XVI Simpósio Brasileiro de Química Teórica

20 – 23 de Novembro de 2011

Ouro Preto – MG, Brasil

Livro de Resumos

XI SBQT 2011 – 30 Anos.

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20-23 de Novembro de 2011

Ouro Preto – MG, Brasil.

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- Coordenação de Aperfeiçoamento de Pessoal do Ensino Superior – CAPES

- Conselho Nacional para o Desenvolvimento Científico e Tecnológico – CNPq

- Fundação de Amparo à Pesquisa do Estado de Minas Gerais – FAPEMIG

- Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP

- Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro – FAPERJ

- Universidade Federal de Ouro Preto – UFOP

REALIZAÇÃO

- UNIVERSIDADE FEDERAL DE MINAS GERAIS – UFMG.

APOIO

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APRESENTAÇÃO

O Simpósio Brasileiro de Química Teórica (SBQT) é o mais importante evento do Brasil na área de química teórica e um dos mais importantes da América Latina. Na sua XVI edição, completa-se 30 anos em que o SBQT contribui de forma extremamente importante na consolidação da pesquisa em Química Teórica no Brasil. A excelência das pesquisas desenvolvidas no país e o prestígio do encontro se manifestam nos "proceedings" publicados em periódicos científicos de grande repercussão internacional como o THEOCHEM (no período de 1993 a 2001) e no *International Journal of Quantum Chemistry* (*IJQC*, desde 2003).

Desde seu início, o caráter interdisciplinar do Simpósio, a qualidade dos trabalhos apresentados e a presença de importantes pesquisadores nacionais e internacionais têm estimulado a participação crescente de profissionais e alunos de pós-graduação e graduação, de diferentes segmentos do meio científico nacional e internacional. Este caráter multidisciplinar responde pelo número crescente de participantes em cada evento - I SBQT (50), II SBQT (100), III SBQT (113), IV SBQT (125), V SBQT (135), VI SBQT (160), VII SBQT (200), VIII SBQT (230), IX SBQT (360), X SBQT (310), XI SBQT (415), XII SBQT (370), XIII SBQT (387), XIV SBQT (374), XV SBQT (429), XVI SBQT (564 inscritos). Essa ampla participação tem contribuído significativamente na formação de novos pesquisadores, principalmente nas áreas de Química e Física Teóricas, com importantes desdobramentos nas áreas de Matemática e Computação.

A expressiva participação de pesquisadores e estudantes das regiões em que a Química Teórica encontra-se consolidada como Minas Gerais, São Paulo, Rio de Janeiro, Pernambuco, Rio Grande do Sul e Distrito Federal e a crescente participação de pesquisadores de outros estados do Norte, Nordeste e Centro-Oeste demonstram a repercussão positiva do simpósio em todo o país, consolidando e descentralizando as pesquisas na área da química teórica.

Outro forte indicativo do sucesso do SBQT é o fato de ser o único encontro nacional com a publicação de seus *proceedings* em periódico indexado de circulação internacional e com arbitragem rigorosa por pares. A publicação dos Anais do SBQT iniciou-se com o VI SBQT quando trabalhos completos apresentados no evento foram publicados no *Journal of Molecular Structure (THEOCHEM)*. Este periódico foi utilizado para a publicação dos Anais do SBQT até o X SBQT. A partir do XI SBQT os trabalhos completos foram publicados no *International Journal of Quantum Chemistry(IJQC)*.

As expectativas em relação à realização do XVI SBQT são de reafirmar e elevar a qualidade das pesquisas que estão sendo realizadas no país, promover a discussão e planejamento de novas linhas de conhecimento da área e ampliar a formação de recursos humanos. A Comissão Organizadora do XVI SBQT está empenhada em propiciar mais uma vez um ambiente de efervescência científica e de motivação para todos os pesquisadores, graduandos e pós-graduandos.

Boa Leitura!

Comissão Organizadora.

WELCOME

The Brazilian Symposium of Theoretical Chemistry (SBQT) is the most important event of Brazil in the field of theoretical chemistry and one of the most important in Latin America. In its XVI edition, the SBQT is completing 30 years and has an extremely important role in the consolidation of the Theoretical Chemistry research in Brazil. A strong indicative of the success of SBQT is the fact that this is the unique national meeting whose proceedings are published in a scientific journal of international circulation with a rigorous peer-review system. The publication of the proceedings started at 1993 with a special issue of THEOCHEM and since 2003 the proceedings are published in the International Journal of Quantum Chemistry.

Since its beginning, the interdisciplinary character of the symposium, the quality of the works presented and the presence of important national and international researchers have stimulated an increasing participation of professionals, graduate and undergraduate students of different segments of the national and international scientific community. This multidisciplinary character is responsible for the increasing number of participants in each event - I SBQT (50), II SBQT (100), III SBQT (113), IV SBQT (125), V SBQT(135), VI SBQT (160), VII SBQT (200), VIII SBQT (230), IX SBQT (360), X SBQT(310), XI SBQT (415), XII SBQT (370), XIII SBQT (387), XIV SBQT (374), XVSBQT (429), XVI SBQT (560 registered) and has contributed prominently to the formation of human resources, mainly to the theoretical physics and chemistry, with important consequences for the mathematical and computational fields. The expressive participation of researchers and students from the regions which the theoretical chemistry research is consolidated such as the southeast states of Brazil, Pernambuco, Rio Grande do Sul and Federal District and the growing participation of researchers from other states of North, Northeast and Center-West demonstrate the positive repercussion of the symposium throughout country consolidating and decentralizing the research in the theoretical chemistry field.

In the four-day event, the theoretical chemists and molecular physicists of the country and abroad, together with the invited speakers, have met to discuss the advances of the field, establish collaborations and exchange information. The expectation for the XVI Brazilian Symposium on Theoretical Chemistry are to reinforce and raise the quality of the researches developed in the country, to promote the discussion and new research lines in this field and contribute to human resource formation. The organizing committee of the XVI SBQT is once more committed to establish this environment of scientific effervescence and motivation for all researchers and graduate and undergraduate students.

Organizing Committee.

Programa do XVI SBQT 2011

Domingo 20/11/2011	Segunda 21/11/2011	Terça 22/11/2011	Quarta 23/11/2011	Quinta 24/11/2011
	Plenária (PL2) - 40 min	**Plenária (PL3) - 40 min**	**Plenária (PL4) - 40 min**	Saída
	Palestra (PA1) - 30 min	**Palestra (PA8) - 30 min**	**Palestra (PA14) - 30 min**	
	Palestra (PA2) - 30 min	**Palestra (PA9) - 30 min**	**Palestra (PA15) - 30 min**	
	Palestra (PA3) - 30 min	**Palestra (PA10) - 30 min**	**Palestra (PA16) - 30 min**	
	Coffee Break - 20 min	Coffee Break - 20 min	Coffee Break - 20 min	
	Sessão Coordenada 11:00 h - 12:20 h 4 Palestras de 15+5 min	**Sessão Coordenada 11:00 h - 12:20 h 4 Palestras de 15+5 min**	**Sessão Coordenada 11:00 h - 12:20 h 4 Palestras de 15+5 min**	
	Almoço - 12:20 h - 14:00 h	Almoço - 12:20 h - 14:00 h	Almoço - 12:20 h - 14:00 h	
	Palestra (PA4) - 30 min	**Palestra (PA11) - 30 min**	**Palestra (PA17) - 30 min**	
Recepção e Registro	**Palestra (PA5) - 30 min**	**Palestra (PA12) - 30 min**	**Palestra (PA18) - 30 min**	
	Palestra (PA6) - 30 min	**Palestra (PA13) - 30 min**	**Palestra (PA19) - 30 min**	
	Coffee Break	Coffee Break	Coffee Break	
	Palestra(PA7)- 30 min	Sessão Coordenada 16:00 h - 17:20 h 4 Palestras de 15+5 min	**Palestra(PA20) - 30 min**	
	Sessão Temática : Uso de GPU na Quimica Computacional 2 apresentações de 30 min		**Palestra(PA21) - 30 min**	
			Plenária (PL 5) - 40 min	
			Pausa (10 min)	
	Sessão de Poster 17:30h - 19:00 h	**Sessão de Poster 17:30h - 19:00 h**	**Assembléia Geral**	
Abertura	Livre - 19:00 h - 21:00 h	Livre - 19:00 h - 21:00 h	Livre - 19:00h - 21:00h	
Plenária (PL1)				
Coquetel de Abertura	**Mesa Redonda: 30 anos de SBQT***		**Confraternização de Encerramento 21:00h**	

*** Sala de seminário no Grande Hotel de Ouro Preto.**

Programa detalhado:

20 de Novembro de 2011 - Domingo

14:00h – 19:00h	Entrega de Material e Registro
19:00h – 19:30h	Sessão de abertura
19:30h – 20:30h	Plenária de abertura (PL1) – Prof. Alfredo Mayall Simas *Química teórica: evolução de paradigmas, novos rumos*
20:30h – 22:00h	Coquetel de abertura

21 de Novembro de 2011 – 2ª feira

8:30h – 9:10h	Plenária (PL2) – Prof. Michele Parrinello *Per montagne e per valloni with metadynamics*
9:10h – 9:40h	Palestra (PA1) – Prof. Andreas Koster *Melting of Finite Systems: A First-Principle Approach*
9:40h – 10:10h	Palestra (PA2) – Prof. Klaus Capelle *"How negative does the correlation energy of many-electron systems get? From lower bounds to new density functionals"*
10:10h – 10:40h	Palestra (PA3) – Profa. Elfi Kraka *"Weak chemical bonds: How can we describe them?"*
10:40h – 11:00h	Coffee Break
11:00h – 12:20h	Sessão Coordenada **A** (4 apresentações)
12:20h – 14:00h	Almoço
14:00h – 14:30h	Palestra (PA4) – Prof. Bernd Winter *Photoelectron spectroscopy from aqueous solutions: Ultrafast charge and energy transfer, and reduced emission angular anisotropy*
14:30h – 15:00h	Palestra (PA5) – Profa. Patrizia Calaminici *Study of Large Clusters with Density Functional Theory*
15:00h – 15:30h	Palestra (PA6) – Prof. Willian R. Rocha *Hybrid Quantum Mechanics/Effective Fragment Potential (QM/EFP) Studies of Organometallic Reactions in Aqueous Solution*
15:30h – 16:00h	Coffee Break
16:00h – 16:30h	Palestra (PA7) – Prof. James Stewart *Past, Present, and Future of Semiempirical Methods*
16:30h – 17:30h	Sessão Temática: Utilização de GPU em Química Computacional
17:30h – 19:00h	Sessão de Posters – Números Ímpares
21:00h – 22:00h	Mesa Redonda: 30 Anos de SBQT - Coord. Prof. Sylvio Canuto Local: Sala de Seminário do Grande Hotel de Ouro Preto.

22 de Novembro de 2011 – 3ª feira

8:30h – 9:10h	Plenária PL3 – Prof. Todd Martinez *Electronic Structure and First Principles Dynamics on Graphical Processing Units*
9:10h – 9:40h	Palestra (PA8) – Prof. Lucas Visscher *Subsystem approaches in computational chemistry*
9:40h – 10:10h	Palestra (PA9) Prof. Ramiro Arratia-Pérez *Optical, magnetic and aromatic properties of heavy transition metal, lanthanide and actinides complexes*

10:10h – 10:40h	Palestra (PA10) Prof. Oscar Ventura *Computational study of the lipscomb and lindskog reaction paths for hydrolytic Zn enzymes*
10:40h – 11:00h	Coffee Break
11:00h – 12:20h	Sessão Coordenada **B** (4 apresentações)
12:20h – 14:00h	Almoço
14:00h – 14:30h	Palestra (PA11) Prof. Benedetta Mennucci *Continuum Solvation Models: what else can we learn from them?*
14:30h – 15:00h	Palestra (PA12) Prof. Ruben H. Contreras *Critical analysis of the through-space transmission of NMR $^{1h}J_{FH}$ coupling constants*
15:00h – 15:30h	Palestra (PA13) Profa Thereza Amelia Soares *Atomistic Simulations of Lipopolysaccharide Membranes of Pseudomonas aerugino*
15:30h – 16:00h	Coffee Break
16:00h – 17:20h	Sessão Coordenada **C** (4 apresentações)
17:30h – 19:00h	Sessão de Posters – Números Pares

23 de Novembro de 2011 – 4ª feira

8:30h – 9:10h	Plenária (PL4) Prof. Walter Thiel *Theoretical Studies of Enzymatic Reactions*
9:10h – 9:40h	Palestra (PA14) Prof. Dieter Cremer *A New Way of Describing Dynamic Processes in Cyclic Jahn-Teller Systems*
9:40h – 10:10h	Palestra (PA15) Prof. José Walkimar *Decomposing the Interaction Energy in the Transition Structure of Bimolecular Reactions*
10:10h – 10:40h	Palestra (PA16) Prof. João B. L. Martins *Structural and electronic properties of adsorption on zinc oxide surfaces*
10:40h – 11:00h	Coffee Break
11:00h – 12:20h	Sessão Coordenada **D** (4 apresentações)
12:20h – 14:00h	Almoço
14:00h – 14:30h	Palestra (PA17) Prof. Ursula Rothlisberger *Mixed QM/MM Simulations of DNA Damage: Defect Formation and Repair*
14:30h – 15:00h	Palestra (PA18) Prof. Kathia M. Honório *Advanced Computational Methodologies and Design of Bioactive Ligands for PPAR Receptor*
15:00h – 15:30h	Palestra (PA19) Prof. Paulo A. Netz *Methods and challenges in DNA modeling and simulation*
15:30h – 16:00h	Coffee Break
16:00h – 16:30h	Palestra (PA20) Prof. Danko Bozanak *Atom in the EM wave - old and new effects*
16:30h – 17:00h	Palestra (PA21) Prof. Gulzari L. Malli *My fifty years in Relativistic Quantum Chemistry*
17:00 – 17:40h	Plenária (PL5) Prof. Kenneth Ruud *Analytic calculations of molecular properties for one-, two- and four-component wave functions*

17:40 – 18:00h	Pausa
18:00h – 19:00h	Assembléia Geral e Entrega de Prêmios
21:00h – 24:00h	Confraternização de Encerramento

Sessão Temática: Utilização de GPU na Química Computacional

21 de Novembro

16:30h – 17:00h	ST1 – Me Arnaldo Tavares (NVIDEA) *Computação em GPU's e seu uso na Ciência*
17:00h – 17:30h	ST2 – Prof. Gerd R. Bruno *Parallel Computing in Semiempirical Quantum Chemistry Calculations using Graphical Processing Units (GPUs)*

Sessões Coordenadas

21 de Novembro – 2ª feira

Sessão Coordenada A

11:00h- 11:20h	P42 – Marcos H. de Oliveira *Incorporation of absorption effects on the electron-molecule scattering cross sections calculations at EPolyScatD*
11:20h – 11:40h	P43 – Kleber Mundim *Temperature Dependence of Chemical and Biophysical Rate Processes: Beyond Arrhenius Mechanism*
11:40h – 12:00h	P323 – Victor H. Rusu *A New Coarse-Grained Force Field for Carbohydrates*
12:00h – 12:20h	P348 – Ademir J. Camargo *Car-Parrinello Molecular Dynamics study of tetrahydroborate(III) ion hydration*

22 de Novembro – 3ª Feira

Sessão Coordenada B

11:00h- 11:20h	P142 – Rafael C. Barreto *On the thermodynamic properties of water around the critical point: Molecular Dynamics simulation using a polarizable model*
11:20h – 11:40h	P278 – Márcio Soares Pereira *The Effect of the Zeolite Cavity on the Mechanism of Dehydrogenation of Light Alkanes over Gallium Containing Zeolites*
11:40h – 12:00h	P397 – Francisco das Chagas Lima Alves *Theoretical Study of the Selective controlled HNO and NO formation in the trans-[RuNO(NH3)4P(OEt)3]3+ reduction*
12:00h – 12:20h	P145 – Giovanni Caramori *Bond Linkage Isomerism of Bipyridine (nitro/nitrito) Ruthenium Complexes*.

Sessão Coordenada C

16:00h – 16:20h	P325 – Geraldo Magela e Silva *Singlet and Triplet Excitons Random-Walk Dynamics in Conjugated Polymers*
16:20h – 16:40h	P341 – Frederico Teixeira Silva *Lennard-Jones potential Parametrization for silicon tetrachloride*
16:40h – 17:00h	P460 – Aloísio de Jesus Santana *Theoretical study of the silane activation by H, F, Cℓ and I atoms*
17:00 – 17:20h	P491 – André Luiz B. Formiga *Multiconfigurational study of charge transfer spectra of cyanoiron complexes*

23 de Novembro – 4ª Feira

Sessão Coordenada D

11:00h- 11:20h	P262 – Frederico Pontes *Structural Properties of Lipid A from P. aeruginosa as a function of phenotypical variation*
11:20h – 11:40h	P295 – Hubert Stassen *Molecular Dynamics Investigations of Prodan in a DLPCBilayer*
11:40h – 12:00h	P357 – Kelly M. Costa *Molecular Docking of the GLCNAcstatin and seven analogues in complex with hOGA*
12:00h – 12:20h	P503 – Thiago C. Correra *Reactivity of sulfate esters and analogs: why is the sulfur center unreactive?*

Palestras Plenárias

"Química teórica: evolução de paradigmas, novos rumos"

Alfredo Mayall Simas

Departamento de Química Fundamental, CCEN,

Universidade Federal de Pernambuco, Recife, PE

Palavras-chave: Química Teórica, Química Quântica, Química Computacional.

Nas últimas três décadas, o SBQT vem testemunhando o enorme avanço da Química Teórica: nos formalismos, na instrumentalização das técnicas, nos modelos, na capacidade computacional e na crescente relevância dos problemas estudados.

Uma teoria da Química precisa explicar e modelar muito bem os quatro estados da matéria: sólido, líquido, gasoso e plasma; bem como suas interfaces. Mas, principalmente, uma teoria da Química precisa explicar e modelar reações químicas.

A instrumentalização da teoria da Química depende do avanço simbiótico entre as técnicas numéricas e os computadores. A crescente paralelização, o processamento em placas gráficas e a tendência para a computação "nas nuvens", já permite vislumbrar indução ao escalonamento linear dos cálculos e à simulação, cada vez mais exata, de sistemas cada vez maiores.

As aplicações da teoria da Química precisam também focar problemas relevantes da atualidade como, por exemplo, a busca por catalisadores tetraeletrônicos que possam promover com eficiência a quebra das moléculas de água; a descoberta de materiais para a estocagem de hidrogênio enquanto combustível; a descoberta de novos materiais com propriedades avançadas; o design de novos fármacos também capazes de serem bem sucedidos nos testes clínicos; ou a proposição de fundamentos inovadores para gerar modelos visando um melhor entendimento da vida e a descoberta de vida sintética.

Com o surgimento da internet, das bibliotecas *on-line*, das redes sociais e da divulgação instantânea das ideias a nível global, podemos também vislumbrar mudanças futuras na maneira de fazer ciência, na velocidade de obter resultados e na forma de dar publicidade aos mesmos – especialmente para a Química Teórica, que depende fortemente de facilidades computacionais.

Nesta palestra, também será abordada a atual evolução das realizações científicas da Química Teórica capazes de gerar modelos, os quais, provavelmente por um bom período, virão a orientar os novos rumos das pesquisas.

Apoio: FACEPE-PRONEX, CNPq.

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"Per montagne e per valloni with metadynamics"

Prof. Michele Parrinello

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Lugano, Switzerland

Key-words: Metadynamics

Computer simulation methods based on empirical potentials or on an *ab-initio* approach over the years have made invaluable contributions to our understanding of many complex chemical and biochemical processes. However, in spite of amazing progress in software and hardware, severe limitations restrict the impact that these simulations might otherwise have. Such limits are evident, for instance, when it comes to study problems in nanosciences or in biochemistry. In either cases both the system size and the time scale of the process typically exceed present say capabilities. The time scale problem is particularly challenging and will be addressed here. The severity of the problem is witnessed by the plethora of methods proposed. We describe here metadynamics which has been introduced in our group [A. Laio and M. Parrinello, PNAS **99,** 12562 (2002)]. We also present recent progress which now allow very complex problems to be solved. We illustrate these capabilities with studies of large protein motions and of homogeneous and non homogeneous solid nucleation from the liquid.

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Electronic Structure and First Principles Dynamics on Graphical Processing Units

Ivan S. Ufimtsev,[1,2] Nathan Luehr,[1,2] Alexey Titov,[3] and Todd J. Martinez[1,2]

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[2]SLAC National Accelerator Laboratory, Menlo Park CA, USA
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Massively parallel processors that can perform more than a hundred arithmetic operations per clock cycle, such as graphical processing units (GPU), have recently become mainstream in the era of petascale computing. However, in addition to the remarkable performance, these architectures posses certain limitations, such as imbalanced performance of single and double arithmetic operations and high sensitivity to various strategies for code optimization. We discuss how precision can be effectively controlled in ground state (HF, DFT) and excited state (CIS, TD-DFT) molecular dynamics by splitting the entire calculation into single precision and double precision parts, providing double precision quality results almost at the speed of purely single precision arithmetic. Using our newly developed TeraChem program, we discuss results from *ab initio* molecular dynamics calculations of solvated proteins with up to 1000 atoms. We show that charge transfer effects are not negligible and comment on the implications for simulations using empirical force fields. If time permits, we also present results for excited states of photoactive proteins using CIS and TD DFT methods, where the entire protein is modeled with *ab initio* quantum chemistry.

"Theoretical Studies of Enzymatic Reactions"

Walter Thiel

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim,

Germany

Combined quantum mechanical/molecular mechanical (QM/MM) approaches have emerged as the method of choice for treating local electronic events in large molecular systems, for example, chemical reactions in enzymes or photoinduced processes in biomolecules. The lecture will outline the theoretical background and the commonly chosen strategies for QM/MM studies of biomolecular reactions [1,2] before addressing current methodological challenges [3-6]. In the second part, it will describe some of our recent work on biocatalysis by enzymes which includes mechanistic studies on cytochrome P450cam [7,8] and xanthine oxidases [9-13]. These studies have addressed, inter alia, the biocatalytic role of single water molecules, the competition between coupling and uncoupling reactions in the wild-type P450cam enzyme and its mutants, and the crucial role of active-site residues in the reductive half-reaction of xanthine oxidases. The examples presented will illustrate the chemical insights and the improved mechanistic understanding of enzymatic reactions that can be provided by QM/MM calculations.

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"Analytic calculations of molecular properties for one-, two- and four-component wave functions"

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In the talk, I will discuss a quasi-energy derivative formalism for self-consistent field states (including Hartree-Fock and Kohn-Sham density-functional theory) for calculating higher-order molecular properties [1,2]. The formalism is expressed fully in the atomic orbital basis for basis sets that are both time- and perturbation dependent, allowing the code to be used in conjunction with linear scaling SCF methodology and making it easy to use in conjunction both with non-relativistic and relativistic methodologies [3].
In order to make the code general and enable calculations of molecular properties of arbitrary order for SCF states, generalized one- and two-electron integral codes have been developed [2,4], in which geometric and magnetic derivatives of the one- and two-electron integrals can be made to arbitrary order. Derivatives of the exchange-correlation kernels appears in density-functional theory are determined using automatic differentiation [5].
Example applications will be presented for selected molecular properties, using both relativistic two- and four-component wave functions as well as non-relativistic wave functions. Particular attention will be given to the analytic calculation of higher-order molecular properties involving molecular vibrations, and in particular analytic calculations of cubic force fields.

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Palestras

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"Melting of Finite Systems: A First-Principle Approach"

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With the rise of nanoscience the melting of finite systems has gained technological interest, *e.g.* in sintering processes. From a theoretical point of view finite system melting can be simulated by first-principle Born-Oppenheimer molecular dynamics (BOMD) runs. In this presentation I will discuss caloric curves and temperature dependent heat capacities of small sodium clusters from auxiliary density functional theory (ADFT) BOMD simulations. The importance of the thermostat choice in these canonical ADFT-BOMD runs will be highlighted. Applications to other clusters and biological systems will be also given.

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"How negative does the correlation energy of many-electron systems get? From lower bounds to new density functionals"

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The correlation energy is a small but crucially important part of the total energy of a many-electron system. While this energy is always negative, it cannot be arbitrarily negative: there is a lower bound on it, known as the Lieb-Oxford bound. In this talk, the existence and consequences of this lower bound on the correlation energy are discussed by using examples of actual chemical and physical systems. While this bound must be respected by all computational methods of quantum chemistry, it has particularly interesting consequences for density-functional theory, where it has been used as a constraint in the construction of better correlation functionals. Recent density functionals that make use of the Lieb-Oxford bound in different ways are presented and their performance is compared for atomic, molecular and solid systems.

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"Weak chemical bonds: How can we describe them?"

Elfi Kraka

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Weak chemical bonds, in particular hydrogen bonds, play an important role in living organisms. They determine the secondary structure of proteins, keep complementary strands of DNA together, and participate in enzymatic catalysis. However, the nature of hydrogen bond interactions is still subject to many discussions and different computational approaches have been applied trying to obtain a more quantitative picture. This includes the investigation of interaction energies, hydrogen bond distances and radii, investigation of electron densities, topological analysis or orbital energies. On the experimental side NMR spectroscopy is today's most applied resource to describe hydrogen bonding. We introduce a new, complementary way that is exclusively based on vibrational spectroscopy.

The vibrational spectra of a molecule should contain ample information on its electronic structure, the strength of its bonds, its geometry, and its conformational flexibility, including information about hydrogen bonding. We suggest unravelling this information by focusing on localized vibrational modes associated with a given structural unit, in our case a hydrogen bond. 1,2 We will show how these localized modes lead to a new unique description of hydrogen bonding.

1. Generalization of the Badger Rule Based on the Use of Adiabatic Vibrational Modes in Vibrational Modes in Computational IR Spectroscopy, E. Kraka, JA Larsson and D. Cremer, J. Grunenberg, Ed.; Wiley, New York, 2010, p.105-149.

2. From Molecular Vibrations to Bonding, Chemical Reactions, and Reaction Mechanism, D. Cremer and E. Kraka, Curr. Org. Chem., 14, 1524-1560 (2010).

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Photoelectron spectroscopy from aqueous solutions: Ultrafast charge and energy transfer, and reduced emission angular anisotropy

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Liquid microjet photoelectron spectroscopy is used in conjunction with soft X-ray synchrotron radiation to explore the sub-10 fs relaxation of core-exited liquid water and transition-metal aqueous solutions. In addition, we investigate how electron emission-angle distributions from the solution/water–vacuum interface compare with those from the respective gas-phase molecules. Relaxation dynamics is revealed from resonant photoelectron spectroscopy measurements. For neat liquid water we find a unique de-excitation channel, involving core-hole delocalization, which is a signature of an energy transfer to a neighbor water molecule. We specifically discuss the role of hydrogen-bonding, and we compare results from H_2O(aq) and D_2O(aq). Such a process is not found for core-excited transition metal ions in water. Instead transient hybridization connected with charge transfers is observed which is revealed from large enhancement of valence signal for photon energy at the absorption edge (2p level). The other topic, i.e., the angular distribution from liquid water and aqueous solution is explored for direct 1s-photoelectrons, using an adjustable electric-field vector of linear polarized synchrotron radiation. In solution, the anisotropy parameter is considerably lower than for gas phase. Possible causes, specifically electron scattering and electronic-structure interactions are discussed.

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"Study of Large Clusters with Density Functional Theory"

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Calculations on large clusters like giant fullerenes and cluster models of zeolites have been performed using the density functional theory (DFT) deMon2k code [1]. Fullerenes con- taining up to 540 atoms as well as cluster models of mordenite-type zeolites containing up to more than 400 atoms have been considered [2]. The calculations were of all-electron type and local and gradient corrected functionals have been employed. The fullerene structures were fully optimized without symmetry constrains. The analysis of the obtained structures as well as a study on the evolution of the bond lengths and binding energies will be discussed. For the zeolite systems [3,4] the only restriction that the position of the hydrogens atoms terminating the zeolites models are kept fixed during the optimization procedure was introduced. Optimized geometries, energetic parameters as well as the results of the analysis of the interaction of single guest CO and CH_3CN molecules with hydroxyls located in the main channel (MC) and in the side pocket (SP) will be presented.

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Hybrid Quantum Mechanics/Effective Fragment Potential (QM/EFP) Studies of Organometallic Reactions in Aqueous Solution.

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Key-words: Hybrid QM/EFP, Alkane Activation, Ligand Exchange, Phosphate

Esters hydrolysis

The study of chemical reactions involving transition metal complexes in solution is a challenging task due to factors like (i) Coordination of the solvent to the metal, (ii) ligand displacement reactions involving the solvent (iii) The correct description of the interaction involving the transition metal compound with the solvent, (iv) the solvent effects on the stability of different spin multiplicities of partially filled d shell, among others. In the last years the Effective Fragment Potential (EFP) [1] has emerged as a powerful method to study organic reactions in solution. In this presentation an overview of the hybrid QM/EFP method will be given and its potential to study organometallic reactions in aqueous solution is discussed and exemplified through the results of recent studies involving C-H bond activation of methane by platinum complexes [2], ligand exchange reactions involving ruthenium compounds [3] and the cleavage of phosphate esters [4].

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"Past, Present, and Future of Semiempirical Methods"

James Stewart

MOPAC

A highly personal overview of NDDO type methods will be given. These methods exemplify semiempirical quantum chemistry in that they show that a combination of theory, reference data, and parameter optimization can result in theoretical structures of useful accuracy. When incorporated as computer programs, the result has been a set of tools that have become widely used. The focus of this talk will be on the philosophical aspects, covering the history of these methods, their steadily-increasing accuracy and range of applicability, current problems and limitations, and speculations regarding the possible futures of such methods.

"Subsystem approaches in computational chemistry"

Prof. Lucas Visscher

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In the conventional approach to electronic structure theory a system is viewed as an unstructured collection of nuclei and electrons, requiring only the specification of nuclear positions and charges and the total number of electrons to start a calculation. This truly *ab initio* approach is very appealing and can for small molecules lead to results that rival high-resolution spectroscopic techniques, thereby providing a numerical laboratory to study electronic properties and reactivity. One realization of this approach is relativistic coupled-cluster method[1] in which electron correlation and relativity are treated on equal footing. I will show some examples of applications[2] done with the implementation available in the Dirac programme suite[3] to illustrate its capabilities. While the application of large-scale supermolecular calculations is still gaining popularity, due to the ever-increasing computational power, such an uncompromising approach also has its disadvantages, however. For complex systems one would ultimately like to understand trends observed upon substitution of functional groups in terms of familiar concepts like chemical bond strength, steric hindrance, atomic or molecular charges, etc. Rather than just obtaining these concepts in an a posteriori analysis, one would ideally like to utilize chemical knowledge concerning the distinction between metal and ligands, solvent molecules, functional groups already in the setup of the calculations. In the flexible subsystem scheme[4] implemented in the Amsterdam Density Functional[5] (ADF) code this is made possible. The theoretical framework for this technique is the frozen-density embedding method[6], and defines the total electron density of a supermolecular system as a sum of densities obtained in individual calculations of chemically well-defined subsystems. We have extended this theory to include also magnetic interactions[7] and introduced a capping approach[8] to treat connections between strongly coupled systems. We are now working on the improvement of currently available kinetic energy functionals by studying the properties of accurate reference potentials[9]. I will give an overview of our experiences[10] with this subsystem formulation of density functional theory and discuss perspectives for its further development as a WFT-in-DFT subsystem method[11].

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Optical, magnetic and aromatic properties of heavy transition metal, lanthanide and actinides complexes

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Key-words: spin-orbit effects, molecular properties

Some recent results on transition metal, lanthanide and actinides complexes will be presented with emphasis in spin-orbit effects influencing their optical, magnetic, aromatic and conformational properties.

We will present the spin-orbit effects acting on the optical transitions and molecular g-tensors of $CeCl_6^{3-}$, $PaCl_6^{2-}$ and UF_6^{-} complexes.[1,2] While non-relativistic molecular theories predicts two absorption bands (Θ,Φ) the relativistic theories predict three absorption bands (Δ_1, Δ_2, Δ_3) due to spin-orbit effects, in quite good agreement with the observed spectra. Moreover, non-relativistic theories predict a positive g-factor, while relativistic theories predict negative g-factors, in quite good agreement with the observed ESR spectra.

We will also illustrate how spin-orbit effects influence the aromatic characteristics of Re_3X_9, and $Re_3X_9^{2-}$ (X= Cl, Br) and $An(COT)_2$ complexes (where An=Ce, Th, Pa, U, and COT= cyclooctatetraene).[3]

The conformational properties of PtF_6 are determined by spin-orbit effects which switches-off the Jahn-Teller effect. These results are supported by ^{19}F and ^{195}Pt high-resolution nuclear magnetic resonance spectra and its undisturbed IR and Raman spectra.[4]

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"COMPUTATIONAL STUDY OF THE LIPSCOMB AND LINDSKOG REACTION PATHS FOR HYDROLYTIC Zn ENZYMES"

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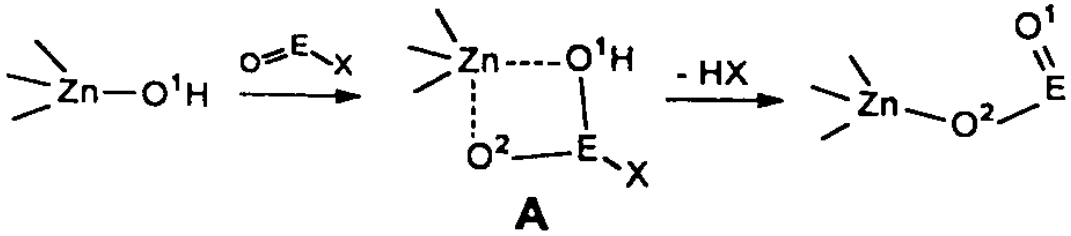
Hydrolytic zinc enzymes (like carbonic anhydrase, peptidases, phosphatases, esterases and nucleases) are highly efficient due to their double functionality. Metal coordination to an oxygen in the substrate allows for electrophilic activation, while a hydroxyl group coordinated to the same Zn atom or a second one, provides the attacking nucleophile. Enzymes exhibiting only one Zn atom must necessarily perfom both functions at this only metal center. It has been postulated in this case that the coordination number of Zn changes from 4 to 5 during catalytic turnover to form an intermediate A,



A

The reaction can proceed through two different paths, either successive proton transfers (which in the case of carbonic anhydrase is called the Lipscomb mechanism) or by internal rotation around the O^2E bond (called the Linskog mechanism). Following and old idea of Bräuer and Vahrenkamp, we performed density functional (DFT) calculations of all the reactants, intermediates, products and transition states involved in both paths for the system L_3ZnOH/CS_2 where L is either none (bare Zn^{+2}), NH_3, imidazole or the more complex tris(phenyl pyrazolyl) borate fragment. Calculations were performed using the B3LYP, PBE1 and M06 DFT functionals and the small 6-31G(d,p) and large 6-311++G(3df,3pd) basis sets. A general study of bond lengths and strengths as well as charge distributions was performed. The results show that while the intermediate A is present in all cases, the Zn atom is not really changing its coordination number. Only in the case of naked Zn^{+2} a real interaction was observed, while no such coordination was noticeable when the ligands were present. Both mechanisms are almost equally probable.

This work was performed as part of the project "Nanotransductores en procesos celulares de señales redox efectuadas por especies reactivas de oxígeno", financed by CSIC, Udelar.

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"Continuum Solvation Models: what else can we learn from them?"

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Molecular modeling is nowadays a well established analytical tool exactly as spectroscopies or other experimental methodologies and we expect that its impact in chemistry, biology, material science and even medicine will enormously increase in the next future. The real spread and success of this expectation will mainly depend on the capacity of the simulations to include environment effects (either a solvent, a protein, a membrane, a polymer, or a composite matrix). This talk highlights recent achievements of one of the most popular approaches to include environment effects in molecular calculations: the polarizable continuum model [1]. Examples of new possible applications of the model will be presented and commented [2].

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"Critical analysis of the through-space transmission of NMR $^{1h}J_{FH}$ coupling constants"

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Key-words: Hydrogen Bond; $^{1h}J_{FH}$; Fermi Hole.

NMR $^{1h}J_{FH}$ coupling constants, SSCCs, are known to show several unusual peculiarities. The main three are as follows, **a)** in many cases their experimental values are reported to be positive and in others, negative; **b)** theoretical values show that in some cases they are substantially contributed not only from the Fermi contact, FC, term but also from the paramagnetic spin orbit, PSO, term, being both of them of similar magnitude, but their respective signs could be either like or unlike; **c)** in many cases it can hardly be expected that the corresponding F---H proximate interactions could be considered a "hydrogen bond", while in other cases it is evident that they are. In this presentation these three points will be critically discussed. For discussing points a) and b), characteristics of both the FC and PSO terms will be discussed performing qualitative analyses based on their expressions in terms of the polarization propagator, PP, formalism, where localized MOs are assumed, as discussed previously (J. Phys. Chem. **A**, 2011, **115**, 7762),. Point c) is discussed in terms of the well known Bader´s QTAIM method as well as recalling the known relationship between the propagations of the Fermi Hole and the FC interaction of SSCCs. This is achieved with a similar approach as quoted above, but analyzing directly the canonical molecular orbitals, CMOs (J. Phys. Chem. A, 2010, **114**, 1044). To this end, CMOs are expanded in terms of natural bond orbitals, NBOs, as given by the Weinhold et al.'s NBO 5.0 program. This approach was dubbed FCCP-CMO, FC Coupling Pathways by using CMOs. In this way it could be determined when the FC term is mainly transmitted through two overlapping electronic clouds owing to exchange interactions present in that region .

Support: UBACYt ; CONICET; FAPESP, CNPq.

Atomistic Simulations of Lipopolysaccharide Membranes of *Pseudomonas aeruginosa*

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Key-words: atomistic simulations, force-field validation, molecular dynamics, lipid bilayers, bacterial adhesion.

Lipopolysaccharides (LPSs) are the major constituent of the outer membrane of Gram-negative bacteria, and a major causative agent of nosocomial illness, eliciting both chronic and acute infections in burn, immunocompromised, and cystic fibrosis pacients. In addition, LPS are believed to play a key role in processes that govern microbial metal binding, surface adhesion, and microbe-mediated oxidation/reduction reactions. Bacterial survival by either forming biofilms or as free planktonic forms is ensured by structural variation in the LPS, such as the presence of inner and outer core and relative expression of O-antigen A- and B-bands. Availability of metal ions in the environment, pH and ionic strength may also alter membrane structural dynamics and stability influencing adhesion, surface charge, immunogenicity and biofilm formation. We have previously developed1 and validated[2,3] an atomistic model of the LPS membrane of *P. aeruginosa*, which has been applied to characterize its structural dynamics and electrostatic profile as function of the presence of B-band, number of acyl chains and availability of metal ions in the environment. It has also been applied to simulate the outer membrane protein OprF from *P. aeruginosa* embedded in the LPS membrane[4]. In this presentation, an overview of previous work on LPS membrane will be offered, and recent simulations to investigate the influence of phenotypical variations of the acyl chains on the flexibility, electrostatic potential and charge distribution of the lipid A will be presented. The dependence of lipid A lateral diffusion, order parameter, molecular shape and diglucosamine tilt angle for symmetrical tetraacyl, pentaacyl and symmetrical hexaacyl lipid A will be characterized and compared against experimental data.

Support: INCT-INAMI, FACEPE, CNPq.

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"A New Way of Describing Dynamic Processes in Cyclic Jahn-Teller Systems"

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The standard quantum chemical approach of describing cyclic Jahn-Teller systems is to calculate the stationary points of the associated potential energy surface ("Jahn-Teller surface") and to assess from there relative energies and the dynamics of the Jahn-Teller system in question. In only a few cases, the complete Jahn-Teller surface has been calculated utilizing, for example, the normal coordinates of a ring to span the surface. However, the latter approach becomes tedious and unreliable for larger rings. The problem can be solved by introducing a set of generally defined ring deformation coordinates that span any space, in which a Jahn-Teller deformation takes place. Ring deformation coordinates are perfectly suited a) to describe bond pseudorotation in Jahn-Teller systems, b) to determine the degree of ring deformation for any ring independent of size and symmetry, and c) to analyze substituent effects on ring structure in a quantitative way. In addition, the ring deformation coordinates complement the ring puckering coordinates previously invented by Cremer and Pople (see, http://smu.edu/catco/, Free Software, Ring Puckering) to a complete set of 3N-6 ring coordinates (N: ring size). By utilizing deformation and puckering coordinates any ring can be described, its geometry optimized, and its vibrational modes calculated in terms of puckering and deformation without any reference to ring bonds and ring bond angles. The usefulness of the ring deformation coordinates is demonstrated by calculating the Jahn-Teller surfaces for different ring systems employing MR-AQCC, EOMIP-CCSD, and CCSD(T).

Decomposing the Interaction Energy in the Transition Structure of Bimolecular Reactions

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Key-words EDA, fragment calculations, molecular interactions, activation energy

The use of Energy Decomposition Analysis (EDA) procedures to study intermolecular interactions and chemical bonds has become a standard method.[1] Decomposition of the molecular or atomic interactions into electrostatic, exchange, repulsion, polarization, and dispersion terms may help us better understand the nature of these interactions and the forces that control (or drive) a chemical reaction. Application of energy decomposition schemes along a reaction coordinate, including the transition structure, is not so common, however. In the present communication we will give some examples of the use of EDA approaches to calculate energy changes along a reaction coordinate and, particularly, to quantify the contributions of the several components of the interaction energy to the activation energy of bimolecular reactions. In the EDA scheme employed in the present case the energy is decomposed into electrostatic, exchange, repulsion, polarization, and dispersion terms. When these terms are added to the bond reorganization energy, which may be the main contributor for some activation processes, it becomes then possible to rationalize the forces that helps stabilize/destabilize a molecular complex, for example, the structure of activated complexes. We employed this approach to study energy changes along the reaction coordinated for some bimolecular reactions such as cycloaddition reactions (Diels-Alder, 1,3-dipolar and [2+2] cycloadditions) and ozonolysis. Decomposition of the energy along the reaction pathway leads to a better understanding of regioselectivity and stereoselectivity. Additionally, we are going to show that bond reorganization necessary for the reactants to attain the activated complex is the main factor contributing to the activation energy in these reactions. Finally, we make some connections to the concept of reaction force as developed by Politzer et alli.[2]

Support: Capes, CNPq, FAPERJ.

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Structural and electronic properties of adsorption on zinc oxide surfaces

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Key-words: Zinc oxide, adsorption, ONIOM, plane wave

There is a considerable interest in understanding the interaction of molecules on metal oxide surfaces, as the role of adsorption on metal oxides is central in many technological areas such as gas sensors and heterogeneous catalysis. One of mostly studied oxides, the semiconductor ZnO has a relatively large direct band gap of almost 3.3 eV. Zinc oxide is a major component of based catalysts which are highly effective for the methanol synthesis from CO/H_2 and CO_2/H_2 mixtures. There are three main surfaces in ZnO wurtzite structure: The ideal polar surface (0001) that expose zinc atoms positioned out with three coordination number; the polar surface $(000\bar{1})$ ended in oxygen, and the prismatic plane $(10\bar{1}0)$ where the zinc atoms and oxygen are in the same plane. As an example, (0001) and $(000\bar{1})$ *ZnO* surfaces show a significant difference in reactivity for the dissociative adsorption of methanol. The activation of carbon dioxide is environmentally important, and is also a molecule used for testing the basicity of metal oxides surfaces. In this study we have used a cluster model and periodic approaches to treat the ZnO surfaces and adsorbed molecules. The cluster approach was carried out with ONIOM hybrid method. The periodic model was performed using LCAO and plane wave. The adsorbed molecules studied were H_2, CO, CO_2 and H_2O. A large number of ZnO units ($Zn_{60}O_{60}$) where used with variable number of layers, specifically four, six and eight layers for the wurtzite structure. The main purpose of this study is to investigate structural and electronic properties of these molecules on the ZnO surfaces and also compare the different theoretical models employed. The theoretical simulation was performed using Density Functional Theory (DFT) implemented in the VASP for the plane wave and Crystal06 for the LCAO, while for the ONIOM method the Gaussian09 package was used with three layers. Interaction energies, orbital stabilization and geometries are comparable to the available experimental data.

Support: CAPES, INCTMN e CNPq.

Mixed QM/MM Simulations of DNA Damage:

Defect Formation and Repair

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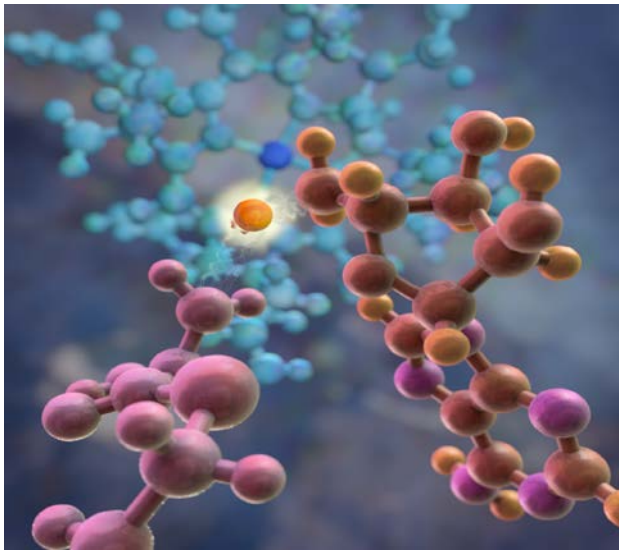

The genetic information encoded in the DNA is constantly challenged by the occurrence of spontaneous changes induced by a variety of internal and external sources such as UV light or chemical carcinogens. These alterations can lead to miscoding during replication and cytotoxic effects. To protect the genetic integrity of the cell, nature has developed a sophisticated control and regulation system involving the concerted action of several DNA repair enzymes that can spot specific DNA damages and correct them back to the original state.

In spite of the pivotal importance of DNA repair, relatively little is known about the molecular mechanisms involved in defect formation, recognition and repair.

In this talk, I will review some of our work based on classical molecular dynamics as well as mixed quantum mechanical/molecular mechanical (QM/MM) simulations in ground and electronically excited states, aimed at a characterization of various chemically or light induced defects, their effects on DNA structure and their correction by DNA repair proteins.

[1] E. Dumont, J. Garrec, and U. Rothlisberger, *Dynamical Effects Play a Pivotal Role for the Formation of Oxidative Intra-Strand Cross-Link DNA Lesions* (submitted)

[2]F. Masson, T. Laino, U. Rothlisberger, and J. Hutter, *A QM/MM Investigation of Thymine Dimer Repair by DNA Photolyase*, ChemPhysChem 10, 400-410 (2009)

[3]D. Bucher, F. Masson, J.S. Arey, and U. Rothlisberger, *Hybrid QM/MM Simulations of Enzyme-Catalyzed DNA Repair Reactions in Quantum Biochemistry*, Cherif F. Matta (Ed.), Vol.2, p. 517-536, Wiley (2009)

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XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
Ouro Preto – MG, 20-23 Novembro de 2011
30 Anos SBQT

"Advanced Computational Methodologies and Design of Bioactive Ligands for PPARδ Receptor"

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Key-words: Metabolic Diseases, PPARδ, chemoinformatics.

This study considers the identification, biological evaluation and design of new ligands for the peroxisome proliferator-activated receptor delta (PPARδ), biological target involved in several metabolic processes, including diabetes and metabolic syndrome. For this study, advanced computational methodologies employed in the discovery and design process of potential agonists and/or antagonists of biological targets were used. Amongst the computational techniques employed in this study, it can be cited: (i) methods based on quantum mechanics, used for the calculation of molecular properties; (ii) statistical methods, employed during the multivariate analysis of the dataset; (iii) methods of molecular docking, used to evaluate the factors that govern the interaction between ligands and biological receptor; and (iv) virtual screening process, that involves the computational analysis of large databases (compound collections) with the aim to determine the binding affinity of molecules into active site of the biological target. Therefore, the main objective of this study is establishing an effective process of development of new bioactive ligands for PPARδ using chemoinformatic methodologies.
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Support: FAPESP, CNPq, CAPES, L'ORÉAL/ABC/UNESCO.

XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
Ouro Preto – MG, 20-23 Novembro de 2011
30 Anos SBQT

"Methods and challenges in DNA modeling and simulation"

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Despite DNA being a very important target for several proteins and drugs, molecular modeling and molecular dynamics simulations with nucleic acids still encompass many challenges. Among these, we can cite the peculiar nature of the DNA interactions, its polyelectrolyte nature, large solvation effects, the complexity of the description of DNA structural parameters and also issues concerning the reliability of the chosen force field. Differently from proteins, DNA does not display a well defined active site and in most of the cases the interactions between ligands and DNA depend on the binding mode, sequence and conformation, in a rather complicated way. After carrying out a detailed study about the advantages and shortcomings of popular force fields in the simulation of DNA, we built a methodology to study the interactions between ligands and DNA, which is intended to be applicable even when there is a lack of detailed experimental information. We start with a docking protocol which uses a modified canonical DNA (with gap) as receptor, in order to sample intercalation and minor groove binding modes. Starting from several independent but energetically favorable docking poses, molecular dynamics simulations are carried out, mapping the interactions, the time evolution of the geometrical descriptors of the nucleotide structures and residence time. The output of molecular dynamics simulations yields also an adequate starting point for refining the docking. This methodology was applied to investigate the interactions between DNA and several ligands as Tröger bases, benzothiadiazoles among others. The results are in good agreement with experimental results, when available, and in other cases point out to some alternative binding modes and unexpected interactions. In the case of Tröger bases, the results suggest that intercalation of one substituent (with aditional contacts in the minor groove) may be preferential binding mode, while minor groove binding through the methanodiazocine bridge, may be responsible for the weaker and non-enantioselective binding which is also observed for the dextrorotatory isomers. In the case of benzothiadiazoles, the presence of a CC π spacer in the molecule was found to be needed to stabilize the intercalation binding mode, yielding very strong interactions and large residence times.

"Atom in the EM wave - old and new effects"

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Interaction of an atom in a (plane) electromagnetic wave is treated in standard text books, but with essential assumption-nuclei is treated infinitely heavy. Strictly speaking this is not correct, which is revealed in the laser cooling of atoms/molecules. The effect is explained semi-quantitatively as scattering of photons from atoms/molecules. In the talk it will be shown what effects one obtains when interaction of the EM wave with atom is treated without the approximation of the infinitely heavy nuclei, and without quantizing EM field. In addition to standard effects, such as resonance transitions and photon energy/momentum exchange, several new ones are obtained.

"My fifty years in Relativistic Quantum Chemistry"

Gulzari L. Malli

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In September 1958 I joined Department of Chemistry, McMaster University, as a graduate student under the direction of Dr. G. W. King and obtained my Master´s degree in May 1960. The title of my dissertation was "LCAO/MO/CI treatment of linear Methylene". In June 1960 I went to the Laboratory of Molecular Structure and Spectroscopy at the University of Chicago as a PhD student in Chemical Physics to work with Professors Mulliken and Roothaan. I tried to work out a few problems in atomic and molecular physics amongst which one was the "Relativistic SCF theory for atoms"; this work was done entirely under the supervision of Prof. Roothaan. However my doctoral thesis dealt with "Vector coupling coefficients for atomic open-shells" and "Relation between electrons and holes in atomic configurations". I obtained my PhD degree in March 1964 and thereafter I worked as Research Physicist at Yale University with Prof. G. Breit, well-known for his relativistic Breit interaction for two-electrons. I returned to Canada in May 1965 at University of Alberta, Edmonton, Canada, but moved to British Columbia at Simon Fraser University in September 1966. In 1972 I was Faculty guest with Prof. E. Bright Wilson at Harvard University and I became Professor Emeritus at the mandatory retirement age in September 2003. Here I will to share the excitement and joy of working in both the non-relativistic and relativistic quantum chemistry since June 1960 until at present highlighting the work of my research associates and myself during the last five decades.

Sessão Temática

Computação em GPU's e seu uso na Ciência

Arnaldo Tavares
Business Development Manager for Latin America
Professional Solutions Group
NVIDIA

A computação em GPU's está revolucionando o mercado de supercomputação e sua aplicação na Ciência, com ganhos tremendos de performance e menor custo de aquisição. Nesta apresentação, abordaremos como a tecnologia CUDA e a linha Tesla permitem obter ganhos de performance nas simulações em diversas áreas da ciência, em especial a Dinâmica Molecular, com AMBER, NAMD e LAMMPS.

Arnaldo Tavares é Business Development Manager para América Latina na NVIDIA, responsável pela linha Tesla e tecnologia CUDA. Graduado em Engenharia pelo CEFET-RJ, possui mestrado em Negócios pela USC (University of Southern California) em Los Angeles, EUA e tem dez anos de experiência no mercado de HPC (computação de alta performance). Já trabalhou na GPlus, um dos maiores integradores para soluções de HPC e visualização 3D, e na Verari Systems, como responsável pelas maiores contas das áreas de óleo/gás, manufatura e pesquisa no Brasil.

Parallel Computing in Semiempirical Quantum Chemistry Calculations using Graphical Processing Units (GPUs)

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Key-words: Semiempirical Methods, GPUs, Parallel Programming

Full quantum chemical treatment of large molecular systems, such as bio-molecules, polymers and new materials, has been pointed as a great challenge for the computational chemists on XXI century. This achievement is only possible with the combined use of high performance computers and efficient parallel programming algorithms.

Nowadays we have been observing a new way to perform high demand calculations with a combined use of Graphical Processing Units (GPUs) co-processors and multi-threaded processors forming high performance hybrid computing systems. As a consequence, many computational chemistry programs have been ported to explore high parallelism of GPU co-processors, including molecular dynamics, DFT, Hartree-Fock, MP2, Coupled Cluster, etc.

Here, we report the first usage of GPUs to accelerate semiempirical quantum chemistry calculations for large molecular systems.

Our efforts have been done to replace some single-threaded parts of MOPAC code with parallel strategies running on both GPU and multi-threaded CPUs. Thus, we modified this code: (1) implementing a parallel version of CGDMS (Conjugate Gradient-Density Matrix Search) linear scaling technique, (2) using numerical libraries (CUSPARSE and SparsKit2) for handling sparse matrices which appears in calculations on large molecular systems, (3) inserting parallel linear algebra libraries (multi-threaded MKL, CUBLAS and MAGMA) and (4) using OpenMP, NVIDIA/CUDA™ and PGI Accelerator™ parallel programming models for introducing new codes to replace the serial ones.

We compared the performance of our parallel code running on a NVIDIA GeForce GTX 480 GPU card to the conventional MOPAC code running entirely on 3.06 GHz quad core, hyper threaded Intel® Core™ I7-950 processor. For some of our implementations, such as CGDMS convergence, the GPU-accelerated code was approximately 140 times faster than diagonalization of Fock matrix in single-point energy calculation for a simulation box with 1000 water molecules and 6000 basis functions.

We believe that this parallel (GPU/CPU) MOPAC code can be useful to produce long molecular simulations using both hybrid QM/MM and QM/QM potentials.

Support: CNPq, CAPES, FINEP and INAMI.

Resumos

"Density Functional Study on the Growing Pattern of B_nP_m Clusters (n = 1 - 4, m = 1 - 4, n + m ≤ 5)"

Verónica Ferraresi Curotto, Reinaldo Pis Diez

CEQUINOR, Centro de Química Inorgánica (CONICET, UNLP,) Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 962, 1900, La Plata, Argentina.

Key-words: BP clusters, Growing pattern, Density Functional theory

Semiconductors formed by group 13/15 elements have increasing importance due to the potential application in the preparation of thin films for electronic devices [1]. The interest in the study of BP atomic clusters is based on the fact that the application in thin films requires a profound understanding of properties at atomic level as well as the growing pattern followed by the aggregates. Results obtained for clusters up to five atoms are reported, with emphasis on the growing pattern followed by the aggregates. B/P aggregates were studied with tools from density functional theory (DFT); using the B3LYP hybrid exchange and correlation functional [2], with cc-pVTZ triple-ζ basis functions [3], as implemented in the Gaussian 03 program [4]. Equilibrium geometries were obtained starting from the BP dimer and adding up boron and phosphorus atoms to grow the aggregates. The increase in the binding energy per atom was used to evaluate the growing. The preferred growing pattern was found to be BP (^{3}A) → BPB (^{2}A) → BBBP (^{3}A) → BBPBB (^{4}A). Molecular electrostatic potentials (MEP), spin densities and charges derived from electrostatic potentials (ESP charges), were calculated to get a quantitative picture of the whole process. Our results, obtained from calculations on clusters of up to five atoms, appear to indicate that B-P clusters tend to grow following a non planar pattern, preferring zones in which ESP charges are large. Moreover, B-B unions are favored over B-P and P-P unions.

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Support: CONICET, UNLP

"Electrochemical and photophysical properties of 2((3-amino-pyridin-4-ylimino)-methyl)-4,6-diterbutylphenol and 2,4-di-tert-butyl-6-(3H-imidazo[4,5-c]pyridin-2-yl)phenol: Experimentals and theoretical studies"

Alexander Carreño[1](PQ), Manuel Gacitúa[2] (PQ), Cristian Linares[1] (PQ), Dessmond McLeod Carey[1](PG), Nancy Pizarro[1](PG), Marcelo Preite[2] (PG), Juan M. Manríquez[2] (PG), Ramiro Arratia-Perez[1] (PG), Andrés Vega[1] (PG), Ivonne Chávez[2,*] (PG).

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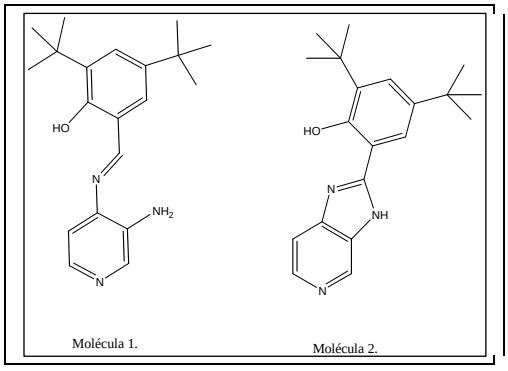
Key-words: Electrochemistry, Photophysics, Gaussian, B3LYP.

We report the synthesis, characterization, electrochemical and photophysical studies of ligands 2((3-amino-pyridin-4-ylimino)-methyl)-4,6-diterbutylphenol (molecule 1) [1] and 2,4-di-tert-butyl-6-(3H-imidazo[4,5-c]pyridin-2-yl)phenol (molecule 2) in order to establish the effect of hydrogen bonding present in both ligands for their potential use in coordination compounds.



The study is supported by theoretical analysis for the interpretation of the experimental results using the software package Gaussian 08 with the B3LYP hybrid functional [2] to explain the luminescent and electrochemical properties.

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Global analytical *ab initio* potential energy surface of the ground state of HOI

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Keywords: potential energy surface, vibrational levels, *ab initio*

Halogen-containing species, like XO and HOX (X = Cl, Br and I), are known by their importance to atmospheric chemistry due to the central role they play on the destruction of stratospheric ozone [1-2]. Extensive *ab initio* calculations using a CASPT2 wavefunction, including scalar and spin-orbit relativistic effects with a quadruple-zeta quality basis set were used to construct a global analytical potential energy surface (PES) of the ground state of the [H, O, I] system. A total of 5344 points were fit to a three dimensional function of the internuclear distances, with a global RMSE of 1.26 kcal/mol. The resulting PES, displayed in Figure 1, describes accurately the main features of this system: the HOI and HIO isomers, the transition state between them and all dissociation asymptotes. After a small adjustment, using a scaling factor on the internal coordinates of HOI, the frequencies calculated in this work agree with the experimental data available within 10 cm^{-1}, thus quite reliable for dynamic studies.

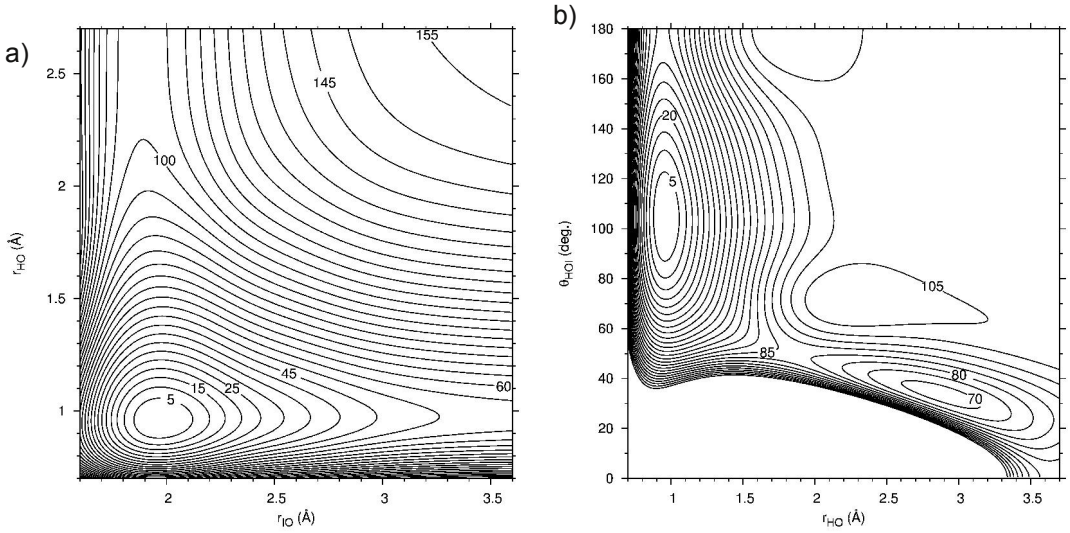

Figure 1. Equipotential contour plot, with increments of 5 kcal/mol, of the fitted [H, O, I] PES for a) θ_{HOI} = 104.7° b) r_{IO}=1.97 Å. The zero of energy is the global minimum.

Support: FAPESP and CNPq.

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ncor oration of a sor tion effects on the electron- olecule scatterin cross sections calculations at olyScat

Gabriel L. C. de Souza(PG)[1,2], Lee Mu Tao(PQ)[1,2], Luiz Eugenio Machado(PQ)[2], Antonio S rgio dos Santos(PQ)[2] and Luiz Marco Brescansin(PQ)[3]

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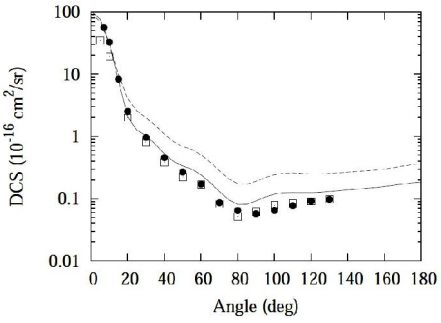
Key-words: Cross Sections, Absorption Effects, Electron Scattering

Although several solid-based ab initio theoretical methods have been developed in the past few decades for the investigation on electron-molecule collisions, most of them can only be successfully applied in the low incident electron energy range. At intermediate energies, numerous open inelastic scattering channels are responsible for absorption effects that play important roles on the collision dynamics. Recently, our group has introduced a modification [1] in model absorption potential of Staszewska et al. [2] which has been successfully applied for electron scattering by several atomic and small molecular targets.

In this work, we present the incorporation of the absorption effects on the EPolyScatD computational code, originally developed by Gianturco et al. [3]. With this implementation, EPolyScatD has become a tool capable to calculate cross sections for elastic scattering of molecules of any symmetry, at intermediate energies, including absorption effects.



The scattering e uations are solved iteratively using the Pad ´s approximant method, as described by Gianturco et al. [3].

As an application of our implementation, in Figure above we show our calculated differential cross sections (DCS) for elastic e^--C_3H_8 at 100eV, obtained with and without the inclusion of absorption effects, along with experimental results of Souza et al. [4] (circles) and Boesten et al. [5] (s uares). Additional results will be presented at the Conference. Below there are references used in this abstract.

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Support: FAPESP, CNP and CAPES.

"Temperature Dependence of Chemical and Biophysical Rate Processes: Beyond Arrhenius Mechanism"

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Key-words: Non-linear Arrhenius, deformed functions, rate processes

A compact formulation is presented here of various effects of temperature on the rates of chemical and biophysical processes as well as in electron conductivity mechanism, where a key quantity is the temperature dependence of the slope of logarithmic plots against inverse temperature.

Physically in the theory of rate processes such slopes are associated to thresholds or to energetic gaps to be overcome for the process to evolve, as for instance in chemical rate reactions. Appreciable deviation from constancy of the slopes, as documented here to occur in a series of examples is accounted for by a linear "*inverse gap versus inverse temperature*" formula which agrees with a recent discussion on deformed Arrhenius plots in chemical and biophysical processes [1] and can be correlated with deviations from Boltzmann distributions, encountered e.g. in non extensive thermodynamics. For the chemical reaction rates, typically of those studied in Refs. [1],[2],[3], the deviation from linearity in Arrhenius plot can be described assuming a linear expansion of "***inverse threshold against inverse temperature***":

$$\frac{1}{E_a} = \frac{1}{E_o} - \alpha \frac{1}{RT} \quad \text{or} \quad \frac{1}{\tau} = \frac{1}{\tau_O} - \alpha \frac{1}{T} \tag{1}$$

where the deformation, dimensionless, parameter α is in the neighborhood of zero. *R* is the ideal gas and T is given in Kelvin. Taking the logarithm of *k* in Eq.**Erro! Fonte de referência não encontrada.** with the condition Eq.(1), in case o the rate reaction process, leads to,

$$\ln k = \ln A + \frac{1}{\alpha} \ln\left[1 - \alpha \frac{E_o}{RT}\right], \tag{2}$$

and the in this new approach the thermal *d*-activation energy is defined as

$$E_a = -\frac{\partial \ln(k)}{\partial(1/RT)} = \frac{E_o}{1 - \alpha \frac{E_o}{RT}} \tag{3}$$

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Support: CAPES and CNPq.

"Molecular Dynamics Study of Uncharged Bupivacaine Enantiomers in Phospholipid Bilayers"

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Key-words: bupivacaine, molecular dynamics, chirality, local anesthetics

Bupivacaine (BVC) is an amino amide local anesthetic with pKa of 8.1. The anesthetic action of bupivacaine is based on its ability to block the voltage gated Na^+ channels in the nervous system. The rbupivacaine (in a racemic mixture) was one of the most widely used LA, due to its quality of anesthesia and prolonged duration of action, however it presents high toxicity The enantiomers R-(+) and S-(-) (shown in Fig. 1) presented different activities. Even if both enantiomers are actives as nerve blockers, the R-(+) is more toxic than the S-(-) form.

Bupivacaine has a high partition in lipid bilayers. In this way, a good understanding of the interaction of each enantiomer with biological membranes could provide insights to improve their efficacy and minimize the side effects.

We have carried out a series of simulations where uncharged DVC, corresponding to the different enantiomers and the racemic mixture, were introduced into a POPC (1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphatidylcholine) phospholipids bilayers at molar ratios LA:Lipid of 1:3. The simulations were able to capture important features of the BVC–phospholipid bilayer interactions: our results show that BVC molecules are found in the hydrophobic tail region. The BVC-R enantioner follows a bimodal distribution while the BVC-S is found, in more uniform distribution, at the bilayer center.

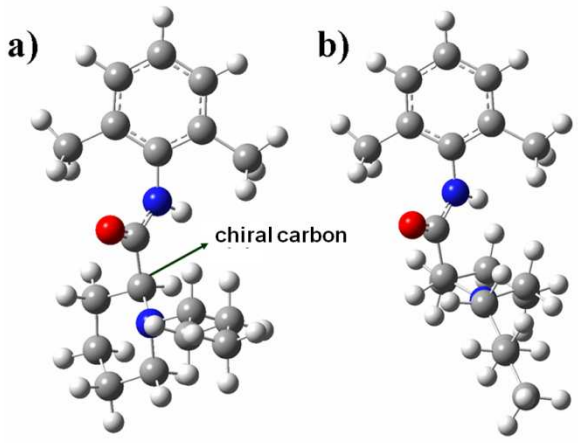

Fig.1*: Structure of Bupivacaine enantiomers a)* S-(-) *and* b) R-(+)

Support: UBA, CONICET and ANPCyT.

Dirac four-component magnetically induced ring current as an aromaticity criterion for heavy-element systems

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Key-words: Relativistic, four-component, ring current susceptibility, aromaticity

The common aromaticity criterion is based on the calculation of nucleus-independent chemical shifts (NICS) values. For heavy systems where relativistic effects are important, this index can be less reliable though. An alternative and more reliable index is based on the magnetically induced current density maps which was pioneered by Lazzeretti and Zanasi[1] as a way to visualize the current flow around a molecule or ring. Quantitatively the integrated induced ring-current susceptibilities, has been introduced as an aromaticity index by Jusélius *et al*.[2] and extended to the relativistic domain by Saue *et al*.[3]
In this study we assess the aromaticity of the uranyl-porphyrin complex by reporting magnetically induced current density maps and induced current strengths. Since strong relativistic effects are expected, the DIRAC four-component code was employed.

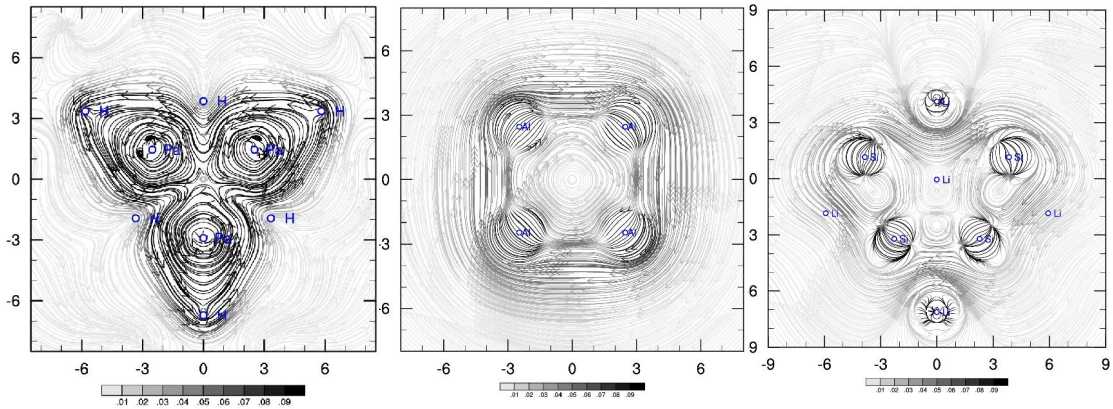

Figure. Sample current density maps showing the current flow around the molecules.

Support: FONDECYT N° 11100446 and UNAB DI-06–10-R.

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Theoretical study of disubstituted pyrrolopyrimidines as focal adhesion kinase

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Key-words: Focal Adhesion Kinase (FAK); Amber force field; pyrrolopyrimidine inhibitors.

We have performed a study of selected 7H-pyrrolo[2,3-d]pyrimidines with FAK inhibitory activities. These inhibitors were placed at the FAK catalytic site analogous to the PDB data in order to obtain the principal conformers of these potential drugs. In addition, we have used molecular mechanics-based energy minimizations and molecular dynamics to understand the interaction of these inhibitors with the amino-acids present in the catalytic site considering the full protein. We have employed AMBER force field to perform the optimization of inhibitors. The calculation using molecular mechanic and the molecular dynamics to probe the conformational space inside the catalytic site, show that the amionacids arginine 14, cysteine 90 and lysine 42 can perform hydrogen bond with those inhibitors. Therefore we have performed MP2 calculations in order to obtain the frontier molecular orbital from the inhibitors and amino acids lysine 42, arginine 14 an cysteine 90 in the catalytic site. The quantum-mechanical results show that the frontier orbital are localized under the cysteine amino-acids, where experimental data suggest a hydrogen-bond with inhibitor of focal adhesion kinase. These results are important to contribute for the development of new FAK inhibitors.

Support: CAPES/REUNI, INCTMN, CNPq.

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QTAIM and NBO studies of glycine conformational preferences

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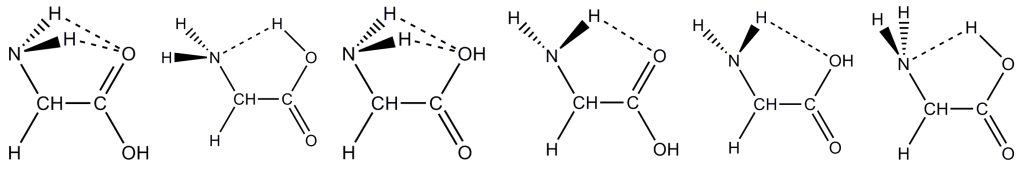
Key-words: Amino Acids, Conformational Analysis, Hydrogen Bonding

Glycine conformational preferences have been mostly explained as due to the formation of intramolecular hydrogen bonding (H-bonding), despite other possible relevant intramolecular interactions that may be present in this molecular system. Indeed, classic (steric and electrostatic) and quantum (hyperconjugative) effects have been invoked to explain the energy difference of conformers of several molecular systems, even those simpler than glycine. Surprisingly, however, not only for glycine, but for all amino acids conformational stabilities these important classical and quantum effects are arbitrarily ignored. Figure 1 shows the glycine conformers (more stable) representation and the commonly indicated most important H-bonding responsible for their relative energies in the literature. However, in the present work, within the framework of the quantum theory of atoms in molecules (QTAIM) and natural bond orbital analysis (NBO), at the B3LYP/aug-cc-pVDZ level, it is shown that actually H-bonding stabilizes just **IIn** glycine conformer. Moreover, these theoretical calculations suggest that the interplay of steric hindrance and hyperconjugative effects rule conformational preferences of this model compound and may not be ignored in the discussion of amino acids conformational analyses.



	Ip	**IIn**	**IIIn**	**IVn**	**Vn**	**VIIp**
Δ*E*	0.00	0.86	1.66	1.20	2.65	5.50

Figure 1: Squematic representantion of the most estable glycine conformers, their relative energies (kcal mol^{-1}) and the supposed H-bonding formation in each case.

Support: FAPESP, CNPq.

Molecular Dynamics and Complex Networks in the study of the thermal stability of Family 11 Xylanases

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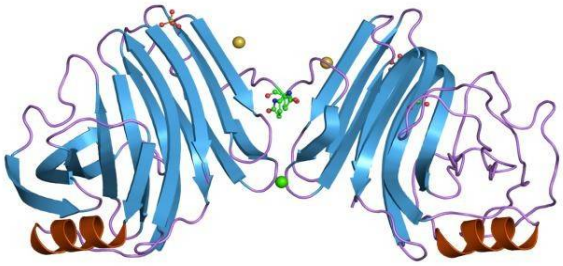
Key-words: Molecular Dynamics, Xylanase, Biofuel, Complex Networks

In the growing global market for biotechnological substrates, Xylanases stand out as key enzymes in fields of strategic importance such as Biofuel production(1). Many of the industrial processes which employ Xylanases can be made more efficient and economically more advantageous by utilizing enzymes of thermophilic and hyperthermophilic origin(1). However, the molecular mechanisms underlying thermal stabilization in Family 11 Xylanases are not well characterized or understood as of yet.(2)

Here, we investigate the mechanisms which confer thermal stability to some thermophilic family 11 xylanases, through Molecular Dynamics simulations and analysis from the perspective of Complex Networks Theory(3). By this, we identify and characterize the importance of each amino acid residue for energy diffusion and stabilization of the protein as a whole, enabling the proposal of protein engineering strategies for enhancing thermal stability.



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Support: FAPESP/CAPES.

Algebraic approach to energy spectra of the Scarf type and generalized Pöschl-Teller potentials

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Keywords: Shape invariance; Superpotential; Sturm-Liouville theorem; Scarf type potential; generalized Pöschl-Teller potentials

The study of exactly solvable problems has attracted much attention since the early development of quantum mechanics. Generally speaking, there are a few main methods to deal with them such as the traditional method [1], exact quantization rule [2], the algebraic method and SUSY approach [3]. The latter two methods are closely related to the factorization method [4]. In this work, we attempt to apply algebraic method to present the exact solutions of the Schrödinger equation with the Scarf type and generalized Pöschl-Teller potentials [5, 6] via the SUSY and shape invariance approach. The key issue is how to find their superpotentials by the Sturm-Liouville theorem. It is recognized that, for the Sturm-Liouville problem, the fundamental trick is the definition of a phase angle which is monotonic with respect to the energy [7].

Support: 20110491-SIP-IPN.

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Theoretical Study of Structural, Electronic and Magnetic Properties of Pentalene and Acene Derivatives

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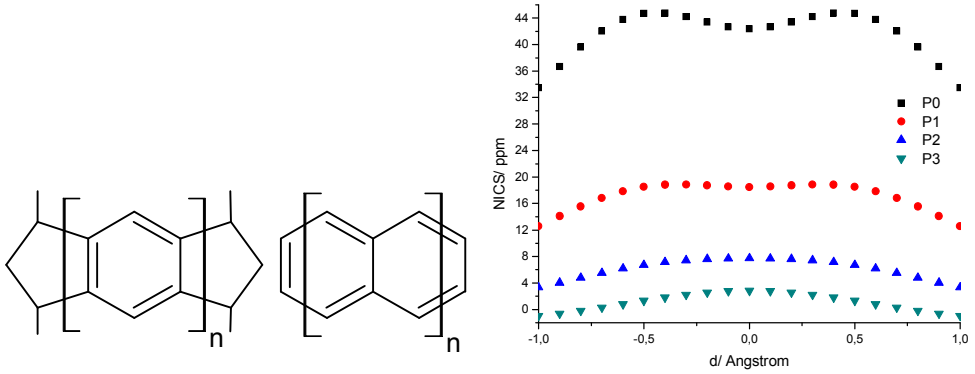
Key-words: pentalene, acenes, NICS, π-stacking, TD-DFT

Fused polycyclic aromatic hydrocarbons displaying extendend π-conjugation, particularly linear polyacenes, have become a primary focus in the field of organic electronics[1]. Extended pentalene derivatives (Fig. 1) represent an interesting alternative to classic polyacenes[2]. These are antiaromatic systems, showing planar conformation[3]. Monomer optimized molecular structures were obtained using B3LYP and BHandH and the basis set 6-31G**, 6-31++G**, 6-31++G**, 6-311++G**. Electronic transitions were obtained at the same level using the TD-DFT methodology. Ground state counterpoise-corrected relative energies for perpendicular displaced dimers and magnetic shielding tensor using the GIAO method were obtained using 6-311++G** basis set with both density functionals. All the calculations were obtained using the Gaussian G03 Rev. E01 software. Our results suggest that the aromatic character of the pentalene derivatives increases by the inclusion of benzene rings between the cyclopentadiene rings. Interaction energy between the monomers also increases with the size of the system. Pentalene derivatives show lower HOMO-LUMO gaps when compared to aromatic polyacene of equal number of rings.



(a) **(b)**

Figure 1. (a) Molecular structure of pentalene and acene derivatives (n=0, 1, 2). **(b)** NICS of the five-membered rings of the pentalene derivatives.

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"Basis set selection for the calculation of the IR fundamental intensities for 1,1-$C_2H_2F_2$."

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Key-words: I.R. Fundamental Intensities, Basis set, vinylidene fluoride.

Accurate quantum mechanical estimates of the gas phase fundamental infrared intensities of 1,1 difluoroethylene have proven to be especially difficult when compared with the results obtained for other small molecules[1,2]. Discrepancies between the theoretical[1,2] and experimental[3,4] values have been found for the C=C stretching band at 1728 cm^{-1} and the CF_2 asymmetric stretching vibration at 1302 cm^{-1}. In this work a wide variety of basis sets have been tested at two electronic correlation quantum levels, MP2 and QCISD, with the objective of determining the basis set that best represents the problematic vibrational modes. The rms error (*root mean square error*), calculated between theoretical and experimental intensities, shows that polarization functions are important for obtaining low rms errors, but use of diffuse functions results in notable error increases. The lowest rms errors were found when 6-31G(d, p), 6-31G(2d, 2p), 6-31G(3d, 3p), 6-311G(2d, 2p) and 6-311G(3d, 3p) basis sets were employed (16,2; 12,9 ; 14,9; 17,3 and 15,7 km/mol (an I.R. intensity unit) respectively, at the QCISD level). Furthermore all the theoretical results for the symmetric CH stretch of 1,1-$C_2H_2F_2$ were much lower than the experimental value of 42.2 km mol^{-1}. This experimental determination was hampered owing to overlapping symmetric and asymmetric CH stretching bands as well as to complication from Fermi resonance. For the 1,1-C_2HDF_2 isotopomer, these bands separate into individual CH band CD stretching bands. Theoretical (calculated with the five best basis sets described previously) and experimental fundamental intensities showed excellent agreement for the isotopomer, implying that the error in the symmetric CH stretch band of 1,1-$C_2H_2F_2$ is probably due to band overlapping and Fermi resonance.

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The role of van der Waals interactions in the adsorption of ethanol on compact transition-metal surfaces

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***K*ey-words**: DFT, ethanol, TM surfaces, van der Waals correction

The development of direct-ethanol fuel cells have great advantages over combustion engines, however, its economic success depends on the designing of stable and low cost catalyst devices for ethanol dehydrogentation, which has not be done efficiently so far. Thus, there is a great interest to understand the interaction of ethanol with TM surfaces, which is the basic step to understand the success or failure of a standard catalyst (transition-metal particles supported on oxides). In this work, we have performed a first-principles study of the interaction of ethanol with close-packed compact TM surfaces (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au). Our first-principles calculations are based on density functional theory (DFT) within the generalized gradient approximation (GGA) employing the projected augmented wave (PAW) method as implemented in VASP. To improve the description of the ethanol/TM systems, we employ also the empirical van der Waals correction proposed by Stefan Grimme (GGA+D2) [1].

We found that van der Waals corrections play a crucial role on the adsorption properties of ethanol on the studied surfaces. A complete different geometry, which affect all the remaining adsorption properties, was obtained by us. For example, GGA yields that the axis formed by the C-C bond is almost perpendicular to the surface, while GGA+D2 yields a parallel orientation for ethanol. Moreover, the C-C bond is closer to the surface for GGA+D2 compared with DFT-GGA calculations. As expected, the adsorption energies obtained by GGA are smaller than GGA+D2 (for example, 310 meV and 852 meV for ethanol/Co(0001), respectively) and increases with the occupation of the TM d-bands. Thus, the obtained results can provide new lights in the mechanisms of ethanol dehydrogenation on TM surfaces.

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The role of localization in the atomic structure of transition-metal nanoclusters by hybrid density functional theory

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***K*ey-words**: DFT, transition-metal, and nanoclusters

Transition-metal (TM) clusters have been widely studied by density functional theory (DFT) within the local density approximations (LDA) and generalized gradienty approximations (GGA) for the exchange-correlation energy functionals [1]. It is well known that LDA and GGA functionals have difficulties to describe particular systems and properties due the incorrect description of the self-interaction. Thus, it is important to obtain a better understanding of the role of the self-interaction problem in TM clusters. In this work, we will report a theoretical investigation of the role of the localization of the d-states in the atomic structure, stability, and magnetic properties of the Co_{13}, Rh_{13}, Hf_{13} clusters, employing hybrid-DFT (Heyd, Scuseria, Ernzerhof - HSE) and DFT+U (Hubbard U term is added to the GGA functional, d-states) approaches.

We found that a partial correction of the self-interaction problem decreases the stability of open structures such as the double simple cubic (DSC), and hence, compact structures such as the icosahedron (ICO) became the lowest energy structure for Rh_{13}. For Co_{13}, the planar structure (hexagonal bilayer - HBL) became almost degenerated with ICO, while there is no change in the relative stability for the Hf_{13} cluster. Therefore, our results suggest that DSC-like structures found for several TM_{13} clusters might be a result of the self-interaction problem, and not a real physical result. Using the sd-hybridization analysis, we found that the sd-hibridization decreases for DSC and increases for ICO for Co_{13} and Rh_{13}. For Hf_{13}, the sd-hibridization decreases for all configurations, and hence, it does not change the relative stability [2].

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"Molecular Basis for Lipase Stability in Supercritical Carbon Dioxide"

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Key-words: molecular dynamics, enzyme stability, supercritical fluids

Lipases are water-soluble enzymes that catalyze the hydroysis of ester chemical bonds in lipid substrates.[1] Lipases have been used historically during yogurt and cheese fermentation, and more recently identified as interesting enzymes for biocatalysis, particularly for their possible role in the synthesis of biodiesel. Lipase industrial use depends on their resilience in unusual environments, such as extreme temperatures and pHs, or non-polar solvents. Supercritical carbon dioxide (sCO_2), in particular, is an interesting medium for biocatalysis and green chemistry, as it is non-toxic and allows the rapid recuperation of substrate and products by depressurization. Surprisingly, despite low viscosity and non-polar nature of sCO_2, it can be used as a solvent for Lipase-catalyzed ester hydrolysis.[2] Here, molecular dynamics simulations are used to probe the molecular basis for Lipase stability in sCO_2. We show that the preservation of the structure of the enzyme depends on the humidity of the solvent. Water is partitioned on the enzyme surface by solvating the polar residues and exposing the hydrophobic catalytic site, which is surrounded by carbon dioxide. The dynamics of solvation and diffusion of sCO_2 on the enzyme are discussed.

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Electronic structure and spectroscopic properties of the low-lying states of CAs

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Key-words: electronic states, spin–orbit coupling, radiative transition.

High-level CASSCF/MRCI calculations with a quintuple-zeta quality basis set are reported characterizing for the first time a manifold of electronic states of the CAs radical yet to be investigated experimentally. Potential energy curves of five quartet and six doublet (Λ + S) states (Figure 1-a) correlating with the three lowest-lying dissociation limits are constructed. The effect of spin–orbit coupling is also included in the description of the states correlating with the first dissociation channel (Figure 1-b). The ground state, $X\ ^2\Sigma^+$, shows R_e = 1.689 Å and ω_e= 1009.8 cm^{-1} followed by the $A\ ^2\Pi$ state, higher in energy (T_e) by 5371 cm^{-1}, with the R_e = 1.785 Å and ω_e= 866.1 cm^{-1}. The spin-orbit coupling constant is 760 cm^{-1} for $A\ ^2\Pi$ state in its equilibrium distance. Estimates of radiative transition probabilities complement this investigation. The $A – X$ transitions associated with the red band systems in CN species, in the case of CAs should arise in the infrared region (T_e = 5371 cm^{-1}), and the $B – A$ (ΔT_e = 20 369 cm^{-1}) should appear in the green region.

(a) (b)

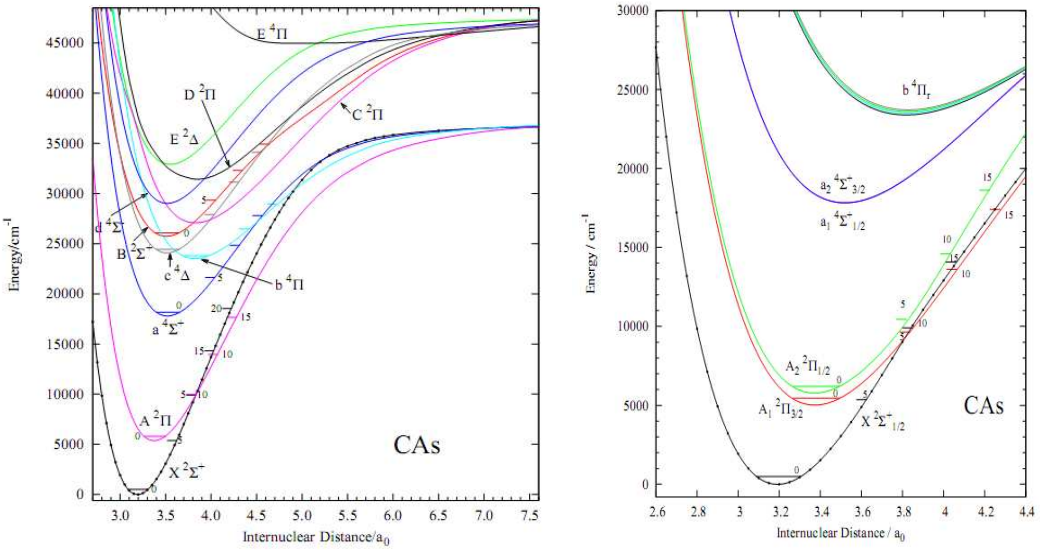

Figure 1. Potential energy curves for: (a) (Λ + S) states and (b) Ω states.

Support: FAPESP.

The metastable BrO^{2+} and NBr^{2+} molecules

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Keywords: Dication Molecules, MRCI, Excited Electronic States

The theoretical study of diatomic dications started early in the history of quantum mechanics, with the investigation of the He_2^{2+} by Pauling, and remains a fruitful research field. In this work using a high-level theoretical treatment, MRCI+Q/aV5Z, several electronic states of the BrO^{2+} and NBr^{2+} molecules were characterized. For the bound states, the vibrational levels and tunneling lifetimes were calculated. NBr^{2+} and BrO^{2+}, in their ground states, are long-lived metastable gas-phase molecules with well depths of 3.38 eV and 2.01 eV. The spin-orbit effects were evaluated for the low-lying (Λ+S) states in order to analyze their influence on the metastability of the species, showed in Figure 1(a), a plot of the spin-orbit eigenstates. The calculated lifetimes for NBr^{2+} (v'' < 35) and BrO^{2+} (v'' < 18) are large enough to be considered stable against tunneling. The adiabatic double ionization energies of BrO and NBr to form metastable BrO^{2+} and NBr^{2+} are calculated to be 30.73 and 29.08 eV, respectively, as displayed in Figure 1(b).

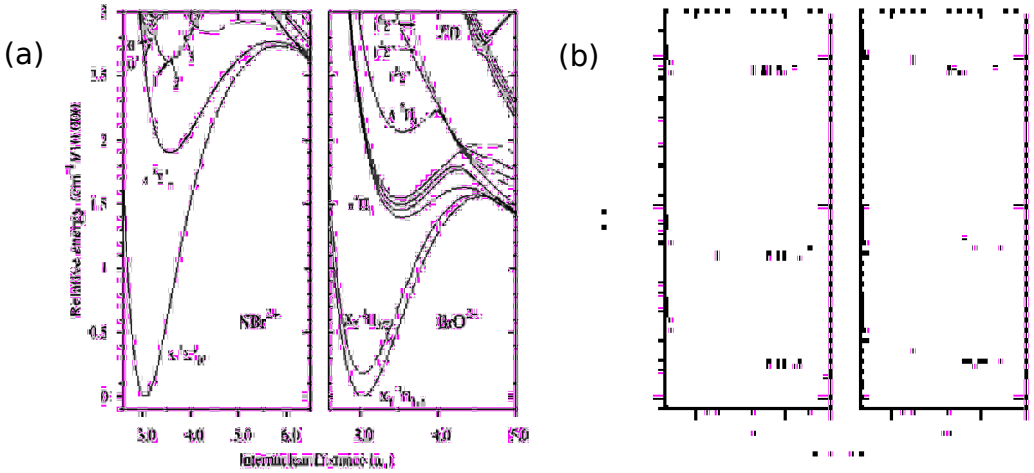

Figure 1: Potential energy curves (a) for NBr^{2+} and BrO^{2+} spin-orbit eigenstates and (b) for ground states of NBr, NBr^+, NBr^{2+}, BrO , BrO^+, and BrO^{2+}.

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Ab initio, Continuum, Cluster-Continuum and Shells Theory of Solvation study of hydroxylamine Stability in Aqueous Solution

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Key-words: solvation, free energy, discrete-continuum models

Hydroxylamine is a potent neutral nucleophile which can exist in two isomeric forms, the neutral NH_2OH and the zwitterionic form NH_3O. In spite of the simple equilibrium involved, theoretical description of the solvation free energy of the highly polar zwitterionic species in aqueous solution may be a challenge and direct experimental detection of this species has been elusive. In this work, we have reported a theoretical study of the hydroxylamine isomerization equilibrium in aqueous solution. Geometry optimization and harmonic frequency calculations were done at PCM/X3LYP/6-31+G(d) level of theory followed by single point energy calculations at MP4/TZVPP+diffuse level. The solvent effect was included through three methods: pure continuum solvation model at PCM/X3LYP/6-31+G(d) level, the cluster-continuum model with one and two explicit solvent molecules and the hybrid dynamical discrete/continuum Shells Theory of Solvation (STS). For the STS method, we have used a cubic box with 32 water molecules plus the hydroxylamine and the molecular dynamics calculations were done at DC-SCC-DFTB quantum method for trajectories. For the solute-solvent interaction energy we have used the PBE/6-31+G(d,p) method and 14 explicit water molecules. The continuum shell was included through the PCM/HF/6-31+G(d,p) method. The results in table 1 shows the pure continuum PCM method and even the cluster-continuum model fail to describe the stability of hydroxylamine isomers when compared with the sophisticated STS approach. The deviation of PCM method is as large as 8.5 kcal/mol. Other study by Rocha and co-workers using Monte Carlo and PCM derived atomic charges predicts an over stabilization of the NH_3O species whereas the report of Fernandez et al predict a value close to our present STS results.

Table 1: Free energy for hydroxylamine isomerisation. Units of kcal/mol.

Method	ΔG^* ($NH_2OH \rightarrow NH_3O$)
PCM (this work)	11.9
Cluster-Continuum (this work)	9.9
Shells Theory of Solvation (this work)	3.4
Rocha (Monte Carlo, JACS **128** (2006) 12374)	-3.6
Kirby *et al* (structure-activity corr., CC **46** (2010) 1302)	0.9
Fernandez *et al* (theoretical pKa, CPL **490** (2010) 159)	2.2

Support: **CNPq, FAPEMIG**

Resonance Spectra of Lignin Components

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Key-words: Lignin, Resonance

Since the discovery of mutagenic DNA strand breaks mediated by transient negative ions (TNIs) [1], considerable has been devoted to low-energy electron interactions with biomolecules. The formation of TNIs, also called resonances, efficiently transfer energy into nuclear degrees of freedom, thus giving rise to a number of reactive channels. With regards to the plasma-based pretreatment of lignocellulosic matter [2], in this work we survey the resonance spectra of lignin components (monolignols and dimers). For this end, we employ well-known semi-empirical methodologies based on bound state calculations [3,4]. This approach is less demanding than scattering simulations and can provide insight into TNI formation (the method if often employed to assign resonance characters in electron transmission spectroscopy [3]). Preliminary results indicate (I) very good correlation between the resonance spectrum obtained with the present methodology and scattering calculations for phenol (precursor of monolignols); (II) very rich resonance spectra for monolignols, with a number of low-lying (< 1.5eV) π^* TNIs, similar in this sense to DNA bases. As a consequence, a number of dissociation channels would be expected.

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Support: FAPESP, CNPq.

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Investigation of electrostatic potentials by means of atomic multipoles from the Quantum Theory of Atoms in Molecules

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Key-words: electrostatic potentials, polarization, QTAIM, CHELPG

The atomic multipoles (charges, dipoles, quadrupoles and higher order terms) allow a rationalization of the electrical properties in molecular systems. Among these properties we can mention the dipole moments derivatives, infrared fundamental intensities and electrostatic potentials. These studies contribute to the development of accurate force fields for use in molecular modeling methods.
The main objective of this work is to advance in the use the atomic multipoles, mainly those from the Quantum Theory of Atoms in Molecules (QTAIM), [1] for the description of electrostatic potentials in proton/molecule systems and to compare the values predicted by QTAIM with results obtained by means of Charges from Electrostatic Potentials using a Grid based method(CHELPG).[2] Another objective is the study of polarization effects induced by the proton on the electrostatic potential and quantities from CHELPG and QTAIM of a molecule. The target molecules were: F_2, Cl_2, BF, AlF, BeO, MgO, LiH, NaCl, CO_2, H_2O, H_2CO, NH_3, PH_3 and BF_3. All the calculations were carried out by using the Gaussian 03 package[3] with the B3LYP density functional and 6-311G(3d,3p) basis sets. All these atomic multipoles are accessible within the QTAIM formalism, whereas only the charge contribution is evaluated by CHELPG.
In almost all the studied cases (except NaCl) the QTAIM formalism, including contributions up to atomic quadrupoles, was more efficient in calculating electrostatic potentials than CHELPG charges in relation to the values obtained directly at the B3LYP/6-311G(3d,3p) level. The CHELPG formalism becomes more competitive only when the predominant contribution to these potentials is that from charges. The lone pairs, described by the QTAIM atomic dipoles, are important in studies of electrostatic interactions (mostly for BF, AlF and PH_3). The polarization induced when a molecule is close to a proton results in substantial changes of atomic multipoles that may affect the observed electrostatic potentials in a large extent (mainly in F_2 and Cl_2).

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Support: CNPQ.

Outer Double Ionization Energies calculated with OVGF method

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Key-words: Outer Double Ionization Energies, Green's Functions, OVGF Method.

Introduction: Vertical ionization energies can be calculated by using Green's functions. The exact Green's functions are unknown and approaches should be used to estimate the ionization energies. One of the most successful approaches is the Outer Valence Green's Function method (OVGF), which has been used in the calculation of outer single ionization energies with deviations under 0.25 eV with respect to experimental data. However, no application of the OVGF method to estimate double ionization energies has been found in the literature.

Objective: To assess the quality of vertical outer double ionization energies of atoms and molecules obtained with the OVGF method in comparison with experimental data and calculated using DFT methods.

Methodology: Vertical outer double ionization energies were carried out with the OVGF method for: CO, N_2, C_2H_2, C_2N_2, O_2, NO, OCS, N_2O, SO_2, CS_2, CO_2, benzene, furan, pyrrole, pyridine, trans-1,3-butadiene, HCl, HBr, Br_2, Cl_2, CH_2Br_2, CF_4, CCl_4, SF_6, H_2O and H_2S, using experimental geometries, and elements of the main group of the 2^{nd} to 4^{th} periods using basis aug-cc-pVTZ and 6-311++G(2df,2pd). The results were compared with those calculated by D.P.Chong[1] using DFT with et-pVQZ basis set and experimental data.

Results and Conclusions: The RMS deviations observed for the double ionization energies for the atoms and molecules mentioned above are in the Table 1:

Table 1: RMS deviations (σ/eV) observed for the study of the vertical outer double ionization of the atoms and molecules.

Systems	*OVGF/ aug-cc-pVTZ*	*OVGF/ 6-311++G(2df,2pd)*	*RPBE/ et-pVQZ*	*KCISmod/ et-pVQZ*	*B97-2/ et-pVQZ*
σ_{atoms}	0.31	0.36	0.34	0.34	-----
$\sigma_{molecules}$	0.6	0.6	-----	-----	0.7

In general, the OVGF double ionization energies are similar to the best calculations carried out by Chong using DFT and a larger basis set. The deviations observed for atoms indicate a better agreement with experimental data (> 0.5 eV) than molecules, which presented larger deviations for compounds containing fluorine atoms or triple bonds.

Acknowledgements: To CNPq, FAPESP and UNICAMP.

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"UV-VIS spectrum of the Pheophorbide *a*, a theoretical study"

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Key-words: Chlorophylls, Pheophorbide *a*, TDDFT, QM/MM, absorption spectrum

The study of tetrapyrroles is important for improving our understanding of electron and energy transfer processes in the photophysical of photosynthetic pigments[1]. Chlorophylls and their derivatives play an important role in these transfer process in both plants and bacteria. The pheoporbide *a* (Pheo, $C_{35}H_{36}N_4O_5$)[2] is a vital pigment for photosynthesis and have also many potential applications such as photodynamic therapy of cancer tumor based on their excited states. The spectrum of pheophorbide *a* shows visible Q bands and near-ultraviolet B bands. These bands are interpreted in terms of the Gouterman four orbital model, involving mainly single-excitation transition from the two highest occupied molecular orbital (HOMO) into the two lowest unoccupied molecular orbital (LUMO). The photophysical properties of Pheo are mainly determined by the delocalized π-electron system along the macrocycle conjugated ring of the molecule. The experimental absorption spectrum[3] in the spectral range between 300 and 700 nm contains four Q-bands and the Soret band, which is typical for porphyrins without a central metal atom. The Soret band consists of more than 10 electronic transitions with different orientations and sizes of the dipole moments[3]. In this work, we will present detailed theoretical analysis of and provide new insights into the UV-VIS spectrum of Pheo in the gas phase and in water. To evaluate the solvent effects for more realistic comparison between theory and experimental data, different procedures using continuum, discrete and explicit model were used to include these effects on the absorption spectrum. The discrete and explicit models used Monte Carlo (MC)[4] simulation to generate the liquid structure. TDDFT calculations were performed to obtain the excitation energies. The continuum and discrete model using TDDFT (B3LYP) showed satisfactory results in comparison with the experimental bands. Explicit model using water molecules making hydrogen bond with the Pheo molecule showed excellent results with average energy in the region of the Soret band of 3.21 eV in excellent agreement with the experimental value (3.09 eV). This corroborates the importance of explicit solvent models in the qualitative and quantitative description of the solvent effects in the absorption spectrum of porphyrins.

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"Analyzing Alzheimer's amyloids with molecular dynamics and normal modes."

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Key-words: Molecular Modeling, Alzheimer's Disease, Molecular Dynamics, Analysis of Normal Modes.

Alzheimer's disease (AD) is a neurodegenerative disease that is the most common form of dementia. Studies have found that aggregates of beta-amyloid peptides (Abeta) are directly involved with the disease; however, the structural characterization of the Abeta dimer still remains difficult through experimental techniques.

We are using normal modes (NM) analysis and molecular dynamics do investigate these aggregates. We divided the work in four steps: i) simulate the molecular dynamics for several peptides together; ii) calculate the low-frequency normal modes of the dimers and tetramers formed during the dynamic; iii) generate a set of conformations of the dimers and tetramers following under the direction of the first twenty normal modes. We are using these normal modes because they are sufficient to represent the global movements of a given protein (Perahia D. et al., Normal Mode Analysis theory and applications to biological and chemical systems. Chapman & Hall, 2000); and iv) use these conformations generated by NM to simulate new molecular dynamics. Until this moment, we performed several simulations containing two or four chains of Alzheimer's Abeta peptide with 42 residues (PDB code 1iyt:A) with a classical approach based on the Gromacs 4.5.1 package employing the GROMOS 53a6 force field with periodic boundary conditions. These peptides were solvated in a box by using SPC/E water molecules in simulations with 4 ns long for each assembly with two or four chains. The VIBRAN module of the CHARMM software (with the CHARMM22 force field) was used to determine the normal modes and normal-mode frequencies of dimers that resulting from these molecular dynamics simulations. These structures were previously fully minimized with the CHARMM through a minimization performed using the steepest-descent algorithm followed by the conjugate gradient method.

We were able to observe the formation of dimers through the interaction between different chains of Abeta and identify which residues bind to maintain this conformation. The methodology will now be used to perform simulations with up to 1 s in duration to analyze the formation of beta sheets in these aggregates.

Support: UFABC, CAPES.

A ressonância em compostos com ligações múltiplas conjugadas.

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Palavras-Chaves: Ressonância, Polienos, Ligações.

Os compostos com ligações múltiplas conjugadas apresentam um papel fundamental para a química. Assim, o isopreno, o beta-caroteno e o retinal, são importantes na visão e na captação da luz no processo de fotossíntese, estando presentes como os principais componentes dos pigmentos. Compostos conjugados também são aplicados como polímeros condutores.

Assim foram estudados por métodos computacionais os compostos: hexa-1,3,5-triino (**1**), hexa-1,3,5-trieno (**2**), hexa-3-en-1,5-diino (**3**) e hexa-1,5-dien-3-ino (**4**), que foram comparadas com o acetileno, o propino, o 1,3-butadiino e o 1,3-butadieno, sendo as duas últimas padrões de ligações conjugadas.

As geometrias dos compostos estudados foram otimizadas pelo modelo computacional MP2/6-311++G(3df,3pd). A densidade eletrônica, ρ(r), foi analisada pelos métodos AIM e NBO, este com a utilização do funcional B3LYP. Todos os cálculos foram realizados pelos programas Gaussian98 e Gaussian03.

Nas moléculas estudadas frente às tidas como padrão temos que os orbitais moleculares π são semelhantes (=). Para as ligações C-C simples observamos um menor comprimento (<) e maiores valores (>) de ρ(r), do maior autovalor da hessiana da densidade eletrônica, λ_1, do laplaciano de ρ(r), $-\nabla^2\rho(r)$ e do caráter covalente. Nas ligações múltiplas observamos que as alterações nessas grandezas são opostas as destas ligações. Estas observações, em conjunto com aquelas do método NBO indicam um aumento da ressonância.

	OM	Ligação C-C	Comprimentos	ρ(r)	λ_1	$-\nabla^2\rho(r)$	Ordem
Hexa-1,3,5-triino (**1**)	=	Simples	<	>	>	>	(covalente) >
		Tripla	>	<	<	<	(iônico) >
Hexa-1,3,5-trieno (**2**)	=	Simples	<	>	>	>	(covalente) >
		Dupla	>	<	<	<	(iônico) >
Hexa-3-en-1,5-diino (**3**)	=	Simples	<	>	>	>	(covalente) >
		Dupla	>	<	<	<	(iônico) >
		Tripla	>	<	<	<	(iônico) >
Hexa-1,5-dien-3-ino (**4**)	=	Simples	<	>	>	>	(covalente) >
		Dupla	>	<	<	<	(iônico) >
		Tripla	>	<	<	<	(iônico) >

Suporte: FAPESP.

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"Heat of formation of phosphorus compounds"

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Key-words: Heat of Formation, Phosphorus Compounds, ccCA, M06-2X.

The heats of formation of phosphorus molecules (P_2, P_4, PO, PO_2, PO_3, P_2O, P_2O_2, and P_4O_6) have been calculated using the correlation consistent Composite Approach (ccCA)[1]. The geometries and harmonic frequencies were obtained at M06-2X density functional method. In ccCA original version is used B3LYP exchange-correlation functional. M06-2X is hybrid meta-GGA functional that improves over the local spin density approximation and the generalized gradient approximation[2]. Table I contains the calculated values of enthalpies of formation at 298 K (in kcal mol^{-1}) and difference with the experimental data.

Table 1: Enthalpies of formation at 298 K (in kcal mol^{-1}).

Systems	**$\Delta(H_{calc} - H_{exp})$[3]**	**$\Delta_f H^o$ (calc)**
P_2	0.529	34.971
P_4	4.600	13.600
PO	-1.106	-5.994
PO_2	-1.092	-66.408
PO_3	-0.237	-101.463
P_2O	1.810	3.690
plan-P_2O_2	1.445	-61.245
P_4O_6	-	-365.190

Using the ccCA composite method, in conjunction with M06-2X functional, we obtained accurate heats of formation for a series of phosphorus compounds. The P_2O_2 planar ring structure (plan-P_2O_2) obtained is found to be energetically favored over the bicycle butterfly-type structure (*bfly*-P_2O_2). Both *trans*-P_2O_2 and *cis*-P_2O_2 are transition states (100.05 and 477.48 cm^{-1}, respectively). The heats of formation calculated, on the average, to within ±2 kcal mol^{-1}. The value of heat formation to P_4O_6 was estimated to be -365.190 kcal mol^{-1}.

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Dynamics of the $CH_3ONO_2 + OH^-$ reaction: An electrostatic potential controlled reaction mechanism.

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Key-words: CH3ONO2, OH^-, BOMD, electrostatic potential

Alkylnitrates are high energy chemical species that are used in applied technologies (explosives, for instance) and environmental (reservoirs of N_2 and regulators of O_3 in the atmosphere)[1]. Thus, the reactivity of these compounds plays a fundamental role in their applications. Recently, Correra and Riveros[1] studied the gas-phase reactions of CH_3ONO_2 with OH^- and F^- by Fourier transform ion cyclotron resonance mass spectrometry techniques and by MP2/6-311+G(3df,2p) calculations. It was suggested that the $E_{CO}2$ (α-hydrogen elimination), $S_N2@C$ (nucleophilic displacement at the carbon) and $S_N2@N$ (nitrogen) reaction mechanisms would explain the reaction products NO_2^- and NO_3^- obtained. However, the $CH_3ONO_2 + OH^-$ reaction the computational and experimental results are in disagreement. The calculations predicted that $S_N2@N$ mechanism is without activation barrier (see table), however the product of this channel was not observed.

Channel	E_{act}
$S_N2@C$	6.2
$E_{CO}2$	0.3
$S_N2@N$	0.1

Table: E_{act} - activation energy (kcal mol^{-1}).

In this context, the main goal of this work resides to explore the reaction $CH_3ONO_2 + OH^-$, particularly the $S_N2@C/S_N2@N$ selectivity, with Born-Oppenheimer direct dynamics (BOMD) trajectory simulations. Reactive and non-reactive scatterings with different initial conditions for collision energies and relative orientations were determined.

In the BOMD simulations only trajectories related to the $S_N2@C$ and $E_{CO}2$ mechanisms were observed. Invariably, all trajectories that simulate the nucleophilic attack of OH^- on the nitrogen atom ($S_N2@N$ mechanism) were deflected towards the methyl group (see figure). We suggest that these results can be rationalized by the molecular electrostatic potentials. Therefore, the reaction mechanism is dynamic driven by the electrostatic potential and that the intrinsic reaction coordinates (IRCs) do not control the selectivity for this reaction channels.

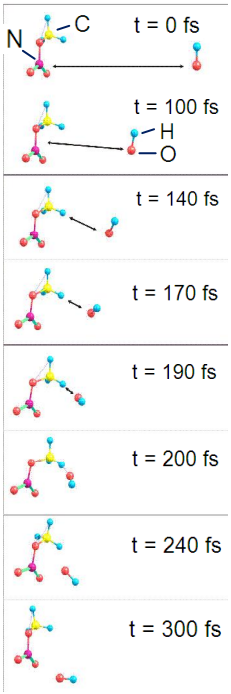

Figure: Structures of a typical trajectory observed in the simulations of $S_N2@N$.

[1] T C. Correra and J. M. Riveros, *J. Phys. Chem. A*, 2010, **114**, 11910 and references within.

Support: CNPq, CAPES, FACEPE, INAMI, PRONEX/FACEPE-CNPq.

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Ab initio Study of Asymmetric Phase-Transfer Catalysis Using Cinchona Alkaloids Derivatives

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Key-words: Phase-Transfer Catalysis, Organocatalysis, Asymmetric Alkylation.

The first successful asymmetric organocatalyzed alkylation reaction with high enantiomeric excess was reported by Dolling and co-workers almost third years ago using cinchona alkaloids derivatives as phase-transfer catalyst (Figure 1). In spite of the high importance of this achievement, no reliable theoretical study on this reaction was reported to date. The main model of asymmetry induction in this reaction is based on the interaction between the aromatic rings (Figure 1).

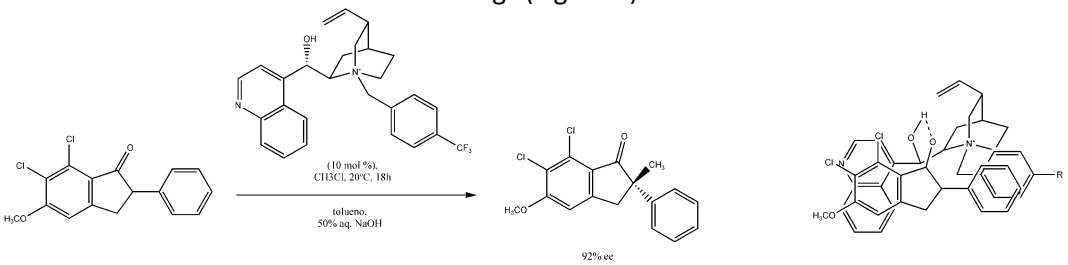

Figure 1

In this work we have reported at the first time a theoretical study of the asymmetric phase transfer catalyzed alkylation reaction reported by Dolling and co-workers. The ab initio calculations were done at X3LYP/6-31(+)G(d) level of theory for geometry and frequency calculations. All the calculations were done with the Firefly program. An extensive search of minimum energy structures for the anion-catalyst complex was performed on the potential energy surface and the two most stables were chosen for investigation of the respective four transition states. The resulting two lowest energy transition states leading to R and S enantiomeric products are presented in Figure 2. The respective activation barriers are 15.0 and 12.3 kcal/mol, leading to 98% of enantiomeric excess of S isomer, in good agreement with the experimental observation of 92%. More refined calculations are in progress and our present results point out the mechanism of asymmetry induction is different from that previously suggested in the literature.

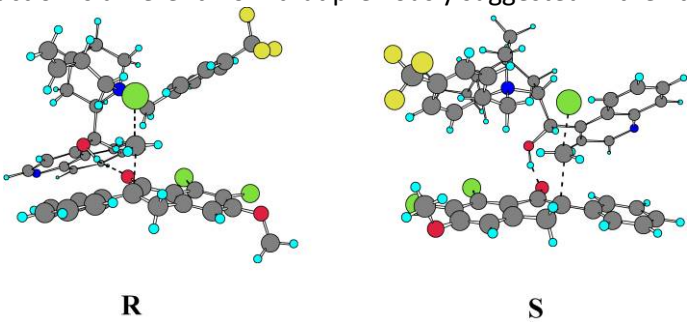

Figure 2

Support: **CNPq, FAPEMIG**

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Coupled cluster calculations of frequency dependent Raman cross sections of polyatomic molecules

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Key-words: CCSD, CC3, response theory, Raman cross sections.

Several studies concerning the calculation of dynamic Raman intensities have shown that the electron correlation effects are strong for these properties. For instance, correlation effects on the dynamic Raman scattering activities were investigated for 10 small molecules, using the aug-cc-pVTZ basis, where the agreement between theoretical and experimental data is 22.5% at the HF, 17.2% at MP2 and 10.8% at the CCSD level [1]. The effect of triple excitations in coupled cluster calculations of Raman cross sections are known only for diatomic molecules where a CC3 study has shown that the triple excitations corrections are substantial for N_2 and CO, where they exceed 10% [2]. The need of a high level treatment of the electron correlation to reach a good agreement between theoretical and experimental Raman intensities motivated us to perform a study where the dynamic Raman cross sections are evaluated with the addition of triple excitations, using the CC3 method, for some polyatomic molecules (H_2O, NH_3, CH_4 e C_2H_2). Since no electronic structure code publically available can perform such calculations, the Raman intensities were computed by our program PLACZEK [1] which computes these properties from numerical derivatives of CC3 linear response polarizabilities evaluated using the electronic structure code CFOUR. The results obtained for H_2O are given in Table 1. For this molecule, the effects of triple excitations are small in the Raman cross sections. By comparing theoretical and experimental data we see that CCS and CC2 give poor results while the CCSD and CC3 data are in good agreement with the experimental data.

Table 1: Differential Raman cross sections (in 10^{-35} m^2sr^{-1}) for H_2O at λ_{ex} = 514.5 nm.

	$\nu_1(a_1)$ 3657 cm^{-1}	$\nu_2(a_1)$ 1595 cm^{-1}	$\nu_3(b_2)$ 3756 cm^{-1}
CCS/aug-cc-pVTZ	8.20	0.37	2.27
CC2/aug-cc-pVTZ	18.10	0.57	3.50
CCSD/aug-cc-pVTZ	10.47	0.39	2.41
CC3/aug-cc-pVTZ	10.95	0.40	2.52
Experimental [3]	10.69±1.4	0.33±0.01	1.80±0.20

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Biogenic Organic Volatile Compounds in Troposheric Chemistry: Limonene reactions with ozone and hydroxyl

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Key-words: limonene, hydroxyl radical, ozone, DFT, IRC, VTST

Biogenic Volatile Organic Compounds play an important role in tropospheric chemistry, mainly in the oxidative processes which lead to the formation and consumption of ozone an also to the production of Secondary Organic Aerosol (SOA). The presence of NOx due to anthropogenic urban emissions can dramatically change gas-phase organic oxidations mechanisms and SOA formation. In this work, limonene reactions with ozone and hydroxyl radical were studied. Thermodynamics and kinetic parameters for the first step of both reactions, which are the rate determinant steps, were calculated using BHandHLYP functional and a double-zeta Dunning basis. Each minimum has all real frequencies and for each transition state only one imaginary vibrational frequency was found, which confirms the first-order saddle point configuration. Additional calculations using the intrinsic reaction coordinate method (IRC) were performed. Rate coefficients were evaluated using the thermodynamic interpretation of the Variational Transition State Theory (VTST). Limonene has two enantiomeric forms: d-limonene and l-limonene and two different double bounds. When limonene reacts with ozone, it follows the Criegee Mechanism, forming two cicle-ring ozonide (POZ) and four sets of carbonyl-oxide Criegee Intermediates and carbonyl products. Two transition states were identified associated to the formation of the two primary ozonides. The rate coefficients for each reaction path were calculated using the activation free energies and the VTST method. A total rate coefficient of 7.90 x 10^{-17} cm^3 $molecule^{-1}$ s^{-1} was calculated for O_3 addition to l-limonene. The result is in good agreement with the experimental value of 2.01 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} for a mixture of d- and l-limonene. The ·OH radical addition to the double bonds was also calculated. Four transition states were identified as associated with the formation of the adducts which lead to four competitive pathways. The total rate coefficient was estimated as 1.40 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. This value is ten times higher than the experimental rate coefficient, indicating that a further refinement of the calculations is needed. Considering that atmospheric ·OH radicals and ozone concentrations about 2.0 x 10^6 molecule cm^{-3} and 7.0 x 10^{11} molecule cm^{-3}, respectively, it can be concluded that the hydroxyl radical addition to the limonene double bonds is the predominant reaction path.

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"Formation of Frenkel's J aggregates from zinc phthalocyanine: a m06 approach"

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Key-words: Density Functional Theory (DFT), J aggregates, Zinc phthalocyanine, m06 hybrid functional.

The development of new materials has received much attention. Particularly, our studies have focused on metal-phthalocyanines (MPc's), due to their technological and medical applications [1]. Experimental studies have suggested that MPc's, under certain conditions, can behave as type J Frenkel's aggregates [1,2]**.** In this communication, we report studies on the possibility of stacking between molecules of zinc phthalocyanine (ZnPc) and understanding of the photophysics of such composites at different levels of aggregation. Initially full structure optimization and frequency calculations were done for the monomer (ZnPc), its dimer, trimer and tetramer. The molecular orbitals involved and the energy first electronic singlet and triplet excited states were calculated. All calculations were based on Density Functional Theory (DFT) and its time-dependent version (TD-DFT) using the m06 hybrid functional [3], the 6-31g(d,p) atomic basis set, and simulating the solvation of such systems in DMSO using the Integral Equation Formalism implementation for the Polarized Continuum Method (IEFPCM) [4]. By the results it was established that ZnPc, when aggregated, tends to behave as type J Frenkel's aggregates. The loss of intensity (estimated by the decrease in oscillator strength) of the transition corresponding to the Q band, the degeneracy loss between the two first two singlet excited states, and the strong bathochromic shift of the Soret band are aspects often reported in the literature to describe systems that behave as type J aggregates, has been observed in the systems studied. The analysis of the frontier molecular orbitals and maps of electrostatic potential suggest the occurrence of strong charge transfer interactions between the macrocycles in the aggregates which corroborates with the possibility of charge transport between ZnPc excitons [2].

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[2] KÖHLER, J. and DANKWARD, S**., J. Phys. Condens. Matter,** p. 115–141, 1996.
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Support: **CNPQ, CAPES** and **FAPEMIG.**

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"Computational study of the temperature dependence of side-chain solvation: implications for protein thermal stability"

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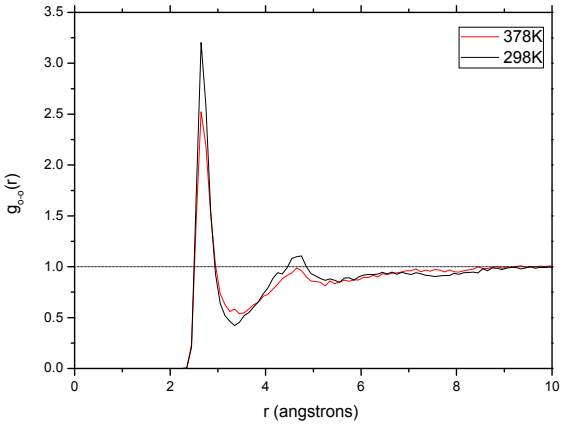
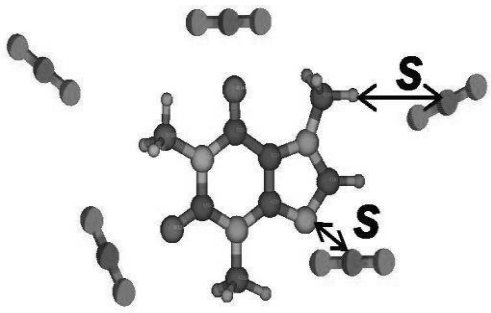
Key-words: Molecular Dynamics, Solvation, thermostability

The study of thermophilic proteins and factors that enhance their stability are of particular interest because it allows for the comprehension of protein folding and raises the possibility of engineering enzymes with enhanced thermal stability and catalytic efficiency for industrial application. Thermostable proteins have advantages for industrial applications since biotechnological processes conducted at high temperatures are usually faster and have significantly reduced risk of contamination [1]. The factors that have been suggested to play a role in the thermostability of proteins are the increase in the number of salt bridges, and a more compact hydrophobic core [2]. However, the comprehension about the factors responsible for the stability of thermophilic and hiperthermophilic proteins is, still, incomplete [1].

This work seeks the understanding of the role of the solvation on protein thermal stability. In order to achieve this, we propose the study of the solvation of amino acids present in the surface of thermostable proteins using classic molecular dynamics simulations at varying temperature. The first step in our analysis involves the simulation of free amino acids and small peptides with sequence AXA and AAXAA (where X is an electrostatically charged residue and A is an Alanine) in aqueous solution. The solvation structures are analyzed through radial pair distribution functions $g_{ij}(r)$, and solute-solvent distribution functions, $g_{ij}^{ss}(s)$ [3]. Subsequently, we study the temperature dependence of free energy change associated with mutations among amino acids using free energy perturbation methods (FEP).



(a)



(b)

Figure 1: (a) Radial distribution function, $g_{o\text{-}o}(r)$ for the interaction between the oxygen from the carboxylate group in the side chain of glutamic acid and oxygen from water in two different temperatures. (b) Diagram showing the variables used to determine the function $g_{ij}^{ss}(s)$.

Support: FAPESP/CNPQ

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On the relationship between ionization energy differences and electron pair repulsion in A–H bonds of AH_n molecules

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Keywords: ionization energy, bond critical points, equivalent bonds.

The chemical bond is a fundamental concept in chemistry that has provided an important basis for rationalizing the structure, properties, stability and reactivity of molecules and materials. In this work, we aim to find a relationship between the differences of ionization energies (ΔE) and the interaction energy (V) between the charge densities (ρ_c) at the bond critical points. The molecular structures of BeH_2, BH_3, BH_2^+, BH_4^-, AlH_3, AlH_2^+, AlH_4^-, CH_4, CH_3^+, SiH_4, SiH_3^+, NH_3, NH_4^+, NH_2^-, PH_3, PH_4^+, PH_2^-, H_2O, H_3O^+, H_2S e H_3S^+ were obtained with the MP2 method with the cc-pVTZ and aug-cc-pVTZ basis sets. The ionization energies were obtained with the electron propagator OVGF method with the same basis sets. The bond critical points properties, position and charge density, of the A–H bonds were obtained at the RHF, B3LYP and MP2 levels with the same basis sets. In Figure 1 we present a correlation between the values of ΔE (the difference between the ionization energies associated with the A–H bonds) obtained at the RHF/aug-cc-pVTZ level with $nVx10^3$, where n is the number of equivalent bonds and V is calculated as the ρ_c^2/r with r being the distance between the bond critical points.

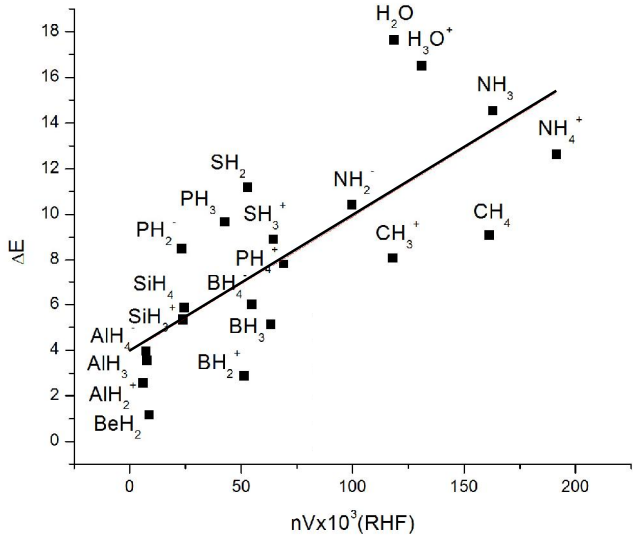

Figure 1. Relation between ionization energy differences and bond electron pair repulsion ($nVx10^3$) for AH_n species. R^2 = 0,56 for linear correlation.

Support: CNPq, CAPES, FACEPE, FINEP, PRONEX, INAMI.

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Kinetic study of the isomerization reaction between cyanopolyynes and isocyanopolyynes

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Keywords: transition state, activation energies, enthalpies of reaction

Cyanopolyynes constitute a series of linear molecules, whose general formula can be expressed by HC_nN (n=1, 3, 5, ...). Nowadays, these molecules are being found in the interstellar medium, where $HC_{11}N$ is the largest of these detected molecules. In contrast, isocyanopolyynes, of general formula $HC_{n-1}NC$, are still scarcely studied. Only the first two members of this series, HNC and HC_2NC, were observed in the interstellar medium. It is possible to find theoretical studies that treat HC_4NC and HC_6NC, but a few electronic properties of these molecules are calculated. Because of that, the intention of this work is to obtain the transition state geometries, activation energies and enthalpies of isomerization reactions from cyanopolyynes to isocyanopolyynes, for n=1 to 9. All calculations were carried out at MP2/cc-pVTZ level by the Gaussian 03 package.

Following the isomerization reaction path, the cyanopolyynes reach their transition state geometries with a kind of "triangular structure" formed by the nitrogen and the other two atoms closest to this end in such cyanopolyynes. Consequently, the activation energies of forward and reverse reactions can be determined and their values are seen in the table below. One can observe that the activation energies of both direct and inverse reactions do not necessarily increase in line with the chain size. Moreover, the isomerization reaction enthalpy values, at 298.15 K, seem to reach a limit as the carbon chain grows.

Table: Energies of activation and forward isomerization reaction enthalpies between cyanopolyynes and isocyanopolyynes at 298.15 K.

Reaction	***Activation Energies (Kcal/mol)***		***ΔH_{for} (Kcal/mol)***
	Forward Reaction	**Reverse Reaction**	
HCN -> HNC	49.5	31.6	18.0
HC_3N -> HC_2NC	69.9	38.5	31.5
HC_5N -> HC_4NC	69.7	37.4	32.4
HC_7N -> HC_6NC	69.7	37.3	32.5
HC_9N -> HC_8NC	70.2	37.6	32.6

The positive values for enthalpies, in all the reactions mentioned, indicate that the forward reactions are endothermic. The rate constants for forward reactions are around 10^{-23} s^{-1} (n=1) and 10^{-38} s^{-1} (n=3 to 9) at 298.15 K. On the other hand, the reverse isomerization reactions present a rate constant around 10^{-10} s^{-1} for n=1 and about 10^{-14} s^{-1} for the reactions with n=3 to 9 at the same temperature. Considering the fact that the reverse reactions are exothermic and show rate constants larger than the ones for forward reactions, it is possible to conclude that the reverse isomerization reactions are more favorable to occur in the interstellar medium.

Support: CNPq, CAPES

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"Novel AMBER99-consistent Force Field for Linear Perfluoroalkanes and Perfluorodecalins"

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Key-words: Molecular Dynamics, AMBER99, perfluoroalkanes

Perfluoroalkanes – alkanes in which the hydrogen atoms are replaced by fluorine atoms – are potential candidates for artificial blood and liquid ventilation therapy agents, due to its elevated capacity of solvation of both, oxygen and carbon dioxide. To understand this solvation behavior, it is necessary to study at the molecular level interactions between perfluoroalkanes and the respiratory gases. In the present work, we focus on the physical chemical properties of the pure perfluorinated liquids employing Molecular Dynamics computer simulations. This tool permits a detailed study at molecular level study furnishing the time evolution of the investigated system.

The simulations have been carried out by the Gromacs 4.0 software package applying the AMBER99 force field. Monitoring physical chemical properties of the pure liquids, such as density (ρ) and enthalpy of vaporization (ΔH_{vap}), as obtained from the standard AMBER99 force field, we observed deviations up to 20% from experimental findings. Thus, a careful reparameterization of the intermolecular potential parameters has been performed. We decided to treat only the fluorine atoms maintaining parameters for the very common tetrahedral carbon atoms unchanged. Atomic charges were calculated for individual molecules following the AMBER recipe via RESP methodology. Varying systematically the Lennard-Jones parameters of the fluorine atom in a series of 11 liquid perfluoralkanes (the linear C_2F_6-C_9F_{20} and *cis*- and *trans*-perfluorodecalin), we failed to establish a uniform parameter set leading to small erros in ρ and Δh_{vap}. However, if we define separate atom types for terminal and internal fluorine atoms (F1 and F, respectively), we succeeded with the Lennard-Jones parameters σ=0.3150 for the F and F1 atoms as well as ε=0.217 kJ.mol^{-1} for F1 and 0.155 kJ.mol^{-1} for the F atoms. This set of parameters produces largest deviations of 6% with the mean deviations of 3,3% and 4% for ρ and $\Delta h_{vap,}$ respectively, in the liquids composed by the selected perfluoroalkanes.

Support: Capes, CNPq and FAPERGS.

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Prediction of Boron-Phosphorous nanographene-like material

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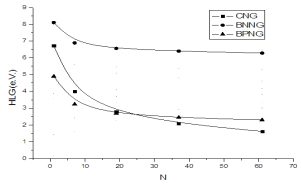
Key-words: CNG, borazine, BNNG, boraphosphabenzene, BPNG,

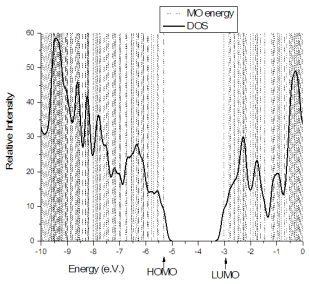
HOMO-LUMO gap, DFT calculation

Nanographene based on Boron-Phosphorous was characterized theoretically (DFT/B3LYP/SVP and TZVPP) by IR, Raman and UV-visible spectroscopies and other microscopic properties. Comparative studies among boron-phosphorous nanographene (BPNG), carbon one (CNG), and boron-nitrogen (BNNG) suggest that is experimentally possible to obtain the BPNG.

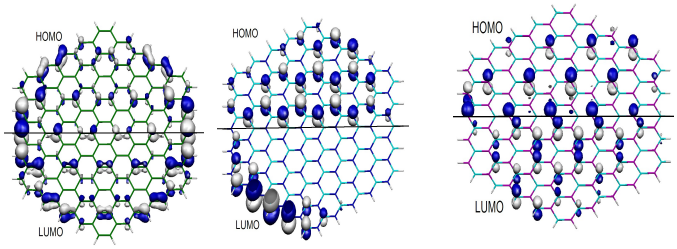
There are several electronic similarities among BPNG, CNG, and BNNG. The CNG, BNNG, and BPNG studied have circulene-like structure with D_{6h} and D_{3h} symmetries for carbon and boron compounds, respectively. The HOMO-LUMO gap (HLG) was obtained and compared for several sizes of those nanographenes.



It is expected that compounds based on BP present intermediary properties in between the CNG and BNNG due to electronegativity difference. The Density Of State (DOS) for BPNG is given below.



The HOMO and LUMO for CNG, BNCG, and BPNG are given below, respectively.



The BPNG can be promising material to obtain nanodevices, its HLG is near to red/VIS region and it is probably as stable as BNNG.

Support: FAPESP.

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QSAR studies of compounds whith oxadiazole larvicidal activity against the mosquite *Aedes aegypti*.

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Key-words: larvicidal activity, QSAR e Oxadiazole.

Oxadiazoles derivates may have activity against larvae of the mosquito *Aedes aegypti.* The intensity of this activity, in turn, depends not only on the nature of the substituent on the phenyl ring, as well as its location. Bioassays larviciding done by the group of professor Daniela Navarro[1], UFPE, showed that in *para*-position to phenyl ring, a substituent such as bromine has an LC50=15,20 ppm, while for the chlorine in the same position LC50=28,10 ppm. To better understand this dependence, we have performed a study of quantitative structure-activity relationship in 9 oxadiazole derivates. Molecular orbital calculations semi-empirical AM1 e DFT with the functional B3LYP/6-311G (d,p), were performed to obtain the electronic properties of these derivates.

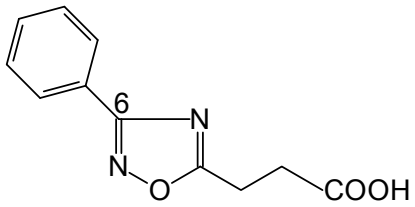

Figure 1: Parent compound and the oxadiazole series studied

The AM1 results have indicated that the more negative the energy of the LUMO and the more positive descriptor π^2, will be most active compound. B3LYP calculations have shown that the activity is better correlated with the charge of the carbon atom 6 of the oxadiazole ring, besides the empirical π^2, i.e., more positive the charge of carbon atom 6 (Figure 1) and more positive the value of π^2, will be the most active compound. The R^2 values for the QSAR equations obtained from AM1 e B3LYP are 0,89 and 0,96 respectively. From these QSAR studies was possible to design new derivates potentially more active which are now being tested in the laboratory.

[1] Neves, R. A. W. F. *et al*; *Chem Pharm. Bull*. **2009**, *57*, 819-825.

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"Glass transition and crystallization of ionic liquids."

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Key-words: ionic liquids, ab initio calculations, Raman spectroscopy.

Salts with low melting point, the so-called ionic liquids, have attracted great interest in recent years due to various applications, e.g. alternative solvents in organic synthesis, and electrolytes for batteries. Several ionic liquids are viscous systems, so that they are easily supercooled with typical glass transition temperature at *ca.* 190 K. In this work, we highlight ionic liquids based on imidazolium, pyridinium, and alkylammonium cations, which can be studied in supercooled liquid, vitreous, and crystalline phases. Structural aspects of different phases of these systems were investigated by Raman spectroscopy and *ab initio* quantum chemistry calculations. The spectra were studied within the low wavenumber range, ω < 200 cm^{-1}, in which relaxation and intermolecular vibrational modes are coupled with relative contributions that are strongly temperature dependent. The high frequency range due to normal modes of the ionic species, *i.e.* intramolecular dynamics, was also studied. Shift of vibrational frequencies, change in band shapes, and relative intensities, between liquid and solid states, unravel modifications of the local environment experienced by the ions. For instance, Figure 1 shows Raman spectra of 1-butyl-2,3-dimethylimidazolium tetrafluorborate, [bmmim]BF_4. The detailed analysis of the Raman spectra requires *ab initio* calculations in order to assign the vibrational frequencies and get insight on ionic arrangements. This work evaluates the importance of hindered nucleation and crystallization on the glass transition of supercooled ionic liquid.

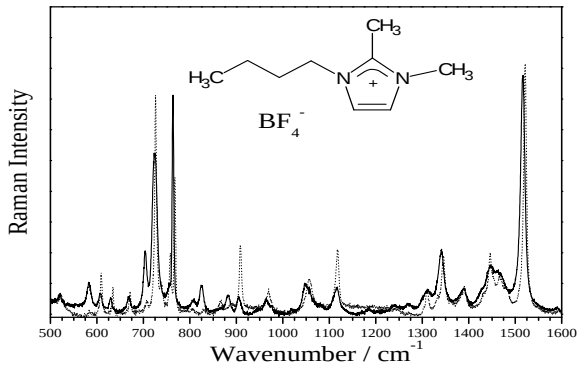

Figure 1: Raman spectra of ionic liquid [bmmim]BF_4 within the 500 < ω < 1600 cm^{-1} range. Full line corresponds to Raman spectrum of the liquid at room temperature, and dotted line to the supercooled liquid (250 K) in which crystal formation is observed.

Support: FAPESP, CNPq.

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"Influência das hidroxilas secundárias na ligação glicosídica em dissacarídeos"

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UFRuralRJ/ ICE/ DEQUIM – BR 465 Km 47, 23890-000 – Seropédica- RJ

Key-words: Análise conformacional, celobiose, hidroxilas secundárias.

Investiga-se neste trabalho como a posição das hidroxilas secundárias na geometria de partida afeta a geometria final e a abundância relativa dos confôrmeros amostrados em mapas conformacionais obtidos para dissacarídeos. Estudos recentes[1] mostram que confôrmeros que diferem entre si somente na conformação destes grupos exocíclicos ao anel podem apresentar diferenças de energia de até 18 kcal/mol.

Com este intuito, foram construídos três mapas conformacionais para a celobiose[1] usando metodologia em nível B3LYP/6-31+G(d,p). Cada mapa conformacional foi construído usando uma única geometria de partida. As três geometrias de partida utilizadas (uma para cada mapa) diferem entre si pela orientação das hidroxilas secundárias, porém escolhidas de modo que o efeito de cooperatividade estivesse presente[2]. Posteriormente, amostragens de confôrmeros nas regiões de energia mínima e para as diferentes orietações dos grupamentos hidroximetilênicos foram efetuadas, para investigação da influência das hidroxilas secundárias sobre as profundidades das regiões de energia mínima encontradas (abundância relativa).

As regiões de energia mínima, independentemente do mapa conformacional (e portanto da geometria de partida), mostraram-se as mesmas tanto em número quanto em posição. No entanto, as profundidades relativas dessas regiões são diferentes (são as profundidades dos poços que definem a abundância relativa).

Os confôrmeros encontrados nas regiões de energia mínima foram amostrados para os três mapas. A orientação das hidroxilas secundárias na geometria de partida não afeta a determinação da conformação glicosídica dos confôrmeros mais estáveis. Porém, a conformação das hidroxilas secundárias deve ser considerada e amostrada, pois esta afeta a abundância relativa de cada um dos confôrmeros que possui conformação glicosídica representativa.

Os autores agradecem à FAPERJ e ao CNPq.

[1] French, A; Johnson, G. P., *Mol Simulation* **2008**, 34, 365
2 Klein, R. A., J. Am. Chem. Soc. **2002**, 124, 13931

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"Computer Simulation of Porous Materials for Removal of Sulfur Compounds in Fuels"

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Key-words: Zeolite, Monte Carlo, Dessulfurization, ONIOM method.

Adsorption isotherms, structures and energies of aromatic (thiophene) and aliphatic (propanethiol) sulfur compounds adsorbed in fausajite zeolites NaY, Cu(I)Y, Ag(I)Y and HY were studied.

We observed that the calculated adsorption energies are in good agreement (differences < 2 kcal/mol) with the available experimental results and increase in the following order: $H^+ < Na^+ < Cu^+ < Ag^+$. These results agree with the formation of π complexes between thiophene and transition metals. The same trend was obtained for propanethiol and in this case we observe formation of S–metal complexes (hard-soft acid-bases type interactions).

We proposed two new clusters to model the zeolite environment: Z40 (1161 atoms) and 2Cages (517 atoms). These models were able to distinguish several adsorption modes and showed that the choice of an appropriate model to represent the zeolite environment is very important not only to provide energies but also the structures of adsorbed molecules. These results were obtained with the ONIOM (PBE1PBE/6-31G(d,p):UFF=QEQ) and for transition metals we used the LanL08f basis sets.

We performed GCMC simulations for these zeolites and obtained good agreement with the available experimental results (differences ≈1 mmol/g) without the need for unusual atomic charges or fitting experimental curves.

Support: FACEPE, CNPq, CAPES, PRONEX, FINEP, Inct-INAMI.

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"Stokes Shift of Uracil in Aqueous Environment"

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Keywords: CASSCF, Stokes shift, S-QM/MM, Uracil

Nitrogenated bases, despite the high electronic absorption, have a low quantum yield. Current studies indicate that this occurs mainly due to the coupling of near excited states by *pseudo-Jahn-Teller effect* and the existence of conical intersections, which allow non-radioactive decays. Biologically, this is very desirable because the lifetime of the excited state decreases, becoming the order of a few tens or hundreds of femtoseconds, drastically reducing the possibility that potentially dangerous photochemical reactions occur.

Although these molecules present their full phenomenology in environment, most studies are carried out with isolated molecules or using microsolvation. This is because a huge computational effort is needed to obtain the geometry of a molecule in the excited state using multiconfiguration methods, like CASSCF.

In this work, to account for the solvent effect in the absorption and emission spectra, we used the *Sequential-Quantum Mechanics/Molecular Mechanics methodology* (S-QM/MM) to calculate the Stokes shift of Uracil in water. Monte Carlo simulations are performed to generate statistically uncorrelated configurations to represent the liquid on which the quantum mechanics calculations are carried out. The theoretical results are in good agreement with the experiments, showing deviations of ~6% from the experimental values.

Acknowledgments: This work has been partially supported by FAPESP, CNPq, CAPES, INCT-FCx and nBioNet (Brazil).

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Relativistic Study of Lanthanide Hexachloride Systems

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Key-words: Relativistic, Lanthanide, Transitions.

The luminescent properties of lanthanide systems, like elpasolites $A_2BMX_6:Ln^{3+}$ are of great interest due to its applicability in the development of optoelectronics devices[1].

In this work we study the octahedral systems $[LnCl_6]^{3-}$ using the ADF software with the two-component ZORA Hamiltonian in order to consider the scalar and spin-orbit effects and the TZ2P basis set. The geometry optimizations energy transitions, orbital compositions and EPR calculations were performed using LDA, PBE, PW91 and BP86 in order to determine which describes more correctly these properties. The geometry obtained was used in the four-component DSW-SCF code to calculate the same properties.

The optimized geometries are in agreement with experimental results for $[CsNaLnCl_6]$ elapsolites[2]. Scalar and Spin-Orbit effects show the same trend but in gas phase the bond length "Ln-Cl" are overestimated, but when we consider the cluster embedded effect the results are better. All GGA functional show the same results but the LDA functional show better results compared with the experiment.

Energy transitions were done using spin-orbit relativistic effect and PBE functional. In the Cerium case the 4f-4f and the 4f-5d transitions are in agreement with experimental results and the embedded cluster does not have any effect in these transitions, while in the Ytterbium case the transitions are not in agreement with the experimental in both cases, phase gas and embedded cluster. In the case of EPR data, we observed similar results for Cerium and Ytterbium systems.

Calculations made with DSW four components for these systems in gas phase show better results for energy transitions and EPR data, this is because the small component have fundamental role in the description of "f" orbitals and its optical and magnetic properties.

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Support: We thank Fondecyt 1110758, UNAB-DI-17-11/R, UNAB-DI-27-10/I projects for funding this work, and FF thanks Conicyt for a graduate fellowship No 63100013.

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On the route of D-mannose conformations

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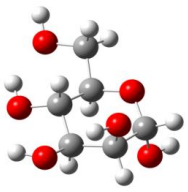
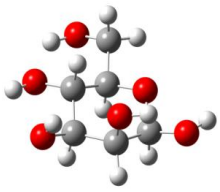
Key-words: D-mannose, B3LYP, monosaccharide

In this work we intend to select the more stable conformers of D-mannose in aqueous solution at room conditions. We started from two initial conformations for each anomer (α and β)[1], that maximize the cooperativity effects. From each optimized structure, 729 conformers were built through rotations of 120° in the dihedral angle of each hydroxyl, starting from the respective initial geometry, generating a total of 1458 conformations.[2] Single point energy calculations using a B3LYP/6-31G* description were performed for all of them. Then, we have selected conformers which have presented energy up to 8 kcal/mol higher than the global minimum (28 for α anomer and 17 for β anomer). Geometry optimization calculations were performed for such selected conformations, and thermal and entropic corrections were introduced. Selecting those conformers with Boltzmann population values greater than 1%, we have obtained a 50.96:44.16 proportion (α:β). This result follows the trend of the experimental data (65.5:34.5 (α:β))[3], found for the system in a solvent with a very low dielectric constant. The solvation of conformers is in progress.

α-mannose

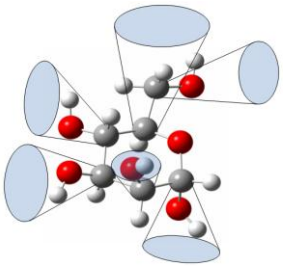


β-mannose



Starting geometry

3x3x3x3x3x3=729



Possible orientations for the hydroxyl groups

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Support: CNPq and FAPERJ.

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"Bioctive Molecules in Phospholipid Monolayers"

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Key-words: molecular dynamics, picolinamide, nicotinamide, lipid monolayers

The elucidation at molecular level of the interactions of bioactive species with phospholipid constituents of biological membranes are of fundamental importance for the description of their mechanisms of action. Among bioactive species, those containing nitrogen atoms are of particular importance due to its direct function or as constituents of nucleic acids. Picolinamide (2-pyridinecarboxamide, PA) and nicotinamide (3-pyridinecarboxamide, NA), shown in Figure 1, are two well known bioactive isomers of pyridine-carboxamide which were found to take part in many important biological processes.

In this work, we study the interaction of NA and PA with lipid monolayers, through Molecular Dynamics simulations. This kind of interactions strongly depends on the lipid head. In this way we take into account two phospholipids: 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and 1,2-dimyristoyl-sn-glycero-3-phosphoethanolamine (DMPE). In order to recreate experimental conditions given in Ref. 1 we simulate a high guest molecule:lipid relation (1:3).

Our results for the DMPC monolayers show that both NA and PA molecules are essentially found at the lipid/water interface and strongly interact with the lipid polar headgroups. Not significant differences were found between these bioactive species with DMPC monolayers, in good agreement with experimental results. By the other hand, dipole potential experiments had shown significant differences between the interaction of NA and PA with DMPE monolayers. Simulations of these systems are in progress. Besides preliminar results shows that the DMPE monolayers are more affected by the PA than the NA bioactive molecules.

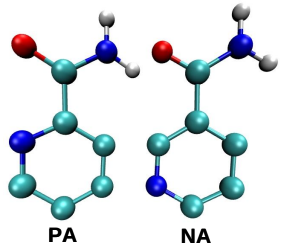

Figure 1. *Structures of Picolidamide (PA) and Nicotidamide (NA)*

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Support: UBA, CONICET and ANPCyT.

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Electronic transitions in local impurity states contained in host ionic lattices allowed by vibronic coupling

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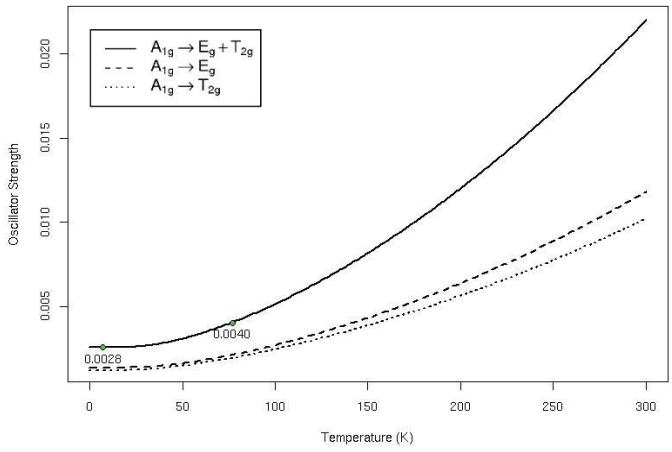
Key-words: Optical oscillator strength, excited states, embedded clusters

Formally forbidden by dipole selection rule, but allowed by vibronic coupling mechanism, electronic transitions of the d→s type, in Cu^{+} and Fe^{2+} impurities in sodium fluoride (**NaF**) and magnesia (**MgO**) respectively, are investigated. The selection rule for these transitions can be broken through vibronic coupling mechanism with vibration modes of suitable symmetry. A method to treat this kind of problem has been presented in a previous work, where a similar system was studied [1].

We have used an embedded cluster model [2] to describe the system. The model was tested with respect to several parameters, such as: cluster size, number of point charges to simulate long range potential, atomic basis set, impurities nearest neighbour equilibrium distance, excitation energy, frequency of normal modes and optical oscillator strength (**OOS**). Several methods have been used (**RHF**, **DFT**, **CASSCF**, and **MR-CI**). The main goal here is to apply, in this problem, a method we have developed to calculate the OOS, which takes vibronic coupling into account [1].

Below we show the graph of the dependence of OOS with temperature for Cu: NaF.



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"GIAO-B3LYP low computational cost scaling factor for 13C NMR chemical shifts calculation"

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Key-words: *nor*-β-lapachone, NMR, GIAO, scaling factor

Although the application of NMR techniques to the determination of the relative spatial orientation of substituents has become a routine task in modern organic chemistry, it is not an easy one. In this scenario, advanced computational protocols have been developed for calculating NMR parameters as an efficient alternatively with low computational task which is able to achieve promising outcomes.[1] In this study, using *Density Functional Theory* (DFT) and the GIAO method (*Gauge Including Atomic Orbitals*), we present a universal scaling factor to determine the NMR ^{13}C chemical shift (δ), which achieves good accuracy in reproducing experimental data with very low computational effort. Geometry optimizations were performed using PM6 and B3LYP/DGDZVP level of theory. NMR δ were computed at the B3LYP with DGnZVP (n = D or T) level using the GIAO method. The scaled δ values (δ_{esc}) were determined using the equation: $\delta_{esc} = a.\ \delta_{cal} + b$, where a and b are the linear regression coefficients obtained from the calculated δ values (δ_{cal}) *versus* the experimental data.[2] In order to verify the applicability of these linear scaling factors, we have chosen the δ calculation of quinoxaline from *nor*-β-lapachone. The determination coefficients (r^2) were between 0.995 to 0.998, which shows a good reproducibility of experimental values. To statistically validate this protocol, we have used r^2 (coefficient of determination), MAD (Mean Absolute Deviation) and RMS (Root mean Square). After scaling of the chemical shifts, both MAD and RMS errors have become smaller. Among the theory levels used to determine the δ_{esc}, GIAO-B3LYP/DGDZVP//B3LYP/DGDZVP ($\delta_{esc} = 0.96.\ \delta_{cal} - 1.59$) has shown the best results, with MAD (1.28) e RMS (1.55). As a result, the scaled factor at GIAO-B3LYP/DGDZVP//B3LYP/DGDZVP level of theory proved to be a potential tool to determine the ^{13}C RMN chemical shifts in this class of organic compounds.

Support: CNPQ

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Photoabsorption Spectroscopy of DMSO at the C 1s, S 2s, O 1s and S 2p regions: a comparison with Acetone.

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Key-words: DMSO, Acetone, NEXAFS, inner shell

Dimethyl sulfoxide (DMSO) is often used as a solvent in laboratories and industries because its great coordination and solvation power. It has a large application in organic reactions due to its great selectivity and stability, even at its boiling point (189^0C). All these characteristics make the DMSO of great interest in spectroscopy studies involving inner shell techniques, as for example the electron energy loss spectrocopy[1]. In this work gas phase total ion yield (TIY) DMSO spectra at S 2s, C 1s, O 1s and S 2p edges are discussed. The experiments have been performed using the Toroidal Grating Monochromator (TGM) beamline at the Brazilian Synchrotron Light Laboratory (LNLS). The assignments were carried out using the improved virtual orbital (IVO) methodology presented in the GSCF3 (Hartree-Fock) and Stobe (DFT) packages. The hole state were calculated with Huzinaga and III-IGLO basis sets. A nonlocal BE88-PD86 DFT method was used. The geometric parameters were calculated using the B3LYP method with 6-311+G** basis sets. The results reflect the difference between the presence of the S=O (symmetry Cs) and C=O (symmetry C2v) groups. The experimental and theoretical results of both ionization potentials and threshold energy are quite similar, confirming the good quality of the carried out calculation, as presented in table 1. These results are compared with acetone at the *K* edge.

Table 1. Some theoretical and experimental NEXAFS data obtained for DMSO.

Inner Shell	Experimental I.P. (eV)	Theoretical I.P. (eV)	Experimental Edge (eV)	Theoretical Edge (eV)
C 1s	291.24*	292.14	287.5 / 288.9	288.7 / 290.4
O 1s	536.67*	537.52	532.6	533.9

*ref: 1

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Support: UFRJ, UFF, LNLS, FAPERJ.

A quasi-classical trajectory study of the OH + SO reaction: The role of vibrational energy

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Key-words: reaction dynamics; molecular energy transfer

A study of the reaction OH +SO using the quasi-classical trajectory method [1] is presented with the aim of investigating the role of the vibrational energy of the reactants in the reactivity. As before [2], calculations were carried out using MERCURY program combined with a previously reported global potential energy surface for $HSO_2(^2A)$ [3]. Different energetic combinations with one and both reactants vibrationally excited were studied. The reactive cross sections, for each combination, are calculated a then fitted to a capture-like model combined with a recrossing factor [4]. Reactivity is affected as vibrational energy is changed. This fact provides a theoretical support for the experimental dependence of the rate constant on temperature.

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Support: Programa BIC/UFJF

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Theoretical Study of Proton Affinity of 1,2,3,4-thiatriazole-5-thiolate Ion

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Key-words: theoretical chemistry, proton affinity, 1,2,3,4-thiatriazole-5-thiolate ion

1,2,3,4-thiatriazole-5-thiolate ion is a pseudo-halide useful in analytical chemistry,[1] as complexing agent,[2] and as a selective catalyst for oxidation reactions of sulfur (IV) to sulfur (VI).[3] Using the Gaussian 03W software package, Hartree-Fock calculations; DFT, through the hybrid functional of density B3LYP; and second-order Møller-Plesset (MP2) were performed to describe the site of greatest proton affinity of an 1,2,3,4-thiatriazole-5-thiolate ion (Figure 1). The basis function used was 6-311G(d)++ computed for all methods. As the partition of charges is not an observable, each scheme to obtain charges may point in a different direction. Mulliken charges, obtained through different methodologies, point as the most likely protonation center the sulfur atom 6S (Figure 1), due to higher concentration of electron density. However, the charges derived from NBO (Natural Bond Orbital) calculations show the nitrogen atom 3N (Figure 1) as the center of higher proton affinity, except for the Hartree-Fock method, which showed a light preference for the nitrogen atom 5N (Figure 1). The comparison of energy between the structural forms thione and thiol indicate that the NBO charge partitioning in this case matches best with the energetic description of the protonated system.

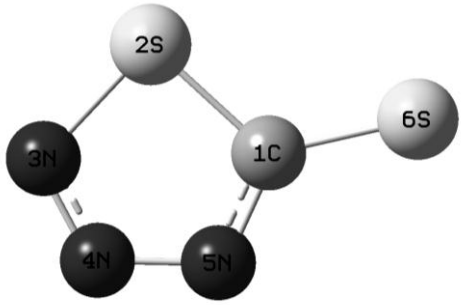

Figure 1. Optimized structure [B3LYP/6-311G(d)++] of 1,2,3,4-thiatriazole-5-thiolate ion.

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"A prototype for phospholipids in cell membrane"

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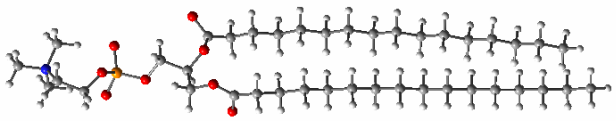
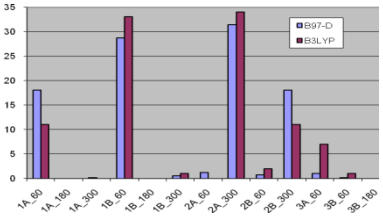
Key-words: Phospholipids, choline, dispersive interactions.

In this work our goal is to obtain a prototype for phospholipids in cell membrane, in order to evaluate quantitatively the interaction energy between a disaccharide and the phospholipidic membrane. To this purpose it is necessary the evaluation of dispersive interactions between the aliphatic chains of the phospholipids, which should be further discounted from the whole interaction energy found. Due to the differences in chemical nature of the hydrophilic and hydrophobic fringes of phospholipids membrane, we are using a methodology based on the B3LYP functional and a specific functional including dispersive interactions (B97-D). We present some preliminary results to the study of both fringes for a choline phospholipid. We decided initially to study both fringes separately due to the already mentioned difference in chemical nature of them. We conclude that the use of a specific functional for dispersive interactions does not change significantly the geometrical and energetical descriptions obtained at the B3LYP/6-31G** level for the hydrophilic fringe.

Hydrophilic fringe  Hydrophobic fringe

Hydrophilic fringe

Comparison of the relative occurrence (25°C, 1 atm) of conformations found as most abundant for the choline hydrophilic fringe[1,2]. No significantly changes were observed in the geometrical parameters that define the conformation of the system.



Hydrophobic fringe

Interaction energy (kcal/mol) for hydrophobic fringes consisting of dimers with eight (8C), nine (9C) and ten (10C) atoms of carbon, in two different approximation geometries – parallel and perpendicular. Calculations in B97-D/cc-p-DZV level.

Dimer	$E_{int}^{paralell}$	$E_{int}^{perpendicular}$
8C	15,99	13,95
9C	18,83	16,07
10C	20,32	17,48

Correction for BSSE is not included yet.

Support: CAPES e CNPq

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"Stability and electronic, structural and mechanical properties of functionalized silica nanotubes. A SCC-DFTB study"

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Key-words: nano-fibriform-silica, dimethylsilane derivatives, SCC-DFTB.

A new class of nano-fibriform-silica has been emerged from natural chrysotile through acid-leaching method[1]. In this process the brucite layer is removed and the remaining products (tridymite) stay in a nanotubular form. Thereby, the surface of these nano-fibriform-silica nanotubes can be functionalized with organic compounds with the aim to reduce the hydrophilicity of the inorganic material enhancing the interaction of the nanotube surfaces with polymers[2].

Stability, electronic and mechanical properties of the armchair tridymite nanotubes and the modified product by dimethyldichlorosilane have been investigated by using Self-Consistent-Charge Density-Functional Tight-Binding approach (SCC-DFB)[3]. All calculations were done by the DFTB+ code[4]. The stability of these derivatives in the zigzag and armchair chirality will be discussed. In table 1, the band gap (BG) and Young's moduli (*Y*) is presented for the armchair tridymite nanotubes. The Young's moduli of the tridymite nanotubes are in the same range as for the chrysotile and imogolite nanotubes.

Table 1. Internal radius (R), band gap (BG) and Young's moduli (Y) of the tridymite.

Type	Tridymite (n,n) nanotubes		
	R (Å)	BG (eV)	Y (GPa)
(8,8)	11.83	9.8	242
(14,14)	20.76	9.9	251
(16,16)	23.73	9.9	235
(18,18)	26.71	9.9	254

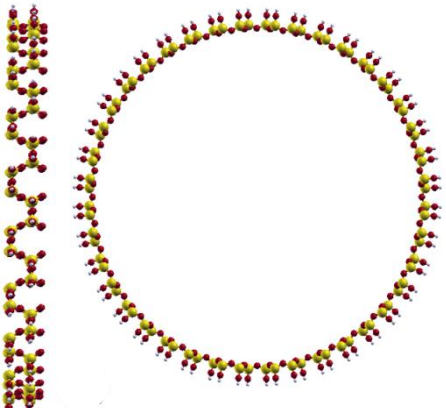

Figure 1. Top view and side view of the armchair nanotubes.

Support: CNPq, CAPES, FAPEMIG, INCT-ACQUA.

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Determination of the relative configuration of a triterpene using GIAO-HDFT calculated chemical shifts.

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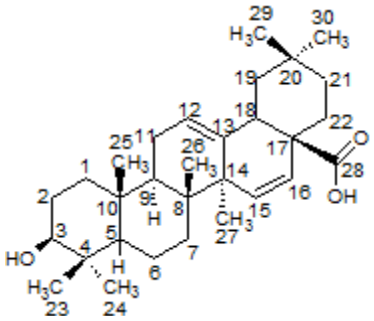
Key-words: triterpenes, NMR, GIAO, scaling factor.

Saponins isolated from *Chiococca alba* are believed to be active principles of this traditional medicinal plant, and there are several hypotheses that correlate the biological activities directly to their aglycone structures. Our goal in this study is to support the structure recently[1] proposed for one of these aglycones (figure) by calculation of ^{1}H and ^{13}C NMR chemical shifts using the methodologies of Baldridge *et al*.[2] and Costa *et al*.[3]



For this purpose, four diastereoisomers were constructed: (1) with 5β (up) and 9α (down) hydrogen atoms, (2) both H-5 and H-9 in α orientation, (3) both H-5 and H-9 in β orientation and (4) H-5 in α and H-9 in β orientation. All of these isomers were submitted to conformational searches using Monte Carlo method and the Merck molecular force field as implemented in the Spartan '08 software package. For each one of these isomers, the more significant conformations (with energies within 0.0–3.0 kcal.mol^{-1} range, accounting for more than 99.0% of the total Boltzmann weighed populations), were selected to energy minimization calculations carried out at the B3PW91/cc-pVDZ level of theory. Chemical shifts were then calculated at the GIAO-B3PW91/cc-pVDZ level of theory for the selected conformers, with population averaged with Boltzmann statistics based on B3PW91/cc-pVDZ free energies.

Through analyses of the ^{13}C calculated chemical shifts, we were able to conclude that isomer 2 is probably the isolated aglycone. Unfortunately, NMR ^{1}H calculated chemical shifts weren't sufficiently accurate to lead to any conclusion.

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Support: FAPERJ.

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"Theoretical study of imidazole adsorption on iron (001) surface."

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Key-words: Adsorption, iron surface, imidazole.

Although spontaneous, corrosion is commonly an undesirable process that should be controlled. Find ways to manage the process of corrosion is of great importance for the oil industry. One feasible way to control corrosion is through the use of corrosion inhibitors, which are substances that offer protection to the metal surface by making chemical bonds with it. It is well known that organic molecules containing electron donor atoms like nitrogen, oxygen or sulfur, act as corrosion inhibitors. Imidazole is one of such molecules. Its structure is described as an organic heterocycle containing two nitrogen atoms, one of them being of pyrrol and the other being of pyridine type.

The aim of this work is to study the adsorption of imidazole on the iron surface to better understand the mechanism of protection by a corrosion inhibitor in a metallic surface.

The methodology used in this work is the density functional theory using the PBE exchange-correlation functional, combined with periodic boundary conditions, plane waves basis set (Bloch's theorem) and pseudopotentials.

Initially, we have studied the preferred site of adsorption of a single imidazole molecule on the (001) iron surface. The imidazole bonded by nitrogen lone pair and having the ring plane perpendicular to the iron surface provided the lowest energy when localized on the top site of the surface. The case where imidazole is bound by the imidazolic ring - parallel position - provided the lowest energy when localized in the hollow site. The former is the most stable in absolute terms. The study was then extended to the adsorption of several molecules in order to describe the passivation film. It was found that there exists a cooperative interaction of adsorbed imidazole molecules.

Support: CNPQ, CAPES e FAPERJ.

Theoretical Study of the XP3 (X = Al, B, Ga) Clusters

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Key-words: molecular clusters, semiconductor clusters, Ab initio calculations, geometrical and spectroscopic characterization, complete basis set limit.

The lowest singlet and triplet states of AlP_3, GaP_3 and BP_3 molecules with C_s, C_{2v} and C_{3v} symmetries were characterized using the B3LYP functional and the aug-cc-pVTZ and aug-cc-pVQZ correlated consistent basis sets. Geometrical parameters and vibrational frequencies were obtained and compared to other results when possible. Relative energies were obtained with single point CCSD(T) calculations using the aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z basis sets, together with extrapolation to the complete basis set (CBS) limit. The main issue related to these species is the question of relative energy of their various isomers. The AlP_3 cluster has two lowest C_{2v} ($^1A_1$) and C_s ($^1A'$) states which are almost degenerate. In all calculations the C_{2v} state is the ground state, which is in agreement to most recent works, while the C_s state, calculated with CCSD(T)/aug-ccpV5Z and CCSD(T)/CBS methods are located above by, respectively, 1.7 and 2.0 kcal/mol. In relation to GaP_3, the singlet C_s ($^1A'$) is clearly the ground state, followed by C_{2v} ($^1A_1$), which is 4.7 kcal/mol above the ground state followed by the C_s ($^1A'$) (9.7 kcal/mol) and C_{3v} ($^3A_1$) (11.6 kcal/mol) states computed at the CCSD(T)/CBS level. The electronic ground state of BP_3 molecule was unambiguously characterized by the first time as a singlet C_{2v} ($^1A_1$) in both B3LYP and single-point CBS calculations using the CCSD(T) method. The first excited electronic state is the triplet C_{2v} ($^3B_2$) lying at 16.5 kcal/mol above the ground state. The next excited structures have symmetries C_{3v} ($^1A_1$) and C_s ($^1A'$), which are 23.3 and kcal/mol above the ground state. Other excited states were also characterized.

Support: CNPq, FAPESP.

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Computational study of thermal diffusion in thermostable proteins

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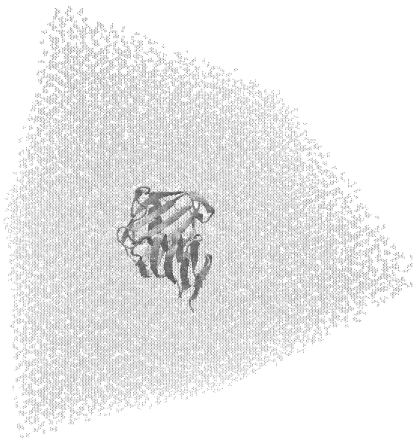
Key-words: Vibrational Energy Diffusion, Molecular Dynamics, Thermal Stability.

Mechanisms of vibrational energy diffusion in biomolecules have been related to stability, allostery and intramolecular signaling. Here we utilize a computational methodology to address energy flow in proteins. The study of thermal diffusion is done using Molecular Dynamics simulations, providing artifices which are not available experimentally: the whole protein is cooled to very low temperatures and only a residue is heated by coupling it to a thermal bath. Thus, the heat flows from the heated residue to the protein, revealing the pathways of vibrational energy diffusion. Because the thermostable proteins may have particular mechanisms of relaxation, distribution and dissipation of vibrational energy, they are interesting systems to which the methodology could be applied. From this analysis, a heat diffusion profile from a thermophilic protein can be identified and compared to another from analogous mesophilic protein, in special, from the Family 11 Xylanases. Importantly, by revealing the mechanisms of anisotropic thermal diffusion of thermophilic proteins, new approaches to rational developing of proteins with modulated stability and activity can be suggested.



Support: FAPESP/CAPES.

otential ner y Surfaces for ∑⁻ ∑ and A olecular Syste s

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Key-words potential energy surfaces, *ab initio* calculations, molecular dynamics.

A stract

Studies related to combustion processes have large interest on both economic and environmental issues. With this motivation, becomes necessary to analyze in detail systems involving Oxygen and Nitrogen, main components of earth atmosphere. Thus, potential energy surfaces for the systems O_2 ($X^3\sum_g^-$), N_2 ($X^1\sum_g$) and O_3 ($^1A_1$) are here studied. To represent such potentials, many-body [1] functional forms are proposed to properly fit the *ab initio* energies. Molecular structure calculations were carried out in the frame of GAMESS package [2] using Multi-Reference Second-Order Moller-Plesset Perturbation Theory (MRMP2) and Coupled-Cluster Method with Singles and Doubles Excitations (CCSD) levels of theory and Dunning basis sets, aug-cc-pVX (X D,T) [3,4]. Exploratory uasi-classical trajectory (QCT) [5] calculations using the obtained potential for O_3 will also be presented.

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Su ort Programa de Apoio ao Rec m Doutor PROPESQ FJF.

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"Evaluation of the Methods G3, CCSD(T), VQMC and DQMC with Electron Correlation in the Calculation of Successive Ionization Potentials for 1°, 2° and 3° - Rows Atoms."

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Key-words: Successive Ionization Potentials, QMC, G3 e CCSD.

Several theoretical methods have been used to adequately describe the electron correlation and provide high accuracy in atomic or molecular properties such as: the Quantum Monte Carlo (QMC) method, Gaussian-3 (G3), and conventional ab initio methods like Coupled Cluster (CC).[1]

The objective of this work is to study successive ionizations of the 1°, 2° and 3° rows atoms using different electron correlation corrections from the methods: Variational Quantum Monte Carlo (VQMC), Diffusion Quantum Monte Carlo (DQMC), Gaussian-3 (G3) and CCSD (T, E4T, full)/aug-cc-pVQZ).

The mean absolute deviations - MAD of table 1 show that G3 and DQMC are the most accurate methods. Both methods present the lowest total mean absolute deviation with a difference of 0.004 eV between them. The results for the 3° row atoms show higher deviations when compared to the 1° and 2° row elements. These larger deviations are possibly associated with the absence of relativistic effects and most appropriate basis functions for the 3º row atoms.

Table 1: Mean absolute deviations for the methods VQMC, DQMC, G3 and CCSD(T) (in eV).

Methods	1° e 2° Rows	3° Row	Total
VQMC	2.983	12.663	9.588
DQMC	0.423	1.912	1.433
G3	0.298	1.965	1.429
CCSD(T)	0.303	2.627	1.879

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Support: CNPQ, CAPES, FAPESP e FAEPEX-UNICAMP.

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Molecular positive ions in the gas phase: structure and stability of $C_2H_4O_2^+$ and $C_2H_4O_2^{2+}$ isomers

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Key-words: molecular ions, interstellar chemistry, DFT methods

Positive and negative molecular ions play an important role in many chemical processes, such as flame and plasma chemistry, industrial processing and in astrophysical environments. In this perspective, methyl formate, acetic acid and glycolaldehyde, all isomers molecules, are the first triad of neutral isomers detected in interstellar clouds. The stellar radiation could lead to the ionization and dissociation of these molecules, enriching the interstellar medium with several molecular ions, such as $C_2H_4O_2^+$, $C_2H_4O_2^{2+}$ and its dissociation products. However, the structure and stability of these ions are very few studied. From the experimental point of view, it has been established that the equilibrium structure of the molecular ions of esters, such as methyl formate, is characterized by presence of equivalent oxygen atoms, differing markedly from the neutral molecules.

The present work investigates the structure and thermodynamic stability of several $C_2H_4O_2^+$ and $C_2H_4O_2^{2+}$ isomers at their ground-state multiplicities. The geometry optimizations were performed using JAGUAR 7.6 program at the B3LYP/cc-pVDZ level. Single-point calculations at the equilibrium geometries were performed at the Left Eigenstate Completely Renormalized Coupled Cluster Method (CR-CCL) using the GAMESS package.

Ninety three minimum structures have been found: 55 related to $C_2H_4O_2^+$ and 38 to $C_2H_4O_2^{2+}$. Figure 1 shows the most stable isomer for $C_2H_4O_2^+$ (A) and $C_2H_4O_2^{2+}$ (B) ions. Structure (A) has equivalent oxygens, in agreement with the experimental results. In addition, methyl formate and acetic acid analogue structures were found only for the monopositive ion, but with higher energies. It is worth to emphasize that both most stable structures are significantly different from the most stable neutral isomers and, therefore, could not be found in a geometry optimization procedure starting from conventional structures.

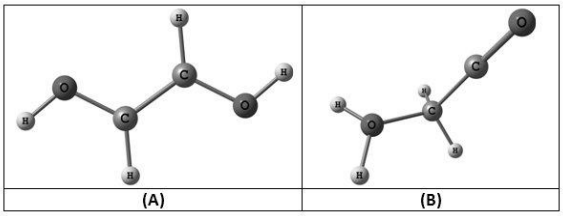

Figure 1 – Most stable structures of $C_2H_4O_2^+$ (A) and $C_2H_4O_2^{2+}$ (B) ions.

Fundamental vibrational intensities calculations at QCISD/6-31G(2d,2p) and MP2/6-31G(2d,2p) levels for BF_3

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Key-words: BCl_3, IR fundamental intensities, Pople basis sets.

Infrared spectroscopy has long stood out among chemical analysis techniques. Each band can be characterized by three spectral parameters, frequency, intensity and band width. These provide information about the behavior of molecular electronic structures during vibrational motions. The intensity value is proportional to the square of the variation of the molecular dipole moment during vibration[1], so the comparison of experimental and calculated intensities is a way to evaluate whether theoretical models are accurate in describing electronic structure changes. This work evaluated the electronic structure changes of boron trifluoride (BF_3), by analyzing the intensities of the infrared vibrational bands calculated using MP2/6-31G(2d,2p) and QCISD/6-31G(2d,2p) levels. The structures were optimized at the same levels of theory as used for their intensities calculations. The MP2 method showed better agreement with the experimental data (RMS error = 11.4 km mol^{-1}), whereas the QCISD method was slightly less accurate with a RMS error of 13.6 km mol^{-1}. These results show that both methods describe the changes in the electronic structures due to vibrational displacements with good quality, since there is an average error of about 8.6 km mol^{-1} associated with their experimental measurements[2]. It is also interesting to note that the carbonyl fluoride molecule (F_2CO), isoelectronic with respect to BF_3 and with similar geometry (trigonal planar, although not as symmetrical), presents a fundamental intensity sum of 851.7 km mol^{-1}, very closed to the sum for BF_3 (832.7 km mol^{-1}). This similarity is also found for the sum of the intensities calculated in the above cited levels, (MP2: 826.6 km mol^{-1} for F_2CO, 861.15 km mol^{-1} for BF_3; QCISD: 850.5 km mol^{-1} for F_2CO and 866.81 km mol^{-1} for BF_3), which shows that the electronic and structural similarities at equilibrium geometry leads to similar behaviors of the electronic structures due vibrational motions. This could be useful in the study of molecules having intensities of difficult assignment, but that have similar intensities with other molecules.

Support: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

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“The VSEPR Model and the Ozone Molecule”

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Key-words: VSEPR model, ozone, dipole moment.

In this work, Gaussian 03[1] package is used to run ab initio calculations that, combined with QTAIM (Quantum Theory of Atoms in Molecules), are applied to study the structure of the ozone molecule, looking for show physical basis for the VSEPR model (Valence Shell Electron Pairs Repulsion) which is able to predict the geometry of ozone and numerous other molecules.

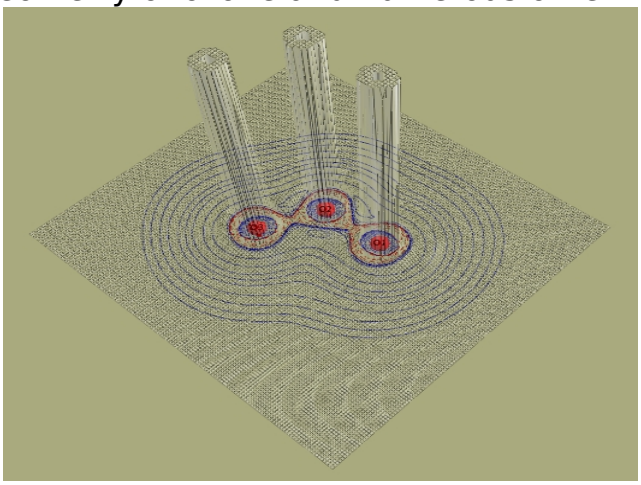

Figure 1. Laplacian Euclidean representation of ozone molecule using Hartree-Fock method and 6-31G (d,p) basis set.

Figure 1 shows the Laplacian representation of the ozone molecule obtained by ab initio calculations using Hartree-Fock method and 6-31G (d,p) basis set, in which is analyzed from AIMAll[2] software. Notice that the charge distribution is maxima in each nucleus, property known as local maximum in ρ(r).
It is also presented a brief historical context of the discovery of ozone and finally we propose an analysis of didactic excerpts that some of the main known books of general chemistry and physical chemistry bring about the issue, trying to identify the presence or absence of some key topics necessary for this approach, such as dipole moment and polarizability.

Support: FAPEMIG.

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"Theory study of C_{60} buckyballs in interaction sulfur dioxide molecules"

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Key-words: Fullerene, DFT, sulfur dioxide.

Fullerenes as allotropic variety of carbon has been of great interest in the scientific community because they are materials with intrinsic properties such as spherical structure derived endohedral formation, specific regioselectivity, receptor electron and include hollow capacity substances such as atoms or molecules inside. The last property was explored in this work in order to investigate possible interactions between C_{60} and sulfur dioxide (SO_2) molecules that are formed by volcanic emissions, decomposition of animal and vegetable matter and combustion of fossil fuels. Also examined is the capacity for containment of C_{60} and characterization of these systems taking into account the structural deformity like pentagonal and hexagonal openings. Calculations were performed at B3LYP/6-31G for better description of the model on computational package GAMESS. The results showed that the C_{60} structure supports only three molecules of SO_2 which shows confinement small area, deformities were observed in the interatomic angles ranging from 104° to 111° (pentagons) and 113° to 124° (hexagons) for two molecules and range from 104° to 110° (pentagons) and 110° to 125° (hexagons) for three molecules, respectively, which leads to infer the addition of only one molecule does not significantly change the angles of C_{60} which are 108° (pentagons)) and 120° (hexagons). This high stability combined with high symmetry, rings tension and greater pentagon separation on C_{60} are possible explanations for the results. Electronic properties like dipole moment was analyzed and the system C_{60} with two SO_2 molecules showed a uncommon value of 0,80 Debye caused by oxygen-carbon bond. These results showed that systems are too limited for storage SO_2 molecules, stables in despite a little deformation, small charge transport and can be functionalized by characteristic reactions fullerenes.

Support: CAPES.

Electronic properties of adsorption of carbon dioxide in the surface of zinc oxide: A first principle study

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Key-words: Zinc oxide, Carbon dioxide, Electronic properties, Density functional theory

Oxide surfaces are important systems in material science. In particular, the surface of zinc oxide is an important step that takes place many catalytical processes, *e. g*., the synthesis of methanol. There are three main surfaces in *ZnO*: The ideal polar surface (0001) that exposes zinc atoms with three coordination number; the polar surface $(000\bar{1})$ ended in oxygen, and the prismatic plane $(000\bar{1})$ where the zinc atoms and oxygen are in the same plane. As an example of catalytic importance of exposed surface, it is kwon that the (0001) *ZnO* surfaces finished in zinc, and $(000\bar{1})$ finished in oxygen show a significant difference in reactivity for the dissociative adsorption of methanol. The activation of carbon dioxide is important due to the air pollution, and is also a molecule used for testing the basicity of metal oxides surfaces. In this study we have used a model of large *ZnO* slab varying the number of layers, specifically four, six and eight layers. The main purpose of this study is to investigate electronic properties of physical and chemical adsorption of CO_2 over the (0001) and $(000\bar{1})$ *ZnO* surfaces. To achieve this purpose we employed first-principles calculations based on density functional theory (DFT). The eigenstates of the electron wave functions are expanded on a plane-wave basis set using pseudopotentials (PP). This method has been implemented into the VASP computer code. It was performed calculations of total and partial density of states for the bulk, and adsorbed species. The results were discussed and compared to the experimental data. As expected, it was found a difference between electronic properties of the CO_2 adsorption, in particular the *band gap* and states of physical and chemical adsorbed CO_2 deposited in the valence band and conduction band. The contributions to the valence band top and valence band bottom come predominantly from O *p* and Zn *d*, respectively.

Support: CAPES, INCTMN e CNPq.

COMPUTATIONAL STUDY OF THE LIPSCOMB AND LINDSKOG REACTION PATHS FOR HYDROLYTIC Zn ENZYMES

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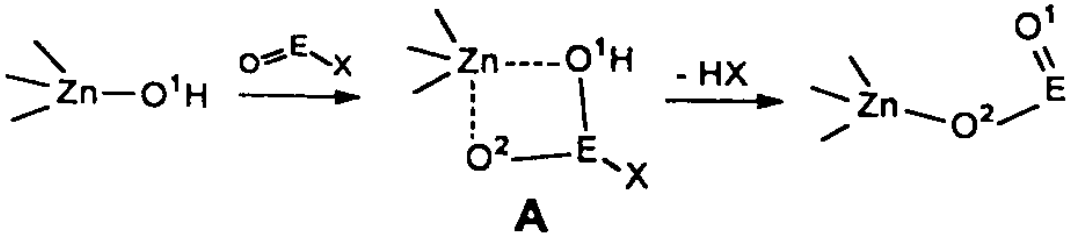
Hydrolytic zinc enzymes (like carbonic anhydrase, peptidases, phosphatases, esterases and nucleases) are highly efficient due to their double functionality. Metal coordination to an oxygen in the substrate allows for electrophilic activation, while a hydroxyl group coordinated to the same Zn atom or a second one, provides the attacking nucleophile. Enzymes exhibiting only one Zn atom must necessarily perfom both functions at this only metal center. It has been postulated in this case that the coordination number of Zn changes from 4 to 5 during catalytic turnover to form an intermediate A,



The reaction can proceed through two different paths, either successive proton transfers (which in the case of carbonic anhydrase is called the Lipscomb mechanism) or by internal rotation around the O^2E bond (called the Linskog mechanism). Following and old idea of Bräuer and Vahrenkamp, we performed density functional (DFT) calculations of all the reactants, intermediates, products and transition states involved in both paths for the system L_3ZnOH/CS_2 where L is either none (bare Zn^{+2}), NH_3, imidazole or the more complex tris(phenyl pyrazolyl) borate fragment. Calculations were performed using the B3LYP, PBE1 and M06 DFT functionals and the small 6-31G(d,p) and large 6-311++G(3df,3pd) basis sets. A general study of bond lengths and strengths as well as charge distributions was performed. The results show that while the intermediate A is present in all cases, the Zn atom is not really changing its coordination number. Only in the case of naked Zn^{+2} a real interaction was observed, while no such coordination was noticeable when the ligands were present. Both mechanisms are almost equally probable.

This work was performed as part of the project "*Nanotransductores en procesos celulares de señales redox efectuadas por especies reactivas de oxígeno"*, financed by CSIC, Udelar.

"Dehydrogenation of Methane by Nb^+ and Nb^{2+} ions: A DFT Study"

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Belo Horizonte-MG – Brasil;

Key-words: DFT, Gas-phase, Reactivity

The conversion of methane is of particular interest for the catalytic industrial applications.[1] Relatively few studies of the reactivity of doubly charged atomic transition metal cations have been performed. [2] Gas-phase reactions can provide important insights about the electronic structures of metal ions without external perturbations, thus providing new information for catalyst design. In this work, DFT calculations have been performed using by B3LYP exchange-correlation functionals and the relativistic Hay-Wadt ECPs for describing the electronic structure of the ionic metal systems. The dehydrogenation process of methane by Nb^+ and Nb^{2+} were studied for all ground and excited spin electronic states of these metal ions. The DFT results indicate slightly endothermic reaction for Nb^+, whereas exothermic reaction was computed for Nb^{2+}. Different reaction mechanisms were observed for Nb^+ and Nb^{2+}, as shown in Fig. 1, with more favorable kinetic conditions observed for Nb^{2+} ion. Theoretical calculations reveal the geometric and electronic structures of all products ions and intermediates. Theoretical results, in accord to experimental data, suggest that $NbCH_2^{2+}$ is formed through a H-Nb^{2+}-CH3 intermediate. The present results are so compared to the previous data of Ta^{2+}.

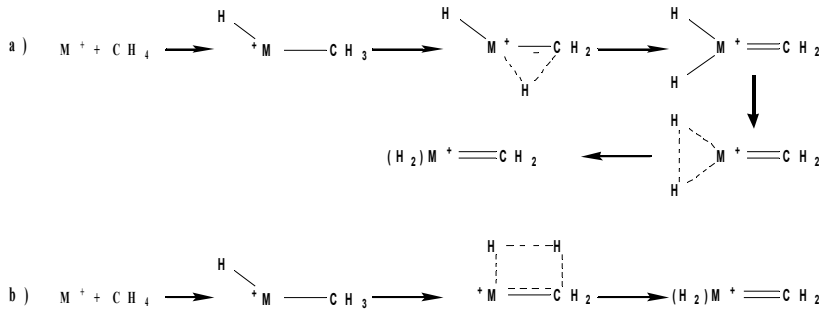

Figure 1: Mechanisms of dehydrogenation of methane.

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Support: CAPES, FAPEMIG

XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
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A Quasi-Classical Trajectory Study of the $H+Li_2 \rightarrow Li+LiH$ Reaction

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Key-words: potential energy surface, $H+Li_2$ dynamics properties

Recently, a new accurate potential energy surface for the ground state $H+Li_2 \rightarrow Li+LiH$ reaction was fitted using *ab initio* electronic energies determined using a pseudo-potential to represent the lithium core and a full CI calculation on a 6-311G(2df,2pd) basis set. Analytical representations of the $H+Li_2$ system were obtained using a Bond Order polynomial expansion for both two- and three-body terms, following the standard many-body method. In this work, Quasi-Classical Trajectories (QCT) are integrated on the fitted surface to determine the $H+Li_2$ dynamics properties, such as reactive cross- sections (RCS), product vibrational distributions, product rotational distributions, and product translational distributions. These properties were obtained integrating the trajectories considering the Li_2 reactant vibrational states v = 0, 1, 2 and 3, reactant rotational states j = 0, 5 and 10 and translational energy varying between 1.0 and 10.0 kcal/mol with a step of 1.0 kcal/mol. For each pair of rovibrational and translational energy values, a batch of 50000 trajectory calculations was performed for initial and final atom-diatom distances of 14 A° (asymptotic region), and a time step of 5.10^{-17} seconds. This value was obtained checking the conservation of both mechanical energy and angular momentum. The maximum reactive impact parameter considered in this work was 8 A°. Tests with batches of one million trajectories were also performed and the obtained results are in a excellent agreement with those calculated with 50000 trajectories. Therefore, the final results are presented considering a batch of 50000 trajectories. The obtained results show that the $H+Li_2$ exoergic reaction is not channeled into both Li_2 vibration and rotation.This is consistent with the absence of a transition state in the present surface. These features are supported by experimental evidence.

Support: CNPq, CAPES.

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Dynamics of Supercooled Ionic Liquids

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Key-words: Ionic Liquids, Raman Spectroscopy, Liquid Dynamics

The interest on room-temperature molten salts, commonly called Ionic Liquids, increased in the last few years due to many applications such as alternative solvents on organic synthesis and electrolytes for batteries. Ionic Liquids based on 1-alkyl-3-methylimidazolium cations have been largely investigated. It is well known that Ionic Liquids like these are good glass-formers and so they can be cooled below the melting temperature, T_m, without crystallizing, thus becoming a supercooled liquid.

Low-frequency Raman spectra of supercooled liquids ($\omega < 100$ cm^{-1}) contain information on vibrational (intermolecular) dynamics and fast relaxation processes (in a time range of picoseconds). The relaxation motions appear as a quasielastic scattering peak and its intensity decreases when the system is cooled, because it is dependent on the dynamics of relaxation.

The dynamics of binary mixtures of Ionic Liquids containing the same anion, bis[(trifluoromethyl)sulfonyl]imide, but different cations, 1-hexyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium, has been studied by Raman Spectroscopy to evaluate recent propositions based on Optical Kerr Effect Spectroscopy (OKE) that nanoscale heterogeneity develops in Ionic Liquids mixtures. The results of these two techniques should be consistent with each other since they both are based on polarizability fluctuations.

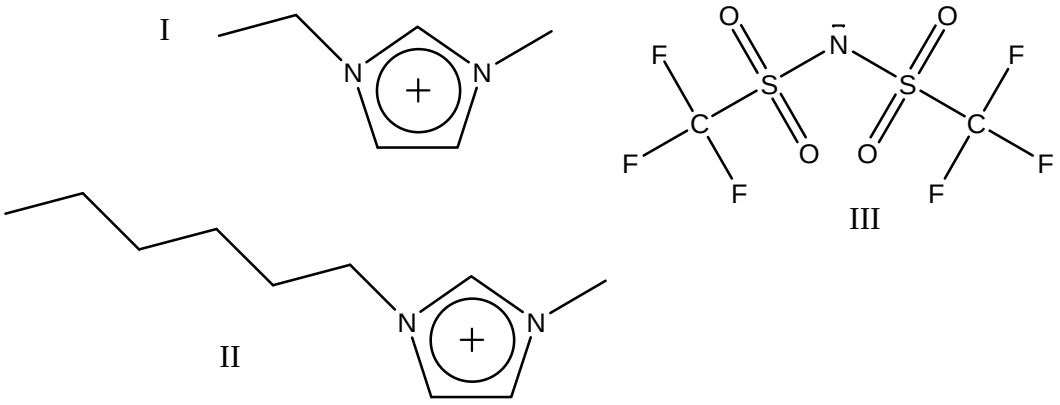

Figure 1. Structures of 1-ethyl-3-methylimidazolium (I), 1-hexyl-3-methylimidazolium (II), and bis[(trifluoromethyl)sulfonyl]imide(III) ions.

Support: FAPESP, CNPq.

Theoretical Study of Covalently Linked α-ciclodextrin Associations

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Key-words: Cyclodextrin, Molecular Tube, Quantum Mechanics

Ciclodextrin Molecular Tubes (CDMTs) are novel materials synthesized by the Harada's procedure developed in the 1990's [1]. The applicability of such nanossistems (Figure 1) is close related to their size. Nonetheless, CDMTs are obtained as a mixture containing entities with various molecular weights.

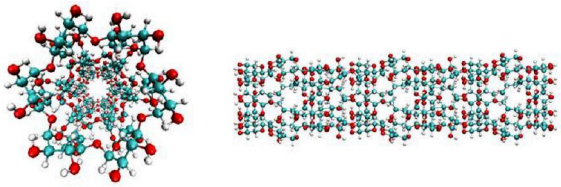

Figure 1. CDMT with 996 atoms obtained through the CycloLink software

The molecular features determining the tube size distribution are not completely understood. In this context theoretical investigations can aid experimentalist to achieve size-controlled synthesis. In this context, by using the previously developed CycloLink software, the relative energies of 156 distinct linked α-CD dimers have been evaluated at the PM3 level of theory.

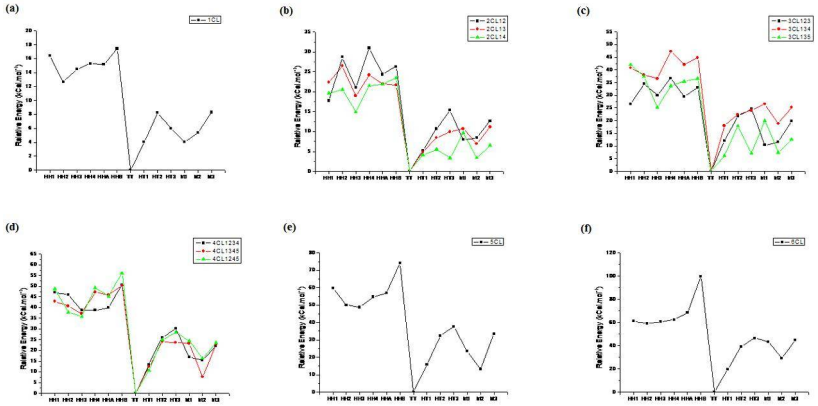

Figure 2. Relative energies evaluated for 156 linked α-CD dimers.

According to the theoretical data (Figure 2), TT linked association has been identified as the most favorable. In addition, the relative stability of HT linked association suggests that the existence of such associations may enlarge the distance between adjacent hydroxyl groups preventing crosslink between CD units, in accordance with experimental observations [2].

[1] Harada, A. et al., Nature 1993, 364, (6437), 516-518. [2] Travelet, C. et al., Soft Matter 2008, 4, 185-1860.

Support: FAPEMIG.

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"Estudo da Enzima Diidroorotato desidrogenase da *Leishmania major (Lm*DHODH*)* por ensaio virtual"

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Palavras-chave: Ensaio Virtual, diidroorotato desidrogenase.

A Leishmaniose se encontra entre as seis endemias consideradas prioritárias no mundo e atinge 12 milhões de pessoas. Os protozoários parasitas da Leishmaniose são dependentes da *via de recuperação* de purino-nucleotídeos. Essa via de recuperação se apresenta como um potencial alvo no planejamento de novos fármacos, sendo que os nucleotídeos desempenham um papel essencial no funcionamento do metabolismo celular, no qual são ativadores e inibidores em várias vias metabólicas, transportando energia para que reações celulares ocorram. A enzima Diidroorotato Desidrogenase da *Leishmania major* (*Lm*DHODH) surge como um alvo promissor para o desenvolvimento de fármacos seletivos no combate a Leishmaniose, uma vez que atua na quarta etapa do processo de síntese de UMP (Uridina Monofosfato) que é o precursor de nucleotídeos. Neste trabalho foram selecionados compostos obtidos da literatura que apresentam atividade contra a DHODH em diferentes parasitos, sendo esses submetidos ao ensaio virtual utilizando os programas de docagem Vina 1.1.1 e FRED 2.2.5. As coordenadas cristalográficas da enzima da *Lm*DHODH foram recuperadas do Banco de Dados de Proteínas (código PDB: 3MHU). A utilização de diferentes programas de docagem reduz a taxa de falsos positivos e aperfeiçoa a probabilidade de identificar novos ligantes. Esse procedimento foi adotado com o intuito de conhecer o sítio catalítico da enzima, fato que contribuirá para a proposta de novos compostos e de um mecanismo de reação em futuros estudos. As energias de interação variaram de -14,0 a -15,0 kJ/mol para o programa Vina e de -59 a -65 kJ/mol para o programa Fred, fato que demonstra a estabilidade da estrutura fármaco-receptor. As moléculas melhores pontuadas, segundo as energias de docagem e as interações mostraram que os resíduos de SER196, GLY71, ASN68, LEU72, ASN 128, LYS44 são importantes, uma vez que fazem interação com a maioria dos inibidores selecionados, dessa maneira eles podem ser explorados no planejamento de fármacos seletivos contra a *Lm*DHODH.

Suporte: CAPES

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THEORETICAL APROACH IN STUDY OF TRANSITION STATE OF CHORISMATE'S SYNTHESIS: A QST2 VIEWPOINT

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Key-words: *QST2, DFT, Chorismate syntase, EPSP.*

Catalized by chorismate synthase enzyme, the seventh and last step of the shikimate pathway, carry out the formation of chorismate, an important precursor in furthers biochemical pathways, as the folic acid, vitamin k, ubiquinone and aromatic amino acids. The chorismate synthase has an absolute requirement for reduced flavin mononucleotide and 5-enolpyruvilvylshikimate 3-phosphate (EPSP) as a substrate. The synthesis of chorismate from EPSP is considered unique in the nature, because does not involve a change in redox state during the reaction, besides presents a different stereochemistry that than expected, that is the 1,4-*anty*-elimination of 3-phosphate and C(6*pro*R) hydrogen, and not *syn*. This mechanism is not totally clear at this time, however some studies suggest that the phosphate group from EPSP leaves the structure of molecule before the withdraw of the hydrogen (H-27) necessary to generate chorismate. Because of the absence of the shikimate pathway in mammals, it is an excellent target for development of new antibacterial agents. Analysis of molecular orbitals with the reactant EPSP performed with B3LYP/6-31+G(d,p) revealed that the HOMO is concentrated in a region of phosphate group, the region in that believe occurs a electrophilic attack by proton H^+, moreover, the LUMO was not located in the region of proton-withdrawing (H-27) at C-6 carbon, which suggest the nucleophilic attack in this hydrogen atom is not favored. Using the QST2 procedure - implemented in Gaussian 03W package, where starting from two species, one reagent and one product, a transition state is suggested as a stable molecule – calculates where were used EPSP as a reactant and chorismate as product, it obtained a transition state that shows the phosphate group separated from of the remaining EPSP molecule and a hiperconjugation that takes place to stabilize the intermediate, preceding the leave of hydrogen 27 atom as viewed in the figure 1. As showed, it was possible to obtain theoretically in DFT (density functional theory) level, a transition structure that supports a well-accepted mechanism as for the chorismate's synthesis reaction. These results shed more light in the elucidation of this important reaction.

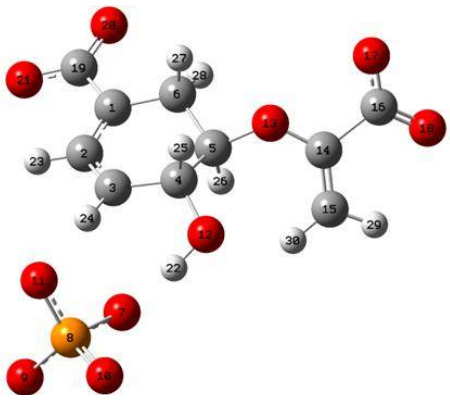

figure 1: Transition structure obtained from a QST2 procedure.

Support: CAPES/FAPEAM.

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"Studies of Molecular Modeling of activities compounds in the *Leishmania (Vianna) braziliensis*"

PINHEIRO, A. S. (G), SILVA, K. A. (G), SOUZA, F. S. (G), ALVES, C. A. (PQ),

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Key-words: Leishmaniasis, docking molecular, molecular dynamics

Leishmaniasis is a parasitic and endemic infection caused by protozoa *Leishmania*. Several drugs are used to treat the disease, but ideal treatment does not exist to this illness, due to high toxicity and low efficacy. The enzymes responsible for energy metabolism of trypanosomatids are strategic targets in drug design, being of great significance to maintaining the parasite's life. In this work, we carried out a study to determine the localization of the active site of the enzyme 6-Phosphogluconolactonase of the specie *Leishmania (Vianna) braziliensis,* through the application of molecular modeling techniques, such as docking and molecular dynamics. The programs used for molecular docking were AutoDock, AutoDock Vina, FRED and DOCK. These programs use different methods to dock the compound to the binding site and are therefore appropriate for comparison purposes. The molecular dynamics was carried out with Dynamo program, and to realize the topographic analysis of cavities we used the CASTp program. This program was used to assist us to pick out residues that may be responsible for the biological activity. The study were realized with the crystallographic model of the enzyme obtained from PDB (3CH7) and three compounds (pentamidine, nerolidol and a sulfonamide 4-methoxychalcone derivate) found in the literature which have values of IC_{50} against the parasite. In this study, based on the results of molecular docking and topographic analysis of enzymatic cavities, the three compounds indicated a region of the receptor to be analyzed as possible active site. Some residues that interacted with the compounds were His168, Asp75 and Phe163, and the best binding energies observed to the compounds were in the range of -40 to -50 Kcal/mol. The results of the molecular dynamics simulations performed to confirm the region of the active site obtained with the three compounds, showed that the ligands remained in the same region, previously pointed out by different methods, which have the same amino acid residues conserved in the active site of the enzyme 6-Phosphogluconolactonase of the *Trypanosoma brucei*. This enzyme has the location of its binding site elucidated and belongs to the same family structure of the enzyme studied here. Thus, these results indicate the proposed site and could be used as a starting point in the design of new inhibitors.

Support: PIBIC-CNPq.

XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
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"Analyze of the active site of enzyme 6-phosphogluconolactonase of *Leishmania (Viannia) braziliensis* species".

SOUZA, F. S. (G), PINHEIRO, A. S. (G), ROCHA, J. A. P. (G), ALENCAR, N. A. N. (PG), ALVES, C. N. (PQ), MOLFETTA, F. A. (PQ)

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Key-words: Molecular dynamics, 6-phosphogluconolactonase enzyme.

Leishmaniases takes place among the most neglected tropical diseases, and there are about 12 million of people infected in the world. Furthermore, there are around 2 million new cases every year. Transmission occurs via the bite of an infected phebotomine sandfly and can also be transmitted through blood transfusions. In Brazil, the disease is caused mainly by the Leishmania (Viannia) braziliensis. The existence of different types of cutaneous leishmaniasis leads to development of drugs as sodium stibogluconate, miltefosine and Amphotericin B. Nevertheless, these compounds are toxics and little efficiency against the disease. To search new compounds against leishmaniases we constructed a data bank with 800 molecules of the Amazon region. The Instant JChem program was used in the process of storage of the molecules in the data bank. From the molecules of the bank we realized a virtual screening with the enzyme 6-phosphogluconolactonase (PDB code 3CH7) of Leishmania (Viannia) braziliensis species. The calculations of molecular docking were carried out with AutoDock 4.0, Vina 1.1.0, DOCK 6.3 and FRED 2.2.5 programs. The use of different docking programs reduces the false positive rate by consensus score, improves the like effective planning of drugs. Then, the molecular docking results we evaluated by consensus score, resulted in 5 compounds: 5-hydroxy-3,4,7,8-tetramethoxyflavone, (+)-Catequin, 5-hydroxy-7,4-dimethoxyflavone, 6,3-dihydroxy-7,4-dimethoxyflavane and nivenolide acid. In the docking results, the energy values observed were in the range of -47.29 to -51.83 kcal/mol. Furthermore, the results showed that the compounds were docked in the same region of the receptor. This region were formed by ARG76, ALA169, GLY161, ARG200, ALA219, HIS167, ASP74, THR47, SER46 and GLY44 amino acid residues. In order to verify the results obtained by docking we carried out a QM/MM molecular dynamics simulation by using Dynamo program. The use of QM/MM offers a possibility to study chemical reactions that are embedded in an environment. The process of molecular dynamics was done with the hybrid method of QM/MM at temperature of 300 K, press of 1 atm, time of simulation of 1000 ps and force field AMBER. The molecular dynamics results suggest that amino acids ARG200 and ALA219 in the active site are likely to form interactions with inhibitors. These results are important for searching new drugs that could inhibit the 3CH7 enzyme because the structures showed great affinity in the active site of enzyme.

Support: PIBIC-CNPq

"Estudo de dinâmica molecular da enzima cruzaína da espécie *T. Cruzi*"

SILVA, K. A. (G), SOUZA, F. S. (G), ROCHA, J. A. P. (G), ALENCAR, N. A. N. (PG), ALVES, C. N. (PQ), MOLFETTA, F. A. (PQ)

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Key-words: Doença de Chagas, cruzaína, dinâmica molecular.

A Doença de Chagas é uma infecção parasitária causada pelo agente etiológico *Tripanossoma cruzi*. A doença possui o *triatoma infestans* como vetor de transmissão e os mamíferos como hospedeiros, sendo esta infecção prevalente no continente Americano. Atualmente, cerca de 15 milhões de pessoas estão infectadas e 90 milhões expostas a doença. No Brasil, estima-se que 8 milhões de pessoas manifestam esta infecção. Os fármacos disponíveis no mercado (Ninfurtimox e Benzonidazol) apresentam sérios efeitos colaterais, elevada toxidez e inatividade na fase crônica da doença. Para o desenvolvimento de novos fármacos, faz-se necessário a seleção de alvos biológicos, e a Cruzaína (ou Cruzipaina) foi o alvo biológico selecionado, pois é essencial em todos os estágios do ciclo de vida do parasito. Esta enzima é uma cisteino protease envolvida no processo de replicação e diferenciação intracelular. Neste trabalho, o programa Dynamo foi utilizado para estudos de dinâmica molecular realizados com a Cruzaína. A estrutura cristalográfica da Cruzaína (1ME3) foi recuperada do PDB, sendo esta complexada ao seu ligante cristalográfico (P10). Os principais resíduos que são importantes na literatura para a Cruzaína e que participam das interações para a estabilização do ligante P10 no sítio ativo da enzima são CYS25, HIS161, GLN19, GLY66, ASP160 e SER61. Através das análises dos cálculos de dinâmica molecular com um tempo de simulação de 1500 picossegundos pode-se verificar que as interações realizadas entre o ligante P10 e os resíduos ASP160, GLY66 e SER61 foram importantes. Assim, através dessas interações com os resíduos encontrados nos cálculos de dinâmica pode-se propor novos inibidores para o alvo biológico estudado.

Support: PIBIC-CNPq

$^4J_{FF}$ transmission mechanisms in 1,4-Peridifluoronaphtalenes

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Key-words: J_{FF}, Through Space, Spin-Spin Coupling Constant

Long-range interactions are usually present in fluorinated organic and bioorganic rigid molecules. Of particular interest are the NMR through space, TS, spin-spin coupling constants, SSCCs between fluorine nuclei (J_{FF}). Although, usually the Fermi contact interaction is the most important contribution, there are cases where the paramagnetic spin orbit term, PSO, is also very important. In this work 1,4-Peridifluoronaphtalenes are taken as model compounds to study the transmission mechanisms of both FC and PSO terms corresponding to $^4J_{FF}$. Total SSCC calculations were performed at the B3LYP/EPR-III level of theory, using Gaussian 03 package. Analyses of the FC term were carried out using both the QTAIM method as well as a qualitative approach based on the polarization propagator formalism, dubbed Fermi Contact Coupling Pathways-Canonical Molecular Orbitals (FCCP-CMO). To this end, CMOs were expanded in terms of Natural Bond Orbitals, using the NBO 5.0 program by Weinhold et al. This procedure allowed us to discriminate between different TS transmission mechanisms of the FC term (concatenated sequences of charge-transfer interactions; direct overlap between the fluorine electronic clouds, etc). On the other hand, the PP qualitative approach for analyzing the TS transmission of the PSO term yields, in these examples, an in-depth insight into the behavior of this type of magnetic electron-nucleus interaction. The σ-framework transmission mechanism can be described which transfer charge to virtual CMOs. The π-electronic system is determined, which is spin-polarized by exchange interactions with the σ-system and are transmitted without needing of π-vacant CMOs. Through-space component is transmitted by the overlapping of electronic cloud of both fluorine atoms, where the exchange interactions are taking place in the overlapping region. For through-space component any virtual CMO was found.

Support: UBACYt ; CONICET FAPESP, CNPq

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Estudo computacional do efeito das ligações de hidrogênio no fenol

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Palavra-chave: fenol, ligação de hidrogênio.

O fenol não é apenas um composto químico comum, mas também é o álcool aromático mais simples, bem como é também um cromóforo do aminoácido tirosina. As ligações de hidrogênio envolvendo fenóis têm sido tema de numerosos estudos tanto teóricos,[1-3] quanto experimentais. Neste trabalho foram estudadas, utilizando métodos computacionais, o fenol (**1**) e suas espécies complexadas com fluoreto de hidrogênio (**2**) e (**3**). As geometrias foram otimizadas utilizando-se o funcional híbrido B3LYP com a função de base 6-31+G(d,p) e o método ab initio MP2 com as funções de base 6-31+G(d,p) e 6-311++G(3df, 3pd). Nos cálculos utilizou-se os programas Gaussian98 e 03 e Molekel 4.3 a visualização gráfica. Os softwares AIM 2000 e AIMQB foram utilizados na análise topológica da densidade eletrônica do composto. Os estudos das geometrias mostraram que com a formação da ligação de hidrogênio há, para o complexo **(2),** um aumento no comprimento das ligações que participam da interação. Já para o complexo **(3)** observamos que houve uma diminuição no comprimento das ligações que participam da interação. Também foram feitos estudos de cargas atômicas, análises energética pelo método Xantheas, NBOs, análise NRT, AIM e análises HOMA, PDI e NICS. Foram observadas mudanças tanto na aromaticidade quanto na estrutura eletrônica do fenol e seus derivados devido ao efeito de formação de ligações de hidrogênio.

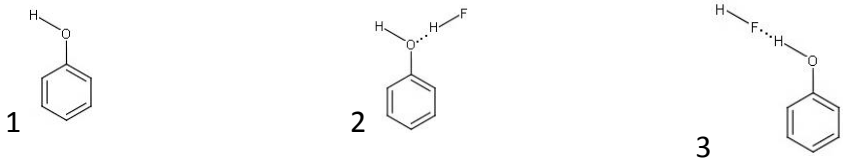

Figura 1. Estruturas das moléculas estudadas.

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Support: FAPESP, CNPq, CAPES.

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A Method to Find Symmetry Elements and the Full Point Group of Molecules

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Key-words: spatial symmetry, point group, symmetry operations.

Molecular symmetry is of great importance in chemistry, physics and spectroscopy, being used, for example, to reduce the computer time in electronic structure calculations and to obtain the selection rules of infrared and Raman spectra. Some approaches are described in the literature to locate point groups using the graph theory [1,2]. The present work describes another method, employing concepts more familiar to chemists and physicists, where the point group is found from the following information: (1) The type of rotor which the molecule belongs (spherical, prolate, oblate, linear or asymmetric), (2) The number of symmetrically equivalent atoms, that is, that atoms whose positions are interchanged trough a symmetry operation (ex. the hydrogens in a water molecule), (3) The interatomic distance matrix, (4) The atomic masses and (5) The polygon or polyhedron formed by the symmetrically equivalent atoms. For instance, an *n*-th order proper rotation axis is found by verifying the existence of a regular polygon formed by *n* symmetrically equivalent atoms of the molecule. The proposed method allows the identification of the full point group of any molecule from a reduced number of symmetry operations. This method is being implemented in a program written in C language and will be incorporated into our code PLACZEK [3], developed for calculations of the intensities of infrared and Raman spectra. The last can explore efficiently the molecular symmetry but doesn´t have a routine for automatic identification of the molecular point group.

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"A SCC-DFTB parameterization of NiX (X= Ni, O, Si, H) atomic pairs for crystals and related systems"

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Key-words: SCC-DFTB, nickel phyllosilicates.

The SCC-DFTB approach has been extensively used to describe large scale systems with lower computational cost than the DFT method[1]. In this work the SCC-DFTB parameterization of the NiX (X = Ni, Si, O, H) atomic pairs has been performed with the aim to describe periodic systems such as Ni, NiO, $Ni(OH)_2$ (brucite analogue) as well as nickel phyllosilicate ($Ni_3Si_2O_5(OH)_4$, lizardite analogue), figure .1. Recent works showed that the nickel phyllosilicate can be used as catalyst precursor for CO_2 reforming of CH_4[2]. The SCC-DFTB optimized geometry of Ni, NiO, $Ni_3Si_2O_5(OH)_4$ and $Ni(OH)_2$ are presented in figure. 1, respectively. The geometrical parameters are compared with the DFT-PBE calculations at table 1. The DFTB+ and Quantum Espresso codes were used to carry out the DFTB and DFT-PBE calculations, respectively.

Support: CNPq, CAPES, FAPEMIG, INCT-ACQUA.

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Table. 1. Interatomic distance r (Å), lattice parameter a (Å), angle α (^{0}) and Δ (Å).

Systems	Properties	SCC-DFTB	PBE	Δ
Ni fcc	a	3.490	3.524	0.034
	r (Ni-Ni)	2.468	2.492	0.024
	α (Ni-Ni-Ni)	60.0	60.0	0.0
NiO sc	a	4.166	4.195	0.029
	r(Ni-Ni)	2.946	2.966	0.020
	r (Ni-O)	2.083	2.097	0.014
	α (Ni-O-Ni)	90.0	90.0	0.0
	α (O-Ni-O)	90.0	90.0	0.0
$Ni(OH)_2$ layer	a	3.074	3.094	0.020
	r (Ni_3-Ni_5)	3.074	3.094	0.020
	r (Ni_3-O_7)	2.032	2.033	0.001
	r (Ni_9-O_7)	2.032	2.039	0.007
	r (Ni_3-H_1)	2.631	2.653	0.022
	α (Ni-O-Ni)	98.31	98.91	0.60
	α (O-Ni-O)	98.31	98.91	0.60
$Ni_3Si_2O_5(OH)_4$ layer	a	5.311	4.195	0.097
	r (Ni_7-Ni_8)	3.082	3.163	0.081
	r (Ni_8-O_5)	2.032	2.058	0.026
	r (Ni_8-O_6)	2.014	1.999	0.015
	r (Ni_8-Si_{17})	3.279	3.292	0.013
	r (Ni_8-H_3)	2.632	2.621	0.011
	α (Ni_7-O_5-Ni_8)	98.61	100.47	1.86
	α (O_5-O_7-O_{10})	81.41	78.71	2.70

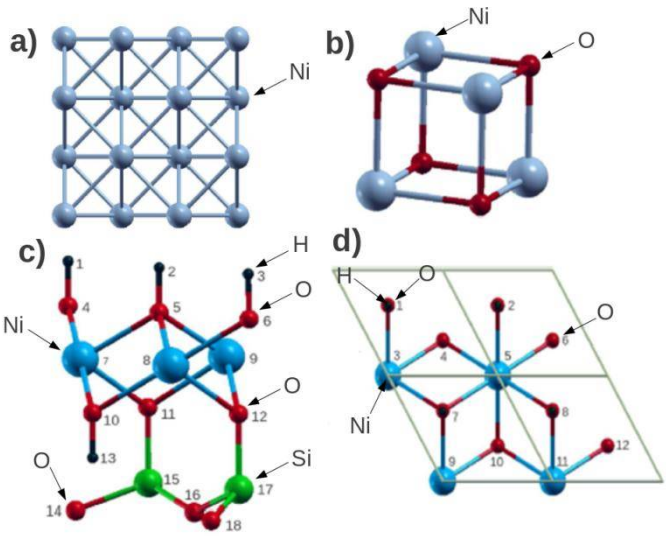

Figure. 1. Face centred cubic (fcc) structure of metallic Ni (a), simple cubic (sc) structure of NiO (b), nickel phyllosilicate structure (c) and the $Ni(OH)_2$ brucite analogue (d) optimized by SCC-DFTB and DFT-PBE methods.

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Interference effect in chemical reactions: the ground-state [2 + 2] and [4 + 2] cycloadditions

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Key-words: interference effect, cycloaddition reactions

Cycloadditions are a type of pericyclic reaction in which the condensation of two unsaturated hydrocarbons leads to the formation of a cyclic compound. It is widely known that, given a [p + q] cycloaddition, the ground-state reaction is favored when p + q = 4n + 2 and unfavored when p + q = 4n. From the Molecular Orbital (MO) point of view, the explanation of these selection rules is based on the Woodward-Hoffmann's orbital correlation diagrams. From the Valence Bond (VB) point of view, Goddard's Orbital Phase Continuity Principle (OPCP) provides results in agreement with both experimental results and predictions of the Woodward-Hoffmann theory, with the advantage of being applicable to molecules of any symmetry. In spite of their success to predict favorable thermal reactions, none of these models are capable to infer the nature of the effect – covalent or quasi-classical (*e.g.* electrostatic) – responsible for their behavior. It is known that the quantum-mechanical interference is the driving force for the formation of chemical bonds. Recently, an energy partitioning method (GPF-EP) was developed, which can determine the interference (*i.e.* covalent) and the quasi-classical contributions for each individual chemical bond or groups of bonds in the molecule. In this perspective, the goal of this work is to examine the nature of the chemical bond in reactants, transition states and products of the ground-state ethylene + ethylene [2 + 2] and ethylene + cis-butadiene [4 + 2] cycloadditions and verify the weight of each energy component in each case. The geometry optimizations and reaction pathways were obtained at the CASSCF(N,N)/cc-pVDZ level. With the VB2000/GAMESS package, Generalized Product Functions (GPF) single-point calculations were performed – the core electrons were treated at the HF level, the valence σ electron pairs were treated at the GVB-PP level and the π electrons, involved in the reaction, at the SCVB level. The results show that the interference energy is responsible for the decrease of the energy in the cyclic products in comparison to the reactants, while quasi-classical effects tend to increase their energy. What is more interesting, however, is the comparison of the contributions to the reaction barrier, *i.e.* the difference in energy between the transition state and the reactants (ΔE_{TS-R}). While the difference in interference energy is almost the same for the two cycloadditions (about 20 kcal/mol), the difference in the quasi-classical energy is 26 kcal/mol for the [4 + 2] cycloaddition and 81 kcal/mol for the [2 + 2] cycloaddition. Therefore, it is shown that the high energy of the transition state of the [2 + 2] cycloaddition is due to quasi-classical effects, rather than covalent ones.

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Solvent effects on core electron binding energies of DL-Valine and DL-Cysteine

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Key-words: Amino acids, Core electron, Solvent effects.

Amino acids, the building blocks of proteins, can assume different geometrical and electronic structure depending on the chemical environment. They are particularly sensitive to the dynamic interactions with the solvent molecules. The solvent environment can determine, for example, if the electronic structure of the solvated biomolecule is neutral or zwitterionic. Although valuable information about the intermolecular forces can be obtained with the increasing number of photoelectron spectroscopy studies on isolated amino acids, there are still scarce theoretical studies focusing the liquid phase. In this work, core electron (K- and L-shell) ionization and energy shifts [1] for both neutral and zwitterionic forms of DL-Valine and DL-Cysteine [2] in gas phase and in different liquid environments (simulated by means of different dielectric constants [3]) are theoretically investigated. The intermolecular interactions between the solutes and the solvents can shift the core electron binding energies, which are thus directly related with structural changes in the local chemical environment. Core electron binding energies are obtained through the difference of the total energies using the valence bond level of theory. The results for various basis set are compared with available experimental data and show not only the effect of the solvents on the binding energy shifts but also the correspondence between it and the structural changings produced by the local chemical environment.

Support: CNPq, CAPES, FAPESP, INCT-FCx and nBioNet.

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Conformational analysis of lignin models: a chemometric approach

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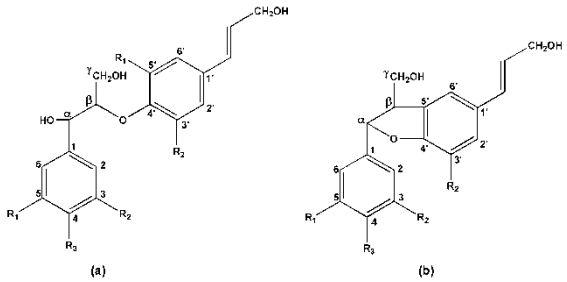
Key-words: Conformational analysis, chemometric, lignin.

Currently, renewable fuels have been studied by several research groups. The importance of this recent scientific field consists in the searching for new substitute for petroleum based fuels. In this sense, several alternatives have been testing, seeking the improvement of biofuels. One of the new and promising alternatives is the use of doped biomass derived from seed cake as catalyst for the transesterification of triglycerides obtained from the same seeds. Aiming to contribute in this challenging field, the present study seeks to model the lignin structure starting from small fragments, namely building blocks (Figure 1). As a first step towards the "bottom-up" building procedure, conformational analysis was carried out using a chemometric tool (Box-Behnken design) to select the main structural parameters to be considered for the final quantum mechanical analysis (the main dihedral angles were identified) considering 24 dimers (guiacyl, syringyl and p-hydroxyphenyl units linked by α-O-4, β-O-4, β-5' and 3-5' bonds). A Box-Behnken 3^4 design was carried out considering four dihedral angles in three different levels (-1, 0, +1) starting from the optimized structures of the dimers (at HF/6-31G theory level). The chemometric procedure applied here allows a fast and useful molecular understanding of the effect of each dihedral angle on the dimers stability, in addition to the coupling effects considering all kinds of liking groups. The two more important dihedrals found from the chemometric analysis for each system were further analyzed by constructing *ab initio* potential energy surfaces. The conformational results for dimers might be used as starting-point to develop larger lignin models (trimers, tetramers, etc.). The final goal is to build up a representative lignin structure using the conformational data of selected building-blocks (Figure 2).

Figure 1. General molecular structures of a (a) β-O-4 and (b) β-5' dimmers studied.



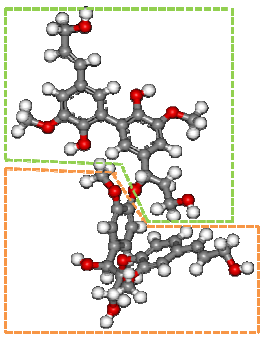


Figure 2. Lignin tetramer model obtained from conformational analysis of dimmers models.

Support: FAPEMIG, CAPES, CNPq, UFJF.

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"Theoretical investigation of the morphology and dynamical properties of amorphous PPV films"

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Key-words: amorphous conjugated polymers, classical molecular dynamics, non-bonded interactions

Amorphous organic conjugated systems are of special interest for optoelectronic devices [1]. Classical Molecular Dynamics (CMD) simulation methods based on parameterized potentials are nowadays used to simulate large systems intending to describe morphological structures to reproduce properties of real samples. However, many questions are under discussion regarding the suitability of model potentials for atomistic simulations [2]. To evaluate local packing properties of amorphous poly(p-phenylene vinylene) (PPV) films, and its sensitivity to different force-field parametrizations, we modeled large supercells (up to tens of thousands of atoms) with 26-ring oligomers employing CMD. These simulations were performed under finite temperature dynamics, employing a home-made reparametrization [3] of Coulomb and van der Waals interactions to UFF (Universal Force Field) [4] adjusted to data available for a set of crystalline structures comprising phenylene and/or vinylene units, coupled to *ab initio* calculations [5,6]. Supramolecular arrangements of our simulated systems have been analyzed by means of statistical correlation functions, over inter- and intra-chain distributions in the range of temperature studied (100K, 300K and 500K). Non-bonded interactions changed local packing properties and the internal chains arrangement with the variation of the, as shown in Figure 1.

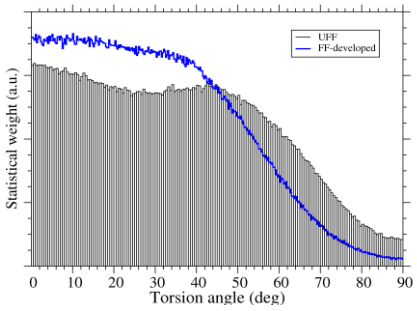

Figure 1: Intrachains torsion angles evaluated for PPV films using both forcefields (UFF and FF-developed). Statistical distribution collected over 15ps of 300K NVT dynamics.

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Support: INEO, CAPES, CNPq, and FAPESP.

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"3D-pharmacophore mapping of β-*N*-bioaryl ether sulfonamide hydroxamates as potential MMPs inhibitors: 1. Molecular dynamics simulations and molecular properties evaluation"

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Keywords: Metalloproteinases, molecular dynamics, melanoma

Introduction and Purpose. Matrix metalloproteinases (MMPs) are a family of zinc dependent proteinases involved in the degradation of the extracellular matrix, and MMP-2 and MMP–9 are overexpressed in several human cancer types as breast cancer, lung cancer, hepatocarcinoma, and notably melanoma.[1] In this study, molecular dynamics simulations (MDS) of a set of novel β-*N*-biaryl ether, sulfonamide-based hydroxamates as potential MMP-2 and MMP-9 inhibitors[1] were performed to correlate thermodynamics, structural, electronic, lipophilic, steric molecular properties to the biological data (IC_{50}, nM). **Methodology.** The 3D models of seventy inhibitors were built up considering a fragment (4-methoxybenzenesulfonamide)[2] bound to a MMP as reference. Geometry optimization was carried out employing MM+ force field, without any constrains, and partial atomic charges were calculated using AM1 method (HyperChem 7.51). The energy-minimized 3D models (steepest descent and conjugate gradient methods) were used as initial structures to perform 1 ns MDS [1,000,000 steps, 1 fs step size, T 298 K] (MOLSIM 3.2).[3] The lowest energy conformation of each inhibitor was selected from MDS, its energy was minimized, and the molecular properties were computed using distinct software. **Results and Discussion.** The total potential energy values found for the minimum-energy conformer of one of the most (**a**) and less (**b**) active inhibitors (Fig. 1) were -26.91 and -61.46 kcal/mol, respectively. The maps of electrostatic potential (MEPs) were computed onto a molecular surface (Gaussian G03W) and are presented in a color ramp from -0.09 (red) to 0.09 (blue) (Fig. 1). The electrostatic potential charges (CHELPG) were calculated using HF/6-31G*. Inhibitor (**a**) showed a higher electronic density distribution (intense red) on the sulfonilamide (β-pos.) and hydroxamate portion. The sulfonyl group provides a vital H-bonding interaction with the MMPs backbone and the hydroxamate moiety is considered the Zn-binding group. The presence of a substituent group at the α-position [dashed line circle (**a**)] by using a N heteroatom linker possible contributes to an interaction with the S1 subsite of MMPs.[1] **Perspective.** The conformational ensemble profiles generated in MDS will be employed to perform an *independent-receptor* (*IR*) 4D-QSAR (quantitative structure-activity relationships) formalism.

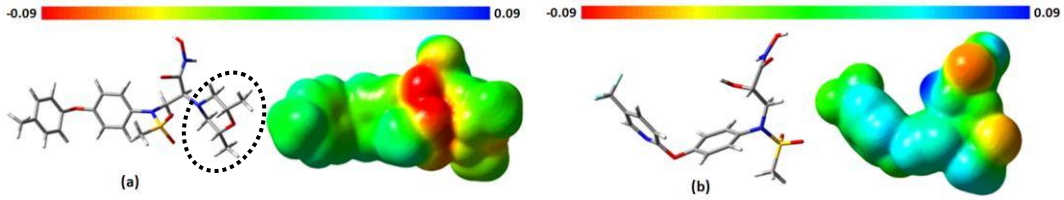

Figure 1. MEPs of a more (**a**) and less (**b**) active inhibitor considering the minimum-energy conformers selected from MDS (Gauss View 4.1). The 3D structures are presented as stick model where the carbon atoms are in gray, oxygen in red, nitrogen in blue, sulfur in yellow, fluorine in cyan, and hydrogen in white.

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Solubility properties of alcohols in sodium octanoate micelles by molecular dynamics simulation

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Key-words: Micelle, association colloids, molecular dynamics, sodium octanoate, octanol, isomers, solubilization

The formation of micelles in aqueous solution may improve the solubility properties of organic molecules, *e.g.*, long chain alcohols and hydrocarbons, producing stable isotropic solutions in a wide range of compositions. The location of any molecule in a micellar solution is determined primarily by the structure of the solute: hydrocarbons and other nonpolar compounds should be located in the hydrophobic core of the micelle whereas molecules bearing polar groups should be found nearer the surface of the micelle.[1] The present work aims to study the spontaneous solubilization process of two isomeric alcohols, 1-octanol and 4-octanol, in a sodium octanoate micelle. These two molecules were chosen to access the effects of the position of the polar group in an aliphatic chain on the equilibrium properties of the reference micellar system. The two model systems consisted of one micelle (N=30), taken from a previous simulation, 5 molecules of the alcohol, 30 sodium counter-ions and 2500 water molecules. The micelle and all molecules were randomly placed in a cubic box. All the simulations conditions and parameters are exactly the same used in a previous work.[2] The simulations reached a total time of 100 ns and after *ca.* 25 ns all energy components reached the equilibrium for both systems. Although all alcohol molecules were incorporated into the micelle in both models systems, 1-octanol molecules were mostly buried within the hydrophobic core, whereas the 4-octanol molecules were preferentially located at the surface of the micelle, resulting in a solvent accessible surface area of (1.2 ± 0.3) nm² per molecule for 1-octanol and (2.2 ± 0.4) nm² per molecule for 4-octanol. The difference in location for the two isomers also changed the average interaction between the surfactant and the solvent, the aggregation numbers of the micelles and the interaction energy of the alcohols with water, while for a single molecule of either 1-octanol or 4-octanol in pure water this effect was negligible.

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Support: FAPESP.

"Investigation of the influence of the central ion on nonlinear optical properties of a porphyrin derivative through the use of quantum mechanical methods"

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Key-words: Nonlinear optics, metal porphyrins, DFT and TD-DFT, first hyperpolarizability, PM6.

The study of nonlinear optical properties (NLO) of organometallic compounds has attracted considerable attention due to the enormous range of technological applications and future perspectives. The main advantages presented by such materials are: 1) great values for the magnitude of nonlinearities; 2) fast response times; and 3) easy structural manipulation that is used to tune the wished property aiming a specific application. It is known that a necessary pre-condition for the observation of NLO properties in this kind of material is the presence of conjugated structure with an efficient π electron delocalization, which is responsible for high values of hyperpolarizabilities in such compounds, and a fast charge redistribution caused by the interaction with intense electromagnetic fields. Our studies have focused on organometallic compounds, particularly metal porphyrins and metal phthalocyanines. In this communication we employed the Density Functional Theory (DFT) and its Time Dependent analogous (TD-DFT) in order to investigate the influence of the central ion (Zn^{2+}, Al^{3+}, Fe^{3+} e Mn^{3+}) on the photophysical and nonlinear optical properties of a cationic porphyrin derivative (meso-tetrakis-(1,3-dimethylimidazolium-2-yl)porphyrin tetraiodide). The ground state geometries and vibrational frequencies for the studied species were obtained using B3LYP/TZVP methodology. The excitation energies, oscillator strengths, etc. were calculated using TD-DFT method with the same functional and atomic basis set. These calculations were made with the use of Gaussian 09 computational package. The first hyperpolarizabilities (β_{TOTAL}), were estimated using the PM6 semi-empiric method (AMPAC 9), with solvated system simulated with the dielectric continuum model COSMO. Through the evaluation of the frontier molecular orbital, it is possible to verify that Mn^{3+} and Fe^{3+} exert a higher influence on the macrocycle electron density, through electron transfer, leading to a distortion of the orbital symmetry between HOMO and LUMO. As a consequence, nonlinear optical properties of these compounds are favored, which can be determined by the estimated values of β_{TOTAL}. For the derivative containing Zn^{2+}, for example, for which an experimentally estimated value of β_{HRS} is available, the discrepancy between the experimental value in DMSO and the theoretical one is 18%.

Support: FAPEMIG, CNPq, CAPES.

The use of Quantum Monte Carlo with Density Matrix to calculate potential energy curves.

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Key-words: Quantum Monte Carlo, density matrix, potential energy curve

Quantum Monte Carlo (QMC) is more likely to be developed than more traditional methods once it is one of the newest alternatives of *ab initio* methods. A recent suggestion for the QMC development proposes the use of Density Matrix in Quantum Monte Carlo (D-QMC). [1] Here, we used D-QMC to describe the potential energy curve (PEC) of some diatomic molecular systems: H_2, LiH and HeH^+.

For this purpose, we employed two D-QMC approaches: Variational Monte Carlo with Density Matrix (D-VMC) and Diffusion Monte Carlo with Density Matrix (D-DMC). For H_2, two basis sets were employed to investigate the influence of the wave function quality on the D-QMC calculation results in both D-VMC and D-DMC approaches. We have used RHF calculations as a starting point to the D-QMC calculations.

For every system studied, we found that the quality of PEC described by D-VMC is similar to the description given by the RHF method for the same basis set (table 1), while the PEC described by D-DMC is essentially coincident with the most accurate literature available results, regardless of the complexity of basis set employed (Figure 1).

Support: CAPES, CNPq.

Table 1 – Hydrogen molecule PEC properties

	RHF		D-VMC	
Basis set	Re (bohr)	De (hartree)	Re (bohr)	De (hartree)
STO-10G	1.34265	0.12651	1.34265	0.1267± 0.0002
TZP-10G	1.38611	0.13354	1.38611	0.1338±0.0001

Re – equilibrium distance, De – dissociation energy

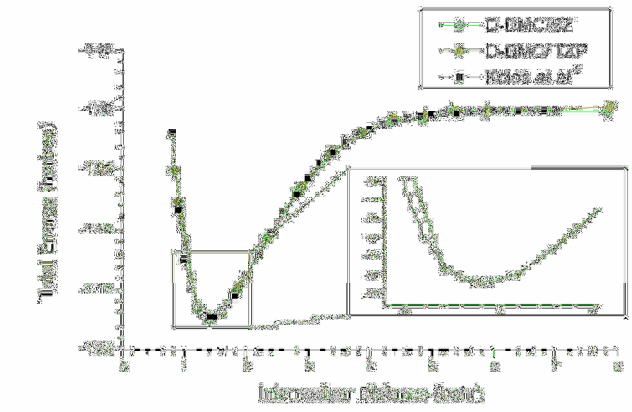

Figure 1. PEC for H_2: two D-DMC curves with different basis sets versus Kolos curve.

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Theoretical and experimental investigation of the bi-dimensional NMR spectrum of 3,4,5-trimethoxydihydrochalcone.

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Key-words: Dihydrochalcone, DFT, bi-dimensional NMR spectrum

Experimental NMR techniques are frequently used in the structural elucidation of natural products due to its versatility as well as the amount of information that can be extracted from analyzing NMR spectra. Using theoretical methods, Atieh and co-authors [1] conducted investigations of putrescine's NMR spectra and obtained experimental spectra well fitted to those simulated with the DFT/B3LYP method. The chalcones are known to present several biological actions, such as HIV-1 replication inhibition in lymphocytes-H9 in mice [2]. The aim of this work was to simulate the bi-dimensional NMR spectra (NOESY and COSY) of the substance 3,4,5-trimethoxydihydrochalcone and compare them to those achieved by experimental techniques [3]. The computer simulation was carried out at DFT (B3LYP/6-31G(d,p)) level for geometric optimization, attainment of the normal modes of vibrations (no imaginary frequencies) and NMR chemical shifts. These data were used as input to obtain NOESY and COSY spectra. Theoretical analysis of COSY and NOESY spectra requires specific basis and inclusion of electron correlation methods. The B3LYP hybrid method is known to use the exchange and correlation functional and the set of basis functions 6-31G allows to describe the valence shell by contracted and primitives Gaussian functions [4]. This set of base functions together with polarization functions (d, p) allows a satisfactory description of atomic orbitals of symmetry d and p [4]. In studies of spectroscopic properties it is important the correct description of electrons in atomic orbitals, since they may interfere with the magnetic field applied to atomic nuclei (Tutorial Spartan 2008). All calculations were done in the Spartan '08 program. Thus, *in sílico* techniques applying DFT level have showed great efficiency in the simulation of bi-dimensional spectra of this substance class.

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"Theoretical Study of the Limonoid 6-O-acetyl-3'-demethylswietephagmin E Isolated from *S. macrophylla*"

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Key-words: Molecular modelling, NMR, limonoids, B3PW91/DGAUSS

The limonoids are a group of triterpenes derivatives with important biological activities, such as inhibition of growth of cancerous tumours, antimicrobial and antiviral activity[1] and insecticide action[2]. The use of NMR techniques in structural elucidation of natural products may lead to uncertainties regarding the chemical shifts or stereochemistry. In this sense, the application of Molecular Modelling (MM) for prediction of experimental data (FTIR, NMR, molecular geometry, among others) is widely used nowadays because it is a fast and efficient tool. In this work we performed the theoretical study of the limonoid 6-O-acetyl-3'-demethylswietephagmin E (L1) (isolated from *Swietenia macrophylla*, found in Amazon region)[3], which possessed two possible structures due to an undefined relative stereochemistry: configuration *R* (L1A) or *S* (L1B) in position C-6, in order to obtain mathematical models for predicting ^{13}C and ^{1}H NMR data, elucidate structural problems and then achieve validation of the method. The software HyperChem Professional™ 7.5 was used in the graphic manipulation of the limonoid and the optimization of the molecule occurred at DFT level and B3PW91/DGAUSS method, employing the program ORCA[4]. The chemical shifts calculated by the theoretical method were compared with those obtained experimentally by linear regression. Statistical analysis was performed using the software MINITAB 14. The correlation obtained for the structure L1A showed the best parameters: for ^{13}C NMR, R^2 = 99.80%, F = 15204.38, Q^2 = 99.74% and s = 2.83; for ^{1}H NMR, R^2 = 96.20%, F = 636.79, Q^2 = 95.39% and s = 0.48. Regarding the comparison of theoretical geometric parameters of compounds L1A and L1B with experimental data of a similar compound, it is verified that in general the bond length, bond angle and dihedral angle data of L1A structure are those closest to the experimental data, corroborating the substance L1A as the most likely structure for compound L1. The results demonstrate that the MM techniques are reliable and have high potential to predict the spectroscopic properties of compounds with similar structures to that studied.

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Support: PIBIC/CNPq.

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Theoretical study of structures on the [H,S,O,F] potential energy surface

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Keywords: HSOF, *ab initio*, sulfur-fluorine compounds

The *ab initio* characterization of atmospherically and astrochemically relevant molecules has become an important step to guide the experimental detection and study of compounds yet to be discovered. As part of an ongoing project on sulfur-containing molecules, the present work is focused on species on the [H, O, S, F] potential energy surface with emphasis on structural, vibrational, and energetics aspects, therefore significantly extending a previous theoretical study of this system at the Hartree-Fock level[1]. MP2 level of theory, using the series aug-cc-pVnZ (n = D, T, Q) of basis sets, with extrapolation to the complete basis set limit, has been applied to the system. Figure 1 displays the relative energies for the seven stationary points located on the surface. Contrary to the previous work, OS(H)F, rather than HOSF, was found to be the minimum energy structure, 9.6 kJ mol^{-1} lower in energy. Geometric parameters were also found to be considerably different than those of Chen *et al.* thus reflecting the importance of including correlation effects in the description of the system. A large energy barrier of 206.1 kJ mol^{-1} prevents the interconversion of the two lowest-lying isomers. The other isomers lie much higher in energy.

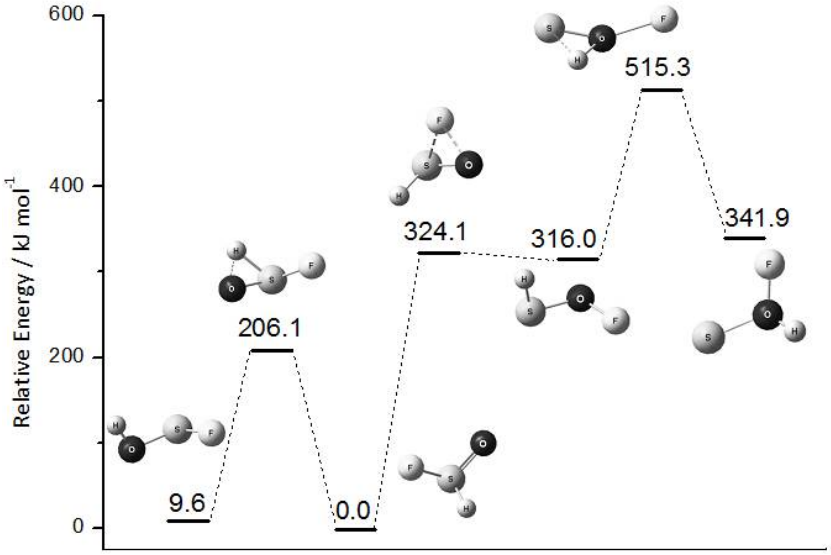

Figure 1. *Energetic profile of the [H,S,O,F] potential energy surface*

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Support: CNPq, FAPESP

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On the Structural and Dynamic Properties of Ionic Aqueous Solutions: A Molecular Dynamics Study

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Key-words: Hofmeister Series, Ionic Hydration, Specific Ion-Effects, Chaotropes, Kosmotropes

The role played by specific ion-effects on the structure of water and macromolecules in ionic solution, is a key aspect to the understanding of different processes in chemistry and biology. In spite of intensively studied, since the seminal work of Franz Hofmeister in 1888, the characterization of the effect of different ions on the structure and dynamics of water alone is still a matter of debate. In this work the structure and dynamics of water in aqueous solutions of sodium halides at different concentrations are studied through molecular dynamics (MD) simulations at room temperature and atmospheric pressure, using the AMOEBA polarizable intermolecular potential. Emphasis is placed on the extent of the ionic induced changes of the water structure. Further, the properties of the ionic solutions are compared with those of water at high pressures. Our results show that the alkali halides studied, induce significant changes on the water H-bond network beyond the first ionic hydration shell. The latter are strongly dependent upon ionic concentration and can be mapped onto pressure (excluded volume) induced structural changes. For the highest concentration studied, NaI is found to exert the largest disruption of the tetrahedral geometry of water,with a pressure equivalent around 500 atm. The water dynamics, probed through the self-diffusion coefficient, is also perturbed by specific ion-effects, in keeping with most, previous MD studies. The concept of kosmotropes and chaotropes is discussed in the light of the present results.

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"Chemical bonding and the equilibrium composition of Grignard Reagents in ethereal solutions"

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Key-words: Grignard reagents composition, *ab initio* calculations, chemical bonding.

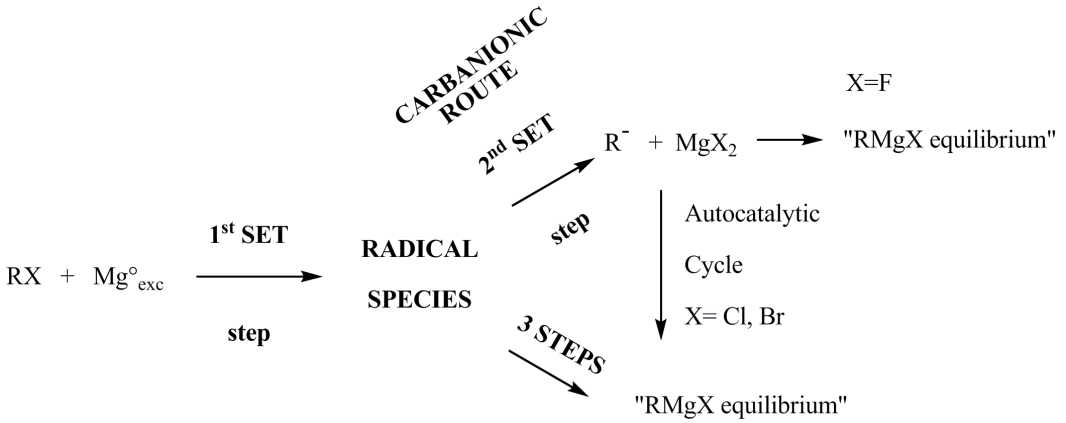
Grignard reaction is one of the most important C-C bond formation reactions and remains as one of the most widely used reactions in chemical synthesis.[1]

Our study present an extensive discussion of the chemical bonding, equilibrium composition and the solvent model interactions in the CH_3MgX species (X= F, Cl and Br). And for the first time it is presented a theoretical approach that includes charged and radical species, as suggested by numerous works in the literature, in the chemical equilibrium associated with Grignard Reagents.[2]

Through fully orbital optimized GVB-RCI calculations we are able to describe the bonding nuances that contribute to account for the different behavior of the Grignard Reagents in function of the type of halogen present. Besides that, we establish that there is no bonding interaction between the solvent molecules and the Mg atom, their interaction being purely electrostatic.

We show through DFT-M06 and GVB-RCI calculations that only by considering ionic and radical species one can get a cogent picture of the equilibrium properties of the Grignard Reagents. We found out that depending on the halogen, different reaction steps are preferably followed to get to the thermodynamic equilibrium.

We proposed two possible pathways for Grignard reaction formation from alkyl halides and Mg°. For alkyl fluorides the equilibrium would be reached through a "carbanionic route" and for alkyl chlorides and bromides a "radical route" is preferably followed. This scheme is depicted in the figure below.



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Support: FAPERJ.

Evaluating the Stability of Charged and Uncharged Multiple Hydrogen–Bonded Motifs in Heterodimers - A Theoretical Insight

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Key-words: Multiple Hydrogen bonds, LMO-EDA, QTAIM, ELF, NBO.

Multiple hydrogen bonds are the most important interaction on supramolecular chemistry, they are responsible for many recognition process in nature such as the stability and selectivity on nucleic acids. The stability of multiple hydrogen-bond arrays depends not only on the number of these associations[1], but also on the secondary electrostatic interactions[2].

Triple and quadruple hydrogen-bond arrays, DDD-AAA, DDD^{+}-AAA, DDDD-AAAA, $DDDD^{+}$-AAAA, $DDDD^{2+}$-AAAA complexes were investigated at the light of energy decomposition analysis, LMO-EDA, as implemented in GAMESS-US, at M06/DEF2SVP level. Additional insight about the covalent character[3] was also provide by using QTAIM, ELF, and Natural Bond Orbitals, NBO, analyzes.

The LMO-EDA results show that in charged motifs such DDD^{+}-AAA are more stable than the uncharged one, due to the increase of orbital polarization POL and electrostatic, ES, contributions. By comparing DDD-AAA and DDDD-AAAA motifs, the increase of polarization term compensates the increase of Pauli repulsion term, making the interaction much more stable (Figure 1).

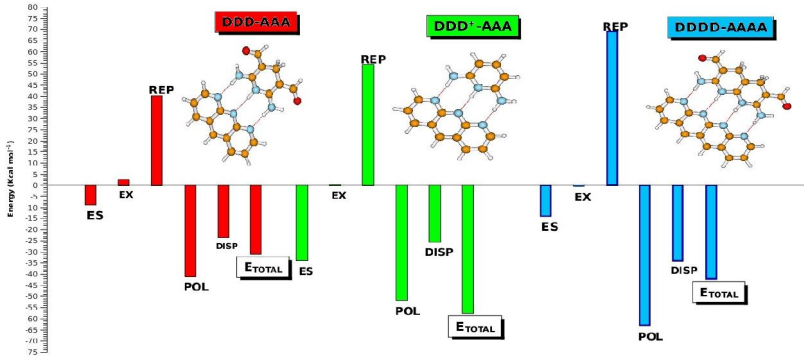

Figure 1 – Energy decomposition analysis, LMO-EDA between triple and quadruple h-bond arrays, where the terms are depicted as following, ES=electrostatic energy, EX=exchange energy, REP=repulsion energy, POL=polarization energy, DISP=dispersion energy, E_{TOTAL}=total energy)

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Simulação molecular do dímero da proteína *E* do vírus do dengue tipo 2

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Key-words: simulação molecular, proteína *E*, dengue

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Dengue é uma doença transmitida pela picada do mosquito *Aedes Aegypti* infectado por um dos quatro tipos de vírus do dengue. Hoje, 2,5 bilhões de pessoas vivem em áreas de risco em países tropicais e subtropicais. Não há substância conhecida com ação antiviral contra os vírus da dengue. A presente abordagem por simulação molecular do problema do dengue foca uma proteína que age fora da célula que tem como uma das suas funções a fusão com a membrana da célula-alvo. O conhecimento da estrutura tridimensional desta proteína de envelope, proteína *E*, a nível atômico é indispensável para a compreensão do mecanismo de fusão. A proteína *E* se apresenta na forma dimérica na fase de pré-fusão em pH neutro, no envelope do vírus, e trimérica na fase de pós-fusão em pH ligeiramente ácido. O comportamento do dímero da proteína *E* em pH neutro em solução aquosa foi estudado usando o pacote GROMACS 4.5.1. Foi usada a estrutura do dímero (código PDB: 1OKE) como configuração inicial. O sistema foi modelado pelo campo de força GROMOS96. As simulações NPT foram realizadas a 300 K e 1 atm. Foram calculadas as raízes quadradas dos desvios quadráticos médios, RMSD, do dímero e dos monômeros em relação à estrutura inicial (1OKE), e à estrutura média obtida por análise dos componentes principais, PCA. O RMSD (1OKE) do dímero apresentou um valor médio de 0,48 nm e RMSD (PCA) de 0,23 nm, portanto a estrutura média é pouco diferente da estrutura inicial, mas os detalhes da estrutura secundária se mantiveram. O RMSD (1OKE) médio do monômero *A* é de 0,37 nm e de RMSD (PCA) de 0,20 nm. Os RMSD (1OKE) e (PCA) médios do monômero *B* são de 0,37 e 0,36 nm, respectivamente. Porém, RSMD entre a estrutura inicial do monômero *B* e sua média é de 0,302 nm, o que implica que as estruturas são diferentes apesar dos RSMD serem parecidos. Portanto, os monômeros apresentaram comportamentos distintos o que resultou em um pequeno desvio quadrático de 0,245 nm entre as duas estruturas médias. A avaliação das estruturas indica que o sistema é estável. Assim, este estudo poderá fornecer estruturas consistentes para a identificação de moléculas inibidoras da atividade da proteína *E* do vírus dengue.

FAPESP, CAPES E CNPQ.

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"On the thermodynamic properties of water around the critical point: Molecular Dynamics simulation using a polarizable model"

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Key-words: Molecular Dynamics, Thermodynamics, Supercritical Water, Polarizable Water Model

The extended simple point charge model (SPC/E) is known to provide reliable physical properties when used to simulate water at room conditions. This is expected, since it is parameterized toward this end. However, it also provides good thermodynamic results when simulated around the critical point. This is interesting because there are marked differences in the water structure in the room and supercritical conditions. The characteristics of the hydrogen bond are very different in the high temperature-pressure and in the low densities regimes, of the critical point. This dissonance raises some simple questions: are there other models capable of reproducing the water thermodynamic properties in these two conditions? Taking into account the molecular polarizability, does it enhance the simulated results? In this work, we chose the AMOEBA water model to study the critical region. AMOEBA is a flexible and polarizable model, parametrized to reproduce *ab initio* calculations, and which provides very good results at liquid and gas phases (small clusters). Using some hundreds of simulations we were able to extract the thermodynamic properties of this model, including its theoretical critical point. It is worth to note that the SPC/E is one of the few models for which the critical point is reported (651K, 0.32g/cm^3, 186atm), and it is well compared to the experimental values (647K, 0.32g/cm^3, 217atm). Among our conclusions we find that the AMOEBA model provides a critical point comparable to SPC/E, and a better thermodynamic behavior (compared to the experimental) around the critical point.

Support: FAPESP, CNPq, CAPES, INCT-FCx, nBioNet e FCT (Portugal)

An ill- osed inverse ro le in en y atic kinetics ack- ean urease denaturation y an anionic surfactant

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Key-words: chemical kinetics, jack-bean urease, neural network procedure

The objective of ill-posed inverse problems theory is retrieving physical information from experimental data by using linear or nonlinear numerical models. This problem is called ill-posed if one or more of three properties of the solution, existence, uni ueness and continuity with respect to experimental errors are not satisfied. In this work a neural network procedure is applied to solve an ill-posed inversion chemical kinetics problem[1] calculation of rate constants for the jack-bean urease denaturation by an anionic surfactant agent, sodium *n*-dodecyl sulphate, from experimental denatured enzyme concentrations. The jack-bean urease denaturation mechanism has three reversible steps. If k_1, k_{-1}, k_2, k_{-2} are the rate constants of the process then the kinetic model is $NU \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} IU \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} DU$ where NU, IU and DU represent respectively the native, intermediate and denatured urease. The efficiency of the neural network was compared with the Levenberg-Mar uardt techni ue[2], commonly used in nonlinear regression methods to solve this kind of kinetics problem. If calculated and experimental physical data are arranged in vectors $P_{\exp}$ and P_{cal} an error function can be proposed as $E = \frac{1}{2}\sum_{j=1}^{m} e_j^2$ with $e_j = P_{cal_j} - P_{exp_j}$ and experimental data. The following values to the error function are obtained by neural network and Levenberg-Ma uardt methods: Noise level at 2 neural network, 2.753 10^{-10} Levenberg-Ma uardt method, 6.058 10^{-7}. Noise level at 10 neural network, 7.164 10^{-9} Levenberg-Ma uardt method, 7.040 10^{-5}. Therefore, the neural network method was more robust than Levenberg-Ma uardt in relation to random noises in the experimental data. The kinetic constants obtained here provide concentrations which are in excellent agreement with experimental results[3].

[1] Lemes, N.H.T. Borges, E. Braga, J.P. *e o . ntell. Lab. S st.* , *96*, 84. [2] Forsythe, G.E. Malcolm, M.A. Moler, C.B. *o uter et ods or at e atical co utations*, 1th ed. Prentice-Hall: London,1977. [3] Nazari, . Mahmoudi, A. Esmaeili, N. Sadeghian, L. Moosavi-Movahedi, A.A. hodafarin, R. *olloids Sur . B* , *3*,139.

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The dependence of topological properties of the hydrogen bond networks on the computer simulation protocols

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Key-words: Hydrogen bond networks, Topological properties, Simulation.

Hydrogen-bonded liquids are very intriguing because they are highly structured, which leads to several peculiar or anomalous properties. The structured behavior of these liquids is attributed to the hydrogen-bond (HB) networks. Previous studies[1] applied Monte Carlo simulation and statistical mechanics of complex networks for obtaining topological properties of HB networks in several systems, such as water, methanol, *t*-butanol and water-alcohol mixtures, and correlated these results with their thermodynamics properties. However, the dependence of the HB networks topological properties on the computer simulation protocol is still unexplored. Thus, we studied the effects of several parameters of the simulation protocols on the topological properties of HB networks. We focused on the number of configurations between samples to perform configurational averages (effects of correlated samples), the effects of the long-range interaction treatments: with and without reaction-field (RF), different potentials for describing the intermolecular interactions between water molecules, and the different criteria for determining the existence of hydrogen bonds. We show that the analysis by local (clustering coefficients, average degrees), semi-global (path lengths) and global (spectral densities) topological properties, and islands statistics as well the small-world behavior of these complex networks were not significantly affected for differences in the simulation protocol (Fig. 1). Except for the clustering coefficient, our results suggest that these analyses are quite robust and the conclusions are generally independent of small differences in the procedures for obtaining these networks.

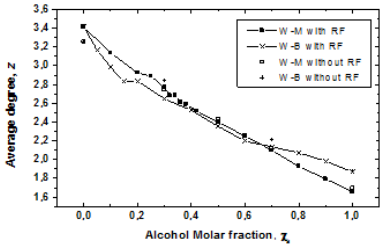

Fig. 1: Average degree, *z* versus methanol molar fraction, χ_s.

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Bond Linkage Isomerism of Bipyridine (nitro/nitrito) Ruthenium Complexes.

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Key-words: Ruthenium nitrosyl complexes, metastable states, DFT, linkage isomerism, LMO-EDA, QTAIM, ELF

Ruthenium nitrosyl complexes have attracted the attention of many researchers groups due to their ability to transport and to release NO, which has remarkable participation in different biochemical, pathological, and physiological processes such as inhibition of tumor growth, regulation of blood pressure, induction of apoptosis, and treatment of Leishmaniasis [1].

Complexes such $[Ru(NO)(NO_2)(bipy)_2]^{2+}$ does not only shown isomerism of nitrosyl group, but also exhibit nitro/nitrito linkage isomerism [2]. In order to shed light on the linkage isomerism, a complete analysis of the nature of Ru-NO and Ru-NO_2 bonds by means of the energy decomposition analysis (LMO-EDA) and topological theories such QTAIM and ELF is employed. Geometry optimizations and harmonic frequencies were performed at BP86/DEF2SVP and BP86/TZVP levels of theory, respectively.

The LMO-EDA analysis of cis-$[Ru(NO)(NO_2)(bipy)_2]^{2+}$ shows that NO_2 binds more strongly to the metal center than the NO group, and that the contribution of electrostatic and polarization terms, modulate the magnitude of the total interaction energy values in Ru-NO and Ru-NO_2 bonds.

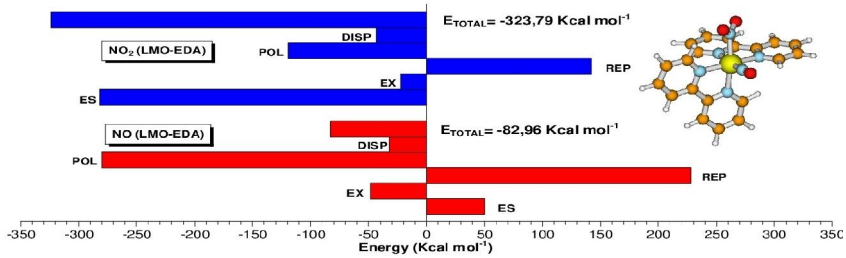

Figure 1 – LMO-EDA analysis of cis-$[Ru(NO)(NO_2)(bipy)_2]^2$ where the terms are depicted as following, ES=electrostatic energy, EX=exchange energy, REP=repulsion energy, POL=polarization energy, DISP=dispersion energy, E_{TOTAL}=total energy)

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[2] O. V. Sizova et al. *Journal of Molecular Structure* (Theochem) 683, **(2004),** 97–102.

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Investigation on the Chalcopyrite´s Surfaces Reconstruction

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Key-words: Chalcopyrite, DFT, Reconstruction, Surfaces

Chalcopyrite (CuFeS2) is the main source of Copper in the world. Traditionally, this metal has been recovered by a pyrometallurgical process. However, the hydrometallurgical treatment is a reliable alternative to extract copper from low grade ores. The reaction with ferric sulphate is the most promising route from the industrial point of view, but, for no clear reasons,[1] the reaction´s kinetic decreases highly in just few hours, limiting the metal recover. Our goal is to investigate the reconstruction of nine chalcopyrite´s surfaces to improve our knowledge about the mineral interfaces with the leaching medium. We carried out DFT calculations (PW91) within the plane waves formalism. The kinetic energy cut off was set as 30 Ry. All the calculations were performed in the PWscf code. Slab models have been used to simulate the surfaces considering a vacuum of 15 Å. The K point´s grids were optimized for each surface studied. The results indicate three different mechanisms. Sulfur terminated surfaces, (001)-S, (100)-S, (111)-S and (112), reconstruct through the sulfur dimerization. Figure 1.a shows the electron localization function on the (001)-S surface which indicates the S-S bond. Metal terminated surfaces, (001)-M (Fig. 1.b), (100)-M and (111)-M reconstruct forming metal-metal bonds. The (110) and (101) surfaces do not reconstruct. There is only a relaxation process in which the metallic atoms move downward if compared with the non reconstructed surfaces.

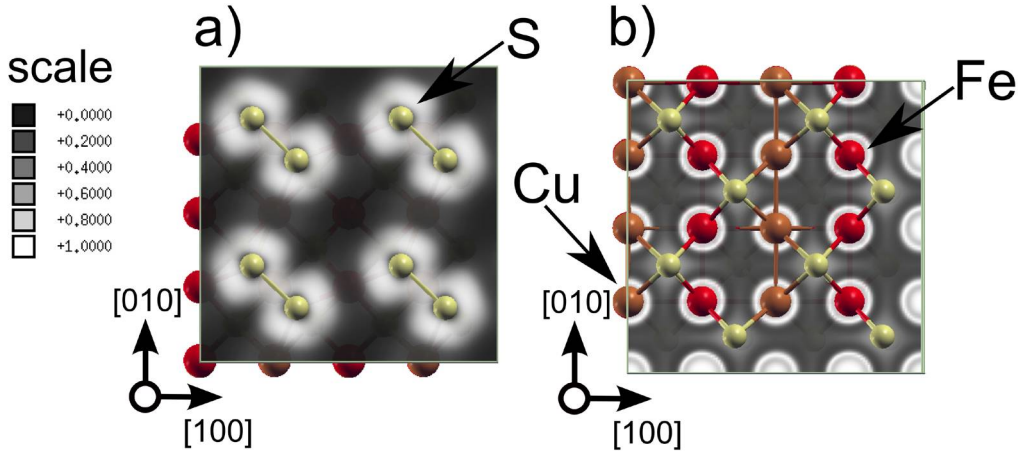

Figure 1: Electron localization functions for the a) (001)-S and b) (001)-M chalcopyrite surfaces

1- *Klauber, C; Int. J. Miner. Process, 2008, 86,(1-4), 1-17.*

Support: FAPEMIG, CNPq, CAPES, INCT-Acqua.

"Theoretical Study of Ethanol Oxidation Catalyzed by Hematite"

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Key-words: catalysis, hematite, DFT, solid state

Carbon deposition over hematite as graphite, amorphous carbon, nanotubes, and nanofibers has been observed experimentally using ethanol as carbon source at high temperatures in a Chemical Vapor Deposition (CVD) reaction [1]. In this work we attempt to find a reasonable mechanism for this reaction. The pathway that has been studied in gas phase is: ethanol first loses a water molecule to become ethene. Ethene is then oxidized to carbon catalyzed by hematite, while its reduction to magnetite takes place. Fe^{3+} may have one to five unpaired electrons, being paramagnetic, thus some methodological challenges should be expected. So this investigation started using small iron models to provide molecular and electronic details about the mechanism and also help the future solid state calculations. Small iron complexes (Fe^{3+} and $[Fe(OH)_6]^{-3}$) were used to model the reaction with ethanol. After that, iron oxide structures were grown to small clusters: $[Fe_2O_2(OH)_8]$ and $[Fe_3O_4(OH)_{10}]$ to approach solid state. For these structures gas phase geometry optimizations and frequency calculations were performed using both MP2 and DFT (B3LYP functional) methods and 6-31G (d,p) basis set. IRC and thermodynamic calculations were carried out in different temperatures and the results compared with experimental data. In Fig. 1 is presented the product of ethanol dehydration brought from the IRC calculations carried out with the transition state structure (v = 739i, at B3LYP/6-31g(d,p)) for this path. The model calculations have been done with Gaussian 2003 suite of programs. The calculated $\Delta G^{\ddagger}$ value for the water loss in ethanol molecule (non-catalyzed process) was 64.4 and 69.6 kcal/mol at the B3LYP and MP2 level respectively. Calculations with the solid state structure (unitary cell of hematite) will be carried out using SIESTA and also ADF/BAND softwares. The active surface of hematite is the 001 [2] and will be constructed using iron and oxygen terminated surfaces.

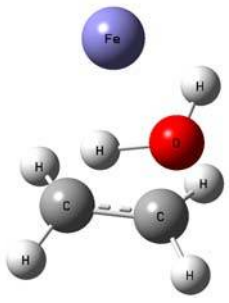

Figure 1: Model for the product of ethanol dehydration.

Support: FAPEMIG, CNpq.

1. Oliveira, A.A.S., et al., Journal of the Brazilian Chemical Society, 2010. **21**: p. 2184-2188.

2. Eggleston, M.C., et al., Geochemical Transactions, 2004. **5**: p. 33-40

A theoretical study of hydrogen bonds between formic acid and acetylene

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Keywords: hydrogen bonds, theoretical calculations, binding energies

B3LYP/6-31++G(d,p) theoretical calculations have been employed to characterize hydrogen-bonded complexes between formic acid and acetylene. Three stable structures have been found. The binding energies of formic acid-acetylene with and without BSSE and ZPE corrections have been determined, as can be seen in Table 1. The most stable structure (I) is shown in Figure.

Table 1. Uncorrected binding energies (ΔE) and binding energies after BSSE and ZPE corrections (ΔE^c) obtained from B3LYP/6-31++G(d,p) calculations.

Complex	ΔE / kJ mol^{-1}	ΔE^c / kJ mol^{-1}
(I)	-15.7	-10.7
(II)	-11.0	-5.8
(III)	-6.2	-1.9

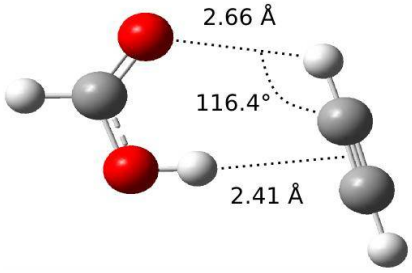

Figure. Most stable complex

As expected, the H-X (X = O or C) stretching frequency is displaced downward and its IR intensity is much enhanced upon H-bond formation. The IR intensities of the stretching and bending modes of the complexed H_b-C≡ and H_b-OC fragments are adequately interpreted through the atomic polar tensors of H_b using the charge-charge flux-overlap modified model. The new vibrational modes arising from complexation show several interesting features, specially the bending modes associated to the proton-donor molecule and the intermolecular stretching mode.

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MKLB and JTS gratefully acknowledges the undergraduate fellowship from Propesq/CNPq and Facepe/CNPq, respectively and VHR acknowledges his graduate fellowship from CAPES.

Hybrid QC/MM Simulations of Metalloenzymes

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Key-words: QM/MM potentials, metalloproteins, polynuclear complexes, multiconfigurational

We have developed and implemented a set of approximations and algorithms into the pDynamo library that permit the simulation of metalloenzymes with various levels of electronic structure description. These include restricted open-shell HF and configuration interaction (CI) with a Davidson diagonalization that permits the treatment of up to 10^5 micro-states for both energy and gradient calculations. An approximate CI selection algorithm allows for the calculation of more challenging polynuclear metal complexes, such as the prosthetic groups of iron-sulfur proteins. Molecular orbital (MO) localization, symmetry analysis, a modified initial guess and the E/ADIIS enhancements were also implemented to improve analysis of MOs and convergence of difficult SCF cases often found for metal centers. Iron-sulfur tetragonal complexes were studied as model systems. Applications of the QC/MM hybrid potential to investigate the rate-limiting reaction in Cytochrome bc1 and the covalent bond-rupture by mechanical stretching of Rubredoxin are also presented.

Support: FAPESP

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A Basis Set and Functional Assessment For The Calculation of The Low Lying Electronic States of Fluorene

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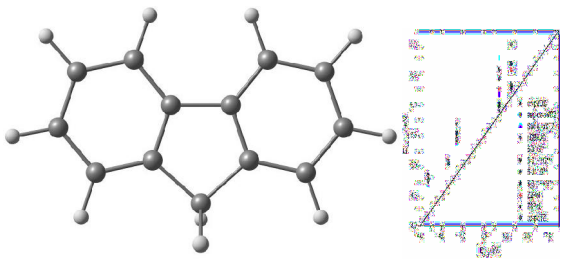
Key-words: Fluorene , TD-DFT, LR-CCSD

Conjugated organic materials are the subject of intensive research for a range of optoelectronic applications[1]. These include light sources such as light-emitting diodes, transistors and lasers, photodetectors, photovoltaics and nonlinear optics[2]. A model for such molecules is fluorene, which molecular structure consists of rigid planar biphenyl units (Fig.1) of C_{2v} symmetry[3]. Low energy experimental absorption spectrum in gas phase is composed by A_1 and B_2 transitions[4]. The aim of this work is to evaluate the performance of the basis sets cc-pVXZ, aug-cc-pVXZ (X=D, T), 6-31G**, 6-31++G**,6-311G**,6-311++G**, Sadlej-pVTZ, Z2Pol and Z3Pol and of the functionals B3LYP, B3LYP/CS00, CAM-B3LYP, PBE0 and LB94 in predicting the observed transitions taking LR-CCSD results as the theoretical reference. All the calculations were done with DALTON 2.0 and NWChem version 6.0 programs. We found that TD-DFT singles method is not able to correctly assign the predicted spectrum while LR-CCSD always describes correctly the experimental data[4]. CAM-B3LYP performed better among the functionals studied. For transitions above 5 eV, diffuse functions are required to properly predict the observed transitions.



(a) **(b)**

Figure 1. (a) Molecular structure of fluorene and **(b)** E_{CCSD} versus E_{exptl}.

References: (1) Montgomery, N.A. and coworkers *J. Phys. Chem. A* **2011**, 115, 2913. **(2)** Clark, J.; Lanzani, G.; *Nature Photonics* **2010**, 4, 438. **(3)**

Support: PROJECT MILLENNIUM n° P07-006-F, FONDECYT Grants 1100283 and 1110758, DGID/UNAB n° DI-01-11/I , and TWAS/CNPq Process n° 190063/2009-2.

Estudo por simulação molecular do monômero da proteína E do vírus da dengue em meio ácido

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Key-words: Dinâmica Molecular, Dengue, Proteína E

Dengue é uma doença transmitida pela picada do mosquito *Aedes Aegypti* infectado com qualquer um dos quatro vírus da dengue. Ela ocorre em regiões tropicais e subtropicais. Hoje, calcula-se que 2,5 bilhões de pessoas vivem em áreas de risco. Os sintomas variam de uma gripe a uma complicação potencialmente letal. No mundo todo, a doença é fatal em cerca de 1% a 5% dos casos. Não existem medicamentos anti-virais específicos para a dengue.

A proteína E do vírus da dengue é uma estrutural que forma parte do envelope do vírus. É importante na interação com os receptores DC-SIGN e na fusão com a membrana celular.

Abordando a proteína E com a simulação molecular, temos como objetivo investigar o comportamento, ao nível atômico, do monômero da proteína E do vírus da dengue quanto à sua estabilidade e quanto aos fatores que a determinam em meio de pH ácido, ou seja, com os resíduos da histidina protonados em solução aquosa, em função da força iônica do meio (0,15 mol/L) focalizando principalmente a região do peptídeo de fusão. A simulação de dinâmica molecular foi feito usando o pacote GROMACS 4.5.3, com a configuração inicial do monômero da proteína E obtida do banco de dados PDB de código 1oke. O sistema foi modelado pelo campo de força GROMOS96. A simulação foi realizada a 300 K e 1 atm no ensemble NPT, num tempo de simulação de 29ns.

A raiz quadrada do desvio quadrático médio, RMSD, mostra que as conformações afastam-se da estrutura inicial, se mantendo em torno de 0,3 nm no decorrer dos primeiros 20 ns de simulação. A partir de 20 ns, houve variações abruptas do RMSD, visto que, as oscilações do RMSD chegaram a valores extremos de 0,57 nm. Entre 22,5 ns e 29 ns, o RMSD se estabilizou, não havendo grandes flutuações.

Levando em conta o curto período de simulação, a evolução da estrutura indica que o monômero da proteína E do vírus da dengue converge para uma estrutura média estável.

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Inverse Virtual Screening Studies of Selected Natural Compounds from Cerrado

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Key-words: Virtual Screening Inverse, docking, Natural products, molecular mechanics, ONIOM, QM/MM.

Several medicinal plants have been studied in recent years in Brazil. However, despite many efforts, the pharmacological mechanisms of many natural products are still unknown. Several biological assays in vivo and in vitro are needed to elucidate this issue, which increase the cost of these researches. The main goal of this study is apply the methodology of inverse virtual screening (TVI), followed by docking studies, and refinement by molecular mechanics (MM) and QM/MM, suggesting pharmacological receptors for 17 selected natural products obtained from cerrado, a typical Brazilian biome. Initially, the structures of natural compounds were generated in online software called sc-PDB, which conducted a search for molecular targets deposited in the Protein data Bank (PDB). The main targets found in this step were refined by the ff03 force field, while the ligands were refined by the semi-empirical method PM6. The ligands were docked against the target protein forming complexes, which were refined again by the ff03 force field. Finally, the binding energy for each complex was obtained by ONIOM (PM6:UFF) method. As a result, these calculations suggested possible molecular targets for these natural compounds. Among targets found are 1EH4, 2A4Z, 1H49, 1JT2, 2BNJ and 3FW9, which are involved in cancer and rheumatoid arthritis pathologies, for example, showing that they are promising molecular targets. The ONIOM energy shows that all of them have binding energy very similar with crystallographic ligand. Our studies suggest that the biological assay for these pathologies found by TVI approach should be carried out before a exhaustive experimental screening. Furthermore, structural changes may be proposed in order to generate compounds able to bind more strongly to the receptor, and become new drugs candidates, optimizing the search for lead compounds.

Support: FAPMIG/CNPq.

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"Docking studies of Glycosides Derivatives with Antitumor Activity"

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Leandro Barbosa (PQ).

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Key-words: Molecular Modeling, cardiotonic glycoside, Na^+/K^+-ATPase.

Cardiac glycosides are drugs used clinically to treat congestive heart failure. These compounds act by inhibiting the plasma sodium potassium adenosine triphosphate (Na+/K+-ATPase), an enzyme responsible for maintenance of intracellular concentrations of sodium and potassium, causing an inotropic and chronotropic positive effect. However, recent studies have shown that some glycosides have cytotoxicity activity in human cells by the same suggested mechanism of action. This study aims to understand the interactions between cardiac glycosides with Na+/K+-ATPase and correlate them with antitumor activity. In this study, fifteen digoxin derivatives were generated, and refined by semi-empirical method PM6, whereas the ATPase (PDB: 3A3Y) was refined by ff03 force field in implicit solvent model. Following, the ligands were docked against the refined molecular target. As a result, binding energy of ligands ranged from -10.2 to -3.1 Kcal/mol using Auto Dock Vina. Additionally, a hydrophobic pocket could be observed in the ATPase. The bulky radicals in lactone ring of cardiac glycosides derivatives can bind into hydrophobic pocket composed by Phe759, Phe762, Tyr284, and without any hydrogen bonds. In contrast, ouabain, a typical cardiotonic glycoside can bind through hydrogen bonds with Ala299 and Thr773, without the hydrogen pocket around lactone moiety (fig 1). Therefore, these compounds show a better antitumoral activity. These results will enable to propose the synthesis of more active and selective derivative glycosides with antitumor activity, suggesting a new chapter in cancer therapy.

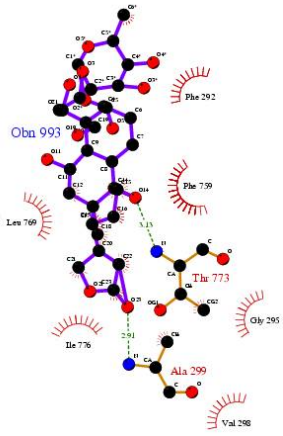

Figure 1: Binding site of Na+/K+-ATPase complexed ouabain

Support: CNPq/PIBIC, FAPEMIG.

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"Triplet energy level prediction of lanthanide(III) complexes using semi-empirical methods"

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Key-words: triplet, lanthanide, semi empirical methods, MOPAC,

The lanthanide(III) complexes with β-diketones are widely described in literature by their high radiative decay efficiency. The energy transfer processes in lanthanide(III) complexes (called antenna effect) depend directly on the triplet energy levels (that is the energy difference between first excited triplet level and ground singlet state) of organic ligands and play a special role in the efficiency of the radiative decay. In this way, the prediction of the triplet energy level is very important to design high efficient lanthanide(III) complexes. Nowadays, the triplet has been predicted by calculations using INDO/S-CIS implemented in Zindo package but the result provided by this methodology is strongly dependent on the chosen active window. This work presents the use of semi empirical methods (AM1, RM1, PM3, PM6) implemented in the MOPAC package to predict the triplet energy level using two levels of calculations: the difference between HOMO and LUMO energies for the singlet ground state (ΔE) and the direct triplet energy calculation (DTE), which is calculated by the difference between fundamental singlet and the first excited triplet. We perform the calculations for free ligands and complexes using both UHF (unrestricted Hartree-Fock) and RHF (Restricted Hartree-Fock) wavefunctions. The ligands selected to perform the calculations were: acac, fod, bzac, btfac, dbm, tta and ntac.

For free ligands both the prediction correlating ΔE and DTE with experimental values fitted a linear curve with a good correlation factor. The best methods in calculations were RM1 (R^2 = 0.92) and PM6 (R^2 = 0.92).
For complexes, ΔE correlated very well with experiment when RHF calculations were performed. DTE correlated very well with experiment when UHF calculations were performed. For both calculations the PM6 was the best method (R2 = 0.90 for ΔE and R2 = 0.87 for DTE).

The results show an alternative way to predict the energy of the triplet level. With the method proposed we are able to choose specific ligands in order to increase the energy transfer rates between organic ligand and lanthanide(III).

Support: INOMAT, CNPq, CAPES and FAPESP.

The Nature of Ru-NO Bonding in Ruthenium Nitrosyl complexes containing polypyrazolylborate (scorpionate) ligand.

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Key-words:$TpRuCl_2(NO)$ complexes, LMOEDA, QTAIM, ELF, NBO

1. Introduction

Transition metal-mediated transformations of nitric oxide (NO) have been biologically and environmentally attractive research fields in these decades. A lot of effort has been put to develop storage/release systems that can deliver NO to desired targets in a controlled manner. It is possible to control the lability of NO in ruthenium nitrosyl complexes by the careful choice of the ligands [1]. For that reason, we have examined the lability of NO^+ and NO^o groups in $[TpRuCl_2(NO)]^q$ complexes by changing the ligands L (hydrogen, pyrazolyl, isoxazole, e isothiazole) at the light of energy decomposition analysis. The results indicate that electrostatic and orbital polarization terms are the most significant to the Ru-NO energy interaction. The NO^+ group coordinates more strongly to Ru in complexes **1** and **2**. However, the the Ru-NO total interaction energy is smaller in **4**-**6**, due to the reduction of electrostatic and polarization terms. The EDA also reveals that neither the nature of the L nor the coordinating atom, when isoxazole or isothiazole ligands are employed, affect the the total Ru-NO interaction energy.

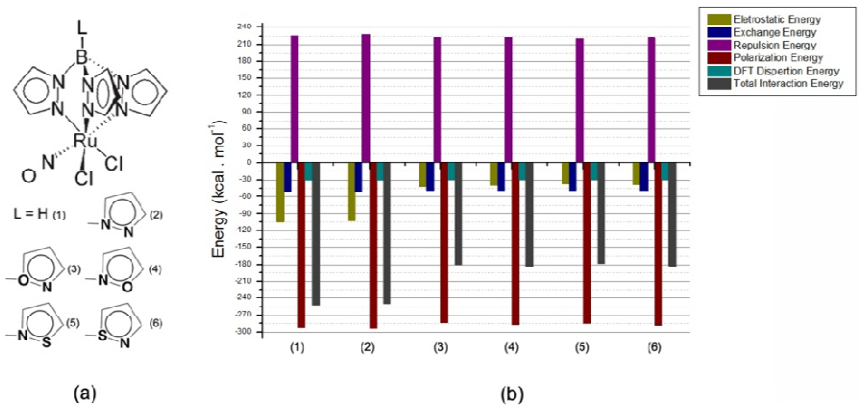

Figure 1. (a) $[TpRuCl_2(NO)]^q$ complexes. (b) energy decomposition analysis for Ru-NO bond in complexes **1**-**6** at M06/def2SVP level of theory.

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Support: FAPESC (Proc. 17.413/20, 5210),CNPq, and UFSC.

"Is there a connection between the upper and the lower energy regions in the HSO_2 potential energy surface?"

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Key-words: HSO_2, PES, Atmospheric Chemistry

The importance of the HSO_2 system in atmospheric and combustion chemistry has motivated several works dedicated to the study of associated structures and chemical reactions. Nevertheless controversy still exists in relation to the possible connection between different energy regions of the potential energy surface (PES) [1-4]. Very recently a path to connect these regions [5] was proposed using the CASPT2/aug-cc-pV(T+d)Z level of calculation but the small energy difference between some of the transitions states present in the mentioned path suggested the necessity of calculations at a higher level. In the present work we report a CCSD(T)/aug-cc-pV(T+d)Z study of the stationary states associated to the indicated connection.

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Support: FAPERJ, CNPq.

A quantum chemical study on the complexation of a macrocycle compound with transition metals divalent of the first period of Inving-Williams order

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Key-words: Irving-Williams; heteromacrocycle; theoretical calculation

The macrocycles compound containing heteroatoms with free electrons pair have great interest research in several fields of applications. Exist, therefore, a continual necessity investigation of the ownerships from coordination of new binders agents macrocycles.

The chemistry of coordination of the heteromacrocycles with oxygen or with nitrogen as heteroatoms is reasonably well known. Were studied the complexes formed with the Irving-Williams order's divalent cations (Mn^{2+}< Fe^{2+}< Co^{2+}< Ni^{2+}<< Cu^{2+}> Zn^{2+}), with atoms of nitrogen complexing these metals and the atoms of sulfur (S) in the position of the atoms of oxygen (Figure 1).

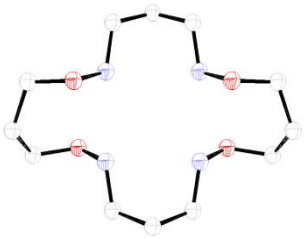

Figure 1. ORTEP of the macrocycle [20]N_4O_4 (1,7,11,17-tetraoxa-2,6,12,16-tetraazacycloicosane) with the atoms of nitrogen as donators. The colors for the atoms of carbon (gray), nitrogen (blue) and oxygen (red).

The calculations were developed at level of theory DFT and this work was developed using the program Gaussian 03. At relation to the methods of DFT, in this work was employee the method hybrid B3LYP, in combination with the base set Lanl2DZ.

The theoretical results obtained of the macrocycle complexing the metals showed that the macrocycle behaves as a ligand of weak field and that modulo of the Interaction energy is most stronger for Ni^{2+} (Figure 2). The macrocycle prefer complexing each cation in its state of biggest multiplicity because of the cation's size cavity and the size cavity's effect of the macrocycle ring.

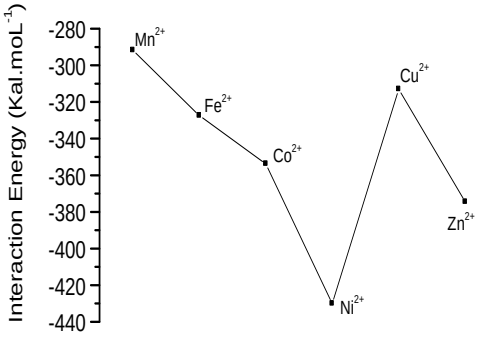

Figure 2. Interaction Energy between metallic cation and the macrocycle [20]N_4S_4.

The complexes more stable obtained for each cation with its multiplicity were Mn^{2+} (sextet), Fe^{2+} (quintet), Co^{2+} (quartet), Ni^{2+} (triplet), Cu^{2+} (doublet) and Zn^{2+} (singlet). This search predicts that the formation's stability of each complex depends of the cation's size and of its multiplicity and that the macrocycle behaves as a weak field ligand.

Support: CNPq.

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“Intense laser field effects on p - d exchange interaction in single manganese doped GaAs”

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Key-words: laser field, GaAs, manganese

We have developed a comprehensive theory about optical control of *p-d* exchange interaction between spins of hole and Mn^{2+} in single-manganese doped GaAs material irradiated by a monochromatic, linearly polarized, intense laser field (LF). The *p-d* exchange interaction leads to formation of magnetic polaron. While the LF induces a *dressed* acceptor Coulomb potential, which transforms single center problem into the one with two *vitual* positively charged centers, resembling hydrogen molecule ion H_2^+. The dichotomy of hole wave functions, which influences the *p-d* exchange interaction as well as binding energy of magnetic polaron, depends strongly on the laser intensity. Increasing the laser intensity reduces the magnetic polaron binding energy. At larger excitation intensity, the magnetic polaron can be completely dissolved.

Support: CAPES e UNIVERSIDADE DE BRASÍLIA.

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S1s Photoabsorption Spectroscopy of the $[NEt_4][Sb(L)_2]$ Complexes, (L=MNT and DMIT).

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Key-words: antimony, complexes, XANES, inner shell

The complexes of poly sulfur ligands represent a very important class of coordination compounds, due their applications in the material science. These complexes can be used, for instance, as charge transfer salts in optical and electronic devices.[1] For these reasons, the valence shell electronic structure of these compounds[2] has been studied by our research group, using the CI methodology. In this work, the S 1s solid state inner shell photoabsorption spectra of antimony complex salts with DMIT (1,3-dithiole-2-thione-4,5-dithiolate) and MNT (1,2-dicyanoethylene-1,2-dithiolate) have been obtained by total electron yield (TEY) detection, using the syncrotron radiation, at the Brazilian National Laboratory of Synchrotron Light (LNLS). Considering the different chemical environments, the assignments of the sulfur atoms were carried out using the improved virtual orbital (IVO) methodology presented in the GSCF3 (Hartree-Fock) and Stobe (DFT) packages. The hole state was calculated with Huzinaga and III-IGLO basis sets. It was also used a DFT method with a nonlocal BE88-PD86. The geometric parameters were calculated by the B3LYP method with 6-311+G** basis sets for the C, N and S atoms and the SBKJC basis set for the coordinated metal. The calculated values were compatible to the crystallographic parameters. The most intense structures observed comparing the XANES spectra of both compounds show the reduction of the number of chemical environments between MNT and DMIT compounds. For the MNT complex, the main structure was identified between 2472 and 2473 eV, assigned as 1s→S-C(π*) and 1s→S-C(σ*). For the DMIT complex, two structures were identified at 2468 and 2471 eV, assigned as 1s→S-C(π*) and 1s→S-C(σ*), with contribution of the metal orbital.

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Support: UFRJ, UFF,LNLS, FAPERJ.

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Theoretical evaluation of spectroscopic and structural properties of Zn(dmit).

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Key-words: dmit, B3LYP, Infrared, UV-Vis, CPCM

The dithiolate ligands have been studied intensively in the last two decades. Physical properties as electric conductivity, ferromagnetism and non-linear optical have been the main focus of these works.[1] In the last years, the 1,3-dithiole-2-thione-4,5-dithiolate (dmit) coordinated with transition and representative elements are receiving relevant attention in new materials science.[2] In this process, our group is carrying out a promising work in the development of new coordination compounds containing dmit and carrying out a vibrational and electronic characterization of anionic complexes.[3] Thus, the objective of this new work is to present a theoretical analysis for the structural, vibrational and electronic characterization in the UV-vis region of compound $[Zn(dmit)]_n$. This compound was synthesized and characterized by elemental analysis.The IR spectrum was obtained in the solid state between 4000 and 150 cm^{-1}. The UV-Vis spectra were obtained between 900 and 190 nm, in DMSO and solid phase. Due to absence of specific crystallographic information for the Zn(dmit), the simulation of metal-sulfur tetrahedral coordination was carried out in this work. The isolated molecules were considered as monomers with incomplete coordination sphere. Thus, the interactions with neighboring molecules are important to complete the Zn-S coordination. The calculations of optimization involved the monomer, dimmer, trimmer and tetrammer and were evaluated together with the vibrational modes of these structures. The B3LYP density functional was used with basis sets double zeta, 6-31G and 6-31+G* present in the package Gaussian 03W. The molecular orbital of the monomer unit were analyzed through the Mulliken population analysis using the programs GaussSum and QM-Forge. The TD-B3LYP method in the vacuum and with polarizable conductor calculation model (CPCM) was carried out to calculate the electronic transitions. The Zn-S intramolecular bond presented value of 2,232Å in the monomer isolated in the vacuum. However, in a tetrahedral coordination with neighboring units, this distance presents value of 2,326 Å. The results show that the methodology is adapted due to a good theoretical-experimental agreement.

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Support: UFRJ, UFF, FAPERJ.

"*In Silico* prediction of structural and spectroscopic properties of PMMA-Fe_3O_4 hybrid material"

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Key-words: hybrid material, DFT, PMMA-Fe_3O_4

Organic/inorganic composite materials have been extensively studied for a long time. Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, ductility, and processability) [1]. Poly(methyl methacrylate) (PMMA)/Fe_3O_4 nanocomposites were prepared *in situ*. This new material was characterized by IR, UV and SAX spectroscopy, the material morphology and thermal properties were evaluated by AFM and TGA/DSC techniques, respectively. Moreover, we have calculated the structural and spectroscopic parameters of the PMMA-Fe_3O_4 hybrid material, comparing them to pure magnetite. In line with that, we got better agreement with experimental data using Slater type orbitals (STO) at DFT level with the PBE functional [2] under periodic boundary conditions with the ADF-BAND program package [3]. In fact, our findings indicate two kinds of iron atoms in the crystalline structure of the hydrid material. The electrostatic calculations show preferential regions for nucleophilic and electrophilic attacks. Furthermore, our results indicate that the magnetite structure increases the thermal stability of PMMA likely due to formation of a crosslinked bond among adjacent polymer chains, thus impeding the oxygen diffusion and significantly decreasing the polymer degradation process rate.

Support: CAPES, FAPEMIG.

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Accurate Gaussian Generator Coordinate basis sets for some atoms of fourth row

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Gaussian Type Functions (GTF) are the most common choice for molecular calculation. Mohallen *et al.*[1] presented an interesting and powerful technique to generate basis sets named Generator Coordinate Hartree-Fock method (GCHF). The GCHF method is the application of generator coordinate (GC) equation to the independent particle model

$$\psi_k = \int \varphi_k(1,\alpha) f_k(\alpha) d\alpha,\ k=1,2,\cdots,n \qquad \text{Eq. 1}$$

where φ_k are the generator functions, f_k are the weight functions, α is the generator coordinate and n is the number of particles. Barbosa *et al.*[2] introduced a new way to generate GTF by means of a polynomial expansion (*p*-GCHF), where each GTF exponent, $\alpha_k^{(w)}$, where *w=s,p,d,f...* symmetries, is determined using the following expression

$$\alpha_k^{(w)} = \exp A\left[\Omega_{min}^{(w)} + (k-1)\Delta\Omega_1^{(w)} + (k-1)^2\Delta\Omega_2^{(w)} + \cdots + (k-1)^q\Delta\Omega_q^{(w)}\right] \qquad \text{Eq. 2}$$

Table 1 shows basis sizes, GCHF, Numerical Hartree-Fock (NHF) energies and energies differences between them and the energy result for copper contracted at 4Z, according to scheme presented by Davidson[3].

Table 1. Ground state Hartree-fock energies for fourth row atoms.

Atom	This work	Energy (E_h)	NHF (E_h)	|ΔE| (mE_h)
V	19s11p6d	-942,880451	-942,884337	3,8868
Cu	19s11p7d	-1638,954221	-1638,963742	9,5209
Zn	19s11p7d	-1777,840583	-1777,848116	7,5326
As	19s13p7d	-2075,351547	-2075,359733	8,1859
Cu	[7s5p4d]	-1638,954099	-1638,963742	9,6430

These results show differences with NHF less than 10 mE_h including the contracted basis for copper, demonstrating that the *p*-GCHF method is capable of generating good contracted basis sets. The aim of this study is to obtain contracted and polarized GTFs for other fourth row atoms for application in molecules.

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Support: CAPES

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Molecular modeling of the interactions between cannabinoid compounds and the CB_1 receptor

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Key-words: CB_1 receptor, homology modeling, ligand-receptor docking

CB_1 receptor is responsible for most of the pharmacological effects of cannabinoid compounds, which have been investigated for the treatment of a large number of medical illnesses, including glaucoma, hypertension, nausea associated with chemotherapy, pain and migraine. The understanding of molecular determinants of ligand binding is critical in drug design, especially when the crystal structure of target protein in complex with a ligand of interest is unknown, which is the case of CB_1 receptor.

In this work, we present a ligand-receptor docking study performed in order to determine the binding modes of selected classical cannabinoids into the CB_1 receptor. Initially, a rhodopsin-based homology model of the CB_1 receptor was built using Modeller. Then, a set of eleven classical cannabinoid compounds were selected from the literature to perform molecular docking studies in the modeled CB_1 receptor structure. In this set, five compounds are psychoactive and six are psychoinactive, according to the effects of their intravenous injection on rhesus monkeys. Site-directed mutagenesis data on the CB_1 receptor were used as guidelines for the docking experiments performed using GOLD 5.0. All docking conformations were ranked with the GoldScore function, and the conformations with the best scores were analyzed using Hermes and VMD.

Our docking results show that in the psychoactive compounds their C3 alkyl side chain is positioned toward the helical bundle interior, while psychoinactive compounds have their C3 alkyl side chain oriented in the direction of the extracellular portion of the receptor. We have also paid special attention to the C4 substituent positioning into the CB_1 receptor, in order to explain the hypothesis of a steric hindrance causing loss of psychoactivity. Our findings suggest that all ligands tend to fit small groups in a tiny space between TM3 and TM7, at the point of interaction between residues K3.28 and S7.39. By the other hand, in compounds with bulky C4 groups, the steric hindrance offered by these residues leads the molecule to turn in the opposite direction, in such a way that smaller groups can be fitted between them. The information gathered by this study can be useful for understanding the molecular determinants of psychoinactivity of cannabinoid compounds, helping so in the design of drug candidates without the undesired psychoactivity.

Support: FAPESP and CNPq

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Modeling Actinide Spectra in Condensed Phase Using WFT-in-DFT and DFT-in-DFT Embedding

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Key-words: Uranyl Chloride, Embedding, Spin-orbit coupling, electronic spectra

Theoretical modeling of actinide species' properties (such as their electronic spectra) require that environment effects are accurately taken into account, since most chemically interesting phenomena occur in condensed phase. This places severe strain on the available methodologies, since one usually must employ wavefunction-based (WFT) methods in order to properly describe electron correlation and spin-orbit effects [1-3]. These are, however, too expensive to use in calculations on large systems, such as solvated species, or in complexes with ligands used for Ln/Ac separation, where Density Functional Theory (DFT) is perhaps the only applicable method. In this contribution we address how, by combining WFT and DFT in a fully QM/QM embedding scheme[4] based on a subsystem formulation of DFT [5], we can obtain accurate spectra for actinide- containing species while reliably describing the environment. We illustrate the performance of WFT-in-DFT embedding in calculations of the low-lying spectrum of NpO_2^{2+} [4] and UO_2^{2+} embedded in $Cs_2UO_2Cl_4$. Moreover, we compare the performance of WFT-in-DFT to that of time-dependent DFT (TDDFT) calculations based on both conventional Kohn-Sham DFT and on a DFT-in-DFT embedding treatment for UO_2^{2+}, therefore extending the investigations done by some of us [6] on the accuracy of TDDFT approaches in describing of electronic spectra of actinides.

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DFT Study of the System Nalidixic Acid/Thymine

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Keywords: nalidixic acid, thymine, DFT

Nalidixic acid is widely used in the treatment of urinary infections. It is known that this compound inhibits the bacterial DNA replication. Several models to describe the interaction between the drug and the DNA have already been proposed. Some of them suggest the interaction of the quinolone group with the nitrogen bases. In this way we are performing this work in order to study these interactions.

In this work the interaction between the anionic and neutral species of nalidixic acid with thymine were studied. The PBE exchange-correlation functional was used, and the 6-311++G(d,p) basis sets were employed in Gaussian 03 program package. The solvent influence was simulated through the polarizable continuum model (PCM). All the possible dimeric structures were analyzed.

Figure 1 contains the four most stable species formed in this system. Figure 1a is the most stable species found for the neutral nalidixic acid form. It is at least 50 kcal.mol^{-1} more stable than the others. Figures 1b, 1c and 1d represent the three most stable structures found for the interaction between thymine and the anionic form of the nalidixic acid. It is clear that the two intermolecular hydrogen bonds in these three species are responsible for their stabilities. The thermodynamical and electronic properties of these compounds will be discussed in details.

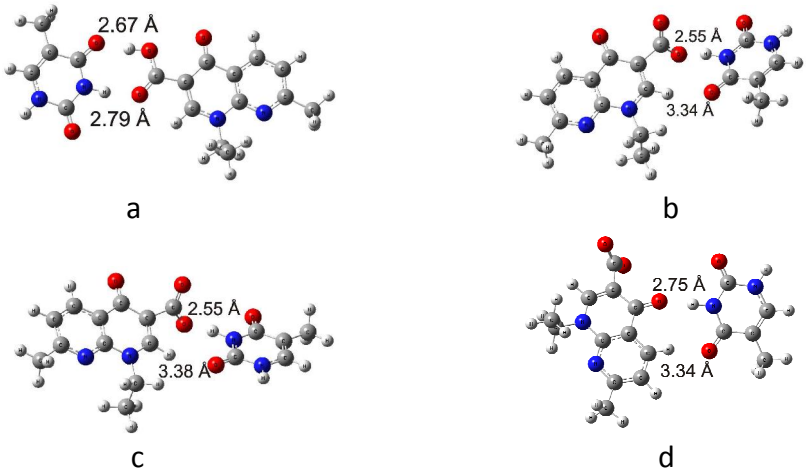

Figura 1: Distinct structures found for the complex of thymine and a) neutral form of nalidixic acid and b), c) and d) with the anionic form of the nalidixic acid.

Support: FAPEMIG, CNPq, CAPES, INCT-ACQUA

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Molecular Dynamics Simulations of the Interaction Between Chitosan and Membrane Cell Models

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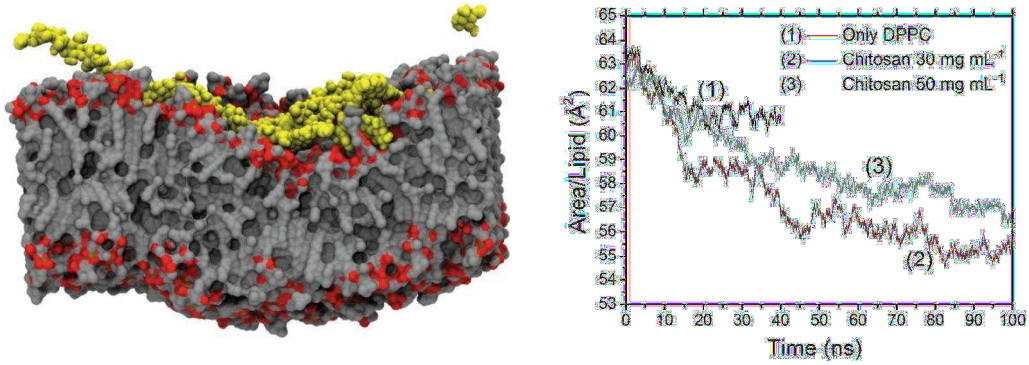
Key-words: Chitosan, DPPC, Molecular Dynamics

Chitosan is a natural polysaccharide obtained by the deacetylation of chitin. These biopolymers are biocompatible, biodegradable and have a wide range of applications in biopharmaceutical and biotechnology industries. The high affinity of chitosan by biological membranes, in acid pH, has been evidenced by experimental results. However, details of the adhesion mechanism are still unknown. To shed some light onto this issue, the interaction between chitosan and dipalmitoyl phosphatidyl choline (DPPC) membranes has been characterized by molecular dynamics simulations. The initial structure was modeled by placing a variable number of chitosan chains at low pH and acetylation degree of 30% at a few Ångstroms from a lipid bilayer surface. 100-ns molecular dynamics simulations were performed to evaluate the influence of chitosan concentration on membrane structure and dynamics. Preliminary results showed that chitosan interacts with the bilayer promoting membrane bending (Figure 1A) and reduction of the area per lipid headgroup (Figure 1B).



(A) (B)

Figure 1 – (A) Final structure for the modeled system with 30 mg.L^{-1}. (B) Area per lipid ratio dependent on Molecular Dynamics Simulation.

Support: FAPEMIG, CNPq, NanoBionet, INCT-INAMI and FACEPE.

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A New Alternative for Pople´s and Dunning´s Gaussian Basis Sets

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Key-words: Generator Coordinate Hartree-Fock method, Gaussian basis sets

Since its development in the eighties, the Generator Coordinate Hartree-Fock (GCHF) method [1] has been used as an important tool to generate universal and adapted Gaussian basis sets to be used in atomic and molecular calculations. In 2003, we published a new way to discretize the integral equation of the GCHF method [2] so that we could improve the efficiency of the GCHF method in generating Gaussian basis sets. This new way of discretizing the integral equation of the GCHF method is done by a polynomial and the name of the method was then changed to polynomial version of the Generate Coordinate Hartree-Fock (pGCHF) method. Here, we now present Gaussian basis sets for the first-row atoms of the periodic table that are an excellent alternative for the well-known Pople´s and Dunning´s Gaussian basis sets since with our first-row basis sets one is able to get results comparable or better than the Pople´s and Dunning´s Gaussian basis sets but with a lower computational cost, mainly when compared to the Dunning´s correlation consistent Gaussian basis sets (see Table 1 as one example).

Table 1 – Optimized B3LYP total energy (in hartree) and computational time for the ground state of the acetone molecule

basis sets	pGCHF	6-31G (3df,3pd)	6-311G (3df,3pd)	cc-pVTZ	cc-pVQZ	cc-pV5Z
Energy	-193.2510342	-193.1825662	-193.2287135	-193.2331578	-193.2492686	**-193.2543032**
CPU Time	**6.67 min**	**4.66 min**	**8.50 min**	**4.00 min**	**51.50 min**	**8h 39 min**

Support: CNPq.

Second order density quantum correction for helium gas equation of state

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Key-words: Helium gas, potential function, second virial, quantum correction

The virial equation of state can be used to predict thermodynamic data at low density and temperature, $p/kT = \rho + B\rho^2 + \ldots$, in which B is the second virial coefficient. A preliminar semiclassical approach will be carried out for HeHe interaction before Bose-Einstein statistic analysed. This semiclassical approach, or quantum approach correction to the Boltzmann statistic gives a second virial expansion[1], $B = B_{class} + (\hbar/2m)B_{q1} + (\hbar/2m)^2 B_{q2} + (\hbar/2m)^3 B_{q3} + \ldots$. Quantum corrections will involve derivative of the potential, and therefore small errors in intermolecular forces will be magnified.

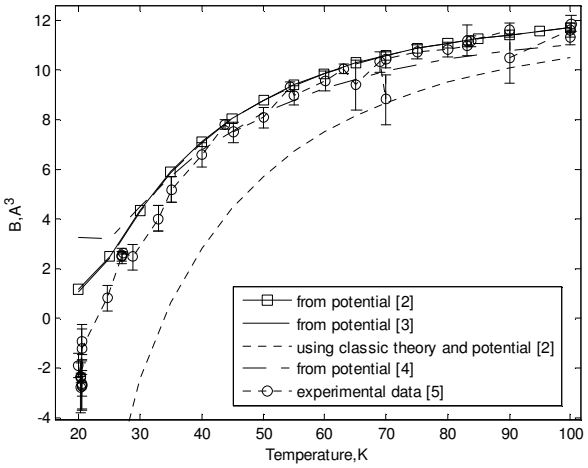

Figure 1- Theoretical and experimental second virial data

Experimental data[5] will be compared with quantum and classical calculation for three recent different potentials [2,3,4] . Calculated quantum second virial, up to third order, are in excellent agreement with experimental data, as shown in figure 1. Classical second virial coefficient is not appropriate to describe HeHe equation of state, even for the highest temperature experimental data available. Quantum correction is essential for this system. Further investigation will be carried out to use Bose-Einstein statistic at lower temperature.

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Support: CNPq,FAPEMIG.

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Quantum parametric sensitivity analysis on model intermolecular potentials

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Key-words: Sensitivity analysis, Bound states, quantum scattering

Model potentials are often used in dynamics and spectroscopy. The potential parameters are established to reproduce some specific properties, such as virial coefficient, cross section or spectroscopic data. To what precision, for a given data, are these parameters needed? This is the subject of sensitivity analysis, which will be carried out here using quantum mechanics. Solution of the Schrödinger equation, with the variable phase method was used to calculate the phase shift. Levinson´s theorem was applied to the recent potentials, Tang and Toennies (TT) [2] , Jeziorska et al. [3] and Varandas [4] , considering the helium-helium interaction. One bound state, for zero angular momentum, was found for Jeziorska et al. or Varandas potentials, whereas for Tang and Toennies no bound state was detected. Potential parameter accuracy, to reproduce experimental evidence [5], was analyzed recursively. The range of acceptable parameters for molecule formation(TT potential) or dissociation (the other two potentials) was determined. Results are as in Table 1 . The most sensitivity parameters are in the short range potential. Dispersion coefficient variation, from about 2% to 10%, will not disturb the molecule formation. These coefficients, in special C_{10}, are more precise than necessary. Functional sensitivity analysis and inelastic parameter cases will also be discussed.

Table 1 : Percentage of potentials parameters variation.

Tang e Toennies[2]		Jeziorska et al. [3]		Varandas[4]	
A	-0.890	β	-0.304	α_0	-9.48
B	+0.067	B	-3.51	α_1	+6.78
C_6	+0.470	B'	-23.6	β_0	-9.64
C_8	+2.02	C_6	-2.34	β_1	+12.7
C_{10}	+6.09	C_8	-10.6	R_0	+6.71
				C_6	-2.13
				C_8	-9.65

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An investigation on the electronic structure of mesoionic compounds

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Key-words: mesoionic compounds, NBO analysis, aromaticity

Mesoionic compounds are a class of molecules which have attracted the interest of scientific community since the late nineteenth century. Their unique structure has proved to be a challenge for researchers who intended to satisfactorily describe and define it. Those compounds are five-membered heterocyclic rings which possess a delocalized π structure clearly separated in two regions: one with a positive charge and the other with a negative one.

In this work it was intended to investigate the electronic structure of three different mesoionic rings (varying X and Z, see figure 1) which had the following basic structure:

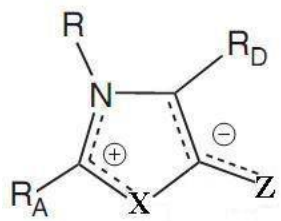

Figure 1 - Mesoionic basic structure

Which:

- R= H or CH_3
- R_A= H, F or CF_3
- R_D= H, CH_3 or NH_2
- X and Z = NCH_3 and S, O and O or S and S

Ground state geometries of 54 structures were fully optimized through DFT calculations using M06-2X functional and a cc-pVTZ basis set. NBO calculations were also made to obtain further electronic structure data. In addition, four aromatic indexes were calculated for each molecule and a multivariate analysis was carried out using the calculated variables.

Results has shown that NOO (X=O and Z=O) mesoionic rings which had F atom as an electron-attractor substituent (Ra) were unstable and have experienced a [X–CZ] bond breaking during the geometry optimization process, therefore, leading to acyclic structures. Also, our results have shown that the frontier orbitals are delocalized throughout the structure which contradicts the localized view stated by recent mesoionic definition (de Oliveira et al; *Phosphorus, Sulfur, Silicon and the Related Elements*, 1996). In addition, principal components analysis have grouped compounds with similar properties, even joining some molecules from different rings and separating some from similar rings – which leads us to believe that the substituent groups play a role as important as the ring structure itself on the electronic structure of those compounds.

Support: CNPq, CAPES, FINEP, INAMI.

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Estudo teórico de propriedades estruturais e mecanismos de formação de polissulfetos

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Key-words: polissulfetos, DFT, calcopirita.

Calcopirita ($CuFeS_2$) é um sulfeto mineral de grande relevância econômica, visto que é a principal fonte de cobre do planeta. O processo convencional de se extrair cobre da calcopirita é através de uma rota pirometalúrgica, no entanto essa não é eficiente para minério com baixo teor de calcopirita. Uma alternativa para os minérios de baixo teor é o tratamento hidrometalúrgico, no qual é feito a lixiviação da calcopirita por uma solução ácida de sulfato férrico. A rota hidrometalúrgica é eficiente nas primeiras horas com uma alta velocidade de reação e uma taxa de recuperação de cobre. No entanto, após algumas horas a reação praticamente cessa, sendo isso atribuído a uma passivação da superfície. Não existe acordo na literatura sobre o que passiva a superfície da calcopirita,[1] no entanto a formação de polissulfetos é uma das hipóteses mais aceitas. Polissulfetos são compostos do tipo (S_n^{2-}) que podem ser formados pela polimerização dos átomos de enxofre na superfície da calcopirita.

A formação de polissulfetos e de enxofre elementar é evidenciada por estudos de espectroscopia RAMAN e TOF-SIMS. No entanto, são escassos estudos na literatura sobre as propriedades químicas e estruturais dos polissulfetos. Dados recentes mostram a formação do dissulfeto, S_2^{2-}, na superfície da calcopirita devido a sua reconstrução.

O objetivo deste trabalho é investigar a rota de formação dos polissulfetos a partir do dissulfeto. Cálculos DFT utilizando o esquema PBE/DZVP2 foram realizados utilizando o programa deMon2K. As propriedades termodinâmicas foram estimadas a 298,15 K. Diferentes espécies químicas aniônicas, S_2^{2-}, S_3^{1-}, S_3^{2-}, S_4^{2-}, S_6^{2-}, S_8^{2-}, S_{10}^{2-}, S_{12}^{2-}, S_{14}^{2-}, S_{16}^{2-}, e neutras, S_2, S_3, S_4, S_6 e S_8, foram investigadas. Os resultados indicam que os polissulfetos com muito átomos de enxofre tendem a se enovelar (figura 1). O mecanismo de iniciação, propagação e de término da formação do enxofre elementar foi proposto. Os aspectos geométricos dos diversos isômeros serão discutidos em detalhes.

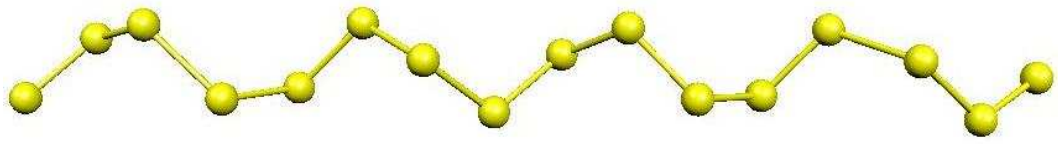

Figura 1 – Geometria mais estável do S_{16}^{-2}.

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Theoretical study of surfaces in $PbMoO_4$

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Keywords: $PbMoO_4$, Density functional theory, periodic calculation

Lead molybdate ($PbMoO_4$) crystals have been widely employed as acousto-optic modulators, deflectors, and ionic conductors. Initially the bulk characterization was made, and then we selected the (001), (011), (111) and (013) surfaces. The simulations have been carried out by means of the CRYSTAL06 computer and are based on density functional theory (DFT) with B3LYP hybrid functional. Pb, Mo and O atoms were described by the follows basis set 6-31G*, 6-31d1 and 311(d31)G[1], respectively.

Optimizations procedures have been employed to determine the structural and electronic properties of bulk and surfaces. The lattice parameters for bulk (experimental in parenthesis)[2],[3] (Å) are: $a = b$ = 5.48 (5.44), c = 11.96 (12.11) and the internal parameters for the oxygen are describe like x=0.238 (0.231), y=0.105 (0.118) and z=0.043 (0.047).

For the bulk, the band gap is indirect (X – Γ), 3.27 eV, in good agreement with experimental data, 3.3 eV. The surface energies and band gap of surfaces are depicted in Table 1.

Table 1: Optical band gap energy $E_{gap\ in}$ (ev), calculated surface energy E_{surf} in (J/m^2) for the selected surfaces

Surfaces	(011)	(001)	(111)	(013)
E_{gap}	4.42	3.18	3.91	4.43
E_{surf}	0.35	0.42	0.67	0.77

The stability order is identified by the sequence: (011)<(001)<(111)<(013), from most stable surface to the least stable one.

The Density of States (DOS) show that the valence bands (VB) has a significantly contribution of oxygen atoms and the conduction band (CB) has a major contribution of molybdenum atoms. The lead don´t have a significant contribution for the CB and VB.

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"Thermodynamic data of the $CH_3SO_3H_2$ atmospheric radical"

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Key-words: isodesmic reaction, enthlapy of formation, ab initio

In a previous study of the atmospheric decomposition of the methanesulfinic acid, the kinetic analysis showed the main product would be the $CH_3SO_3H_2$ radical. In this work, our aim was to conduct a theoretical thermochemical characterization of this species, to which there are not values available in the literature. In this way, we have chosen three isodesmic reactions, listed below:

$CH_3S(O)CH_3 + H_2SO_4 \rightarrow CH_3SO_3H_2 + CH_3SO_2$ (1)
$CH_3S(O)OH + H_2SO_4 \rightarrow CH_3SO_3H_2 + HOSO_2$ (2)
$H_2SO_4 + CH_3SO_2 \rightarrow CH_3SO_3H_2 + SO_3$ (3)

For all species presented above, geometry optimizations and harmonic frequencies were conducted at the UMP2/cc-pV(T+d)Z level of theory. Single point calculations at the UMP2/cc-pV(D+d)Z, UMP2/cc-pV(Q+d)Z and CCSD(T)/cc-pV(T+d)Z levels of theory allowed to obtain more accurate values for energies using the CBS and additivity approximations.

The ΔH_r for the reactions (1), (2) and (3) were determined to be; 310.80 kJ/mol; 333.40 kJ/mol and 196.55 kJ/mol, respectively. The values for ΔH_f at 298K of the $CH_3S(O)CH_3$, H_2SO_4, $HOSO_2$ and SO_3 species were obtained from the literature, as being -150.5 kJ/mol; -735.13 kJ/mol and -373.00 kJ/mol. The values for $CH_3S(O)OH$ and CH_3SO_2 were taken from previous theoretical calculations, as being -337.17 kJ/mol and -218.4 kJ/mol. Using these data, the ΔH_f of the $CH_3SO_3H_2$ was calculated to be -356.43 kJ/mol, -365.90 kJ/mol and -361.21 kJ/mol, for reactions (1), (2) and (3), respectively, with the average value as being -361.18 kJ/mol. Considering that the deviation was ±4.7, and our level of calculation is very accurate, we believe that this value is trustworthy.

Support: CNPq, FAPEMIG

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Mixed Monte Carlo/Molecular Dynamics Simulations of Peptides

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Key-words: simulation, monte carlo, molecular dynamics, peptide folding

Computer simulations are routinely used to study complex molecular systems. In this work we combined the two main simulation techniques, namely Monte Carlo (MC) and Molecular Dynamics (MD). The resulting mixed MC/MD algorithm was used to study the peptides Ala_6 and Ala_{12}. The MC trial moves known as Concerted Rotations with Angles (CRA) [1] were implemented in the GROMACS simulation package (version 4.5.3). The MC/MD simulations consisted of performing one MC trial move (CRA) after 200 MD steps. The leap-frog algorithm was used to integrate the equations of motion during the MD steps. Velocities were kept constant during the MC trial moves, which modify only coordinates of backbone atoms. Simulations of Ala_6 in implicit solvent were run for 2 μs and showed that the MC/MD method yielded equivalent results to the conventional MD simulations. Simulations of Ala_{12} in explicit water were run for 50 ns and showed increased formation of secondary structure (aproximatelly 1.5 times higher) in the MC/MD simulations, when compared with the MD simulations. The MC/MD method could therefore be used to selectively sample alanine-rich regions of larger peptides or proteins. It remains to be established whether the present method can be used to sample hydrophilic residues.

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Support: FAPERJ, CNPq.

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"Testing the ability of various exchange-correlation functionals to describe properties of Mo and Mo_2"

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Key-words: density functional theory; molybdenum atom; molybdenum dimer

In recent years much work has been devoted to the investigation of transition metal clusters. They present unusual structural, electronic, and magnetic properties compared to their bulk counterparts. Their chemical reactivity in catalytic processes is also a matter of interest. In this work the Molybdenum atom and Molybdenum dimer are used as tests for several exchange-correlation density functionals to determine the most adequate functional to be utilized further in the calculation of properties of Molybdenum clusters beyond the dimer. Basis sets of triple-zeta quality, including a set of polarization functions, are used throughout. The functionals tested are BP86, PW91, mPW, PBE, RPBE, revPBE, mPBE, BLYP, OPBE, XLYP, OLYP, KT1 and KT2. All calculations are carried out with the Amsterdam Density Functional (ADF) program. Both the ground and several excited states are investigated in the case of the Molybdenum atom, whereas geometries, electron spin multiplicities, atomization energies and vibrational frequencies are calculated for the dimer. Present findings indicate that the BLYP functional provides the best agreement with experimental data and with theoretical results reported by other authors.

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STUDY OF INTERACTIONS BETWEEN AROMATIC COMPOUNDS AND IONIC LIQUIDS BY COMPUTER SIMULATION

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Key-words: dinâmica molecular, líquidos iônicos, compostos aromáticos.

Ionic liquids (IL) have been applied in green chemistry, in particular due to the certain characteristics such as low vapor pressure and flammability, thermal stability and wide electrochemical window.[1]

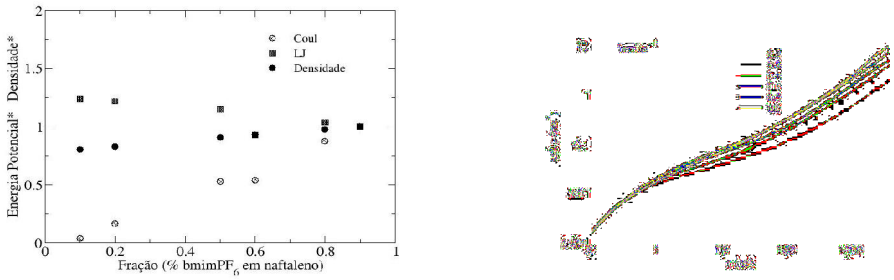

Figure 1. Normalized energies and densities (painel A) as a function of IL mole fraction measured at T=353 K and p=1 atm, and the mean square displacement (MSD) for each studied temperature.

We have investigated the interactions between the 1-butyl-3-methylimidazolium [bmim] hexafluorophosphate with the naphthalene molecules and the transport properties. Figure 1 (painel A) indicates the energy contributions for each IL concentration in naphthalene showing that there is a signature pattern related to the ion association in this system, indicating significative change for Coulomb energy when compared with Lennard-Jones part. We also have calculated the MSD temperature dependence in long time (painel B), where it is possible observe a typical profile of slowing down effect at lower mole fraction of IL in naphthalene, indicating the occurrence of cage effect.

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Support: FAPEMIG

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QSAR studies on pyrimidines as antimalarial prototype compounds

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Key-words: pyrimidines, DFT, QSAR

Despite the growing efforts to eradicate or control malaria, more than one third of the human population lives in endemic areas, with an estimated half-billion of infections annually resulting in about 2 million deaths. Although the development of new treatments such as artemisinin-based combination therapies has been a significant achievement in the fight against malaria, there is still an urgent need for discovery and development of new chemotherapies to control the disease.

In the present work, we report a quantitative structure-activity relationship (QSAR) study performed in order to obtain a reliable and predictive model for the antimalarial activity presented by a series of 2-pyridyl pyrimidines. The data set employed in the QSAR analyses is constituted by 30 compounds selected from the literature, with IC_{50} values measured under the same experimental conditions. All geometries were optimized at the DFT level with the B3LYP functional and the 6-31G** basis set. Eighteen electronic descriptors were calculated with Gaussian 09, and 1197 topological descriptors were calculated using Dragon 5.4. The Kennard-Stone algorithm was employed in order to split the full data set into training (22 compounds) and test (8 compounds) sets, for the purpose of external prediction. The whole set of descriptors was reduced in order to eliminate from the analyses the ones with low correlation coefficients with the biological property. Descriptors presenting a non-uniform distribution with the IC_{50} were also excluded. This reduced set containing 25 descriptors was submitted to the ordered predictors selection (OPS) algorithm, in order to find the most relevant descriptors for PLS regressions.

The best PLS model obtained, chosen on the basis of leave-one-out cross-validation, resulted in q^2 and r^2 values of 0.65 and 0.72, respectively. The model is constituted by three latent variables, combining one physicochemical descriptor (clogP) and four topological descriptors (VRA1, RPCG, RDF080v, Mor31p). The good agreement between experimental and predicted values for both training and test sets indicates the suitability of the selected descriptors used in the model building process. The model obtained in this work was also validated by the leave-N-out cross-validation and *y*-randomization procedures, in order to test its robustness and sensitivity to chance correlations. The results for all of these tests have shown that a reliable, predictive and robust model was found. These findings can be used to guide structural modifications in order to obtain pyrimidines with improved antimalarial activity.

Support: CNPq

Structural and Electronic Properties of the Solid Glycine Polymorphs

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Key-words: glycine crystals, total energy, band structure, DFT calculations.

Aminoacids are the building blocks of protein and peptides macromolecules. Recently, the research for applications of aminoacid crystals as light-emitting materials drives efforts for an improved understanding of their optical processes at the microscopic level. In these crystals, weak chaining occurs between aminoacid molecules due to their zwitterionic states and hydrogen bonds between the amino group N-H and the carboxylic group C-O. In this case, these materials can exhibit a rich (structured) luminescence, which show interesting electron-phonon features. Moreover, glycine, in its solid state, assumes the zwitterionic form NH_3^+-CH_2-COO^-, with three polymorphs α (monoclinic, $P2_1/n$), β (monoclinic, $P2_1$) and γ (hexagonal, $P3_2/P3_1$). While the γ phase is more stable at room temperature, the α polymorph grows spontaneously from aqueous solutions and it is the most studied. While the electronic and vibrational properties of the α phase were well studied, little is known about the electronic properties of the other glycine polymorphs. So, in this work, we have studied, by using the Density Functional Theory within the Local Density Approximation, gradient conjugated techniques, and the planewave pseudopotential method (Abinit code), the structural properties and the electronic structure of the glycine polymorphs. We have used the Troullier-Martins pseudopotentials in the calculations, and our results agree well with both the available experimental data and other theoretical calculations, whenever these comparisons were possible. Based on the obtained results for their band structures, we have speculated about the possibility of application of these crystals as light-emitting materials or as in other biosensor devices.

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Structural and vibrational evaluation of complexes $[Fe(L)_3]^{-3}$, (L=CS_3 and CS_4) and $[Ni(L)_2]^{-2}$, (L=CS_3 and CS_4).

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Key-words: perthiocarbonato, trithiocarbonato, DFT, Infrared, Raman

The synthesis and characterization of coordination compounds with sulfur heterocyclic ligands have been object of intense studies in the last decades.[1] The dithiolenes are the main representative of this class of compounds. However, other polisulfurs as perthiocarbonato (CS_4) and trithiocarbonato (CS_3) are also detached as intermediaries of several chemical reactions, besides acting as addictive anticorrosive and antioxidant for lubricating oils and greases.[2] The elucidation of these properties still was not explored in the literature, being the limited studies to the structural characterization of some few complexes.[3] Thus, this work carries out a complete analysis of structural and vibrational spectroscopy of the anion complexes $[Fe(CS_3)_3]^{-3}$, $[Fe(CS_4)_3]^{-3}$, $[Ni(CS_3)_2]^{-2}$ and $[Ni(CS_4)_2]^{-2}$. The objective is to establish an appropriate theoretical methodology for the analysis of this class of compounds. Some experimental results obtained in the literature were used as reference.[3] The calculations used in the analysis of the electronic spectra involved the previous optimization of the geometry. Also, the vibrational analysis in the Infrared and Raman defined the structures as global minimum energy. The DFT-B3LYP method was used with basis sets double zeta, 6-31G and 6-31+G* present in the package Gaussian 03W. The molecular orbitals were analyzed through the Mulliken population analysis using the programs Gaussun and QM-Forge. Some obtained structural parameters are presented in the Table 1. The results show that the methodology is adequate due to a good theoretical-experimental agreement.

Table 1. Some theoretical and experimental bonds obtained for complexes.

Bond (Å)	Theor. $[Fe(CS_3)_3]^{-3}$	Exp.[3] $[Fe(CS_3)_3]^{-3}$	Theor. $[Ni(CS_3)_2]^{-2}$	Exp.[3] $[Ni(CS_3)_2]^{-2}$
M-S	2.37398 – 2.37452	2.286(3) – 2.323(3)	2.26031	2.21

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Basis set convergence on optical rotation DFT calculations

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Key-words: Gaussian basis sets, optical rotation, DTF.

Recently, a hierarchical sequence of augmented basis sets of double, triple, and quadruple zeta valence qualities plus polarization functions (AXZP, X=D, T and Q) for the atoms from H to Ar were generated[1,2]. At the B3LYP, PBE1PBE, M06, and M06-2X levels of theory, we report a systematic study of Gaussian basis set convergence on frequency dependent optical rotation (OR) ($[\alpha]$) calculations of thirteen rigid chiral molecules at their equilibrium geometries. By direct calculations or by fitting the directly calculated values through one extrapolation scheme, estimates of complete basis set limits (CBS) were obtained.

We examined one of the most popular extrapolation forms - namely, the power form $Y_R(X) = Y_R(\infty) + A\ X^{-3}$, which forms the basis for the CBS model of Helgaker *et al.*[3]. In this equation, we considered only the CBS results obtained from the ATZP and AQZP sets, which will be designed from here on as CBS(3,4).

An inspection of our results[4] indicates some general trends: With rare exceptions, the $[\alpha]_D$ absolute values decrease with the basis set size increase. In general, there is an abrupt change in the OR values from ADZP to ATZP, going, for example, from 37.1 to 26.2 for the molecule 1 and from -143.1 to -139.0 for the molecule 2 (see Fig.1). When compared with the other approaches, the GIAO-B3LYP method gave the smallest error.

Fig.1

TABLE 1. Some calculated GIAO-B3LYP and experimental $[\alpha]_D$ values reported in Ref. [4][a].

	ADZP	ATZP	AQZP	CBS(3,4)	aug-cc-pVTZ[b]	CCSD[c]	Expt.
1	37.1	26.2	23.2	21.0	28.0	69.0	51.2
2	-143.1	-136.0	-134.4	-133.3	-136.4	-117.1	-103.4

[a] All values are in degree/(dm g/cm^3). [b] From Ref. [5]. Calculations carried out from the B3LYP/6-31G* optimized geometries. [c] From Ref. [6]. Calculations carried out with the aug-cc-pVDZ set from the B3LYP/6-31G* optimized geometries.

From our OR results the following conclusions can be drawn. The agreement between theory and experiment worsens with the basis set size increase. It suggests further investigation of other functionals beyond those used here to improve such accord. For all compounds studied, CBS limits were estimated. Theses results can be helpful to calibrate further DFT calculations.

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Support: FAPES, CNPq.

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Molecular aspects of the reactivation process of Acetylcholinesterase Inhibited by Organophosphate and Carbamate

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Key-words: Organophosphate, Carbamate, Docking, QM/MM.

The action of Acethylcholinesterase (AChE) enzyme inhibitors stops the hydrolysis of the neurotransmitter acetylcholine and can lead to an irreversible inhibition of this enzyme[1]. Carbamates (CB) and organophosphorus (OP) are AChE inhibitors, toxic and capable of causing severe poisoning or death to the exposed individuals, and OP can cause irreversible inhibition. These compounds react with the hydroxyl group of the serine residue in the AchE active site, which is directly responsible for acetylcholine hydrolysis[2,4]. The dephosphorylation of this residue (AChE reactivation) is considered the main oxime action mechanism, In fact, it has not been reported yet any universal oxime, able to act efficiently against all the existing neurotoxic agents[3,4]. In our previous work, we have developed and validated a calculation strategy for evaluation of the association and kinetic reactivation constants of oximes. Now, we have extended our discussion for studying the reactivation process of carbamates and other organophosphates with recent published oximes. The docking studies were performed with oximes with biological activity previously reported against AChE inhibited by OP chemical warfare agent ciclosarin (PDB code: 2WHQ) using Molegro Virtual Docker program. In addition, we used QM/MM techniques with Spartan Pro 08, in order to study the reaction mechanism. All transition states, intermediates and precursors were calculated and characterized. The theoretical data show good agreement with experimental results, with R^2 of 0.93 and 0.82 for the docking studies and kinetic parameters of the reaction mechanism, respectively. Our theoretical findings indicate that K005 and HLO-7 compounds could be promising reactivators of AChE inhibited by ciclosarin. In the same line, theoretical calculations, of the same oximes, with the AChE active site inhibited by the carbamate pesticide carbofuran, were performed involving docking and QM/MM techniques.

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Support: FAPEMIG, CAPES, CAPQ, IME e UFLA.

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Thermochemical Study of the Reactions of Methanesulfinic Acid with NO, NO_3 and O_2

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Key-words: Methane sulfinic acid, atmospheric decomposition

Methanesulfinic acid ($CH_3SO(OH)$, MSIA) is an important intermediate in atmospheric decomposition of dimetil sulfide, the largest natural source of sulfur in atmosphere. In order to elucidate the atmospheric decomposition of MSIA, the goal of this work is thermodynamically study the reactions of Methanesulfinic Acid with NO, NO_3 and O_2. The enthalpies e Gibbs free energies of reaction were calculated for seven possible reaction channels. The geometry optimization, vibrational frequencies and thermal properties were carried out at MP2/cc-pV(T+d)Z. Single point calculations were performed at MP2/cc-pV(D+d)Z, MP2/cc-pV(Q+d)Z and CCSD(T)/cc-pV(T+d)Z levels. From these energy values, we made an extrapolation to a complete basis set (CBS) through an exponential fit, and later, estimated the energy at CCSD(T)/CBS level by the use of additivity approximation. The studied channels with the respective Gibbs free energies of reaction are:

$CH_3S(O)OH+O_2 \rightarrow CH_3SO_4H$	$\Delta_rG°=30.9$ kcal/mol	(R1)
$CH_3S(O)OH+O_2 \rightarrow CH_3SO_2+HO_2$	$\Delta_rG°=44.8$ kcal/mol	(R2)
$CH_3S(O)OH+NO \rightarrow CH_3SO_2+HNO$	$\Delta_rG°=25.6$ kcal/mol	(R3)
$CH_3S(O)OH+NO \rightarrow CH_3SO_2+HON$	$\Delta_rG°=68.2$ kcal/mol	(R4)
$CH_3S(O)OH+NO \rightarrow CH_3SO_2(NO)OH$	$\Delta_rG°=32.4$ kcal/mol	(R5)
$CH_3S(O)OH+NO_3 \rightarrow CH_3SO_2+HNO_3$	$\Delta_rG°=-31.2$ kcal/mol	(R6)
$CH_3S(O)OH+NO_3 \rightarrow CH_3SO_3H+NO_2$	$\Delta_rG°=-92.4$ kcal/mol	(R7)

Based on the results above, we conclude that the thermodynamically spontaneous channels, which have a negative Gibbs free energy, are R6, the abstraction of hydrogen from OH group of methanesulfinic acid, and R7, the abstraction of oxygen from NO_3 radical. Kinetic investigations are being conducted for these channels.

Support: FAPEMIG, CNPq.

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Estudo por simulação molecular do monômero da proteína E do vírus da dengue em meio neutro

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Palavras-chave: Dinâmica Molecular, Dengue, Proteína E

A dengue é uma doença febril aguda que acomete principalmente populações em regiões tropicais. Essa doença é causada por um dos 4 serotipos de vírus do dengue transmitido aos seres humanos por um mosquito, o aedes aegypti. O dengue é considerado uma das mais importantes doenças infecciosas re-emergentes na atualidade, com algo entre 50 e 100 milhões de casos por ano dos quais centenas de milhares são e casos de dengue hemorrágica. O dengue hemorrágico é fatal em 1% a 5% dos casos. Estima-se que uma população de 2,5 bilhões de pessoas vive em áreas de risco de transmissão epidêmica. Usando simulação molecular, temos como objetivo identificar quais as possíveis estruturas do monômero da proteína E e, ao nível atômico, identificar quais são os fatores que determinam estas estruturas e quais são as mudanças observadas em função das condições onde a atividade da proteína E se desenvolve. Foi estudado o comportamento do monômero da proteína E em meio neutro, ou seja, com os resíduos de histidina não protonados em meio aquoso de força iônica 0,15 mol/L, por simulação de dinâmica molecular utilizando-se o pacote GROMACS 4.5.3, com a configuração inicial do monômero da proteína E obtida do arquivo PDB sob o código 1oke. O sistema foi modelado pelo campo de força GROMOS96. A simulação foi realizada a 300 K e 1 atm no ensemble NPT. A raiz quadrada do desvio quadrático médio, RMSD, mostra que no decorrer do tempo, as conformações afastam-se da estrutura inicial (média de 0,55 nm) com valores extremos de 0,2 nm e de 0,8 nm. Usando como referência a estrutura média, a média do RMSD caí para 0,33 nm. Durante os primeros 20ns, a estrutura apresenta grandes oscilações, e depois se estabiliza. Observando a estrutura do monômero da proteína E , notamos que ao passar o tempo o monômero assume uma estrutura estável e sem perder as propriedades iniciais.

Fapesp-CNPq

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DFT study of vibrational properties for β-diketonate - Metal complexes

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Key-words β-diketonate ligands, IR spectrum, DFT

The β-diketonate ligands are useful for synthesis of metal complexes, as chelating agents and as bridge between metal cations. Depending on the coordination form, magnetic, electronic and vibrational properties may change severely. Infrared spectroscopy is an important tool to identify different coordination forms. For example, the coordination environment (*cis/trans*) of $M(L_2)R_2$ octahedral complexes (L = β-diketonate ligands, R = another ligand) in η^2 chelate form may be identified by analysis of the M-O stretching vibration. In this work we carry out an analysis of the structure and vibrational spectrum of the $[M(pthfac)_2(NITpPy)_2]$ (M = Co or Mn) complexes (Figure 1).

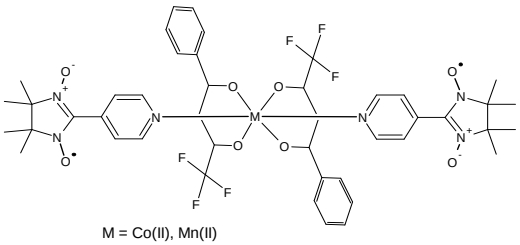

Figure 1 – Example of a $[M(pthfac)_2(NITpPy)_2]$ complex.

The objective is to establish an appropriate theoretical methodology for analysis of this class of compound. Experimental results collected in the literature were used as reference [1]. The vibrational spectra were obtained for optimized geometries using the minimum energy structure. The DFT-B3LYP method was used with the LANL2DZ basis set in the Gaussian 03 software. Stretchings in 1612 and 1372 cm^{-1} were assigned to νC-C e νN-O vibrations of the β-diketonate and nitronyl nitroxide groups, respectively. Theoretical νM-O was observed between 550 and 510 cm^{-1}, compatible with literature data [2]. The molecular orbitals were analyzed through Mulliken population analysis using the Gaussun and QM-Forge softwares. Selected structural parameters are given in Table 1. It shows that theoretical and experimental data are in good agreement.

Table 1. Comparison between selected theoretical and experimental bond lengths.

Bond (Å)	$[Mn(pthfac)_2(NITpPy)_2]$		$[Co(pthfac)_2(NITpPy)_2]$	
	Exp.	Theor.	Exp.	Theor.
Metal-O	2.082 - 2.083	2.158 - 2.167	2.082 - 2.083	2.082 - 2.085
Metal-N	2.156	2.274	2.156	2.155

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Support: Capes, CNPq, FAPERJ.

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"Protein-Protein docking using normal modes and genetic algorithm"

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Key-words: Molecular Modeling, Protein- Protein Interaction, Genetic Algorithm, Analysis of Normal Modes.

Protein-protein docking is a multidimensional problem that can not be explained by a classical lock-and-key mechanism. In the binding processes extensive conformational changes may occur that extend beyond local structure rearrangements. So far, a realistic and computationally efficient assessment of these changes remains a fundamental challenge.The linear combination of normal modes (NM) emerges as an effective approach to reproduce the directions of the conformational changes and capture the structural transition from unbound to bond. However the number of modes and their amplitudes to combine are still required. In this context, we propose a new protein-protein docking approach composed of an automated evaluation of the NM directions to produce a range of NM and amplitudes which are linearly combined and refined in cycles of docking managed by a genetic algorithm (GA). This method was tested against a subset from the protein-protein docking benchmark 4 and was found to predict the structural changes upon binding for rigid docking cases, but requires manual selection of the functional motions for the highly flexible cases. The docking rounds of each generation, frequently sampled acceptable results (<2.5Å) but were promptly discarded due to high energy, and did not survive to the subsequent generations. This if also observed when the best RMS for docking the crystal structures of bond and unbound forms, respectively produces 1AY7 (0.56Å, 0.98Å), 1ACB (1.7Å, 2.6Å) and 1IBR (2.5Å, 3.5Å) with the same parameter set.

Support: Capes, Fapesp, CNRS.

Effect urea on the early stages of mullite precursor formation by molecular dynamics

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Key-words: Molecular dynamics, silanol, aliminuim ion.

Mullite ($3Al_2O_3.2SiO_2$) is a ceramic material that has been used in pieces submitted to large mechanic effort and subjected to high temperatures due to its chemical, physical and mechanical properties. Recent results have shown that these properties are correlated to the synthesis method used in its preparation. Mullite has been synthetized by sol-gel process, which is performed in an aqueous solution of silanol and aluminum ions. The recent results showed a great dependence on the kinetic parameters of mullite crystallization with urea concentration in the aqueous solution. The positive effect of the urea on mullite crystallization is related to its participation in the hydrolysis and condensation reactions of aluminum and silicon, resulting in more homogenous gels. This work shows a computational simulation study based on molecular dynamics of the urea effect of silanol and aluminum chemical interactions in water medium, simulating the early stages of mullite gelation process. The simulation was performed using a Lennard-Jones plus coulombic potential models and in a DL_POLY software package. The simulations were carried out in a NVT statistical ensemble at 298 K. Radial distribution function (RDF) curves showed that urea coordinates water, silanol and di-silanol molecules and aluminum ions, displacing water molecule from their regular position on the first coordination shells. The results also indicated the formation of the $[Al(H_2O)_5(urea)]^{3+}$ chemical specie in the urea based solution instead of $[Al(H_2O)_6]^{3+}$, that was observed in the solution without urea. The resident time of the specie $[Al(H_2O)_5(urea)]^{3+}$ was determined in each solution and their values increased with the increasing of urea concentration for the virtual solution. A close correlation was observed between these resident times and the experimental results of the rate of mullite crystallization. This is a strong indication that the $[Al(H_2O)_5(urea)]^{3+}$ formation is related to the good homogeneity of the mullite precursor experimentally prepared with urea.

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Estudo do mecanismo de fotodissociação do HCFC-133a ($C_2H_2F_3Cl$) utilizando cálculos de estrutura eletrônica multiconfiguracionais.

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Palavras Chave: HCFC, estados excitados, fotodissociação, MCSCF.

A problemática que envolve o consumo do ozônio estratosférico vem sendo largamente estudada nos últimos anos. O mecanismo para este consumo envolve a presença de compostos derivados dos hidroclorofluorcarbonetos (HCFC's) e dos clorofluorcarbonetos (CFC's). As reações envolvem estados eletronicamente excitados, de modo que o entendimento da estrutura eletrônica destes compostos é fundamental para elucidação do mecanismo pelo qual estes se fotodissociam. Assim, este trabalho tem como finalidade estudar os primeiros estados excitados singleto e tripleto ($n\sigma^*$) do HCFC-133a ($C_2H_2F_3Cl$), bem como as curvas de energia potencial destes estados considerando dois graus de liberdade: distância C-Cl e ângulo torcional $\angle_{CF3\text{-}CCl}$. Os cálculos foram realizados utilizando o método SCF multiconfiguracionais (MCSCF), conforme implementado no programa COLUMBUS[1], e as bases cc-pVDZ e aug-cc-pVDZ. Escolheu-se um espaço ativo composto por 4 orbitais e 6 elétrons (CAS(6,4)) sendo estes orbitais $\sigma_{C\text{-}Cl}$, n(Cl, 3p) e $\sigma^*_{C\text{-}Cl}$, relevantes à descrição da quebra da ligação C-Cl. Os resultados mostram que a energia de excitação vertical é 6,27 eV para estado singleto e 5,35 eV para o estado tripleto (CASSCF/aug-cc-pVDZ), com comprimentos de onda de 152 e 178 nm respectivamente, sendo λ_{exp}= 127 nm[2], valor onde detecta-se a saída de FCl durante a fotodissociação. A proximidade entre os valores teóricos e experimental mostra que a saída do FCl provavelmente ocorre no primeiro estado excitado singleto. Na Figura abaixo, são observados dois mínimos locais para o estado singlete à $R_{C\text{-}Cl}$= 3,58 Å e $\angle_{CF3\text{-}CCl}$ = 60° que podem estar associados a este canal de fotodissociação.

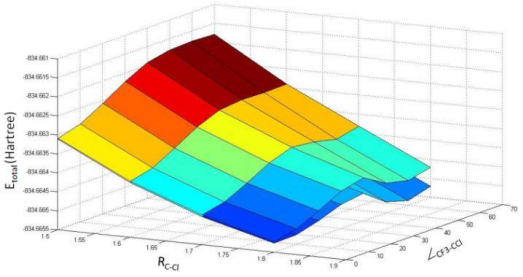

Figura 1: Curva de energia potencial para o estado singleto (CASSCF/cc-pVDZ).

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ensity unctional Theory A lied to Study of che istry reactivity of and i Alloy

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Key-words: Chemical Reactivity, Mg, Mg_2Ni alloy, DFT

Magnesium-based alloys are considered to be the most promising materials for hydrogen storage because of their high storage capacity,the abundance of magnesium in the Earths crust and low cost compared to alternative systems. Of all the magnesium-based alloys, the intermetallic compound Mg_2Ni can be easily synthesized and it reacts readily with gaseous hydrogen to form reversibly the stable hydride Mg_2NiH_4, which, from the engineering point of view, is considered to be a very convenient material for hydrogen storage purposes. sing a density functional approach calculation, the chemical reactivity of Mg and Mg_2Ni alloy towards the atomic hydrogen absorption are systematically investigated. The calculations were performed using the B3PW91 method, the basis set 6-31G is used for the for the hydrogen atom and the effective-core-potential LANL2D for Mg and Ni atoms, according to the formalism of the Gaussian03 program. Our results indicate that magnesium is more reactive than the Mg_2Ni alloy and the local reactivity indicators (Fukui function and electrostatic potential) allow to identify the atoms Ni in the alloy as the most susceptible sites to electrophilic attack.

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"Molecular Modeling and Chemometric Analysis of select natural products with potential antitumoral activity"

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Key-words: Natural products, Molecular Modeling, Chemometry.

Several ways of utilization of natural products derived from plants with medicinal properties is one of the major focus of research for scientists from academia and pharmaceutical industries. In this work, theoretical chemistry methods (Classical and Quantum Mechanics) and chemometric analysis techniques (HCA and PLS) were used to correlate antineoplasic activity with the calculated descriptors of compounds isolated from plants which belonging to aporphine alkaloids, flavonoids and quinines classes. The following descriptors were determined: enthalpy of formation ($\Delta H_f^{o)}$, HOMO and LUMO orbital energy difference ($\Delta E_{HOMO-LUMO}$), parameter of lipophilicity (log P), dipole moment (μ), polarizability, molecular volume and hydration energy. Hierarchical Cluster Analysis (HCA) and Partial Least Squares (PLS) methods ranked compounds in active and inactive in agreement with experimental results (Figure 1). As result (Figure 2), the electronic property $\Delta E_{HOMO-LUMO}$ and the structural property Log P are the most relevant variables to the cytotoxic activity of the tested compounds (r^2~0.87/active compounds).

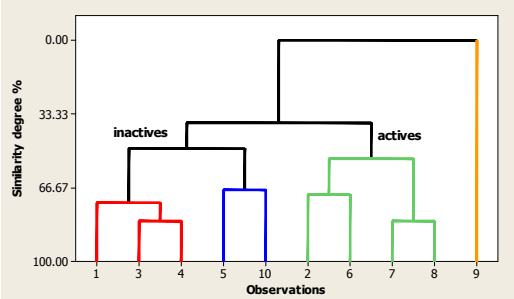

Figure 1: Dendogram obtained from HCA method showing the separation of compounds (active, inactive and the compound 9).

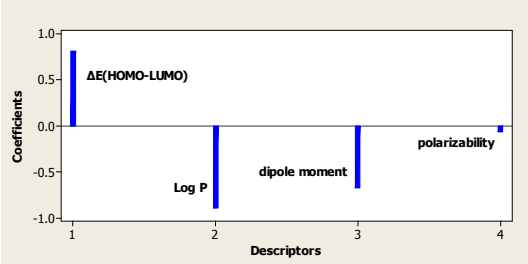

Figure 2. Graph obtained from PLS method showing the relative importance of predictors for the compounds activity.

Support: FAPEMIG.

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Theoretical and vibrational studies of BMIM room temperature ionic liquid, a DFT and NBO approach.

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Key-words: ionic liquids, DFT, NBO, vibrational spectra

The interest in room temperature ionic liquids (RTILs) has been increasing due their excellent properties and wide range of applications. One remarkable property they posses are that they remain in the liquid phase in a wide temperature range; ILs has very low vapor pressures at room temperature, very good chemical stability and high heat capacities, and so on. The elucidation of the molecular interactions within ILs is an important task, for their optimal applications in their vast field of use. In the present study FT-IR and Raman spectral (figure 1) analyses were performed for 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM] [PF_6]. Band Deconvolution Analysis was used to resolve overlapped bands in order to achieve better vibrational assignments. The molecular geometry, vibrational wavenumbers and bonding features in the ground state have been calculated through the DFT with basis set B3LYP. To study significant bonds in the imidazolium ring Natural Bond Orbital (NBO) analysis was also carried out at the HF/6-311+G (d, p) level. The energy gap between the HUMO and LUMO orbitals was of 0.44 a.u. The occurrence of charge transfer bands inside the $BMIM^+$ ion and interactions between the ions $BMIM^+$ and PF_6^- were also confirmed. The more representative interactions are between HOMO→LUMO with stabilization energy of 137.74 kcal/mol, and between HOMO →LUMO+1 with stabilization energy of 49.04 kcal/mol. Figure 2 represent the interaction of one fluorine atom with the hydrogen atom with 5.71 kcal/mol stabilization energy, and is one of factors contributing to the lowering of O_h to C_1 symmetry for the PF_6^- anion.

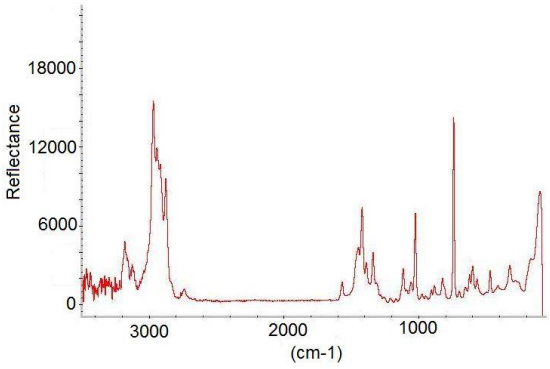

Figure 1

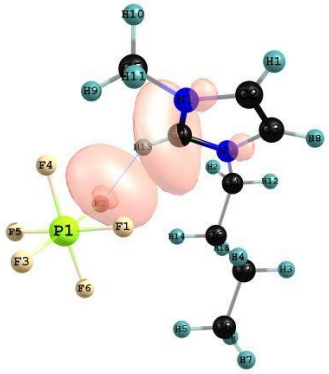

Figure 2

Support: CAPES

Theoretical Study of the Optical Absorption of Glycine Rotamers by Time Dependent DFT Calculations

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Key-words: glycine molecule, electronic structure, optical absorption, TDDFT.

Although being the simplest amino acid, glycine is essential for the biosynthesis of nucleic acids, and acts as inhibitory neurotransmitter in the brain/spinal cord. It has no stereoisomers, but thirteen neutral minimum-energy conformers, or rotamers, in the gas phase were predicted by theoretical studies, three of which being confirmed experimentally. Despite the fact that the structural and electronic properties of these conformers have been studied by both the Hartree-Fock and Density Functional methods, the knowledge about their excited states, as well as their optical absorption is rather scarce. In order to complete these missing informations, we have calculated, by using the Time-Dependent Density Functional Theory within the Adiabatic Local Density Approximation and gradient conjugated techniques (Orca code), the structural properties, electronic structure, and the optical absorption of the three lowest-energy conformers of glycine, as well as of the glycine in its dipolar structure. We have used the 6-311G basis set, and the optical absorption was evaluated by the Casida approximation. Our results agree well with both the available experimental data and other theoretical calculations, whenever these comparisons were possible. Based on our results, we have shown that, while the optical adsorption of the glycine rotamers starts at the UV region of the electromagnetic spectra, for the glycine in its dipolar modification, this adsorption starts at the violet (~ 375 nm). Moreover, we have verified that, in all cases, the strong electronic excitations involve an electron from the carboxyl region (at the HOMO state) to the amine one (at the unoccupied states).

Support: PIBIC/FAPEMIG and FAPEMIG CEX APQ-02418/09.

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"Charge distribution on Carbon Nanotubes: induced electric dipole with non-covalent functionalization"

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Key-words: Carbon Nanotube, HCN, electric dipole moment.

Recently, Carbon Nanotubes (CNT) have been target of many papers due to its physical properties and potential applications. These properties can be tuned up or completed changed by the chirality or by functionalization of the CNT [1]. We have investigated the charge transfer system: HCN and its hydrogen bonding dimer inside zigzag CNTs with different radii (4.70 – 7.87 Å) and length (9.26 and 11.55 Å), the borders are saturated with hydrogen, through B3LYP/6-31G(d) calculation level and NBO charge partition on Gaussian 03 program.

The encapsulation of HCN and its dimer by CNT leads to a charge transfer (CT) complex where the charges migrate from the tube to the HCN and it decreases with the increasing of radius. An interesting observation is that CT leaves a pattern of charge distribution on the nanotube leading to a longitudinal induced electric dipole moment opposite to the electric dipole of HCN (Figure 1) due the neutral character of the system HCN@CNT.

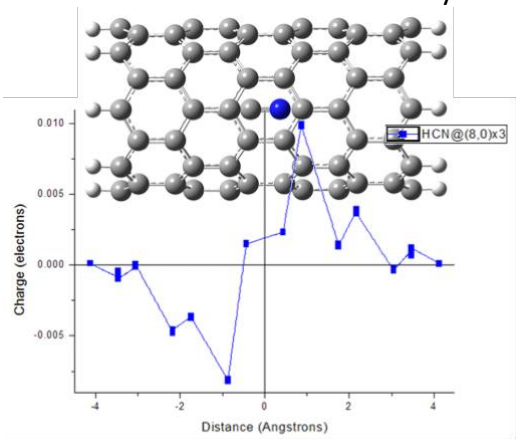

Figure 1. Sum of atomic charges (NBO) of CNT versus distance of mass center. CNT (8,0) with three unit cells.

From Figure 1 we observe that the CNT moiety containing the nitrogen atom of HCN assumes a positive character whereas the CNT moiety containing the C–H bond of HCN assumes a negative character. This pattern is observed on the encapsulation of HCN dimer too. This result can suggest why the CNT changes its conductance feature with non-covalent functionalization. One can imagine the flux of HCN into the nanotube leading to a charge transport on the CNT walls or equivalently submitting a charge flux on the CNT forcing the transport of HCN (in)out-side the tube. The consequences of this pattern on the conductance of nanotube will be investigated through analysis of the band structure for the periodical system.

1. A. G. Souza Filho, S. B. Fagan, *Quim. Nova*, **30**, 1685 (2007);

Support: CAPES, INCT-INAMI, CNPq, FACEPE.

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" Modelling Potential Energy Curves Based on a Simplest molecular-orbital theory of H_2^+ and q-exponential function "

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Key-words: Potential Energy Curves, q-exponential function, molecular dynamics simulation.

Modeling the potential energy curves (PEC) of diatomic systems is of fundamental importance to many issues, including prediction of cluster structures, reactive scattering, molecular spectroscopy, atom-atom collisions, and diatomic ro-vibrational energies. Numerous attempts to analytically model diatomic potentials have been made, such as Morse, Generalized Rydberg, q-Rydberg, Polynomials in coordinate Bond Order (BO), q-BO, as well as Tang-Toennies potential. These potentials usually aim to describe either strongly or weakly bound, neutral or singly charged diatomic and often lose their validity for either small or relatively large internuclear distance. New PEC have been built using hybrid potentials, which different analytical functions for different interaction region of nuclear distance and thereby need more than four adaptable parameters. Our goal is to introduce a new analytical form based on a simplest molecular-orbital theory of H_2^+ and q-exponential function to fit a wide variety of diatomic systems, including neutral and singly charged diatomics, long-range bound diatomics, metastable molecular dications and molecular trications using either one or two adaptable parameters. To verify the quality of this new analytical form, we calculated the vibrational spectra and ro-vibrational spectroscopic constants of H_2, Li_2, NaAr, CdNe, BeH^{++} and LiH diatomic systems. The obtained results are in a good agreement with experimental data available in literature.

Support: CNPq, CAPES.

"Evaluating the DFT Performance to Describe Cation-π Interactions in $[Ru(NH_3)_3(\eta^6\text{-}C_{16}H_{16})]^{2+}$ Complexes"

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Key-words: DFT, Cyclophanes, Cation-π Interaction, LMOEDA.

For several decades, the cyclophanes have attracted the attention of the chemists due to their versatility and capacity to form complexes with transition metals through cation-π interactions [1].

In this work, the performance of different functionals such B3LYP, TPSS and M06, to describe the magnitude of cation-π interactions at the light of energy decomposition analysis, LMOEDA [2] is presented. The obtained values were contrasted with MP2 results. All calculations were performed by using ORCA and GAMESS-US packages, employing Ahlrichs' def2-SVP basis set, and the required ECP for ruthenium(II) [3]. Preliminary testes have shown that LMOEDA is insensitive to the basis set. All functionals have exhibited expected behaviors, the interaction energy of molecular fragments increases rapidly to distances smaller than the equilibrium one, passing through a minimum and approaching zero as the Ru-arene distance increases, Figure 1.

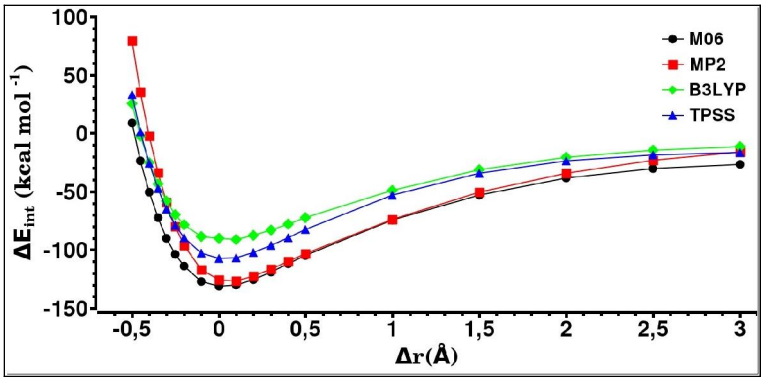

Figure 1. Total interaction energy versus Ru-arene distance in $[Ru(NH_3)_3(\eta^6\text{-}C_{16}H_{16})]^{2+}$ complexes.

M06 is the most suitable functional to describe the cation-π interaction in $[Ru(NH_3)_3(\eta^6\text{-}C_{16}H_{16})]^{2+}$ complexes since it showed a behavior resembled to MP2. Once verified that the M06 is the most appropriate functional to describe cation-π interactions in cyclophanes, several possibilities are in course of study, such the effect of the substituents, the number and size of bridges.

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"Suramin binding sites in human Group IIA phospholipase A2; a Molecular Dynamics Simulation study. "

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Key-words: Phospholipases A2, Suramin, Molecular Dynamics, Affinity Constant, GROMACS and Linear Interaction Energy.

Phospholipases A2 (PLA2 – EC 3.1.1.4) catalyze the hydrolysis of membrane phospholipids, and a total of 15 groups have been identified to date. The human secreted Phospholipase belongs to group IIA (hsPLA2GIIA) and is normally present in various secretions including inflammatory fluids, human tears, intestinal epithelia cells and macrophages, however chronic over-expression of the protein leads to pathological conditions such as arthritis. The hsPLA2GIIA displays high hydrolytic activity against plasma membranes of Gram-positive bacteria and vesicles composed of anionic lipids, and the consensus is that hsPLA2GIIA activity causes disruption of membrane phospholipids and plays an important role in its biological function. The hsPLA2GIIA has a pI of 10.5, and contains a total of 23 positively charged amino acid residues in the active site and on the protein surface, and the hsPLA2GIIA/membrane interaction occurs via the interfacial recognition site (IRS) that that has a predominance of positively charged residues. Suramin is polysulphonated and widely used as an antiprotozoal/anthelminitic drug, which also inhibits a broad range of enzymes, including hsPLA2GIIA. With the aim of understanding this inhibitory effect, the suramin-hsPLA2GIIA affinity constant was estimated by fluorescence emission and compared with results of Molecular Dynamic (MD) Simulations. MD simulations of suramin and hsPLA2GII (PDB code 1POE), were carried out using GROMACS 4.3 software package and the GROMOS-96 (43a2) force field, and show two possible conformations of the bond suramin that are mediated by hydrophobic and electrostatic interactions with residues in the active-site, N- and C-termini. These results also corroborate those obtained by isothermal titration calorimetry data, which demonstrated 2.7 suramin binding sites on the hsPLA2GIIA, which may explain the 90% reduction in hydrolytic activity observed in the presence of 100 nM suramin. hsPLA2GIIA –suramin binding free energy values were calculated using the linear interaction energy (LIE) method by MD simulation and compared with estimate of the affinity constant obtained by increase of the fluorescence intensity. A good correlation was observed between the results of DM and the constants obtained by fluorescence. The results provide insights for designing more potent inhibitors for hsPLA2GIIA.

Support: FAPESP and CNPq.

A Comparative Study of Gas-Phase Molecules in Carbon and Boron Nitride Nanotubes via Potential Energy Curves

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Key-words: Carbon Nanotubes, Boron Nitride Nanotubes, Potential Energy Curves.

Due to the great range of possible application in many fields of science and technology, nanomaterials have been extensively studied in the recent years. Among them we emphasize Carbon Nanotubes (CNT's) and Boron Nitride Nanotubes (BNNT's). Both classes present cylindrical structures in a nanometer scale and their walls are composed of carbon and boron nitride, respectively. Although these structures share some interesting physical and chemical properties, it is worthy to mention that CNT´s present both metallic and semiconductor behavior, while BNNT´s are always of semiconducting nature. This difference is of particular importance in applications where the electronic nature of the material is preponderant. An important example of these applications is associated with the use of nanometric structures as devices for the capture of gas molecules. In this sense, we investigated (via DFT method) the interaction of the CO_2 molecule with CNT´s and BNNT´s using different diameters [SWNT(5,5), SWNT(10,10), SWNT(10,0), SWNT(17,0)] and chiralities (Table below). Furthermore, we determined the potential energy curves, ro-vibrational energies and spectroscopic constants for these systems. The obtained results revealed important properties about of interaction of the CO_2 molecule with both CNT and BNNT.

Chirality	CNT	Binding Energy (a.u)	Equilibrium Distance (Å)
armchair	SWNT (5,5)	0,0046594	3,21
	SWNT (10,10)	0,0046821	3,15
Zig-zag	SWNT (10,0)	0,0043632	3,23
	SWNT (17,0)	0,0046379	3,14

Support: CNPq, CAPES.

The Role of the Frontier Orbitals on 1,3-Dipolar Cycloadditions

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Key-words: Cycloaddition, FERMO, orbital

The FERMO concept[1] emerges as a powerful and innovative implement to investigate the role of molecular orbitals applied to the description of breakage and formation of chemical bonds. In this work, Hartree-Fock (HF) theory and density functional (DFT) calculations were performed for a series of four reactions of 1,3-dipolar cycloadditions[2] (Figure 1) and were analyzed by molecular orbital (MO) energies, charge transfer, and molecular dynamics (ADMP) techniques for direct dynamics using the DFT method. The regioselectivity for a series of four 1,3-dipolar cycloaddition reactions was studied here using global and local reactivity indexes. We observed that the HOMO energies are insufficient to describe the behavior of these reactions when there is the presence of heteroatoms. By using the frontier effective-for-reaction molecular orbital (FERMO) concept, the reactions that are driven by HOMO, and those that are not, can be better explained, independent of the calculation method used, because both HF and Kohn-Sham methodologies lead to the same FERMO.

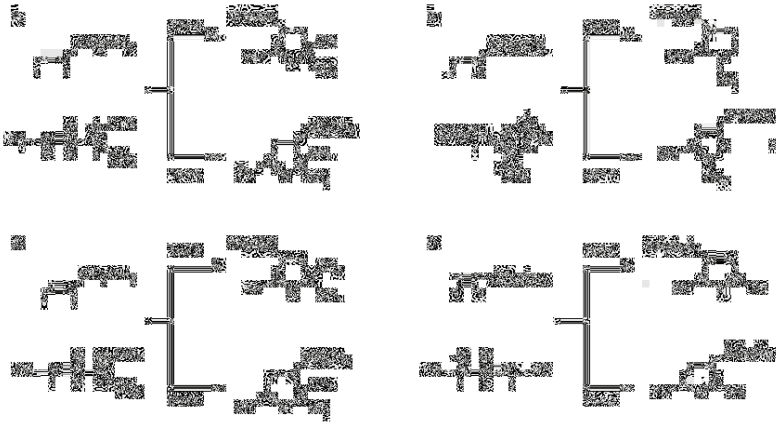

Figure 1: Reactions of 1,3-dipolar cycloaddition investigated.

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Support: CNPq, Fapemig, Capes.

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Theoretical Quantum Study of the $H+Li_2 \rightarrow LiH+Li$ Reaction

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Key-words: $H+Li_2$ reaction, time-independent nuclear Schrödinger equation, quantum scattering, hyper-spherical coordinates, ABC program.

The obtention of potential energy surfaces (PES), of great interest to thorough quantum scattering investigations, is a difficult and laborious task to perform. Maniero and collaborators have recently developed a PES for the $H+Li_2$ system, fitted from the ab initio energies determined through a full CI calculation for the 6-311G (2df, 2pd) basis set and also through a pseudo potential representing the Li. Analytical representations of the surface were obtained using a Bond Order (BO) polynomial expansion for both two and three-body terms, in agreement with the standard many-body method. The present work, carried out with the released PES, contains the theoretical quantum study of the $H+Li_2 \rightarrow LiH+Li$ reaction in the fundamental state with total angular momentum equal and different to zero. Due to the fact that the considered reaction is highly exothermic (yielding an amount of energy of about 33.66 kcal/mol), a great number of rovibrational states and quadratures has been taken into account (even for low energies) in order to accurately describe its dynamical properties. The time-independent nuclear Schrödinger equation has been solved by means of the ABC program (ideally suited to calculating detailed state-to-state quantities - such as the state-resolved differential cross sections - in which the quantum states of the reactants, as well as those of the products, are specified at the same time). ABC simultaneously expands the wave functions of all three possible chemical arrangements in the Delves hyper-spherical coordinate system. The obtained results show that there is no channeling into either the vibration or rotation of the Li_2 molecule. This is consistent with the absence of a transition state in the referred PES, one of the features which are supported by experimental evidence.

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Chemical Speciation Fe^{3+} and the Ligand 4-aminosalicylic Acid – A DFT Study

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Keywords: 4-aminosalicylic acid, chemical speciation, DFT.

The 4-aminosalicylic acid (PAS) is an antibiotic used since 1940[1] in the tuberculosis treatment. This compound has showed to be a safe and efficient medicine for intestinal inflammatory diseases[2], reduction of Mn levels in brain (Parkinson Disease)[3] and as building block for new materials in odontological field[4]. The study of coordination complexes with PAS is quite interesting, since its structure presents three distinct coordination sites. However, from the chemical point of view, this compound has not been studied experimentally or through theoretical methods. There is a great difficult in the crystallization process of the system PAS-Fe^{3+}, that makes its study a challenge. In this way, the use of computational chemistry becomes a very important tool in order to investigate the probable structures of the coordination complexes of PAS and the íon Fe^{3+}.

Density Functional Theory (DFT) was used to study all the possible structures of the systems formed by PAS and Fe^{3+}. The PBE exchange-correlation functional and the basis set DZVP2 to Fe^{3+} and TZVP to the other atoms were used. The thermodynaical properties were estimated at 298.15K, all the possible spin multiplicities were analised.

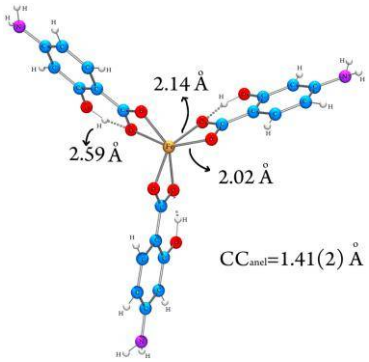

Figure 1: Most stable octahedral complex formed, this sextet complex is at least 7 kcal.mol^{-1} more stable than the others.

Figure 1 shows some relevant structural parameters for the most stable octahedral geometry. It is possible to note that the bonds CC and CO of the carbonil group present distances intermediary between single and double bonds. This structure also presents 3 intramolecular hydrogen bonds. Other properties such as electronic and thermodynamical properties for the different structures studied will be discussed in details.

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Acknowledgments: CAPES, CNPq, FAPEMIG, INCT - Acqua

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"Solvent effects of *m*-xylene on the thermolysis of 4-hydroxy-4-methyl-2-pentanone."

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Key-words: solvent effects, 4-hydroxy-4-methyl-2-pentanone, MMH.

The synthesis and the structural modification reactions of the β-hydroxyketone 4-hydroxy-4-methyl-2-pentanone, also known as diacetone alcohol, have been studied by different methods up today. However, the solvent effects on the kinetics and thermodynamics of this system remain unclear. This research is an attempt to clarify the *m*-xylene solvent effects by a combination of molecular modeling methods: MMH (Multiple Minima Hypersurfaces) for the initial exploration of conformational space, HF (HF/ STO-3G & HF/6-31g(d)) and MP2(MP2/6-31g(d,p)) to refine the models. The MMH method suggests a first solvation shell of four *m*-xylene molecules as the best model to represent the main solvent effects. The association entropy is the major feature for the stabilization of reactant, TS and products. Also, the calculations show that the reaction barrier between reactant and TS diminishes in the presence of *m*-xylene solvent, leading to an increase of the reaction rate constant in *m*-xylene solution compared to the gas phase. A good agreement with the experimental rate constant is only obtained at the MP2 level of calculation. The large values of the Wiberg indices associated to the transformation of the double bond C=O in a single bond, indicates that this is the most important structural change at the transition state. In general the transition state has a 'late' character, structurally nearest to the products than to the reactants.

Support: CAPES, FAPERJ, COLCIENCIAS.

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Vibrational energy flow pathways for the ground state and some valence excited states of the formaldehyde molecule

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Key-words: Formaldehyde, Vibrational coupling, perturbation theory

Vibrational energy flow plays a fundamental role in the chemical reaction and Internal Vibration Redistribution (IVR) phenomena. This work is focused on the analysis of the possible energy flow pathways between the normal vibrational modes of formaldehyde molecule. This compound have been received much attention due to its environmental importance. Our approach is based in the Taylor expansion of the potential energy. The terms with higher degree than quadratic one can be seen as anharmonic terms, usually arising for higher quantum states, associated with classically large amplitudes. If we treat the anharmonicity as a perturbation and consider just up to third degree term, the mixing of the normal mode *i* and *j* along the coordinate of Q_k mode will be given by:

$$L'_i = L_i^0 + \sum_{j \neq i}^{3N} \frac{\omega_{ijk}^0 Q_k}{\lambda_i^0 - \lambda_j^0} L_j^0 \qquad (1)$$

We implemented a program to transform the full matrix of third derivatives of the potential energy surface from the Cartesian nuclear coordinates basis to normal modes basis. The program also performs the perturbation corrections to normal modes and frequencies.

Using MCSCF wavefunctions, we performed the third numerical derivative of the energy using the GAMESS package for the low lying states of formaldehyde ($^1A_1$, $^1A_2$, $^3A_2$). Our results, after transforming to the normal modes basis, showed qualitatively the same behavior for the three states. The symmetric and antisymmetric stretching mode of the CH bond showed a strong coupling principally along the wagging mode of CH_2. We, also calculated the force acting on a atom during the movement of the normal mode k:

$$-\frac{\partial V}{\partial Q_i} = -\frac{1}{2}\omega_{ikk}^0 Q_k^2 \qquad (2)$$

Based in our values of the cubic force constant, we observed that the motion along antisymmetric stretching induces a strong force in the wagging and symmetric mode (ω_{651} = 0,68 Hartree.Bohr^{-3}.amu$^{-3/2}$). This behavior was confirmed by dynamic reaction path calculation. The strong coupling between these modes and the subsequent intramolecular energy relaxation was analyzed in the phase space. The results were used to propose multiphoton excitation schemes designed to carry out specific chemical processes.

Support: PIBIC-UFF-CNPq.

"Fe-PDC as catalyst for oxidation of organic contaminants: computational and experimental evidences"

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Key-words: Fe-PDC, theoretical calculations, Fenton, catalysis

The increase of industrial activity and the development of new chemical products have been significantly improving the quality of life of the population and the progress of other sectors such as agriculture, and environmental chemistry. Thus, the first goal of the present work is to synthesize an iron-dipicolinic acid complex for application in Fenton-like reactions. Furthermore, we intend to test its catalytic activity in the oxidation of organic compounds and to investigate its oxidation mechanism. The theoretical calculations of the reaction mechanism were also performed with several Fe-PDC halogen derivatives. On the experimental side, for the preparation of Fe-PDC, the ferric nitrate (0.6 mM) was dissolved in a PDC (120 mM) solution at the molar proportion of 1:2. The mixture was left under agitation for 48 hours for formation of the light green colored crystals. The complex was characterized by mass spectrometry with electrospray ionization and *Mössbauer* spectroscopy. We carried out theoretical studies to understand the formation of hydroxyl radicals and the overall reaction mechanism. The calculations were performed with Gaussian 98 program. All transition states, intermediates and precursors involved were calculated at the DFT (B3LYP) level using the 6-31G (d, p) basis set. Our results show that Fe-PDC is a good catalyst for oxidation of organic dyes by the Fenton-like mechanism. All theoretical data show good agreement with experimental results. Electrophilic substitution with the halogens studied showed to be advantageous, because it significantly decreased the activation barrier of the chemical reaction. Finally, our theoretical findings also suggest that the oxidation of the dye occurs via a radical mechanism, such as the *Fenton-like* mechanism.

Support: CAPES and CNPq

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Co utational studies etween *Leishmania donovani* α-β tu ulin and sulfona ides derivatives

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Key-words: *Leis ania donovani*, Visceral Leishmaniasis, α-β tubulin enzime

Protozoan infections are parasitic diseases that affect hundreds of millions of people worldwide. In this scenario, Leishmania donovani is a protozoan parasite that causes a disease called visceral leishmaniasis or kalazar. nfortunately, drugs used against kalazar are limited, because they are toxic and there are reports of sudden death[1]. Thus, the importance of new drugs discovery is reflected in our work where the three-dimensional structure of the *Leis ania donovani* α-β Tubulin (LdTub) enzyme was modeled (Figure 1) through homology-modeling. The α-β Tubulin dimer contains α and β subunits which share 40 se uence identity and are therefore basically identical in structure. The alignments of the primary structure between LdTub and template se uence of 1T B (PDB code) showed 82,7 identity. The proposed model was validated and the Ramachandran plot of the LdTub satisfied the tests with 94 of the residues in the most favored regions. After that, we have studied the mode of interaction between the α-β monomers of this enzyme and a class of sulfonamide derivatives as inhibitors of LdTub[2], by using the molecular docking techni ue combined with experimental data for inhibition of the LdTub, our data suggest that sulfonamides derivatives preferentially interact with α-Tubulin subunit (Figure 2). Our findings suggest new compounds in combat leishmaniasis.

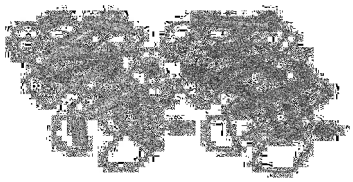

Figure 1: Three-dimensional structure of the *Leis ania donovani* α-β tubulin enzyme.

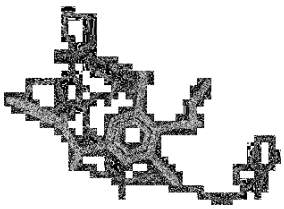

Figure 2: α-Tubulin subunit and compound 8.

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Support CAPES, FAPEMIG, CNP

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Evaluation of Therapeutic Potential for the Control of Alzheimer's Disease: Modeling an Inspiring Cisplatin Analogue

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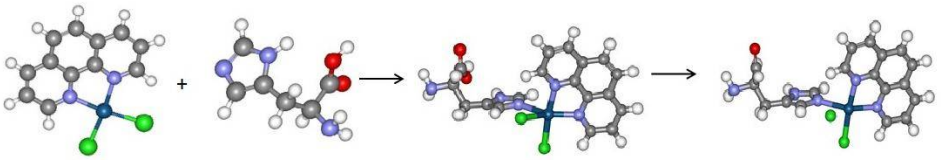
Key-words: Alzheimer, Neurotoxicity, Platinum complex

Neuron and synapse loss together with neurotransmitter dysfunction have been, along with β-amyloid peptide (Aβ) deposition and neurofibrillary tangles, recognized as hallmarks of Alzheimer's disease (AD)[1]. Given the importance of the histidine residues in the Aβ metal binding site, some authors targeted the imidazole side chains as a strategy to inhibit Aβ's neurotoxic activity. The coordination of platinum complexes with histidine residues has been reported as critical in inhibition of the neurotoxic activity[2]. Even with a wide discussion about the enzymatic action of those aggregates, the computational knowledge provided about this matter is scarce. The aim here is to evaluate the coordination model between the histidine-6 (His-6) binding site with the Pt(II)-complex [Pt(1,10-phen)Cl_2] (phen=phenantroline) **(1)**.

The B3LYP hybrid functional has been used for geometry optimization and harmonic frequency calculations, as implemented in Gaussian 03 program. The split-valence basis sets 6-31G(d) and 6-31G(2d) have been used for most atoms except for Pt for which the ECP LanL2MB was used. The species participating of the reaction path are shown in Figure 1. The transition state (TS) is characterized as distorted trigonal bipyramid geometry with the trigonality index equal to 0.53. IRC calculation has confirmed the potential energy surface of the reaction illustrated (Fig. 1).



[Pt(1,10-phen)Cl_2] + His-6 → TS → Local minimum (I1)

Figure 1. Illustration of the reaction of **(1)** with histidine-6 and its related species.

The use of a more polarized basis set showed no significant structural and energy changes only resulting in a higher computational cost.

[1]Mattson, M. P. Nature **2004**, 430, 631-639
[2]Barnham, K. J. *et. al.* PNAS **2008**, 105, 6813-6818

Support: FAPEMIG, BIC-UFJF

Estudo da estabilidade dos complexos formados entre Carboximetilcelulose e Níquel(II)

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Palavras Chaves: Carboximetilcelulose, Níquel(II), Modelagem Molecular

A Carboximetilcelulose (CMC), é um derivado de celulose, amplamente utilizada na indústria alimentícia, farmacêutica, dentre outras. Devido à presença de sítios básicos de Lewis em sua estrutura (-OH e –COOH), a CMC mostrou-se um excelente agente complexante de íons metálicos, tais como Co(II), Al(III) e Ni(II). Entretanto, pouco se sabe sobre a estrutura dos complexos formados, exceto apenas que a relação CMC:Metal parece ser 1:1 ou 1:2[1,2]. Este trabalho, tem como objetivo estudar a estabilidade dos complexos formados entre a CMC (atuando como coordenante monodentado ou bidentado) e Ni^{2+} (coordenado a uma ou duas moléculas de CMC).

Tanto as otimizações de geometrias moleculares quanto os cálculos dos espectros vibracionais foram realizados considerando-se as moléculas em fase gasosa, empregando-se a parametrização PM6[3] disponibilizada no pacote computacional MOPAC 2009. A coordenação do íon $[Ni(H_2O)_6]^{2+}$ é modelada pela retirada de uma molécula de água por cada grupo COO^- ligante presente na molécula de **CMC**.

Os valores dos $\Delta_{reação}H$, foram calculados a partir dos $\Delta_{formação}H$, dos seguintes processos:

$$[Ni(H_2O)_6]^{2+} + xCMC^- \rightarrow [Ni(CMC)_x(H_2O)_{6-x}]^{+2-x} + xH_2O$$

$$[Ni(H_2O)_6]^{2+} + xCMC^{2-} \rightarrow [Ni(CMC)_x(H_2O)_{6-2x}]^{+2-2x} + 2xH_2O$$

onde a CMC^{1-ou2-} atua como ligante monodentado ou bidentado, respectivamente.

Os valores obtidos para os $\Delta_{reação}H$ apontam para o fato de que a bicoordenação do Ni(II) pela **CMC** é mais exotérmica que a monocoordenação. Quando há somente uma molécula de **CMC** coordenante, esta diferença é significativa (cerca de 304kJmol^{-1}) enquanto que para duas moléculas de ligante ela diminui para cerca de 24 kJ mol^{-1}. Apesar da bicoordenação ser mais energeticamente favorável em relação à monocoordenação, efeitos estéreos fazem com que o processo onde dois bicoordenantes participam seja menor que o dobro do valor para o processo com um bicoordenante (diferença de 1115 kJ mol^{-1}).Ainda assim, os valores altamente exotérmicos calculados para as reações de complexação dos íons Ni(II) por **CMC** são coerentes com a alta estabilidade exibida experimentalmente pelos filmes de Ni(CMC) formados em superfícies de eletrodos de níquel em meio alcalino.

Agradecimentos: CNPq (Proc.: 476715/2008-3).

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Proton Transfer in Guanine-Cytosine Base Pair

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Key-words: Proton-transfer, solvent, Guanine, Cytosine.

Proton transfer in DNA bases pair plays important roles in many biological and chemical phenomena and processes, such and genetic mutation, radiation induced DNA damage and photostability of Watson-Crick structure has become a subject of continuous interest for both experimental and theoretical research. The proton transfer form G to complementary C has been observed in double-stranded DNA in nanosecond pulse radiolysis experiments by monitoring the absorbance intensities on UV-vis spectra [1].

In the present work, we report a explicit and statistically converged, *ab initio* determination of the change in structure and energy on the proton-transfer reaction Guanine-Cytosine (G:C) in gas phase and embedded in aqueous solvent. This reaction was modeled by the proton shift along the middle hydrogen bond. We use here a sequential procedure where MC simulations are made to generate structure of the liquid and subsequently quantum mechanical calculations are performed on sampled structures. The results in gas phase show that this reaction is an endothermic reaction with an energy barrier of around 10kcal/mol. The hydrogen bonds between solute and solvent and stability of the triple hydrogen bond will be presented.

Reference:
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Support: FAPEMIG, CNPq.

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H_2^+ Molecular Dynamics in the 8kπ, 9kσ, 9lπ, 9lσ and 10oσ Electronic States

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Key-words: discrete variable representation and Dunham methods; excited electronic energies; rovibrational energies; rovibrational spectroscopic constants

Starting with the Hamilton-Jacobi equation, Campos et al. have applied Hylleraas' method along with the series obtained by Wind-Jaffe to several molecular ions, among which the H_2^+ system, to determine their electronic energies in different states. Up until now, only but a few of these states remained unstudied, and the aim of the present work - the third and last one of a series – is to finally wind up the project of describing the ones for which there exist significant potential wells. This time, we have fitted the potential energy curves for the 8kπ, 9kσ, 9lπ, 9lσ and 10oσ electronic states of the H_2^+ ion, once again employing the Rydberg generalized function. From these fittings, the spectroscopic constants and rovibrational energies have been determined by the same two methods: Dunham's and the discrete variable representation. One more time the theoretically obtained results are in a satisfactory agreement and are expected to provide a comparison source to future works in the experimental field.

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Potential Energy Surface and Canonical Variational Rate Constants for the Camphene + O_3 Reaction.

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Key-words: Terpenes, Ozonolysis, Transition State Theory, Rate Constant

Terpenes account for the major fraction of non-methane hydrocarbons emitted from the terrestrial biosphere, playing a dominant role in the chemistry of the lower troposphere and atmospheric boundary layer. In this work, rate constants for camphene ozonolysis have been obtained using the direct dynamics method.
The theoretical calculations have been performed at DFT level with B3LYP, mPWPW91, mPW1K and the basis sets 6-31G(d), 6-31G(2d,2p), 6-31+G(d,p) and 6-31+G(2d,2p). Beginning at the transition state structure, intrinsic reaction coordinate (IRC) calculations have been performed. Variational transition state theory (TST) has been used to calculate the rate constants in the range 100 - 400K.
Figure 1 shows the minimum energy path at mPW1K/6-31+G(2d,2p) level. According to our results, the cycloaddition of O_3 to camphene is not likely to occur through a pre-barrier complex. B3LYP underestimates the barrier height by 2.13 kcal.mol^{-1}, in relation to the mPW1K with the same basis set, making the value of the rate constant obtained from B3LYP data increase by a factor of 37 in relation to that obtained from mPW1K data. The generalized transition states shift from the saddle point to positive values along the reaction coordinate as the temperature increases, being the variational shift accompanied by a decrease in the ΔG_{max} value of tenths of kcal.mol^{-1}. Such a small decrease in the ΔG_{max} value is expected, since the potential energy surface is too flat (considering the transition state region) and, consequently, the variational effect is small in this range of temperature.

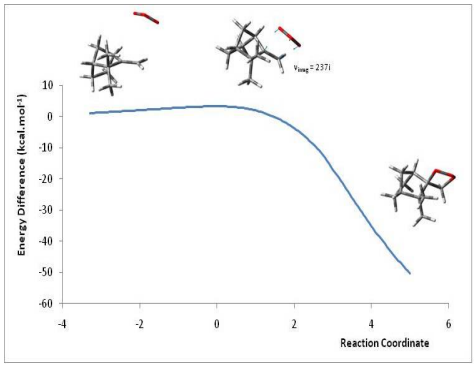

Figure 1: Minimum energy path

Finally, the direct dynamics method has been proved satisfactory for the description of this moderate to large reaction system, with a very good agreement found among experimental (4.5×10^{-18} cm^3.molecule^{-1}.s^{-1}) and theoretical (1.7×10^{-18} cm^3.molecule^{-1}.s^{-1}) values at 298K.

Support: FAPERJ and CNPq.

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A theoretical study of elementary reactions of atomic oxygen with methanethiol

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Key-words: Thermochemical properties, methanethiol, DFT, MP2, CCSD(T).

Chemical processes of sulfur-containing molecules have a significant impact on the atmosphere and the biosphere. In this work, we study elementary reactions of methanethiol molecule (CH_3SH) with the oxygen atom. These reactions are presented in the proposed mechanisms for understanding the sulfur cycle, which is very different from methanol. Thermochemical and structural properties of four reaction paths were calculated using the DFT approximation BB1K and *ab initio* MP2, with the aug-cc-pV(T+d)Z basis set. Single points coupled-cluster calculations on BB1K and MP2 geometries were carried out followed by extrapolation to the complete basis set (CBS) limit to obtain the barrier heights and reaction energies. Therefore, our best results were CCSD(T)/CBS. All electronic structure calculations were carried out with the G03 and G09 codes. The functional BB1K presented very accurate results compared to single-point CCSD(T), and can be very helpful for the thermochemical and kinetic calculations, due to its high accuracy per computational cost ratio. The estimated classical barrier heights ($\Delta V^{\#}$) range from 3.1 to 3.6, 8.7 to 8.9, 1.0 to 1.7 and 1.4 to 2.1 kcal/mol for the reactional paths I , II, III and IV, respectively, as shown in Table below. The breaking and substitution reaction paths are the more accessible ones, which is opposite of what occurs in the methanol+O reactions, where the abstractions are by far more accessible than breaking or substitution [1].

Reactants: CH_3SH+O	CH_3S+OH	CH_2SH+OH	CH_3+HSO	CH_3SO+H
Method/Basis set	I abstraction	II abstraction	III breaking	IV substitution
BB1K/ aug-cc-pV(T+d)Z	4.6	7.8	1.8	2.6
CCSD(T)/ aug-cc-pV(T+d)Z //BB1K	4,4	9.2	2.6	3.0
CCSD(T)/ aug-cc-pV(Q+d)Z //BB1K	*3.6*	*8.9*	*1.7*	*2.1*
CCSD(T)/ CBS_{T-Q}//BB1K	*3.1*	*8.7*	*1.0*	*1.4*
MP2/aug-cc-pV(T+d)Z	9.2	13.2	7.0	7.0
CCSD(T)/ aug-cc-pV(T+d)Z //MP2	4.7	9.2	3.4	4.1
CCSD(T)/ aug-cc-pV(Q+d)Z //MP2	4.1	9.0	2.5	3.0
CCSD(T)/ CBS_{T-Q}//MP2	3.7	8.8	1.7	2.2

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Support: FAPESP, CNPq.

Computational Studies of the Formation of multinuclear platinum compounds Included in α, β, γ-Cyclodextrin and Rotaxanes

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Key-words: Cyclodextrin, binuclear Pt-complexes, ONIOM

Metal complexes have been playing an important role in the study of drugs used in chemotherapy. Binuclear platinum (II) complexes (*bis*-Pt), as those proposed by Farrell[1] (named as 1,1,c,c[1], Fig. 1), show promising antitumor activity in cell lines resistant to cisplatin. *Bis-Pt* as well as other platinum drugs may induce apoptosis by the interaction with DNA and other biomolecules. The bioavailability of the drug is one of the main issues related to the drawbacks of these drugs. Cyclodextrin (CD), in turn, may have an important role in drug controlled release of Pt-complexes[2]. This work is the first proposal for inclusion systems using *bis-Pt* as a guest and distinct CD as hosts.

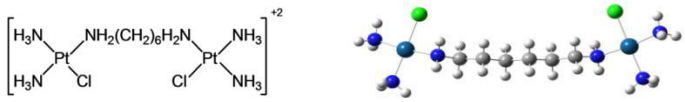

Figure 1. *Bispt* with formula $[\{PtCl(NH_3)_2\}\mu\text{-}H_2N\text{–}(CH_2)_6\text{–}NH_2\text{–}\{PtCl(NH_3)_2\}]^{2+}$; (1,1,c,c)[1].

The aims are to obtain the structures and interaction energies via computational chemistry methodologies. *Ab initio* and ONIOM hybrid methods with (B3LYP/6-31G(d)/LANL2DZ:UFF) were used for geometry optimization and harmonic frequencies calculations for *bis-Pt*@CD complexes using α-, β- and γ-CD as hosts. Among several structures, the inclusion complexes with α and γ-CD (1:1) were found to be stable, with the *bis*-Pt remaining enclosed. The ΔG_{incl} (inclusion free energy) for α-CD (Fig. 2) was -8.42 kcal mol^{-1} at ONIOM level.

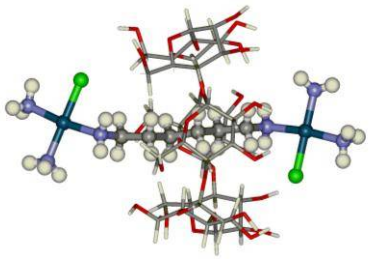

Figure 2. *bis-Pt*@α-CD complex calculated at ONIOM(B3LYP/6-31G(d)/LANL2DZ:UFF).

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SUPPORT BIC/UFJF, FAPEMIG

XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
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"Theoretical Study of Incorporation of Hydrogen in Molybdenum Carbide"

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Key-words: Molybdenum, Carbide, Incorporation of Hydrogen

Transition metal carbides have been employed as catalyst in hydrogenation as an alternative to the metals of platinum group. Particularly, molybdenum carbide has presented a performance in hydrogenation of benzene comparable to noble metals [1,2]. Notwithstanding, the catalyst is deactivated after several hours of reaction. It was recently shown [2] that this deactivation is promoted by strong adsorption of benzene on catalyst surface, which is avoided as long as the hydrogen is available on surface. The goal of this work is to understand the ways by which hydrogen is incorporated to the carbide structure. Accordingly, we are performing DFT calculation with PBE exchange-correlation functional, combined with periodic boundary condition, plane waves basis set and pseudo-potentials on the orthorhombic Mo_2C. Enthalpies for incorporation of hydrogen on the bulk of molybdenum carbide and for adsorption on (001) surface will be reported. So far, results have shown that the incorporation of hydrogen on the bulk is not thermodynamically favored and can be a result of the synthesis procedure. Calculation is in progress concerning the adsorption of hydrogen on Mo_2C surface with and without hydrogen on the bulk. All calculations are been performed on the PWscf code, which is part of the Quantum ESPRESSO suite of programs.

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FAPERJ, CNPq.

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Characterizing new molecular species on the [H, Se, Br] singlet potential energy surface

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Keywords: Selenium-bromine molecules, molecular structure, ab initio, HSeBr

Motivated by the importance of hypohalous acids in reaction cycles in the atmosphere, our group has investigated, at a high level of electron correlation treatment, a series of new molecular species involving sulfur and halogens, and more recently also some compounds containing selenium.[1-3] In this work our focus is on the structural, energetic and spectroscopic characterization of the yet experimentally unknown isomers pairs HSeBr/HBrSe, and the transition state connecting them.

In the electronic treatment, the method CCSD(T) and the basis set series aug-cc-pVnZ for H, and aug-cc-pVnZ-PP for Br and Se (n = D, T, Q and 5) were employed. The energetic results were extrapolated to the complete basis set (CBS) limit using three- and two-parameters formulas shown in equations 1 and 2.

$$E(n) = E_{CBS} + B\exp\{-(n-1)\} + C\exp\{-(n-1)^2\} \quad (n = 3, 4, 5) \qquad (1)$$

$$E(n) = E_{CBS} + B/n^3 \quad (n = 4, 5) \qquad (2)$$

CBS results for the relative energies and structural parameters for the three stationary states are shown in figure 1. Anharmonicity corrections have also been obtained with the configuration interaction (VCI) approach. Figure 1 shows clearly that HSeBr is more stable than HBrSe by about 45 kcal/mol and that the HSeBr bond angle is about 10° smaller than the one in HBrSe. The harmonic frequencies for HSeBr are w_1 = 308.8 cm^{-1}, w_2 = 754.1 cm^{-1} and w_3 = 2410.7 cm^{-1}; the ones for HBrSe are w_1 = 220.2 cm^{-1}, w_2 = 589.8 cm^{-1} and w_3 = 2486.1 cm^{-1}. These results show that the isomers HSeBr and HBrSe can be easily distinguished by IR spectra. We hope that this work will encourage future experimental research related to these yet unknown compounds.

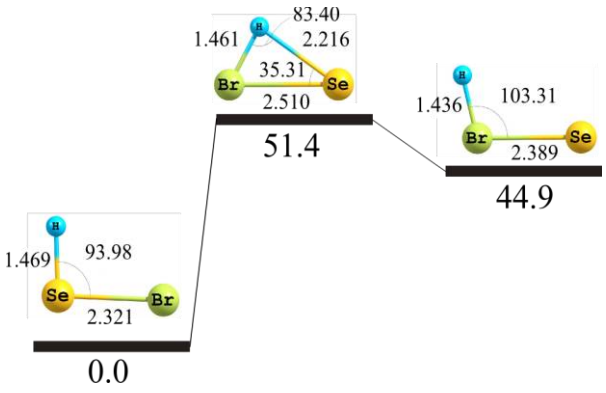

Figure 1. Energy (kcal mol^{-1}) profile and optimized geometric parameters (Å, °) calculated at the CCSD(T)/CBS level theory, including zero-point energies

Support: FAPESP and CNPQ.

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Molecular dynamics simulation of interactions of water-ethanol-NaCl with phospholipids

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Key-words: Ethanol effect, phospholipids bilayer, Molecular Dynamics.

The membrane plasma cells of animals are highly vulnerable to rupture by the presence of ethanol. The aim of this work is to elucidate the membrane stability and function in the presence of different percentage of ethanol, using *in vitro* tests and molecular dynamics simulations. The osmotic fragility of rats' erythrocytes indicates that membrane stability is dependent of ethanol concentration (Figure 1A). In order to characterize the ethanol-phospholipids interactions in molecular level, 20 ns explicit solvent (SPC-water model) molecular dynamics simulations were performed for the dipalmitoyl phosphatidyl choline (DPPC) membrane model with 0.9% of NaCl added ethanol at different concentrations. The AMBER03 force-field was used along with the GROMACS 4.5.4 package on a GPU NVidia Tesla (C1060). The simulation setup (Figure 1B) permitted mimic intracellular and extracellular medium with different ethanol concentration. The preliminary theoretical results, with alcohol at 20%, were validated and displayed a high affinity of ethanol with DPPC and its consequent permeability through membrane. The results demonstrated a good correlation between theoretical and experimental results.

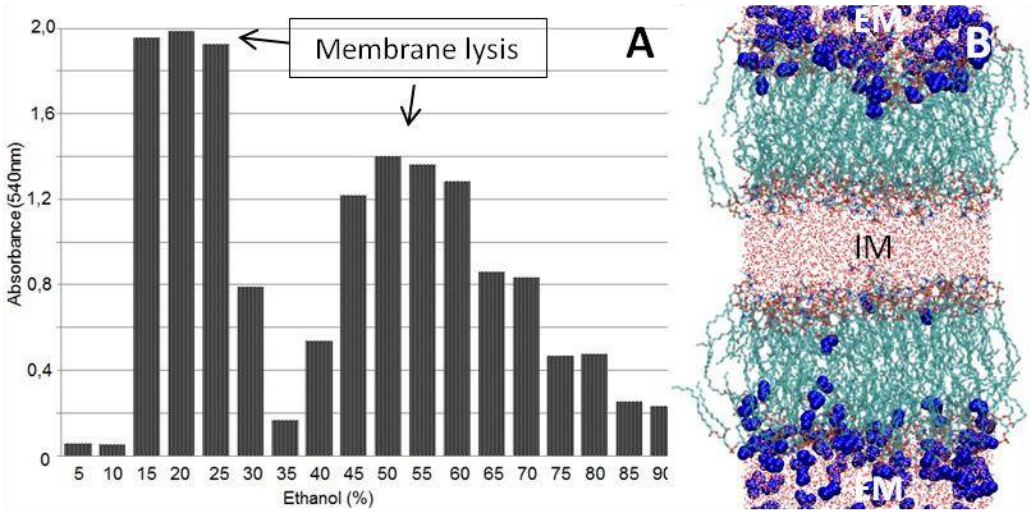

Figure 1. A: Lysis of rats erythrocytes, measured at 540 nm, in ethanol/water at different molar fractions with 0.9% of NaCl. B: Simulated system showing the ethanol pathway thought the membrane bilayer (EM-extracellular medium, IM-intracellular medium).

Support: FAPEMIG, CNPq, Capes.

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"Theoretical quantum-chemical study of the interaction of Co^{2+}-porphyrin with O_2"

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Key-words: fuel cells, Co^{2+}-porphyrin, metalloporphyrins.

The fuel cells are considered as an alternative to substitute current energy sources. The present catalysts are not able to break the bond of O_2, the way they do with H_2. This work has as objective to show the interaction of Co^{2+}-porphyrin with the O_2 through direct mechanism. The calculations were performed in Gaussian 2003^{TM}, using the DFT and the functional B3LYP. for the atom of Cobalt was used the base lanl2dz, for the O atoms the base 6-31G$^+$, for the H atoms the base 3-21G$^+$, for other atoms of the porphyrin, like C and N was used the base 3-21G. To simulate the solvation was used the PCM, and as solvent water, adopted to the temperature of 350 K and pressure of 1 atm, conditions that a PEMFC cell-type. The atomic charges loads were analyzed with the NBO. Two models were used: Co^{2+}-porphyrin (Figure 1) and Co^{2+}-porphyrin with an O_2, H_3O^+ and four electrons (Figure 2). The O_2 after the interaction with Co^{2+}-porphyrin, the oxygen atoms passed the charge 0.0497 (OI) and -0.0960 (OII) to -0.130 and -0.516, respectively, which indicate that O_2 receives negative charge after the interaction with the porphyrin, which indicates facilitation in the process of electrocatalysis, because there was an absorption of negative charge at O_2 The NBO reveal that there is a connection between O_2 and Co, but the donor-acceptot effect indicates a strong interaction ηO*→ ηCo, which facilitate the transport of mass, because the O_2 is close O_2 porphyrin and is more easily transported to the catalyst, which would increase the performance of a PEM-cell.

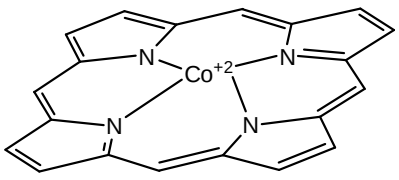

Figure 1 - Co^{2+}-porphyrin

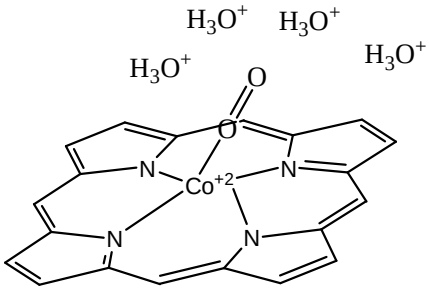

Figure 2 - Co^{2+}-porphyrin with an O_2, H_3O^+ and four electrons

Support: FAPEAM,CAPES,CNPQ.

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Molecular Dynamics Simulations Applied to Design of Enzyme Inhibitor for Trypanothione Reductase in Chagas Disease Treatment

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Key-words: Molecular Dynamics, Chagas' Disease, Trypanothione Reductase, Peptide Inhibitors.

Chagas' disease is one of 13 parasitic diseases that kill millions of people around the world and the treatment remains unsuccessful. Trypanothione Reductase (TR) is presented as a specific and selective parasitic target for chemotherapy against *Trypanosoma cruzi*. We studied the structure and conformational stability of six complexes involving TR and peptide mimetic reversible inhibitors by Molecular Dynamics (MD) simulations applying GROMACS package (version 3.3.1). After preceding steps of energy minimization (5000 steps of Steepest Descent followed by 5000 steps of Conjugate Gradient), all complexes runs throughout 10ns of simulations for acquisition data in a NVT ensemble using the Berendsen thermo-barostat. The systems consists in a dodecahedron simulation boxes containing: Simple Point Charge water model, counter-ions and the TR protein bounded with cofactor FAD and ligands or peptide inhibitors, giving approximately 139 000 atoms. The electrostatic and Van der Walls interactions were evaluated using Particle-Mesh Ewald within a 0.9nm *cut-off*. With this procedure, the methodology allowed us to evaluate multiple conformations of the enzyme focusing their main interactions in each complex resulting in a pharmacophoric map of TR. The results not only clarified the mechanism of action of these peptide inhibitors, but also shown the atomic mapping of the active site and described some chemical groups that modulate the enzyme inhibition. Beside these points, our analysis revealed alternative enzyme binding sites and identified the patterns of interaction by these inhibitors that should be explored in approaches to developing powerful and specific inhibitors of TR.

Support: CNPq.

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A theoretical study of the interaction Solvent- Usnic Acid

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Key-words: Usnic Acid, Hydrogen Bond, water, methanol, DMSO

Usnic acid (Figure 1) is one of the most common and abundant lichen metabolites, well known as an antibiotic, but also endowed with several other interesting properties [1]. The usnic acid is practically insoluble in water but soluble in organic solvents such as, acetone, chloroform, methanol and dichloromethane [2]. This work aims to characterize the relative solubility of usnic acid in water, DMSO and methanol, applying electronic structure and molecular modeling methods. Structural, energetic, electronic and spectroscopic properties of the interaction between the different solvents with usnic acid were evaluated.

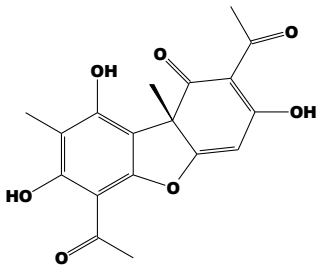

Figure 1 – Structure of usnic acid in enolic form

Our calculations were performed using GAUSSIAN 03 (B3LYP and MP2 methods with the 6-31++G(d,p) basis sets) and GROMACS 4.0.5 (force field 53A6). Our results show that methanol presents three well-defined solvation layers, in contrast with the other two solvents investigated. DMSO presented a broad peak, while no solvation peak was observed for water. Hydrogen bond analyses showed a higher half-life when methanol was used as solvent, followed by DMSO and water. Despite of usnic acid hydrophobic character, these results suggest that persistence of hydrogen bonding plays a key role in its solubity.

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Study of structural effect on nitronyl nitroxide radicals using DFT calculations

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Key-words: Nitronyl Nitroxide, Broken Symmetry, Magnetic Coupling Constant.

Nitronyl nitroxide radicals (NIT) are present in many compounds of interest in molecular magnetism [1]. The magnetic coupling constant (J) is the important parameter because it is sensitive to structural modifications. In the present work we calculated (Gaussian G09W, B3LYP/TZVP) two biradical systems formed by two NIT radicals connected by one or two aromatic rings (Fig. 1). The values of J were calculated for several conformers in C_2 symmetry, considering the dihedral angles between the planes connecting the radicals (C1-C2-C3-C4).

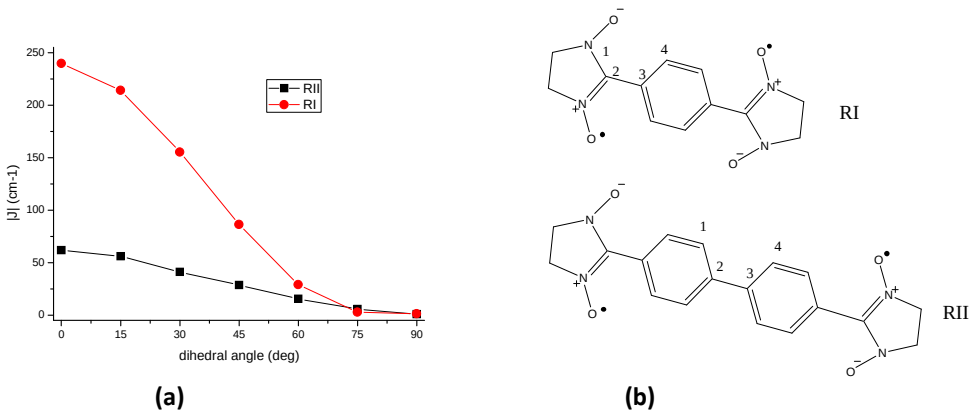

Figure 1 - (a) Dependence of J on the dihedral angle C1-C2-C3-C4; (b) Structures studied.

The J value depends on the distance between the magnetic centers. Therefore, J is much higher for complex RI than for RII. In both cases the magnitude of J decreases by increasing the dihedral angle between the planes containing the radicals. Antiferromagnetic interactions ($J < 0$) depend on the π-π conjugation of the aromatic rings due to superexchange interactions. Increasing the dihedral angle, reduces π-π conjugation and, consequently, the antiferromagnetic interaction decreases. It is interesting that at $\theta = 90°$ the magnetic interaction still exists, even in the absence of π-π conjugation. However the magnitude of J is much smaller than that found at $\theta = 0°$. The distance between the magnetic centers remains almost constant throughout the range of the calculated angles, indicating that the drastic reduction in the value of J is due to the loss of π-π conjugation.

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Support: Capes, CNPq, FAPERJ.

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Estudo da energia de substituição no complexo $[Ca(H_2O)_6]^{2+}$ por ligantes sulfoxilados (OSR_2)

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Key-words: Ca^{2+}, ligantes sulfoxilados, complexos, DFT, PM6.

Um problema comum para a indústria de petróleo é a ocorrência de incrustações geradas ao longo do processo de extração do óleo. Em sistemas marinhos esse processo é resultante da incompatibilidade química entre a água do mar (água de injeção rica em íons sulfato) e a água de formação da rocha reservatório (rica em cátions Ca^{2+}, Ba^{2+} e Sr^{2+}), que em condições termodinâmicas específicas favorecem a precipitação de sais de sulfato. Neste trabalho estudamos a eficiência de diferentes ligantes sulfoxilados na complexação do cátion Ca^{2+}, utilizando os métodos B3LYP/6-31G(d) e PM6. Para a análise da energia de substituição foi usada a variação de energia para as seguintes reações:

$$Ca(H_2O)_6 + OSR_2 \rightarrow Ca(H_2O)_5OSR_2 + H_2O$$
$$Ca(H_2O)_6 + O_2SR_2 \rightarrow Ca(H_2O)_5O_2SR_2 + H_2O$$

R = $N(CH_3)_2$, NH_2, OCH_3, OH, C(CH3)3, CH_3, H, F, Br, Cl, CHO, $COOCH_3$, COOH, CN, CF_3 e NO_2 (R diretamente ligado ao enxofre ou na posição para do anel aromático).

Observou-se que, tanto pelo método B3LYP quanto pelo PM6, os compostos com grupamentos doadores de elétrons apresentam energia de substituição mais negativa que os demais. Isso se deve à doação de elétrons para o oxigênio do grupo sulfoxila, promovida pelos grupos doadores, deixando o oxigênio mais negativo. Como a interação do íon cálcio com o oxigênio dos grupos sulfoxila tem caráter iônico acentuado, o aumento de densidade eletrônica no oxigênio fortalece a ligação, tornando mais favorável sua formação. O efeito contrário é observado para os grupos retiradores de elétrons.

Comparando ligantes sulfoxilados com fosforilados[1] observa-se, em termos quantitativos, que a energia de substituição dos ligantes sulfoxilados tem valores mais positivos do que os valores dos ligantes fosforilados. Isso pode ser explicado pelo fato de o enxofre ser mais duro do que o fósforo, o que faz o enxofre doar menos densidade eletrônica para o oxigênio que interage com o cálcio. Essa situação diminui o caráter iônico da ligação O–Ca, fazendo com que a ligação tenha uma energia de substituição mais positiva.

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Suporte: CAPES, CNPQ e FAPERJ.

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DFT and CCSD(T) study of neutral, positively and negatively charged aluminum clusters

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Key-words: aluminum clusters, PBE0, structures, energetic

Clusters are aggregates of atoms or molecules with intermediate size between individual atoms, or large enough to be called bulk matter. The structures and electronic properties of small and middle clusters differ considerably from bulk matter, and they have a slow and sometimes non monotonic evolution with the number of interacting atoms. Therefore, in order to develop new materials is important to understand the atomic and the electronic behavior when clusters become larger and larger, as the formation of magic and anti-magic clusters. Also, there is a lack of comprehensive studies of their electronic bonding properties as, for instance, the Jahn-Teller effect which controls the maximum degree of symmetry allowed for each cluster. In this study, we have used the density functionals (DFT) PBE0 and M06, as well as the aug-cc-pVDZ and aug-cc-pVTZ basis sets, in order to characterize the electronic structures, geometries and harmonic frequencies of small neutral and charged clusters of aluminum, Al_N ($N \leq 13$). In addition, CCSD(T) single-point calculations were carried out in order to improve the values of electronic energies. Ionization potentials, electronic affinities, cohesive energies are also computed. At the PBE0/aug-cc-VTZ level, calculations show a smooth variation of average geometries and cohesive energies with increasing of cluster size. Geometries of clusters with degenerate electronic wave functions are distorted in different degrees by Jahn-Teller (JT) effects as for Al_6 (O_h), Al_7 (D_{6h}) and Al_{12} (C_{5v}) structures. We also note a great variation of the non-dynamical electron correlation measured by the T_1 method. For instance, values of T_1 are 0.024, 0.082, 0.035, 0.074, 0.029, 0.093, 0.087, and 0.036 for the cluster size varying from Al_2 to Al_9, respectively.

Support: FAPESP, CNPq.

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"Molecular modeling studies of Nucleoside Hydrolase from *Brucella suis*"

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Key-words: Brucella suis; Nucleoside hydrolase; *Docking*; Molecular Dynamics.

Brucella suis is a dangerous biological warfare agent already used for military purposes[1]. This bacteria cause brucellosis, a zoonosis highly infective and difficult to fight[2]. An important selective target for chemotherapy against this disease is nucleoside hydrolase (NH), an enzyme still not found in mammals[3]. We present here the first three-dimensional structure of *Brucella suis* Nucleoside Hydrolase (*Bs*NH). In addition, we performed molecular docking studies, aiming to analyze the three-dimensional positioning of four known inhibitors of *Chritidia fasciculata* NH (*Cf*NH)[4] in the *Bs*NH active site. We have also analyzed the main interactions of these compounds inside the *Bs*NH and *Cf*NH active sites and the relevant factors to biological activity. These results, together with further molecular dynamics (MD) simulations, pointed out to the most promising compound as lead for the design of potential *Bs*NH inhibitors. The enzyme *Bs*NH can become a target in the fight against brucellosis and the NH inhibitors chosen in this work are potent compounds to inhibit this enzyme. The results of energy calculations by docking techniques showed a good linear correlation between the theoretical and experimental results ($r^2 = 0.89$ and $r^2 = 0.88$) for the enzymes *Bs*NH and *Cf*NH, respectively. According to the docking study, it was possible to observe that the compound **1** (Fig. 1) presents a lower intermolecular energy value (-111.61 and -122.37 Kcal.mol^{-1}) compared with other compounds in the active sites of *Bs*NH and *Cf*NH, respectively. Furthermore the MD data confirm the results obtained with the docking study, showing that **1** remains well anchored due to interaction with the amino acids Phe188, His262, Asn60, Asn101 and Asn181 within the *Bs*NH active site during the simulated time.

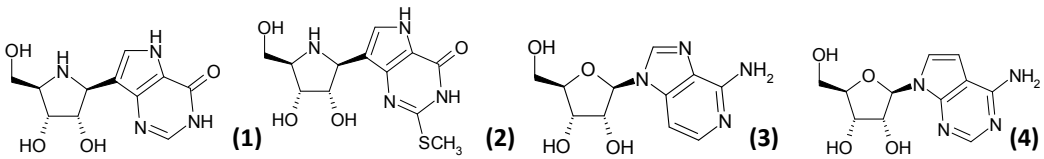

Fig. 1 Structures of the NH inhibitors studied.

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Support: FAPEMIG, CNPq, CAPES, UFLA, IME.

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Performance Evaluation of Density Functionals and Implicit Solvent Models for the Calculation of Cu,Zn-SOD Redox Potentials

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Key-words: Cu,Zn-SOD, Density Functional, Implicit Solvent Models

Superoxide dismutase is a class of metalloenzyme that catalyze the dismutation of superoxide radical anion into oxygen and hydrogen peroxide as shown below:

$$2\ O_2^{\cdot -} + 2H^+ \rightarrow O_2 + H_2O_2 \qquad \Delta G = -24{,}2 \text{ kcal/mol} \quad \text{(eq. 1)}$$

Cu,Zn-SOD is one of the most abundant of this class of enzymes and during catalysis the Cu ion cycles between valence states I and II with the concerted uptake and release of a proton.

This work aims to assess the performance of different density functionals and implicit solvent methodologies on describing the dismutation and oxidation reaction free energies using a simplified model for the enzyme active site.

Density functionals of several classes, namely, LDA, GGA, meta-GGA, hybrid-GGA, and hybrid meta-GGA, were combined with two basis sets, 6-311+G(3df,2p) and 6-31+G(d), to compute the dismutation free energy in water (eq.1). Results are shown on the table below (in kcal·mol^{-1}):

ΔG	VWN5	PBE	BLYP	TPSS	B3LYP	BH&H	M05	M06
6-311+G(3df,2p)	-23,07	-21,13	-20,49	-19,71	-21,27	-23,27	-24,19	-23,72
6-31+G(d)	-21,77	-20,13	-19,42	-18,68	-20,18	-21,99	-23,45	-22,28

A smaller group of functional used in the first set of calculations and the 6-31+G(d) basis set were chosen for the description of the enzyme oxidation reaction. Polarizable continuum model (PCM) calculations employing two distinct solvents, to be specific, water (ε=80) and diethyl ether (ε=4), were used to model the enzymatic/solvent medium. Calculated and experimental free energies in kcal·mol^{-1} for the oxidation reaction are shown on table 2:

Functional	ΔG water	ΔG diethyl ether	ΔG Experimental
PBE/6-31+G*(d)	-16,07	-6,30	-10,8 to -17,8
B3LYP/6-31+G*(d)	-15,17	-5,15	
M06/6-31+G*(d)	-14,33	-7,09	

Free energy results for the dismutation reaction (eq.1) were close to the experimental value for all functionals. The computed Gibbs free energy for the enzyme oxidation reaction for all three functionals produced results in the experimental range only when water is used as the implicit solvent. Calculation using a Poisson-Boltzmann implicit solvent approach, where the complete enzyme is treated explicitly, is currently under its way. The Gaussian03 and Gaussian09 suite of codes were used on all calculations presented in this work.

Support: CAPES and UFABC

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Imogolite based materials: Aluminophosphate and Aluminoarsenate nanotubes

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Key-words: imogolite like structures, inorganic nanotubes, SCC-DFTB.

The synthesis, characterization, and applications of imogolite nanotubes have attracted research attention in the past years. Natural imogolite is a tubular crystalline aluminosilicate mineral with ideal composition $(OH)_3Al_2O_3SiOH$**.** Its well defined tube length and diameter that can be synthesized via relatively mild chemistry, and its chemical properties with hydroxyl groups inside and outside made it an interesting material for many applications in nanotechnology, in particular in aqueous and biological environments. The aim of this work is to investigate new structures derived from imogolite, and make correlations between the composition, diameter and strain energy of aluminophosphate and aluminoarsenate nanotubes. The cylindrical wall of these tubes can be visualized as a rolled-up sheet of gibbsite, $Al(OH)_3$, with silanol (SiOH), P=O or As=O groups linked to the inner surface (Figure 1).

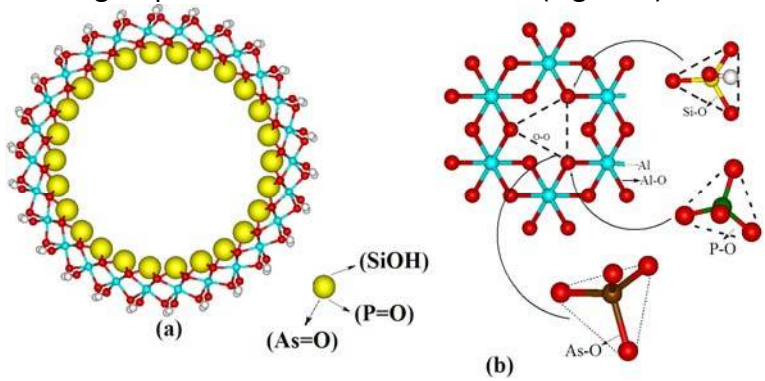

Figure 1 - (a) General scheme for an imogolite derived NT, (b) with SiOH, P=O or As=O groups linked to gibbsite ring on the inner surface.

We have calculated structure, stability, electronic and mechanical properties of the new nanotubes using the density-functional based tight-binding method (DFTB). *Zigzag* (9,0)…(20,0) and *armchair* (5,5)…(15,15) nanotubes with diameters ranging from 14 to 40 Å have been studied. The highest stability of all studied aluminophosphate and aluminoarsenate tubes has (13,0) chirality, while imogolite nanotubes has a minimum at (12,0) tube. An analysis of the electronic densities of states shows that the nanotubes, independent on their chirality and size, are insulators with a wide band gap. The new designed nanotubes have imogolite similar topology, although they present different structural properties, as diameter, structure at the minimum and electronic properties.

Support: FAPEMIG, INCT-Acqua, CNPq.

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"Binding mode analysis of pyrimidines derivatives with *T. gondii* thymidylate synthase and dihydrofolate reductase"

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Key-words: *Toxoplasma gondii*, thymidylate synthase, dihydrofolate reductase.

Toxoplasma gondii causes substantial morbidity, mortality, and costs for healthcare in the developed and developing countries. Current medicines are not well tolerated and cause hypersensitivity reactions. Thymidylate synthase (TS) and dihydrofolate reductase (DHFR) are crucial for the synthesis of thymidylate (dTMP) in dividing cells. Several TS and DHFR inhibitors, as separate entities, have found clinical utility as antitumor agents. However, they are not very potent and are not effective when used as single agents[1]. Gangjee et. al[1] described a series of pyrimidine analogues that act as potential dual TS and DHFR inhibitors. The present work describes the three-dimensional molecular model of the hypothetical T. gondii TS/DHFR structures obtained through the use of the homology modeling technique. In addition, we have investigated the orientations and interaction energies of compounds 1-6 (Fig. 1) with those new structures and human TS/DHFR structures. Molecular modeling techniques, such as homology modeling, molecular docking approaches, molecular dynamics simulations and QM/MM studies were combined with experimental data for inhibition of the TS/DHFR. Our findings suggest that compounds with *meta-para* substituent may increase affinity and selectivity for *T. gondii* thymidylate synthase and dihydrofolate reductase.

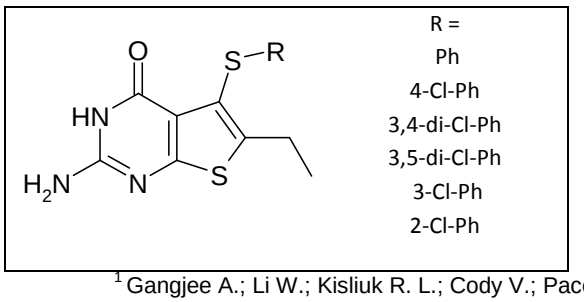

Figure1. Some thymidylate synthase and dihydrofolate reductase inhibitors.

[1] Gangjee A.; Li W.; Kisliuk R. L.; Cody V.; Pace J.; Piraino J.; Makin J. J. Med. Chem. 2009, 52, 4892–4902.

[2]Lovelace, L.L.,Gibson, L.M., Lebioda, L.; **J** Biochemistry. 2007, 46, 2823-2830.

CAPES, FAPEMIG, CNPq

Molecular Modeling of the interaction of the koninginin compounds with the PLA2 enzyme by MMPBSA method

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keywords – PLA2, MMPBSA, molecular dynamics, koninginins

The koninginins are a class of molecules excreted by endophytic fungus *Trichoderma sp*. and are capable to inhibit the PLA2 enzyme. Some of those molecules were tested and thecapability of inhibition of the PLA2 was shown and compared to the α-tocopherol. However, no theoretical explanation was given to understand the Interaction between koninginins and PLA2 In this work we provide some Insights in this sense. Initially, the ligands (two koninginins and tochopherol) were optimized by B3LYP/6-31g*. After, the ligands were docked against active site of PLA2 by Autodock Vina. After this, the molecular dynamics simulation was done in the minimized and docked molecules for 2.4 ns using ff03 force field. All quantum mechanics and molecular mechanic calculation were performed by GAUSSIAN09w and AMBER respectively. Following, using these simulations results the MMPBSA method was used to evaluate the interaction energy between the ligands and receptor compounds. As a result, the energy from MMPBSA method can explain the experimental values.

Table 1 – Calculations of the interaction energy between ligand and receptor. (ΔΔG in Kcal/mol)

Molecule	**$\Delta\Delta G_{tot}$**	**$\Delta\Delta G_{vdW}$**	**Inhibition (%)**
α-tocopherol	-32,41	-46.82	81
Koninginin A	-16,50	-35.27	2,2
Koninginin F	-22,10	-40.49	74,5

As can be seen in this Table 1, the $\Delta\Delta G_{tot}$ confirm the inhibition results and show the role of the van der Waals (vdW) contributions to the overall results. So, the lengths of the aliphatic tail apparently play an important role in the vdW contribution to the total energy. The aliphatic chain in KonF is greater than that observed in the KonA and because and the interaction is more efficiently with the hydrophobic channel present next to the catalytic site of the PLA2, providing the results in the Table 1.

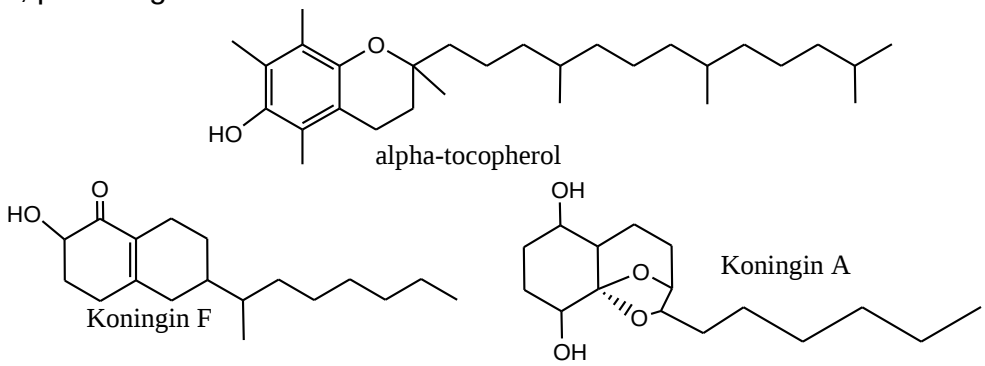

Figure 1 – Compounds used in this work

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Effect of Peripheral and Nonperipheral Substitution on Electronic Parameters of Phthalocyanines

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Key-words: Phthalocyanines , substitutes effect, DFT method.

Phthalocyanines are regarded as synthetic analogues of the porphyrin family[1]. The funcionalization on phthalocyanines can cause changes on the performance of the material, therefore the electrochemical one of the metallic phthalocyanines involves some processes redox[2]. In the present work we report the results of a systematic investigation of the effect of peripheral and nonperipheral (α, β respectively) substitutes on the electronic and structural parameters of metal-free phthalocyanines. All the geometries were calculated using the B3LYP/6-31G(d) level of theory. In addition NBO calculations were performed. All geometries were confirmed to be true minimum energy by the vibrational frequency analyses. The table 1 shows the HOMO/LUMO energies and GAP energy. The calculated geometrics parameters are in accordance with the experimental ones. Figure 1 show the structure of phthalocyanine.

Table 1: HOMO and LUMO energy levels (eV)

Molecule	ΔE (eV)	HOMO(eV)	LUMO(eV)
H_2Pc	2.14	-5.21	-3.07
$H_2Pc(t\text{Bu})_4$	2.09	-5.01	-2.92
$H_2Pc(\alpha\text{-}NO_2)_4$	2.07	-6.13	-4.05
$H_2Pc(\beta\text{-}NO_2)_4$	2.15	-5.76	-3.61
$H_2Pc(SCH_3)_4$	2.02	-4.77	-2.74

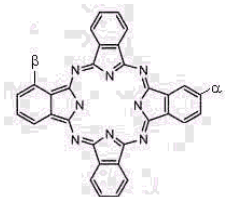

Figure1: Model of Phthalocyanine

These results show the effect of the substituent on the ΔE at the β positions is much smaller than that in the α positions. As can be seen, introduction of the electron-withdrawing groups onto the peripheral positions of the phthalocyanine ring induces a decrease in the electron density of phthalocyanine ring and substitutes typically electron-donating increase HOMO/LUMO energies.

Reference:

1- Guillaud, G.; Simon, J.; Germain, J. P.; *Coord. Chem. Rev.*, 1998; **180**, 1433.

2- Zhong A, Zhang Y, Bian Y.; *J Mol Graph Model.,* **16**, 825, 2010.

Support: FAPERJ, UFF.

Force Field parametrization for Zn(II) present in metalloproteinases

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Key-words: Matrix metalloproteinases , Chemically Modified Tetracycline, Force-Field parametrization.

Matrix metalloproteinases (MMPs) are the family of calcium- and zinc-dependent endopeptidases, which degrade the most components of the extracellular matrix (ECM). The MMPs play a key role in tumor invasion, metastasis and angiogenesis. The inhibition of MMP activity is an interesting therapeutic strategy for the treatment of diseases such as cancer. Thus, synthetic MMP inhibitors (MMPIs) have been designed, such the tetracyclines and chemically modified tetracyclines (CMTs), in specially the CMT-3, which is currently being evaluated in clinical phase II trials as an anti-metastatic.
The present work aims to apply the *ab initio* calculations to determine the structural and catalytic zinc parameters required in order to study MMPs and their interaction with CMTs by means of the AMBER force field. Three distinct molecular zinc tetrahedral models were constructed based on the MMP-9 X-ray and the potential energy surface (PES) scan for bond stretching and angle bending were calculated at B3LYP/SDD/6-31G(d) level. The Figure 1 shows the PES for Zn-N bond calculated by means of distinct approaches depending on the molecular moiety kept frozen, i.e. rigid (R), semi-rigid (SR) and flexible (F) scan. The bond stretching force constant (k) was obtained by fitting a second order polynomial function to the reference data. The results were quite sensitive to the approach used: 250.2 (R), 234.9 (SR) and 157.8 (F) kcal mol^{-1} Å^{-2}, with the latter found in better accordance to the literature expected value. The force field parameters for the zinc complexed with CMTs inhibitors are been performed. The modified AMBER force field will be discussed regarding the suitability for description of structure and energy of MMPs molecular models.

(a) (b)

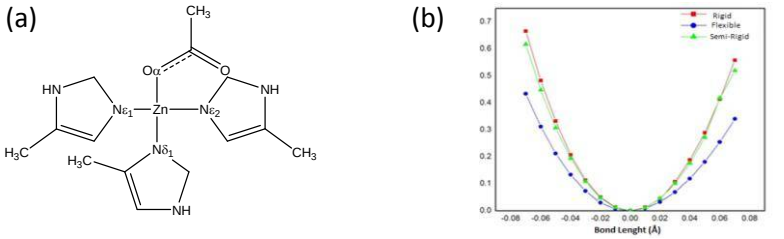

Figure 1.
(a) zinc model
(b) PES for Zn-N bond

Acharya, M; Venitz, J; Figg, W *et al.* Drug Resistance Updates *7,* **2004,** 195**.**

Support: CAPES, FAPEMIG, CNPq.

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Spectroscopic and Structural Properties of the Dication SnF^{2+}

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Key-words: CASSCF/MRCI; electronic states; spin-orbit coupling.

Group IV halides have received special attention due to applications in semiconductor materials. In order to enhance our understanding of these molecules, the electronic structure of **SnF^{2+}** has been investigated. Potential energy curves were obtained at the CASSCF/MRCI level with quintuple-zeta quality basis set, and include seven doublet and six quartet states associated with two lowest-lying dissociation channels (Figure 1a). For the first channel the spin-orbit coupling was considered (Figure 1b). For the ground state, **$X^2\Pi$**, we obtained **R_e= 2,519 Å** and **ω_e= 196,9 cm^{-1}**. Just above, at **T_e= 305 cm^{-1}**, we located the state **$A^2\Sigma^+$** with **R_e= 1,861 Å** and **ω_e= 601,7 cm^{-1}**. At the equilibrium distance spin-orbit splitting was **262 cm^{-1}** for **$X^2\Pi$** ground state, and the calculated atomic spin-orbit coupling constant for **^2P_u** fluorine atom was **391,3 cm^{-1}**, in closed agreement with the experimental value, **404,1 cm^{-1}**. We noted that the inclusion of spin-orbit effects reduce the T_e value by almost half, **164 cm^{-1}**.

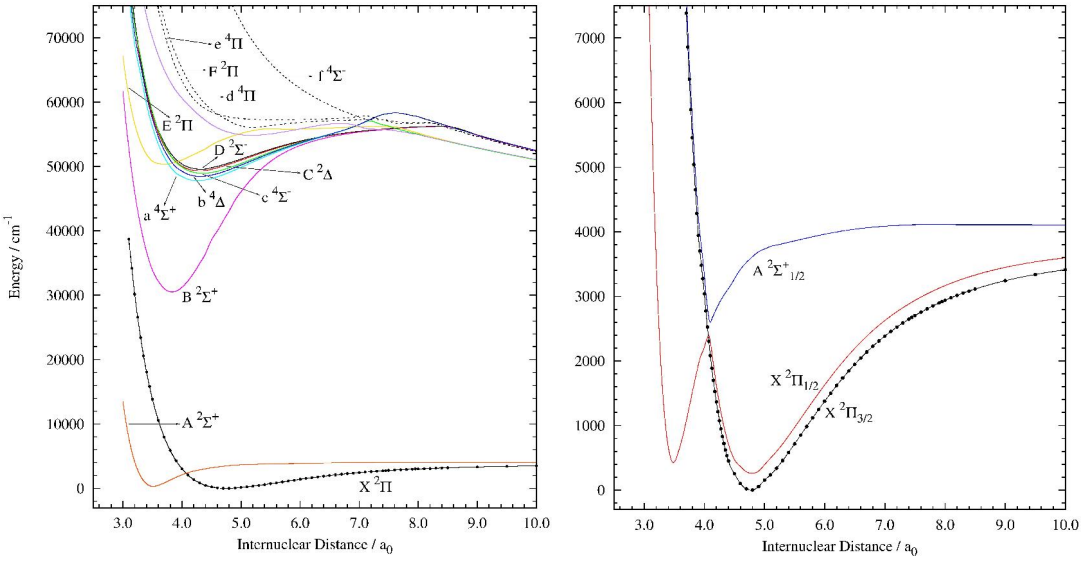

Figure 1: [a] Doublet and Quartet states associated with the two lowest-lying dissociation channels, and **[b]** Spin-orbit states potential energy curves of the dication **SnF^{2+}**.

Support: **CAPES**, **FAPESP**.

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Site Preference of CO adsorption on Ru_4 Cluster from DFT Calculation

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Key-words: Ruthenium cluster, CO adsorption, DFT method

Synthetic fuels represent an interesting alternative to petroleum. One of the most high-profile ways to create synthetic fuel is through what's known as the Fischer-Tropsch (F-T) process. The most widely-accepted FTS mechanism is the carbene model, involving CO adsorption and dissociation[1]. In order to examine CO site adsorption trends on ruthenium cluster a series of Ru_4–carbonyl compounds (Fig. 1) were designed. All calculations were done using the DFT approach with BPW91 functional and Lanl2dz basis sets for Ru atom and 6-31G(d) for C and O atoms. In the optimization process, all possible configurations and spin multiplicities are considered and searched. The shape and energy of the orbitals involved in the Ru–CO electron transfers were evaluated trough NBO calculations. The figure 1 and table 1 shows the energy profile of Ru_4 cluster, adsorptions energies and frequencies of CO molecule.

Table 1: Adsorption energies and frequencies of CO

sites	Eads (eV)	Eads(BSSE) (eV)	υ (cm^{-1})
Top	-1.86	-1.87	1744.18
3f hollow	-1.51	-1.65	1591.77
Bridge	-1.85	-1.99	1618.90

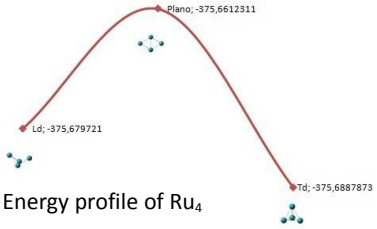

Figure 1: Energy profile of Ru_4

The lowest energy adsorption form was found for bridge site in the Ru_4 tetrahedron geometry. Table 1 show that when we used the BSSE the most stable site for CO adsorption is the bridge site. Experimentally the top adsorption site is more favorable[2]. This difference is due to BPW91 functional, therefore another functional will be tested (PBE1PBE, B3LYP, B3PW91). The CO stretching frequency is observed decrease substantially in going from the free molecule (≅ 2200 cm^{-1}) to the adsorbed species.

Reference:

1- Ponec, V.; Van Barneveld, W. A.; *Ind. Eng. Chem. Prod. Res. Dev.*, **18**, 268 1979.

2- Abild-Pedersen, F.; Andersson, M.P.; Surf. Sci., **601**, 1747, 2007.

Support: FAPERJ, UFF.

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A variational procedure to compute vibrational corrections for hyperpolarizabilities

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Key-words: Hyperpolarizabilities, vibrational corrections

The recognition of the role played by the nuclear motion in calculations of molecular hyperpolarizabilities happened two decades ago. This contribution is often partitioned in two terms named zero-point vibrational average (zpva) and pure vibrational (pv) corrections. The usual methodology to compute these corrections is based on a perturbative scheme known as perturbation theoretic (PT) method. The essence of this method is to expand the electric properties and the electronic energy as power series in the normal coordinates and to express the vibrational wave functions as perturbed harmonic oscillator functions. In this work we develop an alternative methodology based on the variational (VAR) scheme which is convenient to treat low vibrational frequencies and anharmonic cases. Initially we did a study for the ozone molecule, for which we expect the two methods lead to similar results with the aim of testing the VAR methodology. In an initial phase, we include in our calculations only the vibrational states where a single normal mode is monoexcited. The results obtained from the VAR method for the zpva corrections of α and β were 1.48 and 0.55 a.u., respectively. These numbers are in excellent agreement with the values 1.46 and 0.56 a.u. obtained using the PT method. For the correction pv, we obtained through the VAR method the value 1.37 a.u. for α, and the values 14.25 and 0.71 a.u for the terms [μα] and [μ^3] of β. The corresponding figures obtained by the method PT were 1.41, 14.51 and 2.01 a.u.. The only results that are not in good agreement are those obtained for the term [μ^3] of β. Our purpose is to include other excited vibrational states in the VAR procedure in order to obtain good values for this term. In addition, we intend to extend our calculations to the second hyperpolarizability.

Support: CNPq, CAPES, FAPEG, FUNAPE.

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"Donor – Acceptor analysis of the probability current in protein electron transfer reactions"

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Key-words: two state approximation, nonorthogonal basis set, protein electron transfer

In protein electron transfer reaction rate calculation, the electronic part of the Hamiltonian is partitioned into donor – acceptor (D – A) and protein bridge subspace, and an effective two state system is determined for D – A subspace. The Löwdin partitioning is used to perform the two state reduction necessary to compute the D – A tunneling matrix element. An iterative method is developed to determine the donor and acceptor state analysis of the electron probability current for a nonorthogonal basis set for both the weak and strong electronic coupling regimes. The D – A electron probability current is obtained in terms of interatomic tunneling currents and an analytical comparison among pathway models is presented. For a perturbation treatment of interatomic tunneling currents we found a well known expression for the D – A tunneling matrix element in terms of transformed Green functions matrix elements of the isolated protein bridge. Also, the relation of tunneling currents of Stuchebrukhov to pathways of Beratan and Onuchic is discussed. For a simple electron transfer model system we examine spatial distribtution of the tunneling currents flowing through individual atoms in the medium between donor and acceptor sites.

Support: FAPEMIG.

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Simulation of Two-Photon Absorption Properties of Model Organic Compounds

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Key-words: Nonlinear Optics; Sum Over States; PPP.

The application of organic molecules capable of efficiently absorbing two photons encompasses such diverse fields as 3D microfabrication, optical data storage, optical limiting, photodynamic therapy, fluorescence microscopy and the design of molecular sensors. Therefore, several groups worldwide are involved in the design and synthesis of novel molecules with large values for the two-photon absorption (2PA) cross-section δ_{2PA}. An approach, commonly employed in the design of such molecules, is to connect two donor/acceptor (D/A) groups through a conjugated bridge (B). In this poster, we present the results of simulations of the 2PA properties of simple four-center molecular models. The electronic structure of these models was obtained from fully correlated calculations using a PPP Hamiltonian and the 2PA properties calculated using a Sum Over States approach.

In Fig. 1 we show how the 2PA cross-section, of the second excited state of the system, varies as a function of the energy of the donor/acceptor group for systems of the type donor-bridge-donor and acceptor-bridge-acceptor for a symmetric conjugated bridge. We can observe that there is an optimal value of the energy of the donor/acceptor group that maximizes δ_{2PA} and that this value depends on the nature of the group. In Fig. 2 we show the changes of δ_{2PA}, for systems of the donor-bridge-donor type, when we increase the asymmetry of the conjugated bridge. We can also observe that, as in the case of experimentally studied real molecules, the values of δ_{2PA} for our model system decrease as the conjugated bridge becomes more asymmetric. Our simulations further show that, by using much stronger donor/acceptor groups, one could arrive at regions of larger values of δ_{2PA} not yet probed experimentally.

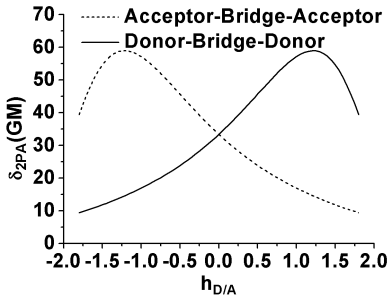

Figure 1. 2PA cross-section as a function of the energy of the donor/acceptor group.

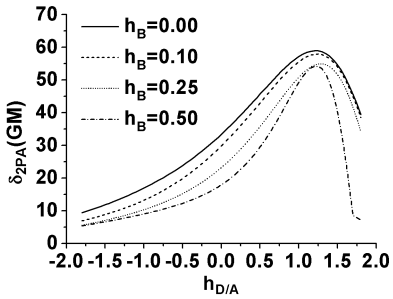

Figure 2. 2PA cross-section as a function of the energy of the donor group, for different asymmetries of the conjugated bridge.

Support: CNPq, FACEPE (Pronex), INCT INAMI and RENAMI.

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Quantum Molecular Mechanics (QMM): an Efficient Non-Iterative Procedure for the Treatment of Large Closed Shell Systems

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Key-words: QMM; Non-Orthogonal Orbitals; Atomic and Molecular Clusters.

When modeling large molecular systems or assemblies, one usually employs methods of molecular mechanics (MM). However, such classical methods do not provide users with wavefunctions, and, therefore, are unable to predict electronic properties, such as the electrostatic potential or the dipole moment. In this poster, we present a non-iterative procedure, based on quantum mechanics (QM), capable of efficiently calculating large molecules or assemblies. The ultimate goal of this procedure, called quantum molecular mechanics (QMM), is to replace the MM part of QM/MM calculations.

The QMM procedure relies on the use of non-orthogonal doubly occupied spatial orbitals ϕ to describe the N-electron wavefunction of the system. These orbitals are pre-optimized in a form similar to the way the MM methods are parameterized, i.e., for each type of orbital (core, bonding or lone pair) the method needs a set of parameters. The key step of the QMM procedure is the calculation of **T**, the inverse of the usually sparse overlap matrix **S** of the spatial orbitals. Having calculated the matrix **T**, the electron density, and consequently the electrostatic potential and other one-electron properties of the system can be easily obtained without ever needing to calculate the one- and two-electron integrals. The total energy of the system can also be non-iteratively obtained by combining the elements of **T** with the one- and two-electron integrals.

We implemented an ab initio version of the QMM procedure by expanding the doubly occupied orbitals using s and p Gaussian primitives. The first studies using this ab initio version of the QMM procedure were performed for the atom of helium and the molecules of H_2 and methane, both isolated and in the form of clusters. For helium, we employed a single pre-optimized orbital for each atom. For the molecules of H_2 and methane, the bonding orbitals were pre-optimized as a function of the internuclear distance. For methane, the orbitals were parameterized only along the symmetric stretching normal mode and shown to be appropriate to also describe distortions along the remaining normal modes. These pre-optimized orbitals were then employed in the calculation of clusters. For these clusters, the interaction energies per atom/molecule obtained using the QMM procedure were very similar to the ones obtained from Hartree-Fock calculations using split valence basis sets.

Support: CNPq, FACEPE (Pronex), INCT INAMI and RENAMI.

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Copper cation interactions with oximes models: A computational DFT study

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Key-words: Oximes, Copper, Complexes, DFT method

Extractants with high selectivity for metal ions are of interest for the removal, separation and concentration of metallic species, extending their application possibilities in the recycling of resources in metallurgy[1]. Oxime reagents have achieved importance in hydrometallurgical practice for the leach/solvent extraction of copper(II)[2]. In the present work we report the results of a systematic investigation of ligand substitution effects on electronic and structure properties of Cu(II)–oxime complexes. First, it was optimized a set of structurally modified copper complexes by groups of different electron ability using DFT method (figure 1). Seven different groups were tested in this step (R1 =NO_2, F, Ph, CH_3, NH_2, ^{t}But, H, R2=H). All these structure were confirmed to be true energy minima by the vibrational frequency analyses.

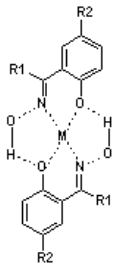

Figure 1

In addiction, NBO calculations were performed in order to account for charge transfer effects between ligand and metal atom. The interaction energy was calculated for all species.

The optimized geometries, frequencies and electronics structures calculated by the B3LYP functional and, 6-31G(d) basis set for describes all the atoms. The results show that the electron donating and withdrawing groups are able to increase and decrease HOMO/LUMO energies respectively. The introduction of electron donating and withdrawing groups leads to decrease and increase in the positive charge of the metal centre respectively. The theoretical vibrational frequencies calculated are in good agreement with experimental data.

Reference:
1-Chu, Y-C.; *Hydrometallurgy*, **84**, 109, 2006.
2- Preston, J.S.; J. *Inorg. Nucl. Chem*.; **37**, 2187, 1975.

Support: FAPERJ, UFF.

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"Influence of ions binding on the dynamics of the LPS membrane of *Pseudomonas aeruginosa*"

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Key-words: Lipopolysaccharide, Gram-negative bacteria, Ions

Bacterial Lipopolysaccharide (LPS) molecules consist of a lipid A - an endotoxin, a nonrepeating "core" oligosaccharide, and the O-antigen - a long variable polysaccharide chain. LPS is credited as the major factor of virulence in humans and other mammals. It acts as a weak non-specific antigen, which is poorly neutralized by antibodies. Unlike its planktonic counterpart, Gram-negative bacteria when forming biolfims can cause septic shock, fever and even lead to death. These microorganisms have a great metal ions sorption capacity in their cell walls. Such characteristic is very important to explain phenotypical variation, mobility and bioavailability of metals in environment. Metal ions and their complexes have been reported to bind negatively charged phosphoryl and carboxyl groups in the LPS. The availability of metal ions is highly dependent on the local environment. In turn, ionic coordination number, solvation shell and net charge are expected to influence packing, stability, adhesion and permeability properties of these membranes. Therefore, the elucidation of the interactions between LPS and different metal ions is expected to shed light into problems such as antibiotic resistance and material adhesion. In this work, we have performed molecular dynamics simulations of the LPS membrane of *Pseudomonas aeruginosa* in the presence of several concentrations of Na^+ and Ca^{2+} ions. While both ions are abundant ions in physiological media, Ca^{2+} ions are commonly found in the LPS of soil-living bacteria. On the other hand, these microorganisms are exposed to high concentration of Na^+ ions in infecting tissues. Differences in the LPS lateral diffusion and acyl chain order parameters suggest that metal ion valence can dramatically affect membrane dynamics, surface charge and stability.

Support: CAPES/CNPq/INCT-INAMI/FACEPE/EMSL

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Influence of Framework Flexibility on the Properties of Exchangeable Cations In Zeolites

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Key-words: Zeolites, Molecular Dynamics.

Zeolites are aluminosilicates whose structure consists of TO_4 tetrahedra (T=Si,Al) that share all its corners with the neighboring tetrahedra, thus forming a three-dimensional highly porous network. The substitution of Si^{4+} with Al^{3+} in the zeolitic matrix leads to the generation of a negative charge, balanced by extra-framework cations, whose location and identity govern the adsorptive and catalytic properties of the material.

Molecular Dynamics (MD) simulations are very useful to help elucidate the locations and mobilities of the exchangeable cations in zeolites. In MD studies of zeolites, the rigid-framework approximation, in which the framework atoms are fixed in their initial positions and only the exchangeable cations and other adsorbed species are free to move, is often applied as a way to save computational time. However, there are no studies in the literature that explicitly show the influence of the framework flexibility in the cationic properties obtained in the simulations.

In this work, we carried out MD simulations of NaX and BaX zeolites in the rigid framework approximation and considering a fully flexible framework to compare the efficiency of both models in the calculation of several properties, such as the location of the exchangeable cations and the absorption spectra of these cations in the far infrared region. Our results show that both models describe adequately the structural and dynamical properties of the zeolites studied. However, the far-infrared spectra calculated with the flexible framework model were worse than those obtained within the fixed framework approximation, which indicates that it is crucial to develop improved force fields to describe more accurately the framework vibrations. Our MD simulations also show that more elaborate models are needed in order to attribute the far-infrared bands observed experimentally.

Support: FAPESP.

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Theoretical study of singlewall and multiwall SiC and BN nanotubes with semi-empirical and Ab-initio methods

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Keywords: Nanotubes, comparisons, quantum calculations

The discovery of nanostructures [1],[2] collaborated to increase the research in this area of nanoscience, where the theoretical studies of these species can contribute to understanding the physical-chemical mechanisms as well as the behavior of these structures [3]. The results of this research can help in the production of materials and devices used in diverse areas of society such as electronics, engineering, aviation and the textile industry. The results of this research can help in the production of materials [4].

In this work we present some results of quantum mechanical calculations with semi-empirical methods AM1, PM6 and Ab-Initio HF, DFT with basis 3-21G, 6-31G of HUZINAGA for nanotubes of SiC and BN in the ARMCHAIR and ZIGZAG conformations formed by one layer known as singlewalls and with many layers, known as multiwalls (fig 1). The calculated data such as energies, dipoles (Fig.2), charge density, |HOMO – LUMO| and DOS can reveal important information to help in the understanding of these structures regarding their individual formation, with one wall, to multiple walls in order to compare the data among them.

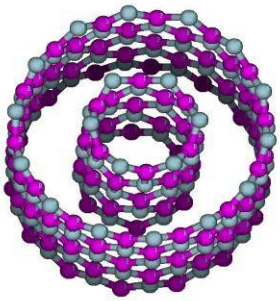

Fig.1: Nanotubes Multiwalls of BN

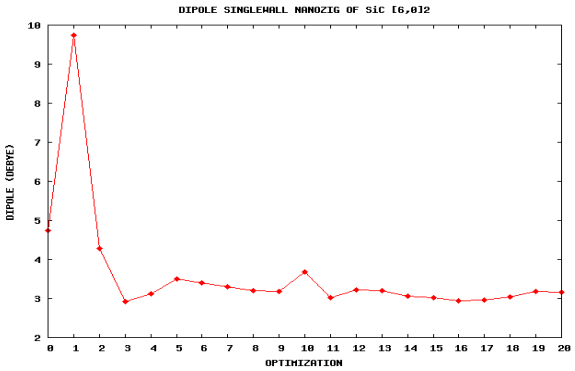

Fig.2: Dipole of zigzag Nanotube of SiC

Support:

[1] Kroto, H.W. *et al*, *1985*, buckminsterfullerene, *Nature,* v.318, p162-163
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[4] Leonardo, L.C. *et al*, 2009, Aplicação de nanotubos de TiO2 fotodegradação do corante verde, *31a SBQ.*

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Theoretical Study of Compounds with Mutagenic Activity and Isolated from *Byrsonima crassa*

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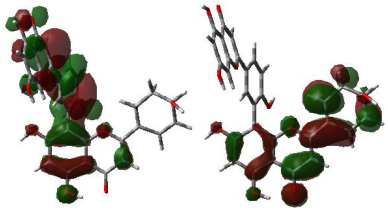
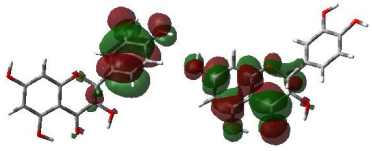
Key-words: DFT, SAR, Flavonoids, Mutagenicity

Byrsonima crassa is a native species of the Brazilian Cerrado formation. Byrsonima species showed convulsive effects in mice, as well as anti-fungal, antibactericidal and antidermatophitic activity. However, the investigation on the cytotoxic, mutagenic and carcinogenic effects of plant compounds is fundamental to reduce the possible inherent risks associated with the use of them. In this work, we calculate the molecular orbitals and electronic properties of amentoflavone (the most mutagenic) and (+)catechin (the less mutagenic). The geometry optimization and calculation of electronic properties were carried out using Gaussian09, with DFT method (B3LYP functional and DGDZVP basis set). Table 1 shows the results obtained from quantum chemical calculation.

Table 1. Electronic properties and molecular orbitals of studied compounds

	amentoflavone	**(+)catechin**	**Frontier Molecular Orbitals**	
Mutagenic Index[1]	2.36	1.09	HOMO	LUMO
E_{TOTAL} (a.u.)	-1907.659	-1105.527	 amentoflavone	
E_{HOMO} (a.u.)	-0.226	-0.226		
E_{LUMO} (a.u.)	-0.087	-0.077	 (+)catechin	
Gap* (a.u.) ($E_{HOMO} - E_{LUMO}$)	0.139	0.149		

From Table 1, we can note that the most mutagenic compound (amentoflavone) has low E_{LUMO} value, suggesting that this one can be electron–acceptor and, probably, can interact with the receptor through a charge transfer mechanism. The good correlation between the Gap values (E_{HOMO}- E_{LUMO}) and experimental data (biological activity) indicates that electronic properties are important to understand the mutagenicity of the studied flavonoids.

Support: FAPESP, UFABC, CAPES, CNPq.

[1]Cardoso, C.R.P.; *et al.* **2006.** *Toxicology.* 225, 55–63.

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Solvatochromic Study of Molecules Derived from the Brooker's merocyanine

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Key-words: Solvent effects, Brooker's merocyanine, Electronic absorption spectrum

The solvent effects are commonly attributed to the change in polarity of the medium. However, physical constants of the solvent such as dielectric constant, dipole moment and refractive index are inadequate to describe the solvent polarity. Thus, the polarity of the solvent has been studied [1,2] using the electronic absorption transition energy of solvatochromic probes (E_T(probe)). The idea is to find an empirical polarity scale which relates the physico-chemical properties of the solvated systems with the nature of the solvent. A widely used scale is the E_T(30) [3], proposed by Reichardt which uses the Betaine 30 as a standard solvatochromic probe.Recent studies, showed that increasing the lipophilicity, through annelation, of some merocyanine derivatives present nonlinear relationship with E_T(30) [4]. The reason of this nonlinearity is not well known and understands this behavior is the motivation of our work. We performed theoretical studies on 2,6-dibromo-4-[(E)-2-(1-methylpyridinium-4-yl)ethenyl]phenolate (MePMBr2) and other two molecules increasing the annelation of the pyridinium group to quinolinium (MeQMBr2) and acridinium (MeAMBr2) groups.

As a first step we performed calculations of the isolated molecules and in solution using the polarizable continuum model to describe the solvent. We studied some structural properties, such as *cis-trans* isomerism and the formation of mesomeric forms, and its effect on the electronic properties of the three molecules in four different solvents (1,4dioxane, DMSO, methanol and water). The calculations on the structural properties were performed in *ab initio* level (MP2 and B3LYP) where we observed that *trans* isomers are more stable and the increase of annelation causes an increase in quinoidal character of the molecule. With respect to the electronic properties, we observe that these molecules are very polarizable, obtaining an induced dipole moment twice as large in water as in nonpolar solvents. And for the electronic absorption spectrum we perform calculations using the time depended density functional (TD-B3LYP, TD-CAM-B3LYP and TD-BHandHLYP) and semiempirical (INDO/CIS) methods. The most intense transition was characterized as π-π*, and the experimental tendency for the solvatochromism was well described only with the semiempirical method and TD-CAM-B3LYP. Our next step will be the improvement of the solvent model including explicitly its molecules in the calculations.

References[1]E.M.Kosower; Wiley,New York (1968).[2]C.Reichardt; Verlag Chemie, Weinheim, New York, (1990).[3]C.Reichardt; *Chem.Rev.* ***94***, 2319 (1994). [4]C.T. Martins, M.S.Lima, E.L.Bastos, O.A.El Seoud*; Eur.J.Org.Chem.*.,1165(2008).

Support:FAPESP, USP, INCT-FCx, Rede nBioNet/CAPES.

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Modified Gaussian basis sets for molecular properties prediction: nonlinear optics and spectroscopic constants

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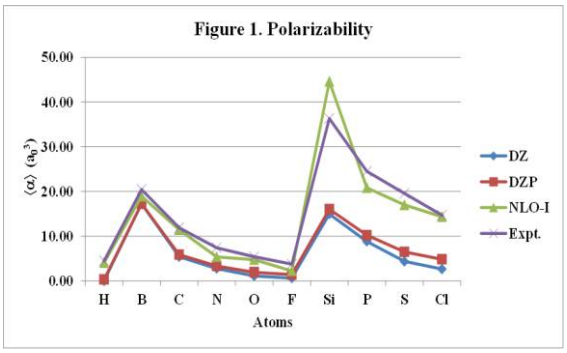
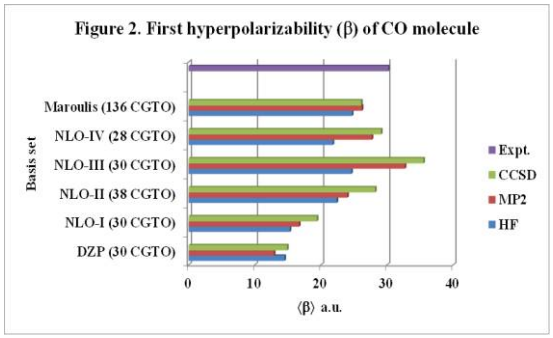
Key-words: Basis set, polarizability, first hyperpolarizability

The theoretical prediction of nonlinear optical properties (NLO) with high accuracy is strongly dependent on the methodology. The electron correlation is known to play a primary role on the calculation of all molecular properties and, it is particularly important for NLO properties. In addition, many studies have also shown a strong dependence on the basis sets used. Most of these studies use very large basis sets, increasing the computational cost significantly, especially where polyatomic molecules are the final goal[1,2].



In the present study, Gaussian basis sets for the H, C, N, O, F, Si, P, S and Cl atoms were adjusted, seeking a low computational cost and good accuracy. After the fitting procedure, we obtained for distinct basis set, called NLO-I, NLO-II, NLO-III and NLO-IV. The basis sets were further used to calculate NLO properties and spectroscopic constants of diatomic molecules. Figure 1 show our calculated values of average polarizability for all atoms with reference basis set (DZ and DZP) and NLO-I. We can observe that the calculated values with NLO-I show an excellent agreement with experimental data. In Figure 2, we present the predicted values for first hyperpolarizability of CO molecule. It can be clearly seen that our basis sets give satisfactory results (see NLO-IV results) at a lower computational cost.



This paper presents a systematic study involving the adjustment of basis sets and calculations of NLO and spectroscopic properties. The results obtained proved the suitability of basis sets, validating the methodology proposed.

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Support: FAPEMIG, CNPq, CAPES and UFJF.

"GANM-Methodology to introduce the flexibility of proteins using genetic algorithm in protein docking

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Key-words: Molecular Docking, Genetic Algorithms, Normal Modes, Rotamer Library

The protein-ligand interaction is involved in several cellular mechanisms. Almost all molecular processes depend on molecules (ligands) that recognize specific bonding sites (receptors) and binds to them. The understanding of these processes is important for drug design. Some of the major challenges in molecular docking are consider both receptor and ligand like flexible. The number of freedom degree for this problem can be reduced with the use of techniques as Normal Modes Analysis (NM). Otherwise, the genetic Algorithms (GA) has been an interesting and efficient tool to simulate the docking problem. In this context, the developments of methodologies that allow consider both global and local conformational changes can be a good and efficient solution for this kind of problem. The methodology, GANM, treats whole receptor as flexible. This software combines genetic algorithms, rotamers library and normal modes analysis. The initial population is composed by a set of backbone with distinct conformations generated following under the direction of twenty normal modes with lower frequencies. We used the first twenty normal modes because they are sufficient to represent the global movements of a given protein. (Perahia D. et al., Normal Mode Analysis theory and applications to biological and chemical systems. Chapman & Hall, 2000). In a second step, after calculated the NM, we generated 40 structures for each 20 normal mode, displacing initial structure (from 0.2 $\dot{A}$)(Angstrom) in both direction of the eigenvector in a predefined range [-4,4] $\dot{A}$ (Perone, Biophis. J., vol. 90, 1583-1593,2006). This protocol generates a significant and sufficiently set of conformations to represent the movement of the protein (Maréchal D and Perahia D, Use of Normal Modes for structural modeling of proteins: the case study of rat heme-oxygenase, Eur Biophys J.; 37(7):1157-65. 2008). The generated structures were clustered for selecting a representative set of conformations using the RMSD as criteria for clustering. We use the RMSD because we wanted a set with different conformations of backbone. This conformations set and rotamer library was used as input to the genetic algorithm. We tested the methodology with three complexes: i) CDK2/DT5, ii) DHFR/MTX, iii) HIV-1 Protease with DMP323, Ritonavir and Indinavir as ligand. The docking rounds of each generation, frequently sampled acceptable results (<2.5Å). The methodology presented good results.

Support: FAPESP, UFABC, CAPES.

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"Photophysics properties and aggregation of methylene blue"

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Key-words: DFT, DCACP´s, photodynamic therapy, methylene blue

The study of cationic and anionic dyes has been carried out because of their different applications. The photophysical and photochemical properties strongly depend on the nature of the surrounding environment. In this work we are interested in the photodynamic therapy (PDT) application of these dyes and the intermolecular interactions involved in it. PDT is a promising treatment against several types of cancer and it is based on a local or systemic administration of a dye, (the photosensitizer, PS), followed by an irradiation with visible light of a wavelength compatible with the absorption of the PS. Only cells exposed to light and PS will undergo the lethal cytotoxic effects of species generated by them (free radicals, especially singlet oxygen). However, the aggregation of the PS is responsible for the decreasing in the effectiveness of the treatment. One of the mechanisms of action of PDT is the transfer of electron or hydrogen atom from the PS to an intermediate molecule (e.g., the solvent itself) making it a radical or an ion-radical. Most of these radicals react with oxygen leasing to the excited state (singlet) or generating O^{2-}, H_2O_2, or OH radical that attack the membranes.

Aiming to study the mechanism of action of Methylene Blue (MB) in PDT, we have performed Density Functional calculations, with B3LYP functional and DGTZVP basis set simulating electron and hydrogen atom (analysed by means of Bond Dissociation Energies) transfers

We have also performed calculations with CPMD program that simulates dispersion forces (DCACP´s, implemented for BLYP functional calculations) to study the aggregation of MB. We have also evaluated the role of the solvent in the aggregation process with IEFPCM continuum solvation model (for aqueous, ethanol and dimethyl ether solutions).

We conclude that that the electron transfer is easier to occur than hydrogen atom transfer. On the other hand, aggregation should occur only in polar solvents because the solvation energy is greater than the dispersion energy.

Support: FAPESP and UFABC

Theoretical study of the N + *trans*-N_2H_2 reaction

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Keywords: barrier heights, reaction energies, N+N_2H_2, DFT, MP2, CCSD(T)

Reactions involving N_2H_x are very important, as for chemical hydrogen storage, and chemical combustion involving other radicals to break chemical bonds. In this work, the reaction involving diazene with nitrogen (N_2H_2 + N → N_2H + NH) was studied with several DFTs approximations (B3LYP, BB1K, M05 and M06 functional families) and the MP2 method. These methodologies with the aug-cc-pVTZ basis set were utilized to optimize the geometries of the reactants, products and transition states as well as to calculate the harmonic frequencies, barrier height and reaction energy. Single point calculations at the BB1K and MP2 geometries were carried out using CCSD(T) with the aug-cc-pVXZ (X=T,Q) followed by complete basis set extrapolation (CBS). Some thermo chemistry results (in kcal/mol) are listed in the table below. Based on the CCSD(T)/CBS, the barrier height and reaction energy should be between 9.5 to 14.0 and -13.0 to -16.0 kcal/mol, respectively. The best density functional approximations results were obtained with BB1K, M05-2X and LC-M06L.

Method/aug-cc-pVTZ	ΔE	ΔH	$\Delta V^{\#}$	$\Delta V_a^{\#}$
BB1K	-12.7	-17.6	10.3	6.6
LC-M06L	-12.6	-17.5	8.3	4.8
M05	-14.8	-19.5	6.3	2.7
M05-2X	-13.9	-18.7	8.8	5.0
M06	-12.3	-17.5	6.5	3.1
M06-2X	-12.9	-17.8	7.4	3.7
M06L	-15.0	-19.9	1.7	-1.5
B3LYP	-19.3	-24.1	2.1	-1.0
MP2	-2.4	-5.6	23.3	22.3
CCSD(T) /CBS//BB1K	-11.0	-15.9	13.1	9.4
CCSD(T) /CBS//MP2	-9.6	-12.8	14.7	13.7

Support: FAPESP,CNPq,CAPES.

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Cálculos Teóricos dos Potenciais de Redução de Lactonas Fitotóxicas Derivadas dos Rubrolídeos

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Palavras chave: Rubrolídeos, Potencial de redução, Fitotoxicidade.

Os γ-alquilidenobutenolídeos são compostos orgânicos isolados de fonte naturais que possuem importantes atividades biológicas. Dentre estes compostos destacam-se os rubrolídeos, constituídos por um anel lactônico de cinco membros substituído. Os rubrolídeos são compostos que possuem semelhança estrutural com os nostoclídeos, os quais possuem reconhecida atividade herbicida. Durante investigação sobre o mecanismo de ação dessas substâncias foram realizados cálculos teóricos dos potenciais de redução de uma série de 13 derivados rubrolídeos. Estes cálculos foram realizados empregando-se a metodologia DFT nos níveis B3LYP/6-31g(d,p) e mPWB1K/TZVP, encontrando-se resultados altamente correlacionados com dados de voltametria cíclica (r^2 = 0,97) obtidos na determinação experimental dos potenciais de redução. Portanto, a metodologia empregada nos cálculos teóricos é um método eficiente para a determinação de potenciais de redução desta classe de compostos orgânicos.

Composto	E_r (V) experimental	E_r (V) teórico
RB1	-2,08	-1,94
RB2	-2,04	-1,93
RB3	-1,28	-0,96
RB4	-1,72	-1,56
RB5	-1,67	-1,46
RB6	-1,69	-1,55
RB7	-1,29	-0,96
RB8	-1,54	-1,33
RB9	-1,53	-1,32
RB10	-1,73	-1,47
RB11	-1,73	-1,50
RB12	-1,71	-1,46
RB13	-1,71	-1,40

Tabela 1. Valores dos potenciais de redução obtidos por cálculos teóricos (B3LYP/6-31G(d)) e por método experimental (voltametria cíclica).

Suporte: Capes, CNPq, FAPERJ e FAPEMIG.

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"Ionic Liquids Simulations with Applications in CO_2 capture"

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Key-words: Molecular dynamics, ionic liquid, capture of CO_2

Molecular dynamics simulations (MD) were performed for 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide [emim]TFSI (painel A). Structural and dynamical properties were calculated in wide range of temperature. CO_2 molecules were included in order to investigate the ability of [emim]TFSI coordinate with the gas molecules in wide range of temperature and mole fraction as well.

A **B**

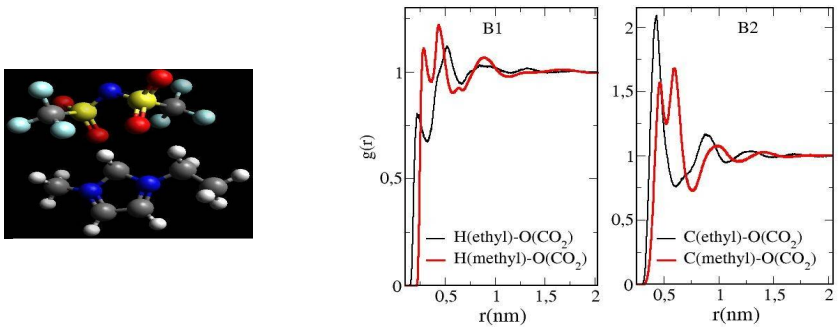

Figure1: Ionic liquid 1-ehtyl-3-methylimidazolium bis(trisfluorosulfonyl)imide (painel A) and radial distribution function, *g*(r), of [emim]TFSI with CO_2 molecules.

Simulations in NpT and NVT ensembles were performed for each system following those compositions: 200 ion pairs of IL at 293, 313, 343, 400 and 450 K. For the systems containing CO_2 molecules were added 1, 20, 50 and 173 molecules of gas.

Figure 1 shows the radial distribution function (painel B) for the interactions between CO_2 molecules and the imidazolium cation. We can see that the coordination of CO_2 molecules is performed by the hydrogen bonds (painel B1) with H atoms from imidazolium ring and from side chain. These results indicate the occurrence of local structure change when we put CO_2 molecules on the IL system.

Support: FAPEMIG.

"Kinetic study of tropospheric reaction between citronellal and OH radical"

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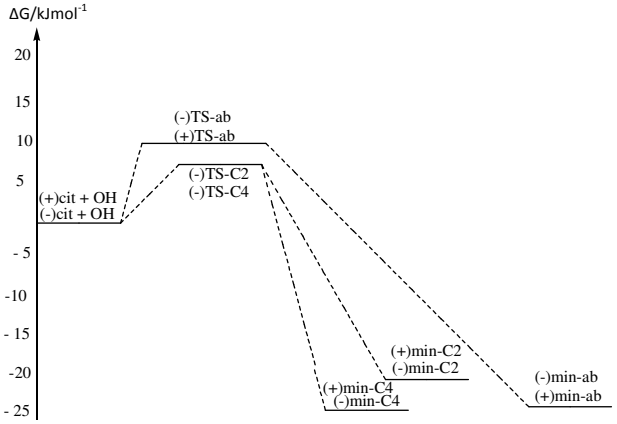
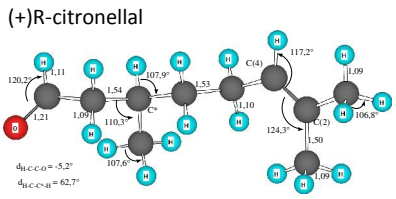
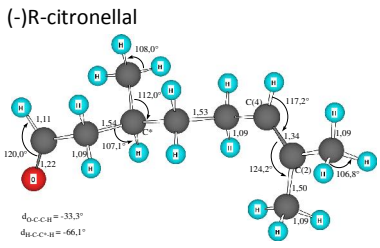
Key-words: volatile organic compounds, citronellal, OH, ozone

In the atmosphere, volatile organic compounds (VOC´s) reacts with hydroxy radicals (OH), ozone (O_3), nitrate radicals (NO_3), or halogen radicals. Since VOC´s are mainly emitted from vegetation during the daytime, the reaction with OH is expected to be the dominant tropospheric removal pathway. Its atmospheric oxidation leads to the formation of ground level ozone, photochemical smog, and secondary organic aerosols. In this way, developing a detailed atmospheric oxidation mechanism for is thus critical in improving regional air quality models which serve to guides regulatory policies. Citronellal is emitted from many types of eucalyptus, being an important volatile organic compound in our country. Citronellal have two forms: (+)R-citronellal and (-)R-citronellal. In this work, we study the reaction between the citronellal and OH radical using ab initio calculations. The optimization was realized at MP2/6-31G(d) level, as well the calculation of vibrational frequencies. Additional calculations single point were conducted with cc-pV(X+d)Z basis set, where X=D, T or Q, to use CBS methodology. The kinetics study was realized based on TST conventional theory.
Though the results obtained we conclude that the reaction between citronellal and OH is fast, but rate constants determined by us are smaller that the experimental ones reported. Moreover ours results show that the abstraction and the addition products are kinetically favorable, which were not detected in the experimental findings.







Support: CNPq, FAPEMIG, CAPES

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A Stratified Computational Model to Predict Geometries of Uranium Complexes

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Key-words: Uranium, ab initio, geometry optimization

This work attempts to find the best combination of methods and basis sets to properly describe the geometry and properties of Uranium complexes of a specific oxidation state by means of computational chemistry.

To describe such complexes, we decided to employ a stratified approach: a combination of a pseudopotential and one basis set for the valence electrons of the uranium atom; another basis set for all atoms that are directly bonded to the uranium atom (the coordination polyhedron atoms); and a third basis set for all atoms not directly bonded to the uranium atom (the ligand atoms).

For the uranium atom, we used the Stuttgart pseudopotentials: one for each oxidation state, together with their various basis sets for the valence electrons. For the coordination polyhedron atoms and for the ligand atoms, we tested all combinations of the following basis sets: STO-3G, 3-21G, 6-31G, 6-31+G, 6-31G* and 6-31+G* with the following methods: RHF, B3LYP, MP2(Full), PBE0, and MPW1PW91; for a total of 450 different model chemistries. Finally, as reference, we considered the coordination compounds UCl_6^{n-} (n being 0 for U(VI), 2 for U(IV) and 3 for U(III)). These compounds contain only uranium and its coordination polyhedron atoms. The following optimal combination was obtained for U(III) and U(IV): B3LYP with the basis sets AVDZ for the uranium atom and STO-3G for the coordination polyhedron atoms. On the other hand, for U(VI) the best combination we obtained is: B3LYP with the basis sets AVTZ2F for the uranium atom and 6-31+G for the polyhedron atoms. These combinations yield mean deviations in bond lengths of only 0.028Å for U(III), 0.019Å for U(IV) and 0.015Å for U(VI).

Then, we addressed the problem of finding the best basis set for the ligand atoms. For that purpose, we used three randomly chosen complexes: one for each of the uranium oxidation states.

We then used two approaches: (a) initial optimization with the polyhedron basis set for all complexes; then freeze the polyhedron and re-optimize the remaining ligand atoms with a larger basis set. (Sequential Methodology); or (b) simultaneous optimizations of all atoms using a three-layer-model (Simultaneous Methodology). As a result of these simulations, the simultaneous methodology, which provides the same result as the sequential methodology, but with the advantage of being simpler, was chosen. The best model was thus defined as:

- U(III)/U(IV) → B3LYP + AVDZ + STO-3G + 6-31+G*
- U(VI) → B3LYP + AVTZ2F + 6-31+G + 6-31+G*.

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H_2-F_2 and O_2-F_2 van der Waals Complex: a complete theoretical study

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Key-words: Potential Energy Surface, Symmetry Adapted Perturbation Theory

In this work we discuss the potential energy surface (PES), at CCSD(T)/aug-cc-PVTZ, for the title systems considering the rigid rotor approximation, with six leading configuration, plus a test one. From the PES we can obtain the global and local minimum. Using simple optimization calculation, with BSSE correction, at MP2/aug-cc-pVTZ, we use as initial point for the SAPT (Symmetry Adapted Perturbation Theory) calculation to determine the energy partition, electrostatic, induction, exchange, dispersion. The SAPT results can give us the energy profile of the complex. The main difference, we would like to point out is the fact the H_2-F_2 is a closed shell system while the O_2-F_2 is an open one, and this fact generate several particularity in the calculation of the PES and the local and global minimum.

For the closed shell H_2-F_2 system we can use the CCSD(T) SAPT, but for the open shell O_2-F_2 it is impossible. To solve this problem we calculate the CCSD(T) SAPT and DFT-SAPT for the H_2-F_2 system to calibrate the DFT(SAPT) for the O_2-F_2 in a way the CCSD(T) and DFT(SAPT) for H_2-F_2 have the same results, giving us the best approximation to use for the open shell system with the precision closer to the CCSD(T).

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"Conformational Equilibrium of *p*-Methyl-Calix[4]arene: A Theoretical Study"

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Key-words: Theoretical calculations, *p*-Methyl Calix[4]arene, Conformational Change

The focus of this work is the conformational study of *p*-Methyl-Calix[4]arene in gas phase and in chloroform, water and toluene solutions using the continuum model approach. To elucidate the solvent effect and reactivity in different media, it is essential to find the respective most stable structures and also their transition states (TS), because the conformational barrier can be influenciated by the solvent [1]. The four known conformations for the *p*-Methyl-Calix[4]arene, are represented in Figure 1. The calculations were carried out at the DFT level of theory, using the B3LYP functional and 6-31G(d,p) basis set.

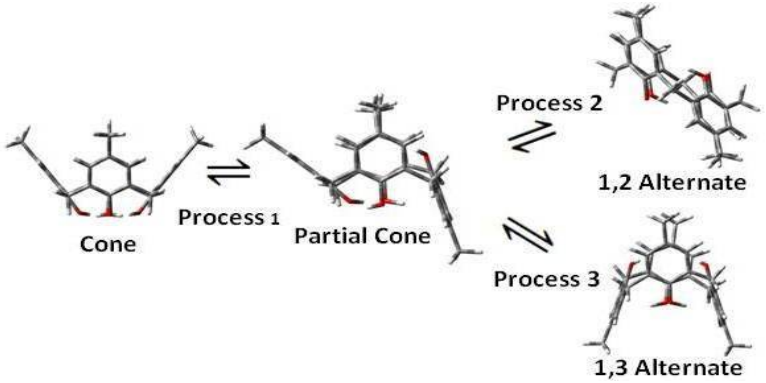

Figure 1: Conformations equilibrium of *p*-Methyl-Calix[4]arene

The table below shows the thermodynamic data calculated for the conformational equilibrium of these species, as well as the energy barriers, using chloroform as solvent. B3LYP calculations for water and toluene solvents were also carried out. In the search for TS structures involved in the partial cone to 1,2-alternate process, and also 1,3 alternate conformer in water solution, the B3LYP IRC results indicated that various TS structures close in energy are present on the multidimensional potential energy surface (PES).

Table 1: B3LYP/6-31G(d,p) thermodynamic data in kcal·mol^{-1}

Solvent: Chloroform	**Process 1**	**Process 2**	**Process 3**
ΔG (ΔG ‡)	**9.0** (16.4)	**1.8** (11.0)	**6.2** (15.1)

Support: CNPq.

[1]. Böhmer, V., *CALIXARENES, MACROCYCLES WITH (ALMOST) UNLIMITED POSSIBILITIES,* Angew. Chem.-Int. Edition in English, 1995. **34** (7): p.713-745.

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Structure, stability and infrared spectrum of capped carbon cones: A DFTB study

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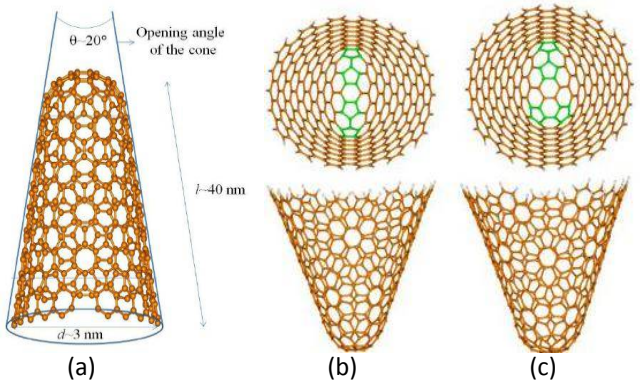
Key-words: Capped Carbon Cones, Carbon Nanohorns; DFTB

The carbon nanohorns (CNHs), have been currently considered as promising drug carrier agents[1], identified in 1999[2] as nearly spherical aggregates of diameter around 80 nm. The single molecular units are structurally organized as a capped cone section with averaged diameter and length close to 3 and 40 nm, respectively, and opening angle of the cone around 20° (Figure 1a)[1]. In the present study, twelve structures of distinct groups of CNHs isomeric are proposed and their equilibrium geometries, stability and infrared spectrum discussed. All the calculations were carried out using deMonNano code and the geometries were analyzed by DFTB (Density Functional based Tight Binding). Table 1 is found some structural properties calculated for isomers shown in Figure 1b-c. The isomers differ in the arrangement of pentagons (green in Figure 1b-c) located at the closed end of the CNHs. The results showed that the number of pentagon-pentagon bonds on the tip is the main factor responsible to provide the distinct topologies, being those avoiding pentagonal adjacencies more stable. In general, the theoretical IR spectra profile is quite distinct among the forms studied. Specifically, the presence of pentagon-pentagon links (Figure 1b-c) can be clearly identified by the presence of absorption bands around 1820 cm^{-1}.



(a) (b) (c)

Table 1- Structural properties of nanohorns isomers.

Structural properties	Isomers 1b-c ($C_{354}H_{30}$)
Opening Angle (°)	38.9
Average Diameter (Å)	14.5
Maximum Diameter (Å)	21.0
Tubule Length (Å)	21.9

Support: CAPES, FAPEMIG, CNPQ.

Figure 1- Nanohorn model in (a) and optimized nanohorns isomers in (b,c).

(1) G. Pagona, G. Mountrichas, G. Rotas, N. Karousis, S. Pispas, N. Tagmatarchis, *Int. J. Nanotechnol.*, 6 (2009) 176. **(2)** S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, K. Takahashi, *Chem. Phys. Lett.*, 309 (1999) 165.

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Gadolinium Complex with Biocatalytic Activity: Sparkle Model Prediction of Preferred Coordinations in Solid State and Solution

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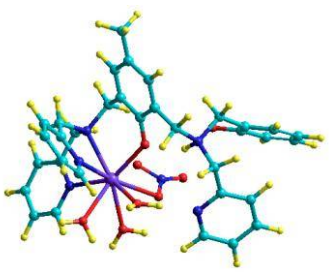
Key-words: Gadolinium Complex, *Sparkle*/PM3, Hydrolase Activity

Experimental studies of a complex containing gadolinium revealed a significant hydrolase-like activity.[1] Although the crystallographic structure showed a mononuclear gadolinium complex, it is believed (potentiometric titration and ESI-MS) that, in solution, dinuclear Gd species are formed (equations 1 e 2). At around pH 7 (optimum activity conditions) the catalytic $[Gd_2L(H_2O)_2(OH)]^{3+}$ **(A)** species is present in higher concentration than the $[Gd_2L(H_2O)_3]^{4+}$ (**B**) species. In this context, we use the semi-empirical *Sparkle*/PM3 model to study the difference in stability between the complexes in the solid state and in solution.

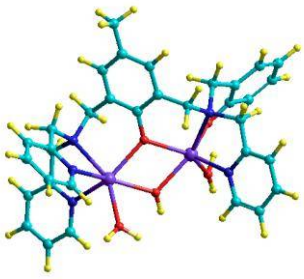
$[GdLH_2(H_2O)_3(NO_3)]^{2+}_{(aq)} + Gd^{3+}_{(aq)} \rightarrow [Gd_2L(H_2O)_2(OH)]^{3+}_{(aq)} + NO_3^-{}_{(aq)} + 3H^+_{(aq)}$ (eq. 1)

$[GdLH_2(H_2O)_3(NO_3)]^{2+}_{(aq)} + Gd^{3+}_{(aq)} \rightarrow [Gd_2L(H_2O)_3]^{4+}_{(aq)} + NO_3^-{}_{(aq)} + 2H^+_{(aq)}$ (eq. 2)

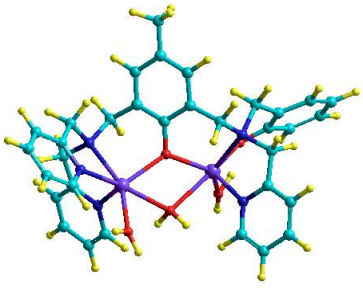
Calculations of the isolated complexes, simulating the solid state according to the Sparkle parameterization, confirm that the mononuclear complex is energetically favored when compared to the binuclear ones by ~270 kcal/mol. However, when the calculation is repeated, this time using the COSMO model, the reverse situation happens. *Sparkle*/PM3 model shows that, in solution, enthalpies of reaction for the formation of both binuclear complexes **A** and **B** from the mononuclear one were -380,26 kcal/mol and -86,01 kcal/mol, respectively. The difference of 294.25 kcal/mol, predicted by *Sparkle*/PM3, between these enthalpies of reaction, confirm the experimental results, indicating greater stability of complex **A**, when compared to complex **B**, in solution.



$[GdLH_2(H_2O)_3(NO_3)]^{2+}$



$[Gd_2L(H_2O)_2(OH)]^{3+}$(**A**)



$[Gd_2L(H_2O)_3]^{4+}$(**B**)

[1]Camargo, M. A. ; Neves, A. ; Bortoluzzi, A. J.; Et al. **Inorg. Chem**. 2008, 47, 2919

Financial Support: CNPq, PRONEX, FACEPE, INAMI, RENAMI.

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"Steered molecular dynamics of the triacylglycerol with the complex biocatalytic composed by the casein and *Candida rugosa* enzyme"

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Key-words: Molecular modeling, molecular dynamics, enzymatic catalysis

The molecular modeling (MM) is a well established set of techniques used to study molecules of scientific interest. In this sense our work use MM to provide theoretical data that should help understand the experimental data obtained in the kinetics assays. Such assays use as substrate the triacylglycerol which is catalyzed by *Candida rugosa* lipase (CRL - triacylglycerol acyl-hydrolases EC 3.1.1.1) to obtain biodiesel. Thus our object is study the interaction energy between CRL and the sodium caseinate (polymeric support) and that between the CRL and triacyglycerol. In this work the casein structure was docked against CRL and a molecular dynamics simulation using explicit solvent (TIP3PBOX for water molecules) in a total time length of 5.0 ns with a time step of 0.001 ps was done. After these the triacylglycerol molecule was placed next to the opened flap in the entrance of the tunnel to accommodate the substrate. This complex reach the minimum equilibrium energy as can be seen in the Figure 1 that also show the equilibrated enzymatic system. Next the steered molecular dynamics simulation was made and the interaction energy evaluated by the MMPBSA procedure supported the data obtained in the kinetic assay in lab.

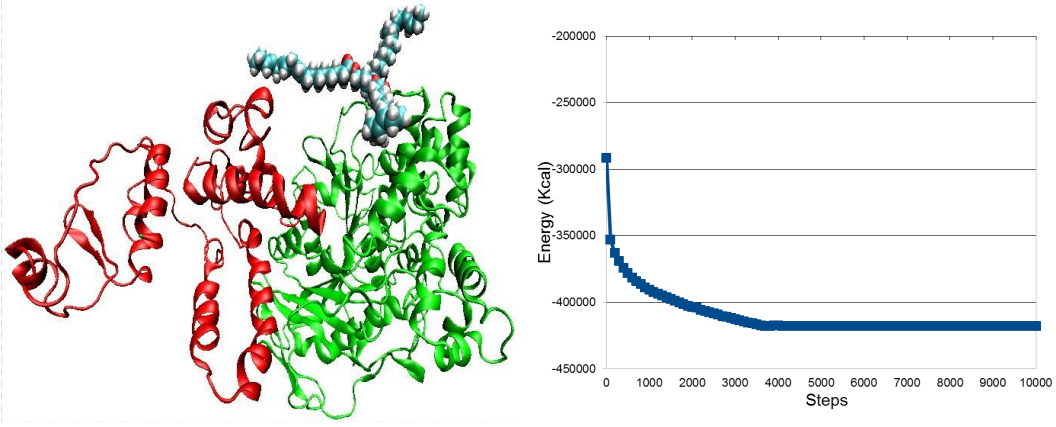

Figure 1- A) CRL (green), α_{S2}-caseína (red) and triacylglycerol.
B) Minimization step plot.

Support: CAPES, UFSJ/CNPq e FAPEMIG.

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Water adsorption over the Fe(100) surface: a MD study

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Key-words: Molecular dynamics, adsorption process, iron, water.

The natural corrosion process of metallic surfaces is of great interest for scientists and engineers. Experimental and theoretical studies have contributed to increase the understanding of interaction between metals and chemicals present in the corrosion processes. The corrosion process generally begins with the adsorption of the gas or liquid chemical species over a metallic surface.

This work shows a detailed analysis about the adsorption process of water molecules over the Fe(100) surface using molecular dynamic simulation. Water molecules are strongly influenced by iron surface, which let to formation of three layers. The dynamic and structural properties of each layer were determined. Figure 1 shows a profile of molecular density in a direction normal to metallic surface, where each peak represents the center of the layer. One can see that the molecular density depends on the distance to surface and decreases with the increase of the distance. Density values related to distances longer than 9.5 Å have the same value of the pure water. The molecular plane of water was parallel to the surface. However, the probability of find out water molecules with this orientation decreased with the increase of the distance from the surface. No preferential orientation was observed for water molecules positioned at distances higher than 9.5 Å. The water diffusion coefficient and residence time also depended on its position, where the residence time of the water molecules decreased in the following order: first layer > second layer > third layer.

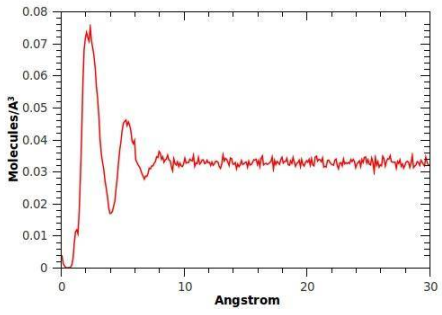

Figure 1. Molecular density profile of water molecules in relation to surface.

Support: CAPES.

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Structural Properties of Lipid A from *P. aeruginosa* as a function of phenotypical variation

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Key words: LPS, Gram-negative bacteria, alcyl chains

Lipid A is the outermost component of lipopolisaccharides (LPS) found in Gram-negative bacteria and main responsible for their toxicity. Its structure is comprised of two phosphorylated N-acetylglucosamine units attached to a variable number of acyl chains. Structural modifications on the chemical primary structure of the lipid A change not only its aggregate shape, but also its physical and biological properties. Experimental measurements suggest that a tilt angle formed by the two glucosamine residues of a Lipid A unit and the membrane plane varies with the number and location of acyl chains, and that it can be correlated with biological activity. To probe this hypothesis we have performed molecular dynamics simulations of bilayers formed by a number of lipid A phenotypes from *P. aeruginosa* PA01. DPPE was used in the bottom layer, as it is one of the most commonly found lipid in this bacterium. Simulations were carried out in the NPT ensemble using the GROMOS 53A6 force field implemented into the GROMACS program. Preliminary data, area per headgroup, lipid A lateral diffusion and order parameters, indicates that symmetric hexaacyl species display a higher structural order than its pentaacyl counterpart and an overall slightly lower value for the glucosamines tilt angle, in agreement with experimental data. Further structural and dynamical analyses for the additional phenotypes are underway. These results should shed light into the basis governing phenotypical variation and LPS remodeling.

Support: CNPq/INCT-INAMI, FACEPE.

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"Structure-Property Relationships on a Terthienoquinoid Derivative: A DFT Study"

Pedro Henrique de Oliveira Neto[a](PQ), Demétrio A. da Silva Filho[a](PQ), M. Carmen Ruiz Delgado[b](PQ), Juan Casado[b](PQ), and Juan Teodomiro López Navarrete[b](PQ)

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Key-words: Mobility, UV- VIS absorption, DFT, TD-DFT

Recently, it was reported an interesting effect observed on a dicyanomethulene-substituted thienoquinoid oligomer: a three-orders of magnitude increase in the electron mobility upon annealing of the spin-coated film. This increase in charge-carrier mobility was also followed by the appearance of an absorption peak, around 1000nm, not seeing in the solution UV-vis spectrum. These experimental results suggest that the annealing procedure is changing the way these molecules pack and this new order is responsible for the observed change in mobility and absorption spectrum. Here we plan to investigate this structure-property relationship by means of quantum-chemical calculations. We will simulate aggregates of two or more molecules and compute relevant parameters to describe the electron mobility (such as the electronic coupling) and the absorption spectrum (such as the excited states) in order to rationalize the structure-property relationships observed experimentally. Exploratory calculations indicate that there is an excited state around 1000nm when a dimer is used in the calculation, indicating that intermolecular interactions play an important role in the observed effect.

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Radial breathing vibration of boron nitride and carbon nanotubes induced by femtosecond laser pulses

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Key-words: Molecular dynamics, femtosecond laser pulses, nanomaterials.

The study of interactions between matter and ultra-short light pulses allows controlled structural modifications on many different molecular systems[1]. In the present study, we have developed theoretical simulations of quantum molecular dynamics of (3,3) "armchair" single-walled boron nitride ($B_{24}N_{24}$) and carbon (C_{48}) natotubes induced by femtosecond laser pulses. The aim of this study is to promote structural changes in nanotubes through the control of the laser pulse parameters which perform the role of a guide of the nuclear motions. The photoinduced dynamics are studied performing a scheme based on *ab initio* molecular dynamics using the SIESTA program[2]. The molecular dynamics simulations are performed by using density functional theory with the generalized gradient approximation (DFT–GGA) employing norm-conserving pseudo-potentials and basis set of linear combination of atomic orbitals (LCAO). The femtosecond laser pulse is modulated by a Gaussian function with the following parameters for boron nitride nanotube: duration τ=125 fs, intensity I_0=1.7×10^{14} W/cm^2 and frequency ω=0.03 eV. For the carbon nanotube, the pulse parameters are τ=150 fs, I_0=2.0×10^{14} W/cm^2 and ω=0.02 eV. The polarization vector of the light is parallel/perpendicular to the axes of the boron nitride/carbon nanotubes, respectively. Both nanotubes have their radial breathing mode activated by the laser pulse. The radial breathing dynamics in the carbon nanotube is very premature starting at the time t=-1000 fs, i.e., before the laser pulse has reached its maximum intensity at t=0 fs. The radial breathing dynamics in the carbon nanotube follows an oscillatory motion with a time period of around 105 fs. In the case of boron nitride nanotube the oscillation period of the radial breathing mode is 35 fs and the dynamics begins at t=57 fs, i.e., after the laser pulse has reached its maximum intensity. Concluding, we have shown here the efficiency of the ultra-fast laser pulses inducing the radial breathing dynamics in carbon and boron nitride nanotubes.

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"SPECTROSCOPIC AND THEORETICAL STUDY OF THE TAUTOMERIC EQUILIBRIUM INVOLVING AZO DYES DERIVED FROM 1-PHENYLAZO-2-NAPHTHOL"

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Key-words: Azo dyes, Raman, Tautomeric Equilibrium

Azo-dyes are of particular interest to chemistry, since they can be easily prepared with a wide range of donor and acceptor substituent groups; in addition, the planarity of the azo bridge is expected to contribute for enhancing electronic delocalization, and consequently the optical activity[1]. For the 1-phenylazo-2-naphthol derivatives, an important characteristic is the tautomeric equilibrium involving the proton transfer from the naphthol to the azo group leading to two isomers called azo (O-H) and hydrazo (N-H)[2-3] (Figure 1).

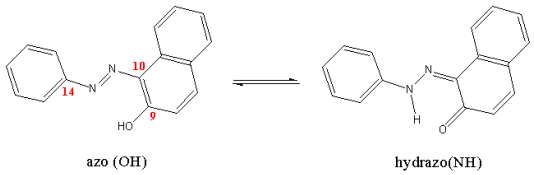

Figure 1. Structures for the azo (OH) and hydrazo (NH) forms of the Sudan I.

The structures of a wide number of azo dyes have been investigated by several spectroscopic techniques, such as Raman, resonance Raman and infrared (IR), as well as nuclear magnetic resonance (NMR) [4]. The presence of both tautomeric forms makes difficult the precise assignments of the experimental spectra; therefore, theoretical calculations at appropriate level can provide information about the structures and spectroscopic properties of individual tautomers.

In this work, experimental and theoretical studies were carried out for four compounds derived from 1-Phenylazo-2-naphthol (Sudan I, Figure 1). Raman, UV/vis, IR and NMR spectra were obtained for all Sudan I derivatives with the Raman spectrum found to be quite sensitive in the tautomeric fingerprint regions. The Raman spectra were carried out in chloroform and dichloromethane solution, suggesting the predominance of the NH tautomer in solution. Several bands were observed and correlated with the predicted values, being the most intense bands centered at 1596 cm^{-1} (γs CC, γs NN, δas CH), 1227cm^{-1} (γ_s CC, γs CN, δ_s CH, δ_{as} NH) and 984cm^{-1} (γ_{as} CC, δ_{as} CH, δ_{as} NH). Experimental analysis of the chemical shift of ^{13}C NMR showed 171.78 ppm for the atom C_9, which is mostly affected by the proton transfer. This value suggests a carbonyl group on the C9 position, supporting the predominance of the NH form.

The structure for the OH and NH isomers (Figure 1) were fully optimized in gas phase at B3LYP level using the 6-311G++G(d,p) basis-set. The final geometries were characterized as minima on the potential energy surface through harmonic frequencies calculation. The ^{13}C and ^{1}H NMR spectra were calculated at the very same in chloroform solution within the PCM formalism and dielectric constant set to 4.71 (chloroform solution). The theoretical Raman spectra presented the main transitions at 1638, 1259 and 1007 cm^{-1}, which are in satisfactory agreement with the experimental data (1596, 1227 and 984 cm^{-1}). The ^{13}C chemical shift predicted for C9 was (182.95ppm) that is also in accordance to the observed value (171.78 ppm), supporting the preference for NH tautomer in solution.

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Support: UFJF, FAPEMIG, CNPQ, FINEP

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"Comparative Modeling and QM/MM Studies of Cysteine Protease mutant of *Theobroma Cacao*"

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Key-words: *Moniliophthora perniciosa, Theobroma cacoa,* cysteine protease

The culture of cacao in Brazil was highly harmed by *Moniliophthora perniciosa*, the fungus that causes witches' broom disease of cocoa. This disease decreases significantly the cocoa production. A genome project started in order to show the genes of cysteine protease involved in the mechanism of resistance/vulnerability between fungus and three. Tnis enzyme is expressed during the process of the maturation of the seed and it is present in necrofitics period of the disease. Furthermore, proteases have a wide application in feed products, detergents and pharmaceutical industries. This study constructed the 3D structure of the cysteine protease of *T. cacao* by comparative modeling. Following, the primary sequence of the cysteine protease of *T. cacao* was submitted to BLASTp obtaining the protein 1PCI|A with 36% of structural similarity as a template. After, three models were constructed (dv1, dv2 and dv3), which were refined and validated by AMBER 9.0 and PROCHECK software, respectively. Among these models, dv1 showed a better Ramachandran Plot with 95% of amino acids in favorable energy region. The final model consists of 171 amino acids, formed by 2693 atoms linked by 2719 chemical bonds. The 3D structure of this enzyme has 7 α-helix, 23 turns and 2 β-sheets. The region of the conserved active site is represented by residues Cys25 and His159. Finally, a mutant model was then generated by replacing His159/Gly. This also was evaluated showing similar dv1 characteristics. Studies of the interaction between the mutant structure with the metal ions Zn^{2+} Cu^{1+}, Cu^{2+} and Cd^{2+} were carried out by QM/MM approach. As a result, the mutant protein is able to complex with all of them, and showed selective for Cd^{+2}. Therefore, this study suggests that mutant cysteine protease of *T. Cacao* can form a ligand selective of metal ions in biological environmental.

Support: FAPEMIG and FAPESB.

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Theoretical Design and Synthesis of Highly Luminescent Europium Complexes

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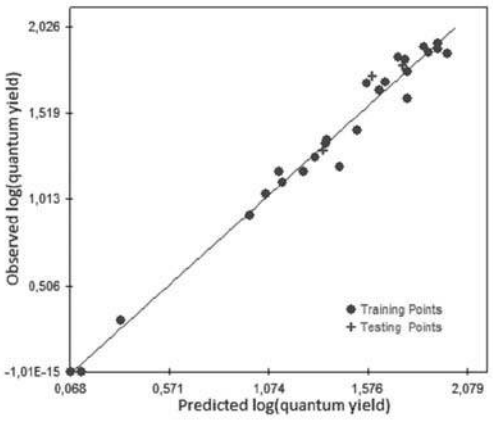
Key-words: Europium; Luminescence; Quantum Yield; Quantum Efficiency.

Luminescent lanthanide complexes possess a wide range of applications. Thus, an understanding of the causes of luminescence is an active area of research. In this work we sought to apply the latest techniques of structure-property relationships to unveil the key structural and electronic factors influencing the luminescence of a series of 28 europium complexes, which had their quantum efficiency and yields measured. Thus, we computed via Simulations Plus Inc. softwares, 325 descriptors for each of the complexes: constitutional descriptors, topological indices, atom-type electrotopological state indices, Moriguchi descriptors, molecular pattern recognition flags, Meylan Flags, descriptors derived from electronic properties, hydrogen bonding descriptors, and molecular ionization descriptors. Then, statistically validated Kernel Partial Least Squares ensemble models for both quantum yield and efficiencies were obtained from a subset of the descriptors. As an example, the corresponding regression for the quantum yields is shown in the figure below.



Subsequently, we generated, in a combinatorial manner, all complexes from all possible combinations of all ligands present in the original 28 complexes. A total of 604160 complexes were thus generated and had their quantum yields and efficiencies predicted. From these, we chose the 18211 best ones to be considered. Finally, we synthesized a number of them, which were characterized via infrared spectra with help from the Sparkle model, and via elemental analysis and ^{1}H and ^{13}C NMR. At present, the quantum yield and efficiencies of the designed and synthesized complexes are being determined in our laboratories. However preliminary results do indicate that their luminescences are indeed exceedingly high.

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Rational design of chimerical antigens based on Top7 scaffold for differential HIV diagnosis

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Key words: gp41, computational design, molecular simulation.

Human immunodeficiency virus (HIV) is a member of the family *Retroviridae* and is the etiological agent for acquired immunodeficiency syndrome – AIDS. Because HIV infection is one of the major public health problems in the world, the screening of blood donors and risk population by highly sensitive and specific diagnostic procedures, is considered crucial. Early diagnosis of two distinct subtypes, HIV-1 and HIV-2, with very similar genomes, is an essential tool to antiviral therapies intervention. The main diagnostic systems are based on the detection of antibodies against the viral GAG and gp120 proteins; however they are unable to identify the infective serotype. The HIV gp41 protein, in turn, could be an important antigen for differential diagnostic test development, since this protein exhibits wide antigenic variety and elicits a strong reactivity during the infection. Here, we describe the development of chimerical proteins loading specific epitopes from HIV-1 gp41 protein. Firstly, we screened HIV-1 gp41 sequences, from South America isolates, in public databases, and several *in silico* analysis were performed to identify the best putative epitopes of this protein. Six epitopes amino acid sequences, ranging in length from 8 to 18 residues, were selected; and their secondary structures were searched in the Protein Data Bank. After determining the epitopes amino acid sequences, computational techniques were employed to transplant them into Top7 acceptor scaffold – a highly stable, computationally designed protein. This procedure resulted in the design of 9 epitope scaffolds, which were submitted to molecular dynamics simulations in order to evaluate the correct insertion site choice and to predict the epitope scaffolds' behavior in aqueous system. The first analysis indicate that 7 chimerical proteins exhibit reasonable replication of the epitope and scaffold shapes, maintenance of the stability of the scaffold and absence of solvent accessible surface modifications. Additional analyses are also being done in order to select the best constructions to experimental production and immunological validation assays. Preliminary results were considered very promising, providing insights for the establishment of a systematic methodology for an *in silico* antigen design aiming diagnostic purposes. All obtained antigens are going to be validated, in terms of their specificity and sensibility as diagnostic input (through cytometric bead array) using HIV pre-validated reference sera panels.

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Nitronium ion adsorption on single-wall carbon nanotubes with Stone-Wales defects

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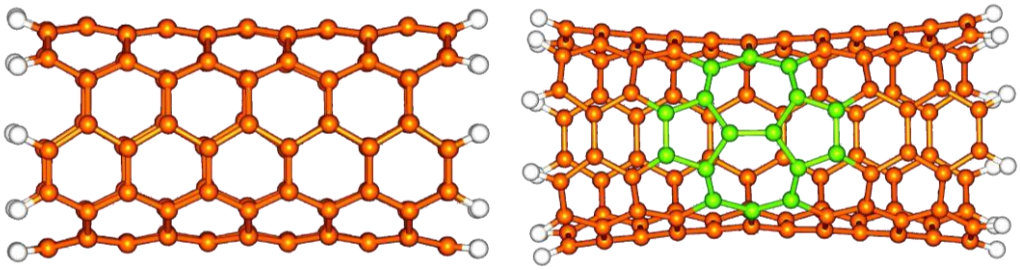
Key-words: SWCNT, Nitronium ion, Stone-Wales

Currently, carbon nanotubes (CNT) have been broadly studied due to their peculiar physical and chemical properties. Several studies have been appeared in the literature addressing CNT application as gas-sensor for CO, CO_2 and NO_x. On the other hand, chemical oxidation has also attracted great interest due its importance for modification of the tube surface.[(1)] Such reaction is diameter-selective and is commonly used for samples purification. However, this processes are not clearly understood yet, nonetheless, the obtained products are frequently used as reagents for chemical processing.

In the present work the adsorption of the oxidant species NO_2^+ (produced from the mixture of H_2SO_4/HNO_3) on the SWNT is discussed. The pristine armchair (5,5) SWCNT and its derivative containing SW defects were chosen as molecular models (see Figure 1).



(a) (b)

Figure 1: (a) Armchair (5,5) SWCNT pristine; (b) Armchair (5,5) SWCNT containing SW defects, the atoms in green represent the Stone-Wales defect (also called 5-7-7-5 defect).

The adsorption of NO_2^+ at several sites on the tube surface was proposed and the structure and relative energies analyzed. The results showed that the system with SW defects is more reactive than pristine system, with binding energy -137kcal/mol to SWCNT with defect and -62kcal/mol to pristine SWCNT.

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"Supersonic Polaron Dynamic in Conjugated Polymers"

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Key-words: Molecular Dynamic, Conjugated Polymers.

The use of organic conductors in developing applications for optoelectronic devices has attracted great attention in recent years. It is well known that conductivity in these materials is related to the velocity of quasi-particles. Furthermore, their interaction with impurities in the material also influence the conductivity. Thus, understanding the quasi particles dynamics in these materials becomes fundamental on science and technology of conjugated polymers. In this work it was investigated the collision between quasi-particle and impurities on supersonic regime. Specifically, it was simulated the motion of both polaron and soliton under a huge external electric field in a polyacethylene chain containing impurities. Our approach consists on a semi-empiric first neighbors tight binding with first order lattice relaxation. In the scope of the Unrestricted Time Dependent Hartree Fock Approximation we performed the dynamic by means of simultaneous solution of Euler Lagrange and Schrodinger equation. Through this method we achieved a good accordance with other works in the absence of impurities and gives phenomenological reasons for conductivity in conjugated polymers containing impurities. Also it was observed that the increase of temperature prevents the polaron to acheive supersonic regime.

Support: CAPES, CNPq and FINATEC.

"Enhanced Deep-blue Photoluminescence in Thienylene Vinylene Derivatives: A Theoretical Investigation"

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Key-words: Mobility, UV- VIS absorption, DFT, TD-DFT

Perepichka and co-workers reported an interesting deep-blue photoluminescence observed in thienylene vinylene molecules (Fig. 1) that is unusually high. This enhanced fluorescence was attributed to the effect of the alkylsulfanyl group on the thiophene ring. Our goal is to use density functional theory to understand the effect of the sulfur atoms in the structure of the molecule and on its electronic properties. We will also compute the absorption spectrum using TD-DFT and the emission spectrum, using CI-S geometry optimization of the excited states, to try to understand the origin of these unusual photo-luminescence efficiency reported. DFT (B3LYP-631G(d)) geometry optimization shows that our target molecule prefers an out-of-plane geometry just like the regular oligothiophene molecules, but short contacts suggests a H-S hydrogen bond that may contribute to the enhancement in the fluorescence.

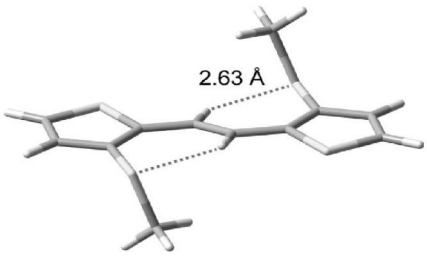

Figure 1.

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Support: CNPq

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Theoretical Evaluation of the Reaction Mechanism of (*Bis*)Platinum Complex with Guanine

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Key-words: (*Bis*)Platinum Complexes, Guanine, DFT

The DNA molecule is a target for several therapeutical agents, which may cause alterations in its replication and transcription. In this sense a study at molecular level of how these interactions occur has a great importance to elucidate the mechanism of action of several drugs. The goal of this work is to understand the first and second step of (*bis*)platinum complexes (*bis*-Pt) interaction with the guanine nucleoside, once this is the main binding site of mono and multinuclear platinum complexes.

The geometries of transition state (**TS1**), reagent (**R-1**) and product (**P-1**) were optimized at the B3LYP/6-31+G(d,p)/LanL2DZ level of theory. TS1 were characterized by an imaginary frequency (-152.03 cm^{-1}). The reaction intermediate (**I1-1**) and (**I2-1**) were obtained through an IRC algorithm, and optimized at the same level of all species cited above (Fig. 1). The rate constants were calculated using the difference of Gibbs free energy between **TS1** and the intermediates **I1-1** and **I2-1** in gas and aqueous phase through the Eyring formalism, $k = \frac{k_B T}{hc_0} e^{\Delta G^{\ddagger}/RT}$.

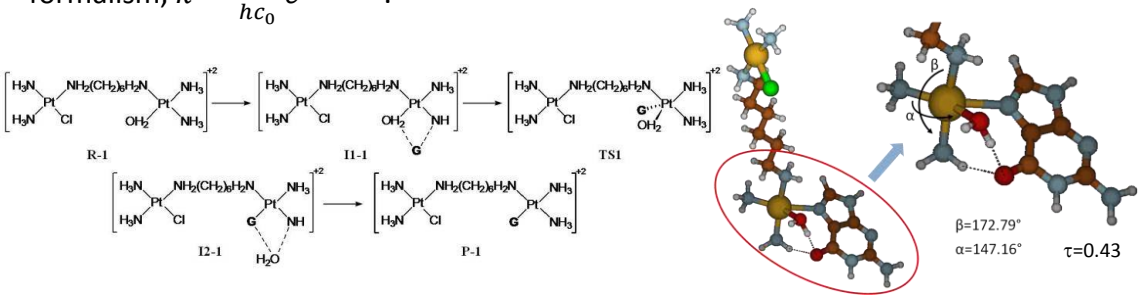

Figure 1: General reactive process for (*bis*)platinum-DNA bases interactions and optimized structure of **TS1**.

The calculated energy barrier (**$\Delta G^{\ddagger}$**) was 29.18 kcal mol^{-1} which generates the rate constant (***k***) for the first step equal to 2.58 x 10^{-9} $M^{-1}s^{-1}$, in gas phase. This result is good when compared to other cisplatin analogues and may be lower when the system is treated by polarizable continuum model. A full *bis*-Pt–guanine reaction is in advanced analysis and new results will be reported soon.

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Support: FAPEMIG.

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"Mechanism of Inhibition of the GAPDH *T. cruzi* enzyme involving iodoacetic inhibitor: A QM/MM Study"

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Key-words: *T. cruzi,* GAPDH, QM/MM, PES

The glyceraldehyde-3-phosphate dehydrogenase (GAPDH) is a key enzyme in the glycolytic pathway of trypanosomatids, therefore, is an important drug targets receiving considerable attention. Herein, we have used Quantum Mechanical/ Molecular Mechanical (QM/MM) combined with Molecular Dynamics (MD) simulations to investigate mechanism for inhibiting of iodoacetic inhibitor in complex with *T. cruzi* GAPDH (3DMT, PDB code). The *f*Dynamo library was used to perform the QM/MM MD simulations, where the inhibitor and side chain of one cysteine residue, Cys166 (present at the active site) were treated with the semiempirical AM1 hamiltonian, while the rest of the system (protein, cofactor NAD+ plus water molecules) was described using the combination of the OPLS-AA and TIP3P force fields. In addition, the potential energy of our scheme is derived from the standard QM/MM formulation. The *f*Dynamo was used to explore the PES as a function of the distances: R1, R2, and R3, R4 (Fig.1a, 1b). The PES were obtained using two anti-symmetric combinations of these distances: the R1-R2 corresponding coordination the transfer of hydrogen from the catalytic Cys166 residue to the nitrogen of His194, while that in the coordinate R3-R4 is related to the nucleophilic attack of the cysteine residue on the alpha carbon of acetate. In addition, the energy barriers were obtained from the surface energy at AM1/MM level and corrected at B3LYP(3-21G(p,d))/MM level. In order to analyze the flexibility of the IAA inhibitor, 1 ns of QM/MM MD was carried out using the GAPDH-IAA complex. The potential energy surface (PES) obtained through combinations of two anti-symmetric distances defined by the coordinates R1- R2 and R3-R4. In this context, it was found that the methodology applied to the study of inhibition was satisfactory in order to elucidate the reaction mechanism, which is established by a concerted process, in which the formation and breaking of connections S-C and C-I occur simultaneously. During this process, the inhibitor remains in the catalytic site acting competitively with the natural substrate of the enzyme GAPDH, since the energy barrier is close to catalysis of the inhibition promoted by iodine acetate. The results reported here are expected to provide useful information for the design of new GAPDH *T. cruzi* inhibitors.

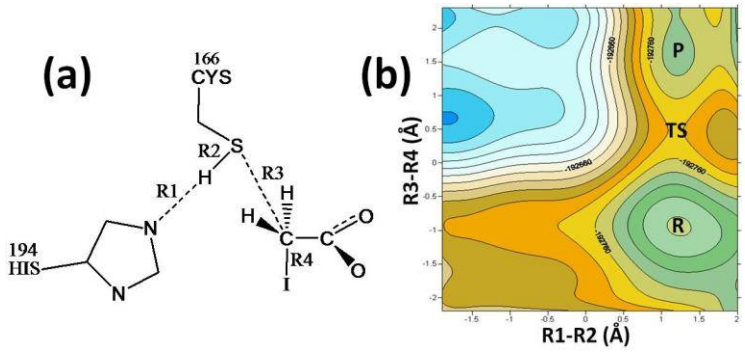

Figure 1. (a) Coordinates for schematic mechanism for inactivating the GAPDH enzyme. (b) PES – Potential Energy Surface.

Support: CNPQ/CAPES.

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Electron-Phonon Coupling in Graphene Nanoribbons

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Key-words: Graphene nanoribbons, band gap, electron-phonon coupling

The exhibition of a bandgap is an important characteristic of systems originated from a particular cut in strips of a graphene sheet, i.e., armchair graphene nanoribbons. This property is particularly crucial when it comes to their technological application as semiconducting structures. It is an important feature that this bandgap can be modified according to some parameter variation such as the width of the nanoribbons. Experimental evidences show that the wider the nanoribbon, the smaller the gap tends to be. Another way to achieve bandgap change is to modify the electron-phonon coupling, which is a parameter that couples the electronic part of the problem with the lattice. It was verified that the electron-phonon coupling has a large impact on scanning tunneling spectroscopy. Varying this constant is an useful approach in models that treats electronic and lattice dynamics simultaneously in a dependent fashion. In this work we investigate the bandgap change as a function of the coupling constant. Here we study armchair graphene nanoribbons using a two-dimensional tight-binding model with relaxation in a first order of expansion. The molecular dynamics was treated classically, while the pi-electrons are described by the time dependent Schrodinger equation. Our results suggest that the coupling parameter that best describes the experimental bandgap is approximately 2eV/Å for armchair graphene nanoribbons smaller than 14 sites of width. Also, when is considered electron phonon coupling, it is observed an electronic collective behavior as a quasi-particle. These two major results are in agreement with both experimental and theoretical data [1, 2].

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Support: CNPq.

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Study of N-methylformamide in non-aqueous media the case NMF-Acetone

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Key-words: MC simulation, N-methylformamide, acetone, hydrogen bond.

This work presents the study of structural and thermodynamic properties of acetone (ACT) - N-methylformamide (NMF) mixtures using Monte Carlo simulation. The study has been performed in order to better understand the molecular mechanisms involved in the enzyme's stabilization in no aqueous media, since there is a significant increase in the use of this technology in pharmaceutical and chemical industries in recent years.

The structural results obtained for the pure liquids were compared with those obtained by neutron diffraction with isotopic substitution and subsequent refinement by the EPSR (empirical potential refinement) method. The simulations were performed in the isothermal-isobaric ensemble with a temperature of 298 K and 1 atm. The intermolecular energy was calculated using the classical 6-12 Lennard-Jones plus Coulomb pair potential. The theoretical values obtained for the heat of vaporization and density are in good agreement with the experimental data for pure liquids. There was a good agreement between experimental and theoretical structure of liquids (especially for NMF).

In the pure liquids' analysis was found structural and thermodynamic differences among them, mainly due to the presence of hydrogen bonds in the NMF and the lack of it in the ACT. In the mixture, the interaction energy between the NMF molecules is larger than between the ACT molecules, also a consequence of the presence of hydrogen bonds in the first ones. It was also found the formation of hydrogen bonds between the two liquids, with an increase in the strength of hydrogen bond interaction between the NMF molecules as ACT was added due to some sort of solvophobic effect. The concentration's influence on the dipolar correlation between the molecules of the liquid has been explored with discussion of the structure in the solvation shells in the mixture. The excess enthalpy of the mixture was calculated and the results were interpreted according to the difference of the hydrogen bonds' quality in the liquid. The results shows that the mixture's formation is exothermic, which agrees with literature's results that indicates a decrease in the volume of the mixture.

Support: CAPES.

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Studies of Hydration and Hydrolysis of the As_2O_3 species

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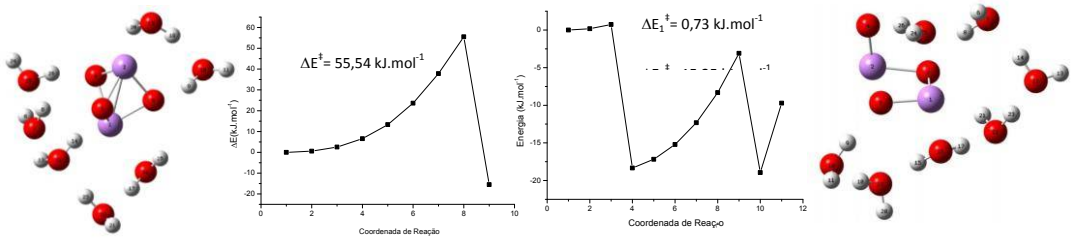
Key-words: As_2O_3, hydration, hydrolysis

Arsenic trioxide is the most important commercial compound containing arsenic and its most notable application is in treatment of acute promyelocytic leukemia[1]. The As_2O_3 molecular species is unknown, so we performed computational studies of the interaction and reaction of its most stable isomer (D_{3h} symmetry structure)[2] with water molecules, simulating hydration and hydrolysis, thus obtaining data about its behavior in such an environment.

We used the Gaussian03 program to obtain structures and vibrational frequencies at the B3PW91/6-311+G(3df) level, considering several options to simulate the hydration of the most stable isomer of arsenic trioxide. Using scans of reaction coordinates, we studied the hydrolysis of As_2O_3 considering different forms of attack: i) oxygen atom of As_2O_3 onto a hydrogen atom of water molecules, and ii) oxygen atom of water molecules onto arsenic atom of As_2O_3.

Analysis of the explicit interaction of As_2O_3 with water molecules showed that the formation of hydrogen bonds between the species causes an increase in the As-As bond length. The presence of more water molecules causes a significant decrease of the energy barrier for hydrolysis characterizing a concerted and assisted mechanism, particularly for the attacks through the oxygen atoms of the water molecules.

Finally, in the search of other hydrated forms of the symmetric D_{3h} structure, the initial configuration of water molecules had enough energy to overcome energy barriers and yield, during the optimization process, a more stable As_2O_3-$(H_2O)_7$ complex with an open structure for the As_2O_3 moiety, as shown in the Figure, which most likely is the structure of As_2O_3 in water.



[1] G. Q. CHEN, et al. *Blood*, **89**, 3345 (1997).
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Support: FACEPE, CNPq, CAPES, INCT/INAMI.

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"In silico binding mode proposition of flavonoid ligands of Tau protein into Alzheimer's Disease"

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Key-words: Alzheimer's Disease, Tau protein, Flavonoids, in silico

An intracellular hallmark of Alzheimer Disease (AD) is accumulation of hyperphosphorylated tau as paired helical filaments (PHF). A significant advance in understanding tau's behavior isolated came when it was recognized that the protein contains isolated short peptide motifs, embedded in an otherwise hydrophilic environment, which have a high tendency for β-structure and aggregation, forming the core of the PHF [1]. In this study was used the smallest fragment responsible for aggregation, the hexapeptide ^{306}VQIVYK^{311}, whose structure has been solved [2].

In the last years, a great number of Tau aggregation inhibitors have been developed, including flavonoids. However, the binding mode of these potential drugs is not well established. Thus we propose a possible binding mode between hexapeptide and inhibitors using Molecular Interaction Fields (MIFs), Pharmacophore Modelling and Molecular Dynamics (MD) procedures.

The MIFs were obtained with GRID22b [3] software using a hydrogen bond acceptor, a hydrogen bond donor, a hydrophobic and aromatic carbon as probe groups. In sequence, bioactive flavonoids were oriented with respect to the hexapeptide after analysis of MIFs and a flavonoid Pharmacophore Model obtained. The last step includes Molecular Dynamics simulations, whose trajectories were obtained and analyzed using the InsightII package [4].

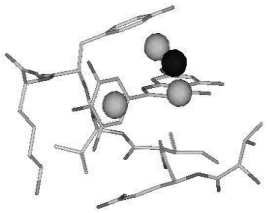

Figure: Proposed binding mode between hexapeptide and flavonoid ligand aligned with its pharmacophore model

Our results point out that the benzopyrone ring of flavonoids is able to stack with Y residues and induce the expected hexapeptide conformational change that could be responsible to inhibit Tau aggregation.

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[2] Sawaya, M. R. et al. Nature 2007, 447, 453-457.
[3] Goodford, P. J. J. Med. Chem. 1985, 28, 849-857.
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Support: FAPESP.

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"The Effect of the Zeolite Cavity on the Mechanism of Dehydrogenation of Light Alkanes over Gallium Containing Zeolites"

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Key-words: zeolite, dehydrogenation, dihydridegallium

The dehydrogenation reaction of light alkanes in gallium containing zeolites was studied using density functional theory (DFT) and a non-framework gallium species in the dihydridegallium ion form (GaH_2^+). The effect of the cavity was incorporated using a cluster with 22 tetrahedron atoms (T22) to model the zeolite. Two different mechanisms were considered when examining the dehydrogenation reaction: a 3-step mechanism and a 1-step concerted mechanism. The 3-step mechanism is favored for ethane dehydrogenation, while the concerted mechanism is favored for isobutane dehydrogenation. The differences between the activation energies through the 3-step and the concerted mechanism are between 1 and 2 kcal/mol for both propane and n-butane dehydrogenation. These results indicate a change in the mechanism of the reaction when larger or bulkier hydrocarbons are considered. This trend has not been observed in previous calculations with smaller zeolite cluster and is, therefore, due to the improved cluster used. From the calculations, it is clear that the effect of the zeolite cavity and active site confinement should be considered for an accurate investigation of the mechanism involved in the aromatization of light alkanes.

Support: CAPES, CNPq, FAPERJ, PRONEX, and Instituto Nacional de Materiais Complexos Funcionais.

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Estudo DFT do mecanismo de decomposição da artemisona

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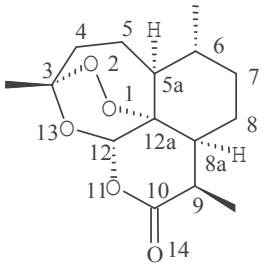
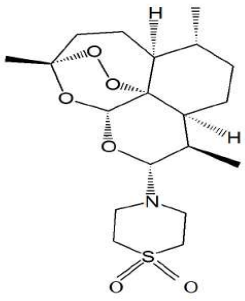
Palavras-chave: artemisona, malária, mecanismo de ação da artemisinina.

Atualmente, a artemisinina (1a) e seus derivados constituem a classe mais importante de compostos antimaláricos. Sugere-se que seu mecanismo de ação seja mediado pela interação de íons Fe(II) do grupo heme do parasita com o grupo peróxido, que se decompõe gerando espécies radicalares reativas e citotóxicas ao parasita. No entanto, programas de síntese vêm sendo desenvolvidos visando obter análogos sintéticos com alta atividade e que apresentem melhor desempenho farmacocinético do que a artemisinina e derivados. Nesse contexto, destaca-se artemisona (1b). Neste trabalho, calculou-se todas as espécies relevantes do mecanismo de decomposição da artemisona, visando identificar propriedades geométricas e eletrônicas que possam justificar sua maior potência frente a artemisinina. Empregou-se o funcional B3LYP e o conjunto base 6-31G(d). Nossos resultados mostram que os intermediários que apresentam o radical centrado no carbono (C_4) são mais estáveis do que a espécie híbrida que apresenta o radical centrado no oxigênio (O_1/O_2). As estruturas com radical secundário e primário em C_4 são 3,64 e 2,28 kcal/mol mais estáveis do que a espécie híbrida. Verificou-se que houve um significante aumento da estabilidade relativa do intermediário com radical centrado no carbono primário da artemisona frente a artemisinina. O estudo das espécies protonadas e a análise das propriedades geométricas e eletrônicas desses sistemas estão em andamento.

FAPERJ



1a



1b

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Periodic study of CO_2 adsorption on tetragonal and monoclinic ZrO_2

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Key-words: Adsorption, Zirconia, PBE1PBE.

Introduction

In recent years ZrO_2 has been extensively studied in different applications, ranging from electronics to catalysis. ZrO_2 is a catalyst for several reactions and active component for the synthesis of methanol from mixtures of CO/H_2 or $CO2/H_2$ [1]. Zirconia presents three well defined phases: monoclinic, tetragonal and cubic [2]. The monoclinic phase is the most widely used in catalytic applications. Its acidity is important for the catalytic activity of this oxide. Thus, the adsorption of CO_2 was studied to compare the acidic property of the zirconia surfaces. Periodic calculations were performed using the program Crystal06 with density functional PBE1PBE.

Results and discussion

Table 1 shows the cell parameter values optimized for zirconia tetragonal phase. The monodentate adsorption is found with carbonate-like formation, on oxides surfaces, with high basicity. The interaction energy found for zirconia tetragonal phase was -461kJ/mol (with BSSE).

Figure 1 shows the result of optimized CO_2 interaction on the tetragonal ZrO_2 cluster. The CO_2 interaction distance was 2.22Å. The interaction with the surface was very strong, which may have led to a change in the CO_2 orbital distribution.

Table 1 – Cell parameters for zirconia tetragonal (Å).

	a	c
Hoffman, 2002	3.67	5.25
Exp. Hoffman, 2002	3.64	5.27
This work	3.61	5.21

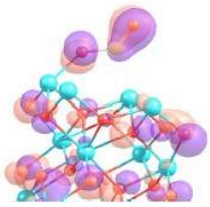

Figure 1 – CO_2 interaction on the ZrO_2 tetragonal surface. Hydrogen atoms for dangling bonding are omitted.

Conclusion

The optimization of tetragonal and monoclinic ZrO_2 cell parameters is in agreement with literature data, showing a good correlation of PBE1PBE functional.

Support: CAPES, CNPq, INCTMN, UnB, UEG-Formosa.

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1 - Tang, Q L, Hong, Q J, Liu, Z P, (2009) J. Catal. 263:114.
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DFT study of electronic properties of polyaniline

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***Key-words**: polyaniline, DFT, B3LYP, BLYP*

Polyaniline (structure presentedin Fig. 1) is widely studied because of its "good combination of properties, stability, price and ease of synthesis by different routes, and uncountable application" [2]. We intend to study long chains and aggregation of polyaniline with DCACPs (Dispersion Corrected Atom-Centered Potentials) implemented in CPMD code for BLYP functional. So, in this work, we performed a methodological study to verify the influence of basis set (6-31 G or 6-311 G with different polarizations combination) and functional (B3LYP and BLYP) on electronic properties and structural parameters of some polyaniline oligomers (with 2 to 8 monomers). All calculations were performed with Gaussian03 code.

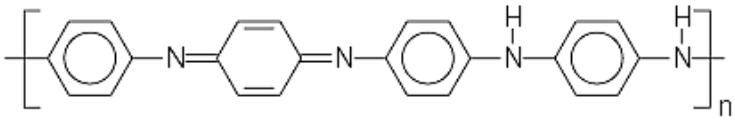

***Figure 1.** Structure of polyaniline.*

The obtained geometries and dipole moments are very similar. HOMO, LUMO and the corresponding gap energies are quite different for BLYP and B3LYP, but the "error" is constant as chain increases. Polarization is important to describe the electron delocalization. So, in further calculations, we intend to use the less time consuming combination BLYP/6-31G(d). Besides DCACPs calculations, we are studying atomic charges to perform molecular dynamics simulations of polyaniline chains.

[1] Amazonas, J. G. et. al. J. Molecular Structure: Theochem 759 (2006) 87–91

[2]Bajpai, A.K. et. al. Journal of Composite Materials 45 (2011) 485-497

Support: UFABC, CNPq, FAPESP.

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A Pseudo-Potential/TDDFT Methodology for the Calculation of Dynamic Raman Activities

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Key-words: Raman Spectroscopy, TDDFT, LR-CCSD, Pseudo-potential

High agreement with experimental data for excitations energies, dynamic polarizabilities and Raman activities can be achieved using extended basis set of triple-zeta quality allied with treatment of the electronic correlation at CCSD level. These requirements limit these studies to small molecules due to the high computational cost. It's desirable to search alternative electronic correlation treatments and smaller basis functions. In this work, we investigate the use of the Density Functional Theory for the treatment of electronic correlation and the use of polarized pseudo-potentials as basis functions. The PBE0 functional is regarded in the literature as suitable for the calculation of these properties. Recently, CAM-B3LYP has been proposed as another functional for this kind of study. For the basis function, the ecp-pStuttgart's[1] pseudo-potential was chosen. CAM-B3LYP/ECP and PBE0/ECP theory levels were investigated taking the CCSD/ECP level as the reference. Electronic excitation energies, dynamic polarizabilities and Raman intensities for CH_4, NH_3, H_2O, C_2H_2 and H_2CO were calculated. The results for both wave-functions were in very good agreement with the reference one. PBE0 performed better than CAM-B3LYP. However, both showed the same limitations when single and double excitations were needed to correctly represent the excited states given that TDDFT is a singles-only method. Figure 1 summarizes the results for Raman activities.

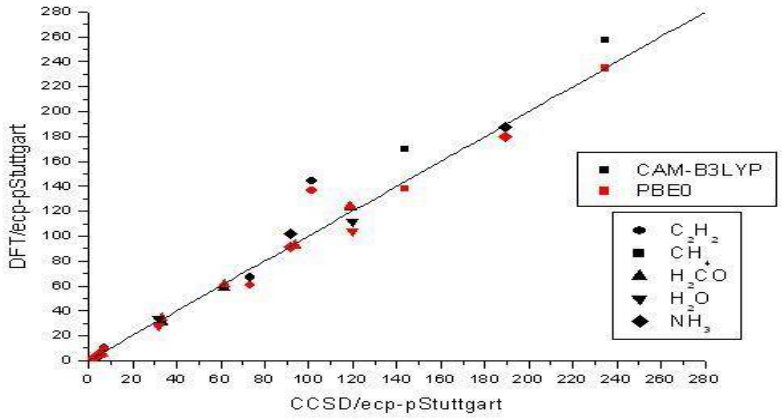

Figure 1: Raman activity $\perp S^n$ (π/2)(514 nm) DFT/ecp-pStuttgart x CCSD/ecp-pStuttgart.

Reference: [1] Vidal, L. N.; Vazquez, P. A. M.; Rev. Bras. de Aplicação de Vácuo,28,21-24,2009;
Support: PIBIC/CNPq, PIBIC/SAE-UNICAMP

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"Preliminary theoretical study of the anti-hypertensive Valsartan: β-Cyclodextrin inclusion complexes"

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Key-words: valsartan, β-ciclodextrin, molecular modeling

Valsartan, a water-insoluble drug, is mainly used in the treatment of hypertension albeit with reduced oral bioavailability. The aim of the development of a valsartan:β-cyclodextrin (VAL:β-CD) pharmaceutical composition is to improve its water solubility and bioavailability. Experimental data shows the possibility of its formation. Molecular modeling features implemented in HyperChem 7.5 program were used in this work in order to elucidate the inclusion complex formation and corroborate experimental results. Preliminary results (Molecular Mechanics calculations, AMBER force field, followed by PM3 Quantum Mechanical calculations, both of them at 298 K, vacuum) are shown in Table 1:

Table 1: Selected properties of pure and complexed VAL obtained at semi empirical level of theory (PM3 Quantum Mechanical method at 298 K, vacuum).

System/property	VAL	β-CD	VAL: β-CD complex
ΔH_f^o / kcal.mol^{-1}	-21.60	-1469,95	-1505.62
μ / D	5.63	0,85	6.02
Log P	4.27	-8,52	-1.33

In order to confirm the optimized geometric structures as minimum on the potential energy surface the vibrational modes were performed (VAL, β-CD and β-CD complex). Besides, these calculations lead to the values of the entalphy of formation and the results showed that VAL is able to form 1:1 stable complex in β-CD. from this point of view (for the complex formation ΔH^o = - 14.07 kcal/mol). We also could observe from Table 1 that the solubility in water of VAL included in β-CD increases (log P decreases and the dipole moment increases).

Acknowledgment: Jensen, C.E.M. (CCO/UFSJ) for experimental discussions.

Support: FAPEMIG.

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Proposal of a new topological index for analysis of inclusion compounds with cyclodextrins

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Key-words: Molecular Dynamics, Cyclodextrins, Molecular Topology

Cyclodextrin (CD) molecules are macrocycles of α-D-glucopyranose linked by glycosidic α-1,4 bonds. These molecules have been widely studied with the purpose of developing host-guest compounds. In this sense, the present study focused on the analysis of the overall profile of the inclusion process involving R,S-amphetamine and α-CD and β-CD, using a new topological parameter called "vector-μ". Molecular dynamics (MD) simulation were carried out for the free species and inclusion compounds, using the AMBER force field as implemented in the MacroModel package (the simulation protocol will be shown in the poster). Figure 1 represents some snapshots from MD simulation for R and S…α-CD complexes. It is worth noting that the inclusion through the tail side (narrow rim) is preferable for both isomers, even though the initial structures have the substrate close to the head face. The guest molecule tracks a very complex pathway to get the opposite side of CD along the MD trajectory. This can be clearly followed by the "vector-μ" (Figure 2) that is quite sensitive to the relative position of host and guest species. Large values of "vector-μ" (peaks in Fig. 2) indicate a dethreading event and low values the inclusion of guest within the host cavity.

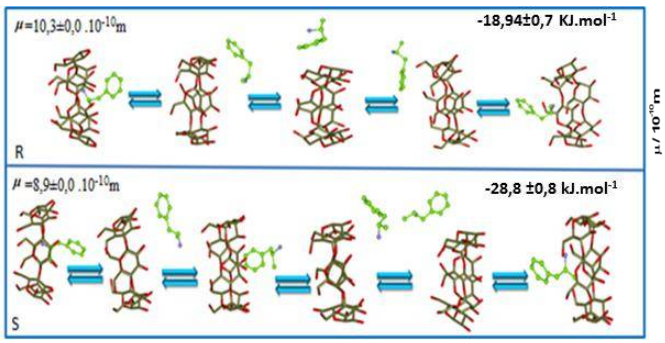

Fig. 1: Snapshots from MD simulation of R- and S…α-CD systems.

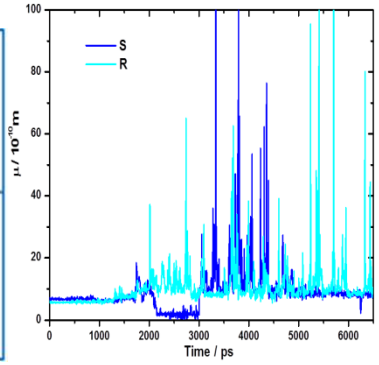

Fig. 2: "vector-μ" as function of MD time.

Support: CAPES, FAPEMIG, CNPq and UFJF.

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"Deformations of the 3*d* and 4*f* electron density in aquo complexes"

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Keywords: deformation electron density, metal-ligand bond.

The investigation about deformation electron density of a metal ion upon coordination with ligands (aquo) is relevant to establish the ligand field effects. For transition metal ions these effects should be large, whereas, for trivalent lanthanides such effects are assumed to be small due to shielding of the 4*f* electrons from the ligand environment by the $5s^2$ $5p^6$ radially extended shells. However, there are evidences that the ligand environment is responsible for a substantial 4*f* electron polarization (or deformation)[1]. Thus, our goal is to evaluate the different effects that cause deformation of the metal ion electron density upon complexation. Thus, we devised several computational procedures to separate and quantify the distinct sources of deformation electron density, which consists in the difference between electron density (ρ_e) of the complex and the sum of the electron densities of the free ion and the water molecules. Each procedure involves calculating the isolated ion and ligands contributions using the following combinations, (*i*) for free ion: pseudopotential ($\rho_{ECP\text{-}ion}$) or point charge ($\rho_{PC\text{-}ion}$), isolated ($\rho_{iso\text{-}ion}$) or with water molecules placed far away in the same symmetry as the equilibrium structure ($\rho_{\infty\text{-}ion}$) and (*ii*) for water: isolated ($\rho_{iso\text{-}H2O}$) or under the effects of ion point charge ($\rho_{H2O\text{-}PC(ion)}$). These combinations separate the effects such as ion × ligand polarization, overlaps and symmetry breaking.

For a preliminary study we have chosen the $[Zn(H_2O)_6]^{2+}$, $[Lu(H_2O)_8]^{3+}$ and $[Lu(H_2O)_9]^{3+}$ complexes, since they are closed-shell systems and have the largest number of 3*d* and 4*f* electrons, so it would be expected the largest deformations. Calculations to obtain electron density were performed the Gaussian03 program at the MP2 level with MDF10 and MWB28 for Zn, MWB28 and MWB60 for Lu ECP/basis sets and 6-311+G(d,p) basis sets for water. Initial results show that there are differences in the electron density deformation of Lu(III) for each procedure, even when the ligands are place at 1000 pm from equilibrium distance, indicating that symmetry breaking is an important effect in the deformation. Comparisons between the two ions should gauge the strength of the ligand field.

[1] E. Furet, K. Costuas, P. Rabiller, O. Maury, *J. Am. Chem. Soc.* **2008**, *130*, 2180.

Support: CNPq, FACEPE, CAPES, PRONEX, inctINAMI, FINEP.

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Adsorption of Methanol on PtPb Anodes for Fuel Cells

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Key-words: DFT, Adcluster, DAM, Platinum and Lead.

Methanol and ethanol are increasingly gain importance as a renewable energetic alternative to fossil fuels, especially in Brazil. The electro-oxidation of these molecules produces undesirable stable intermediates The development of new materials specially designed to avoid these intermediates, will certainly allow the development of cells that can operate directly with these fuels.
In this work, we have used the Dipped Adcluster Model (DAM) [1-2] to study the mechanism of methanol oxidation on Pt_4/C_7 and $(PtPb)_2/C_7$. All calculations were performed with the Gaussian09 program, using the M06 functional and the LanL2DZ basis set. The geometries of the clusters and adclusters were fully optimized. Optimizations were initiated from several different positions of methanol molecule in relation to the cluster models. The absence of imaginary frequencies was used as a criterion to ensure that the optimized structures represent a minimum. Interaction energies (E_{int}) obtained for the system formic acid on pure Pt with this methodology [3] are in very with good agreement with plane wave calculations [4]. We are also performing wave plane calculations, with VASP code, to validate the methodology and also to explore other possible Pt/Pb compositions clusters.

Table 1. Interactions energies (E_{int}, in eV) between methanol and different clusters

Clusters	Pt-Pb-Pb-Pb	Pt-Pb-Pt-Pb	Pt-Pt-Pb-Pb	Pt-Pt-Pb-Pt	Pt-Pt-Pt-Pb
E_{ads}(eV)	2,93234	0,18539	-0,03523	-2,12802	-2,06545

The presence of Pb changes the preferred adsorption position and increases E_{int} between methanol and electrode giving insight about the experimentally observed Pb synergic effect on the oxidation process. The inclusion of dispersion interactions by DCACP's [4] and the choice of the exchange and correlation functional are examples of challenges that are still to be dealt with.

Support: UFABC; FAPESP; CNPQ;

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Molecular Dynamics of Endoglucanase III from *Trichoderma Harzianum*

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Key-words: *Trichoderma harzianum*, Glycosyl hydrolases, Molecular Dynamics

The bagasse of sugar cane is an abundant biomass from Brazilian agroindustry, which holds a promising venue for the production of second generation ethanol. One of the key steps towards the development of a sustainable means of obtaining ethanol from fermentation of soluble sugars resulting from cellulose degradation is the development of efficient cellulolytic enzymes. It is, therefore, important to understand the mechanism of enzymatic hydrolysis of cellulose as well as the general structural and dynamical features of glycosyl hydrolases. In this work we use Molecular Dynamics (MD) simulations to investigate one enzyme of this family of proteins, namely, the endoglucanase III from *Trichoderma harzianum* (EG3h), whose three-dimensional crystallographic structure has been recently resolved by some of the authors. Most endoglucanases contain a cellulose-catalytic domain and one or more carbohydrate-binding modules connected by an unstructured polypeptide linker. EG3h does not contain a carbohydrate-binding module, but still can efficiently catalyze the hydrolysis of cellulose. Here, we report results of MD simulations that help to elucidate the mechanisms by which EG3h effectively binds cellulose so that hydrolysis may proceed. We have compared the crystallographic structures and results from MD simulations performed on the enzyme of high homology, EG3 from *T. reesei*, and also with the carbohydrate-binding module from endoglucanase C from *Cellulomonas fimi.* The simulations reveal that the amino acids that play the most important roles in EG3 binding to cellulose are Gln65, Gln197 and Gln201, which form stable hydrogen bonds in the catalytic cleft, and also the residues Trp23 and Tyr112, which constitute a harboring wall of hydrophobic contacts to the polysaccharide.

Support: FAPESP, CNPq.

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"Photophysics and Photochemistry of Adenine-Thymine base pair"

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Key-words: DNA Base-Pair, Nucleotides, Hydrogen Transfer

UV radiation is one of the main damaging factors of the DNA. After absorbing UV radiation, biomolecules are excited and the excess of energy can be employed in photochemical process or be dissipated through radiative and non-radiative process.

High-level multiconfigurational *ab initio* calculations and extended basis set (CASSCF/CASPT2//ANO-L-VDZP) have been used to investigate the ground and excited potential energy hypersurfaces of adenine-thymine base pair by means of conical intersections, minimum energy paths and linear interpolation in internal coordinates, in order to obtain a comprehensive description of the photophysical aspects involved in proton transfer reactions (single or double) and, subsequently, relaxation or generation of a rare tautomer (Figure 1).

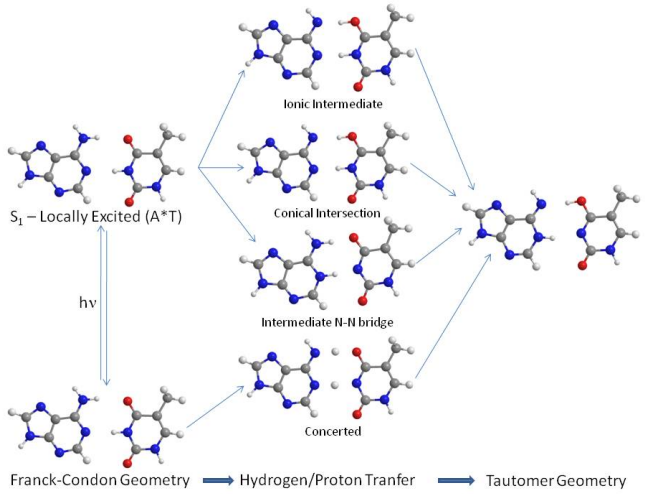

Fig. 1: Scheme of possible mechanisms for the formation of the rare tautomer.

Our results suggests that after excitation to a locally excited state, a conical intersection with a low-lying charge transfer state leads the system to another conical intersection region, but this time with the ground-state.

Support: CAPES, FAPESP, CNPq, LCCA-USP, MEC-FEDER Spain.

Thermochemical Aspects of Emodin Deprotonation Process in Aqueous Solution

Antonio R. da Cunha(PG) , Evandro L. Duarte(PQ), Maria T. Lamy(PQ) and Kaline Coutinho(PQ)

Key-words: Aloe vera, Emodin, deprotonation process

Emodin (1,3,8-trihydroxy-6-methyl-9,10-anthraquinone, EM), is one of the most abundant anthraquinone derivatives found in nature. It can be extracted from different plant sources such as *Aloe vera*, rhubarb, which is widely used in the cosmetic and pharmaceutical industries [1]. Emodin is known to have antibacterial, antiviral, antifungal and anticancer activities [2]. Due these biological and pharmacological activities, several scientific researches examined the structural and electronic properties of this molecule and it interactions with the biological environment [3]. In recent investigation some chemical processes of EM in alcoholic solutions, such as deprotonation and tautomerism, has been analyzed [4]. These processes changes the molecular properties and its interactions with the environment. In this work, we studied the deprotonation process of EM in aqueous solution, using experimental and theoretical techniques. The experimental part was performed to obtain the acidity constant of the first deprotonation of EM in aqueous solution, pK_{a1}=-log(K_{a1}), using measurements of its UV-Vis absorption spectra at different pH values. In the theoretical part, quantum calculations and molecular simulations were performed with different models considering the polarization for solute due to the presence of the solvent. We calculated the value for the pK_{a1}, using the differential free energy of solvation of neutral and deprotonated EM. Our best experimental and theoretical values for pK_{a1} were 8.0 ± 0.2 and 8.2 ± 1.6, respectively. These results are in excellent agreement. Therefore, we conclude that the use of polarizable models for the solute is crucial to well describe the deprotonation process of EM in aqueous solution. Our challenge now is to obtain the theoretical values for second (pK_{a2}) and third (pK_{a3}) acidity constants of EM, since the description of polarizable model for anions is very complex.

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Support: FAPESP, CNPq, CAPES, Rede Nanobiotec and INCT de Fluidos Complexos

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Salt Bridges Control the Kinetic Mechanism of Aldose Reductase: Evidence from Molecular Dynamics Simulations

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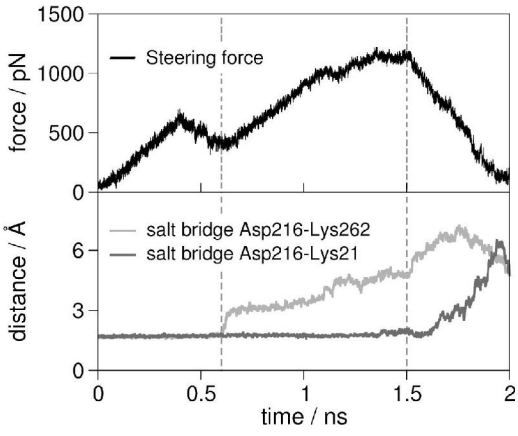
Key-words: Aldose Reductase, Dissociation, Molecular Dynamics

Aldose reductase (AR) is a member of the aldo-keto reductase superfamily of enzymes, which catalyze the reduction of aldehydes and ketones into their respective alcohols in the presence of the cofactor NADPH. As such, AR is able to catalyze the conversion of D-glucose into D-sorbitol, a highly toxic substance involved in health complications such as diabetic neuropathy and retinopathy. The catalytic mechanism involves (1) the binding of both the cofactor NADPH and the substrate to the enzyme, (2) reduction of D-glucose into D-sorbitol, (3) release of the D-sorbitol and (4) the dissociation of the oxidized cofactor NADP from the AR. The latter is the rate-limiting step of the reaction and requires conformational changes in the AR. In this work, we aim to investigate the mechanism of AR-NADP dissociation and determine the conformational changes involved. To reach this goal, we employed two special techniques of Molecular Dynamics Simulations, namely, Locally Enhanced Sampling (LES), which is suitable to unravel possible dissociation paths by reducing the dissociation barrier, and Steered Molecular Dynamics (SMD), in which the ligand-protein dissociation is suitably assisted by an external force on the ligand along a given dissociation path. The LES simulations suggested that the NADP dissociates after the opening of two loops that are initially in a closed conformation and lock the cofactor within the enzyme. The dissociation barrier, computed using the SMD simulations, is due to two salt bridges (Asp216-Lys21 and Asp216-Lys262) that help to keep the loops in the closed conformation. The figure above shows the time history of the external force applied on the NADP and the distance between the residues that form the salt bridges. It is clear that the two observed barriers correspond exactly to the breaking of the two salt-bridges: after the rupture, the loops open and the dissociation proceeds with no resistance, as shown by the rapid decrease of the steering force. Our study provides the first molecular insight on the mechanism of the rate-limiting step of the AR catalyzed reaction and might be useful in developing novel strategies for inhibiting the conversion of D-glucose into D-sorbitol in people with diabetes.



Support: FAPESP

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"Theoretical study of atomic oxygen impurities and the adsorption of CO, NO and O_2 in BC_2N nanotubes"

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Key-words: Density Functional Theory, BC_2N nanotubes, oxygen impurities, molecular adsorption, Van der Waals interactions

Using first principles calculations based on the Density Functional Theory with spin polarization and norm conserving fully separable pseudopotentials, we have studied the structural and electronic properties of oxygen defects (substitution and interstitial) in the (3,3) and (5,0) BC_2N nanotubes. We also study the adsorption of CO, NO and O_2 molecules on these tube surfaces. For the adsorbed molecules detailed calculations are performed by introducing the Van der Waals interactions through the B97-D functional proposed by Stefan Grimme. We observe that the most stable configuration for the atomic oxygen defect is interstitial between a B and a C atom forming the B-O-C configuration. For substitution doping the most stable configuration occur for the O_N (oxygen substitution the N atom). We obtain formation energies of -1.67 and 0.62 eV for these two defects, respectively. The negative value of the formation energy for the interstitial defect shows that it is an exothermic process. The calculated electronic band structures show that the O_N defect lead the system to exhibit a p-type semiconductor character while the interstitial oxygen atom don't introduce any significant changes in the electronic band structure around the band gap region. The interaction between the nanotubes and the CO, NO and O_2 molecules is investigated by the adsorption of molecules in the inner and outer surfaces of the (3,3) and (5,0) BC_2N nanotubes. The calculated binding energies show that the molecules are preferentially adsorbed (lowest binding energies) in the inner surface and perpendicular to the nanotube axis, we obtain binding energies around 0.5 eV. Including van der Waals interactions in the calculations the values of the binding energies doubled. On the other hand, the projected electronic band structure in the nanotubes atoms show that the electronic properties are not changed when compared with the pristine systems. We concluded that the interaction between the nanotube and the CO, NO and O_2 molecules is a physical process, ruled by the Van der Waals interactions.

Support: CAPES and CNPq

ANTI-INFLAMMATORY ACTIVITY OF COPAIBA OIL COMPOUNDS: A DFT AND PCA STUDY

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KEYWORDS: Copaiba oil; DFT; PCA; COX inhibitors

The discovery of an isoform of COX enzyme, named COX-2, started a notable search for compounds that could show selective inhibition to this enzyme. The selective inhibition of this enzyme is more effective in the anti-inflammatory treatment, because of undesired side effects that occurs when COX-1 isoform is inhibited by nonselective compounds. The copaiba oil, composed by a mix of diterpenes, is utilized against inflammation since long time, but there is no indications which compounds present this oil effectively inhibit the COX-2 enzyme. In this work, a set of electronic properties of 17 compounds present in copaiba oil were performed by B3LYP/6-311G**. Following, statistical models were carried out in order to find similarities with the ordinary selective inhibitors of COX-2 . As a result, the statistical model with dipole moment and GAP (difference between HOMO and LUMO energies) descriptors has shown 93.19% of the variance in the analysis. The molecules 5, 14, 16 and 17 (Fig. 1), grouped as actives, were docked into the active site of the COX2 enzyme followed by Molecular Dynamics simulation in order to evaluate the free energy.

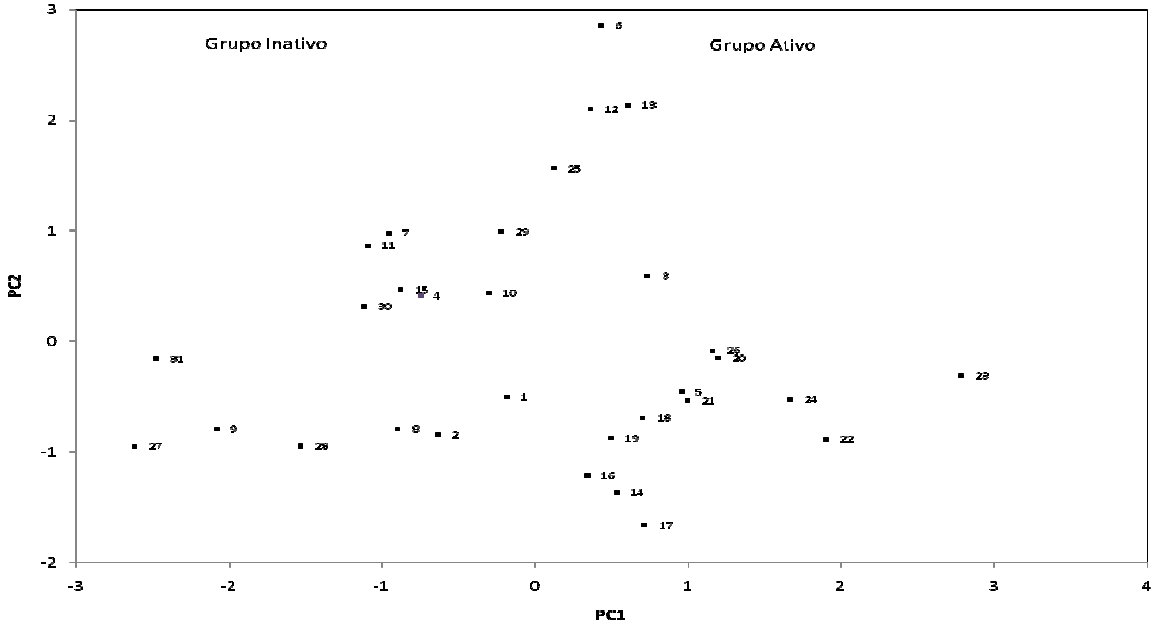

Figure 1 – PCA analysis of the diterpenes compounds found in copaiba oil.

Support: FAPEAM, FAPEMIG

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"Ruthenium(II) Nitrosyl Complexes containing Pyridine Functionalized N-Heterocyclic Carbenes"

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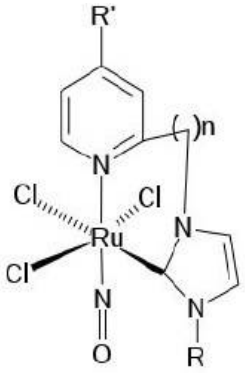
Key-words: Ruthenium nitrosyl complexes, Pyridine functionalized N-Heterocyclic Carbene, DFT, LMOEDA, QTAIM, ELF



Nitric Oxide has long been known for it's unprecedented role in chemistry, being involved in areas such as environment, biology, and technology. With the discovery of its activity in bio-regulation of mammalian cells[1], the research of compounds able to store and transport NO to desired targets greatly stimulated the development of the chemistry of nitrosyl complexes of transition metals, and in particular that of ruthenium[2]. The aim of this work is to study the lability of the Ru-NO bond along a series of substituted ruthenium nitrosyl complexes containing pyridine functionalized N-heterocyclic carbene ligands.

The geometries, harmonic frequencies and bond analysis are obtained by using BP86/TZVPP model. Scalar relativistic effects for the transition metal are considered through ZORA.

The LMOEDA results (Table 1) show clearly that the substituent has a crucial role on the lability of NO group and that the substituent affects mainly the electrostatic, exchange, Pauli repulsion and polarization terms. Additional studies including QTAIM and ELF analysis are in course.

Table 1. Energy decomposition analysis for Ru-NO bond.

Complex	E_{int}	E_{elstat}	E_{exch}	E_{rep}	E_{pol}	E_{disp}
n=0;R=R'=H	-262.72	-109.73	-56.55	253.36	-318.68	-31.11
n=0;R=R'=CN	-238.27	-96.31	-49.50	237.59	-296.19	-33.86
n=1;R=R'=H	-260.34	-112.06	-56.47	256.45	-315.93	-32.33
n=1;R=R'=CN	-238.99	-99.45	-50.62	244.92	-298.52	-35.33

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Support: FAPESC/CNPq (Grant. 17.413.2009-0).

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"Molecular Dynamics Investigations of Prodan in a DLPC Bilayer"

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Key-words: Membrane, Fluorophore, Charge Distribution

Molecular dynamics computer simulations have been performed to identify preferred positions of the fluorescent probe Prodan in a fully hydrated dilauroylphosphatidylcholine (DLPC) bilayer in the fluid phase. In addition to the intramolecular charge-transfer excited state, we considered charge distributions for the electronic ground state of the Prodan molecule by distinct point charge models corresponding to the probe molecule's dipole moment in vacuum as well as polarized in a weak and a strong dielectric solvent. Initially, the Prodan molecules were inserted into the lipophilic region of an equilibrated DLPC membrane. The non-polarized ground state representation of the Prodan molecule maintains its position close to the membrane's center. Increasing its dipole moment, the probe molecule approaches more the polar head group region of the bilayer exposing its oxygen atom to the bilayer's hydration shell. Starting the simulation of the non-polarized ground state representation located within the polar head group region, the Prodan molecule returns to the lipophilic part of the DLPC bilayer.

Support: CNPq, CAPES, NbioNet.

olecular odelin studies of inhi itors of lactate dehydro enase fro *Plasmodium falciparum*

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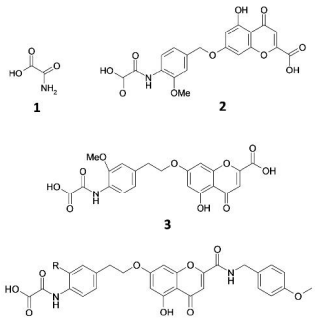
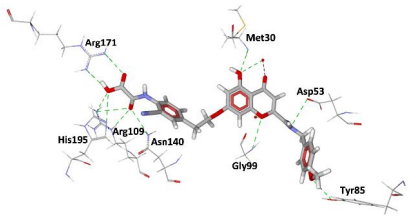
Key-words: Malaria, . *alci aru* , Lactate dehydrogenase, oxamic acids

The high number of people infected by malaria (about 230 million per year) and the emergence of *las odiu alci aru* strains resistant to chemotherapy, has stimulated the search for new drugs against this disease[1,2]. Having this in mind we investigated in the present work, by docking and molecular dynamic (MD) studies, the interactions established between the oxamic acid and five chromene-based analogues of this compound[3] (Fig. 1), with the enzymes lactate dehydrogenases from *las odiu alci aru* (LDH) and *Ho o sa iens sa iens* (*Hss*LDH). The softwares used were Molegro Virtual Docker (MVD) for the docking studies and GROMACS 4.5[4] for the MD simulations. Results show that the compounds studied were able to establish H-bonds with residues important for the catalytic mechanism of LDH, like Arg109, Arg171 and His195 (Fig.2) and that the substituent OMe in position R of compound 6 is able to establish interactions inside *Hss*LDH compromising the selectivity to this compound. Besides, we also observed that five residues belonging to a loop close to the active site of LDH (D EWN), and absent in *Hss*LDH, were able to establish interactions with the ligands along the MD simulation. These results are now been used in the design of new and more selective antimalarials.



i ure : Structural representation of the compounds studied



i ure : Best conformation of the inhibitor 5 in the active site of LDH

Support: CNP , CAPES, FAPERJ.

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olecular odelin studies y Thy idylate Kinase of *Variola Virus*

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[1]*Laborator o Molecular Modelin A lied to t e e ical and Biolo ical De ense, Militar nstitute o n ineerin , 22290-270, Rio de Janeiro, Brazil*

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Key-words: Smallpox Virus, homology modeling, Docking, Thymidilate inase

Smallpox was one of the most devastating diseases in human history and still represents a great menace because of its potential use by bioterrorists as a biological warfare agent[1]. This fact, together with the inexistence of effective chemotherapy against smallpox, motivated us to propose the enzyme Thimidilate kinase of *ariola virus* (*ar*TM) as a potential target to the drug design against smallpox. We first built a homology model of *ar*TM , in the *S SS-M D L*[2] server, using as template the TM from *accinia virus* (*ac*TM). Docking studies, with Molegro Virtual Docker (MVD)[3], were further performed in order to investigate the potential interactions with *ar*TM of known antiviral compounds used against *ac*TM (Table 1). Results suggested a good correlation between experimental and theoretical data[4] and a good selectivity of the compounds related to *Ho o sa iens sa iens* TM (*Hss*TM). Experimental studies are now been performed in order to test this compounds as new drugs against smallpox.

Ta le . Docking results and $_i$ values for the compounds studied.

	***Var*T K**			***Hss*T K**		
Co ound	**ner y Kcal ol⁻**	**ond Kcal ol⁻**	**K_i**	**ner y Kcal ol⁻**	**ond Kcal ol⁻**	**K_i**
5Brd	-127.16	-10.49	7μM	-101.04	-7.66	0.2
5Cld	-129.63	-8.11	15μM	-103.52	-7.77	0.37
5Id	-125.97	-10.43	23μM	-95.79	-8.47	0.35
dT	-123.49	-9.18	25μM	-101.53	-6.00	0.25
BVd	-119.06	-4.11	0.5mM	-90.61	-7.43	1.1
5Fd	-116.32	-9.49	0.7mM	-74.83	-8.88	5
d	-105.17	-11.20	1.0mM	-86.80	-8.71	2.5

Support: CNP , CAPES, FAPERJ

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An lise confor acional e efeito de intera es hi ercon u ativas e fl or-fenois

Marilua A. Moreira (G)[1], F tima M. P. de Rezende (G)[1], Matheus P. de Freitas (PQ)[1], Josue M. Silla (G)[1]

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alavras-chave: NBO ('Natural Bond Orbitals '') , hiperconjuga o, 2- e 3-fl or-fenol.

Os c lculos NBO ('Natural Bond Orbitals'') permitem analisar as transfer ncias de carga de orbitais ocupados para orbitais antiligantes, bem como as implica es energ ticas associadas.[1] C lculos NBO foram realizados a fim de se avaliar as intera es hiperconjugativas ue operam no isomerismo conformacional do 2- e 3-fl or-fenol. Superfícies de energia potencial (SEP) foram construídas considerando-se: o sistema real, o sistema hipot tico com o orbital σ_{OH} removido, o sistema hipot tico com todos os efeitos hiperconjugativos blo ueados. Os resultados demonstram ue o conf rmero *cis* do 2-fl or-fenol o mais est vel e tem o grupo hidroxila no plano do anel arom tico. Ao se removerem as intera es envolvendo o orbital σ_{OH}, o mínimo de energia deslocado (o conf rmero *cis* torna-se um m ximo de energia) e a barreira de energia reduz significativamente, demonstrando ue esse orbital fundamental para a estabilidade da forma *cis* do 2-fl or-fenol. As principais intera es envolvendo o orbital σ_{OH} s o $n_F \rightarrow \sigma_{OH}$ (0,60 kcal mol^{-1}, liga o de hidrog nio fraca) e, principalmente, $\sigma_{CC} \rightarrow \sigma_{OH}$ (1,38 cal mol^{-1}). Quando todas as hiperconjuga es s o blo ueadas para o is mero *orto*, somente um conf rmero est vel (com liga o OH fora do plano do anel), indicando a import ncia de efeitos de transfer ncia eletr nica para a estabilidade dos conf rmeros *cis* e *trans*, particularmente para a intera o $n_O \rightarrow \pi_{C1C2}$ (21,8 kcal mol^{-1} para ambos os conf rmeros). Para o is mero *eta*, a dele o do orbital σ_{OH} n o implica em altera o nas prefer ncias conformacionais (somente a barreira de rota o diminuiu em energia) contudo, uando se removem todas as intera es hiperconjugativas, as formas *cis* e *trans* tornam-se m ximos de energia, sugerindo ue efeitos cl ssicos (est ricos e eletrost ticos) n o s o os nicos fatores operantes do isomerismo conformacional de 2- e 3-fl or-fenois.

1-Santos, F. P. *Disserta ão de Mestrado*, niversidade de S o Paulo, Ribeir o Preto,

Apoio: FAPEMIG e CNPQ

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Prediction of Protein Folded in Native Structures by Generalized Simulated Annealing Coupled to GROMOS Force Field

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Key-words: Generalized Simulated Annealing, Protein Prediction

The genome mapping and sequencing advances are producing an exponential number of amino acid sequences of new proteins, and the comprehension of these protein structures becomes a crucial extension to these progresses. The protein folding, therefore, is the central problem for development of the post-genomic era. Currently, the three-dimensional structure of a protein is obtained by experimental techniques such as Crystallography and X-ray Diffraction or Nuclear Magnetic Resonance (NMR) spectroscopy. However, due to the limitations and high costs of these techniques, determination of three-dimensional structure of a protein is a problem that still challenges the scientists.

In this sense, theoretical and computational studies have increased the understanding of the factors that drive a polypeptide sequence to its native state. This improvement is due mainly to advances in computing power in recent years. The purpose of the protein structure predictions is to provide the conformation of the native state for a given amino acids sequence. In general, it is assumed that the protein sequence is folded in a native state, or a collection of native states, which are found at (or near) the global minimum (free) energy.

The goal of this work is the development of methodologies and protocols, based on the Tsallis thermostatistics, for *ab initio* protein structure prediction using atomistic molecular models. Thus, we use a set of 15 protein models, with length from 13 up to 54 amino acids residues in order to calculate their native structures.

In this work we use an optimization method, the Generalized Simulated Annealing (GSA), coupled to the GROMOS96 Force Field to investigate the protein folding problem.

We were able to find structures very near of the native states. In some structures such as the 1LCX, 2BP4, 1PEF, 1L2Y (PDB ID) we found deviations smaller than 3.0 Å, what is considered a high resolution prediction. Furthermore, 60% of the tested models showed deviations of less than 4.0 Å, which are considered good results.

Support: CNPQ and FAPERJ.

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"Análise conformacional e efeito de solventes em 2-flúor-fenol e 2-flúor-anisol"

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Palavras-chave: Ligação de hidrogênio, Efeito de solvente, Polaridade.

Interações intramoleculares, como efeitos estéricos, eletrostáticos, hipercojugativos e ligações de hidrogênio, são fatores governantes de equilíbrios conformacionais. Dentro desse contexto, realizou-se um estudo conformacional para o 2-flúor-fenol e 2-flúor-anisol, avaliando-se o efeito do solvente (polar e apolar) através de cálculos teóricos em nível MP2/aug-cc-pVDZ.[2] Para todos os compostos, o grupo OR permanece no plano do anel em ambas as conformações estáveis (*cis* e *trans*), exceto para o *cis* 2-flúor-anisol. A questão é: esse comportamento não é observado para o *cis* 2-flúor-fenol por causa de ligação de hidrogênio intramolecular F...HO ou devido ao efeito estérico F/CH_3 no *cis* 2-flúor-anisol? Cálculos NBO indicam que as formas contendo o grupo OR no plano do anel estabilizam-se fortemente devido ao efeito hiperconjugativo $n_O \rightarrow \pi^*_{C1C2}$, enquanto a contribuição hiperconjugativa para a ligação de hidrogênio intramolecular $n_F \rightarrow \sigma^*_{OH}$ é muito modesta (0.6 kcal mol^{-1}); consequentemente, sugere-se que o grupo OH do *cis* 2-flúor-fenol esteja no plano do anel, ao contrário do seu análogo metoxílico, devido à preponderância do efeito estérico F/CH_3 no *cis* 2-flúor-anisol em relação à interação hiperconjugativa $n_O \rightarrow \pi^*_{C1C2}$. Isso pode ser ilustrado pelo comportamento conformacional dos compostos em solução (cálculos incluindo efeito implícito do solvente): na fase gasosa e em solução apolar (cicloexano), o *cis* 2-flúor-fenol é mais estável do que o *trans*, mas em solução polar (acetonitrila), o confôrmero *trans* torna-se mais estável. Isso indica que o confôrmero *cis* não é mais estável do que o *trans* devido à ligação de hidrogênio intramolecular (a qual deveria operar em quaisquer soluções), mas devido à repulsão dipolar O/F no confôrmero *trans*, que é eliminada ou ao menos reduzida em solução polar. Comportamento similar é observado para o 2-flúor-anisol. Sendo assim, derivados metoxílicos não podem ser usados com precisão como compostos de referência para estimar ligações de hidrogênio nos respectivos alcoóis, pois o grupo CH_3 tem efeito estérico pronunciado.

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Apoio: FAPEMIG e CNPQ

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A New Hybrid Algorithm Based on the Dunham and GSA Methods to Fit Potential Energy Curves with Experimental Accuracy

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Key-words: PEC, GSA, Dunham, rovibrational spectroscopic constants

A new hybrid procedure based on GSA and Dunham methods to be used in direct fit of potential energy curves to *ab initio* and spectroscopic data is proposed here. In recent work it was verified that the GSA method is a powerful tool for tuning potential energy surfaces of reactive and stable molecular systems. The procedure to obtain directly an analytic potential energy curve (PEC) of a particular electronic state of a diatomic molecule consists to perform a nonlinear least-squares fit by using the available experimental rovibrational spectroscopic constants. In such case, the objective function is obtained by using the χ2 error function constrained with the relative error between the experimental and theoretical values of spectroscopic constants. For each configuration, generated by the GSA, we use the method Dunham to calculate the rovibrational spectroscopic constants and only configurations that minimize both the fit of *ab initio* points and the relative error between the spectroscopic constants are accepted. We have tested this methodology for the *q*-Bond Order and *q*-Rydberg analytical functions, but it can be applied to other functions providing they are sufficiently flexible to fit the data. The results for H_2^+ and Li_2 diatomic molecules show that the present method provides an efficient way to build up diatomic potentials with spectroscopic accuracy.

Support: CAPES, CNPq, FINATEC.

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"Molecular modeling of Hemoglobin Coimbra : a human protein variant with high oxygen affinity"

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Key-words: structure variant hemoglobin, Hb Coimbra, homology modeling, high oxygen affinity.

Hemoglobin (Hb) Coimbra is a human hemoglobin variant characterized by β99 (Asp→Glu) substitution, which results in increased affinity for O_2 binding and low *heme-heme* cooperativity, followed by increased compensatory red blood cell production (polycythemia) for its carriers [1]. The residue involved in this replacement is located at the α1β2 interface, region affected by the greatest change along allosteric transition between deoxy (T) and oxy (R) configurations. The aim of this work was to solve the T and R structures of Hb Coimbra in order to identify the molecular mechanism involved on its high oxygen affinity. The structure of Hb Coimbra on T and R forms were determinate by homology modeling using native structures as templates (PDB ID: 2DN2 and 2DN1 – corresponding to T and R conformations, respectively), using Modeller and Procheck parameters [2,3]. Molecular dynamics simulation procedures, used with NAMD software, was applied for minimization and equilibration of the mutated structures for 50ps [4]. Experiments indicated that β99 (Asp→Glu) substitution promotes an approximation of the residues inside the α1β2 interface, mainly on R conformation, on which β-99Glu makes a new hydrogen bond with α-97Asn, that does not exist on the native Hb. This event can further help to stabilize the R conformation. We also calculated the differences on geometric parameters of β-99Glu on T and R state, demonstrating that Hb Coimbra has higher stability on the R conformation. The results we present here demonstrate that substitutions on α1β2 seem to be very critical, even on Hb Coimbra, which only differs from the native Hb because of a CH_2 insertion at the β99 residue (that comprehends on Asp→Glu substitution), conferring increased affinity for the oxygen.

Support: FAPESP, CNPq and Fundação Araucária.

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"Casein Kinase I as a target for drug design in Alzheimer's Disease"

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Key-words: Casein Kinase I, Alzheimer's Disease.

Alzheimer's disease (AD) is a progressive neurodegenerative disorder characterized by atrophy of cortex and loss of cortical and subcortical neurons. Recent data indicate the presence of *Casein Kinase* I (CKI) isoforms in vacuolar strands and granulomatous lesions in brains of patients with AD. CKI is an attractive therapeutic target since does not show the usual side effects that occurs in other proteins, whereas the inactivation of one protein triggers the inhibition of several essentials enzimes[1]. This protein encompasses a large family of monomeric serine/threonine protein kinases found in a variety of sub cellular locations[2]. The first tridimensional structure was solved by X-Ray Crystallography in 1995 (Figure 1A), and nowadays 8 structures are deposited in PDB (Figure 1B). In this work, a search was performed in the BindingDB[3] database for CKI inhibitors, and 12 compounds were thus retrieved.

Different pharmacophore models were then derived using the Sybyl 8.0/GALAHAD[4] and Discovery Studio[5] 2.5 software. Results were analyzed, and the best model obtained in consensus was used for pharmacophore-based virtual screening experiments, using the Discovery Studio package and the ChemBridge[6] and ZINC[7] databases. The best-ranked 100 compounds selected are being analyzed inside the CKI active site. In addition, another ligand-based drug design method has been employed, which is based on 2D-similarity of the 12 active compounds. Several novel compounds have been thus selected with significant Tanimoto index, which could be promising CKI inhibitor candidates for future Alzheimier´s disease treatment.

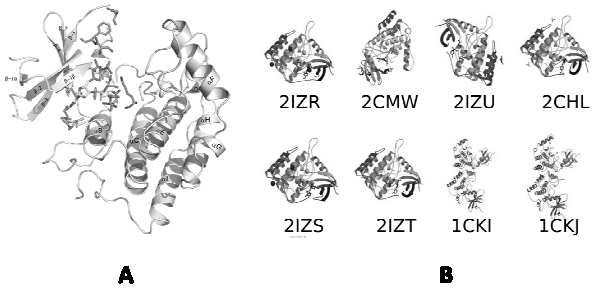

Figure 1. Crystall structure of Casein Kinase I **(A)** and structures deposited in PDB **(B).**

Support: FAPESP, CAPES.

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Ab initio and DFT studies of Dynamic Polarizabilites and Raman intensities of reference molecules: Calibration of polarized SBKJC and Stuttgart pseudo potential basis sets

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Key words: Polarizabilities, Raman, Ab inito, DFT, Sadlej,

Computational implementations for the calculation of molecular polarizabilities and Raman intensities are available using either ab initio or density functional theory (DFT). However, the computation of the mentioned molecular properties requires a large basis set with the inclusion of electronic correlation, to obtain results within experimental precision. This forbids the computations for medium size and large molecules. Our group has developed the polarized SBKJC and Stuttgart pseudo potential basis sets (ECP basis sets) to reduce the computational costs and resources. In this work, this new methodology was calibrated using a set of diatomic halogens and small polyatomic molecules using with the all-electron Sadlej basis set as reference at CCSD and DFT (*i.e PBE0, LB94 and CAM-B3LYP*) levels of theory, resulting. The new strategy is now being applied, at DFT levels (PBE0 and CAMB3LYP), for studying the Raman spectra of a series of organochlorinated pesticides (containing heavy atoms). Up to 50% time savings in the computations and huge amounts of computer resources where achieved without scarifying the theoretical level of the study.

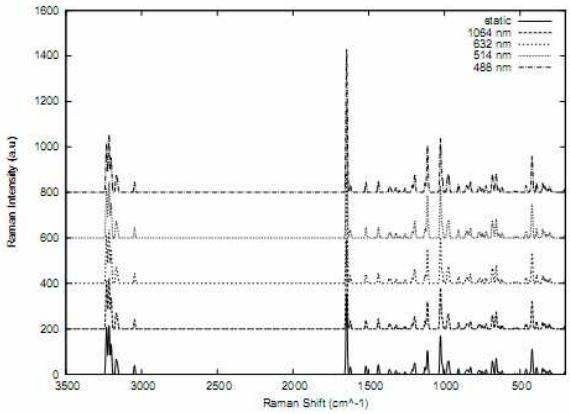

Fig: Raman spectra of DDT molecule computed at CAMB3LYP/pSBKJC level.

References: Vidal Ph.D thesis

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Estudo Computacional de Mecanismos de Reações Diels-Alder, Incluindo Efeito do Solvente

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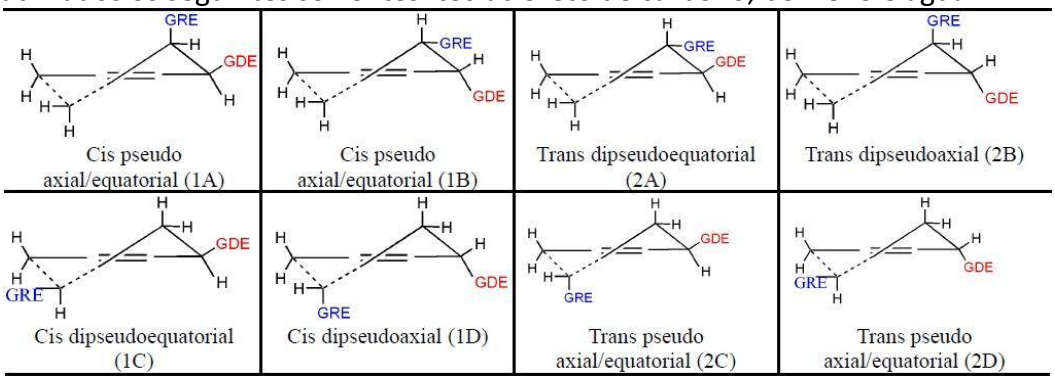
Universidade Federal da Paraíba, João Pessoa.

Palavras-chave: Orbitais de fronteira, Efeito solvente, Diels-Alder.

O objetivo deste trabalho é investigar o efeito do substituinte no mecanismo de reação de Diels-Alder envolvendo o 1,3 butadieno e etileno. Este tipo de reação é uma das mais versáteis em síntese orgânica pelo fator de ser bastante estereoseletiva, além de possibilitar a síntese de moléculas com estruturas complexas [1].

O mecanismo proposto para reações do tipo Diels-Alder é fundamentado nas interações dos orbitais de fronteira [2], de modo que a natureza do substituinte influencia nessas interações. Assim, pretende-se investigar o efeito de grupos doadores de elétrons (GDE) e retiradores de elétrons (GRE) na obtenção das energias de reação e de ativação. Além disso, também será investigado o efeito do solvente na obtenção dessas energias.

A partir da posição dos GRE e GDE é possível obter 08 conformações, mostrados na tabela abaixo. As geometrias dos reagentes, produtos e estado de transição (para o mecanismo concertado) foram otimizadas utilizando-se os métodos Hartree-Fock e DFT (B3LYP e PBE1PBE) com as bases 6-311^{++}G** e aug-cc-pvdz [3]. O efeito de solvente foi incluído no cálculo das energias através do modelo solvatação CPCM (Conductor-like Polarizable Continuum Model). Foram utilizados os seguintes solventes: tetracloreto de carbono, benzeno e água.



Resultados preliminares mostram que as conformações cis dipseudoequatorial (1C), Trans pseudo axial/equatorial (2D) e trans dipseudoequatorial (2A) apresentam as menores energias de Reação e Ativação. O solvente influencia na ordem para a energia de ativação, particularmente quando o solvente é a água.

Agradecimento: CNPq

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Conformational Analysis of Cyclic Phosphazene $N_3P_3(OC_6H_4COOH)_6$

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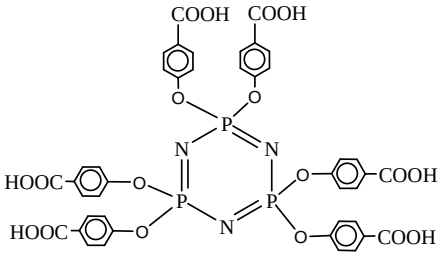
Keywords: cyclotriphosphazenes, ADF-ZORA.

Phosphazenes, particularly polyphosphazenes, have received considerable commercial interest because of their diverse range of interesting properties for potential use in materials science. Appropriately substituted polyphosphazenes have been employed as flame resistant materials, elastomers, membranes, solid ionic conductors, and inert biomaterials.[1] Cyclic or short-chain linear phosphazenes are valuable small molecule models for the polymeric systems, which are often difficult to characterize because of their high molecular weight and structural complexity. Of these model systems, the cyclotriphosphazenes, $[N_3P_3R_6]$, are the most prevalent. Here, we characterize the molecular structure and conformational properties of the cyclic phosphazene $N_3P_3(OC_6H_4COOH)_6$ (1) that has been synthesized by hydrolysis of the corresponding $N_3P_3(OC_6H_4COOCH_2CH_3)_6$.



(1)

All structural and electronic properties were obtained by using the Amsterdam Density Functional (ADF) code with the Zeroth Order Regular Approximation (ZORA).[2] Geometry optimizations were calculated by a standard Slater-type-orbital (STO) basis sets with triple-zeta quality double plus polarization functions (TZ2P) for all the atoms. In all cases frequencies analysis were performed after the geometry optimization, where we obtained only positive frequencies thus verifying local minima.

Due to the high number of bonds with free rotation and the steric hindrance between the OC_6H_4COOH **(2)** fragments, the calculated potential energy surface (PES) of this system is quite complex. Besides this complexity we obtained a global minima and a large number of local minima with quite close energies that reveal the conformational richness of this PES. The calculated local minima show that the most recurrent conformation between the (2) fragments are the T-shaped and π-stacked forms. Furthermore, a detailed study of the interactions in these fragments by decomposing the interaction energy into three physically meaningful components, namely, electrostatic energy, Pauli repulsion, and bonding orbital interactions, reveal, among others, that the electrostatic attraction between the stacked molecules is the most important component of the $\pi-\pi$ stacking interaction which determines the shape and depth of the PES.
It is important to elucidate the electronic structure and conformations of this trimer because is an important model for designing functionalized polymers with specific properties.

Support: Fondecyt 1095135 and 1110758, and PROJECT MILLENNIUM No. P07-006–F.

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Conformational Analysis of the fructose-6-phosphate ligand in GT04 enzymes for QM/MM and MD

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Key-words: UDP-GLcNAc, fructose-6-phosphate, Conformational analysis, QM/MM

Sucrose phosphate synthase (SPS) enzyme is a glycosyltransferase beloing to family 4 (GT04) that catalyze the synthesis of sucrose, which is a process restricted to plants, cyanobacteria and some proteobacteria. SPS catalyzes the first step in the synthesis of sucrose, where a glycosyl group is transferred from uridine diphosphate glucose (UDP-Glc) (sugar donor) to D-fructose-6-phosphate (F6P) (sugar receptor), the result is the formation of UDP and Sucrose-6-phosphate (S6P). Since this is a central regulatory process in the production of sucrose. This work presents, initially the study of Homology Modeling performed to create a three-dimensional model of the UDP-GlcNAc protein and the QM/MM dynamic simulations applied to describe the mobility and flexibility of these enzymes during of the time. the 3D structure of the enzyme was predicted by the theoretical study of the technique of homology modeling using as template a bacterial homologue of Halothermothrix orenii (SPS - PDB code: 2R66) belonging to family GT04 which is complexed with the substrate F6P. Model simulations were generated from molecular dynamics (MD) of hybrid quantum mechanics and molecular mechanics (QM/MM) to determine the interaction energy, and free energy of binding of complex UDP-GlcNAc/F6P. The semi-empirical AM1 Hamiltonian was employed to describe the QM part, while the rest of the system (protein plus and water molecules) was describe using the OPLS-AA and TIP3 force filed, respectively, as implemented in the *f*Dynamo library. The results of simulations reveals after 1.5 ns of computational simulation that the behavior in solution of the enzyme-substrate complex exhibited significant changes in its conformation as a consequence of the effect of the catalytic residue H151 near the glucosyl group, favoring a change in chair-boat conformation. Thus, the molecular dynamics simulation is adequate to describe the conformational changes of the chair-boat S6P ligand and the interactions of the complex enzyme-ligand.

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ENHANCED NONLINEARITES OF FUNCTIONALIZED SINGLE WALL CARBON NANOTUBES WITH DIETHYNYLSILANE OLIGOMERS

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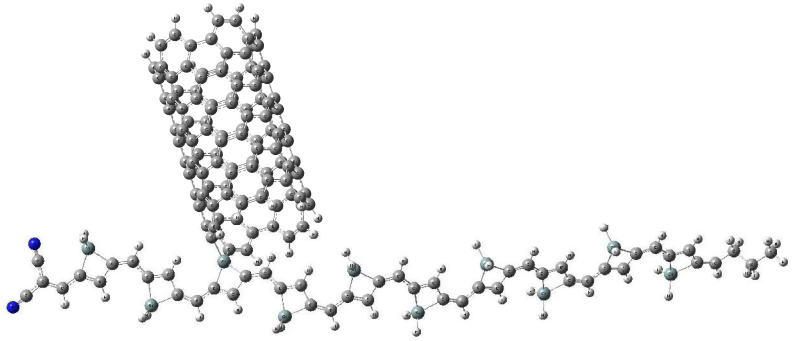
Key-words: Functionalized carbon nanotubes, First hyperpolarizability, DFT

Density Functional Theory (DFT) calculations of the static first hyperpolarizability (β) were performed for armchair (5,5) single wall carbon nanotubes(NTCs) functionalized with some diethynylsilane oligomers. The B3LYP hybrid functional with the 6-31G(d) split-valence polarized basis set were selected in this investigation. The derivatives were designed where an electron donor(*D)* or acceptor(*A)* group was attached to one end of the diethenylsilane decamer and introduced longitudinally on the NTC external surface by the other end. Other derivatives were also designed containing the *D* and *A* groups attached at both ends of the diethynylsilane oligomer that was introduced transversely to the nanotube external surface. The effect of the chemistry modification on the carbon nanotube structure in the magnitude of β was also investigated. Remarkable β values were obtained for all substituted NTCs, in special for ones di-substituted having the *D-A* pairs linked transversely to the nanotube. The largest static β value was predicted for the derivative containing the propyl(*D)* and dicyanovinyl(*A)* groups ($\boldsymbol{\beta}_{mol}$ = 21991 10^{-30}cm^{5}esu^{-1}). Furthermore, all chemically modified carbon nanotubes present very large values of the polarizability. Also, these potential hybrid materials show very small Homo-Lumo energy gap. Our results showed that the model systems of the carbon nanotubes containing Si might be promising applications in opto-electronics and photonics, since that the nanocomposites designed show extraordinary electric properties.



$\boldsymbol{\varepsilon}_{H-L}$= 0.59 eV; $\boldsymbol{\mu}$ = 5.74 Debye; $\boldsymbol{\alpha}_{av}$ = 6597 10^{-25} cm^3; $\mathbf{B}_{vec}$ = -18118 10^{-30} cm^5 esu^{-1}

Figure1. Derivative of carbon nanotube with the largest value **β** value.

Support: FAPEMIG.

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Insights into Ionization States of the Catalytic Residues in HIV-1 Protease by Hybrid QM/MM Molecular Dynamics Simulations

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Key-words: HIV-1 protease protonation, enzyme catalysis, active site reaction.

The HIV protease (HIV-PR) is an enzyme whose catalytic residue consists of two aspartate side chains (Asp25/Asp25'). This protein is a relevant therapeutic target for antiretroviral (ARV) treatment against AIDS. Several works suggest a monoprotonation states for the aspartate residues in the active site of HIV-PR, with one of the residues charged and the other neutral or both sharing a proton. However, there are experimental evidences that HIV-PR could be found in this protonation state but also in other two different states. In the present work we used the combined method of quantum-mechanics and molecular-mechanics simulations (QM/MM) to investigate the functional role of protonation in HIV-PR protease complexed with a substrate. We investigated three different protonation states for the two aspartate catalytic residues (monoprotonation, diprotonation and deprotonation) and analyzed the binding of Gag peptide substrate p2/NC (sequence of amino acid residues SATIM/MQRGN) to the enzyme in these three different states. Our results demonstrate that the non protonation of both aspartic acids catalytic has a strong influence on the dynamic behavior of the HIV-PR flap, making ease its opening with the greater amplitude. Besides, this work showed that the monoprotonation in one of the Asp25 residues results in the strongest interaction between these catalytic residues by sharing the proton. This indicates that protonation of Asp25/Asp25' has effect not only on binding of ligand but also in the flap opening. We expect that these findings will contribute to understand the role of the state of protonation in the catalytic action of HIV-PR.

Supports: CNPQ, FAPERJ e CAPES.

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Theoretical study of $B_XC_YN_Z$ nanotubes: geometry and electronic properties

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Key-words: nanotubes, BN-pair, electronic properties

Since the discovery of boron carbonitride nanotubes ($B_XC_YN_Z$) in 1994 [1], various theoretical and experimental studies of B-C-N ternary material have been reported. Theoretical studies have revealed that the electronic properties of $B_XC_YN_Z$ nanotubes can be adjusted simply by changing their atomic compositions and configurations [2-5]. This feature gives $B_XC_YN_Z$ nanotubes different possibilities for technological applications that carbon and BN nanotubes cannot provide.

In the present work we report a theoretical study of the atomic arrangements on boron carbonitride nanotubes ($B_XC_YN_Z$) with diameter from 4 to 16 Å (Fig. 1). We analyze the role played by nitrogen and boron doping in the structural stabilization of these molecular systems. Stabilization of geometry and energy of carbon and boron carbonitride nanotubes was investigated through semi-empirical quantum chemical method Austin Method 1 (AM1). The advantages of semiempirical calculations are that they are much faster than *ab initio* calculations, and can be used for large organic molecules. Some atomic arrangements and chemical compositions (BCN, $B_3C_2N_3$, and BC_2N) of B-C-N tubular structures proposed in the literature were analyzed. Our results show that the energy associated with boron and nitrogen incorporation depends strongly upon the tube diameter and atomic B-C-N distribution on tubular structures (Fig. 2). Changes in the electronic structure due boron-nitrogen incorporation were also analyzed. Electronic structure of the optimized molecules was obtained through Hartree-Fock theory adopting CEP-4G basis set.

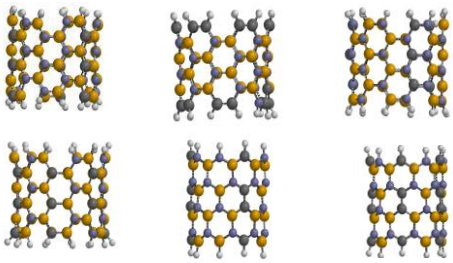

Figure 1: Model molecules. In this ball-tube scheme, yellow balls represents boron atoms, grey balls are carbon, blue balls are nitrogen, and white balls are hydrogen atoms.

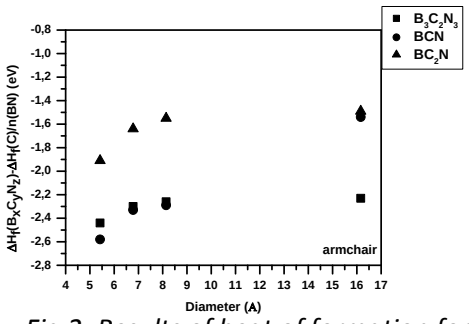

Fig 2: Results of heat of formation for $B_XC_YN_Z$ armchair nanotubes with different diameters.

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Support: CAPES.

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Charge density analysis of energetic molecules: FOX-7 and Nitroguanidine

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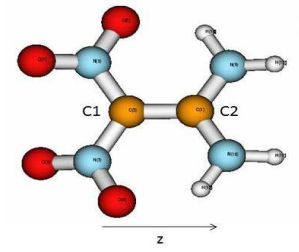
Key-words: Partition of the molecular charge density, energetic materials

Energetic materials – explosives and propellants - include different classes of chemical compounds or mixtures which have important military and civilian applications. These materials can quickly release energy through large quantities of gas and heat. Important properties include the amount of energy released and impact sensitivity; the ultimate goal would be to combine maximum performance with minimum sensitivity. Development of accurate theoretical models for current and future materials is especially important, and safety reasons can be an issue. In this work, we used two different methods to decompose the molecular charge density charge, thus the electron density, of nitroguanidine (NQ), the recently discovered 1,1-diamino-2,2-dinitroethylene (FOX-7) and several derivatives. The purpose was to study in details their molecular properties and relate them to the macroscopic properties of the corresponding materials. The B3LYP/aug-cc-pVTZ method was used to compute the charge densities and to optimize the geometries. The computed B3LYP charge density was decomposed using two methods: the distributed multipole analysis (DMA) and the deformed atoms in molecules (DAM). The effect of systematically adding explosive groups to the molecular framework of both systems was thoroughly investigated. In order to illustrate the results, the table compares the carbon DMA multipole values of FOX-7 and ethylene. It is clearly seen the effect of including the explosive electron-withdrawing NO_2 groups: the carbon C1 charge values become positive, both C1 and C2 dipole values (i.e, the site polarization) increase considerably, with the C1 dipole vector inverting its direction. The quadrupole value of the C2 carbon decreases, thereby indicating the reduction of the C2 delocalized electrons. Similar analysis of other derivatives will be presented.



Multipoles centered on the carbon atoms	
Ethylene	FOX -7
Monopoles (e)	
(C1) - 0,1284	0,0428
(C2) - 0,1284	0,1503
Dipoles (ea_0)	
(C1) 0,0052 (z)	0,0992 (-z)
(C2) 0,0052 (-z)	0,0280 (-z)
Quadrupoles (ea_0^2)	
(C1) 1,228	1,289
(C2) 1,228	0,846

Support: CNPq, FAPERJ, BRAZILIAN ARMY, CAPES.

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Computational Study of Triazoles-based Ligands and their Copper(II) Complexes

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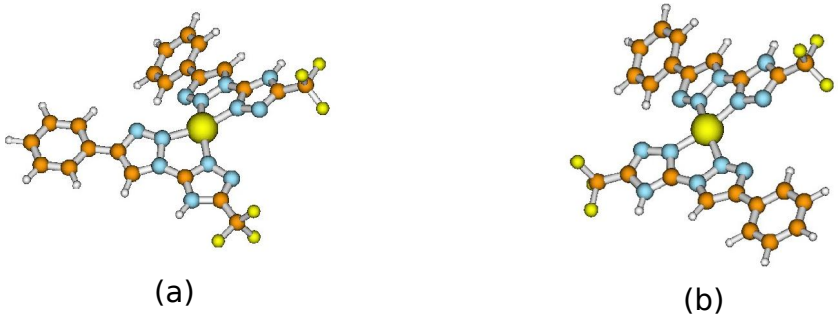
Key-words: triazoles, copper(II) complexes, DFT, LMOEDA.

Triazolic compounds have been reported in the literature as being important biological agents, acting as bactericide, fungicide and potential drug for treatment of cancer [1]. The N-donor triazole rings allows the ligands to coordinate with transition metals such copper or zinc, making them able to form complexes, which present enhanced biological activity in comparison with the isolated ligands [2].

The aim of this work is to investigate the electronic structure of a set of ligands that contain the group 1,2,3- or 1,2,4-triazole as well as their correspondent mono and binuclear complexes with copper(II), including a complete study about the nature of metal-ligand chemical bonding, described in terms of energy decomposition analysis, LMO-EDA, and topological theories (QTAIM and ELF).

Geometry optimizations, and Hessian matrix values for structures of the isolated ligands and complexes were performed at BP86/TZVPP and TPSS/TZVP levels, respectively. All calculations were performed by employing ORCA 2.8 and Gaussian03 packages. The preliminary results indicate the presence of different isomers (Figure 1) with small differences of electronic energy, around 2.0 kcal.mol^{-1}, but with distinct electronic properties as indicated by ELF and QTAIM results.



(a) (b)

Figure 1. Isomers (a) and (b) of mononuclear copper(II) complexes containing fluorinated triazole ligand.

1 - Bagihalli, G.B.; Patil, S.A. J. Coord. Chem. **2009**, *62*, 1690.
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Support: FAPESC (Proc. 17.413/2009-0),CNPq, Capes and UFSC.

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"Theoretical study of conformational equilibrium of calyx[5]arenes"

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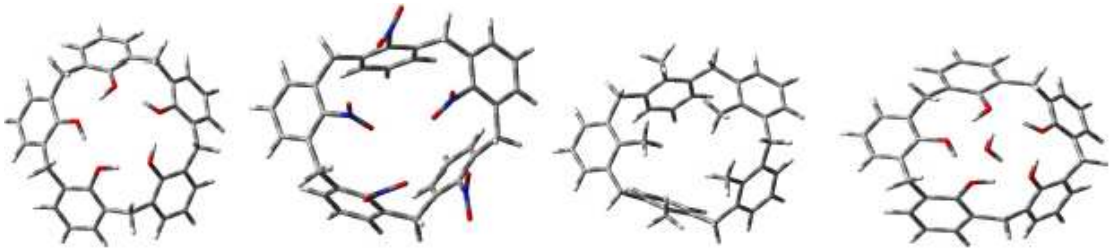
Key-words: solvent effect, conformational equilibrium.

Calixarenes are interesting systems due to the technological and biological aspects. These molecules also have conformational mobility and this equilibrium is strongly affected by intramolecular interactions such as hydrogen bonds and also by the solvent effect. Thus, the most stable calix[5]arene conformer has a cone shape with a hydrogen bond belt formed by hydroxyls groups into one of its cavities. We studied some calix[5]arene with substituents at the hydroxyl position which are not hydrogen bonded. The minima structures and its related transition states were studied at B3LYP/6-31G(d,p) level. The most stable conformer in gas phase is the hydroxyl cone form. When OH groups are replaced by CH_3 and NO_2 the most stable structure is no longer a cone shape (Figure 1). So, the stability of the cone structure is favored by the hydrogen bond between the hydroxyl groups. In order to investigate the intermolecular interactions effects, we are also carrying out calculations including explicit solvent (microsolvation) as a supermolecular approach, aiming to understand the distribution of solvent molecules and the types of interactions through the calixarenes cavities. All calculations are performed using the Gaussian09 program.



(a) (b) (c) (d)

Figure 1: B3LYP/6-31G(d,p) fully optimized structures of the lowest energy structure of Calix[5]arenes (a) with NO_2 and CH_3 structural modifications (b,c) and also calyx[5]arene with one water in the cavity (d)

Reference: Böhmer, Volker; Angew. Chem. Int. Ed. Engl. (1995), 34, 713-745.

Support: CNPq

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Efeito da substituição de átomos de H por F nas propriedades iônicas da N,N-dimetil-nitrosamina

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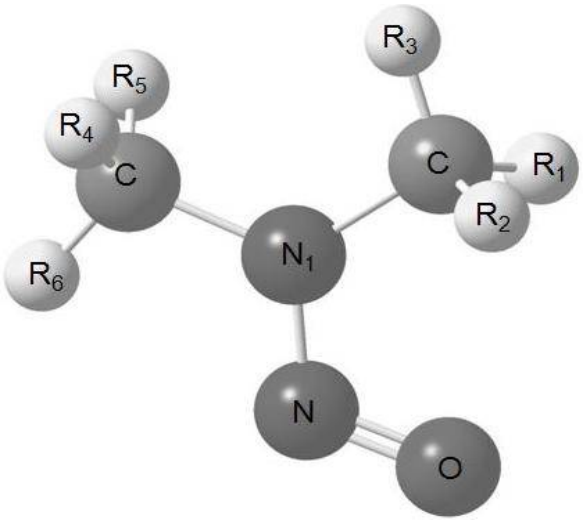
Palavras-chave: Nitrosaminas, Momento de Dipolo, Polarizabilidade.

Um dos mecanismos de ação carcinogênica da nitrosamina envolve a interação direta da nitrosamina com o Fe(III) do grupo Heme[1]. G. B. Addo *et. al.* demonstraram experimentalmente que esta interação se dá através do átomo de O da nitrosamina[1,2]. A planaridade do esqueleto CCNNO (ver figura), juntamente com os resultados das frequências ν_{NO} e ν_{NN}, sugerem uma contribuição razoável de uma estrutura de ressonância dipolar na interação nitrosamina-Fe(III)[2]. Logo, esta interação deve envolver um caráter iônico considerável, daí a nossa motivação em investigar as características iônicas destes ligantes, a saber, o momento de dipolo e a polarizabilidade. Para tal aplicamos um planejamento fatorial (2^6), com a finalidade de entendermos a influência dos substituintes (H ou F) nestas propriedades. Foram realizados cálculos de otimização e frequência de todas as 64 estruturas no *Gaussian09* empregando os métodos DFT/B3LYP e MP2, ambos com a base cc-pVTZ. Os resultados mostraram uma faixa de valores para o momento de dipolo entre ~0,4 D (R_3 = R_4 = R_5 = F) e ~5,08 D (R_1 =R_2 = F), com o método MP2. A substituição do Hidrogênio por Flúor apenas na posição R_3 apresenta o maior efeito (em relação à média) quanto à diminuição do momento de Dipolo (quando comparado à molécula sem átomos de F). A substituição de 2 hidrogênios (R_1 e R_2) provoca o maior aumento no Momento de Dipolo ~0,8 D em relação a nitrosamina não substituída. Algumas substituições levam a uma grande alteração estrutural, com perda da planaridade entre os átomos CCNNO. A polarizabilidade sofre pouquíssima alteração com a substituição.



Apoio: CNPq.

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Cryptolepine and cryptolepine derivatives into stacked DNA base pairs: results from DFT/DCACP and empirical methodologies

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Key-words: Cryptolepine, antimalarial drugs, DFT, DCACP, DNA.

Cryptolepine is an antimalarial agent who also has an excellent cytotoxic activity in B16 melanoma cells. Recent studies show that Cryptolepine interact strongly with non-alternating CG sequences of DNA and behaves as a typical intercalator agent. In this work, we investigate these interactions at the molecular level Density Functional Theory (DFT) calculations using the BLYP functional augmented with dispersion corrected atom-centered potentials (DCACP) for the description of dispersion interactions. Results for DNA inter-base distances and DNA twist angle obtained using a model complex are in good agreement with relevant parameters obtained from the crystallographic structure (PDB: 1K9G). Calculations revealed a strong interaction energy between cryptolepine and CG base pairs of about -38.4 kcal/mol obtained by DFT augmented with DCACP corrections. Several alternate binding modes for criptolepin were considered, but none has managed to produce a binding energy greater then the configuration present in the crystal.
Preliminary results for cripetolepine derivatives, in particular 2,7-dibromocryptolepine and 7-bromo-2-clorocryptolepine, will be presented and discussed. A brief comparison with results obtained using empirical Hamiltonians (GAFF/AMBER94, OPLSAA) will also be presented.

Acknowledgements: UFABC, CAPES, FAPESP.

Comparação da estabilidade relativa de radicais primários e secundários centrados em átomos de carbono e oxigênio saturados

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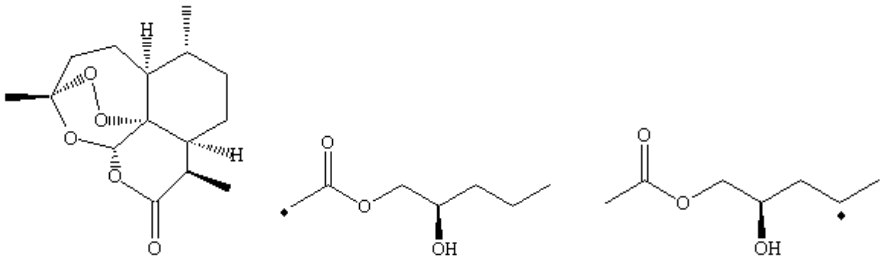
Palavras-Chave: Artemisinina, DFT, malária, estabilidade de radicais.

A malária é uma doença infecciosa parasitária que afeta milhões de pessoas no mundo resultando em um grande número de mortes. A artemisinina (figura 1a), usada no tratamento da malária, é uma lactona sesquiterpênica que apresenta uma ligação endoperóxido, considerada essencial para a atividade antimalárica desse composto. Há indícios de que o mecanismo de ação da artemisinna se inicia com a quebra da ligação peróxido pelo íon Fe(II) do heme, resultando na formação de intermediários radicalares centrados em átomos de oxigênio e de carbono. Essas espécies são consideradas as responsáveis pela inativação do parasita, por processos que envolvem a alquilação do heme ou de alguma proteína específica do parasita. Trabalhos anteriores indicaram que radicais primários e secundários na artemisinina possuem estabilidades similares. O objetivo deste projeto foi estudar a estabilidade relativa de radicais centrados em átomos de oxigênio e carbono de um conjunto de moléculas constituído por 25 compostos saturados, usando o metodo DFT, o funcional B3LYP e o conjunto base 6-31g(d). Os resultados mostram que em cadeias alifáticas, sem heteroátomos, os radicais centrados em carbonos secundários sempre são mais estáveis do que os centrados em carbonos primários. O mesmo ocorre com a substituição de um carbono dessa cadeia por um oxigênio. Entretanto, em alguns compostos, por exemplo o radical N (figura 1b), um radical centrado em carbono primário é 0,40 kcal/mol mais estável do que o radical M (figura 1c), um radical centrado em carbono secundário. Isso indica que alguns radicais considerados menos prováveis possuem estabilidade termodinâmica e viabilidade cinética que permitem sua existência.



(a) **(b)** **(c)**

Figura 1: (a) Artemisinina (b) Radical N (c) Radical M

Suporte: CNPq, FAPERJ

Simulation of EuTc Complex: Absorption Spectrum

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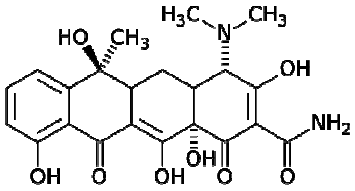
Key-words: Tetracycline, Europium, Absorption Spectrum



Tetracycline (Tc), $C_{22}H_{24}N_2O_8$, is an antibiotic largely used to treat several infections. When Tc is associated to a trivalent lanthanide ion, Eu^{3+}, changes in the absorption and emission spectra arise, showing the antenna effect: Tc transfers the absorbed energy to Eu ion, increasing the emission intensity. The experimental absorption (emission) transition of Tc is seen at 370 nm (510 nm) with the intensity of 1.24 (1.00) and changes to 395 nm (615 nm) with the new intensity of 1.60 (5.63) when Eu is coupled [**1**]. The absorption of Tc in water has been studied using semi-empirical and *ab-initio* methods, after molecular simulation with Lennard-Jones plus Coulomb potential using the Monte Carlo-Metropolis method. For Tc in water, it has been obtained the absorption maximum at 309 nm with semi-empirical ZINDO and 351 nm with TDDFT B3LYP using the Pople basis set. In all of these case have been used one Tc molecule, 9 waters molecules and a large number of point charges to represent the other water molecules of the system. With the polarizable continuum model (PCM) to represent the solvent environment, the absorption maximum is obtained at 347 nm. The calculations for the absorption spectrum of the complex EuTc are being conducted.

[**1**] Courrol, L.C.; Samad, R.E. *Current Pharmaceutical Analysis*, **4**, 238 (2008).

Support: CNPq, CAPES, FAPESP, INCT-FCx and nBioNet

Application of Quantum Chemical Methods for a Series of CB_2 Ligands

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Key-words: Cannabinoids, CB_2 Receptor, Chemoinformatics.

4-oxo-1,4-dihydroquinoline-3-carboxamide is derived from a novel class of selective endogenous agonist, which interacts with the CB_2 cannabinoid receptor and is involved in inflammation, AIDS, cancer and obesity. Thus, the main objective of this work is characterizing the electronic structure of bioactive molecules that inhibit the CB_2 cannabinoid receptor[1]. The structure of the studied molecules, as well as maps of the frontier orbitals are shown in Figure 1. The geometry optimization and calculation of electronic properties (Table 1) were performed using Density Functional Theory (DFT), with B3LYP functional and 6-31G* basis set, implemented in the Gaussian 09 computational package.

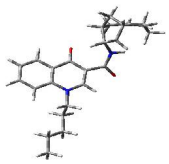
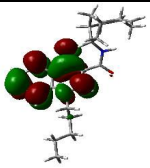
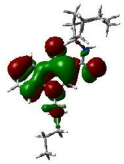
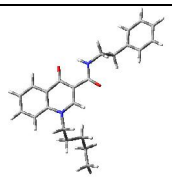
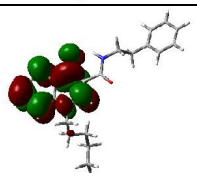
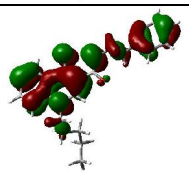
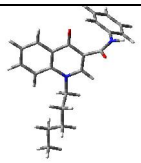
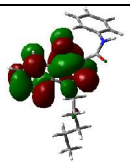
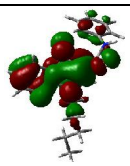
Molecule	2D Structure	LUMO	HOMO
1			
2			
3			

Figure 1. Molecular structure and frontier orbital maps of the studied molecules.

Table 1. Calculated properties

Molecule	K_i (nM)[1]	E_T (a.u.)	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	μ (Debye)
1	13.4	-1230.7109	-0.1663	-0.0500	6.922
2	201	-1152.0540	-0.2139	-0.0454	6.104
3	1000	-1072.9477	-0.1683	-0.0771	7.492

According to Figure 1 and Table 1, we can observe that: *(i)* the total energy of the studied molecules varies significantly; *(ii)* the less potent molecule (3) has a low value of the energy of LUMO, indicating that this one has a more pronounced electron-accepting character; *(iii)* the dipole moment of all molecules is similar. Therefore, the study of electronic structure has great importance to understand the processes that influence the interaction between these molecules and the CB_2 receptor.

Support: Pró-Reitoria de Graduação-USP, FAPESP, CNPq, CAPES.

[1] Stern, E.; Muccioli, G. G.; Millet, R.; Goossens, J.-F.;Farce, A.; Chavatte, P.; Poupaert, J. H.; Lambert, D. M.; Depreux, P.; Hénichart, J.-P.; *J. Med. Chem.*; **2006**, *49*, 70-79.

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Influence of Intramolecular Hydrogen Bonds CH---O and OH---O in Conformational Equilibrium of 5-hydroxy-2-phenyl-1,3-dioxane

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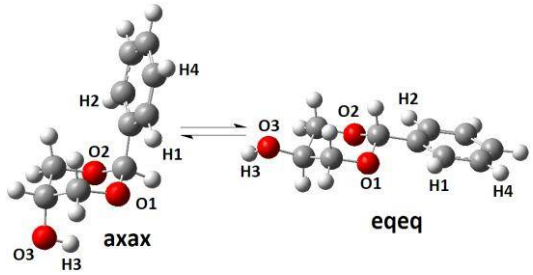
Key-words: Theoretical calculations, Hydrogen bond, Conformational analysis.

Some work on the *cis* isomer of 3-X-cyclohexanols (X=Cl, Br, I, CH_3) and 3-X-1-methoxycyclohexanes (X=F, Cl, Br, I, CH_3) has shown that their conformational equilibra is neither controlled by conformer dipole moments nor by solvent polarity [1], but mostly by the classical syn-1,3-diaxial steric effects. Recently, the occurrence of an intramolecular hydrogen bonds (IHB) in *cis*-3-methoxy-, *cis*-3-ethoxy- and *cis*-3-*N*,*N*-dimethylaminocyclohexanols [2-4], stabilizing the diaxial conformer and suppressing the 1,3-diaxial steric interactions, has been reported. The present work describe how two IHB (HO---H and CH---O) influence in the conformational equilibrium of *trans*-5-hydroxy-2-phenyl-1,3-dioxane (*trans*-HPD) through theoretical calculations. Figure shows the conformational equilibrium of *trans*-HPD. The nine possible rotamers for the diaxial conformation (axax) and diequatorial (eqeq) were optimized with the B3LYP/6-311++g(d,p) using the Gaussian03 software. The energy difference between the more stable rotamer axax and eqeq indicated that the conformation eqeq is 0.45 kcal mol^{-1} more stable than axax. The substitution of hydrogen H4 by NO_2, CHO, CF_3, F, Cl, OH, H, CH_3, NH_2, $N(CH_3)_2$ showed that the energy difference between eqeq and axax conformer decreased 1.33, 1.27, 0.95, 0.75, 0.70, 0.48, 0.45, 0.37, 0.15 and 0.05 kcal mol^{-1} respectively. These results indicate that the effect of these substituent influences directly the strength of IHB C-H1---O1 and C-H2---O2 in both conformations. As the protons H1 and H2 are closer to the oxygen O1 and O2, respectively for eqeq conformation (approximately 2.42 Å) than in axax conformation (approximately 2.53 Å), this conformation suffers more the influence of different substituent in the aromatic ring. As the changes of withdrawing substituent by an electron donor weaker IHB CH---O in both conformations and IHB O3-H3---O1 or O3-H3---O2, which exists only in axax conformer, becomes more important the energy difference between conformers decreases.



Support: CAPES, UTFPR and CENAPAD-SP.

[1] P.R. Oliveira, R. Rittner, J. Mol. Struct. 743 (2005) 69. [2] P.R. Oliveira, R. Rittner, Spectrochim. Acta A 61 (2005) 1737. [3] P.R. Oliveira, D. S. Ortiz, R. Rittner, J. Mol. Struct. 788 (2006) 16. [4] P.R. Oliveira, D.S. Ribeiro, R. Rittner, J. Phys. Org. Chem. 18 (2005) 513.

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A New Coarse-Grained Force Field for Carbohydrates

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Keywords: Parameter set, GROMOS, molecular simulations

Carbohydrates are one of most abundant biochemical products in nature. They are found in living organism serving as structural components, chemical recognition flags and fuel. In addition, carbohydrates and their derivatives constitute major raw materials for many industrial sectors, such as bioethanol production, cosmetic, health and food industry where it has a wide variety of applications from bone implants, to diet formulas to first aid bandages, to name a few.

In nature, carbohydrates are typically found in polymeric forms and/or complexed with other of biomolecules (e.g., proteins, lipids, components of external cell wall membranes, etc). Theoretical description of the behavior of these large biomolecular systems requires simulations of relatively long time scales and demands consequently computational resources. One way to decrease the computational requirements is to use coarse-grained force fields. In this approach, groups of atoms are mapped into beads decreasing the total number of particles in a system at the expense of some chemical detail.

There are currently two coarse-grained force fields for carbohydrates, M3B (based on UFF) and MARTINI. A hexopyranose unit, in both, is comprised of a three-bead model and neglect electrostatic interactions. In this work, we have developed a new GROMOS-based coarse-grained parameter set for carbohydrates that is based on a four-bead model to describe a monosaccharide. Partial charges have been assigned to the different beads in order to take into account electrostatic interactions. The force field correctly describes ring puckering and the electrostatic potential of the atomic glucose ring. Cellulose, amylose, chitin and chitosan are used as validation benchmarks.

Support: CNPq, CAPES, FACEPE and INAMI.

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"Quantum Langevin dynamics study of the thermal transport in conjugated polymers"

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Key-words: Quantum Langevin Dynamics, Dissipation Constant, Conjugated Polymers.

The great potential of conjugated polymers in the development of new technologies for optoelectronic devices has recently received a lot of attention. A significant challenge of these materials science is the thermal transport characterization. The polyacetylene is a classical example where each carbon is bonded to only two neighboring carbons and one hydrogen atom forming a one dimensional harmonic chain. In this systems the temperature can be simulated using an infinite number of oscillators as a thermal bath, i. e., a harmonic chain connected to self-consistent Ohmic heat reservoirs with coupling strength controlled by a dissipation constant. Understanding the effects of this dissipation constant in thermalized molecules is of fundamental for the science and technology of conjugated polymers. In this work we performed numerical simulations to investigate the effects of the dissipation constant in cis-polyacetylene chains. Using an extended version of the Su-Schrieffer-Heeger (SSH) model to include external electric fields and thermal effects, we demonstrate the crossover from ballistic to diffusive thermal transport in these material through an exact analysis using quantum Langevin dynamics.

Support: CAPES, CNPq and FINATEC.

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"Singlet and Triplet Excitons Random-Walk Dynamics in Conjugated Polymers"

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Key-words: Excitons Dynamics, Thermal Effects, Conjugated Polymers.

The exciton randon-walk dynamics in conjugated polymers strongly impacts the efficiency of energy harvesting organic optoelectronics devices. From a technological point of view, the applications of conjugated polymers in organic photovoltaics OPVs and light emitting diodes OLEDs depends critically on the formation, transport, recombination, and separation of excitons under thermal effects. In OLEDs, the injection of charges in the organic material leads to the formation of triplet and singlet excitons, which are then harvested to produce light. Thus, for a substantial progress in these device construction, it is crucial understanding the basic processes involving the exciton dynamics in thermalized molecules. However, such studies remains elusive due to the immense complexities of the systems involved. In this work we performed numerical simulations to investigate the random-walk dynamics of siglet and triplet excitons in a polyacetylene chain. Using an extended version of the Su-Schrieffer-Heeger (SSH) model to include external electric fields and temperature, we show that the excitons random-walk dynamics is related upon the size of the conjugated polymer system as suggested experimentally.

Support: CAPES, CNPq and FINATEC.

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"Diffusion Length of Triplet Excitons in Conjugated Polymers"

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Key-words: Excitons Diffusion, Molecules Envelopment,Thermal Effects, Conjugated Polymers.

The great potential of conjugated polymers in the development of new technologies for optoelectronic devices has recently received a lot of attention. The triplet exciton diffusion length and the molecules envelopment in conjugated polymers strongly impacts the efficiency of energy harvesting organic optoelectronics devices. For successful applications in these material science is fundamental understanding the processes as formation, diffusion length, recombination, and separation of excitons in thermalized molecules. The applications of conjugated polymers in organic photovoltaics OPVs and light emitting diodes OLEDs depends critically of the exciton diffusion length and the molecules envelopment. However, such studies remains poorly described due to the immense complexities of the systems involved. In this work we performed numerical simulations to investigate the triplet exciton diffusion length and the molecules envelopment of two polyacetylene chains. Using an extended version of the Su-Schrieffer-Heeger (SSH) model to include external electric fields and temperature, we show that the diffusion length of triplet excitons is in the few micrometers range and depends upon the size of the conjugated polymer system as suggested experimentally.

Support: CAPES, CNPq and FINATEC.

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Molecular modeling of bioactive neuropeptides, substrates of Angiotensin-converting enzyme

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Key-words: neurotensin, substance P, angiotensin-(1-7), Monte Carlo, conformational analysis, molecular dynamics, Angiotensin-Converting Enzyme I

Angiotensin-I converting enzyme (ACE-I) is important in regulation of cardiovascular functions. In addition to Angiotensin I, ACE is able to cleave several other peptides, such as neurotensin (NT), substance P (SP) and Angiotensin-(1-7) – Ang-(1-7). It was proposed to investigate molecular characteristics of these bioactive peptides for similarities that could mean a molecular recognizing pattern for ACE-I.

Minimum energy conformations were obtained from conformational analysis using MCMM/LLMOD method and OPLS_2005 force field in Macromodel 9.6 software. Ang-(1-7) NMR data were compared with modeled Ang-(1-7) in order to validate these methodology. RM1 Semiempirical and DFT calculations on the selected conformers were performed in order to evaluate electronic structure details. Furthermore, molecular dynamics (MD) simulations in pure water and in 0,15M NaCl solution were performed to access the dynamical behavior of Ang-(1-7) under these conditions.

Backbones' folding pattern was very similar, significatively sustained by non-covalent interactions; conformational freedom was manifested at the side chains. This freedom, however, was mainly observed in amino acids far away from cleavage site; conformers showed conservation at P1-P1'. HOMO and LUMO showed no pattern between the three analyzed peptides. However, HOMO's positions on most peptides were on the carboxi-terminal group, but in other hand, the NT-(8-13) HOMO´s is located at the cleavage site.

Analysis of the MD trajectories, in both pure water and NaCl solutions, display relatively small deviation of Ang-(1-7) from NMR experimental structure with similar structural fluctuation amplitudes. However, computation of appropriate structural time correlation function reveals that the peptide has faster relaxation in saline system than in pure water, probably because ions destabilize intramolecular hydrogen bonds, improving molecule's plasticity. We may speculate that this observation is related to the greater cleavage activity of Ang-(1-7) by ACE-I under saline conditions.

Support: FAPEMIG/FUNEPU.

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"Quantum mechanics study of tyramine electropolymerization and molecular modeling of polytyramine"

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Key-words: polytyramine, electropolymerization mechanism, DFT, Monte Carlo, conformational search, biosensor.

Tyramine polymers can change its state of protonation conveniently at the flexible ethylamine and have been used to immobilize biomolecules in biosensors. This work reports the electropolymerization mechanism study in a wide pH range, as well as a conformational analysis, both aiming polymer features characterization.

Quantum-mechanical calculations of tyramine and its intermediates of electropolymerization of a wide pH range, were performed based on B3LYP/6-311G(2d,p) theory level, using the program Gaussian03. Theoretical models of oligomers were submitted to Monte Carlo conformational searches, under OPLS_2005 force field, using MacroModel package. The energy diagram below **(1)** shows the reactivity trends.

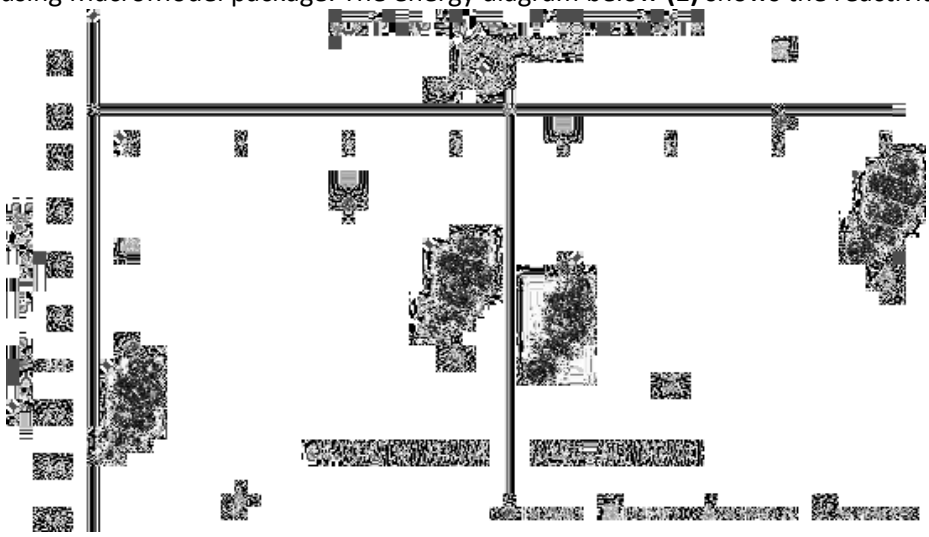

Figure 1. Energy diagram of Frontier Molecular Orbitals: (1)Protonated, (2) Protonated Radical, (3) Bipolar (4) Bipolar Radical, (5) Neutral, (6) Cation Radical, (7) Phenoxide, (8) Phenoxide Radical

In acidic medium, the smallest energy difference was found between the HOMO of the protonated form and SOMO α of the bipolar radical, whereas in basic medium, it was found between the HOMO of the neutral form and SOMO β of the phenoxide radical. CHELPG populational analysis shows more positive values for ortho carbons (related to hydroxyl group), which can indicate advantage in starting a radical chain reaction from them. Furthermore, changes on the hydroxyl bond orders were observed when an electron is removed. The ether-aromatic skeleton of the structures present a spiral behavior, that supports wide distribution of side chains and corroborate to prove the film properties.

Support: FAPEMIG.

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Hansch Analysis of N-Oxide Quinolinyl Chalcones

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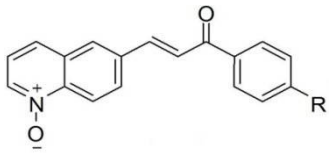
Key-words: QSAR, Chalcones, *Artemia salina*.

Chalcones are an important family of natural compounds, which were tested (LC) against *Artemia salina.* These bioassays are related with cytotoxicity and other biological properties.

Figure 1. N-Oxide Quinolinyl Chalcone Derivatives



Initially, Artemia salina activities were correlated with the following descriptors SFLogP, cLogP, π, σ_p, F, R, ε_{HOMO}, ε_{LUMO}, GAP and LogMW, employing both Quinolinyl and N-Oxide Quinolinyl Chalcones, as a training set, and a low correlation was obtained. A similar analysis was performed using the two families of chalcones separately, and the best correlations were obtained for N-Oxide Quinolinyl Chalcones against F, εHOMO and GAP descriptors. The correlations were evaluated by statistical parameters such as n, r, s, F (Fisher), Q^2, and S-PRESS. QSAR equations (1-3), which consider five different substituents (H, Me, F, Cl and Br) at the position R:

$$\log\left[1/LC50\,(A.\,Salina)\right] = -0.841(\pm 0.98)\epsilon_{HOMO} - 6.866(\pm 5.60)(without\ fluorine)$$
$$(n=4;\ r=0.934;\ s=0.061;\ F=13.717;\ Q^2=-2.053;\ s-PRESS=0.300) \quad (1)$$

$$\log\left[1/LC50\,(A.\,Salina)\right] = -2.268(\pm 1.86)GAP + 5.438(\pm 6.16)(without\ fluorine)$$
$$(n=4;\ r=0.965;\ s=0.045;\ F=27.371;\ Q^2=0.707;\ s-PRESS=0.093) \quad (2)$$

$$\log\left[1/LC50\,(A.\,Salina)\right] = +0.400(\pm 0.098)F - 2.151(\pm 0.048)$$
$$(n=5;\ r=0.991;\ s=0.023;\ F=169.502;\ Q^2=0.942;\ s-PRESS=0.041) \quad (3)$$

The results show that the biding site probably is an electron acceptor and is related with inductive effect (F). Fluorine derivative is found as an outlier due to high biological activity [2], suggesting that additional pKa studies are necessary in order to correlate *Artemia salina* biochemical structure and its biding site.

[1] http://www.kubinyi.de
[2] Jean-Pierre Begue; Fluorine and Health; 2008; 553-622.

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An ab-initio Study of Nucleotide bases and $[Mg(H_2O)_5]^{2+}$ complexes

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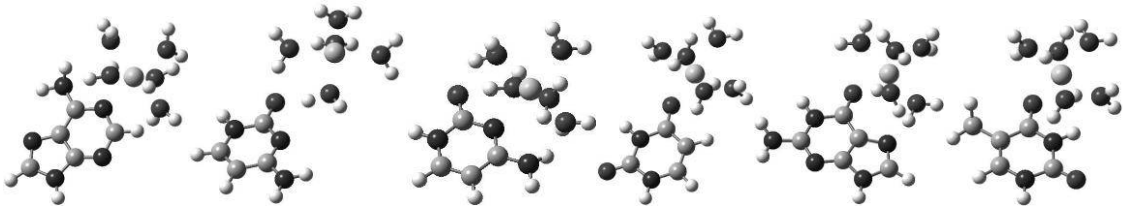
Key-words: Nucleotide bases, Mg2+, complexes, ab-initio.

In this work we made a comparative study of the computational methods HF and MP2 using 6-31G+(2d) and aug-cc-pVDZ basis functions for the complexes (Nucleotide base)-$[Mg(H_2O)_5]^{2+}$, evaluating their binding energies (ΔE) and estimating the dispersion energy (DE) contributions.



Complexes: Adenine, Cytosine 1, Cytosine 2, Uracil, Guanine, Thymine

The geometry of the complexes was fully optimized in vacuum at MP2 level with both basis sets. HF and MP2 energies were used to calculate each of the complexes binding energies as: ΔE = E{complex} – E{nucleotide base} - E$[Mg(H_2O)_5]^{2+}$, the last two terms calculated in separate with their geometries frozen at the optimized geometry of the complex. The dispersion energy contribution was obtained as: DE = $\Delta E_{MP2} - \Delta E_{HF}$. Single point MP2/aug-cc-pVTZ, ΔE and DE calculations for selected complexes, were used to validate the performance of the smaller basis sets used in this study. The binding energies given in Kcal/mol ordered from least stable to most stable nucleotide base are:

HF: **Adenine** (-57.8 to -56.7) **<** Uracil (-62.6 to -61.4) **<** Thymine (-62.8 to -61.4) **<** Cytosine 1 (-74.1 to -73.4) **<** Cytosine 2 (-82.4 to -80.0) **<** Guanine (-92.6 to -91.5).
MP2: Uracil (-62.4 to -61.3) **<** Thymine (-63.9 to -62.9) **<** **Adenine** (-67.1 to -66.8) **<** Cytosine 1 (-76.9 to -76.2) **<** Cytosine 2 (-88.5 to -87.5) **<** Guanine (-94.4 to -94.3).

No changes in the order of stability when going from basis functions 6-31G+(2d) to Aug-cc-pVDZ occurred, confirmed by Aug-cc-pVTZ for Uracil, Cytosine 1 and 2. Differences in ΔE were not greater than 2.5 kcal/mol indicating that 6-31G+(2d) is sufficient to describe the binding energy and that basis set superposition effects are not an issue in this study. However, important differences exist between HF and MP2 results, while HF places Adenine as the least stable complex, MP2 places it as more stable than Thymine and Uracil. Dispersion energy contributions being most notable in Adenine (13.4% - 15.4%) and Cytosine 2 (6.9% - 8.5%), while accounting for less than 4.5% for the rest of the complexes binding energies. We point to the fact that these two bases interact with the Mg^{2+} atom through a Nitrogen atom, while the other complexes do it through the more electronegative Oxygen atom, with a greater electro-affinity and harder electro-sphere.

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"Electronic Coupling in Triindole Derivatives: A DFT-D Study"

Igo Torres Lima[a](PG), Demétrio A. da Silva Filho[a](PQ), Berta Gómes-Lor[b](PQ), M. Carmen Ruiz Delgado[c](PQ) and Juan Teodomiro López Navarrete(PQ)[c]

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Key-words: Electronic coupling, Triindoles, π-staking, DFT-D

The electronic coupling between organic molecules has been computed using several different methodologies, from semiempirical methods, to *ab initio* (HF, MP2 and DFT) techniques. In most of the organic systems, week interactions are responsible for holding these molecules together. These interactions are poorly described by DFT methods. Although there is no direct correlation between the electronic coupling and the dispersion energies, here we will compare the values obtained for the electronic coupling using different DFT methods. Traditional functional, such as B3LYP and PW91 and the two new functionals, developed by Thrular and coworkers: M05-2X and M06-2X. These two funcionals have been parametrized to properly account for noncovalent interactions. The goal is to investigate whether the parametrization used to properly describe the dispersion interactions will influence the values obtained for the electronic coupling. The hole-transfer electronic coupling for the B3LYP/6-31G** optimized dimer at the experimental intermolecular distance 3.68 Å has been calculated to be 34 meV, suggesting that indeed these molecules are promising hole-transport materials.

Support: CNPq

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"Homology modeling of *Leishmania major* and *Trypanosoma cruzi* Fumarate Reductase. Study of the inhibitory capacity of metal complexes by molecular docking."

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Key-words: homology model, SAR, molecular docking

The enzyme NADH-fumarate reductase (FR) is present in several members of the genus *Trypanosoma* but it is not found in mammalian cells [1] providing a unique target against parasitic diseases like Chagas' disease or leishmaniasis. While bacterial FAD-dependent FRs have been widely studied and crystallized [2, 3], less is known on parasitic NADH-dependent FRs and their 3D structures. In this work we report the homology modeling of the 3D structure of *T. cruzi* and *L. major* FR based on *Shewanella frigidimarina* FR (PDB code: 1QO8) selected from a BLAST-P analysis against PDB database. Homology models of *T. cruzi* and *L. major* FR were built by Swiss-Model [4]. The quality of the models was checked using PROCHECK [5] and Prosa-web [6]. Further, the models were subjected to energy minimization using the AMBER 9 [7] software package. The root mean square deviation of the minimized model structures was evaluated from the template by SUPERPOSE [8]. The quality assessment of the models validated their use for further studies. Molecular docking of the NADH cofactor, natural substrate fumarate and different trypanocidal pyridine-2-thiol *N*-oxide metal complexes [9] on FR models was performed using Autodock4.2 [10] shading new light on the binding characteristics of these enzymes. Moreover, docking results showed to adequately predict the FR inhibitory capacity of the metal complexes on both enzymes becoming a valuable tool for future rational drug design.

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Estudos Químico-Quânticos das Propriedades Farmacológicas dos Ácidos Graxos Presentes no Coco Babaçu.

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Key-words: DFT, Coco babaçu, Propriedades farmacológicas

Os ácidos graxos foram vistos, até o inicio do século XX, exclusivamente como uma forma eficiente de armazenar energia, podendo ser sintetizada pelo o organismo a partir de proteínas e carboidratos. Desde então, vária evidências apontam que uma dieta pobre em ácidos graxos é associada a síndromes que podem levar á morte. Com isso, é cada vez maior a procura por fontes contendo estes ácidos, uma dela é a amêndoa do coco babaçu, ela é encontrada no fruto da palmeira (*Orbignya phalerata)*, conhecida popularmente como babaçu. O óleo de coco babaçu é usado na alimentação de pessoas com baixa imunológica, que possuem facilidade em gripar, pessoas com doenças bacterianas e viróticas como tuberculose, pneumonia, herpes, doenças venéreas, autoimunes como o lúpus e a psoríase, entre outras seria de extrema valia. Esta propriedade do óleo babaçu, acredita-se, que é divido seu alto teor de ácido láurico e ácido cáprico.

Esse estudo tem como principal objetivo identificar possíveis propriedades farmacológicas, dos ácidos graxos, encontrados no óleo da amêndoa do coco babaçu. Para isso, utilizamos métodos de DFT com o funcional hibrido B3LYP combinado com o conjunto de base 6-311+G*. De inicio, foi analisado os orbitais moleculares de fronteira e as cargas atômicas obtidas pelos métodos (Mulliken, NPA e Chelpg). Todos os cálculos foram realizados no programa *Gaussian 03W*, já à observação e construção das moléculas foram realizadas pelo *Gauss View 3.07*. Cálculos de frequências foram realizados para verificar o mínimo de energia.

Nos ácidos graxos saturados os HOMO's e LUMO's são localizados no grupo carboxílicos, enquanto que para os ácidos insaturados os HOMO's estão localizados na ligação dupla e o LUMO's sobre os grupos carboxílicos. Dos ácidos graxos presentes no babaçu, os insaturados possui grande aplicação farmacologia, desta forma, a característica desses orbitais contribui para potencialidades desses compostos com fármaco. Dos métodos utilizados para estudar a distribuição de cargas, o método de Mulliken obteve valores de cargas bem distintos.

Support: FAPEPI, CNPq, FINEP.

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"Surface-modified Imogolite by Dehydroxilation"

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Key-words: Imogolite, Dehydroxylation, DFTB

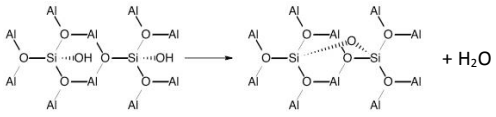
The chemical and physical properties of inorganic nanotubes (NT) allows to be used in several applications such as molecular sieves, chemical sensors and catalytic processes. Their properties depend on size, symmetry and spatial arrangement of NTs. Hence, the synthesis of monodisperse and single-walled nanotubes is of great interest.

The Imogolite ($(HO)_3Al_2O_3SiOH$) is an aluminosilicate nanotube (NT) found in nature with inner radius of 1nm ~100nm in size. This NT is composed of a sheet of gibbsite ($Al(OH)_3$) with silicate groups attached to the inner part of the NT. The imogolite is monodisperse, single-walled and easily obtained. Thus the imogolite is becoming a prototype for the development of new materials.

The modification or functionalization of imogolite has become a new challenge for researchers. Kang et al. [1] demonstrated recently by NMR data that the internal structure of imogolite can be easily changed from thermal processes leading to dehydroxilation. Silanol groups on the inner surface on the tube suffer dehydroxilation and releases water molecules. This process causes the formation of Si-O-Si bonds.

This work investigated the properties of the dehydroxylated imogolite. Successive dehydroxylations were carried out from imogolite (12,0). This is the most stable structure of imogolite. Its unit cell has 24 hydroxyl groups, which splits into two planes. From SCC-DFTB calculations, successive dehydroxylations were performed to explore all possible structures.

Each dehydroxylation is governed by the reaction:



Initially it was only explored a plane of hydroxyls. The ΔE of the dehydroxylation reaction was estimated at 0.3 kcal/(mol.atom). This value does not vary depending on the degree of dehydroxylation. The results indicated that the dehydroxylation process generates preferentially the most symmetric structures, see fig. 1. Electronic, mechanical and structural details will be discussed in detail.

Support: CNPq, FAPEMIG, INCT-ACQUA.

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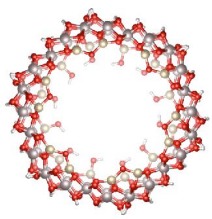

Figure 1. Imogolite (12,0) with 6 dehydroxylations.

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"A Systematic Study of the Lewis Acid-Catalyzed Diels-Alder Reactions Routes to Halogenated Bicyclic Ketones"

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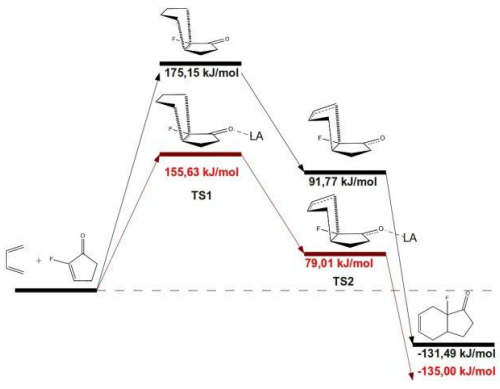
Key-words: Diels-Alder Reactions, PM6, DFT, Lewis Acids, Catalysis

In order to the development of new products with medicinal activities, halogenated bicyclic ketones has been synthesized through Lewis Acids (LA) catalyzed Diels-Alder(DA) reactions, yielding intermediates and precursors of many organic compounds. Nevertheless, few papers have been employing dienophiles as halogenated 5-membered rings keto-alpha-monounsaturated in this kind of reactions[1]. Aiming these goals, a systematic study has been accomplished with the PM6 semiempirical and DFT methods, investigating the LA effects, in order to analyze the equilibrium, thermodynamics and kinetics parameters of these reactions. The PM6 results of the DA reactions, between 7-fluorocyclopent-2-enone and butadiene, have been showing us a non-concerted mechanism with two transition states(TS's). Analyzing the ratio of the rate constants, the second over the first one, through the point view of the kinetics, the second TS formation could be until 10^{14} faster than the first one. So, the first TS formation is the rate determining step. Investigating theses DA reactions with LA = $AlCl_3$, AlF_3, AlH_3, BCl_3, BF_3, BH_3, $SiCl_4$, SiF_4, SiH_4, the average action of LA decreases 20 kJ/mol of the first TS (TS1) activation energy and 11 kJ/mol the second TS one (TS2). However, the trends of the kinetic controls have been maintained. Analyzing the ratio of the equilibrium constants, between the catalyzed reactions over non-catalyzed ones, with values obtained by thermodynamics classical and statistical data, we have been obtained the bellow increasing order: AlF_3(2.3) < AlH_3(2.4) < SiF_4(2.9) < $AlCl_3$(3.0) < $SiCl_4$(4.4) < BF_3(5.5) < BCl_3(7.0) < SiH_4(9.8) < BH_3(10.5). The DFT methods and solvent effects analyses are in progress.



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Support: CNPq, CAPES.

Revisiting the morphology of carbon clusters C_N with $N \leq 25$.

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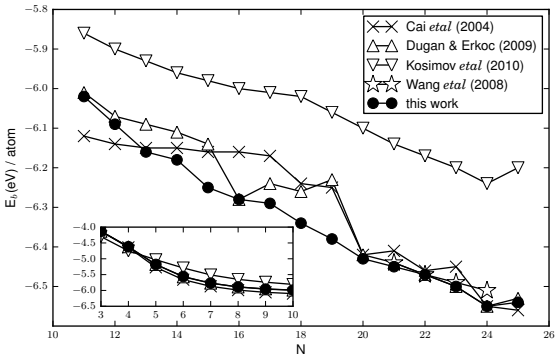
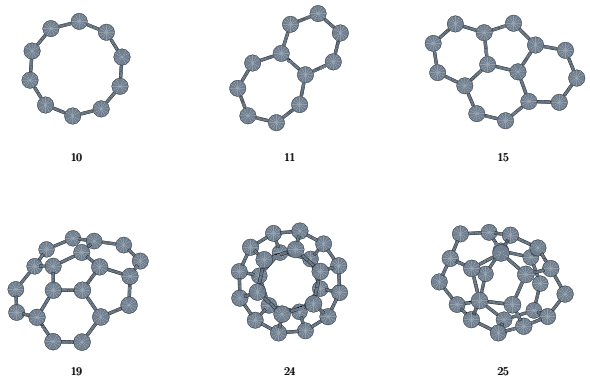
Key words: carbon clusters; graphene; genetic algorithm; density functional theory

We conducted a study of the lowest-energy configurations of neutral carbon clusters, C_N with $N < 25$, with the aim of studying the posterior doping of these structures with metals. The optimization technique we use is a standard genetic algorithm with the addition of two evolutionary operators proposed by our group (annihilator and history operators). As the number of isomers increases very rapidly with increasing cluster size, an empirical Brenner bond-order potential was adopted to describe the carbon two-body and three-body interactions. Following previous studies in the literature, we omit the conjugate-compensation term for simplicity. The plethora of structures range from single ring clusters for $N \leq 10$, flakes of graphene for $11 \leq N \leq 22$ to fullerene-like cages for $23 \leq N \leq 25$. Among the graphene sheets the majority of the structures are planar with few exceptions that show bowl-like shapes ($N = 19, 20, 22$). For sizes larger than $N = 23$ the open edges of the cluster zip up to form a close cage structure. Compared to studies that use the same semi-empirical potential but different optimization techniques our structures are among the lowest in binding energy (see figure below). The isomers we found are further recalculated using a real-space pseudopotential DFT technique (LDA approximation) to verify their stability. In particular we present the vibrational spectra obtained by means of finite-temperature *abnitio* molecular dynamics.





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Mechanistics studies of cisplatin resistance. The copper transporters coordination.

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Key-words: Cisplatin, copper proteins, ONIOM.

Cisplatin is worldwide known as an anticancer drug. Among its disadvantages are the resistance mechanisms that can involve intrinsic and extrinsic causes. Copper efflux transporters proteins[1] (ATP7B and ATP7A) have been implicated in the metal transport outside the cell and thus are associated to the resistance of platinum drugs. This should be due the substitution reaction of the chloro ligands by sulfur on the cysteine. The protein has 1213 atoms in its structure and it is probable that this whole environment can influence the efflux mechanism. With this in mind, QM/MM method through ONIOM approach was chosen for this study. Some ONIOM combinations were used as M06-2x/6-31g(d,p)/LANL2DZ:AMBER and also MP2/6-31g(d,p)/LANL2DZ:UFF. The best results obtained so far were with the last approach. The thermodynamic data calculated at 298K and MP2/6-31g(d,p)/LANL2DZ:UFF showed that the first coordination of cisplatin with the cystein (Cys 14) has the ΔG=-16.37kcal.mol^{-1} and the other possibility is through Cys17 coordination because they are not chemically equivalents. This coordination, yield ΔG=-12.77 kcal.mol^{-1}. Both data attest the exothermic behavior of these monocoordination modes and also indicates that coordination Pt-Cys14 is slightly more stable. The transition states structures are depicted in figure 1. In “a” Pt-Cys14 coordination is showed and in “b” the Pt-Cys17. Just the transition structure of Pt-Cys17 coordination was found until this submission. The TS was defined by only one imaginary frequency (121icm^{-1}) and shows the expected bipyramidal trigonal structure. The TS for the other coordination mode is been pursued as well as the structures for the second substitution step for a full characterization of the desired reaction. Calculations involving solvent effect will be also carried out, aiming to evaluate this effect on the thermodynamics and kinetics of this mechanism.

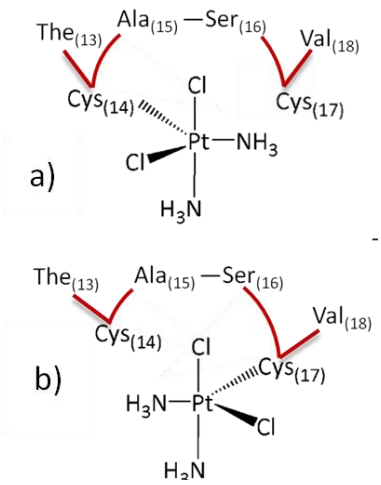

Figure 1: Transition states structures.

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Support: FAPEMIG and CNPq.

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Hybrid QM/EFP study of the aminolysis reaction of monoanionic 2,4-dinitrophenyl ethyl phosphate in aqueous solution

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Key-words: phosphate esters, hydroxylamine, hybrid calculations

In this work, the mechanism of the aminolysis of 2,4 dinitrophenyl ethyl phosphate (2,4DNEPP) with hydroxylamine, an alpha-nucleophile, was investigated by the density functional theory (DFT) formalism. The neutral hydroxylamine can react as a nucleophile and attack the P-O center through oxygen or nitrogen atom. On the other hand, the anionic and zwitteriônica form of the hydroxylamine attack through oxygen. The transition state, reactants and products for the aminolysis reaction were characterized at B3LYP/6-31++G(d,p) considering all three possible attack on the phosphorus atom. Single point energy evaluations were also performed for more precise energy predictions at the MP2 level with the 6-31++G(d,p) and cc-PVTZ basis set.

The theoretical results, in gas phase, show that P-O bond cleavage of the diester, for all models of attack, proceeds through a concerted mechanism and involve a transition state with a trigonal bipyramidal like structure. All reactions show the free energy activation range 12 and 37kcal/mol. Solvent effects on the structures and mechanism for the aminolysis reaction were explored using hybrid Quantum Mechanical/Effective Fragment Potential (QM/EFP). The system under study consisted of the solute molecules (2-4DNPP and hydroxylamine) surrounded by 64 EFP water molecules. Our B3LYP/631++G(d,p)/EFP results show that the cleavage of the P-O bond of the 2,4DNEPP, promoted by neutral hydroxylamine attacking by oxygen atom, also proceeds through a transition state with a trigonal bipyramidal like structure heaving less bonding formation to the nucleophile (P-O = 2.232 Å) than the leaving group (P-O= 1.752 Å). At the MP2/ccpVTZ//B3LYP/631++G(d,p)/EFP level, the aminolysis reaction showed an activation free energy at 25°C of 26.5kcal/mol, which it is 5kcal smaller then in gas phase. The results indicates a stabilizing effect of the solvent in this reaction, showing strong agreement with the experimental value calculated from the second rater constant, 22.0kcal/mol. This result validates the application of the QM/EFP approach to study of the reactions in solution.

References: *Ferreira, D. E. C.; Florentino, B. P. D.; Rocha, W. R.; Nome, Faruk *J. Phys. Chem. B* **2009,** *113,* 14831 and references therein.**

Support: CNPq, INCT-catálise and FAPEMIG.

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Ouro Preto – MG, 20-23 Novembro de 2011
30 Anos SBQT

"Solvation effects in conformational analysis of substituted 1,2,3-triazole linked to glycosyl moieties"

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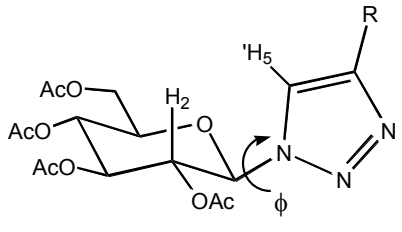
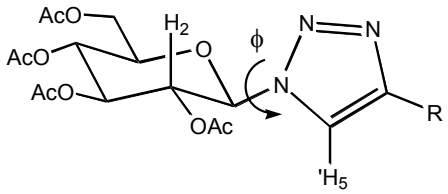
Keywords: Solvation, rotamers, NMR

Nowadays, in absence of crystal structural data, NMR spectroscopy stands alone as the ultimate method for structural characterization of organic compounds. Besides that, molecular modeling methods represent a very useful complementary predictive tool, especially in conformational analysis [1]. Our main goal is to investigate the population distribution of rotamers in solution of a series of 1,2,3-triazole-glycosyl derivatives, using quantum chemical calculations allied to continuum solvation methods in comparison with NMR NOE Diff and NOESY results obtained in $CDCl_3$ solution. The figure below shows two arrangements, 1 and 2, relative to H_2 and $H_{5'}$ spatial orientation, for a series of compounds obtained varying the R substituent. The NMR results indicate the arrangement 1 is always preferable. Using the AM1 method, a preliminary gas phase scan around the torsion angle ϕ was performed which showed: first, that only two isomers are stable, those ones corresponding to arrangement 1 and 2, lacking the rotamers with intermediate torsional angles; second, that arr. 2 is preferable. For a model compound, with hydroxyl and methyl groups replacing respectively acetyl and R groups, it was performed a B3LYP/3-21g geometry optimization with IEFPCM method for solvation in chloroform. This result shows that from gas phase to solution a switch to the arrangement 1 occurs, corroborating NMR results. Furthermore, refinements of molecular structures were obtained using B3LYP/3-21g method and preliminary solvation calculations for the series have similar results as for the model compound.



(Arr. 1)



(Arr. 2)

R: $CH_2CH_2CH_3$; Phenyl; CH_2S-Benzoxazole; CH_2-Benzimidazole.

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Support: FACEPE, CNPq, CAPES.

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Reaction Mechanism of Babassu Coconut Fatty Acids (Oleic and Linoleic) with Grubbs Catalyst First Generation: A Theoretical Investigation

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Key-words: Babassu; Metathesis, Grubbs Catalyst, Activation energy; DFT.

The biomass has been wide used as source of obtaining of the various materials, such as: polymers, fibers, fuels and pharmaceuticals. This interest can be attributed to its renewable character, as well as its ample availability. In function of the different functionalities gifts in its chemical structure, the oil of babassu has excellent characteristics for reactions of metatheses, due to its composition to present unsaturated chains. In such a way, the theoretical study of the mechanism of reaction of olefins of the babassu with catalyzer of Grubbs of the first generation allowed a better understanding of the mechanism of this catalyst attack on unsaturated fatty acids in the oil.

The computations were performed at DFT level of theory using the hybrid functional B3LYP with the basis set for both analog DGDZVP simplified catalyst, $Cl_2(PPH_3)_2Ru{=}CH_2$, and for fatty acids oleic and linoleic. Calculations were performed considering the electron to form singlet structures metalocarbenos for this form is stable. The atomic charges in molecules were obtained by the NBO method. The transition state was obtained using the method QST3, as implemented in Gaussian 03 program.

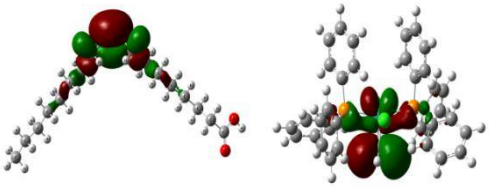

Figure 1. HOMO frontier orbitals for cis-oleic acid, and LUMO for the catalyst.

The results for the fatty acids was optimized that both oleic acid and linoleic acid presented to Trans form more stable than cis, as expected. For the catalyst in their geometrical parameters, it was observed that the base DGDZVP obtained the best. The frontier orbitals of the complex (catalyst-olefin) are formed by a substantial contribution from the HOMO of the acid, which contains unsaturation and the LUMO of the catalyst, which is predominantly metallic (see Figure 1). The activation energy of 39 Kcal mol^{-1} was obtained to the transition state of the oleic reaction.

Support: CNPq, FINEP, UESPI.

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Lennard-Jones potential Parametrization for silicon tetrachloride

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Key-words: Silicon tetrachloride, Lennard-Jones empirical potential, liquid simulation.

It is a common practice the use of the same parameters of empirical potentials, as the Lennard-Jones parameters, for many similar chemical systems. It is the case when parameters of tin tetrachloride[1] have been used for silicon tetrachloride simulations. This is not the best approach since, for example, the mean intermolecular distance of chlorine is 3.724 Å for $SnCl_4$ at liquid phase, and for $SiCl_4$ is 3.293 Å[2] Such deviation may lead to wrong results when the whole system (solvent bulk) is studied. In this work, we intend to obtain a specific set of Lennard-Jones potential parameters for the $SiCl_4$ molecule. The procedure consists in fitting twelve potencial energy curves (PECs), which were obtained from quantum mechanical calculations (fig.1), with the classical potential trough the quasi-newton method.

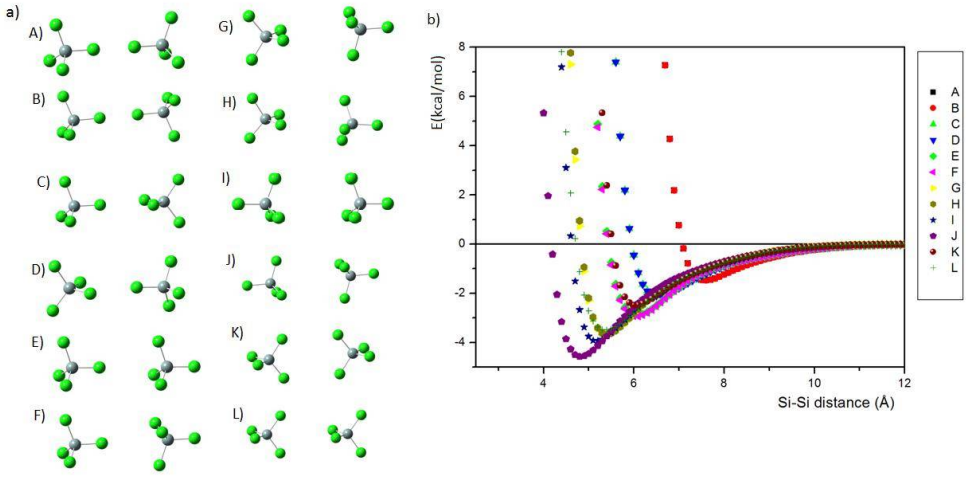

FIG.1a) The 12 conformers of silicon tetrachloride dimer; b) PECs for the twelve dimers orientations.

All quantum chemistry calculations were performed using the GAUSSIAN 09 program package with and without Basis Set Superposition Error (BSSE) correction. The MP2 method was used to treat the electron correlation effect employing the 6-311++G(d,p) basis set. Some PECs are degenerated, like **A** and **B**, for example. At the MP4(SDTQ) level, small differences can be observed Parameters adjustment was carried out with quasi-Newton-Raphson method where the error function is obtained by least squares. The parameters obtained will be used in a further Monte Carlo simulation study of silicon tetrachloride.

Support: FAPEMIG.

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Theoretical Study of the Reduction of the Gallyl Ion to Dihydridegallium in Ga-Exchanged Zeolites

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Keywords: Zeolite, Gallyl, Dihydridegallium

Zeolites are crystalline aluminosilicates largely used as a heterogeneous catalyst, especially in the petrochemical industry. Some of its various uses are in processes of catalytic cracking, hydrotreatment and aromatization. Different species of gallium can be found in Ga-exchanged zeolites, namely framework Ga or extraframework gallium. The main application of these zeolites is in the conversion of small alkanes to aromatic hydrocarbons. In this study, we focus our efforts in extraframework gallium species: the gallyl ion and the dihydridegallium. Studies have shown that the hydride species is the likely active catalyst form of gallium and that the oxidized species cannot be a working catalyst in non-oxidative conditions, which happens to be the case in reactions of aromatization of small alkanes. Furthermore, in the reaction of aromatization of propane an initial low production of hydrogen during the activation of this alkane has been observed, therefore suggesting the existence of an induction period for the reaction. During this period, the gallyl ion would be reduced to dihydridegallium by the evanescent hydrogen produced from the dehydrogenation of the propane molecule over the gallyl ion center. Preliminary studies of this reaction were made using a T5 cluster. The calculations were made in the DFT level, using the B3LYP functional and the LACVP basis set. The Gibbs free energy for the reduction of the gallyl ion and the oxidation of the dihydridegallium were both calculated at 300K and at 723K, the temperature at which the aromatization of propane has been reported to occur. For the reduction reaction, the values obtained were -28,47kcal/mol and -16,86kcal/mol, at 300K and at 723K, respectively. Whilst for the oxidation reaction, these values were -97,59 kcal/mol at 300K and -101,34kcal/mol at 723K. The results show that, indeed, the dihydridegallium is the most stable species in a reducing environment at both temperatures, whereas the opposite is valid in an oxidizing environment. Based on these preliminary studies, we are presently investigating the gallyl ion reduction mechanism, using the same basis set and functional and using a larger T22 cluster, in order to incorporate the effect of the zeolite cavity.

Support: FAPERJ, CNPq, INOMAT.

"Theoretical Study of Sulfatase catalytic action mechanism"

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Key-words: Arylsulfatase, Catalysis, QM/MM

The sulfatases comprise a large family of enzymes that catalyze the sulforila group transfer reactions in biological processes such as hormonal regulation, bone and cartilage formation, among others. The Arylsulfatase (AS) subclass is found in prokaryotic and eukaryotic organisms. Studies have reported the structure of the bacterium *Pseudomonas aeruginosa* AS resolved by X-ray crystallography.[1] Mechanistic proposals of esters hydrolysis catalyzed by AS family members have been presented in the literature[1, 2] however, there is no conclusion yet about which one would be the most likely. In this sense, this work aims to apply computational methods to study the enzymatic catalysis of sulfate esters promoted by AS in an attempt to elucidate such mechanisms. The AS system has enormous number of atoms (4503), based on X-ray structure, and thus hybrid methods based on Quantum Mechanics and Molecular Mechanics (QM / MM) have to be used. The enzyme active site is treated by QM methods while methods based on MM are applied to the rest of the system. The geometry optimization in gas-phase for the active site model of AS was performed using the PBE1PBE functional and the 6-31G(d,p) basis set. This geometry was also defined as a local minimum by the vibrational analysis. This structure is shown in Figure 1, where calcium metal is coordinated with Aspartate in a bidentade form and the other four bonds are designed with methyl sulfate, two Aspartate and one Asparagine.

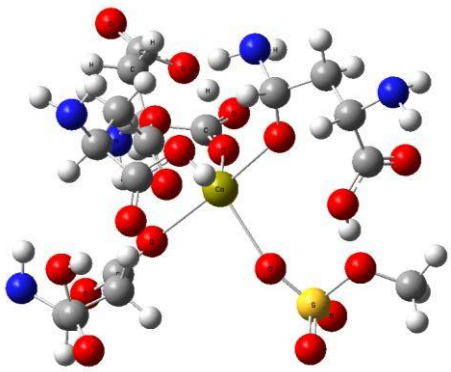

Figure 1 Optimized structure of the active site of AS at the PBE1PBE/6-31g (d,p) level of calculation.

Comparing the theoretical and experimental bonds lengths, Ca—OS=2.46Å (X-ray: 2.57Å) and Ca—OAsn=2.40Å (X-ray: 2.36Å) a good agreement is found. These are incipient results; however, calculations including the solvent effect by means of continuum model as well as microsolvation (supermolecular approach) have been carrying out as well as the transition state searches for the mechanism elucidation.

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Support: CNPQ e FAPEMIG.

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Docking between natural peroxides and the heme group by the PM6 method

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Keywords: Peroxides, Antimalarials, Artemisinin, Heme.

Artemisinin is a sesquiterpene lactone with an endoperoxide function currently used against strains of *Plasmodium falciparum*. Endoperoxides are supposed to act on heme leading to reduction of the peroxide bond and production of radicals that can kill the parasite. In addition, recent studies have shown that artemisinin can inhibit the *P. falciparum* Ca^{2+}-ATPase (PfATP6). The increasing parasite resistance to current drugs endorses the search for new therapies. The main goal of the present study is the identification of new potential antimalarial drugs from natural sources, as well as to find possible correlations between in silico parameters and experimental data. Thus, the interactions of 51 peroxides with heme were studied by the semi-empirical PM6 method. These peroxides were divided into two sets. The first set (training set) was composed by 10 artemisinin derivatives with known biological activity. The second set (test set) was composed by 40 natural peroxides with the primary focus in compounds from the Brazilian flora. Docking studies were performed in three steps. First, a docking between artemisinin, 10 synthetic analogs and heme was carried out in AutoDock Vina 1.0.2. Then, single-point calculation in vacuum and solvent phase, after geometry optimization of each complex, was performed using the PM6 method. A rigid conformational search was performed for all complexes studied to identify the most stable conformer. Finally, we tested correlations between the interaction energies and the experimental data (IC_{50} and K_d) for the compounds of the training set. There is correlation (α = 0.01) between the interaction energy and K_d. The same computational protocol was performed for the test set. The natural peroxides have molecular electrostatic potential (MEP) map similar to that of artemisinin. The interaction energy obtained with the semi-empirical PM6 shows that compound 5 and 24 may be promising antimalarial drugs. They bind to the heme group with interaction energies of -334.86 and -492.43 Kcal/mol, respectively. The binding energy of artemisinin is -233.43 Kcal/mol. Our results show that natural compounds from the Brazilian flora may be candidates to fight malaria.

Support: FAPESB.

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Caracterização espectroscópica da Aegelina por Modelagem Molecular

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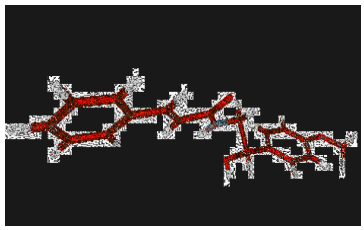
Key-words: Aegelina, espectroscopia de RMN, Elucidação estrutural

O composto N-[2-hidroxi-2-(4-metoxifenil)etil]trans-cianamida, cuja estrutura é mostrada ao lado, é também conhecida por **aegelina,** sendo recentemente obtida[1] em pequenas quantidades, por extração, em vegetais do gênero *Solanum* . Devido às suas propriedades antifúngicas, a **aegelina** é um composto que tem recebido uma atenção especial da comunidade química. Porém, devido à sua pouca abundância e à sua baixíssima solubilidade, a sua caracterização espectroscópica torna-se desafiadora. Além disto, devido à existência de um centro assimétrico, a resolução enantiomérica de sua estrutura tem sido tentada com a conjugação da sinergia da espectroscopia de RMN e de polarimetria. Devido ao fato de que os resultados obtidos pela conjunção destas técnicas ainda não ser absolutamente conclusivo, a modelagem molecular deste sistema é muito bem-vinda.



Este trabalho objetiva modelar, por meio da Teoria do Funcional de Densidade (B3LYP), obtendo-se as geometrias dos enantiômeros **R** e **S** da **aegelina**, assim como os seus respectivos espectros vibracionais, de RMN e sua atividade ótica. As rotações óticas foram calculadas conforme implementação da metodologia descrita por Frish e colaboradores[2] no pacote G03, tendo a radiação da raia-D do sódio como fonte de perturbação sobre as hiperpolarizabilidades.

Os valores de rotação ótica obtidos para os isômeros **S** e **R** da **aegelina** são respectivamente +17,9 e -17,9 °. Os espectros vibracionais calculados para ambos os isômeros são indistinguíveis e bastante congruentes com os seus análogos experimentais. Apesar dos deslocamentos calculados nos espectros de RMN serem distintos para os isômeros **R** e **S**, principalmente no entorno do carbono quiral, estas diferenças são pequenas, o que não permite se afirmar com precisão, somente baseado na comparação entre os espectros experimentais e os calculados, a natureza do enantiômero. Aguarda-se portanto a medida experimental da rotação ótica para a elucidação da estrutura.

Agradecimentos: CNPq (Proc.: 476715/2008-3), **CCAD**/UFPR.

[1] IBRAHIM, O. A., *et al.*, ***J. Chem. Soc. Pak.***, **32** (2010) 565.

[2] STEPHENS, P. J., et al., ***J. Phys. Chem. A***, **105** (2001) 5356.

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"Probability current in protein electron transfer: Löwdin population analysis"

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Key-words: probability currents, non-orthogonal projectors, protein electron transfer

We consider the problem of building an electron probability current density in subspaces of the full Hilbert space in cases where there are overlaps between the subspaces and their complements. In this case the projectors onto these subspaces are non-Hermitian and one has different possible electron population analysis. We show how the electron probability current density can be directly constructed from the probability conservation equation and relate them to population operators. For the Löwdin population operator we investigated the electron probability current density in protein electron transfer problem when the medium is described with a non-orthogonal atomic basis set, and contrast it with the Mulliken analysis. The overlapping atomic population analysis is obtained with a non-orthogonal projector and provides interatomic tunneling currents different from the previous results. Analytical comparison between interatomic currents shows that other interatomic currents can be obtained as a combination of these interatomic currents provided by the non-orthogonal analysis. In case of strong coupling between protein and donor/acceptor states the normalized interatomic current, used recently to build a vectorial pathway model, can depend of the surface in the protein medium between the donor and acceptor site.

Support: FAPEMIG.

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Low energy elastic and electronically inelastic electron scattering from biomolecules

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Key-words: Electron scattering, cross sections, resonances, biomolecules

Recent studies have shown that reactions induced by low-energy electrons may act very efficiently and with a high degree of selectivity in the breaking of chemical bonds in polyatomic systems. In addition, fine control of selectivity can be obtained based just on a suitable choice for the energy of the incident electron. The possibility of manipulating and controlling chemical reactions on the nanoscale points to new opportunities that can be explored both in the field of basic research and in developing new technologies to be applied to different areas of scientific knowledge. In this work we discuss the role played by electronic excitation of gas phase molecules on electron-driven chemical processes. Special attention is focused in the analysis of the influence of polarization and multichannel coupling effects on the magnitude of elastic and electronically inelastic cross-sections. The discussion is based on results obtained for simple organic molecules and some five-membered heterocyclic compounds. The characterization of shape and Feshbach resonances is also considered since the formation of such temporary anionic states represents an efficient mechanism leading to selective breakage of chemical bonds. The relevance of these issues is evaluated in the context of possible applications for the modeling of discharge environments and implications in the understanding of mutagenic rupture of DNA chains.

Support: FAPESP, CNPq, Fundação Araucária.

Car-Parrinello Molecular Dynamics study of tetrahydroborate(III) ion hydration

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Key-words: Tetrahydroborate, Borohydride, Car-Parrinello Molecular Dynamics

The tetrahydroborate (III) ion (BH_4^-) is an important source of hydrogen in combustion cells and it has been extensively used as reagent for both organic and inorganic synthesis. As catalyst it is very effective in the polymerization, oligomerization, and hydrogenation of olefins. In addition, tetrahydroborate has potential to be used in design device to store hydrogen for vehicle applications. In this work, the BH_4^- ion hydration investigation was carried out using the Car-Parrinello code implemented in the quantum ESPRESSO package within the generalized gradient approximation to density functional theory, through the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Vanderbilt ultrasoft pseudopotentials were employed to represent core-valence electron interactions. A plane wave basis set was used to expand the valence electronic wave function with an energy cutoff of 25 Ry and 200 Ry cutoff was used for the expansion of the augmented charge density in the proximity of atoms. A cubic box of 13.0 Å with 61 water molecules and with a density of 0.997g.cm^{-3} was used in the simulation. The system temperature was controlled by Nosé-Hoover thermostat and it was maintained at 300K. The equations of motion were integrated using the Verlet algorithm with a time step of 0.121fs, and the wave function fictitious mass (μ) was set to be 400 au. The boundary conditions and the canonical ensemble NVT were considered in the work. The first 2 ps were used for system equilibration and, additionally, 10 ps simulations were carried out for production and were averaged for analysis. The radial distribution function shows that the first hydration shell was calculated at 3.35 Å and it has an average of 4.8 water molecules. The self diffusion coefficient for BH_4^- was calculated in 2.43x10^{-5} m^2.s^{-1}. The variations of B-H bonds and H-B-H angles during the simulation time show an ion structural change due to water molecules in the first hydration shell. In first shell one can see the breaking and formation dynamics of hydrogen bonds between oxygen of water molecules and the hydrogen of the BH_4^- ion throughout the simulation. The calculated results from Car-Parrinello molecular dynamics simulation for BH_4^- hydration are in good agreement with the experimental data.

Support: CAPES.

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"Theoretical studies of structural and functional characteristics of *Fusarium solani* β-glucosidase by molecular modeling"

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Key-words: *Fusarium solani*, β-glucosidase, Molecular docking

β-glucosidase is a glycoside hydrolase 3 (GH3) and in fungi this enzyme is related with the synthesis of cell wall. *Fusarium solani* is pathogenic fungi responsible for disease on ~100 genera of plants and it is also associated with opportunistic fungal infections and keratitis in humans. Thus, selective inhibitors for β-glucosidase appears as new strategies for suppress fungal diseases. In this study, we have used molecular modeling to predict the three dimensional structure. In addition, to explain the interaction between PUGNAc and six analogues inhibitors and β-glucosidase enzyme was analyzed in order to understand inhibition mechanism of β-glucosidase. The structure three-dimensional of β-glucosidase *from F. solani* (*Fs*bGlc) was predicted by molecular homology using as template code PDB 2OXN from *Vibrio cholera* (*Vc*NagZ). The interaction study for FsbGlc-PUGNAc and VcNagZ-PUGNAc complexes were analyzed by molecular docking. The model was built by Modeller9v8 program and docking simulation was performed using Vina v1.5.4 program with AutoDock Tools 4.2. Our model had 25.5% sequence identity and was validated by Ramachandran plot with 86.6% of amino acid residues within regions of very favorable and RMSD of 0.5 Å. The modeled protein *Fs*bGlc active site remained conserved and docking study showed low affinity energy and good correlation with logK_I values for all PUGNAc analogues in both *Fs*bGlc-PUGNAc and *Vc*NagZ-PUGNAc complexes measured by the kinetic K_i data with $R = 0.898$ and $R = 0.897$ respectively. These results are promising and further studies are needed to validate the dynamic flexibility of the protein modeled. Support: UFPA, LPDF, CNPq, CAPES.

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"Transition energies from ground to inner-shell states of small molecules at IS-CASSCF level"

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Key-words: Inner-shell states, multiconfigurational method

Inner-shell CASSCF method is a multiconfigurational approach to describe the core excited state by making use of the idea of constraining the occupation of the core orbital. The procedure consists in a double-loop SCF cycle, which separates active space orbitals in two groups, the first containing the inner-shell orbital and the second composed by all of the others.[1]

In this work, we have applied the IS-CASSCF method in a group of small molecules in order to obtain transition energies for inner-shell excited states. The effect of dynamic correlation is recovered by multi-reference perturbation theory in the form known as GMC-QDPT. Sensibility of the values of transition energies on the level of calculation and on basis set is reported. Results for formaldehyde are shown in Table 1. As can be seen, the use of perturbation theory generally results in a better agreement with experimental values, especially when triple-zeta quality basis set is used.

State	Basis Set	IS-CASSCF	IS-GMCPT	Experimental[2]
(C $1s^{-1}$ π*) $^1B_1$	**aug-cc-pVDZ**	288.5	287.3	285.6
	aug-cc-pCVDZ	288.0	287.3	
	aug-cc-pVTZ	287.3	285.8	
	aug-cc-pCVTZ	287.3	286.2	
(O $1s^{-1}$ π*) $^1B_1$	**aug-cc-pVDZ**	533.0	533.0	530.8
	aug-cc-pCVDZ	532.3	532.9	
	aug-cc-pVTZ	531.4	530.7	
	aug-cc-pCVTZ	531.3	531.0	

Table 1: Inner-shell transition energies calculated for formaldehyde. In the last column, the experimental values are given. All values are in eV.

[1] A. B. Rocha, *J. Chem. Phys.* **134**, 024107 (2011).
[2] G. Remmers, M. Domke, A. Puschmann, T. Mandel, C. Xue, G. Kaindl, E. Hudson, D. A. Shirley, *Phys. Rev. A* **46**, 3935 (1992).

Support: CNPq, Faperj

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"Modeling Aromatic Staking Interactions In Triindole Derivatives: A DFT-D Study"

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Key-words: Triindoles, π-staking, DFT-D

Among the various theoretical methods, DFT-based calculations have been heavily used to predict geometries of single molecules due to their reasonably computational cost and the reliability of their results. However, DFT methods generally fail to describe the weak interactions such as the dispersion forces found in aromatic staking. Recently Truhlar and coworkers have developed two new functional, M05-2X and M06-2X, parametrized to properly account for noncovalent interactions. These functionals, like others, contain parameters that may work for well for a class of system and not for another. Here we are interested in a *specific* class of molecules, triindole derivatives, for which a validation of these functional is needed. These molecules are important organic semiconductors that forms π-stacks and that have been already characterized experimentally. We will evaluate the ability of these two functionals to properly describe the potential energy surface associated to displacements and rotations of these two molecules one with respect to the other, having the experimental structure (X-Ray) as a reference for such comparison.

Support: CNPq

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Dihedral angles parameterization of herbicides inhibitors of AcetylCo-A Carboxylase (ACCase)

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Key-words: herbicidas, campo de força, dinâmica molecular.

The enzyme acetyl-coenzyme A carboxylase (ACCase) has been identified as one of the most important targets of herbicides and is also a key enzyme in the biosynthesis of fatty acids in both prokaryotes and eukaryotes microorganisms. The molecular dynamics (MD) simulations uses force fields to set energetic and structural data of systems. In general, parameterizations include interactions between bonded and non-bonded atoms. In this work, the potential of the torsional dihedral O-C-C-O (carboxyl and ether) and C-O-C-C (aromatic ether and carboxyl), which are not found in current force fields, were obtained to describe the herbicide diclofop (ACCase inhibitor). The calculations of rotational barriers were performed using the HF/6-31G* base function, with the ORCA 2.8-20 program. The rotational energy barrier of dihedral O-C-C-O and C-O-C-C was converted into the Ryckaert-Bellemans potential (equation 1) to be introduced into the OPLSAA force field.

$$V_{rb}(\emptyset_{ijkl}) = V_0 + \frac{1}{2}[V_1(1+\cos(\emptyset)) + V_2(1-\cos(2\emptyset)) + V_3(1+\cos(3\emptyset)) + V_4(1-\cos(4\emptyset)) + V_5(1+\cos(5\emptyset))] \quad (1)$$

the constants V_n are given in the table 1.

Table 1-Constants of the Fourier expansion

Angle	V_0	V_1	V_2	V_3	V_4	V_5
O-C-C-O	0.155	-0.289	4.487	0.072	1.084	0.142
C-O-C-C	35.087	6.524	-13.572	-19.255	-0.048	1.900

The constants of the Fourier series (equation 1), showed in Table 1, were obtained by a program written in C++, which performs the least square method. After the "fit", the energy difference curve between quantum and classical curve for the O-C-C-O was 0.507 kJ/mol, while for the C-O-C-C dihedral was 2.699 kJ/mol (rotational barrier of 35.000 kJ/mol). The atomic charges (RESP) were derived for diclofop using the NWCHEM 5.1 program. Molecular Dynamics Simulation (GROMACS 4.5.3) of herbicide in explicit water showed that the angles distributions of parameterized angles were found to be around the equilibrium values described by the potential energy curves. Molecular dynamics simulations of ACCase-diclofop complex are in progress to characterize the mechanism of enzyme inhibition.

Support: FAPEMIG, FAPESP and CNPq.

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Study of the interaction between NO and Ni/SiO_2 catalyst by PM6 and DFT Methods

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Key-words: PM6, DFT, Heterogeneous Catalysis

Investigation of the structural stability of compounds by both experimental and theoretical techniques is important for developing new compounds. In catalytic systems, theoretical approaches have become possible through development of computational techniques. The objective of the present study is evaluating a theoretical model to study reaction mechanisms of heterogeneous catalysis. The structure of the catalyst Ni/SiO_2 with adsorbed NO (Fig. 1) was generated and optimized with the GAUSSIAN 03W software using the semi-empirical PM6 and functional density theory (DFT). DFT calculations were performed using the functional hybrid B3LYP, with the appropriate LANL2DZ and 6-31G(d) basis set for the nickel atom and non-metallic atoms, respectively, similar with previous studies.[1] Geometric parameters obtained using PM6 were quite similar to those obtained using DFT. Despite its preliminary study, and consider the vantages and limitations well know of semi-empirical approach, the release of PM6 method with metal parameters motives the use of this method to study the mechanism of heterogeneous catalysis. In a further step, this method will be applied to study the catalytic reduction of more complex and interesting substrates. Both the development of new active and selective catalysts and the investigation of kinetics of hydrogenation address for a better rationalizing in the production of valuable fine chemicals.

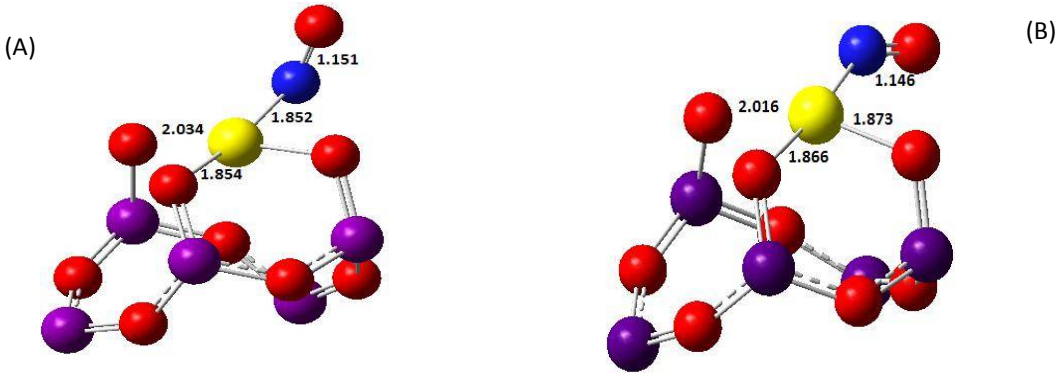

Fig. 1. B3LYP/6-31G*(d)* (A) and PM6 (B) {Ni-$NO^{\delta+}$}/SiO_2 structures. All bond lengths are in Å. Hydrogen atoms were omitted for a better visualization.

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Support: FAPEMIG/UFSJ.

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CONSTRUÇÃO DE BANCO DE DADOS DE MOLÉCULAS BIOATIVAS COM POSSÍVEL AÇÃO NA ENZIMA GAPDH DO *TRYPANOSSOMA CRUZI*

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Key-words: ensaio virtual, banco de dados, *T. Cruzi*

A *Tripanossomíase americana* ou doença de Chagas é causada pelo protozoário *Trypanosoma cruzi* (*T. cruzi*), e considerado pela Organização Mundial de Saúde (OMS) como uma das doenças tropicais parasitárias mais importantes no mundo com cerca de 18 milhões de pessoas infectadas no mundo. Apesar dos altos índices de ocorrência de casos de *tripanossomiasse* pouco se conhece sobre a doença. Os fármacos utilizados para o tratamento da doença são tóxicos e só apresentam atividade na fase inicial. A enzima Gliceraldeído 3-Fosfato Desidrogenase (GAPDH) é importante na via glicolítica, atuando na transformação da glicose em piruvato. A forma *tripomastigota* do *T. Cruzi*, flagelada depende da via glicolitica do hospedeiro para a sua necessidade energética, atuando sobre a GAPDH. Um objetivo importante deste trabalho é utilizar técnicas de ensaio virtual para propor ligantes capazes de inibir a enzima GAPDH do *T. cruzi*, para isso foi construído um banco de dados de ligantes com 503 estruturas que foram submetidas ao método de ensaio virtual através do programa Vina foi selecionado um grupo de cinco moléculas, no qual os parâmetros escolhidos foram a energia de docagem e as interações feitas no sitio ativo da enzima GAPDH. Entre as estruturas selecionadas a molécula 410 foi considerada promissora para a inibição do alvo biológico apresentando uma energia de -10,8 Kcal/Mol e 11 interações com os resíduos de aminoácidos do sitio enzimático.

Support: CNPQ.

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Study of Regioselectivity in Bromination Reaction of Porphyrin-based P450 model

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Key-words: Porphyrins, bromination, regioselectivity, DFT

Porphyrins are vital to the biochemistry of living organisms as they are an integral part of pigment like heme and chlorophyll. In fact, life relies heavily on the biological processes that are performed or catalyzed by porphyrin-containing proteins or coenzymes. Therefore it is natural that porphyrins remain of fundamental interest in both basic and applied fields[1]. Electron withdrawing porphyrins have emerged as an important subclass especially for their oxidative robustness as ligand for porphyrin oxidation catalyst. The regioselectivity of bromination reaction of the porphyrins and metalloporphyrins is largely unknown. In this study we investigated the H_2TCMPP [*meso*-Tetrakis (4-carbomethoxyphenyl) porphyrin], as shown in figure 1, and its brominated species, H_2Br_2TCMPP (8 conformers), H_2Br_4TCMPP (10 conformers), H_2Br_6TCMPP (7 conformers) and H2Br_8TCMPP. Structural and electronic properties of the conformers were evaluated performed using the Density Functional Theory (DFT) (B3LYP/6-31G(d)) in order to analyze the electronic, energetic and structural factors that controls the selectivity in bromination reactions of porphyrins. Time-dependent density functional theory, TDDFT (CAMB3LYP/6-31G(d)) was employed to simulate the UV-Vis espectra of these species, with the solvent effects included by means of the polarizable continuum model (PCM). The structural parameters calculated are in good agreement with experimental results[1]. Our calculations also reproduced the soret band obtained experimentally[2]. The electronic spectra and Boltzmann distribution of the most probable conformers of species of H_2Br_xTCMPP (x = 0, 2, 4, 6 and 8) as well as the discussion of the selectivity of the bromination reaction of meso-substituted porphyrins will be discussed.

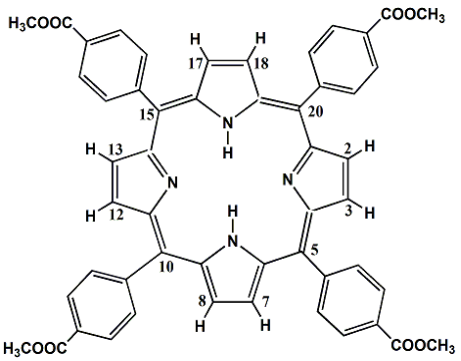

Figure 1 - Schematic structure of the H_2TCMPP

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Musky odor theoretical forecast through *quantum* calculations according to vibrational theory

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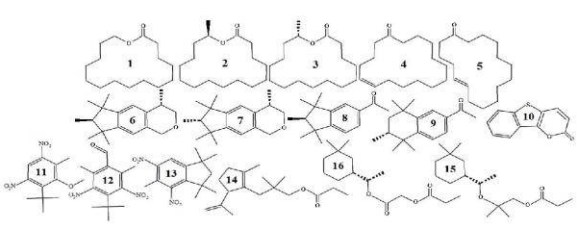
Keywords: musk, *quantum calculation*, theoretical prediction of infrared spectra.

Introductions and aims Regarding odor recognition, Luca Turin defends molecule´s vibrational behavior as the element to provoke an odorant biological reading;[1] therefore, Infrared (IR) spectra obtained *in silico* would give the odor prediction. A novel study on fragrance chemistry is presented hereafter, in which sixteen musks -bottom notes fixative compounds- (Figure 1) have been computationally analyzed in order to have their IR spectra predicted by different methodologies. When experimental spectra were available, they were compared to and, then, judged according to vibrational theory expectation.



Legend:
Macrocyclic musks:
pentadecanolide (1), (*R*)- exaltolide (2), (*S*)-exaltolide (3), cis-globanone (4) and trans-globanone (5);
Polycyclic musks:
(4*S*,7*S*)- galaxolide (6), (4*S*,7*R*)- galaxolide (7), indane (8), tetratalin (9) and tonkene (10);
Nitromusks:
musk ambrette (11), musk ketone (12) and muskene (13);
Acyclic musks:
cyclomusk (14), helvetolide (15) and romandolide (16).

Figure 1. Odorants under study.

Methodology For MM/DM calculations, CFF99/COMPASS forcefield in Discover simulation[2] program was used. Molecules under *vacuum*, into implicit solvent (through the ethanol dielectric constant) and into explicit solvent mixture of ethanol:water (70/30:v/v) were studied. MD trajectories were carried out at 650 K, 1 ns, NVT ensemble. Selected systems were reoptimized until convergence over $1{,}0\times10^{-5}$ kcal.mol^{-1}.Å^{-1}, using Vamp interface for NDDO AM1 Hamiltonian, PM3 and PM6 programs, and by DMol[3] program for DFT calculations (DNP-GGA/PW91) until energy convergence of $1{,}0\times10^{-5}$ Ha, with a 3.7 Å global cutoff.

Results and conclusions None among semi-empirical methods provided satisfactory results for IR prediction, even when implicit or explicit solvents calculations were undertaken. Better correlation between theoretical-experimental spectra was found when using PM6 method over AM1 and PM3. All DFT spectra obtained were matching to experimental data. Adjusting them to postulated vibrational theory, which says that bands around 700, 1000, 1500 and 2200 cm^{-1} are responsible for musky odor, mentioned band are common to the sixteen odorants under analysis; 2200 cm^{-1} is the exception, once it refers to nitriles and alkyl nitriles stretches, groups absent in perfume chemistry.

Acknowledgments Thanks UnB and CNPq for financial support.

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Molecular Docking of the GLCNAcstatin and seven analogues in complex with hOGA

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Keywords: GlcNAcstatin derivatives, CpOGA-GlcNAcstatin C complex, *O*-GlcNAcase, molecular docking.

The substitution of serine and threonine residues of nucleocytoplasmic proteins with 2-acetamido-2-deoxy-b-D-glucopyranose (O-GlcNAc) residues is an essential post-translational modification found within all multicellular eukaryotes. O-glycoprotein 2-acetamino-2-deoxy-β-d-glucopyranosidase (O-GlcNAcase) hydrolyzes O-GlcNAc residues from post-translationally modified serine/threonine residues of nucleocytoplasmic protein. O-GlcNAc has been implicated in several disease states such as Alzheimer's and Parkinson disease, Cancer and type II Diabetes. Herein, we have employed molecular docking using the crystal structure of CpOGA-GlcNAcstatin C complex (PDB entry 2j62) and a homology model of the human O-GlcNAcase (hOGA) enzyme. The genetic algorithm AutoDock Vina (version 1.1.1) was employed to study the details of the interactions established between GlcNAcstatin and seven analogs and both bOGA and hOGA. We choose the better position for each one ranking the affinity energy (EA) obtained from docking in relationship when crystal inhibitor GlcNAcstatin. A recently study has suggested that D174 and D175 within the hOGA family 84 enzyme are the key catalytic residues. These residues correspond to D297 and D298 conserved residues within the CpNagJ that are found in the N-terminal domain. When the active site of hOGA-GlcNAcstatin C complex obtained from docking is compared to the CpOGA-GlcNAcstatin C complex, we can see that the residues D174 (D297) and D175 (D298) present an interaction with GlcNAcstatin, other important residues presenting an interaction with this inhibitor are N280 (N396), N313 (N429), and Y219 (Y335). These results are in agreement with experimental measurements for CpNagJ. Study of the hybrid Quantum Mechanics / Molecular Mechanics (QM/MM) molecular dynamics (MD) simulations are being made to assist docking and quantitatively describe the energy in the biological activity.

Support: UFPA.

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"Understanding the inactivation process of organophosphate herbicides : a DFT study of glyphosate metallic complexes with Zn^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Co^{3+}, Fe^{3+}, Cr^{3+} and Al^{3+}"

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Key-words: glyphosate, complexes, theoretical calculations

Glyphosate is the active component of one of the top-selling herbicides, which is also a potent EPSP synthase inhibitor [1]. When applied directly into the soil, it has low activity, due to the high adsorption by soil constituents [2]. To evaluate the specific interactions between metals in the soil and glyphosate is the main step in understanding the low activity of organophosphate herbicide. Thus, the goal of this work is to investigate the structural, thermodynamic and electronic effects that govern the complexation between glyphosate and some metals in order to rationalize the inactivation process of organophosphate herbicides. The final geometries of compounds and the free energy values of complexation were obtained using DFT at B3LYP/6-311++G(d,p) level. The solvent effect was evaluated using the Polarized Continuum Model (IEF-PCM). Furthermore crystal coordinates of EPSP synthase and glyphosate were taken from the PDB (1G6S). The metallic complexes were docked into the EPSP synthase binding sites using the Molegro Virtual Docker. Firstly, the stability order for metallic complexes of glyphosate with divalent cation was $Zn^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+}$. On the other hand, among the trivalent cations studied, the stability order was $Co^{3+} > Fe^{3+} > Cr^{3+} > Al^{3+}$. Despite the zinc ion being one that forms the most stable complex with glyphosate, it interacts much lesser intensely with the active site of EPSP synthase when compared to other complexes studied. Actually, the glyphosate-Fe complex showed the highest stabilization in the active site of EPSP synthase due to the highest number of hydrogen bonds with the amino acid residues Lys-22 and Gln-171, which seems to be of great importance for stabilization of the complexes at the active site of the enzyme EPSP synthase.

Support: CNPq, CAPES.

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XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
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Thermodynamics of fullerene aggregates in aqueous media

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Key-words: Fullerenes, aggregation, molecular dynamics

Fullerene C_{60} and its derivates are carbon nanostructures that have attracted much attention from many areas of nanoscience. In the recent years, the solubility of C_{60} in many solvents has been investigated due to the emergent technological and biomedical applications. This molecule exhibits extremely low solubility in water and other polar liquids. However, despite the strong hydrophobic character, recent studies suggest that, using different experimental techniques, the C_{60} molecules can form stable colloidal aggregates in aqueous media. These structures have been called nano-C_{60}, because the average diameter size of molecular aggregates that have been found. The biomedical application of the fullerenes has been described as one of the most promising applications of nano-C_{60}. The properties of these structures have been reported in many experimental studies. However, the thermodynamics of nano-C_{60} is not yet well understood. It is known that solvent plays an important role as a mediator of interactions between fullerenes, influencing the stability of nano-C_{60} in aqueous solution.

The goal of this work was to investigate the aggregation mechanism of fullerenes in aqueous media by using classical molecular dynamics simulations. To this end, we employ Lennard-Jones parameters of OPLS-AA force field validated in previous work to simulate the thermodynamical properties of nano-C_{60}. Simulation boxes composed by 4, 8, 16, 32 and 64 fullerene molecules were used to calculate the properties of solutions in a running length of 15 ns in two series of simulations. In the first one, the concentration was kept in 0.10 wt% by varying the mass proportion between the solution components. In second simulations series, the concentration was changed in each solution (0.03, 0.05, 0.10, 0.18 and 0.31 wt%). The obtained results to the solutions with higher concentrations show a tendency to formation of aggregates with particle-size larger than found in lower concentrations solutions. The results also suggest that the aggregation is a process strongly dependent on the concentration. All calculations were performed using the GROMACS 4.5 package.

Support: CNPq, FAPESP, and UFABC.

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"An ONIOM characterization of the catalytic mechanism of Peroxiredoxin V: ¿Why are they so fast?"

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Key-words: Peroxiredoxin V, ONIOM, Catalytic mechanism

Peroxiredoxin V (PrxV) is a thiol-dependent peroxidase, member of the peroxiredoxins superfamily. Two cysteine residues are involved in the catalytic mechanism: a peroxidatic one -Cys47- attacking the substrate (H_2O_2, peroxynitrite $ONOO^-$, or organic peroxides) to give sulfenic acid (RSOH), and a resolutive one -Cys151- reducing RSOH to establish an intramolecular disulfide bond [1], a fact that places PrxV into the 2-Cys atypical peroxiredoxin group [2]. The process occurs with high reaction rates (*e.g.* 10^7 $M^{-1}s^{-1}$ for $ONOO^-$) [3]. Whereas a clear explanation of why these enzymes are so fast is still lacking, recent studies suggest that transition state (TS) stabilization could play a key role in catalysis. It has been shown that Arg127/Thr44/Pro144 residues would be main actors in TS stabilization [4]. To gain insight into the structural features responsible for these observations at a sub-molecular level, a comprehensive characterization of the reaction mechanism leading to RSOH in the protein environment was performed using an ONIOM (DFT:AMBER) strategy. Advantage is taken on the availability of crystallographic structures of PrxV and previous explorations on a free Cys + H_2O_2 reduced representation conducted with *ab initio* correlated methods [5]. Our results show that the enzyme-substrate hydrogen bond network established at the active site could be responsible for the catalytic power of PrxV.

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"Development of Dengue Proteases Inhibitors by Molecular Modelling"

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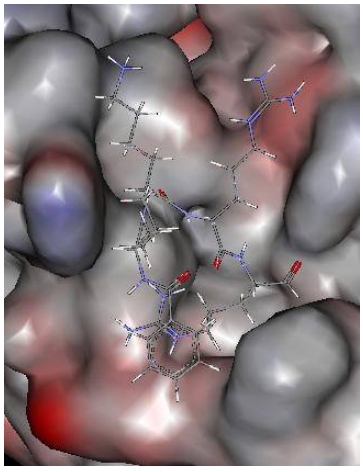
Key-words: Molecular Modelling, protease, dengue, inhibitors.

Dengue virus (DV) belongs to the family of Flaviviridae and is the most prevalent arthropod transmitted virus in humans. The global distribution of the DV infections is comparable to malaria, in which 2.5 billion people are living in the risk area and mostly in the tropical and subtropical region. In addition, no vaccine or antiviral therapies are available for the prevention and treatment. Recent studies showed a serine protease, called NS3pro (PDB: 2FOM), as an important target for development new antiviral agents. This enzyme interferes with viral replication and maturation. Although this enzyme is available in PDB, this is not complex with any inhibitor. Thus, the main goal of this study is describe the active site of NS3pro by molecular mechanic (MM) and docking approaches. Initially, the atomic coordinates of Bz-Nle-Lys-Arg-Arg-H inhibitor were transfered from crystal structure of West Nile virus (WNV) protease, which share 45% sequence identity and 80% sequence, to 2FOM generating a complex between inhibitor and 2FOM. This complex was refined by molecular mechanics (MM) calculations using *ff*03 force field in implicit solvent model. Following, the refinement complex was used for docking studies between 12 tetrameric peptidomimetic inhibithors, which were previously optimized by PM6 semi-empirical method, and prepared protein through Autodock Vina. As a result, the re-dock simulation was able to fit the aldehyde warhead in a convenient position for the nucleophilic attack by Ser164, one of members of catalytic triad (Ser164, His80, and Asp104). The whole binding site is composed by Trp79, His,80, Val101, Asp104, Leu187, Phe159, Ser160, Thr163, Ser164, Tyr179, Gly180, Gly182, Val183, Val184, and Thr190. In addition, hydrogen bonds were formed between His80, Val183 with inhibitor. The binding energy obtained by dock methodology ranged from -6.2 to -5.0 Kcal/mol. These results suggest a good model for further reaction path studies by QM/MM approach, and they address for the development of new generation of antiviral compounds through rational drug design methods.



Support: FAPEMIG.

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Applicability of DFT functionals to study PtPb electrodes with DAM methodology

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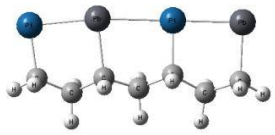
Key-words: DFT, Adcluster, DAM, Platinum, Lead, Formic Acid.

Electrochemical studies using carbon supported anodes demonstrated that the Pb presents an important synergic effect relative to the formic acid oxidation, when the catalyst is composed by Pt and Pb [1]. In this work, we have used the Dipped Adcluster Model (DAM) [2] to study the complete oxidation mechanism of the formic acid. For the computational model, we constructed a PtPb/C cluster with different proportions. Formic acid was studied in several positions to compare its interaction with the catalyst. We have compared three functionals M05-2X, M06 and B3LYP with LANL2DZ small-core pseudopotential basis set as implemented in Gaussian09 software. Geometries of clusters and adclusters (adsorbed molecule plus metallic cluster) were fully optimized. The absence of imaginary frequencies was a criterion to ensure that the optimized structures represent minima in the potential energy surface. Interaction energies (E_{int}) obtained with this methodology (with B3LYP) for formic acid and pure Pt clusters ($0{,}019 < E_{int} < 0{,}189$) are in good agreement with plane wave calculations [3]. Table 1 presents selected E_{int} obtained with all functionals for the cluster presented in Fig. 1.

Table 1. Interaction energies obtained for the cluster presented in Figure 1.

		E_{int} (eV)		
	Formic acid initial position	B3LYP	M05-2X	M06
	OOH	0,189	0,849	0,201
	OH	0,155	0,863	0,150
Figure 1. PtPb cluster.	H	0,019	0,718	-0,006

M05-2X overestimates E_{int}, probably because it was not developed for metals. There is a good agreement between B3LYP and M06. The comparison of formic acid positions on pure-Pt against PtPb clusters gives evidences about the Pb synergic effect relative to the oxidation.

Support: UFABC, CNPq, FAPESP.

[1]G.S. Buzzo et al. J. Braz. Chem Soc. **21** (2010) 185-190.
[2]T. Watanabe et al. Surface Science **603** (2009) 641–646.
[3]C. Hartnig *et al.* Journal of Electroanalytical Chemistry **607** (2007) 133–139.

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Graphene-like Structures of Boron and Silicon: A First-Principles Study

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Key-words: Boron, Silicon, Honeycomb structures, DFT

Since the discovery of superconducting quaternary borocarbides[1] and the high temperature non-oxide superconductor MgB_2[2], boron compounds have gained renewed interest. A still poorly known group of boron containing solids are the silicon boron compounds, for which various phases have been suggested[3-4]. In the present work we investigate the electronic properties of a graphene-like structure made of alternate silicon and boron (Fig. 1), using first-principles spin-polarized density functional calculations.

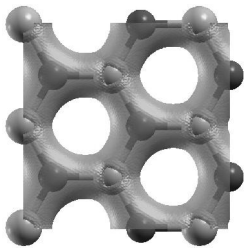

FIG. 1.The hexagonal silicon boron sheet with an electron density similar to that of graphene.

Different from graphene, which is a gapless semiconductor, the hexagonal silicon boron (h-SiB) sheet is predicted to form a metallic material, because of the overlapping between the singly occupied $3p_z$ orbital of Si and the empty $2p_z$ orbital of B. However, due to this weak overlapping h-SiB sheets are not able to be staked into 3D graphite-like structures, leading to a new hexagonal phase. On the other hand, the h-SiB sheet presents a good structural stability, with a cohesive energy of 9.42 eV/unit cell and with a boron silicon bond length of 2.0 Å. In contrast to graphene, the two highest occupied σ-bands and the occupied π-band are crossing the Fermi energy as shown in Fig. 2.

Moreover, the sheets can be rolled into single-wall nanotubes of which we examine the properties of the smaller zigzag and armchair tubes. Both types are predicted to form metallic systems.

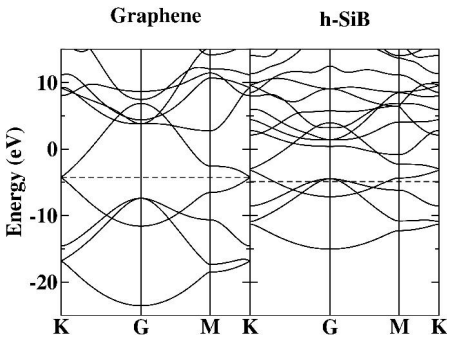

FIG. 2. Electronic band structures along the high symmetry points.

Support: CNPq.

[1] Cava, R. *et al. Nature* **367,** 146 (1994).
[2] Nagamatsu, J. *et al. Nature* **410**, 63 (2001).
[3] Imai, Y. *et al. J. Alloys Compd.* **347**, 244 (2002).
[4] Chen, H. M. *et al. J. Alloys Compd.* **481**, 182 (2009).

Analysis of Quantum Properties of Bioactive Compounds with Affinity for TGF-β1 Receptor

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Key-words: TGF-β1 receptor, bioactive compounds, hartree-fock method

TGF-β (Transforming Growth Factor) is a protein that is involved in many biological processes, including control of cells proliferation and differentiation, apoptosis, embryonic development, endocrine function and tissue repair. TGF-β1 receptor propagates an intracellular signaling that forms a protein complex capable of reaching the nucleus and modulate gene transcription[1,2]. So, the main objective of this study is calculating some quantum chemical properties for a set of compounds that have affinity for TGF-β1 receptor. Structures of the molecules studied in this work can be visualized in Figure 1. Geometry optimization and calculation of the electronic properties (see Table 1) were conducted using Hartree-Fock method, with 6-31G* basis set, implemented in the Gaussian09 computational package.

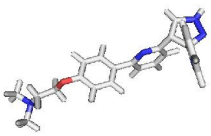
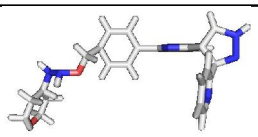
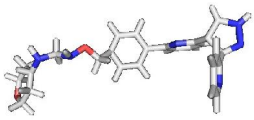
Structure		
		
1	**2**	**3**

Figure 1. Structure of compounds studied in this work.

Table1. Values of calculated properties

Properties	1	2	3
IC_{50} (μM)[1]	0.014	0.093	1.691
E_{Total} (a.u.)	-1231.229	-1437.567	-1476.766
E_{HOMO} (a.u.)	-0.309	-0.299	-0.308
E_{LUMO} (a.u.)	0.069	0.068	0.067
***gap* E_{LUMO}-E_{HOMO}(a.u.)**	0.378	0.367	0.375
μ (Debye)	3.777	4.794	5.101

From the results shown in Table 1, we can observe there is a significant difference among the values of dipole moment, allowing to propose that the compounds can interact with the active site residues of the TGF-β1 receptor by dipole-dipole or other electrostatic interactions. Therefore, the results obtained in this study indicated that the analysis of quantum chemical properties can influence the interaction between the compounds studied and TGF-β1 receptor.

Support: L'Óreal/ABC/UNESCO, FAPESP, CNPq, CAPES.

[1] Gellibert, F.; Gouville, A.; Woolven, J.; Mathews, N.; Nguyen, V.; Bertho-Ruault, C.; Patikins, A.; Grygielko, E. T.; Laping, N. J.; Huet, S.; *J. Med. Chem.* **2006**, 49, 2221.
[2] Massague, J.; *Annu Rev. Biochem*, **1998**, 91, 753.

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Molecular Basis of Hyperthermophilicity of Laminarinases Studied via High Temperature Molecular Dynamics Simulations

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Key-words: Gycosyl hydrolases, thermostability, molecular dynamics.

Glycosyl hydrolases (GH) are enzymes capable of breaking the glycosidic linkage of polysaccharides and have considerable industrial and biotechnological applications. Driven by the later applications, it is frequently desirable that GH display stability and activity under extreme environment conditions, such as high temperatures and extreme pHs. Here, we present molecular dynamics simulation studies aimed to comprehend the molecular basis for the thermal stability of this class of enzymes. The strategy employed in this study was to compare the simulations of the hyperthermophilic laminarinase form *Rodhothermus marinus* (RmLamR), with a thermophilic and a mesophilic homologue enzymes. As most thermostable protein, RmLamR contains a relatively large number of salt bridges. These are not randomly distributed on the structure, but form clusters interconnecting β-sheets of the catalytic domain. It could be seen in the case of the mesophilic enzyme that charge–charge interactions permeating the hydrophobic core contributes to destabilize the structure by facilitating water penetration into hydrophobic cavity. Furthermore, we demonstrate that the mobility of the side-chains is perturbed differently in each class of enzymes. The side-chains of loop residues surrounding the catalytic cleft in the mesophilic laminarinase gain mobility and obstruct the active site at high temperature (363K). By contrast, thermophilic laminarinases preserve their active site flexibility, and the active-site cleft remains accessible for recognition of polysaccharide substrates. At 500K, we studied the denaturation mechanisms in order to evaluate the stability of the different regions of these enzymes. The present results provide structural insights into the role played by salt-bridges and active site flexibility on protein thermal stability and may be relevant for other classes of proteins, particularly glycosyl hydrolases.

Support: FAPESP and CAPES.

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Phase Diagram and Waterlike Anomalies in Core-Softened Shoulder-Dumbbell Complex Fluids

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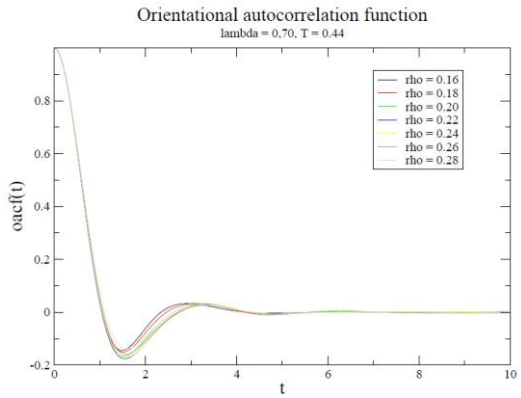
Key-words: Waterlike anomalies, Soft-core potential, Molecular dynamics

Monomeric particles interacting through a core-softened potential like the shoulder potential are perhaps the simplest model able to reproduce waterlike anomalies. This system is, however, isotropic, while most systems exhibiting anomalies in nature are in fact anisotropic. To add anisotropy in one direction to this system the monomers could be linked (with a distance λ), becoming rigid dumbbells. Using molecular dynamics, we have studied waterlike anomalies in a system composed of dumbbell molecules interacting through a core-softened shoulder potential. This system presents anomalous behavior regarding density maximum, diffusivity and structure with same hierarchy as in water and in a much broader region of the pressure-temperature phase diagram than the monomeric model. Besides, in the dumbbell system we can evaluate the rotational behavior, which is also anomalous. Analyzing the orientational autocorrelation function along isochores we found a surprisingly non-monotonic behavior, as seen in the following figure.



Rotational autocorrelation function for shoulder-dumbbell molecules with lambda = 0.70 and several densities

It is known that in SPC/E water the underlying mechanism responsible for the diffusion of water couples its translational and rotational movements. We also evaluate if in the dumbbell system a similar mechanism occurs. In order to achieve this we multiply the diffusivity constant by the reorientational relaxation time and analyze the product. We have found that, for state points within the region of thermodynamic anomalies this product is somewhat constant, meaning that these movements are, at least to some extent, indeed coupled.

Support: Fapergs

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Copper(I) AMBER parameter set for Zn,Cu-SOD bound to oxygen rich ligands

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ABCSim, Centro de Ciências Naturais e Humanas, Federal University of the ABC Region, Rua Santa Adélia, 166, CEP 09210-170, Santo Andre, SP, Brazil.

Key-words: molecular dynamics, metalloenzymes, superoxide, Cu,Zn-SOD.

An empirical AMBER Hamiltonian was parameterized using a model for the copper-zinc superoxide dismutase (Zn,Cu-SOD) active site. The model site constitutes of a central copper(I) atom bound to imidazole rings representing the histidines in the protein. Two ligands of possible relevance to the functioning mechanism of the enzyme were considered in the paramererization: closed shell OOH^- and open shell protonated superoxide ($OOH^\cdot$). A rigid framework was assumed when generating potential energy curves for internal bond and angle degrees of freedom. Equilibrium bond distances and angles and their corresponding force constants were adjusted to these potential energy curves. Density Functional Theory (DFT) along the B3LYP functional and the LanL2DZ basis functions were used for the quantum chemical reference calculations.

Molecular dynamics calculations of Zn,Cu-SOD using a trial parameter set starting from a high resolution crystal structure (PDB code 2C9V) revealed a tendency of the model to underestimate or completely neglect the pyramidalization effect induced by the ligand. Moreover, differences between ligands when forming a complex with the active site make it difficult to obtain a single parameter set for both OOH^- and $OOH^\cdot$. A procedure was attempted to solve this problem by imposing restraints on the model active site for the parameter set determination. Dihedral angles parameters were determined from energy differences generated by DFT calculations on reference structures. Preliminary results for model systems using the newly developed parameter set will be presented. The Gaussian03 code was used for all quantum chemical calculations while the AMBER suite was used for all empirical Hamiltonian calculations in this work.

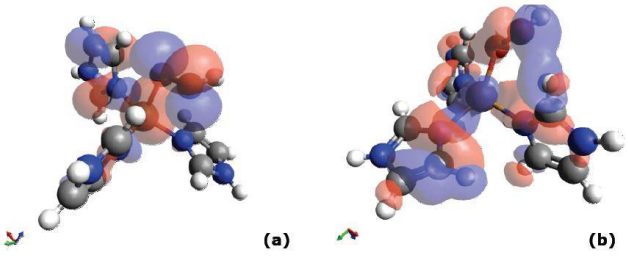

Figure 1: Model active site representation for Cu,Zn-SOD bound to OOH. HOMO isosurfaces are superimposed to the figure. (a) With restraints (b) No restraint.

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Theoretical study of Falcipain-2 using the Docking Molecular technique

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Key-words: Malaria, ligands, enzymatic study.

Malaria is an infectious fever caused by a protozoan of the gender *Plasmodium*. This disease has a high incidence in the Amazon region and is a potential clinical severity. For this reason, we tried to study the Falcipain-2 enzyme (FP2) which is one of the main proteases of *Plasmodium falciparum* (Figure 1). This protease is responsible for degradation of the hemoglobin, the main source of amino acids for the parasite. The docking molecular technique was used to find the best flexible ligand remaining in the proper conformation, it forming the ligand-protein complex toward explore different aspects of biochemical processes. We have selected the following ligands: Chloroquine, Doxycycline, Halofantrine, Hydroxychloroquine and Mefloquine. Ten conformations were generated for each ligand and the best energy conformations were calculated: -4.6 kcal /mol, -5.7kcal /mol, -6.0kcal/mol, -5.2kcal/mol and -6.3kcal/mol. In this study, we used *in silico* methods to investigate the interactions of ligands with FP2, the important residues are TYR93, SER158, HIS183, ILE94, CYS 51, GLY92, GLY49, TYR 90, GLN45, TRP52, ASN 182, GLY 9 and PRO 181. These results can be used to develop new inhibitors of FP2.

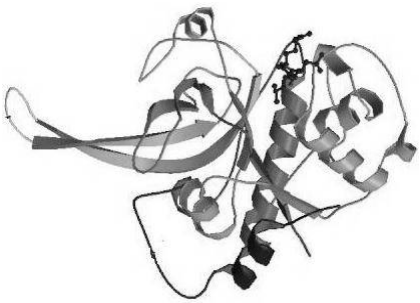

Figure 1. Representation of the enzime FP2 complexed with the ligand crystallography.

Support: UFPA and LPDF.

Theoretical Studies of Renin Inhibitors Associated with Treatment of Cardiovascular Diseases

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Key-words: Hypertension, Renin Inhibitors, Quantum-chemical methods.

Hypertension is a risk factor for cardiovascular diseases and is ranked among the top causes of death in the Western world. It is known that angiotensinogen is the only known substrate of renin inhibition and this phase would be a very effective strategy to combat hypertension[1]. Thus, bioactive compounds can be planned more effectively, with the purpose to control hypertension and associated cardiovascular diseases. In this work, the main objective is the characterization of the electronic effects of three renin inhibitors. The compounds used in this study are shown in Figure 1. The geometry optimization and calculation of electronic properties (Table 1) were performed with the B3LYP functional and 6-311G* basis set, implemented in the Gaussian09 computational package. The value of log P (octanol/water) was calculated using the software ACD/Labs, based on experimental data.

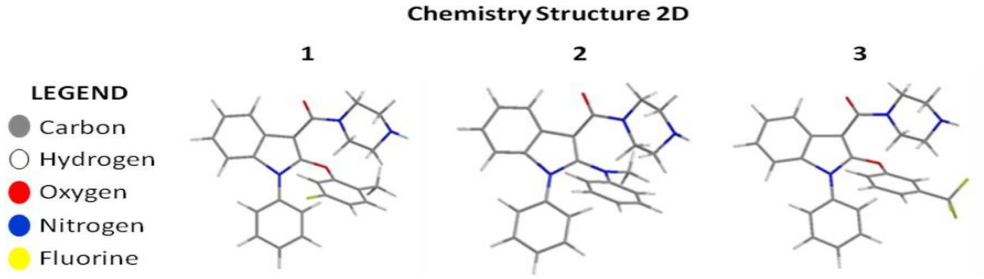

Figure 1. Chemical structure of the compounds studied.

Table 1. Value of electronic properties calculated

	1	2	3
pIC_{50} (μm)[1]	8.300	5.500	5.050
E_{TOTAL} (a.u.)	-1420.0786	-1300.6880	-1618.6241
E_{HOMO} (a.u.)	-0.214	-0.207	-0.217
E_{LUMO} (u.a.)	-0.037	-0.047	-0.047
gap **(E_{LUMO}-E_{HOMO} – a.u.)**	0.177	0.160	0.170
μ (Debye)	6.247	4.646	2.400
log P	4.850	3.890	4.190

The analysis of Table 1 allows us to state that the energy gap for the compounds studied did not have any significant difference; compound 1, that has a high value of dipole moment, indicating a greater interaction with the aminoacid residues that are part of the active site of renin, via interactions electrostatic/dipole-dipole; the coefficient of lipophilicity (log P) of compound 1 shows that this one has a greater ability to cross the biological membrane. Therefore, the characterization of the electronic and lipophilic properties of renin inhibitors is very important for a better understanding of the renin-angiotensin system, responsible for the development of cardiovascular diseases, especially hypertension.

Support: *FAPESP, CNPq, CAPES.*

[1] Scheiper, B.; Matter, H.; Steinhagen, H.; Stilz, U.; Böcskei, Z.; Fleury, V.; McCort, G.; *Bioorg. & Med. Chem.*, **2010**, *20*, 6268-6272.

The Dynamics of the WPD Loop of the Tyrosine Phosphatase YopH Mutant W354F.

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Key-words: Molecular Dynamics, YopH Mutant W354F, WPD loop.

The bacterial protein tyrosine phosphatase (PTP) YopH is an essential virulence determinant in *Yersin* spp., causing gastrointestinal diseases and the plague. YopH correspond to the most efficient catalytic system known, catalyzing the hydrolysis of phosphate monoester dianions with a relative rate constant for the uncatalyzed reaction of ~ $10^{20}s^{-1}$.[1] The active site of the YopH, similarly to the observed in the eukaryotic protein tyrosine phosphatases, is defined with a flexible WPD loop that harbors the general acide/base Asp-356 residue essential for the catalysis. The movement of the WPD loop plays a central role in the PTPase mediated catalytic process., where crystallographic structures have revealed that the WPD loop adopts either open (enzymatically inactive), or a closed (enzymatically active) conformation. In relation to this system, recent studies have been shown that the catalytic activity of the YopH is significantly changed by the mutation of some residues of the active site manly the mutation involving the residues of the WPD loop.[2] Based on recent results obtained from the mutagenesis process applied to the YopH enzyme, we believe that a detailed investigation of the dynamics of the WPD loop, with and without the presence of the substrate in the active site, may provide important insights into the mechanism of action, which could to help design of selective YopH inhibitors to act as antibacterial agents.

In this work, we carried out large molecular dynamics simulations for the wild type YopH and for the YopH mutant W354F in order to analyze the dynamic of the WPD loop of these two proteins and to compare the results. These studies were carried out in the isobaric-isothermal (NpT) ensemble at T=300K and p=1atm with the proteins solvated for 28,331 water molecules positioned in a cubic box with 95.8 Å of side. Before of the large molecular dynamics simulations of 15 ns, both the systems were submitted to two heating steps of 2 ns at 100 and 200K. Details about the simulation protocol will be discussed during the presentation. Consistent with experimental observations, our results show that the WPD loop of the two species investigated presents a flexibility and fluctuates between the open and closed conformation. Our results also show that the mutant specie has a higher WPD loop mobility than the wild protein and the WPD loop in the mutant close and open more quickly of that in the wild protein.

1- Wolfenden, R. *et al Proc. Acad. Sci U.S.A.*, **2003**, 100, 5607-5610.
2- Brandão, T. A. S. *et al J. Am. Chem. Soc.*, **2009**, 131, 778-786.

Support: FAPEMIG, CNPq, CAPES and INCT-Catálise.

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Dockthor: Development and Validation of a new Docking Program using a Diverse Set of Ligands and Molecular Targets

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Key-words: Receptor-ligand docking, Genetic Algorithm, MMFF94 force field

Receptor-ligand docking programs are important tools for structure-based drug design studies. This work presents the new version of Dockthor with: (i) a new and complete computational implementation of the multiple solutions genetic algorithm; (ii) implementation of the MMFF94 molecular force field; (iii) development of auxiliary tools for automatic parameterization of ligands, cofactors and receptors; (iv) a new option for ligand virtual screening studies. This program version is developed in C++ with few fortran routines. The search mechanism is based on a steady-state genetic algorithm (SSGA) with a modified restrict tournament strategy (MRTS) using a phenotypic insertion scheme. The SSGA-MRTS ensures the prediction of multiple ligand binding modes in a single run and also the program ability to deal with highly flexible ligands. Five genetic operators are used during the SSGA evolution step with an adaptive probabilities method. The fitness function is based on the MMFF94 force field using grid maps for the ligand-receptor intermolecular energy calculations.

The Dockthor program was validated in two test sets. The first one comprises five highly flexible HIV-1 protease ligands. The second one consists of 35 ligand-receptor complexes with great ligand structural/chemical diversity and receptors covering 18 protein families. Thirty independent redocking experiments were done for each complex, without any ligand/receptor pre-optimization, using a RMSD ≤ 2.5 Å from the experimental structure as success criterion. The results are considered very good in the following aspects: (i) a success rate about 80% (90%) for the first test set, considering the lowest energy (lowest RMSD) solution in the final population of each run; (ii) a success rate about 94% (99%) for the second test, considering the lowest energy (lowest RMSD) solution; (iii) excepting two cases, all the lowest energy solutions, considering all runs, showed a RMSD ≤ 2.5 Å from the experimental structure.

The very satisfactory results show that the program is able to be used in real receptor-ligand studies. The Dockthor facilities will permit its availability and use by the academic community and research groups acting in the rational drug design field.

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Long Time Scale Molecular Dynamics study of the Bacillus subtilis SecA motor protein: coupling between large amplitude motions and ATP/ADP binding"

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Key-words: SecA, Molecular Dynamics, Poisson-Boltzmann, AMBER

In all living cells, regulated passage of specific proteins across the cell membrane occurs through a universally conserved secretory channel. In bacteria and chloroplasts, the energy for the mechanical work of moving polypeptides through that channel is provided by SecA, a regulated ATPase, which uses ATP hydrolysis as the energy source. It is not well established, though, how the molecule utilizes the ATP chemical energy to perform work. In this work, we use computer simulation as a tool to understand the process. Starting from a recently determined *Bacillus Subtilis* SecA crystal structure (PDB code 1TF2) molecular dynamics simulations performed using the AMBER force field showed a large conformational change when ADP is replaced by ATP in the binding pocket. This indicates a possible mechanism for SecA protein motor functioning. Further replacement of ATP by ADP failed to bring the system back to its initial conformation, showing an asymmetry of its free energy conformational change profile. We were also able to reconcile structural differences between ADP bound crystal structures subjected to monomeric and dimeric crystallization conditions (PDB code 1TF2 vs. PDB code 1M74). In order to characterize the large conformational changes of the protein, normal mode analysis and domain motion (Dyndom) studies are presented in detail. Results from these studies together with electrostatic analysis using a Poisson-Boltzmann approach for the SecA-ADP/ATP binding energy along long scale molecular dynamics trajectories were used to suggest a possible mechanism for SecA motor functioning. The results suggest that the chemical energy might not be used to perform work directly, but for resetting the system to its initial state, allowing the protein to undergo further cycles to generate work.

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ELECTROCHEMICAL AND QUANTUM STUDIES OF THE SERINE, CYSTEINE AND METHIONINE AS CORROSION INHIBITORS FOR COPPER

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Key-words: Aminoacids, Corrosion inhibitors, DFT, Electrochemistry.

It is usual to study corrosion inhibitor molecules by electrochemical or gravimetric methods. However, these experimental procedures do not allow the elucidation of the interaction inhibitor molecules-metal surface and they also do not allow predicting the corrosion inhibition ranking. Computational methods emerge as a powerful tool to overcome these deficiencies of the experimental studies. Furthermore, there is an interest to study environmental friendly molecules as corrosion inhibitors for iron-based and copper-based materials such as aminoacids, because they are non-toxic molecules. Thus, this wok investigates L-serine, L-cysteine and L-methionine as corrosion inhibitiors for copper using electrochemical techniques and computational methods. The electrochemical studies were carried out in 0.5 mol dm^{-3} H_2SO_4 containing 0.01 mol dm^{-3} of the studied aminoacids, at room temperature, with potentiodynamic linear polarization (PLP) and electrochemical impedance spectroscopy (EIS) techniques. The computational study was made using the following softwares: Forcite and $DMOL^3$. The software Forcite was used in conformational analysis of the aminoacids, obtaining low-energy conformers, these structures were relaxed and their properties were calculated by the software $DMOL^3$. Initially, the aminoacids of interest were allowed to interact with the copper surface in 16 different guidelines at distances ranging between 2.5 and 4.5 Å, using a median level of calculation. After finding the orientation of the molecule on the metal surface that presents lower energy value, calculations were made with high accuracy level in order to find the energy of interaction, this sequence of calculations was performed in three different positions on the metal surface, interacting directly on a surface atom, between two atoms and between three. The electrochemical tests showed that aminoacids containing sulfur are the most efficient corrosion inhibitors and tend to form a complex between the molecule and the metal surface, the order of inhibition obtained was serine < cysteine < methionine. The quantum analysis proved that serine was the aminoacid that showed the highest values of interaction energy and lowest selectivity, when considering both molecular orientation and position in relation to the surface. Cysteine presented intermediate values whereas methionine showed the lowest interaction energy and the highest selectivity, indicating the trend of formation of a complex between the molecule and the metal surface.

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Isomers on the $^1[H_3, C, F]$ potential energy surface: A CCSD(T) investigation

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Key-words: methyl fluoride, CCSD(T), dissociation channels

Methyl fluoride (CH_3F), an organo-halogenated that plays a significant role in reactions in plasmas for the production of microelectronic components [3], can be generated directly from the reaction of methyl radical with fluorine atom in their ground states. Wang *et al.* [1] investigated the kinetics for this reaction, as well as the process involving hydrogen abstraction from the methyl radical, using different methodologies for calculating the electronic structure: DFT, MP2, CCSD (T) and CI with an atomic basis set [6-311 + G (3df, 2p)]. The present work reports a state-of-art characterization of fluorine-carbon species on the potential energy surface $^1[H_3, C, F]$. Coupled cluster theory, CCSD(T), using the series of correlation consistent basis sets aug-cc-pVnZ (n = D e T), was employed to obtain the energetic quantities involved in the isomerization processes on this surface. The structure and vibrational spectroscopy for all stationary points on the PES were also investigated.

Seven stationary singlet states have been located on the PES: six of them associated with minima and one with the transition state (located at 101.68 kcal/mol) connecting the global minimum with the dissociation channel CHF + H_2. For the CCSD(T)/aVTZ results, the CH_3F molecule is the global minimum on the surface. Additionally, four other possible barrierless dissociation channels for the global minimum: CH_3 + F, CH_2F + H, $^1CH_2$ + HF, and $^3CH_2$ + HF, located at 108.19, 105.30, 95.34, 84.94 and 98.29 kcal/mol, respectively, were also investigated.

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Support: FAPESP - CNPq.

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The Influence of Phenol Additives in Self-Metathesis Reaction of Olefins

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Key-words: Self-Metathesis, DFT, Grubbs catalyst.

The area of ruthenium-catalyzed olefin metathesis reactions is a remarkable topic in current chemistry because of its relevance as an efficient method to form C=C double bonds. Although the second-generation systems display enhanced activity and thermal stability relative to first-generation catalysts, the formation of secondary metathesis products (SMPs) under certain circumstances can reduce significantly the selectivity of the reaction using this catalytic system. Several studies have shown that the performance of certain olefin metathesis reactions catalyzed by the Grubbs catalyst has been enhanced by the simple addition of phenol. In this study we investigated the influence of the solvent and additives on the main mechanistic steps of the olefin metathesis catalyzed by a second-generation catalyst, as shown in figure 1. Structural and electronic properties of all species along the catalytic cycle were obtained at the Density Functional Theory (DFT) level (CAMB3LYP/BSI). BSI represents the basis set used that is composed of the SBKJC effective core potential and its associated double-ξ valence basis functions for Ru and 6-31G(d) basis set for all other atoms. Solvent effects were included by means of the polarizable continuum model (PCM) in toluene (ε=2.74) and CH_2Cl_2 (ε=8.93). The structural parameters calculated are in good agreement with experimental results[1]. The dissociation of the phosphine, which is the initiation step of the cycle were described with good agreement with the experimental value. Our results predicts a dissociation energy (ΔE_g) of 40.8 kcal/mol, in line with experimental result ΔE_g = 36.9 kcal/mol [2]. To assess the influence of the phenol complexation to the catalyst in the initiation step, we performed a classical Monte Carlo simulation to positioning the phenol molecules based on Boltzmann weighted and then we selected, arbitrarily, one configuration containing the molecules of the first solvation shell. This, cluster (catalyst+ first solvation shell) was submitted to full geometry optimization and frequencies calculations at the CAMB3LYP/BSI level. These results will be discussed in further details during the presentation.

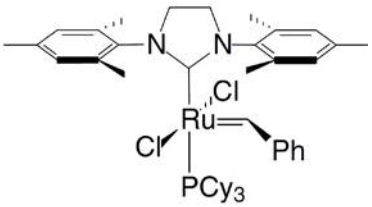

Figure 1 – Structure of second-generation Grubbs catalyst

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Support: FAPEMIG, INCT-Catálise and CNPq.

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A FORMULATION OF THE DYNAMIC COUPLING MECHANISM OF f-f INTENSITIES BASED ON THE OVERLAP POLARIZABILITY OF THE CHEMICAL BOND

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Key-words: lanthanides, actinides, f-f intensities, overlap polarizability.

The most relevant features of the spectral intensities of f-f transitions have been described by the forced electric dipole (FED) mechanism (Judd-Ofelt theory) and the ligand polarizability dependent dynamic coupling (DC) mechanism, which are operative when the f-ion (lanthanide or actinide) is located in a site that is not a center of inversion. The experimental determination of the Ω_λ intensity parameters does not distinguishes between these two mechanisms, from where one can realize the importance of reliable theoretical calculations. DC mechanism is described by point dipoles induced by an incident radiation field in the ligands. In this work, we report on a formulation of the DC mechanism in which these induced dipoles are brought into the overlap regions of the rather weak chemical bonds between the f-ion and the ligands, This is done by assuming that each of these dipole moments is proportional to the overlap polarizability (α_{OP}) of the chemical bond. The immediate advantage of this formulation is that there is an analytical expression for the polarizability of the region of overlap, leading to a clear relationship between the intensity parameters, covalency and structural aspects. The values of α_{OP} were estimated from data (Δε and ρ) obtained with the method INDO/S implemented in the ZINDO program. Several systems (compounds with lanthanide or actinide) were studied. It is important to mention that the parameters Ω_λ obtained with this new formulation better reproduce the experimental data when compared with the old methodology, without the inclusion of α_{OP} (Table 1).

Table 1 – Experimental and theoretical values of Ω_λ for $Eu(TTA)_3 2H_2O$.

Ω_λ (10^{-20} cm^2)	**Experimental values**	**Old estimated values**	**New estimated values**	**%d.c.**	**% α_{op} (d.c.)**
Ω_2	33	19.8	33.56	99.40	0.36
Ω_4	4.6	4.7	4.65	97.82	3.07
Ω_6	-	-	0.24	57.89	32.4

Support: CNPq, INCT-INAMI, CAPES, FINEP

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"Estudo do espectro eletrônico do $[Cr(CN)_6]^{3-}$ e $Co(CN)_6]^{3-}$ usando TD-DFT"

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Key-words: Hexacianometalatos, DFT, espectro eletrônico

Devido as propriedades magnéticas e fotoquímicas exibidas pelos derivados do Azul da Prússia, os cianometalatos, esses compostos têm sido bastante estudados. Essas propriedades estão intimamente relacionadas com as transições eletrônicas destes compostos. Assim, com a finalidade de entender o comportamento dessas transições, bem como a atribuição das bandas do espectro eletrônico, vários cálculos *ab initio* e semi-empírico foram realizados para alguns dos cianometalatos[1]. Bons resultados foram obtidos usando a metodologia CASSCF/CASPT2.[2] O espectro eletrônico de compostos de metais de transição também pode ser calculado usando a DFT empregando o formalismo TD-DFT.

O objetivo deste trabalho é calcular as exitações eletrônicas dos compostos de $[Co(CN)_6]^{3-}$ e $[Cr(CN)_6]^{3-}$ usando os funcionais B3LYP, Beckehandh e PBE0 com o conjunto de base land2dz com correções relativísticas para os átomo metálico e a base aug-cc-pVDZ para os átomos de C e N. Pretende-se também usar o modelo de solvatação Cosmo implementado no programa NWChem.

Os resultados são comparados com o valor experimetal e com os cálculos obtidos pelos métodos configuracionais. A tabela abaixo mostra alguns dos resultados obtidos para a banda de transferência de carga.

Tabela 1 – Banda de transferência de carga M→ L em cm^{-1}.

Complexo	Experimental[3]	CASPT2	Beckehandh	PBE0-cosmo
$[Cr(CN)_6]^{3-}$	38600	40324 [1]	41108	40412
$[Co(CN)_6]^{3-}$	50600	45007[2]	45971	52887

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"Structure and stability of the Si_4Li_n (n = 1 - 7) binary clusters"

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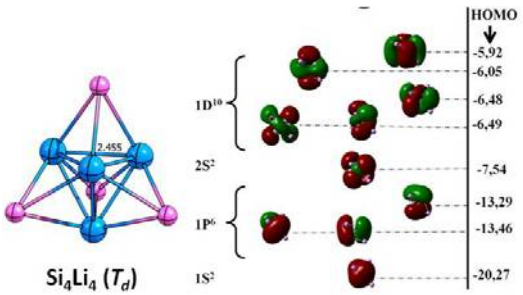
Key-words: Clusters, phenomenological Shell Model, aromaticity.

We have explored in detail the potential energy surfaces of the Si_4Li_n (n = 1-7) binary clusters. We found that the Si_4 fragment changes from a distorted planar rhombic structure to tetrahedral forms, as the number of lithium surrounding it increases. The stability of the title clusters is rationalized in terms of the phenomenological shell model PSM model.

Potential energy surfaces have been explored in detail employing the gradient embedded genetic algorithm (GEGA) program. The GEGA calculations were done using the B3LYP functional in conjunction with the Stuttgart pseudopotentials and their respective basis sets (SDD). The geometries and harmonic frequencies were recalculated for all the title clusters at the B3LYP/def2-TZVPP level of theory. Total energies of the structures that are local minima on the potential energy surface structures were calculated at the CCSD(T)/def2-TZVPP//B3LYP/def2-TZVPP level. To gain some insights into the bonding, a natural population analysis (NPA) was performed. All calculations were carried out with the Gaussian 03 program.

The growth pattern on the studied systems could be conditioned by a complementary or competitive equilibrium between electronic delocalization, adequate number of valence electrons, and the spatial conformation of the nuclei. The stability descriptors obtained from the electronic structure examination suggest that tetrahedral Si_4Li_4 cluster is a closed shell (20 valence electrons) highly stable cluster into the PSM.



Acknowledgements
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Analytical Potential Energy Curve for Cationic Diatomic Systems Based on q-Exponential Function

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Key-words: Analytical Potential Energy Curve, Diatomic Ions, Spectroscopic Properties and q-Exponential Function

The study of potential curves, dissociative channels, vertical double ionization potentials and transition rates for small dications has received growing attention. For almost all neutral and singly charged diatomic molecules, the ground state has only one stationary point, namely that at the minimum. The extended Rydberg function is the most satisfactory theoretical method for describing accurately the behavior of these neutral diatomic systems in the equilibrium region. The Murrell–Sorbie function subsequently has been extended successfully to represent singly charged diatomic ions. However, the extended Rydberg function is not satisfactory for doubly charged diatomic ions because these kinds of molecules have some new features that the potential curves may have both potential minimum and maximum or singly repulsive branch. Wang and co-authors propose a new analytical potential function including an ionic Coulomb repulsion term and a Varandas potential term, which can be used to describe the diatomic ions with both potential minimum and maximum or without any stationary point. In this work we propose new analytical potential functions for doubly charged diatomic ions. These functions are based in the generalized exponential function (q-Exponential) and are most flexible to build up the potential energy curves due to the inclusion of an additional parameter (q parameter). These new function were proposed generalizing the usual Bond Order and generalized Rydberg analytical potential energy function. To validate these new functions, we have calculated the force constant, spectroscopic constants and the rovibrational spectra for the Be_2^{2+}, He_2^{2+}, HF^{2+}, BH^{2+}, CH^{2+} and NH^{2+} molecular systems. The results presented in this work show that the new potential energy curves are sufficiently better when compared with the usual analytical functions and the experimental data.

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"Regiochemical differentiation of phenylpropanoids via GIAO-B3LYP ^{1}H and ^{13}C NMR chemical shift"

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Key-words: eugenol, isoeugenol, chemical shifts, NMR, GIAO

Eugenol (**1**) and isoeugenol (**2**) present different properties and uses, a usual behavior among natural regioisomeric compounds. Although the differentiation of such a pair of regioisomers by NMR techniques is a routine task in modern organic chemistry, it is not always a successful one.[2] In this scenario, the use of computational protocols for calculating NMR parameters as an auxiliary tool in structural elucidation has achieved promising outcomes. In this study we present the use of GIAO-DFT linear-regression-scaled-factor based protocols to determine NMR ^{1}H and ^{13}C chemical shifts (δ) of eugenol and isoeugenol.[3,4] Both isomers were submitted to stochastic (Monte Carlo) molecular-mechanics (MMFF) conformational analysis that led to the selection of 6 conformers for each one (ΔE < 5 kcal/mol). Geometry optimizations performed at B3PW91/cc-pVDZ level reduced to 3 (ΔE < 2 kcal/mol) the accepted conformers for each isomer, which had their NMR δ calculated at the B3PW91/cc-pVnZ (n = D or T) level using the GIAO method. The scaled δ values (δ_{scal}) were determined using linear regression analysis obtained from the calculated and experimental δ values. The statistical validation was carried out using the MAD (mean absolute deviation) and RMS (root mean square) values, in ppm, calculated between δ and δ_{scal}. The more accurate results, for both molecules, for ^{13}C δ_{scal} were obtained using DZ basis set [(**1**) DZ/TZ: MAD= 2.80/2.95 e RMS= 3.31 3.11/; (**2**) DZ/TZ: MAD= 1.65/1.93 e RMS=1.86/2.13], on the other hand, for the ^{1}H δ_{scal} the best results were obtained using TZ basis set [(**1**) DZ/TZ: MAD= 0.33/0.13 e RMS = 0.44/0.14; (**2**) DZ/TZ: MAD= 0.41/0.15 e RMS=0.54/0.18]. Thus as it was expected, for both molecules, the ^{1}H δ_{scal} were more sensitive to the enlargement of the basis set, from D to T, than the ^{13}C δ_{scal}. The results obtained at the B3PW91/cc-pVDZ//B3PW91/cc-pVDZ level, for ^{13}C, and at the B3PW91/cc-pVTZ//B3PW91/cc-pVDZ, for ^{1}H, were accurate enough to allow distinguishing the regioisomers. Thus the approach applied here, to determine (**1**) and (**2**) NMR ^{1}H and ^{13}C chemical shifts, arises as potential tool for differentiation of regioisomers.

Support: FAPERJ

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Aplicação do Método DFT/X3LYP no Estudo da Ligação de Hidrogênio Intramolecular em Compostos β-dicarbonílicos.

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Palavras chave: Compostos *β*-dicarbonílicos, Ligação de Hidrogênio Intramolecular, X3LYP.

A formação de Ligações de Hidrogênio Intramoleculares está relacionada com a estabilidade de vários compostos, em particular dos compostos β-dicarbonílicos: "os compostos β-dicarbonílicos são estabilizados por uma ligação de hidrogênio muito intensa, O-H···O, intramolecular, assistida por ressonância".

Este estudo expõe uma avaliação da formação da Ligação de Hidrogênio Intramolecular em compostos β-dicarbonílicos ($C_3H_2O_2R_2$) substituídos (R= CH_3, CN, H, NH_2, OH e SH), realizada em nível DFT, empregando o funcional híbrido X3LYP com o conjunto de base de Pople 6-311++G(d, p), apoiada pela QTAIM, proposta por Bader.

Dos principais resultados observados, constatou-se uma tendência de deslocamento do modo de estiramento vibracional da ligação O-H, doadora de próton para valores menores de frequência no espectro de infravermelho, causada pela formação da ligação de hidrogênio intramolecular, representando um deslocamento *red shift,* para todos os compostos estudados. De acordo com o substituinte empregado foi verificada uma variação nos valores da força de Ligação de Hidrogênio Intramolecular, sendo a ligação mais estabilizada aquela cujo grupo doador de elétrons é o NH_2, enquanto a mais fraca correspondeu ao composto substituído pelo grupo menos ativador da série em estudo, o grupo CN, de acordo com sequência: NH_2 (79,56 $kJmol^{-1}$) > CH_3 (63,96 $kJmol^{-1}$) > SH (55,90 $kJmol^{-1}$) > H (51,48 $kJmol^{-1}$) > OH (45,50 $kJmol^{-1}$) > CN (39,78 $kJmol^{-1}$).

O método X3LYP conseguiu descrever resultados para os substituintes CN e NH_2 de forma concisa, o que não foi possível para o restante da série, quando comparado a outros funcionais híbridos já empregados para o mesmo tipo de estudo: método DFT, com o funcional B3LYP e o método MP2 que apresentam entre si resultados análogos (Bezerra A. F., *Ligações de Hidrogênio Intramoleculares: Um Estudo Teórico de Compostos β-dicarbonílicos*. Programa de Pós-Graduação em Química, Departamento de Química, UFPB, 2009. Dissertação de Mestrado).

Suporte: CNPq

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"Prediction of three-dimensional structure of a segment of glycoprotein G1 of the *Bunyamwera virus* by molecular modeling"

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Key-words: *Bunyamwera virus*, Glycoprotein G1, Molecular homology.

Many viruses in the family *Bunyaviridae* cause emerging zoonotic infections in humans. Related viruses encephalitis, fever, headache, weakness, myalgia and rash and outbreaks have occurred in worldwide. Bunyamwera serogroup, genus *Orthobunyavirus*, have been isolated in the Amazon region since the late 50. Its genome is three-segmented: small (S), medium (M) e large (L). The M segment encodes two membranes glycoprotein G1 and G2 and another non-structural protein (NSm). The ectodomains of G1 and G2 form a heterodimer on the viral surface, and function as the viral spike proteins and G1 is the viral attachment protein. Thus, glycoprotein G1 is a potential target for vaccine and antiviral drugs. On the other hand, the structural determination of G1 by X-ray techniques was not possible. In this context, the aim of this study was predict the structure three dimensional of a segment of glycoprotein G1 by molecular modeling technique. The structure was predicted by molecular homology using as template PDB 2K9H from *Hantavirus*, and target sequence of glycoprotein G1 was obtained of a strain *B*. *virus*, code *Uniprot* P04505 (478-1433). The structure was modeled from residues 98-151 homologous to the tail of G1 *Hantavírus.* The model was obtained online by SWISS-MODEL Server. Modeled protein had 28% sequence identity and was validated by Ramachandran plot 81.6% of amino acid residues within regions of very favorable and RMSD of 0.2 Å. The results revealed a good stereochemistry quality and the active site remained key residues conserved. Our model protein is promising for further refinement molecular with potential therapeutic. Support: UFPA, LPDF, IEC, CNPq

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S100A12 dimerization analysis via constant velocity steered molecular dynamics simulations

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Key-words: Steered Molecular Dynamics, S100A12, GROMACS

S100A12 is a proinflammatory protein that is considered as a molecular target for the development of novel therapies. This protein can bind Ca^{2+} or Na^{+} by its EF-hand domains and Zn^{2+} or Cu^{2+} by a C-terminal histidine-containing motiff. Differential ion complexation imply in structural changes as well as oligomeric state modulation: from dimers in the absense of divalent ions to hexamers in the presence of Zn^{2+} and Ca^{2+}.

There's little information about the dynamic behavior of S100A12. With this study, and inside a broader context of simulations, we aim to cover this gap and hopefully help the development of novel therapeutical strategies.

We performed several constant velocity steered molecular dynamics simulations using GROMACS 4.5 suite varying both pulling velocity and force constant while monitoring the impact over the secondary structure.

Our results shows that helix I loses most of its secondary structure even in low velocity and low force simulations. This is in agreement with previous simulations which suggests that this helix's conformation is an important factor for the dimerization process.

Furthermore, the optimization of the pulling force and velocity while minimizing the structural impact have immediate methodological application for free-energy calculations via steered molecular dynamics simulations using Jarzynski equallity.

Support: CNPq

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Modified Lennard-Jones potential to predict physical chemical properties at the supercritical state

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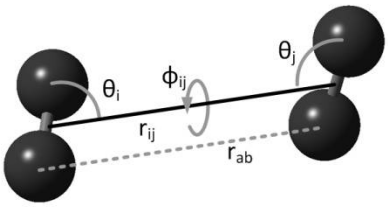
Key-words: intermolecular potentials, fluid properties, supercritical state

A supercritical fluid is a substance at a temperature and pressure above its critical point where distinct liquid and gas phases do not exist. In particular, the measurement of physical-chemical properties at the supercritical region is very difficult. On the other hand, theoretical approaches employing molecular dynamics methods to study fluids on most cases use empirical data to adjust simple model potentials. For this reason, the construction of model potentials based on first principle molecular calculations and its validation are considerable important. Most molecular dynamics calculations use simple intermolecular potentials formulations like Lennard-Jones. Recently, Vrabec[1] proposed a modified two-center Lennard-Jones potential plus point quadrupole moment (2CLJQ) which considers not only the distance between molecules, but also their spatial orientation. Vrabec's potential is constructed in the form, $U_{total} = U_{LJ} + U_Q$,

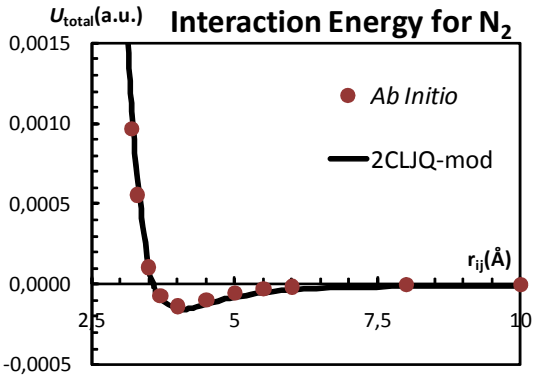


$$U_{LJ} = \sum_{a=1}^{2}\sum_{b=1}^{2} 4\varepsilon\left[\left(\frac{\sigma}{r_{ab}}\right)^{12} - \left(\frac{\sigma}{r_{ab}}\right)^{6}\right]$$

$$U_Q = \frac{3}{4}\frac{Q^2}{r_{ij}^{5}} f(\theta_i, \theta_j, \phi_{ij})$$

where Q is the centered quadrupole moment, obtained experimentally. Vrabec obtained ε and σ from empirical correlations of vapor-liquid-equilibria. However, for the supercritical region of common fluids, results for speed of sound, Joule-Thomson coefficient and isobaric heat capacity present great deviations.[2]

In this work, we computed MP2/6-31G+(d,p) N_2–N_2 interaction energies including basis set superposition error (BSSE) corrections. The plot shows the MP2 data adjusted to the 2CLJQ function. The MP2 (ε, σ) adjusted values were (12.05, 3.65) (dimensionless units), which should be compared to Vrabec original values. This new potential will be tested on molecular dynamics simulations to obtain supercritical properties of N_2.



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[2] COLINA, C.M. *et al Molecular Simulation*. v. 29 (6-7), pp 405-412, 2003.

Support: FAPERJ, CNPq, Brazilian Army.

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Ab Initio Molecular Dynamics Using Many Body Expansion

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Key-words: Ab Initio, Molecular Dynamics, Computer Simulation

In this work we show the implementation of ManBo, an ab initio molecular dynamics (MD) program that uses the many body expansion (MBE) approach. Such approach aims at lowering the computational cost of ab initio simulations while keeping a good accuracy in the calculation of the forces.

In our program we calculate the interaction up to the three-body term. In doing so, the computational cost scales with N^3, thus obtaining a better scalability than using conventional ab initio electronic structure methods. We apply conventional periodic boundary conditions to address border effects and an interaction cutoff to reduce even more the computational cost.

We have found that the MBE introduces very small errors in the forces, of $\sim 10^{-4}$ hartree/bohr, even when using an interaction cutoff. This is the typical tolerance value for the average force in geometry optimizations in gas-phase electronic structure calculations, therefore a quite acceptable deviation in the calculation of atomic forces for MD simulations. We also show that by changing to a little less quality basis set in a conventional ab initio MD, one introduces errors of higher magnitude than that.

We conclude that using MBE in conjunction with ab initio methods is an efficient strategy to perform accurate MD simulations in large molecular systems.

Support: CNPq, FAPEG.

olecular yna ic Si ulations of the intact A γ- α co lex on A

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Key-words: Nuclear Receptor, PPARγ, Molecular Dynamics, Principal Component Analysis.

Despite the major role nuclear receptor PPARγ plays in adipogenesis and in glicose metabolism, it was only recently that a crystallographic structure of the full-length complex was published for the first time[1]. It encompasses not only the heterodimer PPARγ-RXRα, but also fragments of the coativator peptide, two agonists and a DNA recognition se uence, providing a much more realistic and complete snapshot of PPARγ functional complex.

In the present work, we submitted this complex to molecular dynamic simulations using CHARMM force field in order to investigate dynamical aspects such as correlated motions between different domains – which can be important to biological function – and also differences in the dynamical behavior of PPARγ as a monomer and as part of the intact complex.

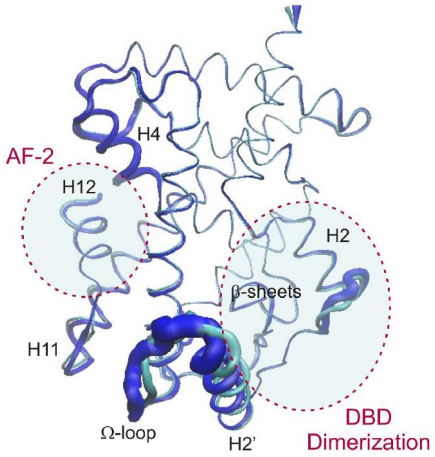

Figure 1. Sausage plot of PC1 for PPARγ simulated as a monomer (cyan) or in the functional complex (blue).

Principal Component Analysis (PCA) of the trajectories allowed to decompose PPARγ global motion into several types of motions and to identify those of higher amplitude among them. The first principal component (PC1) involved mainly the DNA Binding Domain (DBD) dimerization region and the regions near the helix 12 (Figure 1). As further confirmed by Dynamic Cross-Correlation Maps, these regions are correlated, suggesting an important allosteric path connecting the activation domain (AF-2) to DNA, via DBD. Also noteworthy, these correlations were not so evident when PPARγ was simulated as a monomer, indicating they may re uest the whole intact complex to work fully.

[1]Chandra *et al*. Nature, 456, 350-357, 2008.

Support: FAPESP, CNP

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"Multiconfigurational study of charge transfer spectra of cyanoiron complexes"

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Key-words: metallocyanides, CASPT2, charge transfer spectra

We present a multiconfigurational study of the charge transfer spectra of coordination compounds with general formulae $[Fe(CN)_5L]^{3-}$ in which L is a N-heterocyclic molecule (substituted pyridine). These complexes are building blocks used in our systems since pyridine mimics the bonding site at the polymers we are interested in, and pyrazine interconnects different complexes in polynuclear compounds.

For all complexes, DFT geometry optimizations were performed with Gaussian 03 code using TZVP basis sets on all atoms and employing the hybrid functional PBE0. The solvent effect on the geometries was calculated with the PCM model and water or dimethylsulfoxide as solvents.

Single point CASSCF/CASPT2 calculations were subsequently performed on C_{2v} or C_s DFT structures using MOLCAS 7.4. In all these calculations ANO-rcc basis sets were used for all atoms and the choice for the active orbitals followed the standard rules for transition metal complexes.

Apart from ligand field transitions, the calculations show that only one Metal-to-Ligand Charge Transfer (MLCT) band is predicted to be responsible for the experimental spectra. This band is ascribed to a Fe(II)-L(π^*) transition (between A_1 states) and is quite sensitive to solvent. Using the PCM model, the experimental excitations were reproduced with an average error of 2000 cm^{-1}.

Support: FAPESP, CNPq and FWO.

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Computational study on the dechlorination of the pesticides chloropicrin and 1,3-dichloropropene by sulfur species

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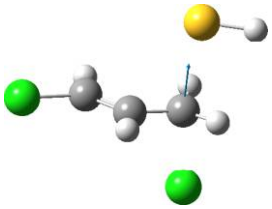
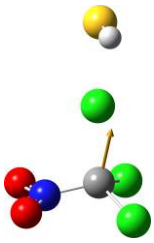
Key-words: hydrogen sulfide species, chloropicrin, dechlorination



Organochlorine chemicals present in the environment are not only of anthropogenic origin. There are over 3000 naturally occuring species containing chlorine, in addition to those produced by human activities. Environmentally, the existance of a large number of industries which effluents contain organochlorine chemicals makes the study of their transformation into harmless compounds, or even their complete mineralization, an important subject.

The chlorinated fumigants chloropicrin (trichloronitromethane) and 1,3-dichloropropene have been used for decades in agriculture as crop fumigants. Even though both compounds are not air pollutant, its chemical interactions in the ground and the possibility of transport to other surface layers is of great concern. Zheng *et al.* studied the simpler dechlorination mechanism of chloropicrin and 1,3-dichloropropene by hydrogen sulfide species using HS^- [1]. They determined that the dechlorination of 1,3-dichloropropene takes place through a S_N2 nucleophilic substitution, but that dechlorination of chloropicrin involves a redox mechanism. In this study we explored the reaction pathways for nucleophilic substitution and reductive dehalogenation of chloropicrin.



In studying the reductive dehalogenation of chloropicrin proposed by Zheng [1] by the results we can conclude that the reactions are highly endothermic, this is not consistent with experimental observations. We studied an alternative mechanism in which the HS- reacts with a chlorine atom of chloropicrin forming the reaction intermediate HSCl. All reactions proposed in this mechanism are exothermic and spontaneous, according to the experimental observations. The transition structure for formation of the HSCl is 58 kJ/ mol above the products, which realizes the exothermicity of the reaction. Furthermore, we studied the nucleophilic substitution of 1,3-dichloropropene, the data indicate that it is an exothermic reaction, which confirms what was observed experimentally. We determined thermochemical data for all the species involved in both pathways using density functional (B3LYP and PBE) and post-Hartree-Fock (MP2) methods. These calculations were performed in gas phase and in solution.

[1] W. Zheng, S. R. Yates, S. K. Papiernik, M. Guo, J. Gan, J. Agric. Food. Chem. 54 (2006) 2280

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Computing the binding free energy of thyroid hormone to a second site of its receptor using non-equilibrium steered molecular dynamics simulations

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and Munir S. Skaf (PQ)[1]

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Key-words: thyroid hormone, molecular dynamics, jarzynski equality

Theoretical estimates of Gibbs free energy differences (ΔG) using molecular dynamics simulations (MD) are one of the challenges in theoretical and computational chemistry. After the discovery of the Jarzynski equality, the field of ΔG calculations methods extended to non-equilibrium computer simulations. The Jarzyinski equality states that the ΔG between two states of a system is the exponential average of non-equilibrium works performed to transform one state to the other, according to the equation: $e^{-\beta\Delta G} = \langle e^{-\beta W} \rangle$. In this study, we applied this equality to calculate $\Delta G_{binding}$ of thyroid hormone to a novel binding site of its nuclear receptor, which was recently discovered by X-ray crystallography. The functional role of this binding site remains unknown and experimental attempts to measure its binding free energy have not yet succeeded. Highly motivated by the need to understand the biological function of this novel site and to estimate the magnitude of its binding strength to thyroid hormone in solution, we have carried out an extensive series of MD simulations, lasting over 800 ns, in order to compute ΔG. Two independent methods were used: Steered Molecular Dynamics Simulations (SMD), from which the W exponential average was computed in connection to the Jarzynski equality, and the Adaptive Biasing Force method (ABF), which allows for increased sampling along the reaction coordinate. We observed a correlation between the initial binding modes of the hormone the SMD simulations and the final W obtained for its dissociation. This observation led us to increase the sampling of smaller works (which are most important for the accurate estimation of the exponential average), using simulations starting from conformations in which ligand and protein are interacting more weakly. The final ΔG value via Jarzynski equality was 8.9 $kcal.mol^{-1}$, which is very close to that obtained with the ABF method (-9.5 $kcal.mol^{-1}$). This binding affinity implies that plasma concentrations of the hormone would be able to activate this second site under physiological conditions.

Support: FAPESP.

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Aflatoxins: a methodology comparison and interaction with DNA

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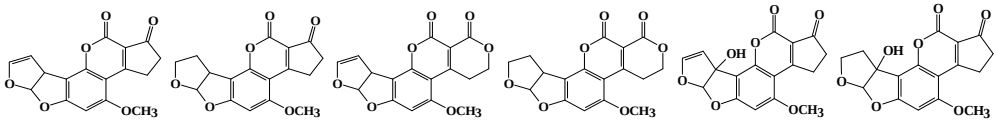
Key-words: Aflatoxin, carcinogenic activity, ab initio and dft methodology

Aflatoxins (AF) are micotoxins produced by fungi biological activity, mainly by *flavus* and *parasiticus* species, *Aspergillus* gender. They can contaminate grains and milk. There are several types of aflatoxins, but the most known are AFB1, AFB2, AFG1, AFG2, AFM1 and AFM2 (Figure 1). All these structures were studied in this work. Experimentally, the AFB1 was identified as the most carcinogenic (hepatic cancer in humans), it is able to interact with protein, causing hepatic intoxication, or with DNA, causing cellular mutations and then cancer. In order to establish the relationship between electronic structure and biological activity, we performed a series of calculation using different methodologies to reproduce some properties related to carcinogenic activity. AM1, HF (STO-3G, 3-21G, 6-31G) and B3LYP (3-21G and 6-31G) were utilized through Gaussian 03 program. The results were visualized by GaussView 3.0. For all the molecules, HF/6-31G generated the higher values of dipole moment (DM). The lowest E_{lumo}-E_{homo} values were obtained using B3LYP/6-31G and for all the methods the frontier orbitals for the aflatoxins of the type 1 were distributed on the furan ring. B1 and G1 presented higher values of DM compared to B2 and G2 and they presented negative components in X axes, while M2 showed higher DM than M1 and showed negative components in X and Z axes. These parameters can contribute with their high reactivity. Docking calculations were performed to preview the interactions of the aflatoxins with DNA. The analyzed receptor was DNA 5'-CGCGAATTCGCG-3'. The main DNA-ligand interactions were π...π type among the rings from the basis and the rings from the ligands. There was a superposition of the ligands on an intercalated mode. We can see that the docking methodology was efficient to preview the binding mode for the aflatoxins with respect to the DNA. The Docking calculations were performed by Ignez Caracelli and Sergio Riardo Pizano Rodrigues, at BioMat, UFSCar.



(a) (b) (c) (d) (e) (f)

Figure 1-(a) AFB1; (b) AFB2, (c) AFG1; (d) AFG2; (e) AFM1; (f) AFM2.

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Cl_2 Dynamical Properties in the Electronic States B'':(2)1_u, (1)2_g, a:(1)1_g , a':(2)0_g^+ , (1)0_g^-

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Key-words: PEC, rovibrational spectroscopic constants, relativistic states.

We have theoretically calculated the Cl_2 dynamical properties in the electronic states B'':(2)1_u, (1)2_g, a:(1)1_g , a':(2)0_g^+ , (1)0_g^- **.** More precisely, we have evaluated the Cl_2 rovibrational energies, ωe, ωexe, ωeye and γe, using the potential energy curves (PEC) of 5 covalent states calculated using relativistic complete open shell configuration interaction approach. To assure the good accuracy of fittings, the relativistic PECs were fitted using the analytical function based on a polynomial q-Bond Order coordinates of tenth degree. From these analytical forms, we evaluated the Cl_2 rovibrational spectroscopic constants for each state using two different procedures. In the first procedure the constants were calculated combining the rovibrational energies and the diatomic rovibrational energy equation. In the second one the constants were determinate using the Dunham method. The calculated properties are in good agreement with both available theoretical and experimental data.

Support: CAPES, CNPq, FINATEC.

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"Theoretical Study of the UV-Vis Spectrum of 1-methylquinolinium-8-olate in Aqueous and Alcoholic Solutions"

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Key-words: Emolecular dynamics; Uv-vis spectrum.

Binary mixtures of organic solvents are usually employed in the studies of solvent effects because the properties of these mixtures can be continuously changed by varying the fraction of their composition. However,many properties of binary mixtures, like densities and dielectric constants, exhibit a nonlinear relationship with their composition. In water{alcohol mixtures, energies of the electronic absorption transitions of the 1-methylquinolinium-8-olate (QB) present this type of nonlinearity with the mixture composition. In this work, we performed theoretical studies of the UV-Vis spectra of the isolated QB and in aqueous and alcoholic solutions, in order to investigate the solute{solvent interactions and the preferential solvation of QB in water-methanol binary mixture. In a first step, we study the QB in two forms, quinoidal and benzenoidal, using quantum mechanics methods and molecular mechanics. We analyzed the preferential conformation of QB using two *ab initio* methods, B3LYP and MP2 with the 6-311+G** basis set and the solvents describe by the polarizable continuum model, PCM. The calculations of the absorption spectrum were performed using two diferent time-dependent density functional methods, TD-B3LYP and TD-BHandHLYP. Using the energetic stability and the electronic absorption transitions, we concluded that the form of the isolated QB is preferentially quinoidal, but it shows a clear tendency in changing to the benzenoidal form increasing the polarity of the solvent. A followed step was test and changes the intra-molecular parameters of the OPLS force field to perform molecular dynamics simulations of QB in explicit solvents. With this re-parametrization, it was possible to reproduce well the experimental value of the electronic absorption transition energy of QB in benzene. Our next step in this study will be the simulation of QB in the pristine solutions (water and methanol) and also in diferent fractions of the binary mixture. Our aim is to understand the in°uence of the microsolvation of QB in its spectral shifts due to diferent fraction of water-methanol mixture.

Support: CNPq, CAPES, INCT de Fluidos Complexos e Rede NBioNet.z'

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Dynamical Simulation of the CH_4-CH_4, CHF_3-CH_4, CH_4-H_2O and CHF_3-H_2O Dimers

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Key-words: CH_4-CH_4, CHF_3-CH_4, CH_4-H_2O and CHF_3-H_2O; Ro-vibrational Dynamics

The hydrogen bond plays a very important role in the structure, function, and dynamics in chemistry, physics, and biology. The hydrogen bonding (A-H...B) is generally described as a relatively weak interaction between an electronegative proton acceptor B and a hydrogen atom, which has a covalent binding to the electro-negative proton donor A. The CH_4-CH_4, CHF_3-CH_4, CH_4-H_2O and CHF_3-H_2O dimers present particular interaction energies involving hydrogen, ordered as follows: CH_4-CH_4 <CHF_3-CH_4 < CH_4-H_2O < CHF_3-H_2O. Futhermore, they have different Coulombic term contribution on the interaction energy: quadrupole-quadrupole (CH_4-CH_4), quadrupole-dipole (CHF_3-CH_4 and CH_4-H_2O), and dipole-dipole (CHF_3-H_2O). Due to the importance of these dimers, we calculated the *ab initio* potential energy curves of CH_4-CH_4, CHF_3-CH_4, CH_4-H_2O and CHF_3-H_2O dimers using MP2, and QCISD levels of theory with a large number of basis functions well as Dunning augmented aug-cc-pVDZ (B1) and aug-cc-pVTZ (B2) basis sets. These energies were fitted employing the Rydberg generalized function. From these fittings, the spectroscopic constants and rovibrational energies were determined. The results are presented in Table 1.

Table 1: Rovibrational spectroscopic constants in units of cm^{-1} for $CH_4\cdots CH_4$, $CH_4\cdots H_2O$, $CH_4\cdots CHF_3$, and $H_2O\cdots CHF_3$ dimers with basis sets 1 and 2.

Dimers	Basis Set	ω_e	$\omega_e x_e$	$\omega_e y_e$	α_e	γ_e
$CH_4\cdots CH_4$	B1	40.37	4.92	0.16	0.03	1.53×10^{-5}
	B2	56.17	4.47	-0.12	0.02	-1.87×10^{-3}
$CH_4\cdots H_2O$	B1	70.02	5.97	0.08	18.29	-102.008
	B2	78.52	6.13	0.13	18.31	-134.530
$CH_4\cdots CHF_3$	B1	44.82	3.88	0.04	4.26×10^{-3}	-8.39×10^{-4}
	B2	50.52	3.03	-0.11	4.21×10^{-3}	-5.93×10^{-4}
$H_2O\cdots CHF_3$	B1	92.31	0.94	-0.9	4.03×10^{-3}	-3.43×10^{-4}
	B2	107.15	4.34	0.18	1.04×10^{-2}	2.16×10^{-4}

Support: CAPES, CNPq, INCTMN

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SAPT Studies for H_2O-CX_4 Complex, with X = H, F, Cl

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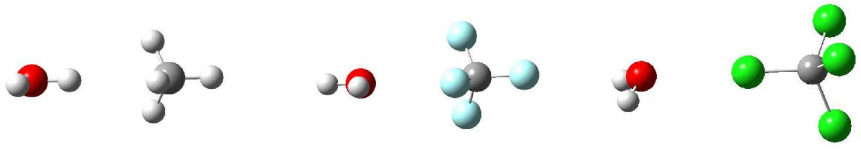
Key-words: Symmetry Adapted Perturbation Theory, van der Waal complex

In this work we discuss the CCSD(T) study and characterization of the interaction energy at the SAPT (Symmetry Adapted Perturbation Theory) level of the global minimum energy configuration of the H_2O-CX_4 complex, with X = H, F or Cl. The SAPT results can give us the energy profile of the complex. Initial search for the optimum parameters (basis set for the midbond points in the "dimer centered plus basis set approach" (DC+BS) and "monomer centered plus basis set approach" (MC+BS) was employed in these studies. In SAPT, the interaction energy is expressed as a sum of perturbative corrections, each correction resulting from different physical effect. This decomposition of the interaction energy into distinct physical components is a unique feature of SAPT which distinguishes this method from the supermolecular approach. For each dimer the geometry is given above, and one can see they are slightly different, the H_2O - CH_4 is bonded as O-H-C, while the H_2O – CF_4 is bonded H-O-C and for the H_2O – CCl_4 is H-O-Cl. The total energy determined by the SAPT methodology are -1.30 kcal mol^{-1} for H_2O – CH_4, -1.45 kcal mol^{-1} for H_2O – CF_4 and -1.60 kcal mol^{-1} for H_2O – CCl_4.



H_2O-CH_4 H_2O-CF_4 H_2O-CCl_4

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THEORETICAL INVESTIGATION OF CHLORINE INTERACTION WITH RHODIUM PHTHALOCYANINE

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Key-words: Rhodium Phthalocyanine, Chemical Sensor, Electronic Properties.

Phthalocyanines classes are aromatic compounds with 18π electrons that can be easily synthesized, and which has high thermal and chemical stability. These features make phthalocyanine the target of intense theoretical and experimental studies to develop new materials and drugs. In the previous study, it performs an experimental analysis of the optical properties in of the Rhodium phthalocyanine (RhPc) exposed to flux of chlorine[1]. The exposition to chlorine affect significantly the absorption bands in the visible region and Raman spectrum, this feature makes it feasible to use as a chemical sensor RhPc. With the aim clarify the mechanism of chlorine interaction and the modification in optical and electrical properties due exposition to chlorine a theoretical study theses structure was performed, describing geometrical parameters, populations analysis, reactivity index, theoretical spectrum visible and Raman. The calculation results show that the Rh – Cl_2 bond length around 2.64Å. It is observed that the Rhodium atom presents a positive charge, with values 1.66, this value change to -3.37 with chlorine interaction, showing a redistribution of the charge in the phthalocyanine. The theoretical spectrum visible results show a peak around 800nm, however the intensity of the peak decrease 38% when interacts with chlorine. The calculated properties are in good agreement with experimental data.

Support: CAPES, CNPq, FINATEC.

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Estudo Teórico da halogenação de 1,1,2-trifeniletileno com ácidos haloisocianúricos

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Palavras chaves: 1,1,2-trifeniletileno, halogenação, ácido haloisocianúricos.

Olefinas substituidas são blocos de construção importantes na síntese orgânica. No caso particular em que três substuintes sejam anéis aromáticos, estes triariletilenos representam o cerne de compostos que possuem atividade biológica sobre os recptores de estrogênio, com aplicação na terapia de câncer de mama, infertilidade e osteoporose.

A incorporação de halogênios a triariletilenos pode fornecer compostos com atividade biológica ampliada, além de intermediários halogenados que podem ser utilizados como substratos em diversas reações de formação de ligação carbono-carbono.

Estudos preliminares da reação de halogenação (Figura 1) da 1,1,2 trifeniletileno com uma nova classe de compostos, os ácidos tri-haloisocianúricos, TXCA, mostrou a seguinte ordem de velocidades de reação: cloração > bromação >> iodação (não observada). A proposta deste trabalho é um estudo teórico mecanístico da reação de halogenação desta olefina. Foram realizados cálculos DFT em nível M06-2X ambos com a base 6-311++G(d, p).

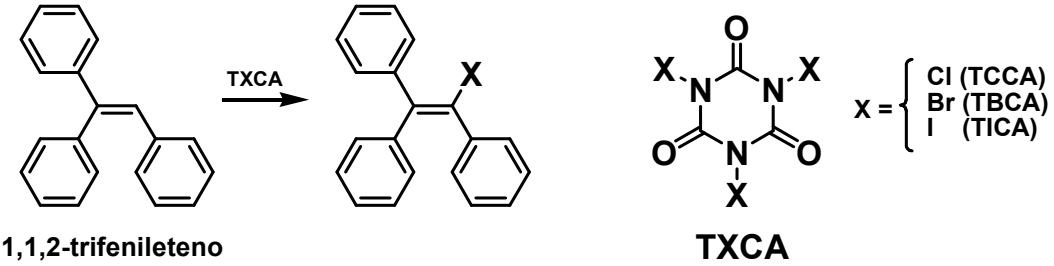

Figura 1. Halogenação de olefinas utilizando ácidos tri-haloisocinúricos

Adotado o mecanismo descrito na literatura (adição eletrofílica), foi investigado se com algum dos três ácidos tri-haloisocianúricos, a reação é termodinamicamente desfavorecida. Com base nos valores de energia observou-se que a reação com TCCA apresentava valor de ΔH de 23,0 Kcal/mol, enquanto para TBCA os valores eram de 33,0 Kcal/mol e TICA, 110,0 Kcal/mol.

Com base nos valores obtidos, pode-se concluir que a reação de halogenação com TCCA é mais favorável energeticamente do que as com TBCA e TICA. Estes resultados equivalem as observações experimentais obtidas.

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"Modelling Dye Behavior: Macrocycle on TiO_2 Surface"

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Key-words: DSSC, DFT, TiO2 Surface, macrocycles

Nowadays among of investigations focuses on semiconductors nanocomposites development to improve efficiency of based dye-sensitized solar cells (DSSCs). Since O'Regan & Grätzel work [1], titanium dioxide has experimental studies and theoretical about their behavior from atomistic view. The metallomacrocycles has a lot promising properties for their use in DSSCs, principally because of it's absorption range 500nm-600nm[2-3]. We investigate of adsorption energy and stability of active organic molecules, like metal-Porphyrin and Metal-Phthalocyanines on reactive face of titanium oxide slabs. Our work is carried out under Density Functional Theory and using generalized gradient approximation for exchange corrections, through plane wave basis and local combination of atom basis set. All the calculations are performed with periodic boundary conditions, simulating a most real system possible. Different ways to attach the molecule on the surface was investigated. The influence frontier orbitals of molecules over the electronic properties and band structure of the periodic surface will be discussed.

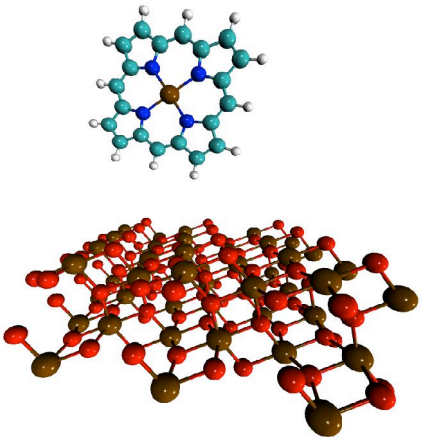

Fig. 1 Iron phorphyrin normal to anatase (101) surface

This work is supported by Millenium Nucleus P07-006-F, UNAB DI-12-09/I and CONICYT through scholarship N° 21110486.

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Reactivity of sulfate esters and analogs: why is the sulfur center unreactive?

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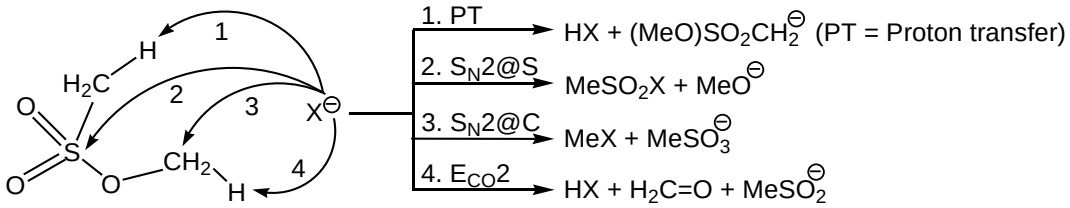
Key-words: sulfate ester, ion-molecule reactions, DFT.

Sulfate esters are an important class of organic compounds because of their broad applications as surfactants, alkylating agents, and their role in aerosol formation and air pollution. Sulfated species also participate in various cellular processes, including pathologies like cancer. For these reasons, the complete understanding of the reactivity of sulfate esters is of interest to a wide audience. An early experimental work[1] studied the reactivity of these species and analogs in the gas-phase by flowing afterglow technique and several reaction channels were investigated:



No S_N2@S products were observed while all other products were characterized. However, no modeling of the mechanism was carried out, leaving some relevant questions unanswered: Why is the sulfur center unreactive? Is this pathway energetically unfavorable or dynamically hindered, like the S_N2@N attack on alkyl nitrates?[2]

To answer these questions transition states and intermediates for the gas-phase pathways were modeled by DFT/B3LYP/6-311+G(3df,2p) level of theory for the X^- + $MeOSO_n(R)$ systems, where X=OH, NH_2, SH, F and OMe, n=1 and 2 (for sulfite and sulfate respectively) and R=Me and OMe.

Our results show that independently of the nucleophile, the S pathway is not energetically favored, except for OH^- and NH_2^- reacting with $(MeO)_2SO$. This indicates that for lower oxidation states, the S center becomes prone to attack by strong protonic nucleophiles.

These results not only expand the expected reactivity of the sulfate esters and their derivatives, but also highlight an important pathway for lower oxidation states, that could be relevant for atmospheric chemistry.

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Support: CAPES, CNPq, Fapesp, INOMAT.

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Semiempirical determination of the base catalytic residue in the elimination step of enzyme EPSP synthase

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Key-words: EPSP synthase, Shikimate pathway, QM/MM

The enzyme 5-enolpyruvylshikimate 3-phosphate (EPSP) synthase is the sixth enzyme of the shikimate pathway and catalyzes the reaction between phosphoenolpyruvate and shikimate-3-phosphate to form the product EPSP and inorganic phosphate. EPSP synthase is a promising target for developing nontoxic antimicrobial agents, herbicides, and antiparasitic drugs, because this pathway is essential in microorganisms, plants and parasites, but absent in mammals. The catalytic reaction of EPSP synthase occurs in two steps, an addition step in which the product is a tetrahedral intermediate (THI) and an elimination step, in which there is the formation of products EPSP and inorganic phosphate. Herein, we have studied the catalytic mechanism used by EPSP synthase involving the THI. The computational model for the QM/MM MD calculations was taking from EPSP synthase (1Q36, PDB code). The semiempirical AM1 Hamiltonian was employed to describe the QM part (THI and residues Asp313, Glu341, Lys22 and Lys411, involved on catalysis) while the rest of the system was described using the OPLS-AA and TIP3P force fields for protein and water molecules, respectively, as implemented in the *f*Dynamo library. All Potencial Energy Surfaces were obtained using two antsymmetric combinations. Where, the d1-d2 coordinates corresponds to proton transfer from methyl group to Glu341, d3-d4 coordinates corresponds to proton transfer from methyl group to Asp313 and d5-d6 coordinates correspond to output of phosphate group from THI. First occurs a double attack of H of Lys22 and Lys411 to phosphate group and consequent release of PO_4^{-3} with formation of a cationic intermediate, after overcoming a barrier of 31 kcal/mol. Then, occurs formation of product EPSP, after overcoming a barrier 12.40 and 17.80 Kcal/mol for Asp313 and Glu341, respectively. The results show that both residues Asp313 and Glu341 may participate, equivalently, in the stage of formation of products EPSP and inorganic phosphate.

Support: CNPQ/UFPA.

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"A DFT Study of Edaravone Derivatives as Antioxidants"

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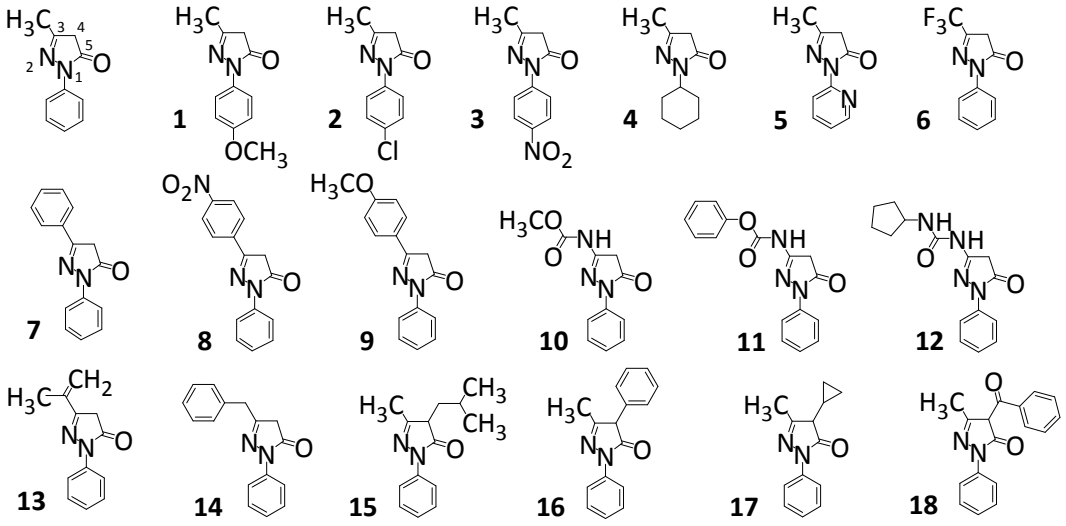
Keywords: Edaravone, ischemia, DFT, antioxidant, tautomerism, scavenging.

Edaravone is a novel neuroprotective agent that was approved for the acute therapy of embolic stroke, and has great potential to protect against toxicity-induced by various radical. Its pharmacological effect arises from its radical-scavenging activity. Nonetheless, the nefrotoxicity of this molecule has increased the research for new edaravone derivatives. Then, the structure-activity study developed here has been used to investigate the antioxidant properties of eighteen edaravone-related derivatives in order to analyze their characteristics as free radical scavengers under several mechanisms using quantum chemical calculations by the DFT method B3LYP/6-31G(d). The HOMO, ionization potential, bond dissociation energies, stabilization energies, and spin density distribution showed that substitutions in the 4 position is more important than in positions 1 or 3 for the reactions of electron or hydrogen abstractions. The spin distribution showed that the π-type electron system determines the stability of radicals and the unpaired electrons are mainly distributed in the pyrazolone ring, *N*-phenyl moiety, and aryl or alkyl groups. Therefore, the most antioxidant potential is related with the derivatives that has showed several resonance effects. Furthermore, structure-activity relationships of these derivatives with electron-donating groups are more favored than electron-withdrawing ones. These results can help in the design of new edaravone derivatives as antioxidant.



Support: CNPq.

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Theoretical Calculations of the Optical Absorption and Fluorescence Emission of the Chlorophylls A and B

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Key-words: chlorophyll, optical absorption, fluorescence, TDDFT.

Chlorophyll is an important pigment in the photosynthesis process because it absorbs light at the blue-red region of the electromagnetic spectra, promoting the excitation of an electron that starts all the chemical reactions involved in this biological process. Besides, it emits fluorescence in the Violet region as a regulating mechanism for the created charge excess by this excitation process. Moreover, there is a lot of experimental studies of both optical absorption and fluorescence emission of the Chlorophylls A and B. From the theoretical point of view, despite the fact that the electronic structures of these pigments were well determined, only the optical absorption of chlorophyll A was determined by Time-Dependent Density Functional Theory (TDDFT) with good agreement with the experimental data. So, in this work, we present here our results, by using the TDDFT within the Adiabatic Local Density Approximation and gradient conjugated techniques (Orca code), the structural properties, electronic structure, the optical absorption, as well as the fluorescence emission of the Chlorophylls A and B. We have used the B3LYP functional for the exchange-correlation term together with 6-311G basis set, and the optical absorption and fluorescence emission were evaluated by the Casida approximation. The fluorescence emission spectrum was obtained within the Independent Mode, Displaced Harmonic Oscillator (IMDHO) model. Our results agree well with both the available experimental data and other theoretical calculations, whenever these comparisons were possible. Based on our results, the observed peaks in the adsorption spectra, as well as the fluorescence emission spectra, were characterized by singlet-singlet transitions due to the electron excitation from HOMO to the LUMO states. Besides, in the fluorescence emission, the electronic transition involves the collective vibrational modes of the long phytol chains of the Chlorophylls.

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Adsorption of Cobalt Phthalocyanine on Functionalized Graphene with Oxygen-Containing Functional Groups

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Key-words: Graphene, cobalt phthalocyanine, functionalization

Graphene (G) is a 2-dimensional crystal lattice formed by carbon atoms with semi-metallic character and high electron mobility[1]. The chemically modified G so-called graphene oxide[2] is a rich structure in oxygen-containing functional groups (carboxyl, hydroxyl, epoxy) that modify the reactivity and electronic properties of G. In this work, we explore how the electronic properties of graphene oxide could be modulated by the adsorption of cobalt phthalocyanine (CoPc). Using Density Functional Theory (B3LYP/6-31G*/LANL2DZ) the adsorption of CoPc on graphene oxide with carboxyl (-COOH) and hydroxyl (-OH) groups was studied (Figure 1). The adsorption energy shows that CoPc weakly interacts with G-COOH as compared with previous results for G–COO^- [3]. In contrast, the cobalt atom of CoPc shows high affinity for the hydroxyl group in G-OH, which suggests that it would be useful as a method of purification of graphene oxide. Compared to pristine G, reactivity descriptors like electrophilicity show that the CoPc adsorption increases electrophilic character in conjugated systems, while electrophilic character in G decrease.

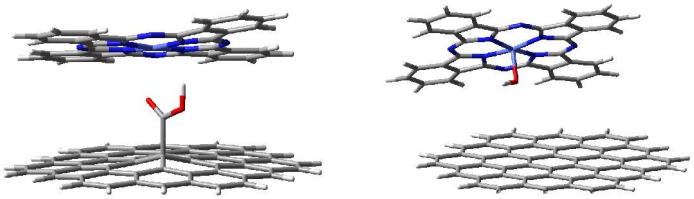

Figure 1. Molecular view of the systems G-COOH-CoPc and G-OH-CoPc

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An improved quantum biochemistry description of the glutamate, AMPA, kainate, and DNQX GluR2 binding pocket domain

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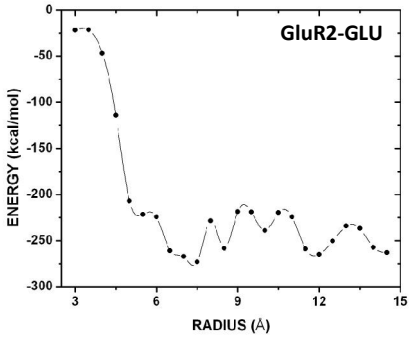
Key-words: GluR2 receptor, glutamate, AMPA, quantum biochemistry

At synapses throughout the brain and spinal cord, the amino-acid glutamate is the major excitatory neurotransmitter. The glutamate-receptor ion channels (iGluRs), namely AMPA, kainate and NMDA receptors, are the major mediators of excitatory synaptic transmission in the central nervous system[1]. Crystal structures of the GluR2 ligand binding core (S1S2) have been determined in the Apo state and in the presence of the antagonist DNQX, the partial agonist kainate, and the full agonists AMPA and glutamate[2]. We take full advantage of this published crystallographic data to perform in this work density functional theory based computer simulations of the glutamate, AMPA, kainate, and DNQX binding energetic to GluR2. The radius of the binding pocket is changed, going beyond of what is generally accepted as the crystallographic binding pocket (cbp) radius. The quantum biochemistry calculations are performed within the framework of the molecular fractionation with conjugate caps (MFCC) strategy[3], using, both, the local density and generalized gradient approximations, LDA and GGA. Stability of the total binding energy is achieved only for radius larger than 8 Å, with a well characterized irregular oscillatory behavior related mainly to the contribution of charged residues. Arg485 and Lys730 (Glu402 and Glu657) are demonstrated to be the most important attracting (repelling) residues in the cbp radius, the binding strength of the formers being higher than that of the latters. Lys449 and Arg660 contribute significantly to the ligands total binding energy beyond the cbp radius. The estimated ligand-GluR2 total binding energy AMPA > glutamate > kainate > DNQX is in agreement with electrophysiological opening of the glutamate and AMPA ionic channels, the kainate partial agonist and the weak GluR2-GLU DNQX antagonism. To the knowledge of the authors, this is the first quantum biochemistry description of the working behavior of the glutamate-receptor ion channel iGluR2, which is one of the major mediators of excitatory synaptic transmission in the central nervous system.



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Calculating the absorption spectra of 4f - 5d heterobimetallic complexes

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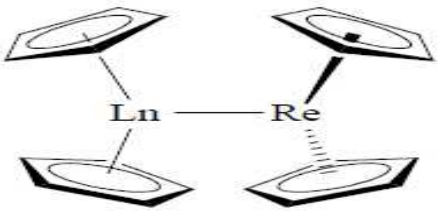
There is an increasing research activity for designing transition metal (TM) sensitized near-infrared (NIR) luminescence from lanthanides (Ln) centers by energy transfer from TM chromophores. Since lanthanide ions are poor at absorbing light directly, due to the low extinction coefficients of the Laporte forbidden f-f transitions, energy transfer from adjacent strongly absorbing TM chromophores is usually used to stimulate luminescence from lanthanides. In this work we employ relativistic calculations in order to describe the bonding between a TM and Ln, and how evolves in the excited states. The ground state TM-Ln bond described in the paramagnetic $Cp_2Ln\text{-}ReCp_2$, where Ln = Yb, bimetallic complexes shows a dipole moment towards the Re center. The absorption properties deal with a f-d transition centered at the Yb atom, which is an ungerade-gerade Laporte allowed transition and thus, it is expected to exhibit high absorption coefficients, and can be selected almost anywhere in the visible or NIR region, due to the heavy TM ion bonded to it. This interaction will facilitate intersystem crossing and give high quantum yield of the energy donor following electronic excitation, relatively long-lived excited states that will facilitate energy transfer to the adjacent lanthanide ion.



Ln=Y (7); Yb (8)

We used the Relativistic Time Dependent Density Functional formalism as implemented in the ADF code via the ZORA Hamiltonian including spin-orbit interaction.

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Potential energy surface and rate constants for unimolecular reactions of Acetaldehyde.

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Key-words: Acetaldehyde, Roaming, Decomposition, Rate constants

Recently, a new decomposition channel has been investigated for formaldehyde by both experimental and theoretical methods. In this new channel, the fragments are separated as in a dissociation dynamics but at a certain inter-fragment distance, the hydrogen atom of one fragment roams to another, yielding decomposition products (H_2 + CO). This channel was called decomposition via roaming atom. Experimental and theoretical works have also suggested the observation of this channel for acetaldehyde. Here, acetaldehyde dissociation and decomposition reactions are investigated by direct dynamics method. The reaction paths have been described with DFT method using B3LYP and BB1K functionals and cc-pVDZ, cc-pVTZ and aug-cc-pVDZ basis sets. Canonical variation rate constants have been determined in the temperature range 1000 to 1600K. Geometrical parameters and vibrational frequencies calculated to acetaldehyde show good agreement with experimental data, with average deviations of less than 4% at all levels of calculation. The geometry of the saddle point for $CH_3CHO \rightarrow CH_4$ + CO shows a three center structure (CCH), with the CC distance about 2.0 Å. This is the conventional decomposition path. The dissociation path shows the typical and expected topology of a barrierless reaction. The saddle point to decomposition via roaming atom was characterized by a three center structure, with CC distance around 3.5 Å. The reaction path for this channel shows the movement of the hydrogen atom from the HCO fragment to the CH_3, forming CH_4 + CO, with activation barrier lower than that calculated for the channel via conventional saddle point. A more detailed investigation of this process shows that the participation of higher spin states is large and that the dynamics of this process is dominated by nonadiabatic effects. So, the Transition State Theory does not apply to the description of the kinetics of this channel, in contrast to other channels of decomposition (via conventional saddle point) and dissociation. Finally, there is an excellent agreement between the calculated rate constants for the unimolecular decomposition (conventional) with the data available in literature.

Support: FAPERJ, CNPq.

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Parameterization of Europium Atom with the Explicit Inclusion of Orbitals of Type s, p and d for RM1 and AM1 Methods.

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Key-words: Lanthanides, Sparkle Model and RM1.

Interest in the synthesis of novel luminescent lanthanide complexes stems from the wide area of application in various fields of science. Thus, the theoretical design becomes an important tool in the search for efficient luminescent complex. Within this context, emerged the Sparkle model that was developed for predicting the ground state geometries of lanthanide complexes.

In this work we present a new parameterization of the ion Eu(III) for the AM1 and RM1 semiempirical methods, with the explicit inclusion of s, p and d orbital in the basis set. With this reasoning, we have limitations in the calculation of lanthanide complexes in the solvent with MOPAC. It´s an aim of this work initiate an improvement in the description of bonds that show the highest degree of covalency.

The parameterization process of this model has a robust statistical analysis to select the set of parameterization, since our whole universe has 144 structures of lanthanide complexes. Thus, we used two methods to identify the structures that should be part of the parameter set: (i) the method of hierarchical grouping known as AGNES and (ii) the DIANA method.

The two models (AM1/Eu and RM1/Eu) showed an improvement compared to the versions of the Sparkle model, considering the low unsigned mean error (UME) for the distances Eu–L (L = O, N, C, S, P, F, Cl, Br and Eu), maintaining the commitment to the low computational cost involved in performing the calculations of the ground state geometries.

AM1/Eu and RM1/Eu models reproduce chemical bonds with more pronounced covalent character satisfactorily. However, greater efforts in the search of new structures, with geometric data and molecular properties, to be included in the parameterization process of this model are required to further minimize the mean error to distances values Eu-L (L = C, S and P) and molecular properties.

Support: CNPq, CAPES, RENAMI, INAMI and FAPITEC.

Thermal conductivity of conjugated polymers

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Key-words: conjugated polymers, thermal conductivity

We have studied the thermal conductivity in conjugated polymers by using a SSH model Hamiltonian coupled to an infinite set of harmonic oscillators. The set of oscillators defines the interaction between each element of the one dimensional backbone lattice with all particles of the heat bath. The resulting set of equations of motion are of generalized Langevin type, obeying the fluctuation-dissipation theorem of second kind, with an exponential kernel, and an effective interaction potential representing the σ and π bonds between neighbors lattice sites. We set different temperature at the ends of the lattice and integrate the equations of motion by using a standard fourth-order Runge-Kutta method. The resulting temperature gradient over the lattice depends mainly of the interaction potential and can be used to study how the heat is transported through conjugated materials. Of particular interest is the transition between ballistic and diffusive transport regimes. As example of application, we tune the model parameters to represent a trans-polyacetylene oligomer. We obtain its thermal conductivity in the scope of the Fourier's Law of thermal conduction and compare our results to experimental data.

Dinâmica Molecular do Fármaco S-Monastrol como inibidor alostérico da Cinesina Eg5

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Palavras chave: S-monastrol, Cinesina Eg5, *Docking*, Dinâmica Molecular.

Cinesina Eg5 é uma proteína motora envolvida na formação e manutenção do fuso mitótico, que desempenha um papel crucial na divisão celular e é, portanto, um importante alvo na terapia do câncer. Uma estratégia para o tratamento de câncer é o desenvolvimento de drogas que interrompem o ciclo celular na fase de mitose. O S-monastrol é uma molécula permeável em células que inibe a cinesina por um mecanismo alostérico. O objetivo deste trabalho é detalhar as interações do ponto de vista microscópico e elucidar os mecanismos moleculares envolvidos na interação entre o S-monastrol com a Cinesina Eg5, através do monitoramento das distâncias do ligante em relação aos resíduos Glu116 e Leu224 situados no sítio ativo. Metodologia: Estruturas Eg5 PDB ID 1II6 (cinesina nativa sem o ligante) e 1Q0B (cinesina complexada com o monastrol) + S-monastrol → *Docking* Molecular (AutoDock) → Dinâmica Molecular (GROMACS, campo de força GROMOS 53A6).
No *docking* do S-monastrol com a cinesina obtivemos apenas um *cluster* para o 1Q0B e cinco para o 1II6, na região correspondente ao sítio ativo, sendo utilizados os três de menor energia como *input* para a DM. A interação entre o ligante e a proteína foi estudada através das distâncias do ligante em relação aos resíduos Glu116 e Leu224, para monitorar a residência (no caso da 1QOB) ou a abertura do sítio ativo (no caso da 1II6). Na DM do 1Q0B atingiu-se a estabilidade após 5ns. No caso da DM do 1II6 com o ligantes em três diferente conformações (3 *clusters*), a conformação de menor energia no *docking* molecular não atingiu a estabilidade, mas as conformações 2 e 3 atingiram a estabilidade após 18 e 17ns. As distâncias entre o ligante e os resíduos Glu116 e Leu224 ficaram na faixa de 0,5-0,7 Å (nos clusters II e III) e entre 1,5 e 1,8 Å (cluster I). Concluímos que pela DM obtivemos resultados muito próximos aos experimentais, constatando a indução da abertura parcial do sítio ativo, que não estava presente previamente.

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Electrical Properties of Cobalt Phthalocyanine Adsorbed on Functionalized Graphene Models

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Key-words: cobalt phthalocyanine, graphene, electrical current, functionalization

We investigate, at a density functional level (B3PW91/6-31G(d)/LANL2DZ), the electric characteristics of 18 complexes of cobalt phthalocyanine (CoPc) and cobalt tetraaminephthalocyanine (CoTAPc) adsorbed on graphene (G) functionalized with CO_2^- or CO moieties, with the aim to explore how the electrical properties of graphene could be modulated[1]. Three models of graphene molecules are used, pristine, defect, and vacancy. The Green´s function procedure encoded in the program GENIP[2] is used to calculate the current-voltage characteristics. It shows that electron transfer is preferably favored in complexes with parallel orientation and with pristine graphene CO_2^- functionalization (≈7μA) when both conjugates, graphene and phthalocyanine, face to each other. This study shows that cobalt phthalocyanine conducts electrical current towards graphene through a covalently attached CO_2^- to the graphene.

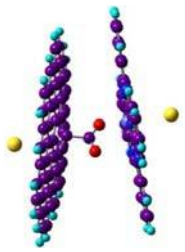

Figure 1. CoPc complex adsorbed in G-CO_2^- attached to Au terminals

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Construction of QSAR models for the activity of thiosemicarbazones against *Morgonella morgonii* and *Klebsiella pneumoniae* using MLR

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Key-words: QSAR, thiosemicarbazones, MLR

The thiosemicarbazones are a class of compounds with broad pharmacological potential applications. In general, the thiosemicarbazones are obtained by condensation chemoselective of thiosemicarbazides with aldehydes and/or ketones. In the reports of biological activities include the following properties: antitumor, antibacterial, antiviral, antiprotozoal, cytotoxic, among others. This work presents the construction of theoretical modeling of Quantitative Structure-Activity Relationship (QSAR) of a group of twelve thiosemicarbazones against microbial *Morgonella morgonii* and *Klebsiella pneumoniae*. The antibacterial activities (expressed as minimum inhibitory concentration - MIC) of the thiosemicarbazones studied were obtained from literature. Calculations semi-empirical and ab initio (Hartree-Fock and DFT) were used to obtain structural and electronic descriptors (lengths of bonds, electrostatic charges from Mulliken, heat of formation, dipole moment, molecular area and volume, hardness, softness, energy of HOMO, LUMO, $HOMO^-$ and $LUMO^+$) computed by the program Gaussian 03W. All descriptors were subjected to a selection statistic (t test; SPSS 15) initial. We discarded the model for those descriptors that showed no significant difference between the responses to high and low values of MIC. Models of activity of thiosemicarbazones against *Morgonella morgonii* included some of the following descriptors: Bond length C_1-C_2, bond length C_3-C_4, bond length of C_4-C_5, bond length of C_5-C_6, bond length C_1-C_6, Mulliken charge of C_2, Mulliken charge of C_6, Mulliken charge of R_{28}. As for the activity against *Klebsiella pneumoniae*, the descriptors selected for testing in various models were: Bond length C_2-C_3, Bond length C_2-hydrogen, Mulliken charge of C_6, Mulliken charge of C_{21}, Mulliken charge of H_{37}, Mulliken charge of H_{38}. The models chosen for each of the strains fulfilled the criteria for statistical significance and the principle of parsimony.

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An electronic structure study on some high-spin Mn(II) Porphyrins: effects of increasing positive charges around the metal center

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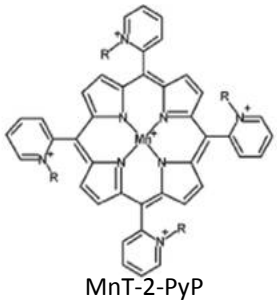
Key-words: Superoxide Dismutases, MnP, Porphyrins, B3LYP

The interest in studying synthetic metalloporphyrins has increased since these complexes are efficient biomimetic systems for a variety of catalytic processes, especially redox-based ones. Synthetic manganese porphyrins comprise the most potent mimics of Superoxide Dismutases (SOD) and redox modulators *in vivo*. Superoxide ($O_2^{\bullet-}$) and its reactive oxygen/nitrogen species progenies are associated to numerous human pathologies, such as stoke, cardiovascular conditions, and radiation injuries. The effectiveness of *ortho* Mn *N*-tetrapyridylporphyrin derivatives (MnT-2-PyP) as SOD mimics has been achieved by appropriate choice of the substituent on the pyridyl moieties to control lipophilicity, charge distribution, and electrostatic facilitation to $O_2^{\bullet-}$ approach. Additionally, cationic pyridinium moieties modulate Mn(III)/Mn(II) reduction potential to yield potent SOD mimics. MnPs of high Mn(III)/Mn(II) reduction potential are reduced *in vivo* from the hexacoordinated Mn(III)P$(H_2O)_2$ form to the corresponding pentacoordinated Mn(II)P(H_2O) species by cellular reductants.


MnT-2-PyP

Hereon we evaluate the effects that the increase of positive charges by methylation of the pyridyl groups exert to some geometrical and electronic properties of aqua complexes of high-spin Mn(II)T-2-PyP compounds.

Geometry optimizations were performed with NWchem 6.0 package, applying unrestricted DFT/B3LYP method (for a sextet spin state) with a 6-311G(d,p) basis set for all atoms except Mn where LANL2DZ ECP was used. Vibrational analysis was carried out, followed by an NBO analysis on the optimized structures with Gaussian 2009 package.

For the Mn(II)P(H_2O) systems studied, the NBO charge in the Mn atom increases with methylation and overall positive charge of the compound. The presence of a single water molecule as axial ligand drives Mn out of the porphyrin plan. An increase in positive charge is accompanied by an increase in Mn-N bond length, while Mn-O bond is shortened. For the Mn(III)P$(H_2O)_2$ systems, the extra coordination water renders Mn nearly within the porphyrin plane. These structural features are in agreement with solution and/or crystallographic data on related systems. Given the difficulty in studying Mn(II)P experimentally, these results may shed some light on the electronic and structural features underlying the catalytic activity of these compounds.

Support: CNPq, CAPES, FINEP and INAMI.

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"Oscillating electric dipole induced by temperature effects in conjugated polymers"

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Key-words: Oscillating Dipole, Thermal Effects, Conjugated Polymers.

Conjugated polymers have energy gaps of typical photo-luminescent materials. This basic property of optoelectronic devices are of current interest from the technological point of view. Particularly, the ground state of polyacetylene is a twofold degenerate insulator with nonlinear excitations in the form of bond alternation domain walls called solitons. In polyacetylene, solitons are free charge carriers, positive or negatively charged, where each one is associated with an electronic state at the center of the energy gap. Understanding the properties of these excitations at thermalized molecules is fundamental for the description and the technology of conjugated polymers. In this work we performed numerical simulations to investigate the soliton behavior in trans-polyacetylene chains under the presence of an external electric field and temperature. Using an extended version of the Su-Schrieffer-Heeger (SSH) model to include external electric fields and temperature using an infinite number of oscillators as a thermal bath, we considered a generalized quantum Langevin equation approach in our equations of motion. Our results suggest an interesting phenomenon associated with the soliton, an internal oscillating dipole with oscillating frequency at the infrared region.

Support: CAPES, CNPq and FINATEC.

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"Interaction of Allylic Carbocations with Benzene: A Theoretical Model of Carbocationic Intermediates of Terpene Biosynthesis"

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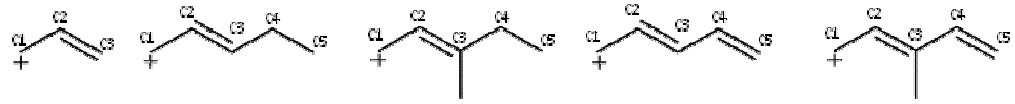
Key-words: Density functional calculations / Electrophilic substitution/Terpene biosynthesis

During the biosynthesis of terpene carbocationic allylic intermediates are formed. Although a high reactivity is expected from this kind of intermediates, there happens no alkylation of the aminoacid side chain of the active site of enzymes that participate of the terpene elongation. To the better understanding of this phenomena, in this work quantum chemical calculations were carried out using the Gaussian 09 program package. Geometry optimizations were performed at level M06-2X / 6-311++G(d,p). Intrinsic Reaction Coordinate calculations (IRC) were carried out to evaluate whether the transition states connected the reactants to the products. Atomic charges were derived of the fit to the electrostatic potential (ESP) according to the ChelpG scheme and of the atomic polar tensor based (APT) analysis. The model reaction was the akylation of benzene, which mimics the side chain of phenylalanine, an amino acid usually found in enzymes involved in terpene biosynthesis. The electrophiles used were a series of allylic carbocations, mimicking terpenoid ones, shown in scheme 1.

Scheme 1:



Results showed that for secondary and tertiary allylic carbocations, as the ones found in nature, the non-covalent interaction is energetically favoured relative to the alkylation of the aromatic ring.

Support: CNPq, FAPERJ, NACAD, CENAPAD-USP.

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"Modelagem molecular da reação de gás sulfídrico com triazinas"

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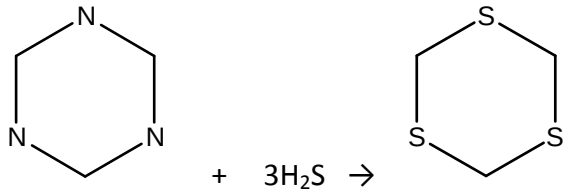
Key-words: Gás sulfídrico, triazinas, modelagem molecular

O gás sulfeto de hidrogênio é um possível contaminante do petróleo bastante comum já na fase de exploração. Além de ser extremamente tóxico é de grande capacidade corrosiva trazendo grande potencial de risco de vida e ambiental às operações nas locações onde se faz presente. Para conviver com esse problema a indústria do petróleo se utiliza de substâncias absorvedoras do gás sulfídrico (H_2S), como a triazina e seus derivados. O objetivo deste trabalho é estudar as reações do gás sulfídrico com as triazinas e tentar identificar os mecanismos pelos quais essas reações se processam, utilizando diversos níveis de cálculos teóricos. Os modelos das reações seguem o esquema abaixo para triazina mais simples (1,3,5-triazina) e pode ser utilizado o conceito de reações isodésmicas.



Resultados preliminares mostram que todas as etapas de substituição do nitrogênio por enxofre no anel são exotérmicas. Isso demonstra uma maior estabilidade energética dos produtos em relação aos reagentes, indicando que esse mecanismo de substituição parece ser preferencial. Isso também pode ser observado durante a simulação computacional onde o aumento da ligação C-N do anel com a aproximação da molécula de H_2S sinaliza para o rompimento dessa ligação e a formação da ligação C-S, que após a simulação, apresentou um comprimento médio de 1,8 Å. Uma simulação em etapas, com uma protonação intermediária da triazina, foi também realizada. De maneira similar, pode ser observado que o ânion dissulfeto também interage com a triazina protonada com o rompimento das ligações C-N e a formação das ligações C-S com valores médios de 1,8 Å. Os resultados para a triazina protonada também indicam que a reação é energeticamente favorável.

Support: FTESM/PETROBRAS.

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"Enantioselectivity and reaction mechanism study of CaL-B towards myo-inositol synthetic derivatives. A computational study."

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Key-words: Lipase, reaction mechanism, molecular modeling, QM/MM, myo-inositol.

The integration between enzyme catalysis and synthetic organic chemistry expands the possibilities of obtaining chemical compounds of biological interest. Within this context, lipases and esterases constitute a class of enzymes of great importance to biocatalysis applied research. The catalytic site of lipases presents a catalytic triad (Ser, Asp/Glu and His) similar to the one observed for the first serine-proteases. The active site is stabilized by hydrogen bond networks, for each particular enzyme, and the oxyanion hole is usually formed by two backbone nitrogen atoms (NH from the amide groups) close to the nucleophile.
In this project, we studied of the enantioselectivity of *Candida antartica* lipase B lipase towards synthetic derivatives of myo-inositol. In this work we investigated the reaction energy barriers, including the formation of the second tetrahedral-intermediate. The complexes were obtained through molecular docking and the tetrahedral intermediates (TI) were obtained through a equilibration and minimization. These protocols comprised firstly of a molecular dynamics simulation of the complexes, restraining the residues not related to the catalytic mechanism and also restraining the distance between the hydroxyl 5 of the myo-inusitol ring with the acyl-enzyme complex. This was followed by an energy minimization using steepest descent and conjugate gradient. The function of lipases depends on the local hydrogen bond network of the reactive site. Inspection of the hydrogen bonds between the acyl oxygen atom and the amide hydrogens of residues in the oxyanion hole revealed the presence of such bonds in all trajectories. An additional water molecule, coordinated to the oxyanion hole, was observed in one of the complexes. Short hydrogen bonds were observed between one the imidazole nitrogen atoms and the reactive oxygen atom of hydroxyl groups of the myo-inusitol derivatives. This hydrogen bond should help the completion of the reaction through the formation of the second TI. The TIs were obtained for the most favorable complexes and these results were used in further QM/MM calculations. In order to estimate the reaction barriers, QM/MM calculations were performed using the QM/MM module of the molecular dynamics package AMBER vs. 11. These simulations are still in progress.

Support: FAPERJ, CNPq, CAPES

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Questioning the Electron Delocalization Concept

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Key-words: GPF-EP, delocalization, interference, chemical bond, conjugation

The electron delocalization concept plays an important role in the language of modern chemistry, being used as an explanation for bond formation and for properties of molecules with conjugated π bonds. However, some questions have been raised in the past concerning the appropriateness of its application to non-aromatic conjugated molecules, questions which were never properly answered.

The main problem with this concept originates from the multiple ways electron densities in quantum systems can be considered delocalized. In a sense, even the density in a single hydrogen atom is delocalized. By recognizing that the concept aims to describe the density changes which occur with the formation of covalent bonds, being clearly distinct from quasi-classical effects such as charge polarization, it becomes possible to rigorously determine the extent to which a system presents “delocalization”. This is done by separating the electron density into its quasi-classical and interference (quantum-mechanical) contributions, the last of which has been shown to be responsible for the covalent part of chemical bonding.

This separation has been carried out for a number of systems using the GPF-EP method, which allows it to be done for individual bonds or groups of bonds. It becomes clear through this analysis that the usual attribution of π bond delocalization in molecules such as 1,3-butadiene is inappropriate and cannot explain its properties. On the other hand, the benzene molecule does present density changes which can be regarded as “electron delocalization” in a sense, though its role in the stabilization of the molecule is quite different from the one traditionally upheld.

Support: FAPERJ, CNPq.

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"Molecular Dynamics Studies of Dengue E Protein Trimer"

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Key-words: dengue E protein trimer, molecular dynamics, protein pockets

The envelope (E) protein of dengue is important for the fusion with the cell membrane. The membrane fusion is the main event that occurs during entry of enveloped viruses into cells. In the case of the dengue virus, which belongs to the class II flavivirus family, this event depends on a pH-induced rearrangement of the E protein units exposing the fusion loops, thereby becoming apt to fusing with the host-cell membrane. In this work, the behavior of the trimer of the E protein at the pre-fusion state, constructed from superposition of 1OKE monomers (all atom structure) to trimer monomers of 1THD (C_α structure), was studied by molecular dynamics simulation in order to observe the stability of the generated all atom structure as well as to obtain information about protein pockets which are possible ligand-binding sites. The simulation was carried out by 500 ns with the GROMACS package modeling the histidine residues in their protonated form, in explicit solvent with an ionic strength of 0.15 $mol.L^{-1}$. Protein pockets were detected using the FPOCKET program. The structure of the trimer suffer great modifications in the first 100 ns (Fig. 1A), reaching RMSD values around 0.6 nm that were maintained until 500 ns, with major oscillations between 300 to 500 ns due fluctuations of some residues at the domain III. The secondary structures of monomers, which are mostly β-sheets, were maintained throughout the simulation. Two pockets at the surface were detected (Fig. 1B): one at the trimer contact with a volume of 770 ± 484 $Å^3$, and the other at the monomer contact with 933 ± 438 $Å^3$.

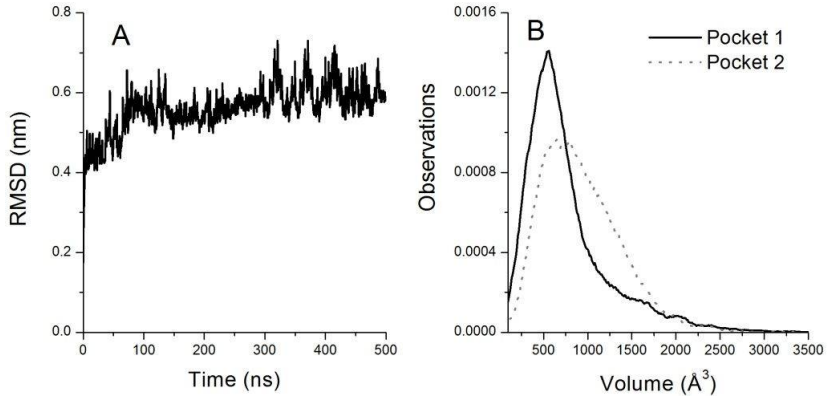

Figure 1 – (**A**) RMSD with relation to the initial structure. (**B**) Pocket volume.

Support: FAPESP e CNPq.

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"Molecular Dynamics study of the Mechanism of Inhibition of Methane Hydrates by Alcohols"

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Key-words: Molecular Dynamics / methane clathrates

Natural gas water clathrates or gas hydrates are systems of polyhedral cells formed by hydrogen-bonded water molecules and stabilized by encaged guest gas molecules, such as methane and/or carbon dioxide. Gas hydrate crystals are formed when water and relatively small gas molecules are present under critical conditions such as high pressure and low temperature. In offshore the exploitation of petroleum and natural gas occurs in some thousand of meters deep, where the formation of plugs of hydrate crystals can difficult or even interrupt the production. Thus, methods aiming to understand and avoid hydrate formation and the flow assurance in the oil wells are of interest. In this work we use molecular dynamics simulations to evaluate the influence of the structure in the mechanism of inhibition of a series of linear alcohols.

The initial positions of the water oxygen atoms were determined from experimental x-ray crystallography of the CH_4 clathrate. NPT molecular dynamics simulations with Tinker program on a periodic box, which varied in size according to the alcohol, were performed. The simulations were carried out for a total time of 200 ps with 50 ps used for temperature scaled equilibration.

It was verified that for long chain alcohols (larger than four carbon atoms), the mechanism of inhibition is different from the one found for small chain alcohols, because the former follow the kinetic mechanism. The low solubility of such alcohols leads to phase separation, which extracts methane from the aqueous phase, decreasing its supersaturation that would prevent the hydrate formation.

Support: ANP-PRH01, CNPq, FAPERJ, NACAD, CENAPAD-USP,
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Solvent Effects on the Metal to Ligand Charge Transfer (MLCT) Transitions in Ruthenium Complexes with Nitrogen Ligands.

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Key-words: DFT, Solvent Effects, MLCT, Ruthenium Complexes.

Ruthenium complexes with nitrogen ligands display an extensive range of applications as, for instance, photosensor devices and antitumoral agents [1]. Many of these compounds are characterized by its strong metal to ligand charge transfer (MLTC) transitions appearing in the visible region of the electronic spectrum. These MLCT transitions are characterized by its large solvatochromic shifts on different solvents [2]. In this study we investigate the solvent effects on the MLCT transitions of the compounds $[Ru(NH_3)_5\mathbf{L}]^{2+}$(**L**= pyridine and pyrazine). The structure of the compounds was optimized using the Beck-Purdew (bp) functional, using the ahlrichs def2-TZVP basis set and the TZVP/J auxiliary basis set for the Coulomb part. Scalar relativistic effects on the ruthenium atom were treated using the ZORA approach [3]. To speed up the calculations the resolution of the identity were used [4]. The structure obtained at the bp/def2-tzvp level shows an excellent agreement with the experimental findings. Prior to the study in solution, we performed a systematic study of the UV/Vis spectra of the complexes in gas phase employing the TDDFT formalism and using several pure, hybrid and meta GGA functionals. In general the results obtained with all XC functionals analyzed deviated largely from the experimental MLCT transition. For instance, the B3LYP result deviates 79 nm from the experimental value obtained in aqueous solution. The solvent effects on the MLCT transition were than treated using the sequential Quantum Mechanics/Monte Carlo Simulation (S-QM/MC) developed by Coutinho and Canuto [5]. Configurations based on the analysis of the center-of-mass distribution functions were selected and the water molecules were included explicitly and also as point charges in the TDDFT treatment. The results, obtained as an average over the selected configurations, shows that the MLCT band shows large solvatochromic shifts in agreement with the experimental values. Further detais of the S-QM/MC simulation, analysis of the hydrogen bonds, and performance of the several XC correlation functionals to describe the MLCT transitions will be given an discussed in the presentation.

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Support: CNPq, INCT-Catálise, FAPEMIG.

Estudos de Dinâmica Molecular das Interações Proteína-Ligantes da Enzima dUTPase de *Plasmodium falciparum*.

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Key-words: Enzima *PfdUTPase*, Dinâmica Molecular, QM/MM.

A busca por novas drogas para o combate à malaria tem se tornado objeto de estudo em todo o mundo. O aumento da resistência da doença aos quimioterápicos clássicos é crescente o que aumenta a necessária e urgente busca por novos alvos moleculares para novos fármacos. Malária faz parte de um grupo de doenças consideradas como negligenciadas. São doenças graves endêmicas de áreas tropicais pobres de países da Ásia, África e América latina.

Utilizando técnicas de modelagem por homologia produzimos, em estudo prévio, o modelo teórico do homotrímero da *Desoxiuridina trifosfato nucleotidohidrolase - PfdUTPase (PDB ID 1VYQ),* enzima essencial ao ciclo de vida do parasita *Plasmodium falciparum*. Essa enzima tem fundamental importância na replicação do DNA, podendo ser considerada um potencial alvo para o desenvolvimento de novos quimioterápicos contra a malária. Neste trabalho investigamos quatro análogos do ligante desoxiuridina trifosfato como inibidores da *PfdUTPase.* Em estudos experimentais, essas moléculas já se mostraram bons candidatos à fármacos, contudo, nenhuma investigação teórica foi realizada para avaliar o papel das interações intermoleculares desses ligantes com a *PfdUTPase*.

As estruturas dos complexos (*PfdUTPase*-inibidor) foram solvatados e neutralizados com o programa LeaP, usando o modelo de água TIP3P em uma caixa octaédrica. Para os ligantes usamos o campo de força *GAFF* juntamente com o esquema de cargas AM1BCC e para a proteína usamos o campo de força *FF99SB.* Equilibramos os complexos em 2*ns* de simulação com o programa AMBER 11 através de Dinâmica Molecular clássica NVT e NPT (1atm e 300K), onde usamos condições periódicas de contorno e o método soma de Ewald para contabilizar as interações eletrostáticas. Adicionalmente foram feitos cálculos de dinâmica molecular QM/MM aplicando os métodos semi-empíricos RM1 e PM3-PDDG para a parte QM, que foi composta por um dos ligantes mais os resíduos intimamente relacionados, totalizando cerca de 120 átomos. Produzimos uma trajetória de 2ns para essas simulações. A análise das trajetórias com a ferramenta *hbound* do programa *CPPTRAJ* revela que o deslocamento de uma molécula de água presente no interior do sítio ativo, quando tratado com QM, prejudica a formação das ligações de hidrogênio entre a porção uracila dos inibidores e os resíduos ILE117 e ASN103, indicando que esta água seja imprescindível para a estabilização do complexo e a inibição enzimática.

Agradecimentos: CNPq, CAPES, FINEP e INAMI

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A Theoretical Study of Electronic Properties of (E)-ethyl 3-amino-2-((5-chloro-2-hydroxy-4-nitrophenyl)diazenyl)butanoate Including Environment Polarization Effects

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Key-words: Environment Polarization Effects, Electronic Properties, *ab initio*.

Enaminones are chemical substances that present a conjugated system of the type N-C=C-C=O with different geometric forms. A particular class of enaminones are the azo-enaminones which are obtained by incorporation of an azo group to the N-C=C-C=O conjugated system. The presence of the azo group plays an important role on the electronic properties of the system. We have calculate the dipole moment, linear polarizability and second hyperpolarizability of asymmetric unit of (E)-ethyl 3-amino-2-((5-chloro-2-hydroxy-4-nitrophenyl)diazenyl)butanoate crystal using a hybrid procedure between the supermolecule approach and an interactive electrostatic polarization scheme where the environment polarization effects are attained by assuring the convergence of this properties in the polarization field of surrounding molecules whose atomic sites are treated as point charges. The interactive procedure was performed considering the atomic sites of the closest 249 asymmetric units as point charges. So, the simulation was developed using a cluster of 5x5x5 unit cells, each unit cell containing only one asymmetric unit. Our results show that in the presence of the embedding charges, the value of dipole moment is increased by 11% while the static values of linear polarizability is decreased by 5% as compared with the isolated situation. All calculation where performed at MP2/6-31+G* using the Gaussian 09 suite of programs.

Support: CAPES, CNPq, FINATEC.

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Implementação do código computacional kcvt para o cálculo de constantes de velocidade segundo CVTST.

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Key-words: kcvt, Teoria de Estado de Transição, Teoria Variacional Canônica

A partir da proposta da teoria de estado de transição generalizado, e em particular do método variacional canônico (CVTST) para o cálculo de constantes de velocidade, vários códigos computacionais foram desenvolvidos com essa finalidade, destacando-se o programa POLYRATE de Truhlar e colaboradores (http://comp.chem.umn.edu/polyrate/). Porém, os programas disponíveis apresentam ou alto nível de complexidade levando, eventualmente, o usuário a cometer erros na determinação de coeficientes de velocidade variacionais, ou tratam o problema com extrema simplificação, gerando resultados duvidosos. Neste trabalho, o código computacional kcvt para o cálculo de constantes de velocidade variacionais canônicas é apresentado. O programa foi escrito em FORTRAN e considera como input os dados de propriedades moleculares (energia eletrônica, freqüências vibracionais, momentos de inércia) obtidas em níveis teóricos (*ab initio*, DFT ou semi-empírico) do ponto de sela e reagente(s) para o cálculo de constantes de velocidade segundo a teoria de estado de transição convencional ou os dados de propriedades moleculares de pontos localizados no caminho de reação de menor energia traçado na superfície de energia potencial. Possibilidades de reações uni e bimoleculares foram consideradas e ainda reações entre átomos ou íons e moléculas. Optando-se pelo input das propriedades dos produtos, constantes de equilíbrio são calculadas e constantes de velocidade para reações inversas são determinadas considerando-se a reversibilidade microscópica. Modificações nas funções de partição eletrônica para o acoplamento spin-órbita e vibracional para correções anarmônicas são possíveis, além da opção de inclusão do efeito túnel. O programa vem sendo aplicado em diversos trabalhos deste grupo de pesquisa e de grupos colaboradores para determinação de coeficientes de velocidade variacionais, com resultados em excelente acordo com dados disponíveis na literatura. Ainda neste trabalho são apresentados os resultados obtidos para a reação de dissociação unimolecular $CH_3NH_2 \rightarrow CH_3 + NH_2$, sua reação inversa e as reações consecutivas no mecanismo de pirólise da metilamina, sendo discutidos os diversos aspectos teóricos envolvidos no cálculo de constantes de velocidade.

Apoio: FAPERJ.

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Molecular modeling and QSAR analysis of a set of pyrrolidine carboxamide derivatives as potential enoyl-acp reductase inhibitors

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Keywords: tuberculosis, pyrrolidine-carboxamide derivatives, molecular modeling, QSAR

Enoyl-acp reductase (ENR) catalyzes a key regulatory step in fatty acid elongation which involves a NADH-dependent stereospecific reduction of α,β-unsaturated acids bound to the acyl carrier protein. These fatty acids are intermediaries in the biosynthesis of mycolic acids, the major components of *Mycobacterium tuberculosis* cell wall.[1,2] A set of pyrrolidine-carboxamide derivatives as selective inhibitors against the ENR from *M. tuberculosis* (InhA) was reported by He and co-workers,[3] and investigated in this study applying molecular modeling and QSAR methods. The crystal structure of five analogues bound to InhA were used as starting point to build up the molecular 3D models of 46 inhibitors in their neutral forms (HyperChem 7.5). The geometry optimization was performed in MM+ force field and partial atomic charges were computed employing the PM3 semiempirical method. Molecular dynamics (MD) simulations of 200 ps at 298 K were previously carried out (MOLSIM 3.2 software).[4] A lowest-energy conformation was selected for each ligand from its conformation ensemble profile (CEP), energy-minimized, and employed to calculate the independent variables or descriptors (electronic, hydrophobic, steric, structural, topological, thermodynamic, etc). The electronic descriptors were computed using the following quantum mechanics methods: HF/3-21G*, HF/6-31G*, B3LYP/3-21G*, and B3LYP/6-31G*. Four data sets, containing all samples, were generated to perform a preliminary multivariate QSAR analysis. The IC_{50} values for InhA (μM)[3] were expressed as negative logarithmic units, pIC_{50} (-log IC_{50}), and varied from 4.13 to 6.85. Partial least squares (PLS) regression and genetic function approximation (GFA),[5] implemented in WOLF 5.5 program,[6] were used as fitting functions. Suitable preliminary QSAR models were obtained for all data sets, but the HF/6-31G* data set (45 samples and 46 descriptors) gave the best models. Hierarchical cluster analysis (HCA) combined with principal components analysis (PCA) scores, and pIC_{50} values distribution were taken into account for splitting the complete data sets (training and test sets). The best QSAR model (training set HF/6-31G*, n = 35; five descriptors; q^2 = 0.61; r^2 = 0.71; LSE = 0.16; LOF = 0.32; outliers = 0) was validated employing the leave-*n*-out crossvalidation and **y**-randomization procedures. Its external prediction power (test set, n = 10) was 90%. Thermodynamic descriptors, torsional angle (θ_4), and the electrostatic potential charge (CHELPG) of C_2 atom (carbonyl group) were better correlated to the pIC_{50} values (Fig.1).These findings must be considered for designing new leads as potential antituberculosis agents.

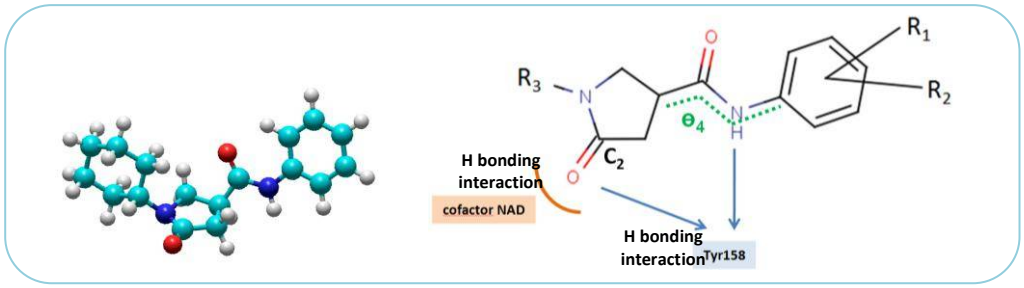

Figure 1. General chemical structure of pyrrolidine-carboxamide derivatives pointing out some descriptors and related interactions in the active site of InhA regarding the best QSAR model.

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Acknowledgments: *CAPES, CNPq, The Chem21 Group,Inc. (MOLSIM 3.2 and WOLF 5.5 licenses).*

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"A VSCF conformational analysis of substituted-ethanes"

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Key-words: Correlation, Conformational Analysis, VSCF

The main purpose of this work is to analyze the Vibrational Self-Consistent Field (VSCF) method efficiency to predict the conformational populations of well-known cases of substituted ethanes: $C_2H_4Cl_2$ (**1,2-DCE**) and $C_2H_4F_2$ (**1,2-DFE**). Experimental data already reported that the preferential conformation of the **1,2-DCE** corresponds to *anti* conformation [1] while in **1,2-DFE**, the *gauche* conformation is preferred [2]. Despite the apparent simplicity of these molecules, previous studies reported by our group [3] showed that conventional quantum mechanics methods do not yield satisfactory results to **1,2-DFE**. Therewith, one can expect that the VSCF method is more suitable to correctly predict the thermodynamics properties, once good preliminary data (MP2/6-311++G(2d,2p)) was obtained for H_2O_2 (S_{298K} = 55.90 cal.mol^{-1}.K^{-1}, compared with experimental data of 55.76 ± 0.12 cal.mol^{-1}K^{-1}). Preliminary MP2/6-311++G(2d,2p) VSCF calculations for *gauche* conformer of **1,2-DFE** showed a non desirable deviation from the observed frequencies ($\nu_{Harmonic}$=154 cm^{-1} and $\nu_{MP2\text{-}VSCF}$=179 cm^{-1} while experimental data is ν=147cm^{-1}[4]), what may be attributed to the basis set used, with Dunning basis set (DZP, TZP) leading to better results.

Support: FAPEMIG, CNPq, CAPES.

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Comparison between Optimized Geometries, Vibrational Frequencies and Uv-Vis of μ- Oxo-bis[pentachlororuthenate(IV)] Anion by DFT, HF and MP2 Methods

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Key-words: ruthenium oxo-bridge, electronic structure, vibrational spectrum

The chemistry of ruthenium complexes has received continuous attention in the latest decades[1]. Theoretical studies involving analyses of electronic structures for $[Ru_2OCl_{10}]^{4-}$ anion is few[2]. A better understanding of the electronic properties depends on the knowledge of the molecular orbital description of its compounds. The aim of the present work is to investigate the differences between the optimized geometries, frequencies and electronics structures calculated by the B3LYP and PBE1PBE functionals in addition to the HF and MP2 methods. The LanL2TZ basis set was used for the ruthenium ion, 6-311G(d) for chlorine and 6-311++G(d) for the oxygen atom. The Linux version of the Gaussian 03 program was used for all calculations. The results show that calculated bond lengths and bond angles using the MP2 method are in good agreement with experiment. The calculated frequencies show discrepancies between the MP2, DFT and HF methods. The electronic spectra were calculated with TD-DFT using the crystalline structures and the structure optimized with MP2. The theoretical results show transitions around 700 and 800 nm, compatible with a weak band in 724 nm. Three transitions around 420, 339 and 302 nm are compatible with intense bands at 495, 384 and 369 nm. This compound shows multiconfigurational behavior, as revealed by the CI coefficients. Our analyses are corroborated by evaluation of the molecular orbitals in different geometries using Gaussun and QM-Forge softwares, based on the c^2 analysis and Mulliken distribution.

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Support: UFF, FAPERJ.

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Theoretical Study of the Selective controlled HNO and NO formation in the *trans*-$[RuNO(NH_3)_4P(OEt)_3]^{3+}$ reduction

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Key-words: nitrosyl complexes, DFT, Molecular Orbital

Nitroxyl (HNO) is a highly reactive molecule attracting current attention due to its close relationship to NO either on their chemical properties either regarding its biological behavior. The nitrosonium cation (NO^+) and the nitroxyl (HNO) have been suggested as responsible for some functions ascribed to nitric oxide such as vasodilatation and cytotoxicity. Earlier studies suggest that HNO is an intermediate form of the EDRF leading to consider HNO as an alternative signaling agent to NO. The molecular geometry optimizations were performed using hybrid functional B3LYP with 6-31+G(d,p) basis set for H, C, P, N and O and the pseudo potential basis set LanL2DZ for Ru. The natural bond orbital calculation was performed using the NBO 3.0 program, as implemented in Gaussian 03 package. The solvent were obtained using the polarizable continuum model (PCM) (water solvent).

The DFT MO calculation shows that the LUMO (Ru dxy 36%, π^*NO 63%) and LUMO+1 (Ru dxy 35%, π^*NO 65%) of the nitrosonium complex ($RuNO^+$) are antibonding orbitals and thus the one-electron reduction would be more localized on the NO^+ ligand, on agreement to the results previously reported. The second electron reduction also would occurs on the nitric oxide ligand since the LUMO of the *trans*-$[Ru^{II}(NH_3)_4P(OEt)_3NO]^{2+}$ ion, is predominantly π-antibonding orbital more localized on the NO ligand (Ru d x^2-y^2 16%, π^*NO 80%) . It is well accepted that the pKa value for the HNO molecule is 11. However an increase on acidity is reported to occur when HNO is coordinated to a metal center as in the $[Fe(CN)_5HNO]$ case for which a pKa value of 7.7 was calculated. Using quantum mechanical calculations the value of 5.5 was obtained for the pKa of the acid *trans*-$[Ru^{II}(NH_3)_4P(OEt)_3HNO]^{2+}$. Since the proton equilibrium is usually fast it is likely that the nitroxyl complex, in the conditions of the experiments (pH < 4.0), would be in the *trans*-$[Ru^{II}(NH_3)_4P(OEt)_3HNO]^{2+}$ form.

Again, according to these calculations it is likely that the nitroxyl ligand would be on the singlet form ($^1NO^-$), which is about 11 Kcal mol^{-1} more stable than the correspondent triplet one ($^3NO^-$). The original *trans*-$[Ru^{II}(NH_3)_4P(OEt)_3NO]^{2+}$ would generate, just after the electron transfer, a triplet species which would undergone a faster spin isomerization to the more stable singlet form.

Due to the above characteristics *trans*-$[Ru(NO)(NH_3)_4(P(OEt)_3]^{+3}$ ion would be a reliable fast NO or HNO donor , which selectivity could be conveniently controlled trough the judicious choice of the electrochemical or the chemical reductor potential.

Support: CNPq,UESPI.

Evaluation of the Mechanism of Action of Novel Platinum (II) Complexes Coordinated to antituberculostatic drugs

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Key-words: Pyrazinamide, Pt-complexes, DFT

Pyrazinamide (PZA) is known as very common used antimycobacterial drug that possesses a well-established role in tuberculosis (TB) treatment[1]. This molecule is classified as a narrow-spectrum agent, as well as isoniazid (INH), another important drug against TB. Its medicinal potential comes from the evaluation of the reaction mechanism by the combination with other broad-spectrum agents.

In this sense, we found interesting to evaluate the coordination of PZA with cisplatin, the most important metal drug in the cancer treatment. In this work we have performed calculations using the density functional theory (B3LYP) in unconstrained geometry optimizations of Pt-PZA molecules. It has been used the 6-31G(d) basis set for all atoms, except Pt (ECP=LANL2DZ). From experimental studies, one can be noted that two new platinum(II) complexes were proposal: *cis*-$PtCl_2(PZA)_2$ (**1**) and the *cis*-$[PtCl_2(DMSO)PZA]$ (**2**).

Scan calculations lead us to believe that the most stable molecule was (**1**), with the geometry seen in fig.1. A difference of 7.15 kcal mol^{-1} was found between two optimized structures, indicating (**1**) as the most stable structure. From a ^{13}C-NMR calculated by the GIAO method, we also could be able to indicate the formation of Pt–O bond in complex (**1**) when compared to the free ligand (178 and 174 ppm, respectively). By an IRC analysis the transition state (**TS**) has been connected to (**2**). As can be seen the displacement vectors point to a clearly exchange of one PZA molecule by one DMSO molecule, suggesting a typical associative mechanism. The Addison parameter for trigonality index shows a TS slightly closer to a square pyramidal geometry ($\tau = 0.42$).

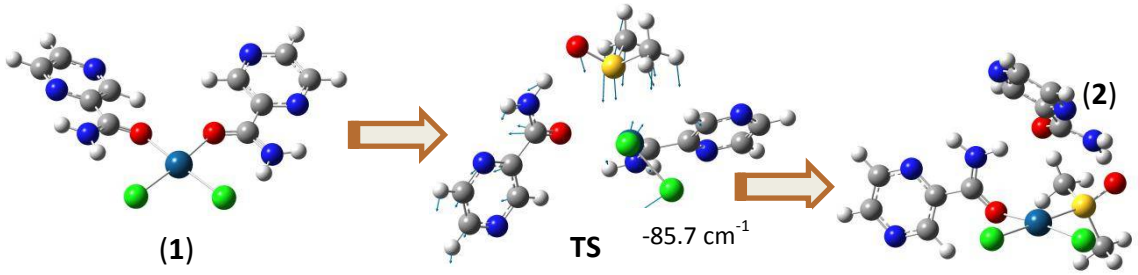

Figure 1. Optimized structures of Pt-PZA related species.

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SUPPORT PROBIC/UFJF, FAPEMIG, FAPERJ

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Direct Dynamics of Unimolecular Reactions of Formamide

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Keywords: Formamide, CASSCF, Variational Transition State Theory

The unimolecular reactions of formamide have been focus of investigation, since formamide is a prototype for peptide bonds.

The present work aims to investigate the ground state unimolecular reactions of formamide in gas phase: (1) $CHONH_2 \rightarrow CO + NH_3$ and (2) $CHONH_2 \rightarrow HCO + NH_2$. Theoretical calculations, including geometry optimizations and frequencies, have been performed at CAS(10,9)/cc-pVTZ level. Other basis sets have been used for comparison. Single point calculations have been performed at MRMP2 level in order to improve the electronic energy.

Here, the unimolecular reactions have been dealt differently, depending on the specific topology of the potential energy surface. The minimum energy path for reaction (1) has been described by IRC calculations, starting from the geometry of the saddle point. For the dissociation path, the CN distance have been taken as the reaction coordinate, and the reaction path was calculated by successive geometry optimizations, keeping the CN coordinate frozen. *Ab initio* calculations have been performed with GAMESS. Canonical variational rate coefficients have been calculated in the range 1500 – 2000K with the kcvt code.

Molecular properties of formamide, calculated at CAS(10,9)/cc-pVTZ are in good agreement with the literature data, with mean deviations of less than 1% for distances and angles and 7% for vibrational frequencies. The calculated energy barrier, including zero point energy corrections is 77.71 $kcal.mol^{-1}$ at MRMP2/CAS(10,9)/cc-pVTZ level. The minimum energy path for reaction (1) is shown in Figure 1. Rate constants are expressed by $k(T) = 4.69x10^{14}exp(-79.63/RT)$ for reaction (1) and $k(T) = 5.06x10^{15}exp(-87.31/RT)$, for reaction (2). Rate constants are in good agreement with experimental data, being $k^{exp}/k^{calc} = 0.72$ (1500 – 2100K).

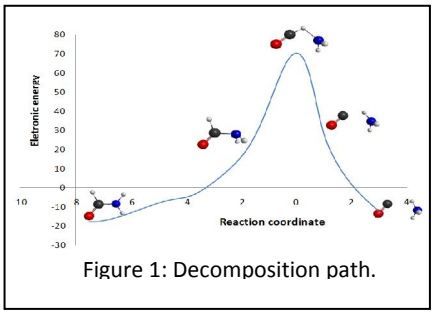

Figure 1: Decomposition path.

These two unimolecular processes are initiated by the out of plane movement of the NH2 fragment. For the decomposition, the OCH bending mode contributes to the formation of a saddle point and the reaction barrier. For the dissociation, the CN stretching mode must be achieved, leading to a barrierless reaction. Finally, these reactions are shown to be not competitive at the ground state, being the decomposition faster.

Support: FAPERJ e CAPES.

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DFT study of the porphyrin ring distortion and aryl-porphyrin rotation in *meso*-substituted porphyrins

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Key-words: porphyrin, distortion, DFT

Porphyrins are ubiquitous in Nature and play important roles in biological processes, such as electron transfer, oxygen transportation and activation, and drugs and xenobiotic metabolism. Whereas chemical modification of the porphyrin ring in hemeproteins either by natural or synthetic paths is expected to altered the physicochemical and biological properties of the protein, a great deal of effort has been devoted to understand the modulation of hemeprotein function followed by structural deformations of the porphyrin. The role of porphyrin deformation in heme biosynthesis itself is well documented. *Meso*-aryl substituted porphyrins are the most studied building blocks for biomimetic models of a variety of hemeproteins (*e.g.*, cyt P450), superoxide dismutase-based redox-modulator drugs, and photodynamic therapy photosensitizers. In these systems, activity is controlled by aryl ring substitution and the mechanism proposed for aryl-porphyrin rotation involves a transition state (TS) in which the porphyrin is deformed to minimize steric interactions.

Hereon the impact that the number and pattern of *meso*-aryl substitution along with the effect that electronic nature of the aryl group exert on porphyrin deformation and on the rotational barrier was investigated. Electron-donor (3-methylphenyl and 4-methylphenyl) and electron-withdrawing (*N*-methylpyridinium-3-yl and *N*-methylpyridinium-4-yl) groups were studied using the following *meso* substitution patterns: 5-aryl-, 5,15-diaryl-, 5,10-diaryl-, 5,10,15-trisaryl- and 5,10,15,20-tetraarylporphyrin.

The mechanism and ring deformation associated with the aryl-rotation of a total of 20 porphyrins were investigated. All the structures and energies were calculated at a DFT/B3LYP/6-31G* level and TS were confirmed by frequency calculation, including correction of zero point energy (ZPE). Contributions of *sad*, *ruf*, *pro*, *wav(x)*, *wav(y)* and *dom*-type deformations were analyzed by PCA.

For all porphyrins investigated, *ruf* is the preferential out-of-plane deformation mode at TS, increases with the number and patter of substitution but is little influenced by the electronic nature of the aryl group. Conversely, the *sad* mode contributes little to the overall out-of-plane deformation, but it is significantly modulated by the electronic nature of the aryl group. Remarkably, the electronic nature of the aryl group inverts the dependence of the rotational barrier on the substitution pattern. These results shed light on the non-additive properties found on unsymmetrically substituted porphyrin-based models.

Support: CNPq, CAPES, UFPB.

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Intermolecular potential energy retrieval by Firsov method: application to He He interaction

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Key-words: Potential Energy, Firsov method, inverse problem

Recovering potential energy function from experimental data is an important step in inverse theory and chemistry. This will provide very accurate potential for the property under consideration. In this work helium-helium interaction is to be obtained from theoretical and experimental cross section[1], using the Firsov method[2]. Theoretical scattering data were generated by a recent HeHe potential[3] and recovered, as in figure 1. The range and accuracy of the inverted potential can be chosen by appropriated total energy employed. Although the whole potential was recovered, that is no taken to imply the inversion is always possible, for experimental errors have to be considered. For example, a systematic error of about 1% in the scattering angle will recover the potential with errors ranging from 0.69% to 7.61%. Experimental differential cross section[1] data will be used, to obtain scattering angle and precise potential energy function.

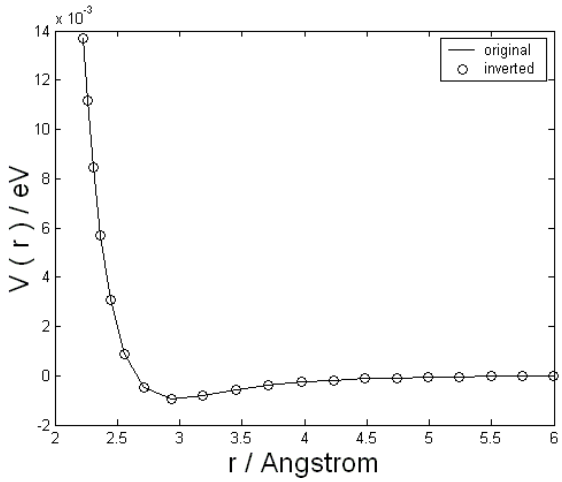

Figure1: Recovered and theoretical potential function.

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Support: CAPES, CNPQ, FAPEMIG

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Homology modeling studies of beta(1,3)-d-glucan synthase of *Moniliophthora perniciosa*

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Key-words: *Moniliophthora perniciosa*, homology modeling, beta(1,3)-D-glucan synthase, glycosyltransferase.

The Witches' Broom Disease, caused by the hemibiotrophic basidiomycete fungus *Moniliophthora perniciosa*, drastically reduced the production of cocoa in Brazil. Phytosanitation, chemical control, genetic resistance strains and biological control, still has flaws in disease eradication process. Effort has been expended in the elucidation of molecular targets, in particular the structural components of fungal cell wall, like the beta(1,3)-D-glucan synthase. This enzyme is essential for the wall cellular construction, which catalyzes the beta(1,3)-D-glucans formation. Protein structure homology modeling approach are able to determine the structure of proteins without performing experimental steps, considering the barriers related to experimental methods for structure determination of molecular targets. The presence of the conserved catalytic residues in members of the same glycosyltransferase family and overall structural analyze suggests that they catalyze glycosyl transfer reactions by similar mechanisms. Therefore, the objective of this study was determine the three-dimensional model of the enzyme beta(1,3)-D-glucan synthase of *M. perniciosa* by homology modeling. Both procedures were performed for build the models: a comparative modeling by satisfaction of spatial restraints in MODELLER and a modeling by assembly of rigid bodies in the SWISS-MODEL software. The models were elected based on analysis of the stereochemistry quality and a quantitative assessment of similarity from the obtained models and to templates. Was obtained reasonable structural model of beta(1,3)-D-glucan synthase enzyme (BegS1). The BegS1 model showed two distinct α/β domains, as feature inverting glycosyltransfer family, and the topology of folded structure showed 7 strands and 13 alpha-helices. The BegS1 model showed the presence of a catalytic cavity formed by the conserved aspartic acid residues (Asp326, 345, 353 and 354 DDxD motif) implicated in substrate binding and/or catalysis. In the BegS1model this cavity it is close by a loop region, as was seen in the GT-2 family structure. It is encouraging to find that the model BegS1 agree well with structures from GT-2 enzyme family.

Support: FAPESB.

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"The force field influence in the process of structural conversion of cellular prion protein simulated at low pH"

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Key-words: Molecular Dynamics (MD), GROMOS, AMBER, OPLS.

Prions are proteins that cause a group of invariably fatal neurodegenerative diseases, one of the most known being bovine spongiform encephalopathy (BSE or mad cow disease)[1]. The cellular prion protein (PrP^{C}), rich in helical structure, undergoes a change in its secondary structure producing the pathological protein (PrP^{Sc}, the prion) in which β-sheet structure prevails. Because of the lack of high-resolution prion structural data, MD simulations can be particularly useful to study PrP misfolding[2]. Employing the force field ENCAD, MD simulations at low pH were performed by Alonso and co-workers. These results indicated that this technique was capable to create some structural instability, producing a gain of β-structure content in the otherwise unstructured N-terminal region[3].

This work proposes to investigate the influence of using different force fields (GROMOS, AMBER and OPLS) in the process of structural conversion of cellular prion protein simulated at low pH, reproducing Alonso's[3] protocol. Thus, for each force field we performed a MD simulation of 30 ns at 298 K, using as its starting point the Syrian hamster PrP^{C} fragment (residues 109-219, PDB code: 2PrP) with HIS, GLU and ASP residues protonated. So, this study pretends to exclude the possibility of artificial structural events resulting from the use of an inadequate force field for assessing the structural conversion process.

From the time evolution of the secundary structure, we observed a stronger loss of helical structure elements in the simulations with the AMBER and OPLS force fields when compared with the GROMOS force field. Furthermore, only the AMBER and GROMOS force fields produced a consistent β-sheet core as indicated by a strand formation in the N-terminal region. Although these structural changes do not provide a perfect β-sheet structure, our results indicate that the AMBER and GROMOS force fields are more appropriate to evaluate the process of structural conversion of the cellular prion protein at low pH.

Support: CAPES.

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"Development of a general program for constructing specific Force Fields"

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Key-words: Force Field

The reliability of classical simulations (mechanics, dynamics or Monte-Carlo) relies deeply on the quality of the Force Field. Commercial packages and even the freely distributed ones provide the user with standard generic force fields. However, for simulation of materials and particularly for heterogeneous catalysis studies, specific force fields are required and those have to be constructed by the user taking into account the peculiarities of the system and the process to be simulated

The goal of this work is to develop a general program to construct specific force fields. The program was written in FORTRAN 95 language. The fit of the parameters was performed either with the Levenberg-Marquardt Method (a least squares method) to minimize a functional of the form:

$$[S] = w_E \sum_{\alpha,i} (\Delta E_\alpha - \Delta E°_\alpha)^2 + w_g \sum_{\alpha,i} (g_{\alpha,i} - g°_{\alpha,i})^2 + w_H \sum_{\alpha,ij} (H_{\alpha,ij} - H°_{\alpha,ij})^2 + \ldots . +$$

Deviations from experimental data

w_E , w_g , w_H being appropriate weights

where the first, second and third terms represent the differences in energy, energy gradient and the hessian matrix elements obtained from *ab inito* and the force field function relative to a given reference configuration of the system, or using the *hessian biased method*, where the parameters are obtained by forcing the force field hessian matrix to reproduce the experimental vibration frequencies.

All the common analytical expressions to represent the bonded and non-bonded terms of the force field are provided giving the user the opportunity of setting up his own force field. Force field terms not included in the present version can be easily implemented into the program.

The program was tested for several systems in order to validate the method employed. The points of the potential surface were obtained at the DFT-B3LYP/LAV2P level, with the Jaguar 7.6 program. The force field parameters were then adjusted to the points obtained by the *ab initio* calculation. The force fields obtained were validated by computing properties of the systems other than those used in the fitting process.

CNPq, FAPERJ, Instituto Nacional de Materiais Complexos Funcionais (INOMAT)

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A Polarizabilidade da Região de Recobrimento da Ligação Química Aplicada para o caso de Materiais Metálicos

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Key-words: Polarizabilidade de recobrimento, ligação química, estado sólido.

Este trabalho apresenta a aplicação dos conceitos de polarizabilidade da região de recobrimento da ligação química (OP) e plásmon de recobrimento (CBOP) para o caso dos metais alcalinos (Li, Na e K) e metais alcalinos terrosos (Be, Mg e Ca) no estado sólido. Em trabalhos prévios foram encontradas relações entre a polarizabilidade de recobrimento (α_{OP}) e o grau de covalência da ligação química e propriedades macroscópicas da matéria. Por outro lado, os materiais metálicos apresentam propriedades eletrônicas e ópticas bastante interessantes. Nos metais alcalinos, o exemplo das anomalias presentes nos espectros de perda de energia, que não podem ser explicadas pelo modelo de elétrons livre já é conhecido. Portanto, neste trabalho, foi feita uma abordagem computacional que envolveu a obtenção de parâmetros da ligação, tais como distância de equilíbrio (R), constante de força (k), integral de recobrimento (ρ), e energia de excitação (Δε). A obtenção desses parâmetros deve ser feita levando em consideração os efeitos do ambiente cristalino. Para mimetizar esses efeitos foi utilizada a aproximação *Frozen-Density Embedding* (FDE) da teoria do funcional da densidade, em que um aglomerado central é tratado de forma auto-consistente e a densidade eletrônica dos átomos visinhos é congelada. Essa metodologia fornece erros médios de 1% entre as distâncias de equilíbrio, experimental e teórica. A figura 1 mostra o perfil da energia em função da distância de ligação (centrados no ponto de equilíbrio) para o caso do sistema de Li na simetria cúbica de face centrada (CCC). A literatura aponta, nos espectros de perda de energia do lítio metálico, uma pico com energia 3,5 eV (abaixo da primeira ressonância de plásmon coletivo) que é atribuído aos chamados estados coletivos de zona de ligação (ZBCS – *zone boundary collective state*). O CBOP calculado para o caso do lítio metálico apresenta energias de oscilação na faixa de 3 – 4 eV. Os resultados são bastante animadores, apesar do seu caráter preliminar.

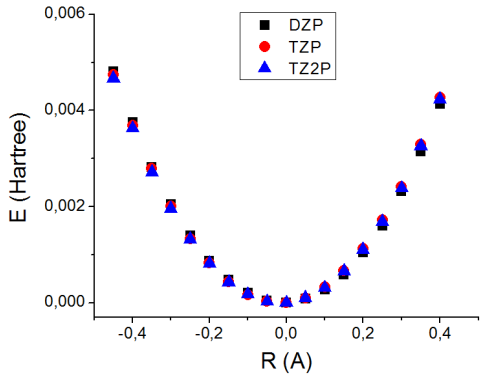

Figura 1: Perfil da energia em função da distância, centrado no equilíbrio para o Li(CCC).

Support: FACEPE, INCT-INAMI, CAPES, CNPq, FINEP.

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"Study of the interaction between Calgranulin C (S100A12) and receptor RAGE)

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Key-words: Calgranulin C, RAGE, Molecular dynamic

Calgranulin C (S100A12) is a member of the S100 family of EF-hand calcium binding proteins. Human S100A12 is predominantly expressed by granulocytes and is markedly overexpressed in inflammatory compartments. Members of S100 family have both intracellular and extracellular functions. The mechanism by which calgranulin C modulates the course of inflammatory process is related to its interaction with the receptor for advanced glycated products (RAGE). RAGE is a 45-kDa cell surface receptor comprising three immunoglobulin (Ig) domains followed by a single transmembrane region, and a short C-terminal cytoplasmic tail. RAGE contains an N-terminal V-type immunoglobulin domain followed by two C-type immunoglobulin domain (C1 and C2). Some studies suggest the interaction of S100A12 with C1 domain of the receptor RAGE, while other studies show that protein interaction with the V domain of the receptor RAGE.

Our goal is to investigate the details of the interaction between S100A12 and RAGE in order to elucidate the region of the receptor which interacts with S100A12 and what are the residues involved in this interaction. Initially we performed molecular dynamics simulations of S100A12 and regions of the RAGE V and C1, together and separately, using the GROMACS 4 suite with the OPLS-AA force field, at the NPT ensemble to verify the stability of the domains. Next was performed protein-protein docking using GRAMM-X. Different models of interaction that will be selected by energy and stereo factors.

Our initial results show that the V and C1 domains of RAGE are stable together and separately, and do not show significant changes when subjected to a concentration of 50 mM NaCl. In general, the global docking shows the preference of binding of S100A12 in the V domain and in the region between V and C1 domains. The selected models will be subjected to molecular dynamics, to investigate the dynamic behavior of the interaction between S100A12 and RAGE. These results will later be used in the calculation of free energy of interaction between S100A12 and RAGE, using the methodology SMD (Steered Molecular Dynamic).

Support: FAPESP

Modelagem Computacional da Redução de NO em Catalisadores de X: Ga_2O_3-In_2O_3 onde X = Ti ou Zn

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Palavras chaves: Adsorção, In_2O_3, PM6.

O NO_x é uma mistura gasosa contendo 95% de NO e 5% de NO_2, liberada pela combustão nos automóveis, que reage na atmosfera, sendo um dos precursores da chuva ácida e do aquecimento global. Nosso objetivo é o estudo de um material cerâmico, baseado num óxido metálico, utilizado em um dispositivo chamado conversor catalítico que é acoplado no cano de escape dos automóveis, cuja função é reduzir o NO_x para N_2. Essa reação é realizada por meio de catálise heterogênea, utilizando cálculos teóricos. Os programas usados para estudo do tema foram MOPAC2009, e o Gaussview e Jmol para visualização das estruturas. Os modelos em estudo foram criados baseando-se em superfícies geradas a partir da estrutura cristalográfica do In_2O_3, obtido no banco de dados de estruturas inorgânicas ICSD, onde partindo da célula unitária construímos uma superfície de In_2O_3 com tamanho de 3a, 4b e 1c, sendo a, b e c parâmetros da célula unitária, essa expansão é feita para que ela se torne mais próxima do modelo real da superfície, e a essa superfície dopada com Gálio, Titânio e Zinco. Iniciamos o mecanismos proposto para reação de redução do NOx para N_2 baseado no artigo de Jug e colaboradores que emprega o agregado $V_2O_7H_4Ti_{33}O_{66}(H_2O)_{17,}$ (2004). Os cálculos de otimização das geometrias dessas superfícies foram realizadas no programa do MOPAC2009, com o método PM6 usado para cálculos de estruturas eletrônicas. Neste processo a energia da superfície é minimizada em termos das coordenadas espaciais dos átomos do sistema. Para tal fim, foi aplicado o método PBC (Condições Periódicas de Contorno) usado em modelagem de sólidos, no intuito de simular a superfície real do conversor catalítico, evitando os efeitos de borda. Na tabela 1 encontramos os valores das energias de adsorção do propeno sobre a superfície do In_2O_3, bem como para a estrutura de In_2O_3 dopada com Gálio, Titânio e Zinco visando analisar o efeito do dopante na estrutura. Verificamos que a energia de adsorção do propeno na superfície dopada com Gálio e Titânio foram maiores que na superfície sem dopante. Dessa forma temos que o gálio e titânio não são bons candidatos a dopante, haja vista que a função do dopante é minimizar a energia de adsorção. Vemos que ao adicionarmos o propeno, conseguimos um resultado aceitável para a energia de adsorção, quando baseado com os valores do artigo de Jug e colaboradores,porém, ainda não podemos falar sobre a eficiência da reação na superfície, pois, não ainda foi possível concluir a reação.

Estruturas	Energias de Adsorção
In2O3	-30.28589 KJ/mol
In2O3 dopada com Ga	-7.22384 KJ/mol
In2O3 dopada com Ti	43.69874 KJ/mol
In2O3 dopada com Zn	-279.03919 KJ/mol

Tabela 1. Comparação entre a energia de adsorção do propeno na superfície 3x4x1 In_2O_3, 3x4x1 In_2O_3 dopado com Gálio, Titânio e Zinco.

Apoio: CNPQ, CAPES, UFPB

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Analysis of interactions of Cyclophilins from *Leishmania donovani* (LdCyp) by molecular dynamics and docking simulations

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Key-words: Leishmania donovani, Neolignans, molecular dynamics and docking

Leishmaniasis is currently a major health problem in the tropical countries of the world, with around 350 million people estimated to be at risk. Visceral leishmaniasis, popularly known as kala-azar, caused by L. donovani is fatal if not treated in time. In recent years, the reemergence of drug-resistant strains of L. donovani in India has called for renewed efforts to identify novel drugs against this pathogen. Neolignans are groups of compounds that show a wide range of biological effects including antileishmanial. The Cyclophilins from Leishmania donovani (LdCyp) are potential targets for the development of antileishmanial therapy. Cyclophilins (Cyps) are an ubiquitous class of proteins as peptidylprolyl cis–trans isomerases (PPIases) and are also known to be intracellular receptors for the drug cyclosporine A (CsA), besides mediating the CsA-induced immunosuppression, also participate in various cellular processes ranging from cell division, receptor maturation, protein folding and its export, and protection against human immunodeficiency virus (HIV) infection to several other important cellular steps. Herein, we have used Molecular Docking to predict the predominant binding mode(s) between Neolignans and Cyps. The genetic algorithm AutoDock Vina (version 1.1.1) was used to perform the docking. In addition, Quantum mechanical/Molecular Mechanical (QM/MM) was used to determine the interaction energy between Neolignans and Cyps. Analysis of interaction energy per residue show that Ala123, Asn124, Gln133 residues and one molecule of water are important to inhibition of Cyps by neolignans. Finally, the results indicate that neolignan and their analogues have the potential to act as leishmanicidal.

Support: UFPA Universidade Federal do Pará CAPES CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico

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Benzophenone conformational analysis

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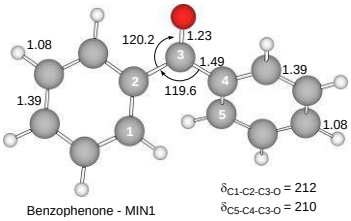
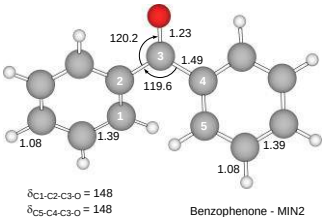
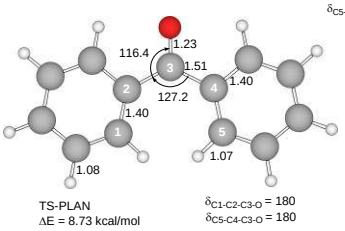
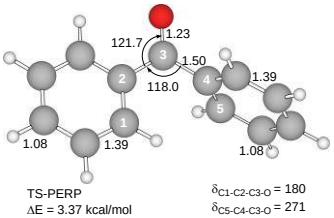
Key-words: benzophenone, sunscreens, conformation, transition states.

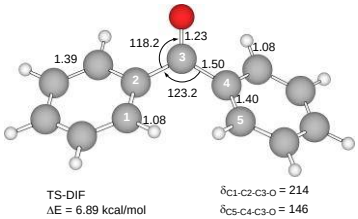
Benzophenone and its derivates are used with numerous applications purposes. These ketones are used worldwide as sunscreens because of its high molar absortivity and mainly due to its capability of absorbing in UVA and UVB simultaneously. In order to investigate the electronic and vibrational properties of these molecules, the first step is to conduct a conformational analysis. In this work the benzophenone molecule was optimized at the MP2/6-31G(d) level of theory. Two minimum energy conformers and three transition states were achieved. The two minimum geometries are non-superimposable mirror images (MIN1 and MIN2). The first transition state is the result of the rotation of one of the benzenic ring until the rings are perpendicular (TS-PERP). In the second transition state, the two benzene rings are in the same plane (TS-PLAN). In the last transition state (TS-DIF), the C=O bond and the benzene rings are not in the same plane, which preclude the conjugation. The geometries of these stationary points are presented below, along with the energies relative to the minimum states (MIN1 and MIN2). From our best knowledge, this is the first time that the existence of these two conformers is related.











Support: CNPq, FAPEMIG.

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Conformational preferences and QTAIM study of bioactive Morita-Baylis-Hillman Adducts

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Key-words: Conformational study, DFT, PCM, QTAIM.

In this work we presented a conformational study of bioactive Morita-Baylis-Hillman Adducts, as well as Quantum Theory Atoms in Molecules (QTAIM) calculations supporting their Structure-Activity Relationship. Relaxed Potential Energy Surface Scan (Gaussian 09W®) were performed using AM1 method, considering important rotational degrees of freedom (sigma bond) to each molecule. Conformational minimum were then submitted to B3LYP/6-31+g(d) calculations with Polarized Continuum Model to simulate water influence. Optimized structures were submitted to QTAIM calculations, using the Morphy98® and AIM2000 package. We observed that the conformations are governed by Intramolecular Hydrogen Bonds (IHB), when it is possible. QTAIM parameters such electronic density and laplaciane at bond Critical Point (BCP) level were able to characterize these interactions. Interestingly, compounds where NO_2 group makes IHB with hydroxyl (examples in Fig.1) show a considerable improvement of parasiticidal activity (lower IC_{50} value), in accordance to redox mechanism of action of NO_2.

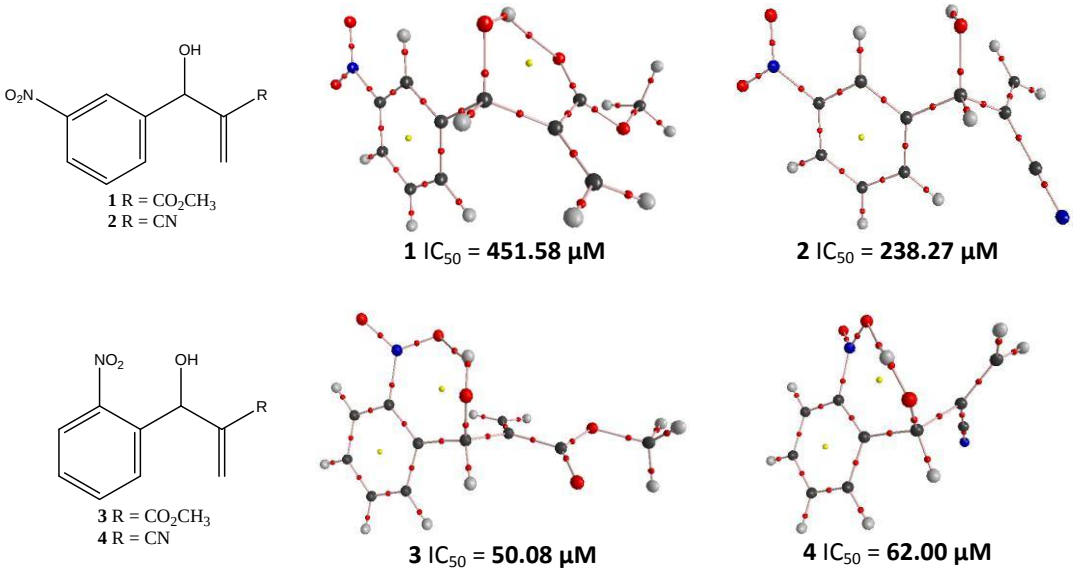

Fig. 1: Conformational preferences, bond critical points and activity of some adducts.

Support: UNIVASF, CNPq, LASOM/UFPB.

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Theoretical Study of Carbon, Germanium and Silicon Nanotubes

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Key-words: Nanotubes, Electronic properties, Theoretical calculations.

Since the experimental results of carbon nanotubes in 1991, the interest on these structures has increased the experimental and theoretical researches on such materials. The growing demand of nanotube based materials is connected to its technological applications, such as energy storage, touch screens and reinforced composite materials [1-3]. The synthesis of nanotubes with other elements such as germanium and silicon are also described in literature. Due to its high specificity and physical properties, they have promising applications in electronics, and optical devices, sensors, among others [2-4]. Moreover, optical spectroscopy is a promising technique for characterizing the geometric structure of nanotubes. Therefore, in this work we studied the structural, electronic and optical properties of carbon, silicon and germanium nanotubes in armchair and zigzag configurations. Figure 1 (a) shows the structures that were optimized using the semi-empirical PM6 method. These optimized structures were used to calculate the properties at the Density Functional Theory using the hybrid B3LYP functional with the 6-31G basis set. Figure 1 (b) shows that carbon nanotube (4, 4) with eight levels structures has a large range of absorption.

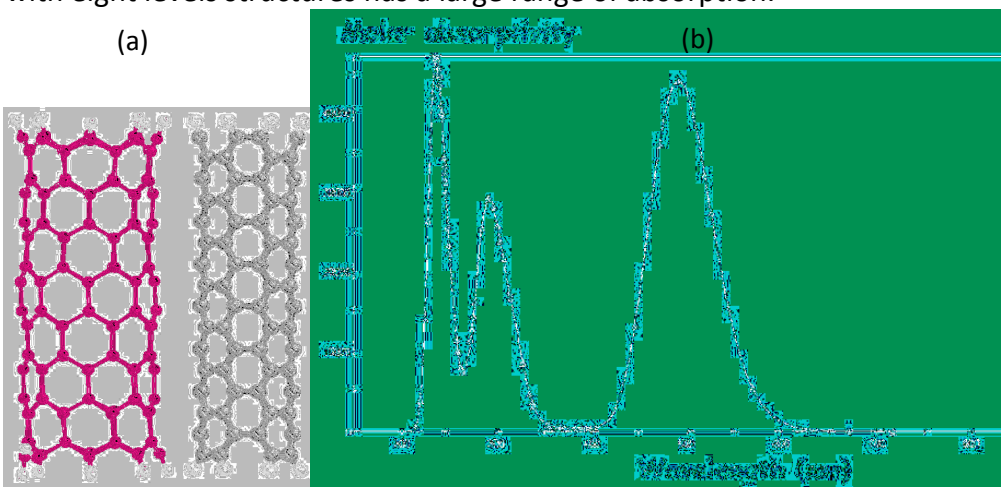

Figure 1. (a) Nanotubes models studied in the zigzag and armchair configuration, respectively. (b) Spectrum of UV-visible transition to the carbon nanotube (4, 4) with eight levels.

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Accelerating semiempirical quantum chemistry calculations using sparse linear algebra GPU libraries for large systems

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Key-words: Semiempirical Methods, GPUs, Parallel Programming, CGDMS

Nowadays we have been observing a new way to perform high demand calculations with a combined use of Graphical Processing Units (GPUs) co-processors and multi-threaded processors. So, many computational chemistry programs have been ported to explore high parallelism of GPUs, including classical molecular dynamics, DFT, Hartree-Fock, MP2, Coupled Cluster, etc.

Analogously, in this work we report the first usage of GPUs to accelerate semiempirical quantum chemical calculations for large molecular systems.

At this moment, our efforts have been done to replace some single-threaded parts of SCF procedure with parallel strategies running on both GPU and multi-threaded CPUs. Thus, we modified the MOPAC code in many ways: (1) implementing a parallel version of CGDMS (Conjugate Gradient-Density Matrix Search) linear scaling technique, (2) using numerical libraries (CUSPARSE and SparsKit 2) for handling sparse matrices which arise in large molecular systems, (3) inserting parallel linear algebra libraries (multi-threaded MKL, CUBLAS and MAGMA) and (4) a combined usage of OpenMP, NVIDIA/CUDA™ and PGI Accelerator™ programming models for introducing new parts of code to replace the serial ones.

CGDMS method replaces diagonalization of Fock matrix in SCF by minimization of energy functional subject to N_e-representability. In CGDMS there is a strong dependence on some linear algebra operations, such as matrix multiplication. The use of GPU version for this operation can be speeded up hundreds of times. Thus, a new strategy of calling full double precision matrix multiplication in CUSPARSE from FORTRAN 95 code was developed.

We have compared the performance of our parallel code running on a NVIDIA GeForce GTX 480 GPU card to the conventional MOPAC code running entirely on 3.06 GHz quad core, hyper threaded Intel® Core™ I7-950 processor. For some parts of our code, such as CGDMS convergence (when 5 CG cycles and 3 purification transformation were applied), the GPU-accelerated code was approximately 140 times faster than diagonalization in single-point energy calculation for a simulation box with 1000 water molecules and 6000 basis functions.

Support: CNPq, CAPES, FINEP and INAMI

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"Computational study of interaction of RC-3095 with gastrin releasing peptide receptor (GRP_R)"

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Key-words: molecular modeling, RC-3095, gastrin releasing peptide, gastrin releasing peptide receptor.

RC-3095 is a selective antagonist of the gastrin releasing peptide receptor (GRPR), a G protein-coupled receptor whose endogenous ligand is the gastrin releasing peptide (GRP). GRP is a 27 amino acid peptide involved in a multitude of physiological functions. Among other effects, GRP acts as a mitogen, morphogen, and proangiogenic factor in certain cancers. GRP activity results from its specific interaction with GRPR. In this context, the perspective of RC-3095 as a drug candidate due its antagonistic action on GRPR was established from studies that demonstrated its efficacy and favorable toxicity profile. Whereas the establishment of the molecular basis of drug-receptor interaction is important for design of more selective and efficient drugs, in this work is proposed the study of the binding mode between the gastrin-releasing peptide receptor and RC-3095. Also, the interaction of gastrin-releasing peptide with its receptor is evaluated. Molecular modeling, molecular dynamics simulations, homology modeling and docking techniques were employed in the establishment of structural and conformational models for the RC-3095, GRP10 (GRP C-terminal decapeptide), GRPR-GRP10 complex and GRPR-RC-3095 complex. From the MD simulations, the overall structure of RC-3095 in membrane environment was found to be different from its structure in aqueous solution. Also, the results showed that the conformation of GRP10 and RC-3095 in aqueous media is more flexible and compact than conformation of RC-3095 in the membrane interface. In the membrane interface, RC-3095 tends to adopt a stable "U" conformation, with the N-terminal region making contacts with the phospholipids while the C-terminal portion remains directed to the bulk solution. With respect to GRPR homology modeling and docking simulations, was to assign the principal residues involved in GRPR interaction with GRP and RC-3095: T303, S304, T296, M298. These results are in agreement with previous site-directed mutagenesis studies on a similar system.

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Investigation on structural optimization and spectroscopic properties of ruthenium(II) polypyridinic complexes

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Key-words: dye-sensitized solar cells, ruthenium(II) polypyridinic compounds, DFT.

Dye-sensitized solar cells (DSSC) are devices capable of convert sunlight into electricity and have been attracting much attention due to their low cost and high efficiency. One of the main component of these solar cells is the dye-sensitizers and one of the most efficient sensitizer is the *cis*-[Ru(dcbH_2)$_2$(NCS)$_2$], also known as N3, Figure 1.

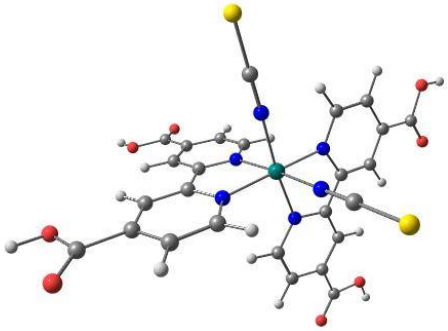

Figure 1. Optimized structure of N3 molecule.

In this work, DFT calculations were carried out for structures based on N3 sensitizer. The data obtained was compared to those experimentally determined for the complex. We have obtained geometries and simulated infrared spectra with B3LYP functional and both LanL2DZ and DGDZVP basis sets. We have also evaluated absorption spectrum by TD-DFT/B3LYP. All calculations were performed with Gaussian 03 program.

Theoretical vibrational spectrum obtained with B3LYP/LanL2DZ resembles the experimental one when including the scaling factor 0.9612. B3LYP with DGDZVP basis was also investigated and some interesting differences from the LanL2DZ, mainly on intensities of some peaks are observed. It is important to notice the identical structures obtained (RMSD ~ 0). Since the LanL2DZ pseudopotential basis set was successfully employed for N3 compound, we will use this methodology to investigate analogous structures, with promising characteristics to be employed in DSSCs.

Support: UFABC, FAPESP.

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Simulação dinâmica molecular da estrutura e dinâmica da água na presença de colágeno.

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Palavras-chave: Colágeno, hidrogéis, dinâmica molecular, simulação.

Soluções aquosas e géis de colágeno são sistemas de grande interesse na ciência dos materiais e na medicina. Devido à complexidade destes sistemas, são necessários estudos com sistemas modelo, como por exemplo, a solução aquosa de oligopeptídeos de (L-Prolil-L-Prolilglicil)$_n$ (PPG*n*). Neste sistema observa-se uma transição de hélice tripla para novelo quando $n \geq 9$ e uma mudança brusca no número de moléculas de águas de hidratação, mesmo para $n = 5$, na temperatura próxima dos 30 °C. No nosso trabalho, realizamos simulações dinâmica molecular com o pacote GROMACS, empregando os campos de força GROMOS 53A6 e AMBER03, solvatando as estruturas e submetendo-as a um protocolo de simulação com aquecimento e resfriamento, em taxas variadas. As simulações do cluster do oligopeptídeos PPG_5 e da Tripla Hélice da PPG_5, realizadas com taxas de aquecimento lento mostraram uma transição estrutural, uma diminuição monotônica do número de ligações de hidrogênio polímero-água, mas um comportamento não monotônico, com recuperação parcial do número de moléculas de água de hidratação. A estruturação da água, monitorada através da função de distribuição radial entre átomos polares do polímero e água, mostra que estes sistemas apresentam reversibilidade, uma vez que o aumento de temperatura implica perda de água de hidratação, e o resfriamento mostra uma recuperação (ainda que parcial) destas águas. De acordo com as análises da função de distribuição radial também se pode concluir que em ambos os sistemas simulados, este efeito age de modo mais pronunciado na segunda esfera de coordenação.

Suporte: CAPES E CNPQ

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Estudo da influência da combinação nível de cálculo x função de base nas intensidades fundamentais do IV de moléculas X_2CY

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Key-words: X_2CY, Intensidades do infravermelho , função de base

Dentre os principais trabalhos teóricos de espectroscopia vibracional de moléculas X_2CY podem-se destacar os resultados publicados por Bruns e colaboradores.[1] Resultados relatados por Faria e colaboradores[2] mostram uma discrepância entre as intensidades fundamentais do infravermelho experimentais e àquelas obtidas teoricamente para as moléculas X_2CY. Dentro desse contexto, com o objetivo de melhorar a acuracidade das intensidades fundamentais do infravermelho de moléculas X_2CY, foi realizada uma análise dos efeitos do nível de cálculos e de função de base para encontrar dados teóricos que tenham uma melhor concordância com os valores experimentais. Através das geometrias teóricas de equilíbrio, foram determinadas, pelo programa Gaussian 03, as intensidades fundamentais do infravermelho dessas moléculas. Os cálculos foram realizados com uma combinação de 4 níveis de cálculo (CCSD, MP2, QCISD e CASSCF) com 21 funções de base, totalizando 84 resultados para cada molécula X_2CY (F_2CO, Cl_2CO, HFCO, H_2CO, F_2CS, Cl_2CS). A combinação nível de cálculo x base que gerou a melhor acuracidade entre as intensidades teóricas e as experimentais foi diferente para cada molécula. O menor erro RMS entre as intensidades para a molécula de F_2CO foi obtido com a combinação MP2/6-311G(3d,3p) sendo ±5,4 km/mol, para as moléculas Cl_2CO, F_2CS, Cl_2CS, H_2CO e HFCO as combinações mais acuradas com seus erros RMS foram respectivamente, ±14,2 km/mol e QCISD/4-31G, ±4,2km/mol e CCSD/4-31G, ± 10,1km/mol e CCSD/6-311++G e CASSCF/6-311++G(2d,2p), ±4,2km/mol e MP2/6-311++G(3d,3p) e QCISD/6-311++G(3d,3p), ± 22,8km/mol e QCISD/3-21G. Os resultados mostram que para as moléculas que possuem cloro (Cl_2CS e Cl_2CO), o erro ultrapassa 10 km/mol. Por outro lado, as moléculas que contêm flúor e hidrogênio, com exceção do HFCO, apresentaram erro entre 4 a 5,5 km/mol. Isso provavelmente se deve ao fato da nuvem eletrônica do cloro ser mais polarizada, fazendo com que as funções de base sejam menos eficazes na representação da nuvem eletrônica dessas moléculas.

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Estudo via simulação molecular da interação do neuropeptídeo Y com modelos de membranas

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Key-words: neuropeptídeo Y, neuropeptídeos, membranas biológicas

As atividades do neuropeptídeo Y (NPY, polipeptídeo constituído por 36 aminoácidos, apresentando uma α-hélice anfipática rígida e sem estrutura definida na região N-terminal) estão relacionadas com a regulação da pressão sanguínea, o consumo de alimentos, a ansiedade, a depressão, o consumo de álcool dentre outras. A grande importância das funções deste peptídeo tem conduzido a uma série de investigações sobre a sua estrutura e sobre sua interação com bicamadas lipídicas a fim de compreender suas interações com a superfície das membranas celulares para encontrar seus receptores. Mutantes do NPY, como o 1icy, 1fvn e toac34, foram também usados a fim de compreender estes mecanismos. . O objetivo deste trabalho é investigar, por simulação molecular, a interação destes peptídeos com modelos de membranas com o intuito de se verificar a existência, ou não, de padrões estruturais que possam contribuir para o entendimento dos mecanismos de interação destes peptídeos com as membranas.

Métodos: Utilizou-se o pacote Gromacs 3.3.1 com o campo de força Gromos96, o modelo SPC para as moléculas de água, um tempo de integração de 0,002 ps e um raio de corte de 1,0 nm, temperatura de 323K e pressão de 1 atm.. Foram realizadas simulações dos peptídeos em presença de uma membrana de dipalmitoilfosfatidilcolina (DPPC).

Resultados: A raiz quadrada dos desvios quadráticos médios (RMSD) em relação à estrutura inicial indica que as estruturas do NPY e dos mutantes são muito flexíveis uma vez que apresentam apenas uma região (resíduos 14-25) com estrutura secundária definida (α-hélice). As energias de interação dos resíduos com as bicamadas mostram grande atração da região C-terminal na interação com as regiões hidrofóbicas dos lipídeos. Este comportamento é confirmado pelas ligações de hidrogênio intermoleculares. Os mapas da projeção da posição dos átomos de fósforo sobre o plano das bicamadas mostram uma clara organização dos átomos promovida pelos peptídeos tanto em relação às moléculas de lipídeos quanto em relação às moléculas de água.

Conclusões: Os peptídeos estudados apresentam afinidade para bicamadas de DPPC porque se aproximam e se aderem com energias de -3108 $kJ.mol^{-1}$, -2942 $kJ.mol^{-1}$, -3097 $kJ.mol^{-1}$ e -3058 $kJ.mol^{-1}$ para o NPY, 1icy, 1fvn e toac34 respectivamente. As estruturas e as modificações dos peptídeos estudados ocorrem quando os mesmos se difundem na membrana. A flexibilidade da região C-terminal causada pelas mutações corroboram para uma rápida inserção desta região na membrana para a ativação do receptor, enquanto a α-hélice se mantem na superfície.

Agradecimentos: CNPq - Fapesp

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Electronic and Dielectric properties of α-Fe and Fe_3Al bulk materials

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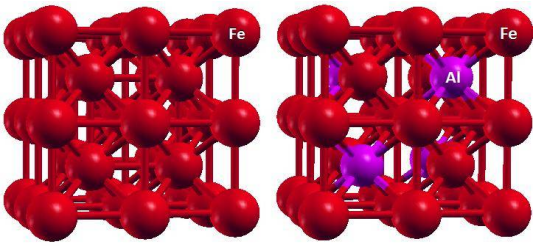
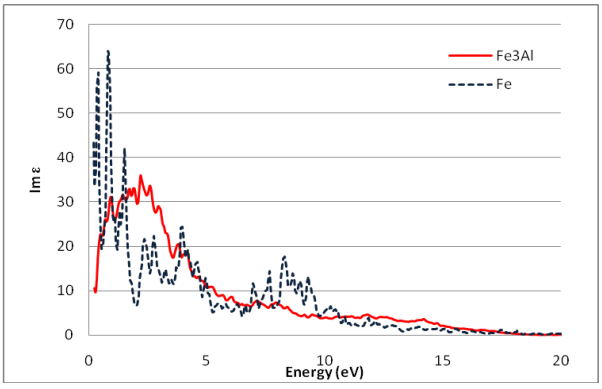
Key-words: electronic properties, dielectric properties, plane wave basis sets

Materials which absorb electromagnetic radiation in the microwave range have several important applications in the electronic and communications industries. Among them, absorptive materials to withhold radar detection are important for defense applications. The accurate knowledge of electrical and magnetic properties of these materials is a requisite for the design of advanced electromagnetic radiation absorption materials. In this work, we computed the electronic, electric and magnetic properties of two materials involving aluminum, known as a good conductor, and iron, abundant in the Earth and also ferromagnetic. We carried out a Density Function Theory (DFT) investigation of the electronic and dielectric properties and magnetic properties through LSDA (local spin density approximation) calculations of the α-Fe and Fe_3Al bulk materials. The Fe_3Al structure differs from the α-Fe just for some substitutions of Fe atoms (see Fig.). We used the PBE functional, plane wave basis sets and norm-conserving pseudopotentials. The Quantum Espresso package was used for all calculations. The structural optimization of both systems was followed by self-consistent field and post-processing calculations to obtain the density of states and the real and imaginary components of the dielectric tensor in the framework of the Random Phase Approximation (RPA). The imaginary part of permittivity (Imε) describes the electric properties of a medium with losses (i.e., that absorbs part of the energy of the electromagnetic radiation). The results of the structural optimization showed that the lattice parameters are in good agreement with experimental results. The major peak of the dielectric function in the α-Fe structure (Imε=63.99) is at the energy of 0.8 eV while in the Fe_3Al structure (35.99) is at 2.2 eV. The Al substitutions in the Fe structure mostly result in a decrease in the absorption, a convenient feature for applications not involving shielding.



α-Fe Fe_3Al



The imaginary part of permittivity for both structures

Support: FAPERJ, CNPq, Brazilian Army.

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Structural Stability in Amyloidogenic and Non-amyloidogenic Variants of the Transthyretin Protein by MD Simulations under High Pressure

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Key-words: ***Amyloid, High Pressure Molecular Dynamics Simulations, Transthyretin Conformations.***

Introduction: The formation of insoluble amyloid fibers is a characteristic of many diseases known as amyloidosis. The transthyretin (TTR) is a homo-tetramer protein of 55 kDa and 127 residues per monomer. Over one hundred mutations have been described for the structure of transthyretin related to amyloid diseases such as Familial Amyloid Polyneuropathy (FAP), characterized by the deposition of amyloid aggregates in the peripheral nervous system.

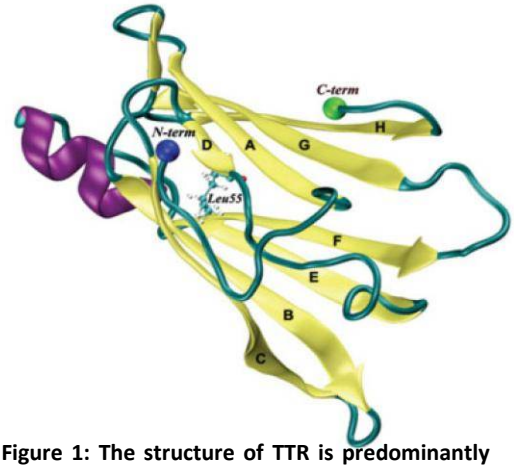

Figure 1: The structure of TTR is predominantly composed of eight *β–tapes* organized into two *β–sheets* (DAGH and CBEF).

Methodology: The dissociation and denaturation of TTR variants have been studied in different conditions of temperature, pH and pressure. Our group has described that the non-amyloidogenic variant as T119M has great stability under 3.0 Kbar, pH 7.5, and 1 ° C (*ref. 2*) compared with amyloidogenic.

We used Gromos96_53a6 Force Field, Reaction Field (radius 1.4 nm) in electrostatic treatment; SPC/E water model, cubical box, 5 ns simulation for stabilization the hydrated layer of protein and ions. Consecutive simulations totalize 40 ns, 5 ns for each pressure step of 0,5 kbar, temperature of 1º C, pH 3,0, and pressure enhancement from 1,0 bar ≅ 1,0 atm to 3,5 kbar.

Thermodynamics Stability: ***A25T<<L55P<V30M<WT<<T119M***;
Aggregation:***A25T>>L55P>V30M>WT>>T119M***.

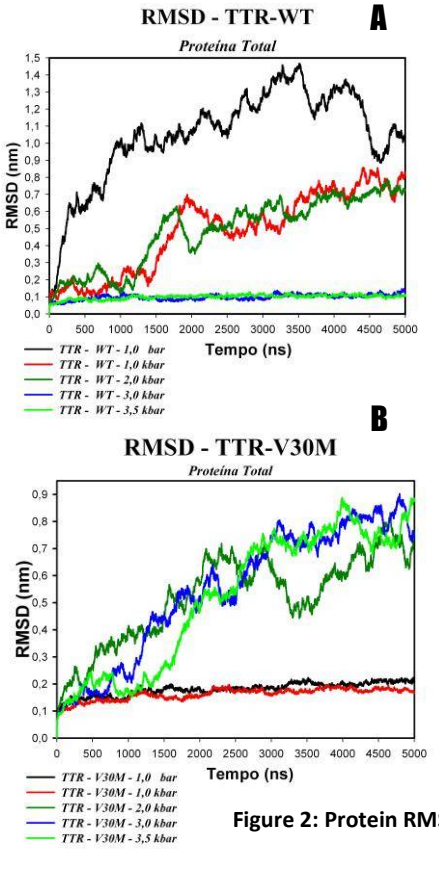

Figure 2: Protein RMSDs – WT-TTR (A), V30M-TTR (B)

Results and Discussion: Multiple and sequential Molecular Dynamics (MD) simulations of WT - and V30M-TTR dimmers were performed at high pressure (up to 3,5 kbar) and in explicit water to assess the structural stability of transthyretin. It was explored the conformational space available to the polypeptide chain upon protein unfolding, and identified potential structural changes leading to amyloid assembly.

The analysis of molecular properties such as secondary structure, hydrogen bonds, and solvent accessible surface area along the MD unfolding trajectories clearly demonstrate that V30M-TTR (fig. 2-**B**) has a much higher tendency to unfold than WT-TTR (fig. 2-**A**). These results are in agreement with previously published experimental data on the conformational stability of dimers of several TTR variants.

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Support: *FAPERJ, CNPq*

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Quantum algorithm search for molecules identification

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Key-words: Grover's algorithm, infrared, data bank search

As showed by Shor[1] and Grover[2] it is possible to simulate and use quantum algorithms in classical computers, also, as example, to find a global minima[3]. We have developed a quantum search algorithm based on Grover's algorithm for the correlation between one infrared spectrum and one molecule stored in a data bank. The quantum bit[4] is the basic unit of information used in the algorithm and one oracle and average inversions that will show the quantum solution to the problem. We have used four groups of registers (r_0, r_1, r_2, and r_3) for frequencies ranges. The boundaries of the ranges for r_0 were: f0=4000, f1=3874, f2=3875, f3=3749, f4=3750, f5=3624, f6=3625, f7=3499, f8=3500, f9=3374, f10=3375, f11=3249, f12=3250 and f13=2999 (all in cm^{-1}). The first register r_0 in the quantum state $|6\rangle$ represents the OH bond, which is between f_{10} and f_{11}, the same for the rest of the spectrum (r_1, r_2 and r_3). The Table 1 shows part of the infrared spectrum for the methanol in terms of quantum bits states. All the process will be similar to all registers in the algorithm.

Table 1: Correlation between the quantum states and the infrared information

Register r_0	$\|0\rangle$	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$	$\|5\rangle$	$\|6\rangle$	$\|7\rangle$
Frequency range	np	f_0-f_1	f_2-f_3	f_4-f_5	f_6-f_7	f_8-f_9	f_{10}-f_{11}	f_{12}-f_{13}
Bond in the range	-	-	-	-	-	-	OH	-
State of the register r_0	0	0	0	0	0	0	1	0

The algorithm performed checking each register. The table 2 shows the progress to find the presence of the peak of the OH bond in the register r_0.

The table 2: Progress in each iteration.

Algorithms	Probability for each iteration					
Iteration	1	2	3	4	5	6
Grover's algorithm	97%	11%	100%	-	-	-
Classical algorithm	0	0	0	0	0	100%

The probability of a correct classification was 99% for all registers. The quantum algorithm has complexity $O(\sqrt{N})$ instead of $O(N)$ as in the classical algorithms, that is important to the real time systems as a river contamination detector.

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Support: CAPES,CNPq.

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A QM/MM Study of the Structural and Electronic Properties of the Methane Monooxygenase Enzyme.

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Key-words: QM/MM, DFT, Methane monooxygenase.

Methane monooxygenase (MMO) is an enzyme that catalyzes the methane oxidation reaction (conversion of the inert methane molecule to methanol). Two forms of the MMO have been found, one soluble and another particulate. However, the best characterized specie it is the soluble, which crystallographic studies revealed to be composed by three protein component: hydroxylase (MMOH), B component (MMOB), and reductase (MMOR). The MMOH, which binds O_2 molecule and catalyses the oxidation, is a dimer, each monomer of which contains three subunits (α,β,ϒ) and a hydroxy-bridged binuclear iron complex. In the MMOH, the diiron center is in the diferric state [Fe^{III}-Fe^{III}] ($MMOH_{ox}$), and can accept one or two electrons to generate the mixed-valence [Fe^{III}-Fe-^{II}] or diferrous state [Fe^{II}-Fe^{II}] ($MMOH_{red}$), respectively (see figure 1).[1]

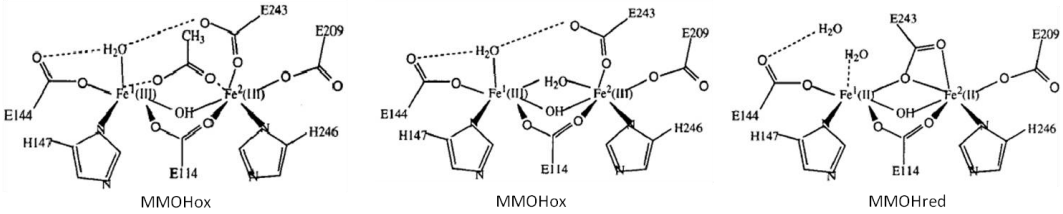

Figure 1: Binuclear Fe center of diferric ($MMOH_{ox}$) and Diferrous ($MMOH_{red}$).

Of the possible MMOH oxidation states, only the diferrous state is capable of reacting with O_2 and start the catalytic cycle. However, there is not yet a formal answer of why only the $MMOH_{red}$ is capable of activate the methane molecule. In the literature there is a good number of theoretical works related to study of the MMOH,[1] but to our knowledge in none of these studies the entire backbone protein was included. Thus, we decided to study the properties of the MMOH including the effects of the entire protein environment. In this work, we applied the ONIOM method in conjunction with DFT formalism to investigate the electronic and structural properties of the species $MMOH_{ox}$ and $MMOH_{red}$. The systems investigated were partitioned in two layer: QM region described by the B3LYP functional and MM part treated by the UFF force field. The structural results obtained for the $MMOH_{ox}$ with the total spin multiplicity 11 are in good agreement with the experimental values. The results obtained for the others possible spin states of the $MMOH_{ox}$ well as the results of the $MMOH_{red}$ will be presented and discussed during the presentation.

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Support: CNPq, FAPEMIG, CAPES and INCT-Catálise.

The ature of the u- ond in u ida ole L Co lexes L and - roto or hyrin Li ands

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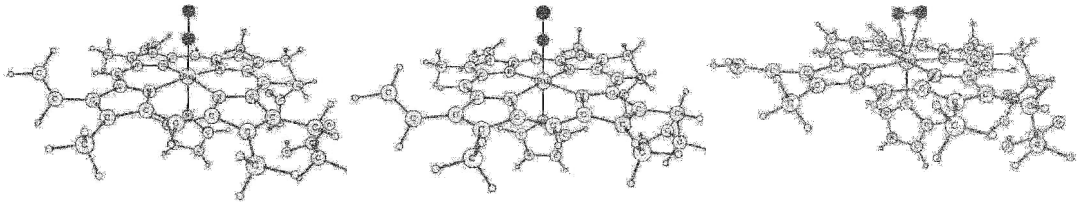
Key-words: Ruthenium nitrosyl complexes, DFT, PPIX, EDA.

The NO is classified as a messenger molecule in several biological processes [1], however there is a problem with their accumulation in the body. The overproduction is an important factor in diseases such as diabetes, arthritis, epilepsy and septic shock. So the main concern of the study involving NO is the search for complex systems capable of transporting and releasing NO in a reversible. To this end ruthenium complexes has shown very promising. The objective is to have an idea about the nature of Ru-NO bond, in [Ru(Imidazole)(PPIX)(L)] complexes, where L NO , NO and NO^-, PPIX Protoporphyrin IX, understanding how PPIX and Imidazole ligands influence their electronic structure by the various forms of interaction between NO and the metal center (Figure 1).



S **S** **S**

i ure Ground State (GS), Metastable States (MS1) and (MS2)

For the geometries and harmonic fre uencies of the complexes have been calculated at DFT level of theory by using the B3L P exchange-correlation functional and SB JC VD ECP for the Ru and 6-31G(d) basis set for the atoms of C, N, O and H. The nature of the Ru-NO has been investigated by means of the energy decomposition analysis (EDA) calculated at B3L P T P level of theory, employing the ORA approximation for atom Ru. For example for L NO , the results EDA indicate that the energy interaction values, $\Delta E_{int,}$ is much more negative for GS e MS2 than for MS1, following the same trend for electrostatic interactions, ΔE_{elstat} and orbital interactions ΔE_{orb}. Also, $\Delta E_{orb,}$ are always more negative than others terms, showing a strong covalent character contribution in the nature of chemical binding of these compounds. Details in the presentation.

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Support: CNP , FAPEMIG, CAPES, INCTCAT LISE.

XVI Simpósio Brasileiro de Química Teórica – SBQT 2011
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"Intermolecular Force Field modeling procedure through quantum mechanical calculations for liquid pyridine"

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Key-words: Pyridine, Force Field, Intermolecular Interactions

Computer simulations are a powerful tool to improve the understanding of complex systems, but the reability of their results are dependent of the employed force field. In this work a novel approach to obtaining accurate intermolecular force fields referenced in *ab initio* quantum chemical calculation was proposed, using liquid pyridine as test system.

The intramolecular force field was taken from a previous parameterization work and kept unchanged(1). The intermolecular force field parameterization strategy consists in sampling pyridine dimers configurations in a trajectory of a molecular dynamic simulation. The choice of dimer configuration was realized based on a difference index, defined in terms of structural and energetic parameters, and automatically permormed by a program named PICKY, that select the most diverse configurations as classified according to their difference indexes. For the selected dimer configurations, the interaction energy was calculated performing MP2 calculations using a cc-pVDZ basis set with correction for BSSE effects using the usual counterpoise procedure. The theoretical interaction energies of the pyridine reference dimers set are fitted by an intermolecular force field constituted by a 12-6 Lennard-Jones potential and a point charges electrostatic potential. This procedure is performed interactively until a convergence of the potential parameters or reference properties.

A molecular dynamics simulation at 298 K and 1 atm with the final parameters produces bulk properties for liquid pyridine is in a good agreement with the experiment: a density of 1.008±0.005 g/cm^3 (an error of 2.8% in respect to experimental value of 0.98 g/cm^3) and a ΔH_{vap} of 40.61±0.28 kJ/mol (an error 1.8% relative to the experimental value of 40.18 kJ/mol).

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Support: CNPq.

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Estudo das reações de S_N2 em fase gasosa: $R_1Cl + OH^- \rightarrow R_1OH + Cl^-$ (R_1=Me, Et, n-Prop, i-Prop, n-But, s-But e t-But).

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Key-words: Substituição Nucleofílica, Eliminação, Teoria de Estado de Transição

Neste trabalho, as reações de substituição nucleofílica, S_N2, foram tratadas pelo método de dinâmica direta para investigação da cinética das etapas elementares e global na superfície de energia potencial de $CH_3Cl + OH^-$ e dos análogos alifáticos $CH_3CH_2Cl + OH^-$; $CH_3(CH_2)_2Cl + OH^-$; $(CH_3)_2CHCl + OH^-$; $CH_3(CH_2)_3Cl + OH^-$; $CH_3CH_2CH(CH_3)Cl + OH^-$ e $(CH_3)_3CCl + OH^-$. Pontos estacionários correspondentes a reagentes, produtos, intermediários pré- e pós-barreira, e pontos de sela foram localizados e caracterizados em níveis MP2/6-31+G(d,p) e B3LYP/6-31+G(d,p). Caminhos de reação foram calculados nos mesmos níveis de teoria. Constantes de velocidade das etapas individuais foram calculadas pelo método variacional canônico na faixa de 200 – 500K.

A diferença de entalpia a 298K calculada em nível MP2/6-31+G(d,p) para a reação $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$ foi de -51,0 kcal/mol, em excelente acordo com o dado da literatura, -50,5 kcal/mol. O mecanismo sugere a formação de um intermediário pré-barreira, estabilizado por 15,3 kcal/mol, em relação aos reagentes isolados a 298K, passando por um ponto de sela localizado a 10,7 kcal/mol abaixo dos reagentes. Dessa forma, a cinética global segue um mecanismo não-Arrhenius. A 298K, a constante de velocidade global calculada foi de 1,1 x 10^{-9} cm^3 $molécula^{-1}$ s^{-1}, em excelente acordo com o dado experimental, 1,3 x 10^{-9} cm^3 $molécula^{-1}$ s^{-1}. Resultados B3LYP/6-31+G(d,p) estão em bom acordo com os resultados obtidos em nível MP2/6-31+G(d,p) para essa reação. As demais reações seguem mecanismos similares para a S_N2, mas apresentam canais competitivos de eliminação de segunda ordem (E2). Em geral, a diferença de energia dos pontos de sela em relação aos reagentes isolados mostra pequena dependência com o aumento da cadeia lateral linear. Resultados obtidos também para canais de substituição com ataque do substituinte pela frente ou por trás do nucleófilo na cadeia são apresentados e discutidos.

Apoio: FAPERJ e CAPES.

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"Theoretical Normal coordinate analysis of the infrared spectra of CH_3Cl, CH_2Cl_2, CH_3Br and $CHCl_3$ molecules."

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Key-words: Greenhouse, infrared, normal coordinate

In this work a normal coordinate analysis has been carried out in order to describe the theoretical infrared spectra of CH_3Cl, CH_2Cl_2, CH_3Br and $CHCl_3$ molecules. All molecular systems are greenhouse gases and the study of their infrared spectra are needed for obtaining important parameters used in the analysis of the global warming potential (GWP) of these molecules. GWP's are currently available for relatively few compounds, although new results are continuously being developed for new species. The geometries were optimized and the vibrational spectrum were computed through ab-initio (Hartree-Fock and MP2) and Density Functional Theory (B3LYP) methods using Dunning's (cc-pVTZ and aug-cc-pVTZ) basis sets. The normal coordinate analysis was performed through the Balga program, with assignment of all absorption bands in the infrared region. B3LYP/aug-cc-pVTZ results lead to the best agreement with experimental results. Therefore, IR intensities and frequencies at this level can thus be used more confidentially in order to estimate the GWP of these molecules [1].

Support: CNPq/UEPB

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CASSCF and MR-SDCI Examination of Chlorimino Radical

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Key-words: NCl radical, spectroscopic constants, CASSCF, MR-SDCI

NCl radical belongs to the 24-electron (halimino) radical series, and therefore is isoelectronic with SO [1]. It is a well-known system which nevertheless has only a few published spectroscopic constants [2-3]. In this work we have studied NCl with a aug-cc-pVQZ-DK basis set and multireference calculations under the GAMESS code. For each distance, the energy was obtained with a CASSCF (12,8) reference followed by a MR-SDCI calculation plus Davidson corrections [4]. The second order CI typically involved 6-7 million configurations. As expected, for the three lowest states the main components are just spin flips of the $(7\sigma)^2(2\pi)^4(3\pi)^2(8\sigma)^0$ configuration. The $^3\Sigma^-$ ground state only gets a significant contribution from the $(7\sigma)^2 \rightarrow (8\sigma)^2$ double excitation. Our list of calculated (at MR-SDCI level) spectroscopic constants is

state	$\tilde{X}\,^3\Sigma^-$	$\tilde{a}\,^1\Delta$	$\tilde{b}\,^1\Sigma^+$	$^3\Pi$
R_e , Å	1.677	1.623	1.611	1.742
ω_e , cm^{-1}	726	829	859	576
D_0, eV	2.40	3.11	3.33	1.11
$\omega_e\chi_e$, cm^{-1}	6.68	6.73	6.77	8.98
T , cm^{-1}	0	11973	17583	42989

The transition energies for the two lowest excited states as calculated at MR-SDCI level are both larger than the currently accepted figures [3].

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Support: FINEP.

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Decomposição da densidade eletrônica e potenciais eletrostáticos de monoterpenos halogenados cíclicos: conseqüências para a desativação de toxicidade

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Palavras-chave: partição da densidade eletrônica, fragmentação, desativação

Algas são organismos simples, mas possuem papel muito importante na vida do planeta: ao mesmo tempo em que são consideradas *o pulmão do mundo,* muitas delas produzem toxinas perigosas inclusive para o homem. Neste contexto, destaca-se a alga *Plocamiun cartilagineum*. Esta alga sintetiza monoterpenos halogenados, substâncias com propriedades citotóxicas. Infelizmente, as algas também podem ser usadas como arma biológica na medida em que são capazes de contaminar as águas de reservatórios, rios e oceanos, inviabilizando a vida aquática e sua utilização para consumo. Assim, torna-se fundamental não apenas saber como controlar a população de algas, mas também como neutralizar as substâncias tóxicas produzidas por elas.

Estudamos seis moléculas de monoterpenos cíclicos halogenados oriundas da *Plocamiun cartilagineum* – dentre elas, o violaceno, o mertenseno e uma molécula obtida a partir do mertenseno. Nosso objetivo foi calcular as densidades eletrônicas das moléculas, e dividi-las segundo o método *distributed atoms in molecules* (DAM). Este método permite identificar visualmente em cada molécula regiões de acúmulo e de depleção de elétrons. Foram também calculados também os potenciais eletrostáticos das moléculas. Estes resultados permitiram identificar os sítios ácidos e básicos de cada sistema. Também calculamos o espectro infravermelho (IV) das conformações mais estáveis.

As geometrias das moléculas foram otimizadas com o método B3LYP/6-311G** e o programa Gaussian03. Varreduras das conformações para cada molécula foram feitas para obter a mais estável. Cálculos de freqüências confirmaram o caráter de mínimo das estruturas e foram usados para obter os espectros IV. As densidades eletrônicas B3LYP foram descompostas segundo o método DAM com programa DAMQT 1.0.

Os resultados permitiram obter os sítios ácidos e básicos das moléculas, e com isto foram identificados em cada caso os sítios e as ligações químicas mais suscetíveis a ataques eletrofílicos ou nucleofílicos. Desta forma, indicamos as ligações químicas mais sujeitas à ruptura, o que permitirá desenvolver mecanismos para desativar os monoterpenos tóxicos produzidos pelas algas.

Apoio: CAPES PRÓ-DEFESA, FAPERJ, CNPq.

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"The Electronic Structure of Manganese Mononitride (MnN) Studied by Multireference methods"

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Key-words: MnN, spectroscopic constants, CASSCF, MR-SDCI

Several diatomics containing a transition metal and a main group element still have no spectroscopic constants in the literature, and even their ground states are unknown or uncertain. In this regard, Quantum Mechanics can provide a quick aid to Astrophysics [1,2].

In this work we have studied manganese mononitride (MnN) using multireference methods. The protocol was the same used by us previously [3]. The zeroth order wavefunction was obtained at CASSCF level, and the resulting set of optimized MOs was used in MR-SDCI calculations. The GAMESS code was used to perform all calculations [4]. The spectroscopic constants were obtained by fitting the calculated potential energy data to Morse curves.

At CASSCF level, three states ($^5\Pi$, $^5\Delta$ and $^3\Sigma$) are very close in energy. The ground state is apparently the $^5\Delta$, with a equilibrium distance of R_e = 1.992 Å. This result is hard to conciliate with the previous DFT results by Andrews (1.636 Å) and Wu (1.632 Å) that suggest the ground state is a quintet.

The second order CISD step brings upon an inversion in the ordering of the states: at MR-SDCI level, the ground state of MnN is $\tilde{X}\,^3\Sigma^+$, with calculated constants R_e=1.580 Å, ω_e=888 cm^{-1} and D_0 = 0.52 eV. At this level, this state can be roughly described by

$$|\,\tilde{X}\,^3\Sigma^+ > \approx 0.805\,|(3\pi)^4(1\delta)^2(9\sigma)^2(4\pi)^0 > + \ldots$$

confirming a previous suggestion by Harrison [2] that the ground state involves a triple bond.

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Support: FINEP.

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A kinetic study of the substrate's H-abstraction step in the mechanism of B_{12} dependant Ethanolamine Ammonia-Lyase

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Key-words: H-abstraction; enzyme catalysis; Kinetics; Tunneling; B_{12} enzymes.

Adenosylcobalamin (AdoCbl, B_{12} coenzyme) dependant ethanolamine ammonia-lyase catalyzes the transformation of ethanolamine into ammonia and acetaldehyde[1]. Kinetics and EPR experimental studies[2] and computational modeling of the possible reaction mechanisms conducted over quite simplified representations of the system[3] support a mechanism of reaction with five elementary steps. According to such proposal, the process starts within the protein with an extremely accelerated homolytic cleavage of the Co–C bond present in B_{12} to yield adenosyl radical (Ado-CH_2·) and cob(II)alamin. Then substrate is activated by H-abstraction from C1, yielding ethanolaminyl radical and 5-deoxyadenosine (Ado-CH_3). The subsequent steps correspond to substrate's radical isomerization, H-reabstraction from Ado-CH_3, and final dissociation to NH_3 and CH_3CHO. Kinetic studies showed H-reabstraction step to be rate determining[4a] and significant tunneling effects were exposed by kinetic isotopic effect (KIE) experiments[4]. Based upong a previous description of the process modeled by us at the DFT/PCM level using more realistic representations[5a] validated by ONIOM studies within the protein[5b] we evaluate here kinetics for the H-abstraction from substrate using conventional and variational transition state theories (TST and IVTST-M) with semiclassical tunneling as implemented in Polyrate 9. Primary KIEs were also determined for substrate [1-^{2}H] and [1-^{3}H]. IVTST-M results and large KIEs show there are important tunneling effects for the first hydrogen abstraction step.

Support: Agencia Nacional de Investigación e Innovación (ANII) - Uruguay.

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Excited electronic state study of some novel fluorescent Schiff bases

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Key-words: electronic structure, excited state, Schiff bases.

Novel benzazolic conjugated Schiff bases were recently synthesized and subjected to extensive photophysical studies on a variety of polar and non-polar solvents at *Laboratório de Novos Materiais Orgânicos*. These fluorescent dyes, which are derived from 2-(4'-aminophenyl)-benzazoles or 2-(4'-amino-2'-hydroxyphenyl)-benzazoles, absorb electromagnetic radiation at the near ultraviolet region and present dual emission of fluorescence at the visible range. Our aim was to select computational methods capable of adequately reproduce the maxima of the absorption spectra of these molecules, and, relying upon them, by means of considerations concerning the electronic structure of ground and excited electronic states of the photoactive species present in solution, to rationalize the photophysical data experimentally obtained. We performed mostly DFT calculations with medium to large-sized basis sets, and they show good qualitative agreement with experiment. For instance, TD-DFT B3LYP/6-311++G(2d,p) calculations showed that for these molecules the dipole moment at the excited electronic state is about 60% larger than that at the ground state − results in perfect agreement with the bathochromic shift experimentally observed with increase of the polarity of the solvent. However, better quantitative agreement with experimental data, especially with respect to precise prediction of the absorption maxima, is still aimed for and is expected to be achieved by employing higher level methods.

Support: UFRGS, FAPERGS and CNPq.

"Theoretical study of native defects of molybdenum carbide"

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Key-words: molybdenum carbide, vacancy, DFT, Plane-Waves

Catalysts and adsorbents for *In situ* upgrading of heavy oils is subject of intense research. However, the lack of fundamental information about the catalysts and the mechanism of reaction is a barrier for improving the technology. The molybdenum carbide, Mo_2C is a most promising catalyst. Previous studies by Pereira[1] have found that the different routes can lead to the nanostructured molybdenum carbides. The stoichiometry can be deficient in carbon or molybdenum. There are many experiments showing that the defects are probably responsible for the difference of the reactivity of molybdenum carbide obtained by the different routes.

In the present study, Density Functional Theory (DFT) calculations have been performed using the Quantum-ESPRESSO package – PWscf. Generalized gradient approximation (GGA) for the exchange and correlation potential (XC) due to Perdew and Wang (PW91) has been used. The electron-ion interactions are described through ultrasoft pseudopotentials. Löwdin population analyses, density of states and electron localization functions have been used to understand the electronic structure of the molybdenum carbides. The carbon and molybdenum vacancies have been investigated and their effects on the geometry and electronic structure of the Mo_2C. The results show that carbon vacancy is more favorable than molybdenum vacancy by 0.15 eV/atom.

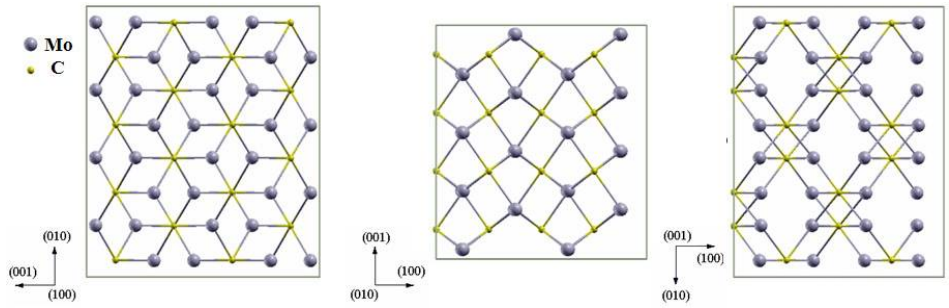

Figure 1. Structure of the Molybdenum carbide.

Support: INCT – Mineral Resource, Water and Biodiversity – ACQUA, CIAM (CNPq/NRC/CONACYT), CNPq, CAPES, FAPEMIG, CENAPAD/UFMG.

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Modelagem Computacional da Redução de NOx em catalisador de CeO_2/MnO_2

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Palavras-chave: Catálise Heterogênea, redução de NO_x, PM6.

Os esforços no campo da catálise heterogênea culminaram no desenvolvimento de um dispositivo chamado conversor catalítico, que é um material cerâmico envolto em uma blindagem metálica capaz de promover a redução seletiva de NOx para N_2, visando solucionar problemas ambientais. Ele é geralmente colocado após a saída dos gases dos motores automobilísticos. Para garantir a máxima eficiência deste processo, vários materiais cerâmicos têm sido testados, como base em óxidos metálicos. Porém os mecanismos desta reação ainda não foram completamente elucidados, pois a reação de redução catalítica seletiva (SCR) pode ocorrer com NH_3, CO, propeno, ou até mesmo CH_4. O óxido de cério suportados por óxido de manganês, possui uma reação SCR com NH_3, assim, este trabalho tem como objetivo investigar qual é o efeito da reação de modo a validar o mecanismo SCR com NH_3 neste material. O modelo foi criado baseando-se em superfícies geradas a partir da estrutura cristalográfica do MnO_2, para gerar o plano de adsorção (001), obtidas do banco de dados de estruturas inorgânicas ICSD[1]. Utilizamos o método PM6[2], e condições periódicas de contorno (PBC), implementado no programa MOPAC2007[3], para o cálculo de propriedades termodinâmicas do sistema. Compararemos os nossos resultados com o trabalho de Jug e colaboradores[4], onde a reação de redução do NO_x para N_2 foi estudada num agregado de V_2O_5 suportado numa superfície de TiO_2. Na primeira etapa desta reação de redução realizamos o estudo da adsorção de NH_3 na superfície. O nosso resultado foi comparado com o de Jug e colaboradores[4], mostrado na Tabela 1, onde neste foi calculado a energia de adsorção de NH_3 em um agregado de V_2O_5 sobre uma superfície de TiO_2, representado pela formula $V_2O_7H_4Ti_{33}O_{66}(H_2O)_{17}$. O nosso resultado mostra que a energia de adsorção do NH_3 no nosso modelo Ce:MnO_2 é cerca de cinco vezes menor, ou seja, o sistema é cinco vezes mais estável do que o modelo proposto por Jug e colaboradores[4]. Assim esta superfície apresentasse como um bom candidato para o estudo da reação de redução do NOx para N_2. Todavia, acreditamos que este valor corresponde a uma energia de adsorção química.

Tabela 1. Comparação entre a energia de adsorção do NH_3 na superfície 2x4x1 MnO_2 e no agregado $V_2O_7H_4Ti_{33}O_{66}(H_2O)_{17}$

Estruturas	Energia de adsorção
Ce:MnO_2	-664,24 kJ/mol
$V_2O_7H_4Ti_{33}O_{66}(H_2O)_{17}$	-128 kJ/mol

Apoio: CNPq, UFPB

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An Evaluation of Singlet and Triplet Excitation Energies Using Time-Dependent Density Functional Theory (TD-DFT)

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Key-words: valence electron excitations, TD-DFT, singlet and triplet transitions

The determination of electronically excited states of large systems is a challenge for theoretical chemistry today. The application of accurate *ab initio* methods is still limited in practice to small and medium-size molecules, and there is a need for reliable approximate methods that can deal with larger systems. A candidate of such methods is TD-DFT, which can be used for large systems and is easy to use at same time. Therefore, it is desirable to have reliable excitation values to validate the approximate methods. Schreiber et al. reported two studies [1,2] which provide excitation data from high-level *ab initio* calculations as well as MP2/6-31G* optimized geometry data for 28 molecules, covering the most important chromophores in organic chemistry. In this work, we are interested in comparing our TD-DFT results with the data reported by Schreiber and co-workers.

All calculations of molecular excitation energies were performed by TD-DFT(SAOP)/et-pVQZ//MP2/6-31G*, using the Amsterdam Density Functional (ADF) package. In this method, SAOP is an asymptotically correct exchange-correlation potential and et-pVQZ is an efficient and high-quality basis set.

In total, we compare 104 low-lying singlet and 63 low-lying triplet excitations energies to benchmark values from literature [1]. The absolute mean deviations were 0.47 eV (0.55 eV for singlet and 0.34 eV for triplet excitations). Our singlet results are as good as those found in literature [3] for other TD-DFT methodologies; however, our triplet results are better of them (absolute mean = 0.34 eV in this work against 0.53 eV for BP86, 0.45 eV for B3LYP and 0.60 eV for BHLYP). The largest deviations were found for cyclopentadiene (+1.60 eV, 2 $^1A_1$) and for naphthalene (+1.52 eV, 2 $^3B_{1.g}$). In total, 19 deviations values (18%) for singlet deviations and 4 (6%) for triplet deviations are great than 1.00 eV. The energy orders of states are, in general, similar to *ab initio* benchmark. In this preliminary study, based on the deviations found, we conclude that TD-DFT(SAOP)/et-pVQZ methodology can be evaluate the electronically excited states. We are doing further studies in order to improve these results.

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Support: PIBIC/CNPq-UERGS.

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"Ab-initio study of the interaction energy between Surfactant and Co-solute"

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Keywords: Giant Micelles, Interaction Energy, CCSD(T)/aug-cc-pVTZ.

The giant micelles have the similar behavior of polymers under flow, but possessing advantage of being formed by molecular interactions. This kind of micelles have created new possibilities and great interest in studies related to their formation, stability and applicability.[1]

This study aims to analyze the molecular interactions energies among different co-solutes and surfactants. Calculations of interaction free energies were performed at the CCSD(T)/aug-cc-pVTZ:MP2/cc-pVDZ level in gas phase. The results are compared on experimental data of stability for giant micelles to verify a possible relationship. Figure 1 presents the molecules studied and results for interaction free energies:

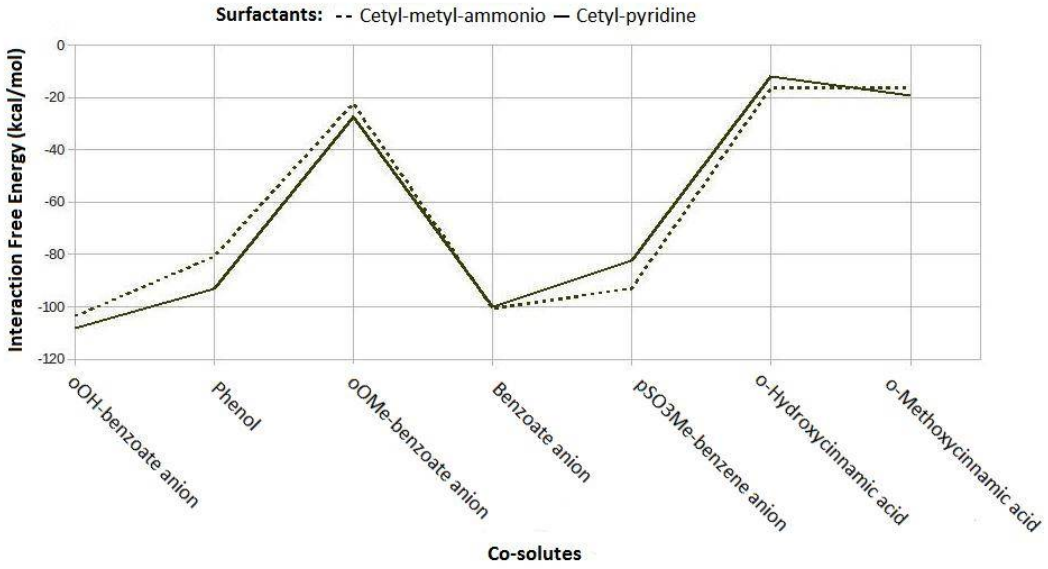

Figure 1: Interaction free energies (kcal/mol) for co-solutes and surfactants studied.

It was observed stronger interaction when employed anionic co-solutes. The exception is the interaction between the phenol and surfactant. It'll be carry out calculations with solvent effect to improve the results.

Support: CNPQ, FAPESP, CAPES, IQ/UNICAMP.

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Efeito dos átomos de flúor em algumas propriedades dos orbitais de fronteira das C-aril- Nitrosaminas

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Keywords: C-aril nitrosaminas, Flúor, Orbitais de Fronteira.

As nitrosaminas possuem grande importância ambiental e para a saúde humana, principalmente devido o seu potencial carcinogênico.[1] Addo e colaboradores[2] publicaram um estudo referente à complexação de nitrosaminas aromáticas ao grupo heme. Verificaram que o ligante N,N-dietil-nitrosamina está coordenado de tal forma à ferro-porfirina que os seus orbitais de fronteira estão em posição favorável a um melhor *overlap* com os orbitais *d* do Fe(III). Com base nesta observação, decidimos investigar o efeito de átomos de flúor nas energias e na localização dos principais orbitais de fronteira (π e π* no grupo nitroso N=O, n(O) e n(N) do grupo amino) no átomo de oxigênio das C-aril nitrosaminas (R_2N-C_6H_5-NO; R=CH_3 e CF_3, ver figura 1), uma vez que estes parâmetros são determinantes para interações efetivas destes ligantes com os metais de transição. Com isso esperamos poder sugerir substituições que induzam interações mais efetivas entre as C-aril nitrosaminas e a ferro-porfirina. Da substituição de 1, 2, 3, 4, 5, ou 6 átomos de H da C-aril nitrosamina de acordo com um planejamento fatorial 2^6 foram obtidos 40 isômeros diferentes. Estas estruturas foram otimizadas no *Gaussian 09*[3] a nível DFT(B3LYP)/6-311++G**. Em seguida foram realizados cálculos *single-point* a nível RHF/6-31+G* com o intuito de analisar os orbitais de fronteira destas estruturas. À medida que os H's da C-aril nitrosamina vão sendo substituídos por átomos de flúor, observamos que as energias dos orbitais de fronteira **n**(N) e $\boldsymbol{\pi_{NO}}$ apresentam um maior decréscimo, quando comparados ao $\boldsymbol{\pi^*_{NO}}$ e **n**(O). Os dois orbitais de fronteira mais localizados no átomo de O são o não-ligante no átomo de O (como seria de se esperar) e o $\boldsymbol{\pi^*_{NO}}$, e estes são muito mais localizados que os outros dois orbitais de fronteira. As localizações do $\boldsymbol{\pi^*_{NO}}$ e do **n**(O) diminuem consideravelmente para algumas estruturas com 1, 2 e 5 átomos de F. Para as outras estruturas as localizações dos mesmos praticamente não mudam. Uma vez que o maior decréscimo de energia (mediante a substituição H → F) é obtido para os orbitais menos localizados, ainda não podemos sugerir para quais estruturas a interação (covalente) nitrosamina-metal deve ser maior.

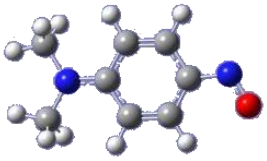

Figura 1: C-aril nitrosamina não substituída, com R=CH_3.

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Estudo computacional de éteres derivados de diidroartemisininas com alta eficácia contra malária resistente a multidrogas

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Palavras - chaves: Malária, Diidroartemisininas, MEP, Docking, Quimiometria

A malária é uma infecção causada por protozoários do gênero *Plasmodium*. São quatro espécies do parasita que comumente infectam os humanos. *P. ovale*, *P. vivax, P. malarie* e *P. falciparum*. O aparecimento de formas de malária, notadamente *P. falciparum*, resistentes aos fármacos disponíveis para o tratamento, tem propiciado pesquisas visando a obtenção de novos antimaláricos que possam atender as necessidades das populações atingidas pela doença. Neste trabalho, derivados da diidroartemisinina foram construídas com a ajuda do programa HyperChem e submetidas à otimização de geometria com o programa Gaussian 98 e a aproximação Hartree-Fock/6-31G. Mapas de Potencial Eletrostático Molecular (MEP) foram obtidos (Molekel 5.4,2009). O estudo dos mapas de MEP demonstrou que os derivados têm uma região de MEP negativa, próximo do anel trioxano, que é responsável pelo complexação com a heme. Docking foi usado para investigar a interação entre os ligantes e o receptor e mostrou que a geometria do complexo formado entre os compostos e a heme ocorre preferencialmente dispondo as moléculas dos ligantes assumindo uma orientação paralela ao plano do anel porfirínico da heme. Também a parte polar dos ligantes contendo a ligação peróxido, em geral, se direciona ao íon Fe^{2+}. Essas orientações foram assumidas como as mais favoráveis considerando serem as mesmas escolhidas com base nos valores mais baixos de energia livre de ligação (energia de interação). Métodos de Quimiometria (PCA, HCA, KNN e SDA) foram usados para classificar os compostos em mais ativos e menos ativos. A PCA possibilitou selecionar os descritores LUMO+1, Polarizibilidade (POL), Refratividade Molar (RM) e L2m como responsáveis pela separação dos compostos em mais ativos e menos ativos). A variância máxima obtida os 3 PCs foi de 99,89%. Aplicação da HCA confirmou os resultados de da PCA. O método KNN forneceu 1NN, 2NN, 3NN e 4NN vizinhos e o modelo foi construído com 4NN, com 100% de informação correta. A utilização do método SDA também classificou o conjunto treinamento com 100% de acerto. Os modelos obtidos poderão ser usados para predizer as atividades de novos derivados.

Apoio: CNPq.

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Is the 5f shell determinant in the Actinide Halide Chemistry? The Answer from Four Component (4C) Dirac and ZORA (2C) Calculations

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Key-words: actinides, spin-orbit, DIRAC, ADF-ZORA

Actinides chemistry is both scientifically interesting and rich in applications. Here we address a fundamental question in the area, is the *5f* shell participation in chemical bonding important, and if the 5f shell determine the geometry in some actinides complexes? To answer this, we choose a group of molecular trihalides AnX_3 (*An=U, Pu, Np, Am, Cm and X=F, Cl, Br, I*) to determine the importance of *5f* shell and the contribution of relativistic effects in chemical bonding. With this purpose we performed a full *4C*-relativistic study for all these systems employing a *DIRAC* code. All calculations were based on the Dirac-Coulomb Hamiltonian an in all cases the *SS* class of integrals were calculated according to the *LVCORR* approach using a *dyall.v2z* relativistic basis function for actinide element and *aug-cc-pVDZ* basis for halides. These calculations provide an extensive description of their electronic structure and chemical bonding, based on a projection analyses and relativistic localized orbitals. Our results suggest that the 5f orbitals are not chemically active and that the difference in covalence between lanthanide and late actinides stems principally from valence s contributions. We also compare these results against *2C*-relativistic calculations obtained via the *ADF* code using the *ZORA-SO* Hamiltonian.

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Replication of Dengue Virus: A Study By Computational Methods.

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Key-words: Molecular Dynamics, Dengue virus, Molecular Docking

Dengue is a tropical disease affecting millions of people, and may lead to the death of the infected. According to World Health Organization (WHO), Brazil is the country with the highest number of dengue and dengue hemorrhagic fever cases combined (D/DHF)[1]. Unfortunately there are no specific medicines for the treatment of D/DHF and, once the disease is contracted, the WHO recommendations are limited to observation and symptomatic treatment. Recent efforts, mainly in academia, have revealed a series of proteins essential to the dengue virus's life cycle, which may be used as targets for new medicines.

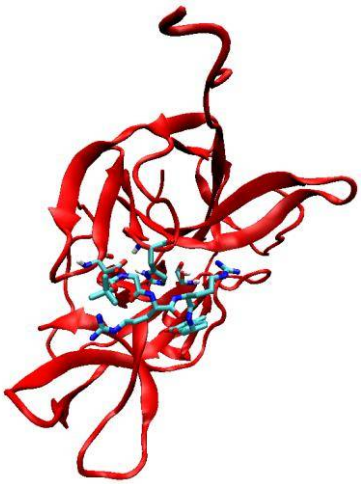

Figura 1: *Docking* of the substrate in the active site of NS3 protein-NS2b. Red protein, and tubes and the substrate amino acids of the active site.

The aim of the present work is understanding the mechanism of action of such an enzyme, the nonstructural protein NS3 protease complexed with the cofactor NS2b (NS3-NS2b), and the identification of molecules capable of effectively inhibit these enzymes, thus preventing the virus from replicating.

Here we will show docking results performed for positioning a substrate (Boc-Gly-Arg-Arg-AMC) in the active site of the protein complex NS3-NS2b, and of molecular dynamics simulations to study the NS3-NS2b complex, alone and in the presence of the substrate in its active site, performed using the programs Autodock 4.2 and Amber 11, respectively.

In the next stage of the work, we will use hybrid QM/MM simulations for understanding the details of the enzymatic mechanism during replication of the virus.

[1] World Health Organization. *Drug for Neglected Diseases Initiative*. 2009 [cited 06/23/2009]; Available from: http://www.dndi.org/.

Support: CAPES and RENAMI.

"Mircrosolvation of Cysteine – a pH-dependency Study of Thermodynamic and Vibrational Properties"

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Key-words: Cysteine, Microsolvation, Infrared Spectra

Water is everywhere. All biological processes occur in aqueous media, making it an essential element for life. This molecule affects the properties of biological molecules, such as conformational stability in the zwitterionic form of amino acids. The Cysteine is a nonessential amino acid characterized by the presence of thiol group (SH). Among its main features, the thiol group becomes important due to its pKa, nucleophilicity, redox, affinity for metal ions and connections, making it very versatile in the regulation of cell function. Previous studies show that amino acids in the gas phase, amino acids are more stable as neutral (N) form. However in solution is found that amino acids tend to prefer the zwitterionic (Z) form. Our goal was to determine from how many molecules of explicit solvent, the Z form of cysteine is more stable than the N form and understand how the presence of the solvent modifies the absorption spectrum in the infrared region. This work presents a computational study of changes in the tautomeric stability and vibrational properties of this amino acid at pH 0.5, 5.2, 9.6 and 13.5. In this study we use the DFT-M06-2X/6-311+G(d,p) method to optimize the aminoacid-water cluster and calculate IR-Spectra. In the study of solvation of the amino acid, we verified the stability of the form CYS_Z over the CYS_N form from five solvent molecules, whose absorption in the infrared region confirmed the higher stability of form Z. At pH 9.6 was reached unexpected tautomer of monoanionic cysteine, CYS_{1A-3}, which proved be the most stable tautomer in gas phase. The addition of water molecules become more stable the CYS_{1A-1} form, from three to seven molecules of solvent, and above this amount the form tripolar form, $CYS_{1A-2,}$ is more stable, up to 30 kcal mol^{-1} in relation to its two tautomers. The addition of water molecules in the system made changes in vibrational properties of cysteine, mainly attributed to hydrogen bonding (HB) between the amino acid and the water molecules. The HB acted by changing the elastic constants of the connections, causing displacement, disconnection and new couplings in the peaks of the theoretical infrared region absorption spectra.

Support: CNPq, CAPES, FINEP, INCT

The Time of Flight Mass Spectrometry Generalized Simulated Annealing - TOFMS_GSA Methodology

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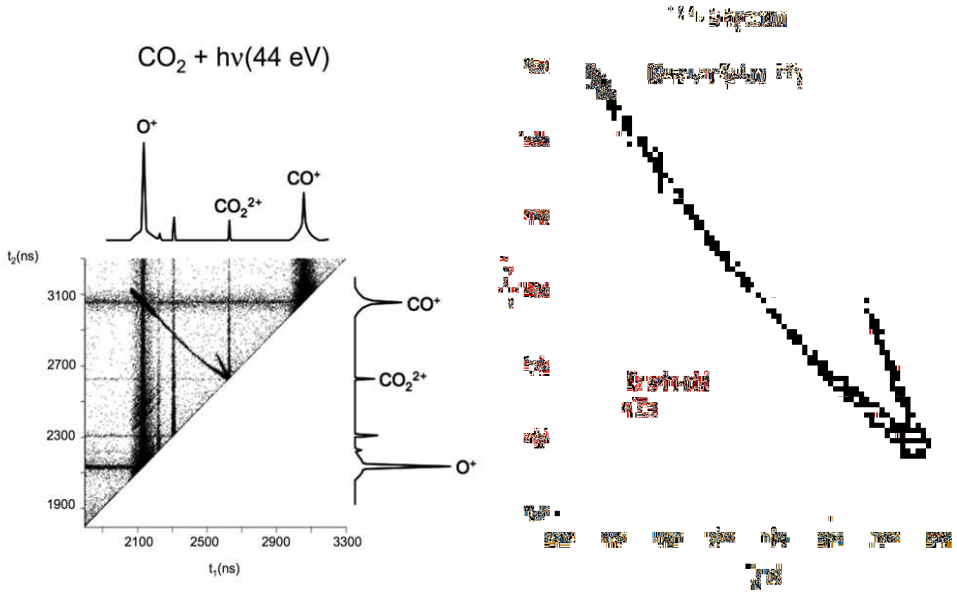
Key-words: Photofragmentation, Simulated Annealing, TOF spectroscopy

We have proposed an alternative methodology to characterize the dynamic features of molecular dication dissociation investigated by time of flight mass spectrometry technique. The double ionization has been studied detecting in coincidence the two fragment ions (PEPIPICO), after the molecular beam has been absorbed the UV light provided by the Synchrotron Radiation Source. The method is based on an extension of the Generalized Simulated Annealing - GSA statistical methodology previously applied in others fields. We have applied it to study some molecular properties like the life time and kinetic energy release. The figures bellows are related to the CO_2 PEPIPICO spectrum and the TOF_GSA simulation, respectively.



Support: CAPES, UnB

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Design of protic solvents for S_N2 and E2 reactions

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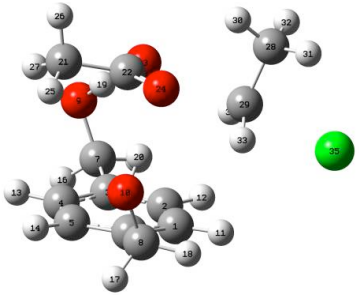
Key-words: S_N2, BDM, TST, Catalysis.

In principle, protic solvents are not recommended for S_N2 and E2 reactions because of their ability of stabilize nucleophiles, thus decreasing their reactivity. However, depending how these solvents interact with the reactants and transition states, the reaction rate can in fact be increased[1]. Since these catalytic effects are still not completely clarified because intrinsic reaction coordinate (IRC) studies were yet not performed, we present a computational study of the S_N2 and E2 reactions between CH_3COO^- and CH_3CH_2Cl in the presence and absence of 1,4-benzene dimethanol (BDM)[1].

Molecular structures, vibrational frequencies, and continuum solvent effects calculations were performed with the Gaussian03 program at the PBE1PBE/6-311++G(d,p) level. The IRC was used to ascertain the proper nature of the transition state, as for instance, the S_N2 reaction shown in Figure 1.

Figure 1



TS with BDM

Table 1. Relative energies (kcal mol^{-1}) for the S_N2 reaction. System: CH_3COO^- and CH_3CH_2Cl.

	System	System-BDM
$\Delta^{\ddagger}E$	13,9	19,0
$\Delta^{\ddagger}G$	15,4	20,7
$\Delta_r E$	–11,2	–11,4

According Table 1, the activation energies ($\Delta^{\ddagger}E$ and $\Delta^{\ddagger}G$) in the presence of BDM is larger than in its absence, when the ion-dipole complex ($CH_3COO^-\cdots CH_3CH_2Cl$) is taken as the reactant. So, apparently BDM is not working as a catalyst in this reaction. The reaction exorthermicity is unaffected by the presence of BDM. This approach was applied to the E2 reactions and we intend to design new protic solvents that can catalyze these reactions. Also, solvent effects have been included by continuum models.

1) J.R. Pliego Jr., *J. Mol. Catalysis A: Chem*., **239** (2005) 228–234.

Support: CNPq, FACEPE, PRONEX, CAPES, FINEP, inctINAMI.

"A Theoretical Study of the Role of Solvent on the Antioxidant Activity of Eugenol."

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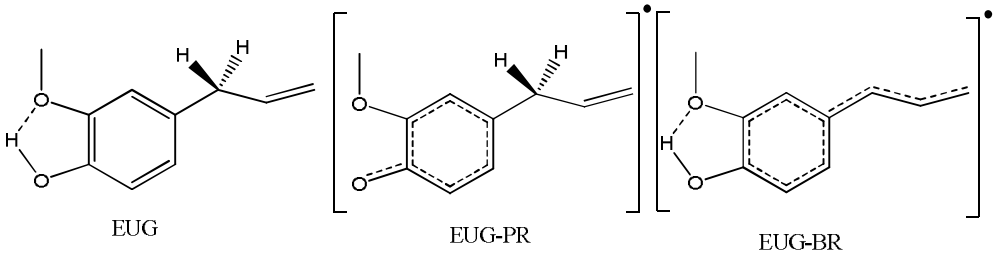
Key-words: Eugenol, Antioxidant, DFT



Eugenol (EUG) is the main substance of the essential oil of clove and has an antioxidant activity. One of the sites for its antioxidant activity is the phenol group, which acts as a hydrogen donor to free radicals. Computational studies conducted for the capsaicin (CAP), which have chemical structures similar to the EUG, called attention to the role of benzylic hydrogens (BH), which presented theoretical and experimental antioxidant activity more effective than the phenolic hydrogen (PH). The goal of present work is to study the antioxidant activity of phenolic and benzylic sites of EUG in gas phase and in the presence of implicit and explicit solvent and propose an experiment to verify this difference in activity. We show by DFT calculations using PBE1PBE/6-311G+(d,p) method, the results of the energies of the radicals have the phenolic radical (PR) as the least stable in all study methods. The presence of implicit solvent weakens the intramolecular hydrogen bond (OH... O-CH3), reflecting the greater tendency of formation of PR of about 4.0 kcal mol^{-1}. The presence of explicit solvent stabilizes more PR than BR. We obtained theoretical spectra of absorption in the UV-VIS region using the semi-empirical INDO/1 method for the radicals in the presence of 19 solvent molecules. PR UV-VIS spectra presents a maximum absorption bands at 359 nm and 552 nm, while BR, at 324 nm and 410 nm.

Support: CNPq, CAPES, FINEP, INCT.

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Inclusion complexation of praziquantel and β-cyclodextrin. Combined Molecular Mechanic and Monte Carlo simulation

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Key-words: praziquantel, cyclodextrin, Monte Carlo.

The treatment of schistosomiasis is made with praziquantel (PZQ) which is a widely effective anthelmintics drug available for human and veterinary use, being the drug of choice for treatment of all kinds of schistosomiasis. However, large doses are necessary to achieve adequate concentrations at the destination due to low solubility of PZQ and its significant first pass metabolism. We use Monte Carlo simulations to generate structures of the water that will act as a solvent around praziquantel molecule with aim to study the formation of the solvation shells of the molecule after complexation into cyclodextrin. The PZQ molecule was positioned into the β-CD cavity at different orientations and MM+ force field calculations considered the center of mass of the isoquinoline ring system. The structure choice presented low enthalpy of formation, with value -18.12 kcal. Mol^{-1}. The Monte Carlo (MC) simulation is performed using DICE program in the canonical NPT ensemble. The system is composed of the β-CD surrounded by 2000 water molecules, at pressure of 1 atm and temperature of 298 K. All QM calculations are made using the Gaussian 09W program to obtain the electrostatic potential for all molecules and density of the orbital molecular. The quantum calculations have been performed at the HF levels with quality bases 6-31G. In this work it had shown an increased of the water number around PZQ/β-CD complexes in relation isolated PZQ molecule. This increase of the water number is due to hydrophilic effect of the cyclodextrin molecule. The HOMO e LUMO orbitals do not present quantitative changes in relation isolate PZQ molecule. Although HOMO of the hydrated system has contribution of electron lone pairs of the water molecule the effect of the solvation shell is not higher to produce a change in the molecular electronic density.

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"Study of the catalytic mechanism of pyrophosphorylase from *Moniliophthora perniciosa* by QM/MM methods"

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Key-words: *Moniliophthora perniciosa,* witches' broom, pyrophosphorylase

The fungus *Moniliophthora perniciosa* is the causal agent of the witches' broom disease of cacao (*Theobroma cacao*). This fungus relies on pyrophosphorylase to catalyze the formation of UDP-N-acetylglucosamine-1-phosphate, an intermediate in the biosynthesis of the fungal cell wall. This enzyme was studied by QM/MM methods in order to understand its catalytic mechanism, and its 3D structure was elucidated in a previous work by homology modeling. The positioning of the substrate in the catalytic site, was based on the similarity with the correspondent enzyme from *Candida albicans*, which was described by crystallographic methods (PDB ID 2YQS) in complex with the substrate and a Mg^{2+} cation. The resulting *M. perniciosa* [enzyme-divalent Mg^{2+} cation-substrate] complex was submitted to molecular dynamics simulations (AMBER 10.0) to refine its geometry. Next, a QM/MM calculation (Gaussian09W) was used to scan the coordinates of the reaction from the reactants to products, considering this reaction as having a S_N2 mechanism (QM: PM6 – applied to reactant molecules; MM: UFF – to the rest of the system). In this system, the nucleophile is oxygen of the phosphate group from N-acetylglucosamine-1-phosphate. It attacks the phosphorus of the alfa-phosphate from the uridine triphosphate to form UDP-N-acetylglucosamine and pyrophosphate. The calculated reaction was exothermic (ΔH = -81,01 Kcal/mol). In the reaction pathway, the most energetic structure had the attacked phosphorus atom in a pentacoordinate configuration. This structure interacts at the catalytic site with the residues Gly-112, Gly-113, Arg-116, Lys-123 and Gly-225 through hydrogen bonds. The Mg^{2+} ion interacts with Arg-116 and Ser-289. All of these residues are described as important to the enzymatic activity in the *Candida albicans*'s enzyme, except Gly-112. It's expected that the geometry of this intermediate will be close to the transition state of the reaction, thus the design of new compounds with similar geometry and with similar interactions with the cited residues may lead to successful antifungal agents against this agricultural disease.

Support: FAPESB.

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"Gaussian basis set of sextuple zeta quality for hydrogen through argon"

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Key-words: XZP basis set, Ab initio, Hatree Fock, CCSD(T), complete basis set

The main purpose of this article is to complete the non-relativistic and relativistic series of increase size basis sets for H-Ar constructed recently by Jorge *et al*., which can be systematically used to reduce basis set truncation error. Segmented all-electron contracted sextuple zeta valence plus polarization function (6ZP) basis sets were constructed to be used in conjunction with the non-relativistic and Douglas-Kroll-Hess (DKH) Hamiltonians. According to our knowledge, it is the first time that a DKH basis set of sextuple zeta valence quality is generated for such elements. The segmented contracted basis sets devised in this work offer the advantage of good accuracy and flexibility. The choice of the polarization functions (p, d, f, g, h, and i) was made from the correlated atomic calculations. The relativistic set was determined from the corresponding original one, i.e., the values of the contraction coefficients were re-optimized using the DKH Hamiltonian. In the present work, we focus exclusively on atomization energies, using the highest level *ab initio* method that can routinely be applied to small molecules with extended basis sets. At the single, double, and perturbative triple-excitation coupled-cluster [CCSD(T)] level of theory, scalar relativistic effects on atomization energies for a sample of molecules were computed. Then, using an extrapolation scheme, scalar relativistic effect complete basis set (CBS) limits were estimated. Additional improvements in the atomization energies were achieved by applying corrections due to core/valence correlation, atomic spin-orbit effects, and addition of tight d and f functions on second-row elements. The 6ZP-DKH+ΔE_{CV}+ΔE_{SO}+ΔE_{tight} atomization energy results showed to be as good as those obtained from extrapolation schemes. Finally, using the BF_3 6ZP-DKH+ΔE_{CV}+ΔE_{SO}+ΔE_{tight} atomization energy and the well established heats of formation of boron trifluoride and fluorine atom, we obtain a heat of sublimation of boron, $\Delta H^0_{f,298}$[B(g)] = 135.1±0.3 kcal/mol, which is near the upper limit and in excellent agreement of the recommendations by JANAF and by Gurvich, respectively. Heats of formation of gaseous carbon tetrafluoride reported previously in the literature agree well with that obtained in this work.

Support: CNPq and FAPES.

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Estudo de artemisininas com atividade contra *Plasmodium falciparum* através do potencial eletrostático molecular, métodos SAR e *docking molecular*

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Palavras - chaves: *Artemisininas, SAR, Mapas MEP e Docking Molecular*

Atualmente, 3,2 bilhões de pessoas, em aproximadamente 107 países ou territórios, vivem em áreas endêmicas (malária), sendo que 300 milhões de novos casos de infecção ocorrem a cada ano, com aproximadamente 1 milhão de óbitos por ano. Neste trabalho, a artemisinina e 14 derivados, com atividade antimalárica, foram estudados. As moléculas fora desenhadas no programa GaussView 1.0. E suas estruturas otimizadas com o programa Gaussian 98, com o método Hartree-Fock/3-21G*. Mapas de Potencial Eletrostático Molecular (MEP) foram calculados e estudados as características estruturais chaves para as atividades biológicas. Estudo dos mapas de MEP mostrou que os derivados têm uma região de MEP negativa, similar ao da artemisinina, próximo do anel trioxano, que é responsável pelo complexação com o heme. A análise de componente principal (PCA) para os três primeiras componentes principais descreveu 94,77% da informação original, e os descritores responsáveis pela separação foram Dureza Molecular (DM), ângulo de torção formado entre os átomos O2-C3-O13-C12a (D4), distância do ferro do heme ao oxigênio 1 do ligante ($dFeO_1$) e índice médio do quadrado da distância (MSD). A análise hierárquica de agrupamento (HCA) mostrou resultados similares a PCA. Os métodos KNN e SIMCA possibilitaram a construção de modelos com 100% de informação correta. Cálculos da interação droga-receptor mostraram que o Fe^{2+} da heme liga-se preferencialmente ao átomo O1 do anel 1,2,4-trioxano. Os modelos obtidos combinados com as informações dos mapas de MEP e dos *docking Molecular* poderão ser importantes no planejamento de novos derivados da artemisinina com atividade contra *P. falciparum*.

Apoio: CNPq.

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"Going where no one has gone before: molecular dynamic simulations as a tool for gene therapy AAV2 vector improvement"

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Key-words: Adeno-associated virus, capsid protein, molecular dynamics.

Adeno-associated virus type 2 (AAV2) has been extensively used as vector for gene therapy applications in animal models and human clinical trials. The first contact between host and AAV2 is achieved by its capsid proteins, specially the one named VP3, which is the most abundant on capsid structure. It has been shown that some mutations on residues of VP3 can improve the infectivity of the AAV2, which have important biological implications. One example is the mutation of the Y444F, located in the binding site, formed by two hairpin structures.

In this context, we used molecular dynamic simulations (MD) to shed light on the alterations of $VP3_{Y444F}$ structure.

The structure of VP3 was taken from Protein Data Bank, code 1LP3. The Y444F mutant ($VP3_{Y444F}$) was constructed using Swiss-PDB-Viewer. The pKa of each residue was calculated by PROPKA server. Both protein structures, wildtype (WT) and $VP3_{Y444F}$ mutant, were simulated in triclinic water boxes, using TIP3P water model and chloride anions at appropriated number to neutralize total charge of the system. Energy minimization was achieved employing steepest-descent with and without position restraint, followed by conjugated gradient and *quasi*-Newton methods, until systems converged to less than 41.84 kJ mol^{-1} nm^{-1}. We also used PME with 1 nm threshold and LINCS algorithm. The systems went to position restraint MD of 500 ps followed by an unrestraint MD of 20 ns. The OPLS/AA was chosen as force field, run on GROMACS 4.0.3 package.

The simulation of WT protein exhibited a closing movement of the loops that forms the binding site. Probably, this movement controls the close attachment of the ligand. In the other hand, the same loops behave completely different in $VP3_{Y444F}$ MD, been apart from each other, and exposing negative charged residues. The both evidences are favorable to binding of heparan sulphate, the most commom ligand of VP3, which is long molecule and positively charged molecule. Therefore, the movement of loops in $VP3_{Y444F}$ may favor heparan sulphate binding, what would improve the interactions between extracellular matrix and AAV2, resulting in more successful infection.

In conclusion, we showed that the MD simulations of VP3 offer an explanation for the biological feature of $VP3_{Y444F}$ mutant virus, been a promising tool to guide another mutagenic studies for viral vector improvement.

Support: CNPq, FAPERJ.

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Effect of Hydrogen Bonds OH---O in the Conformational Equilibrium of *cis*-3-hydroxycyclohexyl methanoate

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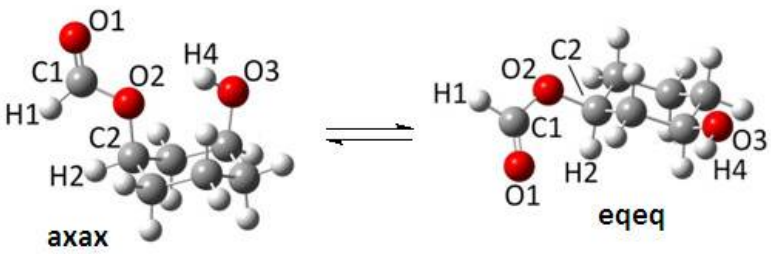
Key-words: Theoretical calculations, Hydrogen bond, Conformational analysis.

Recently, the occurrence of an intramolecular hydrogen bonds (IHB) in *cis*-3-methoxy-[1], *cis*-3-ethoxy-[2] and *cis*-3-*N*,*N*-dimethylamino-cyclohexanols [3], stabilizing the diaxial conformer and suppressing the 1,3-diaxial steric interactions, has been reported. The present work describes how intramolecular hydrogen bonds HO---H (IHB) influence in the conformational equilibrium of *cis*-3-hydroxycyclohexyl methanoate (HCH) through theoretical calculations. Figure shows the conformational equilibrium of HCH. The nine possible rotamer for the diaxial conformation (axax) and diequatorial (eqeq) were optimized with the B3LYP/6-311++g(d,p) using the Gaussian03 software. The energy difference between the more stable rotamer axax and eqeq indicated that the conformation eqeq is 0.48 kcal mol^{-1} more stable than axax. The substitution of hydrogen H1 by NH_2 and CF_3 groups showed that the energy difference between eqeq and axax conformers changed from 0.42 to 0.94 kcal mol^{-1}, respectively. These results indicate that the energy difference increases or decreases because the IHB becomes stronger or weaker depending on the substituent in hydrogen H1. As the group NH_2 is electron density donor, it leaves the oxygen of the ester group more electron rich, strengthening the IHB. Already the group CF_3, to be electron density withdrawing leaves the oxygen of the ester poorer in electrons, weakening the IHB. The distance between atoms O2 and H4 in the conformation axax changed 2.08 to 2.18 when the hydrogen H1 is replaced by NH_2 and CF_3, respectively, confirming the interference of these groups in the strength of the IHB. This distance was 2.10 when the hydrogen H1 was present. Other substituent (F, Cl, Br, OCH_3, CH_3 and OH) are being analyzed and the results will be presented later.



Support: CAPES, CNPq, UTFPR and CENAPAD-SP.

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Interação da MAO-A e MAO-B com menadiona e 1,4-naftoquinona via Docking e Dinâmica Molecular

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Key-words: MAO-A, MAO-B, inibidores, docking, dinâmica molecular

As monoaminooxidases A e B (MAO-A e MAO-B) são enzimas que catalisam a desaminação oxidativa de neurotransmissores e de monoaminas exógenas. Os inibidores da MAO podem atuar tanto no tratamento de depressão como também como agentes neuroprotetores, aliviando os sintomas de pacientes com Parkinson ou Alzheimer. Sendo assim, é de grande interesse o desenvolvimento de novas drogas que atuem como inibidores específicos da MAO-A ou da MAO-B. O objetivo deste trabalho é investigar a interação da menadiona e da 1,4-naftoquinona com a MAO-A e MAO-B através da combinação de Docking e Dinâmica Molecular.

Metodologia: (1) Construção das estruturas dos ligantes e otimização 6-31G* (Gaussian), (2) Estruturas das proteínas PDB ID 2Z5X (cadeia A sem FAD), 2Z5X e 2Z5Y (cadeia A com FAD) para MAO-A e PDB ID 2XFU (cadeia A sem FAD), 2VRL e 3PO7 (cadeia A com FAD) para MAO-B. (3) Docking usando AutoDock/Auto Dock Tools (comparando *blind docking* e grid no sítio ativo). (4) Dinâmica molecular usando GROMACS (campo de força GROMOS 53A6).

Os resultados de docking mostraram interações significativas entre a MAO-A e MAO-B com ambos ligantes, sendo a interação com a 1,4-naftoquinona menor do que com a menadiona, para ambas enzimas. A análise do docking revelou também interação do tipo HB com a porção flavina de cada enzima com 1,4-naftoquinona e menadiona.

A interação mais forte observada no docking foi entre a MAO-B (2XFU sem FAD) e a menadiona, assim, optou-se primeiramente por realizar a simulação Dinâmica Molecular deste sistema. O solvente escolhido foi água tipo SPC. As análises dos resultados, através de pacotes do GROMACS, incluíram: variação de energia potencial e temperatura, desvio médio quadrático (RMSD), raio de giro, mobilidade relativa de resíduos (RMSF), ligações de hidrogênio intramolecular (enzima) e intermolecular (enzima-ligante), gráfico de Ramachandran, superfície acessível ao solvente (SAS) e distâncias entre segmentos da enzima e entre enzima-ligante. Observou-se (Figura 1), que a distância entre o ligante e o resíduo GLY56 do sítio de interação (IV) permanece praticamente inalterada durante a simulação, ao contrário da distância entre o ligante e os resíduos ARG40 (III) e TYR433 (II). A análise da distância entre os resíduos ARG40 e TYR433 (I), levou à constatação de que o ligante se desloca dentro do sítio de interação, afastando-se do resíduo ARG40 e aproximando-se do resíduo TYR433, enquanto as coordenadas da enzima pouco se alteram.

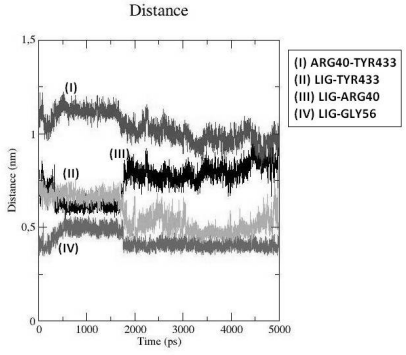

FIGURA 1: distâncias entre resíduos do sítio de interação com o ligante e entre si.

Os demais sistemas obtidos via docking também estão sendo analisados por dinâmica molecular.

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News *Double Zeta* Bases Sets to First Row Atoms Constructed Using the *Generalized Simulated Annealing*

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Key-words: Hartree-Fock Functional, Double Zeta Bases Sets, Generalized Simulated Annealing

The procedure, designated *HF^{Gauss}-GSA* method [1], consists in the direct optimization of the *Hartree-Fock* (*HF*) functional of the atom, taking simultaneously as variational parameters the coefficients of the atomic orbital expansions in the basis functions and the coefficients and the exponents of the Gaussian functions which define the basis functions set. The *HF^{Gauss}-GSA* algorithm is a modification of the stochastic method *Generalized Simulated Annealing* that incorporate constraint conditions.

Using these methodology were constructed new atomic minimal bases for the first row atoms of the Periodic Table. The new basis sets have been used to compute the ground state energy and other properties of the several molecules, at the *HF* and *Configuration Interaction* (*CI*) calculations. In almost all cases was obtained better energies than that ones obtained using the *STO-3G* and *STO-6G* bases. Beside were performed *Multi-Reference HFCI* calculations [2] providing good electrical dipole values.

In this work we are applying the *HF^{Gauss}-GSA* method to obtain news *Double Zeta* (*DZ*) atomic bases for the first row atoms. The first results already indicate the possibility of to improve *DZ* bases, as shown in the following table:

Table I – Atomic energies for the Li and Be atoms obtained with the new and usual DZ bases sets.

Atom \ Base	New *DZ*	Usual *DZ*
Li	-7,4321869202	-7,4317356546
Be	-14,5712514640	-14,5709067067

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Theoretical study of the hydrazine molecule decomposition reacting with hydrogen atom

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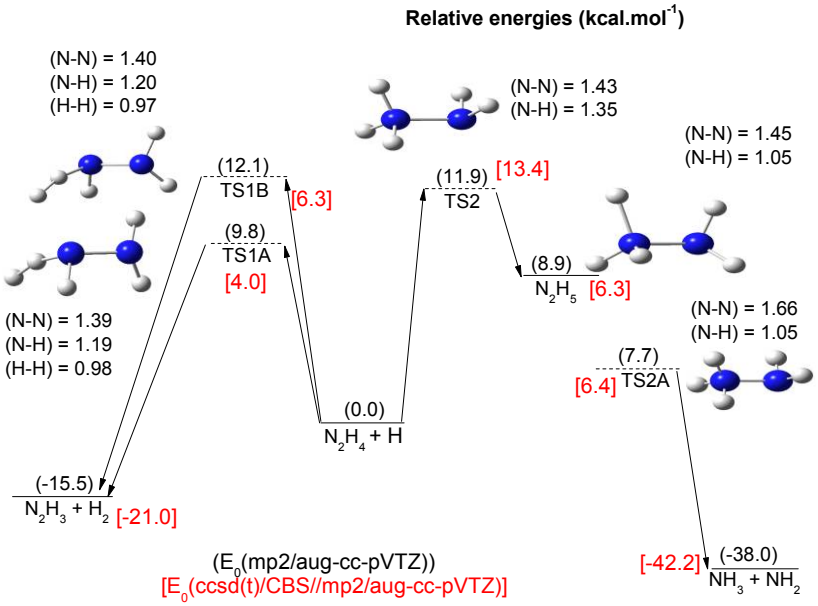
Key-words: Thermochemistry, Transition state, DFT, MP2, CCSD(T).

Hydrazine (N_2H_4) and its methyl derivatives form an important group of molecules that have been used as propellant fuels in rocket and satellite thrusters. In this work we have characterized the reactions between hydrazine and hydrogen atoms, both NN bond and NH bond cleavage: $N_2H_4 + H \rightarrow N_2H_3 + H_2$ (1) and $N_2H_4 + H \rightarrow NH_3 + NH_2$ (2).

Full geometry optimizations were performed using MP2 and DFT methods, with the aug-cc-pVTZ basis set. Single point calculations were carried out with CCSD(T) and aug-cc-pVXZ (X=T,Q) basis set followed by complete basis set extrapolation (CBS). One of our goals is also to evaluate the performance of some class of functional, such as M05, M05-2X, M06, M06-2X, and BB1K, to describe the termochemical properties of these elementary reactions.

The diagram below contains selected results of the reactions 1 and 2 relative energies. All the DFT results present barrier heights lower than MP2 and close to the CCSD(T)/CBS approximation. The M06-2X functional is one that gives results for barrier heights closer to the CCSD(T)/CBS approximation. For the enthalpy, the CCSD(T)/CBS result for the reaction 1, ΔH = -21.11 kcal.mol^{-1}, agrees very well with the experimental value, ΔH = -21.09 kcal.mol^{-1} [1].



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[Support: FAPESP, CNPq]

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Theoretical study of precursors for liquid crystals synthesis using 1,3-dipolar cycloaddition reaction

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Key-words: DFT, liquid crystal, cycloaddition.

Molecules that presenting five members heterocyclic rings are an important class compounds, which already has long time been attracting the researchers interesting because of the diverse chemical transformations available to this ring. These molecules, such as isoxazolines, represent an attractive way to obtain new types of organic materials with potential technological application[1], such as liquid crystals, which was aroused great interest in the organic electronics materials synthesis.

The objective of this work was to realize a theoretical study about the double [3+2] 1,3-dipolar cycloaddition reaction between the benzonitrile oxide and the vinyl acetic acid, whose products present five members heterocyclic rings and liquid crystalline properties. A theoretical calculation was performed with the Gaussian 03 program using DFT methods with PBE1PBE hybrid functional employing a 6-311+G(d,p) basis set including solvent effect (CPCM/THF). Were done the geometric optimization and calculation the transition states.

The calculation showed that probable mechanism starts by a 1,3-cycloaddition reaction between the benzonitrile oxide and vinyl acetic acid to produce the cicloaddition 1:1 product, an isoxazoline. As the reaction moves forward, the concentration of vinyl acetic acid decreases and the isoxazoline produced competes with it by a benzonitrile oxide. But, due the hight reactivity of the isoxazoline and due to smaller energy gap, the second cycloaddition is favoring to occur between the isoxazoline and the oxide. The dominant interactions that control the approach of both reactants depend on the relative levels of the FMOs. The calculation results showed that reaction are possible and both cycloaddition reaction will be controled by LUMO of the 1,3-dipole (benzonitrile oxide) and HOMO of the dipolarophile (vinyl acetic acid and isoxazoline) interactions because these energy gaps are smaller than the competing with 1,3-dipole-HOMO and dipolarophile LUMO energy gaps.

Support: CNPq.

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Microcluster assisted decomposition of methanol to formaldehyde by elementary reactions of hydrogen abstraction

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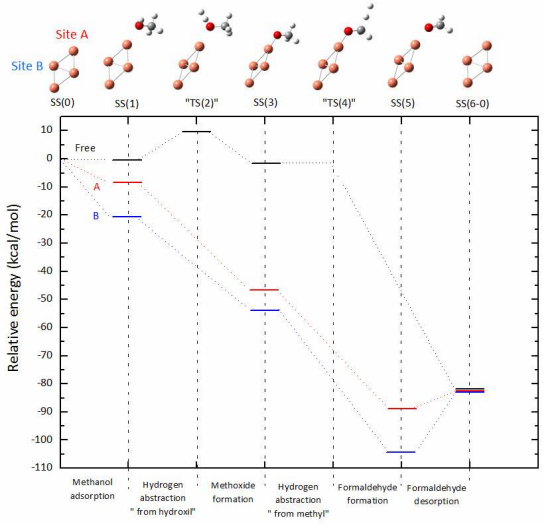
Key-words: M05, copper cluster, methanol

Electronic structure calculations within the cluster approach for a catalyst active site can provide complementary information to experimental studies of catalysis processes. Experimental studies show that small copper cluster with diameter in the order of 16 Å are catalysts of methanol decomposition. We carried out calculations of classical barrier heights, structures and enthalpies for the first two reaction paths of $2H + CH_3OHCu_4$ using the thermochemistry functional M05 with 6-31G*, 6-31G** and a modified for metals 6-31G* basis set for the main group elements, hydrogen and copper atoms, respectively. The electronic structure, intermolecular and intramolecular bond energies were analysed, as well as the energy variations for the reaction on the cluster and in the free reaction. The main objective of this work is to achieve a better understanding on the metal cluster interaction with main group molecules, particulary, those with energetic potential, in order to trace possible reaction mechanisms in their dehydrogenation and/or decomposition. In figure 1 below, it is showed the energy variations along the proposed reaction mechanism, where the sequential hydrogen abstraction, firstly via hydroxil and then from the methyl group, is espontaneous for both adsorption sites.



Support: FAPESP.

Avalia o da intera o de u novo ini idor ro osto na S S de *Solanum lycopersicum* elo todo de ancora ento olecular

Anivaldo Xavier de Souza(PQ)[1,2], Andrea Janaina M. Nogueira[2],

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alavras -chave: Docking, EPSPS

A enzima 5-enolpiruvilchi uimato-3-fosfato sintase (EPSPS), catalisa a rea o entre o fosfoenolpiruvato (PEP) e o chi uimato-3-fosfato (S3P) formando 5-enolpiruvilchi uimato-3-fosfato (EPSP)[1]. A EPSPS essencial para plantas e microorgaismos por ue catalisa a sexta etapa da rota do chi uimato, precursora na biossíntese de amino cidos arom ticos. Essa enzima inibida pelo glifosato ue comercializado como herbicida em todo mundo. Estudos de nosso grupo avaliaram a atividade inibitória de novas dial uilfosforilarilidrazonas sobre a germina o de sementes de *Solanu l co ersicu* (tomate), sendo identificado como ativo o composto dibutilfosforil- -carboxifenilidrazona[2]. Para avaliar a possibilidade deste composto atuar como inibidor da enzima EPSPS, inicialmente foi construído um modelo comparativo para a se ncia prim ria da EPSPS de tomate, tendo como molde a estrutura cristalogr fica da mesma enzima de . *coli*. Este modelo foi usado para um estudo de docking com o composto ativo, com o programa Gold5.0 (CCDC). Para testar a melhor fun o de classifica o do GOLD para o objetivo de estudo, foi realizado inicialmente o ancoramento do intermedi rio tetra drico da rea o entre os dois substrato na enzima EPSPS de . *coli* com as fun es de classifica o Goldscore e Chemscore. Os resultados mostraram ue a melhor fun o foi o Goldscore. Após a defini o da melhor fun o de classifica o, foi feito o ancoramento do dibutilfosforil- -carboxifenilidrazona na EPSPS de tomate. Os resultados mostram ue o composto tem uma boa intera o com a enzima uando comparado com o intermedi rio tetra drico. Essa intera o maior na regi o do sitio ativo onde se processa a rea o entre o S3P e o PEP. Esses resultados mostram ue o composto interage com a enzima na regi o do sítio ativo, ocupando o lugar do S3P e do PEP, possivelmente impedido a rea o entre eles. Isto uma forte indica o ue o dibutilfosforil- -carboxifenilidrazona poderia provocar a inibi o da enzima explicando os resultados obtidos nos testes de germina o. A avalia o de outros compostos sintetizados por nosso grupo de pes uisa bem como um refinamento da avalia o das intera es com m todo semi-empirico est o em andamento.

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"DETERMINATION OF CONFORMATIONAL POPULATION OF CYCLOALKANES USING *AB INITIO* CORRELATED METHODS"

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Key-words: Conformational population, *ab initio,* cycloalkanes, thermal energies.

1. Introduction:

The theoretical determination of thermodynamic properties and so gas phase conformational population (Gibbs population ratio - ΔG) is based on the use of quantum mechanical methods and the standard statistical thermodynamics formalism**.** In the present work, we performed a comprehensive conformational search for cycloundecane, cyclododecane and cyclotridecane molecules using *ab initio* molecular orbital theory.

2. Methodology and Discuss:

In this work we report MP4(SDTQ) and CCSD(T) employing Pople's 6-31G(d,p), 6-311++G(2d,2p) and Dunning's aug-cc-pVDZ basis sets. The thermal correction ($\Delta G_{Thermal}$) to the energy difference in the vacuum (ΔE) leading to the evaluation of ΔG values according to equation (1) is defined as a difference of the internal energy (ΔU) and entropy contribution (TΔS) as given by equation (2).

$$\Delta G = \Delta E + \Delta G_{Thermal} \quad (1)$$
$$\Delta G_{Thermal} = \Delta U - T\Delta S \quad (2)$$

The results reported for cycloalkanes, reveals a large dependence of the conformational population with the low frequency vibrational modes.

4. Conclusion:

An analysis of the adequacy of the standard statistical thermodynamics approach for treating large molecular systems is still of methodological relevance.

Support: FAPEMIG, CNPq.

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Atomic Bases Obtained by the Hartree-Fock Molecular Functional Optimization

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Key-words: Hartree-Fock Functional, Minimal Basis, Generalized Simulated Annealing

In a previous work [1], new atomic minimal bases for the atoms of the first row of the Periodic Table have been constructed by applying a stochastic method - the *Generalized Simulated Annealing*. The procedure, named as HF^{Gauss}*-GSA* method, consists in the direct optimization of the atomic *Hartree-Fock* (*HF*) functional, considering as simultaneous variational parameters, the coefficients of the linear combination of the atomic orbitals and the coefficients and exponents of the Gaussian functions, which define the atomic orbitals. New *Contracted Gaussian Functions* (*CGF*) *3G* and *6G* bases have been obtained. These new bases were tested by computing the ground state energy of a number of molecules at two calculation levels, the *HF* and *Configuration Interaction* (*CI*). In nearly all cases, it was obtained better energies than those achieved by using the *STO-3G* and *STO-6G* bases. In the present work we have expanded the HF^{Gauss}*-GSA* method in order to obtain new bases for the same set of atoms. In this work, however, instead of optimizing the *HF* functional of the atom we are now optimizing the *HF* functional of the molecule using the same variational approach as described above. The first results for the *LiH* molecule yielded a lower *HF* energy, (*-7.9776685349 hartrees*) than those obtained with the bases, the *STO-6G* (*-7.9519562454 hartrees*) and the *CGF-6G* (*-7.9620211907 hartrees*).

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Electrical Properties Calculations of Systems Constituted with First Row Atoms Using MRHFCI Method

Micael Dias de Andrade[1] (PQ), Antonio Moreira de Cerqueira Sobrinho[2] (PQ), Luiz Augusto Carvalho Malbouisson[2] (PQ),

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Key-words: Hartree-Fock, Configuration Interaction, MRHFCI

In previous works [1, 2], we have introduced a new multi-reference configuration interaction method based on multiple *HF* solutions (named as *MRHFCI*). In this method, instead of using a single reference - the *HF* fundamental state, we apply several *HF* extremes as references to expand the state functions. In order to perform the *MRHFCI* calculations, it is necessary to determine multiple *HF* solutions with the appropriate symmetries of point and spin. Thus, we have obtained multiple *HF* solutions for the systems *LiH, BH, FH, CO* and *H2O* using the Slater *STO-6G* bases and the new *CFG-6G* minimal bases introduced in the reference [3]. For the *LiH*, we also used the *Double-Zeta* (*DZ*), *Triple-Zeta* (*TZ*) and *DZ* with polarization functions (*DZp*) bases. With the *MRHFCI* ground states, it was possible to obtain values of the permanent electric dipole moment for the above systems and bases quite close to the experimental values with a reduced number of configurations in the *MRHF* bases. In this work, we are calculating one-electron properties for the molecules mentioned above, using the previous calculated *MRHFCI* states, and new *MRHFCI* calculations for the same systems. Preliminary calculations of the traceless electric quadrupole moment are presented below.

System	Total Energy	MRHF CSF's	Dipole (Debye)	Quadrupole (Buckingham) xx	yy	zz	
LiH STO-6G	-7.9679	13	5.842 (Nuc)	2.508	2.508	-5.017	(Nuc)
LiH DZ	-7.9943	29	5.892 (Nuc)	3.319	3.319	-6.637	(Nuc)
FH STO-6G	-99.522	8	1.799 (Nuc)	-0.833	-0.833	1.666	(CM)
H_2O STO-6G	-75.716	17	1.849 (Nuc)	-2.728	3.616	-0.888	(CM)

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Triple Ionization with Diffusion Quantum Monte Carlo

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Key-words: Quantum Monte Carlo, Ionization, Water

Triply ionized cations are often involved with experiments in photoionization and dissociation processes, enabling a further study on the nature of chemical bond. Furthermore, it's more common to find theoretical and experimental results on single and double ionizations, but triple ionizations are reported sporadically, mainly results involving electronic structure calculations.

Thus, this work aims mainly to study the feasibility of calculation of triply ionized states for the molecule of water with Diffusion Quantum Monte Carlo. The trial wave function is a Hartree-Fock built from the linear combination of Slater Cartesian single zeta basis functions with exponents optimized in the molecular environment. Simulations were performed with 100 walkers previously obtained from Variational Quantum Monte Carlo and moved by 200 x 10^3 steps, with high acceptance and a small time step. The results are in good agreement with theoretical and experimental results.

An important aspect to be emphasized is that the simulations for the ionized states were performed with wave function of the neutral state, which makes this kind of calculation a simpler alternative for triple ionization.

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Structural analysis of the BTCI/Trypsin complex by molecular mechanics and semi-empirical PM6 method

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Key-words: Serine proteases inhibitors, PM6 method, BTCI.

The black-eyed pea trypsin/chymotrypsin inhibitor (BTCI), a Bowman-Birk protein isolated from *Vigna unguiculata* seeds, was described as a potent anticarcinogenic agent due its ability to alter the proliferation and viability of breast cancer cells. The mechanisms of action by which the inhibitor affects the tumor cells are not fully known, but there are evidences that these inhibitors act through the inhibition of trypsin/chymotrypsin-like proteins, that are involved in signal transduction pathways, proteolysis and cell cycle. In this work, we present the comparison of BTCI/Trypsin complex geometry by molecular mechanics using the force fields MM+ and AMBER. The geometry and molecular orbitals of BTCI and trypsin separately were obtained using the semi-empirical PM6 method in Gaussian. The geometry of trypsin and the length of disulfide bonds, which are related to the stability of molecule, showed small variation from the structure deposited in PDB with a RMSD value of 4.99×10^{-7} Å. In relation to orbitals, BTCI and trypsin present a HOMO-LUMO Gap variation of -3.92 and -1.46 eV respectively, indicating the possibility of interaction between these proteins. Further analyses of the complex were performed in order to obtain the interaction energy for the inhibitory complex, frontiers orbitals and components involved.

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Theoretical study of the silane activation by H, F, Cℓ and I atoms

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Key-words: Quantum molecular dynamics, femtosecond pulses, silane activation.

Reactions of silane (SiH_4) with other species have been the subject of many experimental and theoretical studies[1,2] due to their industrial importance in the manufacture of semiconductors. In this study it has been carried out theoretical simulations of quantum molecular dynamics of silane activation reaction by H, F, Cℓ, and I being or not being induced by femtosecond pulses of electromagnetic radiation. All calculations have been performed by using density functional theory (DFT) within the generalized gradient approximation (GGA) and norm-conserving pseudopotentials as implemented in the SIESTA program[3]. We have initiated the molecular dynamics simulations using the following initial structure $H_3Si—H\cdots X$, where X = H, F, Cℓ, and I. We have considered three different H···X initial distances, which are $d_{H\cdots X}$ = 1, 2 and 3 Å. For the simulations induced by laser pulses, the polarization vector of the light is parallel to the Si—H···X axis. The femtosecond light pulse is modulated by a Gaussian function with the following parameters: duration τ=15 fs, intensity $I_0=1\times10^{13}$ W/cm^2 and frequency ω=0.278 eV. Our results show that the hydrogen, fluor and chlorine atoms are able to induce the silane activation reaction leading to the formation of the products SiH_3 and HX. The chlorine atom, exclusively for distance $d_{H\cdots Cℓ}$ = 1 Å, leads the dissociation of all Si–H bonds in silane. When the hydrogen atom is distant from silane molecule ($d_{H\cdots H}$ = 3 Å), it does not become able to induce the silane activation reaction. The iodine atom shows to be inadequate to induce the silane activation reaction. Iodine atom only induces silane bond dissociations for the distance $d_{H\cdots I}$ =1 Å, and in this simulation, all Si–H bonds are broken. The femtosecond laser pulse promotes a distinct reaction pathway when it is used together with fluor to induce the silane activation. In this case, the product of the reaction is $H_2SiF + H_2$, when $d_{H\cdots F}$ =2 and 3 Å. Concluding, we have shown here a comparison about the efficiency of different atoms (H, F, Cℓ, and I) together or not with femtosecond laser pulse to induce the silane activation reaction.

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"Theoretical study of $Ca2^{+}$ - ATPase (PfATP6) and SERCA1 by molecular modeling"

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Key-words: *Plasmodium falciparum,* Molecular modeling, Malaria.

Malaria is an infection caused by protozoa of the genus Plasmodium and can be lethal if not treated early. Currently conventional therapies have been neglected due the constant emergence of parasite resistance. Thus, search for new antimalarial drugs are urgently needed. Several Ca^{2+} pumps were identified in the genome of the parasite and one of them *Pf*ATP6, a Ca^{2+} ATPase enzyme of sarcoplasmic reticulum, known as P-type ATPase are responsible by the active transport of ions across cell membranes. This enzyme has been reported to be the target of the Artemisinin (ART), a sesquiterpene lactone that inhibits enzymes ATPase $Ca2^{+}$ reticulum endo / sarcoplasmic (SERCA) of mammals. In this work, we have carried out molecular dynamics study to describe time-dependent mobility and flexibility for PfATP6-ART complex. The Three-dimensional structure of the *Pf*ATP6 was predicted by molecular homology and enzyme-inhibitor interactions were performed by molecular docking. The molecular dynamics simulations and calculations of interaction energy and free energy of binding for *Pf*ATP6-ART complex was performed by the *f*Dynamo library. So far the data has shown that after 2.0 ns of simulations the behavior in solution of the PfATP6-ART complex exhibited a behavior similar to the structure of X-rays showing hydrophobic residues important like ILE 829 and PHE 256 to a distance around 2-4 Å confirming the literature data. These results are promising for describing conformational simulation of the protein complex in study.

Support: CNPq, LPDF/UFPA.

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Development and applications of the chemical bond overlap polarizability model (CBOP)

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Key-words: overlap polarizability, chemical bond, solid state, embedding

This work presents the study of the covalent character of a chemical bond (CB) in different systems, such as: diatomic molecules, hydrogen bonds (HB) in heterodimers and solid state systems. The concept of the chemical bond overlap polarizability (OP) was also developed using a valence bond (VB) wave function. The results for diatomic molecules led to a covalency scale based on the overlap polarizability quantity (α_{OP}). Using this scale, it is possible to estimate the degree of covalency in homonuclear diatomic molecules, which is impossible by the Pauling scale. For heterodimers, we have calculated the α_{OP} (using a fragment molecular orbitals approach) and the interaction polarizability (α_{int}), using finite field calculations, of a set of organic compounds interacting with water. The results indicate that the HB covalent character increase with the electron donor capabilities of the substituent bonded to the proton acceptor species. Moreover, the decrease in α_{int} suggests an increase of the HB covalent character (Table 1). For solid state systems, was developed a scheme to mimic the crystalline effects where the neighboring atoms are described by a frozen electron density (Figure 1). This method is efficient, providing errors of 1% for the calculated equilibrium distances. The results indicate that the α_{OP} can be a tool for characterizing materials regarding their covalent character and can be measured in the 5–20 eV spectral region. The VB formulation of the OP concept naturally gives rise to some important properties, as the partition of the chemical bond as a sum of atomic and overlap contributions. We have found that the overlap region follows the same selection rules known for electric dipole transitions. Using the VB theory, is possible obtain an analytical expression for α_{OP} that depends on the matrix elements of atomic dipoles, the ionic configuration weight (λ), the overlap integral (ρ), and the first excitation energy (Δε) associated with the CB.

Table 1: Overlap polarizability α_{OP} and interaction polarizability for some dimers.

Systems	α_{OP} (Å)	α_{int} (Å)
$(CH_3)_2O - H_2O$	0.15	–0.020
$CH_3HO - H_2O$	0.08	0.022
$H_2O - H_2O$	0.07	0.073

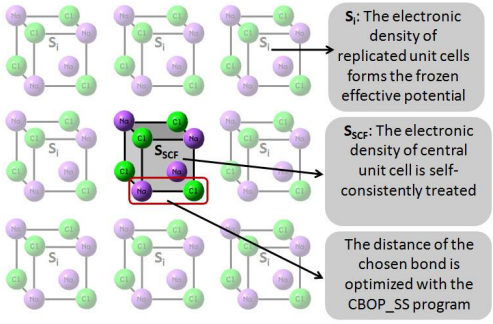

Figure 1: Frozen model for solid state systems

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A procedure to cluster complexes of small ligands and flexible proteins

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Key-words: conformational flexibility, docking, ensemble, T4 lysozyme.

Several computational methods are used to generate protein-ligand complexes and estimate their binding affinities. It has been shown that consideration of protein flexibility is important to improve the estimation of binding energies. This work aims to develop methods for partitioning and rationalizing complexes obtained from docking ligands to an ensemble of protein conformations.

T4 lysozyme mutant L99A/M102Q was chosen as a model system. Configurational ensembles were generated by unrestrained molecular dynamics simulations as well as by selecting structures that reproduce measured NMR chemical shifts. For instance, root mean square fluctuation (RMSF) of the conformations ranged from 0.12 to 1.05 nm, and root mean square deviation (RMSD) relative to the starting structure (PDB 1LI3) ranged from 0.39 to 1.26 nm. AutoDock 4.0 was used to generate complexes between structures in the ensemble and the ligands catechol and toluene. Complexes were superimposed by minimizing the RMSD relative to the starting structure, considering only receptor alpha carbons near the binding site. Poses were clustered based on a partitional clusterization which, for a given cut-off RMSD of ligand positions, takes the complex with largest number of neighbors as a cluster and eliminate them from the pool of complexes, repeating the process until there is no structure left.

Variable cut-offs (0.05 to 0.5 nm) were used. As expected, increasing cut-offs decreased the number of clusters and increased the number of poses in the most populated cluster. Homogeneous clusters were defined as those with a value for maximum deviation from the average binding energy equal to or smaller than 50% the maximum energy deviation for all considered poses. A cut-off of 0.3 nm yielded the best compromise between the total number of clusters and cluster homogeneity.

Support: FAPESP, CNPq

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"Explicit Solvent Effects in Monoglyceride Structure using QM/MM Method"

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Key-words: biodiesel, methanol, transesterification

Biodiesel is produced from triglycerides of fatty acids by a transesterification reaction with a small chain alcohol, usually methanol or ethanol. The transesterification reaction is a carbonyl addition-elimination reaction which proceeds through a covalently bound tetrahedral intermediate. Previous calculations in the gas-phase show details of this reaction mechanism. However, they have not been enough to clarify completely all aspects related to formation and decomposition of the tetrahedral intermediate adduct. The probable reason is the study have neglected the important role of the solvent.

In the present study we analyzed monoglyceride models with apolar linear carbon chain of different length. We performed molecular dynamics simulations of the monoglyceride models diluted in methanol solvent by applying the Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) Method. Our simulations have considered explicit solvent effects of methanol.

Thus, it was possible to evaluate monoglyceride-solvent interactions, alkyl chain effects against the carbonyl monoglyceride and to compare these results with previous theoretical ones presented in literature. So, our research demonstrates the importance of explicit solvent representation in the calculations.

Support: CNPq, FUNDECT, CAPES

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"Dihedral parameters for polytyramine conformational analysis"

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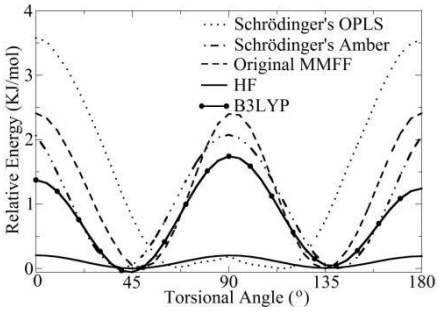
Key-words: polytyramine, parameterization, force field, molecular dynamics

Tyramine is a neurotransmitter that contributes to the functioning of the brain and blood vessels. Used as monomer, its polymer is applied in biosensors. The poly-tyramine structure mainly depends on the parameter that defines the dihedral angle formed between its monomers. In these case, a dihedral parameter diphenyl-ether (DPE) like. This work proposes the derivation of this parameter made by non-linear fitting to Fourier dihedral function, from data obtained in HF and B3LYP/6-31G(d) calculations, as well as a quality assessment of this parameter in comparison with original and modified force field data available for molecular modeling of biological systems. It´s important to note that OPLS were totally parameterized at HF/6-31G(d) level of theory.



	V1/2	V2/2	V3/2	V4/2
Schrodinger´s OPLS	0,0000	0,472	0,0000	0,0000
Schrodinger´s Amber	0,0000	0,750	0,0000	0,0000
Original MMFF	0,0000	3,200	0,0000	0,0000
HF/6-31G(d)	0.0006	0.0026	0.0062	-0.0979
B3LYP/6-31G(d)	-0.0064	0.2173	0.0723	-0.7632

The figure shows the dihedral profiles obtained from table data. These parameters are from OPLS-AA and AMBER, modified by Schrödinger software package, and MMFF original force field (FF), both of Macromodel Software. It also presents the energy profiles derived from HF and B3LYP/6-31G(d) fitting procedure for DPE dihedral. These modified FFs and MMFF were developed for biological molecular systems and are quite similar to B3LYP profile. The parameters added by Schrödinger and the MMFF parameter contain only the term V2/2 and represents a generic ether dihedral X – C_{sp2} – O – X angle type, where X can be any atom while, in this work, parameters of four terms of Fourier series were obtained for C_{Ar} - C_{Ar} - O - C_{Ar} dihedral of DPE. These parameters should better represent the conformational freedom of tyramine´s oligomers in Molecular Dynamics studies that will be performed with the OPLS force field. The HF/6-31G(d) method shows small torsional barriers, so that parameterization with the same method for this FF is essential.

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"Ionic liquids: a description of ionic conductivity temperature dependence beyond Arrhenius mechanism"

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Key-words: ionic liquids, conductivity, non-Arrhenius behavior

Although most of liquids are composed by neutral molecules, a special group has ionic species as components. They have weak interactions that allow the whole material to be in the liquid phase in temperatures below 100 degrees Celsius and are broadly known as ionic liquids.

Besides their low vapor pressure and great chemical and thermal stability, a huge advantage of an ionic liquid is that its properties can be changed just by trying new combinations of cations and anions, which grants great versatility to the ionic liquids.

A known problem associated to these liquids is the non-linear behavior of its ionic conductivity in response to temperature. Linear-kind materials can be modeled by Arrhenius theory, which gives a liner relationship between the logarithm of ionic conductivity and the inverse of temperature. However, ionic liquids often show a non-linear behavior.[1,2]

A possible solution to this feature is the use of a generalization of Arrhenius theory,[3] with which can be showed that the conductivity of ionic liquids is a non-linear function of temperature (Equation 1)

Equation 1: Generalized Arrhenius-relationship between conductivity and temperature

$$\sigma(T) = \sigma_o \left[1 - d\,\frac{\varepsilon_o}{kT}\right]^{\frac{1}{d}}$$

Systems where the logarithm of conductivity as a function of temperature presents a positive curvature have a negative d parameter (d<0) and systems with negative curvature have a positive d parameter (d>0), group in which ionic liquids are inserted.

Support: CAPES, CNPq

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A Theoretical Investigation of Electronic Properties of (E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one including Environment Polarization Effects

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Key-words: Environment Polarization Effects, Electronic Properties, *ab initio*.

In chemistry the chalcones consist of open-chain flavonoids in which the two aromatic rings are joined by a three-carbon α,β-unsaturated carbonyl system, or can be easily obtained from the aldol condensation of aromatic aldehydes and aromatic ketones. In this work the dipole moment, the linear polarizability and the second hyperpolarizability of asymmetric unit of (E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one crystal were calculated using a hybrid procedure between the supermolecule approach and an interactive electrostatic polarization scheme where the environment polarization effects are attained by ensuring the convergence of this properties in the polarization field of surrounding molecules whose atomic sites are treated as point charges. The interactive procedure was performed considering the atomic sites of the closest 342 asymmetric units as point charges. So, the simulation was developed using a cluster of 7x7x7 unit cells, each unit cell containing only one asymmetric unit. Our results show that in the presence of the embedding charges, the value of dipole moment is increased by 14% while the static values of linear polarizability is decreased by 7% as compared with the isolated situation. All calculation where performed at B3LYP/6-31++G** using the Gaussian 09 suite of programs.

Support: CAPES, CNPq, FINATEC.

The strength of the residues interactions for the iGlur2 dimers formation in the apo and Glutamate binded forms

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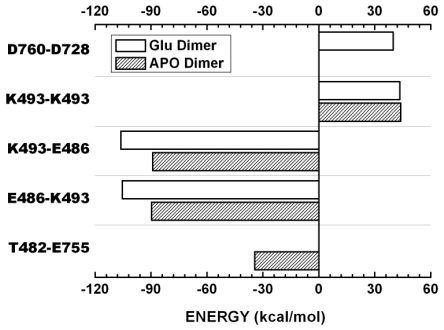
Key-words: GluR2, glutamate, dimer formation, quantum biochemistry

Ionotropic glutamate receptors (iGluR) are important excitatory neurotransmitter receptors in the mammalian central nervous system that have been implicated in a number of neuropathologies such as epilepsy, ischemia, and amyotrophic lateral sclerosis. The tetrameric iGluR includes NMDA, AMPA and kainate subtypes and may provide insight into the mechanisms of synaptic plasticity that underlie learning and memory[1]. The crystal structures of the GluR2 ligand-binding core of the AMPA subtype have been particularly useful in providing initial insights into the conformational changes in the ligand binding domain; however, these structures are limited by crystallographic constraints[2]. The high-resolution data of the structure of the glutamate-binding (S1S2) domain have led to suggestions as to the control of channel gating and desensitization, as well as to the interaction between the involved dimers. This work aims to investigate by quantum biochemistry the influence of glutamate into the binding site on the dimeric interaction domains. Taking full advantage of published crystallographic data, we perform quantum biochemistry calculations within the density functional theory approach and the molecular fractionation with conjugate caps (MFCC) strategy[3] using the local density approximation LDA-PWC and basis 4.4 DNP to calculate the interaction between monomers and dimers. Pairs of residues were chosen with distances up to 5 Å, and the calculations were performed for both dimers considering the Apo state and the co-crystallization with the ligand. As expected, the interaction between the dimers was greater when the ligand was present, but the results showed very close interaction energies (-393.62 kcal/mol and -391.11 kcal/mol for apo state and bound to glutamate, respectively). The BIRD panel shows the interaction energy between the four main pair of amino acid residues contributing the dimer formation.



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Determinação da barreira de rotação da N-metilformamida

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Key-words: N-metilformamida, ab initio, barreira de rotação

A N-metilformamida é amplamente utilizada como solvente polar em várias aplicações da Química Orgânica. Por possuir uma estrutura O=C-NH, representa um modelo simplificado de ligação peptídica, presente em várias biomoléculas. O caminho para o entendimento de sua estabilização passa pela compreensão de ligações fracas de hidrogênio, sendo que estas são de grande importância para sistemas biológicos. Pretende-se determinar a barreira de rotação em torno da ligação N-C para melhor entender sua preferência conformacional, bem como determinar uma expressão analítica que represente esta rotação a fim de ser usada em simulação computacional de líquido. Para tanto, efetuaram-se cálculos de estrutura eletrônica *ab initio* em cada conformação determinada pelo ângulo da ligação N-C. Empregou-se o método *Hartree-Fock* e as bases *6-311G* e *aug-cc-PV5Z*. Esses cálculos foram realizados com o programa *Gaussian 03*. Preliminarmente, analisando o sistema em termos das eletronegatividades dos átomos, espera-se que a conformação *cis* seja a preferencial. Observou-se, porém, a conformação *trans* (figura 1) é a mais estável. Já estão em andamento cálculos empregando Teoria de Perturbação (MP2) e multiconfiguracional (QCISD). Os resultados obtidos permitirão uma análise mais profunda das interações existentes nessa molécula e a razão da maior estabilidade do confôrmero trans.

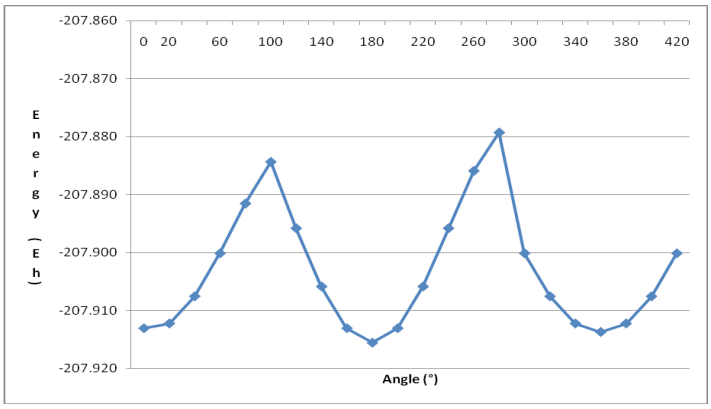

Figura 1 – Barreira de rotação: RHF/aug-cc-PV5Z (cis: 0° e trans: 180°)

Suporte: CNPq.

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