XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Photophysics and Thermoquemistry of 1-8-Naphthalimide in solvents

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Abstract: In the scope of a Sequential QM-MM approximation [1], we investigated the solvent effect on the conformational and electronic structure of 1-8-Naphthalimide in both ground and excited states. We obtained the optimized structure of 1-8-Naphthalimide in acetonitrile, ethanol and water, in ground and in the first excited state. Then we computed the absorption and fluorescence spectra using CASPT2 and TD-DFT approximations. Our absorption results show a solvatocromic deviation of the first absorption band from acetonitrile (331nm) to water phase (343nm) of 12 nm, that is in good agreement with experimental results [2]. In the excited state we tested two different hypothesis for the lifetime of the excitation: (a) a short lifetime, when the solute goes to excited state and the solvent does not have time to relax; (b) a long lifetime, when solute and solvent are both relaxed in the excited state. We found a good agreement between the computed emission energies and experimental results in the first hypothesis for acetonitrile and ethanol, and in the second hypothesis for water. This is reasonable since it was recently revealed by experimentalists [2] that the excited state of 1-8-Naphthalimide has a short lifetime in acetonitrile and ethanol, and a long lifetime in water (2.3ps). Especially in water, it is found in literature an interesting contradiction. Manna A. and Chakravorti S. (2009) [2] disagreed from Samanta et al. (1996) [3] about the protonation state of 1-8-Naphthalimide. Both are experimental results, and there is no theoretical study about this case in literature. In this context we also studied the unprotonated form of 1-8-Naphthalimide in water. From theoretical spectroscopy we found that is not possible to differentiate between neutral and unprotonated form, both has similar absorption and emission spectra. Otherwise we calculate the standard deprotonation free energy of 1-8-Naphthalimide in water and the pKa in ground and first excited states, with Free Energy Perturbation theory in Monte Carlo simulations. We obtained a pKa=9.17±1.0Kcal/mol for ground state and pka=-3.84±1.4Kcal/mol for excited state. This means that 1-8-Naphthalimide is probably neutral in ground state and unprotonated in first excited state. Now we are doing some spectroscopic experiments in different ph to validate our theoretical results. All quantum mechanics calculations was carried out in Molcas 8.0 and Gaussian g09, and the Monte Carlo simulations was performed in Dice program [4].

Key-words: 1-8-Naphthalimide, Photophysics, Thermoquemistry, QM/MM.

Support: This work has been supported by CAPES agency.

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