

Theoretical description of the absorption spectra of solid and liquid benzene

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Abstract

A combination of Monte Carlo simulation and INDO-CI techniques is suggested for the calculation of the absorption spectra of molecular systems in the condensed phase. The $\pi-\pi^*$ states of benzene are selected as appropriate working examples. For benzene the crystalline structure is given and the UV spectrum is calculated directly via a large INDO-CI calculation involving 14 benzene molecules ordered in an orthorhombic face-centred structure. For benzene in the liquid phase five structures are selected after a Lennard-Jones Monte Carlo simulation using 125 benzene molecules. To analyse spectral shifts the same number of benzene molecules in the solid phase are used for the INDO-CI calculation of the UV spectrum of the liquid.

The calculated spectra contain all the essential features of the experimentally observed spectra and good agreement is also obtained for the spectral shifts corresponding to benzene in the gas, solid and liquid phases. Singlet and triplet states are considered.

Introduction

The theoretical investigation of molecular clusters and molecular systems in the condensed phase is a topic of considerable importance and interest [1]. In recent years an increased necessity has been felt for well defined theoretical tools for investigating the properties of crystalline and disordered molecular systems in general [2,3]. The basic strategy for theoretical calculations of small isolated molecules has been laid down and includes sophisticated schemes at both the ab initio and semiempirical levels [4]. For disordered systems, however, the situation is somewhat undefined.

Molecular systems in the condensed phase may be conveniently divided into two categories. The first includes solid systems with well defined structural parameters. Given these parameters, the solid structure can be obtained in an unambiguous and

clear way. In the second category one finds the disordered systems for which the very definition of a single structure is not possible. Many structures or configurational arrangements are in fact equally possible.

Specifically, for the theoretical calculation of the electronic absorption spectra of homogeneous molecular systems in the condensed phase, two basic points must be considered. First, it is necessary to have an efficient quantum mechanical theoretical scheme for handling both the ground and excited states of a very large system, or a large quantity of similar systems. Typically, from a quantum chemistry point of view this calls for a semiempirical procedure able to handle, say 300–500 atoms. The second basic point is particularly important for liquids or disordered systems in general, and it refers to the determination of the structure of the system. A properly defined statistical procedure is necessary in this case [5].

In this paper we present a simple scheme for the

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calculation of molecular systems in the condensed phase. For liquids it essentially amounts to a Monte Carlo simulation followed by quantum mechanical calculation of the absorption spectrum. As our working example we have chosen condensed phase benzene.

Solid benzene has a crystalline structure which was determined some years ago [6–8] and exemplifies systems in the above-mentioned first category. Liquid benzene, however, is studied as a disordered system (the second category above) for which the definition of one single structure or molecular arrangement may not be possible. The UV absorption spectrum of benzene has been recorded many times so this selection for our first theoretical incursion seems very appropriate. It may be added to this that the corresponding π – π^* spectrum of benzene in the gas phase is one of the best known and best assigned molecular UV spectra [9–14]. Our aim in this paper is thus to theoretically describe these well known π – π^* states of gas phase benzene as they appear in the condensed phase; the well known ${}^1B_{2u}$, ${}^1B_{1u}$ and ${}^1E_{1u}$ π – π^* states obtained from the HOMO–LUMO $e_{1g}(\pi) \rightarrow e_{2u}(\pi^*)$ transition. Another attempt to describe the absorption spectrum of liquid benzene has recently been made using an effective hamiltonian for a single benzene molecule [15].

Theoretical approach

All the calculations presented in this paper were made using the INDO-CI method developed by Zerner and co-workers [16], with the original spectroscopic parameterization for benzene [16]. The two-centre coulomb integrals are calculated using the Mataga–Nishimoto expression and the two-centre resonance integrals depend on the scaling factors f_σ and f_π [16]. In this paper we adopt the original $f_\sigma = 1.267$ with $f_\pi = 0.585$ for singlets and 0.720 for triplets. The program we adapted for this project is restricted to CI with a closed-shell reference state and handles efficiently up to about 400 atoms in a given geometry. In the case

of solid benzene the crystalline structure is known [6–8] and therefore the spectrum can be calculated directly. For the case of liquid benzene — as for disordered systems in general — this is not the case and it becomes necessary to theoretically obtain the liquid structure. Therefore, the quantum mechanical calculations are preceded by a Monte Carlo simulation [5].

The experimental structures for solid benzene from X-ray diffraction have suggested three possible orthorhombic face-centred configurations with a *Pbca* space group. There are four benzene molecules per unit cell and a total of 14 benzene molecules are necessary to characterize the solid, corresponding to six benzene molecules face-centred and eight benzene molecules in the vertices. As we shall see, the general absorption band shape varies little from one possible structure to another in the case of solid benzene.

The structure for liquid benzene was studied by Narten [17]. Analysis of the radial correlation function in this study indicates that in the liquid phase each individual benzene molecule is little affected, preserving planarity and essentially the same bond lengths as in the gas phase. We have thus simulated liquid benzene with a total of 125 benzene molecules with intermolecular Lennard–Jones parameters obtained from Evans and Watts [18]. Each benzene molecule is rigid at the equilibrium geometry but all molecules are allowed to translate and rotate. Contrary to Evans and Watts, our simulation does not start from the solid configuration but from a random distribution of molecules in the bulk. The Monte Carlo simulation was performed using the periodic boundary conditions in the NVT ensemble with $N = 125$, (compatible with the density of benzene) and $\rho = 0.899 \text{ g cm}^{-3}$ at $T = 298 \text{ K}$. The calculated C–C radial correlation function is similar to the experimental value given by Katzoff [19]. After thermalization was obtained with 1000 Monte Carlo steps, various structures containing 125 molecules of benzene were sampled. In total, 15 of these structures — one after every 100 steps — were first selected. Each Monte Carlo step corresponds to a motion of all

molecules. Because 125 molecules of benzene is too large a system for quantum mechanical calculation of the spectrum and for obtaining the spectral shifts in a non-biased manner, the same number of benzene molecules in the solid system was used for the liquid. Thus only a portion of the fluid was considered and 14 benzene molecules were then chosen out of the 125 molecules. These were obtained by selecting at random one molecule out of the 125 and then choosing the 13 nearest neighbours.

This selection was made in all 15 structures, giving 15 reduced structures with 14 benzene molecules each. All 15 reduced structures were then used in a SCF INDO calculation and those five with the lowest SCF energies were preferred. These five final preferred structures with 14 molecules each were used for the calculation of the spectrum.

For the calculation and assignment of the UV spectrum of a large system in general it is neither possible nor desirable to make a state-to-state analysis, owing to the very large number of states generated lying very close in energy. Rather, it is better to obtain the band profile. Therefore, in comparing the corresponding theoretical results we show only the resulting calculated absorption spectra.

The calculated band profiles were obtained as follows: after a SCF calculation, the excited states were generated via a single-excited CI. This gave the excited energy and the corresponding oscillator strength, calculated here in the length form. In total, as many as 784 excited configurations were generated. The band profile was finally obtained by convoluting lorentzians with a FWHM of 1000 cm^{-1} .

This general procedure is the same as that we adopted in a previous paper on polycyclic aromatic hydrocarbons [20]. The size of the calculation is, however, much larger in the present case, particularly with respect to the number of CI states generated. This is found here to be necessary, however, to properly describe the ${}^1\text{B}_{2u}$, ${}^1\text{B}_{1u}$ and ${}^1\text{E}_{1u}\pi-\pi^*$ bands of the “supermolecule”.

Results and discussion

The calculated states of benzene in the gas phase are located at $37\,800$, $48\,800$ and $55\,400\text{ cm}^{-1}$, corresponding to ${}^1\text{B}_{2u}$, ${}^1\text{B}_{1u}$ and ${}^1\text{E}_{1u}$, respectively, in excellent agreement with the experimental values of $38\,100$, $48\,600$ and $55\,400\text{ cm}^{-1}$ [14].

Let us now consider the case of solid benzene. In Fig. 1 we show the calculated spectra for solid benzene at -3°C , using the two experimental structures. The “forbidden” B_{2u} and B_{1u} states now have some intensity induced by the crystalline field. In molecular language, the benzene system has lowered its symmetry from D_{6h} and these forbidden states now become allowed with small intensities. The two spectra obtained from the two structures are very similar and they clearly show the same spectral features as for benzene in the gas phase but with the expected band shifts. A clear analysis of the spectrum of solid benzene has been made by Brith et al. [21] among others. All the singlet $\pi-\pi^*$ transitions are red shifted compared to the gas phase. This aspect is nicely obtained in our calculated spectra. The shift is only slight for the ${}^1\text{B}_{2u}$ and more pronounced for the intense ${}^1\text{E}_{1u}$ state, in agreement with the experimental result [21]. It is important to note that the observed shift in absorption spectroscopy is dependent on the experimental resolution. For solid benzene the bands are also broadened by intermolecular interaction and the spectrum is composed of many individual lines, which makes a direct comparison with the theoretical calculations of transition energies more difficult. If one considers the maximum of each band, then the gas–solid red shifts are calculated to be about 400 , 1000 and 2000 cm^{-1} for the B_{2u} , B_{1u} and E_{1u} bands, respectively, compared to the corresponding shifts of 300 , 3000 and 4900 cm^{-1} obtained experimentally. Overall, the calculated absorption spectrum of benzene describes all the essential features of the observed spectrum.

Now we turn to the liquid benzene case. The UV absorption spectrum of liquid benzene has been recorded by many investigators. A comprehensive

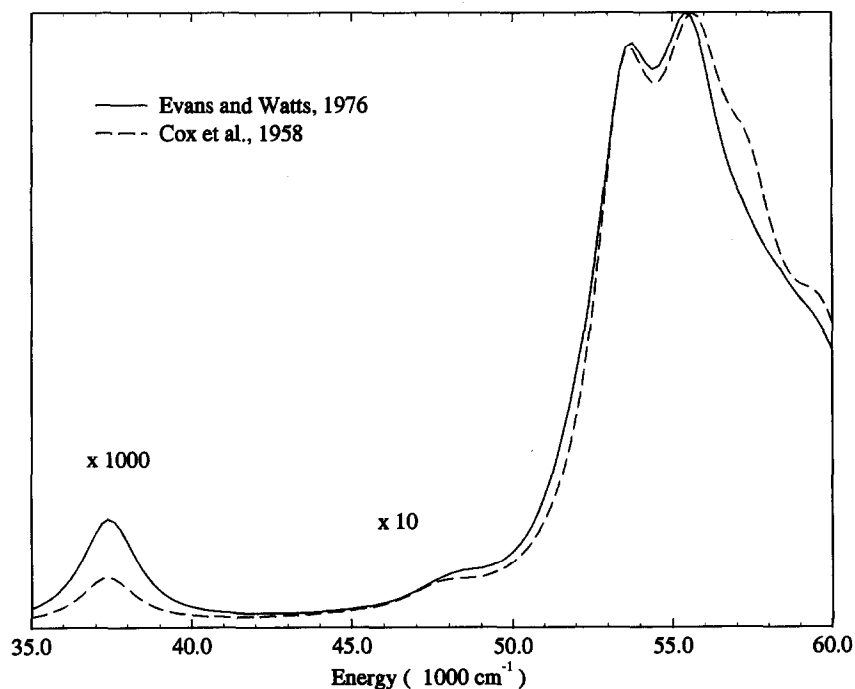


Fig. 1. The calculated UV spectrum of solid benzene at 270 K. Two crystalline structures are used (see text). The first and second bands have their intensities multiplied by 1000 and 10, respectively.

detailed analysis is presented by Inagaki [22]. Again, three absorption systems are clearly identified. The first system comprises a broad absorption system ranging from 37 000 to 44 000 cm^{-1} and corresponds to the first singlet transition, the B_{2u} band. The vibrational structure that characterizes this band system in the gas phase is still discernible even in the liquid phase. The second spectral feature corresponds to the B_{1u} band system, observed as a broad band starting at 46 500 cm^{-1} with diffuse structure, and at about 50 000 cm^{-1} it merges with the most intense E_{1u} band, which has then a maximum at about 53 000 cm^{-1} .

For the calculation of the UV spectrum of liquid benzene five structures were selected, as described in the previous section. For this disordered system one single configuration is not justifiable and more configurations are necessary. Figure 2 shows the calculated spectrum at a temperature of 25°C. As can be seen, each particular selected structure contributes in a different manner to the resultant spectrum. This makes the calculated resultant

spectrum a very rich one with many contributions, and increasing the number of configurations smooths the spectrum and spreads it in frequency. The first thing to be noted in the calculated spectrum is an increase in the intensities of the B_{2u} and B_{1u} bands of the liquid as compared to the solid phase. This is a consequence of the natural disorder of the liquid and the absence of short range symmetry. The gross shape of the spectrum is very similar to the solid phase and again all three bands are clearly discernible. For clarity, the resultant absorption spectrum calculated for the liquid phase is shown, together with the corresponding spectra in the solid and gas phases, in Fig. 3. In agreement with experiment [22] the solid–liquid shift is to the blue side for the intense $^1E_{1u}$ band and to the red for the lowest $^1B_{2u}$ band. The $^1B_{2u}$ in the liquid is also red-shifted compared to the gas phase. The calculated B_{1u} band of the liquid phase is found to range between 42 000 and 50 000 cm^{-1} , where the intense E_{1u} band starts, and shows two maxima in the spectra (Fig. 3). Whereas

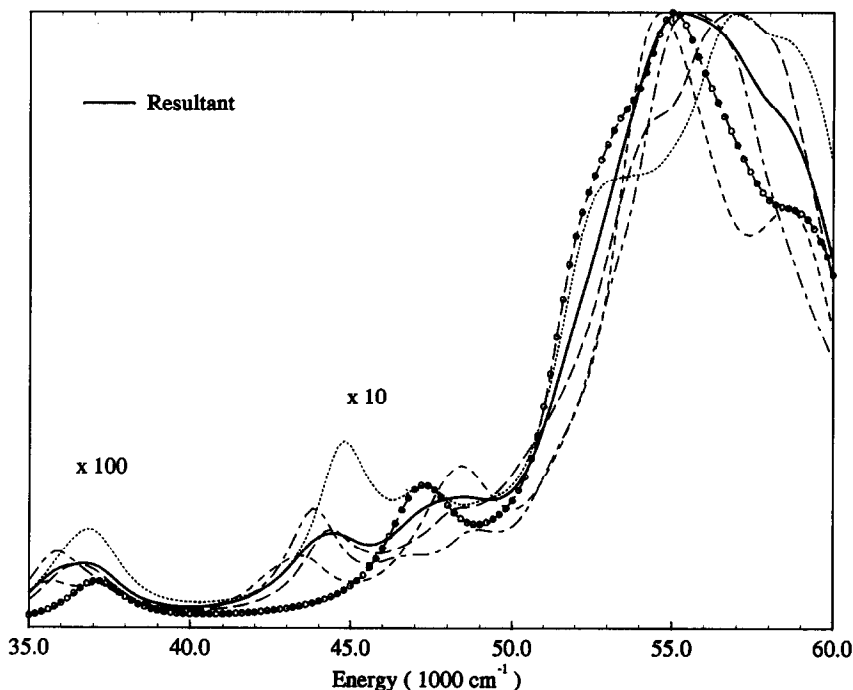


Fig. 2. The calculated UV spectrum of liquid benzene at 298 K. Five structures selected after the Monte Carlo simulation (see text) are used. The first and second bands have their intensities multiplied by 100 and 10, respectively.

the experimental spectrum locates the liquid B_{1u} band slightly at the blue side of the corresponding band in the solid phase, our calculations put it slightly to the red. This is, however, such a broad band both in the theoretical and experimental spectra that a direct comparison is more difficult. However, as can be seen in Fig. 2, the B_{1u} band of the liquid phase is the one which shows the strongest dependence on the structure. It is thus reasonable to expect that perhaps five structures are not enough to give the overall spectral shape for this band. The other two bands are better “converged”. In fact for a general description of the liquid state many configurations may be necessary to reach convergence in the calculated resultant spectrum. In practice, different bands will require different numbers of configurations. The selection of configurations in this study was made by arbitrarily removing sample structures after thermalization of the Monte Carlo simulation.

The calculated B_{1u} band in the solid is pretty narrow compared to the liquid. Whereas for the solid phase it ranges from 47 500 to 48 500 cm^{-1} including many zero-intensity states, in the liquid phase this band is very wide, ranging from 42 000 to 50 000 cm^{-1} . Thus, in going from the solid to the liquid phase the upper edge of the band shifts to the blue and the lower edge shifts to the red side. Again, this exemplifies the difficulty of making a theoretical analysis of spectral shifts associated with very broad bands and low resolution spectra. Experimentally, in both phases the B_{1u} band starts at about 46 500 cm^{-1} and ranges to about 50 000 cm^{-1} but includes, of course, vibronic contributions.

The description of triplet states is essential for interpreting the phosphorescence spectrum. Along the same line of reasoning as for the singlet states, the triplet states of benzene for both the solid and liquid phases were also considered in

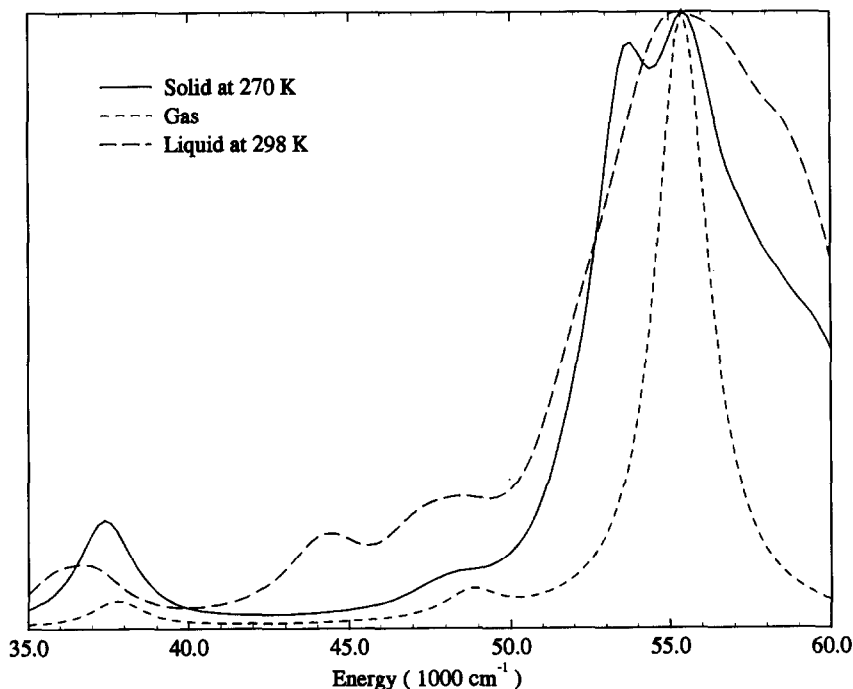


Fig. 3. Comparison of the calculated absorption spectra of benzene in the solid, liquid and gas phases. For the gas phase, artificial intensities are given in the first two bands to help locate these states because they are forbidden by dipole-induced transition from the ground state and have no calculated intensities. The spectral shifts corresponding to the different phases are clearly illustrated.

our investigation. The optical observation of triplet states in general is extremely difficult because singlet–triplet transitions are formally forbidden and absorptions are thus very weak. Hence, the transitions from the ground state to the ${}^3B_{2u}$ and ${}^3B_{1u}$ states of benzene, in particular, are forbidden by both spin and spatial symmetry and their observation by optical methods is very weak [23]. In contrast to optical absorption methods the triplet states of benzene can be observed in the electron-impact spectrum. Doering [24] and Wilden and Comer [25] have recorded the triplet π – π^* states of gas phase benzene and given a comprehensive interpretation. The lowest π – π^* triplet state is observed at $31\,300\text{ cm}^{-1}$ and assigned to the ${}^3B_{1u}$ state. The second triplet is assigned to the ${}^3E_{1u}$ observed at $38\,100\text{ cm}^{-1}$. The triplet state corresponding to the lowest B_{2u} singlet is observed as the third triplet state at $45\,800\text{ cm}^{-1}$ and well above the corresponding singlet.

For the triplet states in gas phase we obtained these three states at $31\,200$, $38\,700$ and $46\,300\text{ cm}^{-1}$ in very good numerical agreement with the experimental values. Similar to the singlet case, the triplet states for the solid and liquid phases were also calculated and the results are shown in Fig. 4. Only one structure [6] is used for the solid and two statistically chosen structures are used for the liquid, which are those with the lowest INDO-SCF energy. Because calculated triplet states have no optical intensity from the singlet ground state (the calculated oscillator strength for the non-relativistic hamiltonian are all zero) all intensities are formally zero. The calculated results depict only the location of the excited triplet states and show the broadening of the excited states. We are not able to find any systematic analysis of the triplet states of benzene in the condensed phase. The calculated results shown in Fig. 4 indicate a clear tendency of shifting to lower energies in going from gas to solid and solid

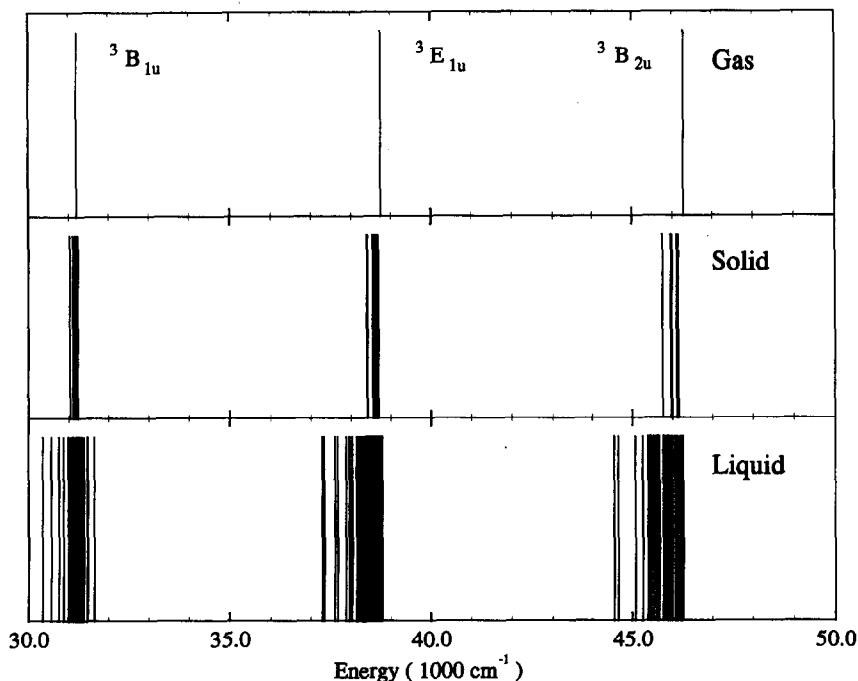


Fig. 4. Comparison of the location of the calculated triplet states of benzene in the gas, solid and liquid phases.

to liquid for the E_{1u} and B_{2u} states. For the first triplet B_{1u} we calculated a higher density of states in the high energy side for the liquid phase compared to the solid phase.

Conclusions

In this paper we have adopted a combination of Monte Carlo simulation and INDO-CI techniques for the calculation of the absorption spectra of liquid systems. This approach is tested for benzene in the condensed phase. For solid benzene the crystal structure is known and the spectrum can be calculated directly via INDO-CI. For liquid benzene we adopt a strategy to be used in disordered systems and simulate the structure with the Monte Carlo method. The calculated results for the spectra of benzene in the condensed phase contain all the essential features of the experimentally observed spectra.

Encouraged by these results we are now studying

the absorption spectra of heterogeneous liquids and, in particular, molecules diluted in several solvents.

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References

- 1 G Scoles (Ed.), *The Chemical Physics of Atomic and Molecular Clusters*, North-Holland, Amsterdam, 1990.
E.R. Bernstein (Ed.), *Atomic and Molecular Clusters*, Elsevier, Amsterdam, 1990.
I. Prigogine and S.A. Rice (Eds.), *Evolution of Size Effects in Chemical Dynamics*, *Advances in Chemical Physics*, Vol. 70, 1988, Parts 1 and 2.
J Jortner, A. Pullman and B. Pullman (Eds.), *Large Finite System*, Reidel, Dordrecht, 1987.
- 2 R.O. Jones and O. Gunnarson, *Rev. Mod. Phys.*, 61 (1989) 689.
A.D. Becke, *Int J. Quantum Chem., Symp.*, 23 (1989) 599.

- R. Car and M. Parrinello, *Phys. Rev. Lett.*, 55 (1985) 2471.
J. Almlöf, K. Faegri and K. Korsell, *J. Comput. Chem.*, 3 (1982) 385.
- 3 W.F. van Gunsteren and P.K. Weiner (Eds.), *Computer Simulation of Biomolecular Systems*, Leiden, 1989.
C.R.A. Catlow, S.C. Parker and M.P. Allen (Eds.), *Computer Modeling of Fluids Polymers and Solids*, Kluwer, Dordrecht, 1990.
- 4 C. Dykstra (Ed.), *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*, Reidel, Dordrecht, 1984.
J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry*, Academic Press, New York, 1973.
P. Jorgensen and J. Simons, *Second Quantization - Based Methods in Quantum Chemistry*, Academic Press, New York, (1981); *Int. J. Quantum Chem.* (1990).
- 5 M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon, Oxford, 1987.
- 6 E.G. Cox, D.W.J. Cruickshank and J.A.S. Smith, *Proc. R. Soc. London, Ser. A*, 247 (1958) 1.
- 7 D.J. Evans and R.O. Watts, *Mol. Phys.*, 31 (1976) 83.
- 8 E.G. Cox, *Proc. R. Soc. London, Ser. A*, 135 (1932) 491.
- 9 J. Philis, E. Pantos, G. Andritsopoulos, A. Bolovinos and A. Ioannidou, *Chem. Phys. Lett.*, 77 (1981) 623.
J. Philis, A. Bolovinos, G. Andritsopoulos, E. Pantos and T.D.S. Hamilton, *Chem. Phys. Lett.*, 77 (1981) 627.
J.P. Doering, *J. Chem. Phys.*, 71 (1979) 20.
R.P. Frueholz, W.P. Flicker, O.A. Mosher and A. Kuppermann, *J. Chem. Phys.*, 70 (1979) 3057.
R.L. Whetten, K.-J. Fu and E.R. Grant, *J. Chem. Phys.*, 79 (1983) 2626.
P.M. Johnson, *J. Chem. Phys.*, 62 (1975) 4562.
R.L. Whetten, S.G. Grubb, C.E. Otis, A.C. Albrecht and E.R. Grant, *J. Chem. Phys.*, 82 (1985) 1115.
N. Nakashima, M. Sumitami, I. Ohmine and K. Yoshihara, *J. Chem. Phys.*, 72 (1980) 2226.
- 10 J.M.O. Matos, B.O. Roos and P.-A. Malmqvist, *J. Chem. Phys.*, 86 (1987) 1458.
S. Kato, *J. Chem. Phys.*, 88 (1988) 3045.
- 11 G. Herzberg, *Electronic spectra and electronic structure of polyatomic molecules*, *Molecular Spectra and Molecular Structure*, Vol 3, Van Nostrand Reinhold, Princeton, NJ, 1966.
- 12 T.M. Dunn, The spectrum and structure of benzene, in J.H. Ridd (Ed.), *Studies on Chemical Structure and Reactivity*, Methuen, London, 1966.
- 13 M.B. Robin, *Higher Excited States of Polyatomic Molecules*, Vol 2, Academic Press, New York, 1975.
- 14 J. Philis, A. Bolovinos, G. Andritsopoulos, E. Pantos and P. Tsekeris, *J. Phys. B*, 14 (1981) 3621.
A. Bolovinos, P. Tsekeris, J. Philis, E. Pantos and G. Andritsopoulos, *J. Mol. Spectrosc.*, 103 (1984) 240.
S. Canuto, *Acta Sud. Am. Quim.*, 6 (1986) 47.
- 15 M. Fernandez, J. Tortajada and L.M. Sesé, *Z. Phys. D*, 9 (1988) 243.
- 16 J.E. Ridley and M.C. Zerner, *Theor. Chim. Acta*, 32 (1973) 111; 42 (1976) 223.
M.C. Zerner, G.H. Lowe, R. Kirchner and U.T. Müller-Westerhoff, *J. Am. Chem. Soc.*, 102 (1980) 589.
- 17 A.H. Narten, *J. Chem. Phys.*, 48 (1968) 1630.
- 18 D.J. Evans and R.O. Watts, *Mol. Phys.*, 32 (1976) 93.
- 19 S. Katzoff, *J. Chem. Phys.*, 2 (1934) 841.
- 20 S. Canuto, M.C. Zerner and G.H.F. Diercksen, *Astrophys. J.*, 377 (1991) 150.
- 21 M. Brith, R. Lubart and I.T. Steinberger, *J. Chem. Phys.*, 54 (1971) 5104.
- 22 T. Inagaki, *J. Chem. Phys.*, 57 (1972) 2526.
- 23 A.L. Sklar, *J. Chem. Phys.*, 5 (1937) 669.
S.D. Colson and E.R. Bernstein, *J. Chem. Phys.*, 43 (1965) 2661.
G.W. King and E.H. Pinnington, *J. Mol. Spectrosc.*, 15 (1965) 384.
J. Metcalfe, M.G. Rockley and D. Phillips, *J. Chem. Soc., Faraday Trans. 2*, 70 (1974) 1660.
- 24 J.P. Doering, *J. Chem. Phys.*, 51 (1969) 2866; 67 (1977) 4065.
- 25 D.G. Wilden and J. Comer, *J. Phys. B*, 13 (1980) 627.