The Use of the Point Charge Model in the Evaluation of Spectral Shifts within the INDO/CIS Approximation

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The point charge model incorporated into the intermediate neglect of differential overlap – configuration interaction singles scheme (INDO/CIS) has been used to calculate spectral shifts in aromatic systems due to intermolecular interactions. The arrangement of the solvent molecules around the central molecule was obtained using the simulated annealing method based on a classical potential energy surface. This method of evaluating the spectral shifts, using the same values for the point charges as used in the solute–solvent simulation where the solute is in its ground state, has been shown to be unreliable when applied to simple Van der Waals systems.

Intermolecular spectroscopy has received much attention in both experimental and theoretical studies recently.[1,2] The effect of small clusters of molecules or a solvent medium on the electronic spectrum of a central molecule, usually referred to as a solute, is important in estimating the dipole moment and polarizabilities of the solute in its excited states.[3] A knowledge of these molecular properties is useful in the design of materials which possess desired non-linear optical properties.

In order to study the effects of molecular environment on the electronic spectrum of a solute using quantum chemical methods, a model which describes the specific interactions of the surrounding molecules with the central molecule has to be chosen. Reaction field techniques are partially useful as the approximation of the solvent as a continuum dielectric and the treatment of the solute as a point dipole at the centre of a sphere or ellipsoid neglects the molecular nature of the solvent and solute. In the point charge model, the atoms of the solvent molecules are treated as point charges located on these atoms and it is this model that is used here to describe the solute–solvent interactions.

In this paper, the shifts in the electronic spectrum of benzene, phenol, pyrimidine and pyrazine due to small clusters of molecules that surround the central molecule have been evaluated using the intermediate neglect of differential overlap (INDO) Hamiltonian[4,5] for the solute, and the point charge model for the solvent clusters. The choice of this model Hamiltonian was dictated by its remarkable success in evaluating the electronic spectra of conjugated systems which has been recorded extensively in the literature.

The solvent molecules studied are H_2O, NH_3 and CH_4 and their arrangement around the solute was calculated using the simulated annealing method[6,7] based on the metropolis Monte Carlo algorithm.[8]

The theory used in the simulation and the evaluation of the spectral shifts are outlined in the following section with the results and discussion presented in the last section.

Theory

The Fraga potential[9] incorporated into the simulated annealing method has been shown to be successful in predicting intermolecular interaction energies and relative orientations of molecules in clusters.[10] It is this approach that has been used here to obtain the structures of the solute–solvent complexes. The geometries of the subsystems were taken from experimental data and were kept fixed in all the calculations reported. According to the Fraga potential, the energy of interaction ΔE between two molecules A and B may be calculated using eqn. (1), where the summation indices (a,b) are over the classes

$$\Delta E = \sum_{a,b}(q_a q_b/R_{ab} - \tfrac{1}{2}[f_a\alpha_a q_b^2 + f_b\alpha_b q_a^2]/R_{ab}^4 - \tfrac{3}{2}\{f_a f_b\alpha_a\alpha_b/[(f_a\alpha_a/n_a)^{\frac{1}{2}} + (f_b\alpha_b/n_b)^{\frac{1}{2}}]R_{ab}^6\} + g_a g_b/R_{ab}^{12}) \quad (1)$$

to which the atoms in the interacting systems A and B, respectively, have been assigned. The definition of the classes, values for the electronic charge q_x, the static polarizability α_x, the effective number of electrons n_x, and the parameters f_x and g_x for an atom belonging to class x, $(x = a,b)$, have been tabulated in detail in ref. 9.

The annealing search algorithm was repeated for various values of the translational displacement step size and, for each value of this displacement, the number of moves allowed for each annealing step was also varied. This was done so as to ensure that the structure evaluated for the cluster will correspond to the global minimum of the solute–solvent complex. In the simulation of clusters with more than one solvent molecule, all of the surrounding molecules were allowed to move according to the algorithm.[10]

The Hamiltonian H_1 of the solute molecule in the presence of the solvent cluster simulated as a set of M point charges $\{q_1, q_2, \ldots q_M\}$ is given by eqn. (2) where H_0 is the solute gas

$$H_i = H_0 - \frac{1}{2}\sum_i^M \sum_{j\in\text{solute}} q_i/r_{ij} + \sum_i^M \sum_{A\in\text{solute}} q_i Z_A/r_{iA} - \frac{1}{2}\sum_{i,j=1}^{M} q_i q_j/r_{ij} \quad (2)$$

phase Hamiltonian within the INDO approximation, the q_is are the point charges assigned to the solvent atoms and Z_A is the nuclear charge of atom A belonging to the solute. The second and third terms on the right-hand side of eqn. (2) correspond to the interaction between electron j of the solute molecule and the point charge q_i and the attraction of the point charges by the nuclei of the solute respectively. The last term is the point charge – solute nuclei interaction. The values for the point charges $\{q_i\}$ in the above equation are the same as that used in the simulation.[9]

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Table 1 Shifts in the π–π^* transitions for phenol–$(H_2O)_n$, n = 1, 2, 3, 5

n	Calculated shift/ cm^{-1}	Experimental shift/ cm^{-1} (ref. 12)
1	−123	−356
2	−225	−93
3	−196	−89
5	−99	

Table 2 Calculated and experimental shifts for benzene with H_2O and NH_3

System	Calculated shift/ cm^{-1}	Experimental shift/ cm^{-1} (ref. 14)
Benzene–H_2O	0	49
Benzene–NH_3	0	±20

Table 3 Shifts in the n–π^* transition peaks for pyrazine with NH_3 and methane

System	Calculated shift/ cm^{-1}	Experimental shift/ cm^{-1} (ref. 15)
Pyrazine–NH_3	−15	117
Pyrazine–CH_4	−7	−32
Pyrazine–$(CH_4)_2$	−9	−38
Pyrazine–$(CH_4)_3$	−21	−70

Table 4 Shifts in the n–π^* transition peaks for pyrimidine with NH_3 and methane

System	Calculated shift/ cm^{-1}	Experimental shift/ cm^{-1} (ref. 13)
Pyrimidine–NH_3	225	285
Pyrimidine–CH_4	33	−57
Pyrimidine–$(CH_4)_2$ (iso)	75	−112
Pyrimidine–$(CH_4)_2$ (aniso)	31	−47

The modification of the one electron part of the gas phase Hamiltonian of the solute can be calculated as the penetration of the point charges into the atomic cores of the solute nuclei. It is this method, that is, the change in H_0 due to the penetration integrals evaluated within the INDO scheme, that is used in the calculations reported here.

The configuration interaction – singles (CIS) procedure has been recently shown to be a successful way to evaluate the spectral transitions in a series of molecules.[11] The spectra of the solute molecules in the gas phase were evaluated using the CIS method. For the solvated molecule, the CIS procedure was repeated with the Hamiltonian as defined in eqn. (2) and the spectrum calculated. In each calculation, the largest possible active space was used to describe the single excitations. From the results of these two calculations, the shift in the spectrum due to the solvent molecule(s) was evaluated.

Results and Discussion

The results of the calculations are presented in Tables 1–4. The spectral shifts in each case have been evaluated with reference to the corresponding gas phase transitions. For the phenol–$(H_2O)_n$, n = 1,2,3,5, systems, multiphoton spectroscopy (MPS)[12] shows a red shift in the lowest π–π^* band of phenol when hydrated by one water molecule. This is due to the proton donor property of the phenol resulting in the formation of the phenolate ion. Further hydration by another molecule causes a blue shift, with respect to the lowest band of the phenol–water complex. In this case, the second water molecule stabilises the phenolate ion resulting in the observed shift as verified by Kasha.[13]

The calculated spectral shifts show that two water molecules are necessary for the formation of the phenolate ion which is then stabilised by the third water molecule. It is therefore expected that two water molecules will behave as proton acceptors towards the phenol.

MPS studies of the interaction of benzene and diaza compounds with small molecules such as H_2O, NH_3 and CH_4 have been reported in the literature.[14–16] In the case of benzene interacting with water and ammonia (Table 2), no shift in the spectrum of benzene was calculated. The orientation of NH_3 and H_2O over the hydrocarbon[10] is very nearly symmetrical, resulting in no net change in the electric dipole moment.

In the case of pyrazine–$(CH_4)_n$, n = 1, 2, 3, the calculated shifts parallel the experimentally obtained shifts remarkably well (Table 3) as is the case for pyrimidine interacting with ammonia (Table 4). However, in the case of pyrazine with NH_3 and pyrimidine with methane molecules, the spectral shift is predicted incorrectly. The predictive power of the method is disappointing for clusters in which the solute–solvent systems comprise polar–non-polar combinations.

As the molecules studied in this paper are mostly polar systems, the first-order contribution is the leading term in the interaction energy that determines the spectral shift. According to first-order perturbation theory, the spectral shift $\Delta E^{(1)}$ is given by eqn. (3) where V is the perturbation operator due to

$$\Delta E^{(1)} = \langle \Phi_0 | V | \Phi_0 \rangle \qquad (3)$$

the point charges that simulate the solvent, given by eqn. (4), Φ_0

$$V = -\frac{1}{2}\sum_{i}^{M} \sum_{j \in \text{solute}} q_i/r_{ij} + \sum_{i}^{M} \sum_{A \in \text{solute}} q_i Z_A/r_{iA} - \frac{1}{2}\sum_{i,j=1}^{M} q_i q_j/r_{ij} \qquad (4)$$

is the gas phase wavefunction of the solute molecule written in the usual notation as $\Phi_0 = |\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2) \cdots \varphi_n(N)\alpha(N)\varphi_n\beta(N)$ with $\varphi_k = \Sigma_p c_{pk}\eta_p$ where η_p are the basis functions centred on the atoms of the solute. Substituting eqn. (4) in eqn. (3) and using the differential overlap approximations, eqn. (5) is obtained, where P_{pp} is the electron

$$\Delta E^{(1)} = \frac{1}{2}\sum_{i=1}^{M}\sum_{p} P_{pp}\left[\sum_{A=1}^{N} \eta_p \left|\frac{q_i}{r_{iA}}\right| \eta_p - \sum_{j} \eta_p \left|\frac{q_i}{r_{ij}}\right| \eta_p\right] + \frac{1}{2}\sum_{i=1}^{M}\sum_{j=1}^{M}\frac{q_i q_j}{r_{ij}} \qquad (5)$$

density contribution from basis function η_p and the summations have been defined previously.

The dependence of the spectral shift on the values of the point charges is evident from eqn. (5) and, in cases where the shift is only of the order of a few hundred cm^{-1} or less, the values chosen for these charges will decide not only the magnitude but also the direction of the shift. The use of the same values for these charges as used in the simulation of the ground state of the solute in the solvent environment is inadequate in representing the electronic polarization of the solvent when the solute is in an excited state.

Furthermore, the hydrogen bonding capabilities of diazines in their excited states has been experimentally verified.[13,16] In cases like pyrazine with NH_3, the method used to calculate spectral shifts should be able to describe intermolecular hydrogen bonding which stabilises the excited state.[17] Replacing the solvent molecules by point charges removes any molecular properties from the solvent, which, in turn neglects specific intermolecular effects which are necessary for the study of the excited state.

In conclusion, the point charge model within the INDO scheme as presented here, has been shown to be unreliable in predicting spectral shifts due to intermolecular interactions. It is proposed that the values of the point charges be evaluated in an iterative manner in which the dipole moment of the solute molecule in the ground and excited states are used and self-consistency in the spectral shifts of interest obtained.

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