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A Monte Carlo–quantum mechanics study of the spectroscopic properties of molecules in solution

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Abstract

A combination of Monte Carlo simulation and quantum mechanics calculation is used to study properties, structure and spectroscopy of molecules in solution. All properties are obtained as statistical averages using uncorrelated structures generated by the Monte Carlo simulation. The auto-correlation function of the energy is calculated and used in the correlation analysis. Examples include the solvatochromic shift of the $n-\pi^*$ transition of formaldehyde and pyridine in water. A detailed and systematic analysis is made starting from the hydrogen bond shell and extending up to the bulk limit. Long range effects are found to be of importance for the total solvatochromic shift. Short range, hydrogen bond, effects are seen to alter the dipole moment of the chromophore both in direction and module, having an effect on the outer solvation shells.

A careful analysis is made of the possible structural changes induced by a solvent in merocyanine dyes. The hyperpolarizability of phenol blue is shown to vary with the resonance between the two, neutral and charge-separated, forms, having a pronounced maximum as obtained experimentally. This indicates that phenol blue undergoes structural changes in polar solvents.

Keywords: Solvent effects; Monte Carlo simulation; Molecular properties and spectroscopy

1. Introduction

Theoretical methods for the study of the structure, properties and spectroscopy of isolated molecules have progressed markedly, since the early pioneering days [1]. Unfortunately, isolated molecules correspond to physical situations that are not very often found in the laboratory. Indeed, most experiments are performed in solution [2]. Several chemical reactions do not occur in gas phase and, biological processes are known to occur only in the aqueous environment, the natural biological solvent. Real challenges are to be found in the study of molecular systems in interaction [3]. Molecular clusters are the subject of intense theoretical and experimental interests [4,5]. Even more challenging, is the study of molecular liquids. The change of the molecular properties due to the interaction of a chromophore with the liquid environment is of utmost importance. The theoretical advance in this area started with the early ideas of Onsager [6] and Kirkwood [7], where the solute is enclosed in a cavity and the solvent is described by a polarizable dielectric continuum. Since two decades ago, this idea has been put in a form that is very suitable for calculations, due to the works of Tapia and Goscinski [8], Rivail and Rinaldi [9], Miertus et al. [10], and more recently by Mikkelsen et al. [11],

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Karelson and Zerner [12], Klamt and Schüürman [13], Cramer and Truhlar [14] and Cances et al. [15]. They have developed a self-consistent reaction field theory where the charge distribution of the chromophore polarizes the solvent and interacts self-consistently with the reacting field (SCRF). This SCRF has been applied to the study of molecules in solvents with relative success. On the advantageous side, the calculations are simplified because the real quantum mechanical calculations are made only on the solute, without any increase in the number of electrons to be treated. Also, the original symmetry is preserved. On the other side, the size and shape of the cavity that encloses the solute is not well defined. This has been the subject of several studies [16] and despite interesting progress it may be said that it is still not well defined. Another approach that is gaining wide acceptance is the use of a combined quantum mechanics/molecular mechanics (QM/MM) approach [17–24] in which the most important part of the problem is treated by QM and the rest by classical force fields. A persistent problem occurs for the specific interaction between the solute and the solvent. For the case of hydrogen bonds several studies have found it necessary to enclose not only the chromophore but the complex formed by the chromophore and one or two hydrogen bonded solvent molecules [12,25]. Later in this paper, we analyze how the dipole moment of the hydrogen-bonded complex differs from that of the original isolated solute.

An important aspect that characterizes a liquid is that there is not only one but several structures to be considered at a given temperature. And, of course, temperature has to be included. Clearly, a realistic treatment of molecules in solution needs to consider the statistical nature [26]. Along these lines, molecular simulation techniques have been used to describe the structure of the liquid and quantum mechanical properties have been obtained as averages after several calculations on different structures obtained by the simulation. Most of these studies have used molecular dynamics simulations [27,28] whereas others have preferred Monte Carlo (MC) simulation [23,24,29,30]. As far as the simulation is performed aiming at generating liquid structures at a given temperature MC methods are more efficient. We have preferred MC simulations for generating structures for subsequent quantum mechanical calculations [30]. This complements the original supermolecular method where the chromophore is calculated with only a few of the solvent molecules explicitly considered. It goes well beyond simple supermolecular and SCRF approaches because (i) it now includes several solvent molecules, selected from the radial distribution function, corresponding to a division in solvation shells; (ii) it includes statistical averages; (iii) it includes explicitly short and long range interactions between the solute and the solvent; (iv) it includes exchange effects, as the wave-function is antisymmetric over the entire super-molecule and finally, (v) the quantum mechanical calculation may explicitly include all the electrostatic, polarization and induction effects. In the next section, we describe how we select the number of molecules to be explicitly considered, how we define solvation shells, and how we select, among the millions of configurations generated by the MC simulation, those structures used in the quantum mechanical calculations. The QM required over the supermolecule is considerably larger than that required over the chromophore alone, but it is certainly doable using semi-empirical QM. In a subsequent section we present results for solvatochromic shifts, influence of hydrogen bonds and change in optical and electrical properties of molecules in solution. We also show how a solvent may dramatically alter the first dipole hyperpolarizability of a dye that changes from a neutral to a zwitterion form.

2. Methods of calculation

2.1. Monte Carlo simulation

The (MC) simulation is performed using standard procedures for the Metropolis sampling technique [31] in the canonical *NVT* ensemble, where the number of molecules N, the volume V and the temperature T are fixed. As usual, periodic boundary conditions in a cubic box [26] are used. In our simulation, we use one solute molecule plus 343 molecules of solvent. The volume of the cubic box is determined by the experimental density of the solvent. Our results in this paper use water as the solvent with, $\rho = 0.9966$ g/cm^3[32] at $T = 25$°C. The molecules interact by the Lennard–Jones plus Coulomb potential with 3 parameters for each atom i (ε_i, σ_i and q_i). For

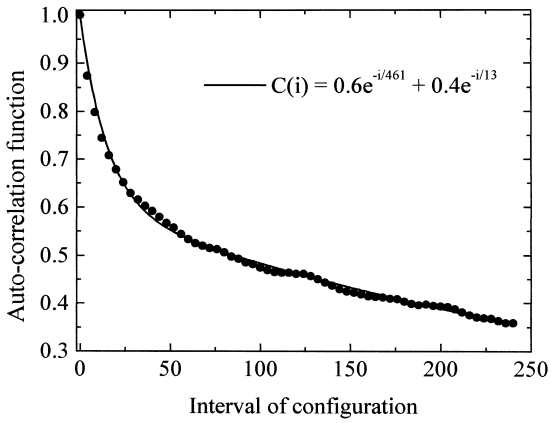

Fig. 1. The calculated auto-correlation function of formaldehyde in water. Best exponential fit is shown.

water molecules, we used the SPC potential developed by van Gunsteren et al. [33]. For the formaldehyde molecule, we used the same potential of Blair et al. [27]. For pyridine we used the OPLS potential developed by Jorgensen [34]. In the calculation of the pair-wise energy, each molecule interacts with all other molecules within a center of mass separation that is smaller than the cutoff radius. For the simulations with water, for instance, $r_c = 10.9$Å. For separations larger than r_c, we use the long range correction of the potential energy [26]. The initial configuration is generated randomly, considering the position and the orientation of each molecule. A new configuration is generated after 344 MC step, i.e. after selecting all molecules sequentially and trying to translate it in all the Cartesian directions and also rotate it around a randomly chosen axis. The maximum allowed displacement of the molecules is auto-adjusted after 17000 MC steps to give an acceptance rate of new configurations around 50%. The maximum rotation angle is fixed during the simulation in $\delta\theta = \pm 15°$. The full simulation [35] involves a thermalization stage of about 1.7×10^6 MC step followed by an averaging stage of 16.5×10^6 MC steps that generates 48000 MC configurations. During the averaging stage some thermodynamical properties, as the internal energy and the heat capacity at constant volume, are calculated and they are in agreement with that calculated for liquid water. The radial distribution function is also calculated during the averaging stage in the simulation.

2.2. The auto-correlation function of the energy

As quantum mechanical calculations will be performed on the structures generated by the MC simulation it is important to optimize the statistics. This point has been largely overlooked in previous calculations. As it is not possible to perform quantum mechanical calculations in millions or even thousands of supermolecular structures, generally only a few of them are chosen. The systematic way to select structures without affecting the true average is via the use of the auto-correlation function of the energy [30]. Structures that are statistically correlated will not give important additional information and will not be used in the QM treatment. For markovian processes the auto-correlation function follows an exponentially decaying function [30,36–38],

$$C(i) = \sum_{j}^{n} c_j e^{-i/\tau_j}$$

where i is the interval of configurations generated in the MC simulation. The correlation step is

$$\tau = \int_0^\infty C(i)\, \mathrm{d}i.$$

Configurations that are separated by $i > 2\tau$ have a statistical correlation that is less than 14% and for $i > 3\tau$ a statistical correlation that is less than 5%. Fig. 1 shows the calculated auto-correlation function of formaldehyde in water. From this and the equation above it can be seen that the correlation step is ~280. Therefore, in calculating the averages for all solutes in water we select structures in an interval of configuration $3\tau \approx 800$ MC steps. The total simulation generates 48000 configurations (see above), thus the averages are taken over 60 configurations, separated by an interval of 800 [30,38,39]. With this, two subsequent structures have a correlation that is only 6%. This procedure is the most systematic way of selecting a reduced number of configurations without compromising the statistical average value [36–38].

2.3. Quantum mechanical calculations

The quantum mechanical calculations are made using the ZINDO program [40] in the super-molecules generated by the MC simulations. The quantum mechanical calculations are then performed for the

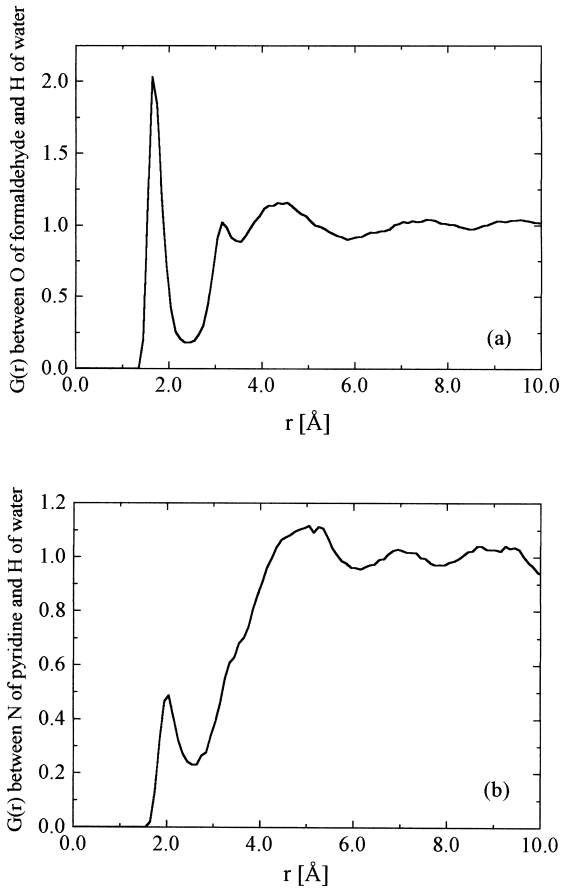

Fig. 2. Pair-wise radial distribution function for the oxygen atom of formaldehyde and the hydrogen atom of water (top) and the nitrogen atom of pyridine and the hydrogen atom of water (bottom). First peak shows the hydrogen bond formation.

super-molecular structure composed of one solute and all solvent molecules within a particular solvation shell. Each solvent water molecule includes eight valence electrons and the Hartree–Fock wave function is anti-symmetric with respect to the entire solute–solvent system. To obtain excitation energies, CIS calculations are performed. The use of size-extensive methods is extremely important in these super-molecular calculations. As the appropriate Boltzmann weights are already included in the Metropolis MC sampling technique [26] all molecular properties are obtained as simple average over a chain of L calculated values. For transition energies, for example,

$$\langle \Delta E \rangle = \frac{1}{L} \sum_{i}^{L} \Delta E_i$$

For all the hydration shells the value of L is 60, obtained previously from the auto-correlation function. For the hydrogen bonds a specific statistics will be performed, where we analyze the number of hydrogen bonds in each configuration, using both the geometric and energetic criteria [41]. For the calculation of the first dipole hyperpolarizability we use the sum-over-states procedures [42]. In total more than 250 excited states, and their corresponding intensities, are used to obtain the hyperpolarizability.

3. Results and discussions

3.1. Hydrogen bond

Solvation shells are defined from the radial distribution function as obtained from the MC simulation. We discuss separately the hydrogen bond formed between formaldehyde and water and pyridine in

Table 1
Statistics of the hydrogen bonds formed between pyridine and water and formaldehyde and water and their contribution to the blue shift of the n–π* transition

Number of HB	Pyridine in water		Formaldehyde in water	
	Occurrence (%)	Shift (cm^{-1})	Occurrence (%)	Shift (cm^{-1})
0	13.3	0	0.0	0
1	53.3	35	23.3	146
2	33.4	277	63.3	313
3	0.0	0.0	13.4	360
Total	100 (72)	112 ± 39	100 (114)	281 ± 65

Table 2
Variation of the calculated shift (in cm^{-1}) of the n–π^* transition of pyridine in water with the solvation shells. *N* is the number of water molecules included. *M* is the total number of valence electrons. *L* is the number of MC structures used for ensemble average

Solvation shell	*N*	*M*	*L*	Distance (Å)	Blue shift
HB[a]	1.2	39.6	60	3.6	112 ± 39
First	29	262	60	6.1	716 ± 30
Second	70	590	60	8.3	805 ± 29
Bulk					900[b]

[a] Average values taken from Table 1.
[b] Estimated from extrapolation (see Fig. 4b).

water. Fig. 2a shows the radial distribution function between the oxygen of formaldehyde and the hydrogen of water. As it can be seen there is a hydrogen bond peak that starts at around 1.4 Å and has a minimum at 2.4 Å, with a pronounced peak at 1.7 Å. We call this the HB solvation, to separate it from the other solvation shells. Some of these configurations have a formaldehyde–water interaction energy that is either too low or even positive. Therefore it is quite appropriate to use also an energetic criterion [39,41]. Thus only those structures with a pair-wise formaldehyde–water binding energy higher than 3.0 kcal/mol are included. Thus using both the geometric and energetic criteria we find a total of 114 hydrogen bonds in the separated 60 MC structures. This gives an average of 1.9 hydrogen bonds. Table 1 gives the statistics obtained for the hydrogen bonds and their contribution to the solvatochromism. The total average blue shift due exclusively to the HB shell is calculated here as 281 ± 65 cm^{-1}. This is lower than that obtained by Blair et al. [27]. We include here only those water molecules that satisfy the energetic and geometric criteria. As a result the average number of hydrogen bonds reduce from 2.6 to 1.9. This hydrogen bond contribution of ~300 cm^{-1} calculated here corresponds to only 15% of the total estimated blue shift of ~2000 cm^{-1} [21,27,39,43–45]. Inclusion of the water molecules in the outer solvation shells (up to 8.4 Å) in the calculations gives a total solvatochromism of ≈ 1950 ± 100 cm^{-1}, in excellent agreement with the estimated blue shift [21,27,39,43–45]. This calculation includes the third solvation shell with a total of 80 water molecules around the solute.

We now discuss the results for the pyridine in water. Fig. 2b shows the radial distribution function between the nitrogen atom of pyridine and the hydrogen atom of water. The HB peak has its maximum at 2.0 Å. In this case, using again the geometric and energetic criteria, we find that the average number of hydrogen bonds is 1.2. This result is in agreement with previously calculated [46] and observed values [47]. The total calculated contribution of the HB solvation to the blue shift is 112 ± 39 cm^{-1} (Table 2). We find that 13.3% of the configurations have no hydrogen bonds. The majority, 53.3%, form one hydrogen bond and gives a blue shift of only 35 cm^{-1}. In complement, 33.4% of the configurations have two hydrogen bonds and give a blue shift of 277 cm^{-1}. The total calculated average blue shift of the hydrogen bonds to the n–π^* transition of pyridine

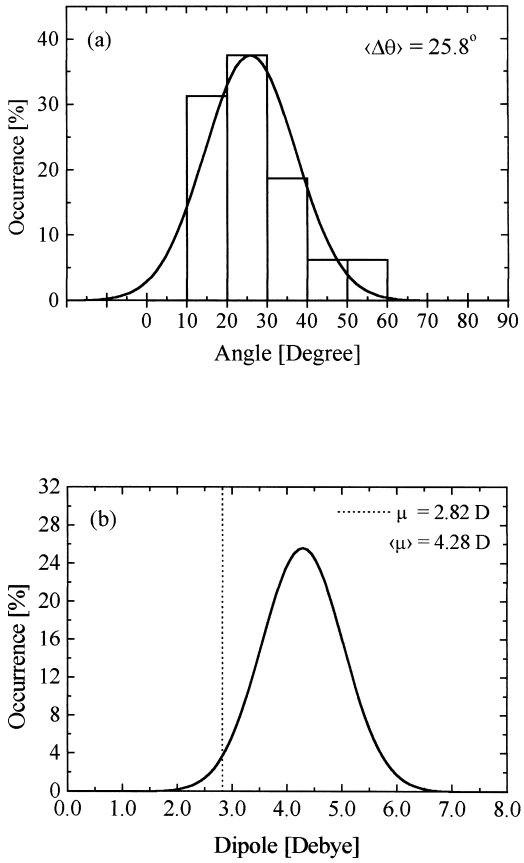

Fig. 3. Calculated distribution of the change in direction and module of the dipole moment of the pyridine–water complex as compared to that for isolated pyridine. See text.

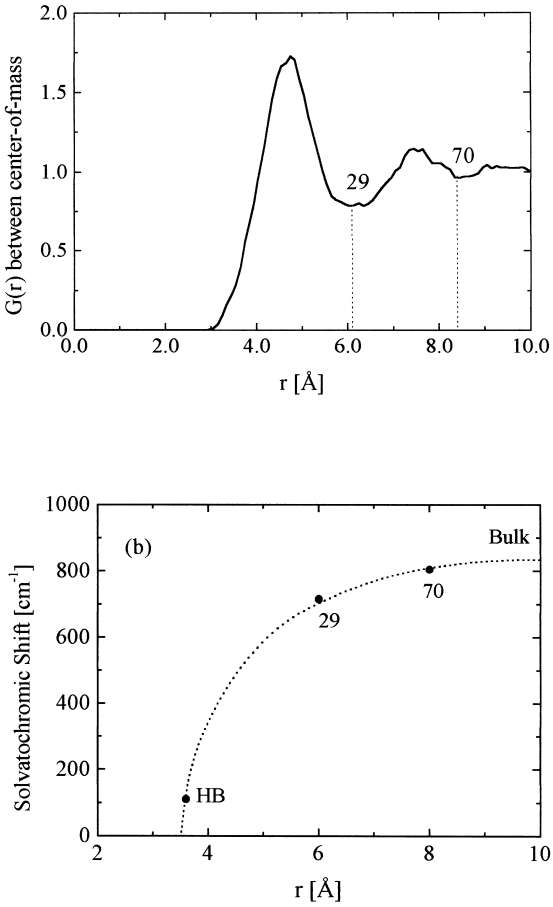

Fig. 4. Pair-wise radial distribution function between the center-of-mass of pyridine and water (top). Below is shown the corresponding solvatochromic shifts of the corresponding solvation shells, including the hydrogen bonds. See text.

in water is 112 ± 39 cm^{-1}. If we consider only those structures that form at least one hydrogen bond, then the total blue shift is now 128 ± 39 cm^{-1}. This is considerably smaller than that inferred from cavity models [46]. This present calculation is the first explicit true calculation of the hydrogen bond contribution to the solvatochromic shift of the singlet n–π^* transition of pyridine in water.

The study of the blue shift of the n–π^* transition of azines in protic solvents, such as water, using SCRF have found that it is necessary to include explicitly one or two hydrogen bonded molecules [12,25]. Thus the chromophore that polarizes the dielectric continuum is not that of the isolated chromophore but, instead, that of the complex. It is of general interest to study the local change in the properties of the chromophore due to the hydrogen bond interaction. We now analyze the change in the dipole moment of pyridine as compared to the complex pyridine–water system. This complex is obtained from the MC simulation of the liquid. It includes the effect of temperature and ensemble averages and it is a better representation of the situation that is found in a real liquid than that obtained with geometry optimization of the cluster [48]. Fig. 3 shows the distribution of calculated values for both the direction and module of the dipole moment. The dipole moment of isolated pyridine lies in the direction of the long C_2 axis and the dipole moment of the complex pyridine–water makes an angle that deviates from the original axis by 26°, on the average. It is interesting to note that the total calculated dipole moment of the complex is 4.3 debye, as compared with that calculated for isolated pyridine that is 2.8 debye. Hence, the average dipole moment of the complex deviates by 26° and is more than 50% larger. Similar results are obtained for the case of formaldehyde–water using ab initio calculations [49].

3.2. Solvation shells

Fig. 4a shows the radial distribution function between the center-of-mass of pyridine and water. Two solvation shells are discernible. The first shell starts at 3.0 Å ending at 6.1 Å. The second ends at 8.3 Å. Integration of the radial distribution function gives a total of 29 and 70 water molecules in these shells, respectively. To obtain the solvation shift we now perform super-molecular calculations involving the solute pyridine and all the molecules in a given solvation shell. The solvent molecules are explicitly considered with all the valence electrons. Table 2 shows the calculated solvatochromic shift and summarizes the results obtained for each solvation shell, including the HB solvation shell, previously discussed. The largest calculation, obtained for the second solvation shell, is composed of the pyridine molecule and 70 water molecules with a total of 590 valence electrons explicitly considered in a totally anti-symmetric ground state wave-function. This gives a calculated blue shift of 805 ± 29 cm^{-1}. The experimental result for the solvation shift of the

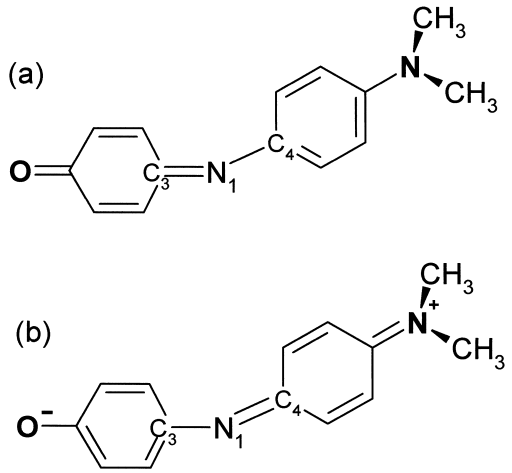

Fig. 5. Phenol blue in its two extreme forms. Neutral structure (top) and charge-separated zwitterion structure (bottom).

singlet n–π^* transition of pyridine in water is not precisely known. For azines, in general, this solvation is estimated to lie in the broad range between 1000 and 3000 cm^{-1} [50]. Our results obtain this shift to lie in the lower side of this range for pyridine. Also, they seem to show that a small number of water molecules cannot adequately describe the pyridine solvatochromic shift (see Fig. 4b). It is clear that one has to include solvent molecules that are located more than 8.0 Å from the center-of-mass of the pyridine molecule. The results shown in Fig. 4b suggest that the calculated energy shift may be extrapolated to the bulk limit. In doing so we obtain an estimated limiting value of ~900 cm^{-1}. This would be our best estimate of the blue shift of the n–π^* transition of pyridine in water. A similar analysis of the solvatochromic shift of the n–π^* transition of formaldehyde in water [39], from hydrogen bond to bulk, gave a limiting value of 2200 cm^{-1}, in good agreement with some previous calculations, in particular those by Blair et al. [27] and the very recent (RISM-SCF) results of Naka et al. [51] and Sánchez et al. [45]. In the case of benzene, a nonpolar molecule, in different solvents we find that the first solvation shell is enough to give the solvatochromic shift [24,30] For polar molecules such as formaldehyde and pyridine it is clear that the effect extends over the second, third and outer solvation shells [39].

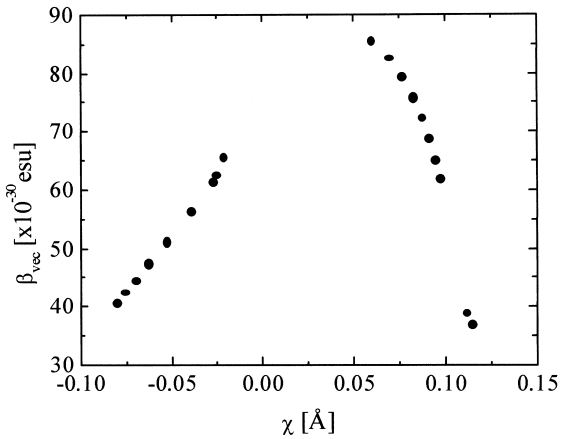

Fig. 6. Variation of the first dipole hyperpolarizability (projected along the dipole moment) with the bond-length-alternation. Negative values of χ correspond to a predominance of the neutral form, whereas positive values correspond to a predominance of the charge-separated value. See text.

3.3. Structural changes

So far we have been discussing those solvent effects that arise from the interaction between the solute and the solvent. There is another solvent effect that is equally important but more difficult to deal with. This is the case of the structural changes induced by the solvent. Geometry changes due to solvent effects have been studied with QM/MM by Gao et al. [52] and using continuum approach by Cammi et al. [53]. Here, we want to consider the case of phenol blue (Fig. 5). This is a well-known dye that may exist in resonance between two forms. One is the neutral form, shown in Fig. 5a. The other is the charge-separated zwitterion form shown in Fig. 5b. Whereas in the gas phase the neutral form is more stable, the zwitterion is believed to prevail in most polar solvents. Geometry optimization of the isolated molecule inevitably leads to the neutral form. However, the calculated properties of phenol blue using this isolated neutral form is in gross disagreement with those results obtained in solvents [54].

The influence of the solvent in the structure of phenol blue can be studied using the concept of bond-length-alternation [55]. This can be obtained by the χ parameter defined below:

$$\chi = r(C_3 - N_1) - r(C_4 - N_1)$$

As it can be seen in Fig. 5, if χ is negative there is a predominance of the neutral form, whereas for χ positive the zwitterion is dominant. The influence of the structure in the molecular first dipole hyperpolarizability will be analyzed here. To obtain the changes in the structure, continuously from the neutral to the zwitterion, it is a common practice to place the molecule in a static homogeneous electric field [56]. Here we find it to be more efficient to place a proton on the oxygen atom and monitor the bond-length-alternation by the proximity of the proton to the oxygen atom. For each oxygen-proton distance the other geometric parameters were re-optimized. With this we found a broader range of χ values than that in Ref. [56]. In this way it was possible to monitor the χ parameter. Fig. 6 shows the calculated values for the dipole hyperpolarizability. These calculations were performed in the corresponding structure of phenol blue after removing the proton. As it can be seen there is a large variation of the hyperpolarizability as a function of the bond-length-alternation. This variation can be traced to the solvent polarity. The maximum seen for the hyperpolarizability is indeed seen experimentally [57] and corresponds to the case of phenol blue in chloroform. The calculated value for the hyperpolarizability as a function of χ changes from 35×10^{-30} esu, in either of the extreme forms of phenol blue, to a value of 85×10^{-30} esu in a more mixed, resonant, form. Morley and Fitton [58] have recently measured the NMR chemical shift of a compound similar to phenol blue and concluded that even in polar solvents only the neutral form exists. This is in contrast to the traditional view and recent resonance Raman results [59]. The maximum value of the hyperpolarizability as a function of the solvent polarity is suggestive of the structural change [57,60,61]. These results are of importance in the analysis of second-harmonic-generation of molecules and is expected to have an impact in the design of nonlinear optical devices.

4. Summary and conclusions

A sequential MC–QM approach has been used to study structure, properties and spectroscopy of molecules in solution. A detailed and systematic analysis of the hydrogen bond contribution to the solvatochromic shift of the singlet n–π^* transition of formaldehyde and pyridine in water has been made. We find that the hydrogen bond contribution is relatively small. The total solvatochromic shift is analyzed as a function of the solvation shells, starting from the hydrogen bond and extending to the outer solvation shells. Long range effects are found to be important. We investigated carefully the change in local properties of the chromophore due to hydrogen bond formation. In the case of pyridine in water, we found that the dipole moment of the dimer pyridine–water, generated in the simulation, in the average, deviates in direction by 26° and is more than 50% larger, in module, than that for isolated pyridine. In all quantum mechanical calculations the solvent molecules are explicitly included with all the valence electrons and the wave-function is antisymmetric with respect to the entire solute–solvent system. The largest calculation, the solvation shift of pyridine in water, for the second solvation shell, involves 60 quantum mechanical calculation of one pyridine molecule surrounded by 70 water molecules, with a total of 590 valence electrons. To obtain statistical averages the quantum mechanical calculations are made on the structures generated by the MC simulation that are statistically nearly uncorrelated. The autocorrelation function of the energy is used to obtain structures that are only 6% correlated. We also analyze the structural changes induced by solvent in resonant dyes. Phenol blue, that may exist in resonance between the neutral and charge-separated forms, is studied using the concept of bond-length-alternation. We showed that the first dipole hyperpolarizability, associated with second-harmonic-generation experiments, has a maximum value for a mixed, resonant, structure. The results obtained for the hyperpolarizability are in excellent agreement with that obtained experimentally, in particular the maximum observed in chloroform. This suggests that phenol blue undergoes structural changes in polar solvents.

Finally, from these examples, it is demonstrated that the combined use of liquid simulation methods, such as MC simulation, and proper QM calculations are convenient and accurate tools for the study of properties and spectroscopy of molecules in solution.

Acknowledgements

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