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Converged electronic polarization of acetone in liquid water and the role in the n–π^* transition

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Abstract

The electronic polarization of acetone in liquid water is obtained using an iterative procedure in the sequential Monte Carlo/quantum mechanics methodology. MP2/aug-cc-pVDZ calculations of the dipole moment of acetone in water are performed on statistically uncorrelated structures extracted from isothermic–isobaric MC simulations. After electrostatic equilibrium the calculated dipole moment of acetone is obtained as 4.80 ± 0.03 D, with an increase of 60% compared to the gas phase value. This solute polarization is used to obtain the shift of 1650 ± 42 cm^{-1} for the n–π^* transition of acetone in water, in agreement with the experimental result of 1500–1700 cm^{-1}.

1. Introduction

The last two decades have seen great advances of quantum chemistry into the area of solvent effects [1,2]. The first modern incursion into electronic structure calculations of solute molecules in a solvent environment was inspired by the original ideas of Kirkwood and Onsager and led to the so-called continuum models [2]. However, as a liquid system is characterized by a large number of possible structures, with equivalent energies at a certain temperature, the use of computer simulation to deal with liquid systems naturally arises [3]. This idea has been used in solvent effects in an early study on the spectroscopy and dynamics of formaldehyde in water [4]. The idea of combining molecular mechanics (MM) and quantum mechanics (QM) originated the so-called QM/MM methods [5–7]. These are available in a series of possible quantum chemical methods [8] including the powerful coupled-cluster method [9]. One variant is the use of computer simulation to generate the structure of the liquid for subsequent QM calculations [10,11]. The advantage of performing the calculations sequentially, in a two-step procedure, is that after the simulation statistical information permits an efficient protocol for the QM calculations. In this way statistically converged results can be obtained with a relatively small number of the usually expensive QM calculations [11–13]. This is the sequential QM/MM methodology [10–12].

A very important aspect in solute–solvent interaction is the understanding of the mutual electronic polarization of the solute and solvent molecules [14–18]. Although this problem has been recognized to be very important for adequate treatment of the solvent effects in QM/MM methodologies it is still lacking a detailed understanding. An important aspect that is missed when performing all-classical simulations is the solute polarization. Most classical simulations of liquids use fixed force field parameters previously optimized that include some *ad hoc* implicit polarization in the electrostatic parameters. For instance, the dipole moment of the reference molecule is increased compared to the dipole moment of the isolated molecule. This increase of course varies depending on the solute and the solvent but a typical increase of 20% is normally found [19]. It is expected that the dipole moment in the liquid phase should be increased but the crucial question now is the proper evaluation of this increase. There have been some important theoretical studies of the electronic polar-

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ization of a reference solute molecule in the solvent environment [14–22]. The dipole moment of liquid systems is not a quantity that is easily amenable to experimental evaluation. Although indirect results can be inferred, for instance, using integrated infrared intensities [23], there are only scarce estimates and a reliable and systematic theoretical procedure is relevant. At this stage a natural procedure is to use computer simulation to generate liquid structures and obtain the dipole moment of the reference molecule in the presence of the solvent. In this work we present a systematic and convergent procedure to obtain the *solute polarization* in the presence of a solvent liquid system. This is then probed in the evaluation of the n–π^* transition of acetone in water. The selection of this n–π^* transition has several motivations. Most of all, the accurate description of this shift in formaldehyde and acetone has been a persistent theoretical challenge [4,6,11,12,14,18,24,25]. But opposite to the case of formaldehyde, in the special case of acetone, the experimental result is known [26–28] and can be used to test the quality of the different theoretical results. Hence, in this work a sequential Monte Carlo (MC) procedure combined with QM calculations is used to obtain the electronic polarization of acetone in water. The procedure is iterated until convergence when the solute is in electrostatic equilibrium with the solvent. Similar strategies have been proposed to look at the solute polarization [15,18]. After convergence, the MC simulation generates liquid structures that are used to calculate the absorption spectrum of the solute in the solvent environment.

2. Calculation details

The MC simulation was performed using standard procedures [3,11] for the Metropolis sampling technique in the isothermal–isobaric NpT ensemble, where the number of molecules N, the pressure p and the temperature T are fixed. We have used the periodic boundary conditions and image method in a cubic box of size L with one acetone molecule embedded in 450 molecules of water in normal conditions ($T = 298$ K and $p + 1$ atm). The acetone and the water molecules interact by the Lennard-Jones plus Coulomb potential [12,19] with three parameters for each interacting site i (ε_i, σ_i and q_i), with the combination rule $\varepsilon_{ij} = (\varepsilon_i\ \varepsilon_j)^{1/2}$ and $\sigma_{ij} + (\sigma_i\ \sigma_j)^{1/2}$. For the water molecules we used the simple point charge (SPC) [29] parameters. For the acetone we used the Lennard-Jones parameters of Gao [6] and the atomic charges are obtained from an electrostatic fit (CHELPG) [30] using MP2/aug-cc-pVDZ in the Gaussian 98 program [31]. The geometry of acetone is the same as that used before [12] to facilitate comparison. The MC simulation was performed with the Dice program [32] and uses procedures described previously [11–13]. After the thermalization, 6.7×10^7 MC steps are performed. The average density is calculated as 0.989 ± 0.007 g/cm^3 in agreement with the result for liquid water. After calculating the auto-correlation function of the energy [10,11], we have sampled configurations with less than 10% of statistical correlation. In total 100 statistically uncorrelated configurations are separated representing the entire simulation. As in previous applications [11–13] statistically converged results are obtained in all cases. To iterate the electrostatic potential several equivalent MC simulations are performed. First (iteration 0) the atomic charges are obtained from a simple CHELPG fit of the MP2/aug-cc-pVDZ calculation of isolated acetone. After the MC simulation using these atomic charges, 100 configurations are sampled, as described above, and the average dipole moment and new charges (iteration 1) are obtained from a similar MP2/aug-cc-pVDZ/CHELPG fit of the acetone molecule, now surrounded by 200 simple-point-charge water molecules (corresponding to all solvent molecules within the cut off radius of 11.5 Å). This changes the dipole moment of acetone from the calculated gas phase value to an in-solution value. These new atomic charges are then used again in another MC simulation to generate new configurations and a new value of the average dipole moment and atomic charges. The procedure is then carried out until we obtain convergence in the dipole moment, when the solute is in electrostatic equilibrium with the solvent. This strategy is similar to that proposed by Aguilar and co-

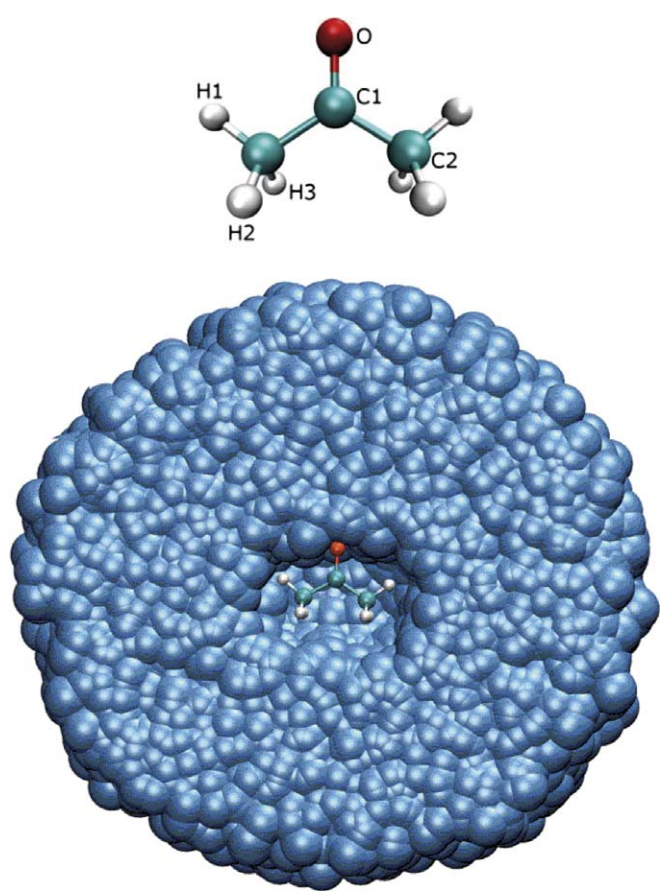

Fig. 1. Isolated acetone molecule and the superposition of 100 acetone–water configurations obtained from the MC simulation of the liquid. Note the configuration space spanned by the water molecules.

workers [18]. The essential difference is that they [18] calculate molecular properties using the average solvent structure and average of the solvent electrostatic potential. We use the converged electrostatic potential to perform another simulation generating structures for the statistical average of the molecular property. After electrostatic convergence statistically uncorrelated configurations are sampled for subsequent QM calculations of the n–π^* transition of acetone in water, using the INDO/CIS in the ZINDO program [33]. Fig. 1 shows a superposition of the 100 MC configurations of one acetone molecule surrounded by 200 water molecules. This illustrates the configuration space that is spanned by the solvent around the solute.

3. Results and discussions

3.1. Electronic polarization of the solute

We now discuss the solute polarization due to the interaction with the solvent molecules. The gas phase dipole obtained for acetone is 2.98 D in very good agreement with the experimental result of 2.93 D [34]. Fig. 2 shows the calculated results for the average dipole moment of acetone in the presence of 200 water molecules represented by point charges. Every (black) circle in Fig. 2 is the average result of a MC simulation followed by 100 MP2/aug-cc-pVDZ calculations of the dipole moment. As it can be seen the average dipole moment in-solution is converged after 5 iterations and substantially increased compared to the isolated acetone molecule. Table 1 gives more detailed information about the electrostatic parameters of acetone in water. Our results thus give a value of 4.80 ± 0.03 D for the dipole moment of acetone in water. The value of 3.6 D associated to the implicit polarization used previously [12] corresponds to an intermediate value between the gas phase and the result obtained in the first iteration. This seems to indicate that the conventional implicit polarization result may not be enough in most cases. We obtain an increase of 1.8 D, corresponding to a sizable induction of 60%. Although this seems a very large increase this is not dissimilar from the recent theoretical estimates of 50–55% using an averaged electrostatic potential [18] or high-level coupled-cluster theory implemented in a linear response approach [14]. In fact, our result is in due agreement with the increase of 1.8 (60%) obtained by Car-Parrinello molecular dynamics [25]. It is not possible to obtain direct experimental results and we have to rely on theoretical estimates of other related properties. The converged electrostatic field of Table 1 is then used, combined with the Lennard-Jones potential, for another MC simulation to obtain the liquid structure to be used in the QM calculations of the solvatochromic shift of the n–π^* transition of acetone in water. Before reporting on this, Table 2 shows the corresponding number of water molecules in the first coordination shell, obtained from the radial distribution functions shown in Fig. 3. Note that the use of atomic charges obtained for acetone in gas phase (iteration

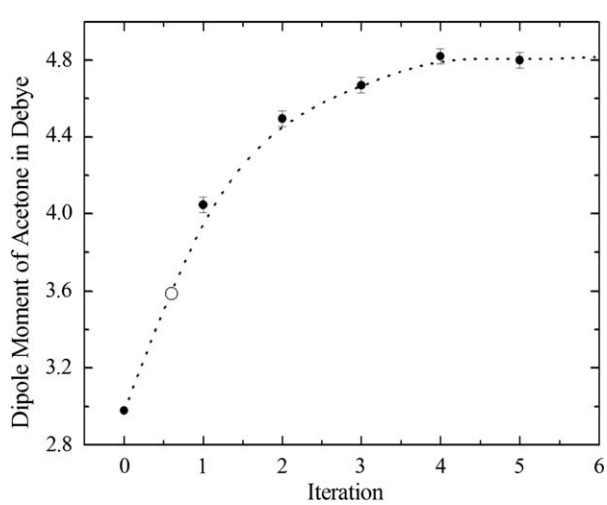

Fig. 2. Convergence of the calculated in-solution dipole moment of acetone in water. Open circle corresponds to the usual value in implicit polarization [12].

Table 2
Coordination number obtained from the integration of the first peak of the $O_{acetone} - O_{water}$ radial distribution function (Fig. 3)

Iteration	r_{O-O} (Å)	N
1	3.4	2.3
2	3.3	2.4
3	3.3	2.7
4	3.3	2.7
5	3.3	2.7
Ref. [12]	3.3	2.2

Table 1
Calculated average values of the atomic charges obtained from CHELPG fitting and dipole moments (in Debye) from MP2/aug-cc-pVDZ calculations using 100 statistically uncorrelated MC configurations

Iteration step	0 (Gas phase)	1 (In-solution)	2 (In-solution)	3 (In-solution)	4 (In-solution)	5 (In-solution)
Q(O)	−0.5318	−0.6562	−0.6998	−0.7169	−0.7226	−0.7307
Q(C1)	0.6843	0.7685	0.7866	0.7881	0.7814	0.7953
Q(C2)	−0.3378	−0.3619	−0.3648	−0.3641	−0.3580	−0.3627
Q(H1)	0.0952	0.1036	0.1038	0.1061	0.1006	0.1050
Q(H2 and H3)	0.0832	0.1011	0.1088	0.1112	0.1140	0.1127
μ	2.98	4.05 ± 0.03	4.50 ± 0.03	4.67 ± 0.03	4.82 ± 0.03	4.80 ± 0.03

See Fig. 1 for the atom types. Uncertainties are statistical errors (standard deviations are 10 times larger).

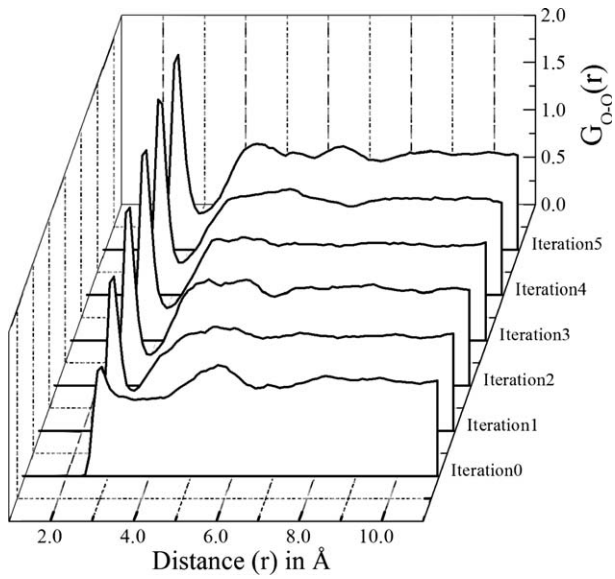

Fig. 3. Radial distribution function of $O_{acetone} - O_{water}$ for the different iteration steps.

0 in Fig. 3) gives unstructured first solvation shell. After convergence the first coordination number is 2.7 water molecules. This number is an approximation to the average number of water molecules that are hydrogen bonded to the oxygen site of the acetone molecule. As Table 2 shows these are also converged quantities.

3.2. Solvatochromic shift

The converged result for the polarized solute in water is now used to obtain the solvatochromic shift of the n–π^* transition of acetone. This shift in water compared to the gas phase has been subjected to several theoretical results and it is known experimentally [26–28] to be within 1500–1700 cm^{-1}. A summary of previous theoretical results is shown in Ref. [14]. In this present work QM calculations are performed including all water molecules up to the third solvation shell. This includes a total of 170 water molecules. Each water molecule considered includes eight valence electrons and the Hartree–Fock wave function is anti-symmetric with respect to the entire solute–solvent system. This includes a total of 1384 valence electrons. One advantage of this procedure is that the wave function is allowed to delocalize over the solvent and this leads to a contribution of the dispersion interaction to the excitation energy [35]. The disadvantage is, of course, that for such a large system we have to recourse to semi-empirical methods. The INDO/CIS method [34] in the spectroscopic parametrization is among the most successful semi-empirical methods for treating absorption spectrum of organic molecules in the ultra-violet and visible region. Table 3 shows the results. Using the same procedure but with the unpolarized solute we obtained the result of 965 ± 31 cm^{-1}. Including the *ad hoc* implicit polarization [12] this gives the result of 1296 ± 41 cm^{-1}. Finally, with the present converged polarized solute the result is improved to the very good result of 1650 ± 42 cm^{-1}. This result is also statistically converged and the histogram of calculated values is shown in Fig. 4 together with the experimental result for a direct comparison.

Table 3
Calculated solvatochromic shift of the n–π^* transition and dipole moments of acetone, isolated and polarized in-water

	Present	Ref. [14]	Ref. [18]	Ref. [25]	Experimentals
ΔE (cm^{-1})	1650	1103	2345	2016	1500–1700 [26–28]
μ_{gas} (D)	2.98	2.92	2.90	3.08	2.93 [34]
$\mu_{in\text{-}solution}$ (D)	4.80	4.44	4.52	4.90	–

See text.

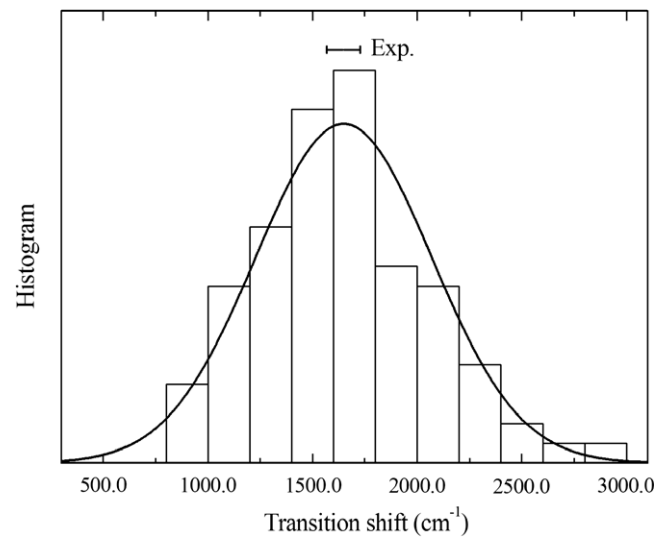

Fig. 4. Histogram of the calculated solvatochromic shift of the n–π^* transition of acetone in water and comparison with experiment (upper horizontal bar).

4. Summary and conclusions

The dipole moment of acetone polarized by liquid water is obtained using quantum mechanical calculations on structures generated by Monte Carlo liquid simulation of acetone in water at normal conditions. An iterative procedure involving several updated MC simulations and MP2/aug-cc-pVDZ calculations is used. Convergence is obtained both for the iterative procedure and the statistical averages. The converged solute polarization gives the value of the dipole moment of acetone in water as 4.80 ± 0.03 D. This result corresponds to an increase of 1.8 D in going from the isolated to the in-water liquid state, leading to the sizable increase of 60%. To probe the reliability of this calculated solute polarization the corresponding electrostatic field is used to generate liquid configurations for subsequent INDO/CIS calculations of the n–π^* transition of acetone. The resulting solvatochromic shift is found as 1650 ± 42 cm^{-1}, in very good agreement with the experimental value of 1500–1700 cm^{-1}.

Finally, this work strongly suggests that the use of implicit polarization in classical simulations requires consideration of the solute–solvent electrostatic equilibrium.

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