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Electronic polarization in liquid acetonitrile: A sequential Monte Carlo/quantum mechanics investigation

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Abstract

The electronic polarization of liquid acetonitrile is investigated using the sequential Monte Carlo/quantum mechanics methodology. Second-order Møller–Plesset and density-functional theory calculations of the dipole moment are performed on statistically uncorrelated structures of liquid acetonitrile generated by the MC simulation. Our best result, obtained at the MP2/aug-cc-pVTZ level, gives an average dipole moment of 4.65 ± 0.19 D, in agreement with an experimental prediction of 4.5 ± 0.1 D. This result corresponds to an increase of 0.71 ± 0.19 D in going from the gas to the liquid state.
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1. Introduction

Understanding the polarization effect in liquid systems is important to rationalize several experiments made in solution [1]. The polarization in water has been the subject of several theoretical studies [2–6]. Liquid acetonitrile is also an important molecular fluid because of its high polarity and ability in acting as a hydrogen bond acceptor [7–9]. Different from water, the acetonitrile molecule has a larger dipole moment [10,11] but does not form strongly associated liquids. It is known, however, to form weakly and small oligomers [12] that are consistent with dipolar stabilization [13]. Acetonitrile is frequently used as a non-aqueous solvent for both, organic molecules and inorganic salts [12,14]. Considering the solvating properties, it is expected a large increase in the dipole moment of liquid acetonitrile compared to the gas phase. Recent density functional theory calculations for small aggregates of acetonitrile [13] have predicted an increase of about 16% relative to the gas phase dipole. An experimental estimate [15] for the dipole moment of liquid acetonitrile exists and needs corroboration.

Many computer simulation studies of pure liquid acetonitrile and different mixtures of solvents containing acetonitrile have been reported [10,11,16–19]. However, much less attention has been paid to the polarization of neat liquid acetonitrile. Direct experimental measurement of the dipole moment in liquids is not possible but a value obtained from integrated far-infrared intensities is available for acetonitrile [15]. Thus, reliable quantum mechanical calculations are now timely and relevant. In this study, we use the sequential Monte Carlo/quantum mechanics (S-MC/QM) methodology [20–24] aiming at obtaining reliable estimates of the dipole moment of liquid acetonitrile. We first generate the structures of the liquid using Monte Carlo simulation and next we sample statistically relevant configurations

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for subsequent quantum mechanical calculations. One crucial advantage of the sequential approach is that after the simulation all the statistical information is available thus permitting an efficient protocol for the QM calculations [4,20–25]. This methodology has also been used successfully to study the electronic polarization of liquid water [4].

The MC simulation is carried out in the isobaric–isothermal (*NpT*) ensemble and the QM calculations are performed at both the second-order Møller–Plesset perturbation [26] and density functional [27] levels of theory, combined with different correlation-consistent basis sets. The structures used for the QM calculations are obtained after calculating the auto-correlation function of the energy to ensure that only statistically relevant configurations are used [21–24]. All average values reported here are indeed statistically converged.

2. Theoretical methods

Standard Monte Carlo metropolis [28,29] simulation is carried out to generate the structures of liquid acetonitrile. The isobaric–isothermal ensemble (*NpT*) has been used and, as usual, periodic boundary conditions with the minimum image method in a cubic box are used. The simulation is performed with the DICE program [30] for a system consisting of 500 acetonitrile molecules at temperature of 298 K and pressure of 1 atm. The acetonitrile molecule (Fig. 1) is modeled by a six-site potential with parameters for the methyl hydrogen and carbon atoms, and the cyanide carbon and nitrogen atoms. This all-atom model was developed by Böhm et al. [16] to simulate liquid acetonitrile. The interactions are described by the 6-12-1 potential composed of the usual Lennard–Jones 6-12 function and the Coulomb interaction.

The simulation consists of a thermalization stage of 2.0×10^7 MC steps, followed by an averaging stage of 5.0×10^7 MC steps. The calculated average density is $\rho = 0.788$ g/cm^3, compared with the available experi-
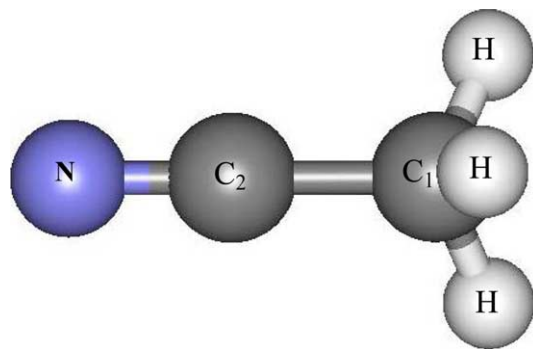
Table 1
Intermolecular potential [16] used for acetonitrile (see Fig. 1)

Sites	ε (kcal/mol)	σ (Å)	q (|e|)
C_1	0.0998	3.0	−0.577
C_2	0.0998	3.4	0.488
N	0.0998	3.3	−0.514
H	0.0200	2.2	0.201
Bonds	r (Å)	Angles	θ (°)
C_1–H	1.087	H–C_1–C_2	109.8
C_1–C_2	1.460	–	–
C_2–N	1.170	–	–
H–H	1.771	–	–

mental density of 0.777 g/cm^3 (see [10]). The cubic box has a size of $L = 34.3$ Å. The intermolecular interactions are spherically truncated within a center of mass separation smaller than the cutoff radius, $R_c = L/2$. As in our previous study [4], long-range corrections have been calculated beyond this cutoff distance [29]. In this simulation, the acetonitrile molecules are kept in rigid [16] geometry (Table 1).

The quantum mechanical calculations are performed at the second-order Møller–Plesset perturbation (MP2) [26] and density functional (B3PW91) [27] theories, implemented in the GAUSSIAN 98 program [31]. We use only augmented correlation-consistent basis sets, aug-cc-pVXZ (X = D, T, Q). The choice for these theoretical methods is based upon our previous experience on the dipole moment of water [4]. The QM calculations are carried out on the structures generated by the MC simulation. We systematically vary the number of molecules in each super molecular cluster, using the center-of-mass radial distribution function. We separated the structures composed of a central acetonitrile molecule and 12, 30, 70, 175, and 253 acetonitrile molecules. These correspond, respectively, to including all acetonitrile molecules within the solvation radius of 4.35, 6.30, 9.00, 13.00, and 15.00 Å. After calculating the auto-correlation function of the energy [20–24,32], we separated 50 configurations with less than 15% of statistical correlation. The QM calculations are then performed on these structures composed of the central acetonitrile molecule and all others within a given solvation shell, these represented by point-charges [16].

3. Results and discussion

3.1. Dipole moments

The calculated dipole moments for isolated acetonitrile are given in the first numerical entry of Table 2 at different levels of quantum mechanics theory. Experimental studies in the gas phase have predicted a dipole moment of 3.92 D [33] and 3.95 D [34]. Our calculated

Fig. 1. The acetonitrile molecule and definition of the atomic indices used in Table 1.

MP2/aug-cc-pVXZ (X = D, T, Q) dipole moments are, respectively, 3.93, 3.94 and 3.95 D, in excellent agreement with these experimental results. On the other hand, the B3PW91 calculations using different augmented correlation-consistent basis sets give slightly larger values, in a range between 4.06 and 4.07 D. In a previous study, for the liquid water [4], the B3PW91/aug-cc-pVDZ and MP2/aug-cc-pVDZ methods have given values in accordance with the experimental result of water. Again, the MP2/aug-cc-pVDZ can be considered a very good theoretical model for investigating the dipole moment of acetonitrile in the liquid phase. To alleviate on the computational demand the MP2/aug-cc-pVXZ method is used only for X = D and T.

Now we will consider the calculated dipole moment for the liquid acetonitrile. Our results, reported on Table 2, were obtained using both MP2 and B3PW91. Each value of the dipole moment for the liquid phase was obtained by performing an average over 50 QM calculations on the structures sampled from the MC simulation. A total of 500 QM calculations were performed at the MP2 and 750 at the B3PW91 levels, giving 1250 QM calculations in total. Using the largest structure composed of the central acetonitrile surround by 253 acetonitrile model molecules (represented by point-charges), we obtained a dipole moment of 4.651 ± 0.189 D at the MP2/aug-cc-pVTZ level, in agreement with the experimental estimate of 4.5 ± 0.1 D [15]. We note that the MP2/aug-cc-pVDZ method also gives good results. In general, the results have shown a good

convergence with the basis set size. Considering the B3PW91 results using the aug-cc-pVXZ (X = D, T, Q) for 1 + 253 molecules the dipole moment is a stable result near 4.81 D.

3.2. Induced dipole moment

To investigate the polarization effects of liquid acetonitrile, it is more interesting to analyze the calculated gas-to-liquid changes. Table 3 gives this induced dipole moment for the different cluster sizes containing $1 + N$ molecules. For this quantity, both MP2 and B3PW91 yield equivalent numerical results but the latter giving systematically larger values. The difference is, however, less than 0.04 D, which is within the statistical error. Also, the use of different basis sets, have only a mild effect in the dipole moment. Using MP2 and B3PW91, with the aug-cc-pVTZ basis set in the largest (1 + 253) structures, the dipole moment increase is 0.709 ± 0.189 and 0.745 ± 0.198 D, respectively. Using all theoretical models, we find that there is essentially an increase in the dipole moment by ~18% relative to the isolated dipole moment. This indicates a moderate polarization effect of the acetonitrile molecule if one compares to the enhancement of the dipole moment in liquid water (~40%) [4]. Density functional theory studies for acetonitrile geometry-optimized clusters [13] have shown that small aggregates lead to a polarization effect of about 16%. Taking into account the average changes in the dipole moment for the small clusters, 1 + 30 molecules,

Table 2
Comparison of the calculated dipole moments (D) using MP2 and DFT methods for different structures of acetonitrile

Method	Structures					
	1	1 + 12	1 + 30	1 + 70	1 + 175	1 + 253
MP2/aug-cc-pVDZ	3.931	4.578 ± 0.259	4.564 ± 0.216	4.608 ± 0.195	4.630 ± 0.193	4.639 ± 0.189
MP2/aug-cc-pVTZ	3.942	4.590 ± 0.259	4.576 ± 0.216	4.620 ± 0.196	4.642 ± 0.193	4.651 ± 0.189
B3PW91/aug-cc-pVDZ	4.063	4.744 ± 0.272	4.729 ± 0.226	4.775 ± 0.205	4.799 ± 0.203	4.808 ± 0.199
B3PW91/aug-cc-pVTZ	4.063	4.744 ± 0.270	4.730 ± 0.225	4.776 ± 0.204	4.799 ± 0.202	4.809 ± 0.198
B3PW91/aug-cc-pVQZ	4.070	4.743 ± 0.271	4.728 ± 0.225	4.774 ± 0.204	4.798 ± 0.202	4.817 ± 0.198

The dipole moments correspond to averages over 50 QM calculations using uncorrelated structures generated by MC simulation. Values are given as $\langle\mu\rangle \pm \sigma$, where $\langle\mu\rangle$ is the average dipole moment of the configuration and σ is the standard deviation.

Table 3
Calculated changes in the dipole moment (D) using MP2 and DFT methods for different radii (in Å)

Radius	Cluster	MP2		B3PW91		
		aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
4.35	1 + 12	0.647 ± 0.259	0.648 ± 0.259	0.681 ± 0.272	0.681 ± 0.270	0.673 ± 0.271
6.30	1 + 30	0.633 ± 0.216	0.634 ± 0.219	0.667 ± 0.226	0.667 ± 0.225	0.658 ± 0.225
9.00	1 + 70	0.677 ± 0.195	0.677 ± 0.196	0.712 ± 0.205	0.712 ± 0.204	0.704 ± 0.204
13.00	1 + 175	0.699 ± 0.193	0.700 ± 0.193	0.736 ± 0.203	0.736 ± 202	0.727 ± 0.202
15.00	1 + 253	0.708 ± 0.189	0.709 ± 0.189	0.745 ± 0.199	0.745 ± 0.198	0.747 ± 0.198

Values are given as average gas-to-liquid dipole moment change, $\langle\Delta\mu\rangle \pm \sigma$, where σ is the standard deviation.

for example, we have also obtained an increase of ~16%. This agreement seems to indicate that most of the polarization effects are already obtained with calculations in small aggregates. However, it is worthwhile to observe that the results reported in Tables 2 and 3 also show that electronic polarization effects leading to increased dipoles in the liquid involves the contribution from acetonitrile molecules beyond the first solvation shells. Therefore, reliable estimates of polarization effects in *liquid* acetonitrile should include these contributions.
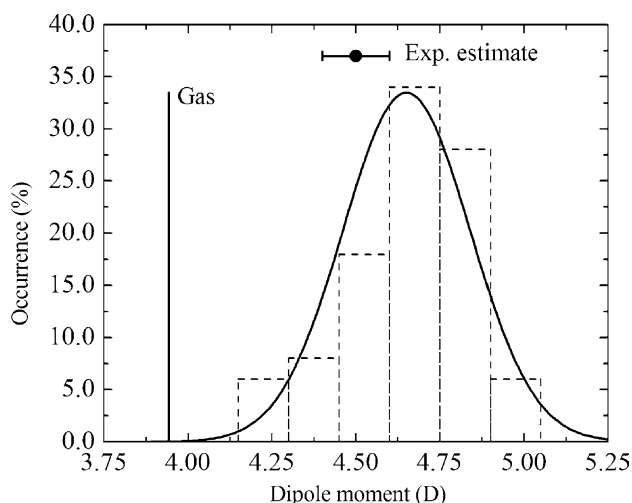

Fig. 2. Statistical distribution of calculated dipole moments of acetonitrile. Results obtained using MP2/aug-cc-pVTZ calculations in the largest structure considered (1 + 253). Also shown are the gas phase calculated value and the experimentally inferred value.
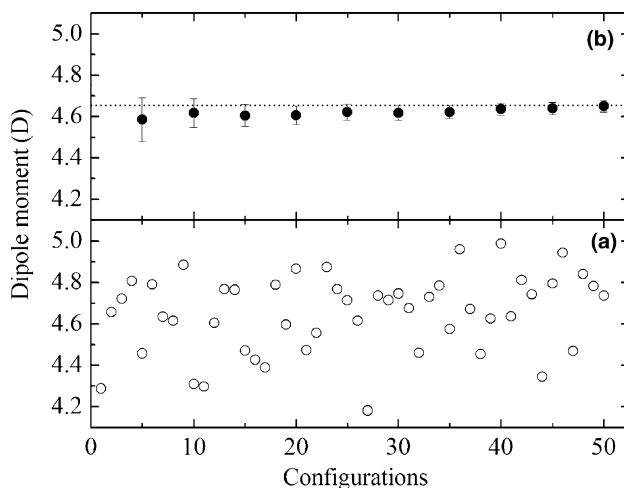

Fig. 3. Statistical convergence of the calculated dipole moment of liquid acetonitrile. Individually calculated values (a) and accumulated average (b) with statistical error are shown. Results obtained using MP2/aug-cc-pVTZ calculations in the largest structure considered (1 + 253).

Before concluding, we analyze the statistical data. In Fig. 2, we show the statistical distribution of the calculated dipole moments obtained with the largest structure in the MP2/aug-cc-pVTZ level. For comparison, the gas phase and the experimentally estimated values are also shown. Finally, Fig. 3 demonstrates the statistical convergence.

4. Summary and conclusions

The gas-to-liquid increase in the dipole moment of acetonitrile is obtained using quantum mechanical calculations on structures generated by Monte Carlo simulation of liquid acetonitrile at normal conditions. Convergence is analyzed both for the statistical averages, the theoretical quantum mechanics model and the number of molecules included. At the highest level considered here, the dipole moment of liquid acetonitrile is calculated as 4.65 ± 0.19 D in agreement with an early experimental prediction of 4.5 ± 0.1 D. This result corresponds to an increase of 0.71 ± 0.19 D in going from the gas to the liquid state.

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