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Electronic polarization of liquid water: converged Monte Carlo-quantum mechanics results for the multipole moments

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Abstract

Sequential Monte Carlo/Quantum Mechanical (S-MC/QM) calculations of the dipole moment of liquid water using extensive and different quantum chemical methods and statistically converged results give an induced dipole moment of 0.74 ± 0.14 D. This corresponds to a dipole moment of liquid water of 2.60 ± 0.14 D, in excellent agreement with the value derived from the dielectric constant and other previous theoretical estimates. Change in multipole moments are also reported using statistically converged MP2/aug-cc-pVQZ calculations.
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1. Introduction

Water is the natural biological solvent and for this, and many other reasons, an essential liquid. One of the most important aspects of water is its great ability to form hydrogen bonds. Another, equally important, is its very high polarization that gives to water its excellent solvent ability [1]. It is expected that the dipole moment of liquid water considerably increases in the liquid as compared to the gas phase. This increase is very important to understand the large dielectric constant of water. Theoretical estimates [2–15] predict this increase to

lie between 15% and 60%. Although the experimental measurement of the dipole moment in liquid water is not possible, the precise value of this dipole moment is a true theoretical challenge and has attracted so much attention [2–17]. Whereas in the gas phase the dipole moment of water has a conclusive value of 1.855 D [18], in the liquid phase its precise dipole moment value has been subjected to some debate. Several previous [2–15] theoretical studies have predicted dipole changes from 0.3 D to a larger change of 1.1 D in going from the gas to the liquid phase. Recent estimates include the ab initio second-order result by Tu and Laaksonen [12] of 2.65 D for the dipole moment of liquid water. Chalmet and Ruiz-López [10] used combined discrete-continuum theories and gave an estimate of increase of 0.8–0.84 D. However,

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Silvestrelli and Parrinello [6] estimated a very large change leading to a value of 3.0 D. There are two aspects related to large values for the dipole moment of the liquid. First, it corresponds to a considerable polarization of the electronic structure that is not accounted for by the best-used conventional force-field potentials [19]. Second, such a large value considerably overestimates the dielectric constant of water. Indeed, for its well-known value ($\varepsilon = 78.3$) it would correspond a dipole moment of water of about 2.6 D [20]. Using cluster-optimized structures including hexamer clusters, Gregory et al. [8] obtained a dipole moment of 2.7 D for water, with an induction form gas-to-liquid of 0.6 D. Recent Molecular Dynamics studies using a polarizable potential [9] suggested a dipole moment close to 2.95 D for the liquid phase. The most recent calculation has been made by Poulsen et al. [14]. Using MCSCF calculations on molecular dynamics structures they obtained a dipole moment of 2.71 D, corresponding to an induced dipole moment of 0.81 D.

In the crystalline phase, the dipole moment has also been of interest. An early and pioneering estimate of the dipole moment of water in the most common phase of ice (Ih) using multipole expansion obtained the result of 2.6 D [13]. Batista et al. [17] have more recently revised the multipole moments using both experimental (dipole and quadrupole) and theoretical (octapole and hexadecapole) moments and obtained a considerably larger value of 3.09 D for this crystalline phase.

Experimentally, only indirect results can be obtained. Experimental studies using X-ray and synchrotron radiation have estimated [21] the charge transfer involved in the OH bond. From this, a value of 2.9 ± 0.6 D has been inferred for the dipole moment in the liquid, a value close to the largest theoretical estimates, but with a very large error bar. Different methods have been used leading to different results for the dipole moment of water. Most of the discrepancy is related to the natural uncertainty associated to the complex and disordered liquid phase. In several previous studies it became clear that cluster or even microsolvation models cannot describe in general the liquid properties [22,23]. A liquid is statistical by nature

and its structure does not correspond to a minimum-energy configuration. The proper description of the liquid state needs a statistical procedure.

In this Letter, we use the sequential Monte Carlo Quantum Mechanics (S-MC/QM) methodology [24,25], with ab initio calculations performed on structures generated by MC simulations to give what we believe is the most consistent value for the dipole moment of liquid water. A strong point here is that statistical convergence is assured by using an efficient sampling technique. Quantum mechanics convergence is also analyzed by considering the role of basis set size and electron correlation effects. In addition, we also analyze the convergence of the results with the total number of polarizing molecules included in the calculations. Our converged value gives an induced dipole moment of 0.74 ± 0.14 D, leading to a dipole moment of liquid water corresponding to 2.60 ± 0.14 D, a value that confirms the correspondence between the known dielectric constant of water and the dipole moment of the liquid at room temperature.

2. Theoretical methodology

Monte Carlo simulations are carried out employing standard procedures [26], including the Metropolis sampling technique and periodic boundary conditions using the minimum image method in a cubic box. The simulations are performed in the NPT ensemble. The total system consists of 450 water molecules at temperature of 298.15 K and pressure of 1 atm. The intermolecular interactions are described by the standard Lennard–Jones plus Coulomb potential with three parameters for each site i (ε_i, σ_i and q_i). For the water molecules we use the recent TIP5P potential [27], which predicts structural and thermodynamic properties of liquid water in very good agreement with experiment. In addition, this model is able to reproduce the water density anomaly close to 4 °C. The effective dipole moment of the TIP5P water molecule is 2.29 D, which is lower than most of the theoretical predictions. The MP2/aug-cc-pVQZ result for the gas phase dipole of the TIP5P water molecule is 1.857 D, in excellent agreement with the experimental value (1.855 D), leading credence

to the choice of the TIP5P geometry as the reference geometry in the present calculations.

In the simulation, the averaged density was found as $\rho = 1.07$ g/cm^3 what leads, in average, to a cubic box of length $L = 23.25$ Å. The intermolecular interactions are spherically truncated within a center of mass separation smaller than the cutoff radius, $r_C = L/2$. Long-range corrections were calculated beyond this cutoff distance. The Lennard–Jones potential contribution is estimated assuming an uniform distribution $G(r) \approx 1$ after the cutoff radius and the electrostatic potential contribution is estimated with the reaction field method of the dipolar interaction. In the simulation the molecules are kept with rigid geometries. The water molecules are kept in their C_{2v} structure with $r_{OH} = 0.9572$ Å and $\angle HOH = 104.52°$. The initial configurations are generated randomly, considering the position and orientation of each molecule. A new configuration is generated after randomly attempt to translate in all Cartesian directions and also attempt to rotate around a randomly chosen axis. The simulations consist of a thermalization phase of 2×10^6 MC steps, followed by an averaging stage of 45×10^6 MC steps. To analyze the electronic structure of liquid water we employ the S-MC/QM procedure [24,25]. The quantum mechanical calculations are performed on the super-molecular structures, generated by the MC simulations, composed of a central water molecule and all TIP5P water molecules within a particular solvation shell. The great advantage of the sequential procedure of the S-MC/QM is that all the important MC statistical informations are available before running into the QM calculations. This considerably reduces the number of super-molecular structures that will be submitted for the quantum mechanical calculations, because the configurations are selected according to their statistical correlation, obtained from the auto-correlation function of the energy [11,28–30]. Using a correlation step of 9×10^5, we separate a total of 50 configurations, with less than 15% of statistical correlation. These 50 structures are used in the quantum mechanical calculations. As we shall demonstrate the selection of these structures does not compromise the statistical average and all results presented here are statistically converged. On

the other hand, this number of QM calculations is still tractable so that several theoretical models and basis sets can be used. The solvation shells were defined from the analysis of the radial distribution function. The electronic structure of each super-molecular structure is then calculated using ab initio methods implemented in the GAUSSIAN 98 [31] program. The quantum mechanical theoretical methods include the second-order MP2 with correlation consistent basis sets such as aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ. In all cases we use 6-component d-type functions. In specific cases other theoretical models such as MP4 and CCD are used. It is important to mention that only size-extensive methods are used. As the appropriate Boltzmann weights are included in the Metropolis MC sampling technique, the average value of the dipole moment is the result of a simple average over 50 uncorrelated configurations. The use of the auto-correlation function of the energy for selecting configurations has been shown before to be an efficient procedure for obtaining converged average values [11,22,28]. All simulation are performed with the DICE [32] MC statistical mechanics program. DICE is a general program for MC simulation with a graphical interface that calculates thermodynamic properties and generates structures for use in most conventional quantum chemistry program.

Using the radial distribution function we separated super-molecular structures composed of the central water molecule and 46, 76, 120, 175 and 230 water molecules with the geometry and charge distribution of the TIP5P model. These will be referred to as 1 + 46 TIP5P, 1 + 76 TIP5P, 1 + 120 TIP5P, 1 + 175 TIP5P and 1 + 230 TIP5P, respectively. These correspond to including all water molecules within the solvation radius of 6.75, 7.95, 9.25, 10.50 and 11.50 Å. In addition, we have also recalculated the electrostatic charges in the same atomic sites of the water molecules using the CHELPG procedure [33] to analyze the role of the relaxation of the surrounding charges [15]. This demands QM calculations that include all water molecules and it is then limited to the 1 + 46 water cluster. The 50 QM calculations of the 47-water system were restricted to the B3PW91/6-31G(d). After these, the CHELPG charges were obtained

at the atomic positions of the non-central 46 molecules. The best results obtained here use averages of 50 QM calculations at the B3PW91/aug-cc-pVQZ and MP2/aug-cc-pVQZ levels using 1 + 230 TIP5P structures.

3. Results and discussions

3.1. Calculated dipole moments

Before discussing the results for the dipole moment of liquid water it is important to analyze the performance of the different theoretical models for the dipole moment of gas phase water. Table 1 shows some of the results obtained using several theoretical methods compared to the experimental value of 1.855 D. As it can be seen, some methods give gas phase dipole moments that are considerably larger than experiment. This indicates that the estimated dipole moment of liquid water using these methods will give artificially larger results and it is the change in the value of the dipole moment from gas-to-liquid that should be investigated.

Considerably large values are obtained with all methods, including density-functional methods, when small basis sets are used. For instance, the gas

phase dipole obtained using the HF/6-31++G(d,p) is 2.286 D, already 0.43 larger than the experimental value. Correlated calculations using small basis sets, even if they include both diffuse and polarization functions, do not give good results. The MP2/6-31++G(d,p), B3PW91/6-31++G(d,p) and the CCD/6-31++G(d,p) give dipole moments that are too large by 0.47, 0.35 and 0.36 D, respectively. The results of Table 1 show, however, that augmented correlation-consistent basis sets give considerably improved results. The B3PW91/aug-cc-pVDZ and MP2/aug-cc-pVDZ give dipole moments of 1.855 and 1.861 D in very good agreement with the experimental result. Including the core electrons in the MP2/aug-cc-pVDZ correlation treatment leads to only a minor change (0.002 D) and will not be further considered. Interesting, as it can be noted the CCD/aug-cc-pVDZ result (1.875 D) is not very much different from the MP2/aug-cc-pVDZ prediction indicating that high-order electron correlation effects are not crucial. Comparison of the results obtained with the aug-cc-pVDZ basis set in the MP2, DQ, SDQ and CCD models shows the systematic participation of the electron correlation effects on the dipole moment. Although double- and quadruple-substitution in fourth-order, DQMP4, increases the dipole moment compared to MP2 by 0.014 D the CCD model gives the same result, indicating that most of the high-order correlation is obtained in fourth-order. The results obtained with the MP2/aug-cc-pVTZ model can be considered very good, but our best theoretical results for the gas phase dipole moment are obtained with B3PW91/aug-cc-pVDZ and MP2/aug-cc-pVQZ leading to the results of 1.855 and 1.857 D, in excellent agreement with the experimental result of 1.855 D.

Now we turn to the calculated dipole moments of the liquid phase. These results are also obtained using several theoretical models and in each case the reported value is an average of 50 quantum mechanical calculations performed on the structures generated by the MC simulation. Thus, in total 1950 QM calculations have been performed. It would be much too cumbersome to report all cases and clearly some theoretical models are inadequate to give a reliable estimate of the dipole moment of water, as discussed before. However

Table 1
Calculated dipole moment (in Debye) for the water TIP5P molecule using different theoretical models in the gas phase

Method	Dipole moment (D)
HF/6-31++G(d,p)	2.286
B3PW91/6-31++G(d,p)	2.206
B3LYP/6-31++G(d,p)	2.201
B3PW91/aug-cc-pVDZ	1.855
B3PW91/aug-cc-pVTZ	1.848
B3PW91/aug-cc-pVQZ	1.846
MP2/6-31++G(d,p)	2.321
CCD/6-31++G(d,p)	2.218
MP2/aug-cc-pVDZ	1.861
MP2/aug-cc-pVTZ	1.850
MP2/aug-cc-pVQZ	1.857
DQ-MP4/aug-cc-pVDZ	1.875
SDQ/aug-cc-pVDZ	1.858
CCD/aug-cc-pVDZ	1.875
CCD/aug-cc-pVTZ	1.871
Experiment [18]	1.855

they are considered because they allow a systematic analysis of the correlation, basis sets and configuration size effect. In these cases only the gas-to-liquid dipole change is relevant. For instance, the HF/6-31++G(d,p) gives a gas phase dipole moment of 2.29 D which is a considerably large value compared to the experimental result of 1.86 D, but the induction in the dipole moment is less than 0.40 D. Including electron correlation effects at the second-order, MP2, does not improve much, increasing the induction to ∼0.50 D. Table 2 shows a short sample of the results for a brief analysis of the correlation effects. First, one may note that the use of the CHELPG charges

systematically decreases the calculated induced dipole moment. This decrease, however, is not appreciable. For the MP2/aug-cc-pVDZ this reduction is found to be 0.016 D. Similar result of 0.015 D is found in the SDQ-MP4 model. Using the MP2/aug-cc-pVTZ this difference is reduced to 0.007 D. The results obtained using the aug-cc-pVDZ allow an analysis of the electron correlation effects. At the MP2 level, using the 1 + 76 TIP5P model, we find that double- and quadruple-substitutions decrease the induced dipole moment by 0.014 D and further considering the higher-order double and quadruple substitutions as obtained by CCD we find only a variation of 0.002 D, thus indicating that high-order excitations give a negligible contribution to the dipole moment in the liquid phase as discussed before for the gas phase also. Indeed the MP2 and CCD results are very similar leading to an induced dipole moment of 0.57 and 0.56 D, respectively. Competitive numerical results are obtained with the B3PW91 and MP2 using aug-cc-pVXZ, with X = D, T, and Q (Table 3). The results show a good convergence with the basis set size. The difference between the MP2 results with the X = T and X = Q for the 1 + 175 TIP5P model, for instance, is only 0.008 D, which is smaller than the statistical error of 0.020 D. Increasing the cluster size to 1 + 230 TIP5P gives this same change of 0.008 D. It is interesting to note the similarities between the results obtained for the MP2 and B3PW91 methods. At this stage the best theoretical result obtained here is that using either the MP2 or B3PW91 with the aug-cc-pVQZ basis set in the largest 1 + 230

Table 2
Calculated change in dipole moment (D) using different theoretical models

Method	System	aug-cc-pVDZ
MP2	1 + 46 CHELPG	0.503 ± 0.257
	1 + 46 TIP5P	0.519 ± 0.136
	1 + 76 TIP5P	0.569 ± 0.135
	1 + 175 TIP5P	0.654 ± 0.135
	1 + 230 TIP5P	0.679 ± 0.136
DQ-MP4	1 + 76 TIP5P	0.555 ± 0.135
SDQ-MP4	1 + 46 CHELPG	0.499 ± 0.253
	1 + 46 TIP5P	0.514 ± 0.135
	1 + 76 TIP5P	0.563 ± 0.133
	1 + 175 TIP5P	0.647 ± 0.134
CCD	1 + 76 TIP5P	0.557 ± 0.134

Each entry is an average of 50 QM calculations using uncorrelated structures of the MC simulation. Values shown are the gas-to-liquid dipole change $\langle \Delta\mu \rangle \pm \sigma$, where σ is the standard deviation.

Table 3
Calculated change in dipole moment (D) using second-order MP2 and density functional methods

System 1 water +	Radius (Å)	Method	Basis set			
			6-31++G(d,p)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
46 CHELPG	6.75	MP2	0.296 ± 0.191	0.503 ± 0.257	0.526 ± 0.274	0.529 ± 0.283
46 TIP5P	6.75	MP2	0.313 ± 0.103	0.519 ± 0.136	0.533 ± 0.140	0.539 ± 0.142
76 TIP5P	7.95	MP2	0.348 ± 0.102	0.569 ± 0.135	0.586 ± 0.139	0.592 ± 0.142
120 TIP5P	9.25	MP2	0.383 ± 0.101	0.618 ± 0.133	0.639 ± 0.138	0.646 ± 0.142
175 TIP5P	10.50	MP2	0.432 ± 0.103	0.654 ± 0.135	0.676 ± 0.140	0.684 ± 0.142
230 TIP5P	11.50	MP2	0.425 ± 0.104	0.679 ± 0.136	0.702 ± 0.141	0.710 ± 0.142
230 TIP5P	11.50	B3PW91	0.518 ± 0.105	0.684 ± 0.137	0.702 ± 0.141	0.711 ± 0.142

Each entry is an average of 50 QM calculations using uncorrelated structures of the MC simulation. Values shown are the gas-to-liquid dipole change $\langle \Delta\mu \rangle \pm \sigma$, where σ is the standard deviation.

TIP5P model that leads to a dipole moment increase of 0.710 ± 0.142 D, representing a total dipole moment of liquid water of 2.567 D.

3.2. Extrapolation and statistical convergence

The sampling of configurations from statistical simulations is crucial for the efficiency of QM/MM methods. Instead of performing quantum mechanical calculations on all the configurations generated by the MC simulation, we use the interval of statistical correlation, to select configurations that give relevant statistical information. We have shown previously that the average over all successive configurations generated in the MC simulation, gives the same result as averaging over only a few statistically uncorrelated configurations [28]. This very efficient way to sample configurations gives statistically converged results. This is one of the advantages of the sequential procedure of the S-MC/QM, in that all the important MC statistical information are available before running into the QM calculations. As in previous works [11,22,28–30] we calculate the auto-correlation function of the energy. Here we select one configuration in each 9×10^5 MC steps and use them to perform QM calculations. This assures that the structures used in the quantum mechanical calculations are statistically relevant and converged values are obtained, as it will be demonstrated below. As the total number of MC steps in the simulation was 45×10^6, the averages, including the quantum mechanical calculations, are then taken over 50 uncorrelated configurations, as discussed before.

As each entry in the Tables 2 and 3 is the result of an average over 50 quantum mechanical calculations on the structures sampled from the MC simulation, it is of great importance to analyze the statistical convergence. Using the MP2/aug-cc-pVQZ in the 1 + 175 TIP5P model as an example, we obtained an average dipole moment of 2.541 ± 0.142 D (induced dipole of 0.684 ± 0.142 D). Fig. 1 shows the histogram of these calculated values. Note that 68% of the calculated dipoles are within the range of 2.40 and 2.68 D, corresponding to the limits of $\langle \Delta\mu \rangle \pm \sigma$. Using the histogram data we convoluted a gaussian curve using Eq. (1),
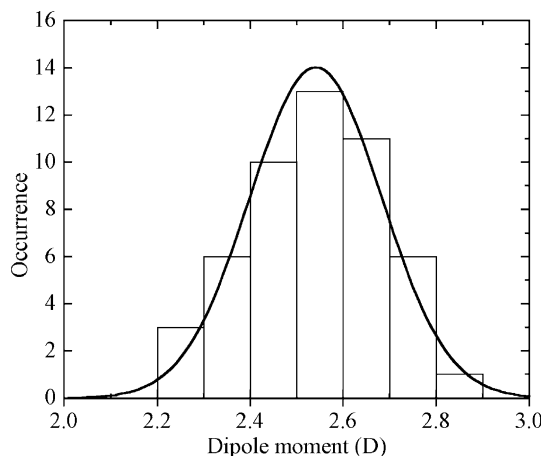

Fig. 1. Histogram of the calculated dipole moments using MP2/aug-cc-pVQZ and the 1 + 175 TIP5P structures obtained from the MC simulation.

$$D(x) = \frac{\exp\left[-(x-\mu)^2/2\sigma^2\right]}{\sqrt{2\pi\sigma^2}} \tag{1}$$

and the calculated average value $\mu = 2.541$ D and the standard deviation $\sigma = 0.142$ D. Note that this is not a best-fit but a two-parameter (μ and σ) gaussian function. The results in Fig. 1 show the excellent distribution of the calculated data points. In complement, Fig. 2 shows the systematic convergence of our best result obtained now with the MP2/aug-cc-pVQZ in the 1 + 230 TIP5P result. As
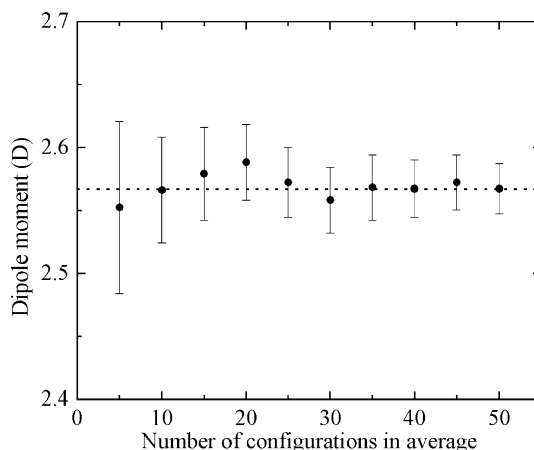

Fig. 2. Convergence of the calculated dipole moment. Illustration is for the MP2/aug-cc-pVQZ using the 1 + 230 TIP5P structures. Error bar represents the statistical error.

can be seen, the convergence is very fast and the use of only 35 configurations is sufficient to give statistically converged result. This is a consequence of the efficient sampling procedure [11,28,30] and similar convergence has been obtained in other previous applications [11,22,28–30]. Fig. 2 also shows that even using this efficient sampling technique the use of only 20 configurations does not lead to a converged result. Tu and Laaksonen [12] have recently used both a cluster model and a molecular dynamics approach to estimate the dipole moment of water in the liquid state at room temperature. The results from the combined molecular dynamics using TIP3P potential and MP2 with large basis set calculations using an average of 20 configurations is 2.65 D, corresponding to an induced moment of 0.77 D. Note that with the same number of configurations we obtained a similar result (Fig. 2). Increasing the number of configurations to the convergence limit decreases this value slightly.

The results of Table 3 indicate that there is a large polarization in liquid water with molecules as far as 10 Å still affecting the calculated dipole. We now focus in the change of the MP2/aug-cc-pVQZ results with the number of polarizing molecules. In the largest system, $1 + 230$ TIP5P model, the calculated induced dipole value is 0.710 D which is 0.026 D larger than in the preceding $1 + 175$ TIP5P model. This increase in value is only slightly larger than the calculated statistical error of 0.020 D. Extrapolating the results to the bulk (Fig. 3) yields a value of 0.74 D, which is now our best estimate corresponding to a statistically converged result for the dipole moment of liquid water of 2.60 ± 0.14 D.

3.3. Quadrupole and octapole moments

Table 4 shows the calculated results for the changes in the quadrupole and octapole moments using the MP2/ aug-cc-pVQZ method. As before, the multipole moments are calculated for the central water molecule surrounded by TIP5P charges using the configurations generated by the MC simulation. Contrary to the case of the dipole moment we find a reasonably fast convergence of the quadrupole moment. The results shown in
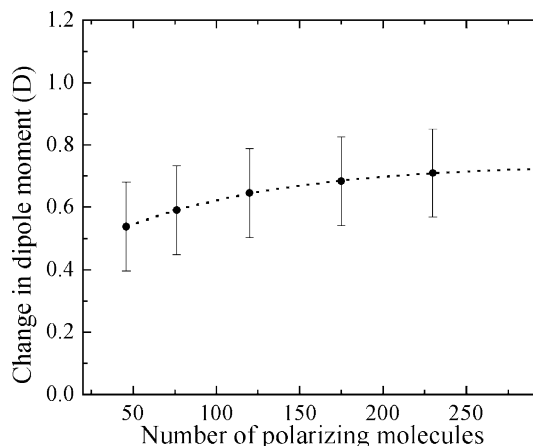

Fig. 3. Extrapolation of the induced dipole moment as a function of the super-molecular size. Each entry represents an average of 50 QM calculations. Results are $\langle \Delta \mu \rangle \pm \sigma$.

Table 4 with the MP2/aug-cc-pVQZ in the $1 + 230$ TIP5P model are the same as those obtained with smaller systems as in the $1 + 176$ TIP5P model or with a smaller basis set as in the MP2/aug-cc-pVTZ. The results for the quadrupole moments are in very good agreement with those obtained previously [12,17]. Quadrupole moments of polar molecules depend on the choice of origin. We chose the origin at the center of mass, similar to Batista et al. [17] but different from Tu and Laaksonen [12], so our results differ slightly with respect to the component along the C_2-axis that corresponds here to the yy component. In general, the results are in good agreement among one another. Quadrupole moment is obtained from the calculated $\langle xx \rangle$, $\langle yy \rangle$ and $\langle zz \rangle$ values using $Q_{jj} = (3jj - r^2)/2$. The results are also shown in Table 4. It is instructive to see the changes in the quadrupole moment upon the change of phase gas-to-liquid. For comparison, we also show the results of Batista et al. [17] for the geometry optimized gas phase water and the experimental gas phase result [34]. Fig. 4 shows the statistical convergence of the quadrupole moments of liquid water as calculated here.

The octapole moments of water have been considered by Batista et al. [17] to be used in their multipole studies of ice Ih, but these moments for liquid water have not been the subject of attention so we give also in Table 4 the calculated results for

Table 4
Calculated quadrupole and octapole moments of liquid water using the 1 + 230 TIP5P model

Quadrupole moment	$\langle xx \rangle$	$\langle yy \rangle$	$\langle zz \rangle$
Liquid (1 + 230 TIP5P)	-4.20 ± 0.06	-6.48 ± 0.04	-7.95 ± 0.06
Gas (TIP5P)	-4.42	-6.46	-7.82
Liquid [12]	-4.27 ± 0.07	-5.94 ± 0.06	-7.99 ± 0.06
Gas (TIP3P) [12]	-4.55	-6.08	-7.95
	$\langle Q_{xx} \rangle$	$\langle Q_{yy} \rangle$	$\langle Q_{zz} \rangle$
Liquid (1 + 230 TIP5P)	3.01 ± 0.08	-0.41 ± 0.07	-2.61 ± 0.08
Gas (TIP5P)	2.72	-0.34	-2.38
Gas (optimized) [17]	2.61	-0.13	-2.48
Gas (experiment) [34]	2.63	-0.13	-2.50
Octapole moment	$\langle xxy \rangle$	$\langle yzz \rangle$	$\langle yyy \rangle$
Liquid	-1.754 ± 0.08	-0.554 ± 0.07	-1.981 ± 0.20
Gas (TIP5P)	-1.325	-0.192	-0.956

Every entry is the average of 50 QM calculations at the MP2/aug-cc-pVQZ. For comparison, the result for isolated (gas) molecule is also shown. All calculations (except that of [12]) use the origin of the coordinate system at the center of mass of the molecule with the y-coordinate as the long C_{2v} axis, and the molecule in the xy-plane. Unit is Debye–Angstrom. Also shown is the experimental result of gas phase and some previous theoretical results.
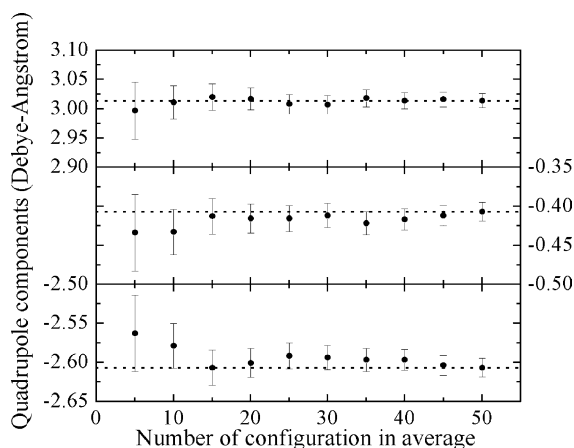

Fig. 4. Convergence of the calculated quadrupole moment components using MP2/aug-cc-pVQZ and the 1 + 230 TIP5P structures obtained from the MC simulation.

the non-zero components $\langle xxy \rangle$, $\langle yzz \rangle$ and $\langle yyy \rangle$ both for the gas and liquid water.

4. Summary and conclusions

From the ab initio and statistical mechanics analysis presented in this Letter we obtain that the induction of the dipole moment upon changing from the gas phase to liquid water at room tem-perature is 0.74 ± 0.14 D. This value is predicted by statistically converged MP2/aug-cc-pVQZ cal-culations using structures generated by MC sim-ulation and the TIP5P potential for water. The influence of other interactions than the coulombic considered here, has been briefly discussed [12] and it has been argued that these are small. Another point to be considered here is the change of ge-ometry of water in the liquid phase. As hydrogen bonds are involved it is expected that the OH distances of the central molecule should slightly increase. This increase has been estimated previ-ously [6,10] to be within 0.002 and 0.013 Å, with large statistical errors. Slight change in the water geometry by increasing both OH distances by 0.01 Å in the MP2/aug-cc-pVDZ level has led to an increase in the dipole moment by only 0.005 D (from 1.861 to 1.866 D). Thus the geometry change will not affect the induced dipole by an appreciable amount. Considering the standard deviation, the largest induction calculated here is of 0.88 D. Hence, we contend that liquid water has an upper bound for the dipole moment of 2.74 D. Our best result gives an average dipole moment value of 2.60 D in excellent agreement with the value associated to the well-known dielectric con-stant of water. This gives strong credence to the increasing consensus that the dipole moment of

liquid water at room temperature cannot be as large as 3.0 D. Changes in the quadrupole and octapole moments are additionally analyzed and they also show the effect of the polarization of liquid water as compared to gas phase.

Acknowledgements

References

[1] K.S. Davies, J.A. Day, Water, the Mirror of Science, Doubleday, New York, 1961.
[2] J. Gao, X. Xia, Science 258 (1992) 631.
[3] I. Tuñón, M.T.C. Martins-Costa, C. Millot, M.F. Ruiz-López, J.L. Rivail, J. Comp. Chem. 17 (1996) 19.
[4] B. Wei, D.R. Salahub, Chem. Phys. Lett. 224 (1994) 291.
[5] D.N. Bernardo, Y. Ding, K. Krogh-Jespersen, R.M. Levy, J. Phys. Chem. 98 (1994) 4180.
[6] P.L. Silvestrelli, M. Parrinelo, Phys. Rev. Lett. 82 (1999) 3308.
[7] Y. Tu, A. Laaksonen, J. Chem. Phys. 111 (1999) 7519.
[8] J.K. Gregory, D.C. Clary, K. Liu, M.G. Brown, R.J. Saykally, Science 275 (1997) 814.
[9] L.X. Dang, T.-M. Chang, J. Chem. Phys. 106 (1997) 8149.
[10] S. Chalmet, M.F. Ruiz-López, J. Chem. Phys. 115 (2001) 5220.
[11] W.R. Rocha, K. Coutinho, W.B. De Almeida, S. Canuto, Chem. Phys. Lett. 335 (2001) 127.
[12] Y. Tu, A. Laaksonen, Chem. Phys. Lett. 329 (2000) 283.
[13] M. Sprik, M.L. Klein, J. Chem. Phys. 89 (7558) 1988.
[14] T.D. Poulsen, P.R. Ogilby, K.V. Mikkelsen, J. Chem. Phys. 116 (2002) 3730.
[15] S. Maw, H. Sato, S. Ten-no, F. Hirata, Chem. Phys. Lett. 276 (1997) 20.
[16] C.A. Coulson, D. Eisenberg, Proc. R. Soc. London A 291 (1966) 445.
[17] E.R. Batista, S.S. Xantheas, H. Jónsson, J. Chem. Phys. 109 (1998) 4546.
[18] S.A. Clough, Y. Beers, G.P. Klein, L.S. Rothman, J. Chem. Phys. 59 (1973) 2554.
[19] A.R. Leach, Molecular Modelling. Principles and Applications, second ed., Prentice-Hall, Englewood Cliffs, NJ, 2001.
[20] K. Watanabe, M.L. Klein, Chem. Phys. 131 (1989) 157.
[21] Y.S. Badyal, M.-L. Saboungi, D.L. Price, S.D. Shastri, D.R. Haeffner, A.K. Soper, J. Chem. Phys. 112 (2000) 9206.
[22] T. Malaspina, K. Coutinho, S. Canuto, J. Chem. Phys. 117 (2002) 1692.
[23] R.C. Guedes, K. Coutinho, B.J. Costa Cabral, S. Canuto, J. Phys. Chem. B, submitted.
[24] S. Canuto, K. Coutinho, Adv. Quantum Chem. 28 (1997) 90.
[25] K. Coutinho, S. Canuto, J. Chem. Phys. 113 (2000) 9132.
[26] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1987.
[27] M.W. Mahoney, W.L. Jorgensen, J. Chem. Phys. 112 (2000) 8910.
[28] K. Coutinho, M.J. Oliveira, S. Canuto, Int. J. Quantum Chem. 66 (1998) 249.
[29] S. Canuto, K. Coutinho, Int. J. Quantum Chem. 77 (2000) 192.
[30] K. Coutinho, S. Canuto, M.C. Zerner, J. Chem. Phys. 112 (2000) 9874.
[31] M.J. Frisch et al., GAUSSIAN 98, Revision A.6, Gaussian, Pittsburgh, PA, 1998.
[32] K. Coutinho, S. Canuto;, DICE: A Monte Carlo Program for Molecular Liquid Simulation, University of São Paulo, Brazil, 1997.
[33] C.M. Breneman, K.B. Wiberg, J. Comput. Chem. 11 (1990) 361.
[34] J. Verhoeven, A. Dymanus, J. Chem. Phys. 52 (1970) 3222.