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Water dimer in liquid water

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Summary. A Self-Consistent Reaction Field Model is used to study the effect of the molecular environment on the electronic distribution and on the equilibrium geometry of the water dimer in liquid water. Computations are performed at the 6-311G++(2*d*,2*p*) MP2 level. Comparison of the results for the monomer and the dimer, in a vacuum and in the liquid, is made in order to gain a deeper insight on the cooperative phenomenon. The discussion emphasizes the trends which should be considered for deriving more sophisticated water-water potentials.

Key words: Water dimer – Self-consistent reaction field – Cooperative phenomenon – Liquid state – Water-water potential

1 Introduction

Understanding the structure and dynamics of water is crucial for all aspects of solution chemistry. Thus, a very large number of statistical mechanical models as well as computer simulation approaches have been developed. In these calculations, a pair-wise additive interaction is used in order to maintain the computational time within reasonable limits. Therefore, the potential for the water dimer plays a central role in this kind of work.

The key feature of liquid water is the ability of a molecule to form four hydrogen bonds with its nearest neighbors. There is ample experimental evidence for local tetrahedral structures in the liquid. At this point, it is necessary to emphasize a cooperative phenomenon between H bonds, which means that the strength of the H bonds depends on the number of bonds in an aggregate. It is assumed that an H bond between two water molecules polarizes both the acceptor and the donor. Consequently, a second H bond formed with a third molecule would be stronger compared with the first one. Experiments [1] demonstrate that such non-additive effects cannot be neglected at all, as some theoreticians have claimed [2–11]. One of the effects of the cooperative phenomenon is the elongation of the donor O–H groups upon formation of an O–H···O hydrogen bond. A slight elongation has been calculated for the water dimer [12] but for larger hydrogen-bonded water clusters, the elongation is more pronounced [11–13]. Then, the O–H groups in condensed media are polarizable and urge us to abandon the model of "rigid" molecules.

Energy functions to carry out Monte Carlo or Molecular Dynamics simulations fall into two main approaches: pair-wise additive and "effective" two-body interaction functions. Energy functions which are pair-wise additive (two-body potentials) are more reasonably derived from quantum chemical calculations and the work of Clementi et al. [14] is one of the major recent efforts in this direction. Far more common is the use of "effective" two-body functions, whose parameters are derived by requiring a fit to a number of liquid properties. The classic work by Rahman and Stillinger [15, 16] describes the first application of such a potential (ST2) to water using molecular dynamics, and the potentials SPC [17], SPC/E [18], BF [19], TIPS3 [20], TIPS2 [21], TIP3P and TIP4P [22] are refined versions of this approach.

The key assumption in "effective" two-body potentials is that many-body interaction energies can be incorporated into the parameters that are evaluated as two-body interaction energies. This leads to partial charges on the oxygen and hydrogen atoms that correspond to a dipole moment of the water molecule of about 2.4 D, considerably enhanced over the gas-phase value of 1.85 D. Then, the study of the water dimer using such "effective" potentials leads to equilibrium geometries with too short intermolecular distances and to overestimated stabilization energies [22]. This result is not surprising since an increase of the oxygen and hydrogen charges enhances the electrostatic interaction and owing to the fact that this term represents the main energy contribution to the total hydrogen bond energy at the equilibrium distance, then the stability of the bond is overestimated.

A quite different situation is obtained when the pair-wise potentials are fitted to *ab initio* results. Obviously, these potentials correctly describe the water dimer in the gas phase but the description of the liquid is rather poor from a quantitative point of view. In order to get accurate values for a wide spectrum of liquid water properties, it is essential to include many body-effects, which are mainly due to polarization. Three- and four-body corrections to the MCY potential [23, 24] have been proposed by Clementi's group and applications of this potential have confirmed the previous conclusion for static [23, 24] and dynamics properties [25, 26] as well. Recently, a new potential, NCC [27], has been derived from the MCY potential which explicitly incorporates many-body effects due to polarization. The reliability of this new potential in simulations of water in the gaseous and liquid phase has been tested [28, 29]. Finally, other authors [30–41] have also proposed a model of polarizable molecules in which the induced dipole moment on each molecule is treated as a separate degree of freedom, fixing the permanent dipole moment at the gas phase value.

All of the potentials mentioned, assume a fixed geometry of the water molecule. As we have already pointed out, the cooperative effect implies the non-additivity of the pair-wise potentials because of the many-body effects but due to the strengthening of the hydrogen bonds it also implies modifications of the intramolecular OH distances. Two type of flexible water-water potentials, that go beyond the rigid molecule approximation, have been employed (the BJH [42, 43] and the MCYL [44] potentials). The performances of flexible potential models to account for molecular vibrations in the liquid have been analyzed by Slanina [45].

Twenty years ago, two of us published a study on the effect of the reaction field on the water dimer by means of a continuous model using the semi-empirical CNDO method [46]. As it will be described below in the methodology section, nowadays it is possible to introduce the polarization of the solute by the reacction field at different levels of *ab initio* computations in a self-consistent way. Both, the electronic and nuclear relaxation, may be taken into account so that many-body effects are introduced. Our aim in this work is to make a detailed analysis of the effect of the polarized environment on the water dimer and monomer, and by comparison of these results to try to get a deeper insight on the cooperative phenomenon.

2 Methodology

Both, experimental [47, 48] and theoretical [12, 14, 49–53] studies, have clearly established that the equilibrium geometry of the water dimer corresponds to a nearly linear structure of the hydrogen bond with C_S symmetry represented in Fig. 1. In this paper, we shall mainly study this structure (called hereafter Dimer I) although a cis-conformation (called hereafter Dimer II), that has previously been considered in solution [46] and which is represented in Fig. 2, will be also analyzed.

The water dimer has been the subject of many previous theoretical studies. For a review, see for instance [54, 55], as well as references 6 to 80 of [45], 1 to 25 of [56] and 1 to 17 of [57]. Nevertheless, in most of these works only partial geometry optimizations have been made. As in our work we are mainly interested in the modifications of the water molecule geometry in the liquid, we have performed in all cases a complete geometry optimization.

In spite of numerous theoretical studies, there is still some controversy on the level of computation to be used in order to get quantitative and reliable results. From the analysis in [12], it appears that at least a triple-ζ basis with polarization and diffuse function is required. The authors conclude that the Hartree–Fock limiting values of the structural parameters are reached with the basis set 6-311G++(2*d*,2*p*) which will be the basis used in this work. Closely related to the choice of the basis set is the treatment of the BSSE. Usually, BSSE is solved by computation of counterpoise corrections [58] although some authors have questioned this approach [59, 60] because it tends to overestimate the BSSE. In particular, for the water dimer, some authors have claimed in favor [56, 61] or

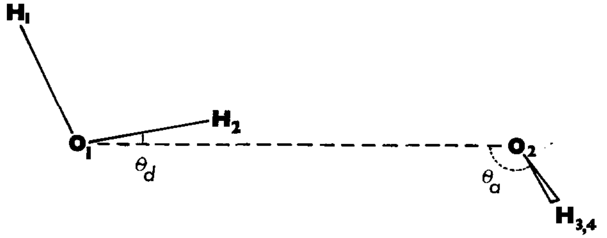

Fig. 1. Linear structure of the water dimer (Dimer I)

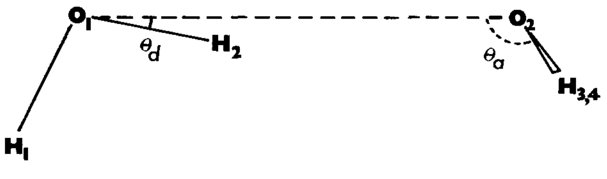

Fig. 2. *cis*-Structure of the water dimer in liquid water (Dimer II) as proposed in [46]

against [12] a counterpoise treatment of the BSSE. Some works have also studied the effect of full counterpoise corrections on the geometry of the water dimer but only a limited geometry optimization was performed [61, 62]. Considering the previous remarks and the fact that a complete geometry optimization must be performed in the present study we have not introduced counterpoise corrections.

The introduction of electron correlation on the supermolecule model may be carried out by the configuration interaction (CI) method and the many-body perturbation theory (MBPT)/coupled cluster (CC) method. CI is clearly inferior because of the lack of size extensivity, which is essential for the determination of interaction energies. The dispersion contribution to the interaction energy has been also calculated for the water dimer [63, 64] using second-order perturbation theory. In our study, both intra- and intermolecular correlation energy will be taken into account at the MP2 level which, as has been discussed in previous work [61], leads to comparable results for binding energies and equilibrium geometries that the CEPA-1 method at a substantially lower cost.

The average effect of the liquid on the electronic and nuclear structure of a particular water molecule or dimer may easily be introduced into quantum chemical computations using a cavity model. In this approach, the liquid is assimilated to a macroscopic continuum characterized by some well defined temperature dependent macroscopic quantity such as the dielectric permittivity at a given frequency. The molecule of interest is then placed in a cavity created in this dielectric continuum. The reaction of the macroscopic medium generates an electrostatic potential which may be obtained by solving Laplace equation for a multipole expansion of the electrostatic properties of the solute performed at the centre of the cavity [46, 65, 66]. The interaction of the molecule with the liquid is given by the hamiltonian:

$$\mathscr{H}_E = -\mathscr{R}_l^m \mathscr{M}_l^m \tag{1}$$

where $\mathscr{M}_l^m$ is a component of the multipole moment of order l and $\mathscr{R}_l^m$ is a component of the reaction field, i.e., the m component of the potential derivative of order l at the origin. Repeated indices stand for a sum over all their possible values: l from 0 to ∞ (in practice a good convergence is obtained for $l \simeq 6$) and m from $-l$ to $+l$. In the linear response approximation, $\mathscr{R}_l^m$ is given by:

$$\mathscr{R}_l^m = -f_{ll'}^{mm'} \mathscr{M}_{l'}^{m'} \tag{2}$$

in which the reaction field factors $f_{ll'}^{mm'}$ only depend on the dielectric properties of the medium and on the cavity shape. Simple analytical expressions are obtained for constant coordinates cavities such as the sphere or the ellipsoid. The electrostatic energy of interaction with the continuum is then:

$$\mathscr{H}_E = -\mathscr{M}_l^m f_{ll'}^{mm'} \mathscr{M}_{l'}^{m'} \tag{3}$$

and using an important theorem which states that the polarization energy is $-\frac{1}{2}$ times the electrostatic interaction, one deduces for the free energy of solvation:

$$\Delta A_S = -\tfrac{1}{2} \mathscr{M}_l^m f_{ll'}^{mm'} \mathscr{M}_{l'}^{m'} \tag{4}$$

Two terms are missing from this model: the cavitation and dispersion energies. In this study, we focus our interest on the structure of the dimer. The only variation of the cavitation term which should be considered is the variation of the cavitation energy when this structure is modified. This variation is expected to be small and we shall neglect its contribution. The dispersion energy may be included in the model [67] but in general its variation is slight with molecular conformation. Its influence on our results will be discussed in the next section. Therefore, as the main terms assumed to vary during the solvation process are the electrostatic and induction ones, the geometry and the electron distribution of the solute will be modified in order to minimize the quantity:

$$\langle\psi|\mathscr{H}_0|\psi\rangle - \tfrac{1}{2}\langle\psi|\mathscr{M}_l^m|\psi\rangle f_{ll'}^{mm'}\langle\psi|\mathscr{M}_{l'}^{m'}|\psi\rangle \qquad (5)$$

where ψ is the multielectronic wavefunction and $\mathscr{H}_0$ the hamiltonian of the free molecule.

Efficient geometry optimization procedures have been implemented [68] using an ellipsoidal approximation for the cavity which is automatically defined from the nuclear coordinates of the atoms. The volume is constrained to be equal to the average molecular volume in the liquid. This volume shows a good correlation with the volume limited by the van der Waals surface and may be evaluated from it (the molecular volume is computed from the expression $1.48 V_{vdW}^{corr}(\text{Å}^3) + 0.42\ \text{Å}^3$, where V_{vdW}^{corr} is a corrected van der Waals volume computed by multiplying the atomic van der Waals radii by a factor of 1.105; this expression has been deduced to fit experimental molecular volume data at 20°C [68]). The axes of the cavity are related to the three axes of inertia of a solid of uniform density limited by the van der Waals surface. This definition allows the use of a deformable cavity during the geometry optimization procedure and leads to an analytical definition of the solvation energy gradient with respect to the cavity parameters.

3 Results and discussion

In order to discuss cooperative effects we shall first present the results obtained for the water molecule both in gas phase and in solution and then those obtained for the water dimer.

Monomer

In Table 1, the optimized geometry parameters of the water molecule in the gas phase ($\epsilon = 1$) and in solution ($\epsilon = 78$) are summarized. Results obtained at the SCF and MP2 levels are both included. The values for the isolated molecule are of course the same that those reported in [12] using the same basis set and the results at the MP2 level are in excellent agreement with experimental data ($R_{OH} = 0.957$ and $< HOH = 104.5$) [69].

The most striking feature of the solvent effect is the lengthening of OH bonds, the predicted variation at the SCF and MP2 levels being similar. This variation is expected in the liquid due to the formation of hydrogen bonds with the neighboring molecules. The continuum model does not take explicitly into account hydrogen bond formation. However, since the main component in the hydrogen bond arises from the electrostatic interaction and since this interaction is represented by the continuum, the effect is well reproduced by the model [70]. As a matter of fact, the *OH* distance as predicted at the MP2 level in solution compares well with the experimental value in liquid water (1.966 Å) [71].

In Table 2, we give the total energies in a vacuum and in solution and the solvation energies. Note that the solvation energies do not include the cavitation

Table 1. Optimized geometries for the water molecule (in Å and degrees)

		$\epsilon = 1$	$\epsilon = 78$	δ
SCF	OH	0.940	0.943	+0.003
	HOH	106.24	105.95	−0.29
MP2	OH	0.957	0.960	+0.003
	HOH	104.37	104.12	−0.25

and dispersion terms. They are the sum of the pure electrostatic interaction energy and the induction energy due to electronic polarization which, as we have pointed out, are the most sensitive terms to modifications of geometry. They may be considered as free energies of solvation which also include the energy consumed by the liquid to reorganize around the solute. A partition of the total free solvation energy into electrostatic and induction contributions allows comparison with some experimental data. The electrostatic free energy for the optimized MP2 geometry in solution is 5.13 kcal/mol and according to the theorem mentioned in Sect. 2 leads to an interaction energy of 10.26 kcal/mol which is in pretty good agreement with the experimental value of 9.92 kcal/mol [22].

The effect of electronic polarization on the water molecule electronic cloud is illustrated in Table 3 taking the optimized geometries at the MP2 level. Comparison of the Mulliken atomic charges shows a net polarization of the system in going from the isolated to the solvated species which is manifested by a substantial increase of the water molecule dipole moment. Experimentally, the dipole moment varies from 1.85 D in the gas phase [72] to 2.6 D in ice [73], which appears to be also a good estimate for the bulk liquid since it is the appropriate value to obtain the dielectric permittivity of liquid water [30]. One should consider that the SCF limit for the dipole moment of water monomer has been estimated at 1.98 D [56] and that limited basis set computations always predict higher moments. The value obtained in the present work at the SCF level

Table 2. Total (in a.u.) and solvation (in kcal/mol) energies of the water molecule

	$\epsilon = 1$	$\epsilon = 78$	E_{solv}
SCF	−76.056832	−76.065783	−5.62
MP2	−76.317352	−76.326161	−5.52

Table 3. Mulliken population, dipole moments (μ) and Mayer indices (B) [74] for the water molecule (computed for the optimized geometries at the MP2 level and using the SCF densities)

		$\epsilon = 1$	$\epsilon = 78$
q_O		−0.4819	−0.5860
q_H		0.2410	0.2930
$\mu(D)$		2.063	2.382
B	[a]	0.9766	0.9368
	[b]	0.9758	0.9359

[a] For the equilibrium geometry in a vacuum

[b] For the equilibrium geometry in the liquid

of computation is 2.016 *D* which is close to the SCF limit. The increase of the dipole moment through the environment effect justifies the use of large values compared to the gaseous phase in effective two-body potentials [15–22]. In Table 3 we also give the values of the computed OH bond order (Mayer indices [74]). Comparing the values for $\epsilon = 1$ and $\epsilon = 78$ at the gas geometry, one sees that the OH bond is weakened by the electronic polarization solvent effect. This is coherent with the fact that after geometry optimization, the bond is lengthened. Notice also that the main solvent effect on the bond orders is due to electronic polarization, the nuclear relaxation representing only a small perturbation which goes in the same direction anyway.

Dimer I

Table 4 summarizes the results for the geometry optimization in the case of the water dimer. For $\epsilon = 1$ our results reproduce those previously reported at the same level [12] with only slight differences on the angles (θ_a, θ_d). The equilibrium *OO* distance predicted at the MP2 level (2.912 Å) is slightly shorter than the experimental value 2.976 Å [48]. This has been atttributed to BSSE and in fact a better agreement is obtained when counterpoise corrections are included [61].

It is first of all interesting to compare the modifications of the water molecule parameters after formation of the dimer with the variations of the geometry predicted for the monomer under the electrostatic solvent effects. If one considers the OH bond length of the H-donor molecule in the dimer and the OH bond length in the monomer, at the SCF level one observes an increase of +0.004 Å which is similar to the increase of the OH bond length predicted by the cavity model in the case of the monomer. At the MP2 level the corresponding bond length differences are greater in the case of the dimer formation which may be interpreted as being due to the inclusion of intermolecular dispersion energy which play a role in hydrogen bond formation [75].

Now, comparing the geometries for the isolated and the solvated water dimer, one sees that the length of the external OH bonds, i.e. those which do not participate in the hydrogen bond, increases with the solvent effect. But the variation is now substantially larger compared to the increase observed for the monomer. This is a first illustration of the cooperative effect. A further conse-

Table 4. Optimized geometries for the water dimer I (in Å and degrees, see Fig. 1 for atom indices)

	SCF			MP2		
	$\epsilon = 1$	$\epsilon = 78$	δ	$\epsilon = 1$	$\epsilon = 78$	δ
O_1H_1	0.939	0.944	+0.005	0.957	0.961	+0.004
O_1H_2	0.944	0.946	+0.002	0.964	0.969	+0.005
O_2H_3	0.941	0.945	+0.004	0.958	0.963	+0.005
O_1O_2	3.035	3.143	+0.108	2.912	2.922	+0.010
$O_2\cdots H_2$	2.094	2.198	+0.102	1.951	1.953	+0.002
$H_1O_1H_2$	106.31	106.12	−0.19	104.58	104.70	+0.12
$H_3O_2H_4$	106.56	106.92	+0.36	104.84	105.38	+0.54
θ_a	130.84	122.89	−7.95	125.07	126.56	+1.49
θ_d	3.33	2.48	−0.85	3.91	1.48	−2.43

quence of the cooperative effect appears for the O_1H_2 bond which participates in the hydrogen bond. The electrostatic solute-solvent interactions lengthens this bond and this suggests that the hydrogen bond is stronger in the liquid. The MP2 average OH distance in the solvated dimer is 1.964 Å which is very close to the experimental value of 1.966 Å in the liquid [71]. The variation of the angle θ_d, which decreases through the solvent effect giving a more linear hydrogen bond, seems to also reflect the strengthening of the hydrogen bond. However, it is not easy to extract definitive conclusions from the variation of the values of the intermolecular parameters because, owing to the flatness of the potential energy surface, they show extreme sensitivity to the computational scheme (see for instance Table 1 of [12]). In a preliminary study using different basis sets, we found that the OO bond length is in general predicted to increase by the effect of the solvent except in the case of the 3-21G basis set which predict a lower OO distance in solution. The overestimation of the hydrogen bond strength by using this basis could explain this specific effect.

In Table 5, the total energies, the solvation free energies and the association energies are given for both isolated and solvated systems. As previously shown [12], the association energy for the isolated systems is predicted to be higher (about 1.4 kcal/mol) when computed at the MP2 level. This is probably due to the fact that at this level, dispersion energy is taken into account. The MP2 value of -5.45 kcal/mol is in very good agreement with the experimental association energy -5.4 ± 0.7 kcal/mol [76], or -5.4 ± 0.2 kcal/mol [77]. A detailed discussion on the experimental determination of association energies from deviations from ideal gas behavior, thermal conductivity or spectroscopy methods is given in reference [78].

In the case of the solvated species, one notices in Table 5 that the association energies are larger. However, it should be considered that the values of the association energy for solvated systems contain a term which is the difference between the free energies of solvation of the dimer and the monomers so that, strictly speaking, they are not true association energies. Estimation of the internal energy may be done as explained above, i.e. by limiting the solvation process to the electrostatic energy term. The values obtained are -6.93 kcal/mol and -8.47 kcal/mol at the SCF and MP2 levels respectively. These values represent a still larger stabilization of the hydrogen bonded dimer in the liquid than that deduced from the values in Table 5. It clearly appears that the hydrogen bond in the water dimer is stronger in the liquid phase. Again, the cooperative effect on hydrogen bond formation is evidenced and confirms the conclusions derived from geometry considerations.

The solvation energies in Table 5 have been calculated as differences of the total energies of the optimized dimer in the liquid and in the gaseous phase.

Table 5. Total (in a.u.), solvation (in kcal/mol) and association energies (in kcal/mol) of the water dimer I

	E_T		E_{solv}	ΔE	
	$\epsilon = 1$	$\epsilon = 78$		$\epsilon = 1$	$\epsilon = 78$
SCF	−152.120155	−152.140995	−13.08	−4.07	−5.92
MP2	−152.643390	−152.664030	−12.95	−5.45	−7.35

Table 6. Electrostatic multipole contributions to the solvation energy for the water dimer I in the computed liquid equilibrium geometry (kcal/mol)

$l =$	1	2	3	4	5	6	Sum
SCF	−1.34	−5.60	−2.85	−1.26	−0.45	−0.15	−11.68
MP2	−1.92	−5.33	−2.91	−1.16	−0.42	−0.13	−11.88

Hence, they include electronic and nuclear relaxation stabilization energies. In order to analyze the multipole contribution to the solvation energies, we give in Table 6 the electrostatic multipole contributions for the dimer in its liquid equilibrium geometry. These values show that the quadrupole contribution is the largest one. This is not surprising because the dipoles of the two water molecules are oriented in slightly antiparallel directions and accordingly they give rise to a substantial quadrupole moment. Contributions over the hexadecapole are small, the series being rapidly convergent.

Electronic population analyses are given in Table 7. Note that the polarization of the electron cloud increases the net charges on all atoms. In particular, the charge on the atoms participating to the hydrogen bond (O_1–H_2–O_2) is greater in solution. This effect is consistent with the increase of the hydrogen bond strength. Besides, the charge transfer and the dipole moment are also enhanced by the solvent effect. It is interesting to point out that the total dipole moment in the dimer (in the gas or in the liquid) is always higher than the vector sum of two dipoles placed on each monomer and having the value of the water molecule dipole moment under the same conditions. This is caused by the charge

Table 7. Mulliken charges, intermolecular charge transfer, dipole moments, Mayer indices [74] and OH bond critical point densities, for the water dimer I (computed for the optimized geometries at the MP2 level and using the SCF densities)

Atomic charges, charge transfer and dipole moments

ϵ	H_1	O_1	H_2	O_2	H_3, H_4	Δq	$\mu(D)$
1	[a] 0.2408	−0.5608	0.3177	−0.5230	0.2626	0.0023	2.848
78	[b] 0.3111	−0.6751	0.3535	−0.6268	0.3186	0.0105	3.267

Mayer indices

ϵ	O_1H_1	O_1H_2	O_2H_2	O_2H_3
1	[a] 0.9732	0.9175	0.0129	0.9595
	[b] 0.9729	0.9130	0.0195	0.9575
78	[a] 0.9261	0.8780	0.0406	0.9187
	[b] 0.9245	0.8710	0.0464	0.9164

Bond critical point densities

ϵ	O_1H_1	O_1H_2	O_2H_3
1	[a] 0.3797	0.3672	0.0219
78	[b] 0.3756	0.3650	0.0221

[a] For the equilibrium geometry in a vacuum

[b] For the equilibrium geometry in the liquid

transfer which, although small in absolute value, leads to a non-negligible contribution because of the relatively large separation between the positive and negative centers.

In order to gain a deeper insight into the polarization effects due to the interactions with the continuum, we also give in this table the Mayer indices and OH bond critical points for the dimer in a vacuum and in the liquid. Looking at the Mayer indices, one sees that the external OH bonds are weakened by the effect of the reaction field, the main effect arising from electronic polarization. In addition, the donor OH bond (O_1H_2) is also weakened while the hydrogen bond (O_2H_2) is strengthened. Keeping in mind the relation between the bond strength and electronic density at the bond critical point [79, 80], the same conclusion is reached by comparing the bond critical point changes in going from the vacuum to the liquid. A more detailed illustration of the electronic polarization of the dimer in the liquid is given in Fig. 3. This figure represents the difference in electron densities between the solvated and the isolated dimer: $\varrho^{sol.} - \varrho^{vac.}$ for the equilibrium geometry in a vacuum. The increase of negative charge on the oxygens and of positive charge on the hydrogens is shown in this figure. Note also that the difference on the electron density of the OH bond critical points falls in a negative region ($\Delta\varrho < 0$) for O_1H_1 and O_1H_2 and in a positive region for the hydrogen bond O_2H_2.

Finally, it is possible to acquire a clear image of the geometry relaxation effect of the solvent by analyzing the forces in solution for the dimer in its gas phase geometry. Of course, these forces are zero in a vacuum (the system is in equilibrium) but in solution the reaction field gives rise to atomic forces that will drive the modifications of the geometry in the nuclear relaxation process. Figure 4 represents these forces schematically. The most noticeable feature is that the solvent favors the proton transfer taking place in the hydrogen bond, whose strength consequently should increase. Conversely, the O and H atoms in the external OH bonds are submitted to opposite forces so that the bond lengths

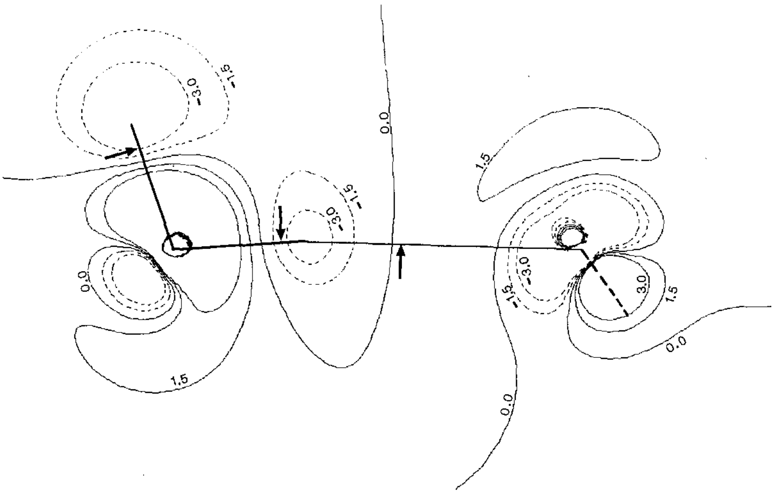

Fig. 3. Representation of $\Delta\varrho = \varrho^{sol.} - \varrho^{vac.}$ (difference between the electron density of the water dimer in the liquid and in the gas phase, for the gas equilibrium geometry). Units of 10^{-3} a.u. *OH* bond critical points are indicated by arrows

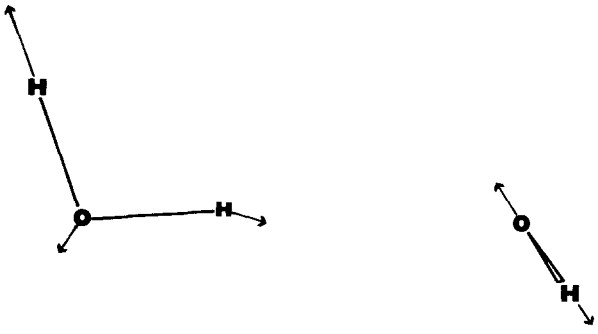

Fig. 4. Schematic atomic force representation for the water dimer in the liquid phase before relaxation of the gas phase geometry

tend to be increased and, consequently, the external H atoms become more accessible to form further hydrogen bonds with other solvent molecules.

Dimer II

The stabilization by the solvent of another conformation of the dimer, called dimer *cis*, has been considered in a previous work [46].

At the *ab initio* level, the existence of an energy minimum for such a conformation is confirmed in the liquid although no such minimum can be found in the isolated dimer. The sum of the molecular energy and of the solute solvent interaction free energy is very close to the value obtained for the normal (*trans*) conformation both at the SCF or at the MP2 level (0.02 kcal/mol above the previous values). If one analyzes the components of these quantities, one notices that the molecular energy is slightly higher but this difference is compensated by a larger solute solvent interaction mainly due to the large dipole moment of the *cis* conformation (see Tables 6 and 8). These differences can be understood by simple electrostatic considerations. In particular, the monomer dipoles are almost parallel, giving rise to positive dipole-dipole interactions but the large total dipole moment of the dimer plays a determining role in the solute-solvent interactions, as opposed to Dimer I in which the anti-parallel configuration of the dipoles has a stabilizing effect on the intramolecular energy but shifts the main contribution of the solute-solvent interaction to the quadrupole term (see Tables 6 and 8).

Regarding the structure of this dimer, note on Tables 9 and 10 that, apart from the relative orientation of the water molecules, the main structural features are quite similar to those of the other dimer: bond lengths, bond angle, length of the hydrogen bond. The Mayer indices and charge transfer are also similar.

These findings support the assumption of the transferability of the properties of each individual molecule from one conformer to another which is a basic assumption for deriving an effective two-body potential.

Table 8. Electrostatic multipole contributions to the solvation energy for the water dimer II in the computed liquid equilibrium geometry (kcal/mol)

$l =$	1	2	3	4	5	6	Sum
SCF	−6.89	−0.30	−3.01	−0.24	−1.56	−0.12	−12.13
MP2	−7.37	−0.32	−3.01	−0.25	−1.37	−0.11	−12.43

Table 9. Optimized geometries for the water dimer II in the liquid (in Å and degrees, see Fig. 2 for atom indices)

	SCF	MP2		SCF	MP2
O_1H_1	0.945	0.962	$H_1O_1H_2$	106.61	105.25
O_1H_2	0.946	0.968	$H_3O_2H_4$	106.86	105.31
O_2H_3	0.945	0.963	θ_a	130.65	132.21
O_1O_2	3.133	2.916	θ_d	3.85	5.12
$O_2 \cdots H_2$	2.190	1.953			

Table 10. Mulliken charges, intermolecular charge transfer, dipole moments and Mayer indices computed for the optimized geometry in the liquid at the MP2 level and using the SCF densities for the water dimer II

Atomic charges, charge transfer and dipole moments

ϵ	H_1	O_1	H_2	O_2	H_3, H_4	Δq	$\mu(D)$
1	0.2337	−0.5593	0.3248	−0.5275	0.2641	0.0008	4.375
78	0.3124	−0.6774	0.3546	−0.6291	0.3197	0.0104	5.116

Mayer indices

ϵ	O_1H_1	O_1H_2	O_2H_2	O_2H_3
1	0.9801	0.9090	0.0206	0.9595
78	0.9255	0.8681	0.0461	0.9164

4 Conclusion

The use of a cavity model to study the water dimer in the liquid phase leads to the conclusion that the dimer hydrogen bond is strengthened from geometric, energetic and electronic density viewpoints under the influence of the solvent. Besides, the solvent stabilizes a second conformation of this dimer which does not exist as an isolated entity. On the other hand, the implicit hydrogen bonds of the external hydrogen atoms in the dimer with other molecules of the liquid also appear to be strengthened. Hence, the structure and properties of the dimer appear to be strongly influenced by the presence of the solvent.

In our results, the charge transfer appears to play a non-negligible role in the hydrogen bond. The non-additivity of this term, together with that arising from polarization, should be considered in the development of theoretical pair potentials.

This study justifies the use of a dipole moment value substantially higher that the gas phase value, in simulations of the liquid state by means of effective pair potentials. However, it states the allowing variation of both intramolecular and intermolecular geometry parameters and atomic charges (and hence, multipole moments) would be necessary in order to get a more sophisticated description of water in the liquid state. This indicates the trends which should be considered for deriving a more sophisticated water-water potential to be used in liquid water simulations. From this study it appears that the minimum requirements for such a potential are an accurate description of the electrostatic and the induction energies. These requirements are quite realistic owing to the recent advances in these fields [81], such as the representation of a molecule by means of distributed multipoles and distributed polarizabilities [82–84]. Other contributions are probably necessary to include [85] in order to accurately describe each molecule in the dimer. Nevertheless, comparison of the two conformers found in this study clearly indicates that such a goal is realistic and that an intermolecular potential, which would account for polarization and charge transfer effects, would be able to represent both conformers in the liquid.

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