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Calculated Physical Properties of a Water Molecule in an Ice-Like Cluster

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Some properties of a H_2O molecule surrounded by the four nearest neighbours arranged as in the ice I geometry have been calculated within a SCF scheme in terms of an extended STO's basis. The effect of the outer molecules is treated as a coulombic perturbation. The different possible geometric configurations of the perturbators have been taken into account. Comparisons are made with the experimental changes of some physical properties of water in passing from vapor to condensed phase.

Es werden einige Eigenschaften des Wassermoleküls, das von seinen vier nächsten Nachbarn in Eis-I-Geometrie umgeben ist, mit Hilfe eines SCF-Schemas mit erweiterter STO-Basis berechnet. Dabei wird der Effekt der äußeren Moleküle als Coulombstörung behandelt. Die verschiedenen möglichen geometrischen Konfigurationen der Störmoleküle sind in Betracht gezogen worden. Die Rechenergebnisse werden mit den experimentellen Änderungen einiger physikalischer Eigenschaften des Wassers beim Übergang von der Gasphase zur kondensierten Phase verglichen.

Introduction

In spite of noticeable progresses in the last years the study of water in its condensed phases, presents some still open problems. At any rate, the persistence in the liquid phase of a more or less extended and stable ice-like tetrahedral structure seems to be largely accepted, and it may be supposed that the differences known to exist between the physical properties of a water molecule in the gas and in the condensed phases can be ascribed to this type of structure.

The most recent "ab initio" calculations on this subject have been mainly devoted to clarify the essence of the hydrogen bond and to attain a quantitative estimate of the related energy. At this regard the papers issued in the last years [1–5] seem to indicate that a complete SCF calculation based on a small cluster of water molecules is sufficient to obtain a correct prediction of this experimental datum. This paper is instead mainly focused to a different objective: the attempt of establishing if a relatively crude model for the effect of the neigbouring molecules

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is sufficient to explain the changes in physical properties which occur when the water molecule is embedded in a condensed phase.

The suggested model and the calculation scheme are discussed in the second section, while the third one is devoted to the discussion of the results.

Model and Calculation Scheme

The adopted model presents the following peculiarities:

1) The changes in the physical properties of water, in passing from gas to condensed phase, are supposed to be related to two different effects:

a) The distortion of the internal geometry, with small lengthening of the OH bond and widening of the HOH angle;

b) the change of the charge distribution caused by the neighbouring molecules.

The first effect is taken into account by the proper choice of the geometry of the molecule and no attempt is made to deduce from the model the new equilibrium positions of the atoms, while the second effect will be treated as due to a perturbation.

Only the first (and, partially, the second) shell of neighbours has been taken into account.

2) Consequently, a water molecule, with a rigid geometry corresponding to that of ice I, is supposed to be surrounded by four other similar molecules, the over-all structure corresponding to a tetrahedral five-member cluster. The distance between the oxygen nuclei is that of normal ice (2.76 Å) and the O and H nuclei, that form the hydrogen bond, are supposed to be collinear.

3) Both the central molecule and the external ones are described by SCF LCAO MO wave functions.

It is known that such an approximation allows to obtain satisfactory results for most of the gas phase observables [6–8].

Since the interaction between the central molecule and the outer ones is treated as a perturbation, a rather extended basis set of STO's has been employed for the description of the former, while a minimal basis set has been considered to be adequate for each of the surrounding molecules.

4) The charge distribution of the perturbing molecules has been adjusted to render it as far as possible suited to the description of the mean situation of a water molecule in the condensed phase. Therefore an iterative process has been carried out starting from an SCF calculation of a water molecule on a minimal basis set of STO's.

The SCF wave function of the isolated central molecule was perturbed by the interaction with its four surrounding ones, neglecting the exchange terms. The iterative process has been then accomplished, by attributing the SCF charge distribution so obtained for the central molecule to the surrounding ones, and so on, up to convergence of the energy. The final wave function has been used in the subsequent calculation stage, where as already stated, the central molecule is described in terms of an extended basis set.

5) Also in this case, the interaction is supposed to be purely coulombic so that exchange and dispersion contributions are neglected. This approximation, that simplifies noticeably the calculation at the actual distances of atoms in the hydro-

gen bond, is a rather drastic one as for as the energy of the bond is concerned, but, hopefully it is not so heavy in considering other physical properties. At this stage, all mutual interactions of the four outer molecules are neglected and their charge distribution is supposed completely rigid.

The hamiltonian of the perturbed central molecule is therefore written as follows:

$$H = H^0 + H' , \tag{1}$$

H^0 being the Hartree-Fock hamiltonian of the unperturbed system and

$$\begin{aligned} H' &= \sum_{j=1}^{N\text{elect.}} V'(j) ; \quad V'(j) = \sum_{\alpha=1}^{4} V'_\alpha(j) \\ &= \sum_{\alpha=1}^{4} \left\{ \sum_{i_\alpha=1}^{3} \frac{Z_{i_\alpha}}{r_{i_\alpha j}} - 2 \sum_{l_\alpha=1}^{5} \int \frac{\varphi^*_{l_\alpha}(k)\, \varphi_{l_\alpha}(k)}{r_{l_\alpha k}} \, d\tau_k \right\}. \end{aligned} \tag{2}$$

φ_{l_α} denotes the occupied molecular orbitals of the perturbing systems, the meaning of the other symbols in (2) being obvious.

6) The SCF solution corresponding to the hamiltonian (1) is employed to evaluate some first and second-order observables to be compared with the corresponding ones evaluated for an isolated water molecule with a geometry characteristic of the gas phase. The last system has been already treated by one of us [8], and the STO's set for the central molecule of the present paper is the same. Since the aim of the calculation is the comparison of the results with the data one can obtain from experiment, one must take into account the fact that particularly in a condensed phase, the perturbation that one can suppose to act on a single molecule, has to be averaged with respect to the different configurations of its surrounding partners. In accordance with the Pauling picture [9], these may be deduced by allowing all the protons to jump from the proximity of an Oxygen atom to another. In our case, since the central molecule is considered fixed in his geometry and position, the different configurations are simply obtained by allowing the four perturbators to rotate around O—O axes (see Fig. 1). Moreover,

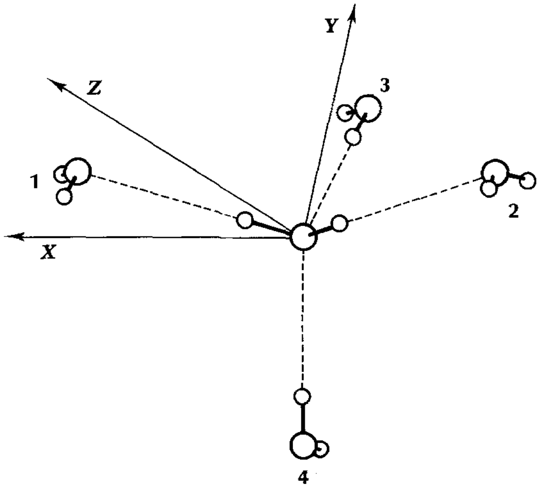

Fig. 1. Geometry of the cluster

if one retains the ice-like geometry, these rotations must be limited only to 120° and 240°, with respect to the original configuration, so that one obtains 3^4 different geometrical configurations. In an infinite crystal, these configurations are all equivalent; in the case of a cluster of limited dimensions the energy and properties of the central perturbed molecule will be generally different for the different configurations of the surrounding ones (although in some cases they coincide, for symmetry reasons). Therefore, the perturbative calculation has been repeated for all the required configurations, and the values of the observables so obtained have been linearly averaged. A similar process has been used in the first stage of the calculation, all minimal set, when the perturbing SCF wave function has been produced.

A Boltzmann average process would mean that the condensed phase has been represented as an infinite replication of non interacting clusters, such as that here considered. Obviously if this cannot be a useful picture of an ice crystal, it is certainly an extremely reductive picture of the liquid phase.

7) The perturbed wave function of the central molecule does not present, in principle, the C_{2v} symmetry characteristic of the isolated molecule. This fact would lead to some unphysical features of the calculated observables. We have therefore imposed an additional constraint to all the SCF perturbing procedures, in order to preserve the symmetry of the wave function identical with that of the unperturbed case. This same constraint has been retained in the first stage of the calculation. As a control of the errors introduced with this last approximation we have performed a complete calculation on the minimal set and for a configuration on the extended set by relaxing the symmetry constraint. In both cases the spurious contributions to the electric dipole moment were not greater than 0.01 D while the z component was varied on the 3th decimal place. The variation of the total energy values was of an unit on the 4th decimal place.

8) In order to have an estimate of the error introduced, by neglecting all outer shells but the first one, an additional calculation involving also the twelve second nearest-neighbours has been carried out. In this case, only one configuration of the molecules has been taken into account.

Results and Discussion

In Table 1 the geometrical parameters for the molecule either isolated or embedded in the cluster are reported. For the first case we have employed the same data as in Ref. [8] which are very close to the experimental equilibrium ones while in the second case the data of Eisemberg and Kauzmann [10] have been utilized. In the same table are reported the coordinates of all the molecules of the cluster in one of the considered configurations, specifically that represented in Fig. 1.

In Table 2 the minimal set orbitals and energies are reported for the central molecule of the cluster. The coefficients are those obtained from the preliminary symmetry constrained SCF process described at point 4 of the previous section, after linear averaging of all the considered configurations. These coefficients are therefore employed in describing the wave functions of the perturbing molecules

Table 1. Geometrical parameters and coordinates for isolated molecule (I) and for the cluster (II)

I	II
HOH = 105°	HOH = 109° 28′
R_{OH} = 1.8103[a]	R_{OH} = 1.90854

Coordinates of the atoms in the configuration shown in Fig. 1

		x	y	z
Central molecule	O	0.0	0.0	0.0
	H_1	1.558266	0.0	1.101950
	H_2	−1.558266	0.0	1.101950

		x	y	z			x	y	z
Mol. 1	O	−4.258235	0.0	3.011280	Mol. 3	O	0.0	4.258235	−3.011280
	H_1	−4.258235	−1.558266	4.113232		H_1	1.558266	4.258235	−4.113232
	H_2	−5.816501	0.0	1.909328		H_2	0.0	2.699969	−1.909328
Mol. 2	O	4.258235	0.0	3.011280	Mol. 4	O	0.0	−4.258235	−3.011280
	H_1	5.816501	0.0	1.909328		H_1	0.0	−2.699969	−1.909326
	H_2	4.258235	−1.558266	4.113232		H_2	0.0	−3.738578	−4.847715

[a] All data are in atomic units.

Table 2. Minimal set STO's, MO's and energies of H_2O molecule in a cluster

Orbital	ζ	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5
$1s_{\mathrm{H}}$	1.27	− 0.00328	0.14238	0.26628	0.41176	0.0
$1s$	7.66	0.99685	−0.22593	0.08123	0.0	0.0
$2s$	2.25	0.01466	0.87159	−0.45169	0.0	0.0
$2p_z$	2.21	0.00264	0.09531	0.80756	0.0	0.0
$2p_x$	2.21	0.0	0.0	0.0	0.63230	0.0
$2p_y$	2.21	0.0	0.0	0.0	0.0	1.0
$1s_{\mathrm{H}}$	1.27	− 0.00328	0.14238	0.26628	0.41174	0.0
ε (a.u.)		−20.52788	−1.24607	−0.44890	−0.58927	−0.39709

$E^{\mathrm{P.M.}} = -75.7541$ $\mu^{\mathrm{P.M.}} = 2.026$
$E^{\mathrm{I.M.}} = -75.7034$ $\mu^{\mathrm{I.M.}} = 1.920$

in the main calculation. In the same table, the total energy and the electric dipole moment corresponding to this charge distribution are compared with the corresponding values for an isolated molecule with the geometry in the gas case.

From the reported data one can see that the average energy for the hydrogen bond results to be:

$$E_{\mathrm{H.B.}} = 5/16\,(E^{\mathrm{P.M.}} - E^{\mathrm{I.M.}}) = 9.9\ \mathrm{kcal/mole}\,.$$

The ratio 5/16 can be understood by considering that in order to separate five molecules (which are assumed to be equivalent to each other) one must break sixteen bonds.

Table 3. Extended basis STO's, MO's and energies for isolated molecule (I.M.) and for a perturbed case (Cluster)

Atomic basis set		
Order number	Orbital	ζ
1	$1s$	13.00
2	$1s'$	7.45
3	$2s$	3.50
4	$2s'$	2.17
5	$3s$	1.50
6, 7, 15	$2p_z, 2p_x, 2p_y$	3.50
8, 9, 16	$2p'_z, 2p'_x, 2p'_y$	2.15
10,11,17	$3p_z, 3p_x, 3p_y$	1.50
12,13,14	$3d_{z^2}, 3d_{xz}, 3d_{x^2-y^2}$	1.50
18,19	$3d_{yz}, 3d_{xy}$	1.50
20,25	$1s_H$	1.00
21,26	$1s'_H$	1.50
22,27	$2p_{zH}$	1.10
23,28	$2p_{xH}$	1.10
24,29	$2p_{yH}$	1.10

$E_{HF}^{I.M.} = -76.0384$
$E_{HF}^{Clust.} = -76.1000$

Molecular orbitals						
Simm. A_1						
	Φ_1		Φ_2		Φ_3	
O.N.	I.M.	Clust.	I.M.	Clust.	I.M.	Clust.
1	0.04813	0.04811	0.02295	0.02268	-0.00530	-0.00525
2	0.95048	0.95058	-0.27020	-0.27142	0.07646	0.06415
3	0.01992	0.01953	0.08886	0.09224	-0.05783	-0.05651
4	-0.01011	-0.00984	0.73840	0.77011	-0.36478	-0.26340
5	0.00726	0.00671	-0.22486	-0.18243	-0.22117	-0.18014
6	0.00420	0.00350	0.01626	0.00746	0.25263	0.25926
8	-0.00428	-0.00361	0.10743	0.09442	0.40615	0.40010
10	0.00356	0.00304	-0.08234	-0.08153	0.24486	0.30521
12	0.00032	0.00024	-0.00073	-0.00297	0.05155	0.03962
14	0.00017	0.00018	-0.00132	-0.00374	-0.00091	0.01691
20, 25	-0.00561	-0.00503	0.20987	0.18186	0.19935	0.13062
21, 26	0.00353	0.00317	0.05704	0.05032	0.07377	0.09269
22, 27	-0.00016	-0.00012	-0.02944	0.02475	-0.02350	0.02025
23	0.00030	0.00031	-0.04932	-0.04839	-0.03989	-0.02894
28	-0.00030	-0.00031	0.04932	0.04839	0.03989	0.02894
ε (a.u.)	-20.58241	-20.60226	-1.36011	-1.34049	-0.58856	-0.58792

Simm. B_1		
	Φ_4	
O.N.	I.M.	Clust.
7	0.22344	0.22263
9	0.38010	0.38668
11	0.15828	0.20356
13	0.07001	0.07089
20	0.17337	0.09929
21	0.18408	0.19878
22	-0.05598	-0.04597
23, 28	-0.04969	-0.04004
25	-0.17337	-0.09929
26	-0.18408	-0.19878
27	0.05598	0.04597
ε (a.u.)	-0.72618	-0.70822

Simm. B_2		
	Φ_5	
O.N.	I.M.	Clust.
15	0.28220	0.29112
16	0.47240	0.44113
17	0.33373	0.38384
18	0.03916	0.01292
24, 29	0.03390	0.01931
ε (a.u.)	-0.51232	-0.52459

The electric dipole moment displays a very small variation, in accordance with the rigidity of the charge distribution in the minimal basis set case. In Table 3 are reported the extended basis set and the corresponding orbitals for the particular configuration of the perturbing molecules described in Fig. 1 and in Table 1.

The orbitals of the isolated molecule on the same basis set, and with the gas geometry, are also reported from [8] for comparison. It can be seen that the most relevant variations involve the most external molecular orbitals, and, particularly, the charge distribution on the hydrogen atoms. Also the coefficients of the oxygen *d*-type STO's result to be remarkably changed.

In Table 4 some comparison is made between the calculated results and those that one may deduce from experiment. At this stage, one is faced by the known difficulty of deducing unambiguously the physical data referring to a molecule embedded in the condensed phase. When possible we have reported the data derived from measurement on ice I but in some cases (e.g. the chemical shift), only the liquid phase data are known. As far as the hydrogen bond energy is concerned, the calculation must now be carried out in a way slightly different from that employed in the minimal set case. Due to the fact that now the perturbing molecules are retained rigid while they are taken away to an infinite distance from the central one, the average energy of the hydrogen bond can be assumed to be one fourth of the difference between the energy of the central molecule perturbed into the cluster and that of the unperturbed molecule with its original gas phase geometry.

Table 4. Calculated and experimental physical properties

	Calc.[a] I.M.	Exp. (gas)	Calc. (mean cluster value)	Max. var.	Exp. condensed phase	ΔCalc.	ΔExp.
Total energy (a.u.)	-76.0384	-76.481^{b}	-76.0971	0.00539		9.2^{h}	5.6—$7.7^{h,i}$
$\mu(D)$	1.926	1.85 ± 0.02^{b}	2.537	0.2823	2.71^{f}	0.61	0.86
$\langle r^2 \rangle$ (10^{-16} cm^2)	5.510	5.10 ± 0.7^{b}	5.727	0.024	12.65^{g}		
χ(c.g.s. p.p.m/mole)	-14.373	-13.1 ± 1.8^{l}	-14.718	0.034		-0.355	$+0.45$
σ_H(g.H) (p.p.m.)	48.4		42.57	0.56		-5.83	
σ_H(g.O) (p.p.m.)	28.41	30.03 ± 0.6^{c}	24.601	0.4		-3.81	-4.58^{j}
σ_O(g.O) (p.p.m.)	346.39		333.05	0.905		-13.34	-36^{k}
$\overline{\alpha}$ (Å^3)	1.170	1.444^{d}	1.258^{e}			0.088	

[a] Arrighini, G. P., Guidotti, C., Salvetti, O.: J. chem. Physics **52**, 1037 (1970).

[b] See Refs. [7] and [8].

[c] For a discussion of this date see: Arrighini, G. P., Maestro, M., Moccia, R.: J. chem. Physics **52**, 6411 (1970), Table 3.

[d] Moelwyn-Hughes, E. A.: Physical chemistry, 2nd edn. New York: Macmillan 1964.

[e] This result is referred to the configuration of Fig. 1.

[f] Hollins, G. T.: Proc. physic. Soc. **84**, 1001 (1964).

[g] Landolt-Börnstein: Zahlenwerte und Funktionen, 6th edn. Vol. 10, II, pag. 21. Heidelberg: Springer 1967.

[h] kcal/mole for an hydrogen bond.

[i] See Ref. [10].

[j] Schneider, W. G., Bernstein, H. J., Pople, J. A.: J. chem. Physics **28**, 601 (1958).

[k] Florin, A. E., Alei, M.: J. chem. Physics **47**, 4268 (1967).

[l] Taft, H., Dailey, B. P.: J. chem. Physics **51**, 1002 (1969).

Therefore one has:

$$E_{\mathrm{H.B.}} = 1/4\,(E^{\mathrm{Cl}} - E^{\mathrm{I.M.}}) = 9.2\ \mathrm{kcal/mole}\,.$$

The hydrogen bond energy data reported in the last column of the Table 4 present a large spectrum of values due to possibility of different definitions of this quantity [10]. Also in this case, to neglect the exchanged interactions causes an overestimate of the quantity.

As far as the electric dipole moment is concerned, static dielectric constant measurements do not lead immediately to a value of this quantity for a molecule in the ice crystal. The values of Hollins [11] reported in the table, or that (2.60) calculated by Coulson and Eisenberg [12] seem to be the most reliable ones and the agreement with our calculated result may be considered satisfactory. For the quadrupole moment variation, we have not found experimental data for comparison.

The deduction of the molecular electric polarizability, in the condensed phase presents some problems analogous to those concerning the dipole moment. In the classical formulae (see for instance [13]) these two quantities appears tied together and, in principle, one could deduce both of them from measurements of dielectric constant and its temperature coefficient. Unfortunately, this type of procedure gives, in the case of highly polar substances, completely unreliable results. Therefore, as far as this quantity is concerned we limit the calculations only to the case of the configuration shown in Fig. 1. Among the reported magnetic properties only the nuclear magnetic shielding constant allows for a rather direct evaluation of the difference between the gas and condensed phase on the basis of the experimental measurements. The reported value for the proton is referred to the association shift introduced in Ref. [14] and it is a datum largely accepted [15]. One can see that the result of the calculation is of the right order of magnitude, although highly dependent from the choice of the gauge of the external field.

Previous calculations [16] have shown that the best results are obtained with the choice that minimizes the total magnetic susceptibility, and, practically, of the oxygen nucleus. As far as the O^{17}shielding value is concerned the agreement with the only experimental result we have found, is decisely unsatisfactory. For the magnetic susceptibility we have reported in the table a very recent result for the gas phase, that seems to confirm the assumption of Eisenberg and Kauzmann that the variation should not be greater than 15%. In contrast with these data, our result shows an increment in passing to the condensed phase.

All the data reported in Table 4 are obtained as averages among configurations that have been considered equivalent. The corresponding values (in the same units) for a Boltzmann average at 0° C (i.e. the temperature to which the experimental values are referred), are the following:

$$E = -76.0993$$

$$\mu = 2.629$$

$$\langle r^2 \rangle = 5.719$$

$$\chi = -14.709$$

$$\sigma_{\mathrm{H}}(g.\mathrm{O}) = 24.495$$

$$\sigma_{\mathrm{O}} = 333.32.$$

Table 5. Observables[a] in presence of the second shell[b]

E	-76.09683	-76.10431
μ	2.5132	2.66419
$\langle r^2 \rangle$	5.7287	5.717
α	8.492	8.495
χ	-14.722	-14.720
σ_H (g.H)	42.674	42.230
σ_H (g.O)	24.628	24.309
σ_O	333.03	335.007

[a] The units are the same as in the Table 4.

[b] The configuration of the perturbing molecules is different from that in Fig. 1.

One can see that no result (with the partial exception of the electric dipole moment) presents sensible variations.

In the fourth column of Table 4 are reported the maximum splittings between two different configurations of the perturbing molecules for each observables. One can see that the result for the dipole moment is the only one for which this splitting has some importance.

As an appendix to the main calculation, the observables of the central molecule have been calculated, by adding the second shell of molecules, in one of their possible configurations to a particular configuration of the first shell which has been chosen with an energy value very close to the linear average.

The calculation has been carried out within the already explained approximations. The results are reported in Table 5; for comparison, in the same table in the first column are reported the results relative to the case of the central molecule perturbed only by the four nearest neighbours to which the second shell has been added.

One can observe that the addition of the second shell brings a not negligible contribution, showing that (particularly in the case of the dipole moment) an addition of at least another shell would probably be needed in order to attain a convergence in the limits of the experience. It is confortable that the obtained result for this last observable comes to be very near to the value deduced from experiment by Hollins. Also the result for proton association shift (-4.1) shows an improvement.

As a conclusion, it seems that the following points can be stated:

1) A coulombic perturbation (classical electrostatic + polarization effects) is sufficient to explain a large part of the variation of the physical properties of a water molecule in passing from an isolated state to a condensed one. As it was already known, this approximation is not suited to attain a quantitative agreement with the experimental energy of the hydrogen bond, and even less, to justifie the equilibrium geometry of the nuclei.

2) At least in the above approximations and with the exception of the dipole moment, the effect of the rapidly fluctuation of the configuration of the nearest neighbours on the considered molecular observables has not a decisive importance.

3) The second shell brings a modification which is not greater (and often largely less) of the 20% of that of the first; unfortunately this fact is not sufficient

to establish the quickness of the convergence of the observables with the growth of the cluster.

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