

## Importance of Electrostatic Interactions between Nonbonded Molecules in Ice

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*Ab initio* calculations on water dimer, trimer,  $Pm11$  polymer,  $I41md$  prototype structure, and ice VIII shows that the dependence of the O-H bond length upon the intermolecular distance mostly depends upon environmental effects due to non-H-bonded molecules. The hydrogen bonds are found to be weaker in ice VIII and  $Pm11$  polymer than in the  $I41md$  structure. This result is consistent with recent experiments on He-H<sub>2</sub>O and H<sub>2</sub>-H<sub>2</sub>O clathrates and emphasizes the role of interactions between nonbonded molecules. These effects can be qualitatively understood by a simple dipole-dipole electrostatic model.

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There is a renewal of interest in the study of the physical properties of ice which is testified by two recently published important papers which bring new information about the hydrogen bonding in this material [1,2]. Ice is a very important substance for the study of hydrogen bonding since it is among the few in which the nearest neighbor interactions are hydrogen bonds. Therefore, the H-bond properties are expected to be less perturbed by other intermolecular interactions in ice than in any other molecular crystal [3]. Moreover, there are many different ice polymorphs which allow the investigation of the H-bond properties for different structures and different surroundings without altering the chemical composition. Conversely, a good modeling of the hydrogen bonding is necessary for the understanding of the structure, thermodynamics, vibrational properties, and phase transitions of ice polymorphs.

In most molecular crystals, the hydrogen bond is almost linear [4] and, thus, the proton potential can be described with two structural parameters: the O-H and O···O distances. Different experimental techniques can be used to probe the H-bond potential with respect to the O···O distance. On the one hand, structural and spectroscopic data collected for chemically different molecular crystals have allowed correlating both the O-H bond length ( $r$ ) and the O-H stretching frequency shift, with respect to unassociated species ( $\Delta\nu$ ), with the intermolecular O···O distance ( $R$ ). These correlations are expressed as empirical laws [5] or rationalized by empirical potentials such as that of Lippincott and Schroeder [6]. On the other hand, in high pressure experiments the O···O distance is "mechanically" varied. Frequency shifts can be measured up to 100 GPa with diamond anvil cells, whereas it is now possible to perform neutron diffraction up to 10 GPa thanks to recent technical developments [7,8], therefore having direct access to the O-H distance.

Such high pressure experiments on ice VIII yield surprising and apparently contradictory results [1,9-11]. Raman spectroscopy shows a noticeable pressure shift

( $\sim -20 \text{ cm}^{-1} \text{ GPa}^{-1}$ ) which should correspond to an O-H bond pressure lengthening of about  $2 \times 10^{-3} \text{ \AA GPa}^{-1}$  whereas the neutron diffraction does not indicate any noticeable variation of  $r$  in the pressure range 0-10 GPa. Nelmes *et al.* conclude that "the average changes in O-H with different chemical environments at constant (ambient) pressure are not the same as those caused by hydrostatic pressure in a single material" [1]. This unexpected behavior is very well accounted for by periodic Hartree-Fock calculations [11,12] which accurately reproduce the equation of state, the pressure dependence of the lattice parameters, and atomic fractional coordinates as well as the  $\nu A_{1g}$  pressure shift.

Ice VIII is an antiferroelectric ordered phase of ice which belongs to the  $I4_1/amd$  space group with oxygen and hydrogen atoms, respectively, in positions 8e and 16h. The asymmetric unit is made of two hydrogen-bonded water molecules lying in perpendicular planes with their dipole moments directed along parallel directions. These units form two independent  $I4_1md$  ferroelectric hydrogen-bonded sublattices with dipole moments directed along the  $c$  axis in opposite directions. In order to get an explicative picture of the interactions governing the behavior of ice VIII under pressure, we have performed a series of *ab initio* calculations on model structures which allow us to discriminate between local and nonlocal interactions. These systems, shown in Fig. 1, are built from the asymmetric unit of ice VIII and are the  $C_s$  water dimer, the  $C_{2v}$  water trimer in which the central molecule forms two H bonds, a linear  $Pm11$  polymer, and the  $I4_1md$  sublattice of the ice VIII structure. In addition to the "ice VIII" structure of the water dimer (dimer 1), the  $C_s$  equilibrium structure in which the dipole moments are nearly orthogonal (dimer 2) has also been calculated. Molecular and periodic calculations have been performed at the self-consistent field (SCF) level with the GAUSSIAN92 [13] and CRYSTAL92 [14] softwares with the standard 6-31G\*\* basis set [15] which appears to be optimal for the periodic calculations as testified by the ice VIII results. Extensive calculations

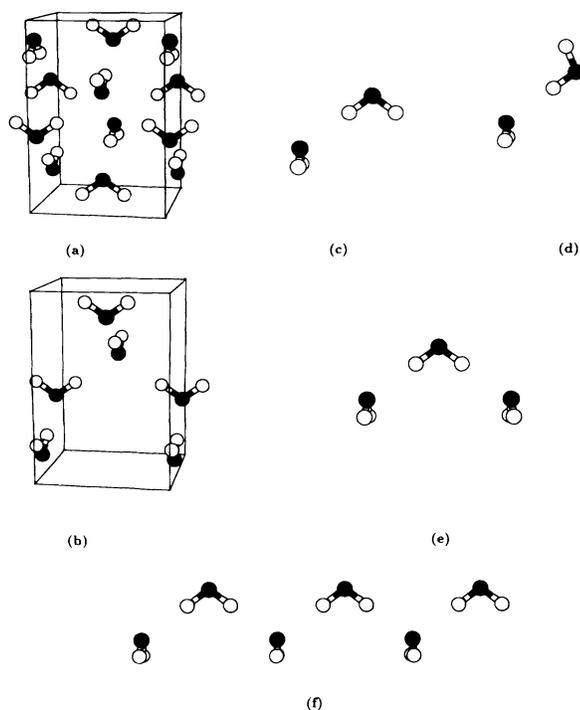


FIG. 1. Structures investigated. (a)  $I4_1/amd$  ice VIII, (b)  $I4_1md$  prototype, (c) dimer 1, (d) dimer 2, (e) trimer, and (f) polymer.

on the water dimer [16] have shown that this basis set yields an optimized structure, in qualitative agreement with those calculated with better basis sets involving diffuse  $s$  and  $p$  functions at the MP/2 level. The neglect of electron correlation is the weakness of the Hartree-Fock approximation. In molecular interactions correlation ac-

counts for dispersion forces which are rather short ranged due to an  $R^{-6}$  decay. The effect of correlation is then expected to be almost similar through the series of related structures. Comparison between Hartree-Fock and configuration interaction results [17] do not indicate any qualitative change of the structure dependence upon intermolecular distance but rather a systematic shift of the numerical values.

In the three-dimensional periodic calculations the reciprocal space integration has been performed using a commensurate net, the meshes of which were determined by the shrinking factor  $S$ .  $S = 4$ , corresponding to 24  $k$  points, has been used for the present calculations; when  $S = 8$  is used the energy change is less than the SCF convergence threshold  $10^{-6}$ . For the polymer, the same shrinking factor has been retained.

The model structures have been partially optimized for five O...O distances (3.03, 2.90, 2.87, 2.80, and 2.77 Å), the bond angle of the proton donor water molecules being constrained at its ice VIII value, and the bond length and angle of the proton acceptor only molecules at the 6-31G\*\* free molecule values. For each structure the energy was also minimized with respect to the intermolecular distance  $R$ . Figure 2(a) displays for the different systems  $r$  as a function of the optimized O...O separation  $R_{eq}$ ; the decrease of the O-H distance with  $R_{eq}$  is consistent with the correlations obtained from experimental data on different compounds. On the contrary, for a given system when  $R$  is varied by an external stress the variation of  $r$  is much weaker and can be in an opposite direction, as shown in Fig. 2(b). Moreover, the curves corresponding to the two dimer structures almost coincide, which indicates that the electrostatic potential anisotropy of the local interaction between two hydrogen-bonded molecules has no noticeable effect on the intramolecular O-H bond

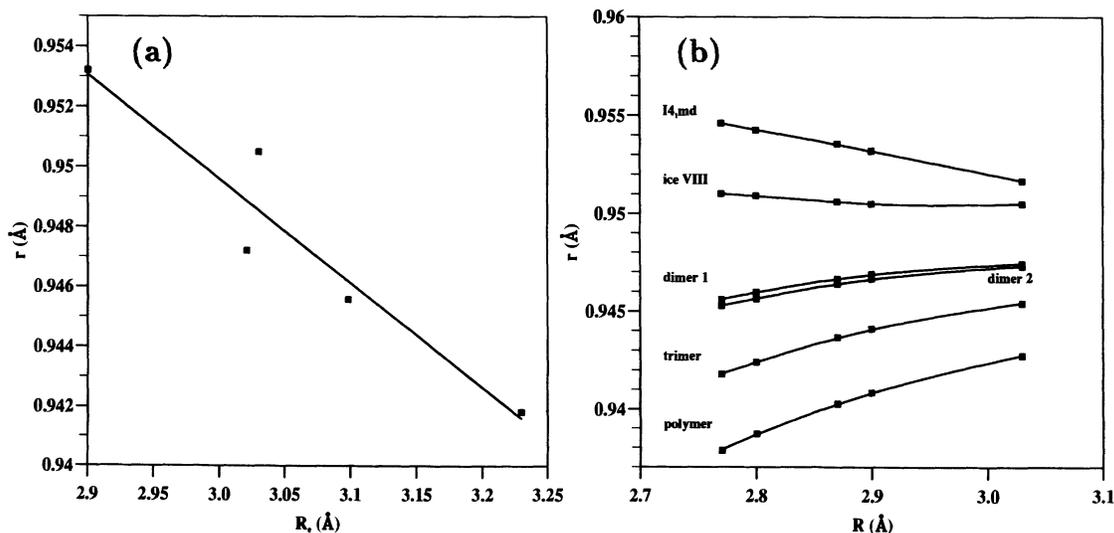


FIG. 2. Dependence of the O-H intramolecular distance upon intermolecular distance: (a)  $r$  vs  $R_{eq}$ , (b)  $r$  vs  $R$ .

length. These two results are in agreement with the available experimental data: on the one hand the  $r$  versus  $R_e$  correlation data collected by Olovsson and Jönsson [4] and by Ichikawa [18] and on the other hand the pressure dependence of the intramolecular O-H bond in ice VIII [1]. They numerically demonstrate that high pressure results cannot be interpreted on the basis of a dependence of  $r$  upon  $R$  obtained from the equilibrium structures of different systems. From such correlations a single well potential in ice (i.e.,  $r = R/2$ ) is expected for  $R = 2.4$  Å. From Raman spectroscopy [10] there is no evidence of a single potential below 70 GPa which contradicts this previous prediction. Moreover, empirical potentials [6,19] which have been built in order to reproduce the experimental  $r$  versus  $R_e$  trend should often be unphysical.

The calculation on the  $I4_1md$  prototype structure provides information on the nature of the interaction energy between the two sublattices of ice VIII. At the SCF level, this interaction energy is small and positive (0.006 08 a.u./cell at  $R=3.0$  Å). It is the sum of the electrostatic and exchange contributions; the former is expected to be the dominant contribution because the shorter interatomic distances between the two sublattices are about 3 Å. An estimate of the dispersion contribution restricted to  $C_6$  coefficients is  $-2.54 \times 10^{-4}C_6$ . With the water molecule  $C_6$  values of the literature [20,21] the dispersion energy is of the order of  $-1 \times 10^{-2}$  and the interaction becomes attractive. It is interesting to note that the equilibrium O...O distance calculated for this system is shorter than that of ice VIII by 0.1 Å. The same difference is found between the  $H_2 \cdot H_2O$  clathrate and ice VIII [22]. The water molecule network of this clathrate corresponds to one of the ice VIII sublattices and the dihydrogen molecules occupy the vacancies. The calculated  $A_{1g}$  vibron frequency difference between the  $I4_1md$  structure and ice VIII is twice that of the clathrate.

These results suggest that long range electrostatic interactions between non-H-bonded molecules could significantly modify the properties of the hydrogen bond in ice. The model of Coulson and Eisenberg [23] shows that the dipole-dipole interaction of a reference water molecule and the rest of the crystal is the most important anisotropic contribution to the electrostatic energy. It can be written as

$$E^{dd} = \mu^2 G, \quad (1)$$

in which  $\mu$  is the molecular dipole moment and  $G$  a structure dependent factor.  $G$  is calculated by summing the dipole-dipole interactions in a sphere around the reference molecule, with a radius large enough to ensure a reasonable convergence of the series. Moreover, this geometrical factor is proportional to  $R^{-3}$ . Assuming the potential of the O-H bond to be harmonic, the variation  $\Delta r$  will be such as

$$\frac{1}{2}k\Delta r^2 + \frac{\partial E^{dd}}{\partial r}\Delta r = 0. \quad (2)$$

Thus,

$$\Delta r = -\frac{4}{k}\mu G \frac{\partial \mu}{\partial r} \quad (3)$$

and

$$\frac{\partial \Delta r}{\partial R} = -\frac{4}{k}\mu \frac{\partial G}{\partial R} \frac{\partial \mu}{\partial r} = \frac{12}{k}G \frac{\partial \mu}{\partial r}. \quad (4)$$

For the polymer, the  $I4_1md$ , and  $I4_1/amd$  structures  $G = 1.06 \times 10^{-2}$ ,  $-2.59 \times 10^{-3}$ , and  $-1.81 \times 10^{-3}$  a.u., respectively, which is in qualitative agreement with the calculated bond shifts and with the slopes of the curves  $r = f(R)$ . For proton fully disordered structures, the averaged dipole moment is zero and one can expect, therefore, that the crystal behavior would be close to that of the dimer.

The series of *ab initio* calculations presented here emphasizes the importance of long range electrostatic interactions in ice. It forms a self-consistent set and therefore the results are expected to have a homogeneous accuracy. The very good agreement between calculation and experiment obtained for the reference system ice VIII (the only one for which a comparison can be made) warrants the reliability of our conclusions.

Our results suggest that realistic H-bond potentials can be derived from accurate *ab initio* calculations on dimers such as those of Rybak [24] rather than from zero pressure experimental data. Such potentials would model the short range interactions whereas long range forces can be accounted for by standard electrostatic, polarization, and dispersion potentials. However, such a strategy is hampered by the difficulty of defining an objective partition of the molecular crystal into molecules in order to have access to molecular multipole moments and polarizabilities in the crystal. The theory of atoms in molecules [25] provides a clue to solve this problem.

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