# Ab-Initio Total Energy Studies of the Static and Dynamical Properties of Ice Ih

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We present a detailed study of the structural and dynamical properties of ice Ih. Methods used include the ab-initio pseudopotential and molecular orbital techniques. In order to simulate the proton disorder present in ice Ih supercells are constructed with the orientation of water molecules determined in such a way that all possible nearest neighbor orientations are included while still obeying the Bernal–Fowler ice rules. For structures considered all structural parameters are relaxed. The dependence of bond length on the orientation of surrounding molecules in both the dimer and fully coordinated system is discussed. All local dimer orientations are accounted for in the supercell of ice Ih considered. The dynamical properties of a 16-molecule supercell model of ice Ih are then investigated via direct determination of the zone center dynamical matrix. Here the dynamical matrix is calculated directly from atomic forces obtained when each atom is shifted away from its equilibrium position. The vibrational modes are then calculated, and the mode frequency as a function of microscopic deformation is discussed.

### I. Introduction

The structure and dynamics of the various phases of ice are determined by the properties of the hydrogen bonding network. The hydrogen bond is notoriously difficult to model in a consistent manner; numerous empirical models have been proposed<sup>1-2</sup> for the interaction of water molecules, but none are entirely satisfactory. In order to fully understand the nature of the hydrogen bond at a microscopic level, a proper quantum mechanical treatment is required. Here we present an ab-initio pseudopotential study of the static and dynamical properties of ice Ih within a fully coordinated structure. Previous ab-initio studies that model ordered periodic ice structures have utilized both density functional<sup>3</sup> and Hartree-Fock<sup>4</sup> approaches. Other recent calculations have used molecular cluster techniques to probe the nature of the hydrogen bond in different geometries.<sup>5-7</sup> Here we attempt to model the disorder inherent in ice Ih in a supercell that contains all possible nearest neighbor orientations of water molecules. The dynamical properties of the lattice are assessed by numerical evaluation of the zone center dynamical matrix. A related technique has recently been used to obtain full phonon dispersions in highly symmetric structures.<sup>8</sup> The paper begins with a description of the choice of unit cell followed by a brief description of the methods employed and then a discussion of both static and dynamic results.

## **II. Unit Cell Choice**

In the structure of ice Ih the oxygen atoms lie on a hexagonal "wurtzite" lattice (space group  $P6_3$ /mmc). In this structure each oxygen atom is tetrahedrally coordinated. Hydrogen atoms occupy the sites between neighboring oxygens in a disordered fashion but subject to the "ice rules".<sup>9</sup> These state that each

oxygen atom is covalently bonded to two hydrogen atoms with the additional constraint that only one hydrogen atom can lie between two neighboring oxygen atoms. An important consideration in modeling the properties of ice Ih is the inclusion of disorder at some level. In the calculations presented here the method requires the use of periodic boundary conditions; hence disorder has to be modeled within a "large" periodically repeated supercell. As has been pointed out previously,<sup>2</sup> each hydrogen bond can be characterized according to the local orientation of the two water molecules involved in the bond. Four possible orientations are possible in the case of ice Ih, two corresponding to bonds parallel to the c-axis, labeled A and B, and two "planar" orientations, labeled C and D. Statistically we expect the ratio of A type to B type and C type to D type to be 2:1. The ratio of (A+B) to (C+D) is constrained by the lattice to be 1:3.

The supercell chosen for the calculations consists of 16 molecules in an orthorhombic unit cell. This relatively small cell size is necessary because of computational constraints imposed by the ab-initio method. We have determined computationally that there are 2970 possible different configurations for hydrogen positions obeying the ice rules (some are equivalent by symmetry). This number is much larger than  $1.51^N$ , where N is the number of molecules predicted on statistical grounds in a infinite lattice<sup>10</sup> due to enhanced positional correlations associated with the imposition of periodic boundary conditions. Out of the 2970 configurations 380 exhibit zero net dipole moment, as is appropriate for a truly random structure. From this set we have chosen a representative configuration with ratios of A type to B type and C type to D type of 3:1. In this size cell configurations with the ratio 2:1 predicted statistically in an infinite lattice do not exist. The lattice vectors and relative coordinates (assuming the perfect tetrahedral geometry) together with a labeling of each hydrogen atom corresponding to the different hydrogen bond types A, B, C, and D are listed in Table 1.

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TABLE 1: Relative Coordinates of the Atomic Positions in the Supercell Used Here<sup>a</sup>

oxygen			hydrogen 1					hydrogen 2			
0.000	0.000	0.000	0.091	0.060	0.045	С	0.909	0.060	0.045	С	
0.500	0.000	0.000	0.500	0.879	0.045	D	0.500	0.000	0.864	А	
0.250	0.500	0.000	0.250	0.379	0.045	С	0.159	0.560	0.045	С	
0.750	0.500	0.000	0.841	0.560	0.045	С	0.750	0.500	0.864	А	
0.250	0.167	0.125	0.341	0.106	0.080	С	0.250	0.167	0.261	В	
0.750	0.167	0.125	0.659	0.106	0.080	С	0.750	0.287	0.080	С	
0.000	0.667	0.125	0.000	0.787	0.080	D	0.000	0.667	0.261	А	
0.500	0.667	0.125	0.409	0.606	0.080	С	0.591	0.606	0.080	С	
0.250	0.167	0.500	0.159	0.106	0.545	D	0.250	0.287	0.545	С	
0.750	0.167	0.500	0.750	0.167	0.364	А	0.659	0.106	0.545	D	
0.000	0.667	0.500	0.000	0.787	0.545	С	0.091	0.606	0.545	D	
0.500	0.667	0.500	0.500	0.667	0.364	А	0.591	0.606	0.545	D	
0.000	0.000	0.625	0.000	0.000	0.761	А	0.909	0.060	0.580	С	
0.500	0.000	0.625	0.409	0.060	0.580	С	0.500	0.879	0.580	С	
0.250	0.500	0.625	0.250	0.500	0.761	В	0.341	0.560	0.580	С	
0.750	0.500	0.625	0.750	0.379	0.580	С	0.841	0.560	0.580	С	

<sup>*a*</sup> The coordinates are grouped into molecular units and each hydrogen is labeled according to the hydrogen bond type it is associated with. The coordinates correspond to the perfect "unrelaxed" geometry, with all atomic sites being determined by the tetrahedral geometry. The magnitudes of the unrelaxed orthogonal unit cell vectors here are 9.000, 7.794, and 7.348 Å, respectively.

#### **III.** Computational Methods

The total energies of the interacting electron system are calculated within the ab-initio pseudopotential method<sup>11</sup> using the CASTEP and CETEP codes. Here the interaction of valence electrons with the ionic cores is replaced by a norm-conserving pseudopotential. The single-particle states associated with the Kohn-Sham equations are expanded in terms of a plane wave basis and the Kohn-Sham equations solved by conjugate gradient minimization of the energy functional. Because of the large cell size used here, only the  $\Gamma$  point was included in Brillouin zone integrations. Forces on the ions are obtained by the Hellman-Feynman theorem and are used to relax ionic positions to the minimum energy by further application of the conjugate method. Also, the total energy is minimized with respect to the magnitude of the lattice vectors using a Newton-Raphson scheme. Accurate minimization using calculated stresses proved difficult because of large errors associated with the finite basis set used. A smooth norm-conserving pseudopotential is used to represent the oxygen ionic cores, and a bare Coulomb potential is used to describe protons. A kinetic energy cutoff of 800 eV is used in expanding the single-particle states. This cutoff is high compared to that needed in other systems due to the "hard" nature of the pseudopotentials associated with first-row elements.

The water dimer potential corresponding to the rotation of the water donor molecule around the O–O axis is computed at the second-order perturbation level of theory (MP2) with the augmented correlation consistent basis set of double- $\zeta$  quality (aug-cc-pVDZ)<sup>12</sup> using the Gaussian-94 suite of programs.<sup>13</sup> It has been established<sup>6</sup> that essential features of the hydrogen bond are sensitive to electron correlation effects. A recent study by Xantheas<sup>5</sup> has shown that gradient corrections to the local density approximation reasonably reproduce essential features such as structures and vibrational spectra of small water clusters, producing results of comparable quality to MP2. This has led us to use the generalized gradient approximation (GGA)<sup>14</sup> to density functional theory to describe electron correlation effects in this system.

The dynamical properties of the lattice are determined by numerical evaluation of the zone center dynamical matrix from atomic forces obtained from systematic displacements of ions away from equilibrium. The dynamical matrix is diagonalized in order to obtain the normal modes of vibration. The numerical method used is outlined in the Appendix. This method gives complete information regarding the frequencies and eigenvectors associated with each mode. The magnitude of the atomic shift used was 0.02 Å, and calculated forces were converged to 0.001 eV/Å. This was achieved by five conjugate gradient iterations starting from the single particle state coefficients of the equilibrium configuration.

#### **IV. Results**

a. Static Calculations. In the supercell calculations both the ionic positions and vector lengths were relaxed in order to find the equilibrium configuration. The final relaxed unit cell (with vector lengths 6.86, 7.29, and 8.30 Å) corresponds to an oxygen-oxygen (O-O) separation of 2.56 Å. This is ~6% smaller than the experimentally measured result, a relatively large error compared to parameters in other structures predicted using this method. This result demonstrates the high sensitivity of the hydrogen bond to the choice of correlation functional as explained below. It was decided to use the calculated lattice parameters, rather than experimental ones, in the subsequent dynamical calculations in order to avoid any anomalous effects due to artificial strain being imposed on the system. The average oxygen-oxygen separations for the A, B, C, and D type hydrogen bonds are 2.551, 2.548, 2.569, and 2.572 Å, respectively. The differences between A and B type and C and D type separations are in agreement with the sign of the differences predicted by calculations on the water dimer in all four orientations detailed below. These differences are approximately an order of magnitude less than in the dimer itself due to the much restricted molecular motion imposed in the fully coordinated structure.

We have computed the water dimer potential as a function of the O-O separation and the dihedral angle corresponding to the rotation of the "free" H atom of the water donor molecule around the O-O axis. The results are shown in Figure 1. Two cases were considered: in the "linear" case the H atom participating in the hydrogen bond is constrained to lie on the O-O line, this constraint is relaxed in the "nonlinear" case. For the water dimer case, we observe a much greater variation in the O-O separations between different orientations compared to the supercell calculation. This is, however, expected due to severe constraints on bond relaxation imposed by full coordination of each molecule in the supercell. The water dimer minimum energy configuration corresponds to the "B" orientation. The energy difference between the *c*-axis "A" and "B" configurations (0.85 kcal/mol or 37 meV/dimer) is computed to be larger than between the planar "C" and "D" configurations





**Figure 1.** Calculated water dimer O–O separation and change in electronic energy difference as a function of the dihedral angle (alpha) corresponding to the rotation of the proton donor molecule around the O–O axis. Filled circles correspond to the "linear" hydrogen bond case; open circles correspond to the "nonlinear" hydrogen bond case.

(0.45 kcal/mol or 20 meV/dimer). Because of the similarity of the O–O separations seen in the relaxed supercell, this implies that the *c*-axis bonds are particularly frustrated in this system. Further relaxation may occur in larger supercells, where particular groupings of bond types may relax the geometrical constraints on bond lengths.

As a benchmark for the accuracy in structural parameters expected using the pseudopotential method, we have performed calculations for the water monomer and dimer. The gas phase modeling of these structures using a periodic based approach was achieved by increasing the cell size until no cell size effects were seen. The O–H bond length in the monomer was calculated as 0.95 Å (expt 0.96 Å), the dimer O–O length calculated as 2.82Å (vs 2.91 Å<sup>15</sup>), and the bond energy as 0.24 eV (vs 0.22 eV<sup>15</sup>). Although the covalent bond length and dimer binding energies are in good agreement with the ab-initio results, the error in the dimer O–O separation is of magnitude similar to that in the fully coordinated case. The principal source of error here is associated with the pseudopotential approximation and the sensitivity of the hydrogen bond to the choice of energy functional.

**b.** Dynamical Calculations. The phonon density of states (DOS) of the ice Ih model calculated here is presented in Figure 2. Strictly this is the density of states calculated from zone center modes of the Brillouin zone associated with our supercell. Because of the limited size of the supercell, this represents an extremely coarse sampling of reciprocal space. In our approach vibrational frequencies are given directly; that is, the frequency output is simply a list of 144 frequencies corresponding to the number of degrees of freedom in the supercell. In order to facilitate presentation, each frequency has been "broadened" by



**Figure 2.** Calculated phonon density of states associated with ice Ih. Only  $\Gamma$  point modes associated with the supercell Brillouin zone are included. Also shown are the density of states obtained by weighting each frequency with the sum of magnitudes of projections onto pure vibrational, librational, bending, symmetric stretch, and antisymmetric stretch modes. The DOS was obtained by broadening each individual frequency by a Gaussian of half-width at half-maximum of 30 cm<sup>-1</sup>.

a Gaussian function of half-width at half-maximum of  $30 \text{ cm}^{-1}$ in order to produce Figure 2. This value is chosen as optimal in retaining the essential features of the frequency spectra. Further, each mode has been projected into components corresponding to the antisymmetric, symmetric, and bending modes of each water molecule in isolation. Molecular motion has been projected into components corresponding to pure librational motion (modes where the orientation of the water molecule about its center of mass changes) and pure vibrational motion (modes where the relative position of the center of mass changes). Also plotted in Figure 2 are the density of states obtained by weighting each frequency by the sum of the magnitudes of each individual component in the five classes of motion mentioned above.

As expected, we see a distinct division of the DOS in frequency space corresponding to mainly vibrational, librational, bending, and stretching modes. There exists, however, important mixing of these regions. We first consider the region of frequencies  $2650-3200 \text{ cm}^{-1}$ , where two distinct peaks are seen. These modes project mainly on the molecular stretching modes. Similar features are seen in ab-initio molecular dynamics studies of ice Ic<sup>3</sup> but with the weight of the higher frequency peak much less than the one computed here. Decomposing the lower frequency peak into its symmetric and antisymmetric components shows the higher frequency part of the peak to comprise mainly antisymmetric components. The width of this peak,



**Figure 3.** Phonon density of states in the vibrational region of the spectra. Also shown are density of states obtained by weighting each frequency with the sum of magnitudes of projections of the center of mass motions along the four bond type directions. The DOS was obtained by broadening each individual frequency by a Gaussian of half-width at half-maximum of  $15 \text{ cm}^{-1}$ .

 $\sim 100 \text{ cm}^{-1}$ , is comparable to the separation of the antisymmetric and symmetric frequencies of the isolated water molecule (3943 and 3832 cm<sup>-1</sup>). The downward shift of the center of this feature with respect to the average molecular stretch frequency is due to interaction with hydrogen bonds. The upper peak in this region comprises equal weightings of antisymmetric and symmetric modes; analysis of individual modes in this region shows individual water molecules exhibiting antisymmetric and symmetric stretch type motion in almost equal numbers. Close examination of this frequency range shows a small amount of mixing with vibrational and bending modes. Practically zero mixing with vibrational modes is seen for the higher energy peak.

The peak in the frequency range  $1650-1800 \text{ cm}^{-1}$  is seen to be of mainly molecular bending origin with small, but not insignificant, contributions from the librational and vibrational projections. The width of the peak is very narrow, a feature also seen in similar studies of ice Ic.<sup>3</sup> The feature in the frequency range  $720-1320 \text{ cm}^{-1}$  is seen to mainly consist of librational motions of individual molecules with some contributions from the translational and bending modes. Essentially zero mixing is seen with the stretching modes in this frequency range, as is expected considering the nature of a librational motion.

Finally, the feature in the frequency range  $120-420 \text{ cm}^{-1}$  is seen to comprise mainly vibrational motion with some librational contribution. Comparison with neutron scattering studies<sup>2</sup> shows the upper edge the vibrational mode region to lie higher in frequency by  $\sim 100 \text{ cm}^{-1}$  compared to the measured upper edge of the vibrational region. This discrepancy is also observed in ab-initio molecular dynamics studies of ice Ic using similar methods<sup>3</sup> and is presumably due to the inadequacy of the GGA energy functional. Although two peaks are seen in this frequency range, our results cannot be directly compared to the experimental neutron scattering studies<sup>2</sup> since only the  $\Gamma$  point was included in the Brillouin zone integrations instead of a very fine integration of reciprocal space.

The vibrational mode region was further investigated by projecting the center of mass motion associated with each molecule along the four nearest neighbor directions for each mode. This allows us to assess the nature of the vibrational region in terms of the different directions associated with the hydrogen bonds. As previously stated, these projections can be labeled A, B, C, and D according to the local orientation of adjacent molecules. In Figure 3 we plot the spectra obtained by weighting the frequencies with the sum of magnitudes of projections in the A, B, C, and D directions, respectively. The width of the Gaussian function used to broaden the frequencies used here is reduced to 15 cm<sup>-1</sup> in order to sharpen the features seen. For easy comparison the spectra have been inversely weighted with the number of bonds of each type. If modes in a particular frequency range were due to vibrational distortions of a particular group of bond types, some evidence may be seen here. Although some differences are seen in the spectra for different bond types, e.g. the B projection contains higher frequency components in the uppermost frequency range here, in general they are all similar. The similarity in all four projections is probably due to the very restricted geometry of the cell used, it being practically impossible to induce a distortion in one bond type without distorting the others.

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#### Appendix

The calculation of the zone center dynamical matrix in terms of atomic forces obtained by distorting individual ionic coordinates away from equilibrium is formulated as follows.

We may write the total energy of the lattice as a Taylor expansion:  $^{16}$ 

$$E = E_0 + \frac{1}{2} \sum_{ij} A_{ij} u_i u_j + \frac{1}{6} \sum_{ijk} B_{ijk} u_i u_j u_k$$
(1)

Here  $E_0$  represents the equilibrium lattice energy and  $u_i$  is a general coordinate of an ion relative to the minimum energy configuration (*i* labels both the ion and a particular Cartesian direction).  $A_{ij}$  describes the harmonic response of the lattice and is used to construct the dynamical matrix from

$$D_{ij} \frac{1}{(m_i m_i)^{1/2}} A_{ij} \tag{2}$$

where the  $m_i$  represent the ionic masses.

The force on a general coordinate is written

$$F_{i} = -\frac{dE}{du_{i}} = -\sum_{j} A_{ij} u_{j} - \frac{1}{2} \sum_{jk} B_{ijk} u_{j} u_{k}$$
(3)

If we assume the starting configuration is not exactly at the

equilibrium configuration (because it is very difficult to fully relax the lattice in complex cells as are considered here), we may write

$$F_i^0 = -\sum_j A_{ij} u_j^0 - \frac{1}{2} \sum_{jk} B_{ijk} u_j^0 u_k^0$$
(4)

Here  $F_i^0$  represents the forces on ions when the relaxation process has terminated and  $u_i^0$  is the "error" in the final relaxed coordinates.

We now independently shift each general coordinate by an amount  $\pm \Delta$  and minimize the total energy with respect to electron wave functions to obtain forces on all ions in this distorted configuration. We now obtain

$$F_i^{\pm\Delta m} = -\sum_j A_{ij}(u_j^0 \pm \Delta \delta_{jm}) - \frac{1}{2} \sum_{jk} B_{ijk}(u_j^0 \pm \Delta \delta_{jm})(u_k^0 \pm \Delta \delta_{km})$$
(5)

where  $F_i^{\pm \Delta m}$  represents the force on coordinate *i* due to a change in coordinate *m* of  $\pm \Delta$ . Using eqs 3 and 4, we may write

$$F_{i}^{\pm\Delta m} = F_{i}^{0} \mp \Delta A_{im} + (\mp \sum_{j} B_{imj} u_{j}^{0}) - \frac{1}{2} \Delta^{2} B_{imm}$$
(6)

Taking sums and differences of the  $F_i^{\pm \Delta m}$  gives

$$F_i^{-\Delta m} - F_i^{+\Delta m} \Delta A_{im} + (\sum_j B_{imj} u_j^0)$$
(7)

$$F_{i}^{-\Delta m} + F_{i}^{+\Delta m} = 2F_{i}^{0} - \Delta^{2}B_{imm}$$
(8)

If the  $F_i^0$  are very small (subsequently the  $u_i^0$  are small) and neglected, then the matrix  $A_im$  can be obtained directly from eq 7. If this is not deemed to be the case, then the  $A_{im}$  can be improved in an iterative fashion as follows. Initially the matrix  $A_{im} \equiv \mathbf{A}$  is estimated from eq 7 neglecting the bracketed quantity. The  $u_i \equiv \mathbf{u}$  are then estimated by inverting the matrix **A** and using the relation  $\mathbf{u} = -\mathbf{A}^{-1}\mathbf{F}$ , where  $F_i^0 \equiv \mathbf{F}$ . This relation is obtained from eq 3 by retaining only the linear term. Equation 8 is used to obtain  $B_{ijj}$  and an improved estimate of  $A_{ij}$  obtained from eq 7 with the additional assumption  $B_{ijk} = 0$   $\forall i \neq j \neq k$ . This procedure is then repeated in an iterative fashion.

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