New observations on hydrogen bonding in ice by density functional theory simulations*

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In this paper, we report on a series of computational simulations on hydrogen bonding in two ice phases (Ih and Ic) using CASTEP with PW91 and RPBE exchange–correlation based on *ab initio* density functional theory. The strength of the H-bond is correlated with intramolecular O–H stretching, and the energy splitting exists for both the H-bond and covalent O–H stretching. By analyzing the dispersion relationship of $\omega(q)$, we observe the separation of the longitudinal optic (LO) mode from transverse optic (TO) mode at the gamma point, seemingly interpreting the controversial two H-bond peaks in the vibrational spectrum of ice recorded by inelastic incoherent neutron scattering experiments. The test of ambient environment on phonon density of sates (PDOS) shows that the relaxed tetrahedral structure is the most stable structural configuration for water clusters.

Keywords: density functional theory, ice, hydrogen bonding, LO–TO splitting

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1. Introduction

Since the discovery of the hydrogen bond (H-bond), it has been generally recognized that the unusual properties of water and ice are due to the existence of H-bonding between water molecules. Hence, H-bonding is regarded as a crucial factor in determining many of the distinctive properties of water and biological complexes.[1–4] Investigating the nature of the hydrogen bonding in water is, thus, of fundamental significance for understanding the bioactivity of biological systems in a hydration environment. Although experiments have presented a distinct dynamic picture of ice, particularly its intermolecular interactions,[5] performing computer simulations of the phonon density of states (PDOS) of ice remains a challenging problem in this field.[6–12]

Despite their simplicity, the two peaks occurring in the region of translational vibrations, which can be attributed to H-bonding, are not thoroughly understood. Li and Ross proposed two H-bond strengths in their lattice dynamic simulation, which appeared to be in good agreement with the measured results.[5,6] However, the concept was not widely accepted[13] and was proven incorrect in our previous work.[14,15] Morrison and Jenkins[16] suggested that the splitting of the optic modes between 200 cm^{-1} and 320 cm^{-1} indicated the coupling between the intramolecular stretching vibrations due to an in-phase and out-of-phase stretching motion associated with adjacent molecules. However, this explanation was phenomenological and lacked theoretical support. He *et al*.[17] theoretically proposed that the special features arise from the directionality, or anisotropy, of collective hydrogen-bond stretching vibrations, which has been disproved by inelastic incoherent neutron scattering (IINS). It is widely accepted that these two peaks cannot be attributed to LO–TO splitting because, as pointed out by Klug *et al*., the difference between the peaks is just 10 cm^{-1}.[18] However, through the analysis of the dispersion curve, we show that the integral of the PDOS does, in fact, originate from LO–TO splitting.

2. Computational methodology and results

Ice is a molecular solid in which the intermolecular bonding consists primarily of H-bonds. In ordinary ice, Ih, the oxygen atoms sit on a lattice of two interpenetrating, hexagonal close-packed structures classified as space group $P6_3/mmc$.[19] As shown in Fig. 1, the water molecules are orientated in such a way that one hydrogen atom lies along an axis joining two oxygen atoms of neighboring molecules, with five water molecules forming a tetrahedron. X-ray diffraction[20] and neutron diffraction[21–23] studies have determined that there are two on-axis O–H distances: the covalent O–H bond length (about 1.00 Å) and the remarkably longer O–H distance (about 1.75 Å) (H-bond). The molecular orientations are correlated in such a way that they maintain this arrangement according to the Bernal–Fowler ice rules, although there is no long-range order in the protons (or rather, hydrogen atoms).[24,25] Cubic ice, Ic, is composed of a metastable cubic crystal lattice. The oxygen atoms are arranged in a diamond structure based on a cubic close packing arrangement.[26] Ice Ic has almost exactly the same density as ice Ih and transfers readily into ice Ih when being warmed

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above −80 °C at atmospheric pressure. The IINS vibrational spectra of ice Ic and Ih are fundamentally the same, having almost the same energy positions for the acoustic and optic peaks and the same bandwidth for the librational modes.[6] The present work focuses on these two ice phases.

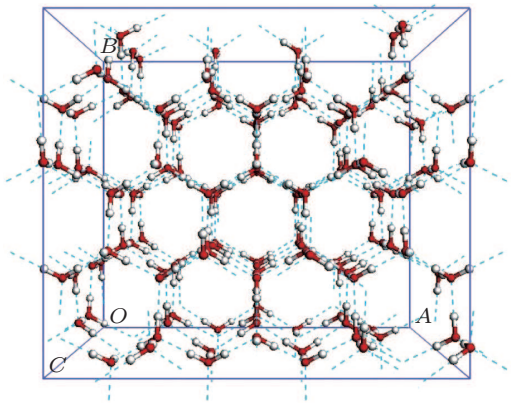


Fig. 1. (color online) A perspective view of a 128-H_2O-molecule supercell in an ice Ih crystal. Each H_2O molecule links four H-bonds with its neighbors to form a tetrahedral structure.

Density functional theory calculations were conducted using the CASTEP package, which has advantages for the calculation of phonon dispersion curves.[27] The detailed setup of the calculations and parameters used in the calculation can be found in Ref. [14] by Zhang *et al*.

Figure 2 illustrates the PDOS diagram for a larger Ih supercell (64 H_2O molecules). These results are consistent with the results of neutron scattering experiments performed on the HET (high-energy transfer) instrument at ISIS, with slight overestimation.[6] In the translational region, the fairly sharp maximum peak occurring at around 190 cm^{-1} and the shoulder on the right-hand side (at around 280 cm^{-1}) can be assigned to acoustic modes. The two sharp peaks located at about 350 cm^{-1} and 430 cm^{-1} (indicated by the arrows) with cutoffs on their right-hand sides come from the two controversial H-bonds of the optic lattice vibration modes. The librational region is from 740 cm^{-1} to 1270 cm^{-1}, and the narrow band around 1600 cm^{-1}, which indicates the bending vibration region. There are four peaks in the intramolecular vibrations: the peaks at 2710 cm^{-1} and 2988 cm^{-1} indicate symmetry stretching and the peaks at 2784 cm^{-1} and 3111 cm^{-1} indicate asymmetry stretching. The frequencies between these four peaks correspond to hybrid vibration modes of both the symmetry and asymmetry stretching modes. We observe energy splitting, not only for the H-bonds but also for the covalent O–H stretching, whereas splitting for the libration and bending modes could not be distinguished. As is well known, frequency splitting occurs in an ion crystal between the TO and LO lattice vibrations by the Lyddane–Sachs–Teller relation. Here we can see that ice, a molecular crystal, presents similar properties.[28]

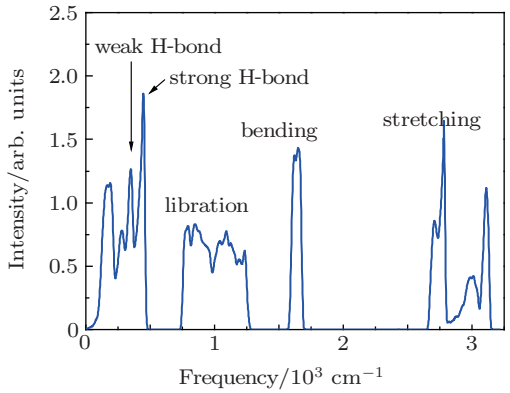


Fig. 2. (color online) CASTE-calculated PDOS diagram for a 64-H_2O Ih supercell by WC potential in Ref. [29]. The main vibration bands are marked. The peaks of the H-bonds and intramolecular O–H stretching bonds show energy splitting.

To discover more about the effect of H-bonding on phonon modes, we systematically examine the effect of the lattice constants in ice Ic, with the Ic crystal model chosen for simplicity.

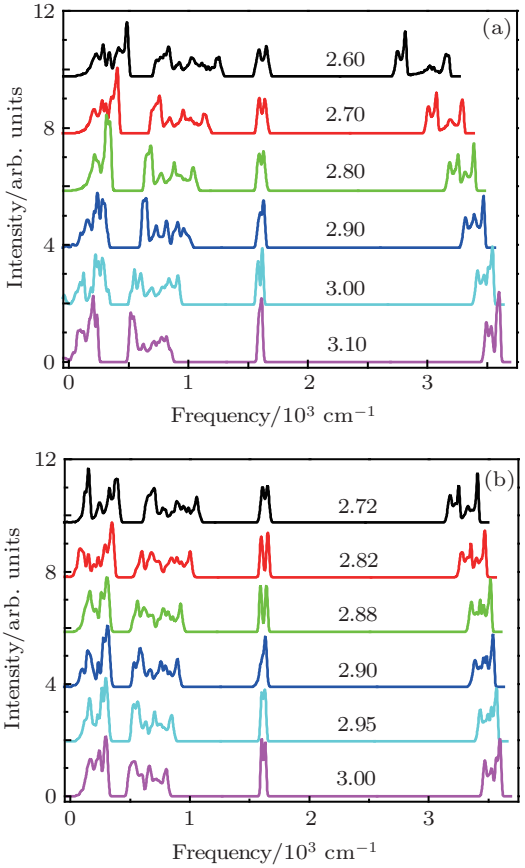


Fig. 3. (color online) CASTEP simulations (XC is PW91[30] for panel (a) and RPBE[31] for panel (b)) of PDOS for different pairwise O–O distances of ice Ic (4 molecules in the crystal cell). The O–O distance increases from 2.6 Å to 3.1 Å with PW91 XC and from 2.72 Å to 3.00 Å with RPBE XC.

When we test the effects of different O–O distances, the results show a clear correlation between the strength of the H-bonds and intramolecular O–H stretching. Figure 3 shows

that, as the distance between neighboring oxygen atoms increases, the intra-molecular O–H stretching frequencies increase, whereas those of the H-bonds decrease. This effect occurs because the coefficient of restitution between the neighbors is reduced as the distance increases. Meanwhile, the strength of the intra-molecular O–H stretching vibration increases with the weakening of environmental effect. A comparison between the results of the two generalized gradient approximation potentials indicates little discrepancy (Table 1). The results using the PW91[30] exchange–correlation (XC) show that as the O–O distance expands, the length of the covalent bond (O–H) decreases from 1.019 Å to 0.990 Å, and that of the H-bond increases from 1.583 Å to 2.105 Å. For the RPBE[31] XC, when the O–O distance increases to 3.00 Å, the simulation PDOS spectrum is in good agreement with the IINS spectrum of ice VIII. Ice VIII consists of two inter-penetrating ice Ic sublattices, and the H-bonding networks in these two sublattices are independent.[32] The H-bonded O–O distance is 2.88 Å in ice VIII, but in this study the PDOS pattern is only in accordance with the IINS of ice VIII when the O–O distance is expanded to 3.00 Å. This discrepancy is due to the neglect of the electrostatic interactions between the two inter-penetrating Ic sublattices in the VIII structure.

Table 1. H-bond (represented as H–O) and intra-molecular covalent bond (O–H) distance with two XC potentials. Their discrepancy is less than 0.5%.

Using PW91 XC			Using RPBE XC		
O–O/Å	H–O/Å	O–H/Å	O–O/Å	H–O/Å	O–H/Å
2.60	1.583	1.019	2.72	1.719	1.002
2.70	1.692	1.009	2.82	1.824	0.997
2.80	1.798	1.002	2.88	1.887	0.994
2.90	1.903	0.997	2.90	1.912	0.993
3.00	2.006	0.993	2.95	1.964	0.991
3.10	2.105	0.990	3.00	2.015	0.989

The left panel of Fig. 4 presents the dispersion curves of ice Ic, which only contains two water molecules in a primitive cell to yield 18 lattice waves. The corresponding integrals of PDOS are shown in the right panel. The CASTEP results exhibit some enhancement with respect to the measurements.[6] The translational vibration is below 400 cm^{-1}, the librational region is from 600 cm^{-1} to 1200 cm^{-1}, the bending mode is in the region around 1600 cm^{-1}, and the stretching vibrations occur from 2900 cm^{-1} to 3300 cm^{-1}. Each band has a clear cutoff in the boundary that does not resemble the neutron scattering spectra because the neutron scattering spectra in the region of high-energy transfer are affected by a large Debye–Waller factor. The dispersion diagram in Fig. 4 indicates that the peak at around 280 cm^{-1} is where the top of the acoustic modes overlaps with the bottom of the optic modes. The first optic branches occurring at around 400 cm^{-1} result in the two H-bonding peaks. A longitudinal wave (flat wave at the top) and the transverse waves splitting nearby point G (i.e., $q = 0$) are clearly distinguishable. The two transverse waves degenerate near point G but split at point Q due to boundary anisotropy. Klug and Whalley[33] suggested an LO–TO splitting value of 80 cm^{-1}. Marchi *et al.*[34] reported that the peak in the PDOS at 227 cm^{-1} was due to TO vibrations, and the peak at 308 cm^{-1} corresponded to the LO vibrations. However, Klug *et al.*[18] summarised these results and restricted the LO–TO splitting up to 10 cm^{-1}. Due to the inactivity of both the infrared and Raman spectra in the LO vibrations, and the poor neutron scattering resolution available at the time of that report, it is not surprising that this conclusion can now be revised.

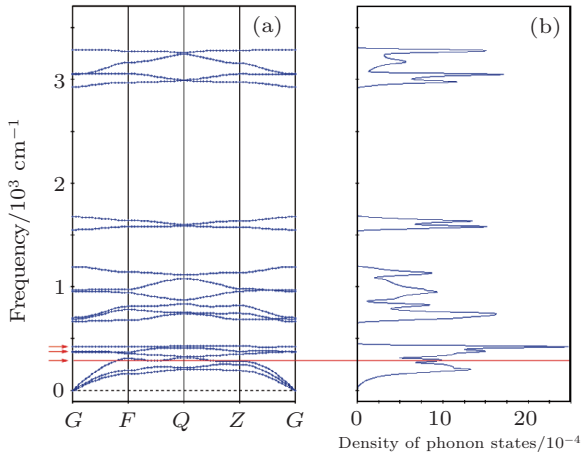


Fig. 4. (color online) Phonon dispersion curves of Ic (two water molecules in a primitive cell). The LO–TO splitting vibration modes at around 400 cm^{-1} can be attributed to the two H-bond peaks in the right panel showing the density of phonon states.

We also change the surrounding lattice to test the effect of the tetrahedral structure. The PDOS simulations are compared in Fig. 5. The primitive cell of ice Ic contains two molecules. When the lattice constants (a and b) are doubled to extend the spacings in the basal plane, only the H-bonded zigzag chain along the c axis remains. If we cut off the c axis link further, it becomes a water dimer. The results show that when the tetrahedral structure changes, the O–O distance increases from 2.756 Å to 2.996 Å and the H-bond elongates from 1.751 Å to 2.016 Å, but the covalent bond decreases from 1.006 Å to 0.982 Å. The corresponding data for the dimer are 2.899 Å, 1.914 Å, and 0.987 Å. From Fig. 5, we can see that the covalent bond becomes stronger as the surrounding structural constraints are removed, whereas the H-bond overlaps with the librational vibrations and cannot be distinguished. The presence of negative frequencies is due to an extraneous level of stress and, hence, structural instability. Our test confirms that the relaxed tetrahedral structure is the most stable structural configuration for water clusters.

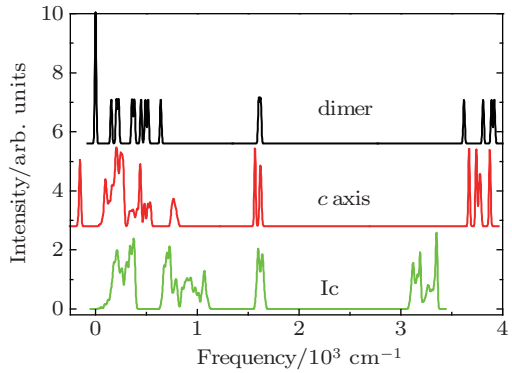


Fig. 5. (color online) Simulation experiments on a cubic primitive ice cell. The spectrum marked as '*c* axis' corresponds to a structure in which the tetrahedral structure is destroyed by double spacing *a* and *b* coordinates with only the *c* axis linked. The upper graph of the H_2O dimer spectrum is shown for comparison.

3. Conclusions

The results of the *ab initio* calculations in this work are in reasonable agreement with the results from the neutron scattering experiments, showing that there exist two types of H-bonds in ice crystal. We have examined the effects of the atomic spacing and molecular configuration in detail and found that the strength of the intra-molecular O–H vibrations increases as the O–O distance increases, whereas that of the inter-molecular H-bonds decreases. By analyzing the dispersion relations, we can clearly distinguish the LO–TO splitting, especially in the translational region; that is, the H-bonding lattice vibrations. Our findings disagree with the Li–Ross model, which attributes the two H-bonds to different coefficients of restitution between neighbors,[5]. They also disagree with the conclusion of Klug *et al.*, in which splitting is restricted at 10 cm^{-1}.[18]

Our results confirm the findings of Klug and Whalley[33] and Marchi *et al.*,[34] who predicted that the splitting of H-bonds in ice occurs at about 80 cm^{-1}. The LO–TO splitting can also be seen in the intra-molecular O–H stretching. However, it cannot be distinguished in the libration and bending regions because of the effect of polarization since the relative displacement of the electric dipole in this region is very small. In summary, the lattice vibration properties of molecular ice crystal are similar to those of ion crystal.

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