Computational analysis of vibrational spectrum and hydrogen bonds of ice XVII

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Abstract

Based on first-principles density functional theory, we investigated the relationship between the vibrational normal modes and the spectrum of the newest laboratory-prepared ice phase, an empty clathrate hydrate structure from gas hydrate named ice XVII. A 48-molecule supercell was designed to mimic the hydrogen-disordered structure. Despite its much lower density than ice Ih, its phonon density of states shows features very similar to those of that phase. In our previous studies of ice Ic and ice XIV, we found two basic hydrogen bond vibrational modes in these hydrogen-ordered ice phases, which contribute two sharp hydrogen bond peaks in the translation region. In this study, we found that this rule also holds in the hydrogen-disordered phase ice XVII. A water molecule vibrating along its angle bisector possesses strong energy, because this vibrational mode involves oscillation against four bonded neighbors. In contrast, a water molecule vibrating perpendicular to its angle bisector has low energy because this mode involves only two of the molecule’s hydrogen bonds. This is an evidence in hydrogen-disordered ice and strengthens our proposal that the existence of two basic hydrogen bond vibrational modes is a general rule among ice family.

1. Introduction

Gas hydrates, which are formed by water and natural gases, are a potential energy source. The water skeleton is stabilized by guest molecules trapped inside cages [1]. In the past, empty water clathrates were thought to be experimentally inaccessible because guest molecules were essential for the stability of the host framework [2–4]. In later studies, Wooldridge and Jacobson et al. suggested schemes to produce metastable guest-free water clathrates in the laboratory [5, 6]. In 2014, Falenty et al. experimentally prepared an empty hydrate named ice XVI by vacuum pumping the neon-filled sII clathrate, opening up research into negative-pressure clathrate hydrates. These low-density ices have recently raised considerable interest from a theoretical viewpoint because they are believed to be stable at negative pressure [7–13]. Strobel et al. found a clathrate structure, named the C0 phase, with the composition (H2O)2H2, formed at high pressures (~400 MPa and 280 K) [14]. Replacing the molecular hydrogen of the C0 phase with carbon dioxide leads to the CO2 hydrate (H2O)3.5CO2, which can be used as a cheap, environmentally friendly, readily producible microporous material for CO2 storage [15, 16]. Ice XVII also shows interesting properties as a candidate for hydrogen storage [17].

Two experimental studies [18, 19] investigated the phase diagram of the H2–H2O compounds and demonstrated the presence of a stable phase, C0, at 360 to 700 MPa and 100 to 270 K, in which the structural model assumes the space group P312121. Smirnov and Stegailov [20] examined these models theoretically and proposed two possible structures: C0-II and ST. del Rosso et al. obtained a non-guest ice structure, named XVII, with space group P6122, at a room pressure below 120 K by removing all molecular hydrogen in the C0 phase [21, 22].
Via consideration of the oxygen positions, a hydrogen-disordered ice XVII supercell with 48 molecules was generated computationally in this study. The vibrational spectrum of ice XVII in the infrared (IR) region was calculated. Here we present IR, Raman, and inelastic neutron scattering (INS) spectra calculated by simulation and discuss the characteristic vibrational modes. Two basic H-bond vibrations were found in a series of investigations of hydrogen bonding (H-bonding) in this ice phase, in accordance with those found in hydrogen-ordered ices.

2. Computational methods

Considering the positions of oxygens as the crystal lattice, the primitive cell of ice XVII contains six molecules. To mimic the hydrogen-disordered structure, a 48-molecule supercell was built, with dimensions $2 \times 2 \times 2$ times those of the primitive cell. We designed a code to generate hydrogens automatically. Of course, the number of possible permutations and combinations of hydrogens is very large. This code generated 416 512 structures and calculated their polarizations. We manually picked a structure with a uniformly distributed dipole moment among ones which has almost zero net polarizations.

The CASTEP code [23], a first-principles density functional theory (DFT) program, was used to perform geometric optimization and phonon calculations. Considering the large spatial variability of the electron gas density, the generalized gradient approximation (GGA) of DFT was applied. Specifically, the exchange-correlation (XC) potential adopted in this work was RPBE [24], which, in our preliminary test, produced a slight redshift in the H-bonding region but had acceptable accuracy for the intramolecular vibrations. The energy convergence threshold of the SCF for geometric optimization was set as $1.0 \times 10^{-9}$ eV atom$^{-1}$. The Energy cutoff for electronic states was set as 830.0 eV. The k-points separation was set as 0.07 Å$^{-1}$. Norm-conserving pseudopotentials were used to calculate the phonon density of states (PDOS).

3. Results and discussion

The calculated PDOS curve of ice XVII is depicted in figure 1 and is contrasted with that of ice Ih. The main features of the curves are almost identical for the two phases. Statistically, the H-bond length in XVII and in Ih were calculated as 1.827 Å and 1.816 Å, respectively. Thus, the longer intermolecular distances in XVII lead to weaker H-bond vibrational frequencies and stronger intramolecular O–H covalent bonds than in Ih. This trend is reflected in figure 1, with a 26 cm$^{-1}$ redshift in the translation region and a 17 cm$^{-1}$ blueshift in the stretching region.

The Raman scattering peaks, which correspond to the frequencies of vibrational normal modes at the gamma point caused by the interactions between photons and phonons, are restricted to the region near the Brillouin zone (BZ) center. The experimental INS data can be compared with the simulated PDOS curves, because the INS measurements collected the phonon signals throughout the whole BZ [25]. A comparison of the INS data ([26]) and calculated PDOS of deuterated ice XVII is shown in figure 2 to manifest the validity of the simulation in this work.

Eight examples of normal modes are shown in figure 3. The perspective view is perpendicular to the optical axis. The green arrows indicate the corresponding vibrational directions, in sizes proportional to the vibrational amplitude. Typical vibrations are highlighted in gold. The vibrational frequencies below 301 cm$^{-1}$ are due to lattice vibrations. Because a unit cell of ice XVII contains 48 water molecules, the number of normal modes in the translation region is $3 \times 48 - 3 = 141$. Three acoustic modes are subtracted.

Two sharp peaks at about 204 and 294 cm$^{-1}$ in the translation region in figure 1 can be seen clearly. To explain the splitting of two peaks of the optical modes in ice, Li and Ross [27] assumed the existence of two types of H-bond. Klug et al [28] discussed longitudinal-optic-transverse-optic (LO-TO) splitting in ice Ih. Morrison and Jenkins [29] suggested that the splitting of the optical modes is due to the coupling with the intramolecular stretching vibrations. In our previous study, the existence of two basic H-bond vibrational modes was first established in ice Ic [30]. These two peaks are contributed by the two fundamental vibrations of H-bonds, the two-bond mode and the four-bond mode. In all ice phases, the water molecules are oriented such that a central molecule is linked with four neighbors via H-bonds to form a tetrahedral structure. In such a local structure, when the central molecule vibrates along its angle bisector, the four linking H-bonds oscillate simultaneously to yield the four-bond mode. Two vibrational motions also proceed along only two H-bonds, corresponding to the two-bond mode. The ratio of the vibrational frequency of these two modes is $\sqrt{2}$ for the ideal Ic structure. Later, in the hydrogen-ordered phase ice XIV, this rule was still found to apply [31]. The universality of the features of INS spectra among all pressure-free ices reveals that the space group and hydrogen long-range order have little influence on H-bond vibration [27]. Thus, the physical mechanism of H-bonding in ices is best understood in terms of the local tetrahedral structure. In figure 3, two examples of normal modes at 209 and 301 cm$^{-1}$ are
Figure 1. Simulated vibrational spectra of ice Ih (blue line) and ice XVII (black line) using the CASTEP code. Because of the longer hydrogen bond length, the spectrum of ice XVII is redshifted in the translation band and blueshifted in the intramolecular stretching band by comparison with ice Ih.

Figure 2. Comparison of experimental INS spectrum with simulated PDOS curve. The data from [26] were measured using deuterated ice XVII, and the calculations were also performed using a 48-molecule model of deuterated ice XVII.
illustrated, with a frequency ratio of 1.44. To keep the center of mass static, complementary vibrational modes emerge around the main vibrations. Of course, deviations from the ideal value of $\sqrt{2}$ exist due to hydrogen disorder and structural deformation of local tetrahedra. The two H-bond peaks found by the INS experiments are composed of a large number of such four-bond modes and two-bond modes. We provide a video that depicts the normal modes at 209 and 301 cm$^{-1}$ to illustrate the dynamics of these water molecules (supplementary material is available online at stacks.iop.org/NJP/21/043054/mmedia). del Rosso showed that the Raman spectrum of the C$_0$ phase in the translation region had a peak at about 218 cm$^{-1}$ [21]. As shown in figure 4, our simulated Raman peak is at 205 cm$^{-1}$, a redshift compared with experimental peak at 223 cm$^{-1}$ [21]. Two small IR peaks are found at 196 and 209 cm$^{-1}$. The selection rules of photon scattering make it difficult to detect the four-bond modes in Raman and IR spectra. However, these strong H-bonds were clearly detected by INS, as shown in the translation band in figure 4.

The libration region extends from 588 to 1037 cm$^{-1}$ with 144 normal modes in the 48-molecule supercell. The molecular vibrations can be divided into three types: rocking (back and forth rotation of the whole molecule around an axis perpendicular to the molecular plane), wagging (back and forth rotation of the molecule around an axis in the molecular plane, perpendicular to the bisector of the HOH angle), and twisting (back and forth rotation around an axis coincident with the HOH angle bisector) [6]. Three examples at 588, 825, and 1037 cm$^{-1}$ are shown in figure 3. The vibration modes at 588 cm$^{-1}$ are all rocking, whereas those at 1037 cm$^{-1}$ all correspond to molecular twisting. The other normal modes are mixtures of rocking, wagging, and twisting, which indicates that the rocking mode is the lowest in energy whereas the twisting mode is the highest. The IR absorption peaks are weak in this region, and the main peak is at 886 cm$^{-1}$, as shown in figure 4. However, the Raman scattering curve shows features similar to those of the INS spectrum.

The 48 normal modes in the intramolecular bending band ranged from 1635 to 1709 cm$^{-1}$ in this model. Because the structure is hydrogen-disordered, it is meaningless to distinguish between in-phase or out-of-phase...
vibrational modes. The maximum frequency at 1709 cm\(^{-1}\) is shown in figure 3. Only one Raman peak, at 1673 cm\(^{-1}\), exists in this band, whereas the IR spectrum shows two main peaks at 1642 and 1661 cm\(^{-1}\). In the bending band, the PDOS spectrum of ice XVII is wider than that of ice Ih, as shown in figure 1. This may be due to the wider distribution of H–O–H bond angles of the water molecules, as shown in table 1. The weak peak at 1643 cm\(^{-1}\) (PDOS) or 1642 cm\(^{-1}\) (IR) is contributed by water molecules with larger bond angles (\(\sim 107.5^\circ\)). Figure 5 shows the smoothed probability density distribution of the bond angle. Water molecules with large bond angles, which participate in eight normal modes, contribute to this weak peak. An example of the normal mode at 1647 cm\(^{-1}\) is inserted in figure 5. All water molecules with large bond angles are highlighted in gold and are positioned around the hexagonal helix structure of ice XVII.

The intramolecular O–H covalent bond-stretching region has 96 normal modes. Only two kinds of vibrational modes—symmetric stretching and asymmetric stretching—exist for each water molecule. This band spreads from 3125 to 3369 cm\(^{-1}\). Two typical modes are shown in figure 3. The minimum vibrational mode at 3125 cm\(^{-1}\) corresponds to the symmetric stretching of these molecules. The maximum vibrational mode at 3366 cm\(^{-1}\) is mainly asymmetric stretching, with some coupled symmetric stretching. Whale et al have found isolated O–H vibrating in the stretching region of ice XV with only one O–H bond oscillate while the

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**Figure 4.** Simulated vibrational spectra of ice XVII. The four images correspond to four vibration bands: translation, libration, bending, and stretching. Each image shows the Raman, IR, and PDOS spectra from top to bottom, respectively. Weak peaks have been amplified for visibility.
Table 1. Comparison of ice XVII and Ih. Data were generated from simulations with identical parameter settings. The units are Angstroms for bond length in the second to fourth columns, degrees for bond angle in the fifth column, cm$^{-1}$ for vibrational wavenumber from the sixth to ninth columns, and g cm$^{-3}$ for density in the last column.

| Ice | H–O  | O–H  | O–H–O | H–O–H Angle | H–bonds | Libration | Bending | Stretching | Density |
|-----|------|------|--------|-------------|----------|-----------|---------|------------|--------|
| XVII | 1.806–1.840 | 0.986–0.988 | 2.791–2.826 | 105–107.9 | 301 | 588–1037 | 1635–1709 | 3125–3369 | 0.81 |
| Ih   | 1.788–1.866 | 0.986–0.989 | 2.784–2.843 | 104.7–106.2 | 327 | 579–1030 | 1651–1706 | 3110–3363 | 0.88 |
other one does not vibrate [32]. Examples were also found in ice XVII in the stretching region similar to the case in ice XV and XIV [31]. There seems to be a third possibility intramolecular vibration mode in addition to symmetric and antisymmetric stretching. We attributed this phenomenon to lattice deformation of local tetrahedral structure of ice XVII. As shown in figure 4, three Raman peaks are seen at 3125, 3235, and 3352 cm$^{-1}$, in agreement with experimental observation at 3108, 3233, and 3340 cm$^{-1}$ [21]. Multiple IR absorption peaks are seen around 3200 cm$^{-1}$, with a distinct peak at 3180 cm$^{-1}$. Consistent with the literature, the vibrational energies increase from symmetric stretching to asymmetric stretching in this region. The Raman and IR peaks are more intense and sharply resolved in the symmetric stretching region than in the asymmetric stretching region.

4. Conclusions

We simulated the newest hydrogen-disordered ice structure, ice XVII, using the first-principles DFT method. The PDOS peaks in our results are in accord with the INS spectrum. The Raman peaks in our results are also in accord with the photon scattering experiments, which manifests the validity of the simulations. Four regions of the PDOS, IR absorption, and Raman scattering spectra were discussed separately.

The most interesting findings are those regarding the vibrational modes of H-bonds. It is well known that three intramolecular hydrogen–oxygen bond vibrational modes exist: symmetric stretching, asymmetric stretching, and bending. Multiple such modes coupled together contribute the two bands, stretching and bending, in the vibrational spectrum of an ice crystal. Combinations of three molecular rotational modes—rocking, wagging, and twisting—constitute the libration band ranging from $\sim$550 to $\sim$1100 cm$^{-1}$. However, the translation band of intermolecular H-bonds is difficult to analyze. We earlier theoretically identified two types of H-bond vibrational modes in hydrogen-ordered ice Ic. Later, we found evidence for the same trend in another hydrogen-ordered phase, ice XIV. In this study, the latest laboratory-prepared ice phase, hydrogen-disordered ice XVII, also shows that these two basic molecular vibrational modes constitute two H-bond peaks. This is the first evidence on the vibrational modes of a hydrogen-disordered ice phase, and further investigations are needed. We deduce that the existence of two basic H-bond vibrational modes is a general rule among the ice family, due to the local tetrahedral structure in ice phases. Moreover, this rule also holds in clathrate ice which may interest in the field of gas hydrates.

Acknowledgments

The numerical calculations were done on the supercomputing system in the Supercomputing Center, Shandong University, Weihai.
Notes

The authors declare no competing financial interest.

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