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Raman and IR Spectra of Ice Ih and Ice XI with an Assessment of DFT Methods

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ABSTRACT:

IR and Raman spectroscopic technology can be directly used to identify the occurrence of ferroelectric ice XI in laboratory or extraterrestrial settings. The performance of 16 different DFT methods applied on the ice Ih, VIII, IX, and XI crystal phases are evaluated. Based on a selected DFT computational scheme, the IR and Raman spectra of ice Ih and XI are derived and compared. When comparing the spectra of ice Ih and ice XI, both IR and Raman, the librational vibrations are found to be the most affected by the proton ordering. The spectroscopic fingerprint of ice XI can be used to distinguish ferroelectric ice XI from ice Ih in the universe. Furthermore, the existence of only one kind of H-bond in ice Ih is demonstrated from the overlapping sub-spectra for different types of H-bonded pair configurations in 16 isomers of ice Ih, which provides an illustration to the historic debate on whether one or two kinds of H-bonds existed in ice.

■ INTRODUCTION

Water is one of the essential natural substances in the universe. The solid phase of water is ice, which have been found in 17 different crystalline structure phases until now.¹⁻¹⁶ In each phase, the arrangements of oxygen atoms are long-range ordered in a specific symmetry with the hydrogen atoms arranged around the oxygen atoms following the ice rules.¹⁷ Some of the ice phases are proton-disordered (Ih,¹ Ic,² III,⁴ IV,⁵ V,⁶ VI,⁷ VII,⁸ XII,¹³ and XVI¹⁶) and the others are proton-ordered (II,³ VIII,⁹ IX,¹⁰ X,¹¹ XI,¹² XIII,¹⁴ XIV,¹⁴ and XV¹⁵).

The ordinary solid phase of water is the proton-disordered ice Ih, the only ice existing on the earth surface. A proton disorder-order transition at low temperatures is known. The proton-ordered phase, ice XI, was discovered from KOH doped ice Ih,¹⁸⁻¹⁹ and was confirmed to belong to the orthorhombic Cmc2₁ space group by neutron diffraction.¹² The ferroelectric character of ice XI was revealed through thermal stimulated depolarization studies.²⁰ Ice XI has been suggested to be related with the process of planetary formation as a considerable electric field might be formed from the ferroelectric ice XI in space.²¹⁻²³ Therefore, a lot of effort has been put on ice Ih/XI studies both experimentally and theoretically.

As IR and Raman spectra can be used to study the structure and dynamics of ice, the IR and Raman spectroscopic characteristics of ice Ih have been reported in numerous studies, especially in the OH stretching vibration region.²⁴⁻²⁹ Only a few works on ice XI have been carried out until now.³⁰⁻³⁵ The polarized Raman spectra of ice XI have been measured based on samples obtained from KOH-doped ice and the vibrational modes in the translational, librational, bending, and stretching region have been assigned by Abe and Shigenari.³¹⁻³² Comparisons between the spectra of ice Ih and ice XI have been presented in the regions of translational and librational vibrations.^{30, 34} The differences between IR spectra of ice Ih and ice XI and the increase of absorbance over a wide frequency range was discussed by Abe and Shigenari.³² In parallel to the experimental studies, several theoretical studies have been carried out.³⁶⁻⁴⁵ The librational modes of ice XI have been studied by density functional theory (DFT) methods and local-MP2 method.³⁹ The IR spectra of ice XI were simulated through Car-Parrinello molecular dynamics (CPMD) calculations by Wójcik et al.,⁴⁰ who found the significant differences between ice Ih and ice XI in the region of librational vibrations, which was further discussed in a succeeding work.⁴¹ Earlier, the structure, stability, and phase transition between ice Ih and ice XI have also been studied based on quantum-chemical computations.⁴²⁻⁴⁵

One can envision that IR and Raman spectroscopic measurements could be utilized to determine whether ice XI exist in extraterrestrial situations. To clarify the relation between the planetary formation and ice XI, IR and Raman measurements would be necessary to carry out both in space and in the laboratory. As the growth of a single crystal sample of ice XI suitable for optical measurements is quite difficult,³¹⁻³² only few studies have carried out for ice XI. At the same time the theoretical studies on the IR and Raman spectra of ice XI are still scarce. To help identify the presence of ferroelectric ice in space, in this work the IR and Raman spectroscopic characteristics of ice Ih/XI according to DFT computations are presented.

■ COMPUTATIONAL METHODS

The unit cell structures of proton-ordered ice VIII, IX, and XI are depicted in Figure 1. The initial lattice parameters and atomic coordinates of ice VIII and IX are taken from

experimental measurements.⁹⁻¹⁰ The unit cell of ice XI is taken from ref. 42, in which the cell parameters and atomic coordinates of all the possible proton-ordered structures of ice Ih are derived for an orthorhombic cell with 8 water molecules.⁴² Among the 16 unique proton arrangements of an 8-molecule orthorhombic unit cell of ice Ih, the no.1 structure in Ref. 42 is the structure of ice XI. The rather small unit cell was chosen as the base for our vibrational computations since the number of H-bond configurations rapidly increases when doubling or further enlarging the cell.⁴⁶⁻⁴⁷

Figure 1. The unit cell structures of ice VIII (a), IX (b), and XI (c). The red balls represent oxygen atoms, white balls represent hydrogen atoms, and dashed black lines represent hydrogen bonds.

Due to accurate description of weak interactions (e.g. H-bond and van der Waals interactions) in the DFT framework being a challenge, different exchange-correlation functionals are assessed as in previous studies.⁴⁸⁻⁵¹ The lattice energies and unit cell volumes of ice VIII, IX, and XI are calculated by hybrid (B3LYP,⁵² PBE0,⁵³ HSE03,⁵⁴ and HSE06⁵⁵) and general gradient approximation (GGA: PBE,⁵⁶ RPBE,⁵⁷ PBEsol,⁵⁸ PW91,⁵⁹ BLYP,⁶⁰⁻⁶¹ and HCTH⁶²) functionals, and some of them with dispersion correction (B3LYP-TS,^{52, 63} B3LYP-Grimme,^{52, 64} PBE0-TS,^{53, 63} PBE-TS,^{56, 63} PBE-Grimme,^{56, 64} and PW91-OBS^{59, 65}). Except for BLYP and HCTH, the methods are employed using plan-wave basis sets with norm-conserving pseudopotentials in the CASTEP⁶⁶ program in Materials Studio 6.1. The energy cutoff value used is 750 eV, the convergence criteria of geometry optimization, SCF, and k-points net used the “fine” set. The BLYP and HCTH methods are employed using the numerical basis sets in DMol³ modulus⁶⁷⁻⁶⁸ in Materials Studio 6.1. The “fine” set is used for the convergence tolerance of geometry optimizations, SCF, and k-points nets. The orbital cutoff used is 3.3 Å and the basis set is triple numerical plus polarization (TNP)⁶⁹ basis set. The performance of each functional for the three ice phases is evaluated by comparison with experimental lattice energies and cell volumes.⁷⁰ PBE, PBE-TS, and BLYP/TNP are further checked by studying the lattice energies of the 16 different proton-ordered structures for ice Ih.⁴² Finally, the IR and Raman spectra within the harmonic approximation of the 16 different possible structures of ice Ih are separately simulated using the PBE functional in CASTEP.

For comparison the IR spectrum for ice XI was also calculated using the PBE0⁵³ functional in combination with the large 6-311G(2d,2p) basis set⁷¹⁻⁷² using the CRYSTAL14 program.⁷³⁻

The spectra of proton-disordered ice Ih is derived by considering the Boltzmann distribution of all the possible proton arrangements satisfying the ice-rules in the 8-molecule unit cell of ice Ih. The Boltzmann-averaged spectra are computed by the aid of the following formula:

$$p_i = \frac{g_i e^{-\varepsilon_i/kT}}{\sum_{i=1}^{16} g_i e^{-\varepsilon_i/kT}}$$

p_i is the probability of structure i , g_i is the degeneracy of structure i ($g_i = 6, 4, 4, 4, 4, 4, 12, 8, 8, 8, 8, 8, 8, 16$ for structure 01-16, respectively)⁴², ε_i is the lattice energy of structure i , k is the Boltzmann constant, and T is the temperature which is here set to 273K. In addition, the OH stretching vibrations are projected into different categories based on the contributions from different H-bond configurations as in previous studies.⁷⁵⁻⁷⁸

▪ RESULTS AND DISCUSSION

Assessment of DFT Methods. H-bonding between water molecules is the dominating interaction in ice. The correct descriptions of ice properties depend on accurate calculations of H-bond interactions, which however pose a challenge for DFT methods. Recently, several benchmark DFT studies have been carried out on various phases of ice, and different kinds of DFT methods have been employed in previous studies on ice,^{49-51, 79-84} but no one functional has been commonly the preferred choice in the studies of ice. Thus, we evaluated the performance of 16 different DFT methods on ice Ih, VIII, IX, and XI.

Table 1. The lattice energy per molecule of ice VIII, IX, and XI without/with cell parameters kept fixed at the experimental values ($a=b=4.68\text{\AA}$, $c=6.80\text{\AA}$ for ice VIII in ref. 85, $a=b=6.73\text{\AA}$, $c=6.73\text{\AA}$ for ice IX in ref. 10, and $a=4.49$, $b=7.78$, $c=7.34$ for ice XI in ref. 86) in the geometry optimization. unit: kcal/mol

	Expt.	B3LYP	B3LYP-TS	B3LYP-Grimme	PBE0	PBE0-TS	PBE	PBE-TS	PBE-Grimme
VIII	13.3 ^a	9.1/8.6	14.8/14.8	15.6/15.5	10.7/10.6	14.1/14.2	10.8/10.6	14.5/14.4	15.5/15.4
IX	14.0 ^a	11.9/11.8	15.2/15.1	15.8/15.7	15.8/13.3	15.8/15.7	14.1/13.9	16.7/16.5	16.8/16.6
XI	14.1 ^{a,b}	13.0/13.0	15.3/15.3	16.1/16.0	14.3/14.2	16.0/15.7	15.1/15.0	17.0/16.7	17.5/17.1
	Expt.	RPBE	PBEsol	PW91	PW91-OBS	HSE03	HSE06	BLYP	HCTH
VIII	13.3 ^a	6.9/4.9	14.3/14.2	11.3/11.1	25.0/22.5	10.6/10.4	10.5/10.3	12.9/12.4	11.1/8.7
IX	14.0 ^a	10.3/9.7	17.3/16.9	14.7/14.5	24.4/22.1	13.1/13.1	13.0/13.0	14.1/14.0	12.9/12.6
XI	14.1 ^{a,b}	11.3/11.2	18.5/17.7	15.8/15.7	24.0/21.6	14.4/14.3	14.2/14.2	14.9/14.9	13.2/13.2

^aReference 50 and 70, ^bReference 87.

The lattice energy per molecule of ice VIII, IX, and XI was calculated by B3LYP, PBE0, HSE03, HSE06, PBE, RPBE, PBEsol, PW91, B3LYP-TS, B3LYP-Grimme, PBE0-TS, PBE-TS, PBE-Grimme, and PW91-OBS with plane-wave methods in CASTEP, and BLYP and HCTH with TNP basis set in DMol³. As listed in Table 1, two types of computational schemes were applied: in one group, the unit cell of each structure is optimized with the lattice parameters fixed at the experimental values ($a=b=4.68\text{\AA}$, $c=6.80\text{\AA}$ for ice VIII,⁸⁵ $a=b=6.73\text{\AA}$, $c=6.73\text{\AA}$ for ice IX,¹⁰ and $a=4.49$, $b=7.78$, $c=7.34$ for ice XI⁸⁶) at zero pressure, whereas in the other group both the cell and atomic coordinates are fully relaxed. In Table 1 and Figure 2, the lattice energies obtained using different functionals are shown. From Figure 2a, we can see that PBE0-TS, PBE-TS, PBEsol, and BLYP work well for ice VIII, where the

error is less than 1.2 kcal/mol in comparison with the experimental result,^{50, 70} and BLYP performs best (underestimation by 0.4 kcal/mol). It was unexpected that B3LYP could show such bad performance for ice VIII with a 4.2 kcal/mol underestimation. After addition of dispersion correction, the performances of B3LYP, PBE0, and PBE are notably improved, indicating that the dispersion interactions become important in high-density ice. The computational schemes with the worst performances is RPBE with a 6.4 kcal/mol underestimation and PW91-OBS with an 11.7 kcal/mol overestimation. For ice IX, PBE, PW91, HSE03, HSE06, and BLYP perform excellent with the error less than 1.0 kcal/mol compared to the experimental value,^{50, 70} in which PBE and BLYP are particularly good with an error of 0.1 kcal/mol. As shown in Figure 2b, for ice IX RPBE and PW91-OBS are also the worst choices with a 3.7 kcal/mol underestimation and a 10.4 kcal/mol overestimation, respectively. For ice XI (see Figure 2c), PBE0, PBE, HSE03, HSE06, BLYP, and HCTH perform with errors less than 1.0 kcal/mol compared to experimental data.^{50, 70, 87} RPBE and PW91-OBS are still the worst computational schemes. Hence, for the lattice energy BLYP combined with the TNP basis set perform best with the average absolute error 3.13% for all the three ice phases. Compared to the other schemes, B3LYP-TS and PBE0-TS perform well with average absolute errors of 9.5% and 10.8%, respectively. However, the method that is best at predicting the energy differences between the ices is B3LYP with the TS dispersion correction scheme. Considering the unit cell volumes in Table 2, the average absolute errors by BLYP, B3LYP-TS, and PBE0-TS are 5.0%, 4.1%, and 8.1%, respectively, compared to the experimental results.^{10, 12, 85-86, 88-89}

Figure 2. The lattice energies of ice VIII, IX, and XI calculated using different DFT methods. Note: ideal cell means the unit cell optimized with the lattice parameters fixed at the experimental values.

Table 2. The unit cell volumes per molecule of ice VIII, IX, and XI. unit: Å³

	Expt.	B3LYP	B3LYP-TS	B3LYP-Grimme	PBE0	PBE0-TS	PBE	PBE-TS	PBE-Grimme
VIII	18.6 ^a , 20.1 ^b	21.5	18.6	17.5	19.8	19.8	20.5	20.0	17.7
IX	25.6 ^c , 25.8 ^d	27.0	23.9	23.9	23.9	23.2	27.0	23.7	23.5
XI	32.0 ^e , 32.2 ^f	32.1	30.2	30.2	30.2	29.3	30.3	29.2	29.0
	Expt.	RPBE	PBEsol	PW91	PW91-OBS	HSE03	HSE06	BLYP	HCTH
VIII	18.6 ^a , 20.1 ^b	26.0	17.6	20.1	14.3	20.3	21.5	20.7	27.4
IX	25.6 ^c , 25.8 ^d	30.8	24.1	26.8	19.1	27.0	25.4	24.9	28.7
XI	32.0 ^e , 32.2 ^f	33.8	27.5	30.0	24.8	30.2	32.1	31.7	33.2

^aReference 85, ^bReference 88, ^cReference 89, ^dReference 10, ^eReference 86, ^fReference 12.

BLYP/TNP, PBE, and PBE-TS methods are further evaluated based on the 16 different proton-ordered structures of ice Ih. The lattice energies of each structure are listed in Table 3. As shown in Figure 3, the trends of the energies of the 16 structures is consistent with the previous quantum-chemical studies,^{42-43,90-91} which also observed negligible functional dependence of the relative energies for the different polymorphs for both a cell with fixed dimensions and for fully optimized cells.⁴²⁻⁴³ As shown in Table S1, the cell parameters from BLYP are close to the parameters of the experimental cell values ($a = 4.4974$ Å and $c = 7.3236$ Å) at 5 K.⁸⁶

To provide an appropriate comparison with the experimental results, the Boltzmann-averaged lattice energy of ice Ih is computed. The results from BLYP, PBE and PBE-TS overestimate the lattice energy by 0.7 kcal/mol, 1.0 kcal/mol and 2.8 kcal/mol, respectively, in comparison with experiment. The energy difference between ice Ih and XI is 0.05 kcal/mol as obtained by the BLYP/TNP computations, which is very close to the value (0.06 kcal/mol) estimated from experimental data by Johari.⁸⁷

Figure 3. The lattice energies of 16 unique structures of ice Ih calculated by PBE, PBE-TS, and BLYP/TNP. The solid lines represent the Boltzmann-averaged values for the 8-molecule unit cell.

Table 3. The lattice energy per molecule of the geometry-optimized 16 distinct proton-ordered structures of ice Ih without/with cell parameters fixed at the values from Ref. 42 termed “ideal values”. unit: kcal/mol

	s01	s02	s03	s04	s05	s06	s07	s08	Ih	XI	Expt.
PBE	15.13/ 15.03	15.04/ 14.94	15.05/ 14.95	15.08/ 14.98	15.10/ 15.00	15.01/ 14.92	15.07/ 14.97	15.11/ 15.01	15.09	15.13	14.1 ^a
PBE-TS	16.97/ 16.70	16.87/ 16.60	16.88/ 16.61	16.91/ 16.64	16.93/ 16.67	16.84/ 16.58	16.90/ 16.63	16.95/ 16.68	16.93	16.97	—
BLYP	14.85/ 14.85	14.72/ 14.72	14.73/ 14.72	14.78/ 14.77	14.81/ 14.80	14.69/ 14.69	14.76/ 14.76	14.82/ 14.81	14.80	14.85	—
	s09	s10	s11	s12	s13	s14	s15	s16	—	—	—
PBE	15.09/ 15.00	15.08/ 14.98	15.09/ 14.99	15.04/ 14.94	15.04/ 14.94	15.10/ 15.00	15.08/ 14.98	15.11/ 15.01	—	—	—
PBE-TS	16.93/ 16.66	16.91/ 16.64	16.92/ 16.66	16.87/ 16.60	16.87/ 16.60	16.94/ 16.67	16.91/ 16.64	16.94/ 16.67	—	—	—
BLYP	14.80/ 14.79	14.77/ 14.77	14.79/ 14.79	14.73/ 14.72	14.73/ 14.72	14.81/ 14.80	14.77/ 14.77	14.81/ 14.81	—	—	—

^aReference 70.

IR and Raman Spectra of Ice Ih/XI. Although BLYP/TNP presents the best performance of all the functionals assessed, we did not use that in the IR and Raman spectroscopic studies since the intensity of each vibrational mode could not be obtained in DMol³. Good descriptions probably can be given by B3LYP-TS and PBE0-TS, but at a quite high computational cost since these are hybrid functionals. Since PBE exhibited good performance in the calculations for 16 isomers of ice Ih and the dispersion interactions have been found to have little influence on IR spectra in liquid water,⁹² the PBE functional was chosen for the simulations of IR and Raman spectra.

A comparison was made with the IR spectrum obtained using the PBE0 hybrid functional⁷¹⁻⁷² with a Gaussian basis set⁷³⁻⁷⁴ for the first of the 16 isomers, ice XI, as shown in Figure S1. It can be seen that the librational frequencies happen to be quite insensitive to whether the PBE or PBE0 computational results are used (e.g. the spectrum from the PBE calculation have large-intensity peaks at 972, 1028, 1072 cm⁻¹ whereas from PBE0 at 971, 1029, 1080 cm⁻¹). However, the bending vibrations and stretching frequencies obtained from the PBE calculation are red-shifted relative to those from the PBE0 calculation (e.g. PBE 1618, 2890, 2920, 3001, 3002 cm⁻¹ unscaled and PBE0 1682, 3253, 3291, 3353, 3363 cm⁻¹). In addition it was checked that the computational level chosen for the PBE calculation was adequate (Figures S2 and S3).

The IR and Raman spectra of 16 isomers of ice Ih were calculated and are presented in Figures S4 and S5. The spectra for the translational, librational, bending, and stretching modes are separately plotted in Figures S4a, S4b, S4c, and S4d for IR, and S5a, S5b, S5c, and S5d for Raman. The 16 different H-bond topologies show distinguishable IR and Raman spectra in the range up to 1700 cm⁻¹, and distinguishable IR spectra also in the high-frequency range. There are no obvious differences in the Raman spectra among 16 different H-bond structures of ice Ih in the OH stretching region (see Figure S5d), which might suggest the Raman spectra of intramolecular vibrations are only slightly influenced by the topology of the H-bond network.

Figure 4. The IR spectra of ice Ih and XI: (a) the low frequency region and (b) the stretching vibration region. The experimental spectra are extracted from Ref. 32.

The Boltzmann-averaged IR and Raman spectra of ice Ih depicted in Figure 4 and 5, respectively, are derived by introducing the specific weighting factor from the Boltzmann distribution of each isomer. To be able to better compare to the experimentally measured spectra, the stretching frequencies are scaled based on small water cluster results⁹³ (see Table S3). As shown in Figures 4 and 5, the computed frequencies are roughly consistent with the experimental measurements. The translational vibrational modes (ν_T) are located below 380 cm⁻¹; librational (ν_L), bending (ν_B), and stretching (ν_S) vibrations are located at the range of 650 – 1190 cm⁻¹, 1610 – 1710 cm⁻¹, and 3090 – 3460 cm⁻¹, respectively. For the IR spectra (see Figure 4a and 4b), the most obvious difference between ice Ih and XI is that a narrower band and sharper peaks in the librational region are observed for ice XI, which is consistent with previous report by Shigenari and Abe³² and by Wojcik et al.⁴⁰⁻⁴¹ In Figure 5 the Raman spectra of ice Ih and XI are shown. As reported in previous studies,^{32, 34, 39} also for the Raman spectra the most apparent difference between ice Ih and XI is in the librational region, where several split sharp peaks are found in ice XI as compared to a continuous weak broad band in ice Ih. Thus, the librational modes are more sensitive to the proton ordering, which is a spectroscopic signature that can be used to distinguish ice XI from ice Ih. No obvious difference between ice Ih and XI is found for the OH stretching part of the spectrum, which might suggest that the intramolecular vibrations are little affected by the proton-ordering.

Figure 5. The Raman spectra of ice Ih and XI. Amplifications are shown as inserts.

OH Stretching Vibrations of Ice Ih. The OH stretching spectra of each ice Ih isomer are split into five different sub-spectra, depicted in Figures 6 and 7. The hydrogen atoms were divided into four different groups based on the types of H-bonded pair configurations A (*h-cis*), B (*h-trans*), C (*c-cis*), and D (*c-trans*) (see Figure S6) as in previous studies,⁷⁵⁻⁷⁸ and the contribution from each group to the total spectra was projected out (in accordance with the number of H atoms of the group and their vibrational amplitudes squared⁷⁵⁻⁷⁸).

Figure 6. The IR spectra in the OH stretching region from 16 unique structures of ice Ih split into different sub-spectra based on the specific contributions from each H-bond group (A, B, C, D).

In Figure 6, the IR spectra of stretching vibrations in 16 different isomers of ice Ih are shown in the range of 3090 – 3460 cm^{-1} . Unlike the distinct distribution of the sub-spectra of each proton group in water clusters,^{75, 77} the sub-spectra in ice overlap in all the 16 cases. This is also observed for the Raman spectra, shown in Figure 7. The OH stretching vibration is very sensitive to the strength of the H-bond^{75, 77} (the Badger-Bauer rule).⁹⁴⁻⁹⁶ We see that in ice each of the H-bonded pair configuration essentially contributes to all the peaks in the OH stretching region. Thus, unlike the existence of different kinds of H-bonds in water clusters (being revealed by the therein separated sub-spectra),^{75, 77} there is only one kind of H-bond in ice. This observation provides an illustration to the historic debate on the existence of two kinds of H-bond in ice.⁹⁷⁻¹⁰⁰

Figure 7. The Raman spectra in the OH stretching region from 16 unique structures of ice Ih split into different sub-spectra based on the specific contributions from each H-bond group (A, B, C, D).

■ CONCLUSIONS

It is suggested that BLYP combined with TNP basis set is a good method for studies on ice with the average absolute error at 3% for the energy and 5% for the volume. B3LYP and PBE0 with the TS dispersion correction can provide an overall fair description of ice with an average absolute error around 10%, as concluded from the present studies on ice VIII, IX, and XI. It is also shown that PBE performs well in studies of 16 different isomers of ice Ih. The IR and Raman spectra of ice Ih and XI are calculated and compared. The librational vibrations are found to be the most affected by the proton ordering from the comparison of both the IR and Raman spectra between ice Ih and XI, in agreement with the measurements by Shigenari and Abe³². This can be used as a spectroscopic fingerprint of ice XI to distinguish ferroelectric ice XI from ice Ih. Furthermore, only one kind⁹⁹ of H-bond, rather than two⁹⁷⁻⁹⁸, was observed in ice Ih as concluded from the existence of overlapping sub-spectra for different types of H-bonded pair configurations in 16 isomers of ice Ih.

SUPPORTING INFORMATION

Optimized unit cell parameters for the 16 proton-ordered structures of ice Ih (Table S1), OH stretching frequencies of water clusters used for calibration (Table S2), Frequencies and IR and Raman intensities for the 16 ice Ih structures using PBE (Table S3, separate text file). IR spectra for ice XI computed using PBE and using PBE0 (Figure S1), IR and Raman PBE spectra for ice XI using different levels of accuracy (Figures S2 and S3), IR and Raman PBE

spectra of the 16 proton-ordered structures of ice Ih (Figures S4 and S5), the H-bonded neighbor geometries in ice Ih (Figure S6).

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Raman and IR Spectra of Ice Ih and ice XI with an Assessment of DFT Methods

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Table S1. The unit cell parameters of the 16 proton-ordered structures of ice Ih after geometry optimization using PBE, PBE with the TS dispersion correction scheme, and BLYP/TNP.

no.	PBE		PBE-TS		BLYP/TNP	
s01	4.41, 7.65, 7.20	90, 90, 90	4.35, 7.55, 7.11	90, 90, 90	4.47, 7.79, 7.29	90, 90, 90
s02	4.42, 7.63, 7.21	90, 90, 90	4.37, 7.54, 7.11	90, 90, 90	4.50, 7.73, 7.31	90, 90, 90
s03	4.42, 7.64, 7.21	90, 90, 90	4.38, 7.57, 7.13	90, 90, 90	4.49, 7.75, 7.30	90, 90, 90
s04	4.42, 7.64, 7.21	90, 90, 90	4.37, 7.57, 7.14	90, 90, 90	4.49, 7.74, 7.31	90, 90, 90
s05	4.42, 7.64, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.49, 7.73, 7.30	90, 90, 90
s06	4.42, 7.63, 7.21	90, 90, 90	4.38, 7.56, 7.14	90, 90, 90	4.50, 7.74, 7.31	90, 90, 90
s07	4.42, 7.64, 7.20	90, 90, 90	4.38, 7.57, 7.13	90, 90, 90	4.49, 7.75, 7.30	90, 90, 90
s08	4.42, 7.64, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.48, 7.75, 7.30	90, 90.3, 90
s09	4.41, 7.65, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.48, 7.76, 7.30	89.4, 90, 90
s10	4.42, 7.65, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.48, 7.76, 7.30	90, 90, 90.1
s11	4.42, 7.65, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.48, 7.76, 7.30	90, 90.2, 90
s12	4.42, 7.64, 7.21	90, 90, 90	4.38, 7.57, 7.13	90, 90, 90	4.49, 7.74, 7.30	90, 90, 90
s13	4.43, 7.65, 7.22	90, 90, 90	4.38, 7.57, 7.13	90, 90, 90	4.50, 7.74, 7.30	90, 90, 90
s14	4.42, 7.65, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.48, 7.76, 7.29	90, 90, 90.2
s15	4.42, 7.65, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.48, 7.76, 7.30	90, 90.1, 90
s16	4.42, 7.64, 7.21	90, 90, 90	4.37, 7.57, 7.13	90, 90, 90	4.49, 7.74, 7.30	89.9, 90.1, 89.7

Table S2. The bonded OH stretching frequencies of small water clusters (H₂O)₂₋₅.

	Calculated	Expt. ^a
(H ₂ O) ₂	3457	3601
(H ₂ O) ₃	3334	3533
(H ₂ O) ₄	3118	3416
(H ₂ O) ₅	3049	3360

Note: the scaling factor is calculated by the formula $c = \frac{\sum \nu_i \times \omega_i}{\sum \omega_i^2} = 1.072$, ν_i is the experimentally measured wavenumber and ω_i is the computed wavenumber from this work. ^aReference 85.

Table S3. Computed vibrational frequencies and IR and Raman intensities of ice XI using the PBE functional and the plane wave basis set with an energy cutoff of 750 eV. unit: cm^{-1}

Translation Modes			Libration Modes			
Freq.	IR	Raman	Freq.		IR	Raman
Calc.	Intensity	Intensity	Calc.		Intensity	Intensity
25.79784	2.3E-06	0.009684	654.2946		0.135585	0.325726
57.85342	0	0.002598	655.9757		0.059538	0.183255
69.52301	0	0.021451	660.489		0	0.00023
93.53978	0.01382	5E-07	661.8796		0	1.855892
98.70972	0.009069	0.001659	677.3546		0.000257	2.046775
130.9715	8.26E-05	0.000046	750.4045		7.94E-05	0.000412
151.9552	0.000487	1.74E-05	751.4869		3.9E-06	2.8E-06
194.5885	2.416094	0.000399	752.6114		0.60627	3.54811
233.6776	0.00033	0.000247	755.5911		1E-07	0
240.3786	0.024041	0.004737	825.0691		0	4.489829
244.5967	0.220002	0.176837	826.6418		0	0.00018
254.1053	0	2.385633	935.5377		4E-07	2.9E-06
257.2154	0	2.94624	942.1517		3.8E-06	9E-07
263.5735	6.773433	5.470218	946.2033		0	1.67E-05
271.6327	9.664121	1.922544	948.0816		0	1.354344
272.921	0.019744	0.015707	949.7798		2.8E-06	0
278.7944	0.008462	0.042777	958.8222		1.7E-06	0.000001
286.3203	0.00063	0.000129	971.9453		11.67128	9.101082
353.1239	0.000491	2.5E-06	1023.866		0	9E-07
365.3615	0.659748	0.16419	1027.73		17.08187	4.503886
369.7208	0.012886	0.226748	1072.022		5.867577	1.948369
			1121.409		0	2.384025
			1137.039		0	0.000061
			1184.559		0.007981	0.00881
Bending Modes			Stretching Modes			
Freq.	IR	Raman	Freq.	Freq.	IR	Raman
Calc.	Intensity	Intensity	Calc.	Scaled ^a	Intensity	Intensity
1616.196	2.475031	1.488379	2889.505	3097.55	68.05285	3008.271
1618.136	5.439601	0.417496	2920.097	3130.344	211.711	18.07486
1629.207	6.7E-06	5.3E-06	2922.181	3132.578	0.004325	0.000233
1664.706	9E-07	2E-07	3000.545	3216.584	0	589.1073
1671.429	0.133057	12.5386	3000.648	3216.695	0.001242	0.001735
1679.237	0	0	3001.25	3217.34	221.2878	287.7263
1689.835	2E-07	4.7E-06	3001.361	3217.459	0.000131	0.003547
1710.388	0.002854	3.476039	3002.242	3218.404	136.4268	698.748
			3002.47	3218.648	13.31854	68.35083
			3136.769	3362.616	3.594124	18.64096
			3137.462	3363.359	2.07E-05	6.05E-05
			3143.087	3369.389	1.48E-05	0.000297
			3152.965	3379.978	5E-07	9.3E-06
			3213.368	3444.731	0.014575	264.7792
			3215.866	3447.409	0.000127	0.006365
			3219.81	3451.636	3.72146	115.9225

^aThe calculated frequencies are multiplied by a scaling factor 1.072.

Figure S1. The IR spectra of ice XI computed using PBE (with plane wave basis set) and using PBE0 (with 6-311G(2d,2p) Gaussian basis set) methods: (a) the low frequency region and (b) the stretching vibration region.

Figure S2. The IR spectra of ice XI computed using the PBE functional with the “fine” and the “ultrafine” settings in (a) the low frequency region and in (b) the stretching vibration region. For the “ultrafine” setting, the plane wave energy cutoff is 830 eV and the k-point net is $6\times 3\times 3$.

Figure S3. The Raman spectra of ice XI computed using the PBE functional with the “fine” and the “ultrafine” settings in (a) the low frequency region and in (b) the stretching vibration region. For the “ultrafine” setting, the plane wave energy cutoff is 830 eV and the k-point net is $6\times 3\times 3$.

Figure S4. The IR spectra for the 16 proton-ordered structures of ice Ih: (a) translational modes, (b) librational modes, (c) bending modes, and (d) stretching modes.

Figure S5. The Raman spectra for the 16 proton-ordered structures of ice Ih: (a) translational modes, (b) librational modes, (c) bending modes, and (d) stretching modes.

Figure S6. The H-bonded neighbor configuration geometries in ice Ih: A (*h-cis*), B (*h-trans*), C (*c-cis*), and D (*c-trans*).