

Anomalous transformations in ice VIIIDennis D. Klug,¹ John S. Tse,¹ Zhenxian Liu,² Xavier Gonze,³ and Russell J. Hemley²¹*Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6*²*Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, USA*³*Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Louvain-la-Neuve, Belgium*

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Synchrotron far-infrared spectroscopy and linear response density-functional theory provide a new interpretation of the unique low-temperature isostructural transition in ice VIII. This study shows that it is a first-order thermodynamic transformation. Previously unexplained discrepancies have been resolved: the transformation between two forms of ice VIII arises from subtle phonon instabilities with an isostructural movement of molecules in the ice VIII structure.

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The structures and properties of the dense phases of crystalline and amorphous ice have revealed many new features that involve the hydrogen bond that remain as challenging subjects for research. Some of these features include phase transitions to high-density amorphous forms of ice, centrosymmetric hydrogen bonds between water molecules, and an isosymmetric transformation. Ice VIII is a high-pressure form of ice with a particularly simple ordered structure, stable above 2 GPa and at temperatures below 265 K (Ref. 1) and consisting of two interpenetrating cubic ice structures where each cubic structure has its dipole moment pointing in opposite directions along the crystallographic c axis. The opposite directed dipole moments give rise to a small tetragonal distortion of the crystal lattice. The tetragonal structure (space group $I4_1/amd$) consists of unit cells with 8 water molecules. If the temperature is raised above 265 K at 2 GPa, ice VIII transforms to a closely related ice VII cubic phase with the same basic interpenetrating lattice structure but with disordered proton positions. At high pressures, ice evolves to a structure with centrosymmetric hydrogen bonds, a transformation that has been the subject of considerable theoretical and experimental study in both ice VII and VIII.²⁻⁶ Ice VIII can also be recovered at ambient pressure at low temperatures and undergoes amorphization on warming above ~ 120 K. This temperature-induced amorphization and its relationship to pressure-induced amorphization (e.g., other phases of ice) has been the subject of numerous experimental and theoretical investigations.

Neutron diffraction studies⁷ provided evidence for a unique isosymmetric phase transition that involves a change in the $z(O)$ coordinate over the pressure range 1–5 GPa. The $z(O)$ parameter is coupled to a tetragonal distortion that defines the distance between the two interpenetrating sublattices in the ice VIII structure. This transformation was also investigated using first-principles electronic structure methods.⁸ Several features of the transformation were reproduced and a partial characterization of the transformation was obtained although the theory indicated a somewhat sharper transition presumably due to kinetic effects. However, neither the experiments nor previous calculations were able to provide detailed thermodynamic information about this transformation. Analysis of early spectroscopic data^{9,10}

suggested that the transformation could be second-order thermodynamic one.⁷ In particular, examination of previous infrared data in particular suggested that the transformation occurred in the 1–4 GPa pressure interval and was characterized by changes in the pressure dependence of a translational E_u mode involving motions of water molecules in the a - b plane of the crystal lattice. Earlier calculations⁸ could not identify softening in selected vibrational modes that could verify this suggestion. Moreover, the data coverage, P - T range and quality of the previously reported spectra were limited.

We have re-examined this unusual transformation using a combination of low-temperature high-pressure synchrotron far-infrared techniques and first-principles linear response phonon calculations. Our results demonstrate that the appropriate interpretation and details of the transformation are entirely different from that previously reported based on limited data, and provide a detailed picture of this transformation and its thermodynamic nature.

Far-infrared high-pressure low temperature spectra of 99.98% D_2O and H_2O samples were obtained using a diamond anvil cell held in a low-temperature cryostat equipped with wedged diamond windows.¹¹ The cryostat was equipped with a lever mechanism that permitted pressure changes from outside the cryostat. Stainless steel gaskets with sample diameters of 200 μm were used; sample thickness of a ~ 3 microns permitted full characterization of the far-infrared band profiles. Ice VIII was prepared by cooling ice VII from 300 K at 6.5 GPa. Pure samples were used to avoid possible clathrate formation with pressure media. Ruby fluorescence was used for pressure measurement.¹² The measurements were performed at the U2A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. An evacuated Bruker IFS-66v spectrometer equipped with a bolometer (Infrared Laboratories) and a 6- μm thick mylar beamsplitter was used to obtain transmission spectra. Spectra were obtained on increasing and decreasing pressure.

Theoretical optimization of the structure and characterization of the pressure dependence of the lattice dynamics of ice VIII were obtained with a planewave pseudopotential method employing the linear response method.¹³ The core electrons were modeled with a generalized gradient approximation^{14,15} (GGA) pseudopotential.¹⁶ An energy cut-

off of 55 or 65 hartrees for the basis set planewaves and a Monkhorst-Pack¹⁷ $4 \times 4 \times 4$ mesh of k -points was used for Brillouin zone integrations for phonon calculations. Monkhorst-Pack meshes of up to 6 6 6 and 8 8 8 and energy cutoffs up to 65 hartrees were used for selected calculations and structural optimizations to obtain convergence of structural parameters and phonon frequencies. Calculations of the phonon spectra used the 12 atom primitive cell and phonon dispersion curves and structural parameters were calculated over the pressure range 0–30 GPa. The internal coordinates and c/a ratio was optimized at each pressure. Calculations were also carried out for D₂O to obtain the isotope dependence for comparison with the experimental results. The calculated structural parameters at zero pressure are $a=4.80$ Å, $c=6.79$ Å, and $z(\text{O})=0.1069$, in good agreement with the reported experimental values of 4.80 Å, 6.99 Å, and 0.1071, respectively.¹ The calculated change in $z(\text{O})$ for the isosymmetric phase transformation is in excellent agreement with experiment.

The spectrum of the sample in the diamond cell was first recorded at 300 K where cubic ice VII (space group $Pn3m$) is the stable phase of ice. After cooling to 254 K at 6.7 GPa, the spectrum sharpened considerably. This sharpening of the spectrum is a direct consequence of the ordering transformation that occurs at ~ 265 K where the proton-disordered ice VII transforms to the proton-ordered ice VIII. The proton disordered lattice of ice VII was characterized by a broad infrared band that essentially reflected the phonon density of states for a phonon branch centered about this frequency range. The pressure dependences of the spectra obtained at 85 K for both D₂O and H₂O for the infrared active modes⁹ with E_u symmetry are shown in Fig. 1(a) and the pressure dependence of frequencies of the absorption bands in the region 100–500 cm^{-1} are plotted in Fig. 1(b). Only one E_u mode due to translational vibrations is infrared active in this frequency region. The other absorption band observed for H₂O at lower pressures and for D₂O up to 8 GPa is an E_u librational lattice vibration. The thin samples allowed observation of the complete absorption bands. The frequencies of the E_u modes for H₂O and D₂O ice VIII at ambient pressure are 160 ± 2 and 163 ± 2 cm^{-1} , respectively, in good agreement with the values of 162 cm^{-1} of Ref. 9 and the frequency of the E_u rotational vibration is 332 ± 2 cm^{-1} , also in agreement with 332 cm^{-1} of Ref. 9. The pressure dependence of the D₂O and H₂O bands are nearly linear at low pressures and extrapolate to the earlier reported results for spectra obtained with recovered samples⁹ but the higher pressure results differ considerably from previous results¹⁰ obtained at 260 K. The insert in Fig. 1(b) shows the data from Refs. 9 and 10 together with the suggested pressure dependence from Ref. 7. The ratios of frequencies at the lowest pressure (~ 0.1 GPa) for the two bands of about 1.0 and 1.38 are entirely consistent with the assignment of these two modes as translational and librational modes. The deviation from the ideal ratios of 1.05 and 1.414 is undoubtedly due to anharmonicity and is similar to that observed previously for other vibrational modes in ice VIII.¹⁸ In addition to the different temperatures (260 K vs 80 K), we note that the maxima of the absorption peaks were not measured due to thick samples used in the previous study, preventing accurate

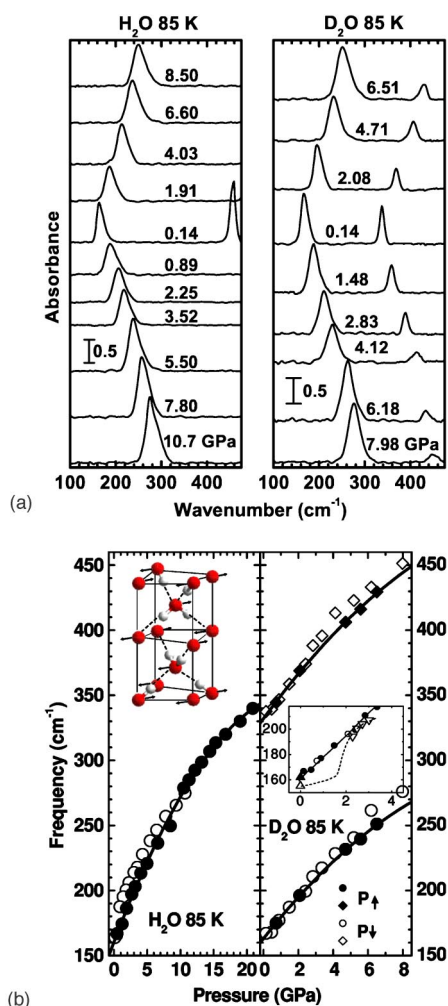


FIG. 1. (a) Pressure dependence of far-infrared absorption spectra of H₂O and D₂O ice VIII obtained at 85 K. The inset shows the infrared active E_u vibrational mode. (b) (Color online) Measured pressure dependence of the frequencies of the infrared active translational and rotational lattice vibrations of ice VIII at 85 K. Solid circles represent data taken on compression and open circles on decompression. The solid lines are the linear best square fits to the data on compression with $\nu = \nu_0 + a \times P + b \times P^2$. In the inset, the triangles \blacktriangle and ∇ are data from Refs. 9 and 10, respectively, where the data point from Ref. 9 had been shifted down by 6 cm^{-1} to match the temperature of 260 K data in Ref. 10. The black triangle in the inset is the data directly from Ref. 9. The dotted line showing the suggested pressure dependence based on this data is from Fig. 2 of Ref. 7.

determination of the frequencies.¹⁰ The present study was obtained on much thinner samples and at lower temperatures and therefore the peak frequencies could be obtained much more accurately. The frequency dependences of both the translational and librational lattice E_u modes were nearly linear for both H₂O and D₂O throughout the pressure interval of the previously reported transition. There is no sign of previously suggested features, which were based on incomplete data and interpreted in terms of a soft infrared-active translational mode and a possible second-order phase transition.

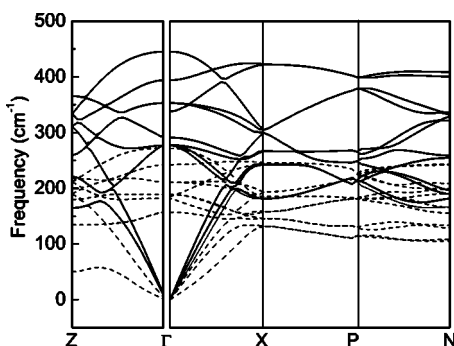


FIG. 2. Calculated phonon dispersion curves for translational modes in ice VIII near the isosymmetric transition (solid lines) and close to ambient pressure (dashed lines).

These surprising experimental results therefore motivated a more detailed theoretical study of the phonons in ice VIII and their role in the isosymmetric phase transformation. The isosymmetric transformation was reproduced in the present calculations and calculated to occur at a volume of $\sim 59 \text{ \AA}^3$ per 12 atom primitive cell. This is identical to the result of an earlier calculation⁸ that employed a different pseudopotential and plane-wave code: the calculated change in magnitude of the change in $z(\text{O})$ agree with that of the experimental result⁷ within the errors for the experiment and theory. In this study, the full phonon spectrum was calculated as a function of pressure to investigate the possibility of softening of particular phonon branches. This more complete treatment is necessary for characterizing the mechanism of the transformation as well as accurate interpretation of the new high-pressure far-infrared data.

The calculated phonon spectra of ice VIII consists of 36 branches of which 3 are due to acoustic modes, 9 due to translational vibrations of water molecules in the ice lattice, 12 modes are librational vibrations, and 12 due to internal vibrations of water molecules.⁹ For the translational vibrations, only the E_u degenerate vibration is infrared active. Two different librational modes with E_u character are also infrared active. The calculated dispersion curves at two volumes calculated with energy cutoffs of 65 hartrees are shown in Fig. 2 and several features are readily apparent. There are no branches that soften to zero frequency in the transition region indicative of lattice instabilities associated with a second-order phase transformation. The phonon dispersion curves for ice VIII at low pressures, however, do indicate a softening of some branches and this may be related to the eventual experimentally observed transformation of ice VIII to an amorphous solid upon heating to $\sim 120 \text{ K}$.¹⁹ This transformation in fact has been attributed to a lattice instability.²⁰ Examination of the phonon dispersion curves at low pressure indicates that this transformation may be associated with an instability that arises when ice VIII is warmed and the dispersion curves further soften as a result of thermal expansion and population of low lying modes in the acoustic branches of the dispersion curves. The present calculations indicate that ice VIII is dynamically stable at ambient pressure, consistent with the known phase diagram of ice and with the experimental observation that ice VIII only transforms to an amorphous form upon heating at ambient pressure.¹⁹

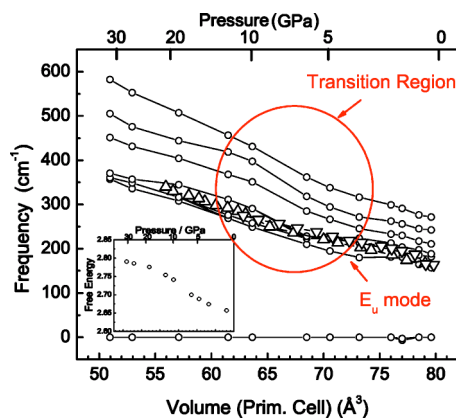


FIG. 3. (Color online) Calculated pressure and volume dependence of the translational lattice vibrations at the Brillouin zone center. The open triangles are the measured frequencies of the E_u lattice mode for the H_2O samples. The triangles with apexes at the top and bottom are for increasing and lowering pressure, respectively. Inset: Calculated pressure and volume dependence of the quasiharmonic phonon contribution to the Helmholtz free energy at 80 K. Units for the phonon free energy are $10^5 \times \text{J}/(\text{mol-prim. cell})$.

The calculated frequency dependence of the translational vibrations displays a unique character that provides insight into the isosymmetric transformation. The volume and pressure dependence of the calculated frequencies at the zone center Γ are shown in Fig. 3. Whereas, at large volumes (low pressures), the pressure dependence of all vibrations are almost linear or only slightly curved, at volumes less than $\sim 70 \text{ \AA}^3$ / primitive cell, the dependence of several modes drops, but then begins to have more normal gradients with increasing pressure for volumes $< \sim 65 \text{ \AA}^3$ / primitive cell. This volume range can be identified as the transition region where the isosymmetric transition is calculated to occur in agreement with experiment.⁷ A particularly interesting feature regarding the pressure dependence of the frequencies is that of the E_u mode. Its frequency has an almost linear pressure dependence in this pressure range in excellent agreement with the experimental result. The calculation therefore indicates that the E_u mode may not provide a clear signature for the transition; this is exactly what is observed. The lowest frequency librational mode is seen only at the lowest pressures in the far-infrared for H_2O but is observed over the full pressure range for D_2O also it has a nearly linear pressure dependence.

Physical understanding of the observations and calculated results is provided by an examination of the normal modes. The E_u mode consists of translational displacements of water molecules in the a - b plane where molecules in each interpenetrating diamond structure lattice move in opposite directions.⁹ The movement of the lattices is coupled with variations in the $z(\text{O})$ parameter and, produces a uniform increase in repulsive interactions with decreasing volume. In contrast, several other vibrations consist of displacements parallel to the c axis or displacements of each sublattice; these modes show slightly different pressure dependences and some of the modes show change in curvature in the transition region.

In order to obtain a more detailed characterization of the transformation, the phonon calculations were used to calculate the volume dependence of the free energy $F(V, T)$ using the quasiharmonic approximation²¹ and the relation,

$$F(V, T) = E(V) + k_B T \sum_{\mathbf{q}} \sum_j \ln \left\{ 2 \sinh \left(\frac{\hbar \omega_j(\mathbf{q})}{2k_B T} \right) \right\}, \quad (1)$$

where $E(V)$ is the static part of the internal energy at 0 K is calculated using the plane-wave pseudopotential method employed here and the sum is over normal mode frequencies in the complete Brillouin zone. The second term is the vibrational contribution to the free energy, $\omega_j(\mathbf{q})$ is the frequency of the j th phonon in the Brillouin zone and evaluated using the density-function linear response method. The slope of the calculated volume and pressure dependence of the phonon contribution to the free energy at 81 K shows small but distinct change in the transition region (Fig. 3, inset). This is characteristic of a classical first-order thermodynamic transition. In this case the free energy behavior indicates that there is a pressure range where the vibrational contribution gives rise to a phase transition at finite temperatures. A small discontinuity is also seen in the calculated equation of state (not shown). We can therefore conclude that the isosymmetric

phase transition in ice VIII is a weak first-order thermodynamic transformation. This picture is consistent with a Landau analysis of this class of transitions that implies that isosymmetric transitions are necessarily first-order.^{22,23}

In summary, synchrotron far-infrared spectra of H₂O and D₂O ices measured under combined high pressure and low temperature high-pressure has led to a major revision of the original suggestions for the characterization of the isosymmetric phase transition discovered by Besson *et al.*⁷ The original explanation was based on ambiguous and limited spectroscopic data. Our results show the power of synchrotron radiation for probing low-frequency excitations at high pressure and low temperatures in diamond anvil cells on thin ice samples. This study demonstrates that the infrared active translational mode has a nearly linear pressure dependence and does not show softening that would be characteristic of a second-order thermodynamic phase transition. The transition appears to be an isosymmetric first order thermodynamic transition but occurs with an extremely small volume change and is therefore consistent with Landau theory models.

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