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Compression of Ice to 210 Gigapascals: Infrared Evidence for a Symmetric Hydrogen-Bonded Phase

A. F. Goncharov,* V. V. Struzhkin, M. S. Somayazulu, R. J. Hemley, H. K. Mao

Protonated and deuterated ices (H_2O and D_2O) compressed to a maximum pressure of 210 gigapascals at 85 to 300 kelvin exhibit a phase transition at 60 gigapascals in H_2O ice (70 gigapascals in D_2O ice) on the basis of their infrared reflectance spectra determined with synchrotron radiation. The transition is characterized by soft-mode behavior of the ν_3 O–H or O–D stretch below the transition, followed by a hardening (positive pressure shift) above it. This behavior is interpreted as the transformation of ice phase VII to a structure with symmetric hydrogen bonds. The spectroscopic features of the phase persisted to the maximum pressures (210 gigapascals) of the measurements, although changes in vibrational mode coupling were observed at 150 to 160 gigapascals.

The high-pressure behavior of ice is fundamental to a number of problems in chemistry and physics. In particular, research has focused on the behavior of the hydrogen bond in materials under compression for many years. On the basis of the behavior of water-containing systems, the concept of symmetrization of the O–H...O bond was developed, which implies that at some critical value of the distance between two neighboring O atoms ($d_{\text{OO}} = 2.42 \text{ \AA}$), a proton occupies the midpoint between them (1). Under sufficient compression, it has been predicted that ice will transform from a molecular solid into an ionic material with symmetric hydrogen bonds (2–4). Experimental evidence of the transformation of high-pressure ice VII (VIII at low temperatures) to such a state have been inconclusive. Moreover, theoretical calculations predict transitions to still denser forms at higher pressures (5–7). Here, we report synchrotron infrared reflectivity measurements to 210 GPa (2.1 Mbar) to explore theoretically predicted phase transitions in protonated and deuterated ices. Phase transitions were observed at 60 and 70 GPa for H_2O and D_2O , respectively, which provides evidence for symmetric hydrogen-bonded states in ice.

Above 2 GPa at room temperature, ice is reported to have the body-centered-cubic (bcc) structure with water molecules disordered around their center of mass. In this structure, each O atom is bonded to four of the eight nearest neighbors by O–H...O or O–D...O bonds in a tetrahedral arrangement (ice VII; Fig. 1). The structure can also be visualized as two interpenetrating

ice I_c (cubic) lattices. The disorder in this structure changes with pressure at 300 K from rotational to proton tunneling along the O–H...O or O–D...O bonds (8). The low temperature-ordered ice VIII has the same atomic arrangement as ice VII, except that the two ice I_c sublattices now have opposite dipole moments. As the O–O distance decreases with an increase in pressure, the barrier between two potential wells for the O–H...O coordinate (where the proton can be found with a maximum probability) decreases and the proton tunneling frequency increases. It has been predicted that ice will transform to a symmetric form (ice X) when the probability of finding a proton at the midpoint between two O atoms becomes equal to that near the potential wells (2). The time-averaged symmetry does not change at this point and is equivalent to that of ice VII. Further compression leads to suppression of proton tunneling and formation of the structure with static, symmetric hydrogen bonds.

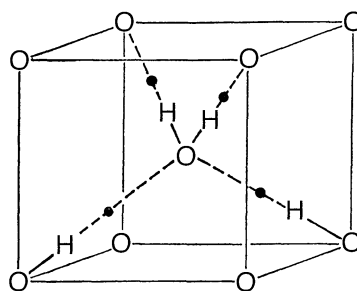


Fig. 1. Idealized structure of ice VII. As in normal ice, at low pressure the H is covalently bonded (solid line) to an O of the same molecule and weakly bonded (dashed line) to an O of a neighboring molecule. The symmetrically hydrogen-bonded state is predicted to occur with decreasing O–O distance on compression when the point of maximum probability of finding the H moves to the middle (solid circle) (2).

Identification of such a transition has been inconclusive because of the difficulty of probing the H (or D) sublattice at the requisite pressures (9, 10). X-ray diffraction data were obtained to 128 GPa (11) but provided no information about the proton sublattice. If we assume that the lattice continues to be bcc, the positions of the O atoms obtained (largely on the basis of the 110 reflection) were found to be consistent with a uniform compression of the O sublattice. Neutron diffraction studies, which are capable of locating the positions of the H and O atoms, have been reported only to 10 GPa (12).

Vibrational spectroscopy provides crucial information on the behavior of ice at ultrahigh pressure, in particular, the evolution of the hydrogen bonds. For example, the Raman-active symmetric O–H stretching mode (ν_1) and the infrared (IR)-active antisymmetric mode (ν_3) will soften with pressure below the symmetrization transition and harden thereafter (13). Raman-active fundamentals in ice VII (ice VIII at low temperature) could be measured only up to 25 and 50 GPa for protonated and deuterated ice, respectively (1, 8). These measurements revealed a softening of O–H stretching modes that is consistent with the approach toward symmetrization, but the intensities of Raman spectra decreased markedly with increasing pressure.

With IR spectroscopy, there is the opposite problem; with increasing pressure, the exceedingly intense O–H absorption results in a broad band, which makes determination of peak positions difficult. Moreover, the diamond windows of the pressure cell are nearly opaque in the frequency range from 1800 to 2400 cm^{-1} , a critical interval for studying the softening of the O–H stretching modes. To reduce the absorption to a measurable range, dilute solutions of HDO in D_2O ice VII have been studied up to 18.9 GPa (14) and 45 GPa (15), and these show the softening of the uncoupled O–H stretching vibrations. For higher pressures, these measurements are complicated by the strong absorption of diamond anvils and the D_2O fundamental stretching mode. The IR absorption measurements of a thin H_2O film up to 110 GPa at room temperature showed enormous line broadening [full width at half maximum (FWHM) 2500 cm^{-1}] above 40 GPa (16), which precluded identification of possible bond symmetrization.

Here we used ultrahigh-pressure synchrotron IR reflectivity spectroscopy, which is ideal for strongly absorbing or opaque samples (17). In addition, with observation of the reststrahlen band, reflectivity measurements constrain the dielectric function even outside the measured frequency range (18). H_2O and D_2O ice VII samples were

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prepared at high pressure (2 to 3 GPa) at room temperature from doubly distilled, deionized water and D₂O (99.9 mol% purity). Three separate experiments were done, two for H₂O and one for D₂O. Water samples together with small ruby chips for pressure determination (19) were loaded into high-pressure chambers 25 to 40 μm in diameter and 15 to 25 μm in thickness in a stainless steel gasket between two type IIa diamonds. Rhenium was used as gasket material for the run reaching 210 GPa. A custom-built cryostat with KCl windows was used to study the effect of temperature, as used recently for measurements on H₂ over a similar pressure range (20). Reflectivity spectra were normalized to the diamond-air interface, and reference spectra for absorption were determined from measurements through the empty diamond cell; all reference spectra were measured at ambient pressure and temperature.

The predicted transition to the symmetric state is related to displacements of the protons into the midpoint between O atoms. Therefore, it has some features of displacive-type phase transitions—namely, soft-mode behavior of the proton-related vibrations. In addition, close to the transition point the transition should have order-disorder character because of strong proton tunneling. Our measurements allow us to observe complex details of this behavior up to and beyond the transition pressure. We analyzed IR reflectivity spectra of H₂O at 13.7 to 80 GPa (Fig. 2) using a classical oscillator model and the Kramers-Kronig transformation procedure (21, 22). The O-H stretch near 3000 cm^{-1} softens with increasing pressure and splits in the pressure range of 25 to 45 GPa. In fact, anomalous line broadening and deviation from the “normal” soft-mode behavior can be interpreted as evidence of proton tunneling at pressures higher than 20 GPa. This broadening is readily observed in absorption spectra of the higher frequency overtone and combination bands (21). The splitting of the stretching mode at 25 to 45 GPa is similar to what has been reported for the uncoupled O-H vibrations of HDO molecules in a D₂O matrix (15). Moreover, we observed intensity exchange from the high-frequency (ν_3) to low-frequency (ν_3') component similar to the reported Fermi resonance phenomenon (15, 23). At higher pressures, the O-H stretching vibration continued to soften to the point where it almost intersected the rotational band ν_R at $\sim 1250 \text{ cm}^{-1}$. We cooled the H₂O sample to 85 K at 55 GPa and found a negligible temperature effect on the frequencies of the stretching and rotational modes.

At 60 GPa the reflectance spectra change abruptly: the ν_3 band became much

weaker and a strong low-frequency IR band was observed (Fig. 2). With further increase in pressure, all bands increased in frequency. Reflectance spectra above 60 GPa show a systematic increase in reflectivity at 600 to 2600 cm^{-1} with increasing pressure. Reflectance spectra of D₂O at high pressures (to 100 GPa at 300 K and 121 GPa at 85 K) are similar to those of H₂O except for the expected mass effect on the frequencies. These results clearly identify a transition at

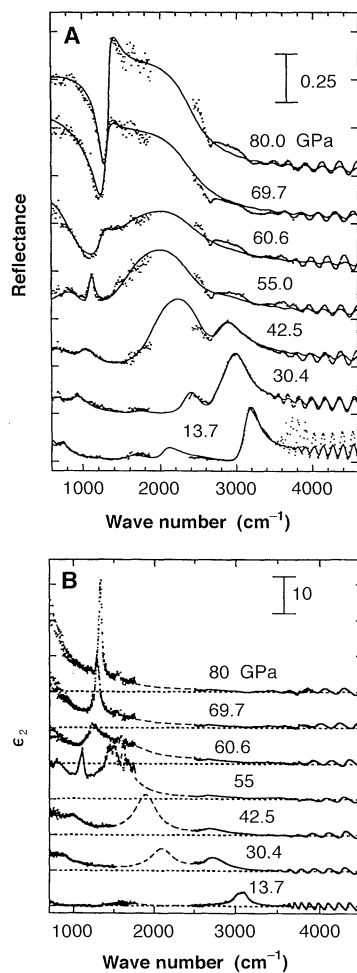


Fig. 2. Spectra of H₂O at 13.7 to 80 GPa (295 K). (A) Representative reflectivity spectra: points, experimental data; lines, oscillator model. Spectra are shifted with 0.25-unit increments in the vertical direction. There are no data in the range of the strong diamond absorption (1800 to 2400 cm^{-1}). Spurious oscillations at high frequencies originate from Fabry-Perot interference between the diamond anvils. The spectral region around 2600 cm^{-1} is complicated by the absorption of diamonds. Peculiarities in the spectra are due to incomplete cancellation of sharp features in reference and sample spectra. (B) Imaginary part of the dielectric constant ϵ_2 of H₂O obtained from a Kramers-Kronig analysis of reflectivity spectra: points, Kramers-Kronig transformation of experimental data; dashed lines, oscillator fit. The curves are offset in the vertical direction for clarity.

60 GPa (70 GPa for D₂O) to a phase having spectroscopic characteristics of a symmetric hydrogen-bonded state.

We pressurized ice far beyond the transition region up to 210 GPa to firmly establish the increasing wave number of the stretching mode with pressure (Fig. 3). At 150 to 160 GPa, a resonance between stretching ν_S and deformational ν_D modes

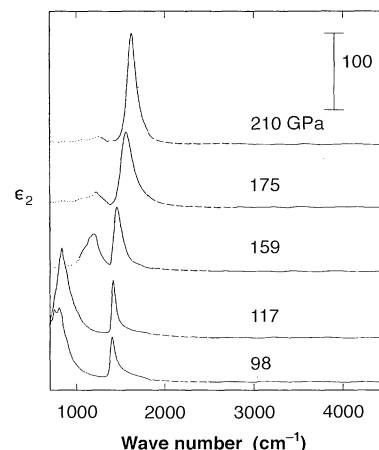


Fig. 3. ϵ_2 spectra of H₂O (295 K) showing the positive pressure shift of the stretching mode ν_S to 210 GPa and the resonance at 150 to 160 GPa. The solid line is from the Kramers-Kronig transformation; the dotted line is calculated from absorbance data (27); the dashed line is the oscillator fit. The curves are offset for clarity.

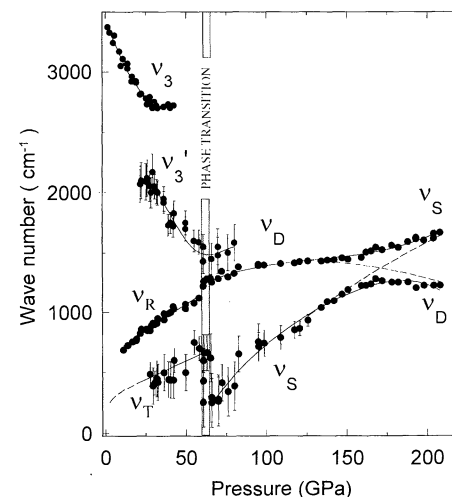


Fig. 4. Pressure dependence of the IR-active vibrational frequencies in H₂O (295 K). The O-H stretching mode is labeled ν_3 and ν_3' at low pressure and ν_S after the phase transition. The dashed line corresponding to the shift of the translational mode ν_T at low pressure is taken from (8). The dashed lines at higher pressure show the proposed resonance. Other modes: ν_R , rotation; ν_D , deformation. Uncertainties due to the broad bandwidth or the diamond absorption are shown as vertical error bars. Where bars are not shown, uncertainties are less than the size of the symbols.

occurred, which is characterized by the approach and separation of the two vibrational levels and a concomitant intensity transfer from ν_D to ν_S . Above this point, the frequency of the stretching vibration exceeded the deformational mode (Fig. 4), indicating that proton tunneling between two potential minima has been suppressed, which is consistent with the presence of static, symmetric hydrogen bonds (24). Further information on the structure, including changes in hydrogen positions and possible distortion of the O sublattice, will be possible if synchrotron x-ray measurements on ice are made in this newly accessible pressure range.

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- We performed the measurements on the U2B IR beam line at the National Synchrotron Light Source (NSLS), using a Fourier transform-IR (Nicolet 750) spectrometer with KBr beam splitter. The characteristics of the beam line are given by G. L. Carr *et al.* [*Rev. Sci. Instrum.* **66**, 1643 (1995)]. Synchrotron light passes through the spectrometer and is focused into the diamond anvil cell to spots 20 to 30 μm in diameter (in the visible), using a custom-built IR microscope with Cassegrain mirror objective (numerical aperture = 0.25, $\times 8$). For absorption measurements, a ZnSe lens placed inside a Mao-Bell diamond-anvil cell collects the light transmitted through the sample and images it on a mercury-cadmium telluride detector (MCT). Reflected light is collected by the same mirror objective, which illuminates the sample, applying a half-mirror beam splitter. A separate MCT detector was used to record the reflectivity, which permitted collection of complementary absorption and reflectivity spectra at each pressure.
- From Kramers-Kronig transformation of the reflectivity spectra, we can obtain both the real and the imaginary parts of the dielectric function, $\epsilon_1 + i\epsilon_2$ [F. C. Jahoda, *Phys. Rev.* **107**, 1261 (1957)]. In contrast, there is no regular procedure to derive both ϵ_1 and ϵ_2 from absorption measurements.
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- We used a standard oscillator model (25) for each of the observed bands, as well as a Kramers-Kronig transformation procedure to relate the absorption and reflectivity spectra (21). Between 60 and 80 GPa, the inclusion of at least three oscillators is required to account for the observed spectra in the lower frequency range. The lowest frequency oscillator (ν_S) has the greatest strength and is below the measured spectral range ($<600\text{ cm}^{-1}$). We believe that this band originates from the stretching mode of the low-pressure phase. A narrow band at 1300 cm^{-1} (ν_D) is a deformational mode of the O–H bond related to the rotational band ν_R of the low-pressure phase. The pressure dependence of the frequency of this band shows a change in slope at 60 GPa. Only those two modes are IR-allowed for the ice X structure. The third weak, broad band is close to the position of stretching mode of the low-pressure phase ν_S' near the transition point (21). The independent oscillator fit to the reflectivity spectra in this pressure-frequency range was not sufficient to model the data, and we obtained much better fits when we included an interaction between stretching and rotational mode as suggested (23). Two interacting oscillators were sufficient to fit the reflectivity spectra above 80 GPa. Aoki *et al.* (16) interpreted absorption near 1200 cm^{-1} as a Fano-type interference between a narrow band and the continuum. We find, however, that the observed line shape does not necessarily require interference, because two independent oscillators (the first, a relatively weak and narrow IR band inside a second, the strong and broad reststrahlen band) also give rise to a Fano-like absorption as a result of the complex behavior of the optical constants (21).
- Alternatively, calculations using a double-well potential model for the hydrogen bond suggest that this could also arise from splitting of energy levels associated with the changing barrier height (21).
- The double-well potential calculations also predict a change in proton motion at these pressures (21). Although the spectroscopic features at 150 to 160 GPa are indicative of a type of Fermi resonance, a second phase transition cannot be ruled out.
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Making DNA Add

Frank Guarnieri, Makiko Fliss, Carter Bancroft*

Recent studies have demonstrated the feasibility of using DNA-based experiments to compute solutions to combinatorial problems. However, a prerequisite for designing a computer useful in a wide range of applications is the ability to perform mathematical calculations. The development of a DNA-based algorithm for addition is presented. The DNA representation of two nonnegative binary numbers is presented in a form permitting a chain of primer extension reactions to carry out the addition operation. To demonstrate the feasibility of this algorithm, a simple example was executed biochemically.

In a pioneering study, Adleman used DNA to solve a directed Hamiltonian path problem (1), thus demonstrating the feasibility of a molecular approach to the solution of combinatorial problems. This approach has been extended by Lipton to the solution of another NP-complete problem, the "satisfaction" problem (2). These elegant studies demonstrated how problems corresponding to Boolean formulas can be solved by a massively parallel processing procedure that makes use of the ability of DNA sequences to hybridize specifically to their complementary sequences.

More recently, Reif has proposed an abstract mathematical model for the performance of parallel molecular computation (3).

It is clearly of interest to design DNA-based computers capable of performing search procedures. However, design of a versatile computer requires development of the bit manipulations for carrying out addition. Mathematical calculations such as addition represent a different problem than the solution of search problems. A search problem can be solved by generating all possible combinations and searching for the correct output, whereas binary operations such as addition require that only the correct output is produced in response to specific inputs. Consequently, the addition operation requires a quite different model for the use of DNA in computing than that used previously for search procedures. As an approach to the development of a generally

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