Neutron Diffraction Study of the Structure of Deuterated Ice VIII to 10 GPa

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The pressure dependence of the structure of deuterated ice VIII has been studied by time-of-flight neutron powder diffraction up to 10 GPa. The precision of the values of the intramolecular bond length O-D is ±0.003 Å or better at all pressures, and the rate of increase of the O-D bond length is found to be 0.0004(4) Å GPa^{-1}. This value is significantly smaller than previous estimates, which all incorporate the assumption that the form of the O-H potential is constant with pressure. It appears that this is not the case.

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There has been a lively interest in the physics of ice ever since Bridgman first examined the phase diagram of water in 1912 [1]. An understanding of the properties, structures, and transitions of this fundamental molecular solid depends on a good modeling of the H bonds. The interatomic potentials can be probed by using pressure to alter the interatomic distances and several such studies have been carried out [2–5]. The principal structural variables are the overall O $\cdots$ O distance and the O-H bond length. Following recent technique developments [6–8], it is now possible to make a direct measurement of these distances by neutron diffraction, over a sufficient pressure range to determine their pressure dependence.

The phase diagram of ice has ten reported phases in the pressure range up to 2.1 GPa, but above this pressure only two phases, ices VII and VIII, are reported to exist up to at least 38 GPa [5,9]. These two phases have closely related structures [10–12]. At temperatures below 0 °C, ice VIII is formed. Its tetragonal structure has two interpenetrating hydrogen-bonded networks, in which the hydrogen atoms order antiferroelectrically (Fig. 1). The oppositely polarized networks are displaced relative to each other along the unique axis by a distance ϵ, as labeled in Fig. 1. The transition to ice VII, which is cubic, involves disordering this structure along the six cubic $\langle 100\rangle$ directions [12].

The structures of deuterated ices VII and VIII have been studied by both angle-dispersive and time-of-flight neutron powder diffraction in the low-pressure range (2.2–2.8 GPa) [10–12]. These studies did not attempt to examine the pressure dependence of the O-D bond length because of the limit of ≈ 3 GPa that has been generally applied to neutron-diffraction studies. This limit has meant that the only previous estimates of the change of O-H (or D) with pressure, $\partial[\text{O-H(D)}]/\partial P$, have been derived indirectly from measurements of either the change in the O-H(D) vibron frequency ν or the overall bond length O $\cdots$ O with pressure, using theoretical models based on some appropriate form of potential.

Klug and Whalley [4] found $\partial \ln(\nu)/\partial P$ to be $-7.3\times10^{-3}\ \mathrm{GPa}^{-1}$ in an infrared study of a dilute solid solution of $H_{0.04}D_{1.96}O$. From this value they calculated $\partial(\text{O-H})/\partial P$ to be 1.8×10^{-3} ÅGPa^{-1} over the range 2–19 GPa, based on a free-molecule potential and the assumption that the variation of ν with O-H is the same as in the isolated molecule. This assumption of a pressure-independent O-H potential was also adopted by Holzapfel [2] to estimate $\partial(\text{O-H})/\partial P$ from x-ray measurements

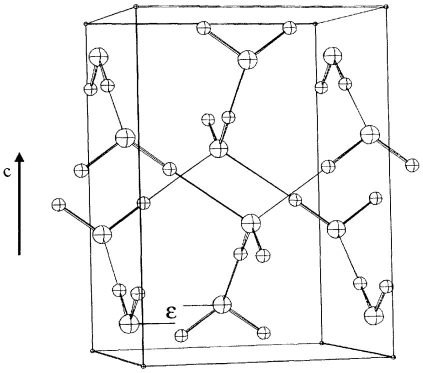

FIG. 1. The tetragonal structure of ice VIII. The separation ϵ between the two oxygen sublattices is shown and the direction of the c axis is marked. The thermal ellipsoids are not drawn to scale. Large spheres represent oxygen atoms and small spheres deuterium atoms.

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of $\partial(\mathrm{O}\cdots\mathrm{O})/\partial P$ [13]. In this case a double-Morse potential was used, with parameters derived from thermodynamic data on water and ice, and $\partial(\mathrm{O\text{-}H})/\partial P$ was found to be 2.5×10^{-3} Å GPa^{-1} over the range 2–10 GPa.

$\partial(\mathrm{O\text{-}H})/\partial P$ can also be obtained from the variation of $\mathrm{O}\cdots\mathrm{O}$ with pressure and an empirical relationship between O-H and $\mathrm{O}\cdots\mathrm{O}$ based on measurements made on many different materials at ambient pressure. Over the range 2–10 GPa, a value of 2.0×10^{-3} Å GPa^{-1} can be derived by direct measurement from the empirical relationship given in Ref. [14]. Matsushita and Matsubara [15] show that another similar set of empirical data can be well described by a double-Morse potential whose parameters are close to those used by Holzapfel [2], and their fit gives a value of 2.5×10^{-3} Å GPa^{-1} for $\partial(\mathrm{O\text{-}H})/\partial P$ over the 2–10 GPa range. Hence it can be seen that various methods of obtaining $\partial(\mathrm{O\text{-}H})/\partial P$ yield values that are self-consistent and lie around 2×10^{-3} Å GPa^{-1} [16]. All these estimates were derived for O-H but, because tunneling is not expected to play a role below 20 GPa [15], the similarity between O-H and O-D in vibrational properties under pressure [17,18] implies that the behavior of the O-D distance is not significantly different from that of O-H.

The models used to derive $\partial(\mathrm{O\text{-}H})/\partial P$ have also been the basis of estimates of the pressure of the transition to so-called "symmetric" ice X [2], where the hydrogen atom becomes equidistant from the two oxygen atoms. The potential models [2,15], and extrapolation of the behavior of ν as a function of $\mathrm{O}\cdots\mathrm{O}$ [3], suggest that this will occur for $\mathrm{O}\cdots\mathrm{O}$ in the range 2.35–2.41 Å, corresponding to a pressure range of 50–80 GPa. Hirsch and Holzapfel [5] observed the A_{1g} mode to disappear at 38 GPa and 100 K and attributed this to the formation of ice X. More recent Raman studies [18] have found no evidence for this transition and show that ice VIII is stable up to at least 51 GPa.

While there is good agreement between the various estimates of $\partial(\mathrm{O\text{-}H})/\partial P$, they are open to question because they are based on assumptions that cannot be justified *a priori*. It is not clear that the O-H potential can be treated as pressure independent [19], and there is no reason to suppose that O-H and $\mathrm{O}\cdots\mathrm{O}$ in ice under pressure will be related in the same way as they are in an average $\mathrm{O\text{-}H}\cdots\mathrm{O}$ bond under varying chemical environments at constant (ambient) pressure. There is thus a need for a direct determination of $\partial(\mathrm{O\text{-}H})/\partial P$ by neutron-diffraction techniques. Because of the O-site disorder found in ice VII [10], it is necessary to study ice VIII to obtain unambiguous results.

As part of a program to increase the maximum pressure available to neutron-diffraction techniques, we have developed a compact (50 kg) opposed-anvil cell (the Paris-Edinburgh cell) suitable for collecting time-of-flight powder-diffraction data at pressures in excess of 10 GPa on the POLARIS diffractometer of the United Kingdom pulsed neutron source ISIS—as described in detail in Refs. [6–8] and [20]. The sample volume (~100 mm^3) has a spheroidal shape—which minimizes pressure inhomogeneities within the sample—formed by the hole in a null-scattering TiZr alloy gasket (between the anvils) and central indentations in the anvil faces. The incident neutron beam passes through one of the anvils parallel to the axis of the cell, and the diffracted beam emerges through the gasket at a scattering angle (2θ) close to 90°. Neutron-absorbing collimation has been designed to eliminate scattering from the pressure-cell materials around the sample.

The sample was 99.8%-enriched D_2O obtained from EURISO-TOP (CEA) [21]. This was loaded as a liquid at room temperature [6,7] and the cell was then taken rapidly to a pressure in the 2.5–3 GPa range, well within the stability range of ice VII. The rapid pressurization and the volume change at the ice VI–ice VII boundary was found to give a good powder specimen. To study the ordered phase, ice VIII, the sample was cooled by passing a stream of cold nitrogen gas over the anvil and gasket assembly. This system enabled a stable sample temperature of 265 K to be achieved, as measured by a thermocouple on the gasket.

Preliminary studies showed that changing the pressure while the sample temperature was below 0 °C resulted in small variations of 5×10^{-3} in the c/a ratio from loading to loading. This was attributed to variable uniaxial stresses within the sample. It was found that the effect was reduced if the sample was warmed to ambient temperature for each pressure change and then cooled back into the ice VIII phase. (Thermal history effects have been reported in other phases of ice and it seems likely that in this case the small volume change at the ice VII/VIII transition [22] relieves the uniaxial stresses with the sample.) Spectra were collected in this way at eight applied loads between 65 and 135 metric tons and corrected for the effects of wavelength-dependent attenuation due to the anvil material (in this case tungsten carbide). This can vary by as much as a factor of 10 over the neutron wavelength range of interest (0.7–4 Å). The procedure used was based on the measured attenuation coefficient of the anvil material and calculations of the average path length, as described in Ref. [8].

The corrected spectra were analyzed by Rietveld profile refinement using the GSAS refinement package [23]. Ice VIII crystallizes in the tetragonal space group $I4_1/amd$ with the oxygen atom at $0, \frac{1}{4}, z$ and the deuterium atoms at $0,y,z$. Thus there are two lattice parameters and three fractional coordinates not fixed by symmetry. In addition, two isotropic thermal parameters, a background polynomial, four pseudo-Voigt peak-width parameters (which model the instrument-resolution, strain, and particle-size contributions to the peak width), and a sample-absorption parameter were also varied. An example of the resulting fits can be seen in Fig. 2.

Since no pressure calibrant was used, the pressure was

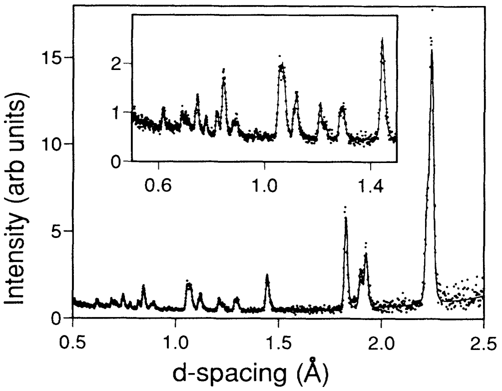

FIG. 2. A spectrum collected from a sample of ice VIII at 9.8 GPa in the Paris-Edinburgh cell. The dots represent the measured data while the solid line represents the results of a Rietveld profile refinement of the data. The inset shows the short d-spacing range enlarged.

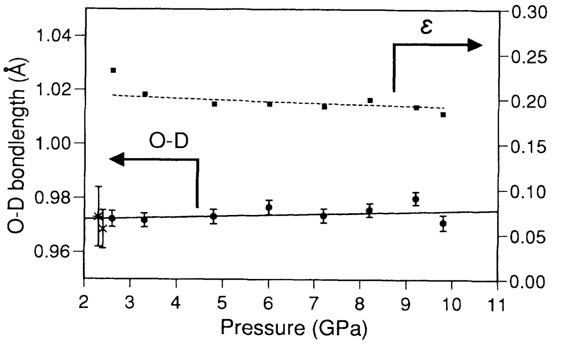

FIG. 3. The pressure dependence of the O-D bond length (circles; left-hand scale) and of the distance ϵ (squares; right-hand scale). The solid line shows a linear least-squares fit to the values of the O-D bond length with a gradient of 0.0004 Å GPa^{-1} and the dashed line shows the variation expected of ϵ if it compresses at the same rate as the c axis. The esd's on ϵ are comparable with the size of the symbols and have been omitted for clarity. The O-D values plotted as an asterisk and a cross represent the results obtained in previous studies [10,11].

calculated from the measured molar volume of ice VIII and the equation of state of H_2O ice VII given by Hemley *et al.* [24]. (The bulk moduli of D_2O and H_2O are known to be the same [25] and the fractional volume change at the VII/VIII transition is known to be less than 10^{-3} [22], so the change in bulk modulus at the transition will be small.) A correction was first made for the effect on the refined values of the lattice parameters caused by the (slight) displacement of the sample along the incident-beam direction as the cell deformed under applied load. And the molar volumes obtained from these lattice parameters were also corrected to take account of the temperature difference between these experiments and those of Hemley *et al.* [24] before deriving the sample pressures. These corrections were small, amounting to less than 0.1 GPa for sample movement and the same for thermal expansion, and the overall uncertainty in the pressure was estimated to be 0.2 GPa. The pressures thus obtained for the eight runs were 2.6, 3.3, 4.8, 6.0, 7.2, 8.2, 9.2, and 9.8 GPa.

Initial refinements were performed without any constraint but the results showed that the angle $\mathrm{D}\text{-}\hat{\mathrm{O}}\text{-}\mathrm{D}$ did not vary within an estimated standard deviation (esd) of 0.5°, and so it was constrained to a mean value of 106.5(5)° in the final refinements. This constraint did not significantly alter the quality of the fit. The values of O-D obtained (with $\mathrm{D}\text{-}\hat{\mathrm{O}}\text{-}\mathrm{D}$ constrained) are plotted in Fig. 3, which also includes the results of previous work in the low-pressure range [10,11]. The results of the present study are consistent with the earlier work, but the esd's are now 3–4 times smaller. This precision remains constant up to the maximum pressure of 9.8 GPa.

The solid line in Fig. 3 shows a linear least-squares fit to the O-D values, which gives a variation of only $0.4(4)\times10^{-3}$ Å GPa^{-1} [26]. The true variation of O-D with pressure is thus significantly smaller than any of the previous estimates ($\sim2\times10^{-3}$ Å GPa^{-1}) [2,4,15]. Contrary to the assumptions underlying these estimates, our results suggest that the principal effect of shortening O···O is to reduce the vibron frequency ν without significantly altering the O-H(D) distance. This indicates that the O-H potential is not pressure independent.

Our results also show that empirical relationships [14–16] between O···O and O-H(D) distances significantly overestimate the effect of pressure on O-D in ice VIII. The average changes in O-H with different chemical environments at constant (ambient) pressure are not the same as those caused by hydrostatic pressure in a single material—at least for the range of O···O studied (2.91–2.73 Å). In fact, the empirical relationships appear to correspond closely to the behavior predicted by a fixed O-H potential.

As we have seen, the estimates of 50–80 GPa for the pressure at which symmetric ice X is formed were also based on the models which give $\partial(\mathrm{O\text{-}H})/\partial P$ of the order of 2×10^{-3} Å GPa^{-1} and above [2,3,15]. Our results, showing a rate of change about 5 times smaller, suggest either that the true centering transition pressure is substantially higher (a simple scaling argument would imply a pressure well in excess of 100 GPa) and/or that, below the O···O range studied in the present work (i.e., less than 2.7 Å), the O-H distance increases more rapidly with decreasing O···O than in the ambient-pressure empirical relationship [14].

Finally, the pressure dependence of the separation between the two networks ϵ—which is expected to become zero in ice X [5]—merits a remark. It shows an initial change up to 4 GPa, which may be associated with the transition from ice VI at 2.1 GPa, and then remains a constant fraction of the c axis up to 10 GPa, as shown in Fig. 3. Because ice VII has a disordered form of the ice VIII structure [11,12], as already discussed, it seems probable that ϵ is related to the diameter δ of the sphere on which lie the six disordered oxygen sites observed in ice VII at 2.5 GPa [10]—certainly ϵ and δ (equivalent to $2r_{\mathrm{ox}}$ in Ref. [10]) have similar magnitudes of $\sim$0.2 Å at that pressure. It is known that this separation of the oxygen sites in ice VII causes the O-D distance to be anomalously short with respect to the mean O position at 2.5 GPa [10] by an amount proportional to δ. If ϵ and δ *are* related, the behavior now found for ϵ in ice VIII suggests that δ varies very little with pressure, and this is relevant to the geometry of centering because D would then remain anomalously close to the mean oxygen position with increasing pressure—even perhaps in ice X.

In summary, we have shown that the initial rate change of O-D with pressure in ice VIII is significantly smaller than had previously been obtained indirectly from optical and x-ray diffraction measurements, or from the empirical ambient-pressure relationship between O-H(D) and O $\cdots$ O distances; the principal effect of pressure up to (at least) 10 GPa appears to be to reduce the O-D force constants without changing the O-D bond length significantly. And it is possible that the pressure required to form "symmetric" ice is somewhat higher than has been estimated. These results illustrate the value of being able to carry out neutron-diffraction studies to pressures in excess of 10 GPa. The need to obtain precise determinations of interatomic distances involving low-Z atoms, over a large enough range of pressure to draw meaningful conclusions, is clearly not peculiar to ice, and the prospect is now opened up of gaining new insights into a whole range of simple molecular systems of importance for planetary physics and at the basis of fundamental physicochemistry.

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