

## Pressure dependence of hydrogen bonding in a novel $\text{H}_2\text{O}-\text{H}_2$ clathrate

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### Abstract

We have carried out Raman spectroscopy and X-ray diffraction to 60 GPa of the 1:1  $\text{H}_2\text{O}:\text{H}_2$  clathrate hydrate, which has water molecules in an arrangement similar to pure ices  $\text{I}_c$  and VII. The pressure dependence of both the  $\nu_{\text{O-H}}$  frequency and the intermolecular distance  $d_{\text{O-H}\dots\text{O}}$  is significantly larger than in pure ice: unexpectedly, both dependencies can be mapped onto those of pure ice by *doubling* the pressure. Nevertheless, the correlation between  $\nu_{\text{O-H}}$  and  $d_{\text{O-H}\dots\text{O}}$  is the same as in pure ice, making the clathrate a model system for ice at pressures reduced by a factor 2. Thus, the transition to a phase with symmetric hydrogen bonds probably occurs in the range 30–40 GPa, which is significantly lower than that for  $\text{H}_2\text{O}$ .

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### 1. Introduction

The structural and dynamical properties of hydrogen-bonded systems, especially water, are crucial to numerous problems in biology, chemistry, geology and physics [1]. Of particular interest is the behavior of the OH stretching mode  $\nu_{\text{O-H}}$  in response to the decreasing nearest neighbor intermolecular oxygen–oxygen distance  $d_{\text{O-H}\dots\text{O}}$ . The general correlation between  $\nu_{\text{O-H}}$  and  $d_{\text{O-H}\dots\text{O}}$  is well known and has been established on the basis of many different hydrogen-bonded compounds [2–4], see Fig. 1. The frequency  $\nu_{\text{O-H}}$  decreases with reducing  $d_{\text{O-H}\dots\text{O}}$  distance due to the increased attraction of the proton by the non-bonded oxygen ion, as shown in Fig. 1. The resulting frequency shift is small at large  $d_{\text{O-H}\dots\text{O}}$  beyond 2.9 Å, but clearly increases at distances below 2.9 Å. The frequencies as a function

of distance have been interpreted with simple empirical potentials (see Refs. [3–5]). Consequently, it is believed that the reduced frequency shift correlates with an increase of the hydrogen bond length  $d_{\text{O-H}}$  upon the approach of the non-bonded oxygen ion [5]. At  $d_{\text{O-H}\dots\text{O}}$  distances in the range 2.45–2.55 Å, the (originally) non-bonded ion has moved in closely and the hydrogen bond length  $d_{\text{O-H}}$  has stretched so that the proton occupies the midpoint between the oxygen ions and thus the hydrogen bond has become symmetric [4]. Indeed, the first compound observed to have a symmetric hydrogen bond is chromous acid ( $\text{HCrO}_2$ ) with a distance  $d_{\text{O-H}\dots\text{O}} = 2.49$  Å [6].

Application of external pressures allows continuous tuning of intermolecular distances and vibrational frequencies of a given compound, such as those containing hydrogen bonds. High pressure experiments have been done on the ices VII and VIII

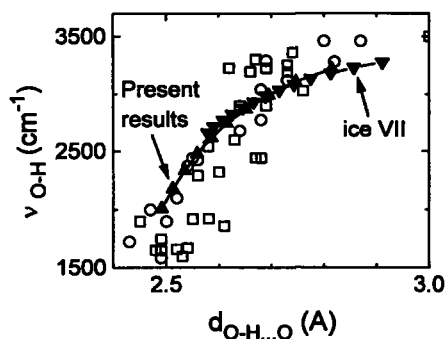


Fig. 1. Frequency of the O–H vibrational mode as a function of oxygen–oxygen distance  $d_{\text{O-H}\dots\text{O}}$ . The upward triangles are our results for the  $\text{C}_2$  clathrate and the downward triangles are for ice VII (data from Ref. [11]). The open circles are data for compounds at ambient pressure compiled by Pimentel and Sederholm [2], and the squares by Ratajczak and Orville-Thomas [3].

up to 50 GPa by Raman spectroscopy [7–9] and up to 128 GPa by X-ray diffraction [10,11]<sup>1</sup>. From the data, Pruzan [13] has compiled a similar correlation between  $\nu_{\text{O-H}}$  and  $d_{\text{O-H}\dots\text{O}}$  as mentioned above (see Fig. 1) down to about 2.5–2.6 Å. Neutron diffraction experiments [14,15], however, have revealed that the hydrogen bond length  $d_{\text{O-H}}$  is nearly pressure independent up to 10 GPa, contrary to the expectation based on the atmospheric pressure behavior. This result was reproduced in calculations by Ojamäe et al. [16] and Besson et al. [15], which confirms that early descriptions [17,18] in terms of empirical potentials are only qualitatively correct. Moreover, further analysis [13] suggests that the  $d_{\text{O-H}\dots\text{O}}$  distances at which the proton would occupy the center point of the hydrogen bond are considerably shorter than mentioned above: 2.29–2.37 Å. This corresponds to pressures in the range 80–100 GPa [9,13]. Experimental evidence for such a symmetrization transition in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  at 60–70 GPa has been obtained very recently by synchrotron infrared spectroscopy [19].

<sup>1</sup> Ice VII is the cubic high-temperature, high-pressure phase, that consists of two interpenetrating diamond lattices. The hydrogen bonds are not symmetric and the protons are randomly oriented along body diagonals. Ice VIII is the low-temperature tetragonal distortion of ice VII with the protons in antiferroelectrically ordered positions. See Ref. [12].

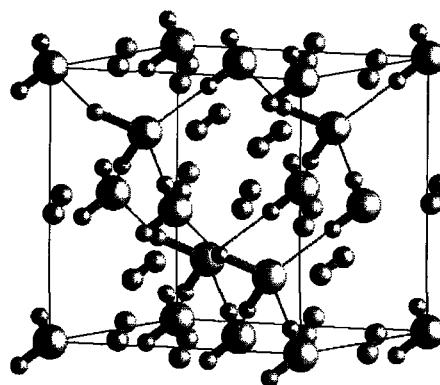


Fig. 2. Crystal structure of the  $\text{C}_2$  clathrate, obtained from single crystal X-ray diffraction data, see Ref. [20]. The origin of  $\text{Fd}3\text{m}$  is set at the 43m site. The  $\text{H}_2$  molecules are shown as light dumbbells in two orientations; however, due to the quantum nature of their rotations, they have an approximately spherical charge distribution. Similarly, the protons (small dark spheres) associated with  $\text{H}_2\text{O}$  are shown in ordered positions; however, X-ray data indicate that are disordered over two of the four possible positions that are tetrahedrally located  $\approx 1$  Å from the oxygen ions (large dark spheres). The hydrogen bonds between different water molecules are indicated as thin dark lines.

We have reported two novel hydrogen–water compounds (clathrate hydrates)  $\text{C}_1$  and  $\text{C}_2$ , the second of which has an unusual stoichiometry near 1 : 1 [20,21]. The  $\text{C}_2$  compound is stable beyond 2.3 GPa at room temperature and it consists of two interpenetrating diamond lattices, one for  $\text{H}_2\text{O}$  and one for  $\text{H}_2$ , see Fig. 2. It can thus be regarded either as ice VII [12] with one  $\text{H}_2\text{O}$  sublattice replaced by  $\text{H}_2$ , or as the metastable low temperature ice  $\text{I}_c$  in which the interstitials have been filled up with  $\text{H}_2$ . We find that the pressure dependencies of  $\nu_{\text{O-H}}$  and  $d_{\text{O-H}\dots\text{O}}$  are in excellent agreement with those of ice VII, if the pressure is scaled *down* by a factor of two. Moreover, the relation between  $\nu_{\text{O-H}}$  and  $d_{\text{O-H}\dots\text{O}}$  is very similar for both  $\text{C}_2$  and pure ice VII, hence we propose that  $\text{C}_2$  can be regarded as a model system for ice VII at half the pressure. In particular, the  $\text{C}_2$  phase is a prime candidate to study symmetric hydrogen bonds in water-bearing materials.

## 2. Experimental

Nine different compositions of  $\text{H}_2$  and  $\text{H}_2\text{O}$ , including one with  $\text{D}_2\text{O}$ , were studied with Mao-Bell

single crystal and megabar diamond anvil cells [22], with T301 and BeCu gaskets. The experimental techniques are described in Refs. [20,21,23,24]. The variations in pressure are about 0.2 GPa below 10 GPa increasing to 3 GPa at the highest pressures of 60 GPa. The accuracy in composition is about 5–10 mol%. All experiments were performed at room temperature ( $295 \pm 5$  K). The samples were probed by several techniques. X-ray diffraction was done on the polychromatic synchrotron beam line X17C at NLSL, Brookhaven [25]. Raman spectra were measured with an Ar laser, a Dilor triple spectrometer and a CCD detector. In addition, visual observations were performed with a high magnification microscope and recorded on video tape.

### 3. Results

Because of the cubic symmetry of  $C_2$  (see Fig. 2), the  $d_{O-H...O}$  distance in the compound is given directly by the lattice parameter  $a$  as:  $d_{O-H...O} = \frac{1}{4}\sqrt{3}a$ . The pressure dependence of  $d_{O-H...O}$  obtained from X-ray diffraction is shown in Fig. 3. The intermolecular distance decreases strongly with pressure, from about 2.8 Å to less than 2.3 Å at 60 GPa. No systematic difference is observed in the experiment with  $D_2O$ , in agreement with earlier findings for ice VII [26]. The solid curve is a weighted fit with the Birch–Murnaghan equation [27] to volume versus pressure, with zero pressure volume  $304 \text{ Å}^3$ , bulk modulus 15.6(2) GPa, and the derivative of the bulk modulus 4.3(6). Although the value of  $d_{O-H...O}$  for  $C_2$  and ice VII start out at the same value at low pressure, the one of  $C_2$  decreases much more rapidly and is more than 0.1 Å shorter at 60 GPa. The scatter in the data increases beyond 30 GPa. There are indications that structural changes may take place beyond 30–35 GPa in the  $C_2$  phase: in several of the runs we observed a splitting of the 220 diffraction lines, which suggests a distortion of the cubic structure.

The Raman spectrum of the  $C_2$  phase in the region of the O–H stretching modes reveals a strong band [20]. On the basis of polarization measurements, we assign the strong band at  $3200 \text{ cm}^{-1}$  ( $2350 \text{ cm}^{-1}$  for O–D, see Fig. 4) to the symmetric

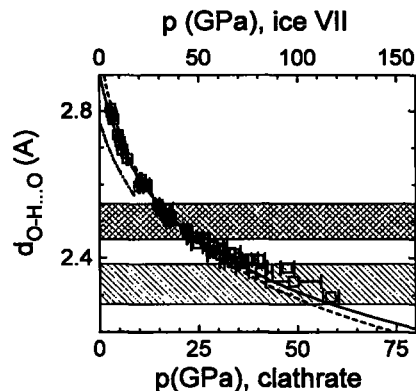


Fig. 3. Oxygen–oxygen distance  $d_{O-H...O}$  as a function of pressure. The squares are our experimental X-ray diffraction data for  $C_2$ . The solid curve is a fit with the Birch–Murnaghan equation [27] to volume versus pressure, with parameters  $V_0 = 304 \text{ Å}^3$ ,  $K_0 = 15.6(2)$  GPa, and  $K'_0 = 4.3(6)$ . The dashed curve is the equation of state for ice VII of Hemley et al. [10] up to 128 GPa. The dashed-dotted curve is a theoretical result for  $C_2$  by Xu and Ching [30]. The cross-hatched horizontal bar indicates the range of  $d_{O-H...O}$  distances at symmetrization of Pimentel and McClelland [4], and the hatched horizontal bar indicates the prediction for ice VII (Refs. [9,13]).

vibrational mode ( $\nu_1$ ) of A symmetry. Because the shape of the spectrum is similar to ice VII and VIII, the shoulders are likely O–H stretching vibrations of different symmetry. At about 13 GPa, the O–H mode overlaps with the two-phonon region of the diamond windows, which form a broad band around  $2500 \text{ cm}^{-1}$ . It was expected that  $\nu_{O-H}$  would be

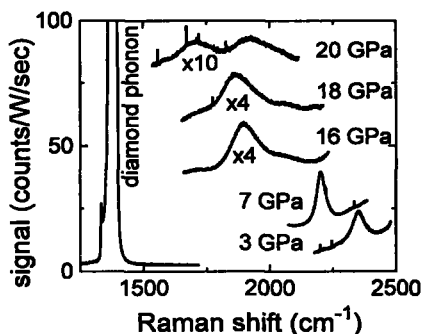


Fig. 4. Raman spectra of the O–D vibrations of the  $C_2$  clathrate at several pressures. The data have been normalized to the counting time and incident laser power. The spectra at 16 and 18 GPa have been multiplied by 4 and the one at 20 GPa by 10 and shifted upwards for clarity. The strong band at  $1400 \text{ cm}^{-1}$  that reaches to about 1000 counts/W s is the diamond one-phonon band.

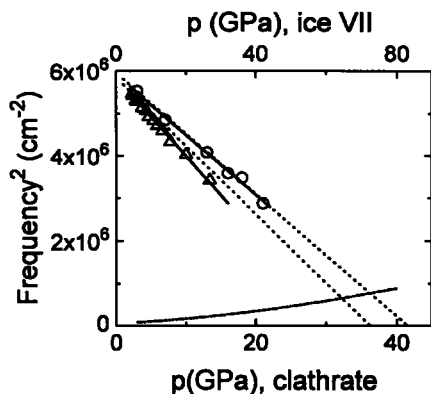


Fig. 5. Squared vibrational frequencies as a function of pressure. The circles indicate the O–D modes of the  $C_2$  clathrate. The O–H modes (frequency<sup>2</sup>/1.374<sup>2</sup>) are indicated with triangles. The drawn lines are linear fits ( $\nu_{O-D}^2(\text{cm}^{-2}) = 5.91(8) \times 10^6 - 1.42(5) \times 10^6 p(\text{GPa})$  and  $\nu_{O-H}^2(\text{cm}^{-2}) = 1.104(38) \times 10^7 - 3.51(6) \times 10^6 p(\text{GPa})$ ). The dashed-dotted curve indicates the translational lattice modes of the  $C_2$  clathrate. The dotted curves are the squared O–D and O–H (divided by 1.374) frequencies of ice VII by Pruzan et al. [8,9,13], which have been extrapolated. Note that the O–D modes frequency of ice VIII by Hirsch and Holzapfel [7] (not indicated) are in good agreement with the data of Pruzan et al.

observed again at higher pressures, however, we were unable to detect it. A similar decrease of intensity has been observed for ice VII and VIII [7,8]. Although this may arise from increased stress gradients in the sample, there is also a significant decrease in Raman cross section, possibly due to charge transfer from the H ions to the O ions [28]. The squared frequency of the O–H mode as a function of pressure is plotted in Fig. 5. It strongly decreases with pressure as expected for a hydrogen-bonded system. It is interesting to note that the frequency decreases at a much faster rate with pressure in the  $C_2$  phase than in ice VII or VIII [7–9].

In order to follow the stretching vibrations to higher pressure, measurements were performed on the clathrate formed from  $D_2O$ , because the O–D mode has a much lower frequency ( $\nu_{O-D} \approx \nu_{O-H}/1.374$ ), and hence the two-phonon band of the diamond windows is avoided. The high-frequency O–D Raman band of the  $C_2$  phase ( $D_2O-H_2$ ) was followed to about 20 GPa pressure (Fig. 4). The band weakens continuously and was not observed

beyond this pressure. Moreover, the frequency reaches the range of the one-phonon band of the diamond windows, which is much stronger than the O–D mode. The  $\nu_{O-D}$  frequency shift with pressure of the  $C_2$  phase is shown in Fig. 5. It also strongly decreases with pressure similar to the O–H mode, yet at a slightly lower rate.

In Fig. 4, it is seen that a second peak develops at  $\approx 20$  GPa, indicating a possible change in the hydrogen bond. No concomitant change was observed in the X-ray diffraction experiments, which probe the oxygen sublattice.

#### 4. Discussion

In Fig. 3, we compare the  $d_{O-H...O}$  distance of the  $C_2$  phase to that of pure ice VII (dashed curve). For ice VII, the X-ray diffraction results of Hemley et al. [10], Fei et al. [11], and results obtained in the present experiment are all in excellent mutual agreement. Interestingly, the curves for the two materials match if the pressure scale for ice VII is reduced by a factor of two. A simple interpretation is that the external pressure is taken up by only one  $H_2O$  sublattice in  $C_2$  phase compared to two in pure ice VII (compare Fig. 2). This implies that the  $H_2-H_2$  and  $H_2O-H_2$  interactions contribute only little to the pressure. This is not unreasonable for the  $H_2-H_2$  interaction, because the distance between the  $H_2$  molecules is much larger than in pure  $H_2$  at the same pressure [29]. For the  $H_2O-H_2$  interaction, we propose that it contributes little because the different species are not nearest neighbors. The dash-dotted curve in Fig. 3 indicates a theoretical calculation by Xu and Ching [30]. It is systematically offset to lower  $d_{O-H...O}$  distance by about 0.1 Å and the theoretical bulk modulus is about 50% higher.

There are several possible explanations for the structural distortions that appear near 30–35 GPa. They can be ascribed to increased pressure gradients of the stiffening  $C_2$  structure, which could explain the increased scatter in the data points in Fig. 3. Another possibility is that the crystal structure distorts away from cubic symmetry. To investigate this in greater detail, experiments should be done on samples with excess hydrogen, which could then act as a hydrostatic cushion for the  $C_2$  compound.

The squared frequency of the O–D mode as a function of pressure is plotted in Fig. 5 as open circles and compared to the results for ices VII and VIII (dotted line, Refs. [7–9]). Again the data of both the  $C_2$  phase and the pure ices are in close correspondence, if the pressure scale for ices VII and VIII is reduced by a factor of two. In Fig. 5, we also compare the squared frequencies of the O–H mode divided by the ratio of reduced masses (1.374) to that of the O–D mode. The two data agree well at low pressure, but at higher pressure, the O–H mode has a smaller frequency than the O–D mode at the same pressure and correspondingly same  $d_{O-H...O}$  distance. This observation can probably be explained by the lighter mass of the proton compared to the deuteron causing its energy levels to be higher in the potential well. As a result, protons will tunnel at a faster rate between the double well in the potential and thus experience effectively a higher anharmonicity. This notion has been invoked to explain the Raman data on ice VII [9,13]. Moreover, at the higher energy levels, the protons will experience more of the anharmonicity associated with the shape of potential well.

From the compressibility (Fig. 3) and the frequency shifts with pressure (Fig. 5), the correlation between the O–H frequency and the  $d_{O-H...O}$  distance can be determined. In Fig. 1, we compare the results for the  $C_2$  phase to those of ice VII [11]. There is excellent agreement for both phases in the region of overlap. This indicates that the O–H frequency shift is only determined by the sublattice in which the  $H_2O$  molecules are located, and not by another non-hydrogen-bonded sublattice (consisting of  $H_2O$  molecules in the case of ice VII and  $H_2$  in the case of  $C_2$ ), which seems at variance with a recent theoretical study [31]. Apparently, the main contribution to the shift is caused by forces along the hydrogen bond, which is exactly the direction of the nearest neighbors in a diamond structure (distance:  $1/2$  times  $\frac{1}{4}\sqrt{3}a$ , see Fig. 2); forces in other directions have less influence, because they are associated with molecules which are at a distance  $\frac{1}{4}\sqrt{3}a$  from the protons. This is in agreement with the observation mentioned earlier that the scaled pressure dependencies of the  $d_{O-H...O}$  distance are the same for both the  $C_2$  phase and ice VII. Therefore, we conclude that it is meaningful to compare the properties

of  $H_2O$  molecules in  $C_2$  with pure ice VII. Thus, with respect to the hydrogen-bonded lattice, the properties of  $C_2$  at a given pressure are a model system for  $H_2O$  at approximately twice that pressure. In addition, the relation between  $\nu_{O-H}$  and  $d_{O-H...O}$  for different chemical compounds [2–4] is in qualitative agreement with the present results. This is not surprising, because this relation was obtained from data on different chemical compounds at ambient pressure whereas the present data are from one compound at different pressures. Moreover, the relation of Refs. [3–5] was determined from infrared (IR) frequencies, whereas the present data are of Raman modes, which are in general associated with different force constants.

The covalent hydrogen bond would no longer exist at a symmetrization transition, therefore, the O–H (or O–D) stretch mode should behave as a soft mode with a frequency  $\nu$  that varies as  $\nu^2 \propto (p - p_c)$  [32]. As shown in Fig. 5, the squared frequency of the O–D stretch mode has a linear dependence on pressure (solid line), that is consistent with soft-mode behavior. If the symmetrization transition is assumed to occur at the pressure where the vibrational frequency tends to zero, a value of about 40 GPa is obtained. We also compare the pressure dependence of the translational lattice modes [20]. If symmetrization is assumed to occur when the O–D frequency reaches that of the lattice modes, the transition pressure is reduced to about 36 GPa. The dashed curve in Fig. 5 is the dependence for O–D in pure ice of Pruzan [13]. As mentioned above, it closely tracks the dependence of the  $C_2$  phase if the pressure for ice is scaled down by a factor of two. Thus, it can be seen that the extrapolation to zero frequency occurs at double the pressure ( $\approx 80$  GPa) for ice VII [13].

Similar behavior is seen in Fig. 5 for the O–H mode of the protonated  $C_2$  phase: the squared frequency also follows a linear pressure dependence. Due to the increasingly lower frequency of the O–H mode compared to the O–D mode, it tends to zero or to the frequency of the translational modes at a lower pressure than for the deuterated  $C_2$  phase. This is consistent with the prediction of Pruzan et al. [13] for ice VII, and the recent observations of Goncharov et al. [19]. It is also consistent with the observation at ambient pressure that  $HCrO_2$  has a symmetric hydrogen bond, in contrast to the deuterated compound

$\text{DCrO}_2$ , which does not [6]. It is expected that  $\text{DCrO}_2$  will symmetrize at high pressure.

It is possible that changes arise in the hydrogen-bonded network as signalled by the second peak that develops in the Raman spectrum near  $\approx 20$  GPa. We do not believe, however, that this is a symmetrization transition, because the O–D vibration frequency is far from degenerate with the lattice mode frequencies, and because the Raman cross section should be zero for protons in a centrosymmetric position between the oxygen ions, assuming an ideal (symmetric) structure. On the other hand, a transition at 20 GPa to a structure with lower symmetry cannot be ruled out.

## 5. Conclusions

X-ray diffraction and Raman experiments on the 1:1  $\text{H}_2\text{O}:\text{H}_2$  clathrate hydrate up to 60 GPa pressure reveal that the pressure dependence of both the intermolecular distance  $d_{\text{O-H}\dots\text{O}}$  and the  $\nu_{\text{O-H}}$  frequency is significantly larger than in pure ice. It appears that both relationships are in close agreement with those of ice VII at twice the pressure. Interestingly, the correlation between  $\nu_{\text{O-H}}$  and  $d_{\text{O-H}\dots\text{O}}$  is very similar, which suggests that  $\nu_{\text{O-H}}$  is mainly determined by nearest neighbor interactions within a hydrogen-bonded network. Moreover, it indicates that the clathrate serves as a model system for ice at pressures reduced by a factor of 2.

From the  $d_{\text{O-H}\dots\text{O}}$  distance (cf. Fig. 3), we infer that the transition to a phase with symmetric hydrogen bonds takes place between 20 and 50 GPa. The O–H vibrational frequency extrapolates to the region of the translational lattice modes or to zero frequency, indicating a hydrogen bond symmetrization transition near 32 GPa for the protonated clathrate and near 40 GPa for the deuterated clathrate. A change is observed in the vibrational spectrum near 20 GPa; however, this is not thought to be a symmetrization transition. Beyond 30 GPa, structural changes may appear in the oxygen sublattice. It is thus possible that the transition to a state with symmetric hydrogen bonds is more complex than previously thought. Therefore, additional evidence should be obtained from IR spectroscopy and from diffraction experiments that are sensitive to the positions of

the protons, using the newly developed synchrotron or neutron sources.

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