Novel H$_2$-H$_2$O Clathrates at High Pressures

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High-pressure optical and x-ray studies of H$_2$-H$_2$O mixtures have revealed the formation of the first hydrogen clathrate hydrates. A rhombohedral hydrate with a H$_2$O sublattice similar to ice II and a H$_2$-H$_2$O ratio of 1:6 is stable between 0.75 and 3.1 GPa (295 K). Above 2.3 GPa, a novel hydrate forms with the H$_2$O molecules in a cubic diamond structure and with a very high H$_2$-H$_2$O stoichiometry of 1:1. The H$_2$ molecules occupy voids in the H$_2$O framework, thus improving the packing efficiency and stabilizing this hydrate to very high pressures of at least 30 GPa.

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The properties of hydrogen and water at high pressures are of fundamental interest to condensed matter physics and chemistry as well as planetary astronomy [1-5]. Despite this importance, the behavior of mixtures of these components has remained unknown at pressures above 0.25 GPa [6]. Whereas mixtures of water and other molecules (such as Ar, Kr, Xe, N$_2$, CH$_4$, etc.) have a strong tendency to undergo phase separation in the fluid phase [6], they often form solid compounds at low temperature and ambient pressure called clathrate hydrates. These are hydrogen bonded networks of water molecules that form cages in which the other, guest, molecules are contained by van der Waals forces (see, e.g., [7]). The total amount of guest molecules relative to water is less than 1:5 $\frac{2}{3}$ [7]. Two cubic clathrate structures have been known for a long time; they have water sublattices that differ from any of the known ice phases [8]. Because these frameworks have cages that are much larger than small molecules such as hydrogen, such hydrogen-water compounds have never been observed [7]. A recent neutron diffraction study at 0.5 GPa, however, revealed a rhombohedral helium clathrate with a novel H$_2$O structure related to ice II with much smaller cages [9]. It is therefore vital to investigate whether hydrogen forms similar small-cage clathrates at high pressures.

Clathrate hydrates are expected to break down at moderate pressures on the order of several GPa, because the compression of the pure gaseous guest species will outweigh the less effective packing of the clathrate phase in the free energy balance at higher pressure [7]. Indeed, a stability limit of 1.8 GPa was recently found in a cubic N$_2$ clathrate [10]. The ice-II type small-cage clathrate was only studied up to 0.5 GPa [9]. Therefore, it is important to assess the high-pressure stability limits of such a clathrate and investigate whether at higher pressure new types of clathrates occur.

In this Letter, we describe the formation of two new compounds (denoted C$_1$ and C$_2$) of hydrogen and water at high pressures. The H$_2$O sublattice of C$_1$ is similar to the ice phase II, thus closely resembling the small-cage helium clathrate [9]. At higher pressures, C$_1$ becomes unstable, and a novel type of clathrate, C$_2$, forms. The H$_2$O sublattice of C$_2$ has a diamondlike structure, similar to the ambient-pressure metastable ice phase I$_c$, whereas the hydrogen molecules occupy voids in the open H$_2$O framework, thus forming a stoichiometric compound with a very high H$_2$-H$_2$O stoichiometry close to 1:1 (see Fig. 1). Interestingly, the structure of the C$_2$ phase is also related to that of the high-pressure ice phase VII which is formed of two separate ice I$_c$-like hydrogen-bonded sublattices, that are interpenetrating but not cross linked [8]; the C$_2$ phase can be viewed as an ice VII structure in which one H$_2$O sublattice is completely replaced by H$_2$.

Figure 1. Structure of the new cubic clathrate (C$_2$ phase). The origin of Fd$_3$m is set at the 43m site. The H$_2$ molecules are shown as light dumbbells in two orientations; however, due to their quantum nature they have an approximately spherical charge distribution. Similarly, the protons (small dark spheres) associated with H$_2$O are shown in ordered positions; however, x-ray data indicate they are disordered over two of the four possible positions that are tetrahedrally located $\sim 1$ Å from the oxygen ions (large dark spheres). The hydrogen bonds between different water molecules are indicated as thin dark lines.
avoid reaction with H$_2$ [12]. The samples were loaded by filling the gasket hole with doubly distilled and de-ionized water and an air bubble. The cell was then placed in a gas loading vessel, in which the air in the bubble was purged and replaced by ultrapure (99.9999%) H$_2$ gas at about 0.2 GPa pressure. The compositions were estimated from the visual appearance of the sizes of the two fluid phases at low pressure—identified by Raman spectroscopy and visual observations—and the known molar volumes of the pure components [13,14]. The accuracy of 5–10 mol% is mainly limited by the estimates of the sizes of the phases. Hereafter, we express compositions in mol % H$_2$. The sample compositions studied were 27%, 29%, 43%, < 48%, and 63%. The experiments were done with increasing load, because during decompressing the most volatile phase may preferentially leak out; after decompression of the 63% sample less than 48% H$_2$ was found [15]. Pressures were determined by the linear ruby fluorescence method [16]. The temperature correction to the ruby scale was taken from Ref. [17] and the accuracy of the pressure is estimated as 0.2 GPa. Temperatures were measured with thermocouples and are accurate to about 5 K. Raman spectroscopy was performed using various Ar$^+$ laser lines for excitation and a Dilor XY triple spectrometer equipped with an l-N$_2$ cooled charge coupled device detector. X-ray diffraction experiments were done on the polychromatic synchrotron beam line X17C of NSLS, Brookhaven National Laboratory. Single crystal x-ray diffraction experiments were also performed using a four-circle diffractometer with monochromatic Mo K$_\alpha$ radiation. All x-ray diffraction experiments were done at 295(± 3) K.

The results of a detailed study of the phase equilibrium in this system at 290–450 K and 0.7–3.2 GPa are shown in Fig. 2, along with the established phase diagram of H$_2$O [18]. The bold curves are three-phase lines involving a H$_2$O-rich fluid phase $F_1$, a H$_2$-rich fluid phase $F_2$, and three crystalline phases, $C_1$, $C_2$, and ice VII. Quadruple points are indicated by large circles. At 0.75 GPa and room temperature, microscopy revealed that birefringent $C_1$ is in equilibrium with $F_1$ and $F_2$. To investigate the structure of the $C_1$ phase, in situ polycrystalline x-ray diffraction measurements were performed at 1.6 and 2.1 GPa with the 63% sample. An example of a diffraction pattern at 2$\theta$ = 8° is shown in Fig. 3. Several patterns at different scattering angles yielded a total of 24 diffraction lines that could be indexed to a hexagonal unit cell with $a = 12.736(2)$ Å and $c = 5.968(2)$ Å at 2.1 GPa. The reflections fulfill the condition $-h+k+l = 3n$ (n is an integer) of rhombohedral structures (Fig. 3). Notably, this structure is distinct from that of the stable phase of pure H$_2$O in the same pressure range (ice VI), which is tetragonal with $a = 6.3$ Å and $c = 5.8$ Å [8]. A subsequent monochromatic x-ray experiment at 1.7 GPa on a single crystal that was carefully grown from the melt confirmed the rhombohedral space group $R\overline{3}$. Refinement with a structure containing 36 water molecules resulted in $R = 0.24$ and $R_w = 0.13$ [19,20]. The H$_2$O sub-lattice is similar to the structure of ice II, and it has six cages per unit cell [8]. Therefore, this new hydrogen

FIG. 2. $P$-$T$ phase diagram of pure water (thin lines) and $P$-$T$ projection of the phase diagram of hydrogen water (symbols and heavy lines). For pure water, only the stable phase lines have been taken from Ref. [8]. The open circles indicate the $F_1+C_1+F_2$ three-phase line, the open squares $C_1+C_2+F_3$, the triangles $F_1+C_2+F_3$, the diamonds VII + $C_1+C_2$, and the crossed squares VII + $F_1+C_2$. The large filled circles indicate the quadruple points $F_1+C_1+C_2+F_3$ and VII + $F_1+C_1+C_2$. The metastable extension of the $F_1+C_1+F_2$ line has been observed below the quadruple point (dashed curve).

FIG. 3. Energy dispersive diffraction pattern of the $C_1$ phase at 2.1 GPa in the 63% sample at 2$\theta$ = 7.990°. The upper scale is calculated from the lower one using $E_d = 88.977$ keV Å. The diffraction lines are indicated by their indices. Other features are not associated with $C_1$, because they did not reproduce in patterns taken at 2$\theta$ = 7.5°, 10°, and 15°. Note that the crystal grains are large compared to the x-ray beam; therefore the intensities cannot be used for structure refinement.
clathrate has a structure similar to the small-cage helium clathrate observed by Londono, Kuhls, and Finney [9].

The Raman spectrum of the C1 phase (Fig. 4) reveals sharp lattice translational modes \( (v_T) \), indicative of an ordered proton structure as in ice II [21]; however, the O-H stretch frequency of 3130 cm\(^{-1} \) is close to that of ice VI, which is surprising in view of the structural differences. The \( \text{H}_2 \) molecules were not observable with x-ray diffraction due to their low scattering cross section, but were clearly observed on the basis of a sharp \( \text{H}_2 \) vibron \( (Q_1) \) and two rotons \( S_0(J) \) in the Raman spectrum. The vibron frequency is only 1 to 2 cm\(^{-1} \) higher than that of pure hydrogen [22]. The \( \text{H}_2 \) content of the solid phase was estimated to be between 10–20 mol% from the intensities of the vibron and roton bands, relative to those in the \( \text{H}_2 \)-rich fluid phase when it was spatially well separated from the C1 crystals. This is consistent with the structure described above, that corresponds to a \( \text{H}_2: \text{H}_2\text{O} \) molar ratio of 1:6.

At 2.3 GPa, visual observations of the 43% and 63% samples revealed that the solid phase C1 and the fluid phase \( F_2 \) are in equilibrium with a newly optically isotropic solid phase \( C_2 \) on the \( C_1 + C_2 + F_2 \) three-phase line (see Fig. 2). The two phases \( C_1 \) and \( C_2 \) coexist between 2.3 and 3.1 GPa because \( \text{H}_2+\text{H}_2\text{O} \) is a binary system. Polycrystalline x-ray diffraction of the 63% sample showed that the \( C_2 \) phase is cubic, with a lattice parameter \( a = 6.434(1) \text{ Å} \) at 3.1 GPa (see Table 1), which is a little less than the equivalent lattice parameter of ice VII \( (2 \times 3.330) \text{ Å} \) [2]. Similar experiments on the 29% sample revealed that \( C_2 \) is stable to at least 30 GPa. A monochromatic x-ray experiment at 2.8 GPa on a single crystal that was carefully grown from the fluid phases showed systematic extinctions that are consistent with space group \( Fd3m \). Refinement yielded a structure with eight water molecules arranged on a diamond structure (Fig. 1), as in ice I \(_d \) [8]. The unit cell volume of \( C_2 \) is much larger than that of ice I \(_d \) extrapolated to the same pressure [8], indicating that there are additional hydrogen molecules in the structure. The locations of the \( \text{H}_2 \) molecules were found in different electron density maps due to the higher quality intensities than were obtained with the \( C_1 \) phase \( (R=0.054 \text{ and } R_e=0.034) \) [20]. The molecules occupy the voids between the \( \text{H}_2\text{O} \) molecules that also form a diamond structure (Fig. 1).

The composition of the \( C_2 \) phase was estimated in two experiments. With the \((43 \pm 10) \text{ mol}\% \text{H}_2 \) sample, we observed only the \( C_2 \) phase and no evidence of phase separation between 2.3 and 6.8 GPa at room temperature; hence this represents the composition of \( C_2 \). Raman spectroscopy of the OH stretching modes with the \(< 48\% \) sample revealed that the \( C_2 \) phase was in equilibrium with ice VII at pressures beyond 3 GPa at room temperature, indicating that the composition of \( C_2 \) is larger than the sample composition. Therefore we conclude that \( \text{H}_2: \text{H}_2\text{O} \) stoichiometry is close to 1:1. The result is in agreement with the above structural assignment with all voids in the \( \text{H}_2\text{O} \) framework filled by \( \text{H}_2 \), as expected for a close-packed structure at high pressure.

Further information on the \( \text{H}_2 \) molecules in the \( C_2 \) phase was obtained from Raman measurements (Fig. 4). The vibron is on the order of 5–10 times more intense than in the \( C_1 \) phase, indicating that the \( C_2 \) phase is rich in hydrogen. The frequency is about 10 to 20 cm\(^{-1} \) higher than in pure \( \text{H}_2 \) [22], and increases with pressure. The linewidth of the vibron is narrower than the \( \text{H}_2 \)-rich fluid phase, which is consistent with the centers of mass of the molecules being localized. The rotons are also very intense, significantly stronger than the lattice translational modes \( (v_T) \), and are very close to those observed for the fluid. This result indicates that \( J \) is still a good rotational quantum number for \( \text{H}_2 \) in the clathrate.

In Fig. 4, the Raman shift of the O-H stretch mode in the \( C_2 \) phase at 2.3 GPa is 3210 cm\(^{-1} \) which is clearly

![Figure 4: Raman spectra of the C1 phase (upper panels) and C2 phase (lower panels) at 2.3 GPa. The upper and the lower central spectra were recorded in the 63% sample, and the remaining ones in the 43% sample. Translational lattice modes (v_T) are indicated with ticks, H_2 rotons by S_0(J), the O-H stretching vibration by v_OH, and the H_2 stretching vibration by Q_1.](image)

**Table 1.** Observed and calculated \( d \) spacings of reflections for the cubic \( C_2 \) phase observed at 3.1 GPa. The lattice parameter is \( a = 6.434(1) \text{ Å} \).

<table>
<thead>
<tr>
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<th>( d ) obs. (Å)*</th>
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<td>422</td>
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*The uncertainty is approximately 0.1%.
smaller than the value of 3290 cm\(^{-1}\) of ice VII at the same pressure [23]. The reduced O-H···O distance is the result of a reduced O-H···O distance: According to the x-ray diffraction measurements, the O-H···O distance is clearly smaller in the C\(_2\) phase compared to ice VII (2.79 vs 2.89 Å) [8]. When the frequencies of the two phases are compared at the same O-H···O distance instead of the same pressure, however, they are identical.

Microscopy, Raman, and x-ray observations were used to determine the P-T phase diagram (see Fig. 2). Two invariant quadruple points, \(F_1 + C_1 + C_2 + F_2\) at 387 K and 2.55 GPa and \(VII + C_1 + C_2 + F_2\) at 396 K and 2.85 GPa, were located. The first point is defined at the intersection of three experimentally observed univariant curves: the melting curve of \(C_1\) \((F_1 + C_1 + F_2)\), the first appearance of \(C_2\) \((C_1 + C_2 + F_2)\), and the melting curve of \(C_2\) \((F_1 + C_2 + F_2)\). The second point is defined by two univariant curves: the breakdown curve of \(C_1\) into ice VII and \(C_2\) \((VII + C_1 + C_2)\) and the eutectic curve of \(VII + F_1 + C_2\). The two points are connected by the univariant curve \(C_1 + C_2 + F_1\). The last univariant related to the two points, \(VII + F_1 + C_1\), can only be measured with compositions smaller than \(C_1\) (14 mol\%) and has not been determined. For more details, see Ref. [18].

In conclusion, we have for the first time studied a molecular mixture containing water to high pressures in excess of 2 GPa and observed two new hydrogen hydrates \(C_1\) and \(C_2\). The discovery of \(C_1\) and the result of Ref. [9] suggest that this structure is favorable for small molecules. The upper stability limit of 3.1 GPa agrees qualitatively with the prediction of Ref. [7] and it indicates that the cage-like structures have a stability range limited to moderate pressures. We have identified a clathrate transition sequence from \(C_1\) to a new type, \(C_2\), that is stable to ultrahigh pressures. It consists of two interpenetrating diamondlike sublattices, one for the \(H_2\)O host molecules and one for the \(H_2\) guests. This structure can accommodate small guest molecules (or medium-size molecules becoming small at high compression) with a high packing efficiency, thus being a favorable structure at high pressures. It should be investigated whether other small molecules such as helium and neon show a similar transition sequence. Finally, because both \(C_1\) and \(C_2\) have higher melting temperatures than the pure ices at the same pressure (see Fig. 2), clathrates are expected to be of considerable importance to planetary interior layers of \(H_2\)-He and ices where high pressures and temperatures prevail.

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[15] A similar effect has been reported earlier in the system \(N_2-He\); see W. L. Vos and J. A. Schouten [Physica (Amsterdam) 182A, 365 (1991)]. We can only place an upper bound on the composition of the sample after unloading, because the \(H_2\)-rich region did not fill up the full thickness of the sample space.
[20] The \(R\) factor is defined as \(R = \frac{||F_{obs}(hkl)|| - |F_{calc}(hkl)||}{|F_{obs}(hkl)||} \sum |F_{obs}(hkl)|\) and the weighted one as \(R_w = \frac{||\sum w(F_{obs}(hkl) - F_{calc}(hkl))||}{\sum wF_{obs}^2(hkl)}\), where \(F_{obs}\) are the observed structure factors, \(F_{calc}\) the calculated ones, and the weights are derived from the counting statistics of the intensity measurements.