Structure and Dynamics of Hydrogen Molecules in the Novel Clathrate Hydrate by High Pressure Neutron Diffraction

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The D\textsubscript{2} clathrate hydrate crystal structure was determined as a function of temperature and pressure by neutron diffraction for the first time. The hydrogen occupancy in the \(\frac{32}{\text{H}_2\cdot136\text{H}_2\text{O}}\), \(x = 0 - 16\) clathrate can be reversibly varied by changing the large (hexakaidecahedral) cage occupancy between two and four molecules, while remaining single occupancy of the small (dodecahedral) cage. Above 130–160 K, the guest D\textsubscript{2} molecules were found in the delocalized state, rotating around the centers of the cages. Decrease of temperature results in rotation freezing followed by a complete localization below 50 K.

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Clathrate hydrates represent a large group of inclusion compounds, with the host framework made up of hydrogen-bonded H\textsubscript{2}O molecules and guest molecules trapped inside the polyhedral cages. Hydrates of natural gases prevail in deep-sea sediments and permafrost, and could play an important role in the formation of planetary nebulae [1–5]. Most recently, a new class of clathrate hydrates containing hydrogen as the guest molecules has been discovered [6,7]. Hydrogen clathrate hydrates are of considerable interest for potential hydrogen storage applications [7,8]; in addition, they also reveal unconventional phenomena associated with the specific nature of the guest molecule, e.g., quantum behavior at low temperature. The most intriguing question of hydrogen occupancy in the cages remained unfeasible to resolve from theoretical calculations because of the obscurity in guest-host interaction and hydrogen distribution in the structure. Previous studies of these and other clathrate hydrates revealed that their cages could be multiply occupied by small molecules [7,9–14]. The unusually high guest/H\textsubscript{2}O molar ratio of 0.45 was proposed for hydrogen clathrate based on indirect experimental evidence [7] and recently confirmed by theoretical calculations [9]. Such a high H\textsubscript{2} occupancy in the clathrate suggests unconventional interactions in molecular H\textsubscript{2} clusters with very short H\textsubscript{2}–H\textsubscript{2} distance at ambient pressure. Here for the first time we report the variation of the D\textsubscript{2} hydrate crystal structure as a function of temperature and pressure by neutron diffraction.

We performed \textit{in situ} synthesis and neutron diffraction experiments with the HIPPO time-of-flight neutron diffractometer at the Los Alamos Neutron Science Centre [15]. Deuterated water and D\textsubscript{2} gas (instead of the hydrogen analogues) were used for the study in order to minimize the background of the collected diffraction patterns. Synthesis of the clathrate was performed in a large volume (~2.5 ml) gas cell under 2.2 kbar of D\textsubscript{2} pressure at 200–270 K. The neutron diffraction data were mostly collected in two sets: on cooling from 200 K to 40 K at ~2 kbar (pressure was slowly decreasing from 2.1 kbar to 1.4 kbar) and during heating from 40 K to 200 K at ambient pressure. Totally, over 30 diffraction patterns were collected and refined by the Rietveld method (Fig. 1) [16]. Over the entire temperature range studied, the deuterium clathrate was found to crystallize in \textit{Fd}\overline{3}m space group with a unit cell parameter \(a \sim 17 \text{ Å}\), known...
as the clathrate cubic structure II. The framework of this structure consists of two types of cages formed by hydrogen-bonded D$_2$O molecules. The unit cell contains eight hexakaidecahedral ($6^{4}5^{12}$) cages (subsequently referred to as “large”) and 16 dodecahedral ($5^{12}$; “small”) cages.

We found that the number of D$_2$ molecules and their distribution in the clathrate structure depend on temperature and pressure. Below 50 K, the guest D$_2$ scattering density distribution is consistent with the model of localized hydrogen molecules in the framework (Fig. 2, left), which was determined by interpretation of difference Fourier maps and confirmed by Rietveld refinement. The D$_2$ molecular scattering factor was calculated assuming a spherical distribution of nuclear density around the molecular center with a fixed radius of 0.37 Å ($\frac{1}{2}d_{H-H}$). The large cage was found to be occupied by four tetrahedrally arranged D$_2$ molecules located at 2.93(1) Å from each other and at a distance of 1.80(1) Å from the center of the cage. Each D$_2$ molecule is oriented toward the centers of hexagons formed by the framework oxygen atoms. A maximum occupancy of only one D$_2$ molecule was determined in the small cage. The scattering density of this D$_2$ molecule was refined as statistically distributed between 20 positions oriented towards the oxygen atoms forming the dodecahedral cage. For both cages, the refined O-D$_2$ distance is 3.34(4) Å.

As the temperature increases, D$_2$ molecules are deintercalated from the large cage, starting at \(\approx 70 \text{ K}\) under ambient pressure and at \(\approx 180 \text{ K}\) under \(\approx 2 \text{ kbar}\). The lowest occupancy of the large cage was found to be 2.0(2), which is probably a minimum value necessary for the stability of the framework structure. The occupancy of the small cage is constant at one D$_2$ molecule nearly up to the decomposition temperature of \(\approx 163(2) \text{ K}\) at ambient pressure (Fig. 3). This observation reflects the instability of the structure with empty small cages, which occurs locally for the small cage occupancy of less than one D$_2$ molecule. Accordingly, the hydrogen occupancy in the clathrate is limited by the stoichiometry $48\text{H}_2/136\text{H}_2\text{O}$. In contrast, previous experimental results [7] and theoretical calculations [9] suggested a higher $\text{H}_2/\text{H}_2\text{O}$ molar ratio of 0.45 with double occupancy of the small cage. Our new data indicate that the D$_2$-D$_2$ and D$_2$-O interatomic distances do not allow double occupancy of the small cage without a significant (14%–19%) compression of these distances.

Increasing temperature resulted in a change of the distribution of D$_2$ molecules in both cages as well. Successful refinement of the data obtained above 50 K could only be achieved by treatment of the delocalized scattering density as a uniform distribution of the D$_2$ molecule on the surface of a sphere (rotator model) [17],

![FIG. 2 (color). Structural view of the thermal variation of the D$_2$ distribution in the large ($6^{4}5^{12}$-hexakaidecahedron, top), and small ($5^{12}$-dodecahedron, bottom) cages in deuterium clathrate. Oxygen atoms are shown as red spheres, deuterium framework atoms–green, and guest D$_2$ molecules–yellow. Below 50 K, the guest D$_2$ molecules are localized: in the large cage four molecules are oriented to the centers of hexagons yielding a tetrahedral cluster; in the small cage one D$_2$ molecule is statistically distributed over 20 positions oriented towards the oxygen atoms forming the dodecahedron. With increasing temperature, the D$_2$ molecules can more freely rotate, yielding a nearly spherical density distribution inside the cages (right).](image1)

![FIG. 3. Temperature dependence of D$_2$ occupancy in the large (diamond symbols) and small (circle symbols) cages of the hydrogen clathrate hydrate structure. Open and filled symbols represent data obtained at ambient and high (\(\approx 2 \text{ kbar}\)) pressures, respectively. Data points with no error bars represent the values, which were fixed in the final refinements but were refined in the range 3.8(2)–4.2(2) for the large cage and 0.9(1)–1.1(1) for the small cage in the initial refinements. No significant correlation between large and small cage occupancy parameters was observed.](image2)
with a refinable radius and the center located at the geometric center of the cavity (Fig. 2, right). In the small cage, the “pure” rotator model (without a localized contribution) is preferable for all data obtained above 50 K. In the large cage, the total guest D$_2$ density at intermediate temperatures (60–200 K) was approximated by a linear combination of spherically delocalized and localized contributions, and their fractions were refined. Figure 4 shows a variation of these fractions with temperature at ambient pressure and under $\sim$2 kbar. At ambient pressure, the onset of the localization of the D$_2$ molecules on cooling coincides with the onset of the insertion of the fourth D$_2$ molecule in the cage at $\sim$130 K. Above 130 K, two or three molecules are rotating inside the cage yielding an average uniform spherical distribution of the nuclear density.

At high pressure, the incorporation of the fourth hydrogen molecule in the large cage is complete at $\sim$180 K (2.05 kbar) on cooling, and localization occurs with the constant clathrate composition. At this temperature, the D$_2$ molecules are mostly delocalized and only about 25% localized fraction refined. That small part of localized D$_2$ molecules may indicate that rotation of four D$_2$ molecules in the large cage is substantially restrained and their average distribution could not be described as spherical with the same accuracy as for 2–3 molecules in the cage. Below 160 K, the localized fraction increases, and at 40–50 K, the D$_2$ molecules were found only in fixed positions. Thus, localization-delocalization behavior of guests seems to be similar at high and ambient pressures when the clathrate composition is the same (below 70 K). However, it differs above 70 K, when at ambient pressure D$_2$ molecules deintercalate from the large cage. Note that the framework structure does not significantly vary with pressure. That allows one to conclude that temperature and cage occupancy are the most important parameters determining D$_2$ molecules distribution.

It should be mentioned that the order-disorder phenomena in general are well known for a variety of clathrate systems, including gas hydrates (3.5Xe·8CCl$_4$·136D$_2$O) [18], intermetallides (e.g., Ba$_6$Ge$_{25}$ [19]), and fullerene derivatives [20]. However, the order-disorder transition in all the above examples exhibits substantial differences from the studied case of deuterium clathrate. Namely, the delocalization of multiple guest molecules in one cage into freely rotating state (with rather large radius of the rotator sphere of 1.45–1.70 Å) is observed for the first time.

Cooling of the clathrate evidences the domination of van der Waals forces over the thermal energy of the D$_2$ molecules, and their localization occurs in the temperature range 50–160 K. Assuming that the D$_2$ molecules are almost nonbonded above 160 K, we can roughly estimate the maximum energy of thermal vibrations as 5/2 kT, and accordingly, the interaction between a deuterium molecule and six framework oxygen atoms as 3.3 kJ/mol. Such interaction results in the strong attraction of D$_2$ electron density by oxygen atoms, decreasing the repulsion between D$_2$ neighboring molecules. This allows the formation of the tetrahedral cluster, which is stable under normal pressure with a D$_2$-D$_2$ distance of

![FIG. 4. Temperature dependence of the number of D$_2$ molecules in the large cage, refined as localized in a tetrahedral cluster (square symbols) and spherically delocalized (circle symbols). Open and filled symbols represent data obtained at ambient and $\sim$2 kbar pressures (pressure was slowly decreasing from 2.1 kbar at 200 K to 1.4 kbar at 40 K; see text for details), respectively. Lines are guides to the eye. At high pressure below $\sim$180 K the total cages occupancy is constant to 4, while at ambient pressure it varies between 2 and 4, that cause the difference in the localization/delocalization behavior.](125503-3)

![FIG. 5. Temperature dependence of the unit cell parameter for the D$_2$O clathrate hydrate at ambient pressure. The minimum at $\sim$130 K reflects the onset of the incorporation of the fourth D$_2$ molecule in the large cage, accompanied by a significant increase of the interaction between the guest D$_2$ molecules and the framework.](125503-3)
2.93 Å; this bond distance is much smaller than that in solid hydrogen at normal pressure (3.78 Å) [21].

Additional evidence for the increased interaction between the D₂ molecules and the framework with localization is found in Fig. 5, which shows the temperature dependence of the lattice parameter (a) for the deuterium clathrate hydrate at ambient pressure. With decreasing temperature to 130 K, a decreases, corresponding to an occupancy of D₂ molecules increasing from two to three in the large cage. Further cooling leads to insertion of the fourth molecule with an increase of a (from 130 K to 90 ± 15 K), followed by a decrease of a (from 90 ± 15 K to 40 K), when the cage filling is complete. That on-cooling increase of the a-parameter (from 130 K to 90 ± 15 K) can be attributed to the increasing interaction between the D₂ molecules and the framework oxygen atoms accompanied by their localization into a tetrahedral cluster.

The D₂ occupancy in the large cage was found to be reversible between two and four molecules per cage by variation of pressure or temperature. The corresponding D₂/D₂O molar ratio varies from 0.35 to 0.26. The maximum D₂ density (0.0159 mol/cm³) in the clathrate is about 400 times greater than that of gaseous H₂ at ambient pressure, about 3 times greater than that of H₂ in a standard gas cylinder, and approximately 2.2 times lower than the density of liquid H₂ at ambient pressure [22]. The H₂ mass fraction in 48H₂·136H₂O clathrate is equal to 3.77%, which is higher than the value in most metal hydrides considered as hydrogen storage materials for mobile applications, e.g., Mg₂NiH₄ (3.59%) and LaNi₅H₆ (1.37%) [23]. The ability of the clathrate to reversibly insert/deinsert substantial amounts of hydrogen suggests that clathrate hydrates are potential hydrogen storage materials.

Similar crystal structure variations may be found for other clathrate hydrates of small guest molecules such as He, Ne, Ar, N₂, and O₂. The information on the localization-delocalization found for the hydrogen clathrate hydrate could be helpful for the study of the dynamic properties and molecular interactions in all gas hydrates and other inclusion compounds.

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