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

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The D_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 $(32 + X)H_2 \cdot 136H_2O$, $x = 0 - 16$ 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_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_2O 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_2O 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_2 occupancy in the clathrate suggests unconventional interactions in molecular H_2 clusters with very short H_2-H_2 distance at ambient pressure. Here for the first time we report the variation of the D_2 hydrate crystal structure as a function of temperature and pressure by neutron diffraction.

We performed *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_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_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 $Fd\bar{3}m$ space group with a unit cell parameter $a \sim 17$ Å, known

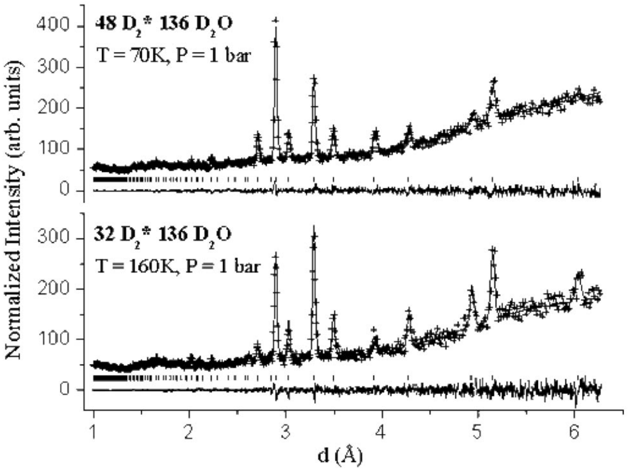

FIG. 1. Rietveld refinement patterns of the neutron diffraction data obtained for deuterium clathrate hydrate with the maximum (top) and minimum (bottom) guest occupancy. The observed intensities are represented by plus signs (every third point is shown), the calculated pattern–by a solid line, allowed Bragg positions–by short vertical bars, and the difference curve is shown below.

as the clathrate cubic structure II. The framework of this structure consists of two types of cages formed by hydrogen-bonded D_2O 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 ~70 K under ambient pressure and at ~180 K under ~2 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 ~163(2) 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 $48H_2 \cdot 136H_2O$. In contrast, previous experimental results [7] and theoretical calculations [9] suggested a higher H_2/H_2O 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],

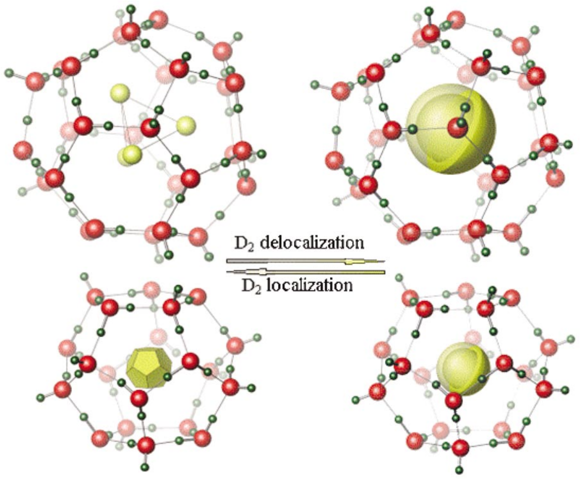

FIG. 2 (color). Structural view of the thermal variation of the D_2 distribution in the large ($6^4 5^{12}$–hexakaidecahedron, top), and small (5^{12}–dodecahedron, bottom) cages in deuterium clathrate. Oxygen atoms are shown as red spheres, deuterium framework atoms–green, and guest D_2 molecules–yellow. 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).

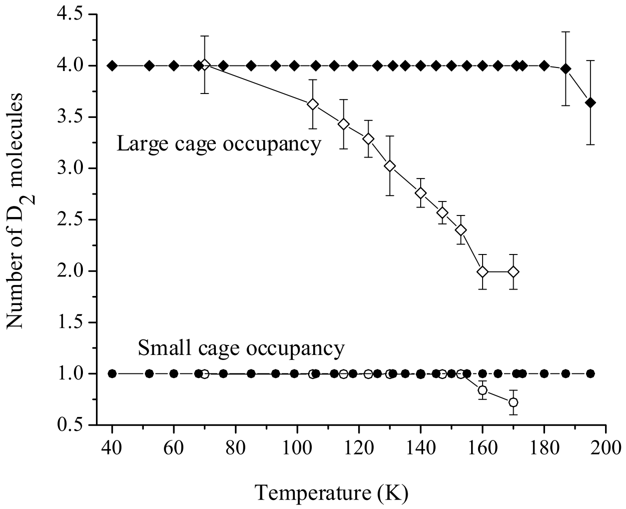

FIG. 3. Temperature dependence of D_2 occupancy in the large (diamond symbols) and small (circle symbols) cages of the hydrogen clathrate hydrate structure. Open and filled symbols represent data obtained at ambient and high (~ 2 kbar) pressures, respectively. Data points with no error bars represent 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.

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 ~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 ~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 ~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.

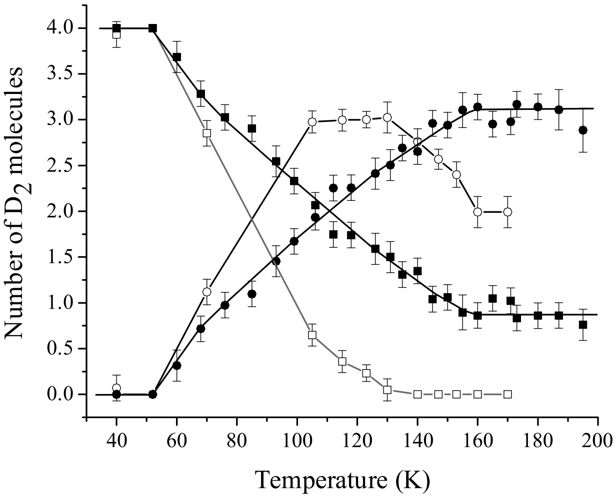

FIG. 4. Temperature dependence of the number of D_2molecules in the large cage, refined as localized in a tetrahedral cluster (square symbols) and spherically delocalized (circle symbols). Open and filled symbols represent data obtained at ambient and ~2 kbar pressures (pressure was slowly decreasing 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 ~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.

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 ($3.5Xe\cdot 8CCl_4\cdot 136D_2O$) [18], intermetallides (e.g., Ba_6Ge_{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

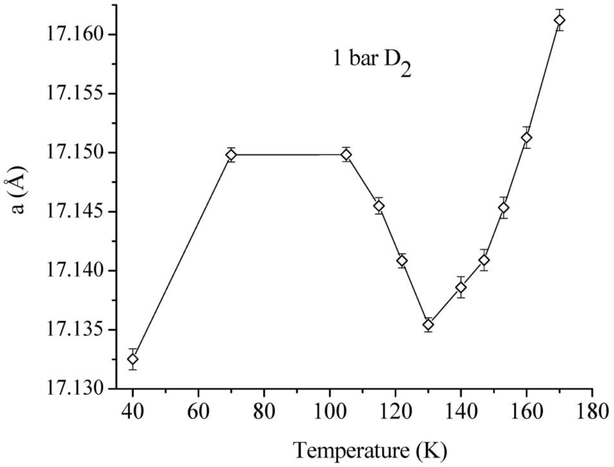

FIG. 5. Temperature dependence of the unit cell parameter for the D_2O clathrate hydrate at ambient pressure. The minimum at ~130 K reflects the onset of the incorporation of the fourth D_2 molecule in the large cage, accompanied by a significant increase of the interaction between the guest D_2 molecules and the framework.

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 D_2 molecules and the framework with localization is found in Fig. 5, which shows the temperature dependence of the lattice parameter ($\boldsymbol{a}$) for the deuterium clathrate hydrate at ambient pressure. With decreasing temperature to 130 K, $\boldsymbol{a}$ decreases, corresponding to an occupancy of D_2 molecules increasing from two to three in the large cage. Further cooling leads to insertion of the fourth molecule with an increase of $\boldsymbol{a}$ (from 130 K to 90 ± 15 K), followed by a decrease of $\boldsymbol{a}$ (from 90 ± 15 K to 40 K), when the cage filling is complete. That on-cooling increase of the $\boldsymbol{a}$-parameter (from 130 K to 90 ± 15 K) can be attributed to the increasing interaction between the D_2 molecules and the framework oxygen atoms accompanied by their localization into a tetrahedral cluster.

The D_2 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 D_2/D_2O molar ratio varies from 0.35 to 0.26. The maximum D_2 density (0.0159 mol/cm^3) in the clathrate is about 400 times greater than that of gaseous H_2 at ambient pressure, about 3 times greater than that of H_2 in a standard gas cylinder, and approximately 2.2 times lower than the density of liquid H_2 at ambient pressure [22]. The H_2 mass fraction in $48H_2 \cdot 136H_2O$ 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., Mg_2NiH_4 (3.59%) and $LaNi_5H_6$ (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, N_2, and O_2. 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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