

HYDROGEN CLATHRATE HYDRATE: CRYSTAL STRUCTURE, KINETICS, PHASE DIAGRAM AND POSSIBLE APPLICATIONS

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ABSTRACT

The detailed crystal structure information for the hydrogen clathrate hydrate was determined by neutron diffraction as a function of temperature (10-300 K) and pressure (1-2000 bar) for the first time. We found that 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 2 and 4 molecules, but keeping single occupancy of the small (dodecahedral) cage in the sII structure. Above 130-160K the guest hydrogen molecules were found in the delocalized state, rotating around the centres of the cages. Decrease of temperature results in the rotation freezing followed by a complete localization below 50 K. We have discovered an extremely fast method of the clathrate synthesis, which allows the complete hydrogen hydrate formation in minutes. High hydrogen capacity (up to 3.77 mass % at ambient pressure), fast kinetics, and readily accessible *P-T* range are the features that make hydrogen clathrate an excellent candidate for a hydrogen storage material.

Keywords: hydrogen clathrate, hydrogen storage

INTRODUCTION

The clathrate hydrates is 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 the planetary nebulae [1-5]. Previous study of these clathrate hydrates revealed that their cages could be multiply occupied by small molecules [6-12]. However, the number and distribution of guest molecules in the clathrates, together with the details of the bonding and crystal structure, have remained unclear.

RESULTS AND DISCUSSION

We performed in situ synthesis and neutron diffraction experiments with the HIPPO time-of-flight neutron diffractometer at the Los Alamos Neutron Science Center [13]. Deuterated water and D_2 gas (instead of 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. Neutron diffraction data were collected at 40-300 K under varying pressures and were used for the crystal structure refinement by the Rietveld method [14]. 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 $a \sim 17 \text{ \AA}$, known

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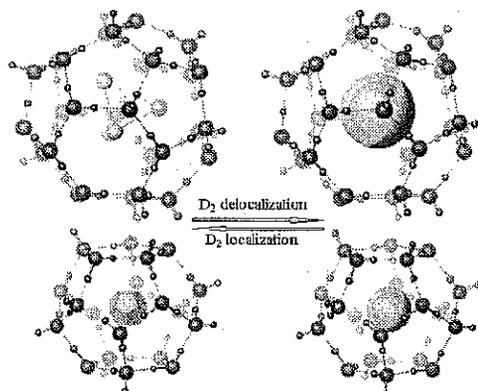


Fig. 1. Structural view of the thermal variation of the D_2 distribution in the large ($6^4 5^{12}$, top), and small (5^{12} , bottom) cages in deuterium clathrate. Oxygen atoms are shown as red spheres, hydrogen framework atoms - green, and guest D_2 molecules - yellow. Below 50 K, the guest D_2 molecules 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).

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 8 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 50K the guest D_2 scattering density distribution is consistent with the model of localized hydrogen molecules in the framework (Fig. 1, left), which was determined by interpretation of difference Fourier maps. The D_2 molecular scattering factor was calculated assuming a spherical distribution of nuclear density around the molecular centre with a fixed radius of 0.37 Å. 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 about 70 K under ambient pressure and at 180 K under 2 kbar. The lowest occupancy of the large cage was found to be two, 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 to up the decomposition temperature of $\sim 163(2)$ K (Fig.2). 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 [10] and theoretical calculations [8] suggested a higher H_2/H_2O molar ratio of 0.5 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 compression of the molecules (about 14-19%). 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) [15], with a refinable radius and the centre located at the geometric centre of the cavity (Fig. 1, 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-

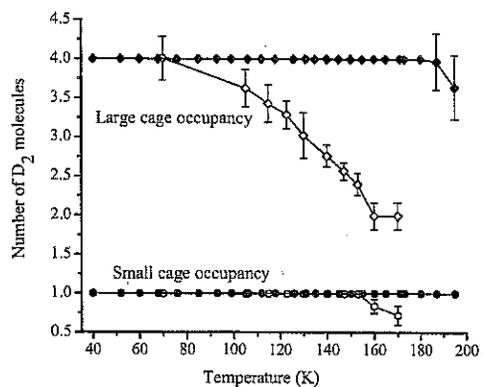


Fig. 2. Temperature dependence of D_2 occupancy in the large (diamond symbols) and small (circle symbols) cages of the hydrogen clathrate hydrate structure. Open symbols represent data obtained at ambient and filled symbols represent data under high pressure (2 kbar).

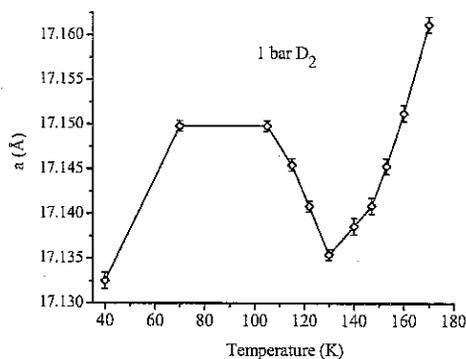


Fig. 3. Temperature dependence of the unit cell parameter for the D_2O clathrate hydrate at ambient pressure. The minimum at ~ 130 K reflects the onset of the incorporation of the fourth D_2 molecule in the large cage, accompanied by a significant increase of the interaction between the guest D_2 molecules and the framework.

200 K was approximated by a linear combination of spherically delocalized and localized contributions, and their fractions were refined. At ambient pressure the onset of the localization of the D_2 molecules coincides with 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 2 kbar pressure incorporation of the fourth hydrogen molecule in the large cage is complete at ~ 180 K. At this temperature the D_2 molecules are almost delocalized and only a small localized fraction refined. That residual 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.

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 non-bonded 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 2.93 Å; this bond distance is much

smaller than that in solid hydrogen at normal pressure (3.78 Å) [16].

Additional evidence for the increased interaction between the D_2 molecules and the framework with localization is found in Fig. 3, 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 3 D_2 molecules in the large cage. Insertion of the fourth molecule (below 130 K) leads to an increase in a , which can be attributed to increasing interaction between the D_2 molecules and the framework oxygen atoms.

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 [17]. The D_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%) [18]. 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 , O_2 . The information on the localization-delocalization found for the hydrogen clathrate hydrate could be helpful for study of the dynamic properties and molecular interactions in all gas hydrates and other inclusion compounds.

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