Communication

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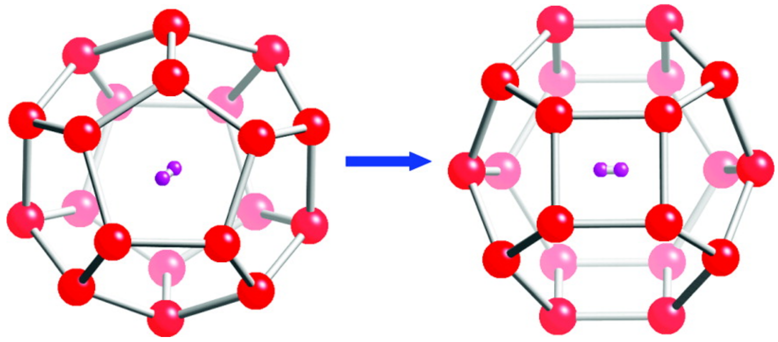

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A Hydrogen Clathrate Hydrate with Cyclohexanone: Structure and Stability

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Clathrate hydrates are crystalline solids in which guest molecules are concentrated within cavities formed from a hydrogen-bonded water host lattice.[1] Three common structures occur, generally as a function of the guest size: sI, sII, and sH, although interactions resulting from the chemical nature of the guest strongly influence hydrate stability. The smallest of hydrate formers (up to about $d =$ 4.0 Å, e.g., H_2, N_2) and larger molecules (between $d = 6-7$ Å, e.g., C_3H_8, THF) form sII, a $Fd3m$ lattice ($a \sim 17$ Å). This structure has two types of cavities: sixteen 5^{12} and eight $5^{12}6^4$ cavities (X^Y, where $Y =$ number of X sided faces per cavity). Molecules in the size range between $d = 4-6$ Å (e.g., CH_4 and C_2H_6) form sI, a $Pm3n$ lattice ($a \sim 12$ Å). This structure also has two cavity types: two 5^{12} and six $5^{12}6^2$ cavities. The structure containing the largest of guest molecules is sH, where two molecules are needed to stabilize this P_6/mmm hexagonal lattice ($a \sim 12$ Å, $c \sim 10$ Å). To form sH, a large guest (between $d = 7.5-9$ Å), such as methylcyclohexane, must occupy the $5^{12}6^8$ cavity (one per unit cell) combined with a guest (e.g., CH_4) that will fit inside the smaller $4^35^66^3$ (two per unit cell) and 5^{12} (three per unit cell) cavities.[2]

Recently, several experimental[3−8] and theoretical studies[9,10] have focused on the incorporation of hydrogen within clathrate phases. Hydrogen hydrates are of interest for several reasons, including as a unique system to investigate quantum effects,[9,10] as a potential gas separation material,[8] and, most notably, as a hydrogen storage material.[11] Historically, hydrogen was thought to be too small a molecule to contribute to the stability of clathrate hydrates.[12] However, hydrogen has been now shown to form a simple sII hydrate,[3] sI hydrate with CO_2,[4] semi-clathrates with various ammonium salts,[5] and binary sII hydrates with several promoter molecules such as THF.[6,7]

THF and other similar sized molecules can only fit into the large $5^{12}6^4$ cavities of sII hydrate, leaving the small 5^{12} cavities vacant. The hydrate structure formed from larger molecules, such as benzene and cyclohexane, has been also experimentally confirmed to be sII.[13] However, unlike molecules which readily form sII hydrate alone (e.g., THF), the largest of the sII formers ($d = 7-7.5$ Å) require a second type of guest molecule for stability, similar to sH. This second "help-gas" molecule is thought to offset unfavorable vibrational frequencies of the host water lattice induced by the presence of the larger molecule.[14]

In this communication, we report that hydrogen plays a similar role to known help-gas molecules (e.g., CH_4) in the sense that it has the ability to stabilize a sII lattice containing cyclohexanone (CHONE), a large molecule unable to form a hydrate on its own. This is also the first direct crystallographic data showing sII formation with cyclohexanone, making it one of the largest known sII formers ($d = 7.3$ Å). On the basis of this evidence, we suggest that, under suitable thermodynamic conditions, the role of hydrogen in hydrate stability is analogous to that of other more common hydrate guests. This implies that hydrogen should be able to stabilize other types of clathrate lattices with different types and sizes of cavities, allowing for greater hydrogen storage potential.

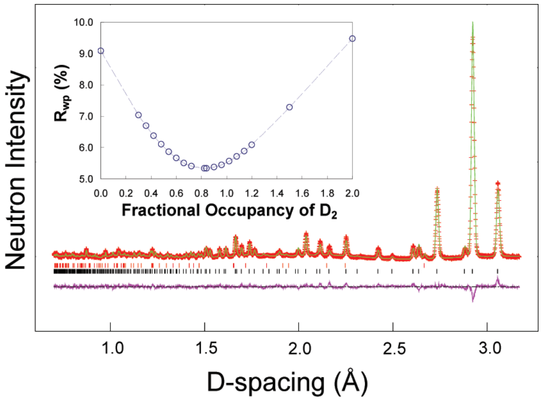

Figure 1. PND pattern of CHONE-D_2 hydrate at 20 K and 0.1 MPa. Points = data, line = model, bottom line = difference. $R_{wp} = 5.34\%$, $\chi^2 = 4.53$. Tick marks: upper = ice, lower = sII. Inset: R_{wp} as a function of D_2 fractional occupancy in the small cavity. Rietveld refinement details in Supporting Information.

High-resolution powder neutron diffraction (PND) measurements on binary CHONE-D_2 hydrate were made using the GPPD instrument at the Intense Pulsed Neutron Source, Argonne National Laboratory (see Supporting Information for experimental methods). All chemical species used were fully deuterated. Isotopic substitution was used to avoid incoherent background scatter from ^1H. Previous neutron diffraction studies on hydrates with D_2[15] were shown to be comparable to laboratory results for hydrates with H_2,[16] so the outcome of this work is assumed to be transferable to hydrogen hydrates. CHONE was previously inferred to fall into the class of large sII forming molecules using H_2S as a help-gas, based upon ^2H NMR line shape symmetry.[17] However, CHONE hydrate had not been previously confirmed as a hydrate former with diffraction.

Figure 1 shows a PND pattern recorded at 20 K and atmospheric pressure for CHONE-D_2 hydrate formed at 70 MPa and 265 K. The lattice parameter, $a = 17.28227(15)$, was significantly larger than that of THF-D_2 hydrate formed and measured at the same $P-T$ conditions, $a = 17.05954(9)$.[15] The larger crystal lattice was the result of spatial expansion in order for the $5^{12}6^4$ cavity to accommodate the substantially larger CHONE molecule. Thus the cavities of the CHONE-D_2 hydrate are larger than those of the THF-D_2 hydrate. Although several experimental reports have confirmed that the small dodecahedral cavity contains only up to one H_2/D_2 molecule[15,16,18−20] (up to pressures of 300 MPa), it is not unreasonable to suggest that a slightly larger cavity could contain two hydrogen molecules, particularly at higher pressures (cf. the $5^{12}6^4$ cavity of pure H_2 hydrate).

However, contrary to this suggestion, the D_2 occupancy of the CHONE-D_2 hydrate was found to be lower than that of the THF-D_2 hydrate. The inset of Figure 1 shows how the quality of fit (weighted R factor, R_{wp}) of the Rietveld model to the neutron data changes as a function of D_2 small cavity occupancy. The best fit

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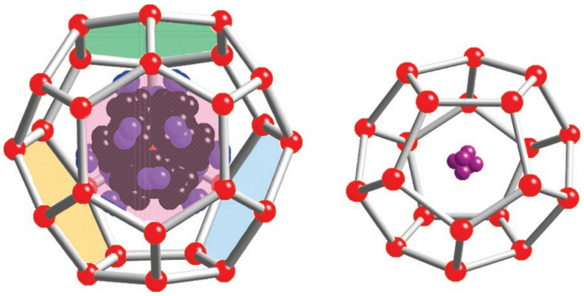

Figure 2. Structure of CHONE-D_2 hydrate. Left: Disordered CHONE in $5^{12}6^4$ cavity, hexagonal faces shaded for clarity. Right: Disordered D_2 in small cavity, multiplicity = 96 (water O = red, CHONE O = blue, C = black, D = purple. Host and CHONE D atoms are omitted for clarity).

R_{wp} of 5.34% was obtained with a D_2 fractional occupancy of 0.828(24) compared with 1.005(16) for the THF-D_2 hydrate.[15]

The Langmuir adsorption mechanism, commonly used to describe hydrate systems,[2] has been shown to be representative of hydrogen filling in the small cages of a THF binary hydrate.[16] The degree of cavity filling is determined by both the hydrogen fugacity and the affinity for the molecule to reside within the cavity (Langmuir adsorption constant). At constant fugacity, the size ratio of the guest to cage is the dominant factor in determining the Langmuir adsorption constant.[21] The increased size of the 5^{12} cage in the CHONE-D_2 binary hydrate, compared to the THF-D_2 binary hydrate, would decrease the guest to cage size ratio and, hence, the Langmuir adsorption constant. This diminished Langmuir constant induced by the larger 5^{12} cavity could explain the difference in filling between the two hydrates, although other effects such as guest−guest interaction could also play a role.

CHONE was found to completely occupy the large $5^{12}6^4$ cavities, in agreement with previous diffraction studies on sII hydrates with large guest formers.[22] The CHONE molecules were localized in the large cavities with the oxygens oriented toward the hexagonal faces. Each atom in a CHONE molecule was statistically distributed over 24 equivalent positions per large cage by the crystal symmetry (Figure 2). Attempts to model CHONE as a delocalized sphere of nuclear density resulted in poorer quality fits to the data. This orientation has been suggested for other oxygen-bearing guest molecules such as TMO[23] and THF.[24] Because the six-membered ring is approximately 0.8 Å larger than the five-membered ring, this is likely to be the most stable configuration for the $5^{12}6^4$ cavity to accommodate the large CHONE molecule.

Similar to previous studies,[15,20] the disordered D_2 molecule was localized in the center of the small cavity at 20 K (Figure 2). In this position, the site multiplicity of the atoms on the rigid body can either take on values of 96 or 192 depending on the orientation. However, the D_2 cavity filling and refinement statistics were independent of arbitrary rotations of the rigid body, thus no preferred orientation of the D_2 molecule was observed.

Generally, the stability of clathrate hydrates is governed by the interactions between the guest and host lattice. Thus guest molecular size plays an important role in hydrate stability as size variations lead to variations in the distance over which stabilizing interactions operate. In the case of sII hydrates such as THF, hydrate stability occurs in the absence of small cage occupancy, with large cavity occupancies being greater than 99%. Due to the small size of hydrogen (d = 2.9 Å), multiple occupancies are required in the large cavity to create a stable hydrate condition for pure hydrogen hydrate. Hydrogen also contributes to hydrate stability via interactions with the small cavity; for example, THF-H_2 hydrate is stable to higher temperatures than pure THF hydrate.[6] However, in this case, THF forms sII hydrate readily without a second guest. Because CHONE does not form a simple hydrate, the contribution of hydrogen to the hydrate lattice stability is further elucidated. That is, it appears that hydrogen has an analogous behavior to other help-gas molecules such as methane or xenon. Therefore, from these results, we suggest that hydrogen is capable of stabilizing other types of hydrate lattices that require a second guest for stability, for example, sH hydrate.

Like the CHONE-D_2 hydrate, sH hydrate typically forms with two types of guest molecules: a large molecule between 7.5 and 9 Å, and another small help-gas molecule. If hydrogen can act as a help-gas molecule for sH hydrate with one hydrogen molecule in each of the smaller cavities, the increase in hydrogen storage capacity would be on the order of 40% when compared with THF-H_2 hydrate. More generally, as a direct result of this study, it can be inferred that hydrogen should be able to stabilize other less common types of hydrate structures, or even entirely different classes of inclusion compounds that could potentially store even greater amounts of hydrogen.

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Supporting Information Available: Experimental technique and Rietveld refinement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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