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Observation of Interstitial Molecular Hydrogen in Clathrate Hydrates**

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Abstract: *The current knowledge and description of guest molecules within clathrate hydrates only accounts for occupancy within regular polyhedral water cages. Experimental measurements and simulations, examining the tert-butylamine* + H_2 + H_2O *hydrate system, now suggest that* H_2 *can also be incorporated within hydrate crystal structures by occupying interstitial sites, that is, locations other than the interior of regular polyhedral water cages. Specifically,* H_2 *is found within the shared heptagonal faces of the large* $(4^35^96^27^3)$ *cage and in cavities formed from the disruption of smaller* (4^45^4) *water cages. The ability of* H_2 *to occupy these interstitial sites and fluctuate position in the crystal lattice demonstrates the dynamic behavior of* H_2 *in solids and reveals new insight into guest–guest and guest–host interactions in clathrate hydrates, with potential implications in increasing overall energy storage properties.*

When water and low-molecular-weight compounds are mixed at high pressures and low temperatures, crystals of hydrogen-bonded water cages, known as clathrate hydrates, can form. The clathrate hydrate structure is differentiated from other solid forms of water by the incorporation of a single guest molecule inside regular polyhedral water cages, stabilizing the crystal structure.[1] Notable exceptions to this heuristic model include very small molecules such as H_2 and N_2, which can multiply occupy larger water cages at moderate pressures.[2–4] The ability to capture compounds within a water framework is currently an area of both scientific and practical interest for applications including energy storage, carbon sequestration, and hydrocarbon production.[5–7] Whether considering singly or multiply occupied water cages, the accepted knowledge is that the stability of the clathrate framework is dependent on the interaction between enclathrated guests and the host water lattice.[8,9] Specifically, if clathrate occupancies are reduced below a certain threshold, ice or water will be thermodynamically preferred, suggesting a critical and balanced interaction between guest and host molecules. This constraint of guest molecules inside individual water cages has been well-supported from single-crystal X-ray diffraction, neutron diffraction, and quantum chemical calculations.[2,10–15] Herein, we provide evidence from experiments and simulations on the structure VI clathrate hydrate system that suggests hydrate guests may also occupy interstitial sites within the host water lattice, which is in contrast to the conventional definition of guest molecules residing only in the interior of well-defined polyhedral water cages.

Structure VI (sVI) hydrates are the thermodynamically stable phase of *tert*-butylamine (tBuNH$_2$) + H_2O for temperatures below 271 K at 0.1 MPa. The sVI unit cell contains 12 octahedra 4^45^4 cages and 16 larger heptakaidecahedra $4^35^96^27^3$ cages, forming a cubic ($a = 18.81$ Å) crystalline structure where tBuNH$_2$ occupies the large cage and the small cage remains vacant.[16] Unlike the other more common hydrate structures (I, II, H) that easily form binary systems (occupancy with two different guests), sVI has been experimentally observed with only a single guest, tBuNH$_2$. Despite possessing the highest theoretical H_2 storage capacity for a clathrate hydrate structure, attempts to synthesize binary sVI hydrates with H_2 or CH_4 have shown a rapid and complete transition to structure II hydrate at temperatures greater than 243.15 K.[17–19] Herein, we show that by reducing the system temperature to 123–153 K, the transition from sVI to sII can be significantly delayed on the order of several days, allowing for the exploration of the native sVI environment preceding the structural transition to sII.

After pressurizing pre-formed sVI tBuNH$_2$ hydrate samples (9.31 mol% tBuNH$_2$) with H_2 at 70 MPa and 143 K, Raman spectroscopic analysis reveals a distinct H_2 vibron centered at about 4136 cm^{-1} (Figure 1 A). Interestingly, this vibron lacks the spectroscopic characteristics typically found for H_2 in hydrates.[3] Specifically, whereas in the Raman spectra of other binary H_2 hydrates structures (sI, sII, sH; Figure 1 B–D) each enclathrated H_2 environment is clearly defined by ortho/para H_2 peaks separated by about 6 cm^{-1}, the new H_2 environment (1A) is comparatively much broader (spanning a total of about 40 cm^{-1}) and without clear features,

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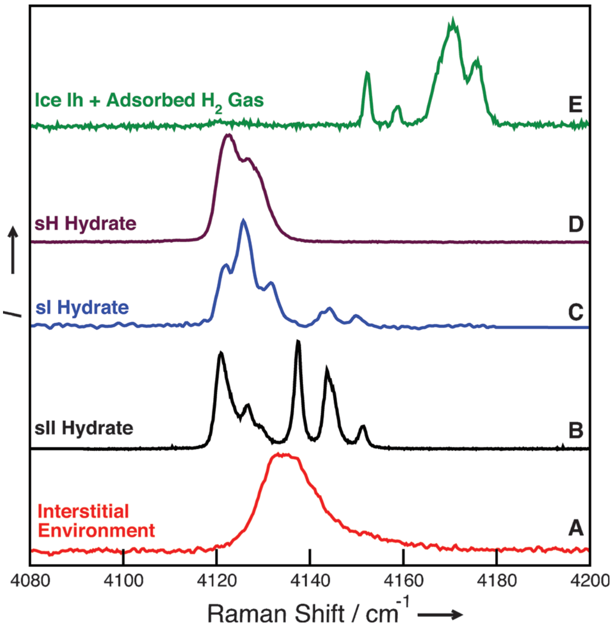

Figure 1. Raman vibrational spectra of H_2 in known clathrate hydrate environments of sI, sII, sH, and ice Ih (B–E), and in the proposed interstitial environment(s) in sVI (A), highlighting differences in features, position, and width. All of the Raman spectra were measured at 0.1 MPa and 83 K.

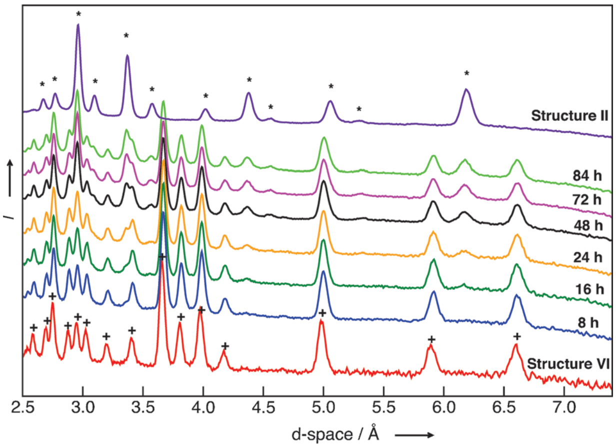

Figure 2. In situ neutron diffraction data from the General Materials Diffractometer (GEM; detector bank 3), covering the complete sVI-to-sII transition acquired at 70 MPa and 190 K over a range of 84 h of exposure to D_2. Diffraction peaks are denoted as sVI (+) and sII (*).

suggesting possible convolution of several environments. Additional experiments studying ortho/para H_2 conversion after LN_2 exposure suggest a minimum of two unique sites (Supporting Information, Figure S7). Given that sVI hydrates are thermodynamically driven to transition to sII after the addition of H_2, it is expected that only three phases would exist throughout the transition process: sVI (initial structure), sII (final structure), and possibly ice Ih as an intermediate byproduct of crystal reformation.[17,18] In comparing the observed H_2 environment (1A) to a pure H_2 hydrate sII sample formed at 114 MPa/263 K (1B) and H_2 in ice Ih[7,20] (1E), the peak shift, shape, and width are significantly different, suggesting the observed H_2 vibron cannot be associated with H_2 in sII or ice Ih, but possibly a native sVI environment. As the formation process of the initial sVI hydrate sample was conducted using H_2O and *t*BuNH$_2$ at the stoichiometric concentration for sVI clathrate formation (16*t*BuNH$_2$ + 156 H_2O), it is assumed that all of the large $4^35^96^27^3$ cavities are fully occupied by a single *t*BuNH$_2$ molecule. By process of elimination, this suggests only the 4^45^4 small cage of sVI would be available for H_2 enclathration and potentially responsible for the vibron in Figure 1 A.

To more accurately characterize the hydrate structure(s) present during the transition process, in situ neutron diffraction was performed at 70 MPa and 190 K over a period of 84 h in the presence of D_2 (Figure 2). The structure of the initial hydrate sample was indexed as cubic $I\bar{4}3d$ ($a = 18.60401(2)$ Å) confirming a pure sVI phase.[16] As D_2 was added to the system, the sample slowly began to transition, showing characteristic sII reflections within the first 8 h. After 84 h, approximately 28 % of the initial sVI had converted into sII ($Fd\bar{3}m$, $a = 17.4806(1)$ Å).[1] To finalize the transition to sII, the sample was heated to 263 K and held for 8 h, during which complete conversion to sII was observed, and was then cooled back to 190 K for the final acquisition. Throughout the entire transition experiment, only two crystal structures were detected, sVI and sII. The lack of a distinct third phase suggests that the H_2 vibron observed from the Raman spectroscopic measurements (Figure 1 A) could only be derived from H_2 enclathration in either sVI or sII. Furthermore, when combined with the Raman analysis discussed above, the data confirm that the H_2 signal is a result of enclathration into sVI. Additionally, during the neutron scattering experiment, it was observed that immediately following the initial pressurization with D_2 to 70 MPa, the sVI lattice expanded from 18.6040(12) Å to 18.6645(09) Å (Supporting Information, Figure S2).

From previous work, it is known that hydrate lattice constants are affected by at least three variables: temperature, pressure, and occupancy of guests. The reported expansion was observed at constant temperature and following an increase in pressure, which acts to compress the lattice, suggesting the expansion may result from D_2 insertion into sites within the sVI lattice.[4,21] To quantify the effect of H_2 penetration into the hydrate lattice and its expansion, molecular simulations studying sVI unit cell dimensions as a function of guest filling were performed. These simulations showed that, as expected, the insertion of H_2 molecules in the sVI lattice resulted in gradual increase in lattice constant of the crystal and with a loading of approximately 8 H_2 molecules per unit cell, a comparable increase in lattice constant as in the case of the neutron experiment was observed (Supporting Information, Figure S5).

To probe possible H_2 occupancy within native sVI environments, a series of classical molecular dynamic (MD) simulations for the *t*BuNH$_2$ + H_2 + H_2O system was performed. Based on earlier experimental efforts studying sVI + H_2 binary hydrates and our DFT calculations (Supporting Information, Table S2), it was expected that H_2 would be unable to occupy any native sVI environment as the large

($4^35^96^27^3$) cages were fully occupied by tBuNH$_2$ and the small (4^45^4) cages were shown to be too constrained for enclathration.[17,18,22] Surprisingly, the simulations revealed that H_2 readily diffuses into the sVI lattice (Figure 3A), assisted primarily by the metastability of the host water network. The results show that upon entering the sVI crystal, H_2 did not occupy either of the well-defined sVI water cages, but instead was localized in two interstitial sites (Figure 3B).[23,24] In one site, H_2 migrates through the crystal lattice, and resides in the heptagonal-shared face of the $4^35^96^27^3$ water cages (Figure 4A). In the other site, the inability of H_2 to occupy either of the two thermodynamically stable cage types in sVI induces local disruption of the water hydrogen bond framework, specifically in the 4^45^4 cages, resulting in cavities with disrupted hydrogen bonds that can also stabilize H_2 (Figure 4B). A study on the residency times of individual H_2 molecules upon diffusion into the bulk sVI structure revealed that approximately 55% of the total time was spent in a disrupted small cage environment, 40% inside of heptagonal shared face, and 5% as a co-guest with tBuNH$_2$ inside the large cage. It should be emphasized that when H_2 was observed in these interstitial spaces, it was typically stabilized on the order of 10–20 ns, whereas the transition step or "hop", from one interstitial space to another occurred quickly (< 5 ps), revealing that the timescale for the localization of H_2 at interstitial sites is roughly four orders of magnitude greater than the diffusion step (see the Supporting Information for videos illustrating these processes).

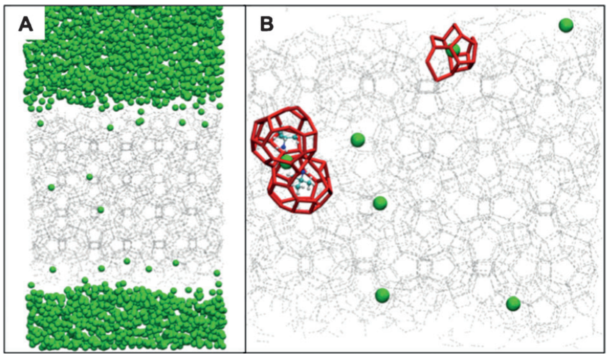

Figure 3. A) Simulated system consisting of 27 sVI unit cells (4212 H_2O molecules with 432 tBuNH$_2$ molecules) and 2393 H_2 molecules at 230 K and 85 MPa. B) Snapshot from the simulation showing seven H_2 molecules within the sVI lattice, highlighting the two dominant types of interstitial sites in red. Green spheres represent the center of mass of H_2 (size increased for clarity), and gray dotted lines correspond to hydrogen bonds between water molecules.

Prior to this study, hydrate guest occupancies in interstitial sites had not been considered, and these results provide new insight into guest–guest and guest–host interactions, highlighting the dynamic environment of both guest and host molecules in the clathrate structure. While this finding of interstitial occupancy exists only as a metastable state during the sVI to sII transition, these results suggest that it may be possible to discover other combinations of clathrate hydrate structures plus guests to form thermodynamically stable interstitial guest occupancy, which would have significant implications in increasing overall storage capacity for a variety of applications.

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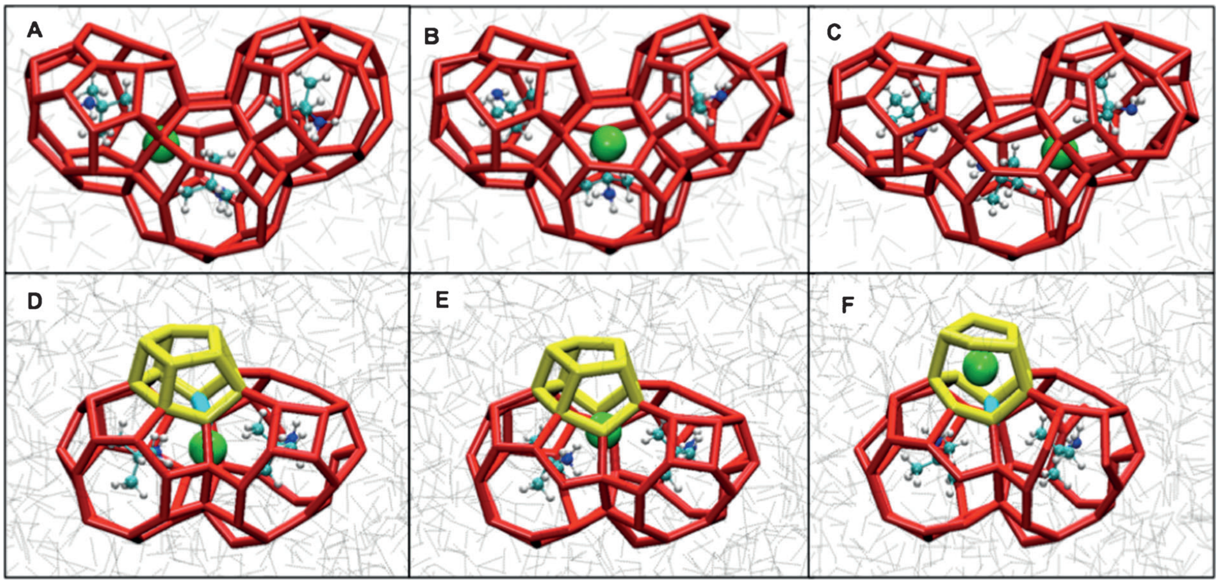

Figure 4. A–C) Pathway and interstitial sites occurring during the H_2 (green) migration between two heptagonal faces shared among three fully occupied $4^35^96^27^3$ cages (red). D)–F) Pathway for stabilization of H_2 in cavity formed from disrupted hydrogen bonds (blue) in the small 4^45^4 cage (yellow).

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