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Multiple H_2 Occupancy of Cages of Clathrate Hydrate under Mild Conditions

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ABSTRACT: Experiments were carried out by reacting H_2 gas with N_2 hydrate at a temperature of 243 K and a pressure of 15 MPa. The characterizations of the reaction products indicated that multiple H_2 molecules can be loaded into both large and small cages of structure II clathrate hydrates. The realization of multiple H_2 occupancy of hydrate cages under moderate conditions not only brings new insights into hydrogen clathrates but also refreshes the perspective of clathrate hydrates as hydrogen storage media.

The success of the future hydrogen economy relies on the technologies of efficient and profitable hydrogen production and storage. Among candidate materials for hydrogen storage, clathrate hydrates have the advantages of environmentally friendly features and comparatively high storage efficiencies (up to ~5 wt %).[1] First-principles electronic calculations have suggested that the hydrogen storage capacity of clathrate structure I can be even higher (~9.2 wt %) because there is the possibility for the small cages to host three hydrogen molecules and for the large cages to host six.[2] As a result, hydrogen hydrate has continued to provoke much interest in the scientific community since it was first reported in 2002.[3] Unfortunately, its prospects were dimmed by the extreme formation conditions of hydrogen hydrate, requiring a pressure of ~200 MPa at 284 K, which is much higher than that acceptable by industry (<30 MPa). Efforts have been made to bring the formation pressure down by loading H_2 into the empty cages of stable clathrates [e.g., tetrahydrofuran (THF) hydrate],[4,5] but this occurs at the price of sacrificing the storage capacity because H_2 occupies only the small cages. Although the storage efficiency can be improved by making use of the tuning effect[5−7] of THF and other hydrates, this method, because of the single H_2 occupancy of the small cages, still reaches storage capacities of up to only 3.4 wt %, far away from the acceptable storage capacity (5 wt %). Since the number of cages with a unit cell of a specific clathrate hydrate is fixed, the more H_2 molecules are loaded into each of the large and small cages, the higher the storage capacity will be. Although theoretical calculations predict multiple occupancy of H_2 molecules in the small (5^{12}) and large ($5^{12}6^4$) cages,[8,9] these have been realized only at extremely high pressures. To date, under moderate pressure conditions, only the single occupancy of the small cages has been demonstrated. Thus, the loading of multiple H_2 molecules into both types of cages under moderate conditions is the key to developing clathrate hydrates for hydrogen storage. We have developed a novel method of reacting H_2 gas with N_2 hydrate at 15 MPa and 243 K. The idea was to substitute the smaller H_2 molecule for the larger N_2 molecule in N_2 hydrate, allowing multiple H_2 molecules to be loaded into the clathrate cages.

The N_2 hydrate was prepared by reacting N_2 gas with finely powdered ice (<50 μm) in a 100 mL pressure cell at ~20 MPa and 253 K. After evacuation for 30 min while the pressure cell containing ~2 g of N_2 hydrate was sitting in dry ice, H_2 gas was charged into the pressure cell up to 15 MPa at 77 K. Finally, the pressure cell was stored in a 243 K freezer, and the H_2 gas was allowed to react with the N_2 hydrate for 4 days. When the cell was placed in the freezer initially, its pressure increased because of the temperature increase, so gas was released from the cell to keep the pressure stable at 15 MPa. Nitrogen hydrate is one of the least stable hydrates in terms of its $P-T$ behavior and thus was a good choice for this reaction, which can be considered as a type of metathesis reaction. The reaction products were recovered at 77 K for characterization with Raman spectroscopy and powder X-ray diffraction (PXRD). Raman spectra were recorded in the H−H and N−N stretching mode vibration regions at 77 K with a Raman spectrometer (Acton Research Corporation, model Spectropro 2500i) equipped with a Witec confocal microscope and an Ar^+ laser (Spectra-Physics, model 177G) operating at 514.5 nm with a power of 100 mW. For each spectrum, the laser scanned a sample spot of ~15 μm for ~6 min. For the measurement, the aluminum sample holder was placed in a liquid nitrogen bath in a box with an outlet to release the evaporated N_2 gas to the ambient atmosphere. PXRD analyses were carried out at 153 K on a Bruker D8 Advance powder X-ray diffractometer (Cu Kα, λ = 1.5406 Å).

The reaction product was confirmed to be a type II structure hydrate by PXRD (Figure 1) and Raman spectroscopy (Figure 2), similar to N_2 hydrate and H_2 hydrate. Comparison of the H_2 Raman spectra (Figure 2) with those of pure H_2 hydrate and consideration of theoretical analyses[8−10] indicated that multiple H_2 molecules were loaded into both types of cages. It can be seen that spectrum II in Figure 2 is generally similar to the spectrum of pure hydrogen hydrate, with peaks for one H_2 in the 5^{12} cages and one to four H_2 in the $5^{12}6^4$ cages. However, some minor differences between the two spectra can be identified. Previously, it was reported that the line shapes and

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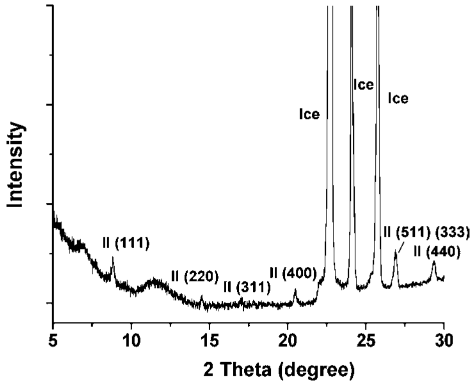

Figure 1. PXRD pattern of the material produced by reacting N_2 hydrate with H_2 gas at 243 K and 15 MPa for 4 days. The indexing of the pattern for structure II hydrate is indicated.

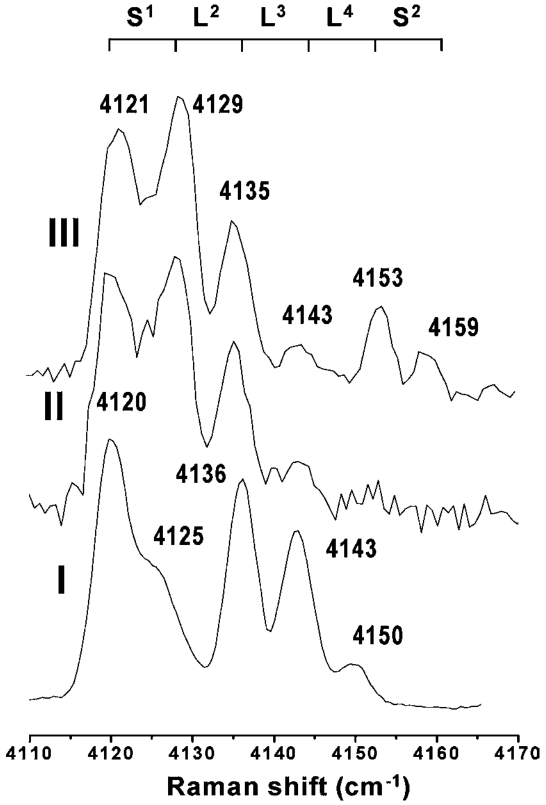

Figure 2. Raman spectra of the products of the reaction of N_2 hydrate with H_2 gas at 243 K and 15 MPa for 4 days. The peak assignments were made with reference to the theoretical studies of Wang et al.[8,9] and the experimental results of Strobel et al.[10] and Giannasi et al.[11] Spectrum I: H–H vibrons of hydrogen hydrate[10] (4120 cm^{-1} [$Q_1(1)$] and 4125 cm^{-1} [$Q_1(0)$] for a single H_2 molecule in a 5^{12} cage; 4136, 4143, and 4150 cm^{-1} for up to four H_2 molecules in a $5^{12}6^4$ cage). Spectrum II: H–H vibrons of the reaction product (4120 cm^{-1} and part of 4128 cm^{-1} for a single H_2 molecule in a 5^{12} cage; part of 4128, 4135, 4143, and 4150 cm^{-1} for up to four H_2 molecules in a $5^{12}6^4$ cage). Spectrum III: H–H vibrons of the reaction product (4120 cm^{-1} and part of 4129 cm^{-1} for a single H_2 molecule in a 5^{12} cage; part of 4129, 4136, 4143, and 4150 cm^{-1} for up to four H_2 molecules in a $5^{12}6^4$ cage; 4153 and 4159 cm^{-1} for two H_2 molecules in a 5^{12} cage).

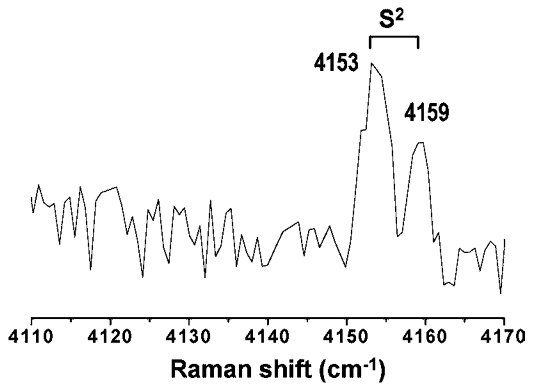

Figure 3. H–H vibrons of the reaction product (4153 and 4159 cm^{-1} for two H_2 molecules in a 5^{12} cage).

peak positions of hydrogen hydrate depend on the temperature.[11] Because the reaction temperature (243 K) and pressure (15 MPa) for our experiments were very different from those for preparing the sample for spectrum I, it is reasonable to consider that the differences in line shapes and peak positions were caused by the differences in the reaction conditions. Spectrum III, of a different sample spot, is different from spectrum II, with two extra peaks at 4153 and 4159 cm^{-1} on the high-frequency side. On the basis of our previous theoretical analyses,[8,9] these two peaks represent double occupancy of H_2 in the 5^{12} cages. It is noteworthy that these two peaks are quite close to those of hydrogen gas. Because the peak positions were calibrated with the $Q_1(1)$ (4155 cm^{-1}) peak of hydrogen gas, the 4153 cm^{-1} peak should be due to a material different from hydrogen gas. Moreover, the sample holder was located in a liquid nitrogen bath and liquid nitrogen was always evaporating and venting out from the sample box during the Raman measurements, so the hydrogen gas from possible hydrate dissociation would be extremely diluted and quickly removed by N_2 gas. Hydrogen molecules trapped in ice pores can be identified at 4170–4180 cm^{-1} in Raman spectra,[6,10] which is ~20 cm^{-1} higher than the two peaks in our Raman spectra, so these peaks are not from ice-trapped hydrogen molecules. With these considerations, we believe that the two peaks at 4153 and 4159 cm^{-1} originate from the hydrogen molecules in doubly occupied small cages. This appears to confirm that both the large and small cages are able to accommodate multiple hydrogen molecules (a maximum of two in 5^{12} cages and four in $5^{12}6^4$ cages). However, we do note that the reaction products were not homogeneous on the time scale of our experiments. In some portions of the prepared sample, only peaks corresponding to two H_2 molecules in the small cages were found (Figure 3), in addition to the variation in hydrogen occupancies in both the large and small cages in other parts of the sample. Peaks for N–N stretching were always present (Figure 4), indicating the possibilities that part of the N_2 hydrate had not reacted and/or some N_2 molecules might remain in some cages. In the case of double H_2 occupancy of small cages without H_2 in the large cages, the latter were occupied by N_2 molecules. There are a number of possibilities for the coexistence of N_2 and H_2 in the same cage. It has been found that there can be one N_2 in a small cage and two N_2 in a large cage, so the possibilities for the coexistence of H_2 and N_2 could be one N_2 and one H_2 in a small cage and one N_2 and one to three H_2 in a large cage. Theoretical calculations on all of these possible configurations showed that their Raman frequencies are located in the two regions 4170–4210 and 4140–4150 cm^{-1}. For example, the H_2 Raman frequency for

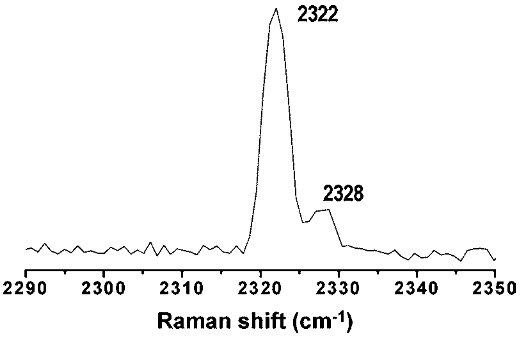

Figure 4. N−N stretching modes of the reaction product (2322 cm^{-1} for N_2 in hydrate cages and 2328 cm^{-1} for N_2 gas).

one H_2 coexisting with one N_2 in a small cage is ~4210 cm^{-1}, while for the coexistence of one H_2 molecule with one N_2 molecule in a large cage, the Raman frequency is ~4140 cm^{-1}. As a result, the peaks in the 4150−4160 cm^{-1} range in the experimental Raman spectra must be due to two H_2 in small cages that do not coexist with N_2 molecules in the same hydrate cage. The peaks in the 4129−4150 cm^{-1} range in the experimental spectra are from multiple H_2 in the large cages that also do not coexist with N_2 molecules in the same hydrate cage, as they are almost perfectly consistent with those of pure hydrogen hydrate. Although multiple occupancies of H_2 in both types of cages of the hydrate have been realized under mild conditions, considerable efforts in optimizing the experimental conditions are required to improve the sample homogeneity and production rates. Since multiple occupancy of H_2 in clathrate cages had previously been obtained only at very high pressures (several hundred MPa), its realization under mild pressure (~15 MPa) is a major breakthrough for practical applications in industry.

On the basis of the results obtained, both the small and large cages of clathrate hydrates can accommodate multiple H_2 molecules under moderate pressure conditions when hydrogen gas is reacted with N_2 hydrate. Although the reaction product obtained with the current method was not homogeneous, with various H_2 occupancies and with some N_2 hydrate remaining, the realization of multiple occupancies of H_2 in both the small and large cages under mild conditions reestablishes the possibility of clathrate hydrates as hydrogen storage media. It is clear that the detailed conditions for optimum capacity must still be worked out.

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Notes

The authors declare no competing financial interest.

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