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Fast molecular transport in hydrogen hydrates by high-pressure diamond anvil cell NMR

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In situ proton NMR spectra and T_1^{-1} and T_2^{-1} relaxation rates of filled-ice hydrogen hydrates at pressure reveal fast translational motion of the H_2 molecules within the ice frameworks. The NMR spectra to 3.6 GPa gave surprisingly narrow resonances of the H_2 guests. Pressure effects on T_1^{-1} and T_2^{-1} of the H_2 indicate that molecular rotation and diffusion contribute together to the relaxation, from which correlation times τ_{rot} and τ_{dif} were separately determined. Liquidlike fast diffusion of the H_2 with little pressure sensitivity was deduced from τ_{dif}, indicating that the ice framework allows active guest translation even in extensively compressed states.

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I. INTRODUCTION

The properties of hydrogen hydrates at high pressures are of increasing importance in solid-state physics, pure and applied chemistry, and energy engineering science.[1–4] At pressures to 0.4 GPa, structure II hydrogen clathrate hydrate crystallizes from a fluid mixture of H_2-H_2O at moderately low temperature.[2,3] Its high H_2:H_2O molar ratio of 1:2 is attractive as a hydrogen-storage material in a chemically benign material.[3] Although the growth of this hydrate appeared too slow for such application, an improved preparation technique with >100 times faster synthesis rate was recently developed.[5] This method uses a mixture of ice Ih and H_2 for the synthesis, with the surprisingly rapid reaction resulting from anomalously fast diffusion of hydrogen in ice Ih.[6] Thus, hydrogen transport in ice and hydrate is a primary issue in both basic and applied hydrate researches.

A distinct feature of H_2 is its smallest size among the molecules. It is much smaller than polyhedral cages of clathrate hydrates, so that four H_2 molecules can simultaneously fill up the largest cages in the hydrate. H_2 is even smaller than intrinsic small interstices of some ice polymorphs. Thus, ice Ih may dissolve up to ~0.1 mol % of H_2 into these interstices. At pressures higher than 0.4 GPa, two other ice polymorphs spontaneously dissolve a far larger amount of H_2 to produce the first discovered pair of dense hydrogen hydrates, called C_1 and C_2.[1] These hydrates have the structures of ice II and Ic and are also called filled ices.[7] The filled-ice II is stable to 3 GPa with a composition H_2:H_2O=1:6. The filled-ice Ic is stable to at least 60 GPa with H_2:H_2O=1:1. We emphasize that these filled ices are stable to one or two orders of magnitude higher pressure than conventional clathrate hydrates. In other words, pressure plays a very profound role in controlling the properties of these filled ices. The physics of molecular transport in the filled-ice hydrates are therefore of critical importance.

II. EXPERIMENTAL METHODS

We applied a high-resolution diamond anvil cell (DAC) NMR method to these filled ices. Pressure was generated using a specially designed nonmagnetic DAC within a magnetic field up to 7 Tesla.[8] This DAC was designed to generate a force large enough to compress larger sample volume, which partly reconciles intrinsic low sensitivity of NMR. A diamagnetic gasket (UNS C17510) with susceptibility matched to the sample keeps the sample field homogeneous to the sub-ppm level.[9] We designed a remarkably sensitive radio-frequency (rf) probe that enables solid-state high-resolution NMR even at gigapascals. Our previous design with 5 mm in diameter[10] already gave a record in its sensitivity and worked fine for NMR of liquids.[11] However, its sensitivity can be still insufficient for solid-state samples of broad bandwidth, especially for ice and hydrate samples that involve strongly dipolar-coupled protons. Such samples generally require higher sensitivity than those giving only sharp resonances.

According to the standard scheme of increasing hardware sensitivity of NMR,[12] we reduced the volume of rf coil while keeping the sample at its center. We fabricated a coil of four turns with 1.2×2.5 mm^2 in a rectangular cross section and 1.2 mm in length, and made of a 75 μm-ϕ silver wire. Note that the coil dimension is much smaller than two opposite diamond anvils with 5 mm in total thickness and 4 mm in diameter. In order to install such a small coil, we laser drilled each anvil to excavate four straight holes with 150 μm in diameter and 2.5 mm in length, along the direction parallel to the anvil's 1.0 mm-ϕ culet surface. The drilling was made using a commercial cutting tool (COMBI Laser System, Bettonville, Wijnegem, Belgium). Like the previous design,[10] direction of the rf field generated by the rf probe is parallel to the gasket surface, so that the field can dip into the sample chamber even if shielding current flows within the metallic gasket. We will report all the fabrication techniques of this rf probe separately.

We prepared our filled-ice samples as follows. A large 400 μm-ϕ sample chamber was drilled into a slightly preindented gasket of 250 μm thickness. We then partially filled the sample chamber with desired volume of H_2O along with an air bubble. The piston-cylinder (P-S) pair of the DAC was sealed to avoid H_2O evaporation and then placed into a gas-loading vessel into which H_2 gas at 1500 bar was filled. To exchange the air bubble by H_2, the *P-S* pair was quickly opened and sealed again within a few seconds. We did not lose any H_2O during this process, which assured that the desired mixing ratio of $H_2:H_2O \sim 1:6$ was obtained. We finally set the rf coil wire through the diamond holes for the NMR analysis.

We compressed the H_2-H_2O two-fluid sample at room temperature, while optically observing the crystal growth through the diamond. At 1.9 GPa, the whole H_2O part was suddenly frozen into an inhomogeneous mixture of ices, presumably consisting of ice VI and small amount of H_2-filled-ice II. The much larger freezing pressure than pure H_2O (at 0.9 GPa) is due to a large amount of dissolved H_2 into the water. After the freezing of the H_2O part, polycrystalline filled-ice II gradually grew by consuming the ice VI and the fluid H_2. The filled ice was growing concentrically into the ice VI body starting from the H_2 fluid pore, so that the growth rate was limited by H_2 diffusion through the filled-ice II. The growth was completed within several hours, indicating that the H_2 diffusion in the filled ice is much faster than in other solids. By further compression, a mixture of filled-ice Ic and ice VII appeared after self-decomposition of the filled-ice II, as expected from the phase diagram.[1]

III. RESULTS AND DISCUSSION

Broadband powder NMR spectra were collected at 291 K with a $\pi/2$-$\pi/2$ solid echo sequence with pulse spacing of 10 μs (Fig. 1). We expected these spectra would be almost featureless due to strong dipolar coupling between its even denser ^{1}H spins than those in ordinary ices. The observation in both NMR spectra of sharp resonances at their near center, indicating a highly mobile species, was there surprising. The acquisition time of Fig. 1(a) was much shorter than T_2^* of L_1, but was longer than T_2^* of L_2 and G_1, so that the area intensity of L_1 was instrumentally reduced. The linewidth of L_1 was also instrumentally broadened. We settled this problem by using a $\pi/2$-π Hahn-echo sequence with pulse spacing of 500 μs. Only the L_1 component gave the Hahn echo, making it possible to obtain intrinsic line profile of L_1, which is no longer an ideal Lorenzian (Fig. 2). In spite of this distortion, the two broadband spectra (Fig. 1) were well fitted with two Lorentzian (L_1 and L_2) and one Gaussian (G_1) peak; other combinations give statistically worse results.

We have two potentially mobile species in the filled ices, those are hydrogen-bonded protons and H_2 molecules. Both of them could give Lorentzian peaks, and the former have more positive δ than the latter.[4] Thus L_2 is assigned to H_2O protons and L_1 is assigned to H_2. The G_1 was not detected when the sample was in the liquid state so that it did not come from the background. Its half-width (Δ_{G1}) is identical with that of static pure ices at 37±1 kHz (Ref. 13) (Fig. 1). This coincidence strongly suggests that the G_1 is assigned to the static part of the ice framework. Its extreme linewidth can only be explained by the strongest dipolar coupling within the ice. Therefore, the static G_1 protons coexist with the mobile L_2 protons within the same filled-ice frameworks. However, the chemical shift of the former (δ_{G1}) is apparently different from the latter (δ_{L2}). This discrepancy may be alleviated if we can strictly evaluate the line shape of L_2, which could have a broad asymmetric shoulder at its lower chemical shift wing, reflecting the axial nature of chemical shift

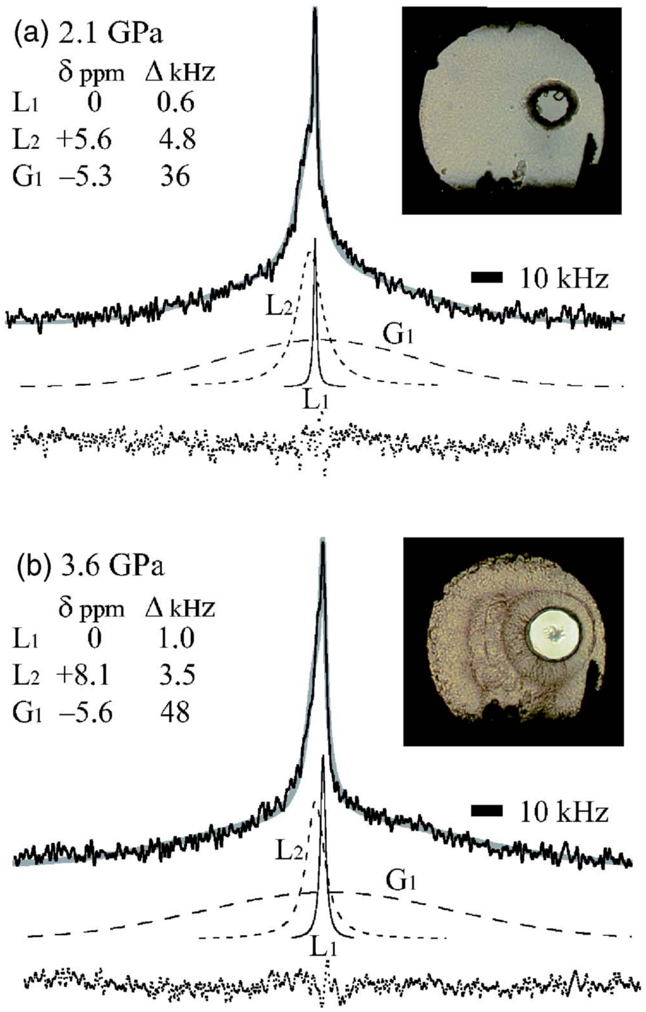

FIG. 1. (Color online) Solid-echo powder NMR spectra and optical micrograph of the relevant samples. The spectra were obtained with a 300 MHz and 300 W solid-state spectrometer. The typical $\pi/2$ pulse length was 1.5 μs. For each figure, the upper part shows the observed spectrum and its fitting curve, the middle part shows model fitting peaks, and the lower part shows the residual. (a) The filled-ice II phase (C_1). The small pore in the figure is H_2 fluid that did not react, which is about one-tenth of total H_2 in the sample. The NMR signal of H_2 mostly came from the reacted filled-ice part because of its larger molar ratio and shorter relaxation time. 2698 transients with 1 s repetition time were averaged. (b) The mixture of filled-ice Ic (C_2) and pure ice VII phases. On further compression, the bright transparent part of polycrystalline filled-ice Ic was formed by the reaction between the fluid H_2 and part of the filled-ice II. The remaining filled-ice II then decomposed into the darker part consisting of a mixture of filled-ice Ic and pure ice VII. 8000 transients with 2 s repetition time were averaged.

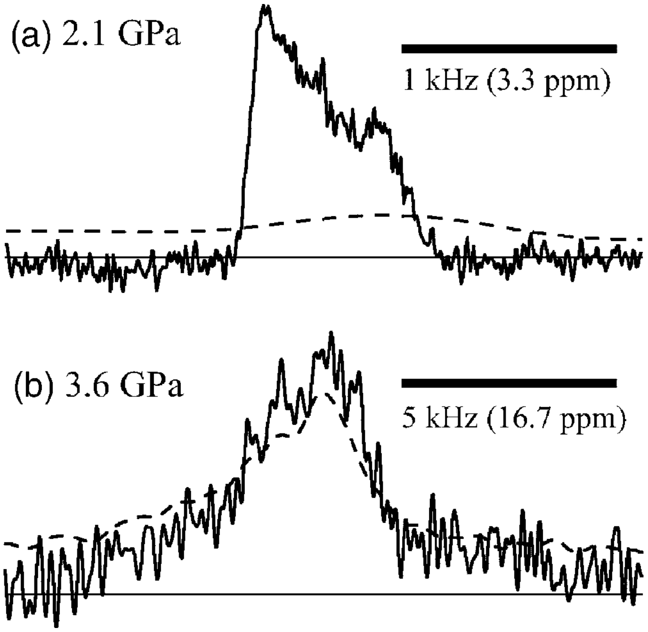

FIG. 2. Hahn-echo spectra of L_1 which gave the intrinsic line shape. Broken lines show the central part of the solid-echo spectra shown in Fig. 1. Note the instrumentally reduced intensity of the broken line in (a).

tensor of hydrogen-bonded protons.[14] Such a broad shoulder cannot be separated from G_1, giving arbitrally lower δ_{G1} than its actual value. To determine the correct line shape of L_2, we must have far better spectra than shown in Fig. 1, which is beyond the scope of this work.

Now we consider the nature of H_2 species. Relaxation times of L_1 were measured at two Larmor frequencies, $\omega_I/2\pi=200$ and 300 MHz (Fig. 3). NMR relaxation of ^1H in molecules forming a crystal is usually induced by two types of motions, which are molecular rotation and translational diffusion.[15] The H_2 molecules in these filled ices are almost free rotors but their angular momentum is modulated when they collide with the surrounding ice framework. With increasing pressure, their rotational correlation time τ_{rot} decreases because of the more frequent collisions of H_2 with the compressed framework. The τ_{rot} of the confined guest molecule is smaller than ω_I^{-1} so that the "extreme narrowing" condition applies, where both relaxation rates $T_{1\text{rot}}^{-1}$ and $T_{2\text{rot}}^{-1}$ become identical, independent of ω_I, and proportionally decreasing with τ_{rot}.[16] The observed T_1^{-1} is consistent with such behavior of $T_{1\text{rot}}^{-1}$. However, another relaxation process must contribute to T_2^{-1}, which behaves differently from T_1^{-1}.

In contrast to τ_{rot}, the diffusion correlation time τ_{dif} increases with increasing pressure because of the increase in activation energy of diffusion, due to narrower channel size through which the H_2 molecules diffuse. Then transverse relaxation rate by diffusion $T_{2\text{dif}}^{-1}$ also increases, which is consistent with the observed T_2^{-1}. Thus, we reconfirm the mobile nature of L_1 from its T_2^{-1} trend. The $T_{1\text{dif}}^{-1}$ should be smaller than $T_{2\text{dif}}^{-1}$ so that τ_{dif} is larger than ω_I^{-1}, where the general theory of diffusion relaxation gives[17]

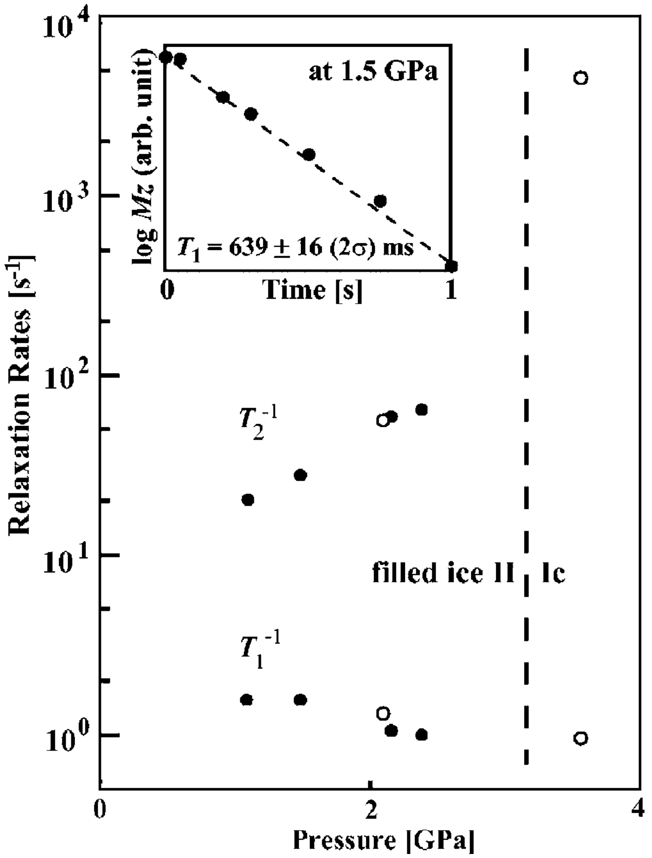

FIG. 3. Relaxation rates of L_1. Filled circles were at 200 MHz and open circles were at 300 MHz. T_1 was measured by a saturation recovery sequence after comb pulses. T_2 was measured by a Carr-Purcell-Meiboom-Gill sequence. These sequences forced the L_2 and G_1 resonances to decay much faster than L_1. A single exponential relaxation was observed at all pressures (inset).

$$T_{1\text{dif}}^{-1}=(\Delta_{\text{dif},X}^2+\Delta_{\text{dif},Y}^2)\frac{\tau_{\text{dif}}}{1+\omega_I^2\tau_{\text{dif}}^2},$$

$$T_{2\text{dif}}^{-1}=\Delta_{\text{dif},Z}^2\tau_{\text{dif}}+\frac{T_{1\text{dif}}^{-1}}{2}, \qquad (1)$$

where $\Delta_{\text{dif},X}$ to $\Delta_{\text{dif},Z}$ are three components of fluctuating local field felt by the diffusing nuclei (in Hz). Our filled-ice samples were fine powders without preferred orientation, which induces isotropic local field on average, $\Delta_{\text{dif},X}^2=\Delta_{\text{dif},Y}^2=\Delta_{\text{dif},Z}^2=\Delta_{\text{dif}}^2/3$. The value of Δ_{dif} can be accurately determined from the geometry of H_2 sites and diffusion path. Although this information is not available, we can approximate it by Δ_{G1} (Fig. 1), because the local fields in ices are primarily controlled by their proton density.[13] The local fields felt by H_2 and H_2O protons in the filled ices come from the H_2O protons of the same density, while they are sensed at different positions. We ignore minor contributions from H_2-H_2 interactions and the effect of increasing density by compression, and obtain

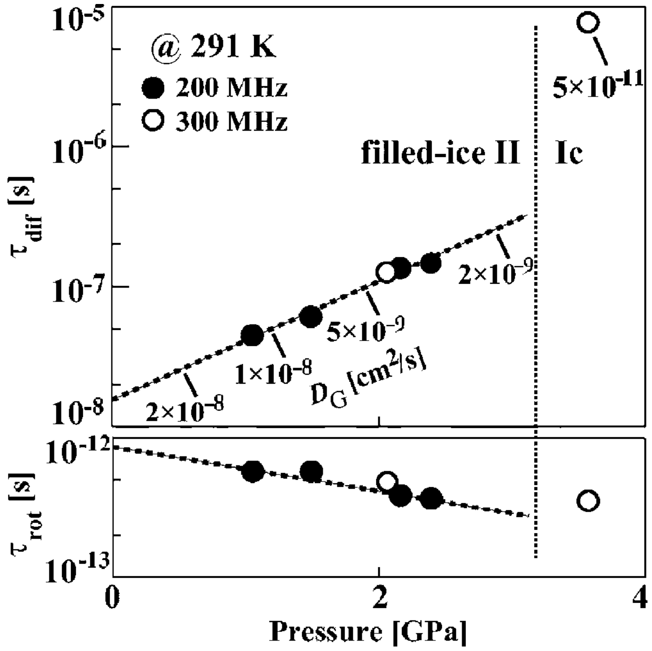

FIG. 4. Two correlation times and D_G of the guest H_2.

$$T_1^{-1} = T_{1\mathrm{dif}}^{-1} + T_{1\mathrm{rot}}^{-1} = \frac{2}{3}\frac{\Delta^2}{\omega_{\mathrm{I}}^2 \tau_{\mathrm{dif}}} + \alpha\tau_{\mathrm{rot}},$$

$$T_2^{-1} = T_{2\mathrm{dif}}^{-1} + T_{2\mathrm{rot}}^{-1} = \frac{1}{3}\Delta^2\tau_{\mathrm{dif}} + \alpha\tau_{\mathrm{rot}}, \qquad (2)$$

where $\alpha = 2.74 \times 10^{12}$.[16] Neglecting the first term of T_1^{-1}, which is much smaller than the second term, we have

$$\tau_{\mathrm{rot}} = \frac{T_1^{-1}}{\alpha},$$

$$\tau_{\mathrm{dif}} = \frac{3(T_2^{-1} - T_1^{-1})}{\Delta^2}. \qquad (3)$$

Then a random walk model gives a guest diffusion coefficient $D_G = \langle r^2 \rangle / 2n\tau_{\mathrm{dif}}$. The $\langle r^2 \rangle$ is the mean square displacement taken from the relevant crystal structure,[1,18] and n is the dimension of diffusion. For rhombohedral filled-ice II, $n=1$ is assumed because the distance to neighbor site along a axis is 4 times larger than that along the c axis. This implies the diffusion is anisotropic within each crystal. For cubic filled-ice Ic, $n=3$ is assumed, which implies the diffusion is isotropic. Figure 4 shows the estimated τ_{rot}, τ_{dif}, and D_G as a function of pressure. The diffusion activation volume of H_2 in filled-ice II, $V_G^* = RTd \log_e D_G / dP = 2.2$ cm^3/mol, is only 40% of that volume for solid hydrogen at a comparable pressure range.[19] The very small V_G^* indicates that guest molecules undergo facile translation motion over a wide pressure range. This distinctive feature arises from the delicate size balance between the guest H_2 and intrinsic interstices of the ice II framework. If the guest is larger than the interstice, the filled ice should not form. If the guest is smaller, the filled ice might form but only at a very limited pressure regime. The H_2-filled-ice II was stable up to 2.4 GPa, which is a factor of 6 larger pressure than the stability limit of pure ice II.[20] It is striking that the fast molecular transport occurred throughout this much extended pressure regime.

The H_2-filled-ice Ic exhibits a factor of 20 smaller D_G than the filled-ice II at the same pressure (Fig. 4). It is still too fast as a diffusion phenomenon in solid crystalline state. Ice Ic framework has 6 times more interstices than ice II, which is more loosely interconnected and easily compressed.[1] Despite of this softness, the filled-ice Ic is stable at least to 30 GPa. It will be a suitable topic of NMR at higher pressure for which we are working now.

The D_G in filled-ice II extrapolated to zero pressure (D_G^{II}) is 3×10^{-8} cm^2/s (Fig. 4). The diffusion coefficient of guest H_2 in ice Ih (D_G^{Ih}) is $\sim 10^{-4}$ cm^2/s, whereas that of framework H_2O (D_F^{Ih}) is $\sim 10^{-10}$ cm^2/s, both at zero pressure.[6,20] A rather large factor of 3×10^3 difference between D_G^{II} and D_G^{Ih} should be associated with the difference in their guest occupancy. Relative to the filled ices, ice Ih interstices are only very weakly filled with hydrogen, whereas the ice II is filled by 80% of maximum guest capacity at 0.5 GPa and almost fully filled at >1 GPa.[18] Thus, the guests in the latter must have many more trials to jump into the neighboring sites. In other words, actual diffusion species in the latter is guest site vacancies, rather than the guest itself. The 3×10^2 times larger D_G^{II} than D_F^{Ih} indicates that the fully filled guests in ice II are still much faster than the ice framework molecules at the condition of fastest diffusion (zero pressure and near the melting temperature). Thus, despite of the factor 3×10^2 smaller D_G due to the full packing, the previously reported "liquidlike" character of H_2 in ice Ih (Ref. 6) is also maintained in the filled-ice II. The fast synthesis of hydrogen hydrates from ice (Ref. 5) is therefore a universal feature of ices of various crystal structures at wide pressure range.

IV. CONCLUSION

NMR at high pressure of filled-ice hydrogen hydrates reveals fast molecular transport of H_2 in the ice frameworks. Molecular rotation and diffusion contribute together to the relaxation of H_2. The former correlation time is smaller than ω_{I}^{-1}, decreasing with pressure, and mainly affects T_1^{-1}. The latter correlation time is larger than ω_{I}^{-1}, increasing with pressure, and mainly affects T_2^{-1}. A liquidlike diffusion coefficient with little pressure sensitivity was deduced from the latter. The fast transport of H_2 is a universal feature of ice polymorphs that have interstices within their structures.

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