

Diffusion dynamics of hydrogen molecules confined in clathrate hydrate

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Hydrogen hydrate is a clathrate hydrate in which H₂ is accommodated into the host cages formed by water molecules. The stability of the clathrate hydrates is dominated by the van der Waals contacts between the guest molecules and the cages. A hydrogen molecule is too small for any of clathrate cages and so the hydrogen hydrate is stabilized only under pressure higher than 2 kbar. However, it was reported that the stabilization pressure is much lowered (ca. 100 bar) by adding tetrahydrofuran (THF) as a helper gas^{1,2}, leading extensive studies on hydrogen hydrates. The H₂-THF hydrate has the typical clathrate sII structure and THF molecules are accommodated in hexakaidecahedral “large” cages, while H₂ molecules are in pentagonal dodecahedral “small” cages.

The purpose of this work is to clarify the dynamics of H₂ molecules in the hydrate by means of the quasielastic neutron scattering (QENS) technique. Owing to large incoherent scattering cross section of H atom, we can preferentially observe the motions of H₂ molecules when THF and water molecules are fully deuterated. We have preliminary performed the QENS measurement using IN5 spectrometer with the energy resolution of 25 μ eV at ILL (France). Here the occupancy x of H₂ molecules in the small cages is estimated to be 0.3 from the reported relation between x and the formation pressure. A QENS broadening corresponding to the motion of H₂ molecules was clearly observed above 180 K, in addition to the contribution from the rotation of TDF (tetra-deuterofuran). The QENS component was fit to the Lorentzian function and the relaxation time was estimated to be ca. 10 ps. In this work, we have carried out the QENS experiment at HFBS

at NIST (USA) to examine the dynamics in the time range between 100 ps and 10 ns.

In the measurement on HFBS, relaxation attributable to H₂ motions was not detected. Recently, Pefoute *et al.* demonstrated that clear QENS signals from H₂ molecules appeared at $100 < T < 250$ K in the timescale of 1-10 ps³.

Furthermore, it was reported by Tait *et al.* that no relaxational process was observed below 150 K in the time range from 1 ps to 10 ps⁴. These results are summarized in Fig. 1. Apparently, it is difficult to understand all results consistently. To settle the dispute about the H₂ motion, we are planning to perform further QENS measurements to explore the motion in the missing time region between 10 ps and 100 ps.

[1] L. J. Florusse *et al.*, *Science* **306**, 469 (2004). [2] H. Lee *et al.*, *Nature* **434**, 743 (2005). [3] E. Pefoute *et al.*, *J. Phys. Chem. C* **116**, 16823 (2012). [4] K. T. Tait *et al.*, *J. Chem. Phys.* **127**, 134505 (2007).

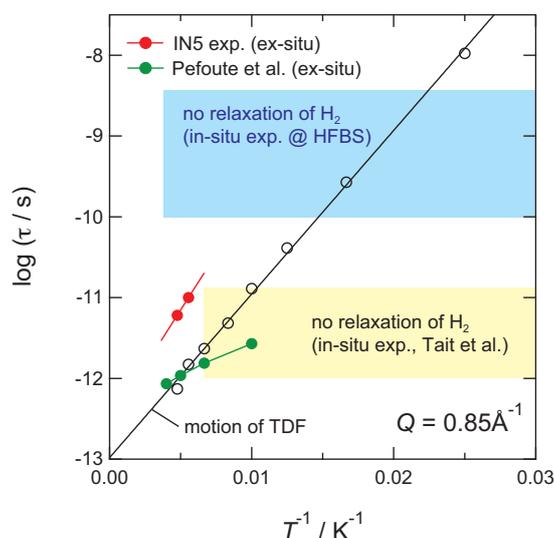


Fig. 1. Arrhenius plot of the relaxation times for the motions of H₂ and THF molecules.