

Diffusion process 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 performed the QENS measurement using a chopper-type tof spectrometer IN5 at ILL (France). The energy resolution of IN5 used in our experiment is 25 μ eV. In the actual experimental procedure, the deuterated stoichiometric THF hydrate (d₈-THF-17D₂O) was prepared and then kept under H₂ gas pressure of 140-160 bar at ca. 260 K for a day to incorporate H₂ gas in the cages. Once H₂ molecules are trapped into the cages, they do not desorb below 200 K even at 1 bar. Therefore, we measured QENS spectra after releasing the applied pressure to reduce the background from H₂ gas. The occupancy x of H₂ molecules in small cages is estimated to be 0.3 from the reported re-

lation between x and the formation pressure.

A clear QENS broadening was observed in $S(Q, \omega)$ of the H₂-THF hydrate above 150 K. From a similar measurement for pure THF hydrate (d₈-THF-17D₂O), we know that the quasielastic scattering due to the rotation of d₈-THF is also observed in this temperature range. Therefore, we fitted the QENS spectra to the combination of the elastic component, a KWW component with fixed relaxation times and β (for the THF rotation), a Lorentzian function (for the H₂ motion), and a constant background. The obtained relaxation times are plotted as a function of inverse temperature in Fig.1. The activation energies for the H₂ and THF motions were estimated to be 23 kJmol⁻¹ and 3.9 kJmol⁻¹, respectively. Further QENS studies are in progress to obtain the overall dynamical map of hydrogen diffusion in the clathrate hydrate.

References

- [1] L. J. Florusse *et al.*, Science **306**, 469 (2004).
- [2] H. Lee *et al.*, Nature **434**, 743 (2005).

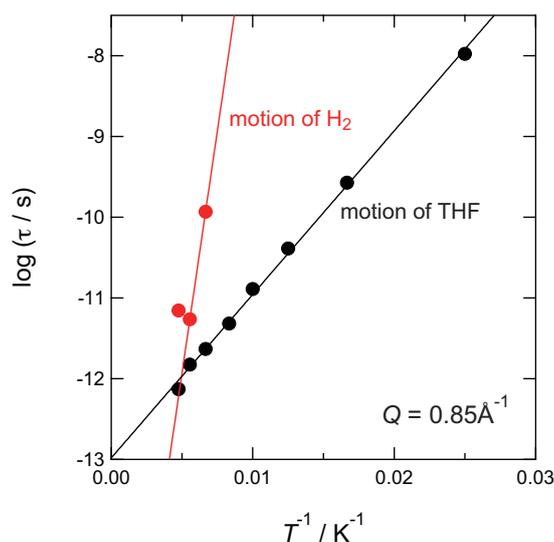


Fig. 1. Arrhenius plot of the relaxation times for the motions of H₂ and THF molecules.