

Hydrogen dynamics 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, 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.

We aim to investigate the dynamics of the H₂ molecules in the clathrate hydrate by means of quasielastic neutron scattering (QENS) techniques. The QENS measurements for H₂-TDF were carried out using the two spectrometers IN5 at ILL (France) and HFBS at NIST (USA). In the *ex-situ* measurement on IN5, a QENS broadening corresponding to the motion of H₂ molecules was clearly observed, in addition to the contribution from the rotation of TDF. On the other hand, no relaxation was detected at 5 < T < 260 K in the *in-situ* measurement on HFBS. So far, two groups have reported QENS works on this system, but their results conflict with each other [1, 2]. To settle the issue, we have carried out *in-situ* QENS measurements on DCS at NIST. Since the motion of TDF was observed over the wide temperature range even though it was deuterated, the *in-situ* measurement is highly effective to make the exact subtraction of the contribution

from TDF. The incident wavelength used are 4.8 Å and 8.5 Å, giving rise to energy resolutions of 118 μeV and 25 μeV, respectively.

Figure 1 shows the QENS spectra of TDF and H₂-TDF hydrates taken at T = 210 K and Q = 0.85 Å⁻¹. No difference between them was detected. The similar results were obtained at all temperatures measured (80 < T < 210 K), suggesting that H₂ molecules do not move on the 1-100 ps timescale. From the results obtained so far, it appears that QENS originating in the H₂ motion were observed in the *ex-situ* measurements but not in the *in-situ* ones. The subtraction procedure of the TDF contribution may cause misinterpretation of the data. We thus conclude that the motions of H₂ are not in the time range accessible to neutron scattering (1 ps - 10 ns) and should be slower than the range.

References

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- [2] K. T. Tait *et al.*, J. Chem. Phys. **127**, 134505 (2007).

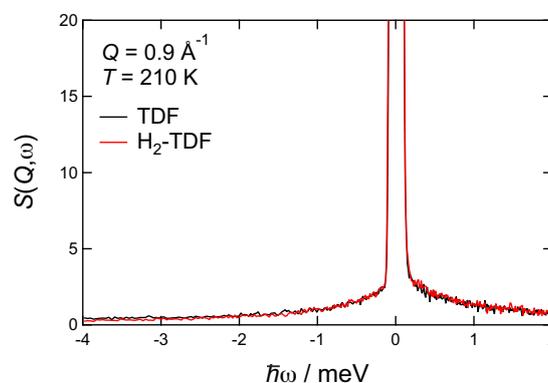


Fig. 1. QENS spectra of TDF and H₂-TDF hydrates taken on DCS.