Experimental report

07/03/2019

Proposal:	**6-07-29**	**Council:**	4/2017

Title: Microscopic diffusion of hydrogen molecules in ice clathrate under high pressure

Research area: Physics

This proposal is a new proposal

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Samples: D2O-H2

Instrument	Requested days	Allocated days	From	To
IN5	3	3	26/03/2018	29/03/2018

Abstract:

Hydrogen clathrate hydrate is an inclusion compound in which a hydrogen-bonded crystalline ice structure encages hydrogen molecules. It has been suggested as candidate material for hydrogen storage applications and attracted considerable attention during the last decade. In addition, it is likely to exist in nature since hydrogen and water ice are common constituents of the universe. We recently performed a high-pressure inelastic and quasi-elastic neutron scattering experiment on IN5 to characterize the self-dynamics of the encaged hydrogen molecule. This experiment was performed in a gas pressure cell up to 5 kbar using helium as pressure transmitting medium. Here we propose to conclude such measurements using a similar setup with argon as pressure transmitting medium.

During this experiment, we successfully completed our study of the dynamics of H_2 and D_2 molecules in hydrogen hydrates at ambient and high pressure.

Hydrogen hydrate samples were prepared at the Helmholtz-Centre Berlin (Germany) by exposing deuterated ice spheres at 244 K to H_2 or D_2 gas at 0.28 GPa. Inelastic and quasi-elastic neutron scattering measurements at temperatures between 1.5 and 75 K were performed on IN5 using different neutron wavelengths in the range 3.0-6.0 Å. A cylindrical gas pressure cell of aluminum alloy (internal diameter of 6 mm) was employed to generate high pressures up to 5 kbar.

At moderate pressures, simple hydrogen hydrate form the so-called clathrate structure II (or sII), with one hydrogen molecule occupying the small cage and several ones (up to four) occupying the large cage. The dynamics of one H_2 (or D_2 or HD) molecule encaged in the *small* cage of clathrate sII at low temperature has been investigated in the past by means of inelastic neutron scattering experiments [1-3] and theoretical works [2,3], and is a fascinating example of roto-translational quantum dynamics of a nanoconfined light molecule. On the other hand, the quantum dynamics of hydrogen confined in the *large* cage of the structure had not been characterized experimentally before our study.

During the assigned 3 days of beamtime, we measured 4 different samples and the empty cell. We first measured a D_2O-H_2 hydrate sample (8 mm in diameter) occupying clathrate sII at ambient pressure and 1.5 K, using 4 different neutron wavelengths (3.0, 3.5, 4.8, and 6.0 Å). The spectra measured on this sample are reported in Figure 1. Each inelastic peak or band in the spectra can be assigned to a quantum roto-translational transition of H_2 confined in the small or in the large cage of the structure. In Figure 1, rotational transitions are indicated by changes of the rotational quantum number J and translational transitions are labelled by changes of Δn.

Then we compressed a D_2O-H_2 hydrate sample (6 mm in diameter) to 0.5 GPa using argon as pressure transmitting medium. The sample transformed into the high-pressure structure filled ice II (or structure C1), as indicated by the diffraction pattern obtained directly on IN5 during the experiment.

We measured spectra of this sample at 0.5 GPa and 6 temperatures between 1.5 and 75 K. To investigate the effect of substituting the encaged H2 molecules with D_2, we also measured a clathrate sII D_2O-D_2 hydrate sample (8 mm in diameter) at ambient pressure and 6 different temperatures in the range 1.5-40 K.

Finally, we compressed a D_2O-D_2 hydrate sample (6 mm in diameter) to 0.3 GPa using helium as pressure transmitting medium, but unfortunately the pressure cell started to leak.

The results obtained during this experiment and during our previous IN5 beamtime (exp 6-07-5) provided a range of new valuable information on the quantum dynamics of H_2 and D_2 molecules trapped within nanocavities of the two hydrate structures, namely clathrate sII and structure C1. We identified two excited translational energy levels for H_2 encaged in the large cage of clathrate sII and one for D_2. The transition from the ground state to the first excited translational state of H_2 ($J=1 \longrightarrow 1$, $\Delta n=1$) appears in the spectra as a triplet at energies of 1-3 meV (see Figure 1). The existence of three peaks is likely to be related to the existence of translations involving one, two, or three H_2 molecules at the same time. The temperature and pressure dependences of those modes were also studied. The effect of substituting H_2 molecules with D_2 turned out to be an anomalous change in the peaks position.

We observed that the effect of applying pressure on the sample is a shift in energy for all peaks associated with transitions involving a change in the translational state of the H_2 molecules in the small or in the large cages of sII. The peak associated with a purely rotational transition (J=1⟶0, Δn=0) was insensitive to pressure variation.

Finally, we observed that the effect of inclusion of helium in the structure is a spectacular suppression of all peaks associated with a change in the translational state of H_2 in the large cage.

Those results constituted an important part of the EPFL/ILL PhD thesis dissertation of Umbertoluca Ranieri [4] and are matter of an article recently published [5].

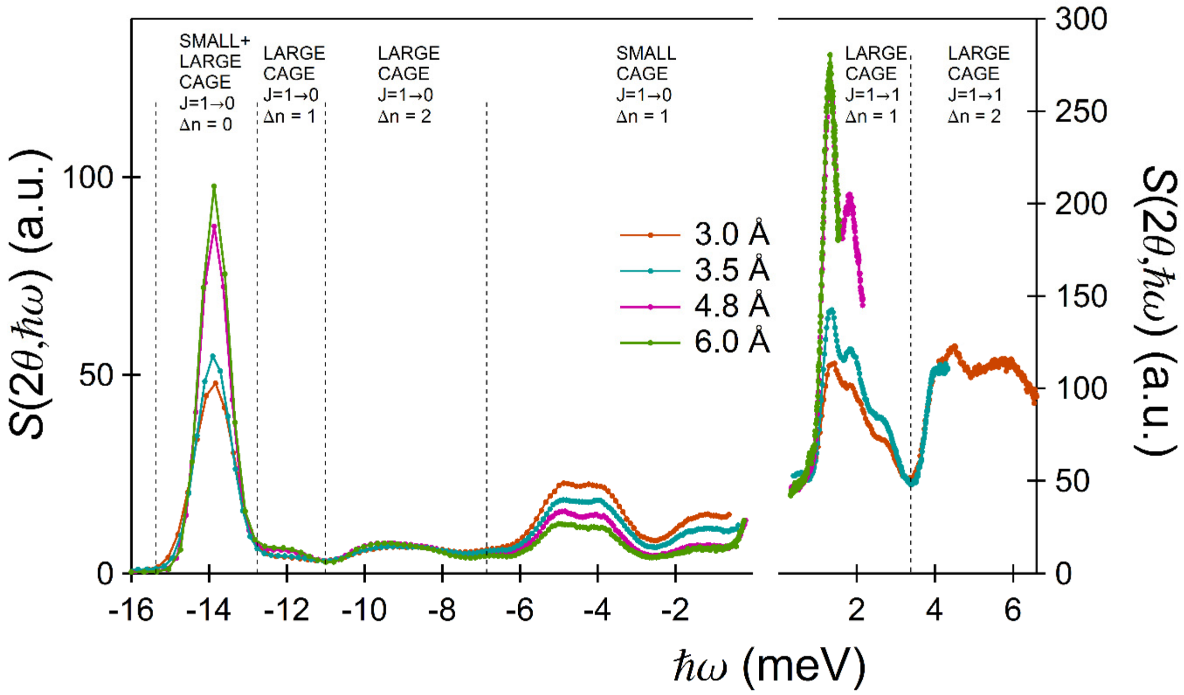

Figure 1: Spectra of clathrate sII D_2O-H_2 hydrate at ambient pressure and 1.5 K, measured using the indicated incident neutron wavelengths during beamtime 6-07-29 on IN5. The elastic line is not plotted; positive and negative $\hbar\omega$ have different y-axis scales.

References

[1] L. Ulivi et al., Phys. Rev. B 76, 161401(R) (2007).

[2] M. Xu et al., Phys. Rev. B. 83, 241403(R) (2011).

[3] D. Colognesi et al., J. Phys. Chem. A 117, 7314 (2013).

[4] U. Ranieri, PhD Thesis, “Guest dynamics in methane hydrates and hydrogen hydrates under high pressure.” École Polytechnique Fédérale de Lausanne, 2018.

[5] U. Ranieri et al., “Quantum dynamics of H_2 and D_2 confined in hydrate structures as a function of pressure and temperature.” J. Phys. Chem. C 123, 1888–1903 (2019).