Experimental report

17/09/2018

Proposal: **INTER-365** **Council:** 10/2016

Title: Internal time on IN6

Research area:

This proposal is a new proposal

Main proposer: **Umbertoluca RANIERI**

Experimental team: Umbertoluca RANIERI

Local contacts: Michael Marek KOZA

Samples: D2OH2
D2OCH4

Instrument	Requested days	Allocated days	From	To
IN6	2	2	30/01/2017	01/02/2017

Abstract:

During this experiment we completed our study of the self-dynamics of methane molecules in methane clathrate hydrates at high pressure.

The CH_4–D_2O methane clathrate hydrate sample in phase sI was prepared at the Department of Crystallography of the University of Göttingen (Germany) using 99.9% deuterated ice, following the procedure described in refs [1,2]. Quasielastic neutron scattering measurements at 1.0 GPa were performed on IN6 using an incident neutron wavelength of 5.12 Å. The VX5 Paris-Edinburgh press was used to generate high pressure.

In the framework of the ILL/EPFL PhD thesis of Umbertoluca Ranieri [3], we employed quasielastic neutron scattering to characterize the diffusive dynamics of methane molecules in methane hydrates occupying different clathrate structures or structure coexistences. By changing pressure, we were able to form pure clathrate structure I (sI), pure clathrate structure H (sH), coexistence of sI and sH and coexistence of sI and structure II (sII).

During this beamtime, we measured methane hydrate during transformation from sI to sH. The sI-sH sample was prepared by compressing methane clathrate hydrate originally in sI to 1.0 GPa at liquid nitrogen temperature and then warming it up to 295 K. The relative amount of sH was found to slowly increase over time and the transformation into pure sH was completed within ~12 h. An example of IN6 spectrum recorded during this time is reported in Figure 1 and shows a very weak quasielastic signal. This is in contrast with the clear quasielastic signal we measured for the sI-sII sample with the same instrumental conditions (see Figure 1).

These results highlight the very particular nature of the interfaces between coexisting sI and sII (one stable and one metastable phase of methane clathrate), compared to the more common scenario of the transition between sI and sH (two stable phases) and have been published in ref [4].

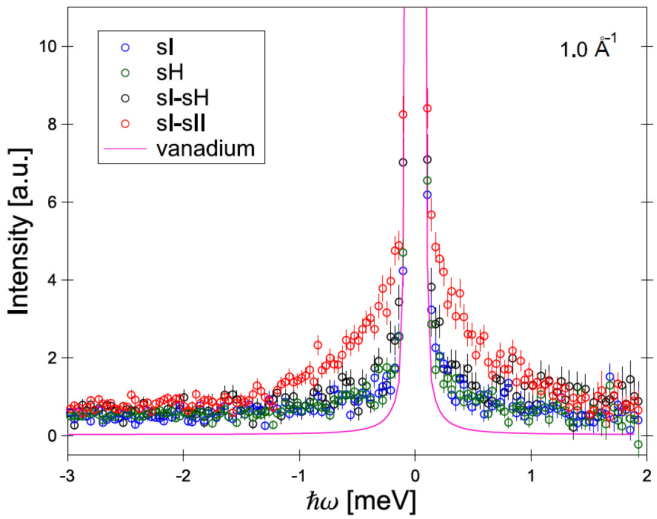

Figure 1: Examples of QENS spectra of methane hydrate at Q=1.0 Å^{-1} in pure clathrate sI (at 0.4 GPa and 290 K), in pure clathrate sH (1.4 GPa and 290 K), in clathrate sI-sH (1.0 GPa and 295 K), and in clathrate sI–sII (0.8 GPa and 282 K). The instrumental resolution function is also shown. Reproduced from ref [4].

References

[1] W. F. Kuhs et al., J. Phys. Chem. B 110, 13283-13295 (2006).
[2] T. C. Hansen et al., J. Chem. Phys. 144, 054301 (2016).
[3] U. Ranieri, PhD Thesis, "Guest dynamics in methane hydrates and hydrogen hydrates under high pressure." École Polytechnique Fédérale de Lausanne, 2018.
[4] U. Ranieri et al., Nature Communications 8, 1076 (2017).