Experimental report

15/05/2024

Proposal: 7-03-232 **Council:** 4/2023

Title: Nematic ordering in hydrogen hydrates at high pressure and low temperature

Research area: Physics

This proposal is a new proposal

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Samples: H2-D2O

Instrument	Requested days	Allocated days	From	To
IN5	3	3	13/11/2023	16/11/2023

Abstract:

Gas hydrates have received considerable attention in the last decades due to their extensive natural occurrence on Earth and extraterrestrial bodies, and to their significant applications in sustainable technologies. In particular, hydrogen hydrate (HH) drew attention of scientists as one of the most promising materials for hydrogen storage. DFT simulations performed by our group indicate that HH in the C2 phase, its stable phase above 2.5 GPa, is characterized by nematic ordering of the hydrogen molecules at temperatures below 80 K. Nematic order plays a prominent role in disparate material classes such as the cuprates, some ruthenates or the iron-based compounds and may be interrelated with superconductivity, but has never been observed in gas hydrates. Here we propose to investigate the H2 rotational dynamics in H2-D2O samples in the C2 phase at 3, 5 and 8 GPa in the 5 to 100 K range by using the HP-QENS technique developed in the past years by our group in order to characterise the predicted nematic state.

IN5 Report experiment 7-02-215 - 233 cycle

Nematic ordering in hydrogen hydrates at high pressure and low temperature

Introduction

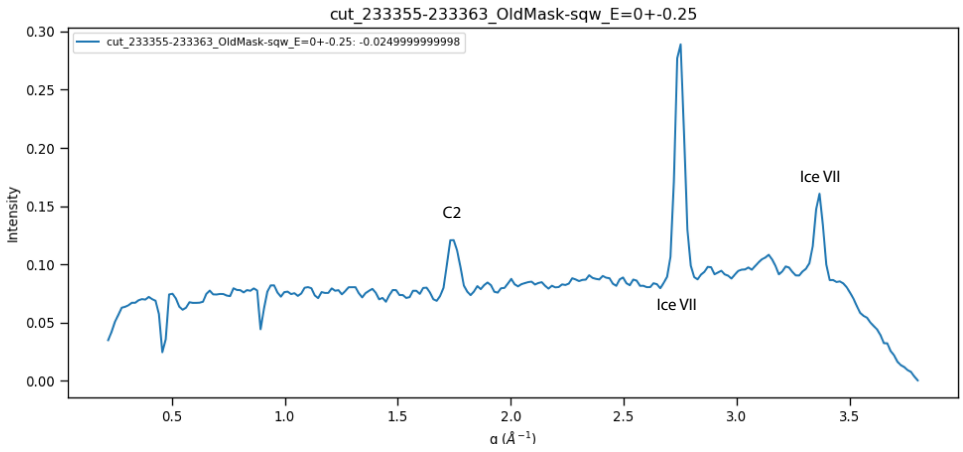
Gas hydrates have received considerable attention in the last decades due to their extensive natural occurrence on Earth and extraterrestrial bodies, and to their significant applications in sustainable technologies. In particular, hydrogen hydrate (HH) drew attention of scientists as one of the most promising materials for hydrogen storage. Classical MD simulations performed by our group indicate that HH in the C2 phase, its stable phase above 2.5 GPa, is characterized by nematic ordering of the hydrogen molecules at temperatures below 80 K. Moreover, quantum calculations show that the potential that the hydrogen molecules feel due to the water molecule cage, lifts the degeneracy in m of the J=1 rotational level which causes a splitting of about 5 meV. In this experiment we measured the ortho-para transition of the hydrogen molecules inside the filled ice structure C2. We found a splitting in the J=1 rotational level in good agreement with the numerical simulations.

Sample preparation

Sample was H2-D2O sample prepared in Florence. We prepared capsules of sample and loaded two clump modules (#1 and #2). Anvils were made od Sintered Diamonds. We used TiZr gaskets.
The clamp #2 was inserted in the PE press.

3 Å

We acquired spectra at 3 Å to check the diffraction. At the beginning no peaks were visible (probably we were in the SII phase) but we could see some quasi-elastic contribution, meaning that there was hydrogen in the cell ***(#233350-#233352***).
We compressed until we observed peaks from Ice VII and C2 phase. From the Ice VII equation of state we were at 4.2 GPa ***(#233353-233354***). We compressed further and stopped at 6 GPa (1200 bar) ***(#233355-233363***).
We started to cool the cell and acquired diffraction data while cooling ***(#233364-233397***)



4.8 Å

#233398-233442 acquisition at 4 K

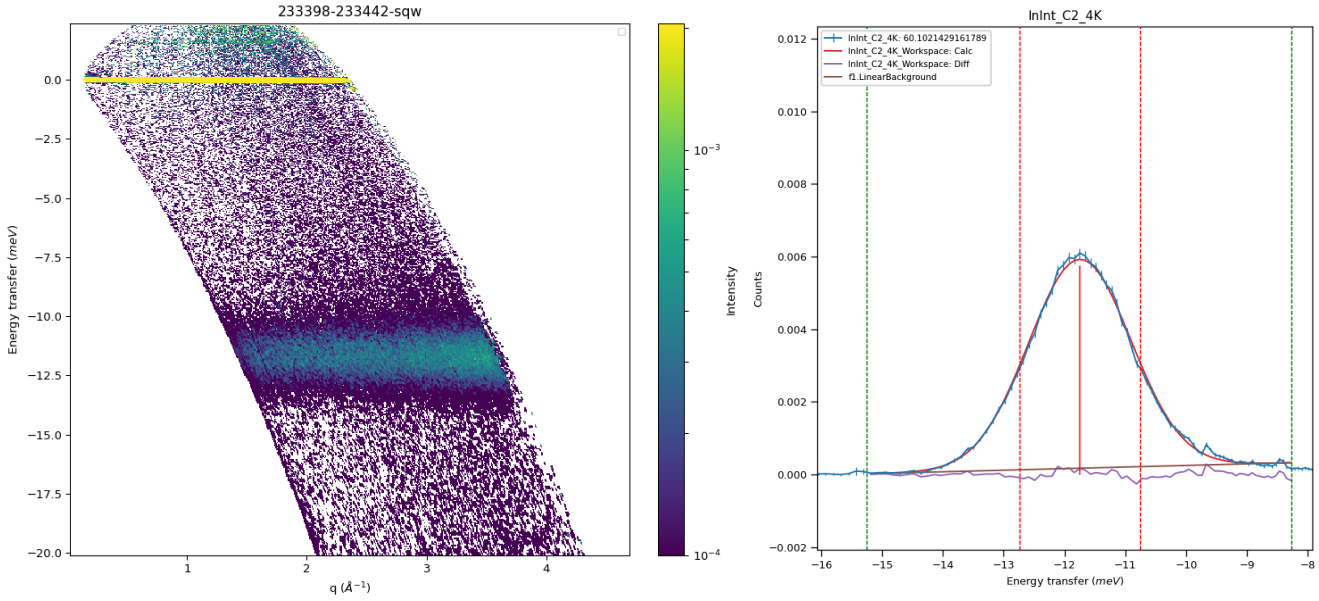


Figure 1: Complete S(Q,omega) after data reduction (left) and integration along Q (rigth)

If we integrate over Q we obtain one peak, slightly asymmetric. This peak can be fitted with a Gaussian function centered at -11.6 meV. We can then bin the data at different Q values to study the Q evolution of the peak. Q binning is 0.1 $Å^{-1}$.
We obtain constant HWHM and roughly constant central value.

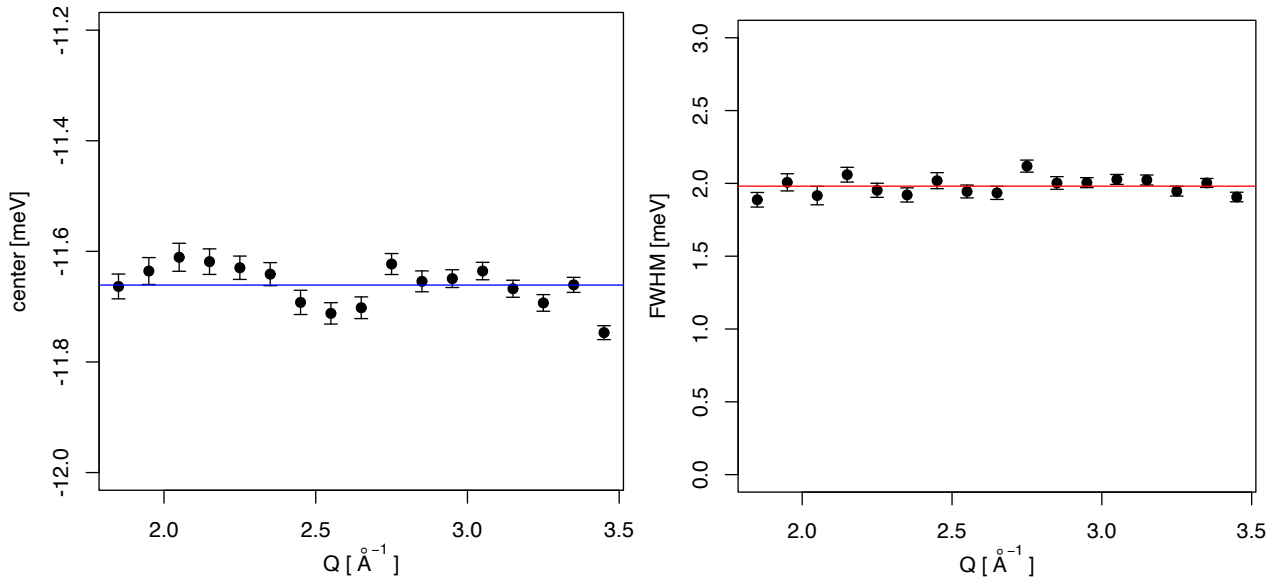
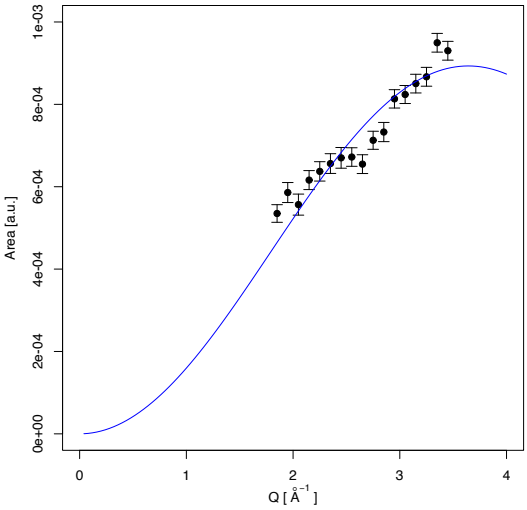


Figure 2: position of the gaussian peak and HWHM

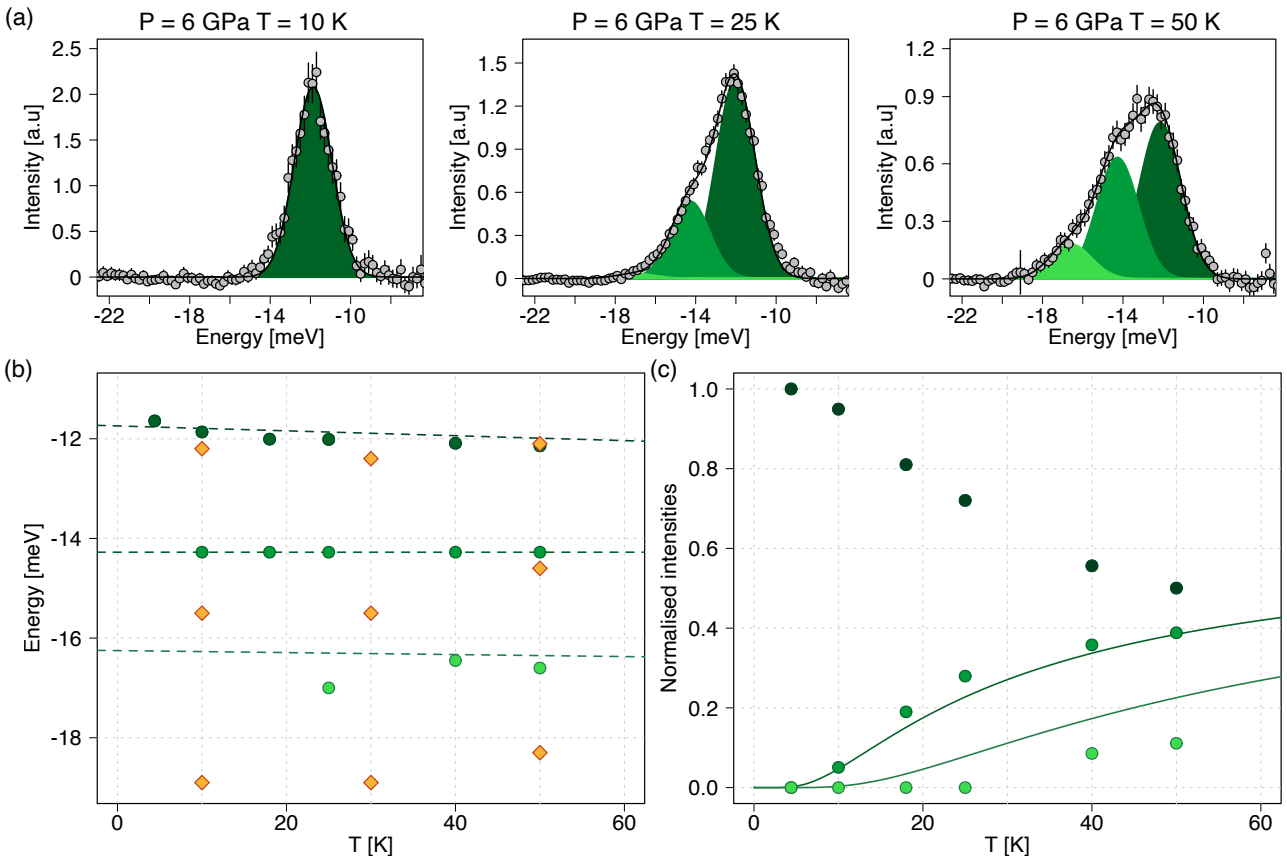
For the intensities we can fit them with the following function: $y = Be^{-Q^2<u^2>/3} j_1^2(\frac{d_{HH}}{2}Q)$.



If we constrain d_{HH} to the literature data (0.741 Å) we obtain B=(0.0114±0.0006) and $< u^2 >$ = (0.13±0.02) $Å^2$
Similar results on the Q dependence are obtained at higher T.

Temperature evolution

We then collected other 5 other temperatures:



We observe a progressive filling of the successive levels as the temperature is raised. The energy level positions are in good agreement with simulations. For the intensities the second peak follows nicely the Boltzman distribution while the third peak seems to populate more slowly.

Q analysis at 50 K

All three peaks have a Q dependent intensity in good agreement with a Bessel function. The mean square displacement at this temperature is of 0.19 $Å^2$