Experimental report

14/11/2023

Proposal: 6-07-102 **Council:** 10/2022

Title: Dynamics of molecular hydrogen in the strong spatial confinement of microporous carbons

Research area: Physics

This proposal is a new proposal

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Samples: Nanoporous carbon beads

Instrument	Requested days	Allocated days	From	To
IN16B	4	4	18/09/2023	25/09/2023
PANTHER	4	3		

Abstract:

This proposal aims at studying the diffusion of molecular hydrogen (H2) and the ortho- to para-H2 transition in strong spatial confinement in a nanoporous carbon with sub-nm pore sizes particularly from low cryogenic temperatures up to temperatures of technical relevance, i.e., 2-100 K. Diffusion dynamics of solid-like ortho-hydrogen confined in these narrow pores will be studied on the high resolution IN16B backscattering spectrometer at five temperatures (20, 50, 77 and 100 K) and different H2 pressures (corresponding to different loadings). The para-to-ortho transition line has a three-fold degeneracy which is lifted as a function of the local symmetry of the adsorption site, with line-shifts that are dependent on the intensity of the interaction between the H2 molecule and the host surface. These interactions can be studied using inelastic neutron scattering at the PANTHER instrument. The combination of quasi-elastic neutron scattering (QENS), INS, gas adsorption analysis and carbon structure modeling will help to identify the role of H2 confinement and diffusional properties in nanopores

Experimental Report for Proposal 6-07-102

Dynamics of molecular hydrogen in the strong spatial confinement of microporous carbons

(18.09.-25.09.2023, D16)

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Aim of the experiment:

The aim of this proposal was to study the diffusion of molecular hydrogen (H_2) and the ortho- to para-H_2 transition in strong spatial confinement in a nanoporous carbon with sub-nm pore sizes particularly from low cryogenic temperatures up to temperatures of technical relevance, i.e., 2-100 K. Diffusion dynamics of solid-like ortho-hydrogen confined in these narrow pores were studied on the high resolution IN16B backscattering spectrometer at five temperatures (20, 50, 77 and 100 K) and different H_2 pressures (corresponding to different loadings). The para-to-ortho transition line has a three-fold degeneracy which is lifted as a function of the local symmetry of the adsorption site, with line-shifts that are dependent on the intensity of the interaction between the H_2 molecule and the host surface. These interactions can be studied using inelastic neutron scattering at the PANTHER instrument. Facilitating the Panther instrument to study the para-to-ortho-transition in more detail was not possible due to an unresolved issue with the Fermi chopper. The previous experiments at the D16 instrument of ILL, facilitating a disordered and highly microporous material have been recently summarized in a publication submitted to carbon journal [1]. The main results from our previous SANS experiments at D16 for different materials (see reports **1-04-218, 1-04-235 and 1-04-242**) was that for pressures up to 1 bar at application relevant temperatures around 77 K only very small pores of ≈ 6-8 Å size (so called ultramicropores) are occupied with a highly densified phase. The density in the smallest pores is approaching or even exceeding the bulk solid density [1], whereas in larger pores the gas only starts to noticeable densify at pressures well above one bar. This material was also to be studied using QENS and INS, but due to its high Oxygen and Hydrogen contents, we have decided to investigate an ordered mesoporous carbon (soft templated carbon – STC) exhibiting a considerable fraction of micropores [2].

Experimental details:

The experiments were conducted using the gas sorption analyzer available at the ILL at various pressure points up to 20 bar and temperatures down to 10 K using H_2. The sample was degassed at 250 °C under vacuum using the degassing station of the AutosorbIQ3 (Qantatec) of our home lab facilities. The degassed sample was left under Nitrogen atmosphere and sealed in a special air-tight glass cell. The sample was then transferred into the Argon-glovebox and filled into the sample holder, thus preventing contamination with air and humidity. The sample stick was removed from the glovebox and the sample was put under vacuum (10^{-6} mbar) at room temperature for 2 h. Afterwards the sample was placed in the OrangeCryostat and cooled to 2 K and fixed window scans (FWS) were performed during the cooling period. A full QENS spectrum at 2 K was collected, which helps to calculate the instrumental resolution function, as lattice vibrations at this temperature are not expected. A QENS spectrum for vanadium was also recorded at 2 K, as well as the empty cell at all temperature where a full QENS spectrum was recorded.

The measurement sequence was performed as follows:

1. The sample was heated/cooled to 77 K to perform H_2 injection up to a desired uptake (2.4, 6.37 and 10.05 mmol/g)
2. Subsequent cooling to 2 K with a ramp of 1 K/min and collection of FWS at 0 and 2 µeV.
3. Holding at 2 K for 30 min and simultaneous collection of FWS
4. Heating protocol with 1K/min and FWS up to the desired temperatures to perform full QENS spectra (25, 50, 77 and 100 K) for 3-4 h.
5. Cooling to 77K for the next H_2 injection.

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[1] Experimental Team
[2] Local Contact
[3] Supervision

Collected data and results:

Figure 1 shows the fixed window scans (FWS) for the first dose of 2.4 mmol H_2/g collected at a) 0 and b)0.02 meV. The sample cell temperature was set to 77 K and the dosed H2 was at room temperature. Thus we believe that the gas entering the pore system should consist of the room temperature equilibrium mixture of para:ortho H_2 of 1/3. After equilibrium adsorption was reached (~20 min) the sample was cooled to 50 K, indicated by the blue square points in Figure 1. The intensity of the elastic line is increasing as the temperature is decreasing, which can be partly attributed to the decreased dynamics of the hydrogen. The same trend is observed at 0.002 meV until the intensity is reaching a maximum around 50 K. The following decrease of intensity at higher energy transfers can be attributed to a decrease in ortho-H_2, which exhibits a large incoherent scattering cross section. Furthermore, below 25 K the intensity is changing rapidly as the confined H2 seems to get immobilized as well more ortho-H_2 might have converted to para-H_2. A more detailed deliberation of the para:ortho ration can be extracted from the energy gain- and loss-spectra we plan to collect at Panther. After cooling to 10 K we collected a full QENS spectrum for 1.5 h, with a subsequent heating to 25 K. Now the intensity is increasing with increasing temperature which we attribute a para:ortho transition as well as an increase in mobility. After the collecting the QENS spectrum at 50 K for 4 h an increase in intensity at 0.02 meV can be seen. This might be due to an increase of ortho-H2 as well as to increased mobility of confined H2.

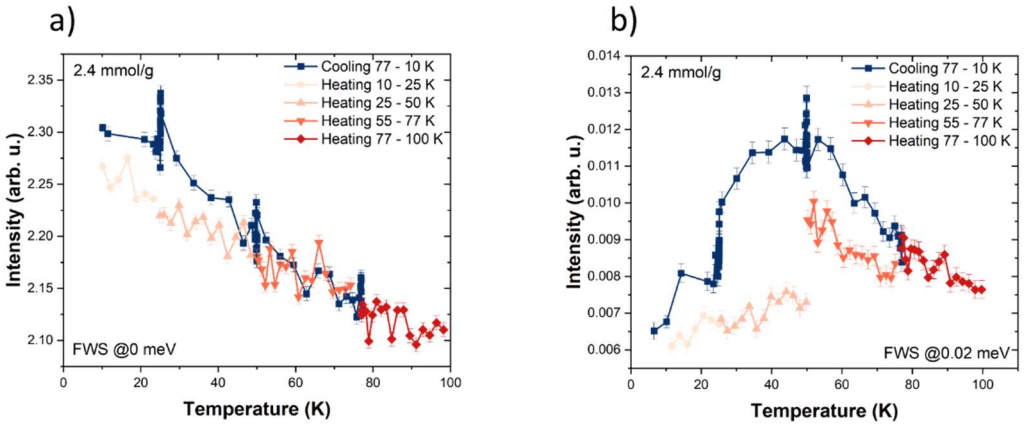

Figure 1: Fixed window scan collected at different temperature and at a H2 loading of 2.4 mmol/g: a) elastic line at 0 meV and b) at 0.02 meV

In figure 2 a)-d) the collected QENS spectra at different temperatures and H_2 loadings are shown. It is evident that with increasing gas amount the overall intensity is increasing, as more H_2 molecules are present in the pore space. At 25 K the QENS spectrum at the highest H_2 loading seems also to show a slight increase in width, which will be further investigated by fitting of the data sets. At 50 K the increase in width with increasing temperature can be attributed to an increased mobility of H_2 molecules, especially at the highest dosing, as we believe that the hydrogen is populating the ordered mesopores as well as the ultramicropores. From earlier SANS experiments we conclude that for pressures up to 1 bar the H_2 is only adsorbed in the smallest pores (< 1 nm), thus at higher loadings we might identify a second diffusional time constant of H_2 adsorbed in mesopores. The fitting of the QENS spectra will be carried out in the Mantid software packages available at ILL.

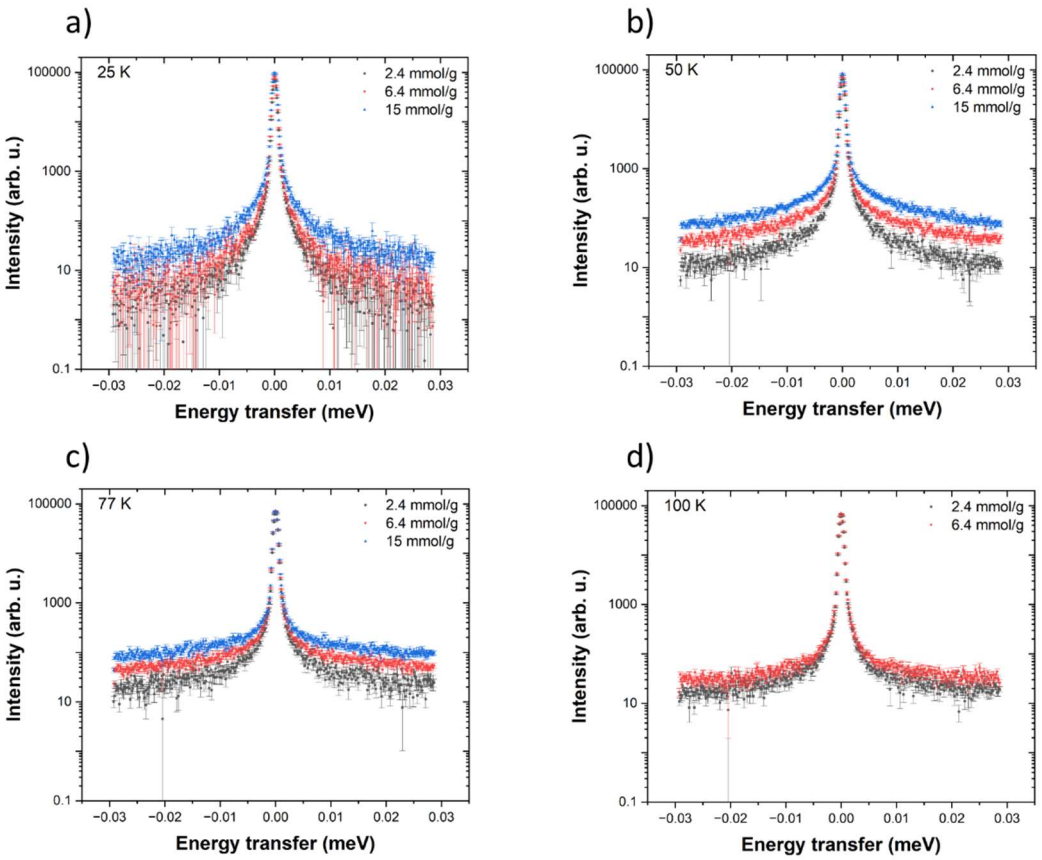

Figure 2: full QENS spectra collected at different loadings and temperatures: a) 25 K, b) 50 K, c) 77 K and d) 100 K

Further experimental investigations and data analysis:

The STC model material gives rise to a clear separation of the meso- and micropore scattering, which helps to understand the pore filling mechanism in more detail. A similar material with higher volume fraction of micropores was recently investigated using Quasi-Elastic neutron scattering (QENS) at IN16b (proposal 6-07-102 and the respective report) and is intended to be measured also by inelastic neutron scattering (see also proposal 7-05-603). From those experiment details about adsorbate diffusion within nanopore confinement [3] and the ortho-to-para H_2 transition [4], as well as differences in adsorption behavior can be elucidated. From SANS we can identify the position of the hydrogen molecules within the porous structure, thus generating a holistic picture of the effects of confinement on the adsorbate density as well as the dynamics.

References:

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