# Experimental report

23/01/2024

**Proposal:** 7-05-555 **Council:** 10/2022

**Title:** Hydrogen mobility in activated MoS2 catalysts

**Research area:** Chemistry

**This proposal is a new proposal**


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**Samples:** MoS2 powder

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| WASP | 7 | 0 | | |
| IN5 | 4 | 3 | 02/06/2023 | 05/06/2023 |


**Abstract:**

The layered crystal molybdenum disulfide, MoS2, is one of the most studied candidate catalyst for replacing the rare and expensive platinum in hydrogen. Its activity can be enhanced considerably by the creation of active sites via plasma treatment.
Despite intense recent research efforts, there is a lack of understanding how hydrogen moves and reacts in the activated catalysts. This is important, because two alternative reaction mechanisms have been proposed for water electrolysis at MoS2 surfaces, which differ in the step of recombination to molecular hydrogen. Here, we propose to use QENS and spin-echo spectroscopy to study hydrogen diffusion in untreated and plasma-treated MoS2 samples. In using well-defined powder samples we will be able to extract the diffusion of hydrogen in this important catalyst material with unprecedented precision.

**Experimental Report 7-05-555 „Hydrogen mobility in activated $MoS_2$ catalysts "**

## 1. Introduction

Climate change is one of the central societal issues at present and, hence, decarbonization of the global energy system is urgent. In this context, hydrogen gas is an important energy carrier, because it can easily be stored for later use in fuel cells and it can be produced by water electrolysis on the basis of renewable energies [1]. However, for the process of water splitting low-cost catalysts are needed to replace the highly active, but expensive platinum catalysts.

The layered crystal molybdenum disulphide, $MoS_2$, has shown promising behaviour as a catalyst for the hydrogen evolution reaction (HER) [2,3]. In fact, its activity can be enhanced considerably by the design of active sites via controlled formation of small-scale structures [3], by tailoring the binding energy of reactive species by means of doping [4-8] and by improving mechanical contact to the electrode and enhancing bulk conductivity [7]. Plasma treatment is a very versatile tool to modify a material in several ways to meet these requirements [8,9,10].

Previously we have performed a detailed study on the motion of hydrogen in $MoS_2$ single crystals using QENS at ILL and MLZ as well as photoelectron spectroscopy (XPS) at BESSY, Berlin [11-13].

Considerably different diffusion properties have been found for hydrogen atoms and molecules, respectively. Hydrogen atoms move parallel to the $MoS_2$ basal planes with a diffusion coefficient of about $1 \times 10^{-9}$ $m^2/s$ at room temperature. No spatial confinement is observed on the length scale of cold neutron TOF spectrometers. The data allow interpretation in terms of continuous Brownian diffusion or jump diffusion with a continuous distribution of jump lengths. For electrolytically loaded samples, in addition, there is motion of recombined hydrogen molecules within the material. Using QENS, the motion of hydrogen molecules is observed below 500 K and has been assigned to jump diffusion of rotating molecules with a diffusion coefficient of around $5 \times 10^{-8}$ $m^2/s$. Diffusion studies contribute to elucidate, which transport mechanisms are necessary in the water splitting reaction.

## 2. Samples and Experiment

The aim of the present experiment was to extend the QENS study to treated powders based on commercial $MoS_2$ nanopowder (Sigma Aldrich). Three samples were prepared:

**S1:** This sample was treated with low-temperature hydrogen plasma (30 min, 11 W, 0.1 mbar $H_2$). The sample was mounted in an annular sample cell.

**S2:** Powder was loaded with hydrogen by water electrolysis. (4 h, 0,5 molar sulfuric acid, 3 V applied tension). In a first step the $MoS_2$ powder was deposited onto graphite paper electrodes. After electrolysis the powder was removed from the support by treatment in an ultrasonic bath in deionized water and finally precipitated onto aluminium foil. The foil was rolled and placed into a circular sample cell.

**S3:** For this reference sample, as-received $MoS_2$ powder was placed into an annular sample cell.

The experiment was scheduled at IN5, 2-4 June 2023. S3 and the empty cell measurements were completed on 28-29 September 2023, after the original experiment had been interrupted by a power failure. S1 and S2 were measured at 300 K, 10 K, 100 K, 200 K, 400 K, 500 K, and a second time at 300 K. S3 was measured at 10 K, 100 K, 300 K, 500 K, and a second time at 300 K employing an incoming wavelength of 5 Å. Data reduction and analysis was carried out using the Mantid software [14].

## 3. Preliminary analysis

**S1 (Figure 1)**: At the first 300 K measurement before any cooling/heating, a quasi-elastic broadening can be observed. This is apparent in all three samples. Since S1 and S3 were not treated in aqueous solutions, it indicates that water from the air adsorbs onto the $MoS_2$-powder in ambient conditions. There is no broadening of the spectra at 10 K, 100 K and 200 K, respectively. At 400 K, a QENS broadening is observed, suggesting the presence of dynamics in the sample (Figure 1). On further heating to 500 K this signal disappears, either because the dynamics become too fast relative to the

instrument resolution, or because of a loss of H from the sample, as it has been observed for hydrogen in $MoS_2$ crystals. Upon cooling to room temperature, no QENS signal is apparent.
The spectrum measured at 400 K can be fitted using a convolution of the 10 K resolution with a delta function, a flat background and one Lorentzian to account for the broadening (Figure 1, right).

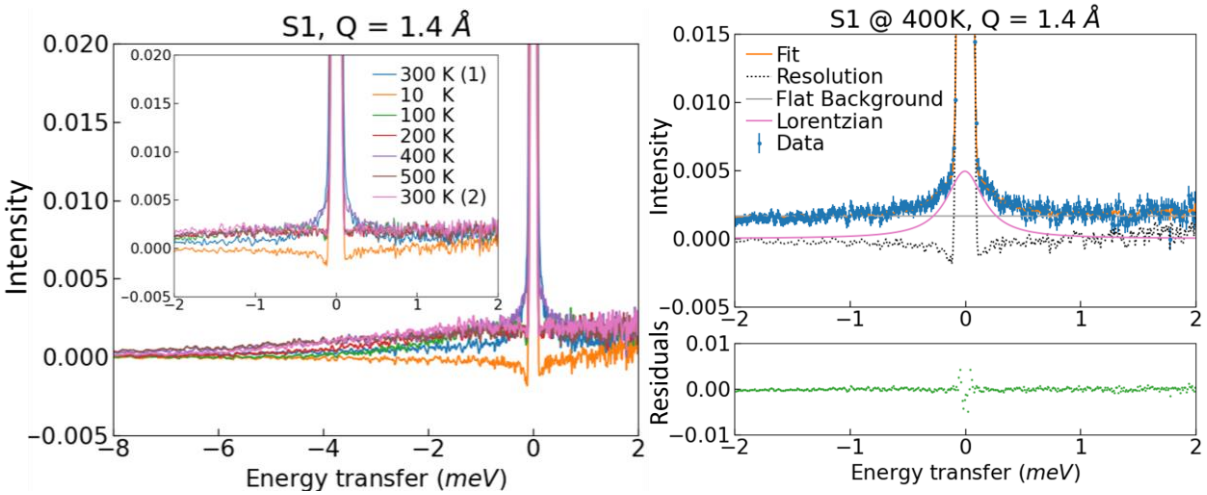


Figure 1: QENS spectra of plasma-loaded $MoS_2$ at various temperatures at Q = 1.4 $Å^{-1}$ (left) and fitting of the 400 K data (right).

**S2 (Figure 2):** An initial measurement at 300 K reveals the presence of some dynamics similar to S1, possibly caused by adsorbed water. On cooling to 10 K and then heating to 100 K this broadening disappears, and there is no indication of dynamics. At 200 K, a very small broadening of the elastic peak is observed, showing the onset of dynamics. Further heating to 400 K results in a strong QENS signal, which decreases on heating to 500 K. Again this decrease of quasi-elastic intensity is probably related to loss of the diffusing species due to the high temperature. However, the onset of faster dynamics is also a possibility. In contrast to S1, on cooling to 300 K a small QENS signal remains. Similarly, to S1, the spectrum measured at 400 K can be fitted using a convolution of the 10 K resolution with a delta function, a flat background and one Lorentzian to account for the QENS signal (Figure 2, right).

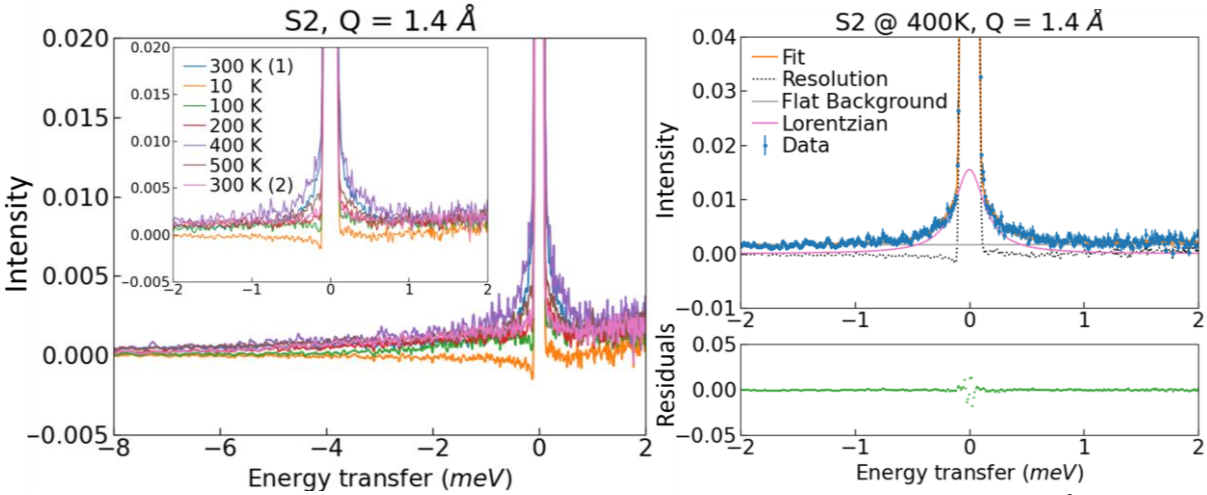


Figure 2: QENS spectra of electrolysis-loaded $MoS_2$ at various temperatures at Q = 1.4 $Å^{-1}$ (left) and fitting of the 400 K data (right).

**S3 (Figure 3):** The QENS broadening observed at 300 K(1) in this untreated reference sample indicates that water adsorbs onto the sample at ambient air condition. As expected due to this being untreated

$MoS_2$ powder, no QENS signal is apparent on cooling first to 10 K and then heating to 100 and 500 K. The second measurement at 300 K confirms that, at the investigated temperatures, no dynamics are present in this reference sample in the TOF spectral range.

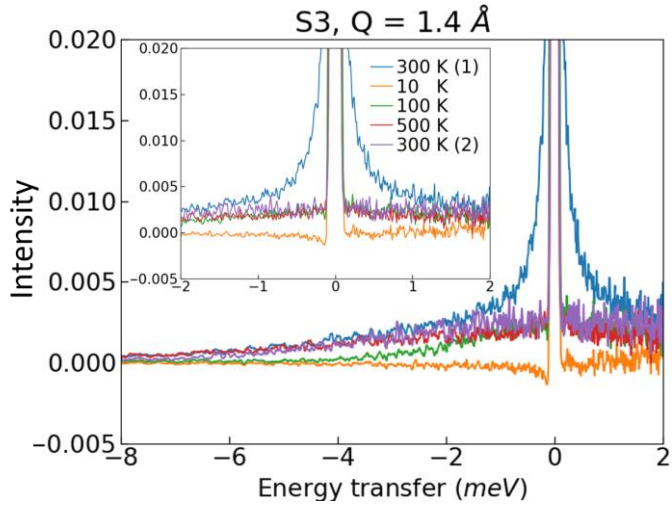


Figure 3: QENS spectra of as-received $MoS_2$ powder at various temperatures at Q = 1.4 $Å^{-1}$.

Further analysis of the QENS data of all three samples, including the detailed study of the Q-dependence as well as the temperature dependence of the QENS broadening and of the intensities, is ongoing. This analysis will comprise a detailed comparison to our single crystal $MoS_2$ QENS data.

**4. References**

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