# Experimental report

29/08/2022

**Proposal:** 7-05-541 **Council:** 4/2021

**Title:** Investigation of nanoscale mechanism of unusual hydrogen isotope separation in MIL53 (Al) at elevated temperatures

**Research area:** Materials

**This proposal is a new proposal**


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Jitae PARK
Veronika GRZIMEK
Margarita RUSSINA

**Local contacts:** Jacques OLLIVIER


**Samples:** MIL-53(C8H5AlO5)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN5 | 5 | 4 | 23/09/2021 | 27/09/2021 |
| IN6-SHARP | 5 | 0 | | |


## Abstract:

The goal of this proposal is the development of materials for cost-efficient hydrogen isotope separation, which would enable high degree of separation at high operational temperatures. For this purpose, we use a novel strategy employing flexible nanoporous structures. Recently, we have discovered a breathing transition from large pore (lp) to very large pore (vlp) in well known flexible MOF MIL-53 (Al), which respond only to a heavier hydrogen isotope. As a results, the breathing transition in MIL-53, D2 in 1:1 H2/D2 mixture is adsorbed preferentially on MIL-53, leading to the high D2 selectivity even at high temperature. The aim of the proposed experiments is to investigate the nanoscale mechanism of the isotopic molecular transport within the framework during breathing transition using in-situ neutron spectroscopy. This investigation will provide a key information on diffusion of isotopes in flexible MOFs and hence on the nanoscale nature of the isotope separation. The results will serve as a guideline for further development of the next generation of materials using quantum sieving approach

Experimental report of the experiment 7-05-541

# "Investigation of nanoscale mechanism of unusual hydrogen isotope separation in MIL53 (Al) at elevated temperatures"

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Local contact: Jacques Ollivier

## Objectives

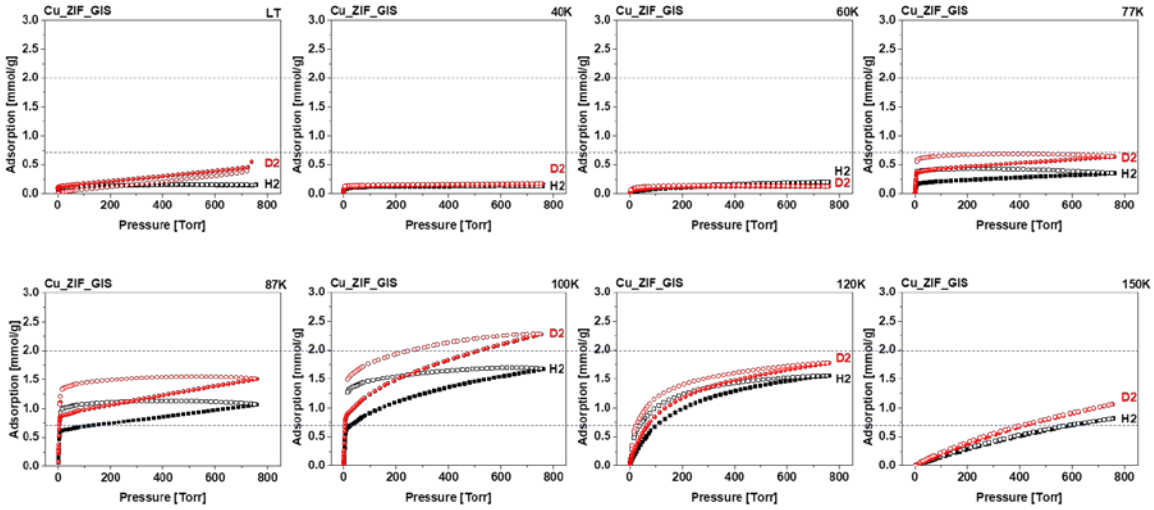
Local flexibility is a unique property of some metal-organic frameworks (MOFs) that clearly distinguishes them from other inorganic porous materials, such as zeolite and porous silica. A Cu-ZIF-gis has cylindrical pores with a cross-sectional diameter of 2.32 Å – 2.44 Å, and two isolated pores with narrow bottlenecks of 1.39 Å and 1.30 Å, respectively. Therefore, Cu-ZIF-gis did not absorb Nitrogen (kinetic diameter, 3.68 Å) at 77 K and 1 bar, but exhibited hydrogen adsorption isotherms with large hysteresis. The total void volume is 17 % per unit cell where about 10 % corresponding to two isolated pores is not usable. strongly absorbs Hydrogen molecules with very large desorption energy of 22.8 kJ/mol, and exhibits a temperature-dependent gating effect. Consequently, the dynamic behavior of adsorbed hydrogen isotopes during the phenomenon of the 'gating effect' may exhibit differently, and will be fundamentally very interesting. However, this has so far been lacking in research. Therefore, we propose to conduct neutron spectroscopy studies on NEAT to investigate the dynamics of hydrogen isotope.

## Achievements (limited 250 words)

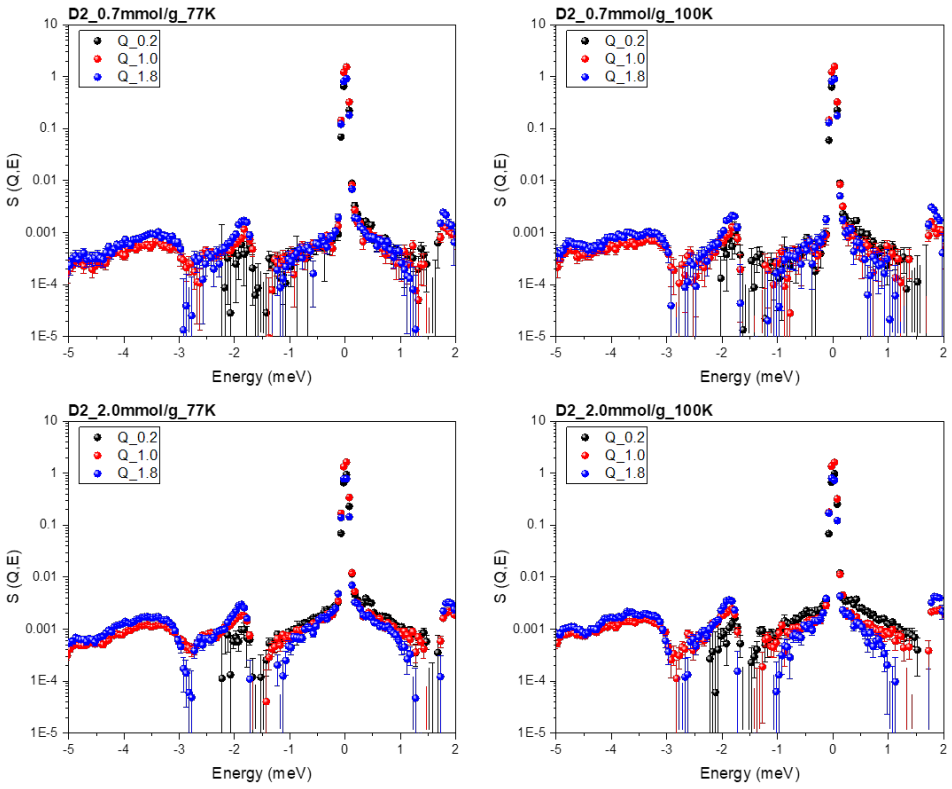
Owing to this gate effect of Cu-ZIF-gis, the adsorption amount of $H_2$ and $D_2$ increases up to 100K and then decreases. Thus, we measured and the MOFs with a series of different loading (0.7, 2.0 mmol per gas), and temperatures (25 K, 77 K, 100K, 150K) per two different gases (H2 and D2). The scattering data of all conditions was collected and currently being analyzed. The major problem for the data analysis present the spurious contribution at low and medium angle range, which makes the quasielastic signal asymmetrical. We are working on the possible solutions to this problem. This investigation will provide a different way to control the gate effect and also key information on the diffusion of isotopes in Cu-ZIF-gis.

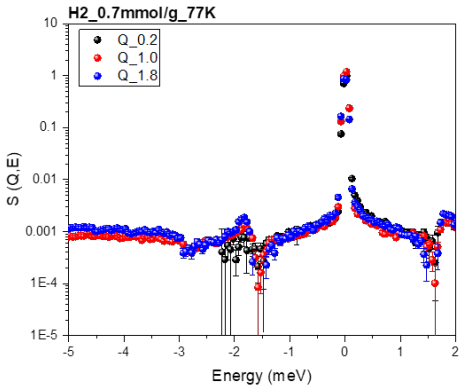
1. **Initial background isotherm measurements**

The loading amounts of gases are decided by using various temperature isotherms. The amount of loading gas is decided based on two factors, the first is the starting point of adsorption at 77K and the second is the maximum amount of adsorption. In order to see the difference between hydrogen and deuterium, two factors are decided only exist deuterium uptake point.




2. **Plot results (raw data)**

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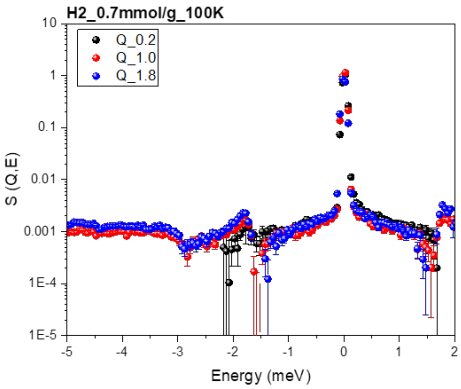
Q_0.2
Q_1.0
Q_1.8
S (Q,E)
Energy (meV)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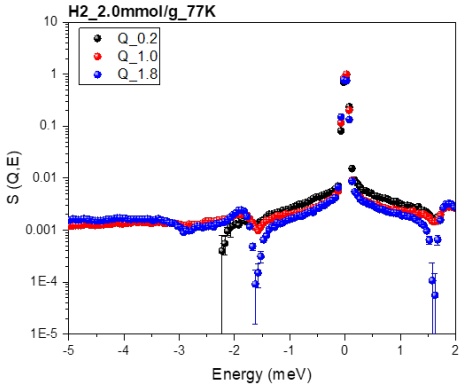
Q_0.2
Q_1.0
Q_1.8
S (Q,E)
Energy (meV)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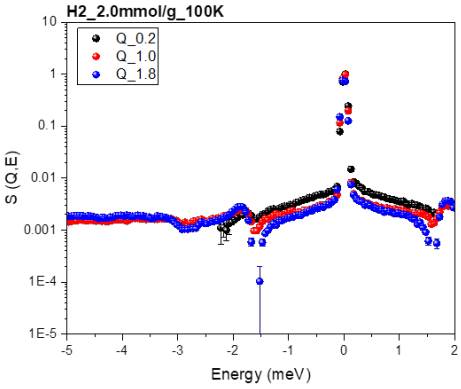
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