Hydrogen mobility and reactivity in MoS_2 catalyst

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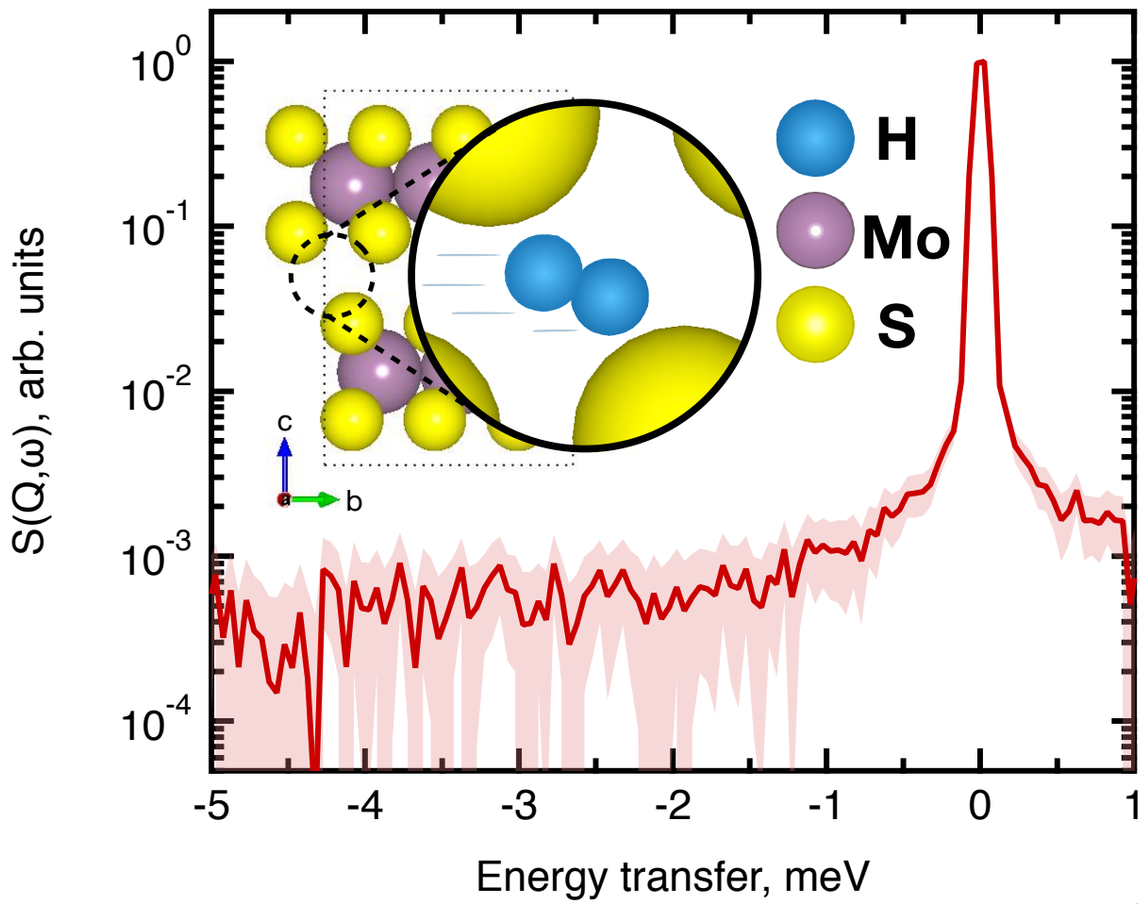

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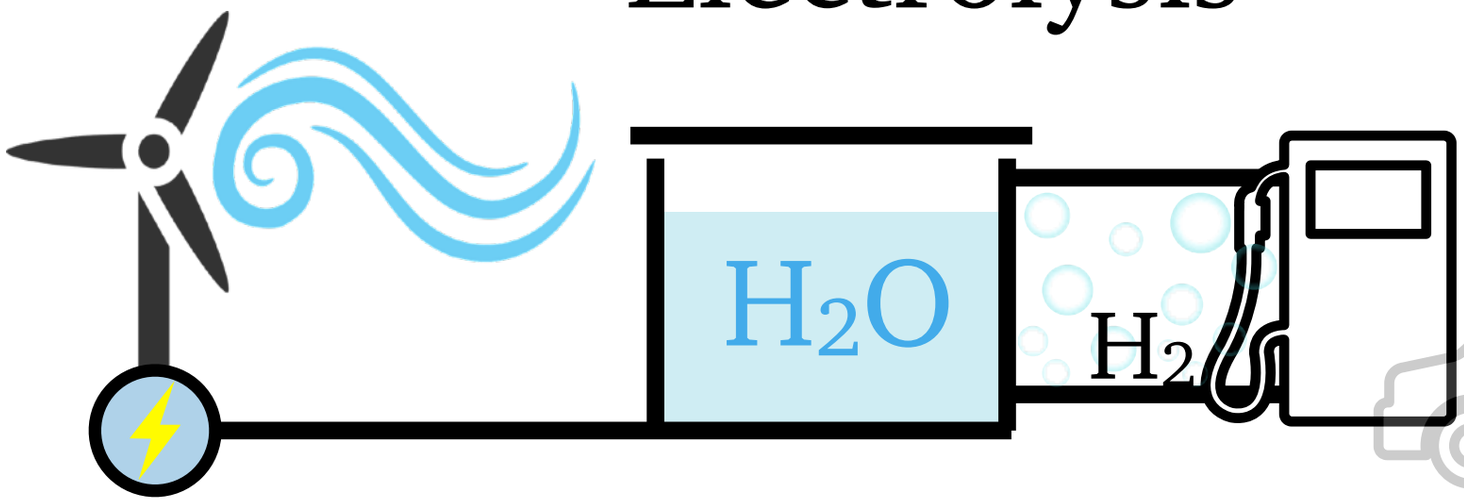
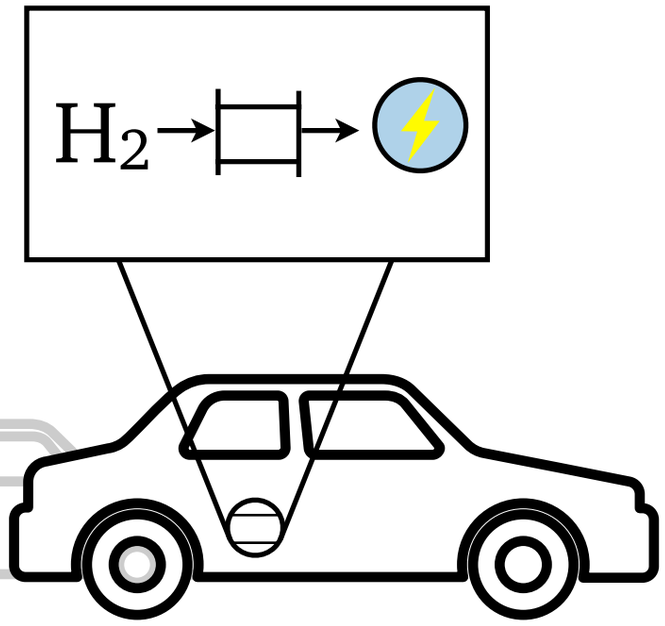
Electrolysis



Fuel cell stack



Electricity → H_2 → Electricity

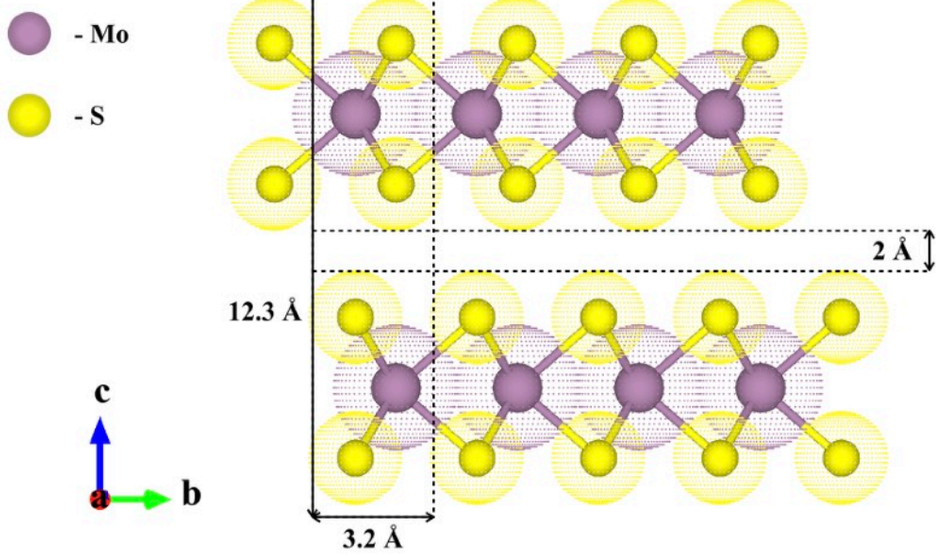
Catalyst

- For large-scale applications a **cheaper alternative to platinum** catalyst is required, since it contributes to ~ 20 % of the total costs of H_2 production[1]

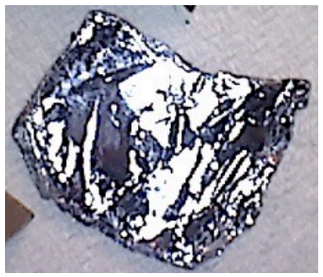
- MoS_2 is a catalyst candidate for the hydrogen evolution reaction (HER)

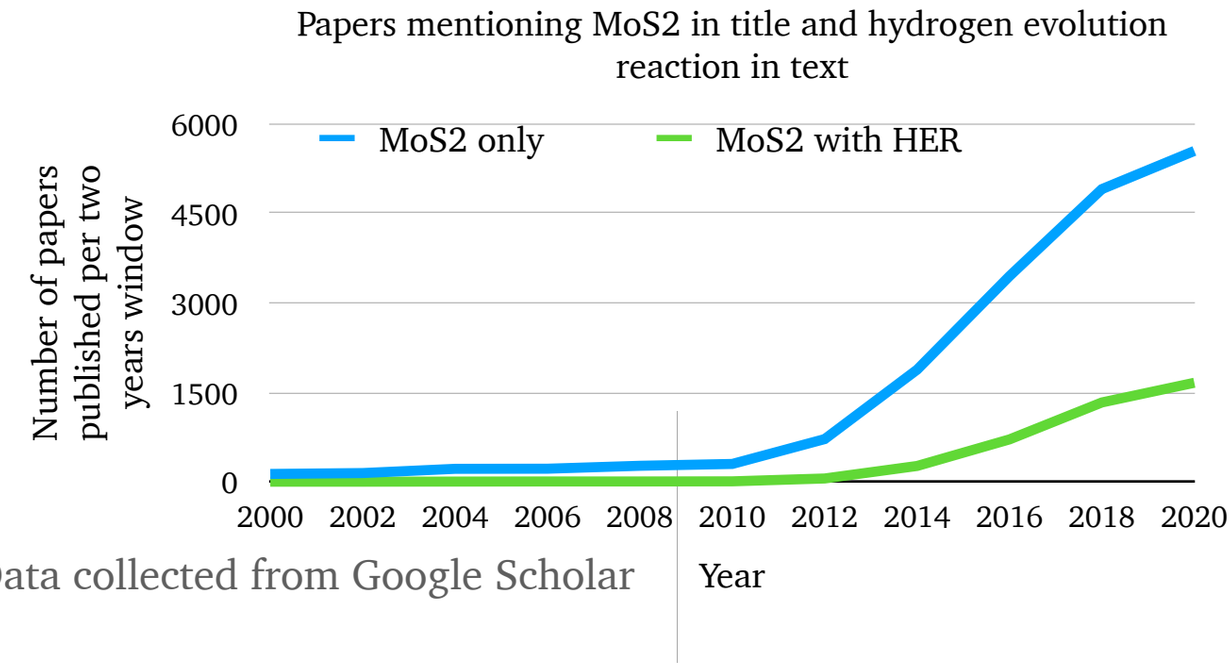
- MoS_2 can be ~10^5 times cheaper than Pt if produced in large quantities[2].

The structure of MoS_2



MoS_2 crystal





[1] Technical Report NREL/TP-6A20-72740 August 2019

[2] https://doi.org/10.1038/s41467-020-17121-8

Hydrogen evolution reaction (cathode)

Reaction: $2H^+ + 2e^- \rightarrow 2H_2$

Occurs in two steps:

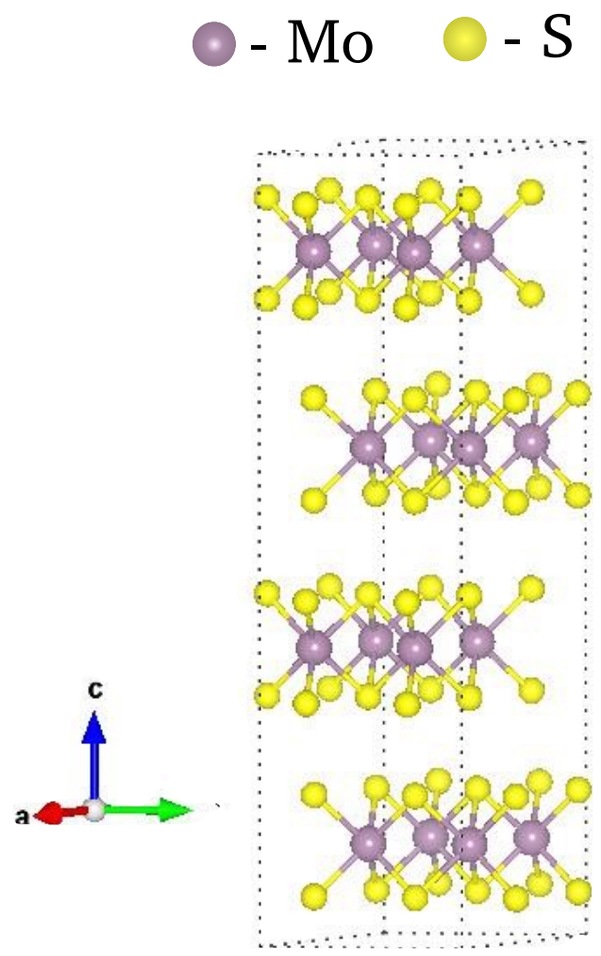
1. Volmer step - hydrogen adsorption: $H^+ + e^- \rightarrow H_{ad}$

2. Either Heyrovsky or Tafel step - recombination:

   2.1. Heyrovsky: $H_{ad} + H^+ + e^- \rightarrow H_2$

   2.2. Tafel: $H_{ad} + H_{ad} \rightarrow H_2$

It is believed that only edge S atoms are reactive. Hence diffusion of H_{ad} to non-reactive sites (spillover effect) is important, since it helps to vacate reactive sites for further H adsorption.



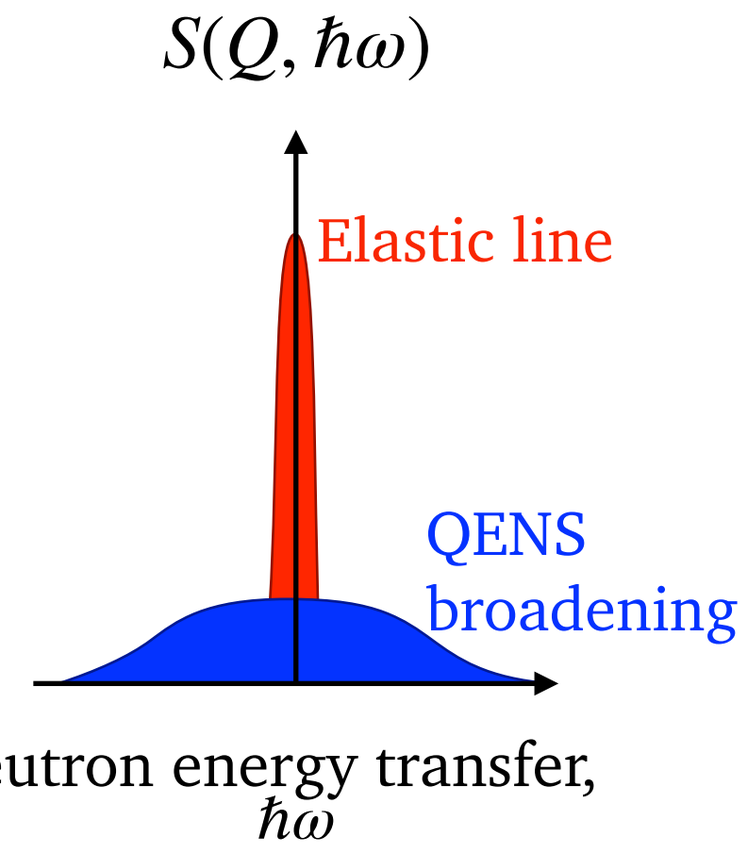
MoS_2

Quasi-elastic neutron scattering

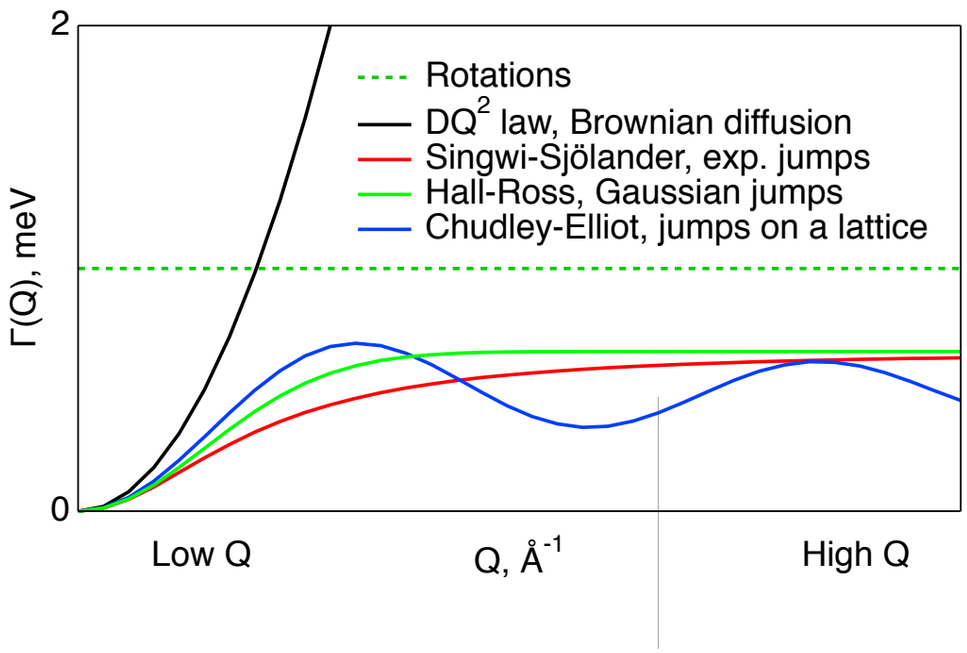
The QENS signal usually has a form:

$$S(Q,\hbar\omega) = A_0(Q)[A_{el}(Q)\cdot R(\hbar\omega) + A_{qe}(Q)\cdot\sum L_i(\Gamma_i(Q),\hbar\omega) * R(\hbar\omega)]$$

$A_0(Q)$ - total intensity coefficient, $R(\hbar\omega)$ - resolution function, $L(\Gamma(Q),\hbar\omega)$ - Lorentzian function with HWHM $\Gamma(Q)$, * - convolution action.



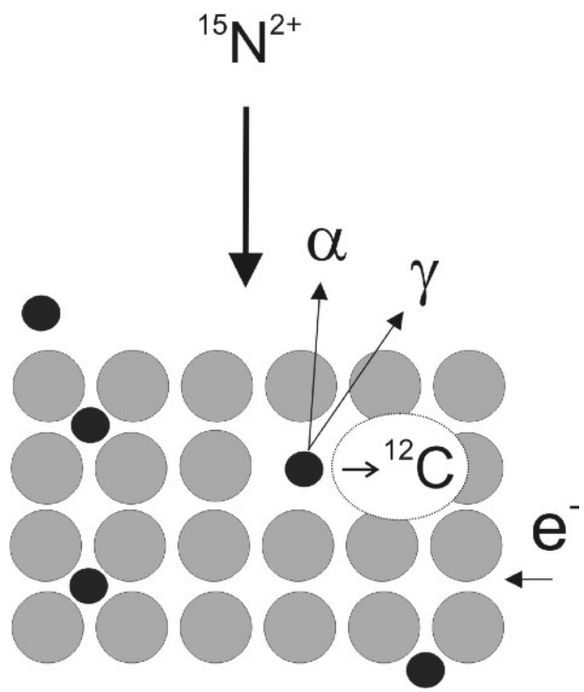
The width $\Gamma_i(Q)$ gives information about the type and rate of the corresponding diffusion mode.

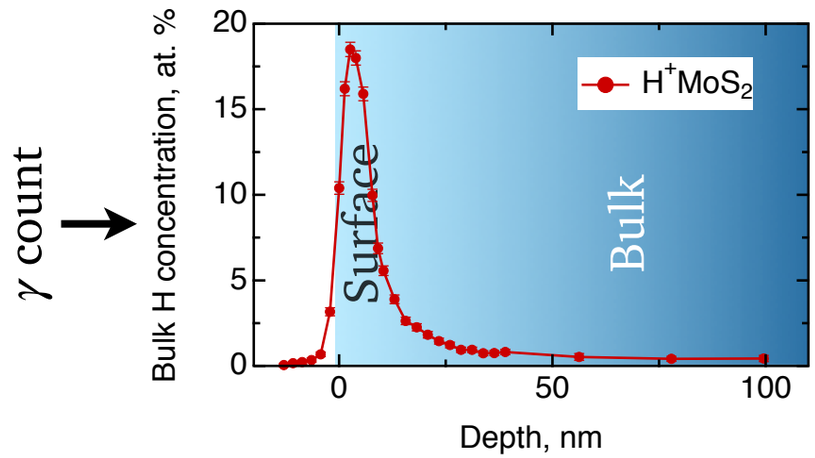


Supplementary methods

Nuclear Reaction Analysis (NRA) yields hydrogen concentration profile perpendicular to the sample's surface.

Reaction: $^{15}\mathrm{N} + {}^{1}\mathrm{H} \rightarrow {}^{12}\mathrm{C} + \alpha + \gamma$, with a sharp resonance at 6.416 MeV energy of nitrogen ions.

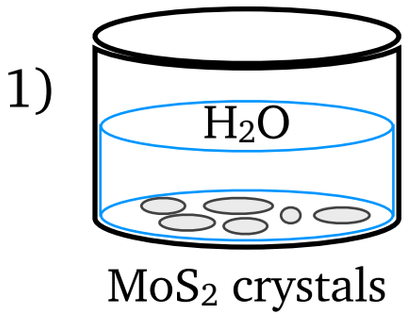


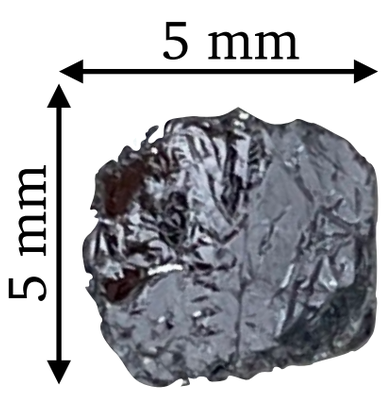


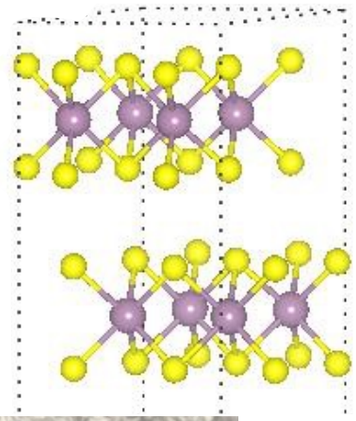
Samples - hydrogen loaded MoS_2 crystals

1. Soaked in water, H_2O/MoS_2

Aim - isolate the dynamics of **adsorbed water**, which could be present in other samples.

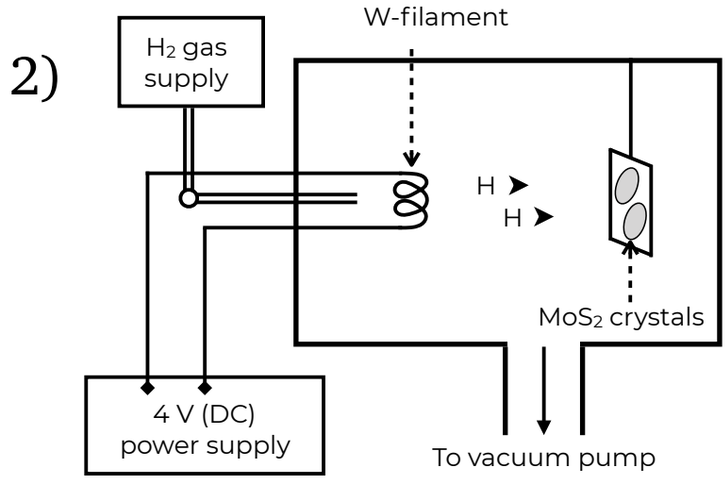






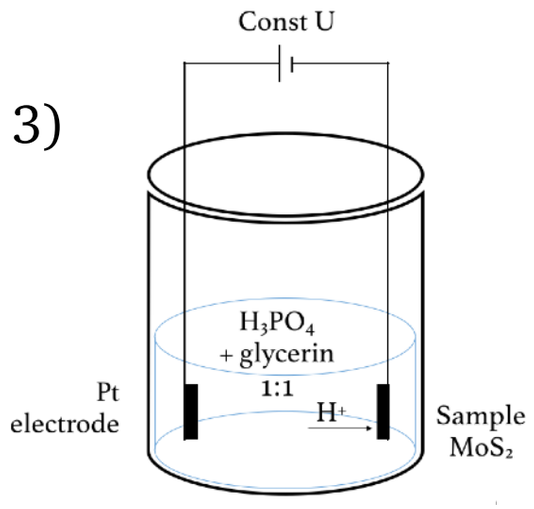
2. Atom beam bombarded, H/MoS_2

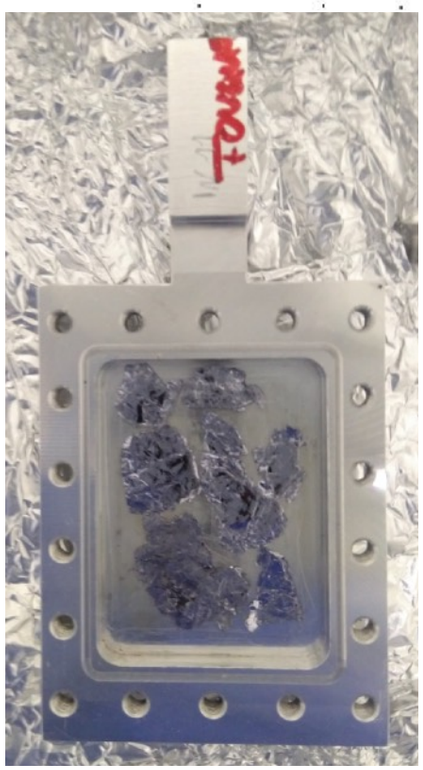
Aim - study the diffusion of **H atoms only**.



3. Loaded via electrolysis, H^+/MoS_2

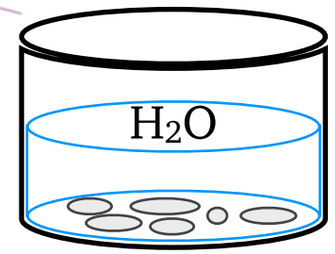
Aim - study the diffusion of **hydrogen** species, which are incorporated into MoS_2 during **electrolysis**.





MoS_2 crystals in a sample holder for QENS experiments

Characterisation of H_2O/MoS_2



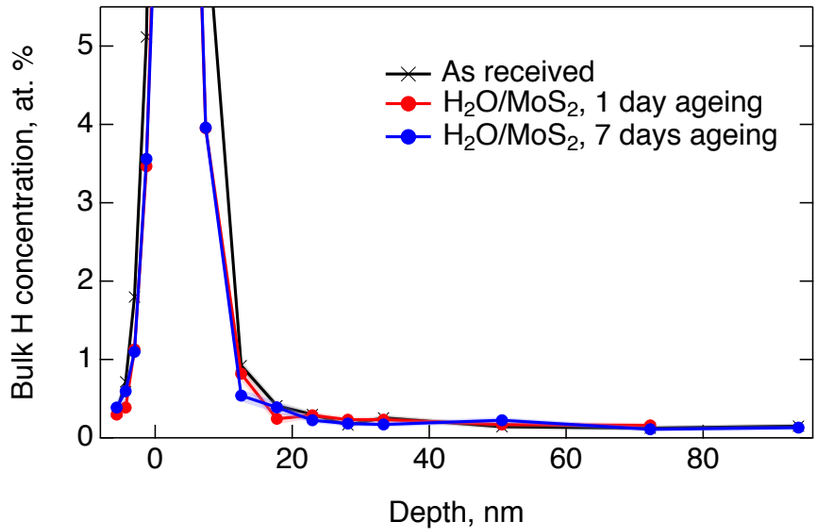
MoS_2 crystals

Water cannot penetrate deep into the bulk of MoS_2.

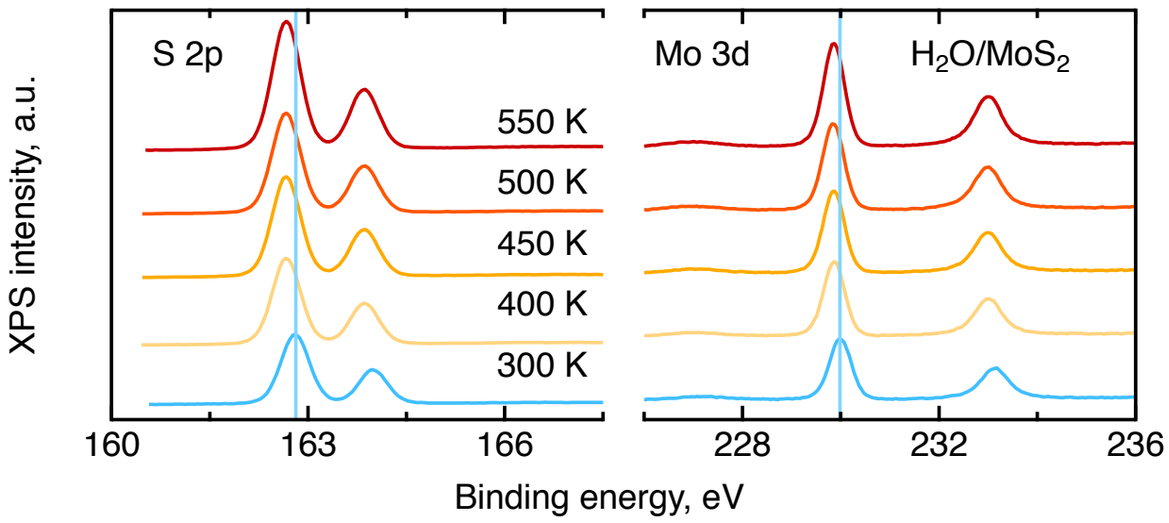
It also does not affect the chemistry of the MoS_2 surface.

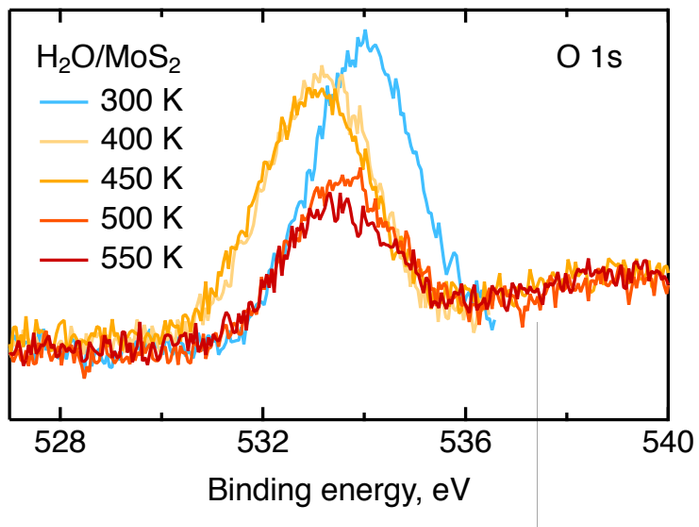
→ Water is physisorbed near the surface.

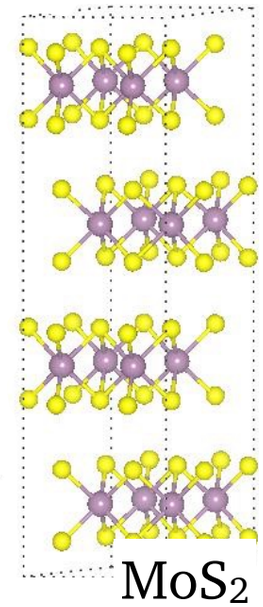
Nuclear Reaction Analysis
NRA @ RUBION



XPS @ BESSY II synchrotron



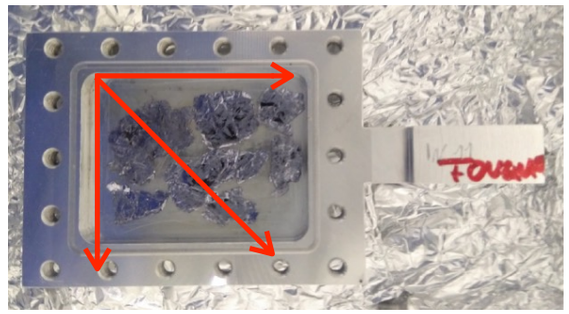




MoS_2

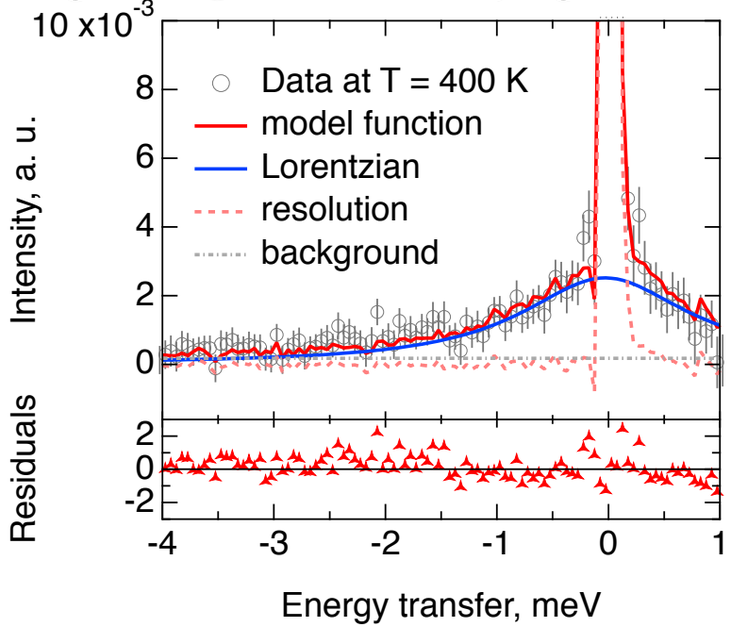
Dynamics in H_2O/MoS_2

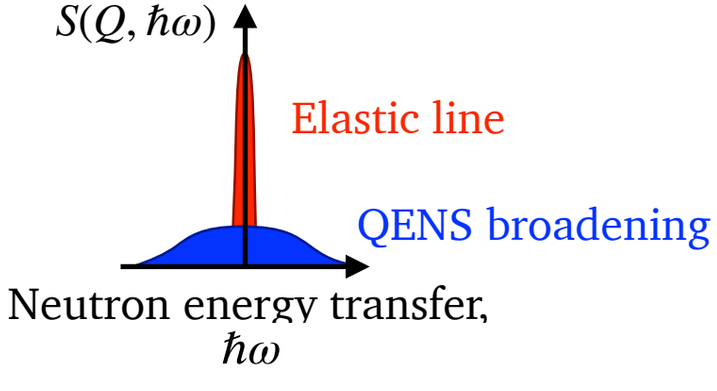
Diffusion is found mostly in-plane, i.e. parallel to the MoS_2 layers.



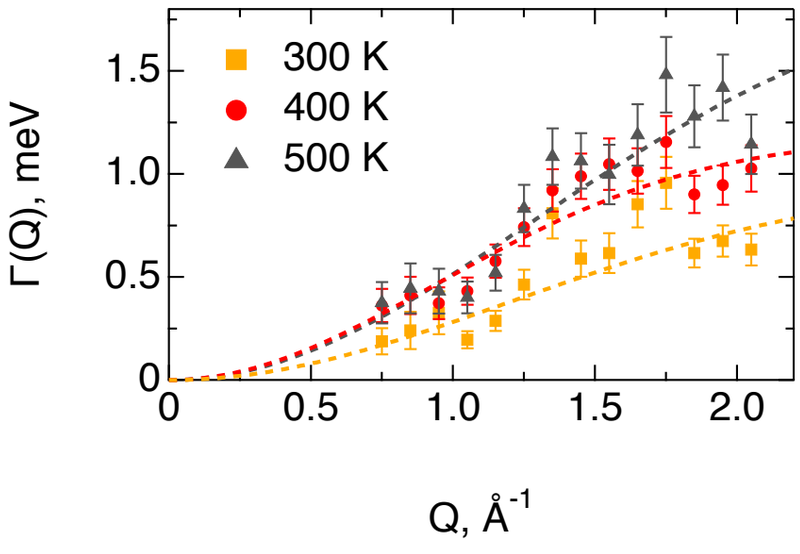
Clear QENS broadening
only one Lorentzian observed

QENS @ IN6-SHARP, Q = 1.35 Å^{-1}





The QENS broadening, $\Gamma(Q)$,
shows a jump behaviour, similar to
H diffusion in liquid water.



Fit by the Hall-Ross model (or Singwi-Sjölander),
Average jump distance: $l = 1.6$ Å
Diffusion coefficient: $D_{||} \approx 1 \cdot 10^{-8}\ m^2/s$

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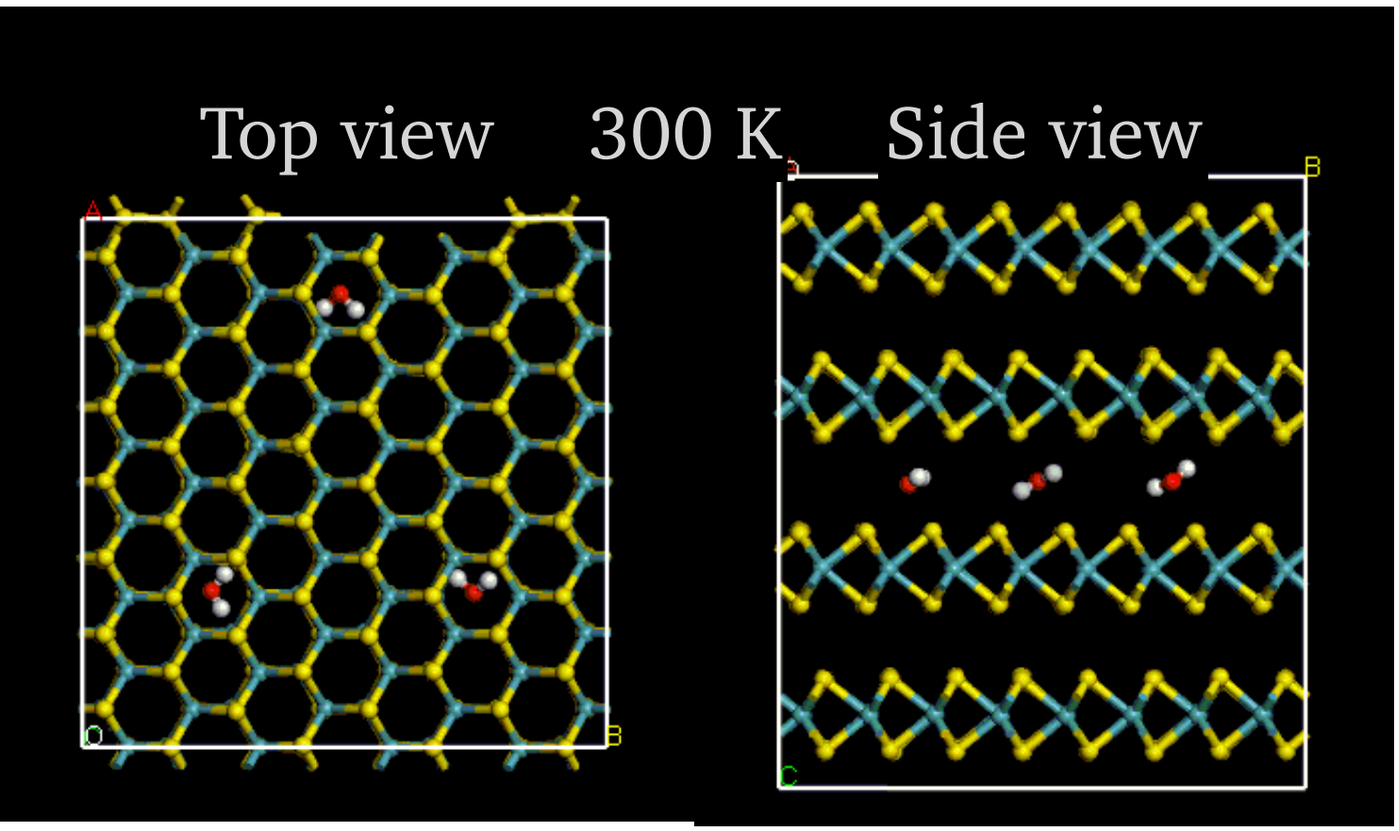
Water dynamics in MoS_2

Classical molecular dynamics simulations with a modified *pcff* forcefield.

According to classical MD simulations, inside MoS_2 water can only perform rotational motion, which is very fast already at 100 K.



→ The diffusing water **cannot** be in the bulk, but is in surfaces/cracks

Characterisation of H/MoS_2 (atom beam bombarded)

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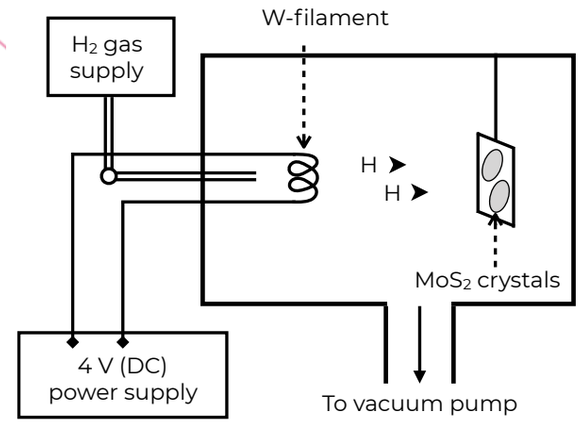
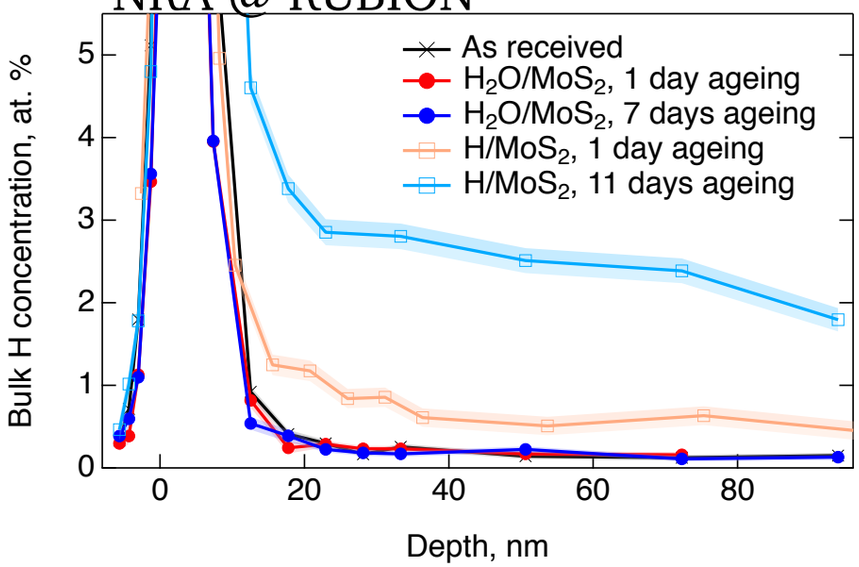


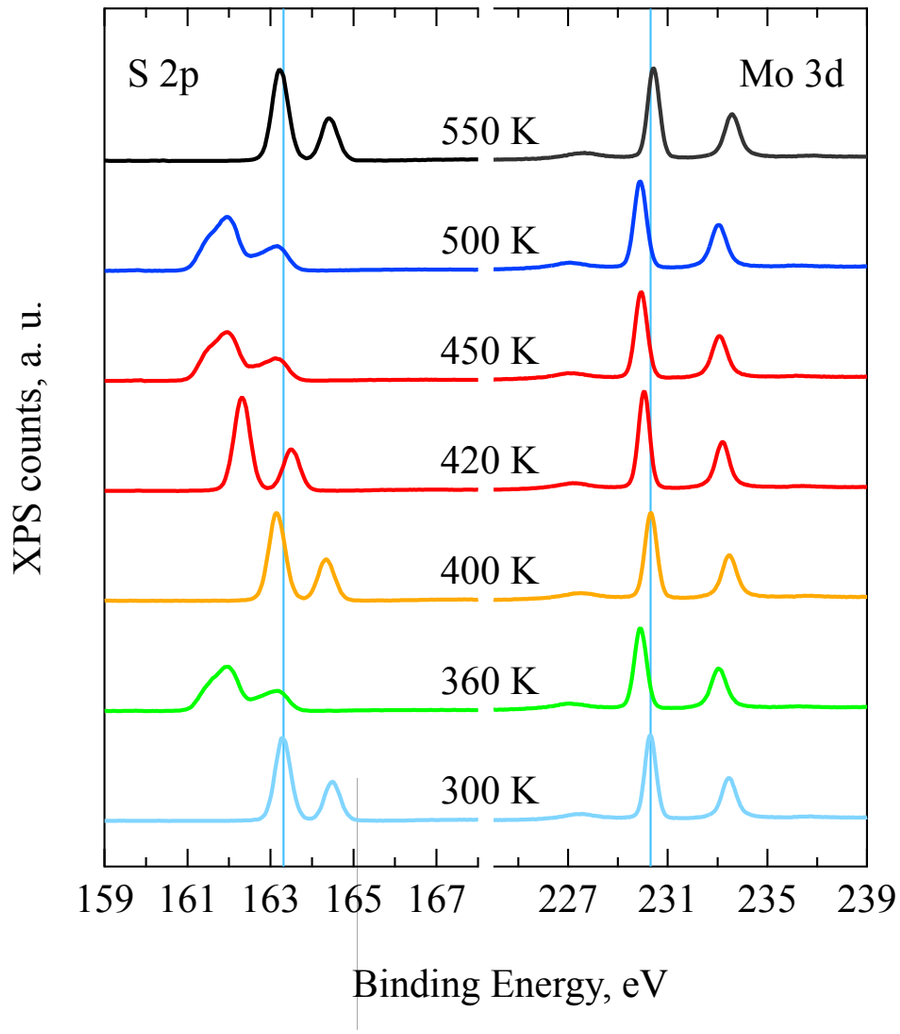
Hydrogen atoms do penetrate MoS_2 layers. The estimated $D_\perp \approx 10^{-21}\ m^2/s$.

NRA @ RUBION



XPS @ BESSY II synchrotron

MoS_2 loaded with H via atom beam bombardment



At least two reduction-oxidation cycles are observed in the XPS spectra.

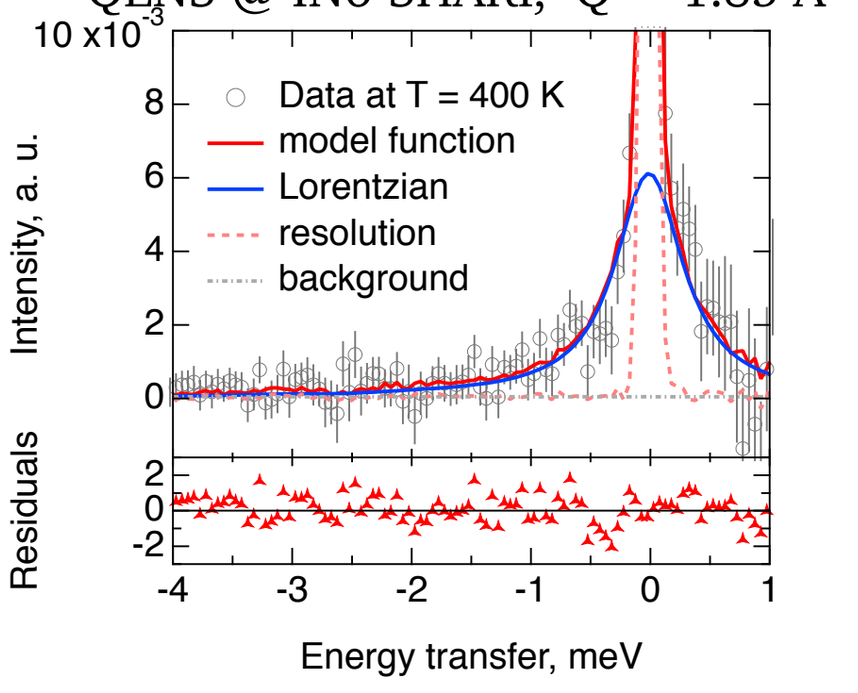
These two cycles may correspond to hydrogen atoms adsorbed with different binding energies, for example, as -SH group and near S vacancies.

Hydrogen dynamics in H/MoS_2

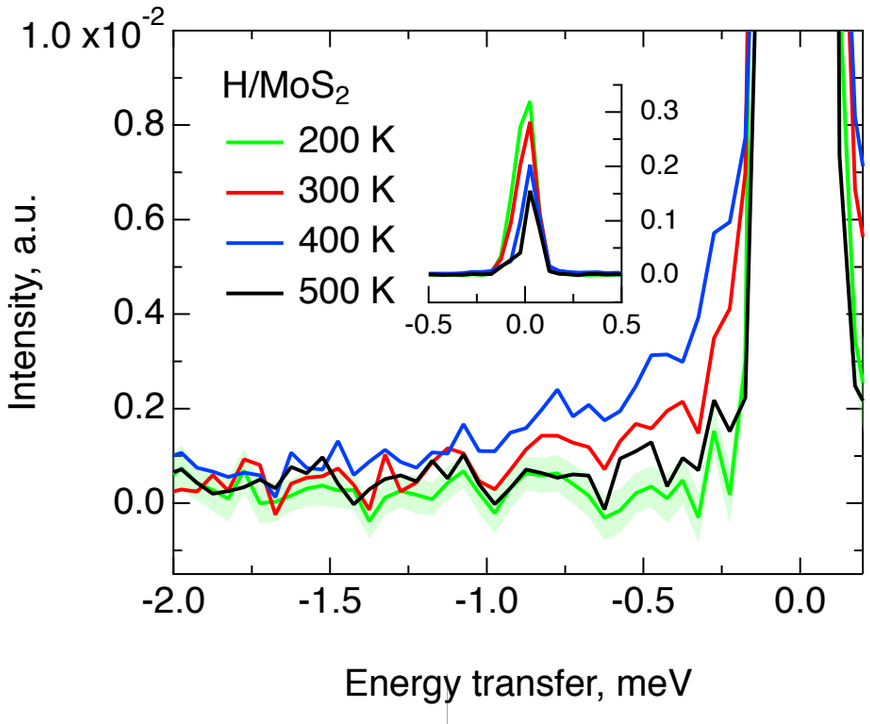
Diffusion is measured mostly in-plane, i.e. parallel to the MoS_2 layers. The crystals were baked out at 390 K prior to the experiment.

One Lorentzian is enough to fit the QENS broadening.

QENS @ IN6-SHARP, Q = 1.85 Å^{-1}

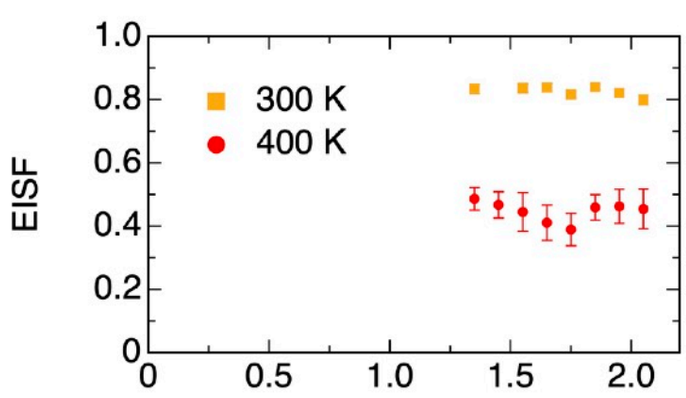


The QENS broadening vanishes at 500 K:
→ Total desorption of mobile hydrogen.

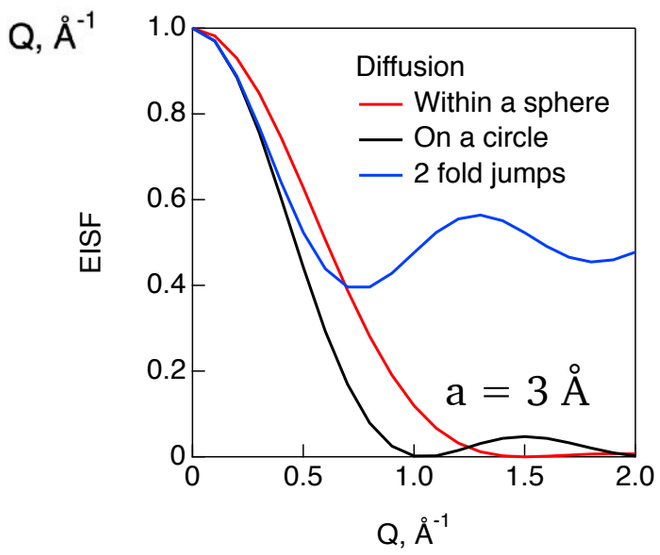


Hydrogen dynamics in H/MoS_2

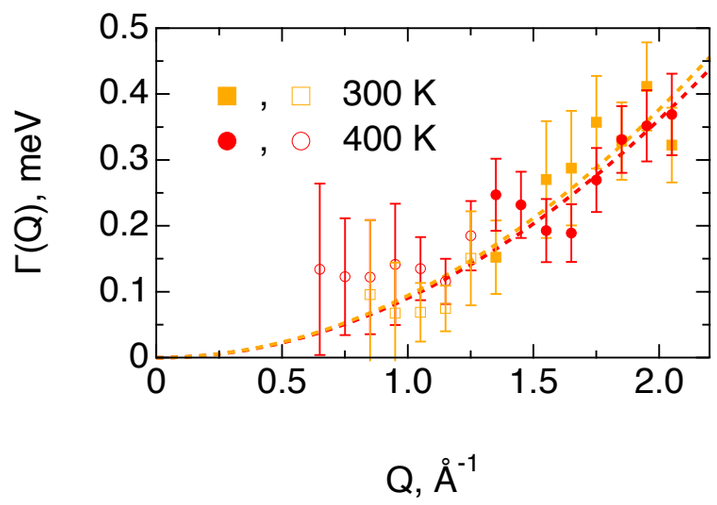
No spatial restrictions for H were found.
Around 50 % of H atoms are mobile at 400 K, rising to 100 % at 500 K.



$$EISF = \frac{A_{el}}{A_{el} + A_{qe}}$$

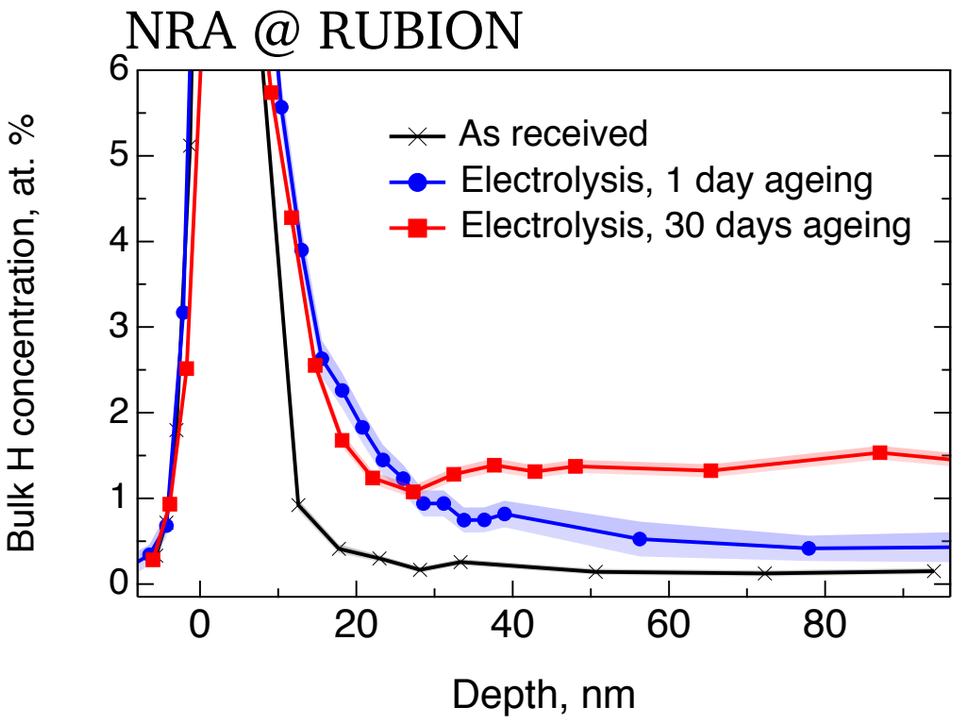


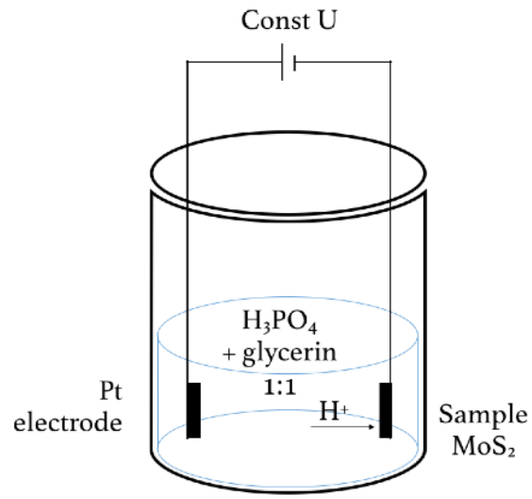
QENS broadening follows a DQ^2 law for Brownian diffusion, with $D_{\parallel} = 1 \cdot 10^{-9}\ m^2/s$.



We see unobstructed Brownian diffusion of H atoms parallel to MoS_2 layers.

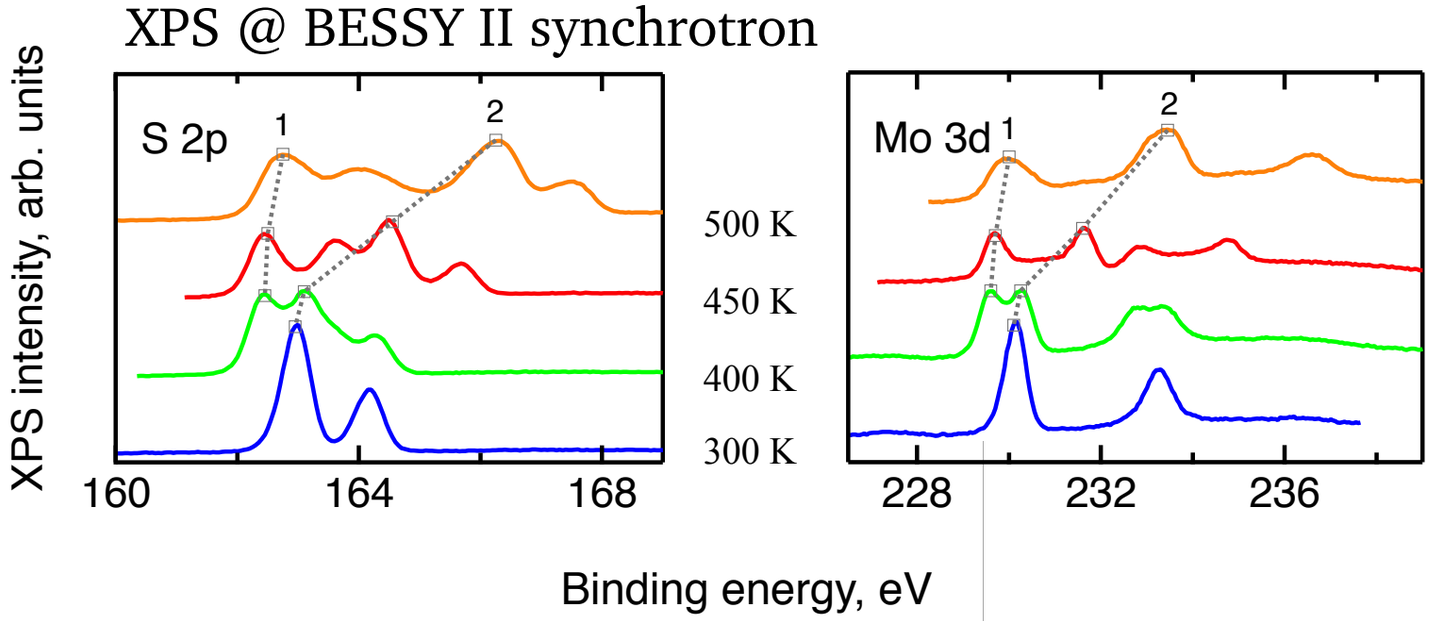
Characterisation of H^+/MoS_2





For the **electrolytically loaded H+/MoS_2** crystals hydrogen diffusion into the bulk is also observed.

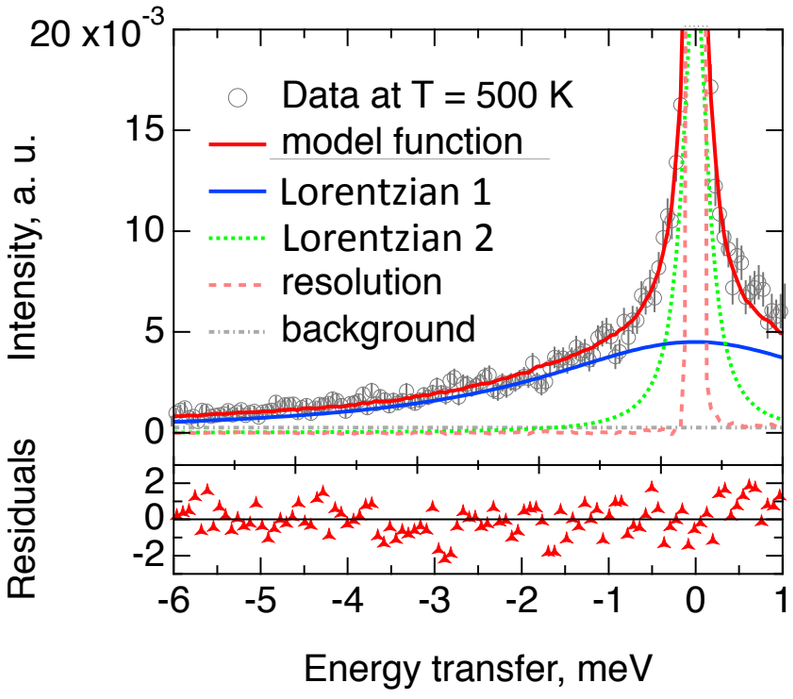
XPS reveals strong oxidation due to hydrogen desorption from the surface, with no significant source of H atoms in the bulk.



Hydrogen dynamics in H^+/MoS_2

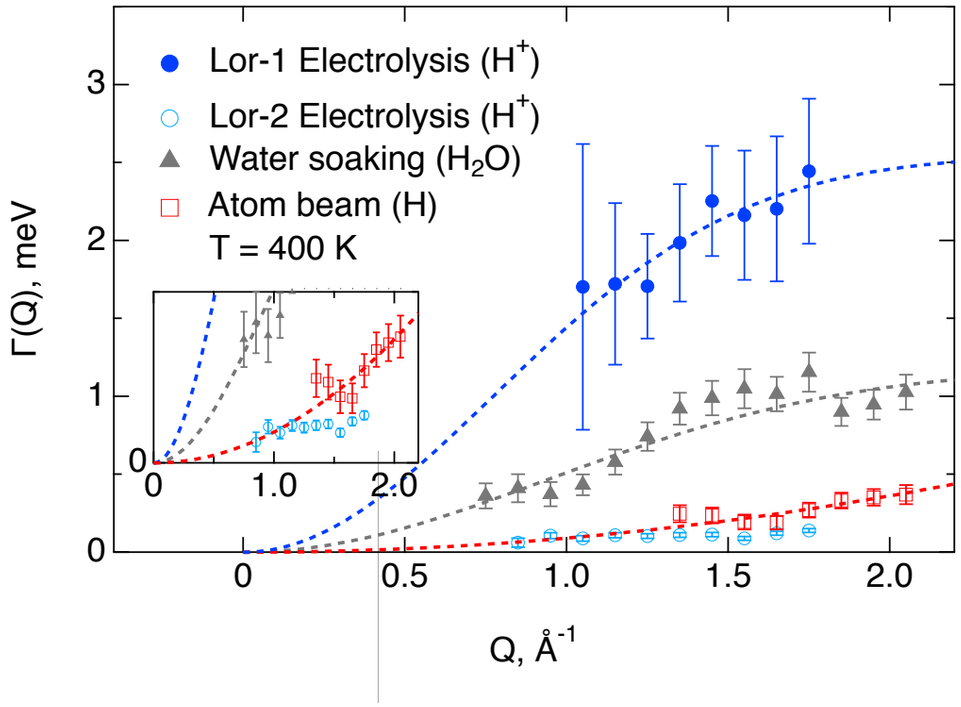
Here the main studied geometry is in-plane, i.e. parallel to the MoS_2 layers. However, the out-of-plane set-up was also measured.

QENS @ TOFTOF, MLZ, $Q = 1.65$ Å^{-1}

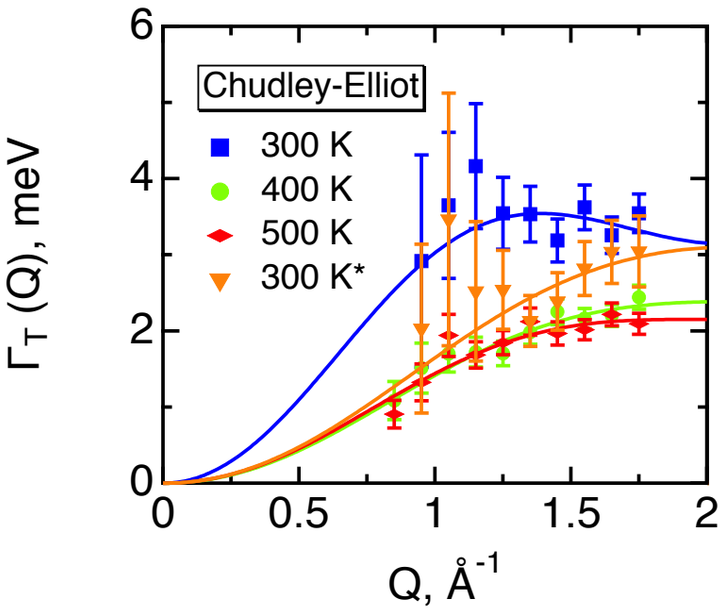


This time *two* diffusion modes can be discerned.

One is clearly different from what was observed earlier. The other one is close to H/MoS_2, but it still exists at 500 K.



Hydrogen dynamics in H^+/MoS_2

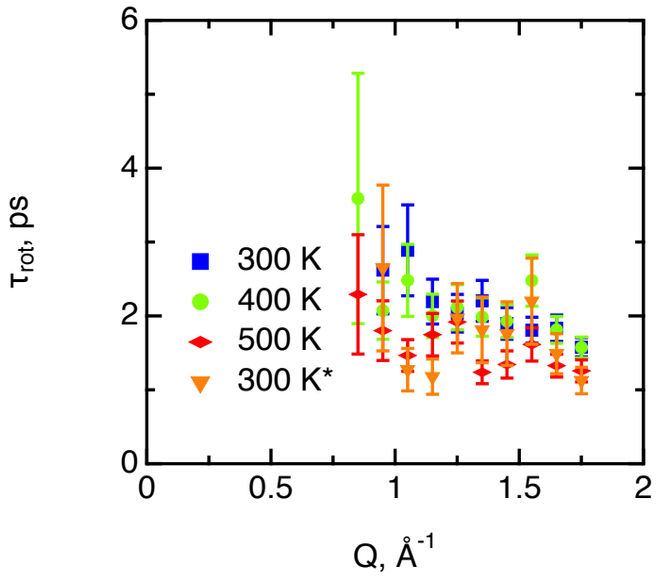


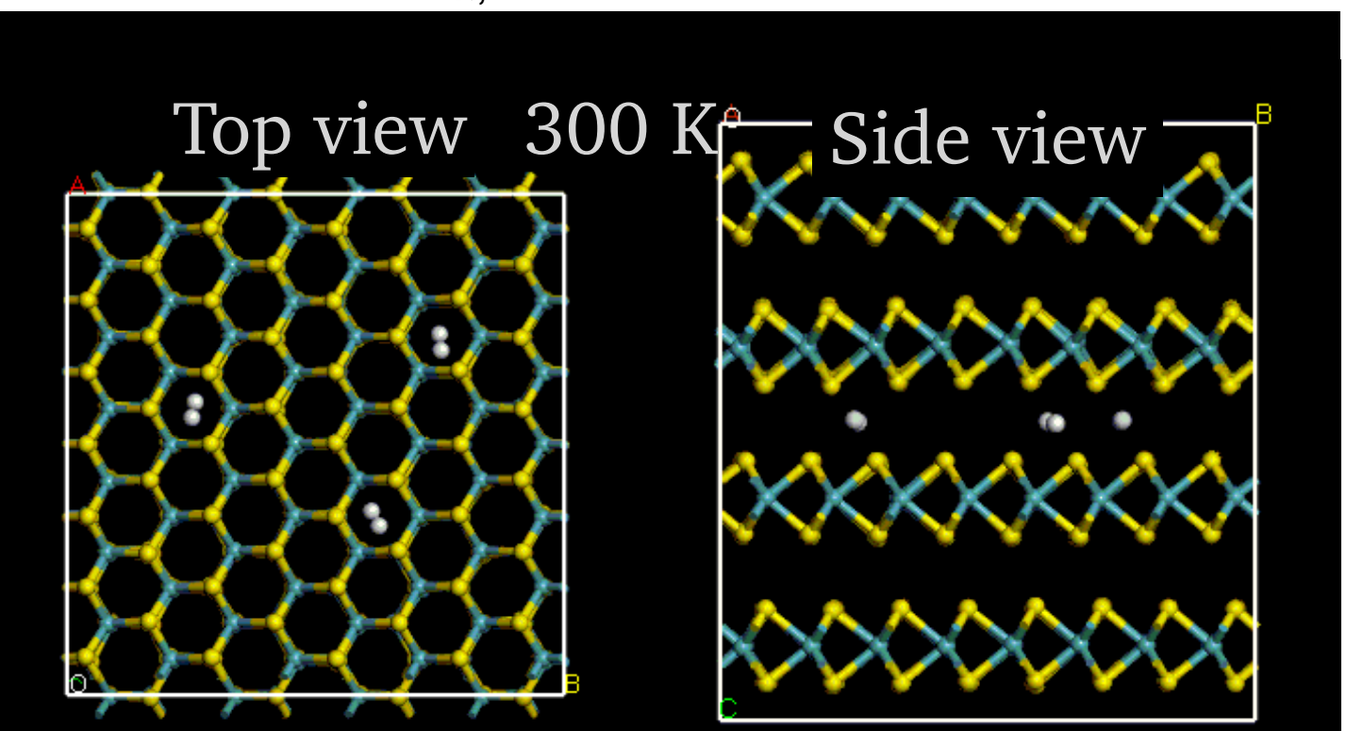
Average jump distance:

$l = 2.3$ Å $< a = 3.2$ Å

Diffusion coefficient:

$D_{\parallel} \approx 4 \cdot 10^{-8}\ m^2/s$



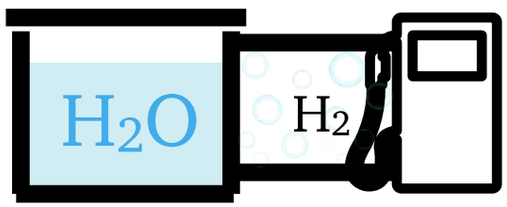


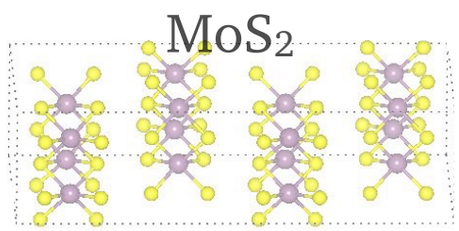
Characteristic rotational time from experiment: $\tau_{rot} \approx 2\ ps$;
from classical MD: $\tau_{rot} \approx 0.2\ ps$.

Conclusions

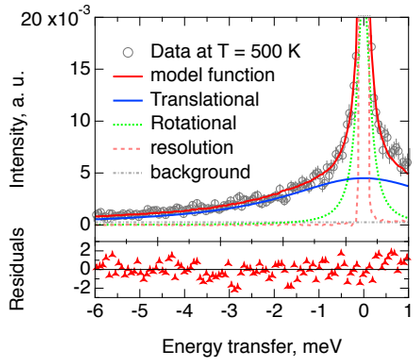
- **Liquid water** can access defective regions of MoS_2, but does not affect the surface chemistry;
- The proportion of mobile H atoms in **atom beam loaded** samples increases with temperature, reaching 100 % slightly below 500 K;
- The diffusion of **H atoms** in MoS_2 is fast, meaning that spillover effect is likely to work well;
- **Recombined H_2 molecules** are the fastest among the hydrogen species observed, but are trapped inside the material even at 500 K.

Electrolysis

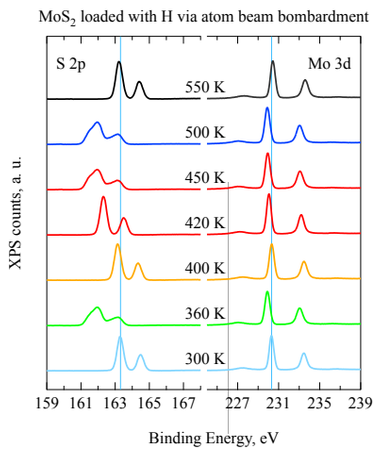




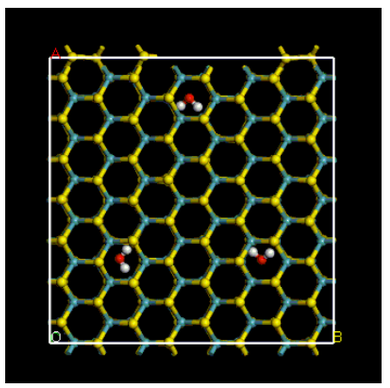
QENS



XPS



MD



Acknowledgments

ILL
Vitalii Kuznetsov

Leran Lu
Monica Jimenez Ruiz
Thomas C. Hansen
Manon Letiche
Michael M. Koza
Andrea Piovano
Ketty Beauvois

Westfälische Hochschule
Franziska Traeger

Norbert Kazamer

GREMI Univ. Orléans
Eva Kovacevic
Andrea Jagodar

FRM-II
Wiebke Lohstroh

BESSY II/Karsruhe IT
Alexei Nefedov
Thomas Strunkus

RUBION
Detlef Rogalla
Hans-Werner Becker
Varvara Foteinou

Funding

grant agreement no. 730872 CALYPSO plus
and no. 731096 FILL2030


Thank You!