universität innsbruck
Institut für Ionenphysik
und Angewandte Physik

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The $[Mo_3S_{13}]^{2-}$ nanocluster; an ion towards clean energy

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Supervisor: Martin K. Beyer

MIP Seminar – 20.11.19

Chemical Physics Group

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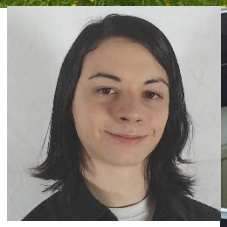
Cooperation partners

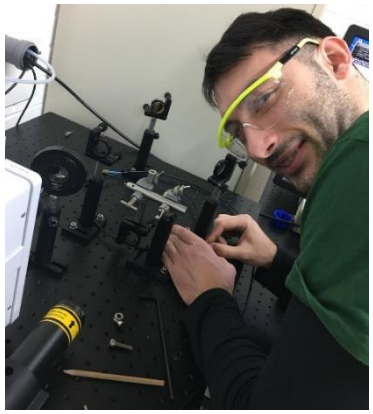
M.-L. Grutza

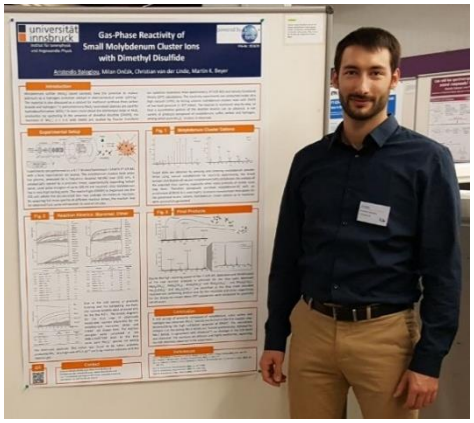
Ph. Kurz



PhD Life:

- Plan, conduct, and evaluate experiments
- Instrument maintenance
- Project management
- Scientific articles and conferences
- Extraordinary tasks (e.g. decontamination)





3 articles, 10 conferences,
and 1 poster prize

MolSulCat

powered by klima+ energie fonds

Supervision of 3 students
Collaboration with Freiburg

[1] https://www.energieforschung.at/projekte/876/molekulare-mechanismen-der-wasserstoffentwicklung-und-der-methanolsynthese-mit-molybdaensulfidkatalysatoren

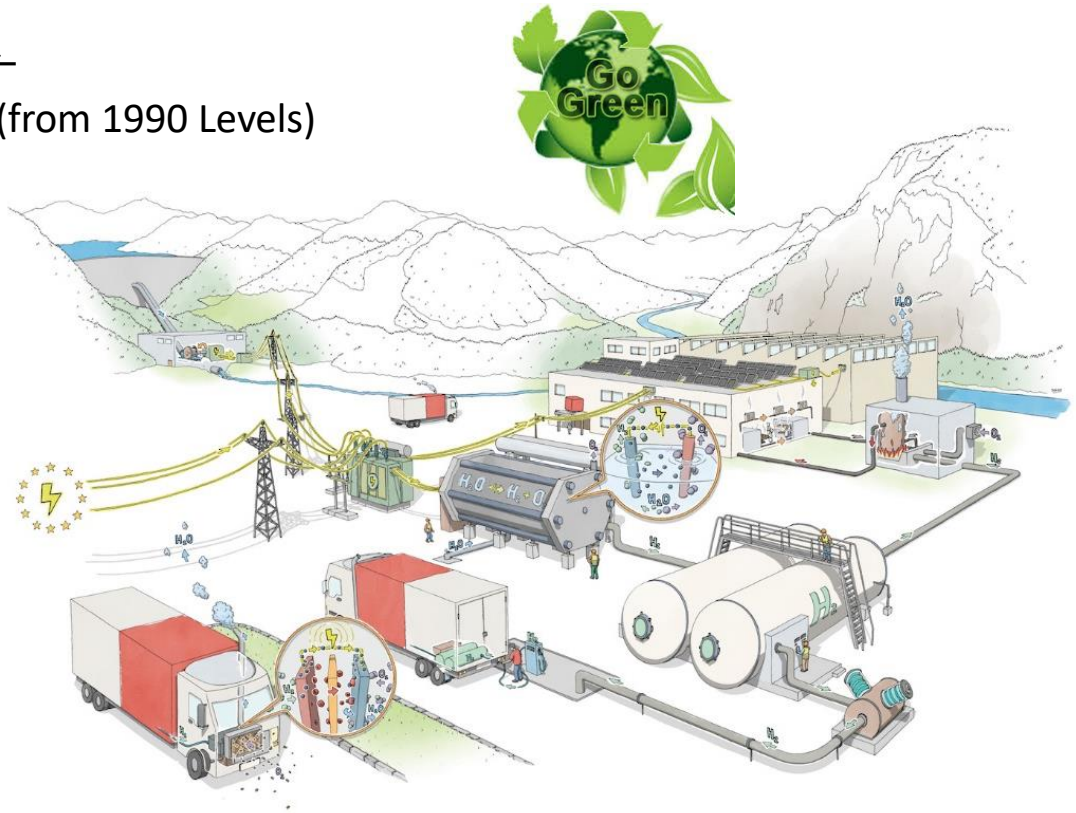
Motivation

EU 2030 Energy & Climate Framework

- 40% reduction of greenhouse gas emissions (from 1990 Levels)
- 32% share for renewable energy sources
- >32.5% improvement in energy efficiency

→ **Efficient Power-to-Hydrogen!**

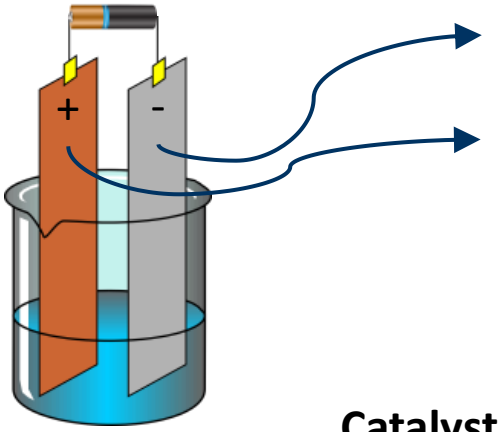
1. Surplus (green) energy
2. Water splitting → H_2
3. Chemical energy storage
4. For fuel cells & heating



Question: Can we make H_2 production more efficient?

[2] https://ec.europa.eu/clima/policies/strategies/2030_en
[3] www.demo4grid.eu/project/

Electrolysis of Water

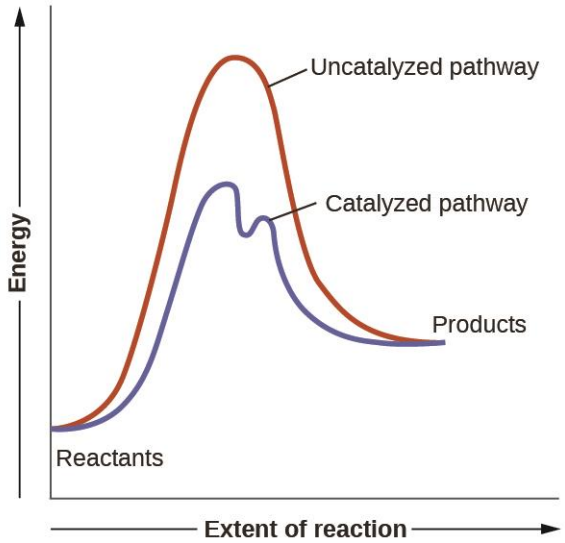


$$2H^+ + 2e^- \rightleftharpoons H_2$$ **Hydrogen Evolution Reaction (HER)**

$$H_2O \rightleftharpoons \frac{1}{2}O_2 + 2H^+ + 2e^-$$ Oxygen Evolution Reaction (OER)

Efficiency?

Catalyst lowers activation energy *via* intermediate steps



Catalyst Materials:

Pd – 30.5 $/g

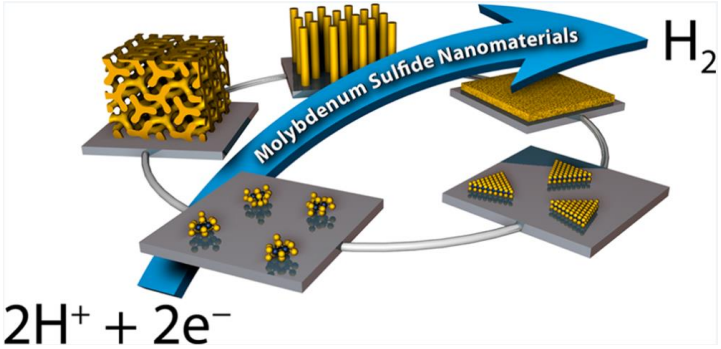
Pt – 27.4 $/g

Ru – 8.0 $/g

MoO_3 – 0.026 $/g

Molybdenum Sulfide – an HER Catalyst

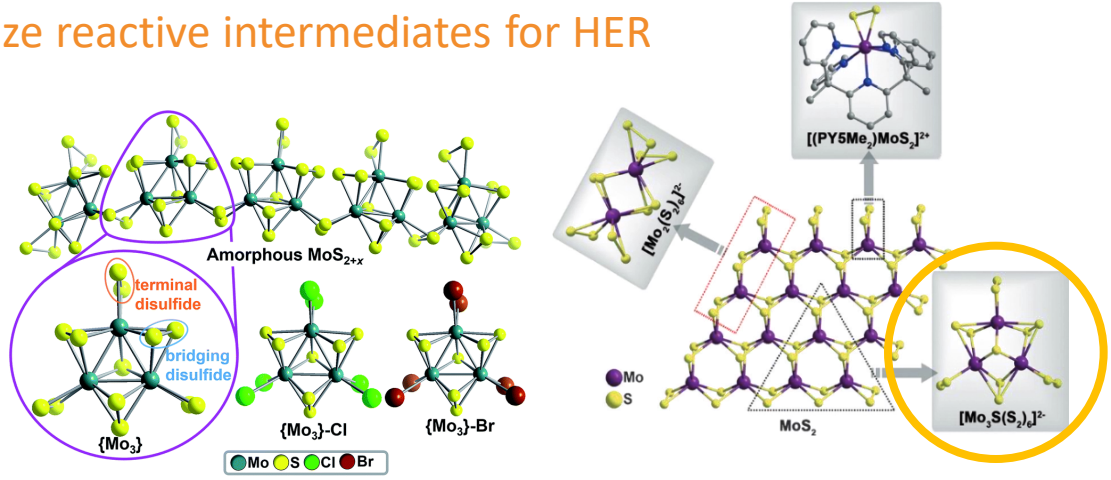
- High activity, excellent stability, precious metal-free
- Appropriately nanostructured MoS_2 to expose a high density of active edge sites



$[Mo_3S_{13}]^{2-}$ as a gas-phase model:

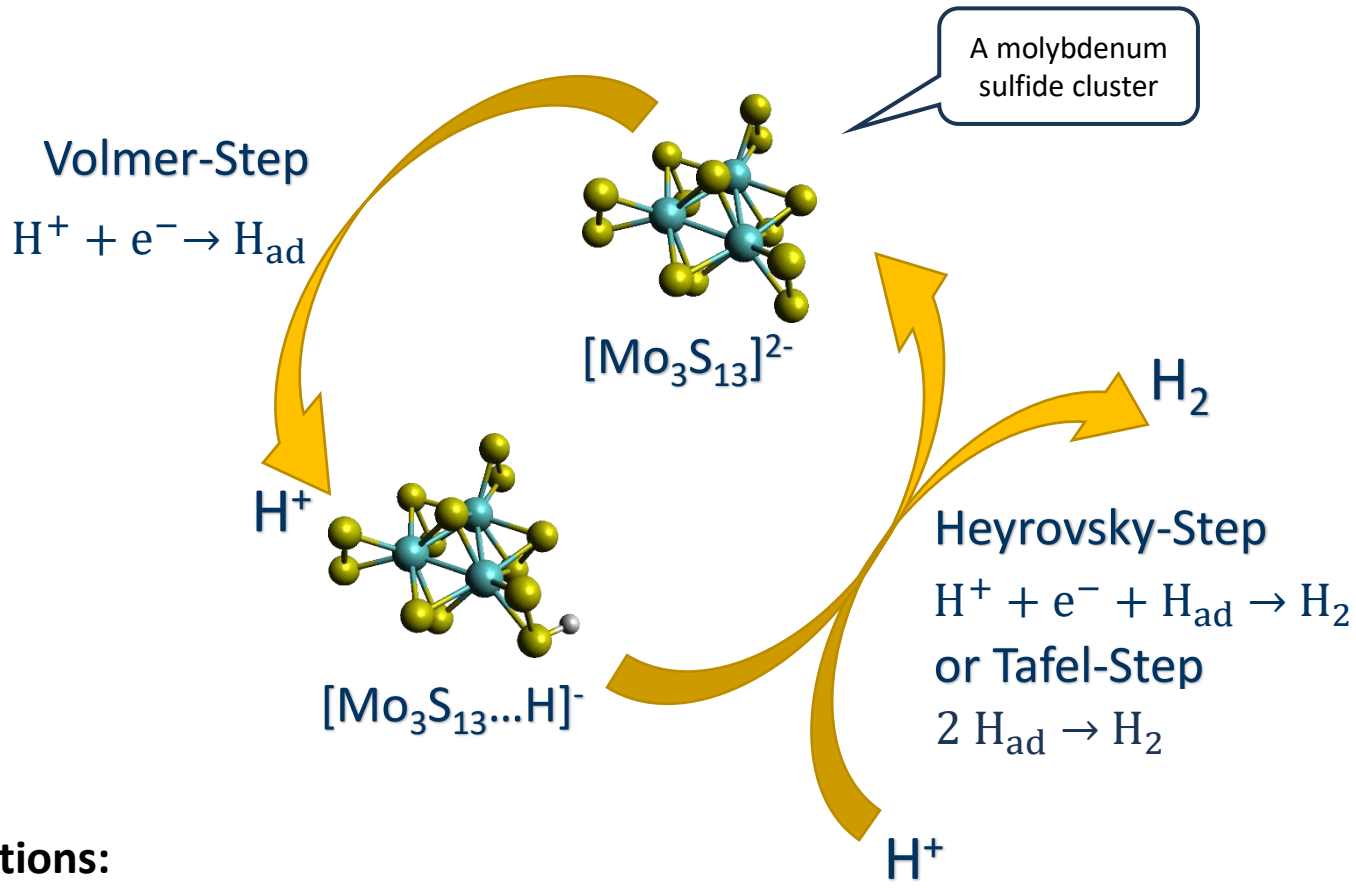
- Key building block for MoS_2 and MoS_x
- Heterogeneous and homgeneous HER catalyst
- Better understanding of HER catalysis (M.-L. Grutza et al., 2018)

→ Identify active centers & characterize reactive intermediates for HER



[5] J. D. Benck, et al., *ACS Catal.*, **2014**, 4, 3957-3971 [6] M.-L. Grutza et al. *Sust. Energy & Fuels*, **2018**, 2, 1893-1904 [7] Y. Wu et. al., *Angew. Chem. Int. Ed.*, **2015**, 54, 15181-15185 [8] C. Streb et al., *Sust. Energy & Fuels*, **2018**, 2, 1020-1026

Do you know HER?



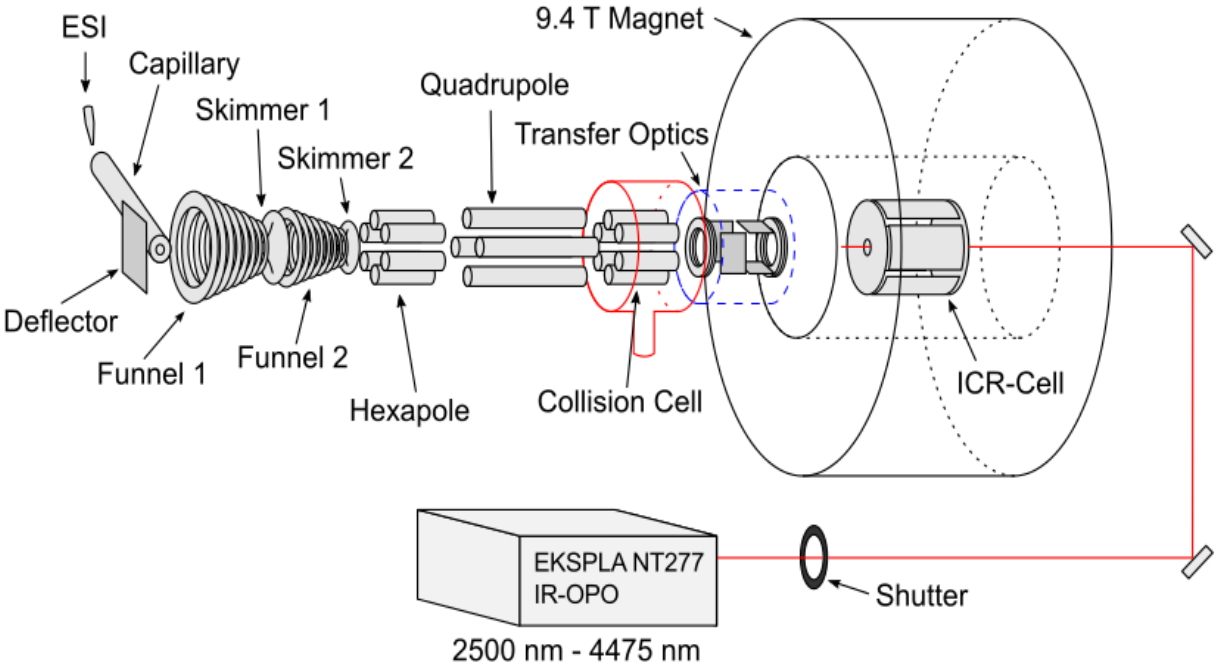
Open questions:

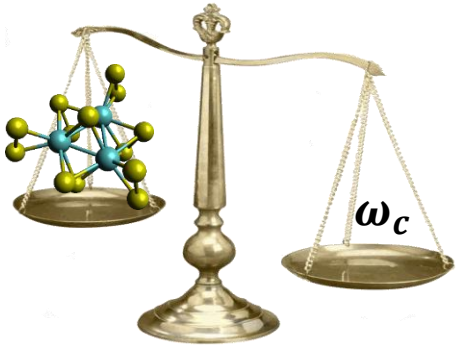
- Role of different S_2 moieties?
- H-adsorption sites?
- Mechanistic studies on MoS_x?

Experimental Setup

9.4T Fourier Transform – Ion Cyclotron Resonance Mass Spectrometer

Bruker Apex Qe 9.4T FT-ICR MS





Ion Cyclotron Frequency:

$$\omega_c = \frac{B_0}{m/z}$$

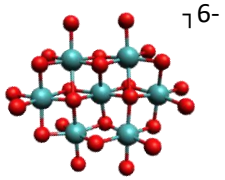
<u>A (nearly) complete chemistry lab:</u>

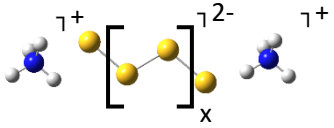
1. Collision Induced Dissociation (CID)
2. Ion Spectroscopy (IR & UV/Vis)
3. Ion-Molecule Reactions

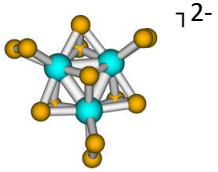
Sample Preparation

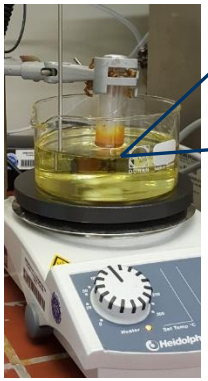
1) $MoO_3 + NH_{3(aq)} \xrightarrow{\text{evap.}} (NH_4)_6Mo_7O_{24} \cdot 4H_2O$

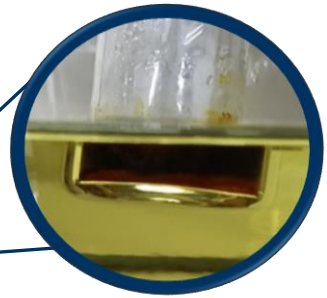
2) $(NH_4)_6Mo_7O_{24\,(aq)} + (NH_4)_2S_x \xrightarrow{90°C,\ 15h} (NH_4)_2Mo_3S_{13} \downarrow$

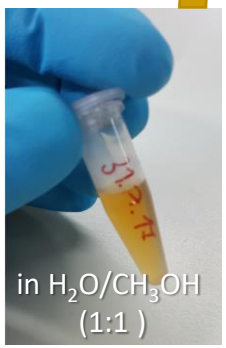




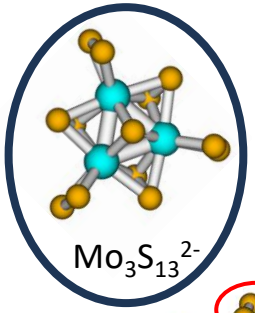




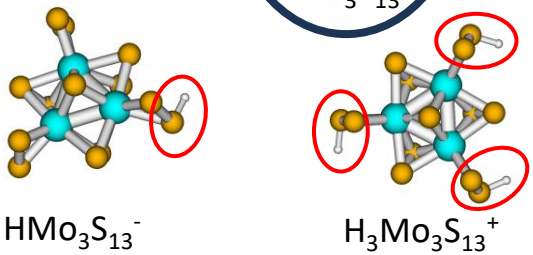


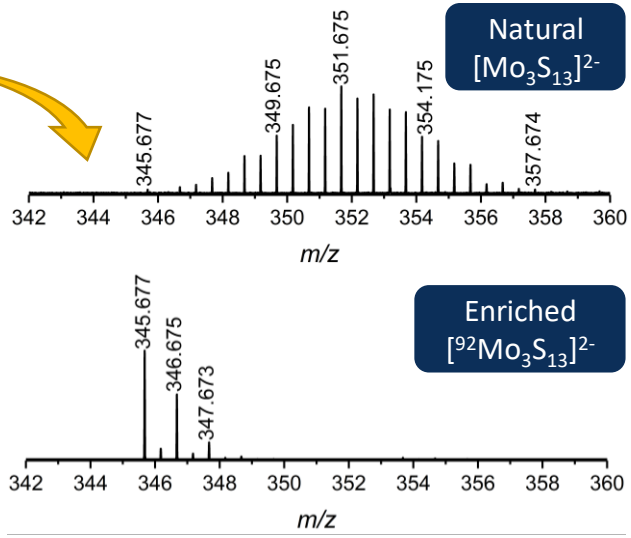


Electrospray



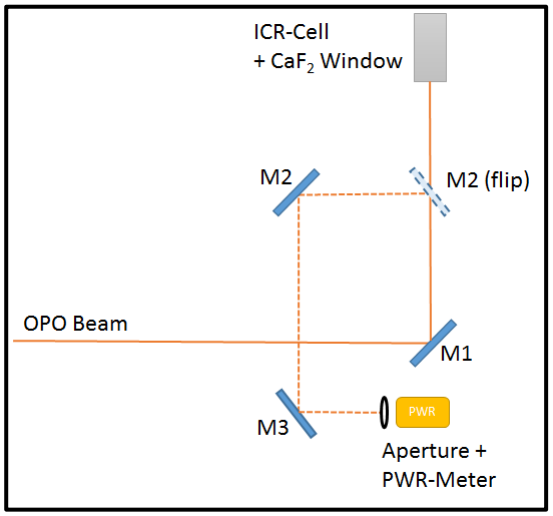
MS

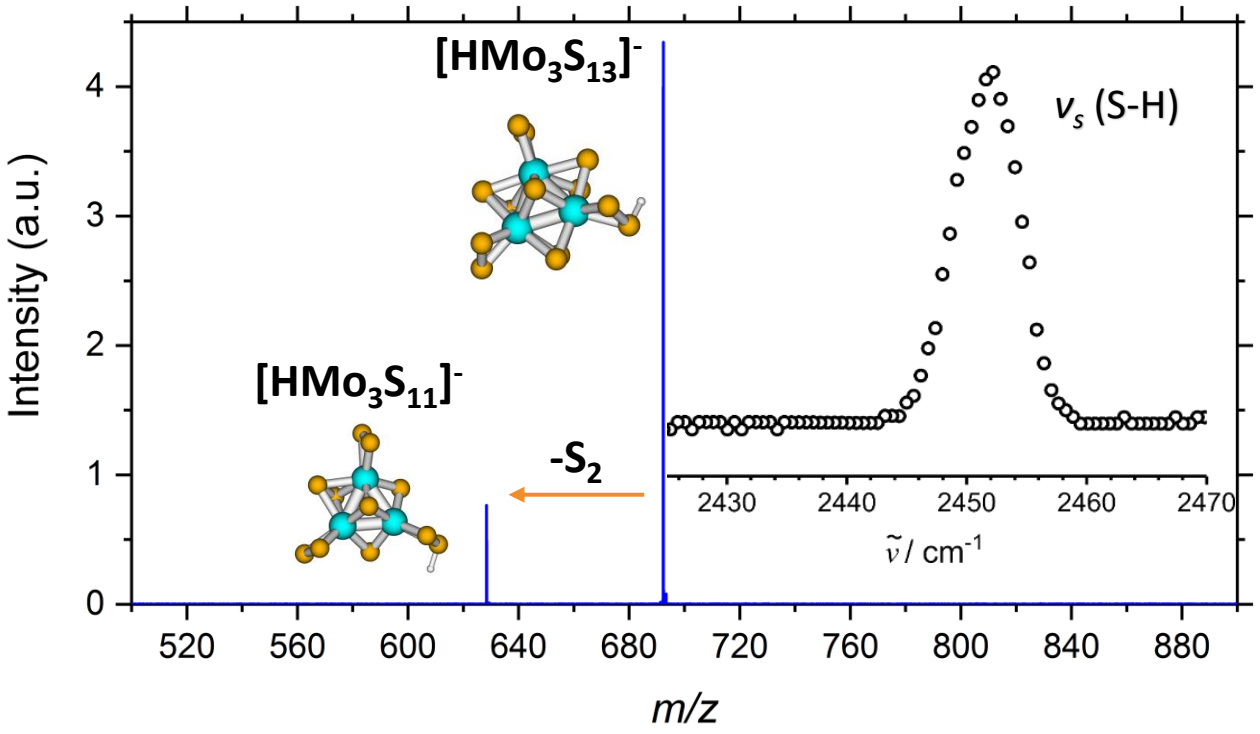




[9] M. Plattner, A. Baloglou et al., *J. Am. Soc. Mass Spectrom.*, **2019**, 30, 1946-1955 DOI: 10.1007/s13361-019-02294-4
[10] A. Baloglou, M. Ončák et al., *J. Phys. Chem. C*, **2019**, 123 (13), pp 8177–8186 DOI: 10.1021/acs.jpcc.8b08324

IRMPD Spectroscopy Technique



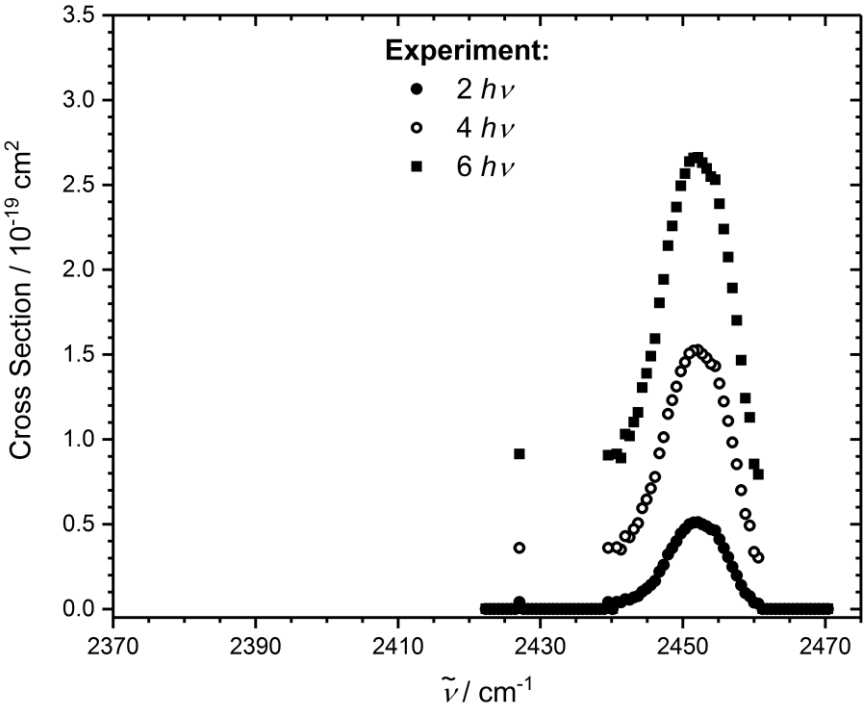


Measurement:

Fragmentation $\frac{\sum_{i=0}^{n} I_i}{I_0}$, photon flux Φ,

irradiation time t_{irr}

IRMPD Spectrum of $[HMo_3S_{13}]^-$



Measurement:

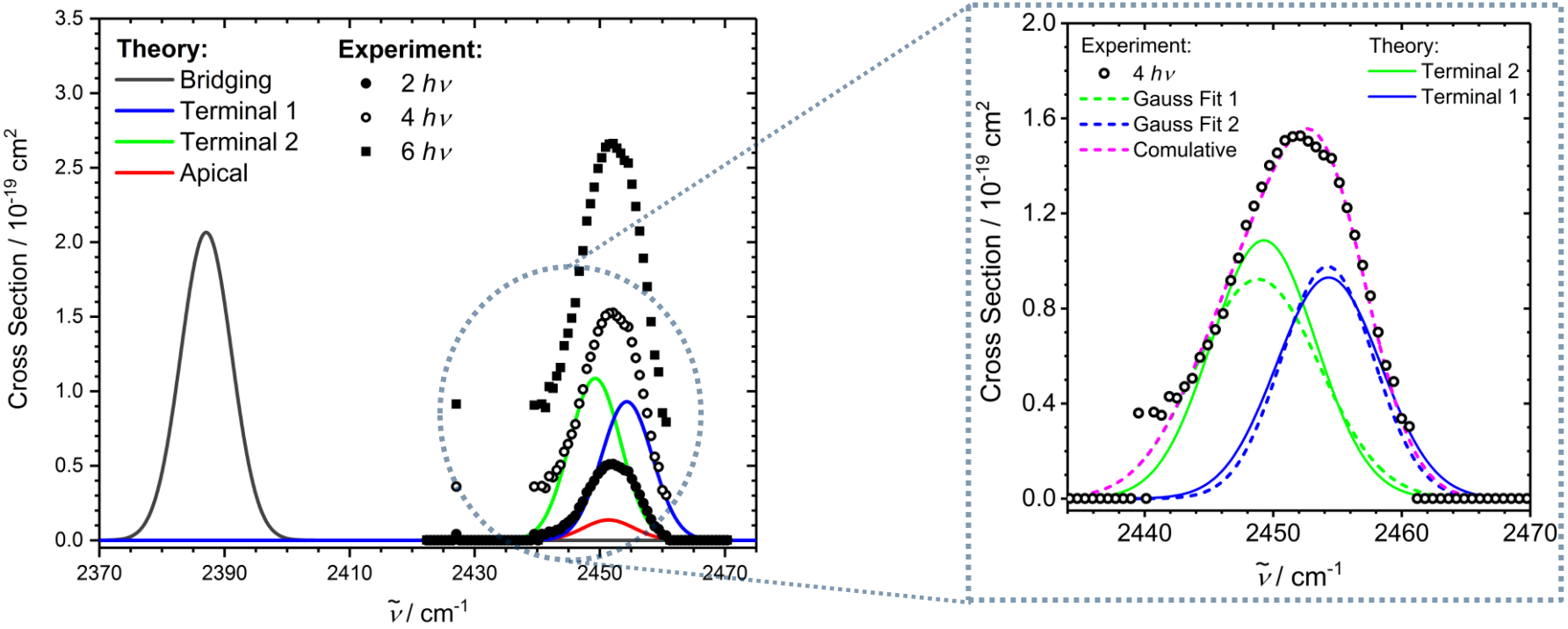
Fragmentation $\frac{\sum_{i=0}^{n} I_i}{I_0}$, photon flux Φ, irradiation time t_{irr}

Analysis: Photodissociation cross sections

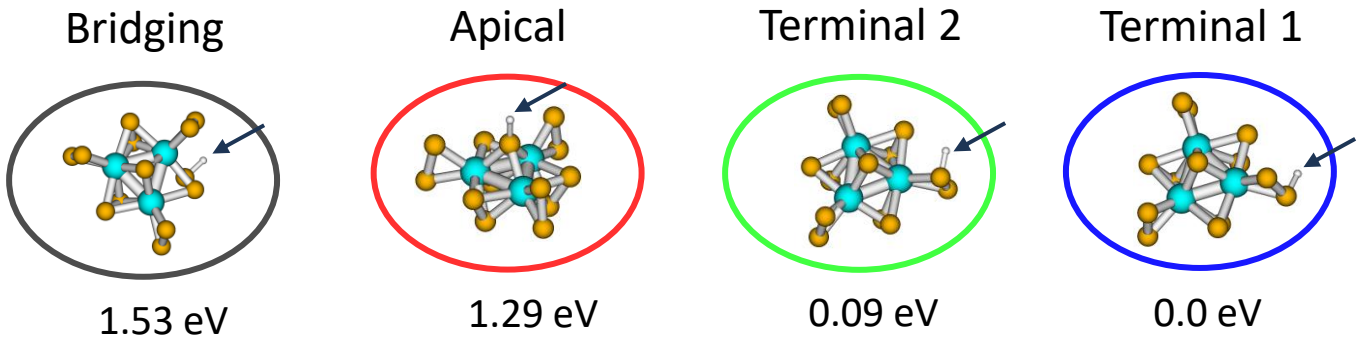
Lambert-Beer:

$$\sigma_{\mathrm{tot}} = \frac{1}{\Phi t_{\mathrm{irr}}} \ln\left(\frac{\sum_{i=0}^{n} I_i}{I_0}\right)$$

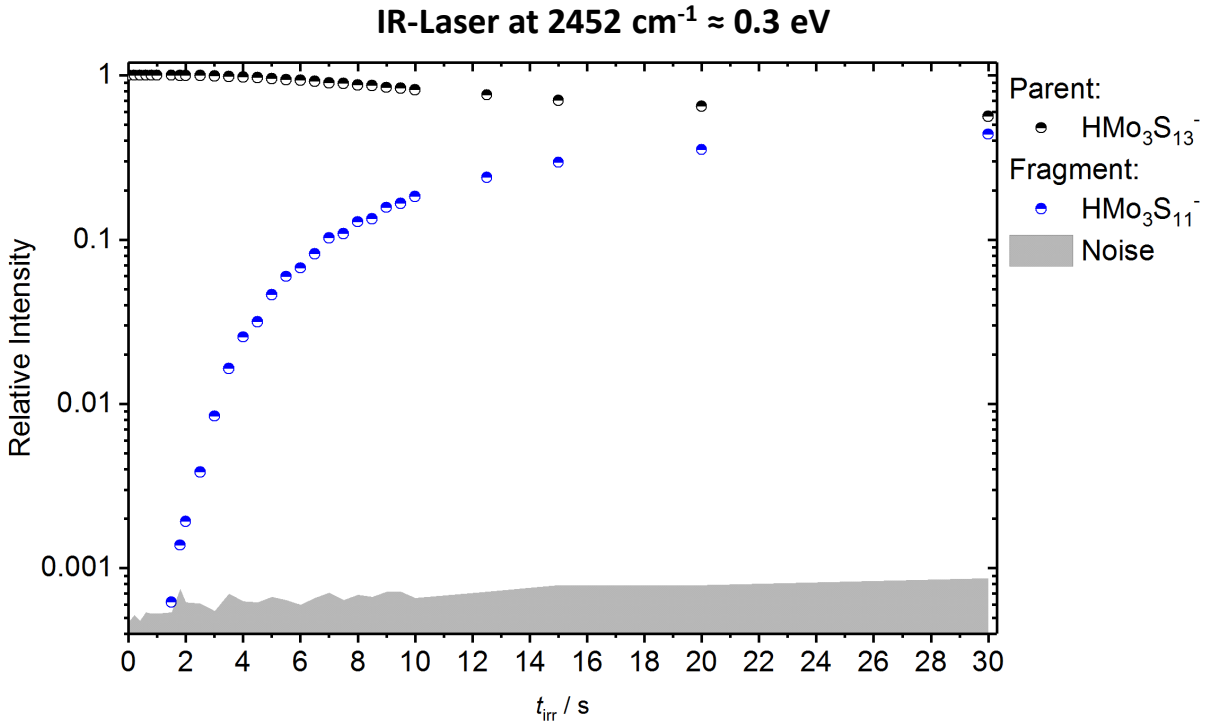
IRMPD Spectrum of $[HMo_3S_{13}]^-$

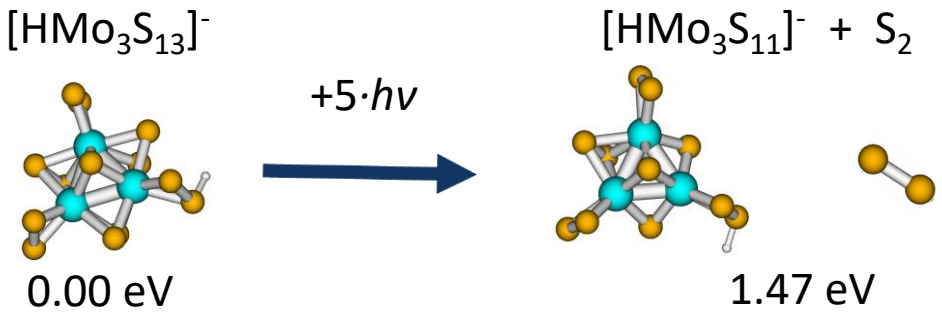


H-adsorption sites:



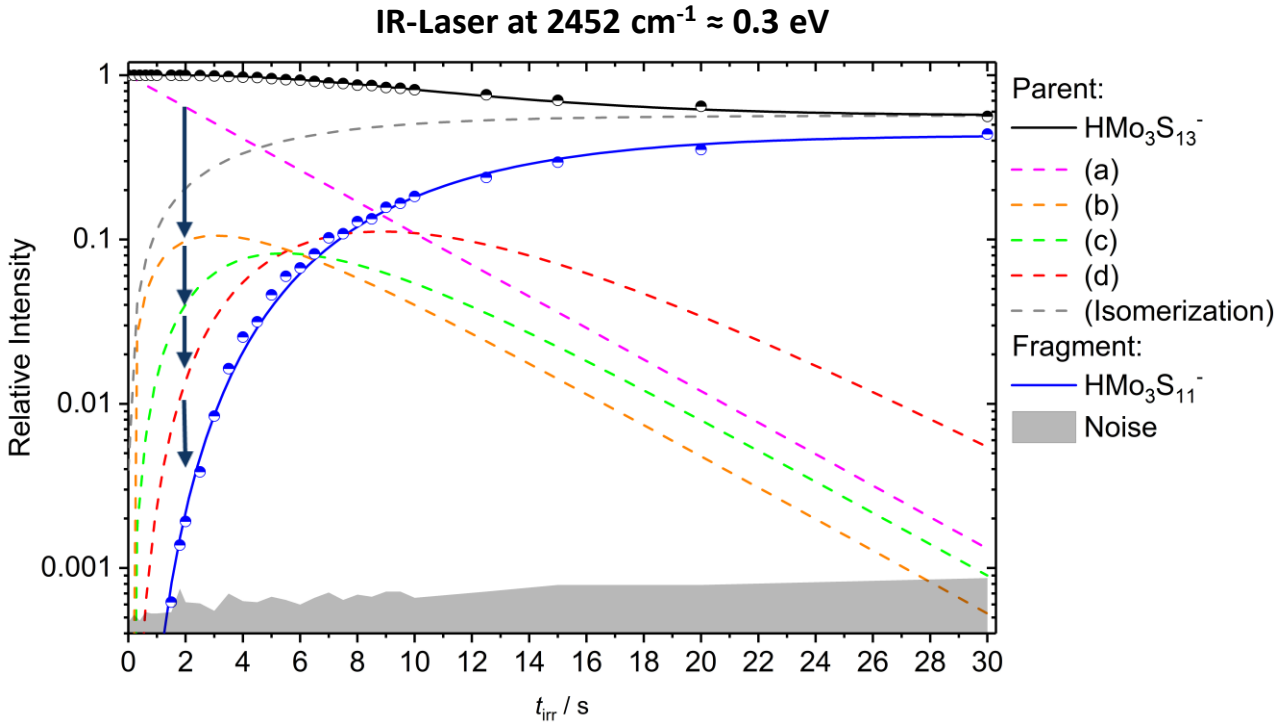
IRMPD Kinetics of $[HMo_3S_{13}]^-$

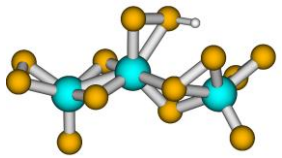




[10] A. Baloglou et al., *J. Phys. Chem. C*, 2019, 123 (13), pp 8177–8186 DOI: 10.1021/acs.jpcc.8b08324

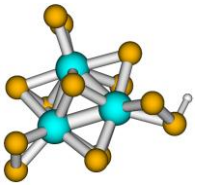
IRMPD Kinetics of $[HMo_3S_{13}]^-$





Xb
0.98 eV

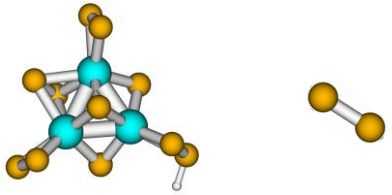
$[HMo_3S_{13}]^-$



0.00 eV

+5·*hν*

$[HMo_3S_{11}]^-$ + S_2

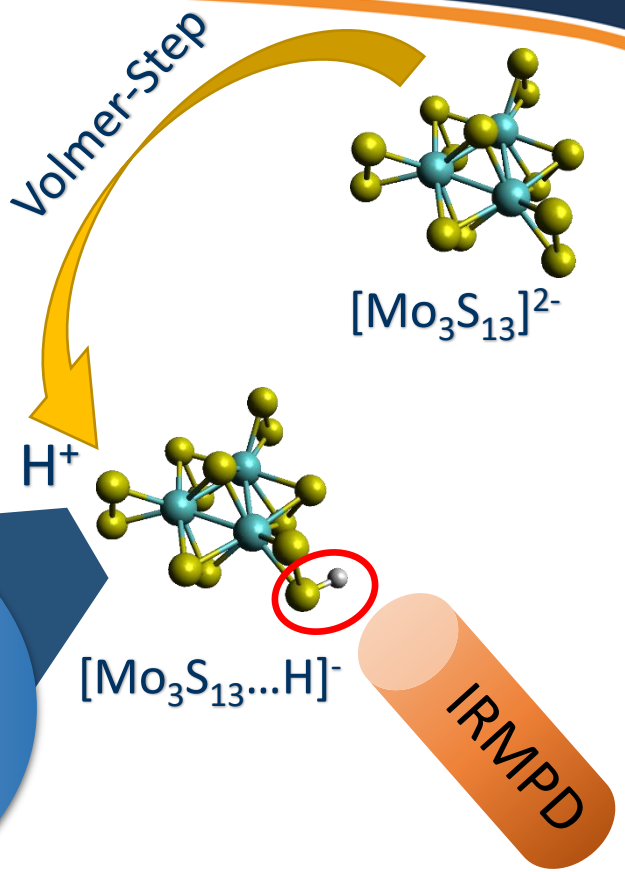


1.47 eV

[10] A. Baloglou et al., *J. Phys. Chem. C*, 2019, 123 (13), pp 8177–8186 DOI: 10.1021/acs.jpcc.8b08324

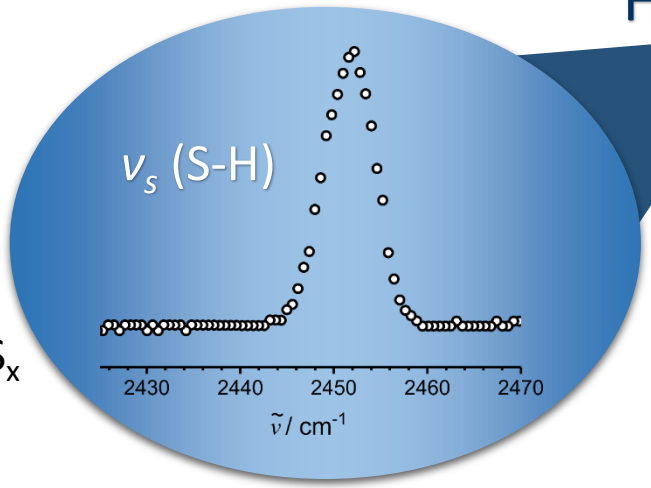
Summary

- $[Mo_3S_{13}]^{2-}$ gas-phase model for HER catalysis
- FT-ICR MS and IRMPD technique
- Pinpointing H-adsorption site on terminal S_2



Outlook

- Determine proton affinity
- Analyze UV/Vis Spectra
- Study reactions forming MoS_x



Publications & Awards

- A. Baloglou, M. Ončák et al.,"Gas-Phase Reactivity Studies of Small Molybdenum Cluster Ions with Dimethyl Disulfide", *Top Catal,* **2018**, 61(1-2), 20-27
- A. Baloglou, M. Ončák et al., "Structural Properties of Gas Phase Molybdenum Sulfide Clusters $[Mo_3S_{13}]^{2-}$, $[HMo_3S_{13}]^-$, and $[H_3Mo_3S_{13}]^+$ as Model Systems of a Promising Hydrogen Evolution Catalyst", *J Phys Chem C*, **2019**, 123 (13), 8177–8186 DOI: 10.1021/acs.jpcc.8b08324
- M. Plattner, A. Baloglou et al., "Structural Properties of Gas-Phase Molybdenum Oxide Clusters $[Mo_4O_{13}]^{2-}$, $[HMo_4O_{13}]^-$, and $[CH_3Mo_4O_{13}]^-$ Studied by Collision-Induced Dissociation", *J Am Soc Mass Spectrom,* **2019**, 30, 1946-1955 DOI: 10.1007/s13361-019-02294-4
- Best Student Paper Award at IC4N 2019, Corfu: "Gas-Phase investigations of Nanoclusters $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ as Model Catalysts for the Hydrogen Evolution Reaction"