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# Computational heterogeneous electrocatalysis: How does it work and which questions can be answered at which cost?

Stephan N. Steinmann

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# Computational heterogeneous electrocatalysis: How does it work and which questions can be answered at which cost?

Stephan N. STEINMANN

# Research interests

## Reactivity at (electrified) interfaces

**Surface state:** Fang, Ding, Zhang, [Steinmann](#), Hu, Mao, Feliu, Tian *J. Am. Chem. Soc.* **2020**, 142, 9439.

**OER:** Curutchet, Colinet, Michel, [Steinmann](#), Le Bahers. *Phys Chem Chem Phys* **2020**, 22, 7031.

**HER:** Abidi, Bonduelle, [Steinmann](#) *ACS Appl Mater Interfaces* **2020**, 12, 31401.

## Solid-state

**g-CN:** Li, Melissen, Le Bahers, Sautet, Masters, [Steinmann](#), Maschmeyer, *Chem. Mater.* **2018**, 30, 4253.

**MoS<sub>3</sub>:** Sahu, [Steinmann](#), Raybaud, *Cryst. Growth Des.* **2020**, 20, 7750.

**MnO<sub>2</sub>:** Manceau, [Steinmann](#), *ACS Earth Space Chem.* **2023**, 7, 1459.

## Method development for solid/liquid interface

**Force fields:** Clabaut, Beisert, Michel, [Steinmann](#) *J Chem. Phys.* **2022**, 157, 194705.

**Solvation energy:** Clabaut, Schweitzer, Goetz, Michel, [Steinmann](#) *J Chem Theory Comput.* **2020**, 16, 6539.

**Electrostatic embedding:** Abidi, [Steinmann](#), *ACS Appl Mater Interfaces* **2023**, 15, 25009.

# How do noble metal electrocatalysts look like?

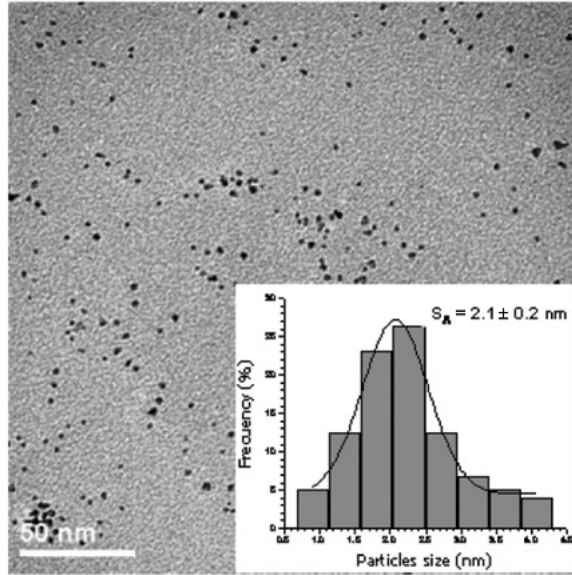
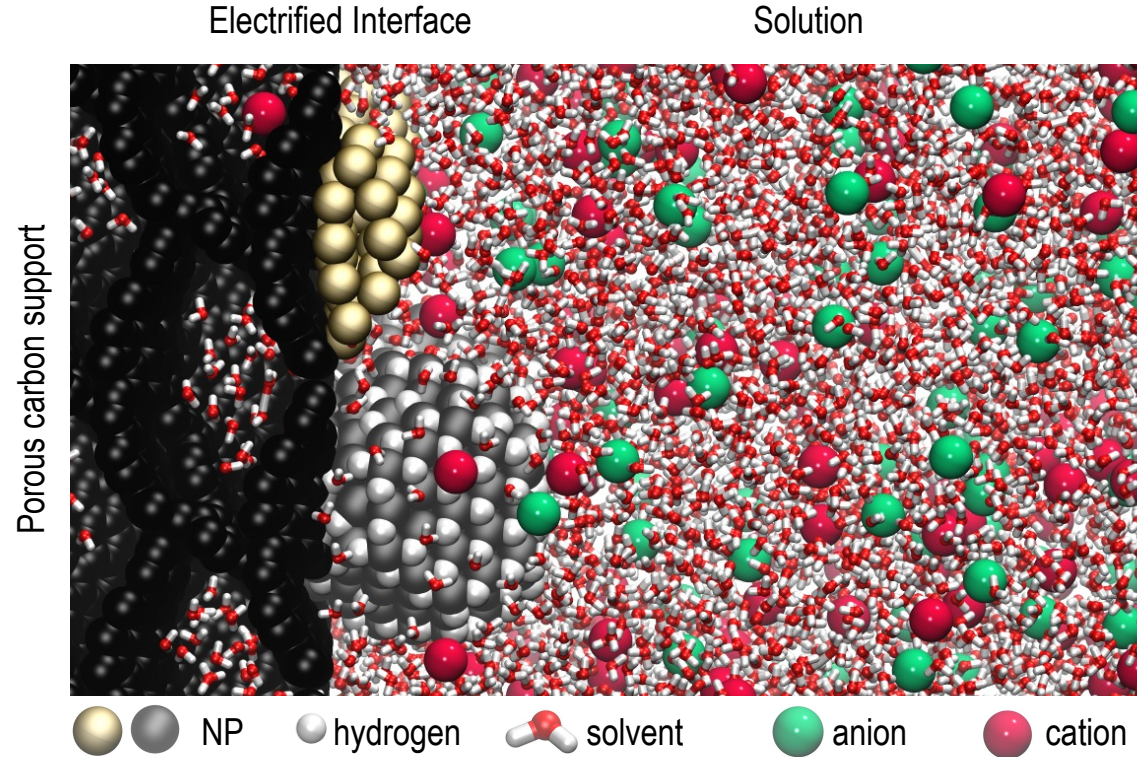


Figure 1: A typical TEM image of the Pt nanoparticles with size distribution histogram.



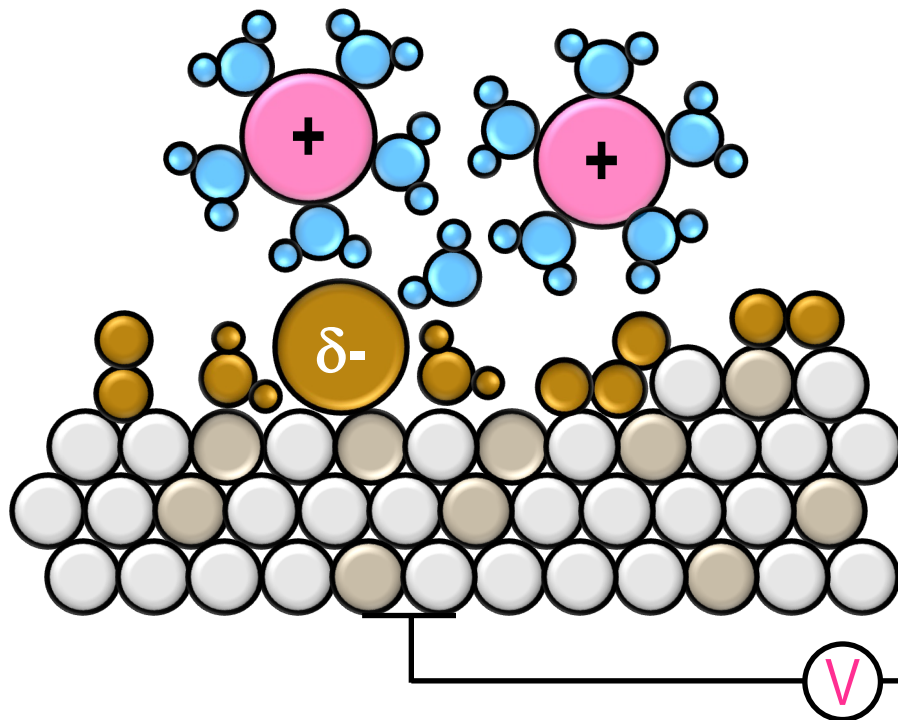


# Atomistic models for electrocatalysis?

Solvent

Ions

Adsorbates



Restructuring

Reactivity

Electrochemical potential

# Models in practice

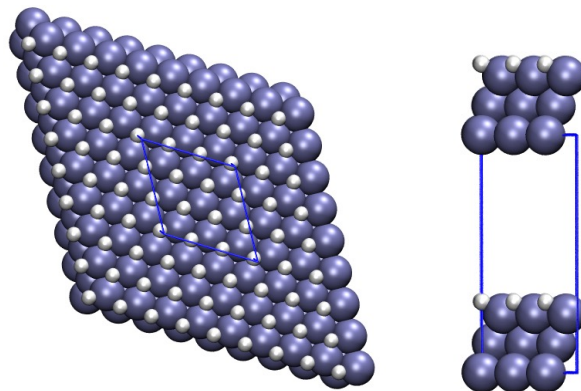
Large nanoparticles  
→ Periodic surface model

Solvent

None

Implicit

QM/MM



Electrochemical potential

Implicit: CHE

Explicit: GC-DFT

# Grand-Canonical DFT

Grand-Potential  $\Omega$  :

The energy of GC-DFT

$$\Omega(U) = E(q) - U \times q$$

U: potential  
q: charge

E(q): Electronic energy at charge q

Poisson-Boltzmann Equation neutralizes q

**Implicit solvent + Electrolyte**

## Grand-Canonical DFT

Grand-Potential  $\Omega$  :  
The energy of GC-DFT

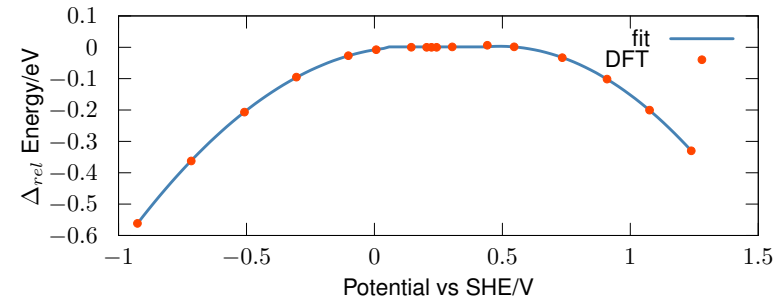
$$\Omega(U) = E(q) - U \times q$$

$U$ : potential  
 $q$ : charge

$E(q)$ : Electronic energy at charge  $q$

Poisson-Boltzmann Equation neutralizes  $q$   
**Implicit solvent + Electrolyte**

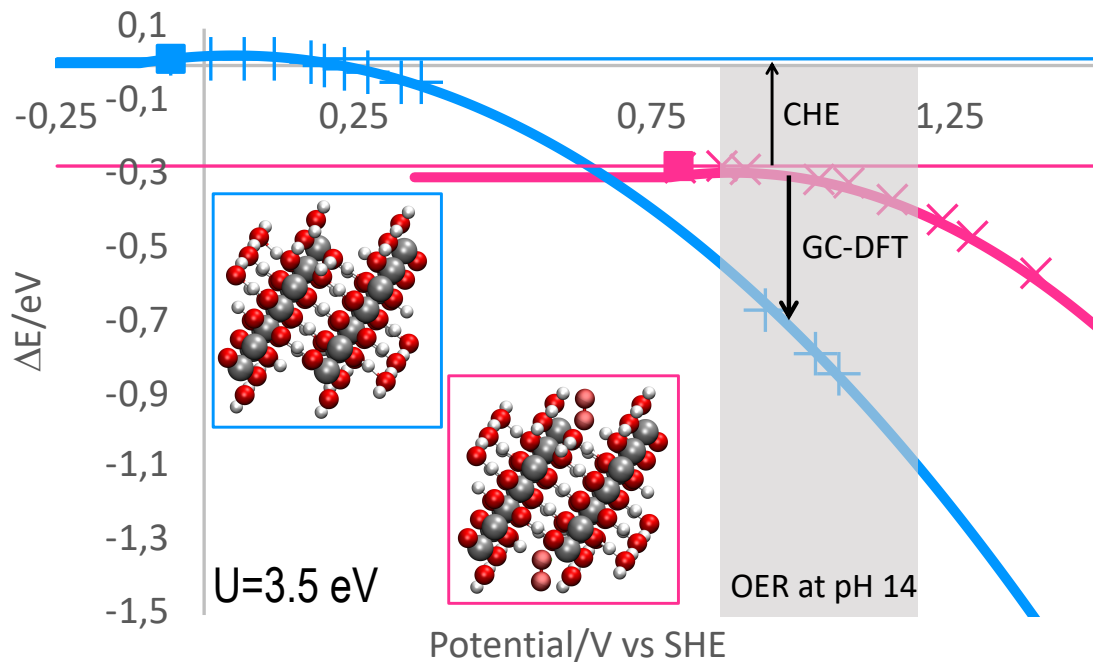
Semi-conductor: A piece-wise parabola



Conductor: A Single parabola

# Grand-Canonical DFT in practice

The impact of electrode polarization is system dependent



The **potential modifies** the qualitative behavior of "chemical" steps

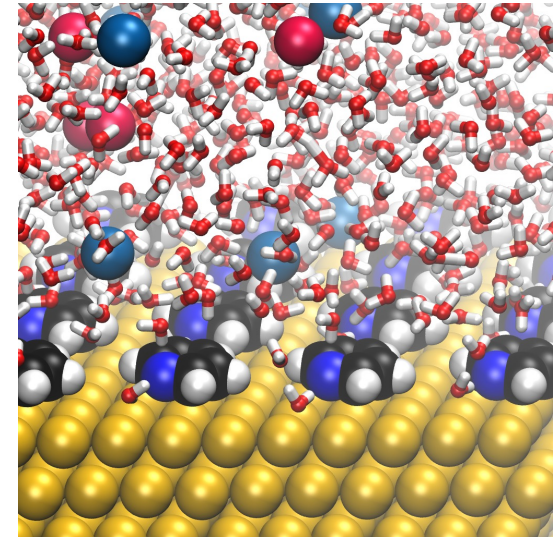
# How to model the water/metal interface?

Diffusion at interfaces is slow:  
~500 ps for equilibration

DFT for metals is costly  
~140 kCPUh for 10 ps, est. 8 years for 500 ps

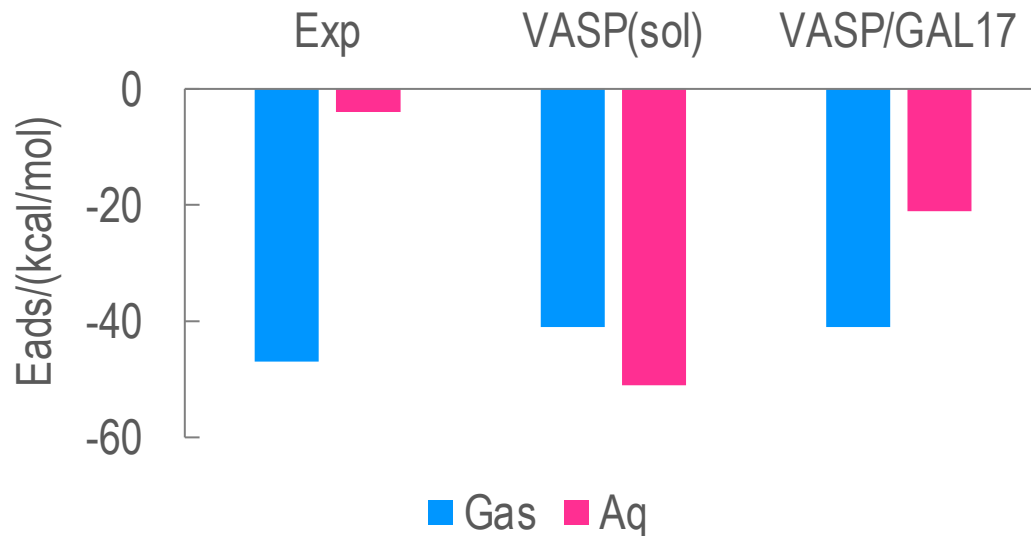
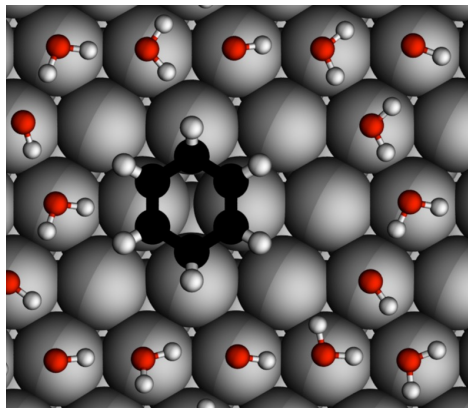
Interaction is neither weak nor strong  
Problem for force fields

Interfaces are amorphous:  
Large cells required





# Aromatics at Pt(111)/water interface



→ **Semi-quantitative** agreement between theory and experiment

# What about kinetics?

Transition states determine the kinetics of reactions

The number of atoms needs to be conserved from the reactant to the product

Chemical steps:  $\text{H}^* + \text{CO}_2^* \rightarrow \text{HCOO}^*$   $\mapsto$  “standard”

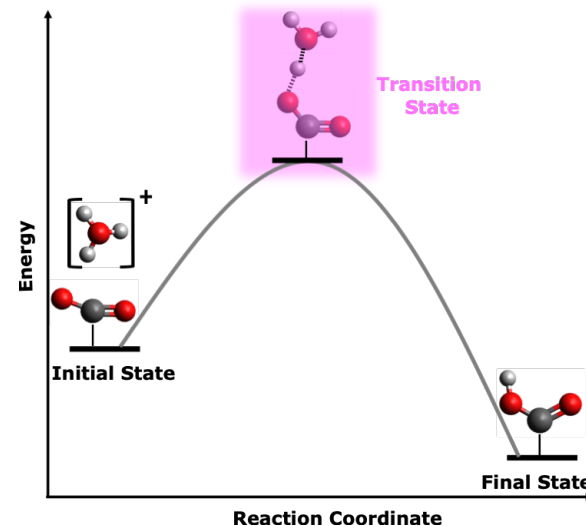
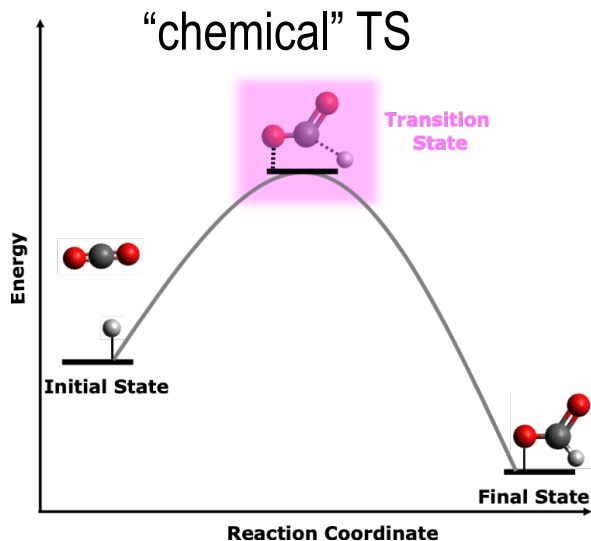
Electrochemical steps:  $\text{H}^+ + \text{e}^- + \text{CO}_2^* \rightarrow \text{HCOO}^*$   $\mapsto$  non-standard

## Transition states in electrocatalysis

**(Electro-)chemical transition states**

Transition states determine the kinetics of reactions

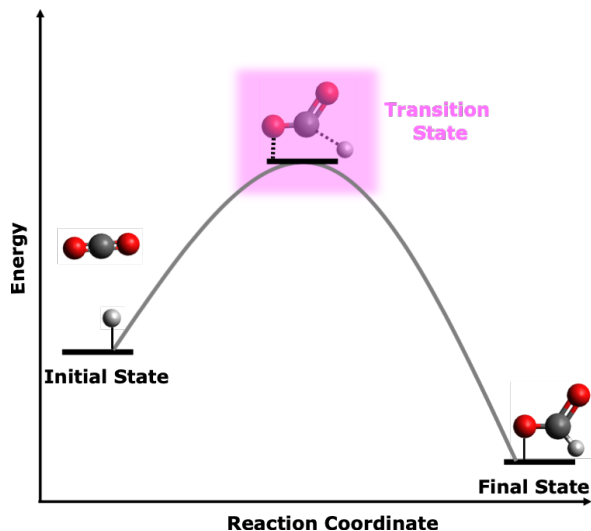
“electrochemical” TS



Most computational work in electrocatalysis ignore transition states

# Transition states in electrocatalysis

## Chemical steps



Standard techniques in heterogeneous catalysis

2 weeks to 1 month of real time\*

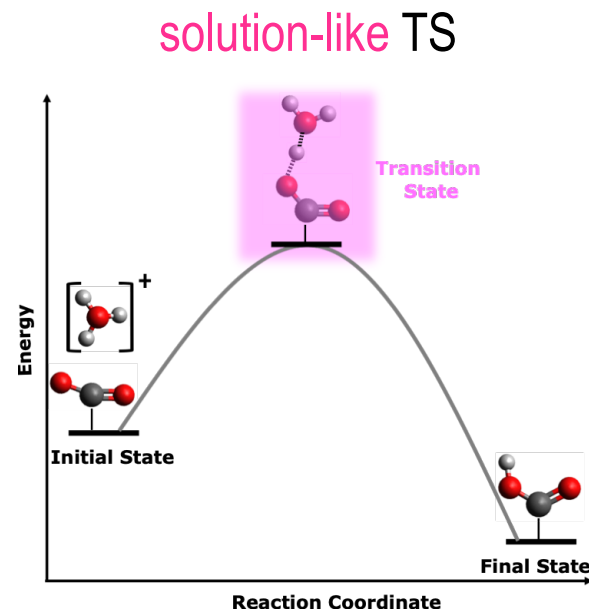
\*not 100% of human time

# Transition states in electrocatalysis

## Electrochemical steps

Difficult to identify

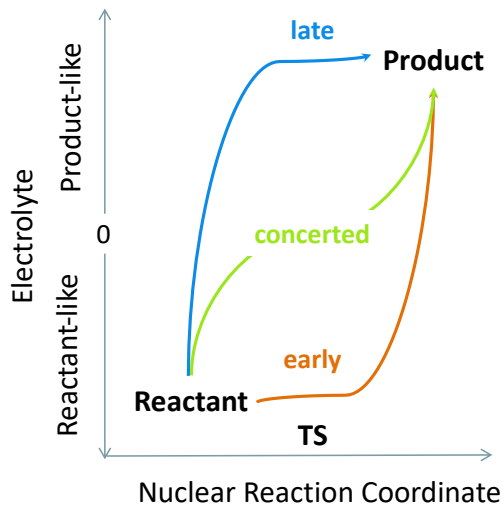
1-3 month of real time\*



\*not 100% of human time

## Transition states in electrocatalysis

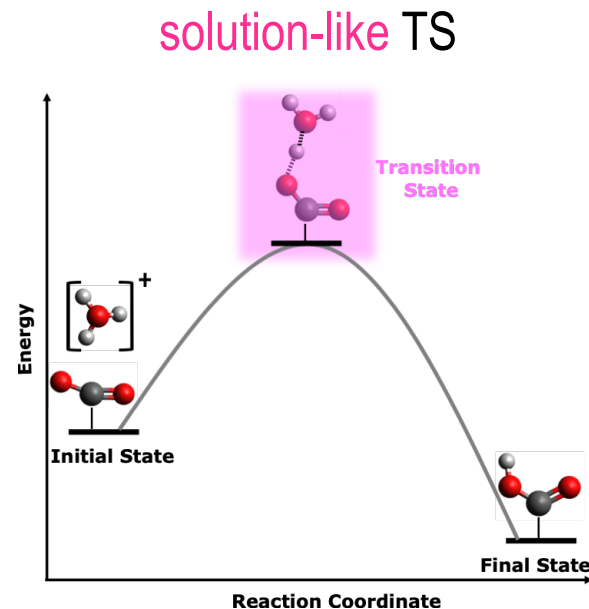
## Electrochemical steps



Reorganisation of:

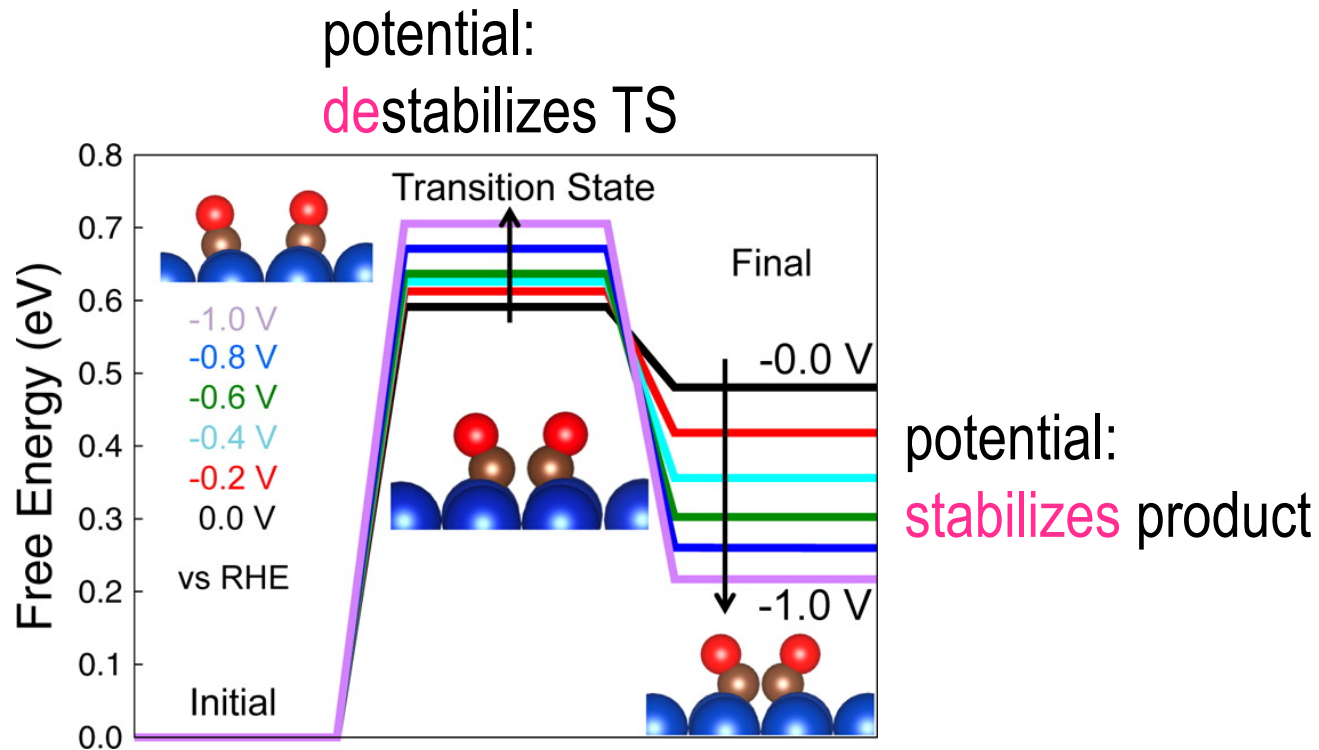
- Solvent
- Adsorbate@surface

- Marcus theory?
- Active research



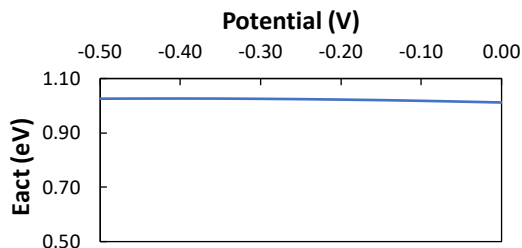
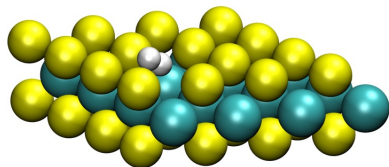


## Transition states in electrocatalysis

**Oddly behaving transition states can be found**

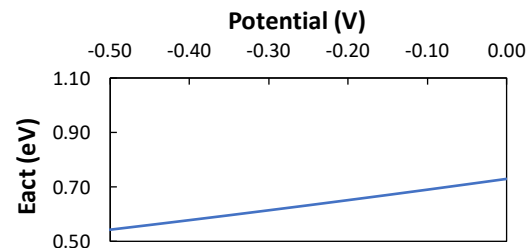
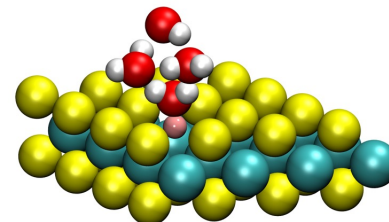
# HER mechanism on V<sub>S</sub> defect

Chemical (Tafel) step



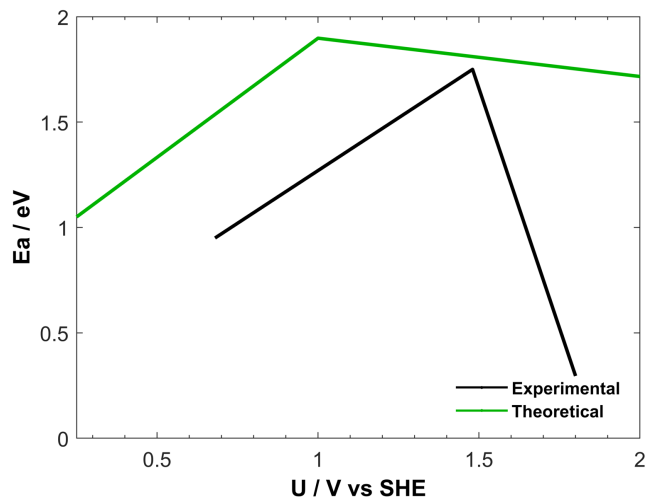
Slope:  
Symmetry factor from GC-DFT

Electrochemical (Volmer) step

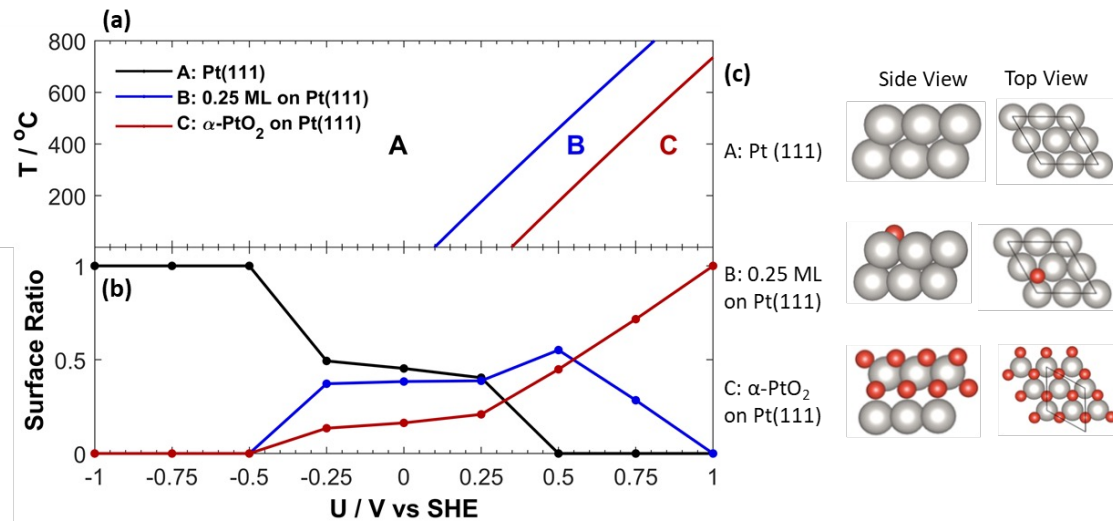


# Importance of the surface state

Accelerating CH<sub>4</sub> oxidation over Pt via an electrochemical potential



Effective activation energy



Surface state as a function of  $T$  and  $U$

# Partial take home message

Periodic surface models are most convenient

The effect of the electrochemical potential can be modeled with GC-DFT

Implicit solvents are very practical but have limitations

TS: rarely considered and painful to identify for electrochemical steps

The surface state changes dramatically as a function of the potential

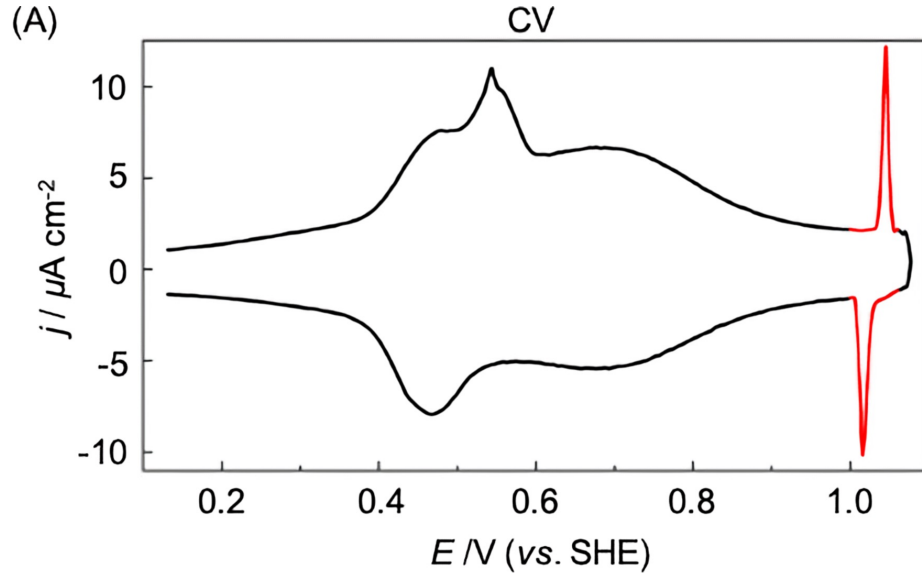
# 1. Sulfate on Au(111)

2. HER on MoS<sub>2</sub>: Screening of dopants

3. Structural complexity

4. Reaction pathways

# The gold sulfuric acid interface is prototypical



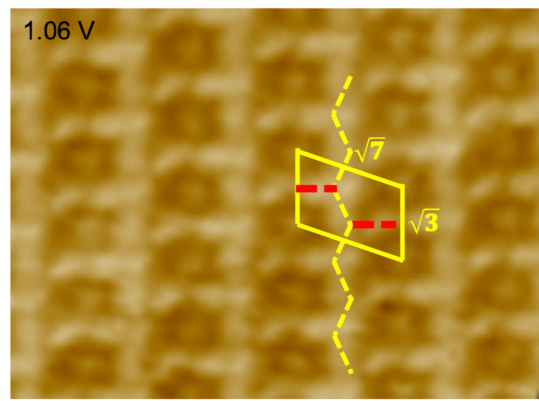
Indication of a phase transition

→ What is the structure?

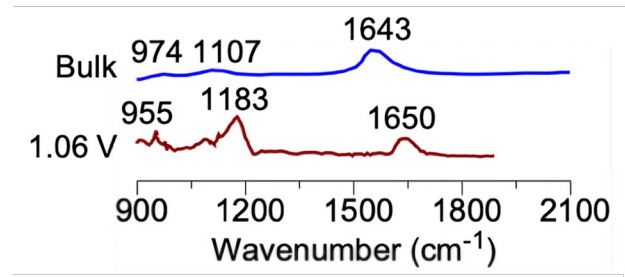


# Experimental characterization of ordered phase

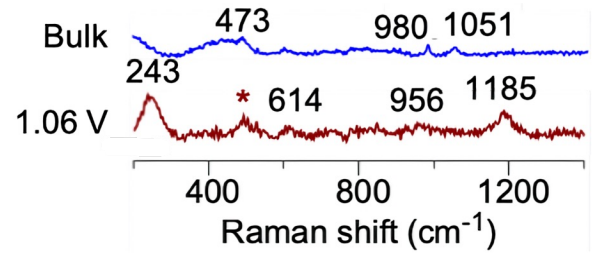
EC-STM



EC-IR



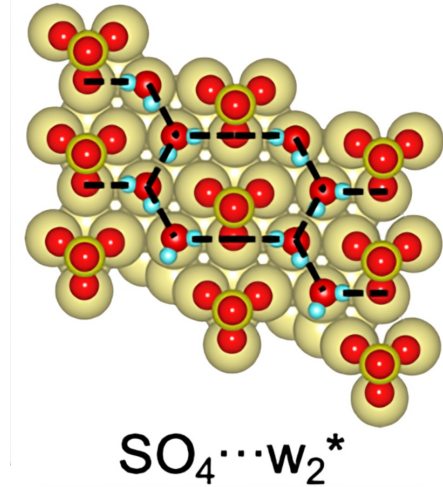
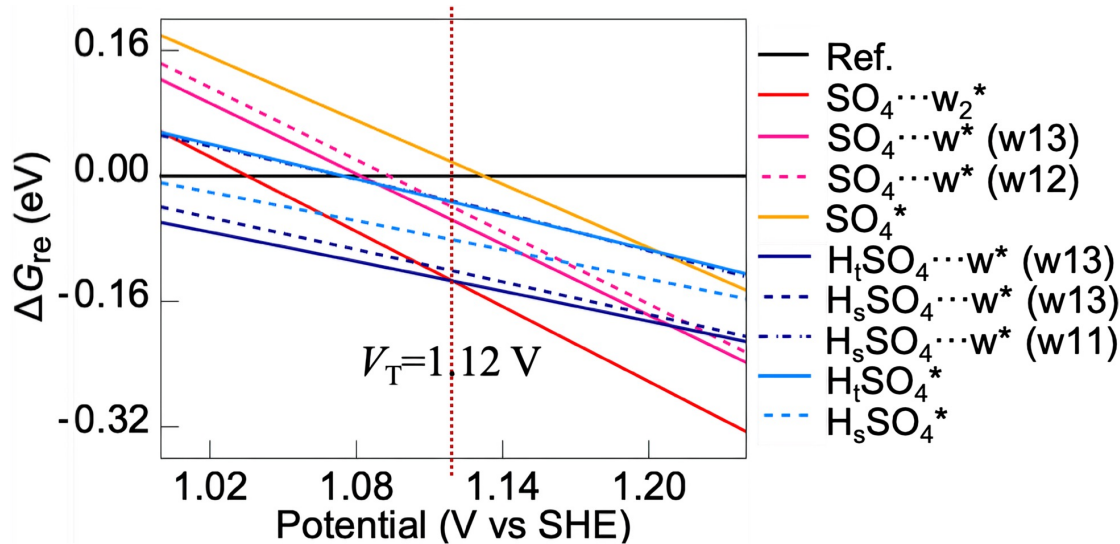
EC-Raman (SHINER)



Characterization can barely be better

→ But still, what is the atomic structure of this phase??

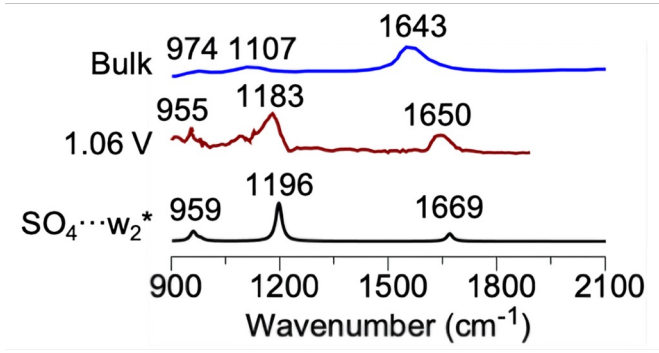
# Computational identification of ordered phase



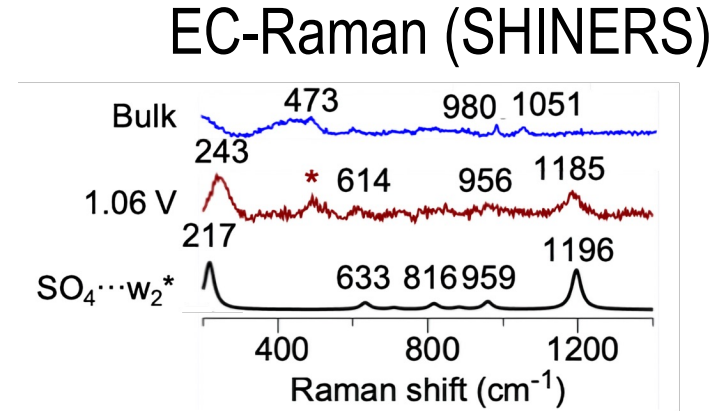
At positive potentials a very ordered water/SO<sub>4</sub> adlayer becomes most stable

SO<sub>4</sub>@Au(111)

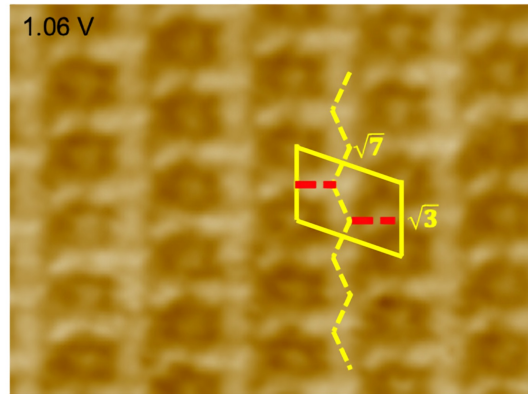
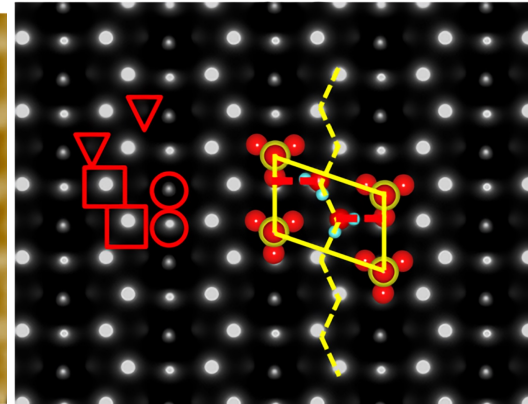
# Experiment and computations agree!



EC-IR



STM

SO<sub>4</sub>⋯w<sub>2</sub>\*

# Partial take home message

Microscopy and spectroscopy for electrified interfaces are challenging

When available: Interpretation not always obvious

Computations can “convert” signals into atomic structures

→ More insights for (electro-)chemists

1. Sulfate on Au(111)

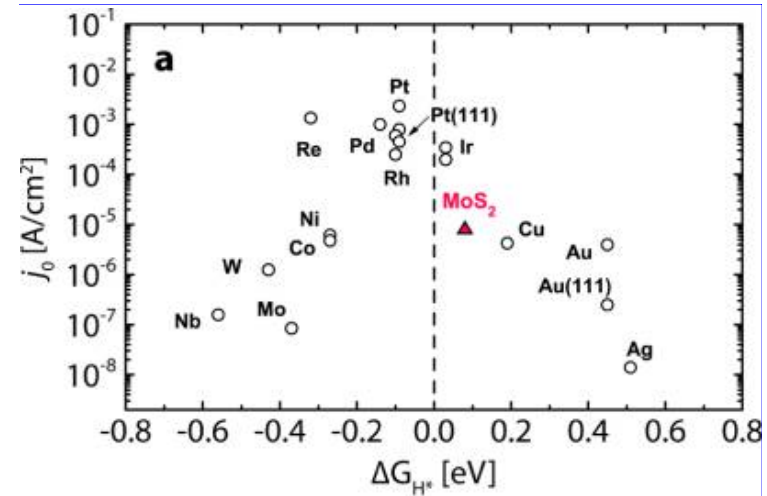
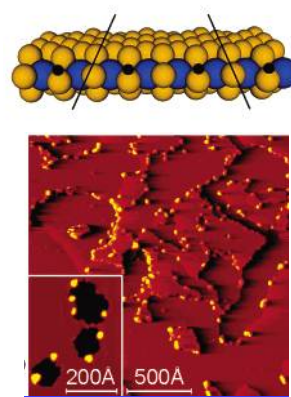
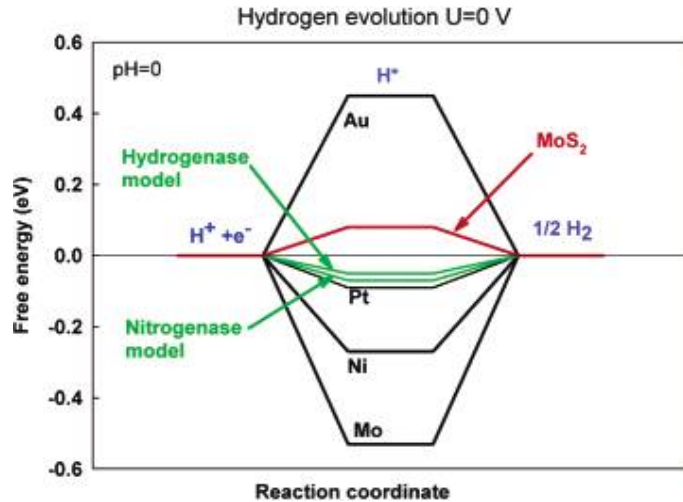
**2. HER on MoS<sub>2</sub>: Screening of dopants**

3. Structural complexity

4. Reaction pathways

Hydrogen evolution reaction on  $\text{MoS}_2$ 

# $\text{MoS}_2$ as an Hydrogen Evolution Reaction Catalyst



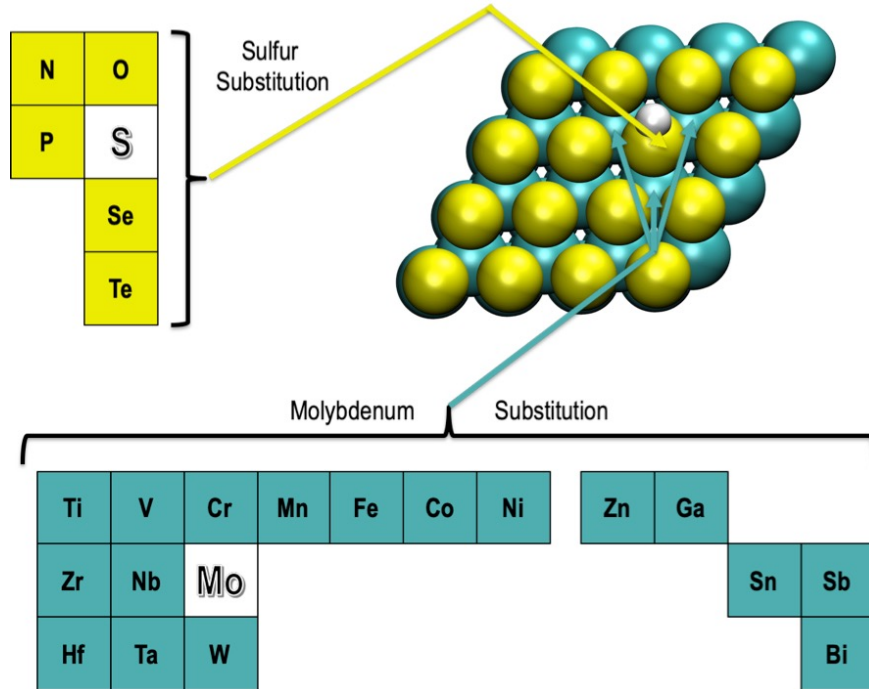
$\text{MoS}_2$  is one of the best low-cost HER catalysts in acidic conditions

”one of the best”, but not a good one



Hydrogen Evolution Reaction on MoS<sub>2</sub>


## Can We Activate the Basal Plane?



Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo				
Hf	Ta	W				

Zn	Ga	
	Sn	Sb
		Bi

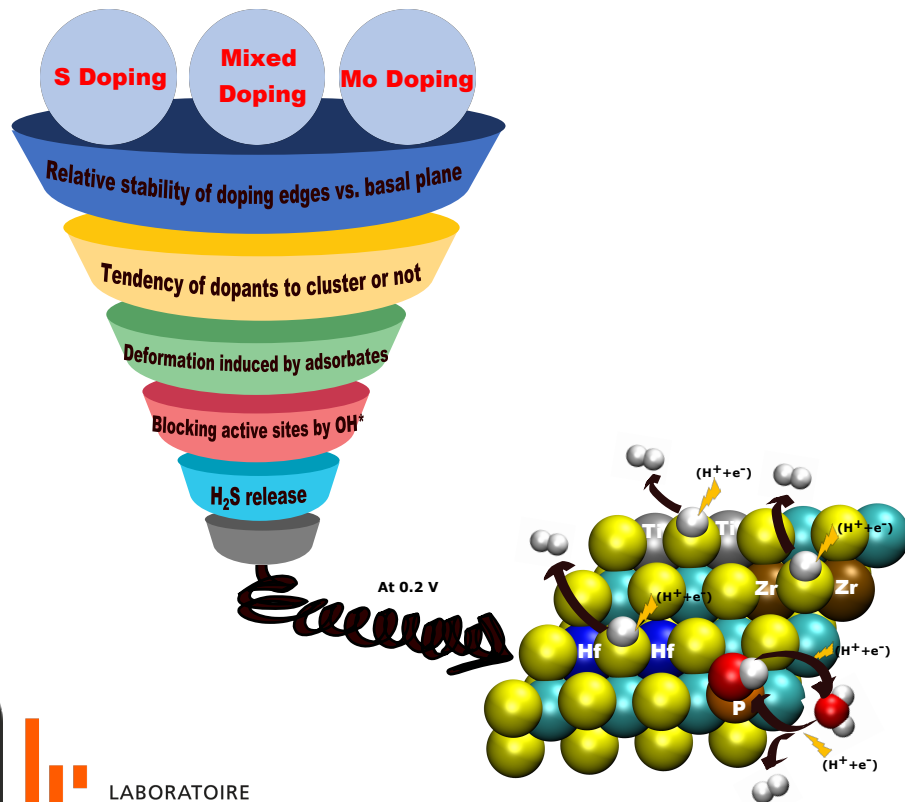
Mo: Element to substitute

**Element:** Better stabilized on Mo-edge**Element:** Better stabilized on S-edge Edge substitution strongly preferred Basal plane substitution possible

Doping stability is one of the key issues

# Hydrogen Evolution Reaction on MoS<sub>2</sub>

## Can We Activate the Basal Plane?



At -0.2 V vs SHE:  
few dopants create active sites:

Mo/P via OH/H<sub>2</sub>O cycling  
Ti<sub>2</sub>/S, Hf<sub>2</sub>/S and Zr<sub>2</sub>/S via Volmer-Heyrovsky

~1 year  
PhD

# Partial take home message

## Material screening

Computers are patient and non-intelligent

Strong and necessary assumptions limit the scope

Do not forget about *stability*

→ Computationally expensive and not always that useful

1. Sulfate on Au(111)

2. HER on MoS<sub>2</sub>: Screening of dopants

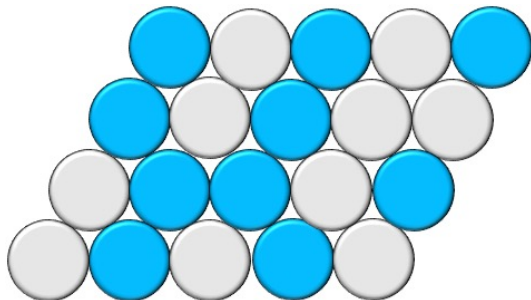
**3. Structural complexity**

4. Reaction pathways



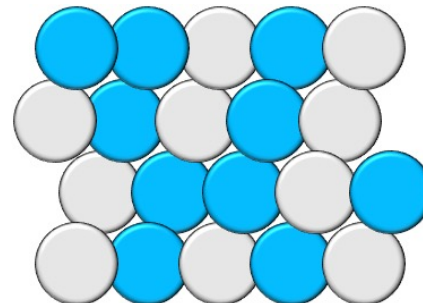
# Alloy Re-Organization under Reactive Conditions

In-plane  
Island formation

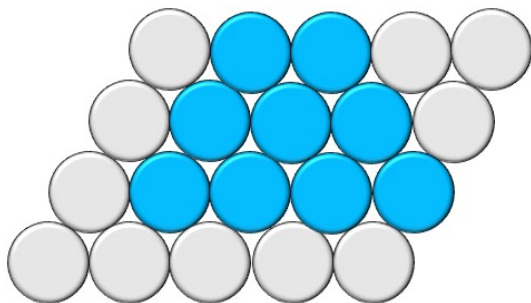
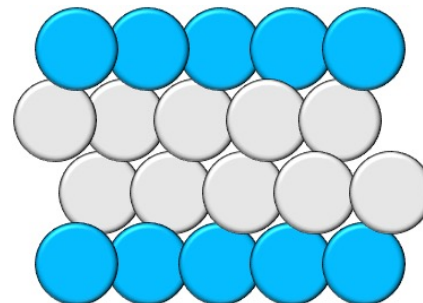


Random

Vertical  
Segregation

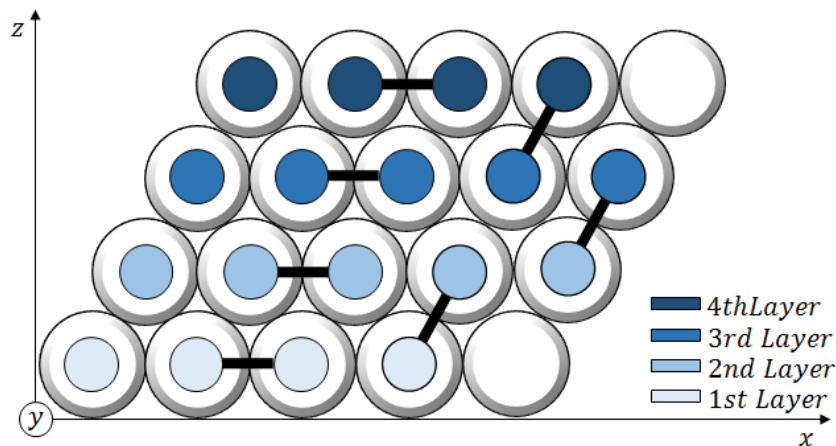


Ordered

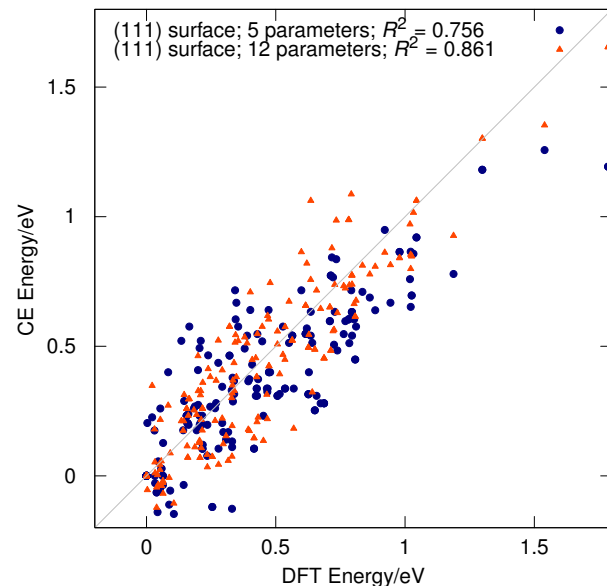




# Cluster expansion of alloy arrangement



Refined model: quantitative improvement, but same trends



226 DFT configurations bare alloy  
150 configurations with 1  $C_2H_2$   
52 configurations with 2  $C_2H_2$

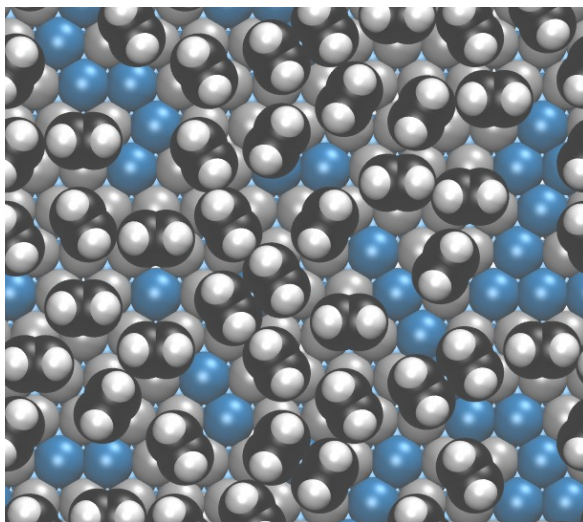


# Typical Configuration of $Ag_{0.76}Pd_{0.24}$ @ 1 bar of $C_2H_2$

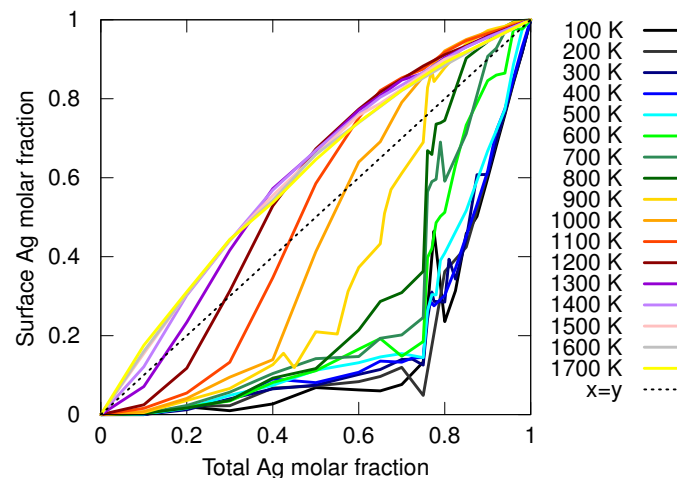
Dense packing:

Lateral Interaction are key

**Pd:** Covered with  $C_2H_2$



**Ag:** Acts as spacer



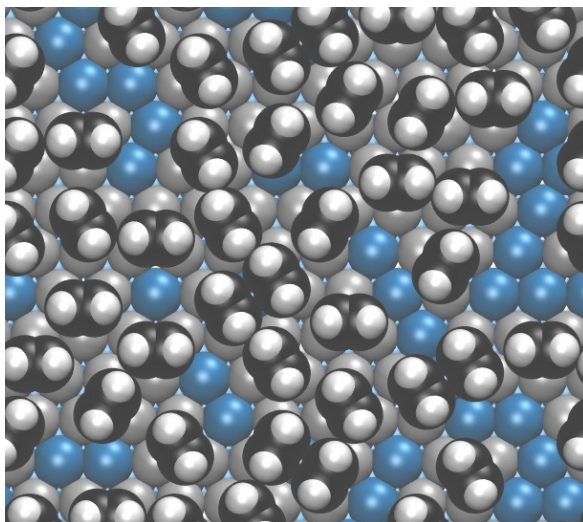
Monte Carlo simulations are required



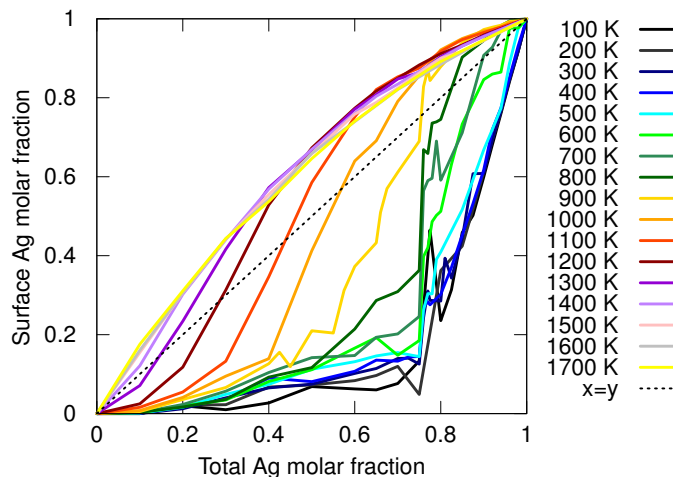
# Typical Configuration of $Ag_{0.76}Pd_{0.24}$ @ 1 bar of $C_2H_2$

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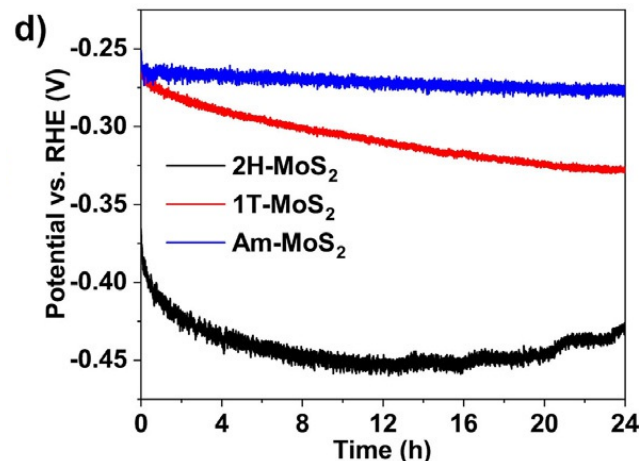




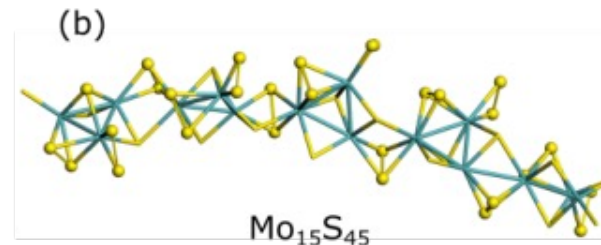
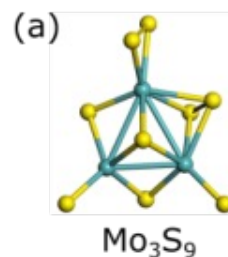
Hydrogen Evolution Reaction on  $\text{MoS}_3$ 

## Increasing the Number of Edge Sites?

Highly dispersed, amorphous  $\text{MoS}_2$  – or –  $\text{MoS}_3$  has many edge-sites

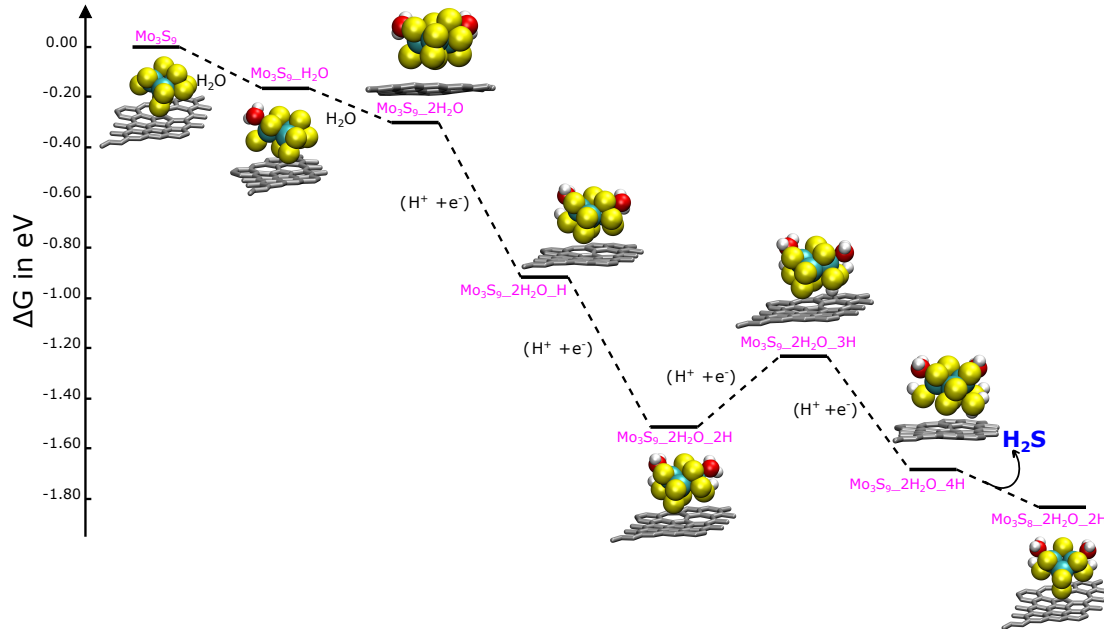


Amorphous, building block look like:



Wu, Longo, Dzade, Sharma, Hendrix, Bol, De Leeuw, Hensen, Hofmann, *ChemSusChem* **2019**, *12*, 4383.

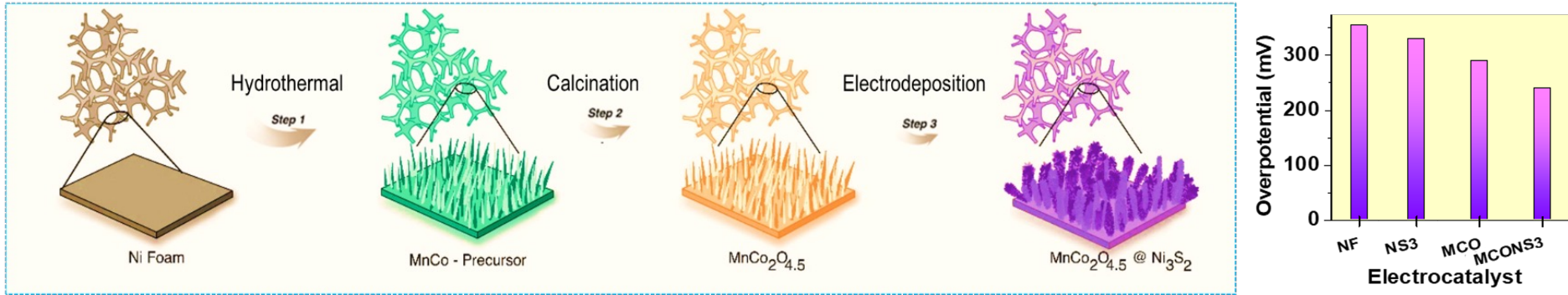
Sahu, Steinmann, Raybaud, *Cryst. Growth Des.* **2020**, *20*, 7750.

Hydrogen Evolution Reaction on  $\text{MoS}_3$ How Stable is  $\text{MoS}_3$  under HER Conditions?

~ 6 months  
post-Doc

Desorption of at least 1  $\text{H}_2\text{S}$  is easy, even at 0 V vs SHE, pH 0

# Hybrid material for oxidation of water and urea



Ni foam is not very active

$\text{Ni}_3\text{S}_2$  (NS3) overlayer

manganese cobalt oxide (MCO) overlayer

Covering MCO with  $\text{Ni}_3\text{S}_2$

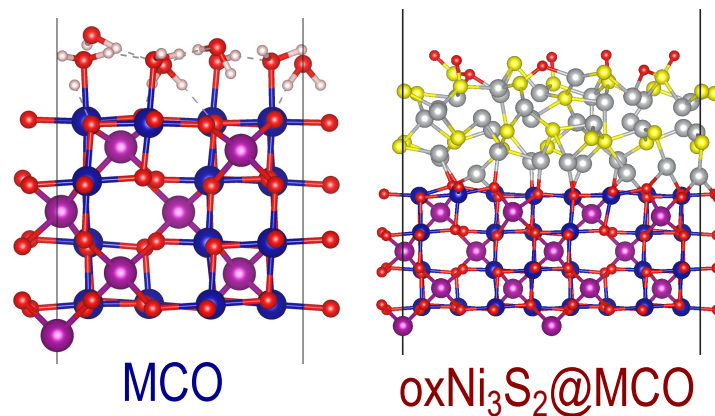
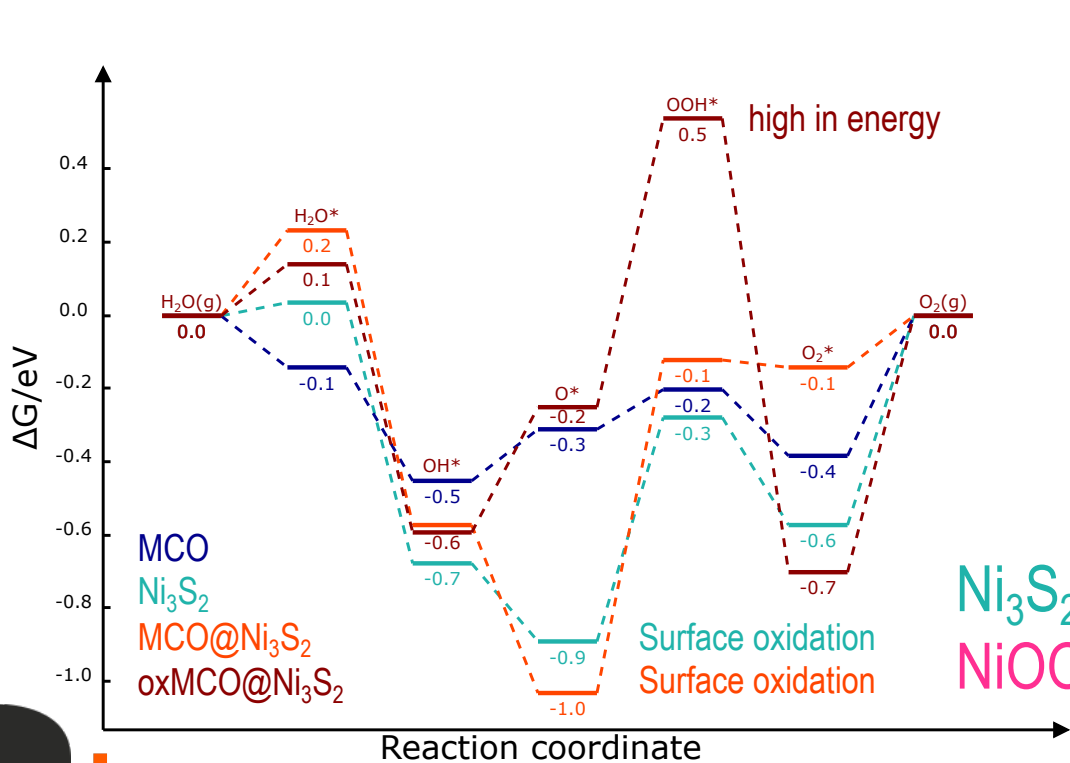
→ Small improvement

→ improvement

→ **even better, but why?**

## OER on hybrid material

## Reaction energy profile of OER

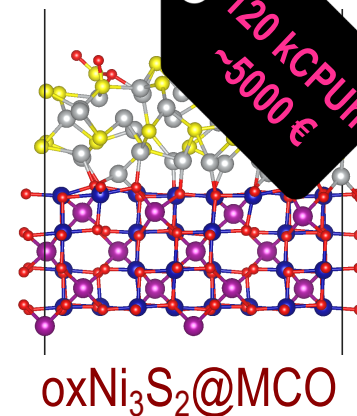
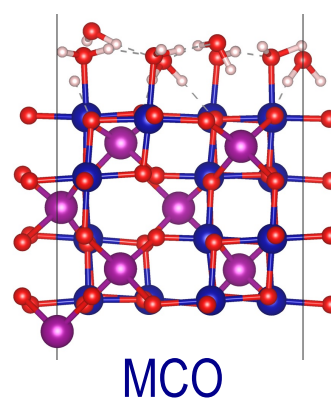
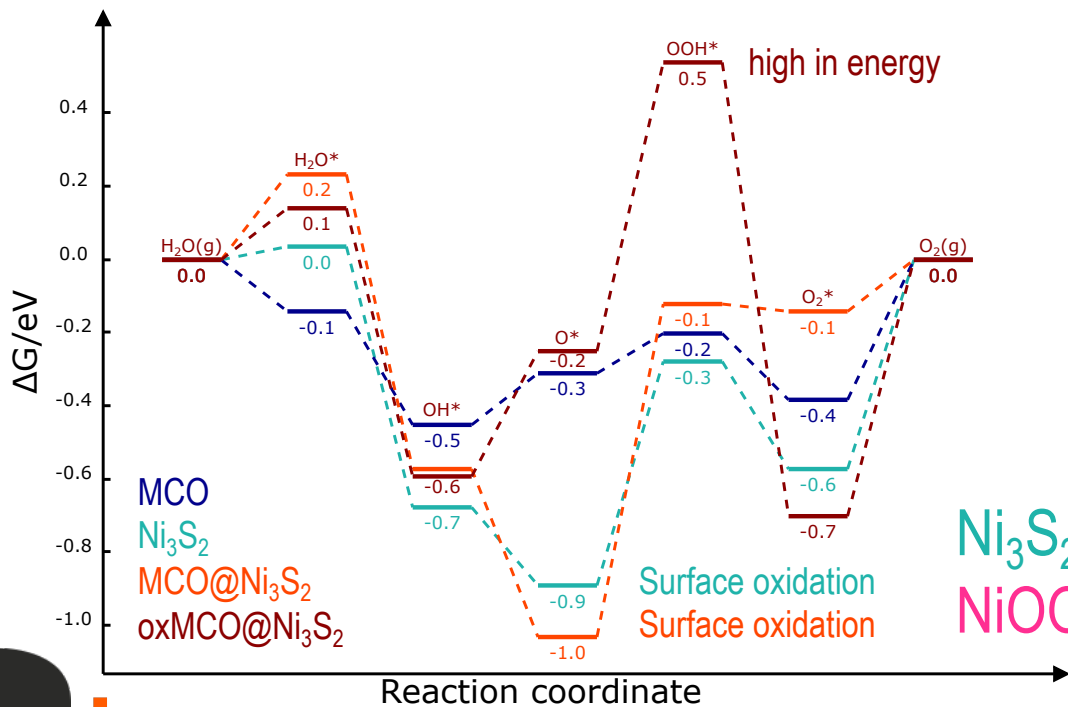


$Ni_3S_2$  is not stable under OER conditions  
 $NiOOH$  would be a better model

Conductivity and active surface area explain high experimental performance

## OER on hybrid material

## Reaction energy profile of OER



$Ni_3S_2$  is not stable under OER conditions  
 $NiOOH$  would be a better model

Conductivity and active surface area explain high experimental performance

# Partial take home message

## Structural complexity

Each system is different

Models, scope and confidence vary a lot

Amorphous structures are the worst for computational (electro-)chemists

Computations do not always lead to the expected insight

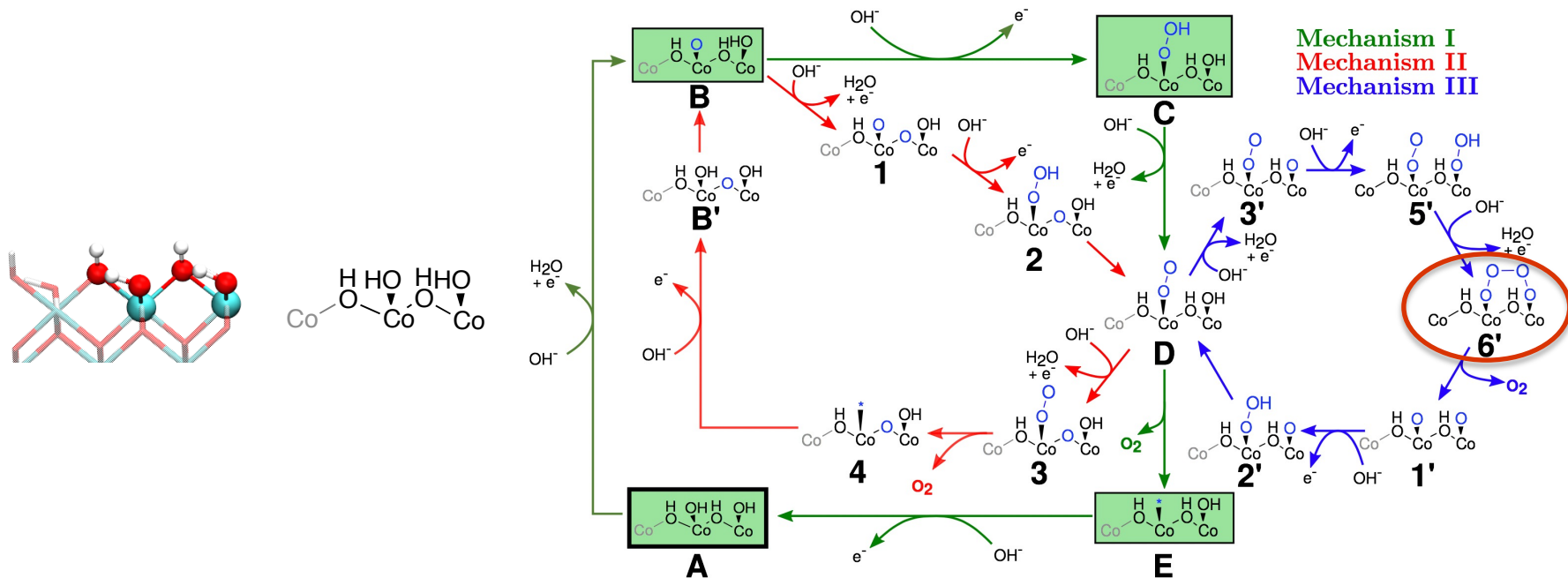
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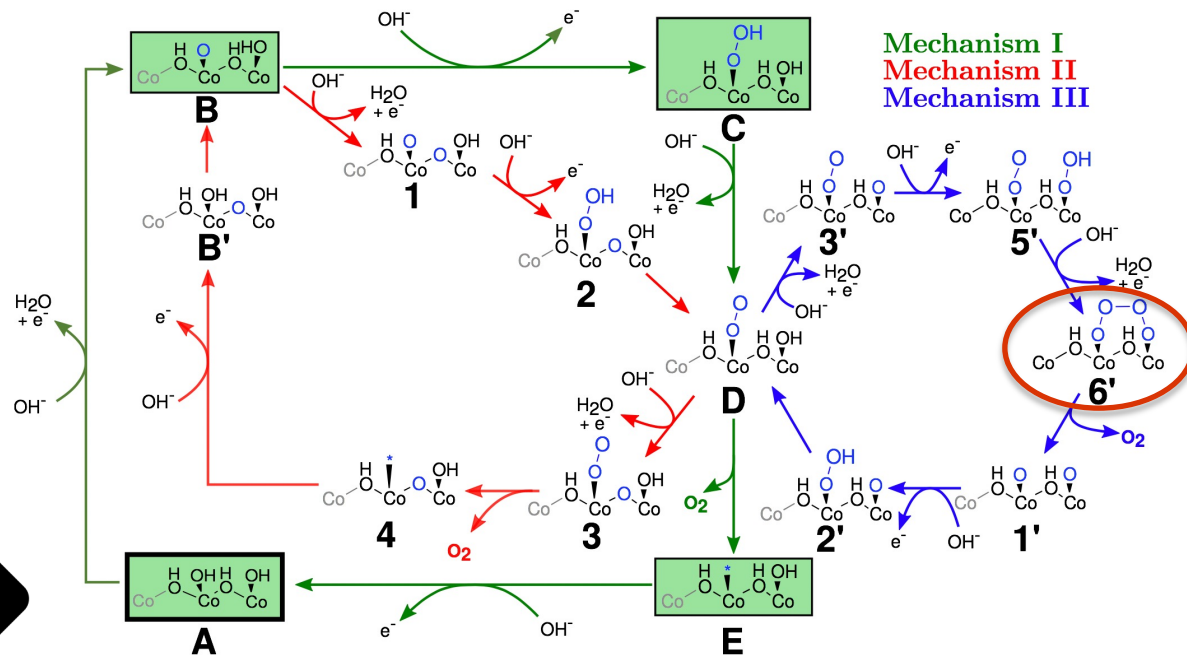
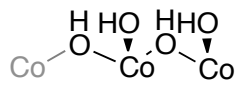
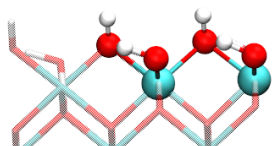
# Revisited mechanism for alkaline OER with GC-DFT



Considering barriers and overpotentials, mechanism III is likely

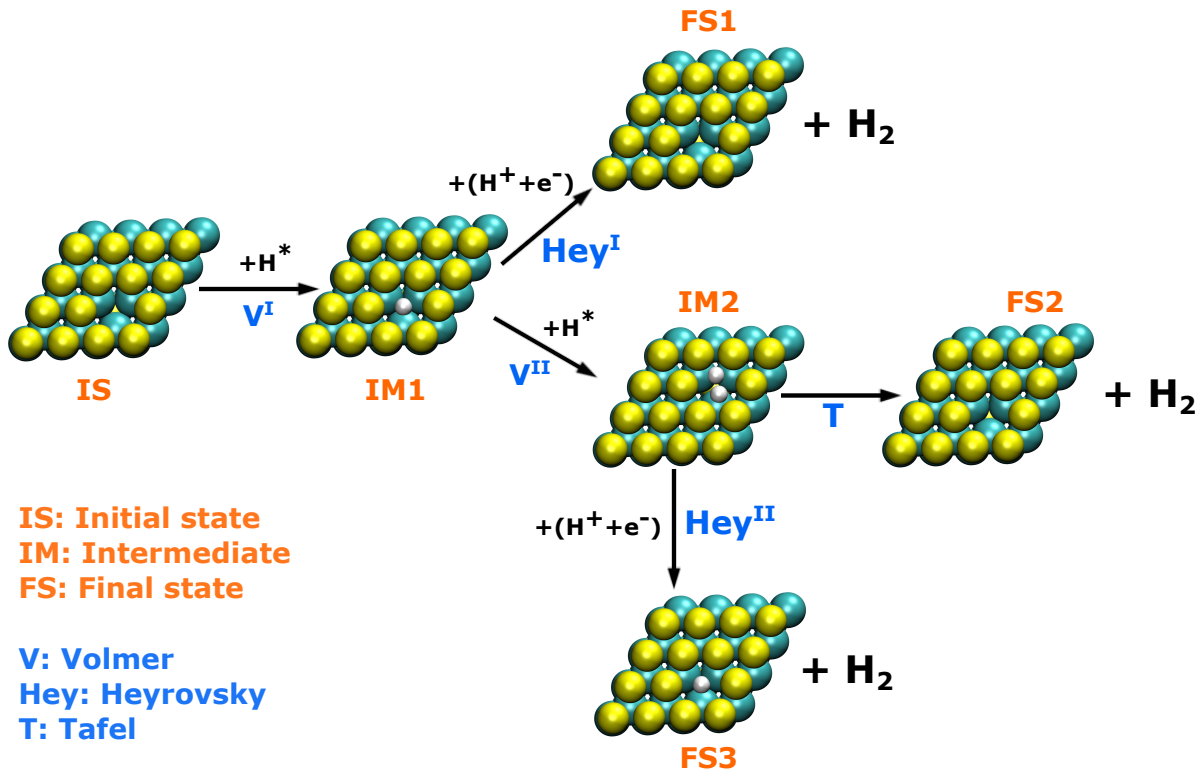


# Revisited mechanism for alkaline OER with GC-DFT



Considering barriers and overpotentials, mechanism III is likely

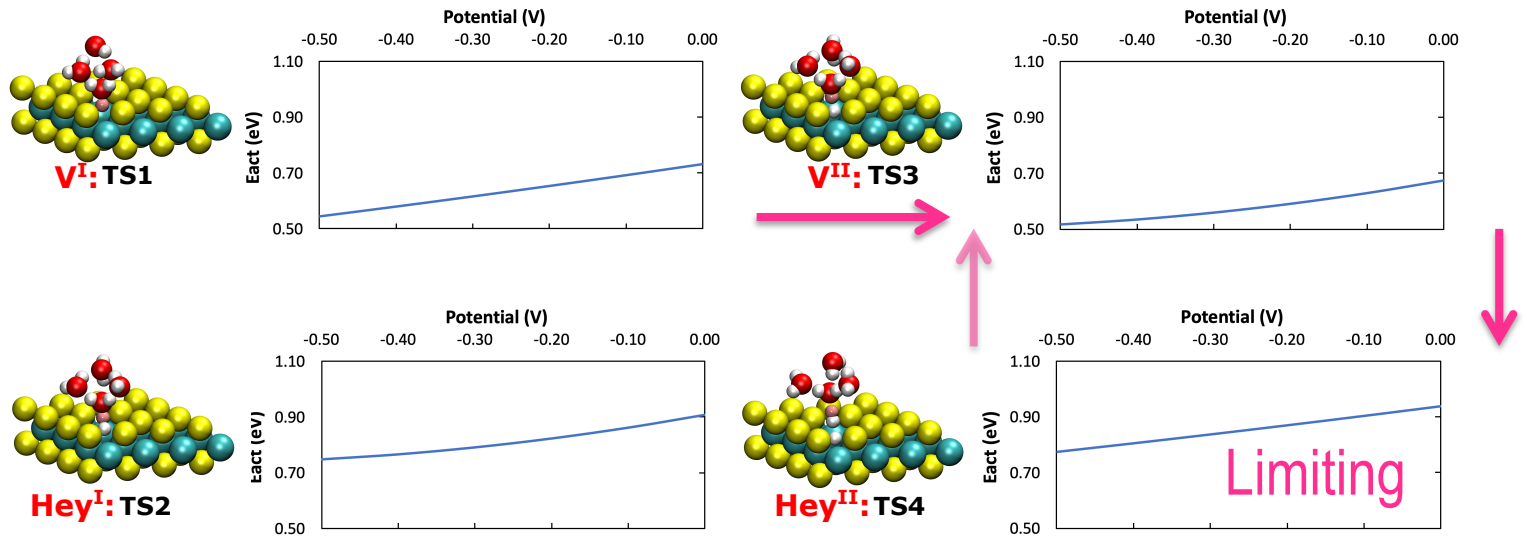
# HER mechanism on V<sub>S</sub> defect



**IS:** Initial state  
**IM:** Intermediate  
**FS:** Final state

**V:** Volmer  
**Hey:** Heyrovsky  
**T:** Tafel

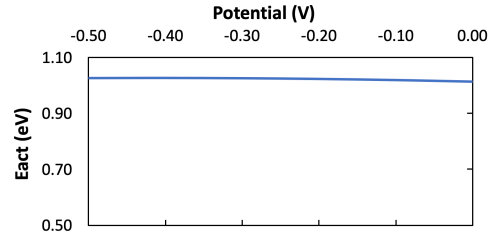
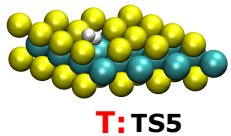
# Activation energies from Grand-Canonical DFT



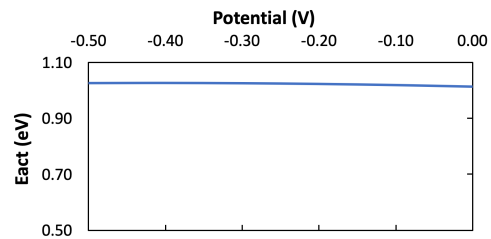
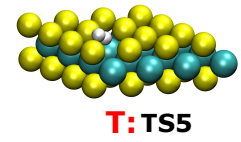
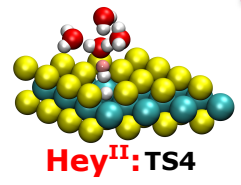
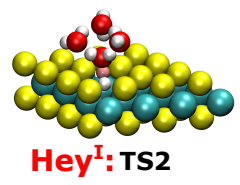
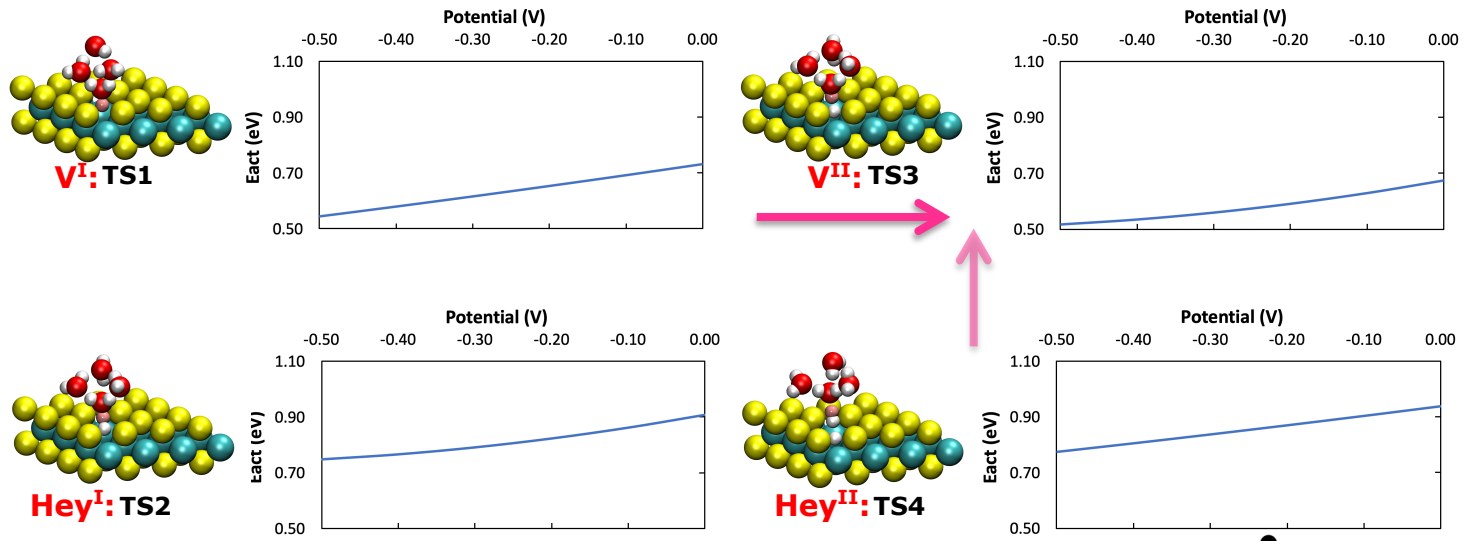
~0.8 eV barrier

**V: Volmer**  
**Hey: Heyrovsky**  
**T: Tafel**

**TS: Transition state**



# Activation energies from Grand-Canonical DFT



**V: Volmer**  
**Hey: Heyrovsky**  
**T: Tafel**

**TS: Transition state**



# Partial take home message

## Reaction pathways

Time consuming

Detailed insight, sometimes hard to (in-)validate by experiments

Activation energies are necessary for detailed mechanisms

Symmetry factors can be computed - but with which precision?

# Conclusions

Delicate **competition** between "chemical" vs "electrochemical" reactions

→ Can be addressed by GC-DFT



Amorphous or ill-characterized materials

→ **Structural complexity = major bottleneck**



In many cases computational studies are neither cheap nor fast



→ **Developments** are necessary for modelling solid/liquid interfaces



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LABORATOIRE  
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IMUST  
UNIVERSITÉ DE LYON

La Région  
Auvergne-Rhône-Alpes



TotalEnergies

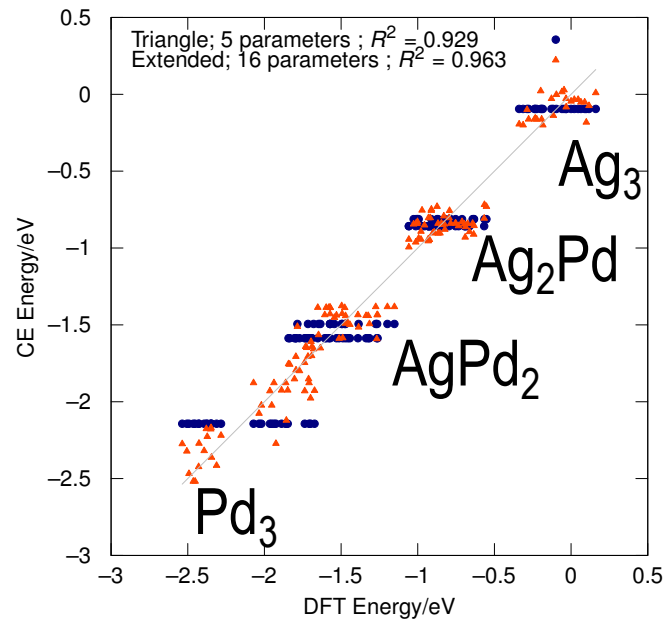
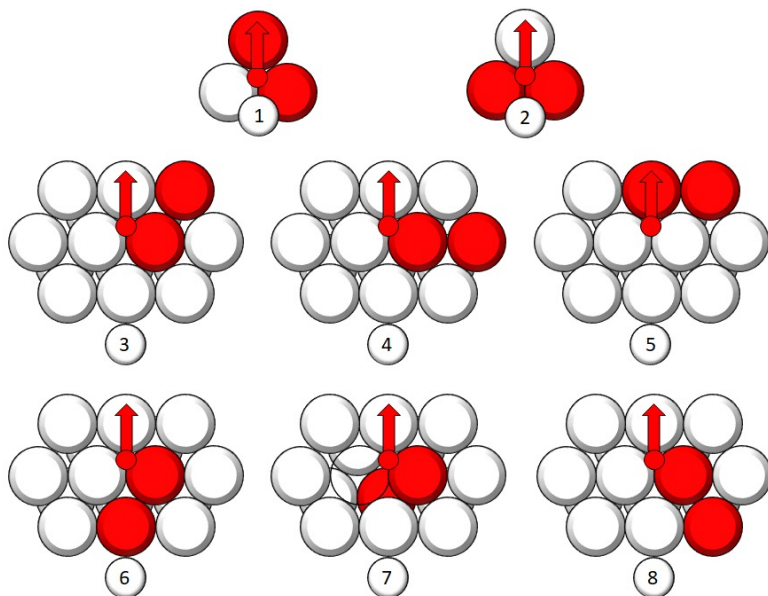


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# Cluster Expansion of Adsorption Energy



150 DFT configurations

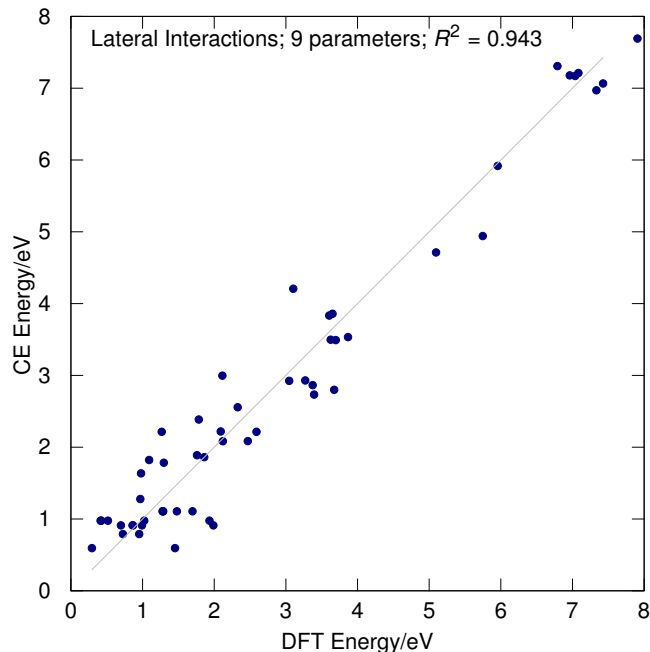
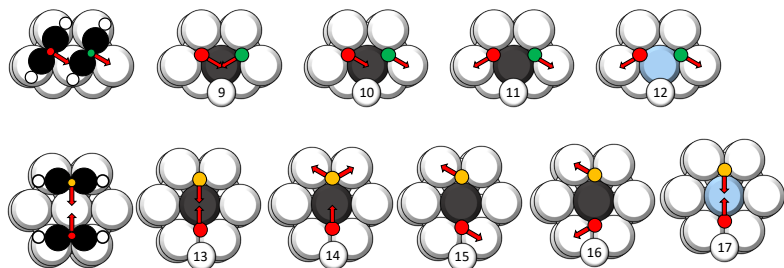
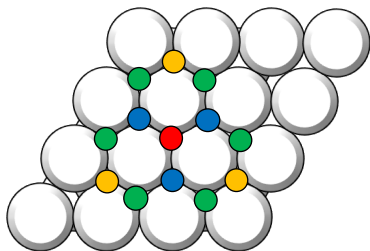
Refined model:

Spreads between ensembles is important for  $Pd_2Ag$  and  $Pd_3$





# Cluster Expansion of Lateral Interaction Energy



52 DFT configurations