

Ab initio molecular dynamics applied to liquid water systems

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Funding:



VILLUM FONDEN



Outline

Molecular dynamics

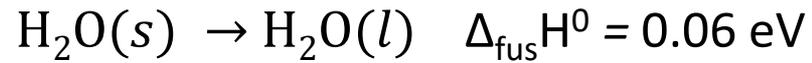
Examples: Simulated annealing,
Reaction energies

Rare event sampling

Examples: Meta dynamics

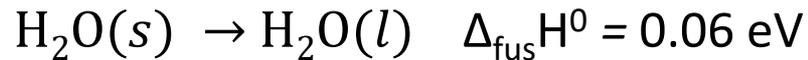
Why molecular dynamics?

Basic issue, liquid water is not a ground state structure



Why molecular dynamics?

Basic issue, liquid water is not a ground state structure



We need a method that can capture the dynamic nature of liquid water

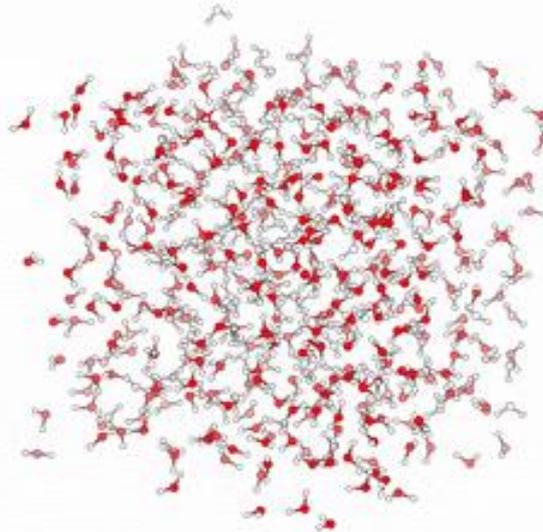


Figure from:
[https://en.wikipedia.org/
wiki/Molecular_dynamics](https://en.wikipedia.org/wiki/Molecular_dynamics)

Constant energy molecular dynamics

Newtonian dynamics

$$\frac{dp_i}{dt} = F_i$$

Atomic forces (F_i) can be obtained from *ab initio* methods such as DFT or *non ab initio* methods such as interatomic potentials.

Constant energy molecular dynamics

Can be used to study:

Structural properties (densities, coordination numbers)

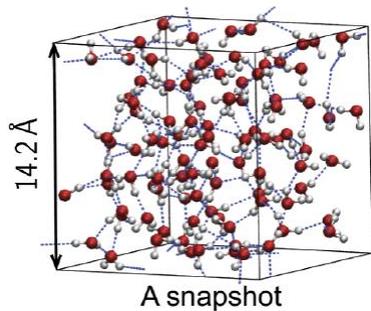
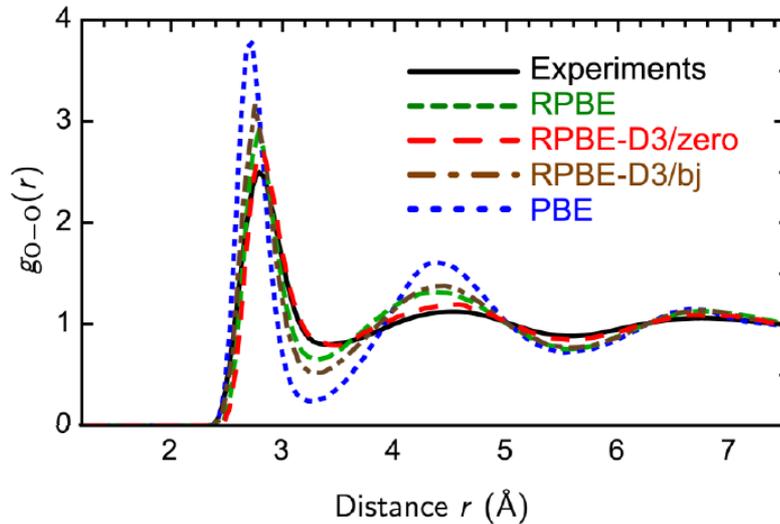
Dynamics (diffusion constants, vibrations)

Rare events (reactions), if they occur

Cannot provide energy differences!

Structural properties

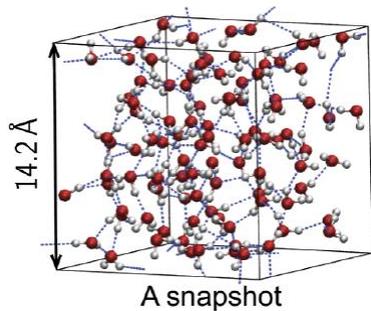
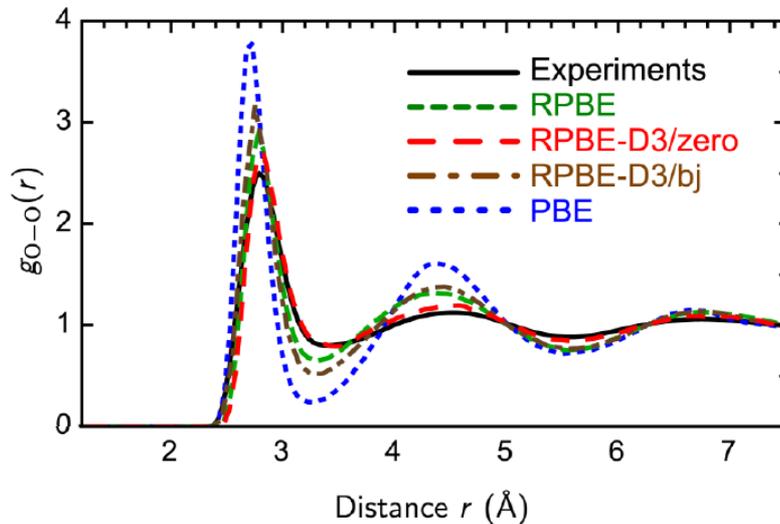
Radial distribution function (Pair correlation function)



Experiments are
neutron or x-ray
diffraction.

Structural properties

Radial distribution function (Pair correlation function)



Experiments are neutron or x-ray diffraction.

Probability of finding a B type atom at r from an A type atom.

$$p_{A-B} dr = 4\pi r^2 g_{A-B}(r) \rho_B dr$$

Number of B neighbors within r_{max} from A

$$n_{A-B}(r < r_{max}) = \int_0^{r_{max}} p_{A-B} dr$$

Dynamic properties

Vibrations

Hydrogen power spectra (S).

Fourier transform of the self-velocity autocorrelation function

$$S(\omega) = \int_0^{\infty} \langle v(t)v(0) \rangle \cos(\omega t) dt$$

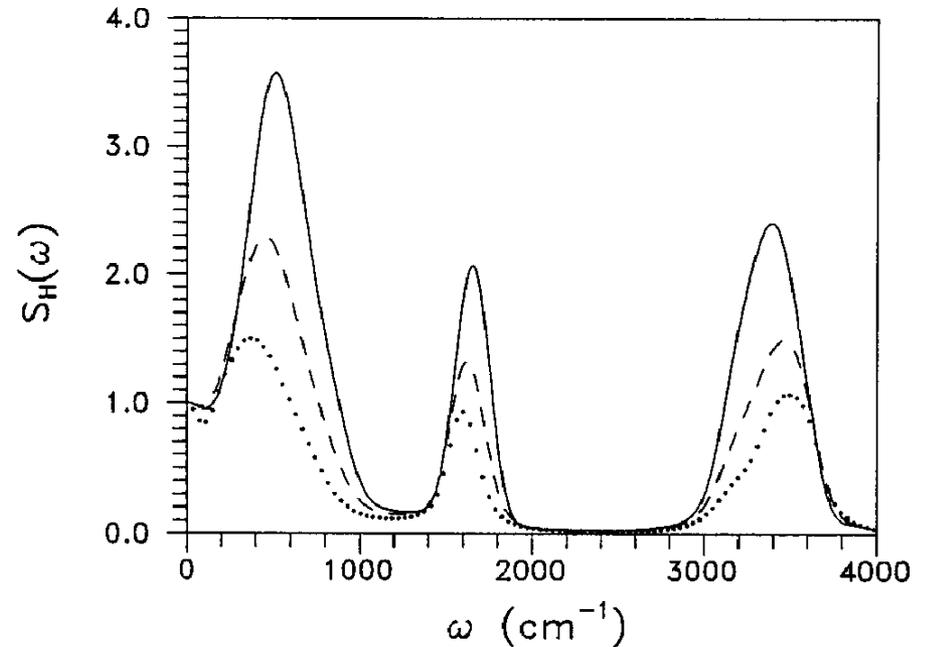
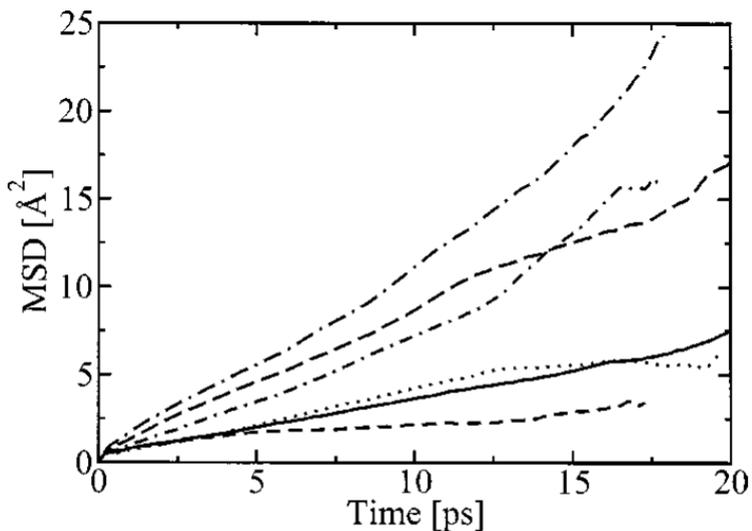


FIG. 11. Normalized hydrogen power spectra for water along the coexistence curve: $T=298$ K (—), $T=403$ K (---), and $T=523$ K (····).

Dynamic properties

Diffusion



DFT	T (K)	MSD ($\text{\AA}^2 \text{ps}^{-1}$)
BLYP	324	0.31
PBE	337	0.40
TPSS	351	0.14
OLYP	310	0.75
HCTH120	315	0.65
HCTH407	307	0.94
Exp	298	1.3

FIG. 7. MSDs as obtained for simulations with the BLYP, PBE, TPSS, OLYP, HCTH120, and HCTH407 functionals using solid, dotted, dashed, long dashed, dash dotted, and long dash dotted lines, respectively.

“Constant” temperature molecular dynamics

The dynamics is modified by a thermostat (Nosé, Andersen, Langevin, etc.)

Nosé thermostat:
$$\frac{dp_i}{dt} = F_i - \zeta p_i \quad \frac{d\zeta}{dt} = \frac{3Nk_B}{Q} (T - T_0) \quad T = \frac{2E_{kin}}{3Nk_B}$$

Nosé dynamics has no random components

S. Nosé, *J. Chem. Phys.*, **1984**, *81*, 511–519

Wm. G. Hoover, *Molecular Dynamics: Lecture Notes in Physics*, Volume 258, Springer-Verlag, 1986

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Nosé dynamics has no random components

Trajectory (time) averages become the canonical ensemble averages

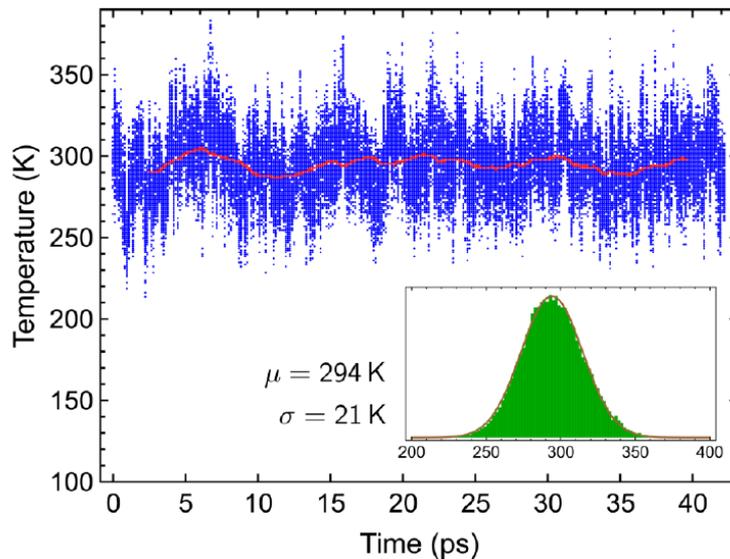
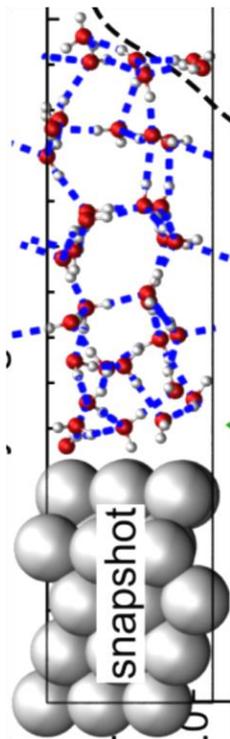
$$\lim_{M \rightarrow \infty} \frac{1}{M} \sum_{j=1}^M E_j = \langle E(T_0) \rangle_{canonical}$$

S. Nosé, *J. Chem. Phys.*, **1984**, *81*, 511–519

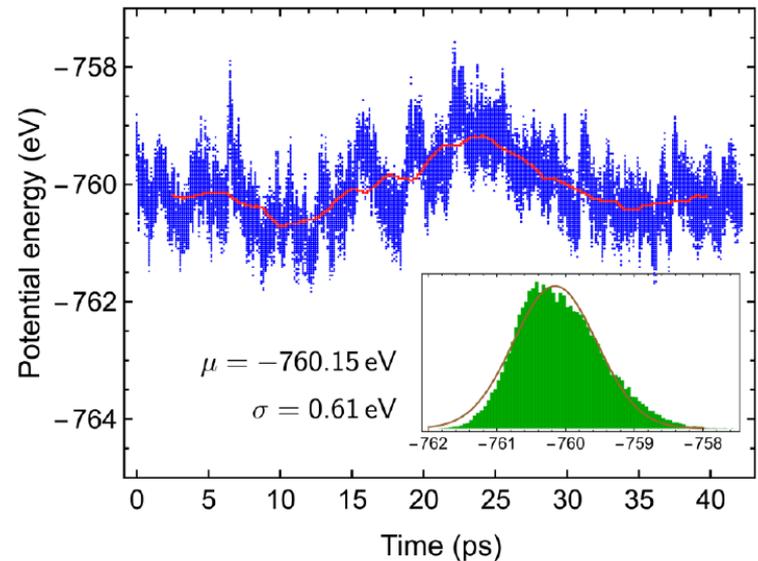
Wm. G. Hoover, *Molecular Dynamics: Lecture Notes in Physics*, Volume 258, Springer-Verlag, 1986

“Constant” temperature molecular dynamics

Temperature and energy fluctuations



Performed with Langevin thermostat
but the behavior is similar to Nosé



From statistical mechanics

$$\sigma_E^2 = T^2 N k_B c_v$$

“Constant” temperature molecular dynamics

Can be used to study:

Structure properties

Approximate dynamics

Rare events (reactions), if they occur

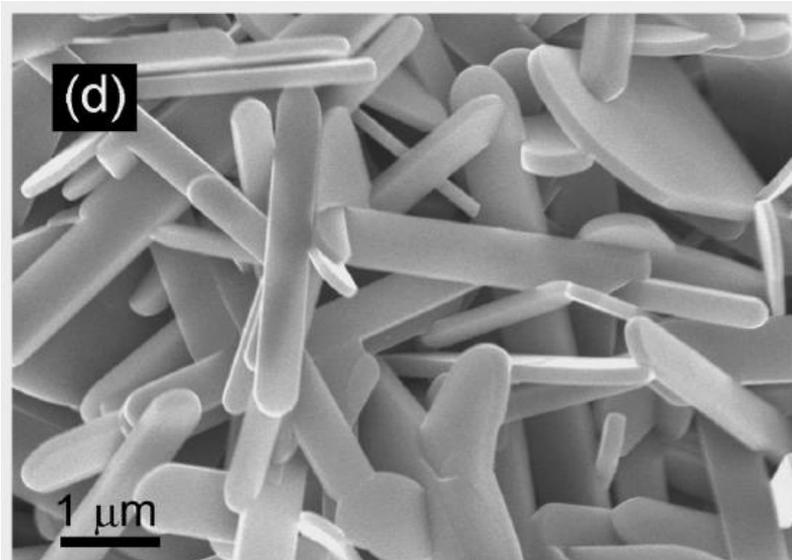
Simulated annealing (global optimization)

Reactions energies

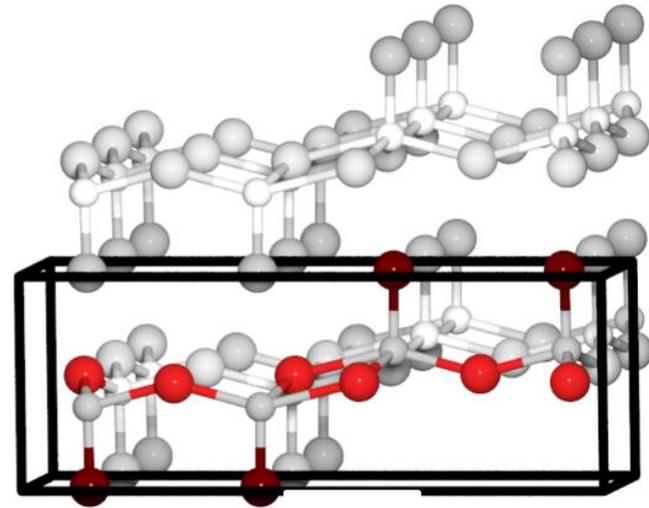
Example

Structure of $V_2O_5 \cdot nH_2O$ xerogels
from simulated annealing

Crystalline V_2O_5



Bulk V_2O_5 is a layered compound

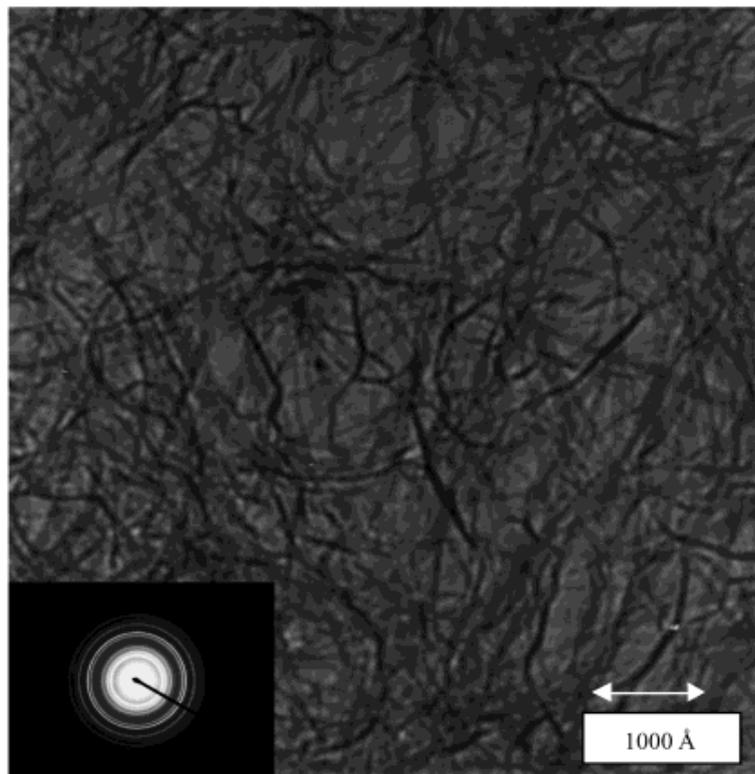


red = **bridging O**

dark red = **double bonded V=O**

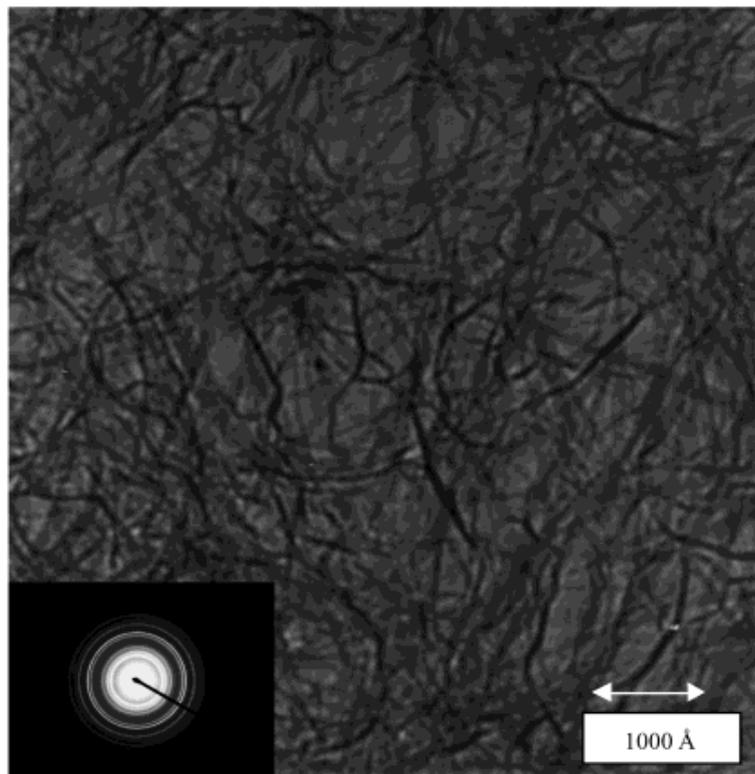
gray = **vanadium**

$V_2O_5 \cdot nH_2O$ xerogels

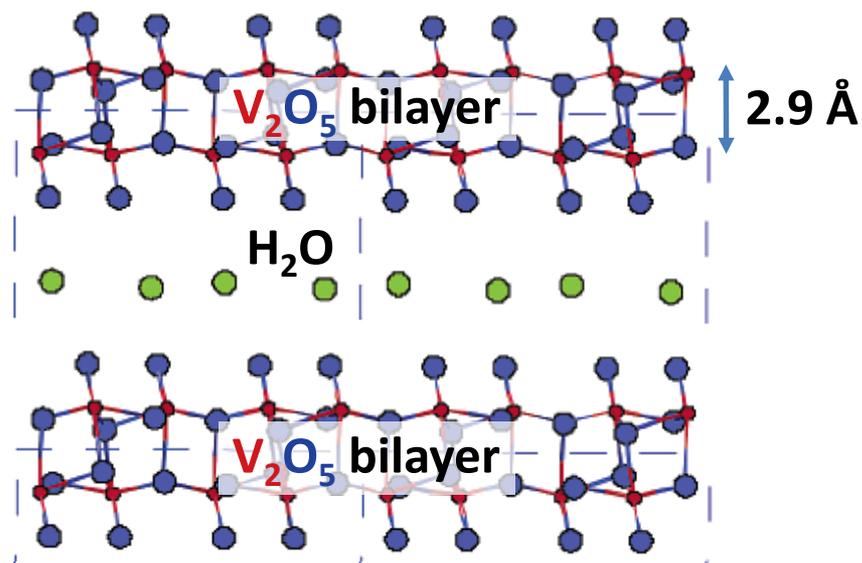


“The $V_2O_5 \cdot nH_2O$ xerogel was synthesized by melting of crystalline V_2O_5 at $800^\circ C$ and pouring the melt into deionized water under vigorous stirring. The resulting dark red solution transformed to gel within 4 days.”

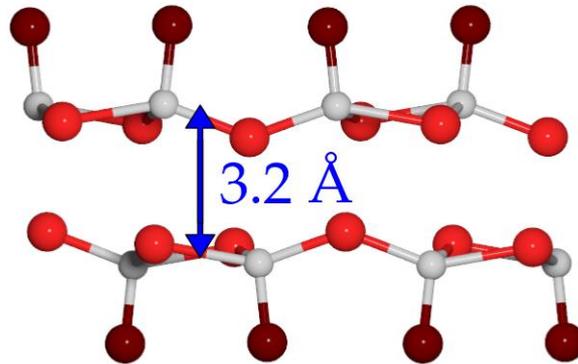
$V_2O_5 \cdot nH_2O$ xerogels



Structural model based on XRD



Issue 1: Bilayer stability

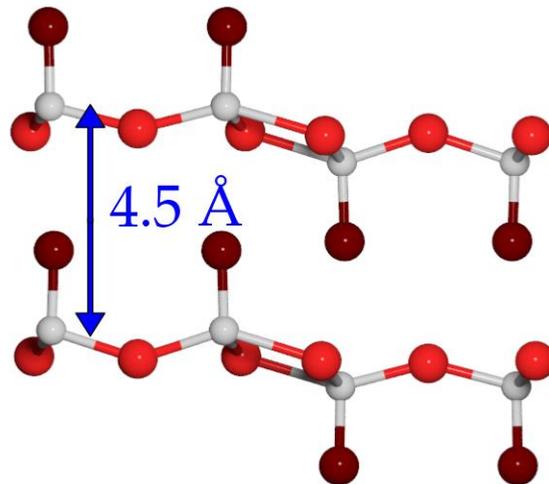


$$\Delta E / n_{\text{V}_2\text{O}_5} = 0 \text{ eV (ref)}$$

Bilayer in the absence
of water:

Higher energy

V-V distance is **almost
correct**



$$\Delta E / n_{\text{V}_2\text{O}_5} = -0.07 \text{ eV}$$

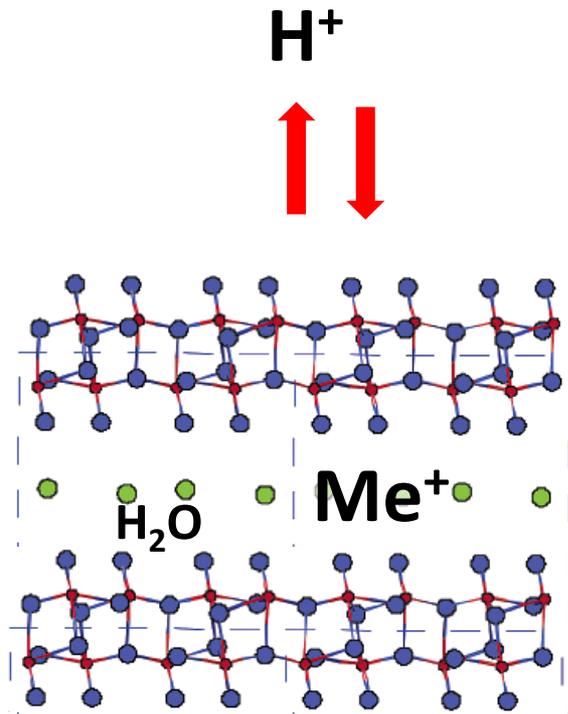
Double layer cut from bulk:

Lower energy

V-V distance is **too large**

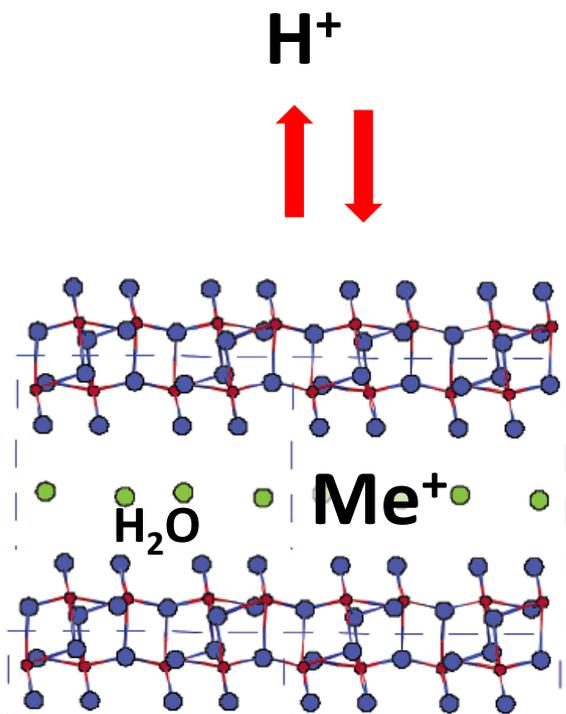
Issue 2: Inherent acidity

H⁺ exchange with cations

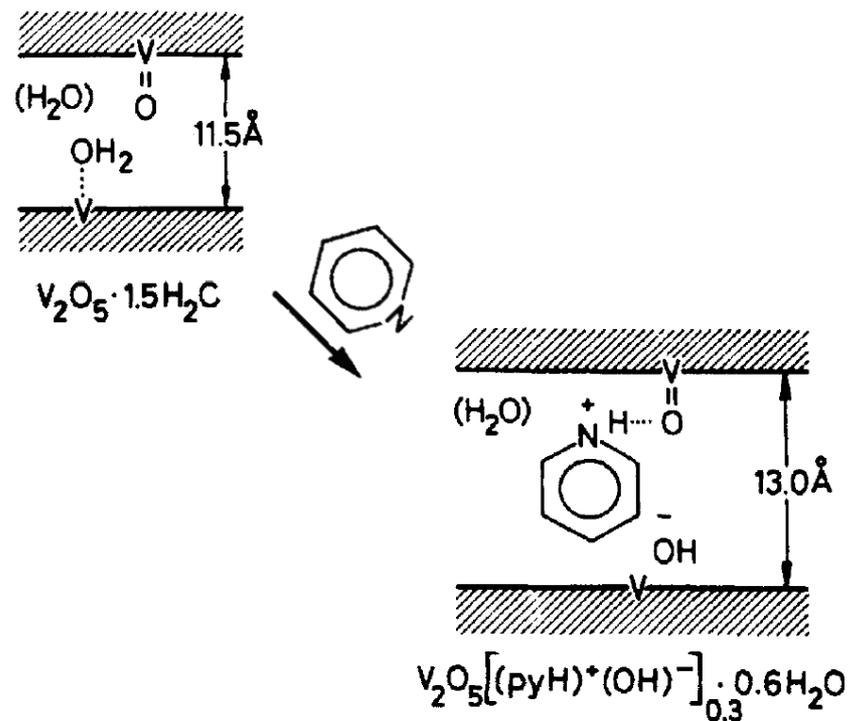


Issue 2: Inherent acidity

H⁺ exchange with cations



Protonation of intercalated pyridine measured by IR



J Livage, et al., *MRS Proceedings* p 167 (1988)

E. Ruiz-Hitzky, et al., *J. Chem. Soc., Faraday Trans. 1*, **1986**, 82, 1597-1604

Methodology

Modeling that include both V_2O_5 bilayer and H_2O ($8V_2O_5 \bullet 14H_2O$)

Ab initio molecular dynamics with Nosé thermostat

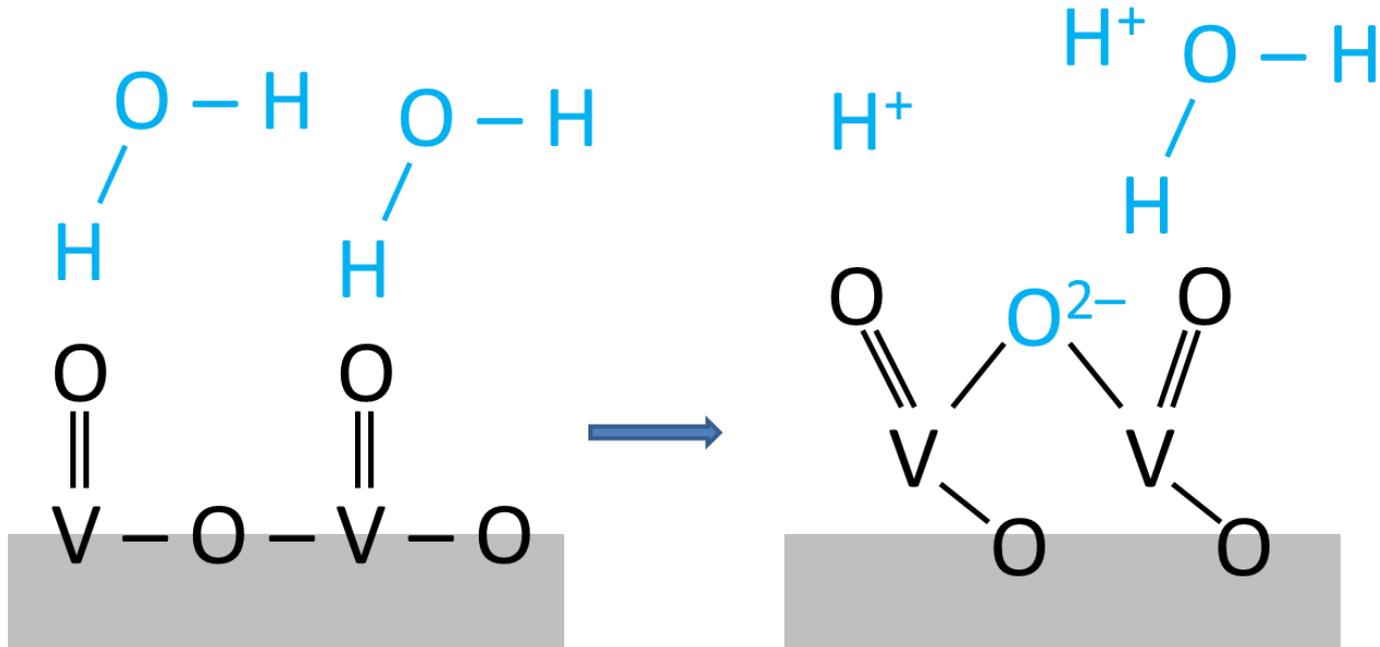
DFT with PBE+D2 performed in VASP

Unit cell and structure optimization

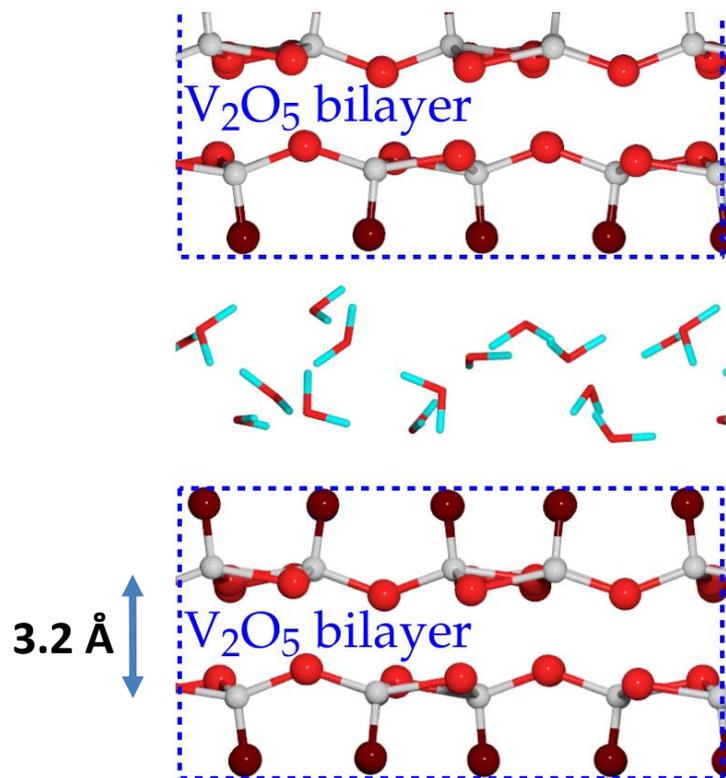
1. Simulated annealing for 10 ps from 600 K to 250 K (fixed unit cell)
2. Full structure and unit cell relaxation (atomic forces < 0.03 eV/Å).
3. Repeat 1. and 2. five times and report the most stable structure.

We conducted several parallel runs of 1.-3., which end up in markedly different structural motifs.

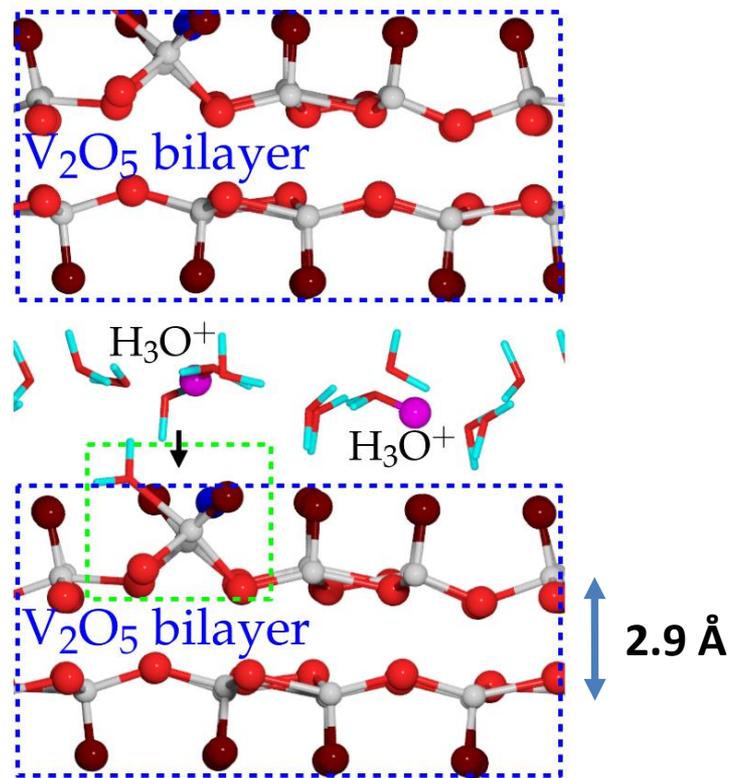
Solution: Water adsorption at bilayer



Models for $V_2O_5 \cdot nH_2O$ xerogels



$$\Delta E / n_{V_2O_5} = 0 \text{ eV (ref)}$$

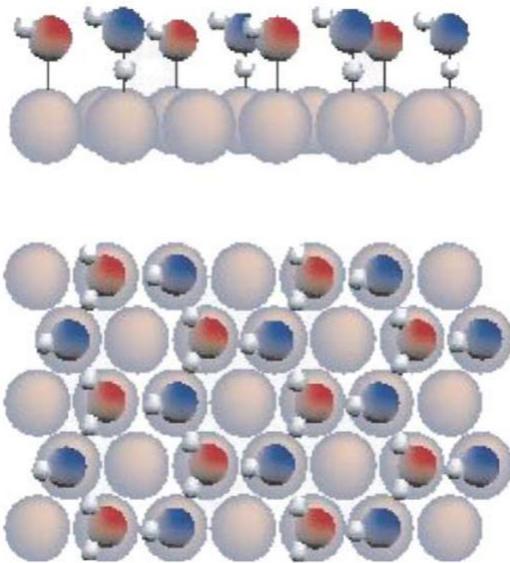


$$\Delta E / n_{V_2O_5} = -0.27 \text{ eV}$$

Example

Reaction energies
for water-Pt(111) electro-chemistry

Static water bilayer model



The bilayer model is based on the experimental structure for $2/3$ ML H_2O on Pt(111) at low T and in UHV.

Computational studies using the bilayer model have made assumptions concerning coverage and structure of H_2O at the interface.

Methodology

Ab initio, constant temperature Nosé molecular dynamics at 350 K

DFT with PBE+D3 in VASP (vdW important for water properties)

$$\langle E \rangle_t = \frac{1}{t - t_0} \int_{t_0}^t E_{DFT}(t') + K(t') dt'$$

$t - t_0$ is > 30 ps (with $\Delta t = 1$ fs)

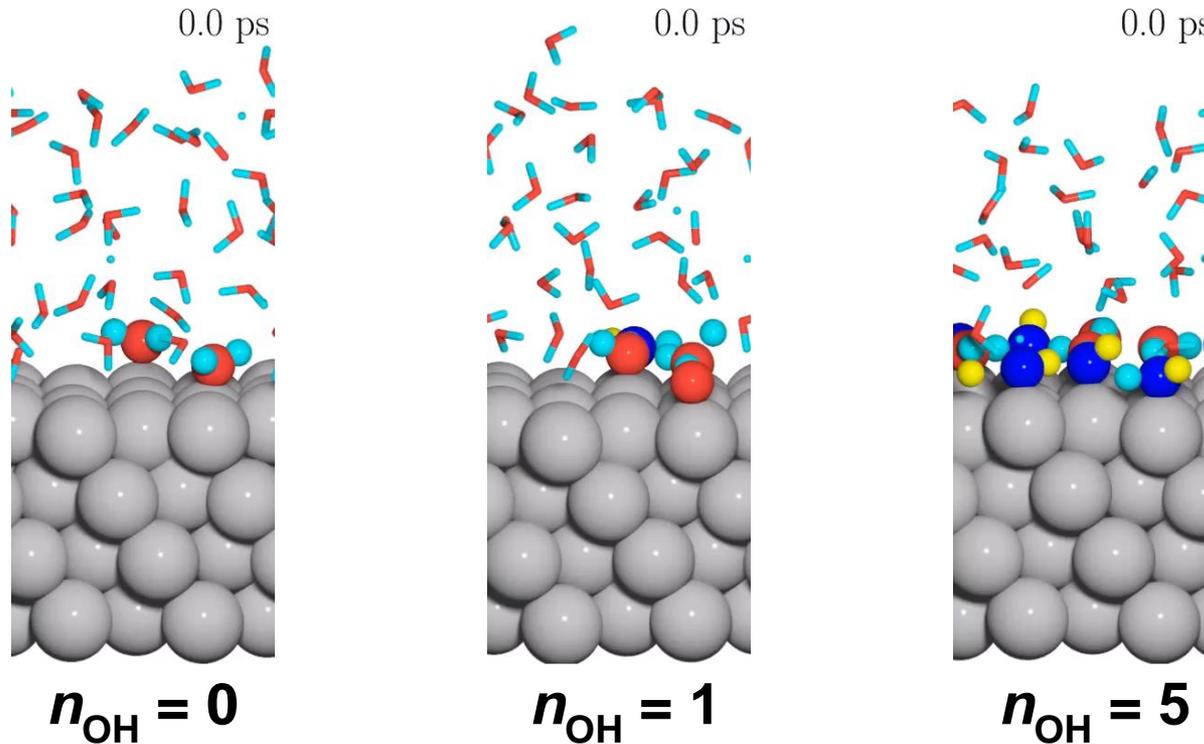
We perform 2 to 3 runs of each interface

Reaction energies for *OH formation

$$\Delta E = \langle E_{n\text{OH}+(32-n)\text{H}_2\text{O}/\text{Pt}(111)} \rangle_t + \frac{n}{2} \langle E_{\text{H}_2(\text{g})} \rangle_t - \langle E_{32\text{H}_2\text{O}/\text{Pt}(111)} \rangle_t$$

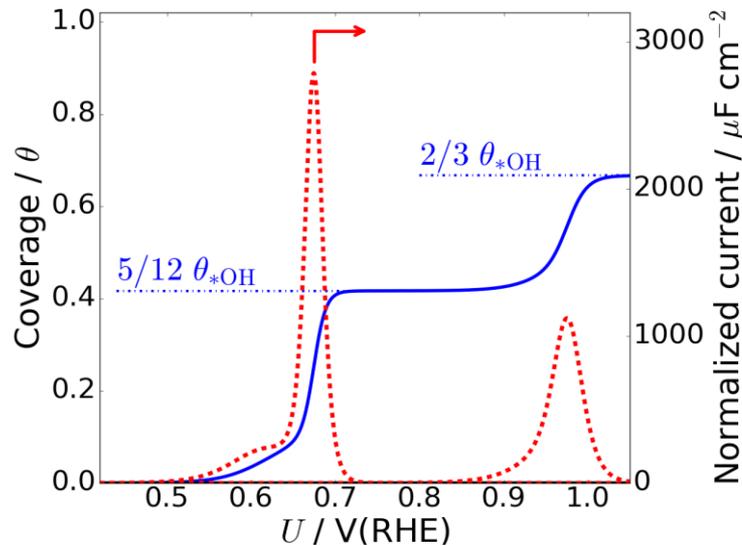
(We estimate changes in entropy and zero point energy)

MD on interfaces with different number of *OH



Also investigated $n_{\text{OH}} = 2, 4, 6, 8, 9$, and $n_{\text{O}} = 4$

*OH coverage vs electrostatic potential



Constructed from:

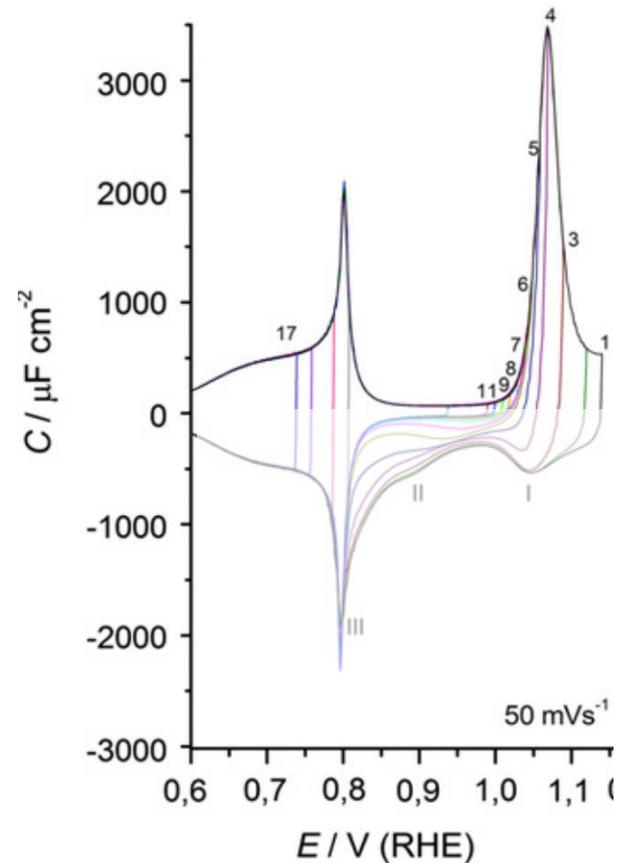
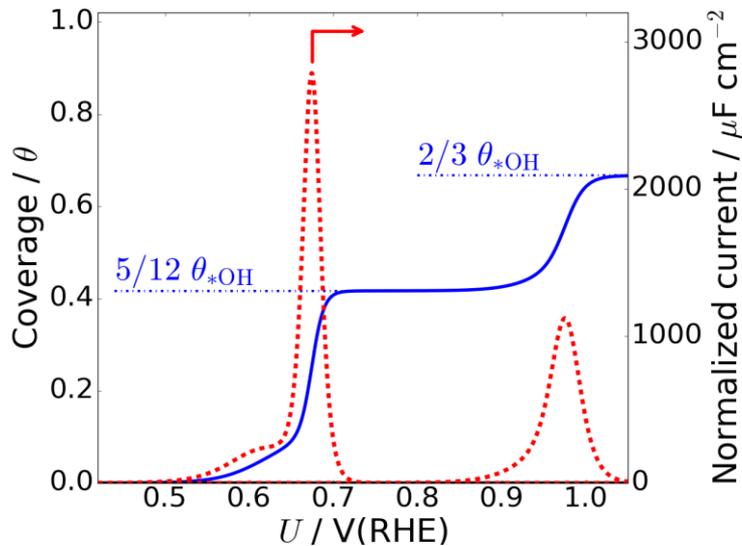
Reaction free energies



Computational hydrogen electrode

$$G(\text{H}^+(\text{aq}) + e^-) \approx \frac{1}{2} G(\text{H}_2(\text{g})) - eU$$

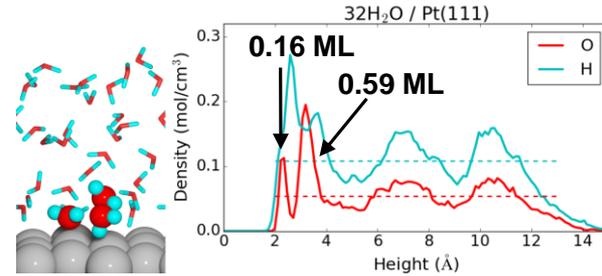
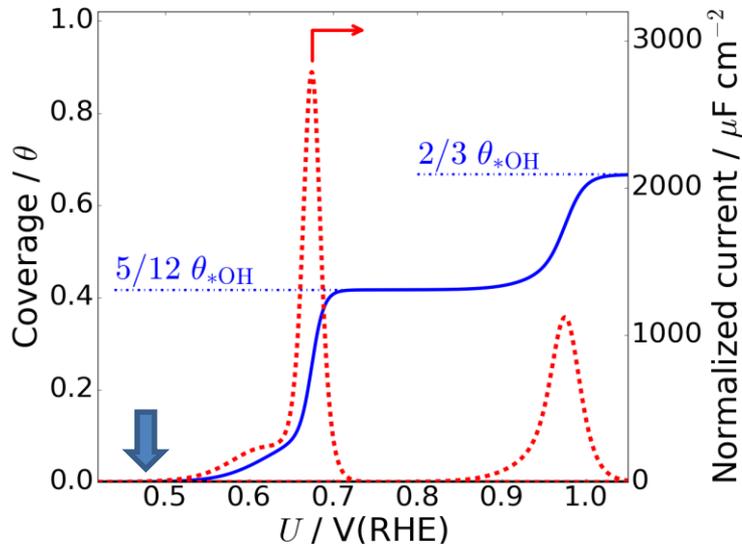
*OH coverage vs electrostatic potential



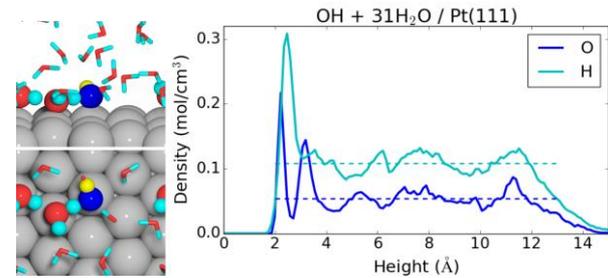
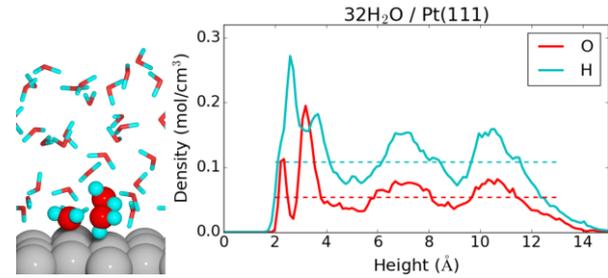
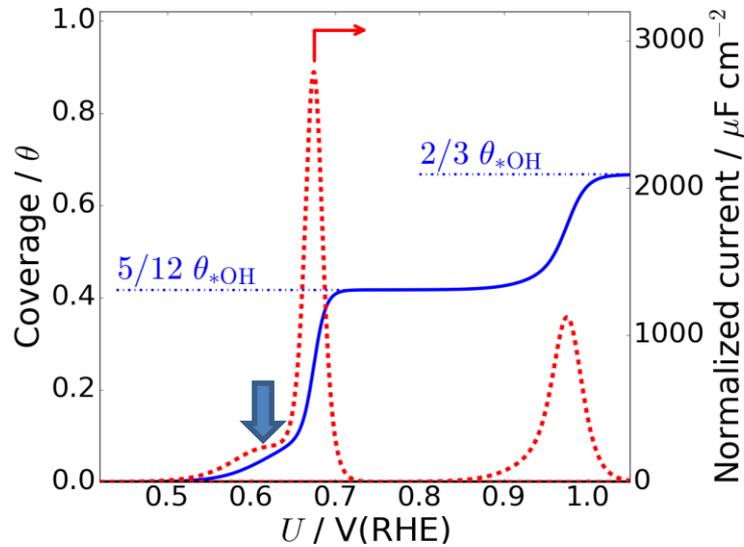
**Cyclic voltammogram of Pt(111) in
0.1 M HClO₄**

A. M. Gómez-Marín, *et al.*,
J. Electroanal. Chem. **2013**, 688, 360-370.

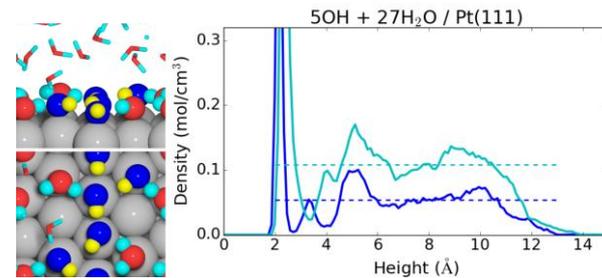
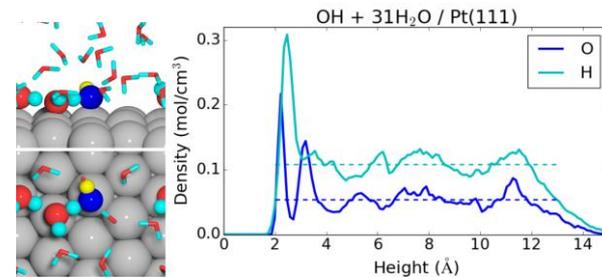
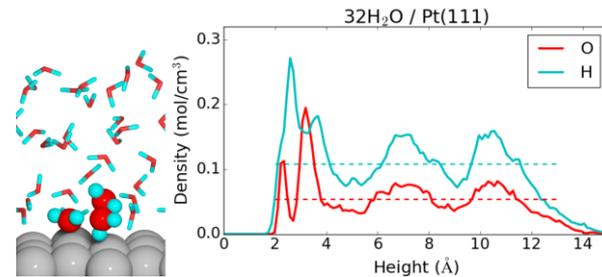
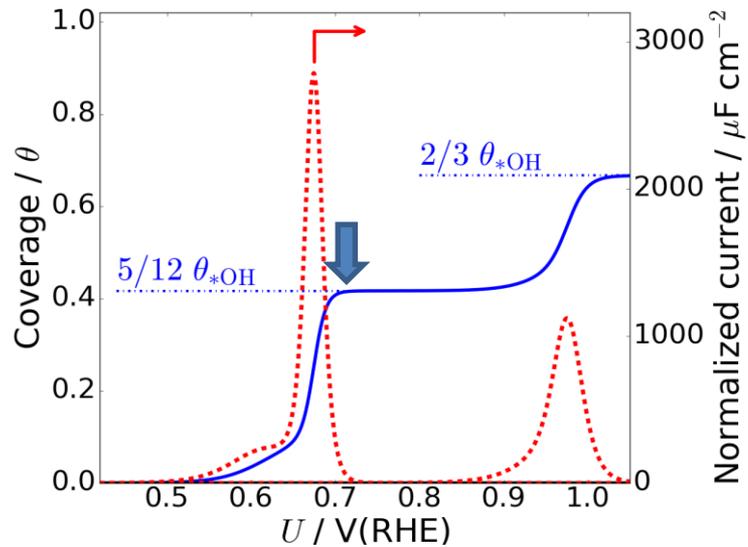
*OH coverage vs electrostatic potential



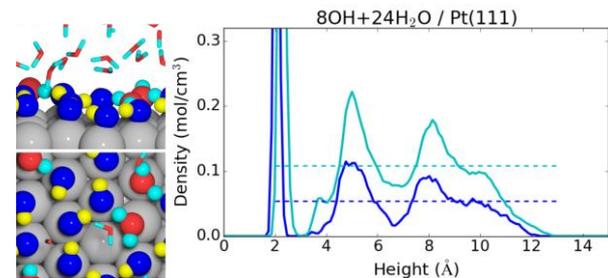
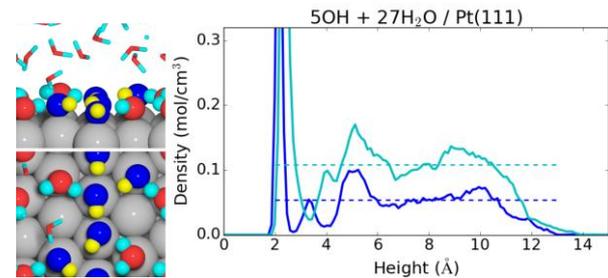
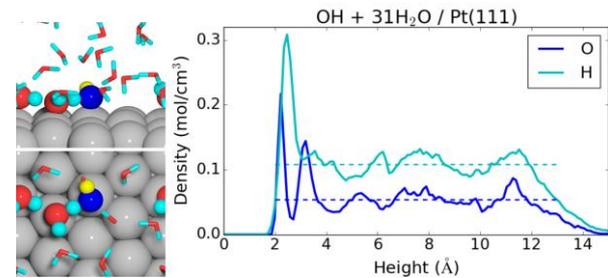
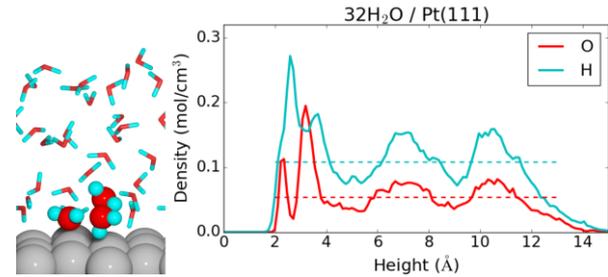
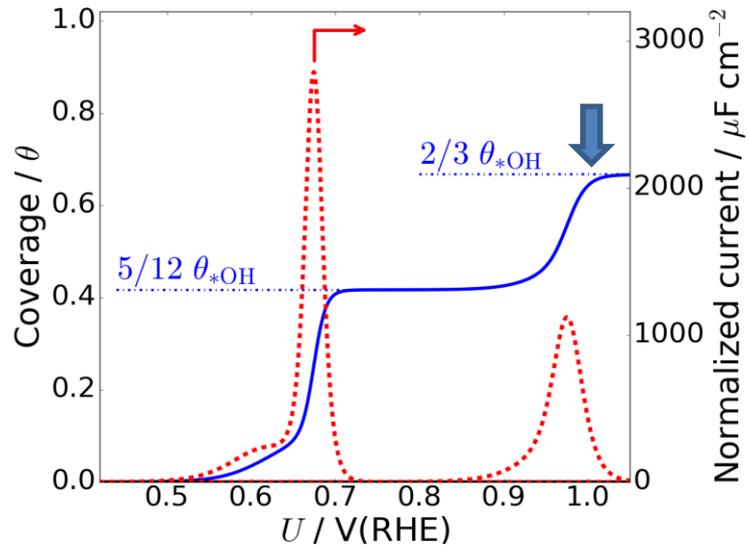
*OH coverage vs electrostatic potential



*OH coverage vs electrostatic potential



*OH coverage vs electrostatic potential

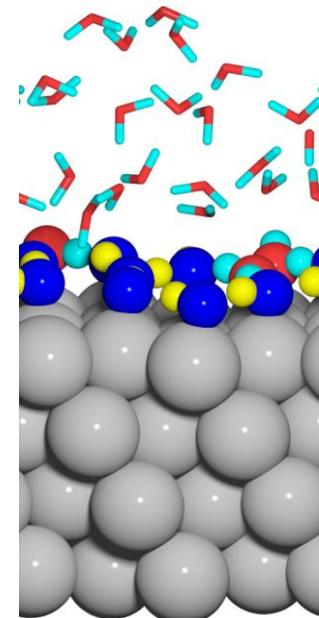
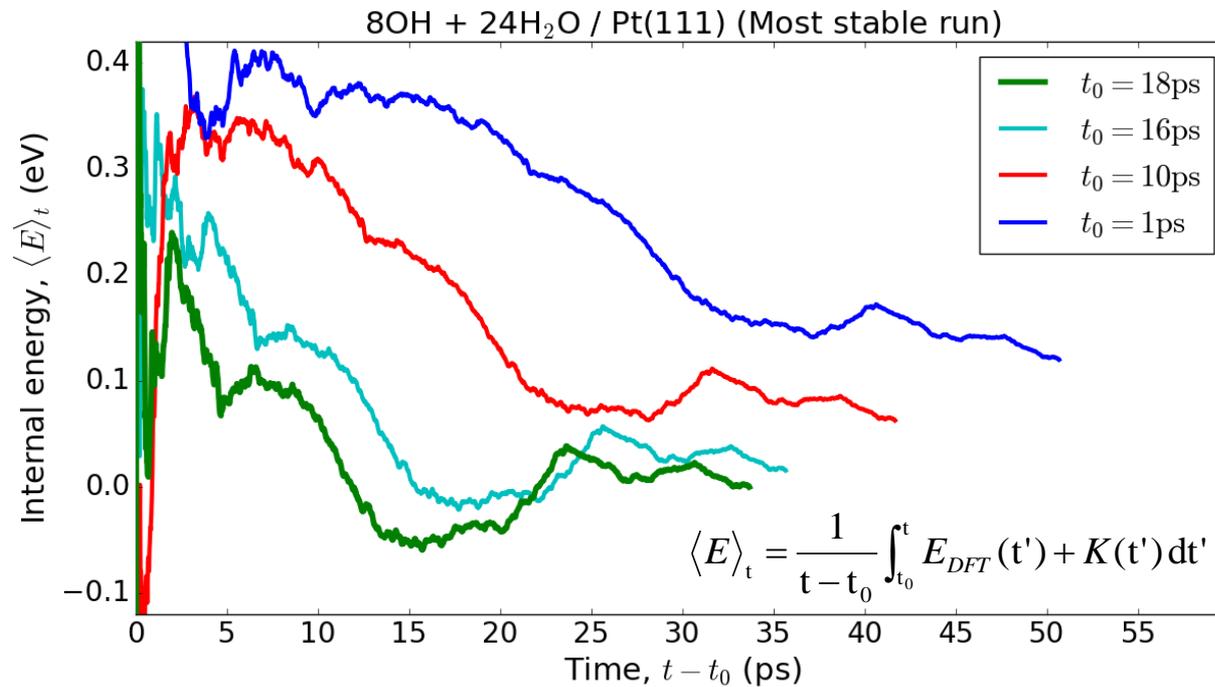


“Costly” insight

**The amount of sampling required for
high accuracy only becomes apparent
after extensive sampling**

Initial thermalization

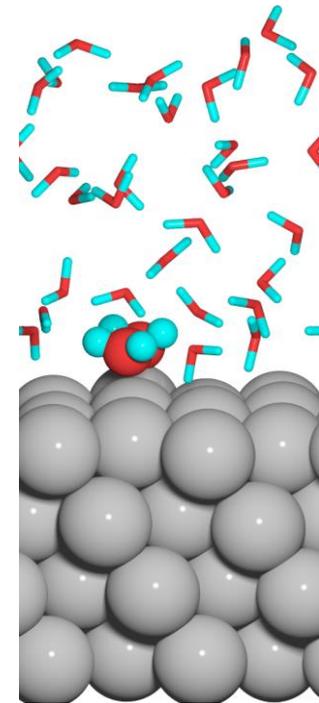
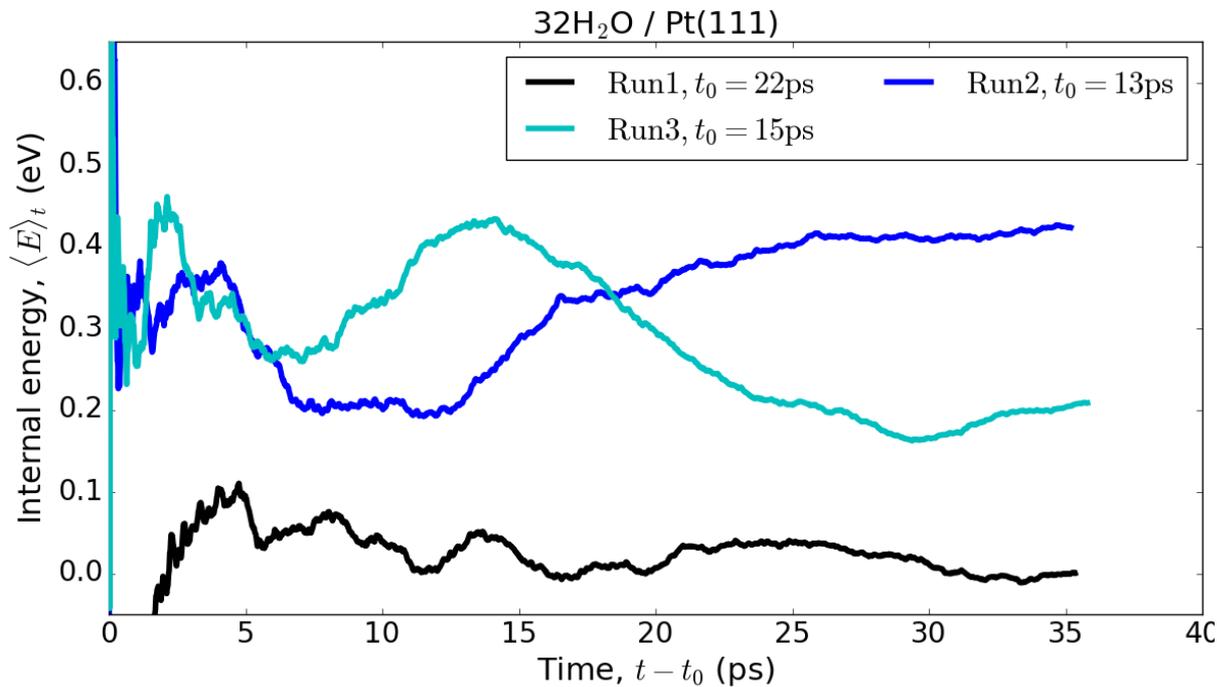
Initial “thermalization” often takes ~20 ps



Trapped in unfavorable minimum

Liquid water is a “glass” with many local potential energy minima

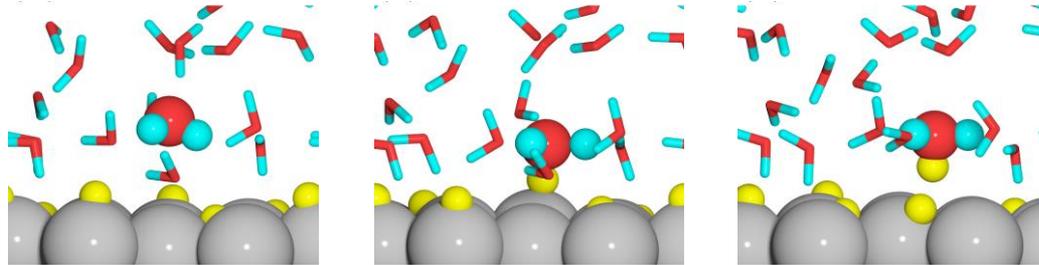
The average energy in ~ 50 ps MD run may depend on the initial conditions (the system is “stuck” in the local minimum where it started)



Rare event sampling

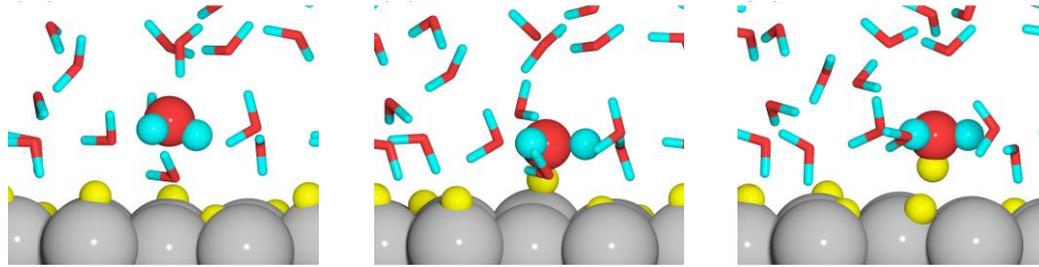
Rare event sampling

Such as $\text{H}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^-$



Rare event sampling

Such as $\text{H}^* \rightarrow \text{H}^+(\text{aq}) + \text{e}^-$



If irreversible, the free energy has decreased

$$F_{after} < F_{before}$$

(The “rare event” should happen after some simulation time to not be caused by initialization)

If reversible

$$\Delta F(A \rightarrow B) = -k_B T \ln \frac{\sum \tau_B}{\sum \tau_A}$$

(From probability distribution, i.e. ratio of time spend in each state)

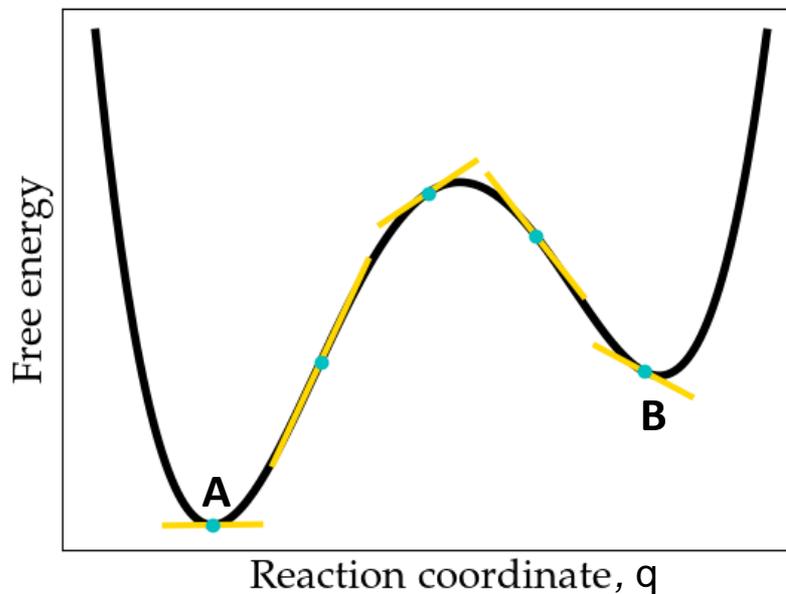
Rare event sampling

Probing the free energy profile of reactions from the required work

Thermodynamic integration

$$\Delta F(A \rightarrow B) = - \int_{q_A}^{q_B} \langle f(q) \rangle_t dq$$

Metadynamics



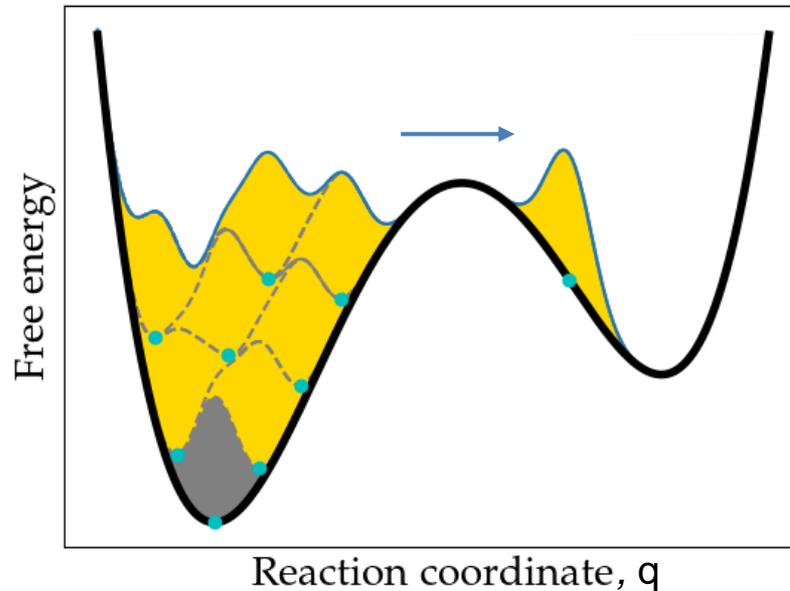
Rare event sampling

Probing the free energy profile of reactions from the required work

Thermodynamic integration

$$\Delta F = -h \sum_j \exp\left(\frac{-(q_j - q)^2}{2w^2}\right)$$

Metadynamics



*Multiple reaction coordinates are possible. There are several other methods.

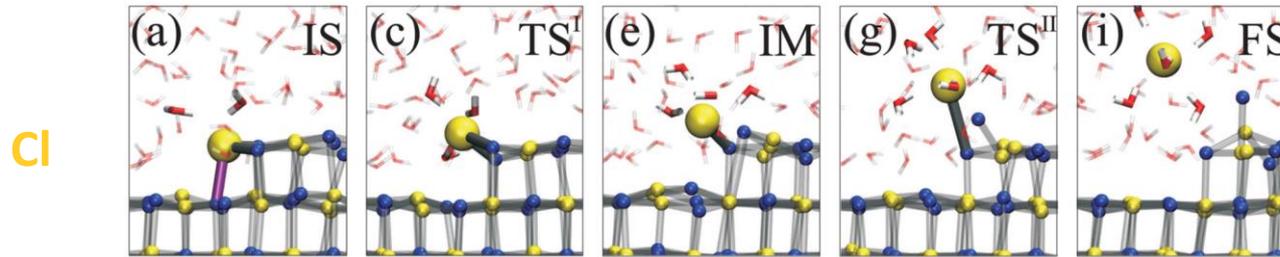
T. Bucko, *J. Phys. Condens. Matter*, **2008**, 20 (6), 64211. (VASP implementation)

Example

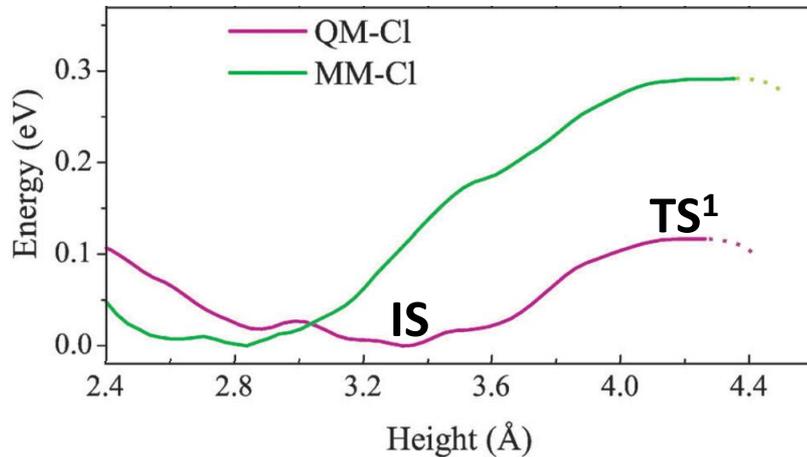
NaCl dissolution in liquid water studied with metadynamics

Dissolution mechanism

Initial dissolution step (is Cl^- solvation)

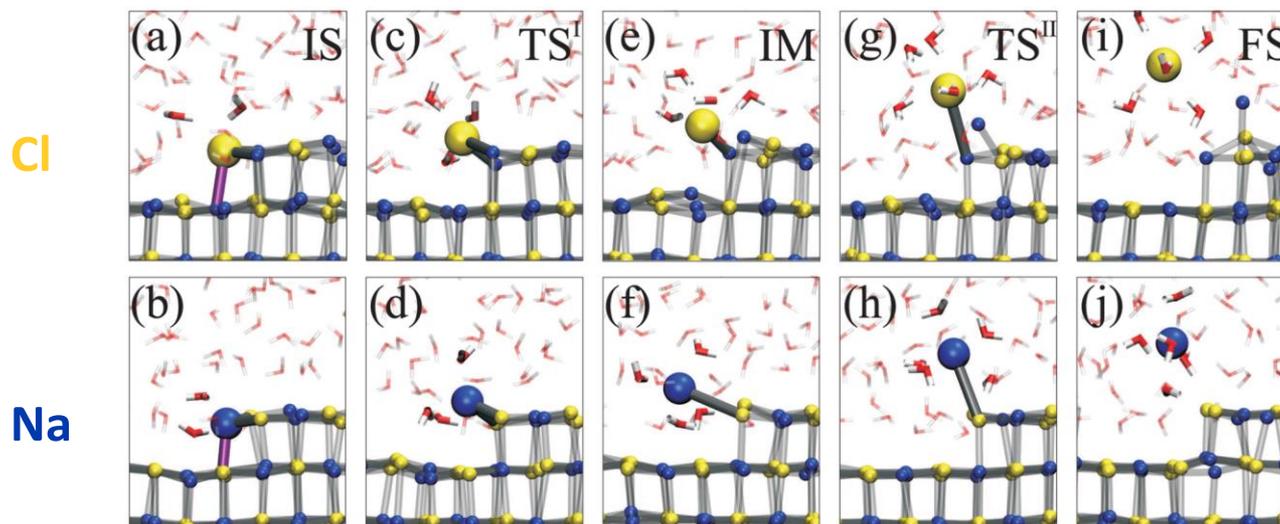


Free energy (metadynamics) with Cl height used as reaction coordinate.

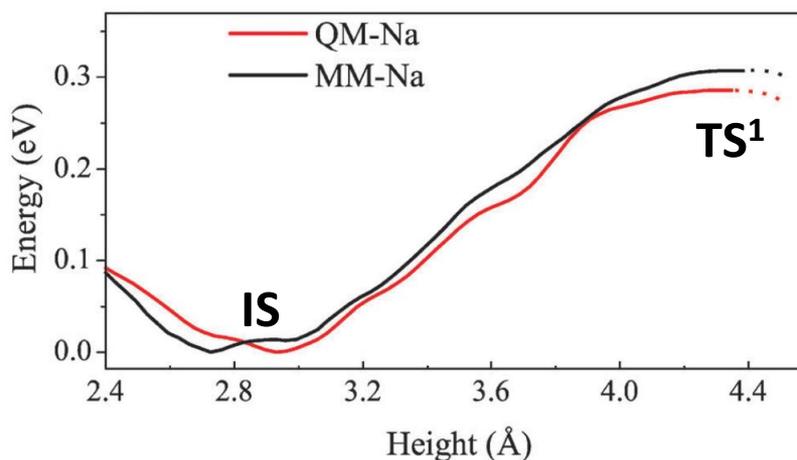
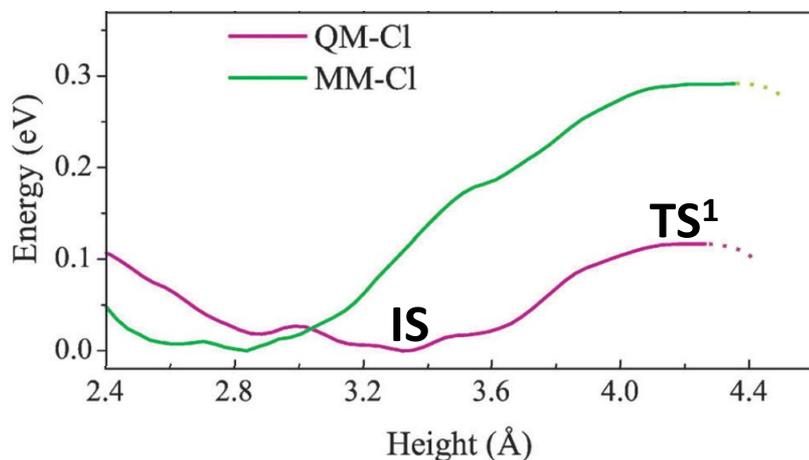


Dissolution mechanism

Initial dissolution step (is Cl^- solvation)



Free energy (metadynamics) with Cl/Na height used as reaction coordinate.



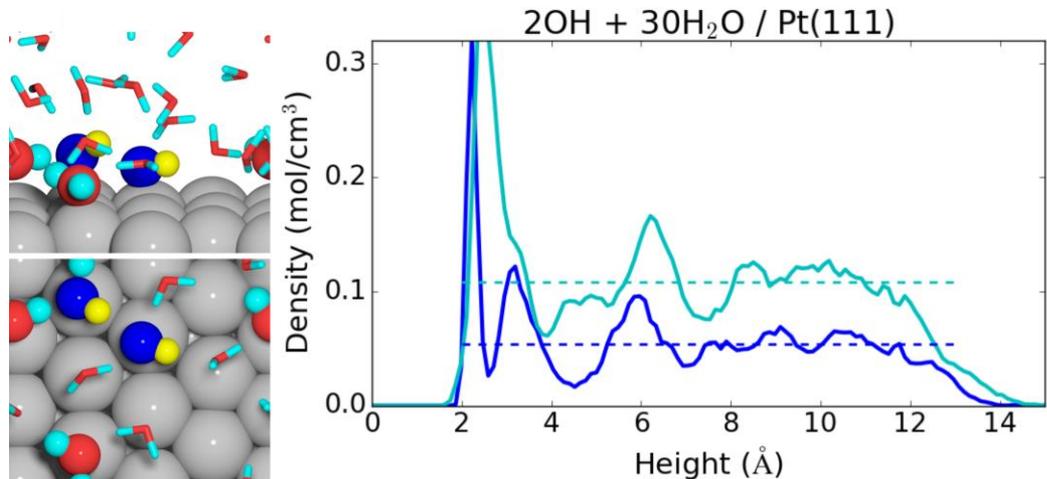
Example

O₂ adsorption-solvation barriers at liquid water-Pt(111)
studied with metadynamics

O₂ adsorption-solvation

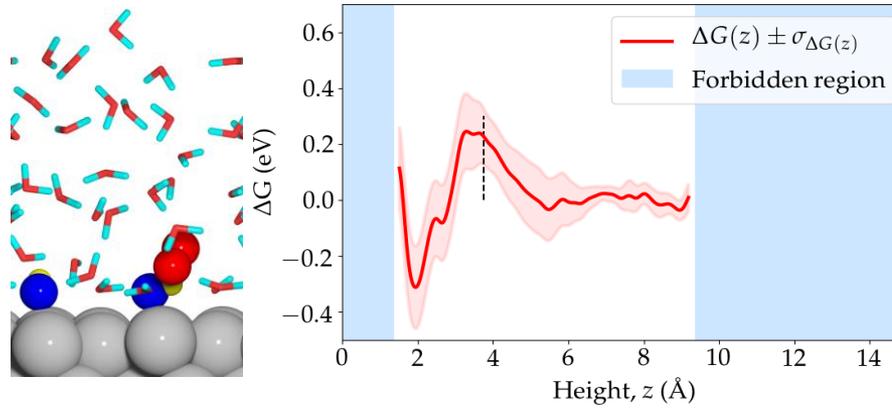
Can O₂(aq) access the surface of the 2OH + 30 H₂O / Pt(111) interface?

O₂(aq) +



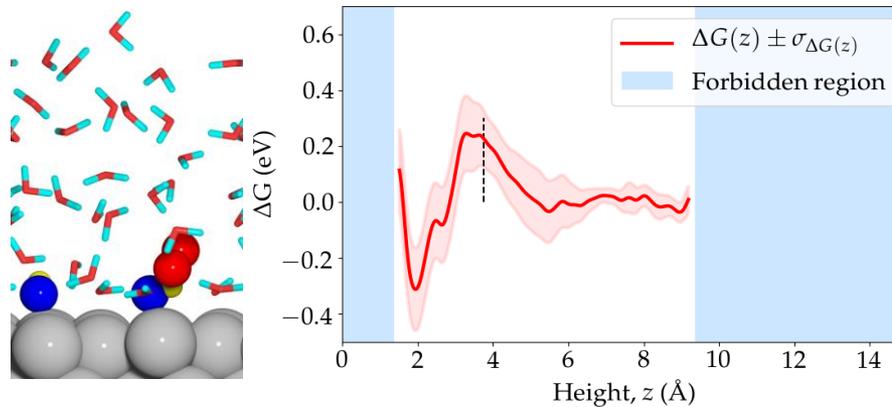
O₂ adsorption-solvation

The height of O₂ above Pt(111) is used as reaction coordinate

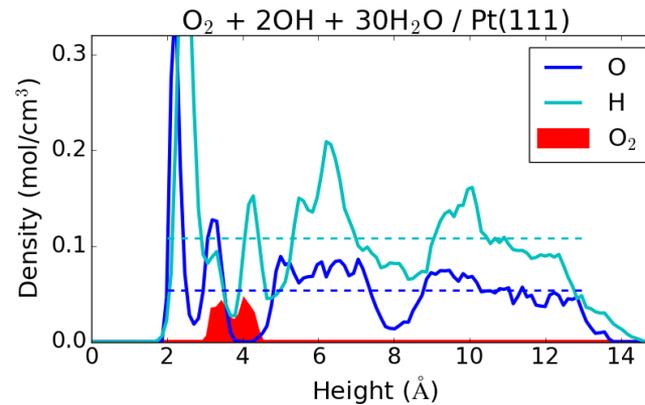


O₂ adsorption-solvation

The height of O₂ above Pt(111) is used as reaction coordinate

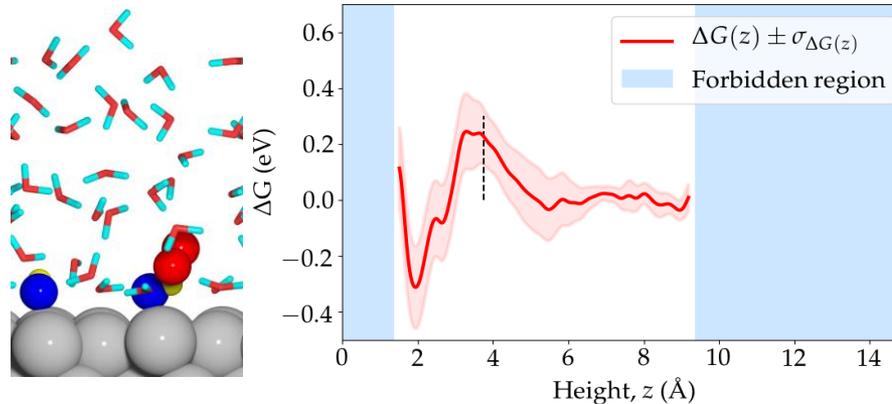


Atomic densities with O₂ at the transition state



O₂ adsorption-solvation

The height of O₂ above Pt(111) is used as reaction coordinate



Decomposition of the free energy (ΔE from normal MD simulations)

	O ₂ (2 Å)	O ₂ (4 Å)	O ₂ (7 Å)	O ₂ (g)
ΔG	-0.3 eV	+0.3 eV	0 eV	
ΔE	-0.6 eV	-0.1 eV	-0.1 eV	0 eV
$-T\Delta S$	+0.3 eV	+0.4 eV	+0.1 eV	

Entropy barrier!

Summary

Ab initio molecular dynamics

Necessary because liquids are not ground state structures

Can provide energy differences / reaction energies

$$\lim_{M \rightarrow \infty} \frac{1}{M} \sum_{j=1}^M E_j = \langle E(T_0) \rangle_{\text{canonical}}$$

Liquid water is different from ice-like water, example water-Pt(111)

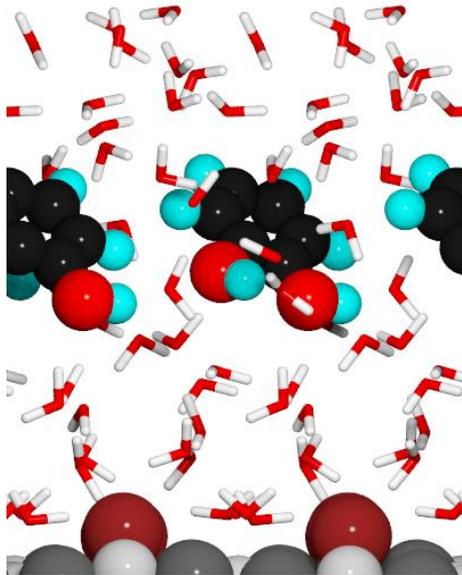
Rare event sampling

Methods like metadynamics provide free energy profiles
of rare events / reactions

Importance of van der Waals correction

optB88-vdW

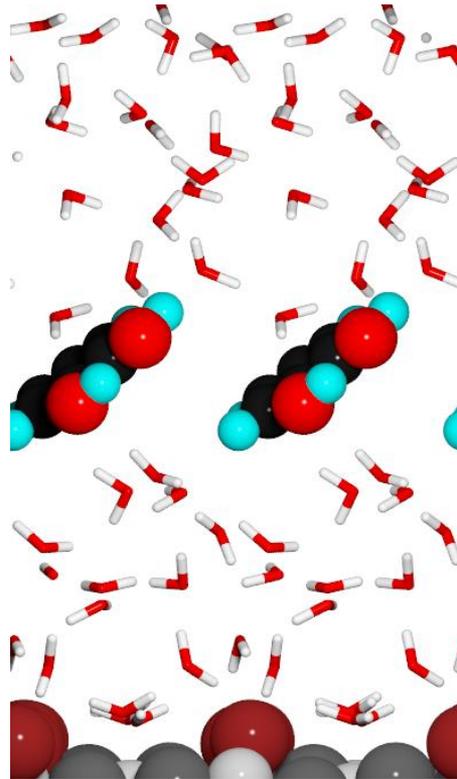
Includes van der
Waals correction



Energy **favorable**
solvation

PBE

no van der Waals
correction



Energy **unfavorable**
solvation

Catechol is very
solvable

31.2g catechol per 100g
water at 20°C