Solid-liquid interfaces and external bias

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Norderney

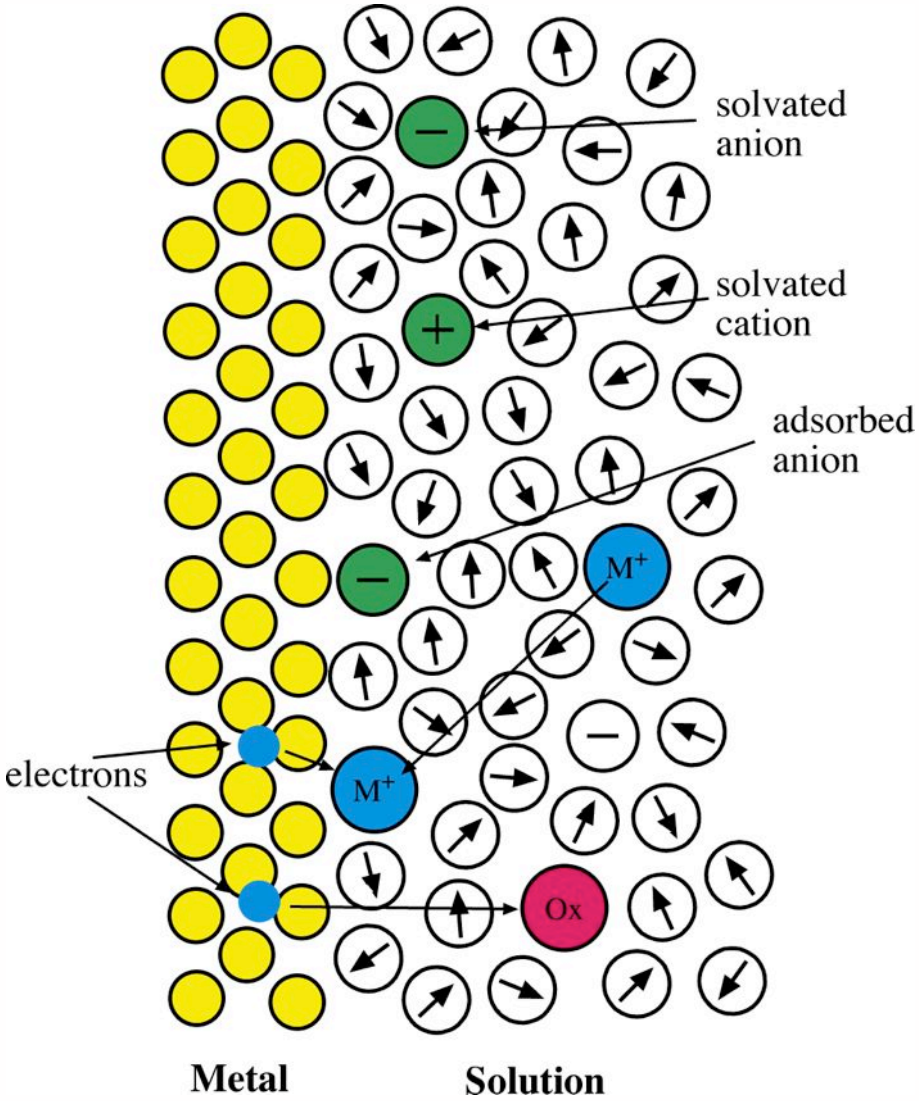
July 25, 2013

1. First-principles modeling of the electrochemical interfaces

2. Structure of aqueous electrolyte/metal interfaces

3. Adsorption and simple reactions at electrodes in the presence of the water

Electrochemical double layer



"Interfacial Electrochemistry", Elizabeth Santos and Wolfgang Schmickler, Springer, 2010.

Open questions

- Exact structure of water at the electrochemical solid-liquid interface: ice-like or liquid?

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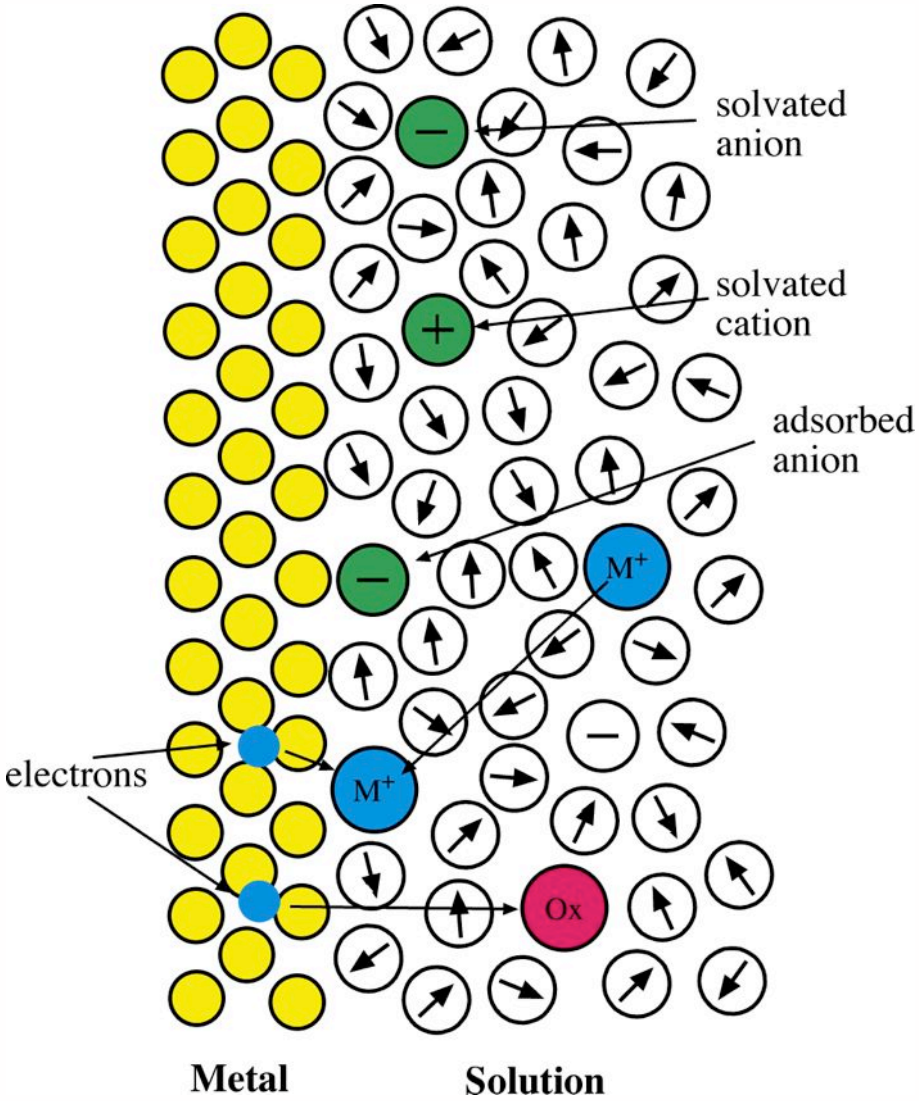

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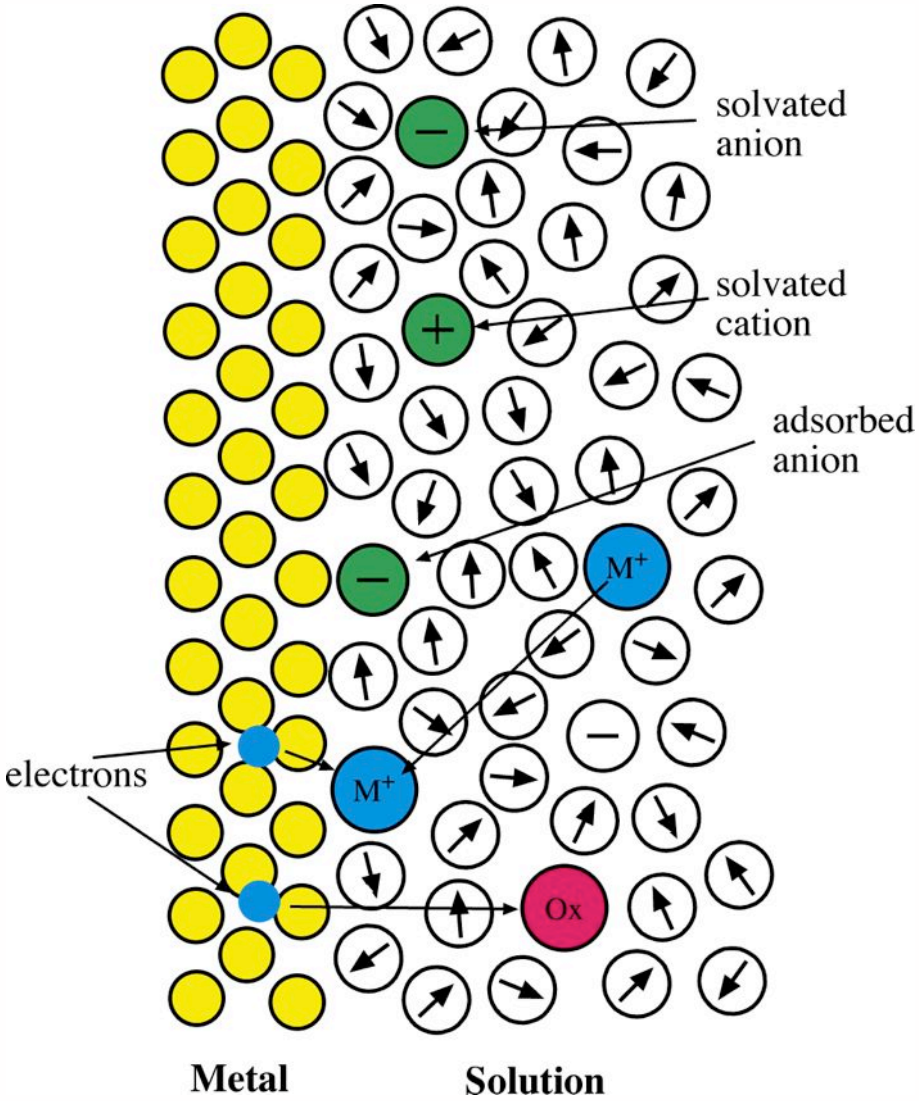

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- Is the strength of specific adsorption influenced by the presence of the electrolyte ?

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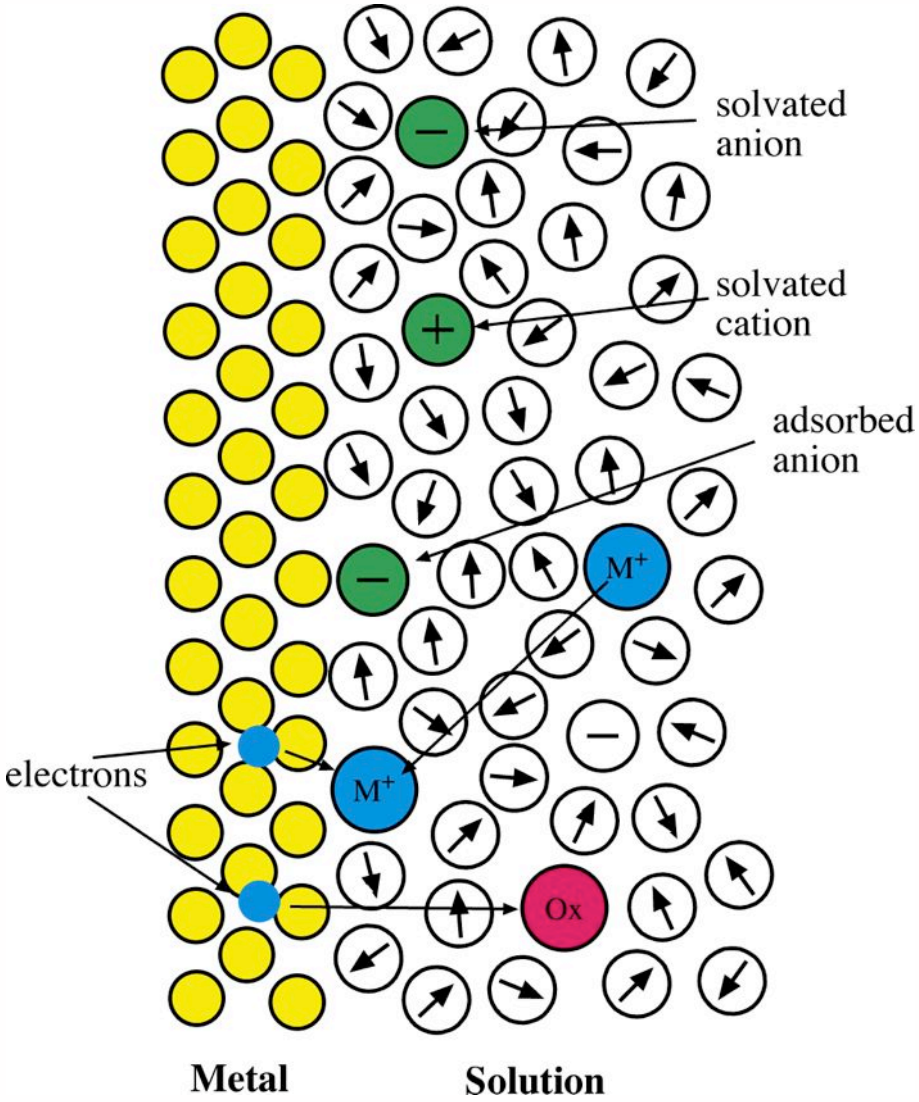

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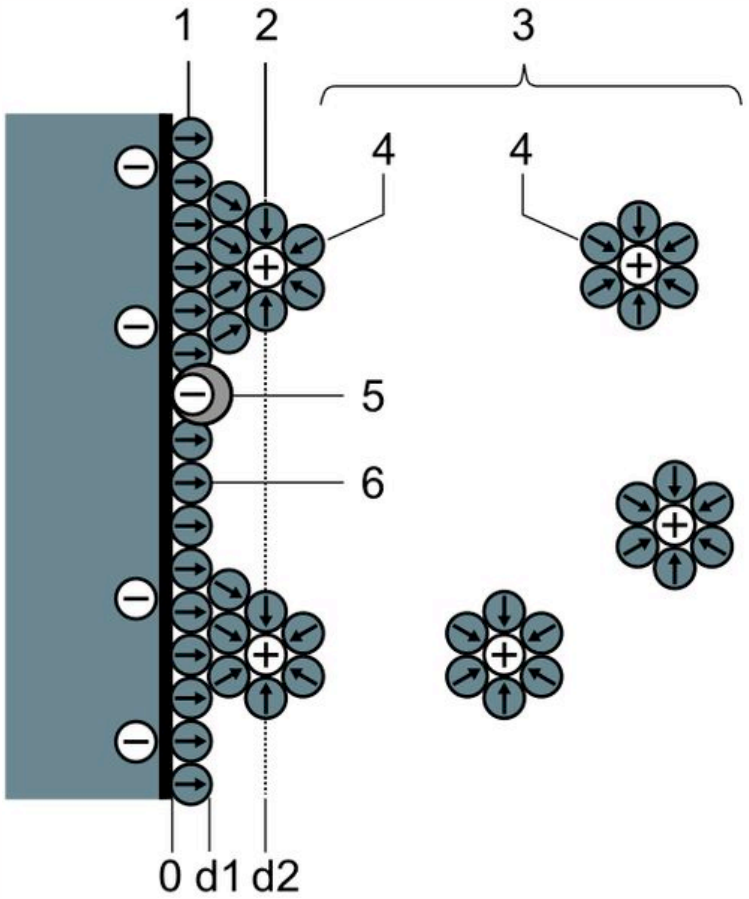
Open questions

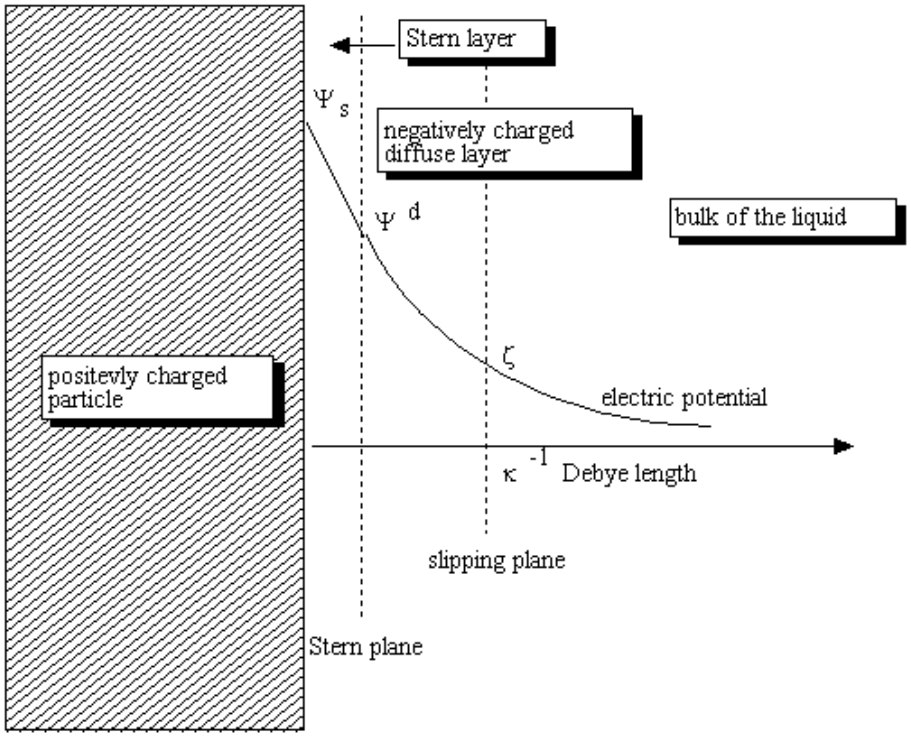
- Exact structure of water at the electrochemical solid-liquid interface: ice-like or liquid?
- How do solvation shells change at the vicinity of the interface ?
- Is the strength of specific adsorption influenced by the presence of the electrolyte ?
- What is the microscopic role of the electrode potential ?
- ...

Double layer (Wikipedia)

Atomistic sketch



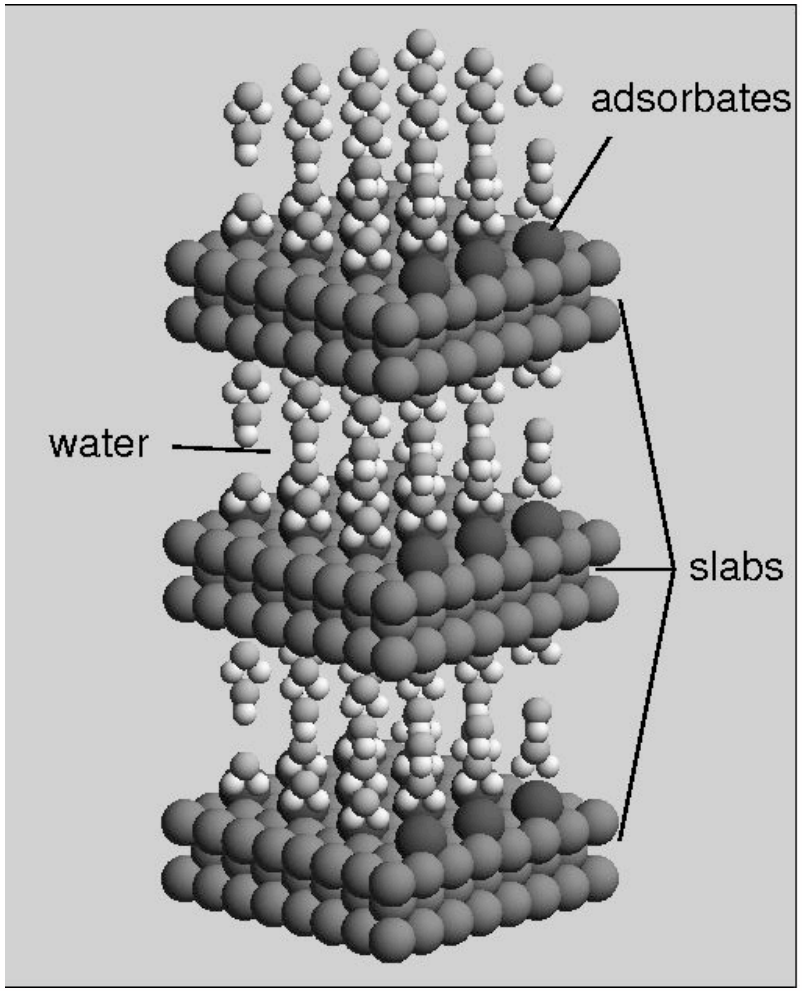
Continuum sketch



1 Inner Helmholtz layer, 2 outer Helmholtz layer, 3 diffuse layer,
4 solvated ions, 5 specifically adsorbed ions, 6 solvent molecules

Density functional theory calculations in a plane wave basis

Super cell approach



Numerical details

Description of electronic wave functions by plane waves numerically very efficient

⇒ Super cell approach

Typically 10 - 100 atoms per super cell,
but up to several thousands of atoms possible

Results should be independent of layer thickness and distance

Many-body effects in DFT described by the exchange-correlation functional that is not known in general

⇒ Approximations: GGA necessary

Collaboration with University Vienna:
Vienna Ab initio Simulation Package (VASP)
G. Kresse, J. Furthmüller, J. Hafner

Varying electrode potentials

Electrochemistry: electrode potential additional important external parameter

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Theoretical consideration of electrode potential not trivial

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Effective incorporation of electron potential is possible: Computational hydrogen electrode

J.K. Nørskov *et al.*, J. Phys. Chem. B **108**, 17886 (2004).

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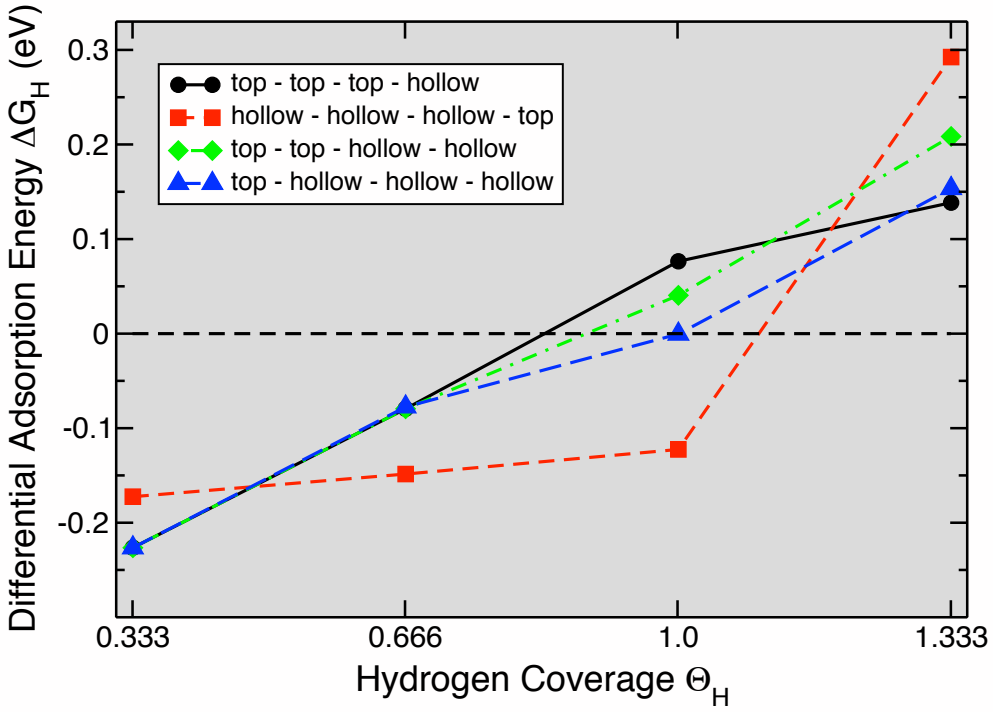
Differential adsorption energies H/Pt(111)



At standard conditions, hydrogen evolution

$$\mathrm{H}^+ + e^- \leftrightarrow \frac{1}{2}\mathrm{H}_2$$

is in equilibrium

$\Rightarrow$ processes with $\Delta G_\mathrm{H} < \mu_\mathrm{H} = -eU$ occur under equilibrium conditions

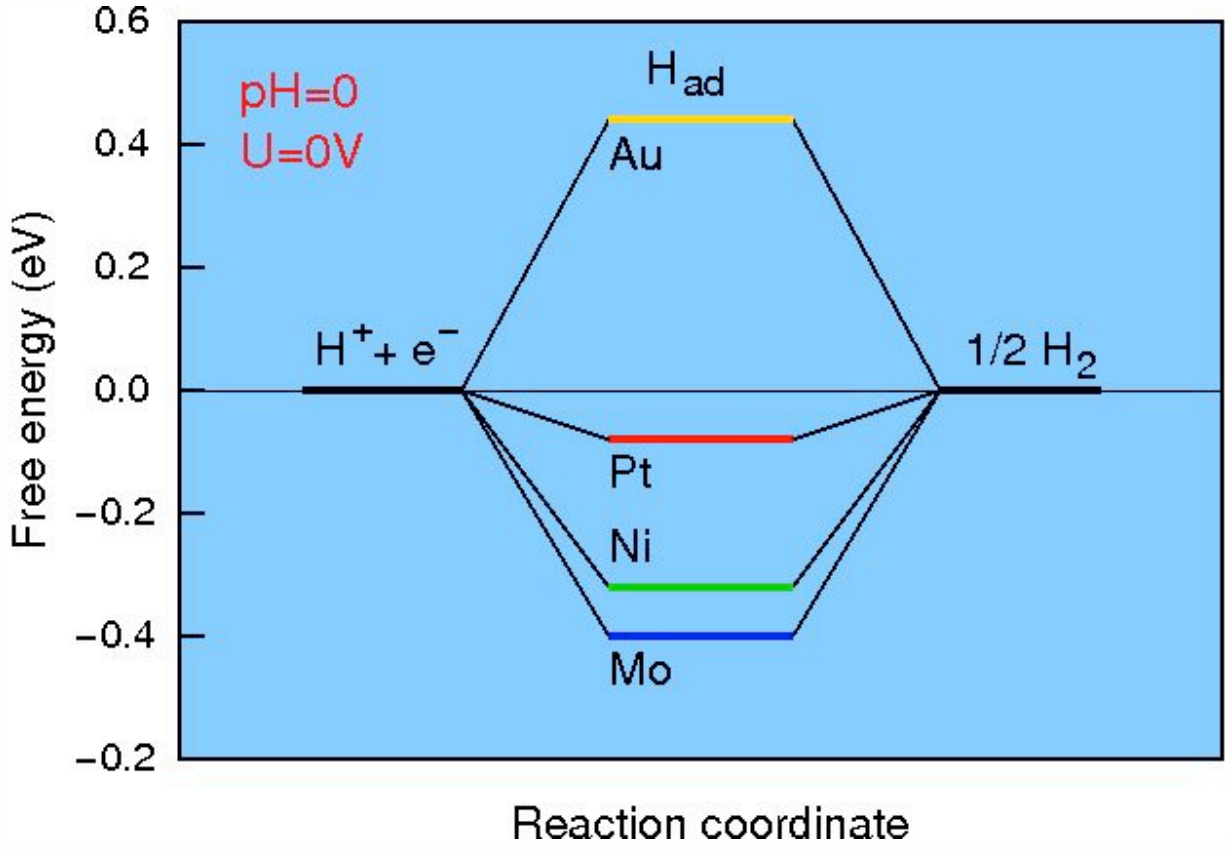
Change in electron number n between reactants and product considered via $\Delta G = \Delta G(0) + neU$

At standard conditions, a Pt(111) electrode is covered by a hydrogen layer

Chemical trends in the hydrogen evolution

J.K. Nørskov *et al.*, J. Electrochem. Soc. **152**, J23 (2005).

Free energy diagram for hydrogen evolution at equilibrium (U=0 vs NHE)



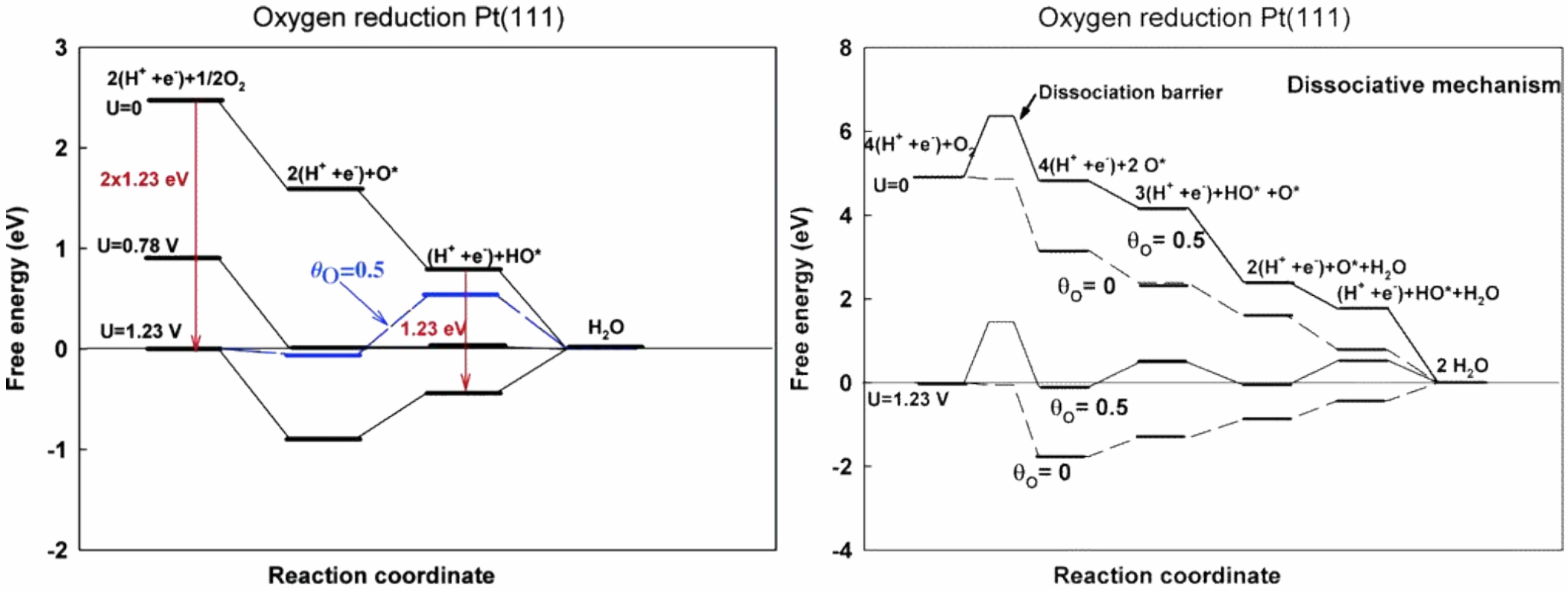
On Pt(111), hydrogen evolution in equilibrium with the intermediate H adsorption state
$\Rightarrow$ Exceptional role of Pt as an electrocatalyst

Oxygen reduction reaction (ORR)

J.K. Nørskov *et al.*, J. Phys. Chem. B **108**, 17886 (2004).

$$\Delta G = \Delta G(0) + neU$$

ORR two- and four-electron processes

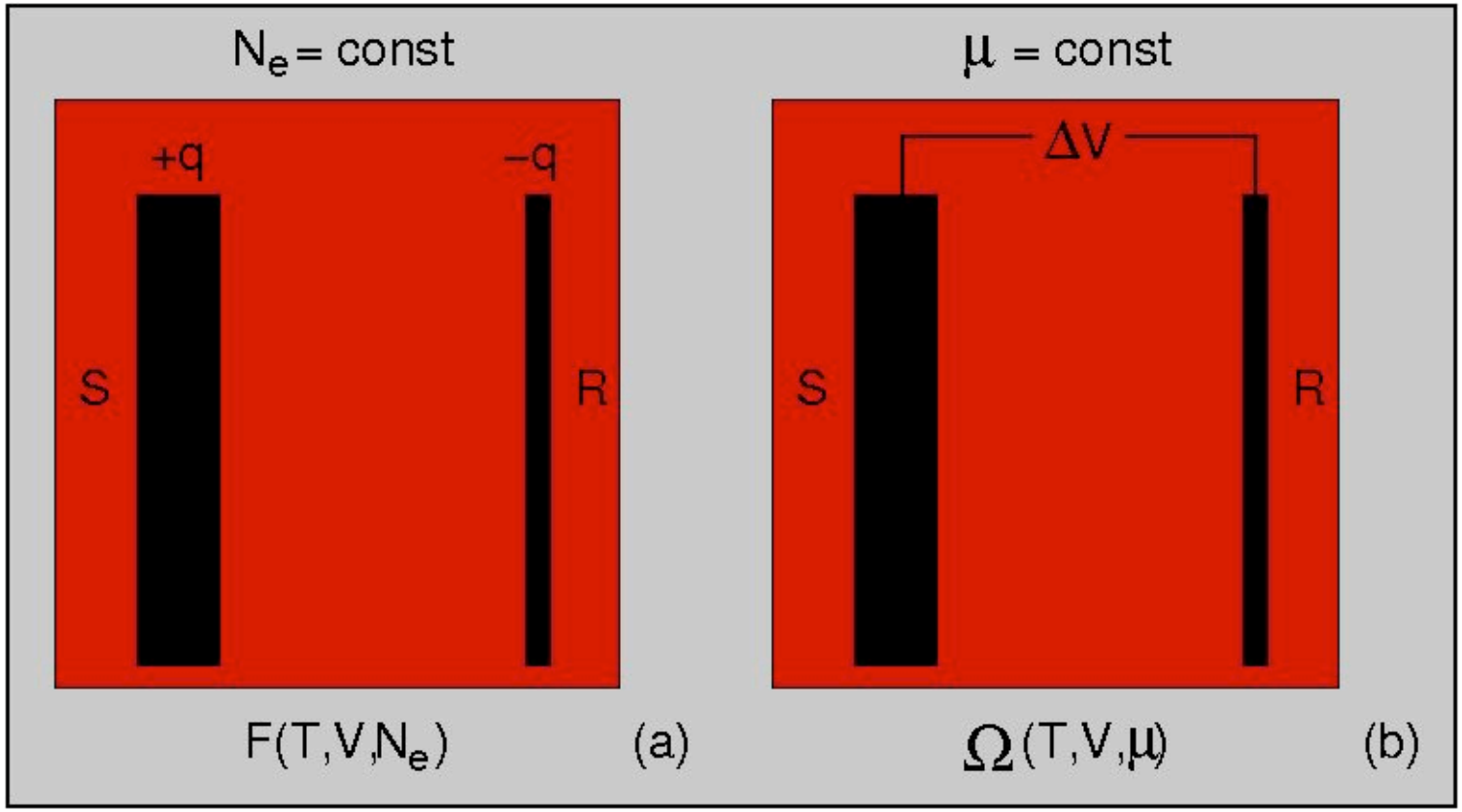


No explicit consideration of electrode potential and electrochemical environment

Charged systems in periodic DFT calculations

A.Y. Lozovoi *et al.*, J. Chem. Phys. **115**, 1661 (2001)

Charging up the slabs also leads effectively to a variation in the electrode potential, but in periodic calculations the unit cell has to be neutral

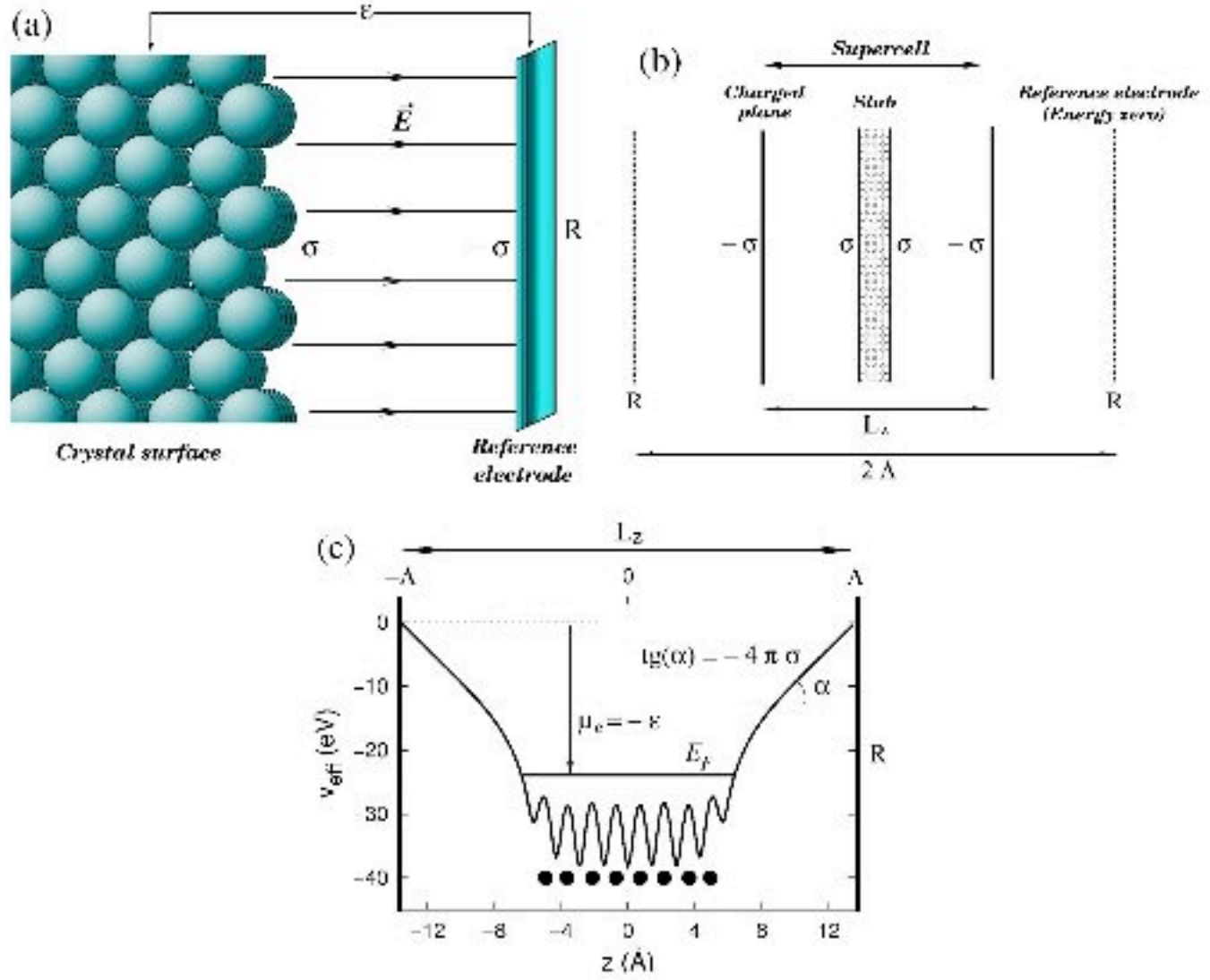


Two different modes are possible to treat charged slabs corresponding to a canonical and a grand-canonical formulation

Reconstruction of charged surfaces: Pt(110) and Au(110)

A.Y. Lozovoi and A. Alavi, Phys.Rev. B **68**, 245416, (2003)

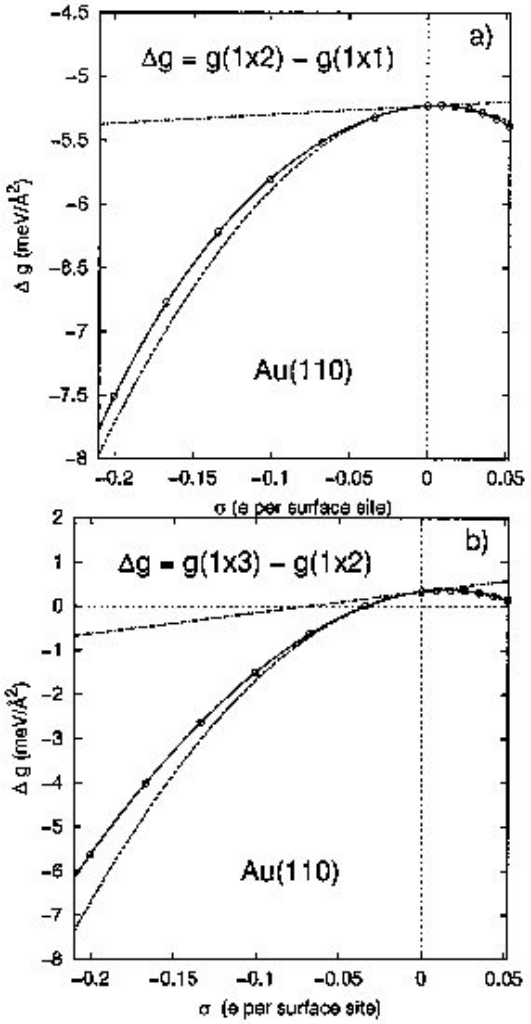
Setup of supercell calculations



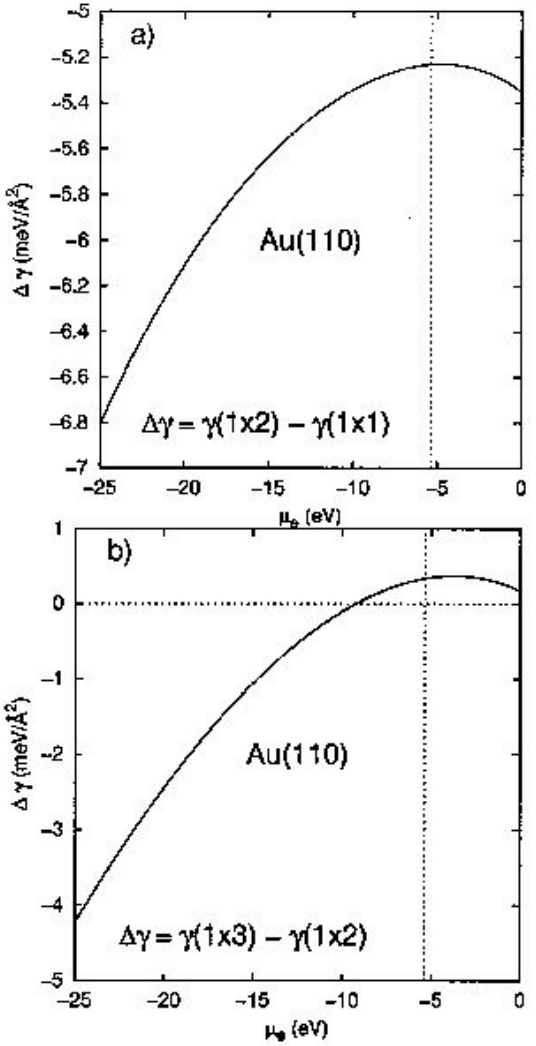
Au(110): Lifting of (1×2) missing-row reconstruction

A.Y. Lozovoi and A. Alavi, Phys.Rev. B **68**, 245416, (2003)

Constant charge



Constant potential

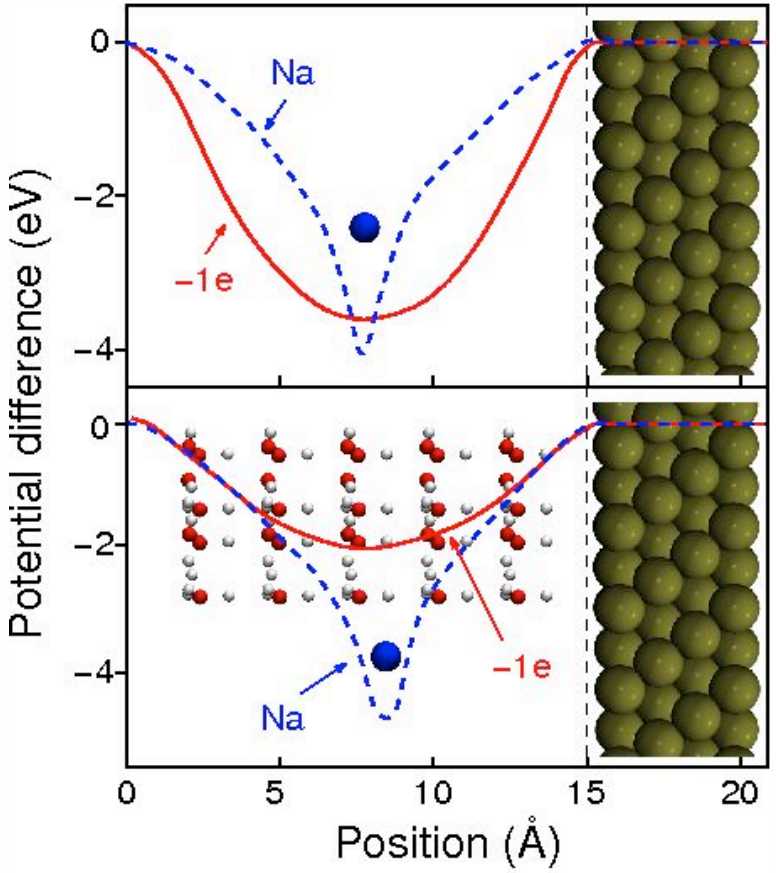


Analogous bevavior in constant-charge and constant-potential mode

Interface with a constant charge background

C.D. Taylor *et al.*, Phys. Rev. B **73**, 165402 (2006).

Potential with and without a water layer



Constant charge background: automatic default procedure in periodic DFT codes to compensate a charged system

Poisson equation for region with a constant charge background:

$$\nabla^2\phi(\mathbf{x}) \;=\; 4\pi\rho_o \;. \qquad (1)$$

General solution:

$$\phi(\mathbf{x}) \;=\; 4\pi\rho_o\Big(\sum_{i,j} C_{i,j}x_i x_j + \sum_i C_i x_i + C_0\Big) \;. \qquad (2)$$

Artefacts due to parabolic solution outside the metal electrodes reduced through the presence of polarizable water layers

Energy expression in the presence of a constant charge background

C.D. Taylor *et al.*, Phys. Rev. B **73**, 165402 (2006).

$$\frac{\partial E_{\mathrm{DFT}}}{\partial q} = \frac{\partial E_{\mathrm{slab}}}{\partial q} + \frac{\partial E_{\mathrm{slab-bg}}}{\partial q} + \frac{\partial E_{\mathrm{bg}}}{\partial q} , \tag{3}$$

E_{slab}: energy of the charged water/electrode system, $E_{\mathrm{slab-bg}}$: interaction between the system and the background charge, and E_{bg} energy of the background.

$$E_{\mathrm{slab-bg}} = \int \rho_{\mathrm{bg}} V_{\mathrm{slab}} d^3x , \quad E_{\mathrm{bg}} = \int \rho_{\mathrm{bg}} V_{\mathrm{bg}} d^3x , \tag{4}$$

V_{slab}: electrostatic potential of the charged water/electrode system in the absence of the background charge. Note that $\rho_e = -\rho_{\mathrm{bg}} = q$.

$$\Rightarrow \frac{\partial E_{\mathrm{DFT}}}{\partial q} = \mu - \int \frac{V_{\mathrm{tot}}}{\Omega} d^3x . \tag{5}$$

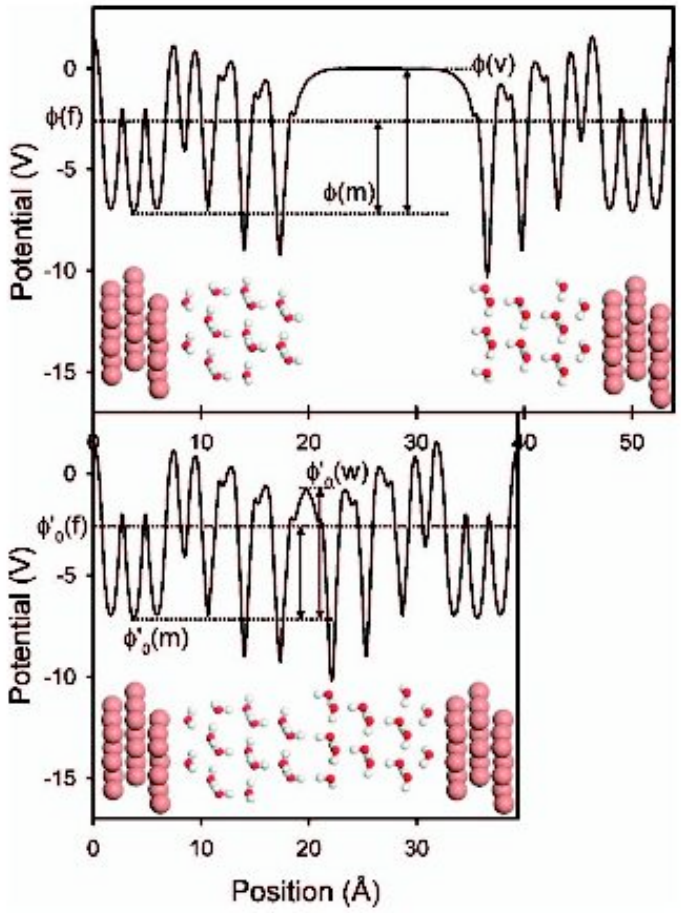
$$\Rightarrow \text{Grand canonical free energy } E = \int_0^q \mu dQ = E_{\mathrm{DFT}} + \int_0^q \left[\int \frac{V_{\mathrm{tot}}}{\Omega} d^3x \right] dQ . \tag{6}$$

Electrode potential for a constant background charge

C.D. Taylor *et al.*, Phys. Rev. B **73**, 165402 (2006).

"Double-reference method"

Electrostatic potential profile



First reference: vacuum level for uncharged system

$$\phi_0(m) = \phi(m) = \phi'(m) - \phi'(v) \qquad (7)$$

Index 0: system without vacuum

$$\begin{aligned} \phi_0(z) &= \phi'_0(z) - \phi'_0(m) + \phi_0(m) \\ &= \phi'_0(z) - \phi'_0(m) + \phi'(m) - \phi'(v) \end{aligned} \qquad (8)$$

Second reference: Fixed region far from the electrode at its position in the $q = 0$ calculation (potential $\phi_0(w)$) while the rest of the system is relaxed in response to the applied charge

$$\phi_q(z) = \phi'_q(z) - \phi'_a(w) + \phi_0(w) \qquad (9)$$

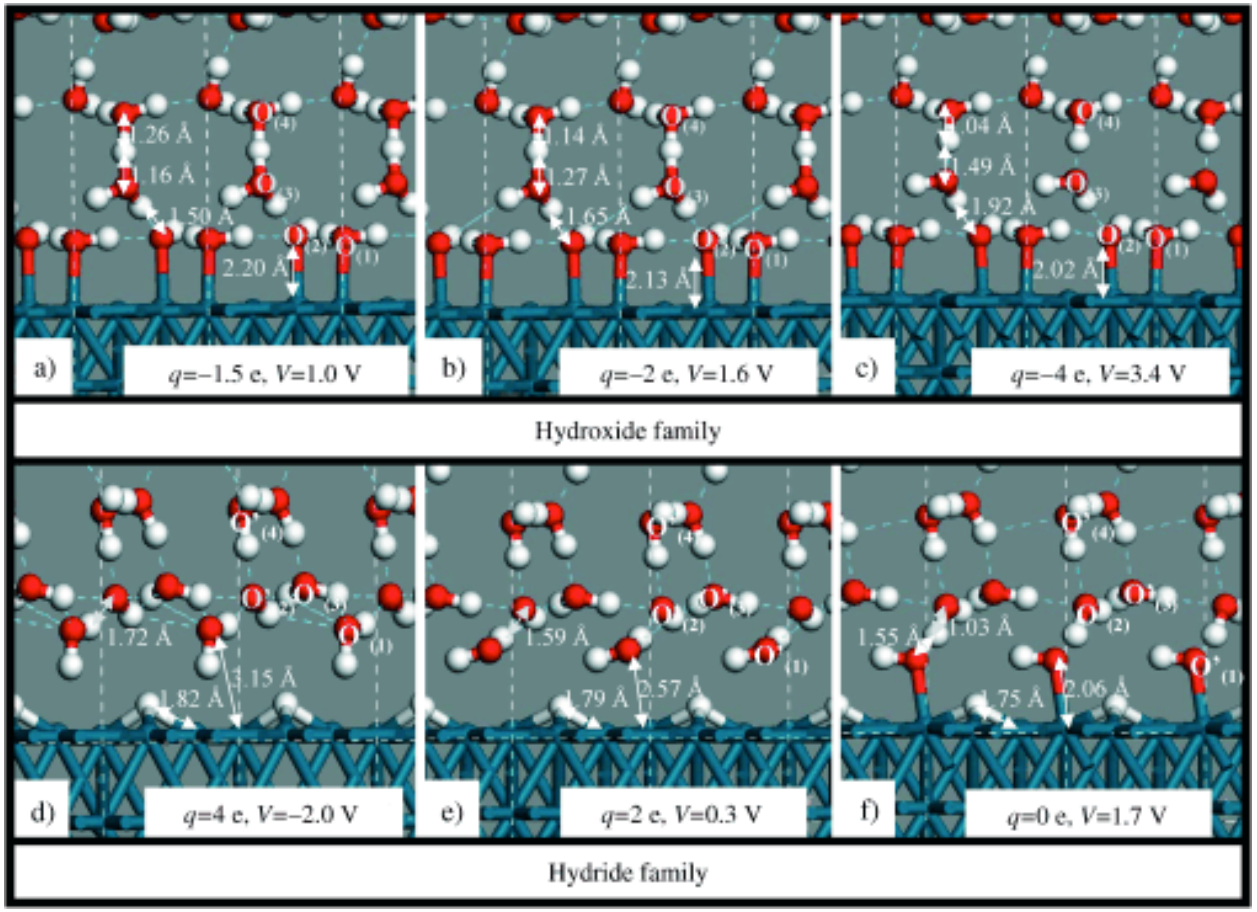
Absolute potential:

$$\phi_{\mathrm{NHE}} = -4.85\mathrm{eV} - \phi_q \qquad (10)$$

Applications: Electrochemical Activation of Water over Pd

J.S. Filhol and M. Neurock, Angew. Chem. Int. Ed. **402**, 402 (2006)

Evolution of the structure of the palladium/hydroxide interface as a function of applied potential

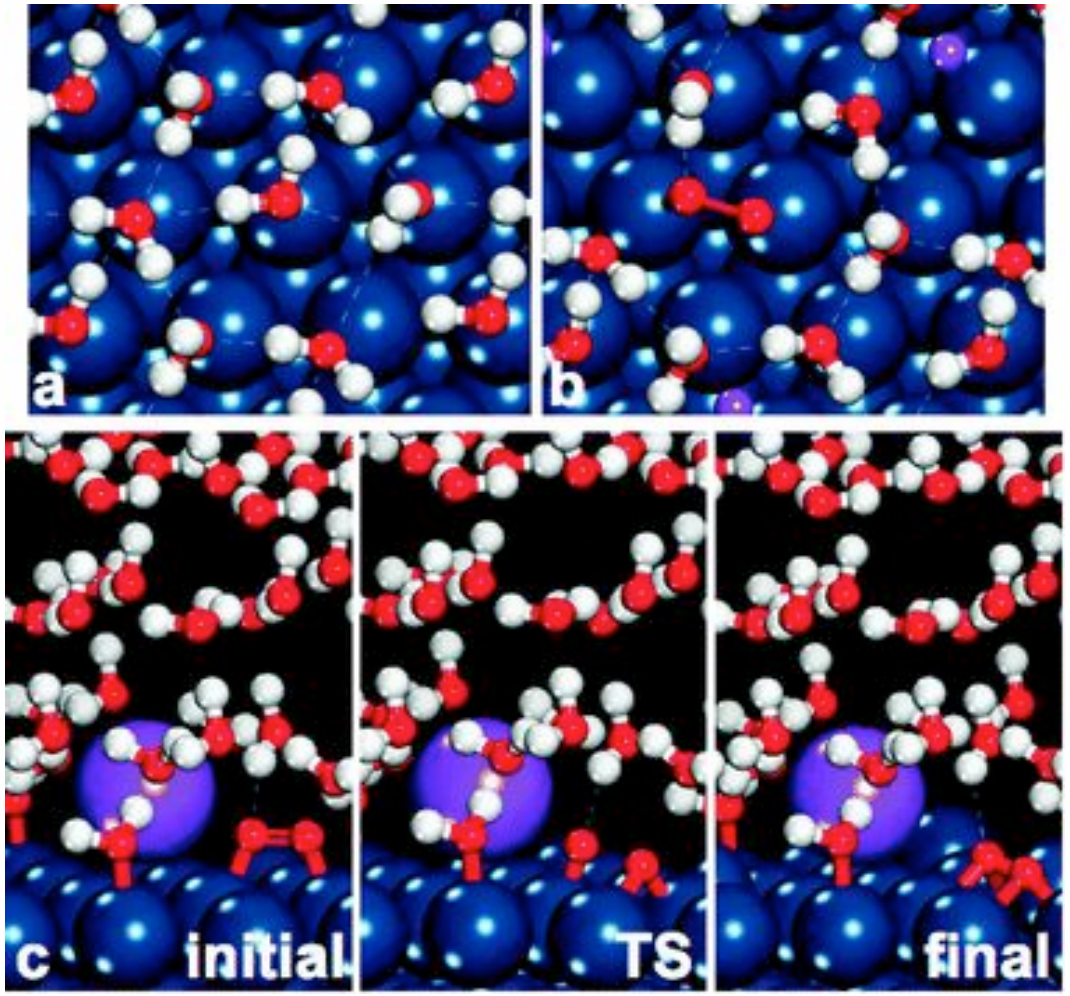


H_2O/Pd/Au structure and H_2O-Pd/Au distance as a function of an external electric field

Oxygen dissociation at an electrode surface

S.A. Wasileski and M.J. Janik, PCCP **10**, 3613 (2008).

O_2 dissociation on Pt(111) in the presence of water and Na at various potentials

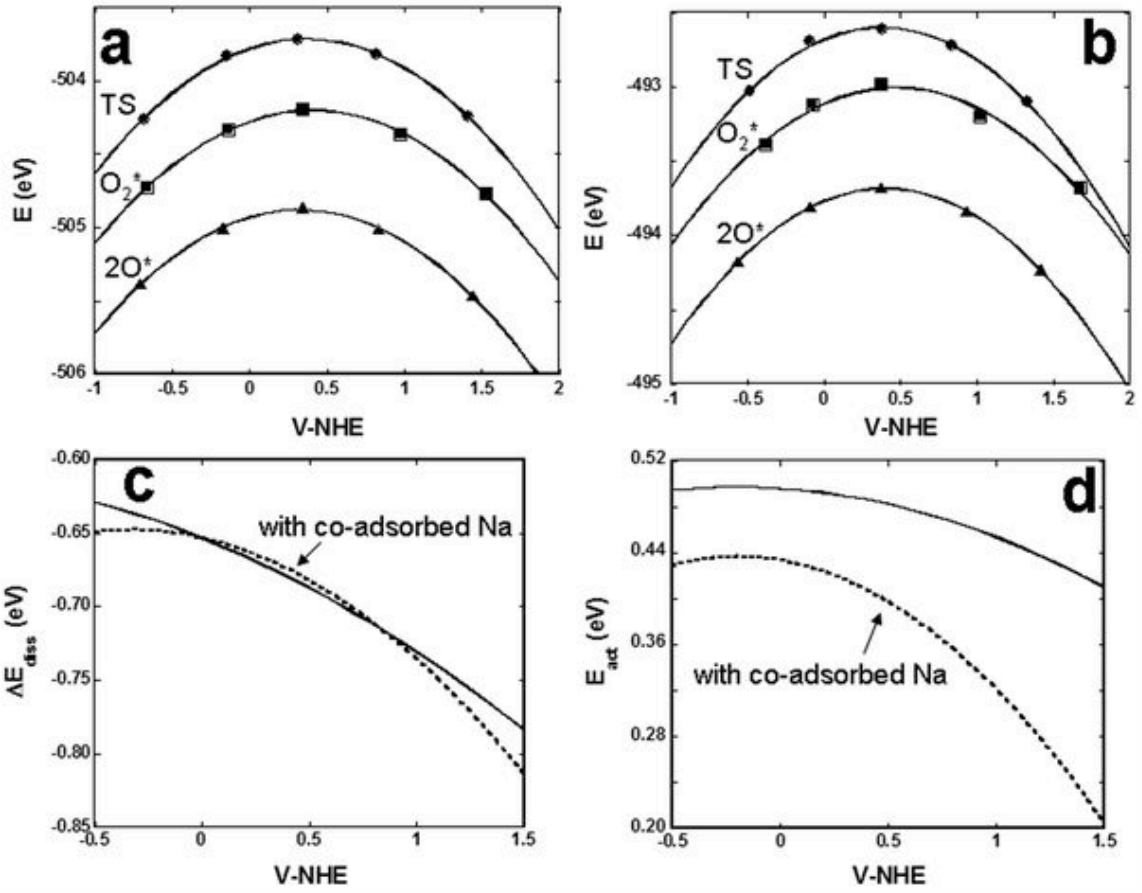


O_2 dissociation path with coadsorbed Na

Potential dependence of O_2 dissociation

S.A. Wasileski and M.J. Janik, PCCP **10**, 3613 (2008).

Potential dependence of initial, transition and final state energies for O_2 dissociation on solvated Pt(111)



Variation in the structure along a reaction path can lead to changes in the workfunction corresponding to a variation in the electrode potential

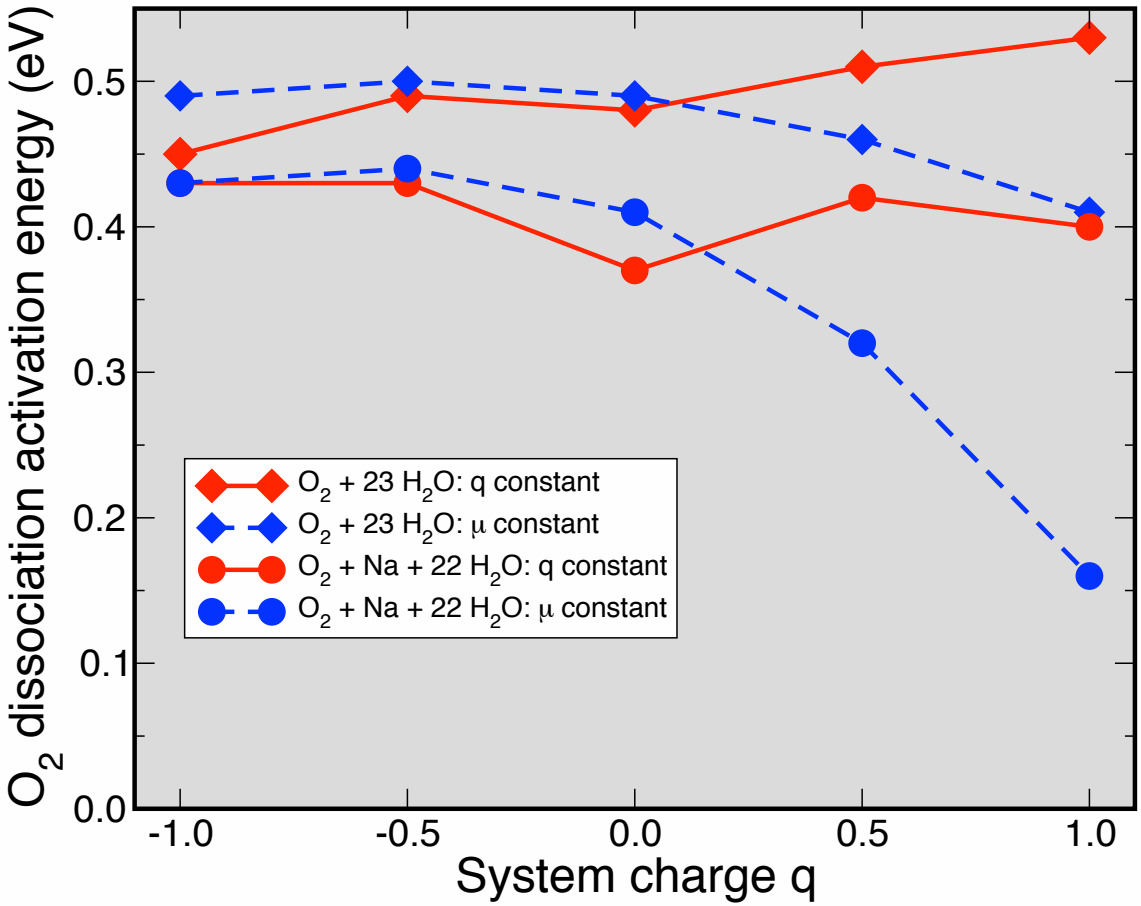
Quadratic fit referenced vs. NHE

$$E(\phi) = A\phi^2 + B\phi + C \qquad (11)$$

in order to generate continuous energy vs. potential curve

Oxygen dissociation activation energy

S.A. Wasileski and M.J. Janik, PCCP **10**, 3613 (2008).



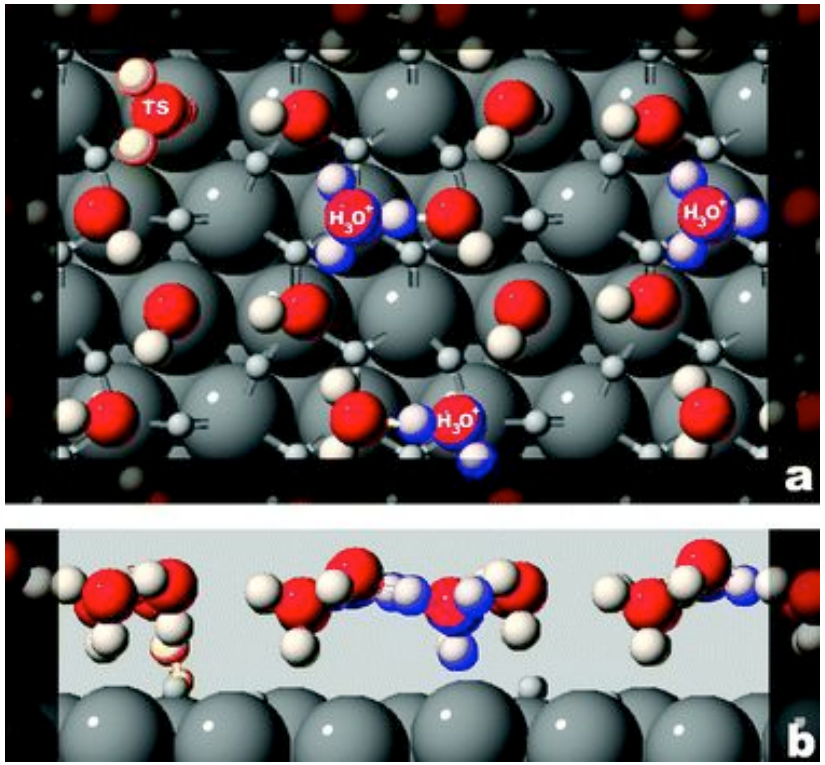
Reduction of the O_2 dissociation barrier in the presence of Na

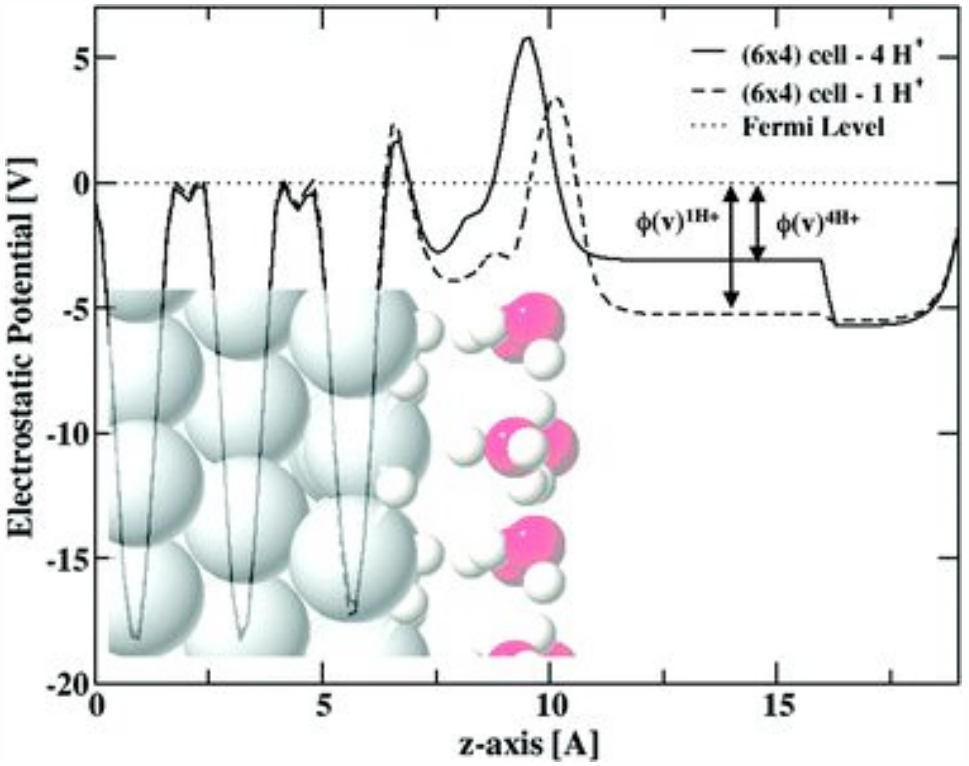
Significant difference between results for constant charge and constant chemical potential at the potential of the initial state

Explicit consideration of counter ions

E. Skúlason, J. Rossmeisl, J.K. Nørskov *et al.*, PCCP **9**, 3241 (2007); CPL **466**, 68 (2008)

Change of electrode potential by varying the number of protons/electrons in the double layer





Excess H atoms are included in the water layer which results in the formation of solvated protons in the water layer and transfer of electrons to the metal

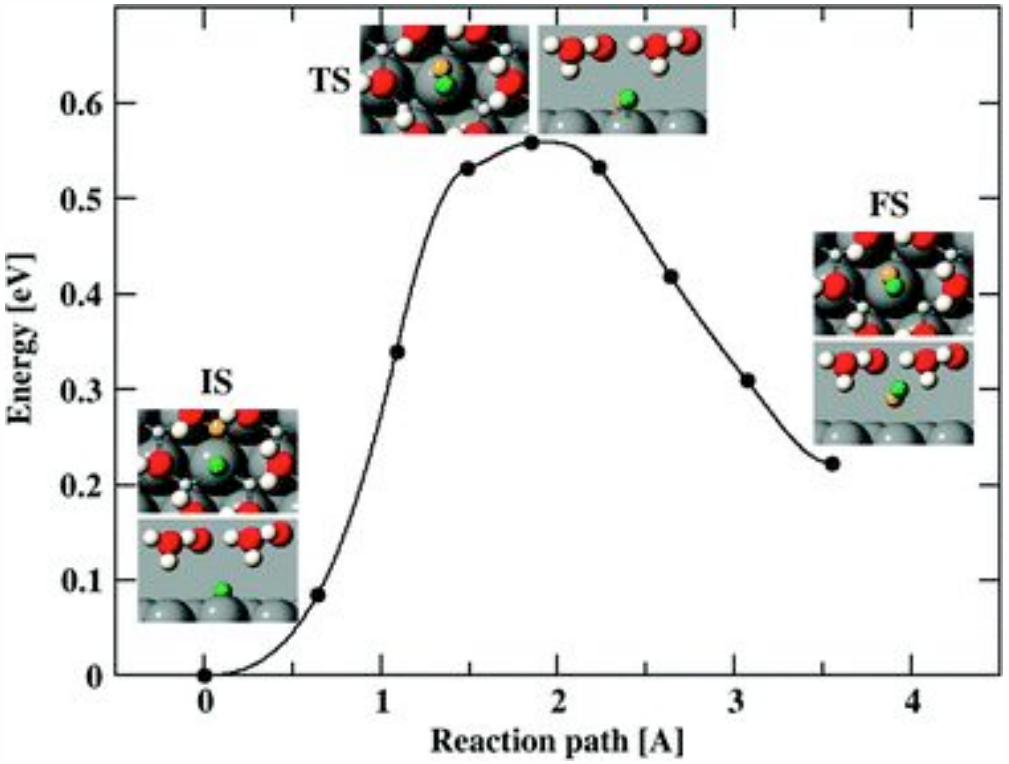
Problem: only one water bilayer, protons confined to the first water bilayer, electrode potential can vary along reaction paths

Tafel reaction as a function of the electrode potential

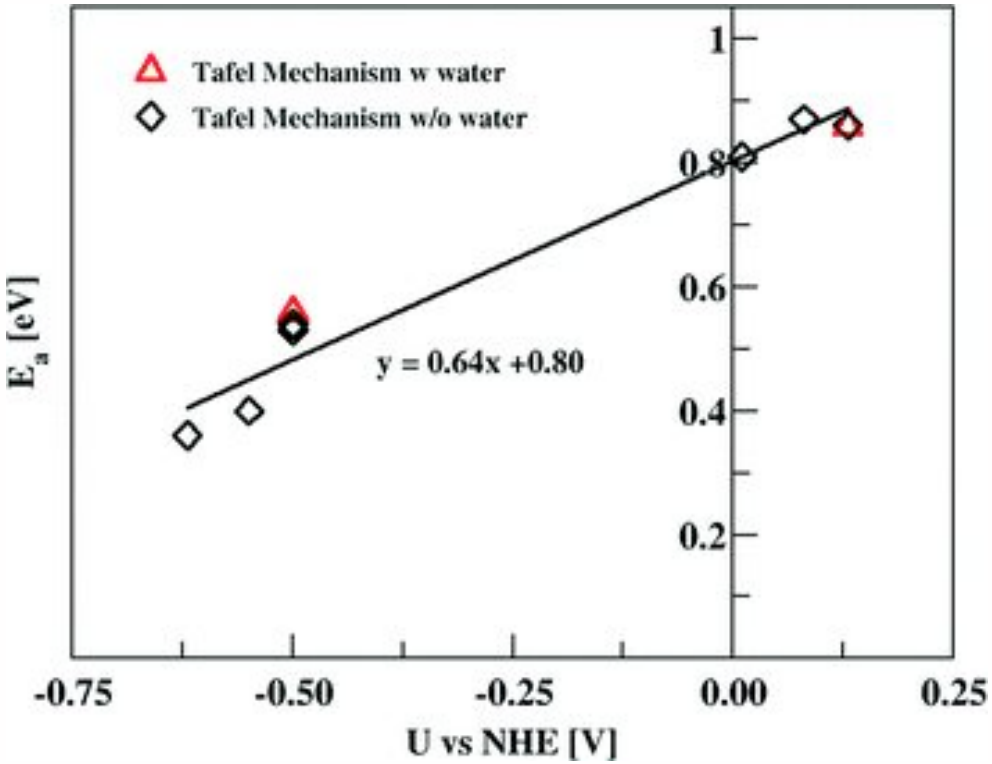
E. Skúlason, J. Rossmeisl, J.K. Nørskov *et al.*, PCCP **9**, 3241 (2007).

Tafel mechanism: $2\mathrm{H_{ad}} \rightarrow \mathrm{H_2}$

Reaction path



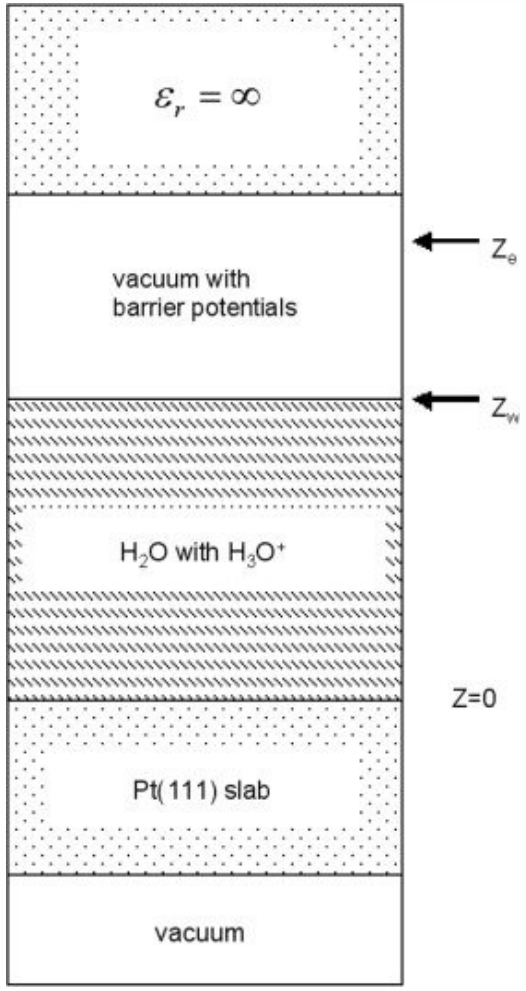
Activation energy

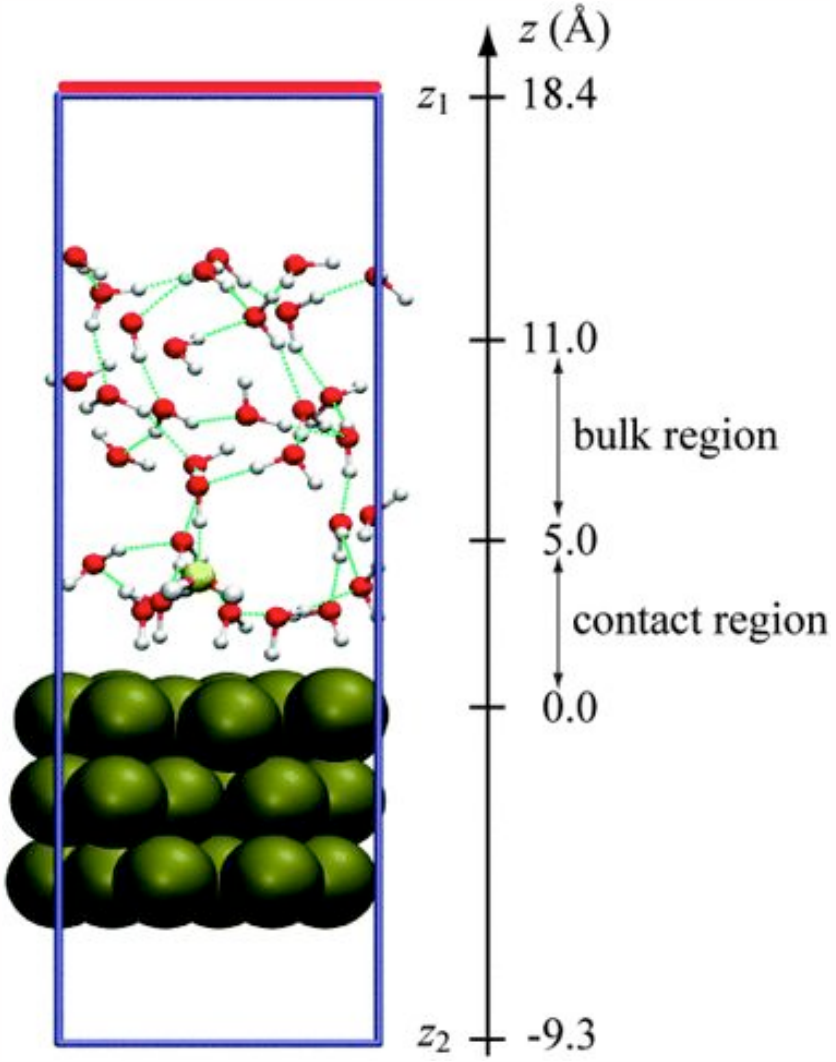


Note: in addition to electrode potential U, pH is also an independent variable

Non-periodic slab calculations with effective screening medium

O.Sugino *et al.*, Surf. Sci. **601**, 5237 (2007); PCCP **10**, 3609 (2008).

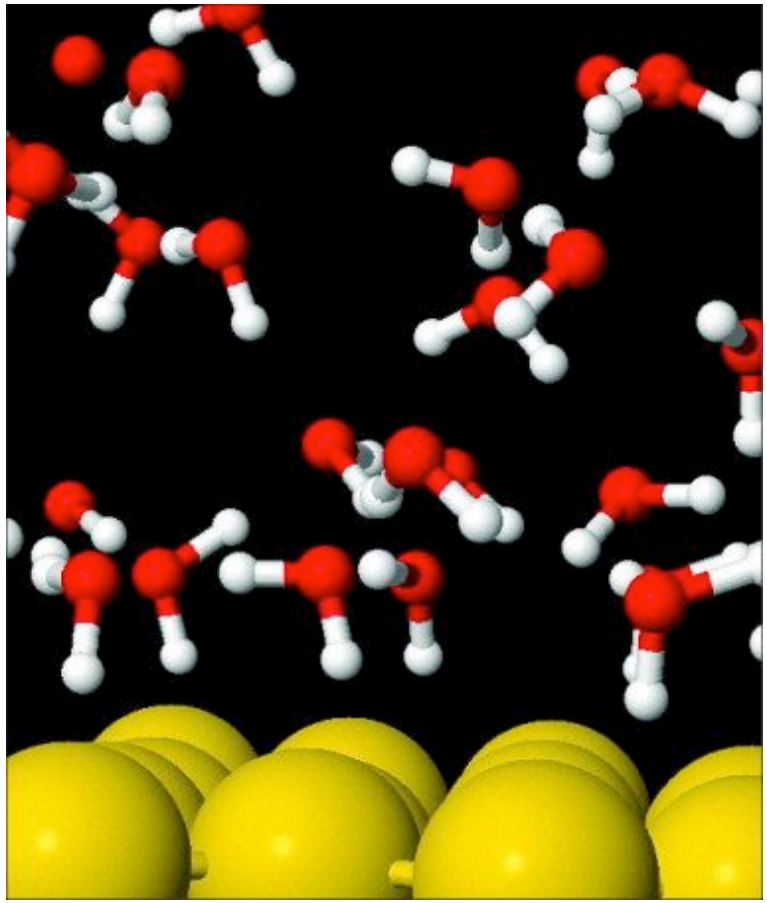




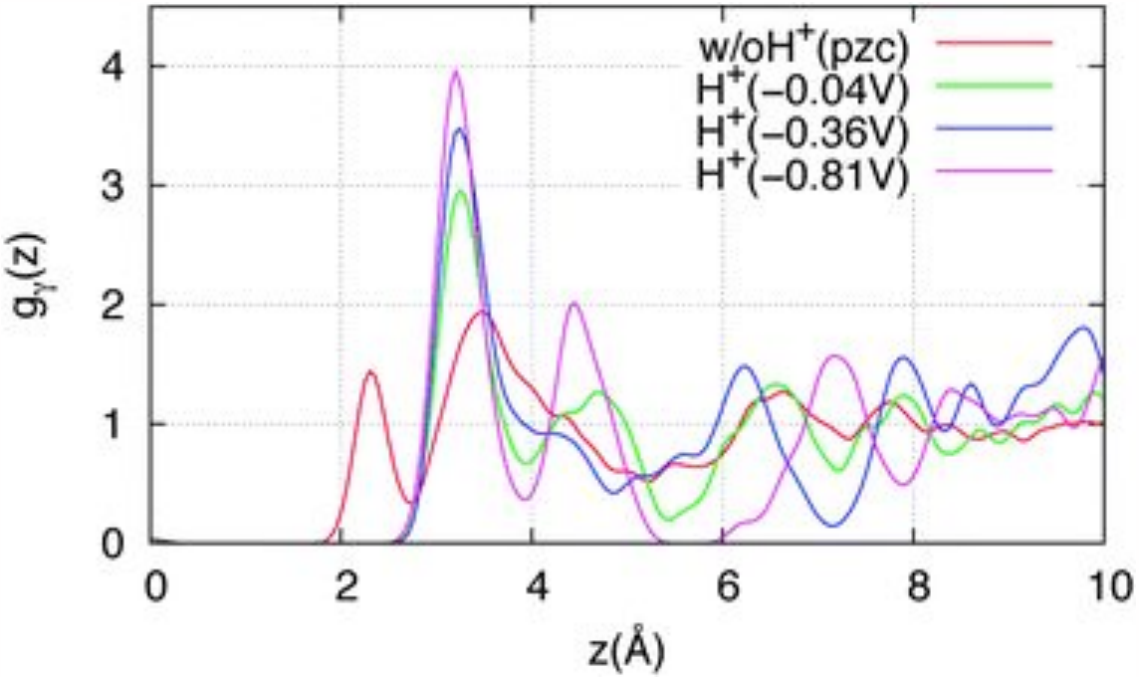
Structure of the water/platinum interface

M. Otani, O.Sugino *et al.*, PCCP **10**, 3609 (2008).

AIMD snapshot



Structure: distribution function



No bias: O-down structure stable

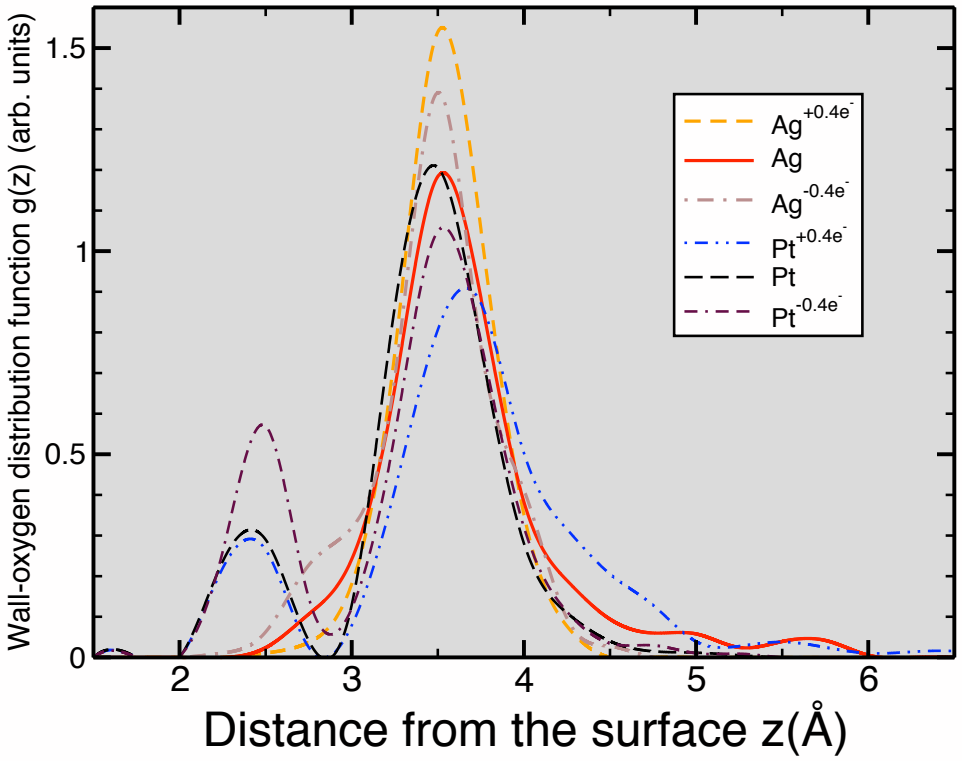
Negative bias: H-down structure stable, moderate increase of the density of contact layer with increasing bias

Charge-induced effects

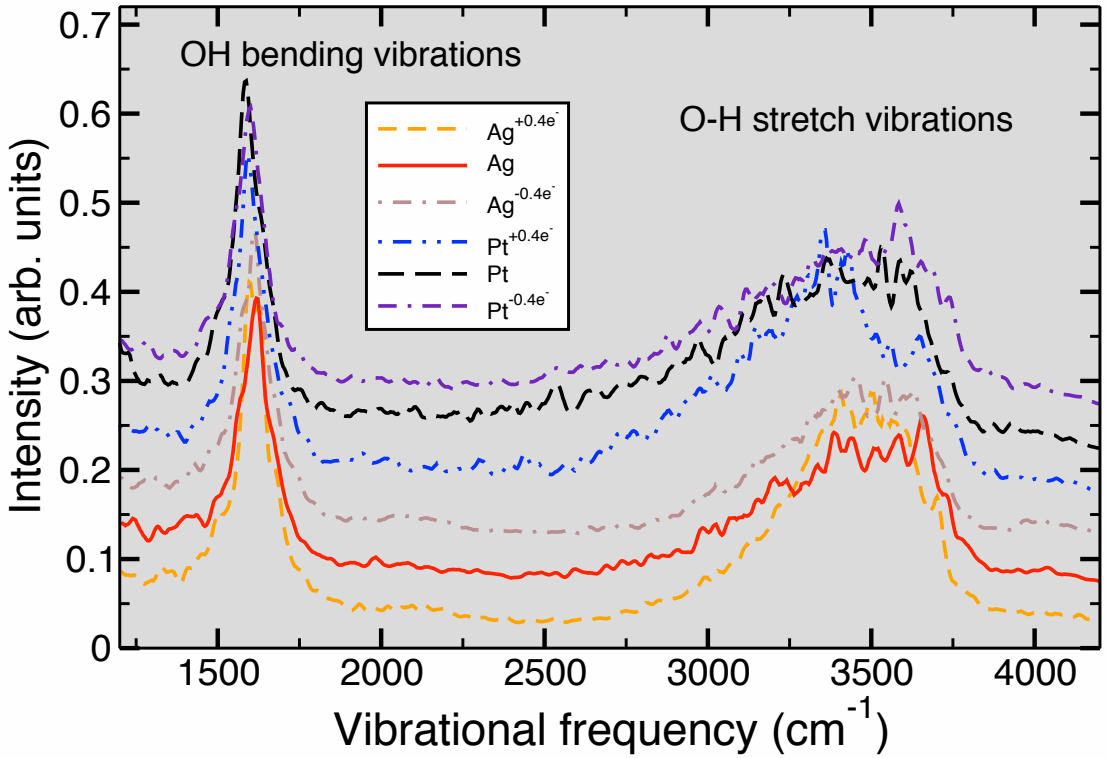
Sebastian Schnur and Axel Groß, New J. Phys **11**, 125003 (2009).

Countercharge modeled by uniform charge background

O-wall distribution function



Vibrational spectra



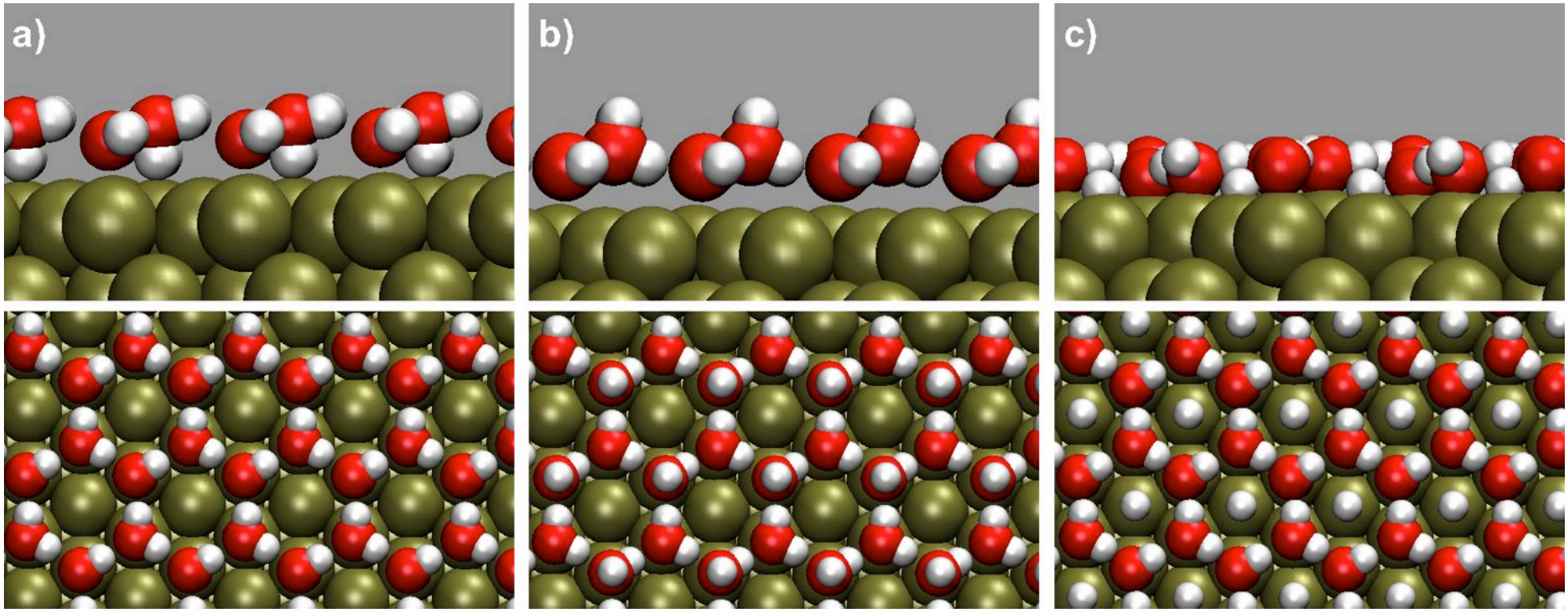
Problem: artefacts due to uniform charge background

Towards an atomistic first-principles modeling of electrochemical electrode-electrolyte interfaces

Stepwise approach to model electrochemical electrode/electrolyte interfaces by considering systems with increasing complexity

Water bilayer structures

H-down, H-up and half-dissociated water bilayer structures

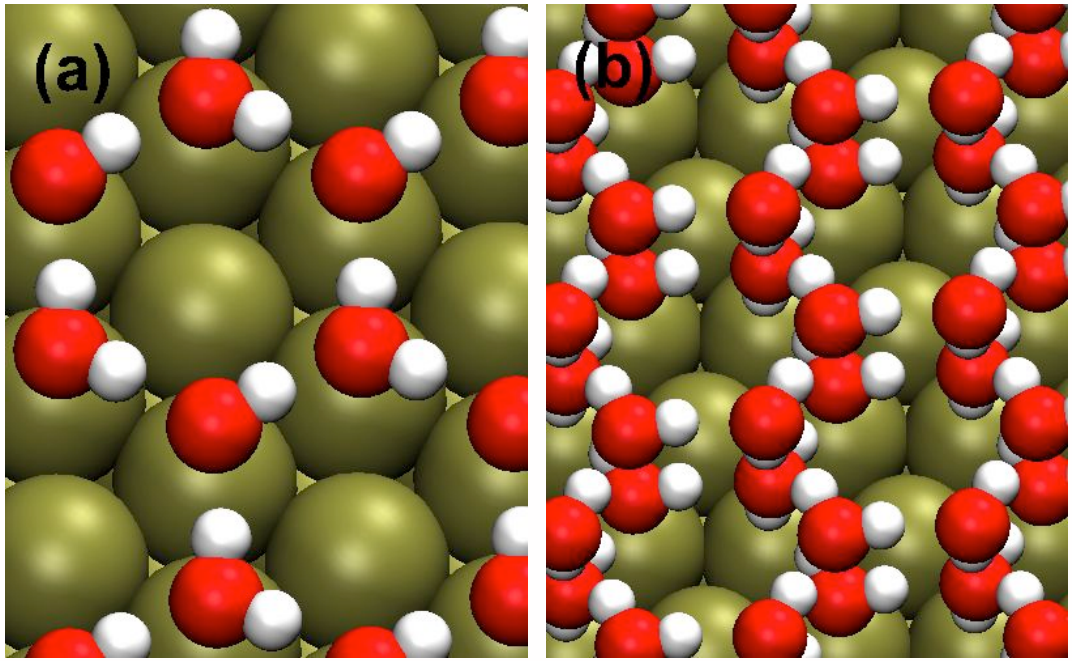


H-down and H-up layer often energetically almost degenerate

Pt(111) covered by water bilayers

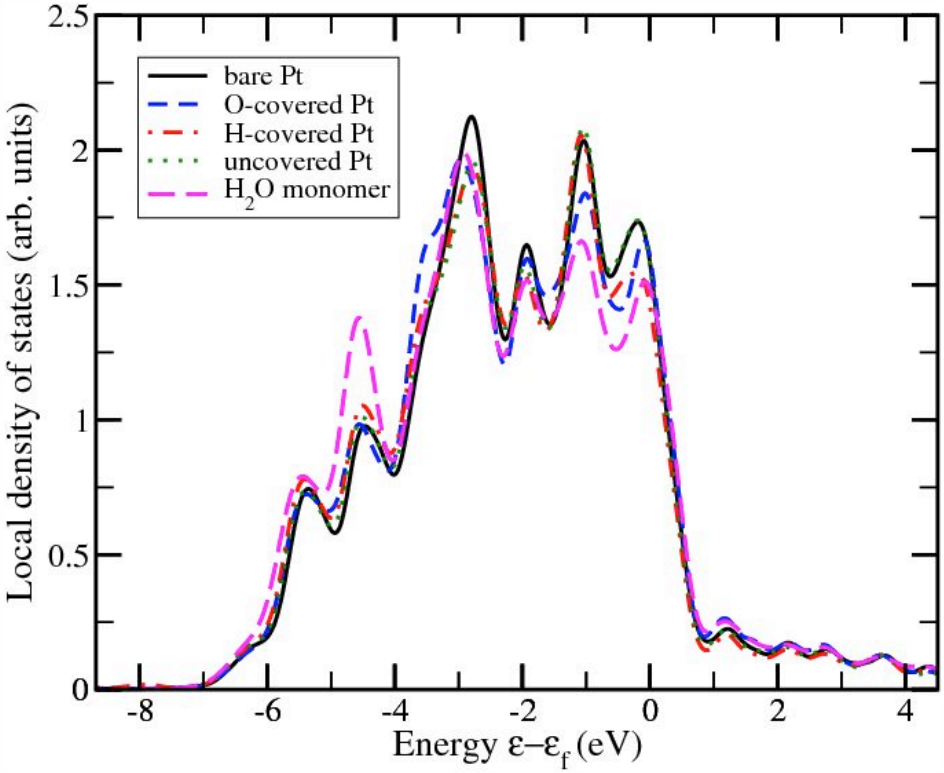
Yoshihiro Gohda, Sebastian Schnur, Axel Groß, Faraday Diss. **140**, 233 (2009).

Geometric structure



Structure of a water bilayer and double bilayer on Pt(111)

Electronic structure

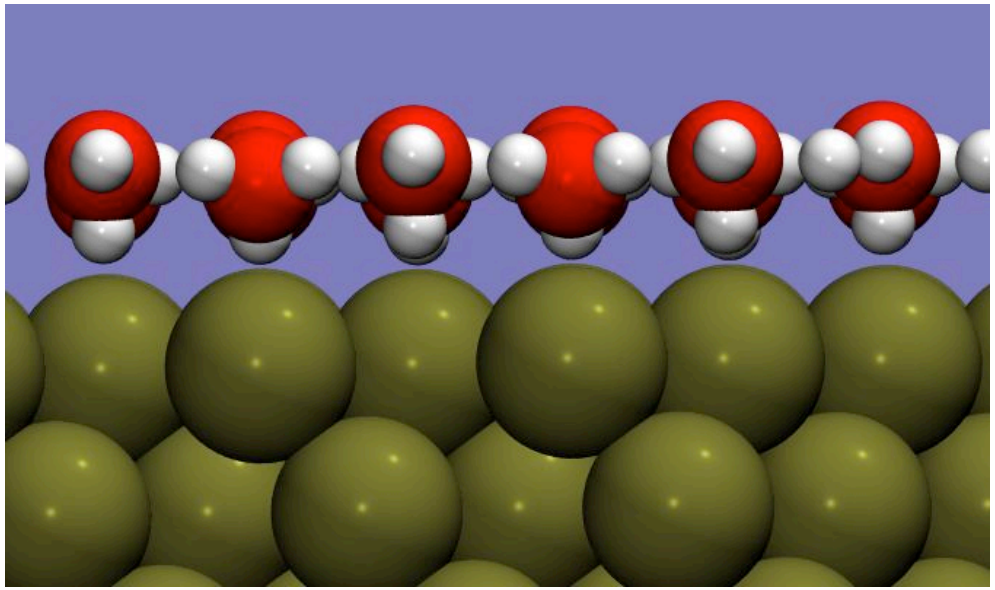


Pt(111) local d-band density of states

Electronic structure of Pt(111) hardly changed by the adsorption of water

Water-induced work function change

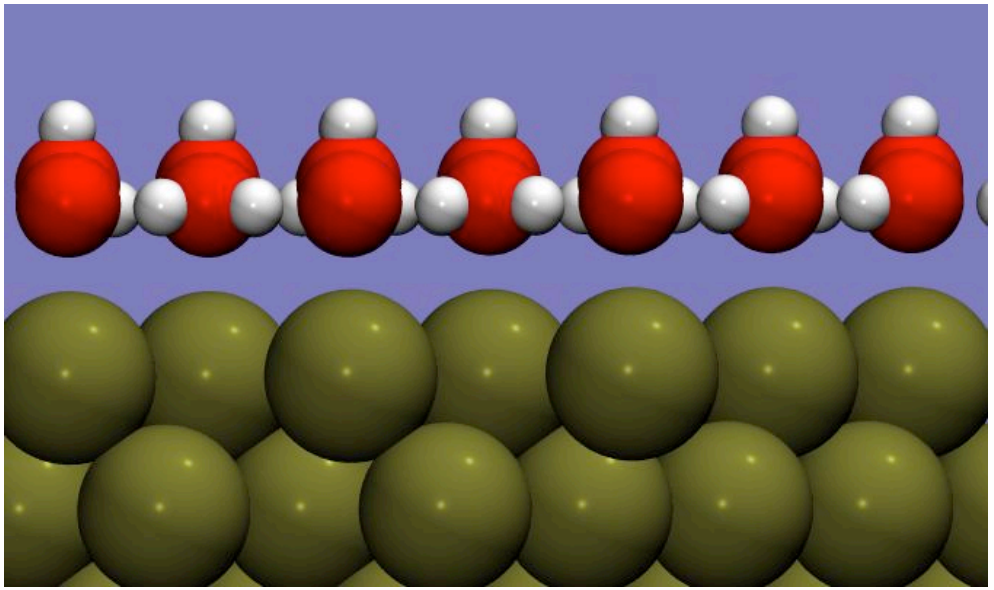
H-down water bilayer



$E_{ads}^{H_2O}$ = -487 meV

$\Delta\Phi$ = -0.23 eV

H-up water bilayer



$E_{ads}^{H_2O}$ = -450 meV

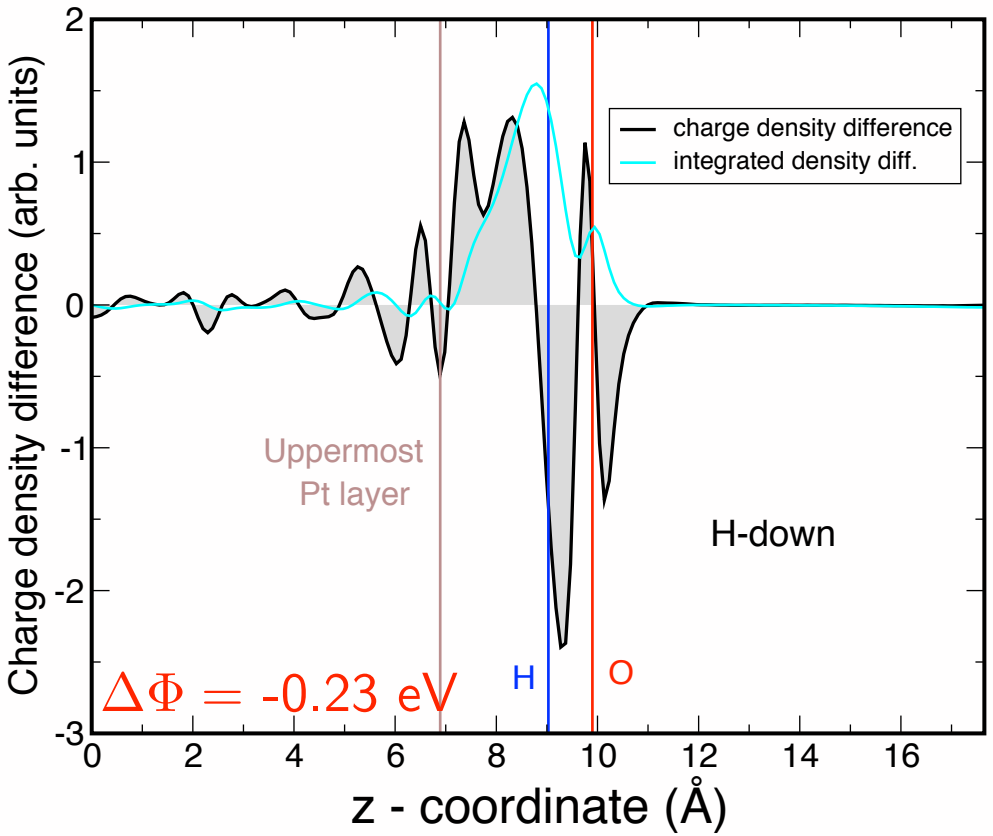
$\Delta\Phi$ = -2.27 eV

2 eV difference in work function change between H-down and H-up bilayers, but both bilayers lead to a reduction in the work function of Pt(111), although dipole moments of the two free bilayers have opposite signs

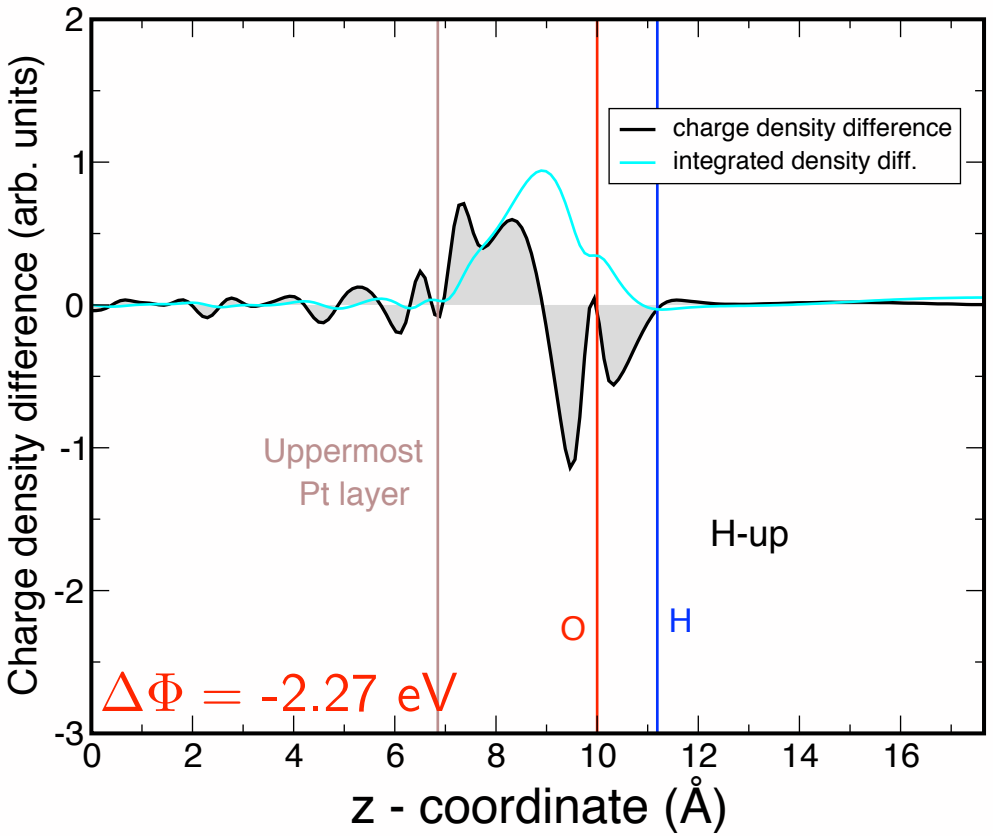
Water-induced charge density difference plots

$$\Delta\rho = \rho(\mathrm{H_2O/Pt(111)}) - (\rho(\mathrm{H_2O}) + \rho(\mathrm{Pt(111)}))$$

H-down water bilayer



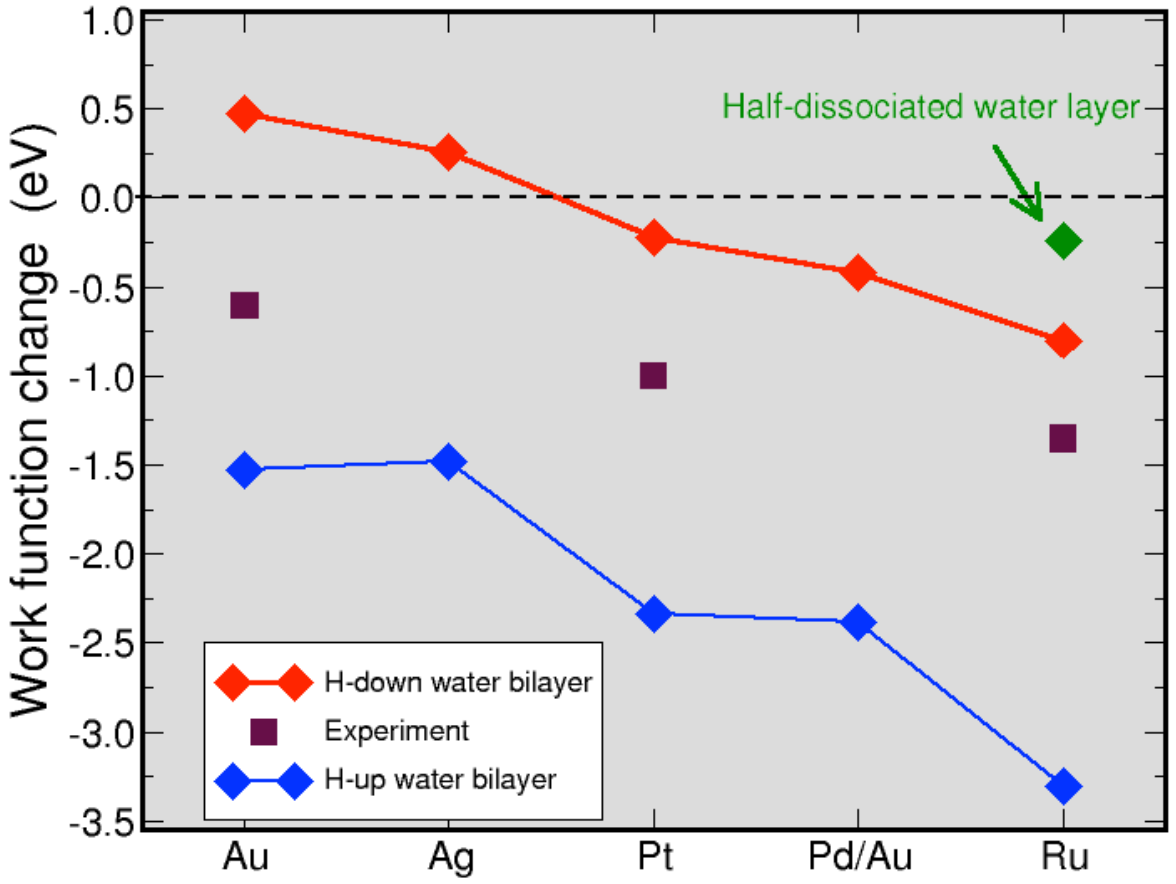
H-up water bilayer



Charge accumulation between water bilayer and Pt(111)

Chemical trends in water-induced work function change

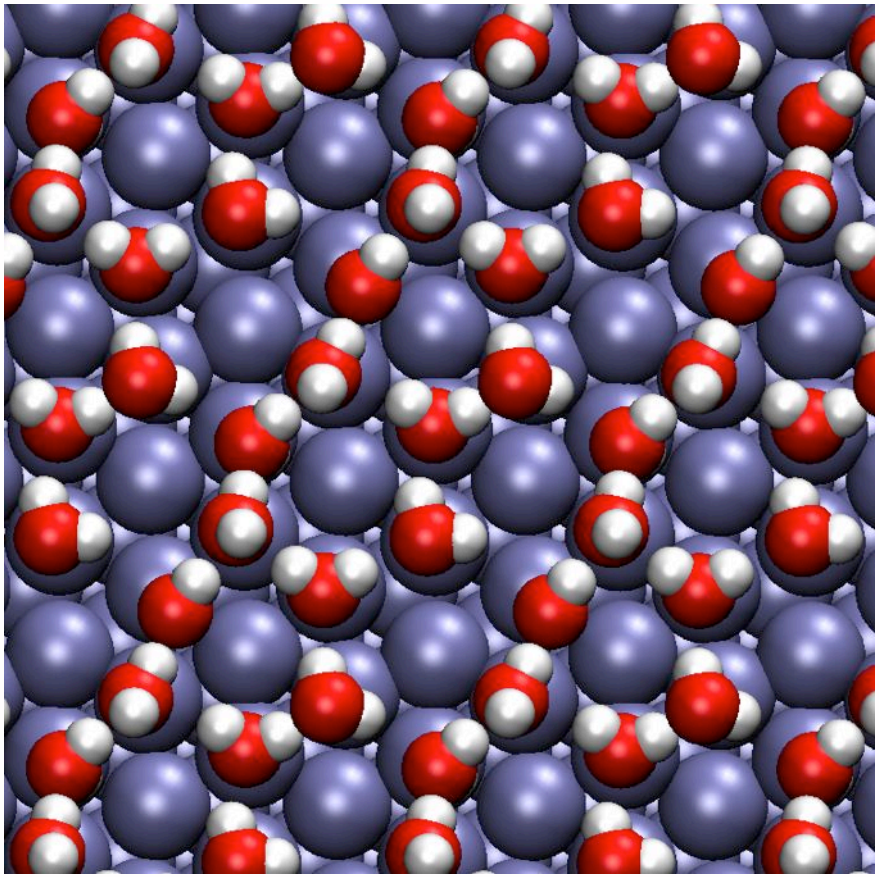
Sebastian Schnur and Axel Groß, New J. Phys **11**, 125003 (2009).



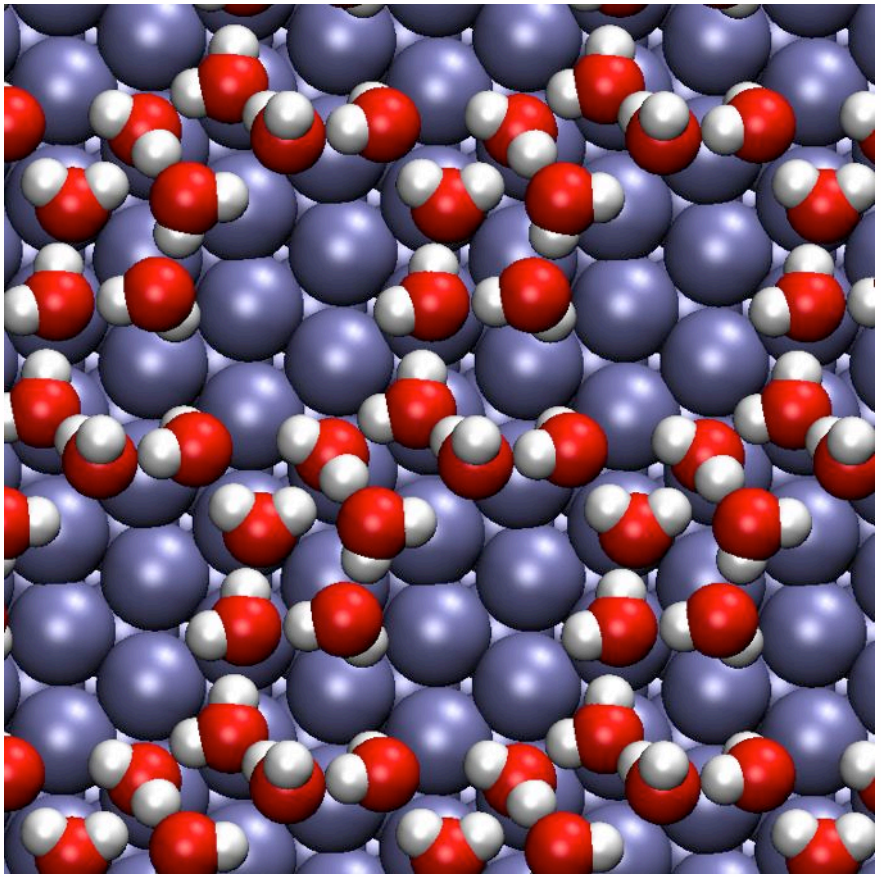
Overall work function change correlates with water-metal interaction strength, but surprisingly large discrepancies to experimental results

Ab initio molecular dynamics simulations (AIMD) of water on Ag(111)

T = 1.5 ps



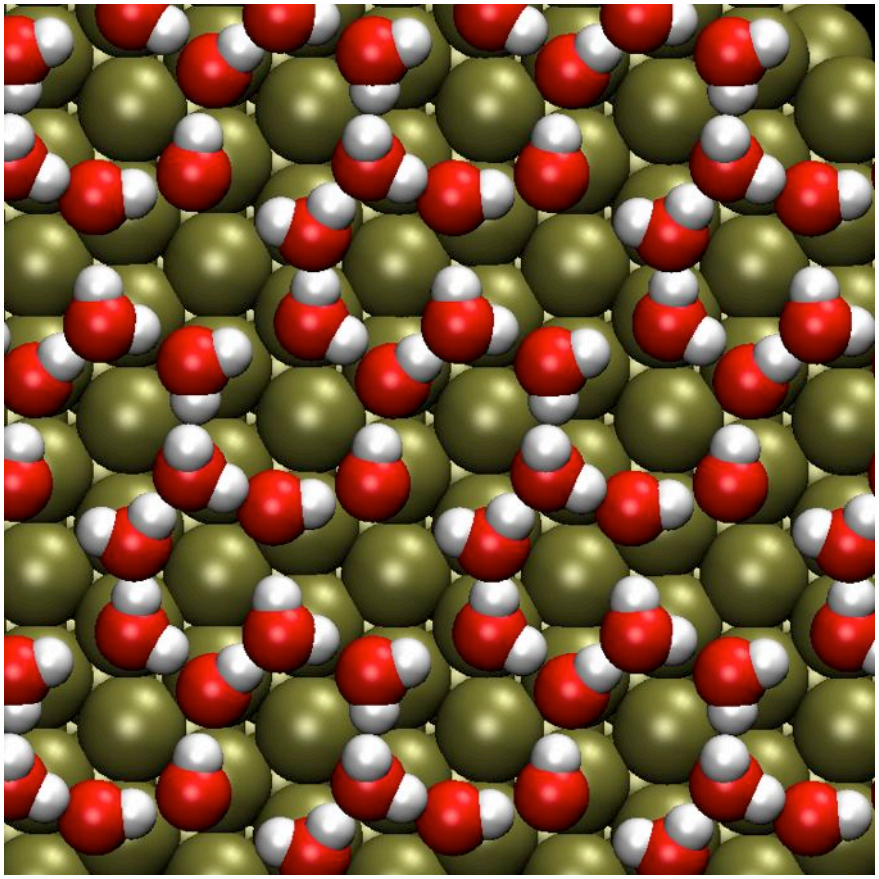
T = 7.5 ps



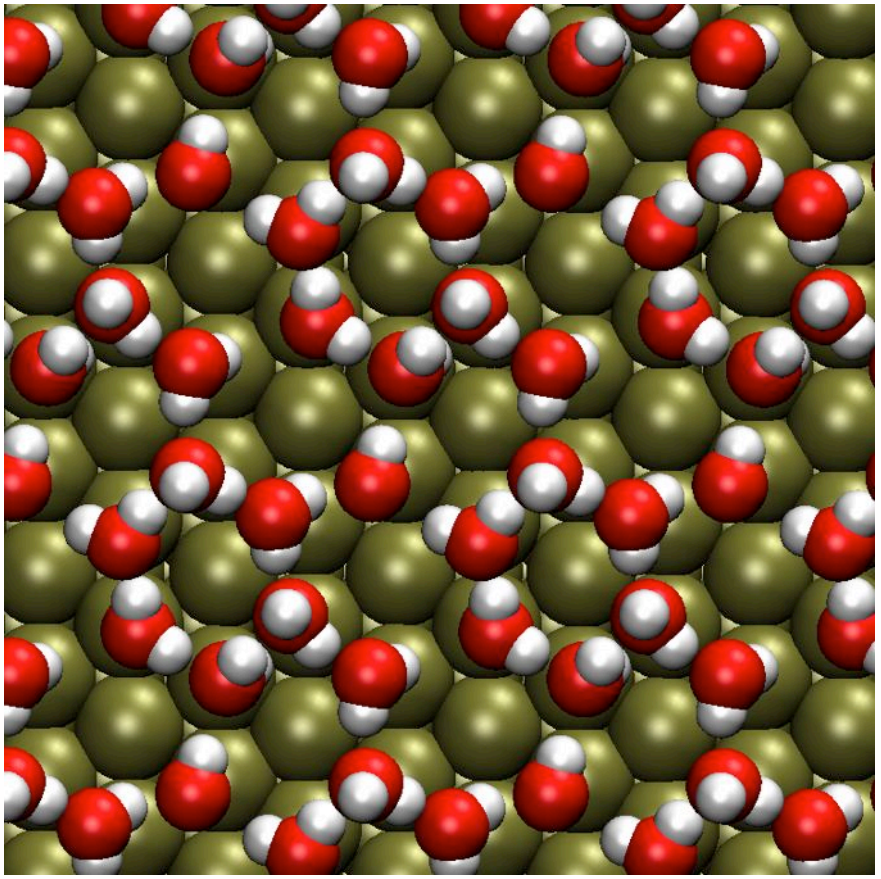
Hexagonal ice-like structure at room temperature broken up after 7.5 ps

AIMD simulations of water on Pt(111)

T = 1.5 ps



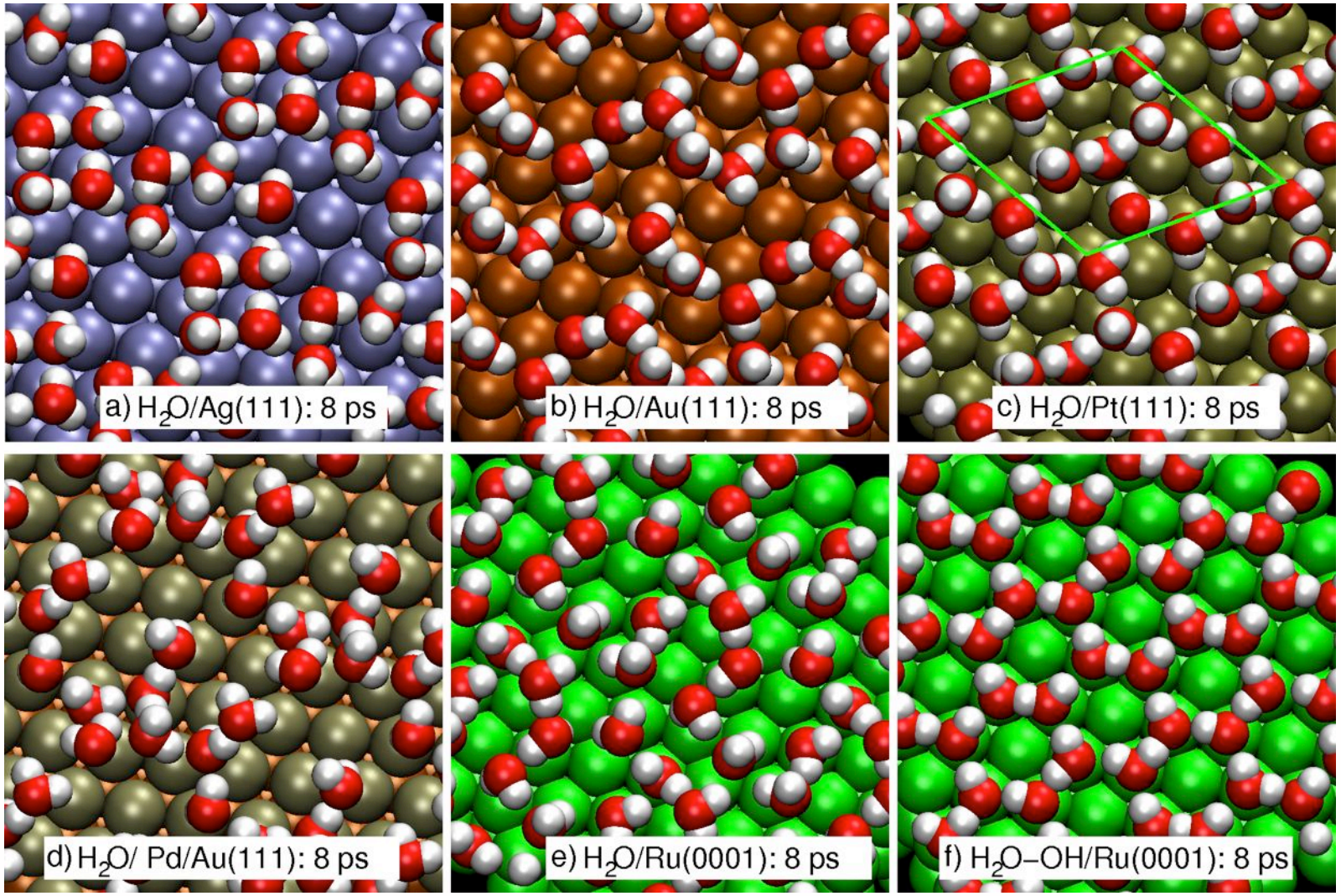
T = 7.5 ps



Hexagonal ice-like structure at room temperature still intact after 7.5 ps

AIMD simulations of water layers at room temperature

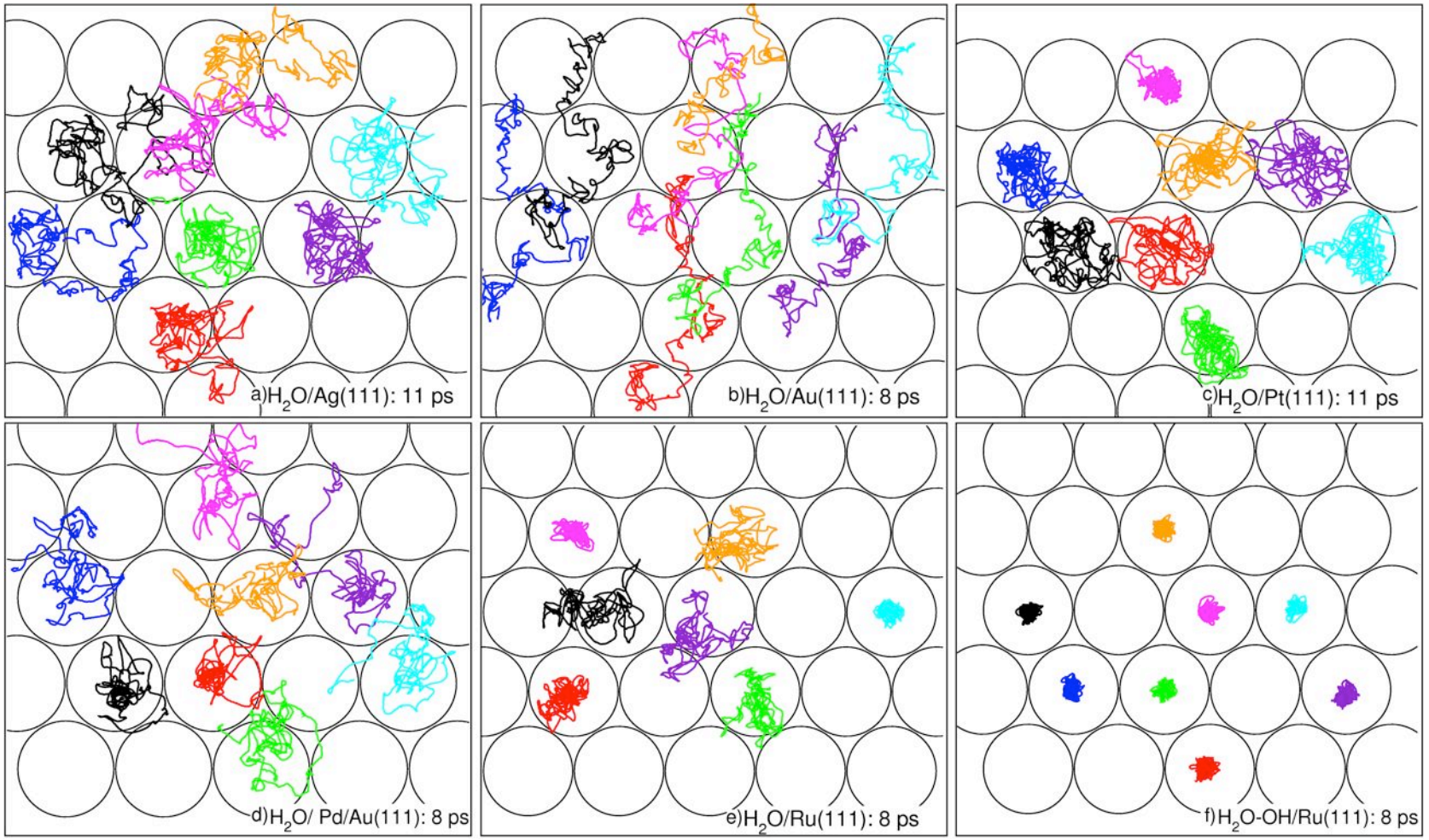
Sebastian Schnur and Axel Groß, New J. Phys **11**, 125003 (2009).



On noble metal surfaces (Au, Ag), ice-like bilayer structure not stable at room temperature.

Water trajectories at room temperature

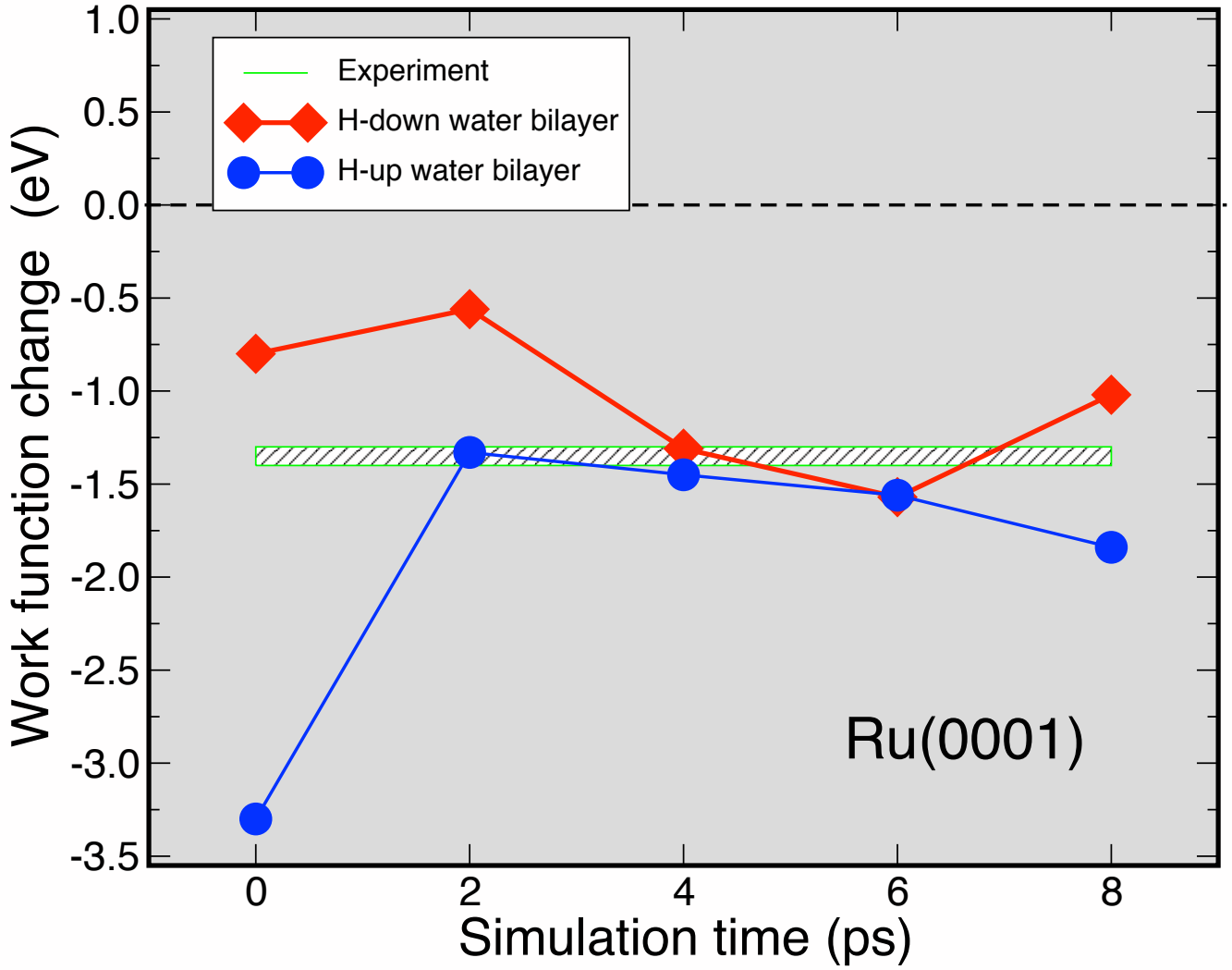
Sebastian Schnur and Axel Groß, New J. Phys **11**, 125003 (2009).



On noble metal surfaces (Au, Ag), ice-like bilayer structure not stable at room temperature.

Time evolution of work function change

Sebastian Schnur and Axel Groß, New J. Phys **11**, 125003 (2009).

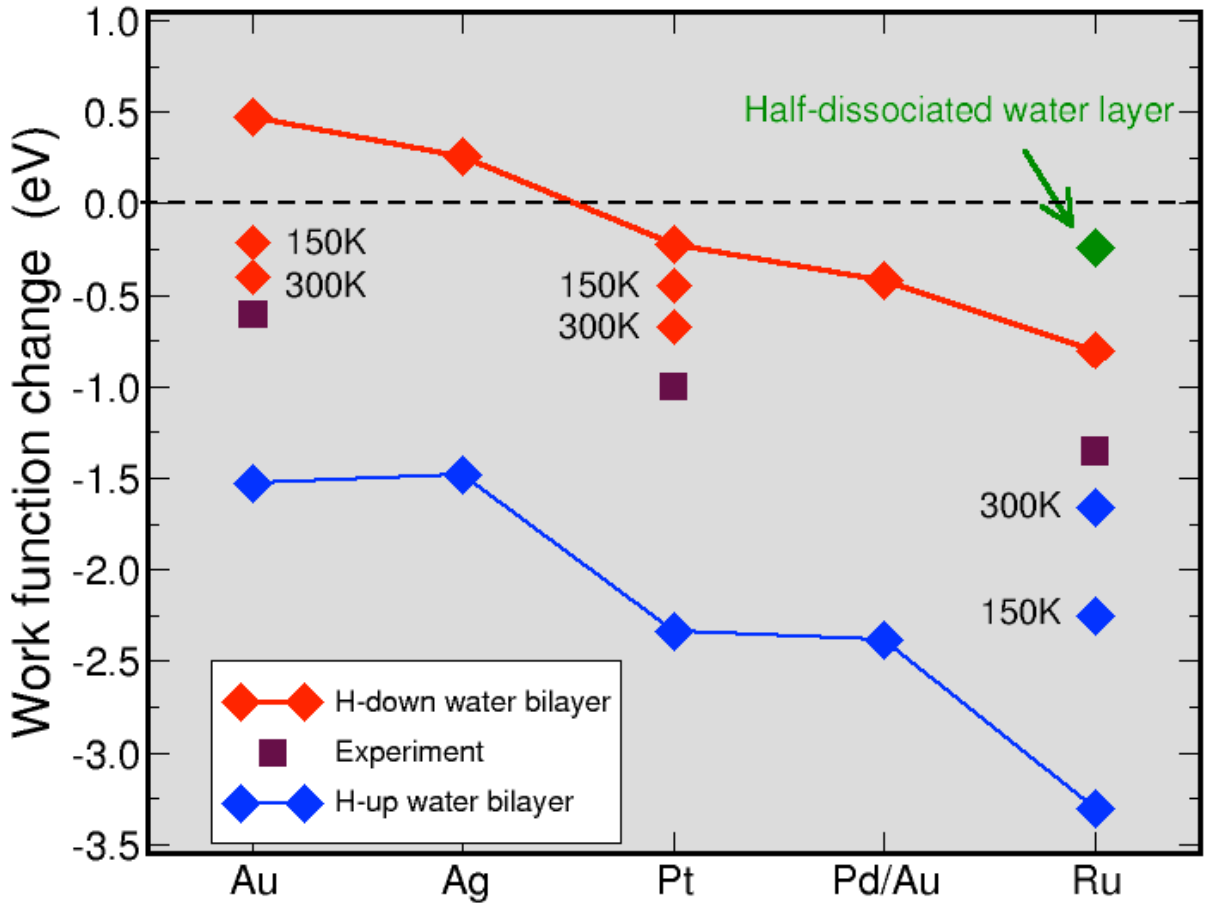


Thermal averaging ⇒ good agreement between theory and experiment

Exp.: W. Hoffmann and C. Benndorf, Surf. Sci. **377-379**, 681 (1997); Y. Lilach *et al.*, J. Phys. Chem. B **105**, 2736 (2001).

Work function change for thermalized water layers

Sebastian Schnur and Axel Groß, Catal. Today **165**, 129-137 (2011).



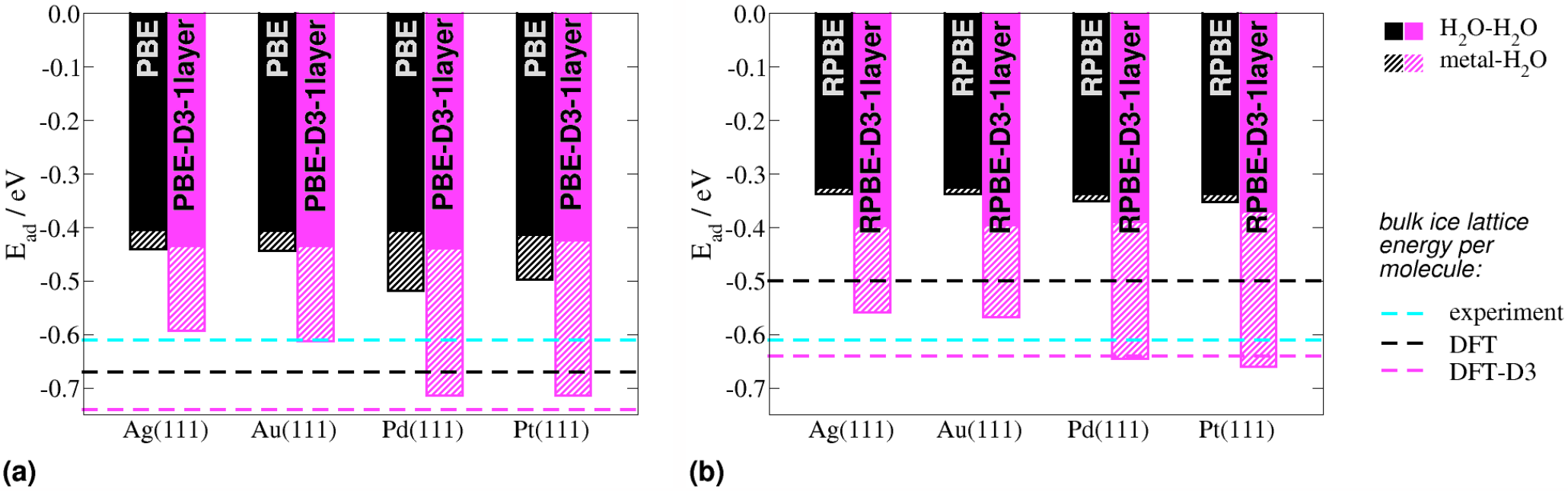
Averaging done over 2 ps ab initio molecular dynamics runs

Wetting of water on (111) metal electrodes

Katrin Tonigold and Axel Groß, J. Comput. Chem. **33**, 695-701 (2012) .

Water is known to wet Pd(111) and Pt(111), but not Ag(111) nor Au(111)

PBE **vs.** **RPBE**

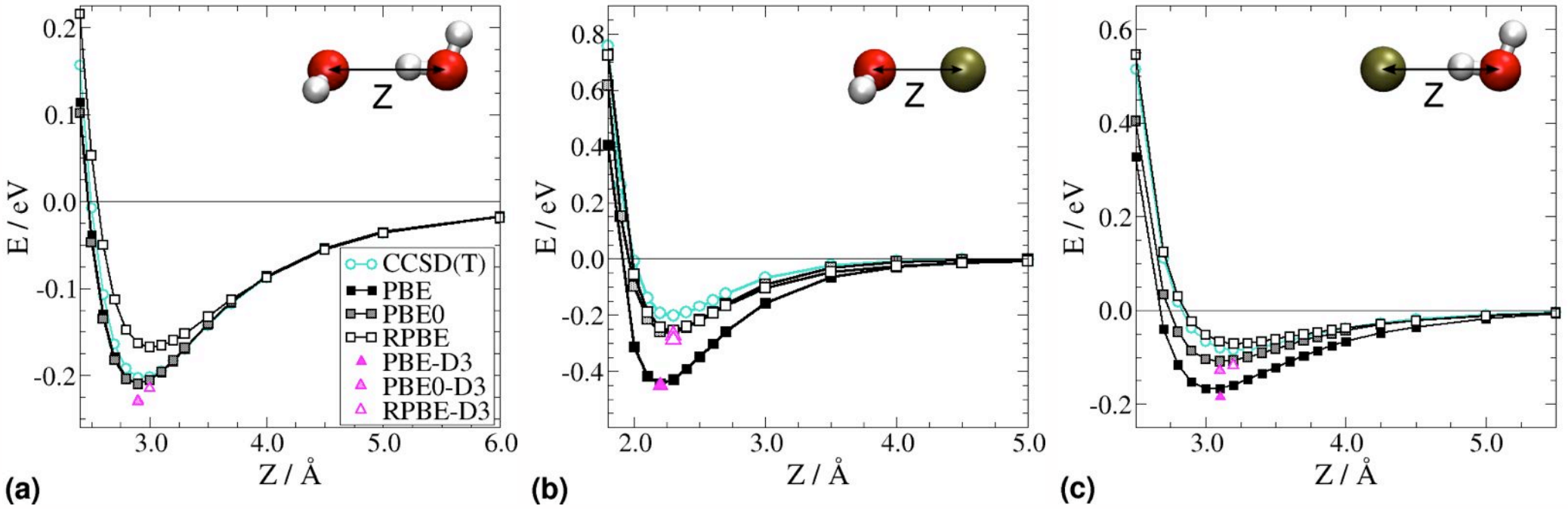


RPBE-D3 correctly reproduces wetting behavior

PBE vs. RPBE with and without dispersion corrections

Katrin Tonigold and Axel Groß, J. Comput. Chem. **33**, 695-701 (2012) .

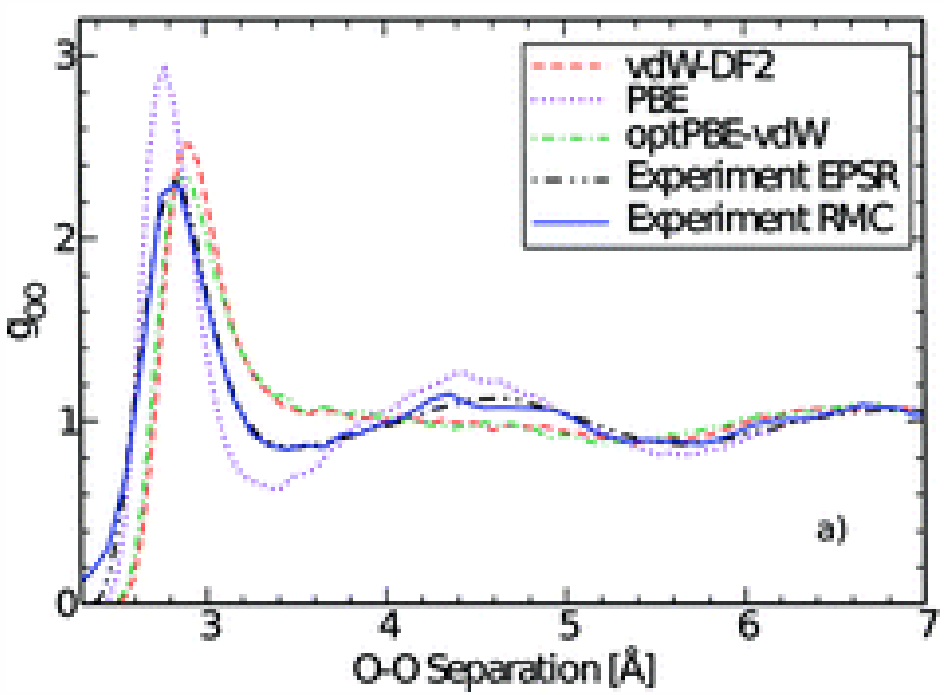
Comparison DFT-D calculations with *ab initio* results

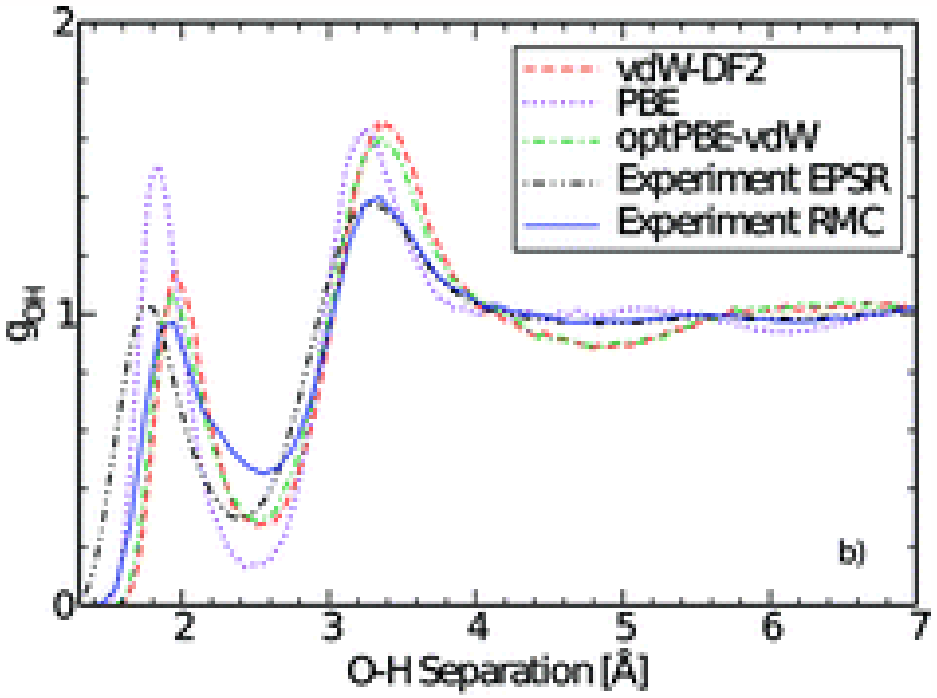


RPBE-D3 also improves description of water-Au and water-water interaction

PBE Water

Problem: PBE water over-structured





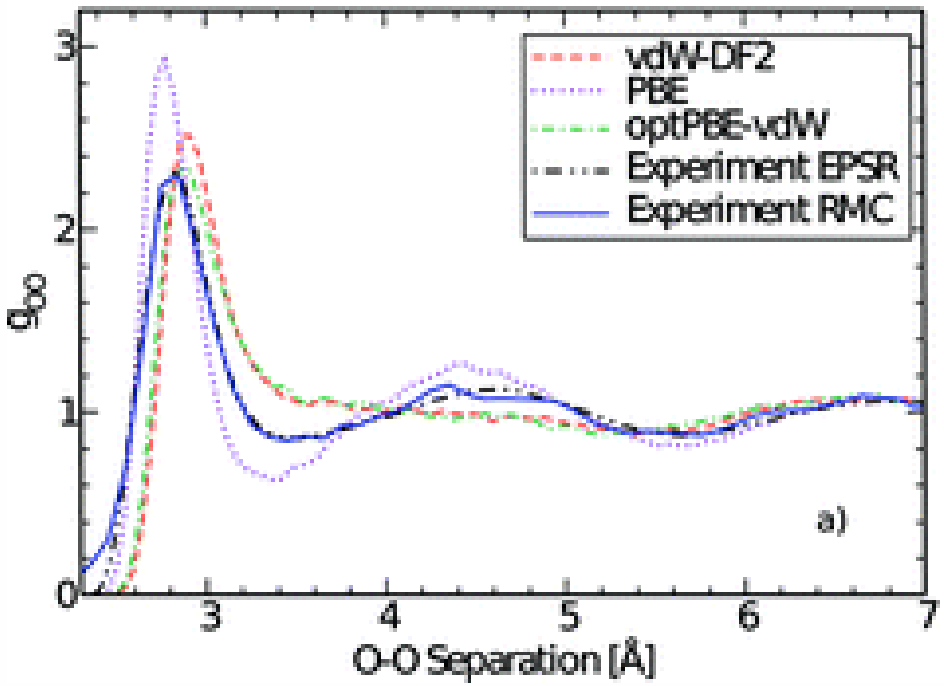
Møgelhøj, Kelkkanen, Wikfeldt, Schiøtz, Mortensen, Pettersson, Lundqvist, Jacobsen, Nilsson, Nørskov, JPCB **115**, 14149 (2011) .

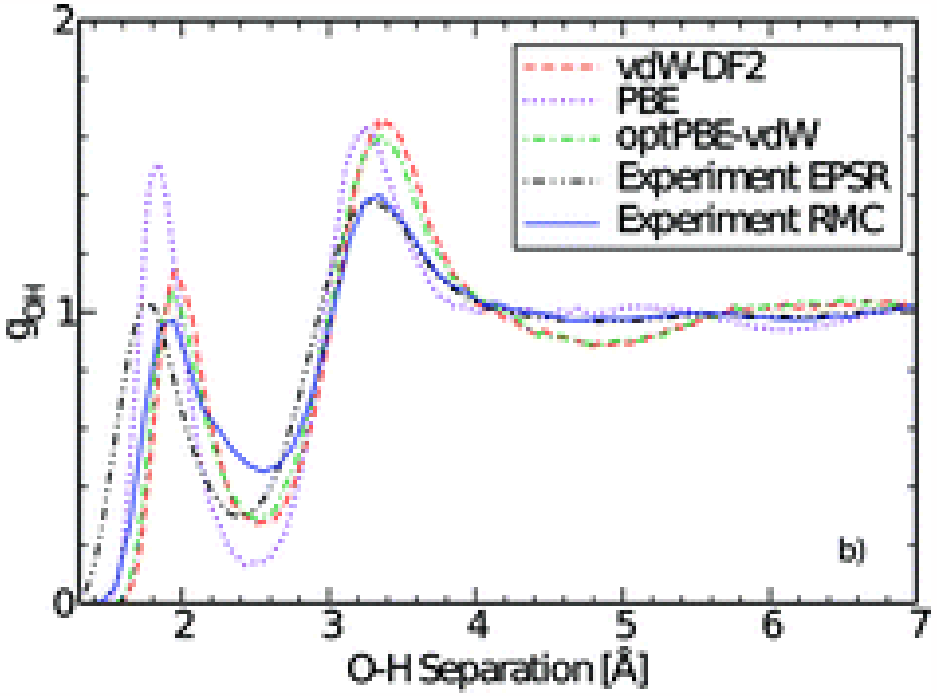
see also J. VandeVondele *et al.*, JCP **122** 014515 (2005); L.-M. Liu, M. Krack, A. Michaelides, JCP **130** 234702 (2009).

Idea: replace directional hydrogen bonding (overestimated by PBE) by non-directional van der Waals interaction

PBE Water

Problem: PBE water over-structured



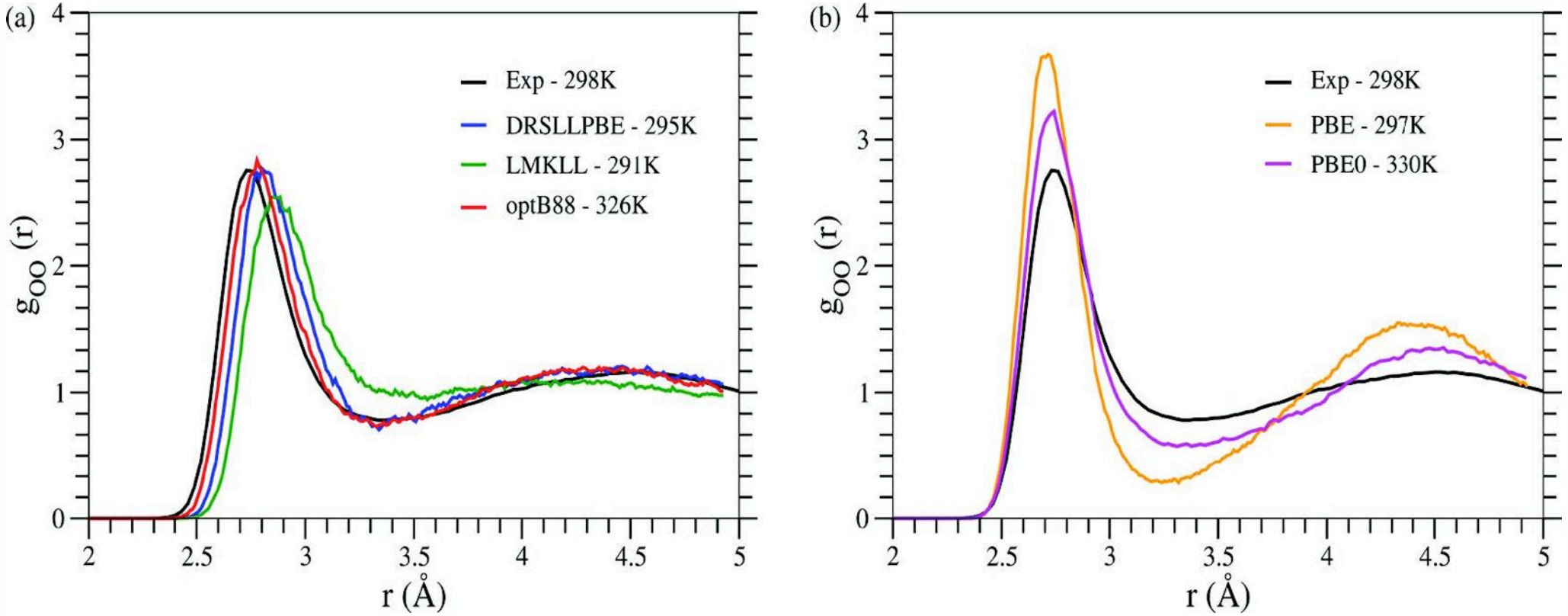


Møgelhøj, Kelkkanen, Wikfeldt, Schiøtz, Mortensen, Pettersson, Lundqvist, Jacobsen, Nilsson, Nørskov, JPCB **115**, 14149 (2011) .
see also J. VandeVondele *et al.*, JCP **122** 014515 (2005); L.-M. Liu, M. Krack, A. Michaelides, JCP **130** 234702 (2009).

Idea: replace directional hydrogen bonding (overestimated by PBE) by non-directional van der Waals interaction

optPBE-vdW functional not satisfactory

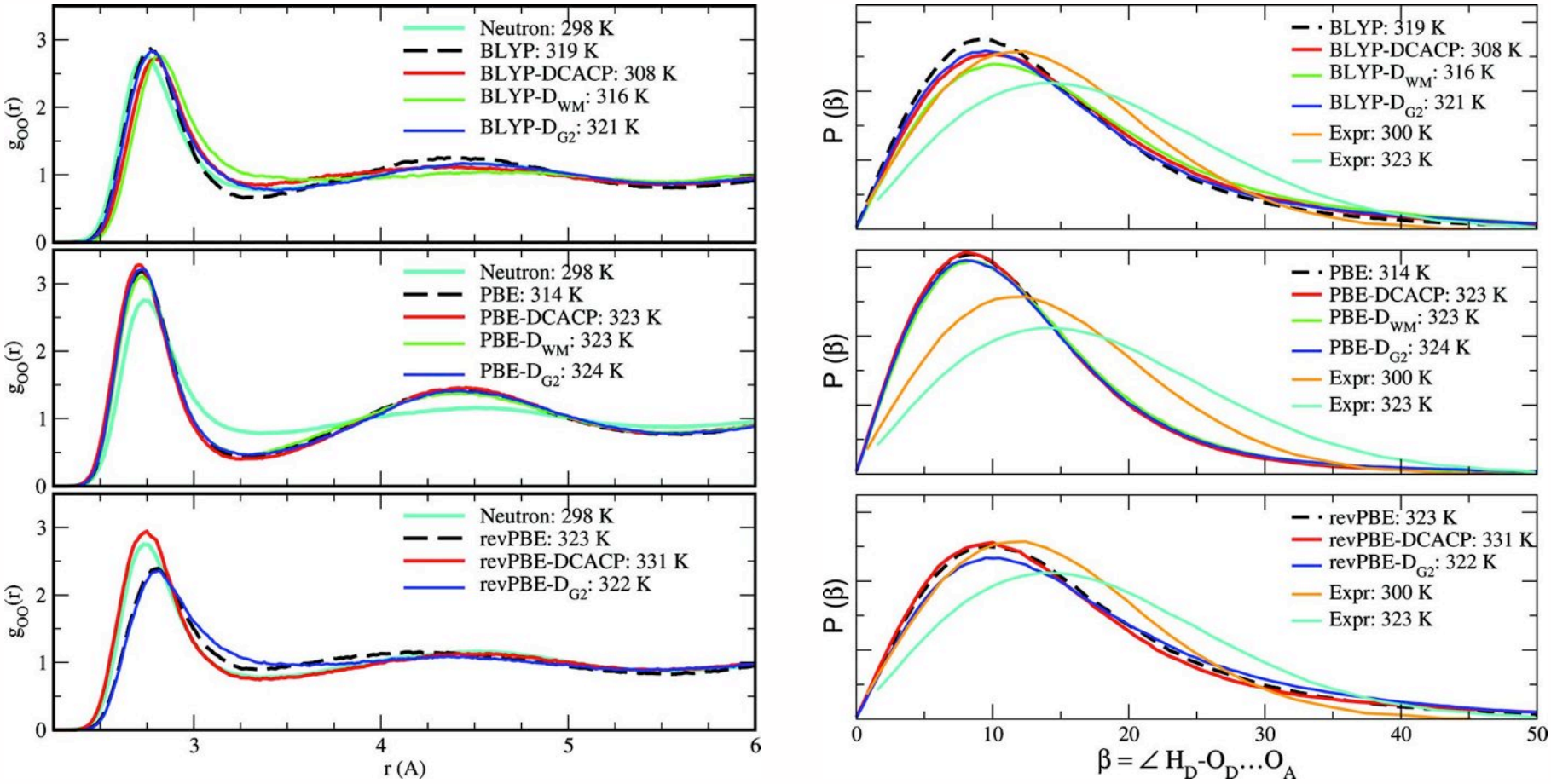
optB88-vdW Water



C. Zhang, J. Wu, G. Galli, and F. Gygi, J. Chem. Theory Comput. **7**, 3054 (2011) .

optB88-vdW functional satisfactory

Further vdW waters



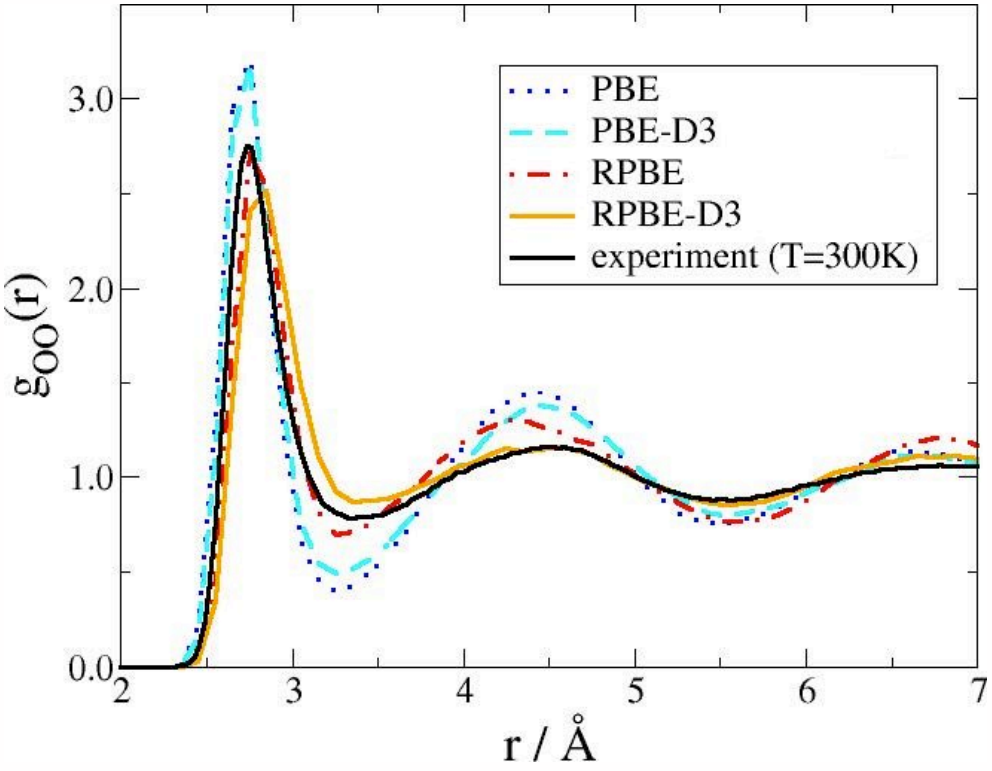
I-C. Lin, A.P. Seitsonen, I. Tavernelli, and U. Rothlisberger, J. Chem. Theory Comput. **8**, 3902 (2012) .

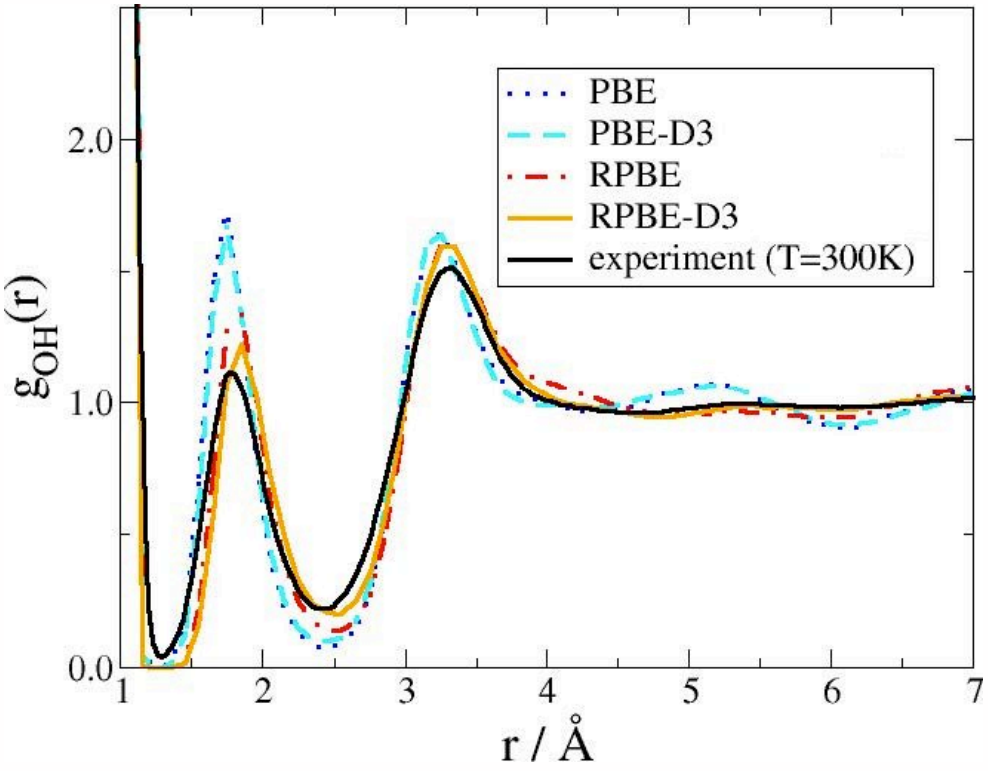
Broad variety of results for different vdW functionals

PBE vs. RPBE water with and without dispersion corrections

Katrin Tonigold and Axel Groß, in preparation.

Preliminary results



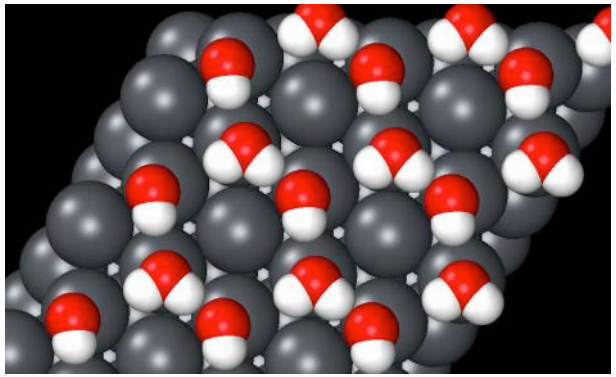


RPBE-D3 exhibits acceptable properties and describe metal electrodes well

Water on other metal substrates: H_2O/Pb

Xiaohang Lin and Axel Groß, in preparation

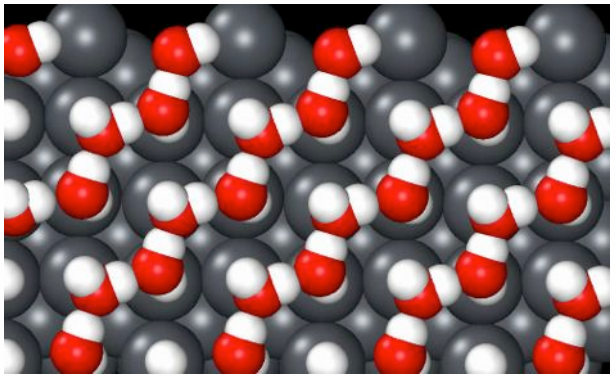
H_2O/Pb(111)



$\Theta_{H_2O} = 2/3$

$E_{ads} = -0.254\,\text{eV}$

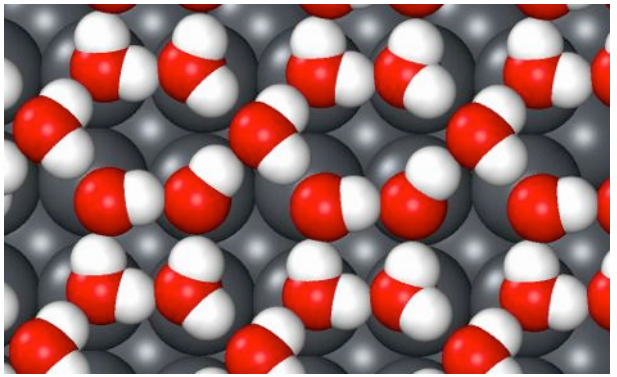
H_2O/Pb(100)



$\Theta_{H_2O} = 1$

$E_{ads} = -0.359\,\text{eV}$

H_2O/Pb(100)



$\Theta_{H_2O} = 5/4$

$E_{ads} = -0.396\,\text{eV}$

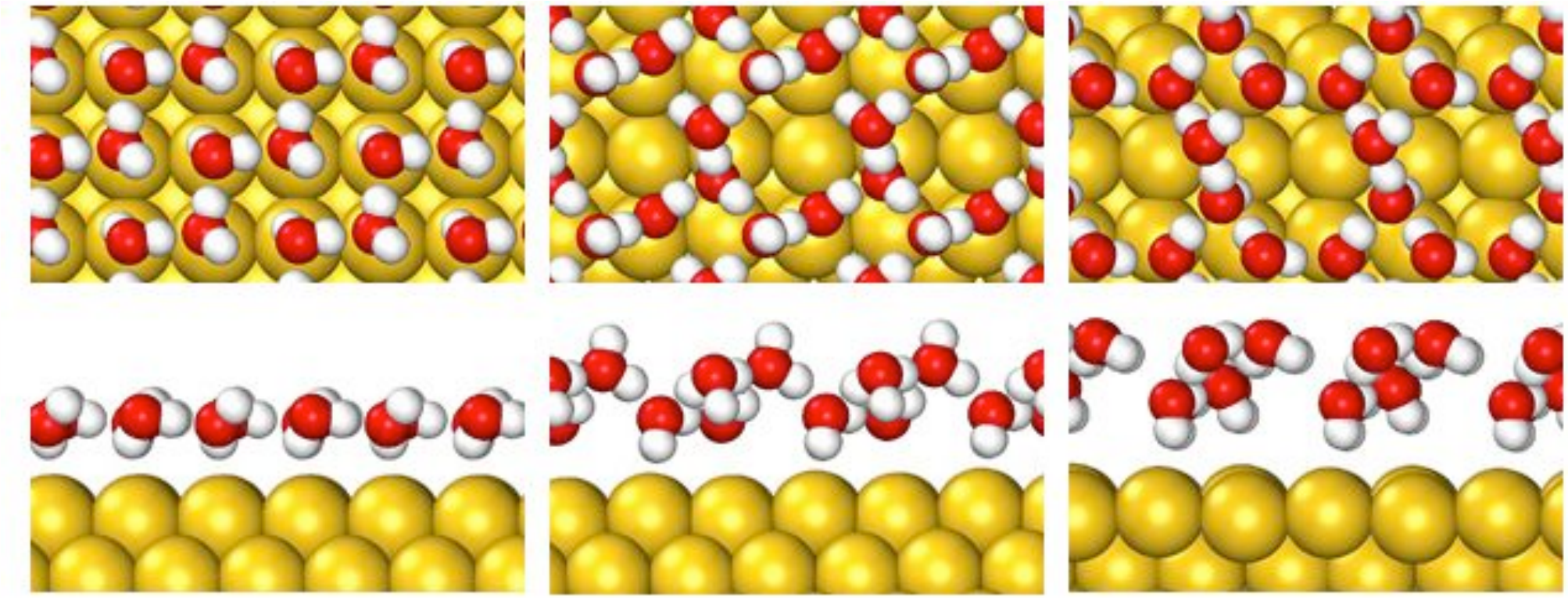
Nearest-neighbor distance in Pb ($d_{NN} = 3.50\,\text{Å}$) much larger than for late transition metals

$\Rightarrow$ Nominally higher water coverages per substrate atom stable

Water on other metal substrates: H_2O/Au(100)

Xiaohang Lin and Axel Groß, Surf. Sci. **606**, 886-891 (2012).

$T = 0\,\mathrm{K}$ $T = 140\,\mathrm{K}$ $T = 300\,\mathrm{K}$

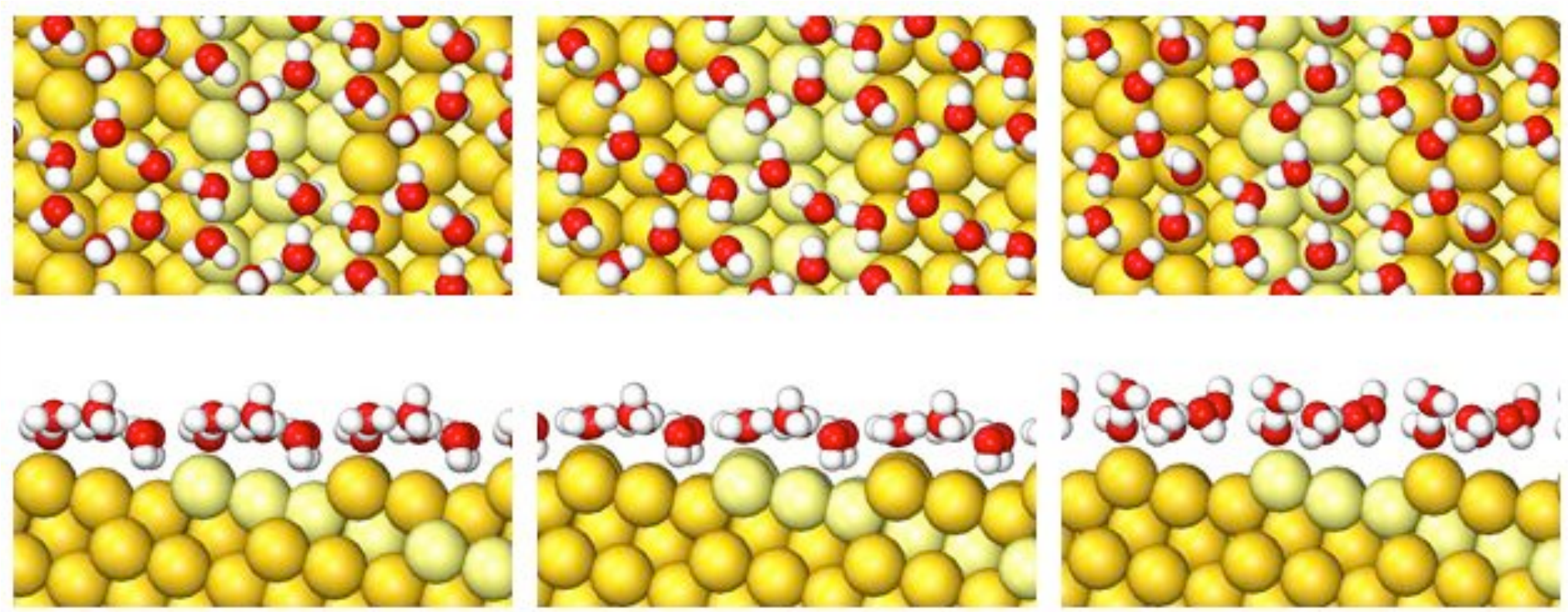


No hexagonal water arrangement on Au(100), 2×2 unit cell most probably insufficient

Water on other metal substrates: H_2O/Au(511)

Xiaohang Lin and Axel Groß, Surf. Sci. **606**, 886-891 (2012).

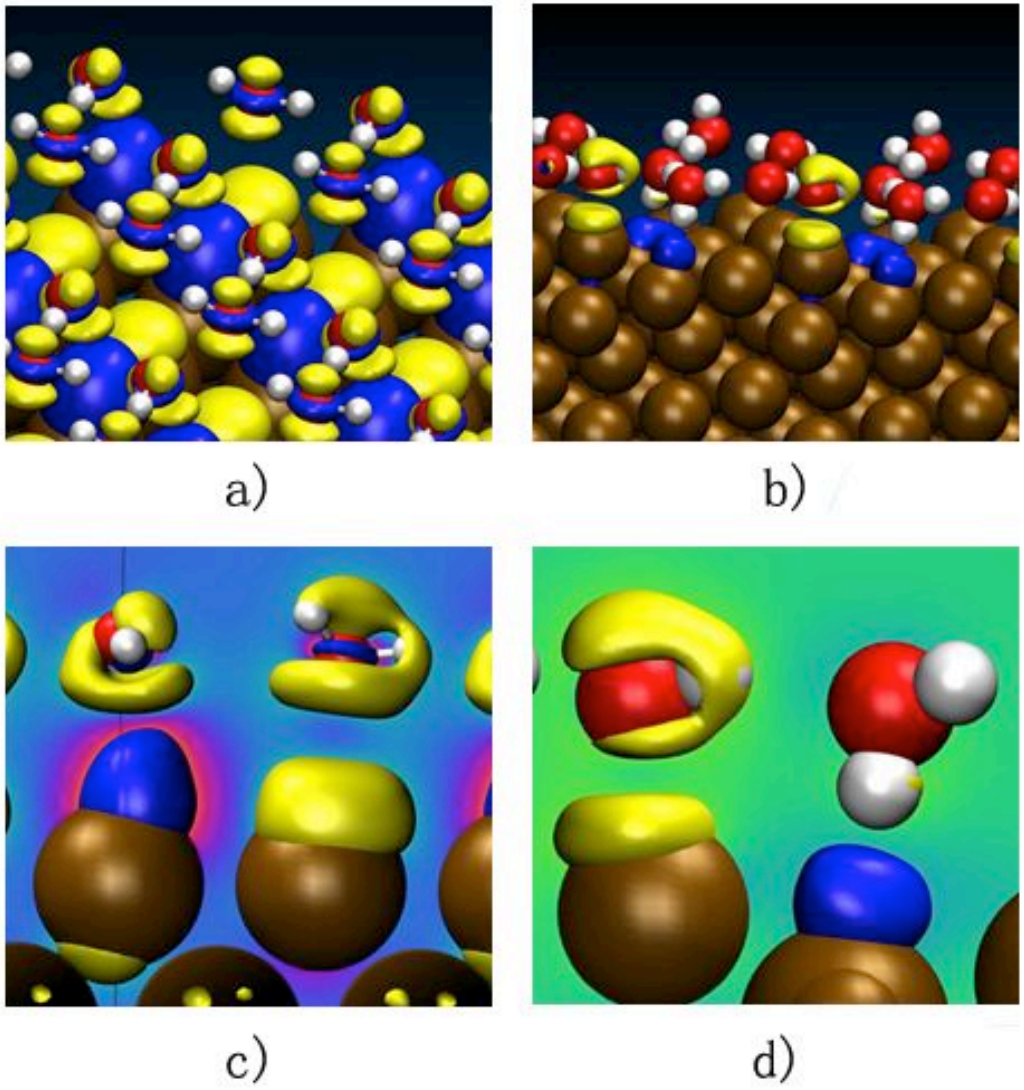
$T = 0\,\mathrm{K}$ $T = 140\,\mathrm{K}$ $T = 300\,\mathrm{K}$



Stable water structure on Au(511), consisting of hexagons, rectangles and octagons

Charge density differences H_2O on Au(100) and Au(511)

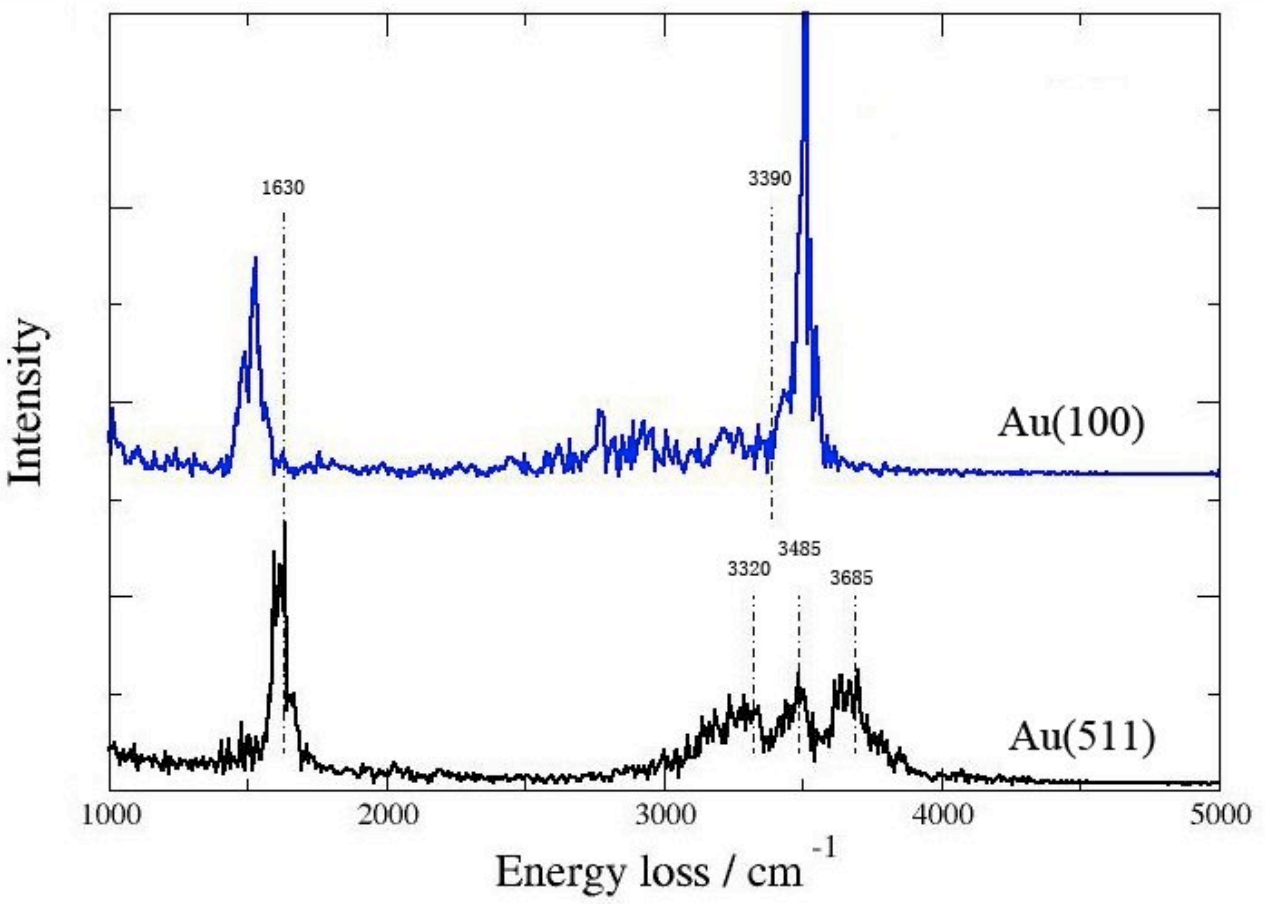
Au(100) Au(511)



Au(511): water structure pinned at Au step edge atoms

Vibrational spectra of water on Au(100) and Au(511)

Vibrational spectra derived from AIMD runs at $T = 140\,\mathrm{K}$

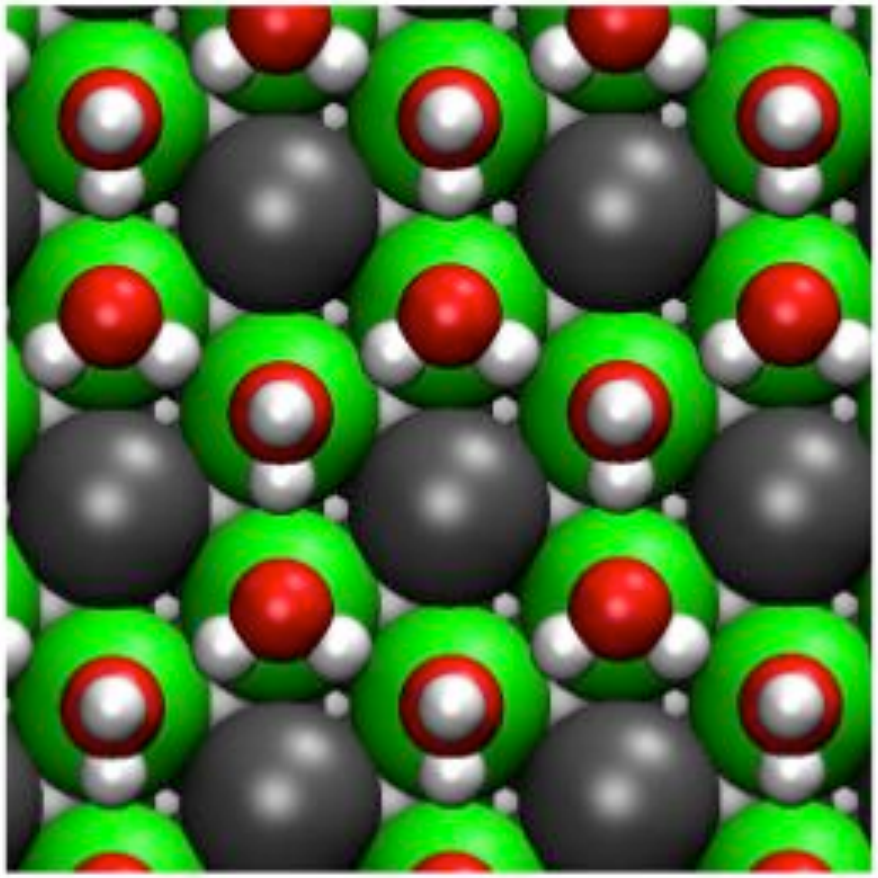


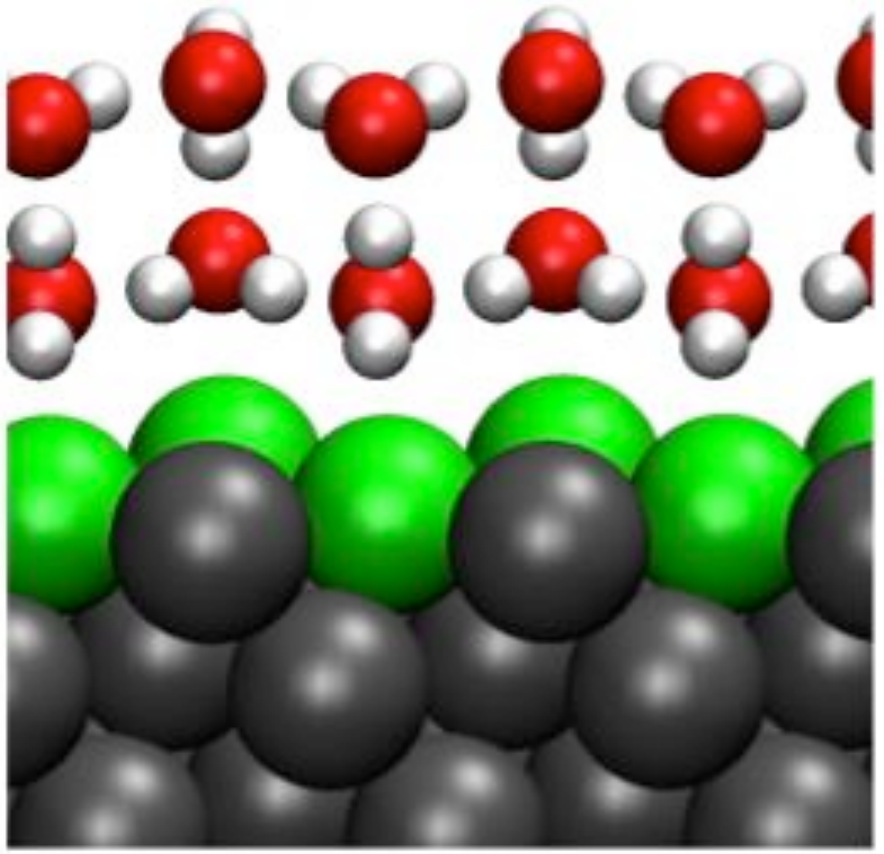
Dashed lines: experimentally observed peaks (H. Ibach, Surf. Sci. **604**, 377 (2010).)

Mode-splitting in O-H stretch region around $3500\,\mathrm{cm}^{-1}$ on Au(511) reflects coexistence of hydrogen-bonded and non-hydrogen bonded H atoms in water layer

Water on PtRu bimetallic substrates

Julia M. Fischer and Axel Groß, in preparation



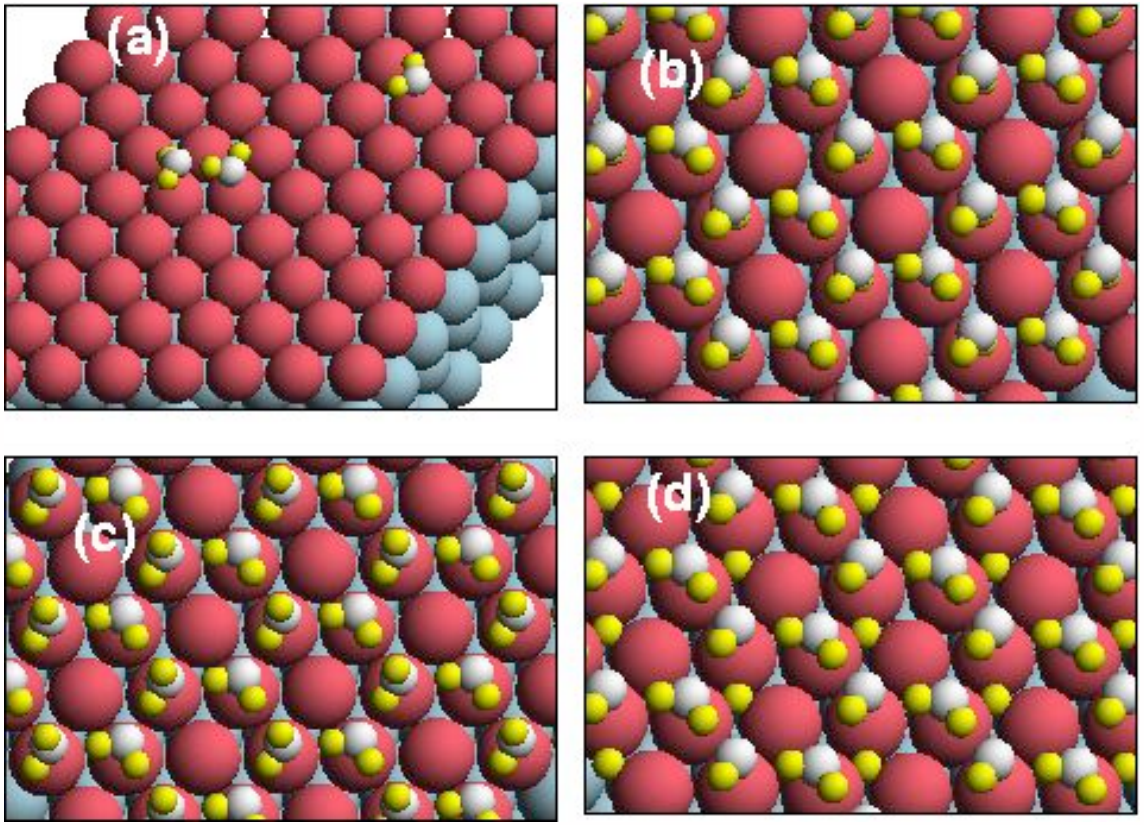


Water molecules bound to more strongly interacting Ru atoms

H adsorption in the presence of a water overlayer

A. Roudgar and A. Groß, Surf. Sci. **597**, 42 (2005)

Water structures on Pd/Au(111)



H_2O structure: a) monomer and dimer, b) H-down bilayer (ice Ih), c) H-up bilayer, d) half-dissociated bilayer

H adsorption energies

θ_{H_2O}	$E_{ads}^{H_2O}$	$E_{ads}^{H\,fcc}$	$E_{ads}^{H\,hcp}$
1/4	-0.308	-0.634	-0.592
1/3	-0.295	-0.606	-0.610
1/2	-0.419	-0.582	-0.602
1	+3.135	–	–
3/4	-0.465	-0.561	–
2/3(b)	**-0.528**	**-0.633**	**-0.596**
2/3(c)	-0.499	–	–
2/3(d)	-0.327	–	–
0	–	**-0.690**	**-0.655**

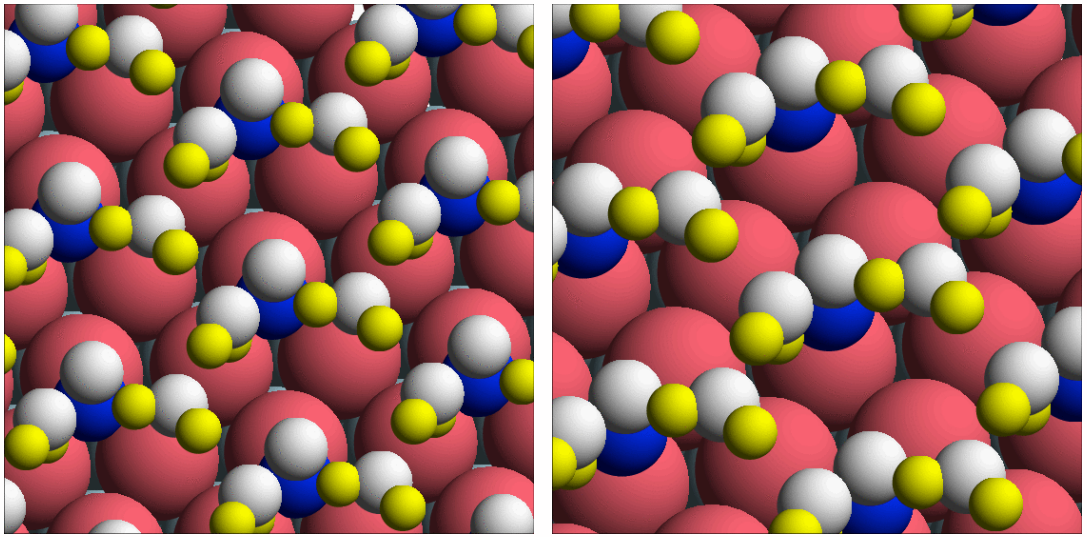
H_2O adsorption energies in eV/H_2O and H adsorption energies ($\theta_H = 1/3$) in eV/atom on Pd/Au(111)

H adsorption energies only slightly changed by the presence of water

CO adsorption in the presence of a water overlayer

A. Roudgar and A. Groß, Chem. Phys. Lett. **409**, 157 (2005)

CO/water structures on Pd/Au(111)



CO/H_2O structures (H-down): a) CO in fcc hollow, b) CO on-top

CO adsorption energies

site	E_{ads}^{CO} H-down	E_{ads}^{CO} H-up	E_{ads}^{CO} clean
fcc	-1.831	-1.894	-2.023
hcp	-1.866	-1.923	-2.043
bridge	—	—	-1.827
on-top	-1.243	—	-1.413

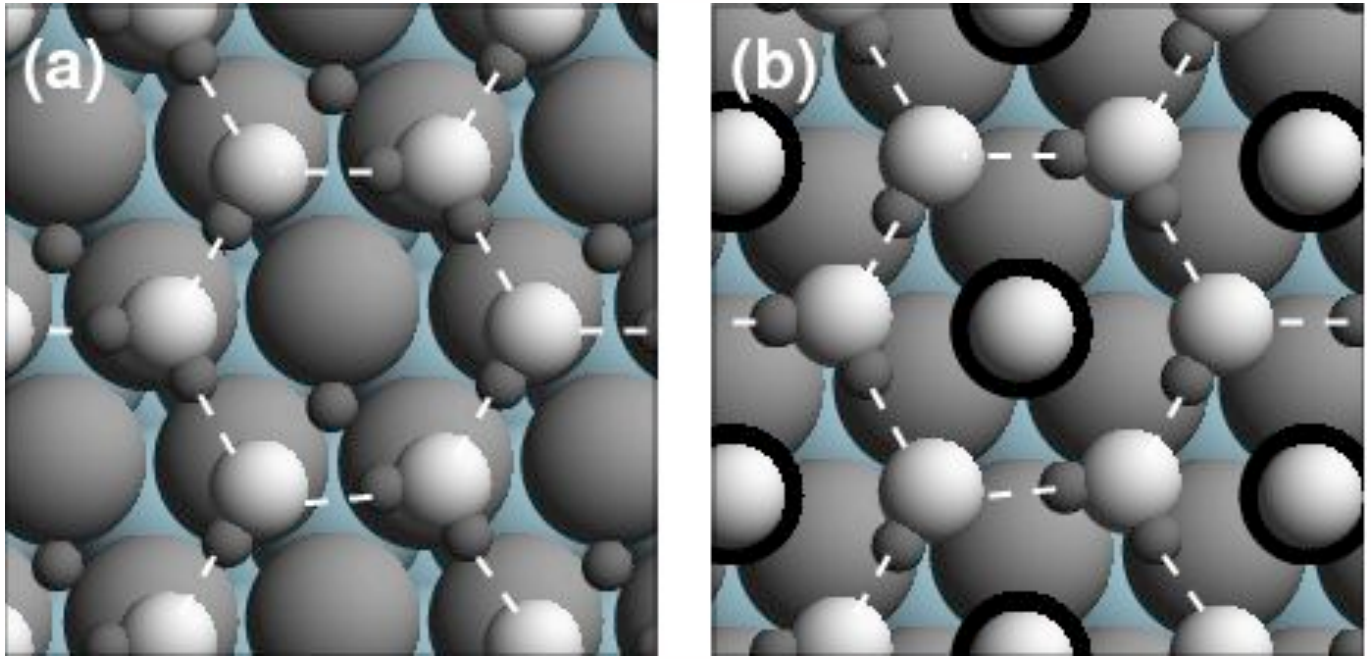
CO adsorption energies ($\theta_{CO} = 1/3$) in eV/molecule on H_2O/Pd/Au(111)

Both H_2O and CO are polar molecules. Still the dipole-dipole interaction between CO and H_2O in the ice-Ih structure on Pd/Au(111) only $\lesssim$ 50 meV

Water relaxation upon CO and H adsorption

A. Roudgar and A. Groß, Chem. Phys. Lett. **409**, 157 (2005)

CO/water and H/water structures on Pd/Au(111)



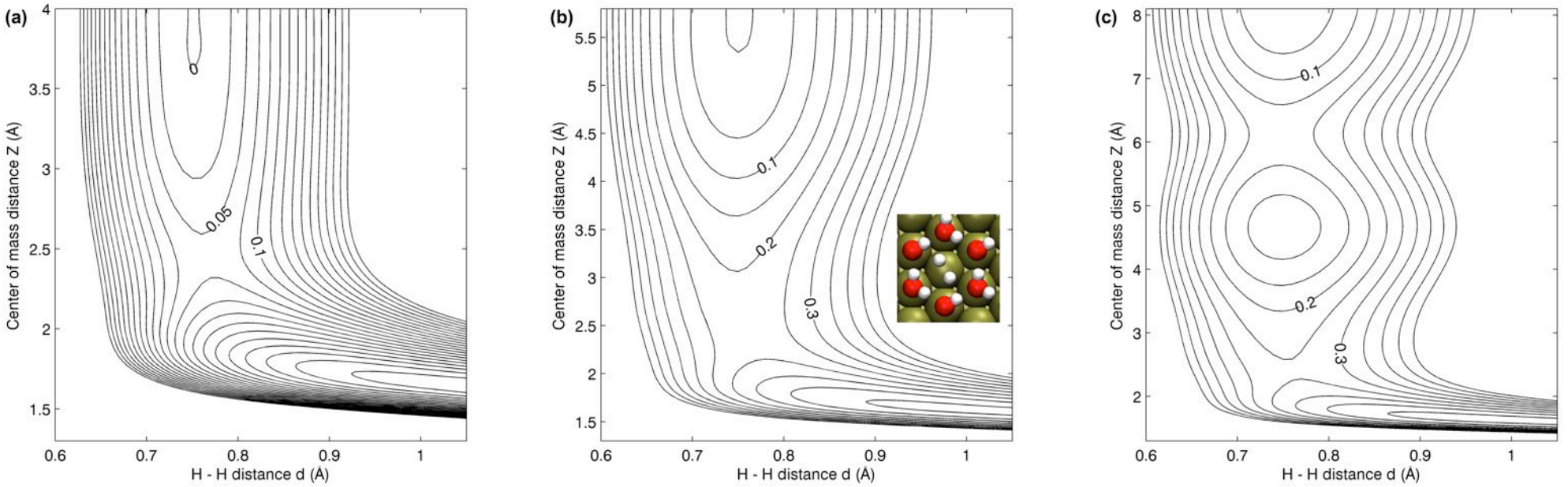
Relaxed water structures in the presence of CO and H

Because of the strong CO-metal interaction, a shifted water bilayer is energetically more favorable

Potential energy surface of H_2/Pt(111)

Yoshihiro Gohda, Sebastian Schnur, Axel Groß, Faraday Diss. **140**, 233 (2009).

Without water | One water bilayer | Two water bilayers



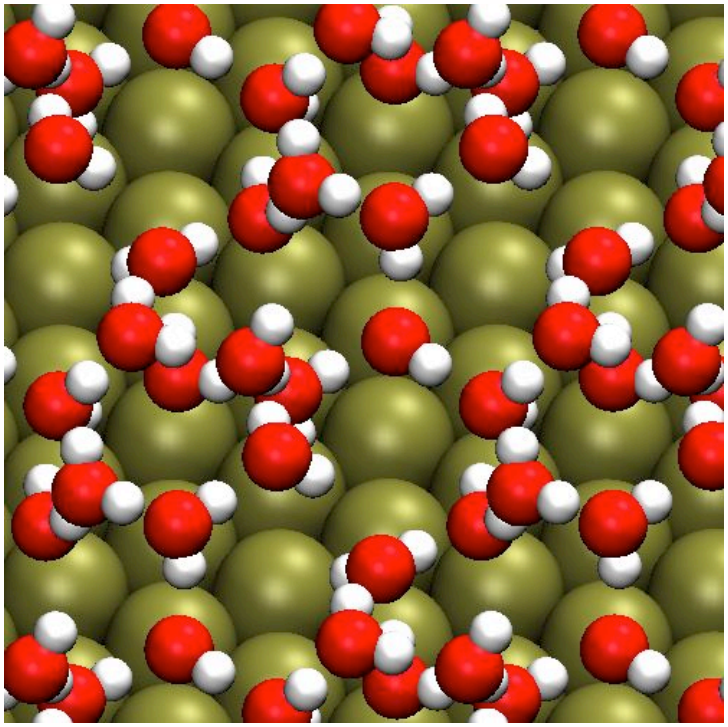
PES as a function of the H_2 distance from the surface and the H-H separation

Barrier height: Superposition of H_2/Pt(111) dissociation barrier and H_2-water repulsion

Disordered water structures

Disordered structures created by removing water molecules from the two water bilayers

Structure



Example of a disordered water structure

H_2 dissociation barrier heights

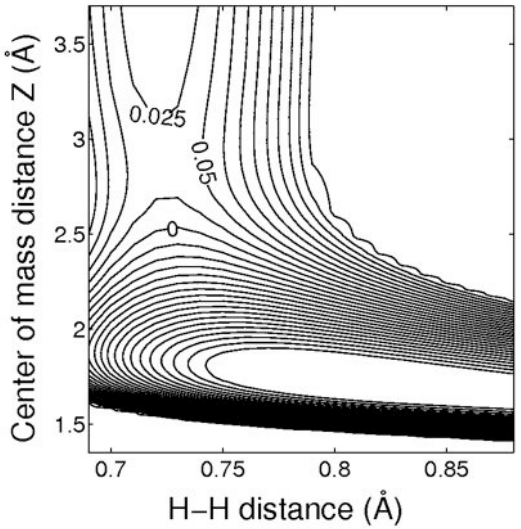
	Lower layer						
#	0	1	1	2	2	2	3
E_b	270	296	284	276	275	323	189
	Upper layer						
#	0	0	1	1	2	3	3
E_b	173	172	162	139	97	9	0

Dependence of the dissociation barriers E_b in meV in the lower and the upper water layer on the number of molecules removed from the water layers (#).

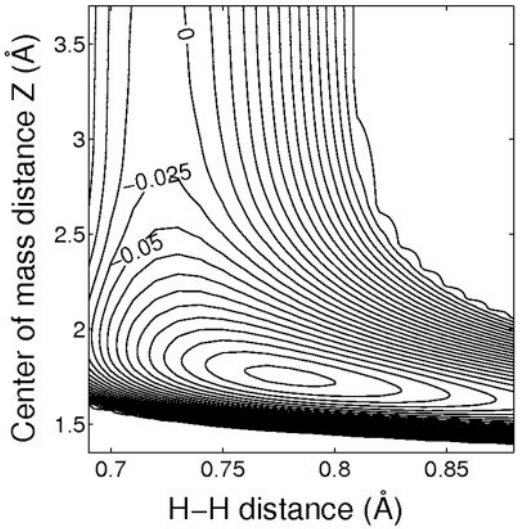
Barrier heights significantly lowered for disordered water structures $\Rightarrow$ thermal averaging required to determine free energy barriers

H_2 dissociation at further water/metal interfaces

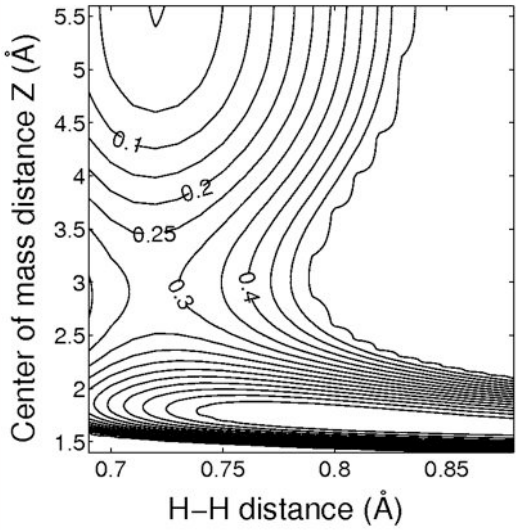
H_2/Ru(0001)



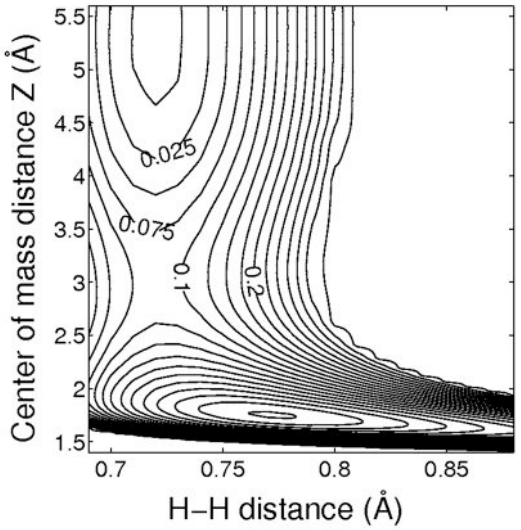
H_2/Pd/Au(111)



H_2/H_2O/Ru(0001)



H_2/H_2O/Pd/Au(111)



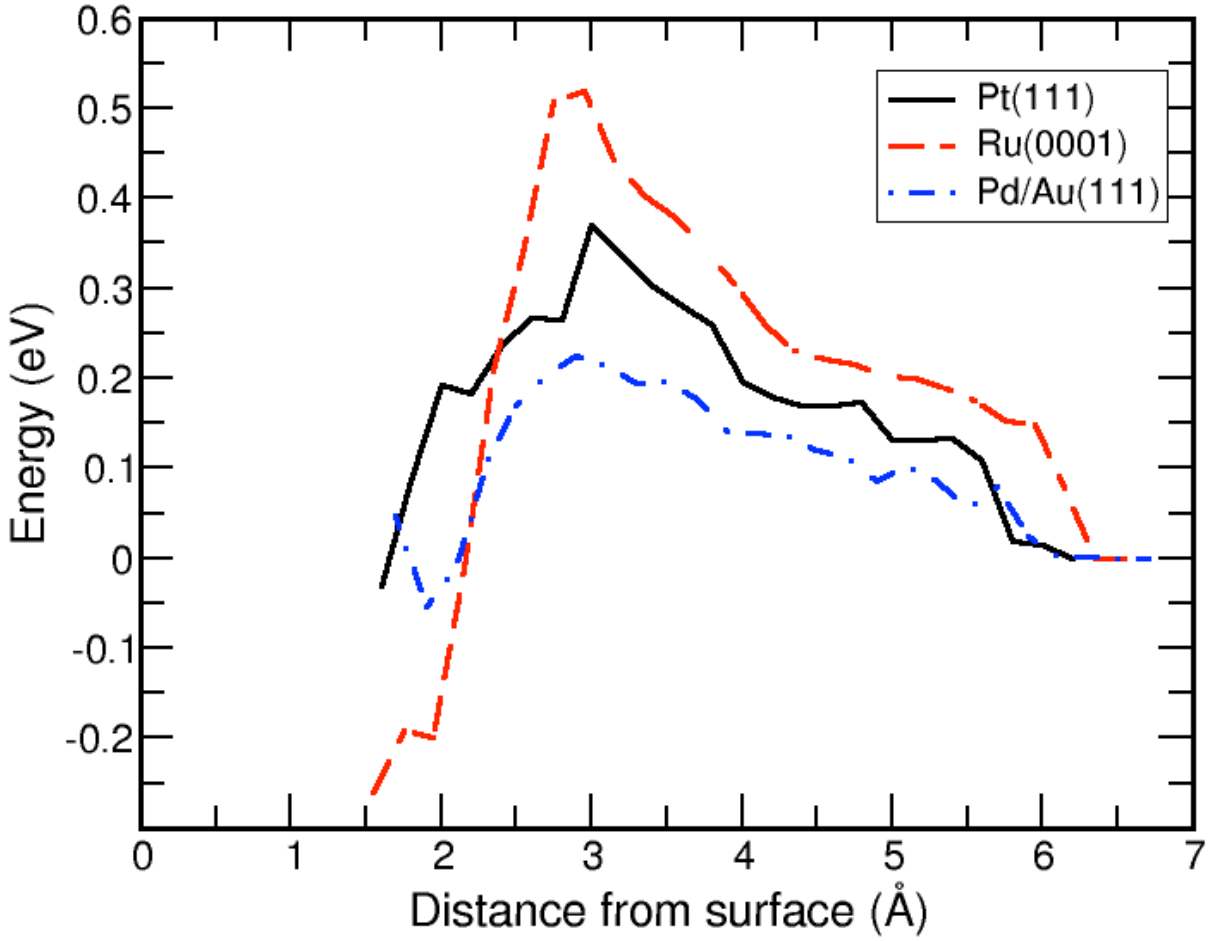
Barriers for H_2 dissociation at water/metal interfaces

		ΔE (meV)	z (Å)	Metal NN distance (Å)
Pt(111)	clean	54	2.4	2.77
Pt(111)	H-down	221	2.5	
Ru(0001)	clean	30	2.8	2.68
Ru(0001)	H-down	290	3.0	
Ru(0001)	H-up	369	2.8	
Pd/Au(111)	clean	0	-	2.86
Pd/Au(111)	H-down	91	3.0	

Strong correlation between metal lattice constant ($\equiv$ size of the water ring) and the change of the H_2 dissociation barrier when a water layer is included

H_2 dissociation barrier at water/metal interfaces at room temperature

Sebastian Schnur and Axel Groß, Catal. Today, **165**, 129 (2011).



Free energy determined by constrained AIMD runs along dissociation path

Further increase of barriers by 150 meV due to thermal motion of the water atoms

Ab initio molecular dynamics simulations of H_2 dissociation on water-covered Pt(111)

Trajectory

Discussion

H_2 dissociation through thermalized disordered water layer

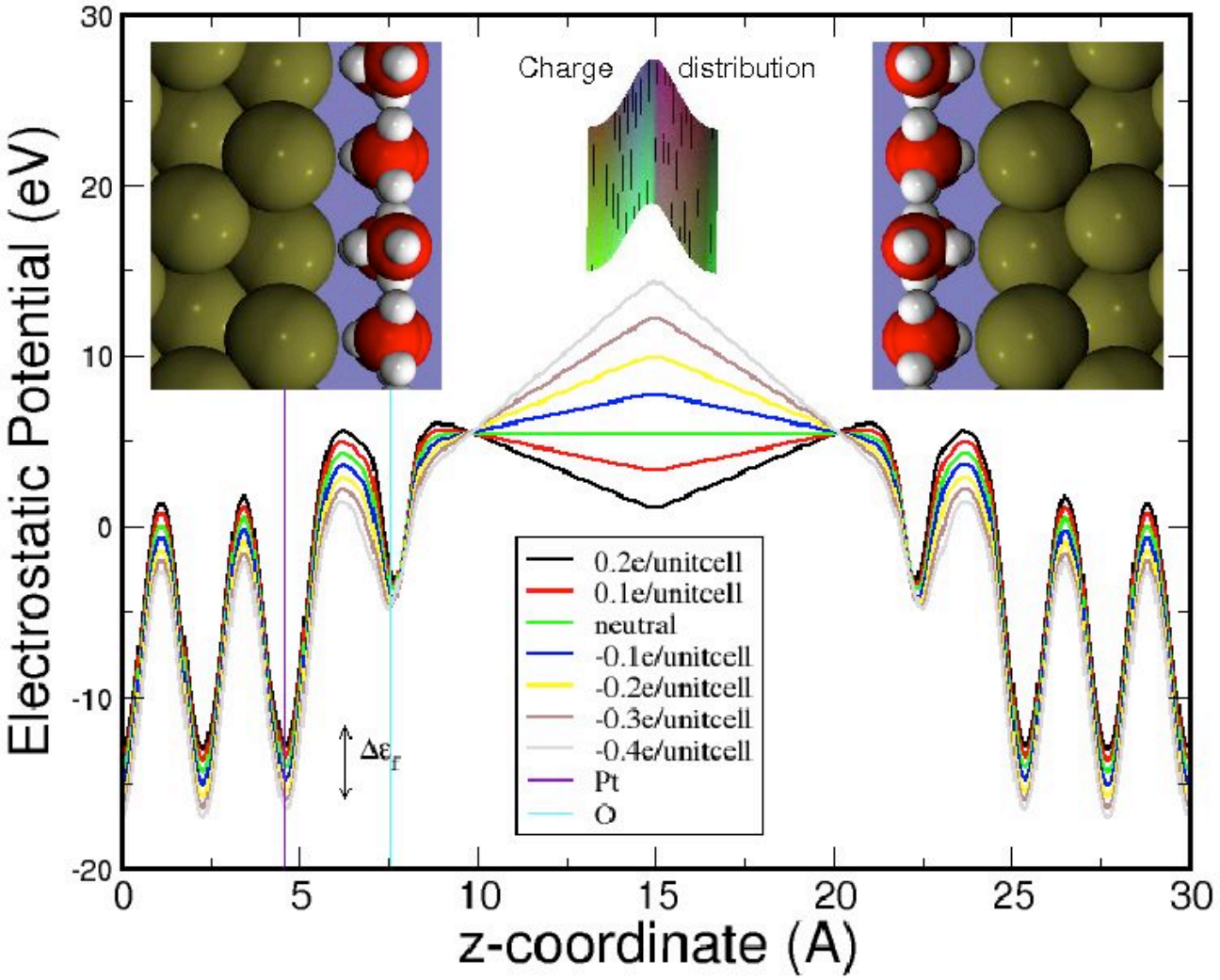
After dissociation, H atoms can move almost freely beneath the water layer

H atoms end up at top sites

Disordered water layer rearranges upon H adsorption

Implementation: Explicit counter charge in supercell

S. Schnur and A. Groß, Catal. Today, **165**, 129 (2011).

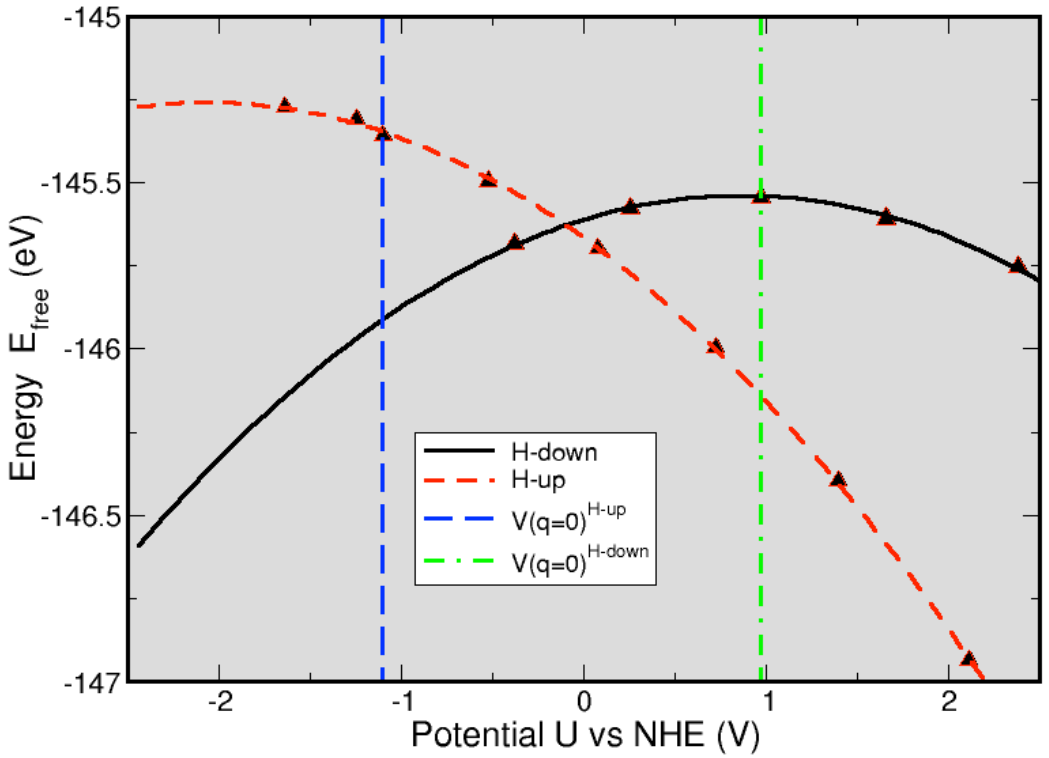


Advantage: Separation of counter electrode and considered system

Application: stability of water layers as a function of the electrode potential

S. Schnur and A. Groß, Catal. Today, **165**, 129 (2011).

$$E_{\text{free}} = E_{\text{total}} - \mu q$$



Capacities derived from these curves are a factor of two smaller than experimental results
Agreement improved when results from AIMD runs are used

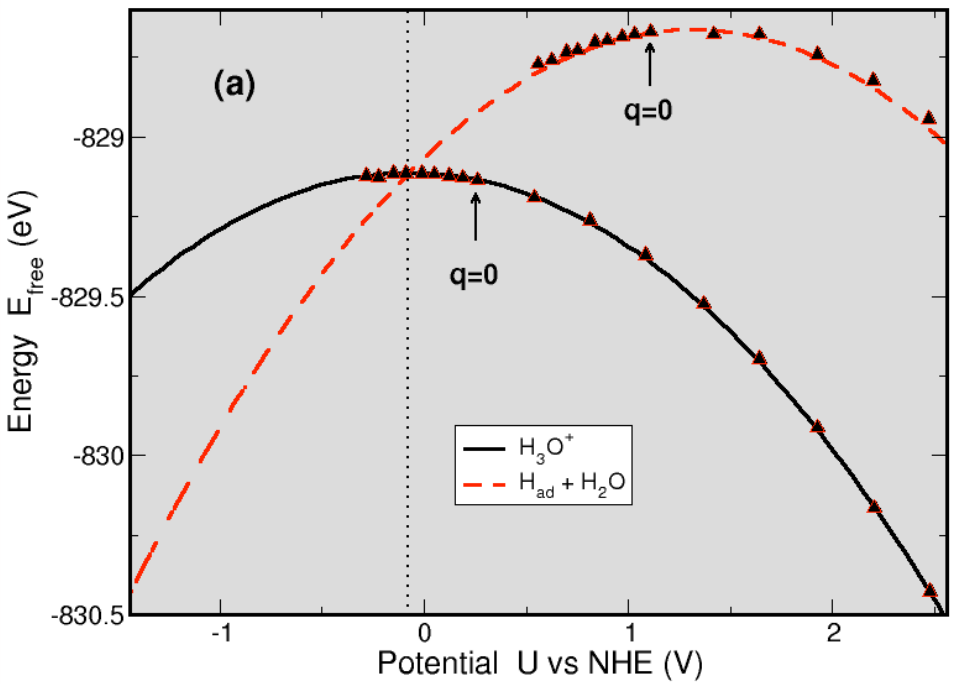
Volmer reaction on Pt(111)

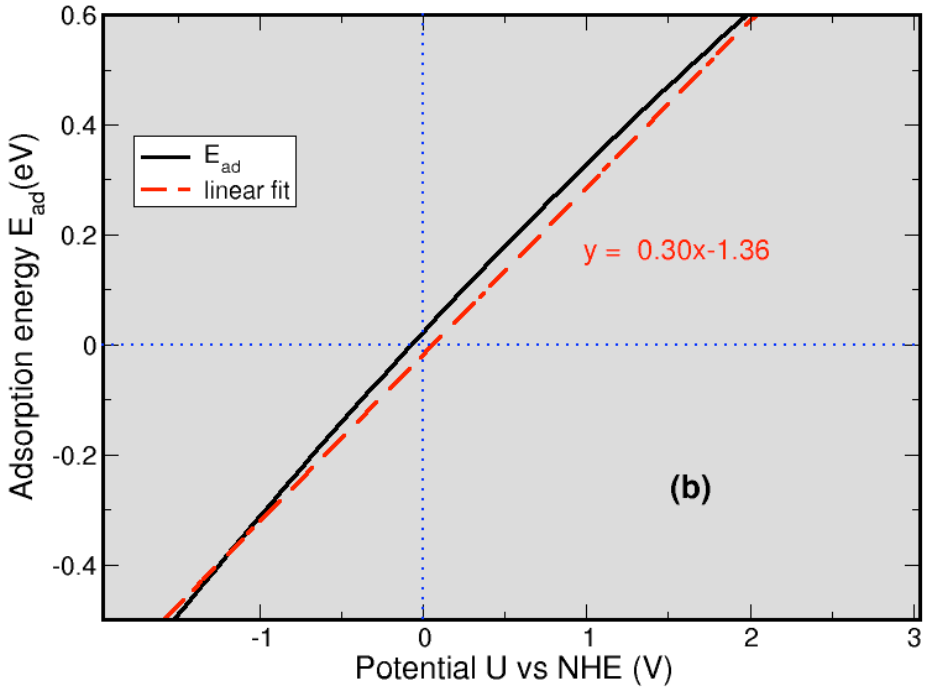
S. Schnur and A. Groß, Catal. Today, **165**, 129 (2011).

Hydrogen evolution according to the Volmer-Tafel-mechanism

$$\mathrm{H_3O^+} + e^- \leftrightarrow \mathrm{H_{ad}} + \mathrm{H_2O} \quad \text{Volmer reaction} \tag{12}$$

$$2\mathrm{H_{ad}} \leftrightarrow \mathrm{H_2} \quad \text{Tafel reaction} \tag{13}$$



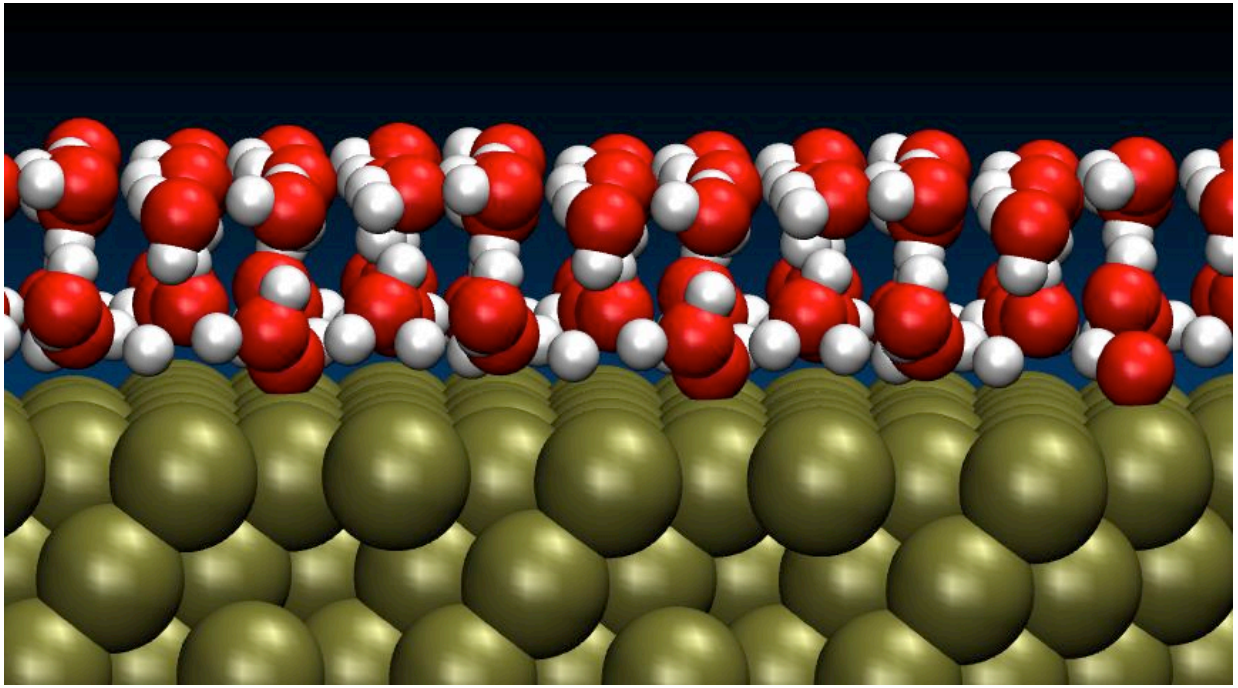


On Pt(111), hydrogen evolution in equilibrium with the intermediate H adsorption state
$\Rightarrow$ Exceptional role of Pt as an electrocatalyst

J.K. Nørskov *et al.*, J. Electrochem. Soc. **152**, J23 (2005).

Water structure on H-covered Pt(111)

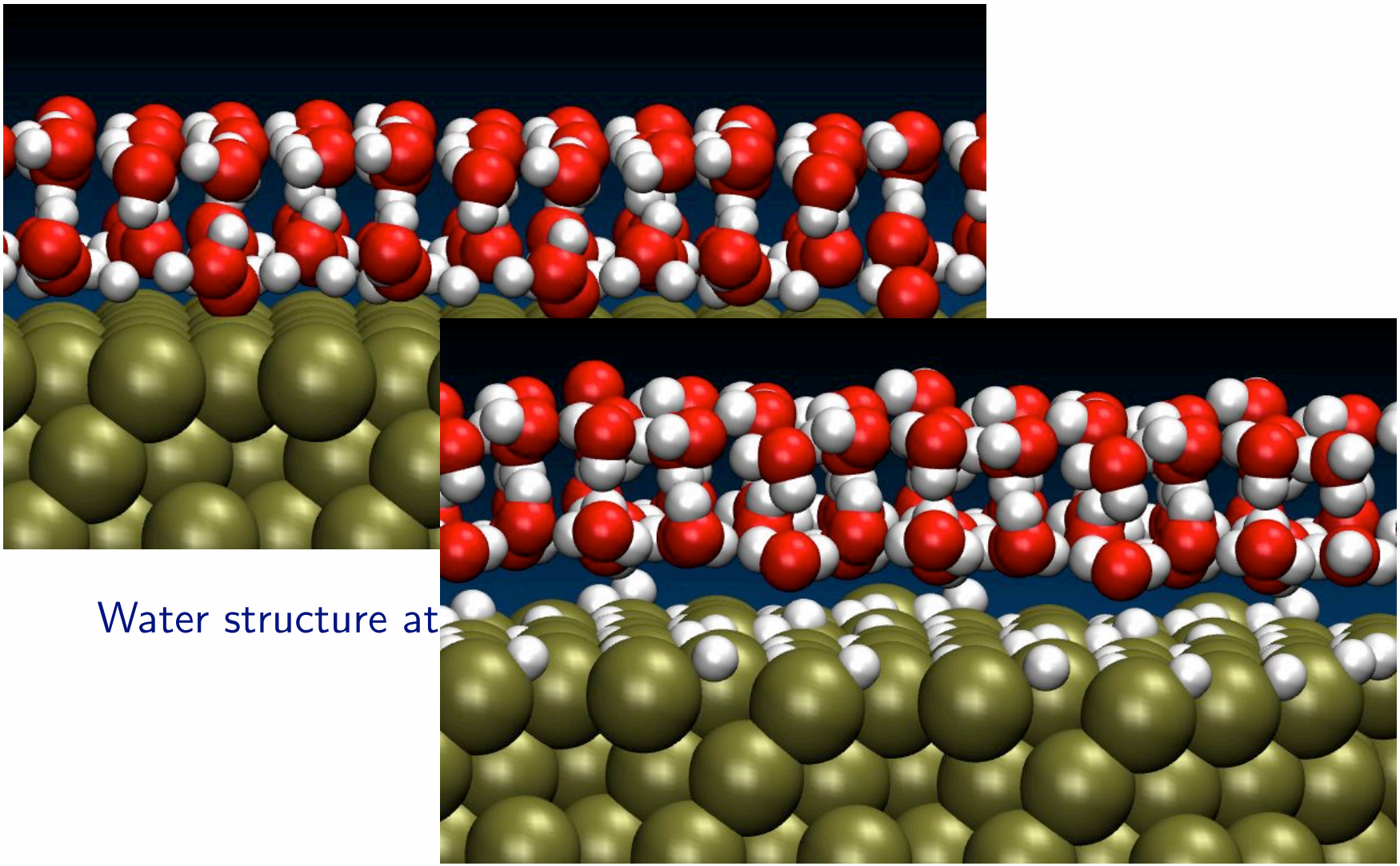
T. Roman and A. Groß, Catal. Today **202**, 183190 (2013).



Water structure at 300 K on clean Pt(111)

Water structure on H-covered Pt(111)

T. Roman and A. Groß, Catal. Today **202**, 183190 (2013).

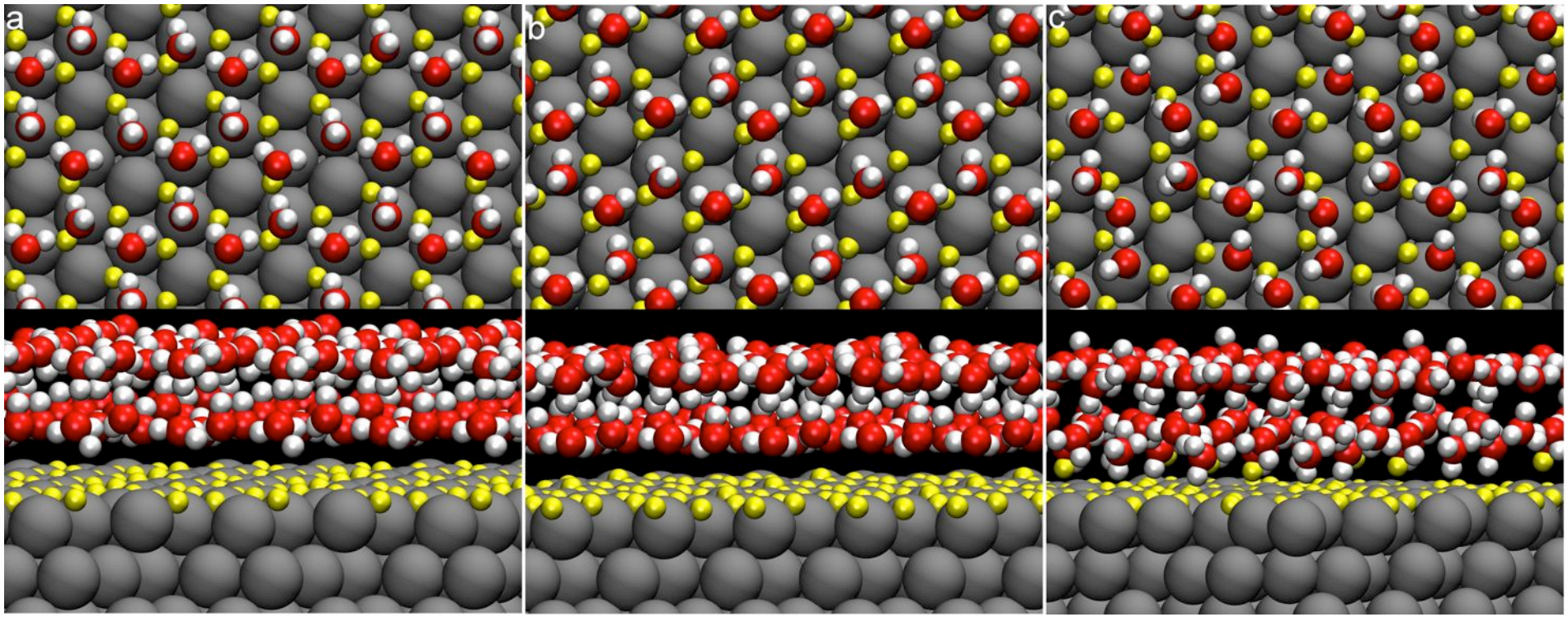


Water structure at 300 K on H-covered Pt(111)

Water on hydrogen-covered Pt(111)

T. Roman and A. Groß, Catal. Today **202**, 183190 (2013).

H_2O/H(0.92 ML)/Pt(111) H_2O/H(1 ML)/Pt(111) H_2O/H(1.08 ML)/Pt(111)

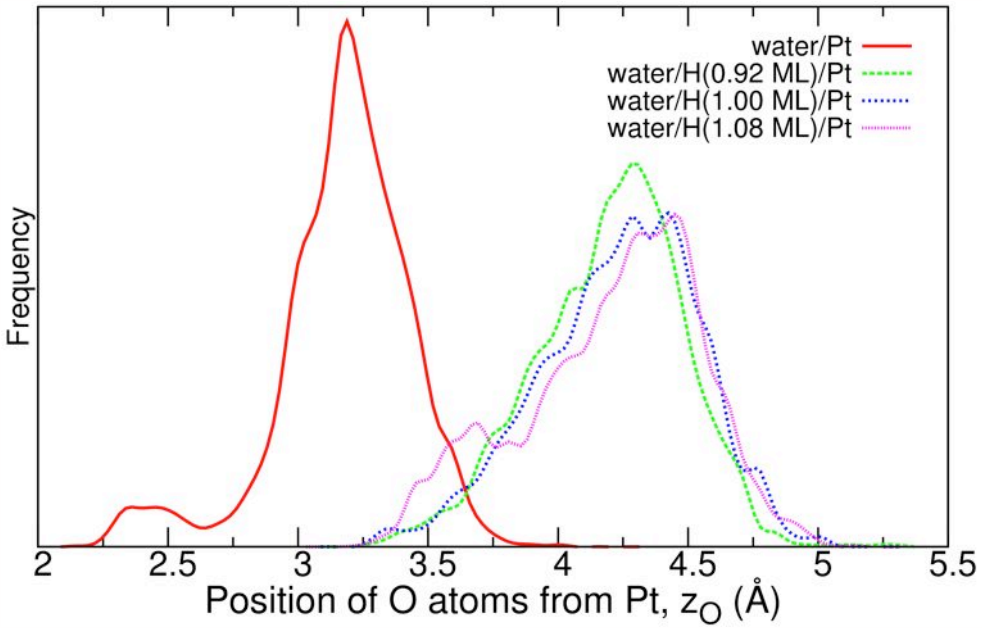


Second layer hydrogen atom (opd hydrogen) considered as active species for hydrogen evoluation reaction

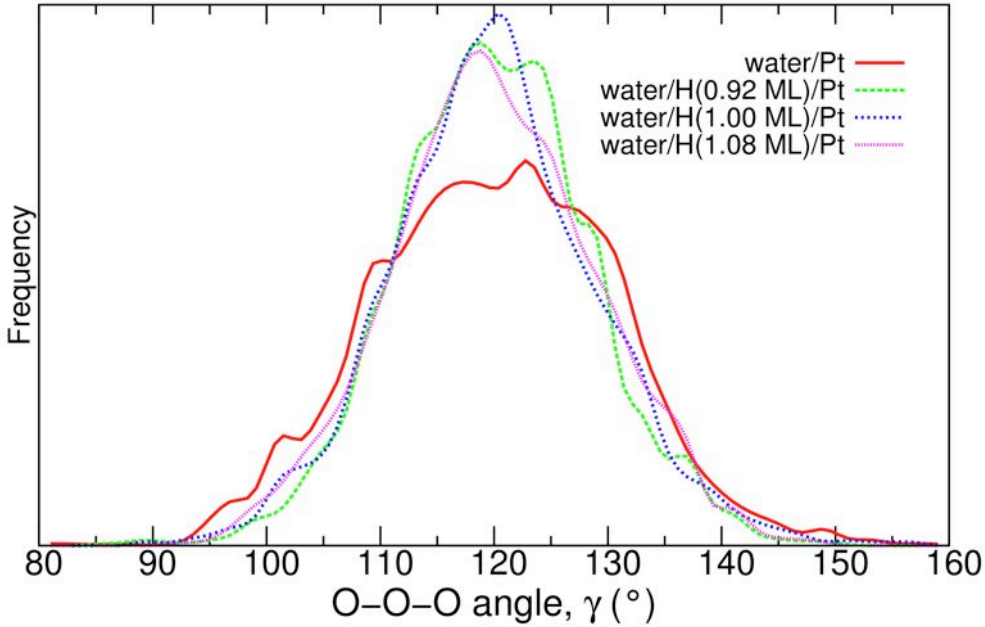
Water on Pt(111): distributions

T. Roman and A. Groß, Catal. Today **202**, 183190 (2013).

O-Pt distance



O-O-O angle



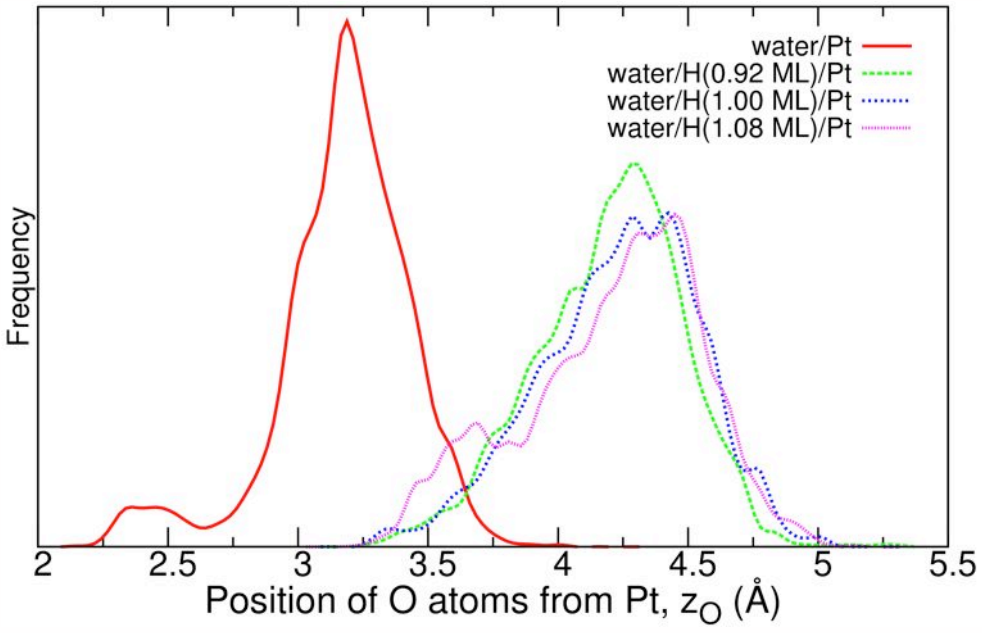
Ice structure: O-O-O angle $\gamma = 120°$

Order of water layer on H-covered Pt(111) stronger than on clean Pt(111)

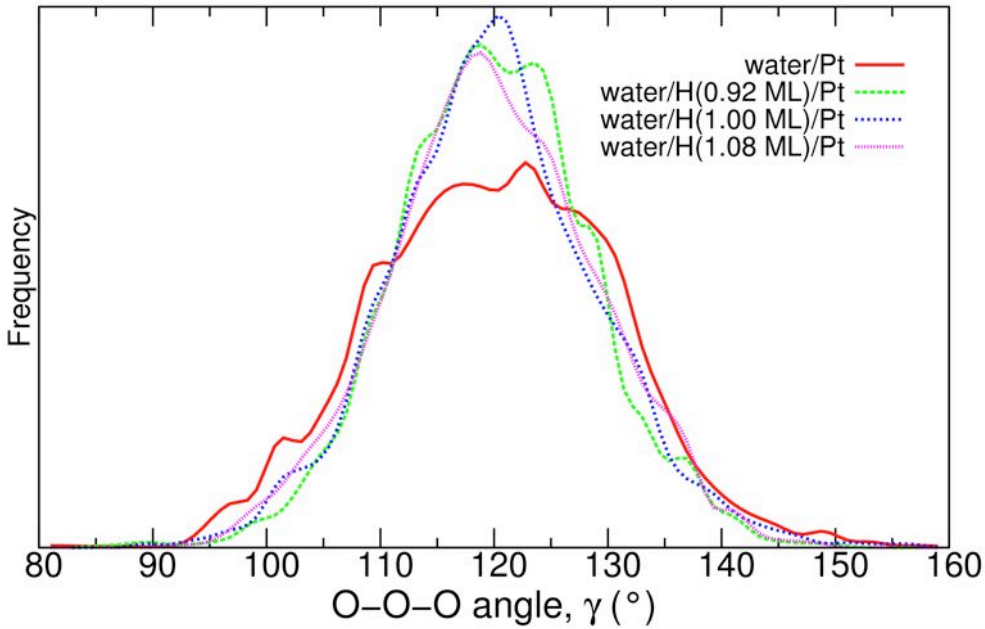
Water on Pt(111): distributions

T. Roman and A. Groß, Catal. Today **202**, 183190 (2013).

O-Pt distance



O-O-O angle



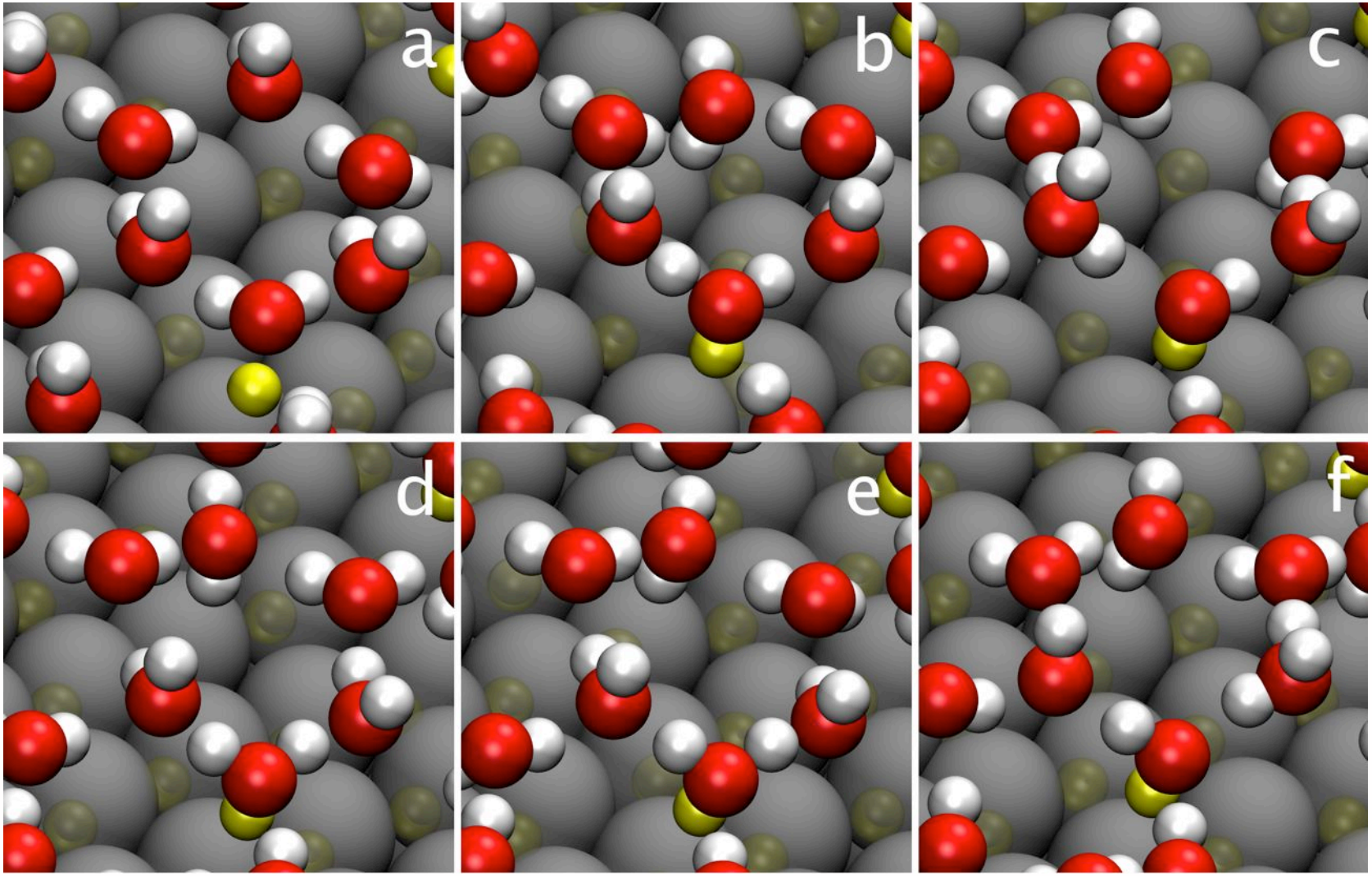
Ice structure: O-O-O angle $\gamma = 120°$

Order of water layer on H-covered Pt(111) stronger than on clean Pt(111)

Ice adsorption energies on Pt(111) and H/Pt(111) very similar, but water monomer interaction with H/Pt(111) weak $\Rightarrow$ stronger water-water interaction

Proton transfer into the water layer

T. Roman and A. Groß, Catal. Today **202**, 183190 (2013).

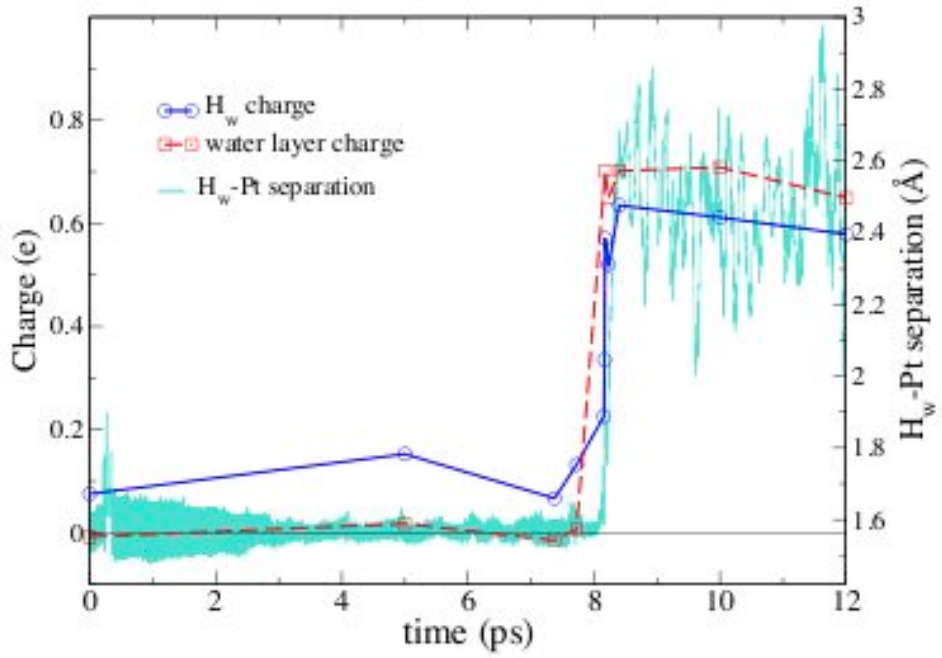


Second layer hydrogen atom (opd hydrogen, solid yellow ball) transfered into the water layer followed by further proton diffusion (Grotthuis mechanism)

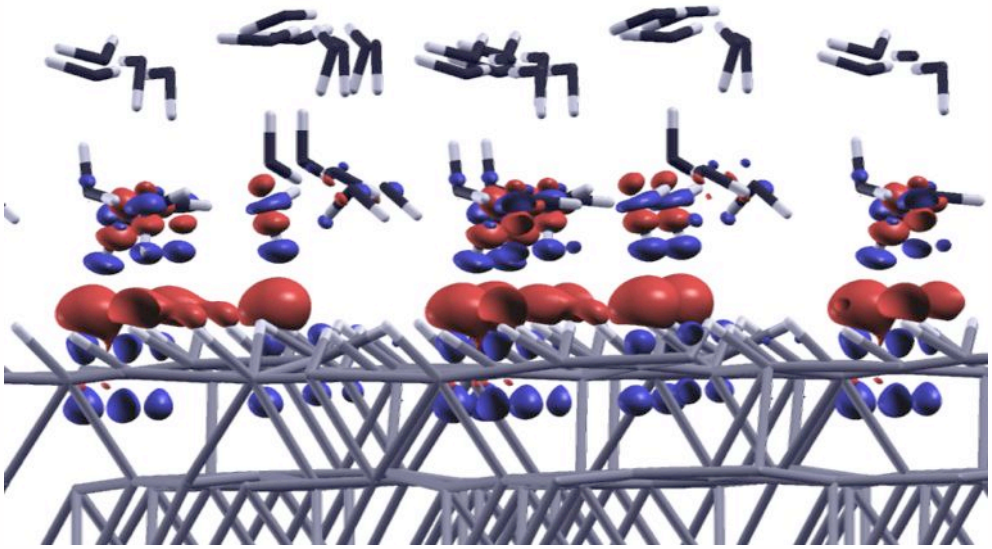
Charge of transfered proton

P. Quaino, N. Luque, G. Soldano, R. Nazmutdinov, E. Santos, T. Roman, A. Lundin, A. Groß, and W. Schmickler, Electrochim. Acta (2013).

Time evolution



Charge distribution at 10 ps



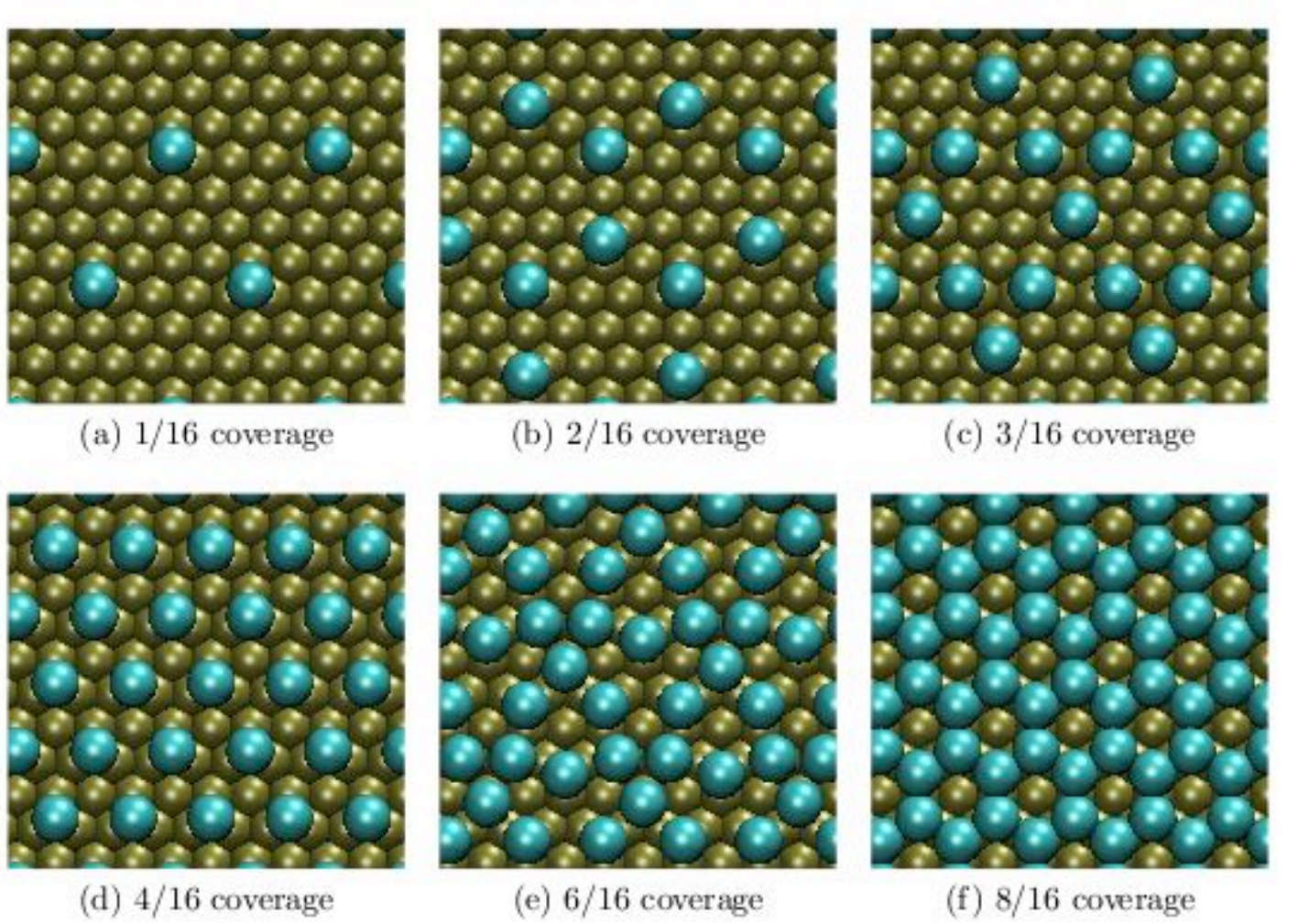
Ice structure: O-O-O angle $\gamma = 120°$

DFT-hydrogen atom not fully ionized upon transfer into the water layer

Adsorption of anions at electrode-electrolyte interfaces

T. Roman, F. Gossenberger, and A. Groß

Halides (F^-, Cl^-, Br^-, I^-) often present at electrode-electrolyte interfaces

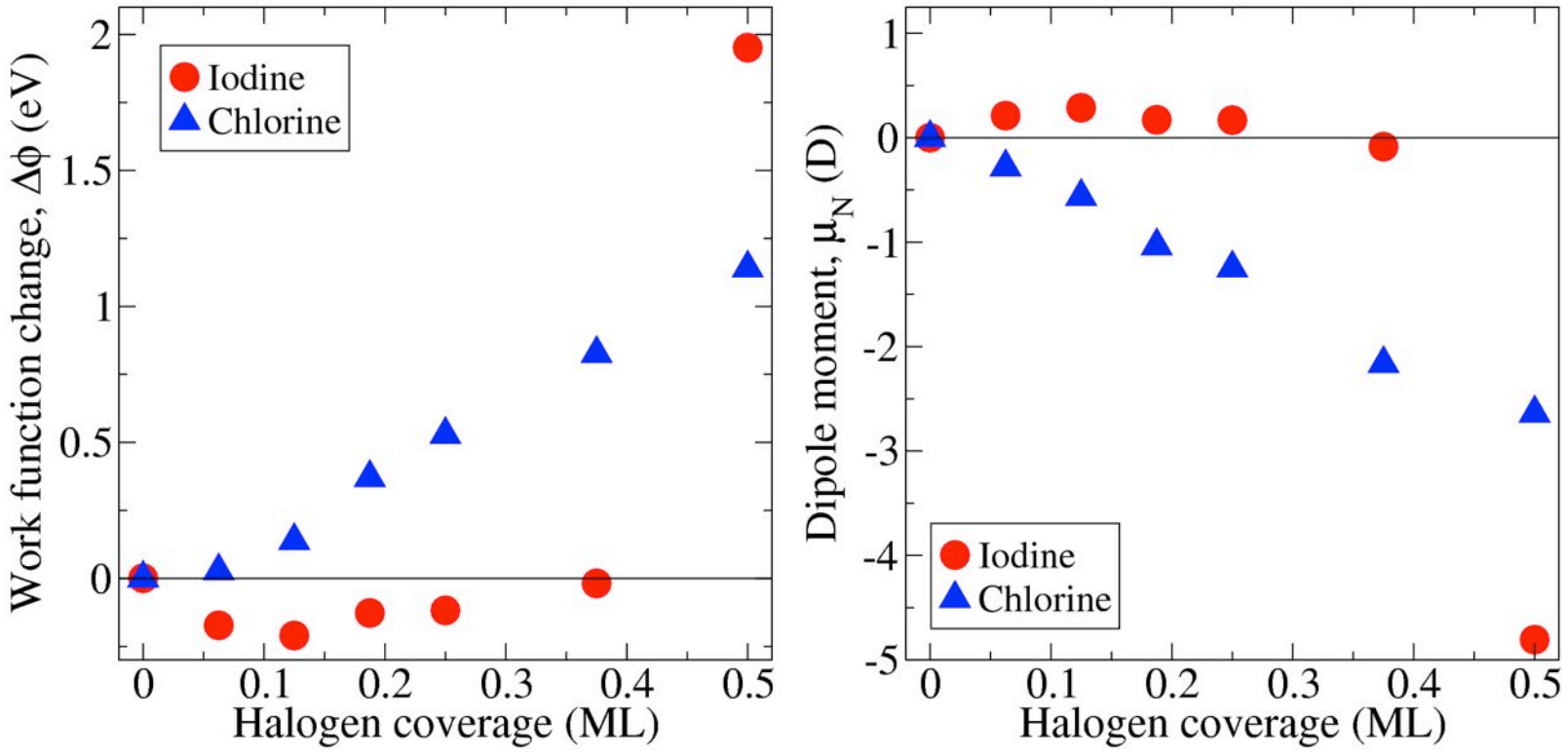


Energy minimum structures of chlorine adsorbed on Pt(111) as a function of the coverage

Halogen adsorption on Cu(111)

T. Roman and A. Groß, Phys. Rev. Lett. **110**, 156804 (2013).

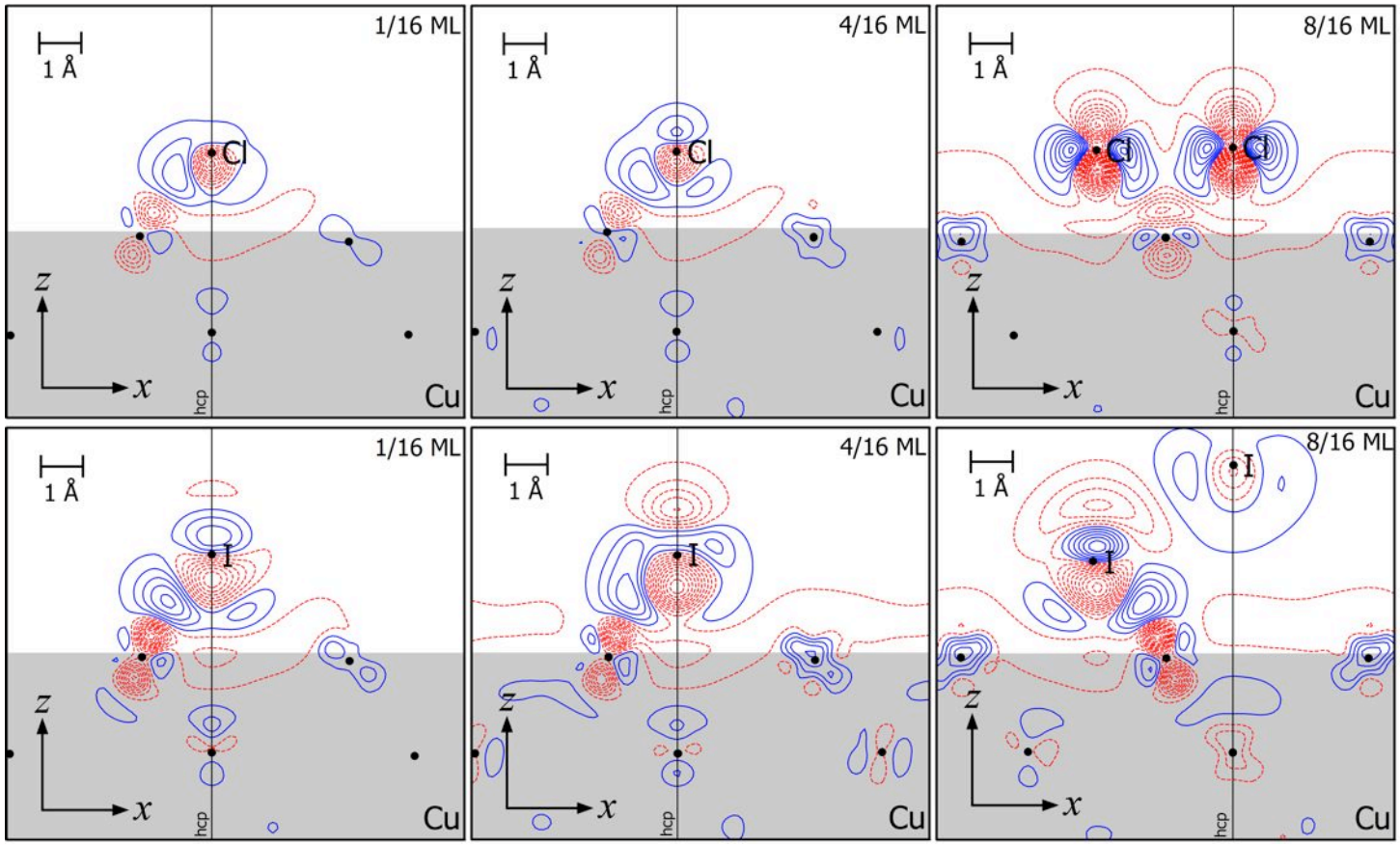
Halogen adsorption on metal substrates well-studied in surface science



Iodine-induced work function change of Cu(111) exhibits anomalous trend in agreement with experiment

Charge-density difference plots of Cl/Cu and I/Cu

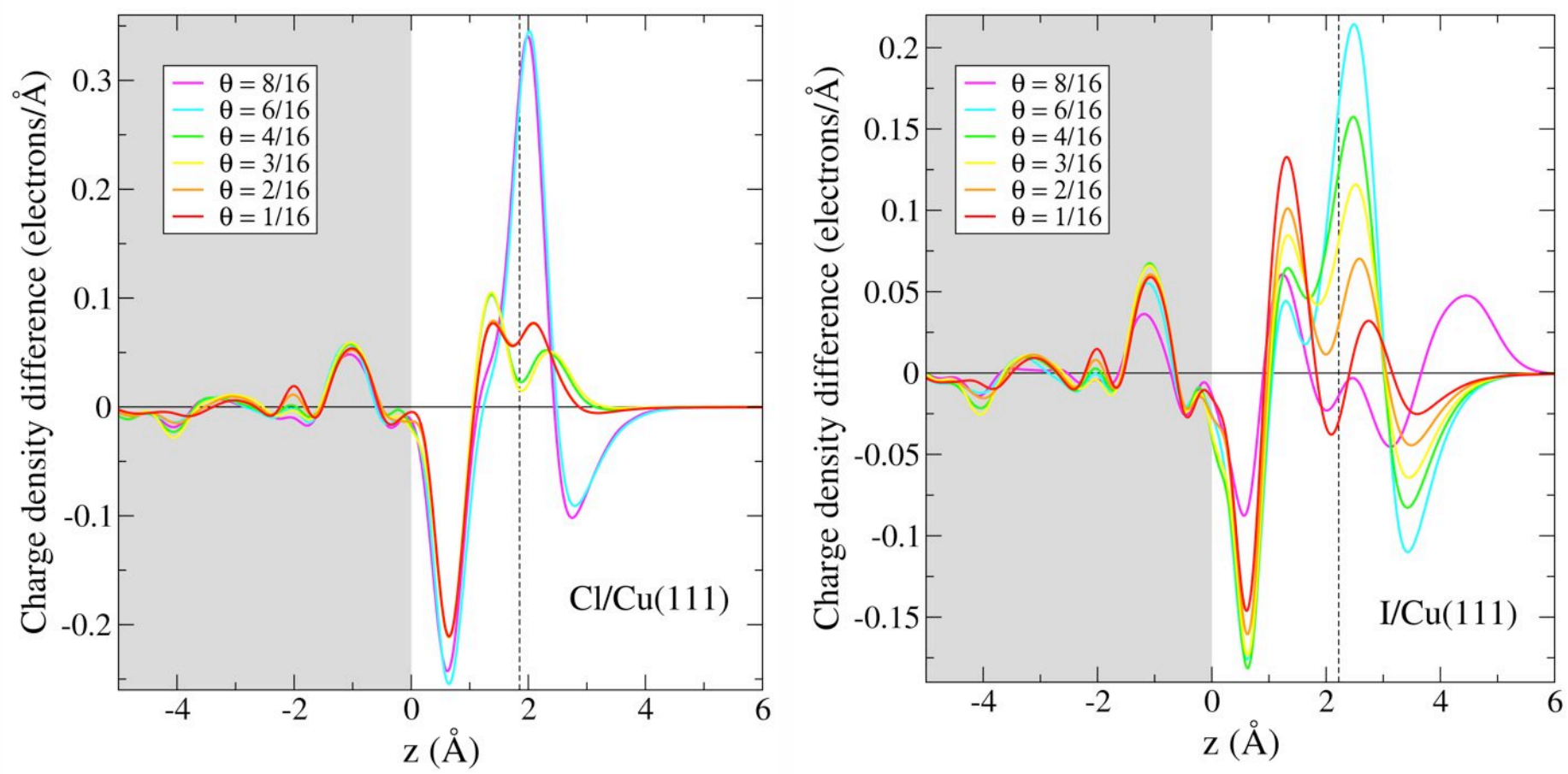
T. Roman and A. Groß, Phys. Rev. Lett. **110**, 156804 (2013).



Both Cl and I exhibit net charge accumulation, but I/Cu shows much stronger polarization than Cl/Cu

Laterally averaged charge density difference

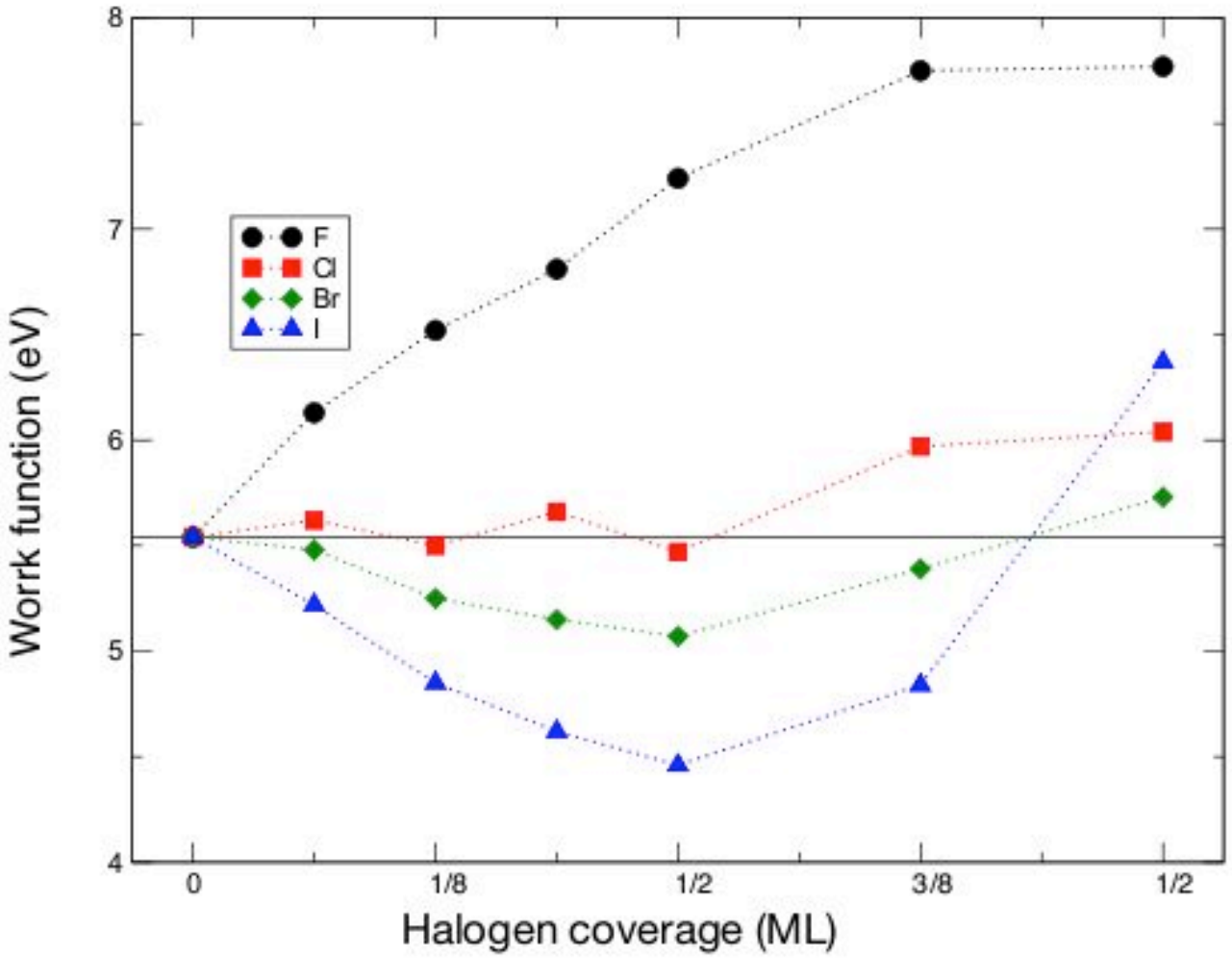
T. Roman and A. Groß, Phys. Rev. Lett. **110**, 156804 (2013).



Anomalous iodine-induced work function change caused by the large charge depletion at large distance from the surface

Halogen-induced work function change of Pt(111)

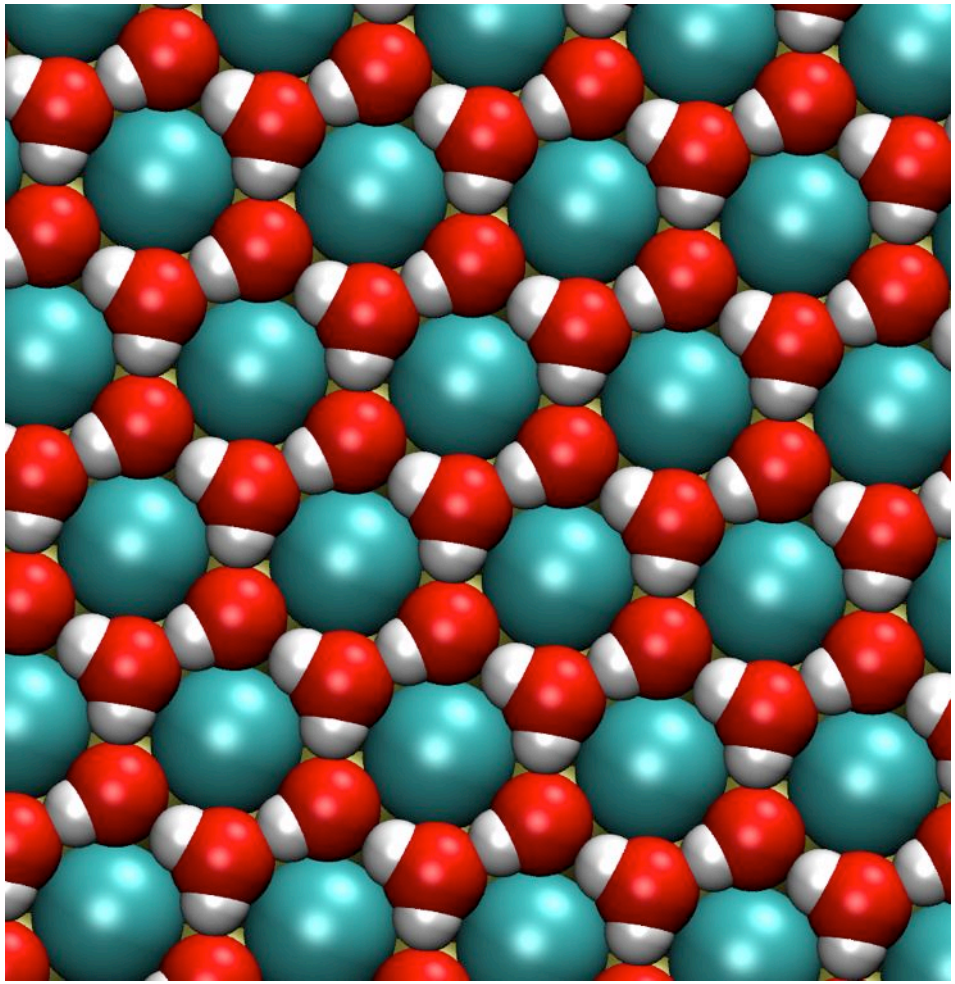
F. Gossenberger, T. Roman, and A. Groß, in preparation

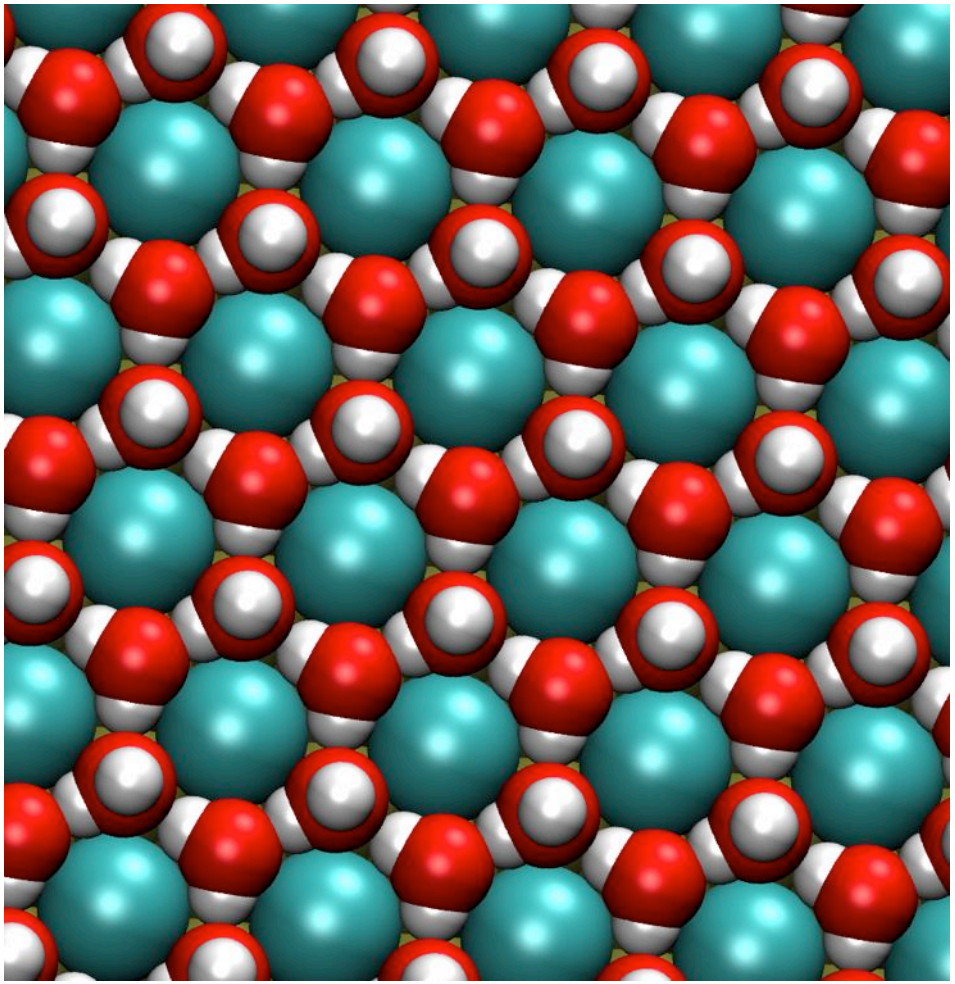


Similar trends as on Cu(111)

Co-adsorption of water and halogens

F. Gossenberger, T. Roman, and A. Groß, in preparation

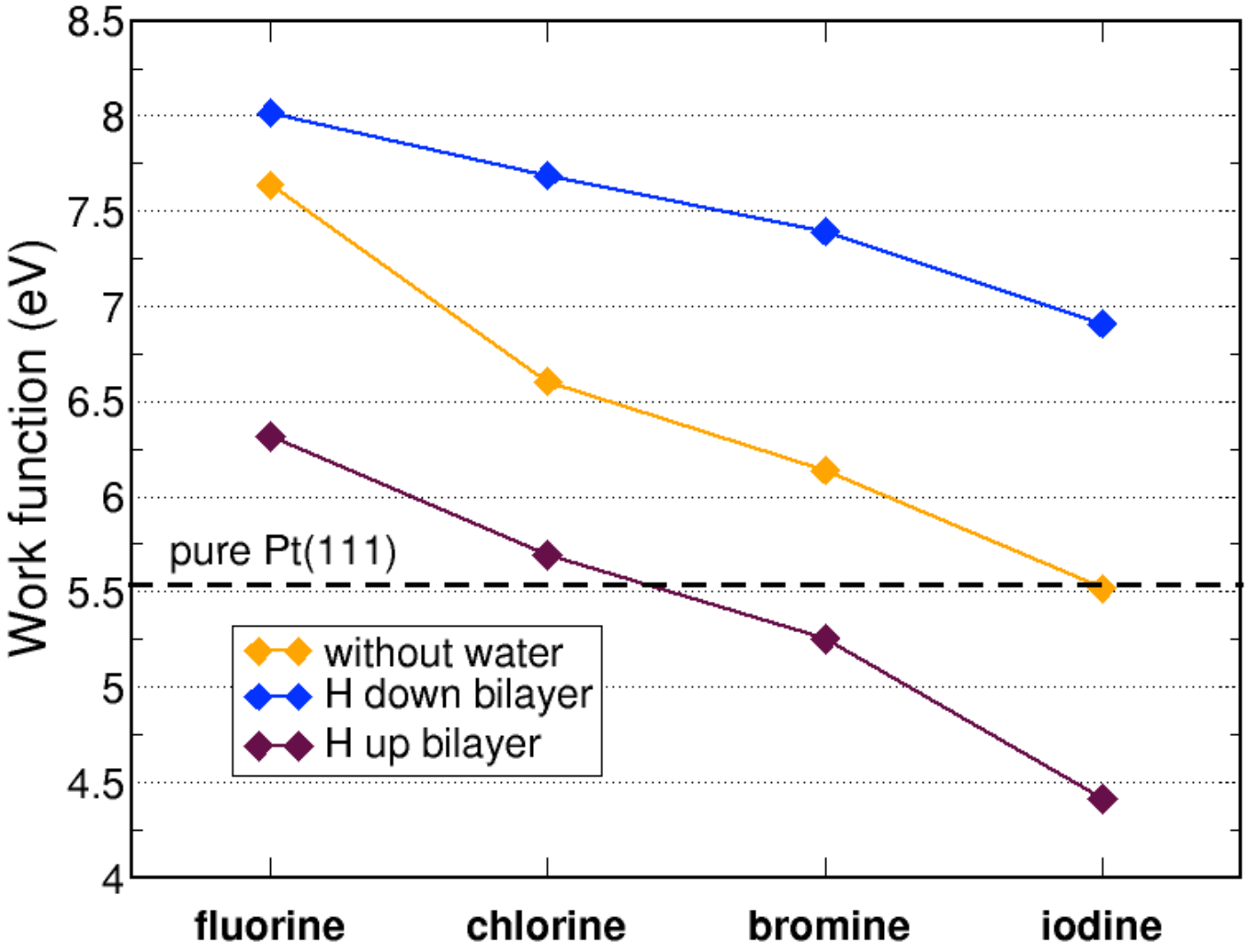




Repulsive interaction between water and halogens: water layer shifted away from the surface

Work function of water and halogens on Pt(111)

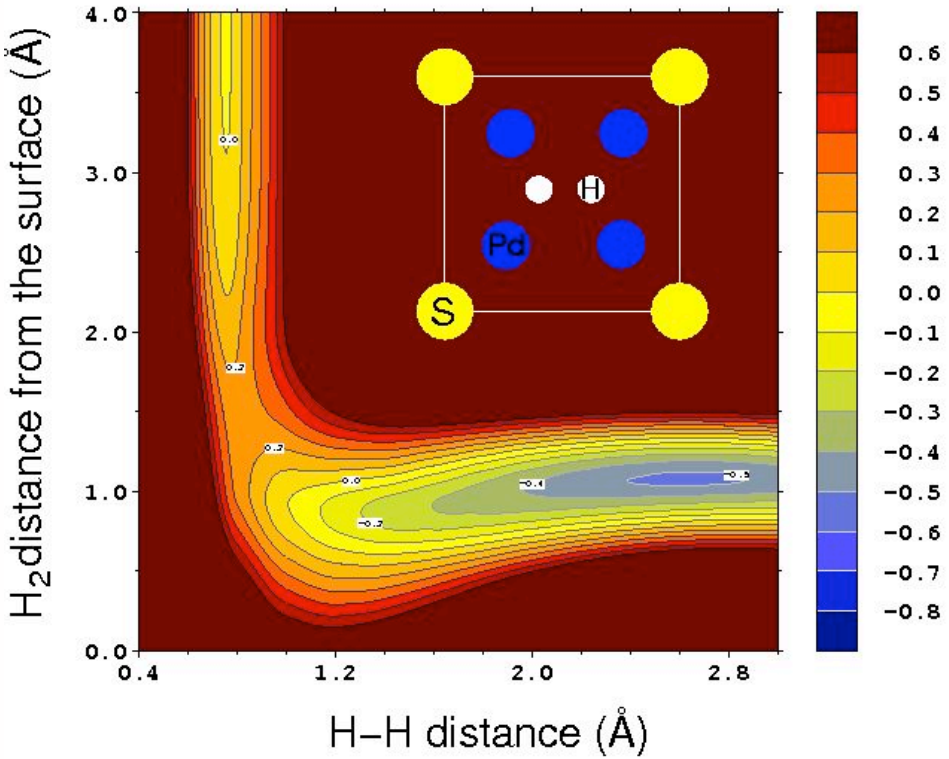
F. Gossenberger, T. Roman, and A. Groß, in preparation



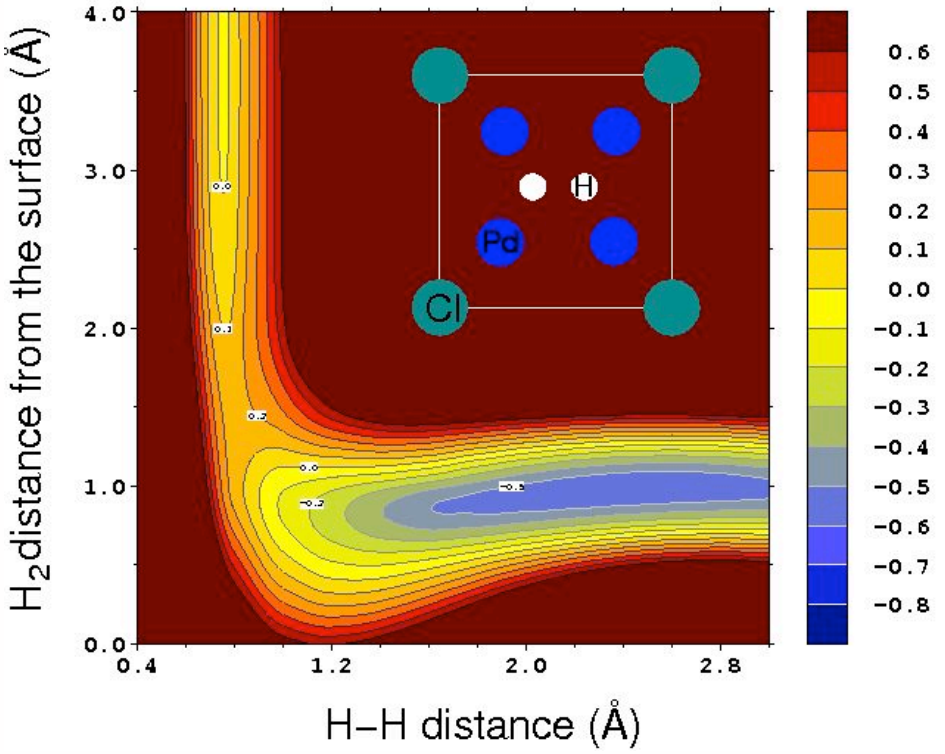
No apparent polarization of the water layer

Potential energy surface of H_2 on $S(2 \times 2)$ and $Cl(2 \times 2)$/Pd(100)

H_2/S(2×2)/Pd(100)



H_2/Cl(2×2)/Pd(100)



Chlorine leads to similar PES as sulphur, just minimum adsorption barrier 0.1 eV lower

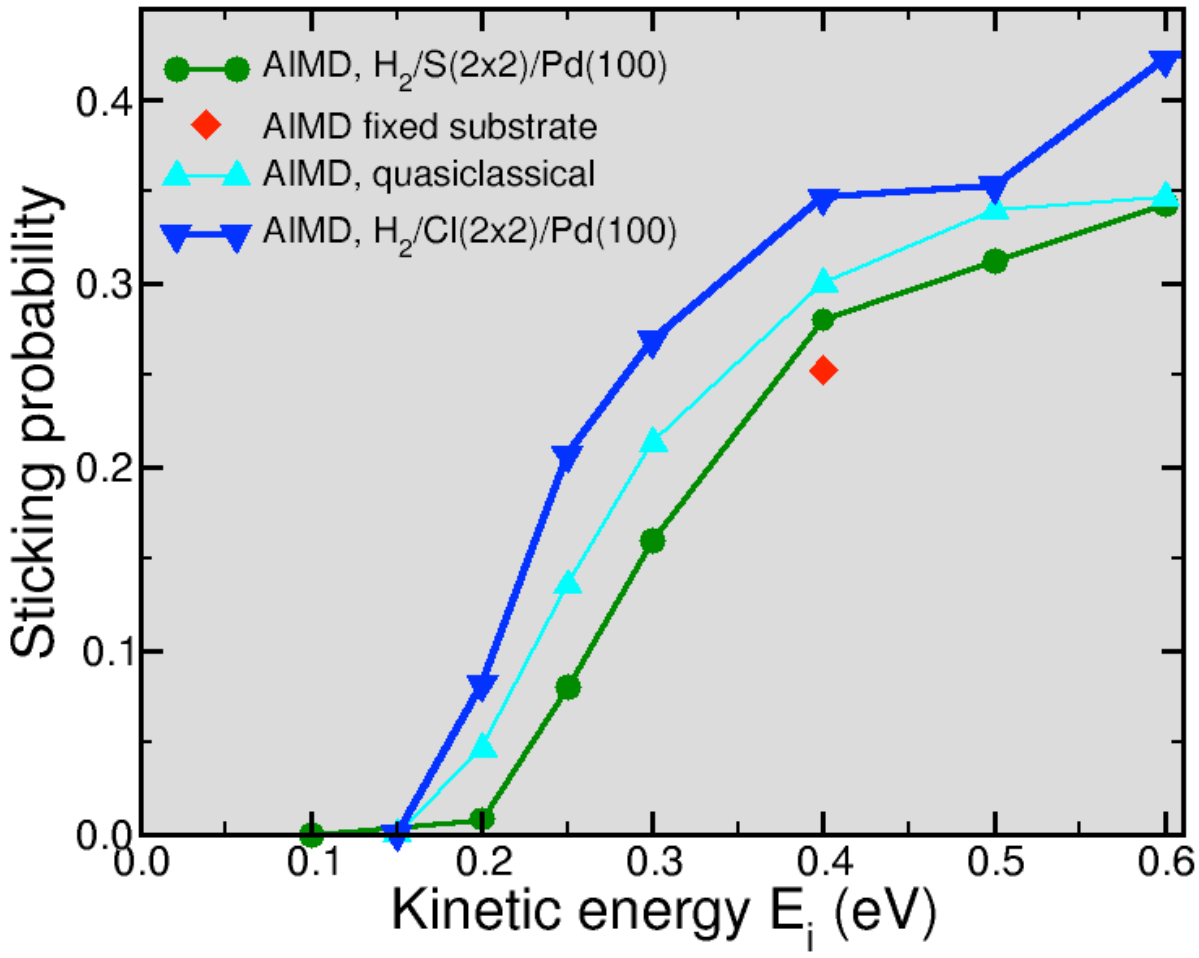
H_2 interaction with Cl(2×2)/Pd(100)

Scattering

Dissociation

Sticking probability of $H_2/Cl(2 \times 2)/Pd(100)$

A. Groß, Surf. Sci. **608**, 249254 (2013).



Sticking probabilities of $H_2/Cl(2 \times 2)/Pd(100)$ and $H_2/S(2 \times 2)/Pd(100)$ rather similar, just shifted by the difference in the minimum barrier height

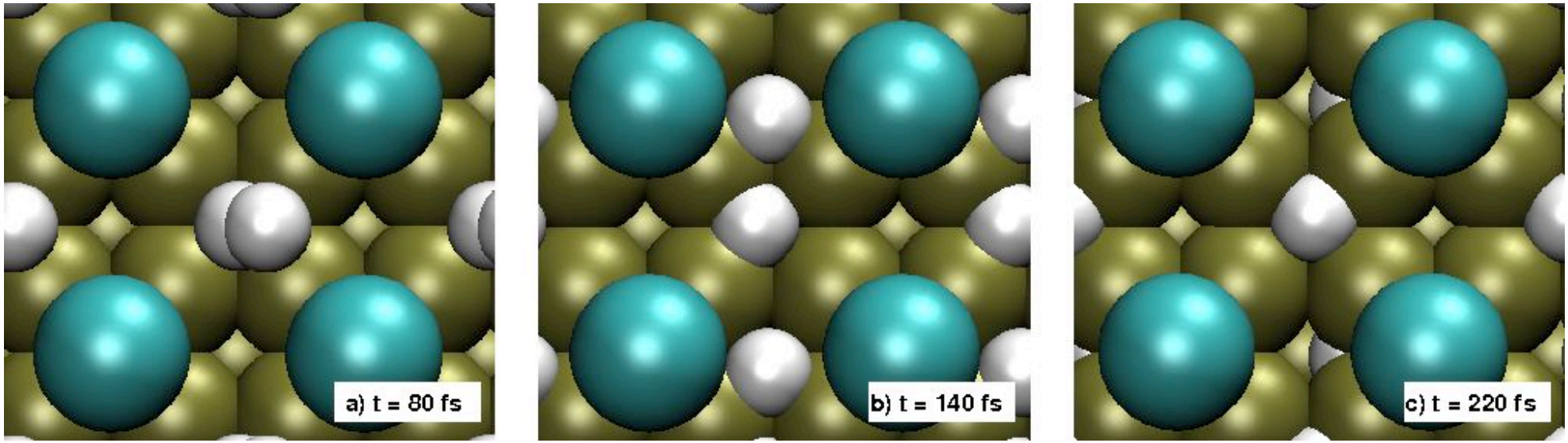
Subsurface penetration of $H_2/S(2 \times 2)/Pd(100)$

A. Groß, Surf. Sci. **608**, 249254 (2013).

Trajectory

Subsurface penetration of $H_2/Cl(2 \times 2)/Pd(100)$

A. Groß, Surf. Sci. **608**, 249254 (2013).

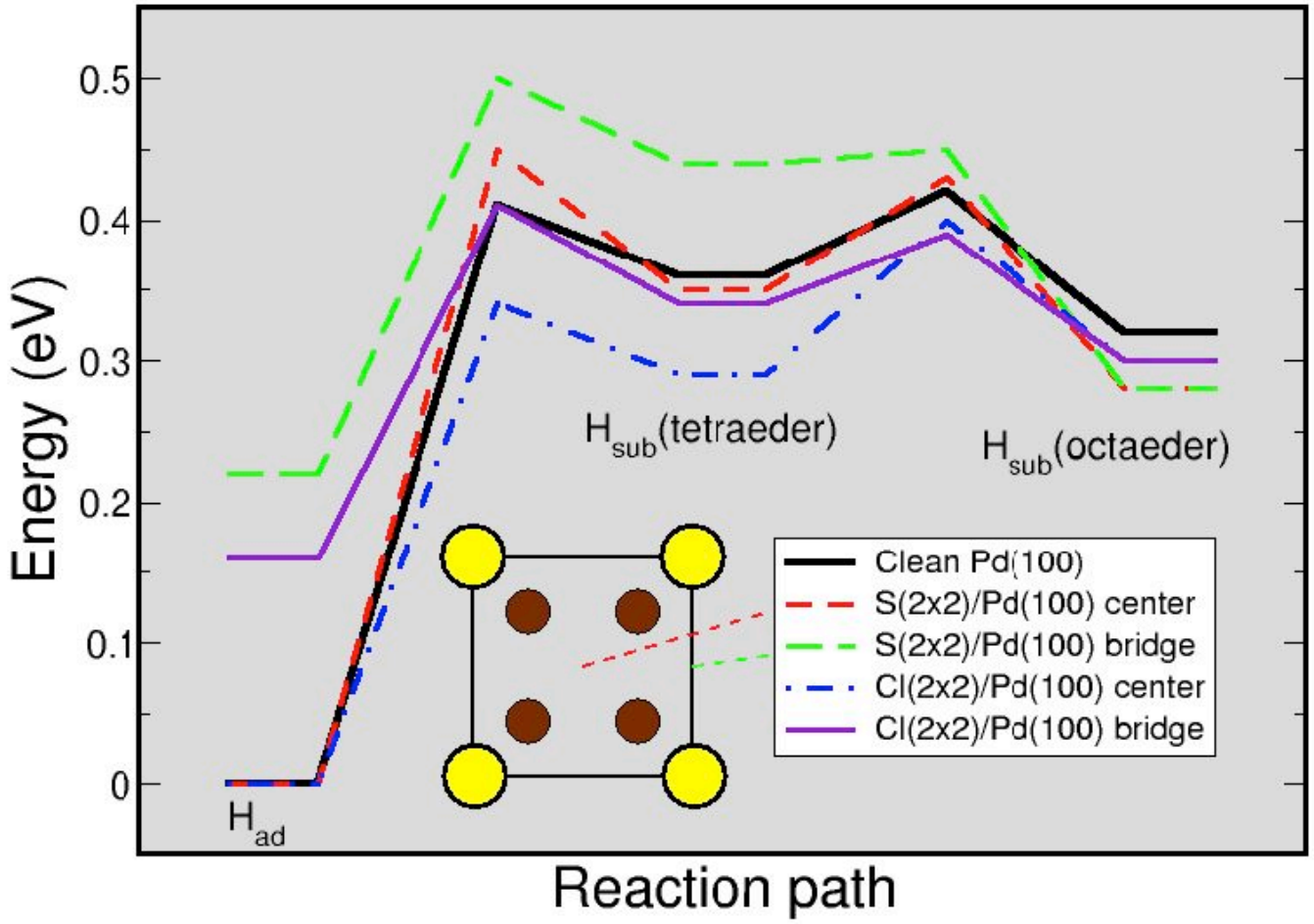


Subsurface penetration of one hydrogen atom through the hollow site near the chlorine atom

Without chlorine or sulphur coverage, no single subsurface penetration events observed for H/Pd(100) but rather concerted subsurface penetration

Absorption paths of H on S- and Cl-covered Pd(100)

A. Groß, Surf. Sci. **608**, 249254 (2013).

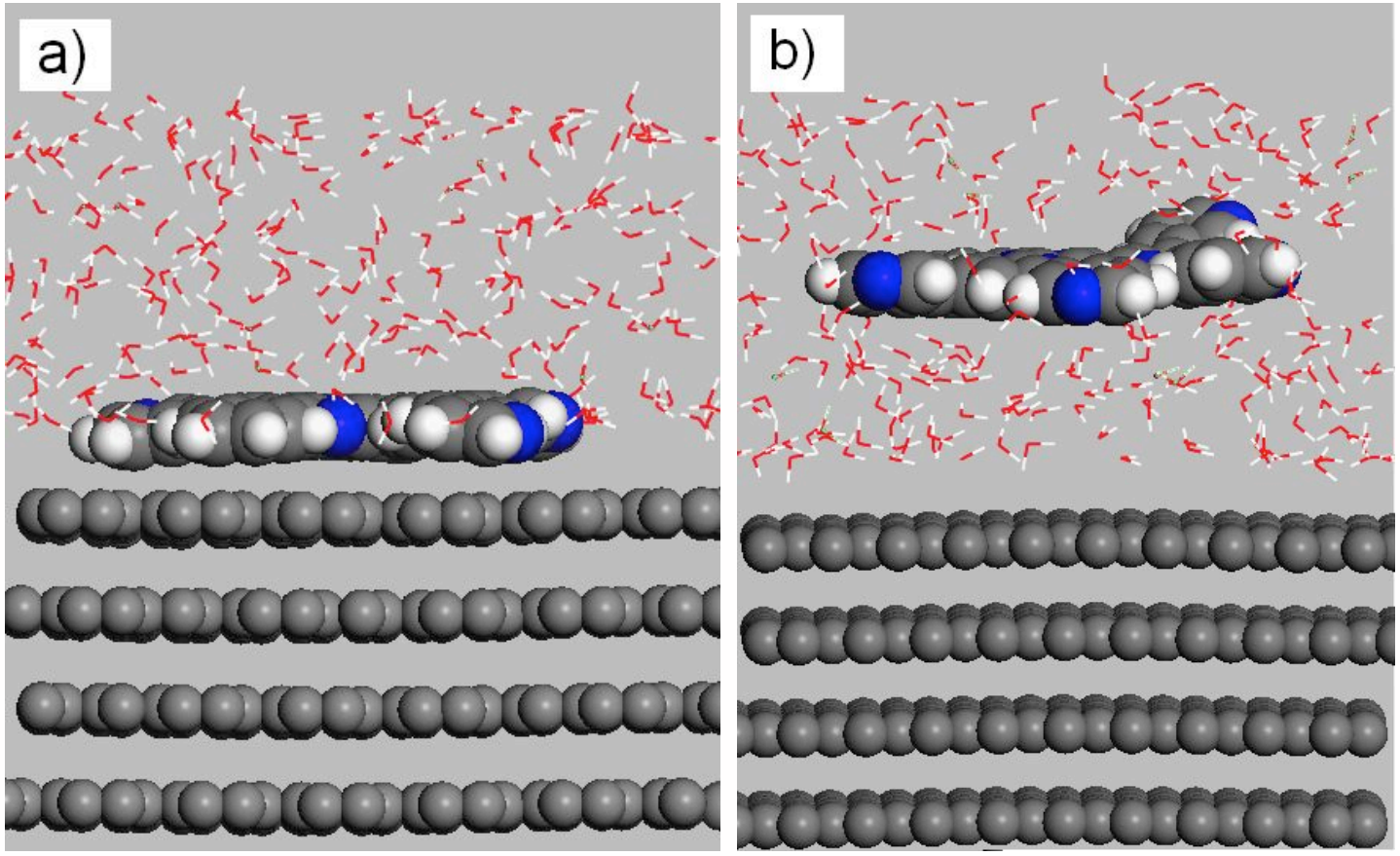


Subsurface penetration facilitated through the destabilization of the H-adsorption sites close to the adatoms

Adsorption at the solid-liquid interface

D. Künzel, A. Groß, Beilstein J. Nanotechnol. **4**, 267 (2013).

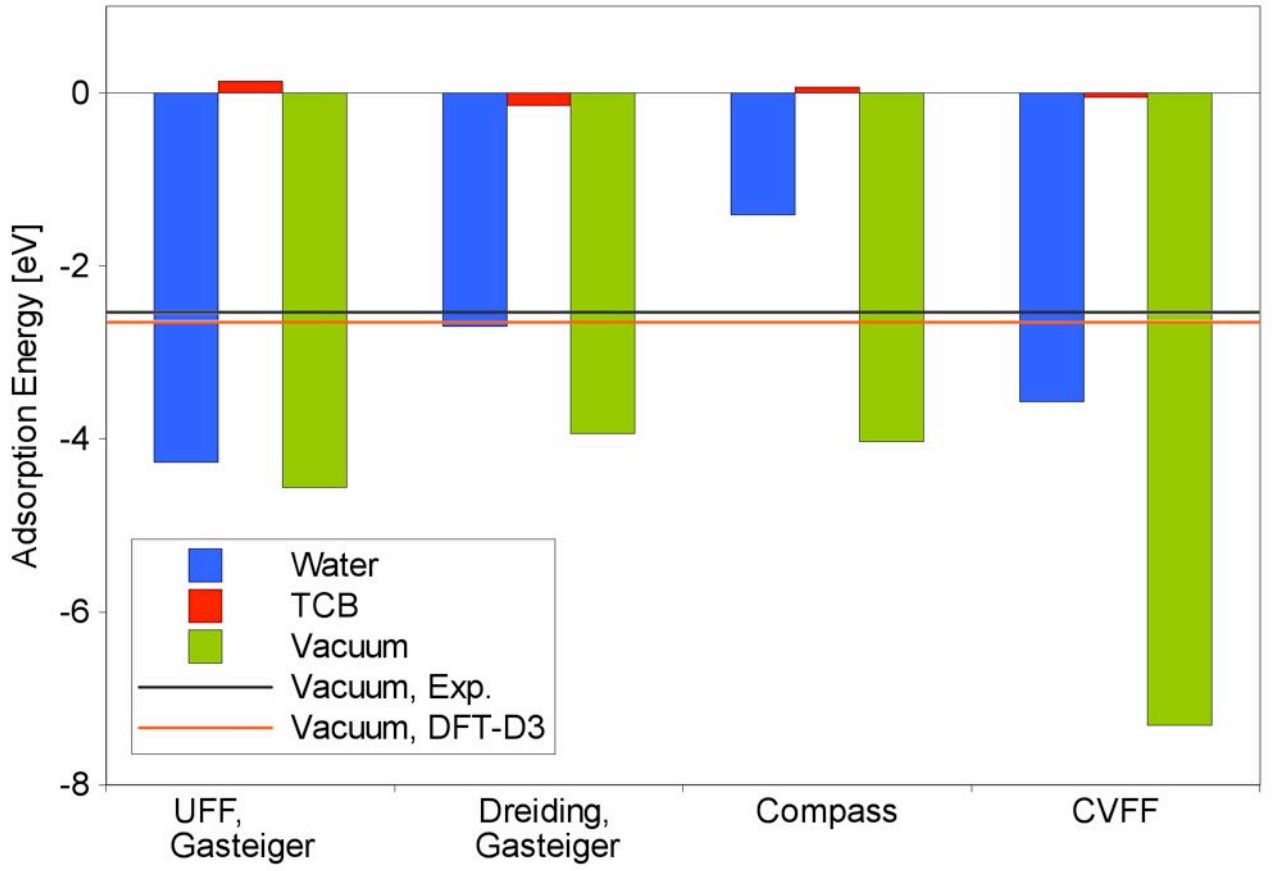
Reference state: solvated molecule



Calculation of thermal averages

Free energies of adsorption of BTP on graphite

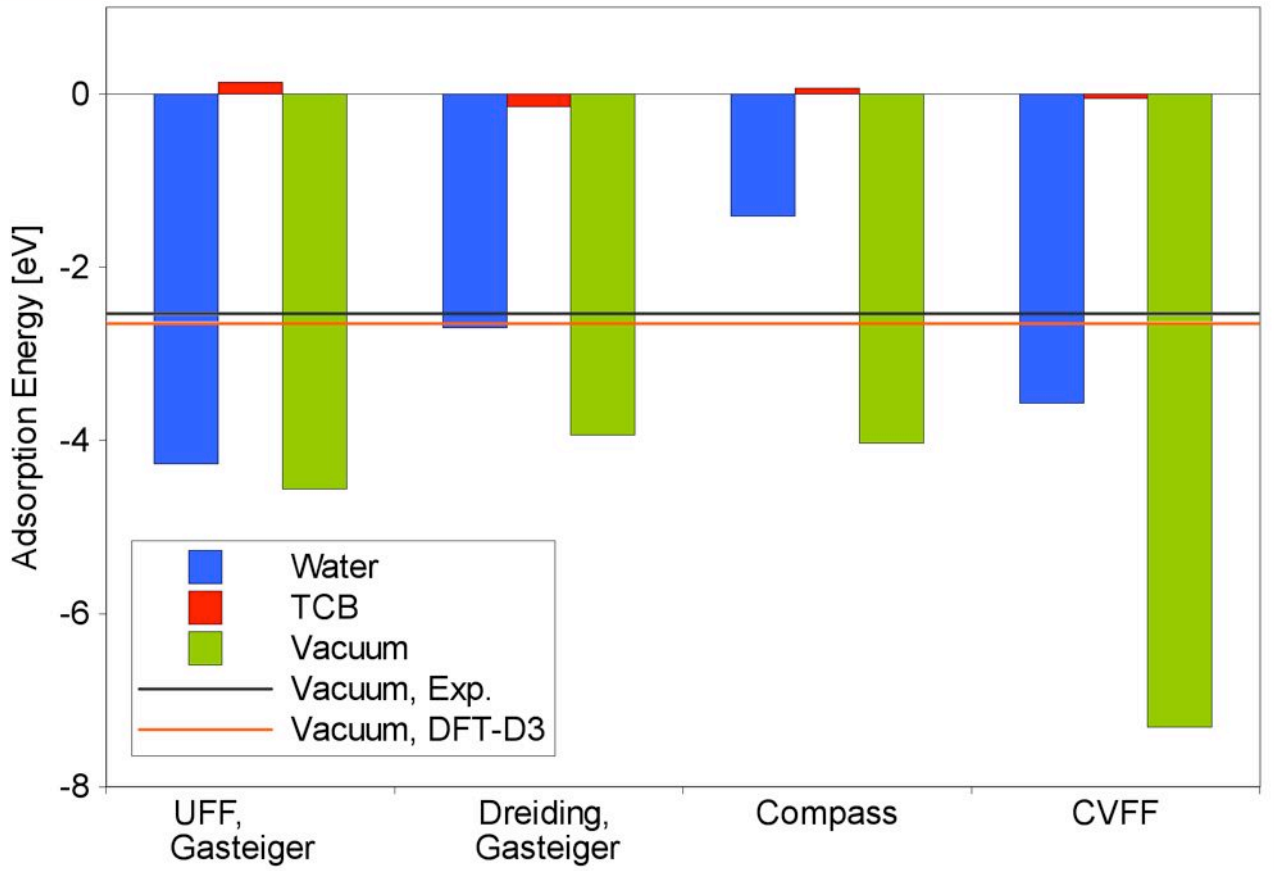
D. Künzel, A. Groß, Beilstein J. Nanotechnol. **4**, 267 (2013).



Small variation in adsorption energies: error cancelation

Free energies of adsorption of BTP on graphite

D. Künzel, A. Groß, Beilstein J. Nanotechnol. **4**, 267 (2013).

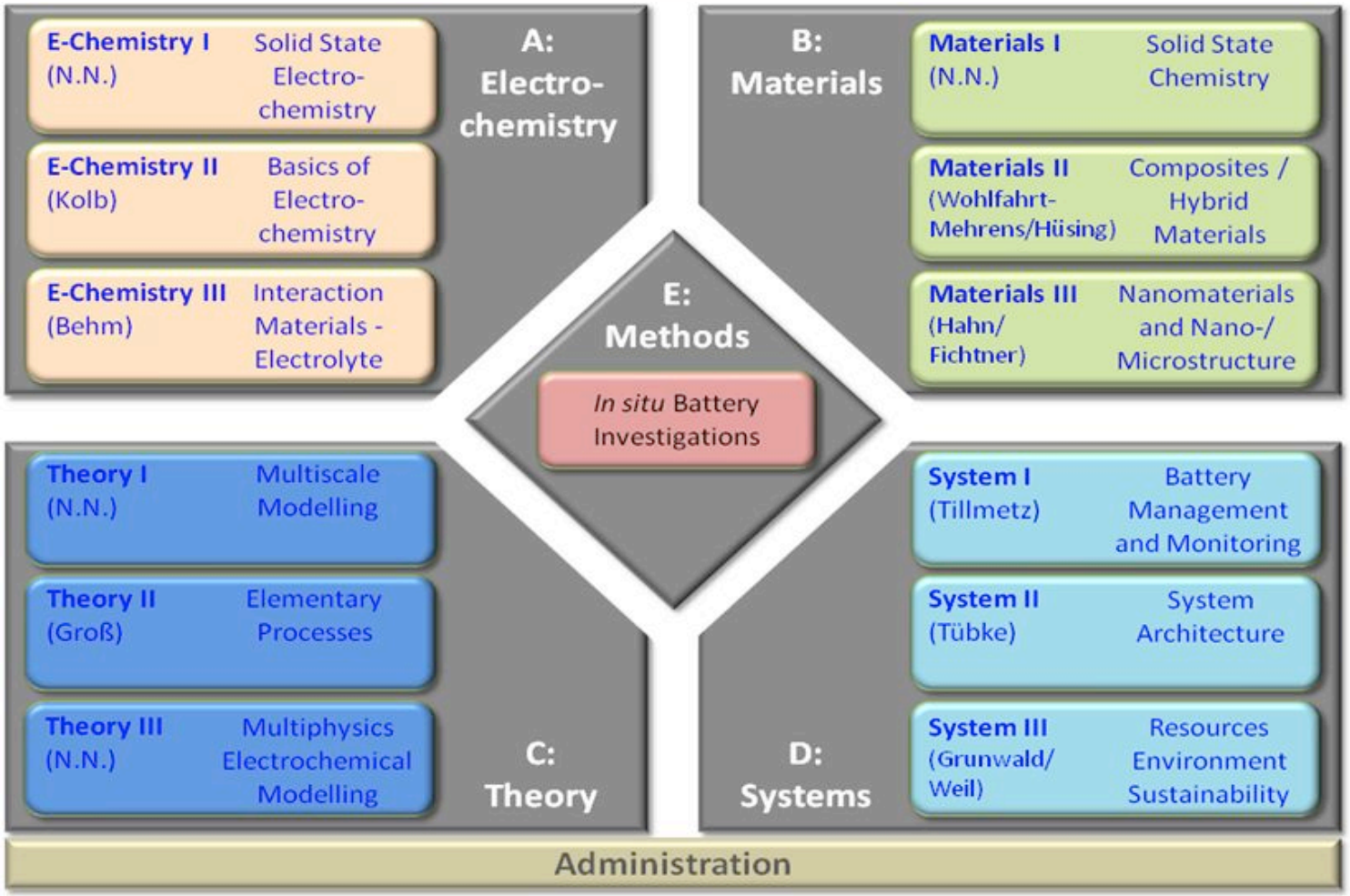


Small variation in adsorption energies: error cancelation

Adsorption of BTP molecule on graphite in TCB thermoneutral ⇒ graphite acts as a template that stabilizes the formation of ordered BTP layers

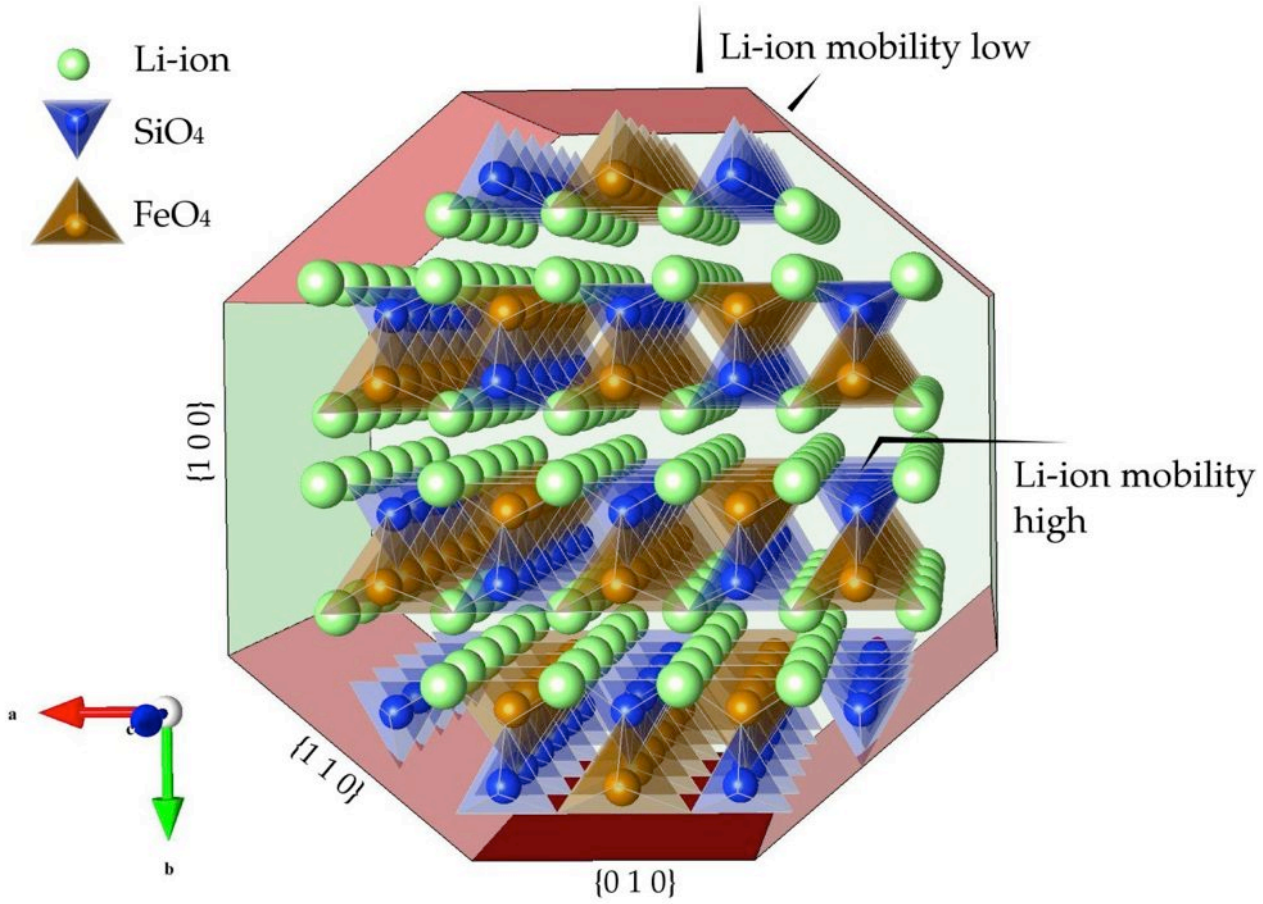
Helmholtz Institute Ulm (HIU)

HIU Electrochemical Energy Storage – established January 1, 2011



Project in the HIU: Structure of Li_2FeSiO_4 nanocrystallites

N. Hörmann and A. Groß, submitted to J. Solid State Electrochem.



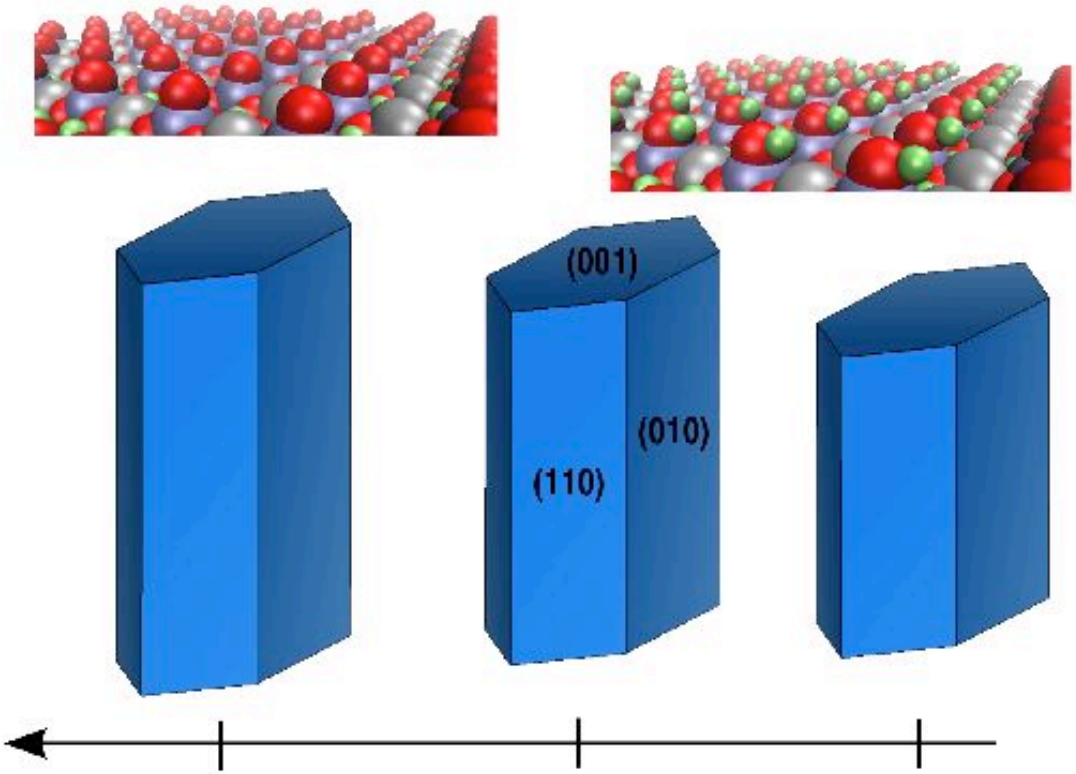
Preparation of nano-sized Li_2FeSiO_4 crystallites in order to reduce transport limitation

Collaboration with N. Hüsing (Univ. of Salzburg) and M. Wohlfahrt-Mehrens (ZSW Ulm)

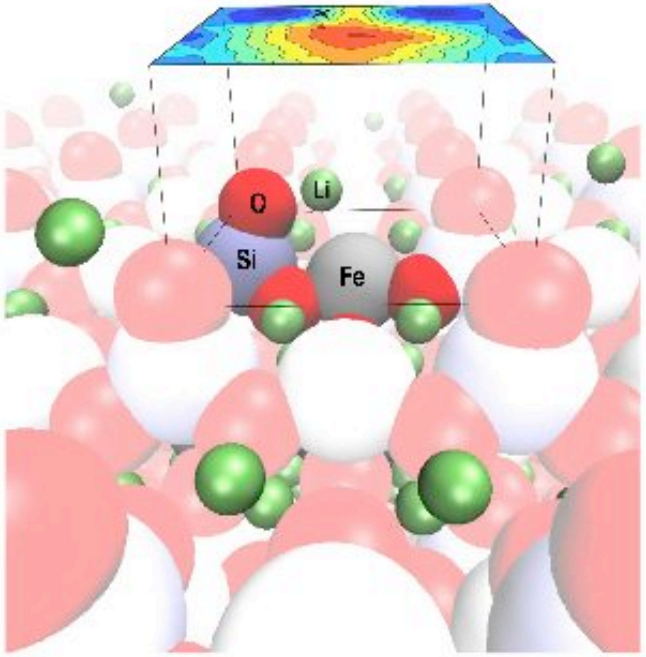
Surface properties of Pmn2/1 Li_2FeSiO_4

N. Hörmann and A. Groß, submitted to J. Solid State Electrochem.

Equilibrium morphology (Wulff-shape) as a function of Li chemical potential

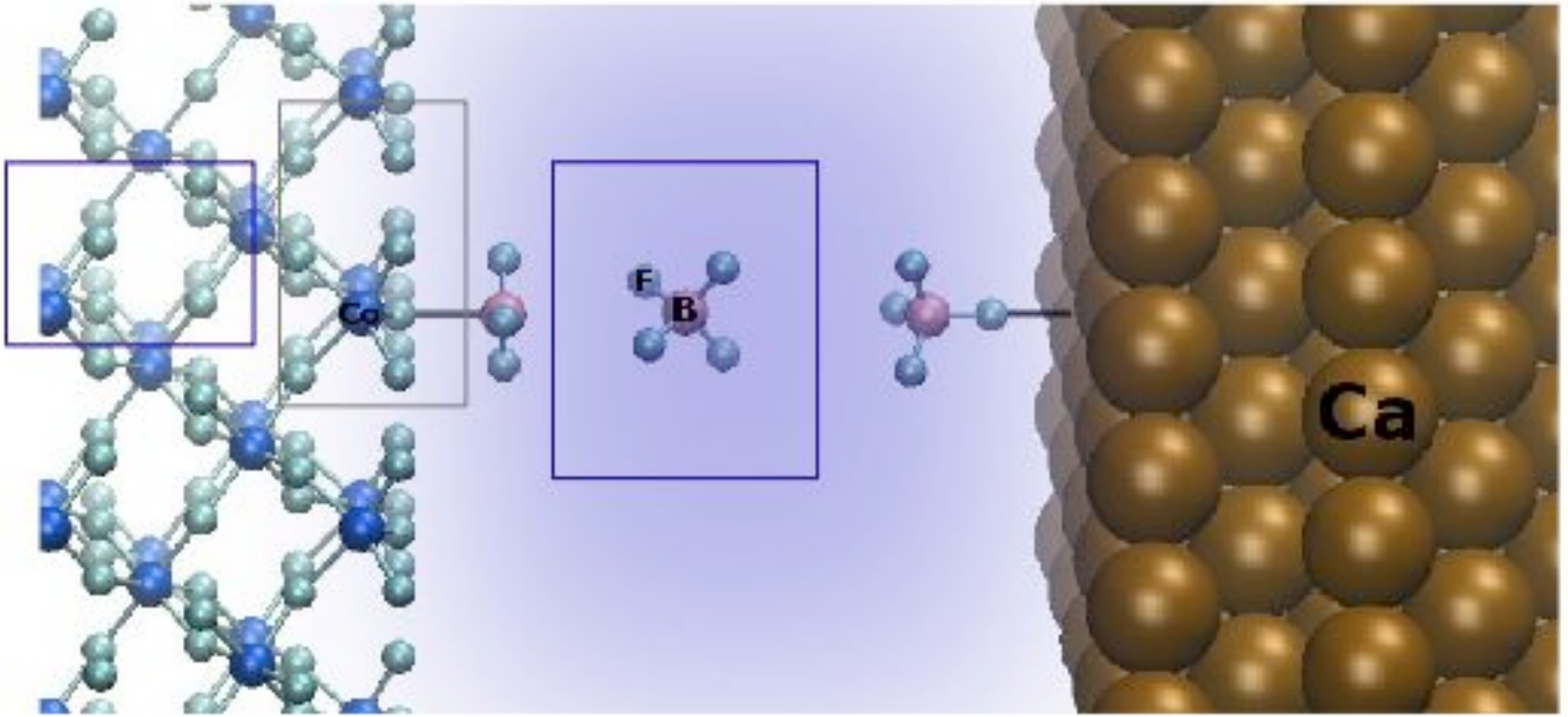


Potential energy landscape for Li Diffusion on (001):



Transport in batteries with liquid electrolytes

Katrin Tonigold and Axel Groß

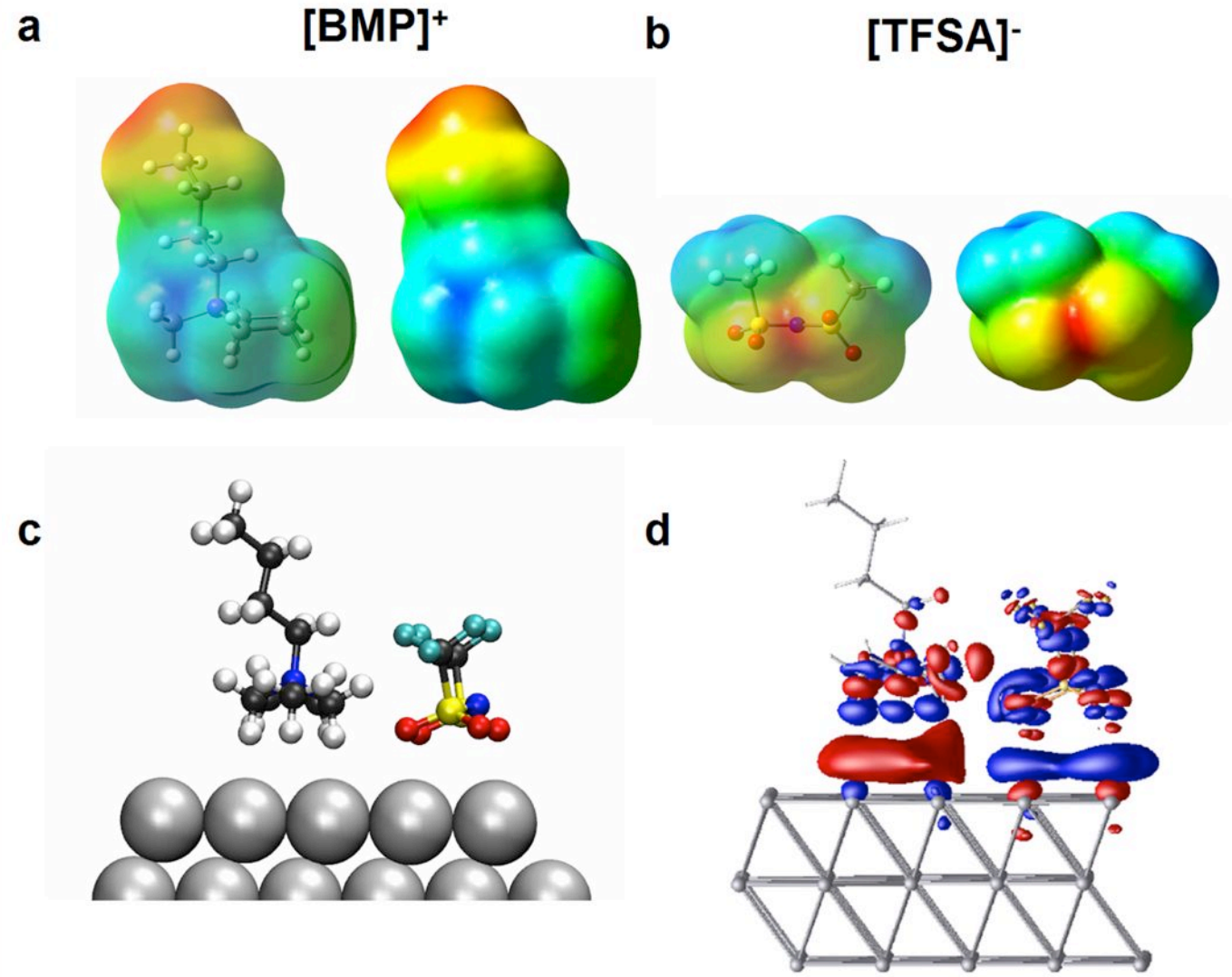


Search for shuttle molecules for fluoride-ion batteries

Collaboration with Maximilian Fichtner, KIT, HIU

Ionic Liquids on Ag(111)

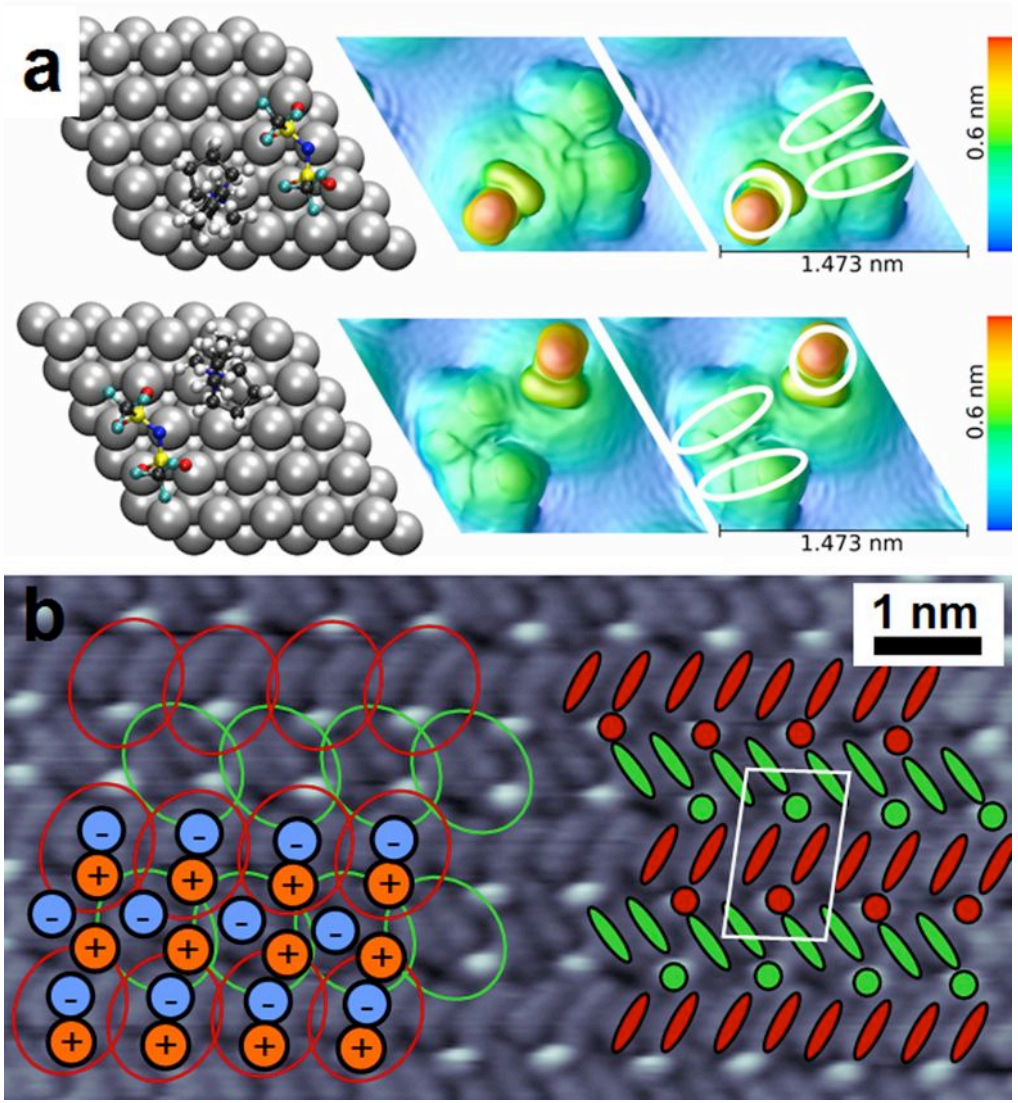
F. Buchner, K. Forster-Tonigold, B. Uhl, D. Alwast, N. Wagner, A. Groß and R.J. Behm, to be submitted.



E_{ads} (PBE) = -0.05 eV, E_{ads} (PBE-D3) = -1.30 eV

STM study of ionic liquids on Ag(111)

F. Buchner, K. Forster-Tonigold, B. Uhl, D. Alwast, N. Wagner, A. Groß and R.J. Behm, to be submitted.



DFT yields interpretation of STM images

Conclusions

The theoretical description of processes on surfaces based on first-principles electronic structure calculations is able to elucidate microscopic mechanisms and thus contributes to enhance our understanding of electrochemical processes at the solid-liquid interface

Acknowledgments

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Christian Mosch
Tanglaw Roman
Sebastian Schnur
Katrin Tonigold

TU München

Ataollah Roudgar
(now Vancouver, Canada)

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DAAD (German Academic Exchange Servive)
AvH (Alexander-von-Humboldt Foundation)
Baden-Württemberg Stiftung
Adenauer Stiftung

Computer time

NIC (John-von-Neumann Computing Center, Jülich)
kiz (Computer Center, Ulm University)
bwGrid