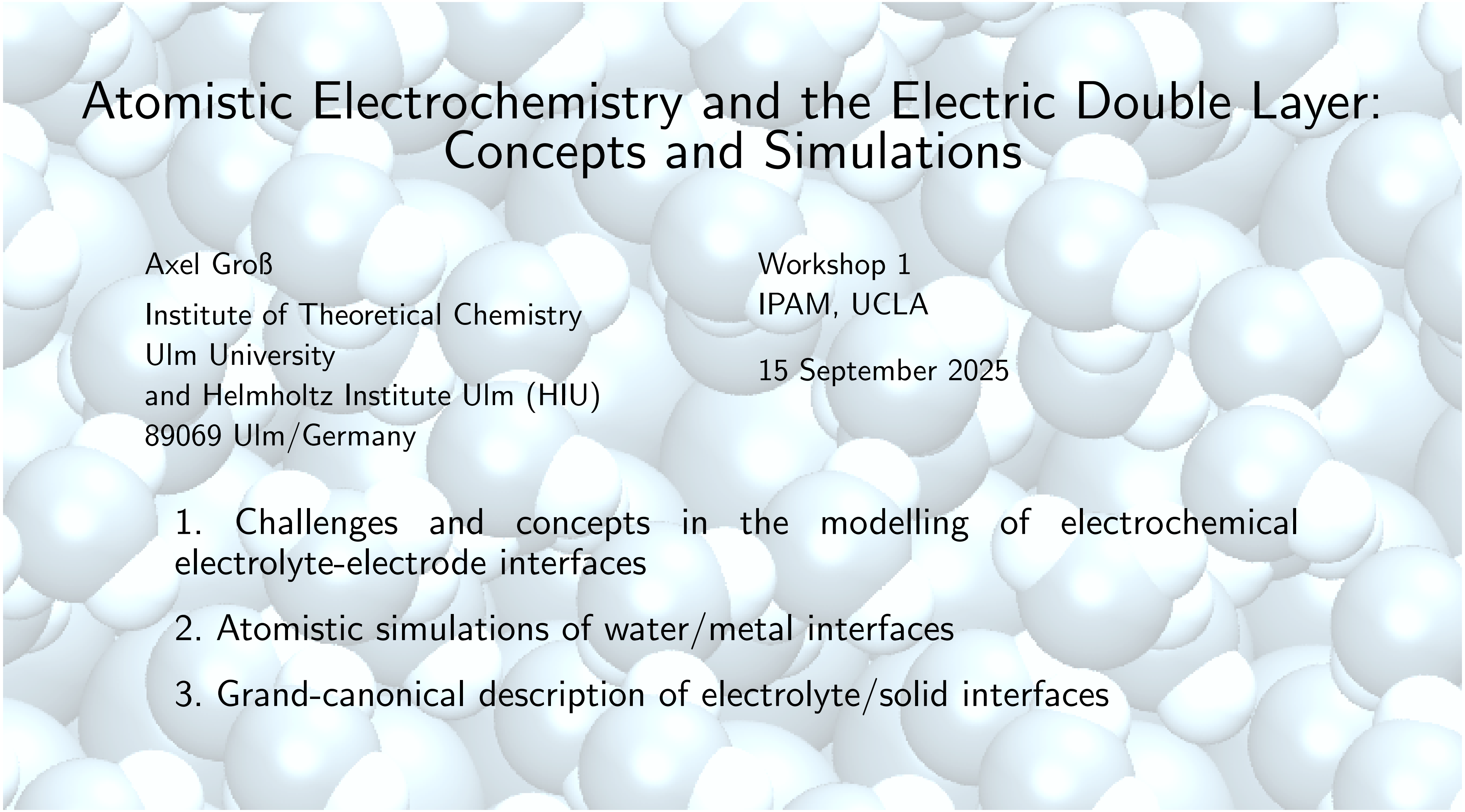


Atomistic Electrochemistry and the Electric Double Layer: Concepts and Simulations

Axel Groß

Institute of Theoretical Chemistry
Ulm University
and Helmholtz Institute Ulm (HIU)
89069 Ulm/Germany

Workshop 1
IPAM, UCLA

15 September 2025

1. Challenges and concepts in the modelling of electrochemical electrolyte-electrode interfaces
2. Atomistic simulations of water/metal interfaces
3. Grand-canonical description of electrolyte/solid interfaces

From free electrons to bound electrons

Renewable energies

Definition: energy carriers from sources, which continuously regenerate on a human time scale such as sun light, wind, rain, tides, waves and geothermal heat

From free electrons to bound electrons

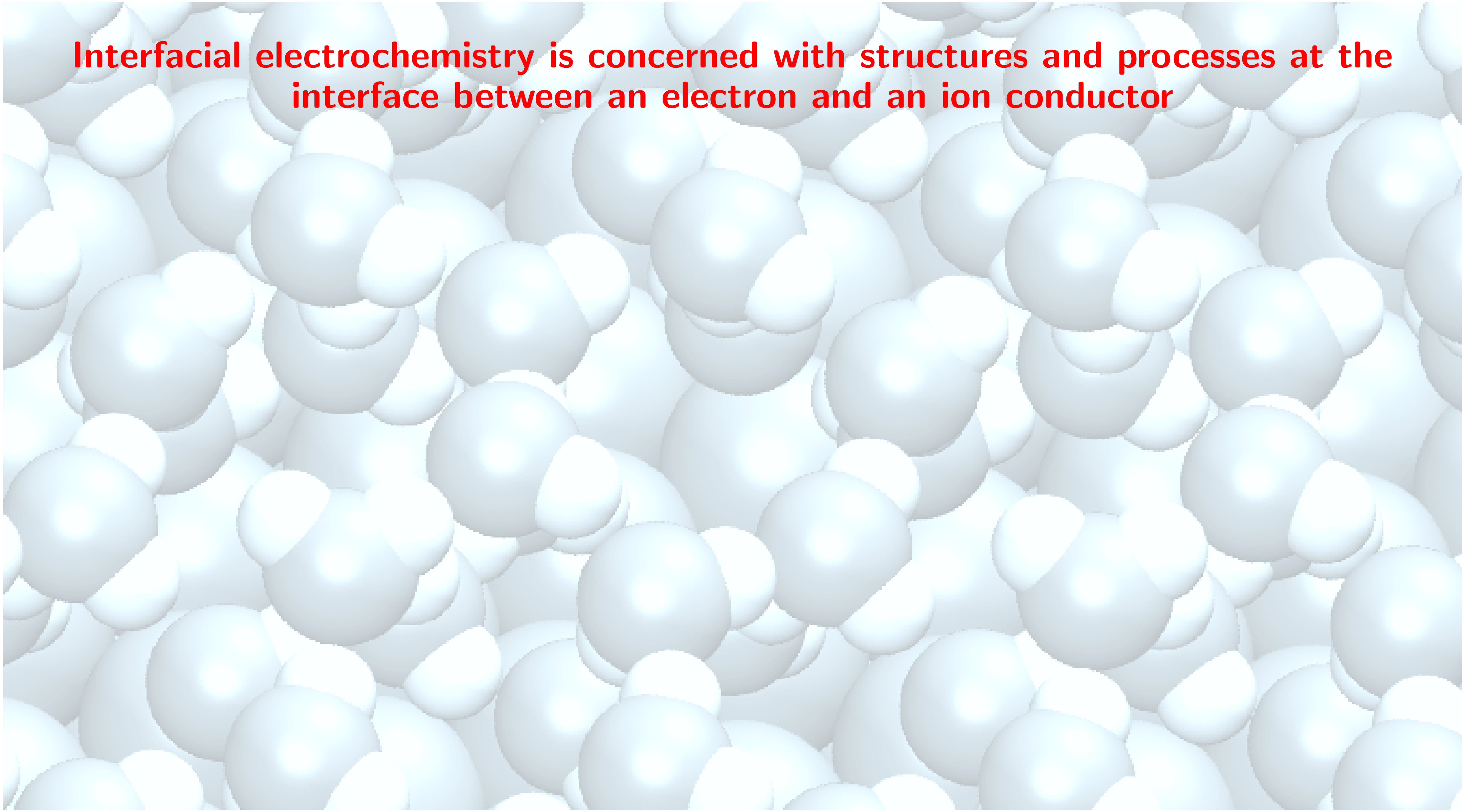
Renewable energies

Definition: energy carriers from sources, which continuously regenerate on a human time scale such as sun light, wind, rain, tides, waves and geothermal heat

Problem: renewables energies are often volatile ⇒ Energy need to be stored

Most efficient energy storage system: chemical bond

Electrochemical energy storage and conversion



Interfacial electrochemistry is concerned with structures and processes at the interface between an electron and an ion conductor

Electrochemical energy storage and conversion

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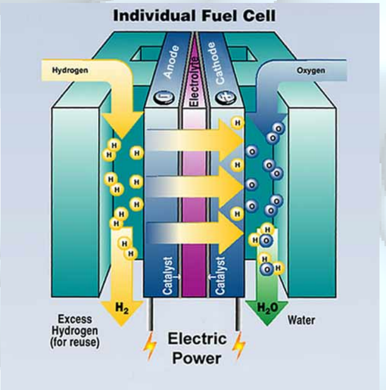

Fuel cells

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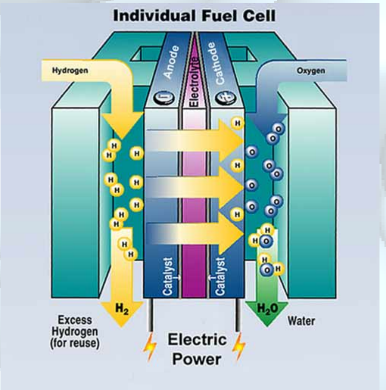

Fuel cells

Batteries

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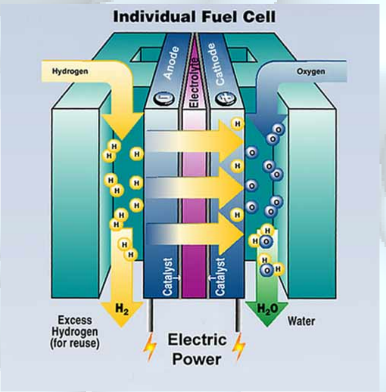

Fuel cells

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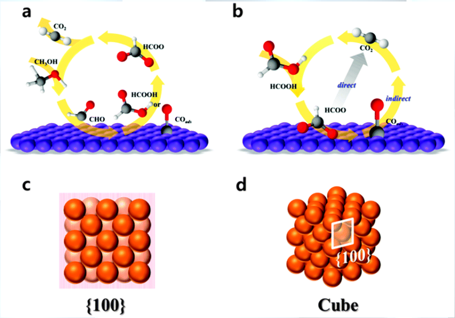

Electro-catalysis

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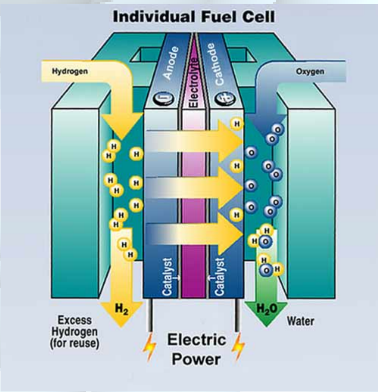

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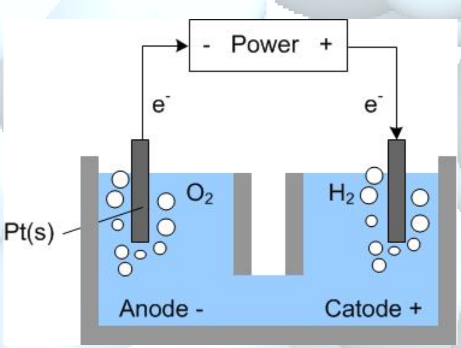

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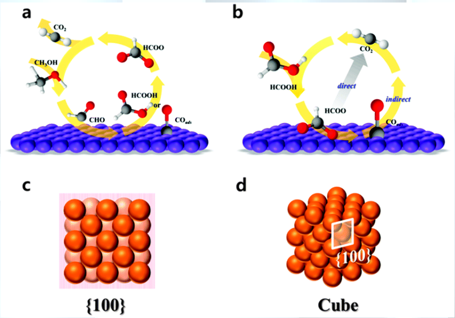

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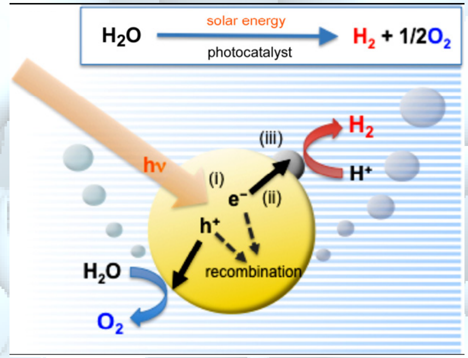
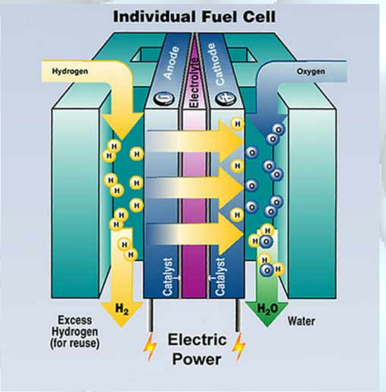


Photo-catalytic water splitting



Fuel cells

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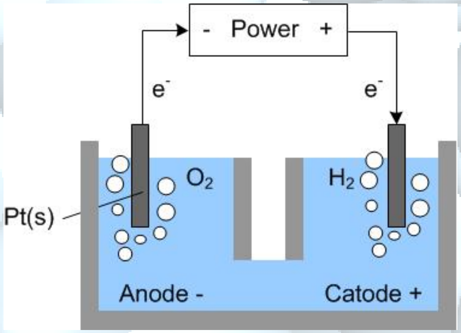

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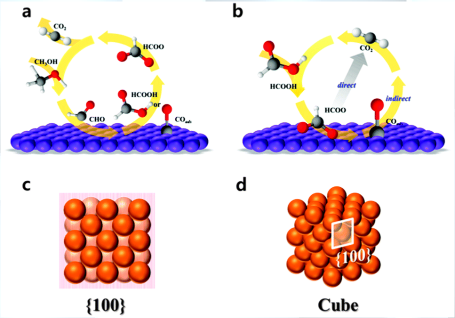

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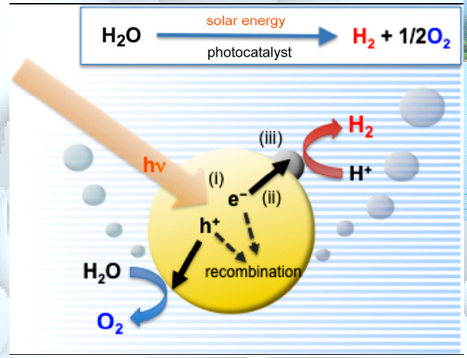
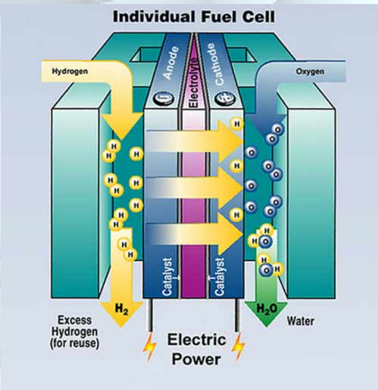


Photo-catalytic water splitting

Corrosion



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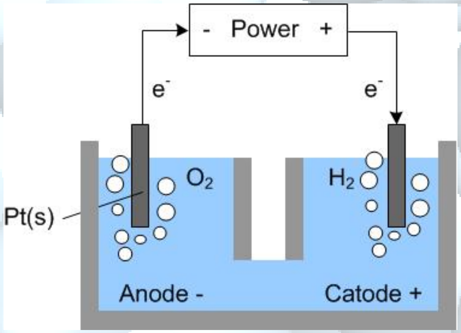

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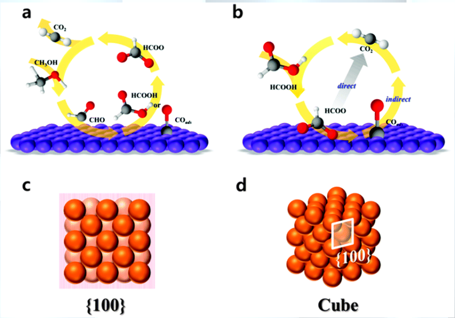

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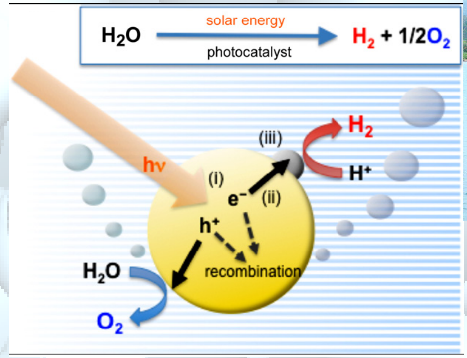

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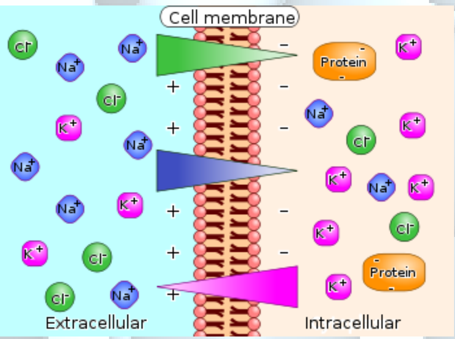
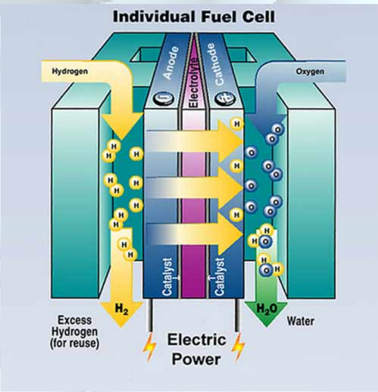


Life science



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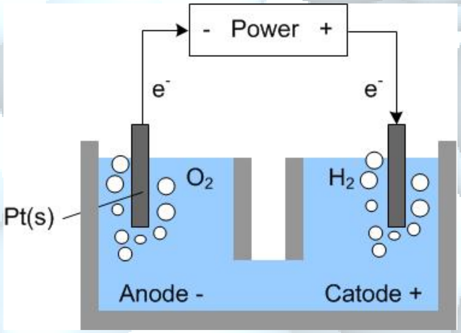

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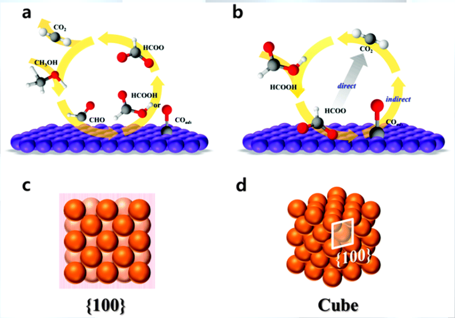
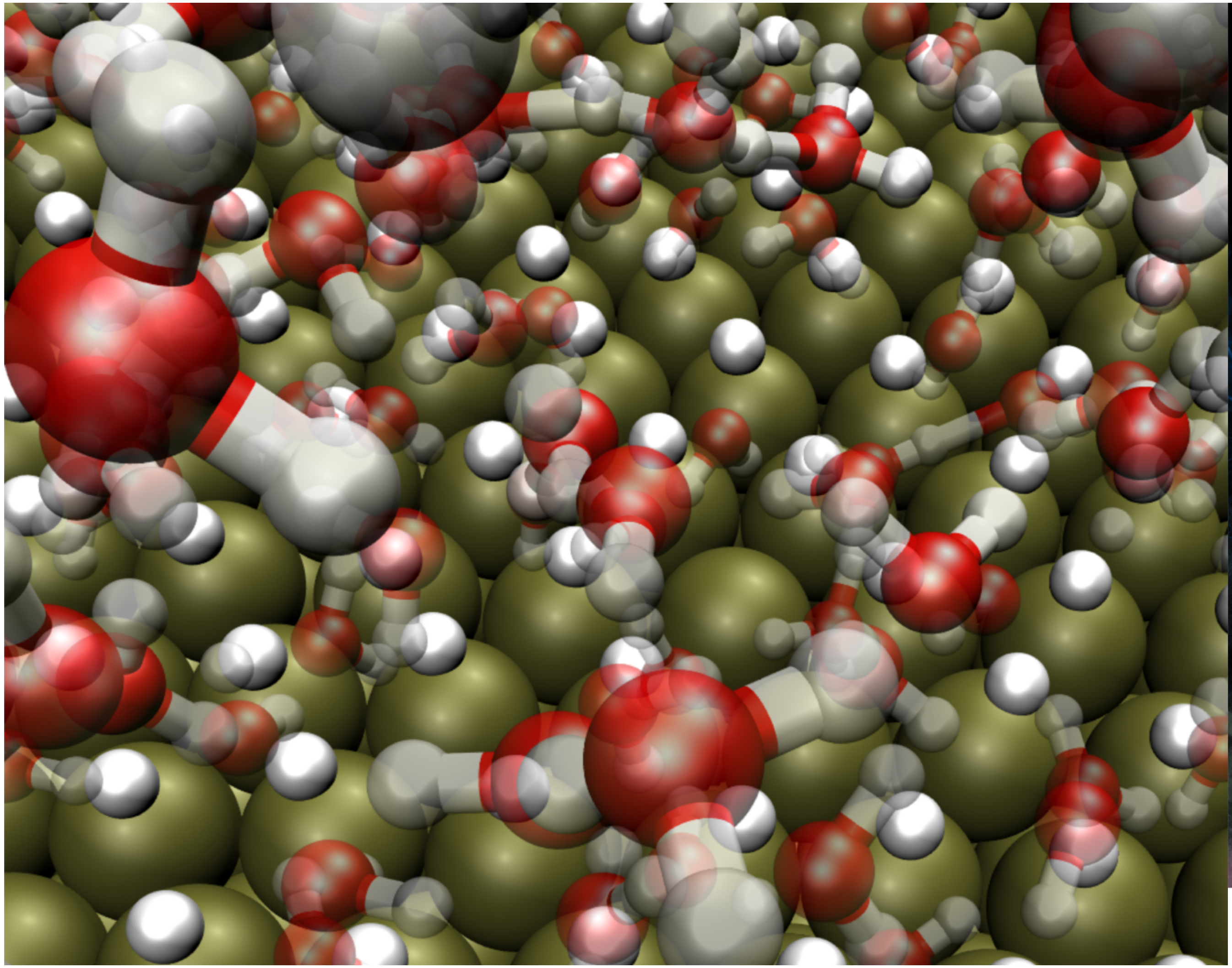
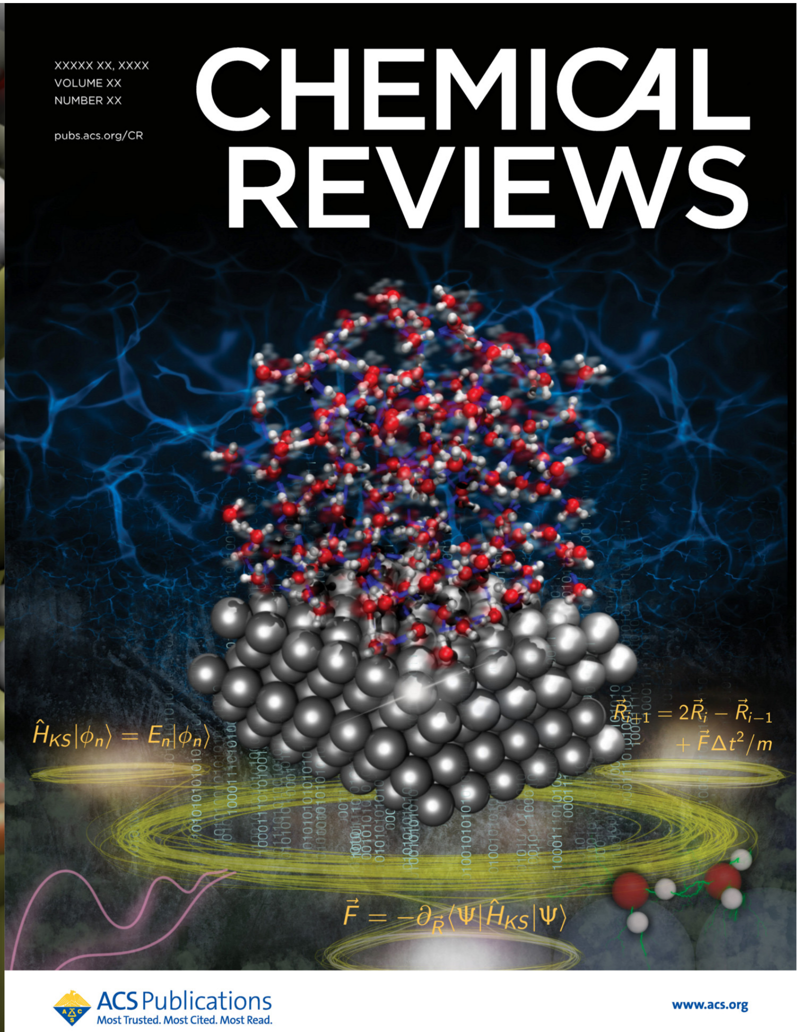


Electro-catalysis

Electrochemical electrolyte/electrode interfaces

Perspective: A. Groß, J. Phys. Chem. C **126**, 11439 (2022); Review: A. Groß, S. Sakong, Chem. Rev. **122**, 10746 (2022).





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CHEMICAL
REVIEWS

$\hat{H}_{KS}|\phi_n\rangle = E_n|\phi_n\rangle$

$\vec{R}_{i+1} = 2\vec{R}_i - \vec{R}_{i-1} + \vec{F}\Delta t^2/m$

$\vec{F} = -\partial_{\vec{R}}\langle\Psi|\hat{H}_{KS}|\Psi\rangle$

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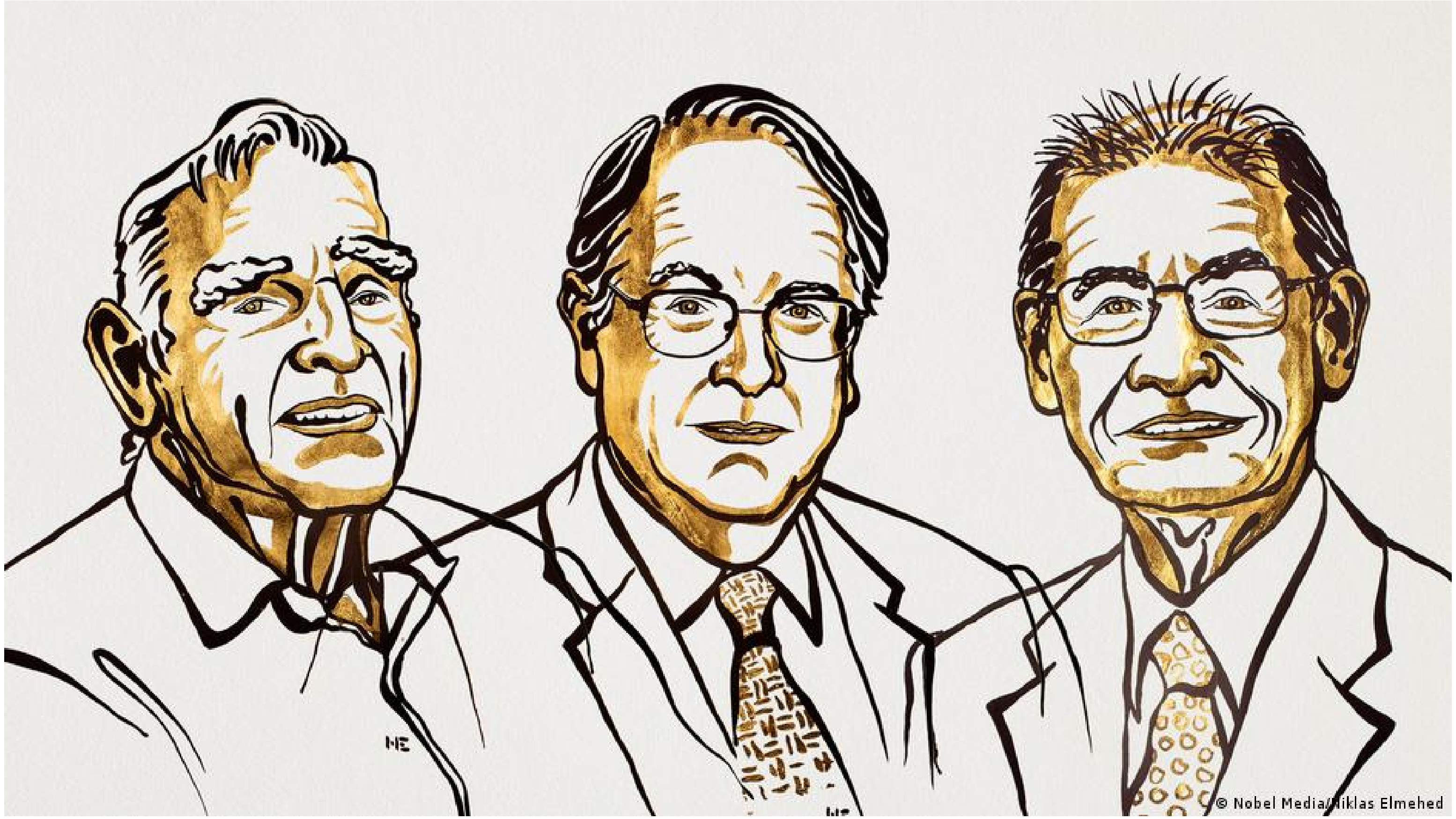
How can we deal with this complexity of electrochemical electrolyte/electrode interfaces which in principle requires to perform statistical averages in the case of liquid electrolytes?

Nobel Prize for Chemistry 2019



Quelle: Nobel Media

John B. Goodenough　M. Stanley Wittingham　Akira Yoshino

Nobel prize for Chemistry 2019 “for the development of lithium ion batteries”

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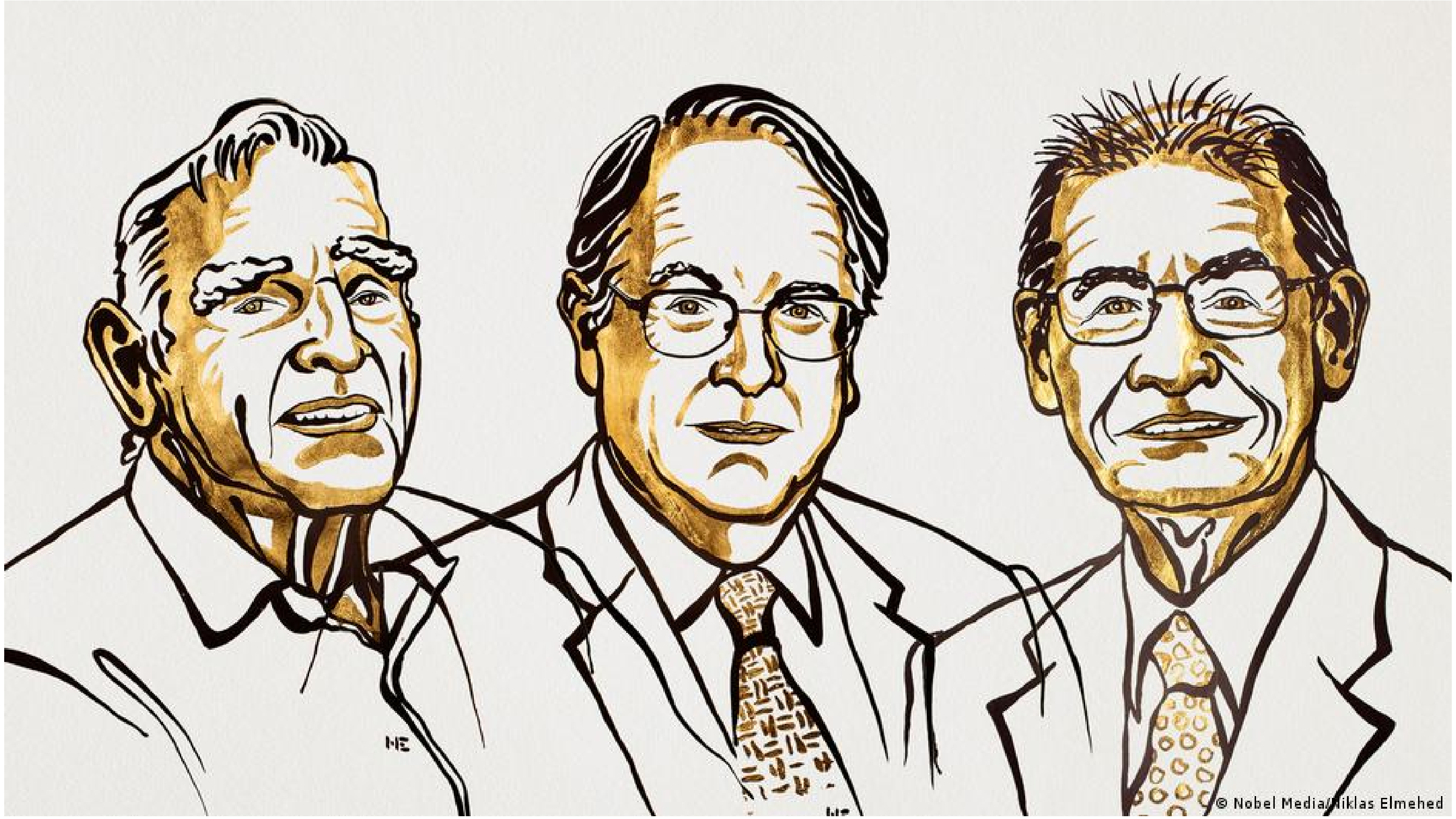

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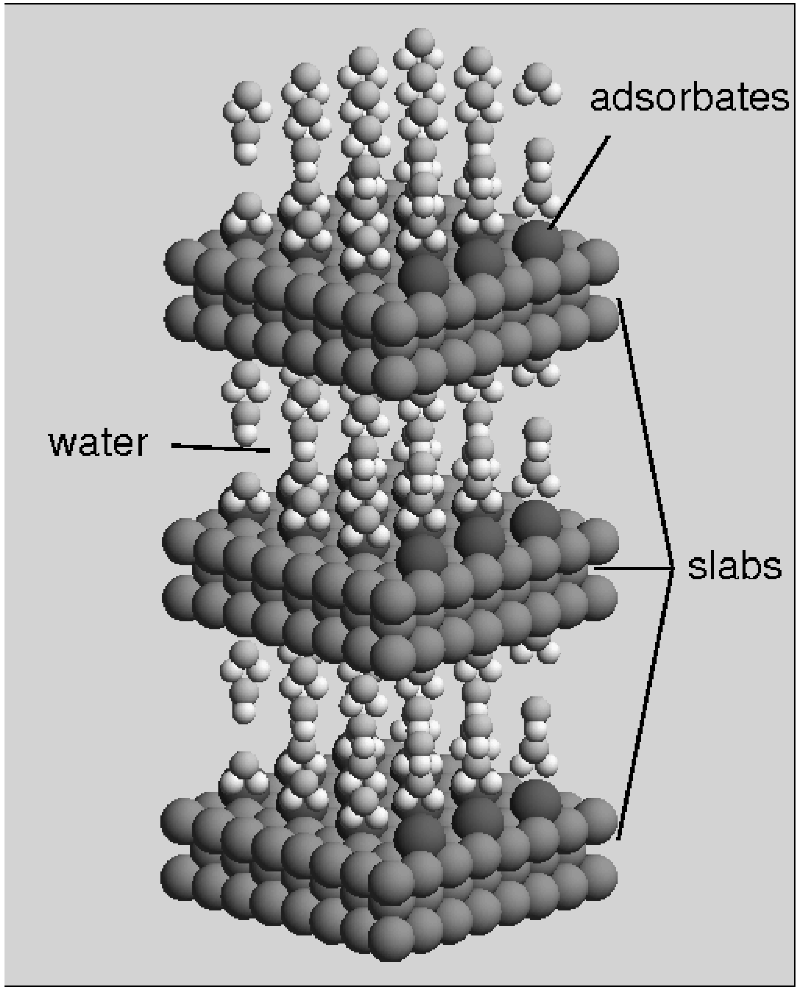
Nobel prize for Chemistry 2019 "for the development of lithium ion batteries"

⇒ Development of Li-ion batteries is not only based on technological advances, but also on demanding successful basic research

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

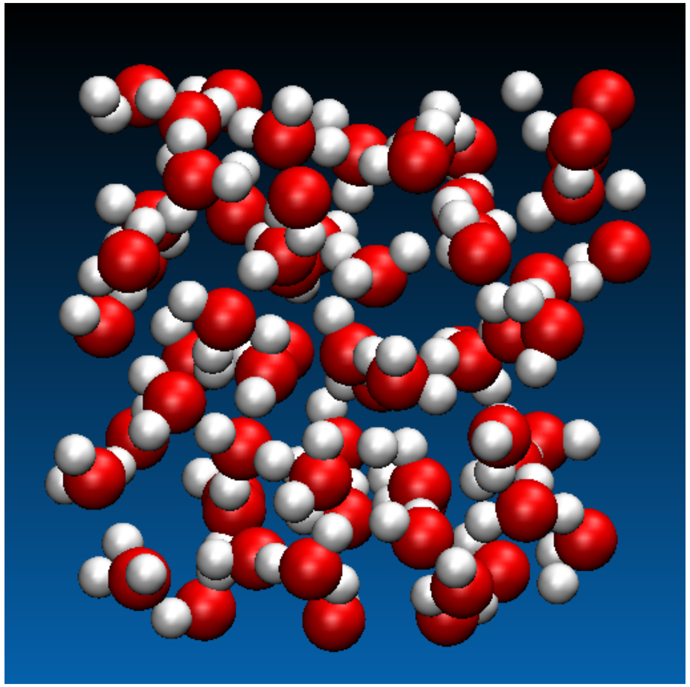
⇒ Approximations: GGA together with dispersion corrections

Collaboration with University Vienna:
Vienna Ab initio Simulation Package (VASP)

G. Kresse, J. Furthmüller, J. Hafner

Challenges in the theoretical treatment of electrochemical solid/liquid interfaces

Liquid electrolytes require to perform statistical averages, i.e., free energies instead of total energies have to be determined



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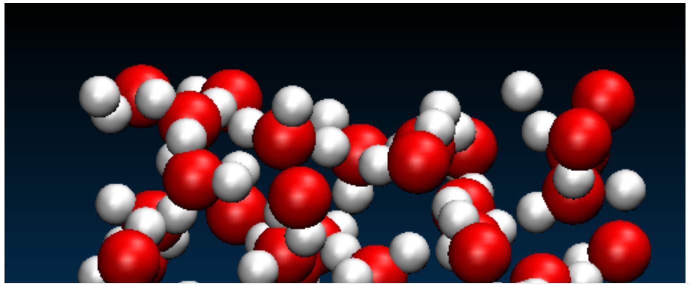

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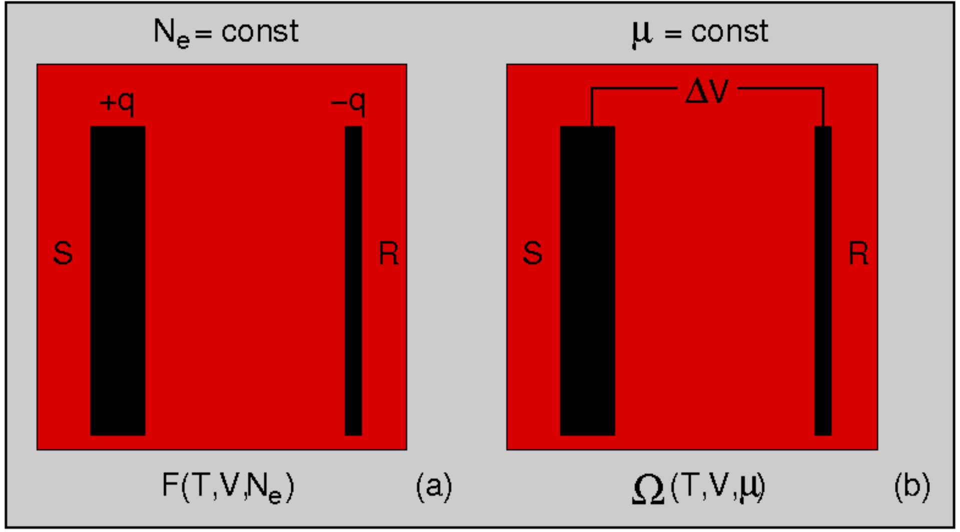

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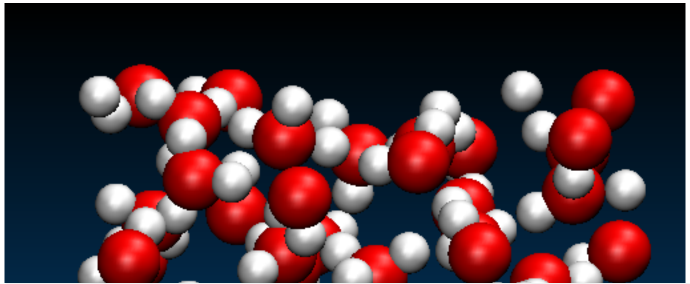

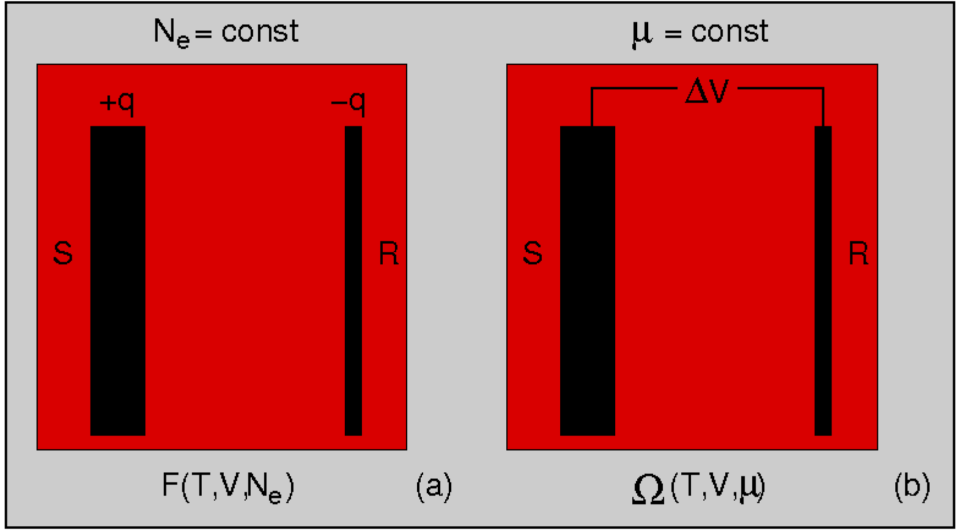

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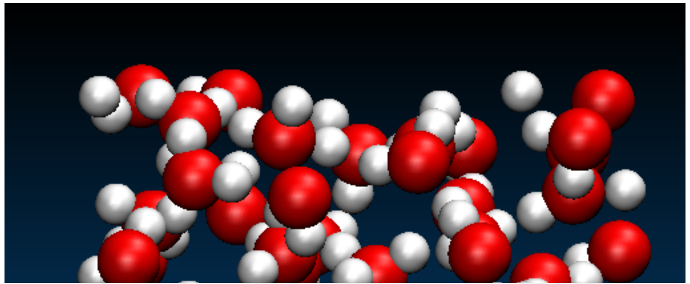

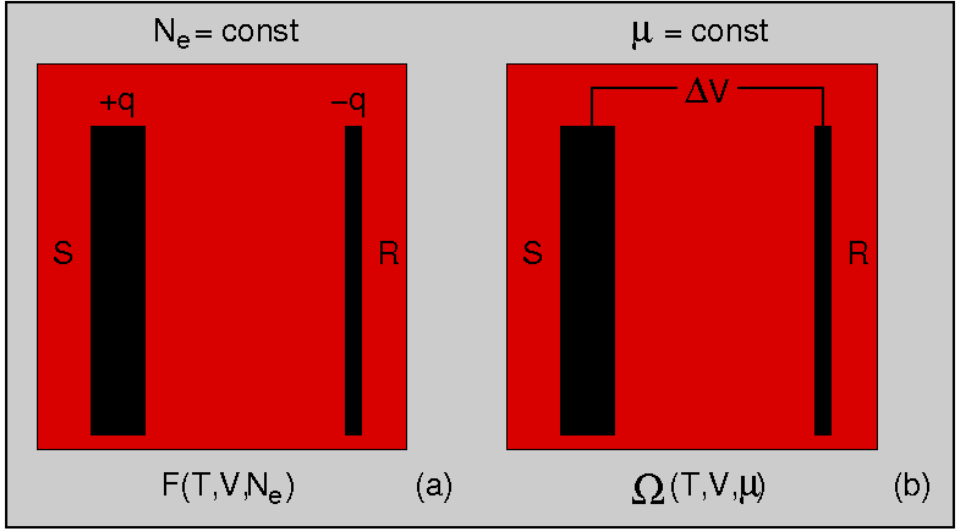

Proper ansatz: Reliable quantum chemistry calculations of these interfaces should be performed under potential control with an appropriate number of electrolyte molecules considered and their statistical nature taken into account through averaging over sufficiently long ab initio molecular dynamics simulations

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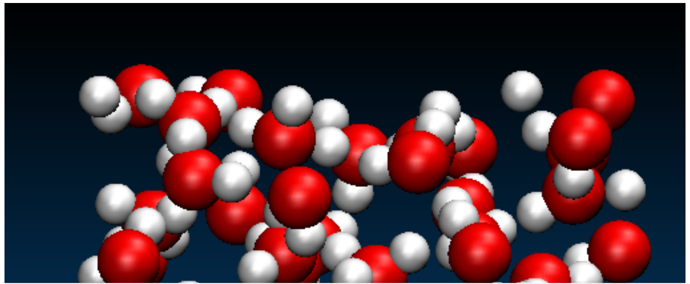

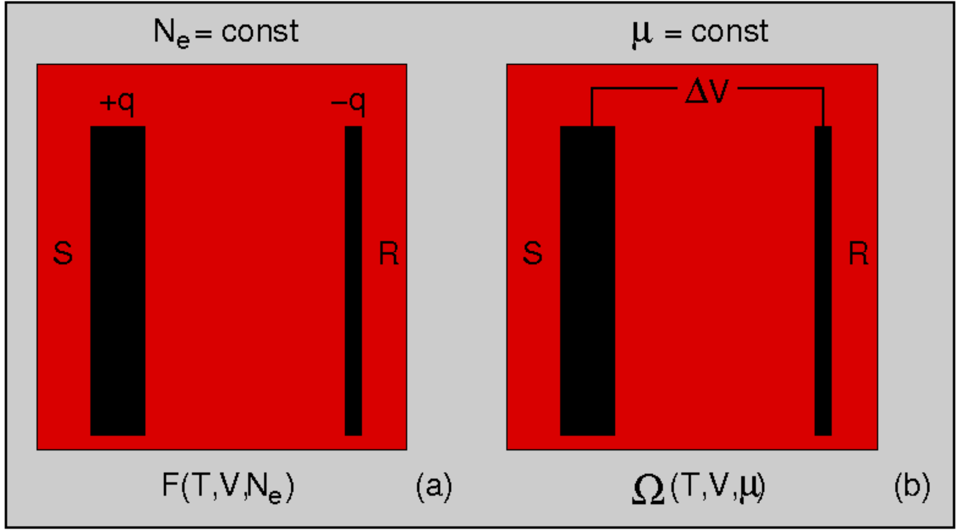

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Proper ansatz: Reliable quantum chemistry calculations of these interfaces should be performed under potential control with an appropriate number of electrolyte molecules considered and their statistical nature taken into account through averaging over sufficiently long ab initio molecular dynamics simulations

Unfortunately, such an approach is currently not possible and will probably not be possible for a long time due to technical and numerical obstacles

Electrical Double Layer I

A. Groß and S. Sakong , Curr. Opin. Electrochem. **14**, 1 (2019).

An electric double layer (EDL) forms whenever two conducting phases meet at an interface.

Wolfgang Schmickler, Reference Module in Chemistry, 2014.

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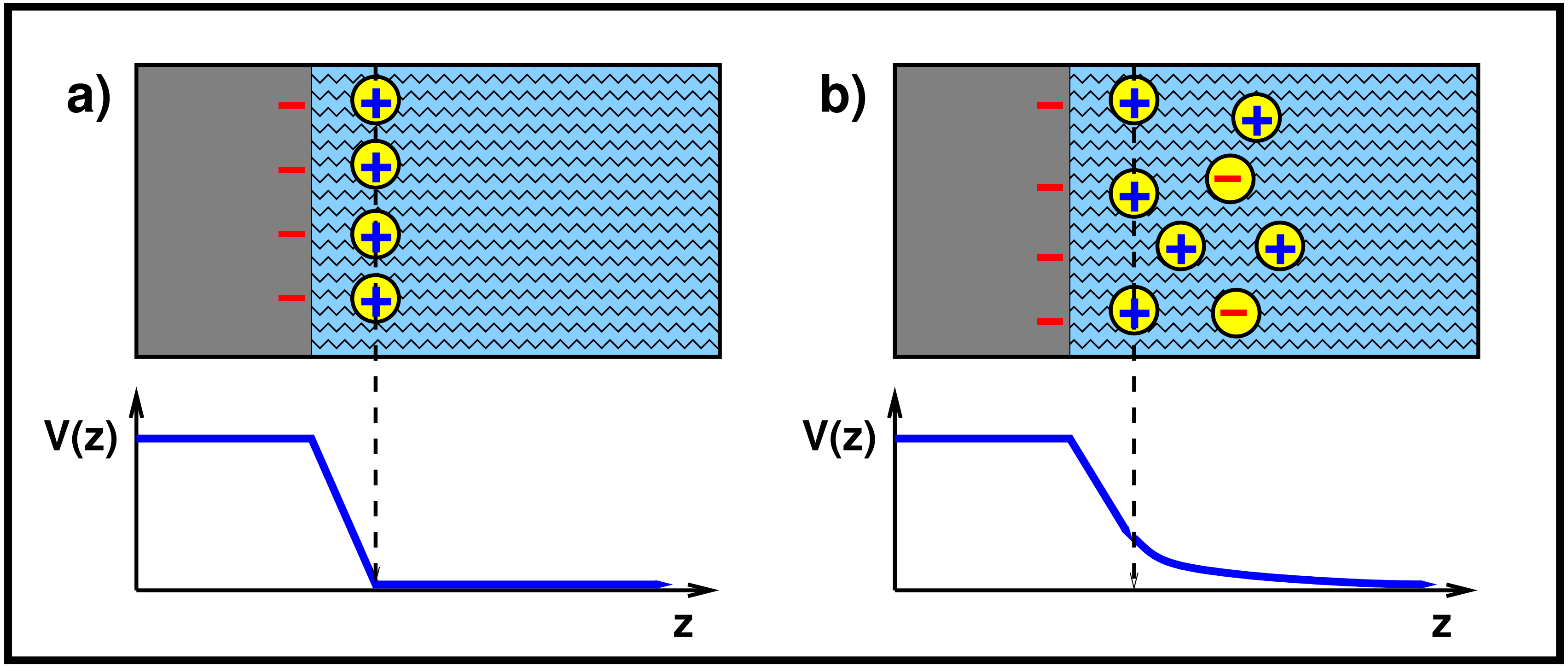

Helmholtz model

Diffuse layer added

Stern (1924): combined Helmholtz model with diffused layer proposed by Gouy and Chapman

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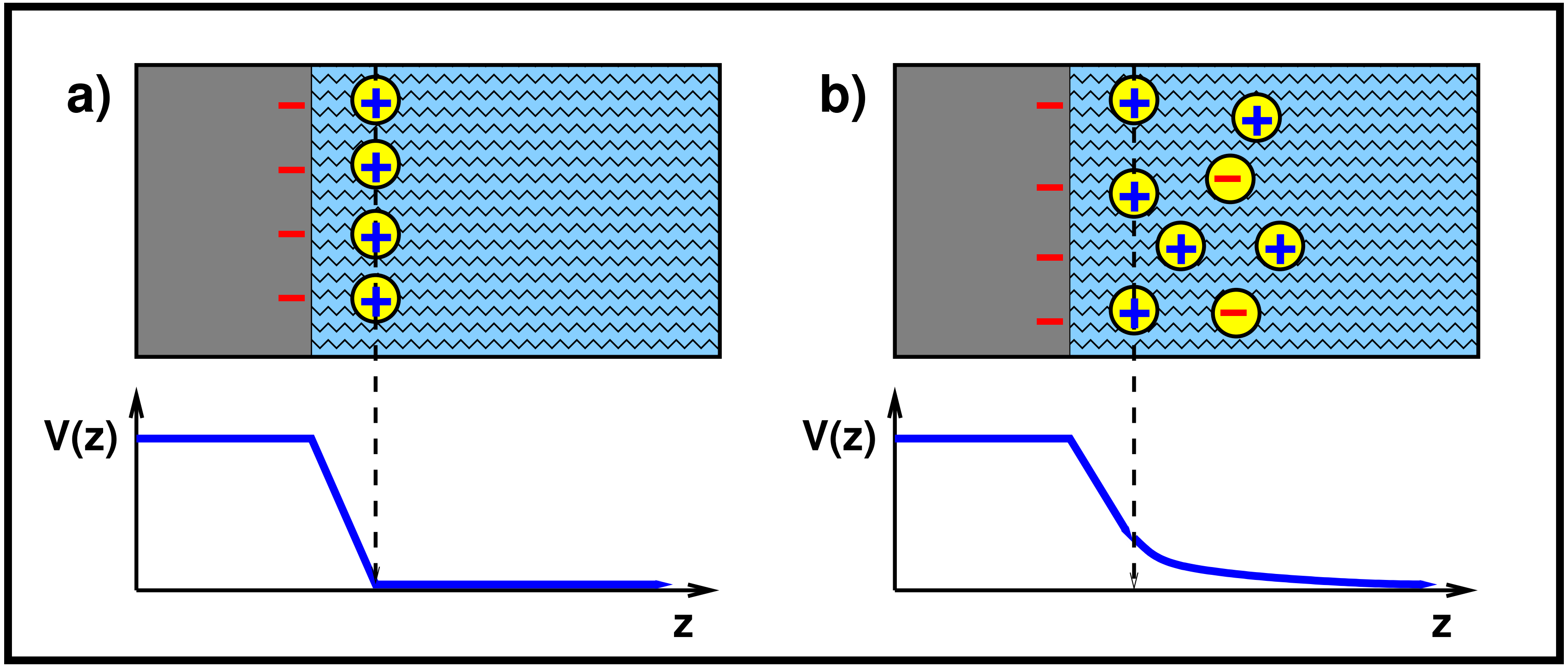

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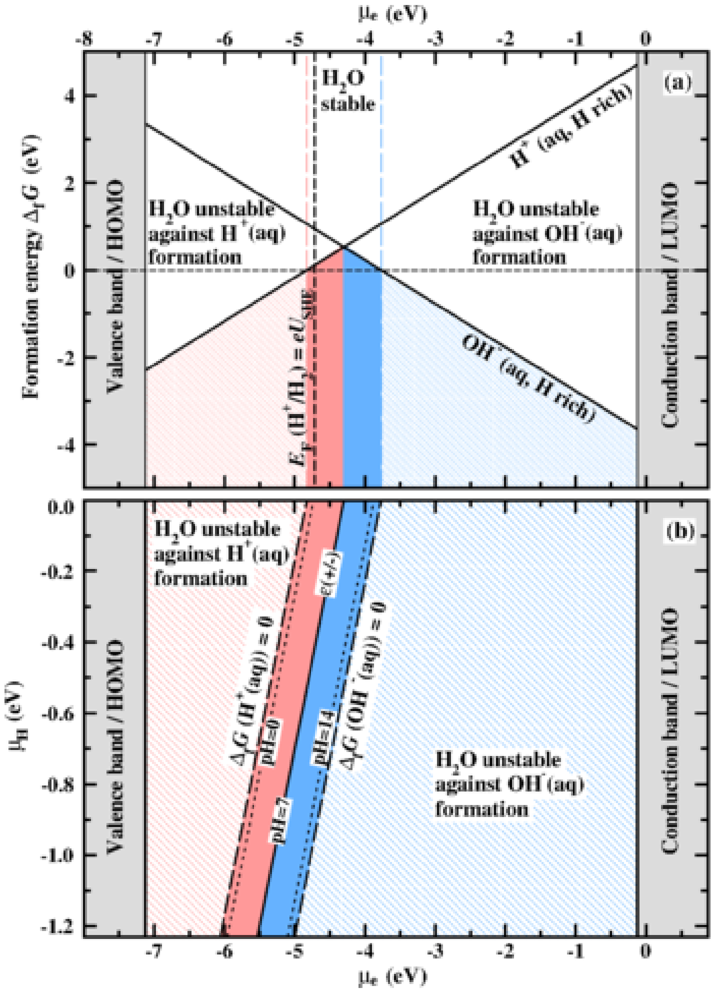
In electrochemistry, often no explanation is provided why the EDL forms

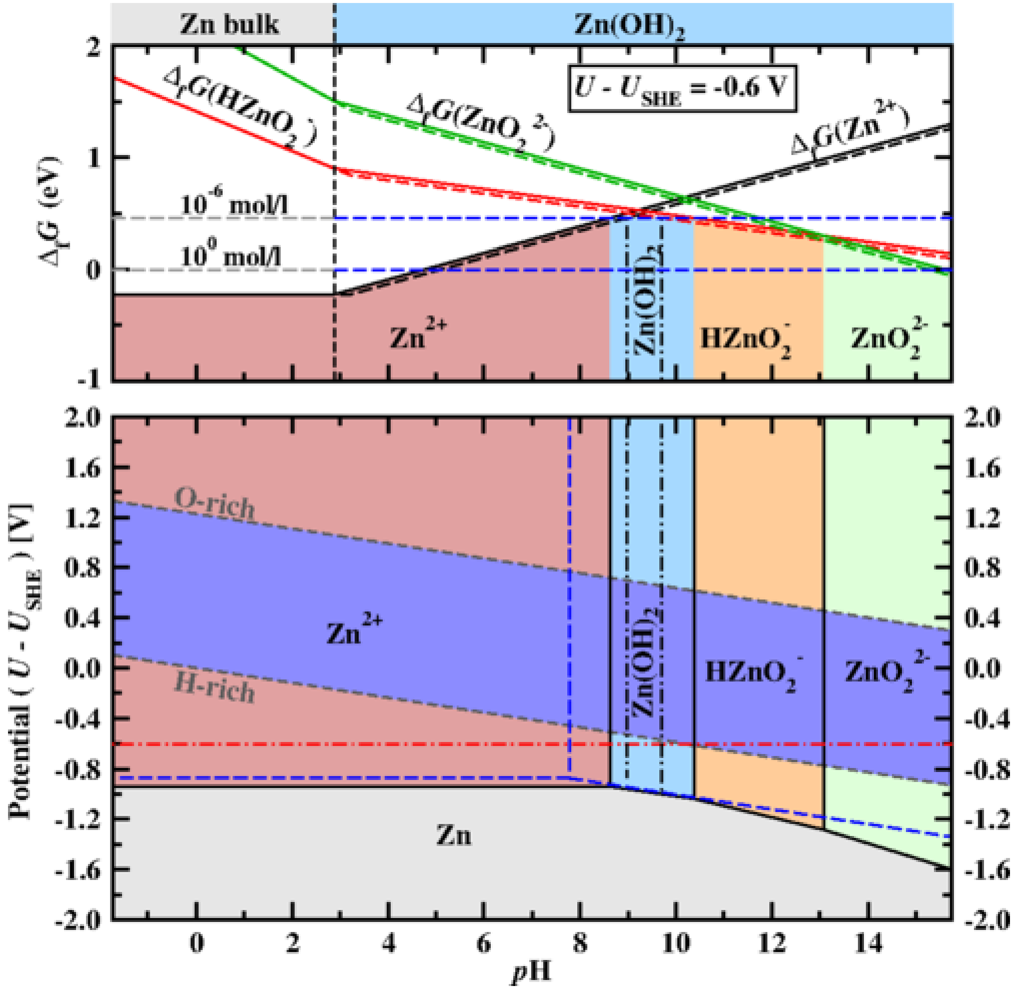
Extending the Concept of Defect Chemistry from Semiconductor Physics to Electrochemistry

M. Todorova and J. Neugebauer, Phys. Rev. Applied **1**, 014001 (2014).

Water



Zinc oxide and hydroxide



Connecting Semiconductor Defect Chemistry with Electrochemistry

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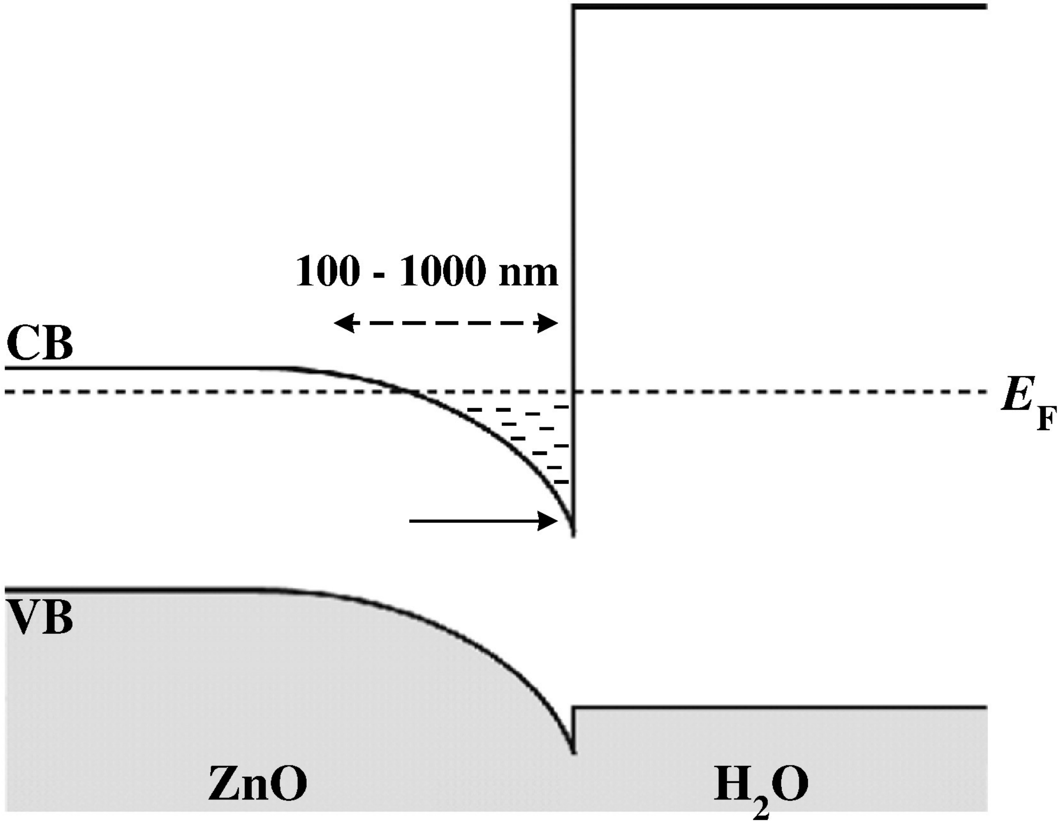

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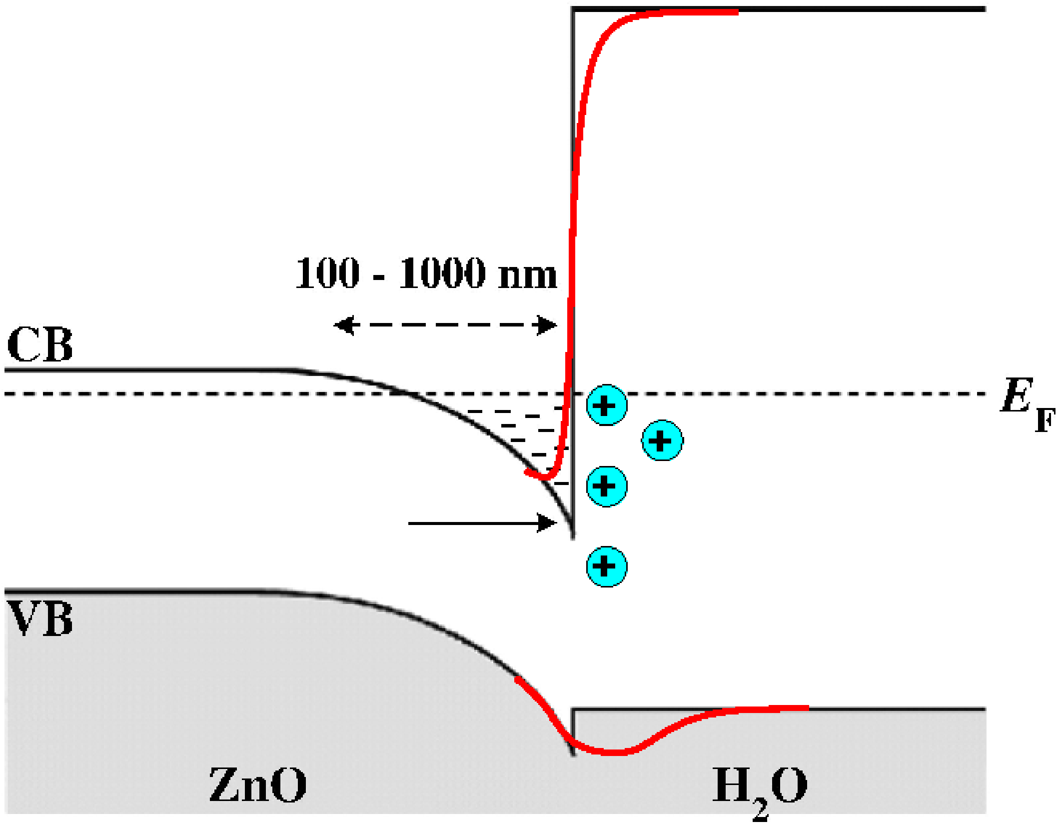

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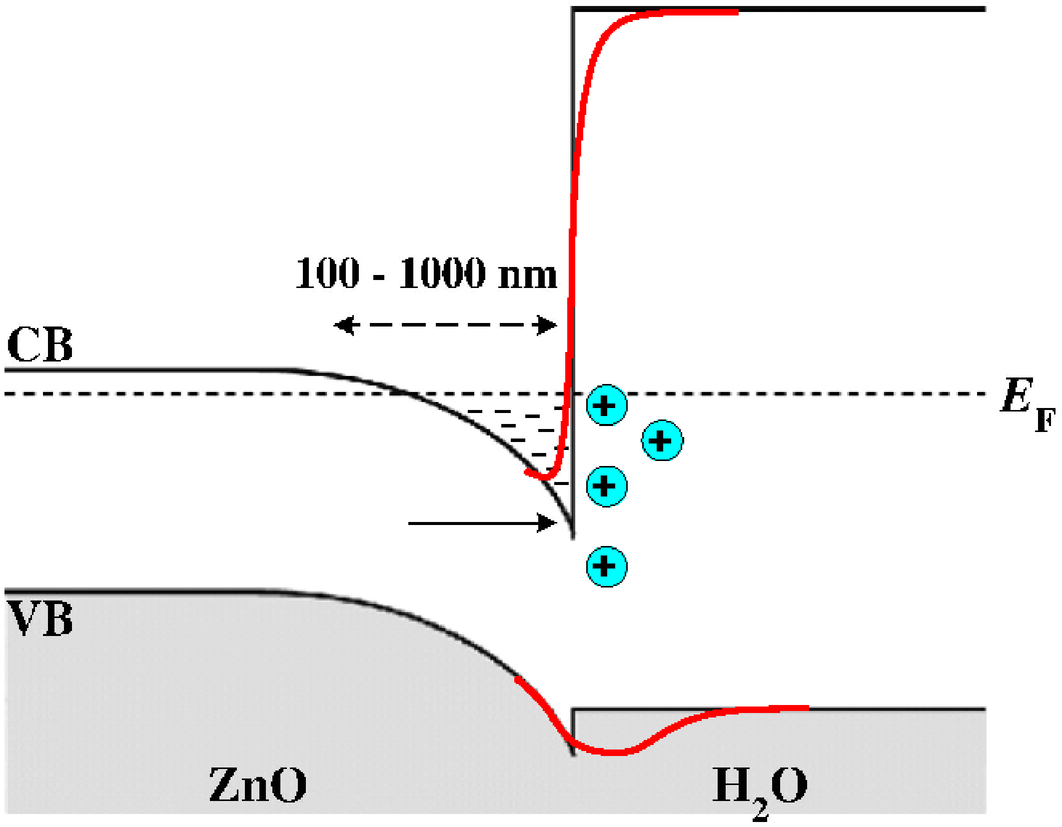
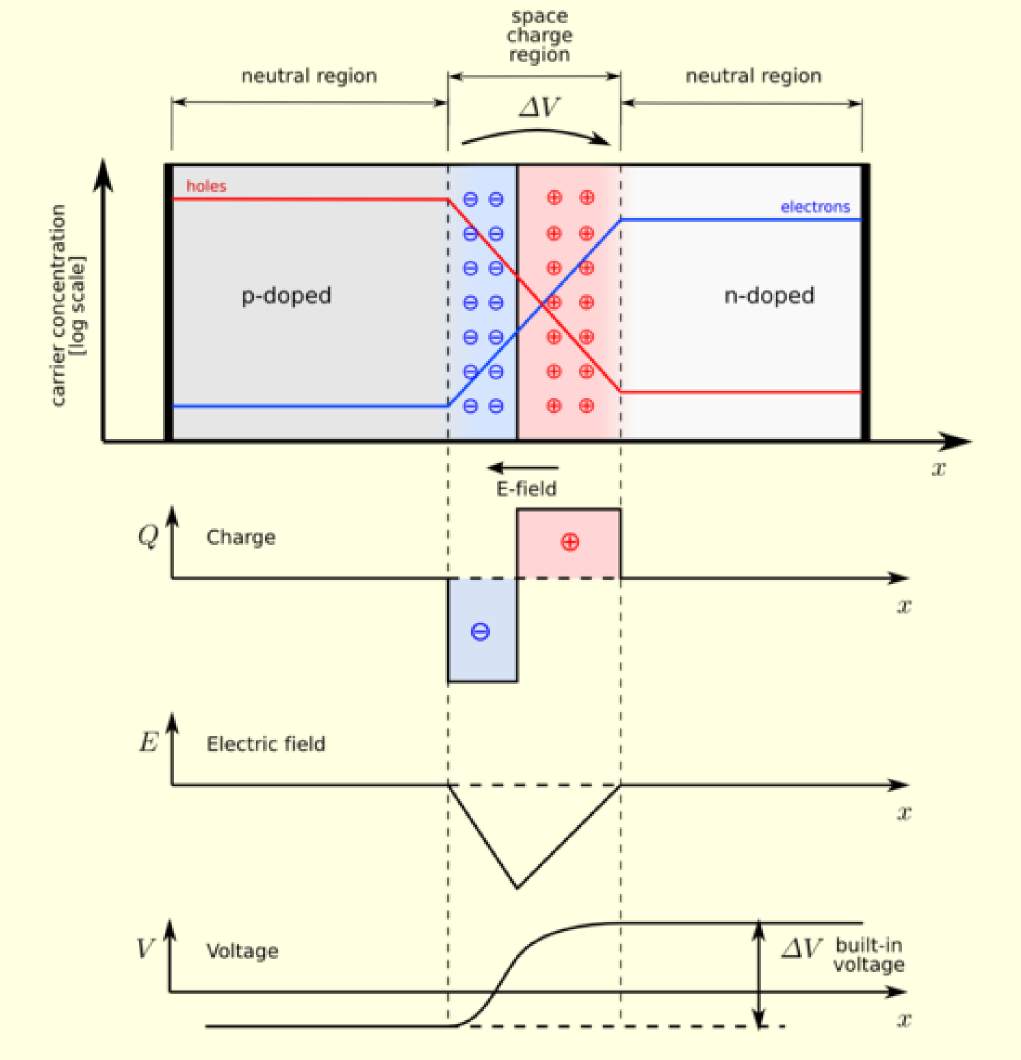


Difference between solvated ions and defects: ions are more mobile

Electrical Double Layer II

Analogy with interfaces in semiconductor physics



p-n junction

Interface between an electron and a hole conductor

Potential drop across interface

Space charge layers

Electrochemical interface has strong similiarities to a p-n junction or a Schottky contact

Source: Wikipedia

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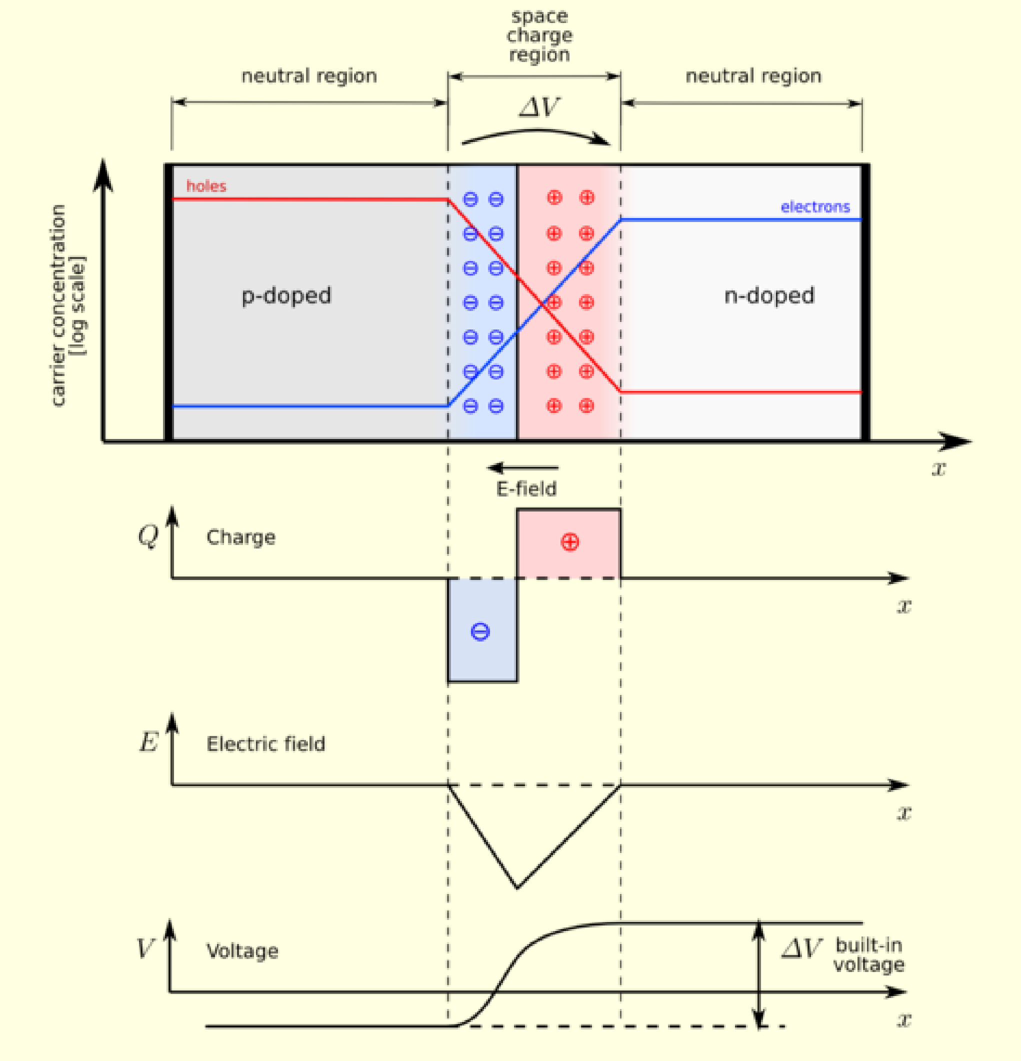

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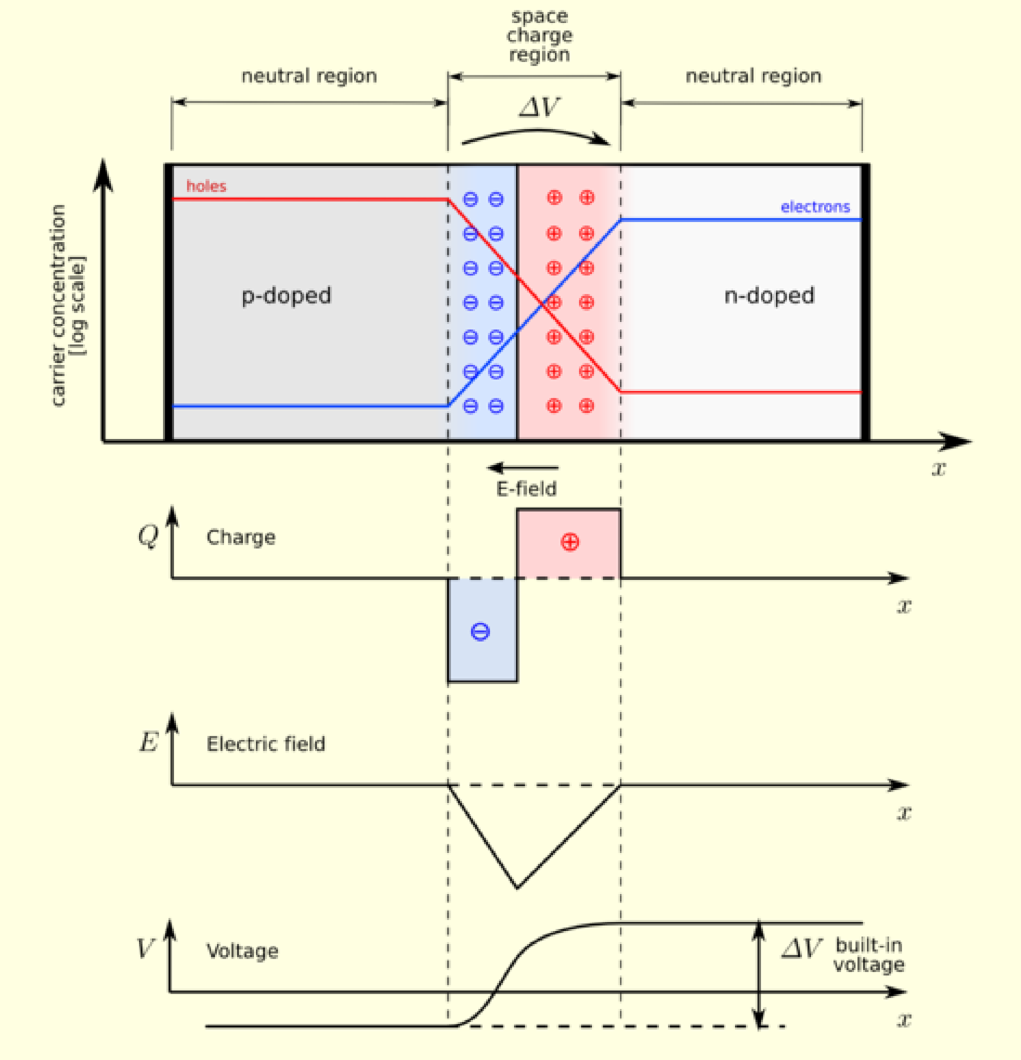

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Driving force for the formation of the space charge layer: The Fermi energy has to be constant throughout the whole system

Why is this argument hardly used in interfacial electrochemistry?

Source: Wikipedia

Electrochemistry and potentials

Electrochemistry characterized by a multitude of potential definitions,
some expressed in units of a voltage, some in units of an energy

Electrochemistry and potentials

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VIEWPOINT

Potentially Confusing: Potentials in Electrochemistry

Cite This: *ACS Energy Lett.* 2021, 6, 261−266

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Shannon W. Boettcher, Sebastian Z. Oener, Mark C. Lonergan, Yogesh Surendranath, Shane Ardo, Carl Brozek, and Paul A. Kempler

“A potential quantifies the capacity of a system to do work .”
“The word “potential” alone should be avoided unless the type of potential is made clear.”

Electrochemistry and potentials

Electrochemistry characterized by a multitude of potential definitions, some expressed in units of a voltage, some in units of an energy

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“A potential quantifies the capacity of a system to do work .”
“The word “potential” alone should be avoided unless the type of potential is made clear.”

In Li-ion type batteries, the cation is at a higher potential in the cathode than in the anode!

Electrochemistry and potentials II

Electrode potential: How do you picture the role of the electrode potential for yourself?

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Late Prof. Dieter Kolb:

“The electrode potential plays a similar role in cyclic voltammograms as the temperature in temperature programmed desorption.”

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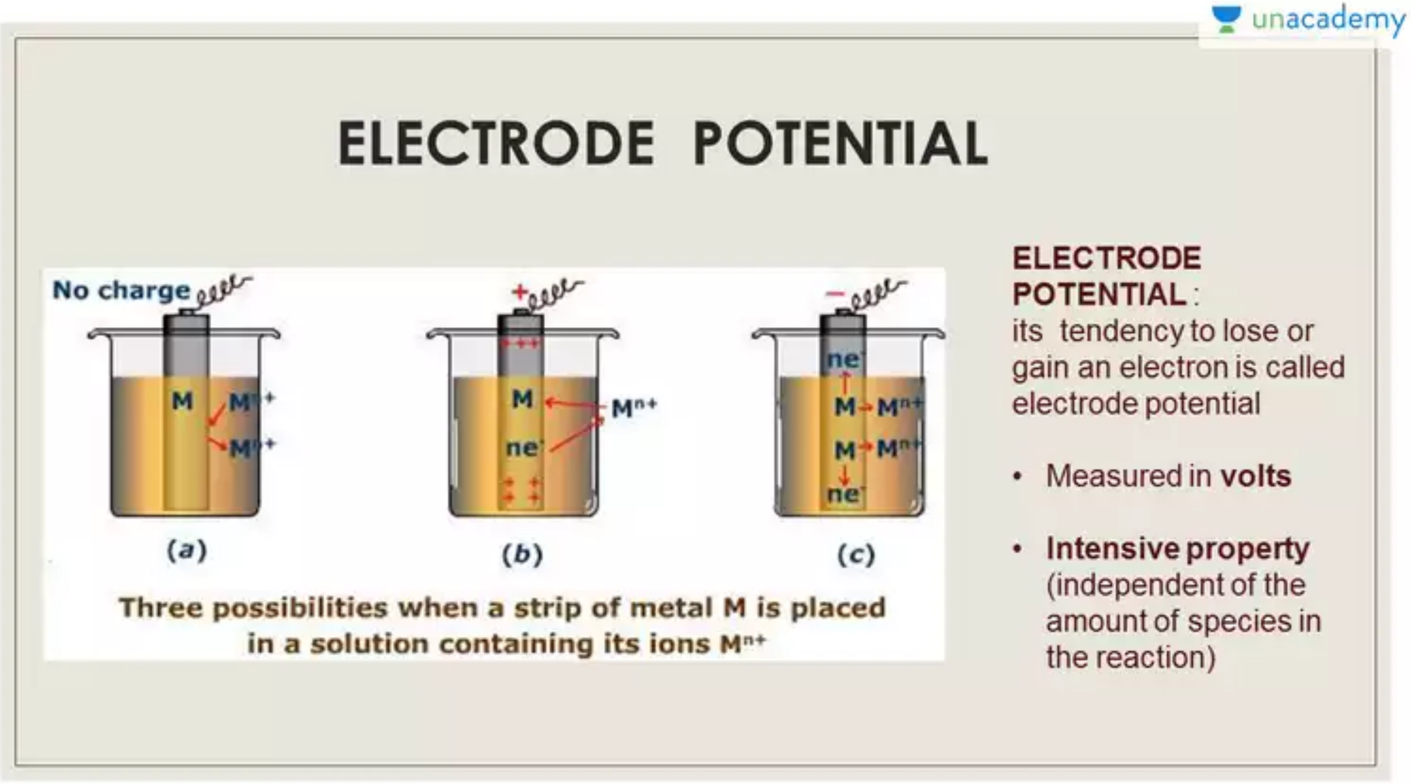

ELECTRODE POTENTIAL

Three possibilities when a strip of metal M is placed in a solution containing its ions M^{n+}

ELECTRODE POTENTIAL: its tendency to lose or gain an electron is called electrode potential

- Measured in **volts**
- **Intensive property** (independent of the amount of species in the reaction)

https://unacademy.com/lesson/electrode-potential-and-emf-in-hindi/FM3JYV88

Electrode potential

From Wikipedia, the free encyclopedia

In electrochemistry, electrode potential is the voltage of a galvanic cell built from a standard reference electrode and another electrode to be characterized.

By convention, the reference electrode is the standard hydrogen electrode (SHE). It is defined to have a potential of zero volts.

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In electrochemistry, the standard hydrogen electrode (abbreviated SHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials.

The hydrogen electrode is based on the redox half cell corresponding to the reduction of two hydrated protons, $2H^+_{(aq)}$, into one gaseous hydrogen molecule, $H_{2(g)}$.

Electrochemical potential I

J.K. Nørskov *et al.*, J. Electrochem. Soc. **152**, J23 (2005); H.A. Heine, J. Rossmeisl *et al.*, PCCP **12**, 283 (2010);
K. Reuter and M. Scheffler, PRB **65**, 035406 (2001)

Standard conditions (zero pH, $U = 0$): $\mathrm{H}^+(\mathrm{aq}) + e^-$ is in equilibrium with $\frac{1}{2}\mathrm{H}_2(\mathrm{g})$

Finite pH and electrode potential:

$$\mu(\mathrm{H}^+(\mathrm{aq})) + \mu(e^-) = \frac{1}{2}\mu(\mathrm{H}_2(\mathrm{g})) - eU_{\mathrm{SHE}} - k_{\mathrm{B}}T\ln(10)\mathrm{pH} \tag{1}$$

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The absolute electrode potential

S. Trasatti, Pure & Appl. Chem.**58**, 955 (1986)

“The “electrode potential” is often misinterpreted as the electric potential difference between a point in the bulk of the solid conductor and a point in the bulk of the electrolyte solution.”

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“The energy of electrons in a vacuum just outside the phase is in fact adopted by physicists to measure the electronic energy in the bulk .... This reference state is suitable to relate the potential scale of electrochemists with the energy scale of physicists.”

Electrochemical potential II

Thermodynamic equilibrium:

Electrochemical potentials, concentrations and hence also the electrode potential have to be uniform in the whole considered system

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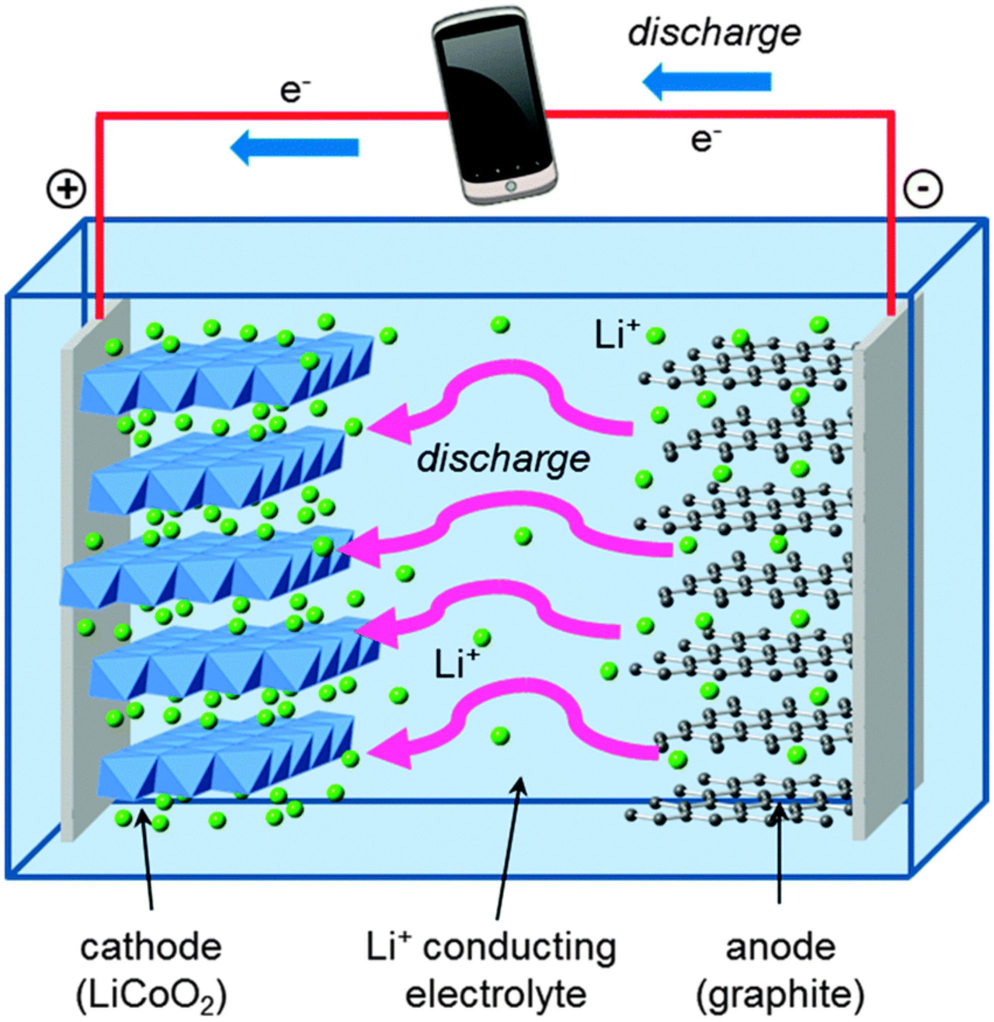
$\Rightarrow$ The electrode potential is nothing else but the Fermi energy or the electrochemical potential of the electrons

Operating mode of batteries

Li-Ion Battery (LIB)



M.S. Islam and C.A.J. Fisher, Chem. Soc. Rev. **43**, 185 (2014).

Reaction upon discharge:

$$x\ \text{Li (anode)} + \text{Li}_y\ \text{(cathode)} \rightarrow \text{Li}_{x+y}\ \text{(cathode)}$$

Energy gain upon the Li transfer: ΔG

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Difference of electrical potential between two terminals of a device when disconnected from any circuit

$$V_{\rm OC} = \frac{-\Delta G}{xF} = (\mu_{\rm Li}^{\rm A} - \mu_{\rm Li}^{\rm C})/e$$

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Typical value for Li-ion batteries: $V_{\rm OC} \geq 4\,\text{V}$

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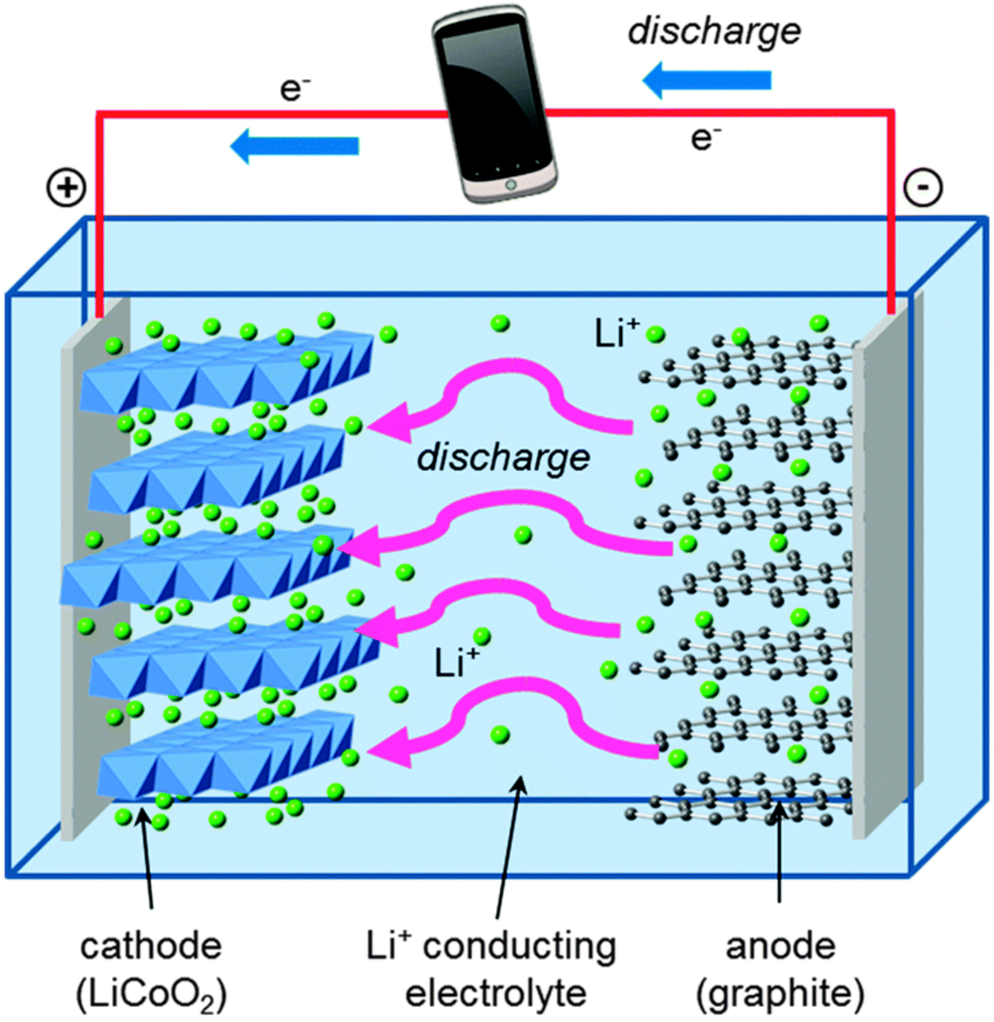

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Note: a battery is never "charged"

OCV and alignment of electrochemical potentials

Axel Groß and Sung Sakong, Curr. Opin. Electrochem **14**, 1 (2019).

Decomposition of the chemical potentials μ_{Li}:

$$V_{\mathrm{OC}} = (\mu_{\mathrm{Li}}^{\mathrm{A}} - \mu_{\mathrm{Li}}^{\mathrm{C}})/e \;, \qquad \mu_{\mathrm{Li}} = \tilde{\mu}_{\mathrm{Li}^+} + \tilde{\mu}_{\mathrm{e}^-} \tag{2}$$

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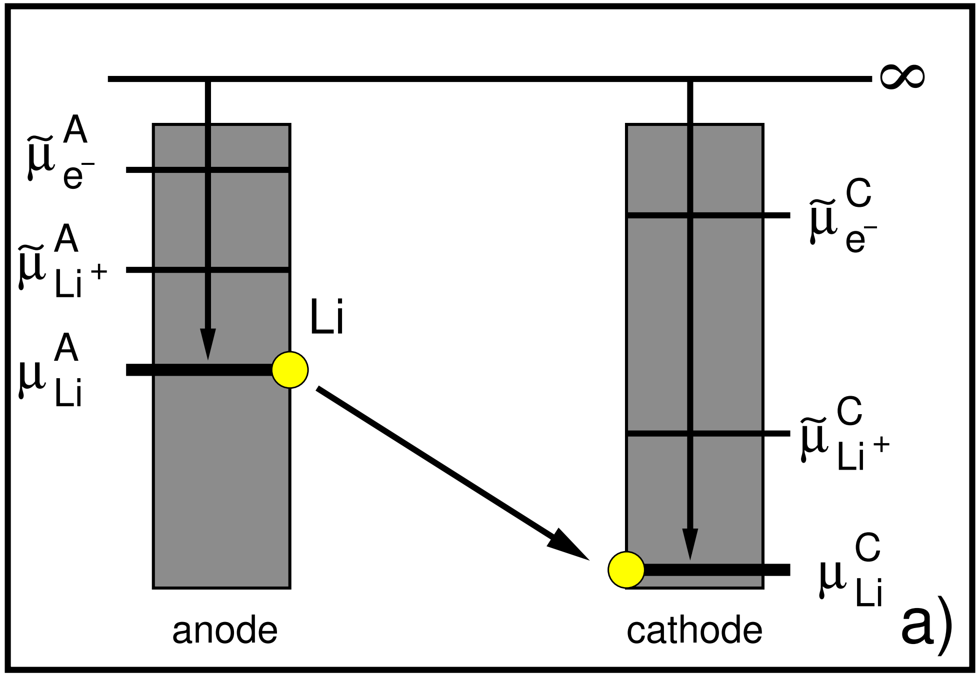

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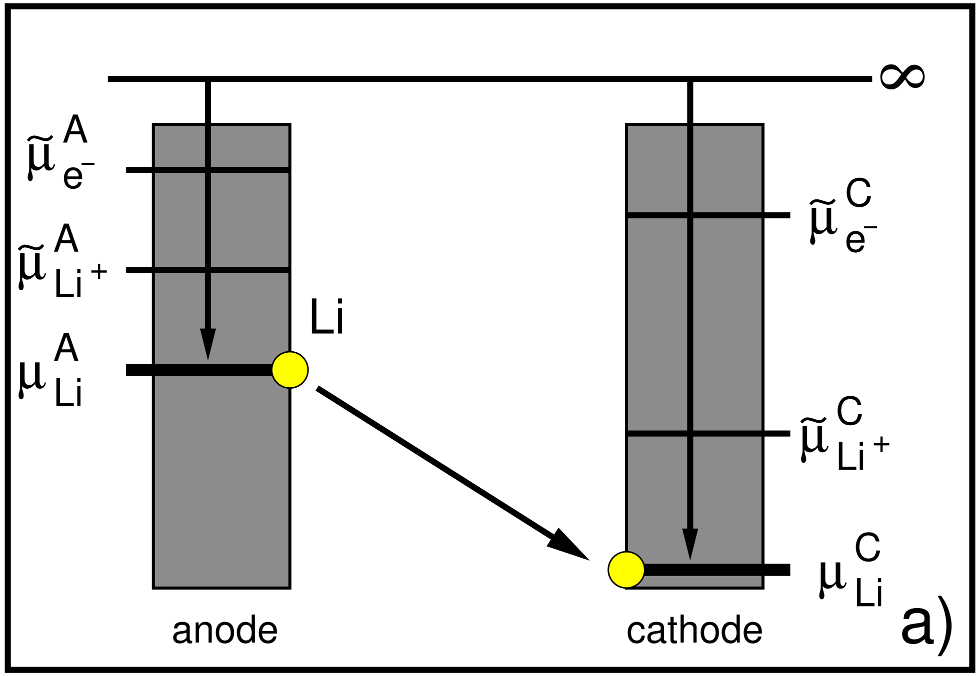

What does happen when the electrolyte is introduced?

OCV and the formation of an electric double layer

Axel Groß and Sung Sakong, Curr. Opin. Electrochem **14**, 1 (2019).

Upon introduction of the electrolyte, $\tilde{\mu}_{\mathrm{Li}^+}$ has to be constant throughout the cell

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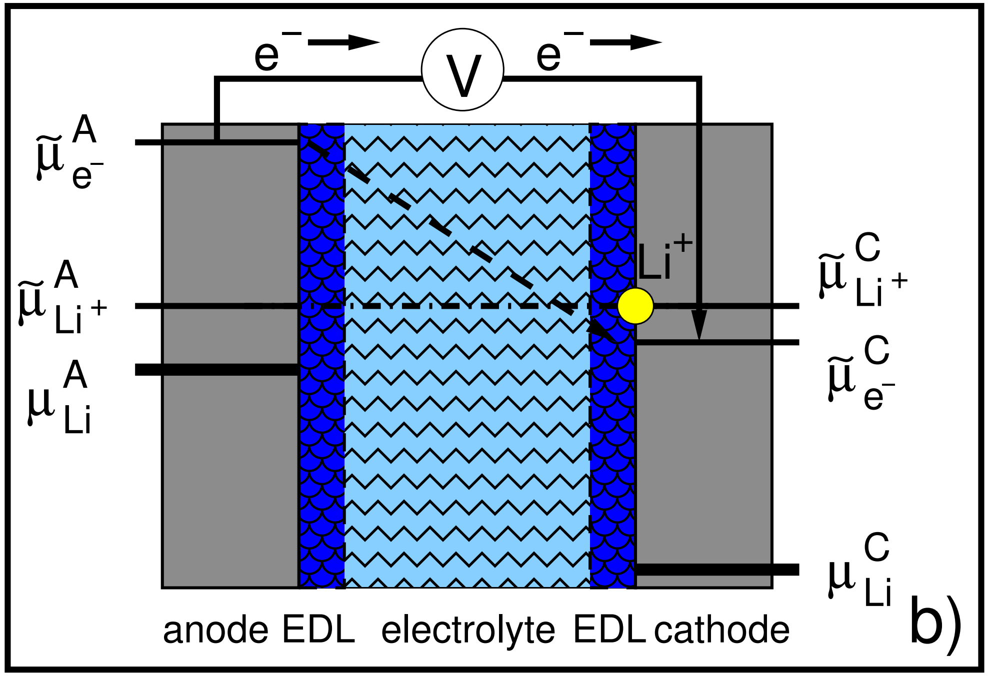

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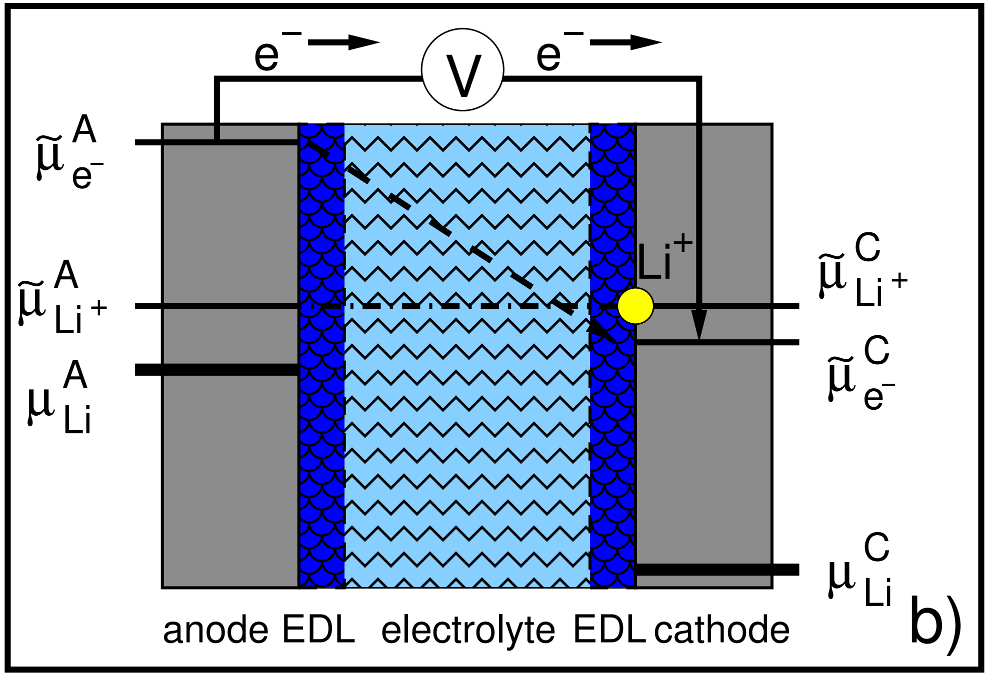

Formation of electric double layers at both the anode and cathode upon establishing the equilibrium in the ion distribution.

$$\Rightarrow V^{\mathrm{el}}_{\mathrm{OC}} = (\tilde{\mu}^{\mathrm{A}}_{\mathrm{e}^-} - \tilde{\mu}^{\mathrm{C}}_{\mathrm{e}^-})/e \ , \qquad (3)$$

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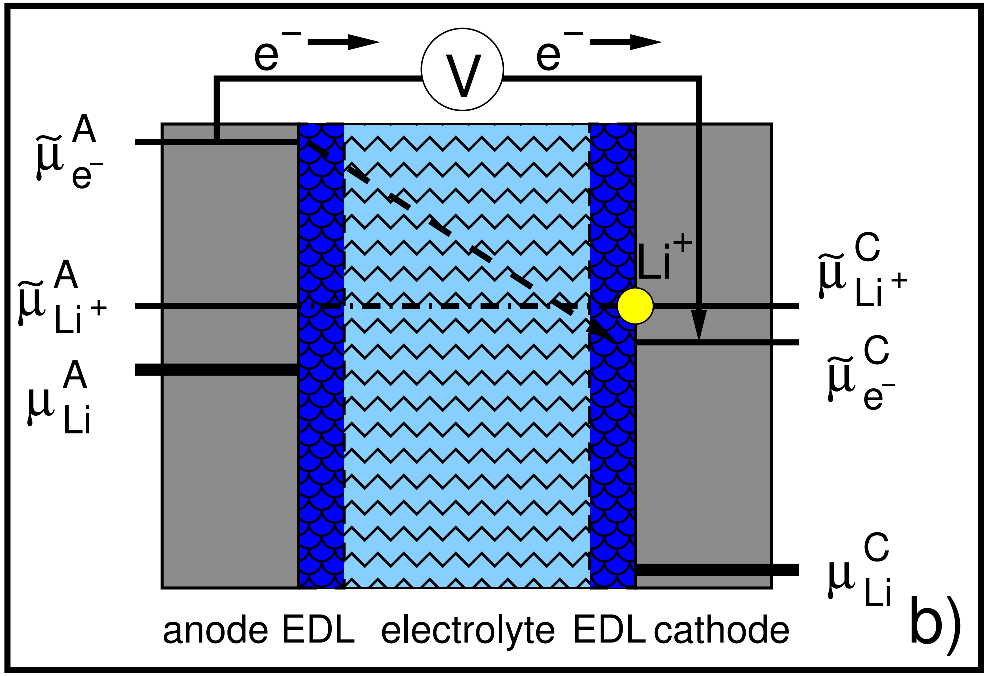

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⇒ **OCV is entirely given by the difference of the Fermi energies in anode and cathode**

Is Li metal the best anode material?

Many papers state that Li is the best anode material because it hat the lowest redox potential

metal	Li	Na	K	Rb	Cs	Mg	Ca	Sr	Al	Zn
E^0 (V)	-3.04	-2.71	-2.93	-2.98	-3.03	-2.7	-2.87	-2.88	-1.66	-1.20

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Source: Kittel, Introduction to Solid State Physics

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⇒ Na and K are in principle better "charge carriers" than Li

A metal anode with a low cohesive energy should be coupled with a cathode with a high metal insertion energy

Why are flammable electrolytes used in batteries?

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Electrolyte have to be stable with respect to the large difference in the potential between charging and de-charging

Only few electrolytes are stable at the high voltage of Li-ion batteries ($\geq 4.5\,\mathrm{V}$).

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Alternative concepts: ionic liquids, water-in-salt electrolytes

When a nobel laureate is wrong

John B. Goodenough and Kyu-Sung Park. The Li-Ion Rechargeable Battery: A Perspective, JACS **135**, 1167 (2013).

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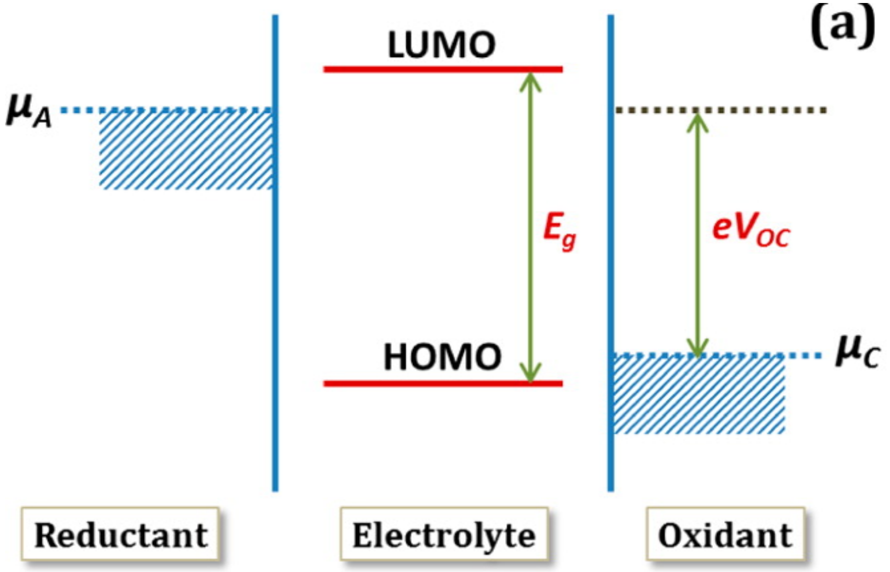

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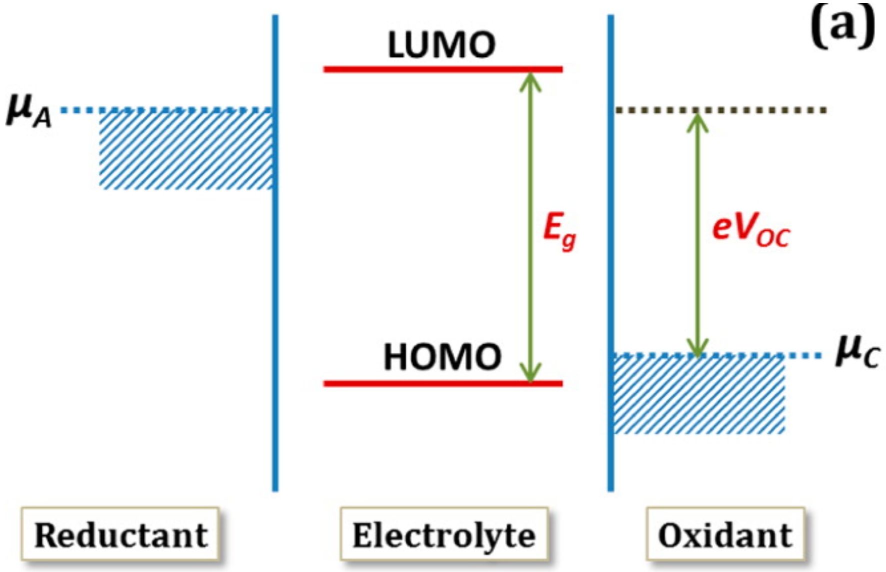

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P. Peljo and H.H. Girault, Energy Environ. Sci. **11**, 2306 (2018):
Electrochemical potential window of battery electrolytes: the HOMO-LUMO misconception

Elektrochemical potential window

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Simple counter example with respect to the concept of Goodenough:
Water has a "band gay" of about 9 eV, but decomposes at voltages above 1.23 V

Elektrochemical potential window

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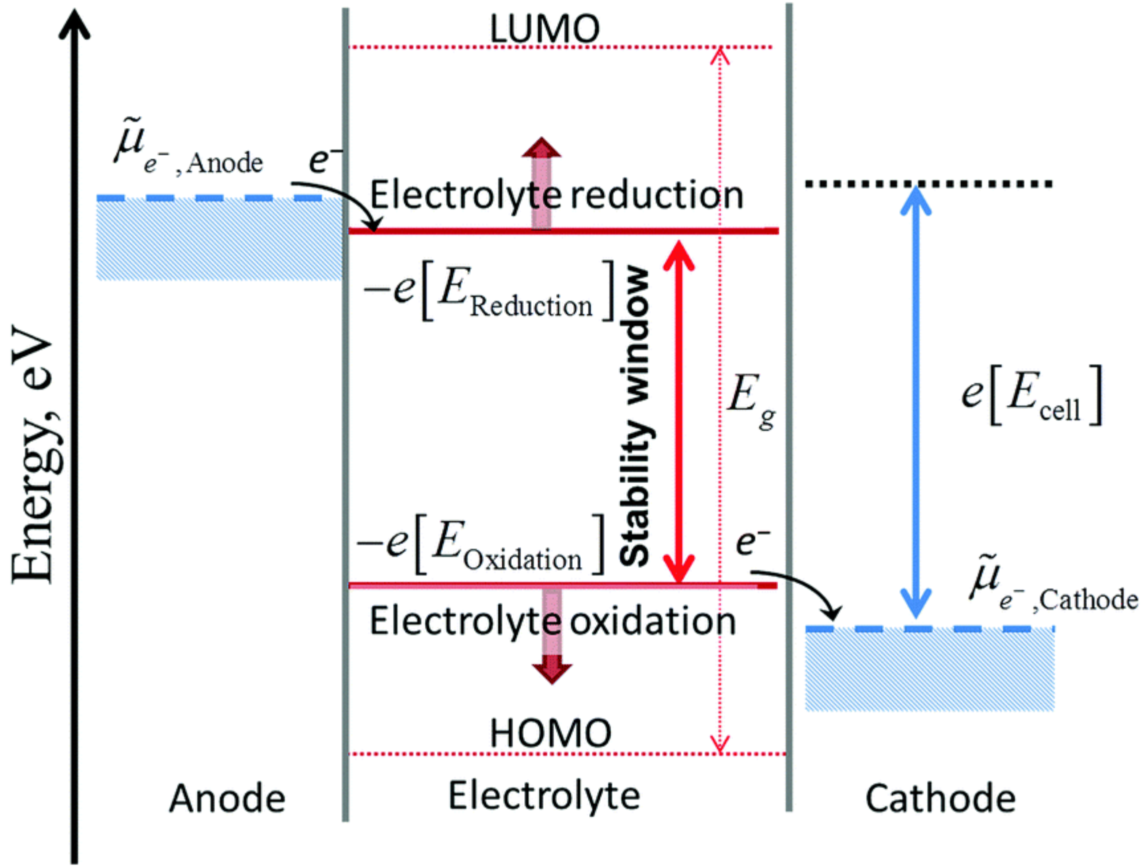
Correct picture involves the redox potentials of the electrolyte

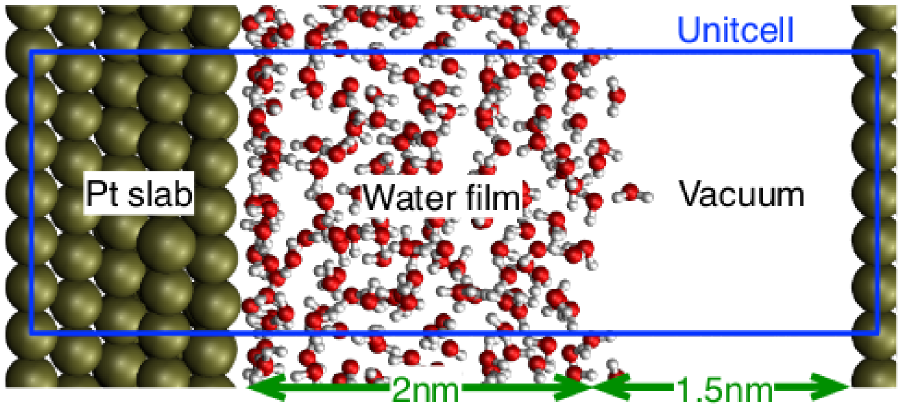


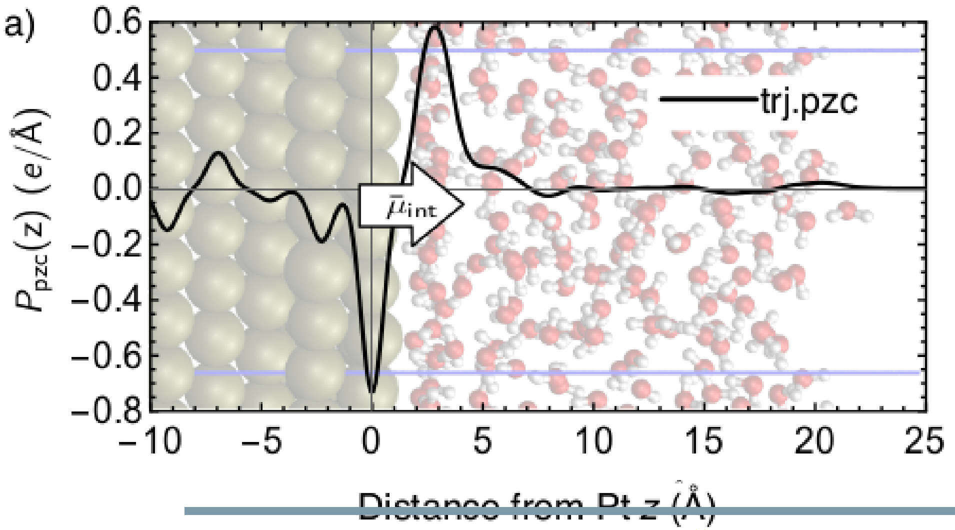
AIMD simulations of a water film on (6×6)Pt(111)

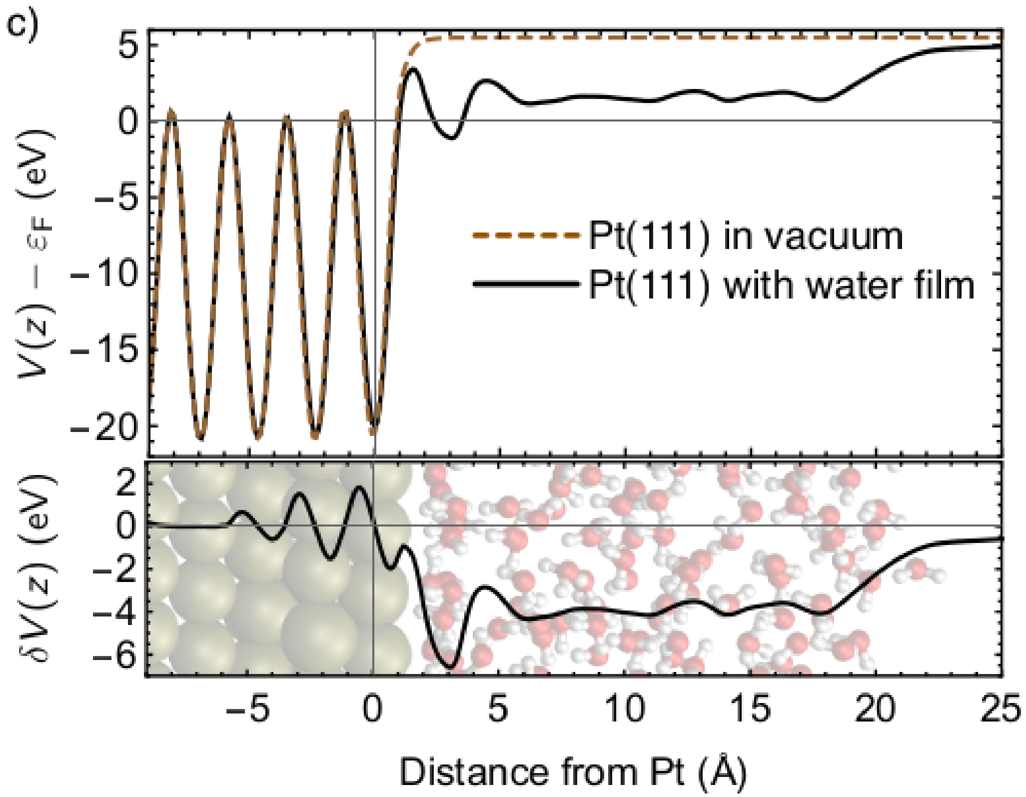
Sung Sakong and Axel Groß, JCP **149**, 084705 (2018), O. Magnussen and A. Groß, JACS **141**, 4777 (2019).

AIMD simulation for 40 ps with six water layers in a 6×6 surface unit cell corresponding to 144 water molecules

a) Snapshot of trj.pzc





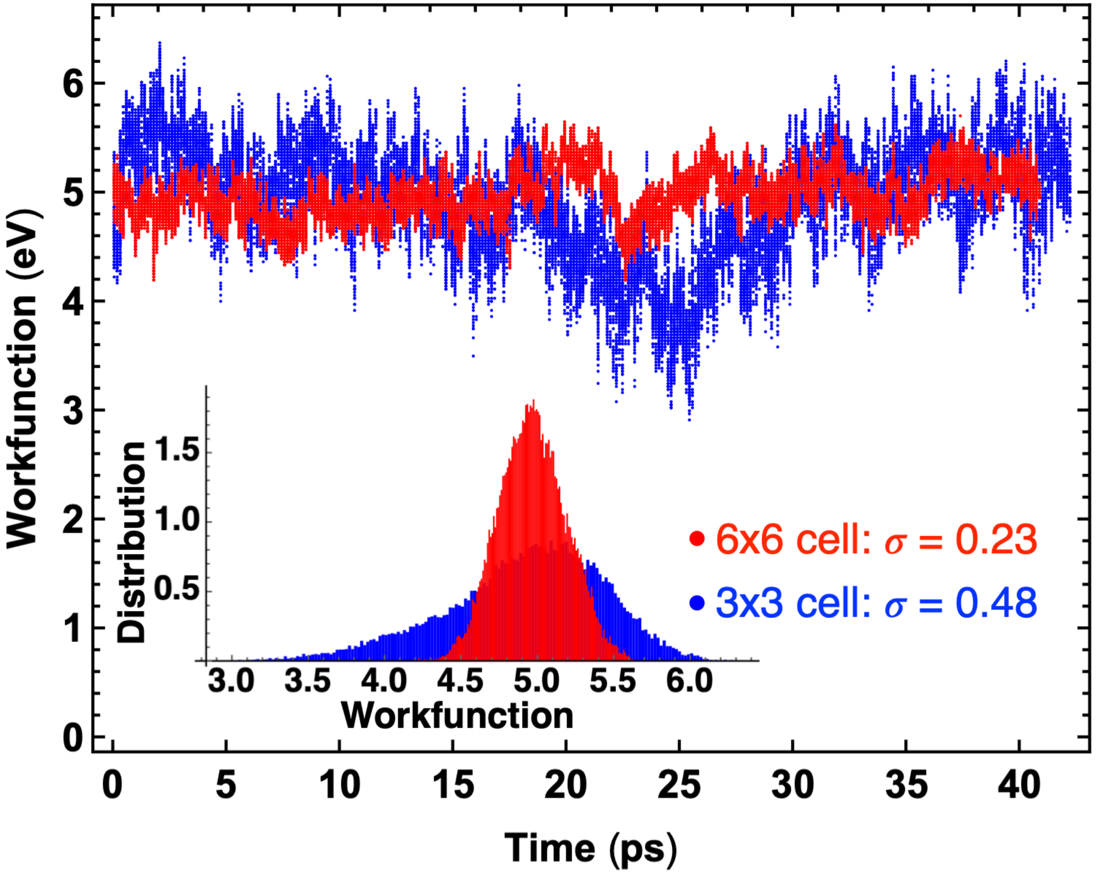


AIMD simulations: system size dependence

Sung Sakong, Katrin Forster-Tonigold, and Axel Groß, J. Chem. Phys. **144**, 194701 (2016)

Sung Sakong and Axel Groß, J. Chem. Phys. **149**, 084705 (2018)

Comparison of AIMD simulation for 40 ps with six water layers in a 3×3 surface unit cell with 36 water molecules and in a 6×6 surface unit cell with 144 water molecules



Smaller variance for larger surface unit cell

Work function changes

Sung Sakong and Axel Groß, J. Chem. Phys. **149**, 084705 (2018)

AIMD simulations of a water film on Pt(111) with different amounts of ions and adsorbed species

Trajectory	ΔH	Φ (eV)	pH	U (V)	$\mathrm{NAC}_{\mathrm{Pt}}$ (e)
trj.pzc	0	4.96 ± 0.23	7.0	0.52	-1.25
trj.H_3O^+	$+1$	4.85 ± 0.25	0.4	0.41	-1.56
trj.OH^-	-1	5.05 ± 0.19	13.6	0.61	-0.93
trj.H_{ads}	$+1$	4.92 ± 0.20	7.0	0.48	-1.27
trj.OH_{ads}	-1	4.93 ± 0.21	7.0	0.49	-1.08
trj.36H_{ads}	$+36$	4.91 ± 0.20	0.1	0.47	-1.03
trj.2H_3O^+	$+2$	4.86 ± 0.20	0.1	0.42	-1.84

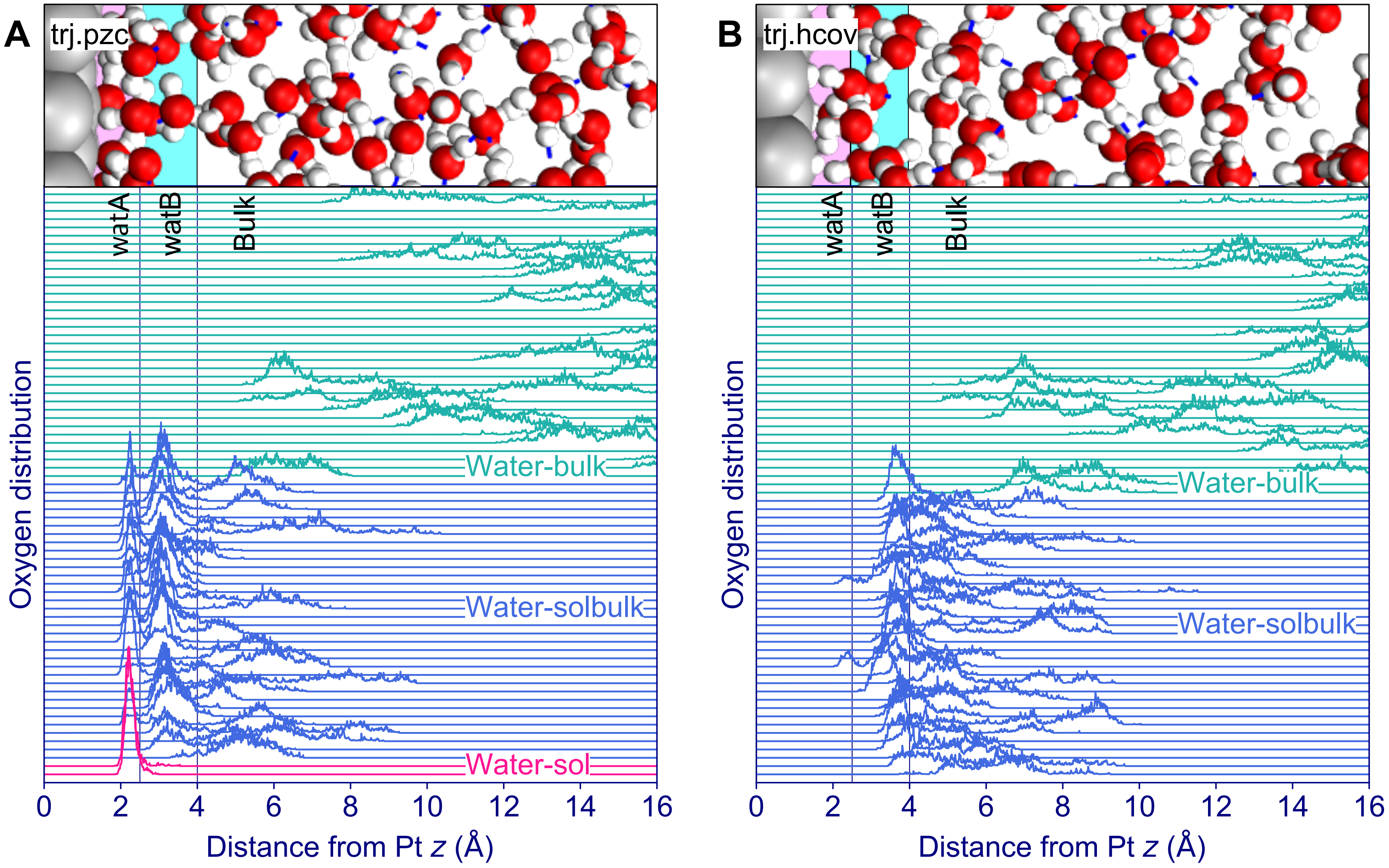
Small work function changes for adsorbed species:

Screening of adsorbate-induced surface dipoles by water molecules

Detailed structure of a water film on Pt(111)

S. Sakong, A. Groß, PCCP **22**, 10431 (2020); A. Groß, S. Sakong, Chem. Rev. **122**, 10746 (2022).

Clean Pt(111)   Hydrogen-covered Pt(111)

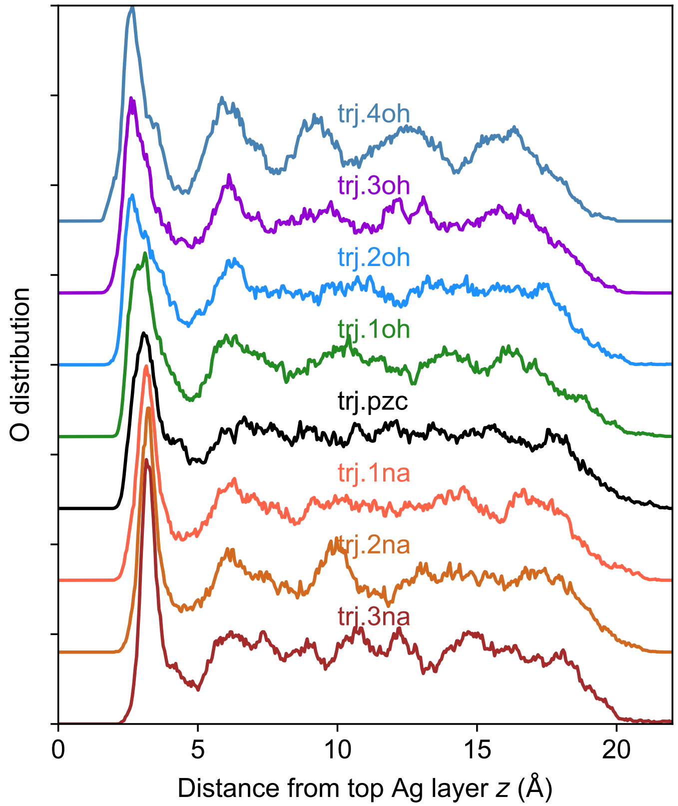


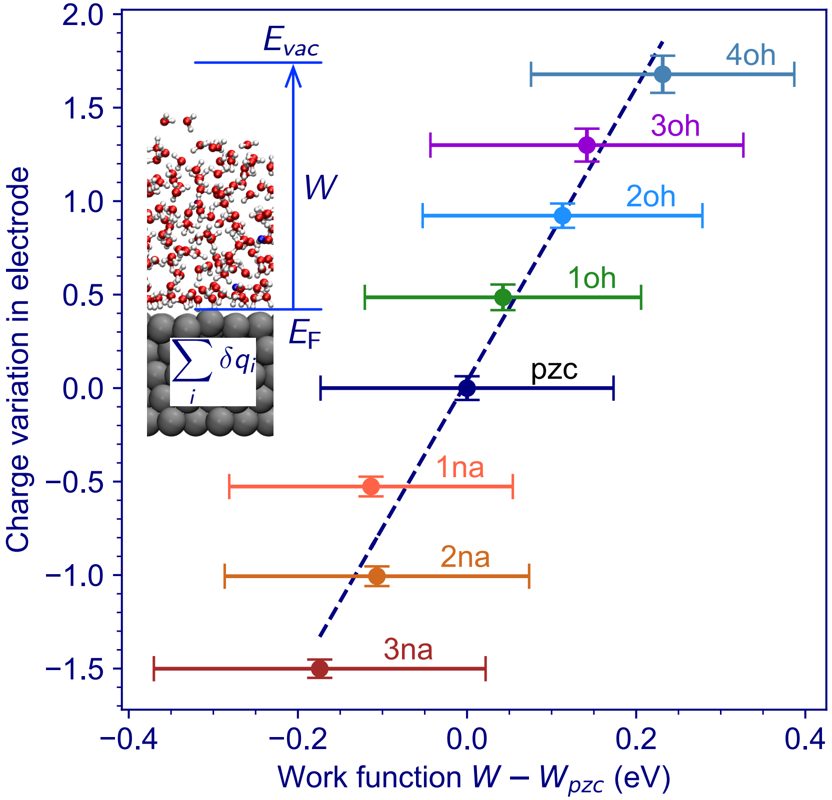
Frequent exchange of water molecules between the first (solvation) layer and bulk water

AIMD simulations of a water film on (6×6)Ag(111)

Sung Sakong and Axel Groß, in preparation

AIMD simulations with removed H atoms or added Na atoms, otherwise H_2 evolution





$U_{pzc} = -0.5\,\mathrm{V}$, width due to finite size effects

Results suggest a constant capacity, no diffuse layer considered in these simulations

Entropic effects in water layers on metal surfaces

F. Domínguez-Flores, T. Kiljunen, A.Groß, S. Sakong, M:M. Melander, JCP **161**, 044705 (2014)

Determination of free energy contributions from AIMD simulations

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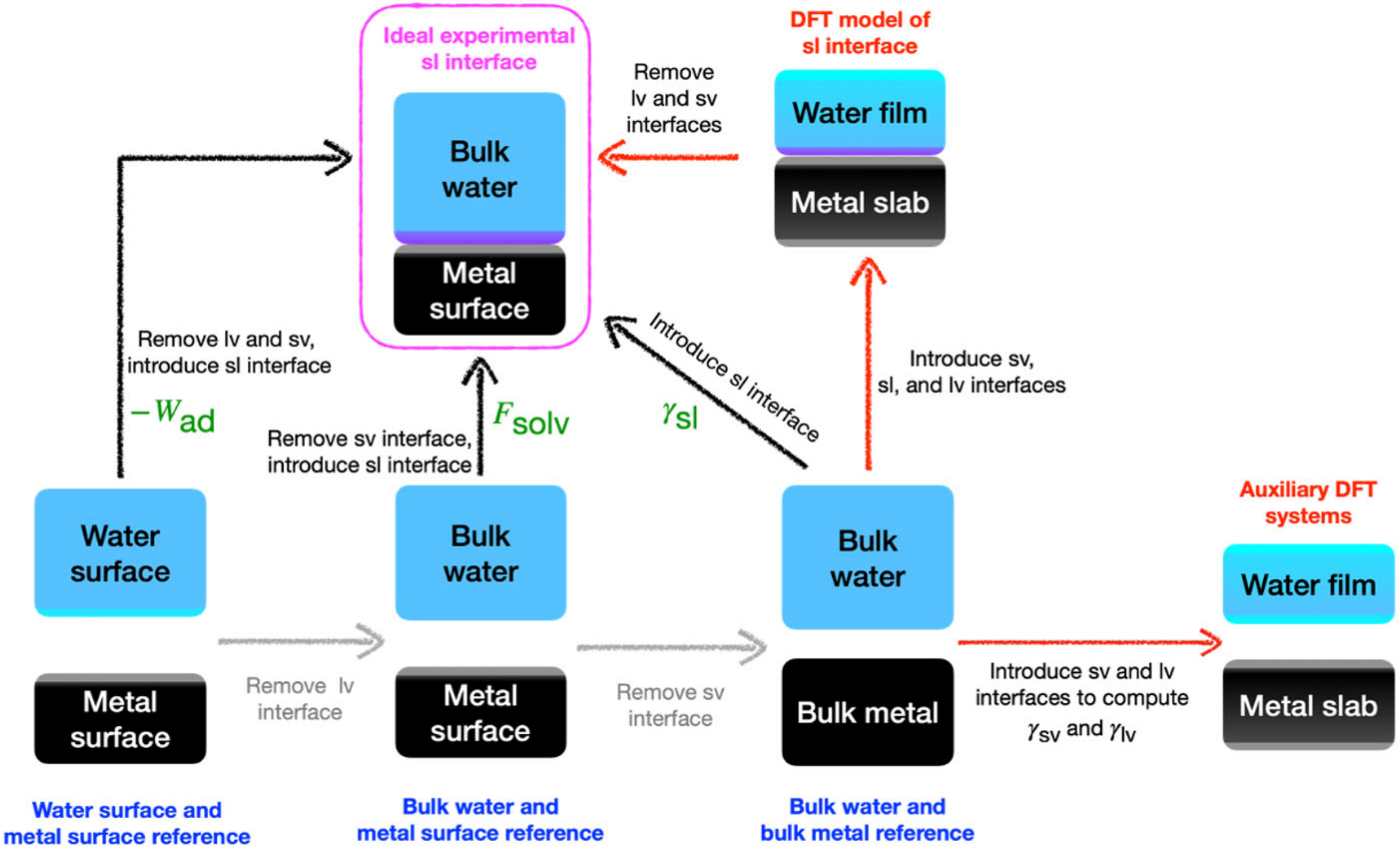
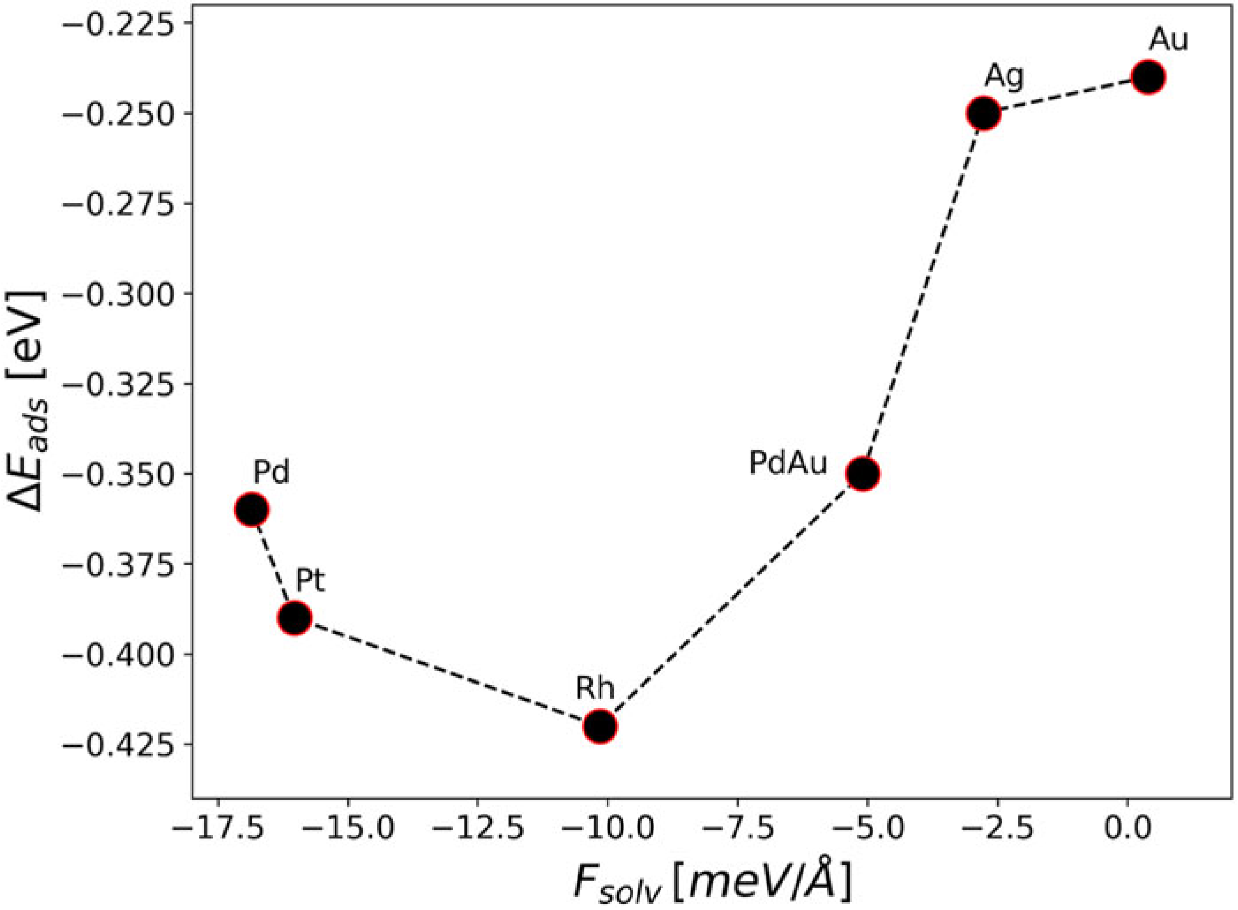


Thermodynamic cycle used to assess the formation of solid–liquid interfaces

Water adsorption energies

F. Domínguez-Flores, T. Kiljunen, A.Groß, S. Sakong, M:M. Melander, JCP **161**, 044705 (2014)

Water adsorption energies ΔE_{ads} as a function of the free energy of solvation F_{solv}

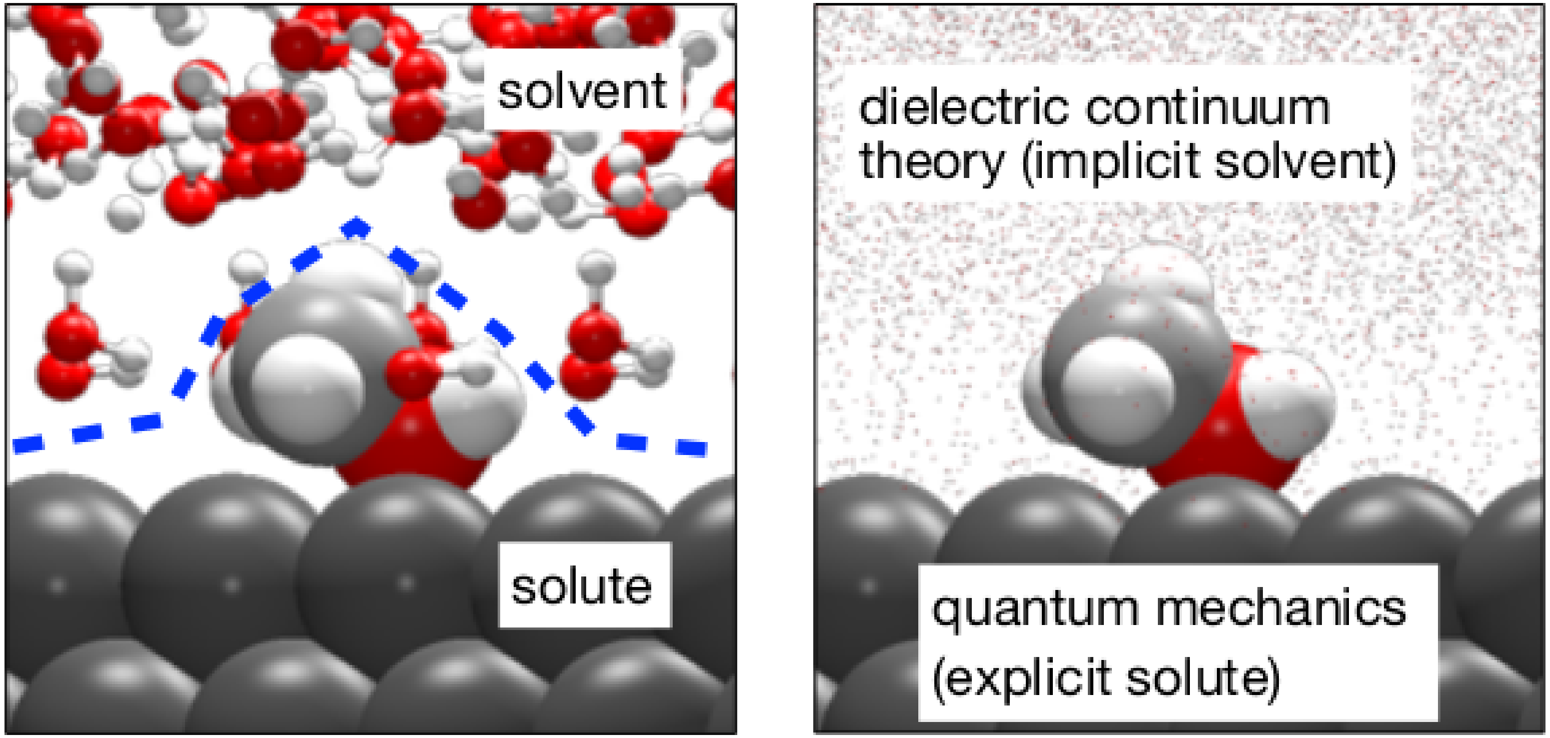


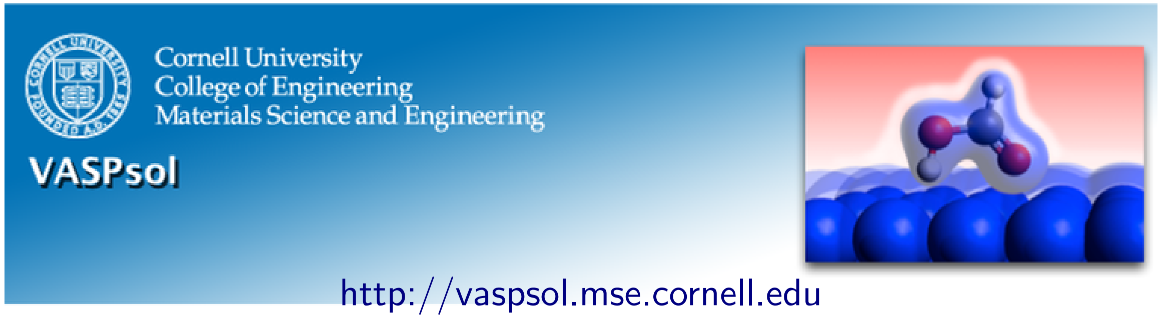
Too strong binding suppresses the entropic contributions

Implicit solvent approach: methanol oxidation

S. Sakong and A. Groß, ACS Catal. **6**, 5575 (2016).

Explicit vs. implicit description of solvent



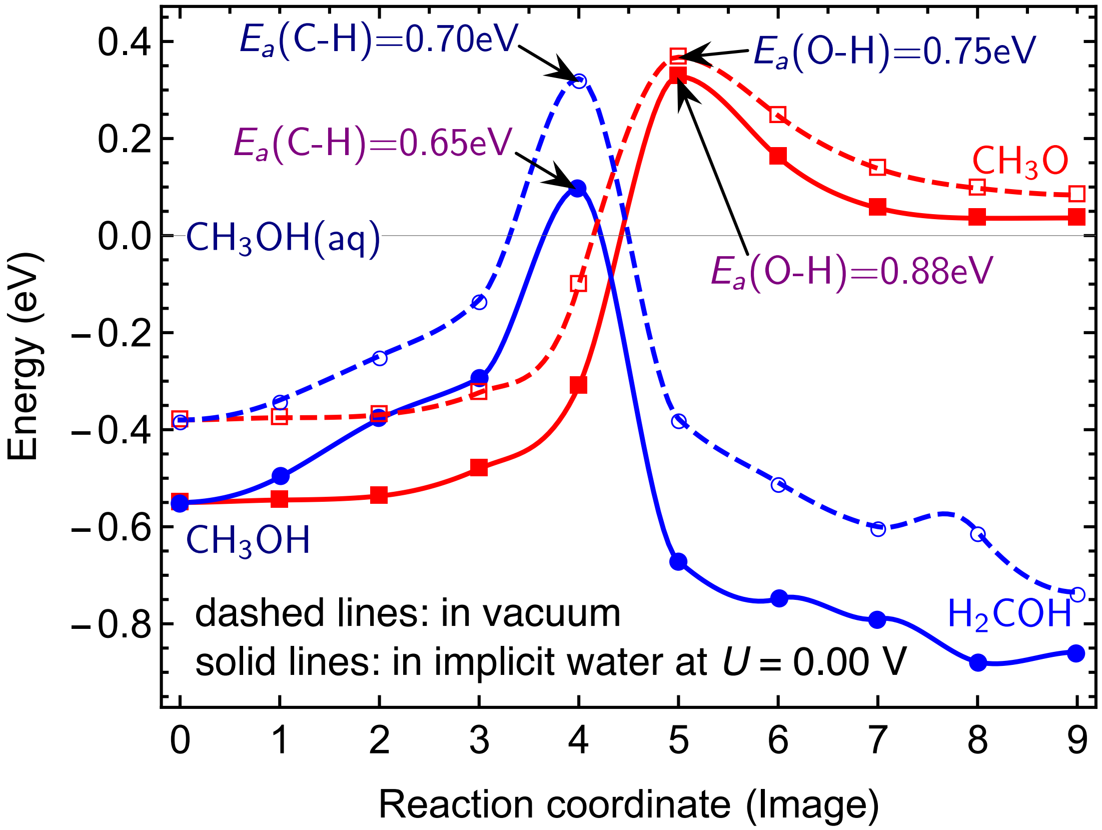


http://vaspsol.mse.cornell.edu

K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig J. Chem. Phys. **140**, 084106 (2014).

Influence of solvent on reaction barriers

S. Sakong and A. Groß, ACS Catal. **6**, 5575 (2016).



	Barriers in vacuum	and in implicit solvent
Red: $CH_3OH^* \rightarrow CH_3O^* + H^*$	0.75 eV	0.83 eV
Blue: $CH_3OH^* \rightarrow H_2COH^* + H^*$	0.70 eV	0.65 eV

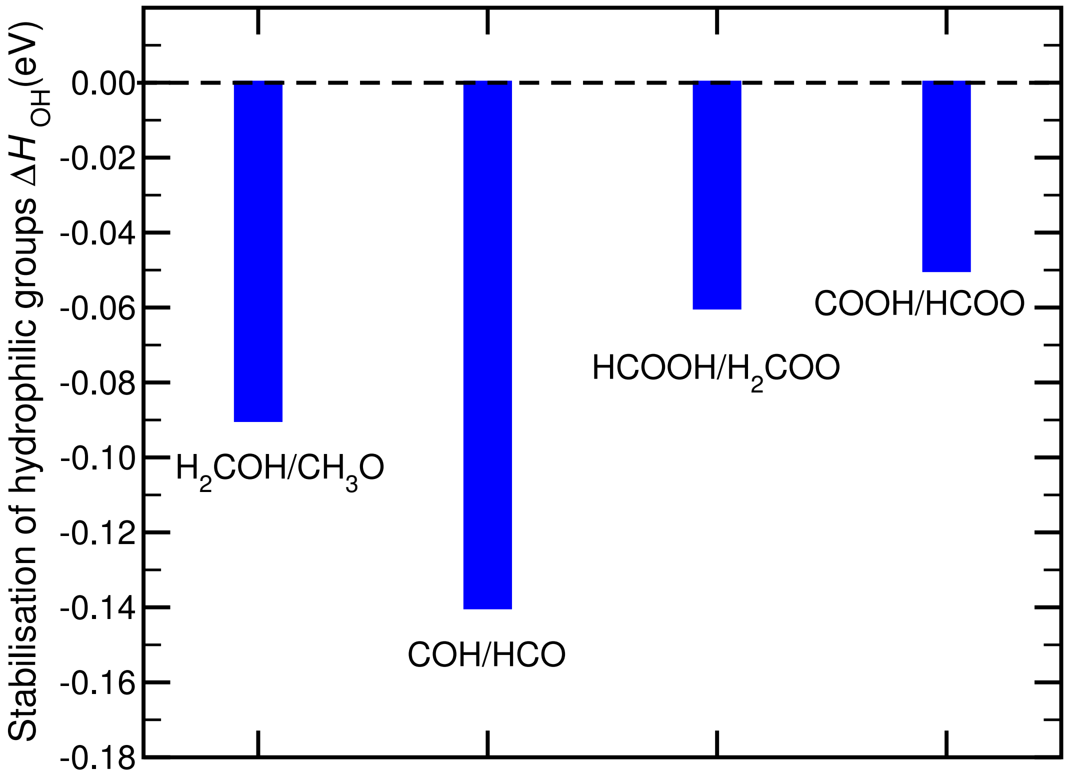
Presence of solvent favors C-H bond breaking pathway through stabilization of the OH group

Stabilization of adsorbed species in aqueous electrolyte

Sung Sakong and Axel Gross, Electrocatal. **8**, 577-586 (2017).

Adsorbed isomers at solid-gas vs. solid-liquid interface

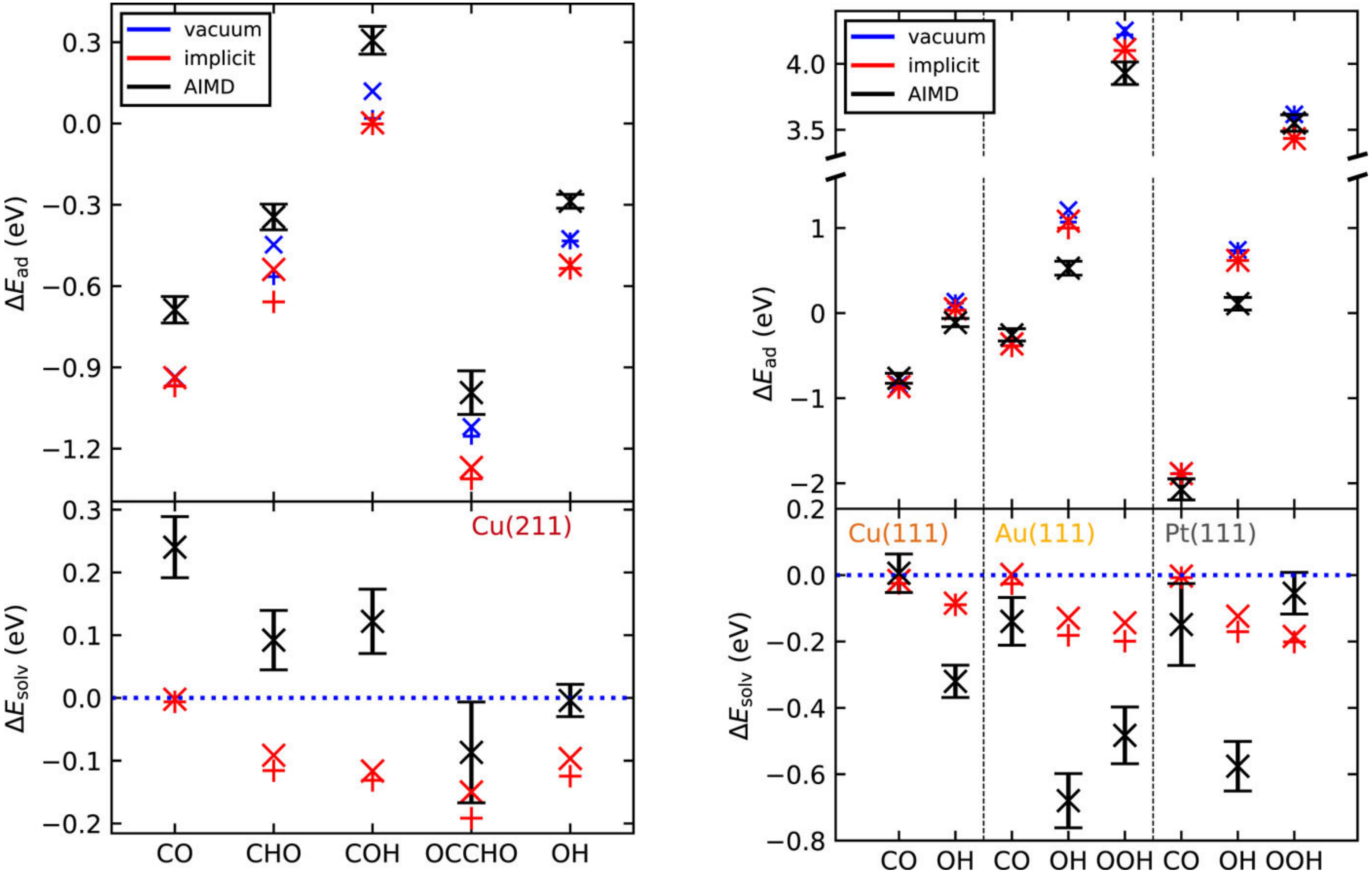
$$\Delta H_{\mathrm{OH}} = (\Delta H^{\mathrm{l}}(\mathrm{H_2COH}) - \Delta H^{\mathrm{l}}(\mathrm{CH_3O})) - (\Delta H^{\mathrm{g}}(\mathrm{H_2COH}) - \Delta H^{\mathrm{g}}(\mathrm{CH_3O})) \ , \qquad (5)$$



Adsorbed isomers with a hydrophilic hydroxyl group stabilized by aqueous electrolyte

Comparison adsorption energy in implicit and explicit water

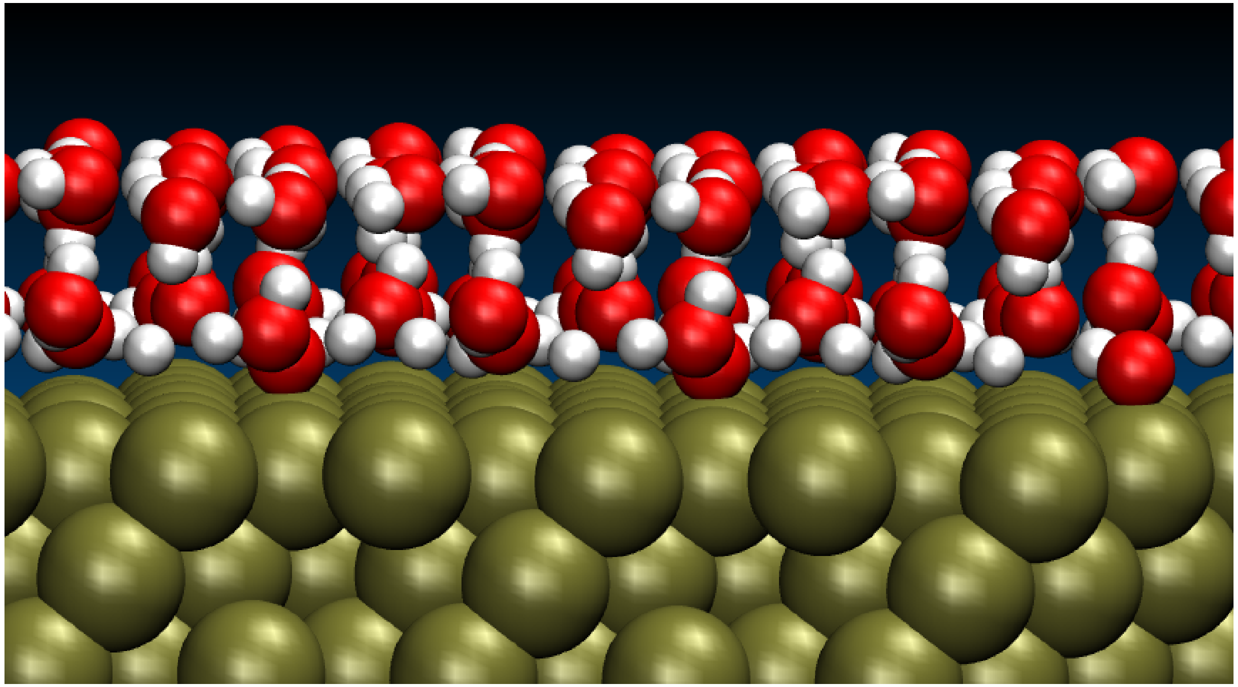
H.H. Heenen, J.A. Gauthier, H.H. Kristoffersen, T. Ludwig, and K. Chan, J. Chem. Phys. **152**, 144703 (2020)



Differences by up to 0.6 eV in the solvation energies between implicit and explicit solvation which vary strongly across metals and facets

Water structure on H-covered Pt(111)

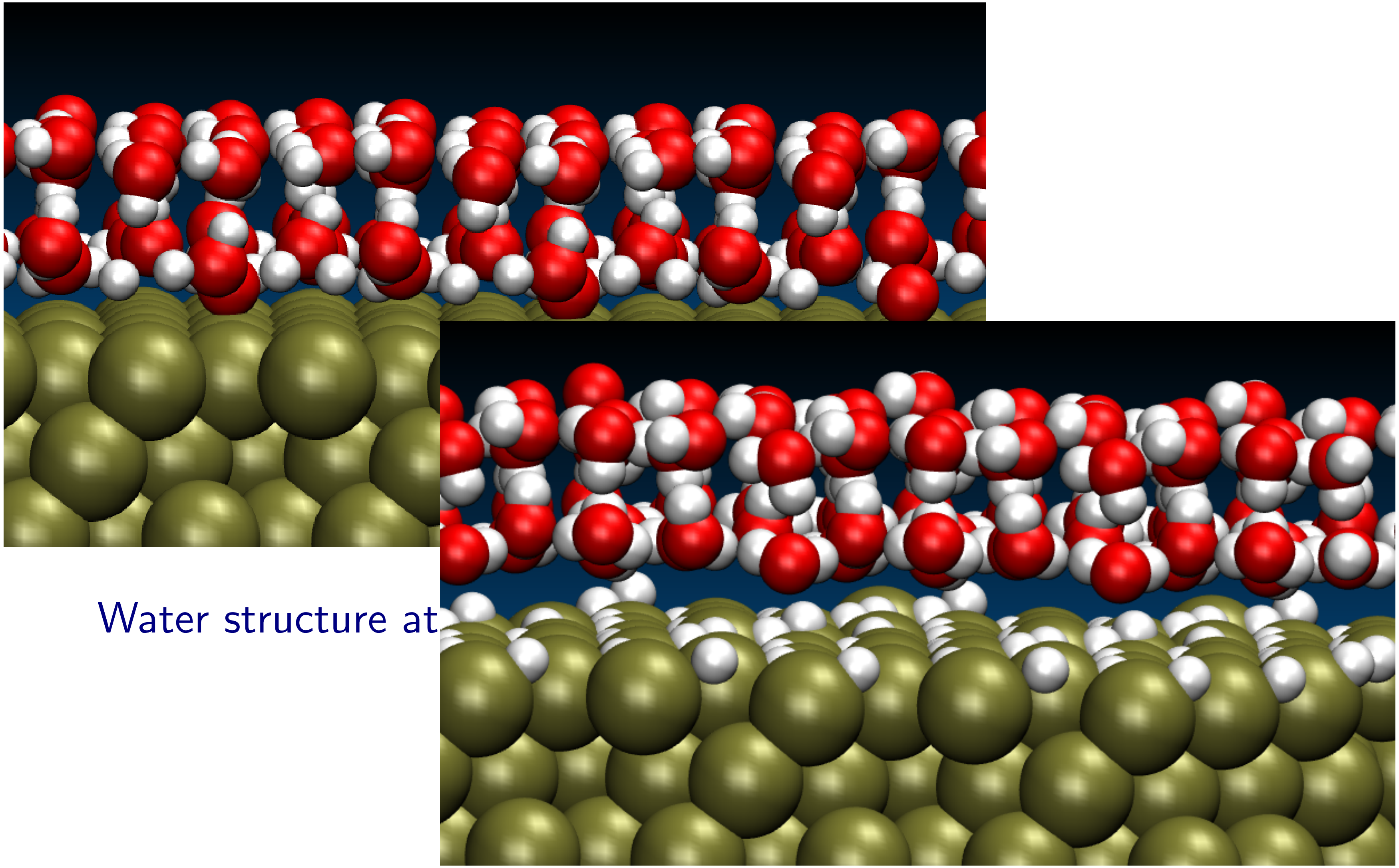
T. Roman and A. Groß, Catal. Today **202**, 183–190 (2013).



Water structure at 300 K on clean Pt(111)

Water structure on H-covered Pt(111)

T. Roman and A. Groß, Catal. Today **202**, 183–190 (2013).



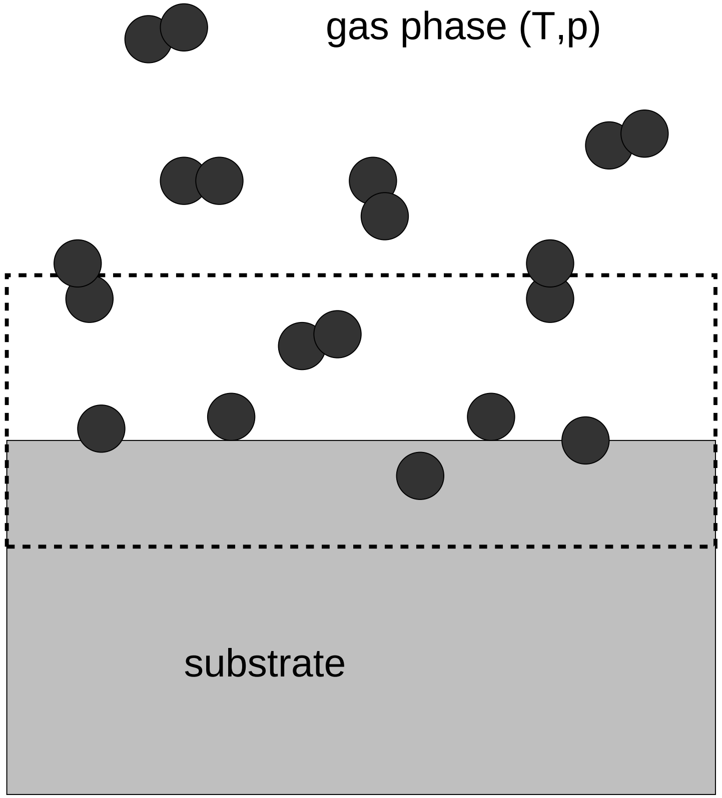
Water structure at

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

Adsorption energies at finite temperatures and pressures

K. Reuter and M. Scheffler, Phys. Rev. B **65**, 035406 (2001)

Equilibrium situation



Sketch of a substrate in equilibrium with a surrounding gas phase

Gibbs free energy

Gibbs free energy of adsorption

$$\Delta\gamma(T,p) = \gamma(T,p,N_{\mathrm{ads}}) - \gamma_{\mathrm{clean}}(T,p,0) \quad (6)$$

$$= \frac{1}{A}\Delta G^{ads}(T,p) \quad (7)$$

$$\approx \frac{N_{\mathrm{ads}}}{A}\left(E_{\mathrm{ads}} - \Delta\mu_{\mathrm{ads}}(T,p)\right) \quad (8)$$

Entropic contributions neglected in eq. (8)

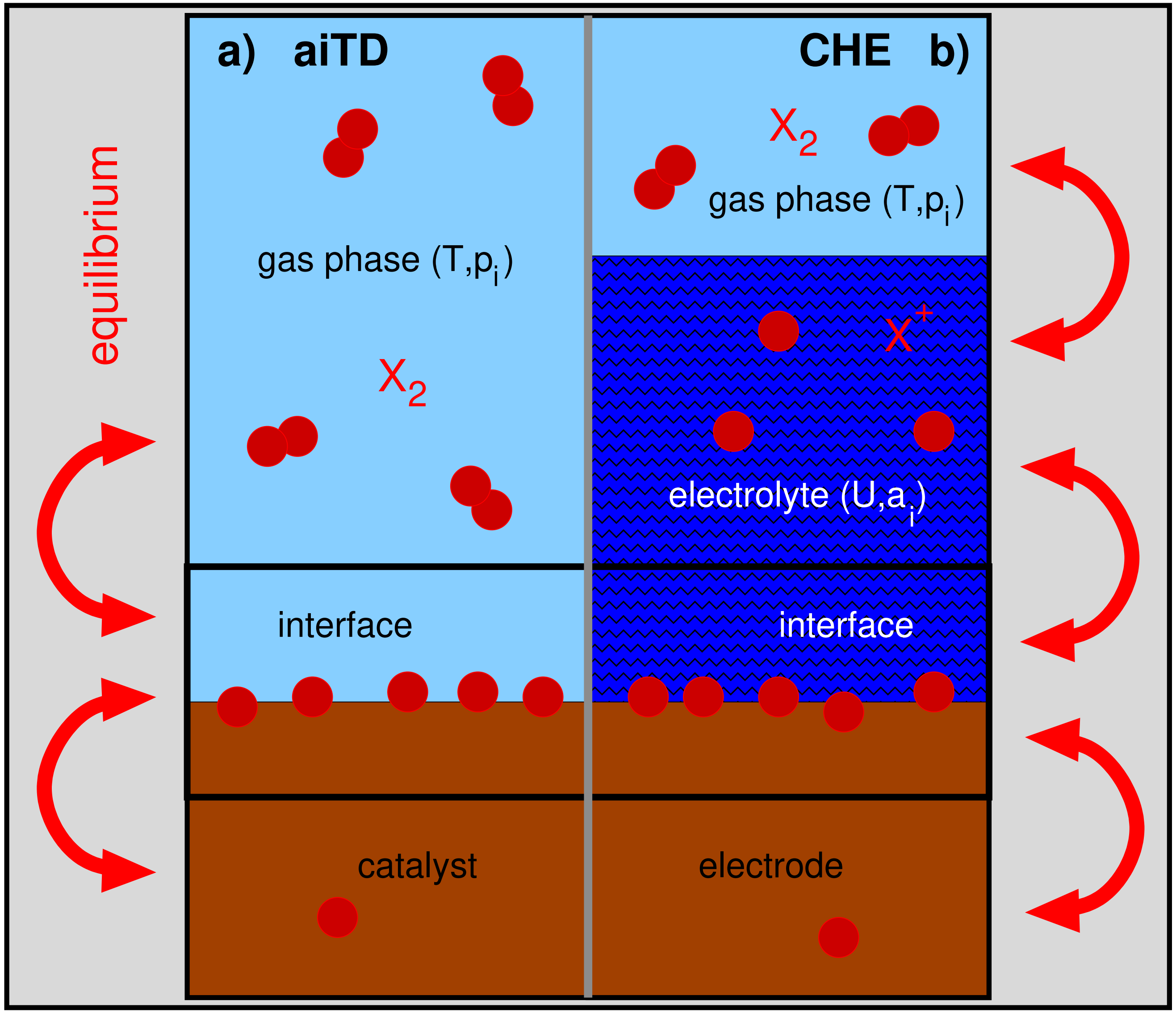
Chemical potential of the ideal gas

$$\Delta\mu_{\mathrm{ads}}(T,p) = \Delta\mu_{\mathrm{ads}}(T,p^0) + \frac{1}{2}k_{\mathrm{B}}T\ln\left(\frac{p}{p^0}\right) \quad (9)$$

ab initio thermodynamics ⇒ environment-dependent adsorbate structures

CHE vs. ab initio thermodynamics

A. Groß , Curr. Opin. Electrochem. **27**, 100684 (2021).



Electrochemical equilibrium adsorbate structures

J.K. Nørskov *et al.*, J. Electrochem. Soc. **152**, J23 (2005); H.A. Heine, J. Rossmeisl *et al.*, PCCP **12**, 283 (2010);
K. Reuter and M. Scheffler, PRB **65**, 035406 (2001)

Standard conditions (zero pH): $\mathrm{H}^+(\mathrm{aq}) + e^-$ is in equilibrium with $\frac{1}{2}\mathrm{H}_2(\mathrm{g})$

Finite pH and electrode potential:

$$\mu(\mathrm{H}^+(\mathrm{aq})) + \mu(e^-) = \frac{1}{2}\mu(\mathrm{H}_2(\mathrm{g})) - eU_{\mathrm{SHE}} - k_{\mathrm{B}}T\ln(10)\mathrm{pH} \tag{10}$$

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Equivalently for the standard chlorine electrode
(redox potential $\mathrm{Cl}^-(\mathrm{aq}) \leftrightharpoons \frac{1}{2}\mathrm{Cl}_2(\mathrm{g}) + e^-$: $U_{\mathrm{SHE}} = 1.36\,\mathrm{V}$)

$$\mu(\mathrm{Cl}^-(\mathrm{aq})) - \mu(e^-) = \frac{1}{2}\mu(\mathrm{Cl}_2(\mathrm{g})) + e(U_{\mathrm{SHE}} - 1.36V) + k_{\mathrm{B}}T\ln a_{\mathrm{Cl}^-} \qquad (11)$$

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Free energy of adsorption

$$\Delta\gamma(U_{\mathrm{SHE}}) \approx \frac{N_{\mathrm{ads}}}{A_s}\left(E_{\mathrm{ads}} - e(U_{\mathrm{SHE}} - U^0) - k_{\mathrm{B}}T\ln a_{\mathrm{A}^-} + k_{\mathrm{B}}T\ln(10)\mathrm{pH}\right) \ . \tag{12}$$

Computational electrodes ⇒ environment-dependent adsorbate structures,
avoids determination of solvation energies

Electrochemical equilibrium adsorbate structures

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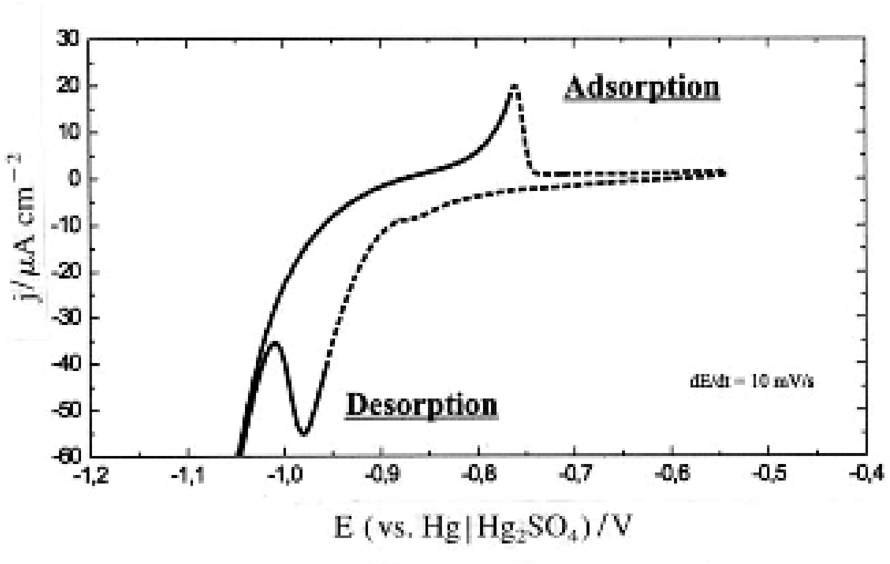
Free energy of adsorption

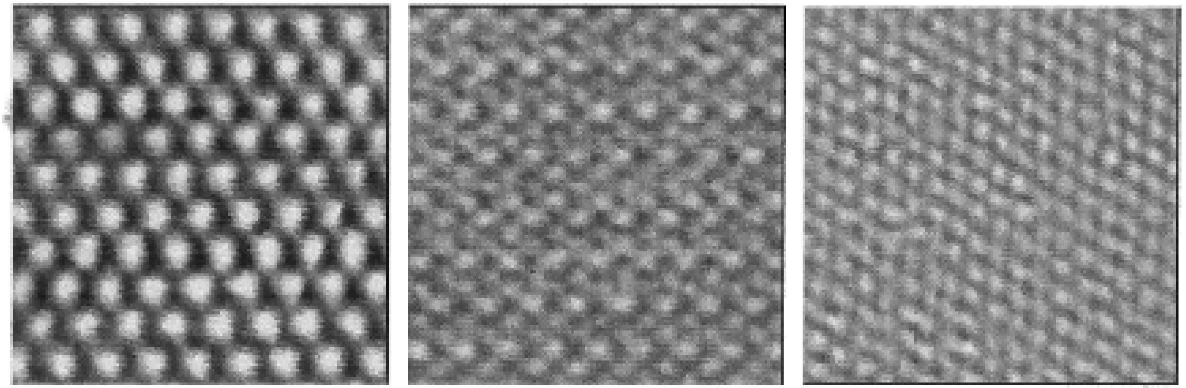
$$\Delta\gamma(U_{\mathrm{SHE}}) \approx \frac{N_{\mathrm{ads}}}{A_s}\left(E_{\mathrm{ads}} - e(U_{\mathrm{SHE}} - U^0) - k_{\mathrm{B}}T\ln a_{\mathrm{A}^-} + k_{\mathrm{B}}T\ln(10)\mathrm{pH}\right) \;. \qquad (15)$$

Computational electrodes ⇒ environment-dependent adsorbate structures,
avoids determination of solvation energies

Electrochemical experiment: Cl on Cu(111)

P. Broekmann *et al.*, J. Electroanal. Chem. **467**, 307 (1999)





(√3×√3)R30°-Cl

(√3×√3)R30°-Cl + Cu (1×1)

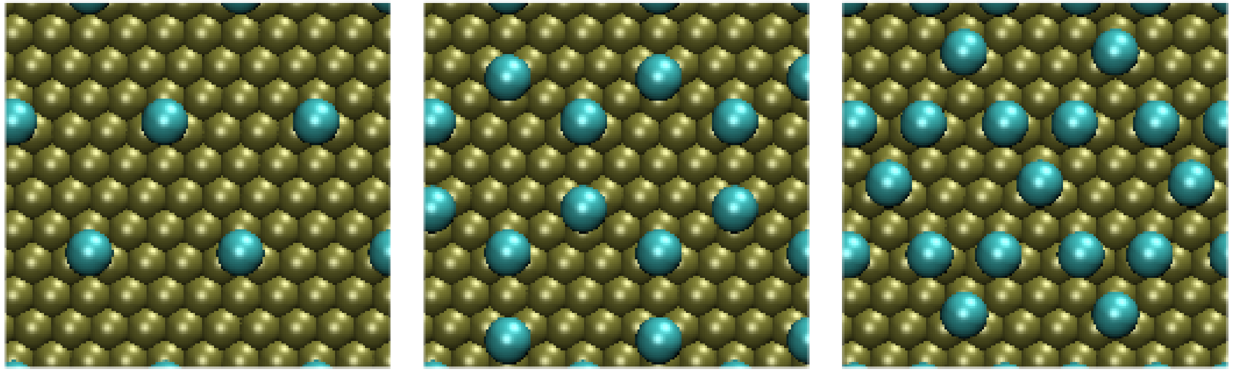
Cu (1×1)

Cyclic voltammogram and STM images of Cu(111) in 10 mM HCl

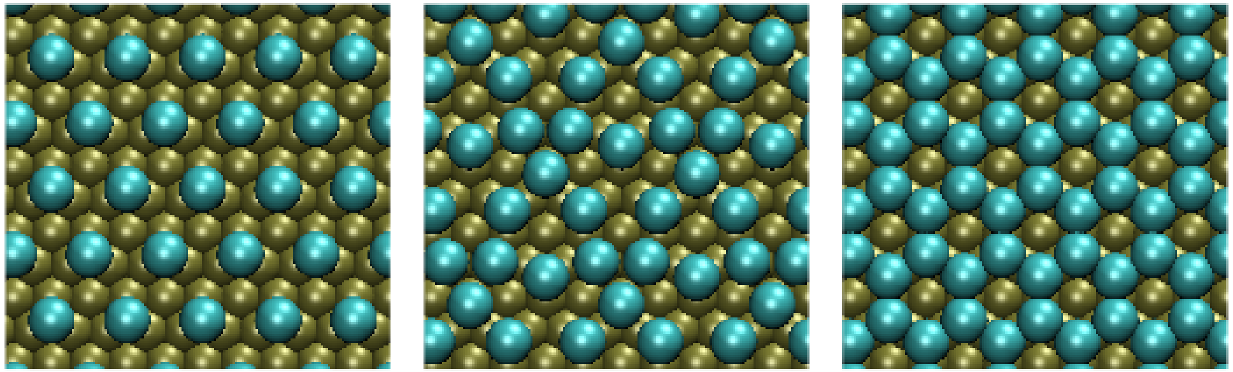
Adsorption of anions at electrode-electrolyte interfaces

T. Roman and A. Groß, PRL **110**, 156804 (2013);
T. Roman, F. Gossenberger, Katrin Forster-Tonigold, and A. Groß, PCCP **16**, 13630 (2014).

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



(a) 1/16 coverage (b) 2/16 coverage (c) 3/16 coverage

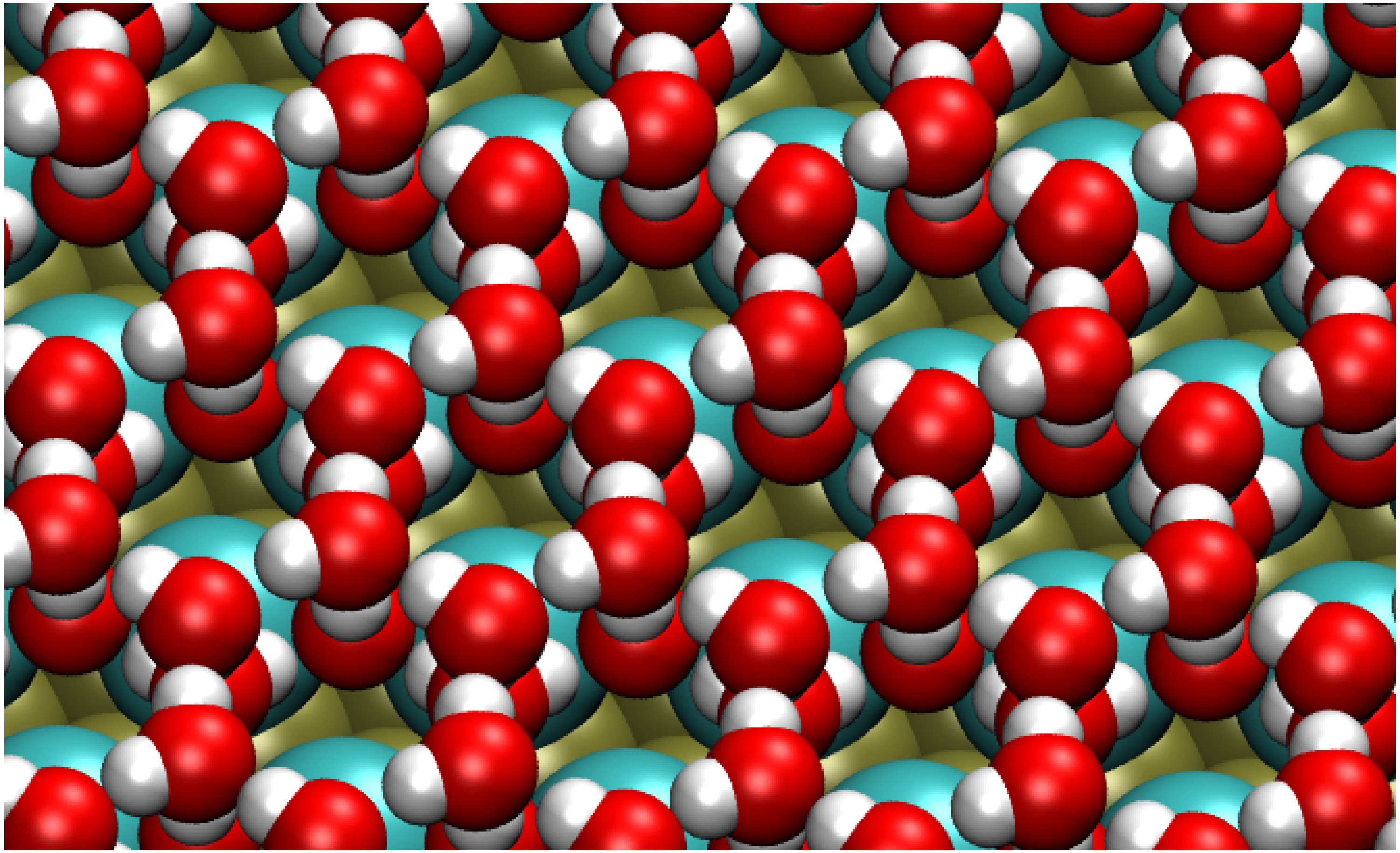


(d) 4/16 coverage (e) 6/16 coverage (f) 8/16 coverage

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

Water layer above chlorine-covered Pt(111)

A. Groß et al., J. Electrochem. Soc. **161**, E3015 (2014)

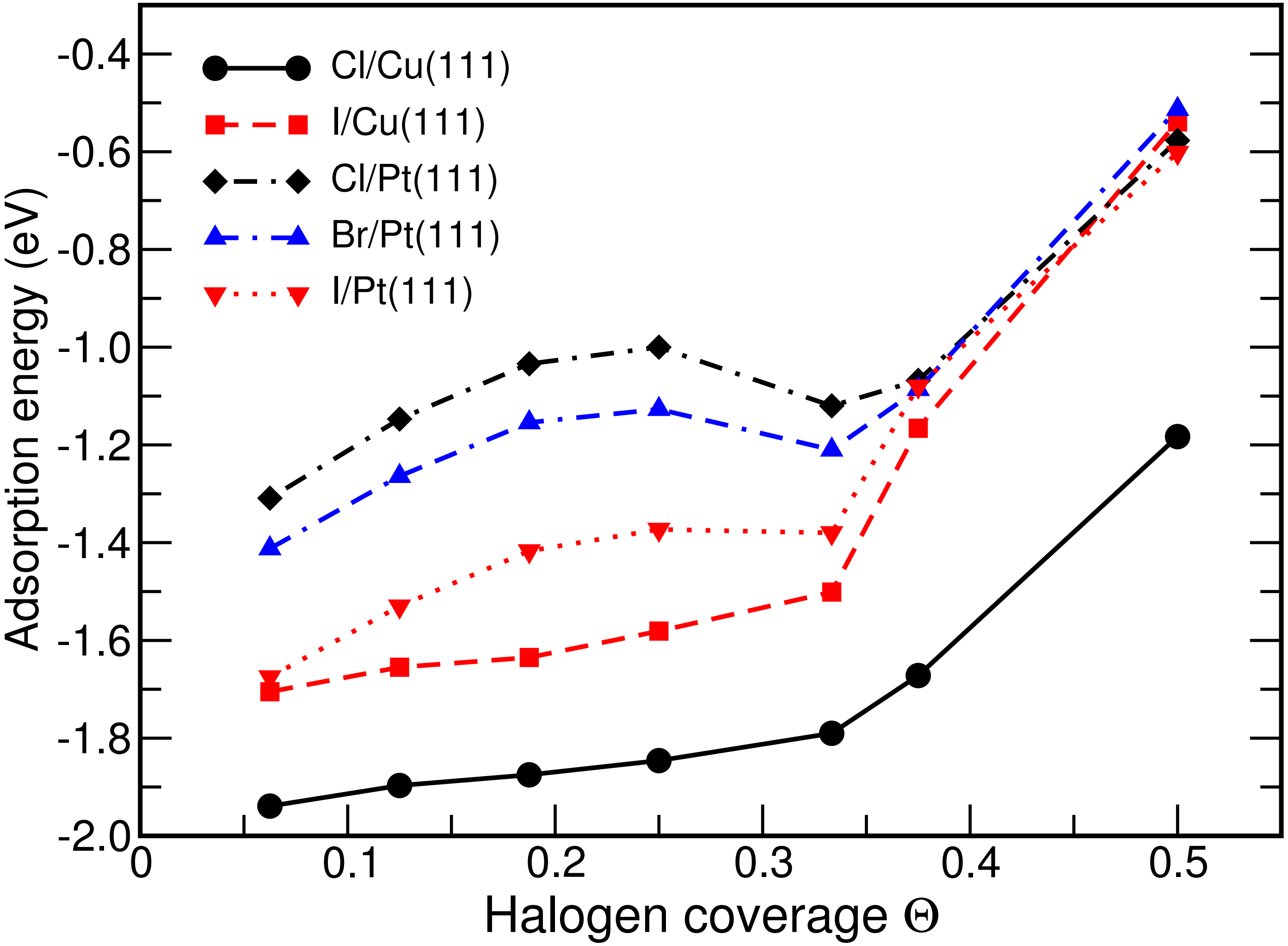


Compact water layers above chlorine atoms

Weak influence of the water layer on chlorine adsorption

Adsorption energies of halides on Cu(111) and Pt(111)

F. Gossenberger, T. Roman, and A. Groß, Surf. Sci. **631**, 17 (2015).



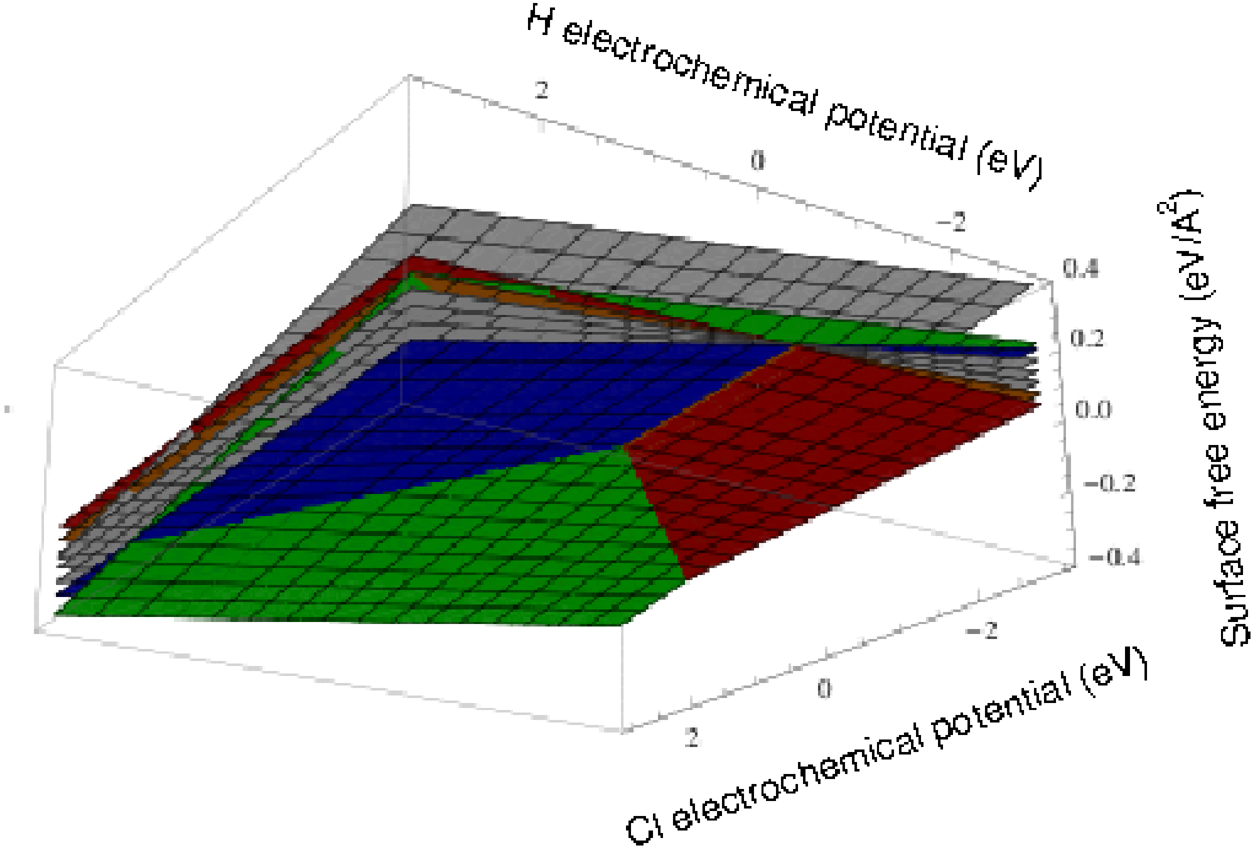
Stability of structure in equilibrium hard to judge from the representation of adsorption energies

Co-adsorption of Cl and H on Pt(111)

F. Gossenberger, T. Roman, and A. Groß, Electrochim. Acta **216**, 152 (2016).

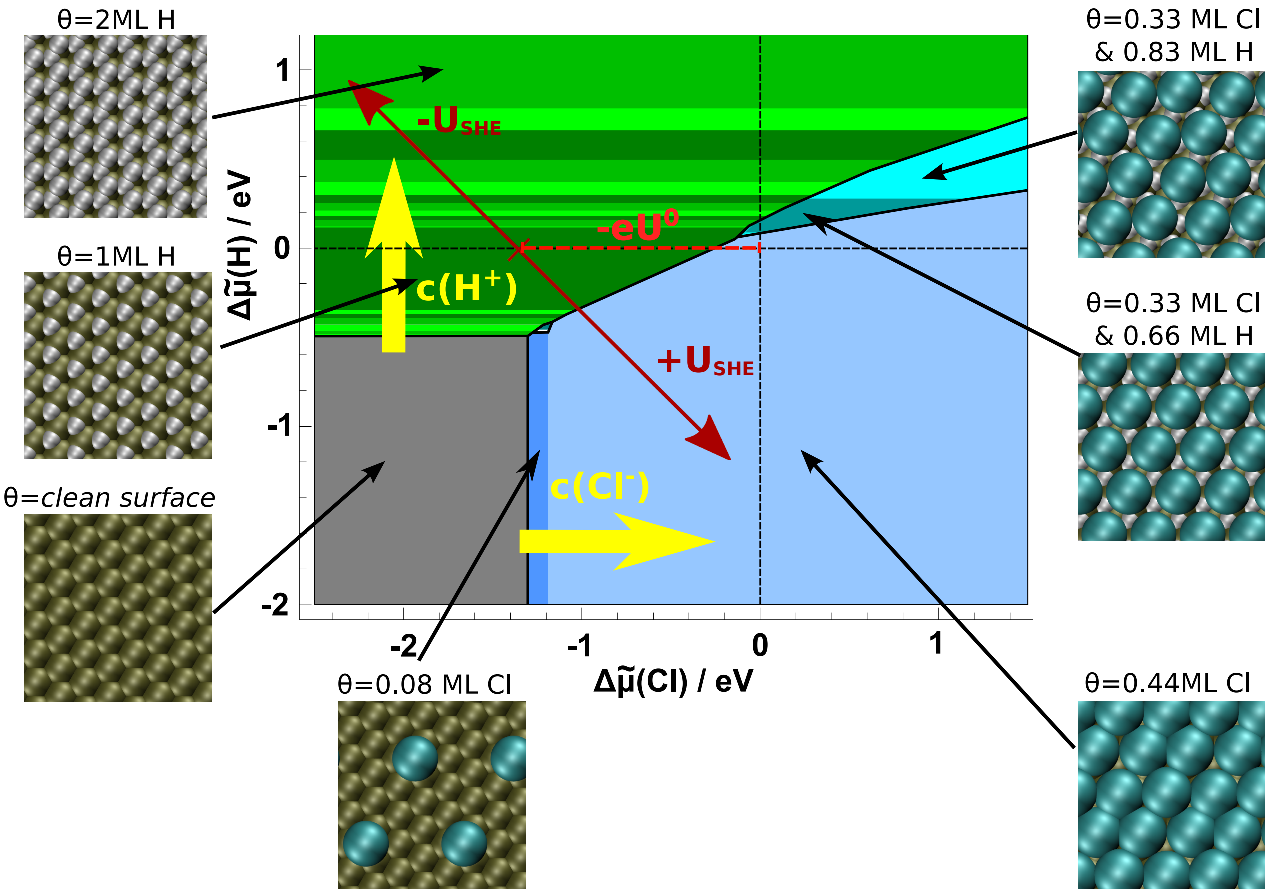
Thermodynamic formalism can be extended to several adsorbates A, B, . . .

$$\Delta\gamma(A,B,T,p) = \frac{1}{A}\left(E_{\mathrm{ads}}(N \cdot A, M \cdot B) - N\Delta\mu_{\mathrm{ads}}(A,T,p) - M\Delta\mu_{\mathrm{ads}}(B,T,p)\right) \quad (16)$$



Phase diagram of Cl and H co-adsorption on Pt(111)

F. Gossenberger, T. Roman, and A. Groß, Electrochim. Acta **216**, 152 (2016).



Repulsion between adsorbed H and Cl

Adsorption of hydrogen and chlorine has a competitive character

N. Garcia-Araez *et al.*, J. Electroanal. Chem. **576**, 33 (2005)

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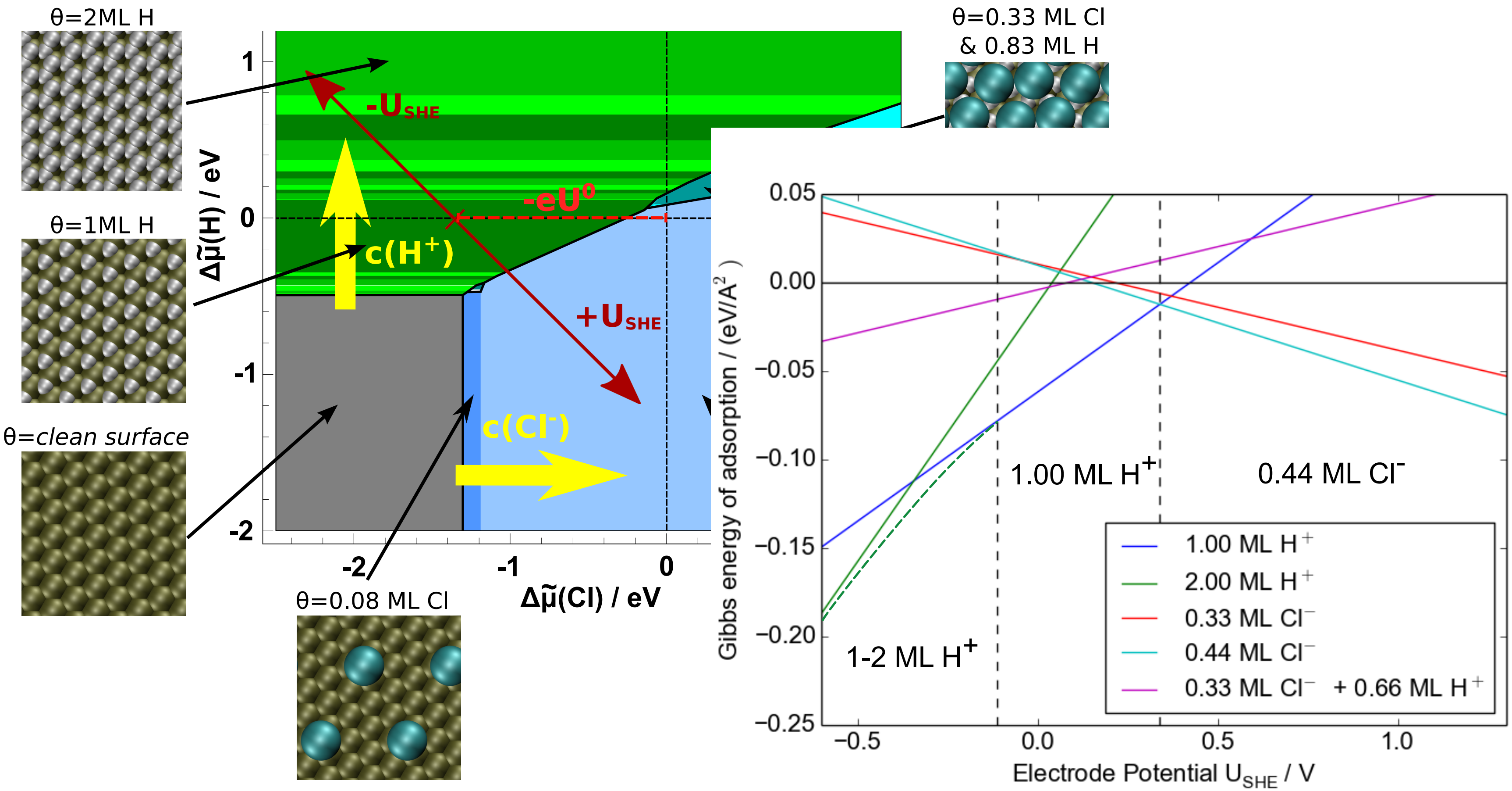

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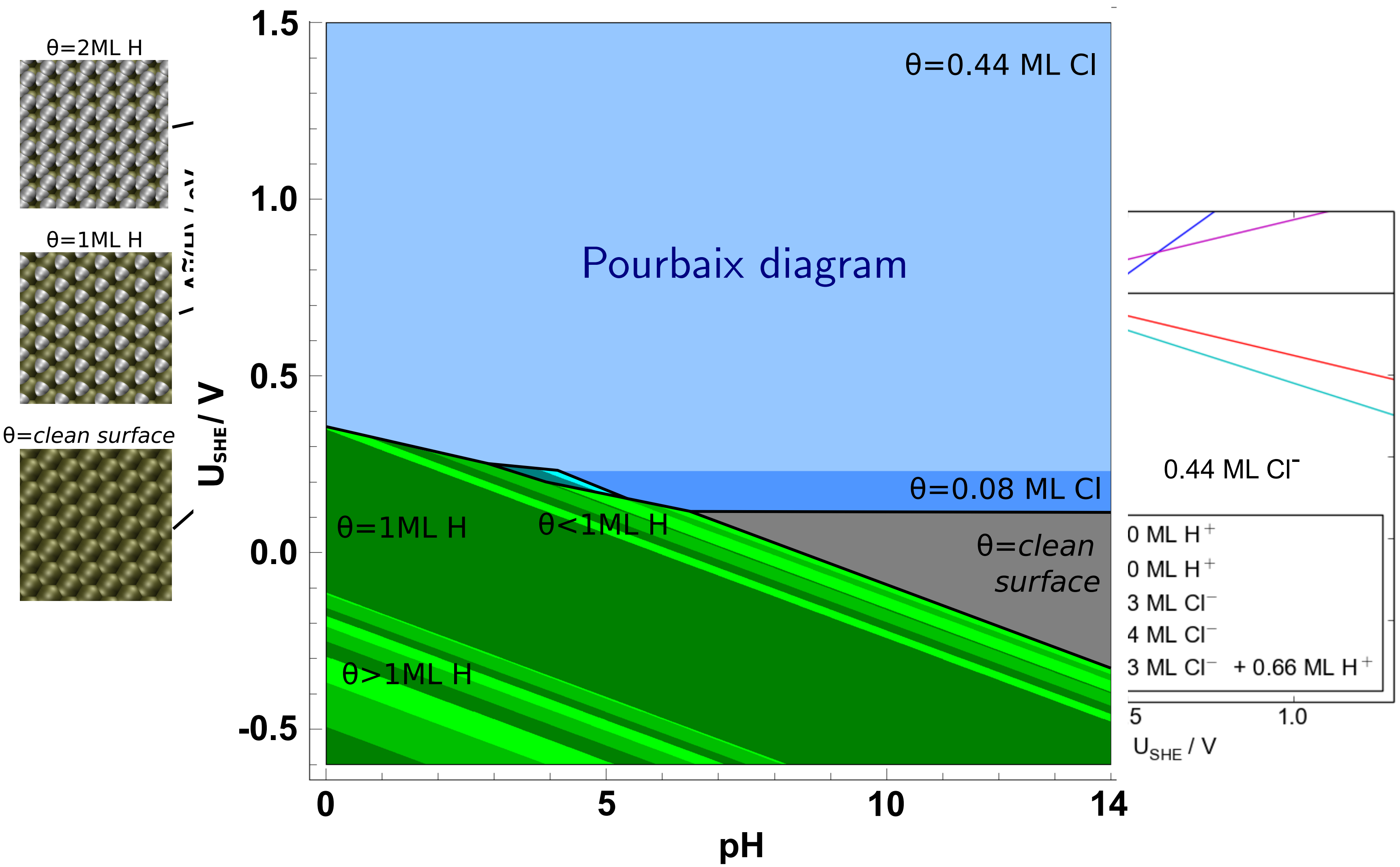

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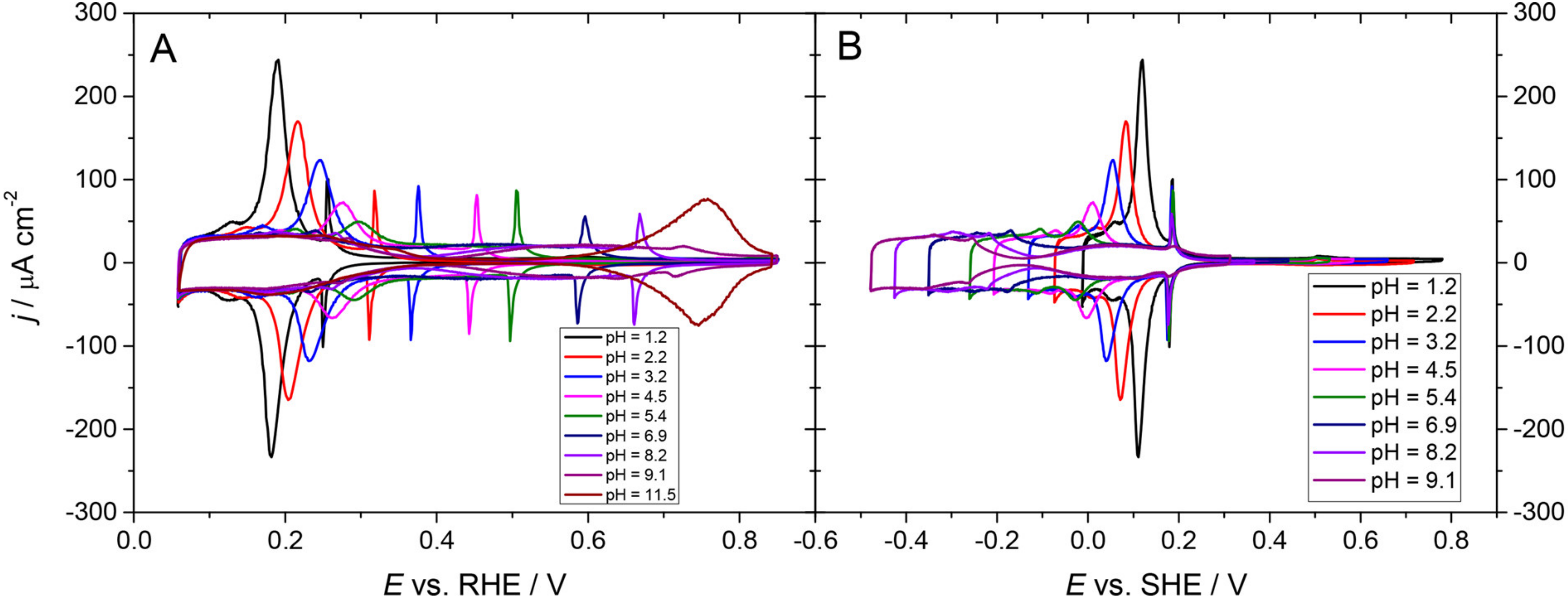
N. Garcia-Araez *et al.*, J. Electroanal. Chem. **576**, 33 (2005)

“Non-Nernstian” trends in Br and H co-adsorption

G.A.B. Mello, V. Briega-Martos, V. Climent, J.M. Feliu, J. Phys. Chem. C **122**, 18562 (2018).



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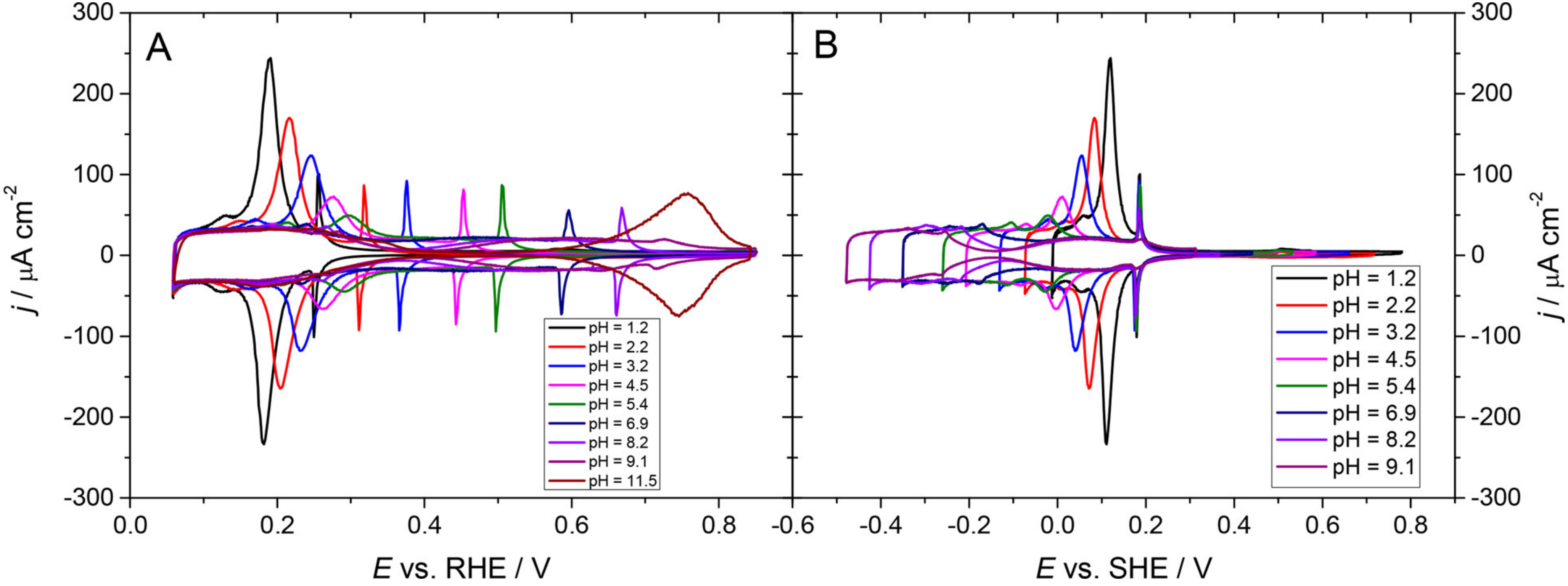

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Peak associated with Pt(111)(4×4)-7Br to Pt(111)(3×3)-4Br transition independent of pH on the SHE scale

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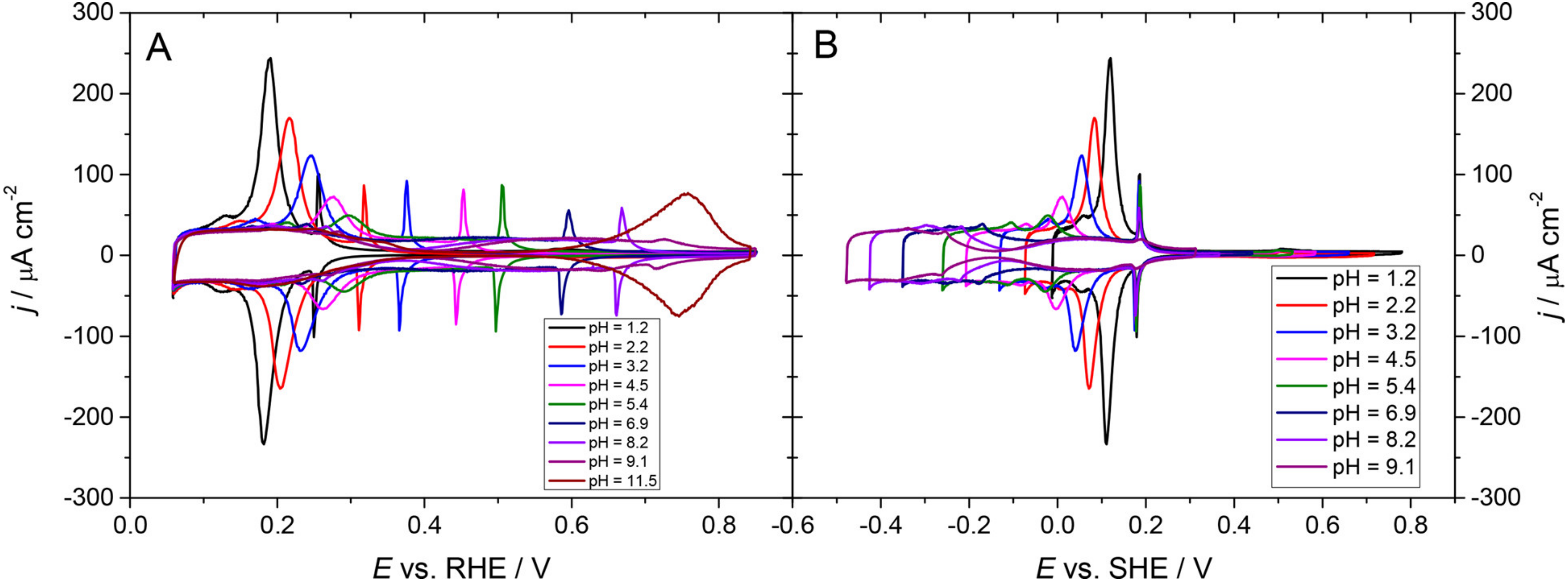

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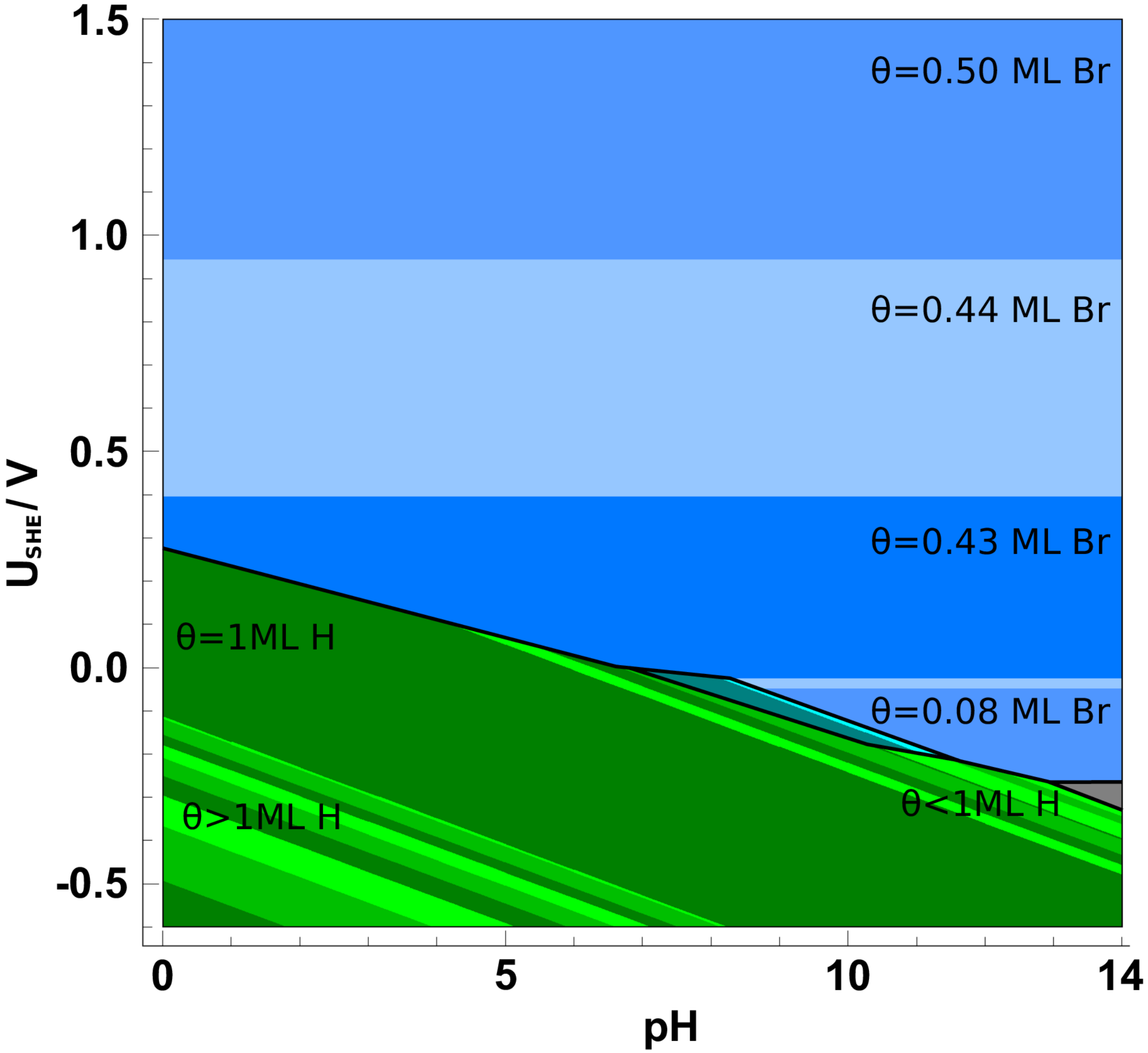
Hydrogen adsorption/desorption peak depend on pH on the RHE scale

Calculated Pourbaix diagram of Br and H on Pt(111)

F. Gossenberger, T. Roman, and A. Groß, Electrochim. Acta **216**, 152 (2016); X. Lin, F. Gossenberger, and A. Groß, Ind. Eng. Chem. Res. **55**, 11107 (2016); A. Groß, J. Phys. Chem. Res. C **126**, 11439 (2022)



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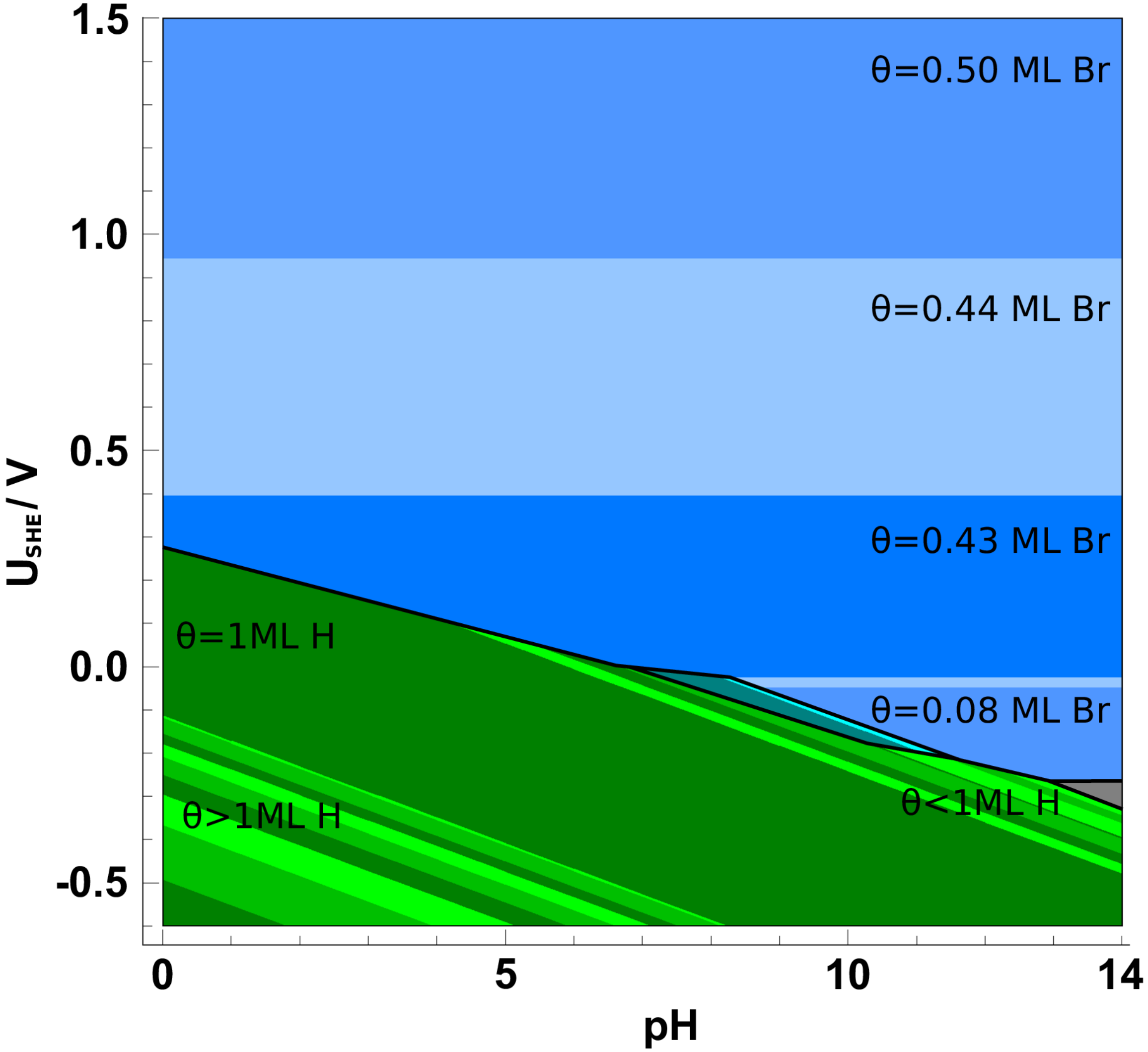

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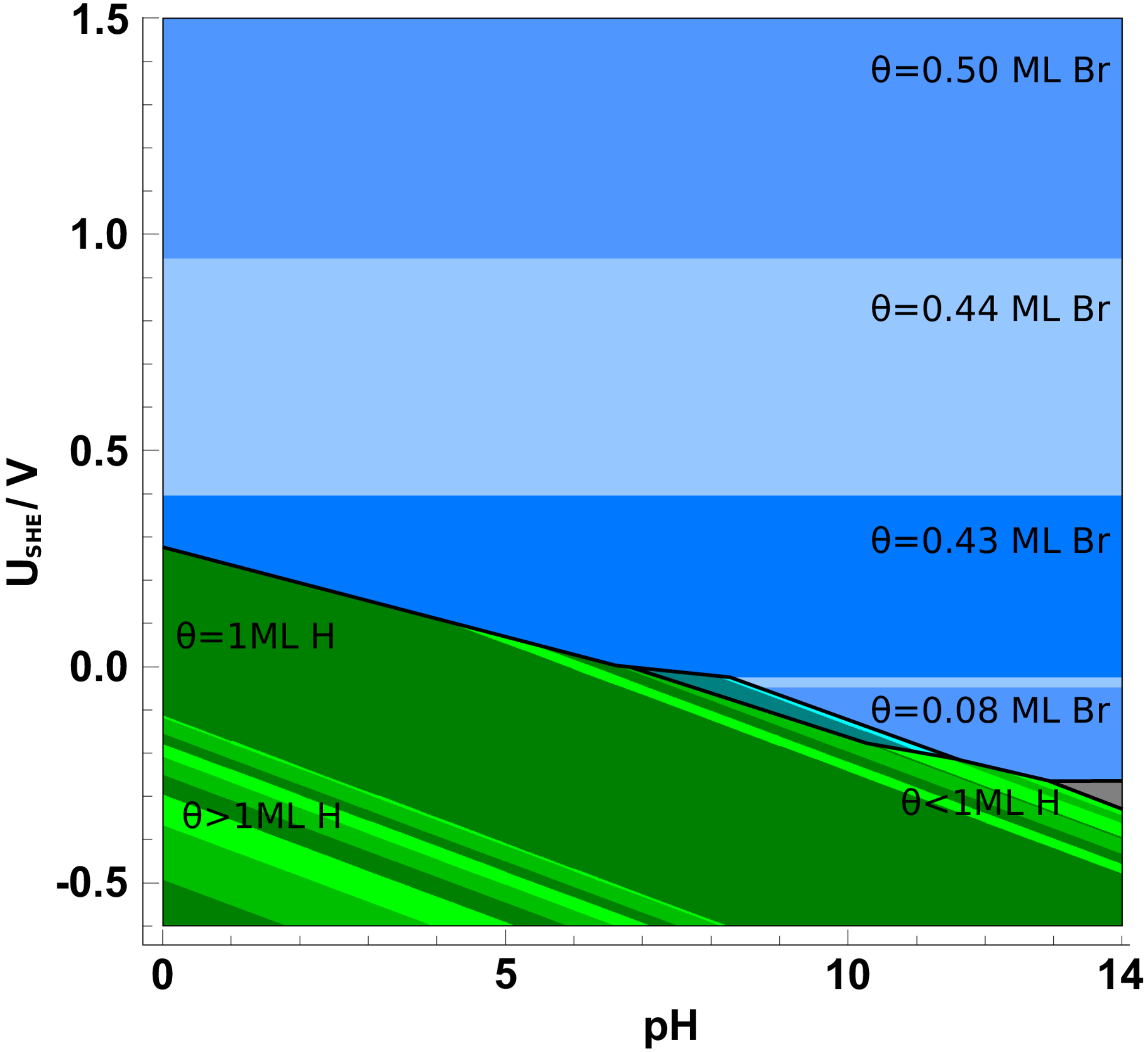

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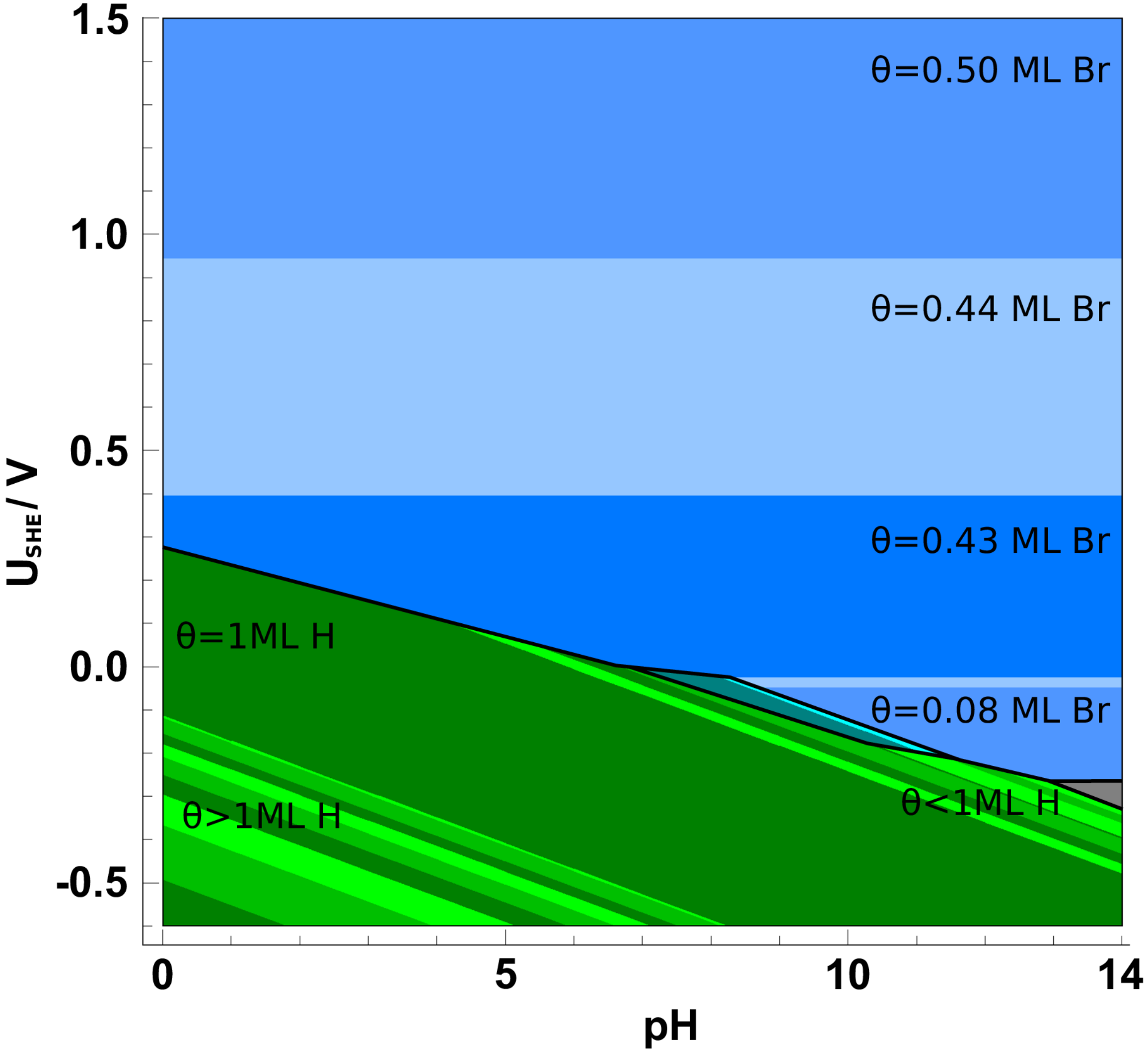

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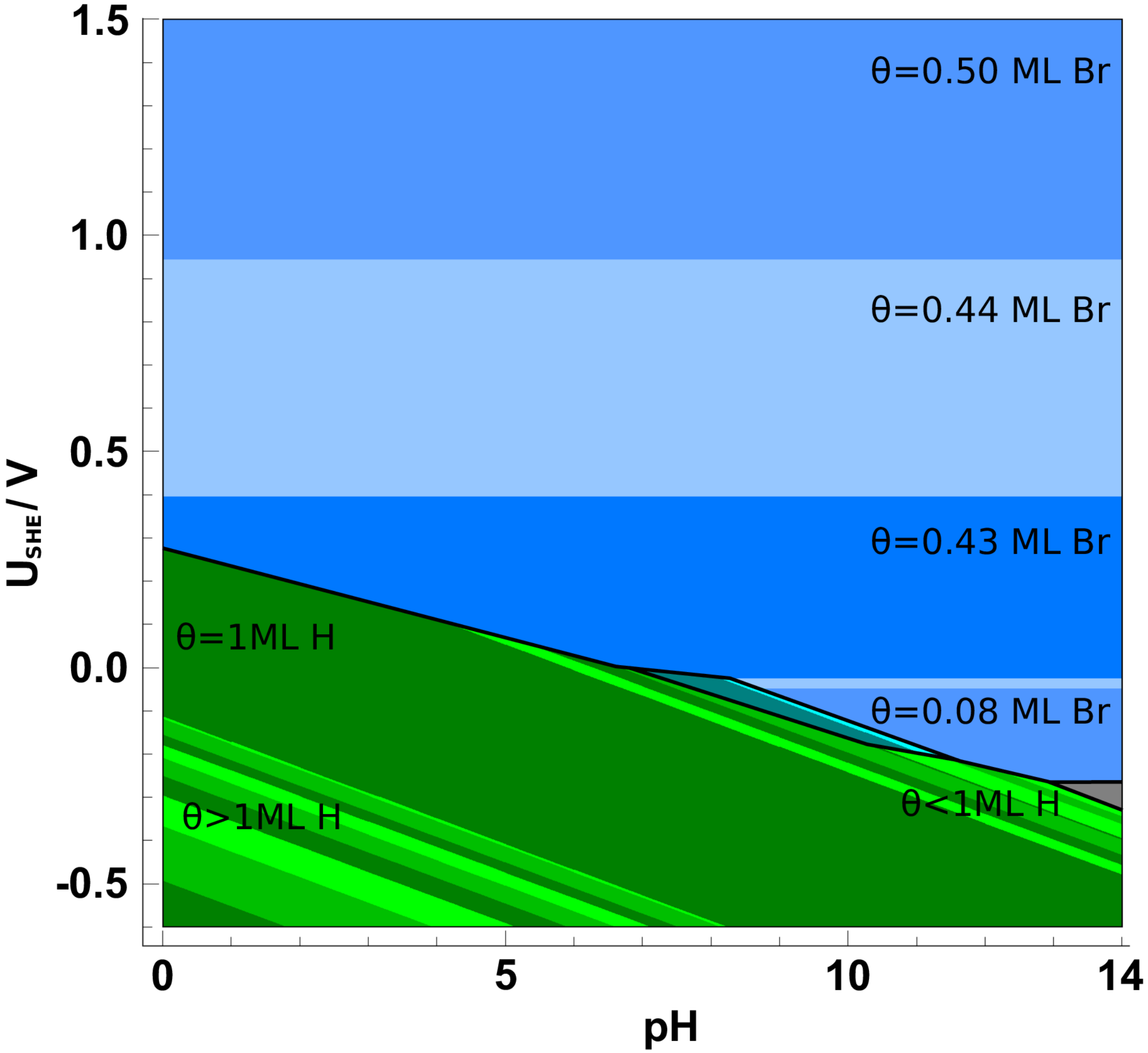

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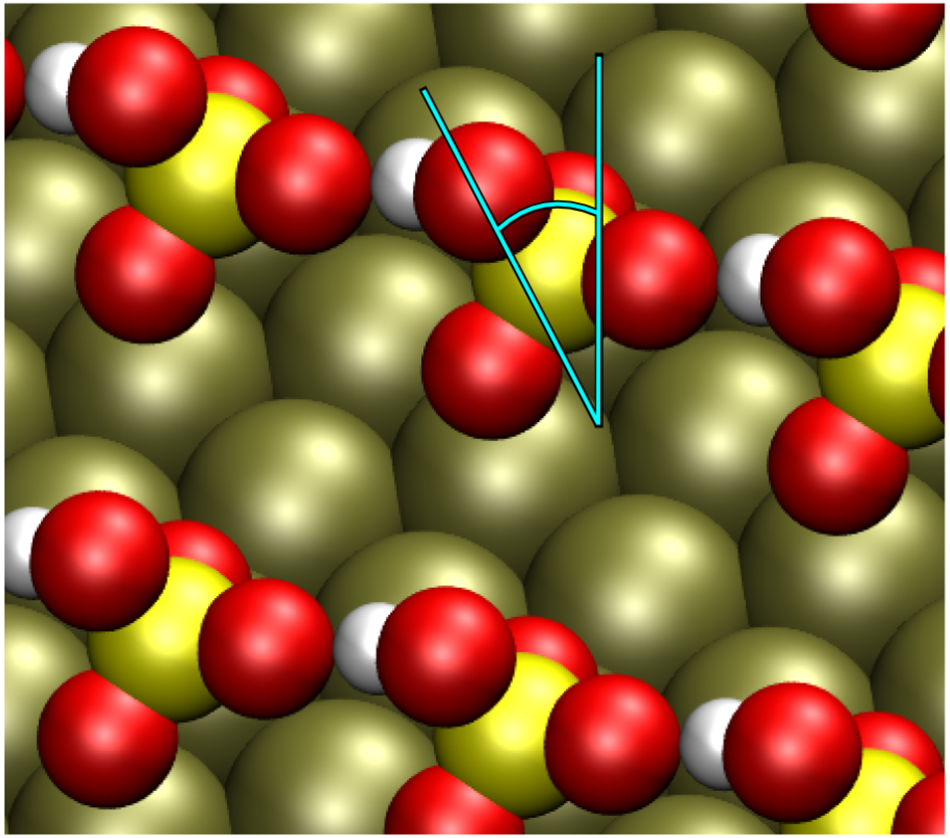
A slope $\neq$59 mV/pH of hydrogen phases does not necessarily indicate a non-Nernstian behavior

Sulfate and bisulfate adsorption on Pt(111)

F. Gossenberger, F. Juarez , and A. Groß, Frontiers Chem. **8**, 634 (2020).

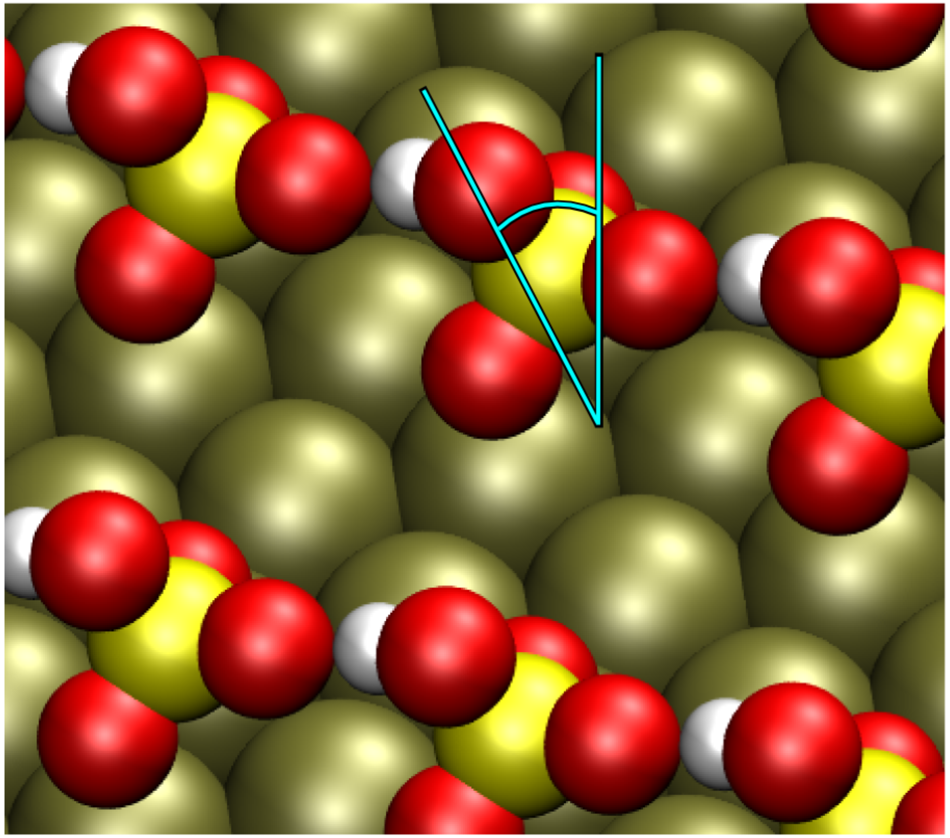


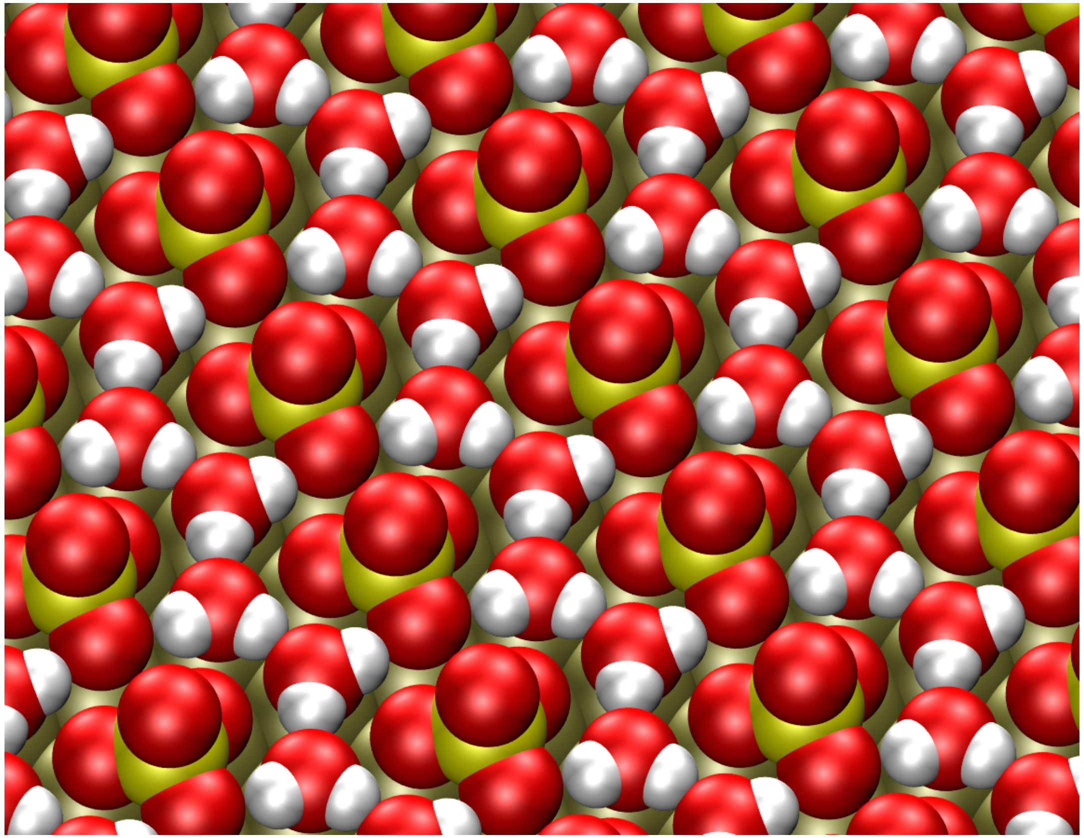
$(\sqrt{3} \times \sqrt{7})R19.1^\circ$ bisulfate rows

Water needs to be included both implicitly and explicitly

Sulfate and bisulfate adsorption on Pt(111)

F. Gossenberger, F. Juarez , and A. Groß, Frontiers Chem. **8**, 634 (2020).





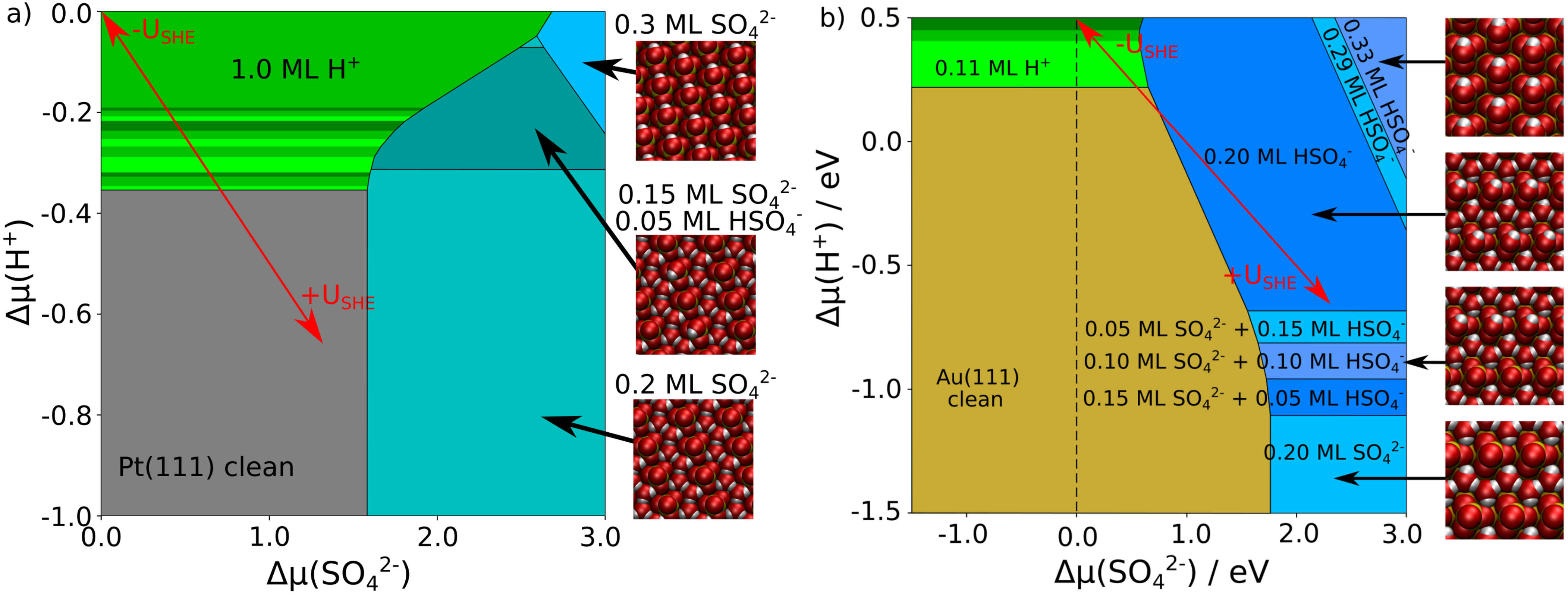
$(\sqrt{3} \times \sqrt{7})R19.1^\circ$ bisulfate rows

Sulfate rows stabilized by the bridging water molecules

Water needs to be included both implicitly and explicitly

Phase diagrams of sulfate on Pt(111) and Au(111)

F. Gossenberger, F. Juarez , and A. Groß, Frontiers Chem. **8**, 634 (2020).

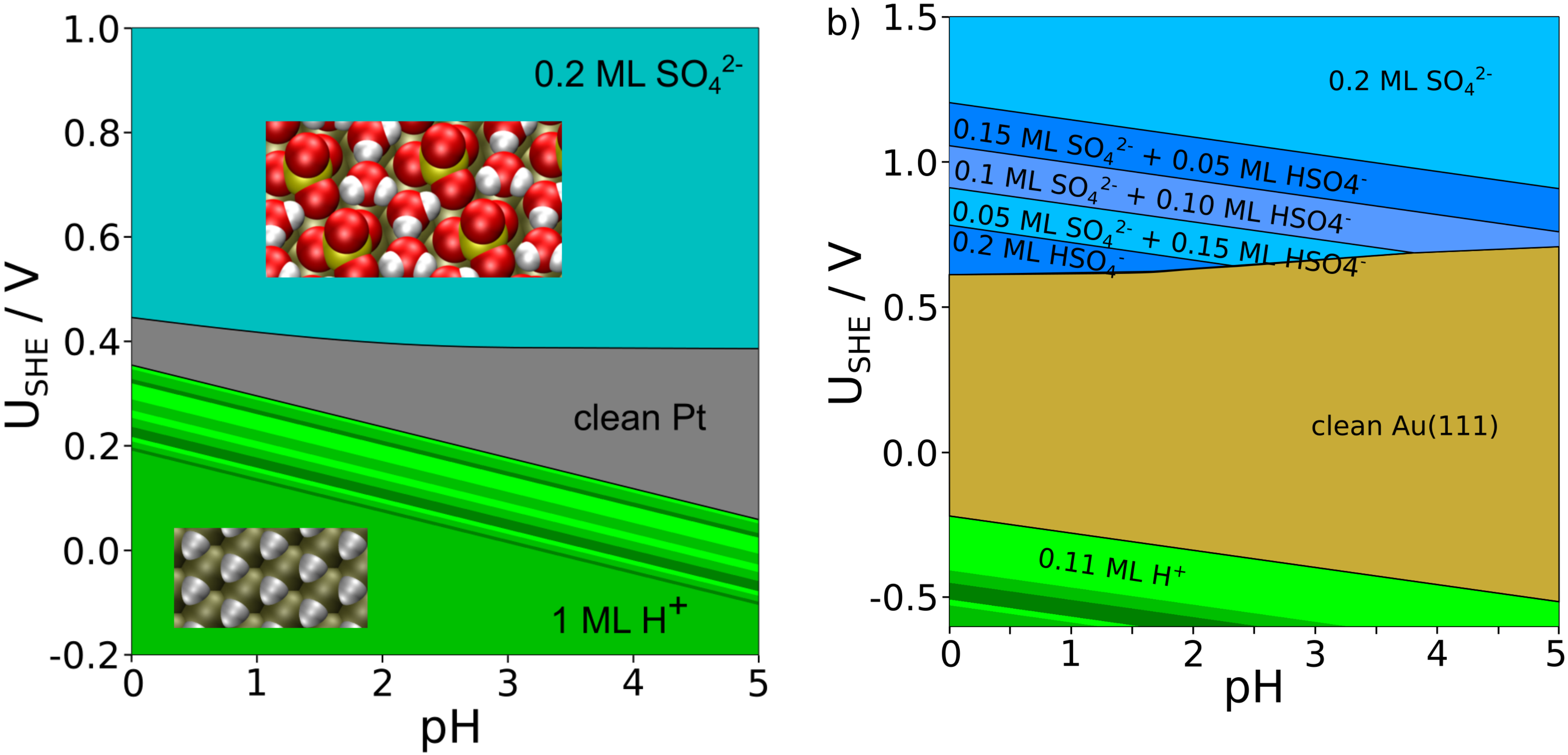


Water included in a combination of implicit and explicit modeling

Pourbaix diagrams of sulfate on Pt(111) and Au(111)

F. Gossenberger, F. Juarez , and A. Groß, Frontiers Chem. **8**, 634 (2020).

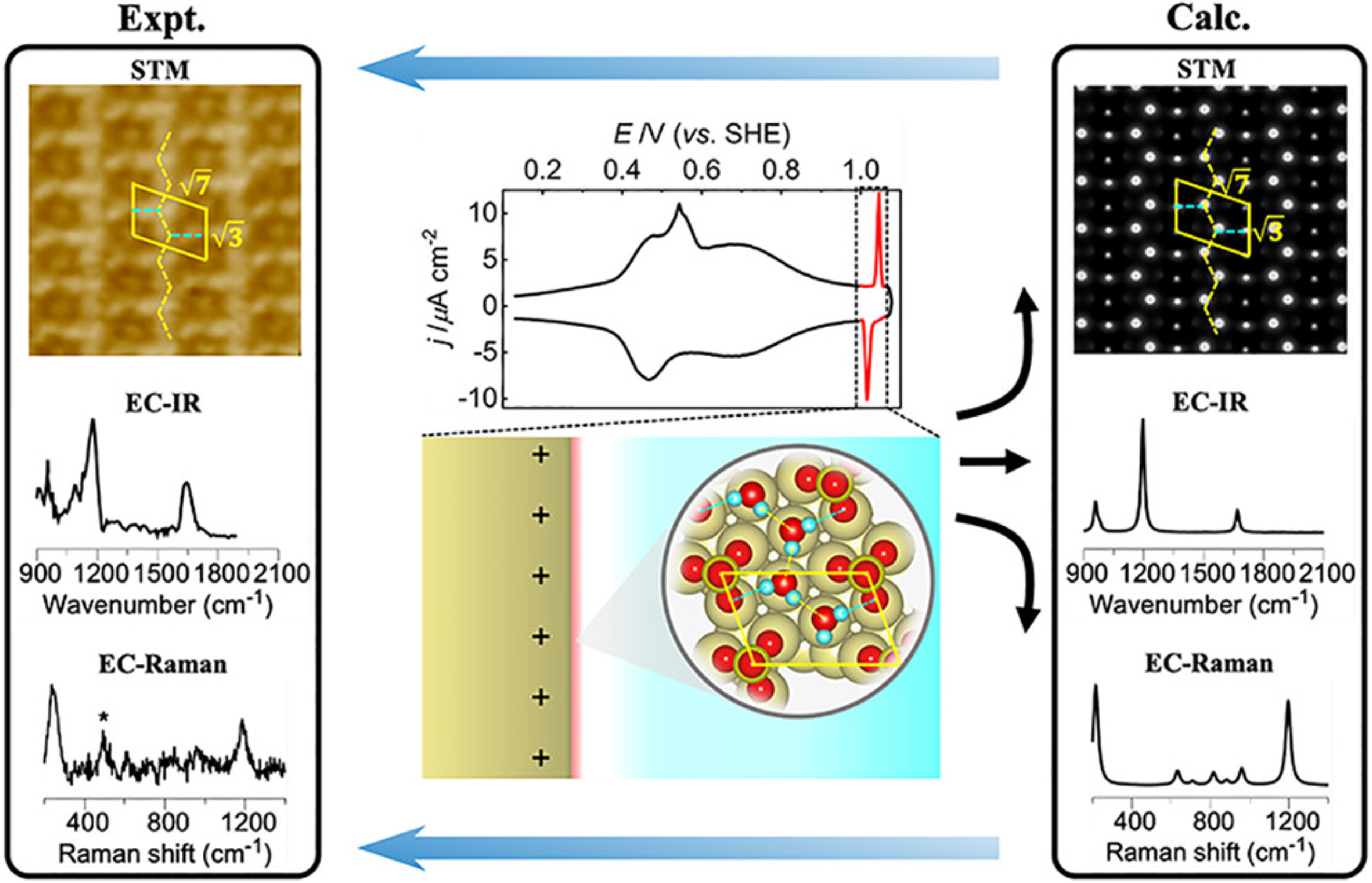
A. Groß , Curr. Opin. Electrochem. **27**, 100684 (2021).



Qualitative and almost quantitative agreement with experiments

Interface of Au(111) electrode-sulfuric acid solution

Y. Fang, S. Ding, M. Zhang, S.N. Steinmann, R. Hu, B. Mao, J.M. Feliu, Z. Tian, JACS **142**, 9439 (2020).



Transition from diffuse mixed sulfate-bisulfate layer to striped sulfate structure

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 processes at surfaces and interfaces

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