2269-26

Workshop on New Materials for Renewable Energy

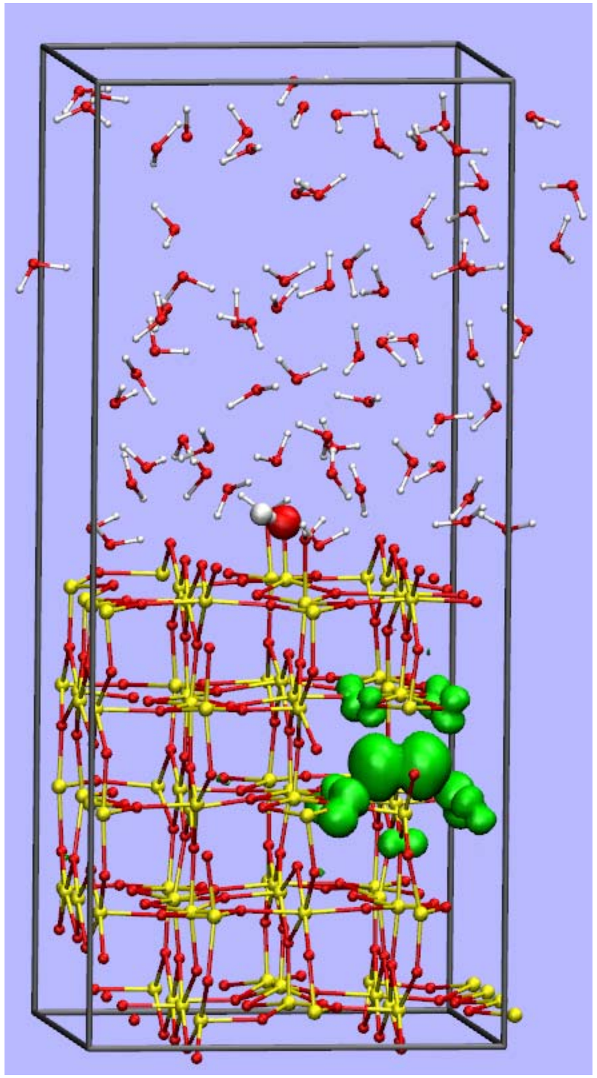
17 - 21 October 2011

The thermochemistry of oxidative dehydrogenation of a water molecule at a TiO2 (110) water interface

Michiel SPRIK

Dept. of Chemistry, University of Cambridge
U.K.

Oxidative hydrogenation at the rutile TiO2(110) water interface



Collaboration:

Jun Cheng

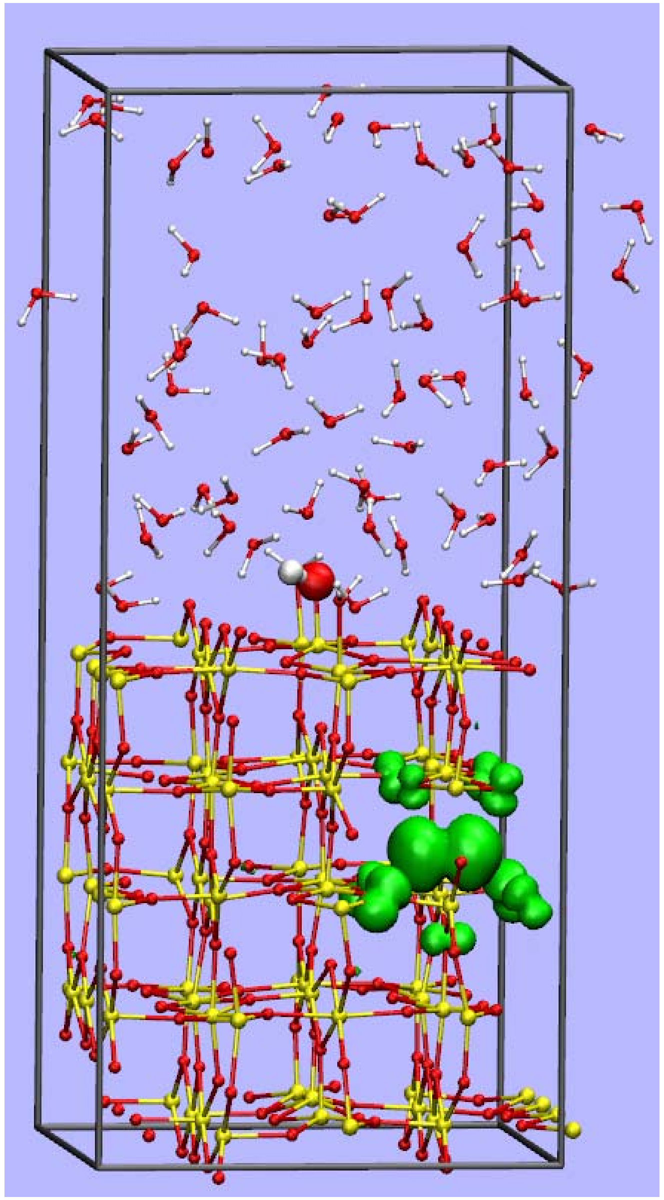
Marialore Sulpizi

Joost VandeVondele

Funding: **EPSRC, UKCP**

Department of Chemistry
University of Cambridge

Formation of a surface hydroxyl group



Oxidative dehydrogenation of water

$$*\mathrm{OH_2} \rightarrow *\mathrm{OH}^{\bullet} + \mathrm{H}^{+} + e^{-}$$

Separated in a deprotonation

$$*\mathrm{OH_2} \rightarrow *\mathrm{OH}^{-} + \mathrm{H}^{+}$$

and an ionization

$$*\mathrm{OH}^{-} \rightarrow *\mathrm{OH}^{\bullet} + e^{-}$$

or trapping of a hole

$$*\mathrm{OH}^{-} + \mathrm{h}^{+} \rightarrow *\mathrm{OH}^{\bullet}$$

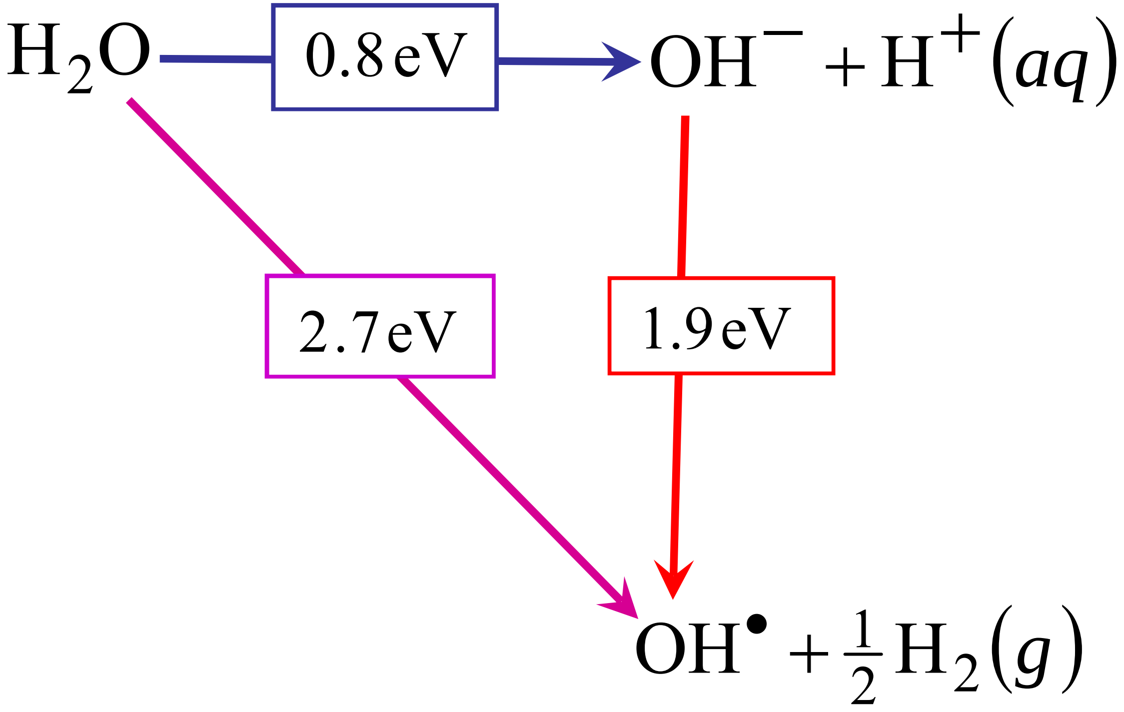
Spin density in TiO_2

(*Jun Cheng*)

Abstracting the first hydrogen from water

$$H_2O(l) \rightarrow OH^{\bullet}(aq) + \tfrac{1}{2}H_2(g)$$

Experiment



H_2O

$0.8\,\mathrm{eV}$

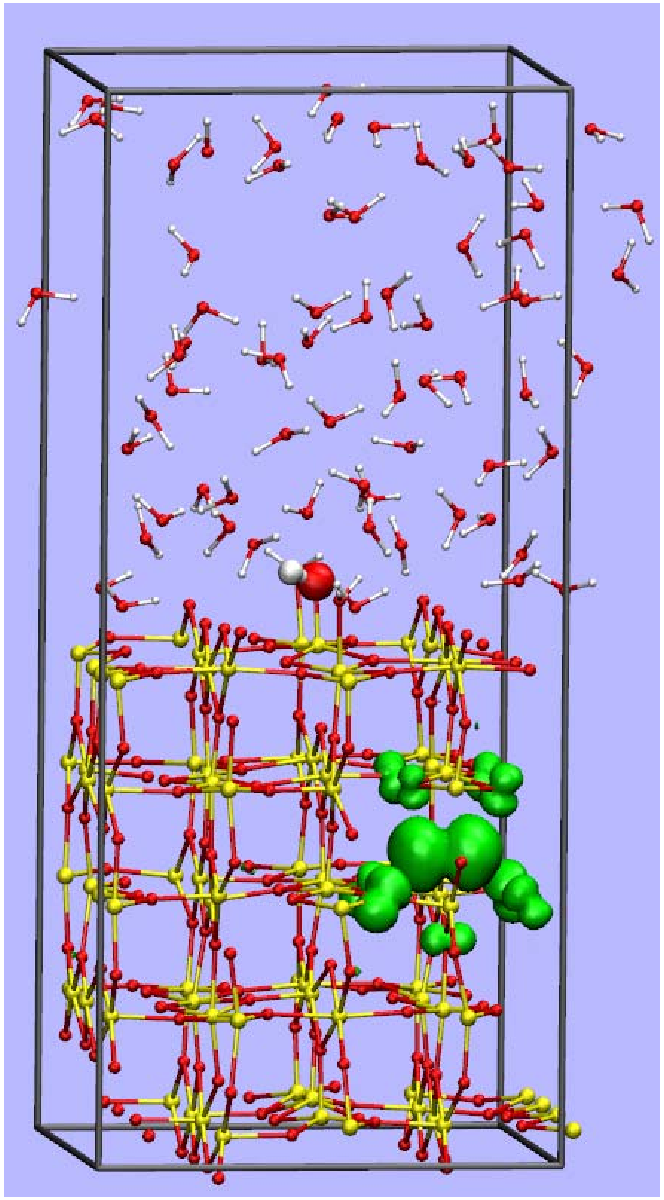
$OH^{-} + H^{+}(aq)$

$2.7\,\mathrm{eV}$

$1.9\,\mathrm{eV}$

$OH^{\bullet} + \tfrac{1}{2}H_2(g)$

Formation of a surface hydroxyl group



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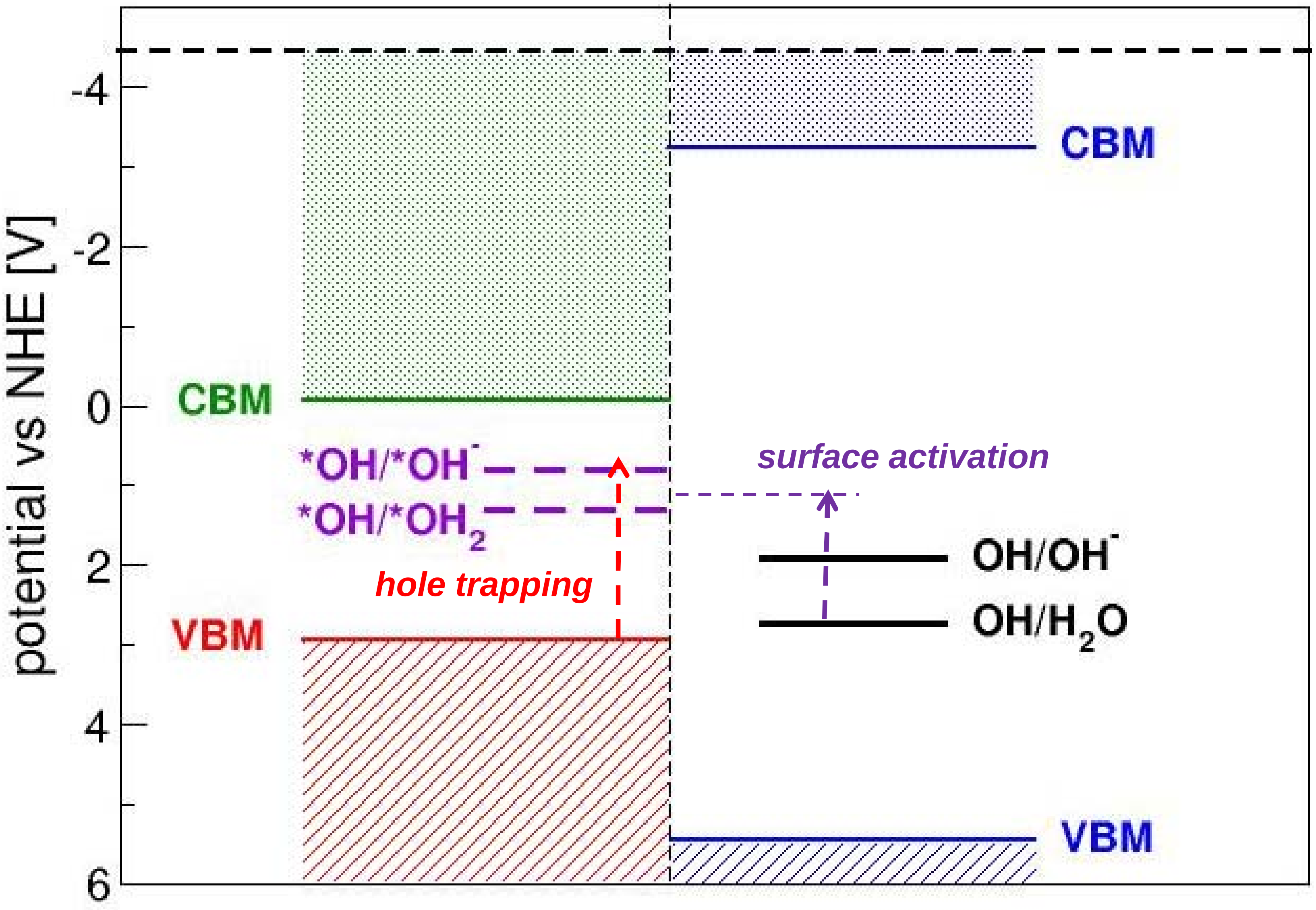
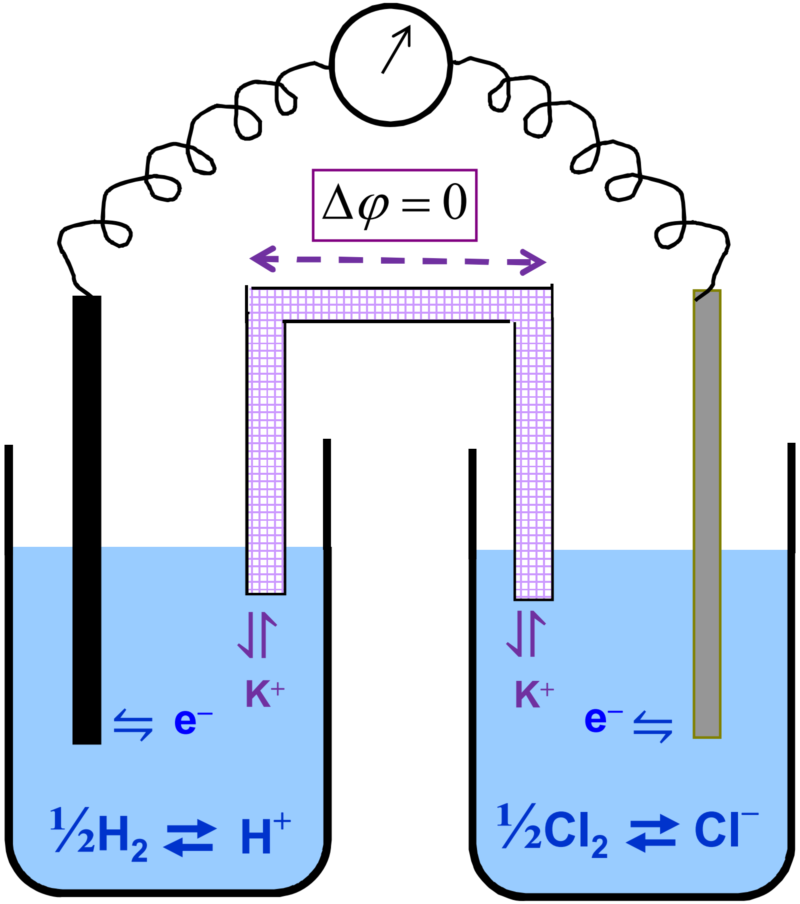
Spin density in TiO_2

(*Jun Cheng*)

Where are the redox levels of adsorbed H_2O?



Open circuit voltage of redox electrodes



No current

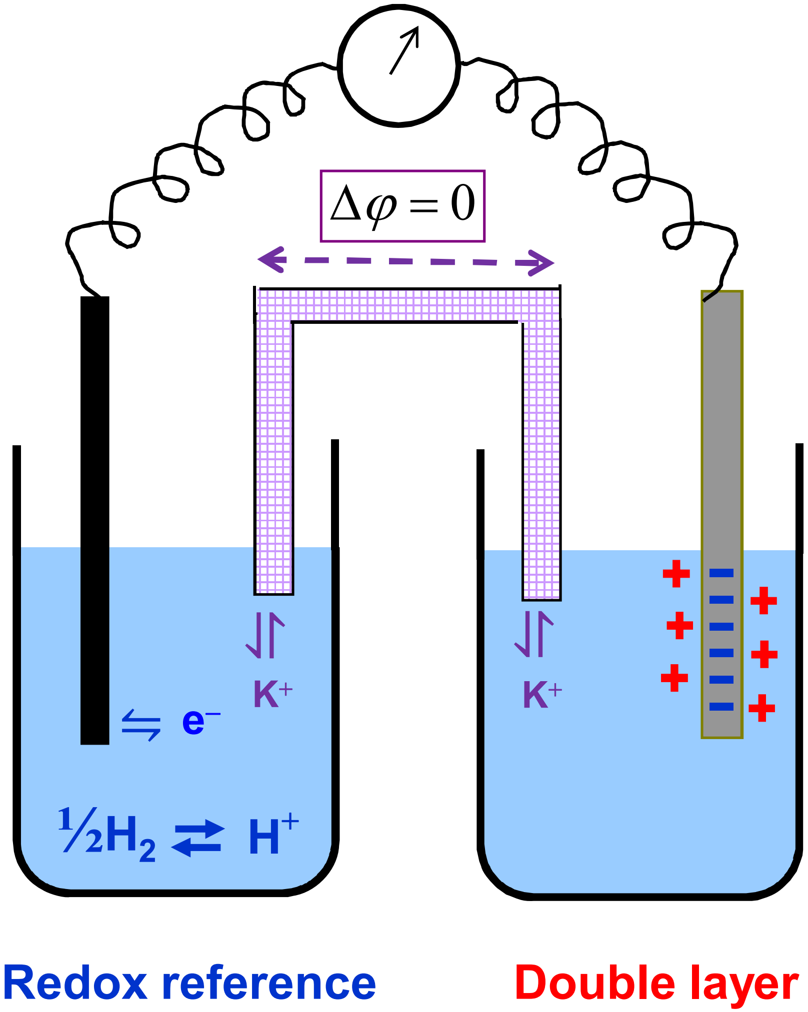
Electrode reactions in equilibrium

$$E = -\frac{\Delta_r G}{2e}$$

$$E = E^o + \frac{k_B T}{2e} \ln \frac{p_{H_2} \, p_{Cl_2}}{\left[H^+\right]^2 \left[Cl^-\right]^2}$$

Nature of electrodes irrelevant

No control by a redox process



Electrode acts as a capacitor

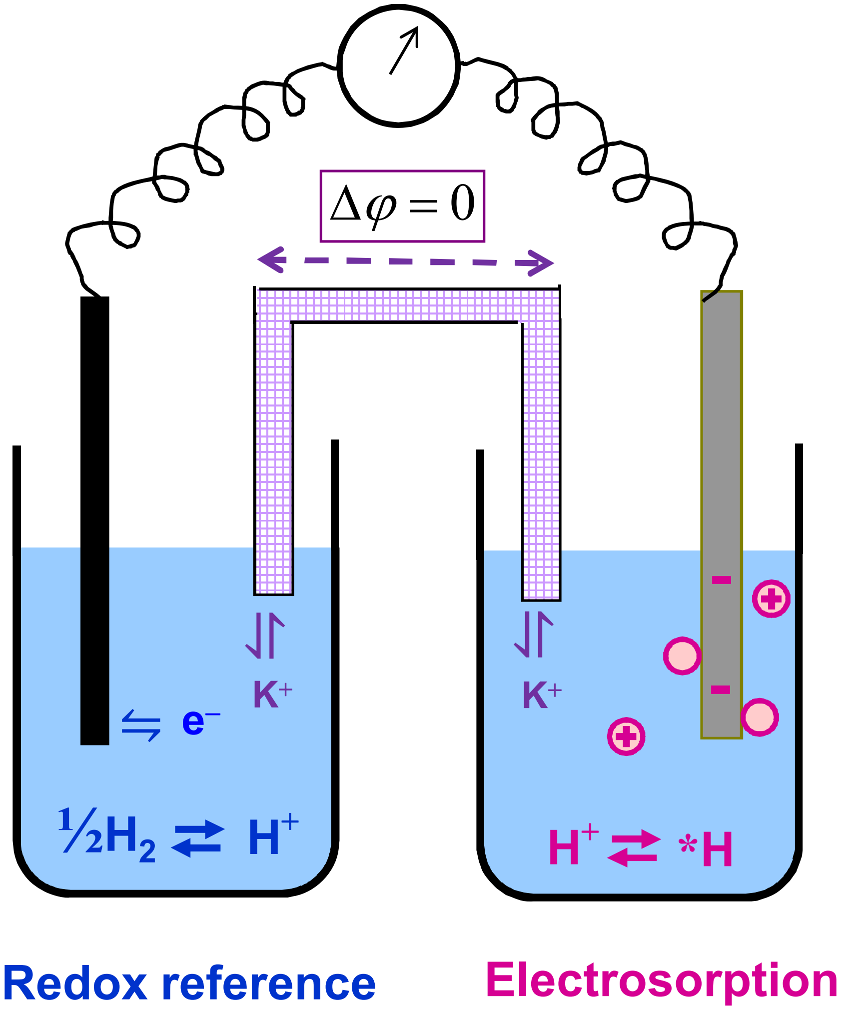
$$E = \varphi_{\text{pzc}} + \frac{Q}{C(Q)}$$

Nature of electrode matters.

$$\varphi_{\text{pzc}} \propto \varepsilon_{\text{fermi}}$$

Point of zero charge for metals

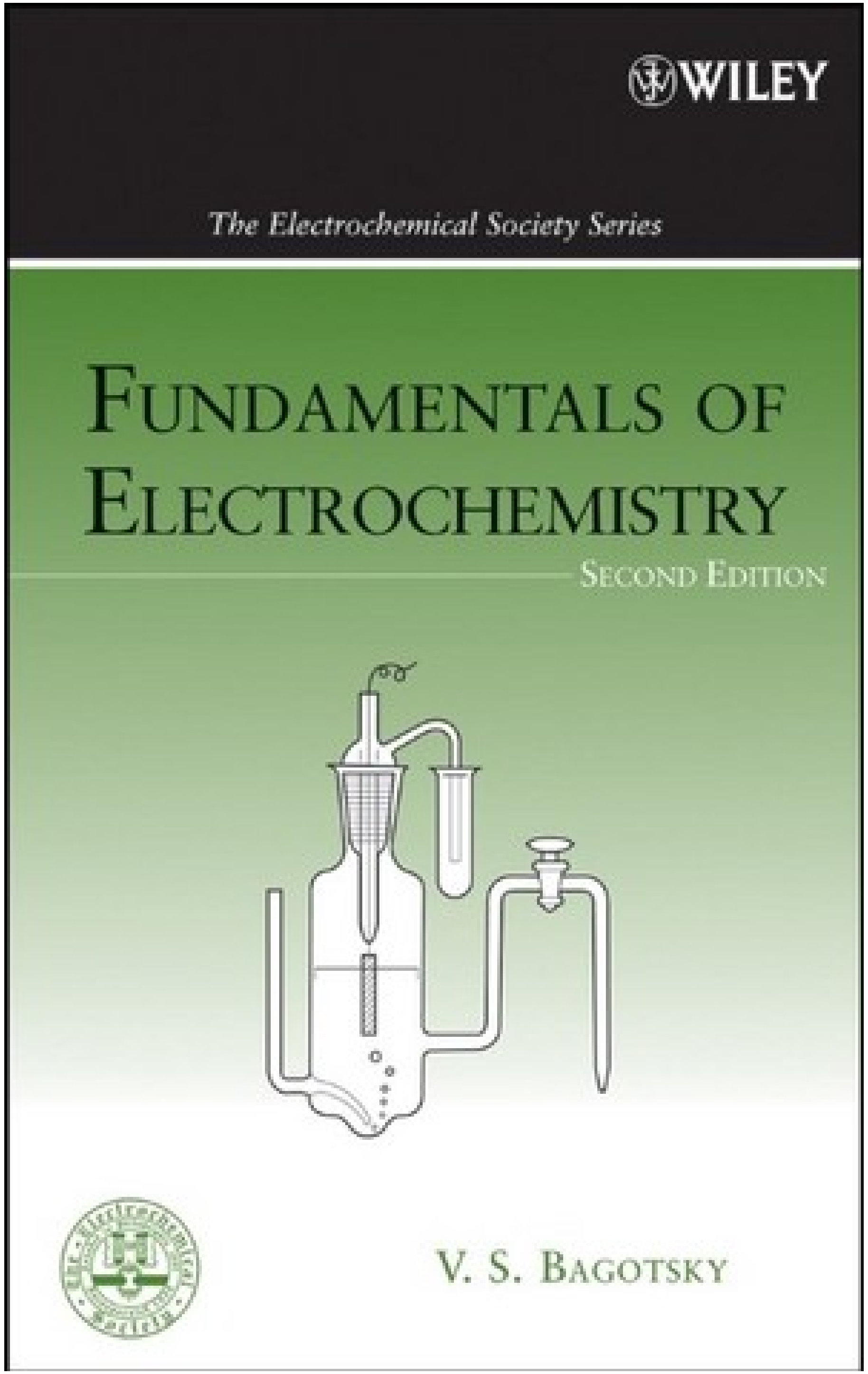
Redox active species adsorbed on surface



Example: Volmer reaction

$$H^+(aq) + e^-(m) \rightarrow *H$$

Step in Hydrogen Evolution Reaction



WILEY

The Electrochemical Society Series

FUNDAMENTALS OF ELECTROCHEMISTRY

SECOND EDITION

V. S. BAGOTSKY

We need a common energy reference

Normal hydrogen electrode (NHE)

$$X^{-} + H^{+}(aq) \rightarrow X^{\bullet} + \tfrac{1}{2}H_2(g)$$

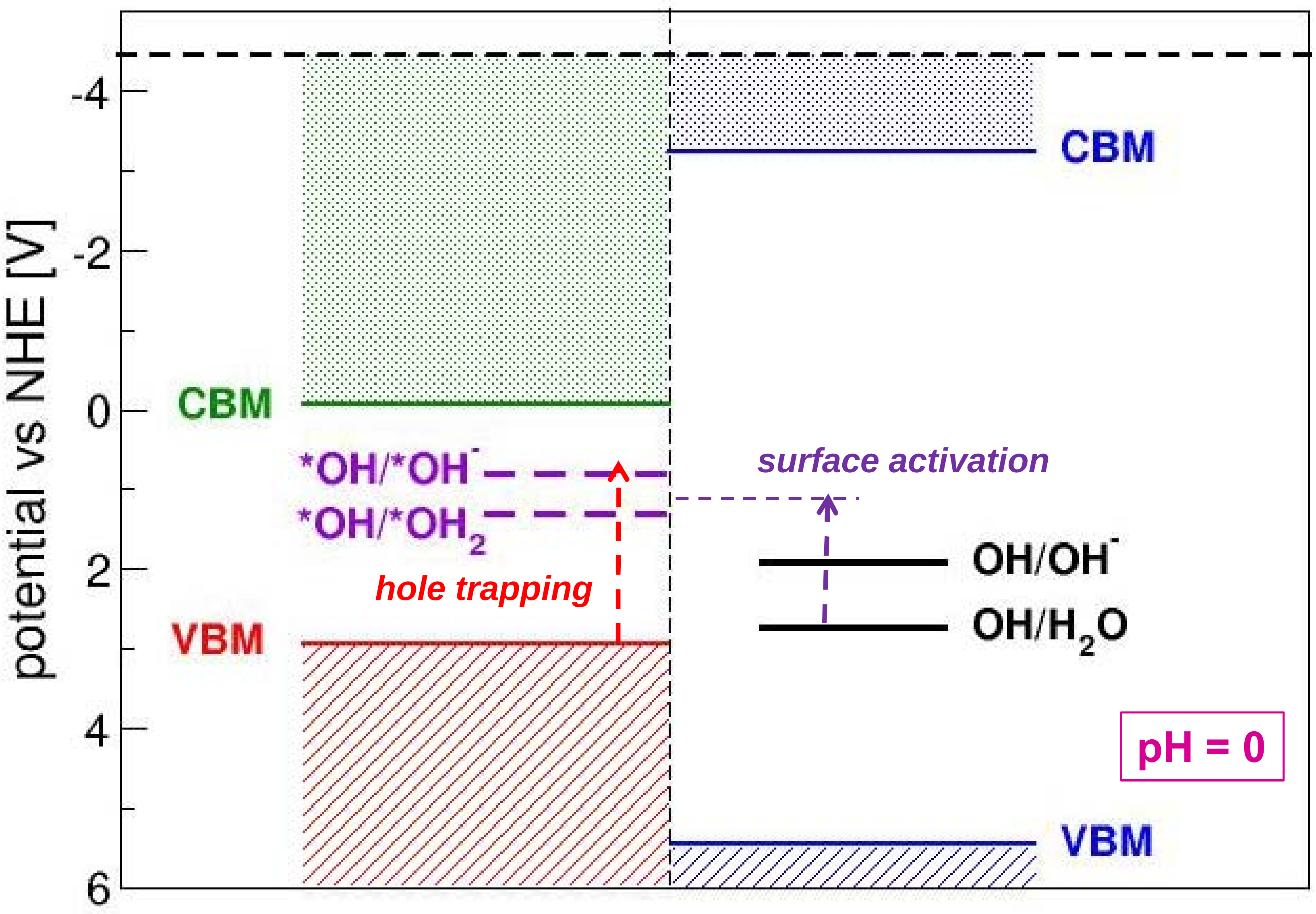
Oxidation free energy of X^- by H^+

$$eE^{o}_{X} = \Delta_{ox}G^{o}_{X^-}$$

How to construct a molecular dynamics normal hydrogen electrode?

NHE half cell

Where are the redox levels of adsorbed H_2O?



$H_2O \rightarrow OH + H$ in solution

exp.

$$\begin{tikzcd}
H_2O \arrow[r, "0.8"] \arrow[dr, "2.7"'] & OH^- + H^+ \arrow[d, "\boxed{1.9}"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

BLYP

$$\begin{tikzcd}
H_2O \arrow[r, "0.7"] \arrow[dr, "2.1"'] & OH^- + H^+ \arrow[d, "\boxed{1.3}"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

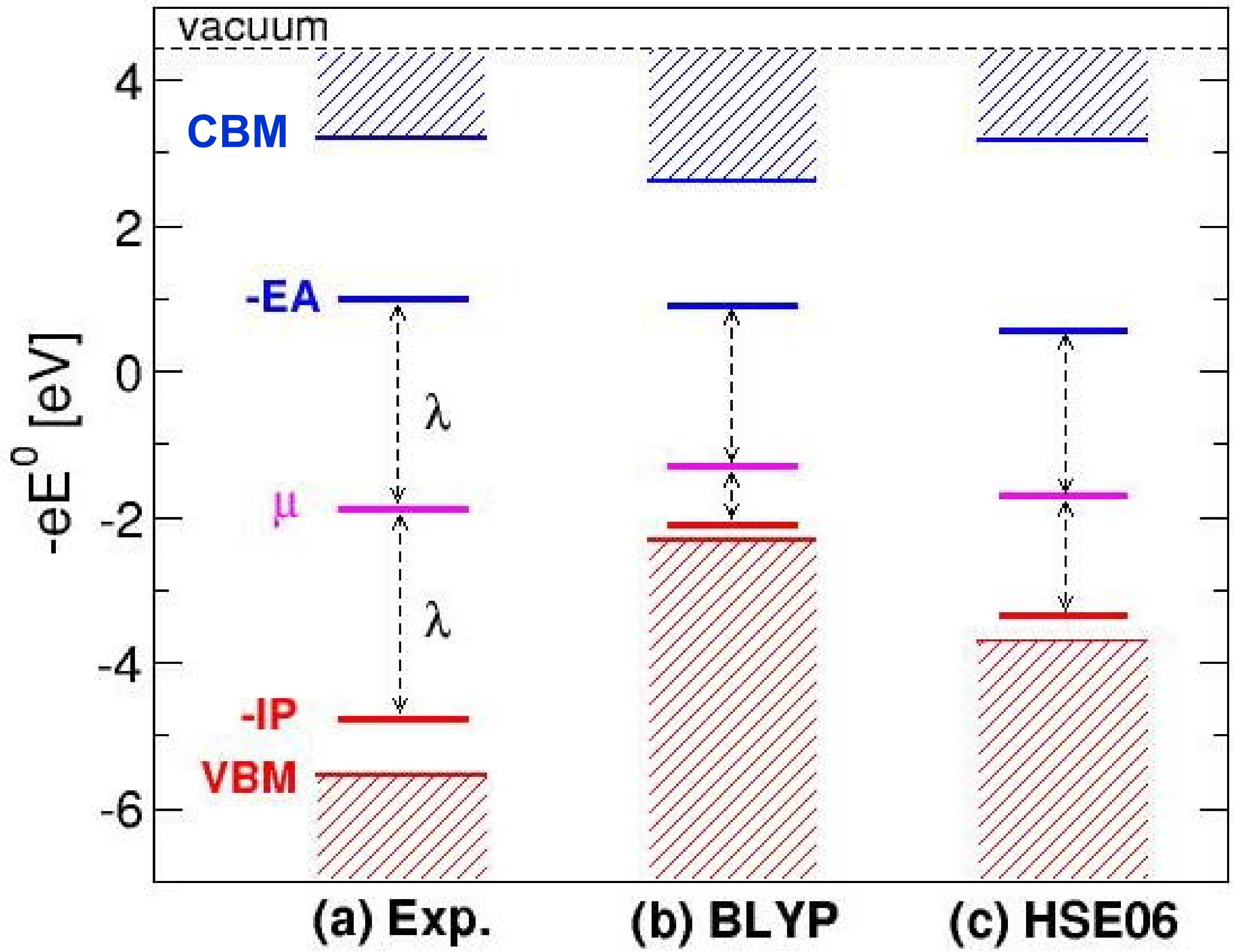
Energies in eV

HSE*

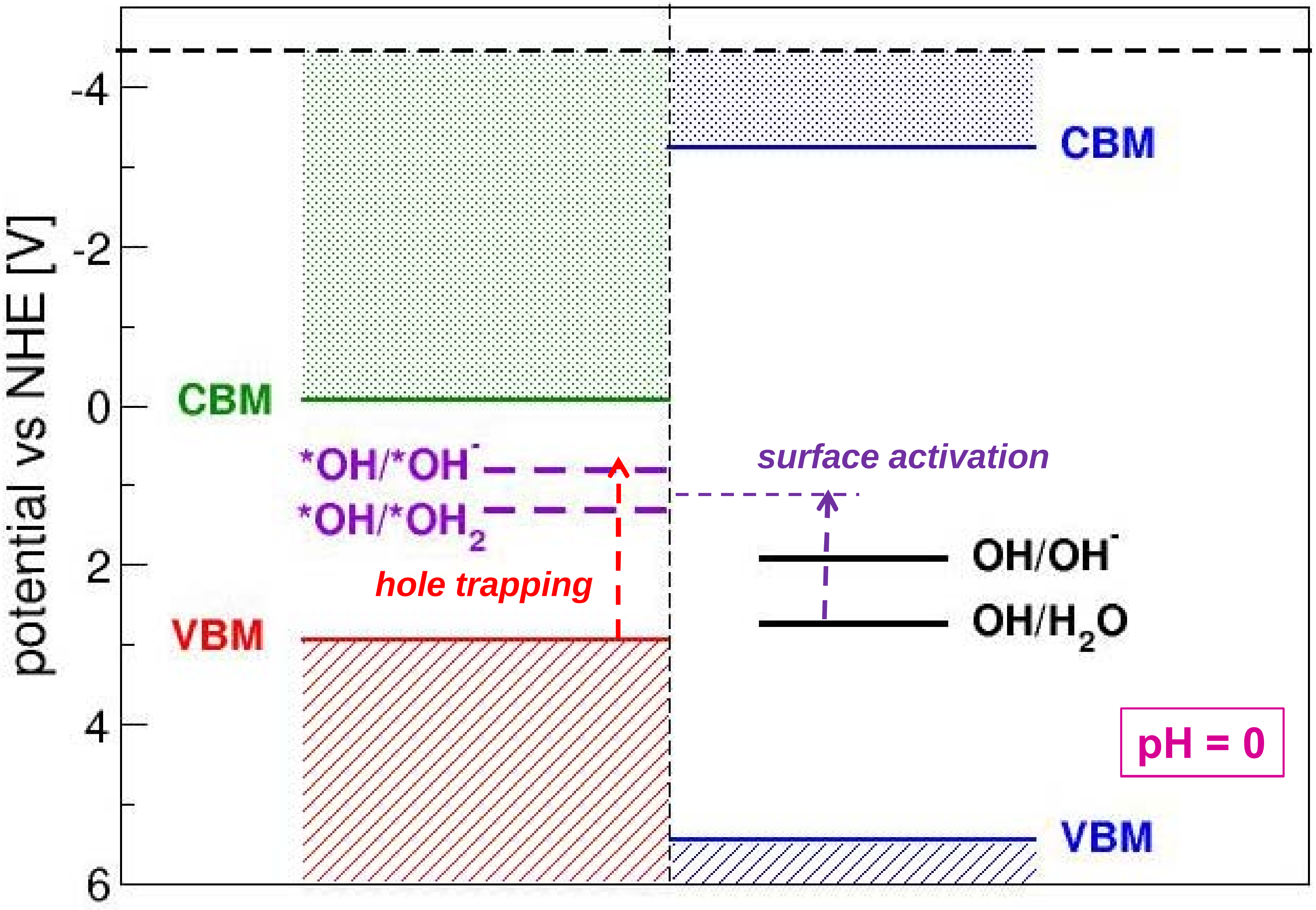
$$\begin{tikzcd}
H_2O \arrow[r, "0.7"] \arrow[dr, "2.5"'] & OH^- + H^+ \arrow[d, "\boxed{1.7}"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

*Guidon, M.; Hutter, J.; VandeVondele, J.
"Auxiliary Density Matrix Methods for
Hartree-Fock Exchange Calculations."
J. Chem. Theory Comput.(**2010**),*6,* 2348.

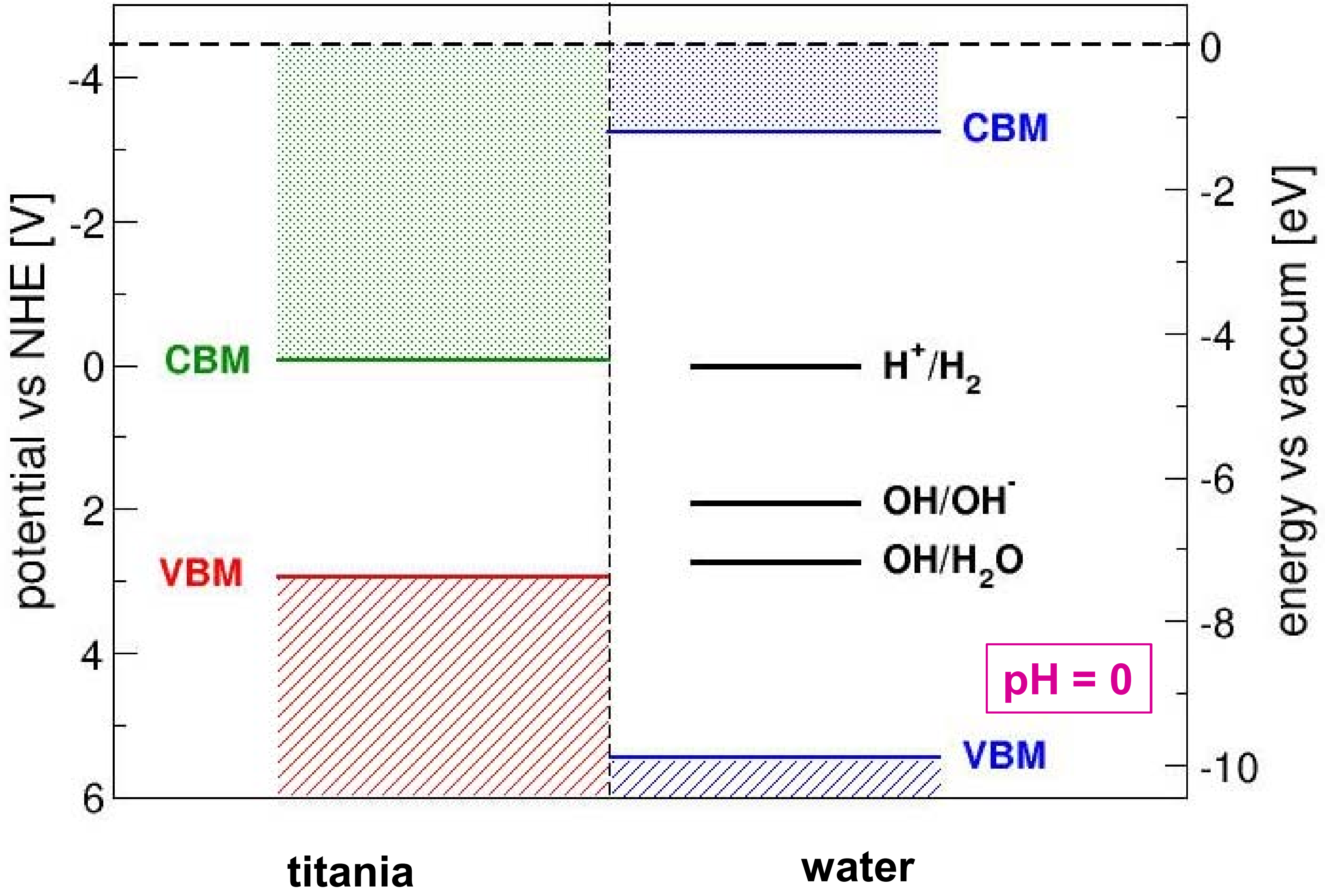
Vertical and adiabatic levels OH/water



Where are the redox levels of adsorbed H_2O?

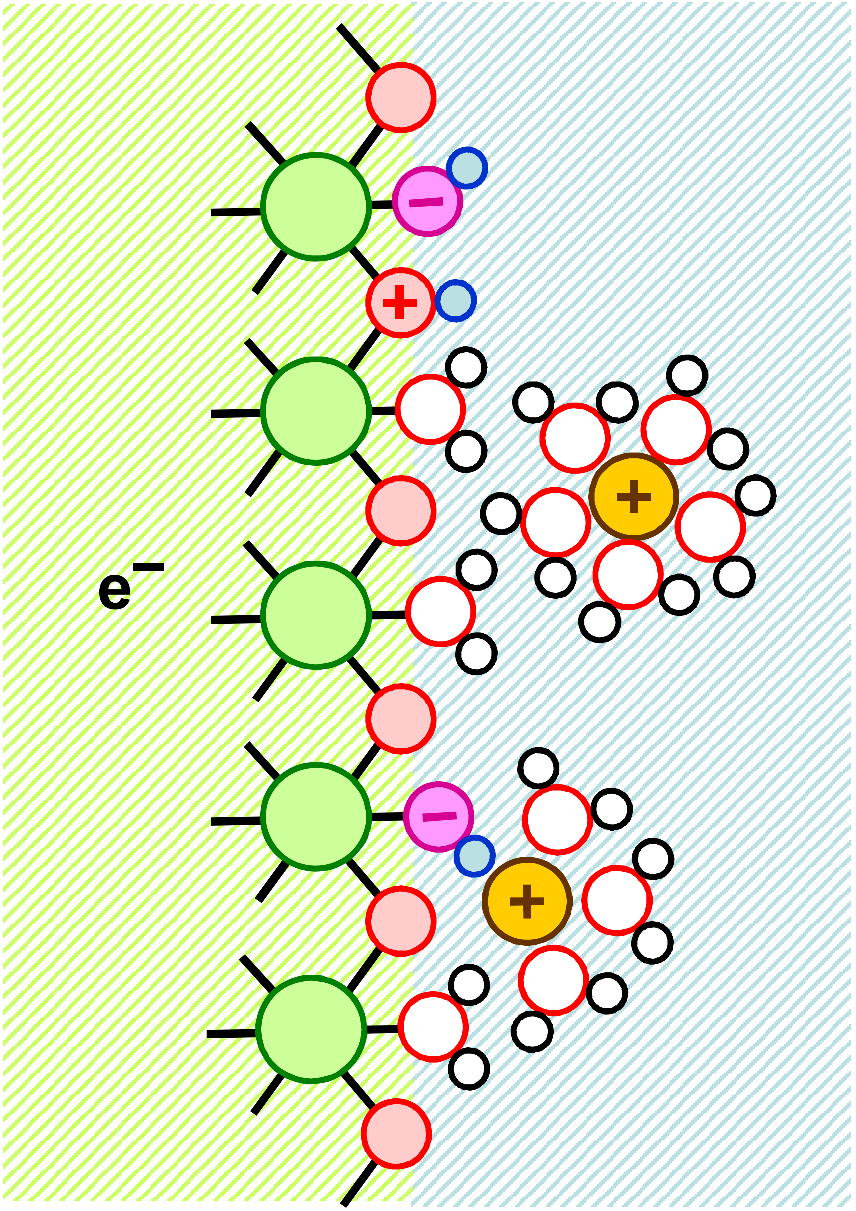


OH/H_2O aligned with TiO2 (110) rutile electrode



Experimental data

Electrical double layer at a TiO_2 water interface



- Excess electron charge

  electrons in conduction band
  holes in valence band

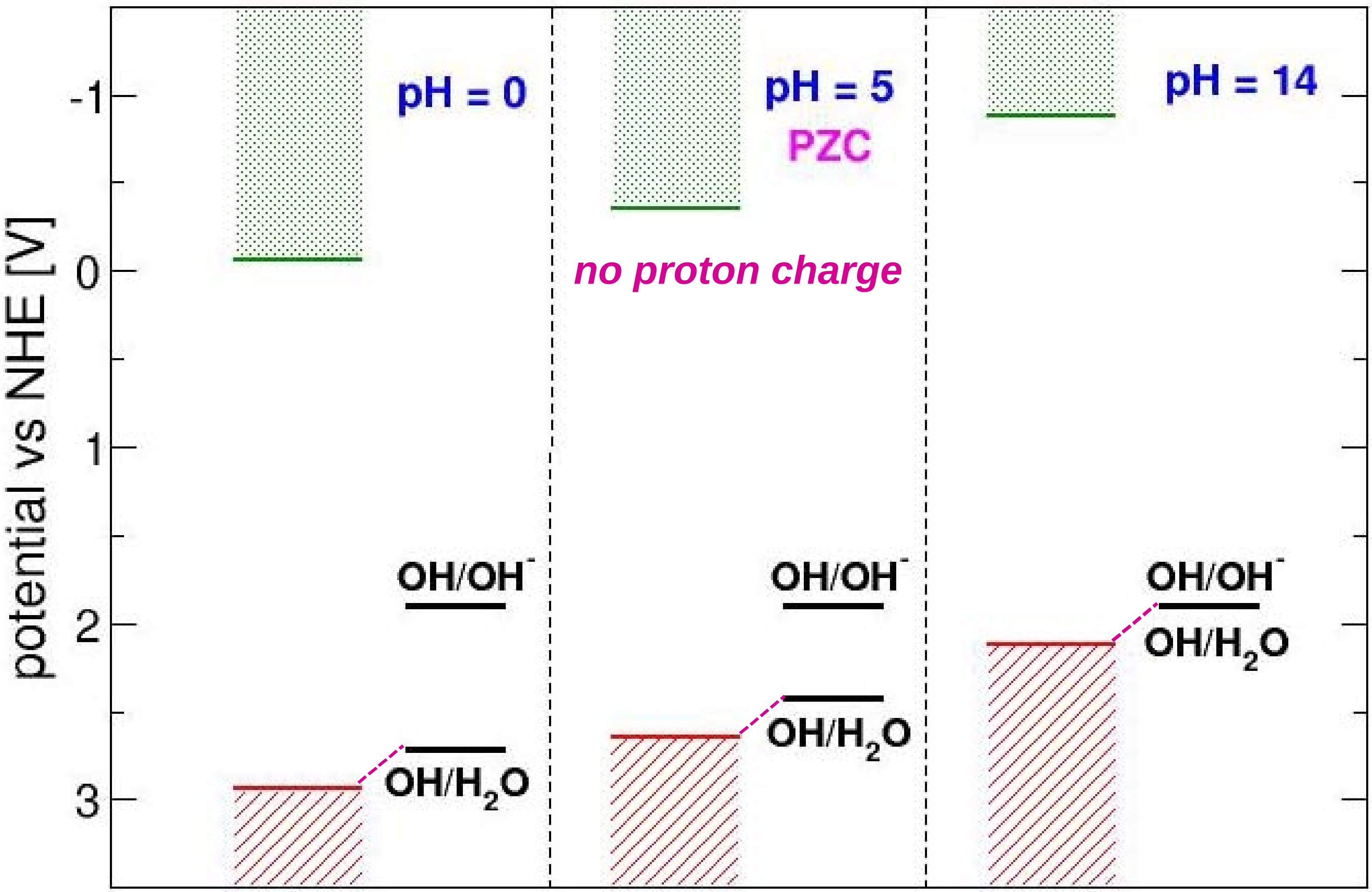
- Excess proton charge

  deprotonaton terminal waters
  protonation bridging oxygens

- Ionic counter charge

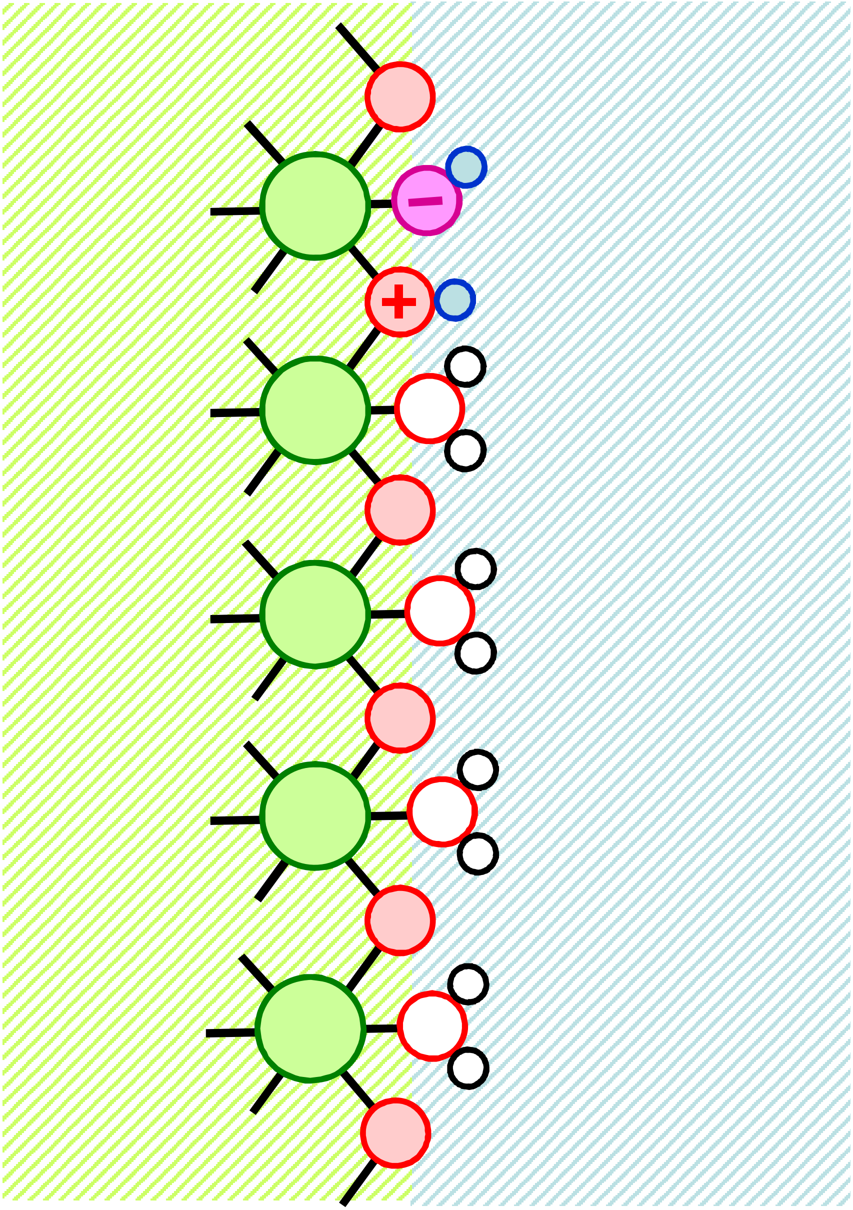
  cations and anions from
  electrolytic solution

pH dependence redox levels



Experimental data

Reference state point of our calculation



Point of zero charge (PZC)

Zero net proton charge

$\mathbf{pH_{PZC} = 5}$

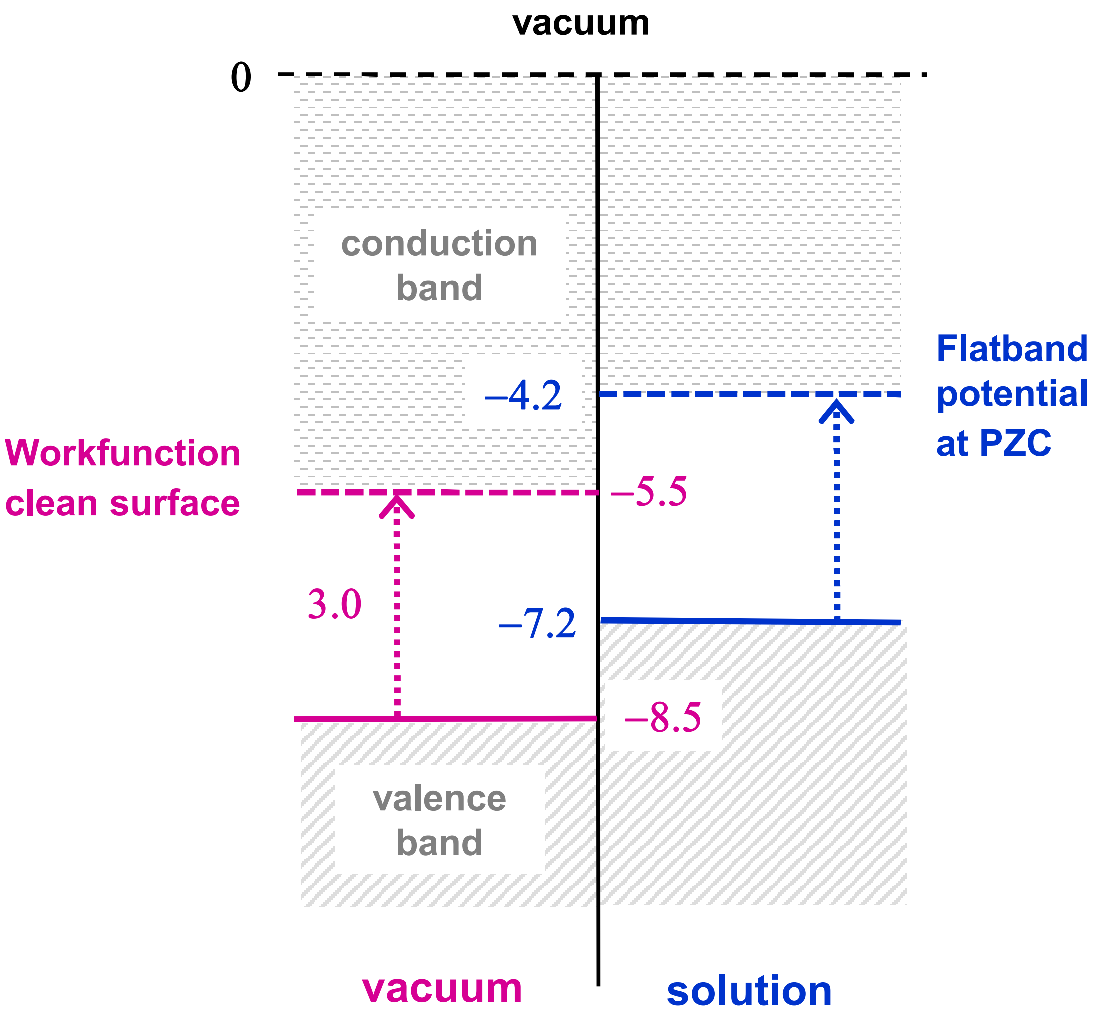
Flatband potential (FB)

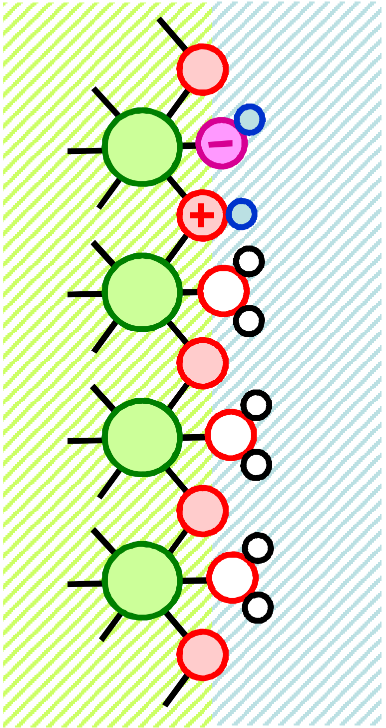
No space electronic charge

$\boldsymbol{\varphi_{FB} = -\ 0.25\ V}$

Experimental data

TiO_2 electronic energy levels at PZC: solvent effect





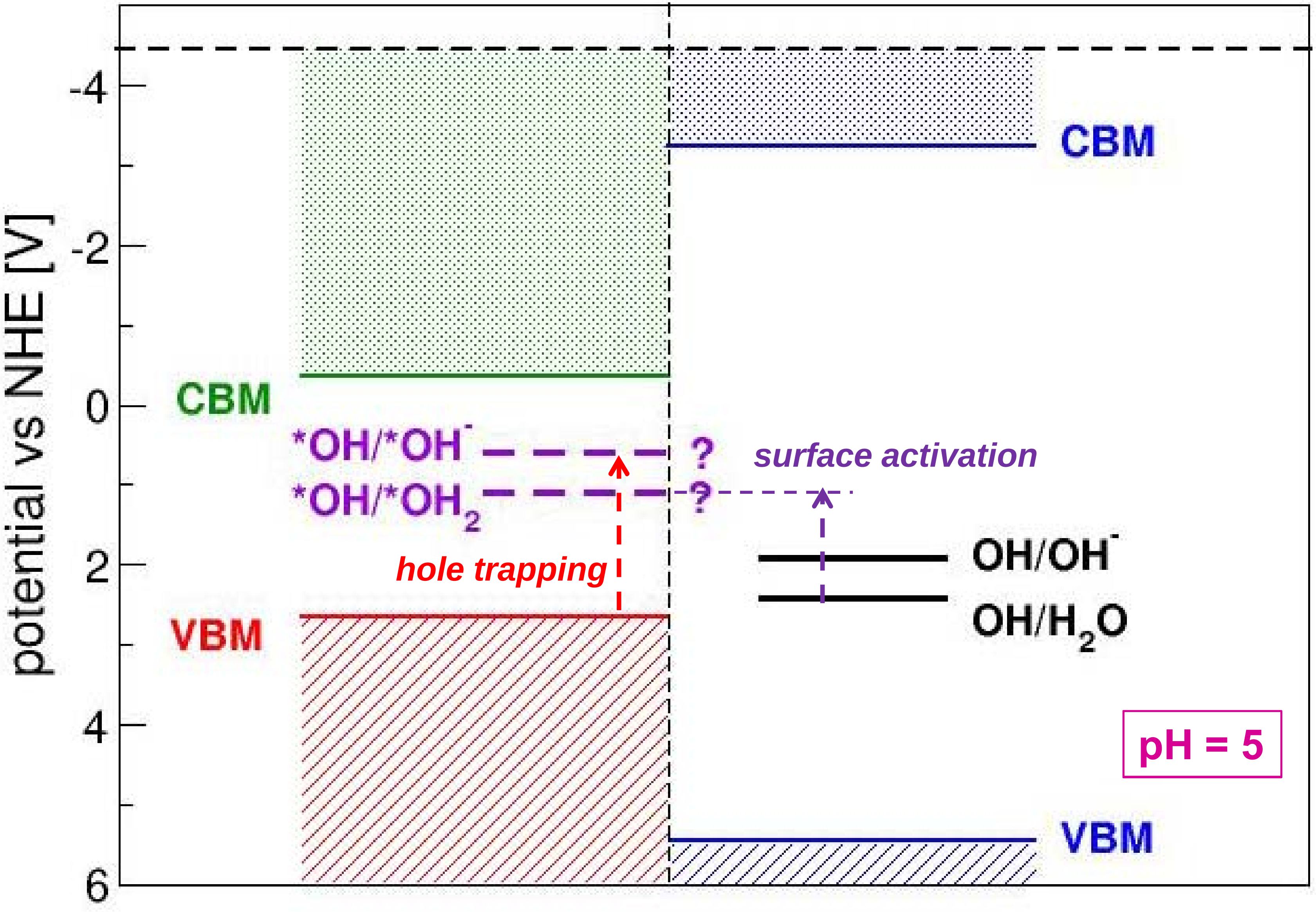
PZC TiO2 (110) rutile is 5

Energies in eV

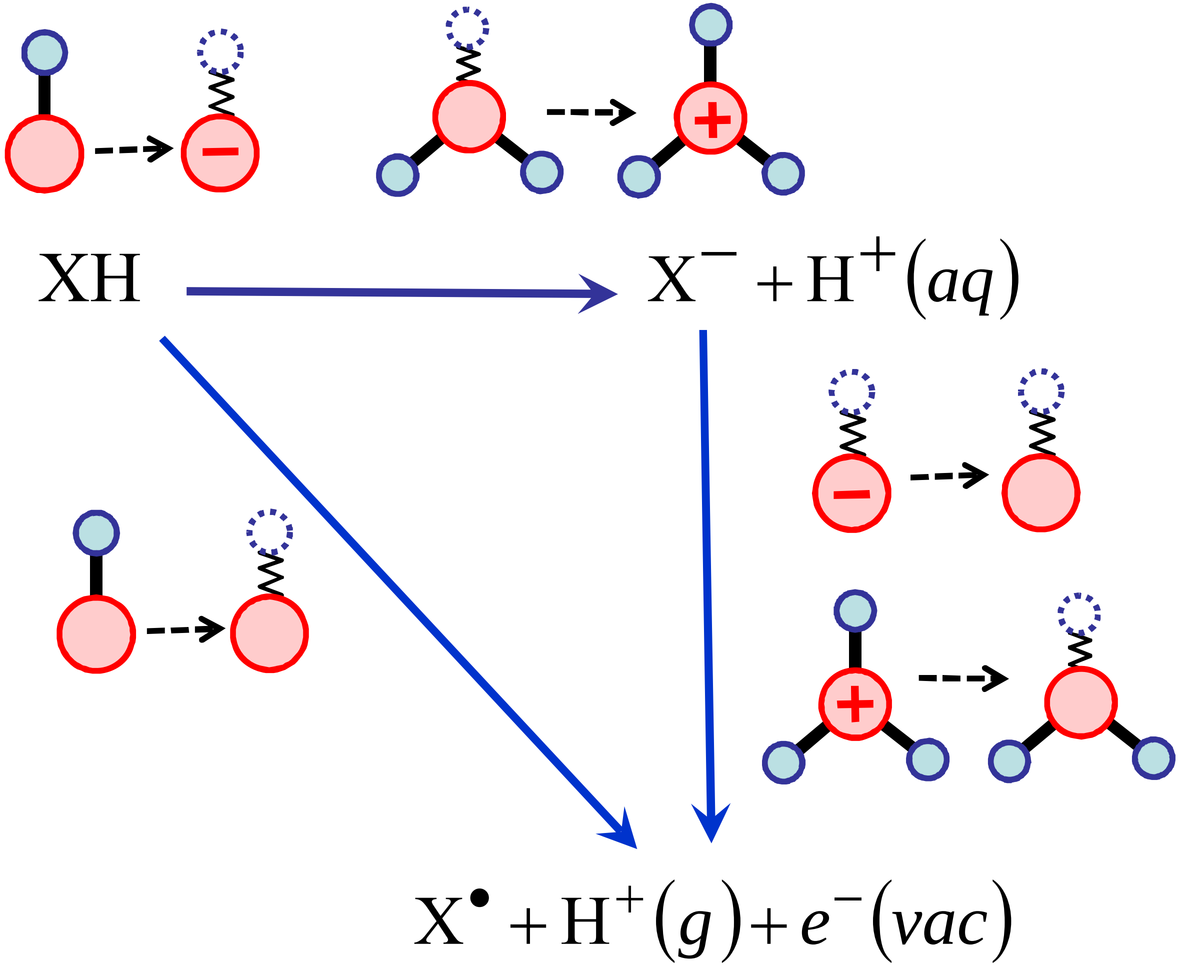
Onda and Petek, PRB (2004) 70, *045415*

Kavan, Graetzel et al JACS (1996) 118, *6716*

Where are the redox levels of adsorbed H_2O?



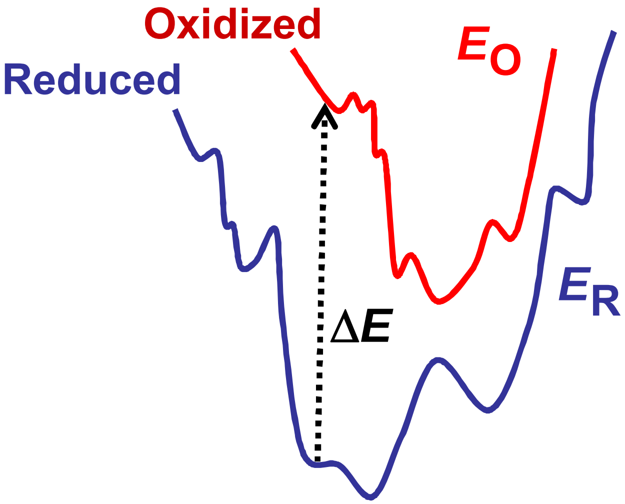
Reversible discharge of proton + electron



$$\begin{tikzcd}
\mathrm{XH} \arrow[r] \arrow[dr] & \mathrm{X}^- + \mathrm{H}^+(aq) \arrow[d] \\
 & \mathrm{X}^\bullet + \mathrm{H}^+(g) + e^-(vac)
\end{tikzcd}$$

Free energy perturbation plus analytical thermochemical corrections

From vertical to adiabatic ionization energy



Two potential energy surfaces

$E_\mathrm{R}\left(\mathbf{R}^N\right)$: PES **reduced**

$E_\mathrm{O}\left(\mathbf{R}^N\right)$: PES **oxidized**

Vertical energy gap

$$\Delta E\left(\mathbf{R}^N\right) = E_\mathrm{O}\left(\mathbf{R}^N\right) - E_\mathrm{R}\left(\mathbf{R}^N\right)$$

Mapping potential

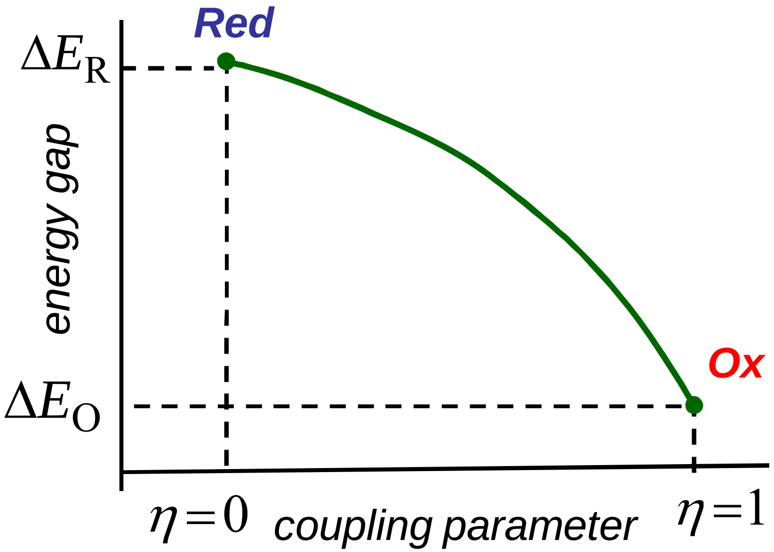
$$E_\eta\left(\mathbf{R}^N\right) = \eta\, E_\mathrm{O}\left(\mathbf{R}^N\right) + (1-\eta) E_\mathrm{R}\left(\mathbf{R}^N\right)$$

Coupling parameter derivative

$$\frac{\partial}{\partial \eta} E_\eta\left(\mathbf{R}^N\right) = \Delta E\left(\mathbf{R}^N\right)$$

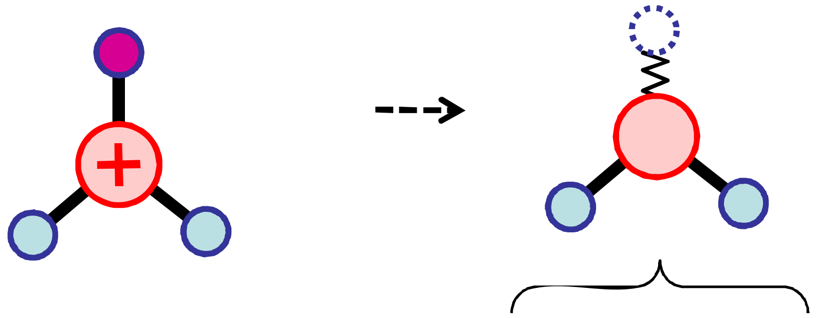
Oxidation free energy

$$\Delta A = A_\mathrm{O} - A_\mathrm{R} = \int_0^1 d\eta \left\langle \Delta E\left(\mathbf{R}^N\right) \right\rangle_\eta$$



Reversible deprotonation

Switching the proton charge off and on again



real proton

dummy proton (no charge)

BO surface ***protonated*** *system*

BO surface ***deprotonated*** *system*

Harmonic potential holding ***dummy*** *in place*

Mapping potential

$$E_\eta\left(\mathbf{R}^N\right) = (1-\eta)\boxed{E_{\mathrm{XH}}\left(\mathbf{R}^N\right)} + \eta\boxed{E_{\mathrm{X}^-}\left(\mathbf{R}^{N-1}\right)} + \boxed{V_r\left(\mathbf{R}^N\right)}$$

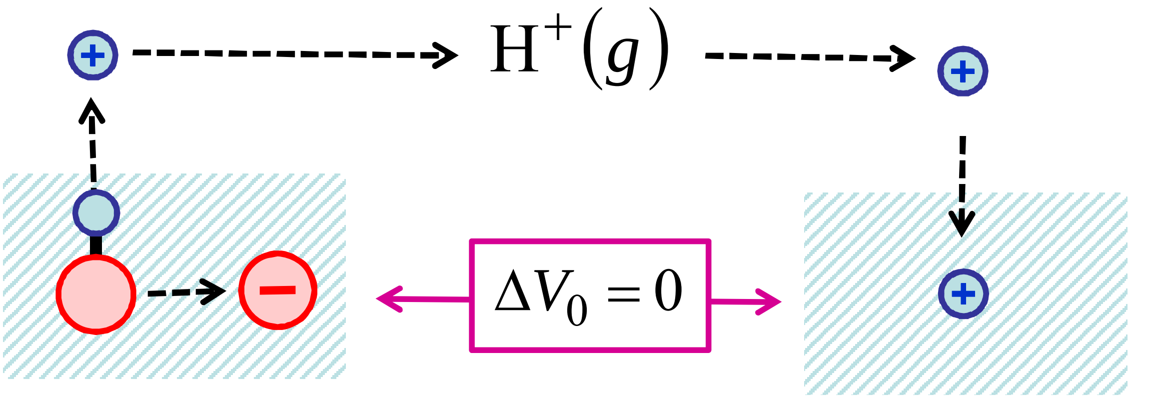
Vertical proton gap:

$$\frac{\partial}{\partial\eta}E_\eta\left(\mathbf{R}^N\right) = E_{\mathrm{X}^-}\left(\mathbf{R}^{N-1}\right) - E_{\mathrm{XH}}\left(\mathbf{R}^N\right) = \Delta E\left(\mathbf{R}^N\right)$$

Restrained deprotonation free energy

$$\Delta A = A_{\mathrm{X}^-} - A_{\mathrm{XH}} = \int_0^1 d\eta \left\langle \Delta E \right\rangle_{r\eta}$$

Half cell method for determination pKa



$$\Delta_{\mathrm{dp}}A + \boxed{V_0}$$

$$\Delta_{\mathrm{s}}G_{\mathrm{H}^+} - \boxed{V_0}$$

Adiabatic deprotonation energy

Solvation free energy H^+

$$2.3\,k_{\mathrm{B}}T\,\mathrm{p}K_a = \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}}E_{\mathrm{XH}} \right\rangle_{r\eta} - \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}}E_{\mathrm{H_3O^+}} \right\rangle_{r\eta} + k_{\mathrm{B}}T \ln\left[c^{\mathrm{o}}\Lambda^3_{\mathrm{H}^+}\right]$$

Bias V_0 in the electrostatic reference should cancel

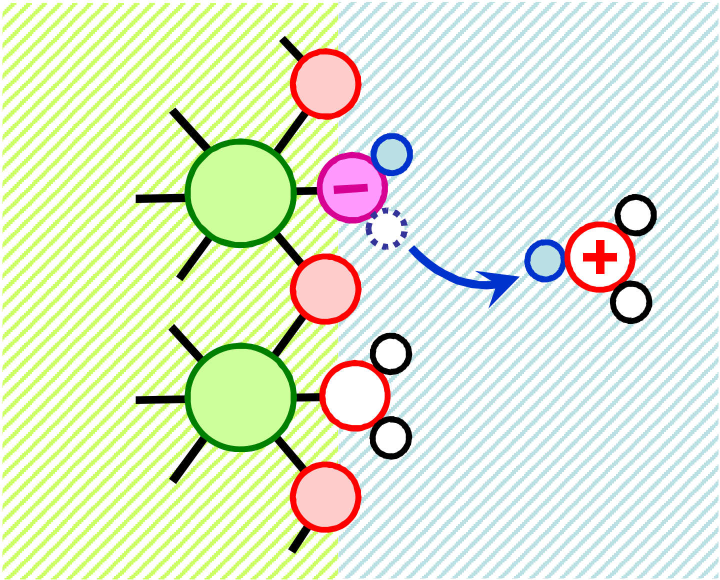
Small acids: Comparison to experiment

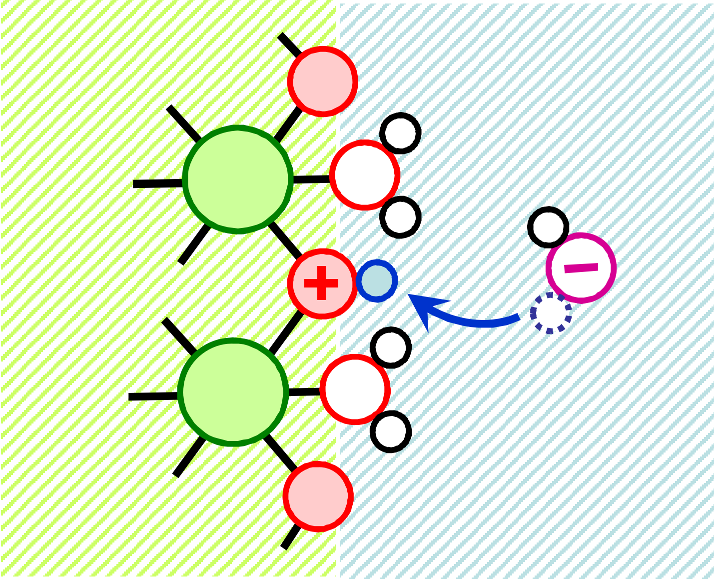
Energies eV	$\Delta_{\mathrm{dp}} A_{\mathrm{XH}}$	$\mathrm{p}K_a$	exp.	$\Delta\mathrm{p}K_a$
HCl	15.1	–7	–7	0
H_3O^+	15.35	–3.2	–1.74	–1.5
HCOOH	15.8	5	3.75	1
H_2S	16.0	8	7.0	1
CH_3SH	16.1	11	10.3	1
NH_4^+	16.1	11	10.2	1
Errrors	statistical uncertainty < 0.1 eV			**MUE =1**

$$\Delta_{\mathrm{dp}} A_{\mathrm{XH}} = \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}} E_{\mathrm{XH}} \right\rangle_{r\eta}$$

(*Sulpizi*)

Surface acidity and point of zero charge





Deprotonation of terminal H_2O

$$pK_{a1} = pK_{aH_2O_t}$$

Protonation of bridging O

$$pK_{a2} = pK_W - pK_{bO_b}$$

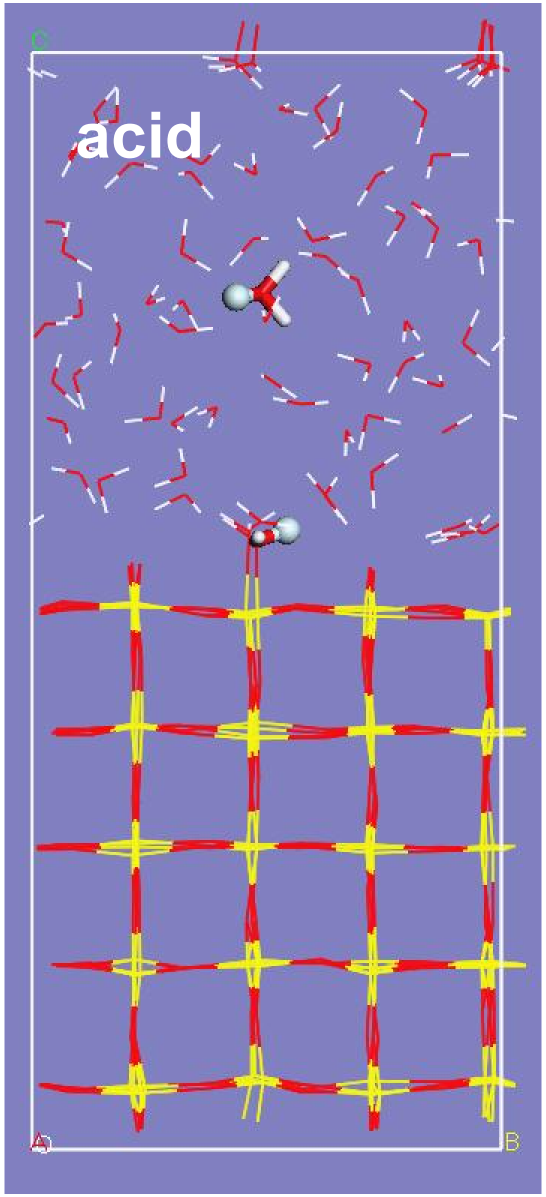
$$\mathrm{PZC} = \tfrac{1}{2}\left(pK_{a1} + pK_{a2}\right)$$

pH at zero net proton charge

$$\Delta pK_a = pK_{a1} - pK_{a2}$$

Surface dissociation constant

Acidity of the TiO_2 (110 rutile) water interface



Cell: $11.9 \times 13.2 \times 30.8$ Å^3

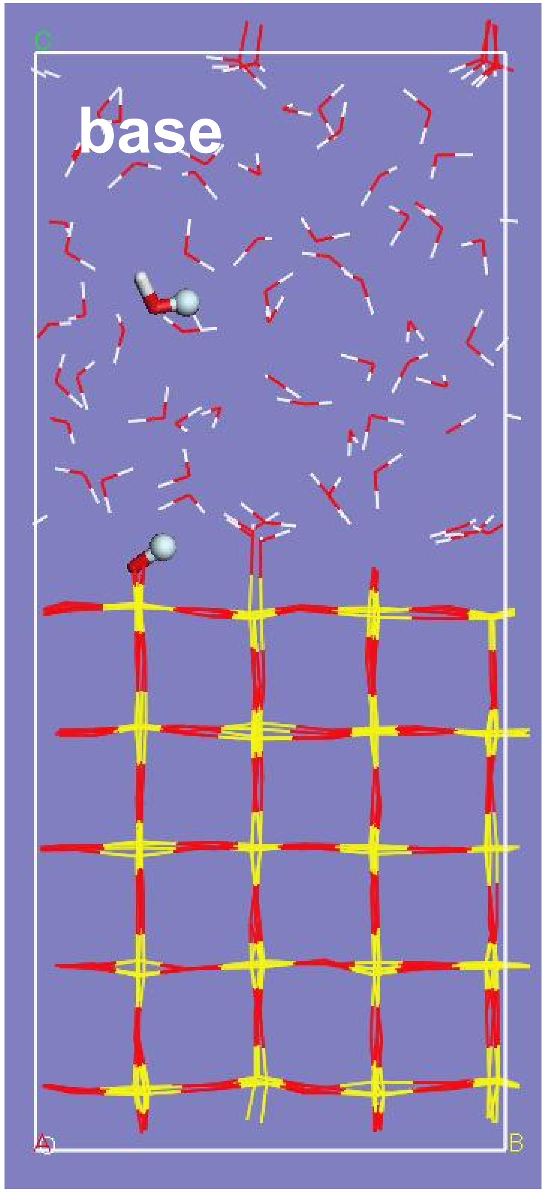
80 TiO_2 units

(5 O-Ti-O layers)

71 H_2O molecules

PBE functional (DVZP)

$$\mathrm{TiOH_2 + H_2O \rightarrow}$$
$$\mathrm{TiOH^- + H_3O^+}$$

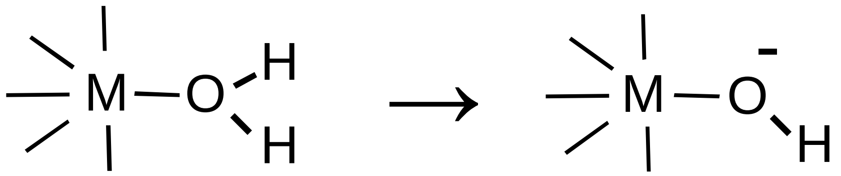


$$\mathrm{Ti_2O + H_2O \rightarrow}$$
$$\mathrm{Ti_2OH^+ + OH^-}$$

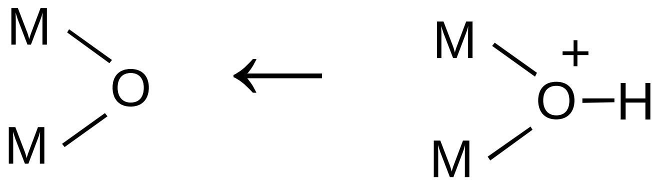
(*Jun Cheng*)

Acidity of three rutile (110) surfaces compared

t(erminal) OH



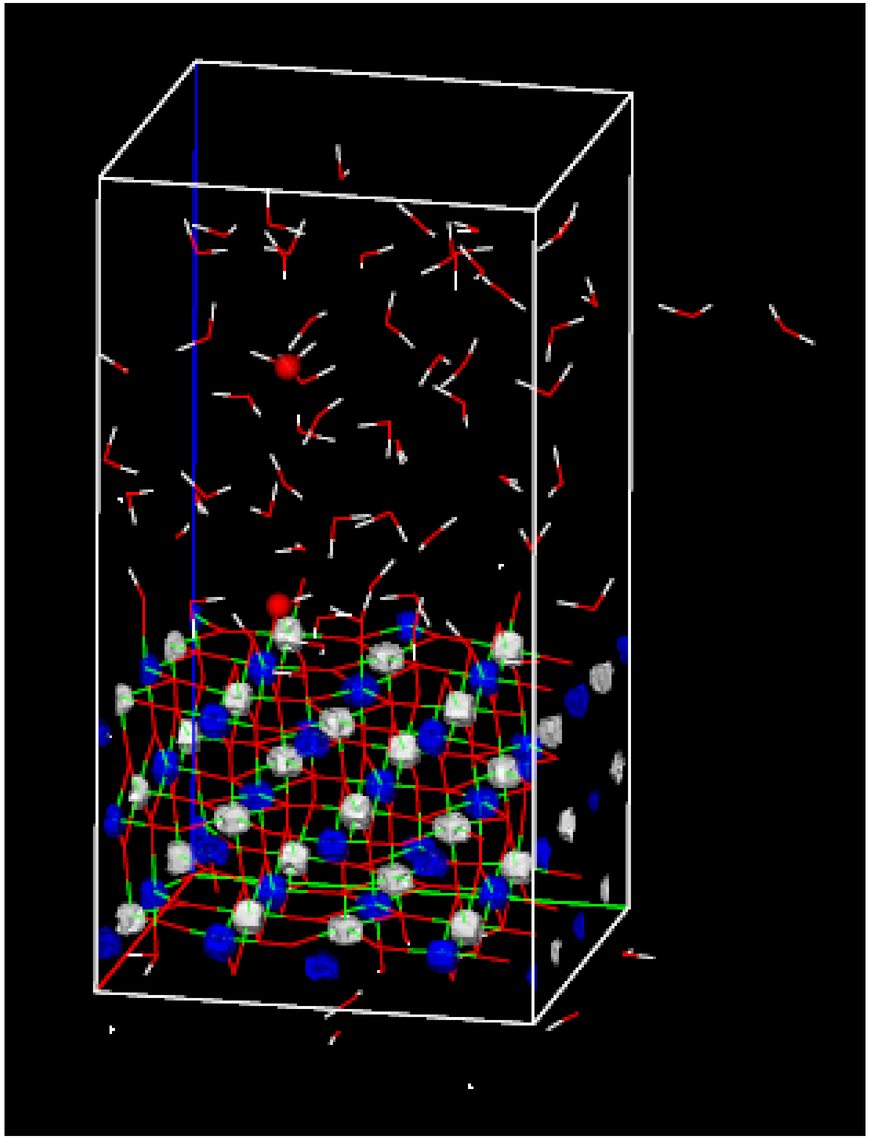
b(ridging) OH



	conf	tOH	bOH.	PZC	PZC(exp)	ΔpK_a
TiO_2	d^0	6.	**-4**	1	5	10
MnO_2	d^3	5	2	3	5-7	3
SnO_2	d^{10}	–1	10	4	4-6	–11

1 pK unit = 0.059 meV

Acidity of the MnO_2 (110 rutile) water interface



Cell: $11.5 \times 12.4 \times 23.8\ \text{Å}^3$

48 MnO_2 units

(3 O-Mn-O layers)

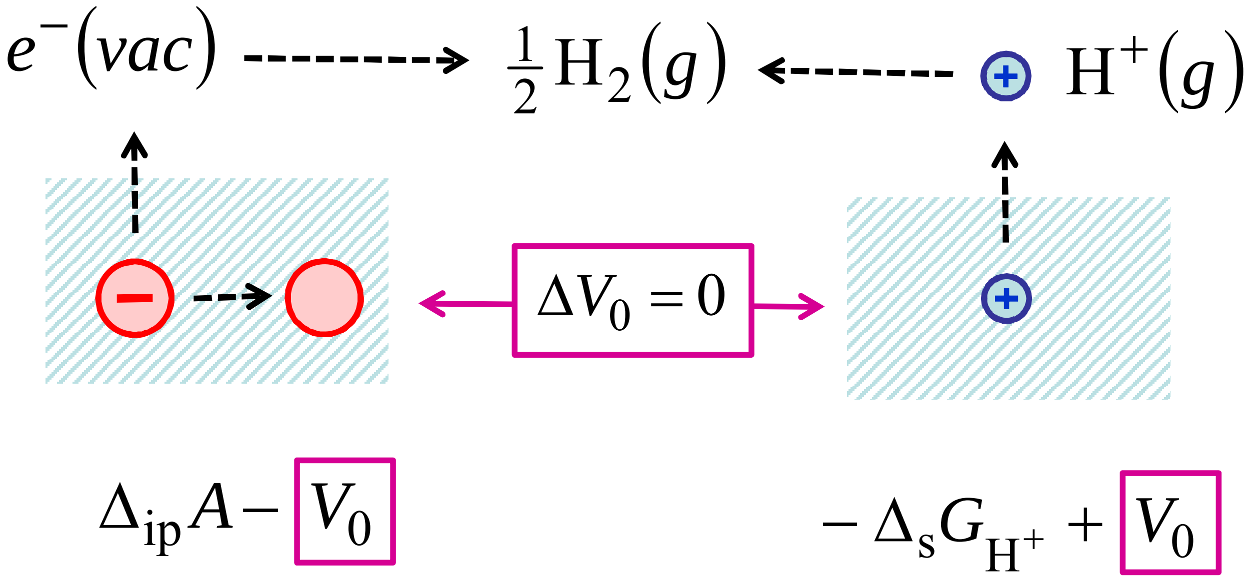
58 H_2O molecules

PBE functional (DVZP)

Spin polarization

(*John Kattirtzi*)

Half cell method for electrode potentials



$e^-(vac) \dashrightarrow \frac{1}{2}H_2(g) \dashleftarrow H^+(g)$

$\Delta V_0 = 0$

$\Delta_{ip}A - \boxed{V_0}$

$-\Delta_s G_{H^+} + \boxed{V_0}$

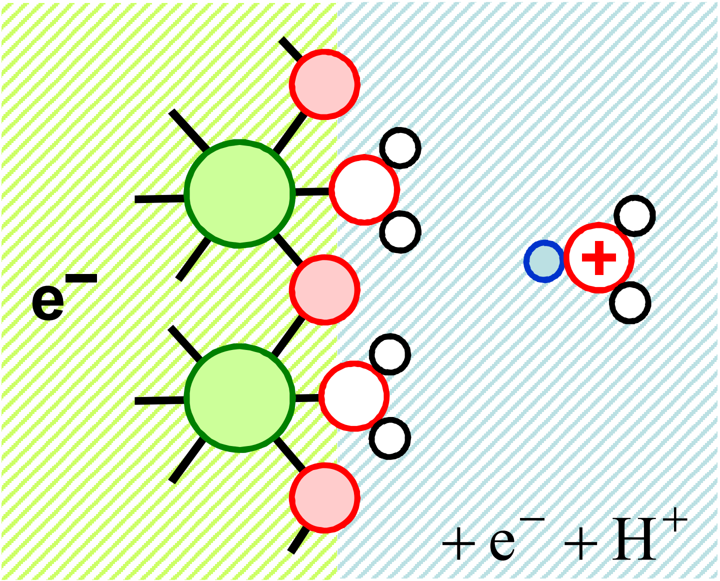
Adiabatic ionization potential

Desolvation free energy H^+

$$eE^\circ = \int_0^1 d\eta \left\langle \Delta_{ip}E_{X^-}\right\rangle_\eta + \int_0^1 d\eta \left\langle \Delta_{dp}E_{H_3O^+}\right\rangle_{r\eta} - \Delta_{zp}E_{H^+} - \Delta_f G_{H^+(g)}$$

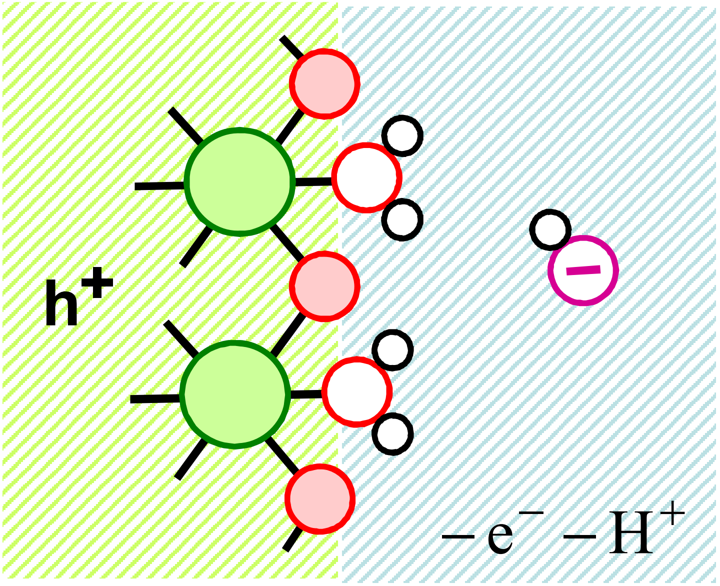
Bias V_0 in the electrostatic reference should cancel

Potentials for oxide electrode



Electron affinity *vs* NHE

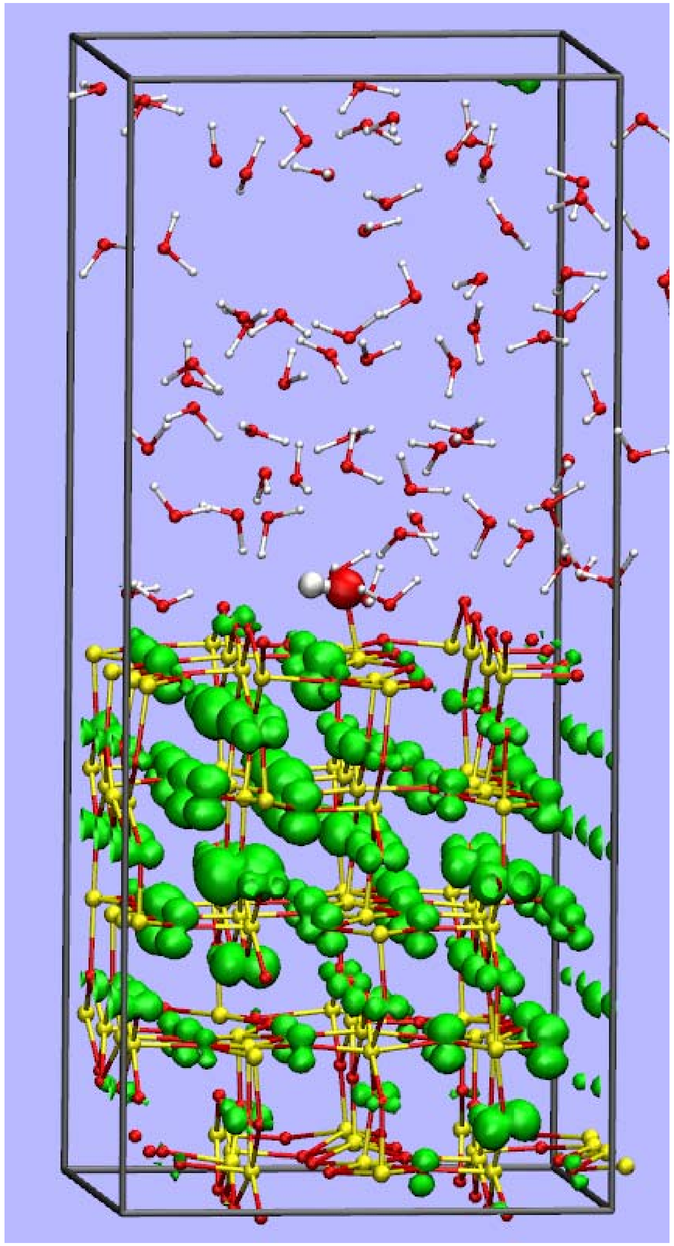
Inserting **electron** in **solid**
+
and **proton** in **solution**



Ionization potential *vs* NHE

Removing **electron** from **solid**
+
and **proton** from **solution**

DFTMD Model system TiO_2 water interface



Cell: 11.9 × 13.2 × 30.8 $Å^3$
(water layer ≈15 Å across)

80 TiO_2 units

71 H_2O molecules

Gaussian basis (DVZP)

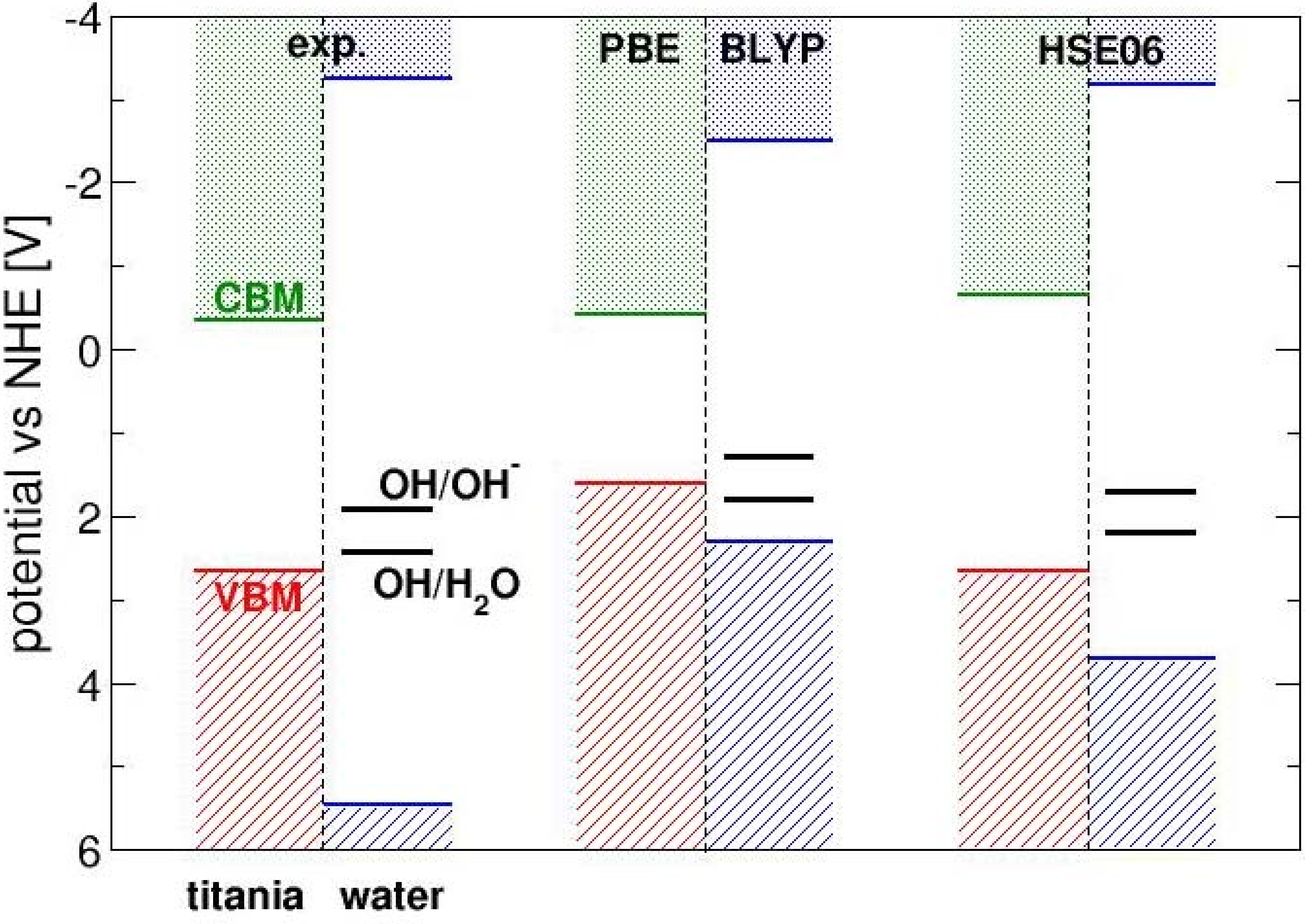
MD trajectories of 5-10 ps

DFTMD code: **CP2K**

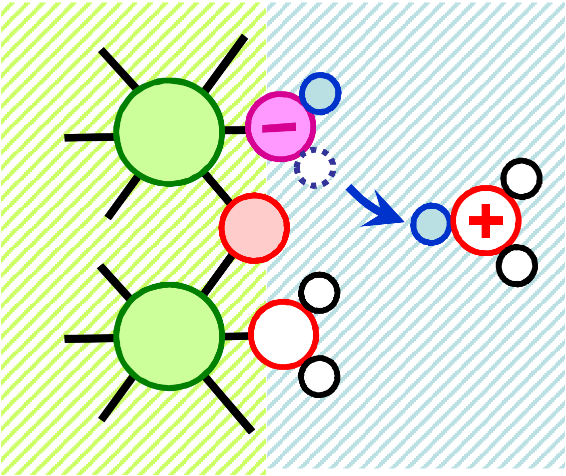
Solid slab and NHE in the same periodic DFTMD model system

Spin density (PBE)

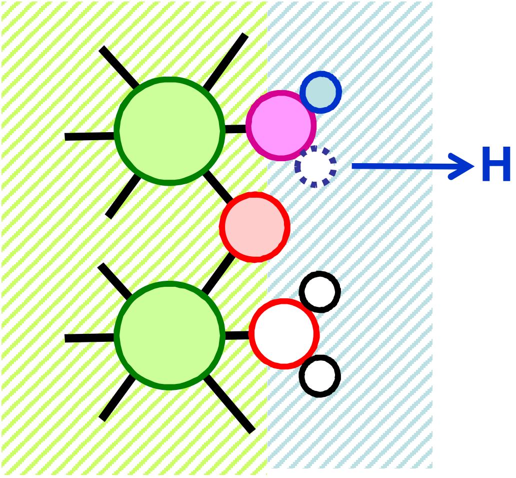
Level alignment at PZC

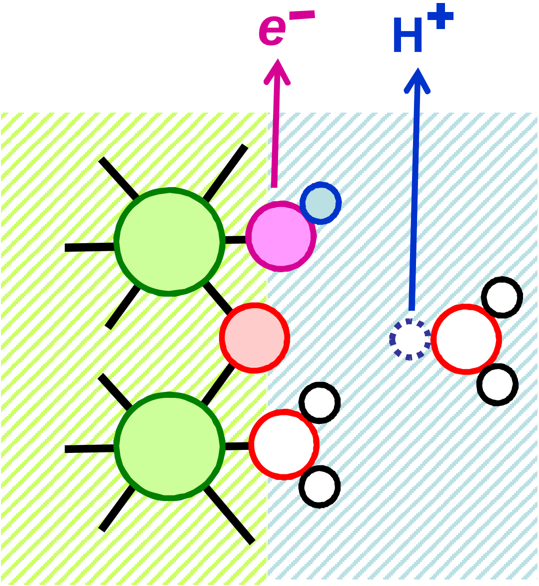


Oxidative dehydrogenation of a terminal water

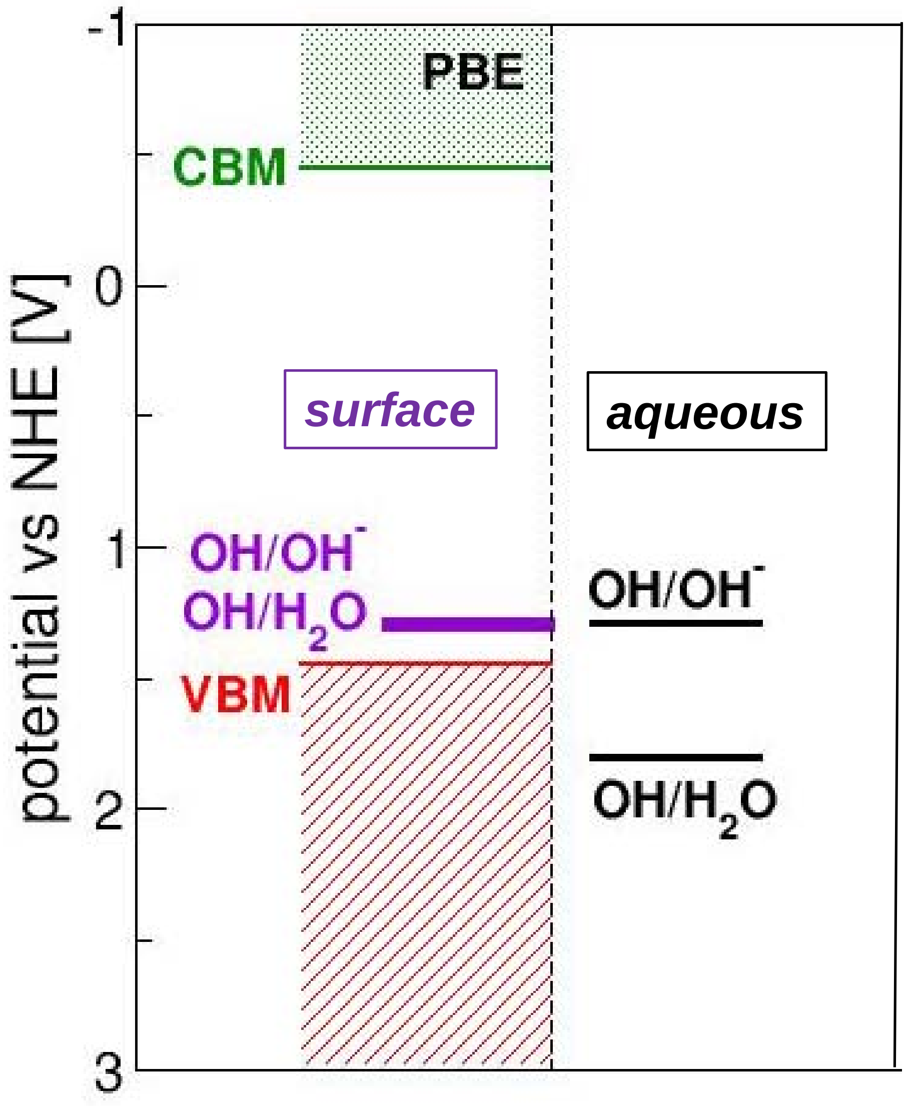


$$\begin{tikzcd} \mathrm{TiOH_2} \arrow[r] \arrow[dr, dashed] & \mathrm{TiOH}^- + \mathrm{H}^+ \arrow[d] \\ & \mathrm{TiOH}^\bullet + \mathrm{H}^+ + e^- \end{tikzcd}$$





Surface activation of ODH of H_2O at PZC

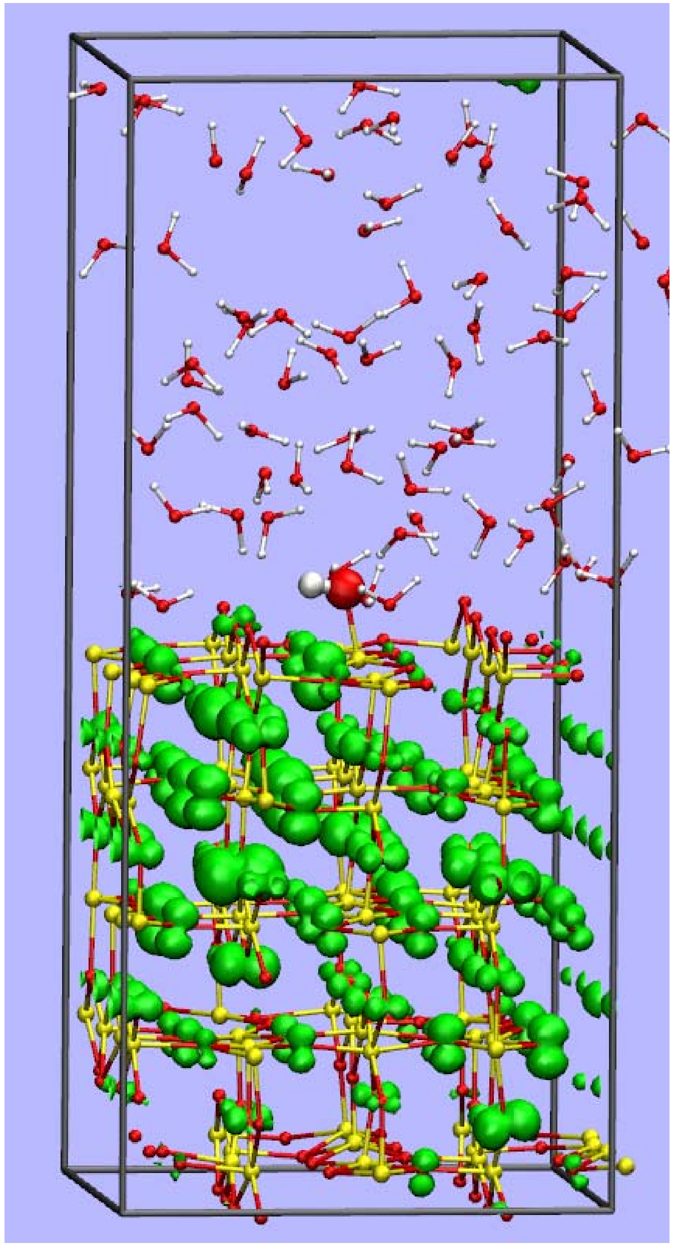


- Adsorption decreases pKa
- **No electronic activation**

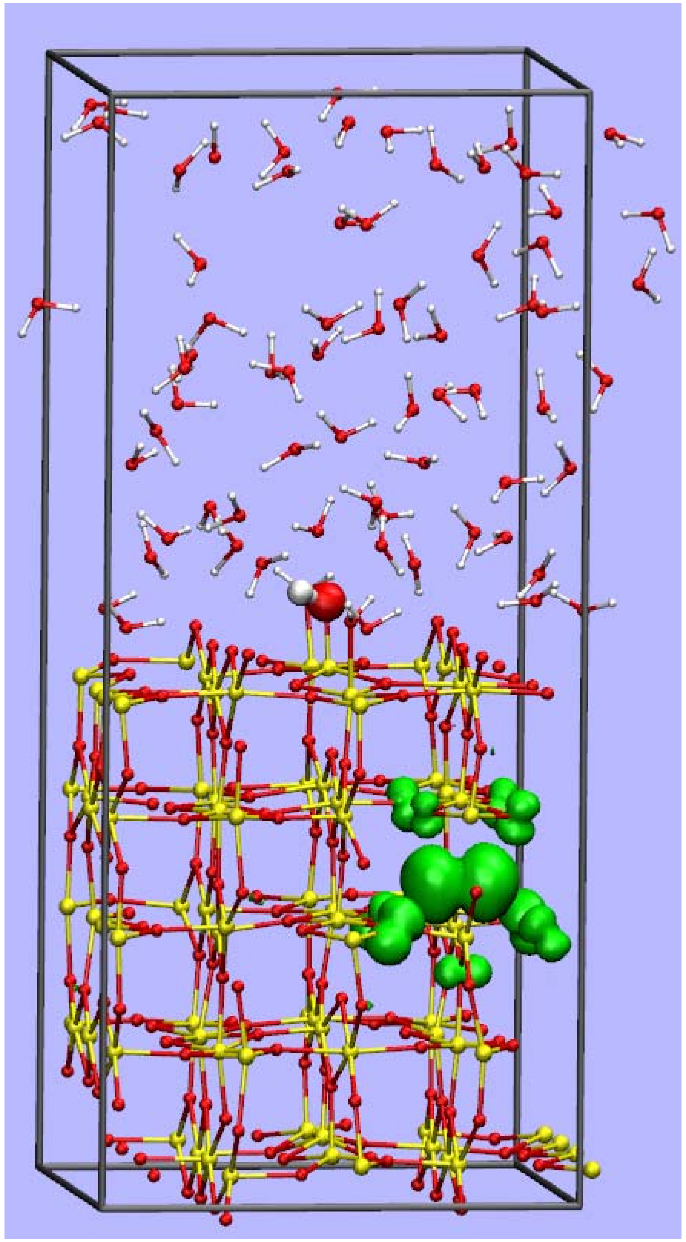
Fooled by the GGA?

Surface OH^- - hole pair

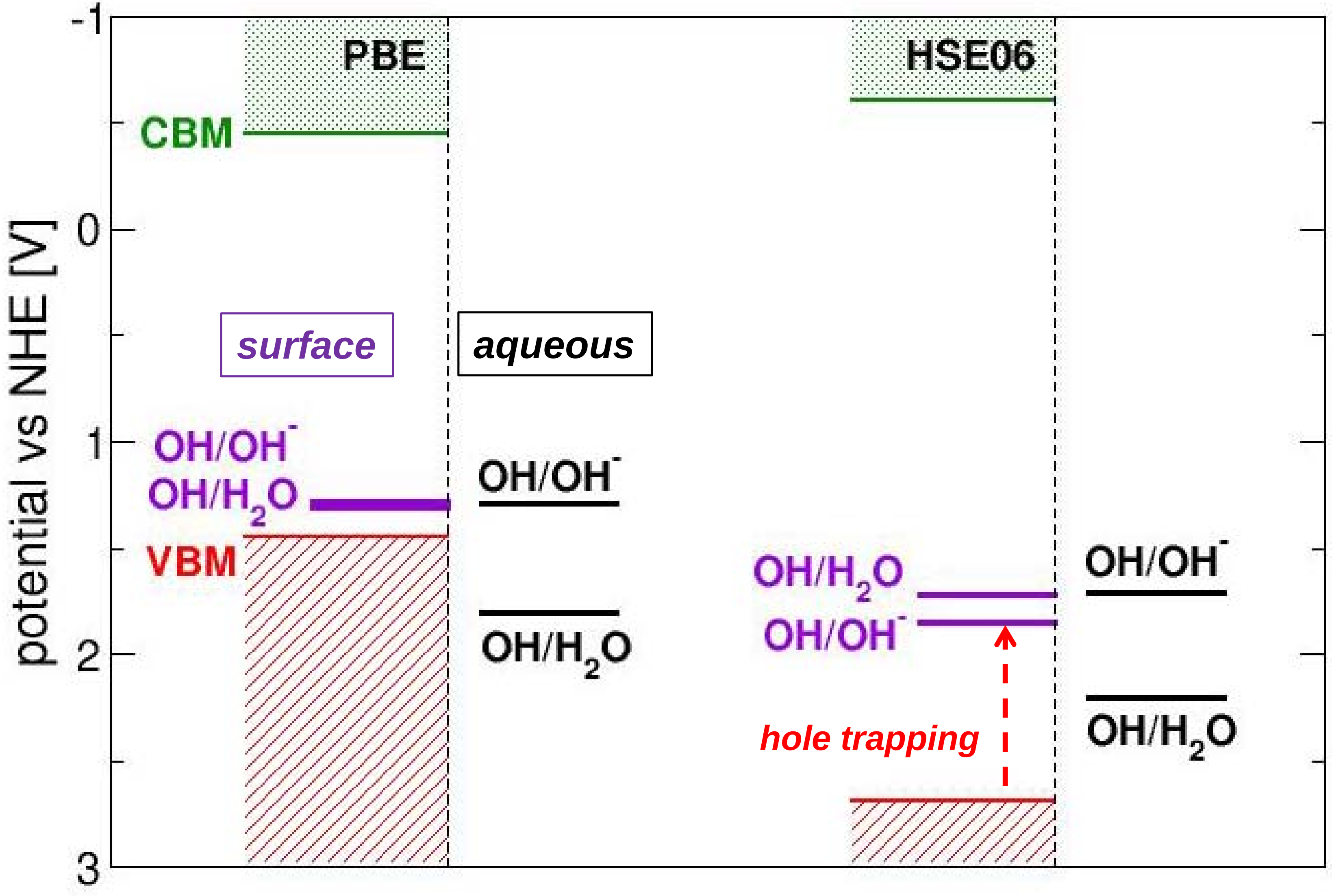
PBE



HSE06

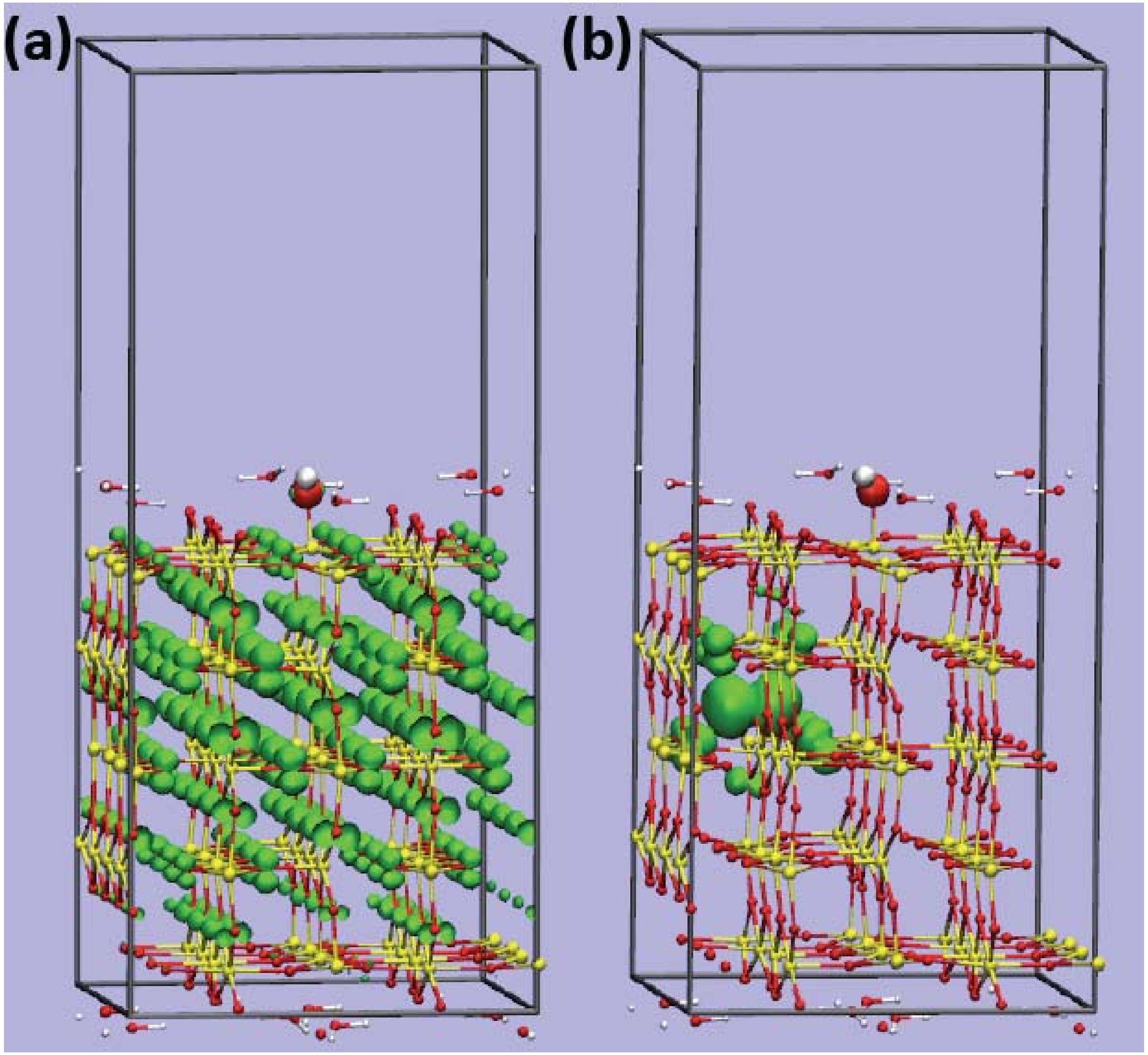


Surface activation of ODH of H_2O at PZC

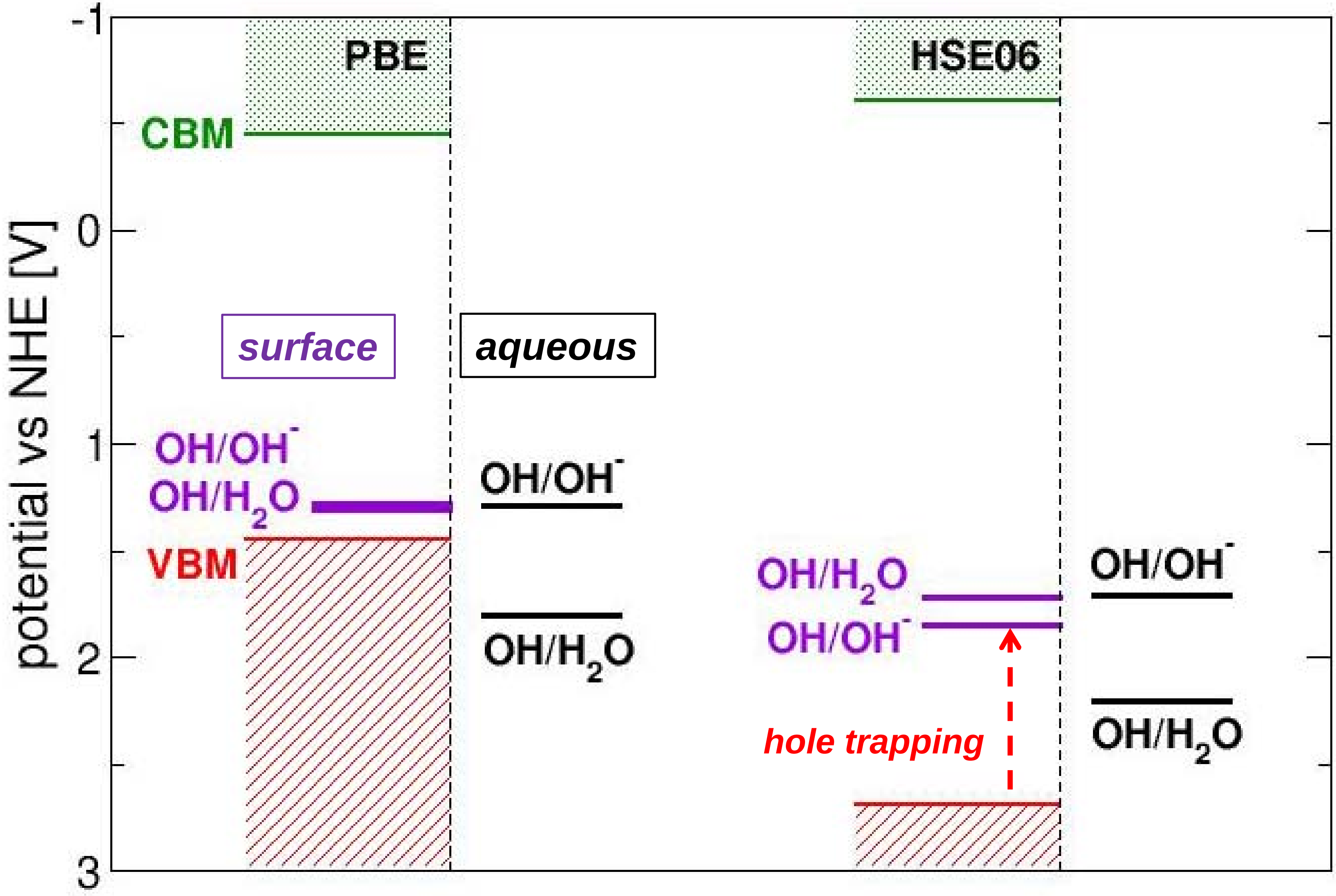


No electronic activation, increase in acidity only

The 1 mono-layer of water model system

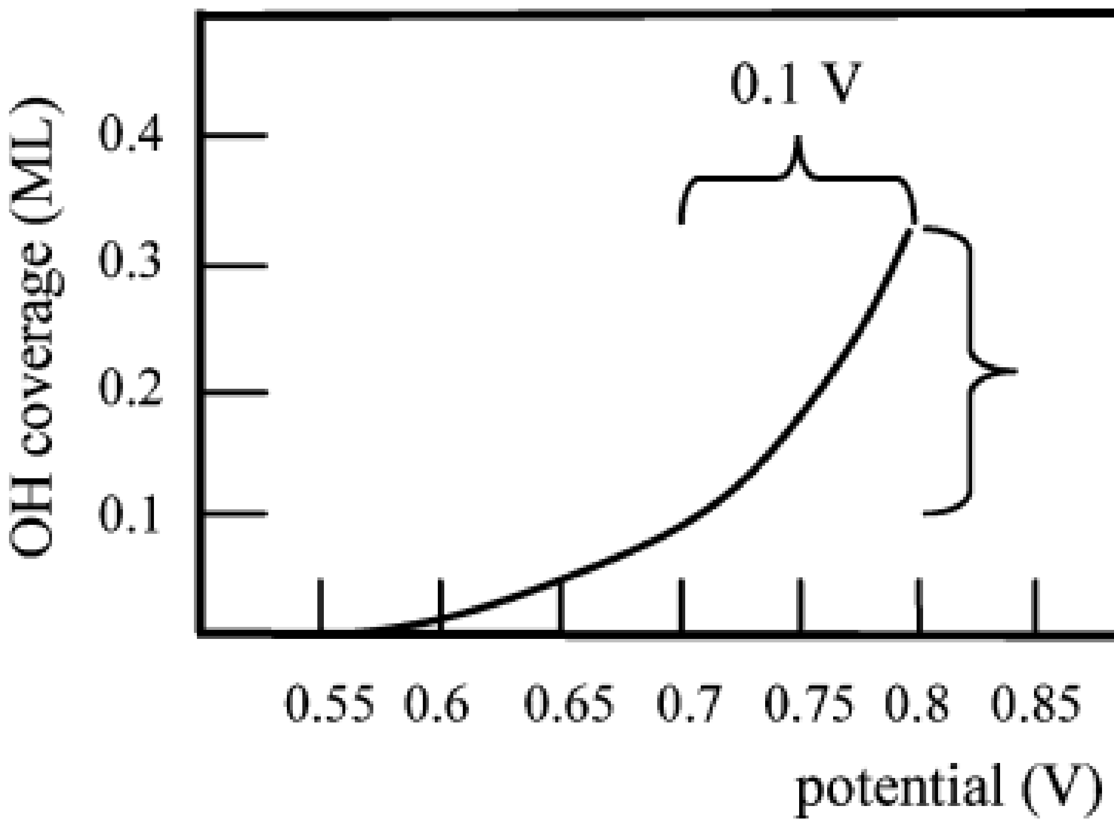


Surface activation of ODH of H_2O at PZC



No electronic activation, increase in acidity only

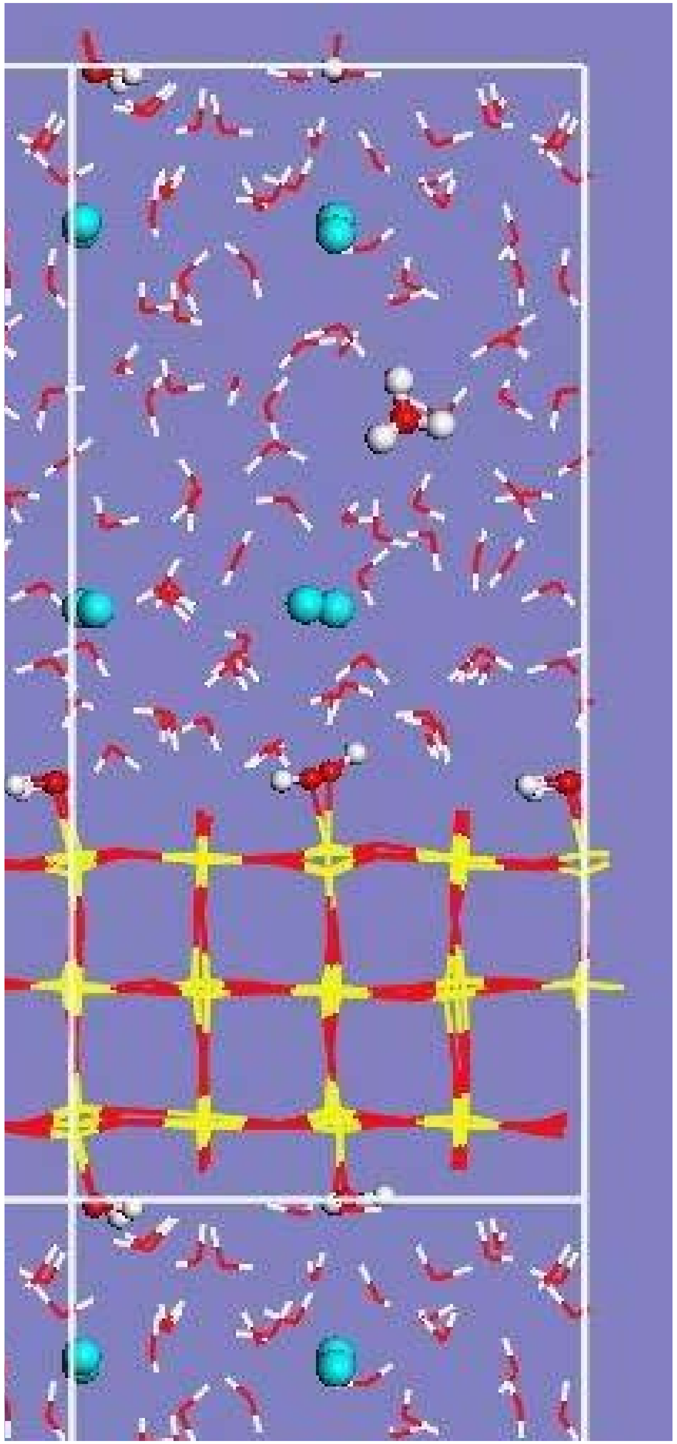
Surface activation of ODH on Pt(111)



Why is Pt so much more effective?

(1) Climent, V.; Gomez, R.; Orts, J. M.; Feliu, J. M. *J. Phys. Chem. B* **2006**, *110*, 11344–11351.

(2) Wakisaka, M.; Suzuki, H.; Miotsui, S.; Uchida, H.; Watanabe, M. *Langmuir* **2009**, *25*, 1897–1900.



Compact (Stern) double layer model

Cell: 11.9 × 13.2 × 29.2 $Å^3$

48 TiO_2 units

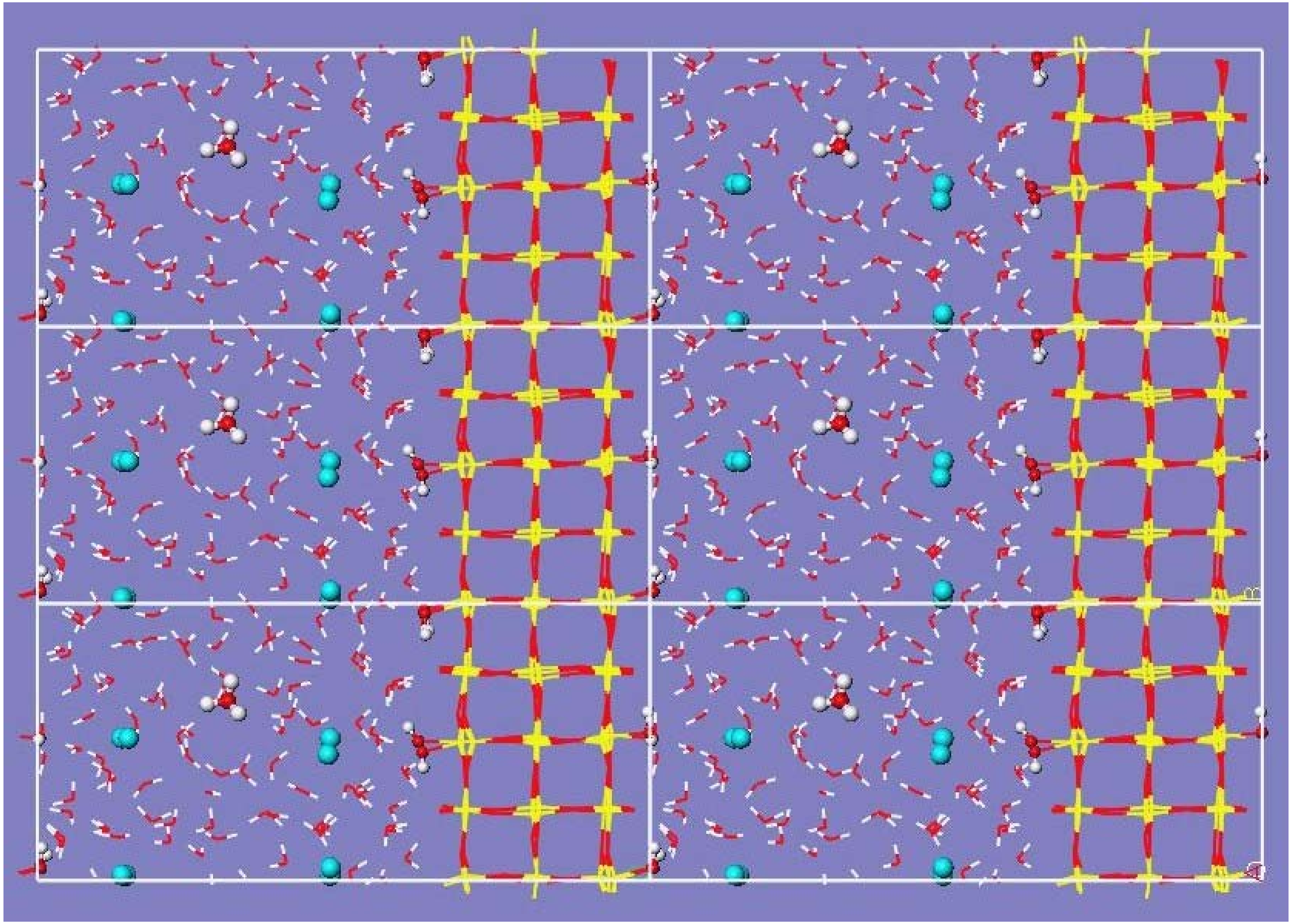
97 H_2O molecules

2 × 4 = 8 Na^+ ions

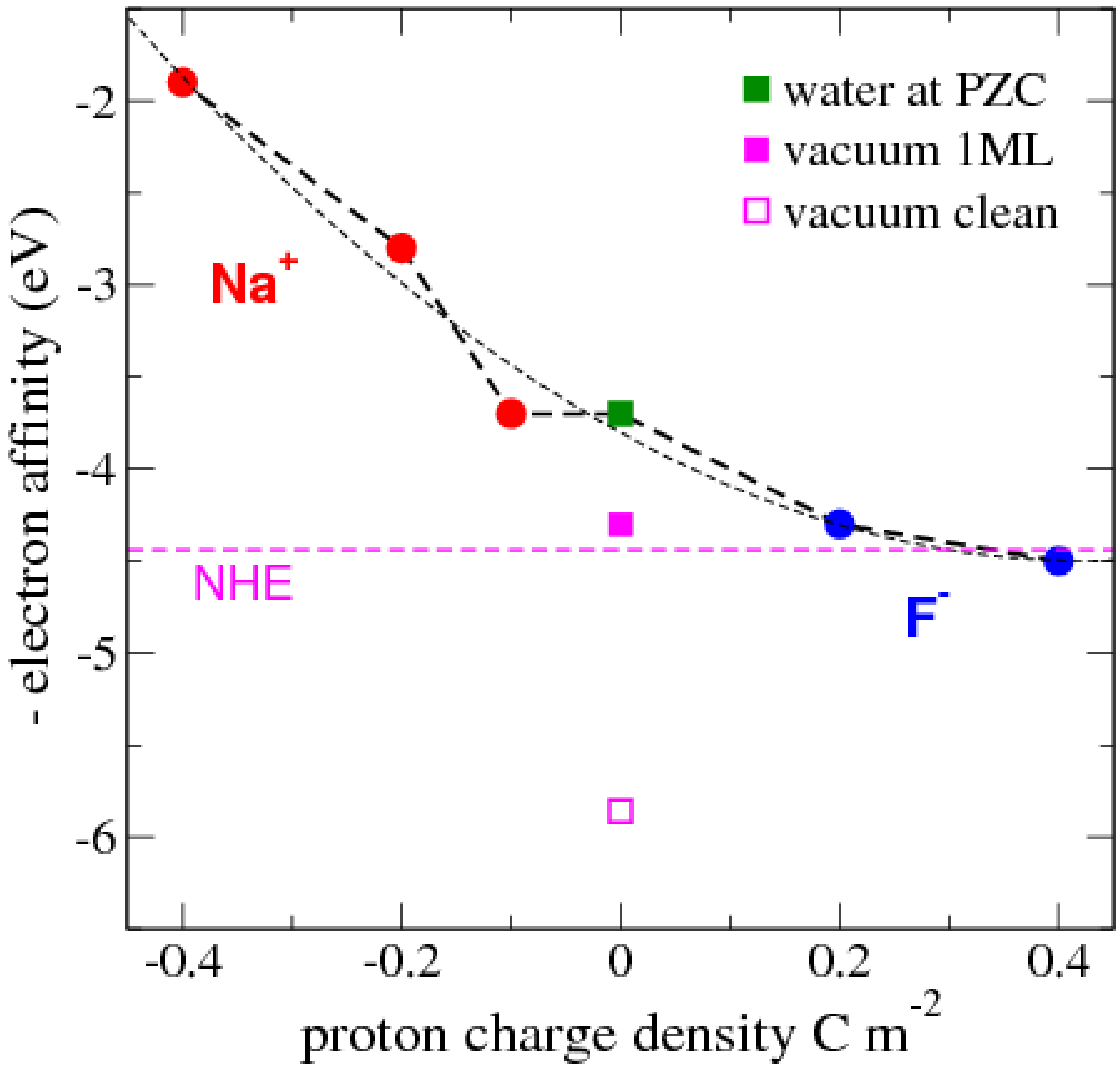
PBE functional (DVZP)

Double layer on both sides of the slab

Compact (Stern) double layer model



Charging the TiO_2 water interface



← pH

Capacitance

$$\frac{1}{C} = \frac{dV}{dQ}$$

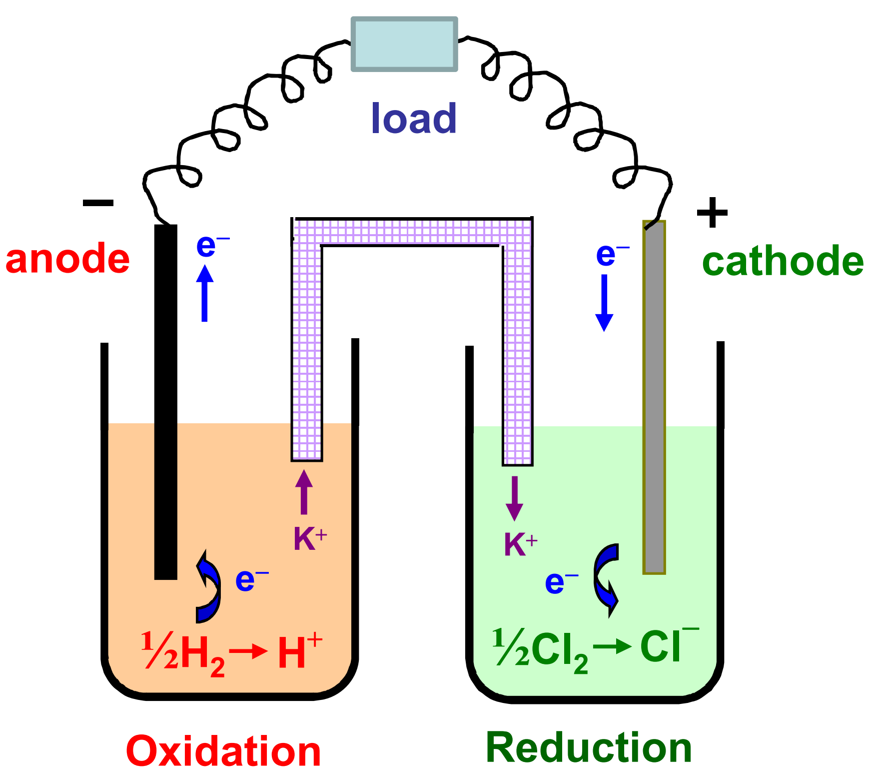
at PZC

Calc. $\mathrm{C = 0.3\ Fm^{-2}}$

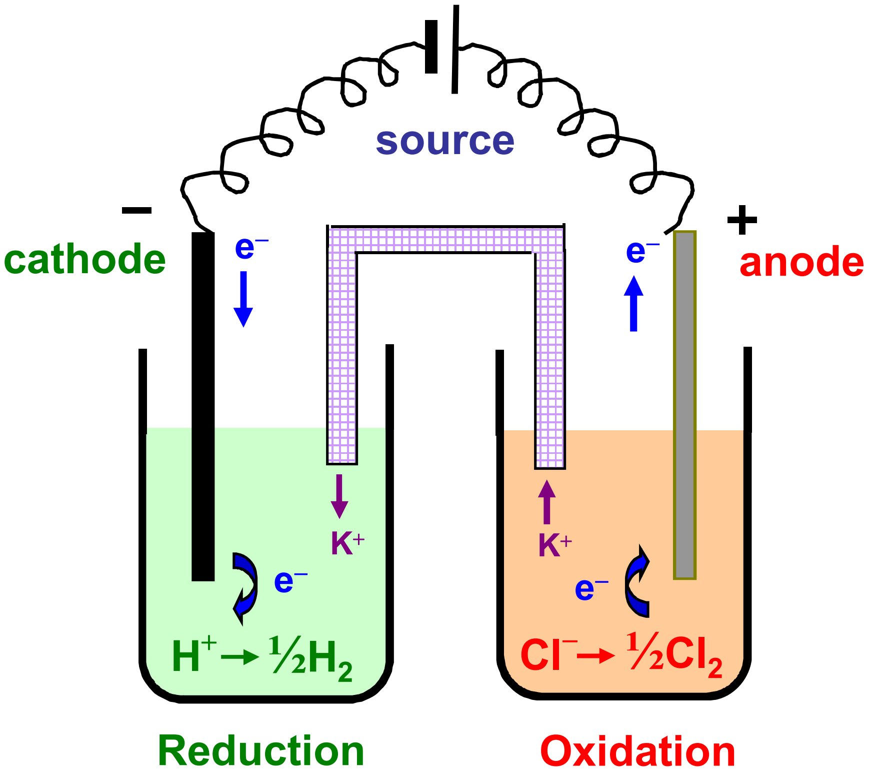
Exp. $\mathrm{C = 1.0\ Fm^{-2}}$

pH dependence flatband potential is overestimated

The two modes of an electrochemical cell

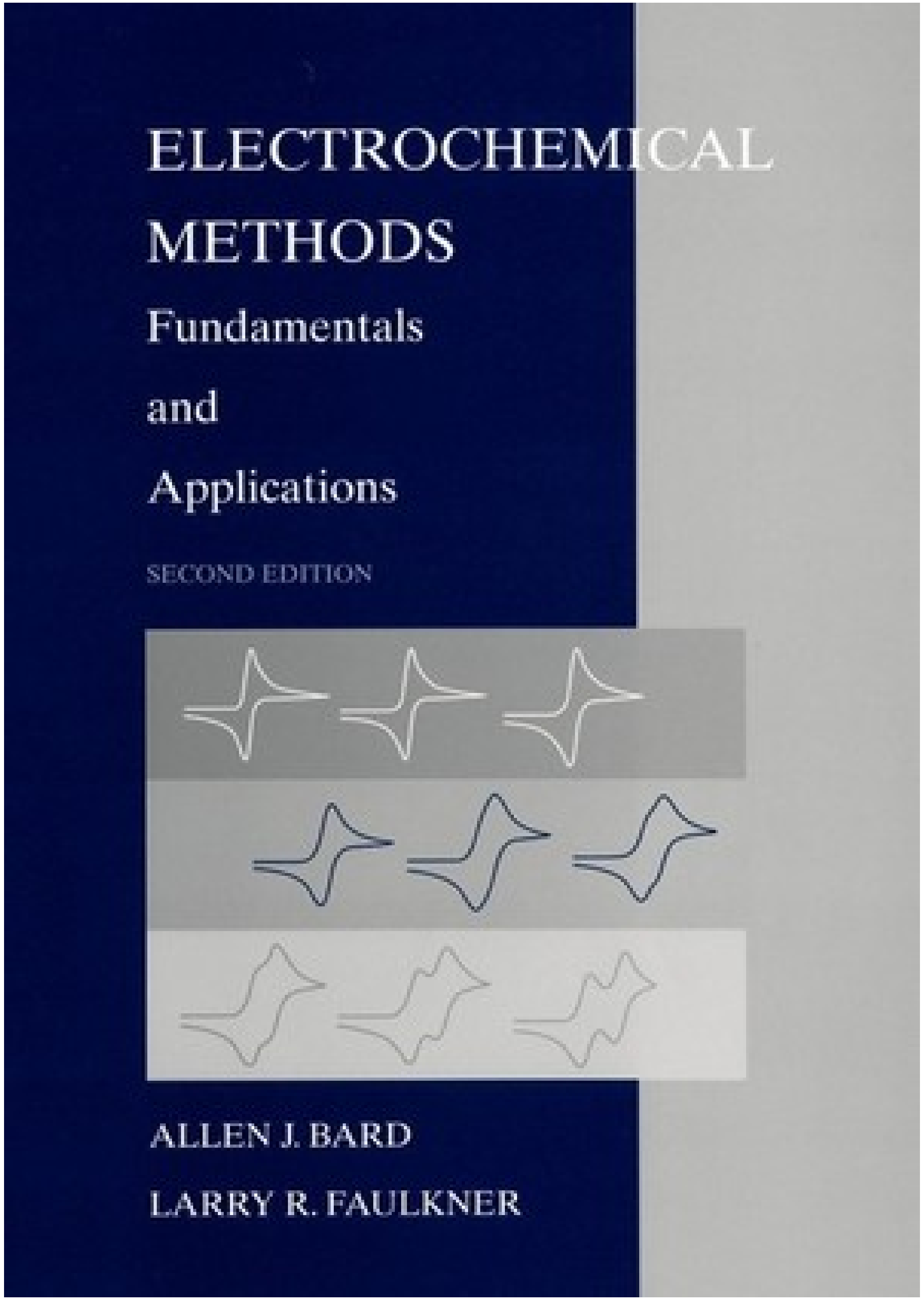


Generating electricity



Driving reactions

Cyclic Voltammetry



ELECTROCHEMICAL METHODS

Fundamentals

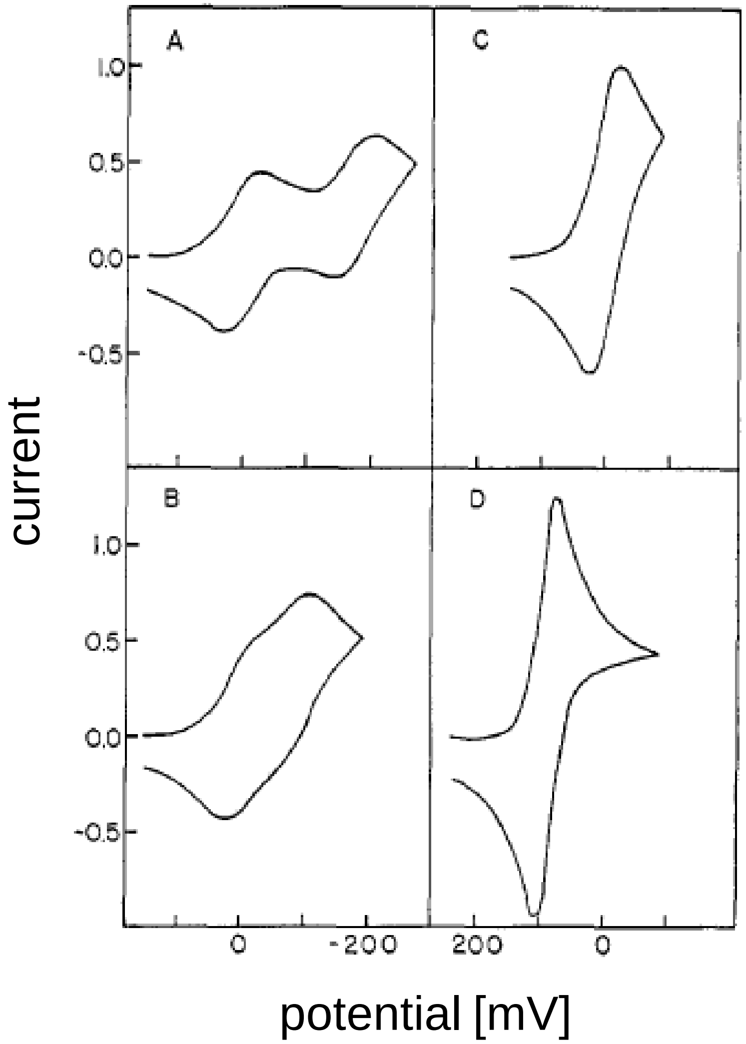
and

Applications

SECOND EDITION

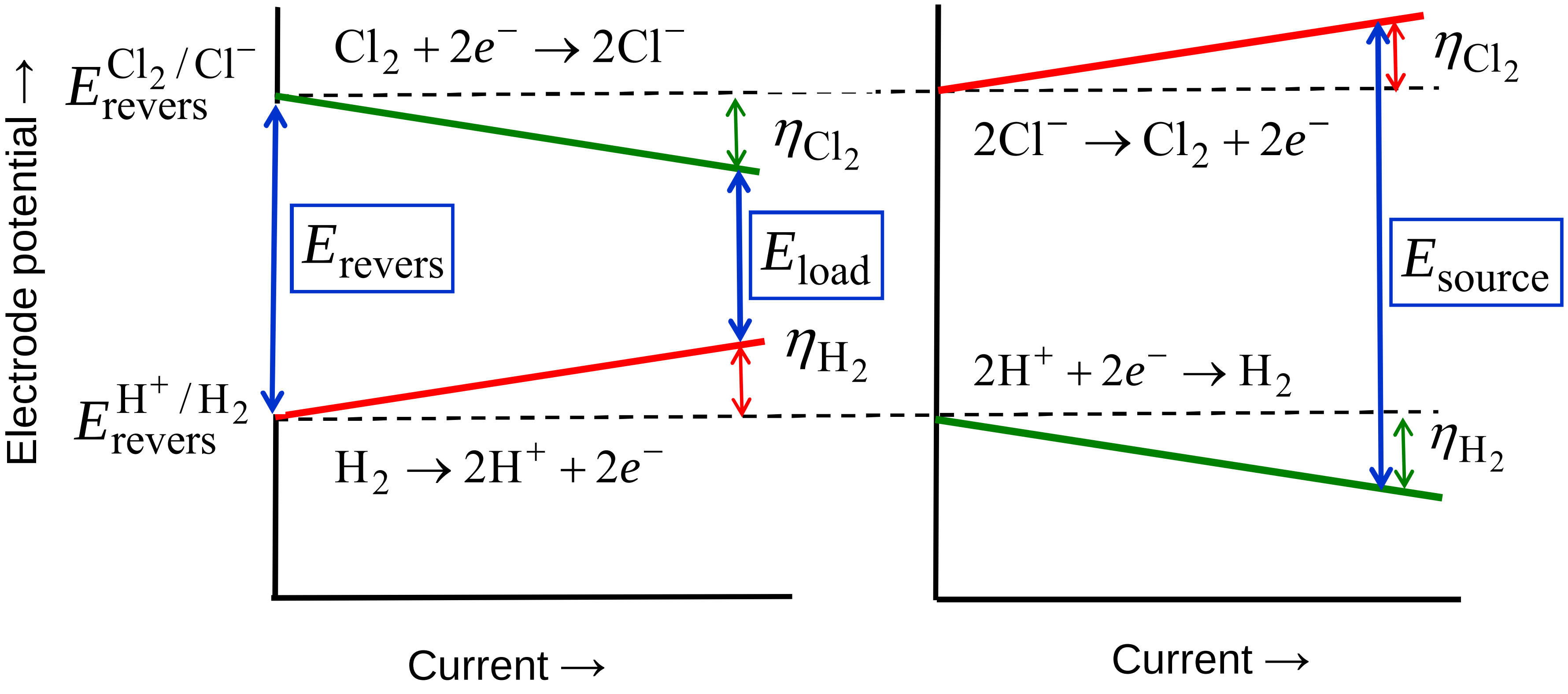
ALLEN J. BARD

LARRY R. FAULKNER



Not ready for this yet

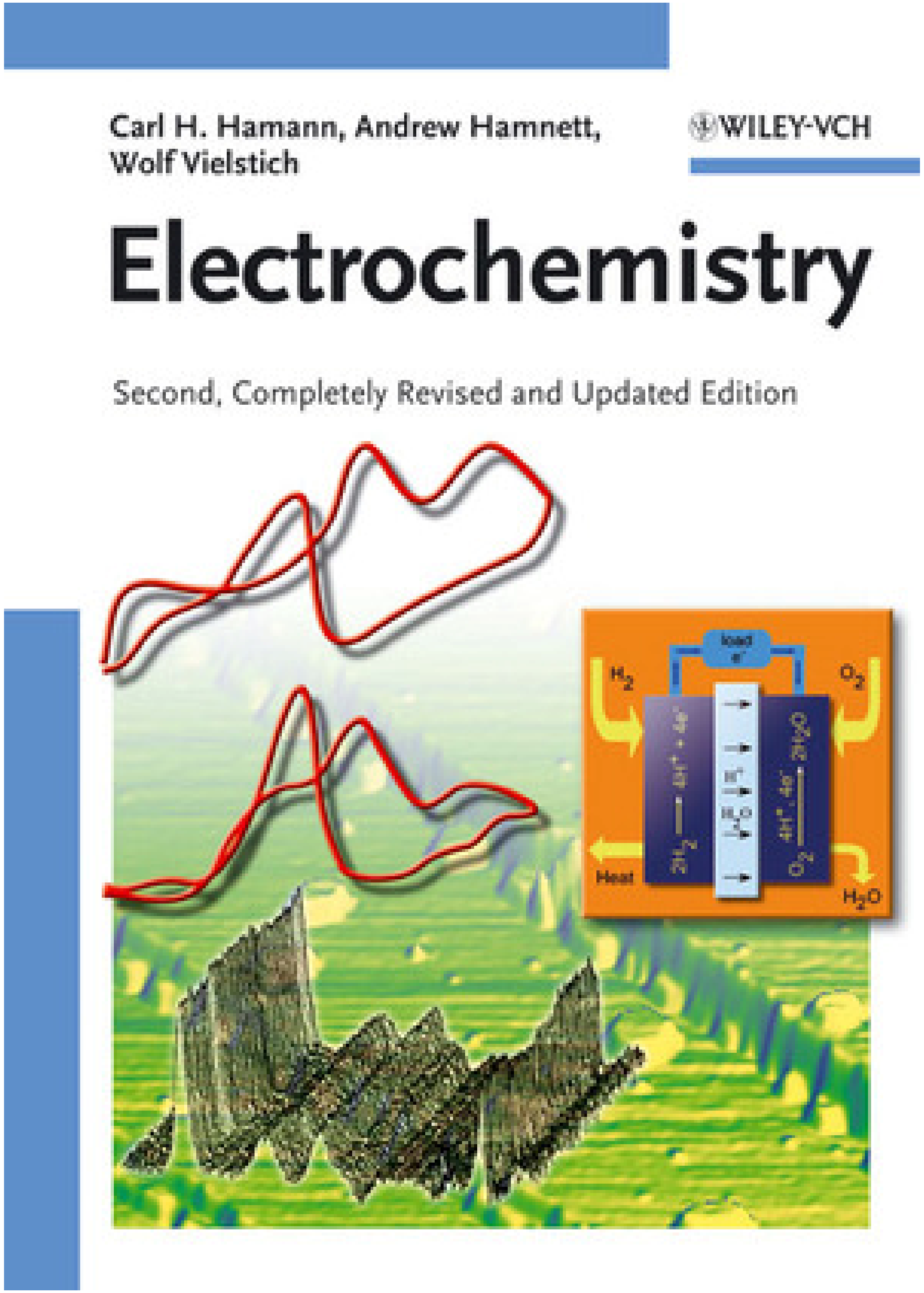
Overpotentials are wasting energy



Generating electricity ***Driving reactions***

Energies of barriers and intermediates can already give a clue

Reference for the previous slide



Carl H. Hamann, Andrew Hamnett,
Wolf Vielstich

WILEY-VCH

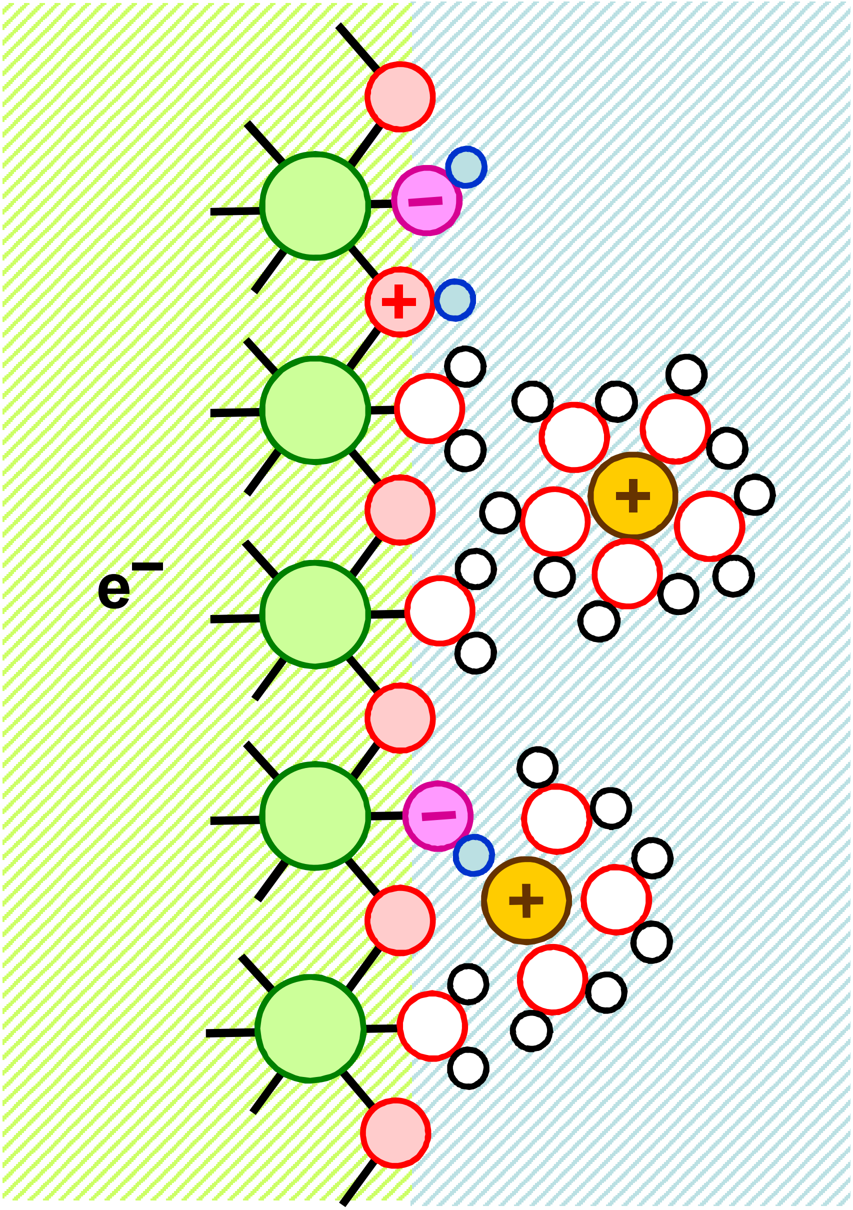
Electrochemistry

Second, Completely Revised and Updated Edition

But, yes

Electrochemistry is hard for theorists ...

Electrical double layer at a TiO_2 water interface



- Excess electron charge

  electrons in conduction band
  holes in valence band

- Excess proton charge

  deprotonaton terminal waters
  protonation bridging oxygens

- Ionic counter charge

  cations and anions from
  electrolytic solution

Rates: Compare vertical and adiabatic IP's

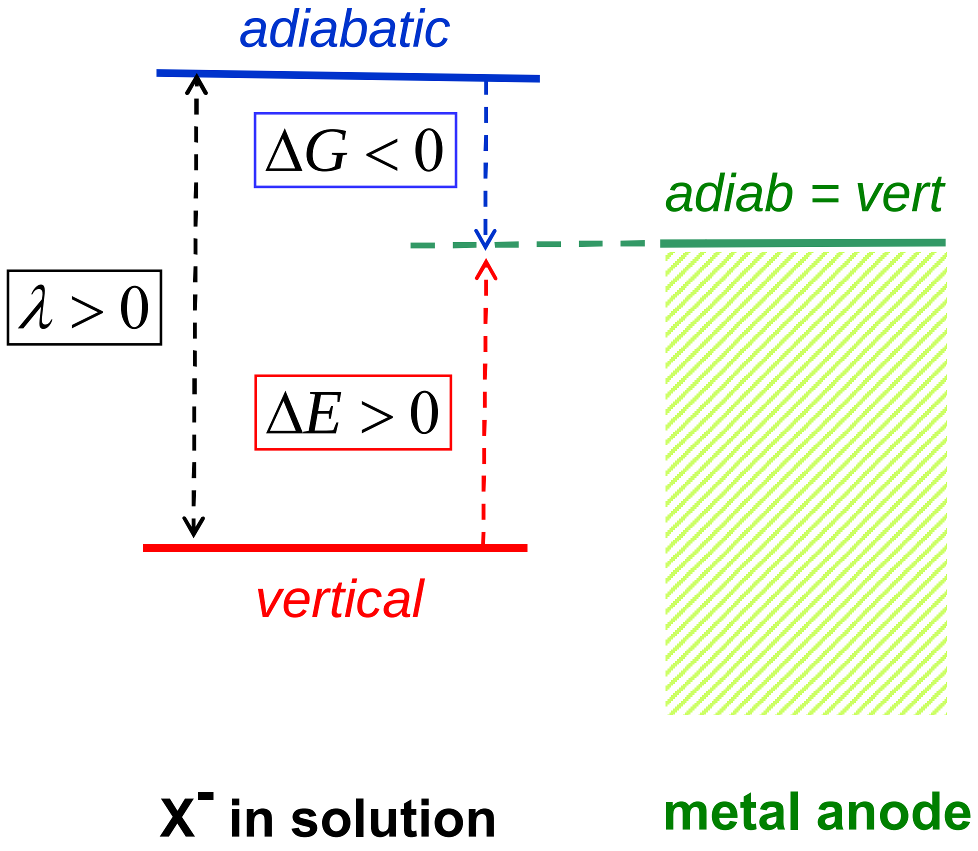
$$\boxed{\mathrm{X}^{-}(aq) \xrightarrow{\Delta G < 0} \mathrm{X}^{\bullet}(aq) + e^{-}(m)}$$

equilibrium constant

$$K = \exp\left[-\frac{\Delta G}{k_{\mathrm{B}}T}\right]$$

rate constant

$$k \propto \exp\left[-\frac{(\Delta E)^2}{4\lambda\, k_{\mathrm{B}}T}\right]$$



People involved

Jun Cheng

Marialore Sulpizi

Joost VandeVondele

Regla Ayala

Francesca Costanzo

John Kattirzi

Density functional molecular dynamics method

Credo

Treat solute and solvent at the same level of density functional theory

Code

CP2K (cp2k.berlios.de)

- Gaussian basis set (+ plane waves for density)
- GGA and now also Hybrid functionals
- Born-Oppenheimer dynamics
- Free energy calculation

J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter,
Comp. Phys. Comm. (2005), ***167****, 103.*