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FREE WEBINAR SERIES IN CORROSION SCIENCE

9 June 2021

Molecular modeling of corrosion inhibitors

Anton Kokalj & his colleagues at
Department of Physical and Organic Chemistry

Jožef Stefan Institute, Ljubljana, Slovenia

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Atomistic ~~Molecular~~ modeling of organic corrosion inhibitors

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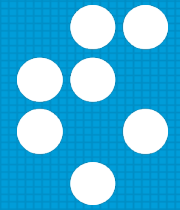
Modeling corrosion inhibitors



1) MEPTIC: **M**olecular **E**lectronic **P**roperties **T**o **I**nhibition-efficiency **C**orrelation
   relies on associating inhibitor molecular properties (without any consideration of a metal substrate) with experimentally determined inhibition efficiency

2) Machine-learning methods

3) Physics-based modeling

   atomistic modeling of interactions between components of corrosion system
   gives deeper physical insight, but is technically more complicated & computationally much heavier

   multi-scale modeling using ICME paradigm
   emerging approach, currently at the level of implementations in corrosion inhibitor research

Quantifying inhibitor performance

inhibition efficiency (η)
a number that indicates how "good" is a given inhibitor

$$\eta = \frac{R_p^{inh} - R_p^{blank}}{R_p^{inh}}$$

PROS:

- normalized: $\eta \in [0,1]$
- under simplifying assumptions: $\eta \approx \Theta$ (surface coverage)

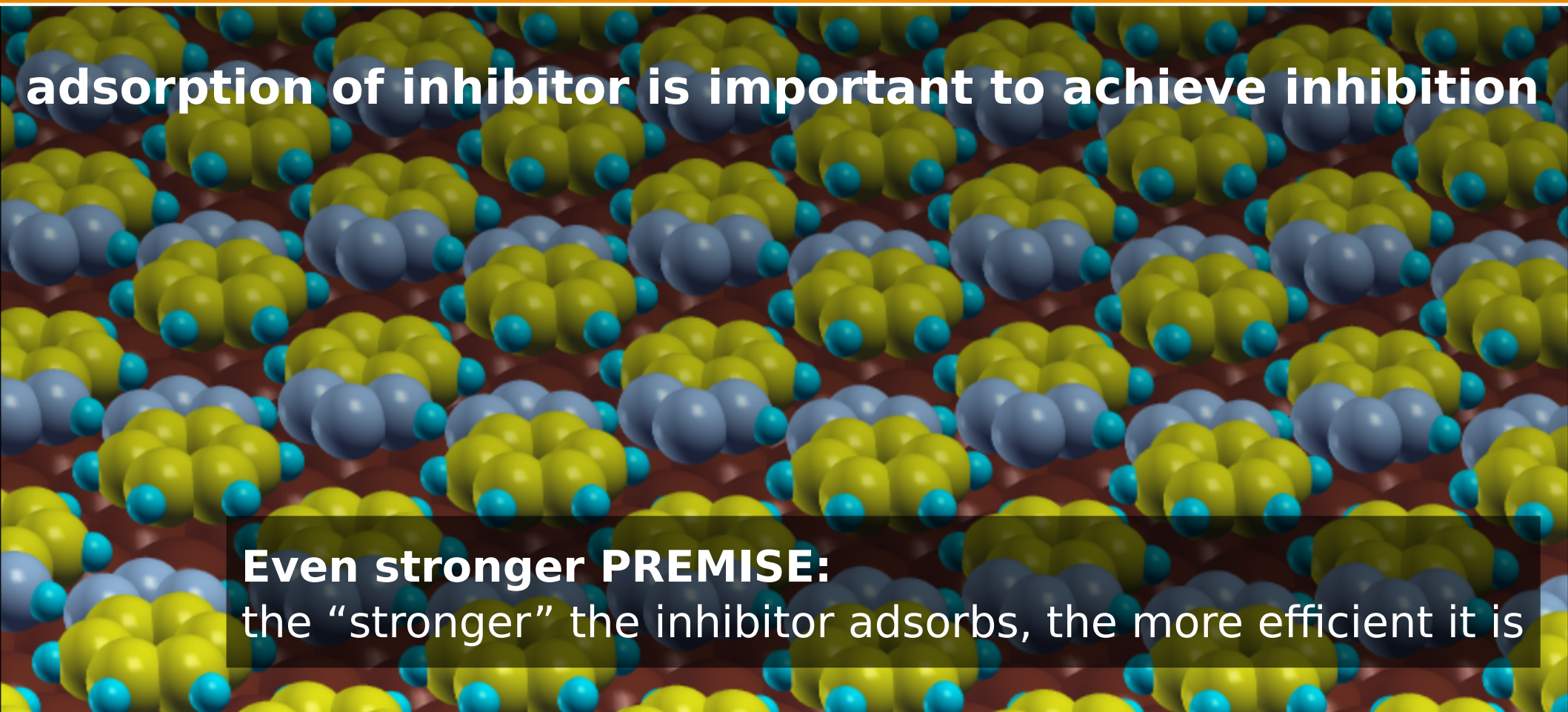
CONS:

- highly "non-linear"

Corros. Sci. **179** (2021) 108856

PREMISE:
the greater is the inhibitor adsorption affinity, the more efficient is the inhibitor

Generally accepted premise



adsorption of inhibitor is important to achieve inhibition

Even stronger PREMISE:
the “stronger” the inhibitor adsorbs, the more efficient it is

Units …

1 eV ≈ 100 kJ/mol

≈ 25 kcal/mol

MEPTIC premises

MEPTIC: **M**olecular **E**lectronic **P**roperties **T**o **I**nhibition-efficiency **C**orrelation relies on associating inhibitor molecular properties (without any consideration of substrate) with experimentally determined inhibition efficiency

Popular molecular electronic parameters:

- eigenvalues of HOMO (ε_{HOMO}) and LUMO (ε_{LUMO})
- HOMO–LUMO gap ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$)

HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital

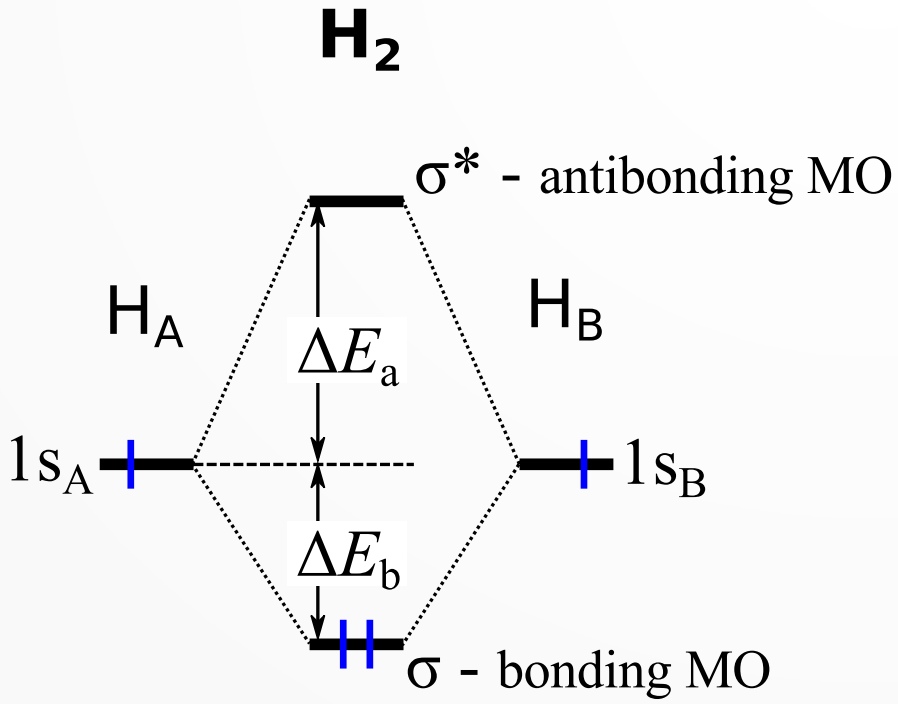
Premise:

the **smaller** the HOMO–LUMO gap the **stronger** the molecule–surface interaction, the **stronger** the interaction the **better** the inhibitor

HOMO & LUMO

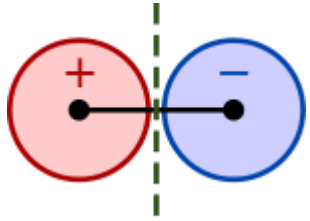
Why is a HOMO–LUMO gap important for the molecule–surface interaction?

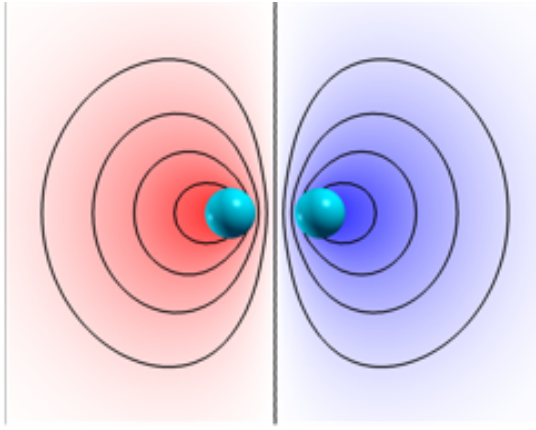
A chemist's view of bonding

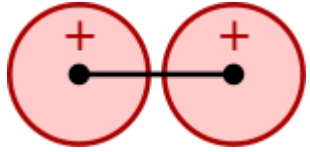


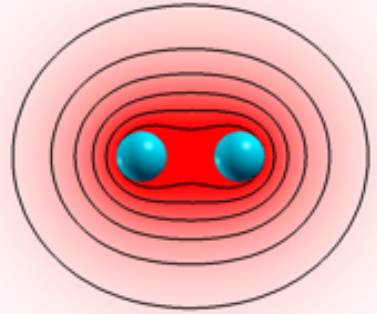
net attraction

(two-orbital two-electron interaction)

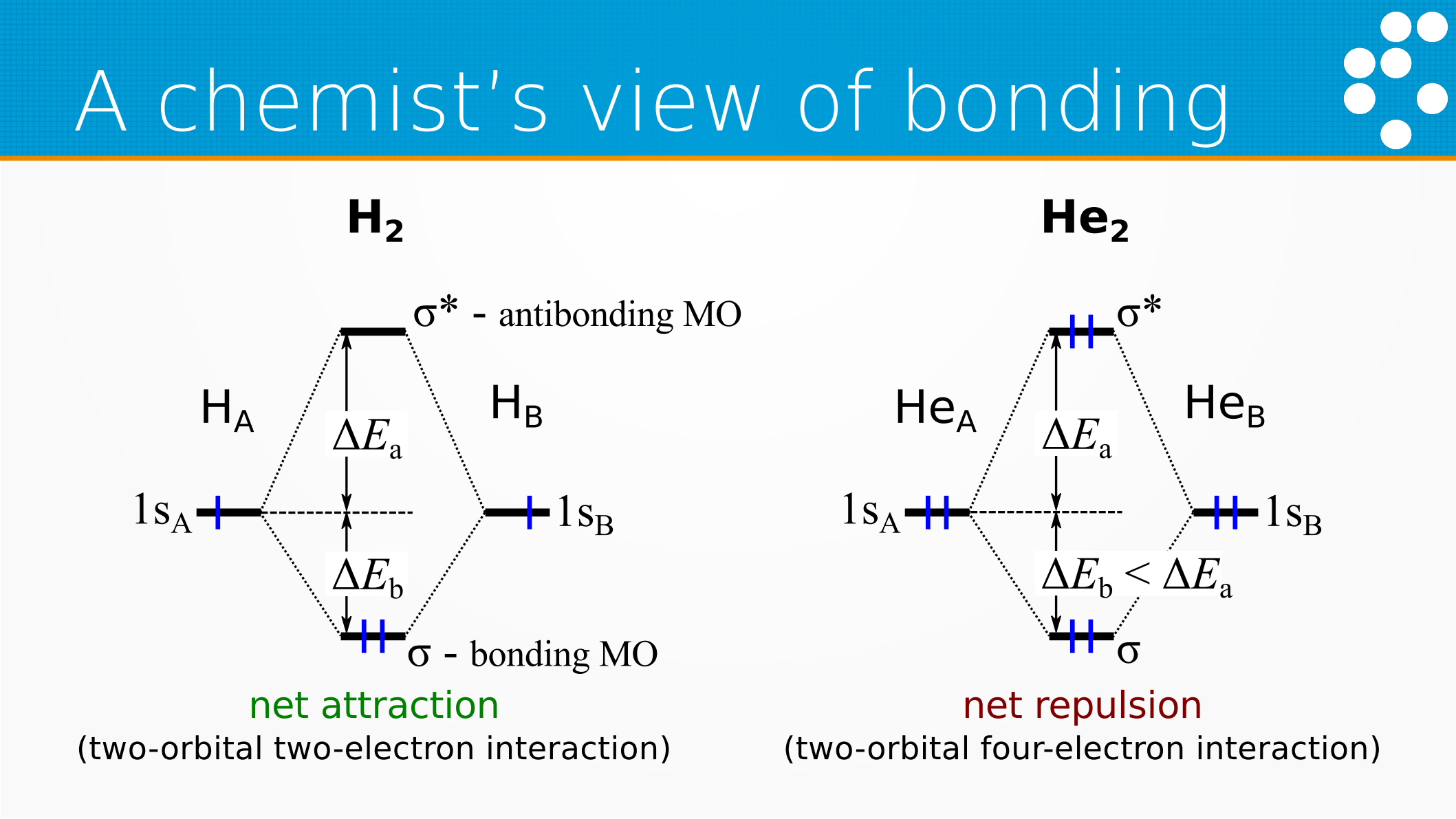




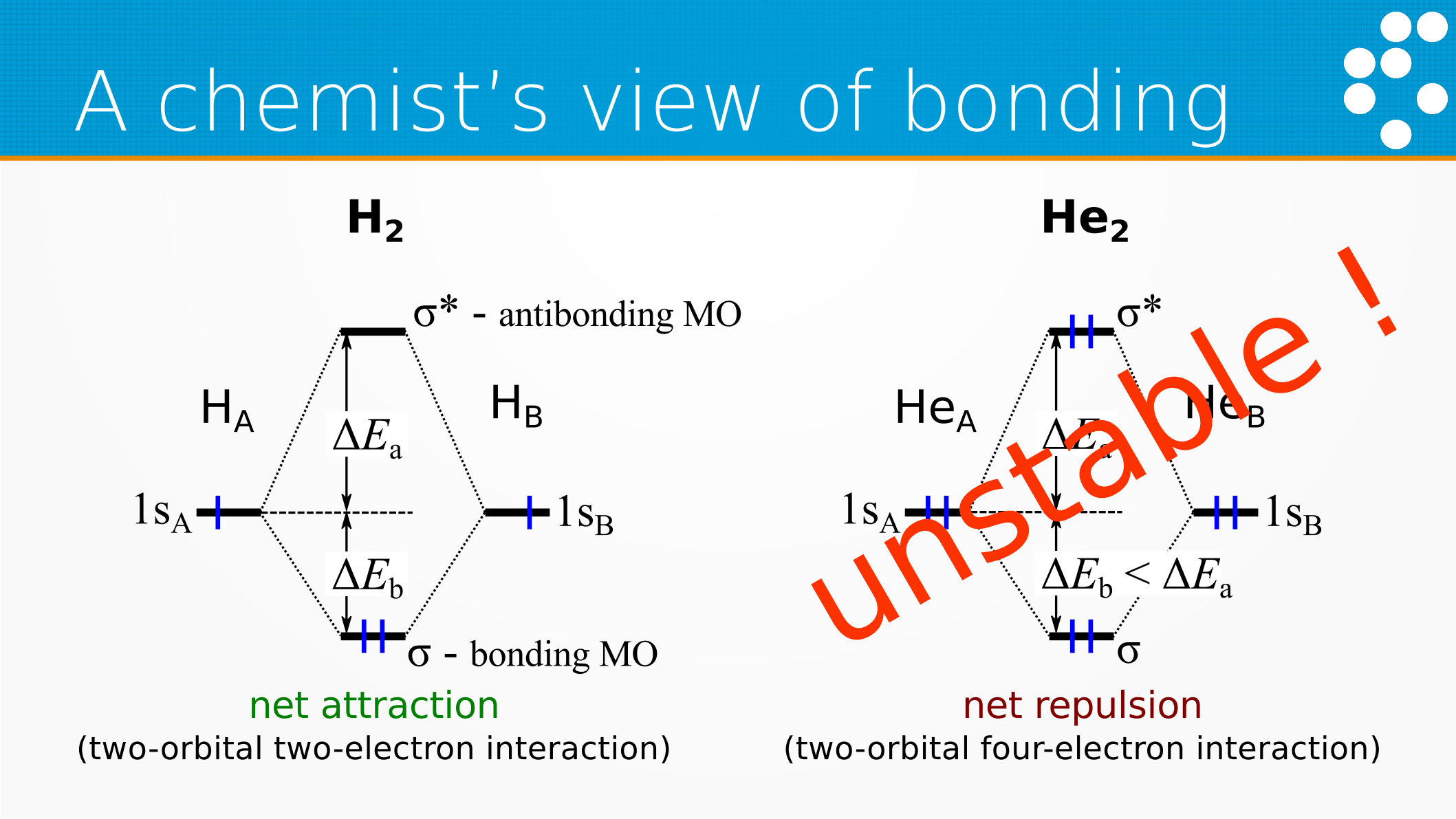




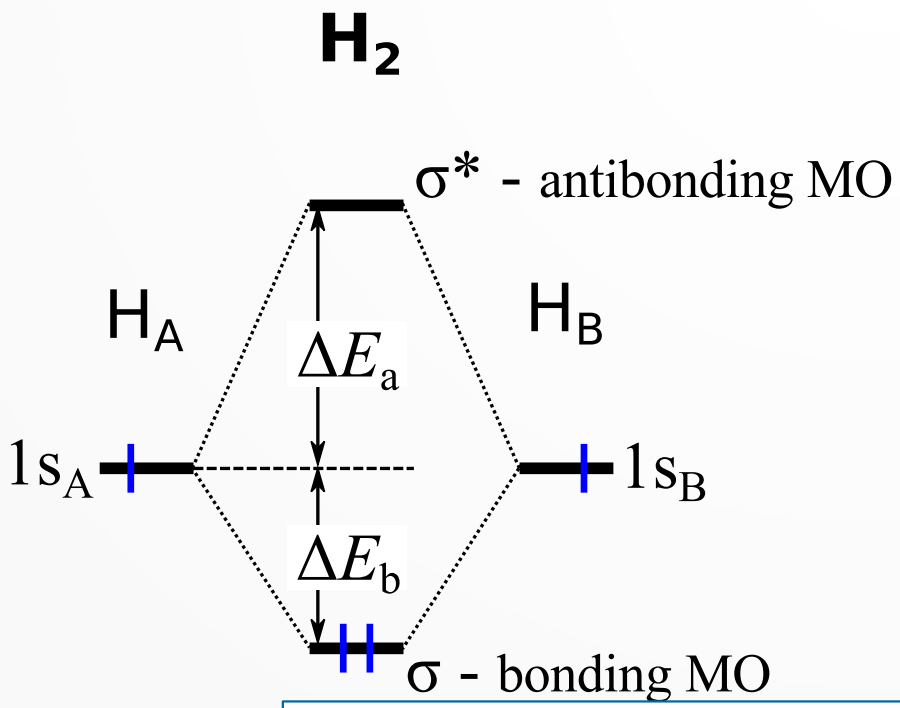
A chemist's view of bonding

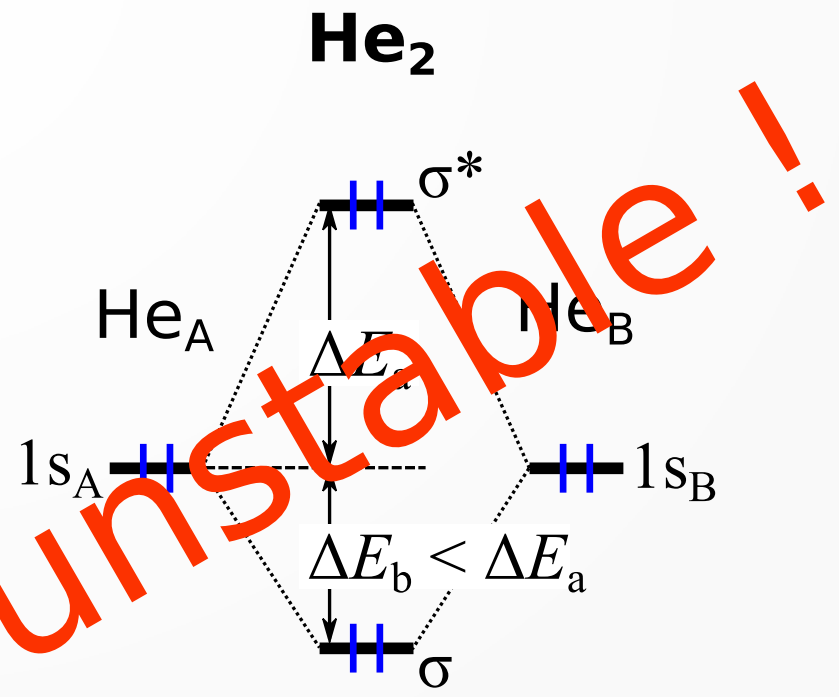


A chemist's view of bonding



A chemist's view of bonding



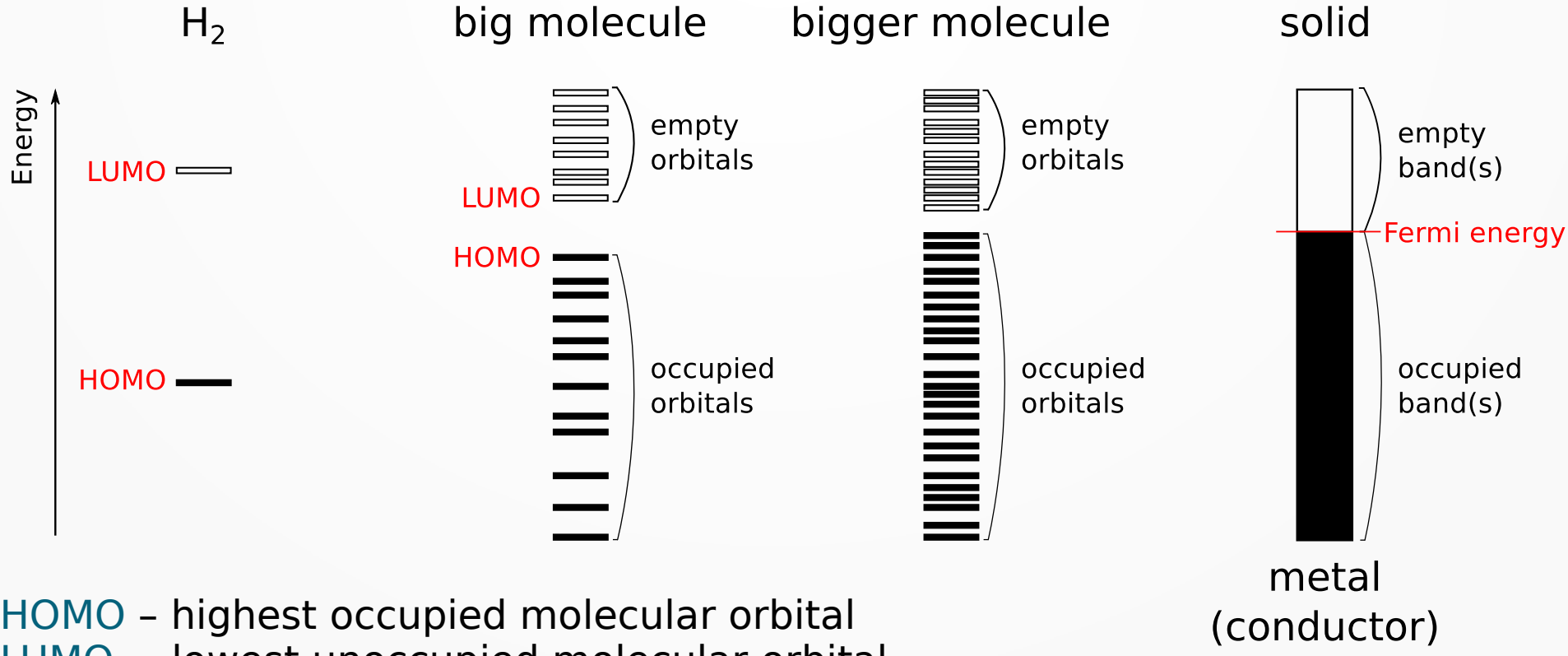


net

(two-orbital two

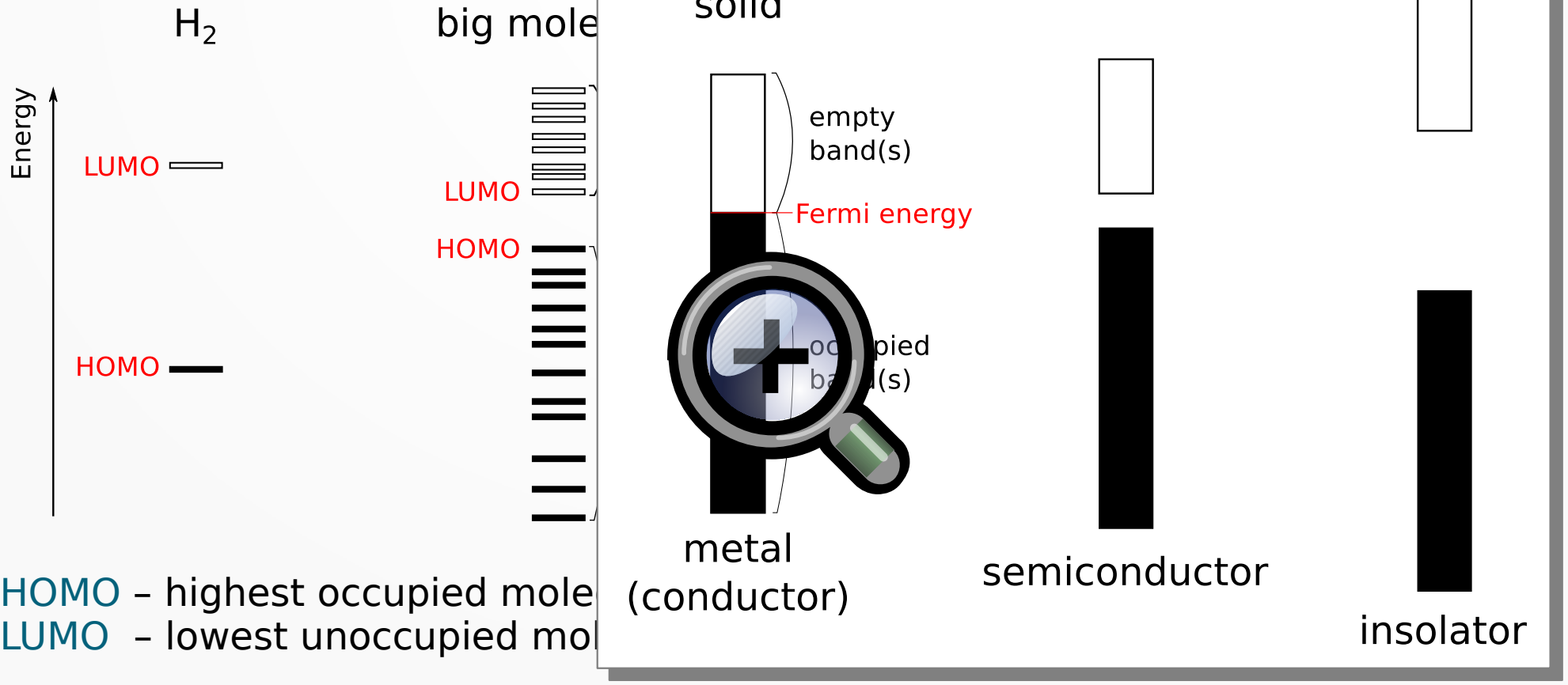
keep antibonding states empty

From H_2 to solid



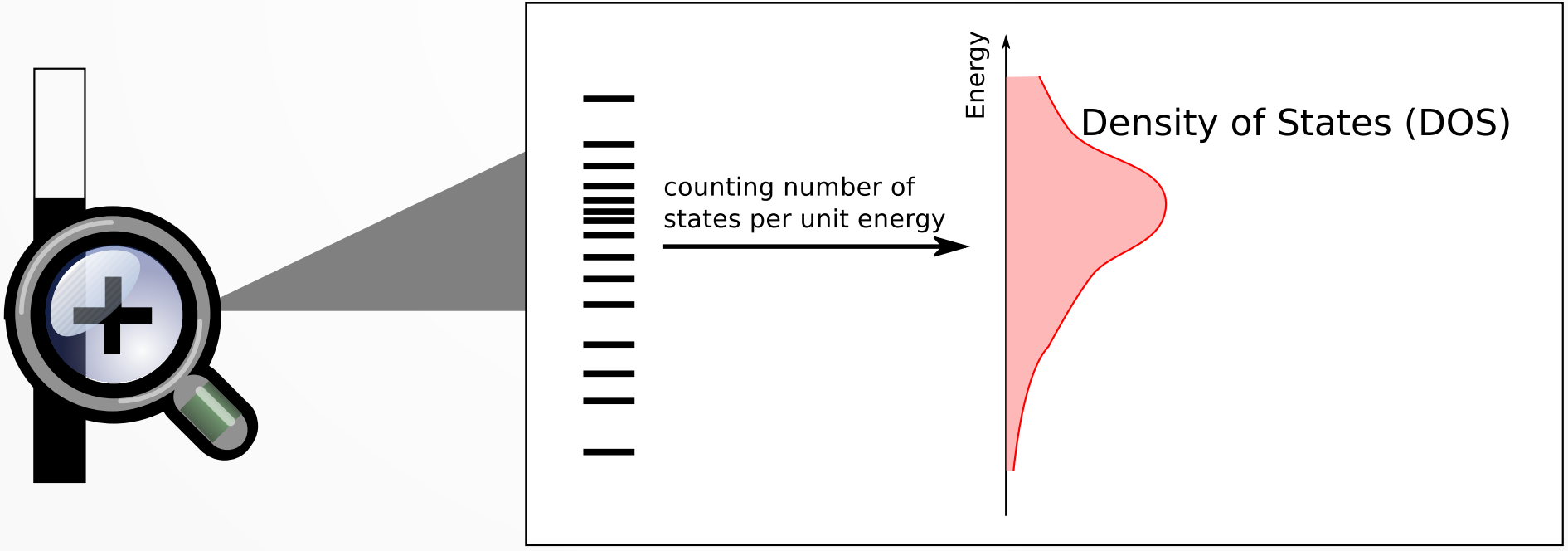
HOMO – highest occupied molecular orbital
LUMO – lowest unoccupied molecular orbital

From H_2 to solid

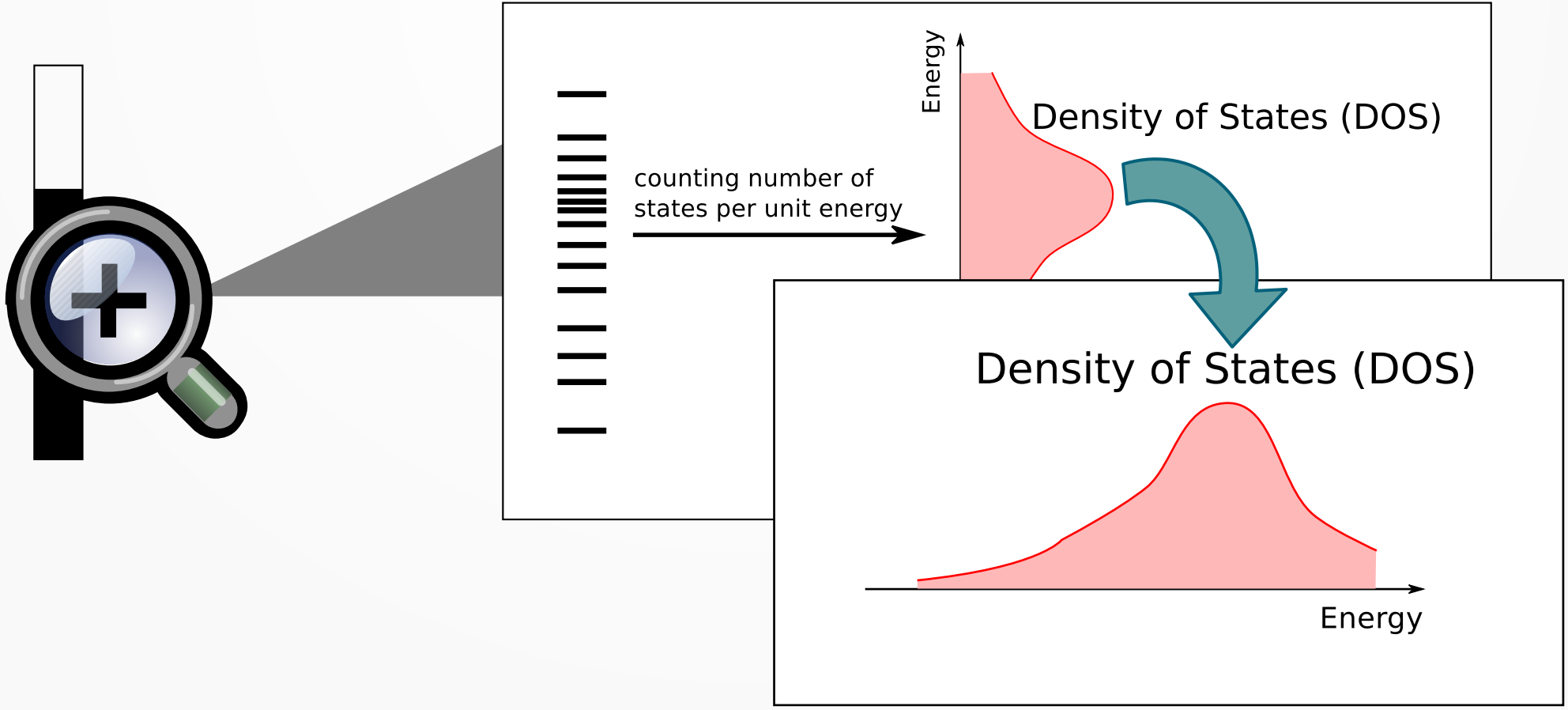


HOMO – highest occupied mole
LUMO – lowest unoccupied mol

Density of states (DOS)



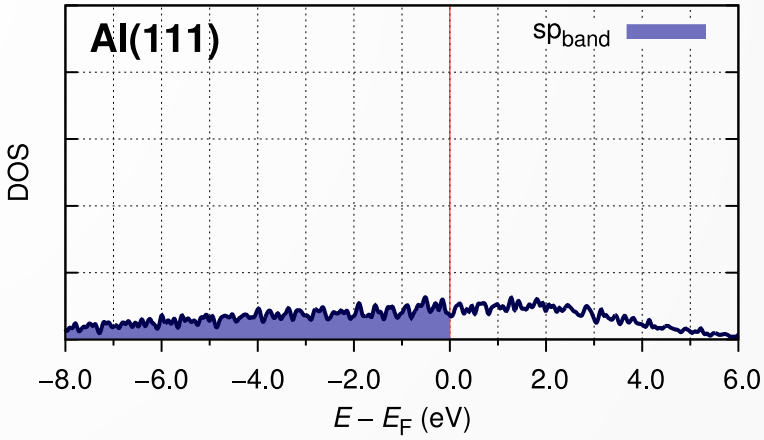
Density of states (DOS)



Electronic structure of metals

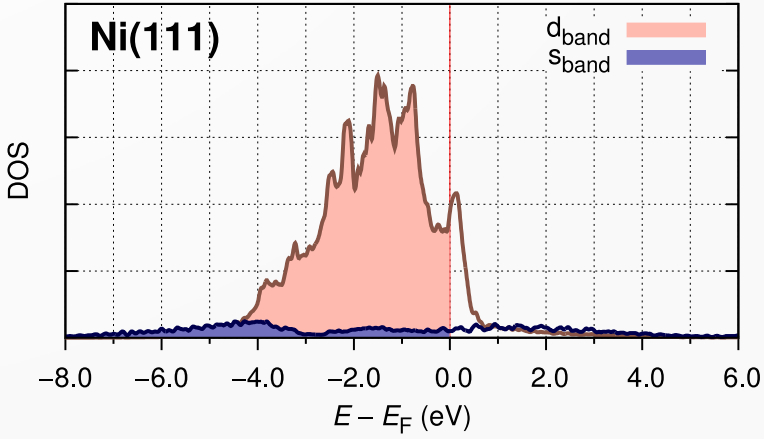
Two types of bands:

- delocalized (broad) sp-pands
- localized (narrow) d-bands



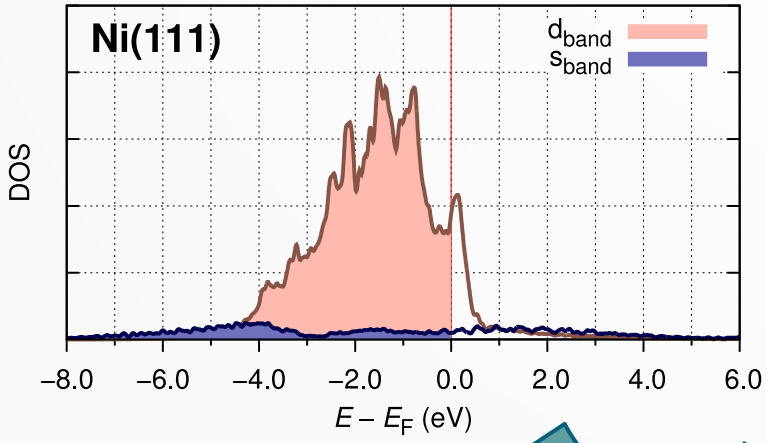
Transition metals (TMs):

- s-band is half filled for all TMs
  (similar bonding for all TMs)
- variation in bonding comes from d-bands

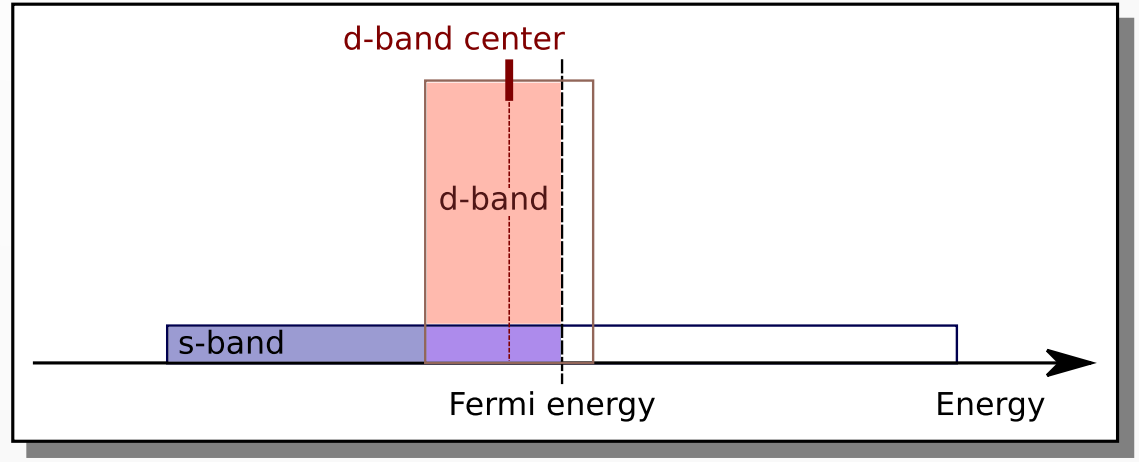


Electronic structure of TMs

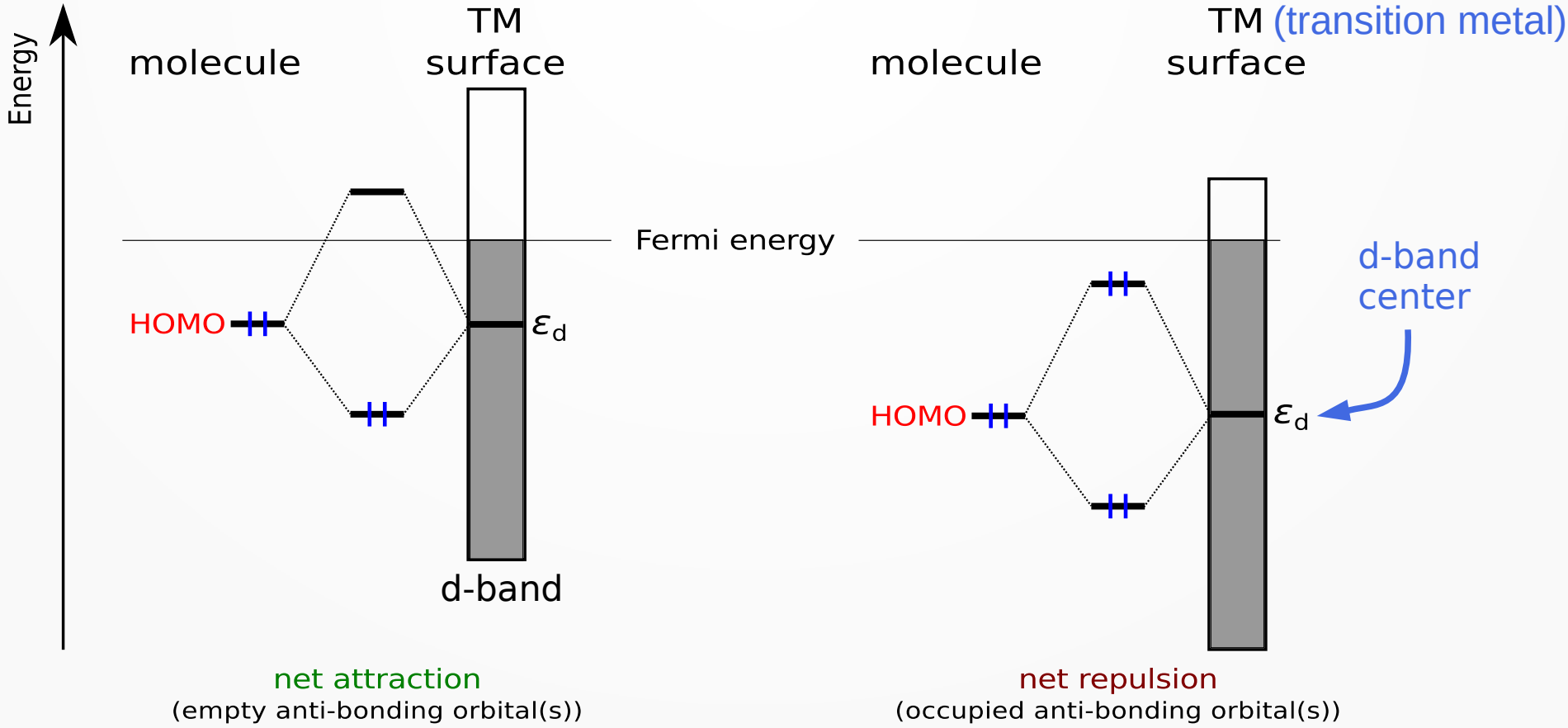
Hammer-Nørskov chemisorption model: d-band center (ε_d)



$$\varepsilon_{\mathrm{d}} = \frac{\int_{-\infty}^{+\infty} \varepsilon \, \mathrm{DOS}_{\mathrm{d}}(\varepsilon)\mathrm{d}\varepsilon}{\int_{-\infty}^{+\infty} \mathrm{DOS}_{\mathrm{d}}(\varepsilon)\mathrm{d}\varepsilon}$$

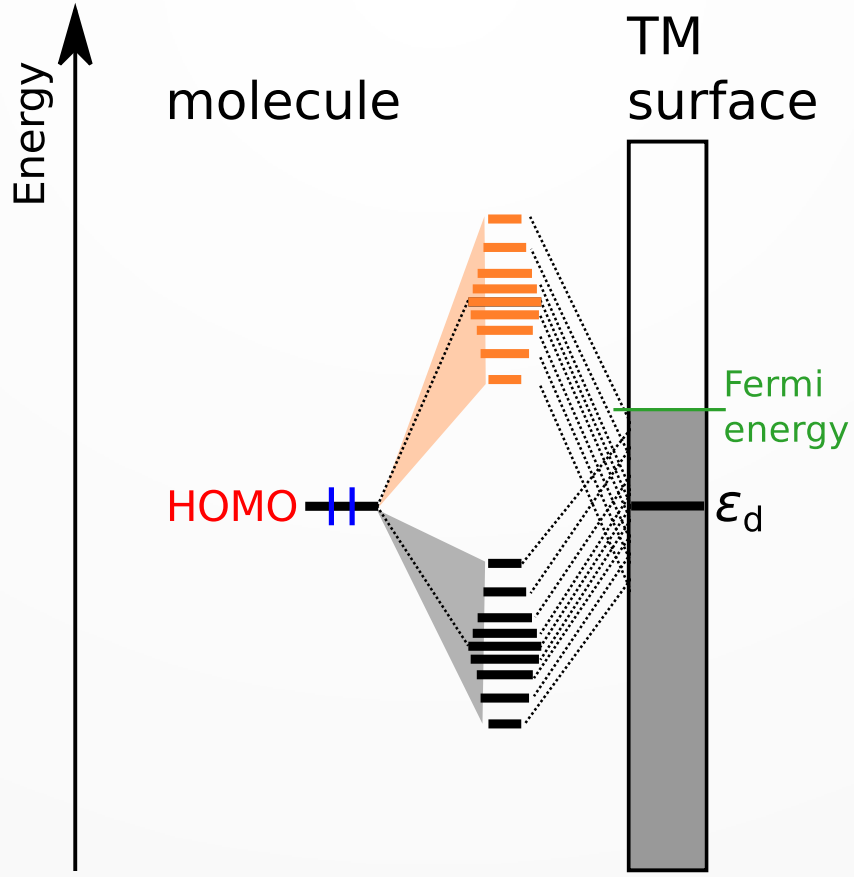


Molecule–TM-surface bonding



Molecule–TM-surface bonding

TM ≡ transition metal



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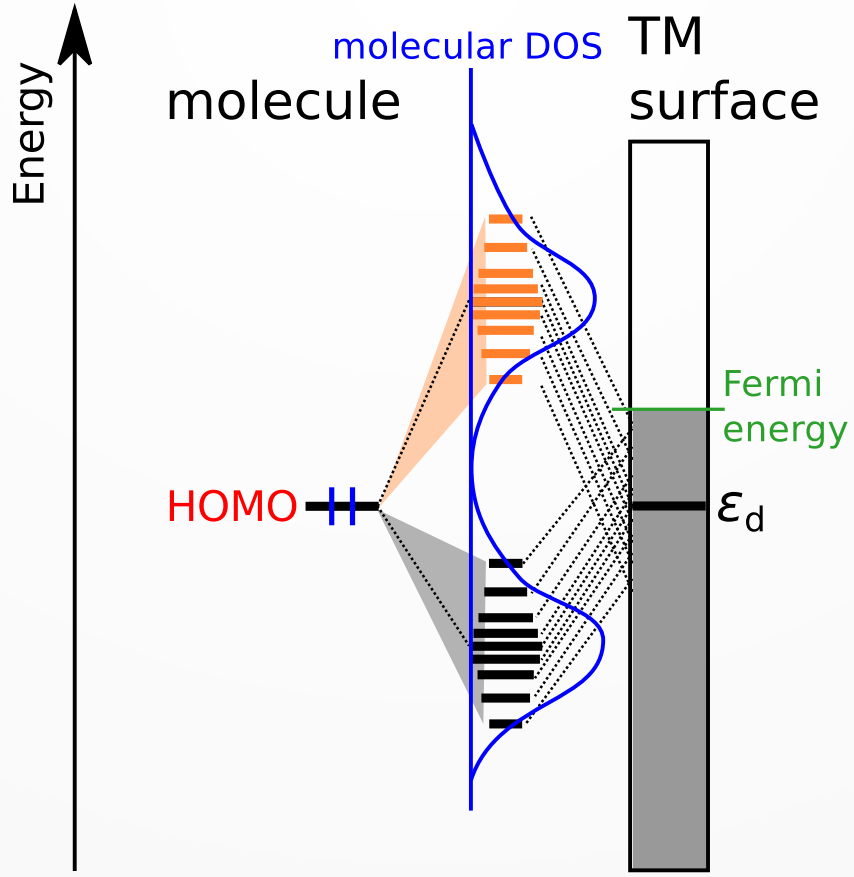
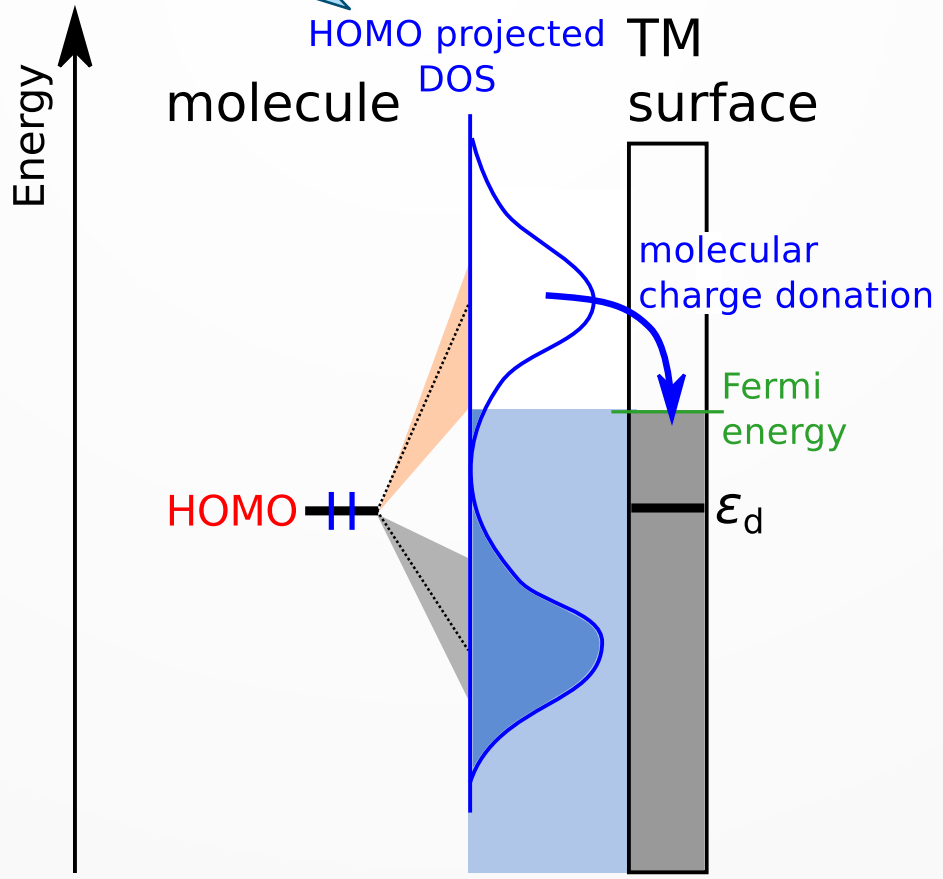


Molecul surface bonding

integrates to two electrons



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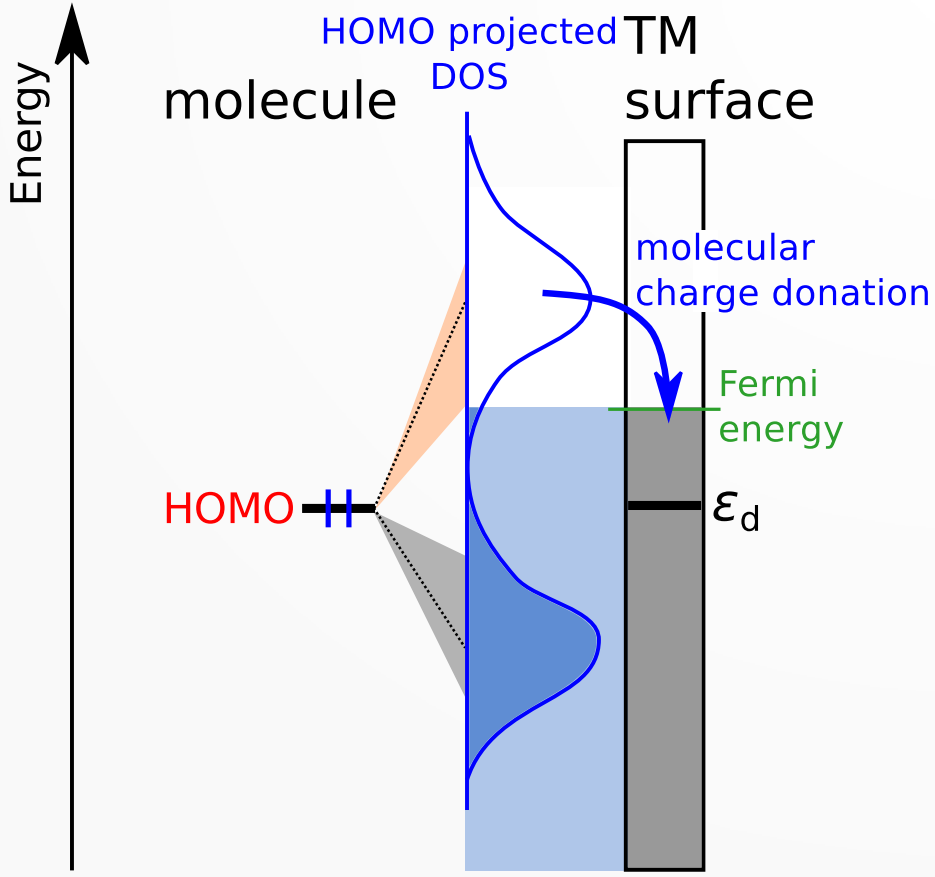
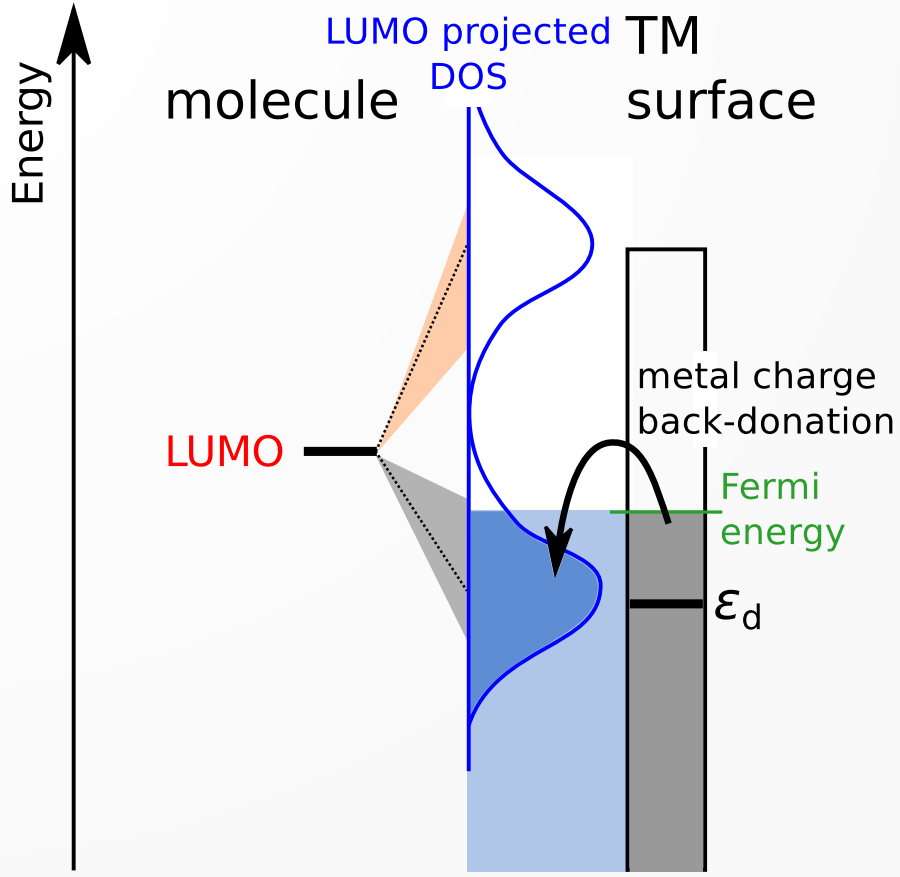
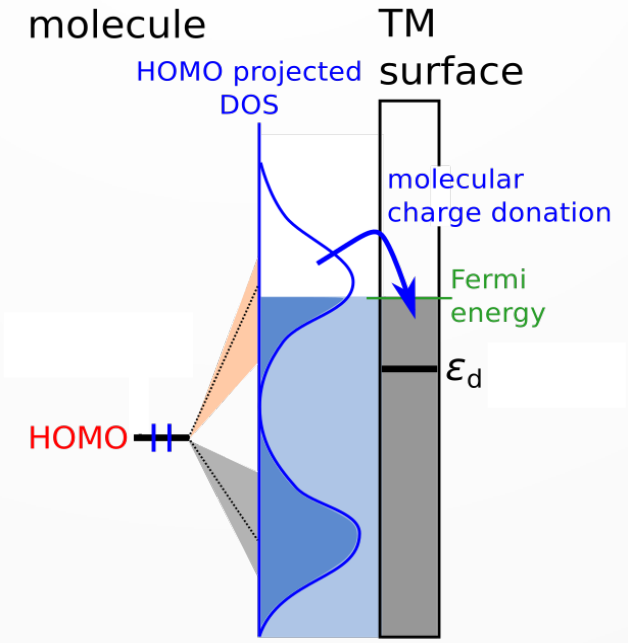




Tuning molecule–surface bonding

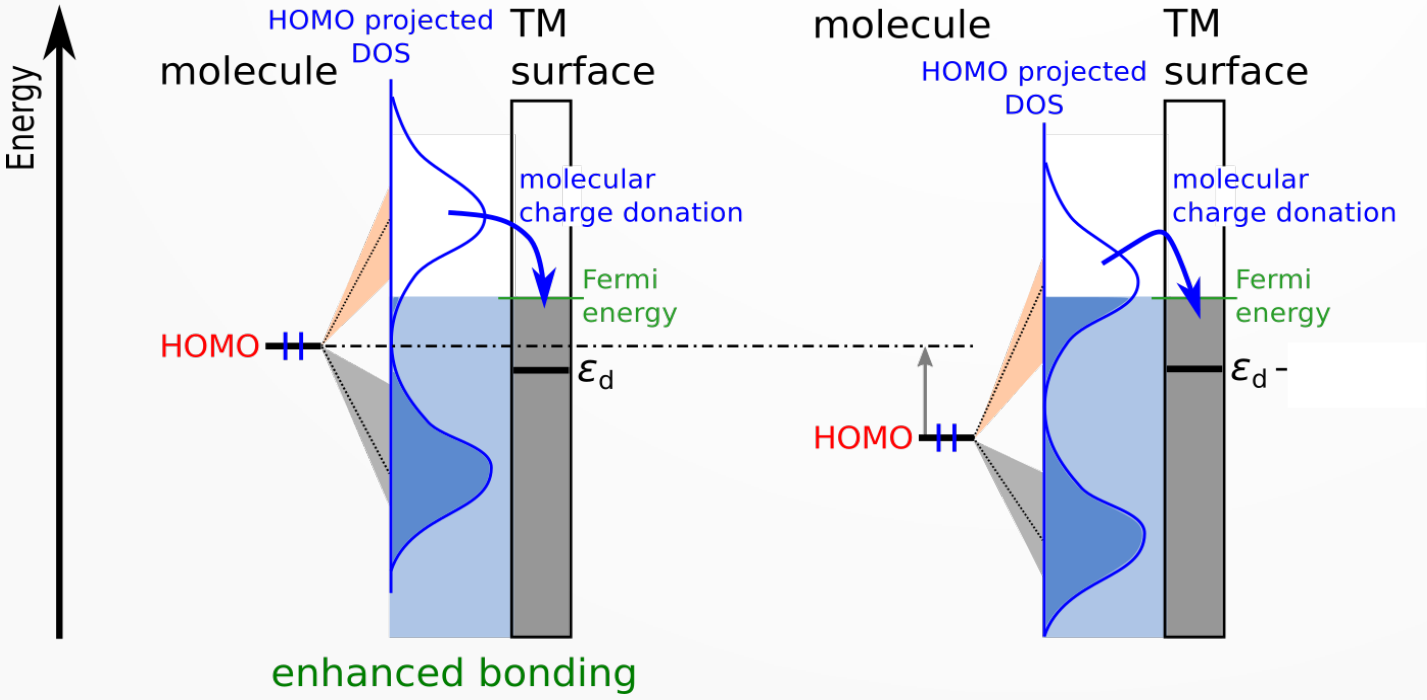
TM ≡ transition metal



Tuning molecule–surface bonding

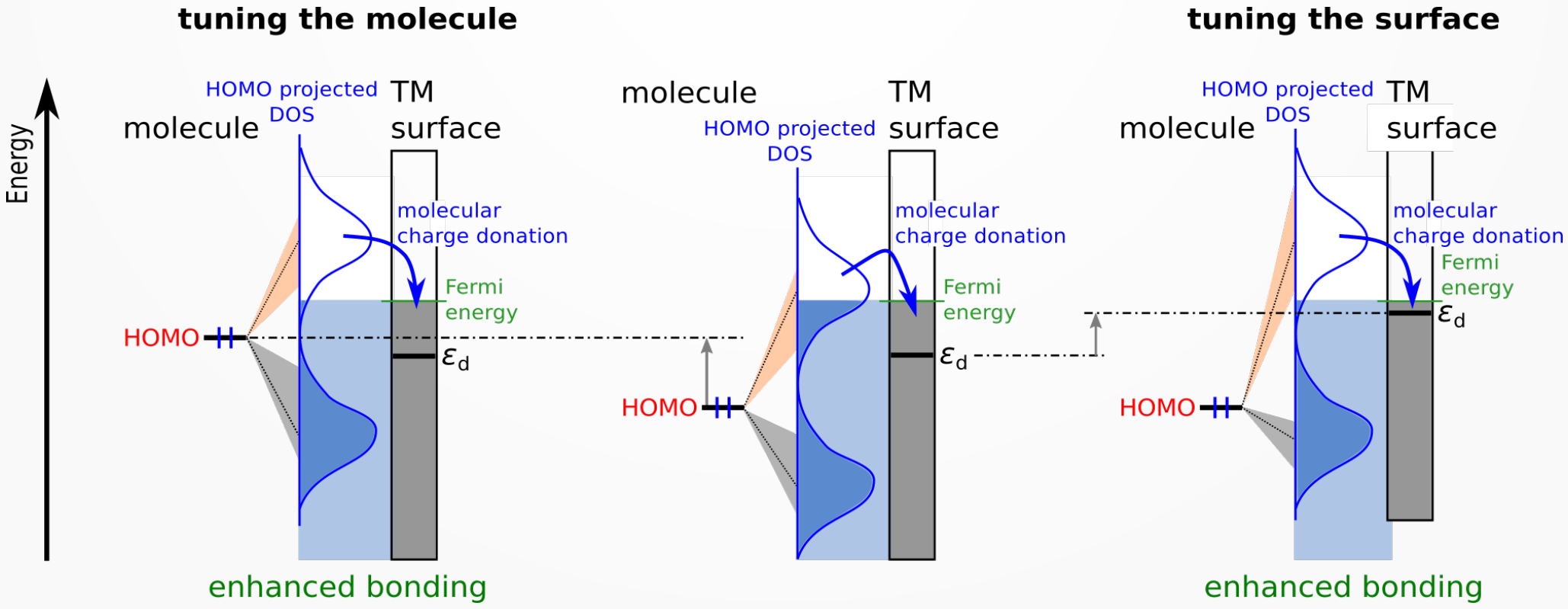
TM ≡ transition metal

tuning the molecule

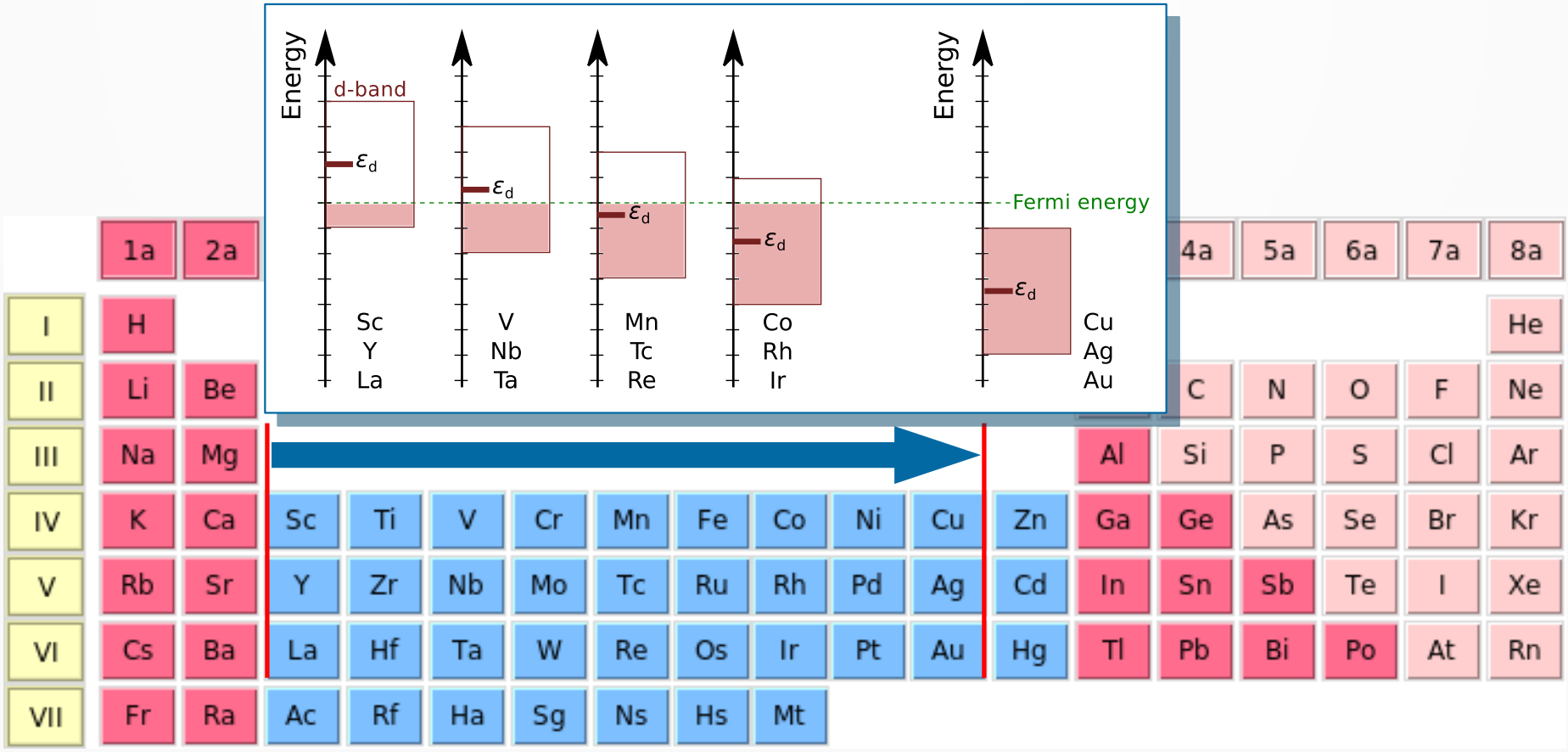


Tuning molecule–surface bonding

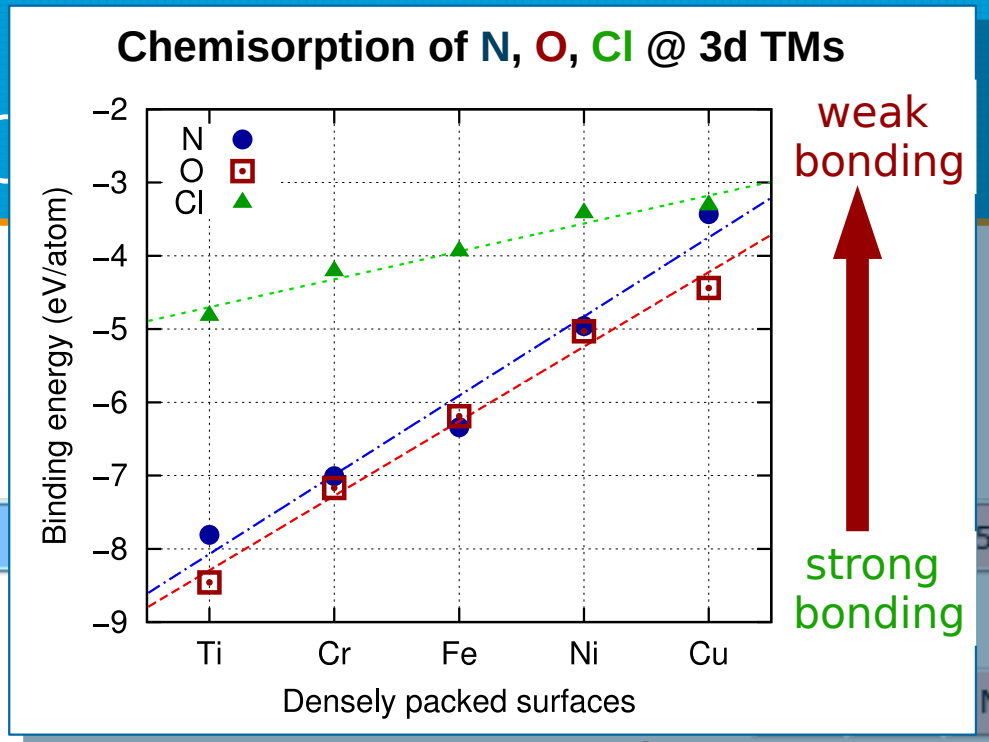
TM ≡ transition metal



Position of the d-band



Position c



	1a	2a	3b	4b													5a	6a	7a	8a
I	H																			He
II	Li	Be															N	O	F	Ne
III	Na	Mg													Al	Si	P	S	Cl	Ar
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
VI	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
VII	Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt											

Kokalj, Chem. Phys. **393** (2012) 1–12

The HOMO–LUMO premise

Molecular perspective: strong molecule–surface interaction implies:

- high eigenvalue of HOMO (ε_{HOMO})
- low eigenvalue of LUMO (ε_{LUMO})

$\varepsilon_{LUMO} > \varepsilon_{HOMO}$

- small HOMO–LUMO gap ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$)

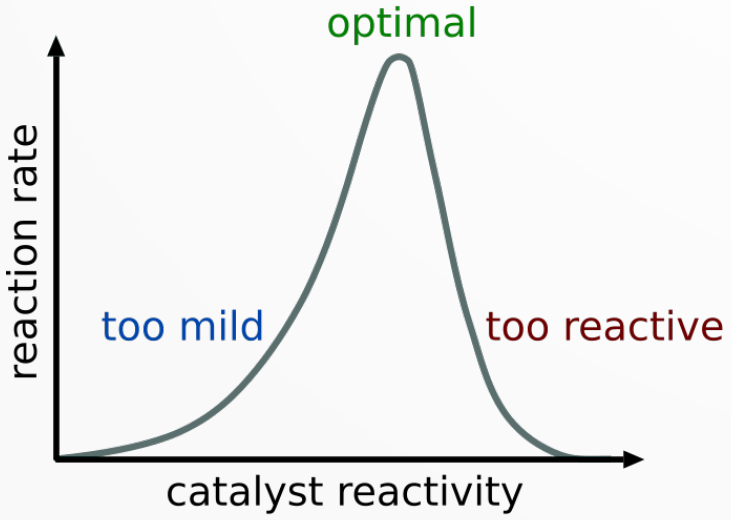
… for the argument to work, everything else should be kept compatible (similar, homologous cases)

But:
does a stronger inhibitor–surface interaction entails a better inhibitor?

The stronger, the better?

A possible objection to “the stronger, the better” premise

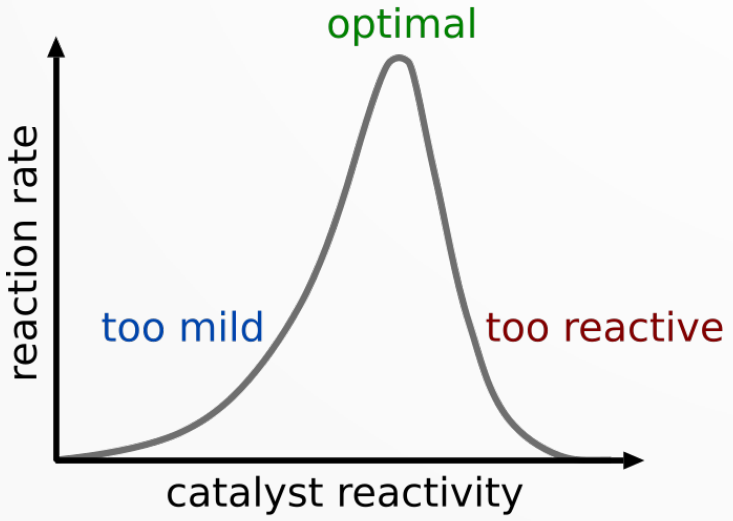
Sabatier principle in heterogeneous catalysis



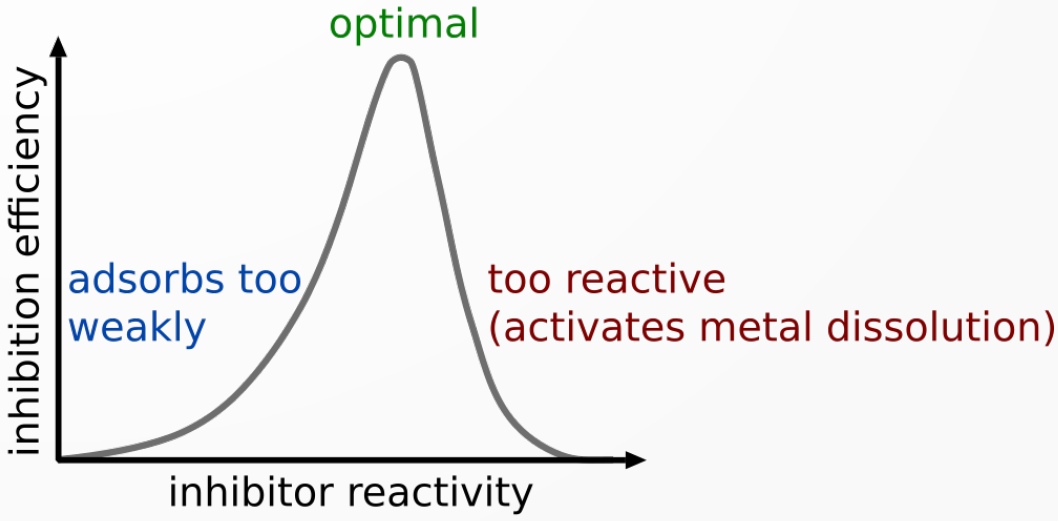
The stronger, the better?

A possible objection to “the stronger, the better” premise

Sabatier principle in heterogeneous catalysis

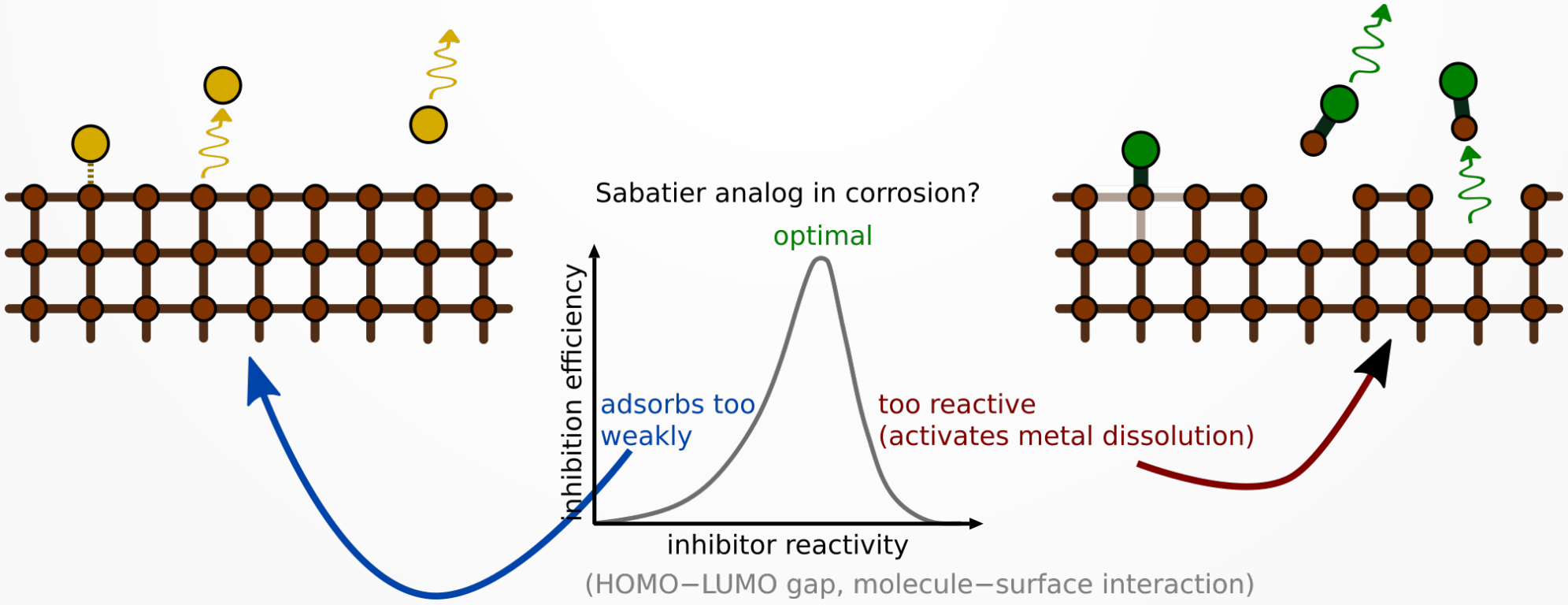


Sabatier analog in corrosion?

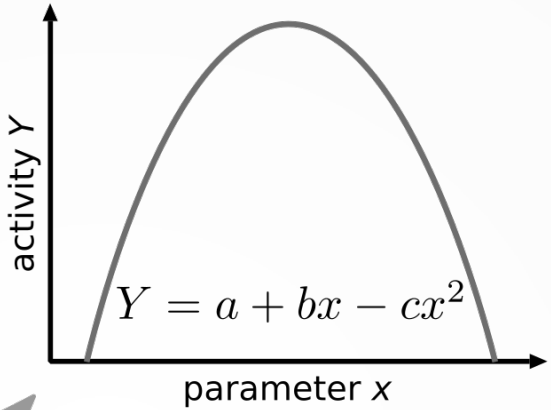


(HOMO−LUMO gap, molecule−surface interaction)

“Sabatier principle” in corrosion?

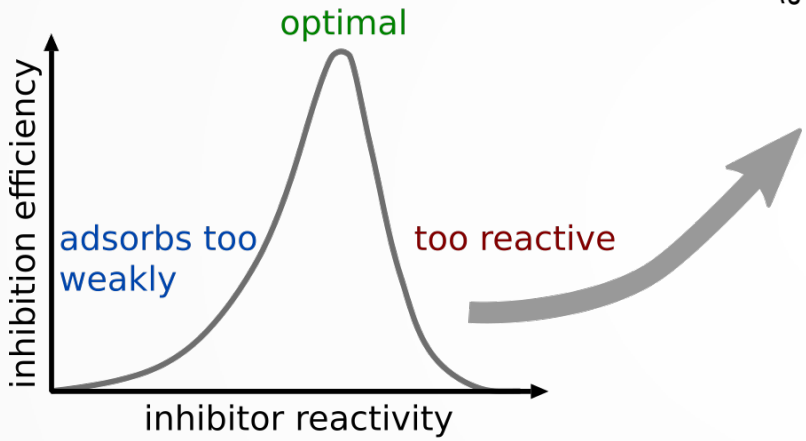


QSAR: Hancsh correlation



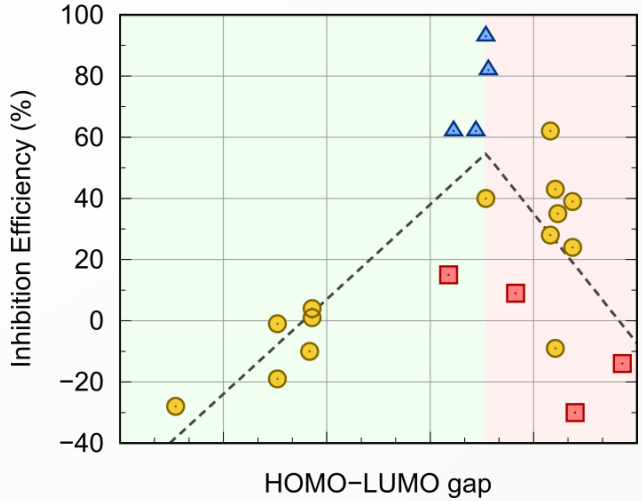
QSAR = quantitative structure activity relationship

Sabatier analog in corrosion?



(HOMO−LUMO gap, molecule−surface interaction)

Lukovits et al., Corrosion **57** (2001) 3–8



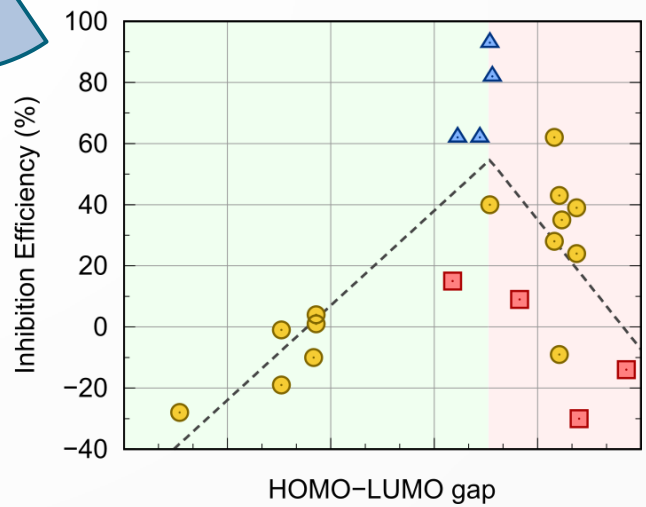
- wrong reading of the paper resulted in "ΔN < 3.6 rule":

  "if ΔN < 3.6, the inhibition efficiency increases with increasing ΔN"

- ΔN < 3.6 rule is useless;
  this condition is always fulfilled

  Kokalj, Corros. Sci. **180** (2021) 109016

Lukovits et al., Corrosion **57** (2001) 3–8



The stronger, the better

Let's test the MEPTIC approach ...
(i.e., the HOMO–LUMO "business")

Experimental characterization of 24 heterocyclic organic compounds (mainly azoles)

System: copper in 3 wt.% NaCl aqueous solution

COIN DESC

M-era.Net

Daniel Crespo

UNIVERSITAT POLITÈCNICA DE CATALUNYA BARCELONATECH

Frank Renner

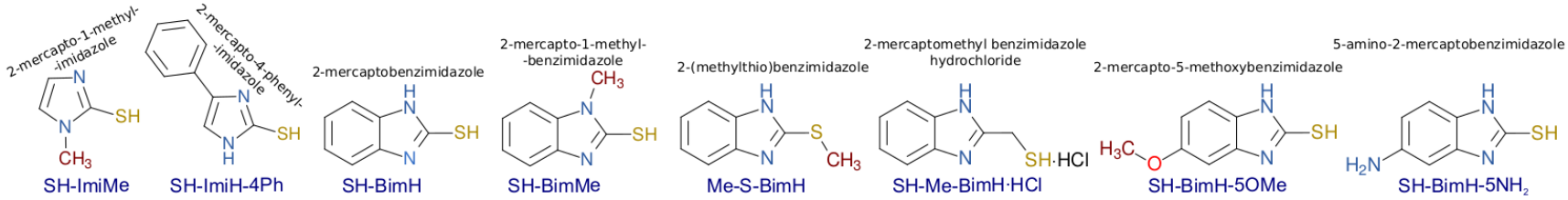
universiteit hasselt

KNOWLEDGE IN ACTION

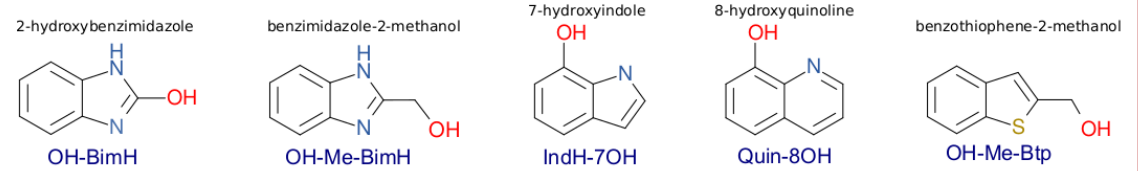
Arjan Mol

TU Delft Delft University of Technology

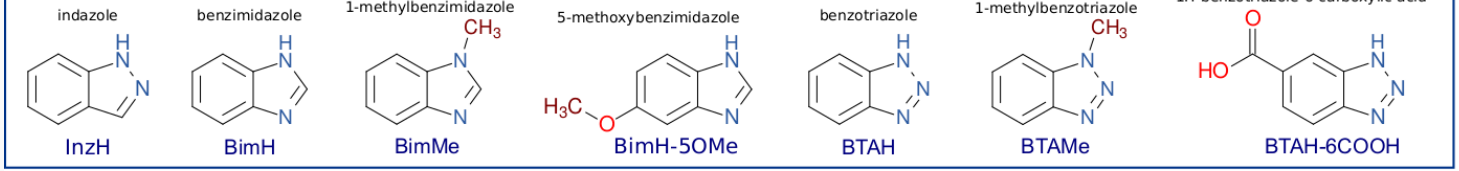
group-1: mercapto-azoles



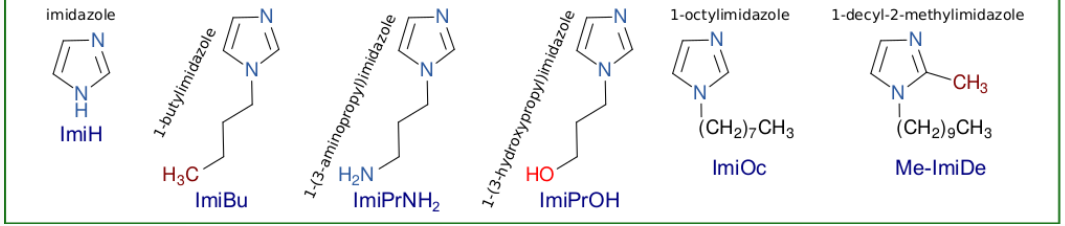
group-2: hydroxy-heterocycles



group-3: benzazoles

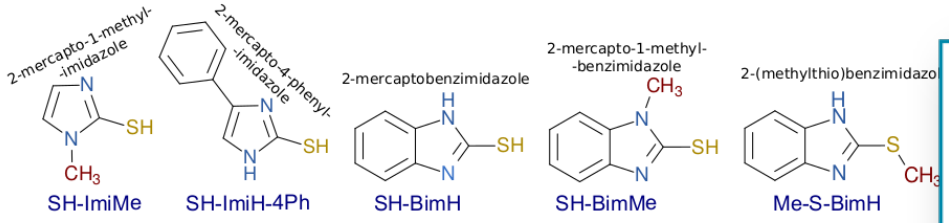


group-4: imidazoles

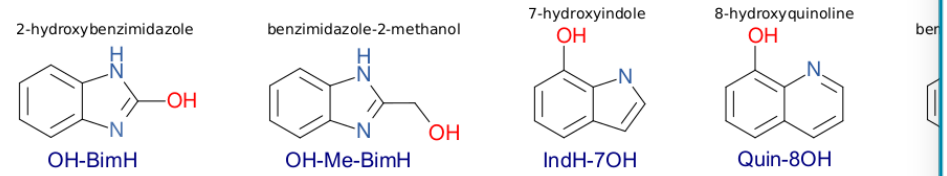


Kokalj et al. Corros. Sci. **179** (2021) 108856

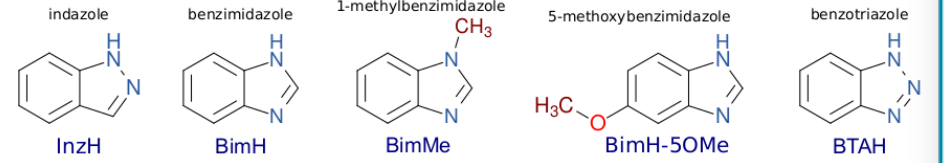
group-1: mercapto-azoles



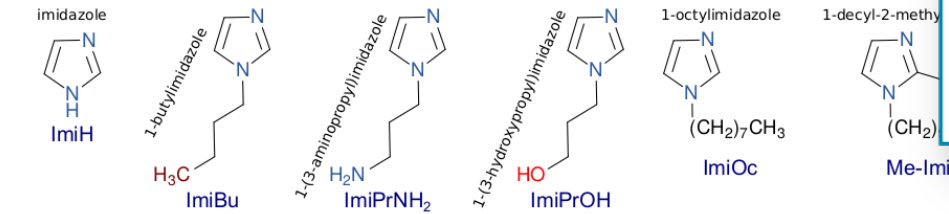
group-2: hydroxy-heterocycles

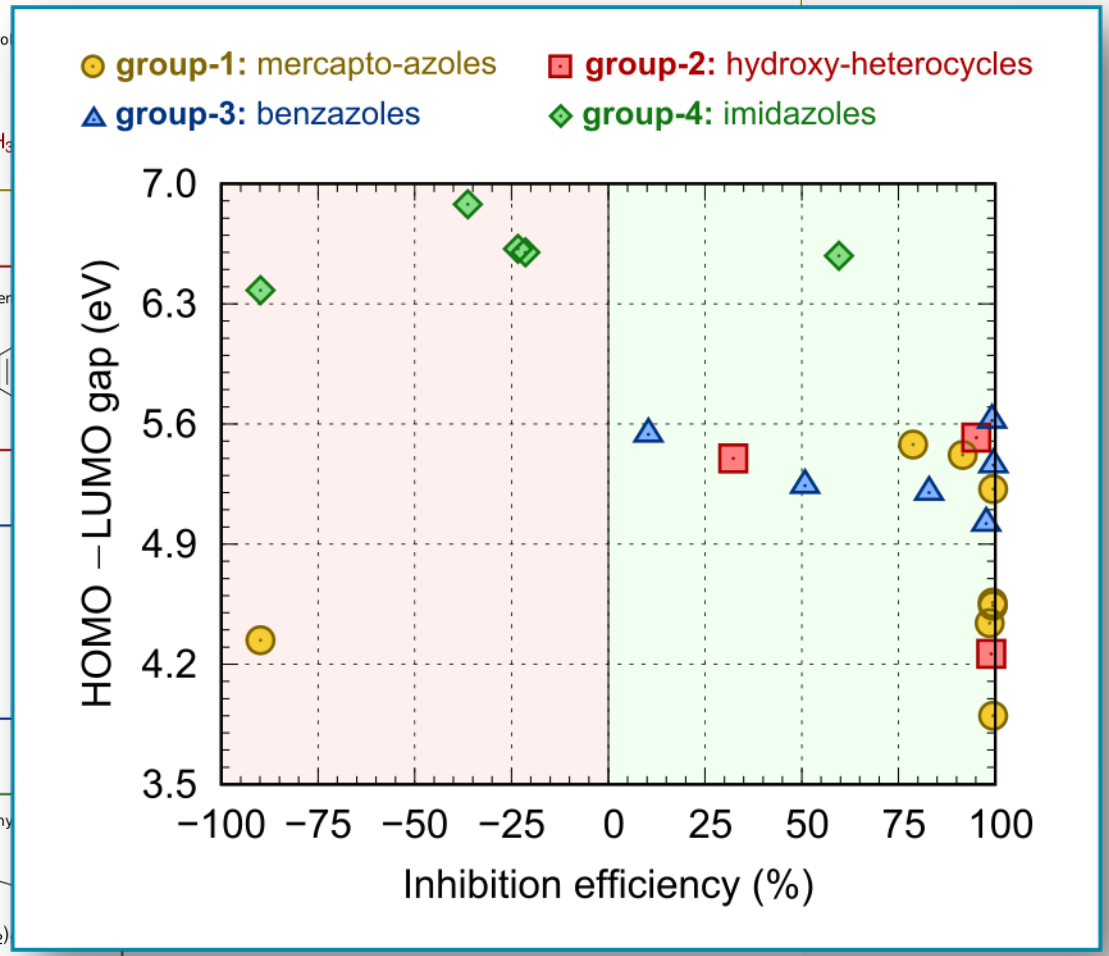


group-3: benzazoles

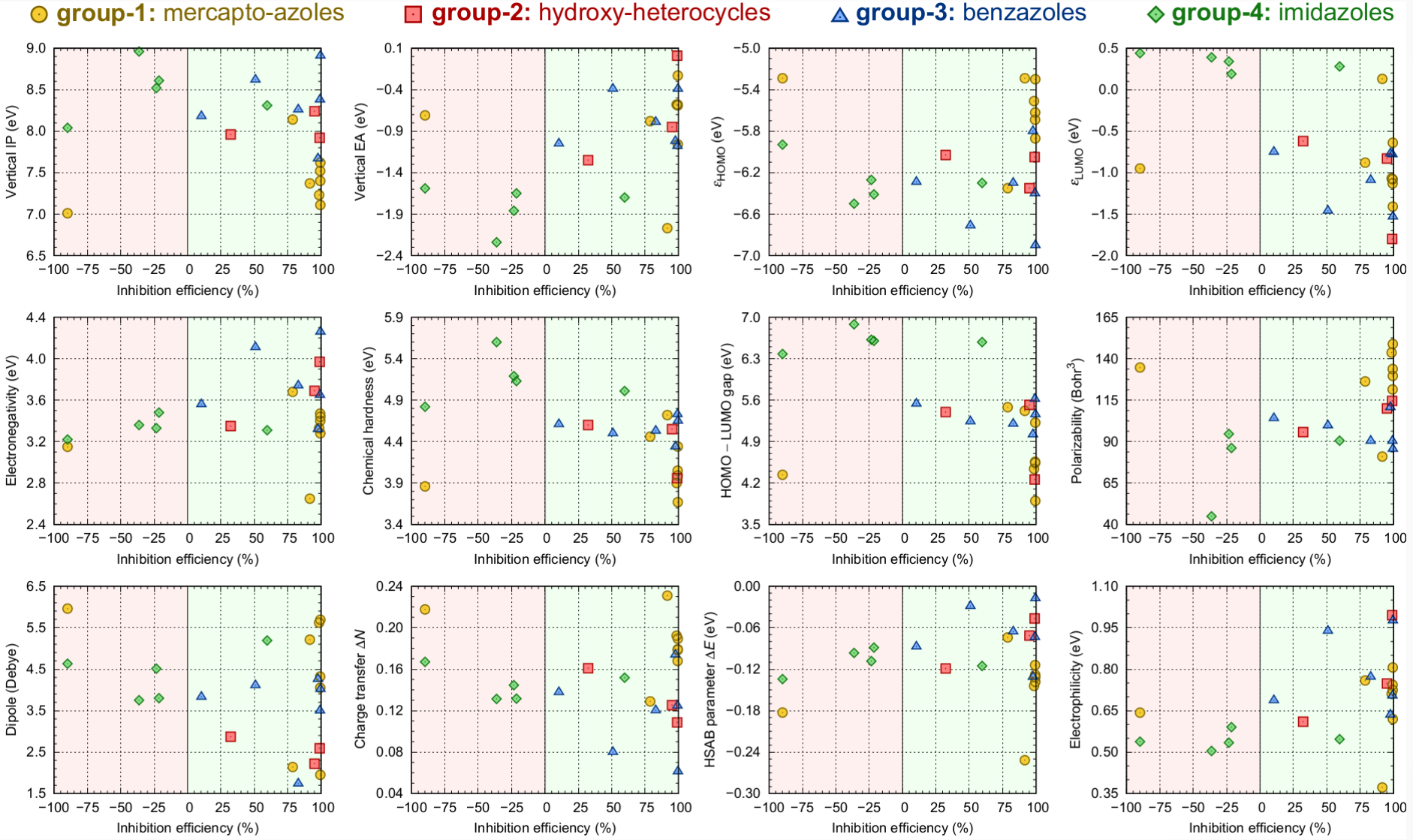


group-4: imidazoles





Kokalj et al. Corros. Sci. **179** (2021) 108856



A. Kokalj et al. Corros. Sci. **179** (2021) 108856

Take home message

- A single molecular electronic parameter is (almost) useless to predict corrosion inhibition efficiency
  (e.g., a smaller HOMO–LUMO gap does not imply a better inhibitor)

- A model is needed:
  - data driven models: machine learning methods
  - physics based models

Toward data-driven model ...

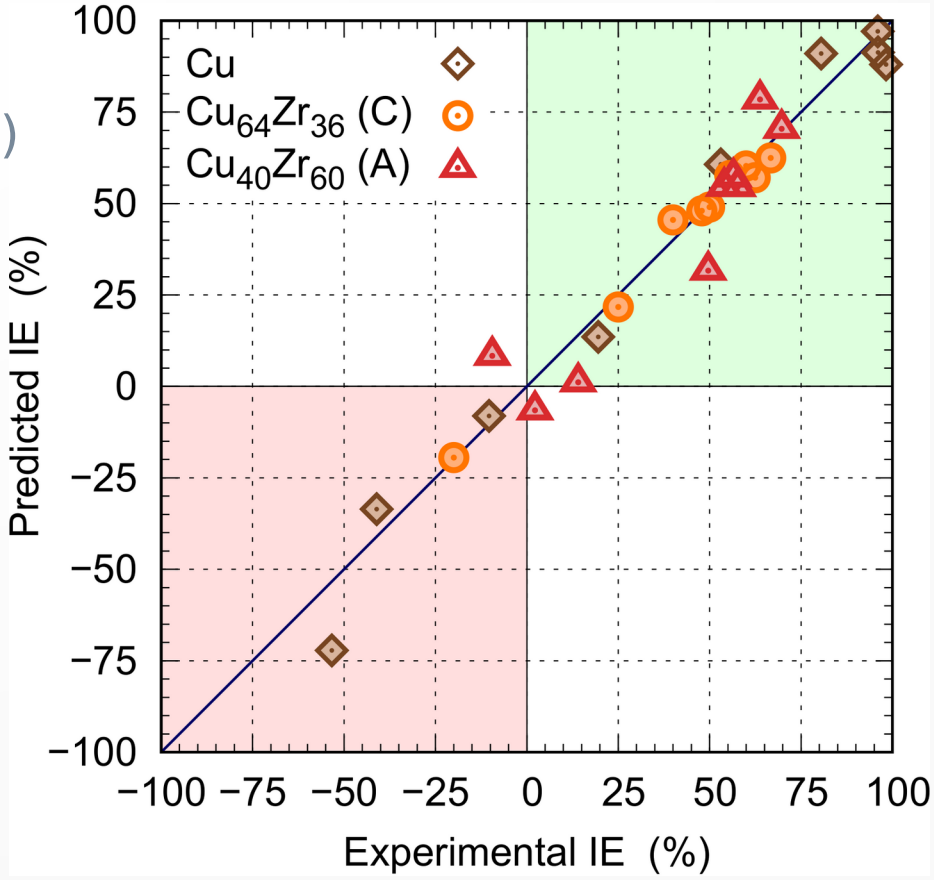
4-parameter regression models
(imidazole compounds on Cu/Zr materials)

PROS:

- *in silico* screening of similar inhibitors

CONS:

- lack of physical insight



Kokalj et al. Corros. Sci. (2021) under submission
Xie et al. J. Alloy Compd. **879** (2021) 160464

Physics based models

Explicit atomistic modeling of interactions between components of corrosion system

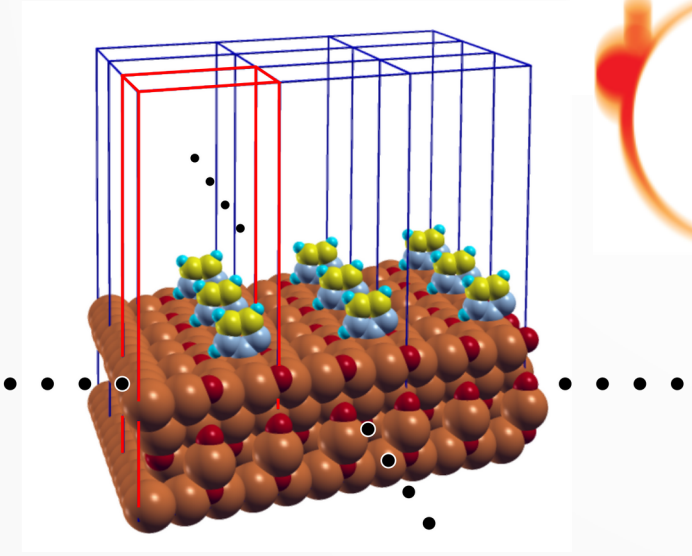
provides a physical insight, but is technically more complicated & computationally much heavier

quantum-mechanical (unbiased) vs. empirical force-field methods (reliable only for “parameterized” systems)

Multi-scale modeling using ICME paradigm

emerging approach, currently at the level of implementations in corrosion inhibition research

Computational method



slab model of a surface
(periodic boundary conditions)

QUANTUMESPRESSO

PWTK

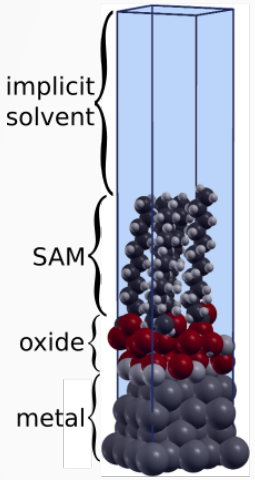
XCrySDen ...

DFT = density functional theory
(computationally affordable
first-principle quantum-mechanical method)

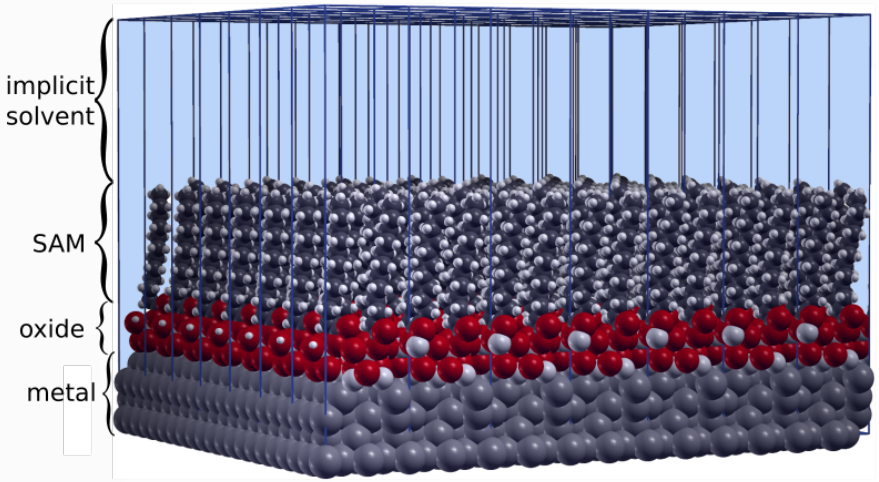
Method: DFT (GGA-PBE functional)
+ semi-empirical dispersion correction (Grimme DFT-D)
+ Hubbard U correction (aka GGA+U) for TM oxides

Basis Set: plane-waves (+ pseudopotentials)

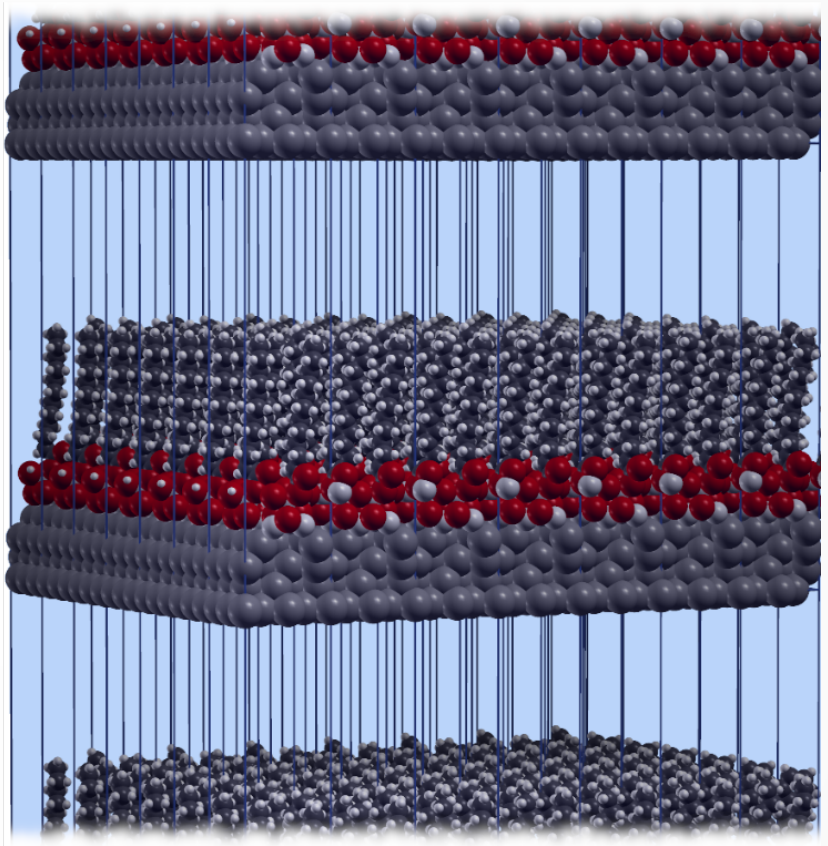
one supercell



many supercells (PBC applied laterally)

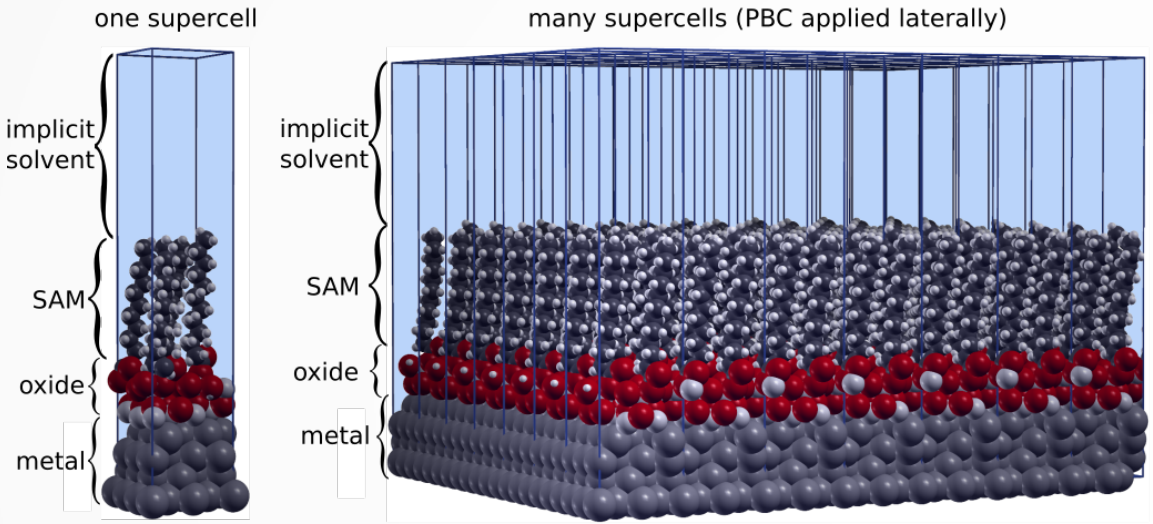


multi-slab model
(PBC applied also along the surface normal direction)

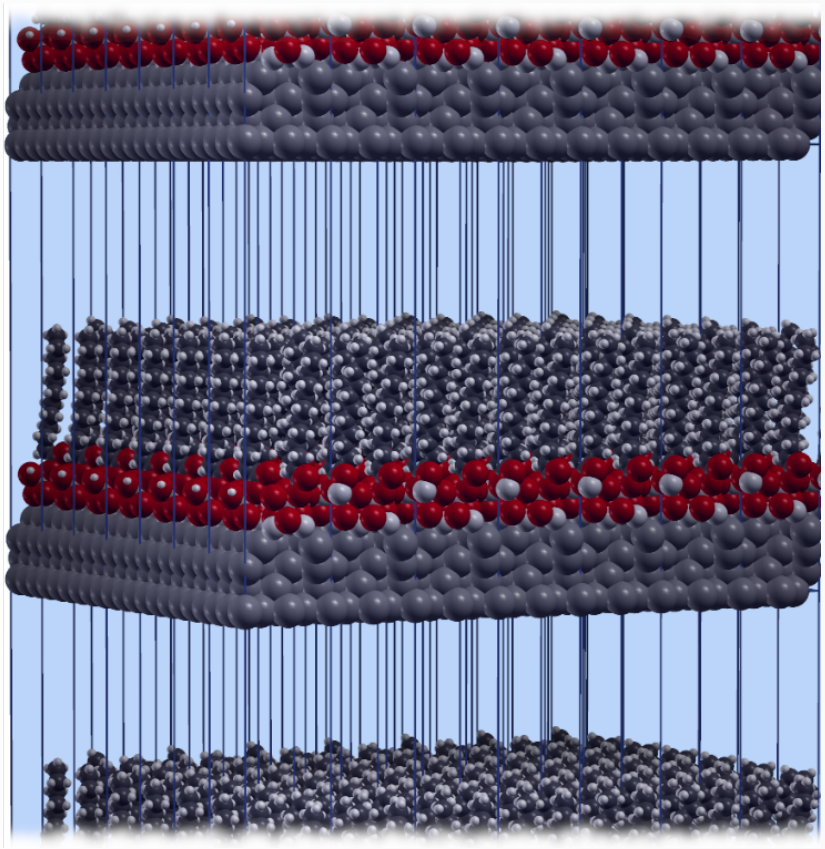


used by plane-wave DFT codes

Atomistic modeling ...



multi-slab model
(PBC applied also along the surface normal direction)



used by plane-wave DFT codes

PROS:

- model is assembled atom by atom
- allows to study hypothetical scenarios

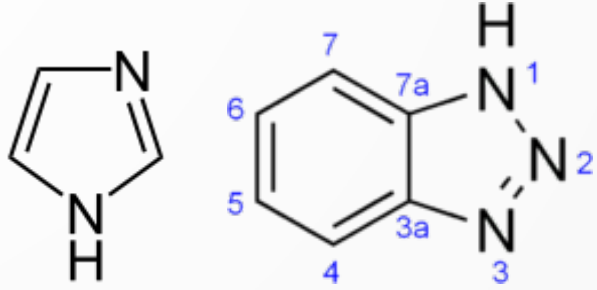
CONS:

- models can be too simple or even irrelevant for real cases

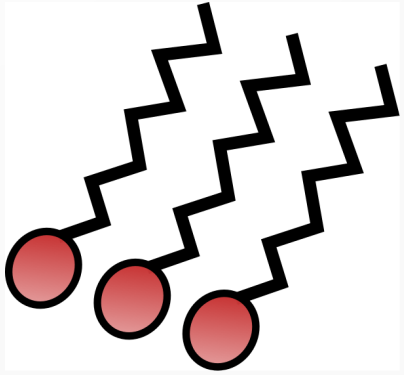
Reductionistic approach

Start simple and elaborate incrementally ...

- azole molecules @ Cu surfaces



- surfactant inhibitors @ Al surfaces



Inhibitor–surface bonding

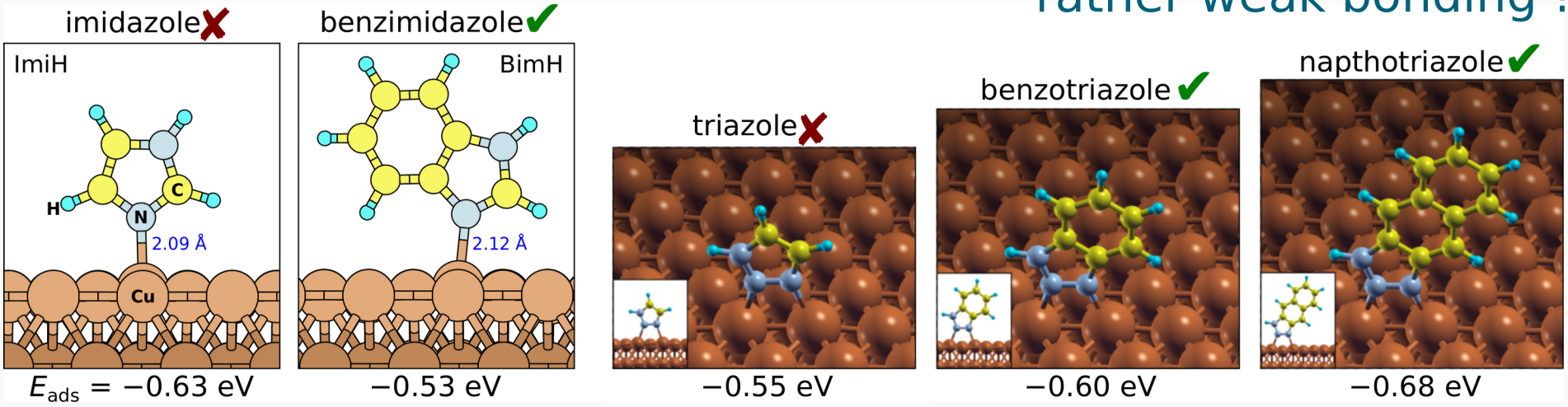
plain molecular adsorption @ Cu(111)

MolH + * → MolH*

(* = adsorption site,
MolH* = adsorbed molecule)

✘ = bad inhibitor ✔ = good inhibitor

rather weak bonding !



Corros. Sci. **98**, 457

ChemPhysChem **12**, 3547

Inhibitor–surface bonding

weak bonding of intact azoles to copper surfaces
(below about 1 eV)

Cl–Cu(111) bond strength > 3 eV

Arrhenius equation for rate constant:

activation energy

$$k = \nu \exp\left(-\frac{E^*}{k_\mathrm{B}T}\right)$$

frequency prefactor

Boltzmann constant

Inhibitor–surface bonding

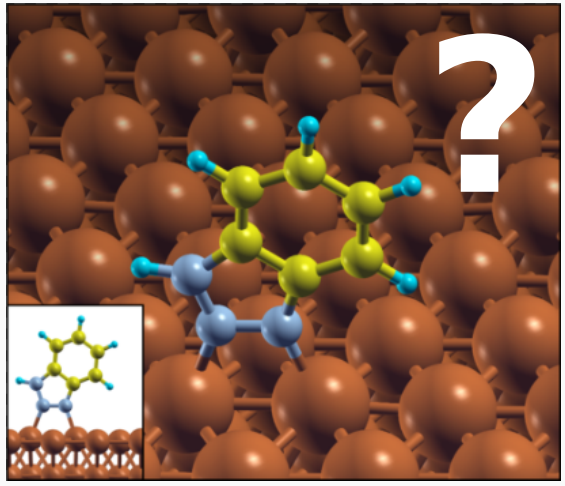
weak bonding of intact azoles to copper surfaces
(below about 1 eV)

typical residence time of a molecule on the surface at $T = 300$ K

$$\tau = \nu^{-1} \exp\left(\frac{E_{\mathrm{des}}}{k_{\mathrm{B}} T}\right) \approx 10^{-6}\ \mathrm{s}$$

for $E_{\mathrm{des}} = 1$ eV (at $T = 300$ K): $\tau = 10\ \mathrm{s}$

molecule must adsorb stronger than 1 eV
to persist on the surface at room T !



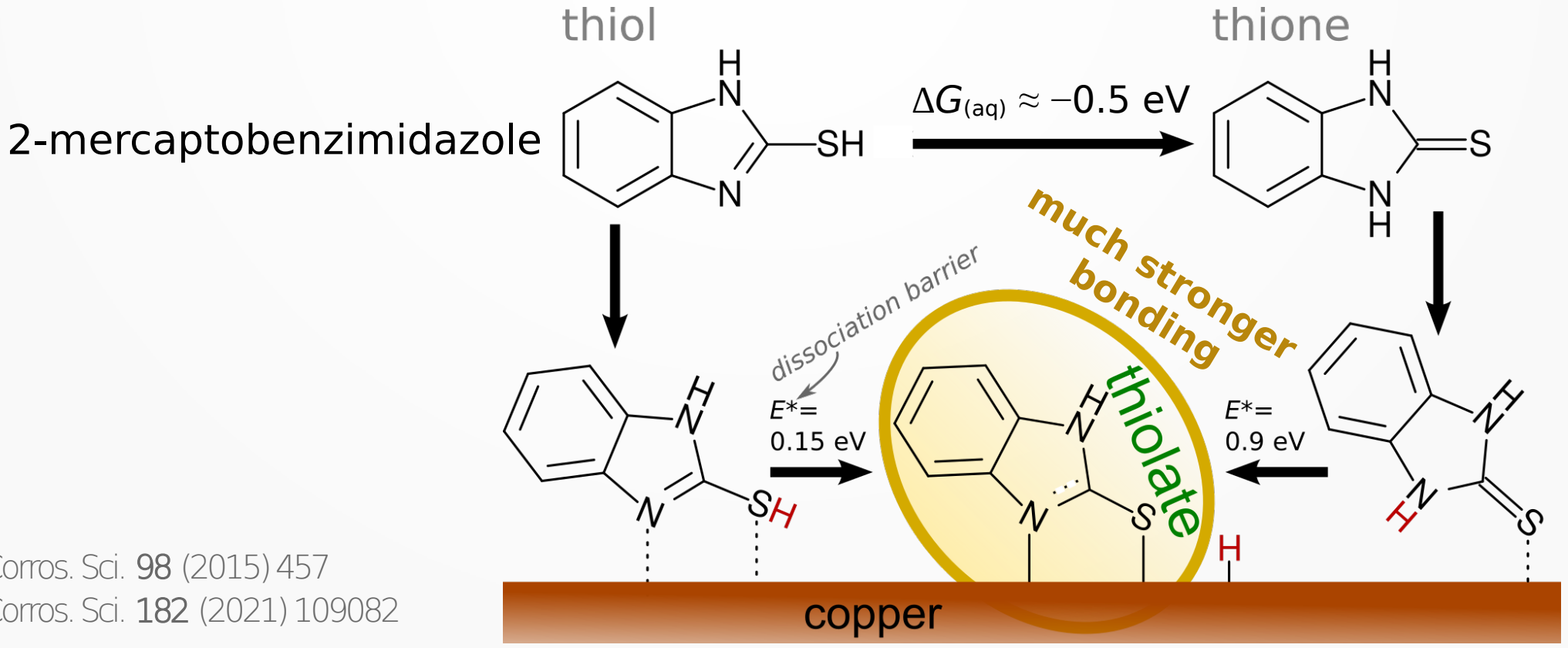
$E_{\mathrm{desorption}} = 0.60$ eV

Heterogeneous catalysis …

Transition–metal surfaces are good bond cleavers

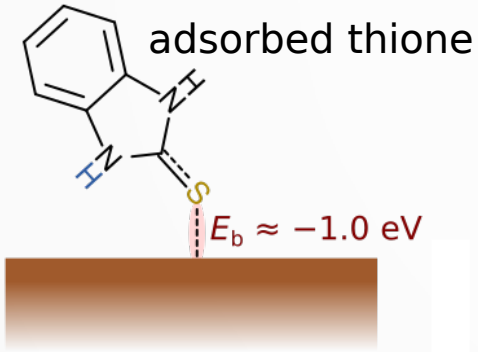
S–H, O–H, N–H, C–H intramolecular bonds
cleave particularly easily @ transition-metal surfaces

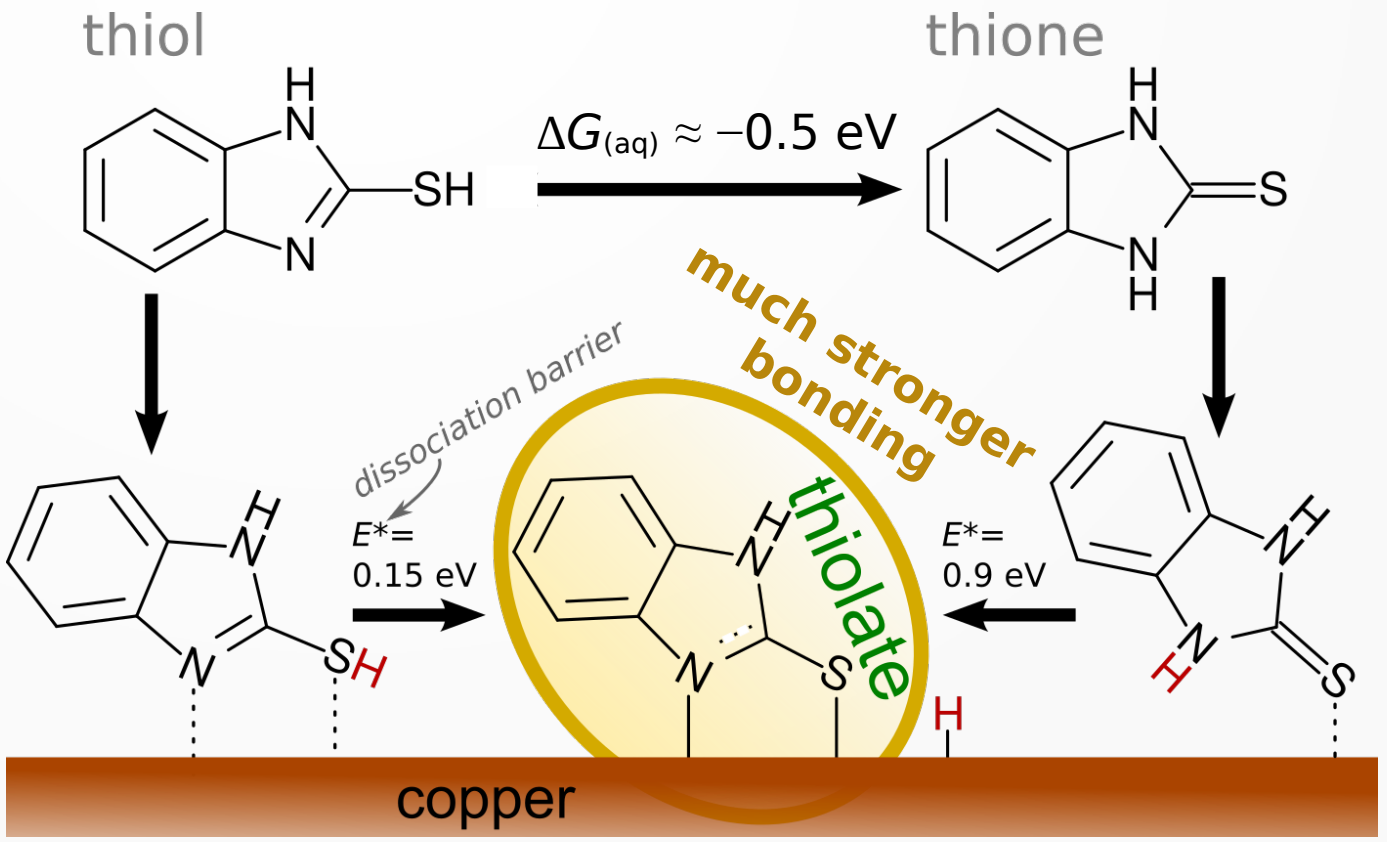
Dissociative adsorption



Corros. Sci. **98** (2015) 457
Corros. Sci. **182** (2021) 109082

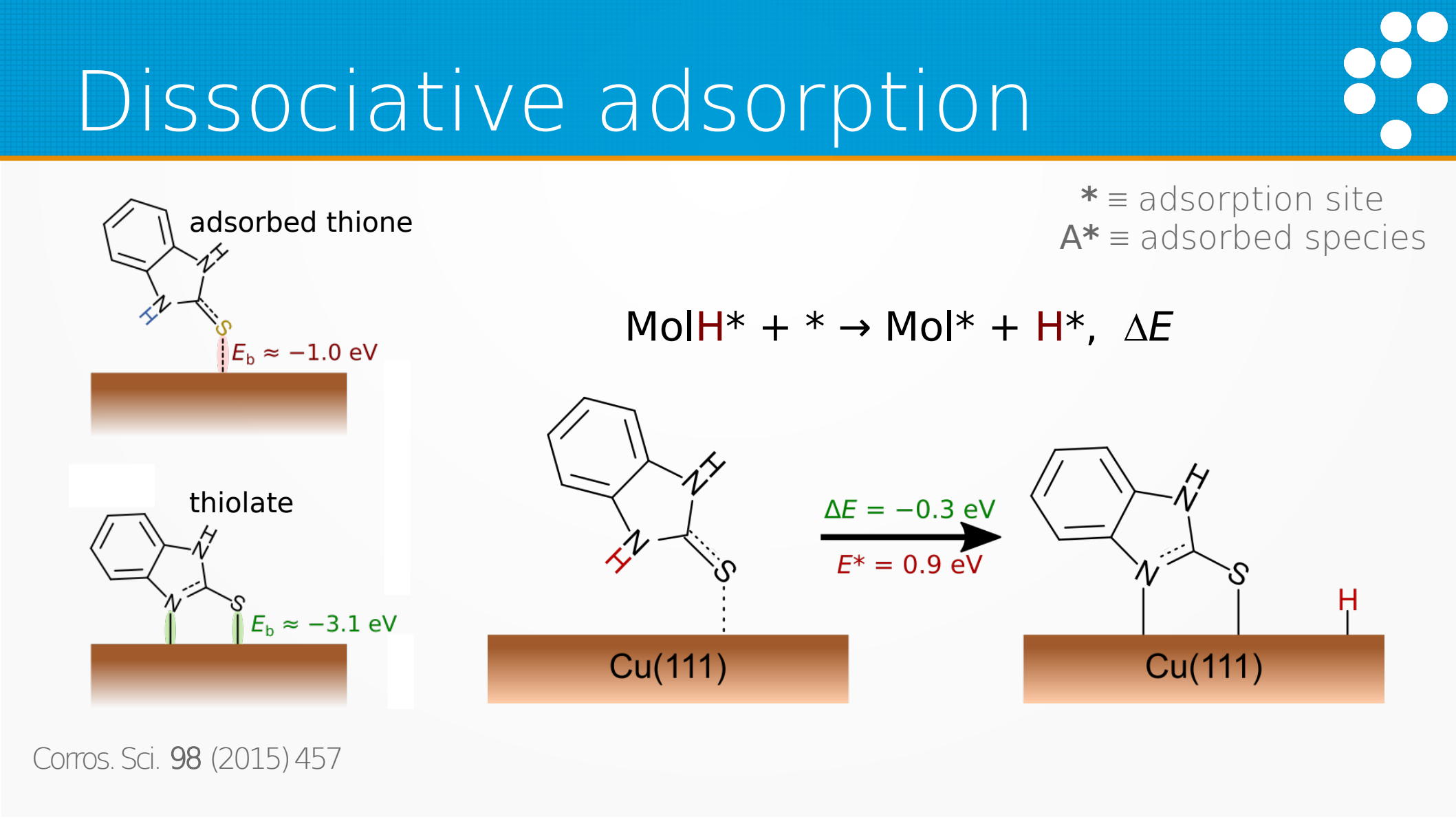
Dissociative adsorption





Corros. Sci. 98 (2015) 457

Dissociative adsorption



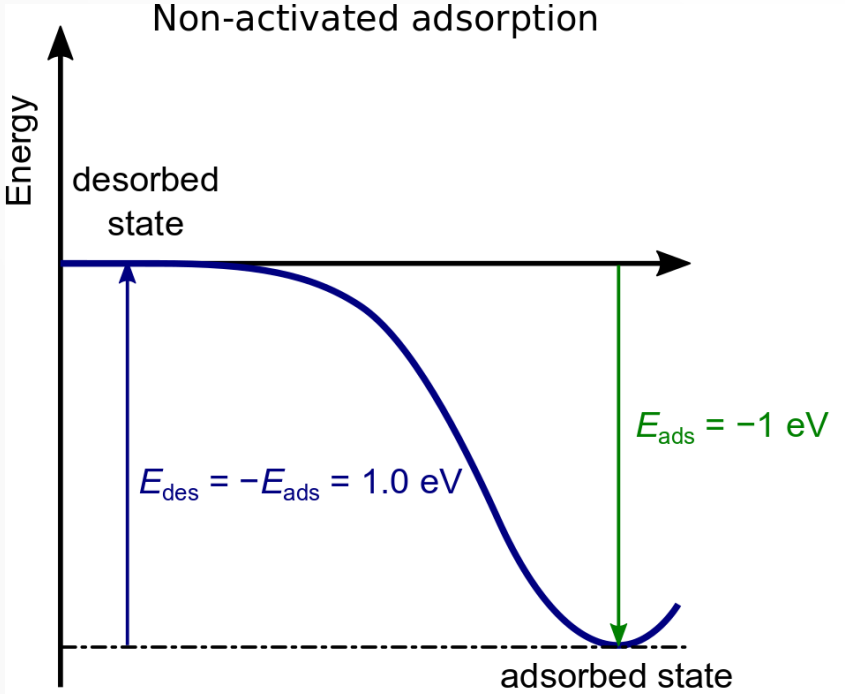
* ≡ adsorption site
A* ≡ adsorbed species

$$MolH^* + * \rightarrow Mol^* + H^*, \quad \Delta E$$

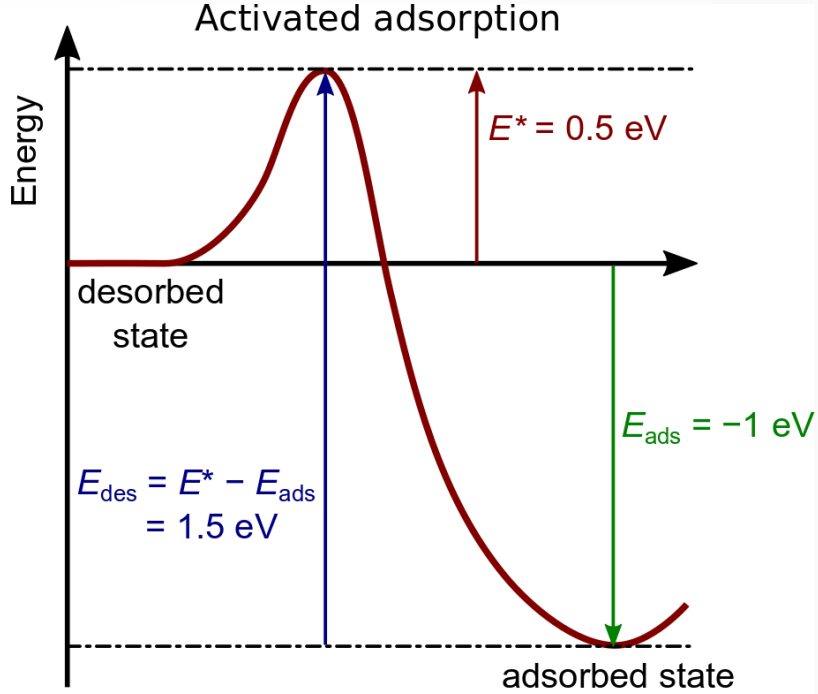
Corros. Sci. **98** (2015) 457

Non-activated vs. activated adsorption

typical residence time of a molecule on the surface at $T = 300$ K



$$\tau = \nu^{-1} \exp\left(\frac{E_{\mathrm{des}}}{k_{\mathrm{B}} T}\right) \approx 10 \text{ s}$$



$$\tau = \nu^{-1} \exp\left(\frac{E_{\mathrm{des}}}{k_{\mathrm{B}} T}\right) \approx 50 \text{ years}$$

Dissociative adsorption

- $MolH + 2* \rightarrow Mol* + H*$

  surface defects promote dissociation

  Kokalj et. al., J. Phys. Chem. C **118**, 944

$* \equiv$ adsorption site

$A* \equiv$ adsorbed species

- $MolH + O* + * \rightarrow Mol* + OH*$

  chemisorbed oxygen promotes dissociation

  Gustinčič & Kokalj, Metals **8**, 310

- $MolH + OH* \rightarrow Mol* + H_2O$

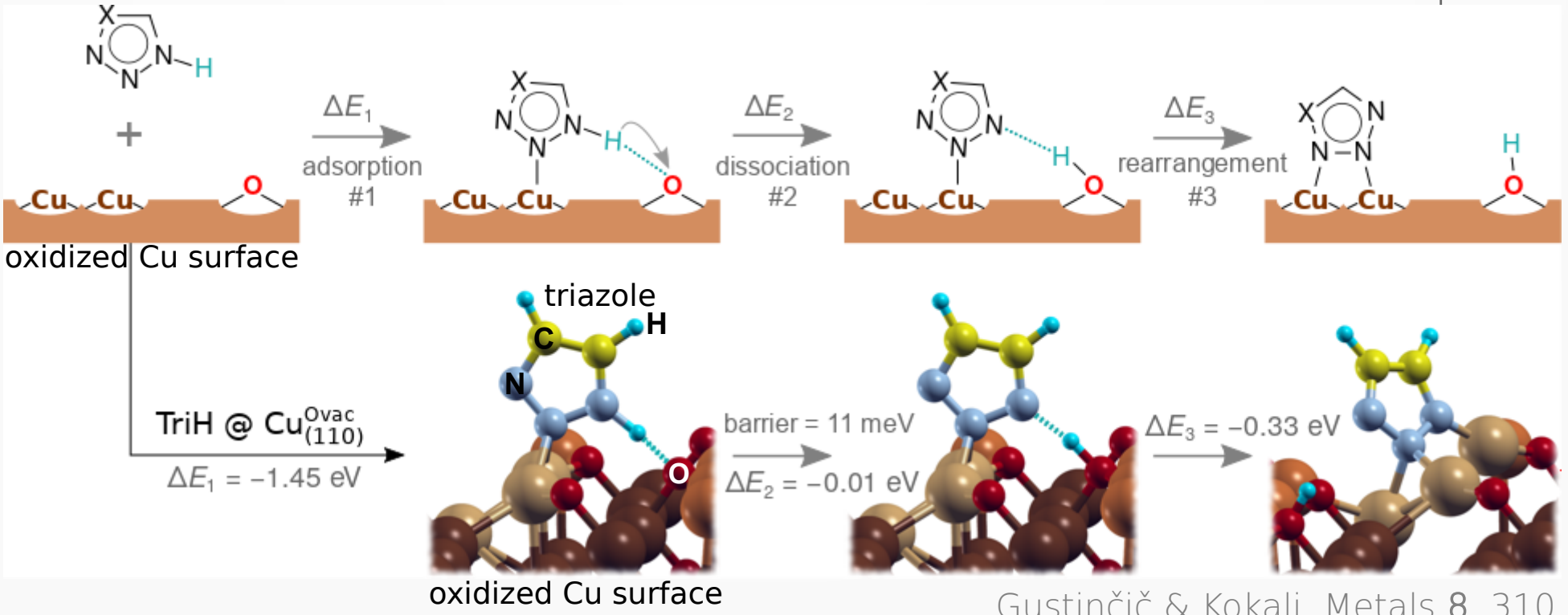
  chemisorbed hydroxyls promote dissociation

  Kokalj, Faraday Discuss. **180**, 415

Dissociative adsorption

$$\mathrm{MolH} + \mathrm{O}^* + * \rightarrow \mathrm{Mol}^* + \mathrm{OH}^*$$

* ≡ adsorption site
A* ≡ adsorbed species

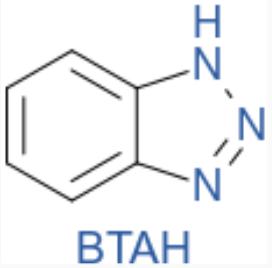


Gustinčič & Kokalj, Metals 8, 310

Dissociative adsorption

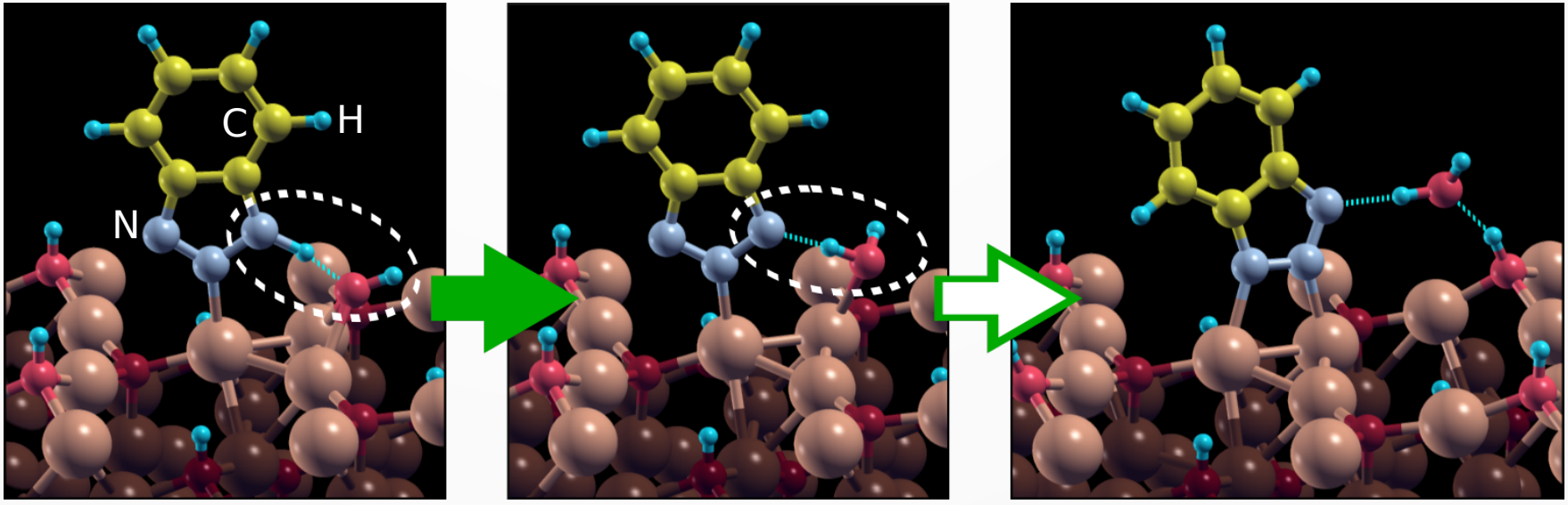
$MolH + OH^* \rightarrow Mol^* + H_2O$ (X* ≡ adsorbed species)

benzotriazole



BTAH

BTAH$_{(ads)}\cdots$OH **BTA**$_{(ads)}\cdots H_2O$



$\Delta E \approx -0.2$ eV $\Delta E \approx -0.3$ eV

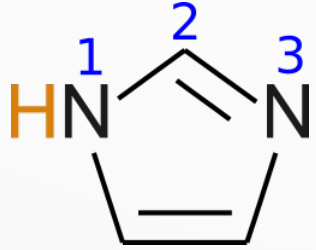
Kokalj, Faraday Discuss. **180**, 415

Surface vs. solvent

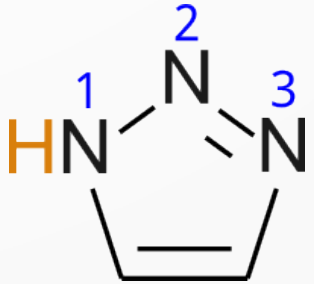
- surface = 2D system
- solvent = 3D system
- chemistry of solvent ≠ chemistry of surface

- **Example:**

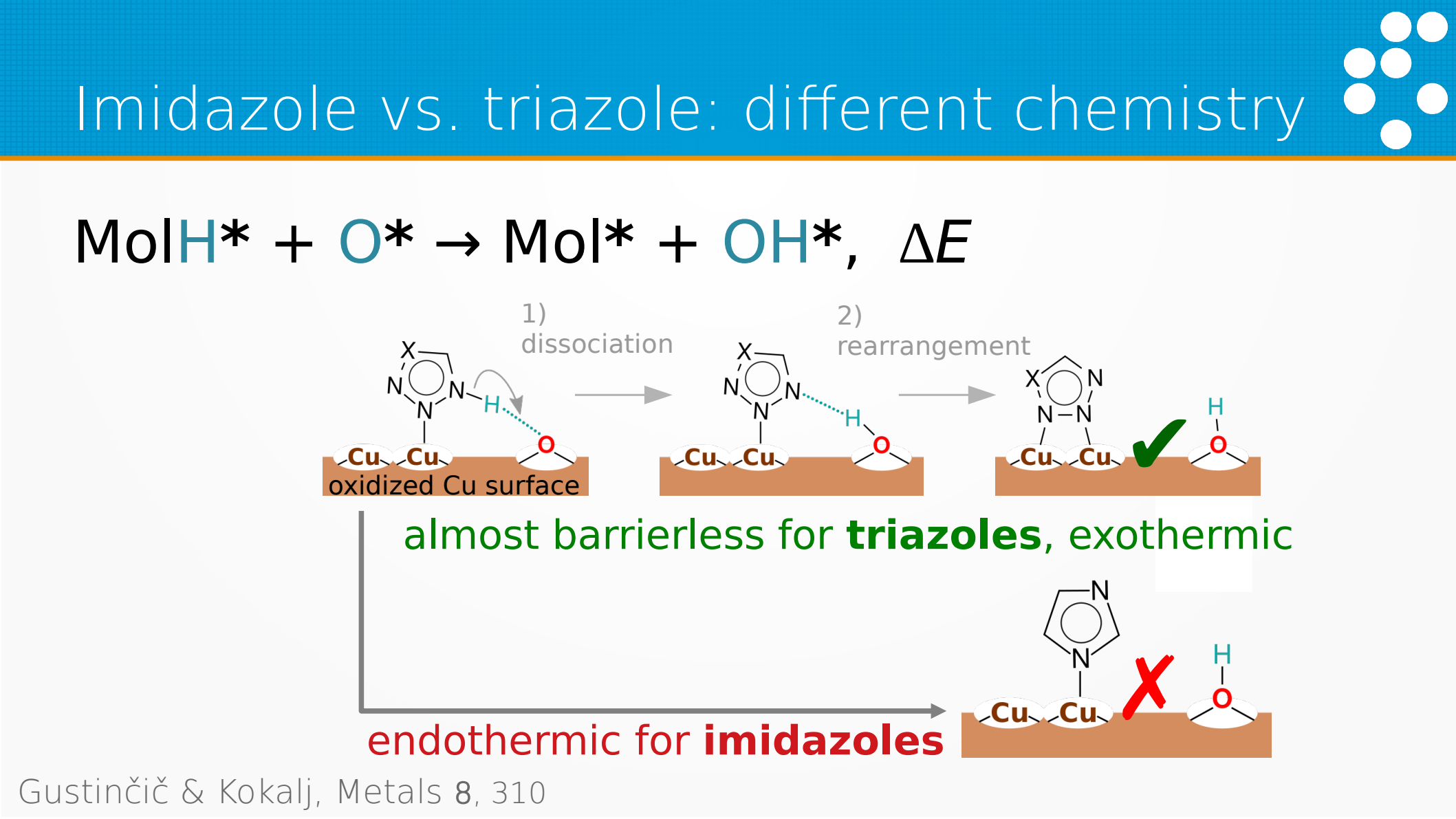
imidazole



triazole

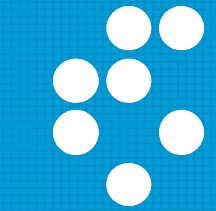


Imidazole vs. triazole: different chemistry

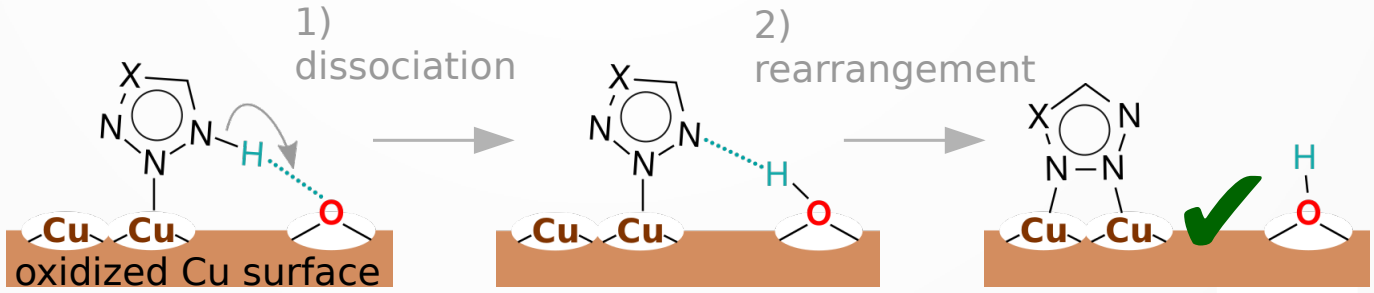


Gustinčič & Kokalj, Metals 8, 310

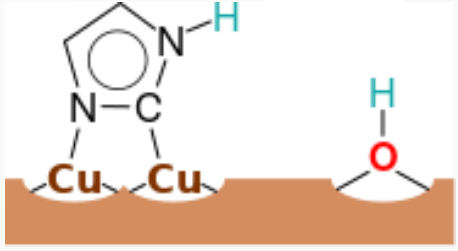
Imidazole vs. triazole: different chemistry



$$\mathrm{MolH^*} + \mathrm{O^*} \rightarrow \mathrm{Mol^*} + \mathrm{OH^*},\ \Delta E$$



almost barrierless for **triazoles**, exothermic



C–H dissociation exothermic for **imidazoles**

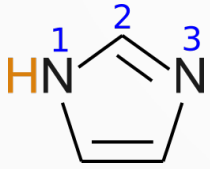
Kokalj et al., Appl. Surf. Sci. **479**, 463–468

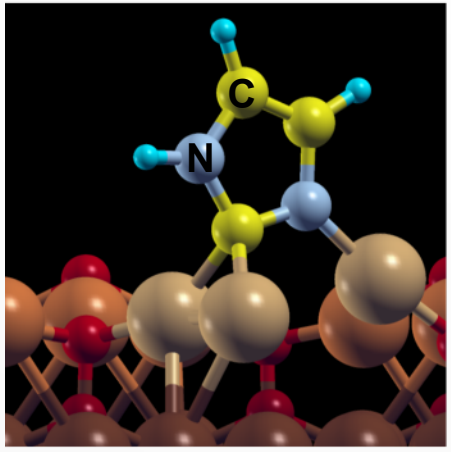
Imidazole vs. triazole: different chemistry

$$MolH^* + O^* \rightarrow Mol^* + OH^*, \quad \Delta E$$

imidazole

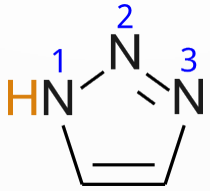
C2–H dissociation

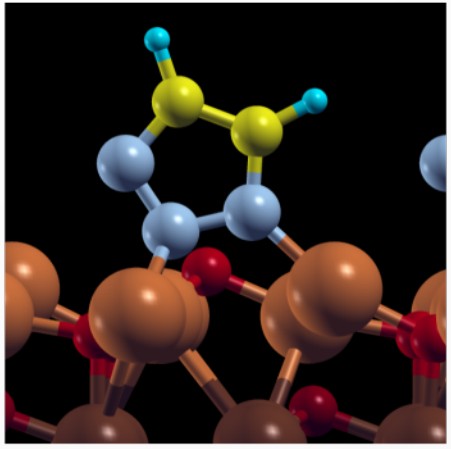




triazole

N1–H dissociation





similar thermodynamic stability

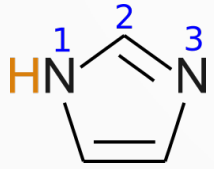
Kokalj et al., Appl. Surf. Sci. **479**, 463–468

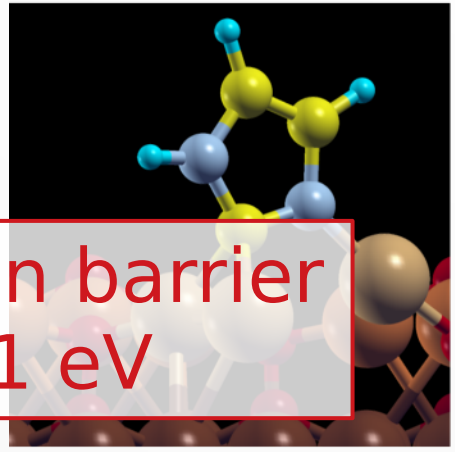
Imidazole vs. triazole: different chemistry

$$MolH^* + O^* \rightarrow Mol^* + OH^*, \quad \Delta E$$

imidazole

C2–H dissociation

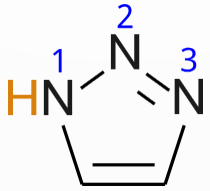


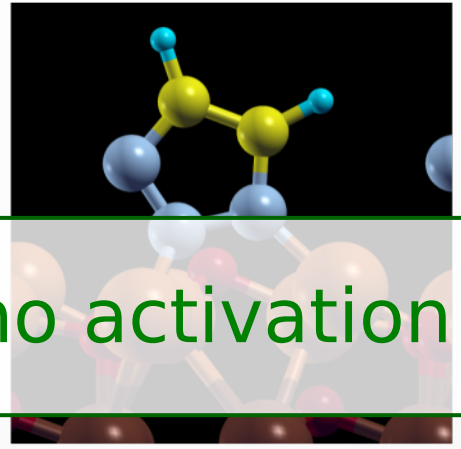


activation barrier
= 1.1 eV

triazole

N1–H dissociation





no activation barrier

similar thermodynamic stability

Kokalj et al., Appl. Surf. Sci. **479**, 463–468, Gustinčič & Kokalj, Metals **8**, 310

Inhibitors @ Al surfaces

In cooperation with **Philippe Marcus, Dominique Costa** et al.

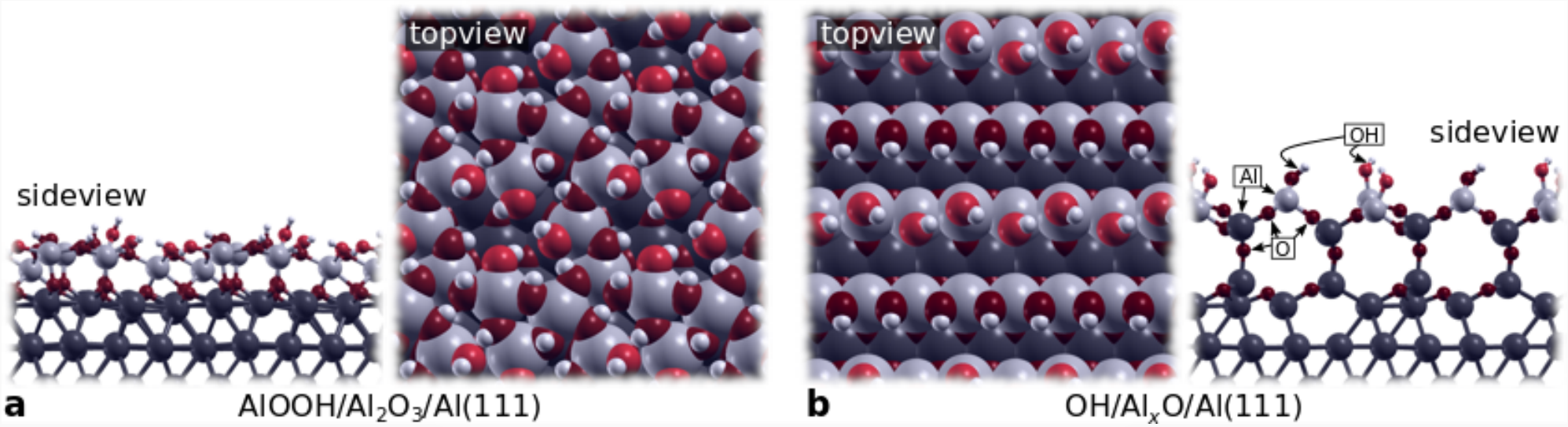
ParisTech

PSL

Aluminum

Al surfaces are oxidized & (possibly) hydroxylated

Al surface models

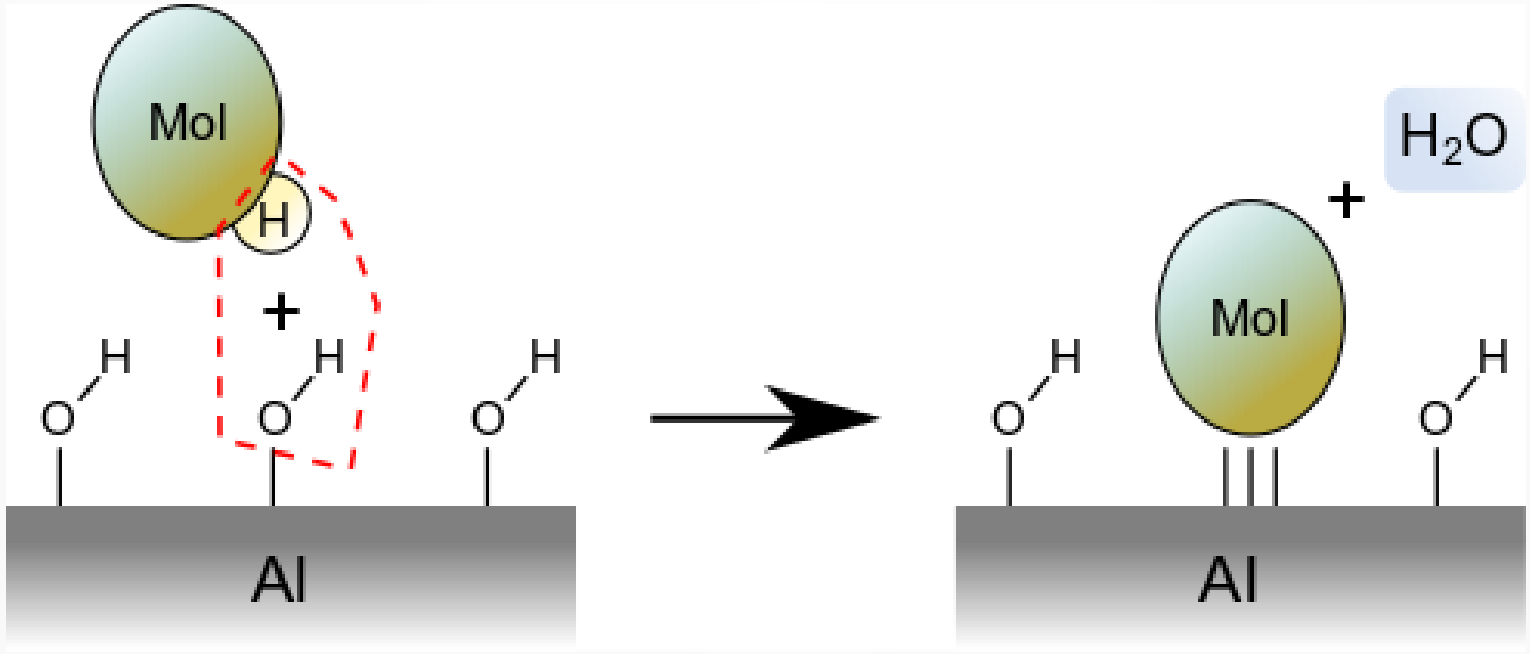


Poberžnik et al., J. Phys. Chem. C **122**, 9417, Appl. Surf. Sci. **525**, 146156
Milošev et al., J. Electrochem. Soc. **166**, C3131, *ibid.* **167**, 061509, *ibid.*, submitted

Inhibitors @ aluminum

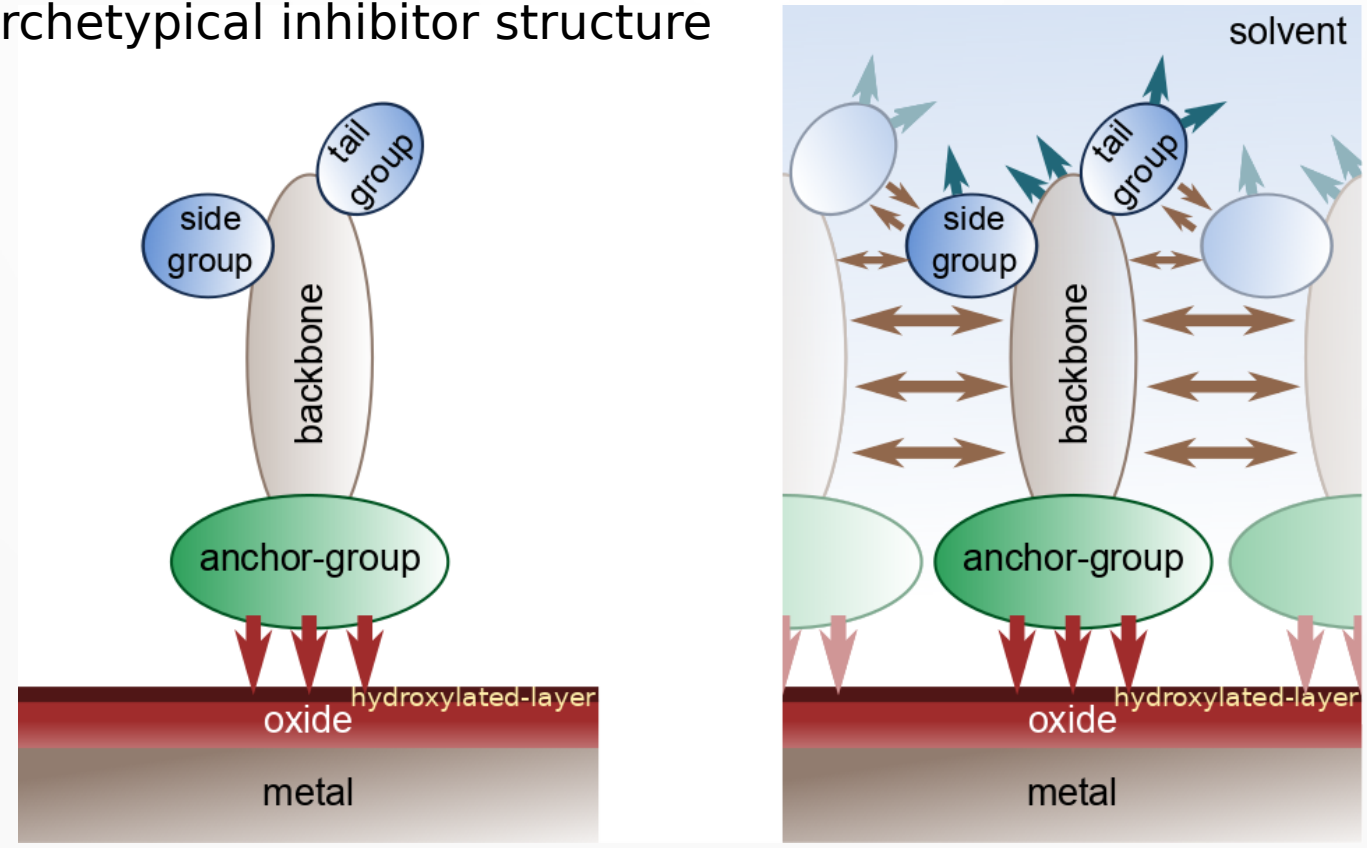
MolH + OH* → Mol* + H_2O

(condensation adsorption)



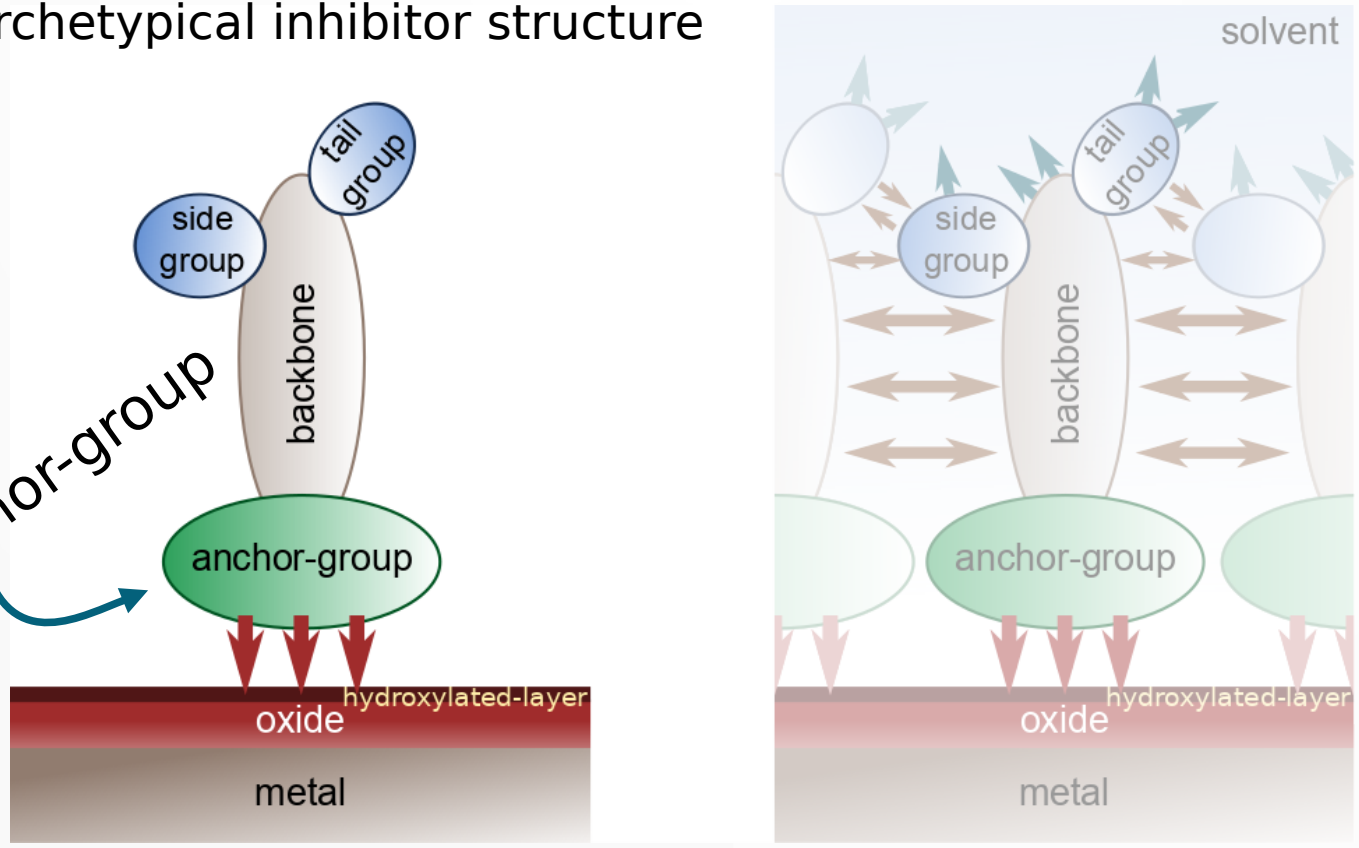
Inhibitors @ Al surfaces

archetypical inhibitor structure



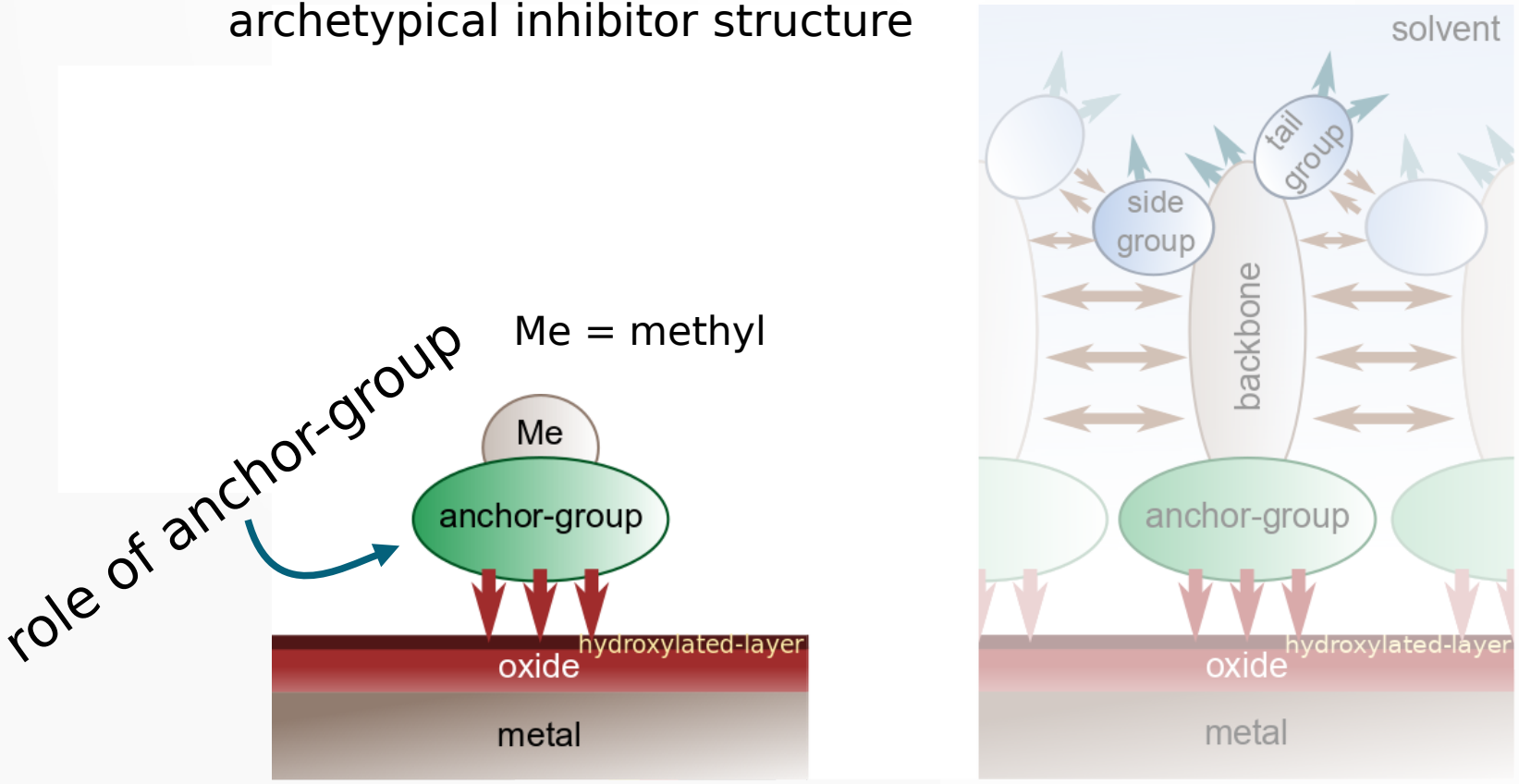
Inhibitors @ Al surfaces

archetypical inhibitor structure

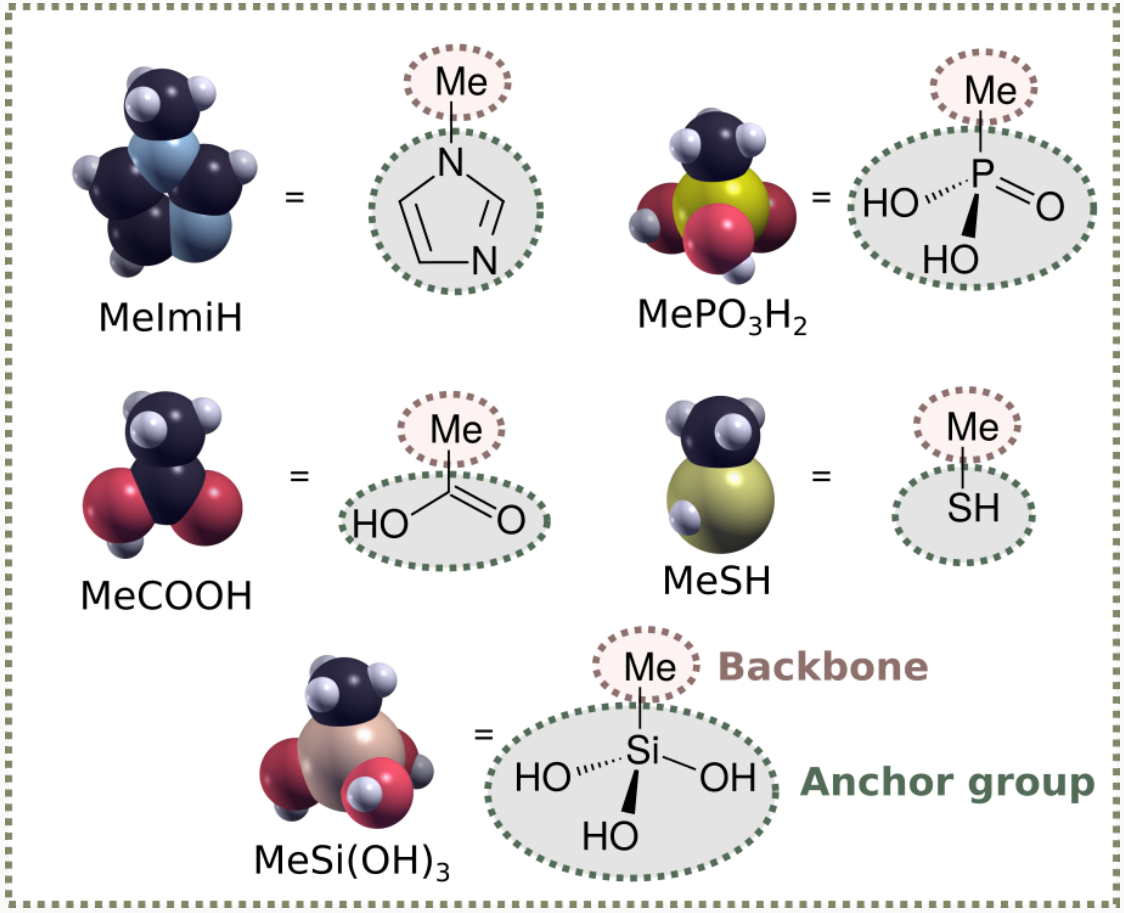


Inhibitors @ Al surfaces

archetypical inhibitor structure



Anchor groups



Me = methyl
(minimal backbone)

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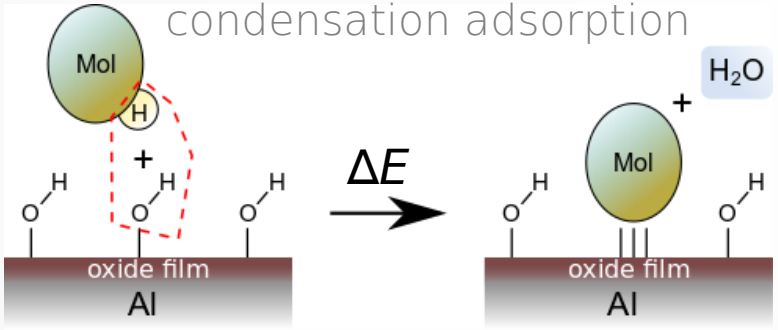
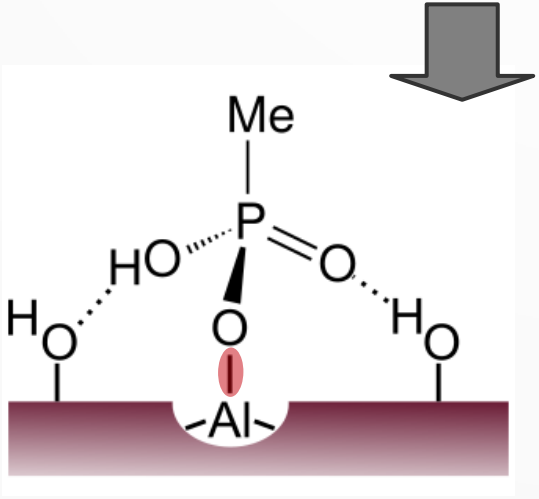
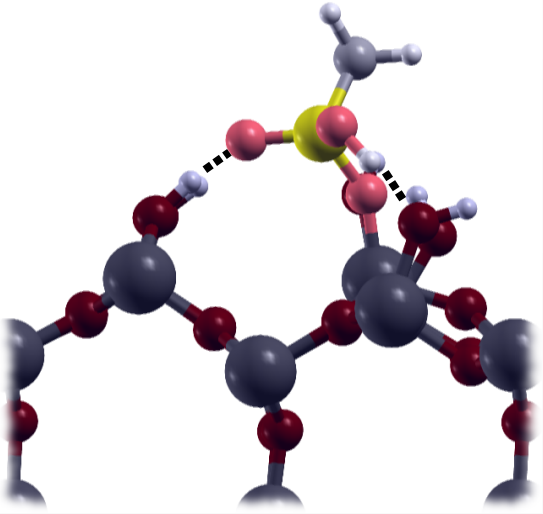
Anchor = phosphonic acid

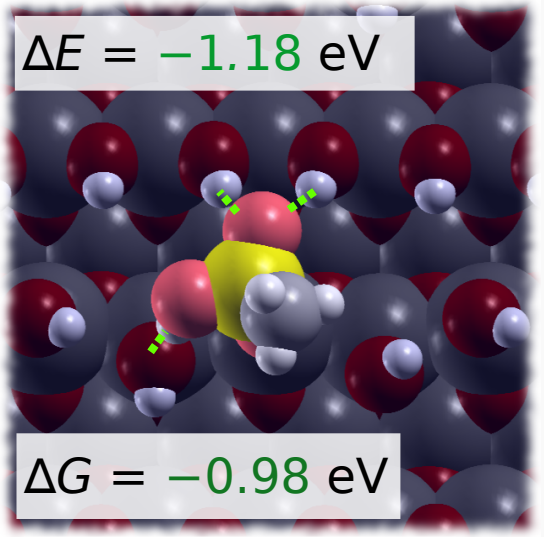


Beware: ΔE does not measure the molecule–surface bond strength due to bond-breaking & bond-making

Info: PO–Al bond strength ≈ 4.6 eV

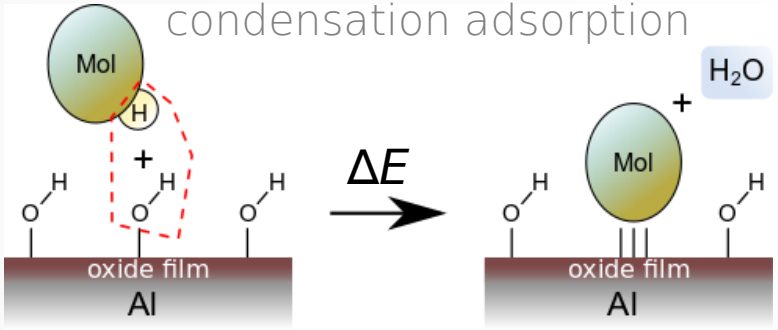






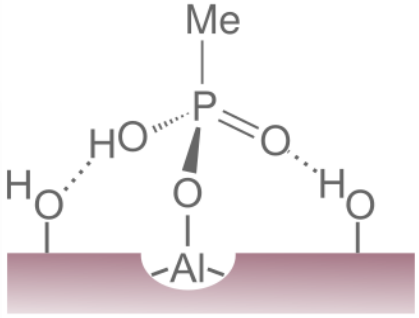
T = 298.15 K, p = 1 atm

Anchor = silanol



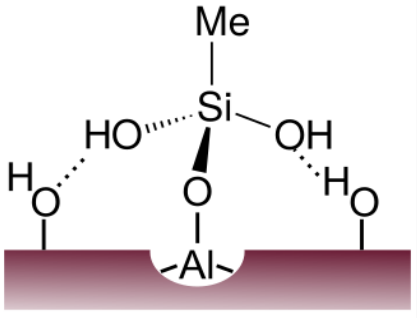
T = 298.15 K
p = 1 atm

ΔE = −1.18 eV



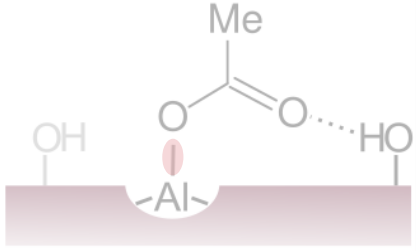
ΔG = −0.98 eV

ΔE = −0.87 eV



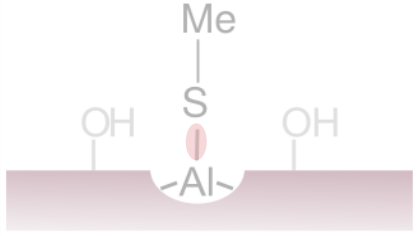
ΔG = −0.60 eV

ΔE = −0.29 eV



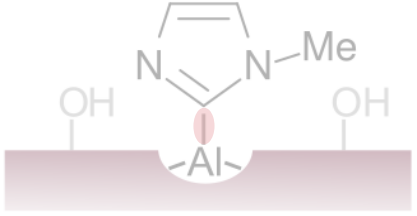
ΔG = −0.19 eV

ΔE = +0.35 eV



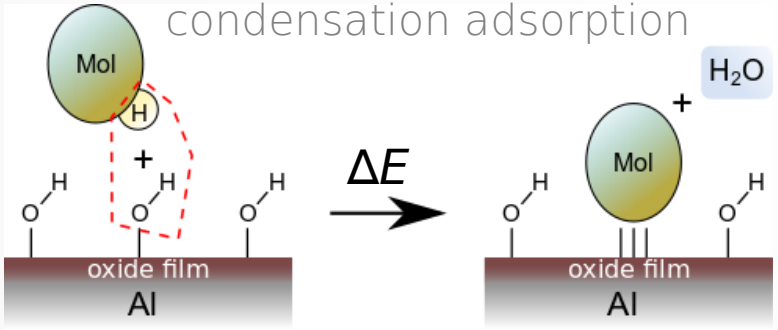
ΔG = +0.52 eV

ΔE = +0.96 eV



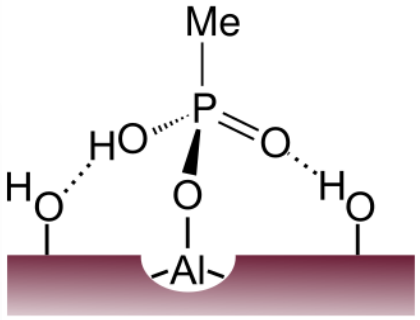
ΔG = +1.11 eV

Anchor = carboxylic acid



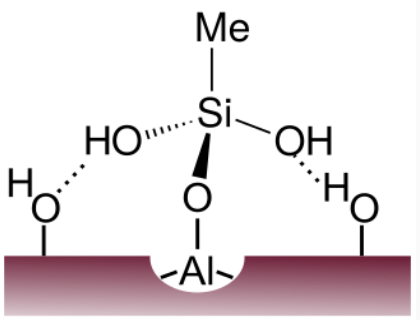
T = 298.15 K
p = 1 atm

ΔE = −1.18 eV



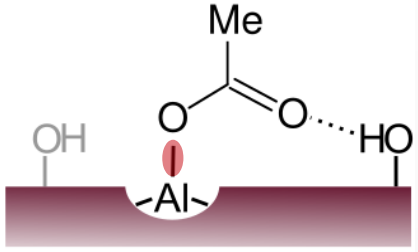
ΔG = −0.98 eV

ΔE = −0.87 eV



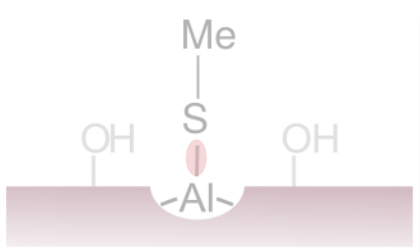
ΔG = −0.60 eV

ΔE = −0.29 eV



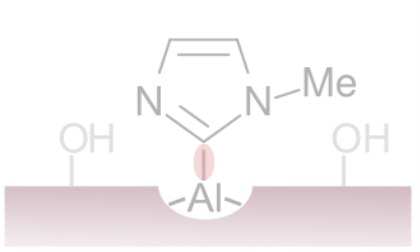
ΔG = −0.19 eV

ΔE = +0.35 eV



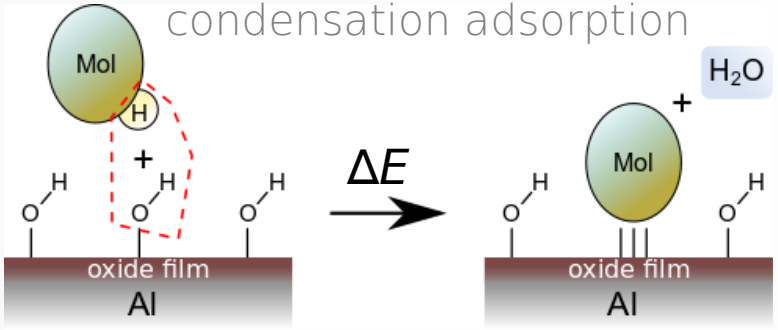
ΔG = +0.52 eV

ΔE = +0.96 eV



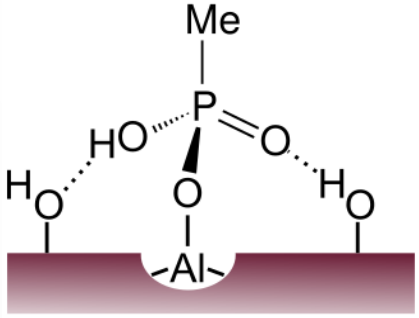
ΔG = +1.11 eV

Anchor = thiol



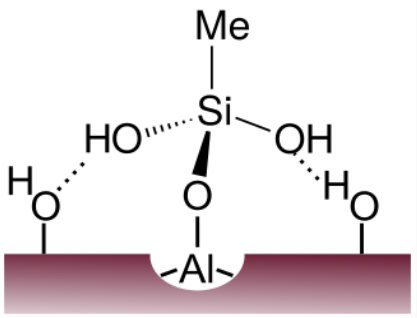
T = 298.15 K
p = 1 atm

ΔE = −1.18 eV



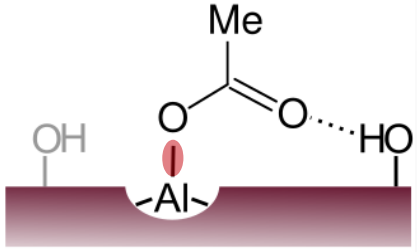
ΔG = −0.98 eV

ΔE = −0.87 eV



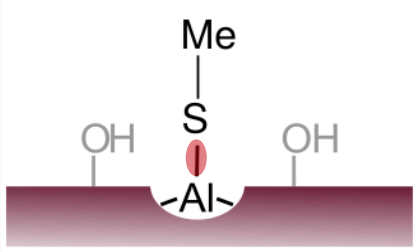
ΔG = −0.60 eV

ΔE = −0.29 eV



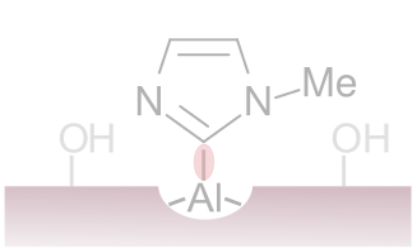
ΔG = −0.19 eV

ΔE = +0.35 eV



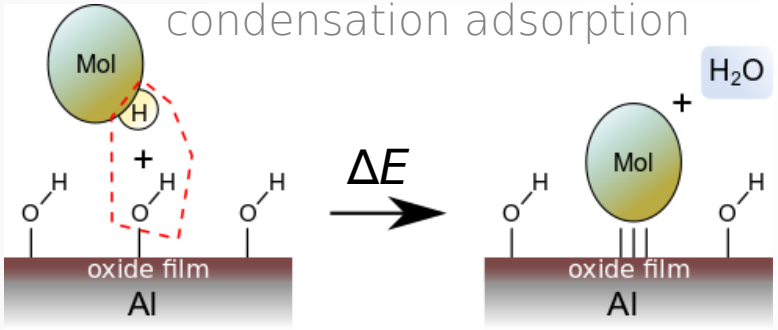
ΔG = +0.52 eV

ΔE = +0.96 eV



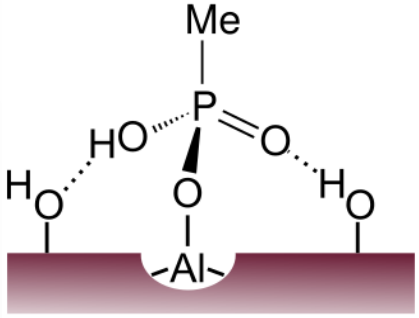
ΔG = +1.11 eV

Anchor = imidazole



T = 298.15 K
p = 1 atm

ΔE = −1.18 eV



ΔG = −0.98 eV

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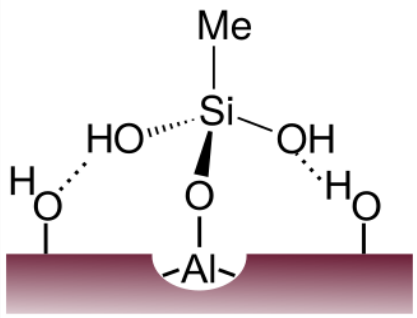
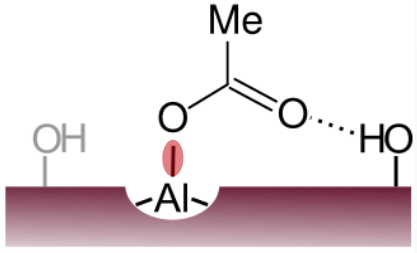


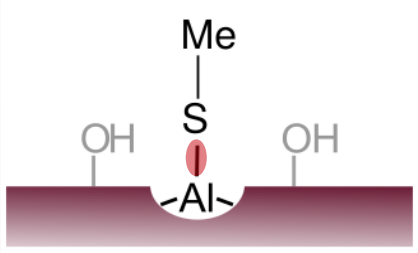
ΔG = −0.60 eV

ΔE = −0.29 eV



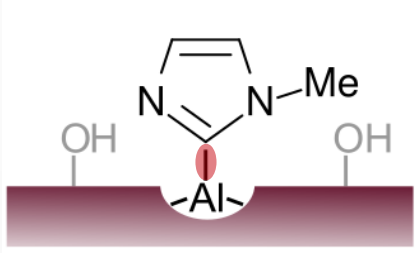
ΔG = −0.19 eV

ΔE = +0.35 eV



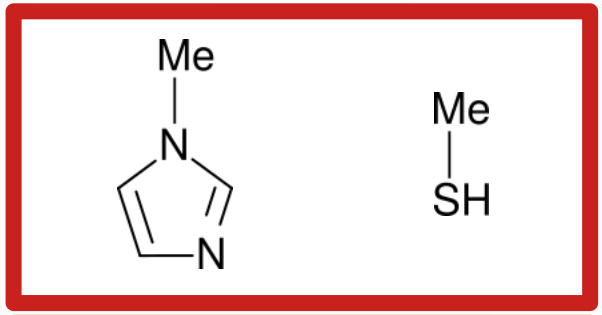
ΔG = +0.52 eV

ΔE = +0.96 eV

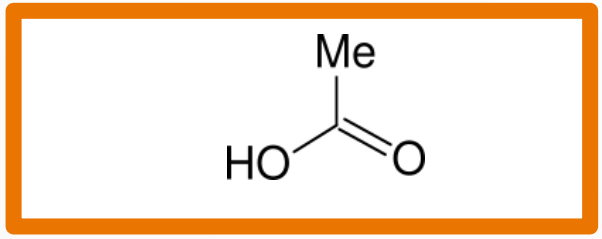


ΔG = +1.11 eV

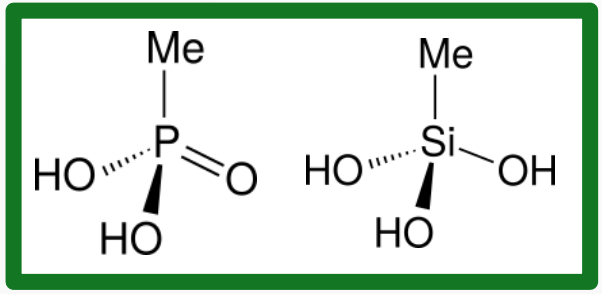
Anchor groups: bottom line



not good



additional stabilization



good

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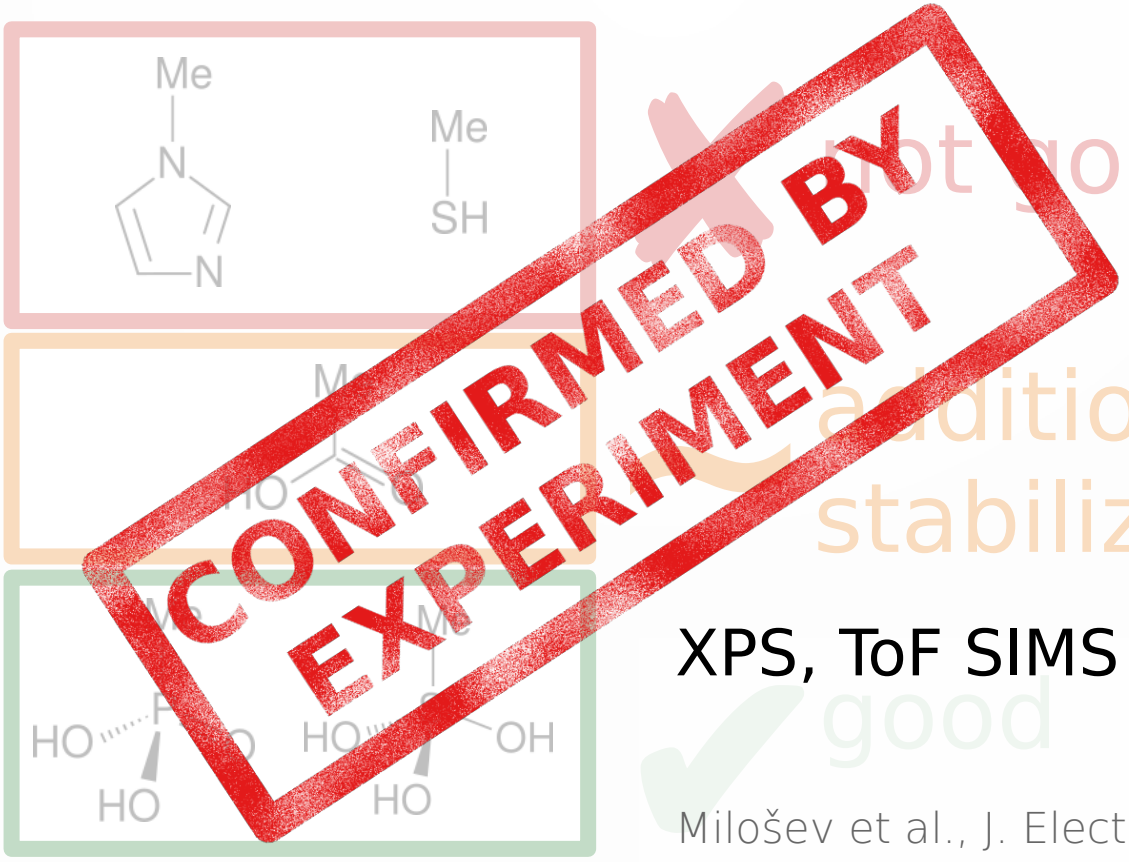
Anchor groups: bottom line



XPS, ToF SIMS

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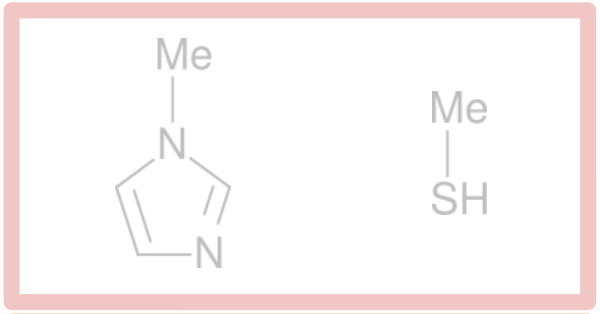
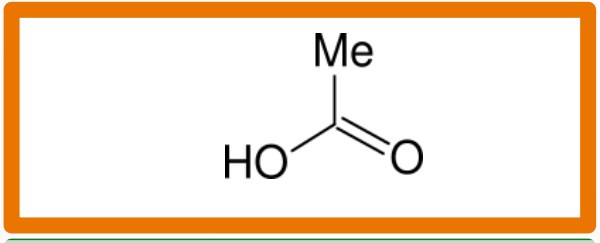
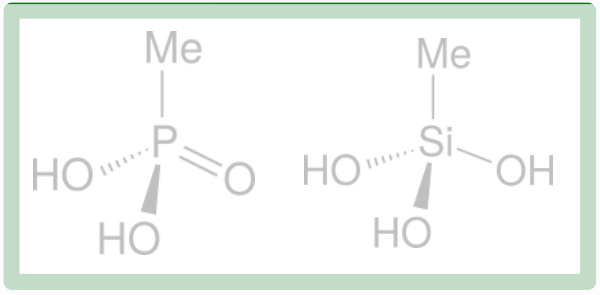
Carboxylic acids



not good

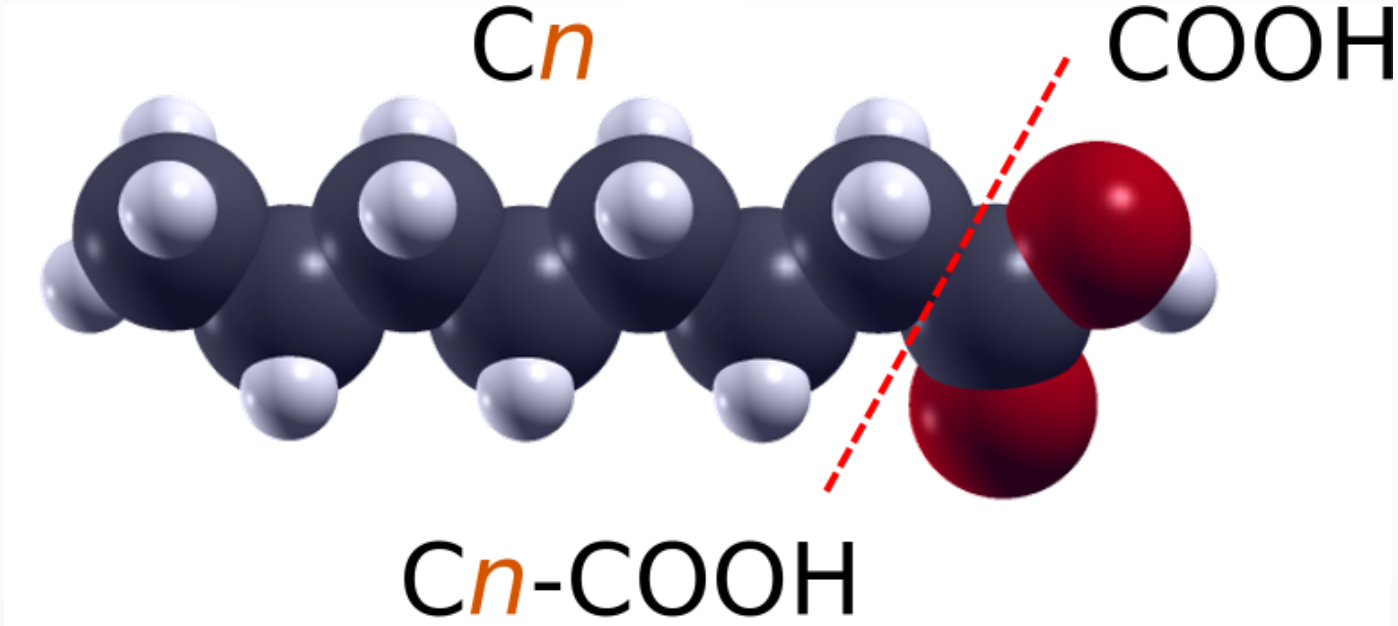


additional stabilization



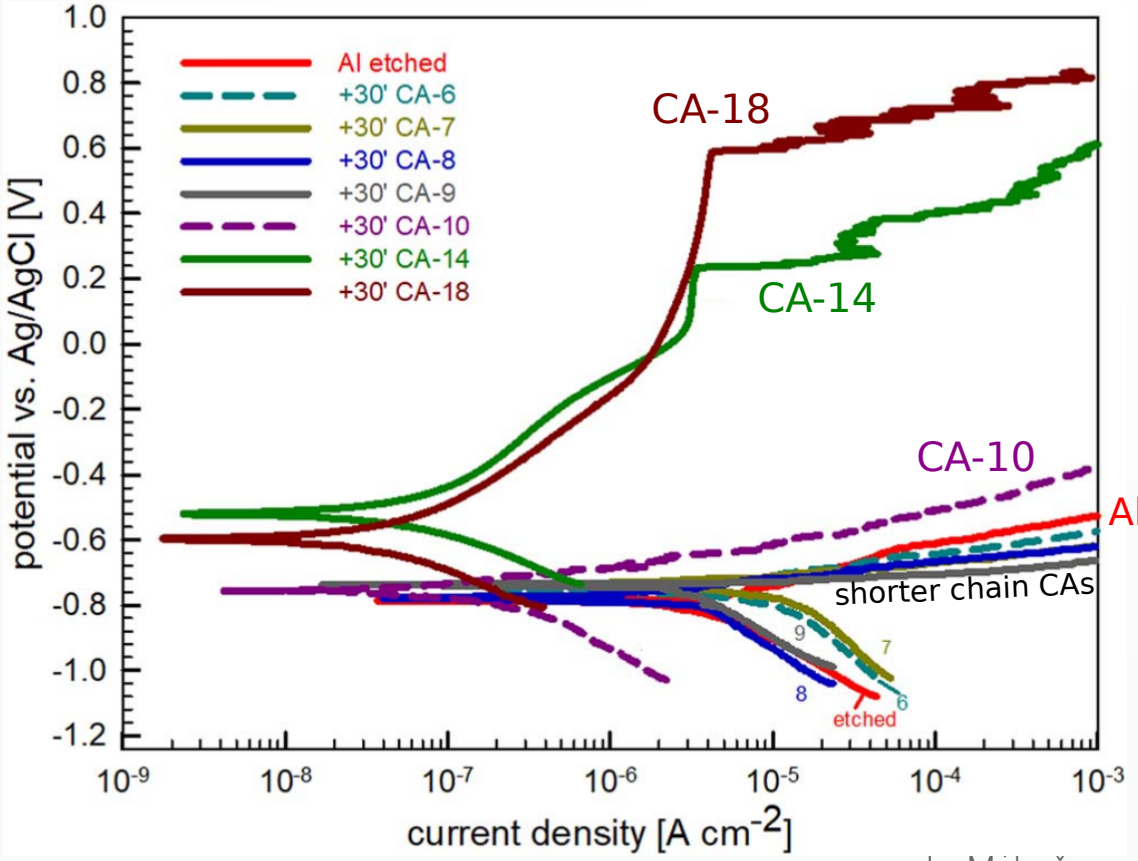
good

Carboxylic acids – designation



octanoic acid = C7-COOH = CA-8

Carboxylic acids – CA

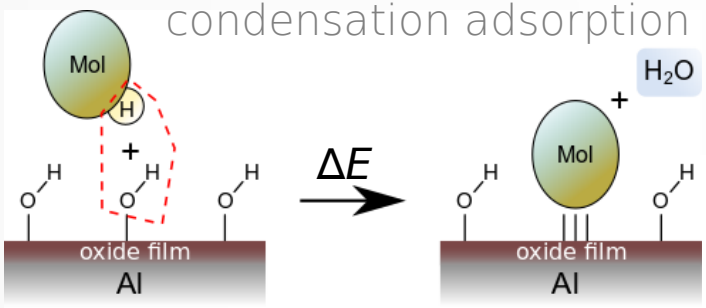


only long-chain CAs are efficient inhibitors

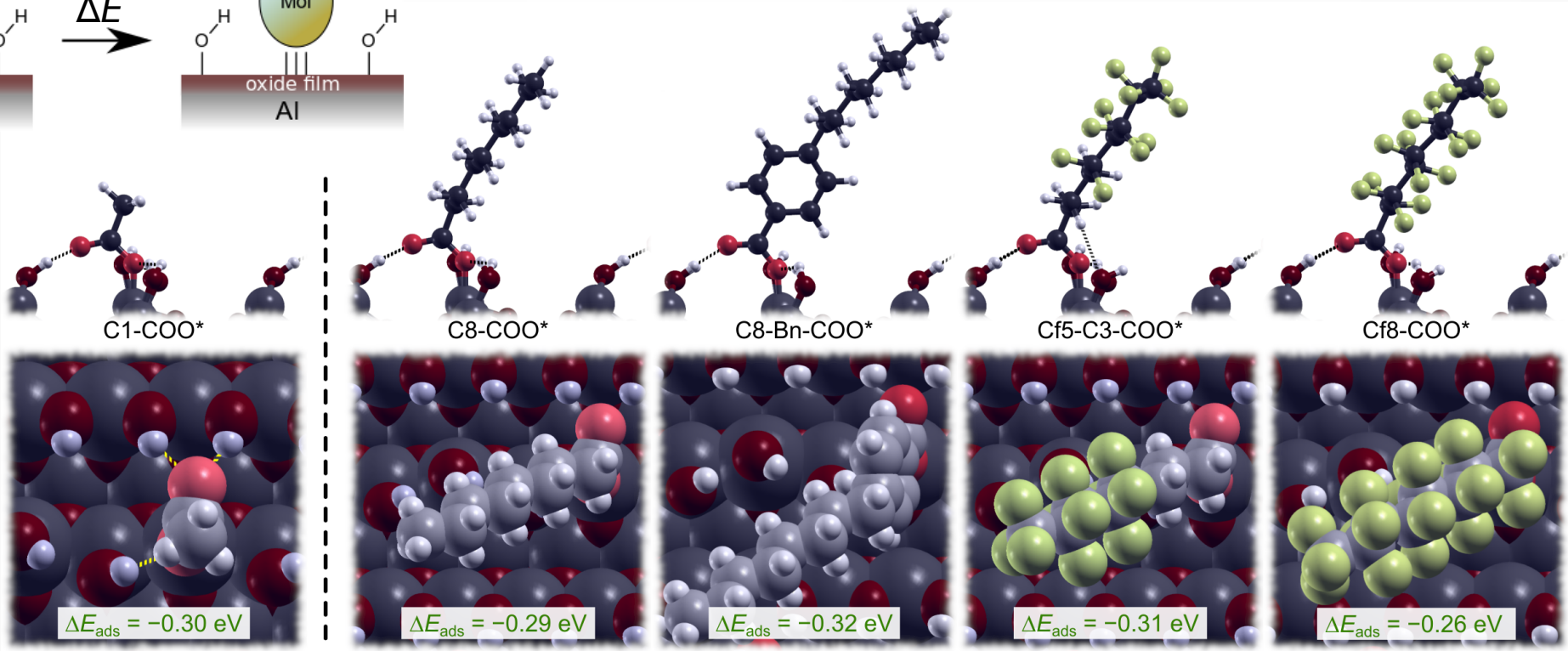
WHY?

I. Milošev et al., J. Electrochem. Soc. **166**, C3131

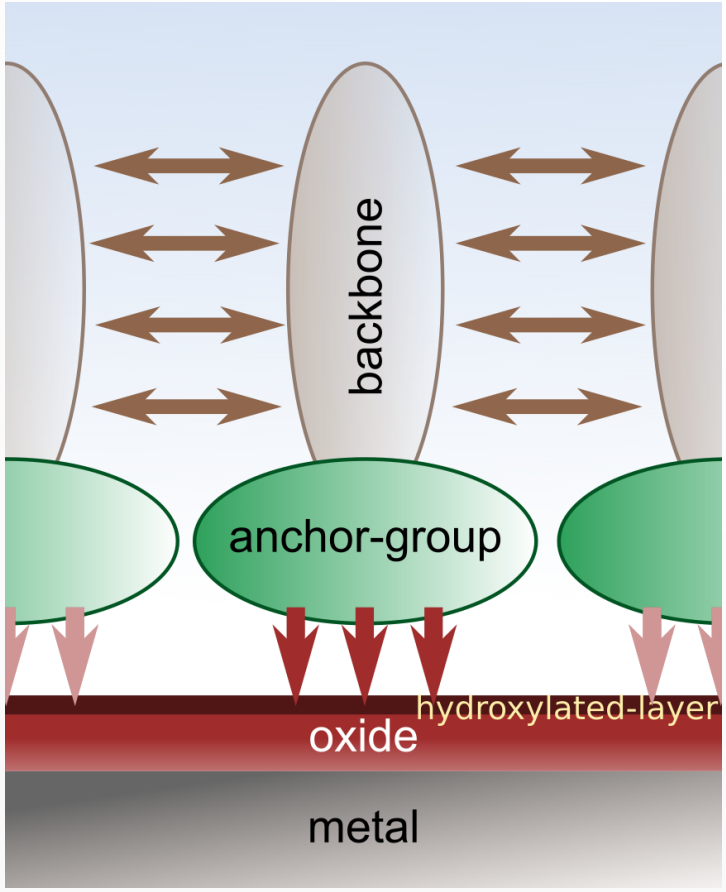
Carboxylic acids – standalone



Milošev et al., J. Electrochem. Soc. (2021) submitted

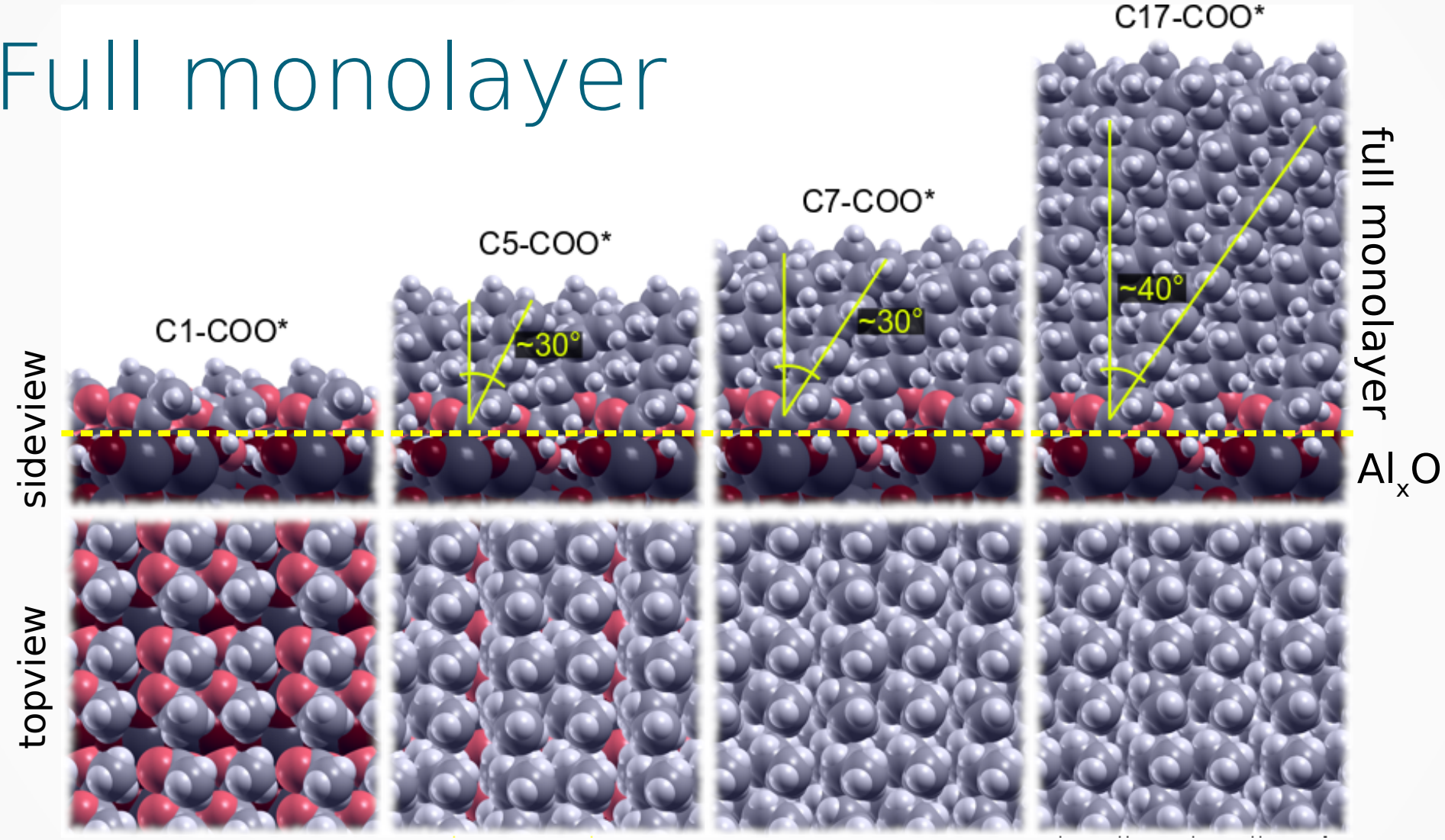


Role of backbone

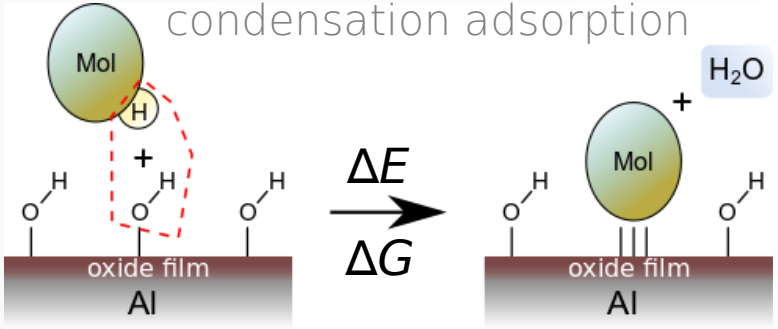


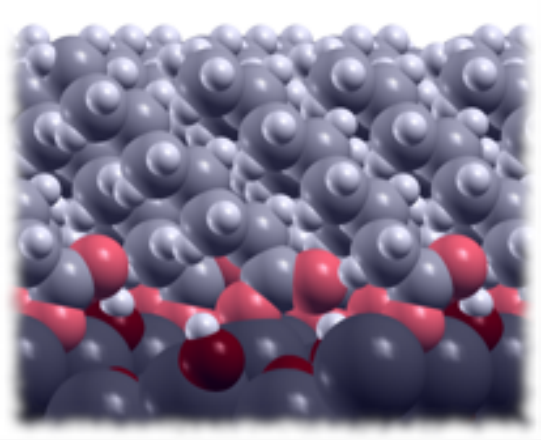
backbone governs lateral interactions

Full monolayer

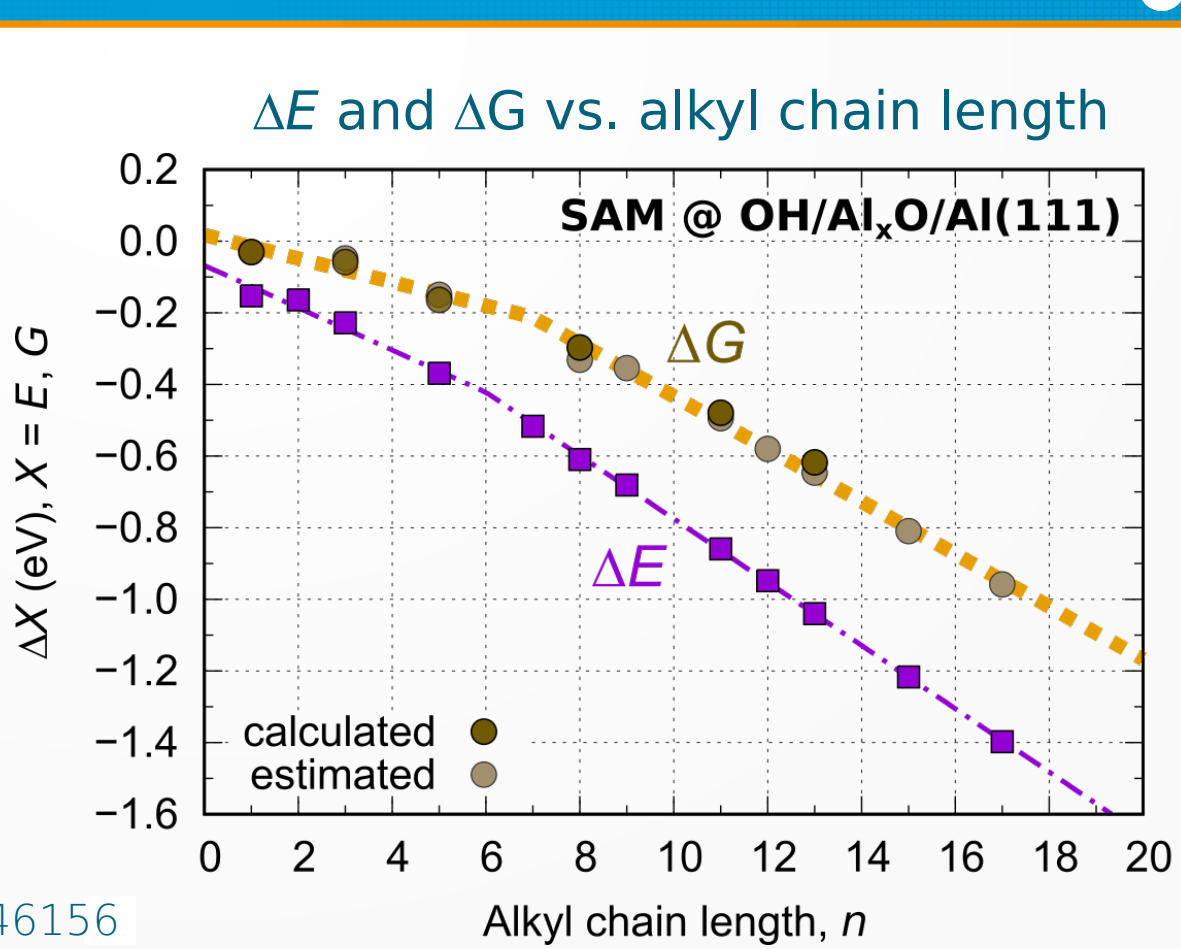


Decoding lateral interactions



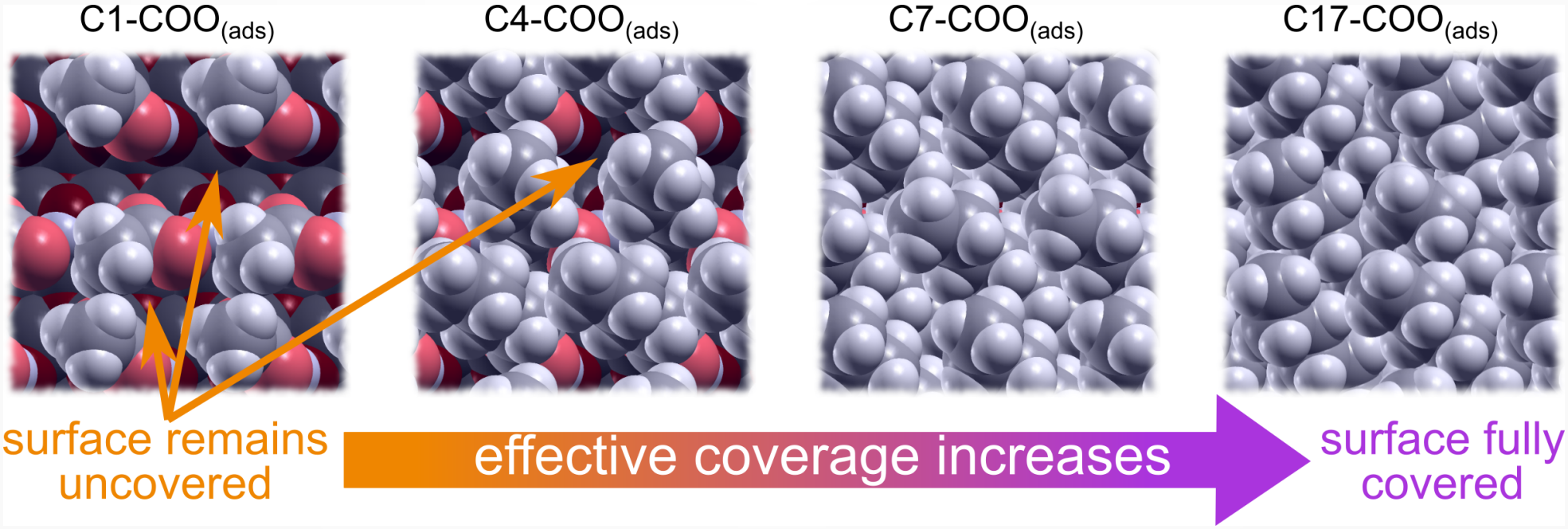


T = 298.15 K
p = 1 atm



Poberžnik et al., Appl. Surf. Sci. **525**, 146156

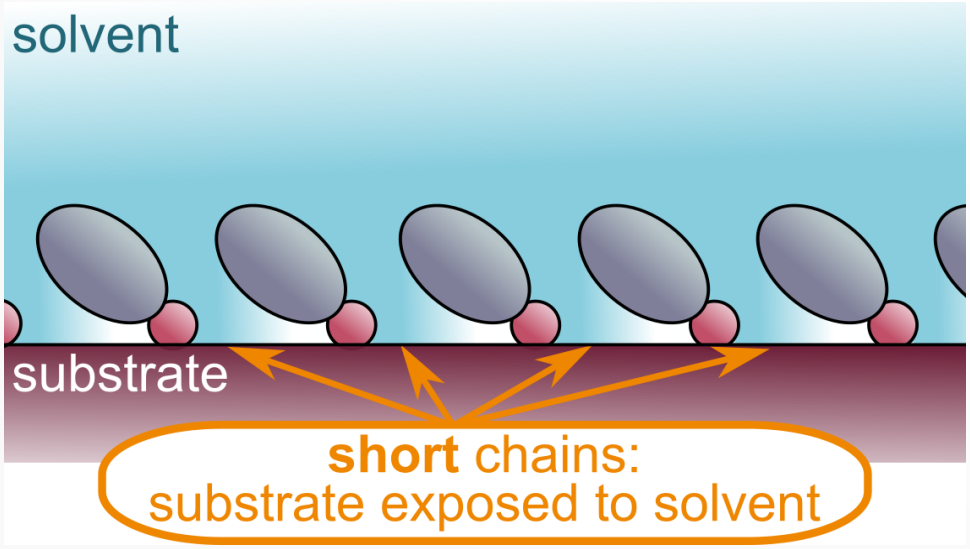
Effective coverage

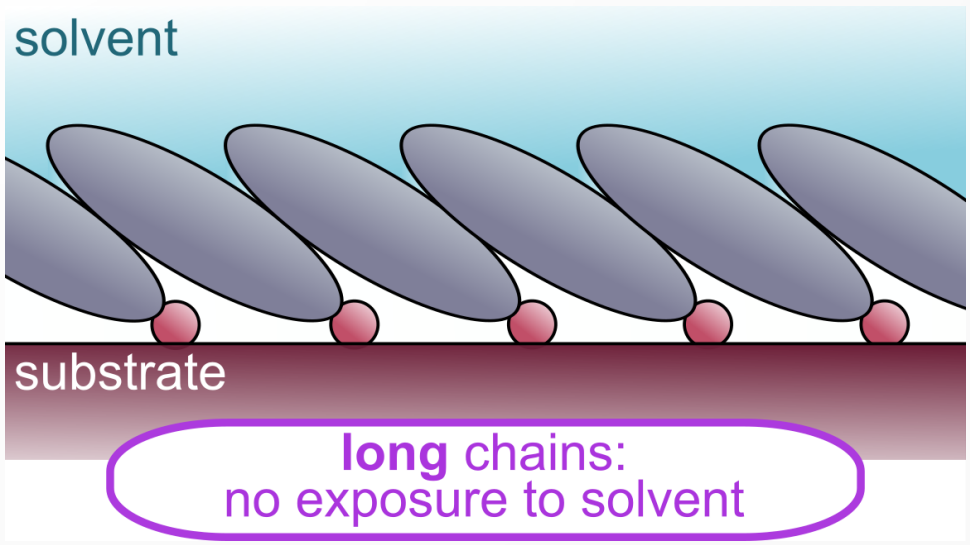


longer alkyl chain = smaller gaps = greater effective coverage

Milošev et al., J. Electrochem. Soc. **166**, C3131

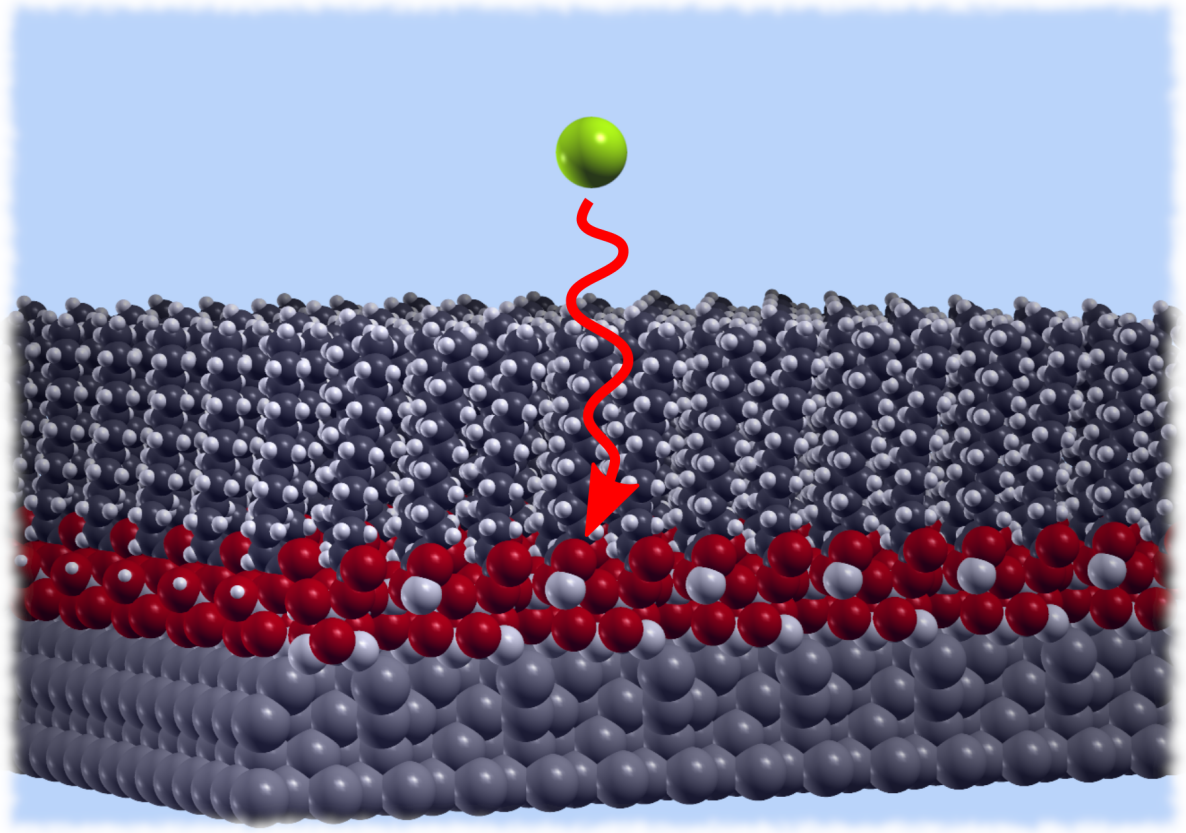
Effective coverage





Milošev et al., J. Electrochem. Soc. **166**, C3131

Penetration of Cl^- through SAM



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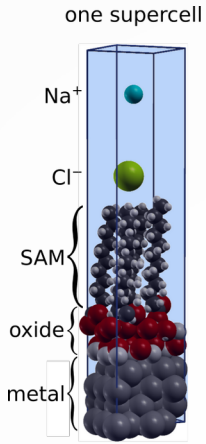
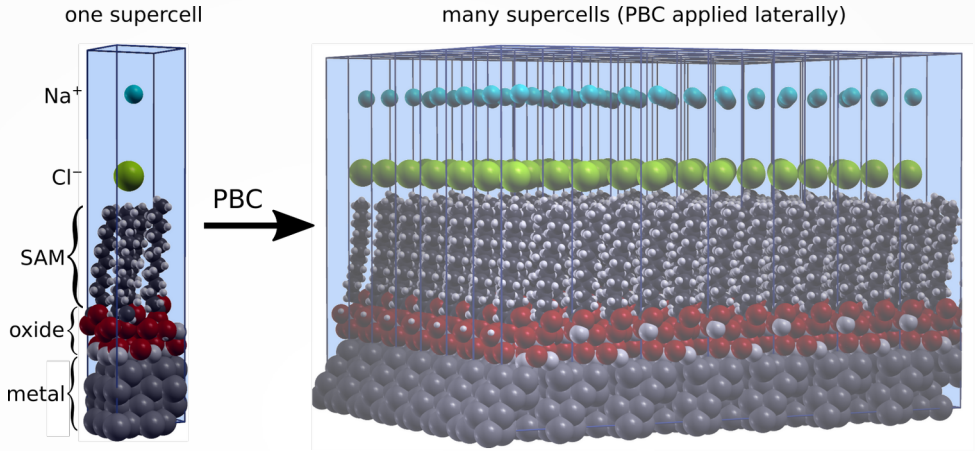
Beware of PBC (periodic boundary conditions) !



PBC & divergent Coulomb interactions:

add Na^+ to make supercell neutral

Beware of PBC (periodic boundary conditions) !



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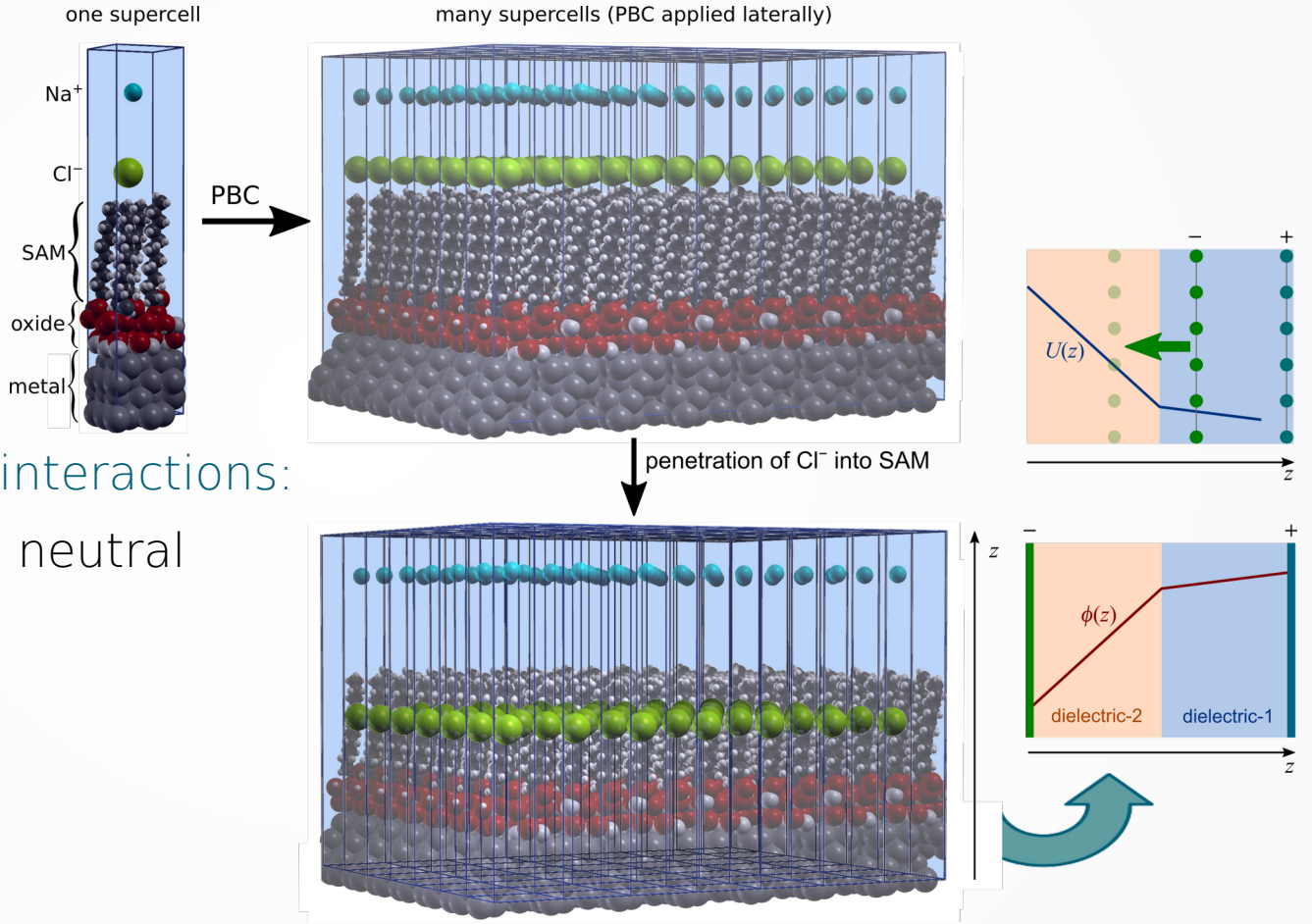
Beware of PBC (periodic boundary conditions) !

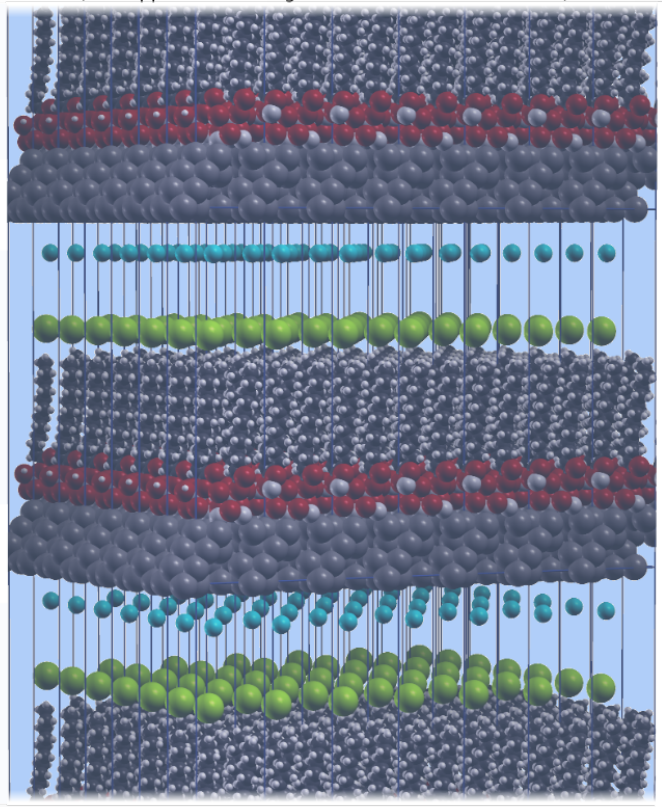


PBC & divergent Coulomb interactions:

add Na^+ to make supercell neutral

3D PBC: beware of artifacts

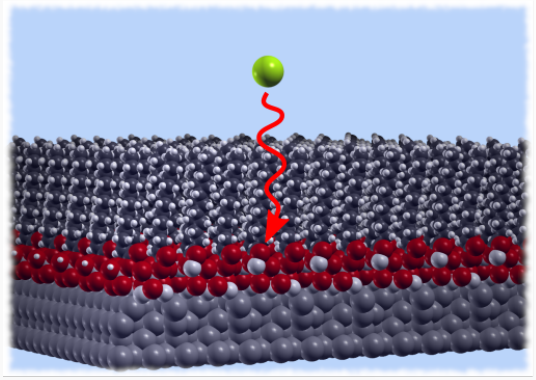
multi-slab model
(PBC applied also along the surface normal direction)

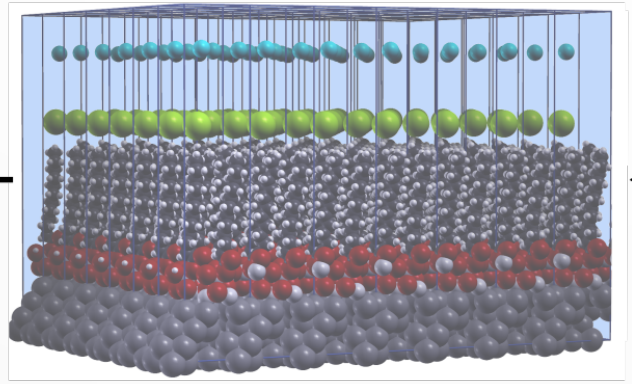


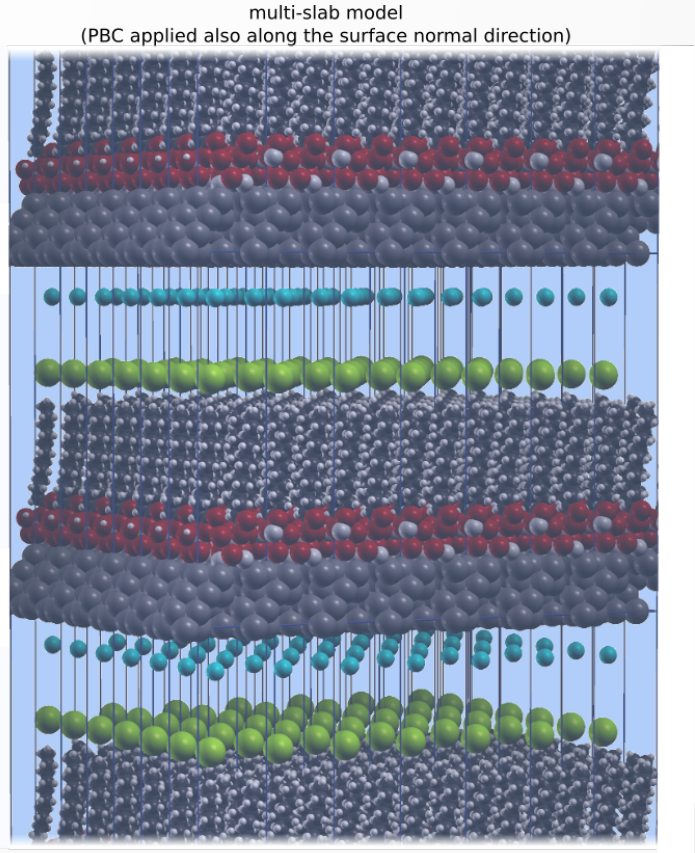
used by plane-wave DFT codes

3D PBC: beware of artifacts

reverse engineer to get rid of PBC artifacts







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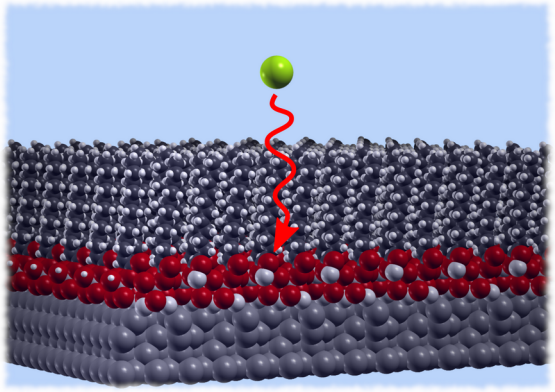
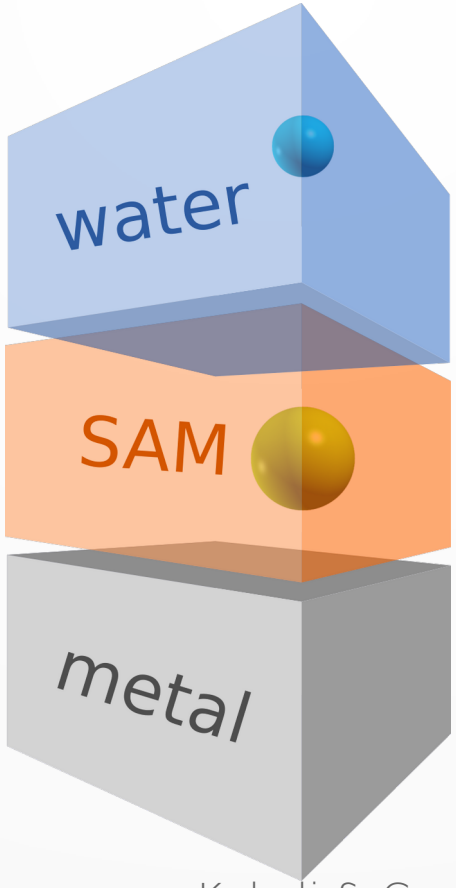
Penetration of Cl^- through SAM





Simplified model calculations:

- metal/SAM/water described by implicit continuum slabs
- ions treated explicitly
- elastic penalty for Cl^- penetration into SAM neglected

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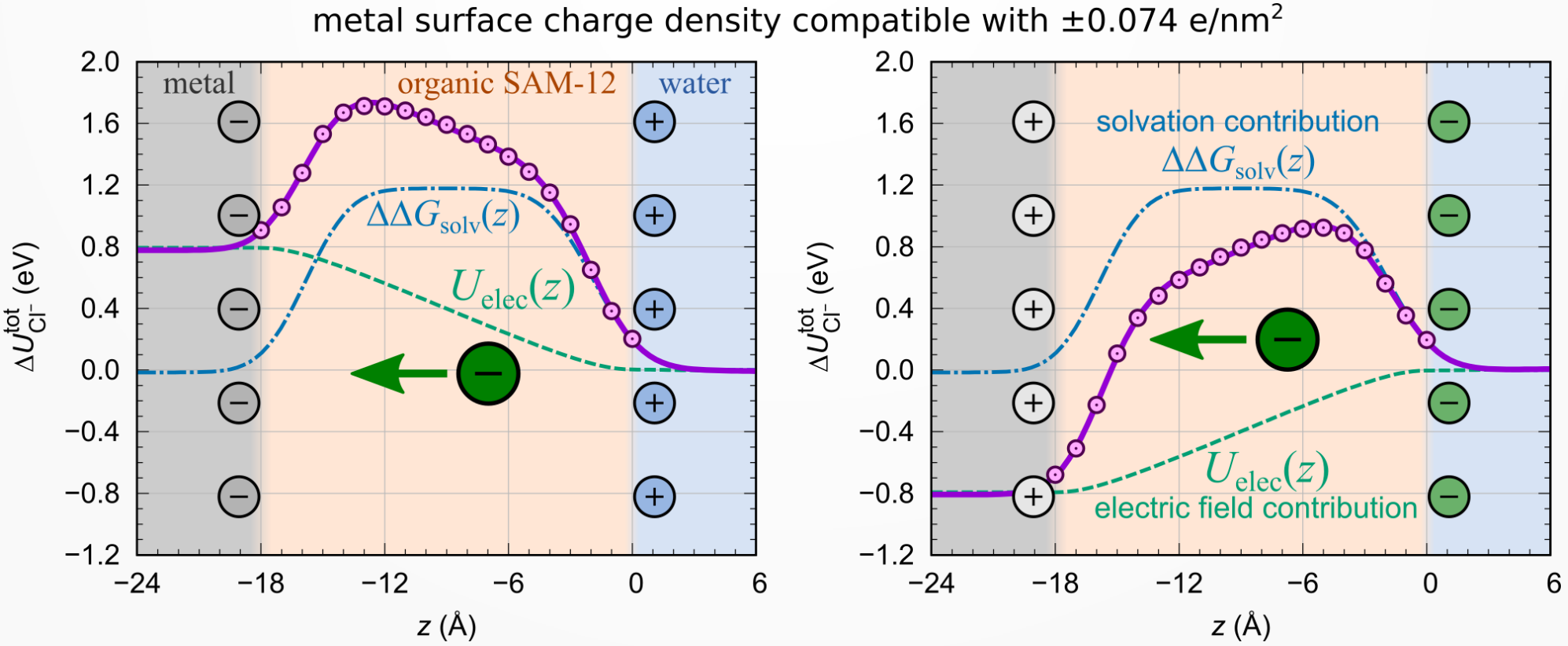
Penetration of Cl^- through SAM



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Penetration of Cl^- through SAM

Contributions to the penetration barrier:

- inferior solvation of ions in SAM ($\Delta\Delta G_{solv}$)

$$\Delta G^{\mathrm{Born}}_{\mathrm{solv}} = -\frac{q^2_{\mathrm{ion}}}{2r_{\mathrm{ion}}}\left(1-\frac{1}{\varepsilon}\right) \quad \text{[in Hartree atomic units]}$$

$$\Delta\Delta G^{\mathrm{Born}}_{\mathrm{solv}} = \Delta G^{\mathrm{Born}}_{\mathrm{solv}}(\mathrm{SAM}) - \Delta G^{\mathrm{Born}}_{\mathrm{solv}}(\mathrm{water}) = \frac{q^2_{\mathrm{ion}}}{2r_{\mathrm{ion}}}\left(\frac{1}{\varepsilon_{\mathrm{SAM}}}-\frac{1}{\varepsilon_{\mathrm{water}}}\right)$$

- contribution due to electric field in the Helmholtz double-layer (U_{elec})
- elastic penalty (currently neglected)

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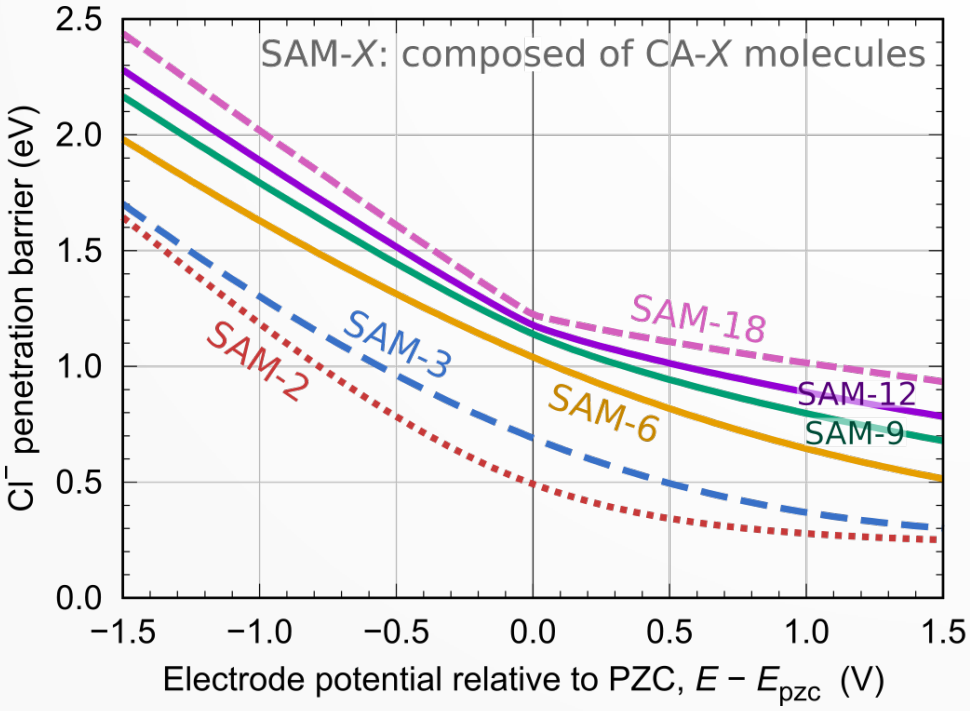
Penetration of Cl^- through SAM



Simplifying assumptions:

- CA molecules fully cover the surface irrespective of the alkyl chain length
  (expt.: only long-chain CAs form a complete SAM)
- surface is fully covered by SAM at all electrode potentials
- elastic penalty for Cl^- penetration is neglected
- ...

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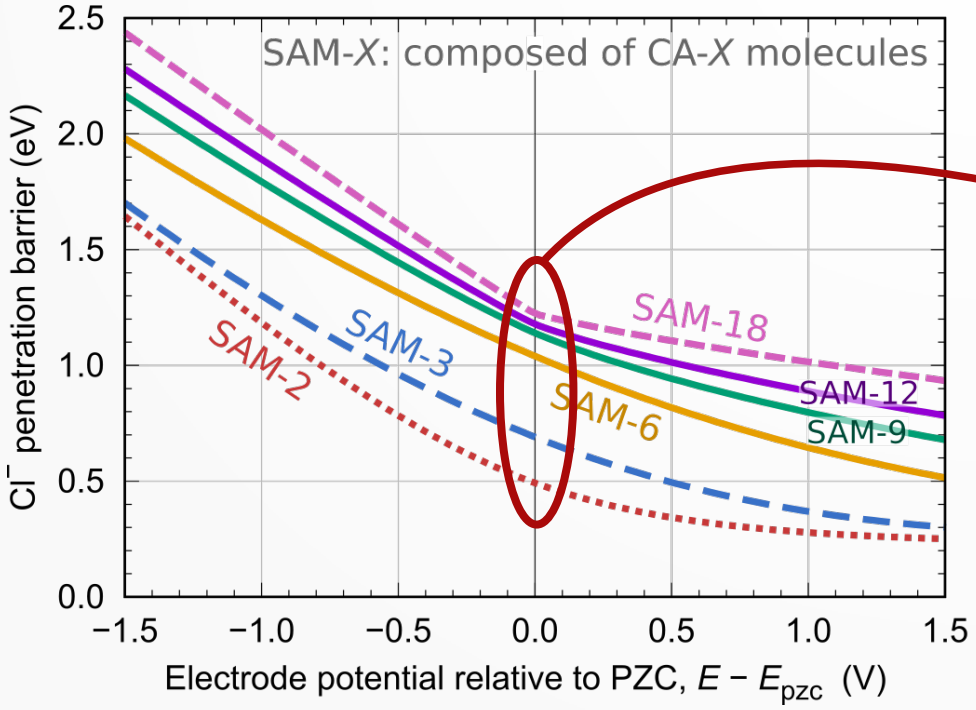
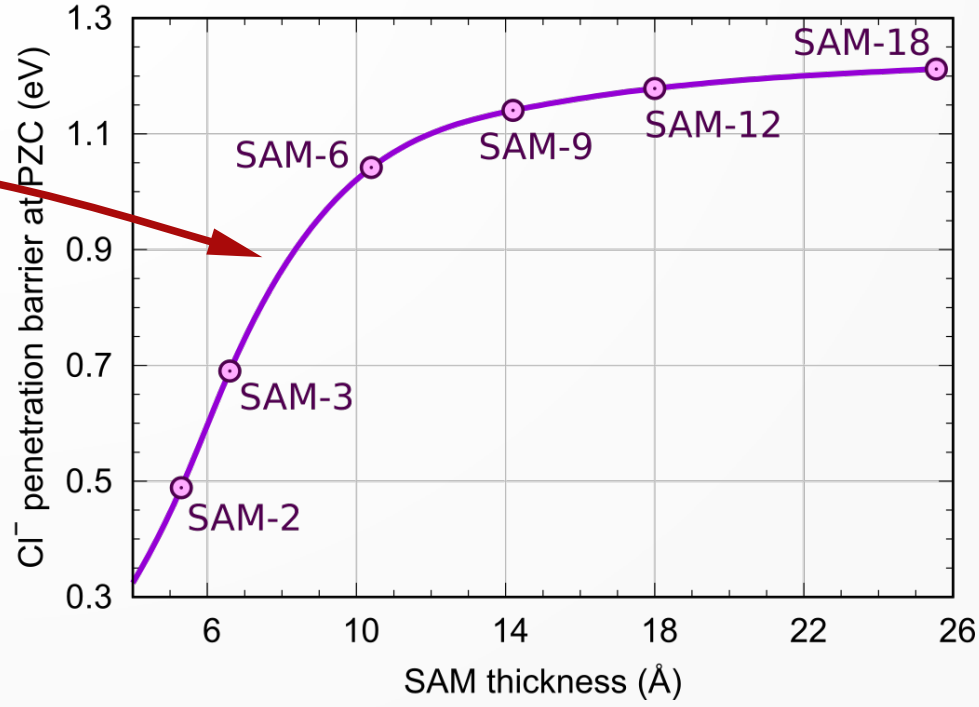
Penetration of Cl^- through SAM





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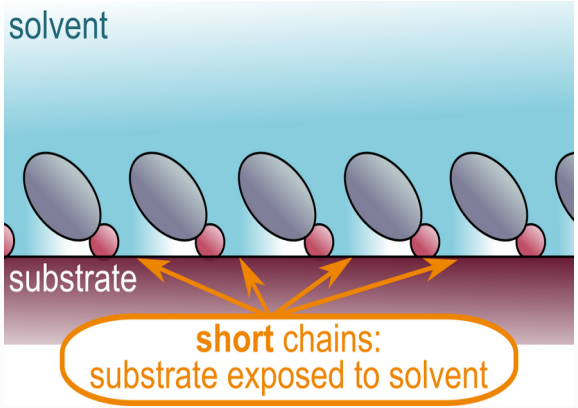
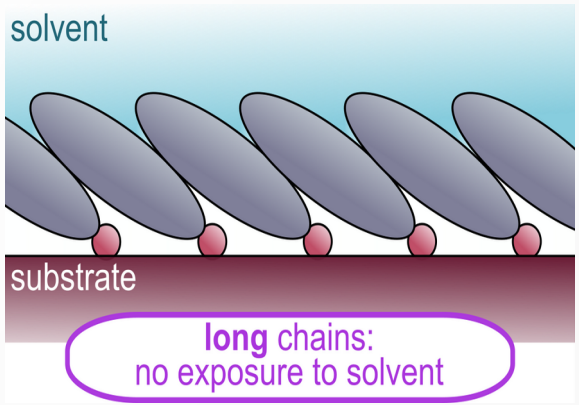
Summary

- SAM stability: anchor–surface adhesion + intermolecular lateral cohesion
- lateral interactions between alkyl chains are maximized by tilting
- longer alkyl chains:
  - display stronger lateral cohesion (needed for CA's SAM formation)
  - more efficiently hinder the access to material's surface





Conclusions

The purpose of this presentation was to show with several examples that …

DFT modeling can provide several details and useful insights that may be of relevance for corrosion inhibition and can subsequently help to explain investigated phenomena

Molecular modeling of organic corrosion inhibitors: calculations, pitfalls, and conceptualization of molecule–surface bonding

Anton Kokalj*

Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Abstract

Molecular modeling of corrosion inhibitors has gained momentum in the last decade. This paper describes various approaches, starting with the so-called MEPTIC (Molecular Electronic Properties To Inhibition-efficiency Correlation) approach that is among the most commonly used in the literature, and illuminates some pitfalls that appear more or less frequently therein, such as the "$\Delta N < 3.6$ rule", inferences based on correlations obtained for only a few inhibitors, attributing significance to total energies, reliance on too small differences, etc. The relevance of the often used molecular electronic parameters in the MEPTIC approach a
examined, because the basic premise of many modeling studies i
of inhibitor molecules. To this end, the conceptualization of mol
of the explicit modeling of inhibitor adsorption, either by quantu
molecular-dynamics methods, are discussed, such as the use of t
and solid/vacuum instead of electrified solid/liquid interfaces, ap
between physisorption and chemisorption, and bond-breaking an

Keywords: B. Modeling studies, C. Interfaces, C. Neutral inhibit

Corros. Sci. (2021) submitted

Molecular Modeling of Corrosion Inhibitors

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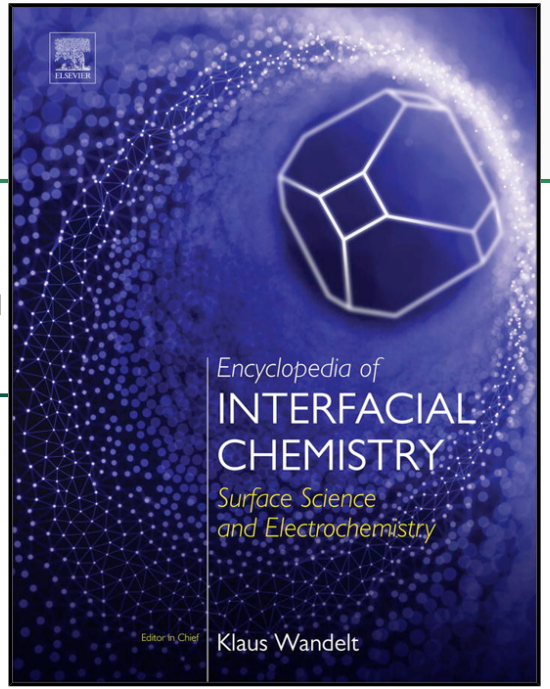
D Costa, Institut de Recherche de Chimie Paris/Research Group of Physical



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IJS

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Jožef Stefan Institute, Slovenia

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NWO Netherlands Organisation for Scientific Research

Thank you for your attention