« Réactivité de Surface d'Alumines : des Conditions UHV à l'Interface Solide-Liquide et de l'Oxyde Massif au Film Mince supporté »

Dominique Costa
Laboratoire de Physico-Chimie des Surfaces, UMR 7045
ENSCP Chimie-Paristech, 11 rue P. et M. Curie,
75005 Paris

IR
CP

Horizon 2014
Institut de Recherches Chimie Paris

- Chimie Théorique et Modélisation (CTM)
  (Carlo Adamo, Alain Fuchs, Dung Di Caprio)
- Interface Electrochimie, Energie (I2E)
  (B. Diawara, multi-échelle appliqué à la corrosion)
- Physico-Chimie des Surfaces
  (D. Costa, Réactivité de Surfaces, DFT)

Approche Multi-Echelle de la croissance de films passifs

Métal (MEAM)

Cr ou FeCr

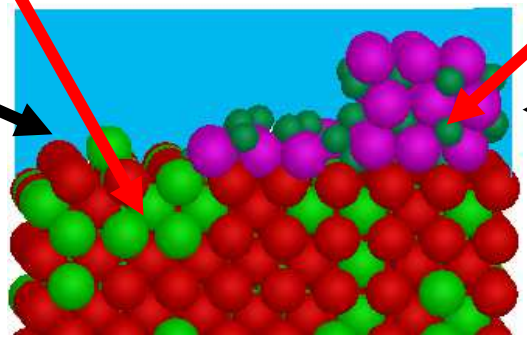
Oxyde (DFT)

Cr_2O_3

Dissolution

Diffusion de Surface

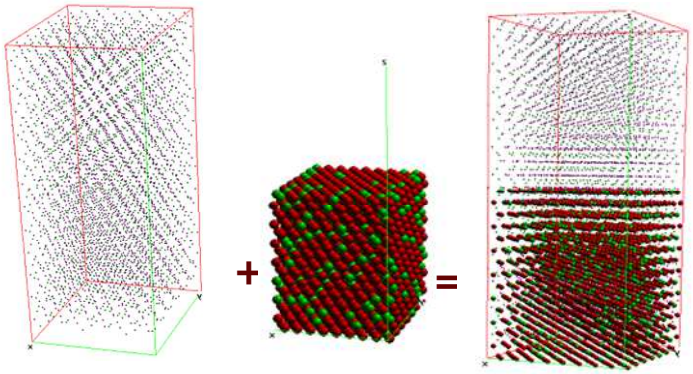
Diffusion de volume



Nucléation et croissance de la couche d'oxyde

- **Transfert électronique**
- **Formation des lacunes**
- **Diffusion ionique**

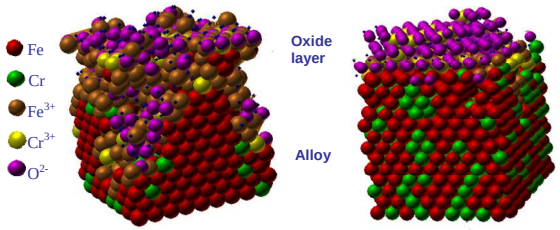
Simulation à l'échelle mésoscopique de la croissance du film passif



Virtual oxide lattice

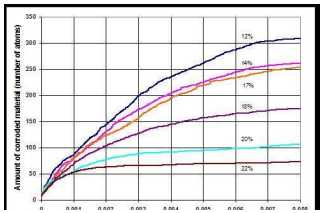
Alloy lattice

Alloy embedded in the virtual oxide lattice



(a) %Cr <14%)

(b) %Cr >16%)



Equipe de Physico-Chimie des Surfaces, Axe de Modélisation

- En résonance avec les grands axes de l'équipe de Physico-Chimie des Surfaces, il s'agit de décrire à l'échelle atomique la réactivité de surfaces métalliques et d'oxydes et de films minces d'oxydes sur métaux et alliages.

- L'accent est ainsi mis sur la **réactivité des oxydes vis-à-vis d'entités chimiques corrosives, ou inhibitrices de corrosion**, ainsi que sur la **compréhension des interactions molécules-surface pour de petites molécules organiques et d'intérêt biologique**.
- Le rôle du solvant (eau) dans les propriétés d'interface est pris en compte .

Oxide/Water Interfaces from Experiments

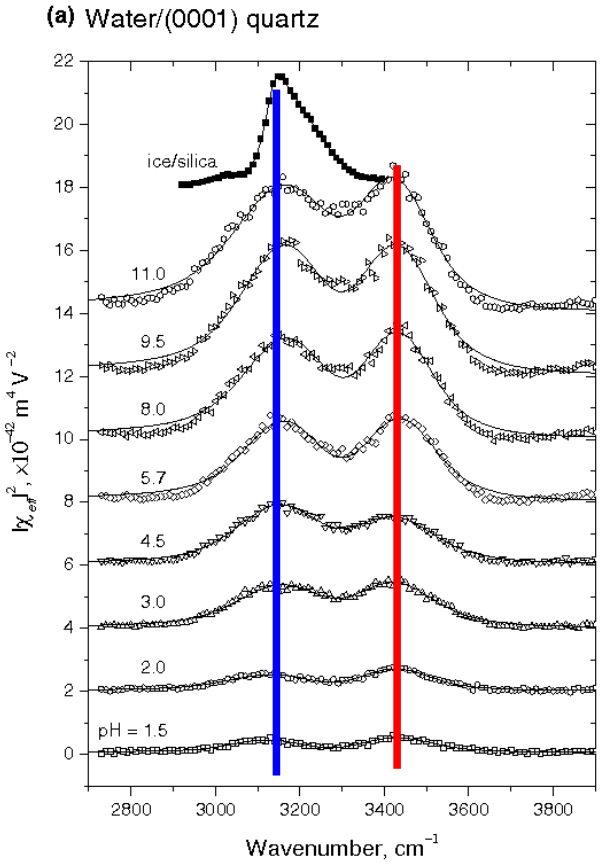
VSFG : Vibrational Sum Frequency Generation, non-linear spectroscopy

Exps : Shen et al. (USA)

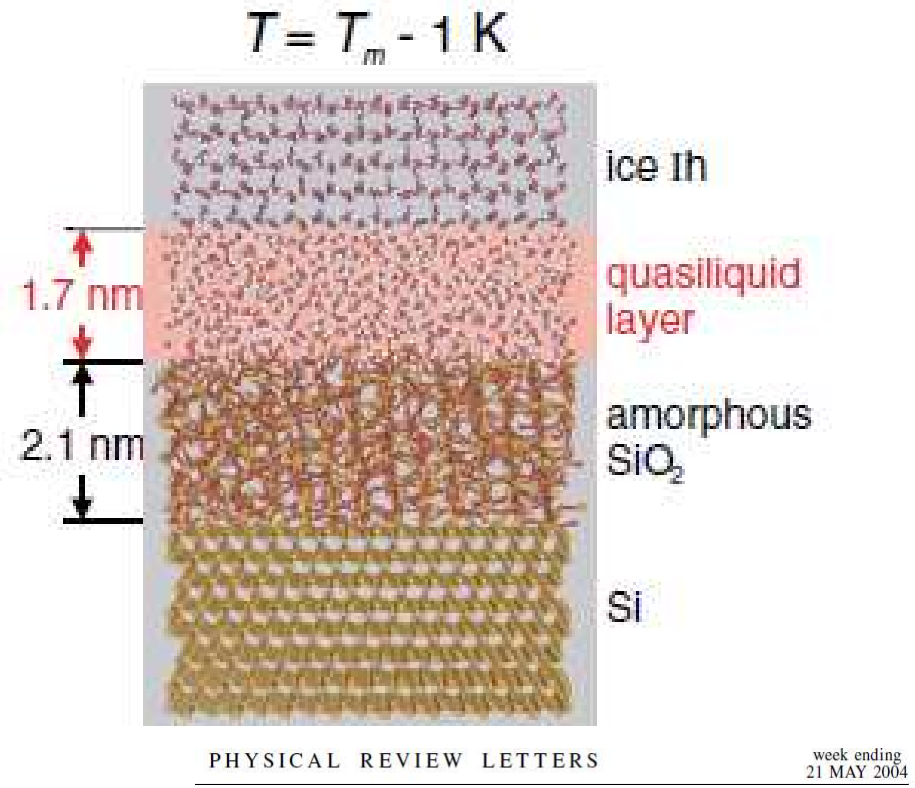
High Energy Transmission Reflexion

Exps : Engemann

Ice-like layer at the contact with Quartz

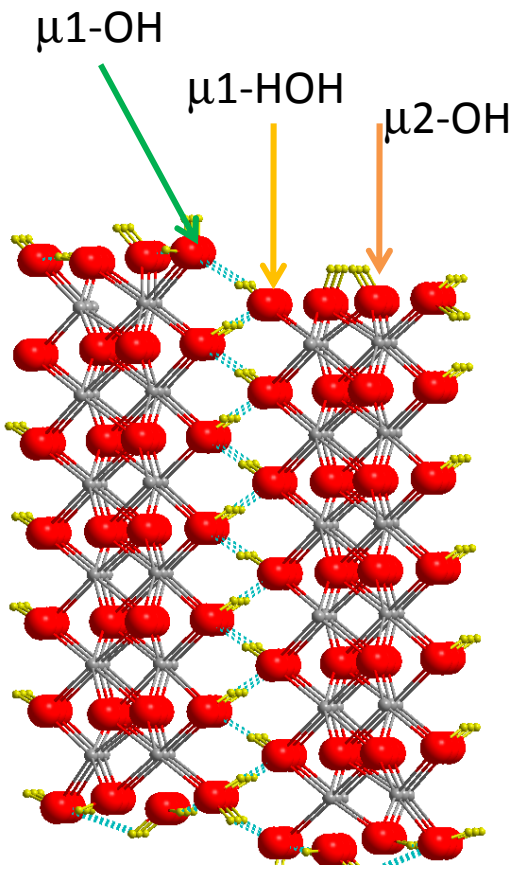


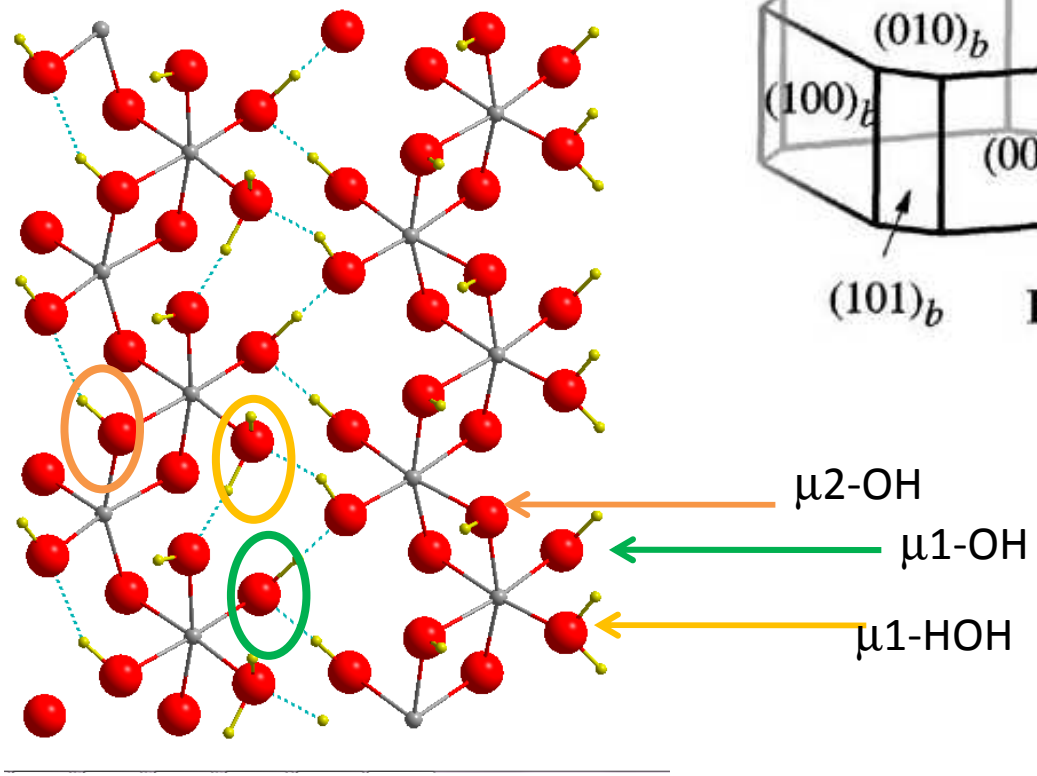
Liquid-like layer at the contact with amorphous

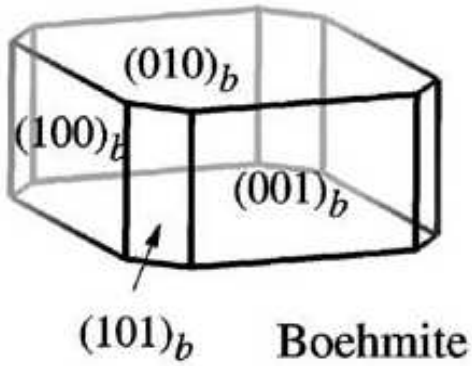


HARD MATTER HAS THE LAST WORD !

Boehmite (101) surface





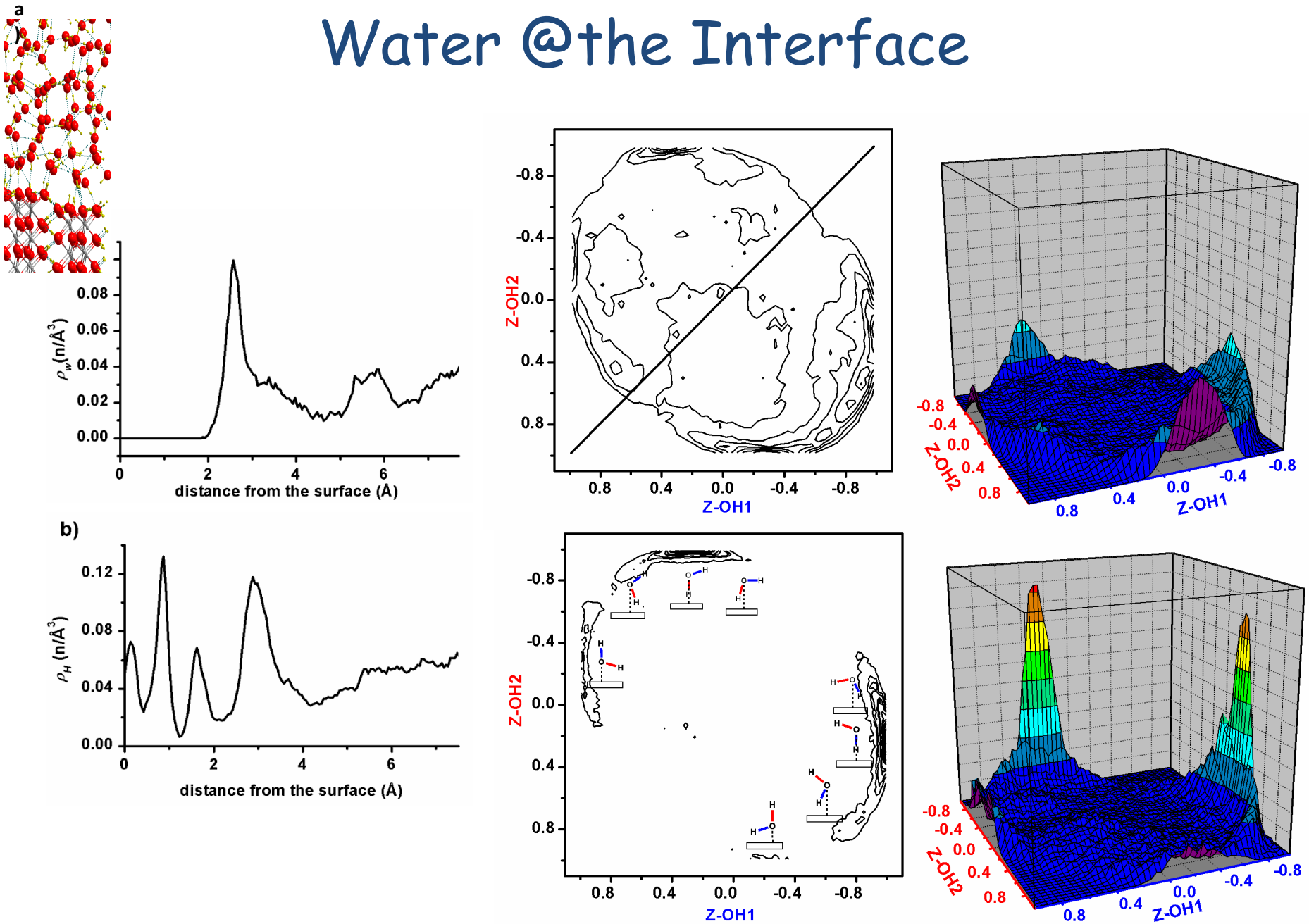


Three types of OH groups
Music's charge zero
pZc of boehmite 8-9

The Calculated Proton Association Constants for Several Important Surface Reactions at Various Important (Hydr)oxides[a]

Surface group	Formal charge	log K	L
Al–OH	$-\frac{1}{2}$	10.0	2.59
Al_2–O	−1	12.3	2.43
Al_2–OH	0	−1.5	2.43
Al_3–O	$-\frac{1}{2}$	2.2	2.49

Water @the Interface

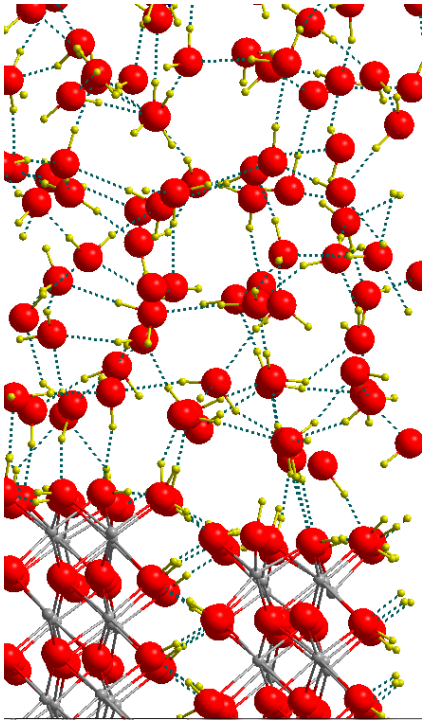


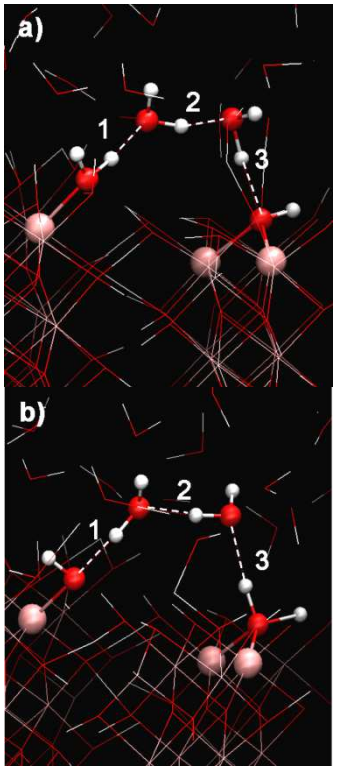
b)

Motta , Gaigeot, Costa, J. Phys. Chem C 2012

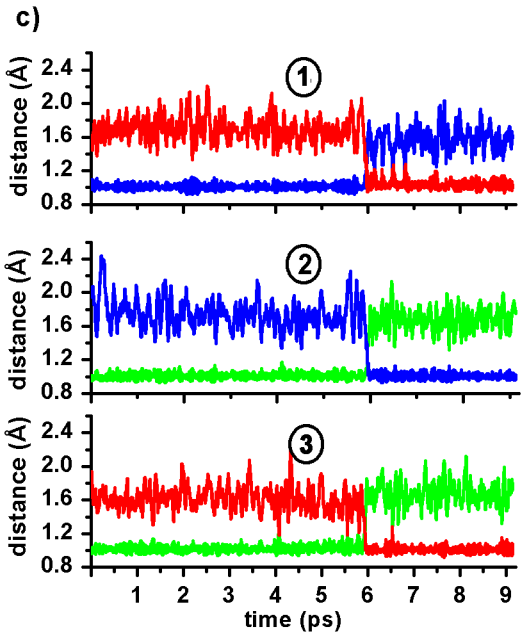
Conductivité protonique@steps

a)





Grotthus mechanism for H exchange



μ1-HOH + μ2-OH ⇌ μ1-OH + μ2-HOH ΔpK(μ1-OH) = 1.4

MUSIC predicts 2-3 units pK difference (Jolivet et al 2004)

Décembre 2013: Workshop « Oxydes/Solution » CFCAM, Paris

Ab Initio Study of the dioxygen reduction on oxidized Al at the solid-liquid interface

T. Ribeiro, D. Costa, F. Mercuri, G. Pacchioni, S. Zanna, M-P. Gaigeot, P. Marcus

- Cathodic reduction of O_2
- The metal is covered with an oxide film
- Water

- Ab initio modeling of complex aspects:

cathodic reduction on a metal covered with an oxide film on metal in the presence of solvent

Experimental Evidence (XPS)

- Al_2O_3/Al, Al-rich, reactivity towards O_3 and Cl_2
- Oxide film 20Å, non reactive towards O_2, reactive towards O_3, inner barrier with a high potential drop

10312 *Langmuir, Vol. 16, No. 26, 2000*

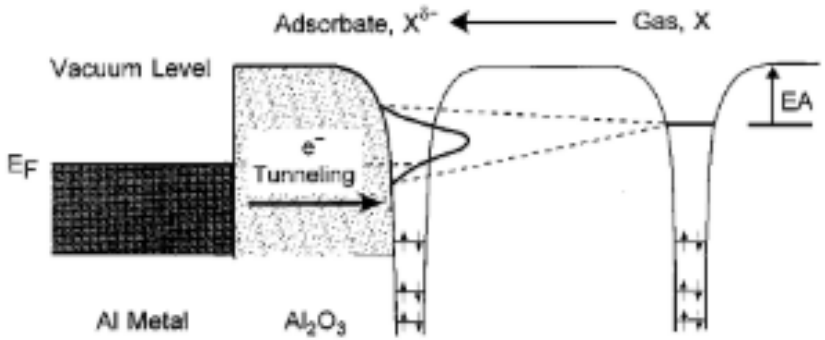
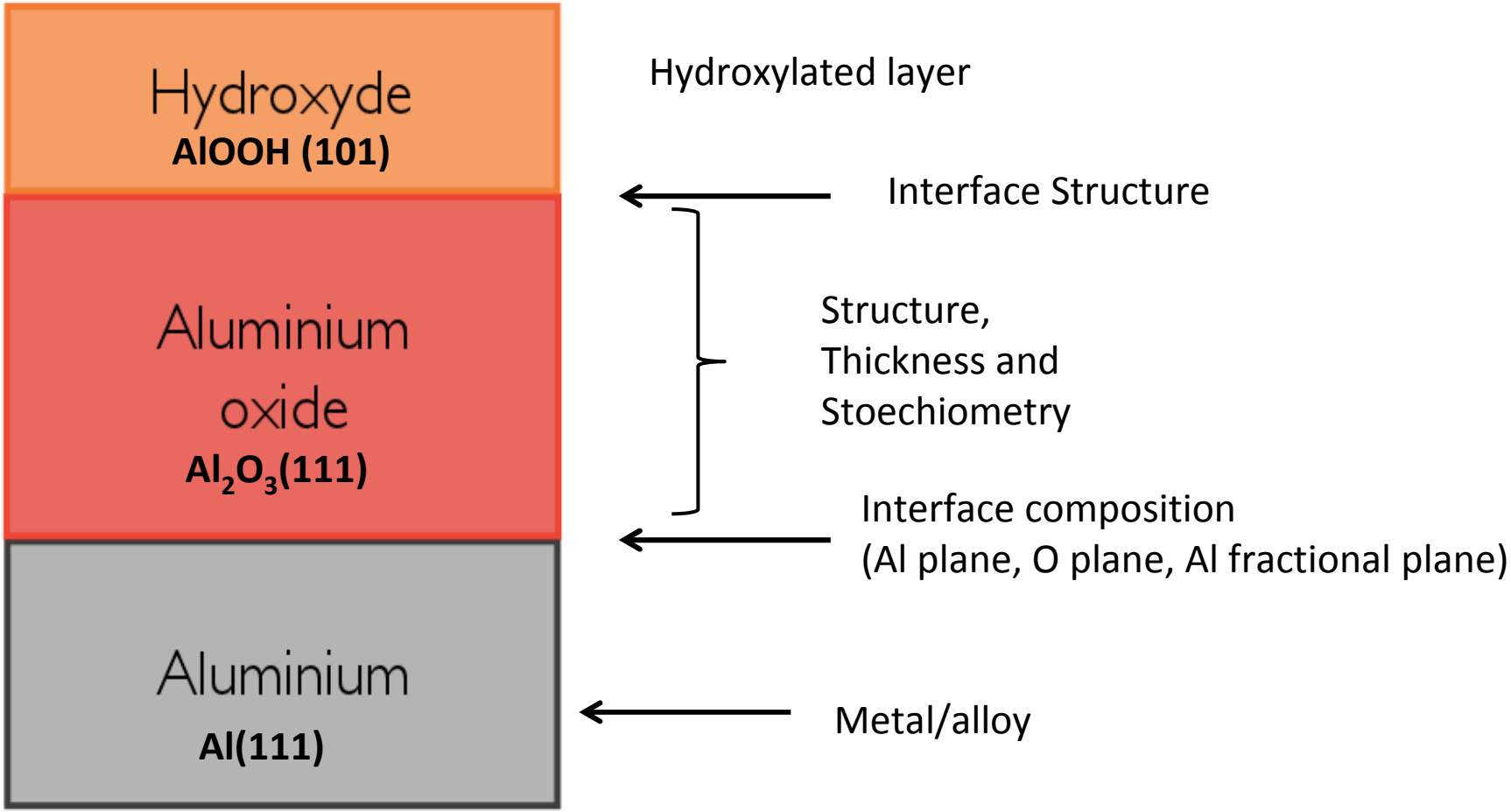


Figure 6. Schematic potential energy diagram of electron tunneling from the Al metal to the broadened and lowered affinity level of the X molecule. The tunneling causes charging of the adsorbed molecules ($X^{\delta-}$).

Model Elaboration

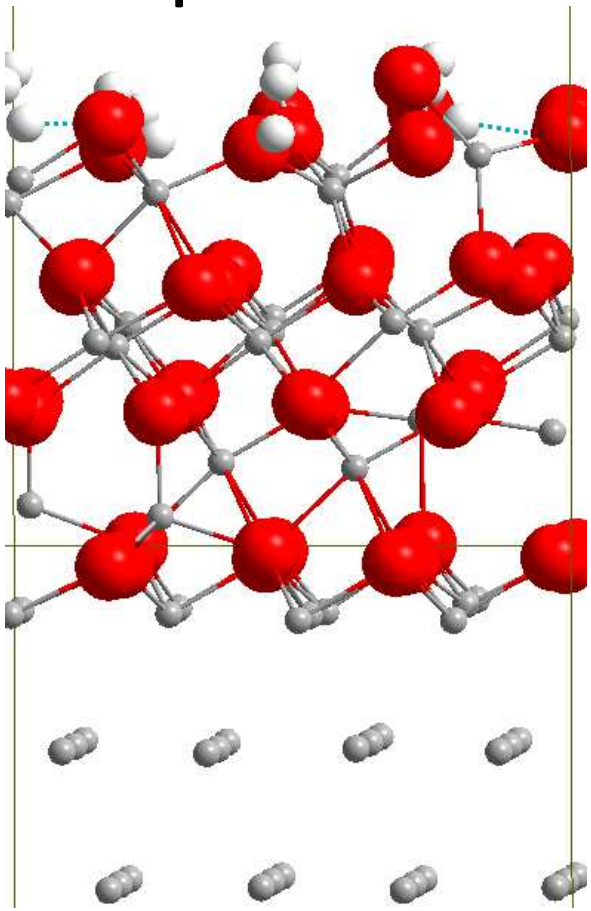
A tuneable Model of Epitaxial Al(111)/γ-Al_2O_3(111)/AlOOH



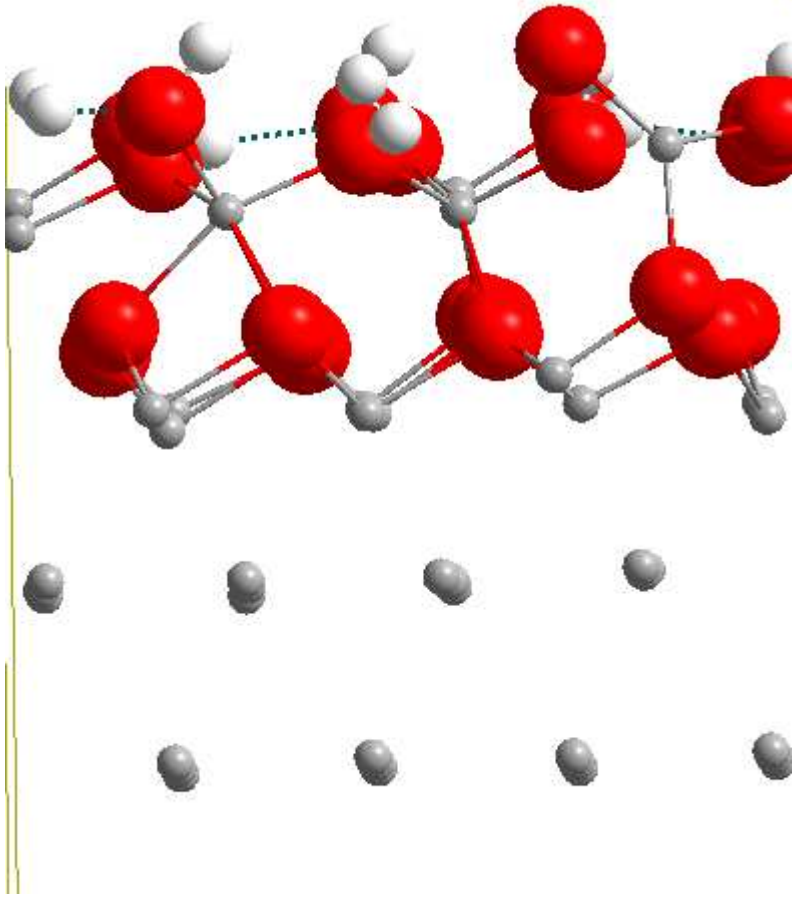
Several films are built to account for different thermodynamical conditions (O_2, H_2O)

Films modélisés (1)

Film Epais 9Å



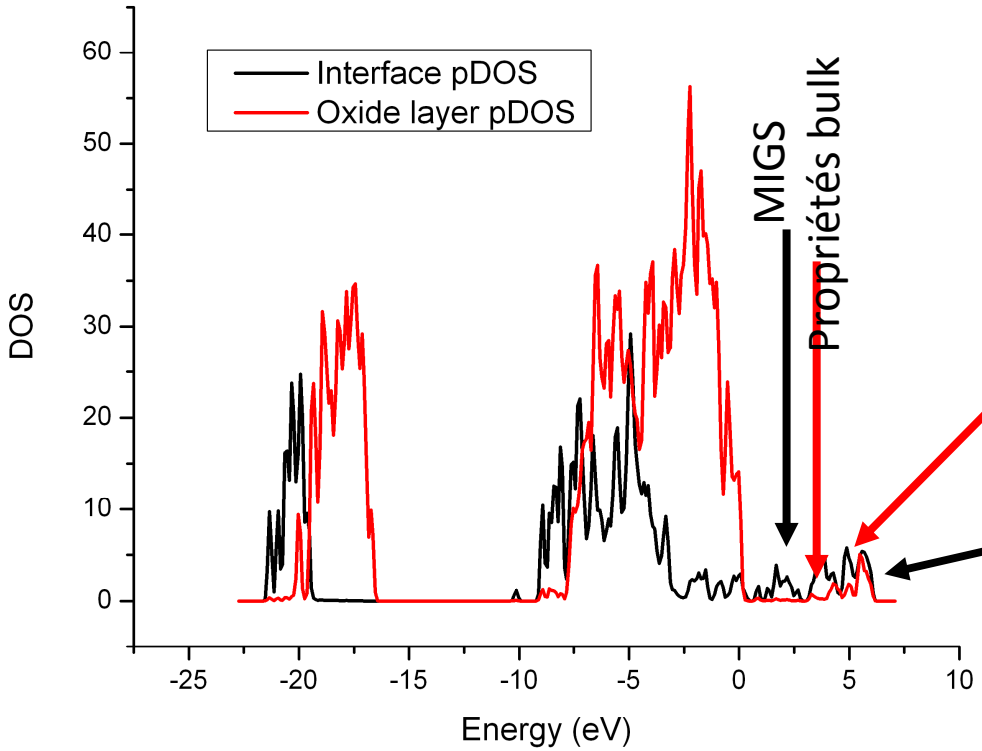
mince Al-rich 4.8Å

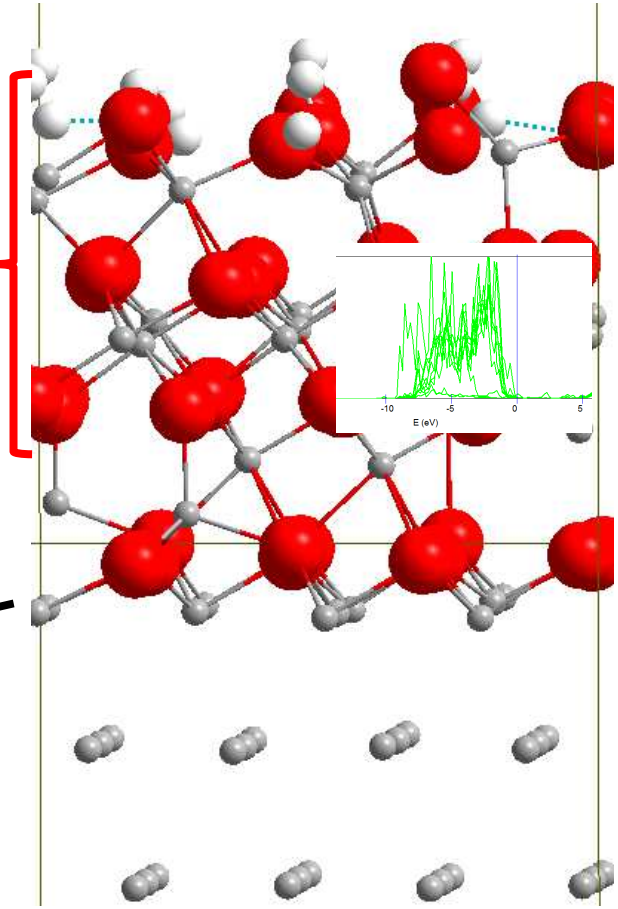


Φ_e = 6.35 eV

4.16eV

DOS du Film Epais

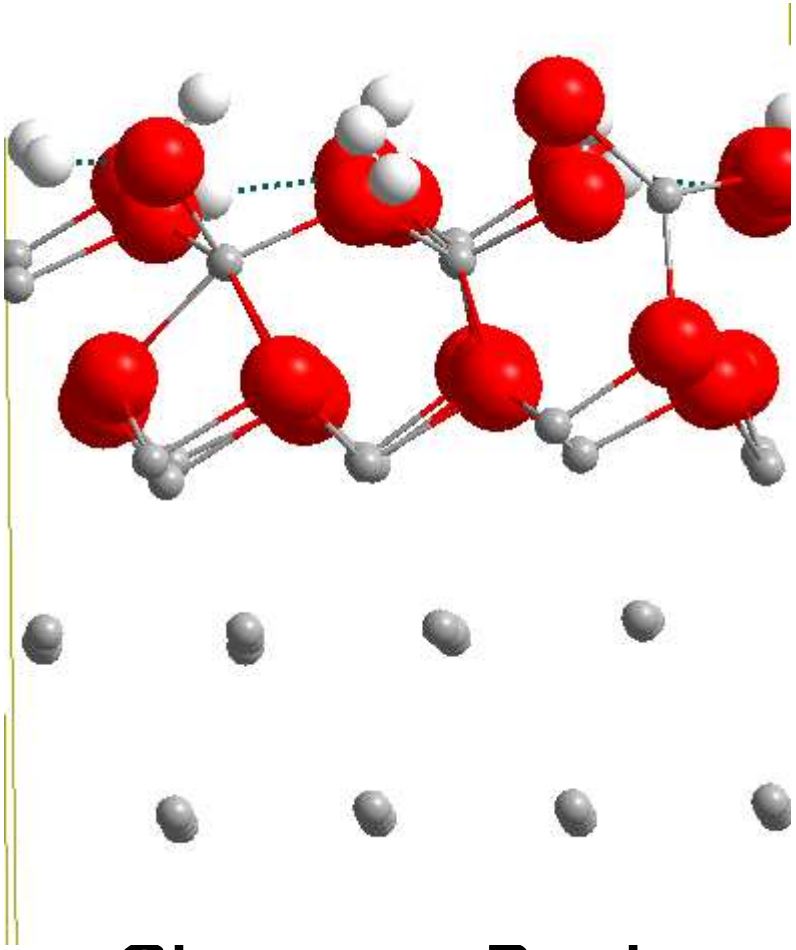


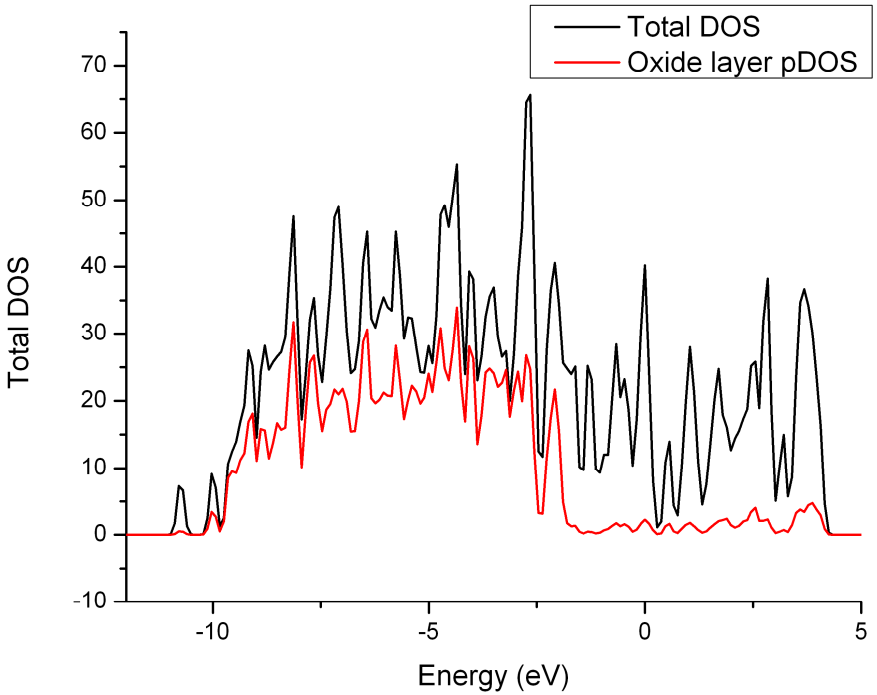


Charges Bader: Transfert film-> métal

Film Mince

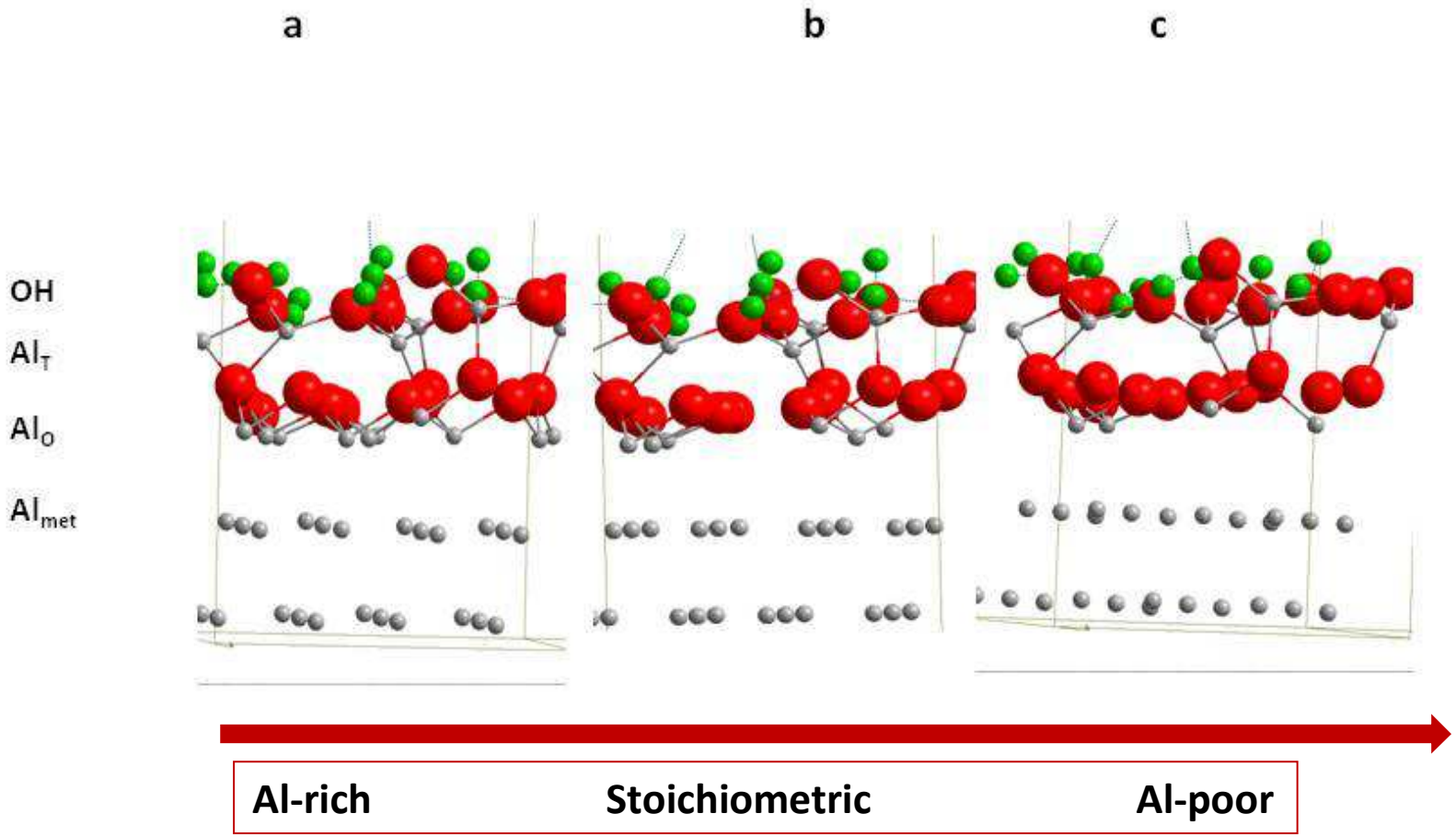
Mince Al-rich





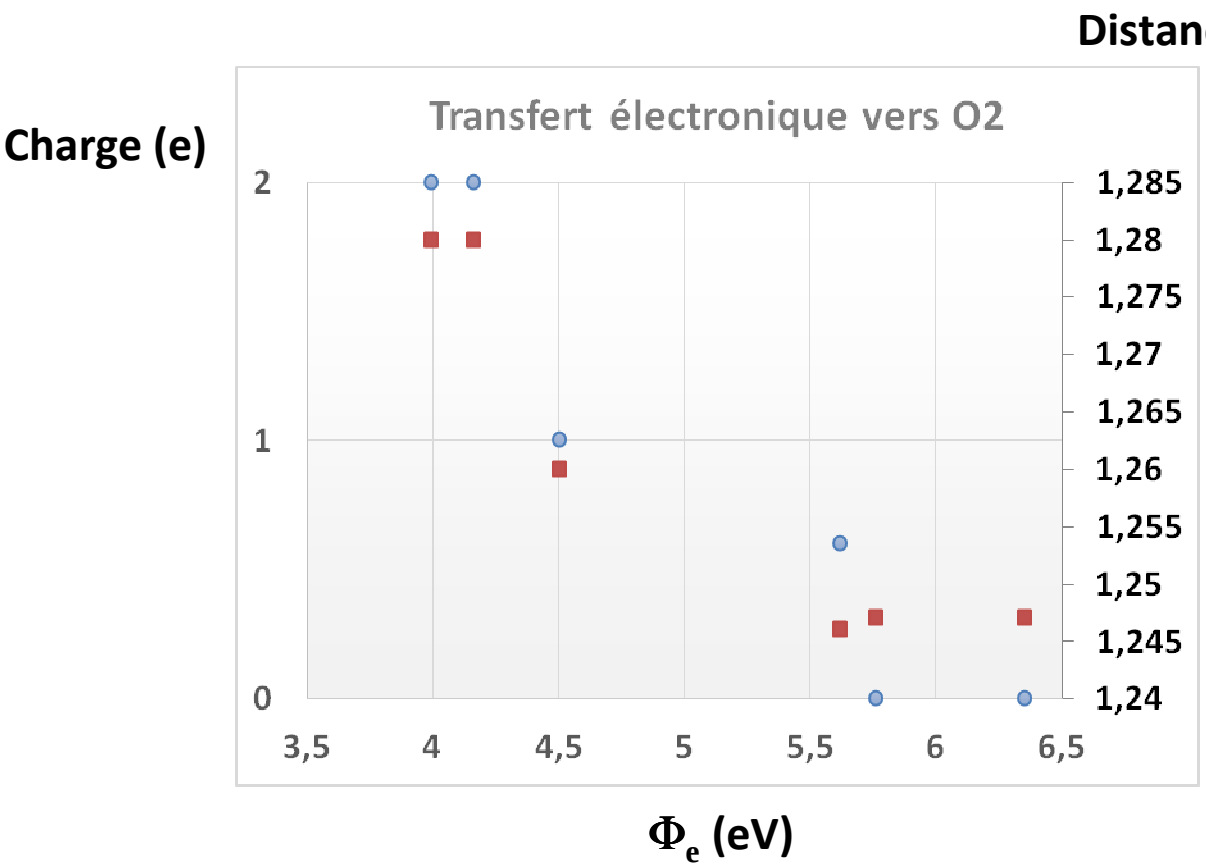
Charges Bader: Transfert métal->film

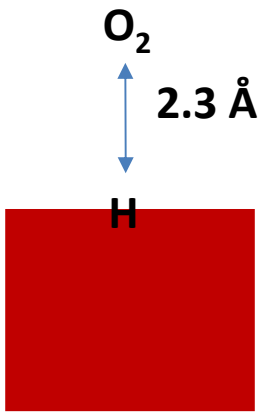
Films modélisés (2)



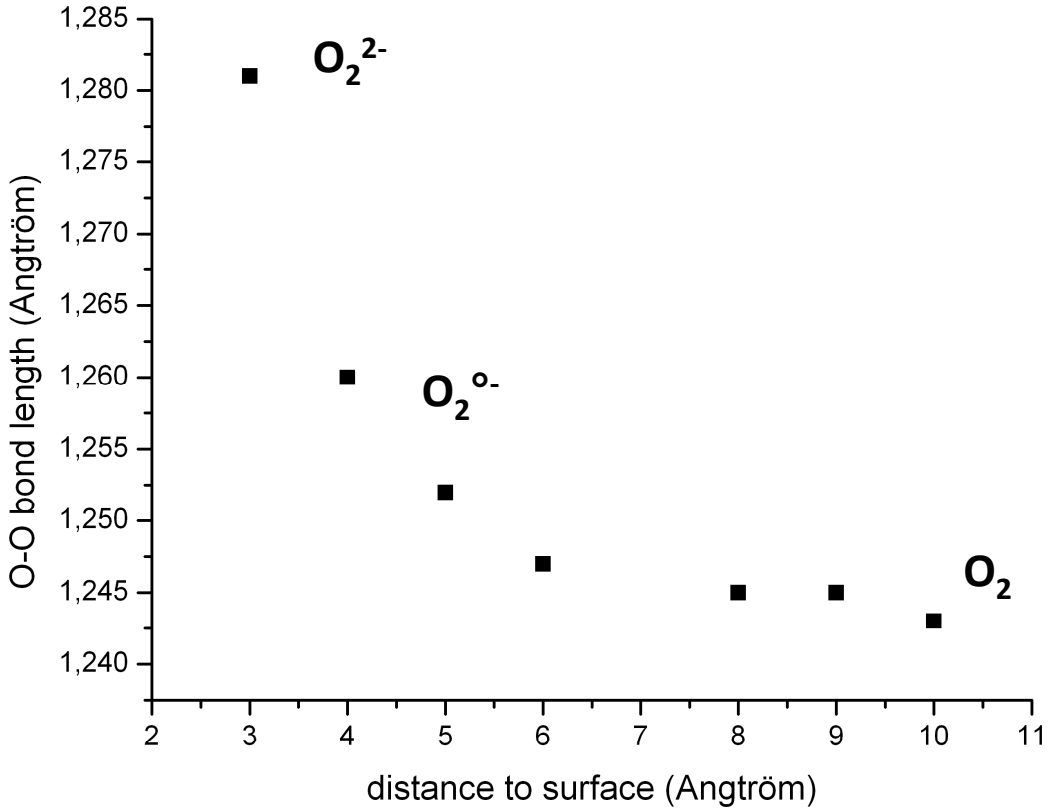
Φ_e = 4.16 eV 5.62eV 5.76 eV

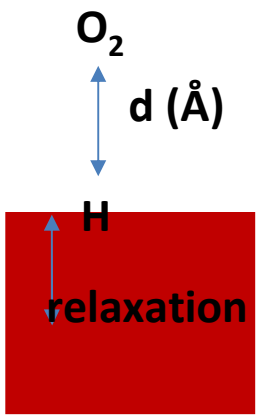
Transfert de charge vers O_2





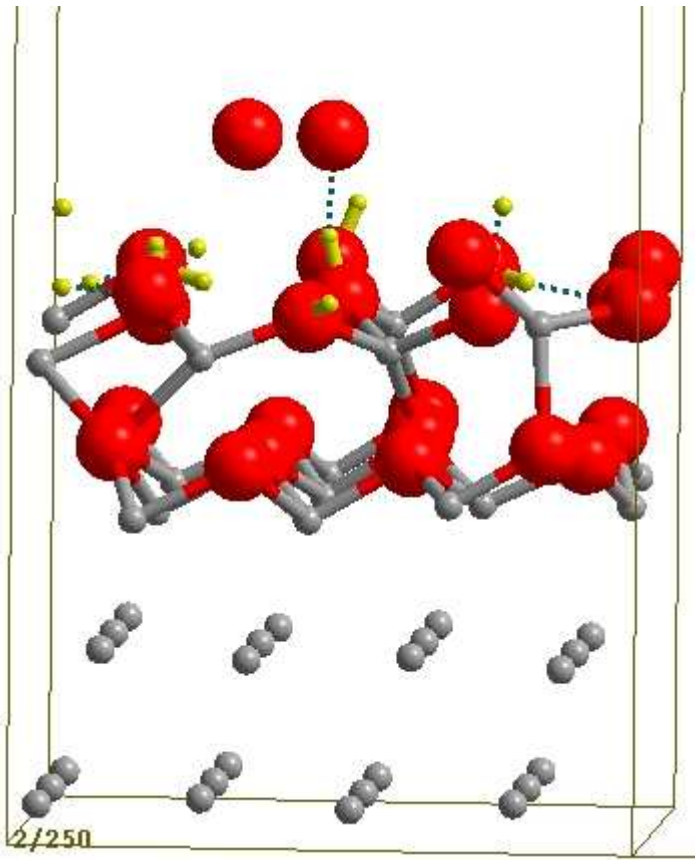
$Er = EA(O_2) - \Phi e + Erelax$, film mince Al-rich





O_2 Reduction, a two e- process

- $O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$ and $H_2O_2 + 2e^- + 2H^+ \rightarrow 2\ H_2O$
- Spontaneous reactions, no activation barrier
- ΔE_{react}= -4.3 (-5.8)eV
- Hydroxylated oxide acts as a proton reservoir
- Bader charge analysis shows that electrons originate from the interface layer and surface

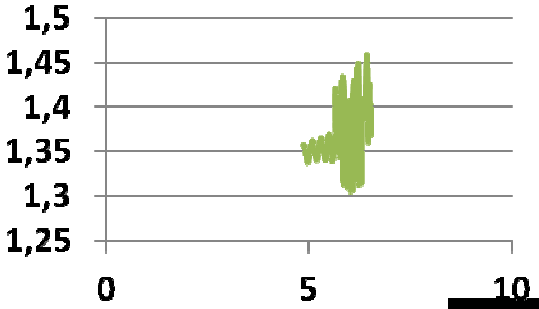


Acidic character of the hydroxylated oxide.

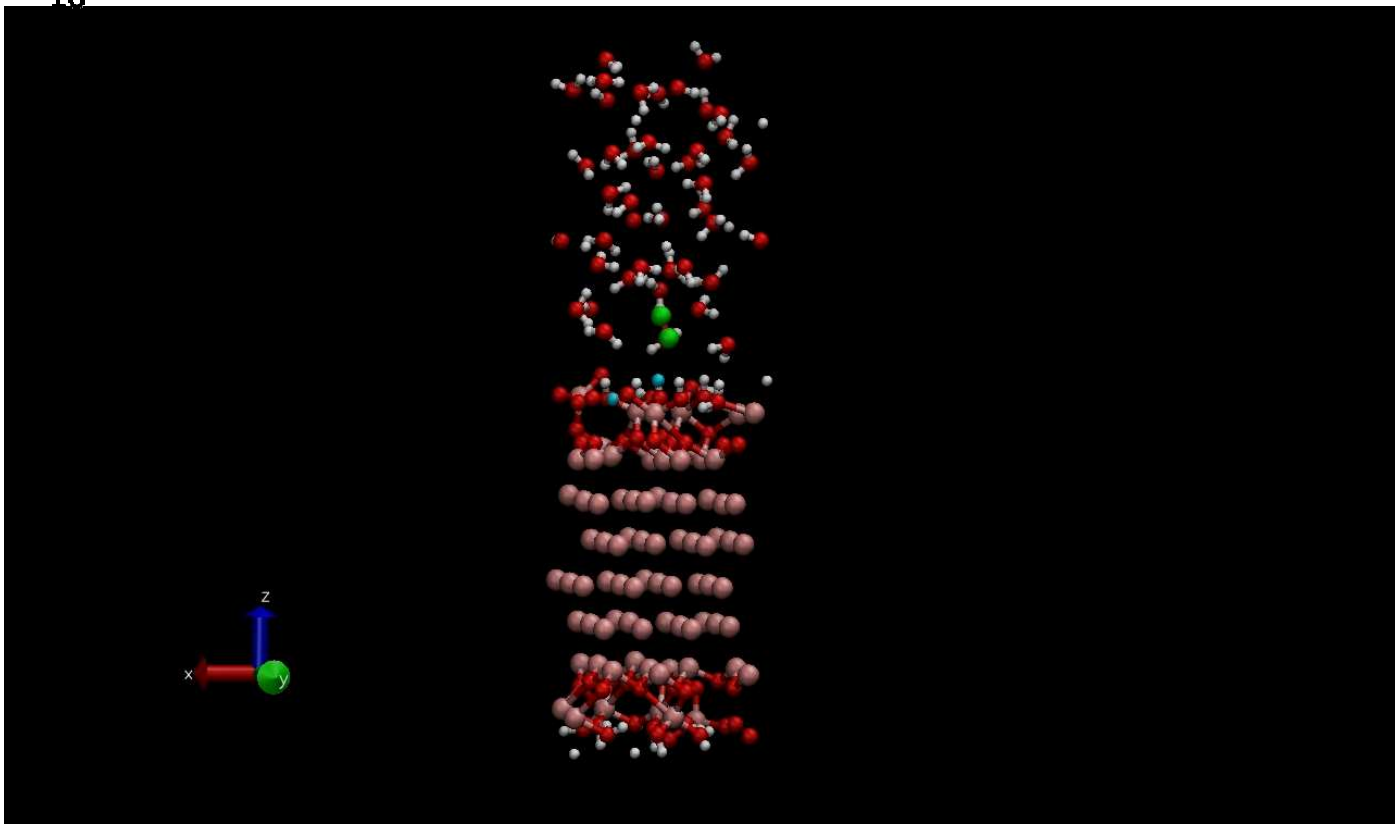
O_2@MgO/Mo; O_2@MgO/Ag

Frondelius et al, *Phys. Chem. Chem. Phys.,* 2010, 12, 1483

O_2 reduction at the Al_2O_3-Water interface



Transfer of e- to O_2 occurs even at 7 Å from the surface



Merci pour votre Attention