Interfaces entre des solides d'oxydes et l'eau liquide étudiées par dynamiques moléculaires DFT-MD

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ATIGE

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Expertise

Group : 9 permanent researchers, 3 Post-Doc, 3 PhD
Theoretical and Computational Chemistry
Multi-Scaling Molecular Dynamics (MD) Simulations

DFT-based MD

Classical MD Cℓ-MD
Force Fields Development

Coarse grained MD

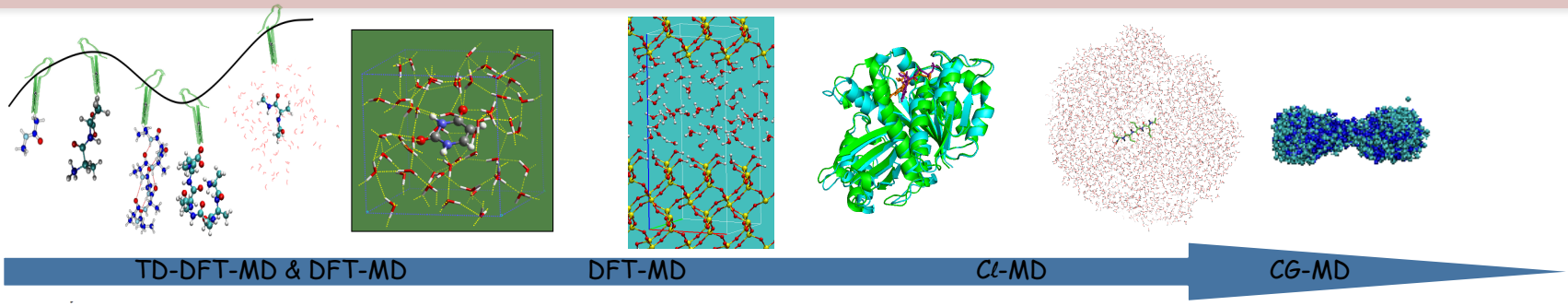
Biased MD

Tackle several size- and time- scales

Tackle a large range of properties
in chemistry & physics

Structure | Dynamics | Chemical Reactivity | Proton Transfers | Thermodynamics | Fragmentation | Vibrational Spectroscopy | Mass Spectrometry

Gas phase, liquids, interfaces, clusters, biomolecules, proteins embedded in droplets



User and Developer of Theoretical Methods & Analysis Methods

User and Developer of Numerical Codes [CpH-MD, MDVRY, MCClus, MDClus]

Theory useful for the interpretation of experiments

Specialist of Theoretical Vibrational Spectroscopy :
extract & interpret signals from MD, including T°, anharmonicities and couplings to environments

Motivations for investigating solid/liquid and liquid/air interfaces

Structure and dynamics of the liquid at the interface

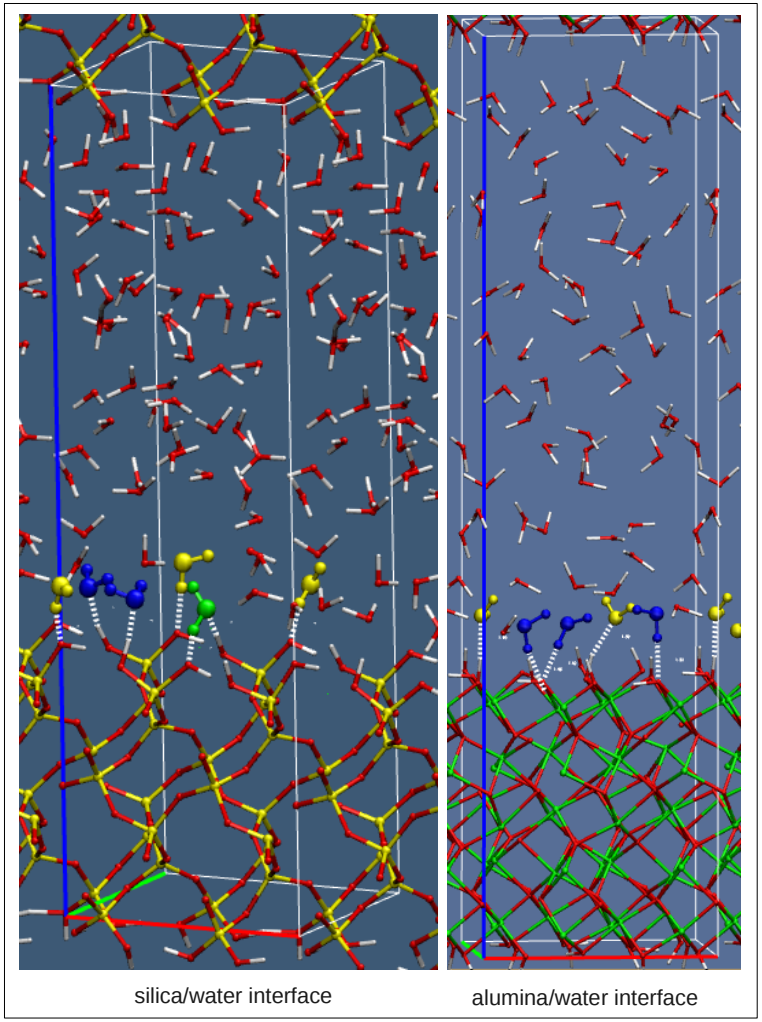
Structure of the solid at the interface

pKa of sites at the solid/liquid interface, links with the organisation of the liquid at the interface

Organisation of ions, electrolytes, organic molecules at the interface

Chemical reactivity at the interface

One pivotal probe: vibrational spectroscopy at the interface extracted from the dynamics.
Synergy with experiments of vibrational spectroscopy, coupling simulations and experiments.



Theoretical methodology : DFT-based MD (semi-empirical MD)

DFT-MD of Solid oxides/water interfaces

Coll. M. Sulpizi (Mainz, Germany), M. Sprik (Cambridge, UK),
J. Phys. Cond Matter 2012, J.C.T.C. 2012
CP2K package, BOMD, BLYP+Dispersion, 400 atoms in the cell, 330 K

α-quartz Surface (0001)

α-quartz : (0001) hexagonal Surface

Supercell : 9.820 X 8.504 X 22.300 $Å^3$

Fully hydroxilated surface

400 atoms simulated

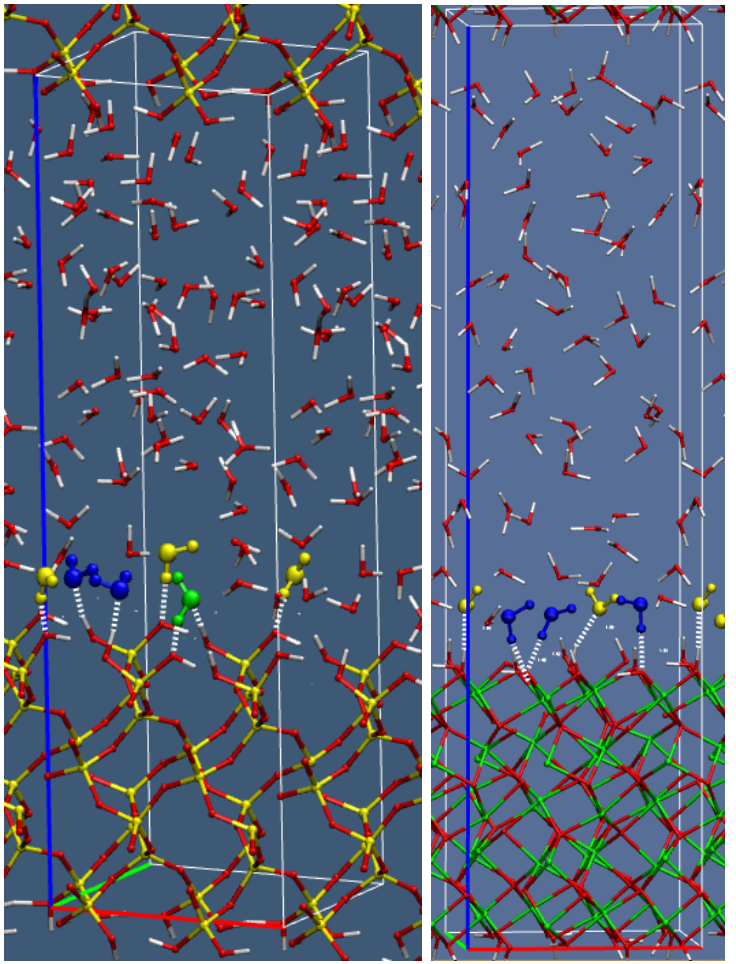
α-alumina Surface (0001)

α-alumina (corundum) : R-3c space group

Supercell : 9.514 X 8.239 X 25.237 $Å^3$

Fully hydroxilated surface

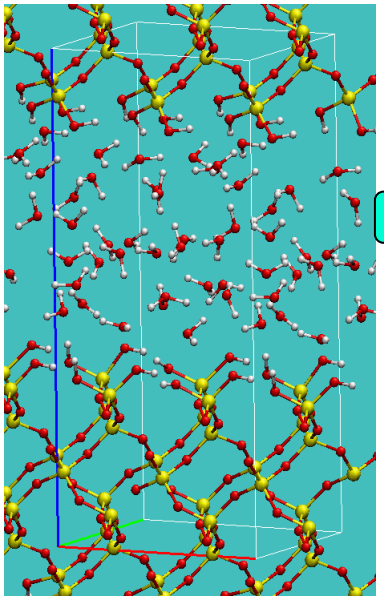
400 atoms simulated

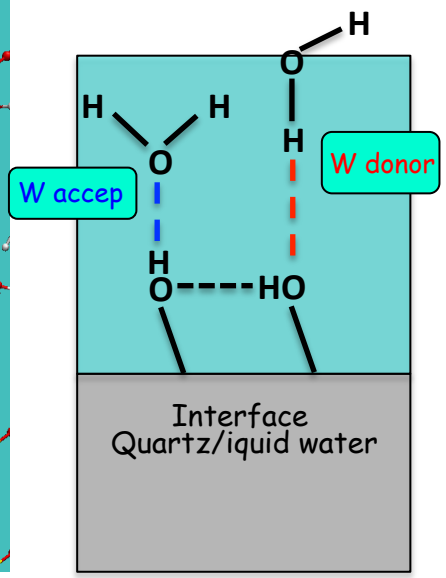


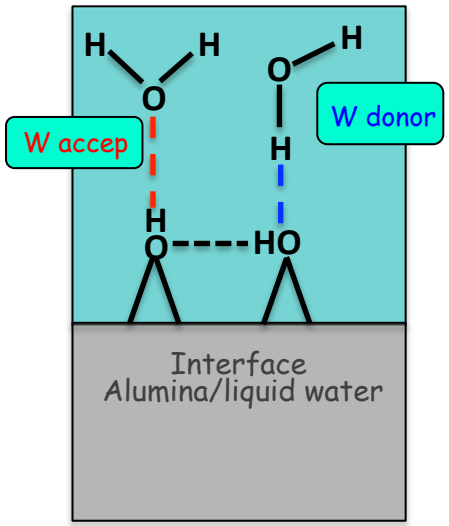
silica/water interface

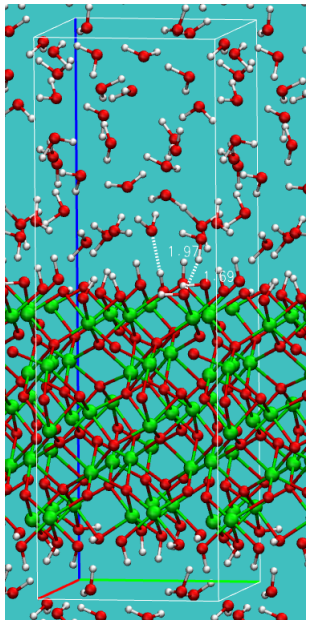
alumina/water interface

Hydrogen bond strengths of water at solid interfaces : silica oxide/ and alumina oxide/ water interfaces









Water donor

Hw … O(Sil) HB 1.82 Å

Hw-Ow 0.988Å

« Weak Hbonds »

« liquid like »

Water acceptor

Ow … HO(Al) HB 2.00 Å

Hw-Ow 0.994 Å

Water acceptor

Ow … H(Sil) HB 1.64 Å

Hw-Ow 0.996Å

« Strong Hbonds »

« icelike »

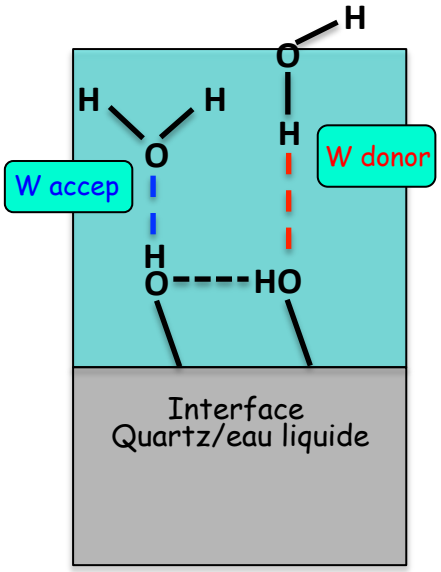
Water donor

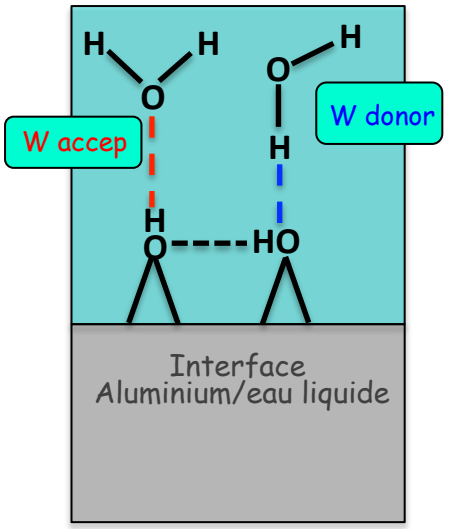
Hw … OH(Al) HB 1.70 Å

Hw-Ow 1.004 Å

Reversal of role & properties of water molecules acceptor/donor of Hbonds at the 2 interfaces

pKa calculations of surface sites : silica oxide/ and alumina oxide/ water interfaces





pKa of Silanols : 5.6 (our calculation)

Acidic
Easily release a proton in solvent
➔ Strong Hbond with water

pKa of Aluminols : 16.6 (our calculation)

Basic
Does not easily release a proton in solvent
➔ Weaker Hbond with water

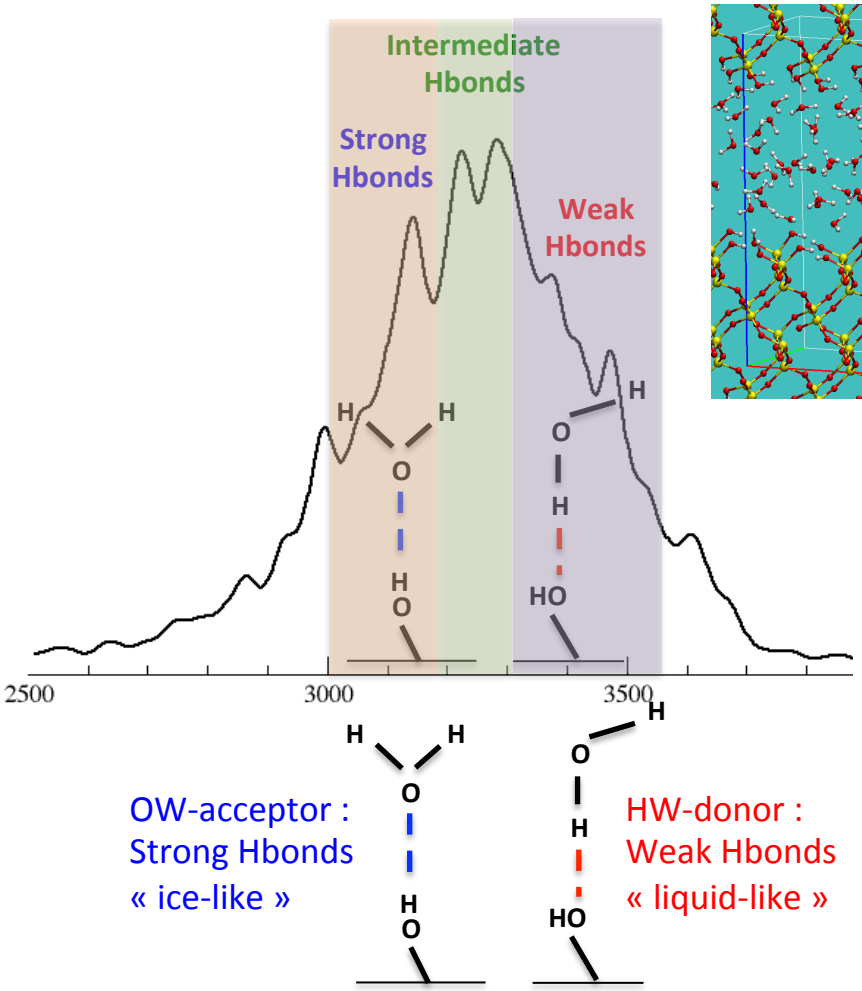
Structural properties/HBonds of first interfacial layer are consistent with pKa values of surface hydroxyl groups at the interface

Acid/Basic characters of Silanols/Aluminols determine/« dictate » the arrangement of the water molecules Hbonded to the surface and modulate the water properties

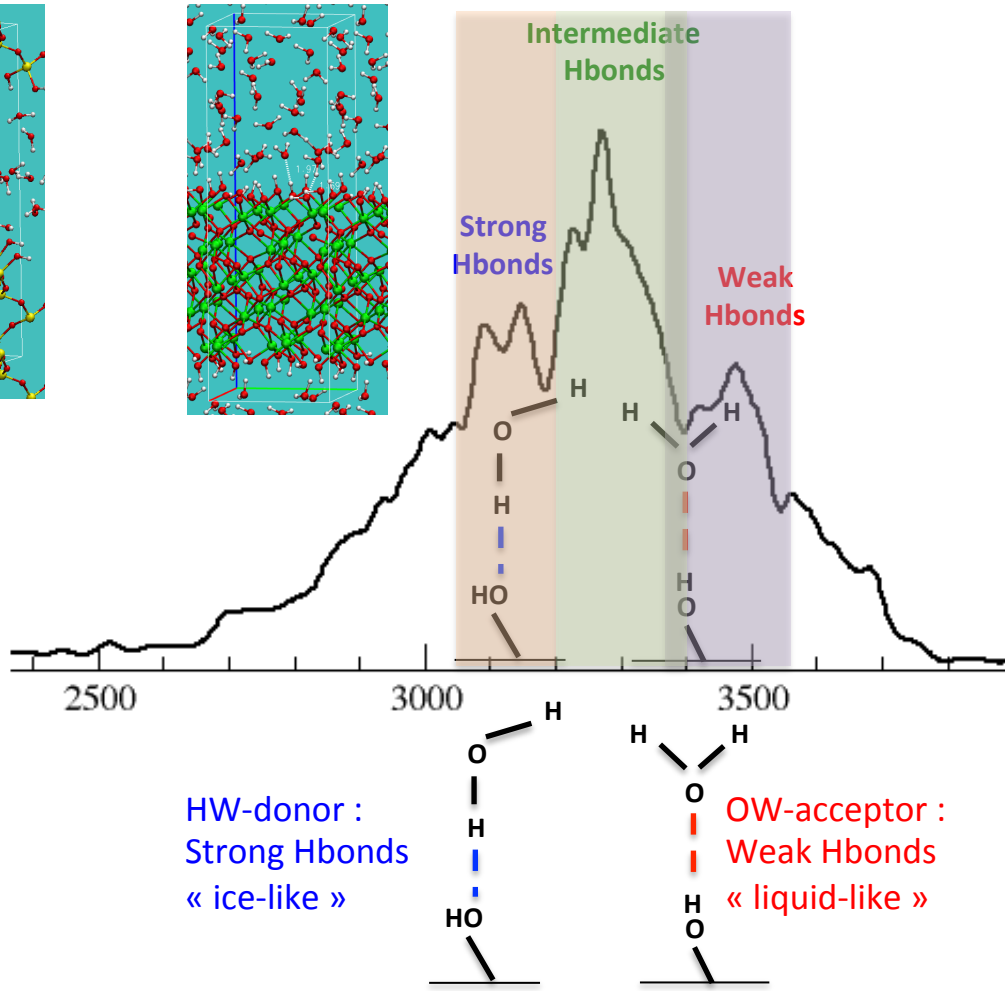
Vibrational IR signatures of water at solid/liquid interfaces

$$I(\omega) = \alpha(\omega) n(\omega) = \frac{2\pi\omega\left(1 - e^{-\beta h\omega}\right)\mathcal{D}(\omega)}{3hcV} \int_{-\infty}^{+\infty} \mathrm{dt} \left\langle \vec{M}(t).\vec{M}(0) \right\rangle e^{i\omega t}$$

Interface Quartz/liquid water



Interface Alumina/liquid water



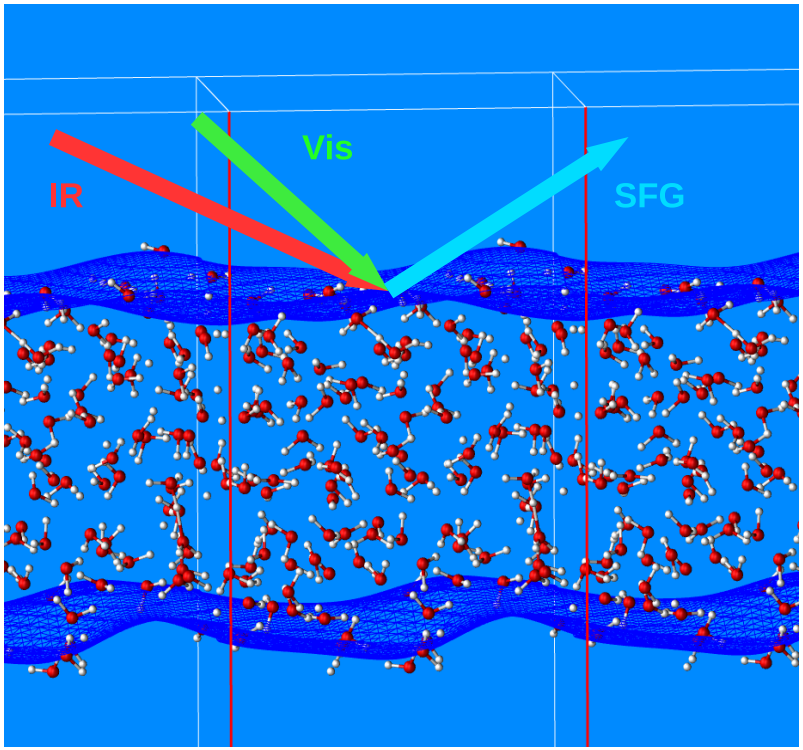
Reversal of H-bond signatures between the two interfaces : donor/acceptor - weak/strong H-bonds

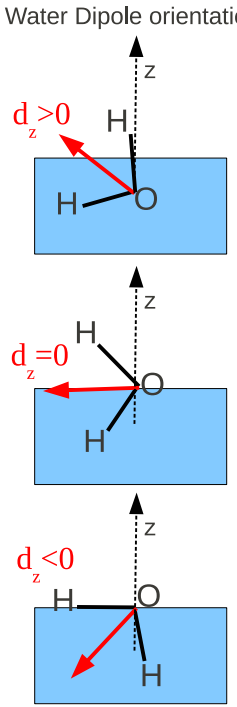
→ Interpretation of SFG signatures from DFT-MD of the interfaces (+true signal under calculation)

VSFG Spectroscopy at the liquid water/air interface

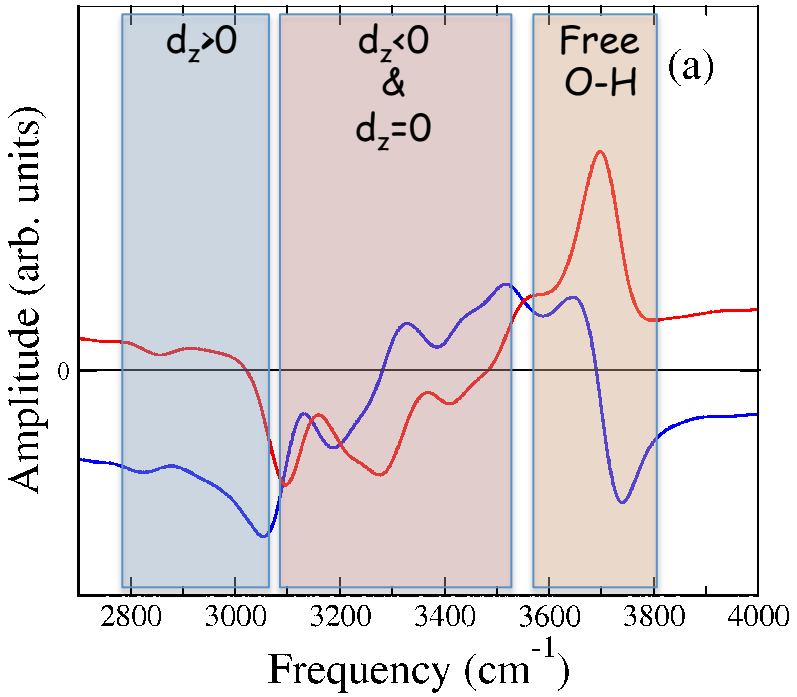
Coll. M. Sulpizi (Mainz, Germany), M. Sprik (Cambridge, UK), Salanne (Paris)
J. Phys. Chem. Letters 2013

$$\chi_{ijk}(\omega) = \frac{i\omega}{k_B T} \int_0^\infty dt\ exp(i\omega t) \sum_{m=1}^{Nmol} \sum_{l=1}^{Nmol} \boxed{< \delta\alpha_{ij}^m\ \delta\mu_k^l >}$$





phase resolved :
real & imaginary parts



Theoretical IR & Raman spectra → interface thickness of 2-3 ang

[Assignments on imaginary part (red)]

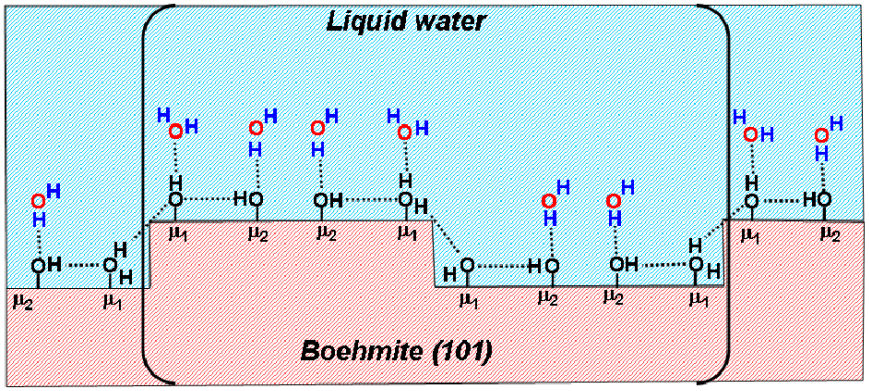
Interfacial water molecules : almost no Hbond within the interface ;
mostly Hbonded with the subsequent liquid layer

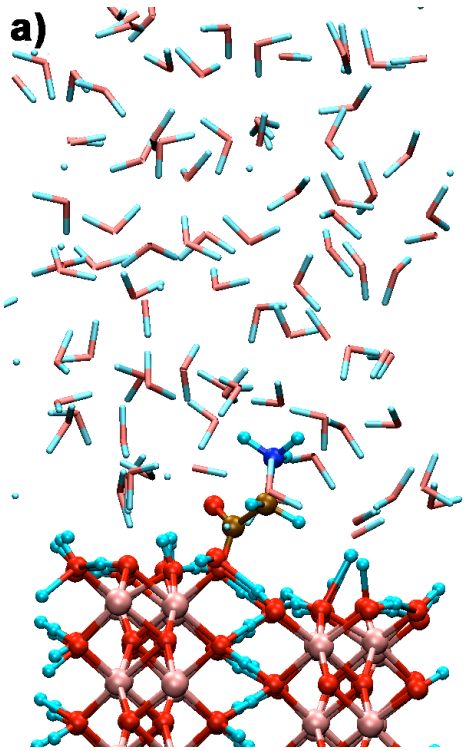
DFT-MD of boehmite/water interface and the adsorption of glycine

Coll. D. Costa (ENSCP ParisTech), JPCC 2012 (116:12514, 116:23418)

CP2K package, BOMD, BLYP + D2, 640 atoms in the cell, 330 K
Supercell : 14.05 X 11.70 X 32.4845 $Å^3$

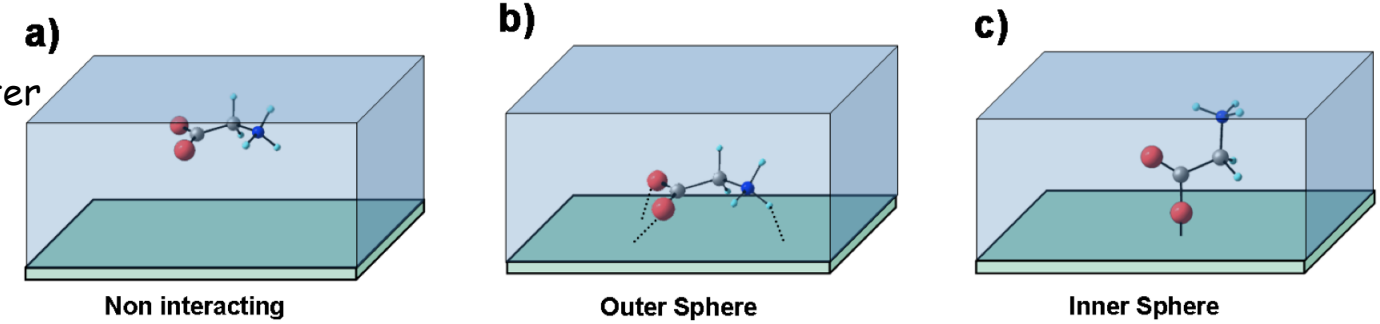
Hydroxylations of boehmite at the aqueous interface
& organisation of interfacial water molecules
(JPCC 2012 116:12514)



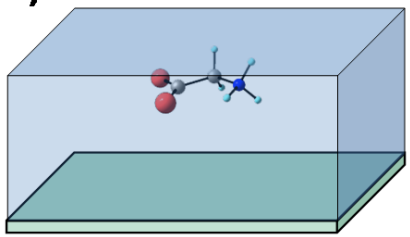


Energetically most favorable adsorption mode of Glycine at the aqueous boehmite/water interface?

(JPCC 2012 116:23418)



a)

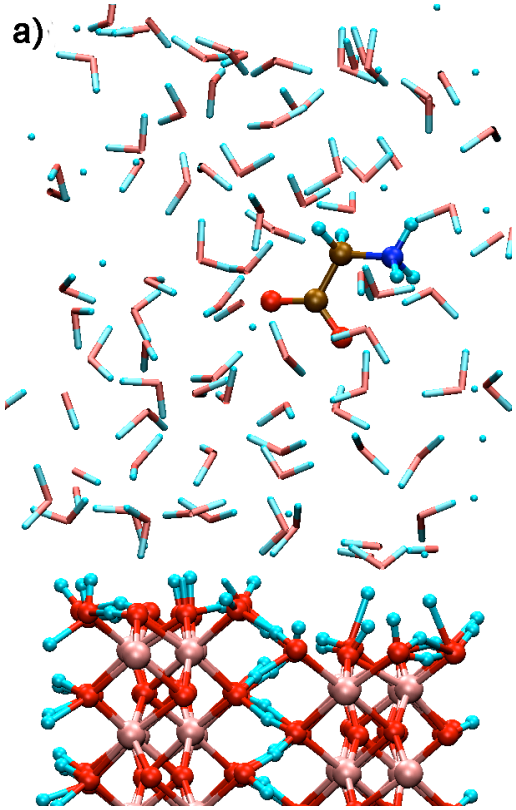


Non interacting

Organisation of solvent around Glycine

(radial distribution functions)

a)



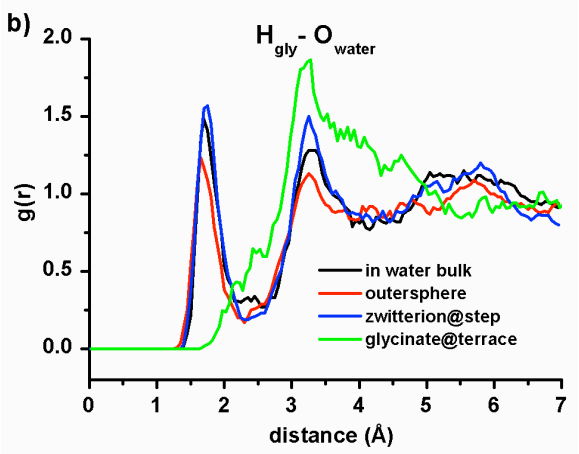
Glycine is a Zwitterion

NH_3^+ : 3*0.95 H-bonds to H_2O in total

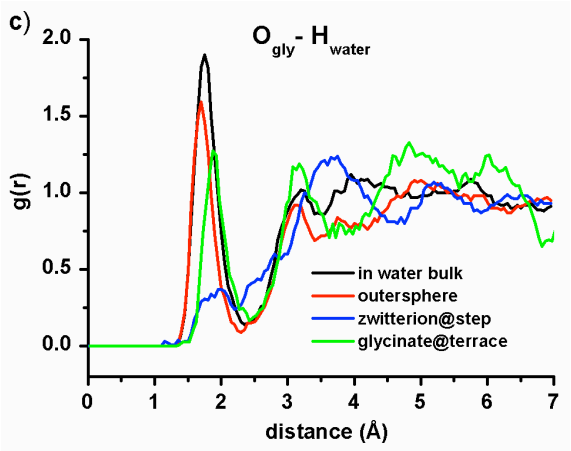
COO^- : 2*2.3 H-bonds to H_2O in total

Same results as for DFT-MD of Gly in liquid water

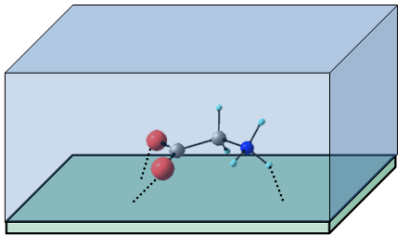
b)



c)

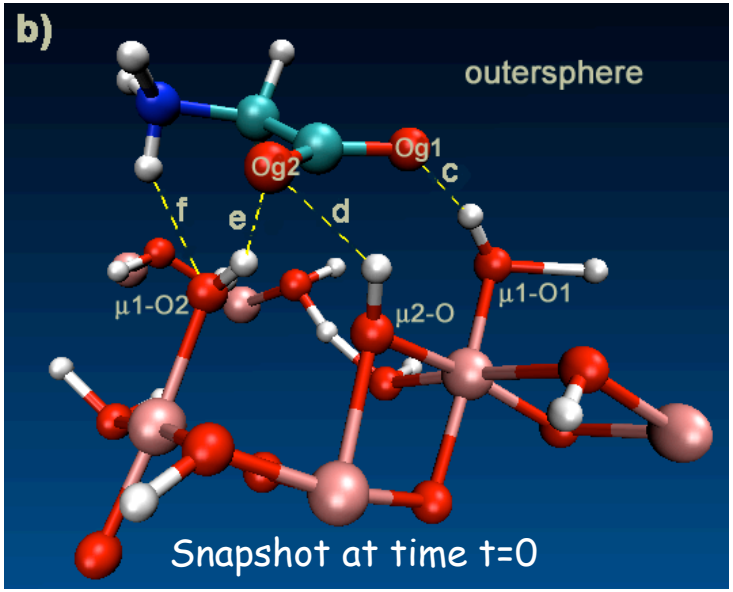


b)

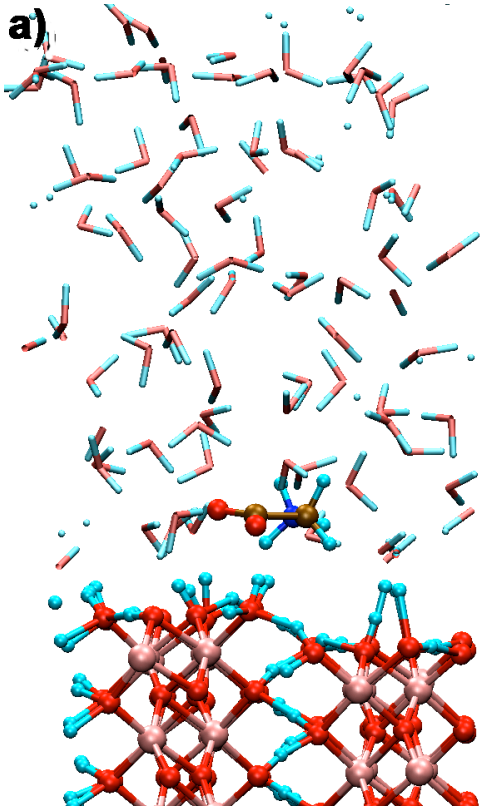


Outer Sphere

Organisation of Hbonds Gly-Water & Gly-Boehmite



a)



Gly : general orientation parallel
to surface (perpendicular : not stable)
along the surface step

Glycine is a Zwitterion

Hbonds Gly-water :
NH_3^+ : 2*0.75 H-bonds in total
COO^- : 2*1.70 H-bonds in total

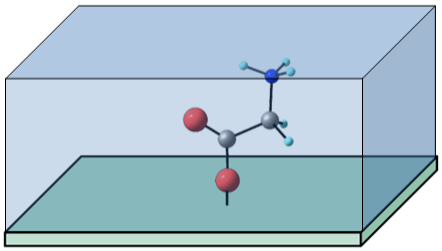
Slightly less Hbonds in total than when Gly is in the bulk
Strengths of Hbonds reduced wrt bulk

Hbonds Gly-Boehmite :
1 NH+ … mu1-O2
1 COO^- … mu1-O1H
1 COO^- … mu2-OH (long)

Hbonds Fluxional (formed/broken along time)

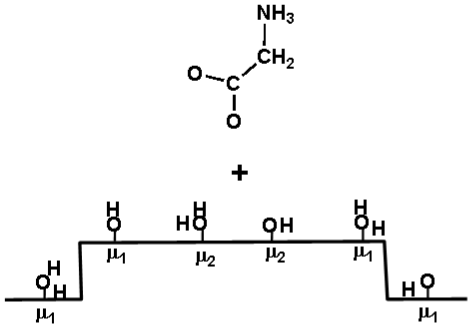
$\langle \Delta E^{KS} \rangle$ = -20.5 kJ/mol
wrt to Gly immersed in bulk

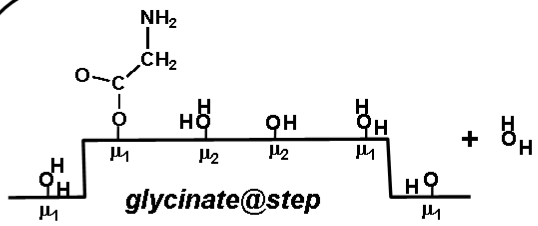
c)

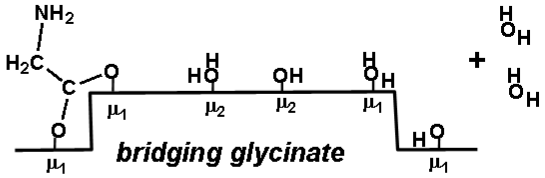


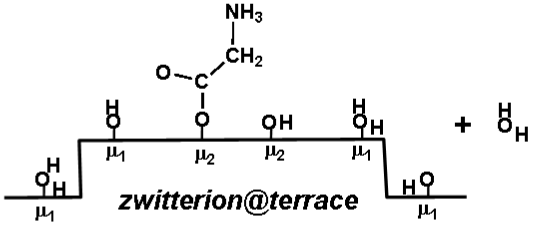
Inner Sphere

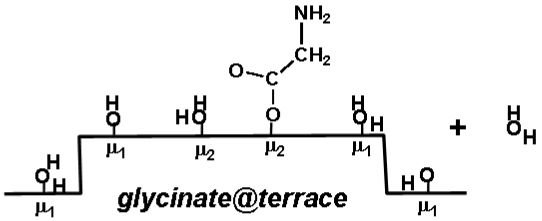
Several condensation reactions of Glycine COO^- termini with the different Al surface sites

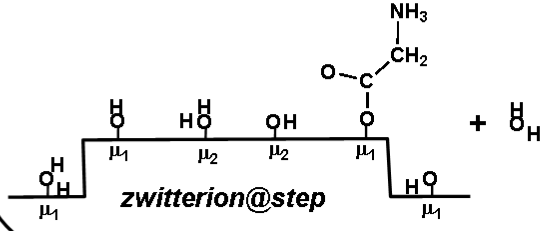






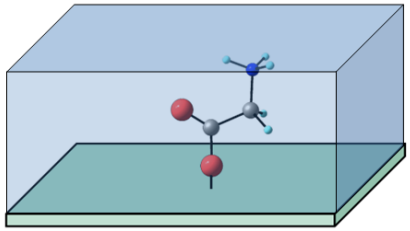






DFT-MD on all 4 possibilities

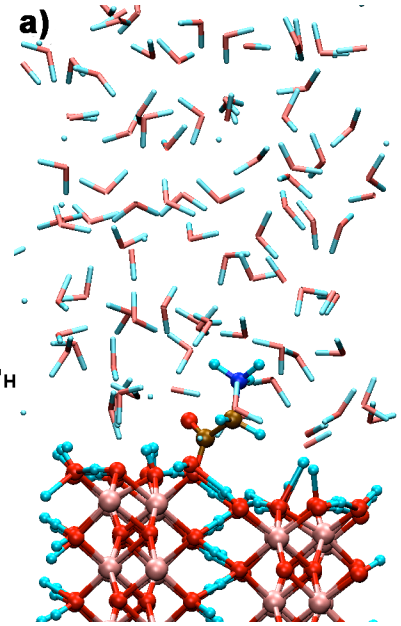
c)



Inner Sphere

Two most stable inner-sphere structures

a)



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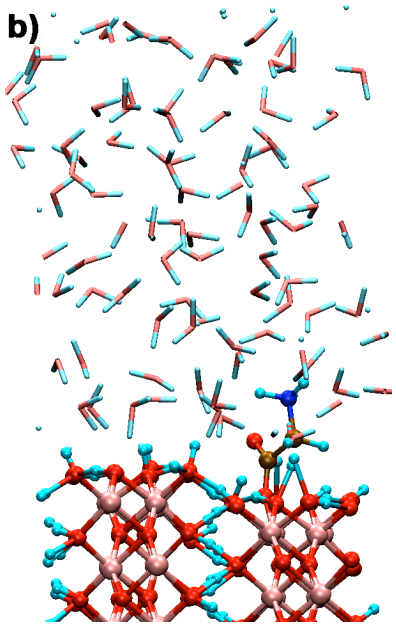

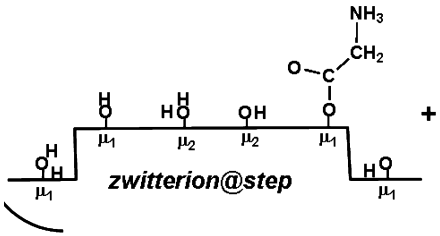

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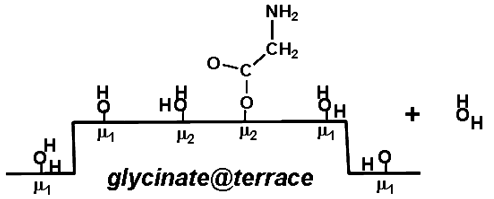
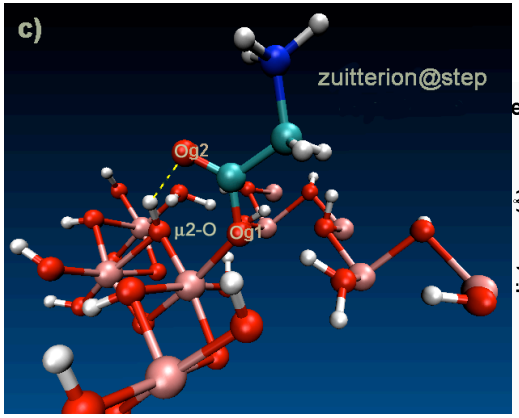
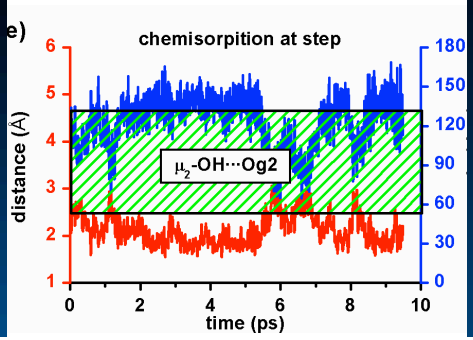
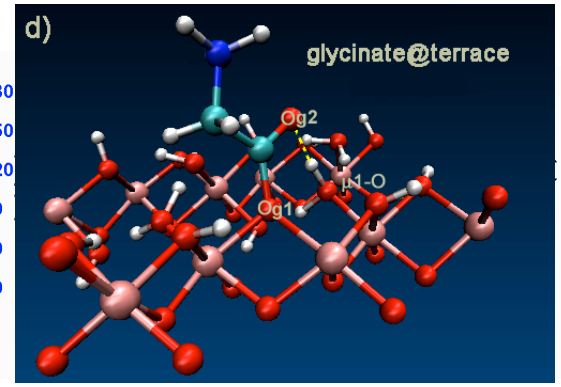
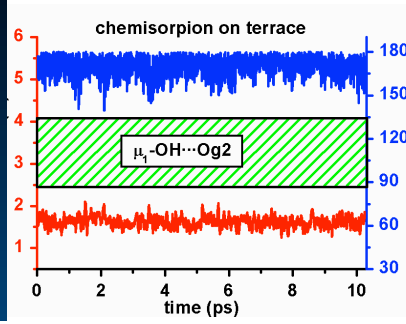










< ΔE^{KS} > = -113.6 kJ/mol

< ΔE^{KS} > = -161.3 kJ/mol

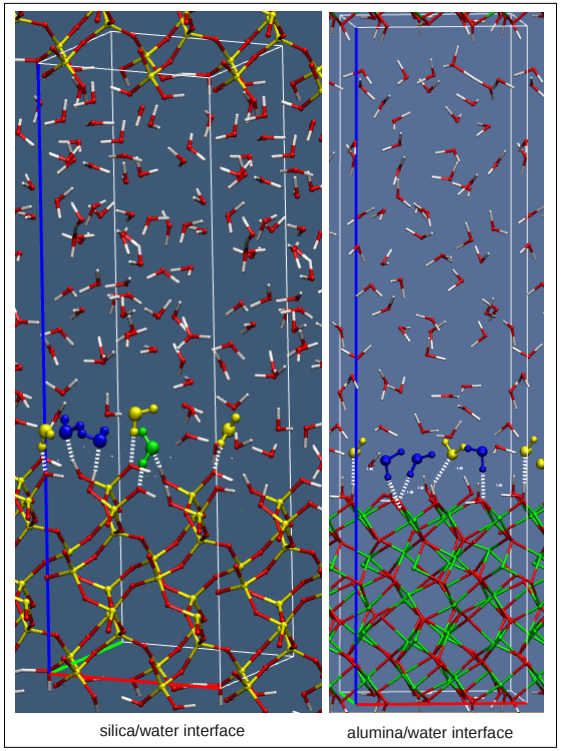
(taking into account the organisation of interfacial water)

$NH_3^+(NH_2)$ Hbonded to 3(2) H_2O ; 1 *COO* Hbonded to mu2-*OH* or mu1-*OH*

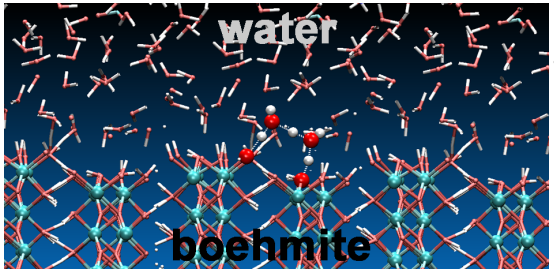
- DFT-MD: Liquid structure, solid structure, pKa, IR spectra

  Full VSFG spectrum currently calculated from DFT-MD

  JCTC 2012, J.Phys.Cond.Matt 2012



- Boehmite/Water interface (Coll. D. Costa, Paris)



- Proton transfers at the step
- Peptide @ the interface

JPCC(1) 2012, + JPCC(2) 2012

- VSFG signal of liquid water/air interface
  (DFT-MD, JPCLetters 2013)

- Electrolytes at the interface, electrochemistry, batteries …

  Vibrational spectroscopy as a special observable

- DFT-MD and semi-empirical MD ; reference trajs useful for classical force field developments

Collaborators on these works :

Morgane Laplaud-Pfeiffer (PhD, 2012-2015)

Marie-Laure Bonnet (Post-Doc, 2012-2013)

Alvaro Cimas-Samaniego (MdC Evry France)

Michiel Sprik - Cambridge UK

Marialore Sulpizi - Mainz Germany

Dominique Costa - ENSCP France, Alessandro Motta, Italy

Group of M Bonn – Max Planck Institute Mainz, Germany

Group of J. Gibbs-Davis – University of Alberta, Canada