Amorphous Silica-Water , Boehmite AlOOH Interface studied by DFT-MD and adsorption of biomolecules

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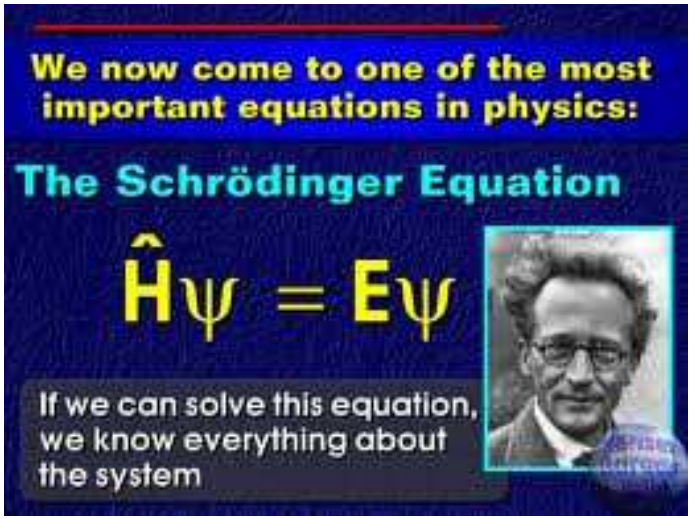
First Principles Calculations

« structural, dynamics and electronics understanding »



- Bond breaking and making
- Reproduces surface properties (relaxation, structure, acid-base character..)
- Calculation of Spectroscopic Properties

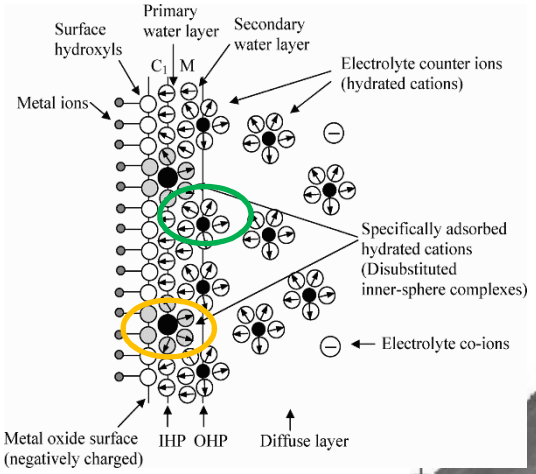
Adsorption of small biomolecules

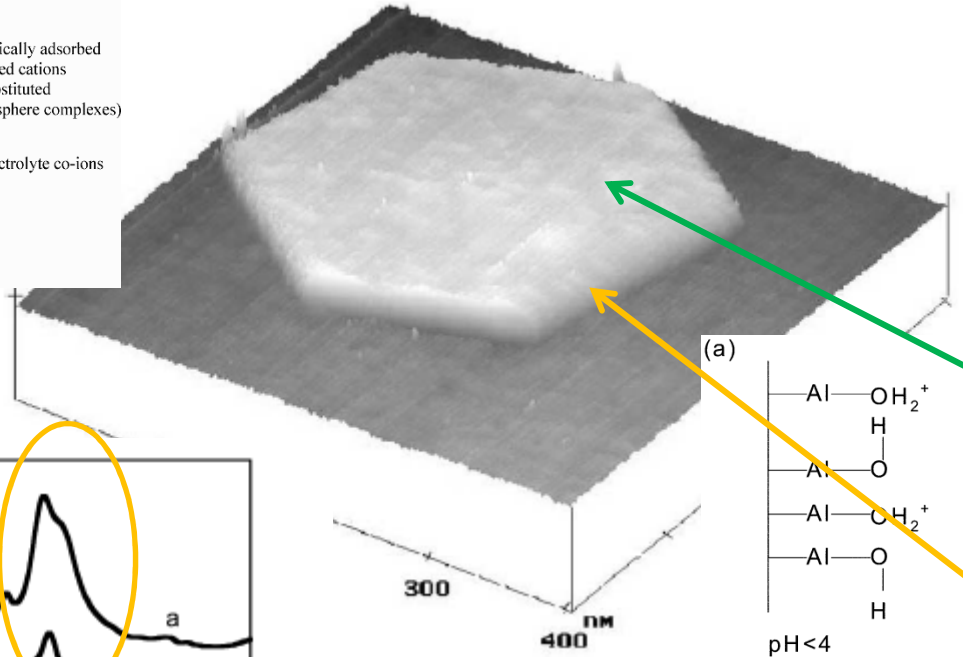
- Electrostatic does not explain everything
- interpretations of spectroscopic data require more insight on the local interactions

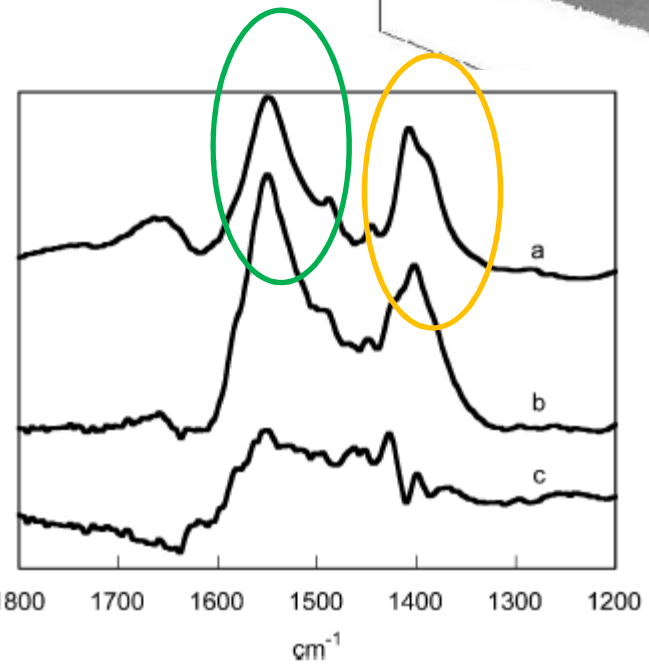
Role of specific surface sites in presence of water

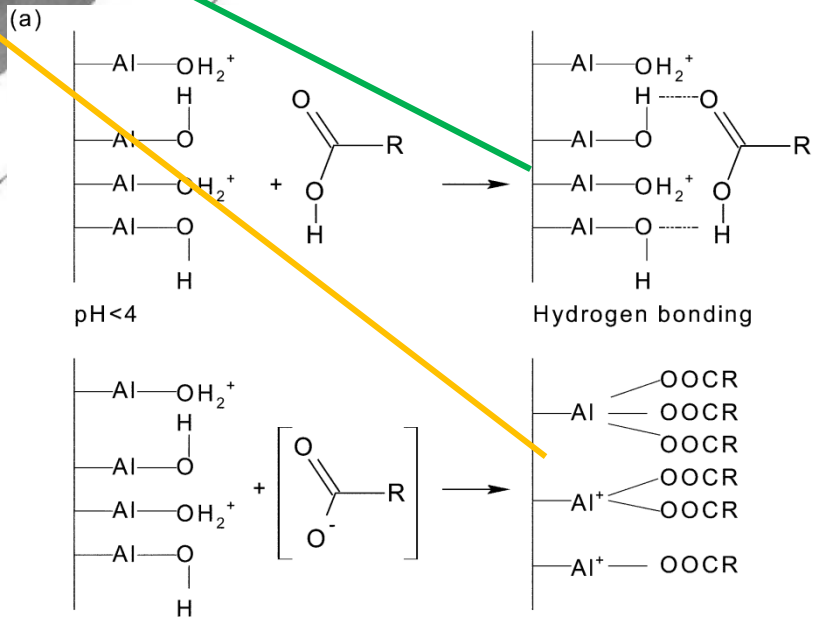
In the recent three years Born Openheimer Molecular Dynamics is developing for surfaces-water interactions

Experimental evidence of adsorption@specific surface sites







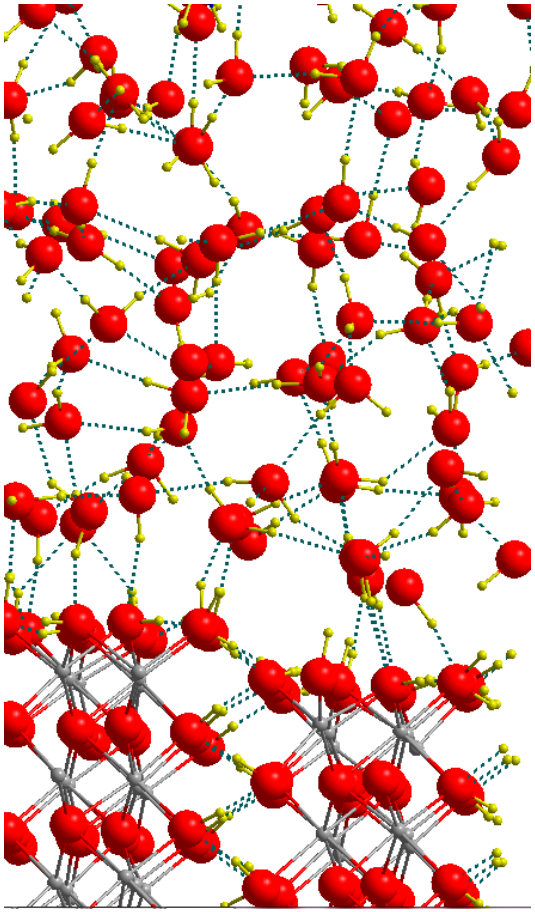


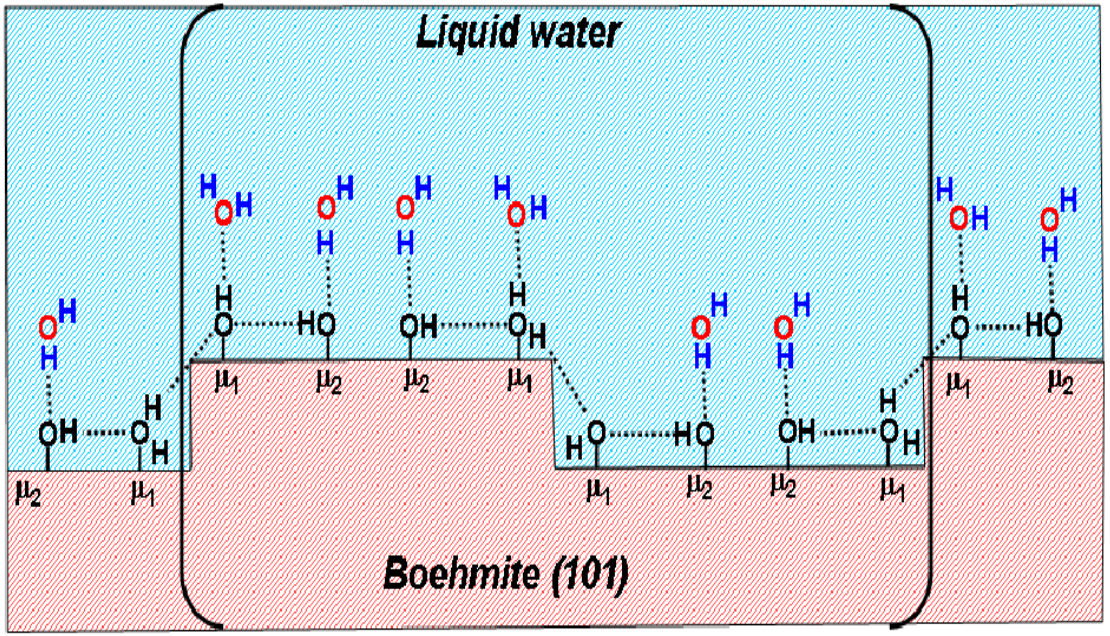
J. Rosenqvist et al. / Colloids and Surfaces A: Physicochem. Eng. Aspects 220 (2003) 91–104

B. Kasprzyk-Hordern / Advances in Colloid and Interface Science 110 (2004) 19–48

Hydroxylation of boehmite at the aqueous interface & organisation of interfacial water molecules

a)

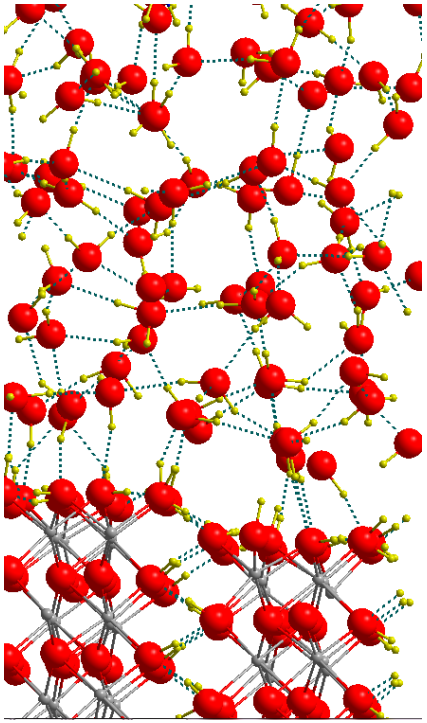


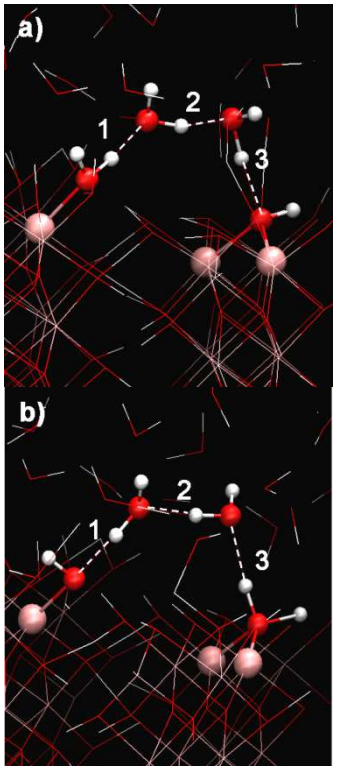


Motta, Gaigeot, Costa *JPCC* 2012 116:12514

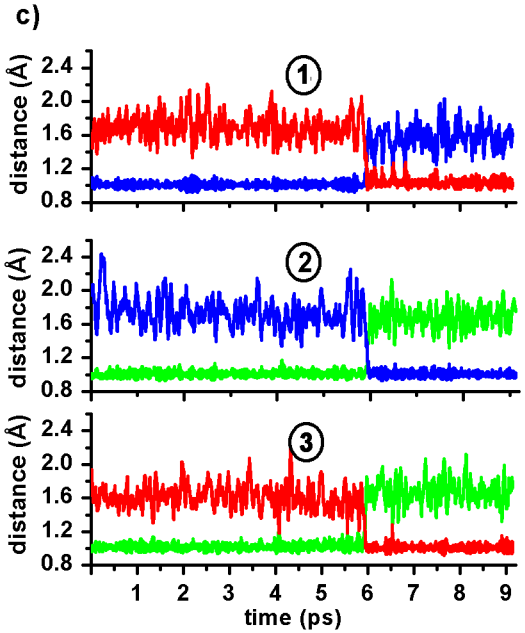
Protonic Conductivity@steps

a)





Grotthus mechanism for H exchange

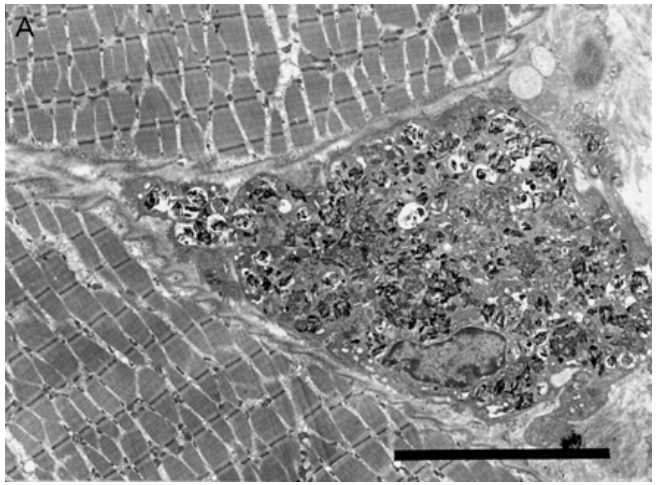


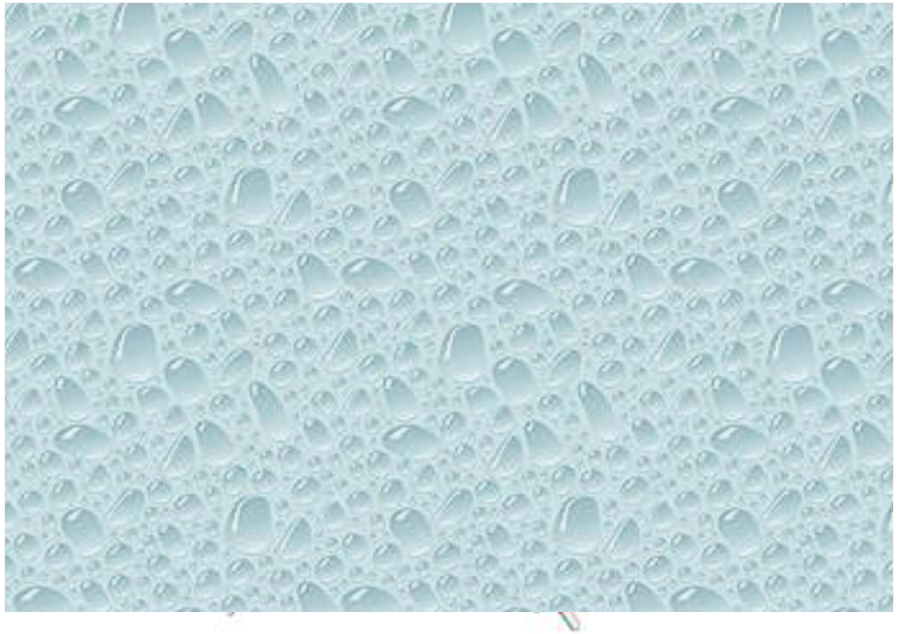
$$\mu1\text{-HOH} + \mu2\text{-OH} \rightleftharpoons \mu1\text{-OH} + \mu2\text{-HOH} \qquad \Delta pK(\mu1\text{-OH}) = 1.4$$

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

Boehmite Toxicity ?

Boehmite used as vaccine adjuvant induces **Macrophagic *myofasciitis* lesions** (Gherardi 1998)

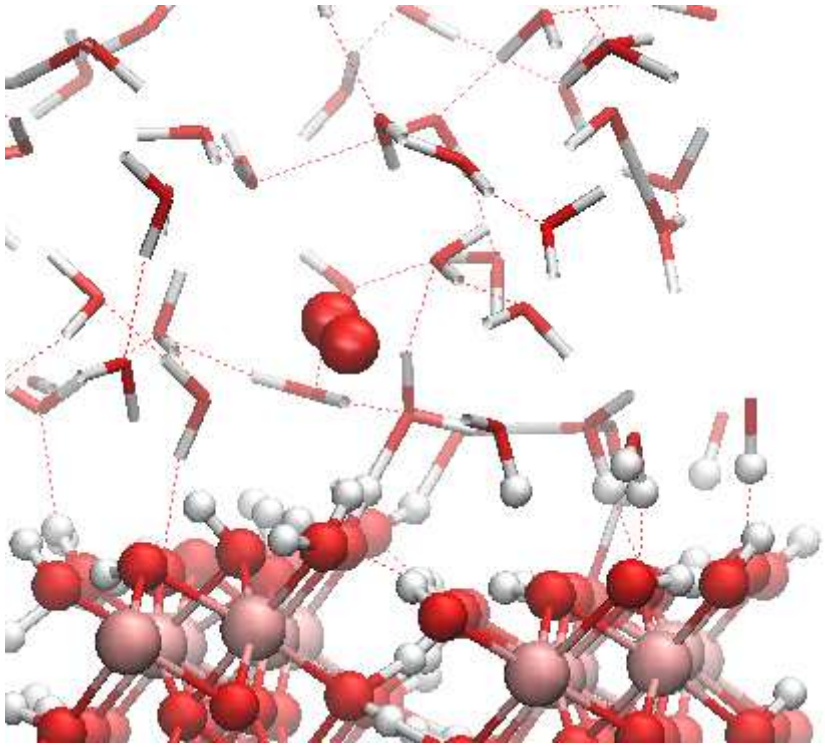


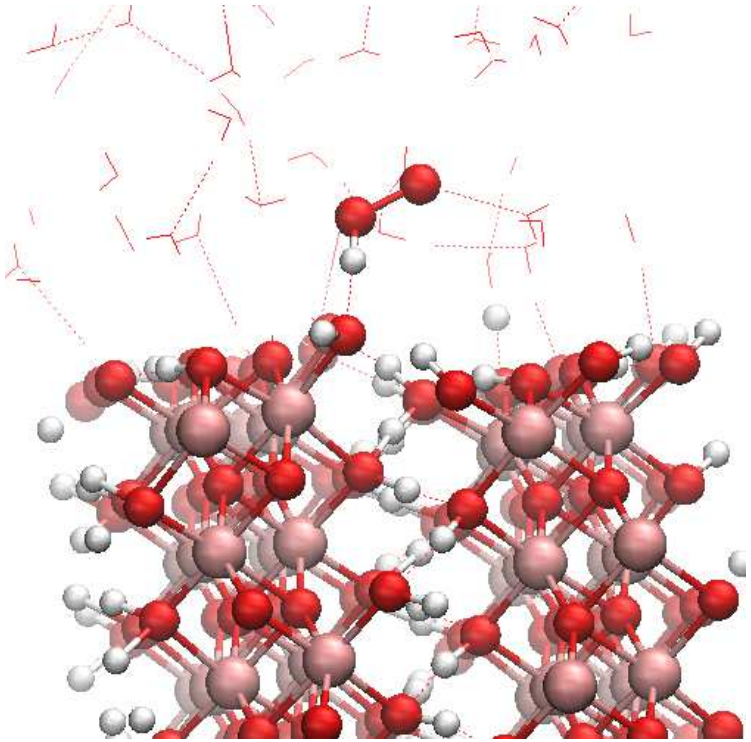


Al^{3+} acts as a pro-oxidant
Stabilisation of Reactive oxygen Species

X. Lopez (Espagne), C. Exley (UK)

$O_2^{\circ -}$@boehmite and OOH°@boehmite



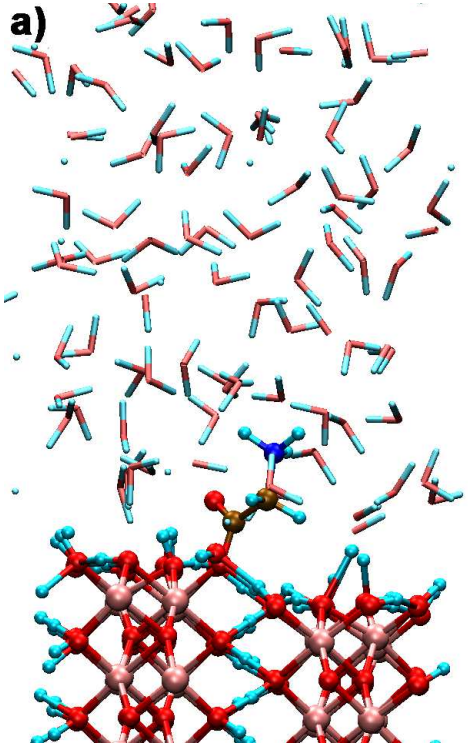


-0.7 eV more stable

OOH° four times more oxidant than O2°-
Active in Oxidative Stress

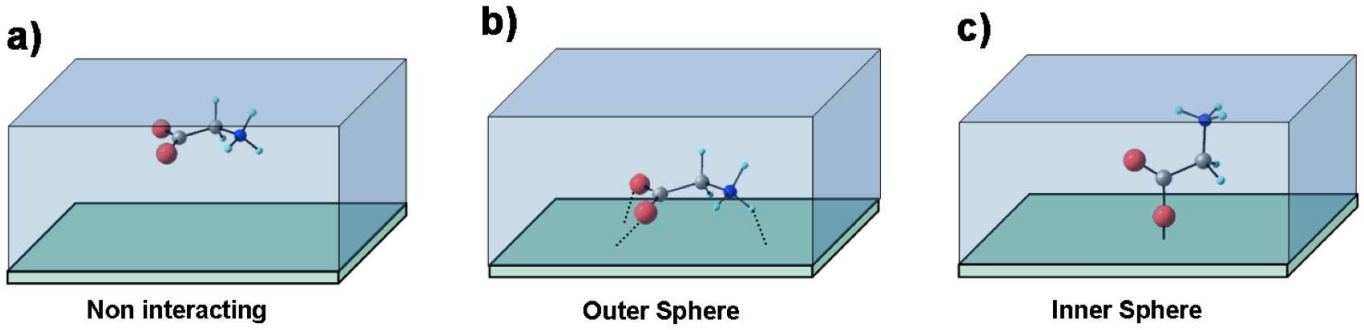
Ribeiro et al, *J Inorganic Biochemistry,* **128C**, 164-173, 2013

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

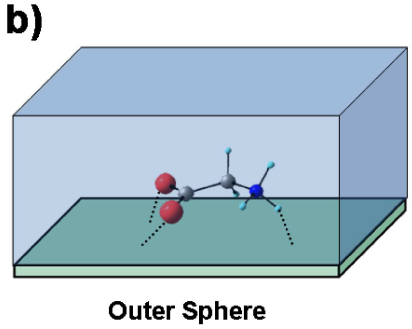


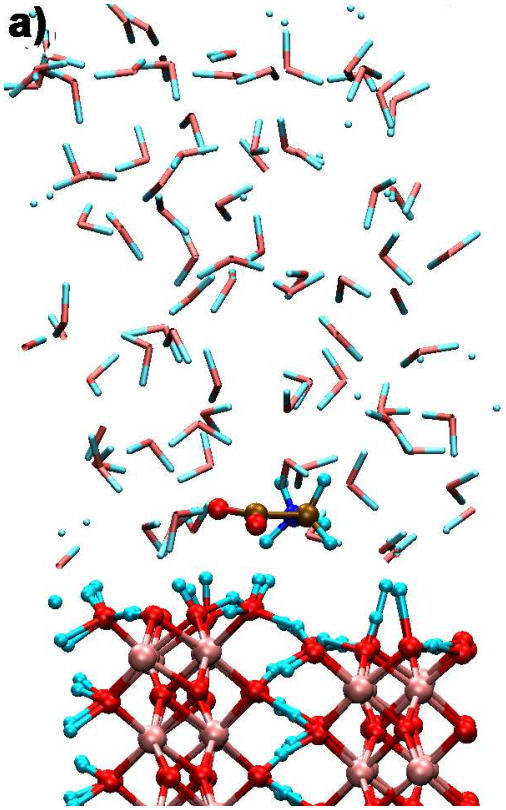
Energetically most favorable adsorption mode of Glycine at the aqueous boehmite/water interface?

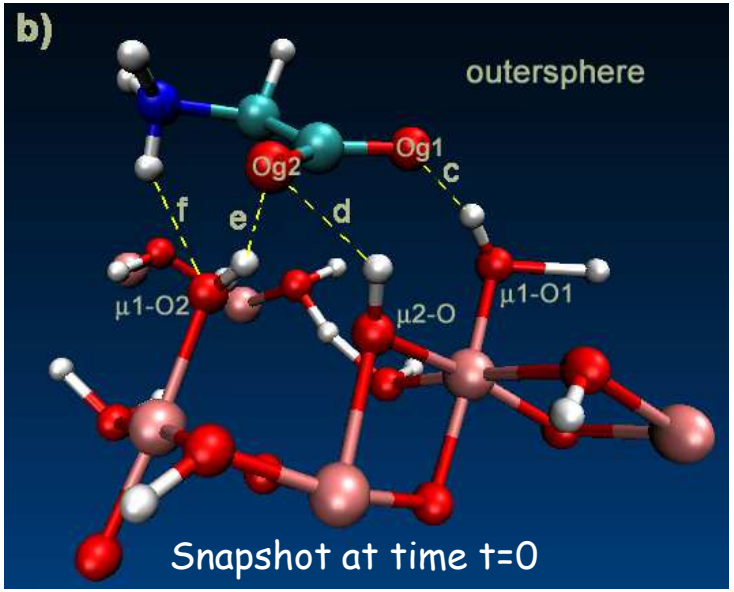
(Motta, Gaigeot, Costa, JPCC 2012 116:23418)



Outer Sphere Adsorption Gly-Boehmite

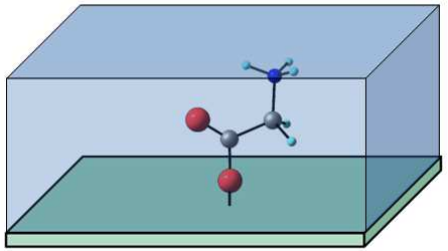






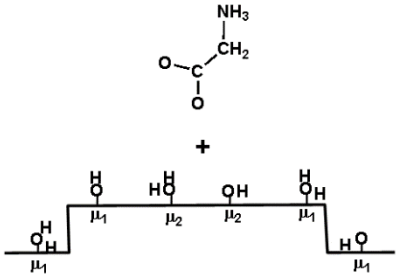
$< \Delta E^{KS} > = -20.5$ kJ/mol

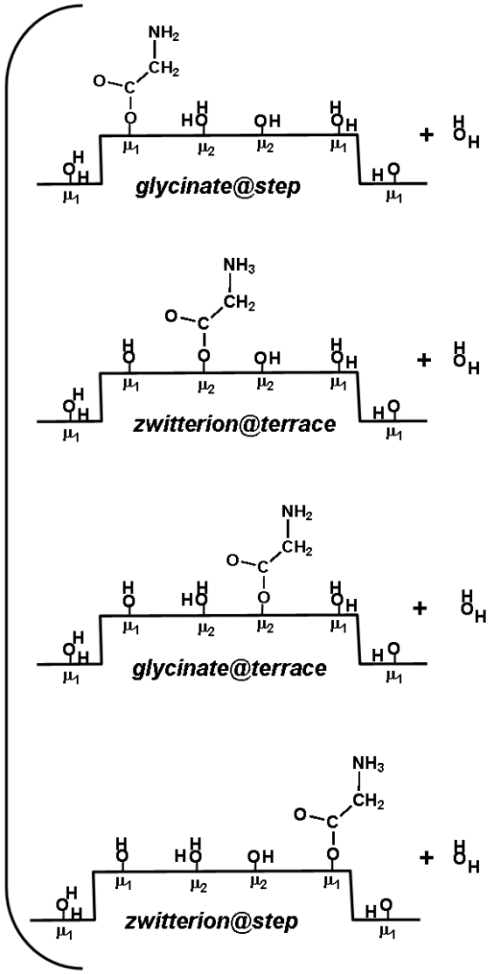
wrt to Gly immersed in bulk water

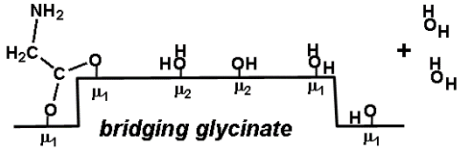


Inner Sphere

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



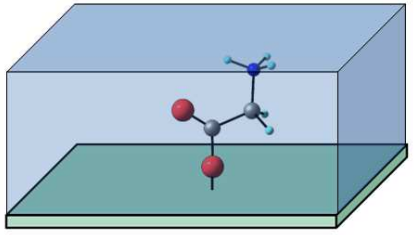




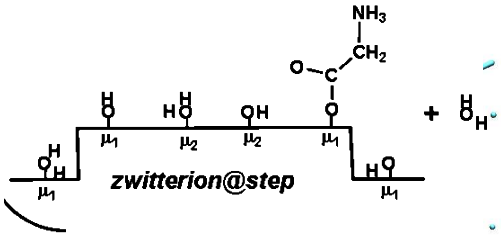
DFT-MD on all 4 possibilities

Two most stable inner-sphere structures

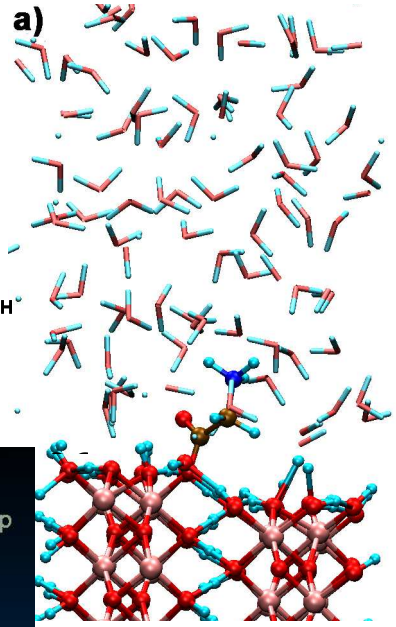
c)



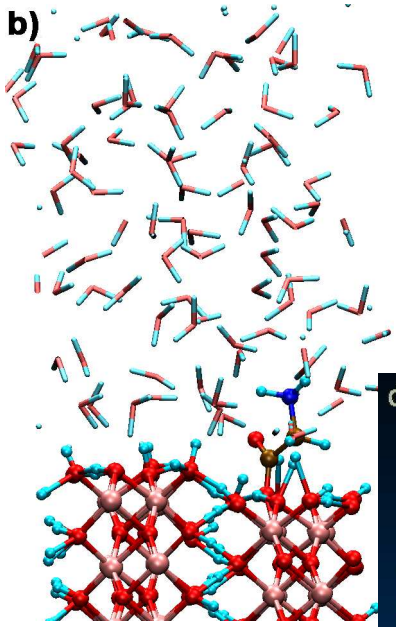
Inner Sphere

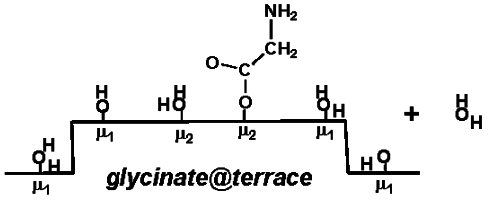


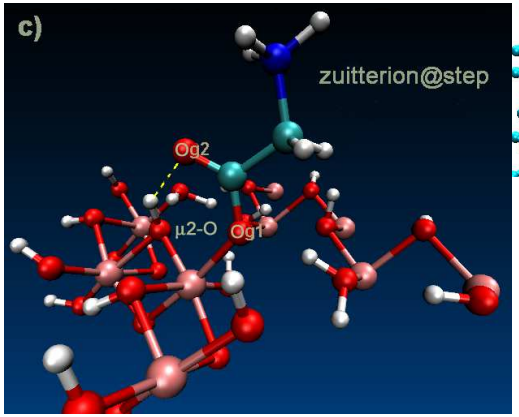
a)



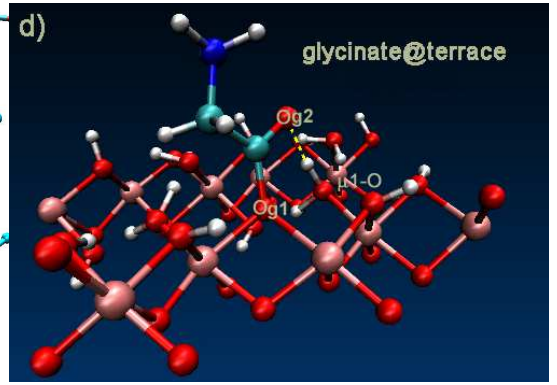
b)







< ΔE^{KS} > = -113.6 kJ/mol



< ΔE^{KS} > = -161.3 kJ/mol

The most stable conformation is found when the surface charge is maintained:

an anion substitutes an OH group

a neutral group substitutes a HOH

Summary

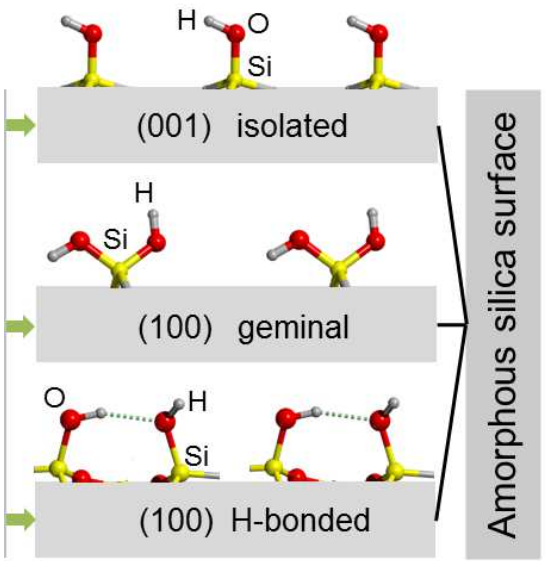
For a small molecule on a simple surface, several adsorption configurations have to be considered and adsorption energies are not simply predictible

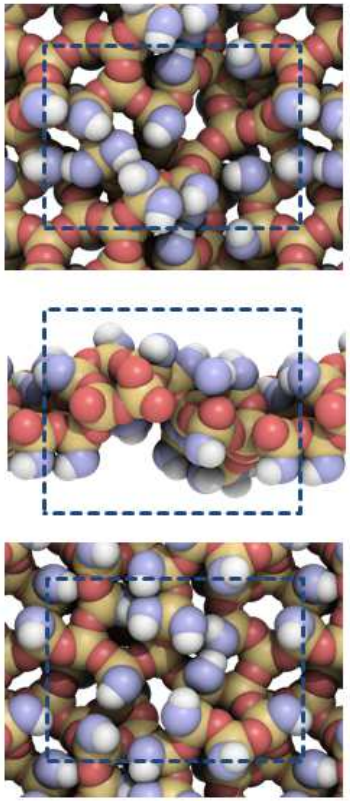
=> A high level of theory is required

Inner adsorption is much more stable than Outer sphere adsorption @step and @terrace

At step, an adsorbed molecule might be oxidized by OOH°

Amorphous Silica: A representative ab initio Model



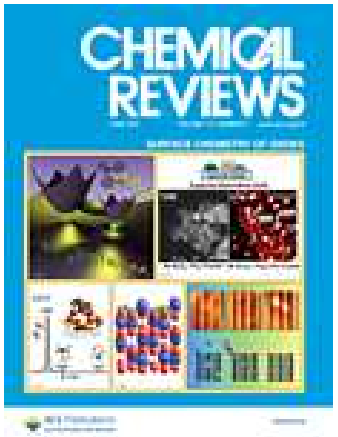


SiOH 5.8/nm^2
experimental estimates on a hydroxylated surface (4-5 OH/nm^2).

On the top surface, 23% silanols are geminal ones, in good agreement with experimental values.

35% of the silanols are involved in H bonds.

F. Tielens, C. Gervais, F. Mauri, J-F Lambert, D Costa Chem Mat., 20, 3336 (2008)



Rimola et al., 113, 4216, 2013

Combined NMR Experiments and DFT-D

DFT-D calculations to help in interpretating experimental NMR data.

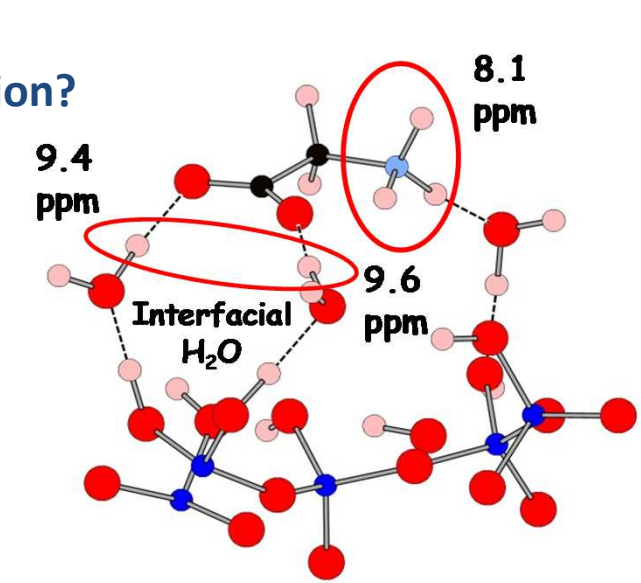
glycine on isolated, vicinal, geminal silanols.

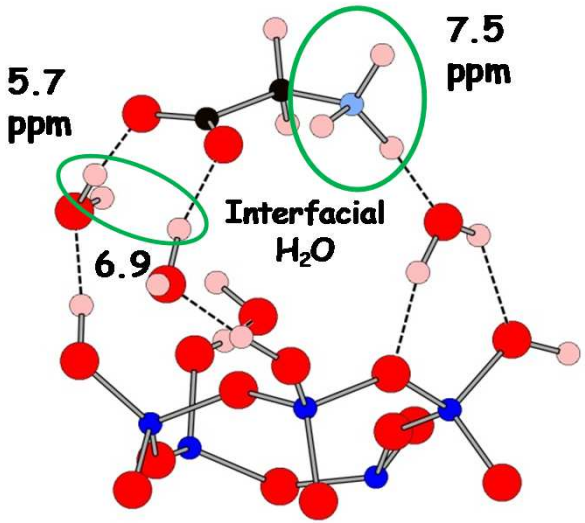
Calculated NMR shifts => vicinal silanols, with water coadsorbed.

Strentgth of Adsorption @ isolated < vicinal < geminal nest

Water co-adsorption is favored.

Role of surface sites ?
Role of Water in adsorption?

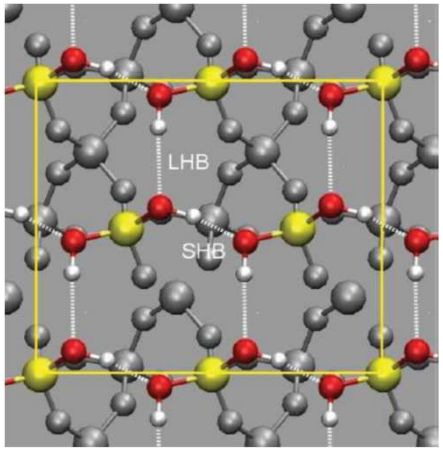




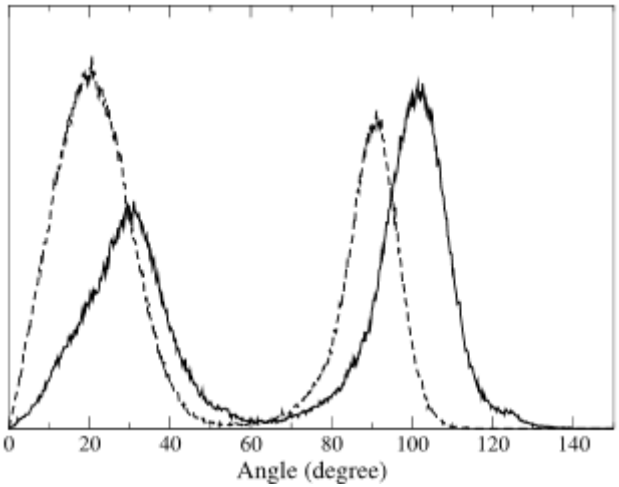
*Folliet et al, JPC C **117**:4104 (2013)*

Silanols on Quartz (0001)

OH orientation in vacuum

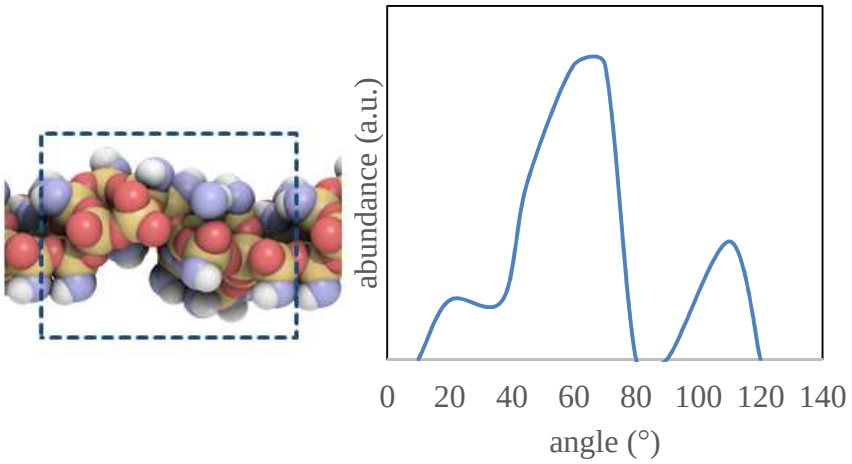


OH orientation in water

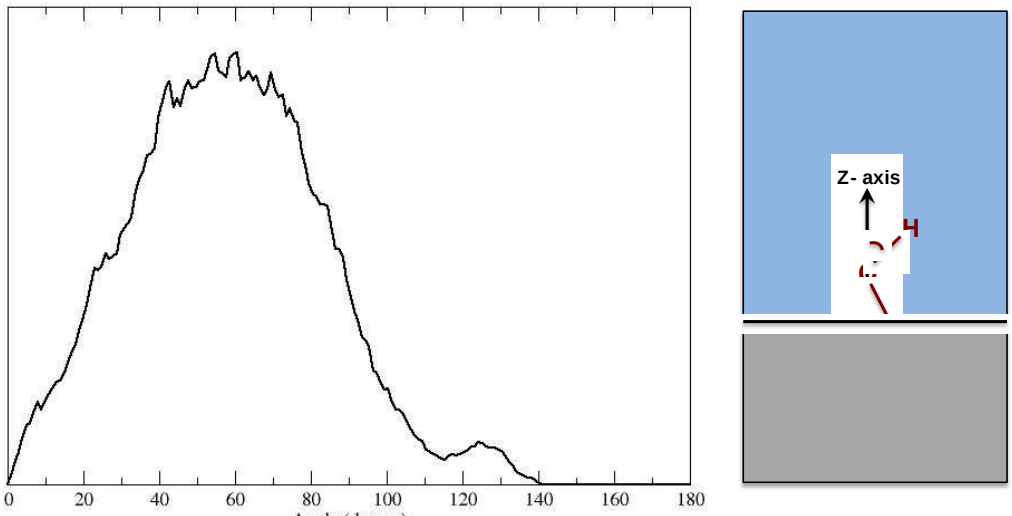


Silanols on amorphous Silica

OH orientation in vacuum



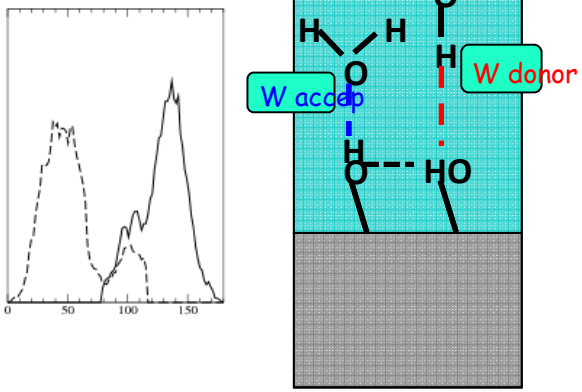
OH orientation in water



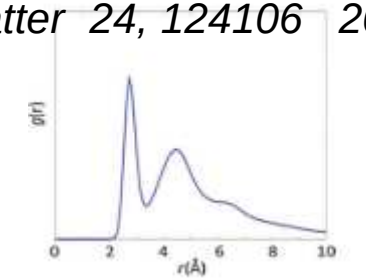
Cimas et al, submitted

Interfacial Water layer

@Quartz

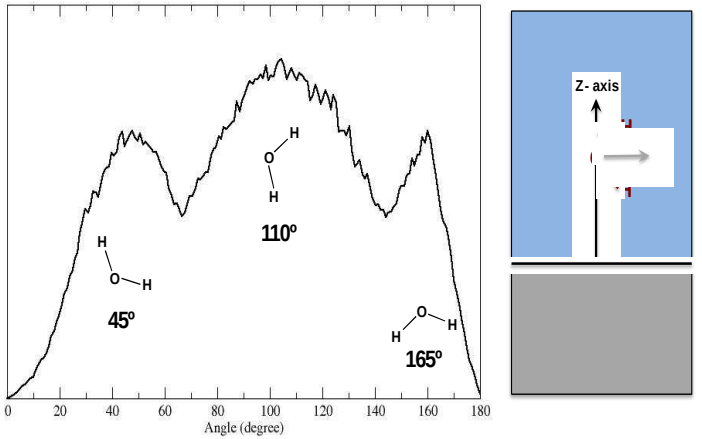


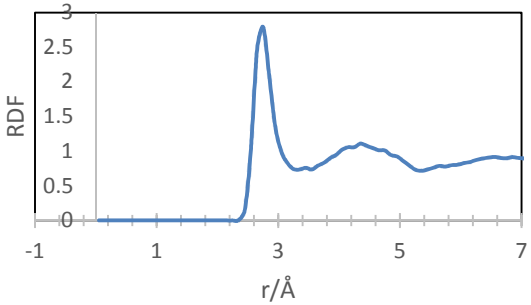
Gaigeot M-P. et al, J. Phys. Cond Matter 24, 124106 2012



Musso et al. Phys Chem Chem Phys 14 10507, 2012

@amorphous silica

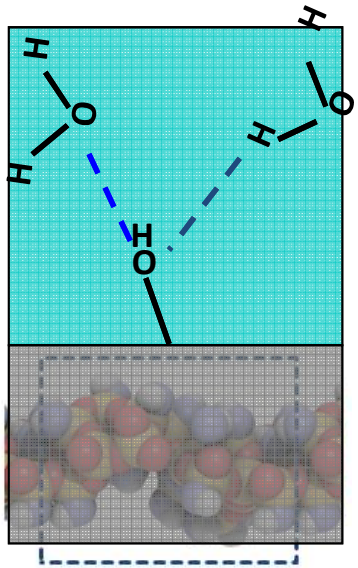


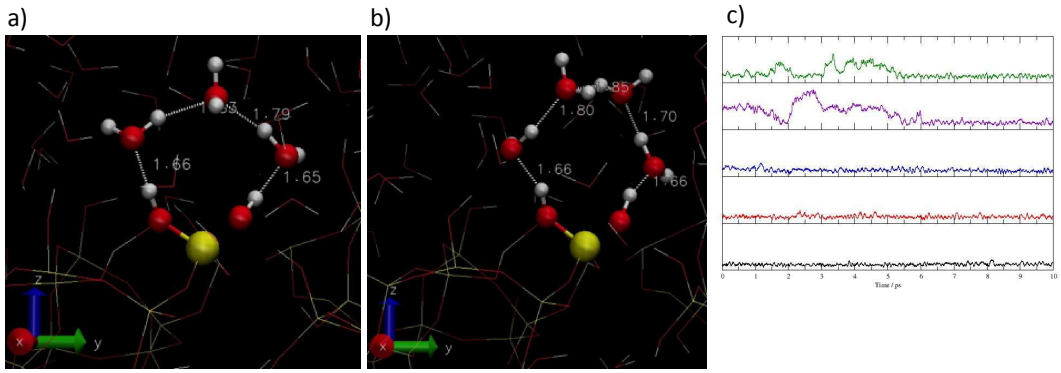


No structured interfacial water layers

Isolated vs Geminal Silanols @amorphous silica

Ring formed during > 50% of the trajectory or more





Ring Opening → Adsorption

Summary

- Amorphous Silica exhibits a picture dramatically different from 0001 quartz
- In average water is not organized @amorphous silica
- Appearance of a local organisation in a global disorder
- Water Cycles are formed at geminals, which may allow insertion of an adsorbate

THANKS TO

A. MOTTA, Catania
M-P GAIGEOT
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M-P GAIGEOT
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C GERVAIS
F TIELENS
J-F LAMBERT

GENCI
HPC EUROPA