



Master 2 Sciences de la Matière : Chimie concepts et applications

FROM BOEHMITE TO γ -ALUMINA EDGES : REVISITING THE NATURE OF SITES AND DECIPHERING ^1H NMR EXPERIMENTS

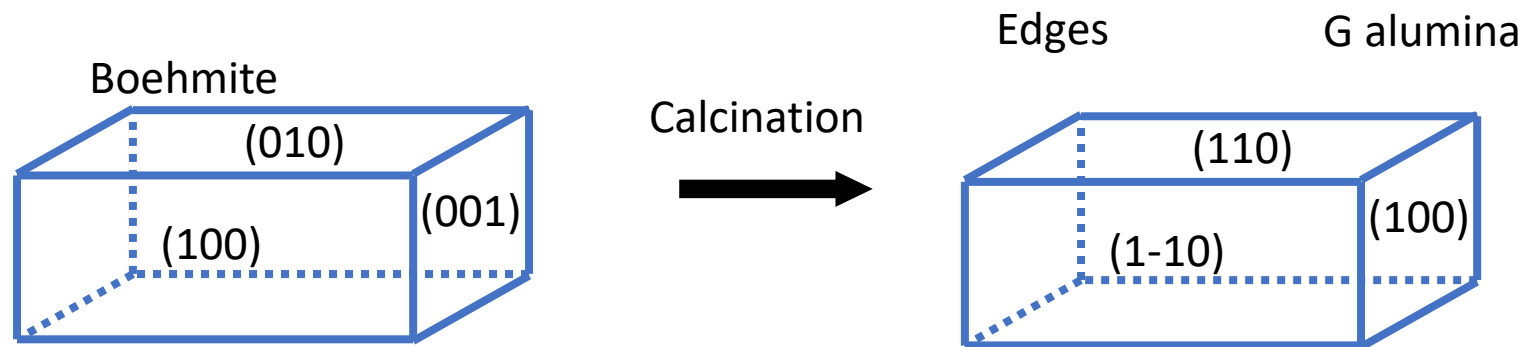
Thomas Pigeon

SUPERVISORS : CELINE CHIZALLET AND PASCAL RAYBAUD (IFPEN)

γ -alumina

Synthesized by par boehmite calcination^[1] : $\gamma - AlO(OH) \xrightarrow{450^\circ C} \gamma - Al_2O_3$
 → Topotactic transformation (Overall Particle shape conservation)

Simplified scheme



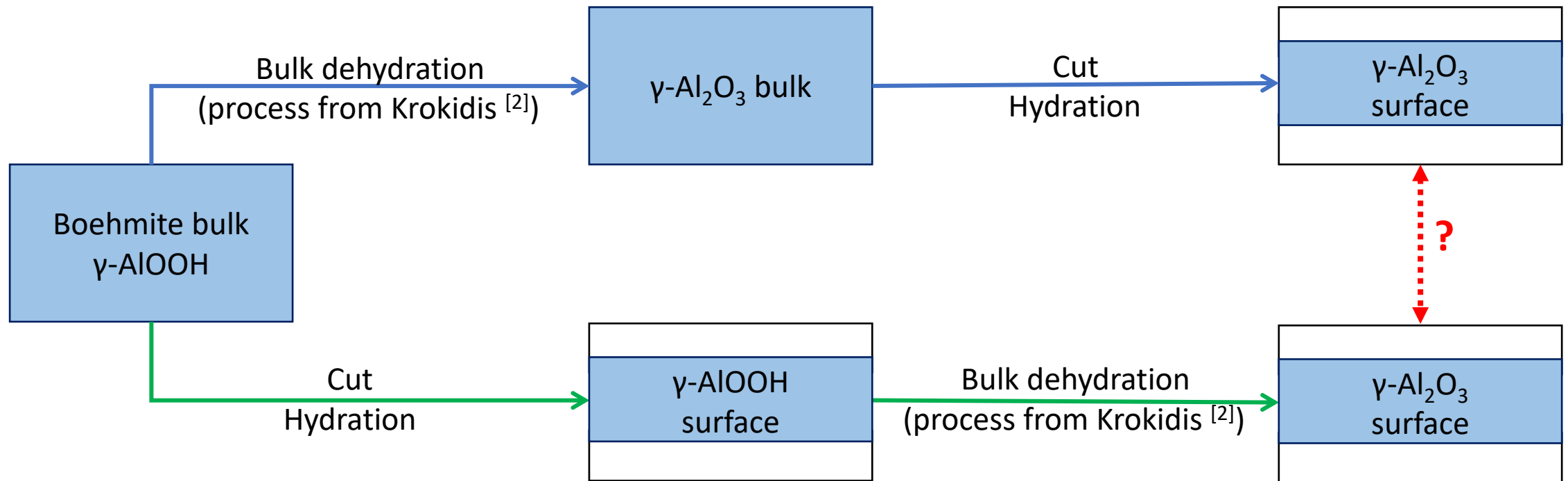
[1] F. Schuth, K. Sing, J. Weitkamp, *J. Handbook of Porous Solids*. Wiley-VCH, **2002**.

[2] D. Chiche, C. Chizallet, O. Durupthy, C. Chanéac, R. Revel, P. Raybaud, J.-P. Jolivet, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11310.

3 INTRODUCTION

Boehmite has mainly 4 surfaces ^[1] : (100), (010), (001) and (101)

1st method: from alumina bulk



2nd method: from boehmite surface

[1] D. Chiche, C. Chizallet, O. Durupthy, C. Chanéac, R. Revel, P. Raybaud, J.-P. Jolivet, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11310.

[2] X. Krokidis, P. Raybaud, A.-E. Gobichon, B. Rebours, P. Euzen, H. Toulhoat, *J. Phys. Chem. B.* **2001**, *105*, 5121.

Methods

- Vienna Ab-initio Simulation Package ^[1], pseudo-potential : Projector Augmented Wave

- Basis set: plane waves, periodic boundary conditions
- Energy cutoff : 400 eV
- Exchange correlation functional: PBE ^[2]
- Dispersion correction: dDsC ^[3]

- Chemical shifts: linear response method (GIPAW ^[4]) calculated for (T, p) conditions close to the pretreatment conditions of the samples used in NMR experiments achieved by D. Wisser at CRMN

- *Ab initio* thermodynamics (dependence on T and P_{H₂O}) ^[5]

$$\begin{aligned}\Delta_{Ads}G(T, P_{H_2O}) &= G_{Slab+n H_2O}(T) - G_{Slab+p H_2O}(T) - (n - p)G_{H_2O}(T, P_{H_2O}) \\ &\approx E_{Slab+n H_2O} - E_{Slab+p H_2O} - (n - p) G_{H_2O}^*(T, P_{H_2O}) \\ G_{H_2O}^* &= E_{elec}(H_2O) + G_{H_2O}^{rot}(T, P_{H_2O}) + G_{H_2O}^{trans}(T, P_{H_2O})\end{aligned}$$

[1] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, 47, 558–561.

[2] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.

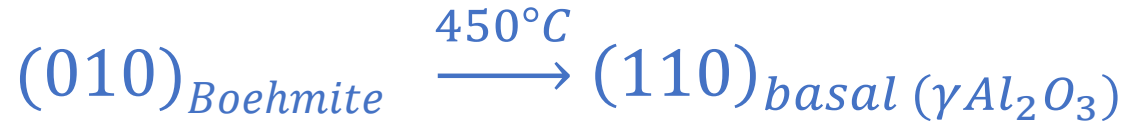
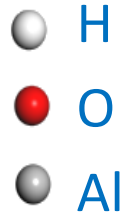
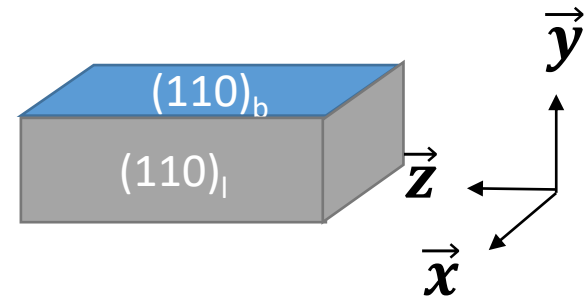
[3] S.N. Steinmann, C. Corminboeuf, *J. Chem. Theory Comput.*, **2011**, 7 (11), 3567–3577

[4] C. Pickard, F. Mauri, *Phys. Rev. B* **2001**, 63, 245101

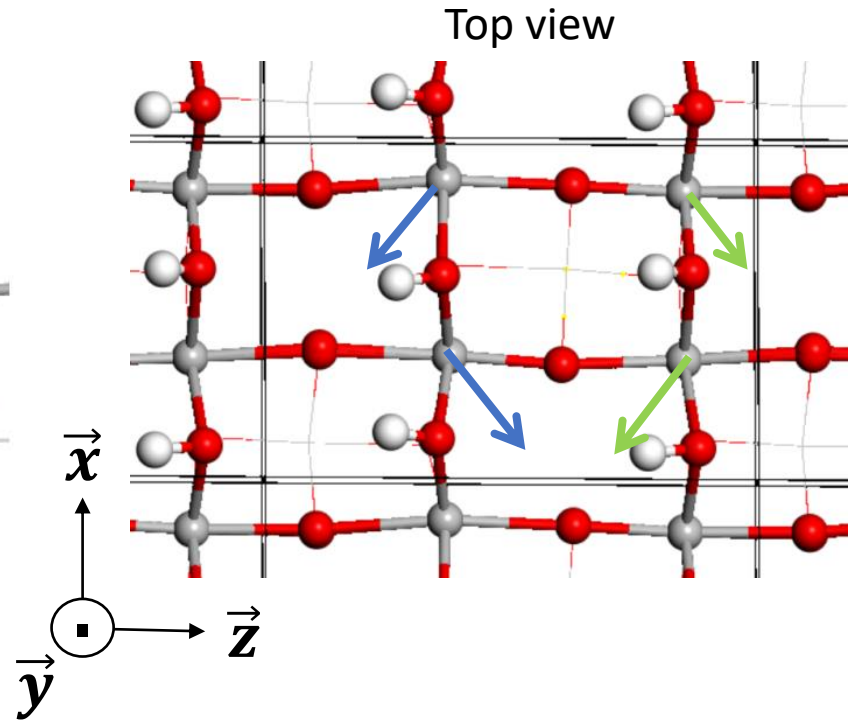
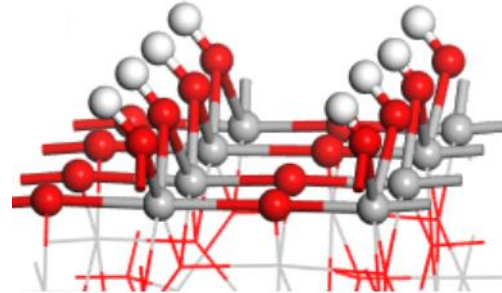
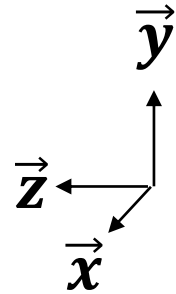
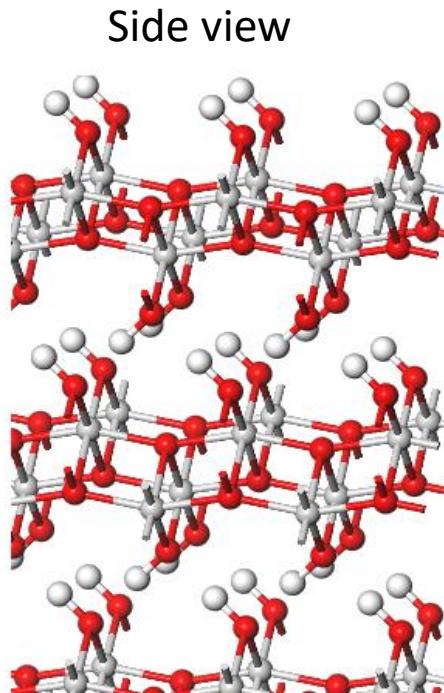
[5] Joseph, J., W., McDouall, *Computational Quantum Chemistry*, Royal Society of Chemistry, Cambridge, **2013**.

- I. Revisiting surface models
- II. Edge models construction

(010) boehmite surface dehydration

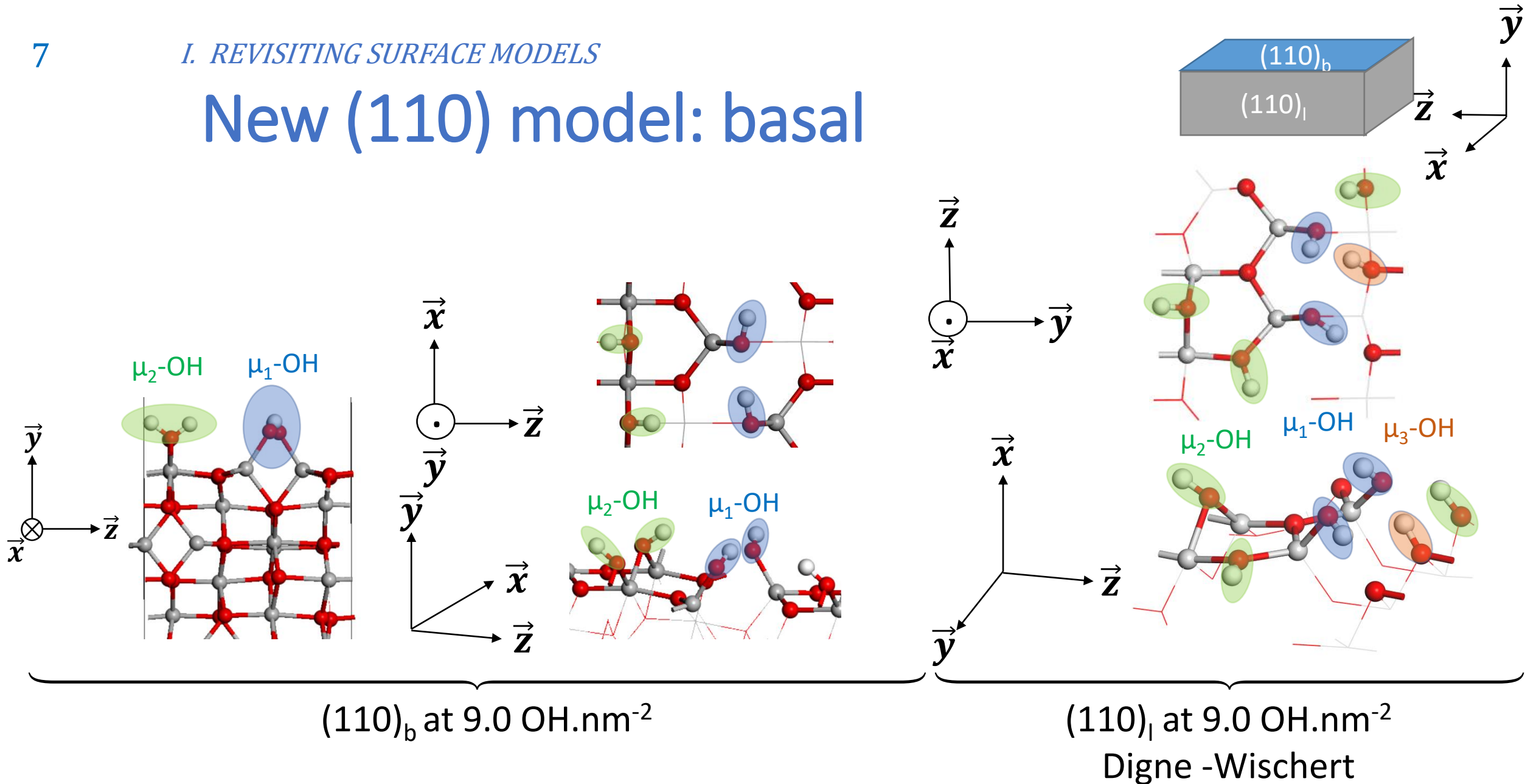


Surface dehydration
not favorable at
calcination
conditions



The surface cannot be dehydrated but surface Al atoms can migrate

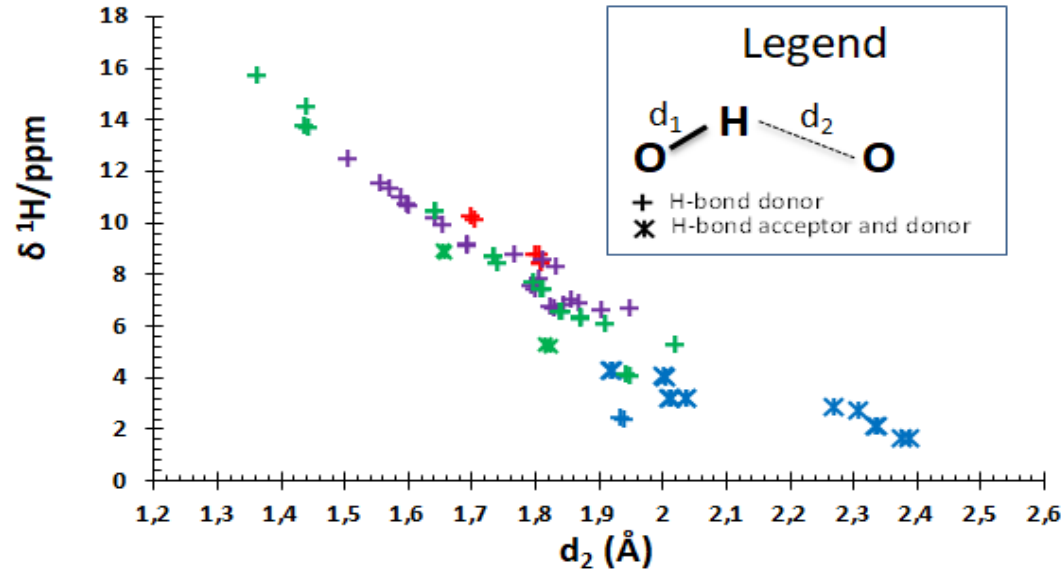
New (110) model: basal



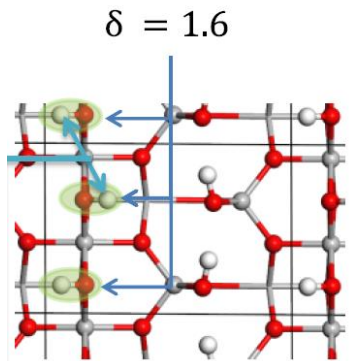
This model differs from the (110)-Digne-Wischert model

New (110) model: basal

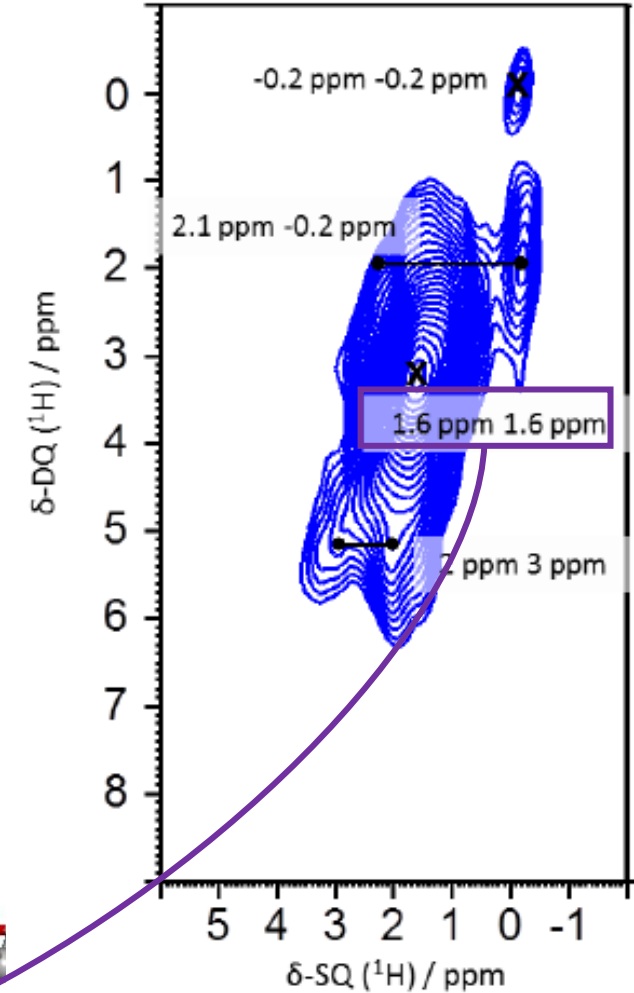
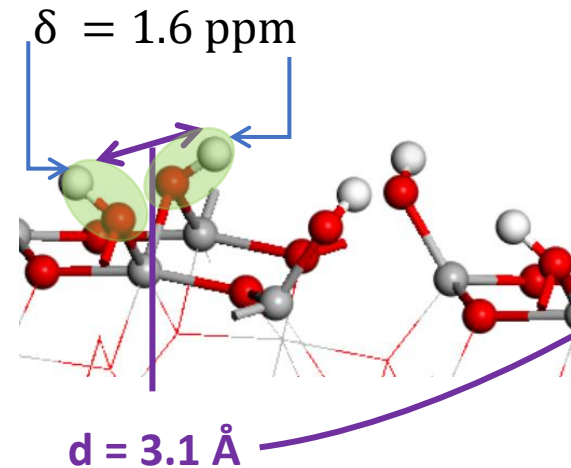
H-bonds increases chemical shiftt



→ isolated μ_2 -OH rows on the $(110)_b$ surface

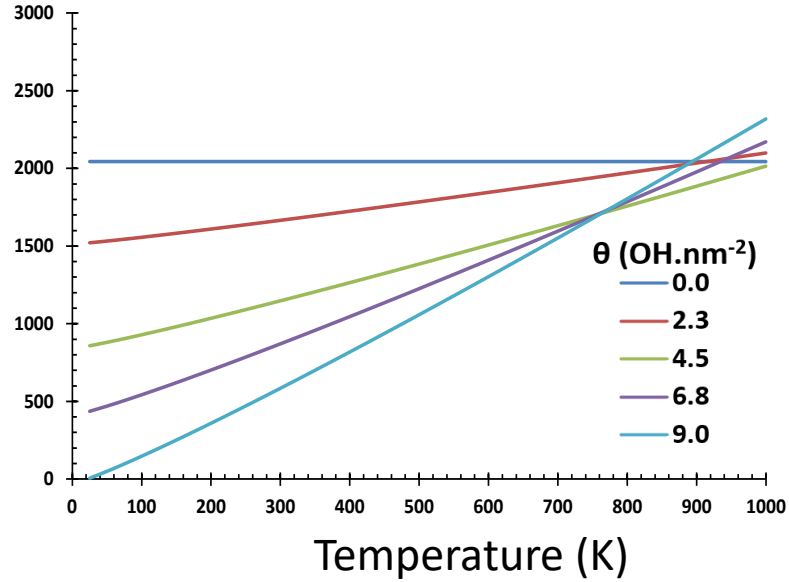
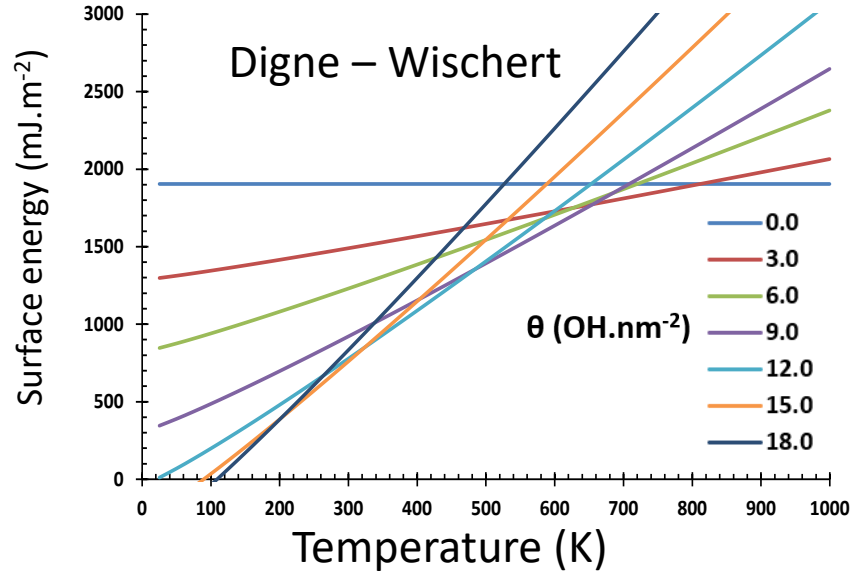
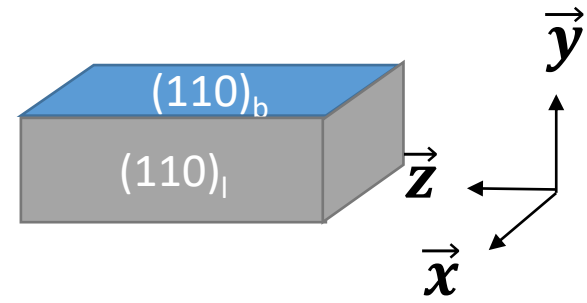


Double quantum spectra
→ Through space correlation between ^1H



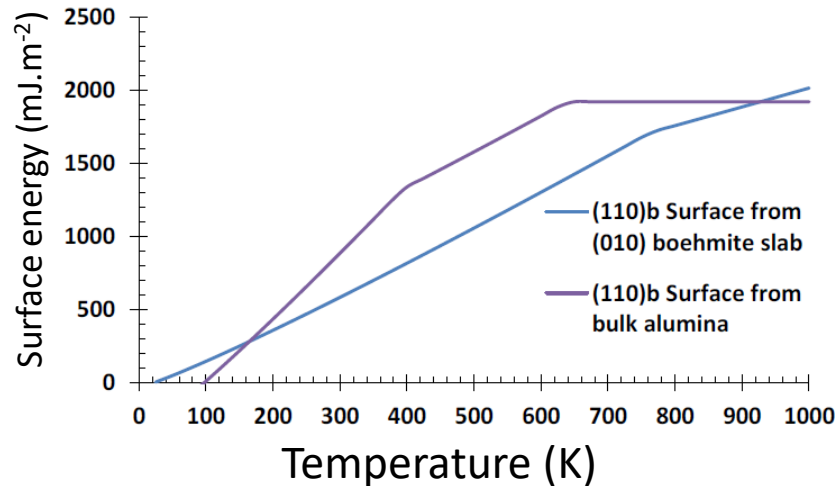
Double quantum spectrum of Pural SB3 [1]

Thermodynamic analysis



Basal

All diagrams
are plotted at
 $P_{\text{H}_2\text{O}} = 10^{-6}$ bar



The new model have a
lower surface energy on
almost the whole
temperature range

Are both construction methods equivalent ?

- $(110)_b$: No
- $(110)_l$: Yes (not presented here)
- (100) et (111) : Partially, dehydration methods is more “complete” (not shown here)

We confirm the relevance of the existing models^[1,2,3]

3 alternative and relevant models (based on energetic analysis):

- $(110)_b$ isolated μ_2 -OH
- $(110)_l$ L1 (not shown) isolated μ_2 -OH
- (111)P1_2 (not shown) isolated μ_3 -OH

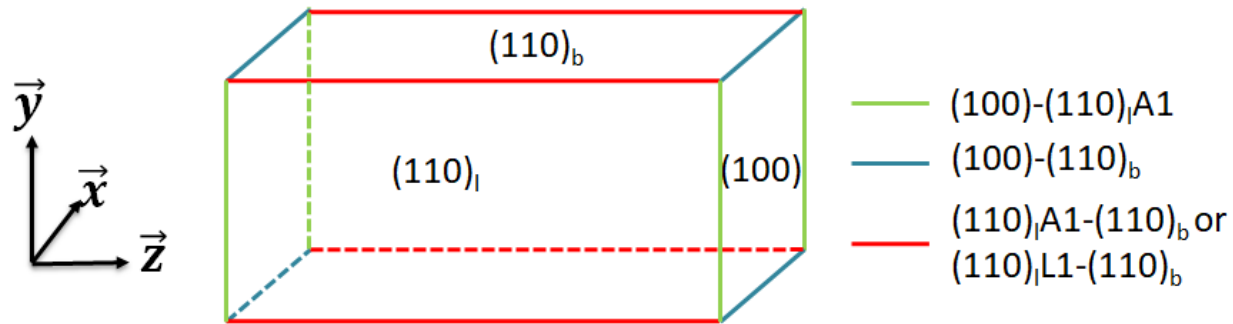
[1] M. Digne, P. Sautet, P. Raybaud, H. Toulhoat, *J. Catal.* **2002**, 211, 1.

[2] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, *J. Catal.* **2004**, 226, 54.

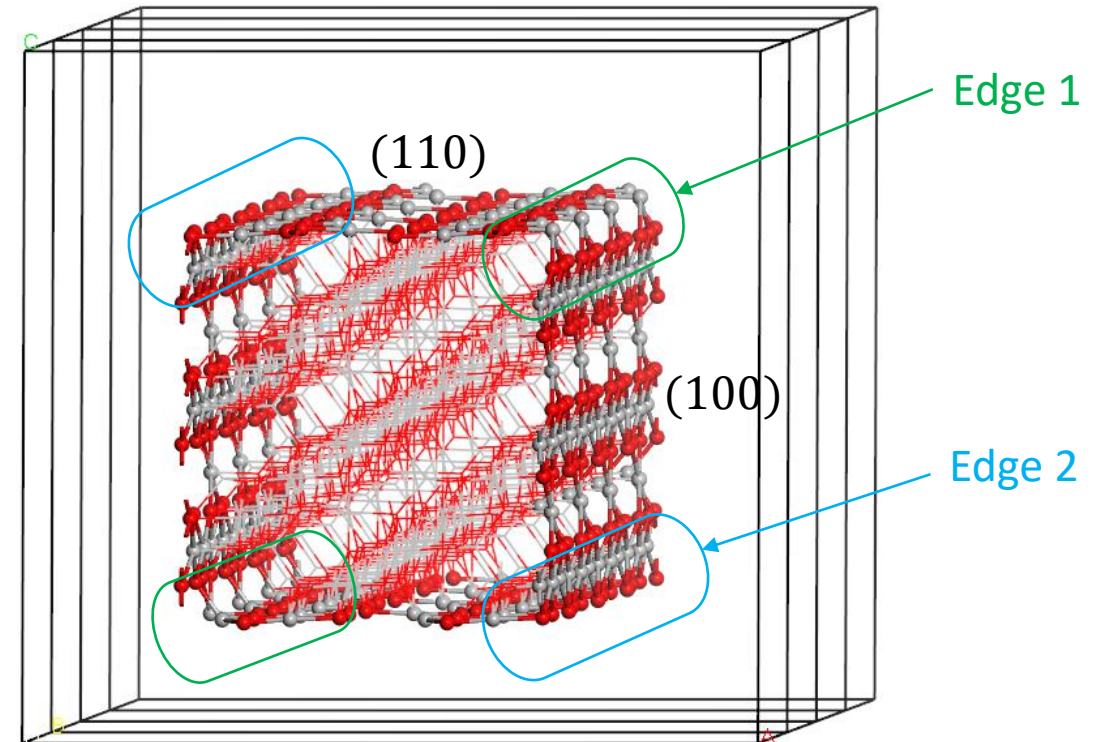
[3] R. Wischert, C. Copéret, F. Delbecq, P. Sautet, *Angew. Chem.* **2011**, 123, 3260.

Method

Starting from surface models to build nano-rods



44 x 32 Å
240 atoms

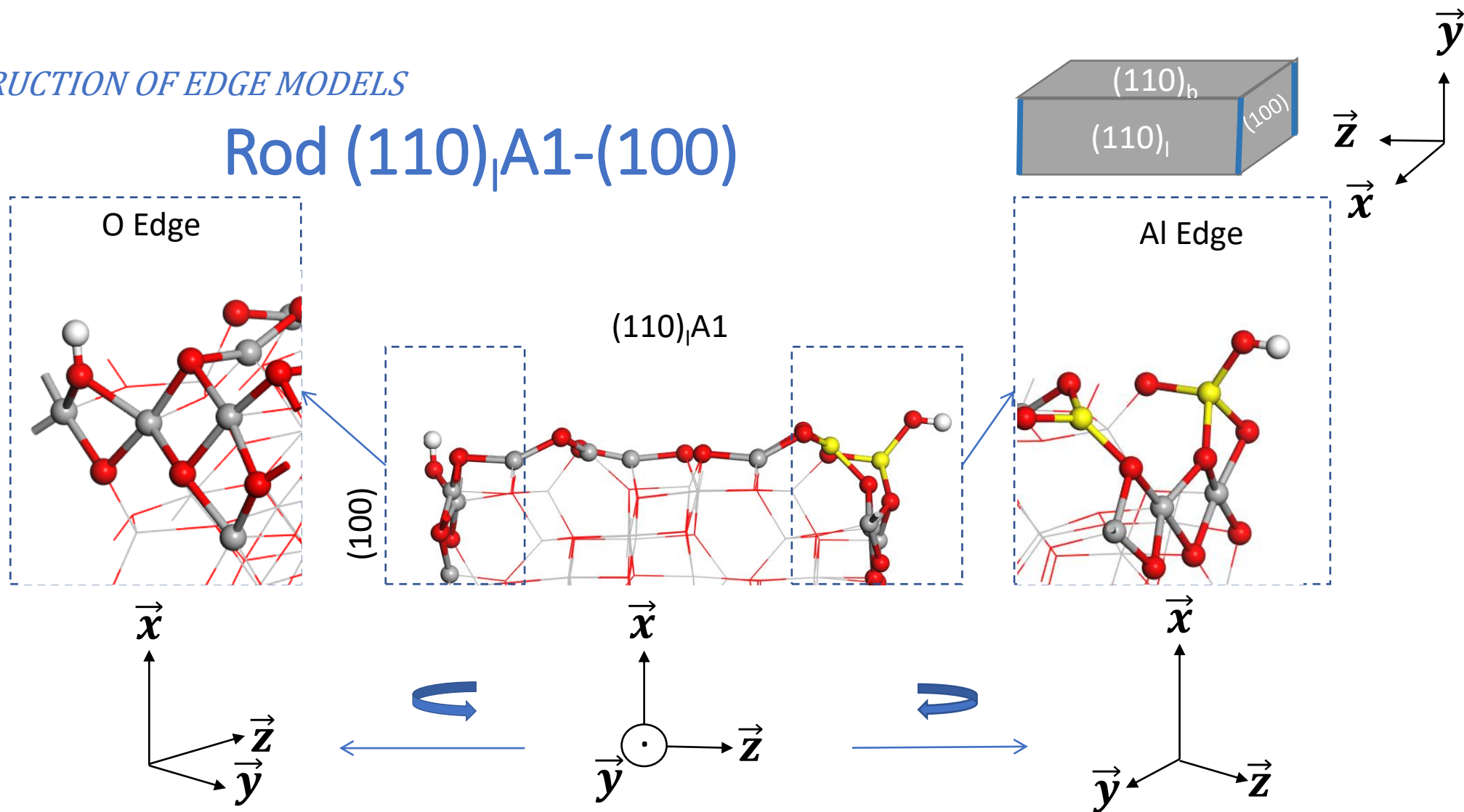


Fixing hydration on the surfaces according to targeted conditions (T, P_{H_2O})

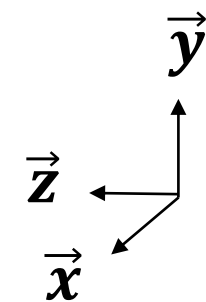
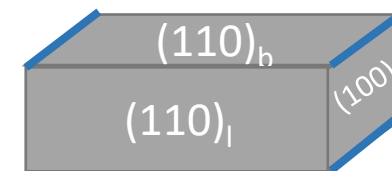
Then, explore edge hydration in (T, P_{H_2O}) conditions

Rod $(110)_I A1-(100)$

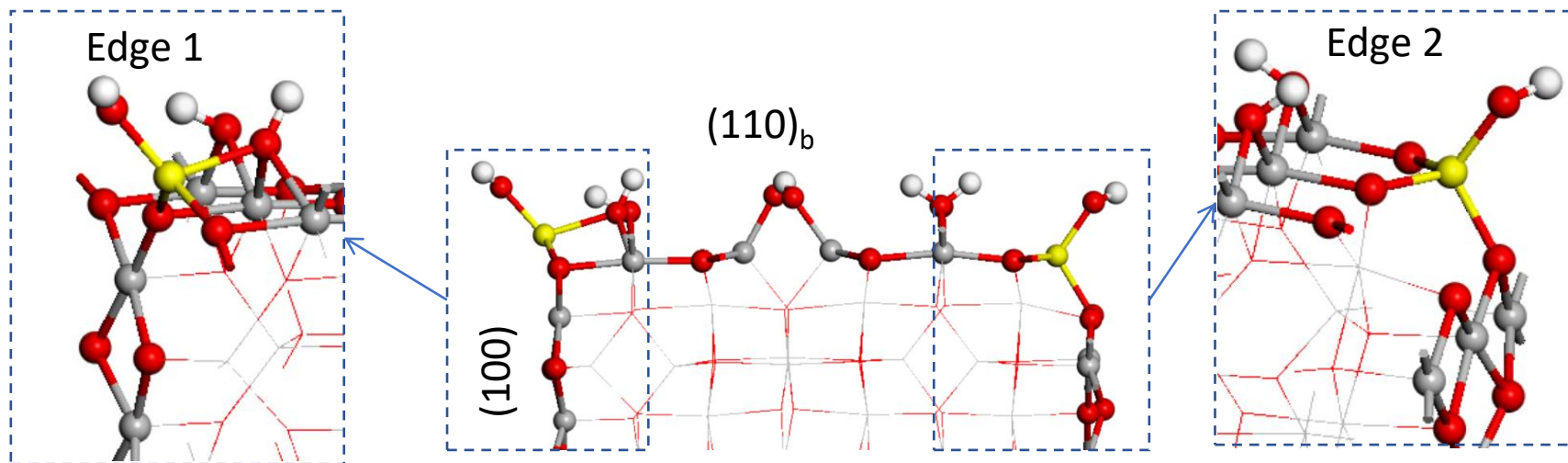
$T = 800 \text{ K}$
 $P_{\text{H}_2\text{O}} = 10^{-6} \text{ bar}$
 (close to NMR
 pretreatment
 conditions)



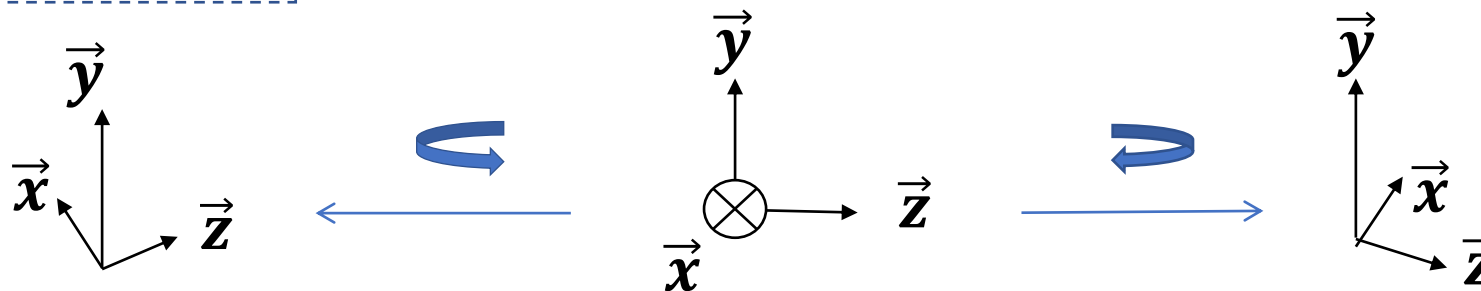
One edge exhibits $\text{Al}_V\text{-OH}$, the second one only O and $\mu_2\text{-OH}$

Rod (100) - $(110)_b$ 

$T = 700 \text{ K}$
 $P_{\text{H}_2\text{O}} = 10^{-6} \text{ bar}$
 (close to NMR
 pretreatment
 conditions)



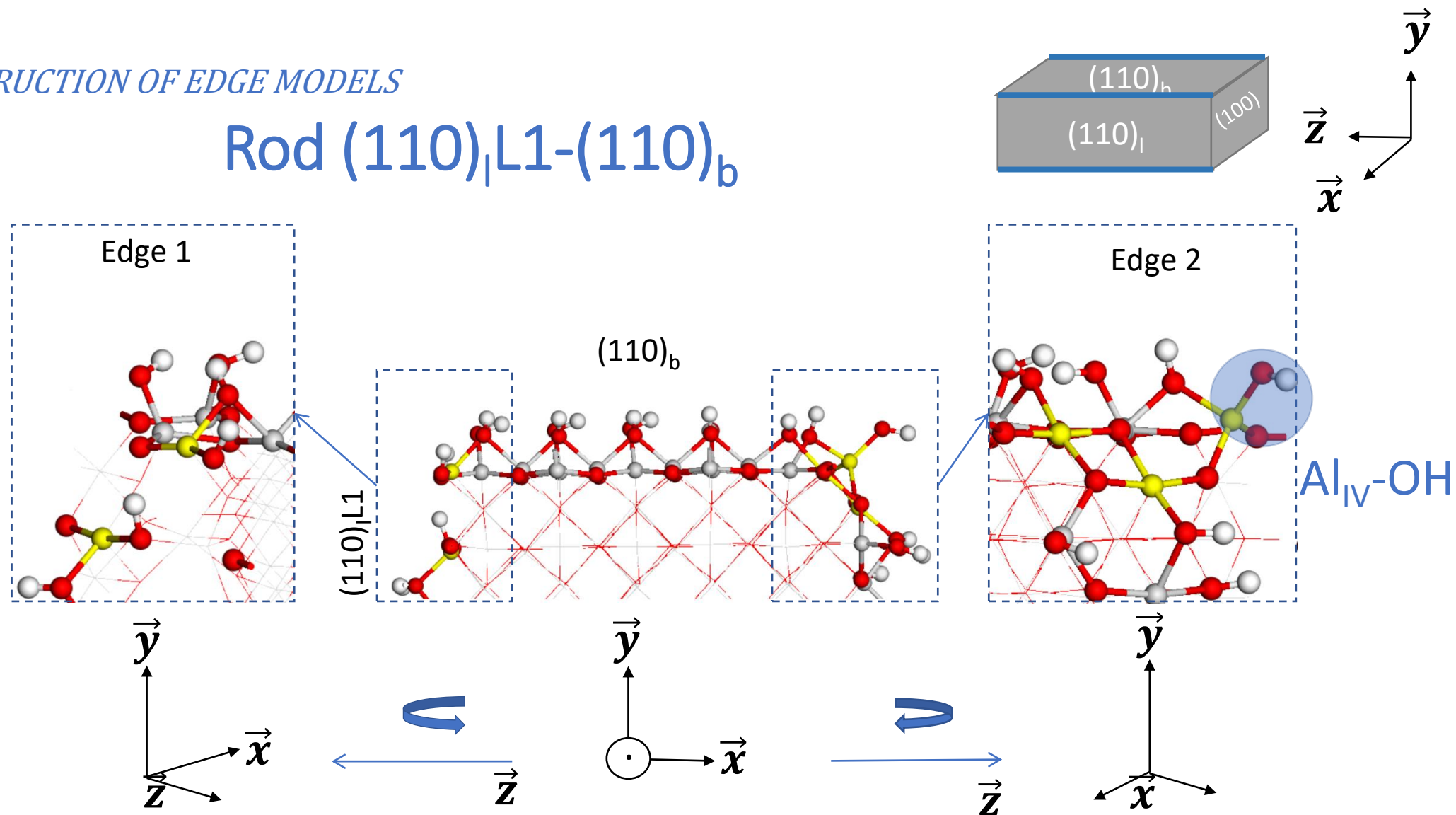
Pretreatment
 $700 \text{ K} \leq T \leq 800 \text{ K}$
 $10^{-4} \text{ bar} \leq P_{\text{H}_2\text{O}} \leq 10^{-6} \text{ bar}$



Both edges exhibit $\text{Al}_{\text{IV}}\text{-OH}$

Rod $(110)_l$ L1- $(110)_b$

$T = 700$ K
 $P_{\text{H}_2\text{O}} = 10^{-6}$ bar
 (close to NMR
 pretreatment
 conditions)



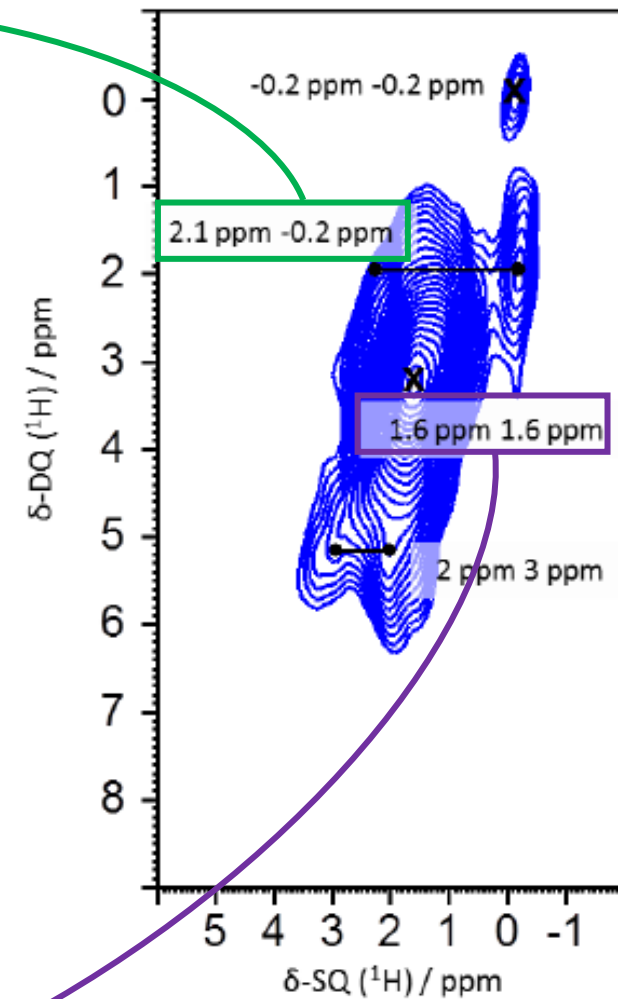
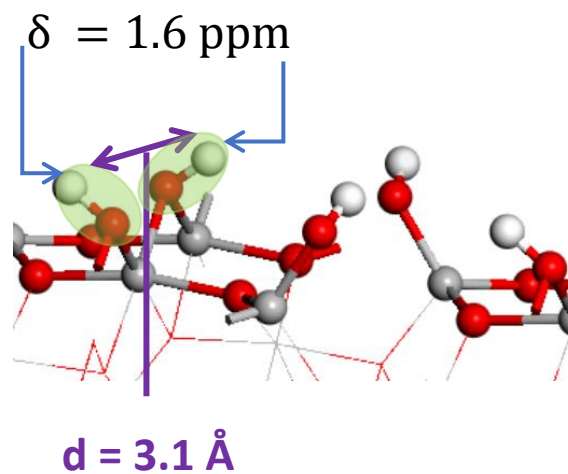
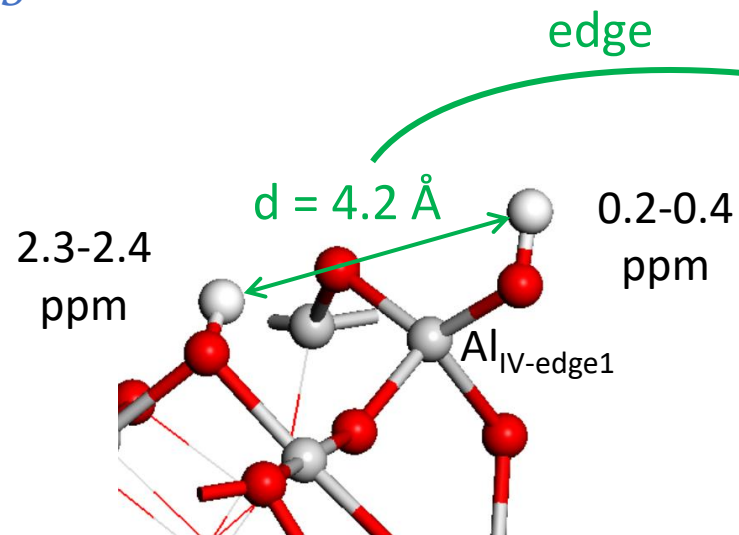
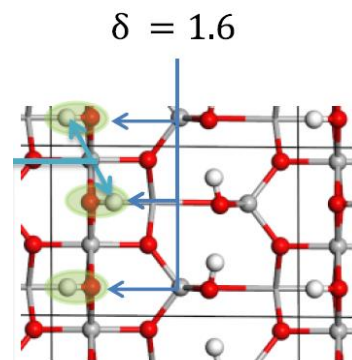
Edges exhibiting Al_{V} Lewis sites and $\text{Al}_{\text{IV}}\text{-OH}$

Double quantum spectra

→ Through space correlation between ^1H

→ isolated $\mu_2\text{-OH}$

rows on the $(110)_b$ surface



Double quantum spectrum of Pural SB3 [1]

Comparison of calculated and observed proton chemical shifts

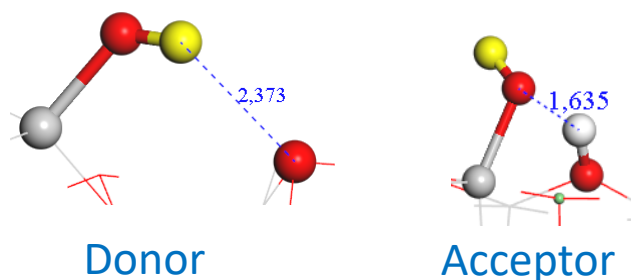
→ Acceptors and isolated are in the expected range (except μ_3)

→ But only isolated μ_1 at edge position have a chemical shift around 0 ppm

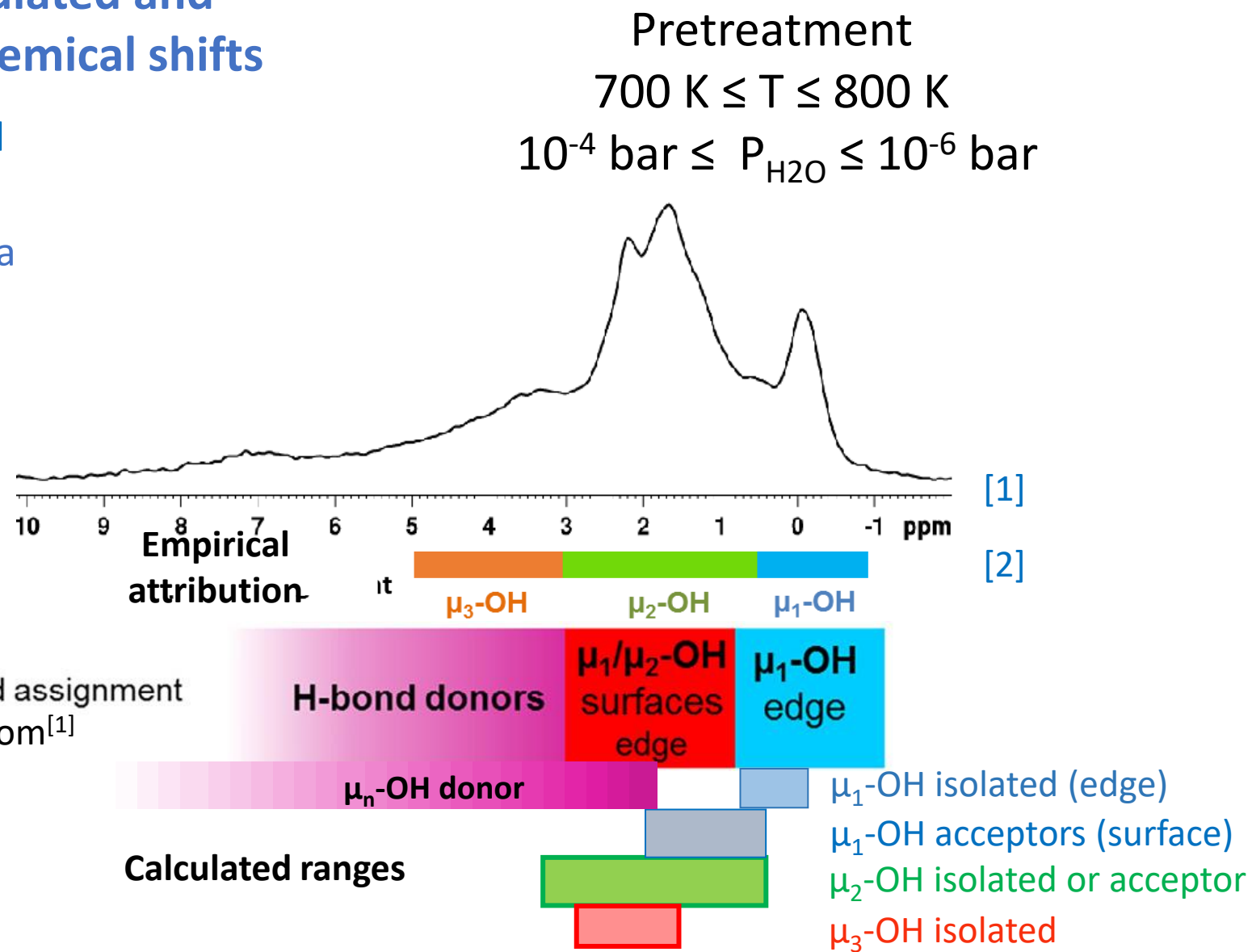
→ Many μ_1 at surface are H-bond donors (2-4ppm)

Isolated μ_2 and acceptor are in a large range

→ Strong impact of the bridged Al coordination $\delta(\mu_2-(Al_{IV}, Al_{IV})) > \delta(\mu_2-(Al_{VI}, Al_{VI}))$



Revisited assignment from^[1]



[1] A. T.F. Batista, D. Wisser, T. Pigeon, D. Gajan, F. Diehl, M. Rivallan, L. Catita, A.-S. Gay, A. Lesage et al., *J. Catal.* **2019**, 378, 140

[2] M. Taoufik, K. C. Szeto, N. Merle, I. Del Rosal, L. Maron, J. Trébosc, G. Tricot, R. M. Gauvin, L. Delevoye, *Chem. Eur. J.* **2014**, 20, 4038.

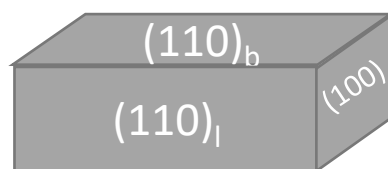
CONCLUSION

Confirms from another approach the previous surface models

→ 3 new models to complete the picture (isolated μ_2 μ_3)

→ There are two different (110) surfaces, basal more stable

→ Provide a rationalization for the auto-correlation peak by the free μ_2 -OH on (110) surfaces



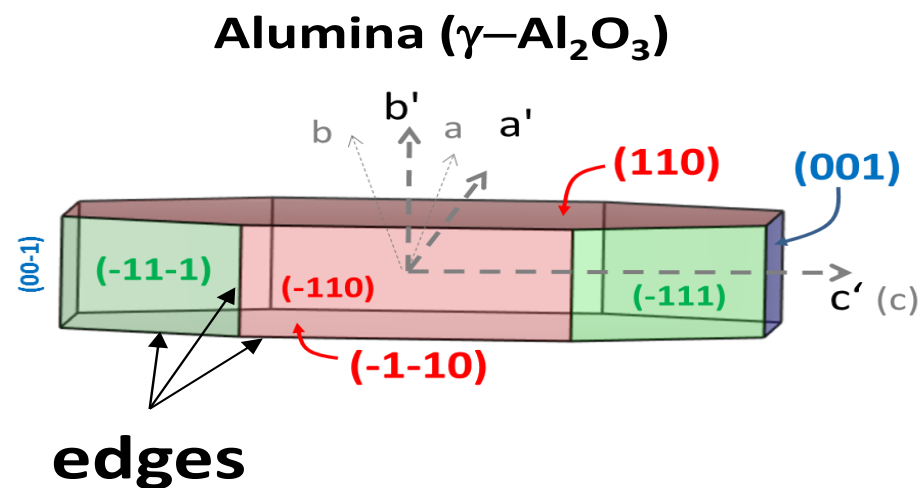
3 new edge models :

→ Validates the quality of the models and the attribution of the 0 ppm peak

→ Provide a rationalization for the auto-correlation peak by the free μ_2 -OH and free μ_1 -OH at edge position

We finally complete and revisited our attribution of the ^1H spectra

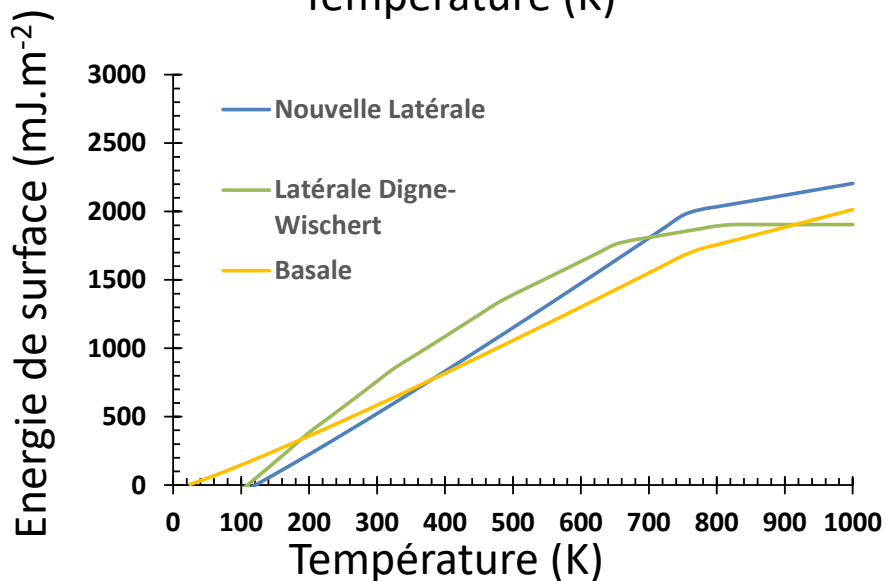
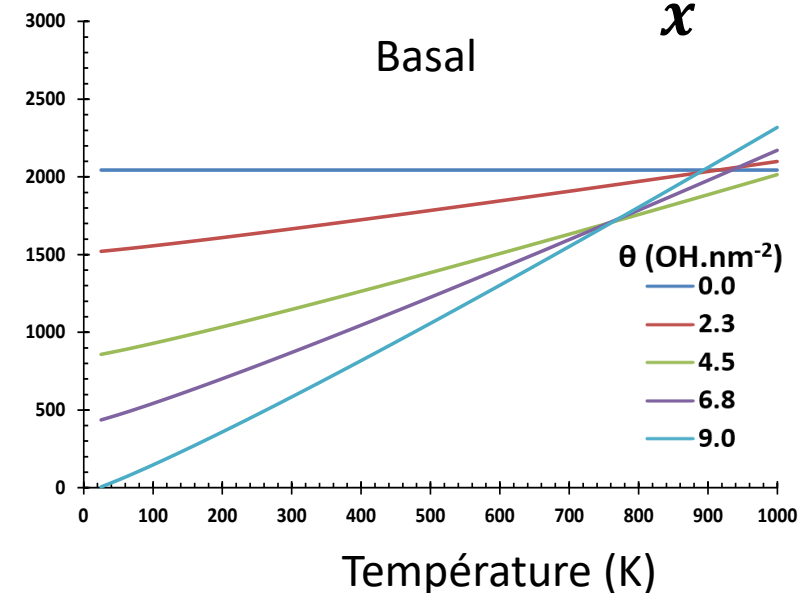
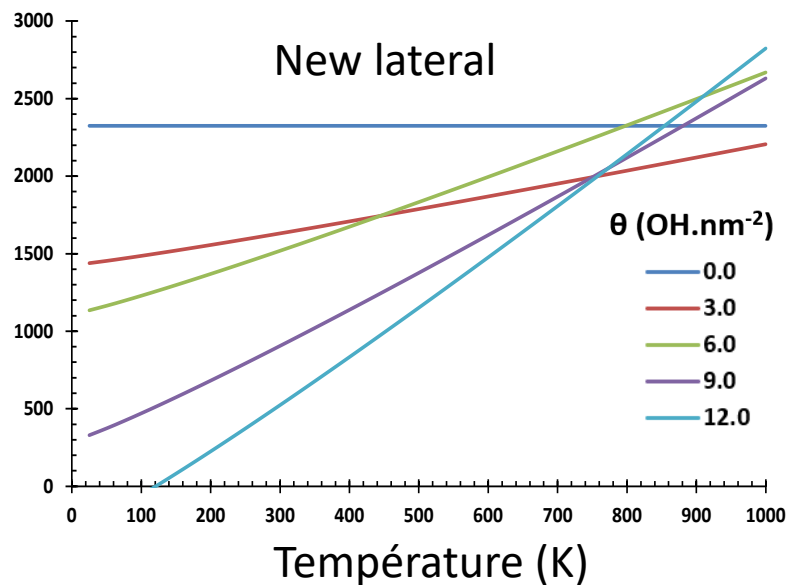
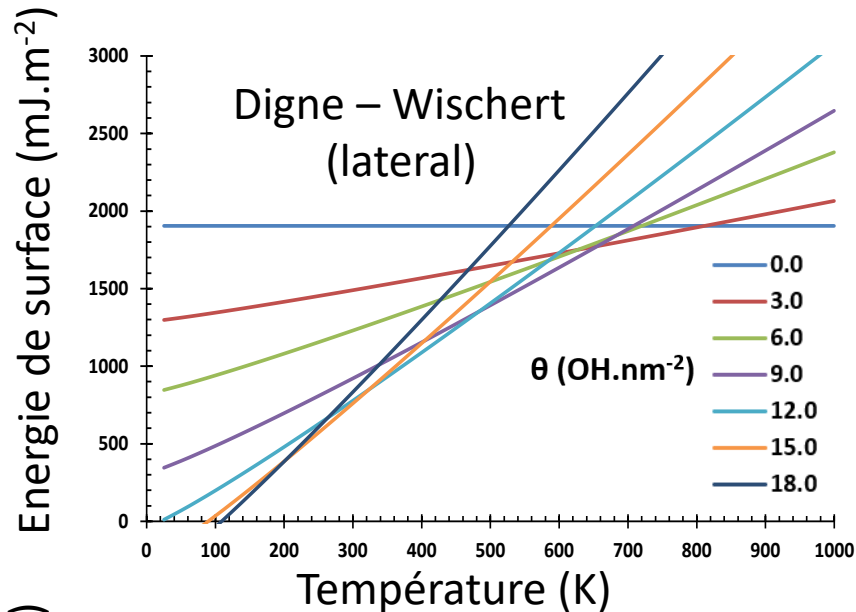
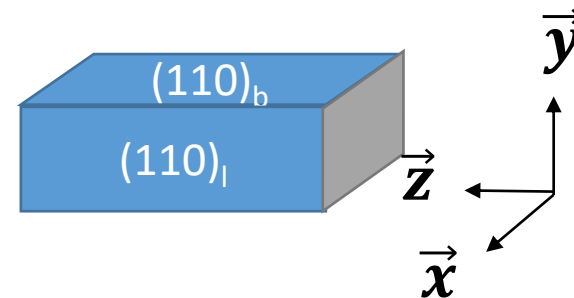
Rod models including (111) surface (limitation due to the size)



^{17}O NMR parameters (δ , C_q , η) ^[1] (not exploited calculation results)

Appendices

Other alternative (110) lateral surface models

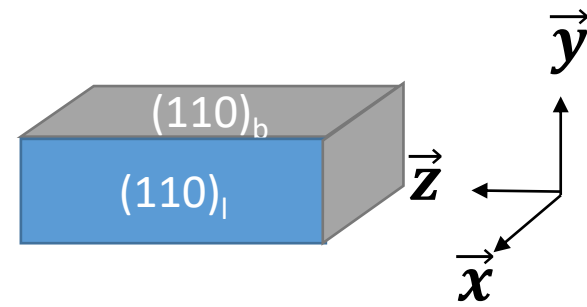


$$P_{\text{H}_2\text{O}} = 10^{-6} \text{ bar}$$

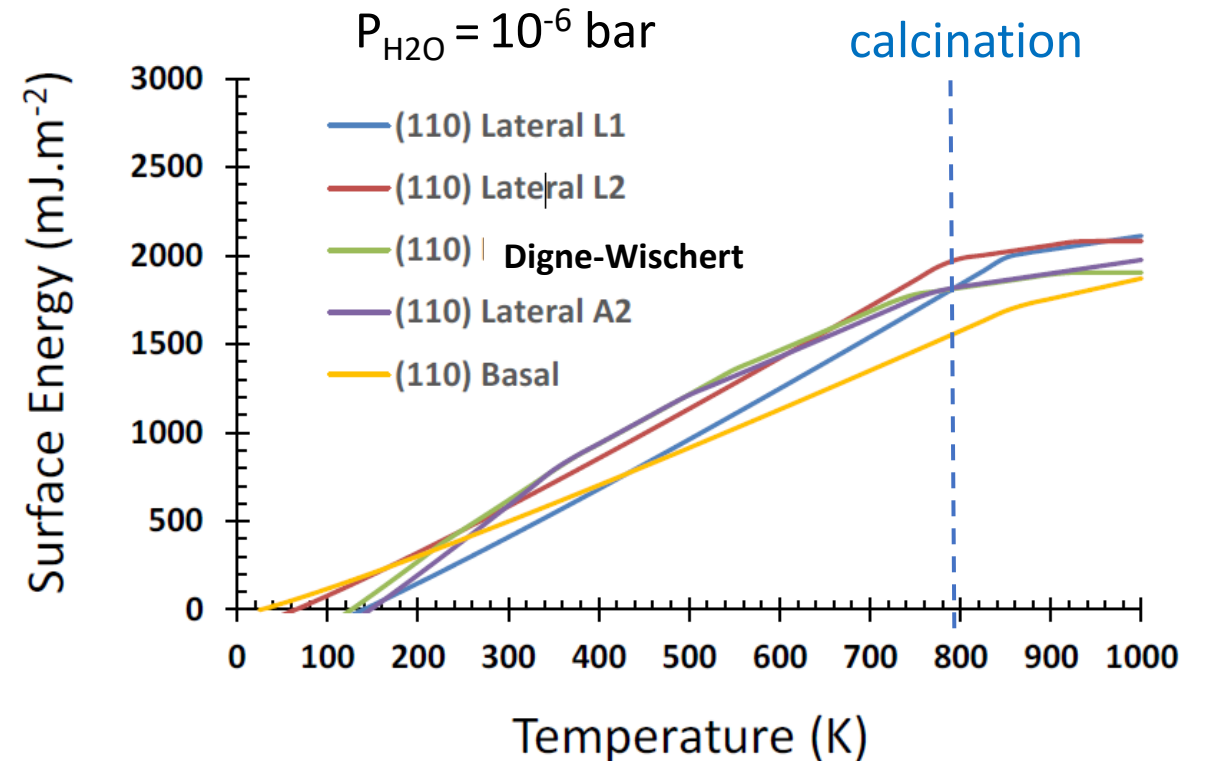
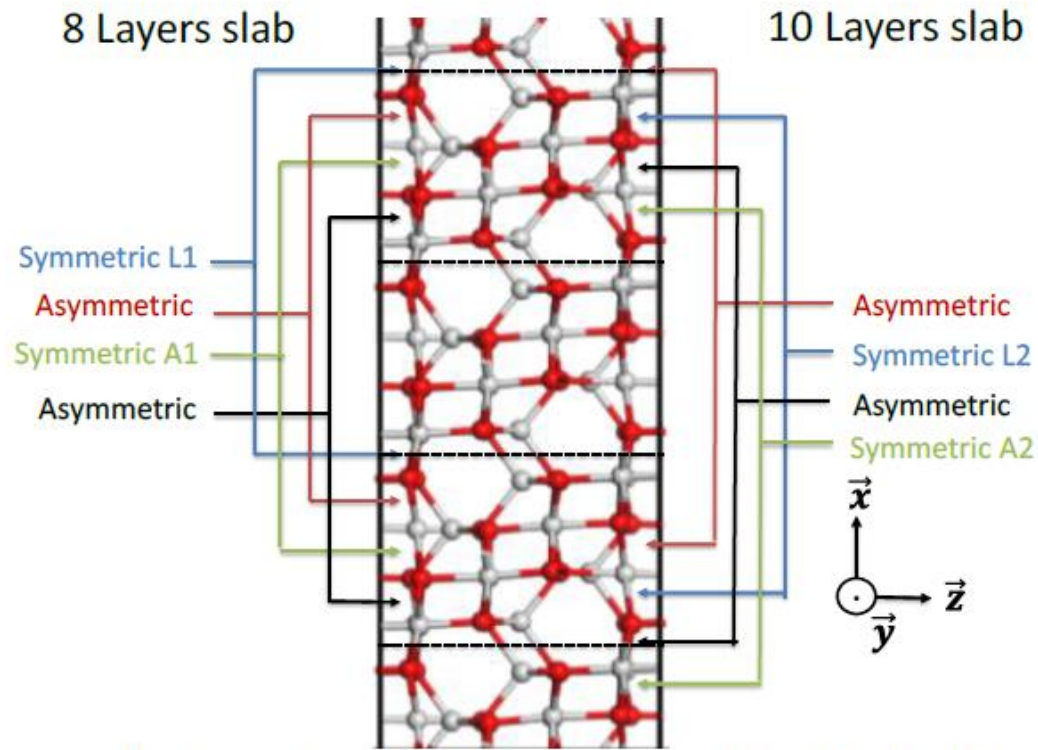
The new models have a lower surface energy on almost the whole temperature range

I. SURFACE MODEL CONSTRUCTION

Other alternative (110) lateral surface models



Construction from the Krokidis bulk

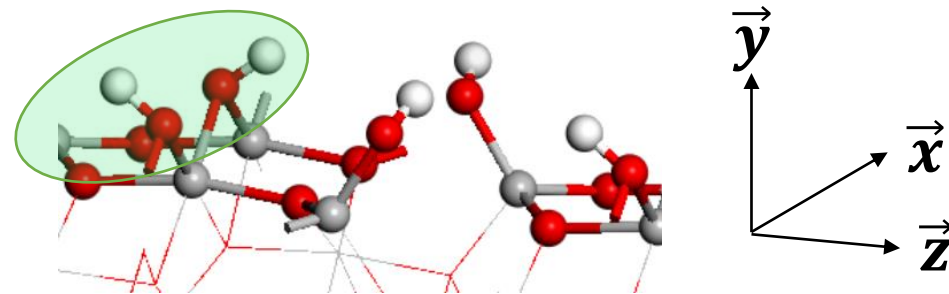
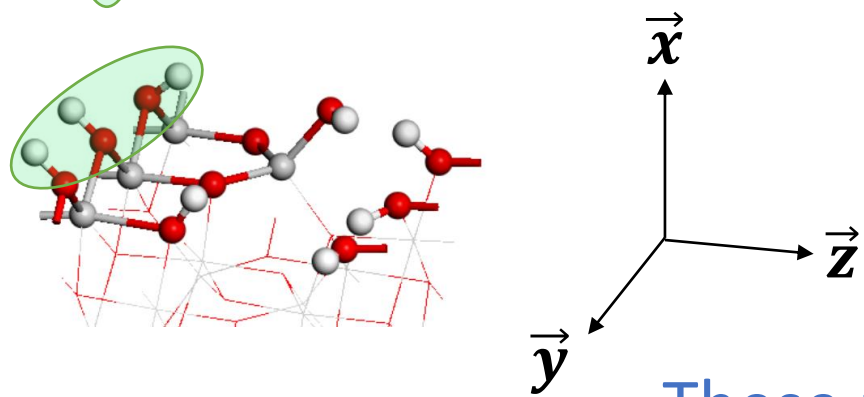
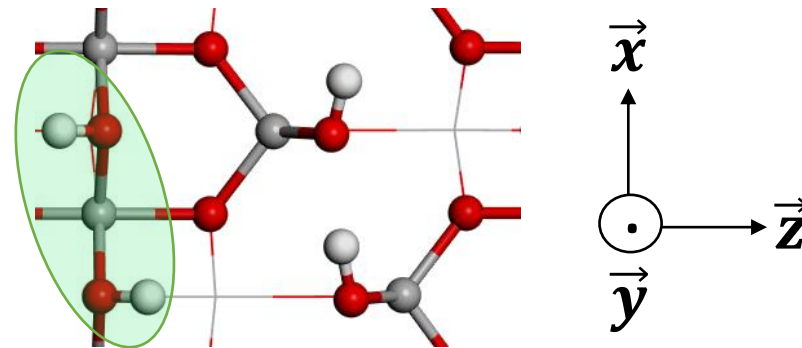
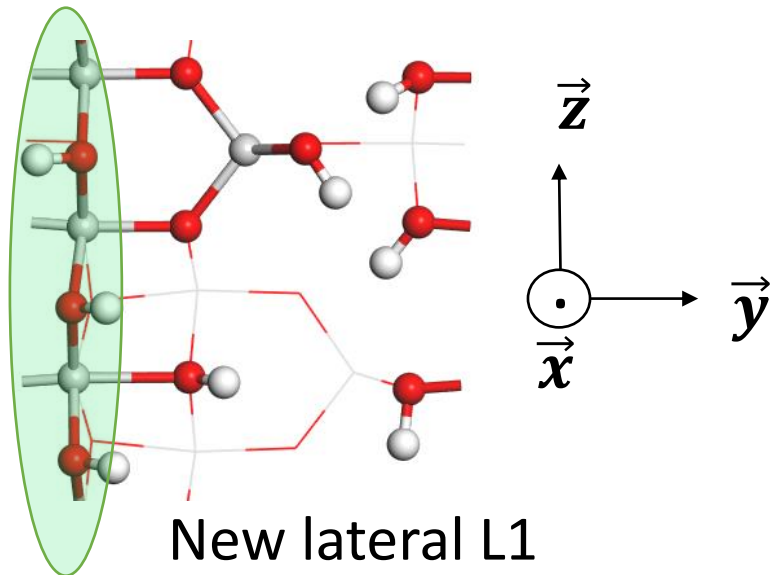
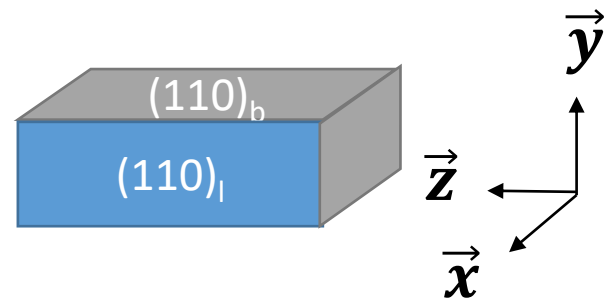


The revisited models exhibit a lower surface energy on a wide temperature range

For the calcination temperature: Digne-Wischert models are favored

I. SURFACE MODEL CONSTRUCTION

Other alternative (110) lateral surface models



These new models present aligned
Highly stable free OH- μ_2 -(Al_{Vl}Al_{Vl})