

SIMULATING NC-AFM IMAGING OF CALCITE IN UHV AND WATER



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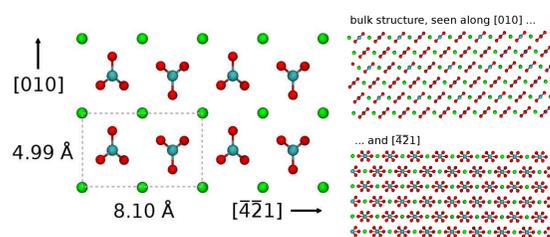
CALCITE (10 $\bar{1}$ 4) SURFACE

Calcite is a stable polymorph of calcium carbonate (CaCO_3), one of the most abundant minerals on earth.

It has a rhombohedral crystal structure ($R\bar{3}c$), with unit cell vectors $a=b=4.99 \text{ \AA}$ and $c=17.06 \text{ \AA}$. $\angle(a,b)=120^\circ$, and c is perpendicular to a and b .

The $10\bar{1}4$ cleavage plane is charge neutral and therefore very stable. It has been studied in high resolution AFM in UHV and water, and by other experimental methods (LEED, XPS) as well.

The $10\bar{1}4$ surface unit cell consists of two CaCO_3 units and measures $4.99 \times 8.10 \text{ \AA}^2$. The calcium (green), carbon (cyan) and one of the oxygen (red) atoms lie in the surface plane. The other two oxygens are above and below the plane.



CALCITE IN VACUUM

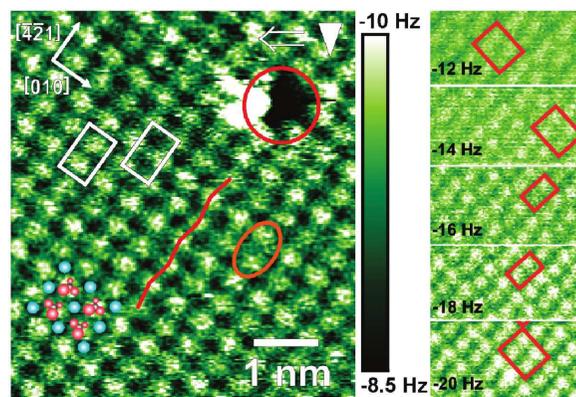
EXPERIMENTAL DATA

Image from FM-AFM in UHV with a Silicon tip [1]

zig-zag line: oxygen atoms protruding from the surface.

row pairing (red ellipse): alternating brightness between adjacent rows of oxygen atoms.

2x1 reconstruction (red rectangles): a true surface property, but only imaged at certain Δf values.

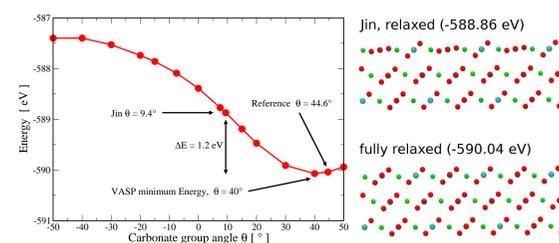


[1] Schütte J., Rahe P., Tröger L. *et al.*, *Langmuir* **26**, 8295 (2010).

SURFACE STRUCTURE FROM DFT

PAW-PBE calculations of 16 CaCO_3 molecules in 4 layers + vacuum gap using the VASP 4.6 code.

Row pairing mechanism proposed by Jin *et al.* [2]: oxygen atoms protruding from the surface are at two different heights, because every other carbonate group is rotated by 35° towards the surface.



CONCLUSIONS

The relaxed surface shows only minor differences compared to bulk Calcite structure.

Electronic structure calculations can not directly predict row pairing or 2x1 reconstruction.

The proposed row-paired system is energetically unfavorable and there is no barrier separating it from the energetic minimum.

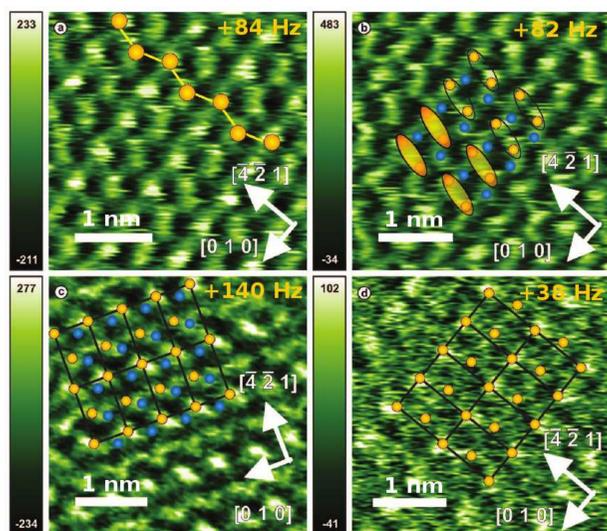
[2] Jin M., Shimada E., and Ikuma Y., *J. Ceramic Soc. Japan* **107**, 1167 (1999).

CALCITE IN WATER

EXPERIMENTAL DATA

Images from FM-AFM [3] with a Silicon tip ($f_0=160 \text{ kHz}$, $k_0=40 \text{ N/m}$, $Q=8$) in water and 0.15–1 M KCl. The oscillation amplitude is 0.2–0.5 \AA .

Varying contrasts can be observed depending on Δf set point and pH of the solution.



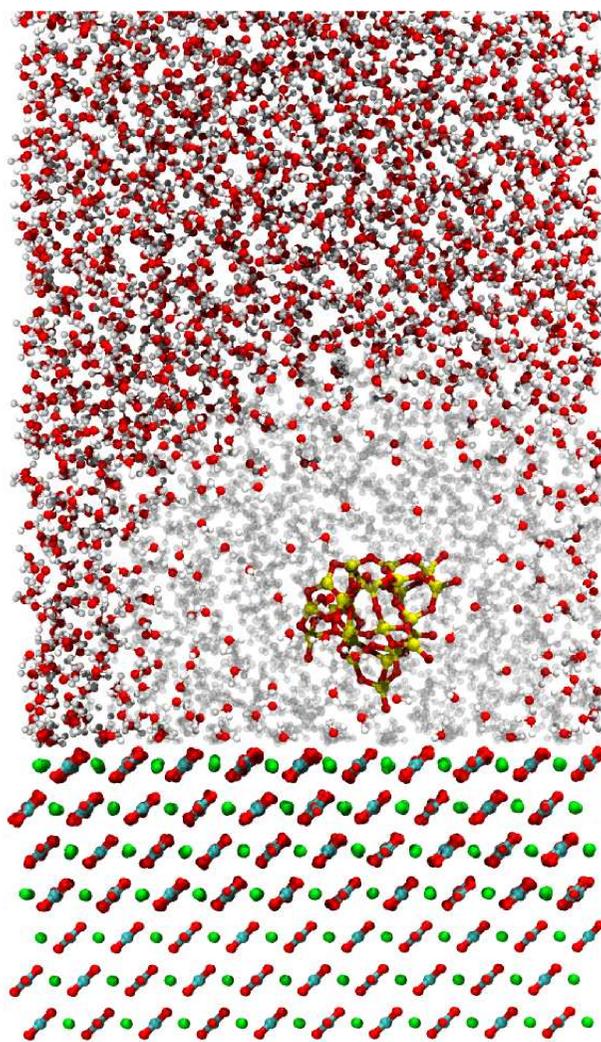
[3] Rode S., Oyabu N., Kobayashi K. *et al.*, *Langmuir* **25**, 2850 (2009).

MOLECULAR DYNAMICS SIMULATIONS

We want to understand the role of the liquid in the contrast imaging mechanism.

At $T=300 \text{ K}$, the water molecules' entropic contribution to the free energy ($F = U - TS$) of the system is very important. We have to resort to molecular dynamics simulations using empirical interaction potentials to average system properties in the correct statistical ensemble (N,V,T or N,p,T).

With the GROMACS code ('fast, flexible, free') on a linux cluster, running 1 ns MD of 20.000 atoms takes less than 2 days on 4 CPU cores.



INTERACTION PARAMETERS

There is no consistent force field with all the parameters needed in this system. We have to combine force fields for a Calcite–water interface [4] and bulk SiO_2 [5], and missing parameters are assigned according to Refs. [6,7].

[4] Raiteri P. *et al.*, *J. Phys. Chem. C* **114**, 5997 (2010).

[5] Vashishta P. *et al.*, *Phys. Rev. B* **41**, 12197 (1990).

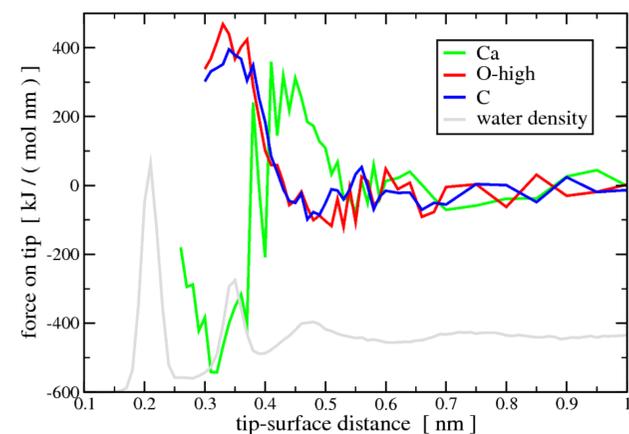
[6] Su X. and Garofalini S.H., *J. Mater. Res.* **19**, 752 (2004).

[7] Du J. and Cormack A.N., *J. Am. Ceram. Soc.* **88**, 2532 (2005).

FORCE CURVE CALCULATIONS

The simulation box measures $40 \times 40.5 \times 100 \text{ \AA}^3$ with periodic boundary conditions in x , y and z . It contains 8 layers of calcite (3200 atoms, bottom 4 layers are 'frozen' to their initial positions). The 'tip' is modeled from a 72 atom SiO_2 nanocluster. It is placed at distances from 2.6–10.0 \AA above the surface and its top part is frozen as well. Then, the remaining box is filled with 4020 water molecules ($\rho=1.0 \text{ g/cm}^3$). The entire system contains around 20.000 atoms. The box shape and volume are constant, and a Nosé-Hoover thermostat is used to simulate an N,V,T ensemble.

For every tip-surface distance, the system is equilibrated for 0.5 ns at $T=300 \text{ K}$ and then the force on the center of mass of the frozen part of the tip is averaged over 0.5 ns. In this manner, force curves are harvested above the calcium (green), carbon (blue) and upper oxygen atoms (red).



CONCLUSIONS

Force curves from our simulations are compatible with the observed contrast images.

Very promising first results, but further work is necessary to fully understand the rearrangement of the liquid during tip oscillation.

Consistency of the interaction potentials must be tested in a systematic way.