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Atomic scale characterization, manipulation and dissipation on insulating surfaces

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Atomic scale characterization, manipulation and dissipation on insulating surfaces

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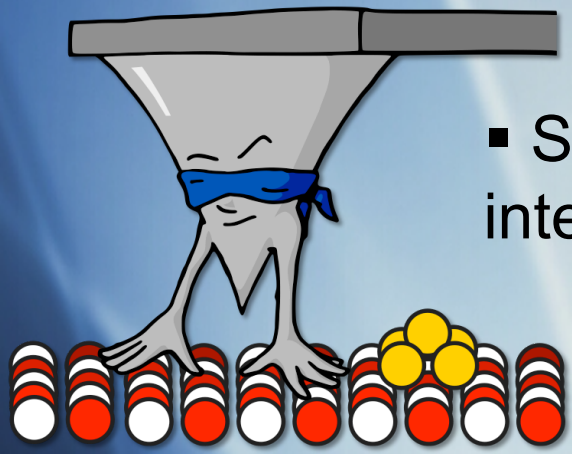
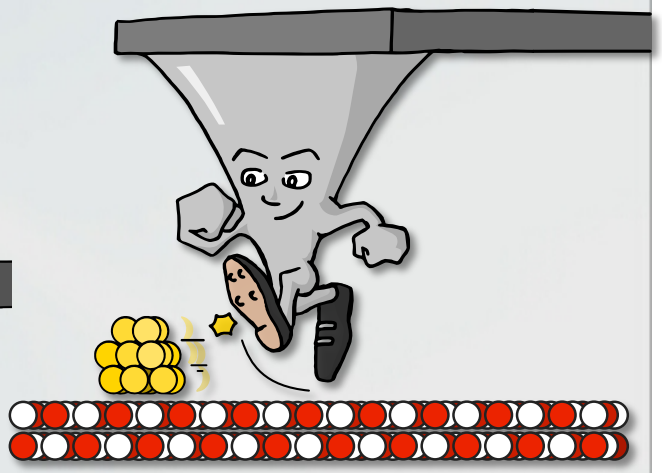
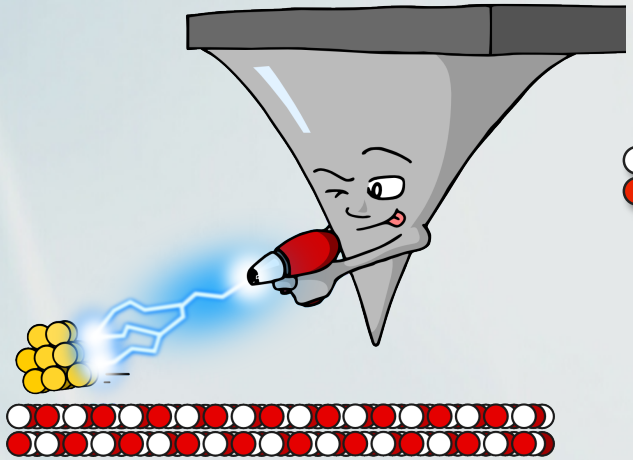
SPM modelling



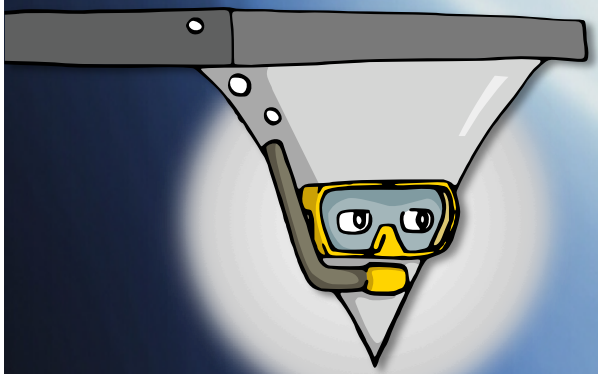
- STM/AFM interpretation



- Nanomanipulation

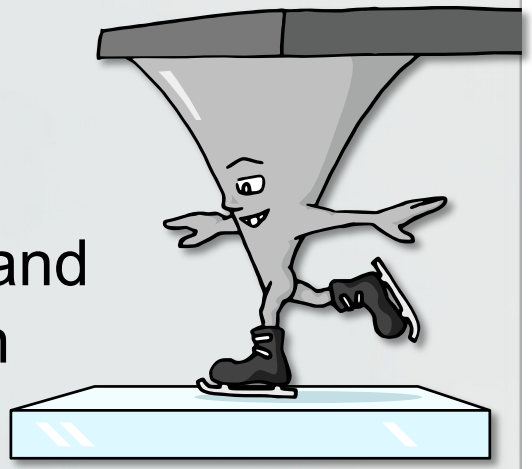


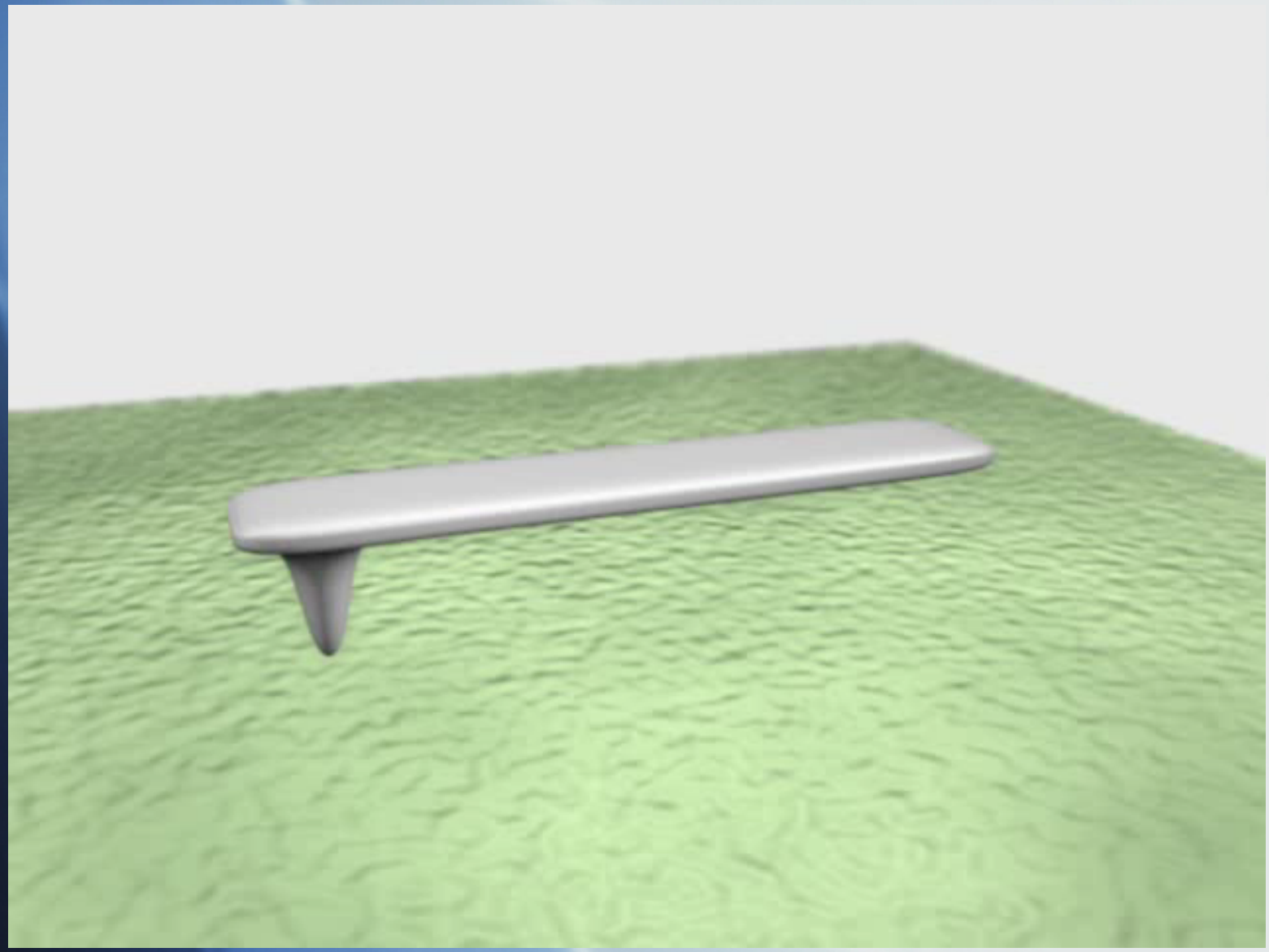
- Charge transfer



- AFM in water

- Friction and dissipation





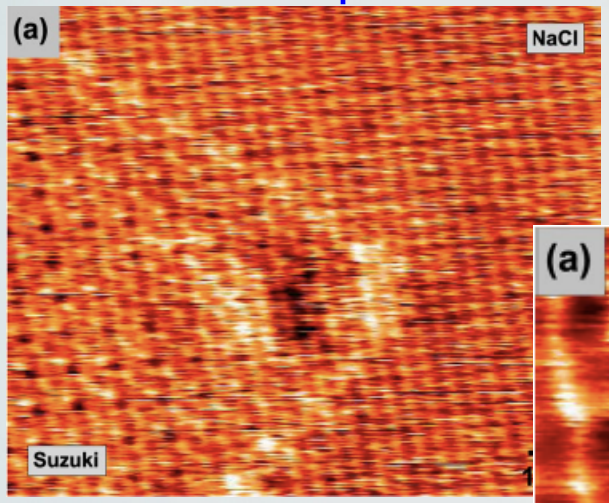
Doping insulators

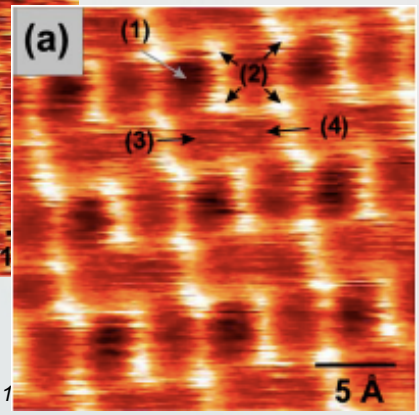
A. S. Foster *et al.* Phys. Rev. Lett. (2009) 102 256103

• Doping of monovalent insulators with di- or multivalent impurity ions leads to the segregation of the so-called Suzuki phase[1] at the surface – recently shown in high resolution AFM images of $NaCl:Mg^{2+}$.

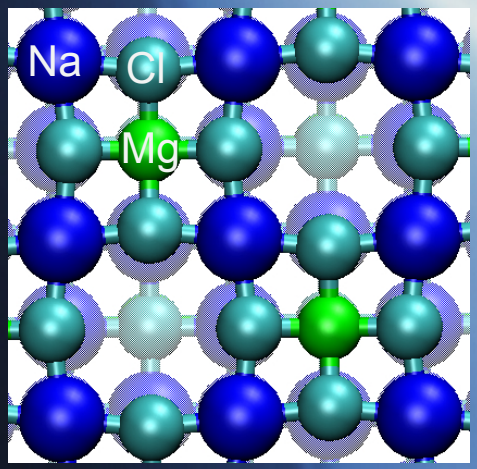
[1]K. Suzuki, J. Phys. Soc. Jpn. 10, 794 (1955) and 16, 67 (1961)

• The impurities are compensated by a nearby cation vacancy, producing a stable phase with similar geometry, but very different elements to the host.





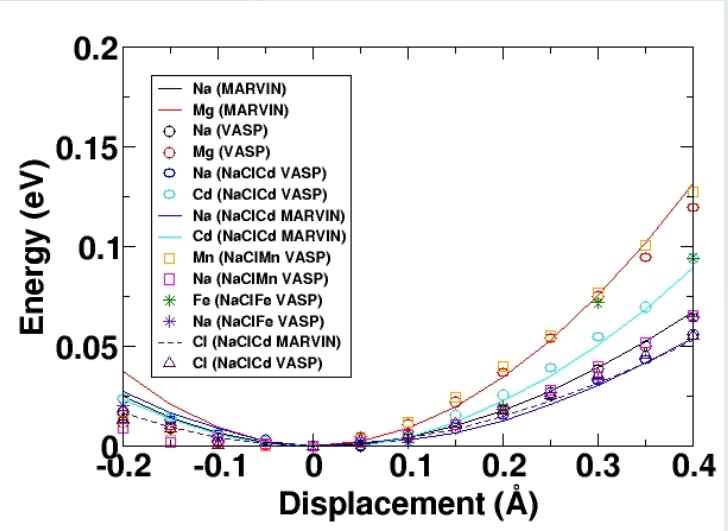
Phys. Rev. Lett

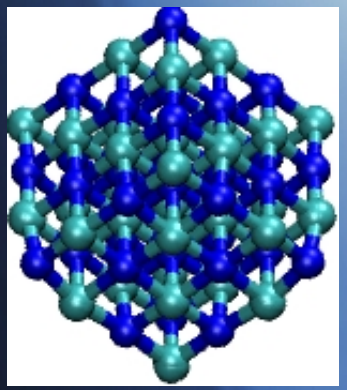


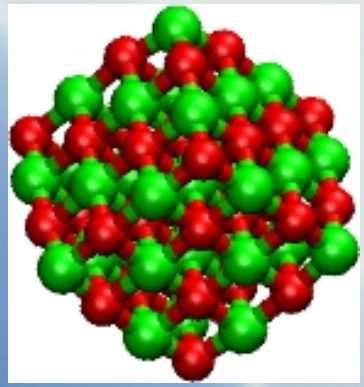
• Suzuki phases can be formed from many systems and impurities e.g. $NaCl:Cd^{2+}$, $NaCl:Fe^{2+}$, $LiCl:V^{2+}$, $MgO:Mn^{4+}$. Their properties in regard to molecular adsorption, nanocatalysis and nanomagnetism are particularly interesting.

Methods

- *ab initio (PAW-PBE-VASP)* calculations of bulk and surface used as benchmark for fitting of atomistic potentials.
- Structure matches experiments and *ab initio*.
- Atomic displacement profiles also match.





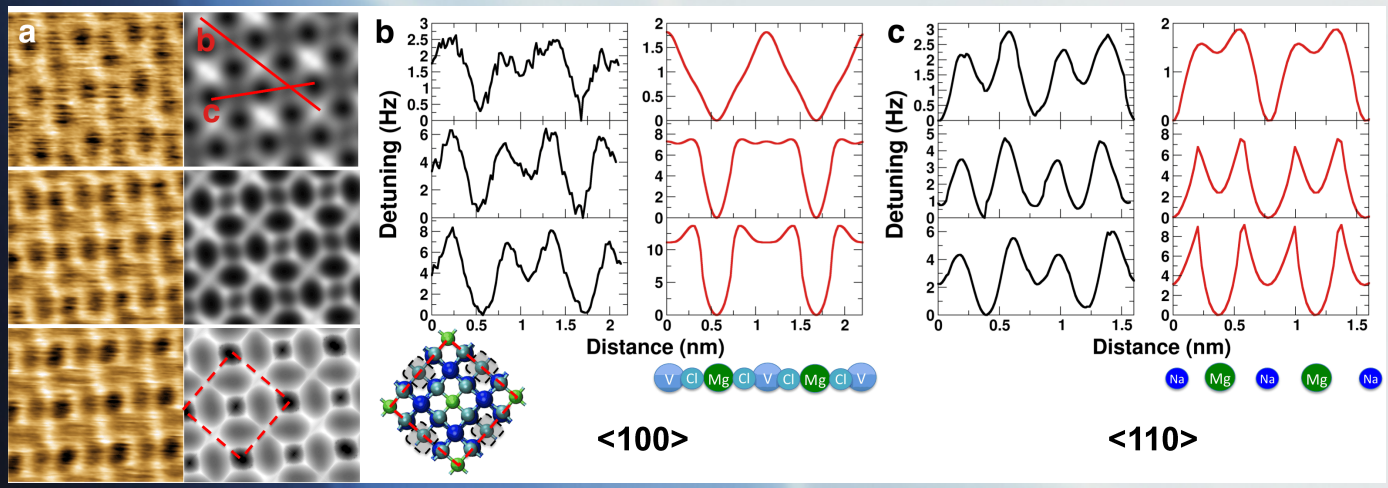


- Considered several tip models, including NaCl:Mg and NaCl:Cd based models.
- Upper third of tips and lowest layer of surface frozen, all other atoms allowed to relax fully.

NaCl:Mg

- Simulated images with a Cl-terminated NaCl tip match experimental contrast pattern, frequency change and contrast magnitude as a function of tip-surface separation.

- Clear evidence that experiment was imaging the Suzuki structure on the surface with vacancy sites as maximum contrast i.e. minimum attraction. All sublattices are resolved.

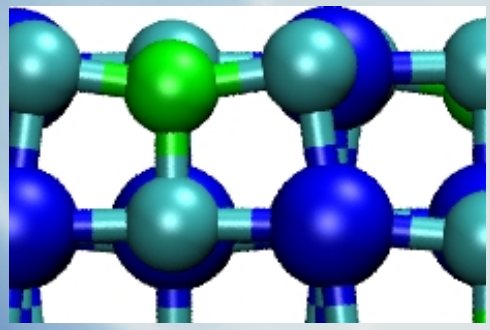


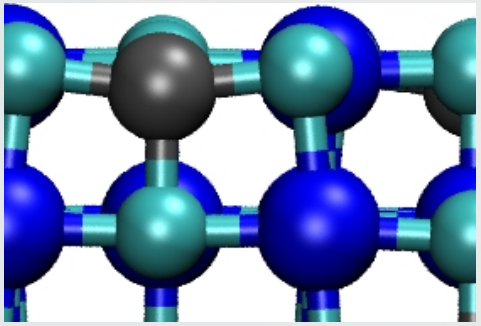
- Other tips produced characteristically different contrast or were much less stable than an NaCl tip.

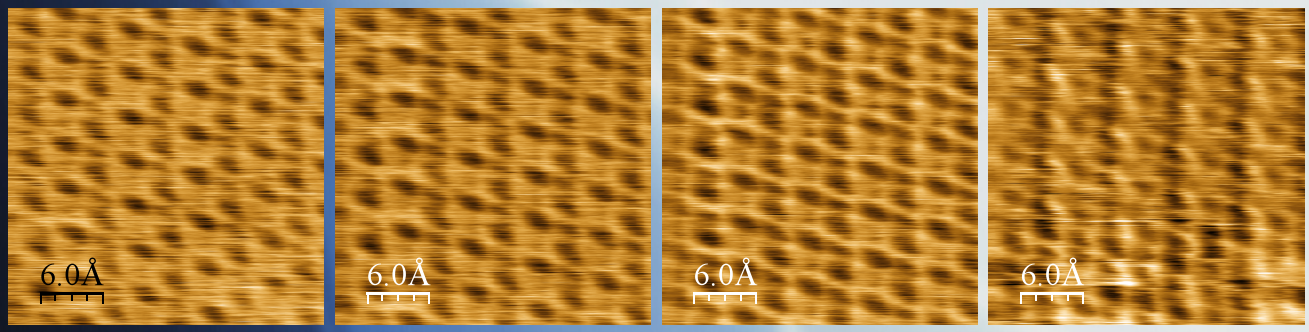
NaCl:Cd

• NaCl also doped with Cd^{2+}, resulting in the appearance of similar Suzuki islands at the surface.

• Calculated surface geometries are similar, although Cd induces larger displacements at the surface.





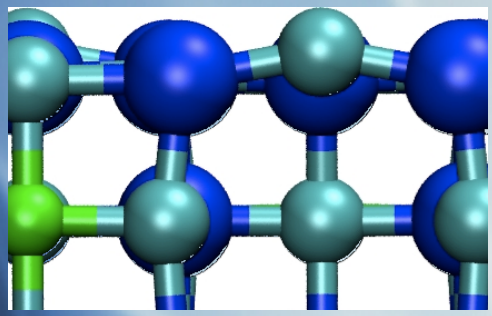


df = 109 Hz df = 112 Hz df = 115 Hz df = 118 Hz

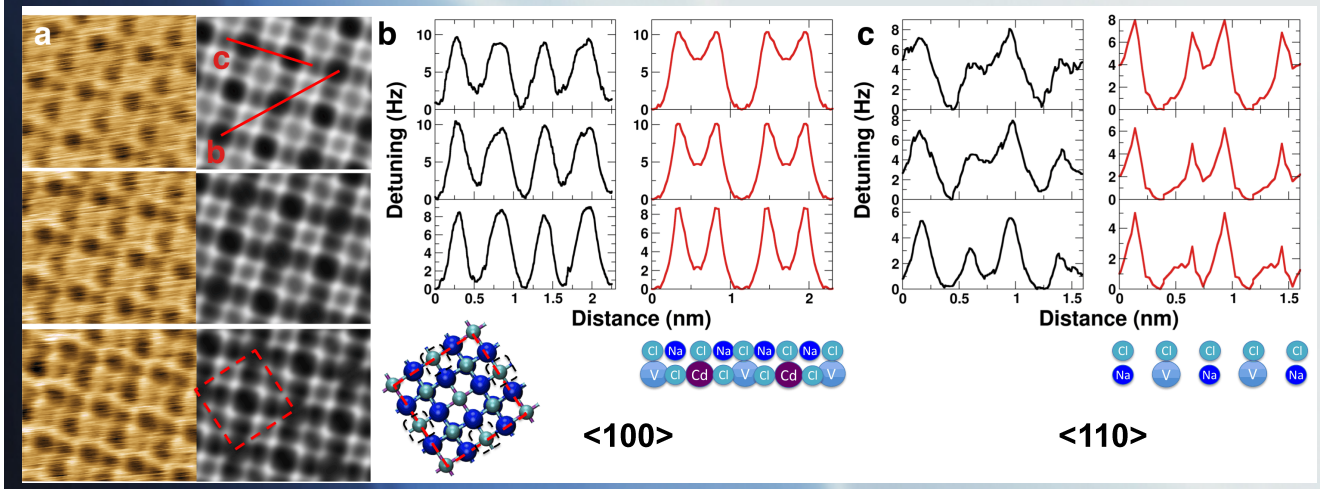
• Experimental images show a different contrast pattern, which cannot be seen in simulated images of NaCl:Mg for any tip – no match in simulations…

NaCl termination?

- Termination by an “ideal” NaCl layer has not been considered in earlier works.



- From *ab initio* surface energy calculations, NaCl:Mg Suzuki termination is favoured by 0.3 eV over NaCl termination.
- For NaCl:Cd the difference is less than 0.1 eV.

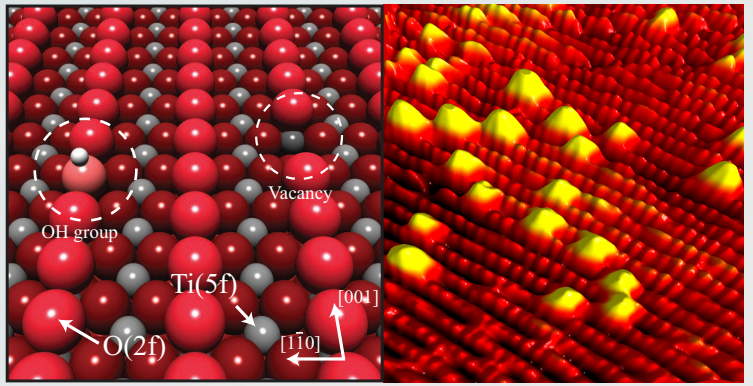


- Simulated images of the NaCl terminated surface with a Na-terminated tip match experiment.

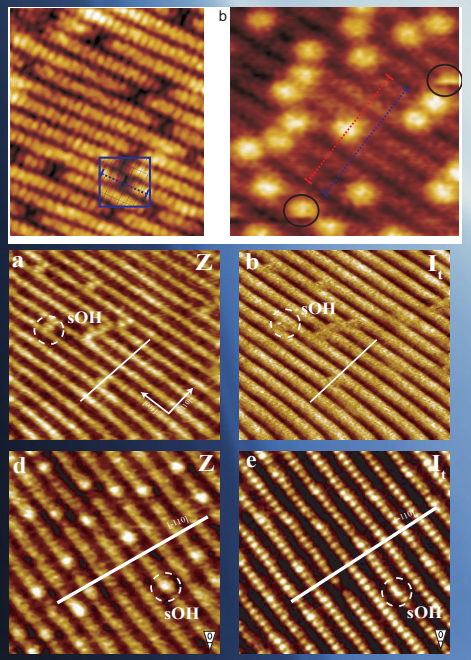
Benchmark oxide

Nanotechnology 17 (2006) 3436, Phys. Rev. B 76 (2007) 205415, Phys. Rev. B 78 (2008) 045416

• TiO_2 remains a model oxide for many surface science studies, particularly for Scanning Probe Microscopy (SPM).

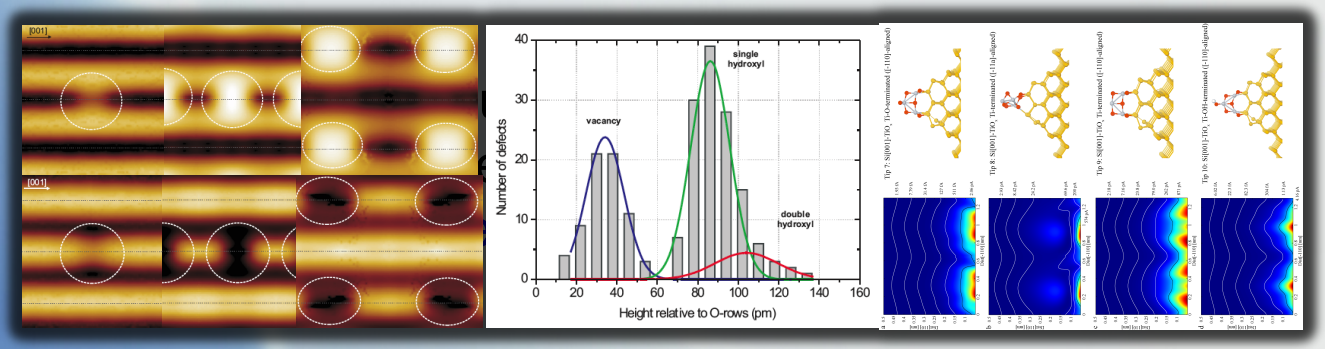


• Technologically important as a catalytic substrate, both in photo- and nano-catalysis. Also a common biomedical substrate.



• Wide gap semiconductor or Narrow Gap insulator, can be imaged in STM and AFM.

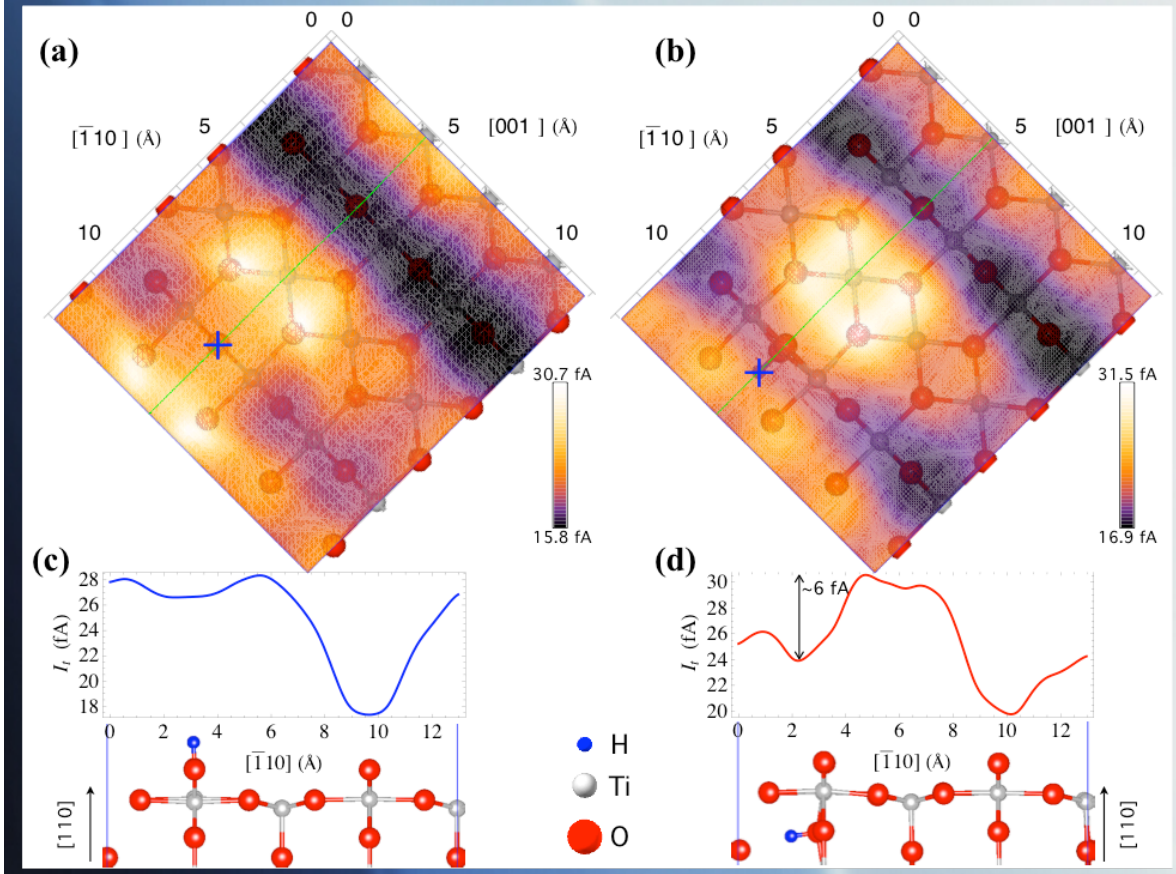
• Even in UHV, residual adsorbates can be seen on the surface after a few hours.

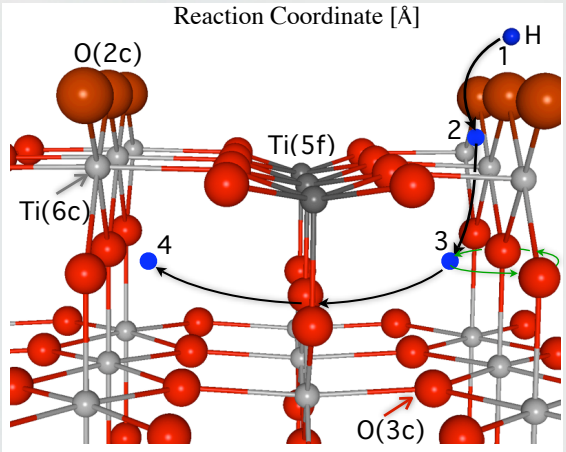


Now you see me! Now you don't!

Phys. Rev. Lett.102, 136103 (2009)

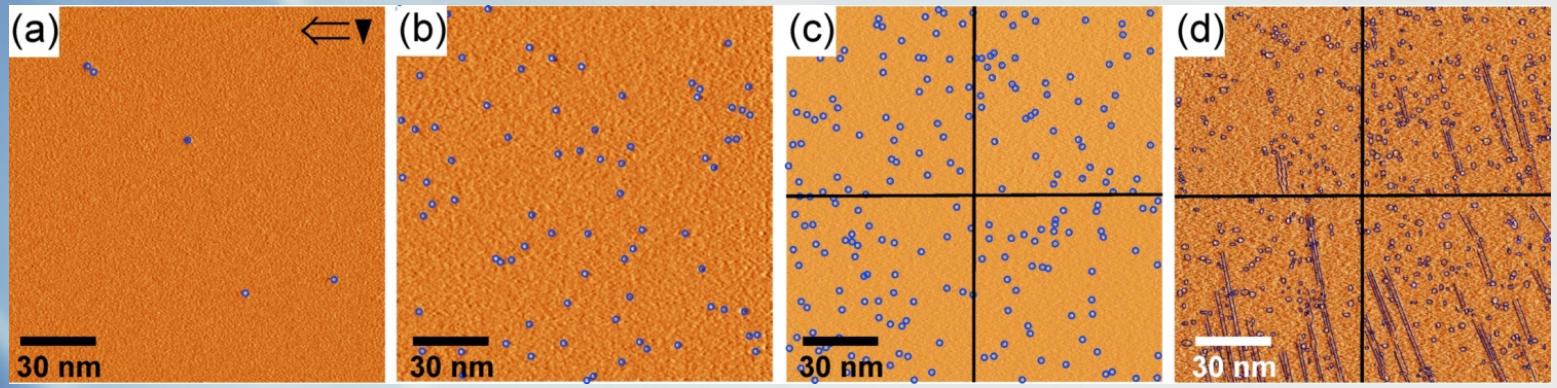
- Combining STM and AFM provides access to information not available from a single channel alone.



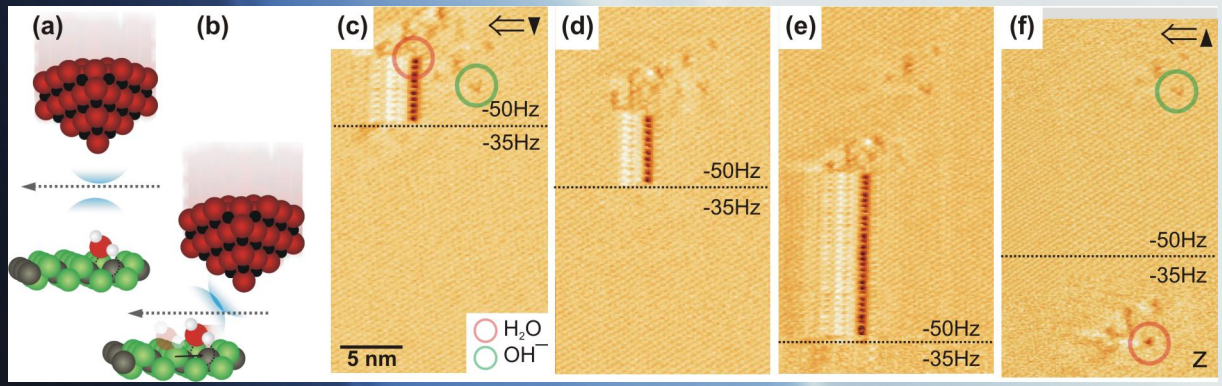


- Proton is manipulated by the tip – it is pushed from the surface to subsurface site. Barrier ~1 eV.

Chemistry and mobility of water on the CaF_2 (111) surface



• AFM images as a function of time show the gradual deposition of water and the eventual manipulation of some of the resultant defects.

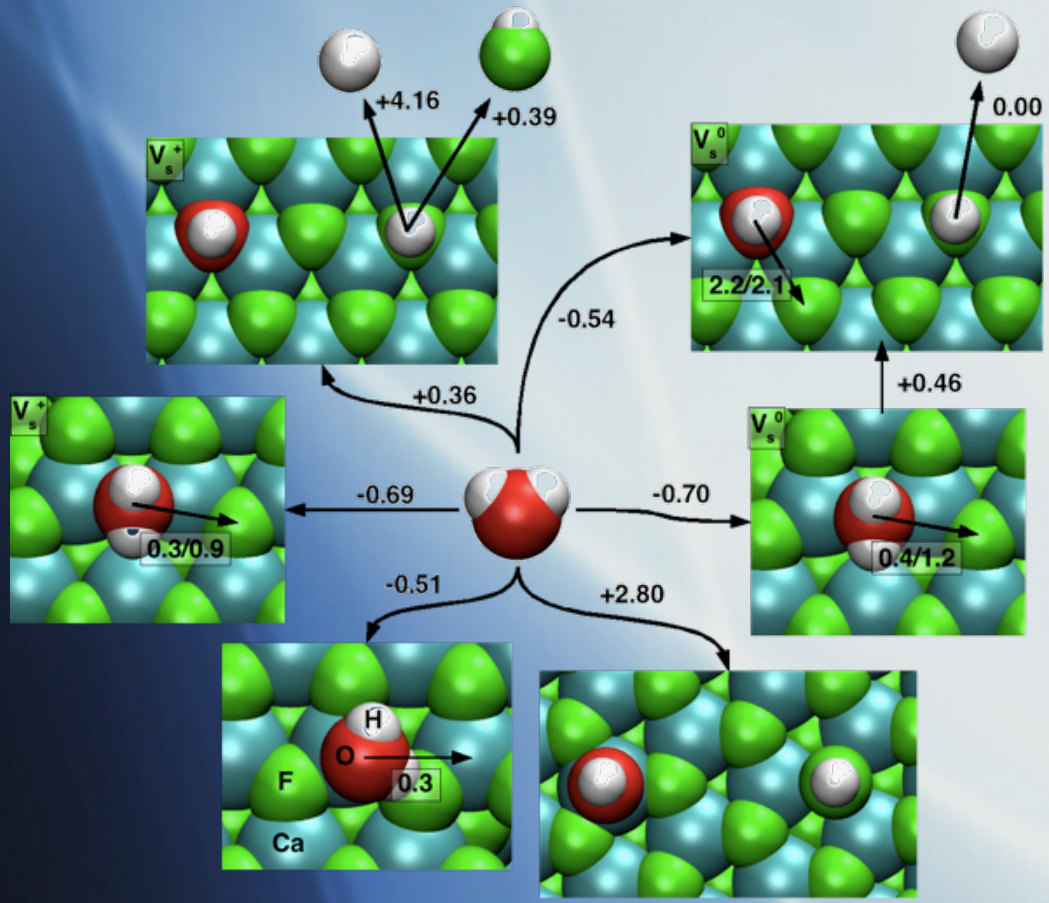


• Controllable manipulation can be seen when approaching the tip closer to the surface. Only certain defects are moved.

Modelling manipulation

Phys. Rev. B 80, 115421 (2009)

• We use first principles calculations to characterize the barriers for adsorption, reaction and migration on the surface.



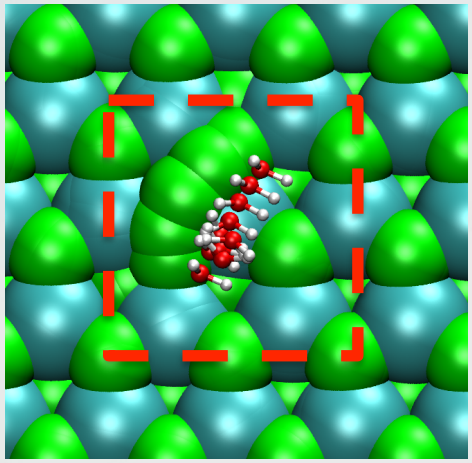
• Water is too mobile on the ideal surface and must adsorb at vacancies.

• Initial immovable species are OH groups at neutral F-centres?

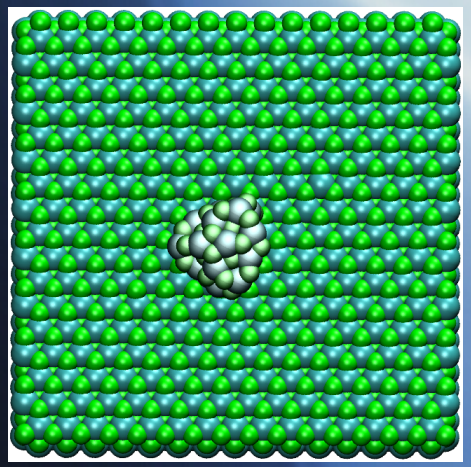
• Over time, charged vacancies diffuse to the surface and trap molecular water – the manipulable species in images?

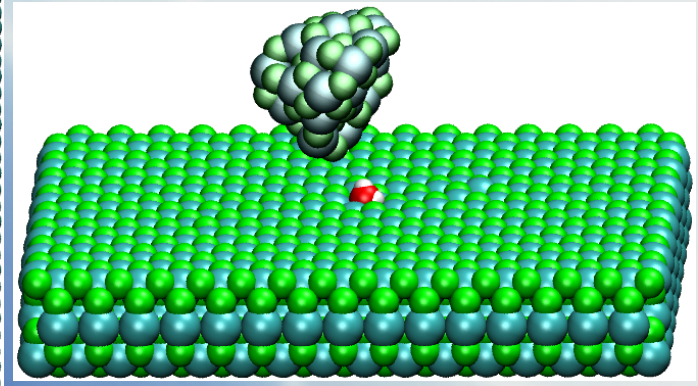
Modelling manipulation

• Barrier for water diffusion calculated at each tip position on a 7000 point grid, covering the area around the path and from 0.6 to 0.2 nm tip-surface distance.



• Manipulation experiments generally have contrast characteristic of imaging Ca
- negatively terminated tip.

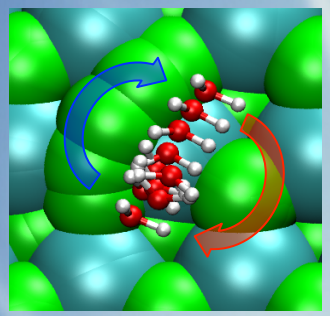




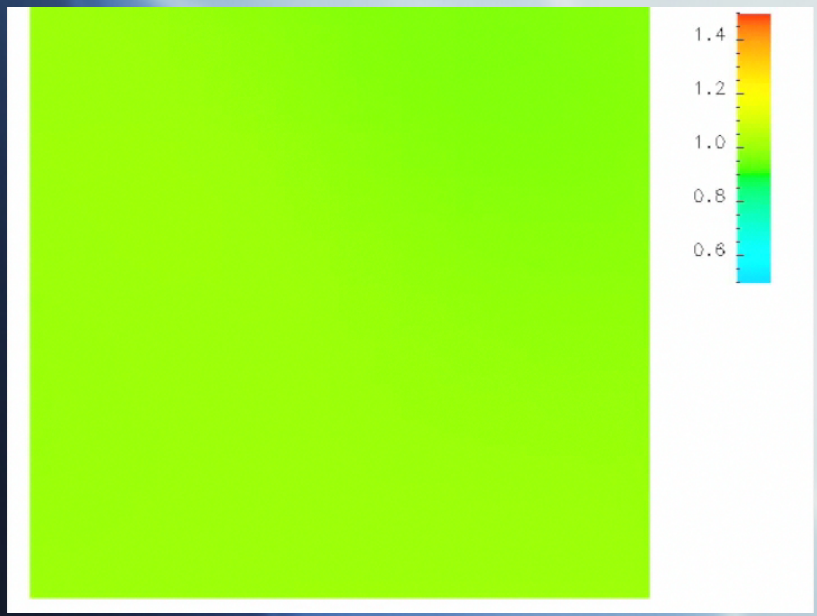
• Oxide tips interact too strongly with water and cannot reduce the barrier before desorption.

• Annealed a large CaF_2 cluster to form a realistic tip contaminated by the surface – F termination.

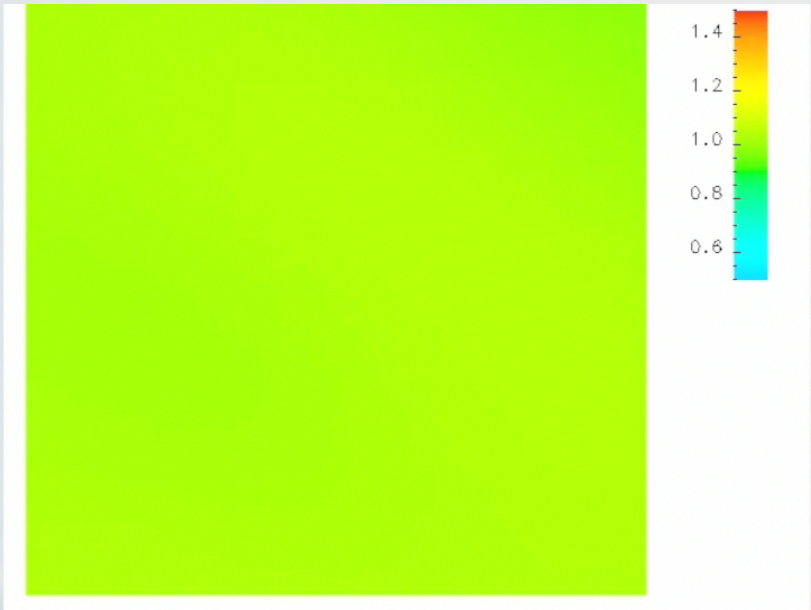
Barrier development



• Plots of the barrier as a function of tip height demonstrate the influence of the tip on the barrier and identify the areas of maximum manipulation probability – irreversible?



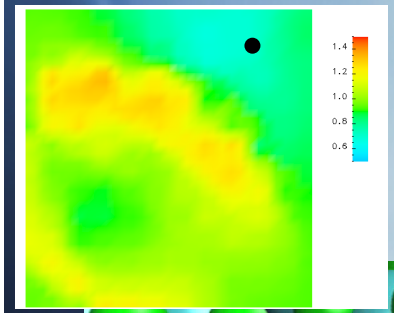
Forward barrier



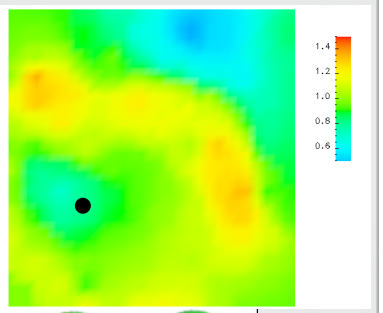
Backward barrier

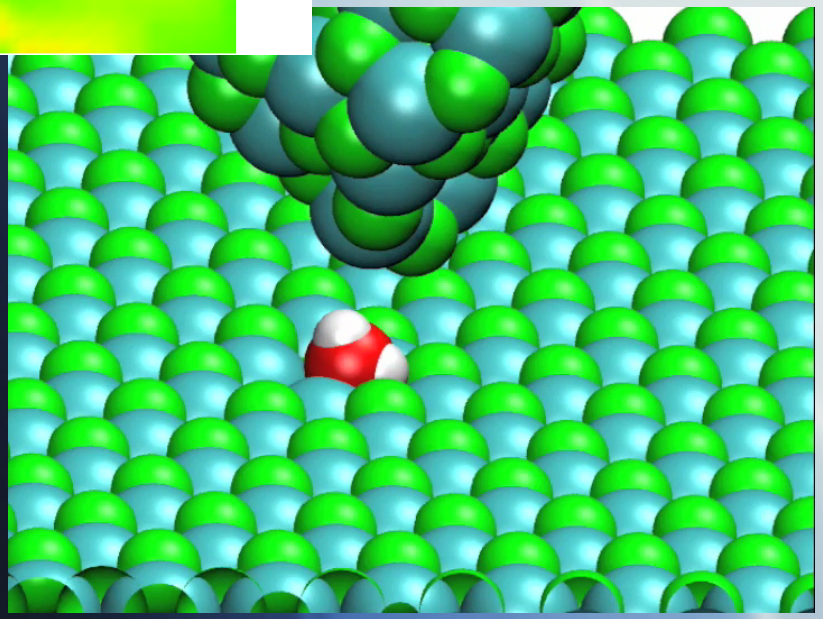
Mechanism of manipulation

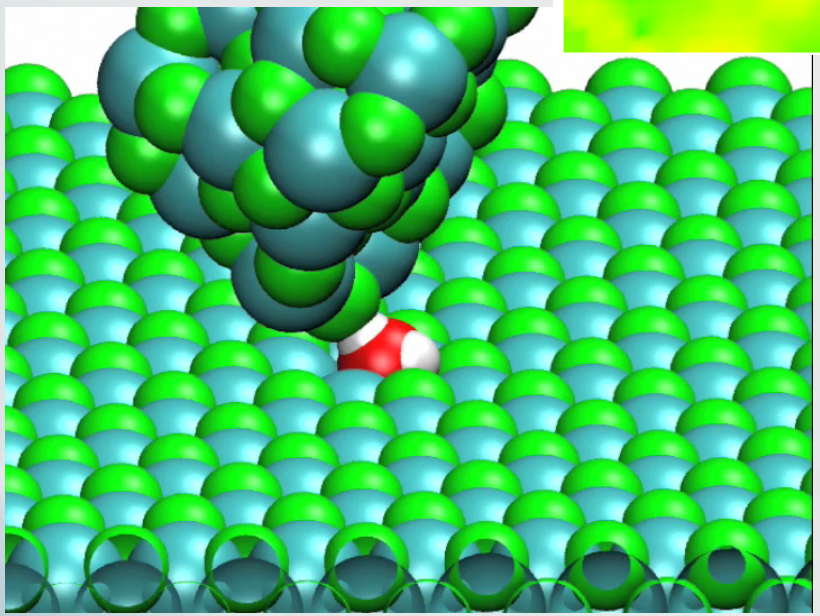
• Key low barrier area appears already at about 0.45 nm – repulsion of fluorine under the tip makes vacancy part of diffusion easier, while H-F attraction aids molecular motion.



• Closer to the surface, the tip can act as part of the molecule's diffusion path.



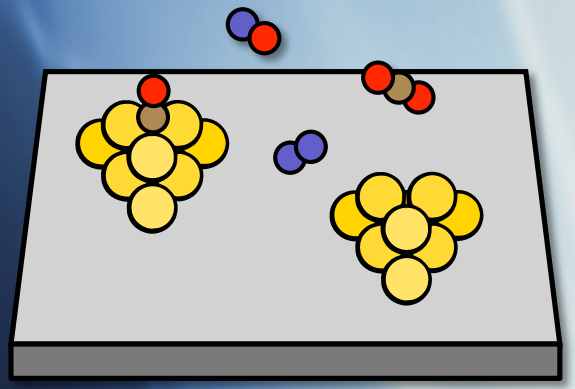


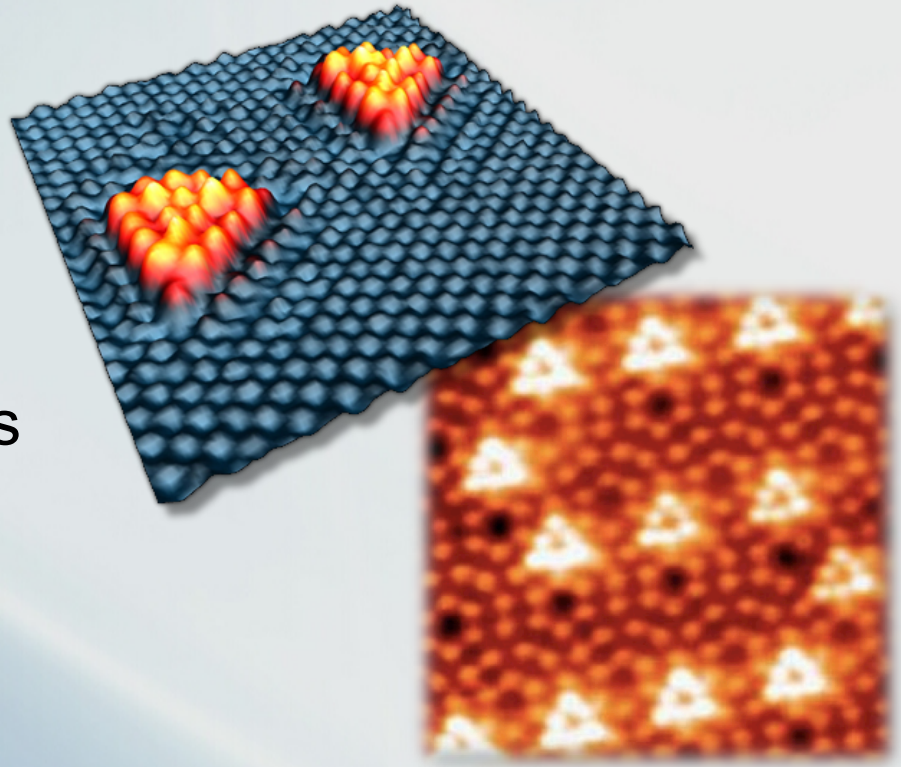


Nanocluster manipulation

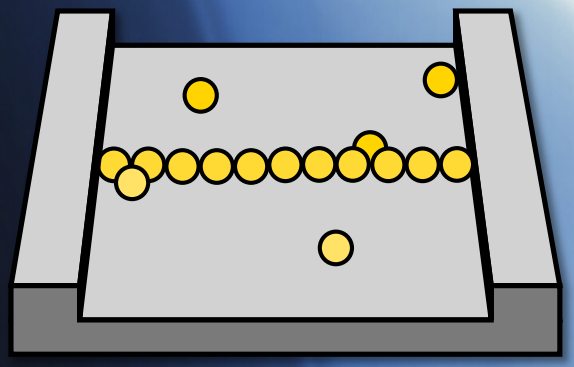
on *insulating* surfaces

- Catalysis



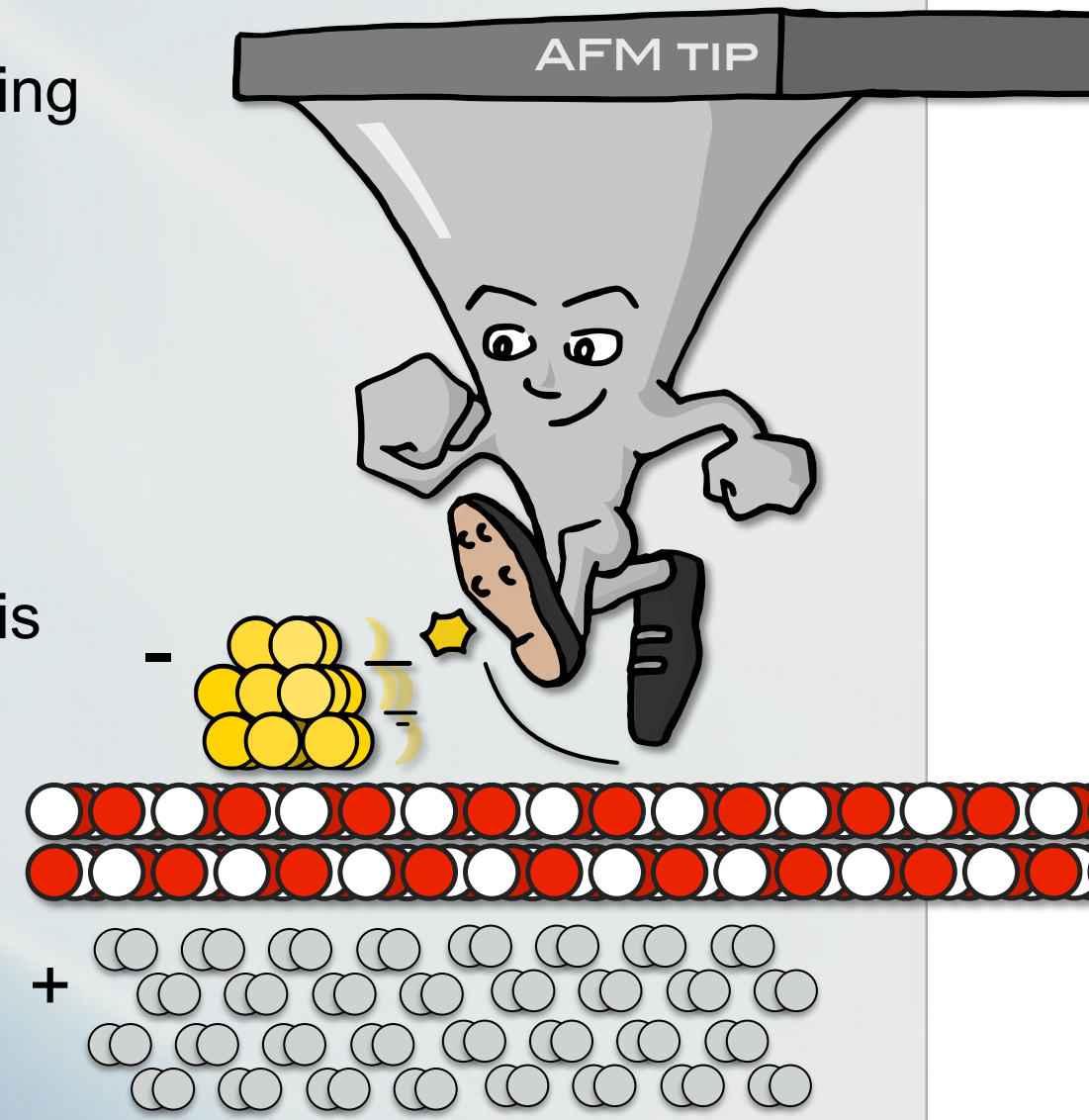


- Nanostructures

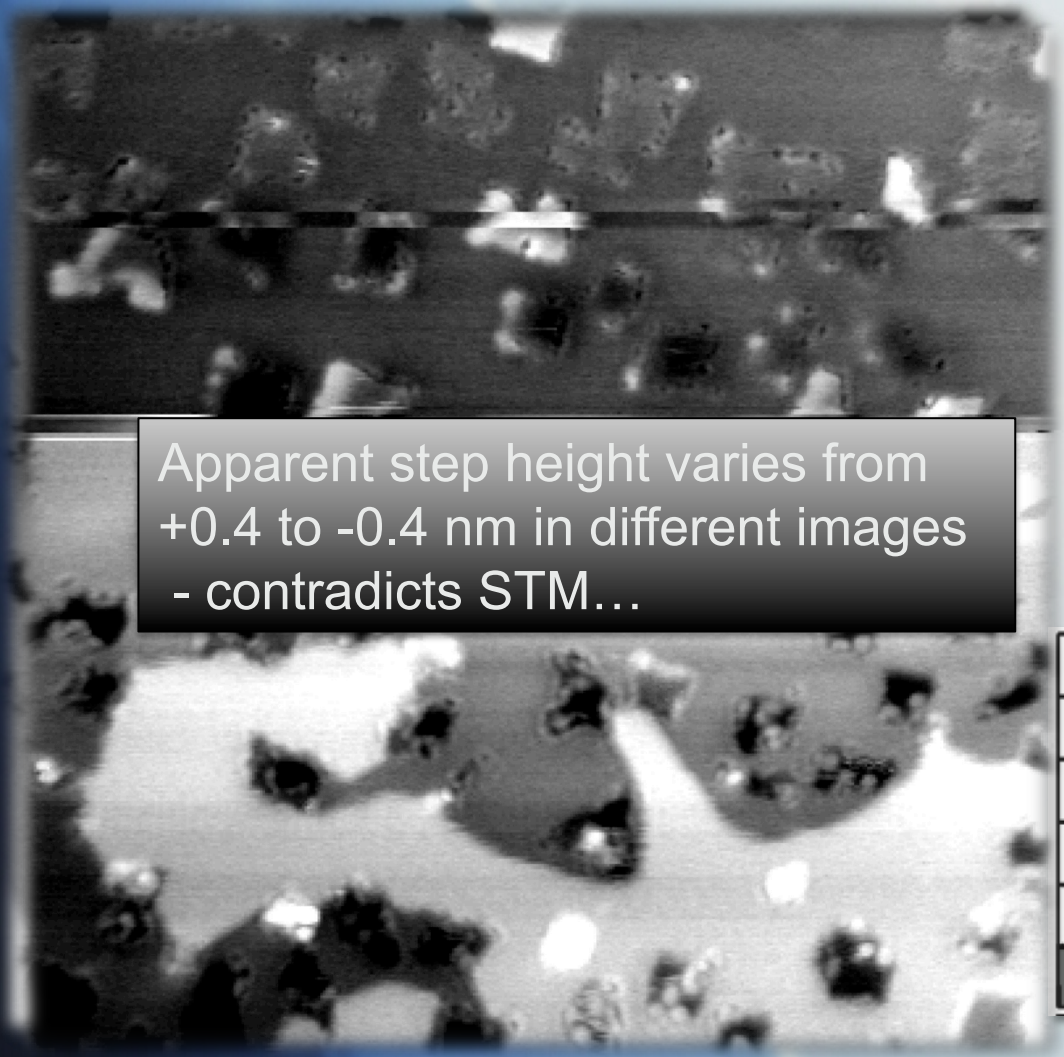


Cluster nanomanipulation on thin films

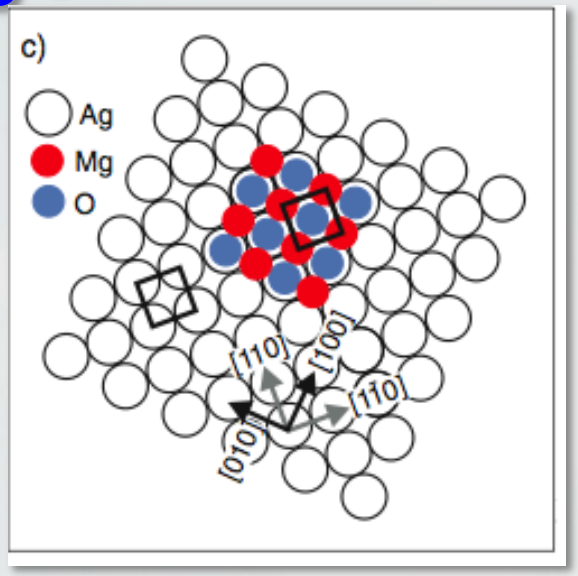
- charge transfer through insulating film
- thin film thickness additional degree of freedom for catalyst design
- MgO on Ag suitable for catalysis **and** nanomanipulation?

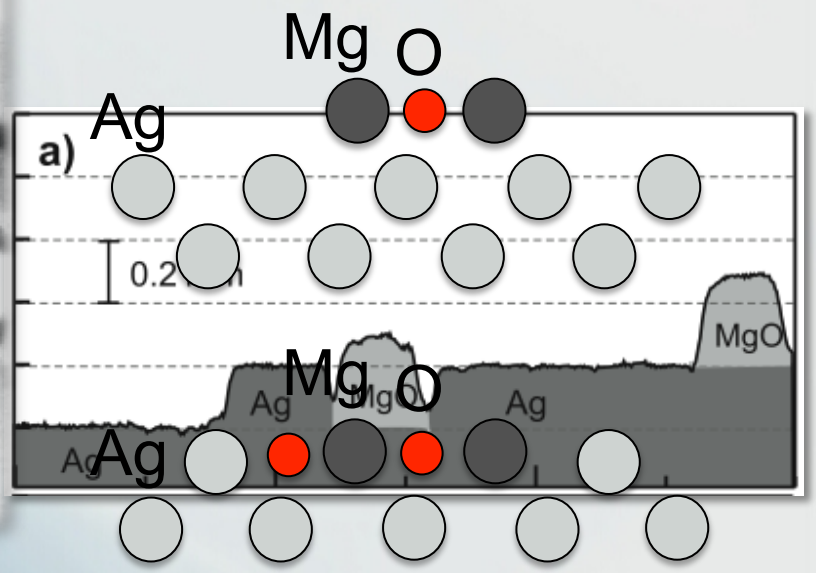


Island growth of MgO



Apparent step height varies from +0.4 to -0.4 nm in different images - contradicts STM…

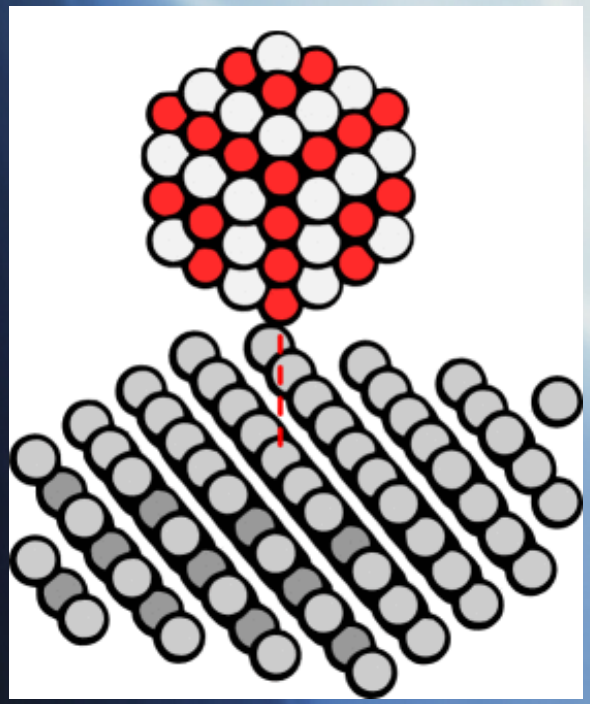


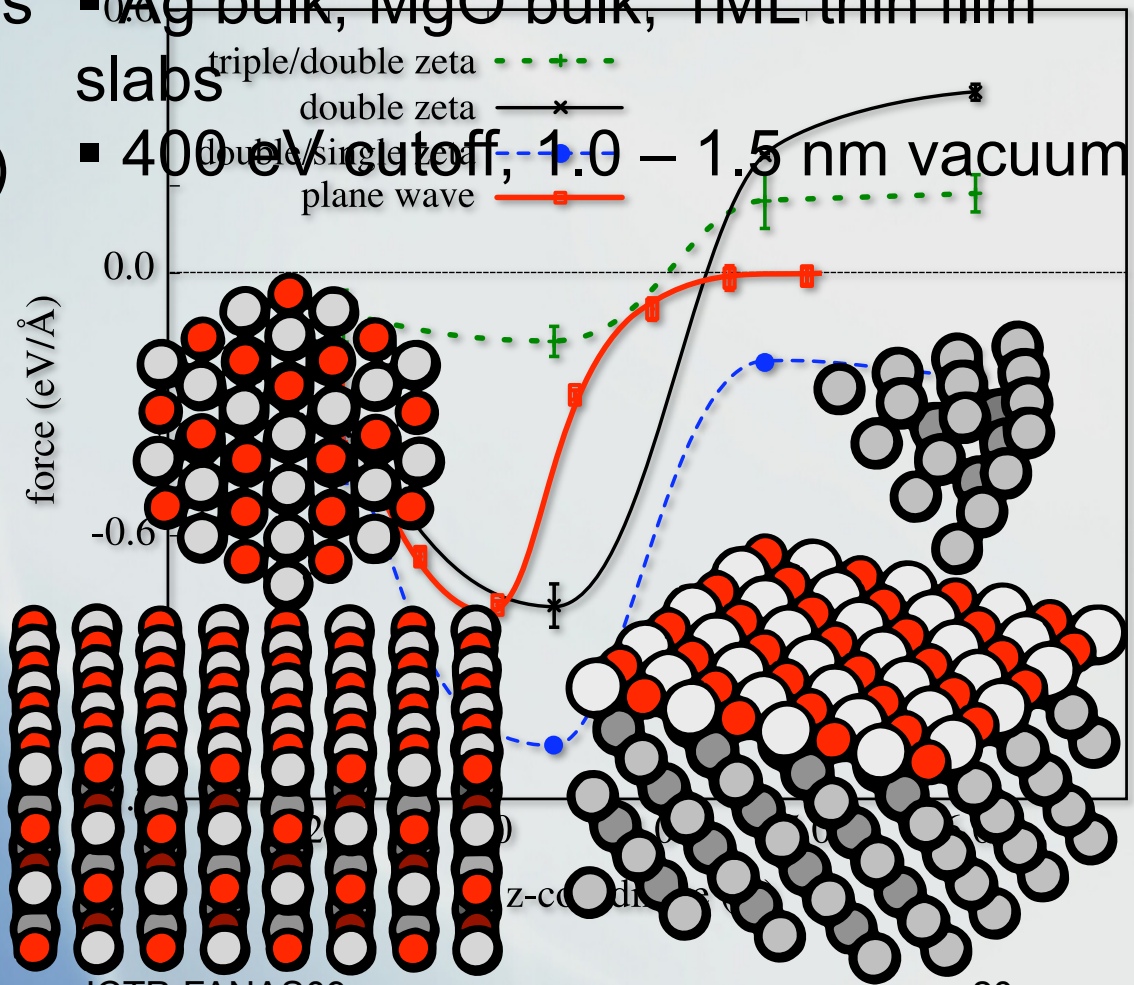


Computational AFM force spectroscopy

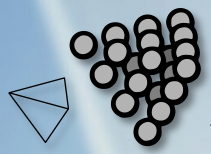
- first-principles calculation of AFM forces
  - SIESTA (LCAO)
  - VASP (plane wave)

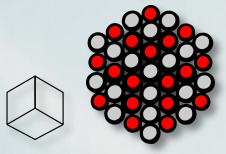
- MgO and Ag tips (64 and 20 atoms)
- Ag bulk, MgO bulk, 1ML thin film slabs
- 400 eV cutoff, 1.0 – 1.5 nm vacuum

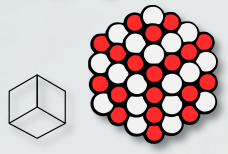




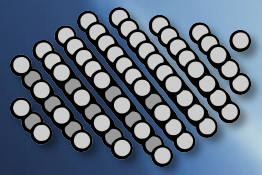
Force spectroscopy


Ag tip

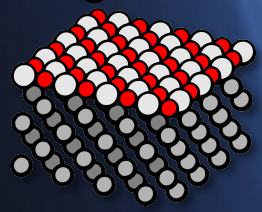

Mg tip

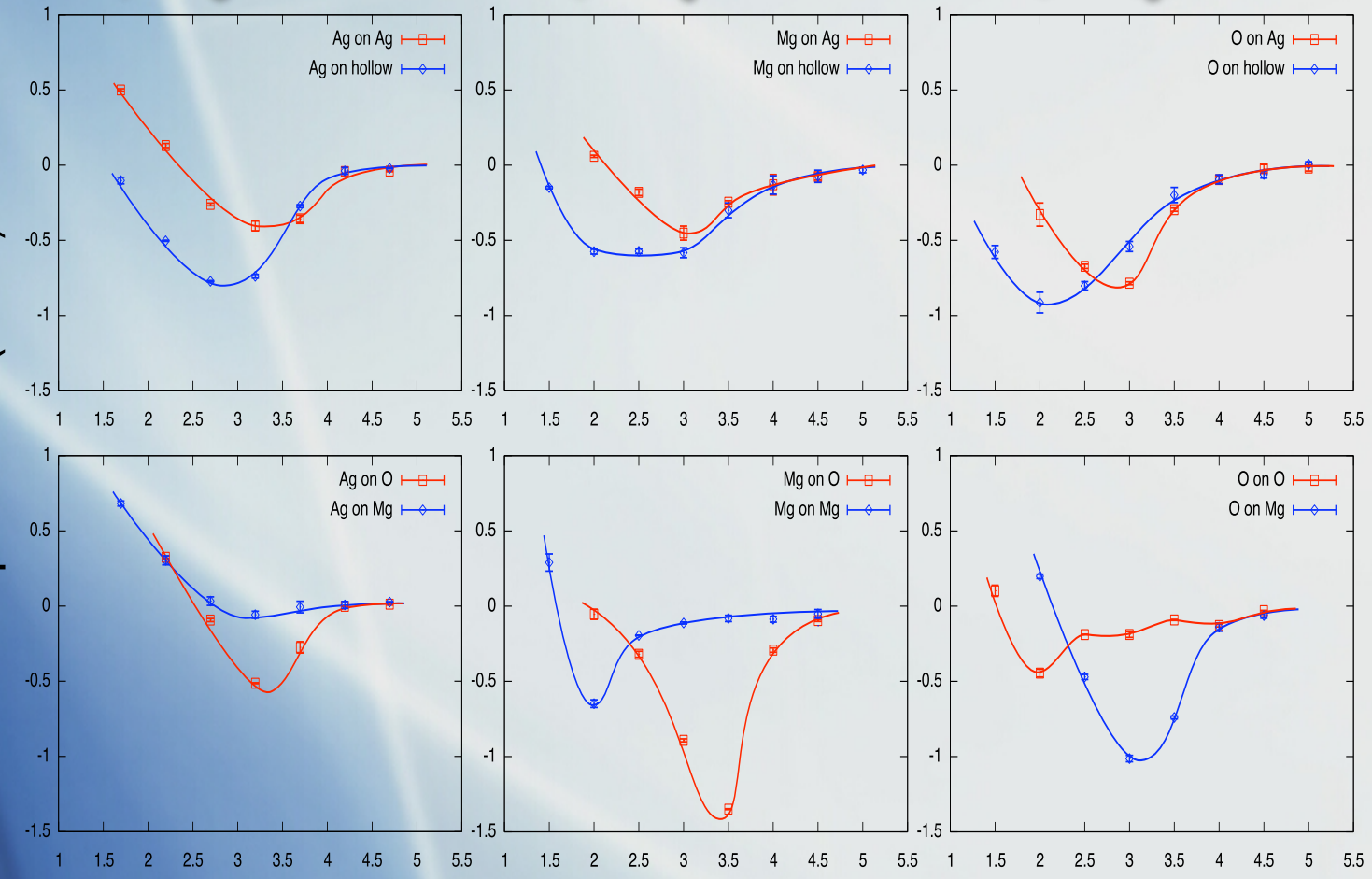

O tip

Ag bulk

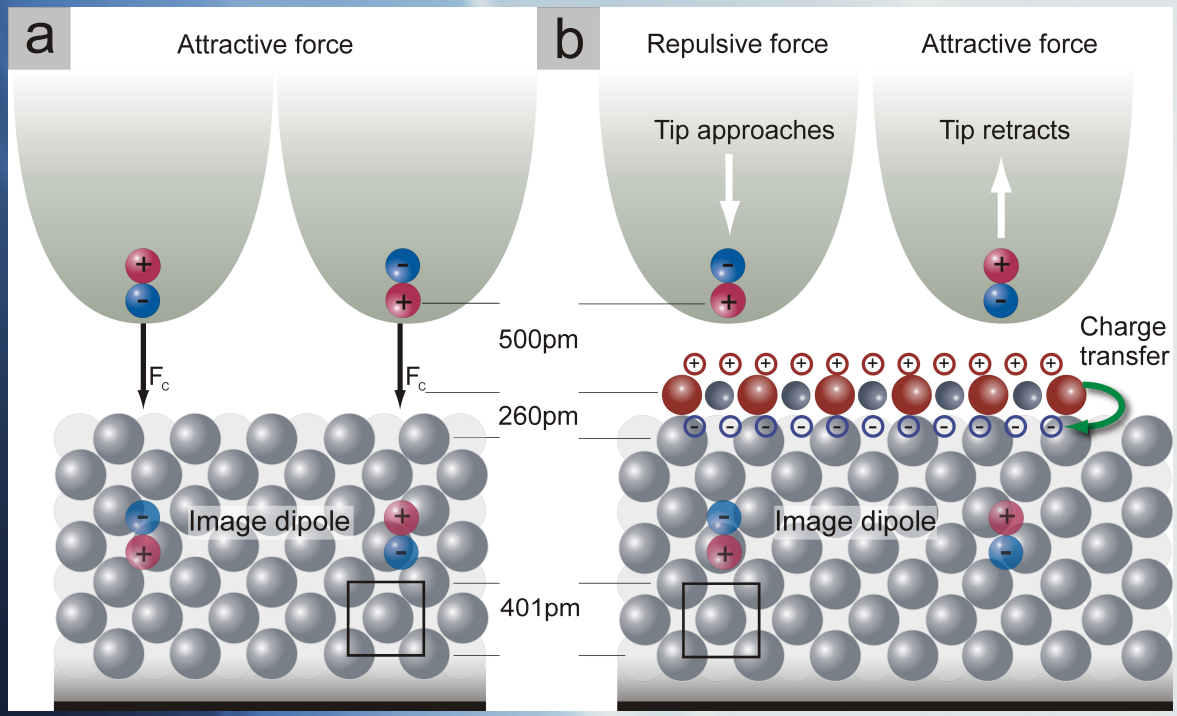


MgO film

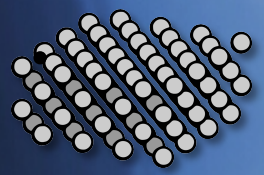


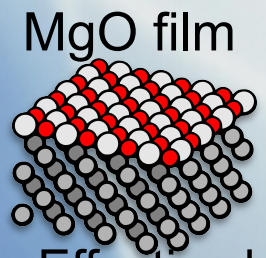


Designing a tip



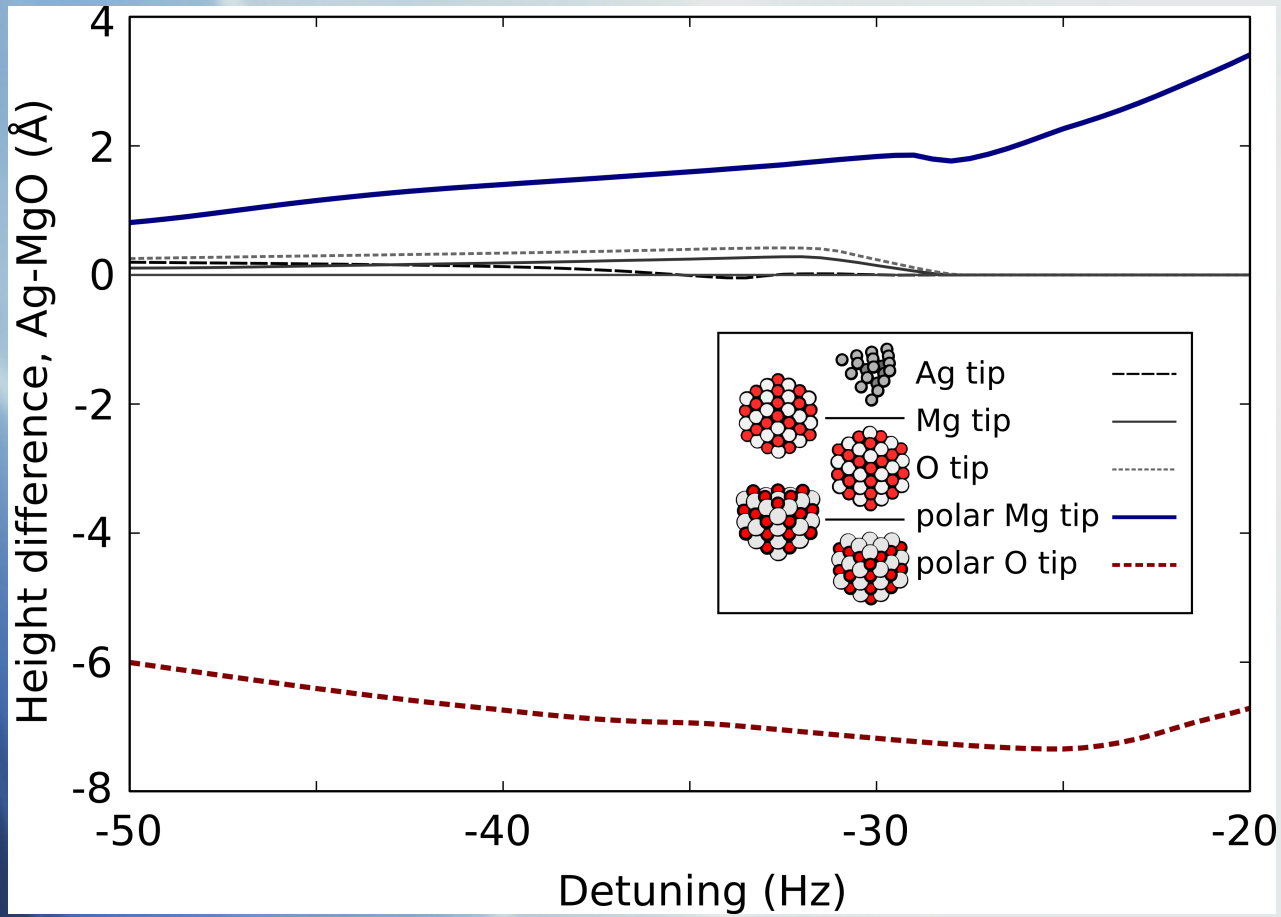
- Neutral tips will always give roughly the real step height.
- What about polar tips?
- Long-range electrostatic forces make no difference to imaging silver…
- …but couple with dipole of MgO thin film.





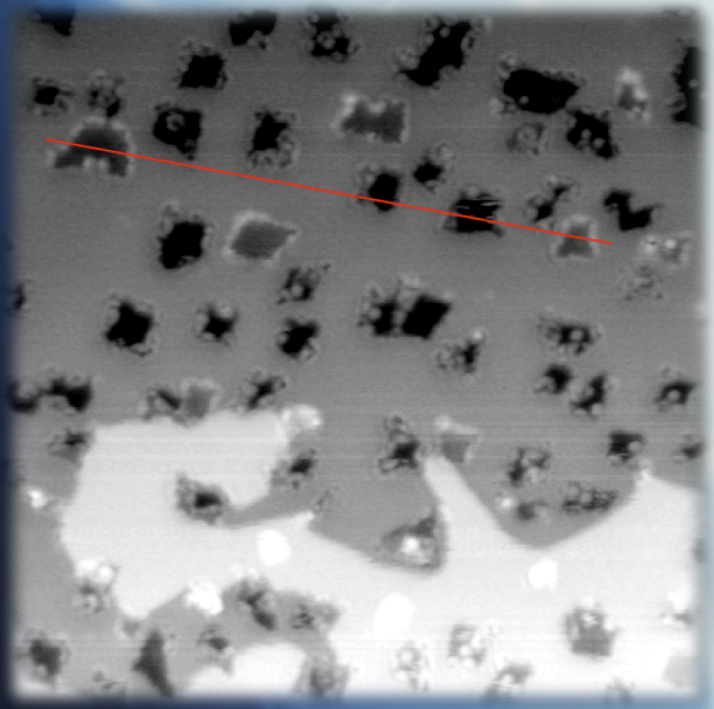
Effective height a function of the polarity of the tip.

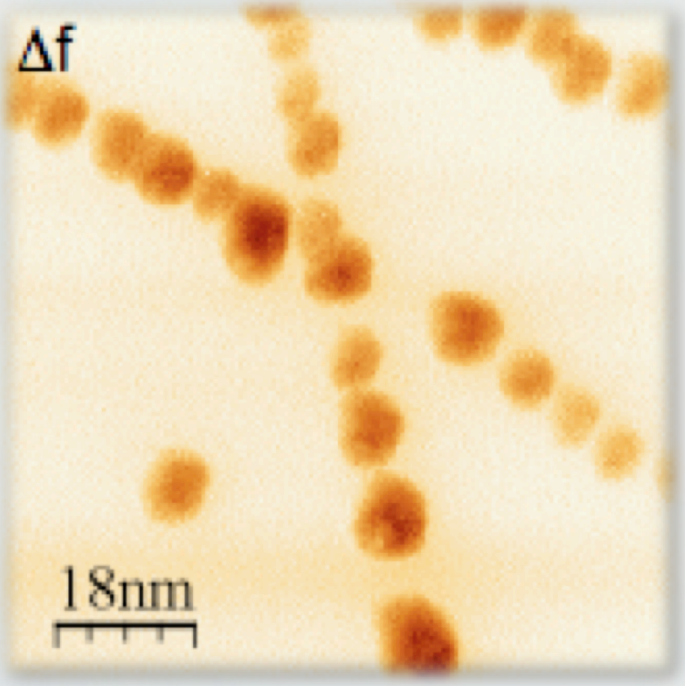
Designing a tip



Nanomanipulation?

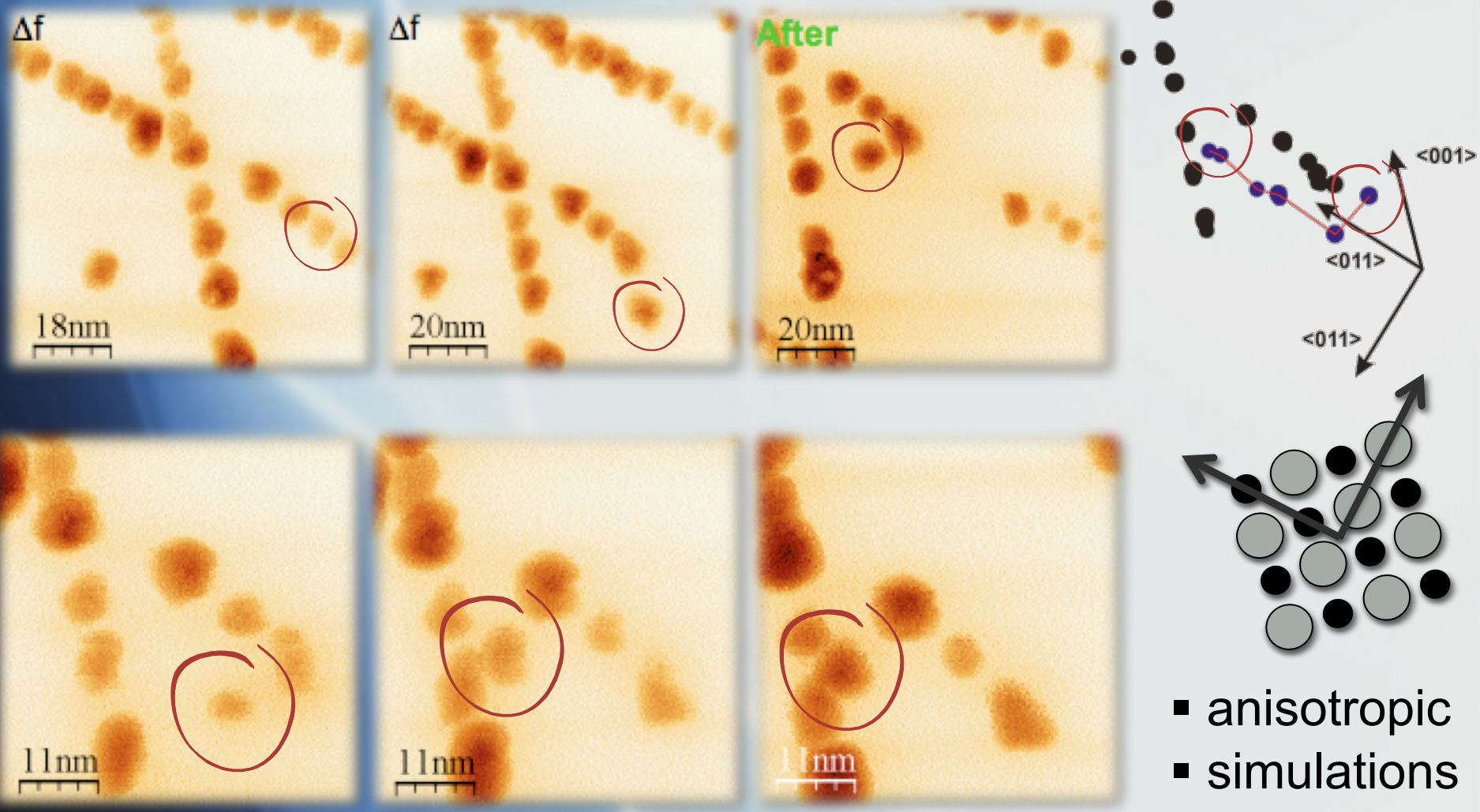
- controlled growth of MgO on Ag difficult
- working on improving surface quality





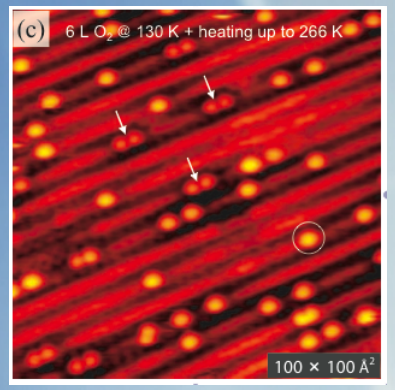
- other systems also investigated
- successful nanomanipulation of Au clusters on NaCl

Nanomanipulation?



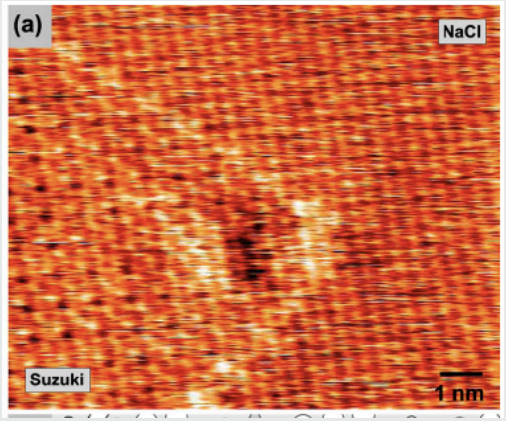
- anisotropic
- simulations to follow ...

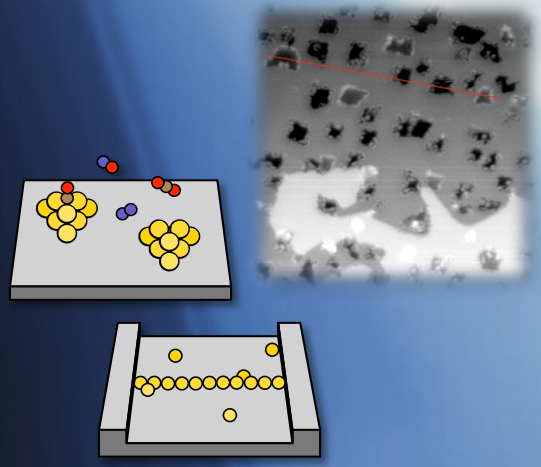
The future



• Coupling of adsorbates on **TiO_2** – contrast as a function of separation.

• Ongoing studies of **Suzuki islands** to take advantage of the unusual surface properties in nanocatalysis and nanotemplating.





• Imaging of **MgO thin films** strongly influenced by polarity of tip… nanomanipulation?

Publications

- Sublattice identification in non-contact atomic force microscopy of the NaCl(001) surface
  - *R. Hoffmann, D. Weiner, A. Schirmeisen and A. S. Foster* Phys. Rev. B 80 (2009) 115426 [pdf]
- Structure and diffusion of intrinsic defects, adsorbed hydrogen, and water molecules at the surface of alkali-earth fluorides calculated using density functional theory
  - *A. S. Foster, T. Trevethan and A. L. Shluger* Phys. Rev. B 80 (2009) 115421 [pdf]
- Imaging of the hydrogen subsurface site in rutile TiO_2
  - *Georg H. Enevoldsen, Henry P. Pinto, Adam S. Foster, Mona C. R. Jensen, Werner A. Hofer, Björk Hammer, Jeppe V. Lauritsen, and Flemming Besenbacher* Phys. Rev. Lett. **102** (2009) 136103 [pdf]
- Role of the tip size and orientation, tip-surface relaxations and surface impurities in simultaneous AFM and STM studies on the TiO_2 (110) surface
  - *Henry P. Pinto, Georg H. Enevoldsen, Flemming Besenbacher, Jeppe V. Lauritsen and Adam S. Foster* Nanotechnology **20** (2009) 264020 [pdf]
- Chemical identification of ions in doped NaCl by scanning force microscopy
  - *Adam S. Foster, Clemens Barth, and Claude R. Henry* Phys. Rev. Lett. **102** (2009) 256103 [pdf]
- Understanding the atomic-scale contrast in Kelvin Probe Force Microscopy
  - *Laurent Nony, Adam S. Foster, Franck Bocquet and Christian Loppacher* Phys. Rev. Lett. **103** (2009) 036802 [pdf]
- STM topography and manipulation of single Au atoms on Si(100)
  - *F. Chiaravalloti, D. Riedel, G. Dujardin, H. Pinto and A. S. Foster* Phys. Rev. B **79** (2009) 245431 [pdf]
- The role of van der Waals forces in the adsorption and diffusion of organic molecules on an insulating surface
  - *O. H. Pakarinen, J. M. Mativetsky, A. Gulans, M. J. Puska, A. S. Foster and P. Grutter* Phys. Rev. B **80** (2009) 085401 [pdf]
- The so-called dry laser cleaning governed by humidity at the nanometer scale
  - *D. Grojo, Ph. Delaporte, M. Sentis, O. H. Pakarinen and A. S. Foster* Appl. Phys. Lett **92** (2008) 033108 [pdf]
- Imaging the real shape of nano-objects in scanning force microscopy
  - *Olli H. Pakarinen, Clemens Barth, Adam S. Foster and Claude R. Henry* J. Appl. Phys. **103** (2008) 054313 [pdf]
- Detailed scanning probe microscopy tip models determined from simultaneous atom-resolved AFM and STM studies of the TiO_2 (110) surface
  - *Georg H. Enevoldsen, Henry Pinto, Adam S. Foster, Mona C. Christensen, Angelika Kühnle, Michael Reichling, W.Hofer, Jeppe V. Lauritsen, and Flemming Besenbacher* Phys. Rev. B **78** (2008) 045416 Editors' suggestion [pdf]
- First principles study of adsorption, diffusion and charge stability of metal adatoms on alkali halide surfaces
  - *M. H. Hakala, O. H. Pakarinen and A. S. Foster* Phys. Rev. B **78** (2008) 045418 [pdf]