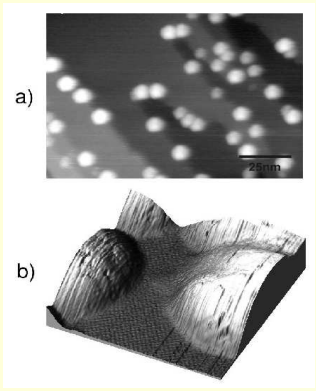
Simulating nc-AFM imaging of Au clusters on the KBr surface

O. H. Pakarinen*, C. Barth**, A. S. Foster*, R. M. Nieminen* and C. Henry**

*Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 HUT, Finland
**CRMCN-CNRS, Campus de Luminy, case 913, 13288 Marseille Cedex 09, France
email: opa@fyslab.hut.fi

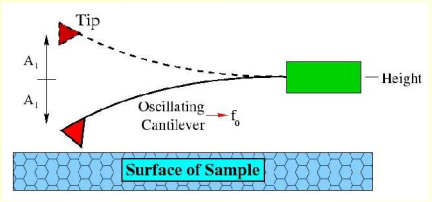
Motivation

- Gold nanoclusters are catalytically active → real applications: better car catalysts etc.
- Origin of activity is under discussion
- nc-AFM is a natural tool for this research, but it failed to image the clusters with atomic resolution



Experimental topography images of KBr (001) surface
a) Surface after deposition of 0.08 ML of gold.
b) High magnification 3D image with atomic resolution on KBr surface, but poor imaging of gold clusters (C. Barth and C.R. Henry, *Nanotechnology*)

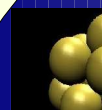
nc-AFM



- Tip-surface interaction causes a frequency shift to the cantilever oscillation
- To obtain atomic resolution, the tip has to be very close to the surface, few Å in its lowest point
- Images need to be interpreted → simulations

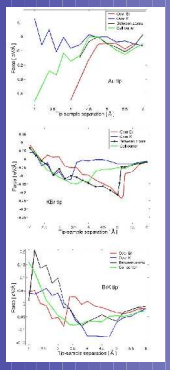
nc-AFM imaging simulations

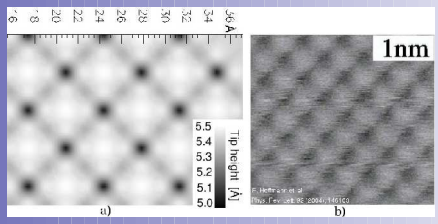
- DFT simulations with 3 tips on gold cluster and KBr(001) surface
- Force-distance data can be transformed to frequency shifts over different surface sites
- Topographic images can be drawn



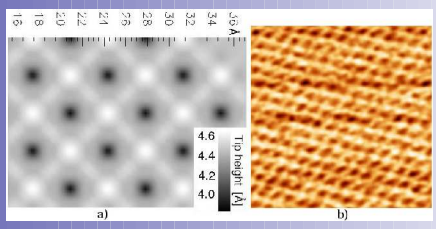
Au_{13} tip approaching Au cluster on KBr surface

Force-distance curves obtained from KBr(001) surface scan simulations





a) Simulated KBr surface imaged with **K-terminated tip**
b) Experimental nc-AFM image of KBr(001) surface



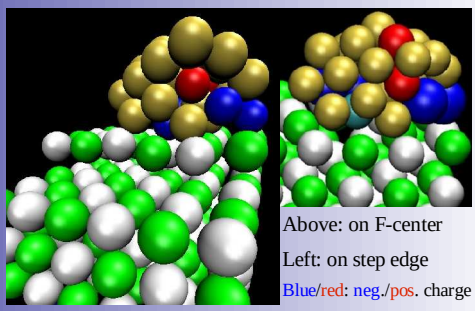
a) Simulated KBr surface imaged with **Br-terminated tip**
b) Experimental nc-AFM image showing similar structure

Charge transfer from KBr surface to Au cluster

- Recent results suggest charge transfer as origin of activity of Au
- Our results show that for filled Br-vacancies the extra charge localizes to **Au atom in vacancy**
- Single Au atom desorption is shown to fill vacancies in **KBr(001) but not in MgO(001)**
- These results indicate that single Au atom desorption may **fail to produce active clusters**

Amount of charge transfer for clusters over different surface sites

Cluster site	ΔQ [e⁻]
Plain surface	0.81
Above step edge	0.89
Filled K-vacancy	0.37
Filled Br-vacancy	1.26
F-center	1.21



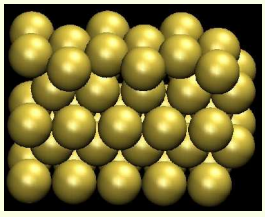
Above: on F-center
Left: on step edge
Blue/red: neg./pos. charge

Technical details

- Density functional theory calculations with SIESTA code
- LCAO basis, multiple-zeta, polarized orbitals
- GGA xc-functional
- Pseudopotentials (fully non-local Kleinman-Bylander)
- Scalar relativistic corrections
- About 100 atoms in simulations
- Forces relaxed below 0.02 eV/Å
- Accuracy tested by comparing single atom adsorption energies and free cluster structures and energies to other calculations and experiments

Now calculating

nc-AFM simulations on Au(001) surface



- 1x5 reconstruction
- Scanned with Br tip
- 104 atoms in surface
- Represents also a large gold cluster

Conclusions

- nc-AFM simulations of KBr(001) in good agreement with experiment, also new effects seen & later confirmed
- nc-AFM imaging of Au clusters difficult, different explanations for this were studied
- Charge transfer from substrate to cluster studied
- Clear qualitative difference between two cluster growth methods was found