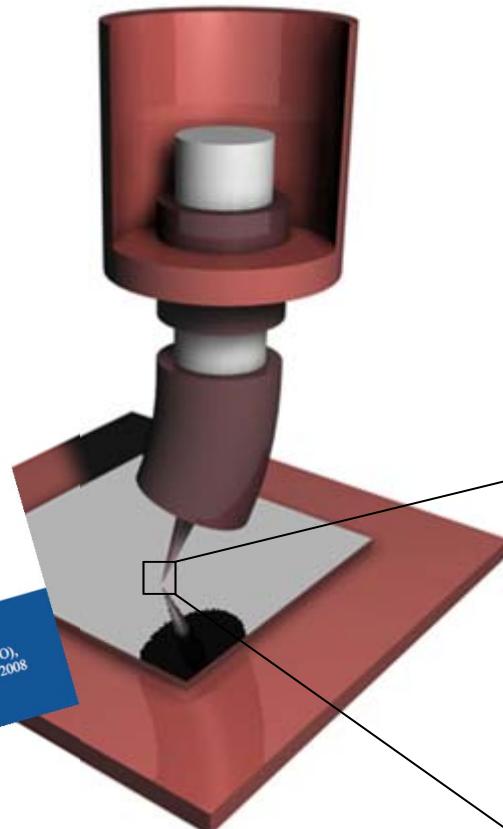
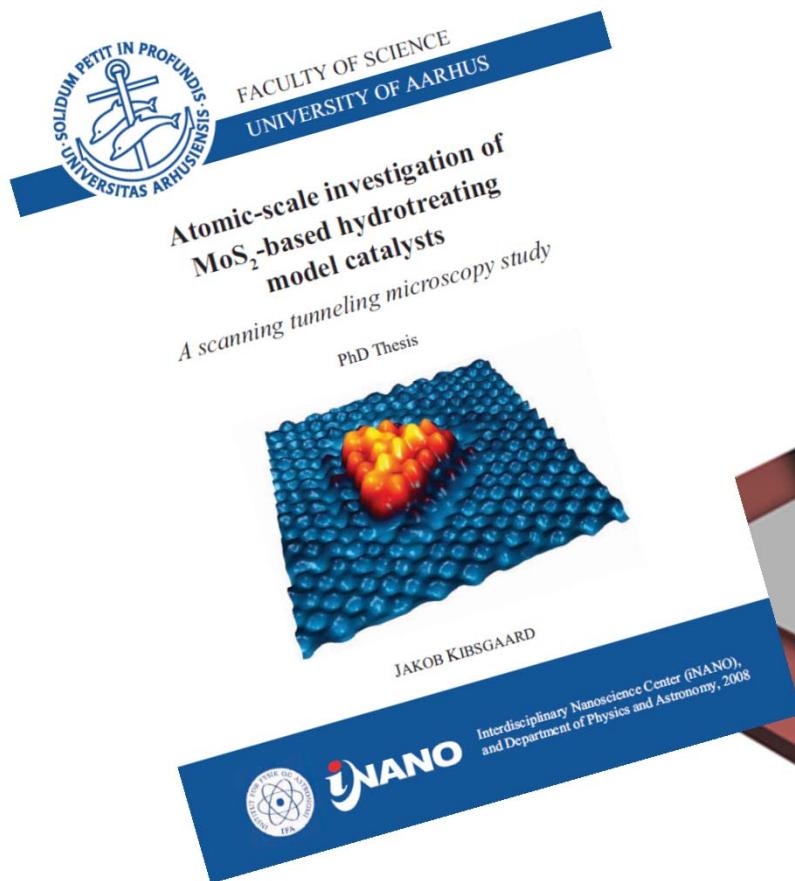
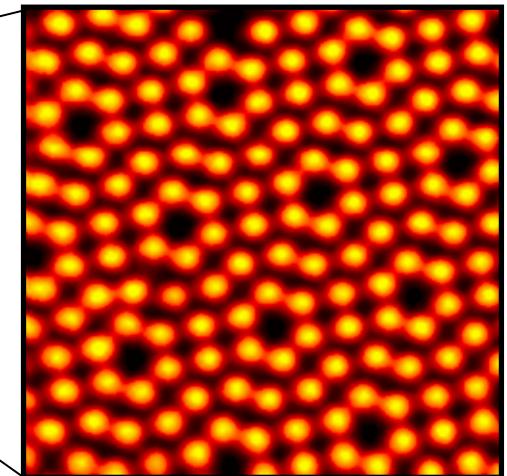


Scanning Tunneling Microscopy (STM)

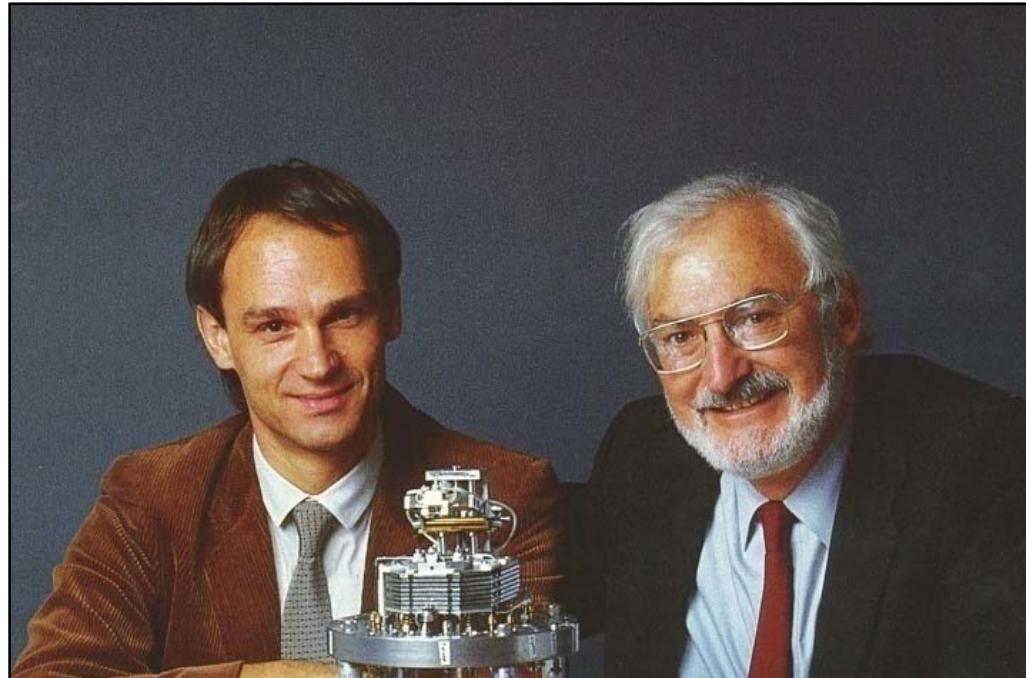


Si(111)-7x7 Surface

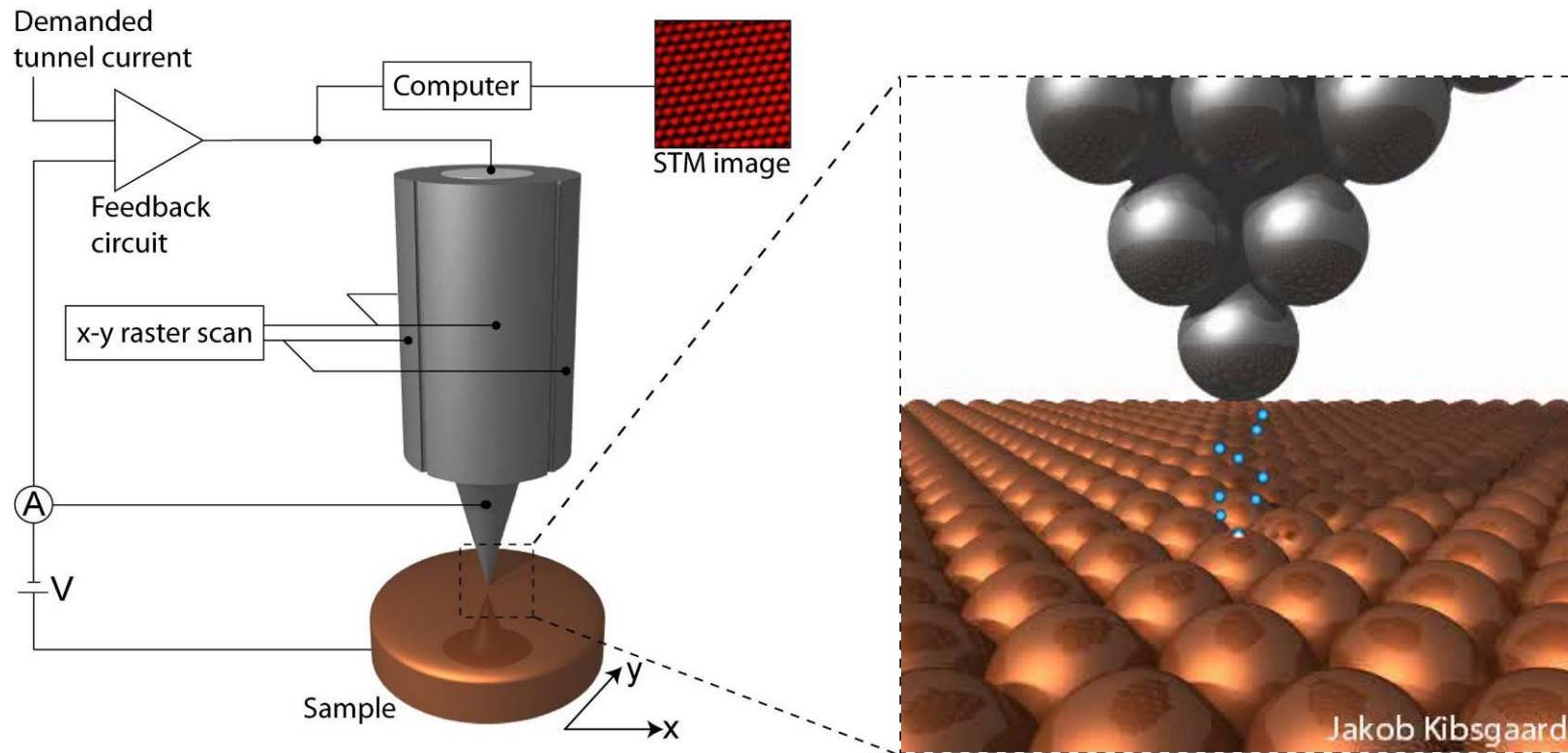


In this lecture, we will develop a basic understanding of the physical principles underlying Scanning tunneling Microscope (STM)

STM was developed in 1981 by Binning and Rohrer at IBM Zurich.



Awarded the Nobel prize in 1986



General conceptual procedure:

- Produce tip with size on order Å
- Apply voltage across tip and sample
- Measure **current** as the tip is moved along, *but not touching*, the sample

An analysis tool that measures:

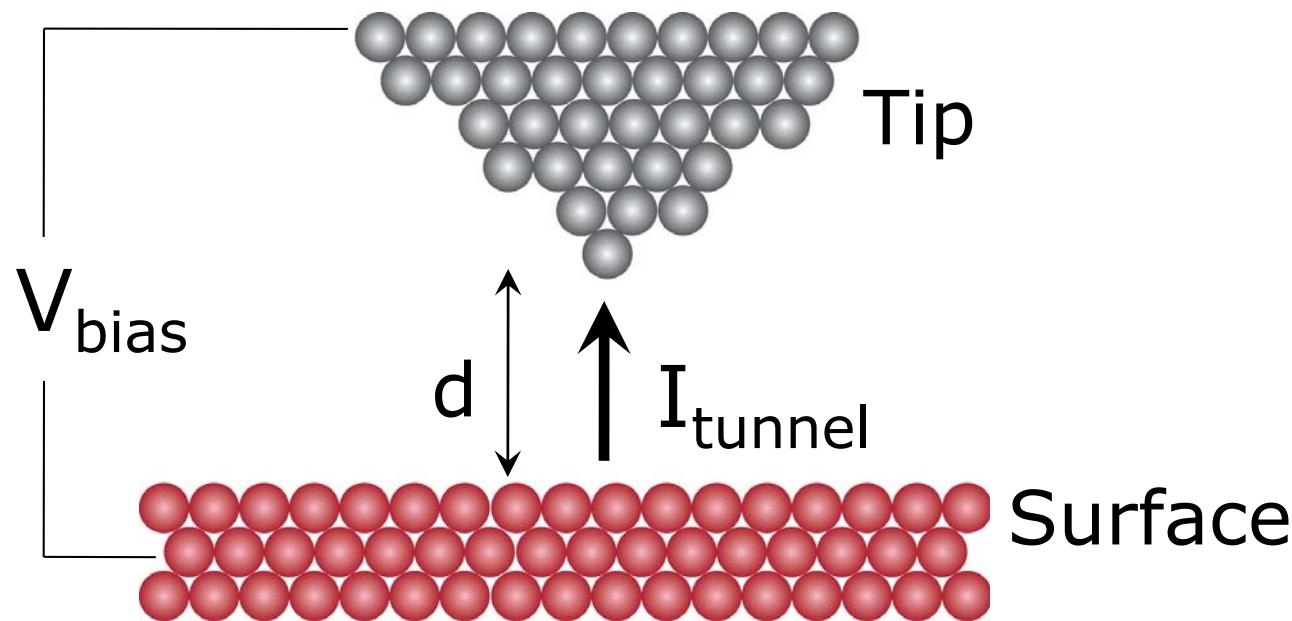
- Surface structure with true atomic resolution
- Surface electronic structure, spatially resolved
- Individual molecules, atom defects and surface atoms
- STM has revolutionized our understanding of surfaces
- STM is often mentioned as one of the most important nanotechnology tools

Study surfaces:

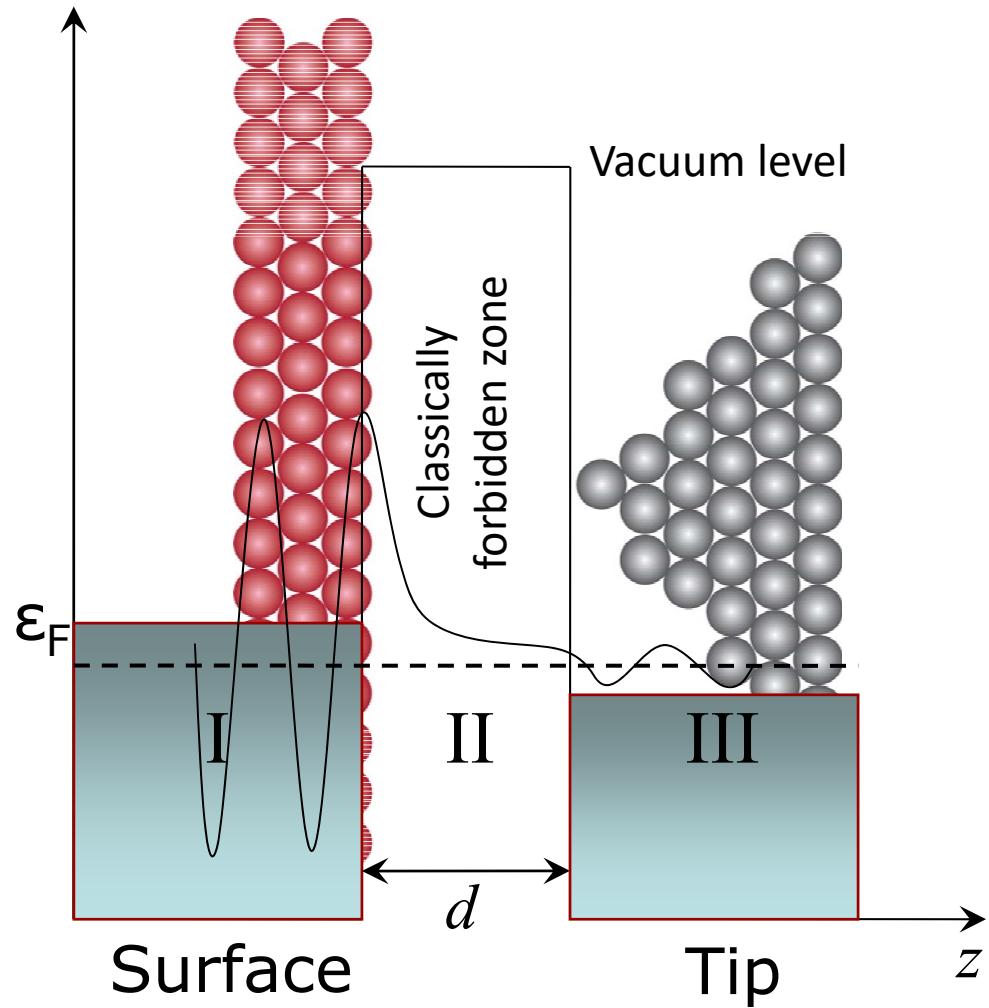
- 3D symmetry broken, bulk concepts inapplicable
- New phenomena in 2D: Adsorption, desorption, diffusion, nucleation and growth, and reaction mechanisms and rates

Applications:

- Heterogeneous catalysis
- Corrosion, friction, wear
- Microelectronics
- Nanotechnology
- Energy and environmental problems



Potential energy



Schrödinger Equation in region II

$$\frac{-\hbar^2}{2m_e} \frac{d^2\psi}{dz^2} = (\epsilon - V)\psi$$

$$\psi(z) = \psi(0)e^{-\kappa z}$$

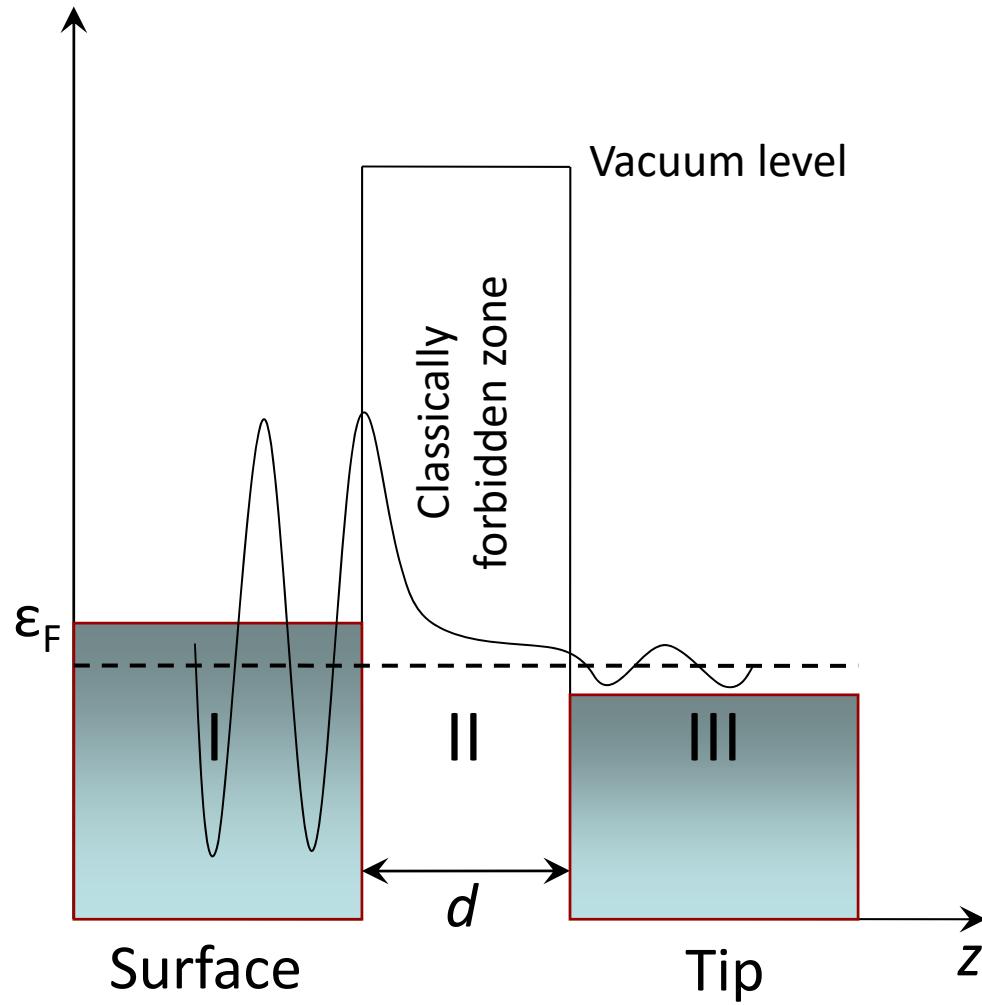
Where κ is the decay length of the electron wavefunction:

$$\kappa = \frac{\sqrt{2m_e\phi}}{\hbar}$$

The probability for an electron to tunnel from a filled sample state to an empty tip state is:

$$w \propto |\psi(d)|^2 \\ = |\psi(0)|^2 e^{-2\kappa d}$$

Potential energy

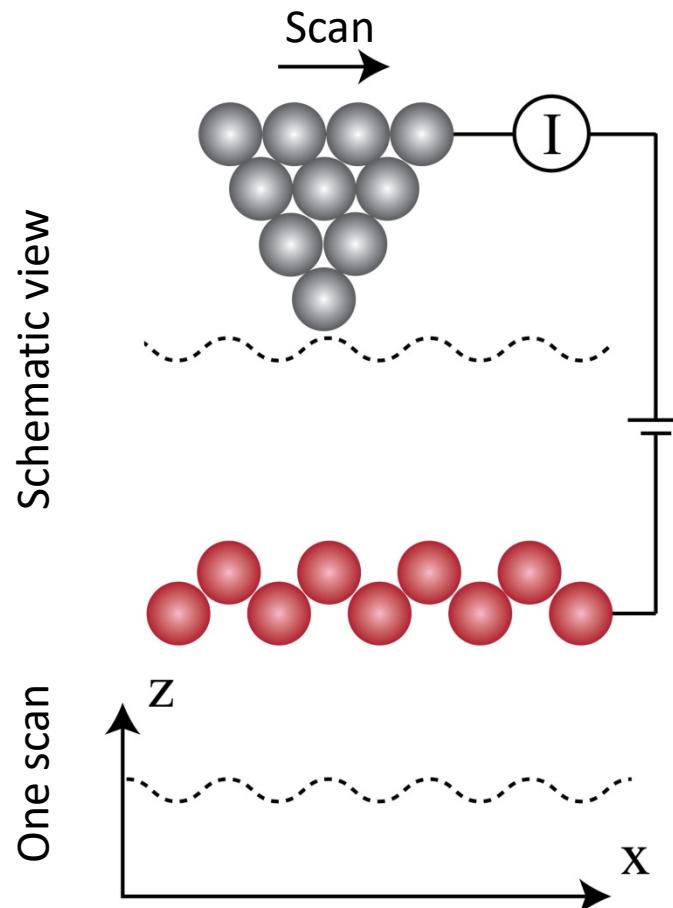


The tunneling current between tip and sample behaves as:

$$I_t \propto \exp(-2\kappa d)$$

- If tip and surface are typical clean metals in vacuum, $\phi \sim 4\text{eV}$ (work function) and $\kappa \sim 1/\text{\AA}$ (decay length).
- Therefore, for each **1 Å change in d** , the tunnel current changes by **1 order of magnitude!**
- So to a first approximation, the STM gives a direct topograph of the surface structure.

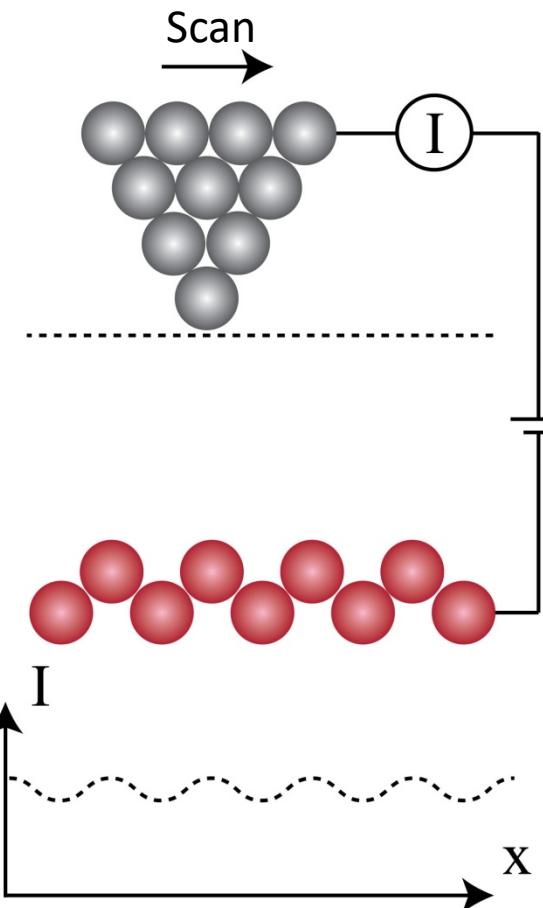
Constant current mode



Advantage: Good tip stability

Disadvantage: Slow + requires feedback

Constant height mode

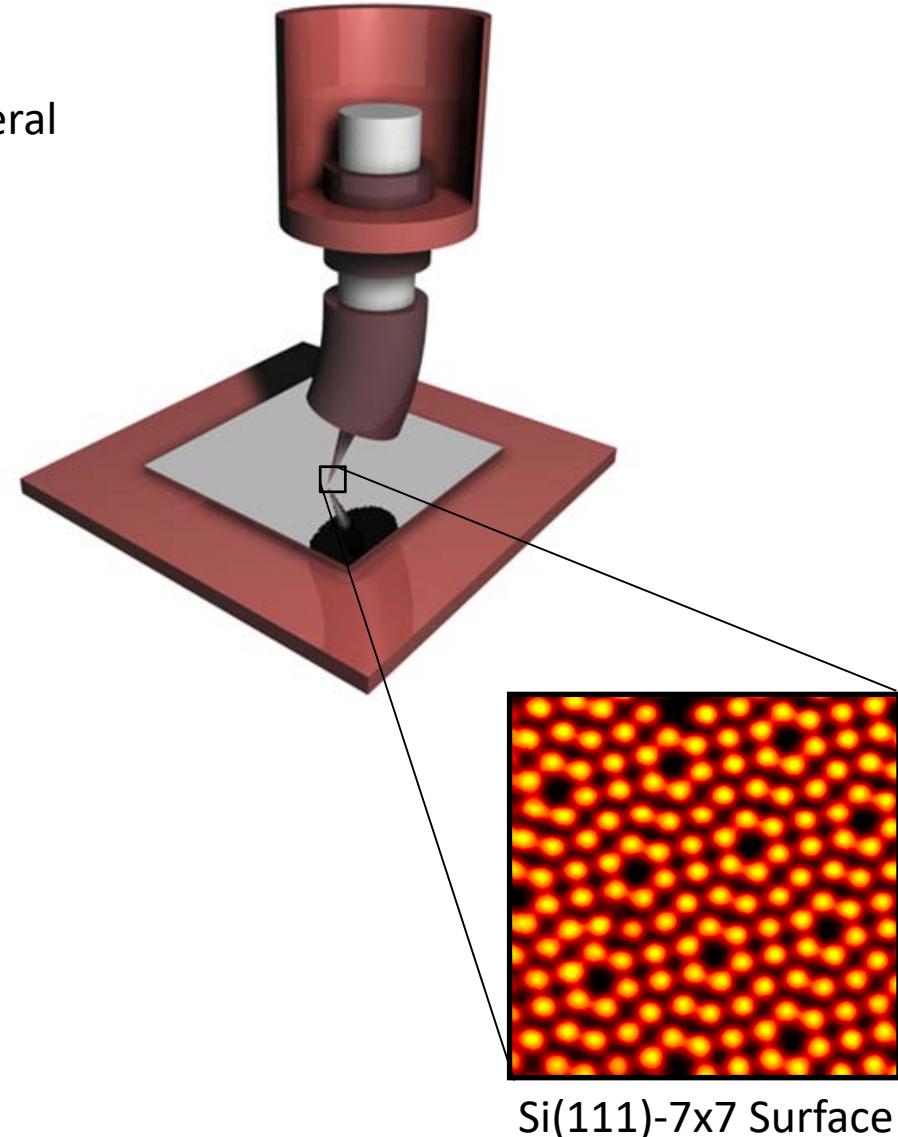


Advantage: Faster scanning (no feedback)

Disadvantage: Tip instabilities

Challenge (for atomic resolution studies) :

To measure corrugations of ~10 pm with a lateral resolution of 50-100 pm, using construction elements with dimensions of mm.

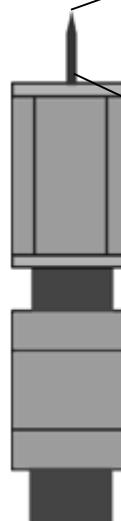


Problems:

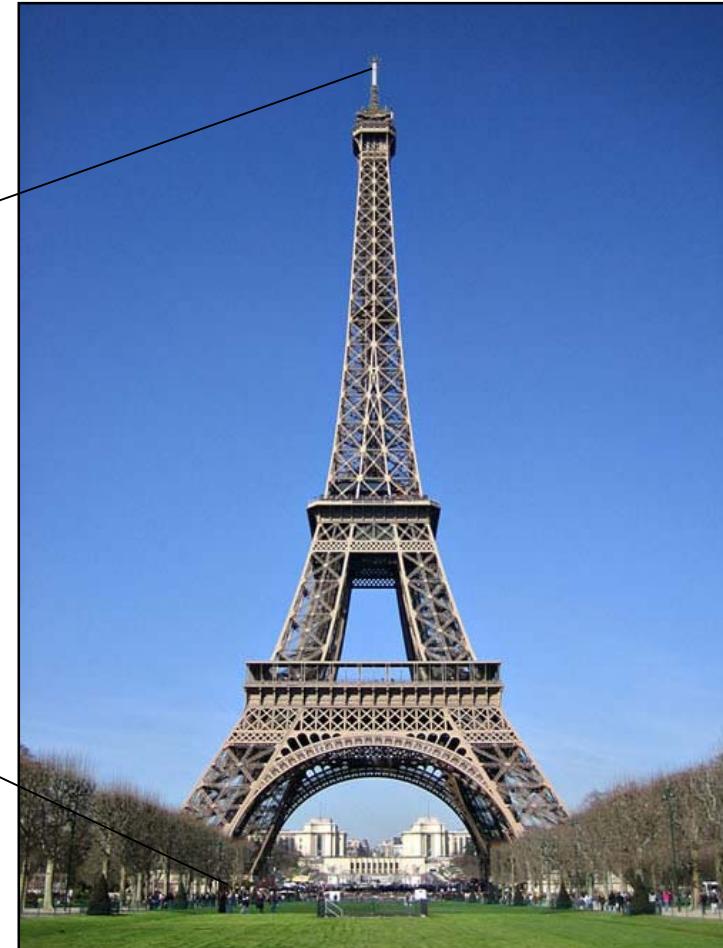
- Coarse positioning and raster scanning
- Vibration isolation
- Thermal drift
- Atomically sharp tip
- Low-noise electronics
- Application under UHV

Challenge scaled to Eiffel tower:

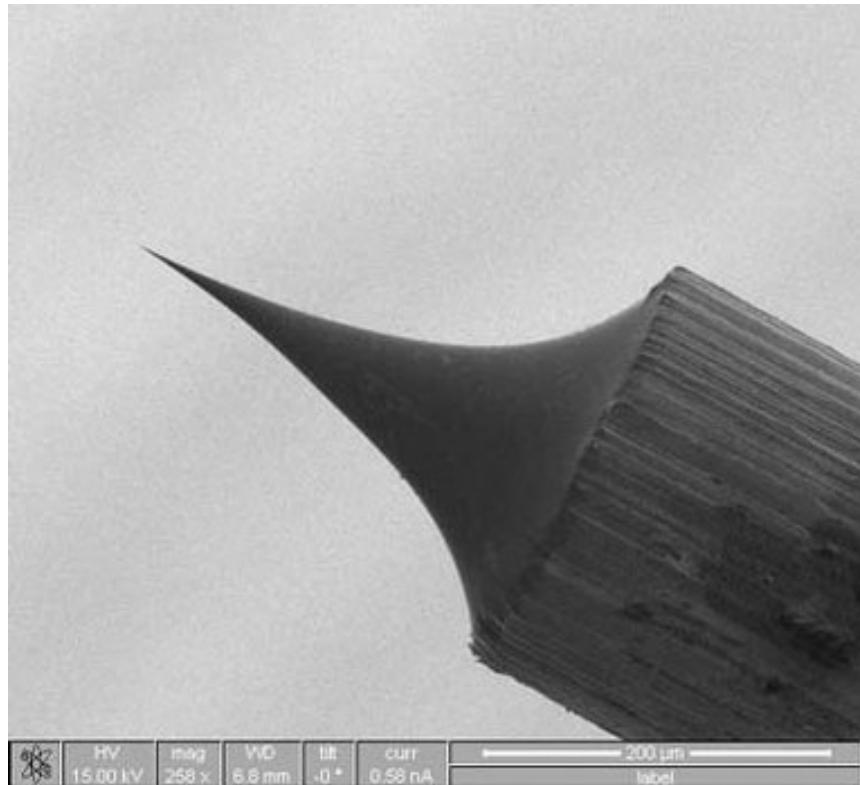
Place the top of the Eiffel tower 1 mm over Champs-Élysées and control the top with a precision better than $\sim 1\mu\text{m}$!



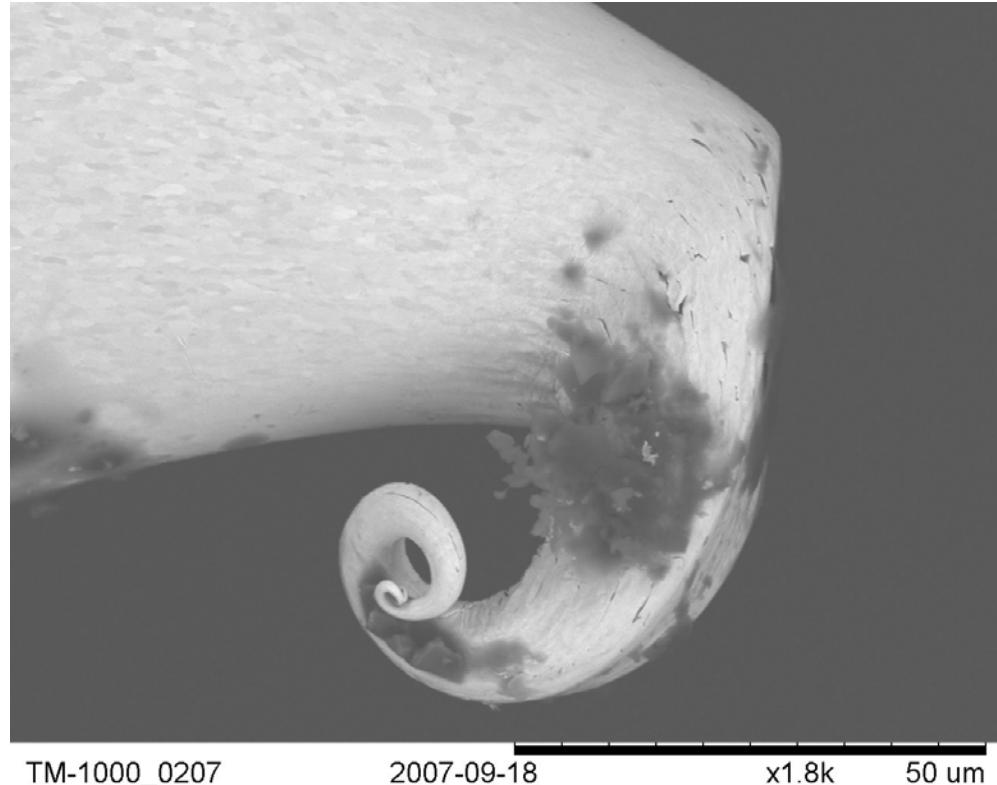
STM tip: $\sim 1 \text{ mm}$



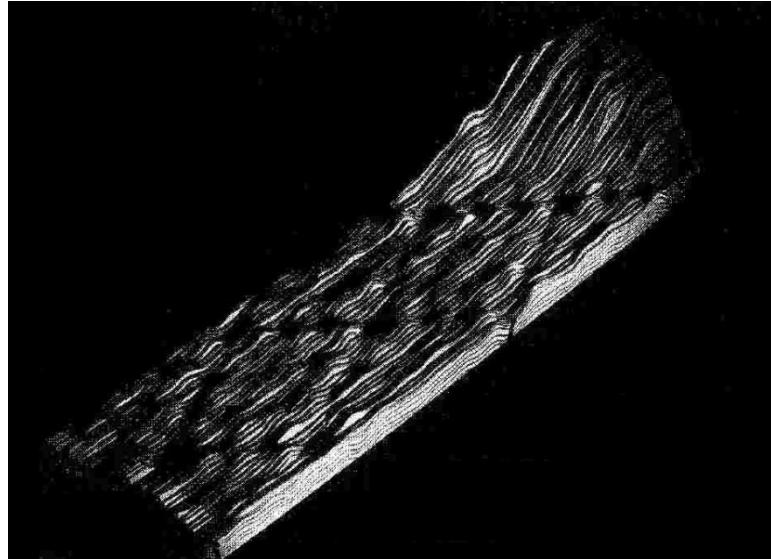
Eiffel Tower: 320 m



Ideal STM tip

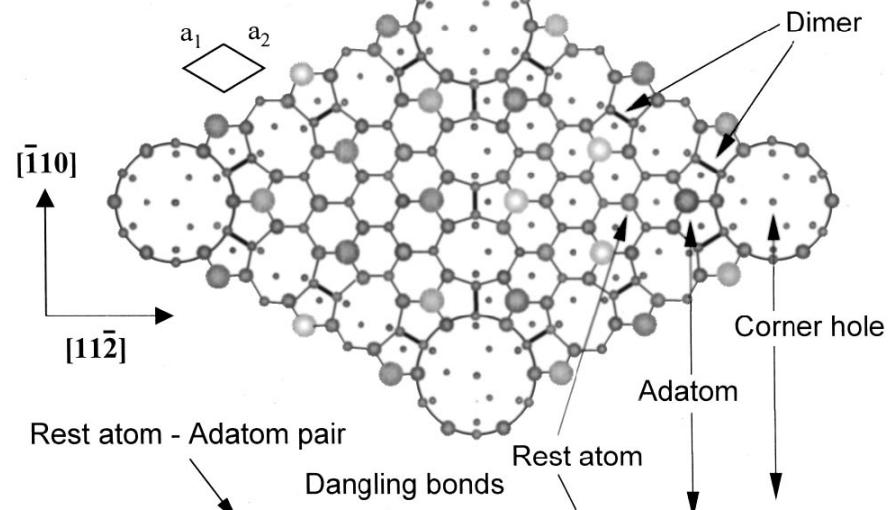


SEM images of a STM tip after close contact with a HOPG surface

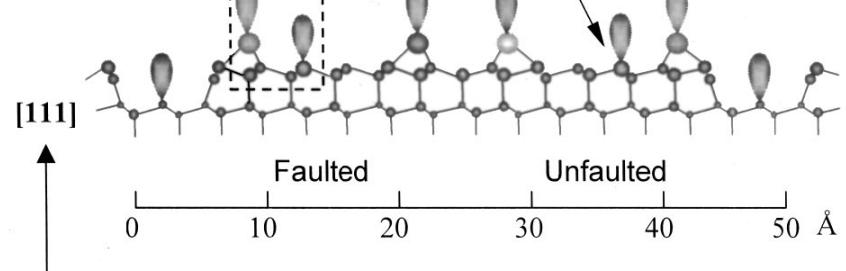


7 × 7 reconstruction on Si(111) resolved in real space from G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett., 50:120–123, 1983.

Top view

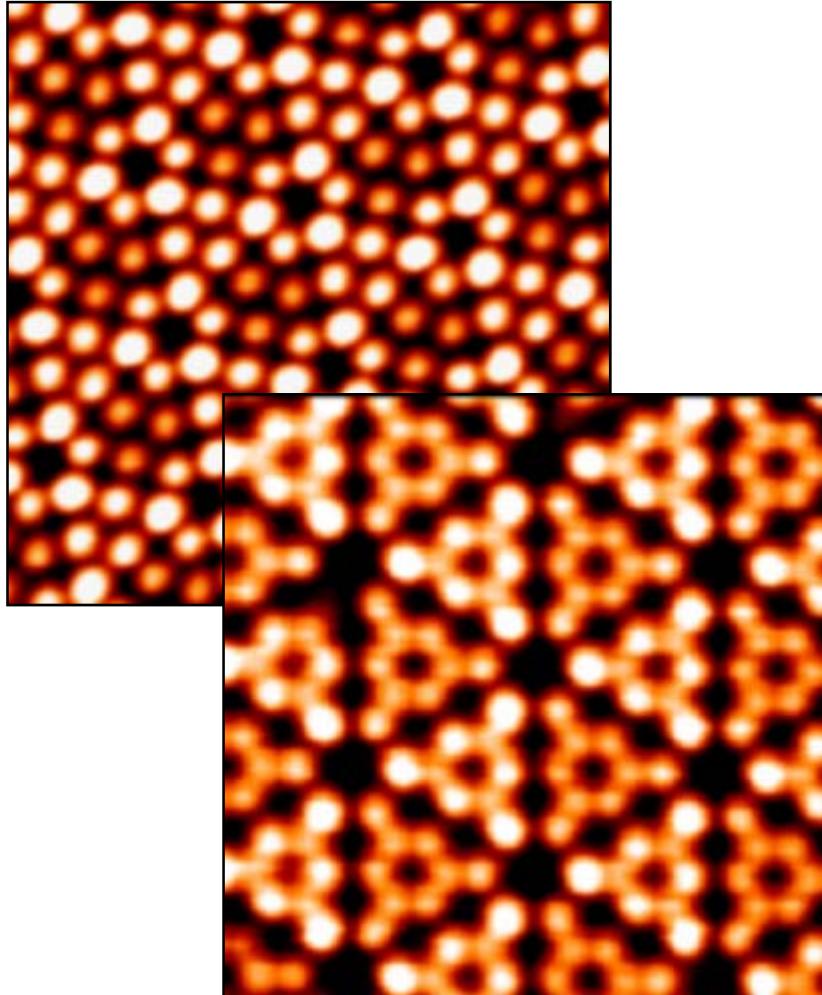


Side view



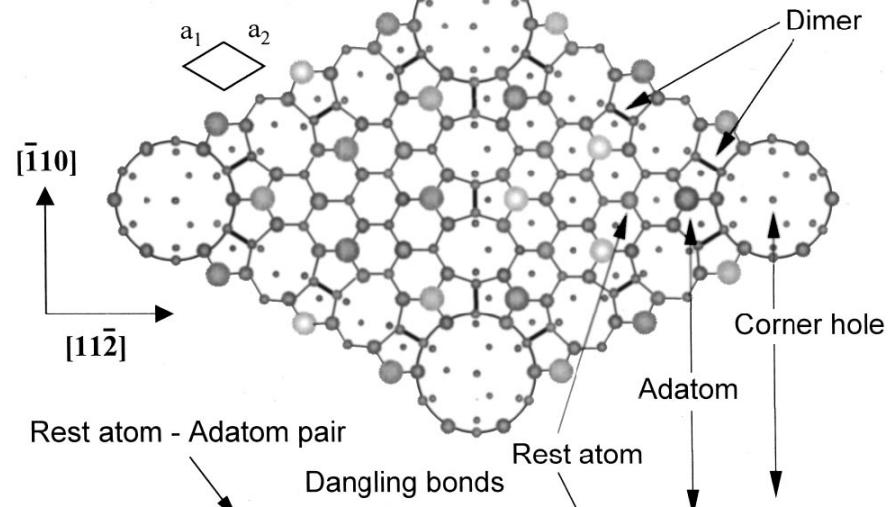
Dimer-adatom-stacking fault model

Surface model from Y. Cao, et al, Journal of Chemical Physics 115, p3287 (2001)

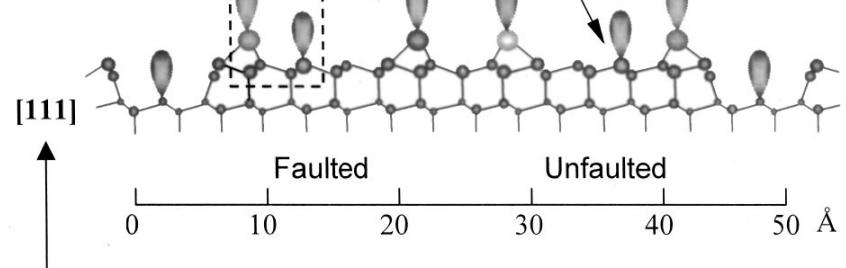


STM imaging depends on the tunneling parameters (V_t , I_t)

Top view

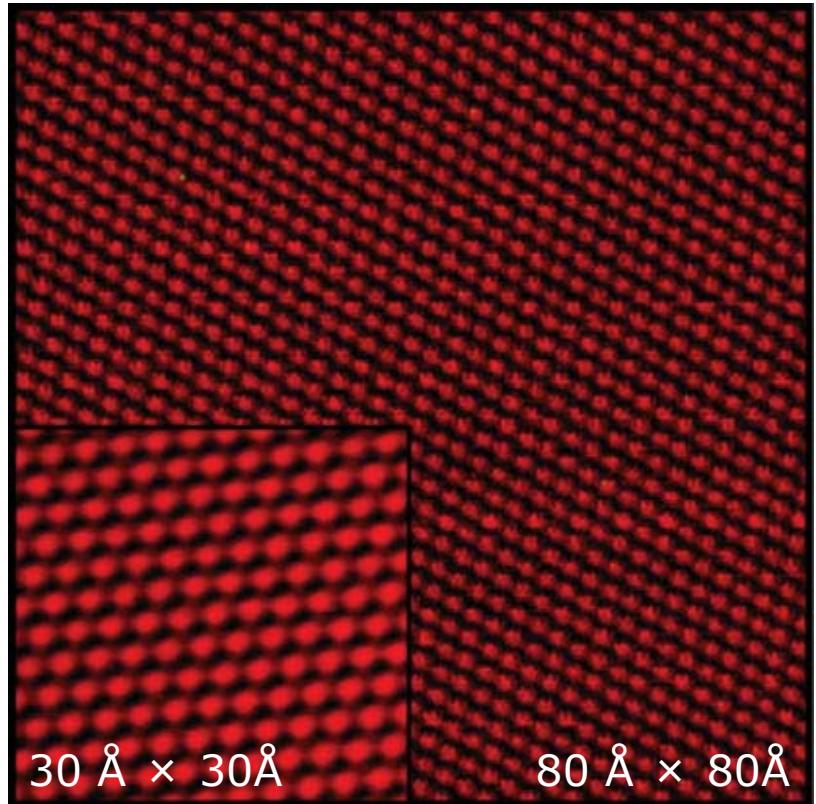


Side view



Dimer-adatom-stacking fault model

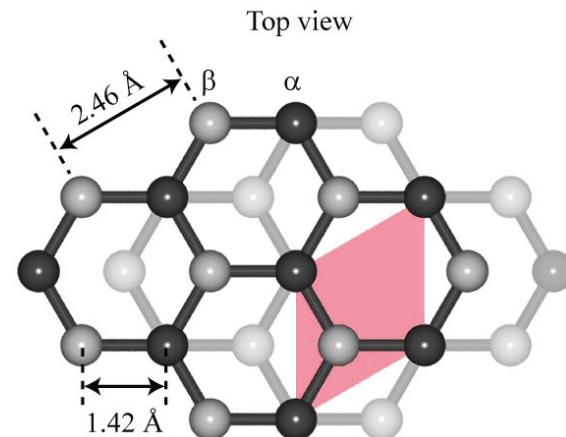
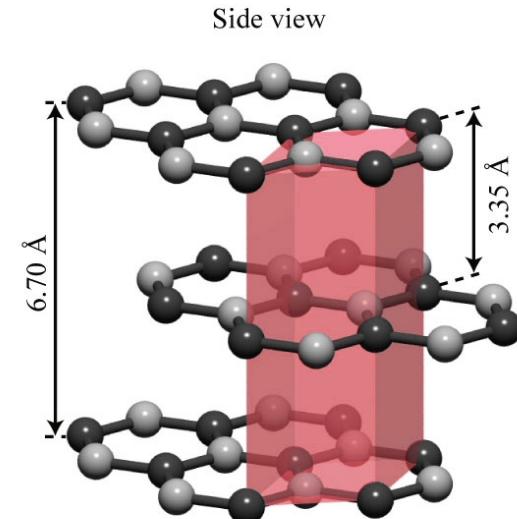
Surface model from Y. Cao, et al, Journal of Chemical Physics 115, p3287 (2001)



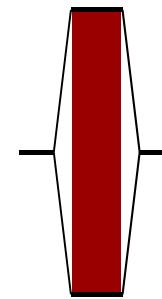
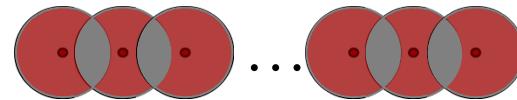
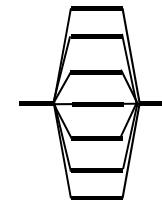
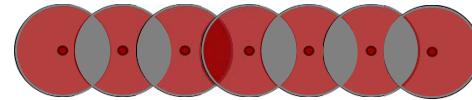
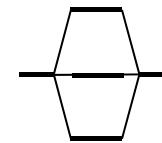
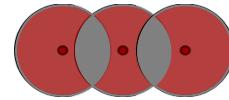
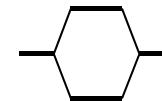
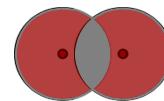
Only every other C atom is imaged

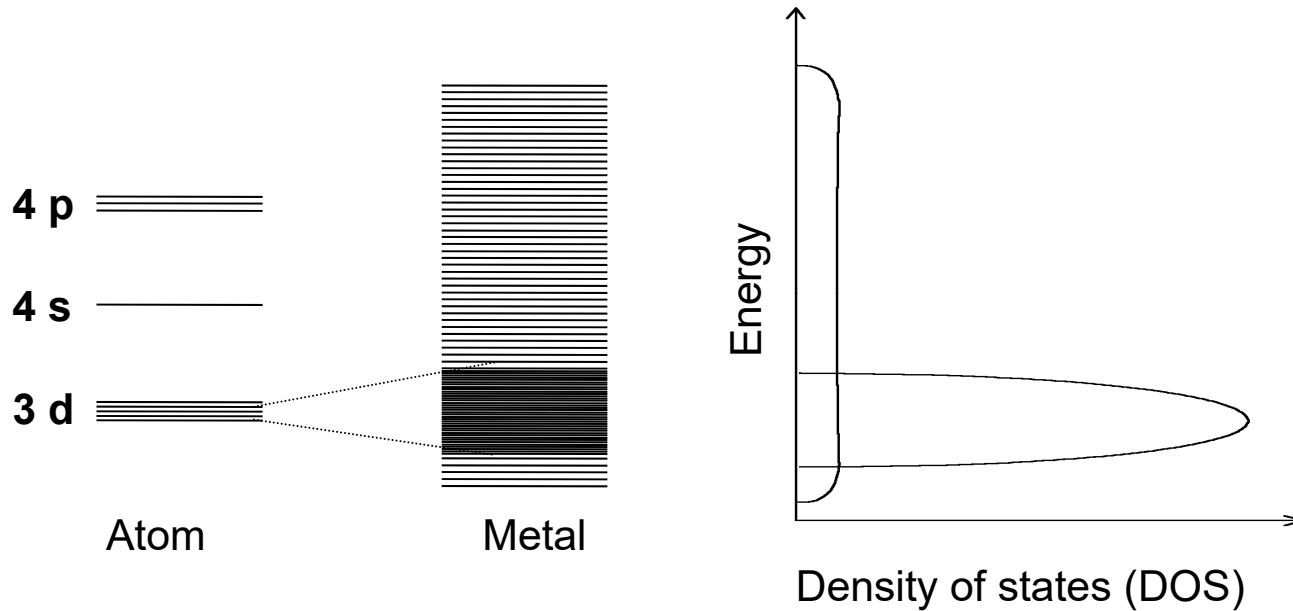
=> STM does **not** image a purely geometric structure

Structure of graphite:



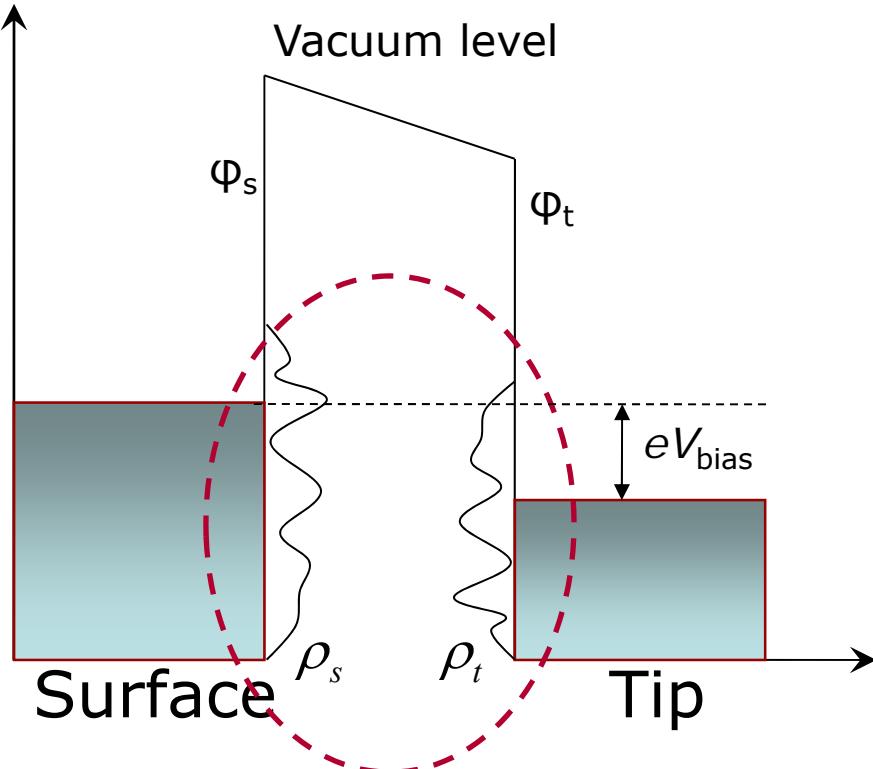
Electronic structure of metals can be described with band structure like an extended molecule





Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period	H												B	C	N	O	F	He
2	Li	Be											Al	Si	P	S	Cl	Ne
3	Na	Mg											13	14	15	16	17	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uup	Uuh	Uus	Uuo	
Transition Metals (d-block)																		
Lanthanides																		
Actinides																		

Potential energy



Solving the problem requires

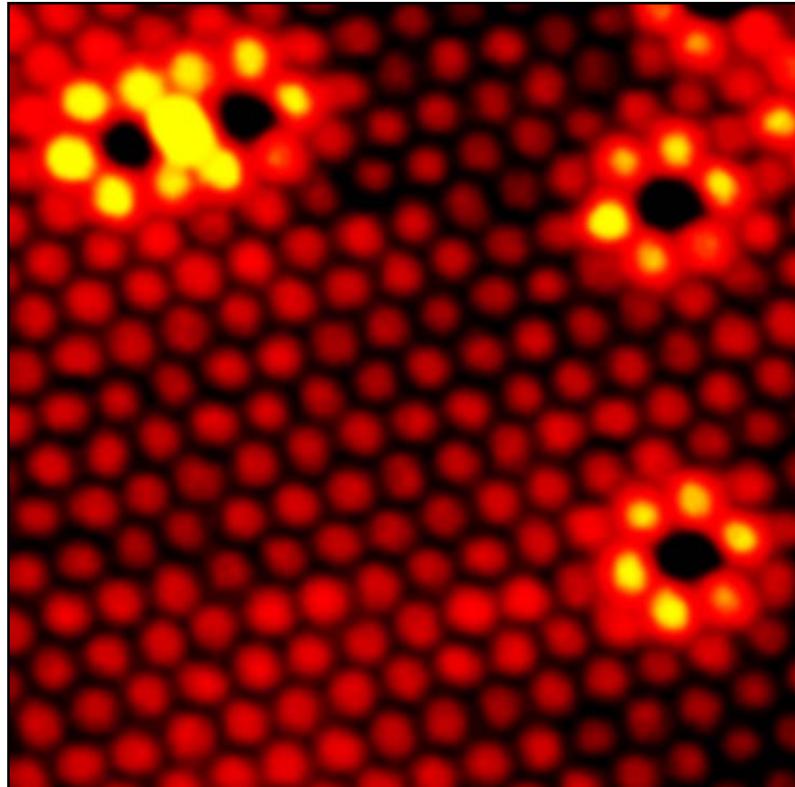
1. Knowledge on the surface structure
2. Exact knowledge on the tip structure (which is most often undefined)
3. Knowledge on the tunneling barrier

Local DOS of surface for given tip position r_0 and energy ε_F

$$I_{s \rightarrow t} \propto V_{bias} \sum_s \left| \psi_s(\vec{r}_0) \right|^2 \delta(\varepsilon - \varepsilon_F) = V_{bias} \rho_s(\varepsilon_F, \vec{r}_0)$$

So, unlike the first order approximation in which STM images topography,

... the tip is actually mapping out a contour of constant LDOS at the Fermi level of the surface.



The Au atoms substitute Ni atoms in the surface.

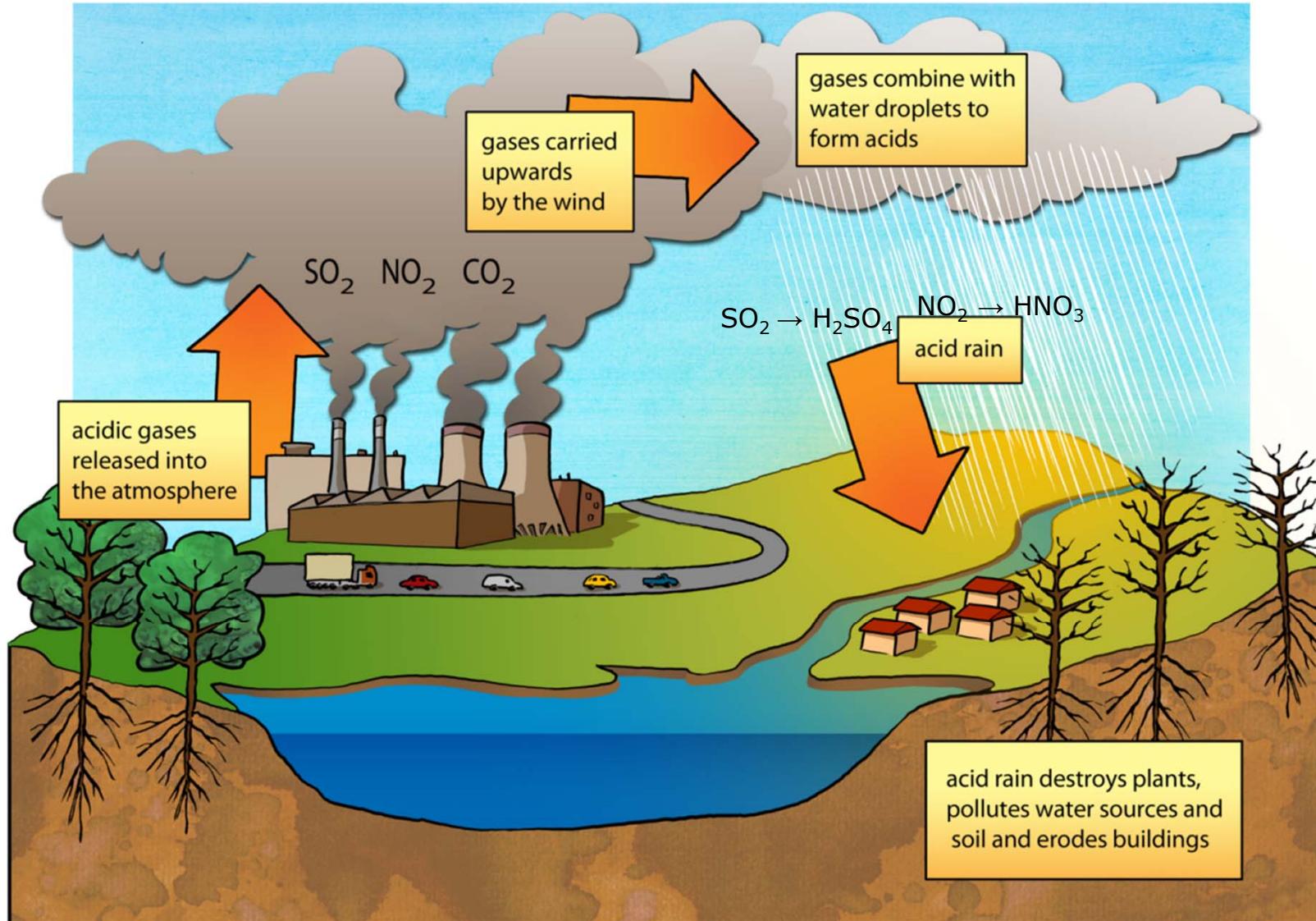
The LDOS at the Au atoms is smaller than at the Ni atoms – therefore the Au atoms are imaged as holes! (Even though they physically protrude from the surface).

The LDOS of the Ni atoms surrounding a Au atoms is increased – i.e. the chemical properties of these Ni atoms are influenced by the presence of the Au atoms!

$$I_{s \rightarrow t} \propto LDOS$$

*No chemical identification of surface atoms with STM
STM images of complex systems not easily interpreted*

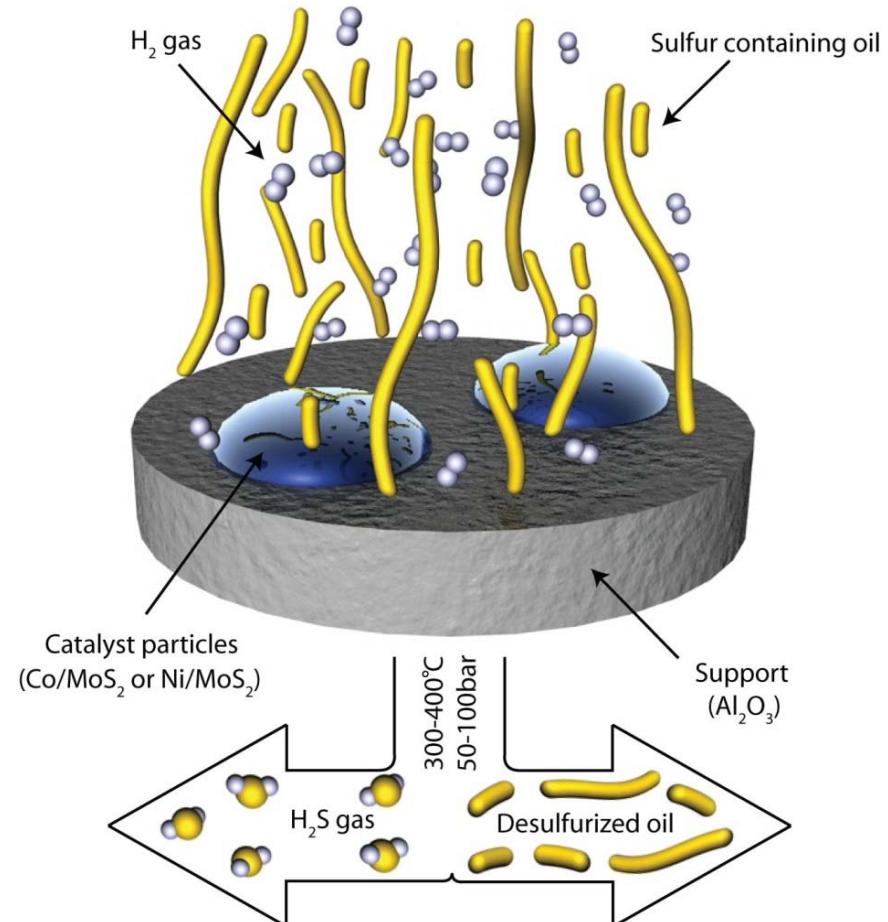
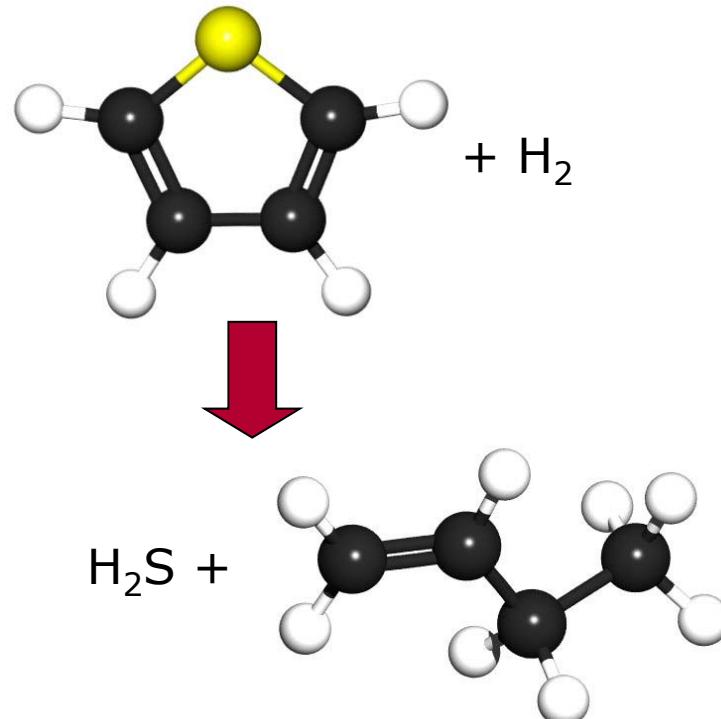
Sulfur emission → acid rain



Hydrodesulfurization - (HDS)

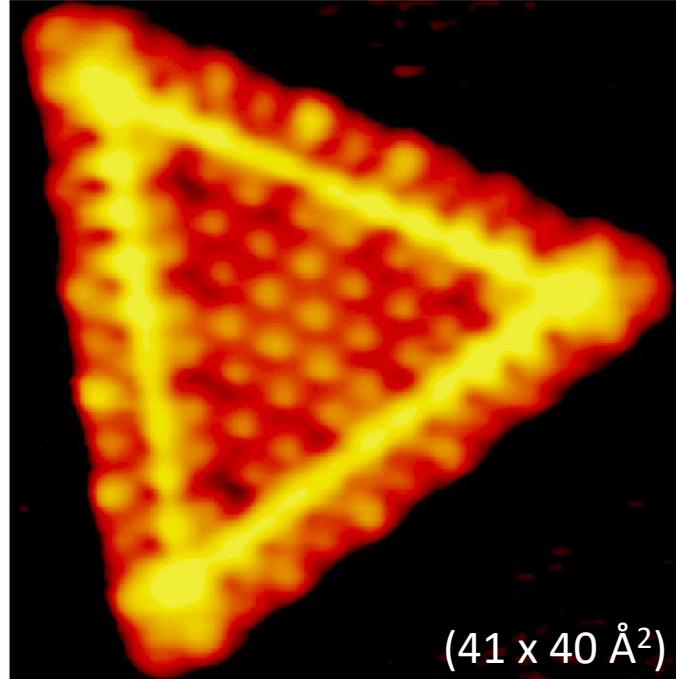
Hydrodenitrogenation - (HDN)

Hydrogenation - (HYD)

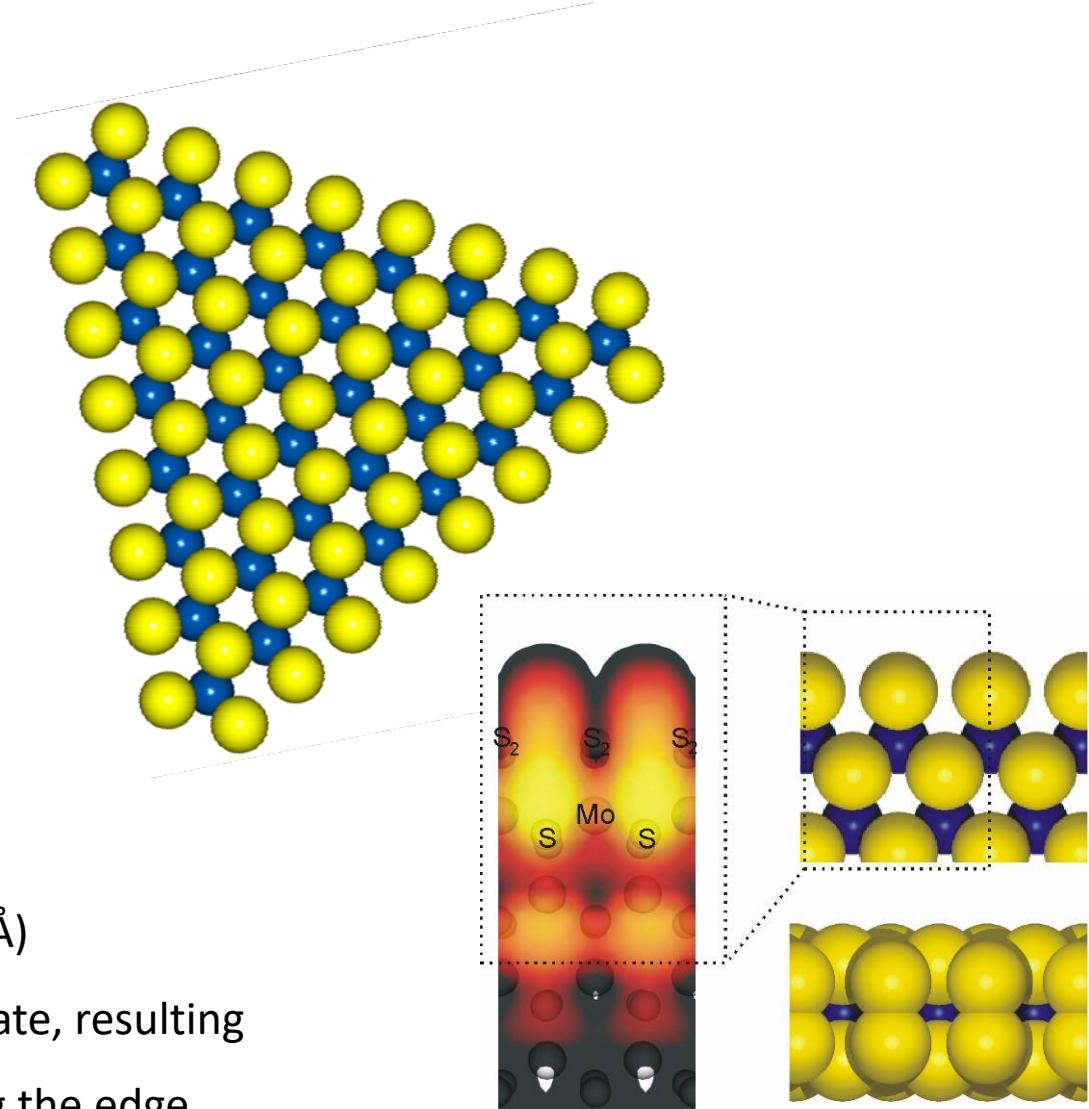


Active particles characterized by *in-situ* measurements: single-layer MoS₂-like clusters, size: $\sim 20 \text{ \AA}$ at 400°C

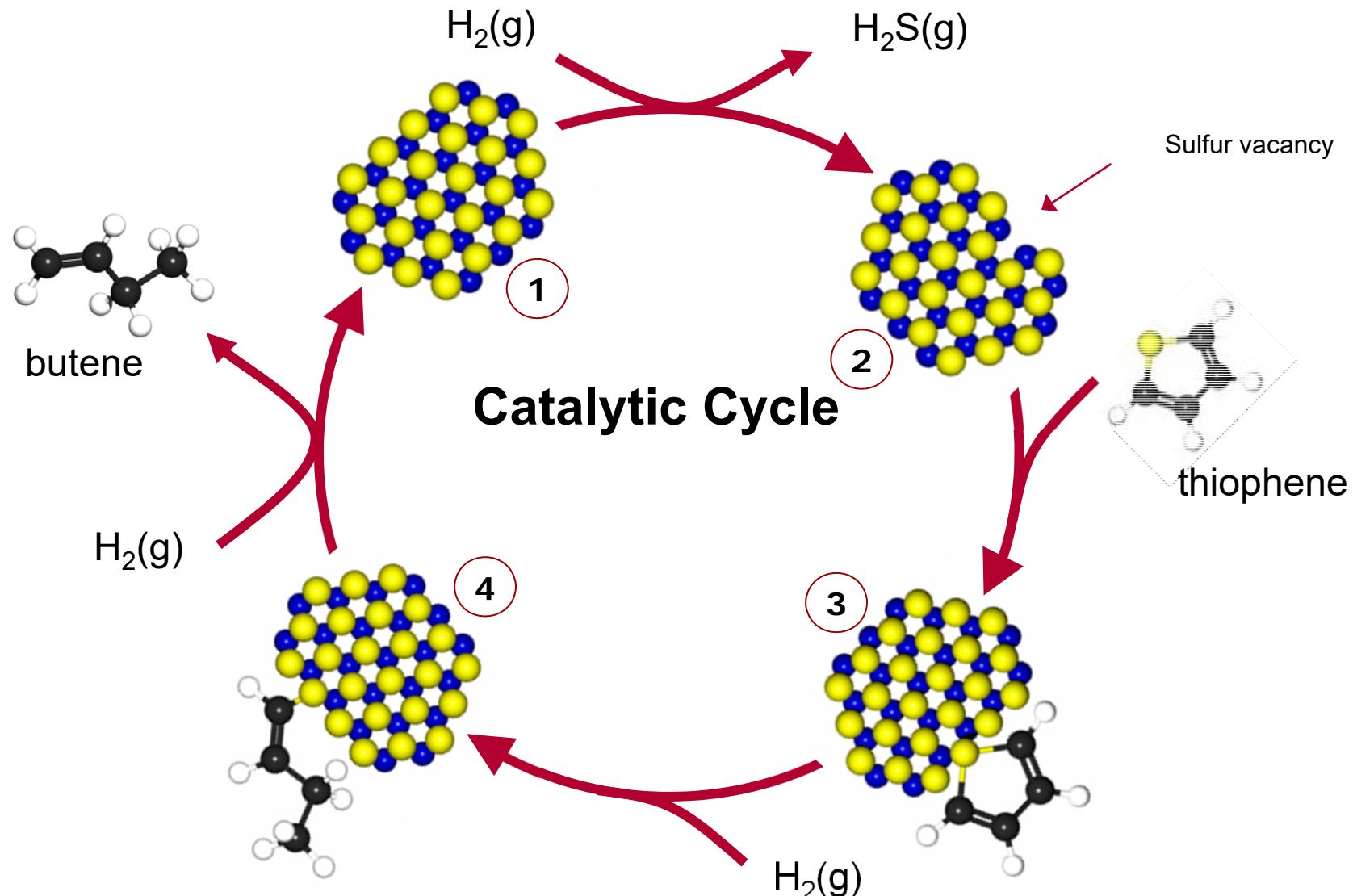
Topsøe, Clausen and Massoth in *Hydrotreating Catalysis*, Springer Verlag (1996)



- Triangular shape
- Single S-Mo-S layer (Height: 3.16 Å)
- One-dimensional metallic edge state, resulting in the observed bright brim along the edge

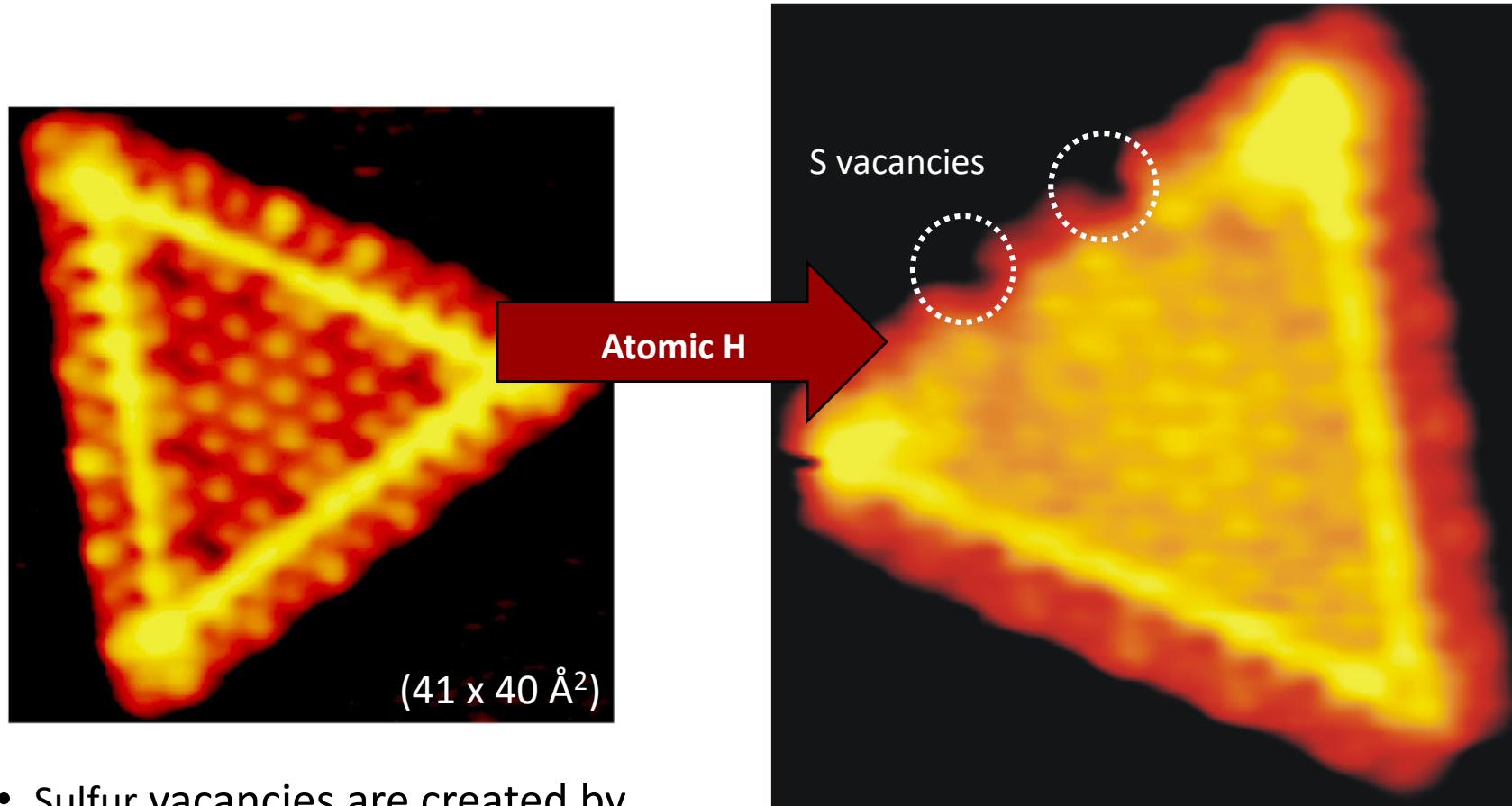


S. Helveg, J.V. Lauritsen, F. Besenbacher *et al.* PRL **84**, p951 (2000)



Topsøe, Clausen and Massoth

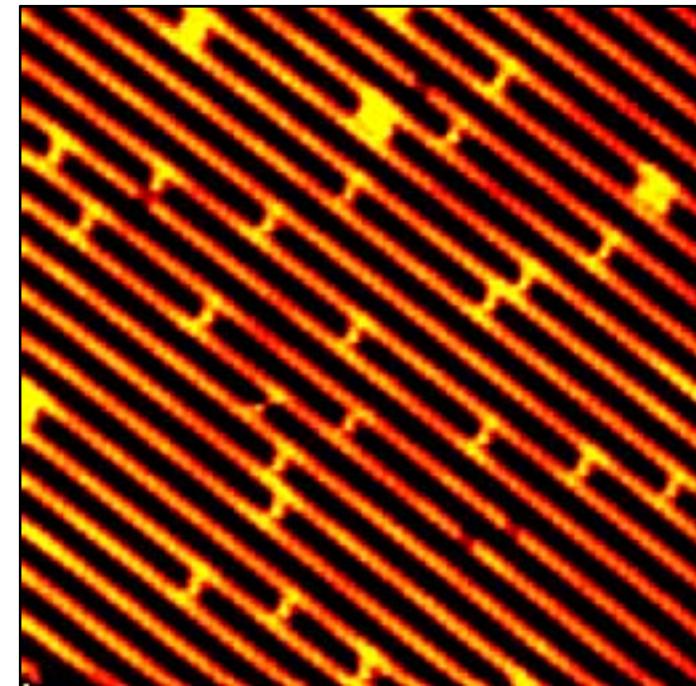
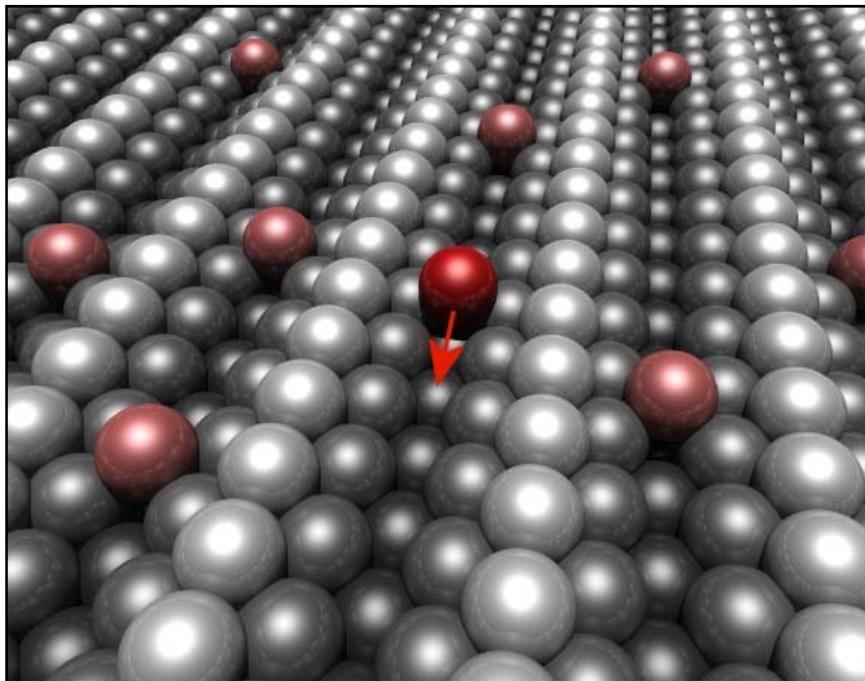
in *Hydrotreating Catalysis*, Springer Verlag (1996)



- Sulfur vacancies are created by exposing the MoS₂ clusters to atomic hydrogen =>
- Direct imaging of catalytically active sites!

S. Helveg, J.V. Lauritsen, F. Besenbacher *et al.* PRL **84**, p951 (2000)

Diffusion of Pt adatoms on the missing row Pt(110)-(1x2) surface

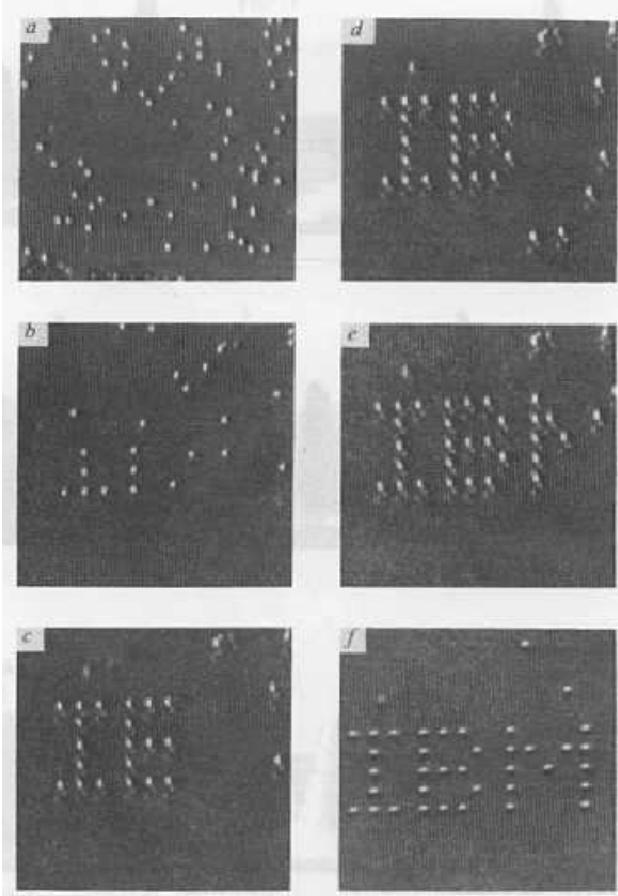


High speed STM's: Over 30 images/s!

=> Follow dynamic processes in real time

61° C, 13 s/image, $150 \times 150 \text{ \AA}^2$

Linderoth, T. R., et al., Phys. Rev. Lett. (1997) 78 (26), 4978

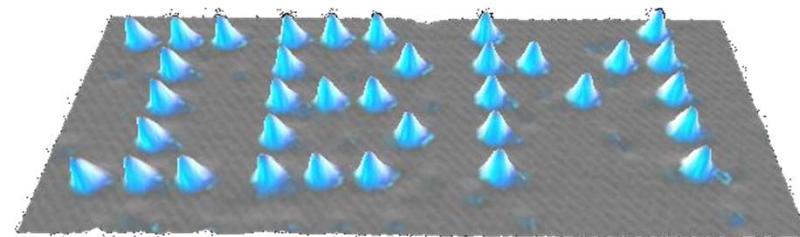
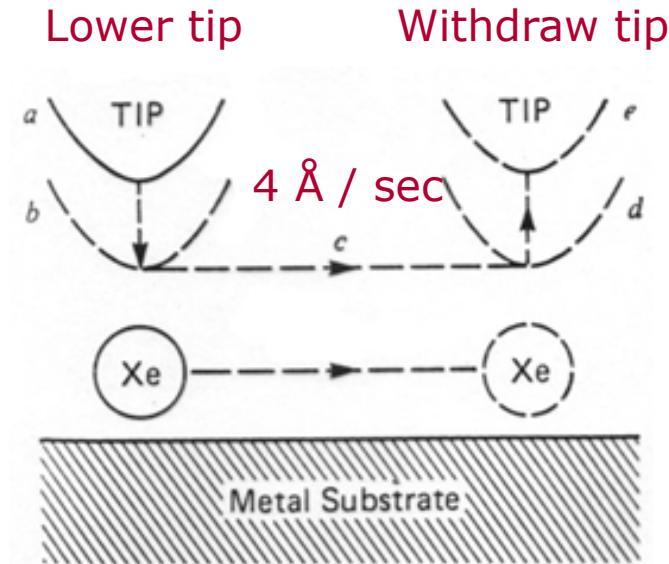


Xe atoms on Ni(110)

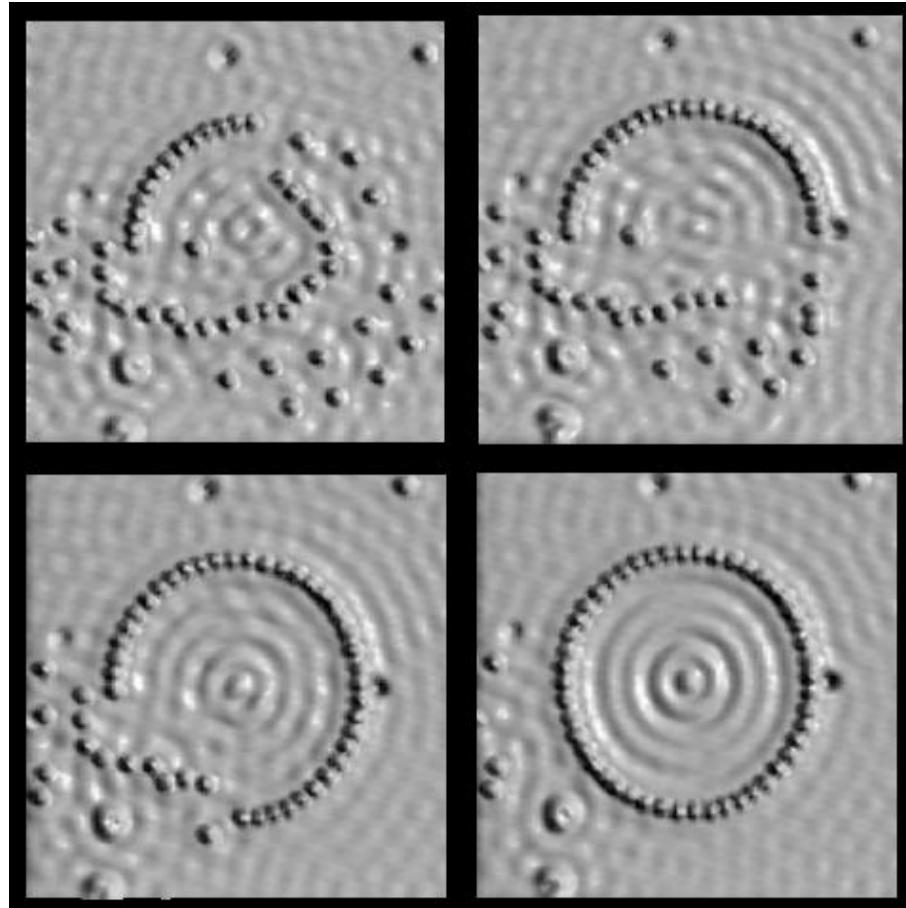
(a): The surface after Xe dosing.

(b) – (f): Various stages during the construction.

Each letter is 50 Å from top to bottom.



Eigler and Schweizer, Nature **344**, p524 (1990)

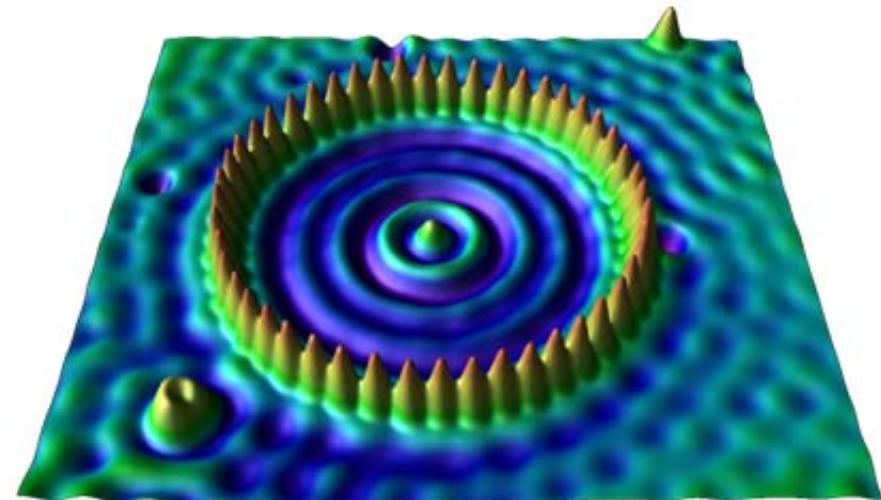


Fe Atoms on Cu(111) at 4K

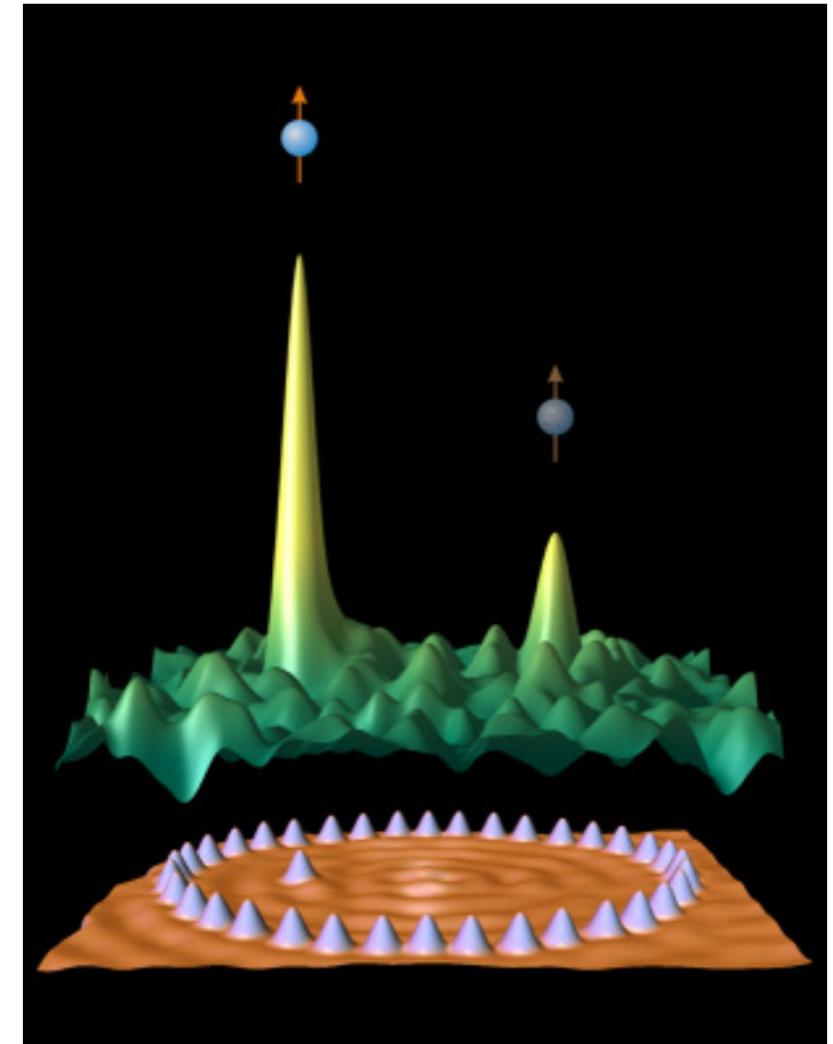
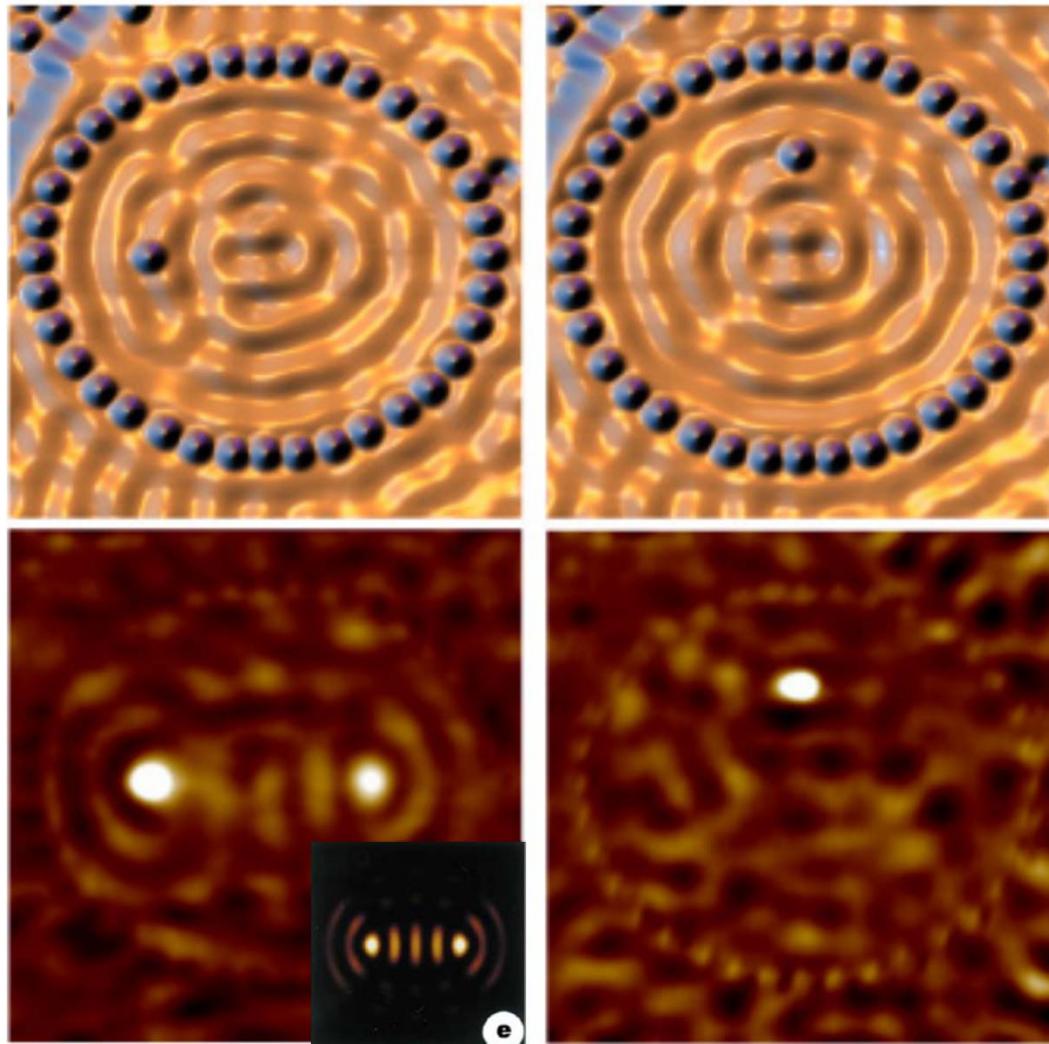
The Fe adatoms confine the surface state electrons laterally because of strong scattering



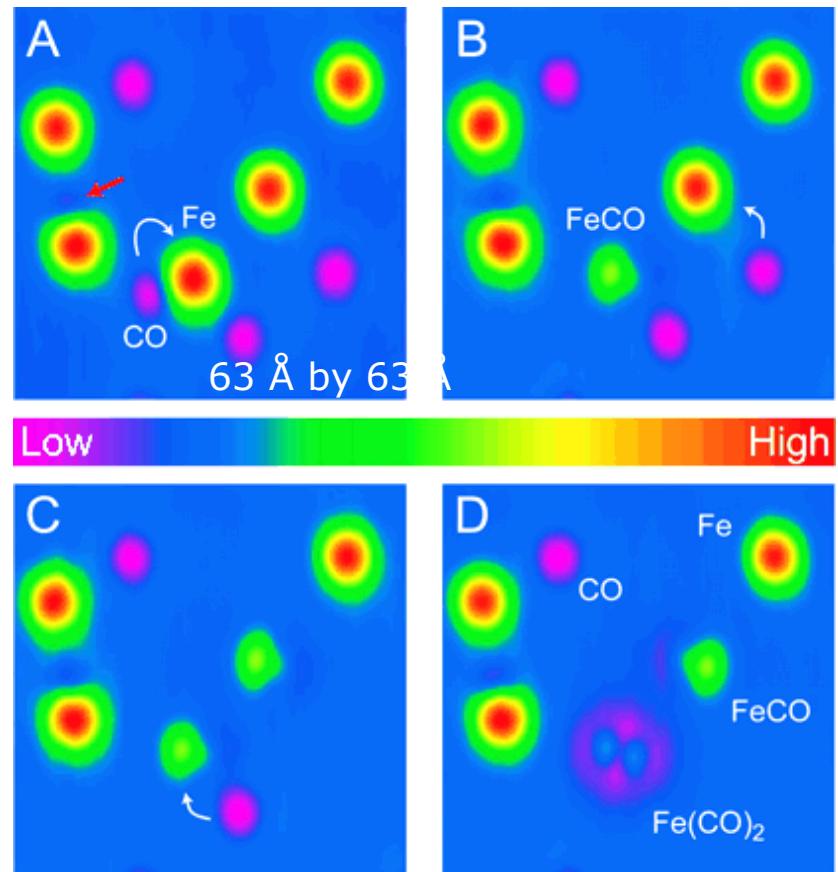
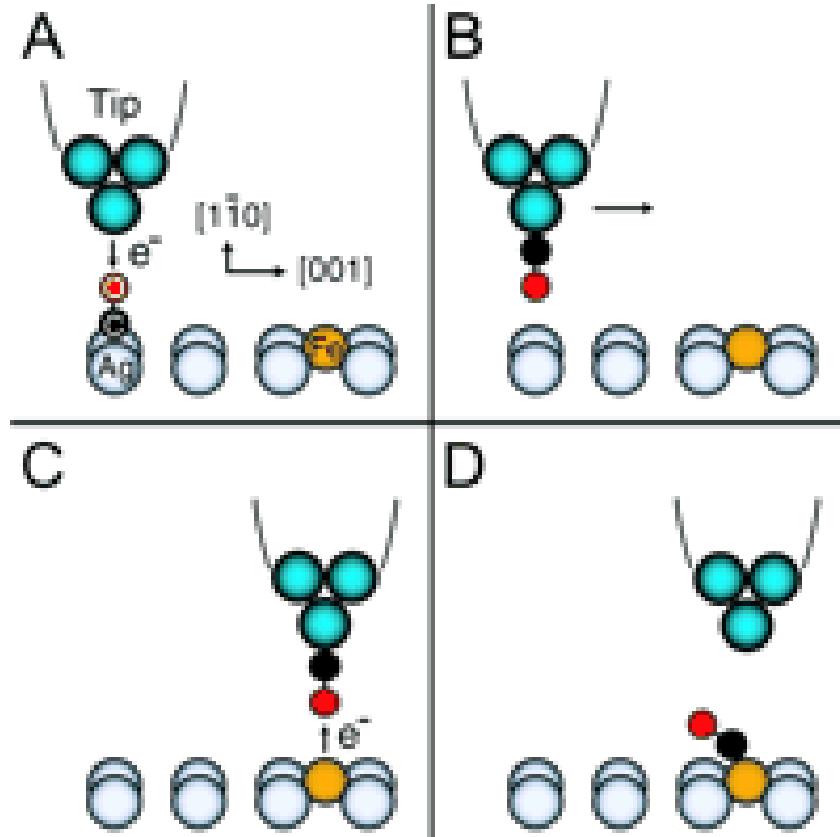
Standing wave pattern in DOS



D.M. Eigler et al. Science **262**, p218-220 (1993)



Eigler, Nature 403, 512. 515 (2000)



Formation of $Fe(CO)$ and $Fe(CO)_2$ induced by moving the CO molecules by the STM.

H. J. Lee, W. Ho, Science **286**, p1719 (1999)

<http://www.research.ibm.com/articles/madewithatoms.shtml>

