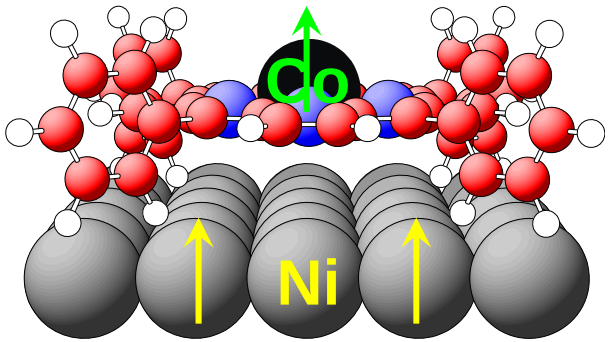
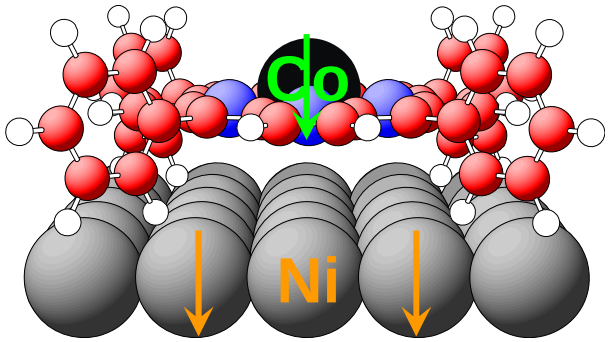
Repetition V

- Near Edge X-ray Absorption Fine Structure
- reflects density of unoccupied states
- Absorption processes and decay (soft X-rays)
- Sampling depths (total electron yield, secondary, Auger, Fluorescence)
- Multiplet structure (chemical, electronic sensitivity)
- XMCD (sum rules)
- XMLD
- Magnetism (spin and orbital moment, magnetocrystalline anisotropy)

Experimental results: XMCD

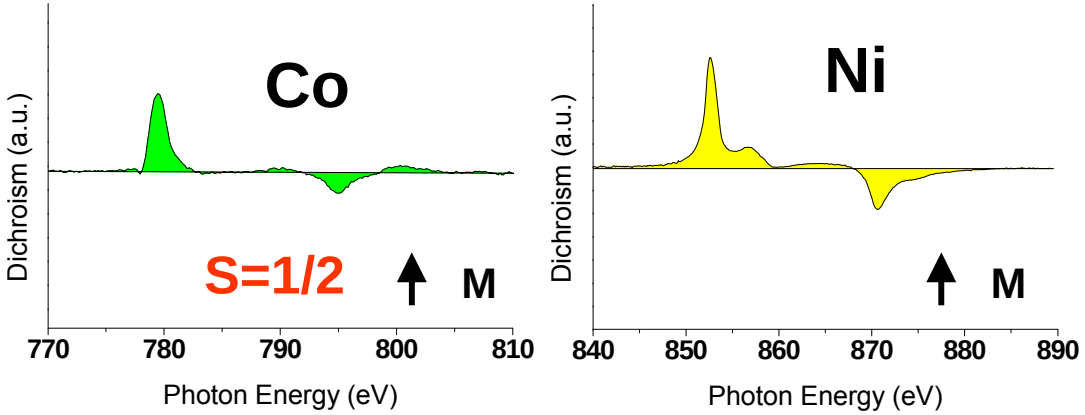


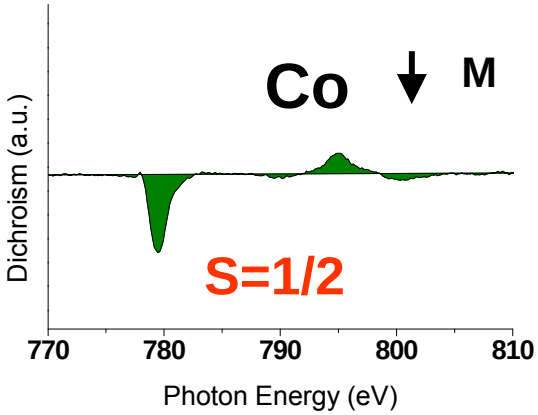
CoTPP/Ni(001)

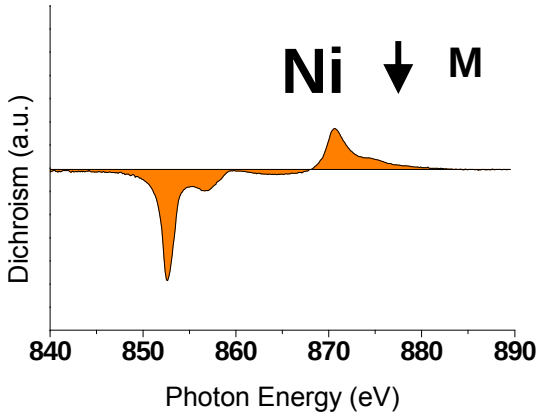


CoTPP/Ni(001)

XMCD: L-edges

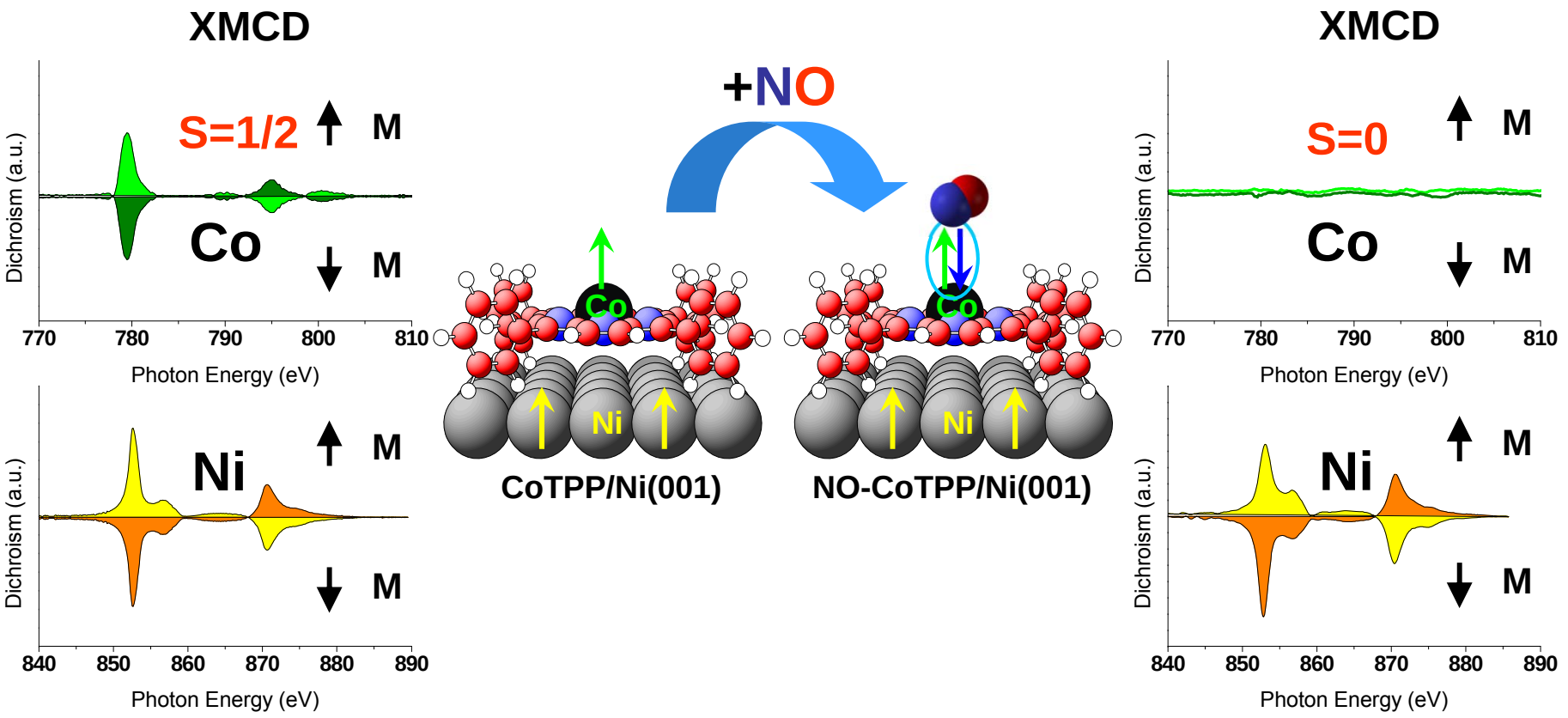






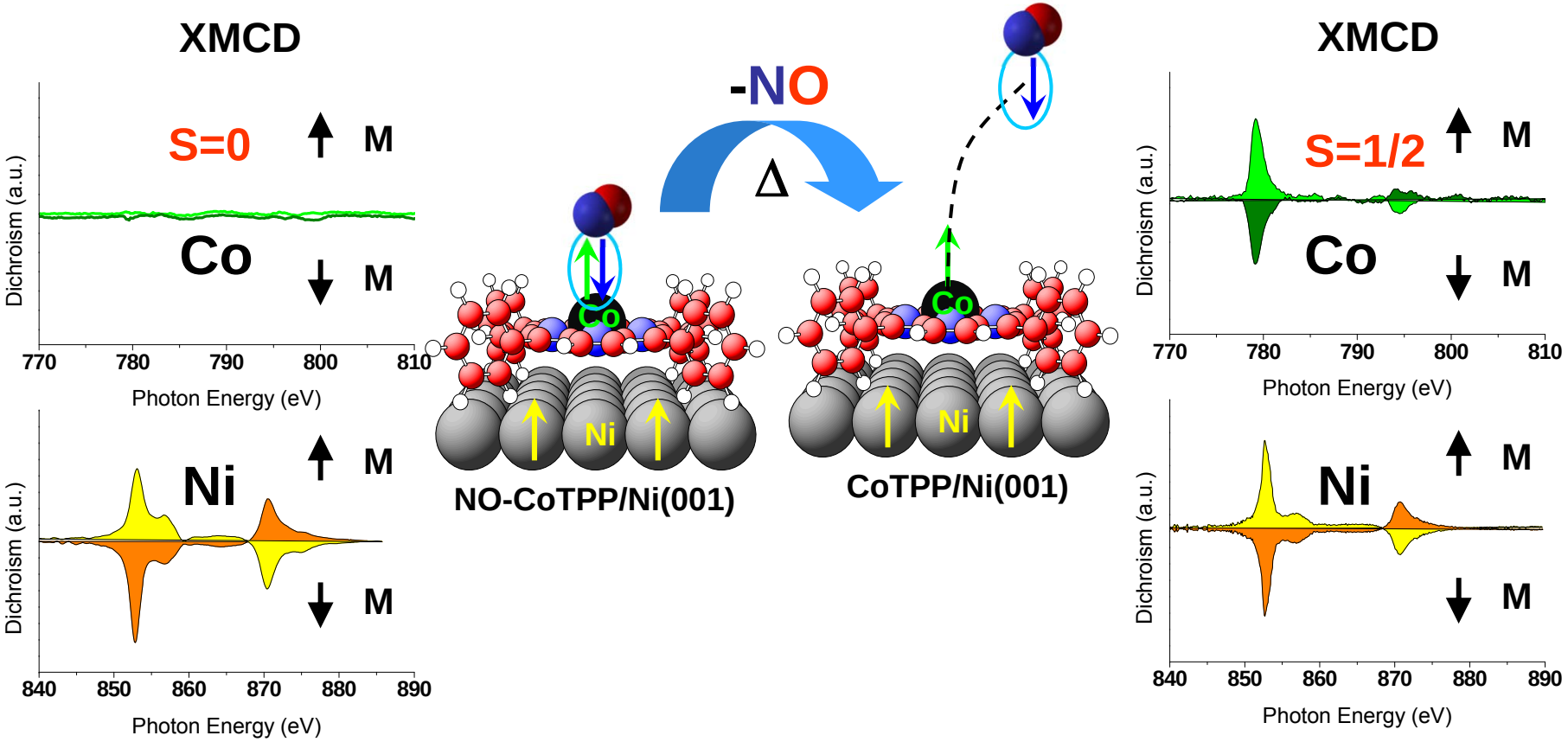
ferromagnetic (FM) coupling of molecular spins with the substrate: RT **On-state**

Experimental results: XMCD



switching-off molecular spins in presence of the substrate-field by NO **Off-state**

Experimental results: XMCD



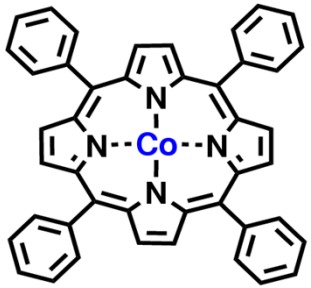
switching-on molecular spins after thermal desorption of NO

On-state

Research design: molecule, substrate and technique

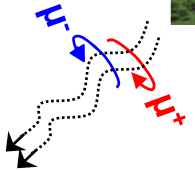
X-ray (SLS) Magnetic Circular Dichroism

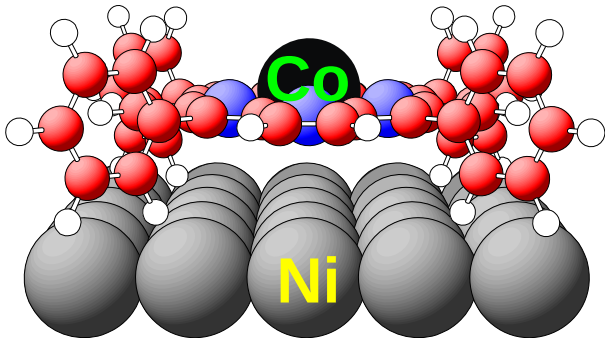
(XMCD)



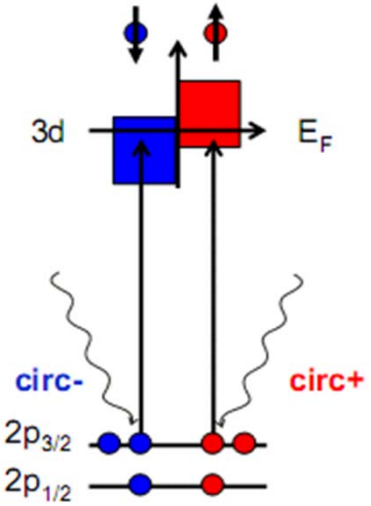
CoTPP

S=1/2

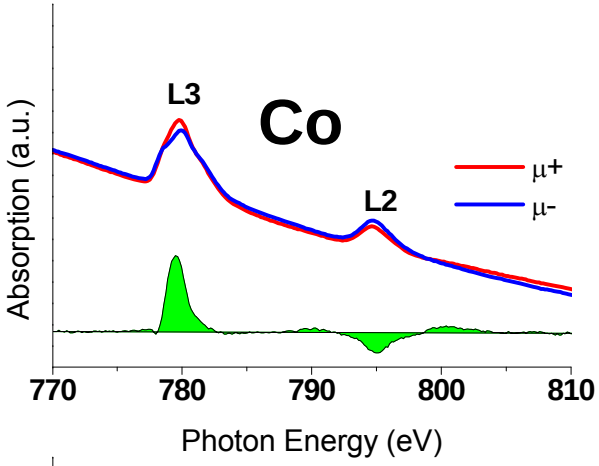


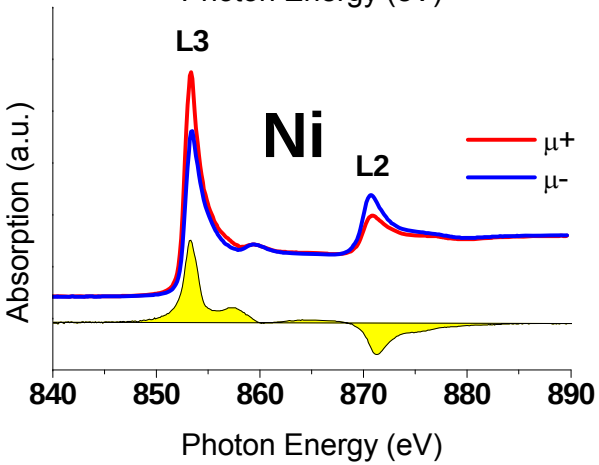


CoTPP/Ni(001)



XAS: L-edges





Repetition VI

- Magnetic domains
- Slow electrons (surface/interface sensitivity)
- PEEM with soft X-rays as source (XMCD image)
- Polarized X-ray source
- PEEM with slow electrons as source
- Research example nanocrystals

Repetition IV

- Winkelaufgeloeste Photoelektronenspektroskopie ARPES / Fermi Surface Mapping
- Diffusion / Random Walk in 2D
- Fick‘s Laws
- Atomistic Diffusion Mechanisms / Defects / Steps
- Mass Transfer / Anisotropy
- Cluster Diffusion

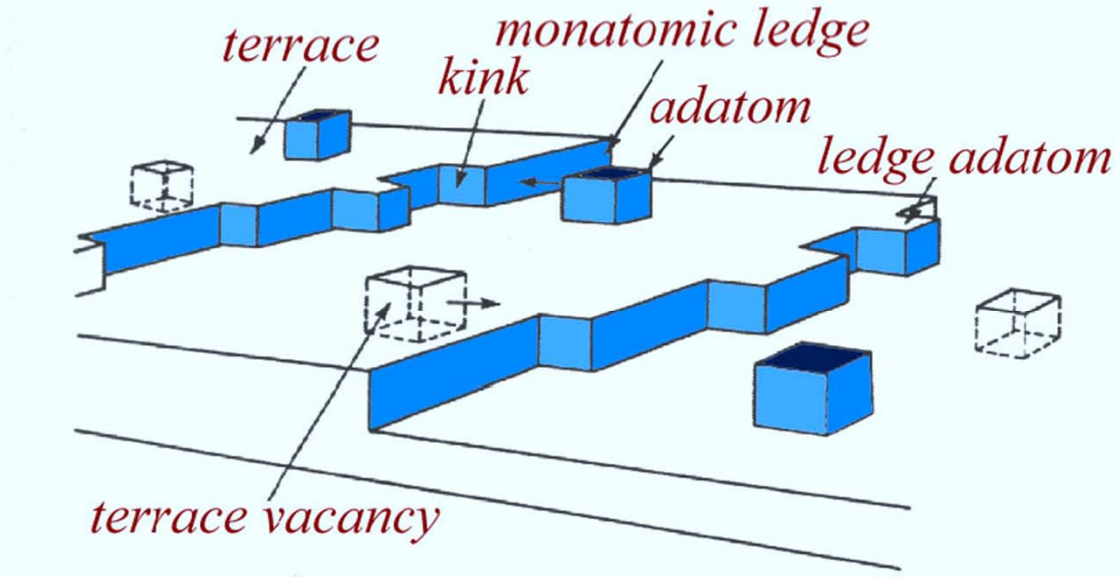
Diffusion Mechanisms

- Depending on the landscape:
  - Intrinsic diffusion (no sources and traps)
  - Mass transfer diffusion (generation and/or trapping)

Intrinsic Diffusion

- Adparticle motion is monitored within a single terrace → Spatial limit ~ 100 nm

- In practice: no strong distinction from tracer diffusion



Mass Transfer Diffusion

• Real surfaces contain defects (steps, kinks, adatoms or vacancy clusters, etc.)

• If average separation between defects < diffusion length → number of mobile particles (and diffusion) become strongly temperature dependent

• If adatoms and substrate are the same chemical species:

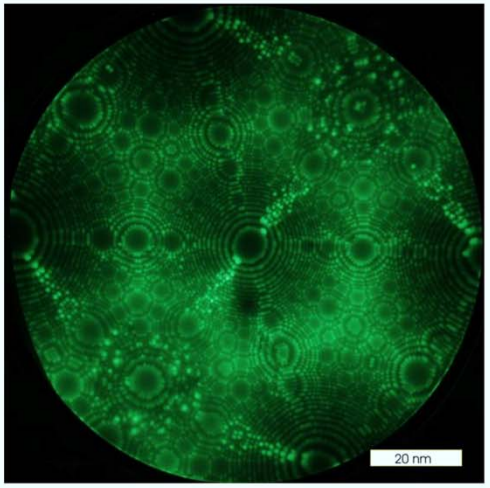
$$D = \frac{\nu_0 a^2}{z} \exp\left(-\frac{\Delta G + E_{diff}}{k_B T} \right)$$

ΔG = energy of adatom formation

(→ two types of energy barriers!)

Experimental Techniques

1) Direct observation:

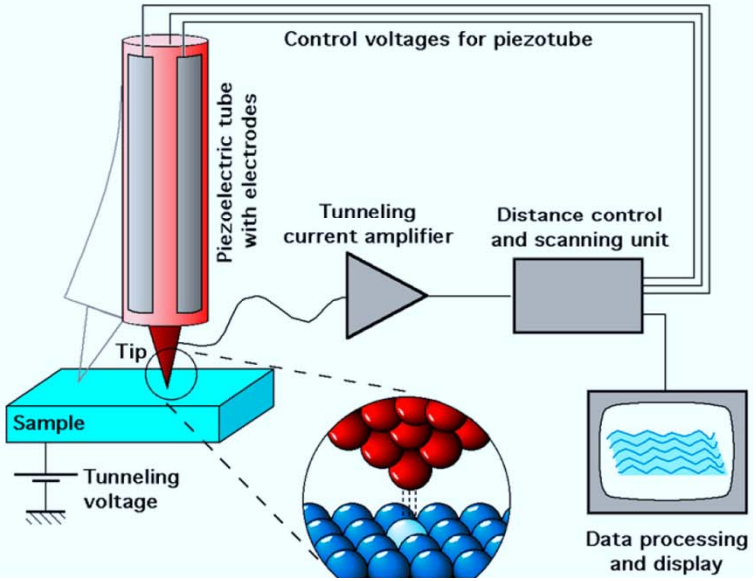


• Field ion microscopy (FIM)
→ "image-anneal-image" technique

- Limited to refractory or noble metal surfaces

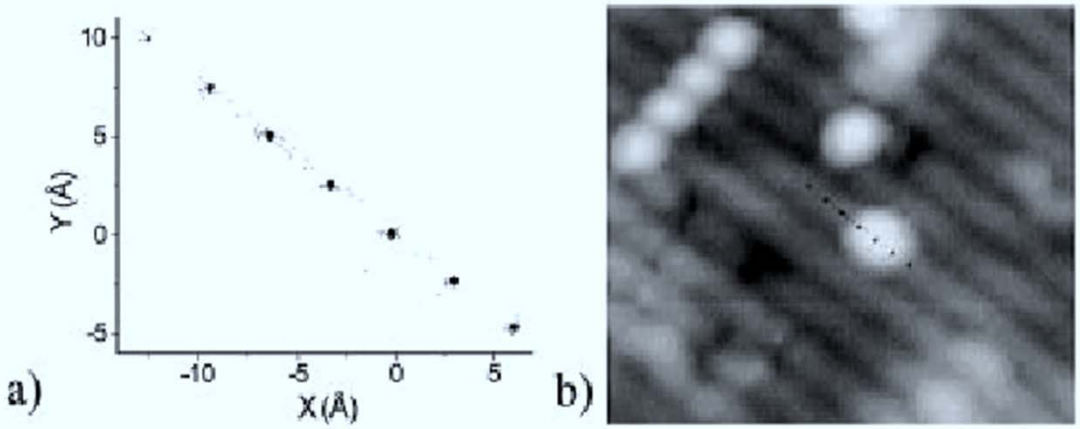
• Scanning tunneling microscopy (STM)
→ "image-while-hot" technique
→ „cook-n-look" technique

- STM "movies" can be recorded
(at 0.01-1 frames per second)



Experimental Techniques

- Scanning tunneling microscopy (STM) → "atom-tracking" technique
  - STM tip locked onto an adparticle by 2D lateral feedback
  - Example: Si on Si(100) (Swartzentruber, PRL 1996)



  - Electric fields from the STM tip influence surface diffusion!

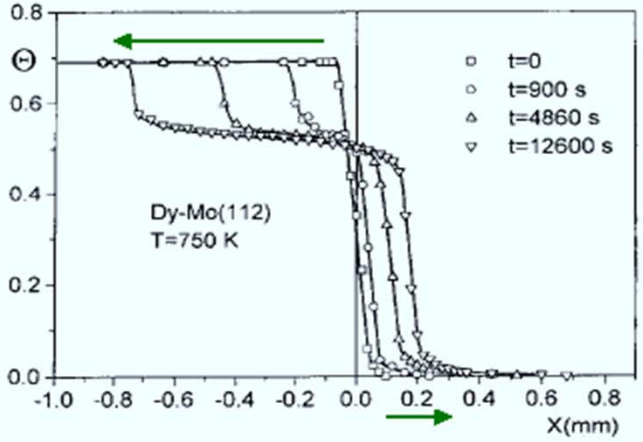
Experimental Techniques

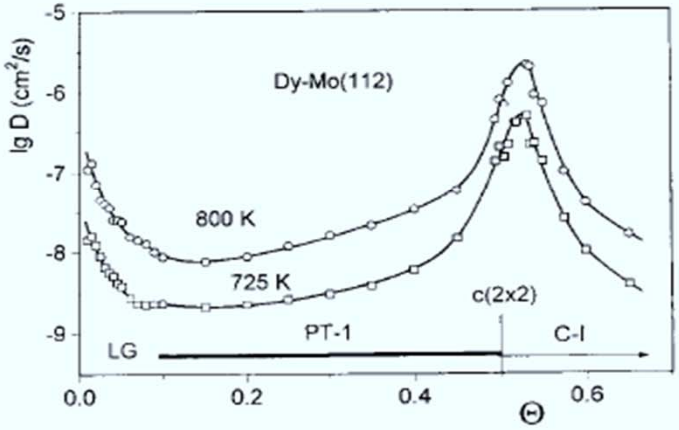
2) Profile evolution method:

- Smearing of a sharp initial concentration profile is monitored

  - Initial profile deposited using a mask
  - AES, SIMS, SEM or local work-function…
  - D(Θ) can be evaluated

- Example: Dy on Mo(112) (Loburets et al., SS 1998)





Experimental Techniques

3) "Capillarity" techniques:

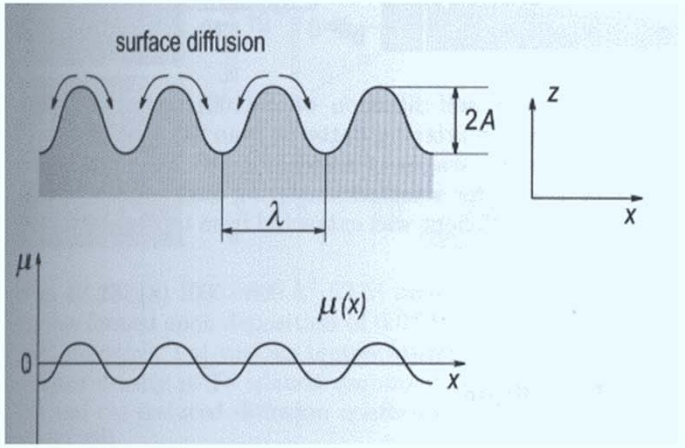
- A surface is perturbed from its lowest energy configuration...

... and allowed to relax via diffusion

- Relaxation rate → Coefficient of diffusion

- For a sinusoidal profile (Mullins, JAP 1999):

$$A(t) = A_0 \exp\left[-\frac{\gamma D n_0 V^2}{k_B T} \left(\frac{2\pi}{\lambda} \right)^4 t \right]$$

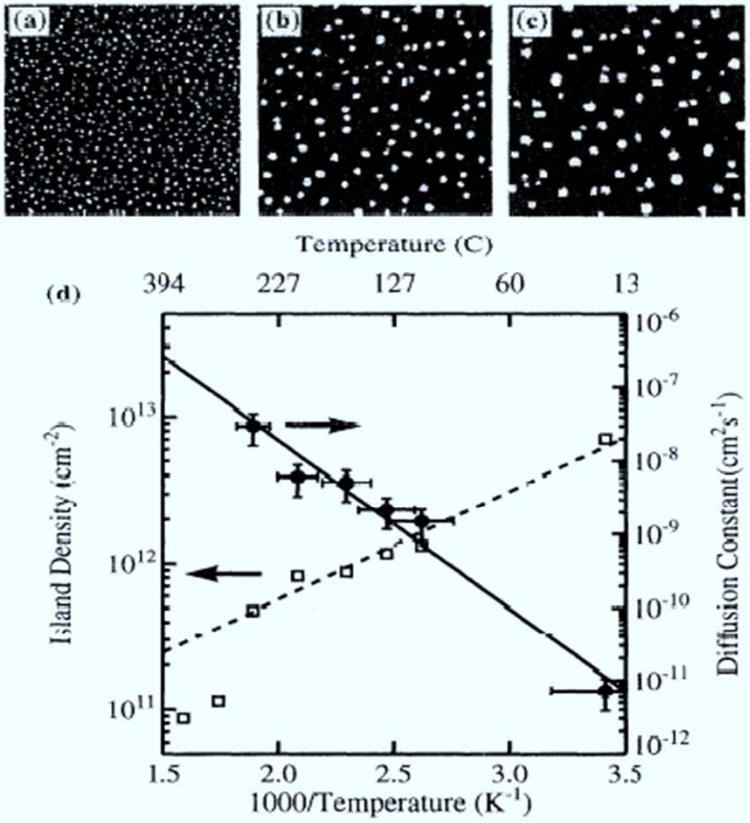


γ = surface tension; V = atomic volume; n_0 = surface density

Experimental Techniques

4) Island growth techniques:

- Number density of islands after submonolayer deposition is monitored
- Example: Fe on Fe(100) (Stroscio et al., PRL 1993)



$$N \propto \left(\frac{R\Theta}{\nu} \right)^{1/3}$$

deposition rate

hopping rate

Further Reading

- K. Oura et al., Surface Science, Springer 2003, chapter 13
- A.G. Naumovets & Yu.S. Vedula, Surf. Sci. Rep. 4 (1985) 365
- R. Gomer, Rep. Prog. Phys. 53 (1990) 917
- G.L. Kellogg, Surf. Sci. Rep. 21 (1994) 1

Oberflächenphysik

27/04/2010

Local Probes and Experiments I:

Scanning Tunneling Microscopy (STM)
Inelastic Tunneling and
Scanning Tunneling Spectroscopy (STS)

Prof. Dr. Silvia Schintke & Prof. Dr. Thomas A. Jung

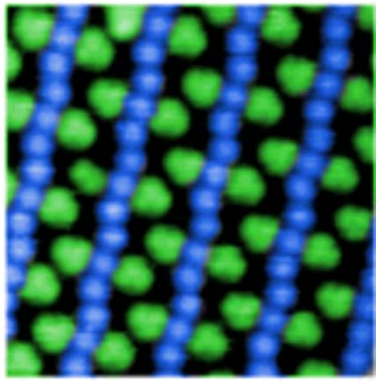
heig-vd
Haute Ecole d'Ingénierie et de Gestion
du Canton de Vaud

PAUL SCHERRER INSTITUT
PSI

UNI
BASEL

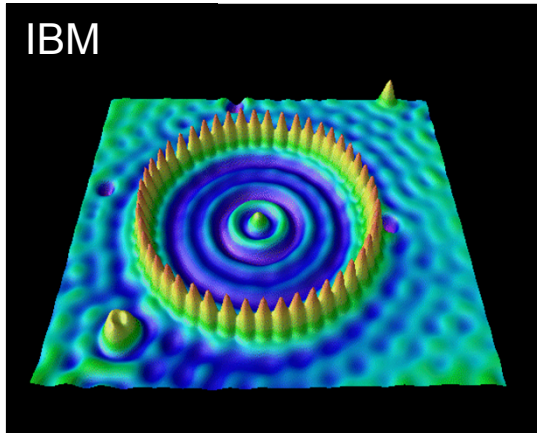
STM – local probe for surface science

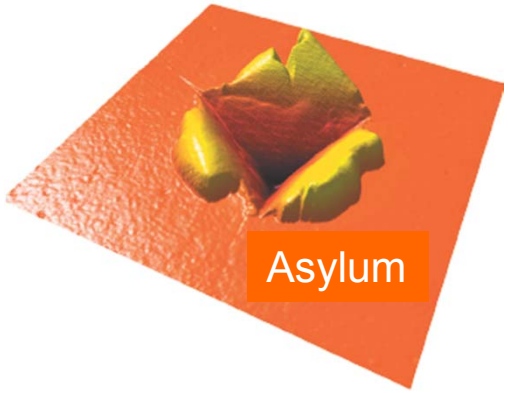
surface analysis @ nanoscale
- scanning probe methods (STM/AFM)
  - working principle of STM
  - tunnel current
  - examples and image interpretation
- scanning tunneling spectroscopy (STS)
  - local electronic structure



STM image: self-assembled molecular layer
Nanolab, Uni Basel

surface modifications @ nanoscale
- manipulation of atoms or adsorbates
- nanoindentation



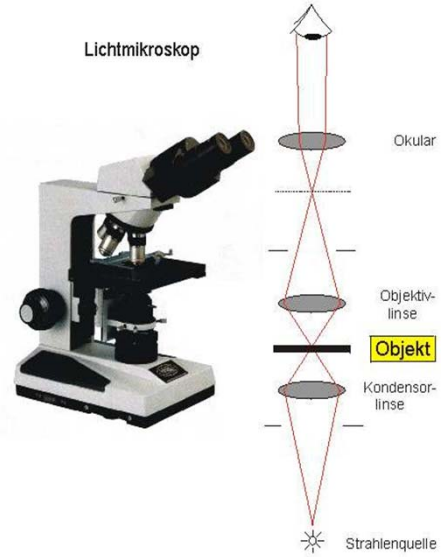


Microscopes

For the visualisation of millimeter to nanometer structures

Light Microscope

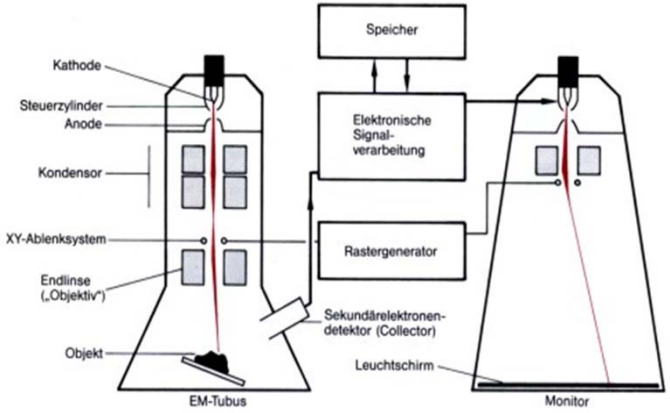
since about 1750



geometric optics
resolution about 500 nm
Light-Intensity contrast

Electron Microscope (SEM)

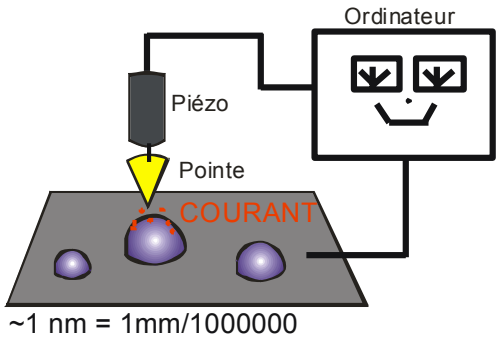
since about 1955



e-beam raster-scan
resolution 5 nm
secondary electron counting
projection image

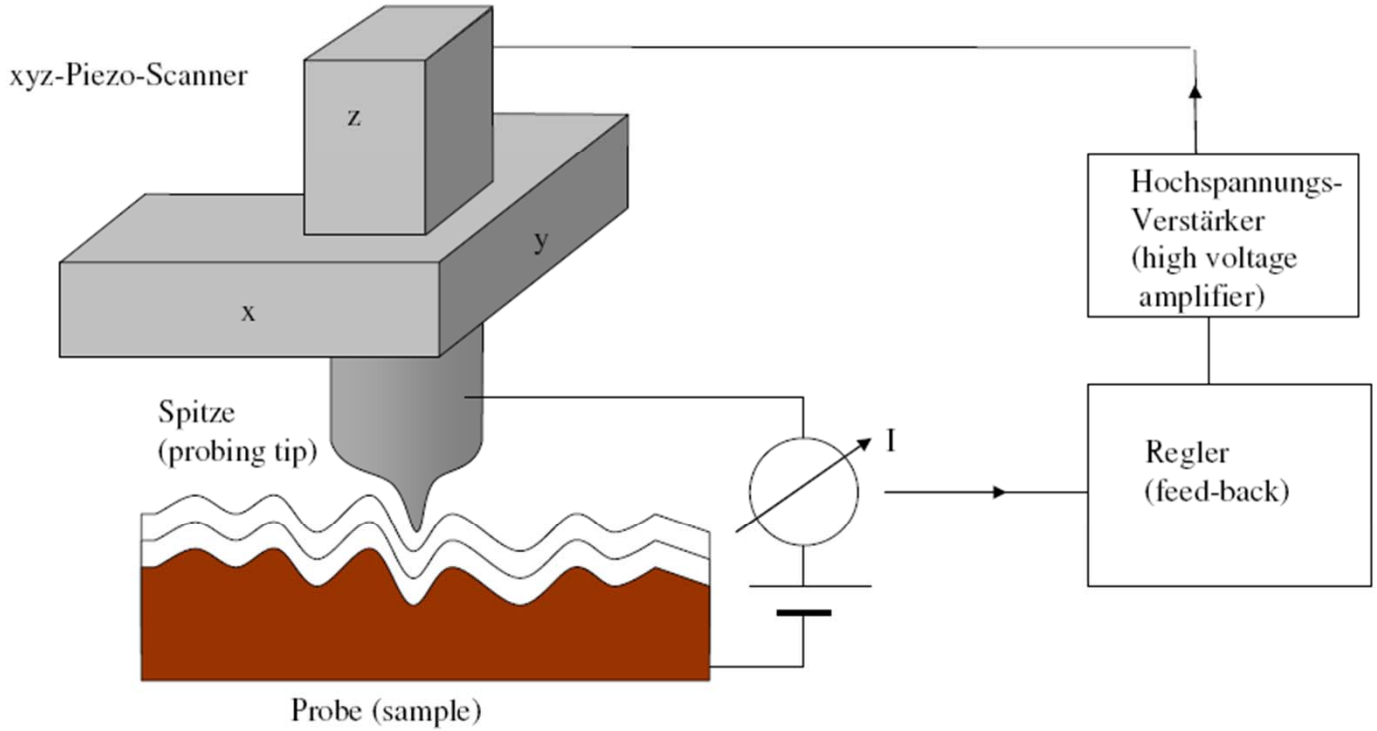
Scanning Probe Microscope (SPM)

since about 1981



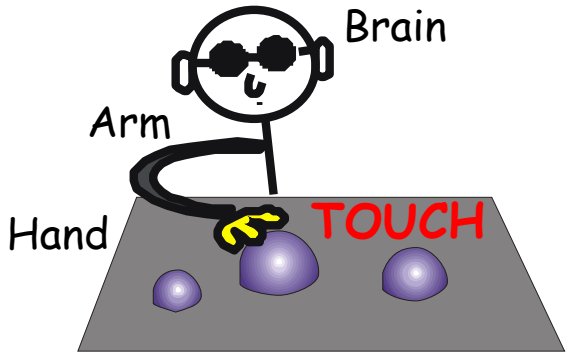
Local probe piezo-scan
resolution 0.1 nm
3D map of surface

Rastertunnelmikroskop (STM)

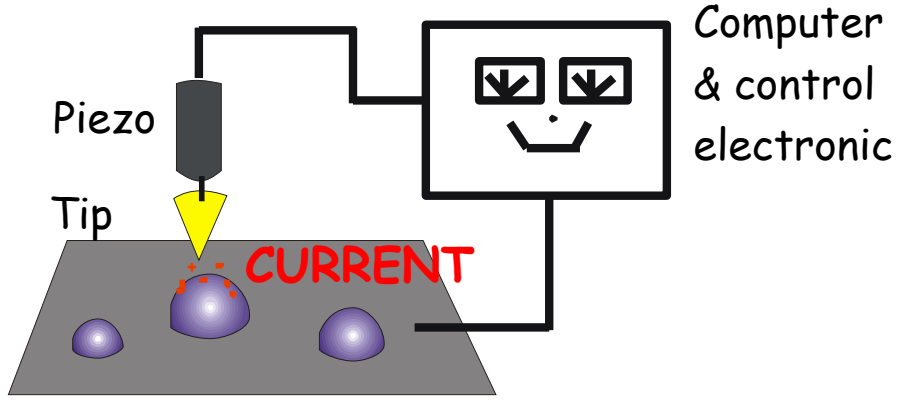


Ein Regler hält den Tunnelstrom (≈pA-nA) zwischen Spitze und Probe konstant. Es werden Kontouren konstanten Tunnelstroms abgerastert.

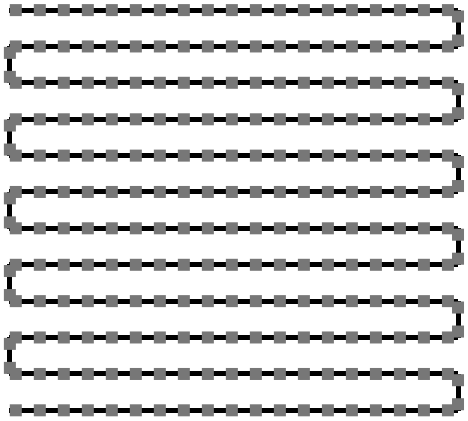
Scanning Tunneling Microscopy

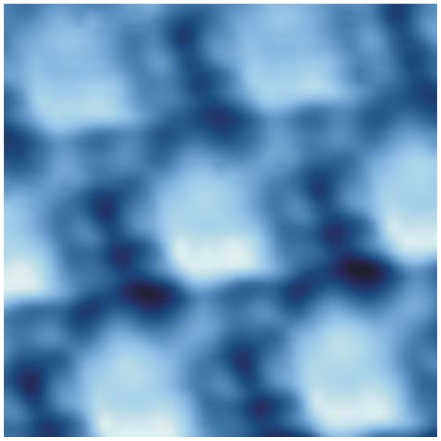


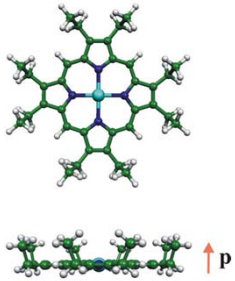
~1 mm



~ 0.1 nm = 1mm/10 000 000

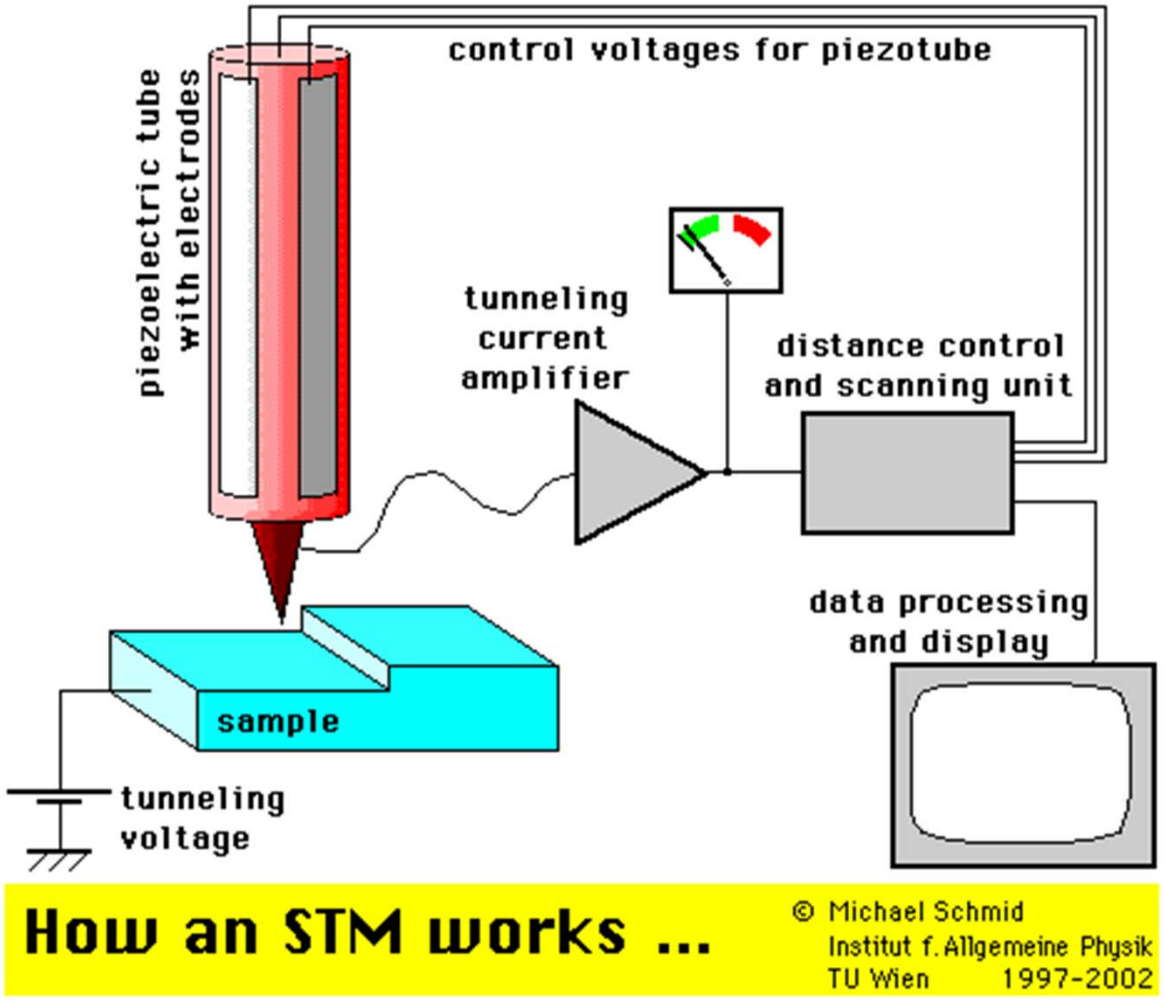




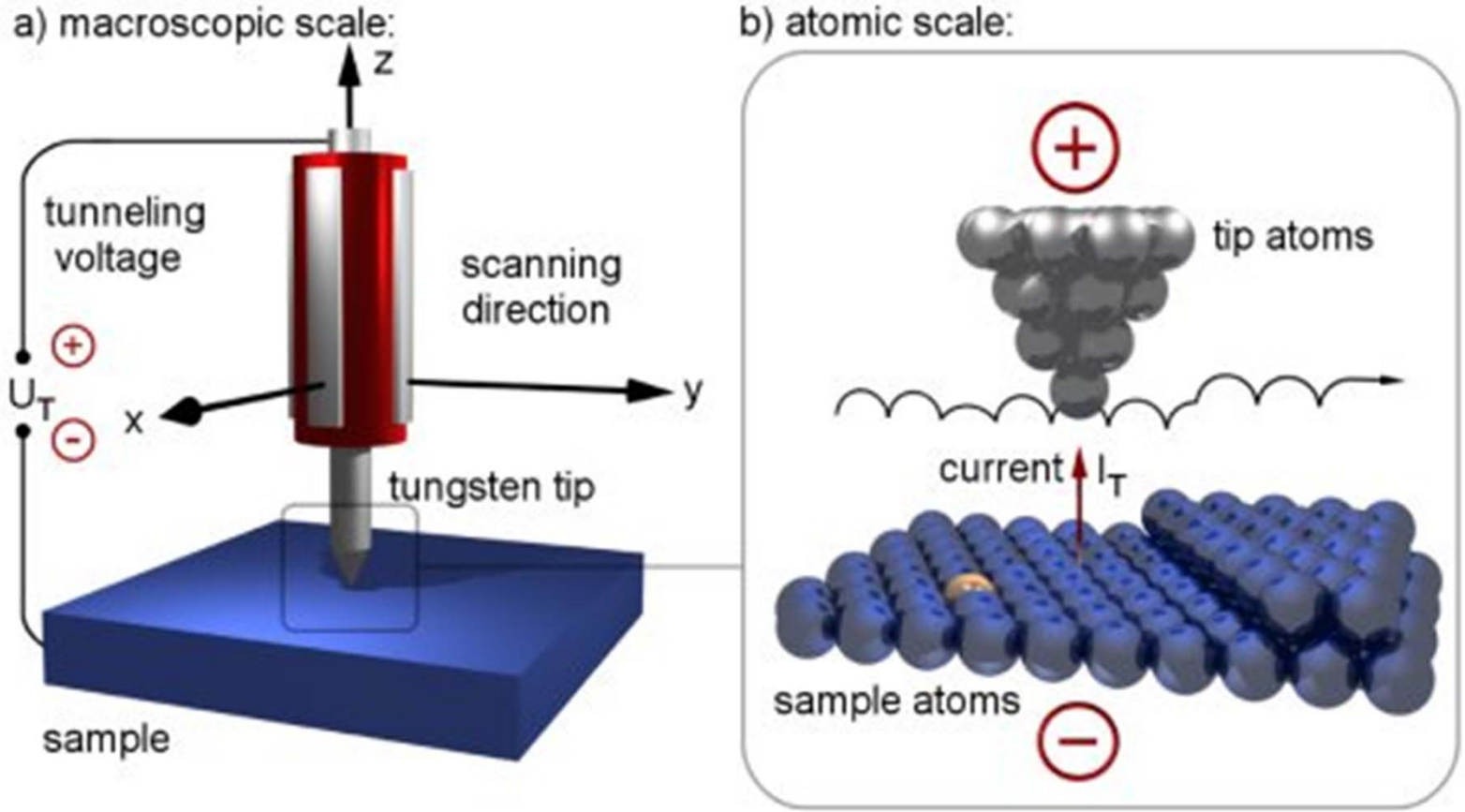


CuOEP on Cu(111) (averaged image)
3.0 nm × 3.0 nm, U = -0.55 V, I = 24 pA
L.Ramoino, S.Schintke et al., to be published

Image acquisition **(constant current images)**

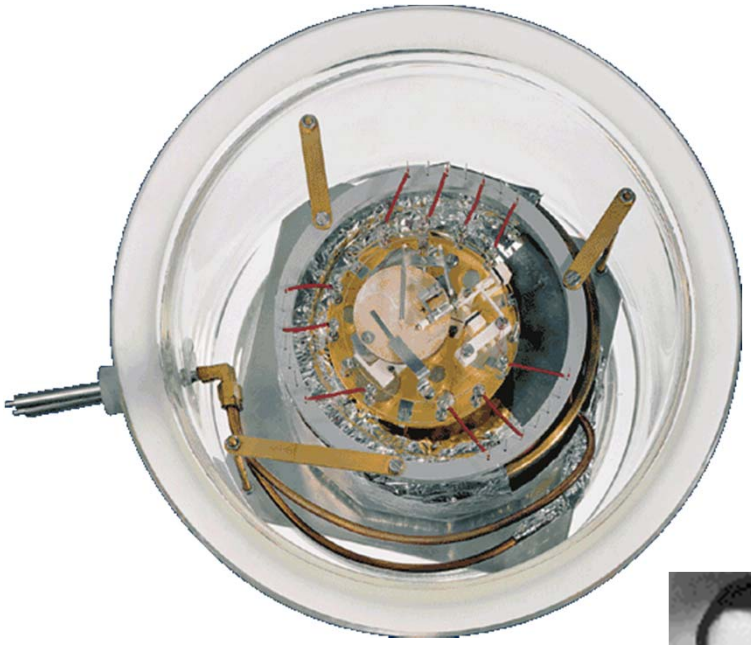


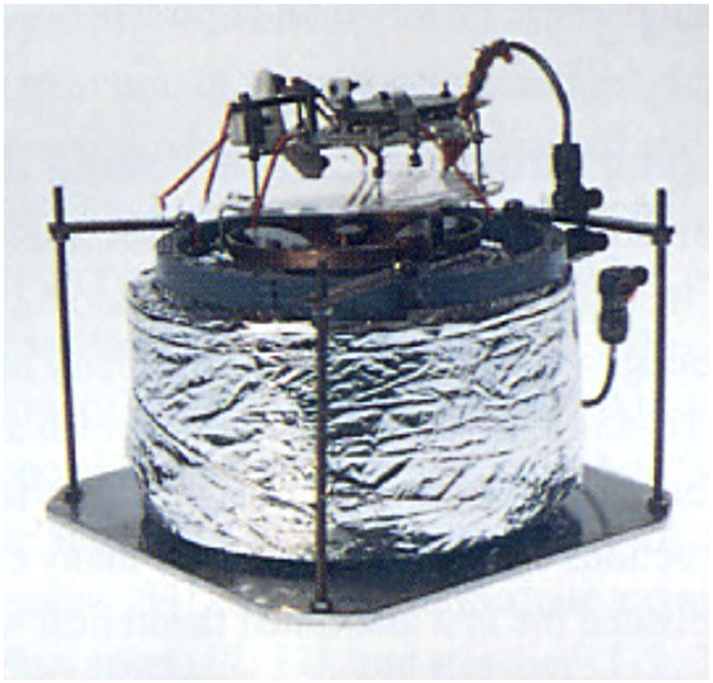
Piezo unit and tip displacement

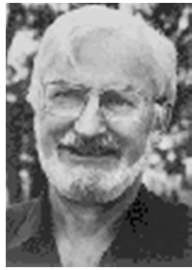


The first Scanning Tunneling Microscope

1981 development at
IBM Rüschlikon, Switzerland

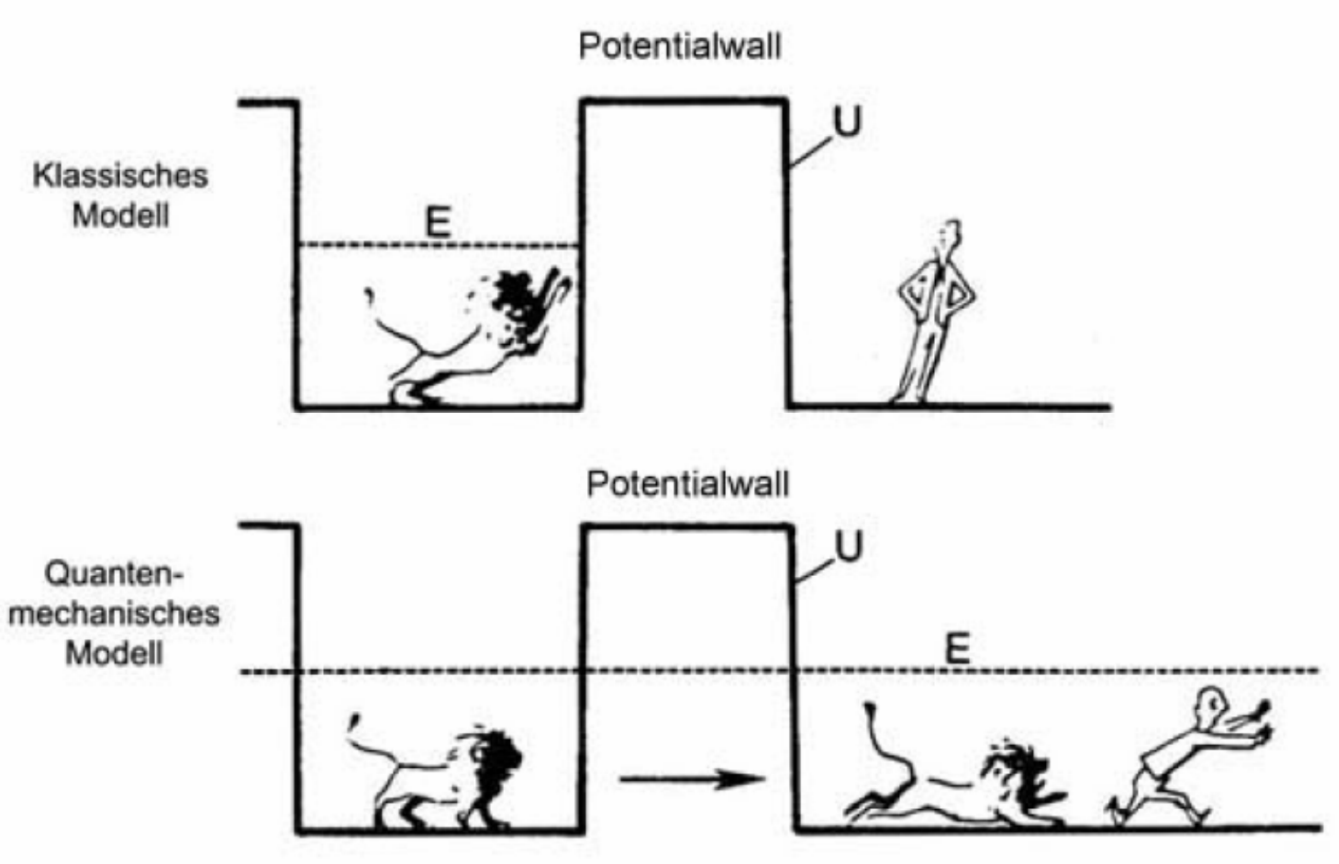






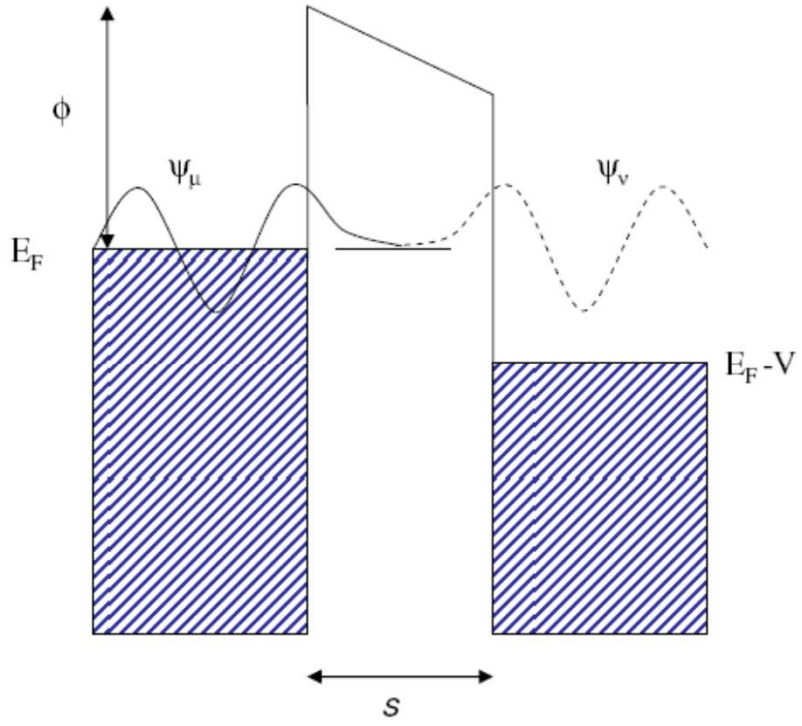
G. Binnig and H. Rohrer
Nobelprize for physics 1986

Quantum Mechanic Tunneling



Tunneleffekt

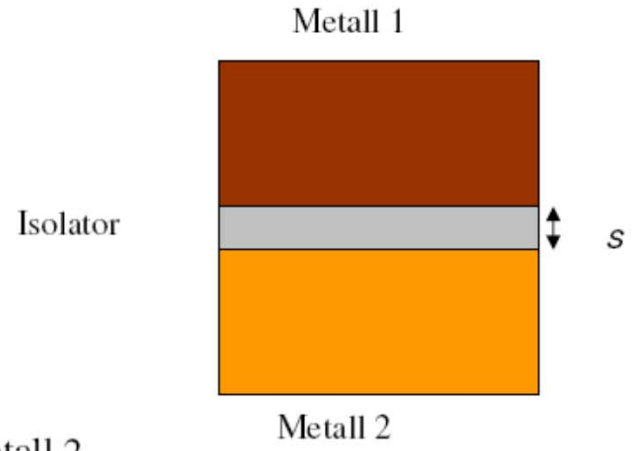
Schon zu Beginn der Quantenmechanik wurde der Tunneleffekt vorausgesagt. Der Überlapp der Wellenfunktionen führt zu einer Transmission von Elektronen durch ein klassisch verbotenenes Gebiet. Zwischen zwei Metallen, die durch Vakuum oder ein Oxid getrennt sind, fliesst ein Tunnelstrom.



Tunneleffekt

$$I = f(U)\exp\left(-A\sqrt{\phi}\, s\right)$$

J. Frenkel, *Phys. Rev.* **B 36**, 1604 (1930)



I: Tunnelstrom
U: Extern angelegte Spannung
s: Distanz zwischen Probe und Spitze
ϕ: Barrierenhöhe

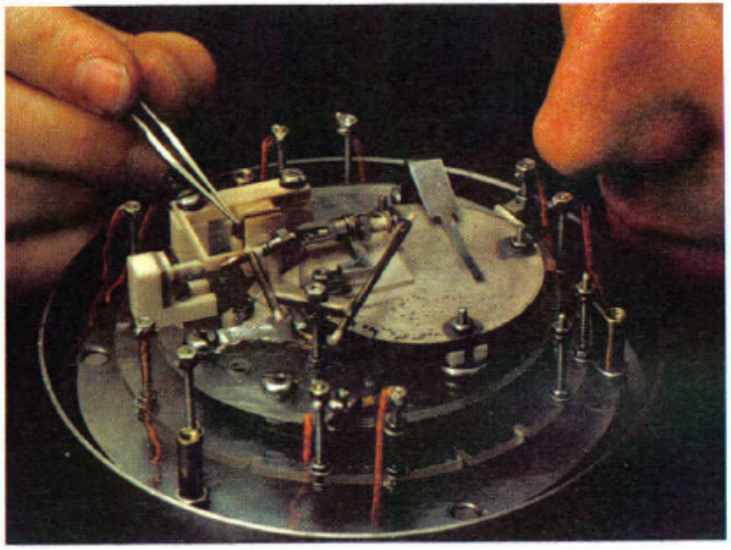
$\phi \approx \frac{\phi_1 + \phi_2}{2}$ ϕ_1, ϕ_2 Austrittsarbeiten von Metall 1 und Metall 2

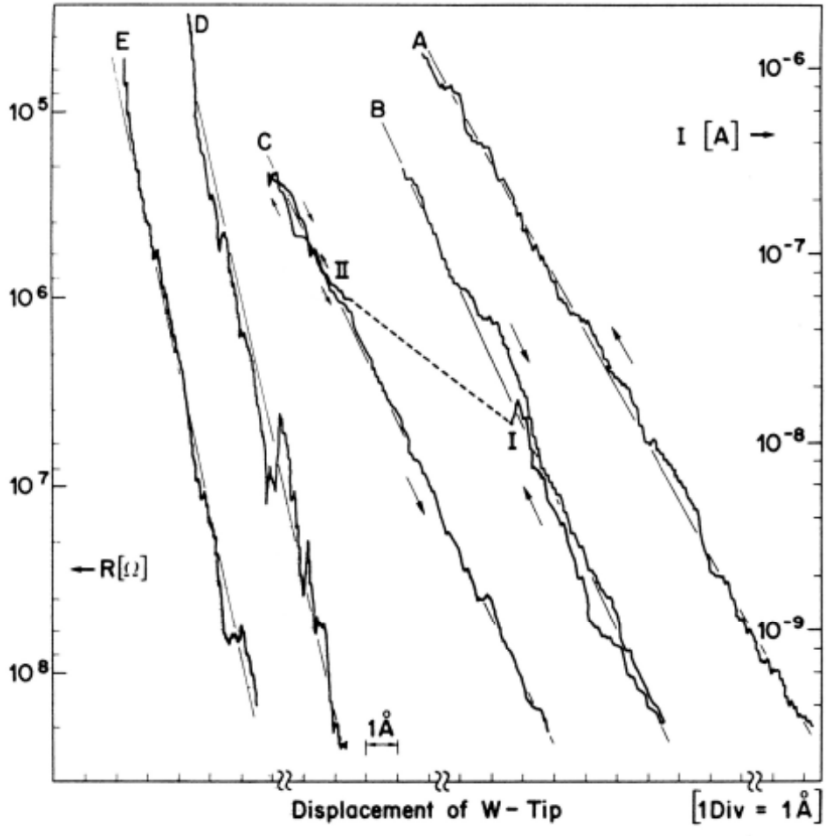
$A = 2\sqrt{\frac{2m}{\hbar^2}}$ = 1.025 $Å^{-1}eV^{-1/2}$.

f (U) : Funktion der elektronischen Struktur von Probe und Spitze
Für freie Elektronen f (U) ~ U

Der Tunnelstrom hängt exponentiell vom Abstand s ab. Für typische Austrittsarbeiten von ϕ=4.5eV ändert sich der Strom etwa um eine Grössenordung, wenn die Distanz um 1Å verändert wird. Historisch wurde zuerst das Oxidtunneln realisiert. Erst mit dem STM konnte Vakuumtunneln beobachtet werden.

Tunnelstrom



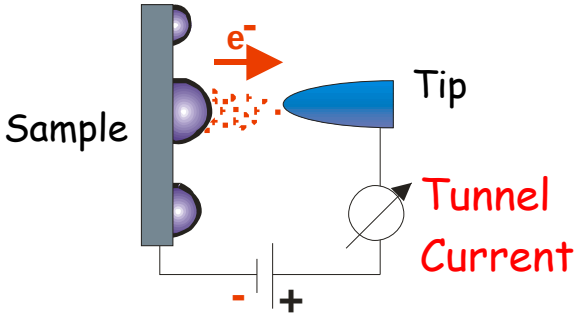


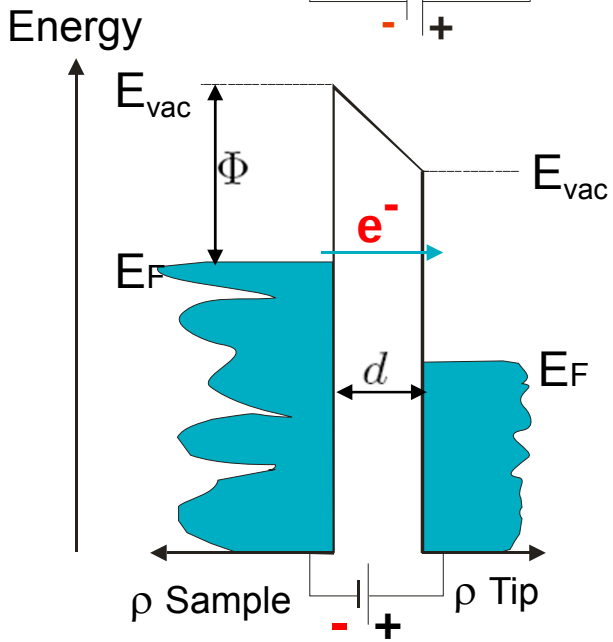
Exponentieller Abfall des Tunnelstromes mit dem Abstand

STM

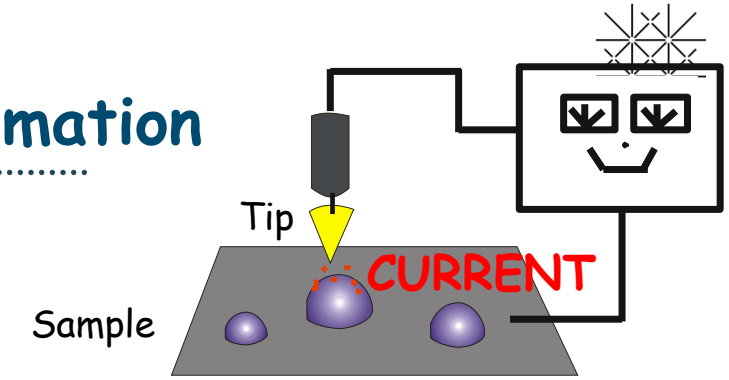
Nanosurf AG, Liestal

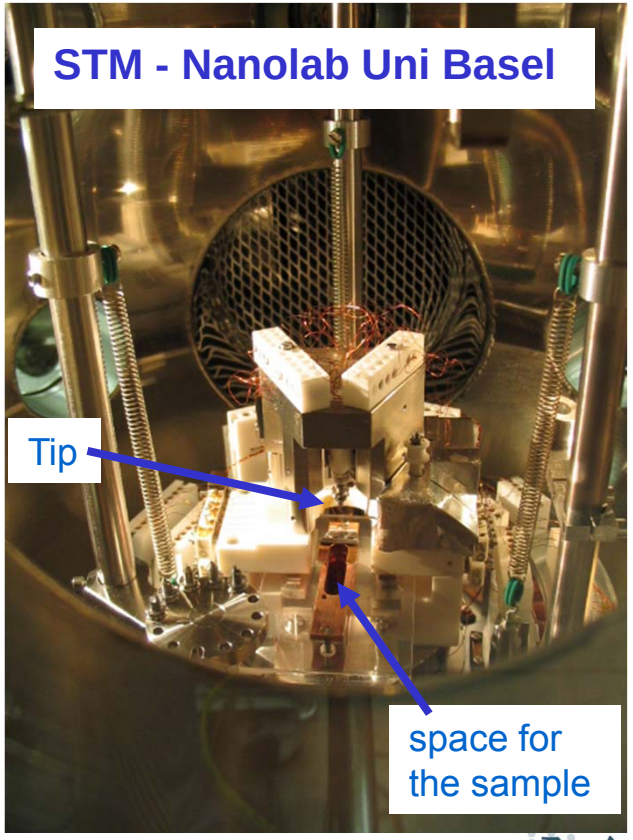
Tunnel Current – simple approximation



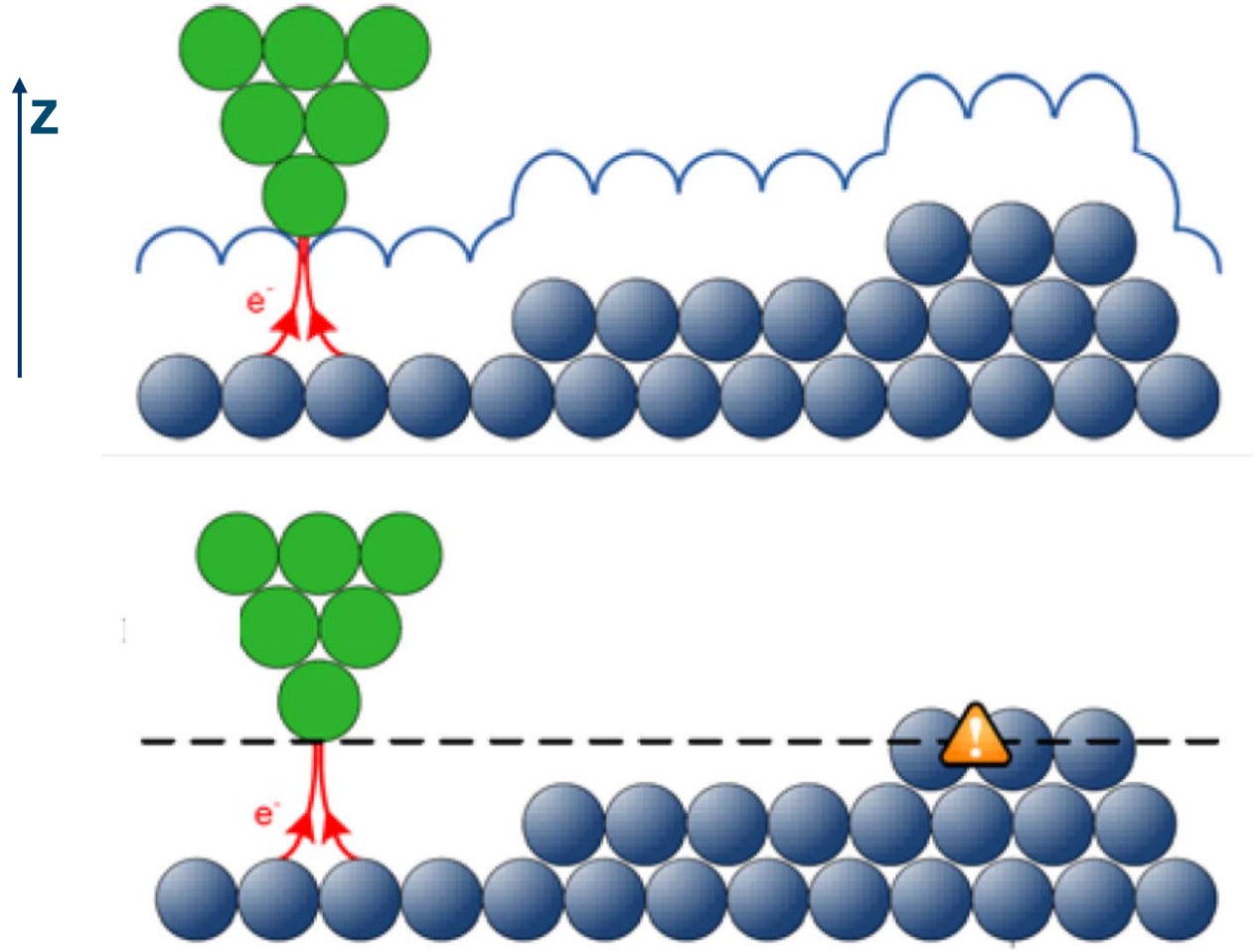


$$I_t \approx c_1 \cdot U_{bias} \cdot e^{-c_2\sqrt{\Phi}\cdot d}$$





Measurement modes: constant current vs constant height

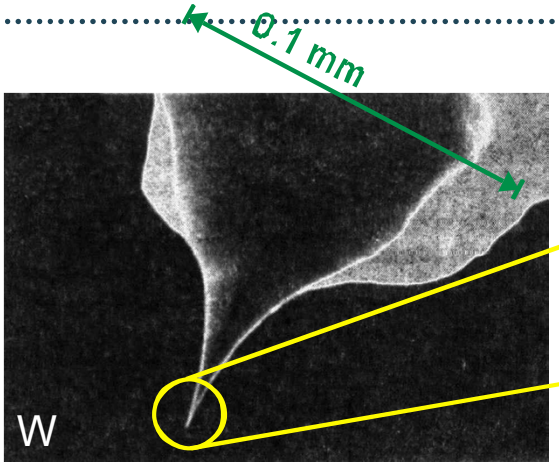


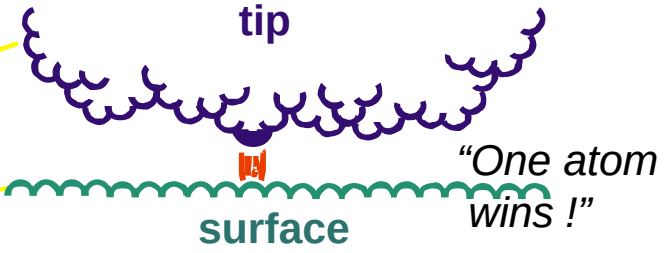
at each position (x,y)
record signal:
tip displacement in z direction

at each position (x,y)
record signal:
tunnel current I_t

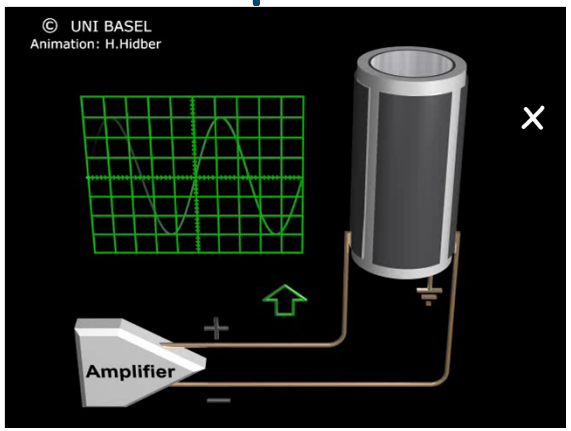
The « finger » and the « arm »

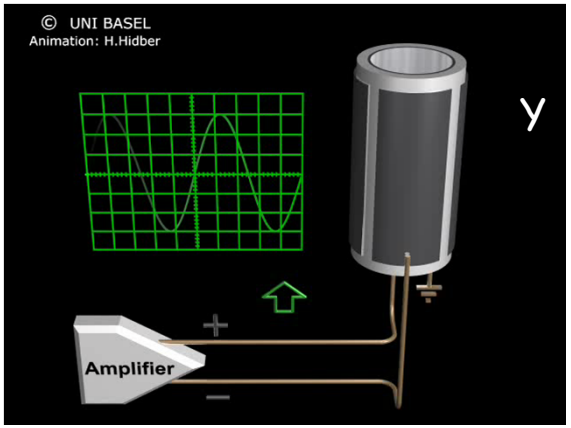
"Finger" = tip

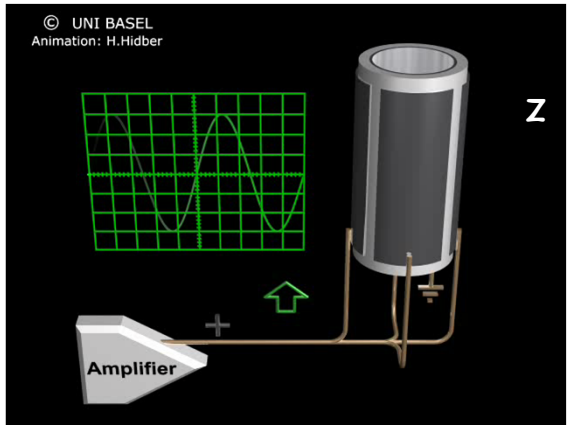




"Arm" = piezoelectric actuator

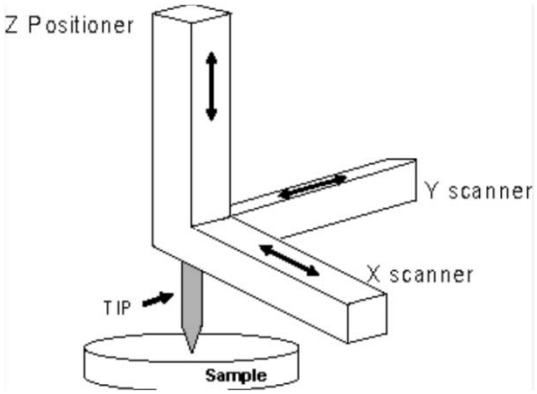




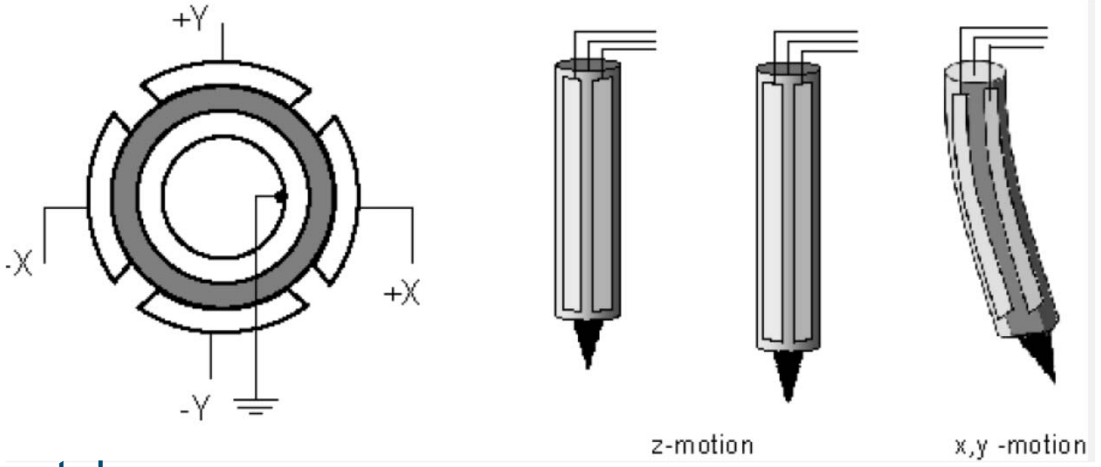


Animations: H. Hidber, University of Basel

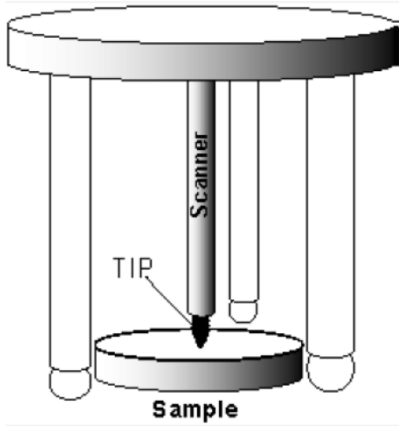
Piezo scan unit



tripod scanner

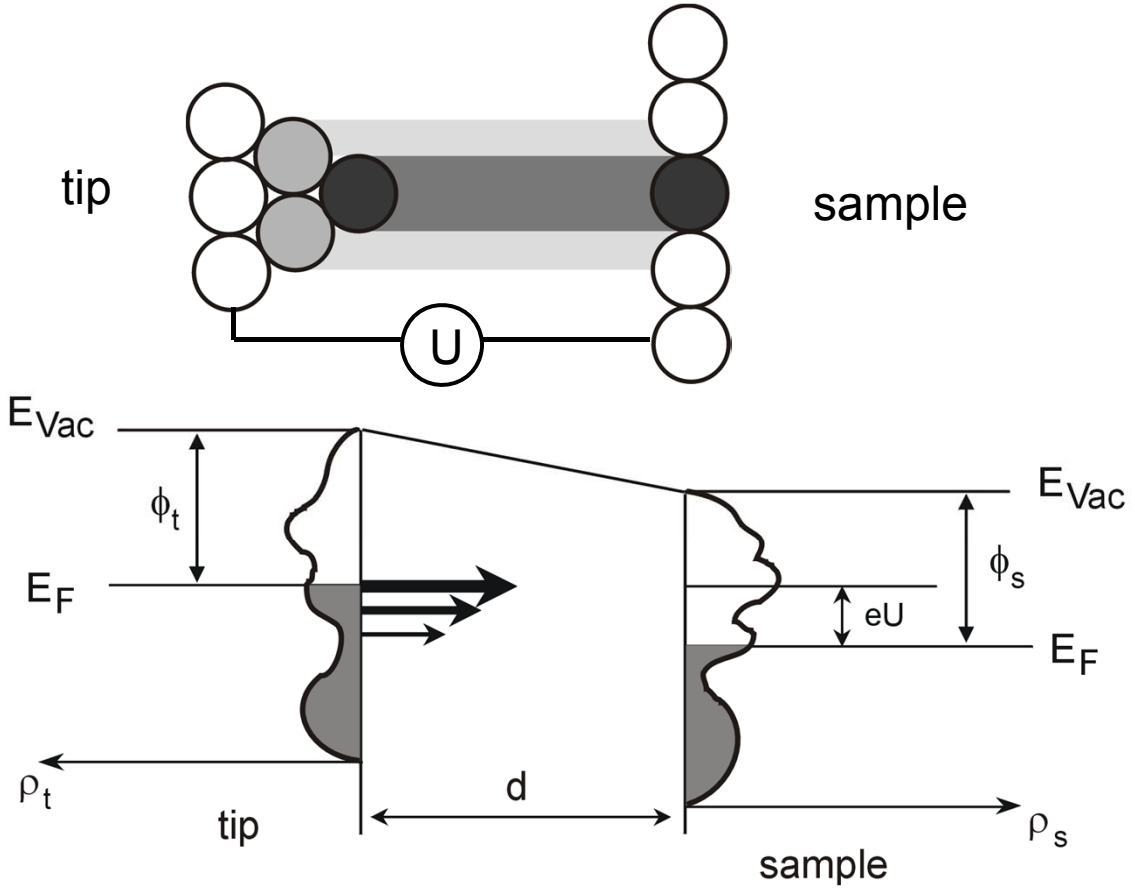


tube scanner



beetle type STM

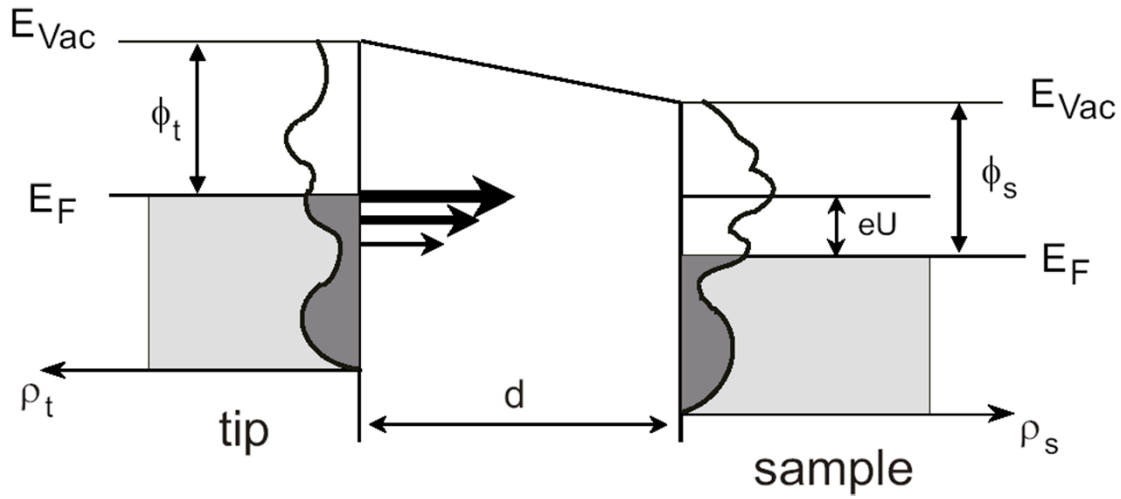
Tunnel Current in STM



Tunneling current: $I_{tunnel} \sim U\, \rho_t\, \rho_{s(x,y)}\, e^{-const\ d}$ (Tersoff and Hamann)

=> sensitivity to local electronic structure of the sample

Scanning Tunneling Current



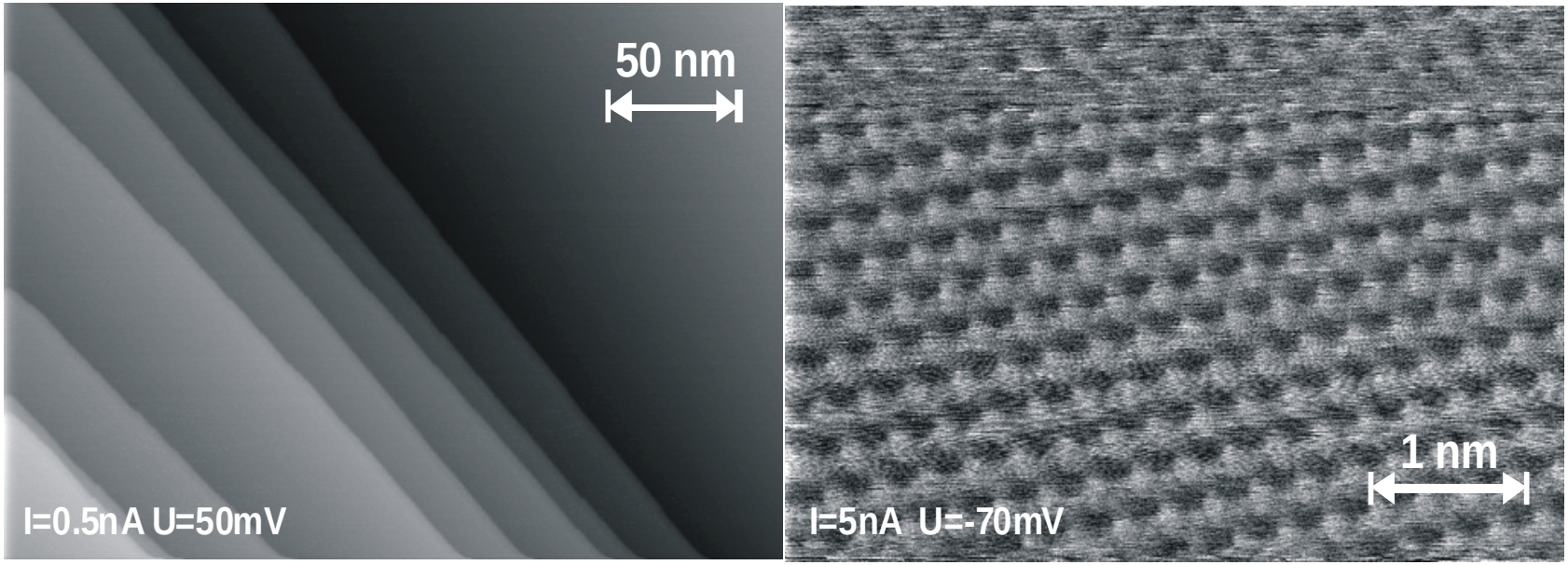
Bardeen approximation PRL 6, **57** (1961)

$$I \propto \int_0^{eU} \rho_s(E)\rho_t(\pm eU \mp E)T(E,eU)dE$$

$$T(E,eU) = \exp\left(-\frac{2z\sqrt{2m}}{\hbar}\sqrt{\frac{\Phi_s+\Phi_t}{2}+\frac{eU}{2}-E}\right)$$

STM Application for Surface Analysis and Surface Material Science & Engineering

Atomic resolution
Metals



steps of monatomic height

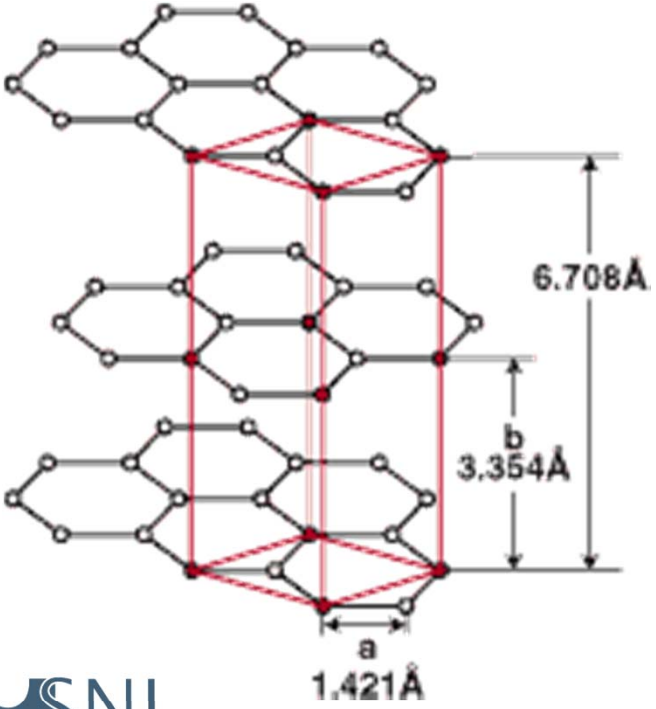
atomic resolution

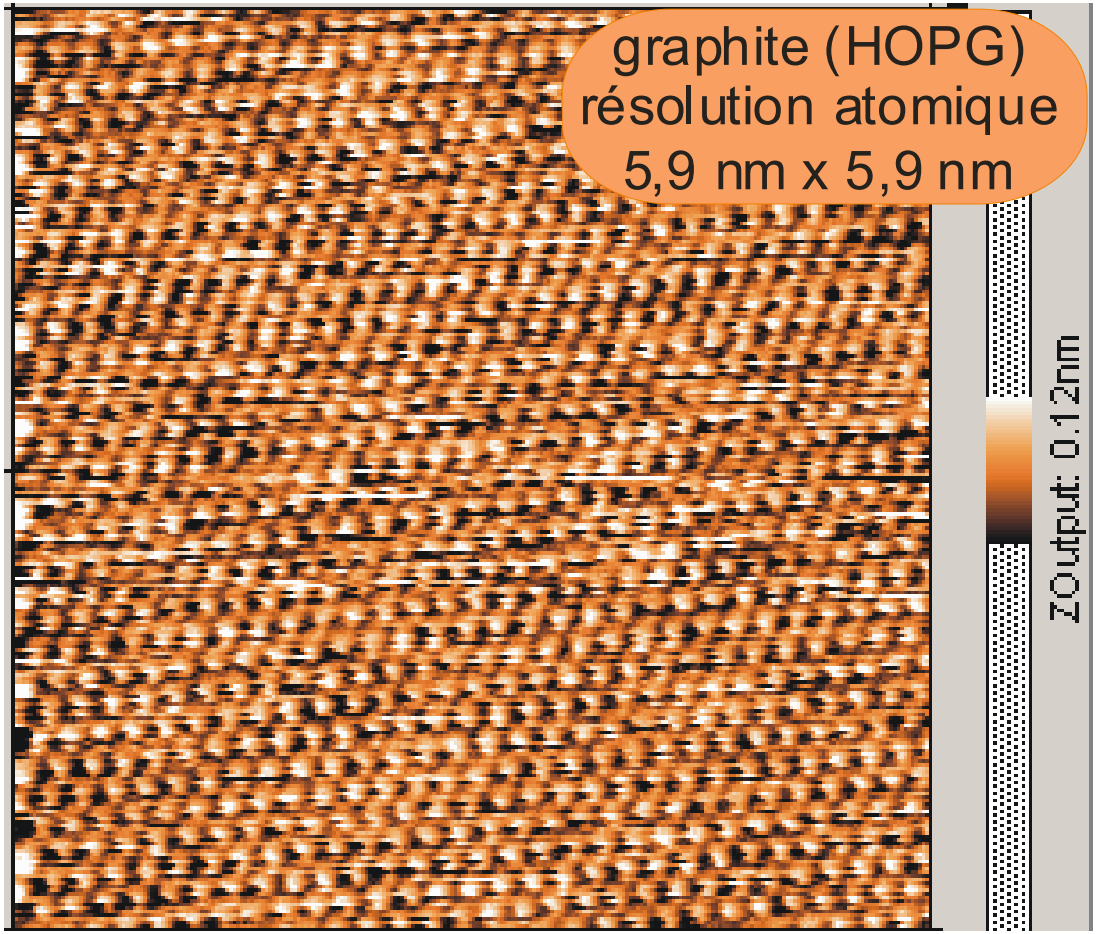
(raw data on Ag(111))

$$I \propto \int_0^{eU} \rho_s(E)\rho_t(\pm eU \mp E)T(E,eU)dE$$

$$T(E,eU) = \exp\left(-\frac{2z\sqrt{2m}}{\hbar}\sqrt{\frac{\Phi_s+\Phi_t}{2}+\frac{eU}{2}-E}\right)$$

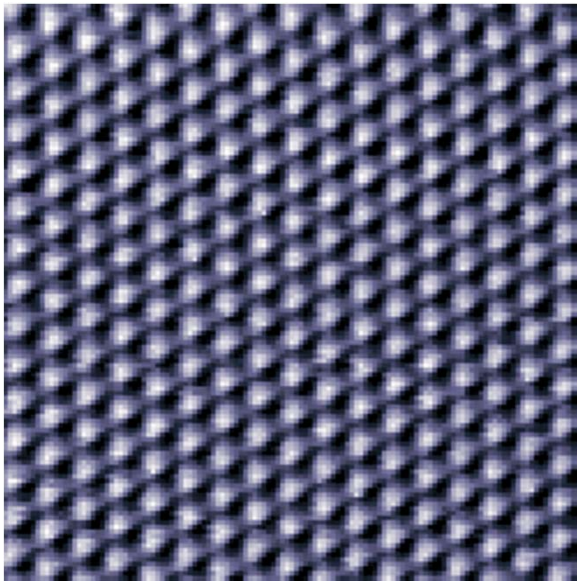
Graphite: HOPG (highly oriented pyrolythic graphite)



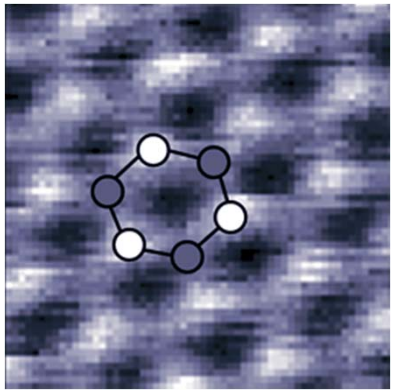


Atomic Resolution Images on HOPG

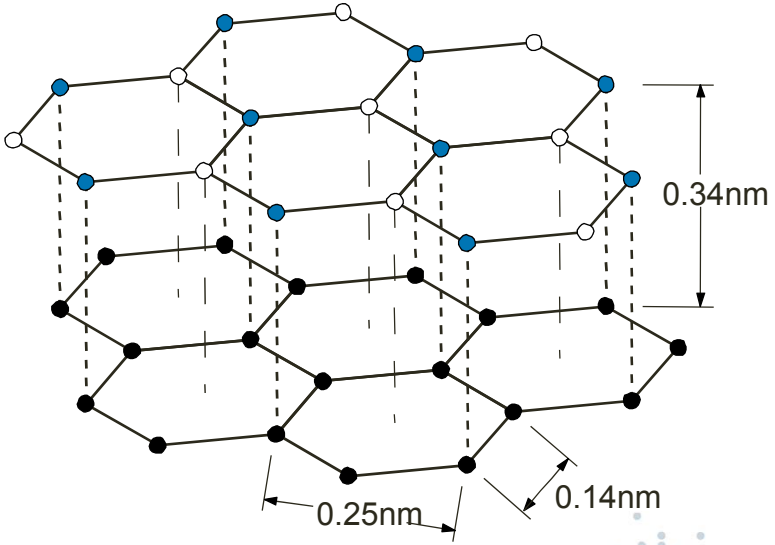
STM image raw data of HOPG



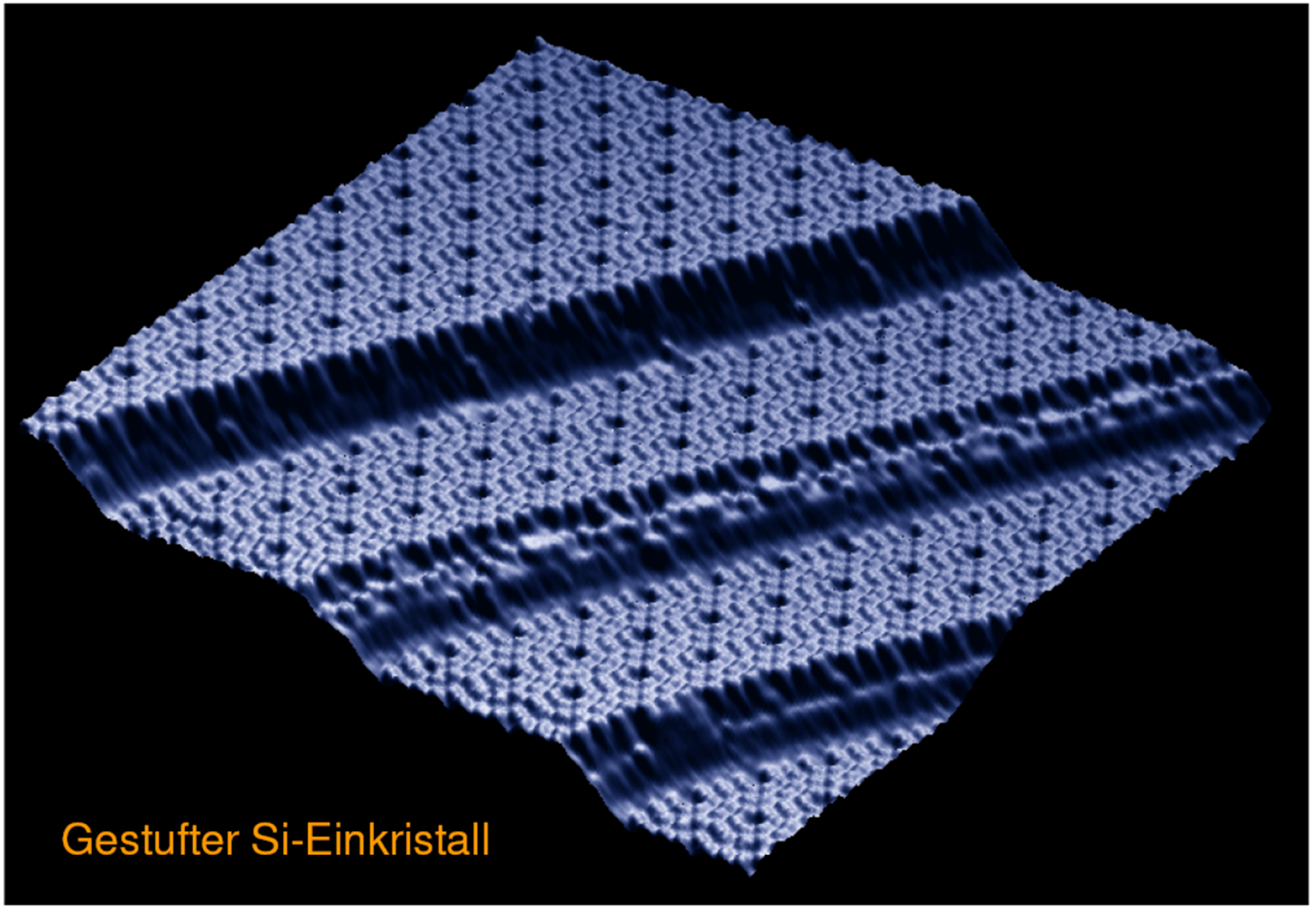
scan size: 4 nm



From the lattice model of graphite one can see that there are two different positions of the carbon atoms in the graphite crystal lattice (see e.g. R.C. Tatar)



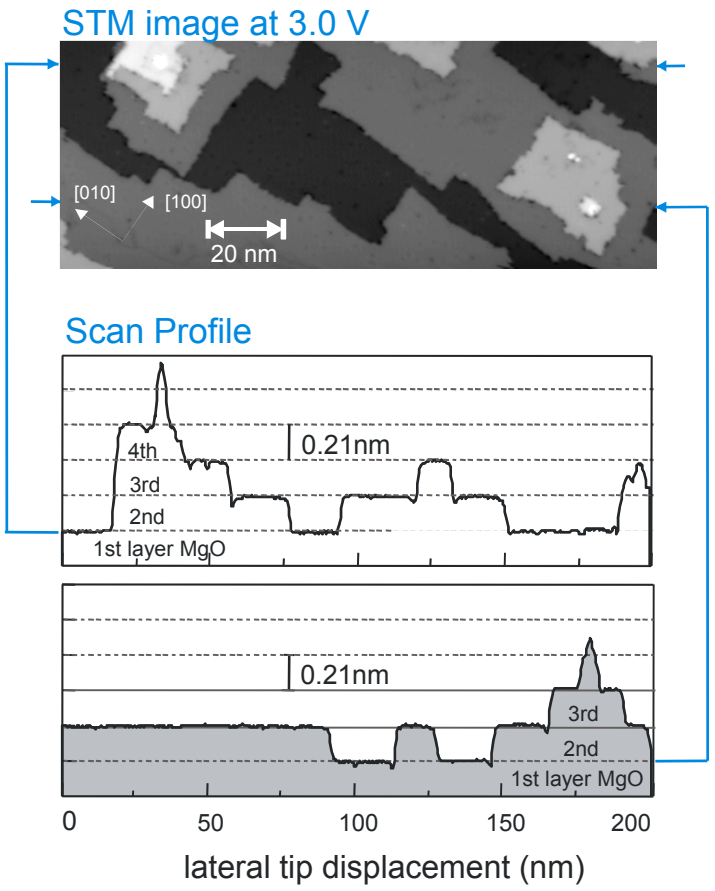
Semiconductors: Silicon

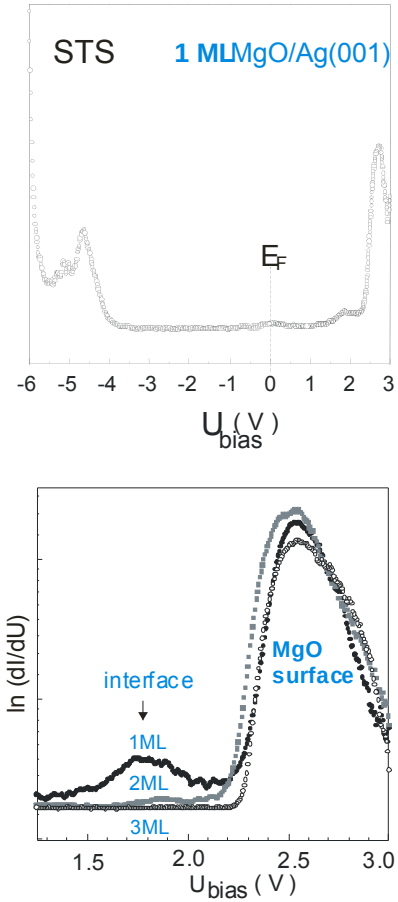


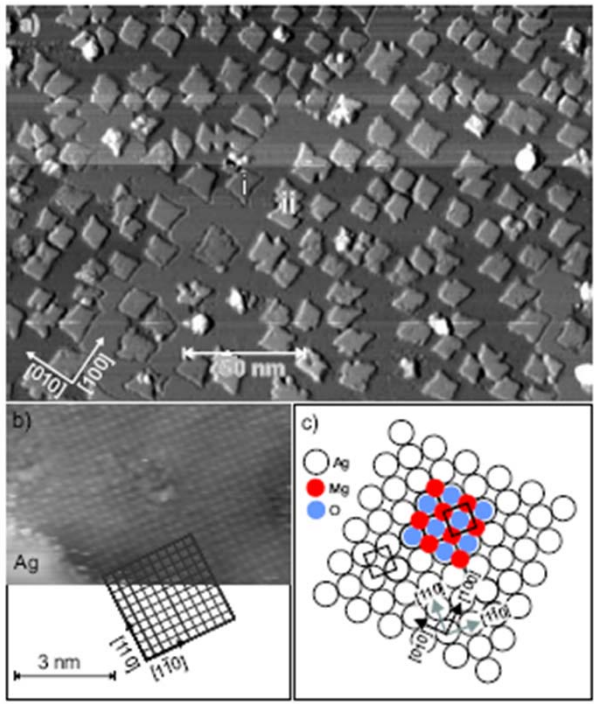
Ultrathin insulators
MgO/Ag(001): Insulator at the limit

nature physicsportal
researchhighlights

UNI BASEL







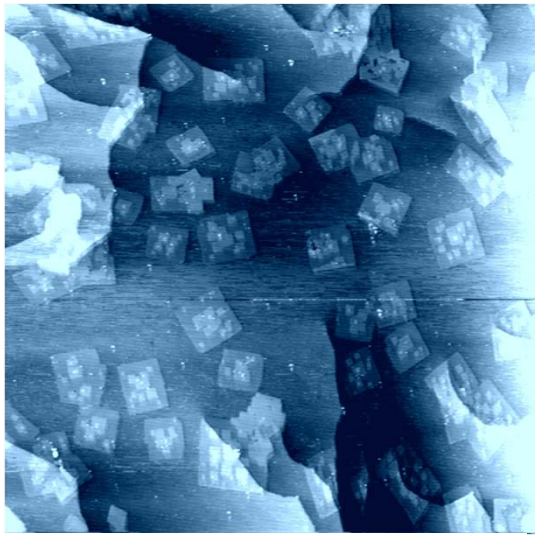
S. Schintke et al., *Insulator at the ultrathin limit: MgO on Ag(001)*, Phys. Rev. Lett. **87**, 276801 (2001)

S. Schintke and W.-D. Schneider, *Insulators at the Ultrathin Limit: Electronic Structure studied by Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy*, J. Phys.: Condens. Matter **16**, R49-R81 (2004)

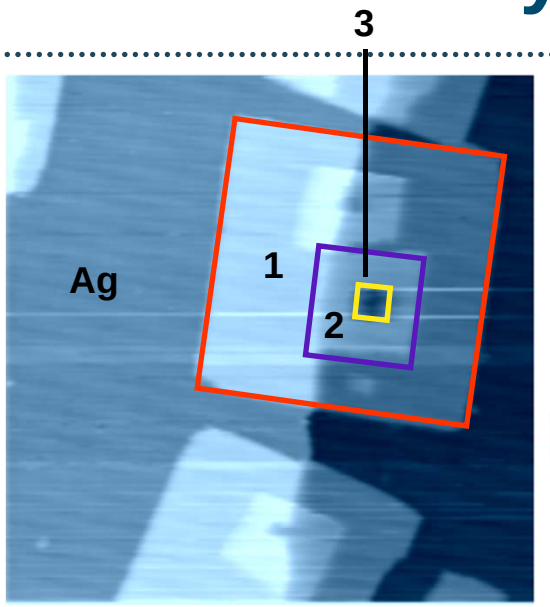
SNI SWISS NANOSCIENCE INSTITUTE

NANO

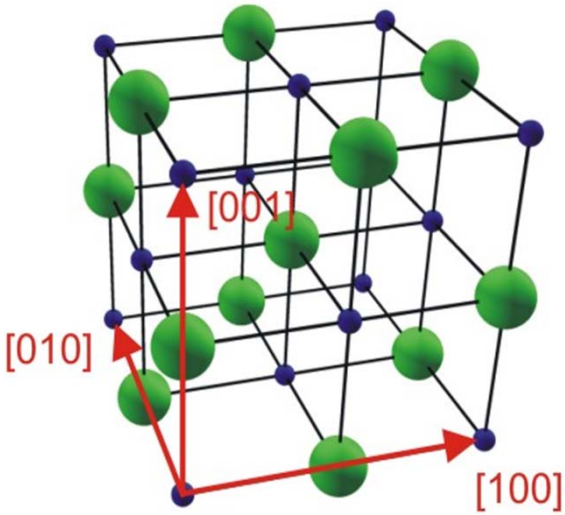
Ultrathin insulators: NaCl layers



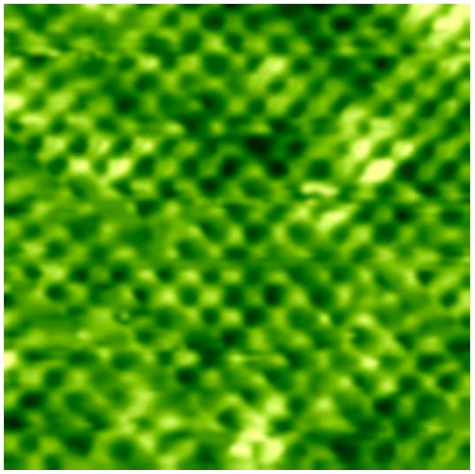
NaCl on Ag(111)
1.25 μm x 1.25 μm



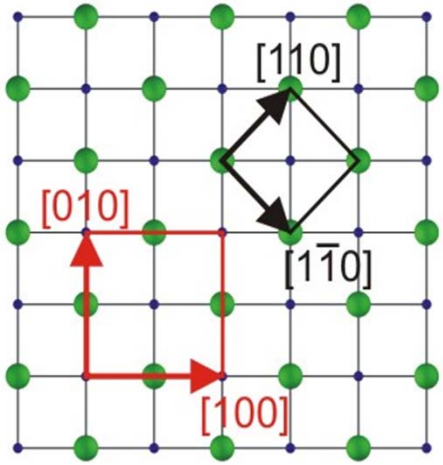
NaCl on Ag(111) 200 nm x 200 nm
U = 4.0 V, I = 15 pA



atomic resolution: <u>one</u> type of the ions is imaged

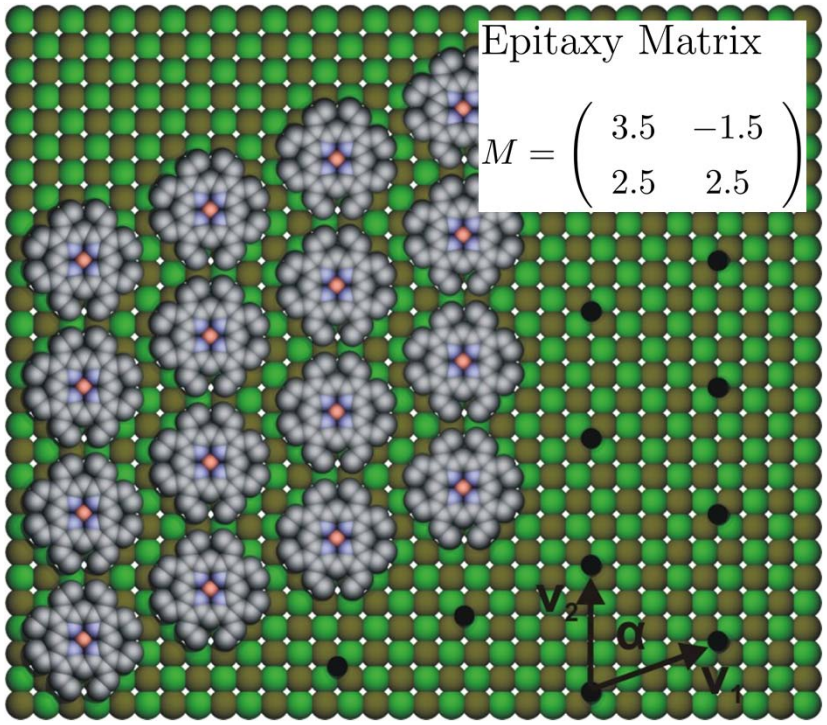


NaCl on Cu(111)
5 nm × 5 nm
U = -1.5 V, 50 pA



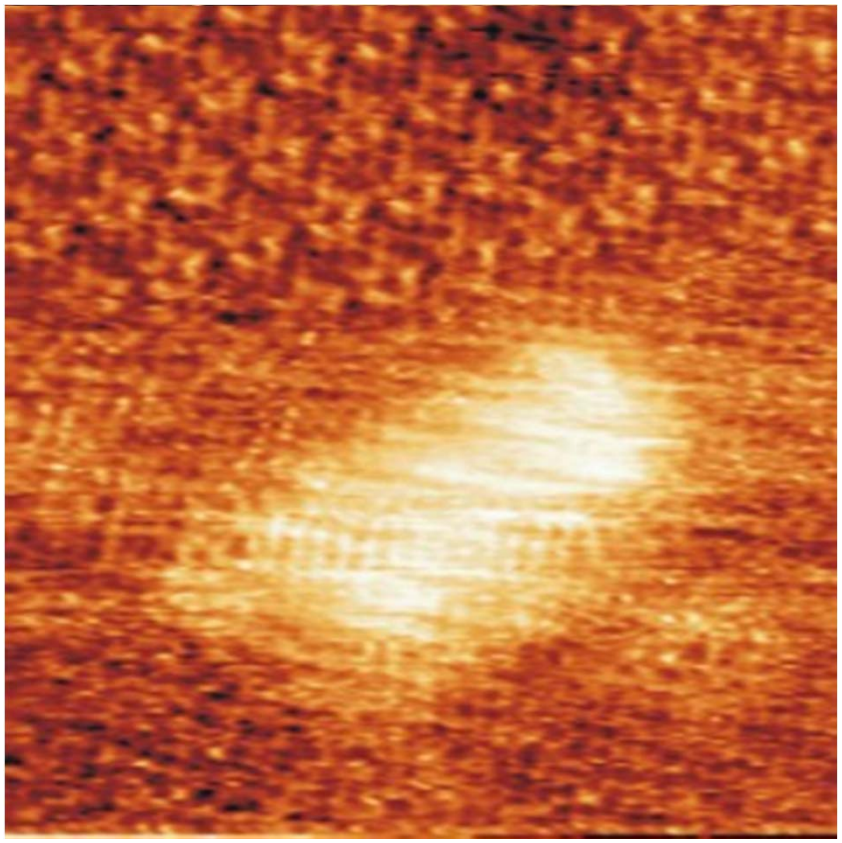
a_0 = 5.65 Å

CuOEP Self-Assembly on Salt



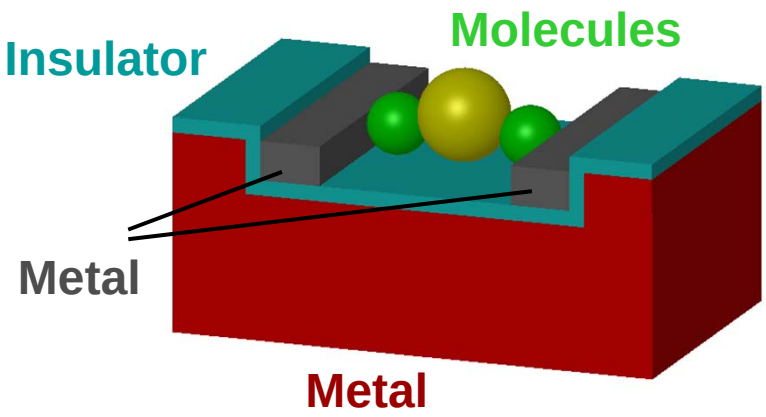
	model	experiment
v_1	14.6 Å	14.3 ± 0.3 Å
v_2	13.5 Å	13.5 ± 0.3 Å
α	68.2°	69.0 ± 1°

CuOEP on NaCl/Ag(111)

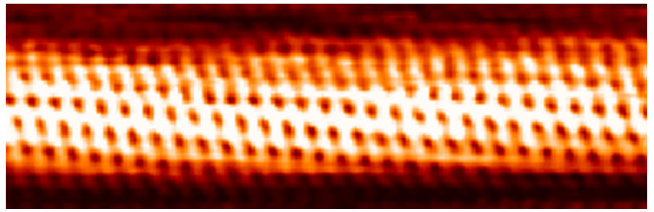


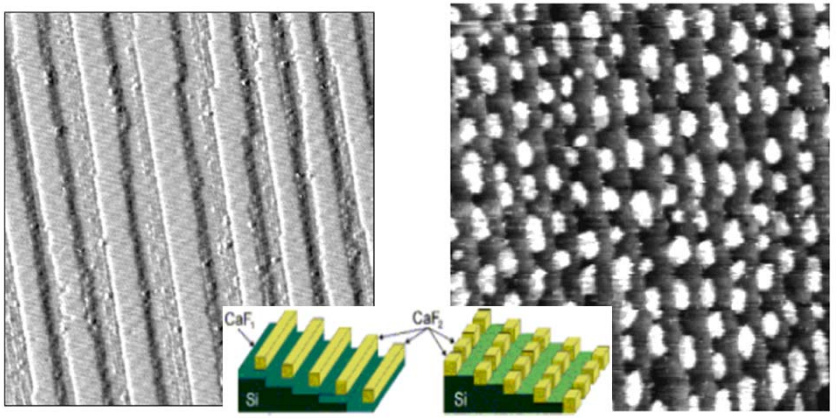
15 × 15 nm, U = -0.25 V, I = 81 pA

Towards Molecular Electronics

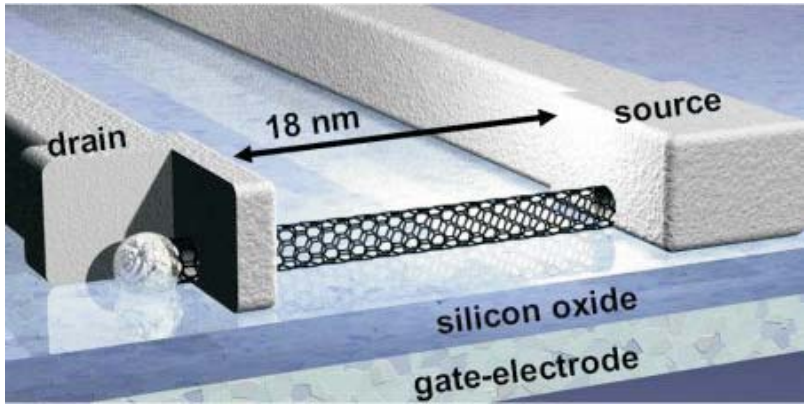


Carbon Nanotube





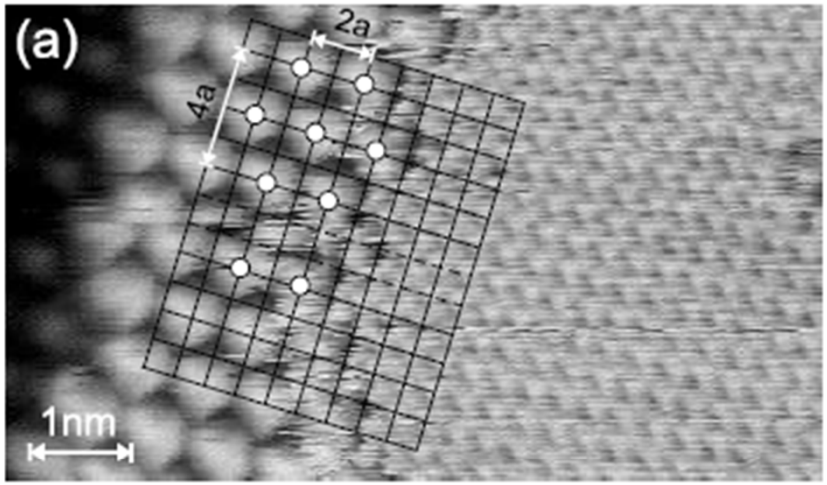
Himpsel, Jung et al. MRS Bulletin **24** (8) 1999

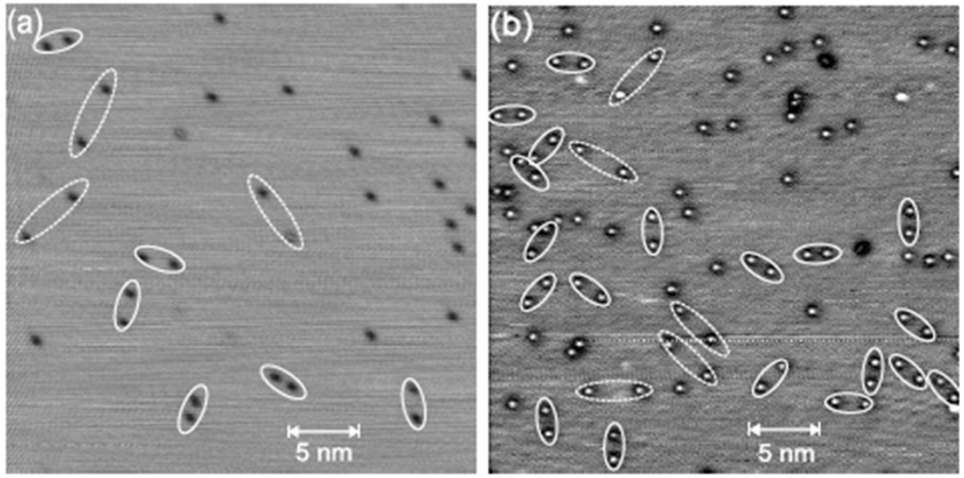


Infineon: carbon nanotube FET

Oxygen on Ag(001): molecular superstructures; far- ranged dissociation

Atoms





Atoms:
S. Schintke, S. Messerli et al., J. Chem. Phys. 114, 4206 (2001)
Molecules:
S. Messerli, S. Schintke et al., Chem. Phys. Lett. 328, 330 (2000).

Oxygen/Ag(001)

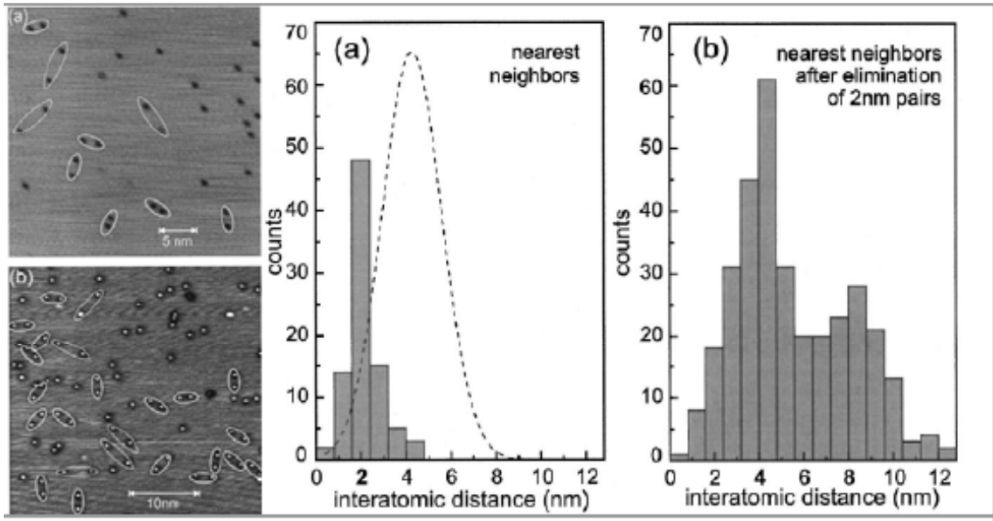


Fig. 3.1 Left: Pairing of oxygen atoms on Ag(001) at different coverages observed in STM images (50 K).
Right: Distribution of interatomic distances analysed from STM data.

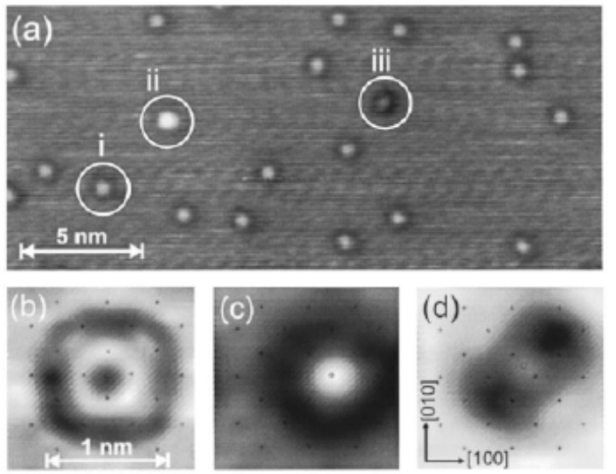
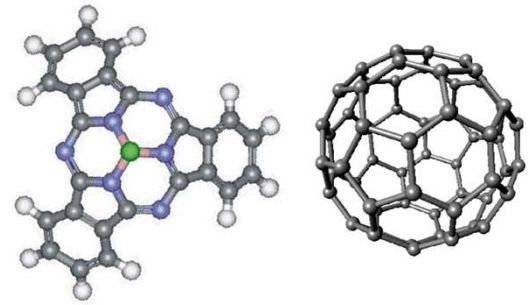


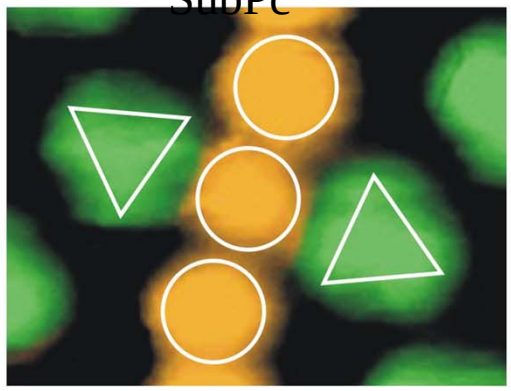
Fig. 3.2: Binding sites of oxygen atoms. Top: experimental STM data (50 K). Bottom: Calculated STM images a) hollow site, b) on-top site, c) bridge site.

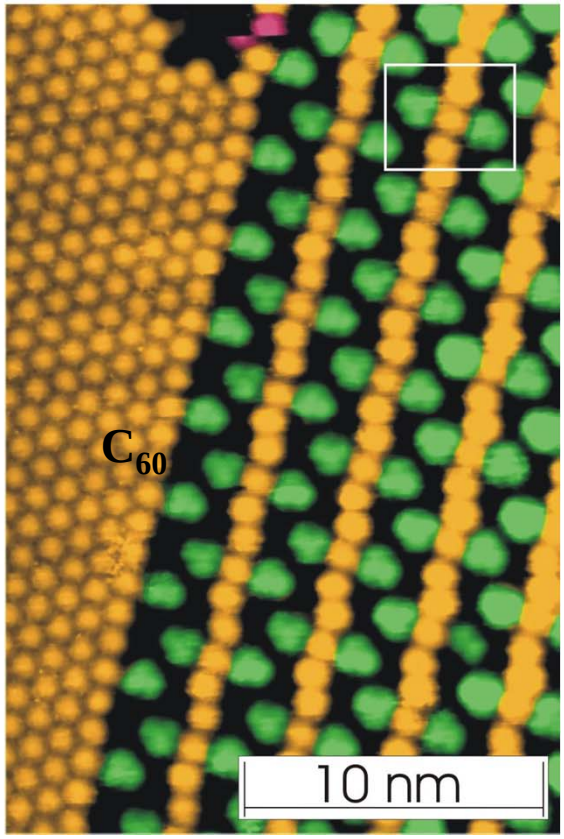
S. Schintke, S. Messerli, K. Morgenstern, J. Nieminen, and W.-D. Schneider, Journal of Chemical Physics **114**, 4206-4209 (2001)

Self-intermixed monolayer



SubPc

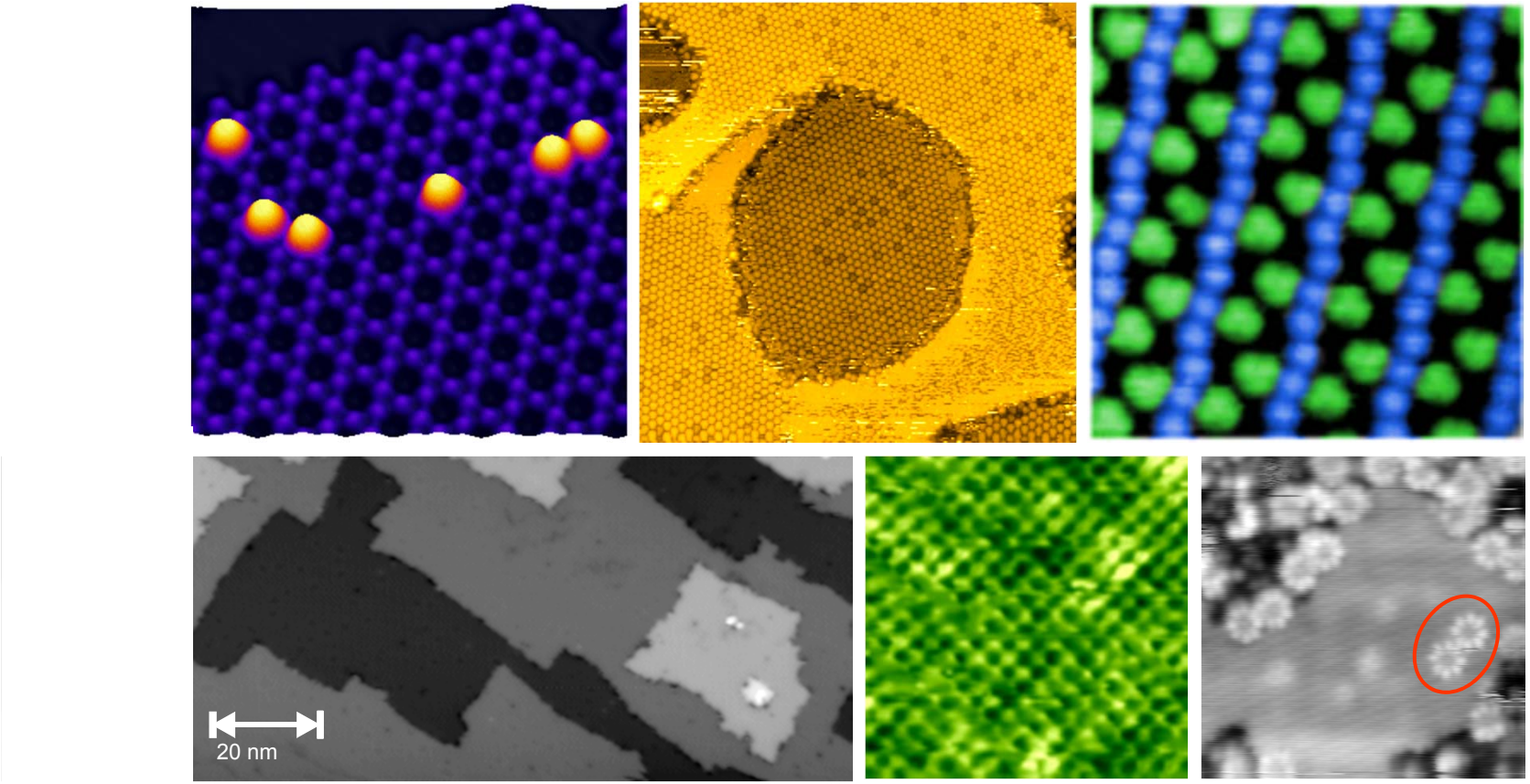




Scan range 4.3nm x 3.2nm. V_{bias}=1.3V, I_t=20pA. Scan range 17nm x 25nm. V_{bias}=1.3V, I_t=20pA.

M. de Wild *et al.*, *ChemPhysChem* **10**, 181 (2002)
M. de Wild *et al.*, *Chimia* **10,** 56 (2002)

Further STM images from research



www.nccr-nano.ch (Uni Basel)

2. STM beyond imaging

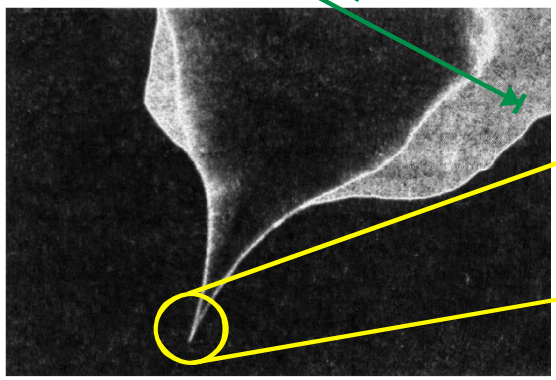
- STM a tool for nanofabrication:
  - Adsorbate manipulation

- STM a local spectroscopy tool:
  - Scanning Tunneling Spectroscopy (STS)
  - Inelastic Tunneling Spectroscopy (IETS)
  - Local Photonemission spectroscopy

« Nanotool »: STM-Tip

Materials: Tungsten (W), Iridium (Ir), Platinum-Iridium (Pt-Ir), Gold (Au),…
e.g. cut or electrochemically etched

Pt-Ir-tip

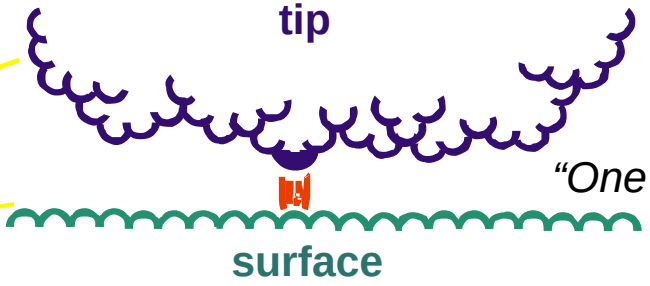


W-tip

Scanning electron micrographe of an STM tip
(Hamann, Hietschold, Rastertunnelmikroskopie)

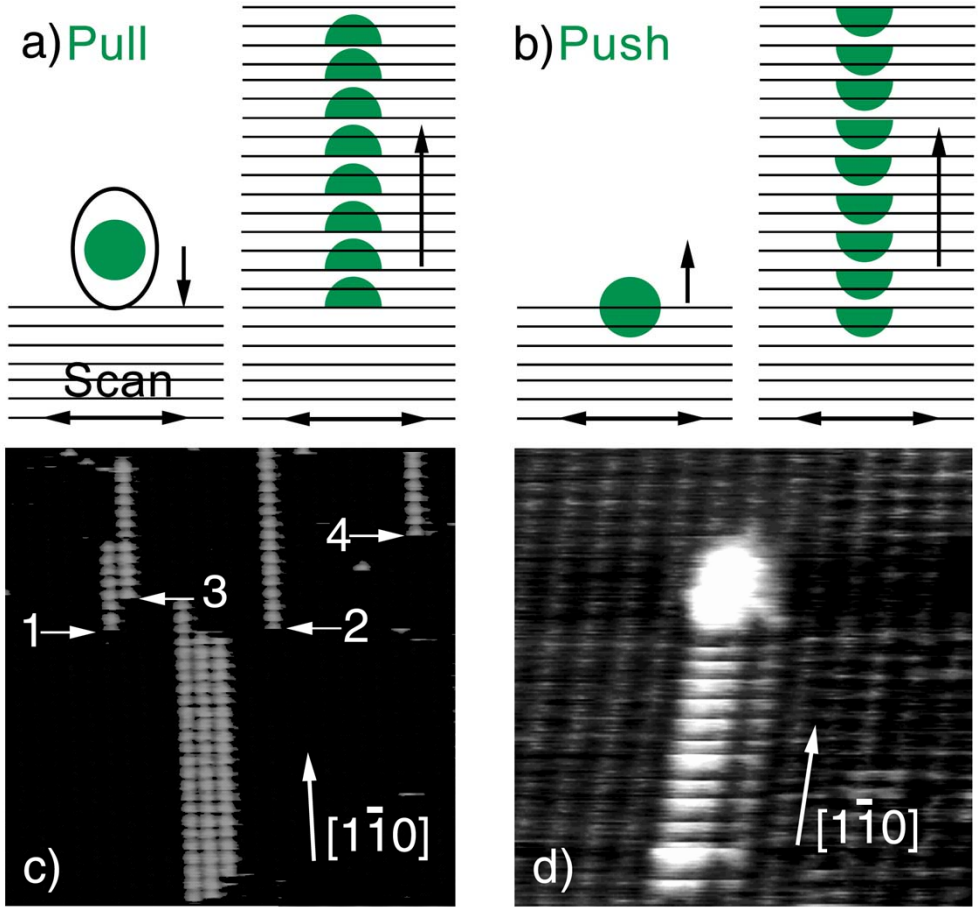
Matterhorn (“tip”)

Pingpong-ball (“atom”)



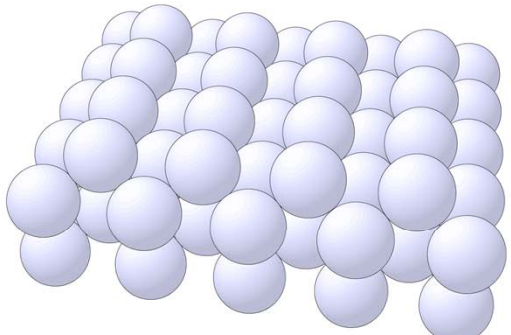
“One atom wins !”

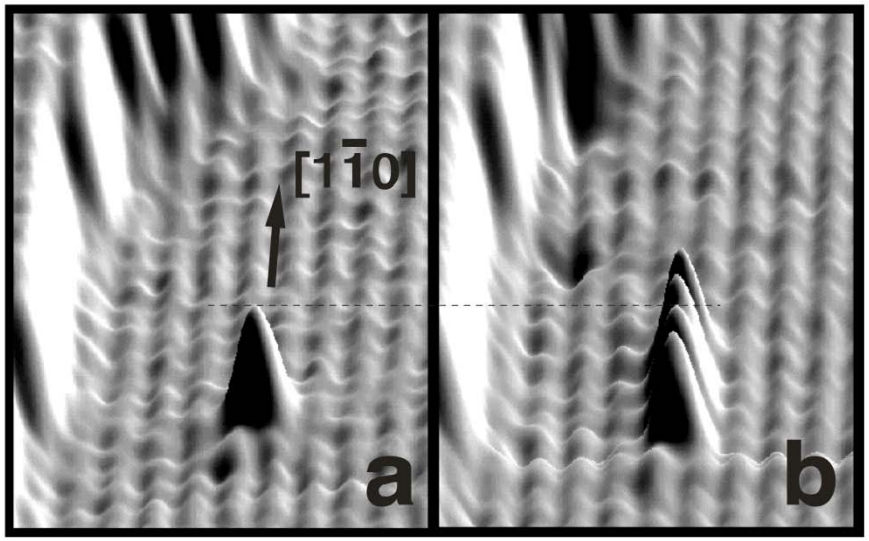
Tip-sample interaction



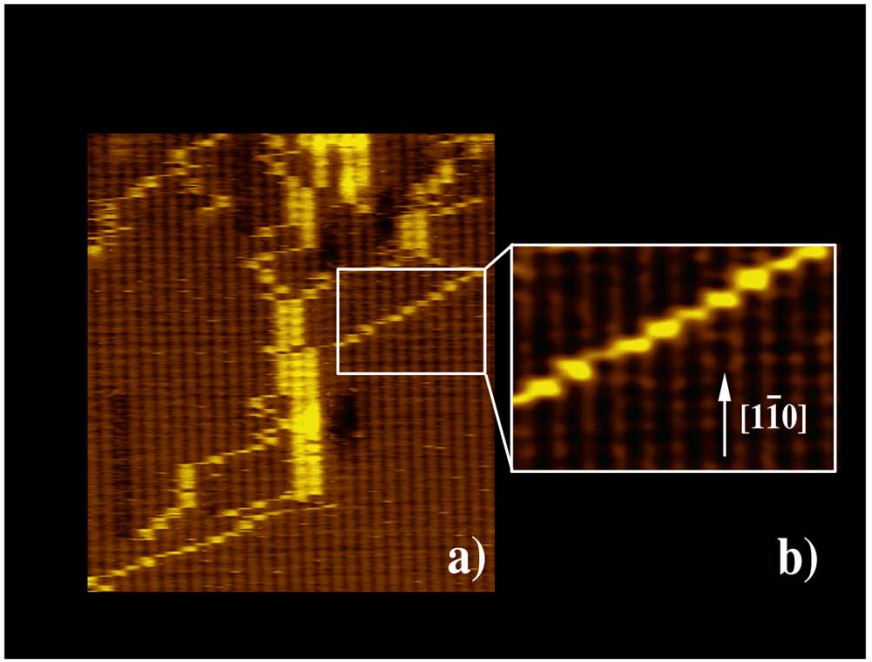
Low-temperature manipulation of Ag atoms and clusters on a Ag(110) surface,
J.T. Li, W.-D.Schneider, and R. Berndt, *Appl. Phys. A*, 66, 575 (1998).

Tip-sample interaction



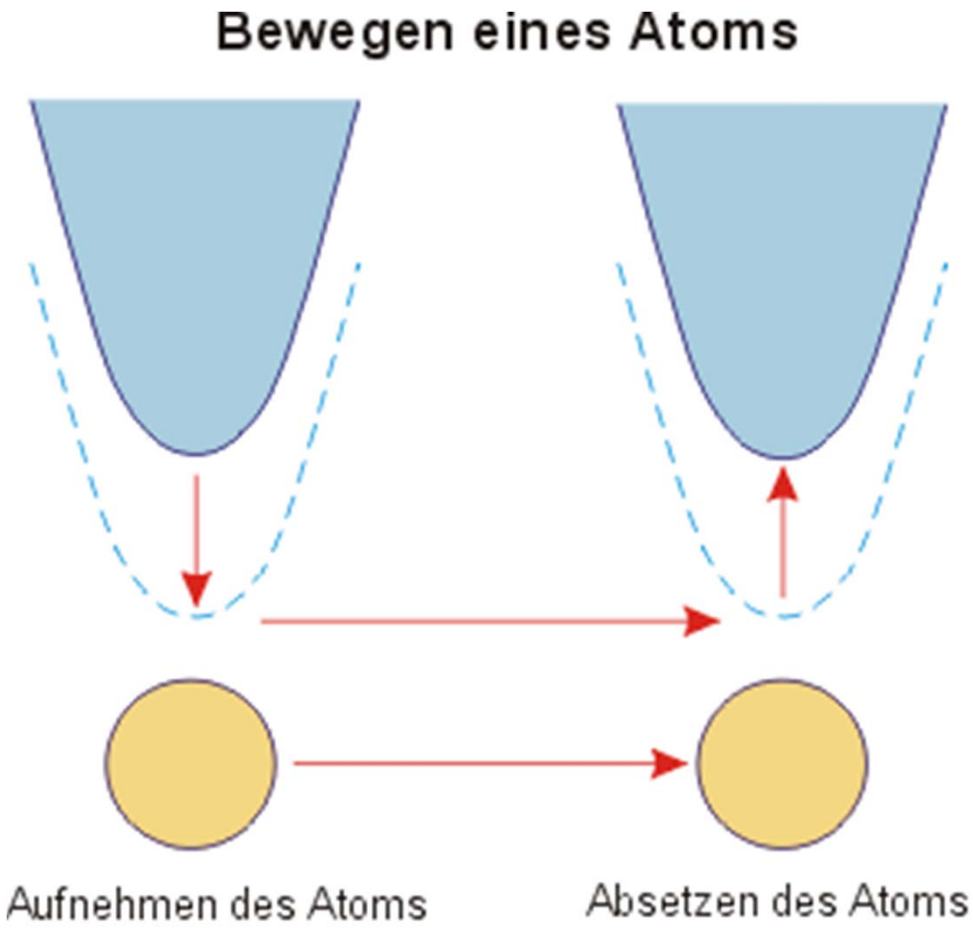


Diagonal Ag adatom motion along
[1-11] direction (atom exchange)

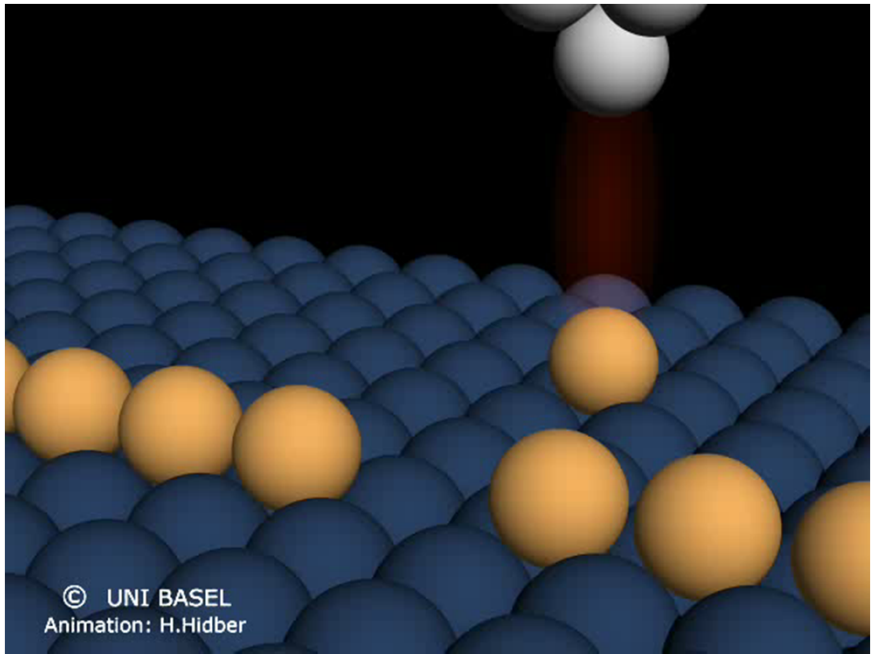


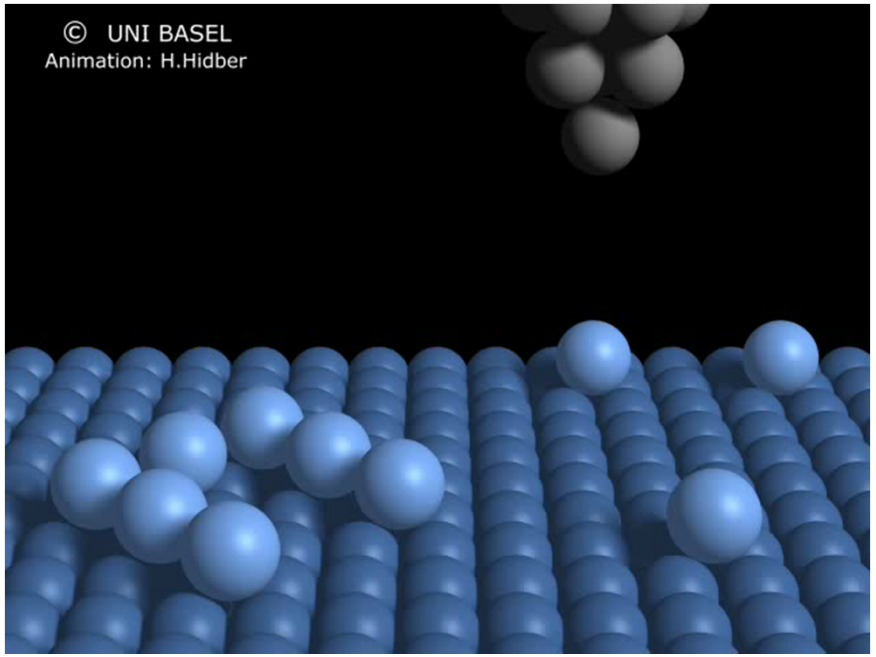
Low-temperature manipulation of Ag atoms and clusters on a Ag(110) surface,
J.T. Li, W.-D.Schneider, and R. Berndt, *Appl. Phys. A*, 66, 575 (1998).

Adsorbate manipulation by STM



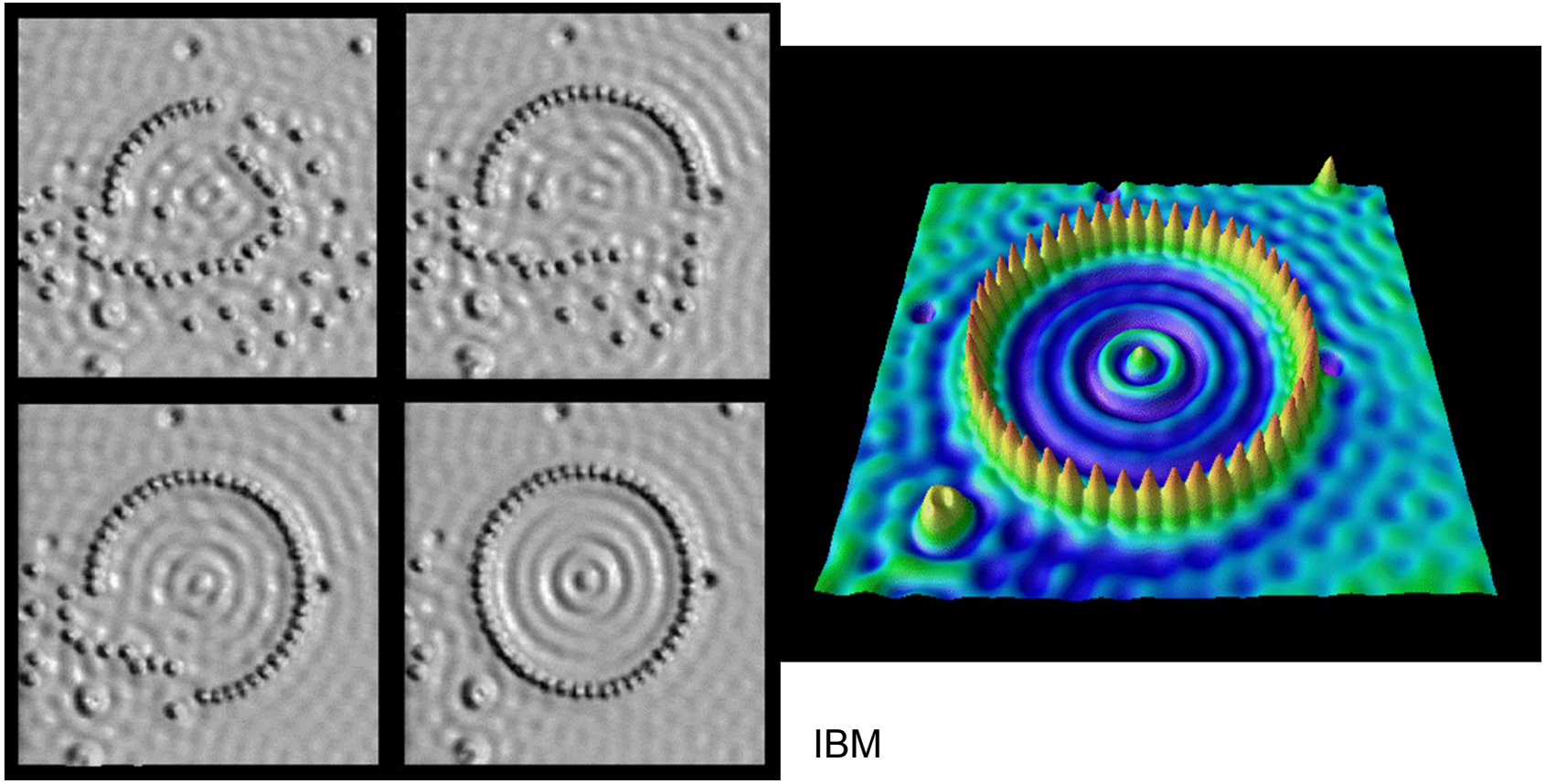
Déplacer des atomes ou molécules





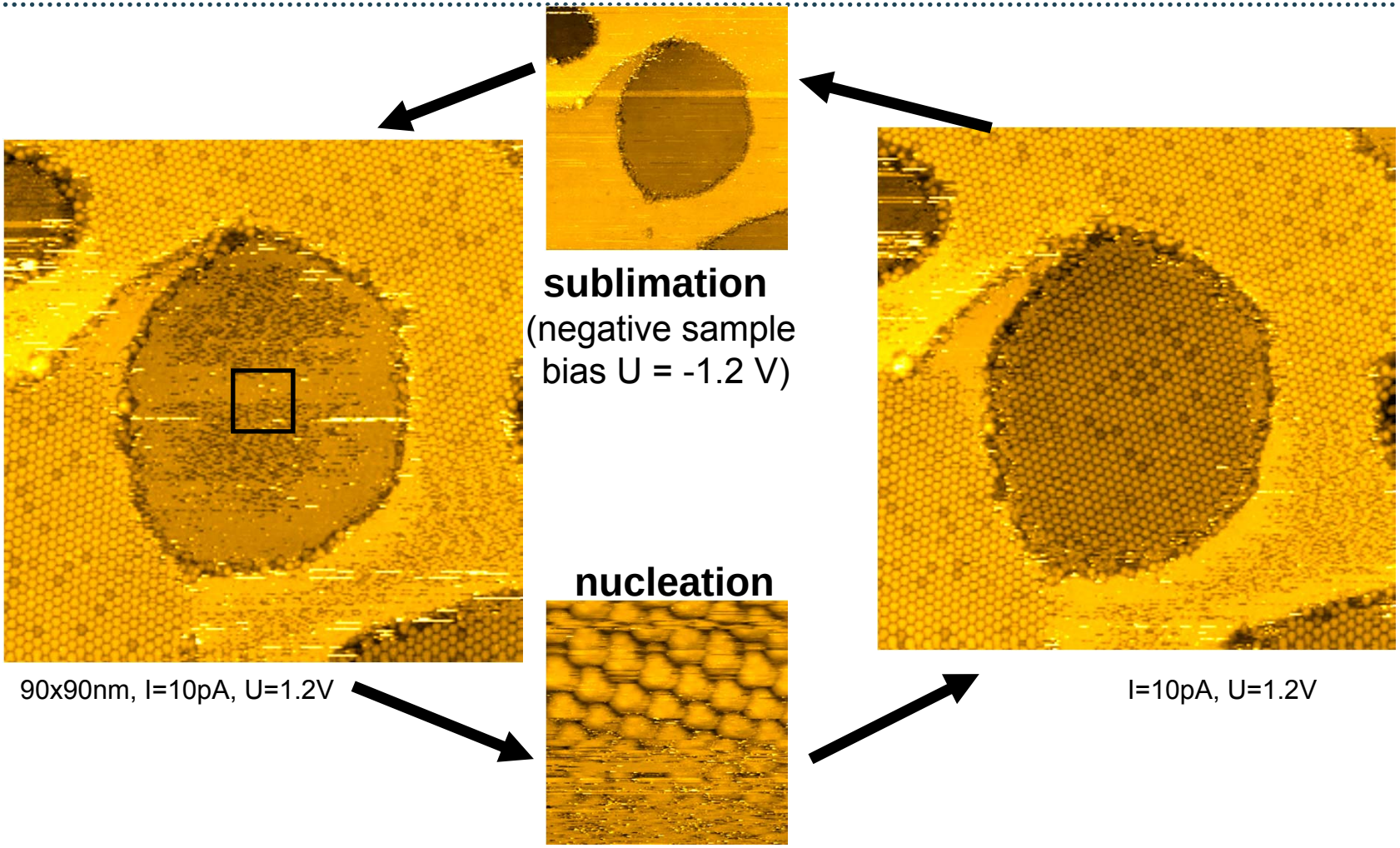
Animations: H. Hidber, Université de Bâle

Quantum Corral



IBM

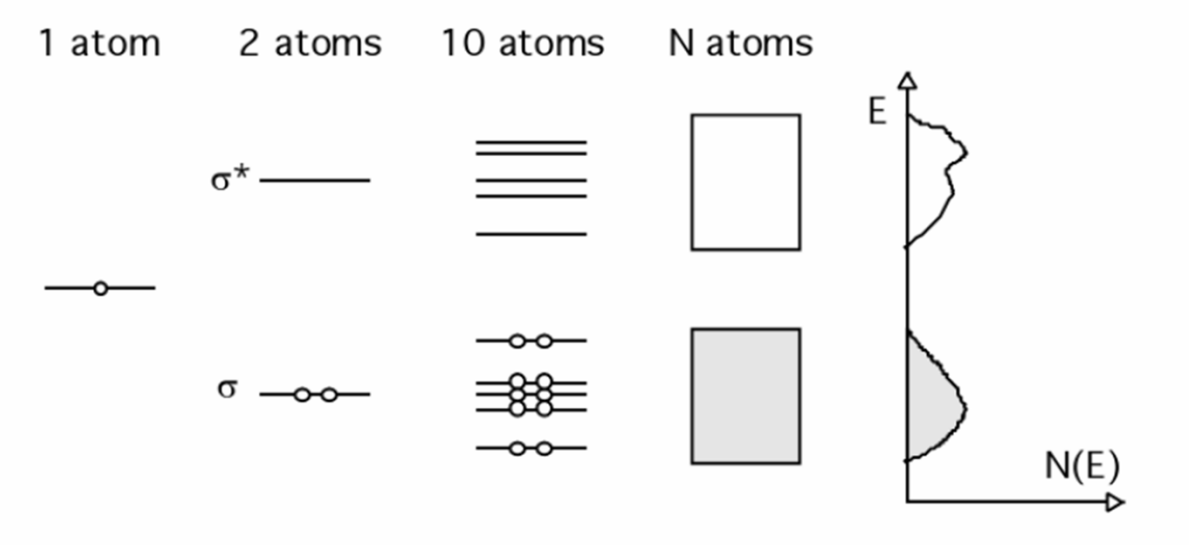
Reversible 2D Phase Transition controlled by the STM tip



Controlled phase transition 2D fluid <=> 2D solid

STS (scanning tunneling spectroscopy)

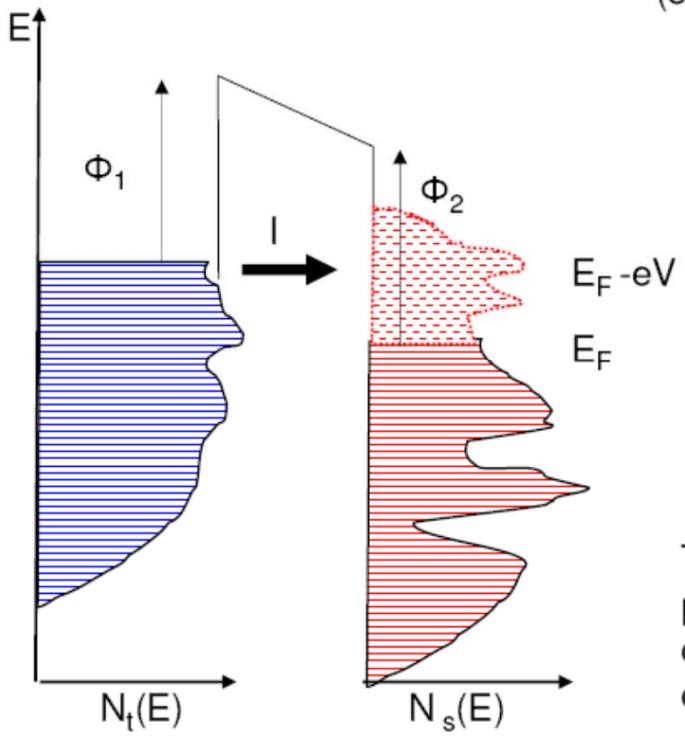
Density of States (DOS)



Density of States (DOS), N(E) is the number of energy levels bewteen E and E+dE (states per eV)

States can have s,p,d,f or mixed (hybrid) character
Bands may be separated by band-gaps E_g

Voltage dependence of tunneling current



By changing the voltage, the density of states can be recorded as function of the voltage (e.g., band structure of semiconductors)

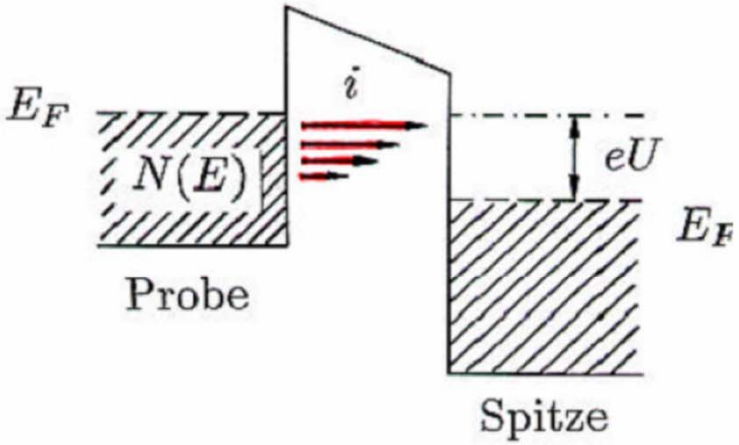
$$I \propto \int_0^{eV} N_1(E) N_2(E - eV) T(E,V) dE$$

where N_1 N_2 are the densities of states at the Fermi niveau and T(E,V) the transmission probability.

$$T(E,V) = \exp\left\{-2s\left[\phi - E + \frac{eV}{2}\right]^{1/2}\right\}$$

The contribution of the states to the tunneling process decays exponentially with their energetic distance to the Fermi niveau. Core levels do not contribute at all.

Spektroskopie



Spektroskopie

Lokale Messung der I/U-Charakteristik bei $x, y, z = const$ (R.J. Hamers, R.M. Tromp and J.E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986))

Information über lokale elektronische Zustandsdichten N(E) enthalten in

$$I/U$$

$$dI/dU$$

$$\frac{dI}{dU}/\frac{I}{U} = \frac{d\ln I}{d\ln U}$$

CCT's mit $+U$ und $-U$

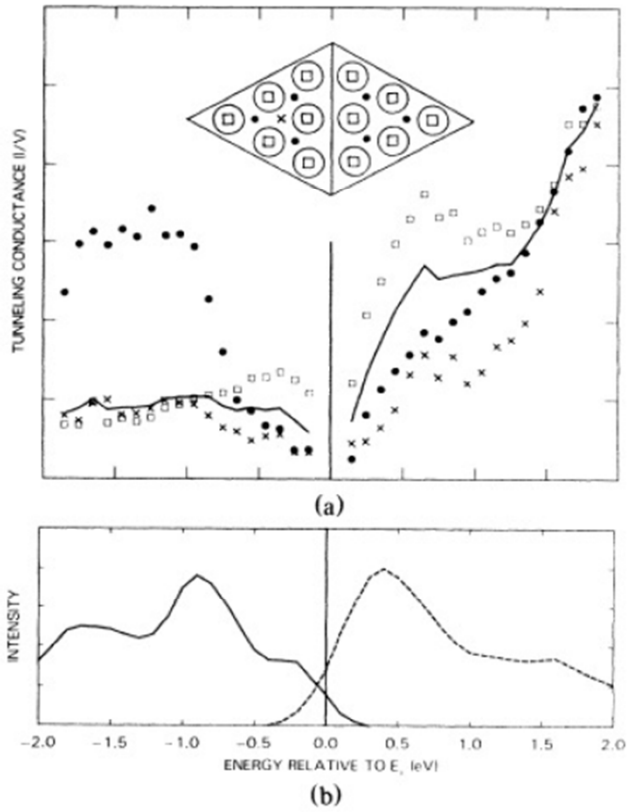
Stabilisierungsspannung U_0 und U sind Parameter

Zustandsdichte der Wolframdichte im Bereich der Fermienergie ändert Sich wenig, d.h. es wird primär die Zustandsdichte der Probe beobachtet (+; unbesetzte Zustände, -, besetzte Zustände)

Tunnelspektroskopie von Si(111)7x7

I(V)/V

UPS/IPS



R. Hamers,
Phys. Rev. Lett. 56, 1972 (1986)

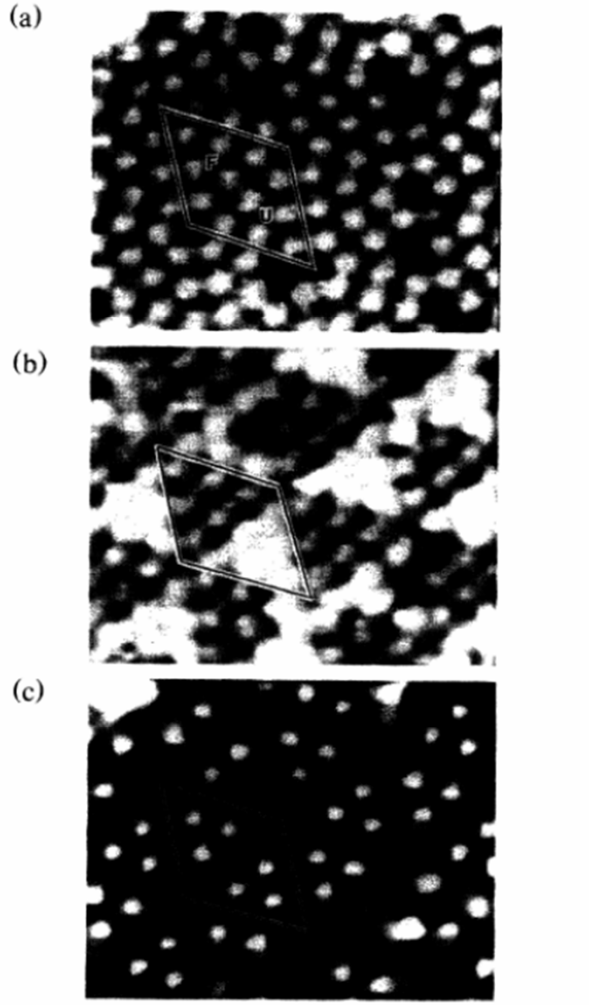


FIG. 1. Simultaneously acquired topograph and current images: (a) STM topograph with +2 V applied to the sample, and current images with (b) +1.45 V and (c) −1.45 V applied to the sample.

Tunnelspektroskopie von GaAs(110)

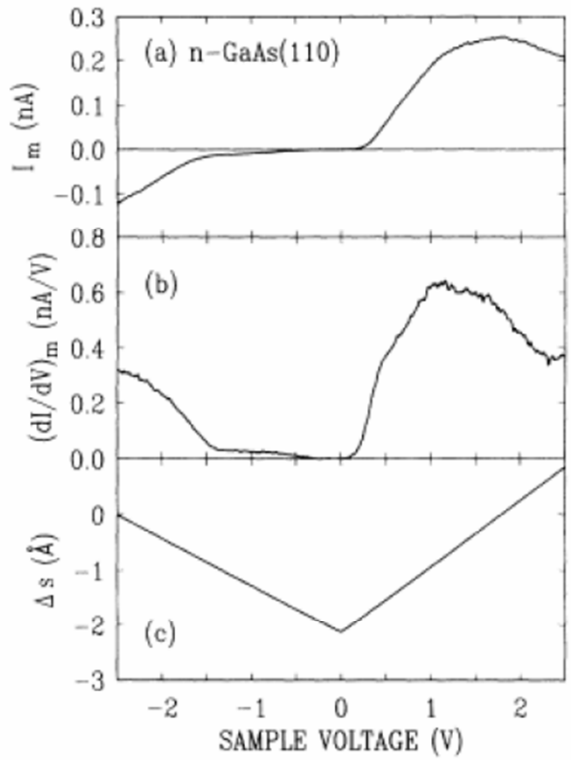


FIG. 1. Raw data from an *n*-type GaAs(110) surface, showing the (a) measured tunnel current and (b) measured conductance, as a function of sample voltage. The applied variation in tip-sample separation is shown in (c).

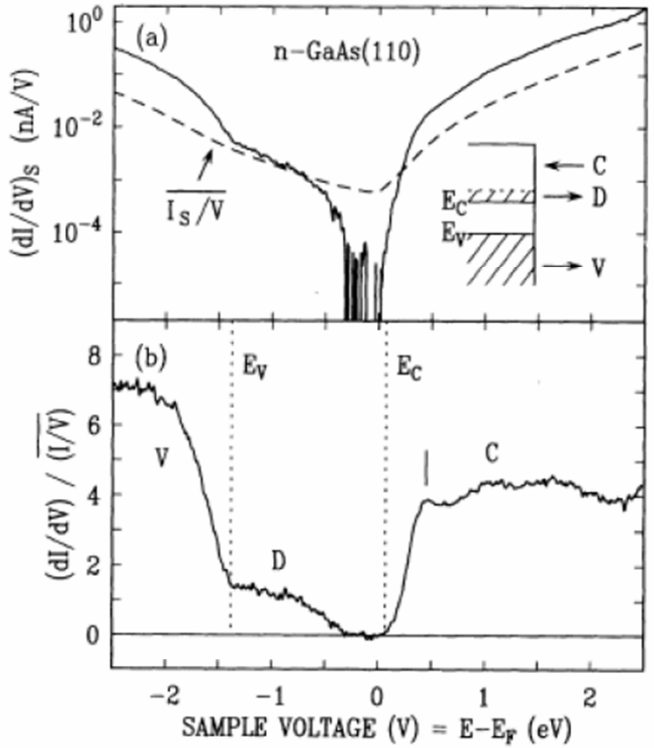


FIG. 3. Analyzed spectral data for *n*-type GaAs(110), showing (a) the differential conductance at constant tip-sample separation, and (b) the ratio of differential to total conductance. The dashed line in (a) shows the total conductance, broadened over a voltage width of 1.5 V. The components of the spectrum are indicated in the inset: *C*—conduction band, *V*—valence band, and *D*—dopant induced. Valence- and conduction-band edges are indicated by dotted lines, labeled E_V and E_C, respectively. The thin vertical line at 0.45 V marks a surface-state feature.

R. Feenstra et al., Phys. Rev. B 50, 4561 (94)

Tunnelspektroskopie auf Supraleitern

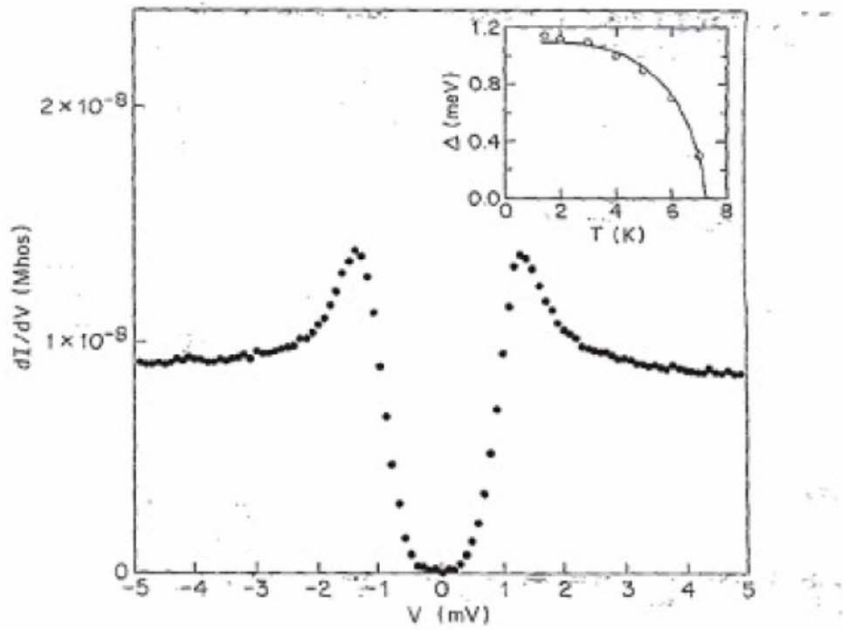


Fig. 2.7. dI/dV vs. bias voltage V for $NbSe_2$ at 0T applied magnetic field used to determine the gap at 1.45K. Inset: The gap vs. temperature and the corresponding BCS-fit. From [35].

H.Hess et al., Phys.Rev. Lett. 62(2), 214(1989)

Inelastic Tunneling Spectroscopy

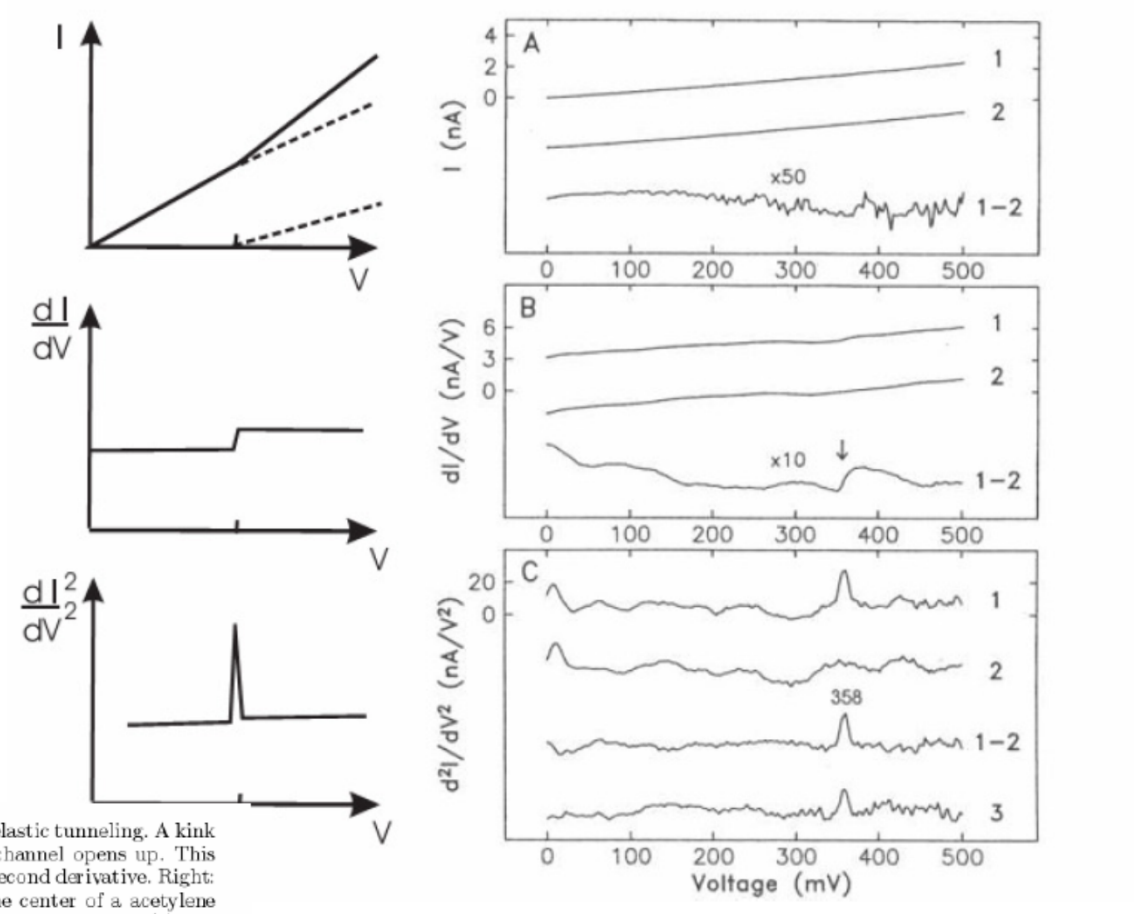


Fig. 2.8. Left:Current vs. voltage curves with elastic and inelastic tunneling. A kink is observed when the inelastic electron tunneling current channel opens up. This kink becomes a step in the first derivative and a peak in the second derivative. Right: (A) I-V-curves recorded with the STM tip directly over the center of a acetylene molecule (1) and over the bare Cu(100) surface. (B) dI/dV on the molecule (1) and on the substrate (2). (C) dI^2/dV^2 on the molecule (1) and on the substrate (2). The difference spectrum (1-2) shows a peak at 358mV. (3) is an average of 279 scans. From [41].

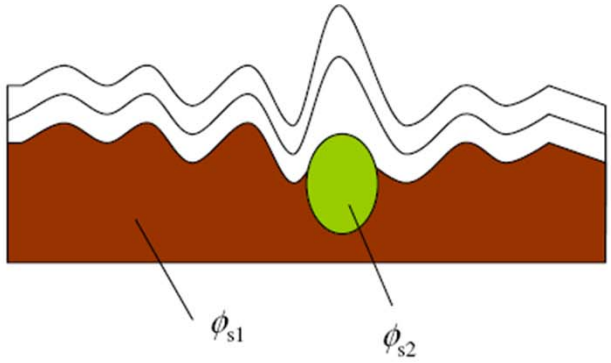
B.Stipe,M.Rezaei,W.Ho:Science 280, 1732 (1998)

Constant current mode

$$\ln(I) = \text{konst.} \quad \Rightarrow \quad \sqrt{\phi}\, s = \text{konst.}$$

If barrier height constant ⇨ **s=constant**

If barrier height varies ⇨ **ϕ(x,y), s(x,y) affect topography z(x,y)**



**Contour z(x,y)
at constant current**

Chemical contrast in an alloy

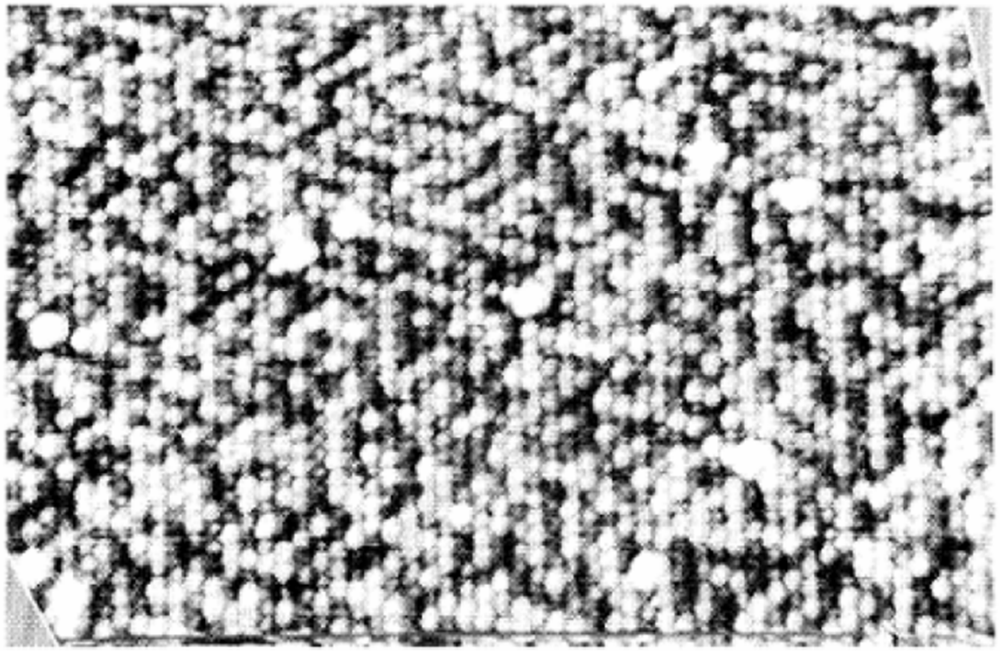


Fig. 2.14. STM image of the (111) surface of a $Pt_{25}Ni_{75}$ single crystal. A voltage of 5mV and current of 16nA were applied. A rather strong "chemical" contrast is observed, where the dark species is attributed to Pt und the bright features to Ni. The contrast is related to the interaction between tip adsorbates and the surface. Image size is 125Åx 100Å. From [50].

Oberflächenzustände auf Cu(111)

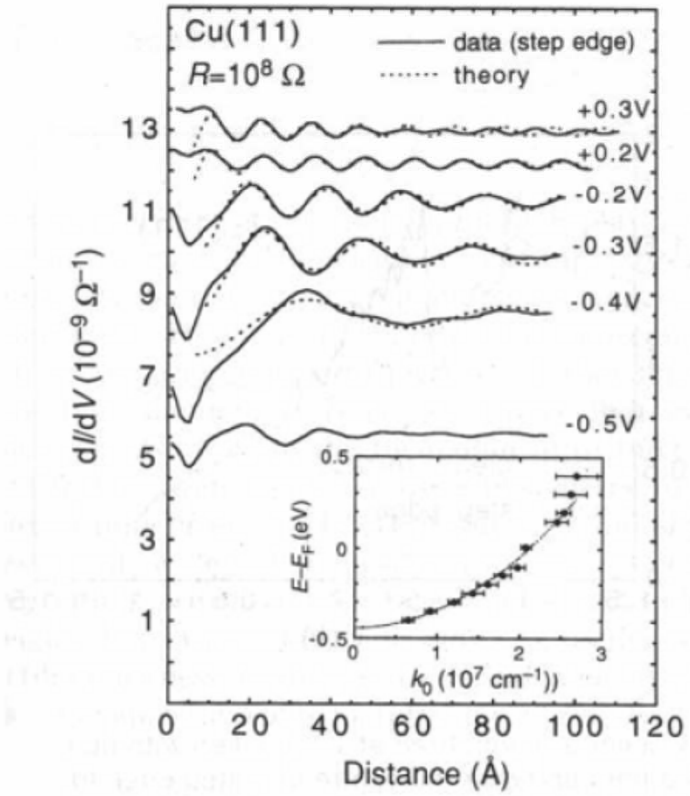
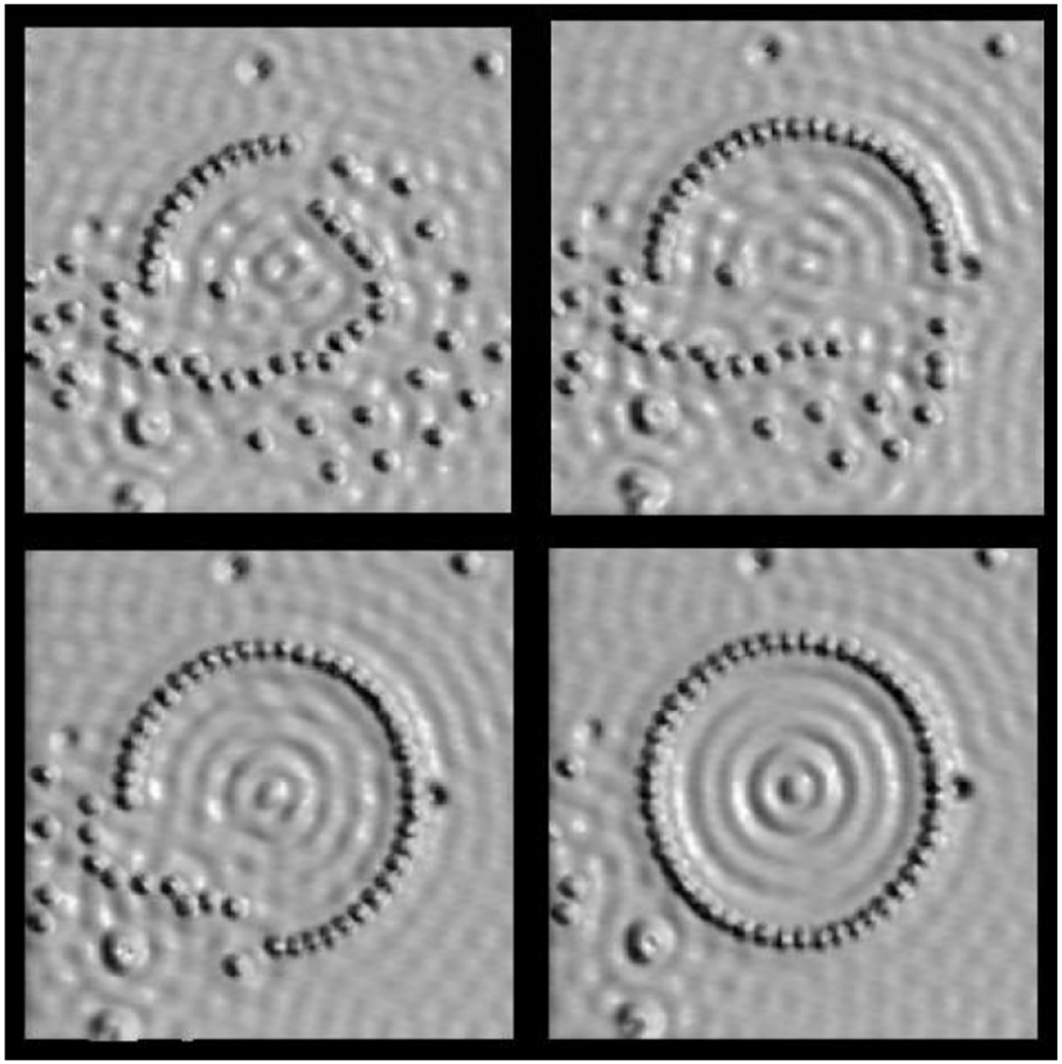


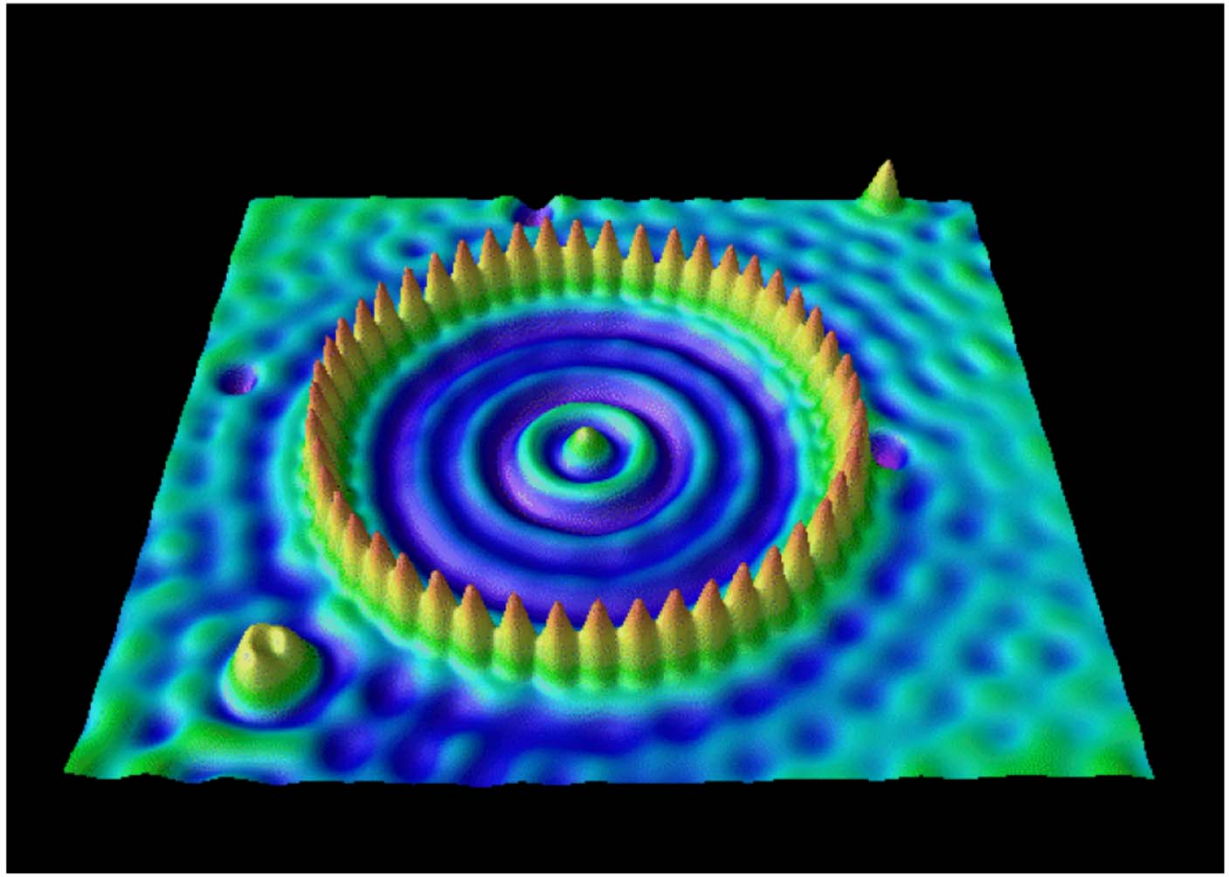
Fig. 2.16. Spatial dependence of dI/dV across a step edge on Cu(111) at 4K. For details see text. From [80].

Surface state scattering



M.F. Crommie, C.P. Lutz and D.M. Eigler, *Nature* 363 (1993)

Quantum corral



M.F. Crommie, C.P. Lutz and D.M. Eigler, *Nature* 363 (1993)

„Confined electrons“

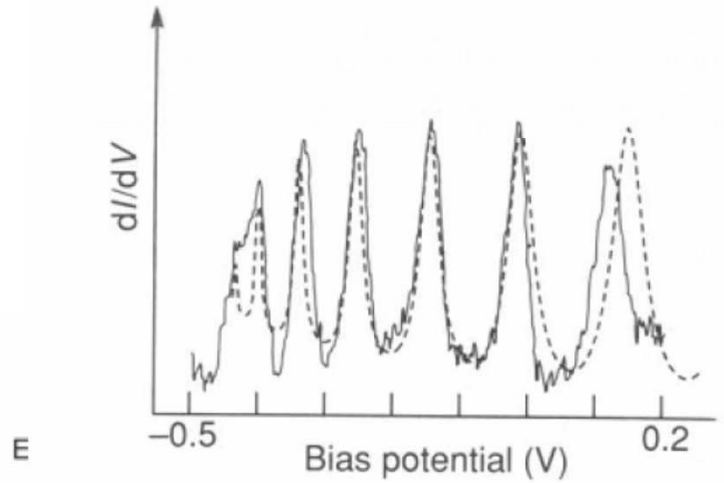
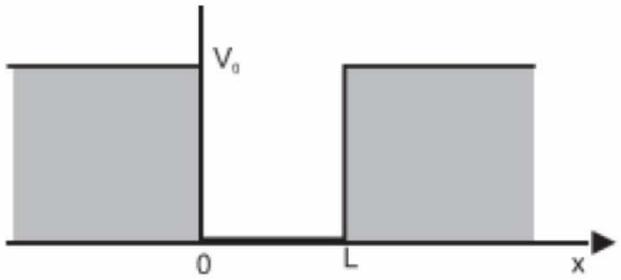


Fig. 2.18. The experimental (solid line) and theoretical (dashed line) voltage dependence of dI/dV, with the top of a STM located at the center of a 88.7Å diameter, 60-atom circle of Fe atoms on a Cu(111) surface. From [84].



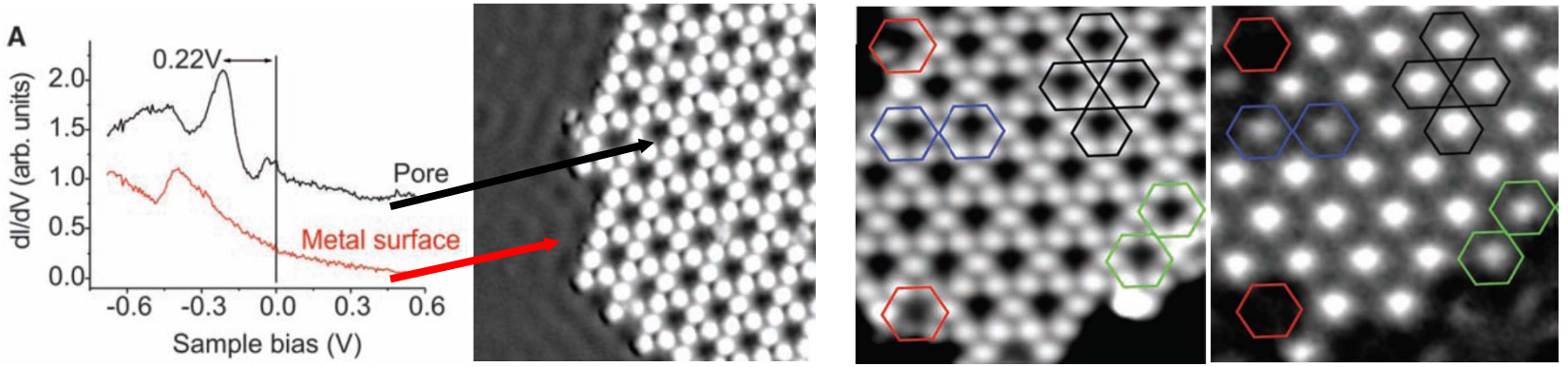
$$E_n = \frac{h^2}{8mL^2} n^2$$

E.Heller,M.Crommie,C.Lutz,D.Eigler:Nature 369, 464 (1994)

2D bandstructure

Detection of confined states in a porous supramolecula network

STS is a powerful tool to probe the local electronic density of states (LDOS) of a quantum entity.
STS performed inside the hexagonal DPDI pores shows, in the corresponding dI/dV curve, a confined electronic state at -0.22V (black curve).
No peak is seen on the metal surface for the same voltage (red curve).



J.Lobo-Checa et al, Science, 325,300 (2009).

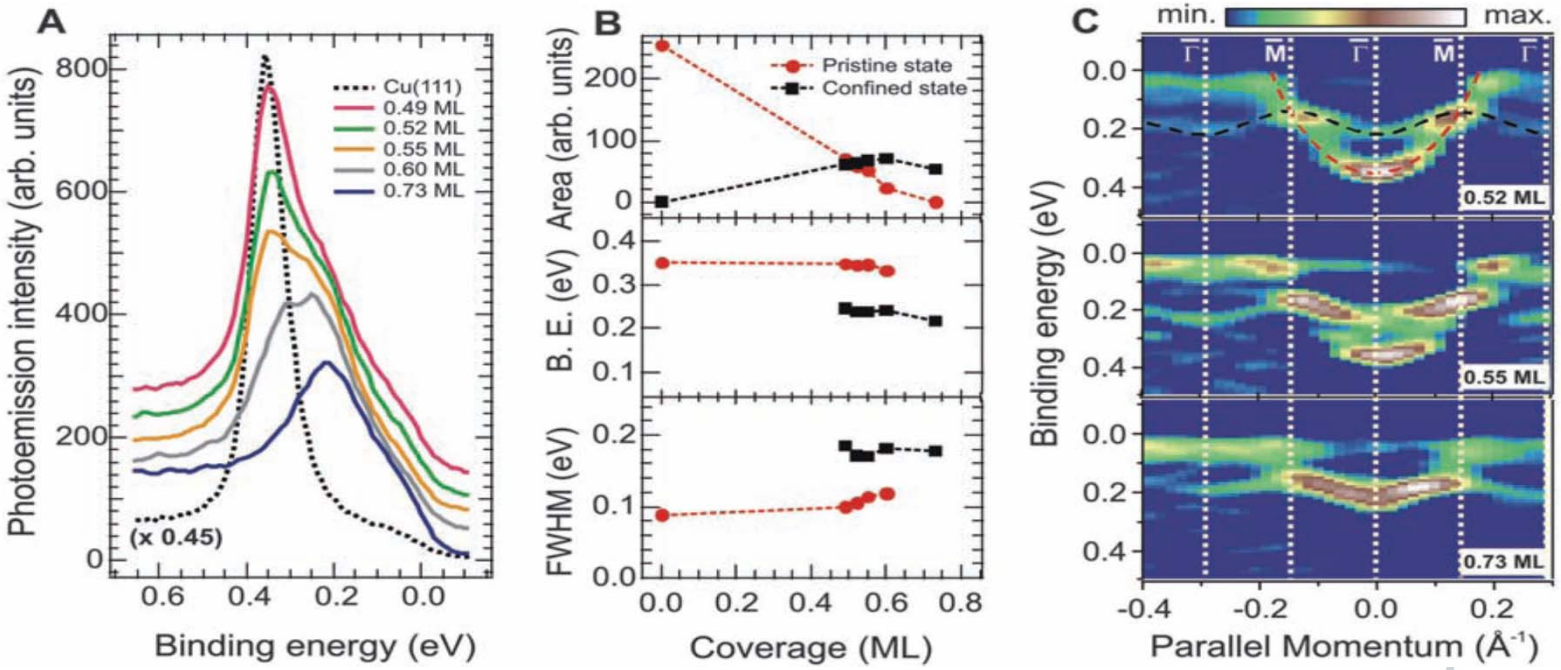
2D bandstructure (STS+ARPES)

ARPES is a surface analytical technique that helps us to identify the binding energy of the confined electrons with respect to their momentum.

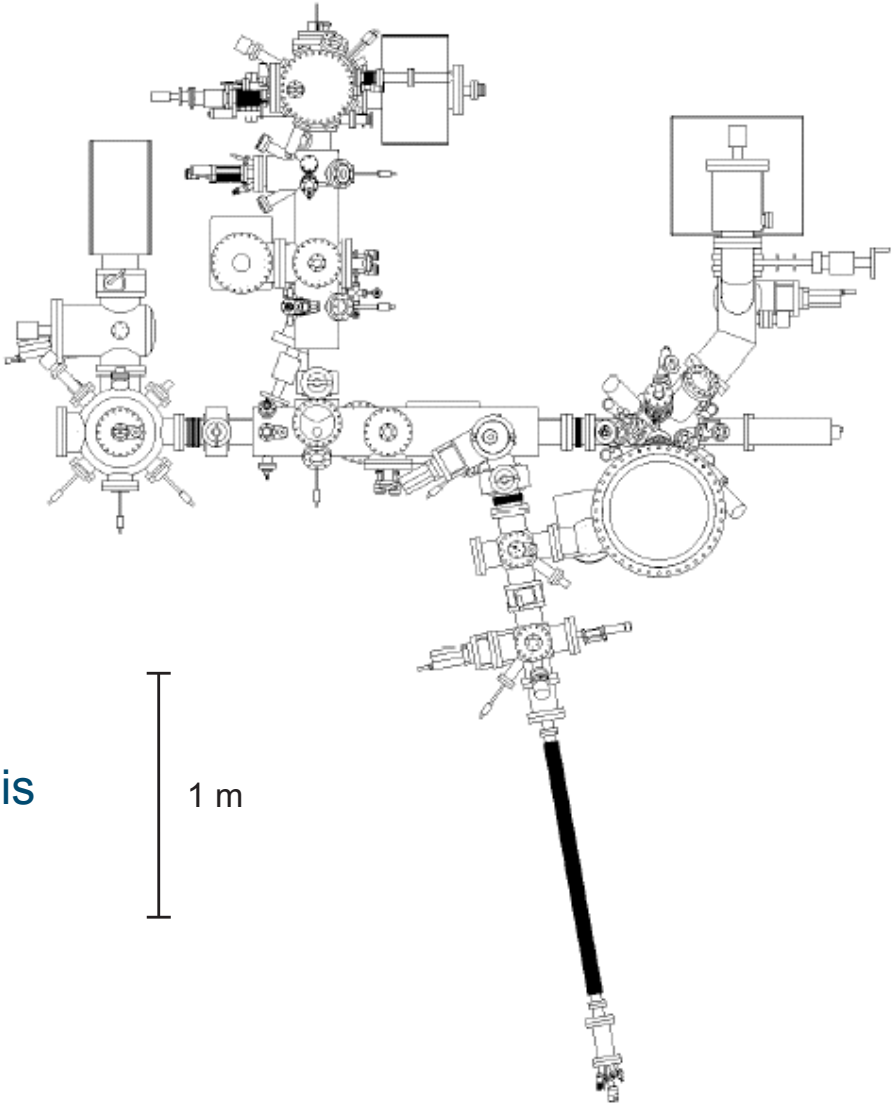
The red dotted line in fig c shows the E(k) relation of the free surface electrons and the black line (first sub-band) corresponds to the first confined state.

The energy gap between the sub-bands is ~90 eV.

With increasing molecular coverage, the number of the confined states increases and the surface state forms a continuous band in 2D supramolecular structure.



Come an study more: STM/STS - Nanolab Uni Basel



- UHV 10^{-10} mbar
- *in situ* sample preparation and analysis
- multiple evaporation facilities
- STM (home-built RT, Omicron LT)
- XPS, UPS, AES, LEED