

Inhalt

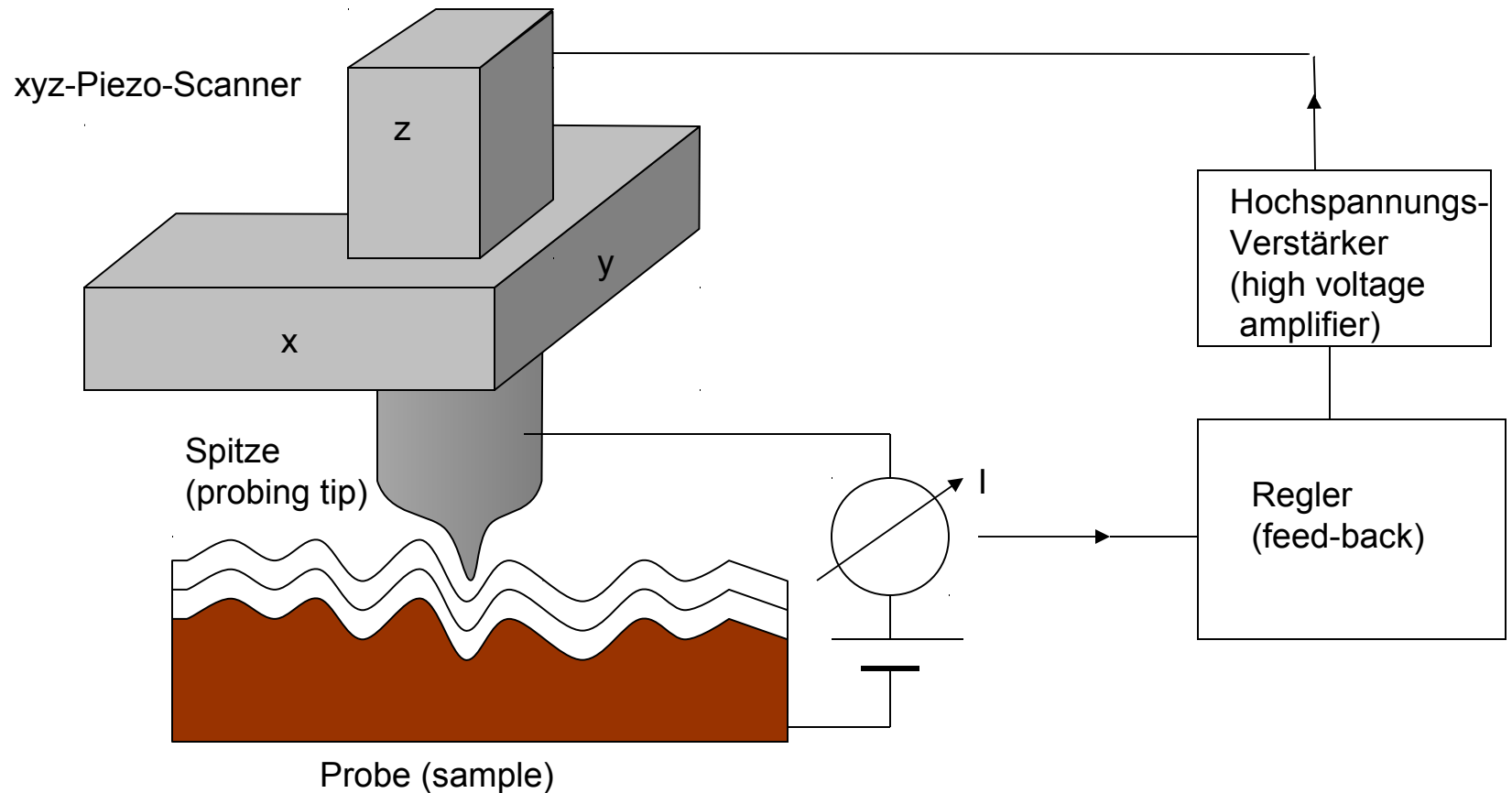
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01.10.13	Nanostructuring 2 (Selbst-Organisation, Substrate „Template“ Effekte)
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03.12.13	Kolloidale Methoden und inverse Mizellen
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Nanostrukturen-Analysemethoden

Scanning Probe Microscopy

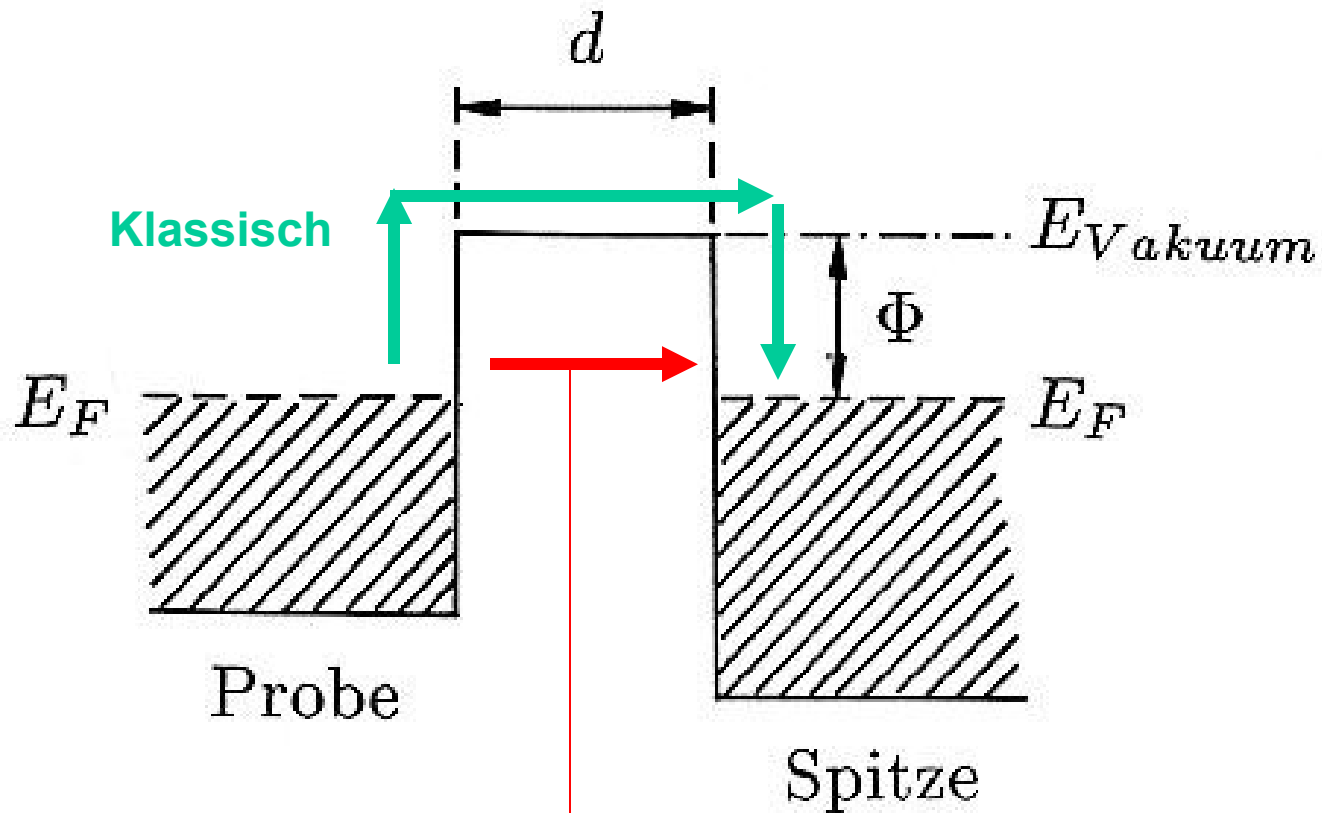
- **Scanning Tunneling Microscopy**
 - Tunnel Current
 - G. Binnig and H. Rohrer, Nobelpreis 1986
 - Experimental Setup
- **Friction Force Microscopy**
 - Force Calibration
 - Atomic Stick Slip
 - Tomlinson Model
 - Nano-manipulation
- **Atomic Force Microscopy**
 - Short- and Long-Range Forces
 - Kelvin Probe Force Microscopy
 - Measurements on Semiconducting Devices
 - Molecules on Insulating Surfaces
 - Manipulation

Rastertunnelmikroskop (STM)



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

Tunneleffekt



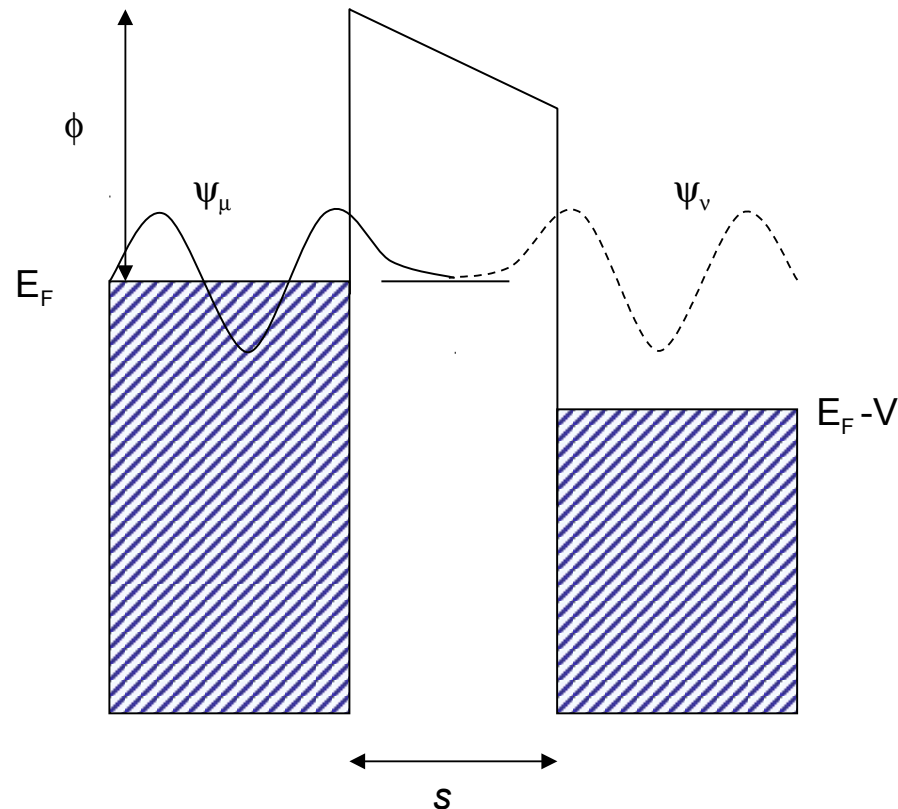
**Quantenmechanisch:
Tunnelstrom**

$$I_T = f(U)e^{-A\sqrt{\Phi d}}$$

$$I_T \approx 1nA$$

Tunneleffekt

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



Tunneleffekt

$$I_T = f(U) e^{-A\sqrt{\phi}s}$$

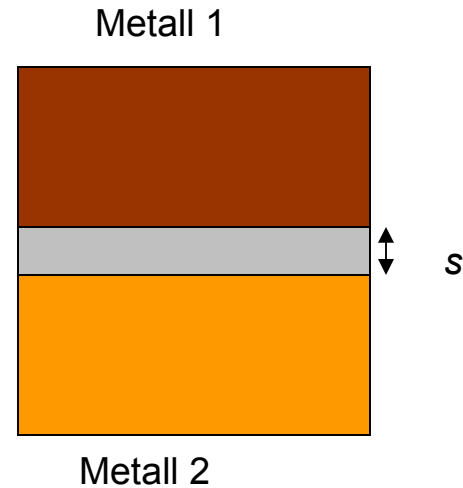
I_T : Tunnelstrom

U : Extern angelegte Spannung

s : Distanz zwischen Probe und Spitze

ϕ : Barrierenhöhe

Isolator



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

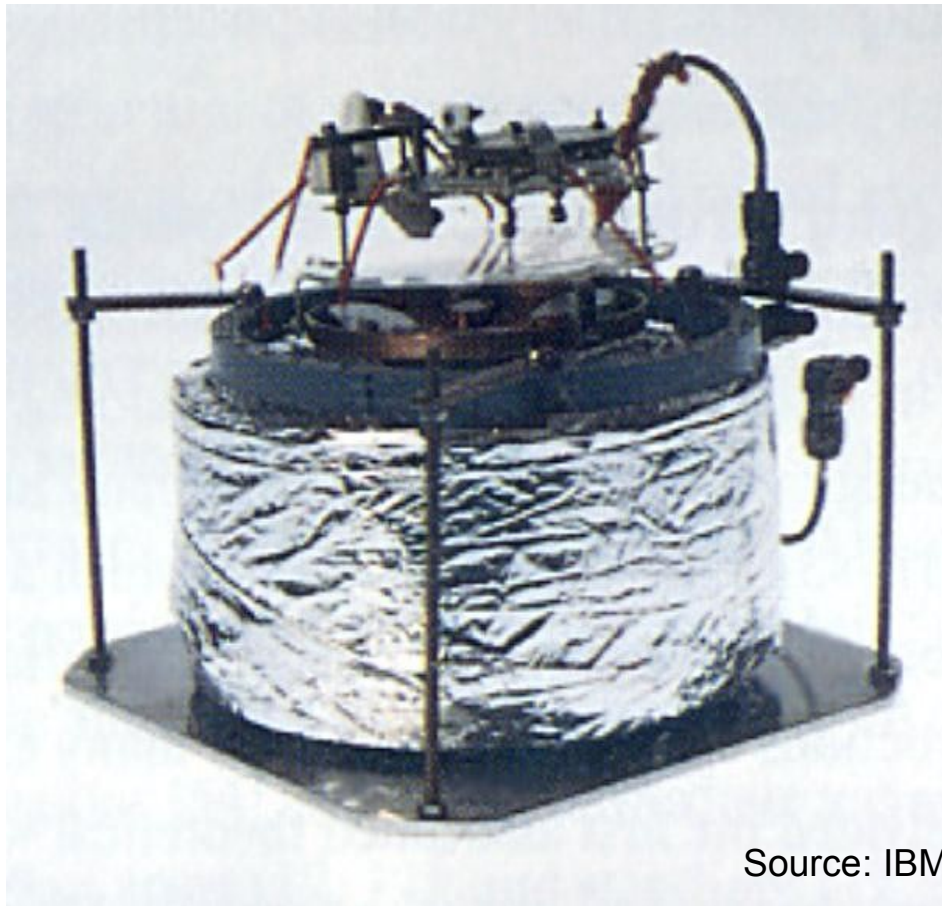
$$A = 2\sqrt{\frac{2m}{\hbar^2}} = 1.025 \text{ \AA}^{-1} eV^{-1/2}$$

$f(U)$: Funktion der elektronischen Struktur von Probe und Spitze

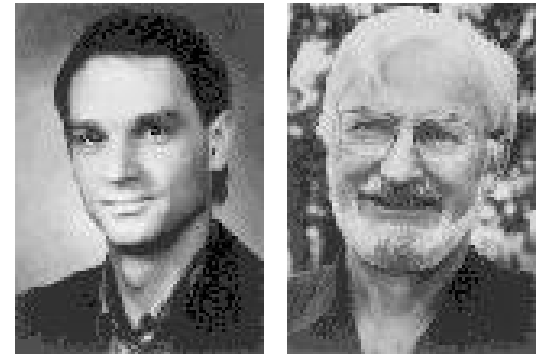
Für freie Elektronen $f(U) \sim U$

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

Scanning Tunneling Microscope (STM)



Source: IBM



G. Binnig and H. Rohrer
Nobelpreis 1986

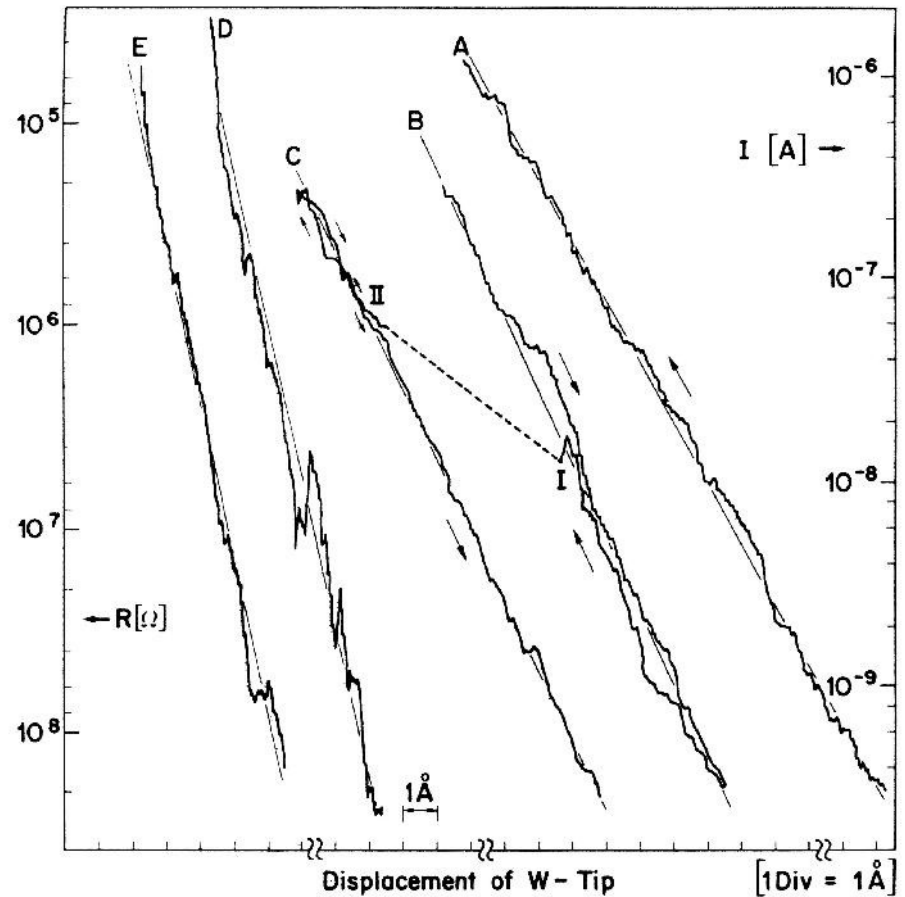
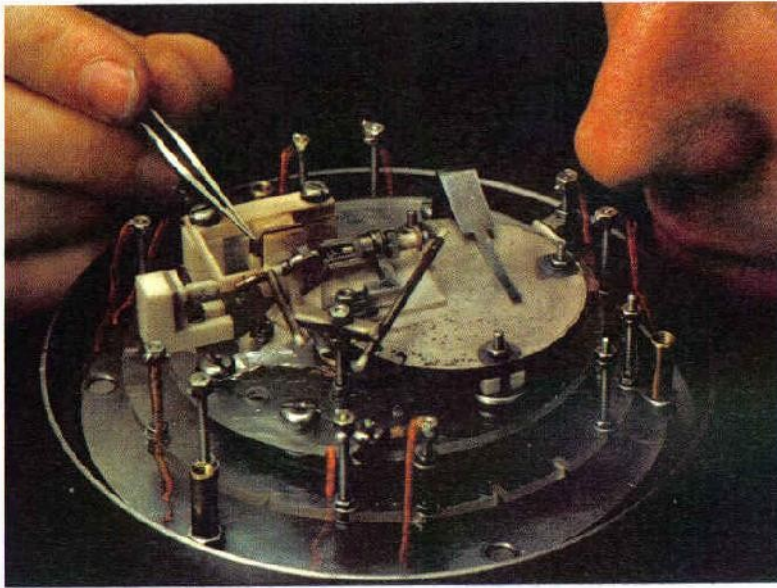
IBM Rüslikon
Switzerland

G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. 50, 120 - 123 (1983)

G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. 49, 57 - 61 (1982)

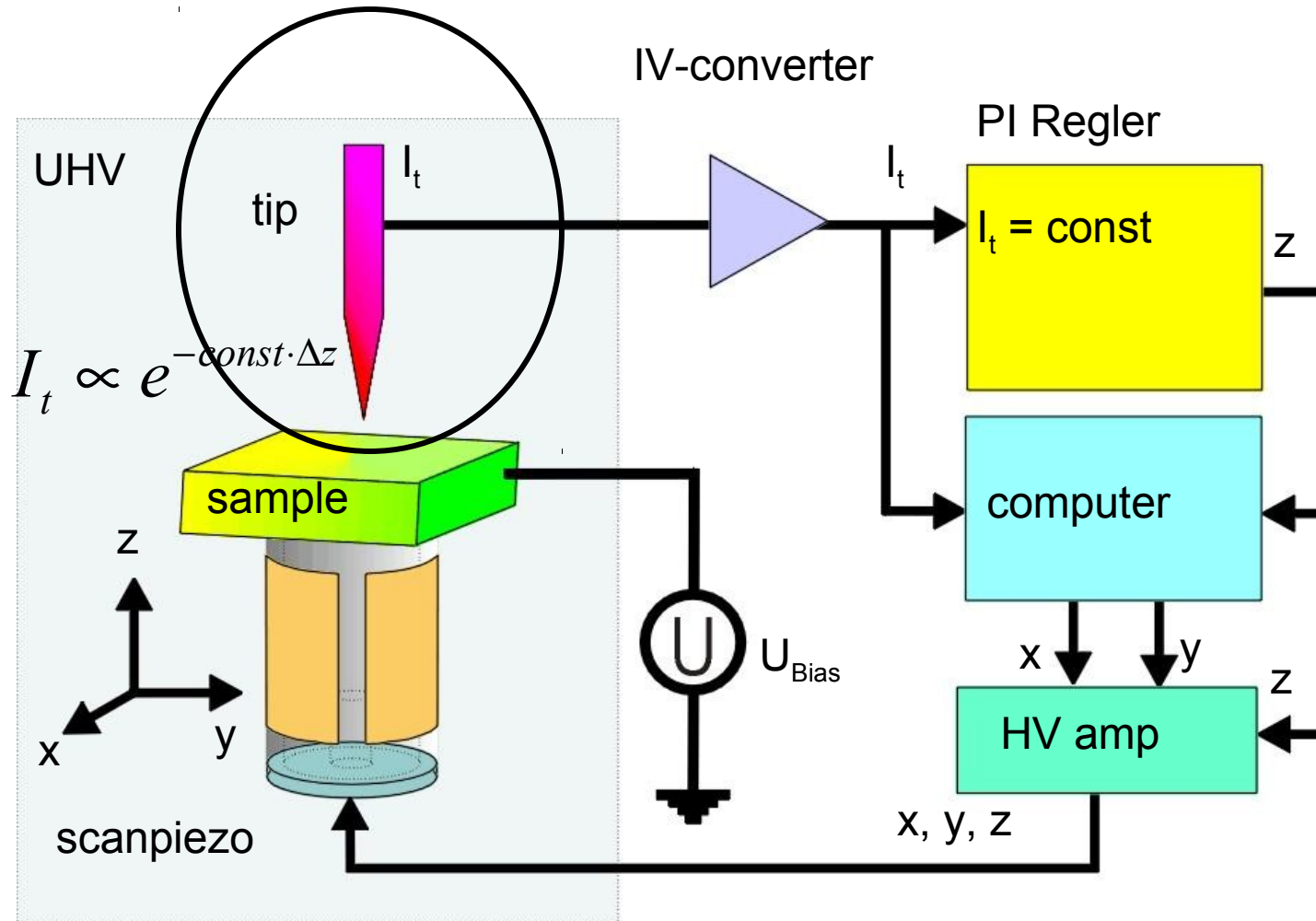
G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Appl. Phys. Lett., Vol. 40, Issue 2, pp. 178-180 (1982)

Scanning Tunneling Microscopy (STM)



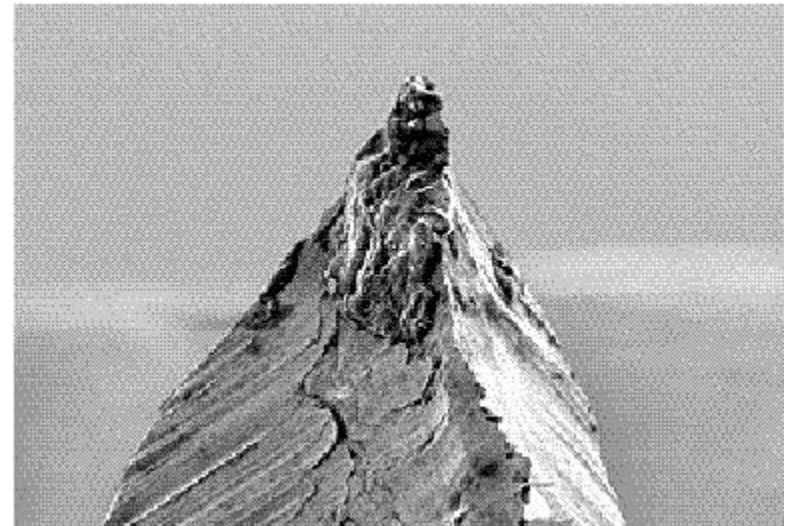
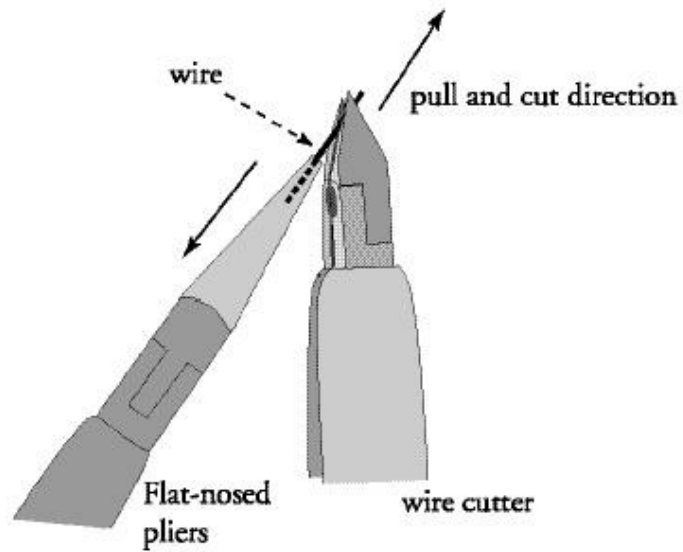
Exponentieller Abfall des Tunnelstromes mit dem Abstand

Blockschaltbild STM



Spitzen

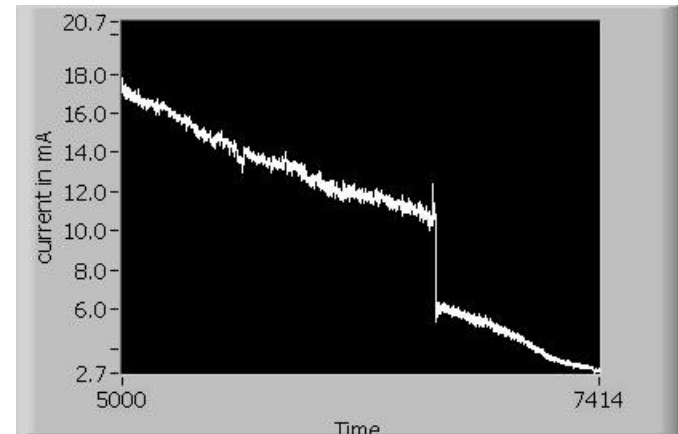
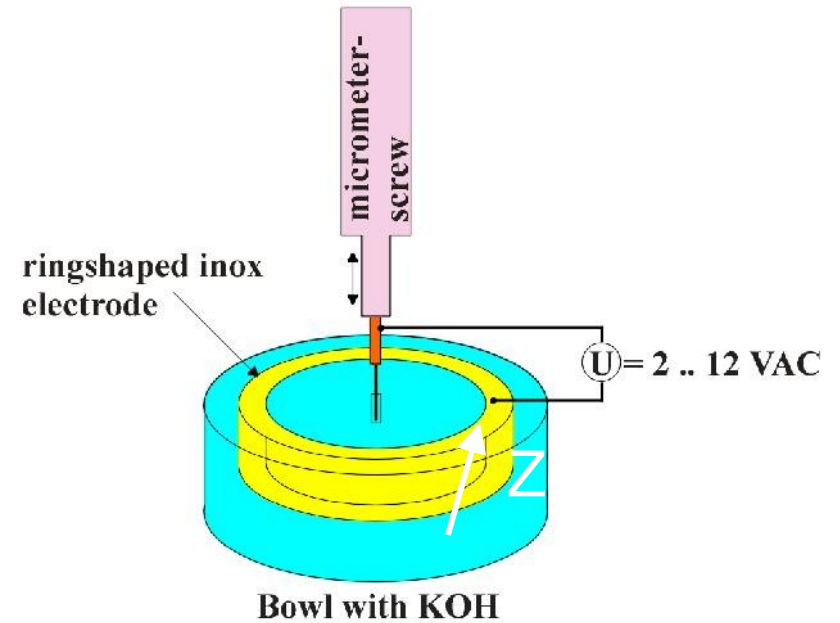
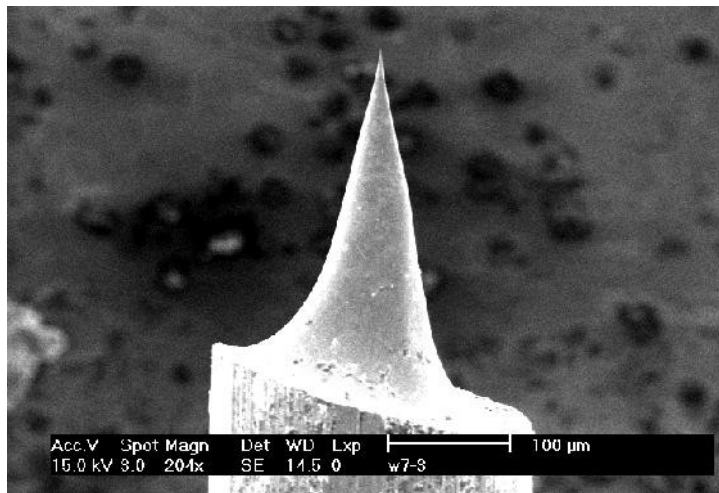
1. Abgerissener Ptlr Draht



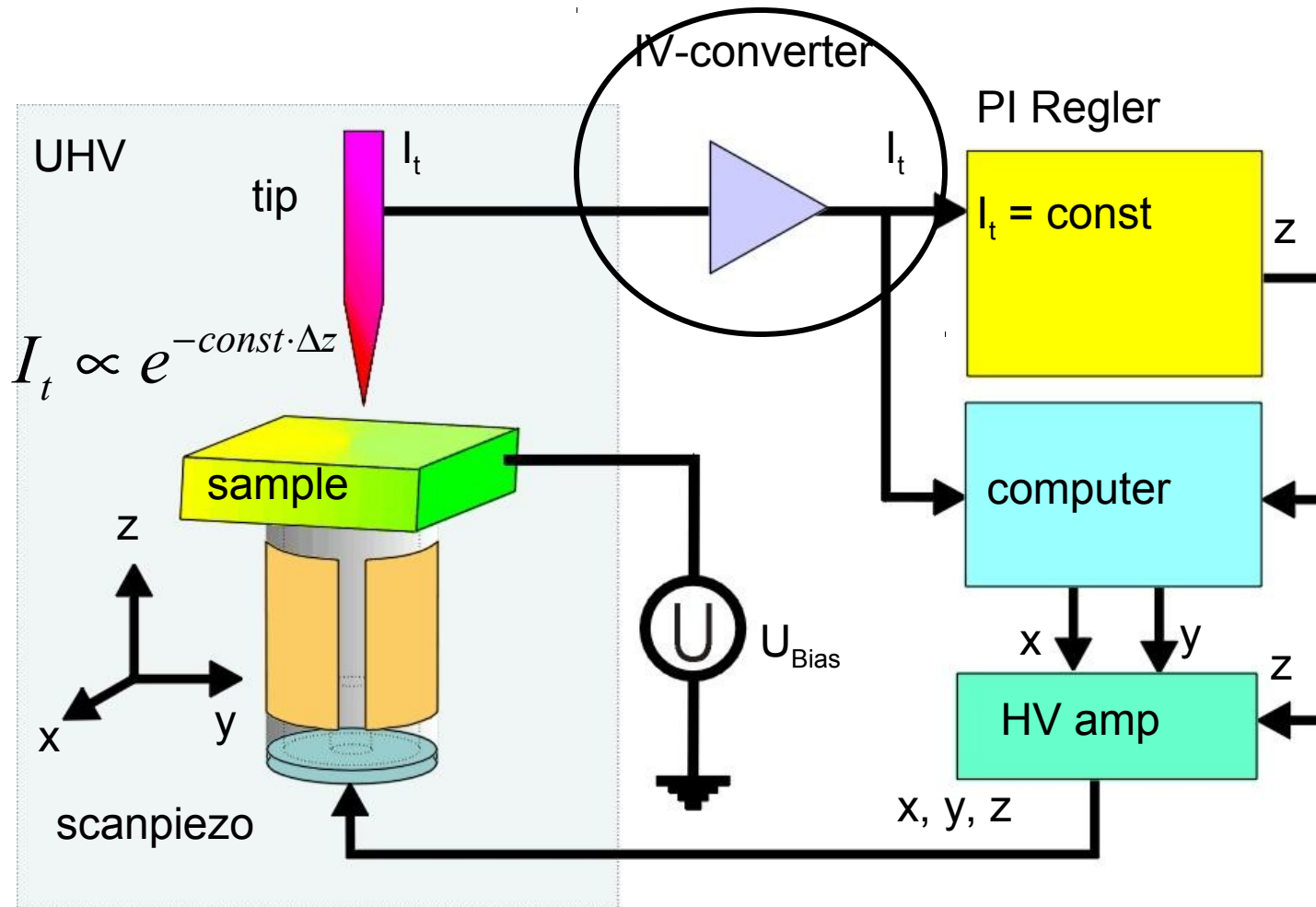
Oder...

Spitzen

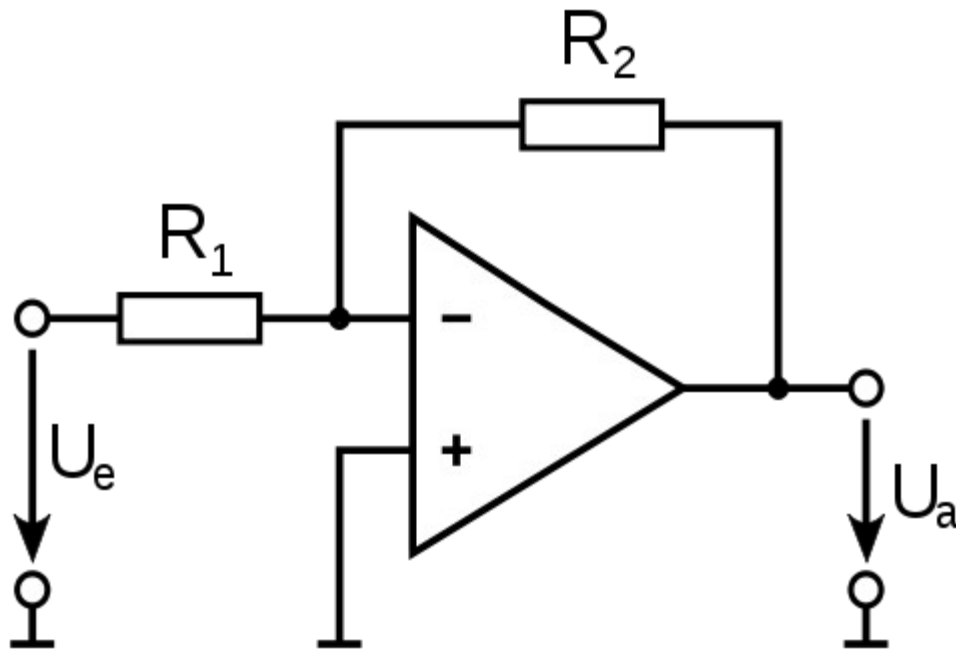
2. Elektrochemisch
geätzte Wolframspitzen:



Blockschaltbild STM

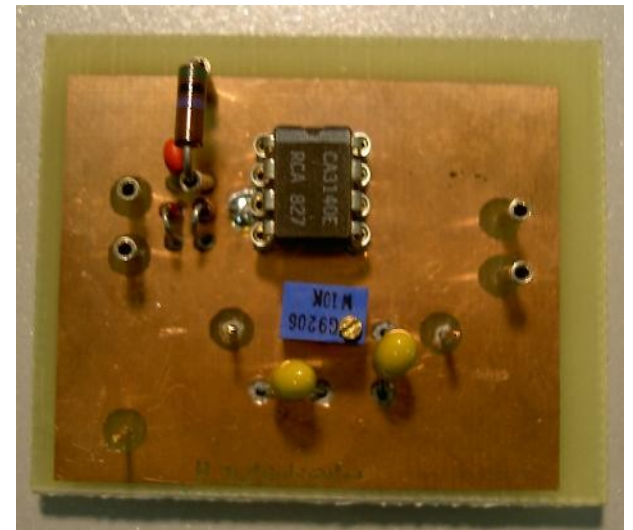
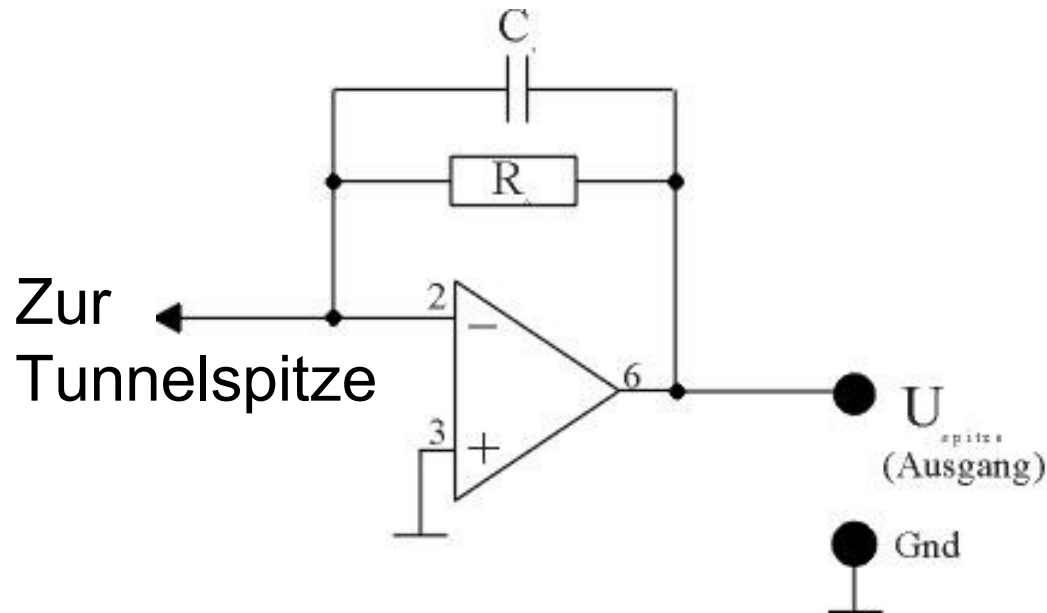


Invertierender Verstärker



$$U_a = -\frac{R_2}{R_1}U_e$$

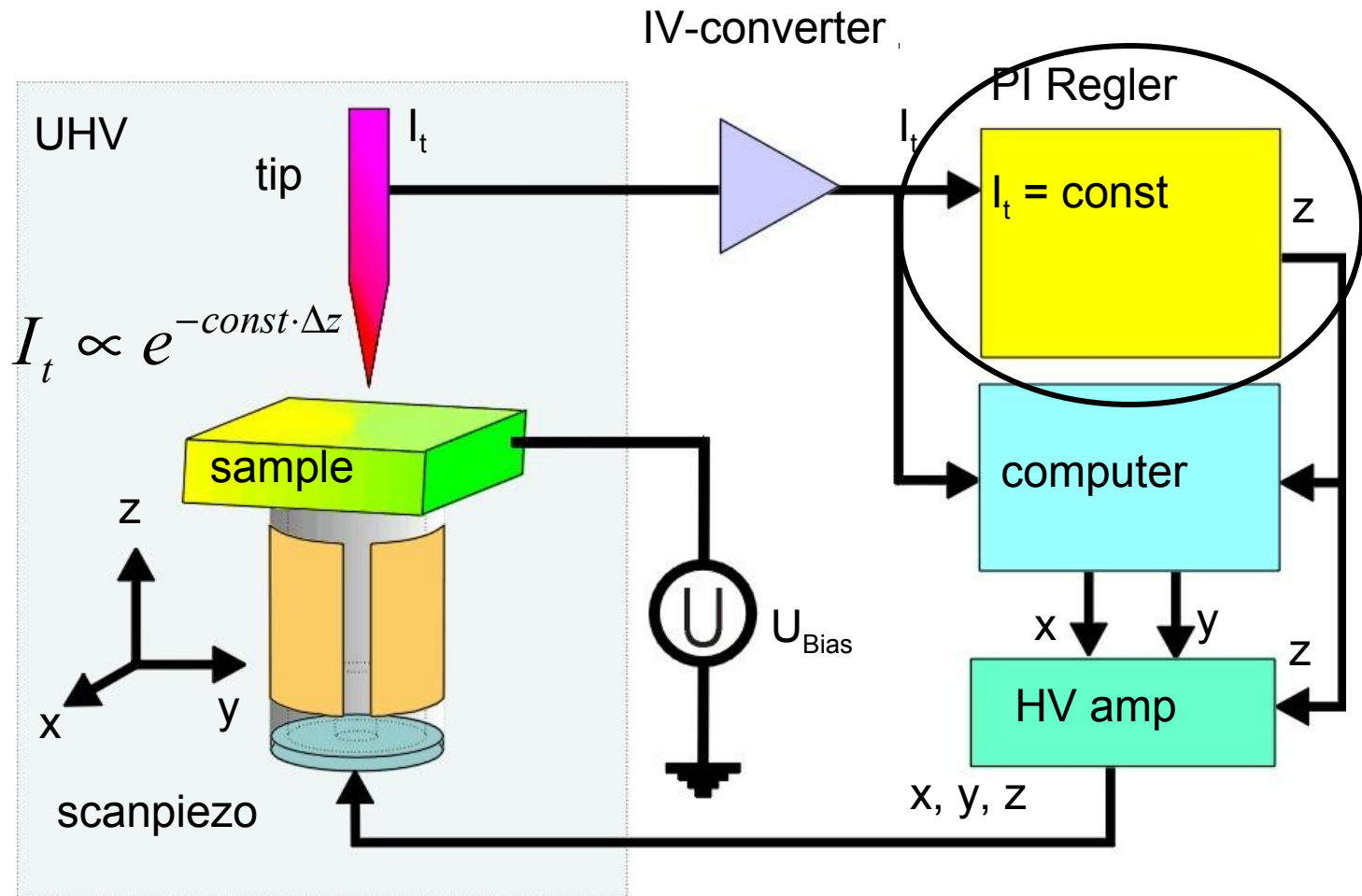
Strom-Spannungswandler



$$U_A = -R \cdot I_t$$

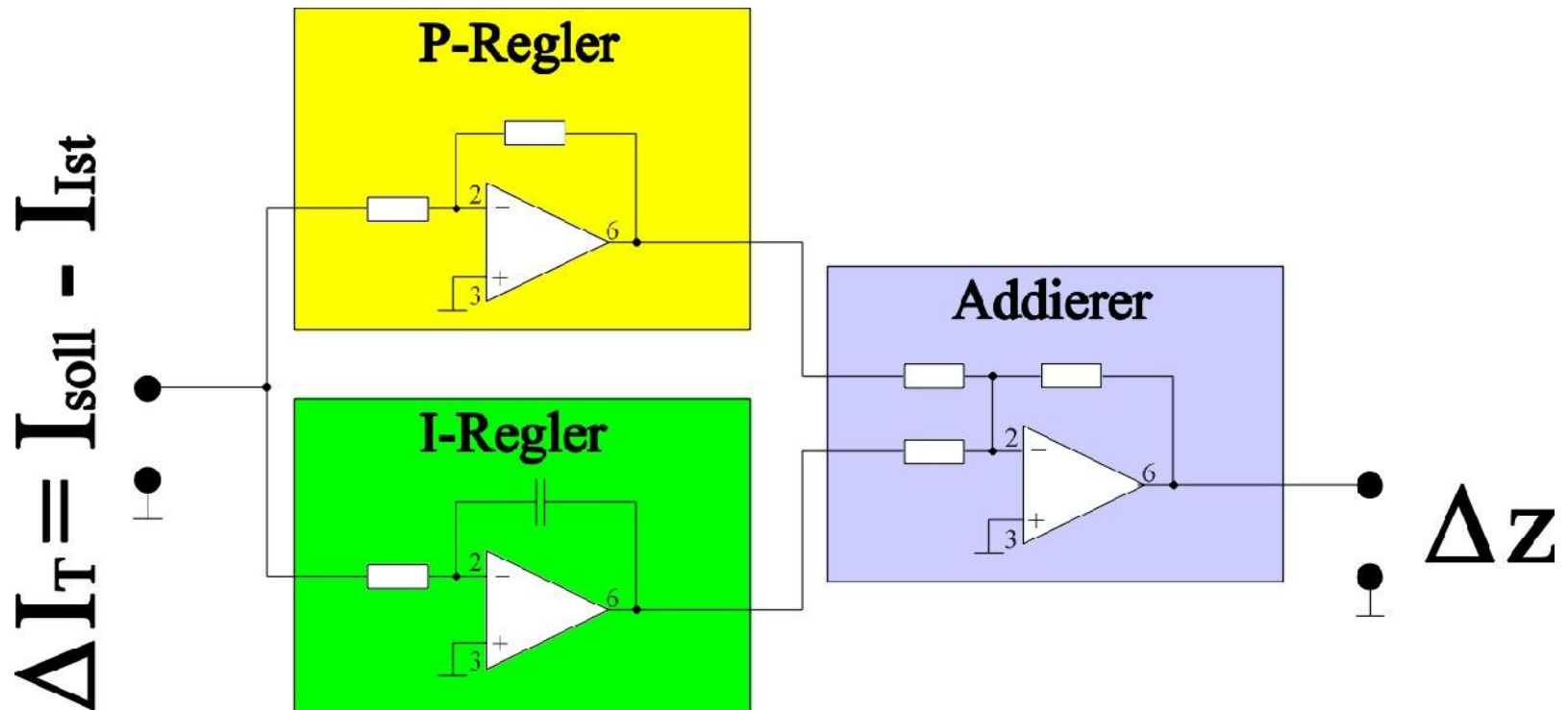
Bei $R = 100\text{M}\Omega$ entspricht $U_A = 1\text{V}$
einem Tunnelstrom von 10nA

Blockschaltbild STM

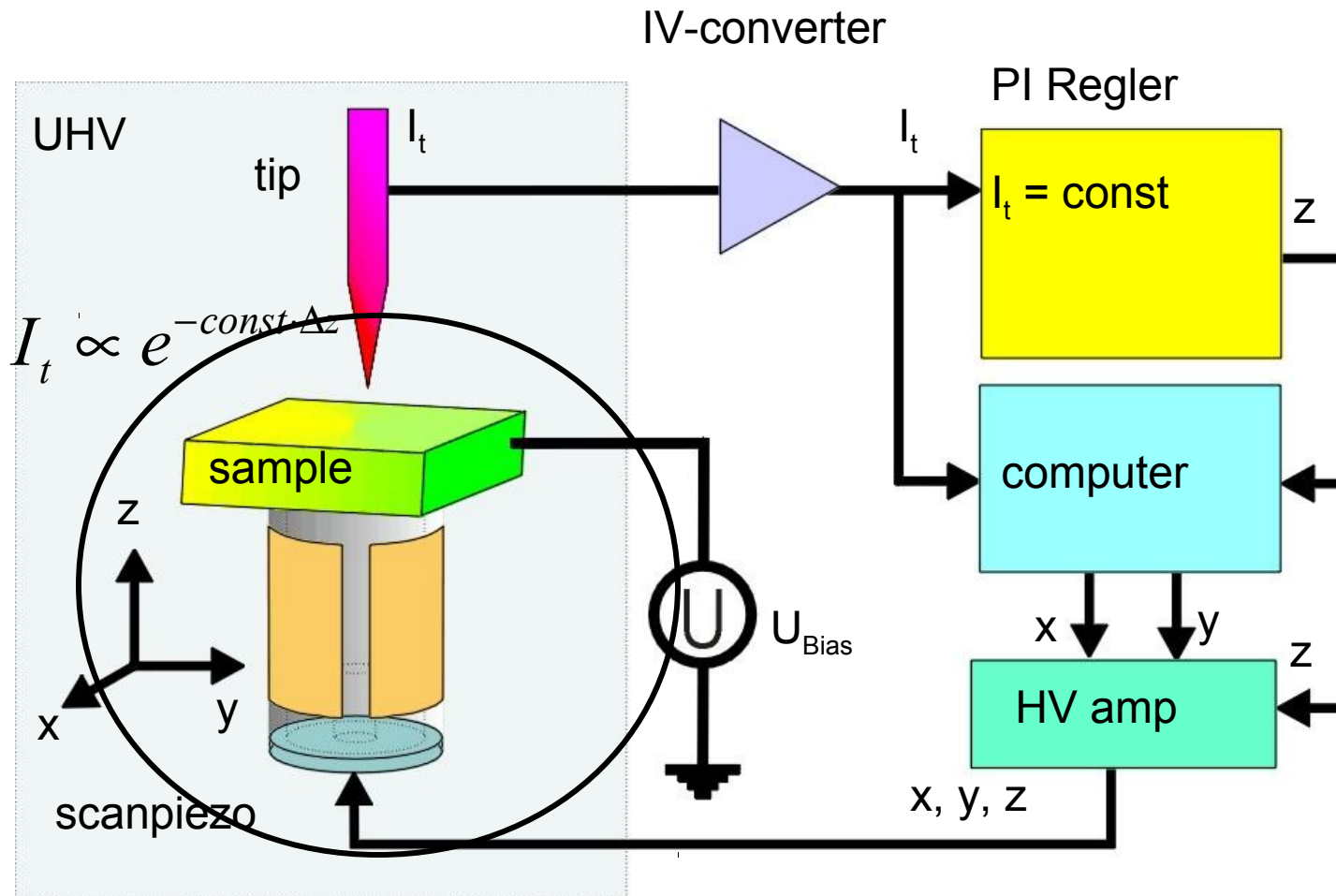


PI Regler

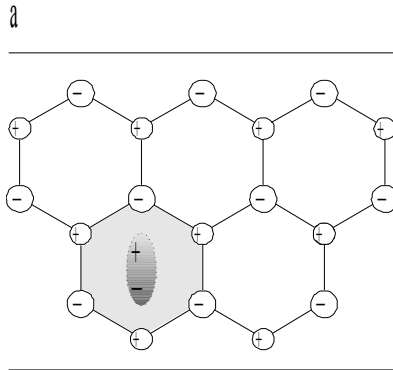
Regelt den Abstand Spitze-Probe so, dass der Tunnelstrom konstant bleibt



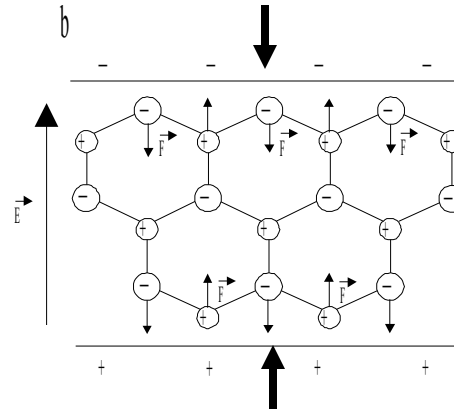
Blockschaltbild STM



Piezozos



Verschiedene
Ladungsschwerpunkte



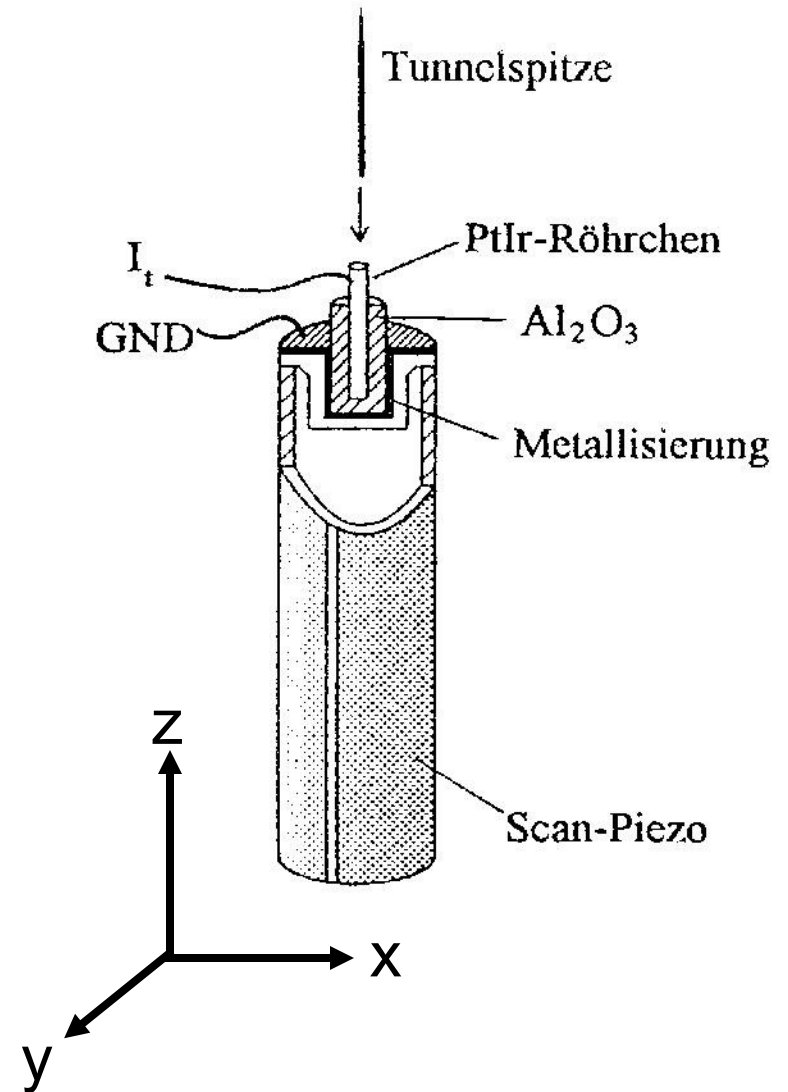
Verformung
durch
Anlegen einer
elektrischen
Spannung

Typische Piezoelektrische Materialien:

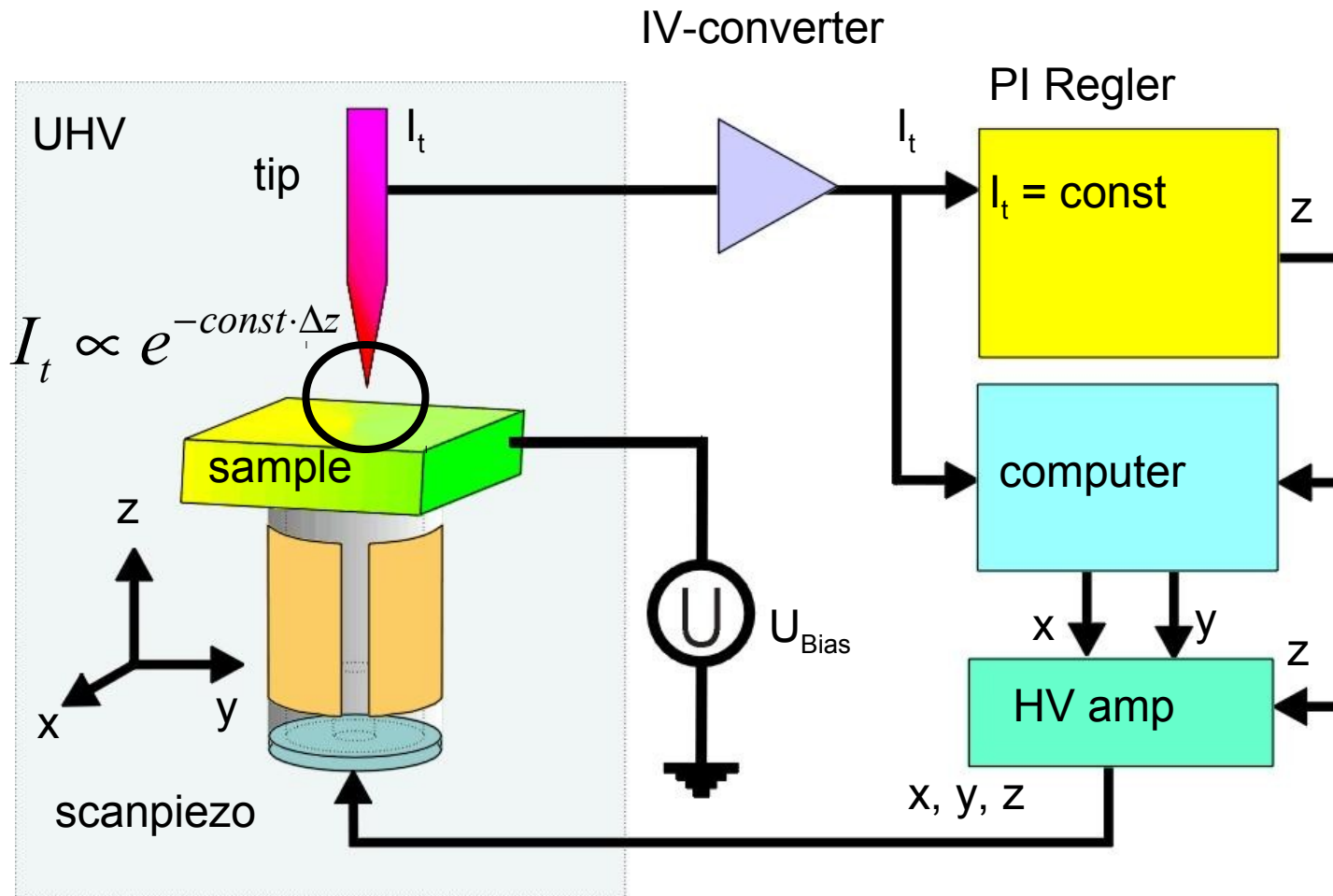
- Quarz
- Bariumtitanat
- Bleizirkontitanat (PZT)
- Etc.

Piezotubes

XYZ-Stellglieder

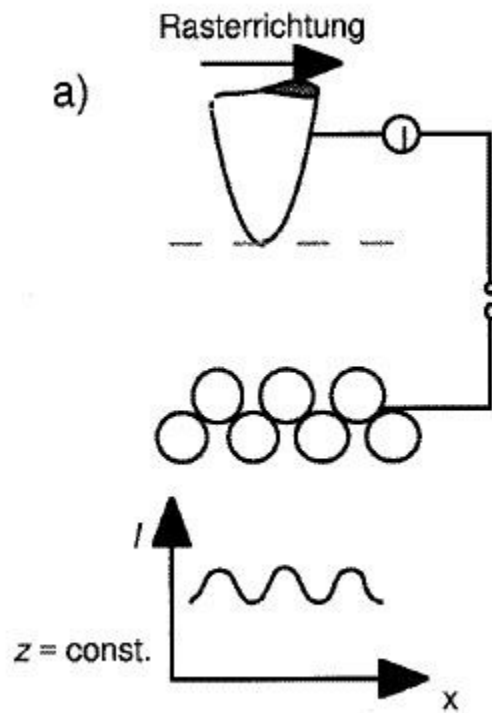


Blockschaltbild STM

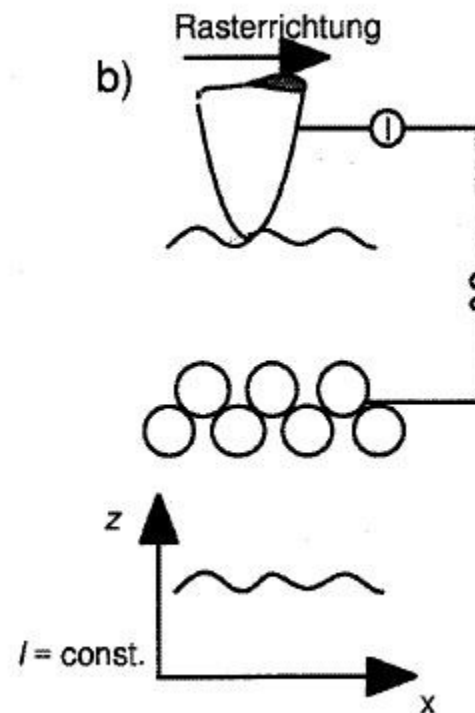


Messmodi

Constant Height



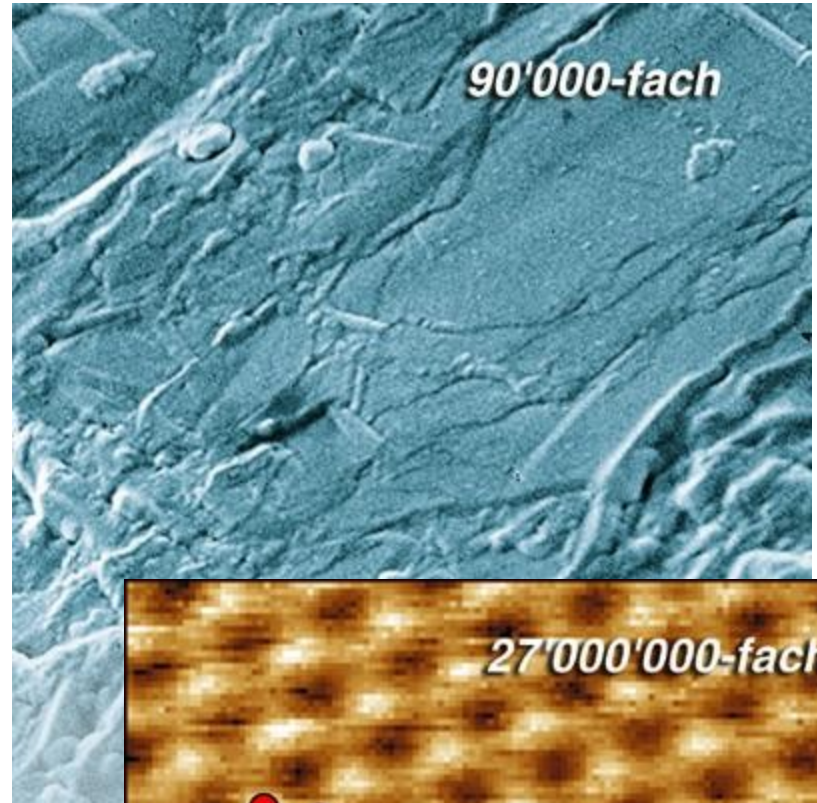
Constant Current



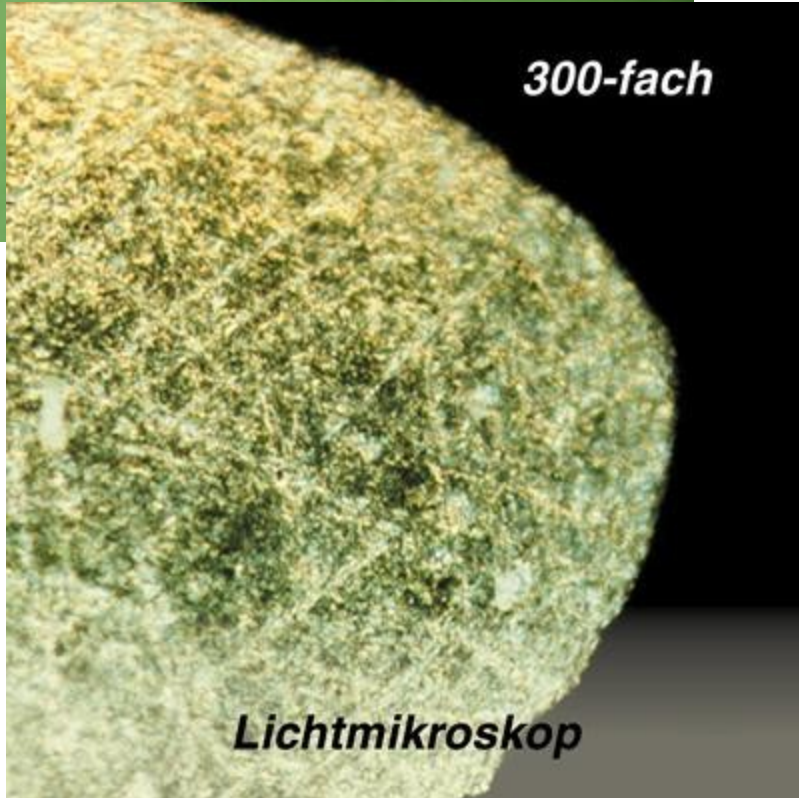
Originalgrösse



90'000-fach

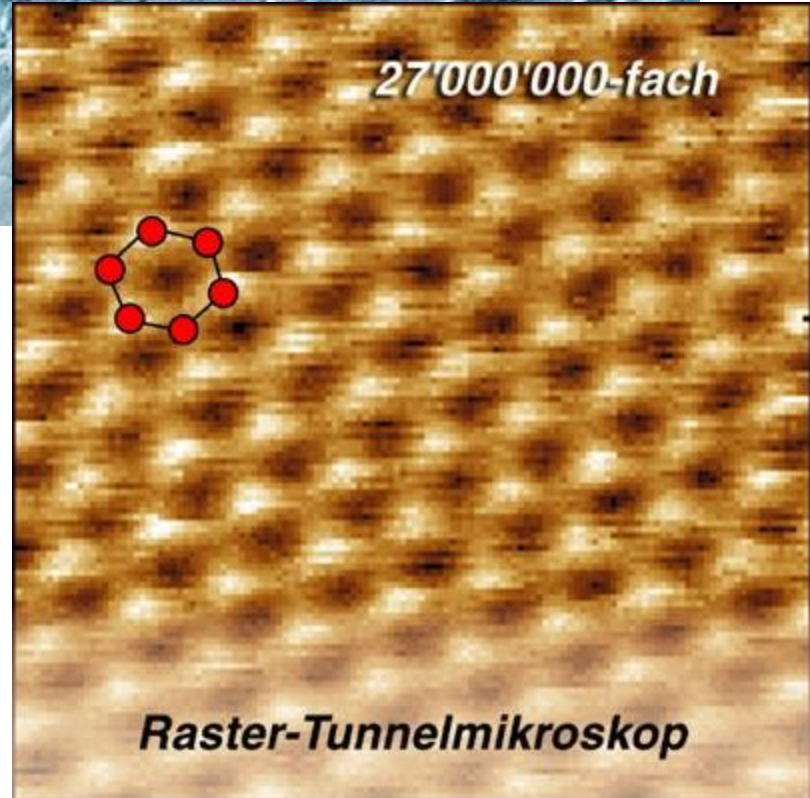


300-fach



Lichtmikroskop

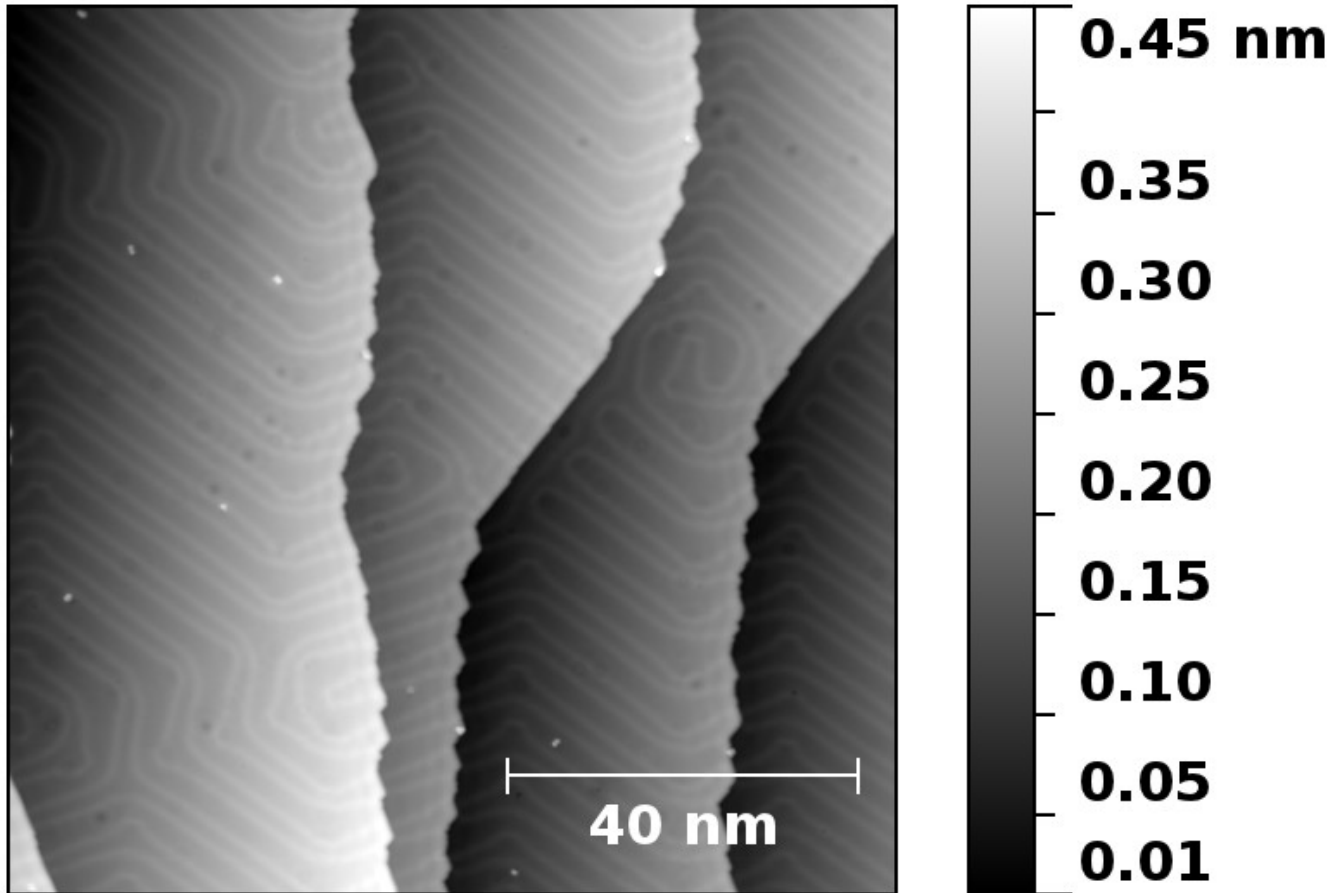
27'000'000-fach



Raster-Tunnelmikroskop

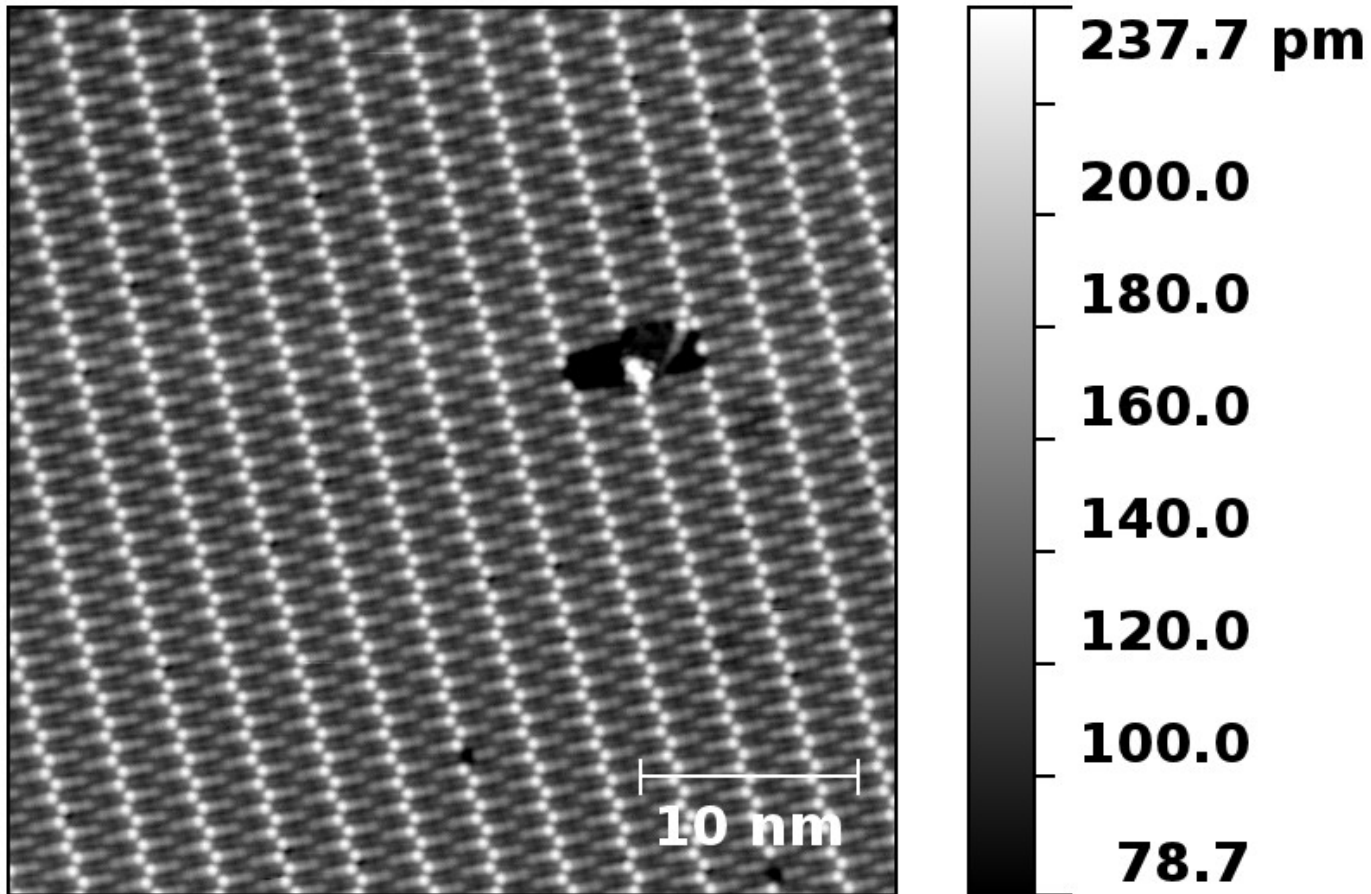
Au (111) surface

$V_{\text{bias}} = 200\text{mV}$, $I_{\text{T}} = 10\text{pA}$, $T = 4\text{K}$



DA molecules on Ag(111)

$V_{\text{bias}} = 200\text{mV}$, $I_{\text{T}} = 2\text{pA}$, $T = 4\text{K}$

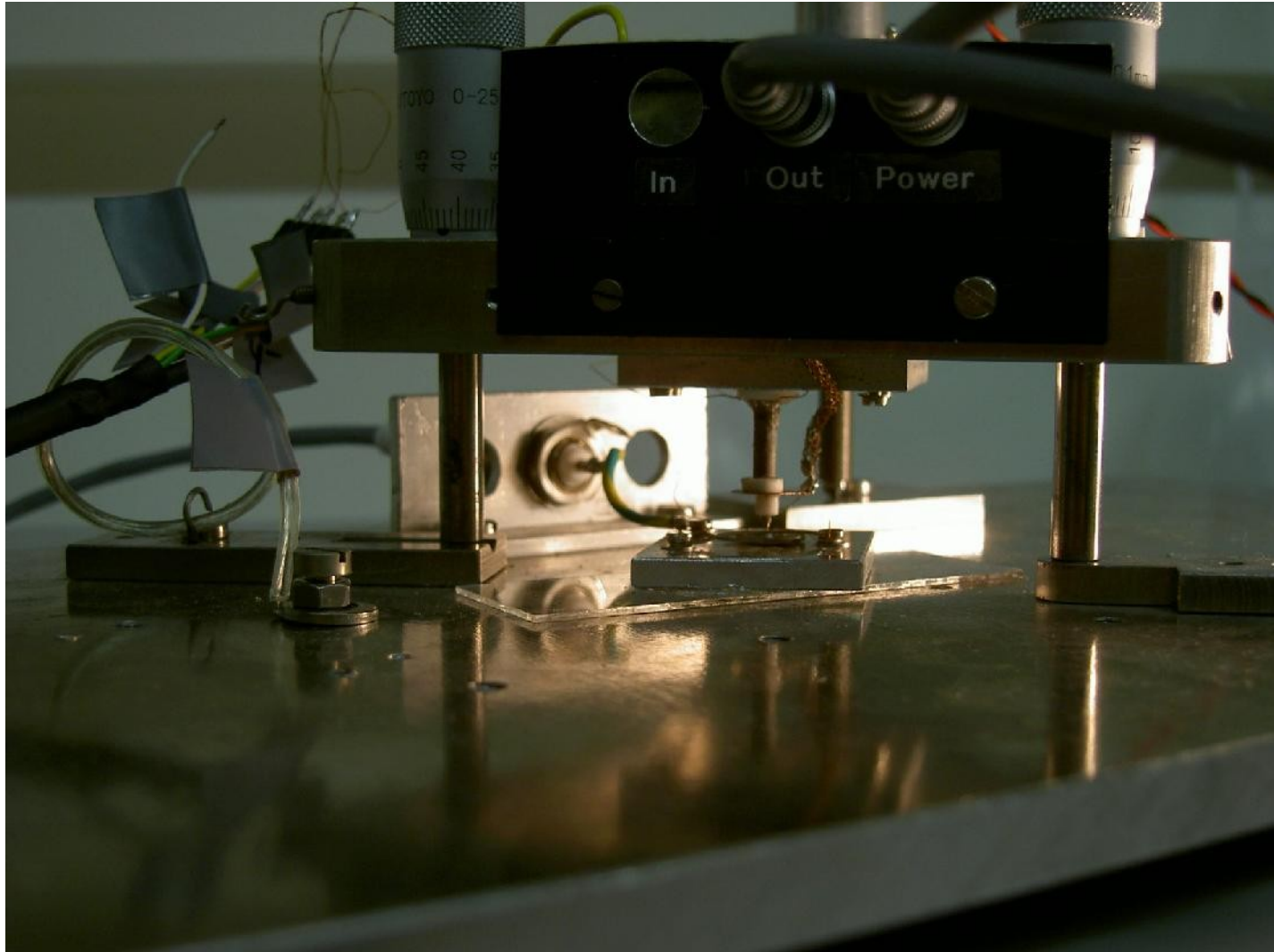






Nanosurf AG, Liestal

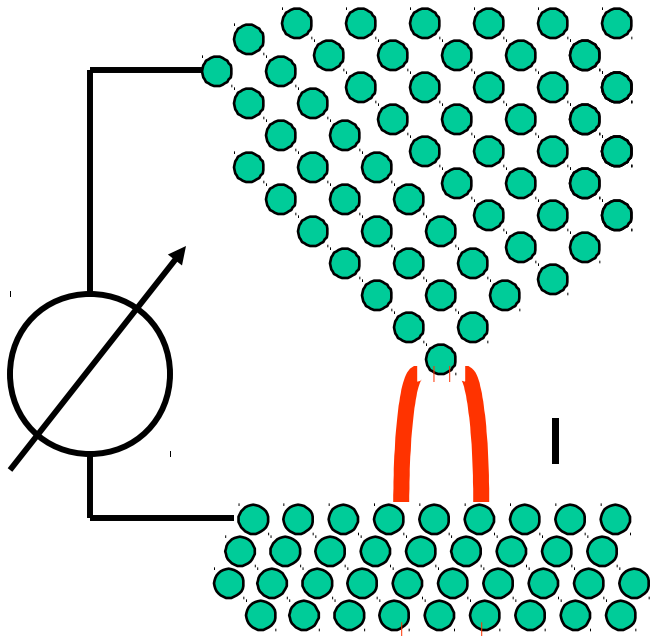
Do-it-yourself-STM Projektstudie



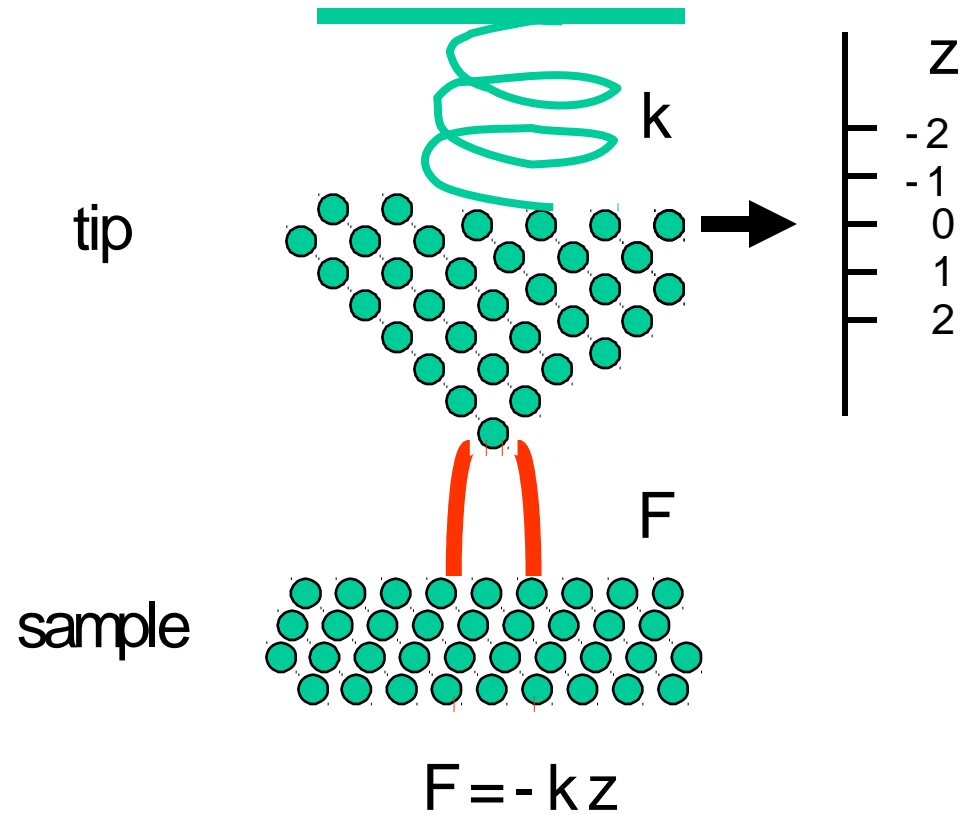
Blockkurs SPM !

Scanning X Microscopy

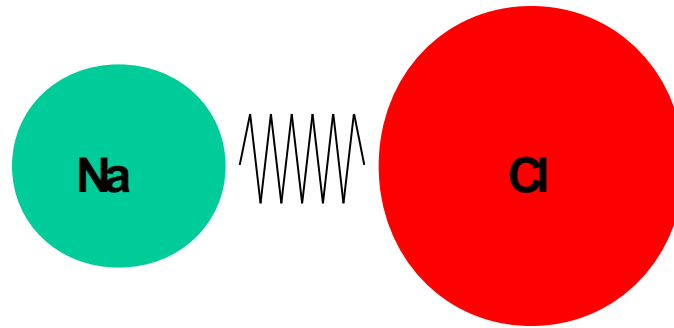
S Tunneling M



S Force M



Kräfte zwischen zwei Atomen

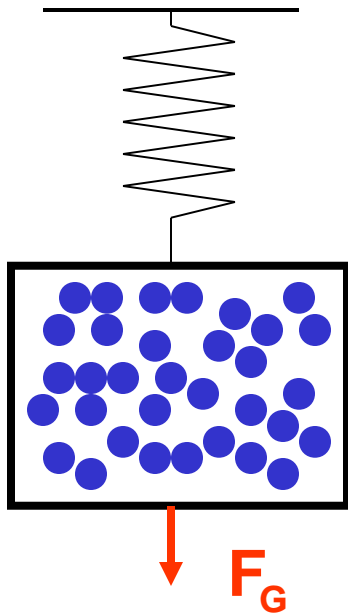


Chemische Bindung

$$F_{\text{chem}} = 1\text{eV} / 0.1\text{ nm}$$

1.6 nN

„Kräfte Spüren“



1 nm³ Wasser (33 Moleküle)

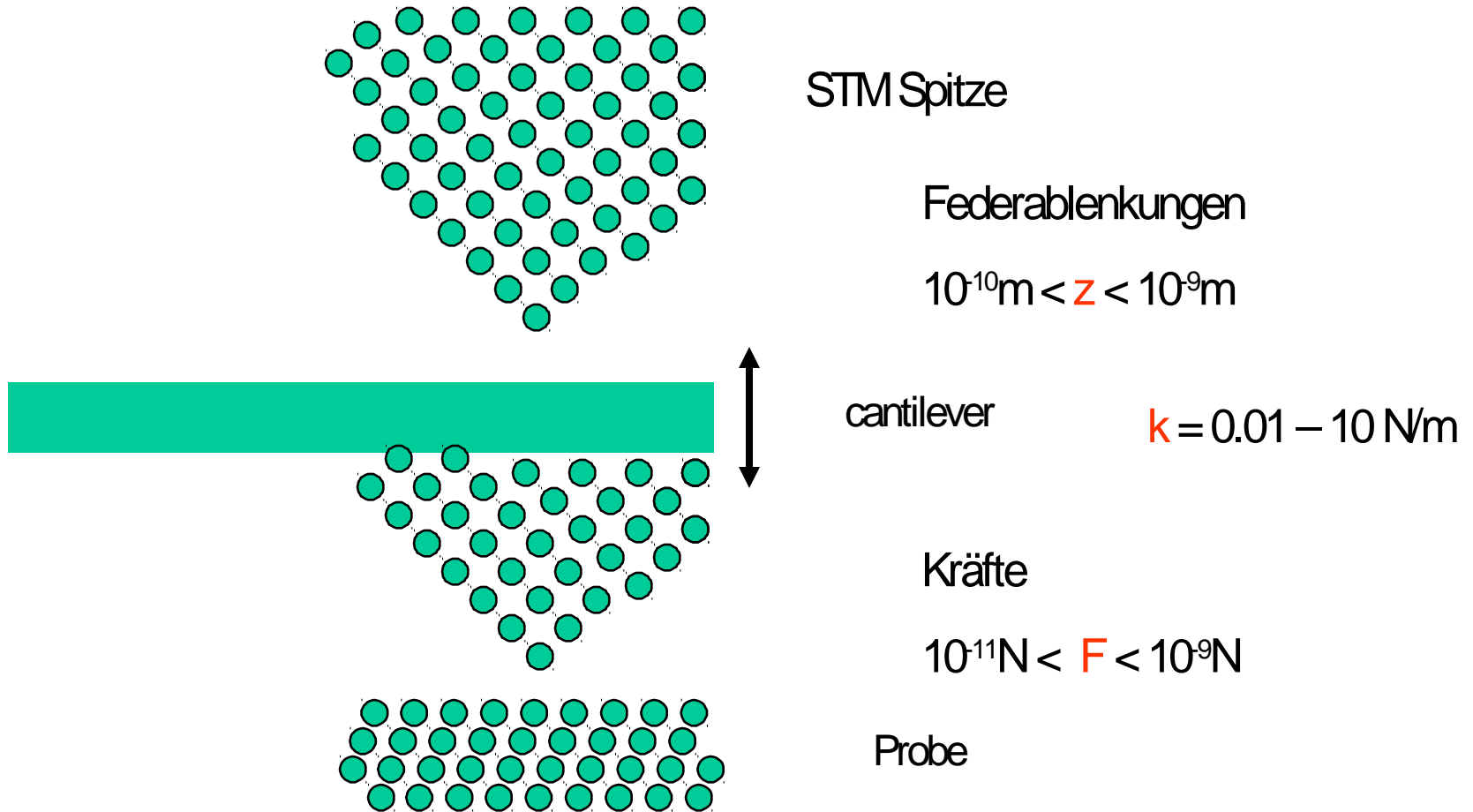
$$F_G = 10^{-23} \text{ N} = 10^{-14} \text{ nN}$$



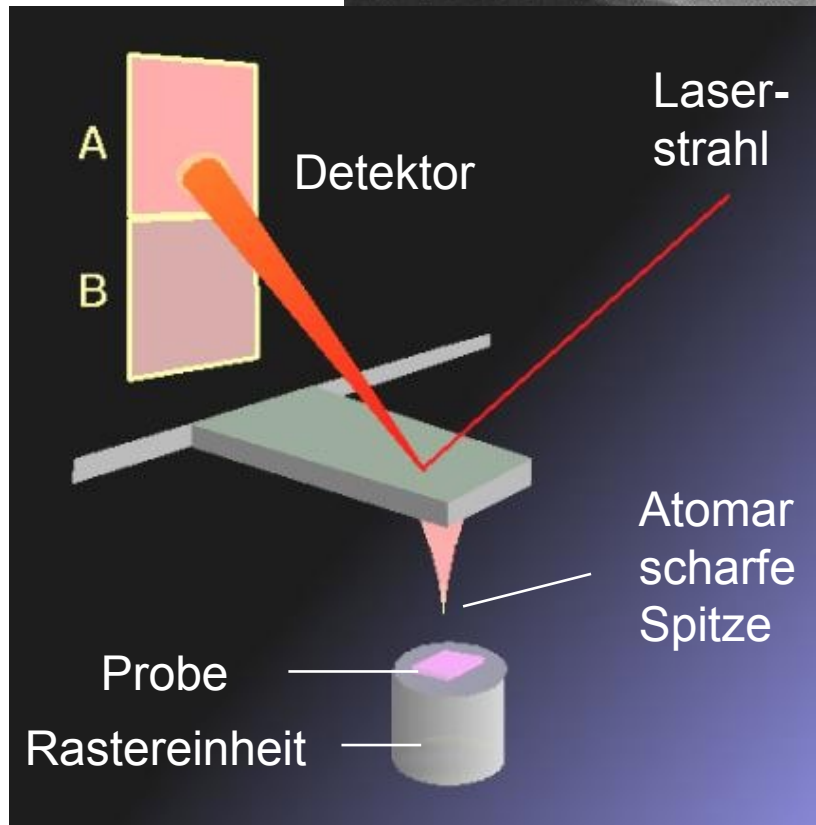
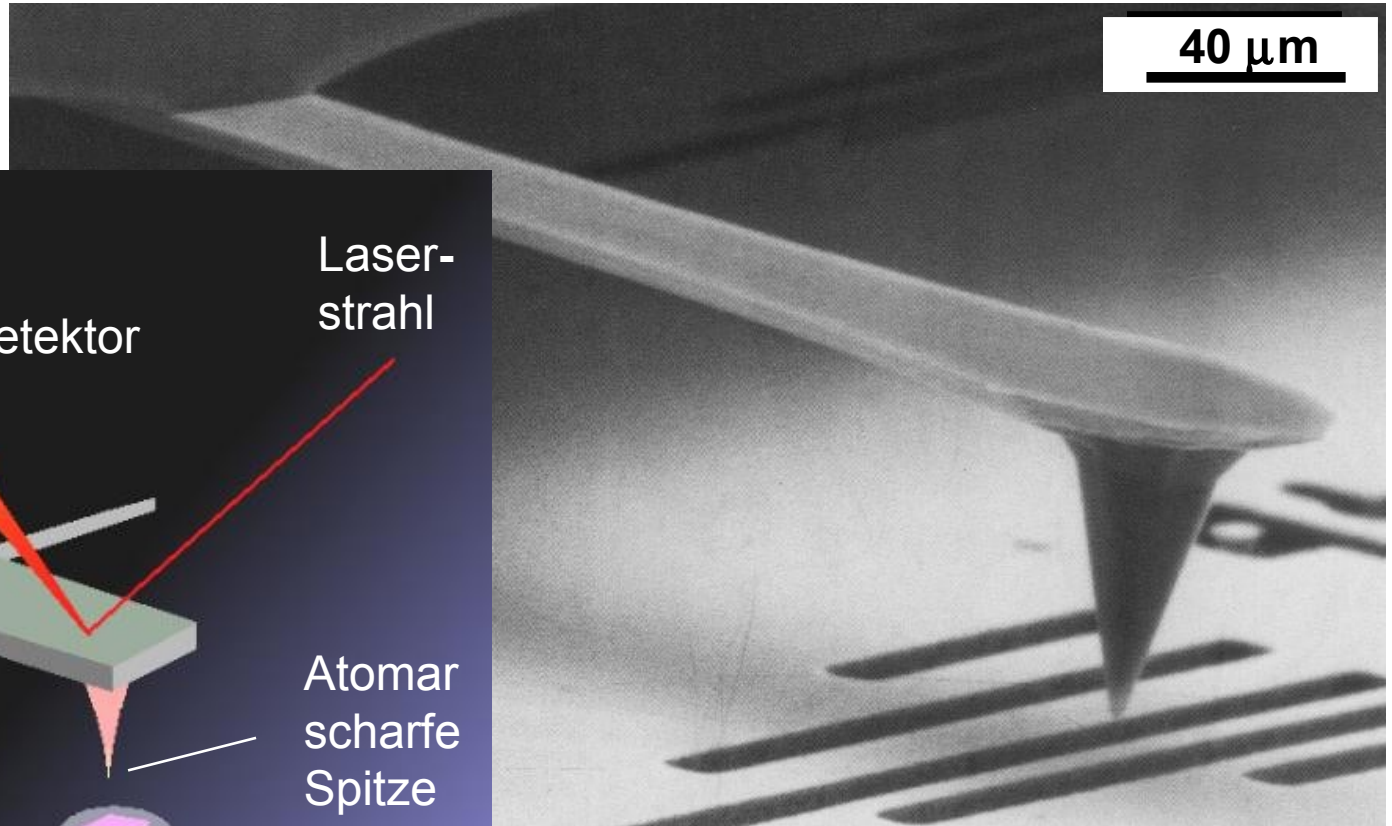
0.01 g

$$F = 0.1 \text{ mN} = 10^5 \text{ nN}$$

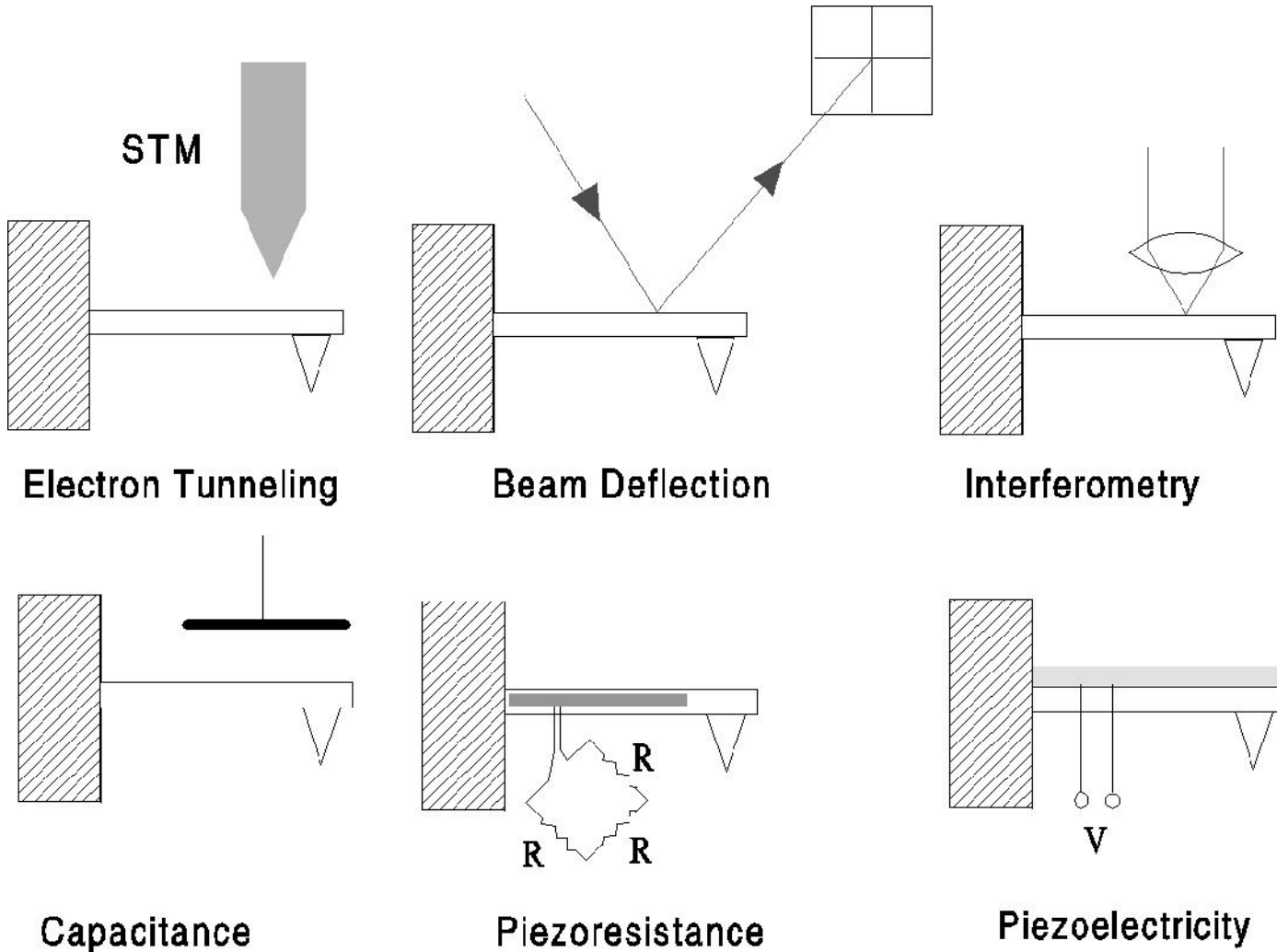
Prinzip des ersten AFMs



„Beam deflection“-Methode



Ablenkungssensoren



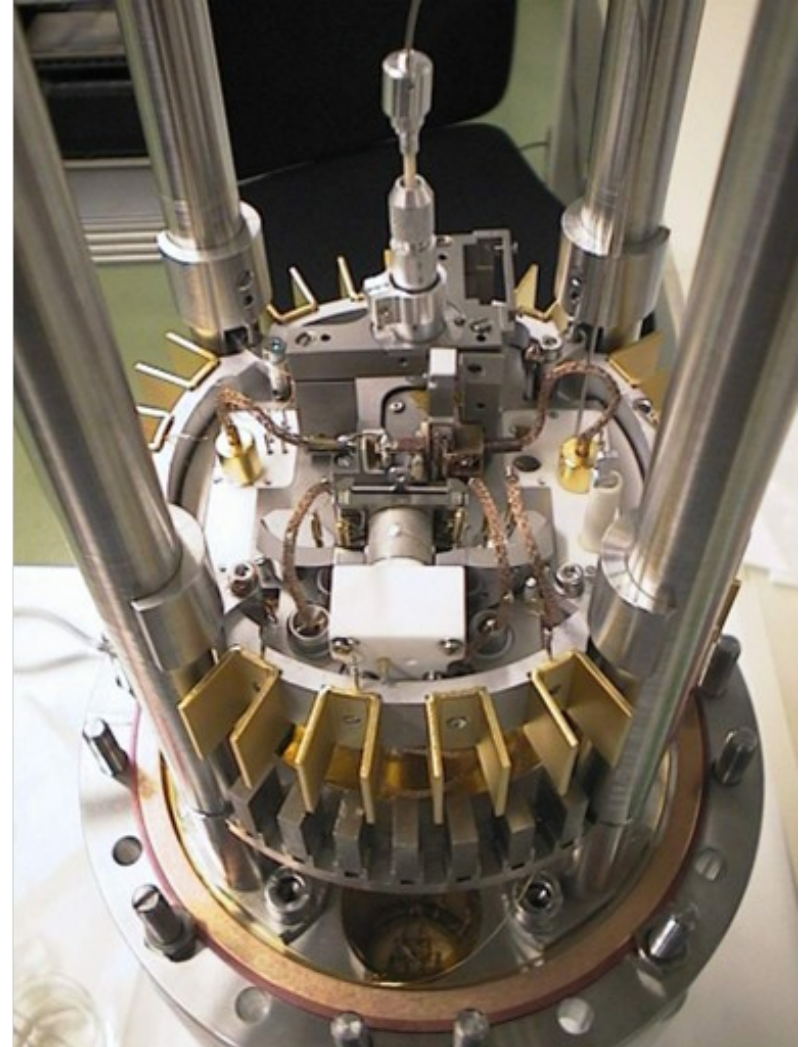
Multimode (Bruker)



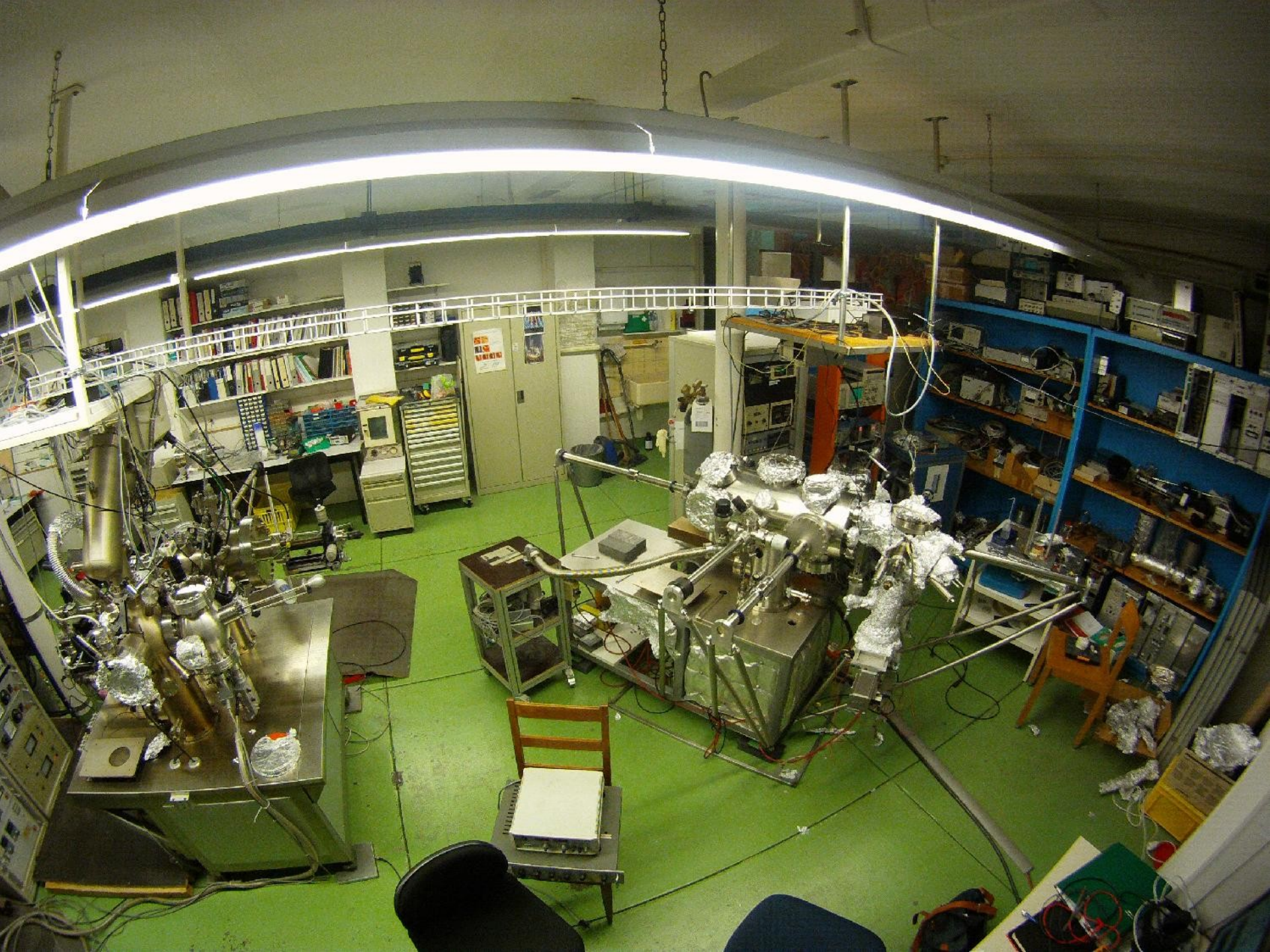
Nanosurf



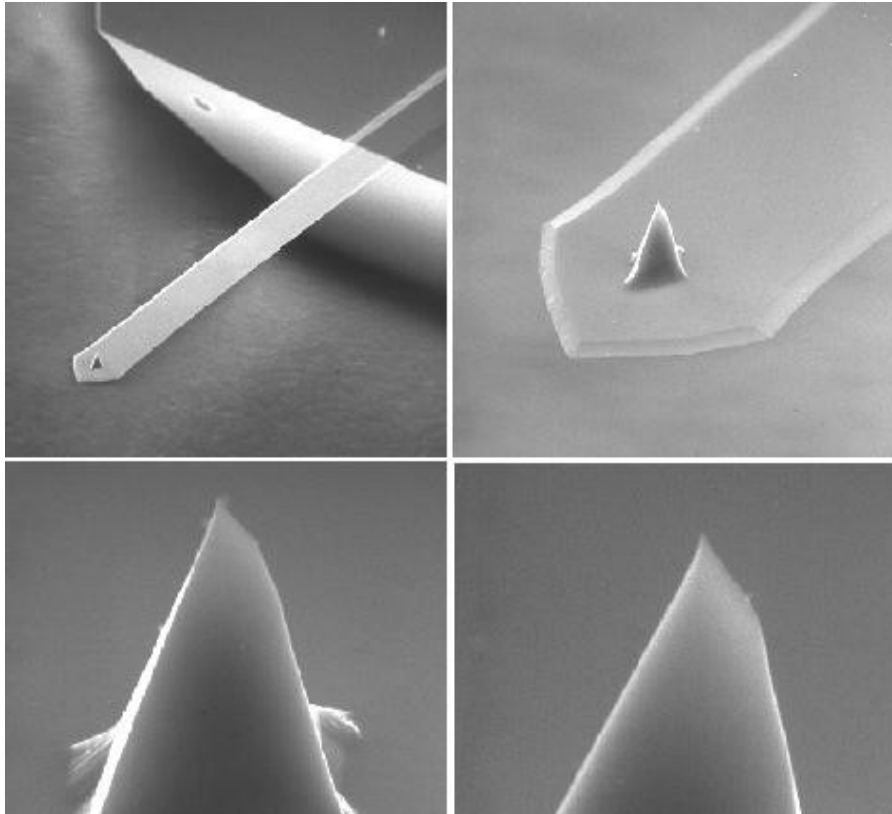
Beispiele



Uni Basel, UHV AFM/STM



Microfabrizierte “Cantilever”



Länge : $l = 450 \mu\text{m}$

Breite : $w = 45 \mu\text{m}$

Dicke: $t = 1.5 \mu\text{m}$

$E = 1.69 \cdot 10^{11} \text{N/m}^2$

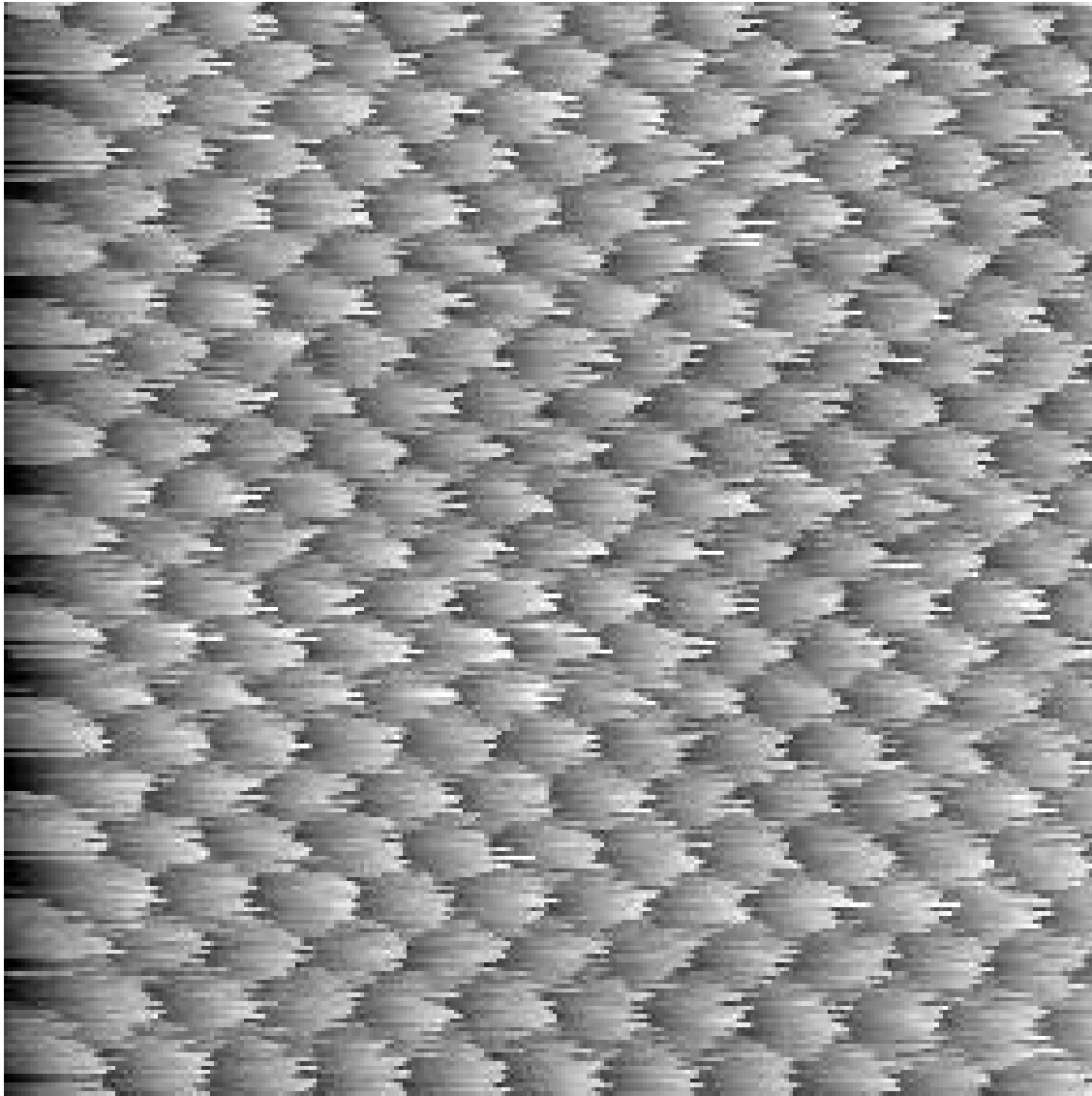
Spitzenhöhe: $12 \mu\text{m}$

Spitzenradius: 10nm

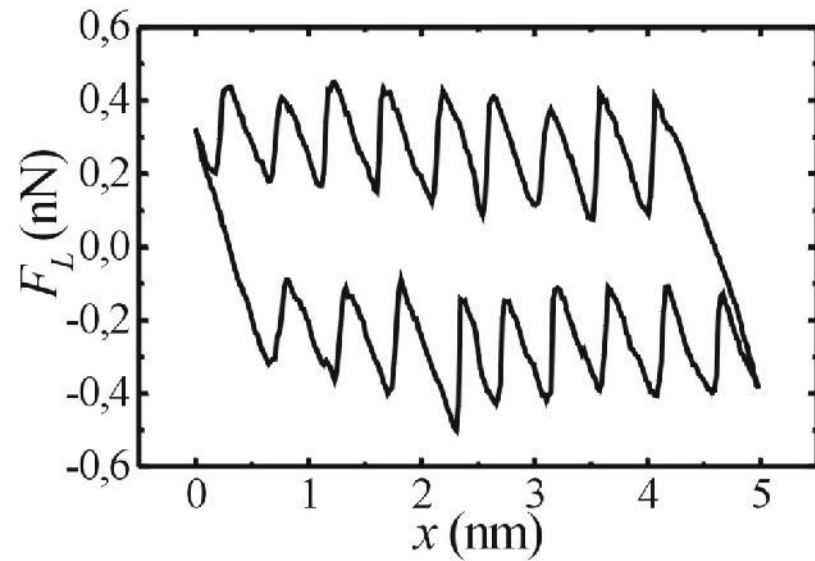
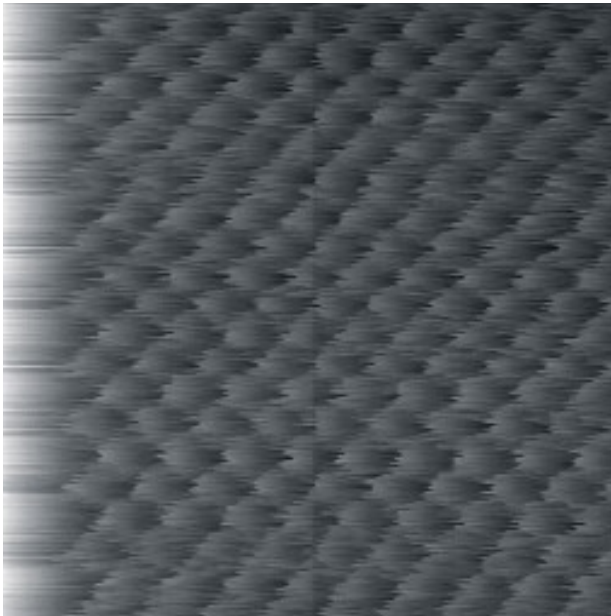
Federkonstante k :

$$k = \frac{Ewt^3}{4l^3} = 0.15 \text{ N/m}$$

atomare Reibung von NaCl Oberflächen



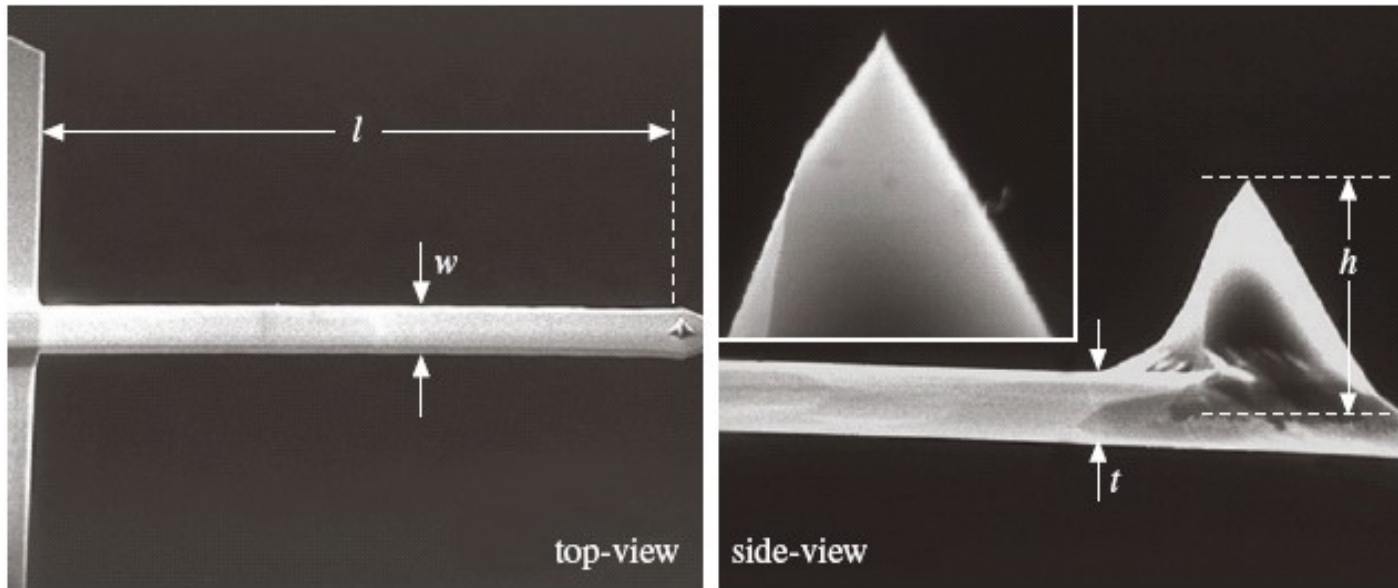
Atomic stick-slip



(friction map and friction loop on NaCl(100) in UHV)

Force Calibration

- Simple if **rectangular** cantilevers are used
- Cantilever width, thickness and length, tip height: from **SEM pictures**



Force Calibration

- Cantilever **thickness** also from the **resonance frequency**:

$$t = \frac{2\sqrt{12}\pi}{1.875^2} \sqrt{\frac{\rho}{E}} f_0 l^2$$

- ρ , E : density and Young modulus

(Nonnenmacher et al., JVSTB 1991)

- For pure silicon:

$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

Force Calibration

- **Normal and lateral spring constants** of cantilever:

$$c_N = \frac{Ewt^3}{4l^3} \qquad c_L = \frac{Gwt^3}{3h^2l}$$

- G: shear modulus
- For pure silicon:

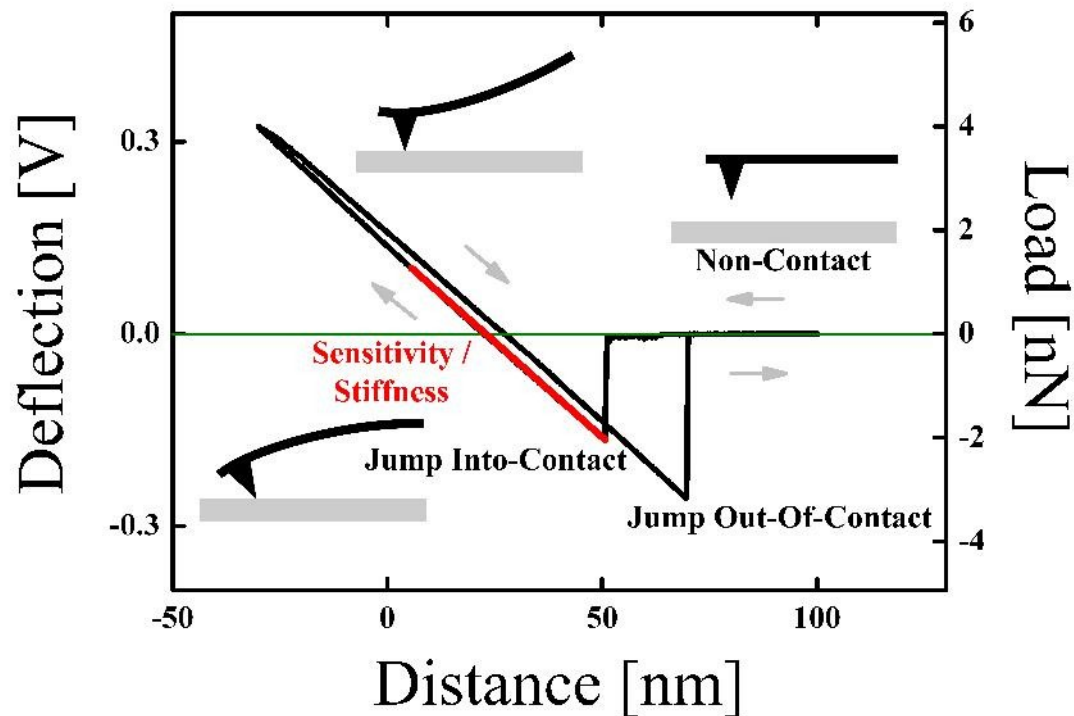
$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

$$G = 0.5 \cdot 10^{11} \text{ N/m}^2$$

Force Calibration

- Next step: **sensitivity of photodetector**
- Force-distance curves on hard surfaces (e.g. Al_2O_3):



- Scanner movement = cantilever deflection
- Slope \rightarrow sensitivity

Force Calibration

- **Normal and lateral forces:**

$$F_N = c_N S_z V_N \qquad F_L = \frac{3}{2} c_L \frac{h}{l} S_z V_L$$

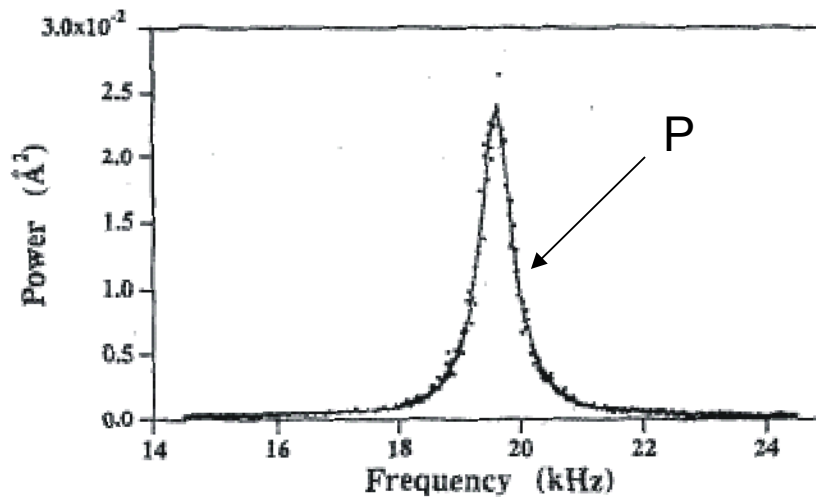
(if the laser beam is above the probing tip!)

- V_N , V_L : normal and lateral signals

Force Calibration

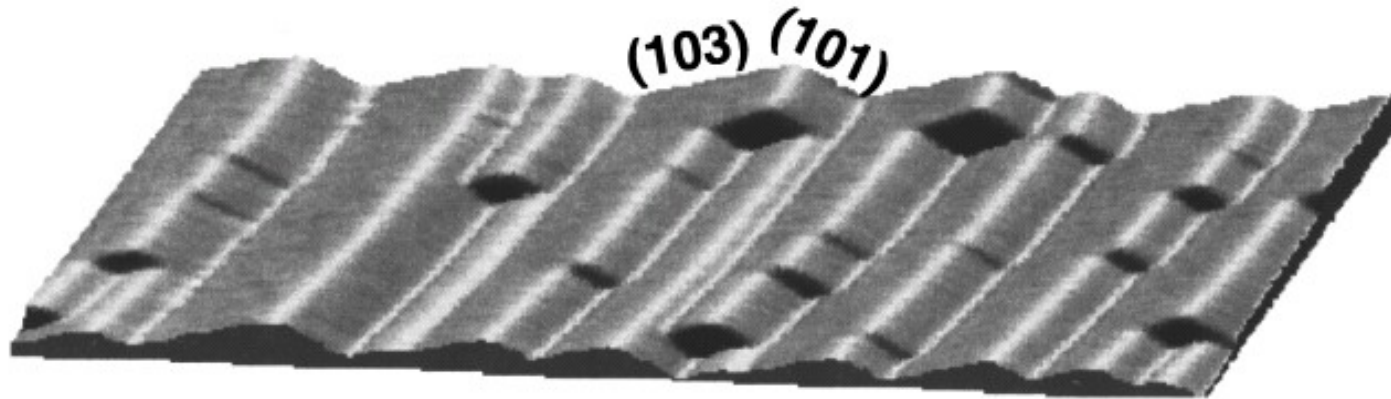
- Alternative method: Spring constant **from thermal power spectrum** (Hutter et al., RSI 1993)
- Correct relation (Butt et al., Nanotech. 1995):

$$c_N = \frac{4k_B T}{3P}$$

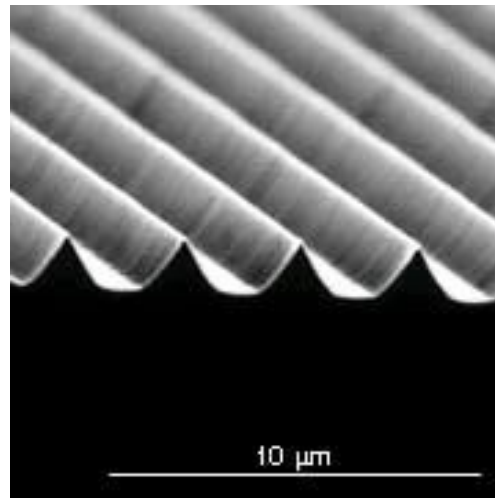


Force Calibration

- Alternative method: Scanning over profiles with **well-defined slope** (Ogletree et al., RSI 1996)



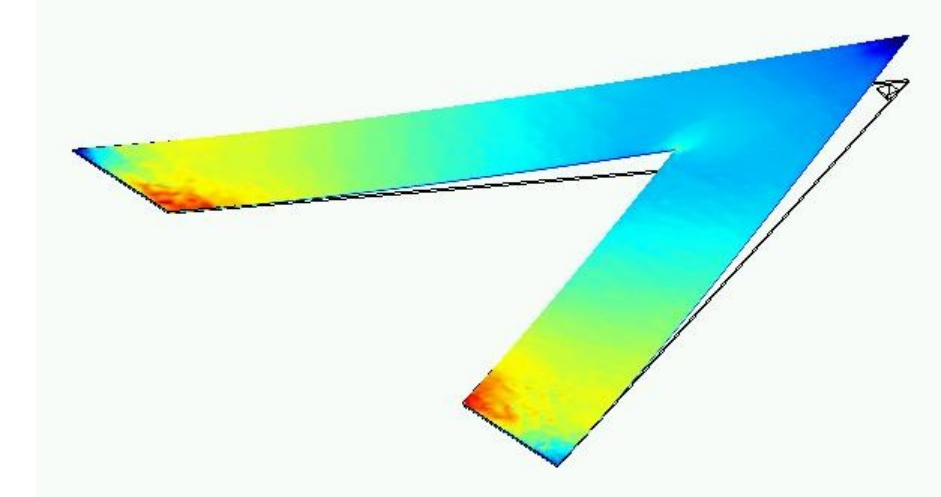
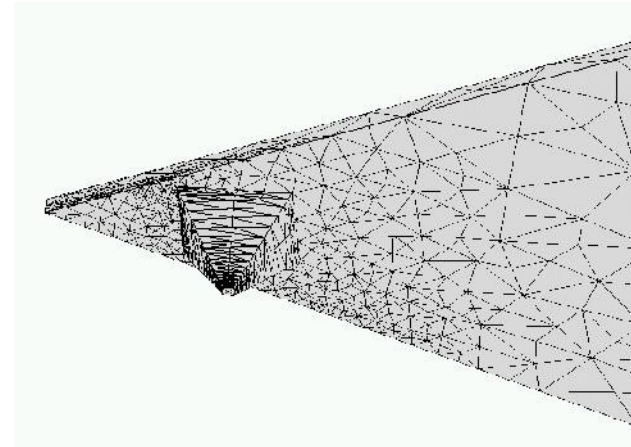
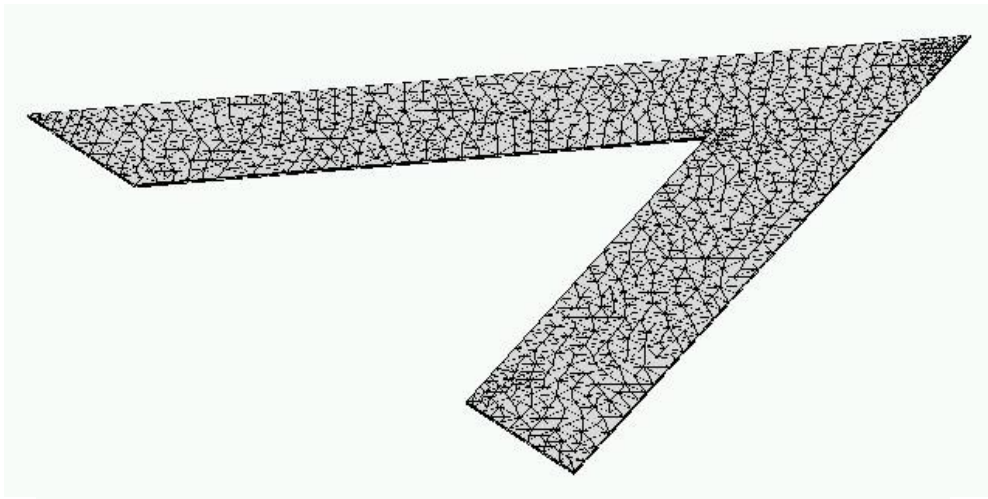
Commercially available grating:



(TGG01, NT-MDT,
Moscow)

Force Calibration

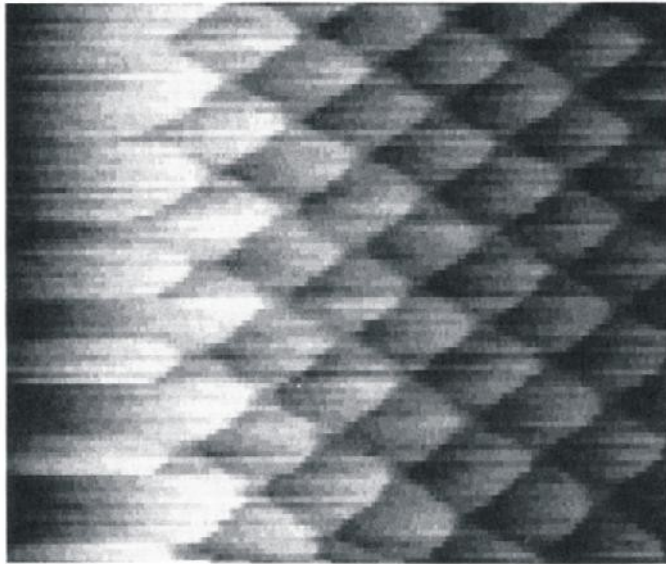
- Different shapes → **Finite elements analysis**



(Femlab™ 3.0)

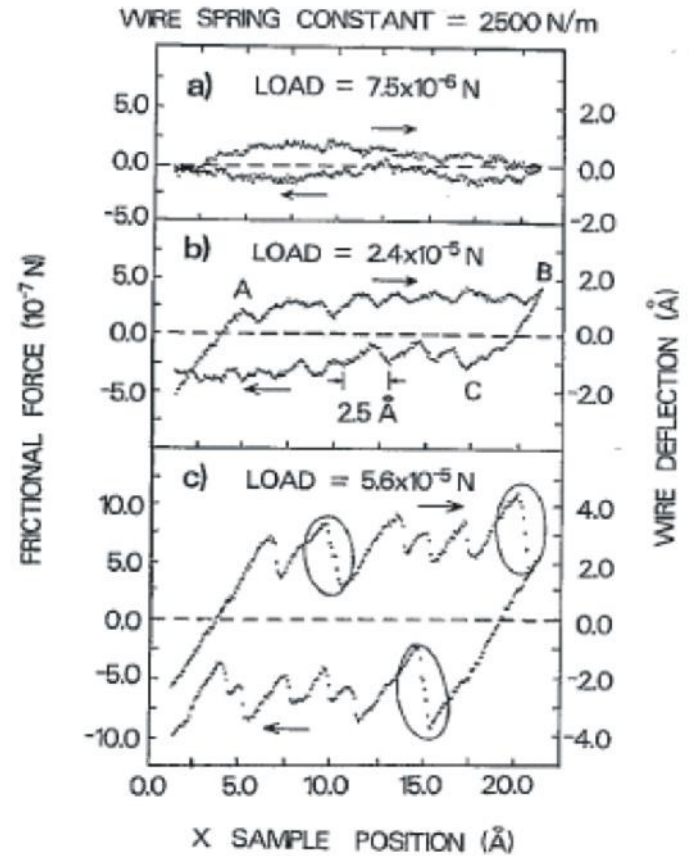
Atomic-Scale Measurements

- Atomic friction on **graphite**:



2 nm

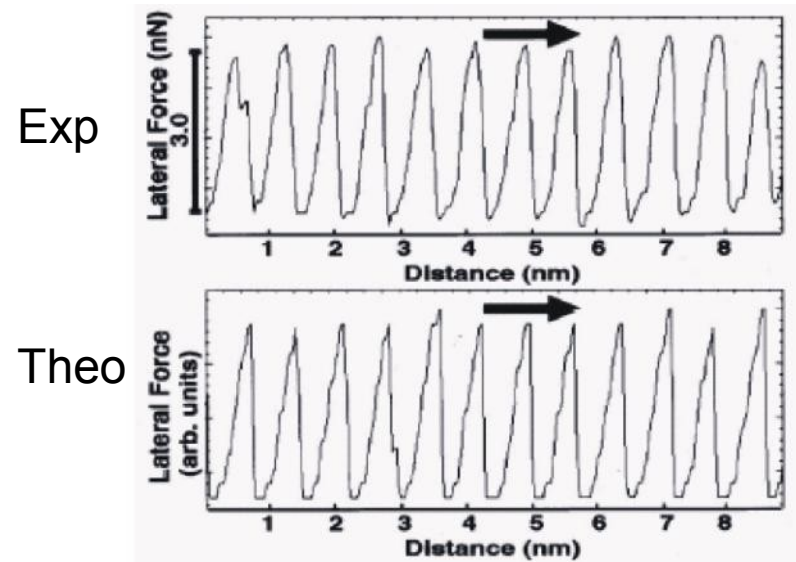
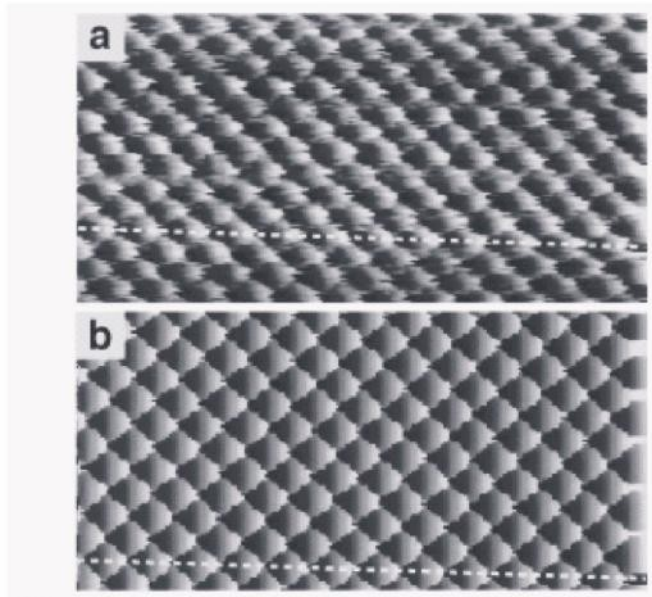
(Mate at al., PRL 1987)



Atomic-Scale Measurements

- Friction on **insulating surfaces** (Lüthi et al., JVSTB 1996):

KBr

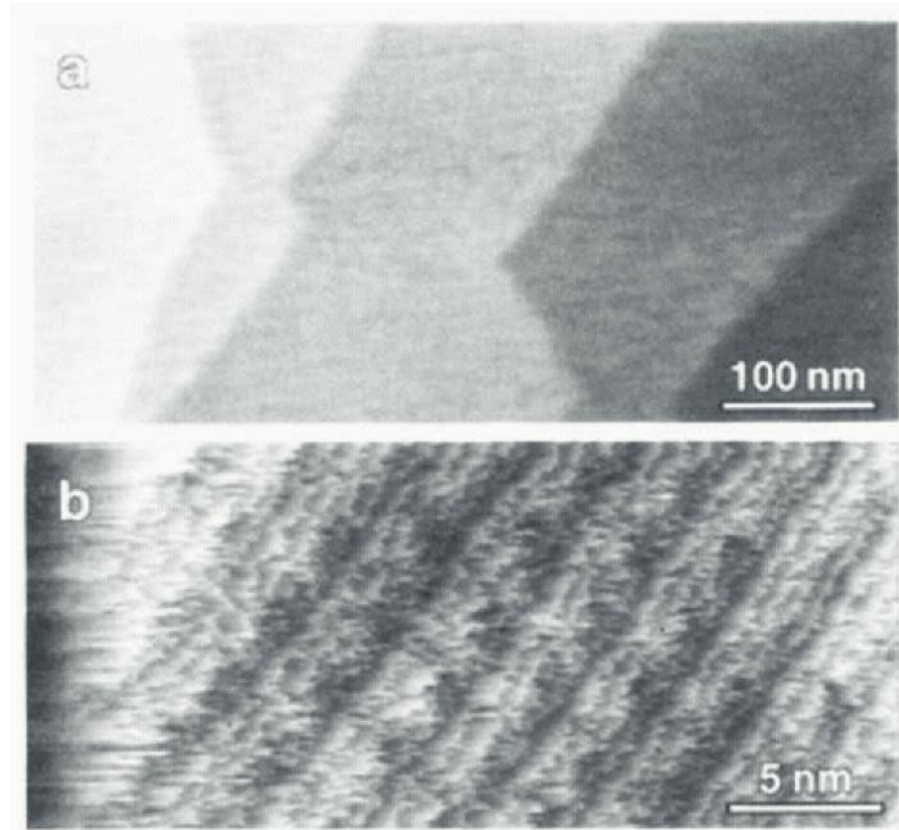


- No individual defects are observed

Atomic-Scale Measurements

- Friction on **semiconductors** (Howald et al., PRB 1995):

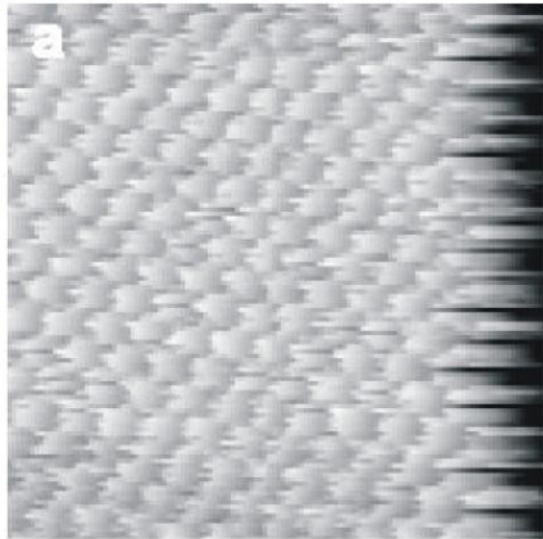
Si(111)7x7



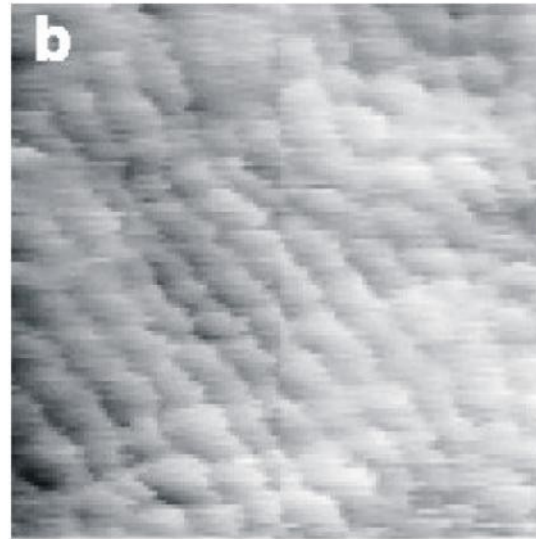
(tip coated with PTFE)

Atomic-Scale Measurements

- Friction on **metal surfaces** (Bennewitz et al., Trib. Lett. 2001):



Cu(111)

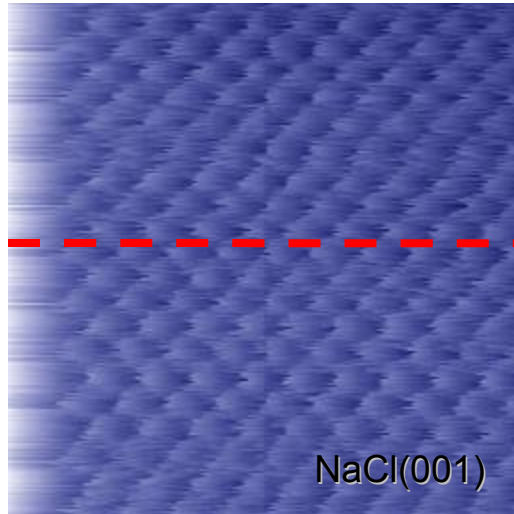


Cu(100)

Irregular features on the (100) surface (less packed!)

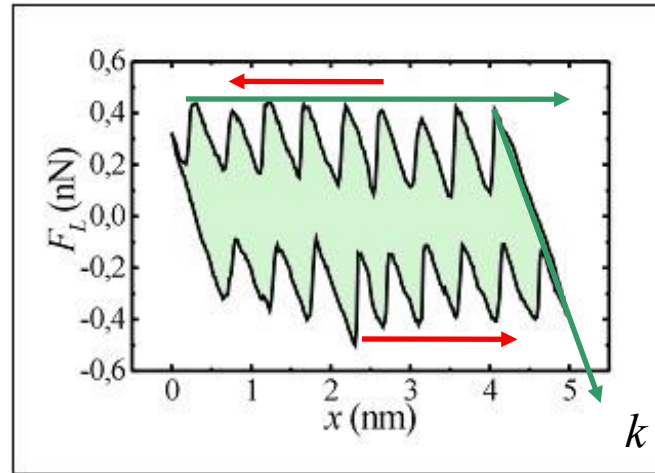
Atomic friction on crystal surfaces

Our model systems: alkali halide surfaces (easy preparation, simple structure)

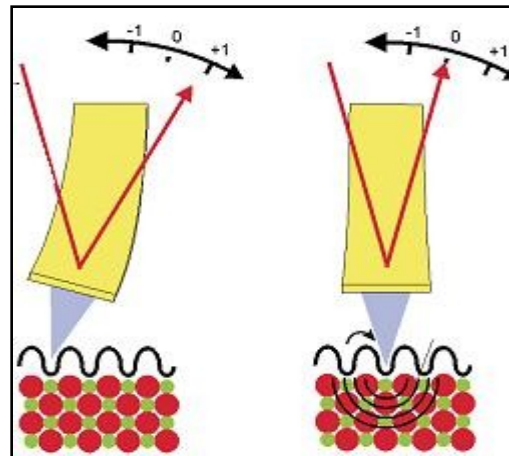


5 nm

Tomlinson model:
(Phyl. Mag. 1929)



$$F_L^{\max} = \frac{2\pi V_0}{a}$$

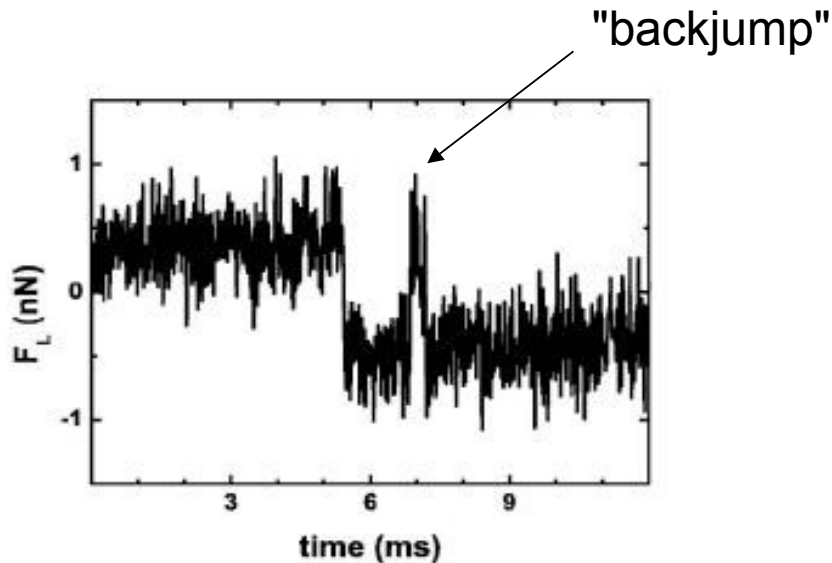
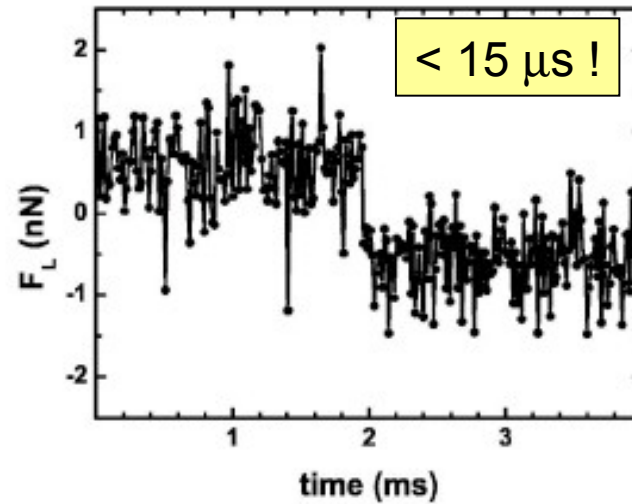
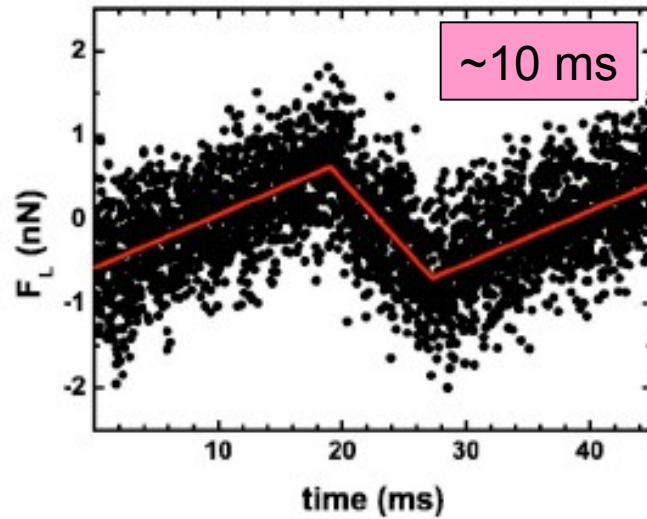


$$V_0 \sim 1 \text{ eV}$$

$$k \sim 1 \text{ N/m}$$

Atomic-Scale Measurements

- Wide distribution of slip durations:



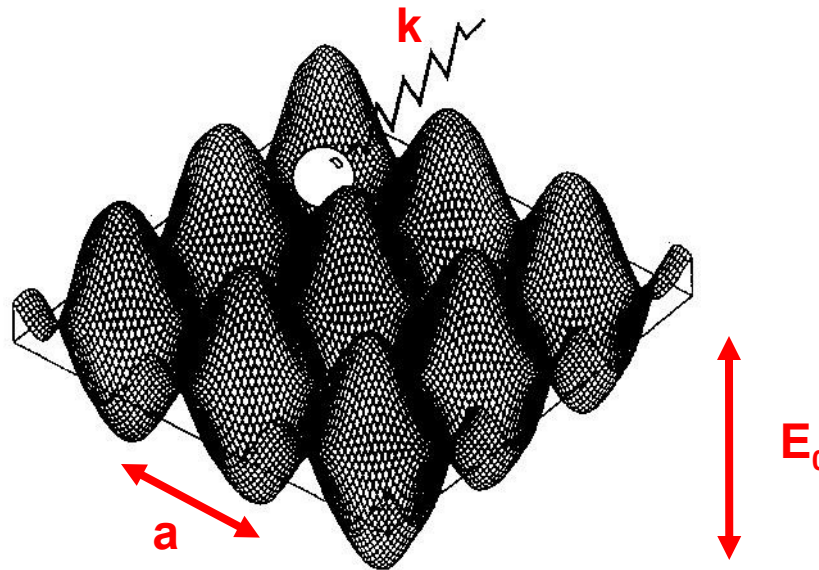
Why?

Modelling Atomic Friction

- The tip is subject to

- 1) periodic interaction with the underlying surface

- 2) elastic deformation of the cantilever



- In 1D the corresponding potential energies are represented by

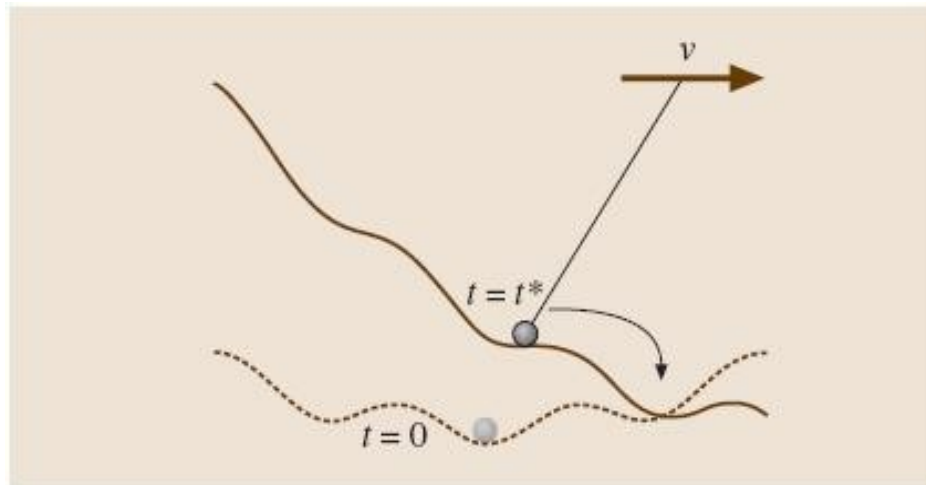
- 1) a sinusoid

- 2) a parabola

Modelling Atomic Friction

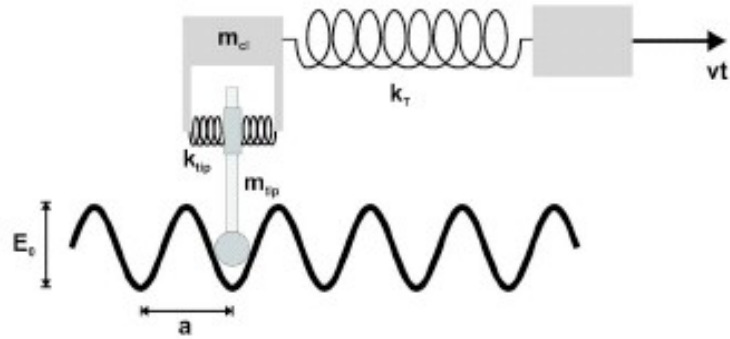
- Total energy of the system:

$$U_{\text{tot}}(x, t) = -\frac{E_0}{2} \cos \frac{2\pi x}{a} + \frac{1}{2} k_{\text{eff}} (vt - x)^2$$



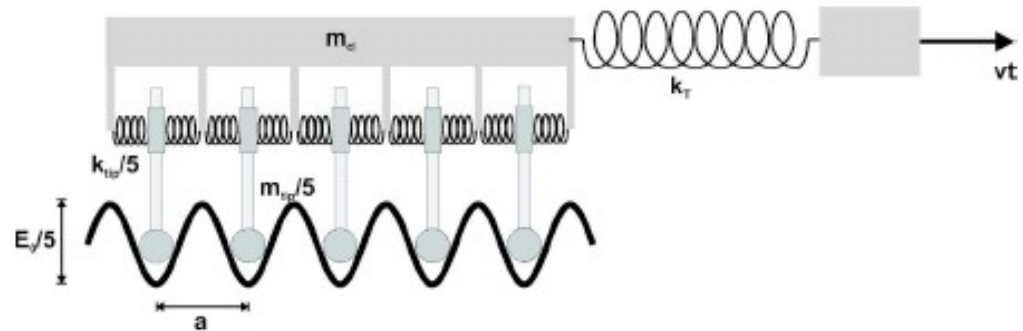
- The tip can "stick" to the minima of the potential profile

Modelling Atomic Friction



single contact

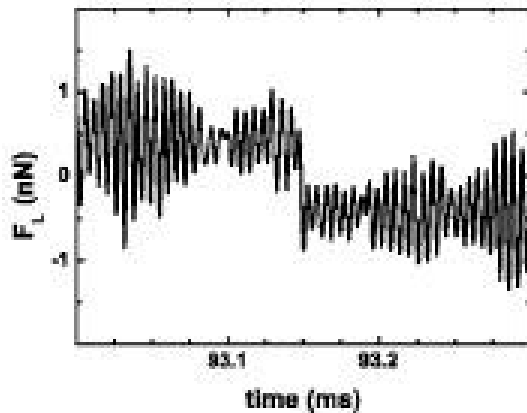
multiple contact



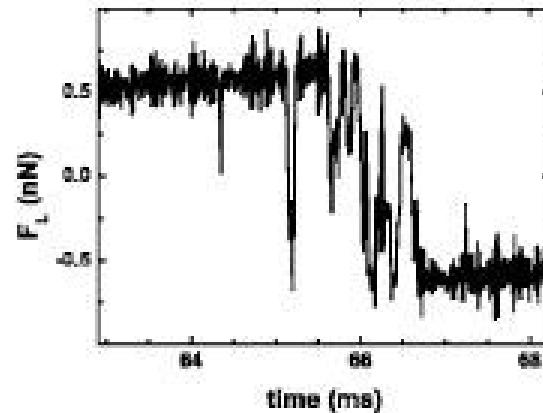
Modelling Atomic Friction

- Tip \rightarrow Langevin equation (including thermal noise)
- Cantilever \rightarrow Newton equation (without thermal noise)

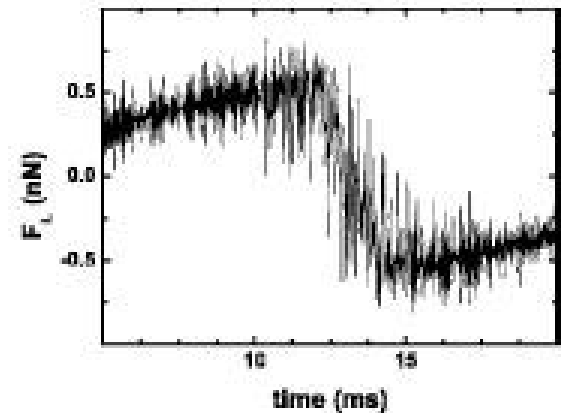
One tip



Three tips



Five tips

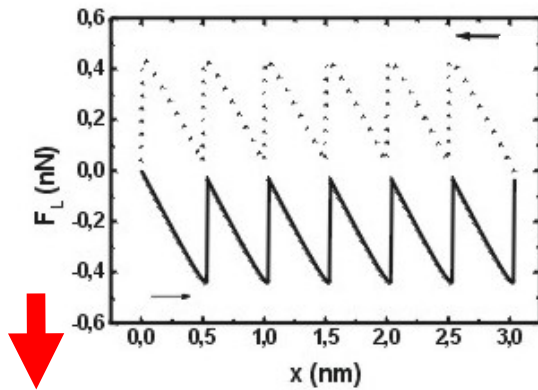


- Long slip times are found with multiple tips only
(Maier et al., PRB 2005)

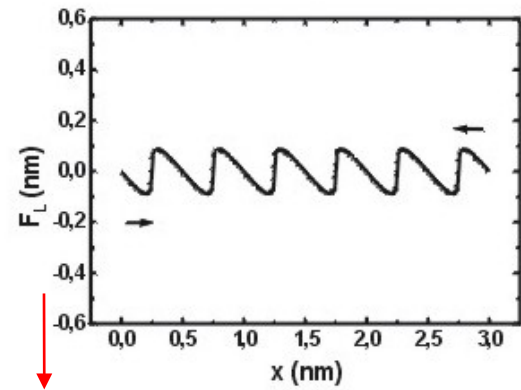
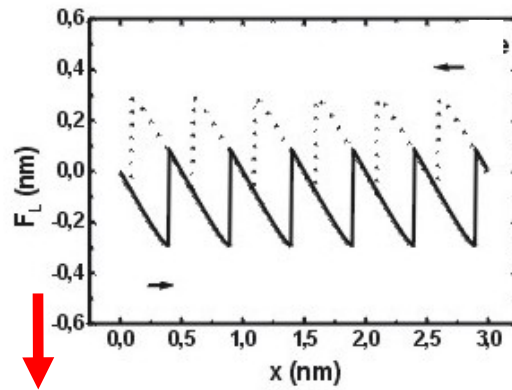
Superlubricity

- From the Tomlinson model (without thermal activation):

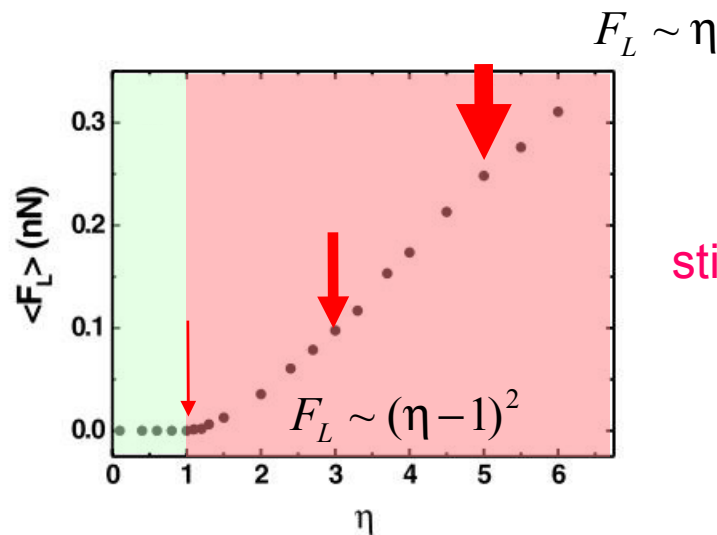
$$\eta > 1$$



$$\eta < 1$$



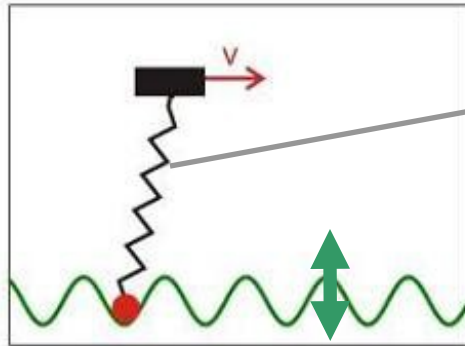
superlubric regime



stick-slip regime

“Dynamic superlubricity”

A third way to reduce friction: Tomlinson model with TIME modulation



$$V_{\text{elas}} = \frac{k\alpha^2}{2}$$

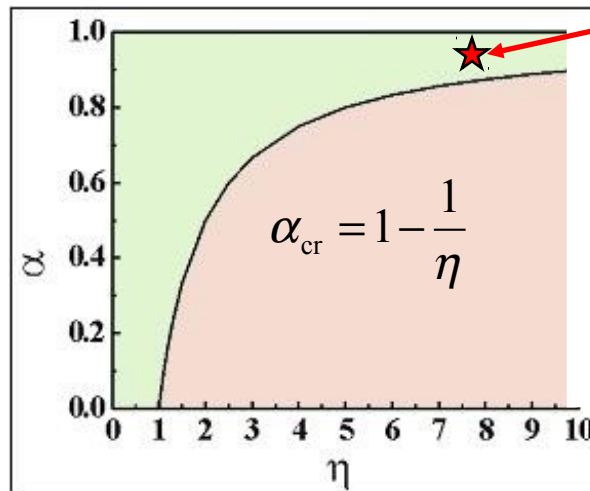
$$V_{\text{int}} = V_0 \cos \frac{2\pi x}{a}$$

$$\eta = \frac{(2\pi)^2 V_0}{k\alpha^2}$$

Phase-diagram in the η - α plane:

$$V_0 \rightarrow V_0(1 + \alpha \cos \omega t)$$

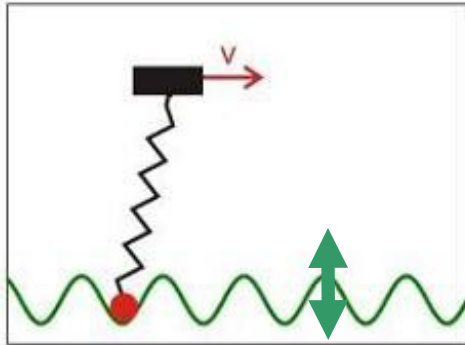
$$\eta_{\text{eff}} = \eta(1 - \alpha)$$



High loads
can be applied!

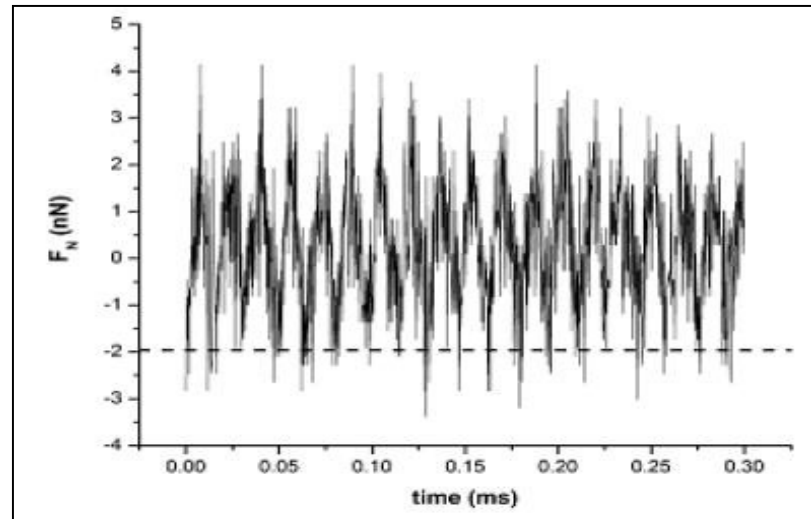
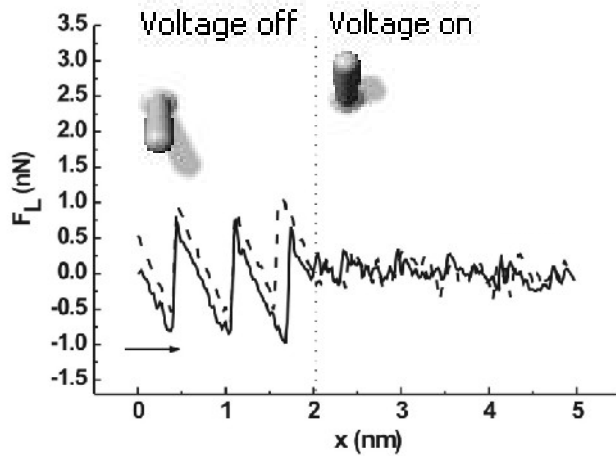
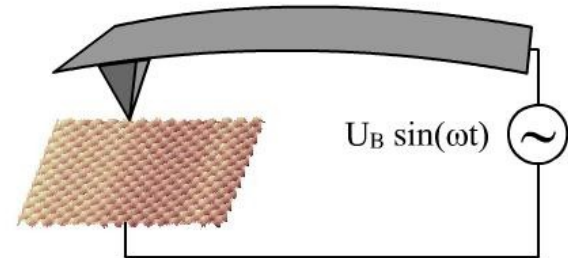
“Dynamic superlubricity”

A third way to reduce friction: Tomlinson model with TIME modulation



NaCl(001)

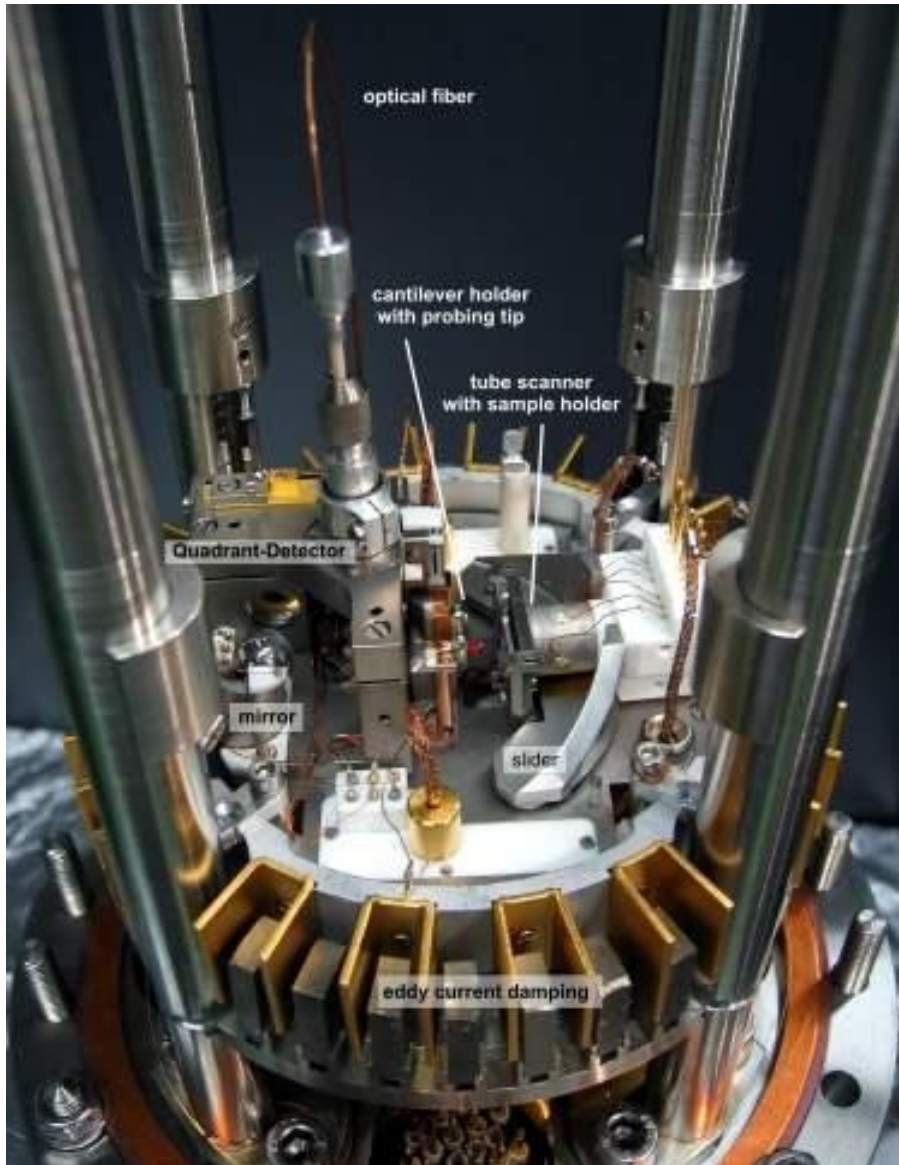
AC actuation
of the nanocontact:



Wieviel Kraft braucht man für einen molekularen Schalter?

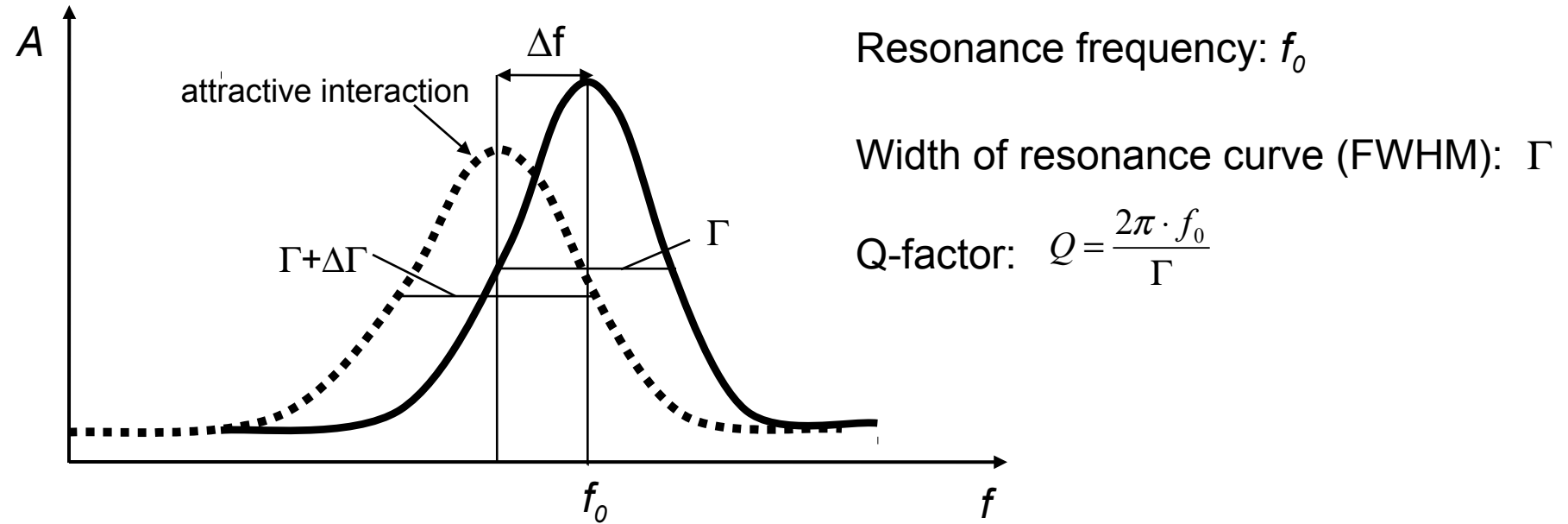


Noncontact-AFM (nc-AFM)



- UHV: Base pressure below 1×10^{-10} mbar
- Operation at room temperature
- Mixed mode: AFM/STM
- Beam deflection method
- Bandwidth of the photodetector: 3MHz
- Evaporation of molecules from a k-cell kept at 165°C or 170°C

Quantitative understanding of nc-AFM



Conservative forces \Rightarrow shift of resonance curve Δf

Dissipative forces \Rightarrow broadening of curve $\Delta\Gamma$

Forces in nc-AFM

Frequency modulation: $f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}$ $\Delta f = -\frac{f_0}{2k} \frac{\partial F_{tot}}{\partial z}$

⇒ measured topography = surface of constant $\frac{\partial F}{\partial z}$

$$F_{tot} = F_{chem} + F_{mag} + F_{el} + F_{vdW}$$

bonding between
tip and sample
atoms
(only for $d < 5 \text{ \AA}$)

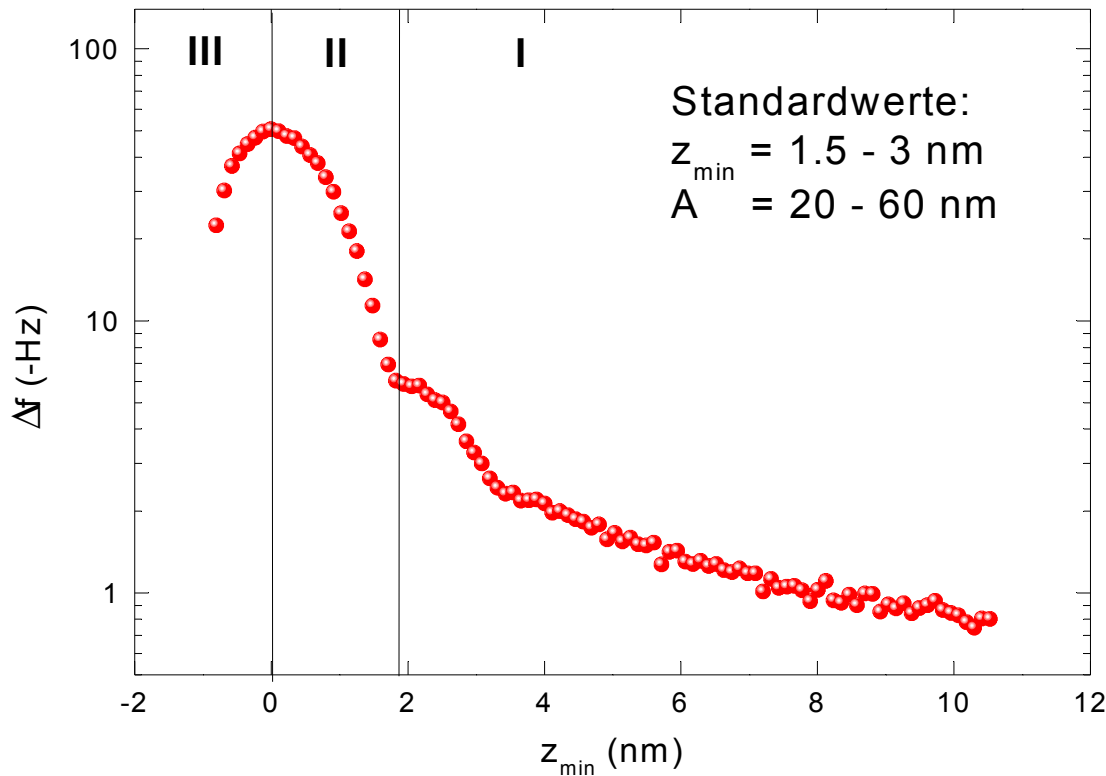
only for
magnetically
sensitive tips

$$F_{el} = -\frac{1}{2} \frac{\partial C}{\partial z} V^2$$

$$F_{vdW} = -\frac{HR}{6d^2}$$



Dynamic Mode, non-contact

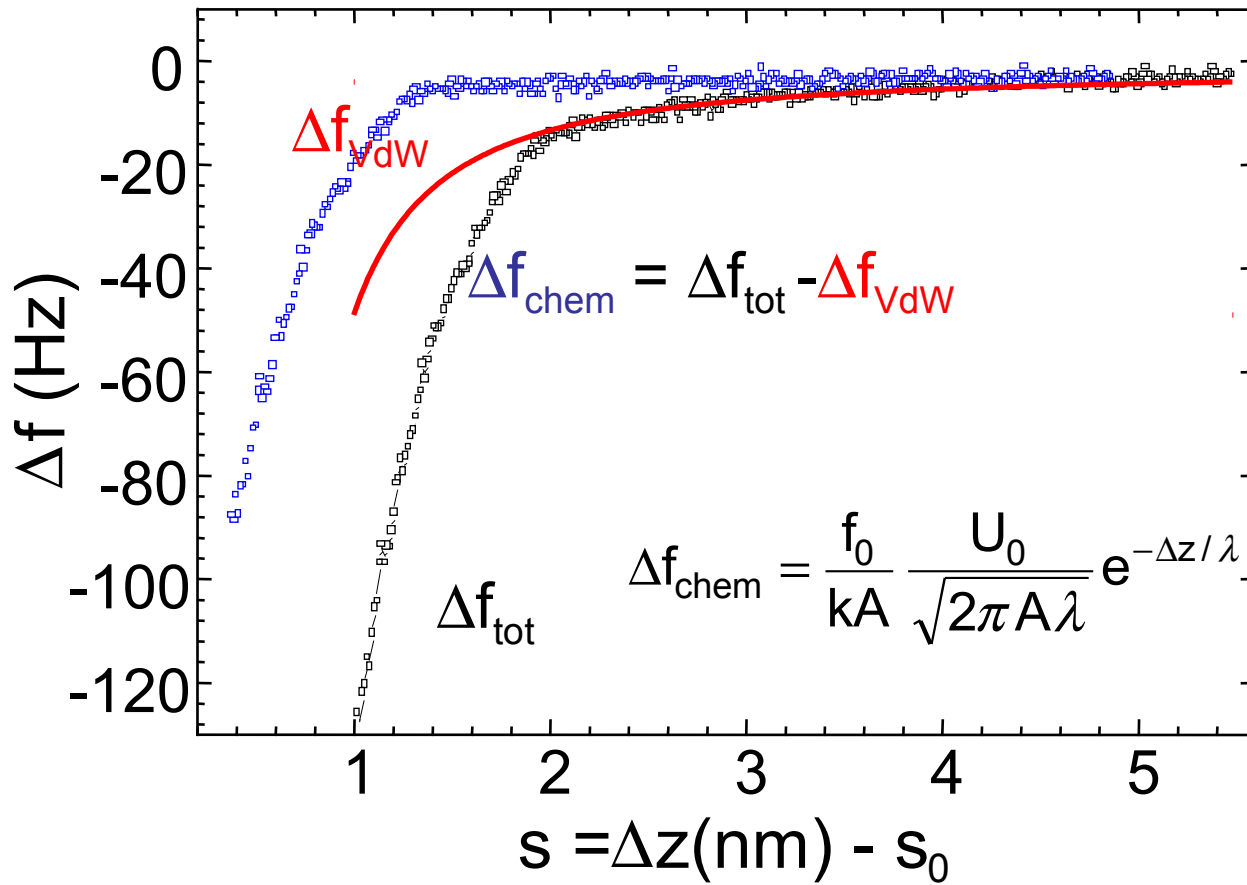


region I:
attractive forces
non-contact mode

region II:
attractive forces
atomic resolution

region III:
repulsive forces
tapping mode

Short range interaction

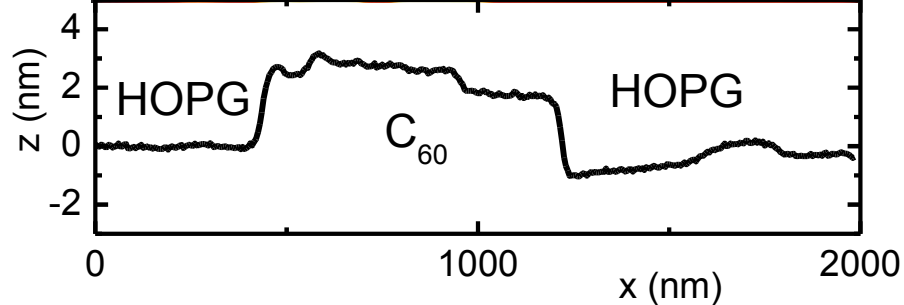
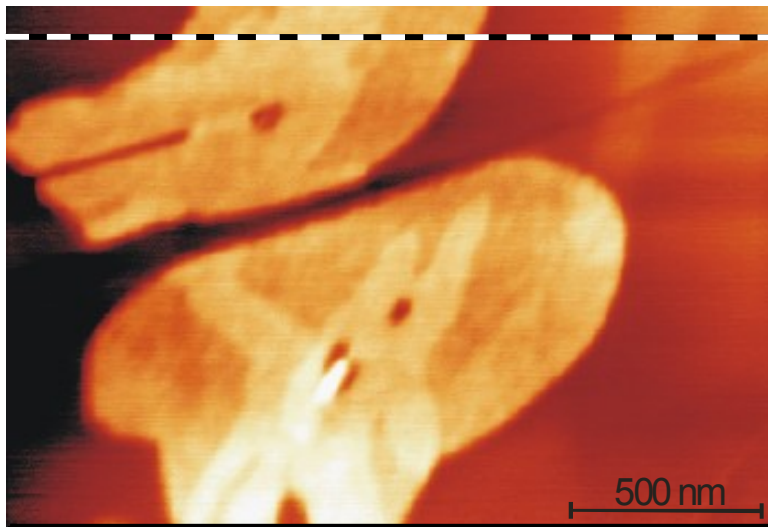


$$\begin{aligned}\lambda &= 0.35 \text{ nm} \\ U_0 &= -4.7 \text{ eV} \\ s_0 &= 0.45 \text{ nm}\end{aligned}$$

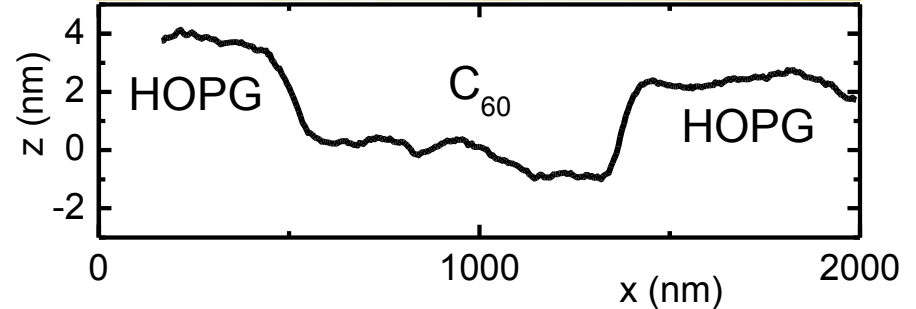
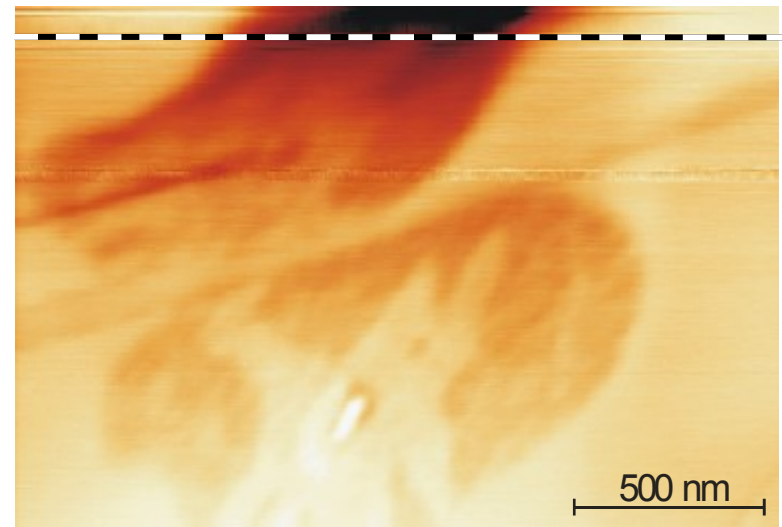
inhomogeneous sample: HOPG + $\frac{1}{2}$ monolayer C₆₀

Topography

$V_{\text{bias}} = 0 \text{ V}$



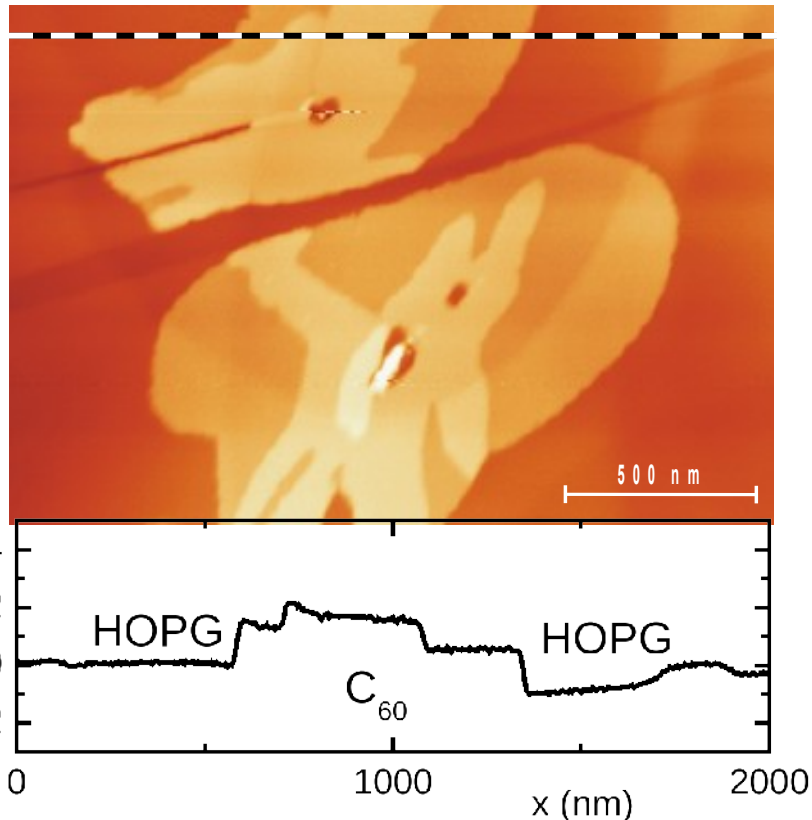
$V_{\text{bias}} = 1.34 \text{ V}$



→ contrast inversal: HOPG ↔ C₆₀

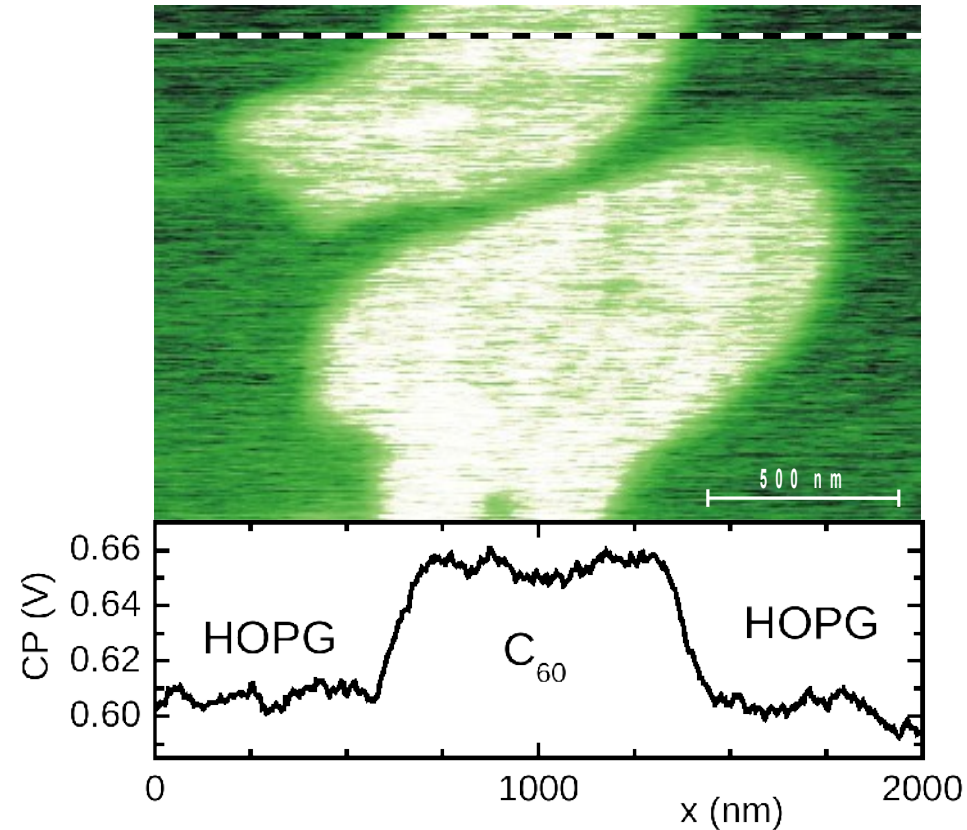
inhomogeneous sample: HOPG + $\frac{1}{2}$ monolayer C60

topography



HOPG: $V_{CP} \cong 0.61$ V

contact potential

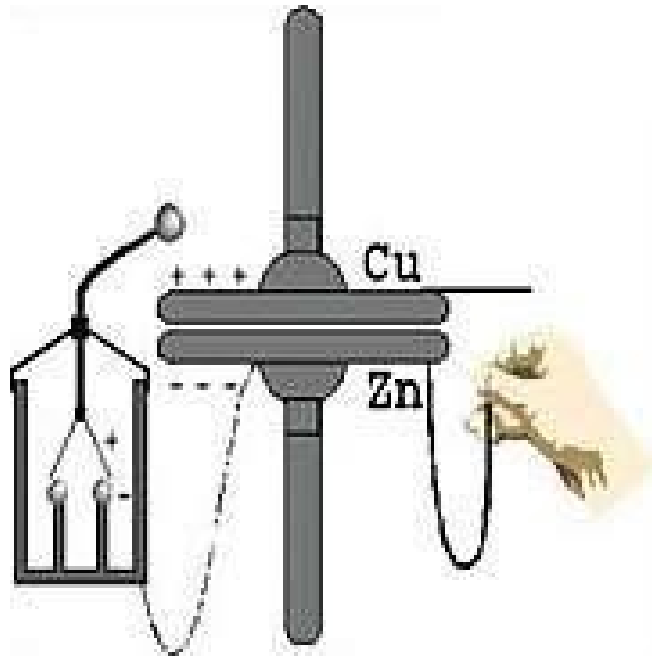


C_{60} : $V_{CP} \cong 0.66$ V

\Rightarrow NC-AFM: residual electrostatic force for fixed V_{bias}

Makroskopische Kelvin-Sonde

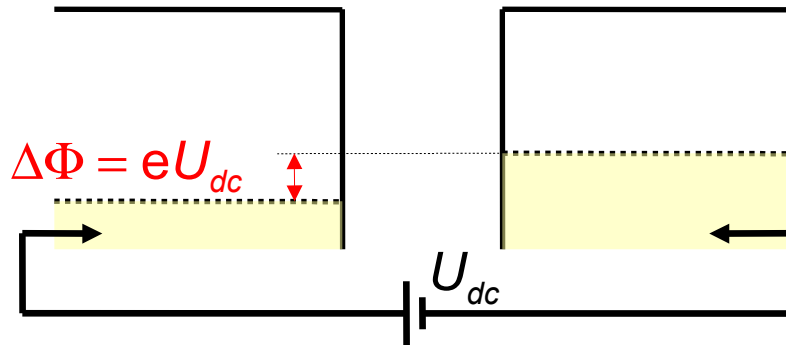
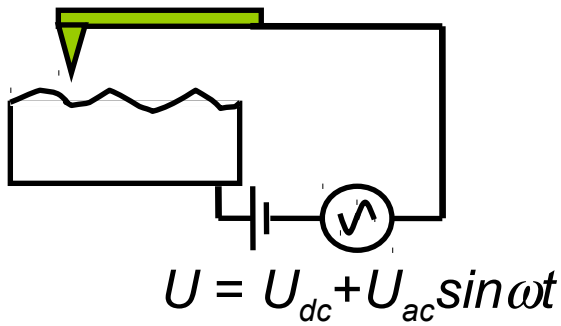
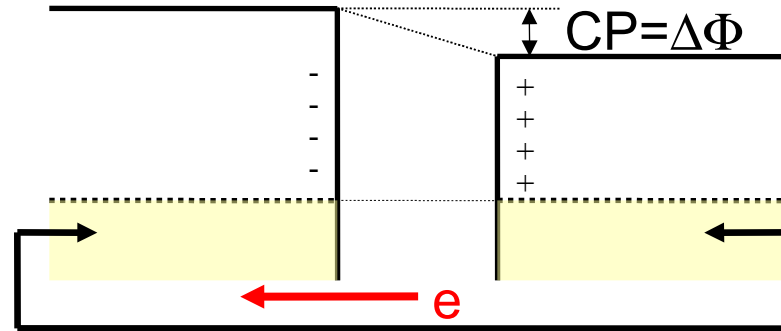
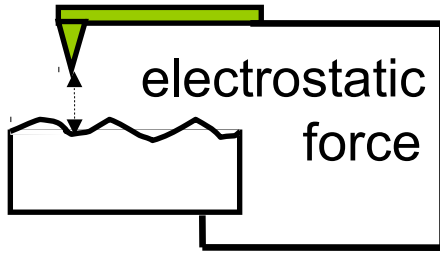
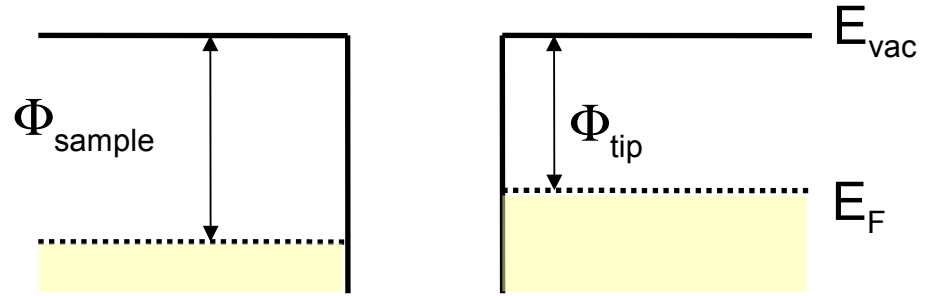
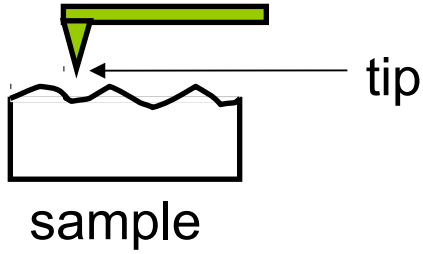
Lord Kelvin 1861



Verschiebestrom

$$I(t) = (U_{dc} - U_{CPD}) f \Delta C \cos \omega t.$$

Kelvin Principle



Electrostatic Forces in nc-AFM

$$F_{el} = -\frac{1}{2} \frac{\partial C}{\partial z} V_{eff}^2 \quad \Rightarrow \quad F_{el} = -\frac{1}{2} \frac{\partial C}{\partial z} (V_{bias} - V_{CP})^2$$

$$V_{CP} = 1/e \cdot (\Phi_{tip} - \Phi_{sample})$$

contact potential

Φ - work function

apply bias:

$$V_{bias} = V_{dc} + V_{ac} \cdot \sin(\omega t)$$

Kelvin Probe Force Microscopy

$$F_{el} = -\frac{1}{2} \frac{\partial C}{\partial z} V_{eff}^2 = F_{dc} + F_{\omega} + F_{2\omega}$$

$$F_{dc} = -\frac{\partial C}{\partial z} \left[\frac{1}{2} (V_{dc} - V_{CP})^2 + \frac{V_{ac}^2}{4} \right]$$

$$F_{\omega} = -\frac{\partial C}{\partial z} (V_{dc} - V_{CP}) V_{ac} \sin(\omega t)$$

$$F_{2\omega} = \frac{\partial C}{\partial z} \frac{V_{ac}^2}{4} \cos(2\omega t)$$

AM-KPFM

Amplitude Modulation

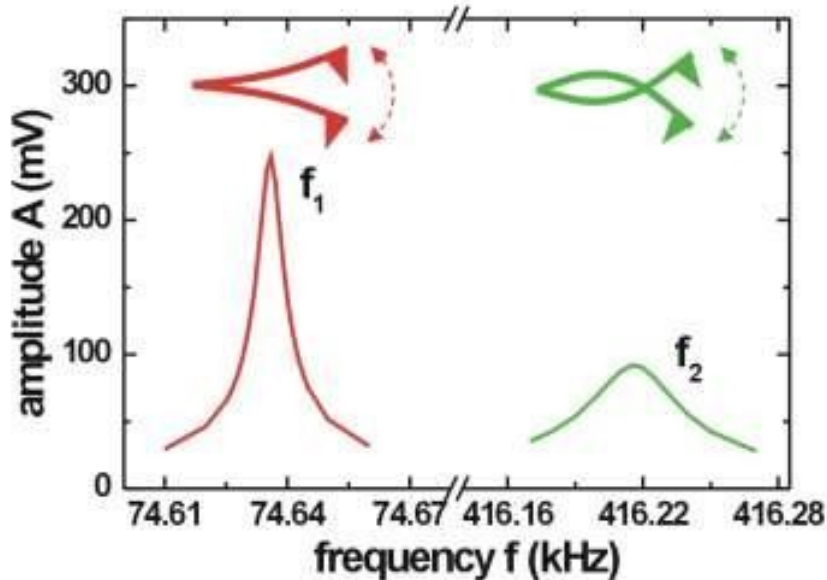
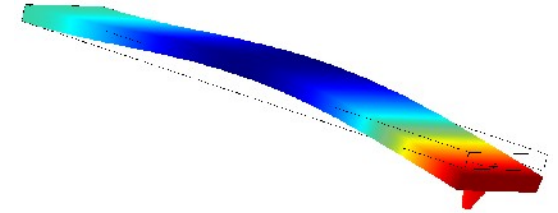
FM-KPFM

Frequency Modulation

AM – KPFM

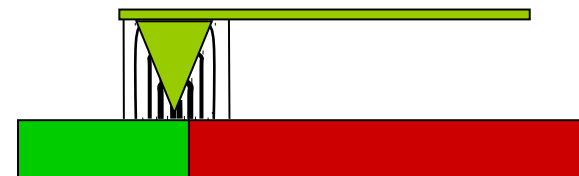
Amplitude Modulation Detection

$$F_{\omega} = -\frac{\partial C}{\partial z} (V_{dc} - V_{CP}) V_{ac} \sin(\omega t)$$

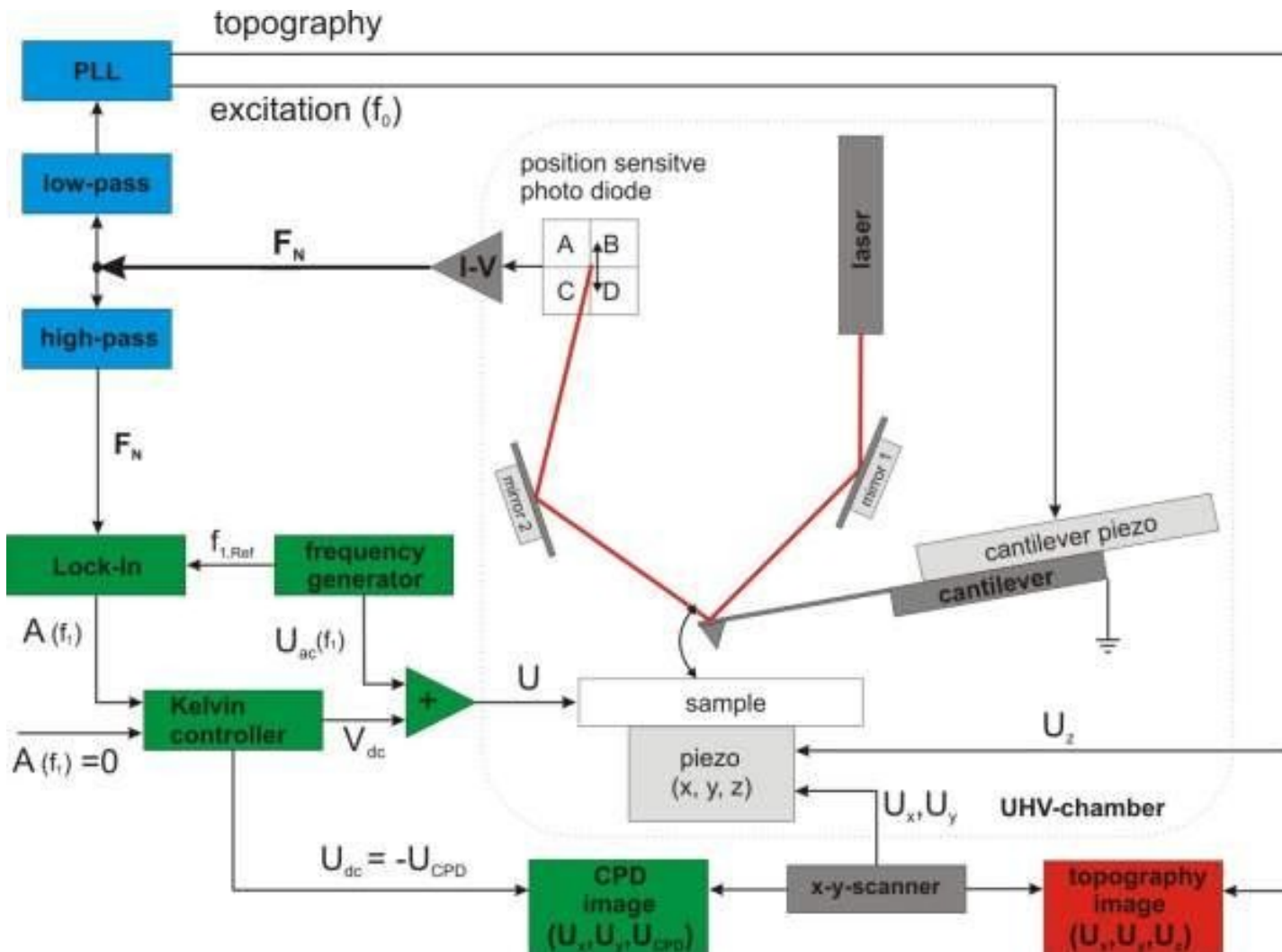


- tune ω to the second resonance f_2
- detection of the oscillation amplitude A_{ω} with a lock-in
- limiting factor: bandwidth of the photodiode

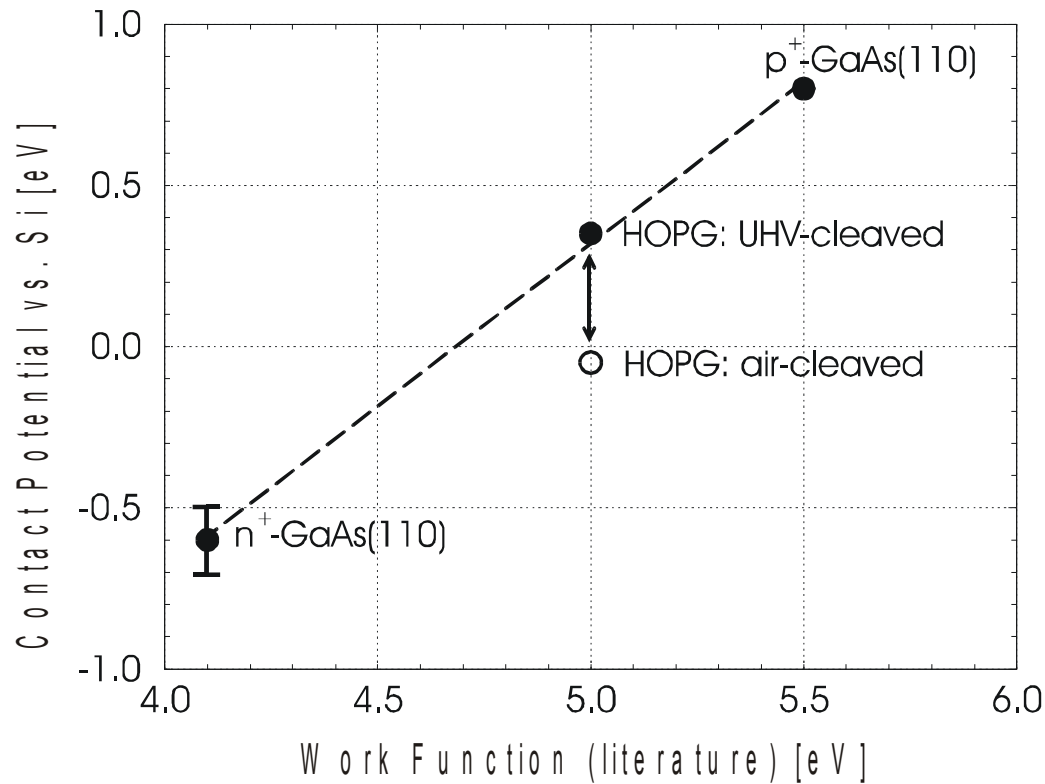
$$A_{\omega} \propto F_{\omega}$$



Experimental Setup nc-AFM & AM-KPFM



KPFM calibration and absolute work function



Φ -Si-Cantilever = 4.70 (± 0.1) eV

$U_{ac} = 100$ mV

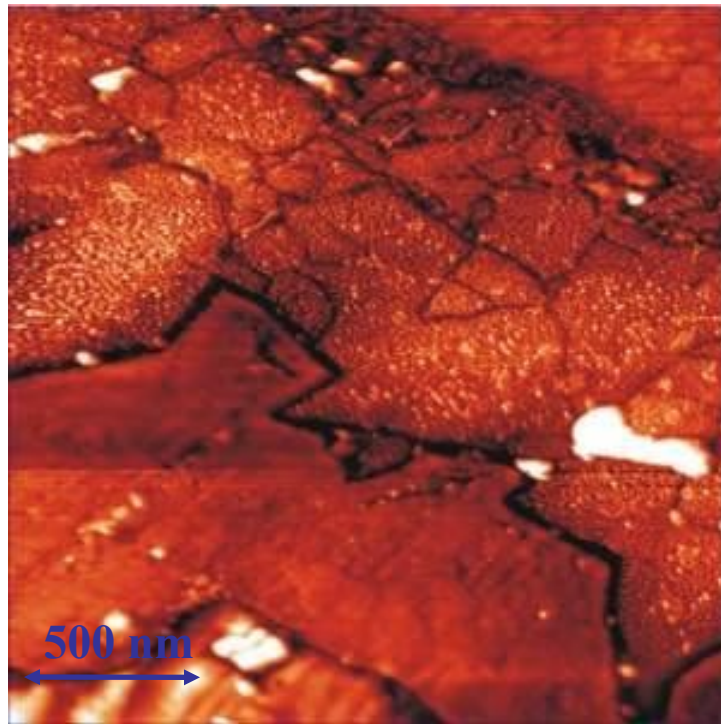
→ absolute and quantitative work function determination

Polished Cross Section of a CuGaSe₂ Solar Cell

CuGaSe₂ solar cell device: $V_{oc} = 820$ mV, $\eta = 4.6$ %

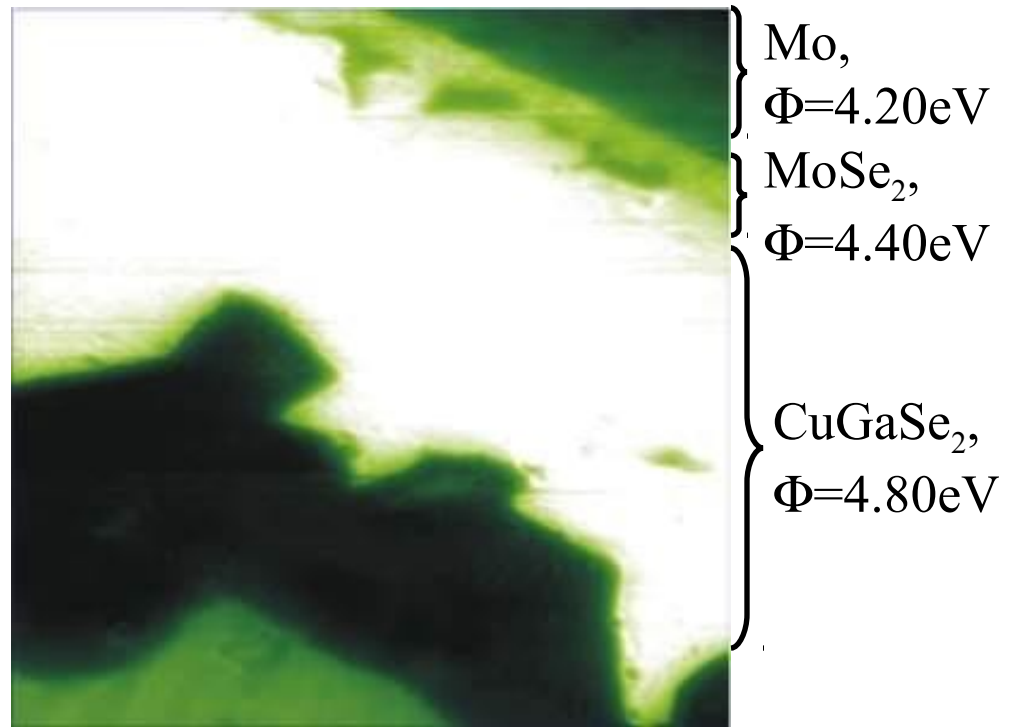
polished and Ar-ion sputtered cross section

topography



$\Delta z = 65$ nm

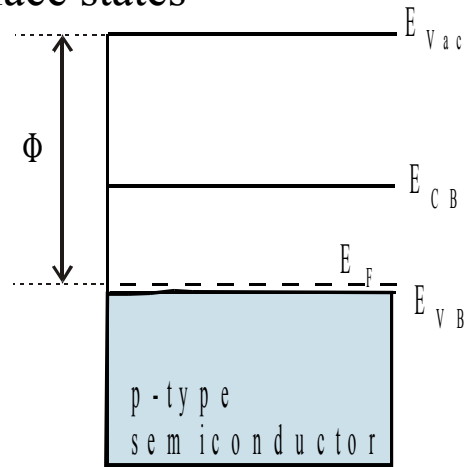
work function



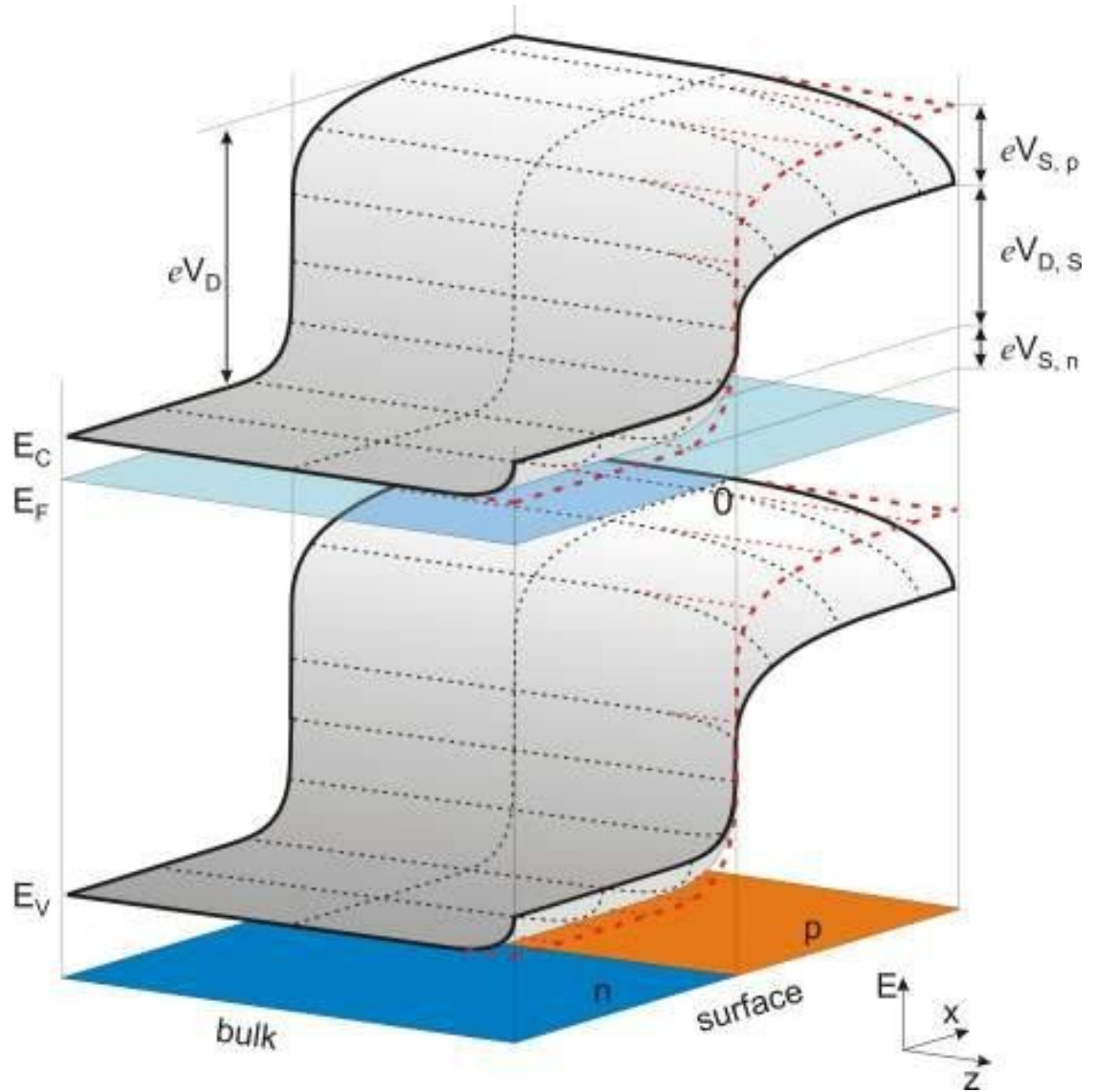
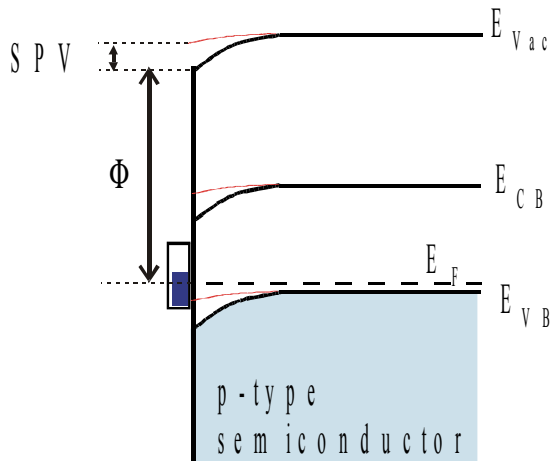
n-ZnO:Ga,
 $\Phi = 4.0$ eV

Surface Effects

no surface states

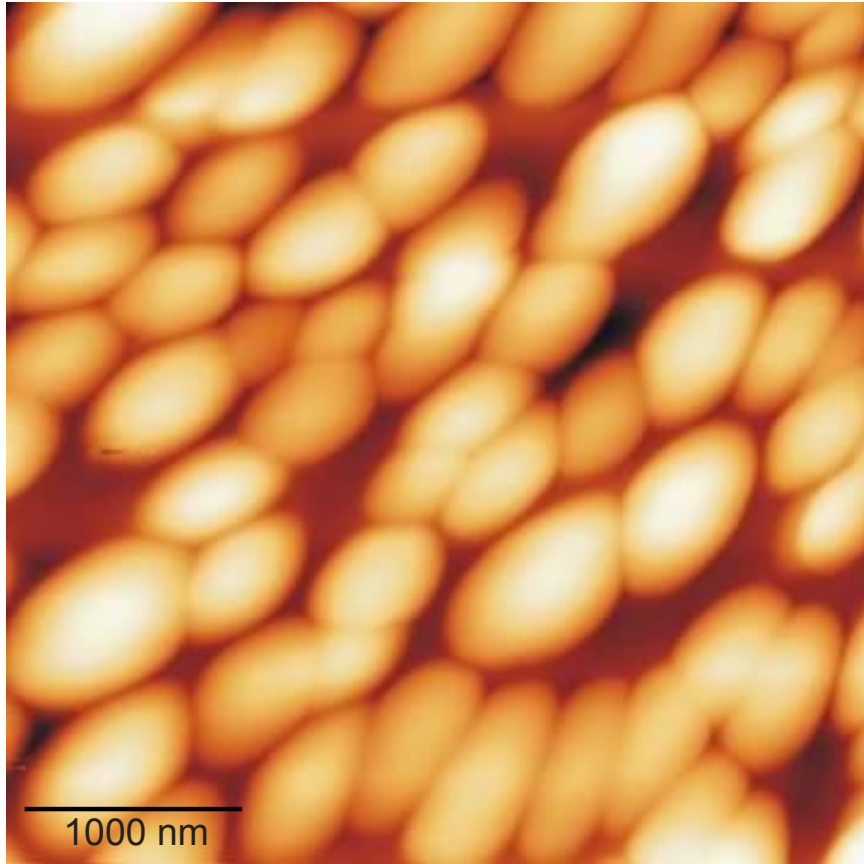


surface states

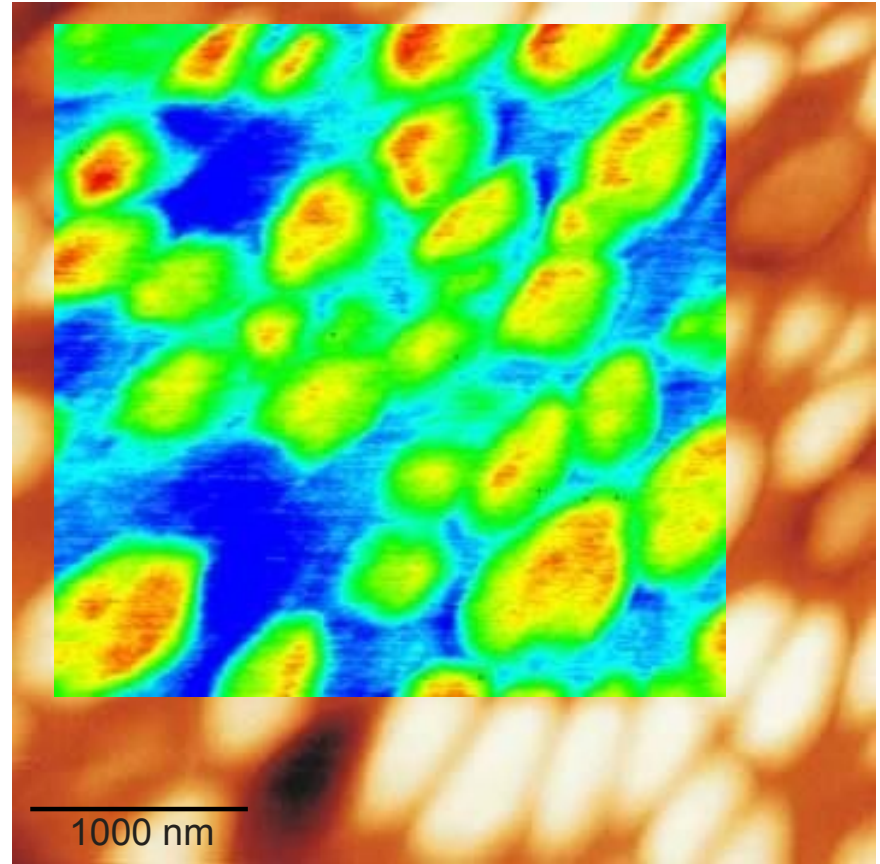


Surface Photovoltage

MDMO-PPV/PCBM – 675nm



0 nm  105.6 nm

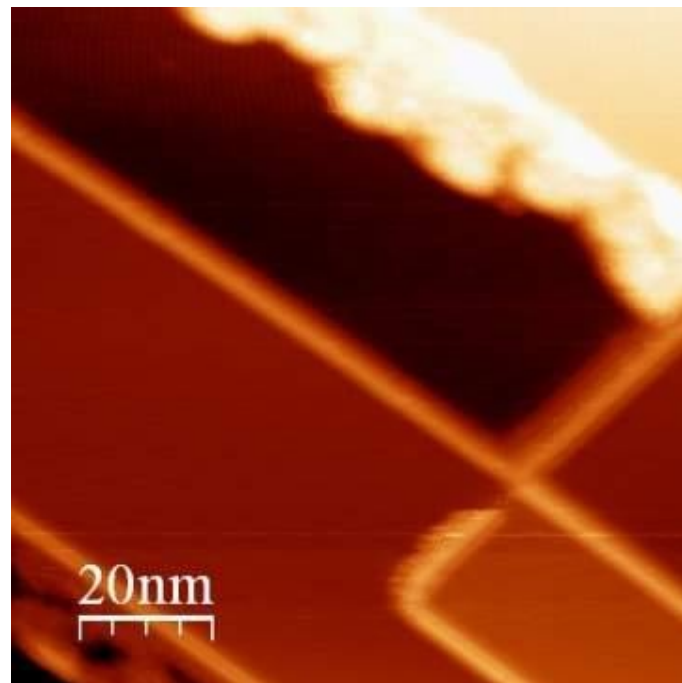
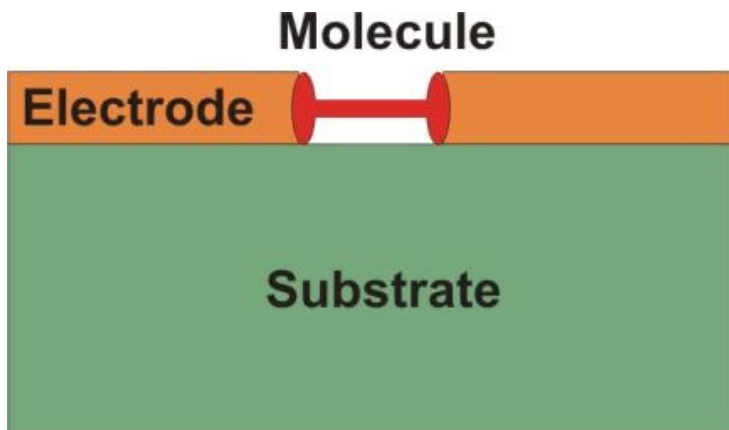


4.19 eV  4.62 eV

-50 mV  220mV

Motivation

Molecular electronics

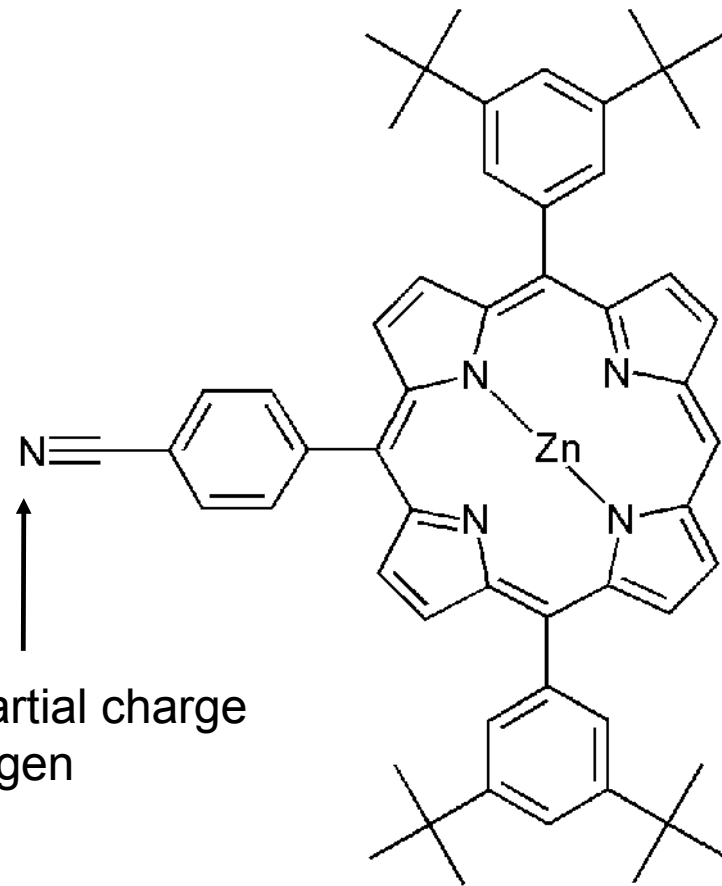
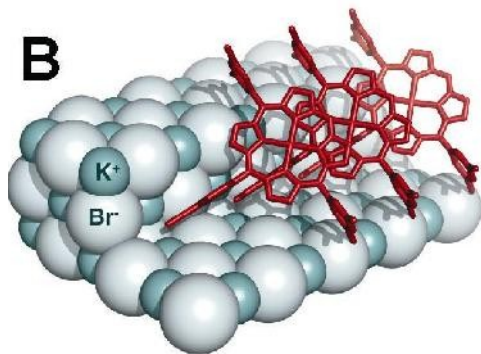
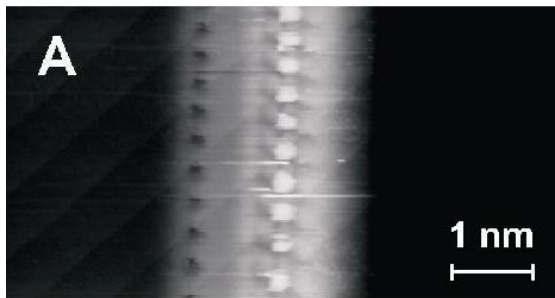


Molecules on Insulators:

- No STM possible – nc-AFM mandatory
- Low diffusion barrier but high intermolecular interaction
- Low temperatures – easier to “fix” molecules but not so easy to find applications

Asymmetric Cyano-Porphyrins

Natural light harvesting complexes

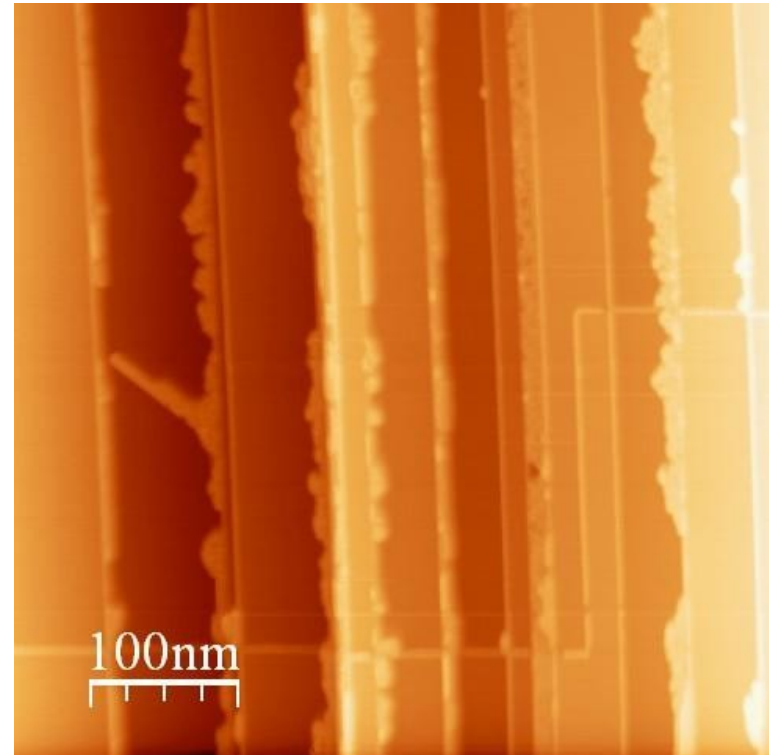


S. Meier et al., *Small*, 2008, 4, 1115

Wire Formation

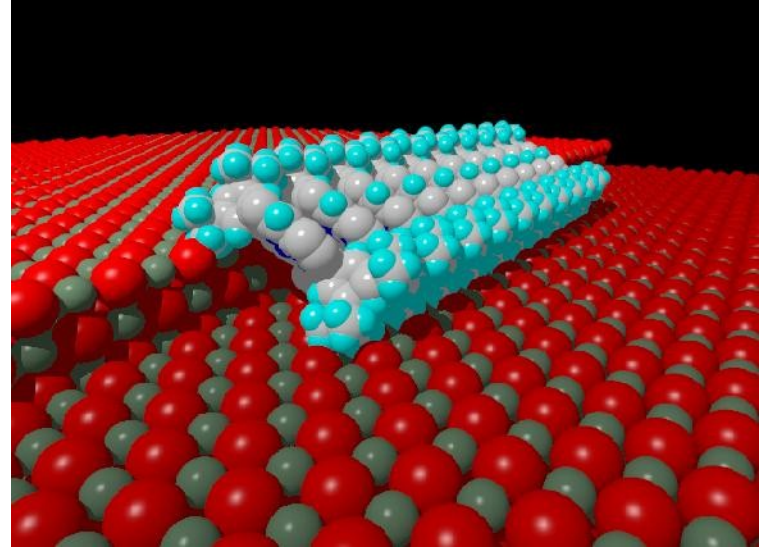
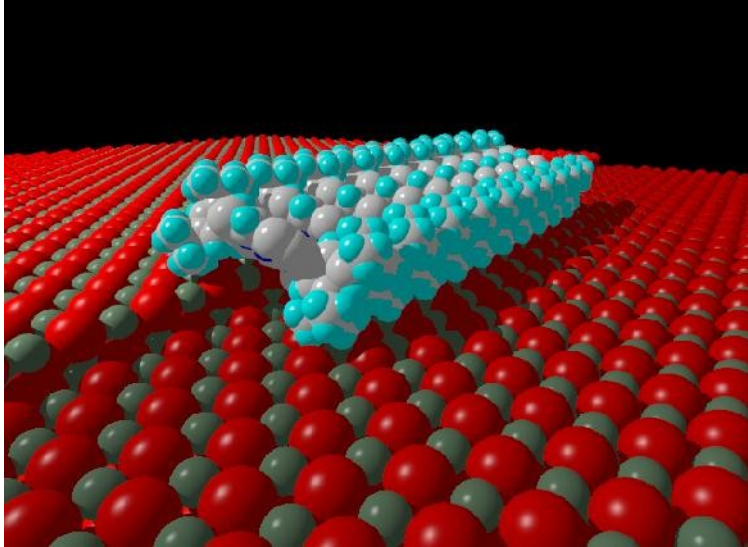
Decoration of step edges on KBr(100)

- In situ cleaved KBr with 0.5 ML of molecules
- Steps (< 1nm) are decorated with monowires
- Higher steps act as nucleation sites for structure growth across terraces

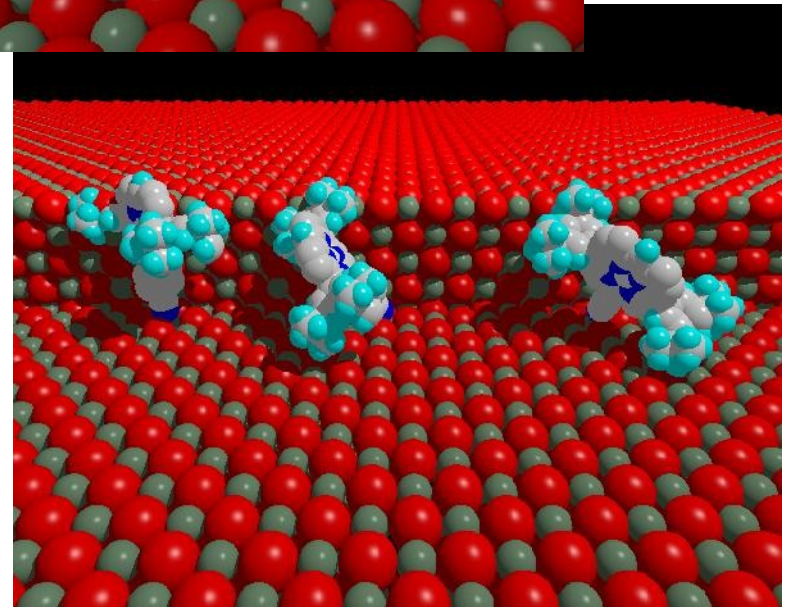


Wire Formation

Structural model

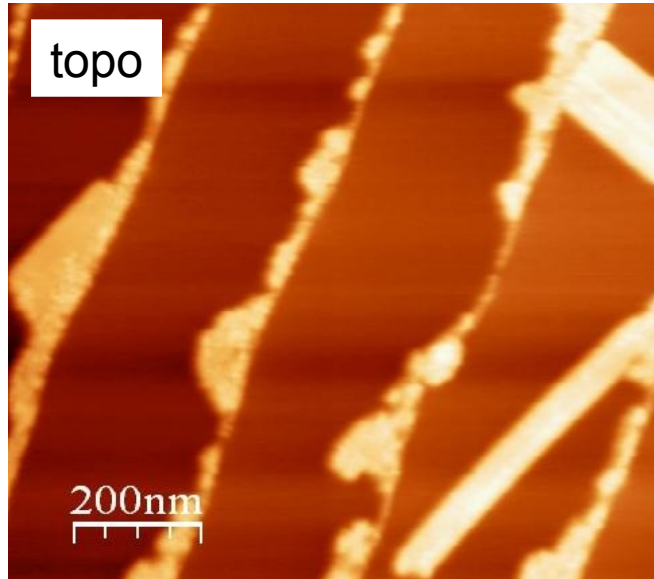


- The tilt angle of the molecules is determined by the side groups, the π - π stacking and the step height.
- Steps higher than 3 ML prevent a π - π stacking.

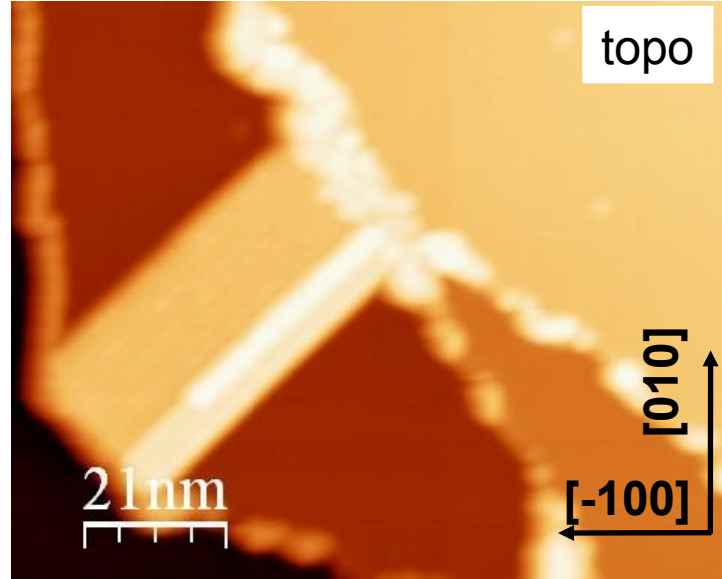


Molecular Assemblies

Multiwires on KBr



$f_0 \approx 174054\text{Hz}, \Delta f = -8\text{Hz}, Q = 15k, A = 5\text{nm}$

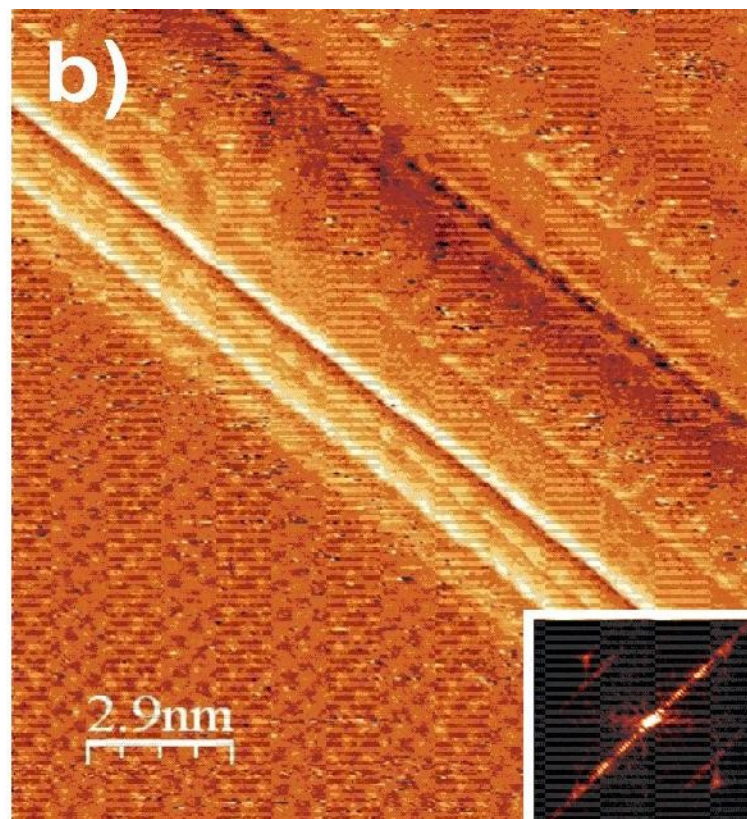
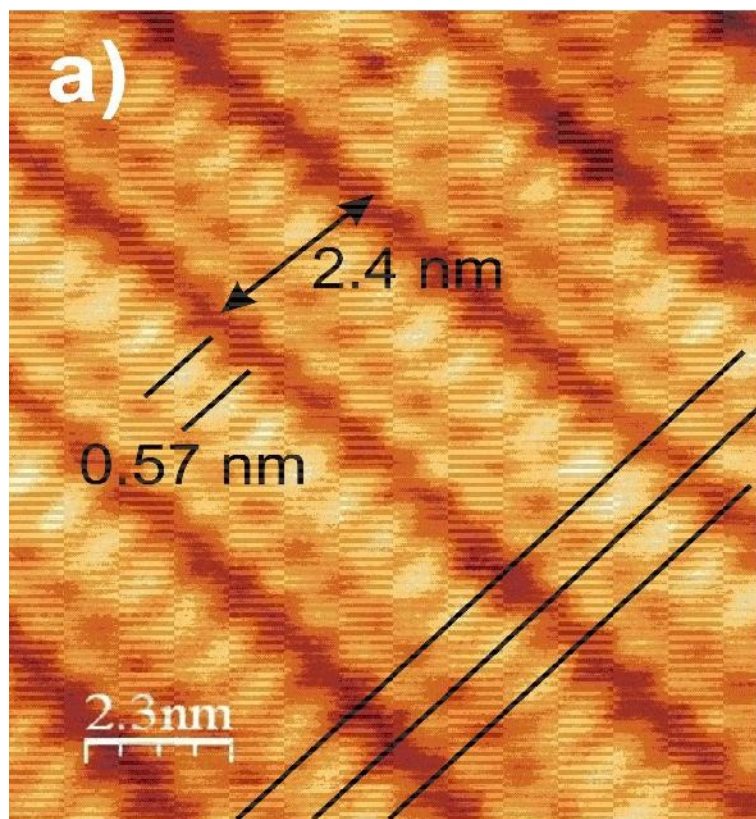


$f_0 \approx 173886\text{Hz}, \Delta f = -52\text{Hz}, Q = 15k, A = 5\text{nm}$

- Multiwire growth across terraces
- The $\langle 110 \rangle$ directions are clearly preferred
- Different heights are visible

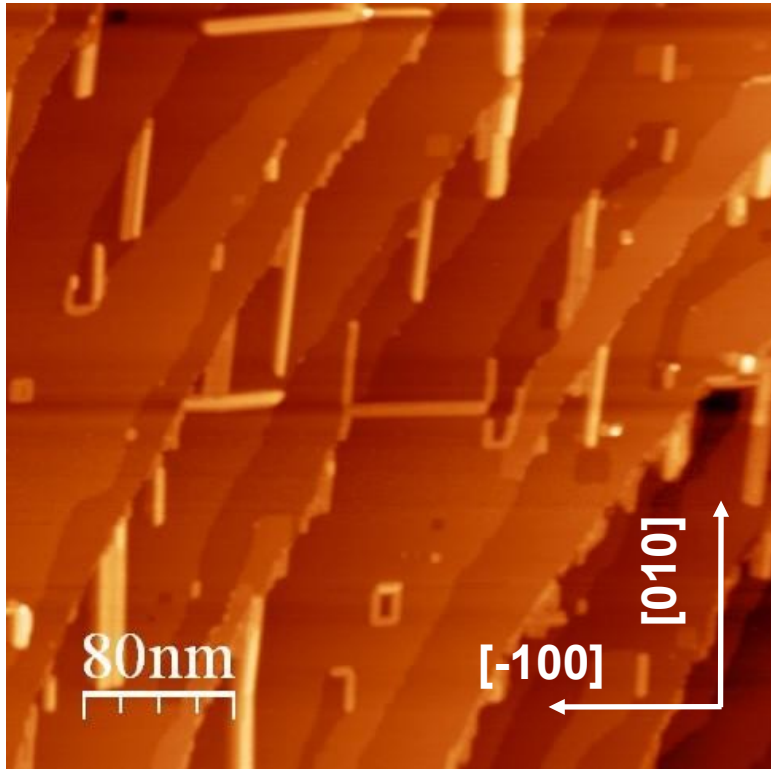
Molecular Assemblies

High resolution imaging

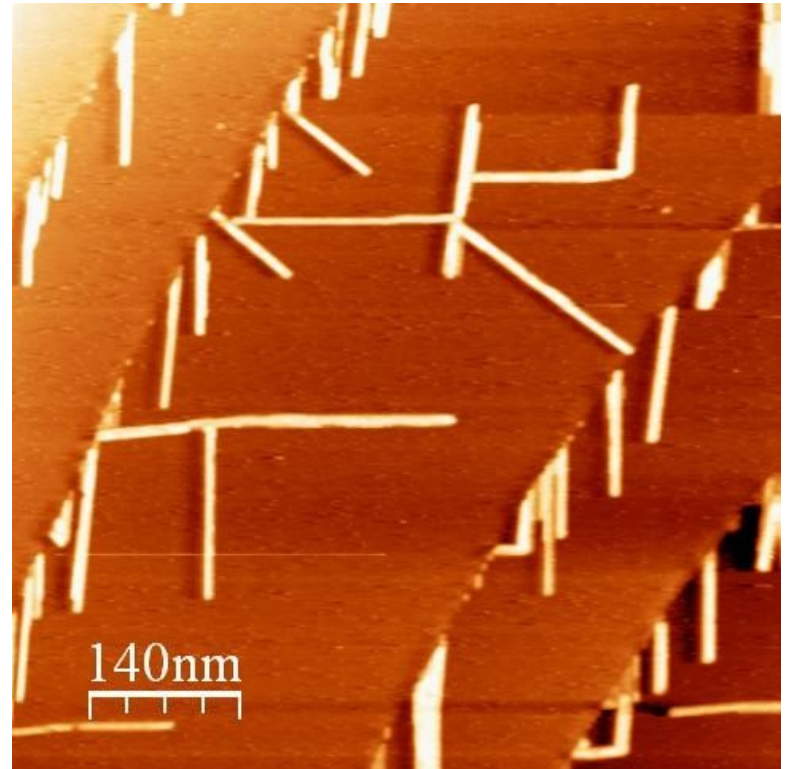


Molecular Assemblies

Molecular wires on NaCl



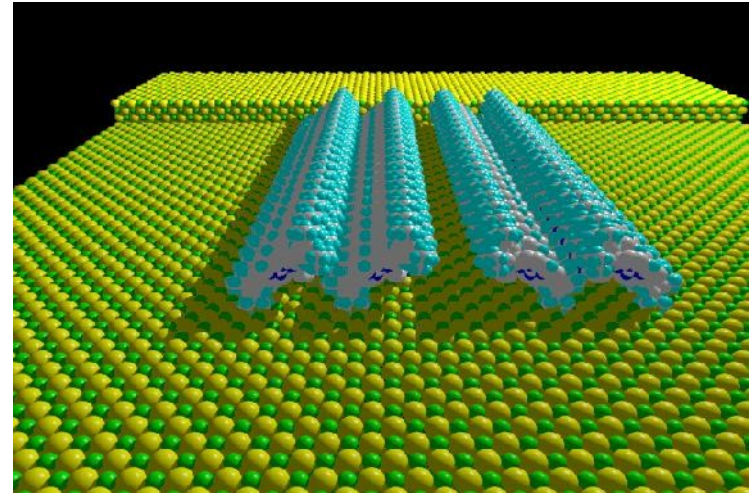
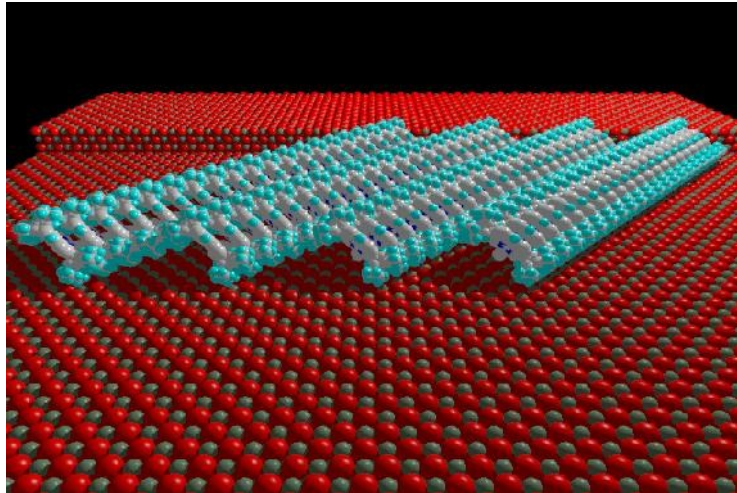
$f_0 \approx 170992\text{Hz}$, $\Delta f = -9.5\text{Hz}$, $Q = 15k$, $A = 40\text{nm}$



$f_0 \approx 170992\text{Hz}$, $\Delta f = -11\text{Hz}$, $Q = 15k$, $A = 40\text{nm}$

Molecular Assemblies

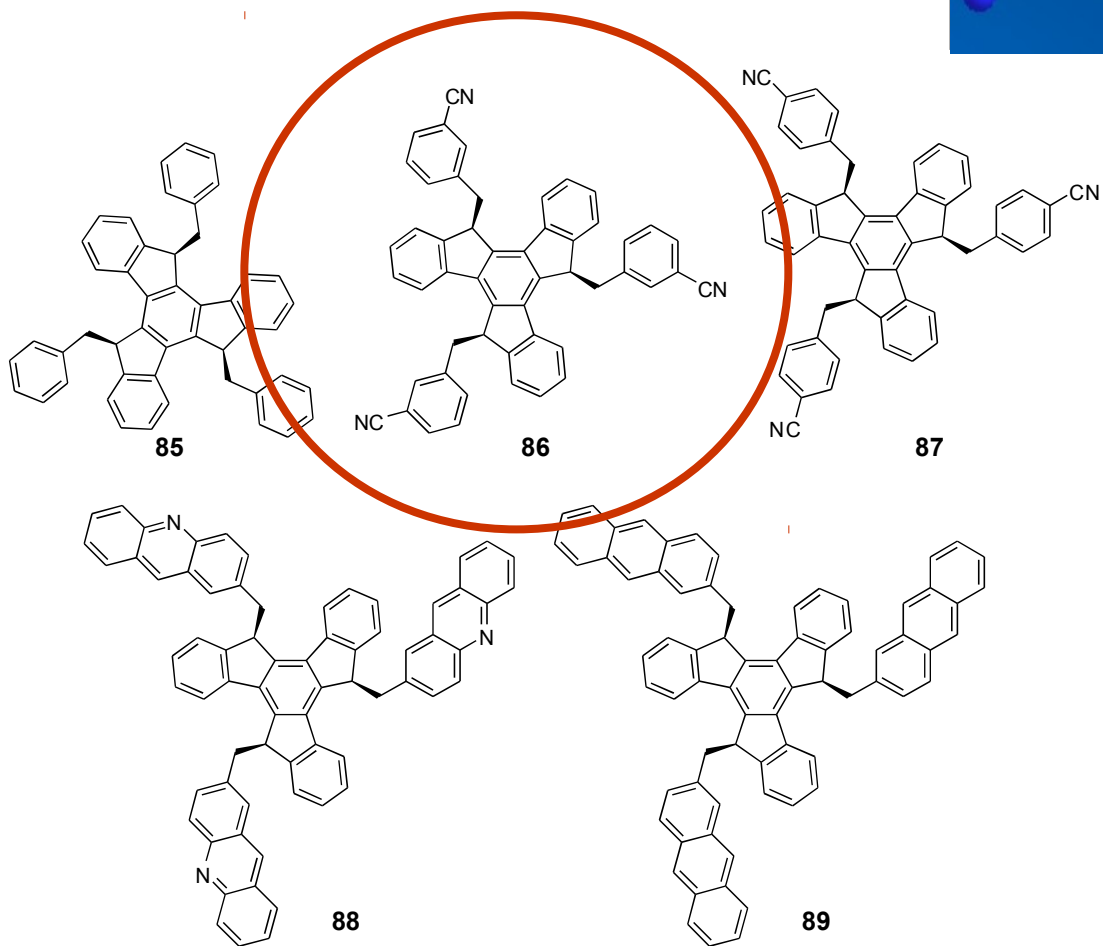
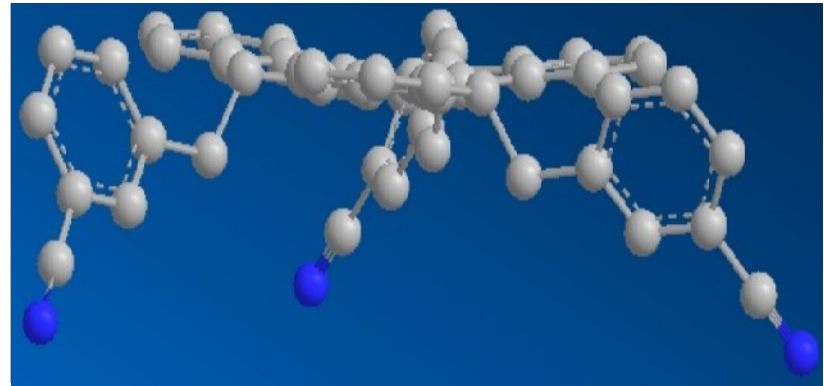
Structural model



- Intermolecular equilibrium separation $\sim 5.7 \text{ \AA}$
- Directed growth by the substrate

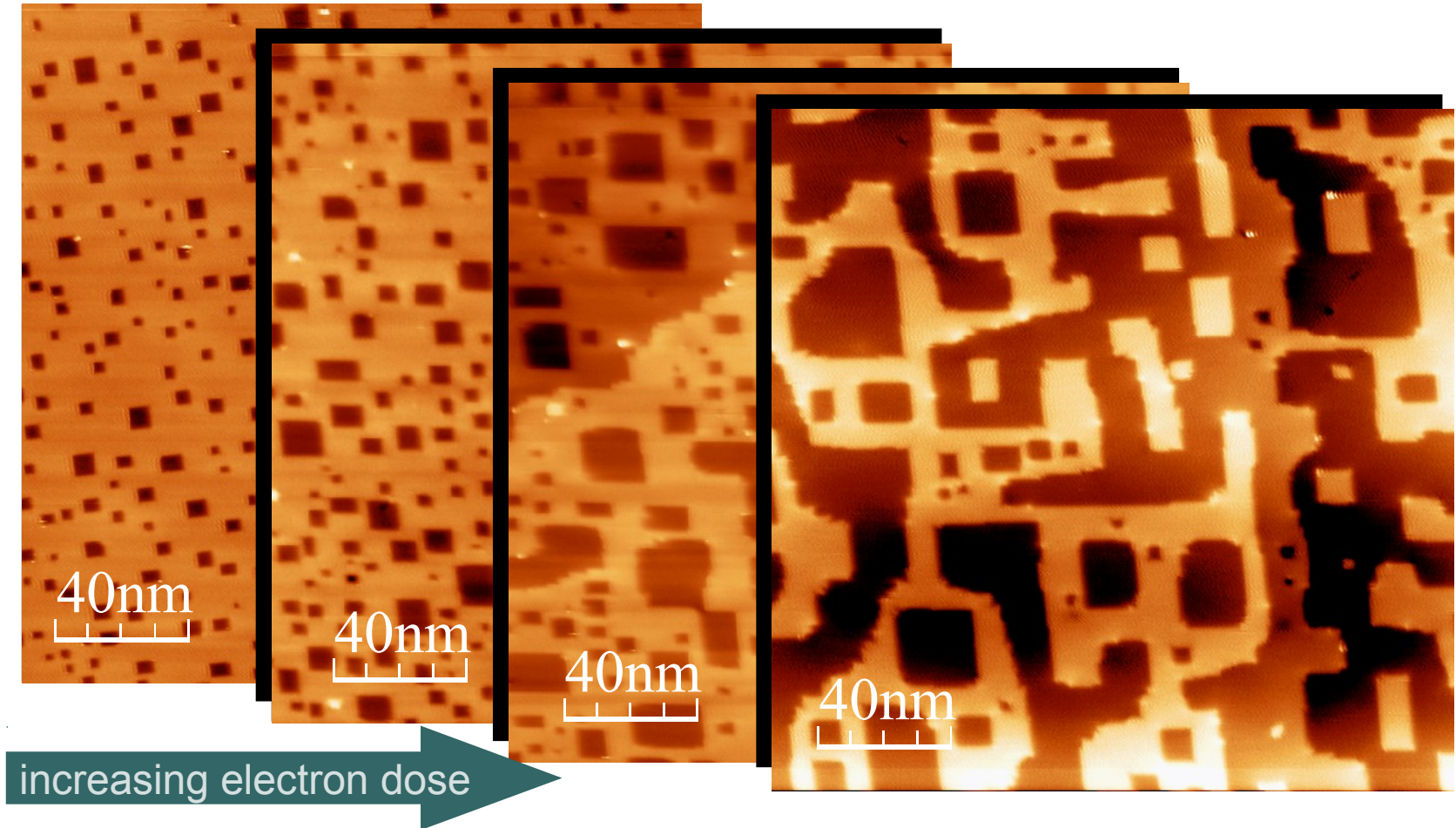
Functionalized Truxenes

Structure



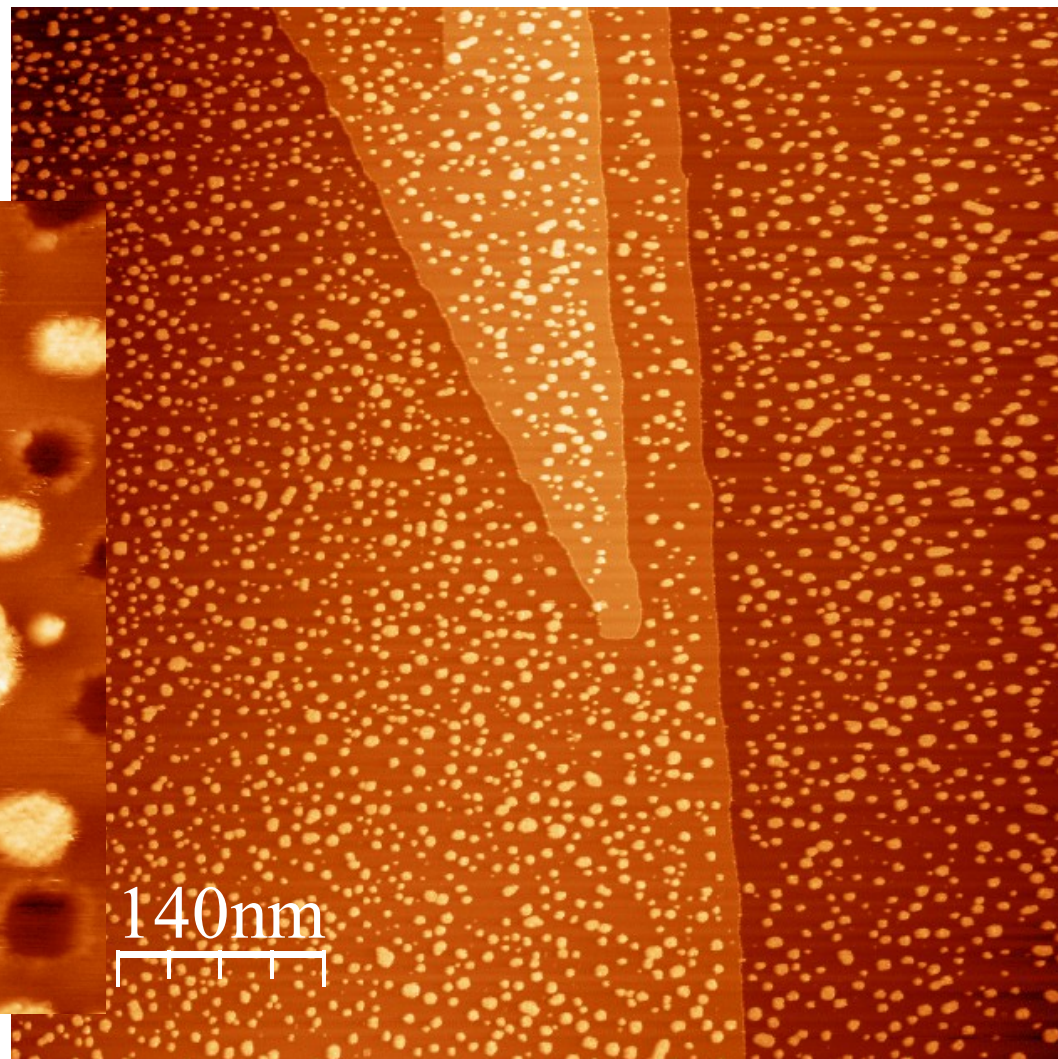
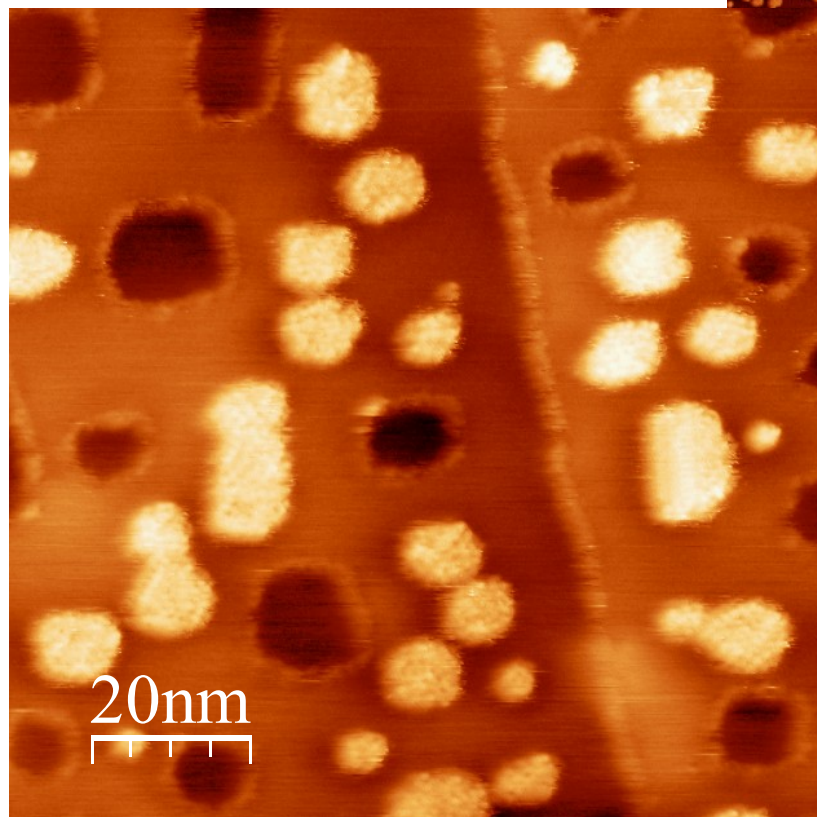
Single Crystal KBr

Substrate patterning by electron irradiation



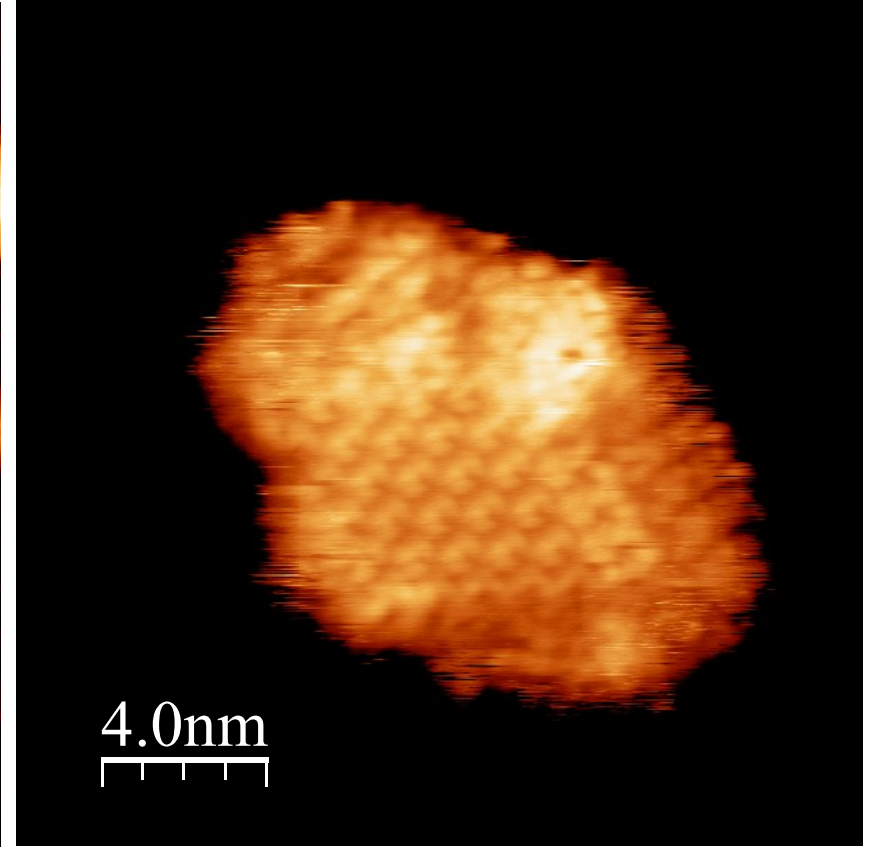
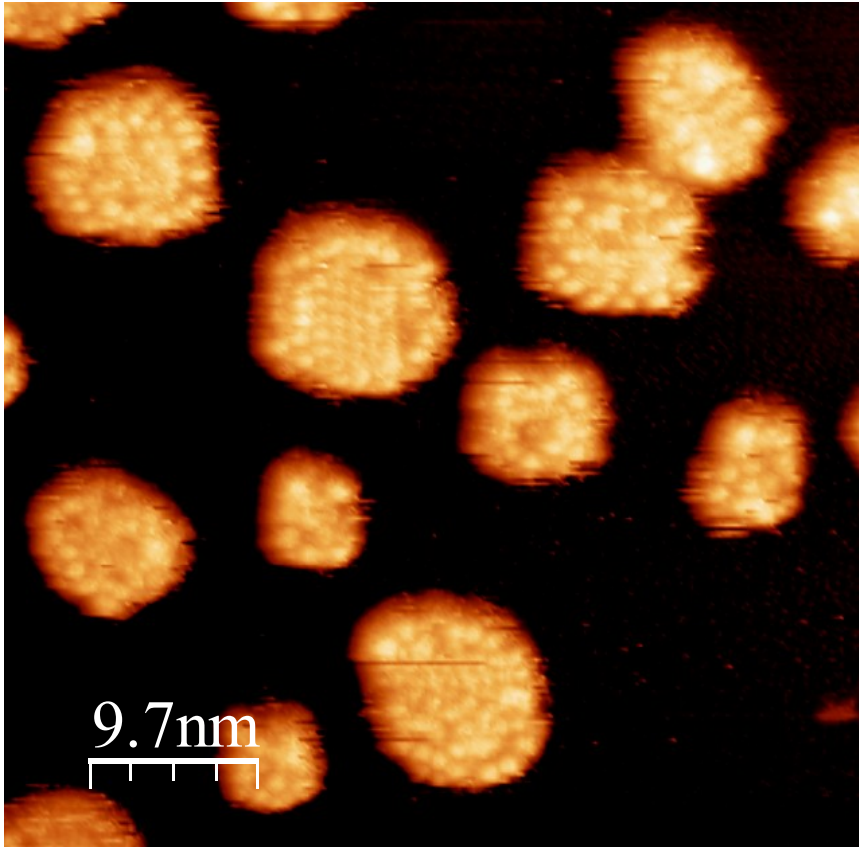
Truxenes on patterned surface

Filled and unfilled pits



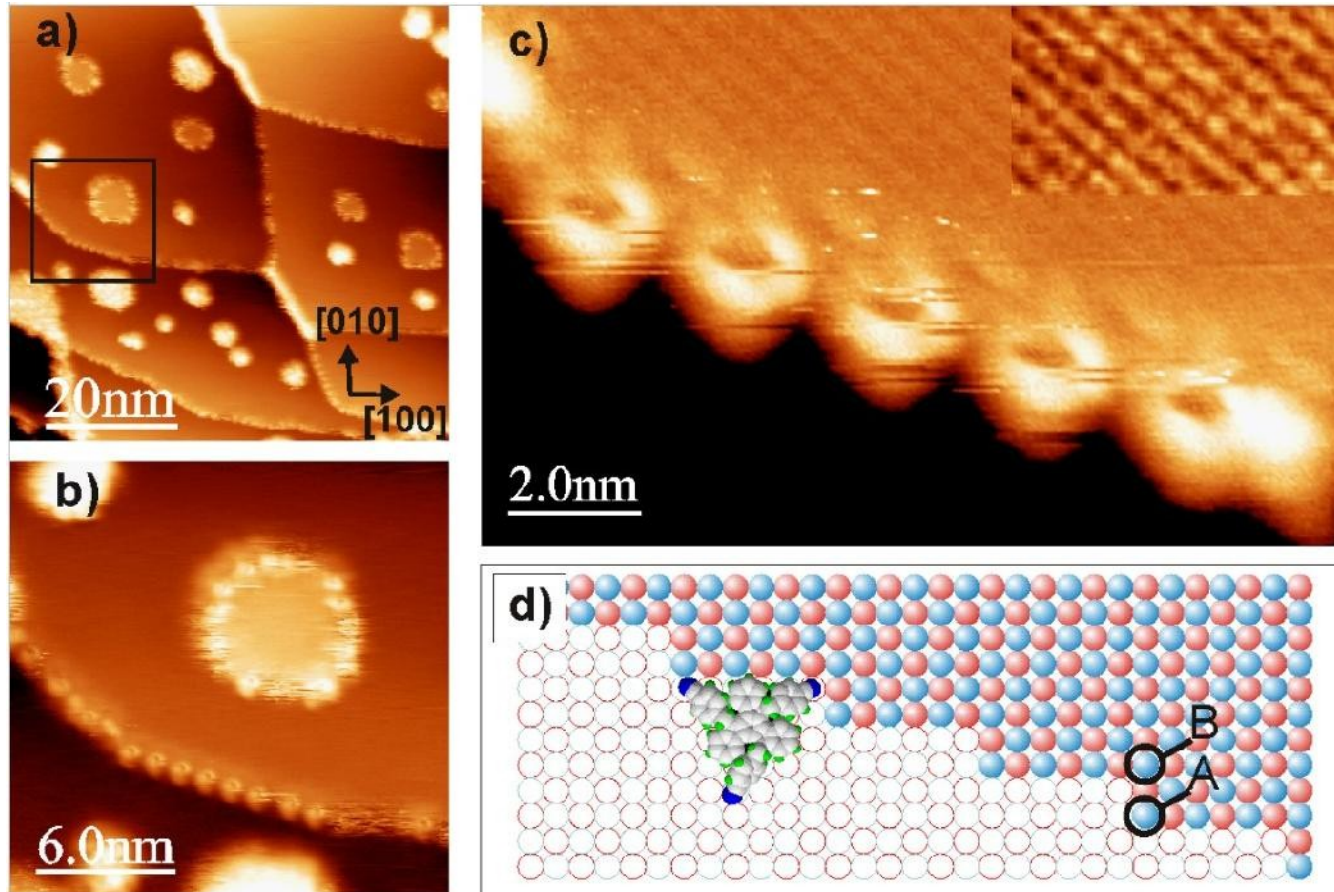
Truxenes on patterned surface

Organization within the pits



Imaging a Single Molecule

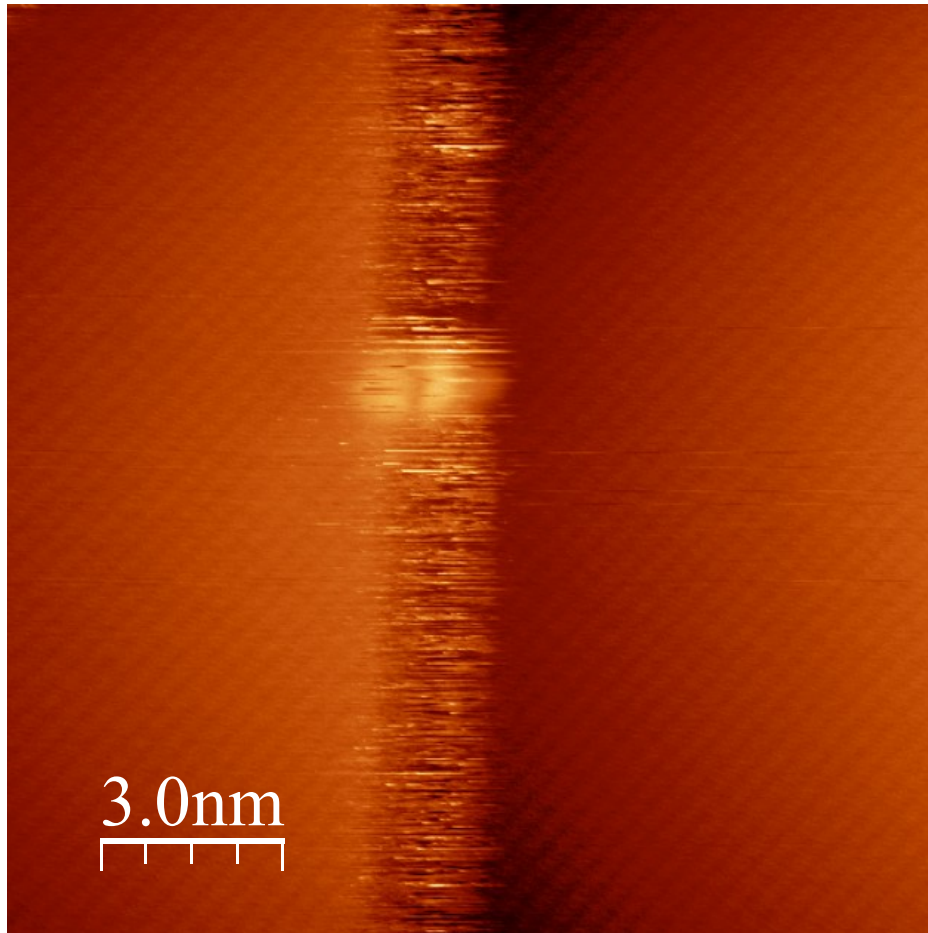
Measurements at RT



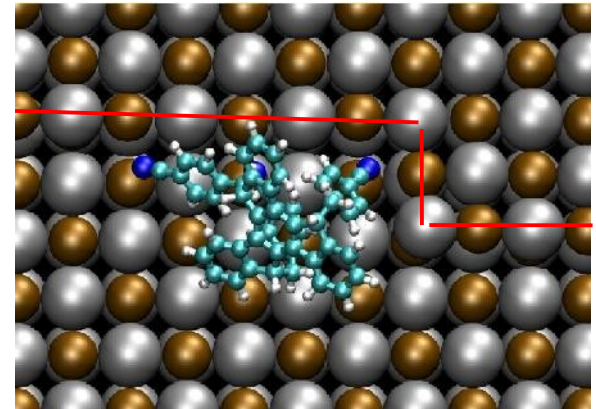
- Re-arrangement of the substrate, edges are running in the $[-3\ 1\ 0]$ direction
- no chemical interaction with the surface
- adsorbed on K or Br terminated double atomic kink

Imaging a Single Molecule

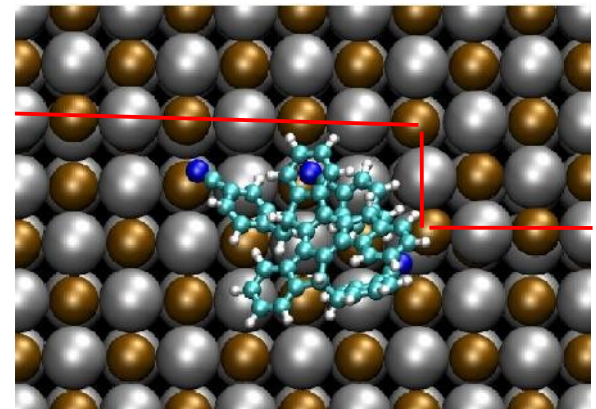
Measurements at RT



Br terminated, $E_b = 1.33\text{eV}$

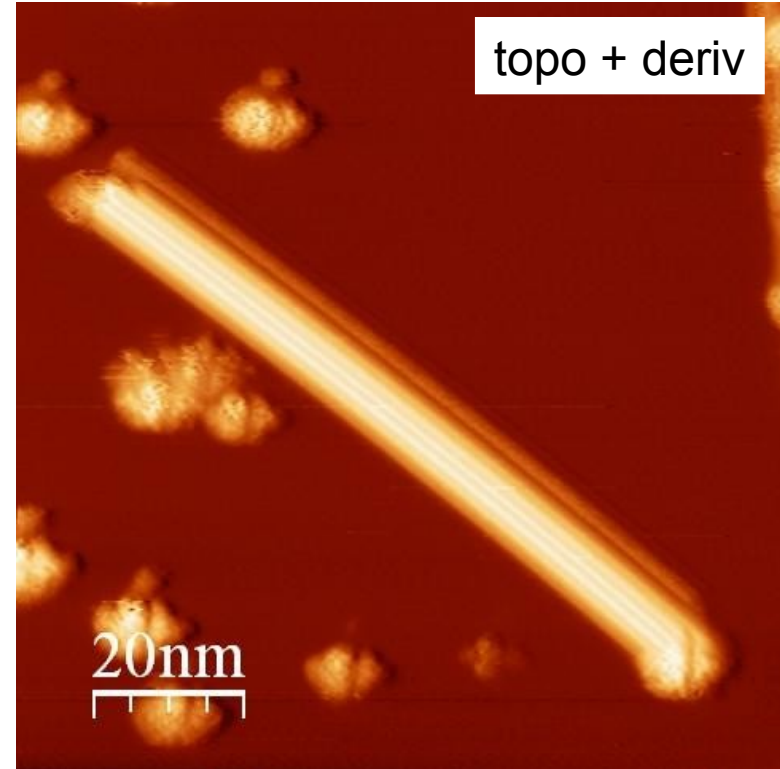
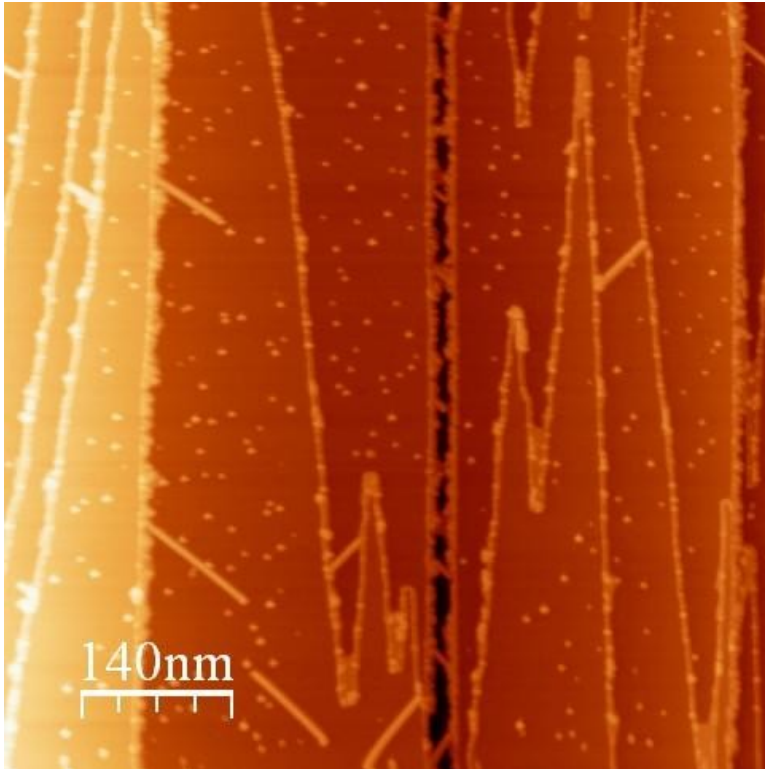
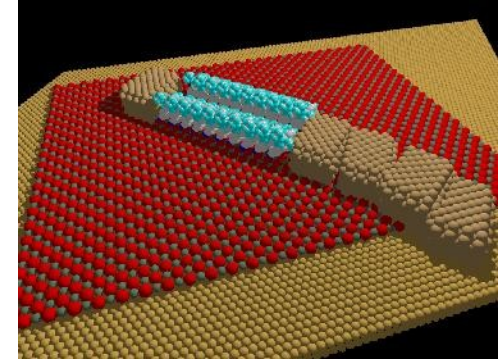


K terminated, $E_b = 1.17\text{eV}$



Contacting Molecular Assemblies

Au-Molecules-Au

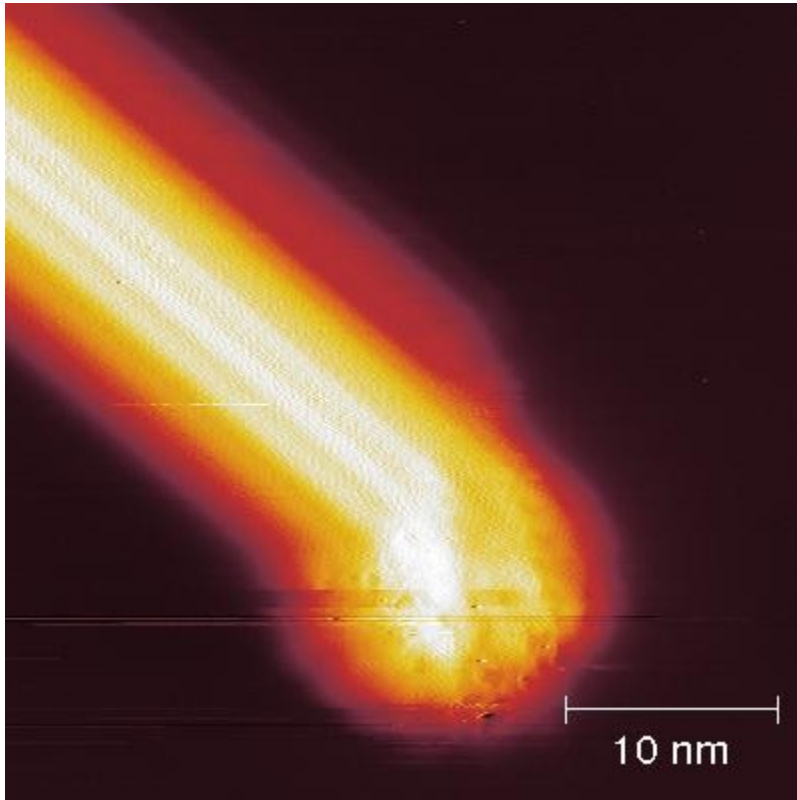


- Molecules arrange at steps and across terraces
- The growth is started/stopped at gold clusters.

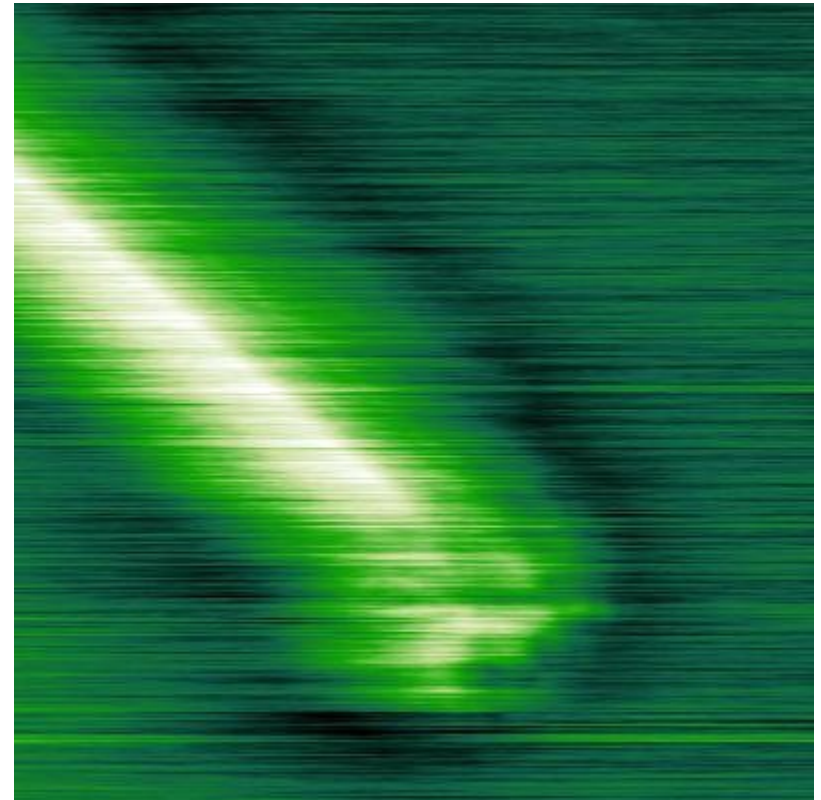
Contacting Molecular Assemblies

KPFM

Topography



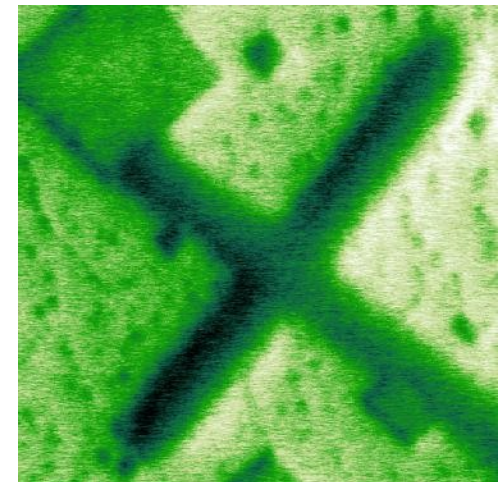
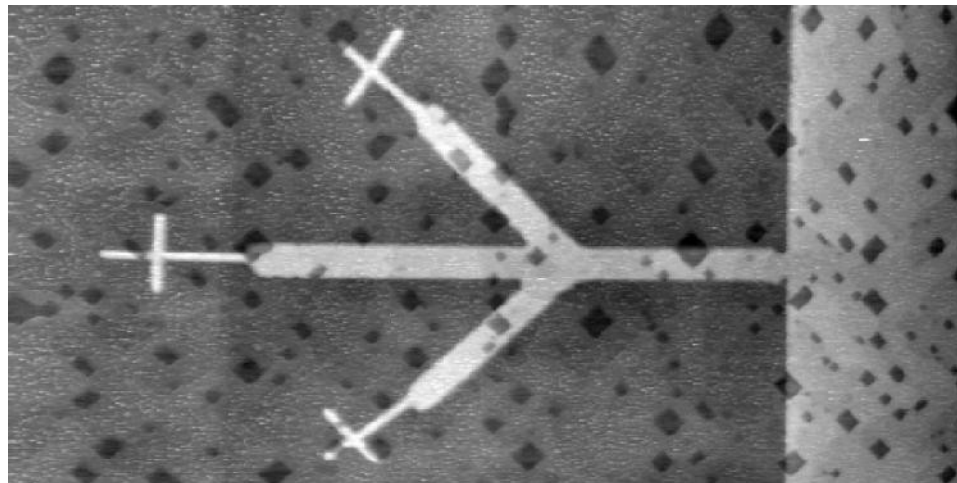
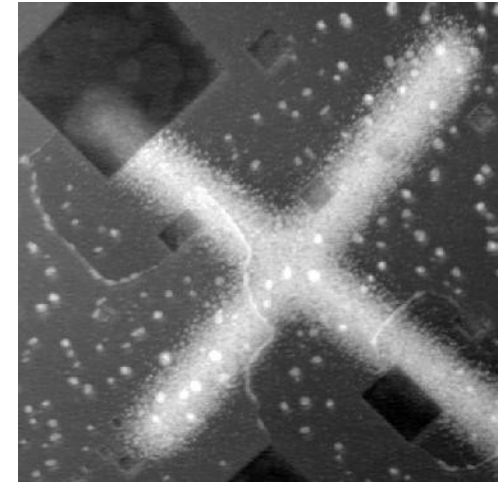
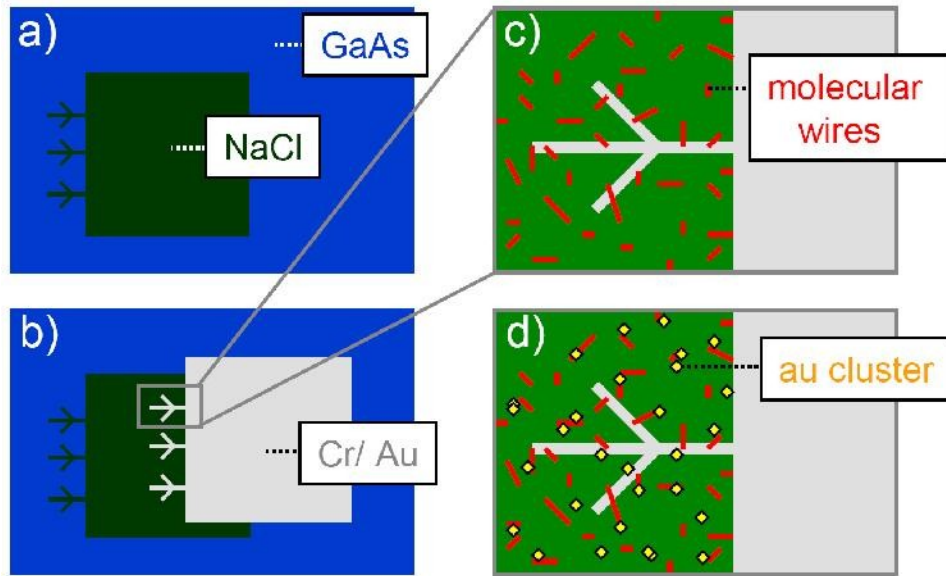
LCPD



LCPD= -0.5...0.2eV

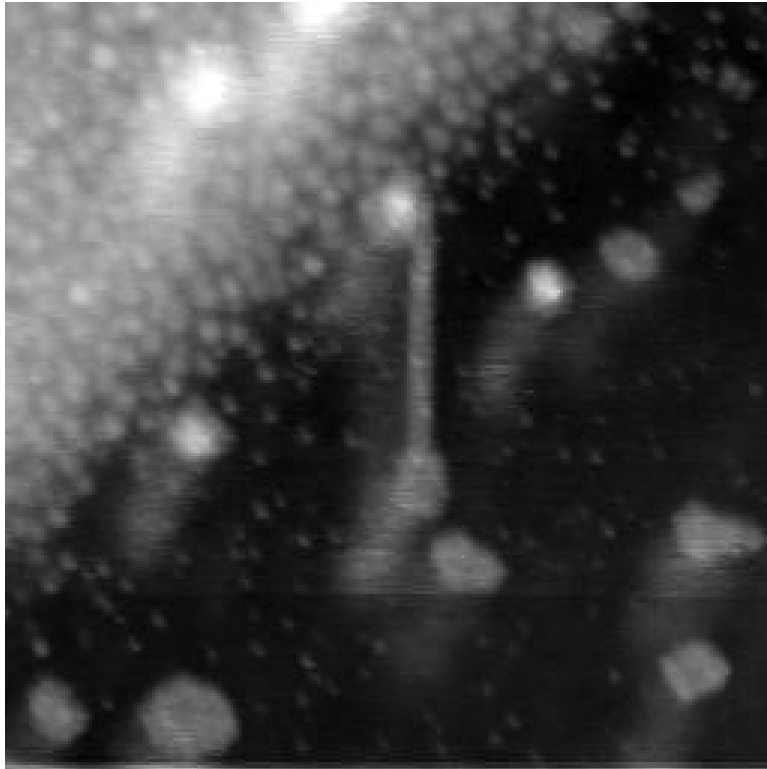
Contacting Molecular Assemblies

Nanostencil (IBM Rüschnikon)

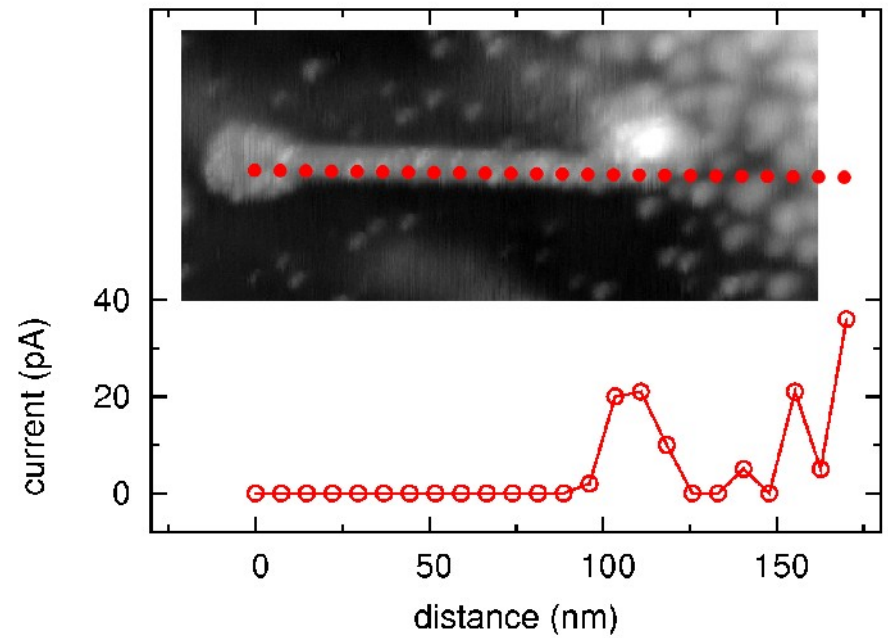


Contacting Molecular Assemblies

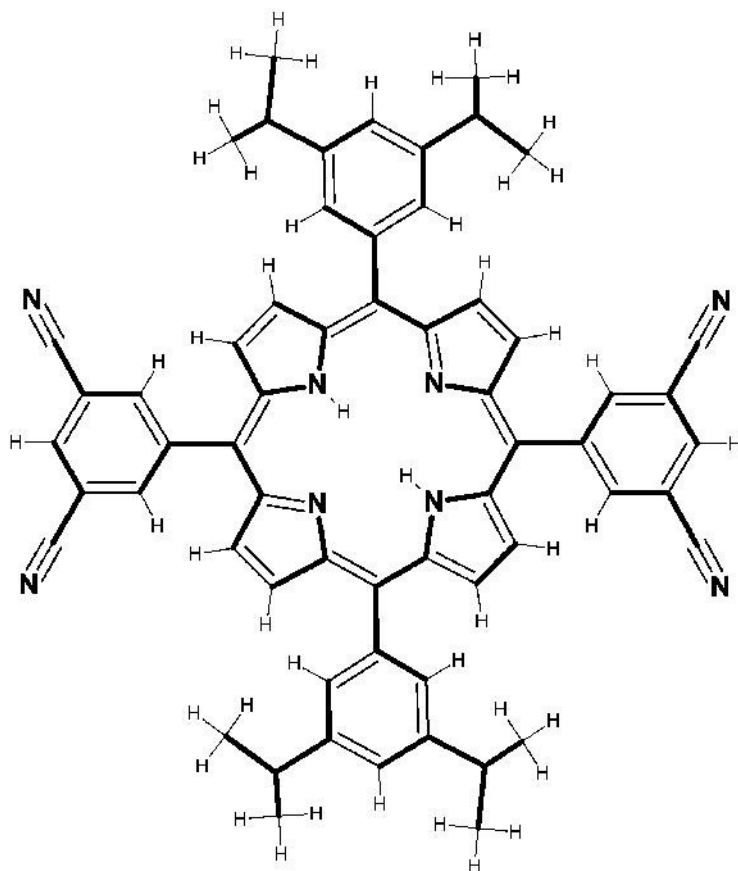
Nanostencil (IBM Rüslikon)



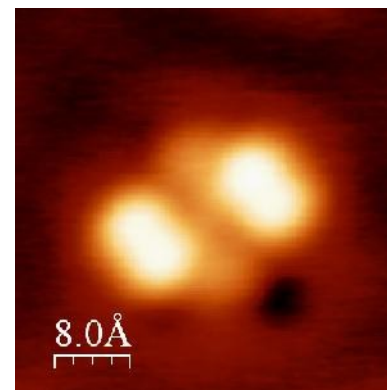
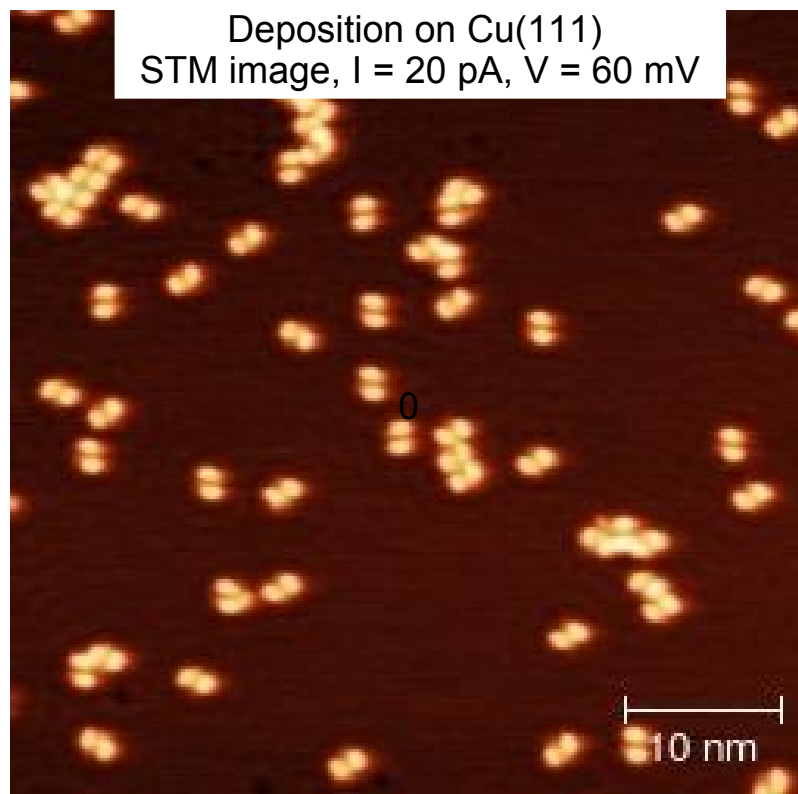
300x300nm²



Porphyrin with bicyanophenyl legs



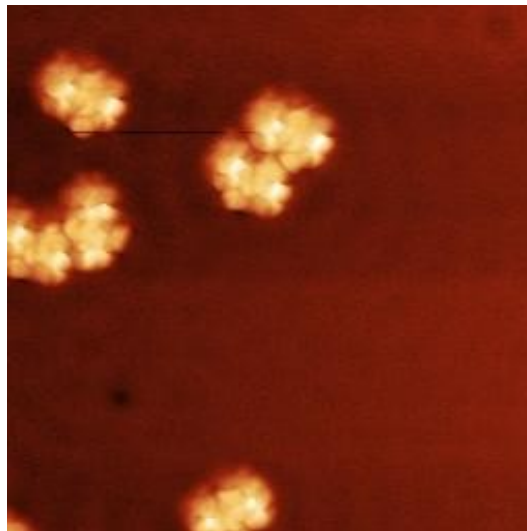
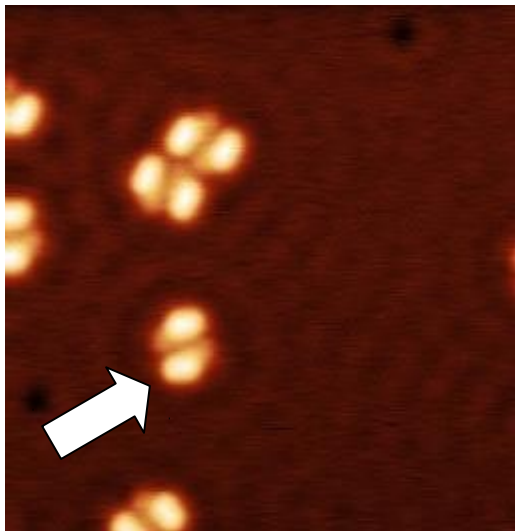
2-bicyanophenyl, 2-aryl H₂-porphyrin
synthesized by F. Diederich (ETH, Zurich)



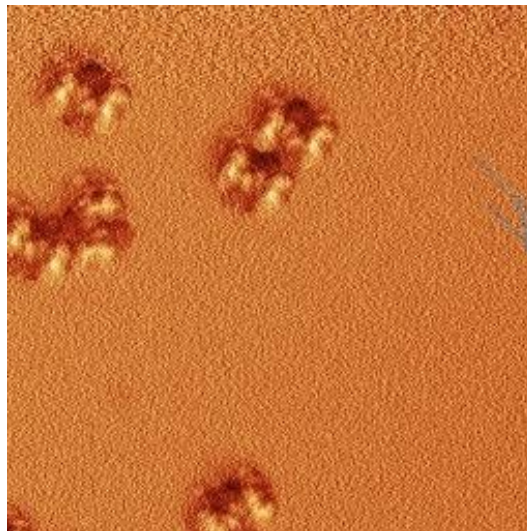
Vertical manipulation: Catch the molecule...

Method: Z spectroscopic curve in the **center** of the molecule

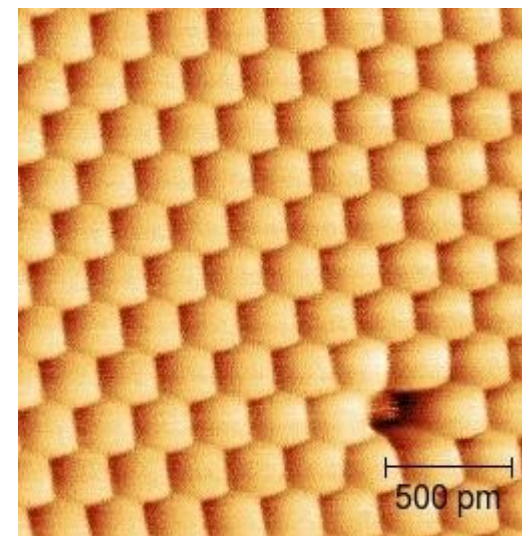
STM Topography



Simultaneous Frequency Shift

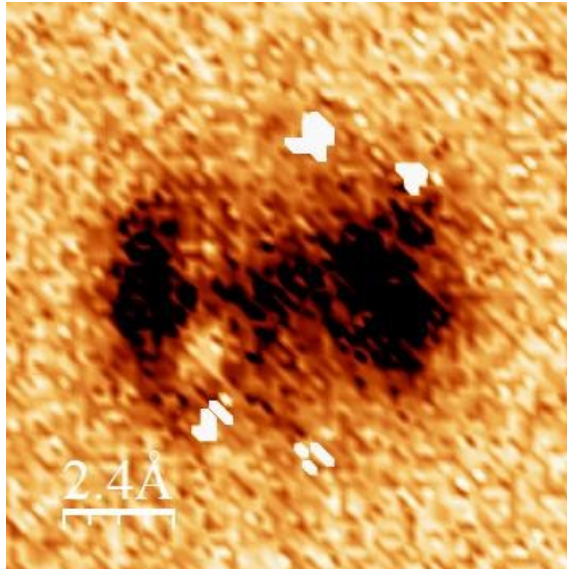


Friction measurement with a molecule linked to the tip

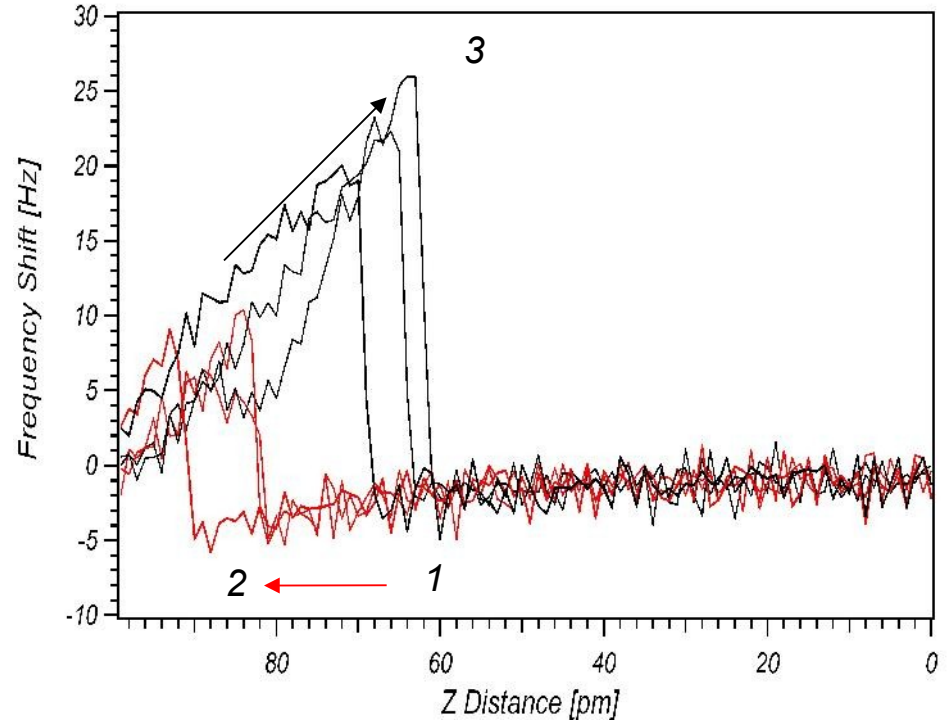


Atomic resolution on Cu(111)

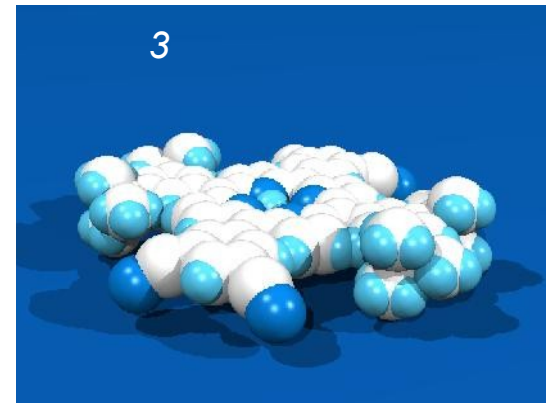
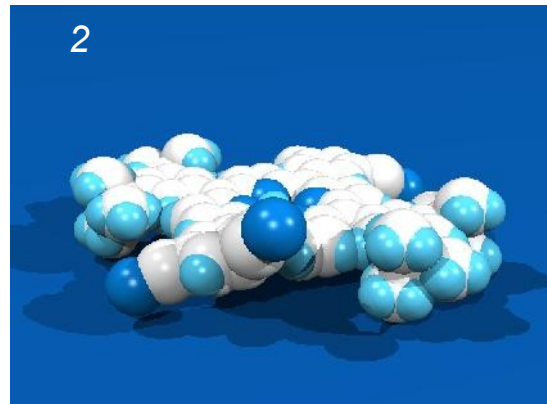
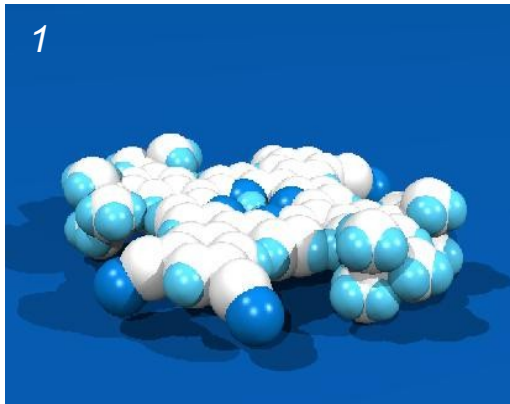
3d-force spectroscopy: Observations of localized instabilities



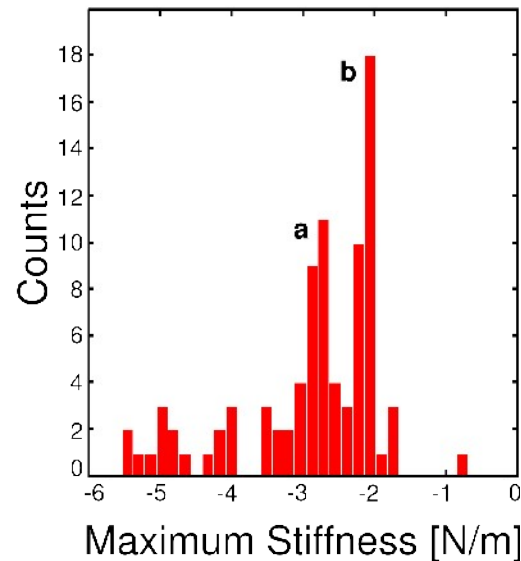
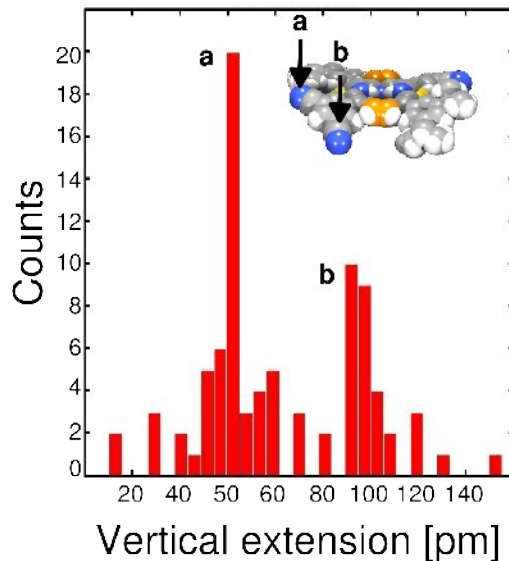
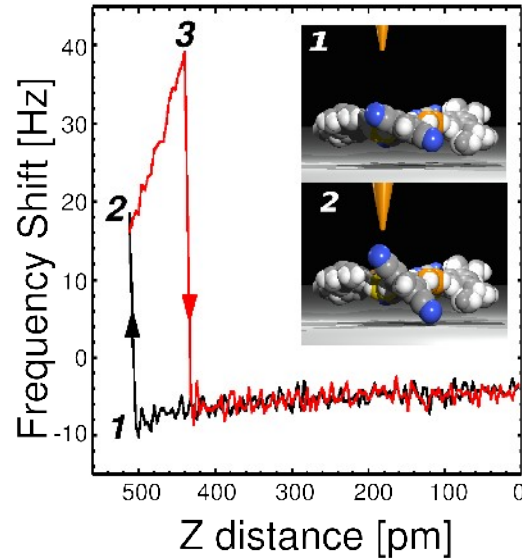
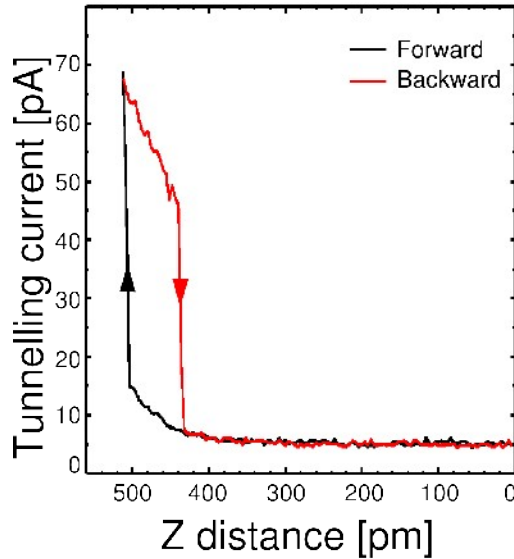
Three-dimensional
Force Field Spectroscopy



Origin of the hysteresis



Vertical switching and statistics



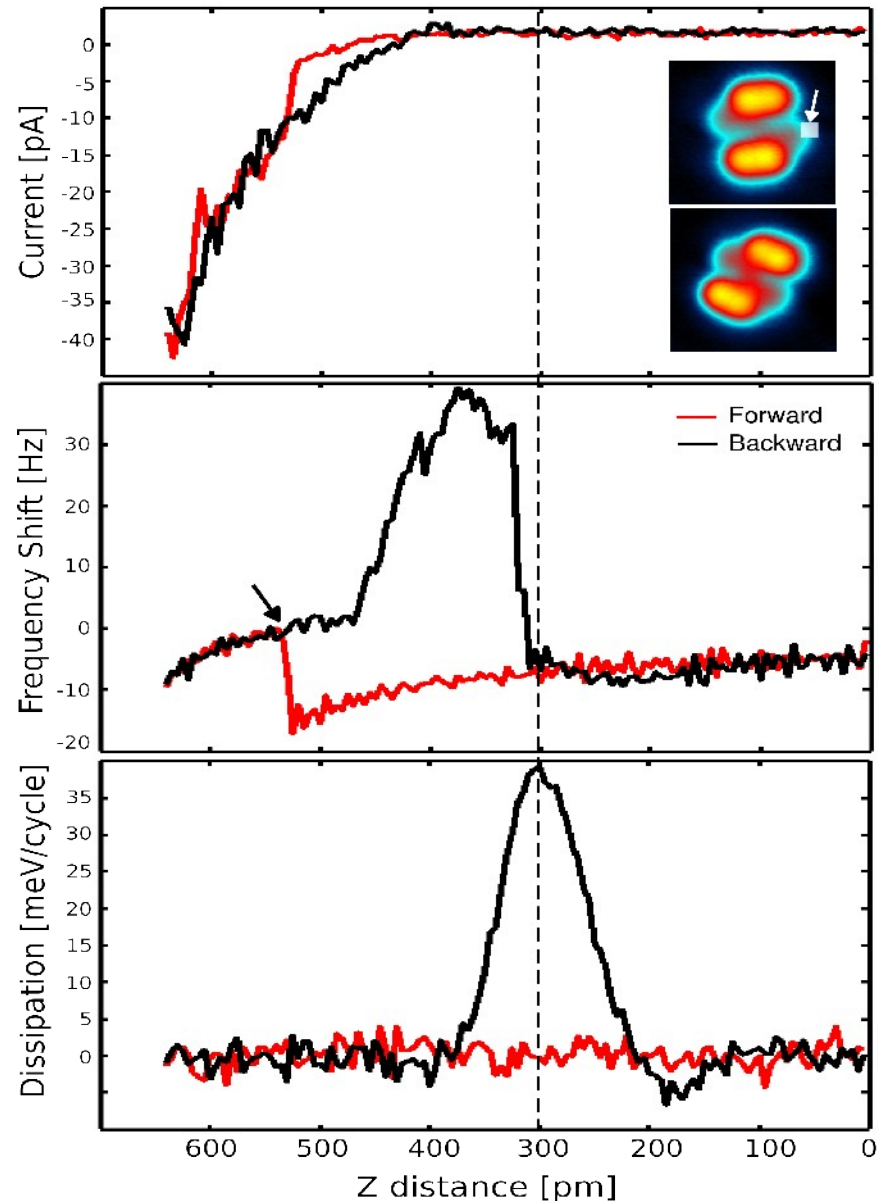
Vertical switching:

- **Tip-molecule junction between a CN function and the Cu-terminated tip.**
- **Attractive interaction force (= -150 pN) to create the bond.**
- **Possibility to lift the porphyrin leg up by retracting the tip.**
- *Elastic process independent of the targeted CN functions as well as the enantiomeric form.*

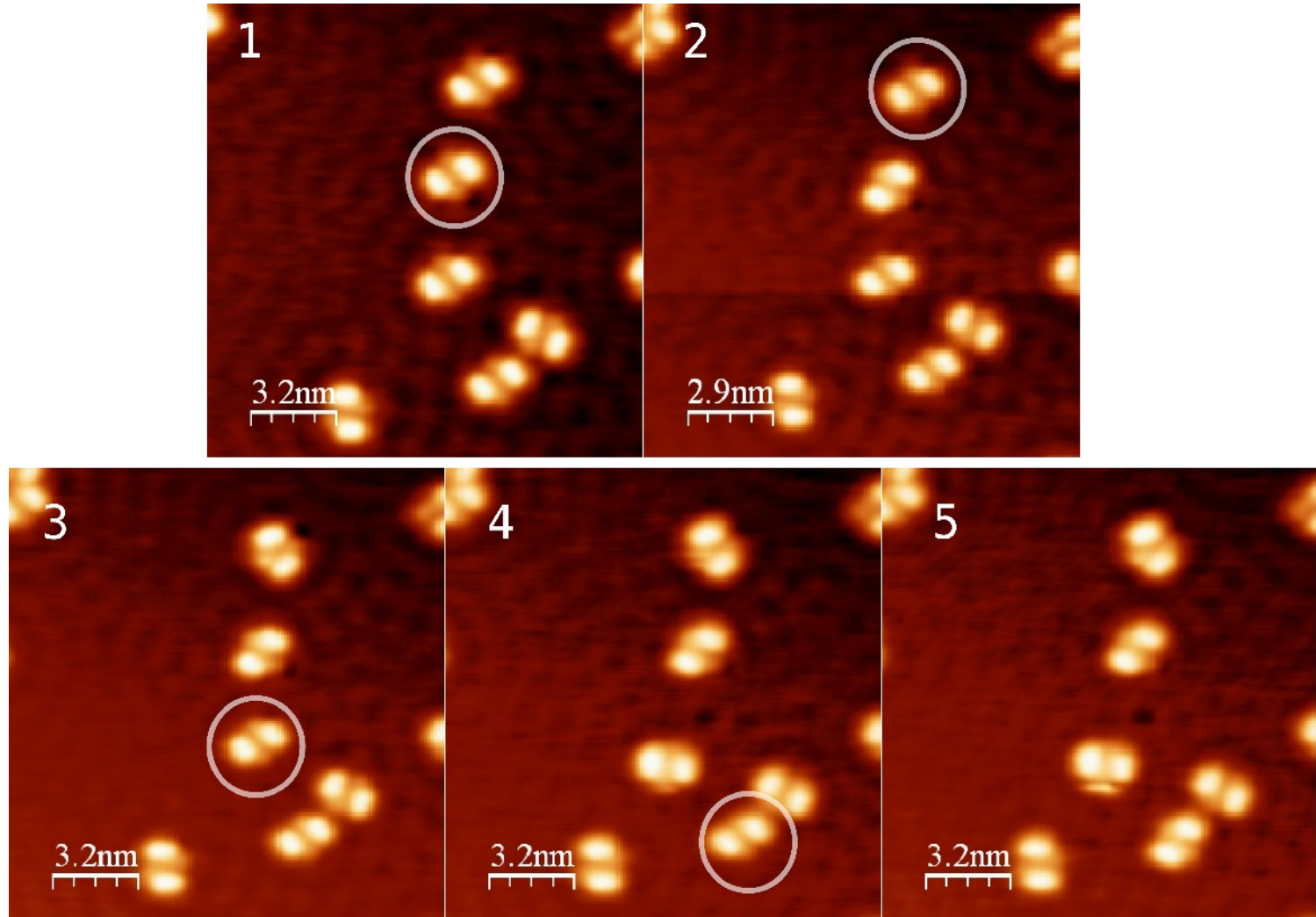
Rotation by controlled force interactions

Rotational switching of the molecule:

- **Tip-induced motion of the porphyrin by manipulating the CN function with a single z spectroscopic curve.**
- **Rotation of 60° with respect to the initial conformation.**
- **Absolute interaction force = - 500 pN during manipulation, dissipated energy = 30-80 meV/cycle.**
- **Fully elastic process (no tunnelling current and bias variation).**

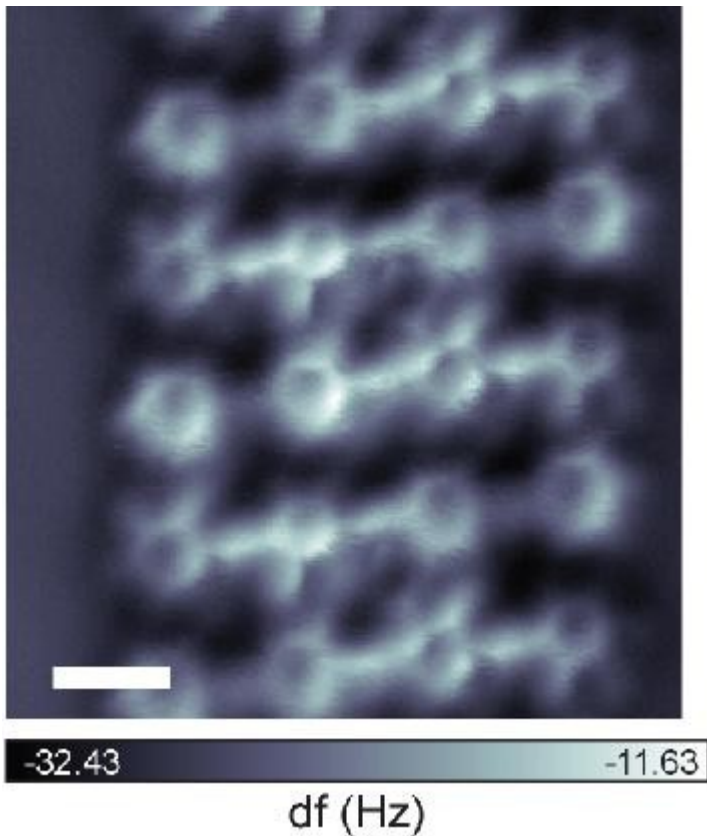
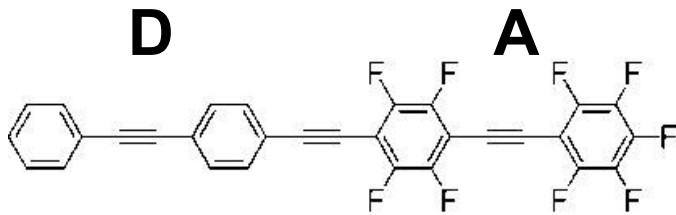


Rotation of molecules clockwise and anticlockwise

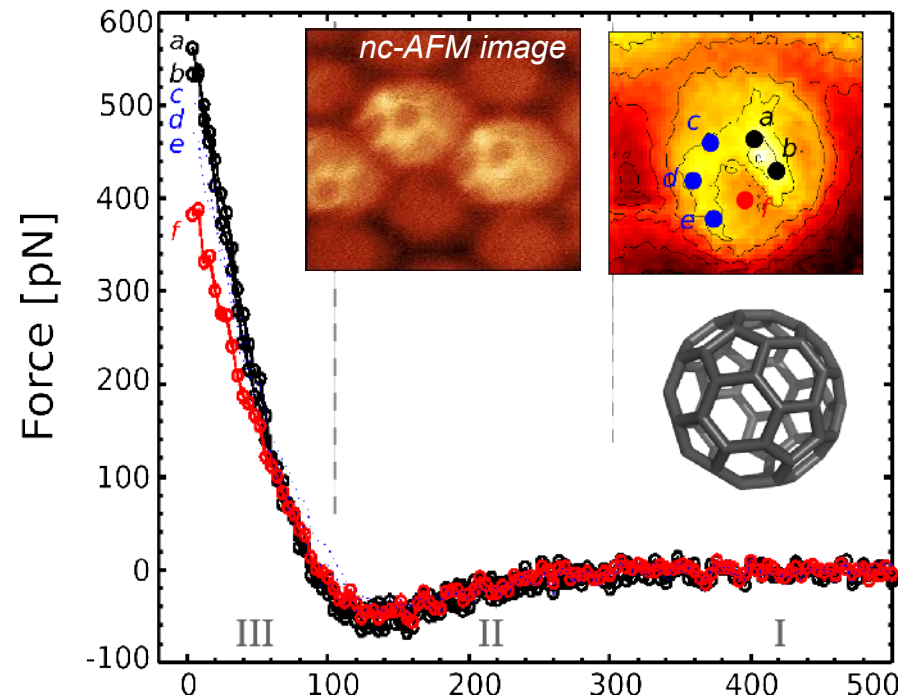


= Possibility to rotate molecules in both directions (clockwise and anticlockwise) without consideration to their symmetry

nc-AFM Messungen



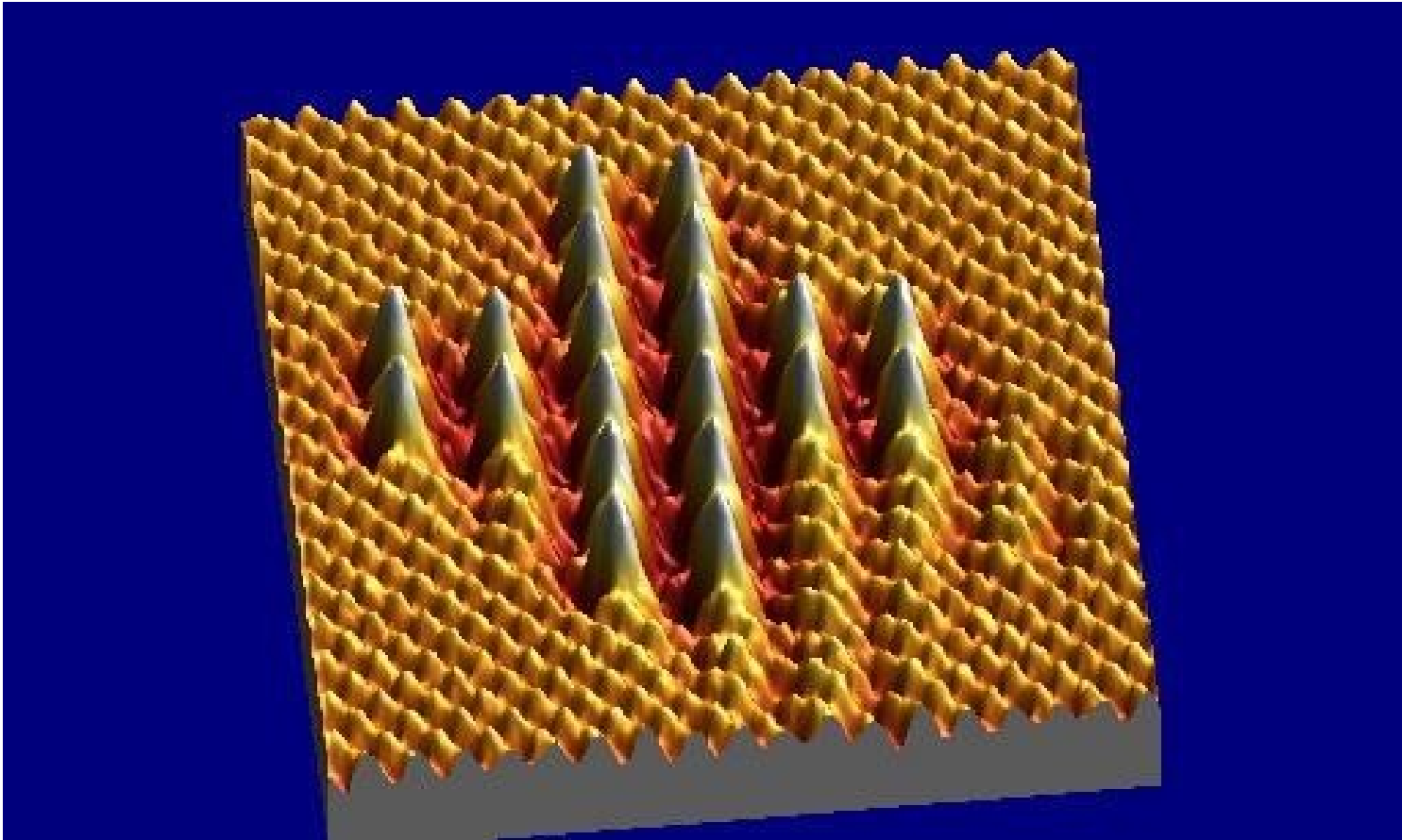
DA molecules on



C_{60} on Cu(111),
Kraftspektroskopie



A Small Swiss Cross made by AFM at room temperature
torsional resonance imaging



S. Shigeki et al.