

# Nanostrukturen-Analysemethoden

## Scanning Probe Microscopy

### • Scanning Tunneling Microscopy

- Tunneleffekt
- G. Binnig and H. Rohrer, Nobelpreis 1986
- Experimenteller Aufbau

### • Friction Force Microscopy

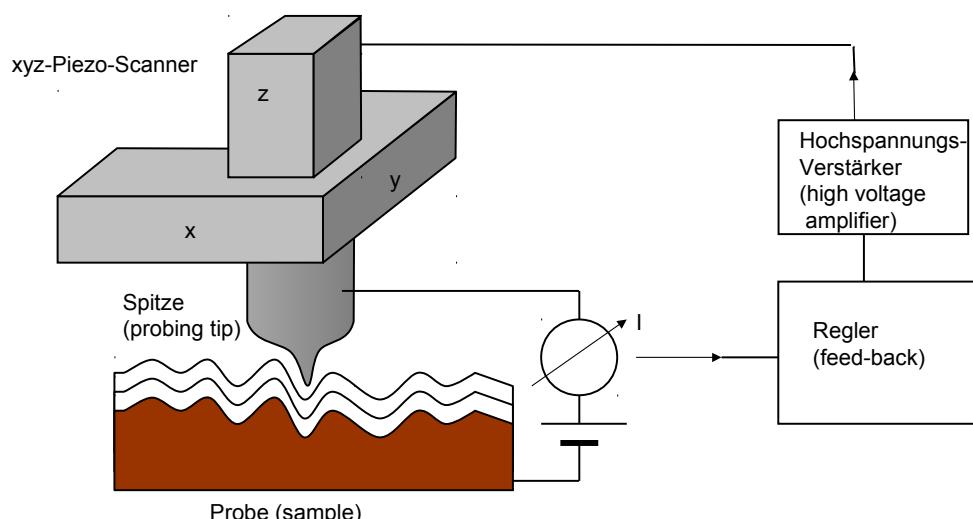
- Force Calibration
- Atomic Stick Slip
- Tomlinson Model
- Nano-manipulation

### • Atomic Force Microscopy

- Short- and Long-Range Forces
- Kelvin Probe Force Microscopy
- Measurements on Semiconducting Devices
- Molecules on Insulating Surfaces
- Manipulation

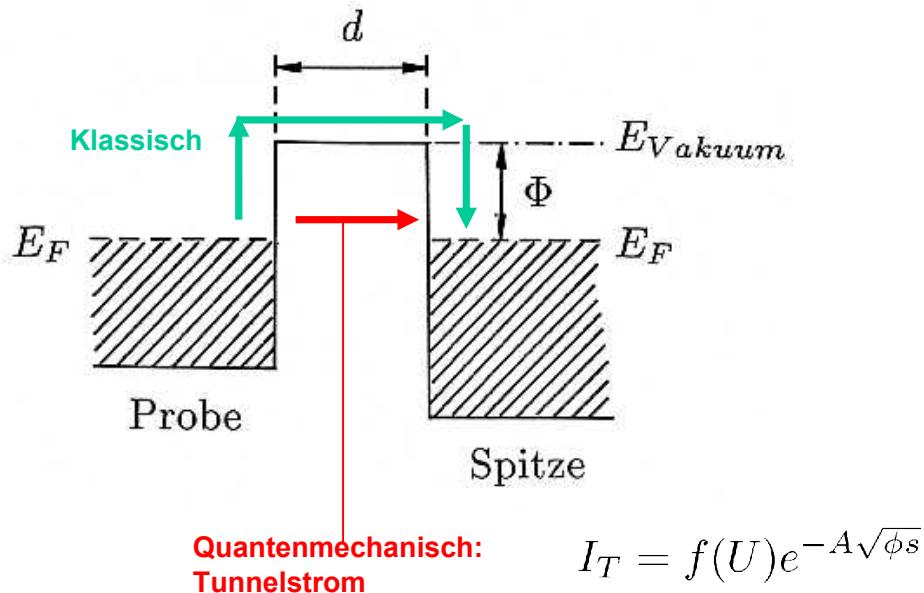
Thilo Glatzel, [thilo.glatzel@unibas.ch](mailto:thilo.glatzel@unibas.ch)  
NANOlino Lab

## Rastertunnelmikroskop (STM)



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

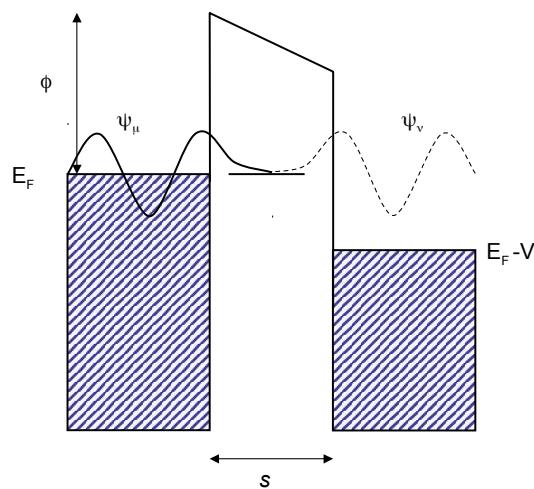
## Tunneleffekt



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

## 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.



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

## Tunneleffekt

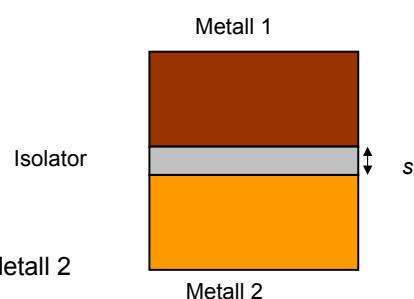
$$I_T = f(U) e^{-A\sqrt{\phi s}}$$

$I_T$ : Tunnelstrom

$U$ : Extern angelegte Spannung

$s$ : Distanz zwischen Probe und Spitze

$\phi$ : Barrierenhöhe



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

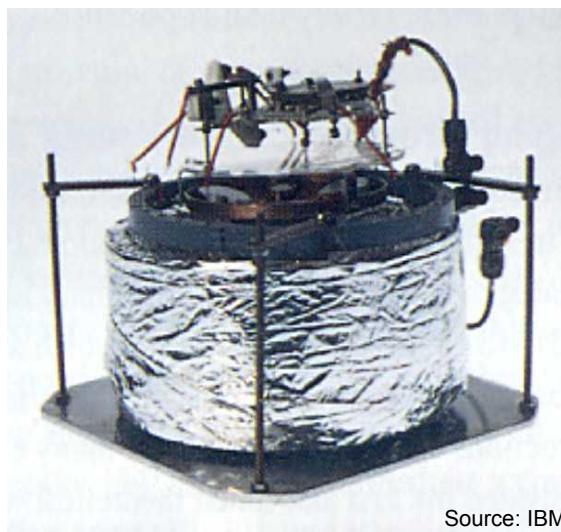
$$A = 2 \sqrt{\frac{2m}{\hbar^2}} = 1.025 \text{ Å}^{-1} eV^{-1/2}$$

$f(U)$ : 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  $=4.5 \text{ eV}$  ändert sich der Strom etwa um eine Größenordnung, wenn die Distanz um  $1 \text{ Å}$  verändert wird. Historisch wurde zuerst das Oxidtunneln realisiert. Erst mit dem STM konnte Vakuumtunneln beobachtet werden.

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

## Scanning Tunneling Microscope (STM)



Source: IBM

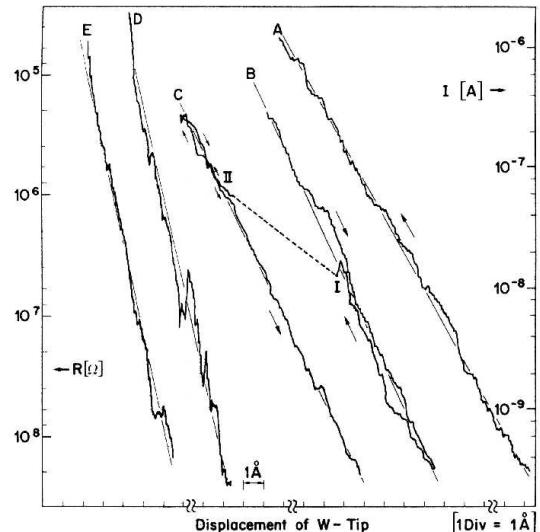
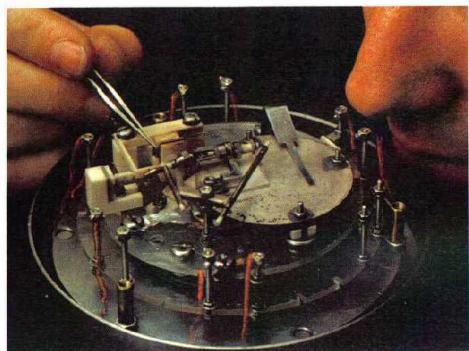


G. Binnig and H. Rohrer  
Nobelpreis 1986

IBM Rüschlikon  
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)

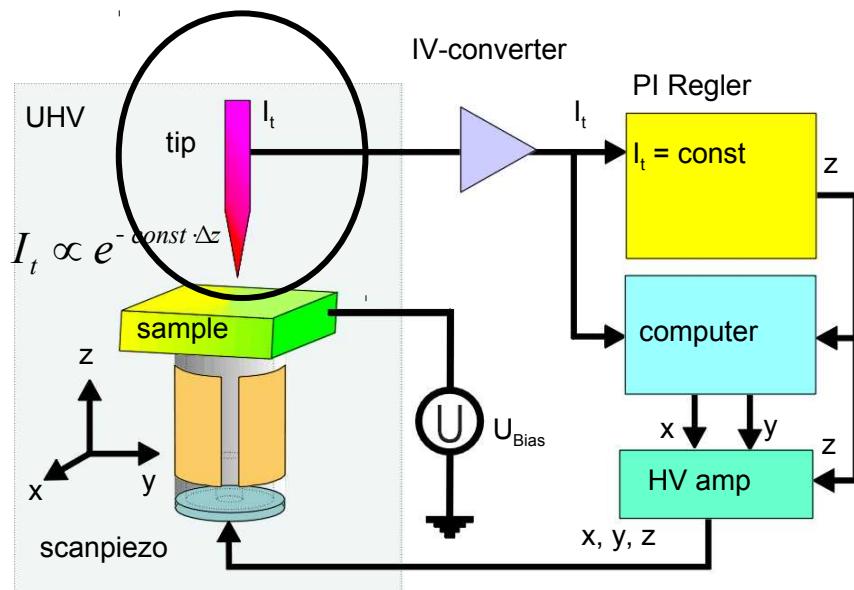
## Scanning Tunneling Microscopy (STM)



Exponentieller Abfall des Tunnelstroms mit dem Abstand

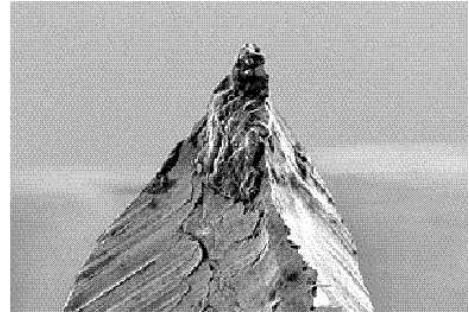
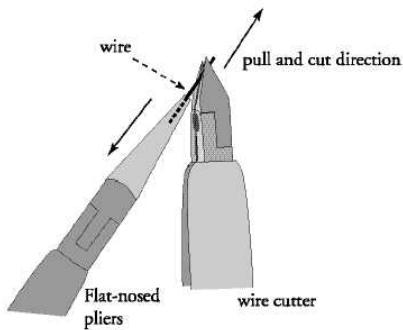
G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Appl. Phys. Lett., Vol. 40, Issue 2, pp. 178-180 (1982)

## Blockschaltbild STM



# Spitzen

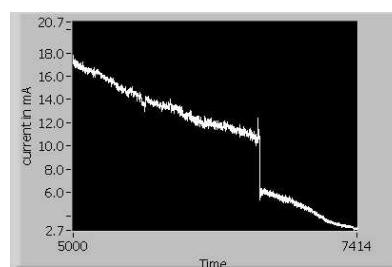
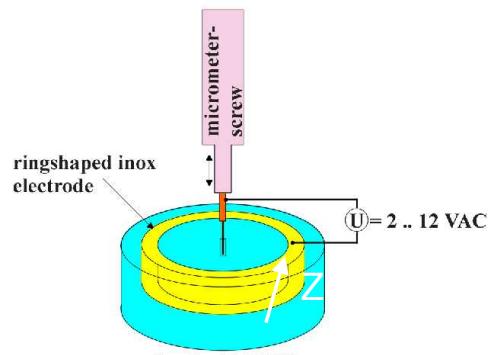
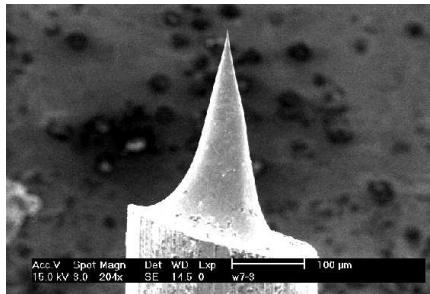
## 1. Abgerissener PtIr Draht



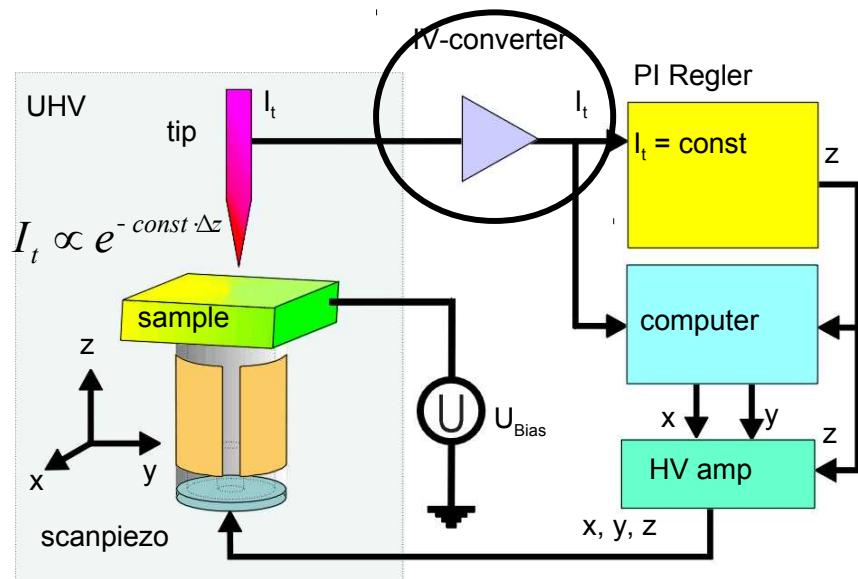
Oder...

# Spitzen

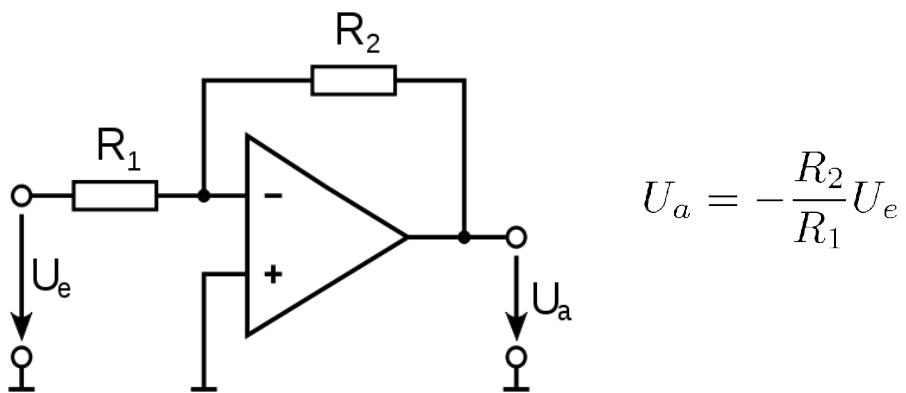
## 2. Elektrochemisch geätzte Wolframspitzen:



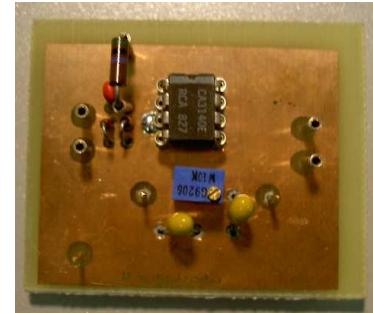
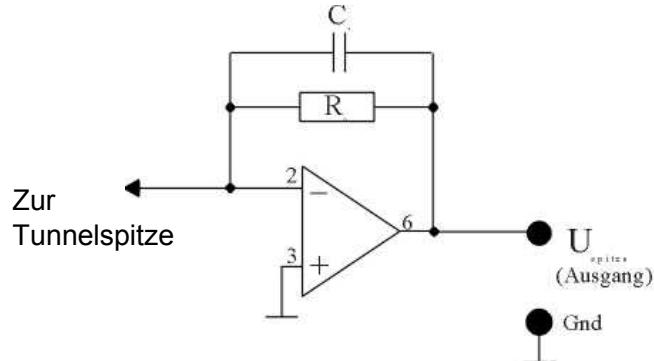
## Blockschaltbild STM



## Invertierender Verstärker



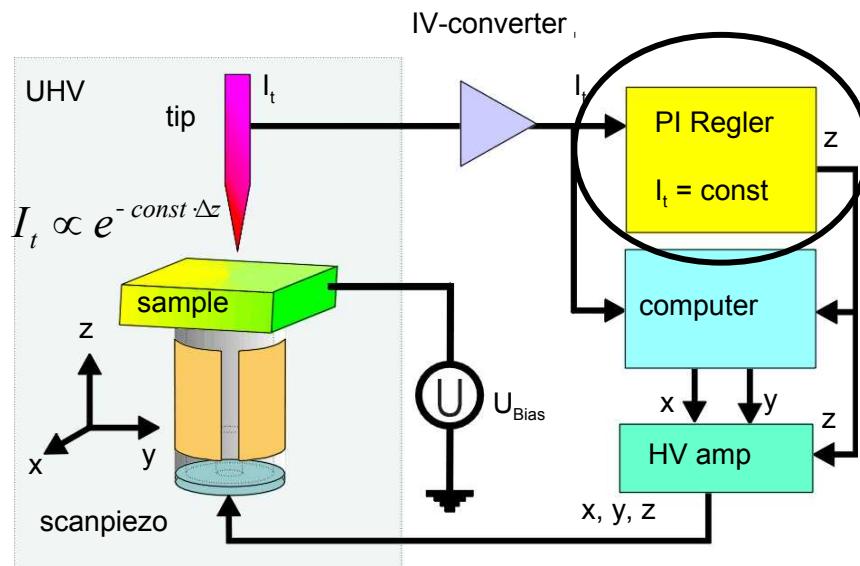
## Strom-Spannungswandler



$$U_A = -R \cdot I_t$$

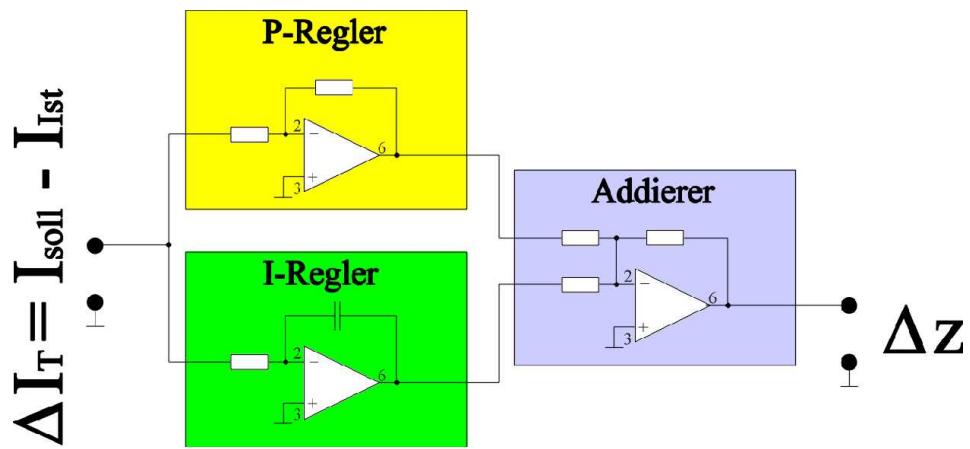
Bei  $R = 100\text{M}\Omega$  entspricht  $U_A = 1\text{V}$   
einem Tunnelstrom von  $10\text{nA}$

## Blockschaltbild STM

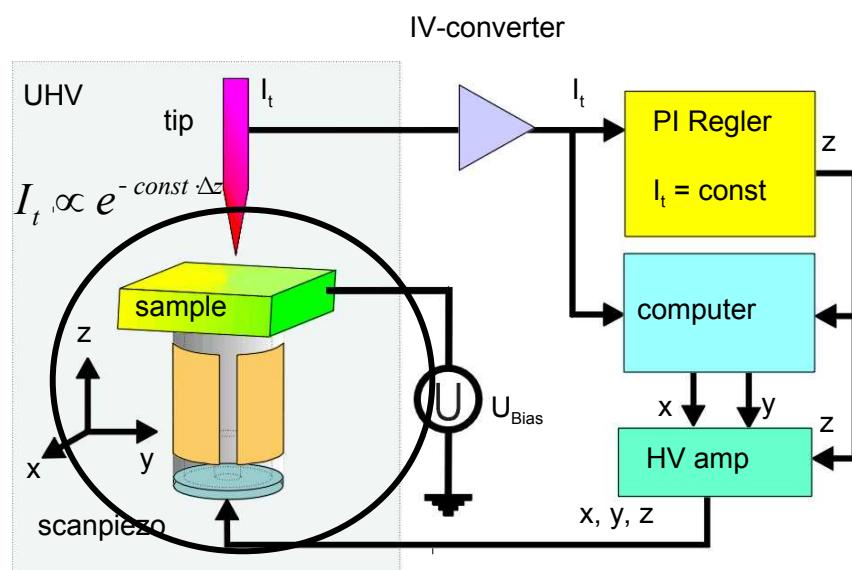


## PI Regler

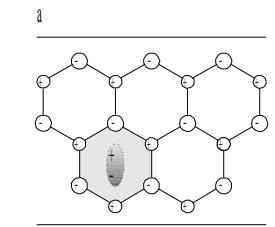
Regelt den Abstand Spitze-Probe so, dass der Tunnelstrom konstant bleibt



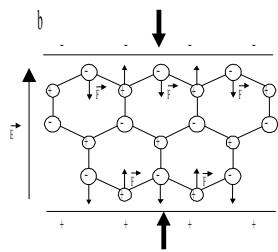
## Blockschaltbild STM



# Piezos



## Verschiedene Ladungsschwerpunkte



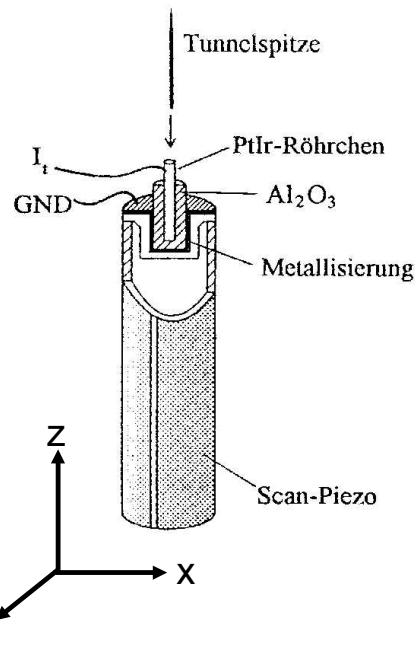
Verformung  
durch  
Anlegen einer  
elektrischen  
Spannung

## **Typische Piezoelektrische Materialien:**

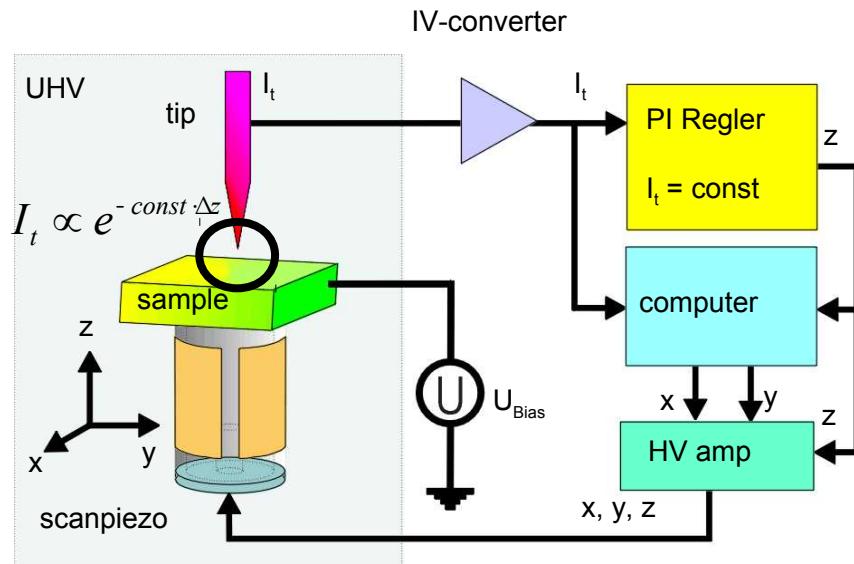
- Quarz
  - Bariumtitanat
  - Bleizirkontitanat (PZT)
  - Etc.

# Piezotubes

## XYZ-Stellglieder

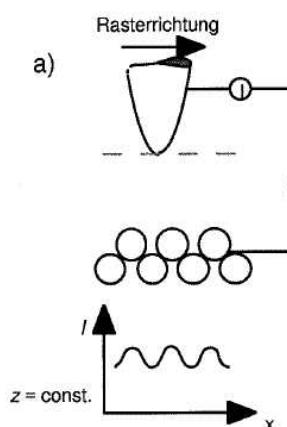


## Blockschaltbild STM

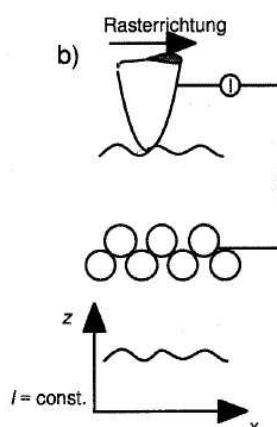


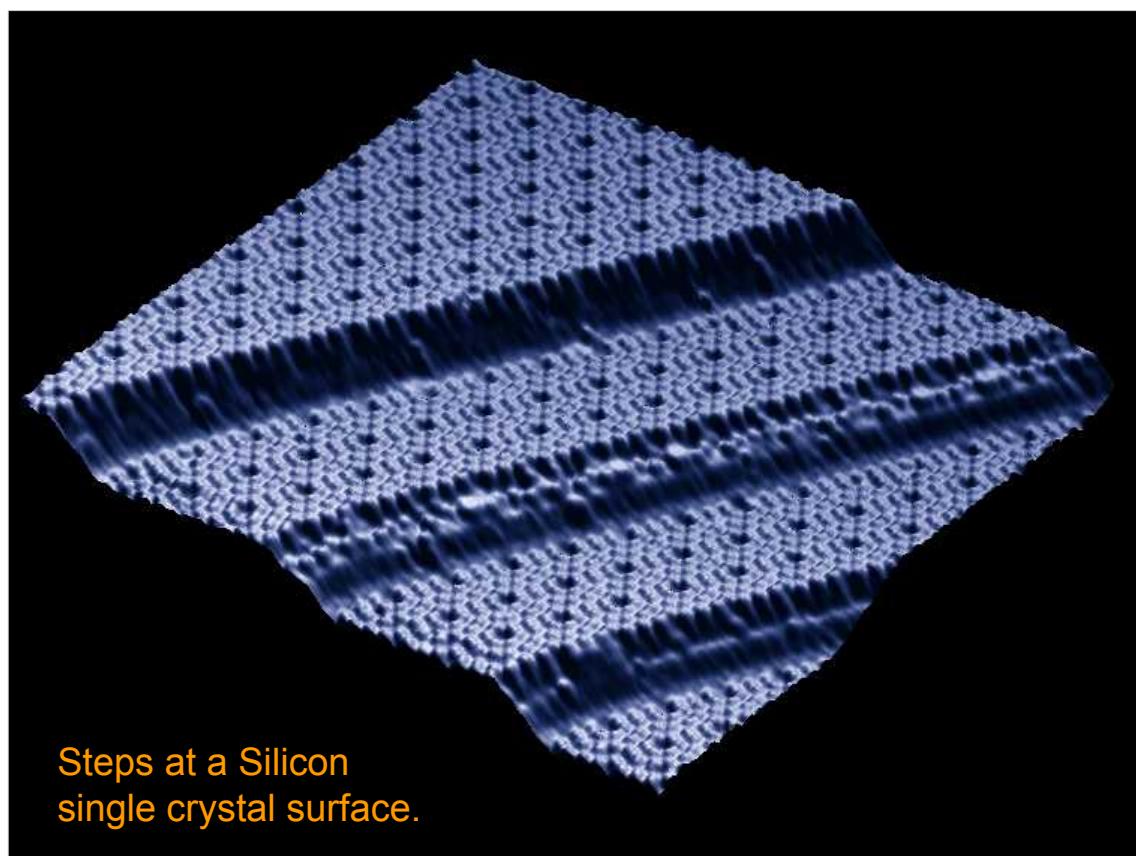
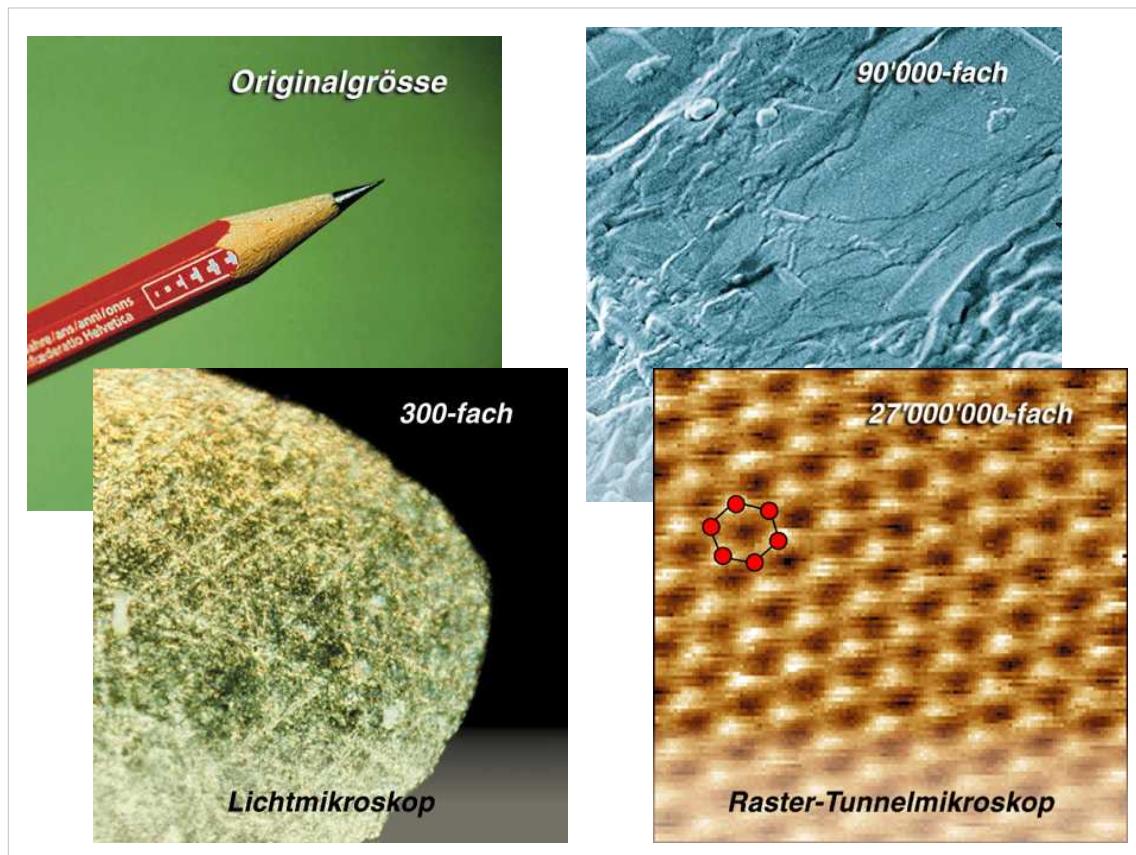
## Messmodi

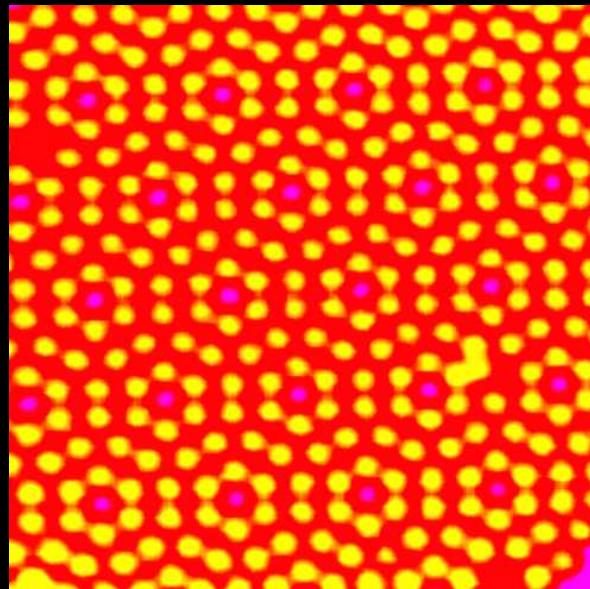
### Constant Height



### Constant Current



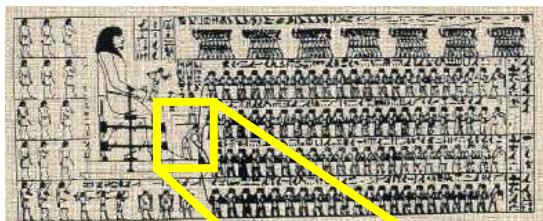




Si(111)7x7 reconstructed surface

## Importance of Friction

Long time ago...

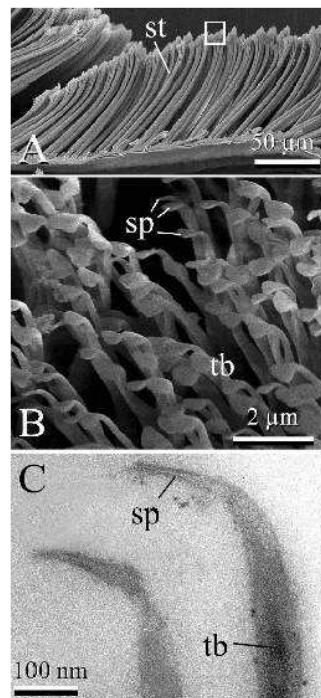


Nowadays...



In all cases: It is highly desirable to reduce and control friction

## Gecko uses nanometer-sized contacts to climb walls

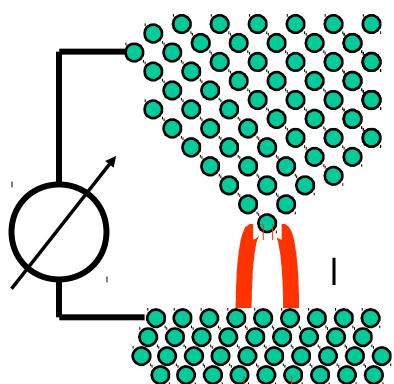


Gecko is able to control the contact area on all length scales

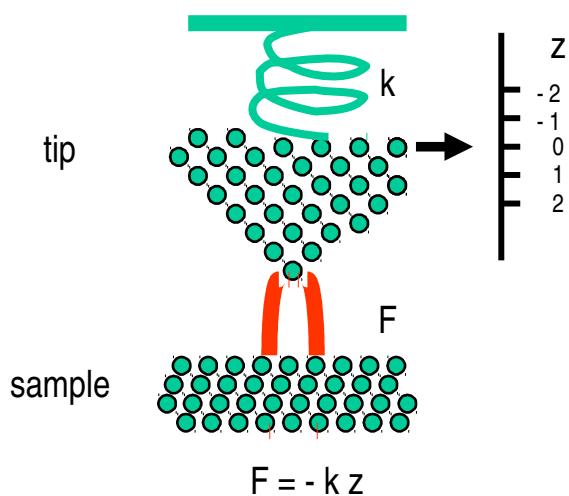
From B. Persson and S. Gorb  
JCP, 119, 11437 (2003)

## Scanning X Microscopy

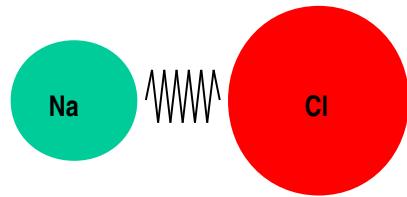
### S Tunneling M



### S Force M



## Kräfte zwischen zwei Atomen

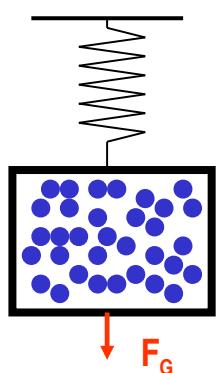


Chemische Bindung

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

$$1.6 \text{ nN}$$

## „Kräfte Spüren“



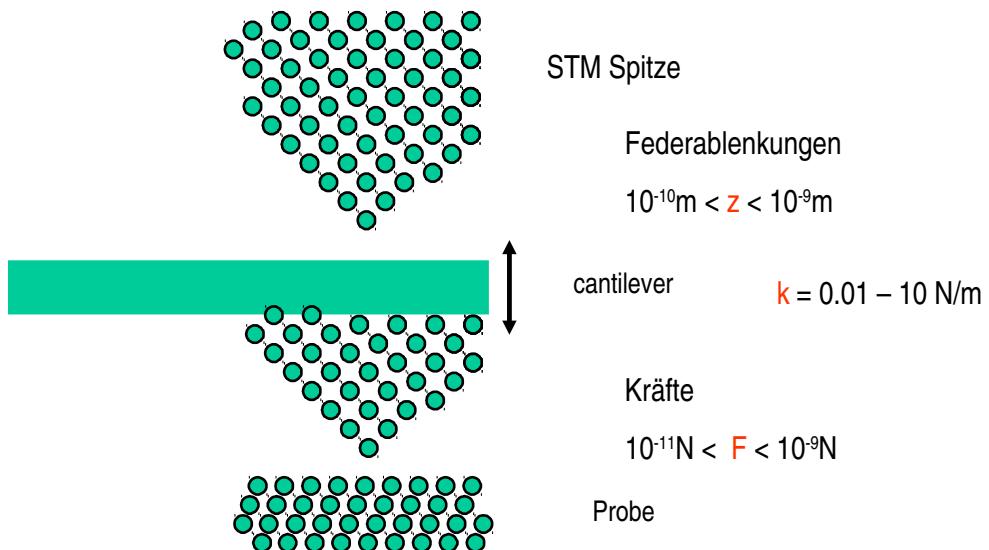
1 nm<sup>3</sup> Wasser (33 Moleküle)

0.01 g

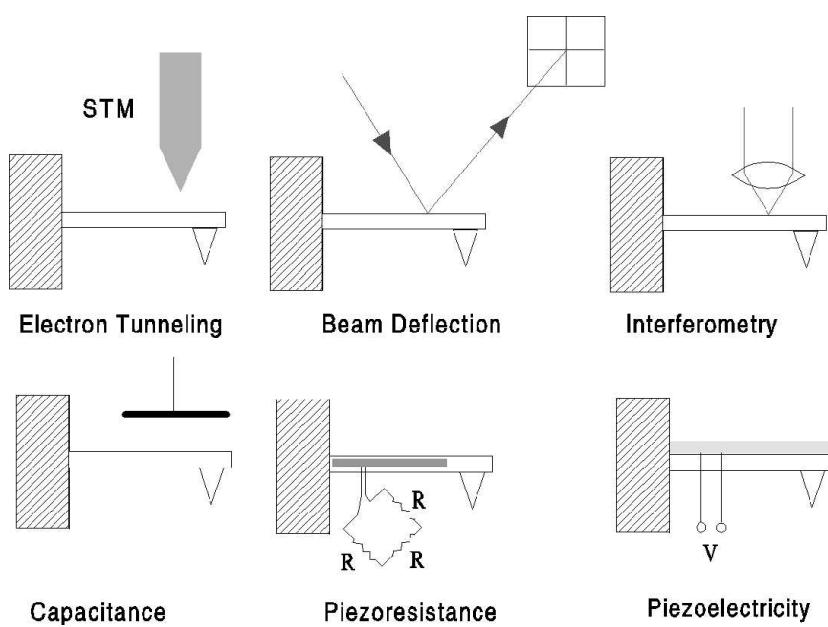
$$F_G = 10^{-23} \text{ N} = 10^{-14} \text{ nN}$$

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

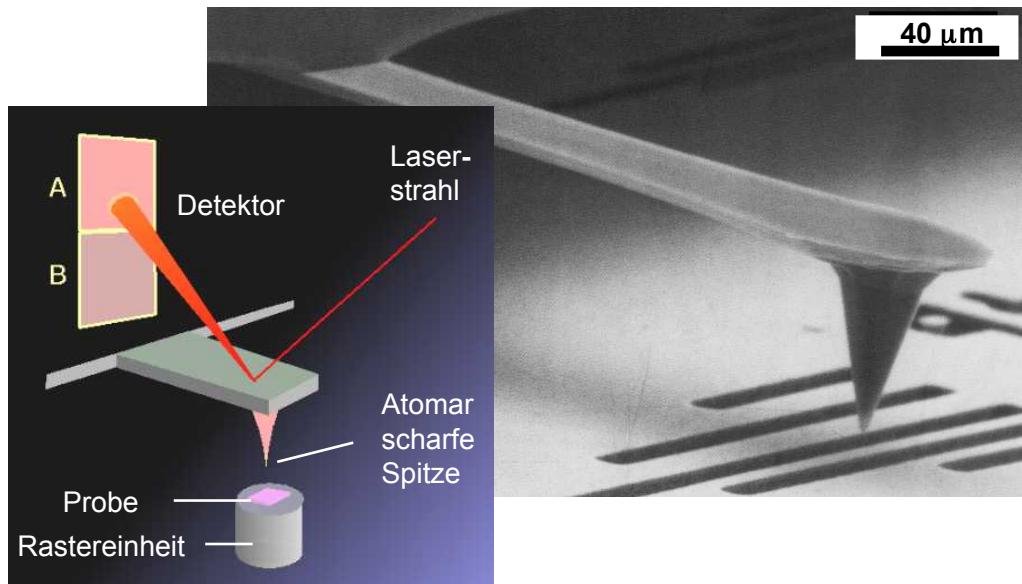
## Prinzip des ersten AFMs



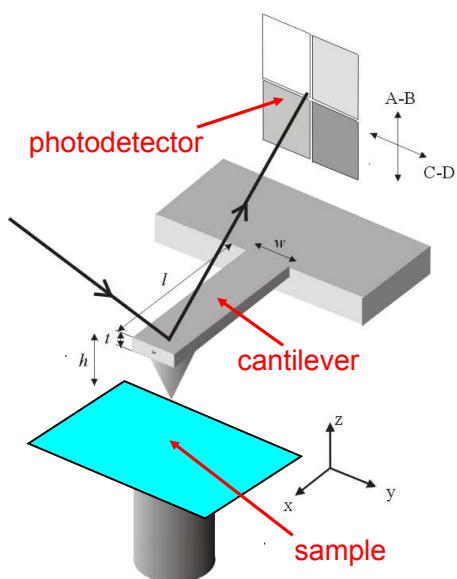
## Ablenkungssensoren



## „Beam deflection“-Methode

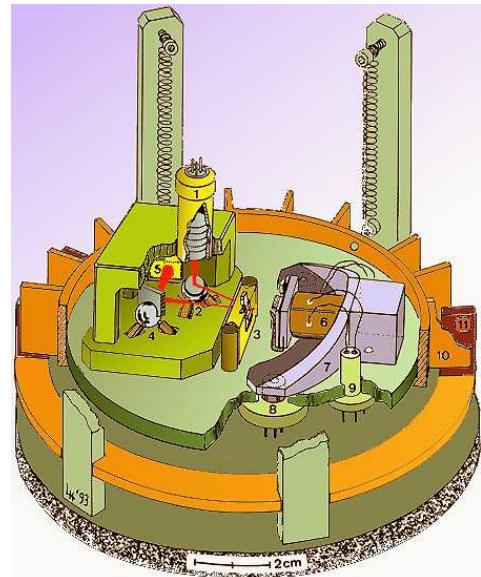
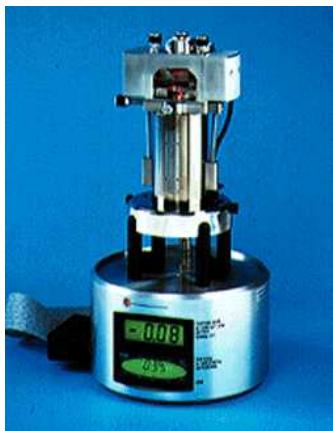


## Atomic Force Microscopy (beam deflection)

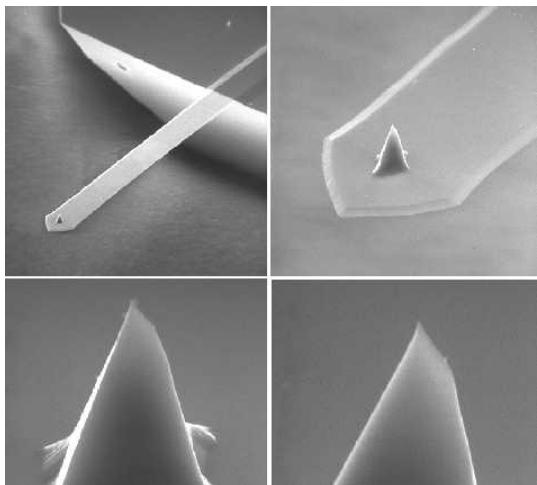


- The normal and lateral forces on a sharp tip sliding on a surface are sensed using a laser beam
- Forces < 1 nN can be measured

## Beispiele



## Microfabrizierte "Cantilever"



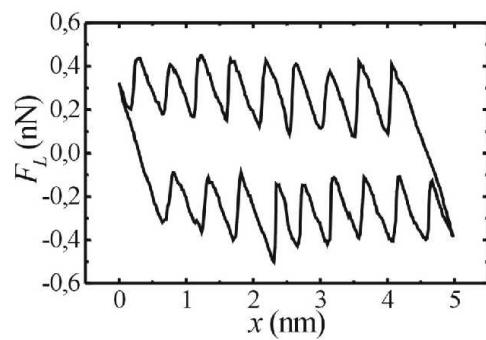
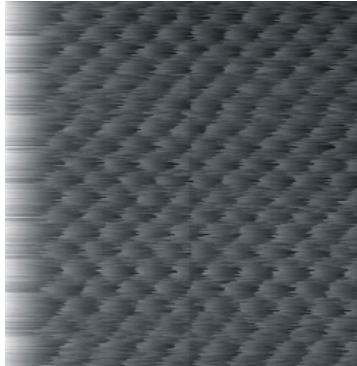
Länge :  $l = 450 \mu\text{m}$   
Breite :  $w = 45 \mu\text{m}$   
Dicke:  $t = 1.5 \mu\text{m}$   
 $E=1.69 \cdot 10^{11} \text{ N/m}^2$

Spitzenhöhe:  $12 \mu\text{m}$   
Spitzenradius:  $10 \text{ nm}$

Federkonstante  $k$ :

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

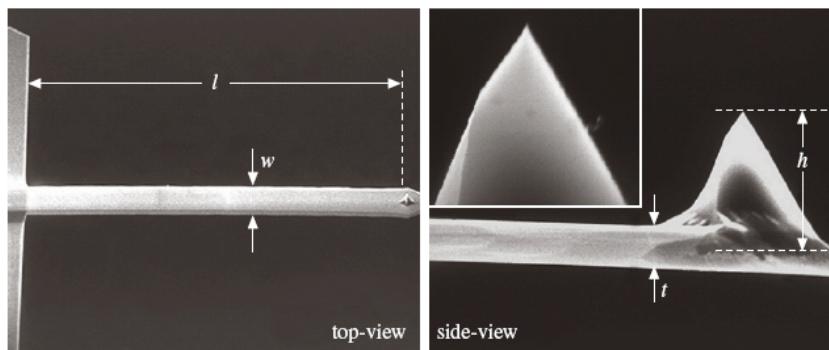
## Atomic stick-slip



(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**:

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

- $\rho$ ,  $E$ : 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:

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

- $G$ : shear modulus

- For pure silicon:

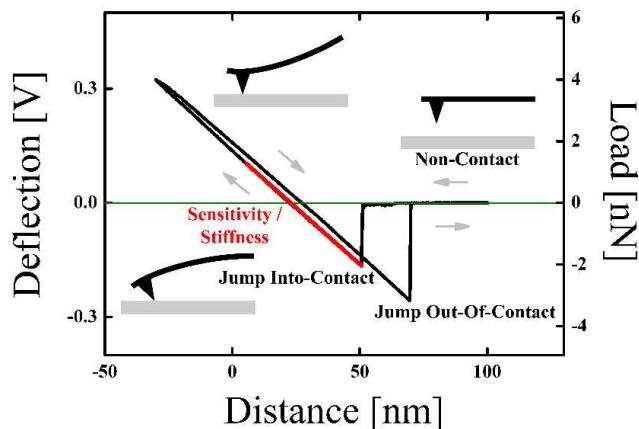
$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

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

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

## Force Calibration

- Next step: **sensitivity of photodetector**
- Force-distance curves on hard surfaces (e.g.  $\text{Al}_2\text{O}_3$ ):



- Scanner movement = cantilever deflection
- Slope → sensitivity

## Force Calibration

- **Normal and lateral forces:**

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

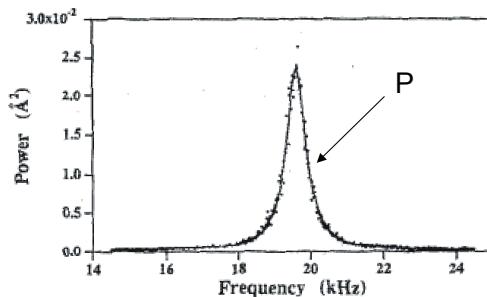
(if the laser beam is above the probing tip!)

- $V_N, V_L$ : normal and lateral signals

## Force Calibration

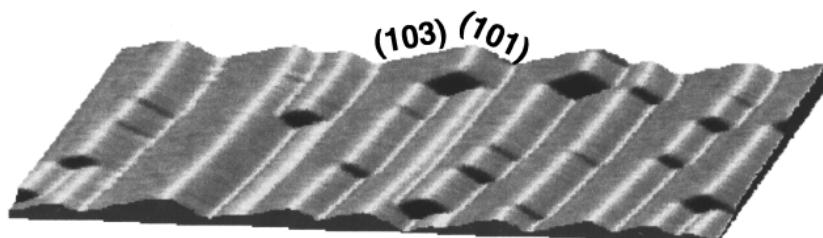
- Alternative method: Spring constant **from thermal power spectrum** (Hutter et al., RSI 1993)
- Correct relation (Butt et al., Nanotech. 1995):

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

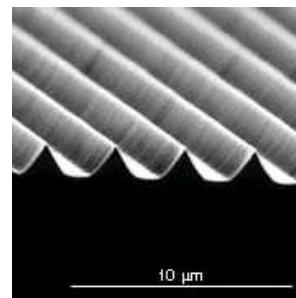


## Force Calibration

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



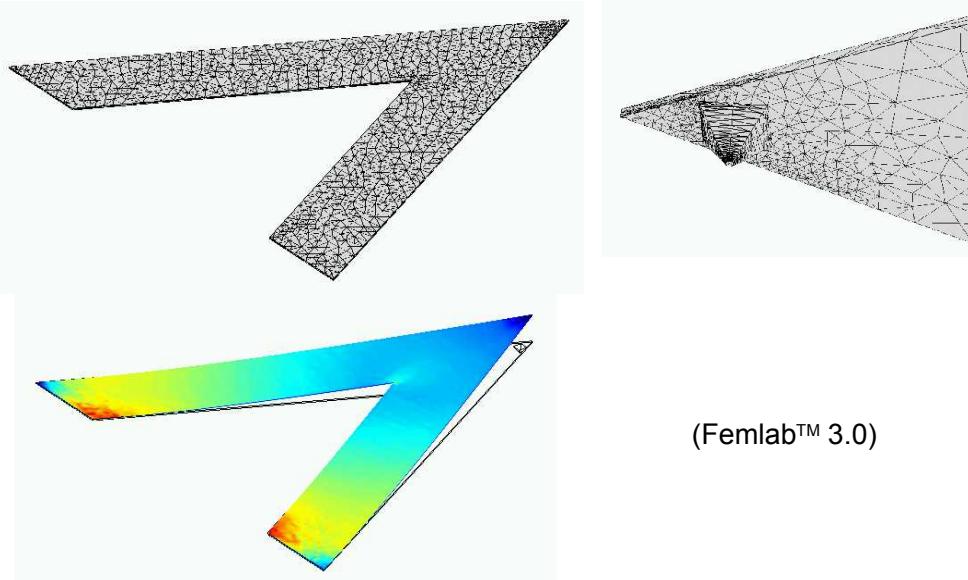
Commercially available grating:



(TGG01, NT-MDT,  
Moscow)

## Force Calibration

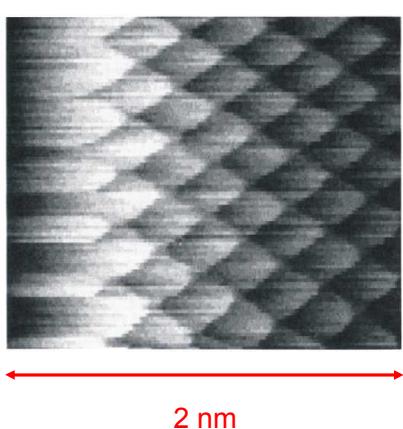
- Different shapes → Finite elements analysis



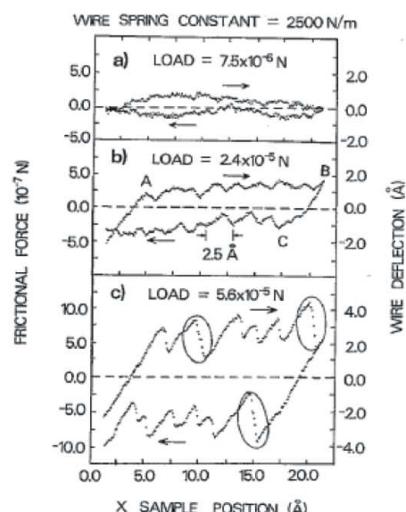
(Femlab™ 3.0)

## Atomic-Scale Measurements

- Atomic friction on **graphite**:

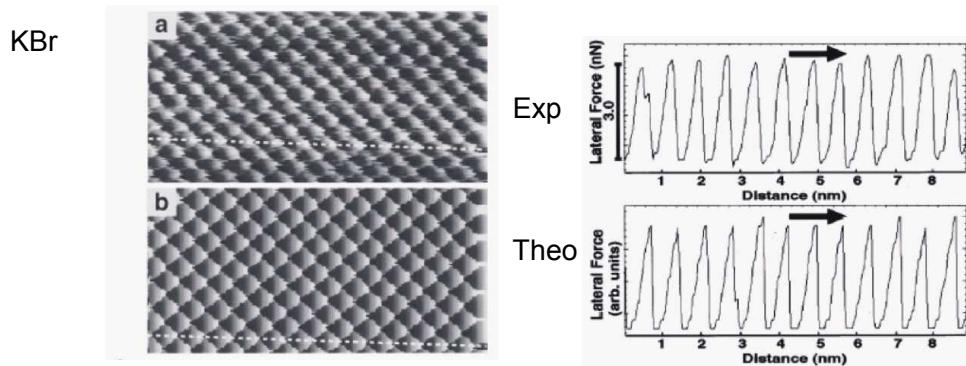


(Mate et al., PRL 1987)



## Atomic-Scale Measurements

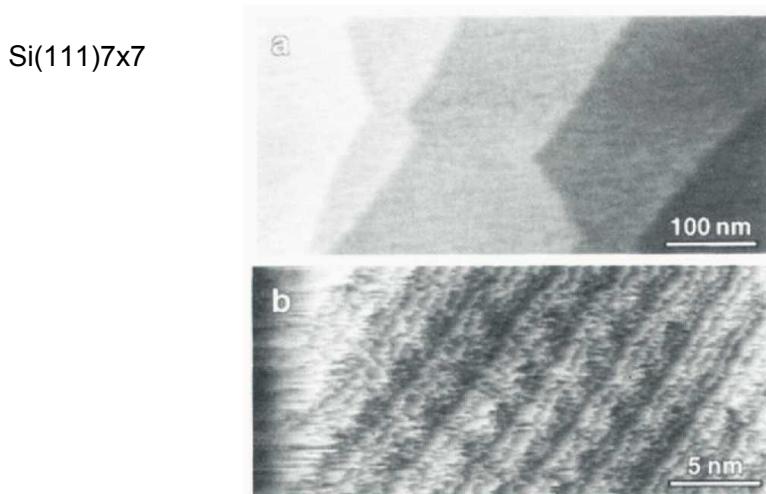
- Friction on **insulating surfaces** (Lüthi et al., JVSTB 1996):



- No individual defects are observed

## Atomic-Scale Measurements

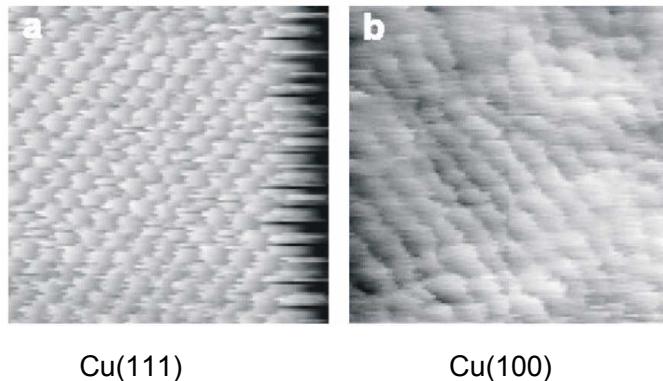
- Friction on **semiconductors** (Howald et al., PRB 1995):



(tip coated with PTFE)

## Atomic-Scale Measurements

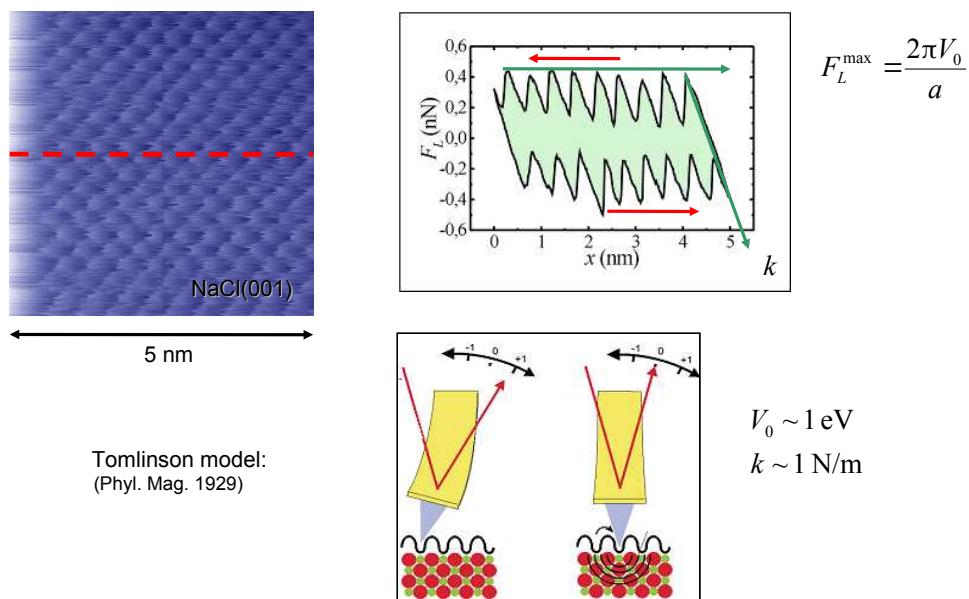
- Friction on **metal surfaces** (Bennewitz et al., Trib. Lett. 2001):



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

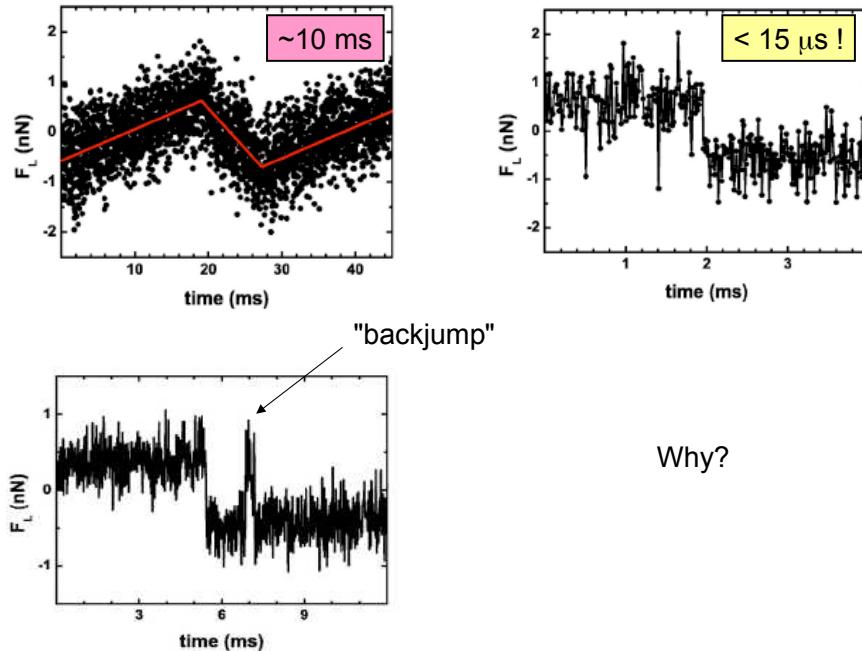
## Atomic friction on crystal surfaces

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



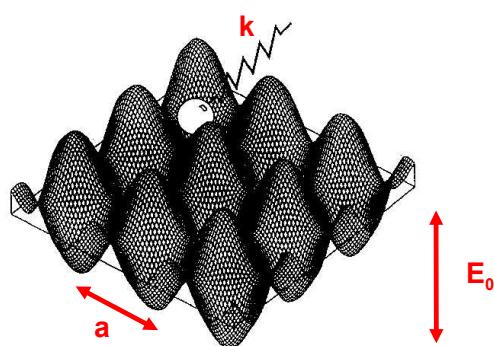
## Atomic-Scale Measurements

- Wide distribution of slip durations:



## Modelling Atomic Friction

- The tip is subject to
- periodic interaction with the underlying surface
  - elastic deformation of the cantilever

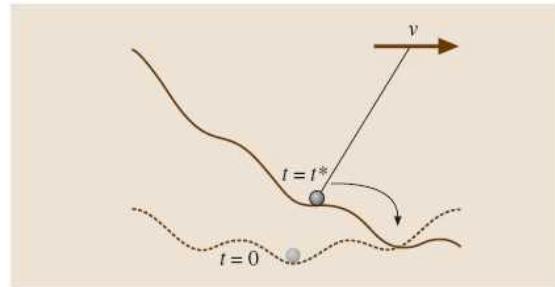


- In 1D the corresponding potential energies are represented by
  - a sinusoid
  - a parabola

## Modelling Atomic Friction

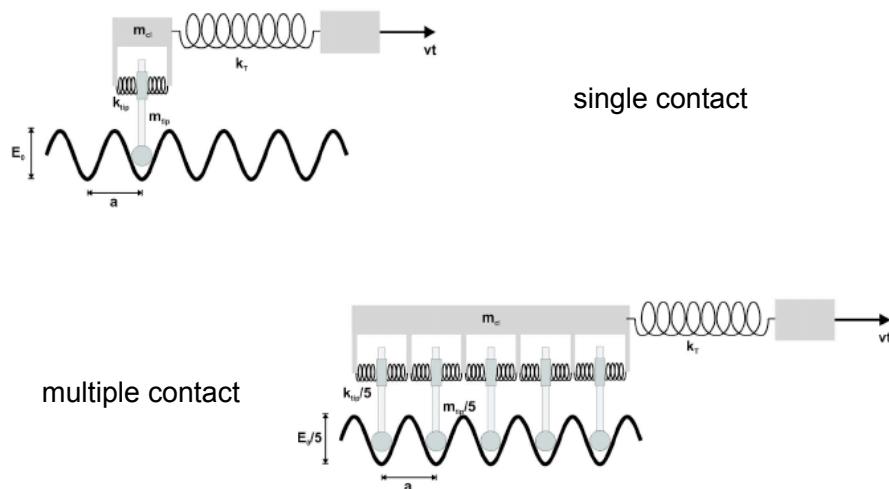
- Total energy of the system:

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



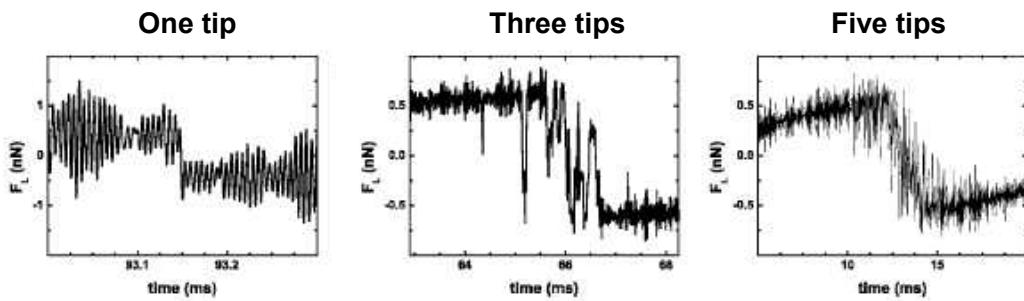
- The tip can "stick" to the minima of the potential profile

## Modelling Atomic Friction



## Modelling Atomic Friction

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

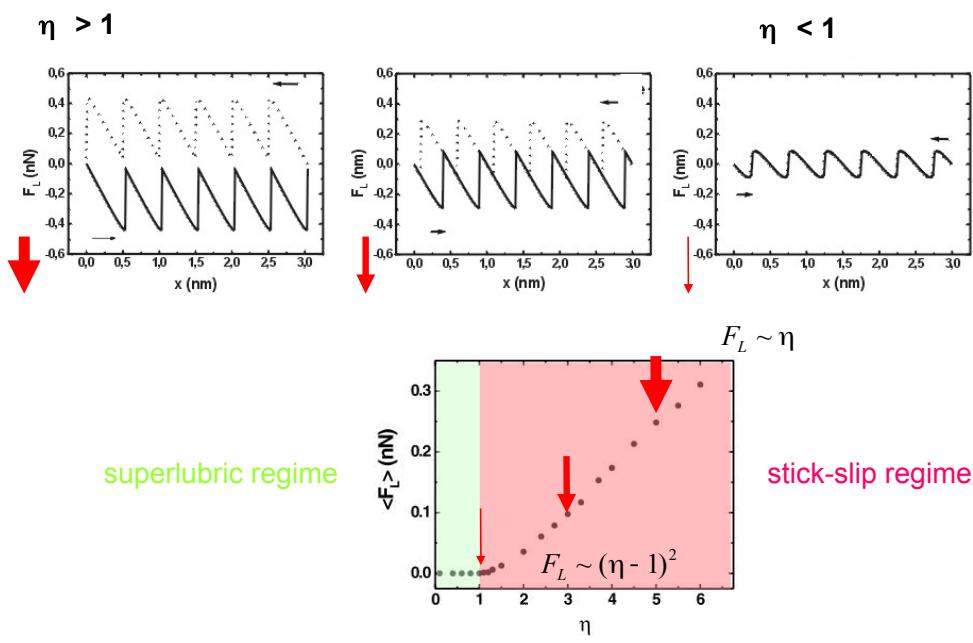


- Long slip times are found with multiple tips only

(Maier et al., PRB 2005)

## Superlubricity

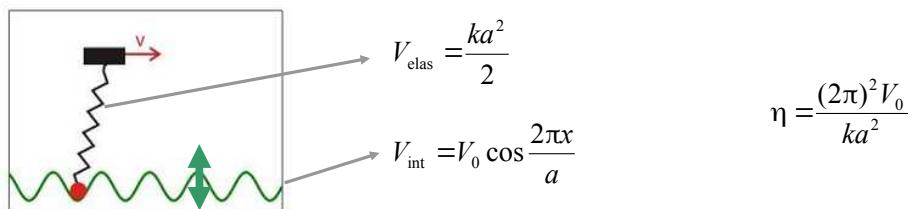
- From the Tomlinson model (without thermal activation):



A. Socoliuc et al., Phys. Rev. Lett. 92 (2004) 134301

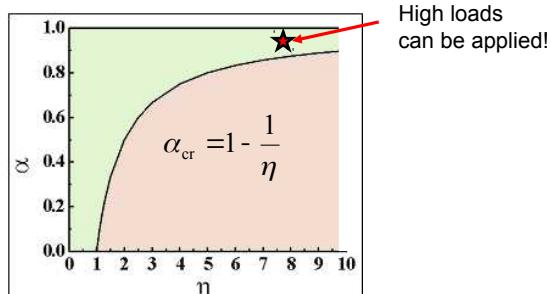
## “Dynamic superlubricity”

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



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

Phase-diagram in the  $\eta$ - $\alpha$  plane:

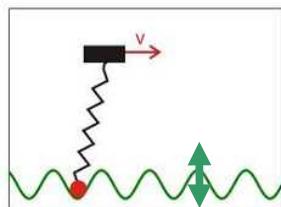


High loads  
can be applied!

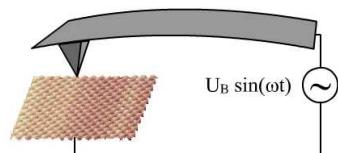
E. Gnecco et al., J. Phys.: Condens. Matt. a20 (2008) 354004

## “Dynamic superlubricity”

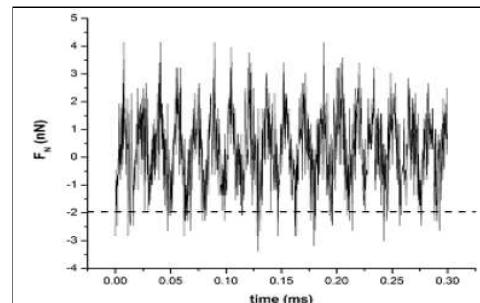
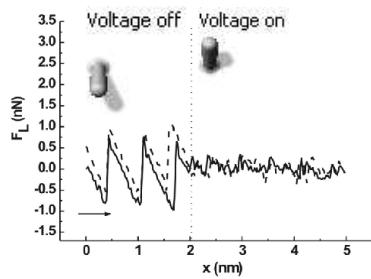
A third way to reduce friction: Tomlinson model with TIME modulation



AC actuation  
of the nanocontact:

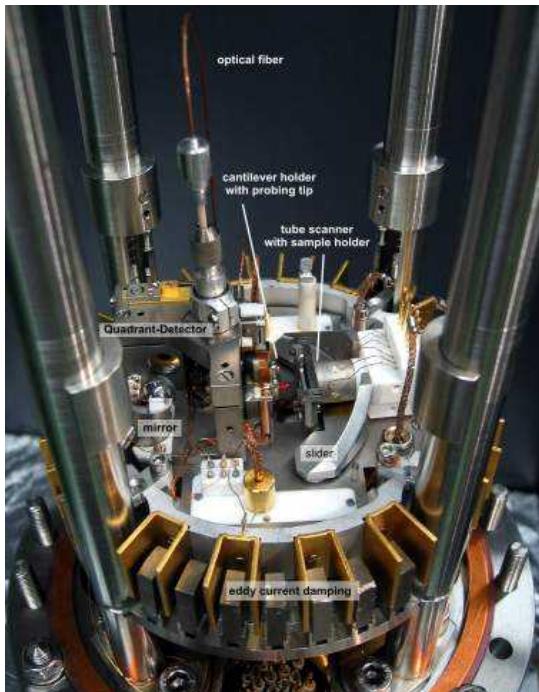


NaCl(001)



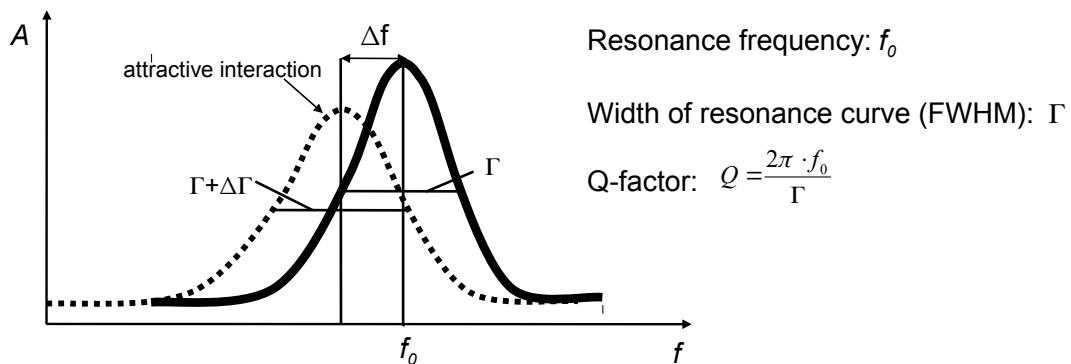
A. Socoliuc et al., Science 313 (2006) 207

## Noncontact-AFM (nc-AFM)



- UHV: Base pressure below  $1 \times 10^{-10}$  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  $\Delta f$   
Dissipative forces  $\Rightarrow$  broadening of curve  $\Delta \Gamma$

## Forces in nc-AFM

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

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

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

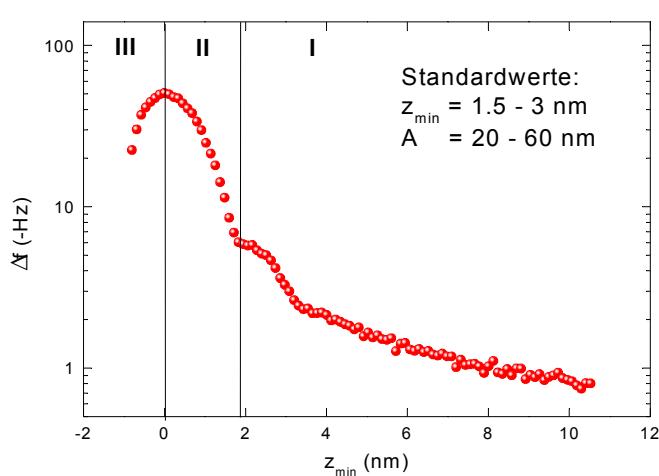
bonding between tip and sample atoms  
(only for  $d < 5 \text{ \AA}$ )

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

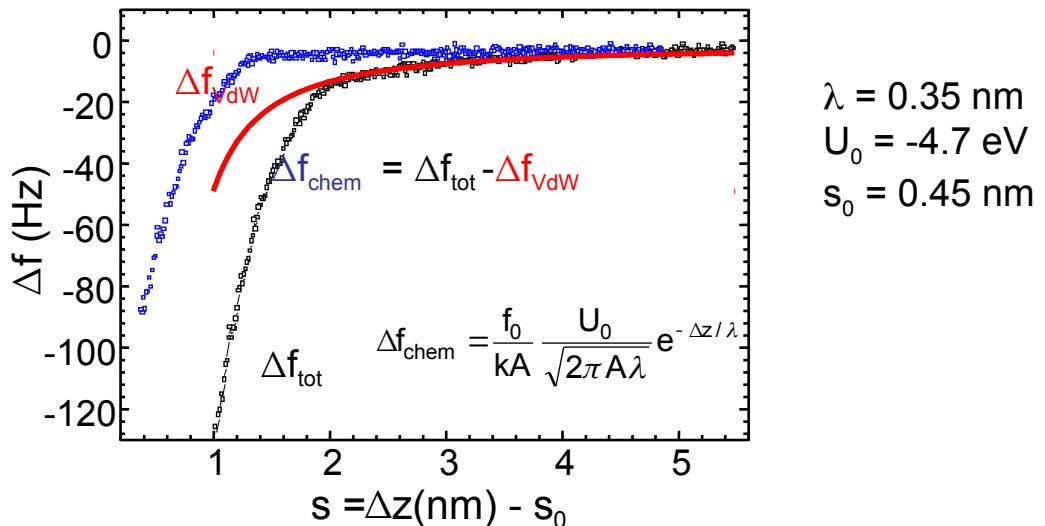


region I:  
attractive forces  
non-contact mode

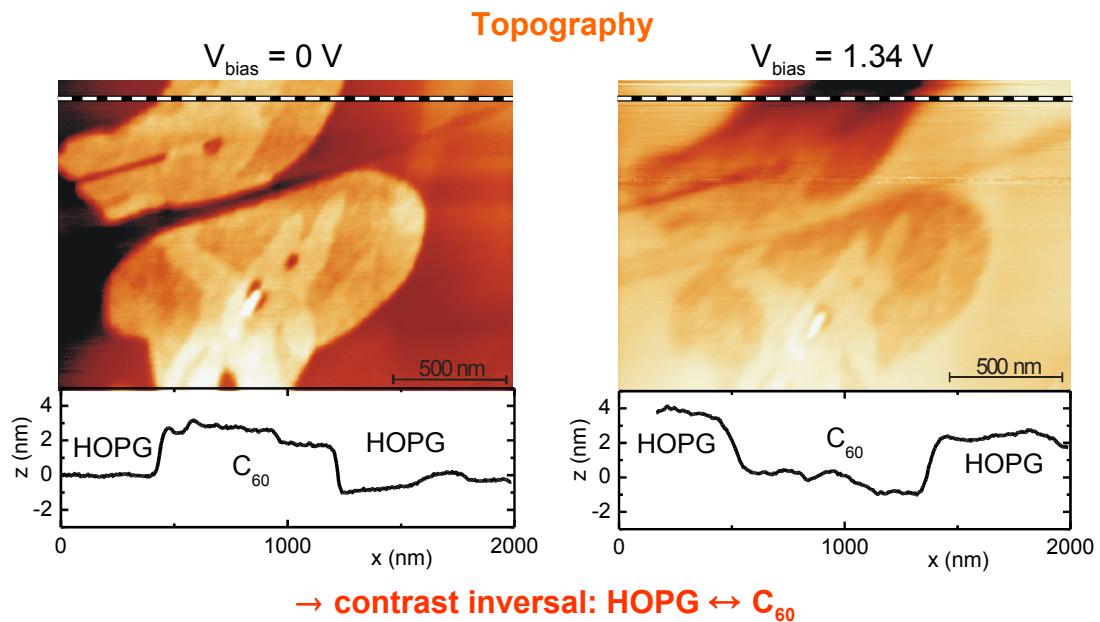
region II:  
attractive forces  
atomic resolution

region III:  
repulsive forces  
tapping mode

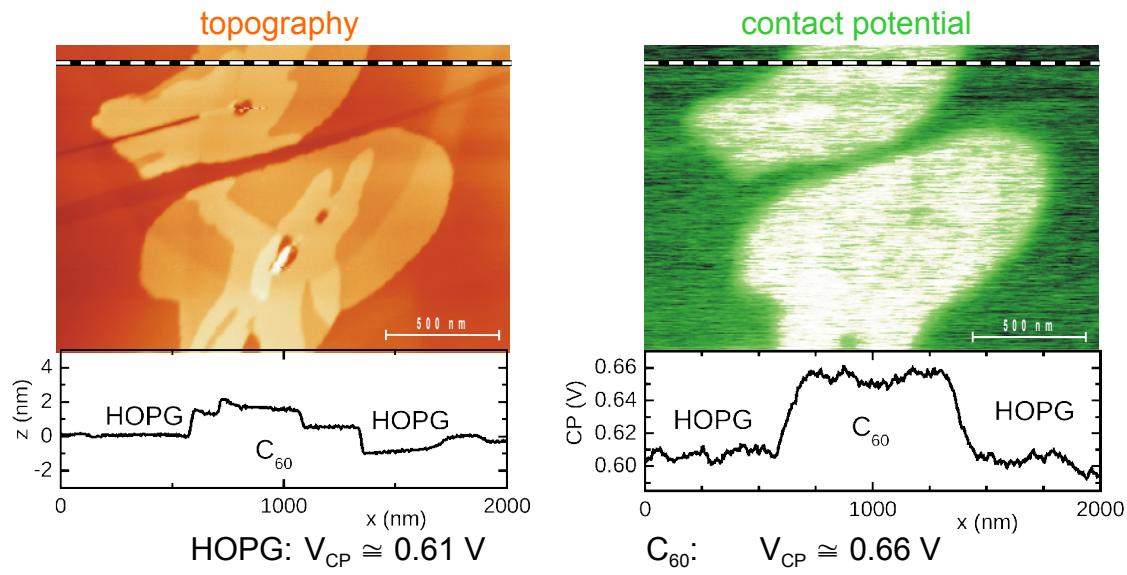
## Short range interaction



inhomogeneous sample: HOPG +  
 $\frac{1}{2}$  monolayer C<sub>60</sub>



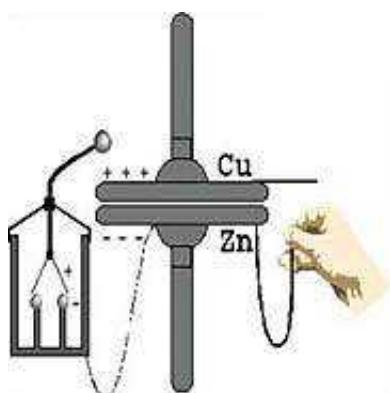
## inhomogeneous sample: HOPG + ½ monolayer C<sub>60</sub>



⇒ NC-AFM: residual electrostatic force for fixed  $V_{bias}$

## Makroskopische Kelvin-Sonde

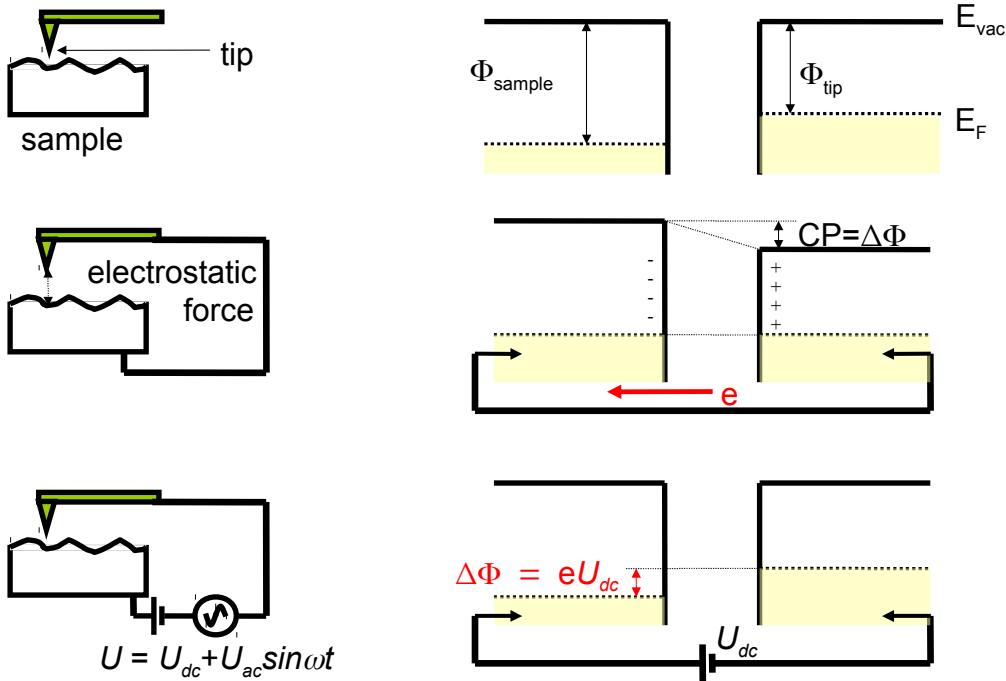
Lord Kelvin 1861



### 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  
 $\Phi$  - work function

apply bias:

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

# Kelvin Probe Force Microscopy

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

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

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

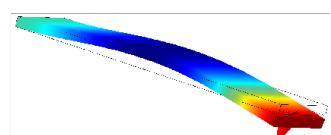
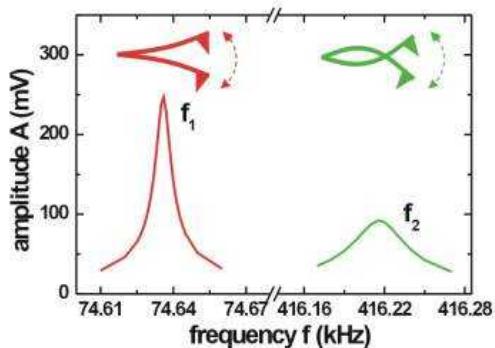
$$F_{2\omega} = \frac{\partial C}{\partial z} \frac{V_{ac}^2}{4} \cos(2\omega t)$$

**AM-KPFM**  
Amplitude Modulation

**FM-KPFM**  
Frequency Modulation

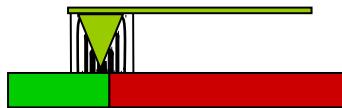
## AM – KPFM Amplitude Modulation Detection

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

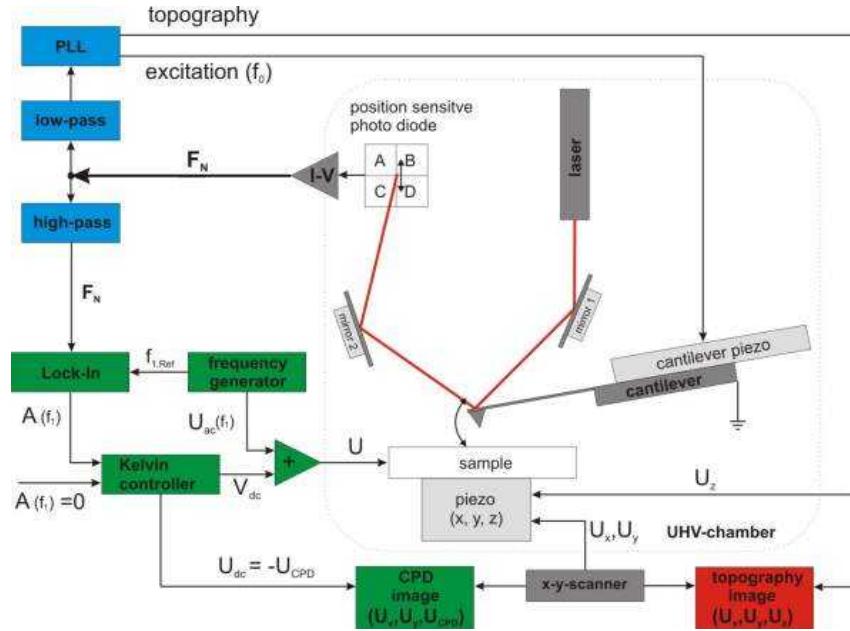


- tune  $\omega$  to the second resonance  $f_2$
- detection of the oscillation amplitude  $A_\omega$  with a lock-in
- limiting factor: bandwidth of the photodiode

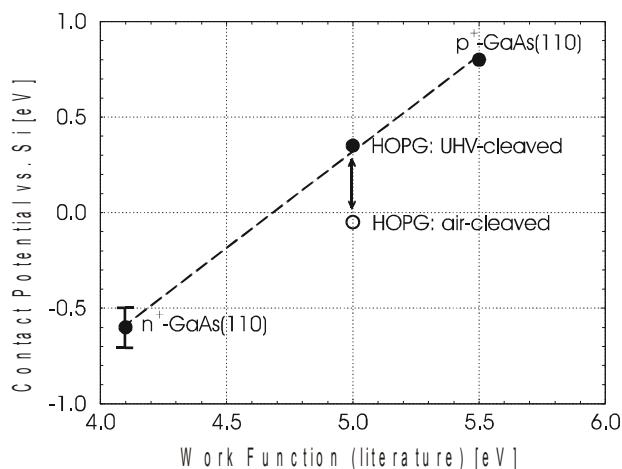
$$A_\omega \propto F_\omega$$



# Experimental Setup nc-AFM & AM-KPFM



## KPFM calibration and absolute work function



$\Phi\text{-Si-Cantilever} = 4.70 (\pm 0.1) \text{ eV}$

$U_{ac} = 100 \text{ mV}$

→ absolute and quantitative work function determination

## Polished Cross Section of a CuGaSe<sub>2</sub> Solar Cell

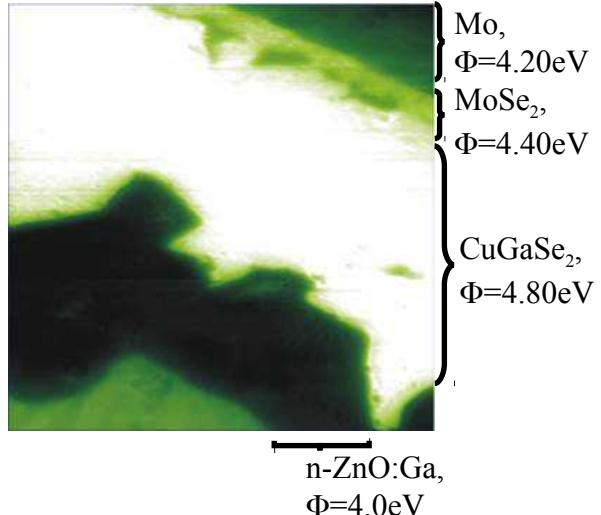
CuGaSe<sub>2</sub> solar cell device:  $V_{oc} = 820$  mV,  $\eta = 4.6\%$

polished and Ar-ion sputtered cross section

topography



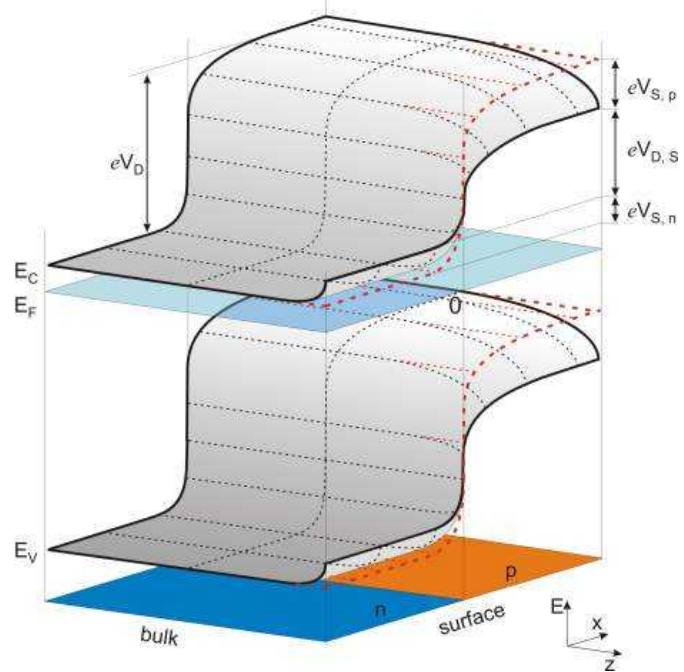
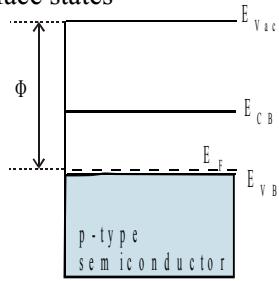
work function



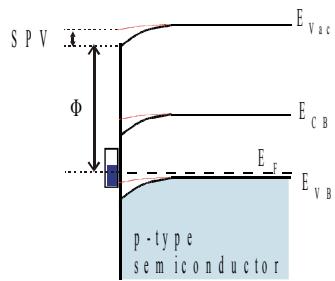
Glatzel *et al.*, APL **81**, 2017 (2002)

## Surface Effects

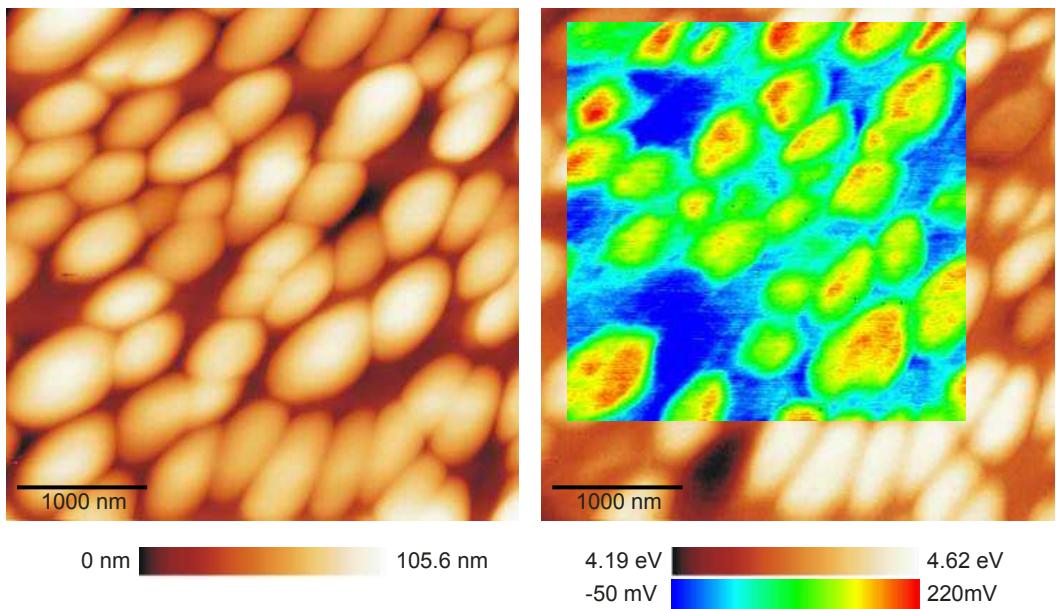
no surface states



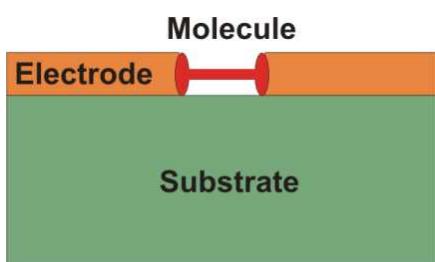
surface states



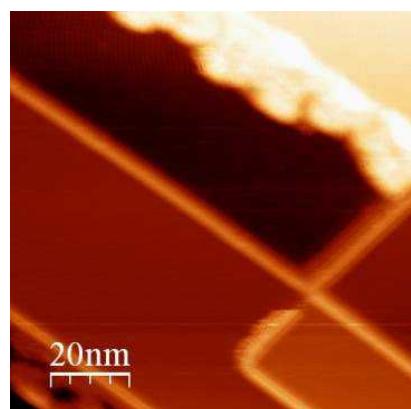
# Surface Photovoltage MDMO-PPV/PCBM – 675nm



## Motivation Molecular electronics



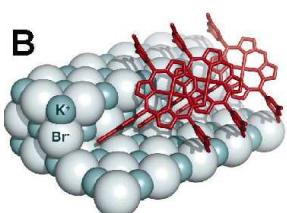
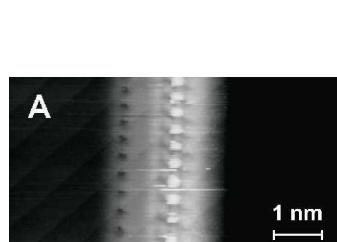
Molecules on Insulators:



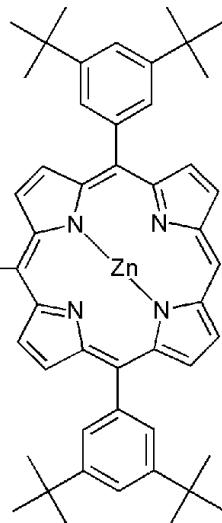
- No STM possible – nc-AFM mandatory
- Low diffusion barrier but high intermolecular interaction
- Low temperatures – easier to “fix” molecules but not so easy to find applications

## Asymmetric Cyano-Porphyrins

Natural light harvesting complexes



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

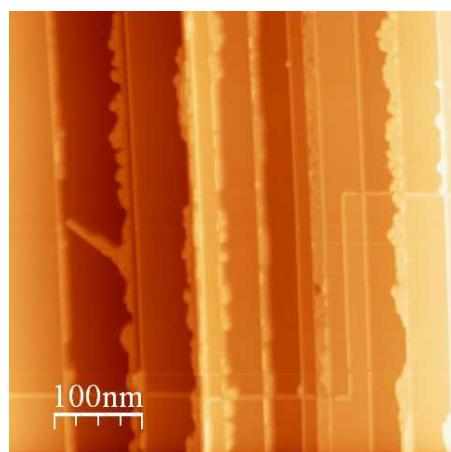


Balaban et al., Acc. Chem. Res. 2005, 38, 612 – 623

## Wire Formation

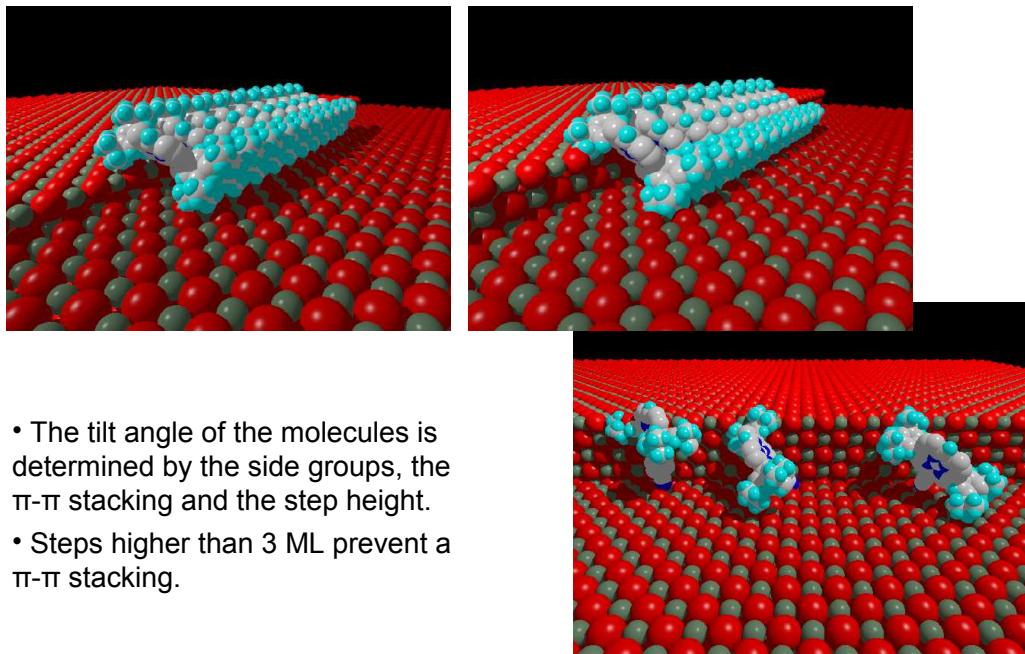
Decoration of step edges on KBr(100)

- 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

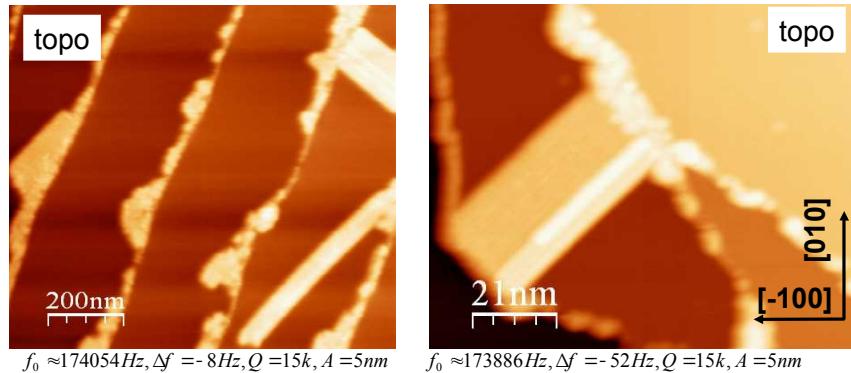


L. Zimmerli et al., J. Phys.: Conf. Ser., 2007, 61, 1357

## Wire Formation Structural model



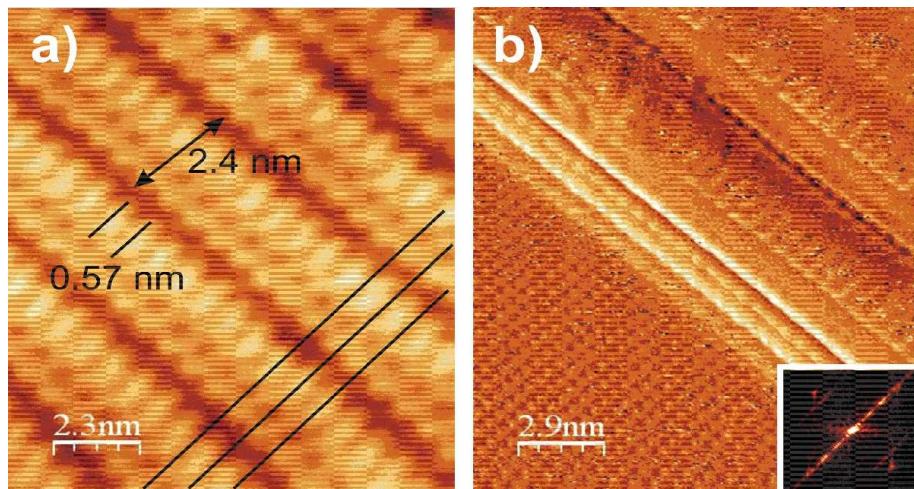
## Molecular Assemblies Multiwires on KBr



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

## Molecular Assemblies

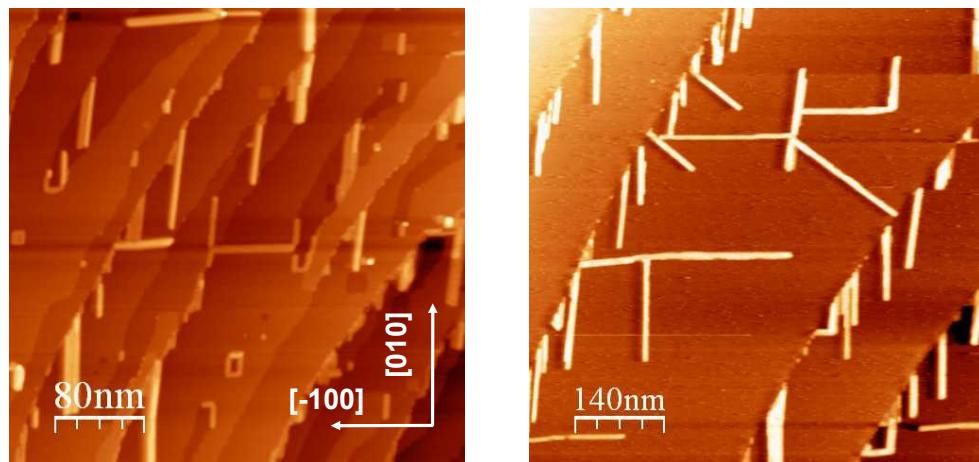
High resolution imaging



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

## Molecular Assemblies

Molecular wires on NaCl

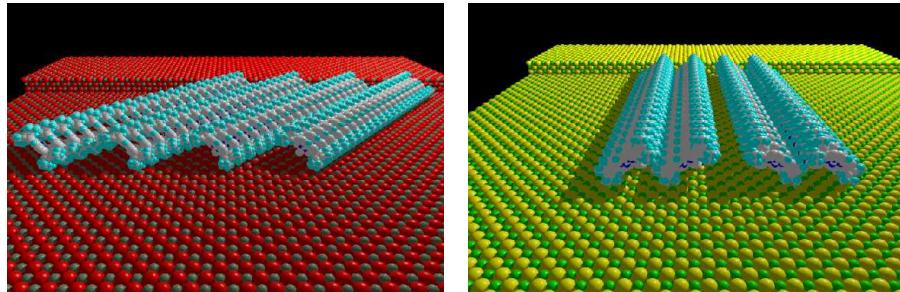


$f_0 \approx 170992\text{Hz}, \Delta f = -9.5\text{Hz}, Q = 15k, A = 40\text{nm}$

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

## Molecular Assemblies

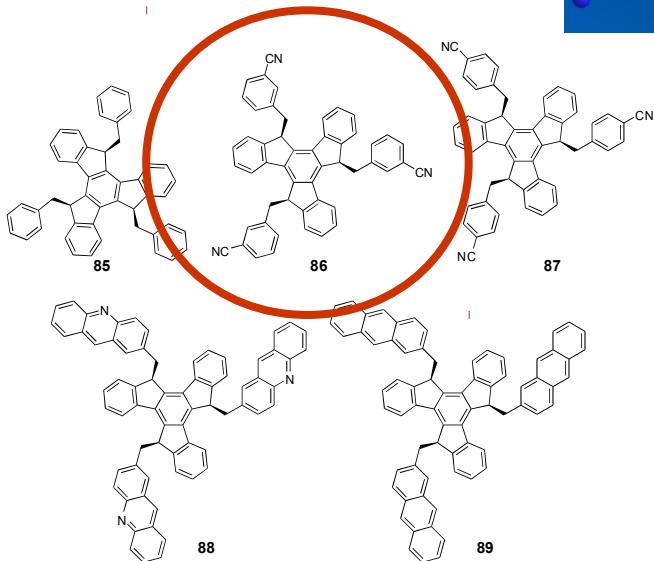
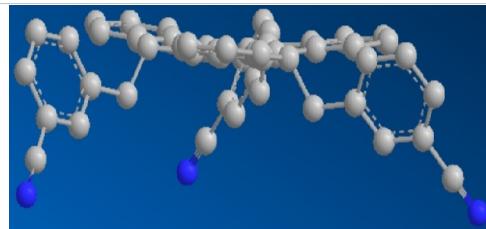
### Structural model



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

## Functionalized Truxenes

### Structure



evaporation onto  
the sample at RT

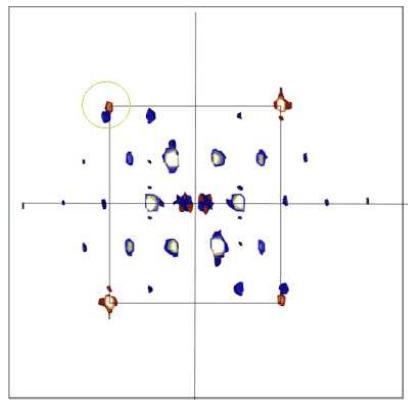
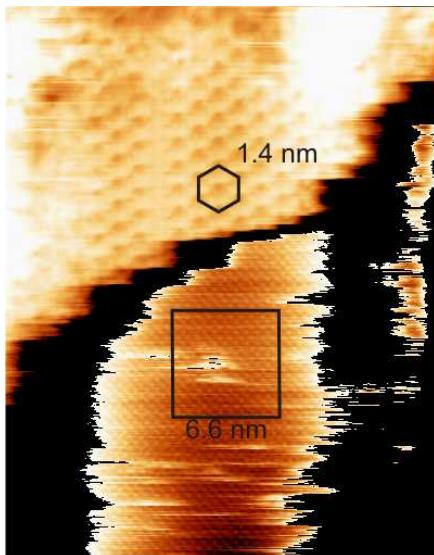
40nm

and the result of  
post annealing at  
155 C for 15 mins

20nm

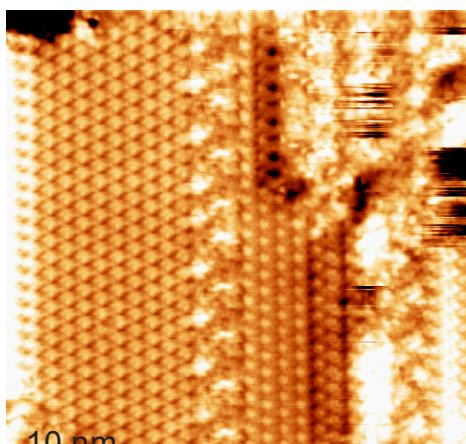
## Truxene Self Assemblies

Hexagonal coordination on KBr

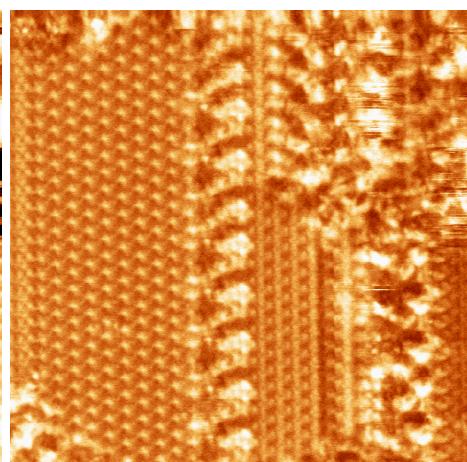


## Truxene Self Assemblies

Various distinct structures

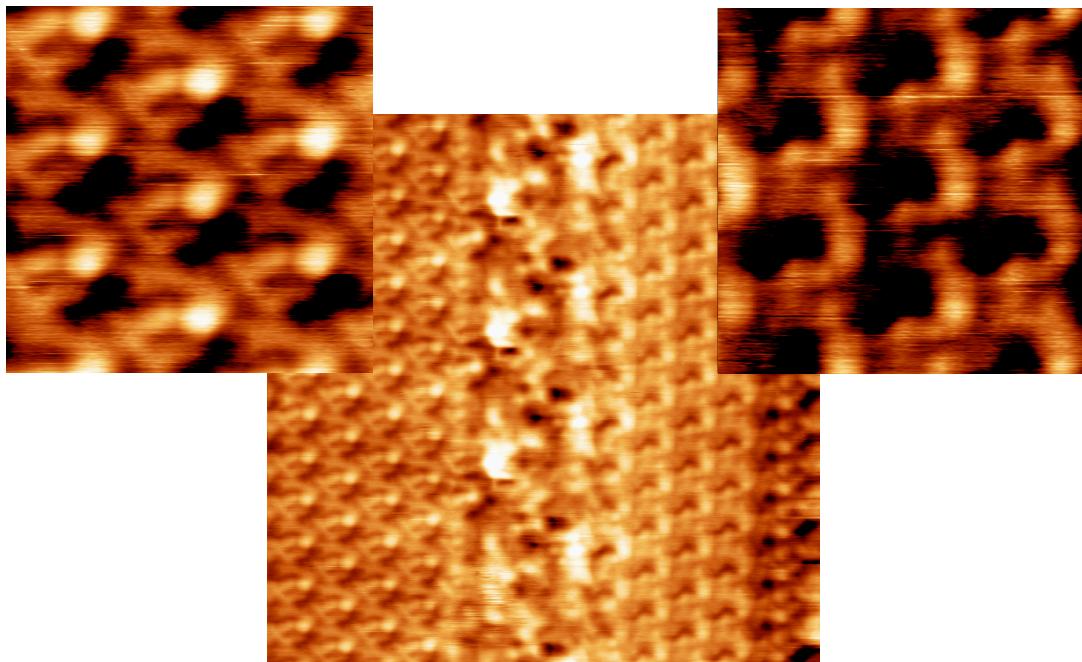


topography



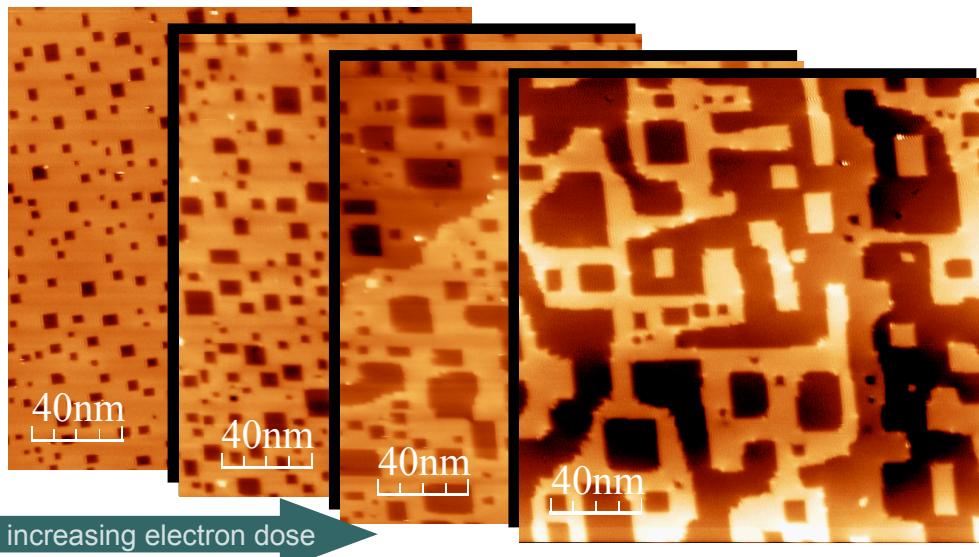
## Truxene Self Assemblies

Heigh resolution measurements



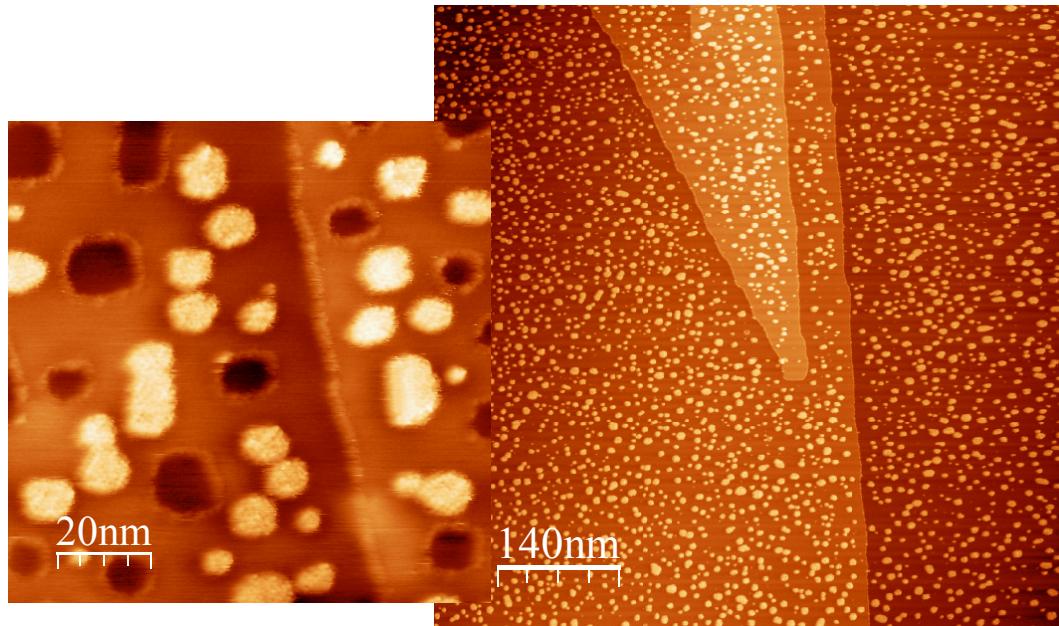
## Single Crystal KBr

Substrate patterning by electron irradiation



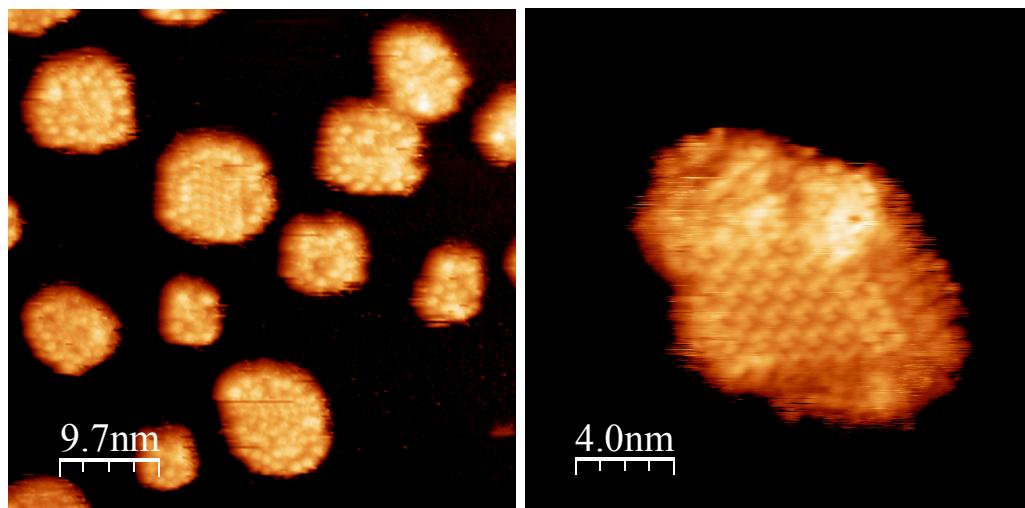
## Truxenes on patterned surface

Filled and unfilled pits



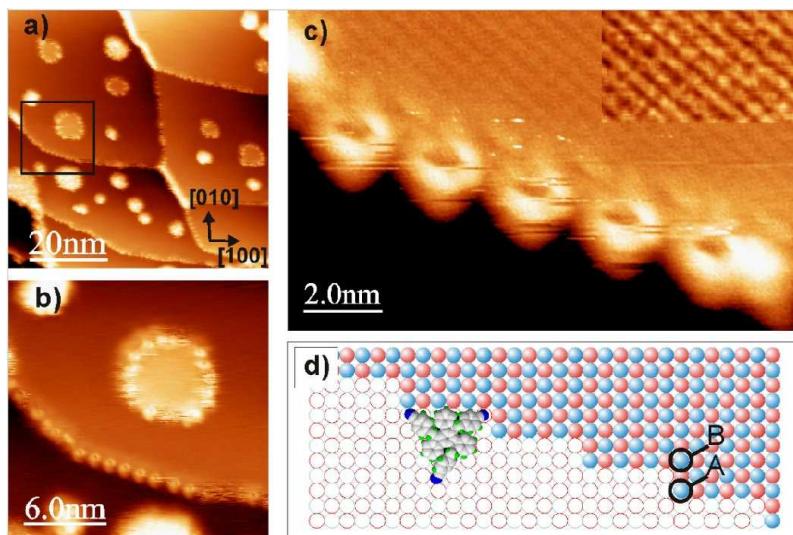
## Truxenes on patterned surface

Organization within the pits



## Imaging a Single Molecule

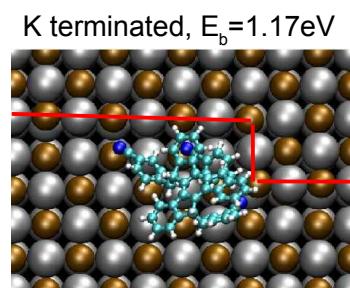
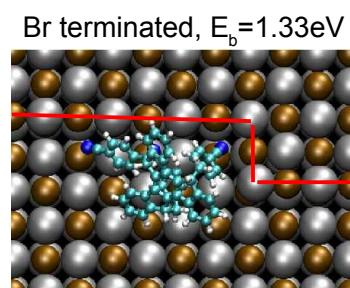
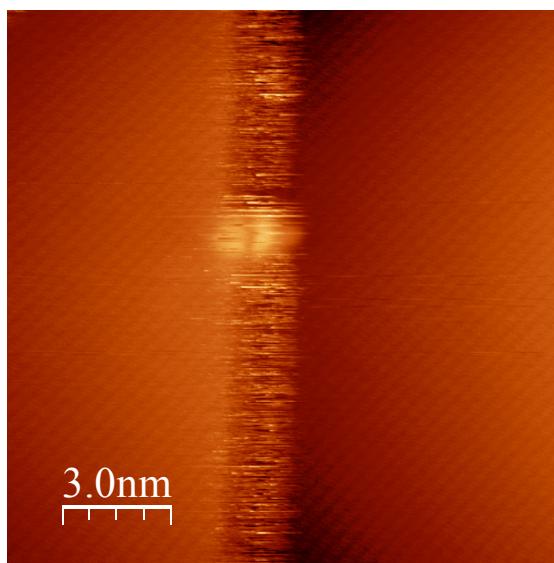
Measurements at RT



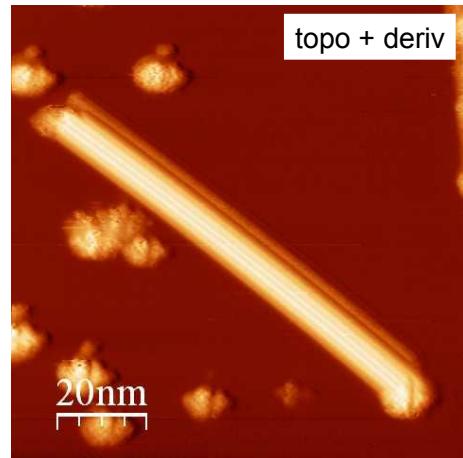
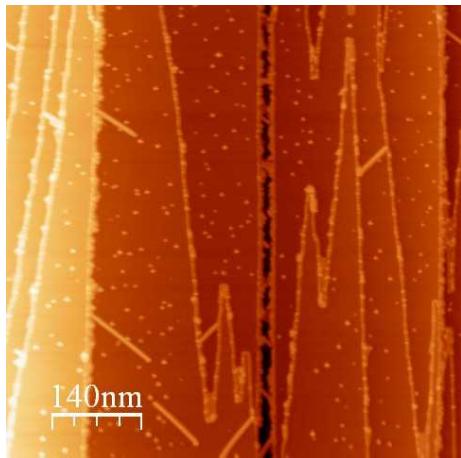
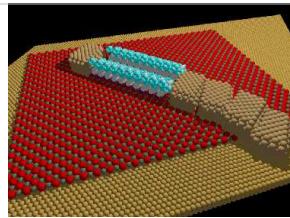
- Re-arrangement of the substrate, edges are running in the [-3 1 0] direction
- no chemical interaction with the surface
- adsorbed on K or Br terminated double atomic kink

## Imaging a Single Molecule

Measurements at RT



## Contacting Molecular Assemblies Au-Molecules-Au

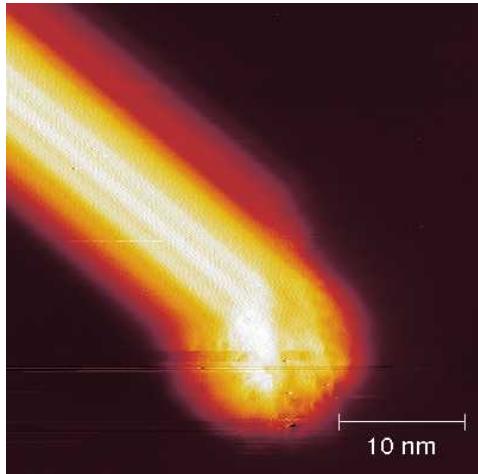


- Molecules arrange at steps and across terraces
- The growth is started/stopped at gold clusters.

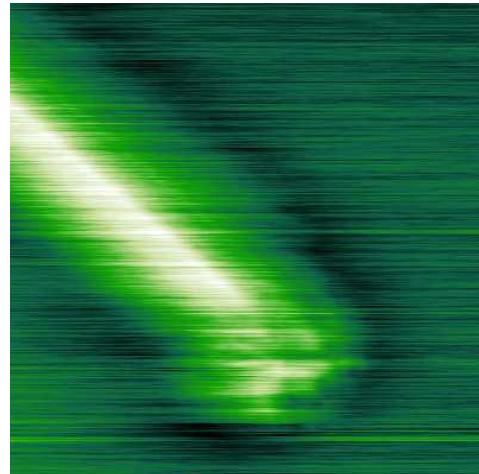
Glatzel et al., Appl. Phys. Lett., 2009, 94, 063303

## Contacting Molecular Assemblies KPFM

Topography



LCPD

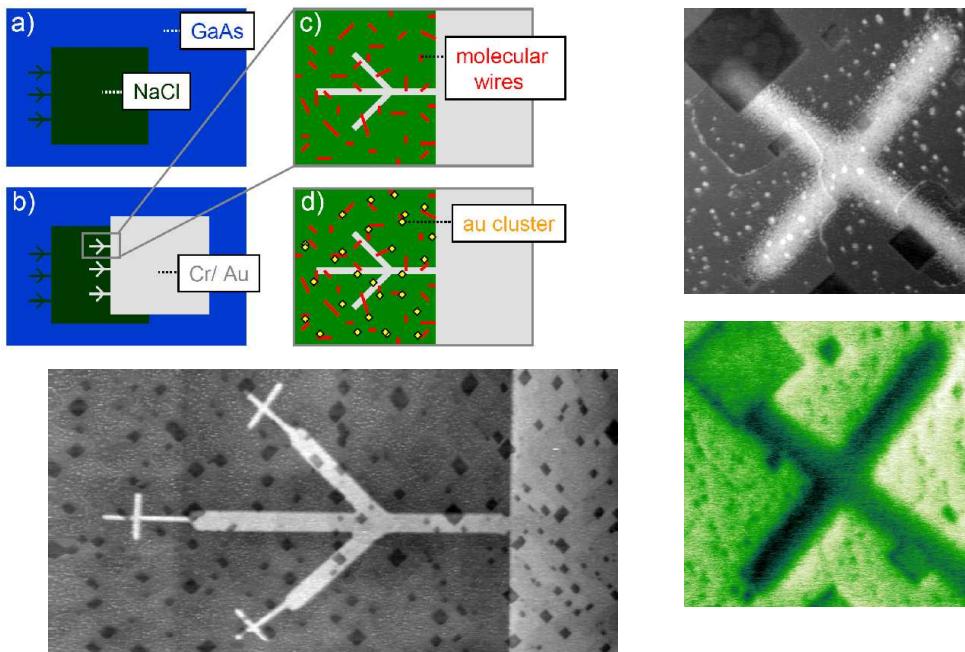


LCPD= -0.5...0.2eV

Glatzel et al., Appl. Phys. Lett., 2009, 94, 063303

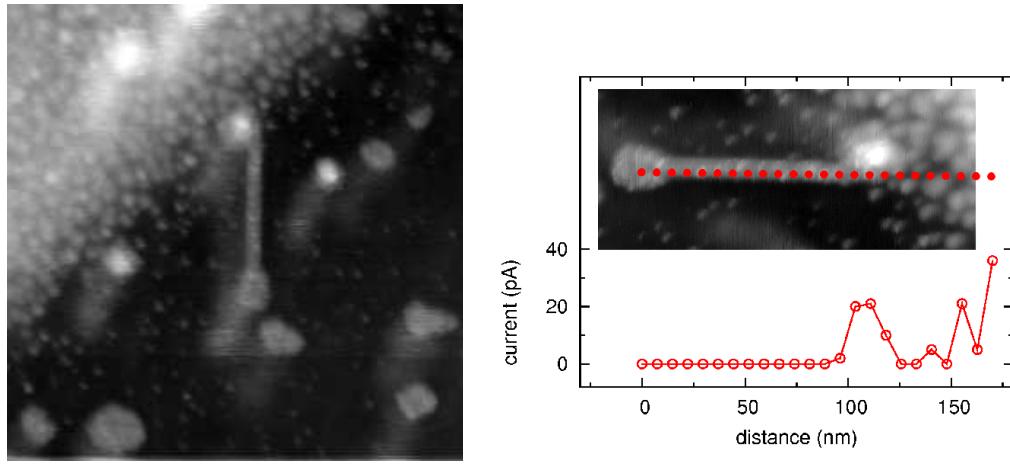
## Contacting Molecular Assemblies

Nanostencil (IBM Rüschlikon)



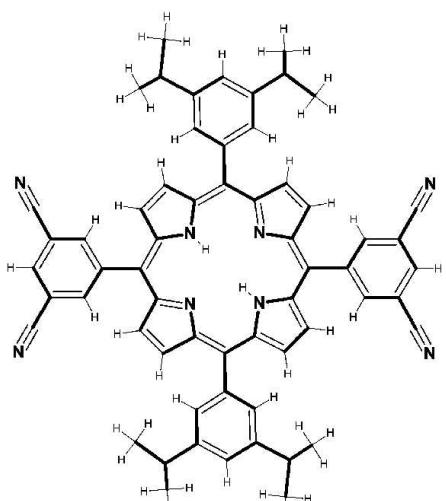
## Contacting Molecular Assemblies

Nanostencil (IBM Rüschlikon)

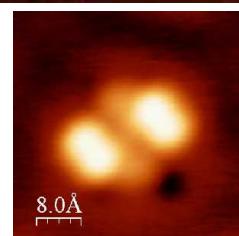
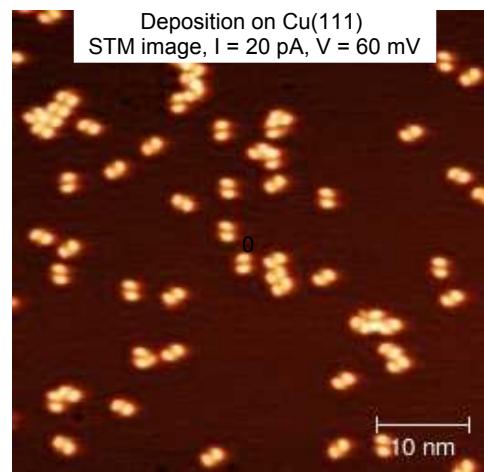


300x300nm<sup>2</sup>

## Porphyrin with bicyanophenyl legs



2-bicyanophenyl, 2-aryl H<sub>2</sub>-porphyrin  
synthesized by F. Diederich (ETH, Zurich)

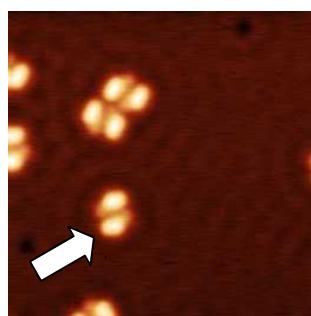


R. Pawlak et al.

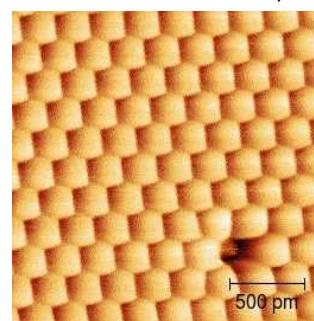
## Vertical manipulation: Catch the molecule...

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

STM Topography  
Simultaneous Frequency Shift

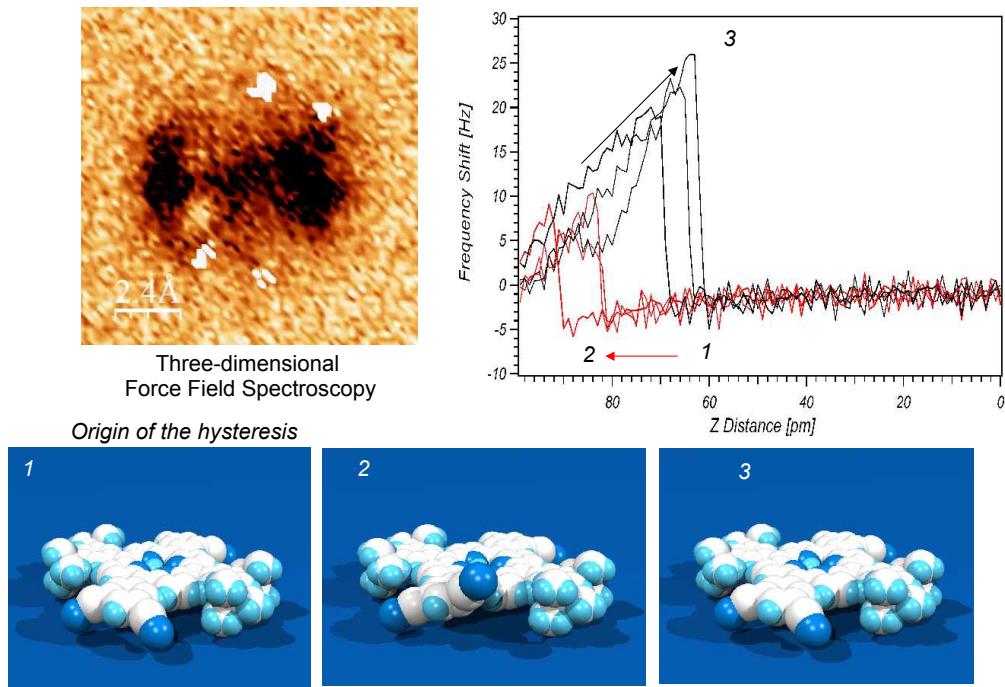


Friction measurement with  
a molecule linked to the tip

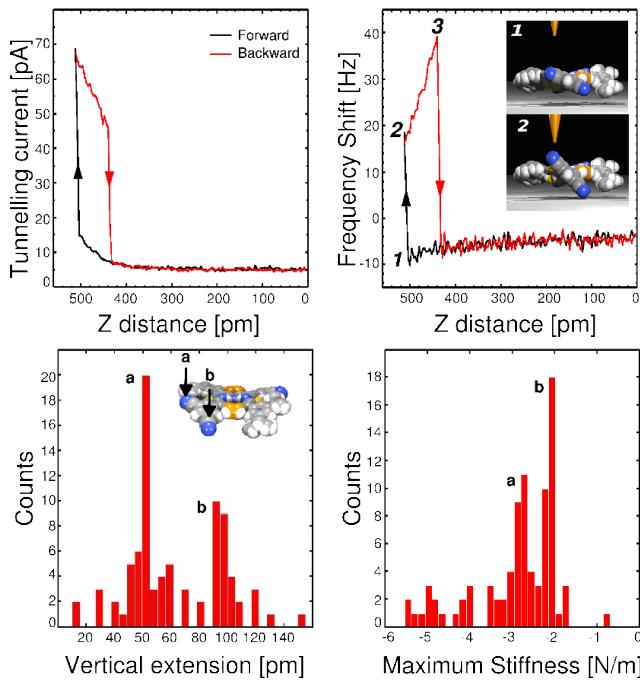


Atomic resolution on Cu(111)

## 3d-force spectroscopy: Observations of localized instabilities



## Vertical switching and statistics



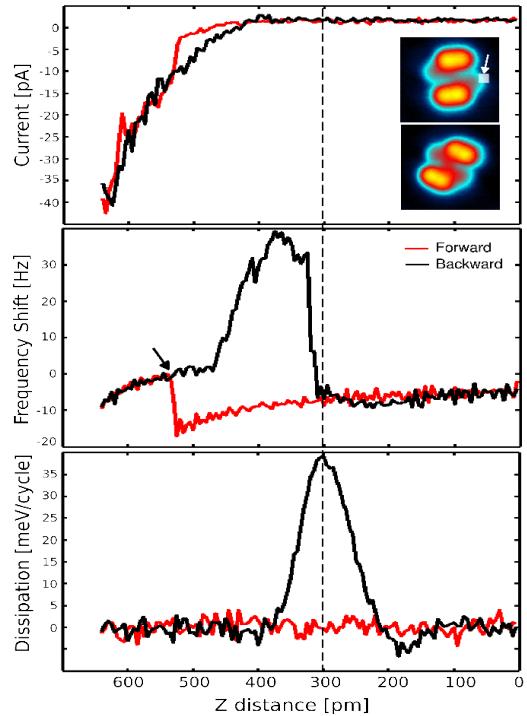
### Vertical switching:

- Tip-molecule junction between a CN function and the Cu-terminated tip.
- Attractive interaction force ( $= -150 \text{ pN}$ ) 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.

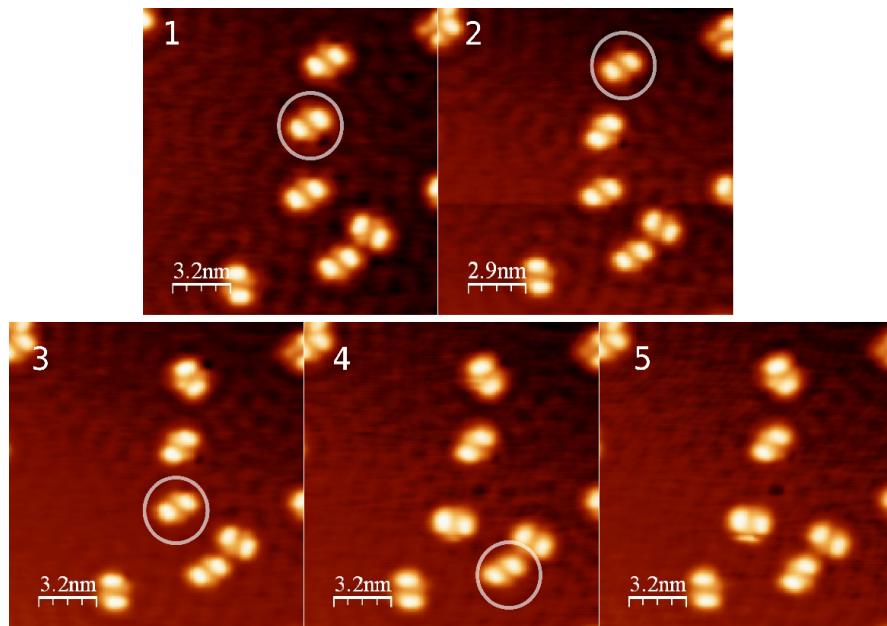
## Rotation by controlled force interactions

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).



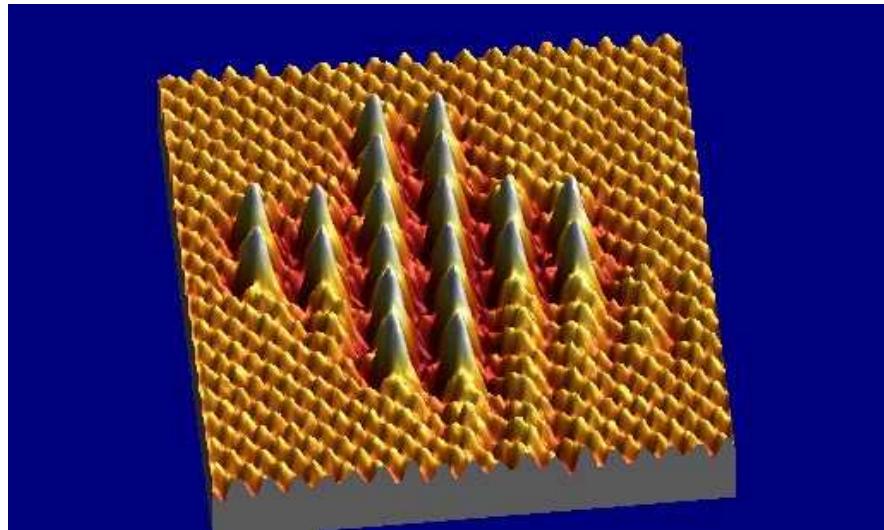
## Rotation of molecules clockwise and anticlockwise



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

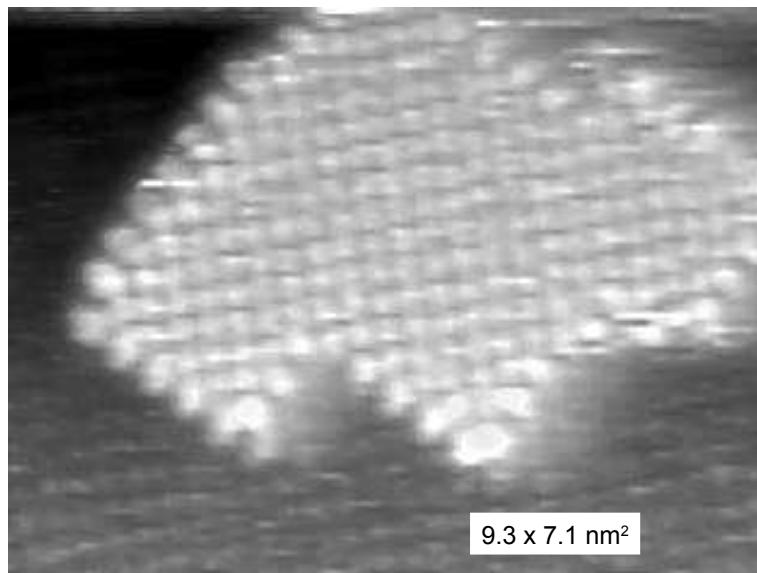


A Small Swiss Cross made by AFM at room temperature  
torsional resonance imaging



S. Shigeki et al.

## Die “Nano-Schweiz”



NaCl-Insel mit AFM abgebildet