National Center of
Competence in Research
“Nanoscale Science”

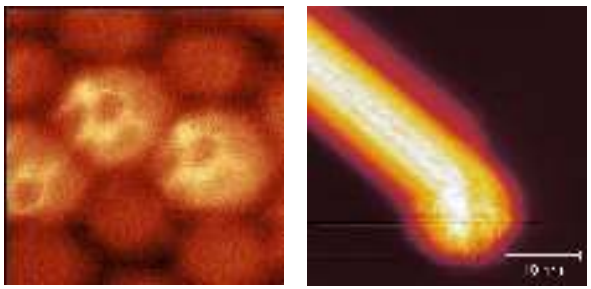
Thilo Glatzel, thilo.glatzel@unibas.ch

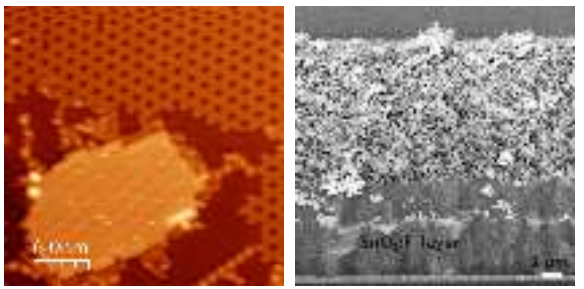
Molecular and carbon-based electronic systems

Single molecule deposition and properties on surfaces

Bottom Up

Top Down





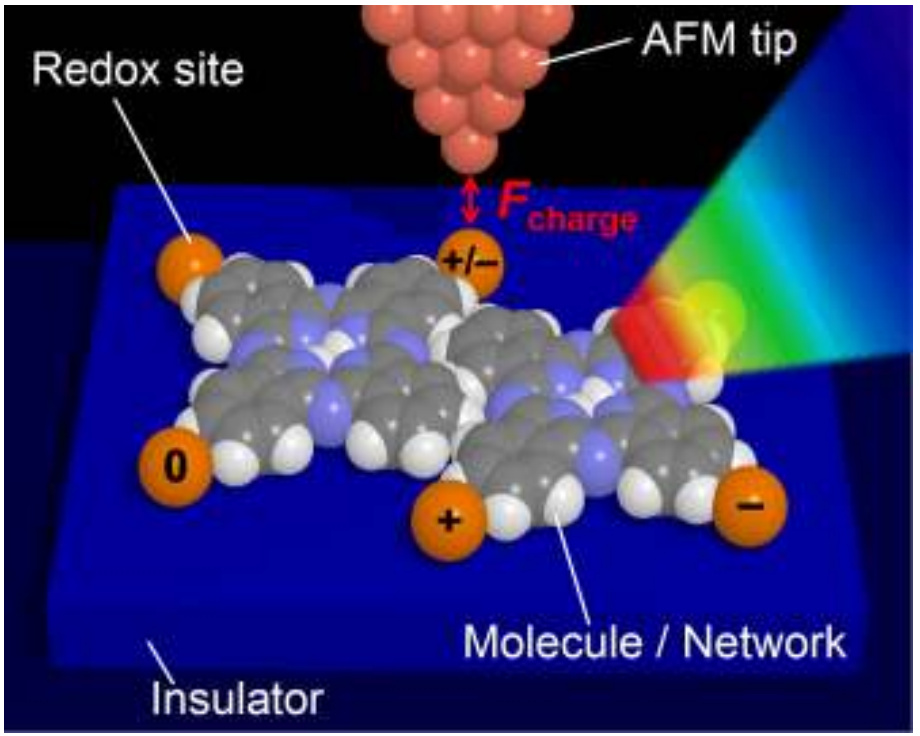
Fundamental Knowledge
&
Functional Devices

UNI BASEL

SNI SWISS NANOSCIENCE INSTITUTE

Motivation

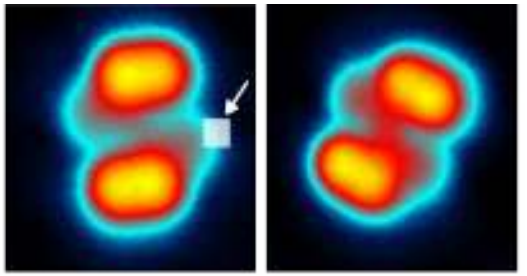
opto-electronic charge transfer processes in molecules

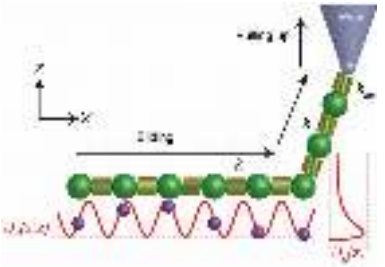


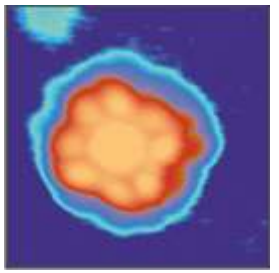
- locale surface potential at atomic scale - surface photovoltage
- transfer to room temperature
- stabilization and **manipulation** of molecules/atoms
- quantification of the observed signals (forces and energy)
- development of new measurement methods

Overview

- **Introduction into SPM techniques**
  - interaction forces
  - detection mechanism & setup
- **Properties of single C_{60} molecules**
  - orientation of single molecules
  - mechanical properties
- **Manipulation of porphyrin molecules**
  - structural analysis
  - 3D force spectroscopy
  - controlled molecular manipulation
- **Formation of a molecular wire**
  - on surface reaction
  - determination of pulling forces
- **Electronic Information at submolecular scale**
  - Donor and Acceptor molecules
  - Optoelectronic excitation of CuPc







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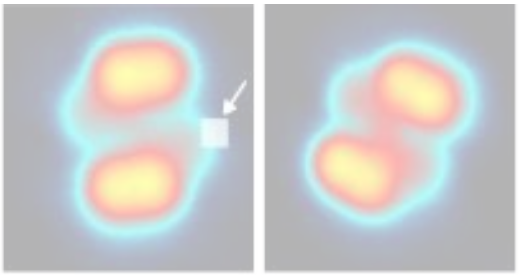
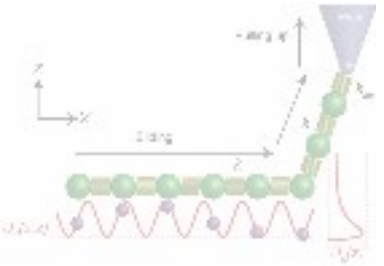
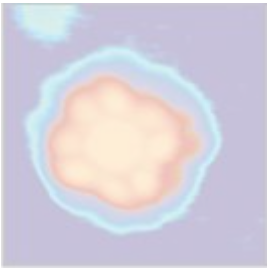
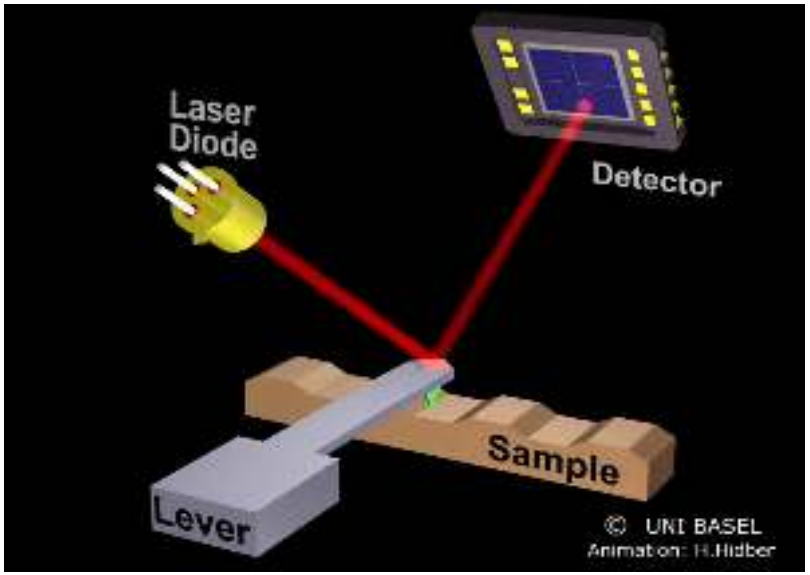




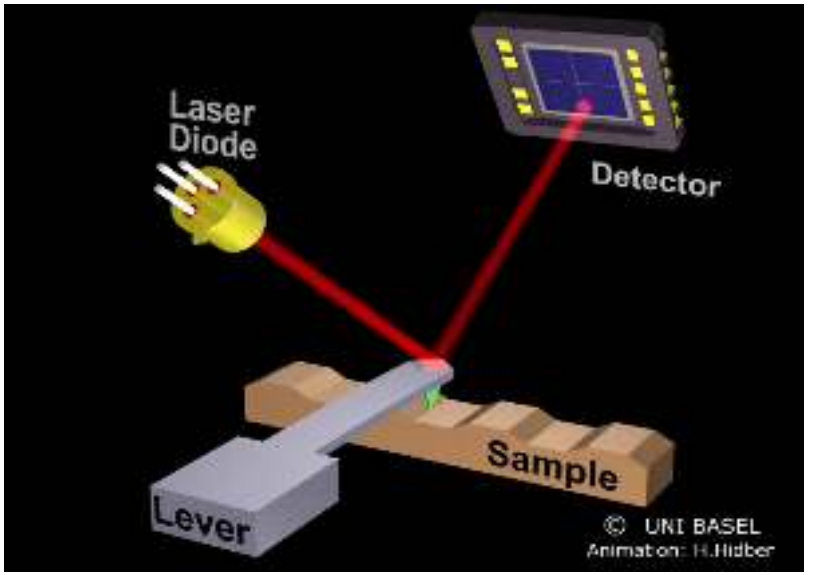


Atomic Force Microscopy

contact AFM



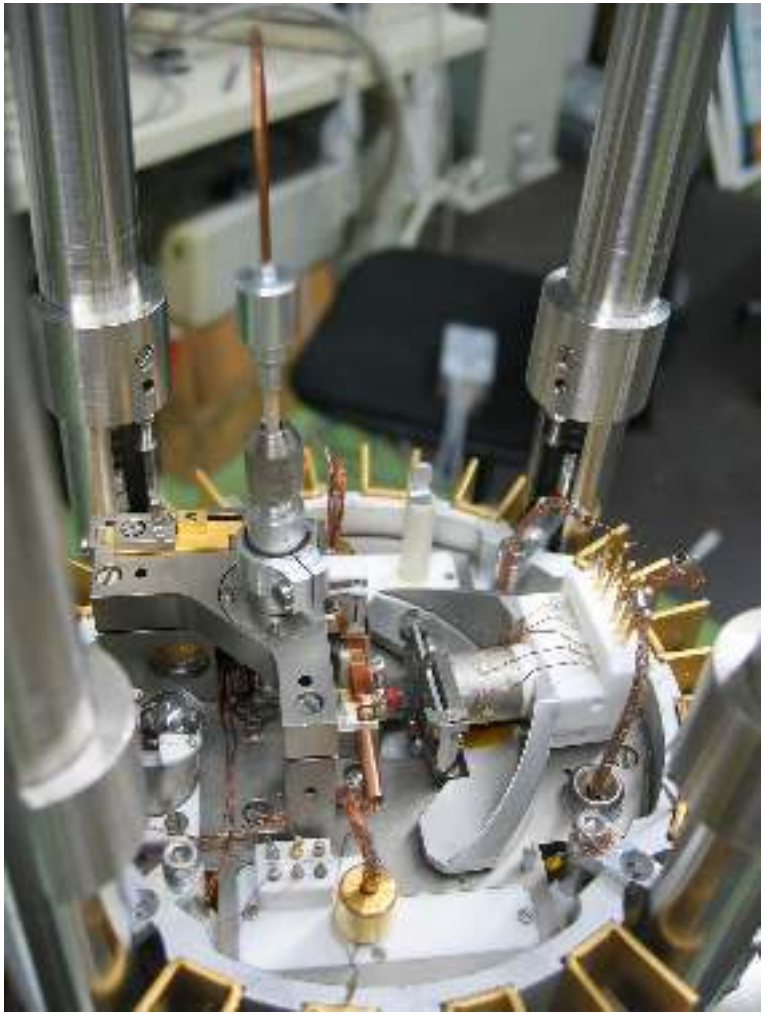
dynamic AFM



Experimental Setup
AFM/STM

Nanosurf, ambient AFM (Flex-AFM)

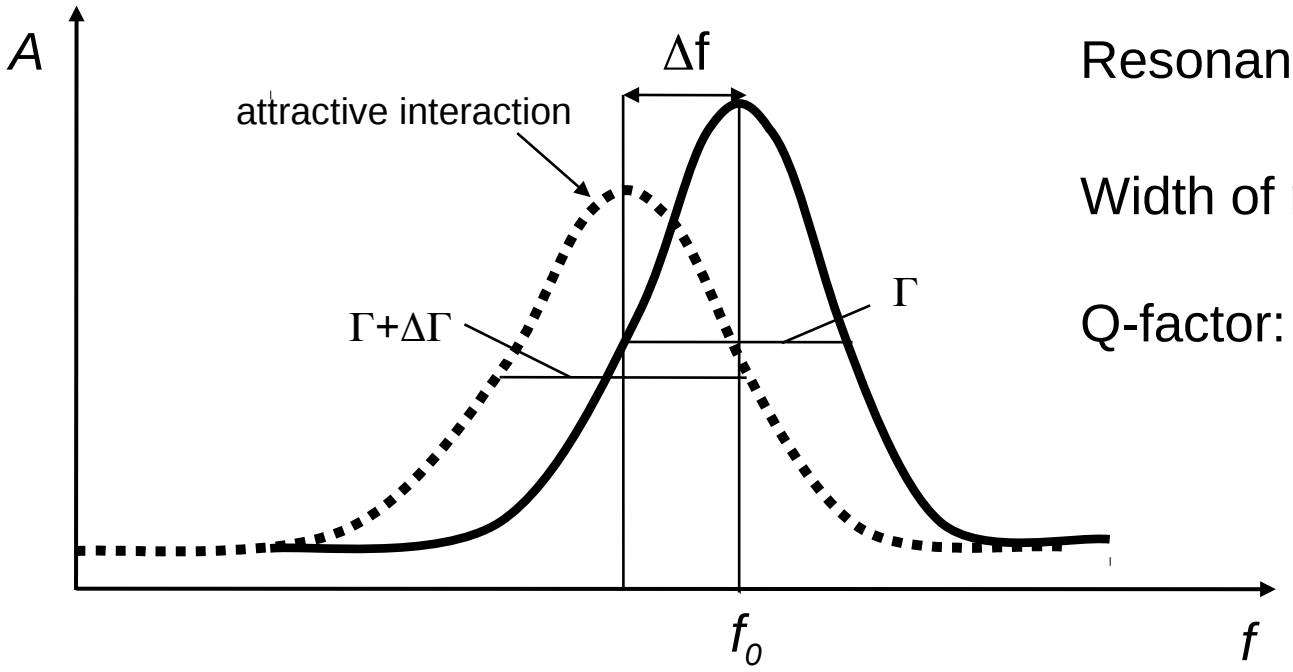
home-build RT-AFM, UHV



Multimode AFM

LT-STM/AFM, Omicron

Quantitative understanding of nc-AFM



Resonance frequency: f_0

Width of resonance curve (FWHM): Γ

Q-factor: $Q = \frac{2\pi \cdot f_0}{\Gamma}$

Conservative forces $\Rightarrow$ shift of resonance curve Δf
Dissipative forces $\Rightarrow$ broadening of curve $\Delta\Gamma$

Forces in nc-AFM

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

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

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

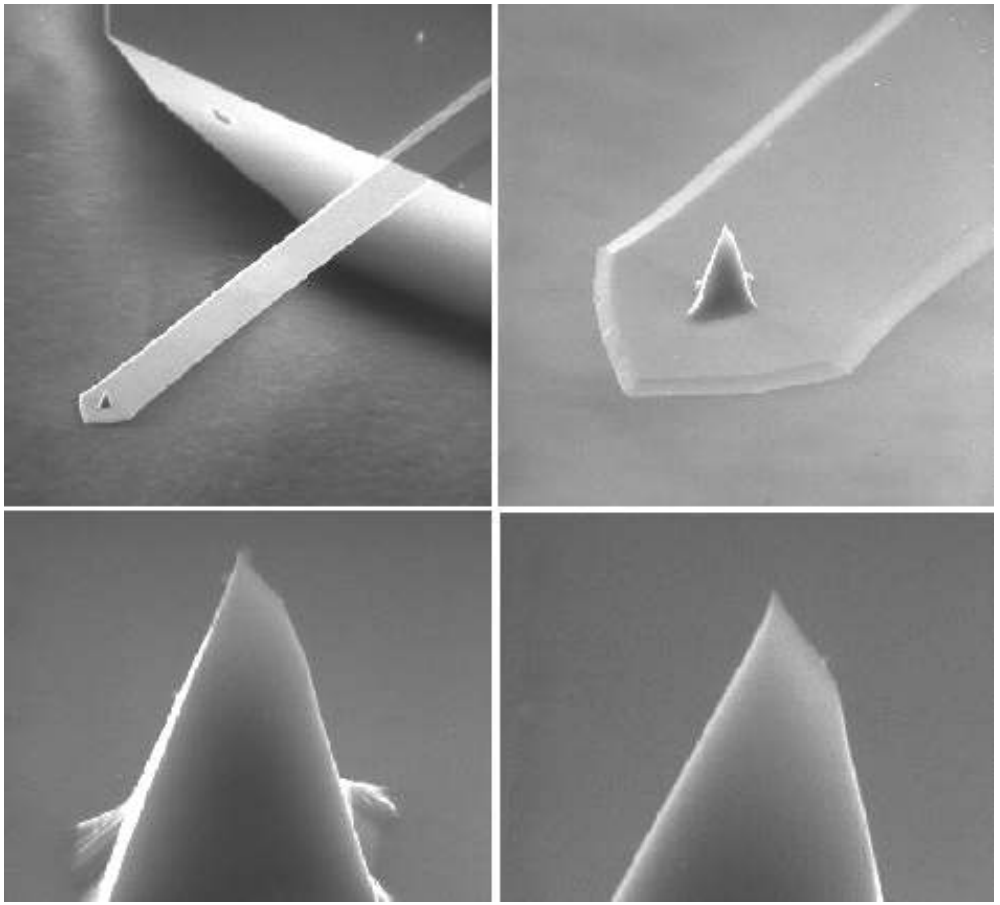
bonding between tip and sample atoms (only for d < 5 Å)

only for magnetically sensitive tips

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

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

Microfabrizierte “Cantilever”



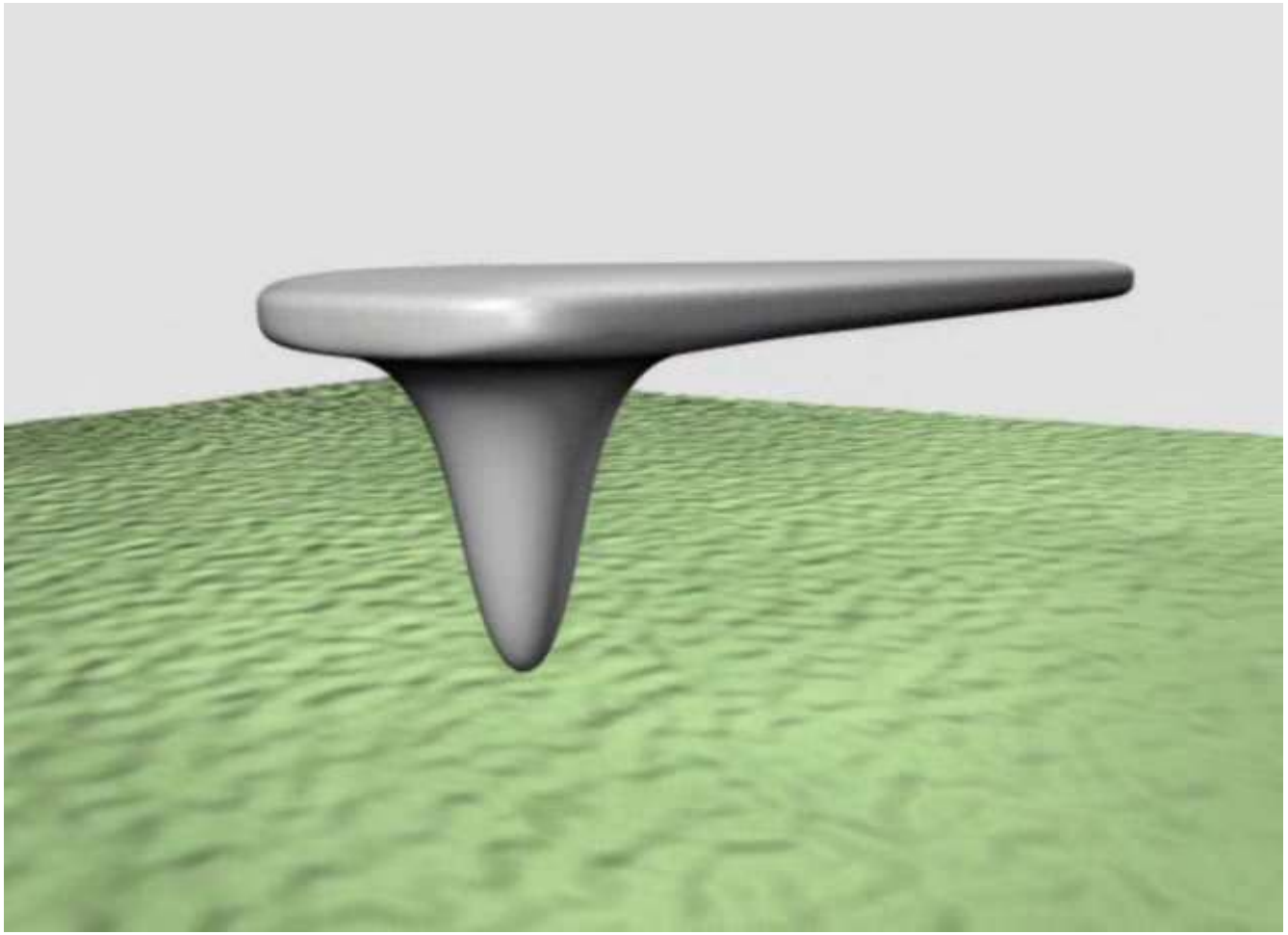
Länge : l = 450 μm
Breite : w = 45 μm
Dicke: t = 1.5 μm
E=1.69 10^{11}N/m^2

Spitzenhöhe: 12 μm
Spitzenradius: 10 nm

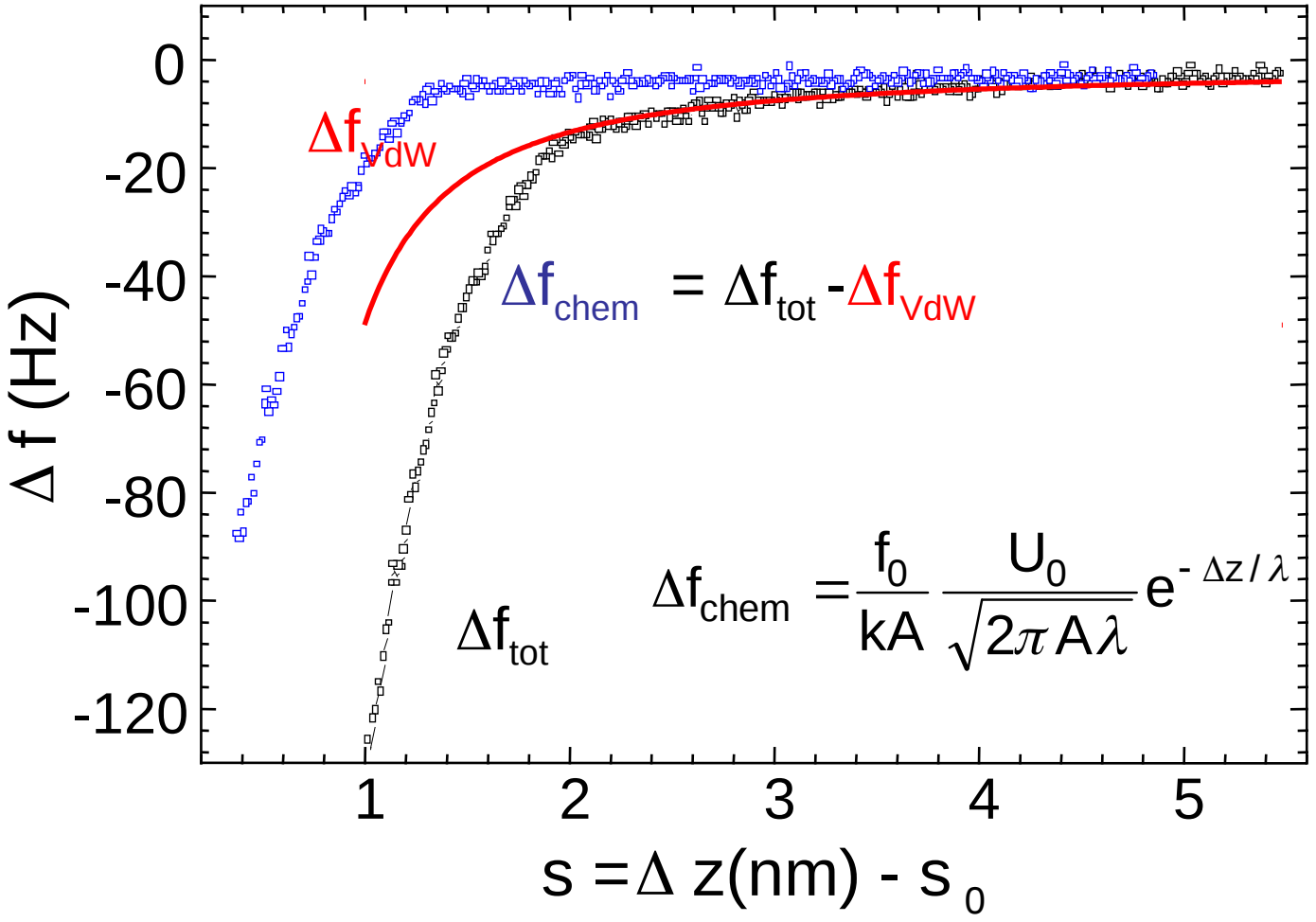
Federkonstante k:

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

nc-AFM scheme



Short range interaction

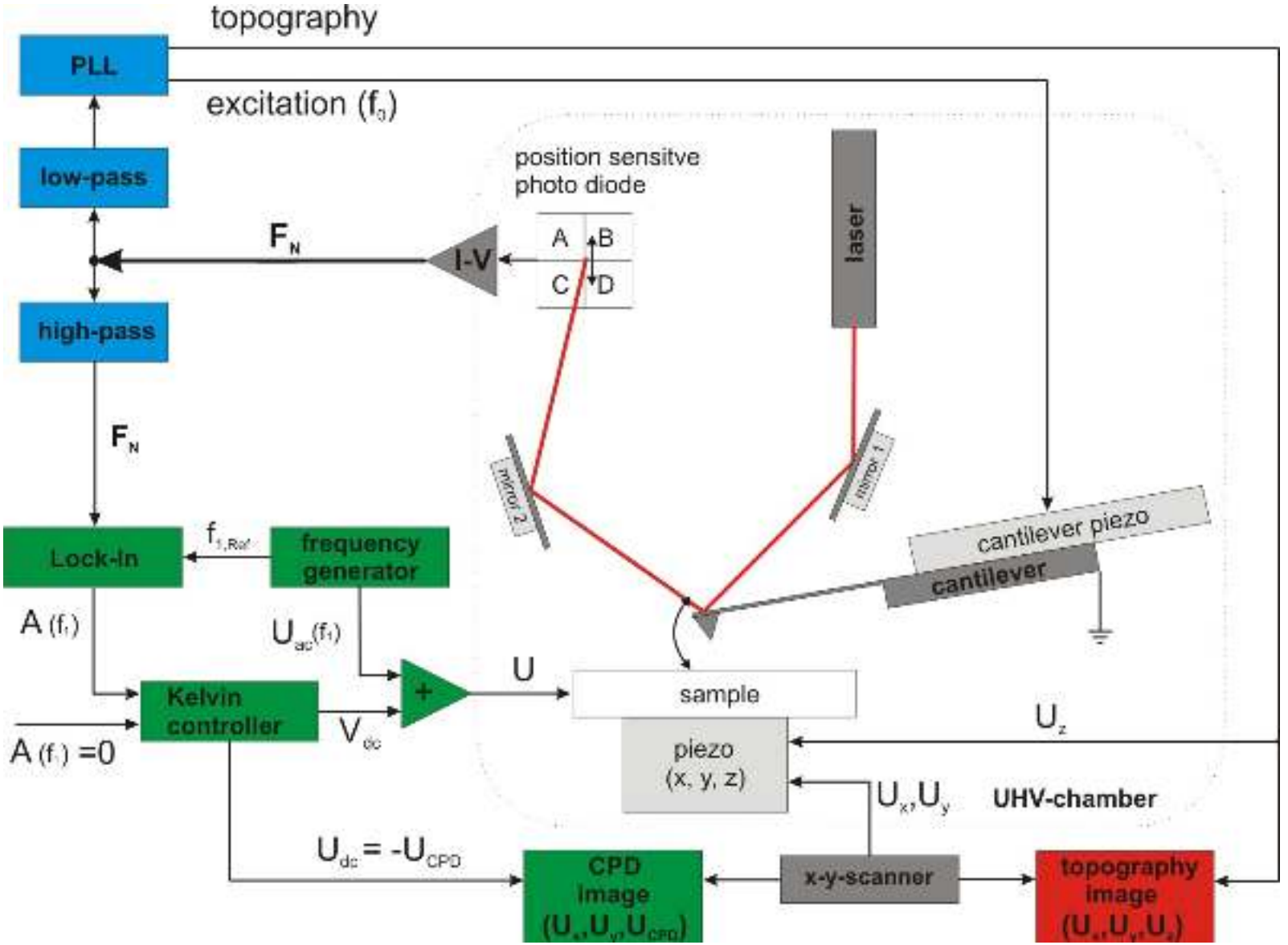


λ = 0.35 nm

U_0 = -4.7 eV

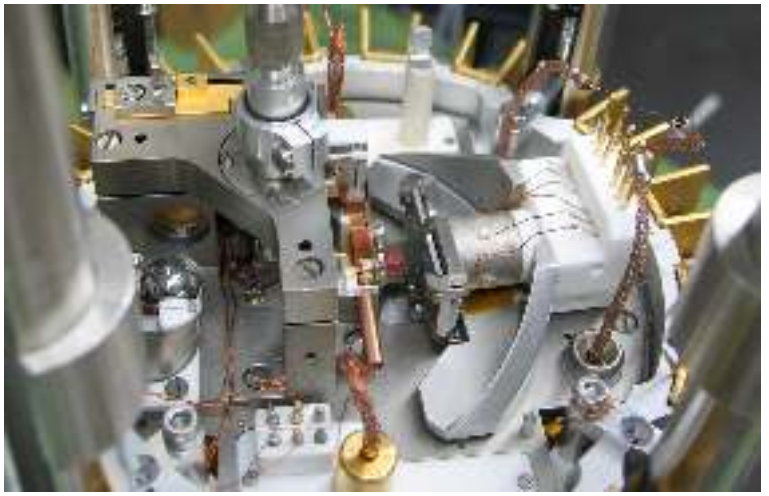
s_0 = 0.45 nm

Experimental Setup
nc-AFM and KPFM

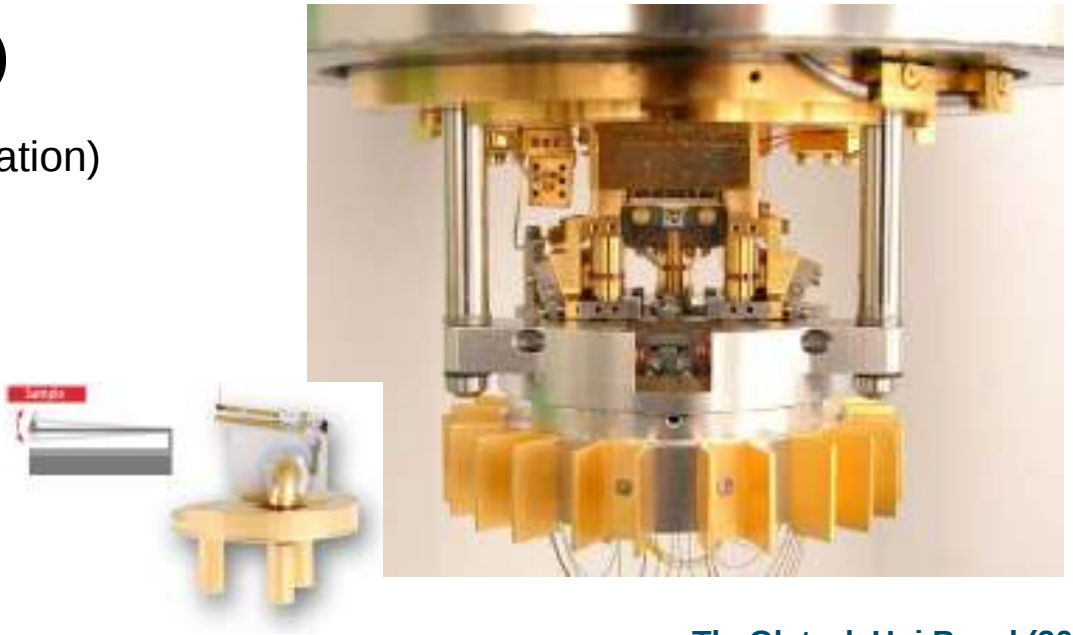


Experimental Setup
UHV AFM/STM

- **Room temperature AFM (UHV)**
  - UHV: Base pressure below $1x10^{-10}$ mbar
  - Operation at room temperature
  - Mixed mode: AFM/STM
  - Beam deflection method
  - Bandwidth of the photo detector: 3MHz
  - Nanonis Dual-OC4



- **Low temperature STM/AFM (UHV)**
  - Tuning Fork from Omicron (qPlus configuration)
  - Low temperature measurement (5K-77K)
  - High-resolution imaging of molecules
  - Determination of the „force needed to move an adatom on a surface“



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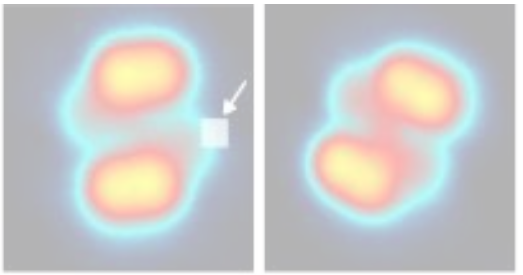
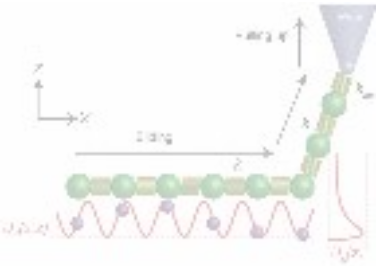
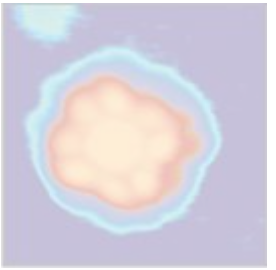
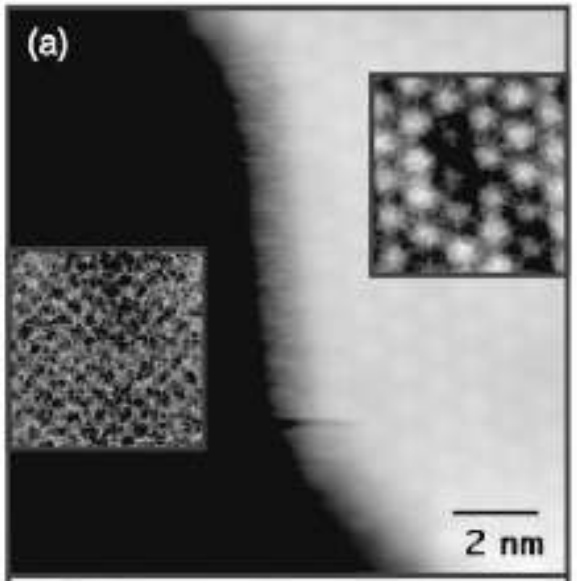




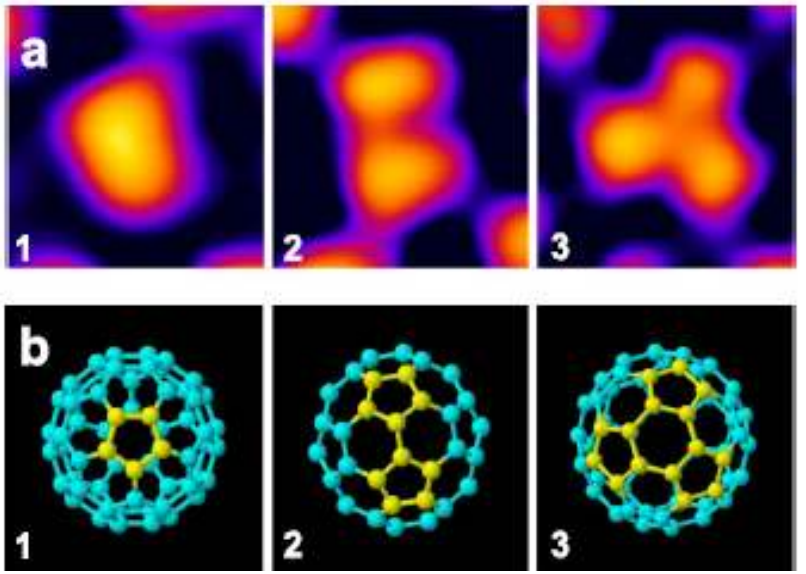


C_{60} state of the art

nc-AFM, C_{60}/KBr(001)



STM, C_{60}/Au(111)



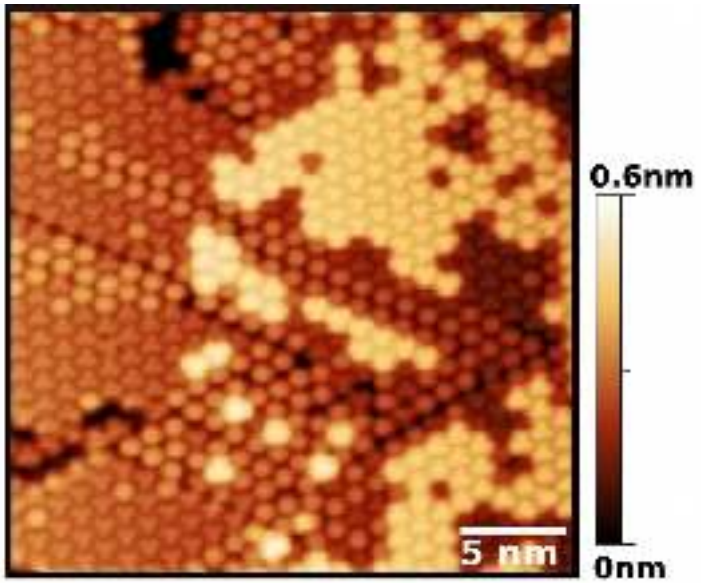
Possible C_{60} orientations

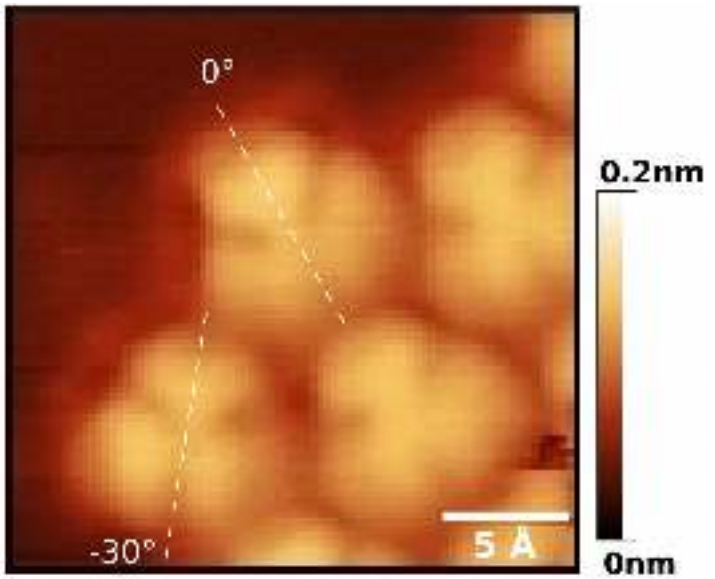
[1] G. Schull *et al.*, *Phys. Rev. Lett.*, **99**, 226105 (2007)
[2] S.A. Burke *et al*., *Phys. Rev. Lett.*, **94**, 096102 (2005)
[3] S.A. Burke *et al*., *Phys. Rev. B*, **76**, 035419 (2007)

High Resolution Imaging

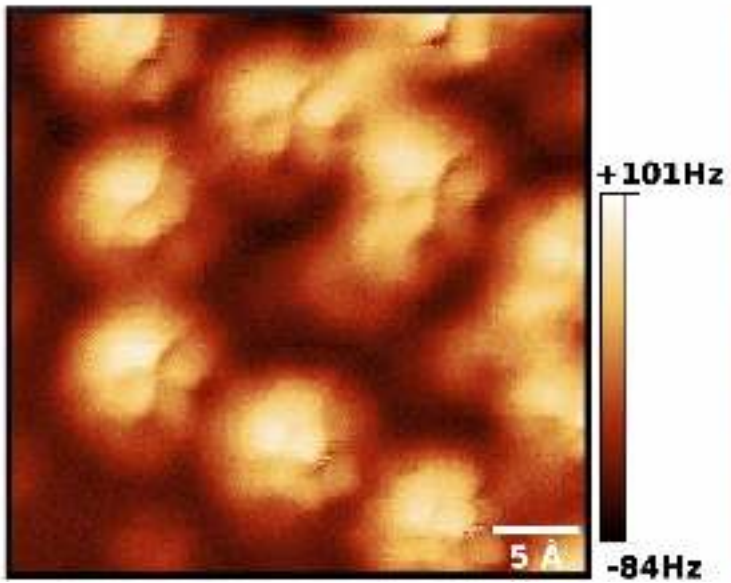
C_{60} on Cu(111)

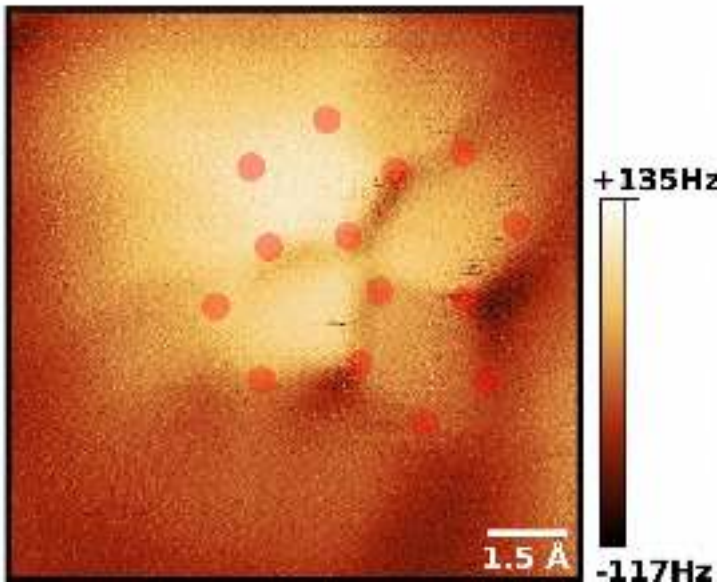
Scanning Tunneling Microscopy (STM)





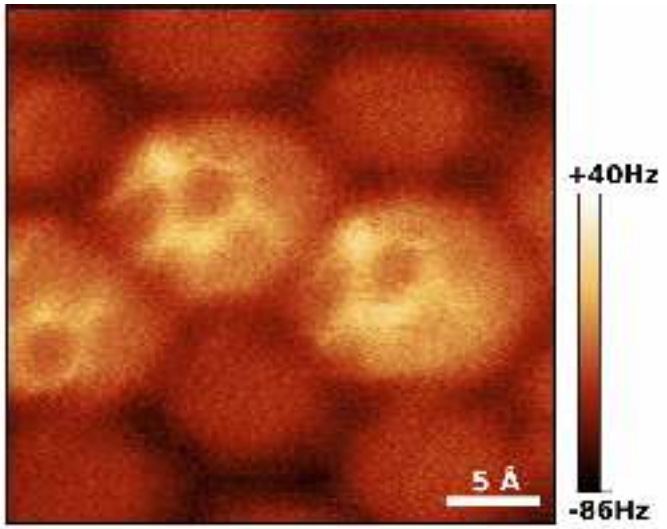
Atomic Force Microscopy (STM)

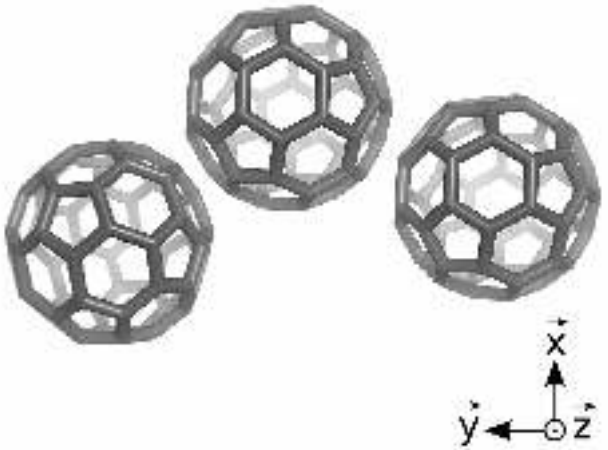


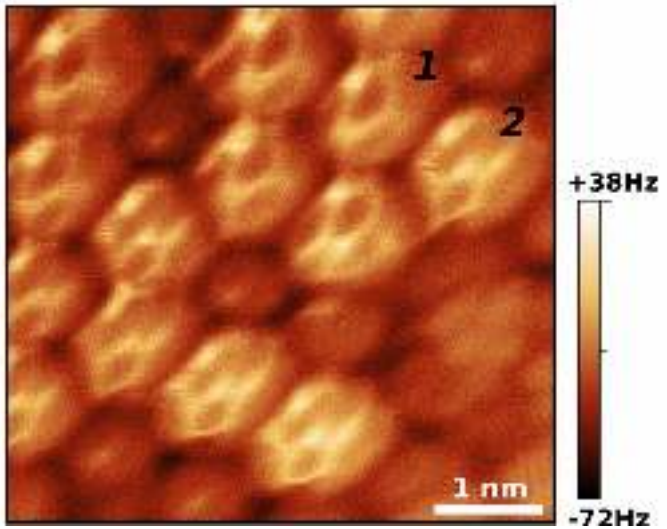


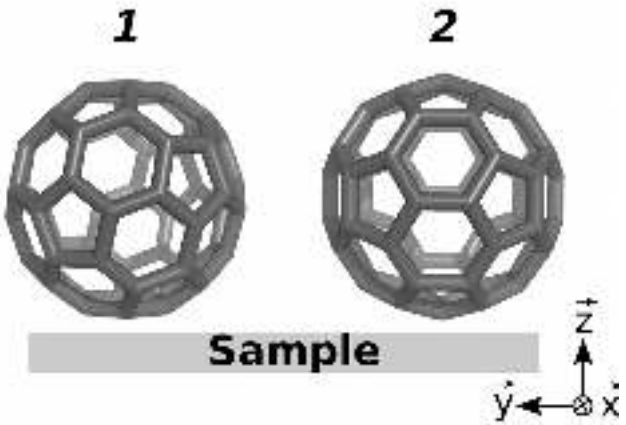
High Resolution Imaging of C_{60} Molecules

tuning fork AFM measurements









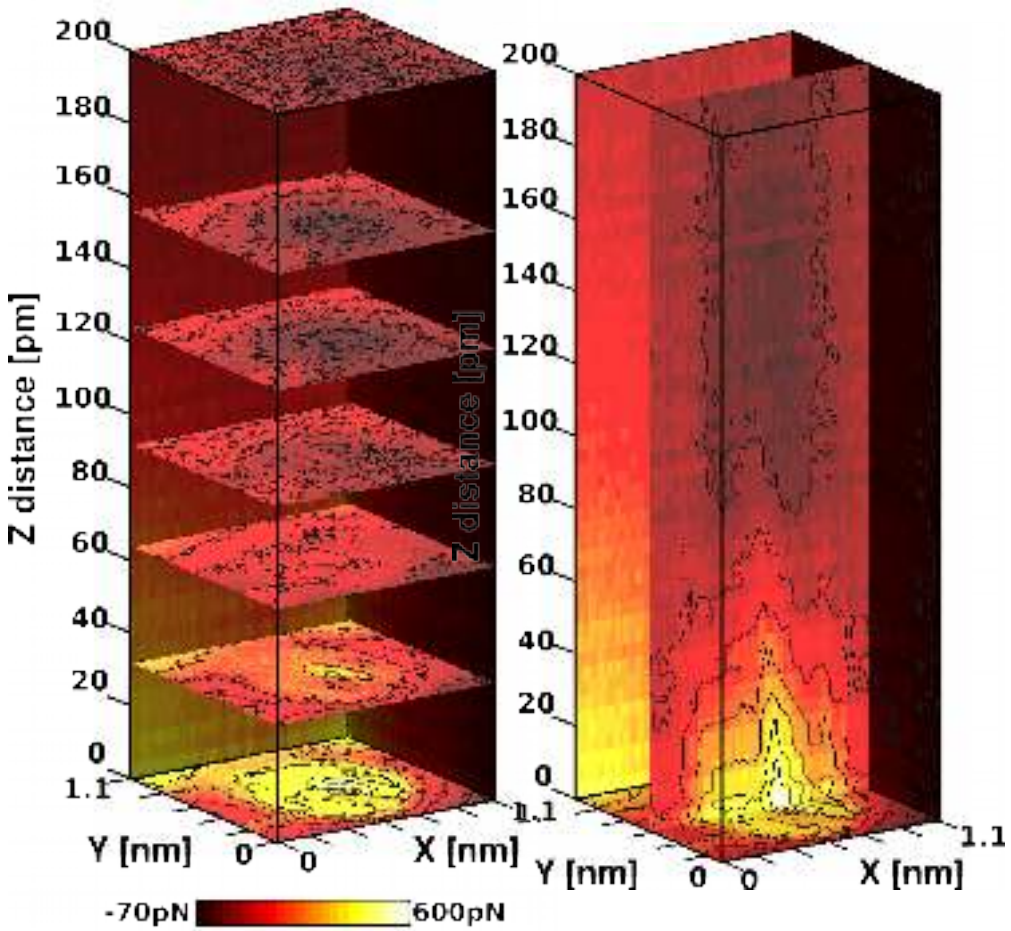
➔ Constant-current AFM measurement (STM feedback I = 50 pA, V = 6 mV, A =80 pm)

R. Pawlak et al., ACS Nano 5, 6349-6354, (2011)

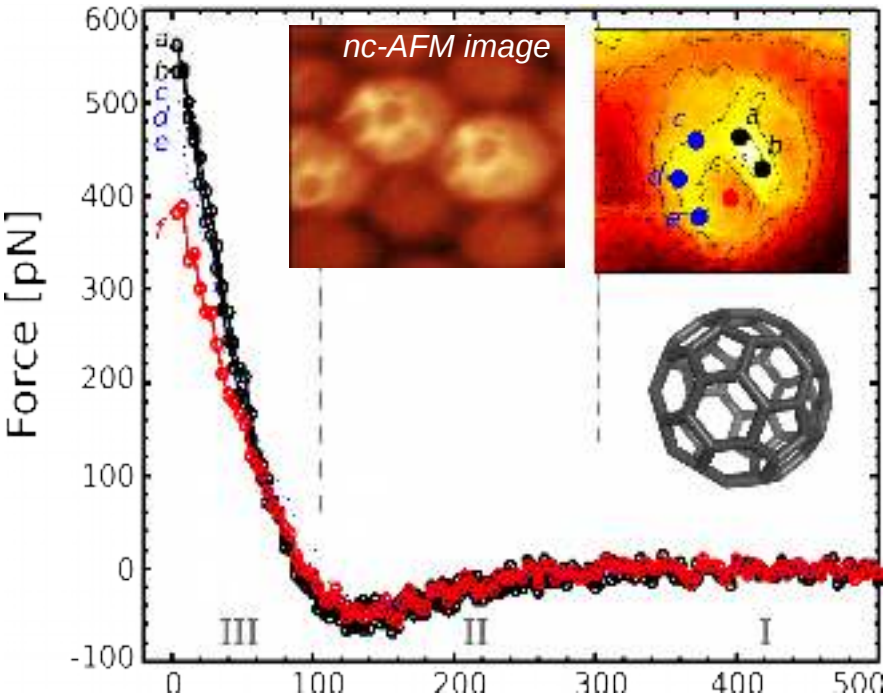
High Resolution Imaging of C_{60} Molecules

local mechanical properties

3D-force field above a single C_{60}



61 x 61 points, Δf(z) with 256 points, atom tracking



- High-resolution imaging of the C_{60} chemical structure
- Site-specific tip-sample force variations above the C_{60} structure detected with 3D-spectroscopy
- Above carbon atoms vertical force gradient is found to be ~9 N/m and ~7 N/m
- Above the center of the carbon ring ~4 N/m.

R. Pawlak et al., ACS Nano 5, 6349-6354, (2011)

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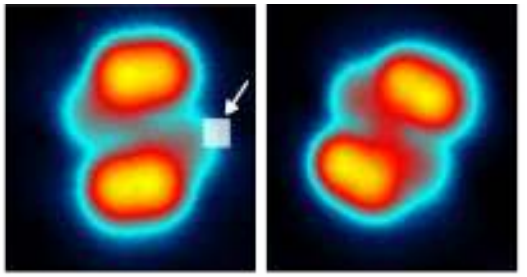
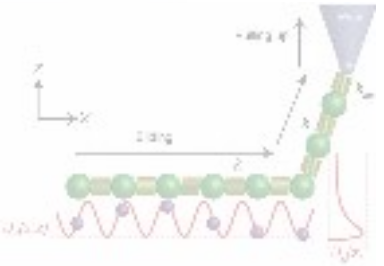
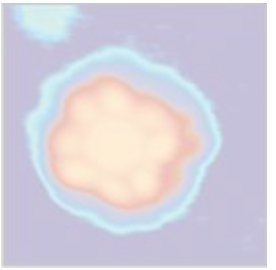
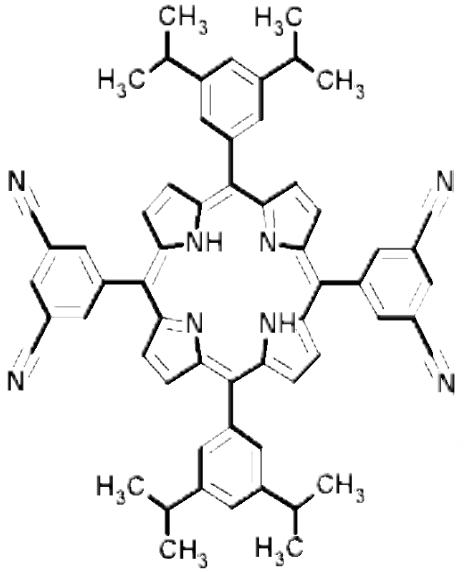
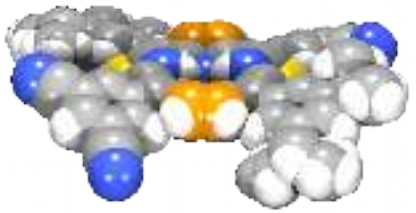






Porphyrins on Cu(111)
AFM/STM investigation at LT

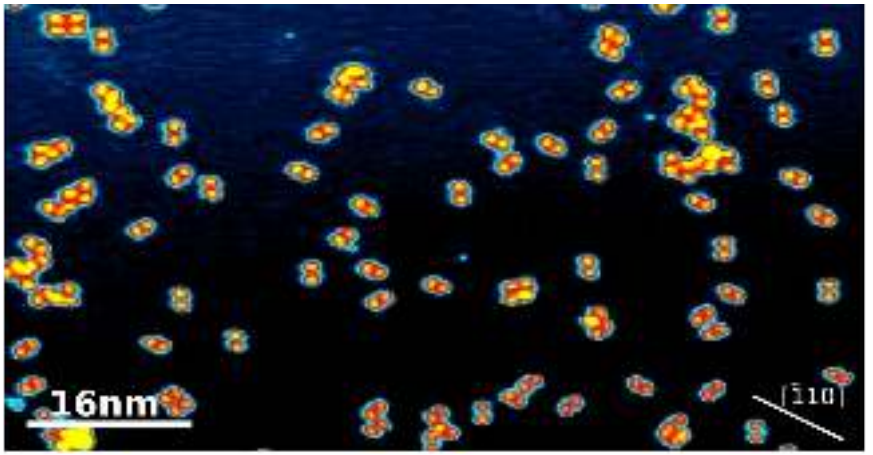


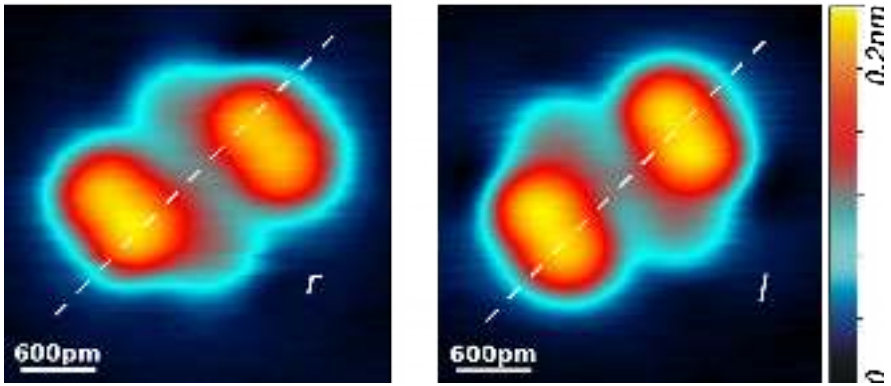


(F. Diederich, ETH Zurich).

CN endgroups:

- metal-ligand interaction
- strong dipolar moment
- Anchoring sites for molecules on insulating surfaces





STM overview after deposition on the sample kept at 80K,
(I = 30 pA, V = 60 mV)

- Symmetry breaking after adsorption on Cu(111)
- Saddle conformation

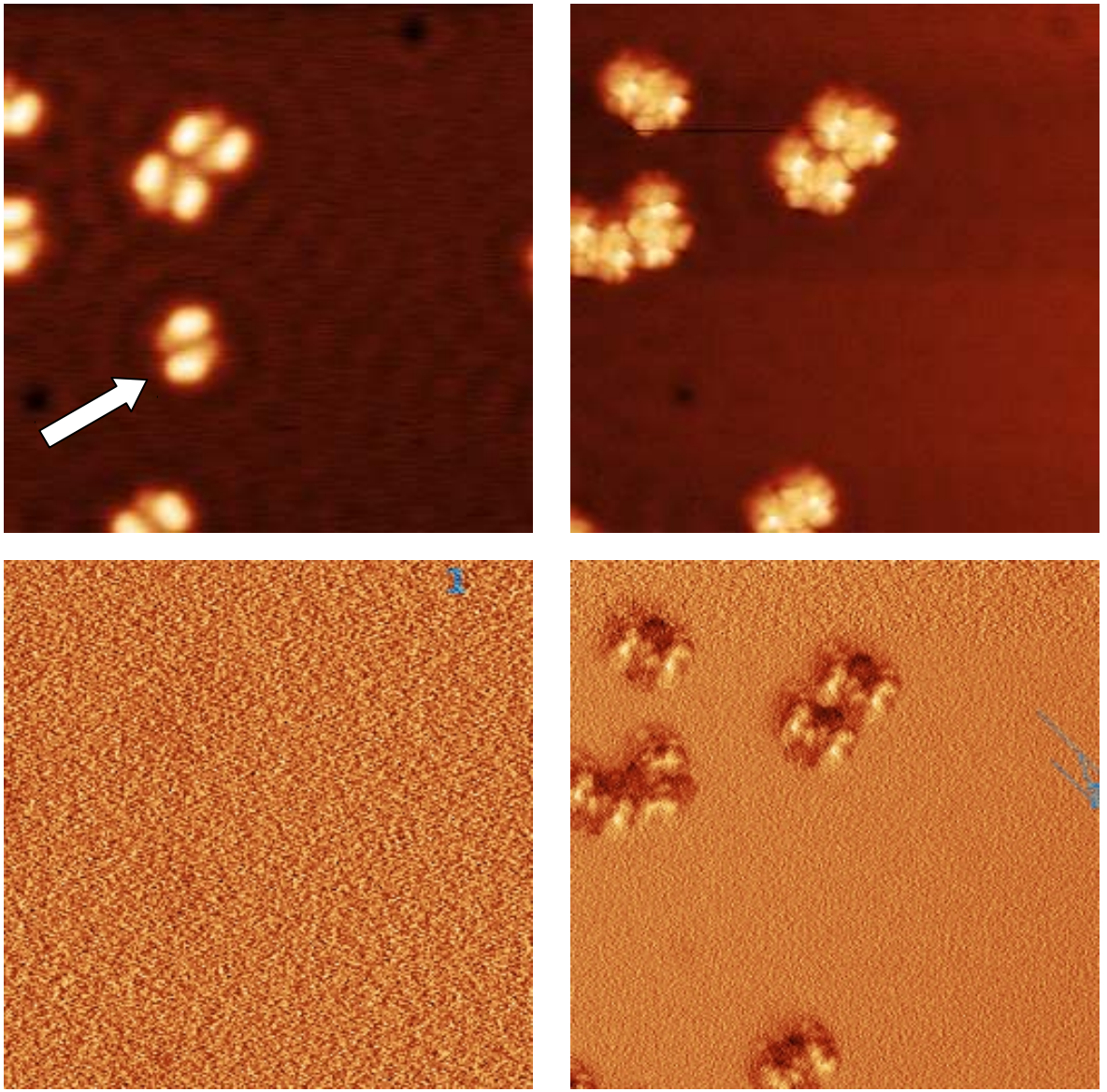
R. Pawlak et al., ACS Nano 6, 6318-6324, (2012).

Vertical Manipulation

catch the molecule with the tip...

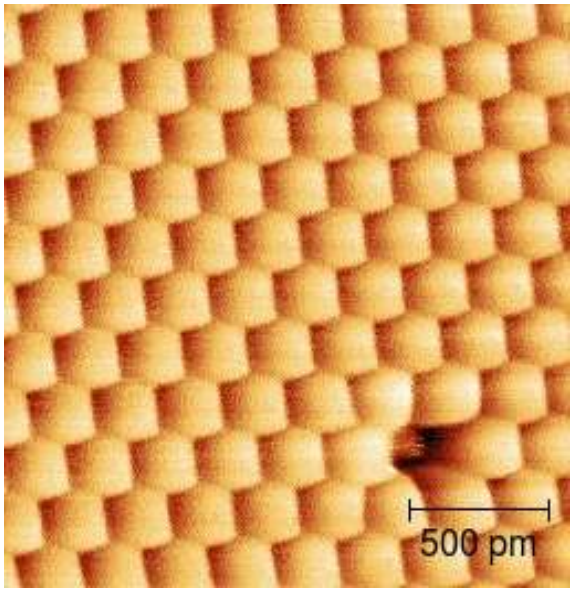
STM Topography

Frequency Shift



Method: z-spectroscopic curve in the center of the molecule

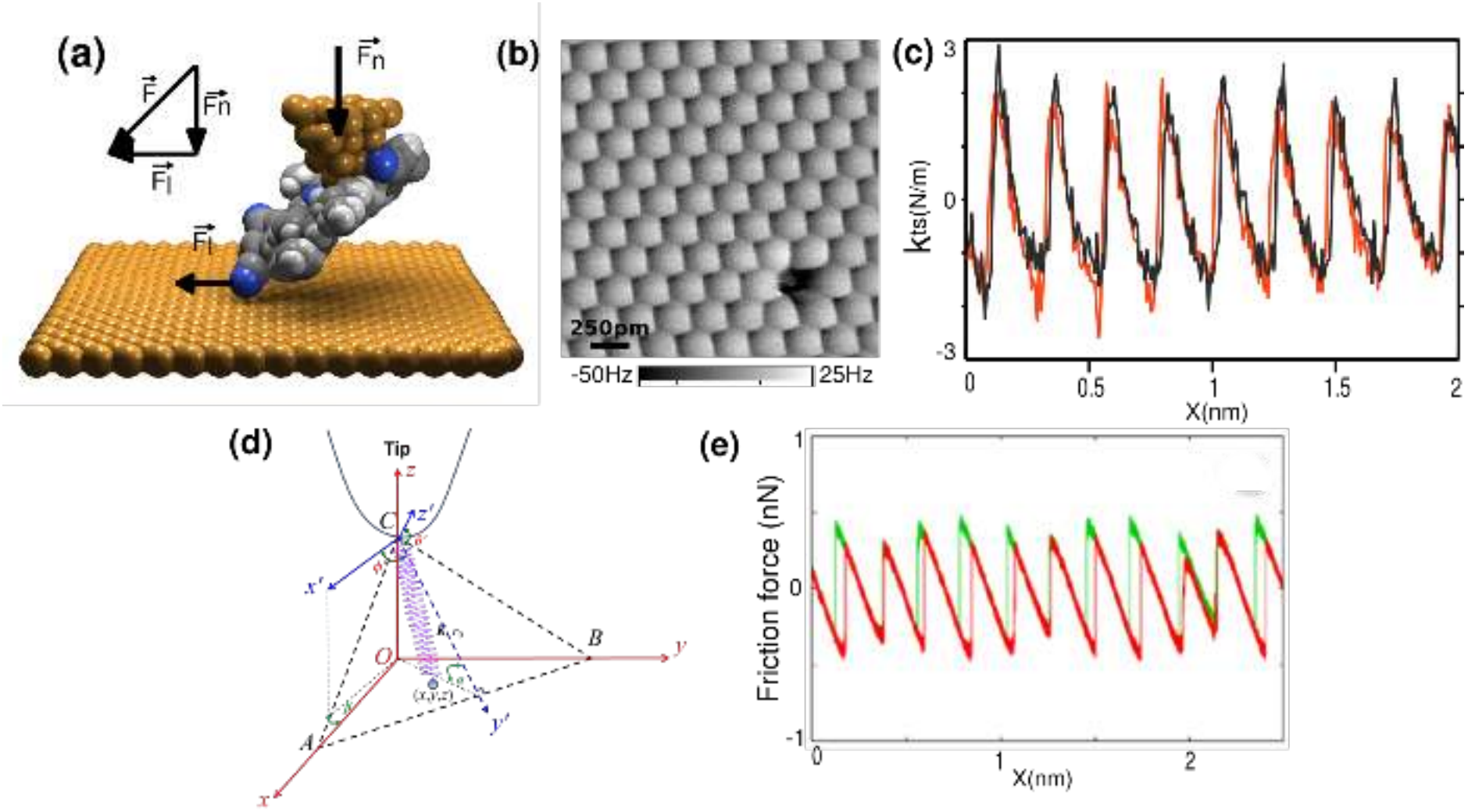
Friction measurement with a molecule linked to the tip



Atomic resolution on Cu(111)

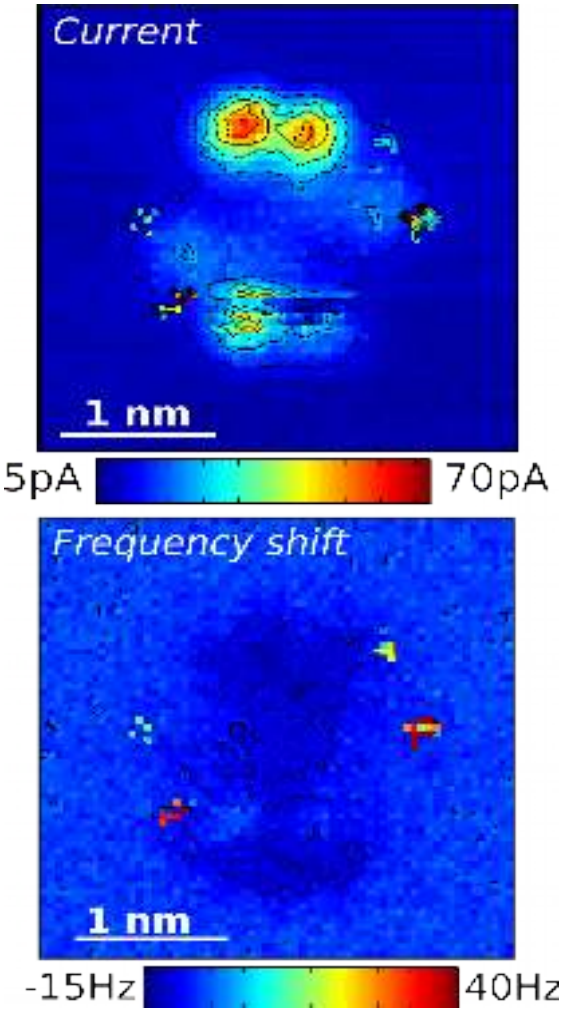
Vertical Manipulation

friction with a single molecule

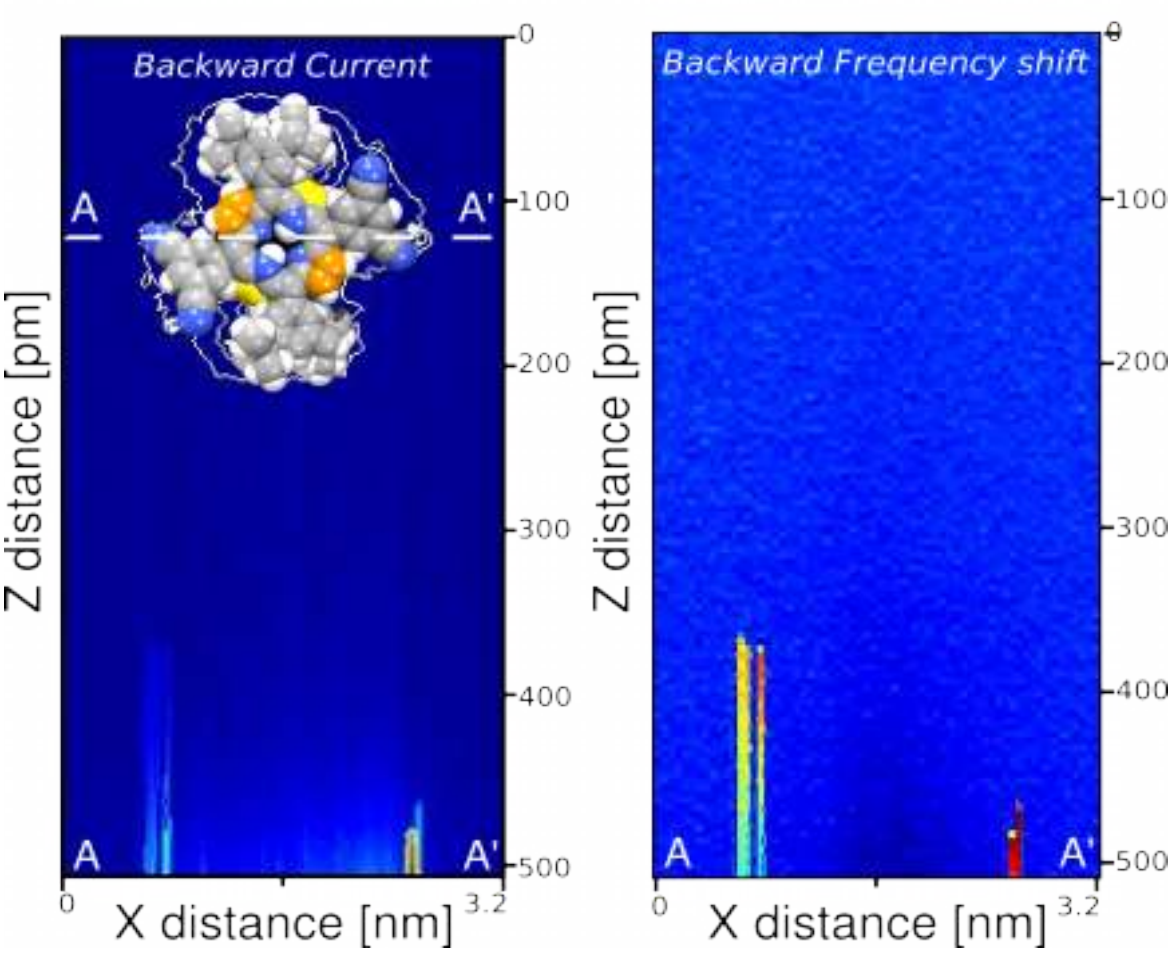


3D-spectroscopic measurement

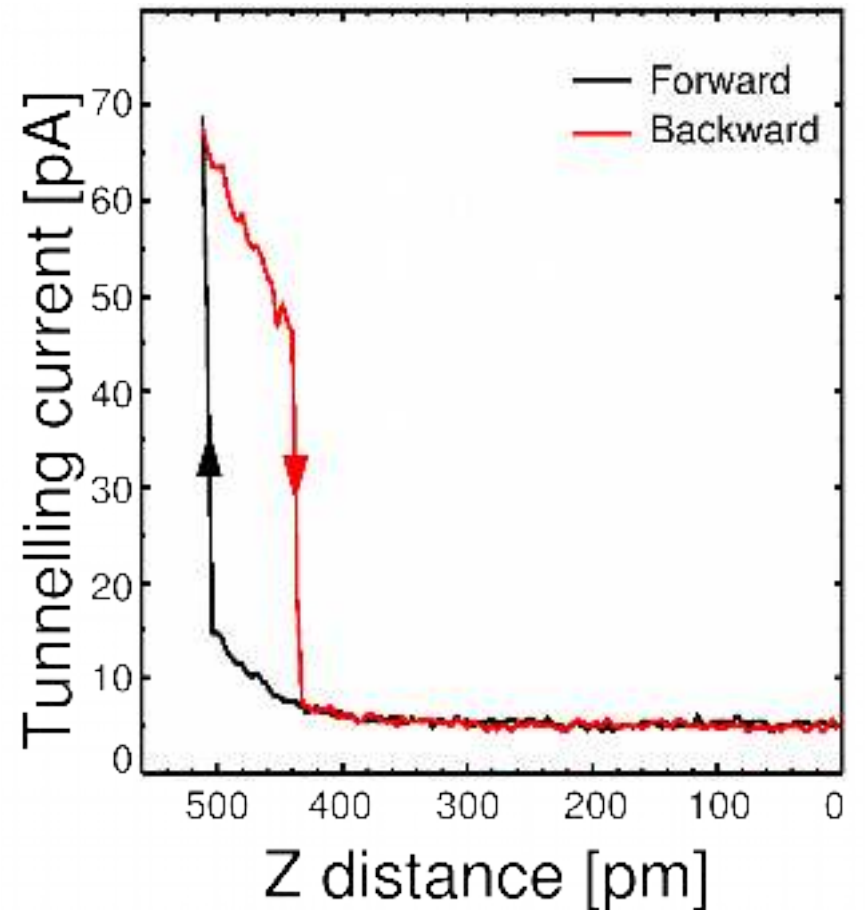
· T = 4 K, f_o = 26438 Hz, Q = 30808, A = 60 pm, V_{tip} = 300 µV,
· acquisition time = 10-15 hours, grid size : 60x60x128 pt (2x2x0.5nm),
· grid mode with atom tracked positionning

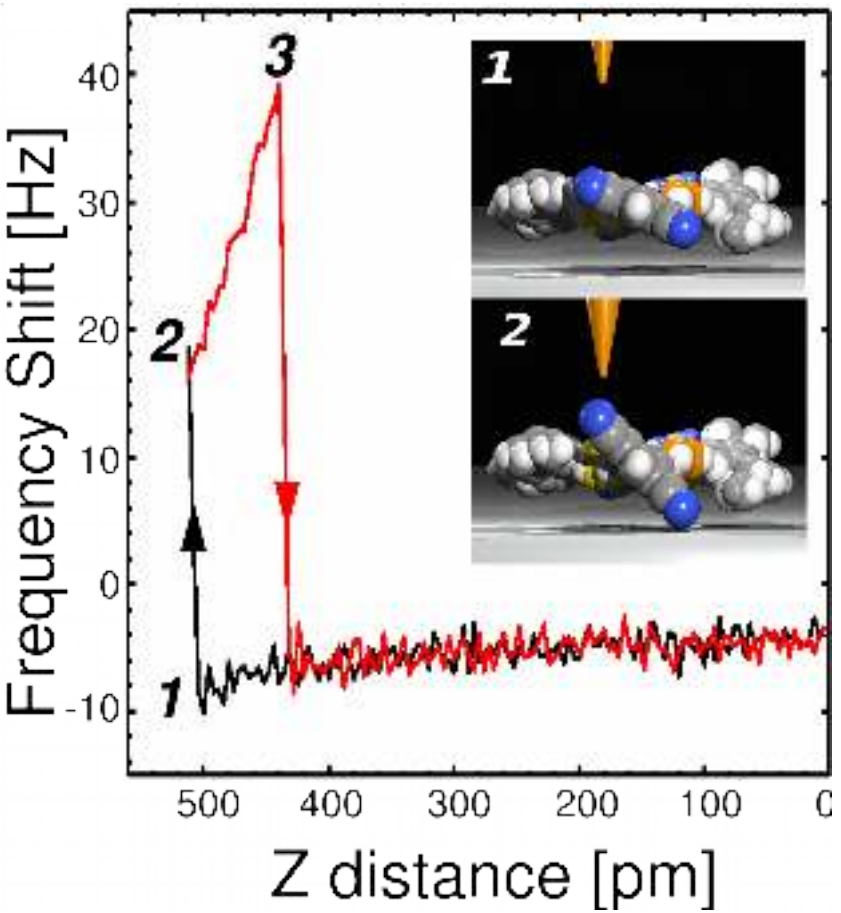


*It(x,z) and **Δ**f(x,z) cross-sections*



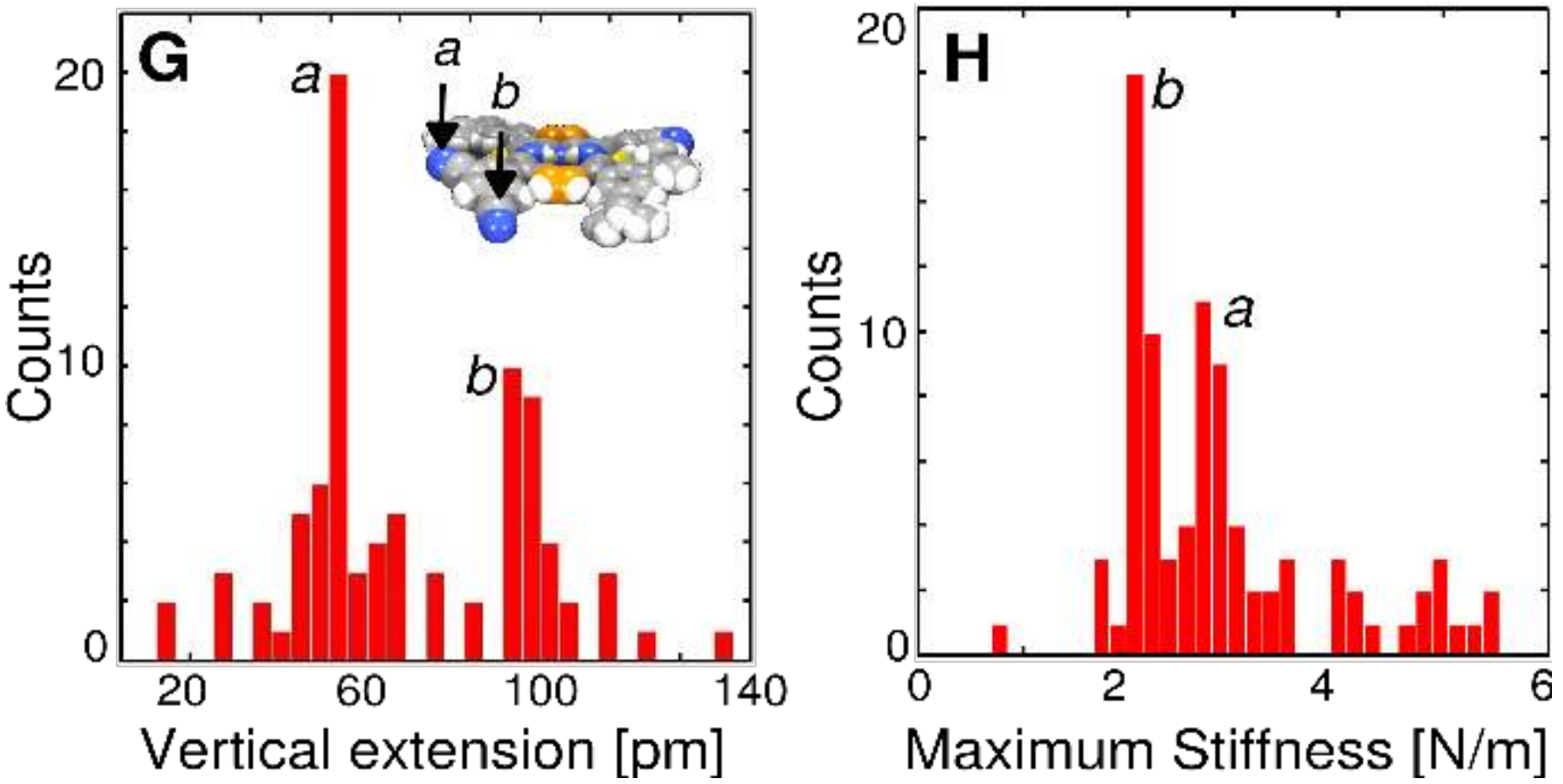
Vertical switching of the dicyanophenyl leg





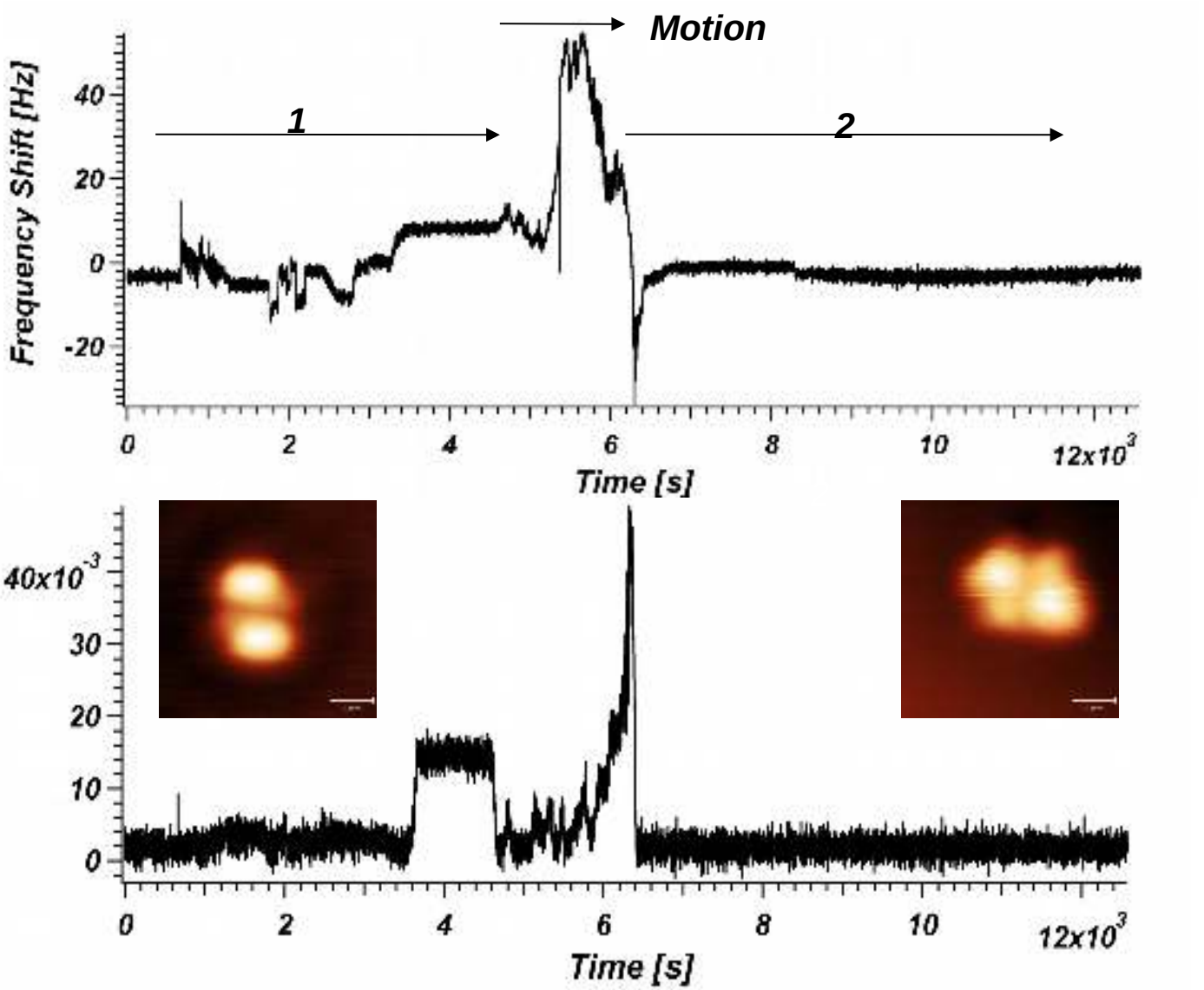
R. Pawlak et al., ACS Nano 6, 6318-6324, (2012).

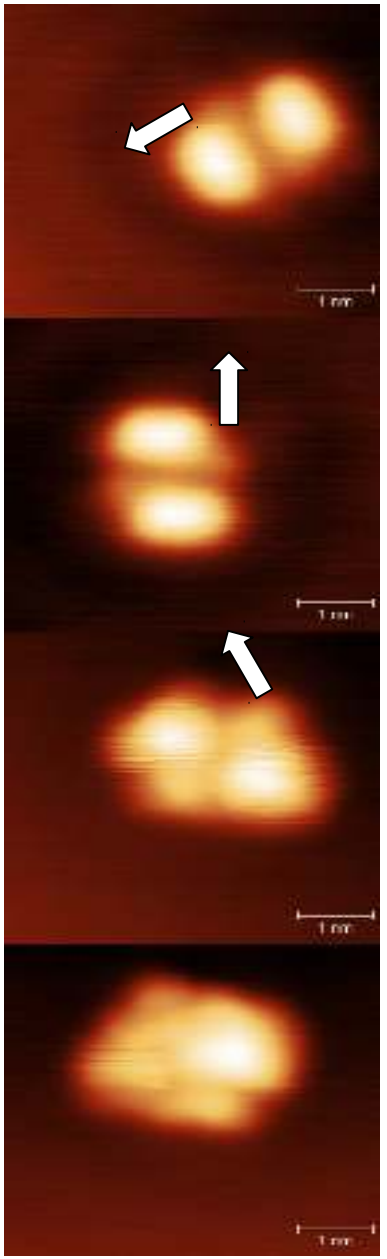
Vertical switching of the dicyanophenyl leg



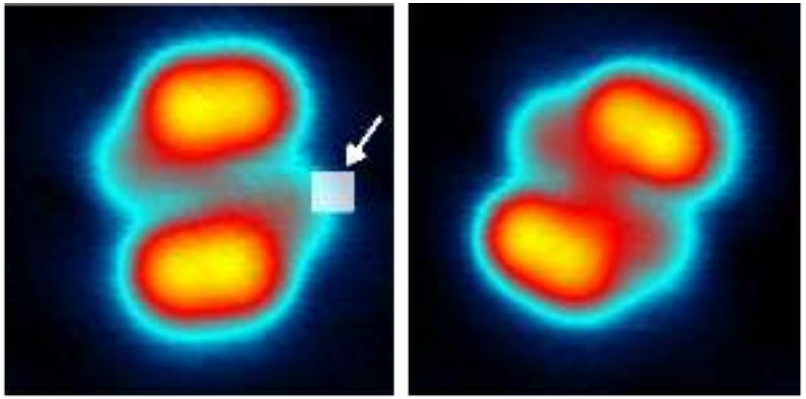
R. Pawlak et al., ACS Nano 6, 6318-6324, (2012).

Lateral Manipulation





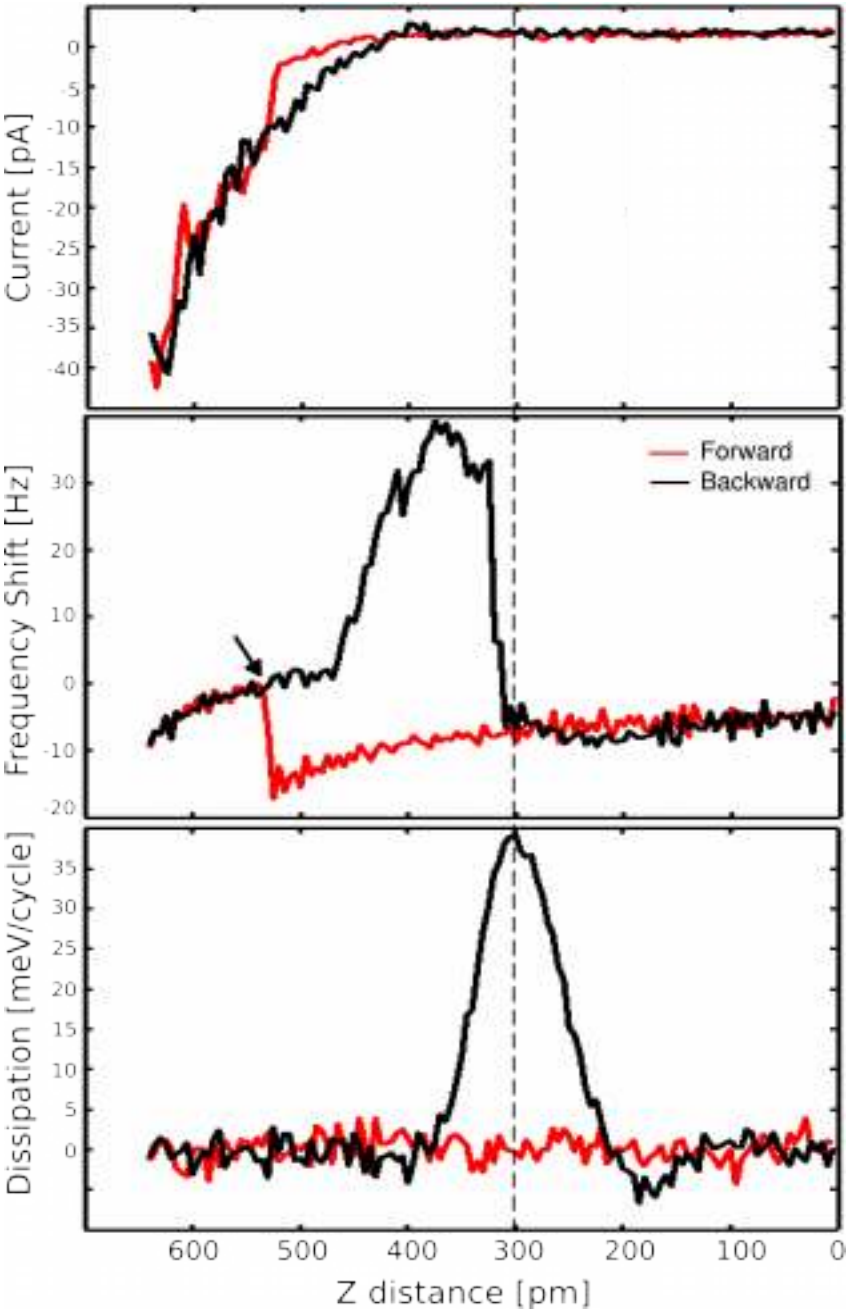
Controlled rotation



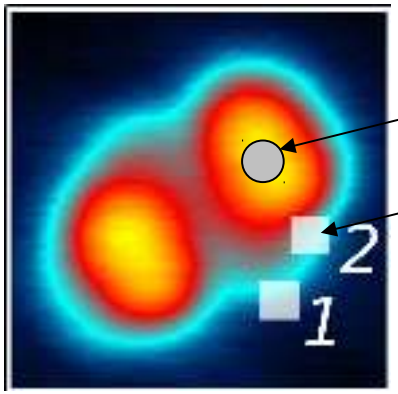
Rotation of **60°**

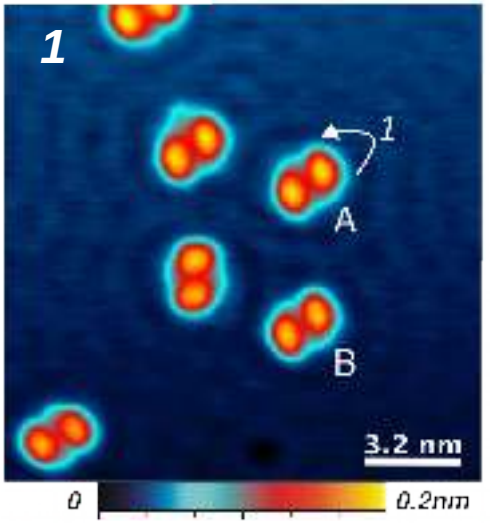
Absolute interaction force = **- 500 pN**

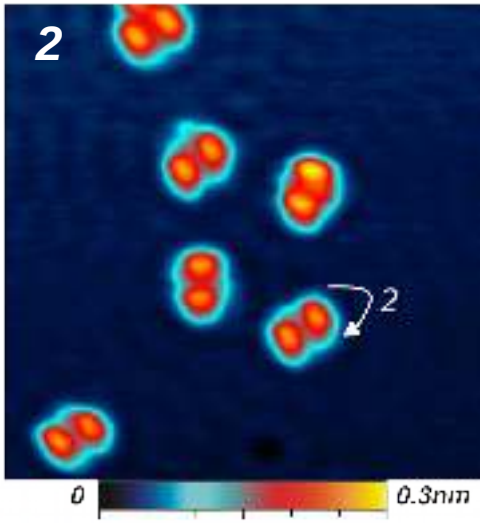
dissipated energy = **30-80 meV/cycle**

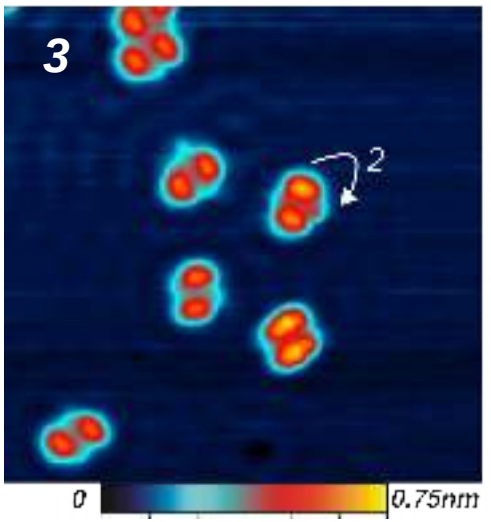


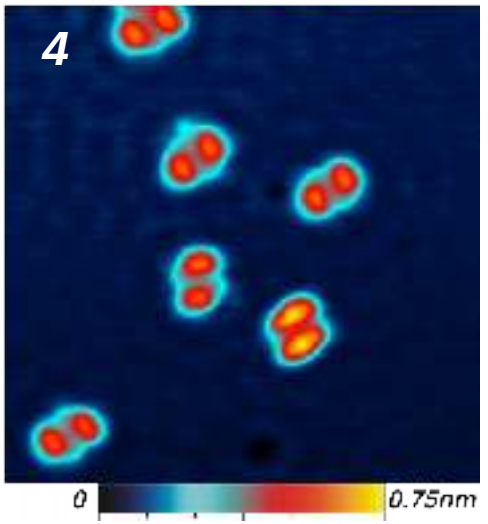
Influence of the targeted CN function





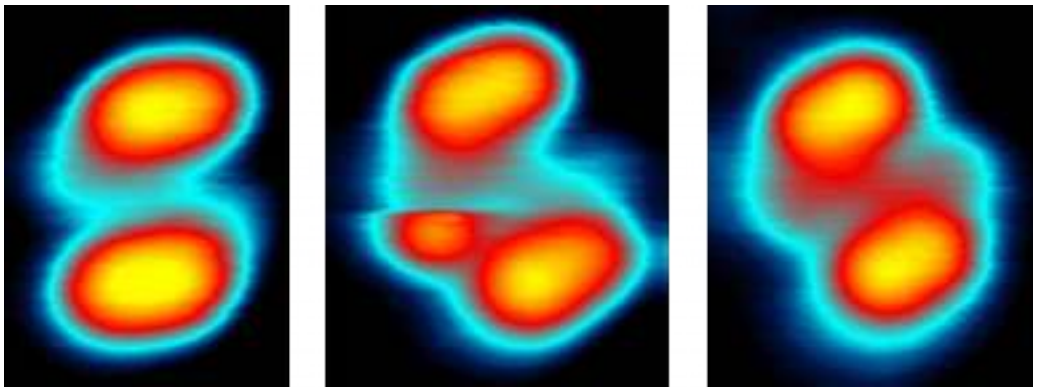


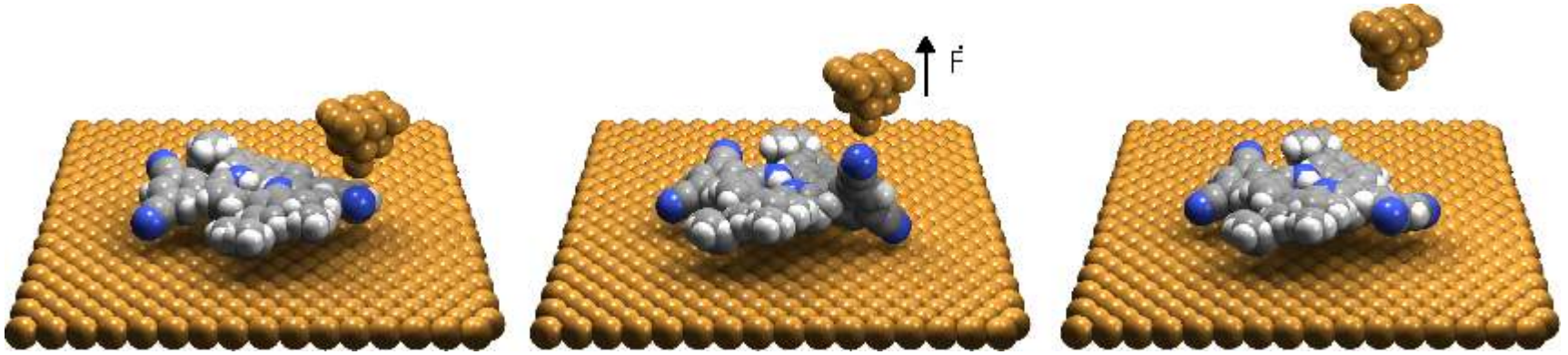




- **95 %** of induced rotations
- **15 %** of unusual conformations after motion
- Control of the rotation direction (**clockwise** or **anticlockwise)** depending on the targeted N atoms.

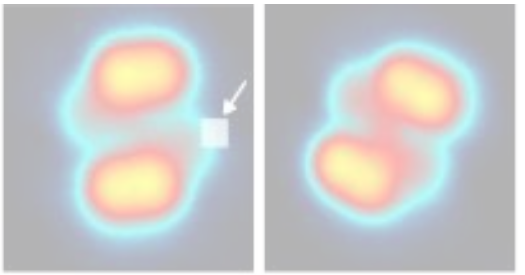
Mechanism

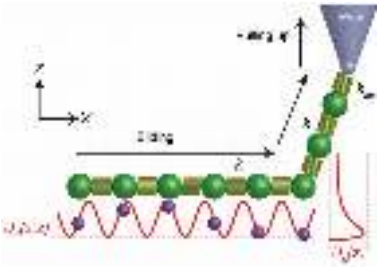


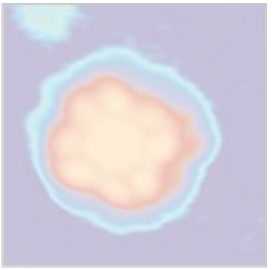


Overview

- **Introduction into SPM techniques**
  - interaction forces
  - detection mechanism & setup
- **Properties of single C_{60} molecules**
  - orientation of single molecules
  - mechanical properties
- **Manipulation of porphyrin molecules**
  - structural analysis
  - 3D force spectroscopy
  - controlled molecular manipulation
- **Formation of a molecular wire**
  - on surface reaction
  - determination of pulling forces
- **Electronic Information at submolecular scale**
  - Donor and Acceptor molecules
  - Optoelectronic excitation of CuPc

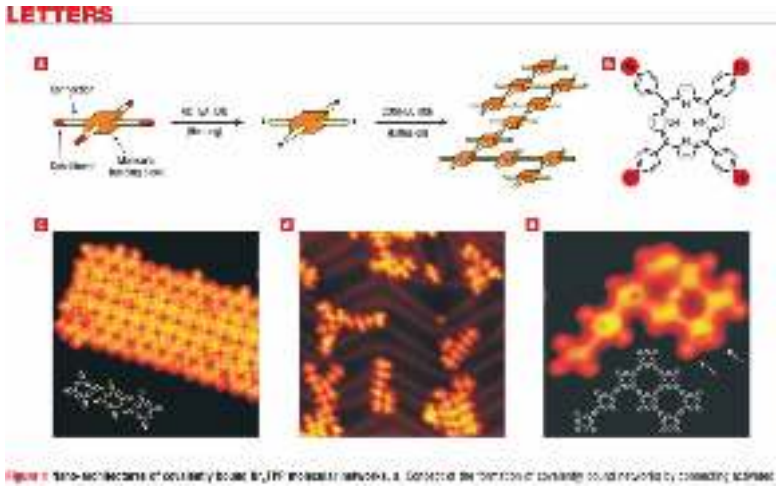




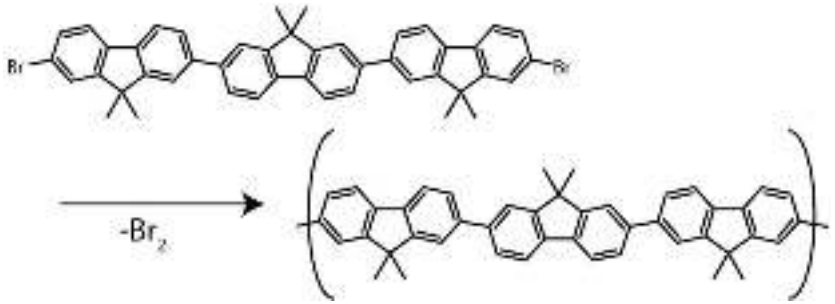


Surface chemical reactions for a long-molecular wire

Ullmann coupling reaction



L. Grill et al., Nat. Nanotechnol. 2, 687 (2007).



Conductance measurement

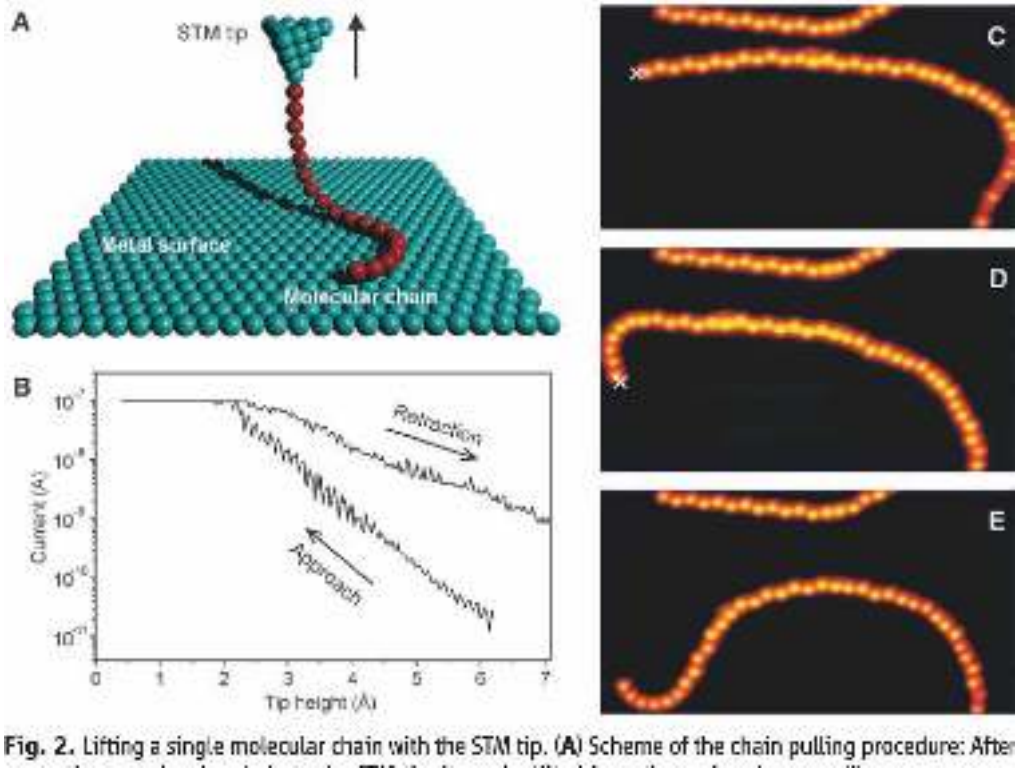
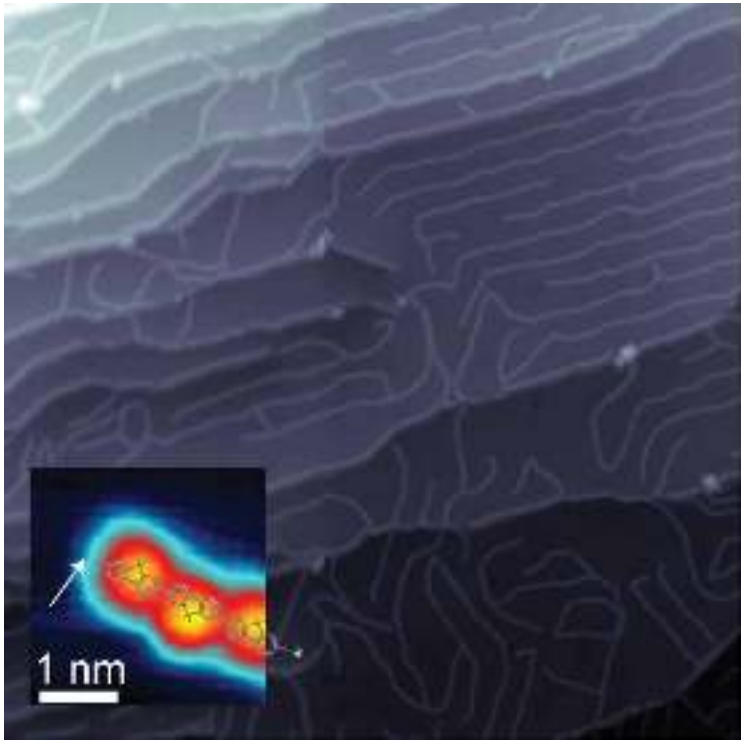


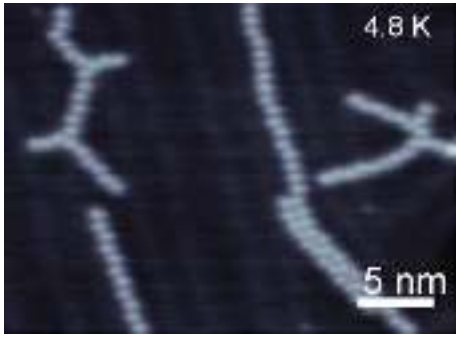
Fig. 2. Lifting a single molecular chain with the STM tip. (**A**) Scheme of the chain pulling procedure: After

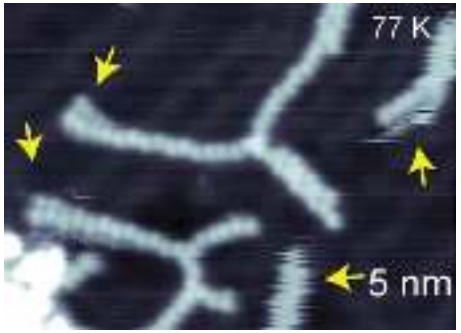
L. Lafferentz et al.,, Science 323, 1193 (2009).

STM topography of conjugated molecule wire on Au(111)



The “tail” is moving by thermal energy.

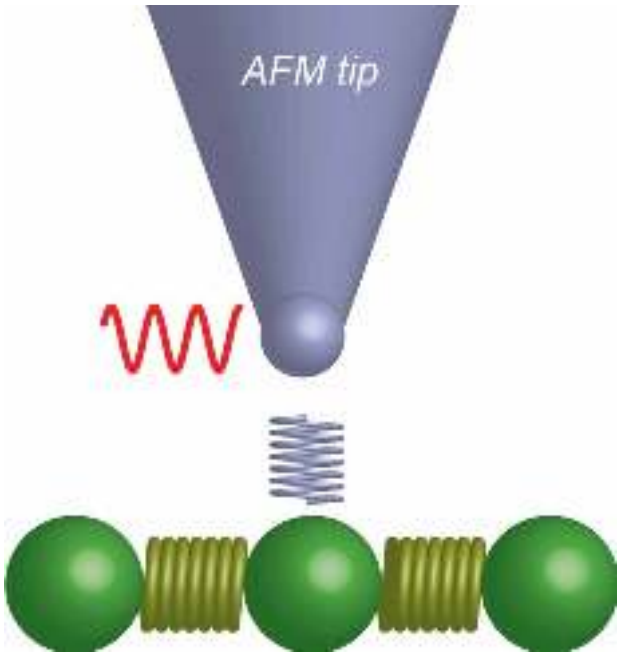




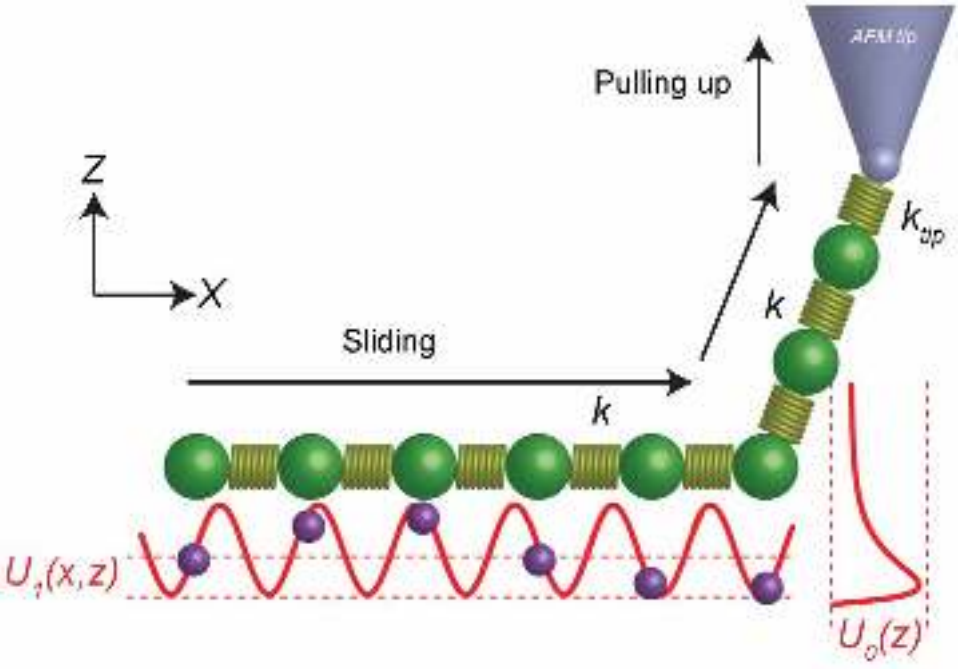
Low binding energy to the substrate (physisorption)

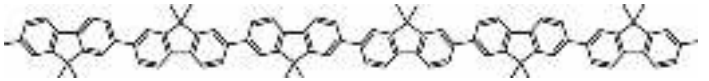
Tip-sample interaction

Conventional

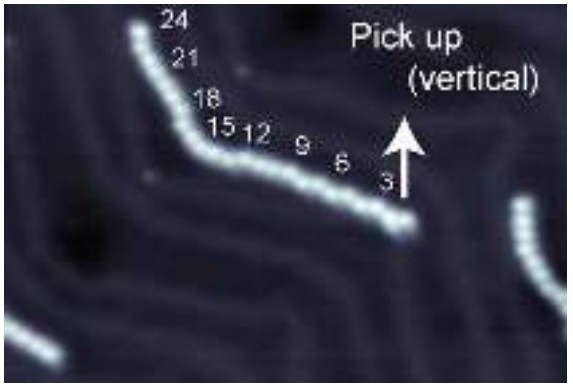


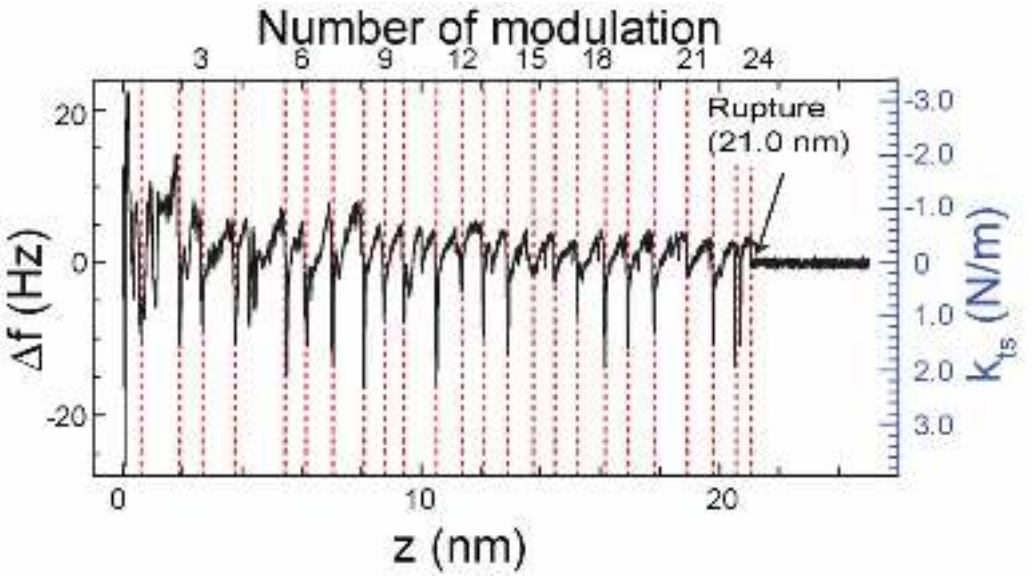
Puling wire by AFM

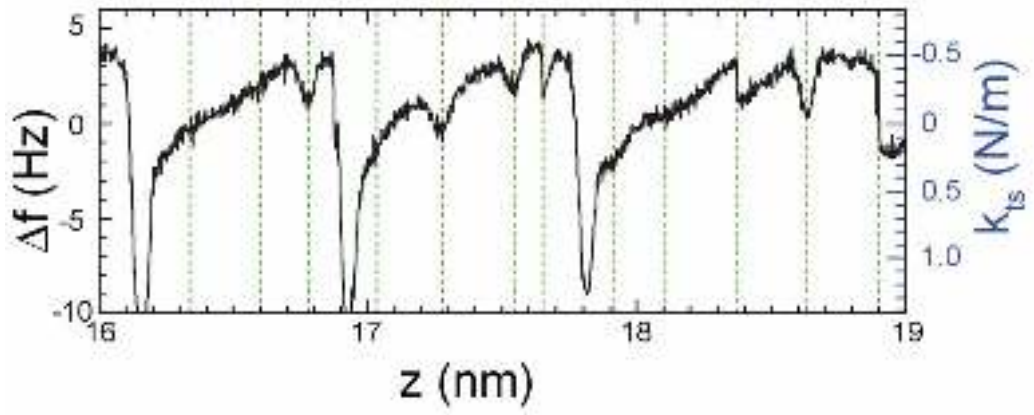




Mechanical response of the wire

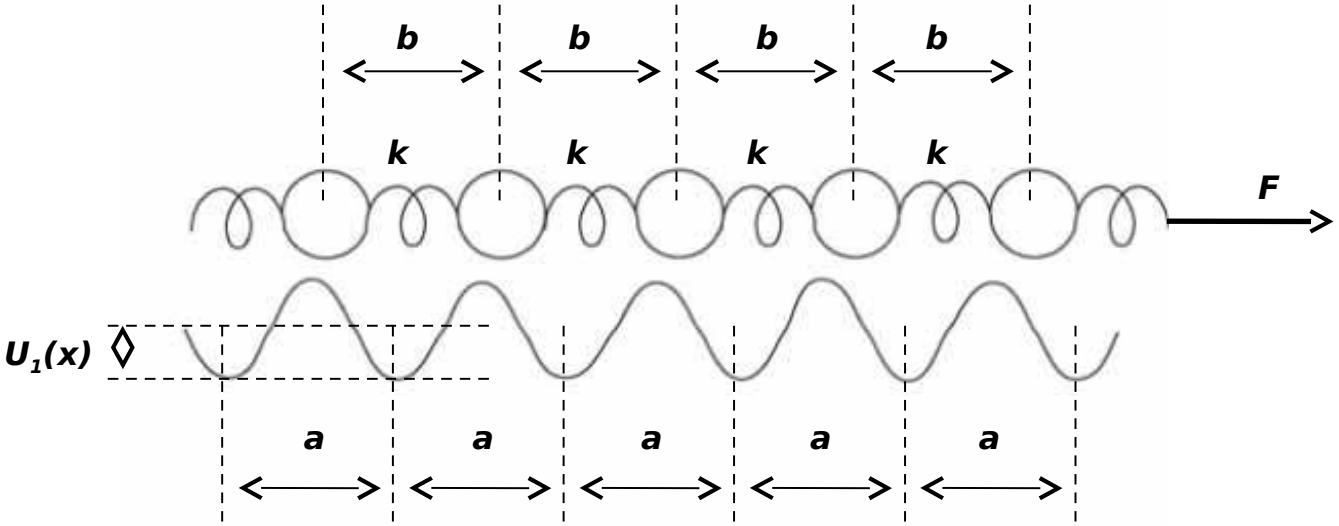






Model calculation
Frenkel-Kontorova model

Equivalent spring k and equilibrium length b
Unit-substrate interaction, sinusoidal potential with amplitudeU1(x) and periodicity b



O. M. Braun and A. G. Naumovets Sur. Sci. Rep. 60 79 (2006)

Model calculation