Contacting a single molecular wire by STM manipulation

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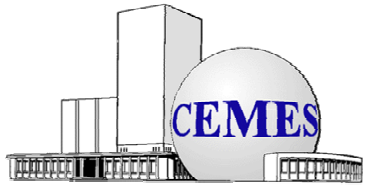
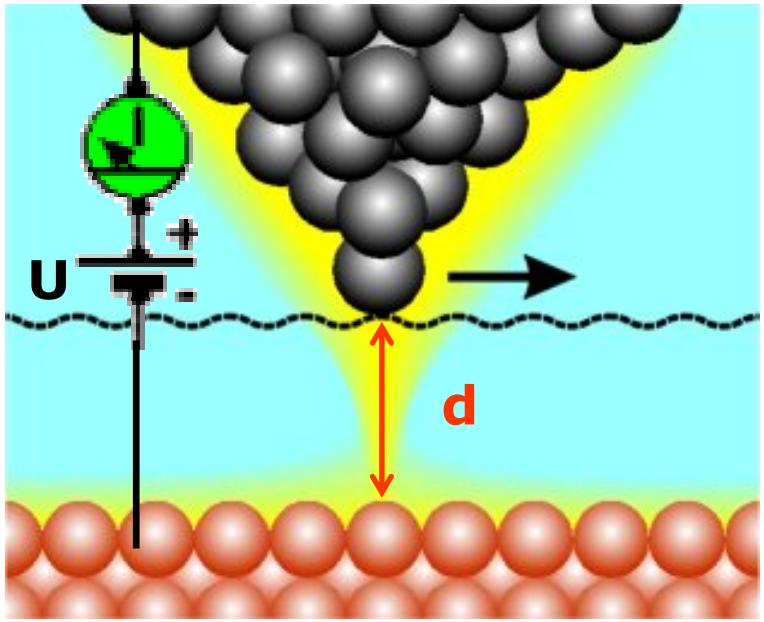
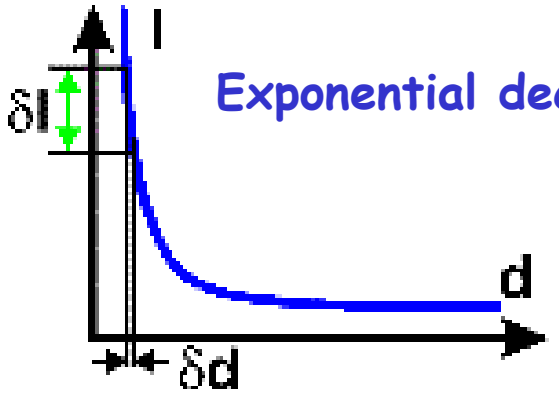


Nanoscience Group
CEMES-CNRS Toulouse

Scanning Tunneling Microscope

1982 Gerd Binnig and Heinrich Rohrer





$$I \propto U \cdot k \cdot e^{-kd}$$

Very small changes in the tip-sample separation induce large changes in the tunneling current

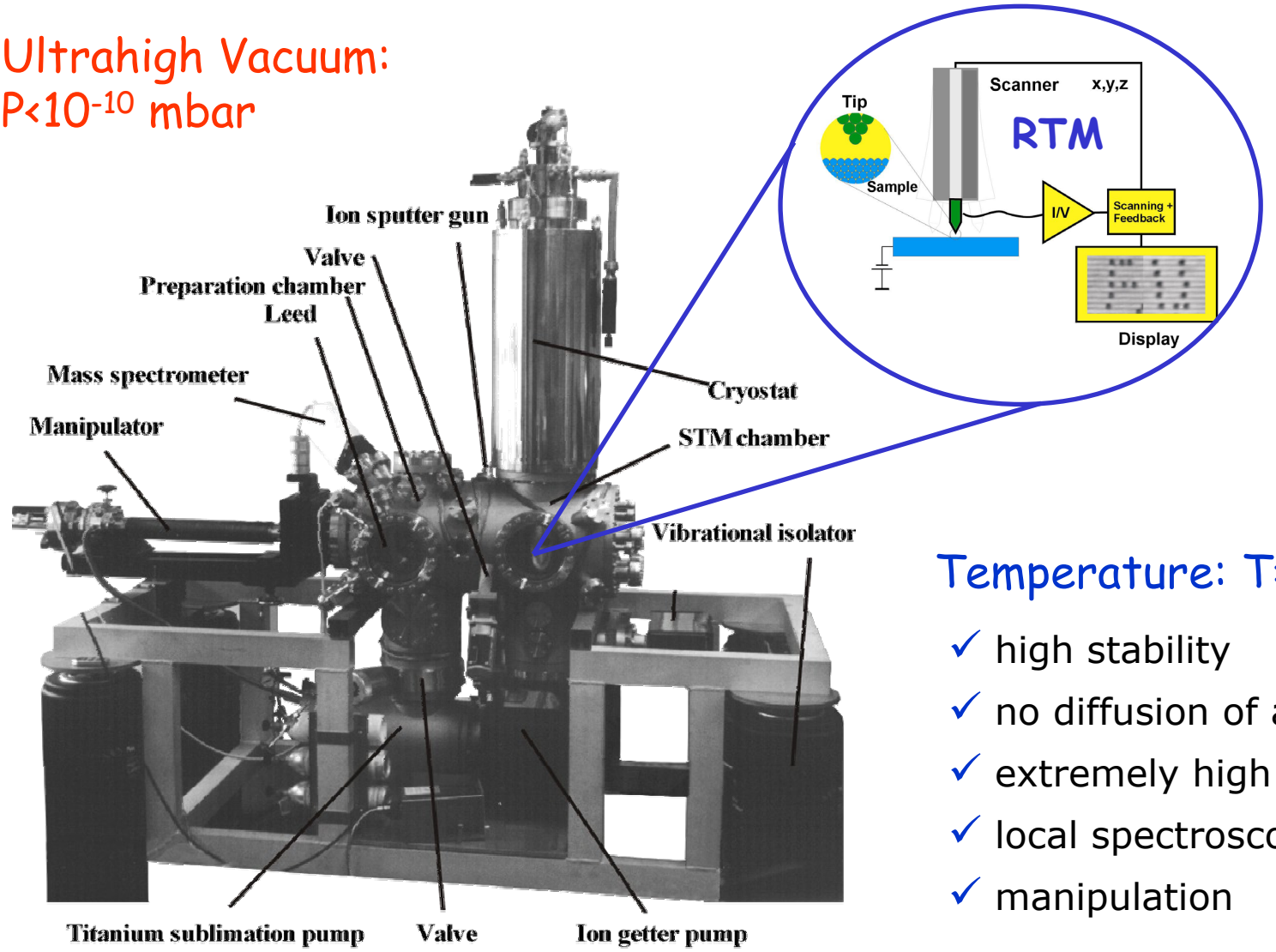
atomic resolution

$$I \propto \rho_s(\vec{r}_t, E_F)$$

local density of states (LDOS)

Low temperature STM

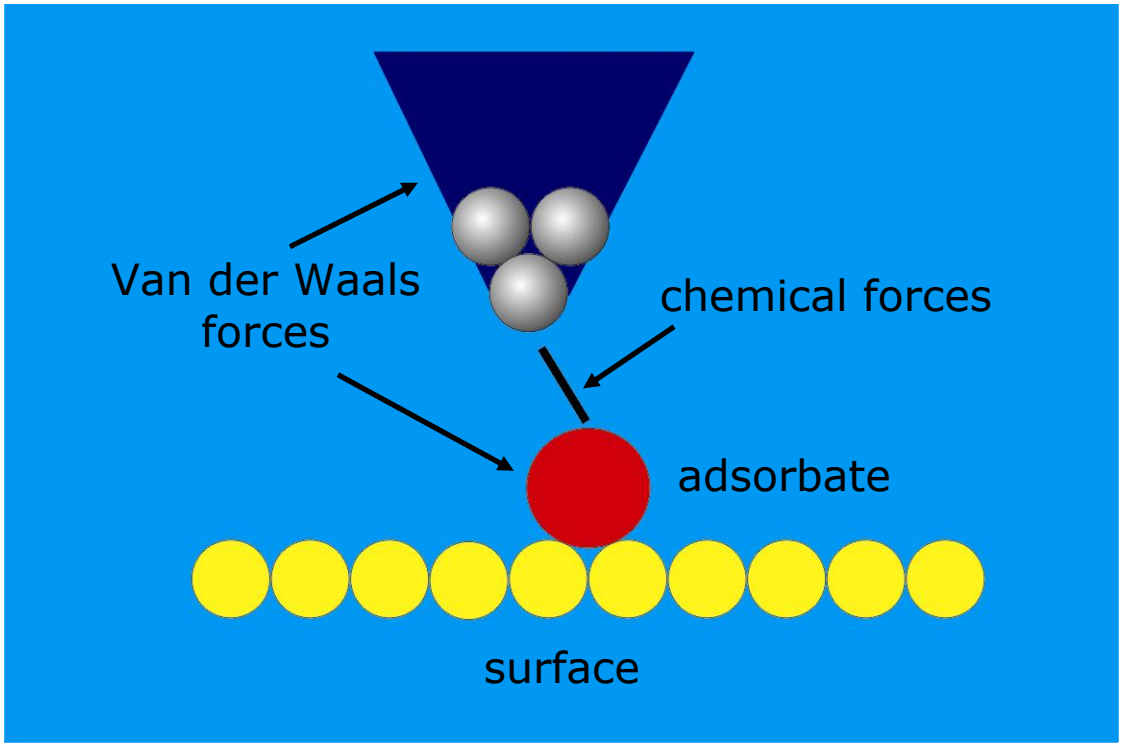
Ultrahigh Vacuum:
$P<10^{-10}$ mbar



Temperature: T=8 K

- ✓ high stability
- ✓ no diffusion of adsorbates
- ✓ extremely high vacuum
- ✓ local spectroscopy
- ✓ manipulation

Manipulation with the STM tip



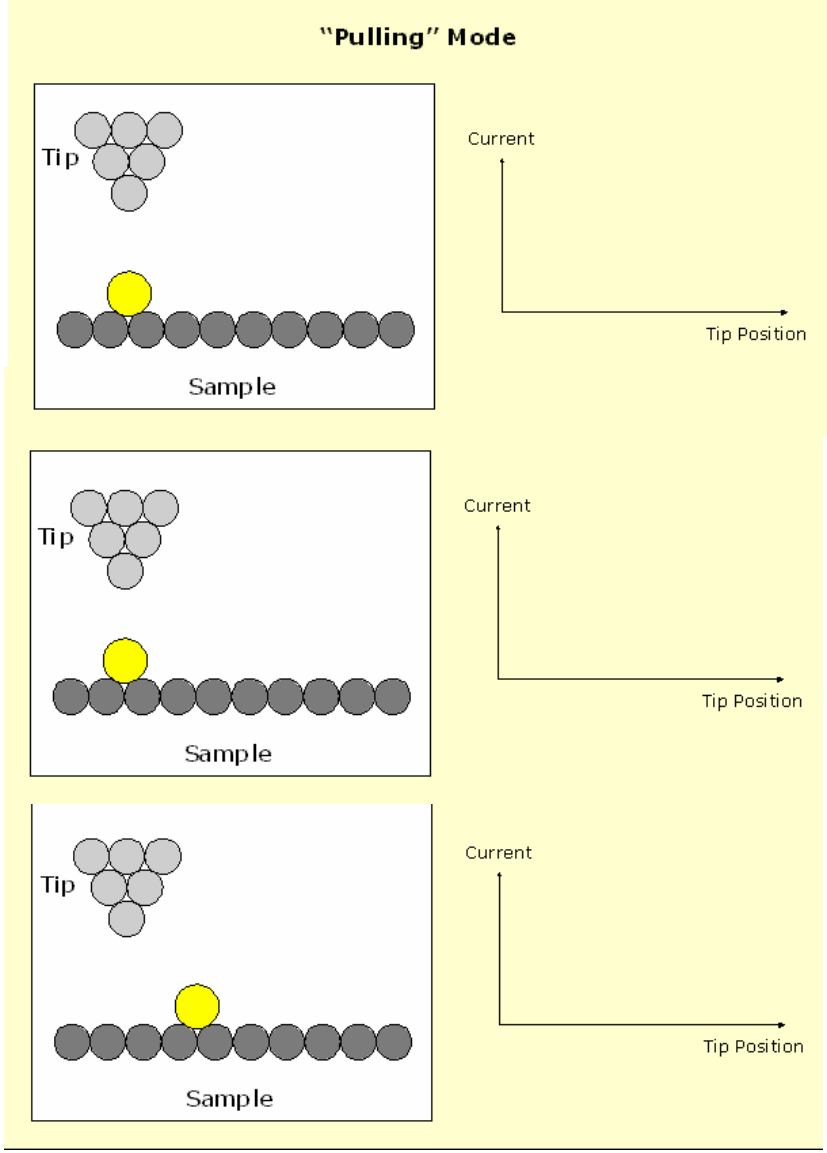
Lateral Manipulation:

The adsorbate moves without loosing the contact to the surface

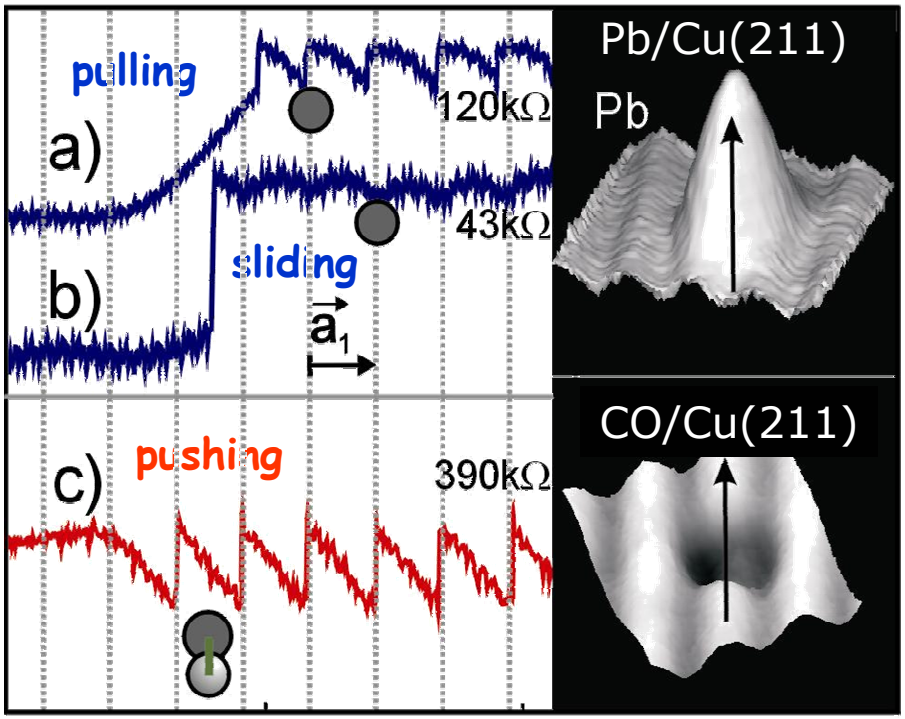
Vertical Manipulation:

The adsorbate is picked up and deposited elsewhere

Lateral Manipulation



How does the tip moves the particles?



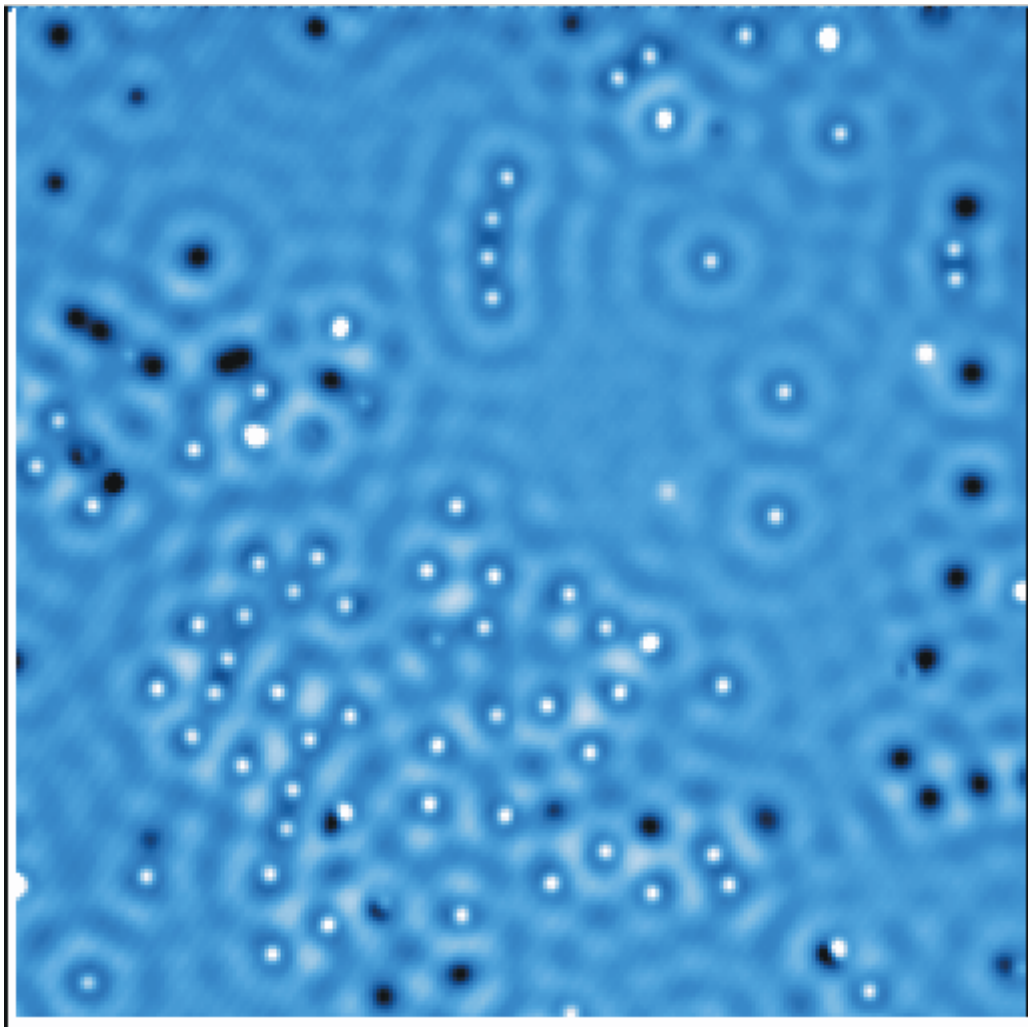
L. Bartels, G. Meyer, K.H. Rieder, Phys. Rev. Lett. 79, 697 (1997)

Signal recorded during the manipulation

Nanostructures

"Quantum Corral" of Ag Atoms

Ag(111)

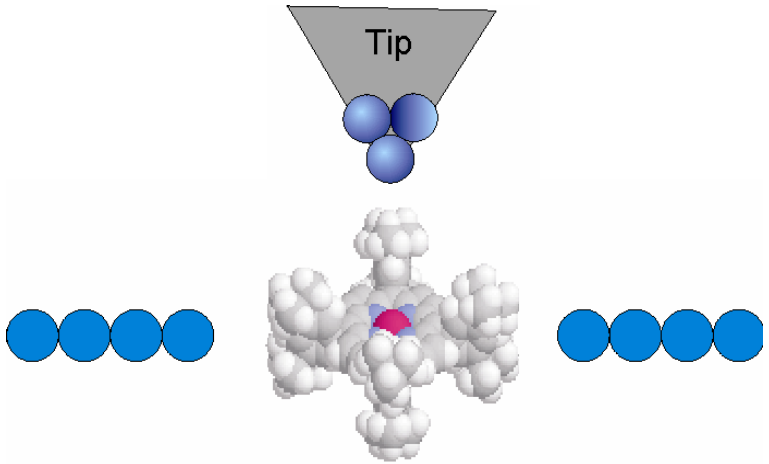


Kai-Felix Braun, FU Berlin

Standing waves of the electrons in the surface state

Manipulation of complex molecules

Application of the single atom manipulation techniques to large specially designed molecules

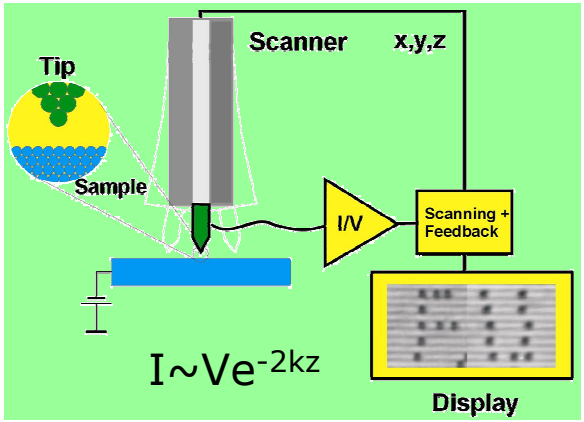


Controlled modification of the electronic properties of a molecule

Contact between a molecule and a metallic electrode

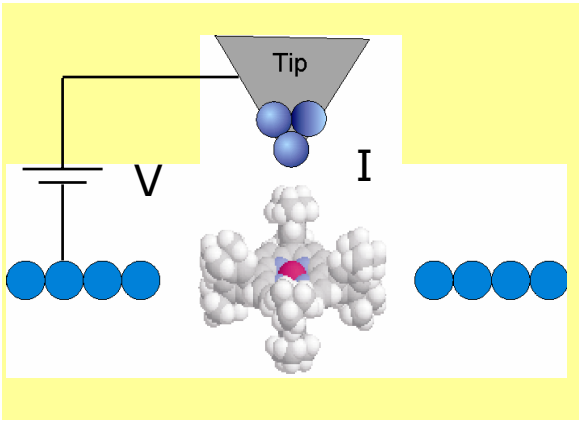
→ Molecular Electronics

LT-STM: from imaging to manipulation



Imaging

- Atomic resolution
- Control of the geometry of the system

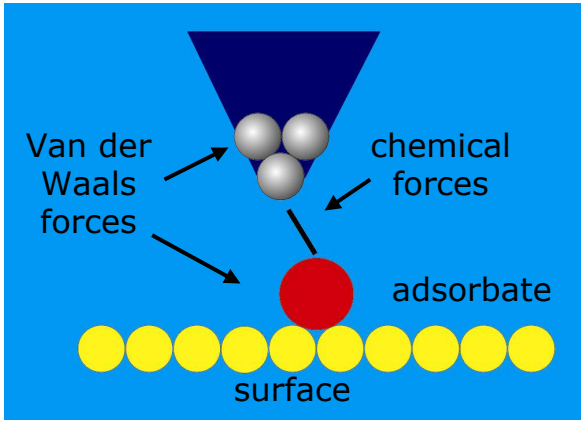


Current measurements

- Controlled 2-Terminal electron transport through a molecule

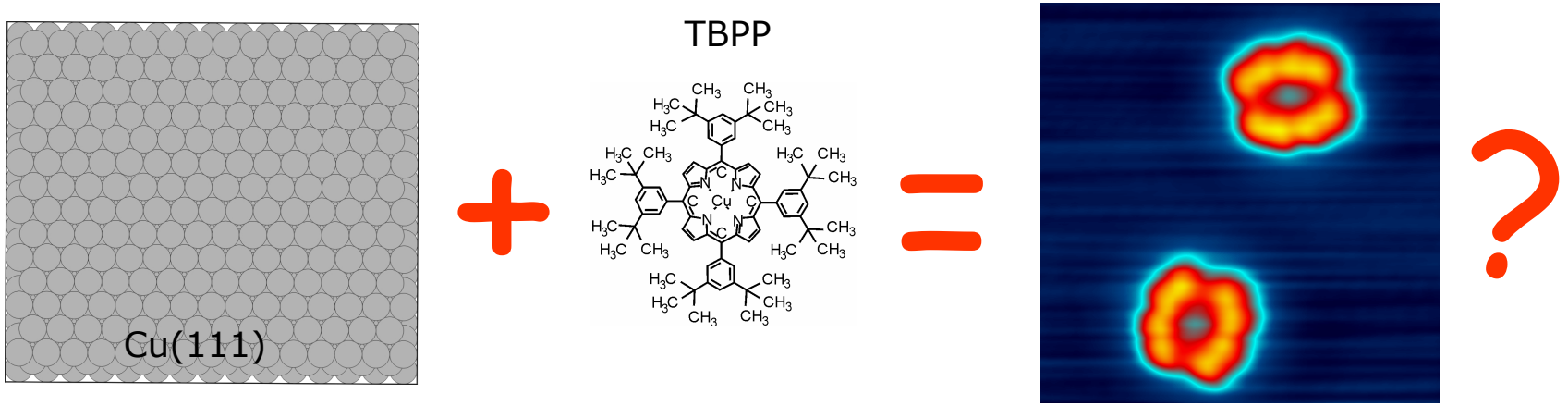
Manipulation

- Mechanics of a molecule on a surface
- Induce conformational changes



Interpretation of STM images

Which information can be extracted from the STM image of a molecule on a surface?



- ✓ The molecule perturbs the LDOS on the surface
- ✓ Characteristic local tunneling footprint of the molecule

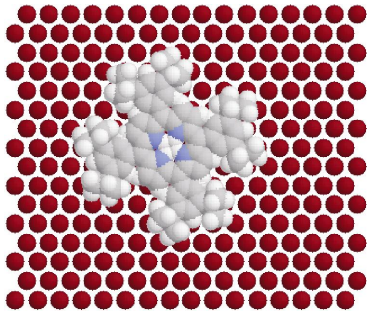
Adsorption geometry?

Conformation?

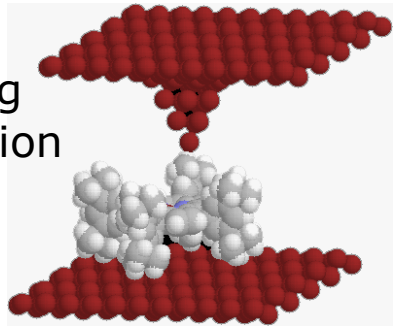
MM-ESQC

Elastic Scattering Quantum Chemistry (C. Joachim, Toulouse)

Molecular Mechanics:
Optimization of the molecular deformation on the surface

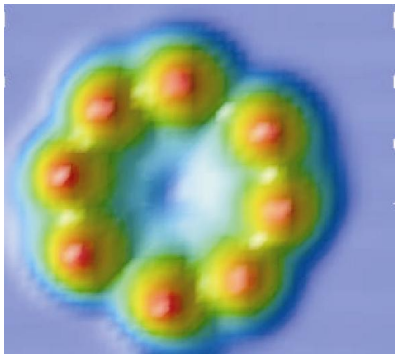


ESQC:
Calculation of the full scattering matrix of the STM tunnel junction over the entire molecule

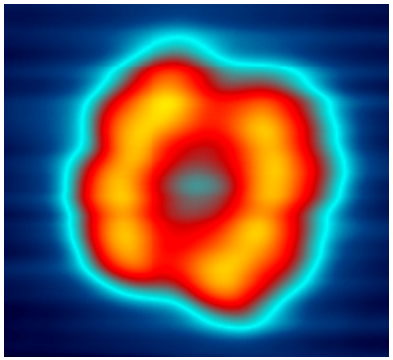


- Images
- Electronic properties
- Conformational changes

Calculation of the STM image

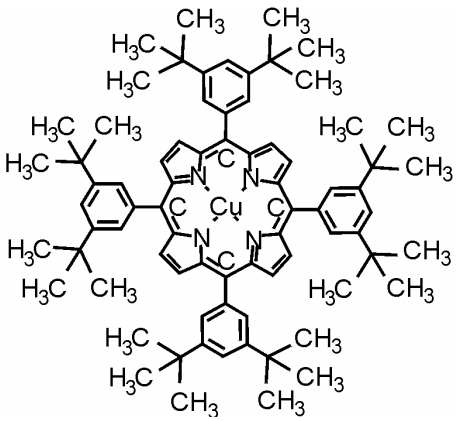


Comparison with the experimental image



Molecular switch

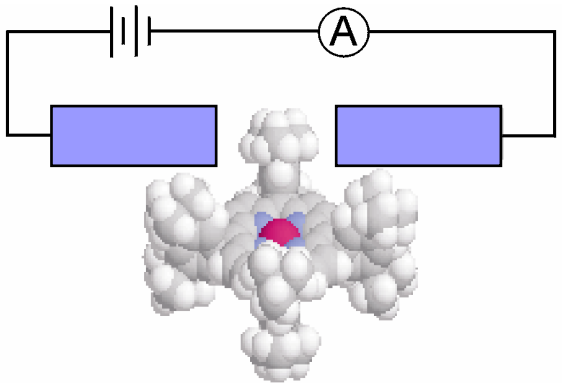
Cu-tetra-3.5-di-ter-buthyl-phenyl-porphyrin



TBPP

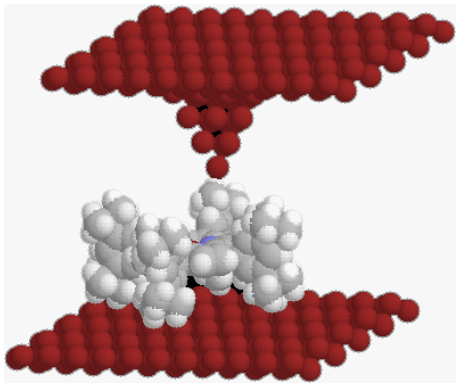
- In the gas phase the TBP-groups are perpendicular to the porphyrin ring
- The lateral groups can rotate

Idea:



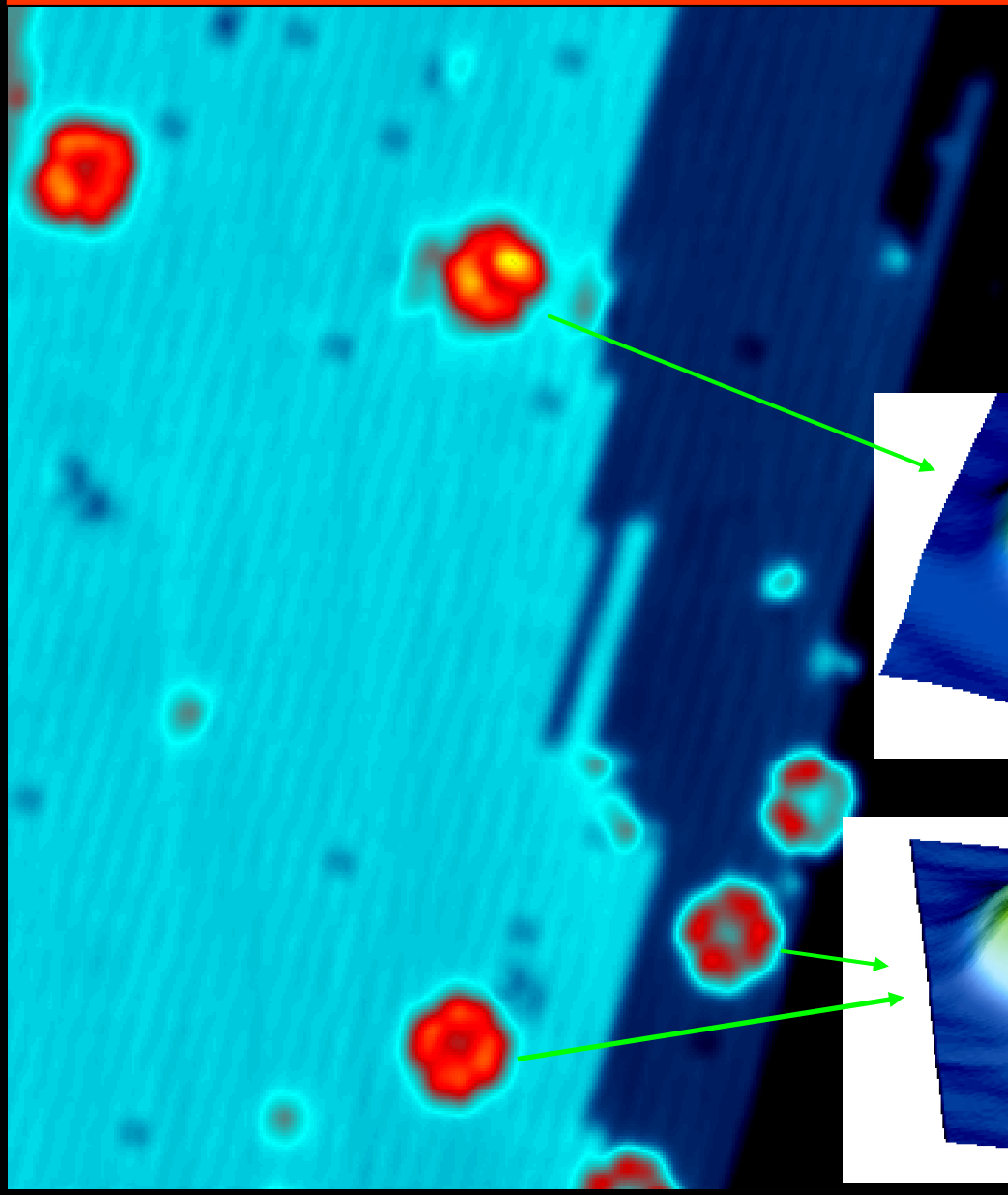
... by the rotation of a leg

Experiment:

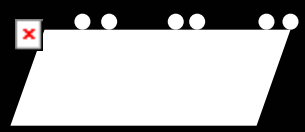


... under the tip of an STM

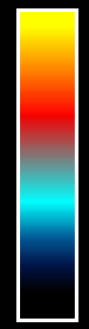
TBPP on Cu(211)



Cu (211)

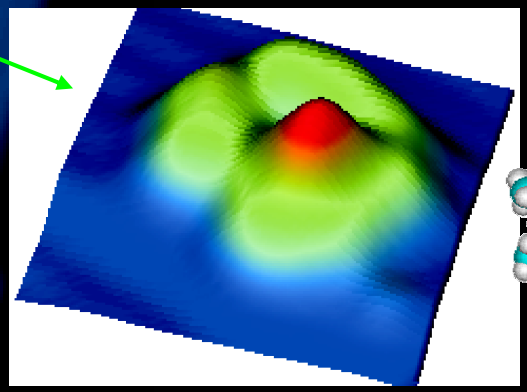


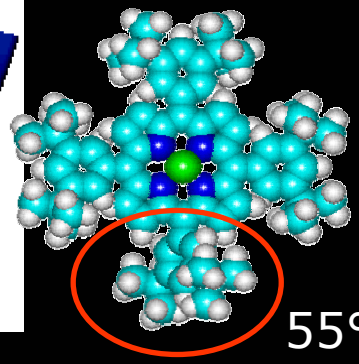
(111) facets + (100) steps



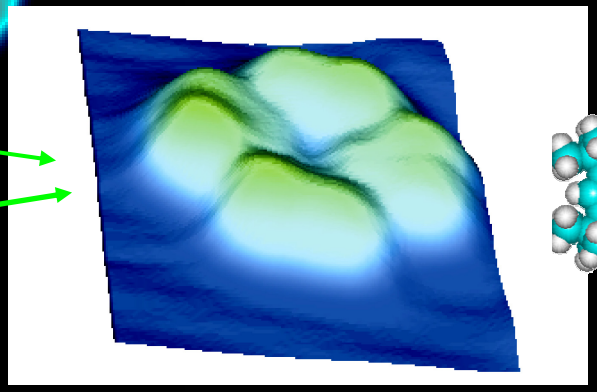
1.8 nm

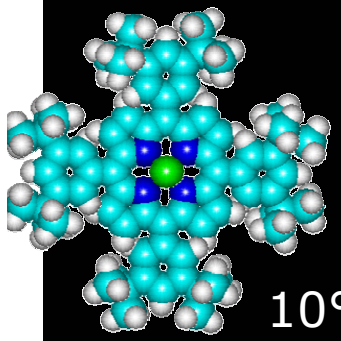
0 nm





55°





10°

Manipulation of a leg

Lateral Manipulation

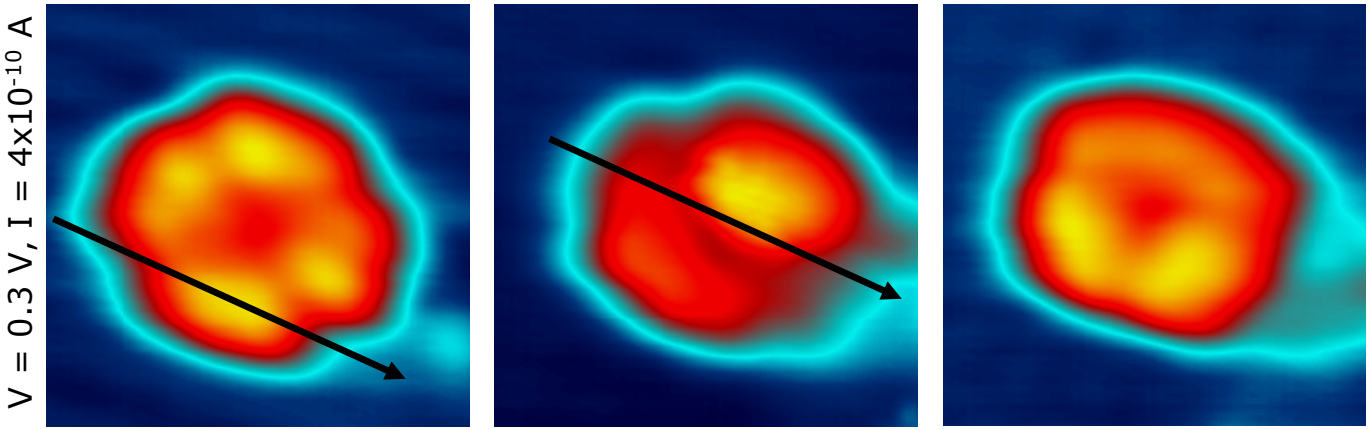


Image:
R = 7.5 x 10^8 Ω

Manipulation:
R = 6 x 10^4 Ω

Vertical Manipulation

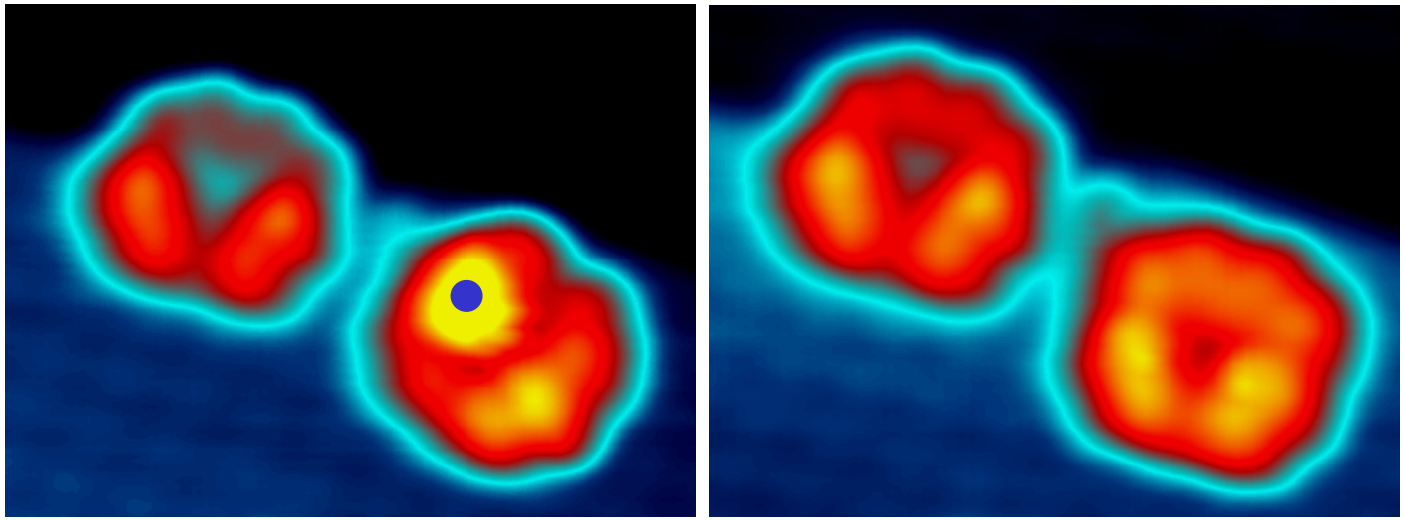
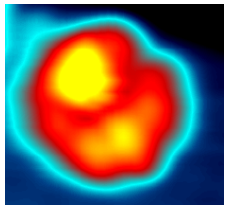


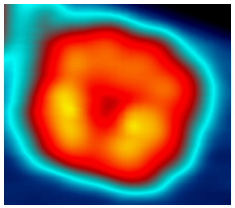
Image:
z_o = 0.75 nm

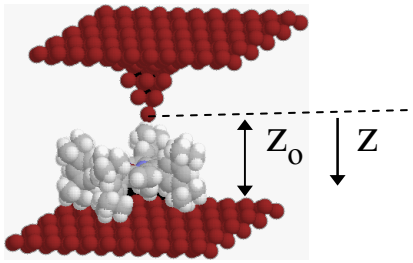
Manipulation:
Δz = 0.45 nm

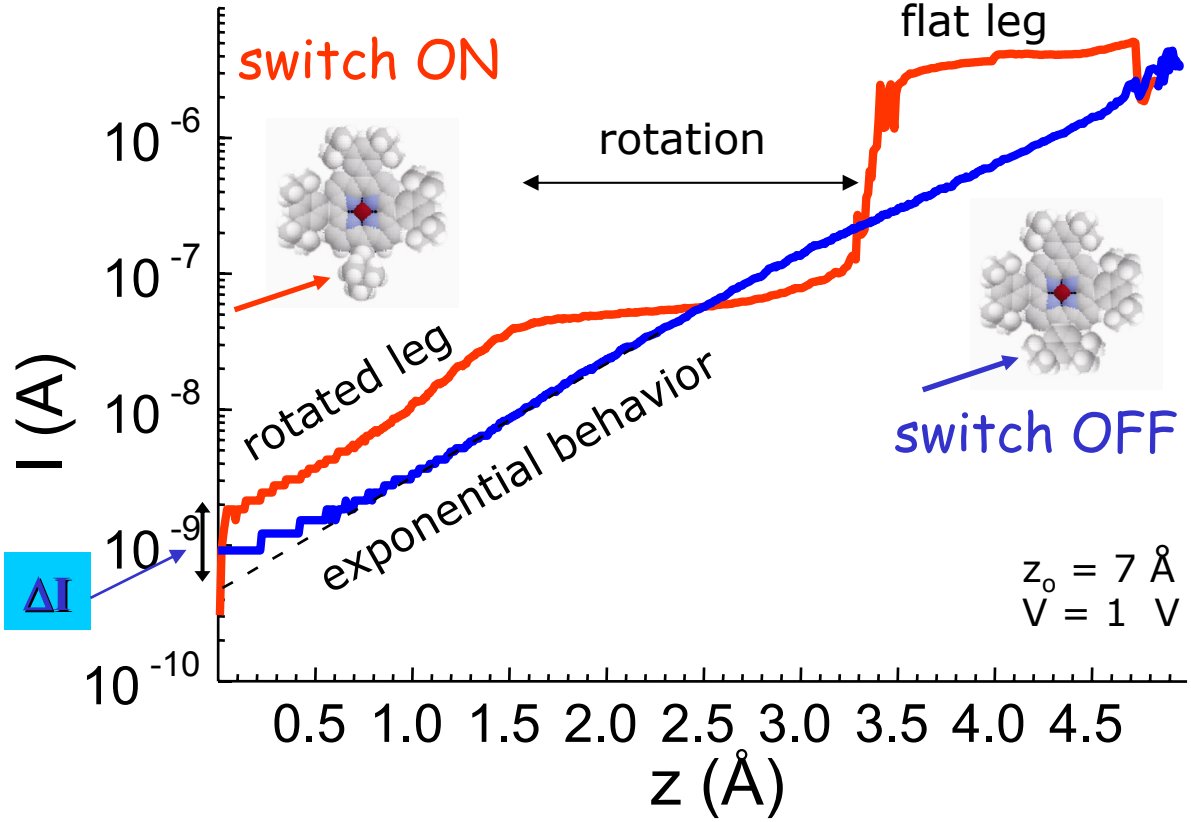
I(z) by switching

vertical manipulation



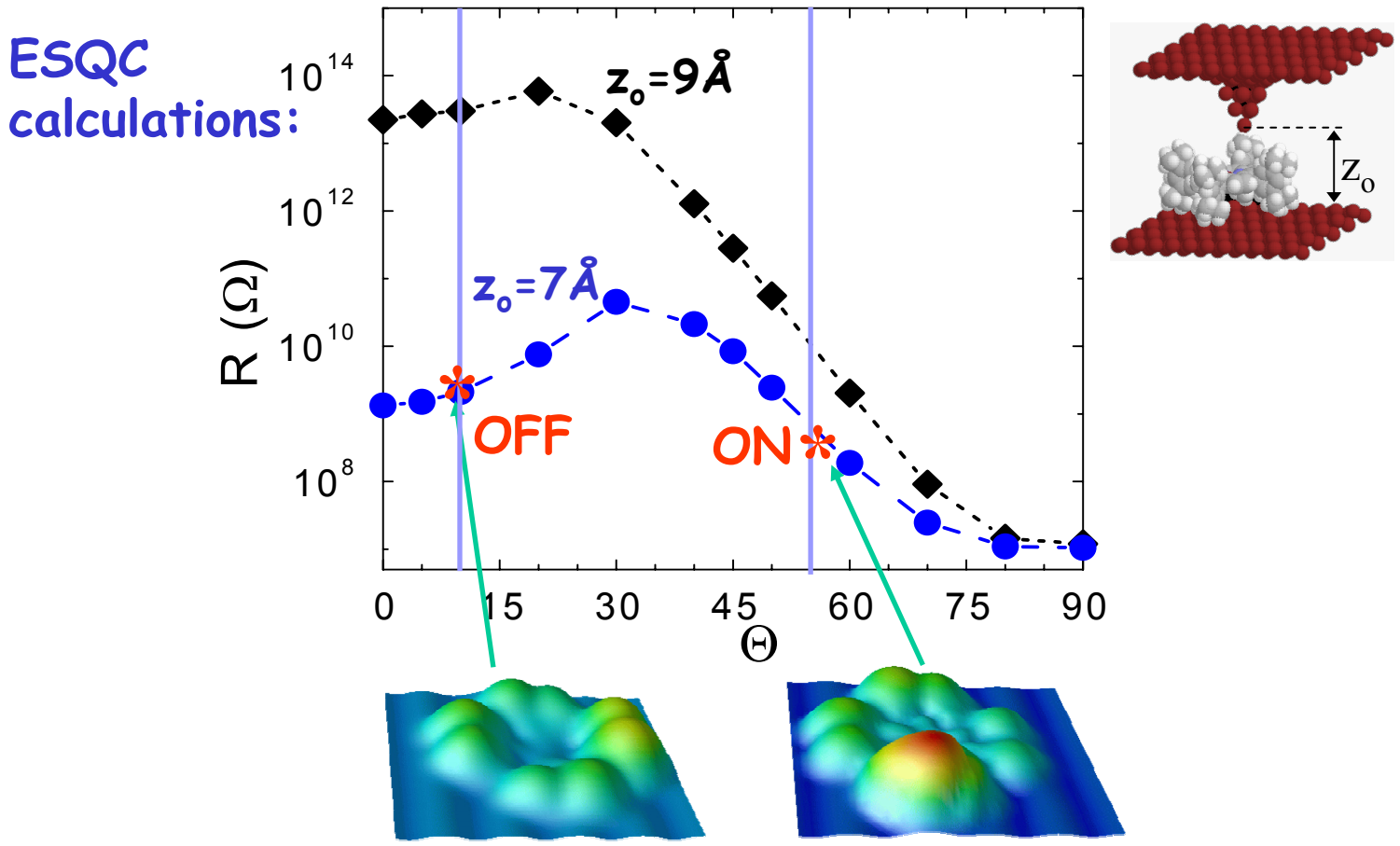






Molecular switch: Theory

Resistance versus leg's orientation

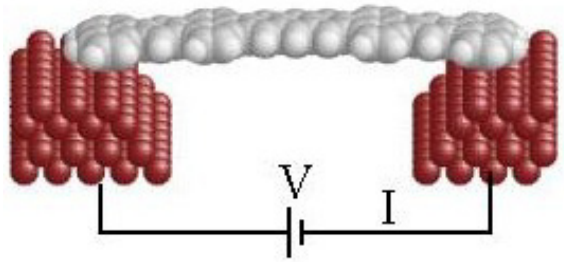


F. Moresco, G. Meyer, K.H. Rieder, H. Tang, A. Gourdon, C. Joachim, Phys. Rev. Lett. 86, 672 (2001)

Contacting a single molecule

Problem:

Electronic properties of the contact between an isolated molecule and metallic electrodes



Previous results:

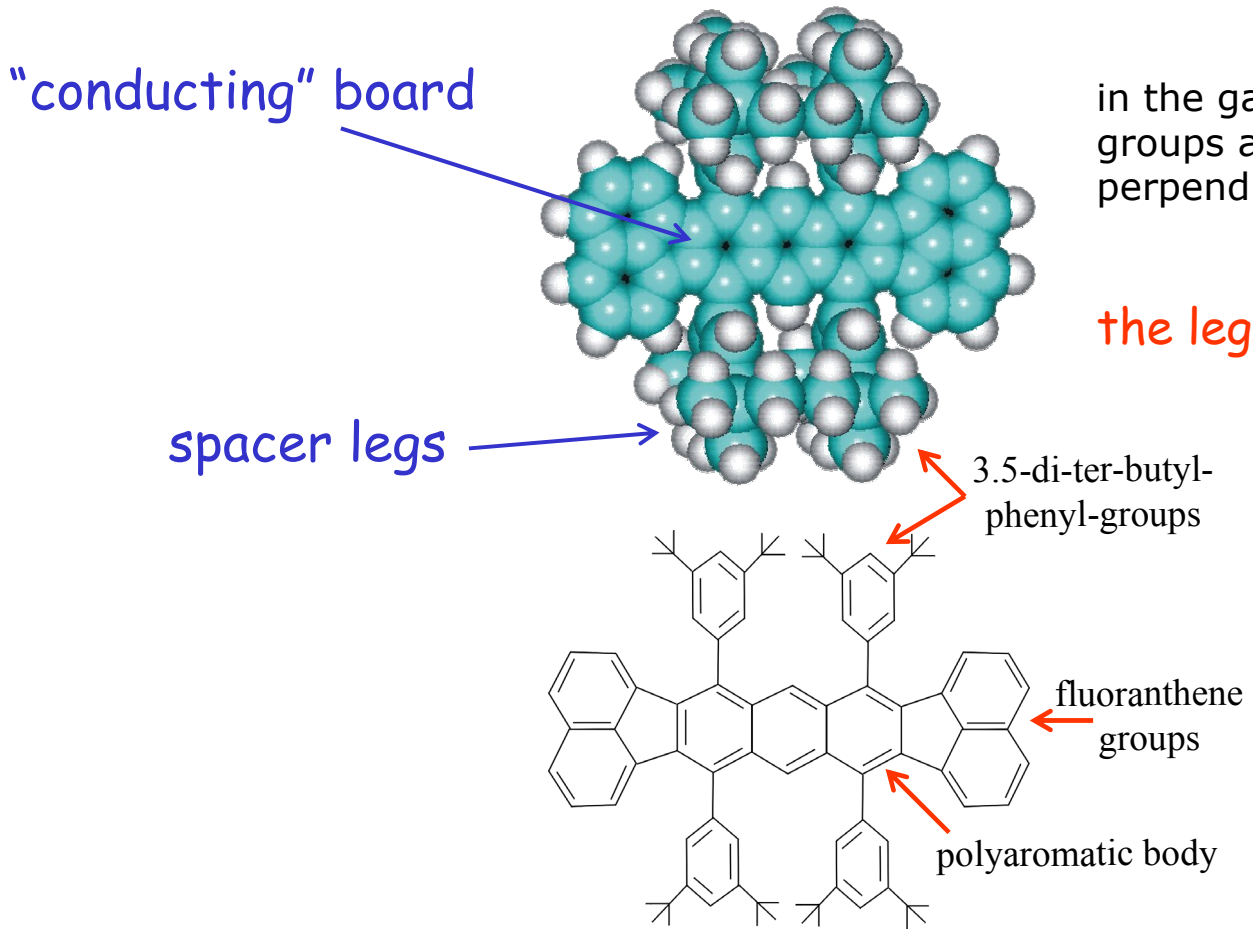
- ✓ Ensemble of molecules
- ✓ Break junction measurements
- ✓ Calculations: electron transport in junctions

LT-STM:

- ✓ Individual molecules
- ✓ Atomic control of the geometry of the system
- ✓ Manipulation

→ Special molecules, which can be connected with a metallic electrode in a planar way.
Suitable metallic electrodes: step edges or nanostructures.

Lander ($C_{90}H_{98}$)



in the gas phase the lateral groups are oriented perpendicular to the board

the legs can rotate

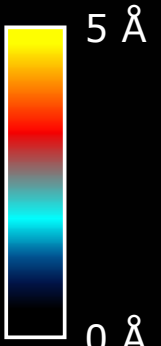
model system for a molecular wire on a metallic surface

A. Gourdon Eur. J. org. Chem. 1998, 391 (1999)

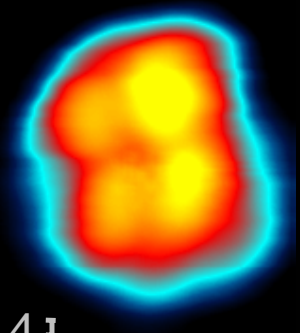
Lander/Cu(111) terraces

2 different configurations

During deposition: T_{sample}<80 K

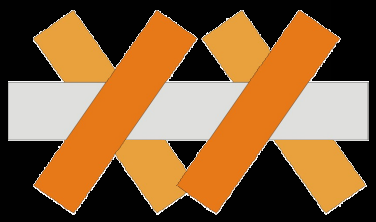


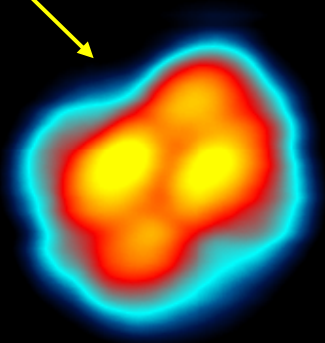
The board is not visible, but is always oriented parallel to the legs with the shorter distance

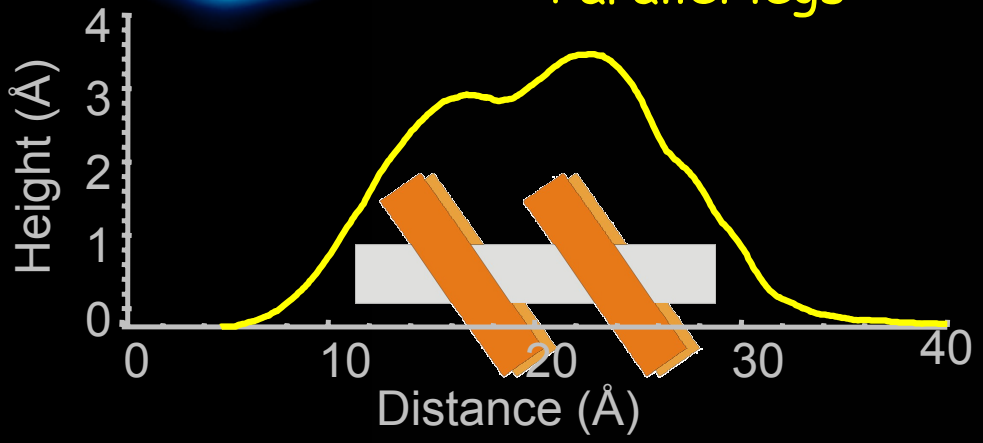


Parallel legs

Crossed legs







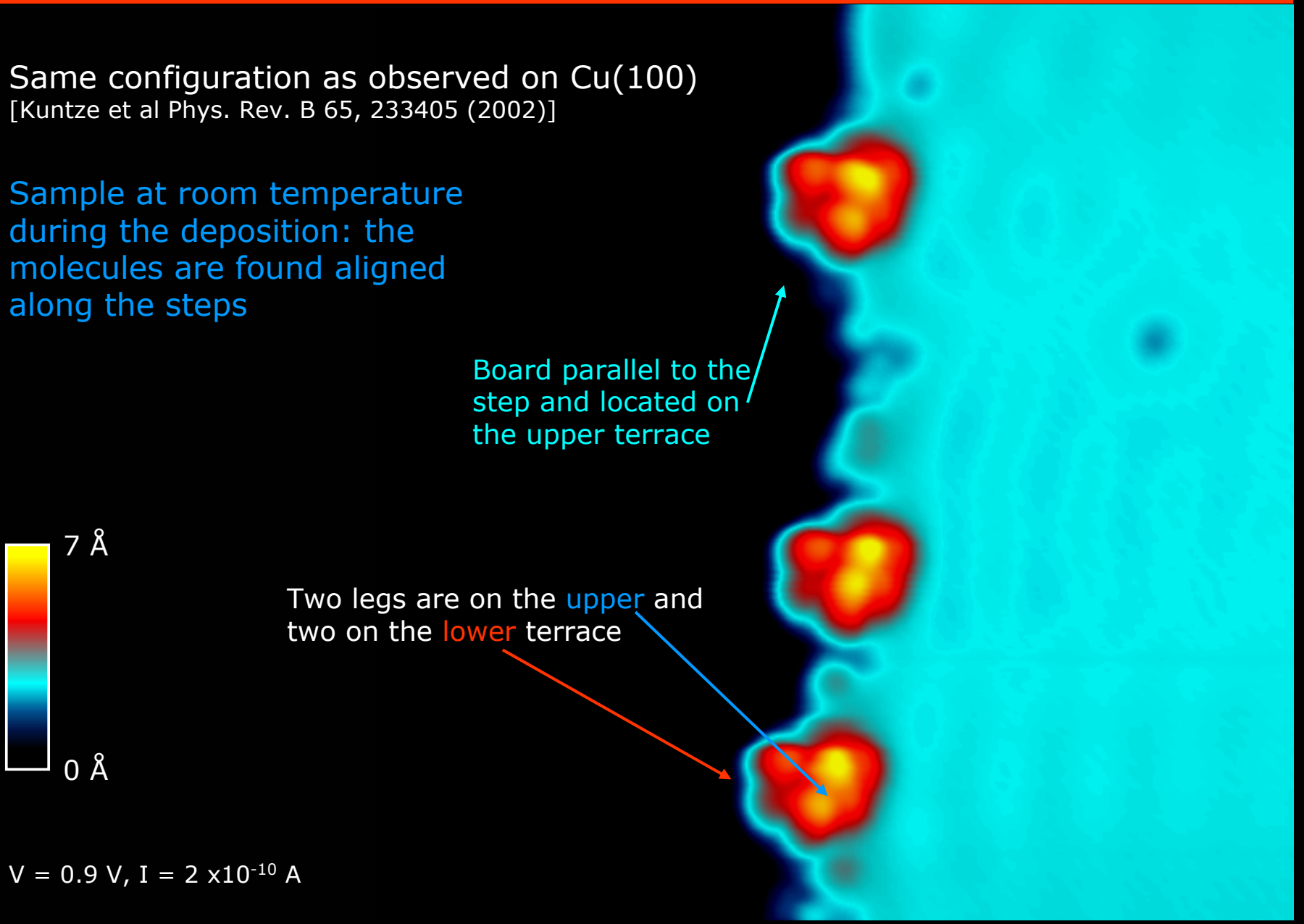
Rosei et al. Science 296, 328 (2002)
Kuntze et al Phys. Rev. B 65, 233405 (2002)

V = 0.9 V, I = 2 x10^{-10} A, T = 8K

Lander/Cu(111) step edges

Same configuration as observed on Cu(100)
[Kuntze et al Phys. Rev. B 65, 233405 (2002)]

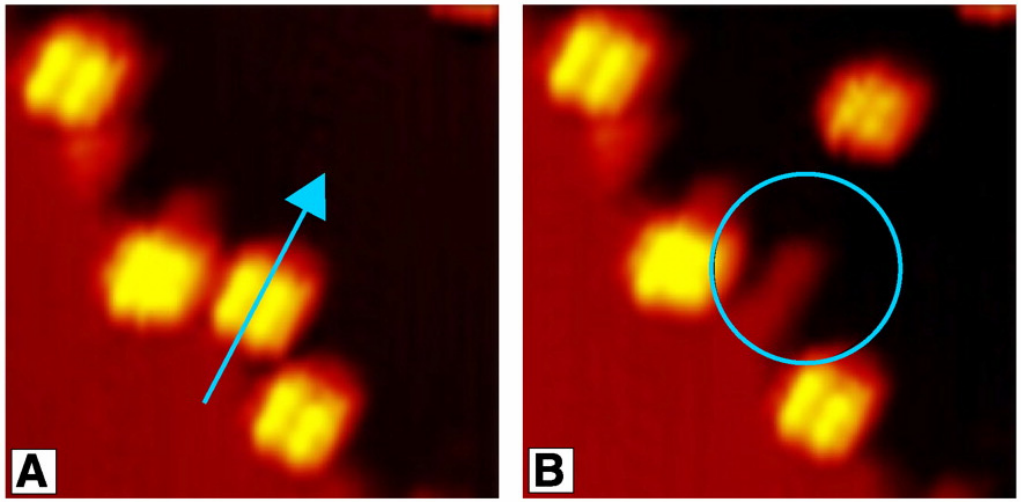
Sample at room temperature during the deposition: the molecules are found aligned along the steps



V = 0.9 V, I = 2 x10^{-10} A

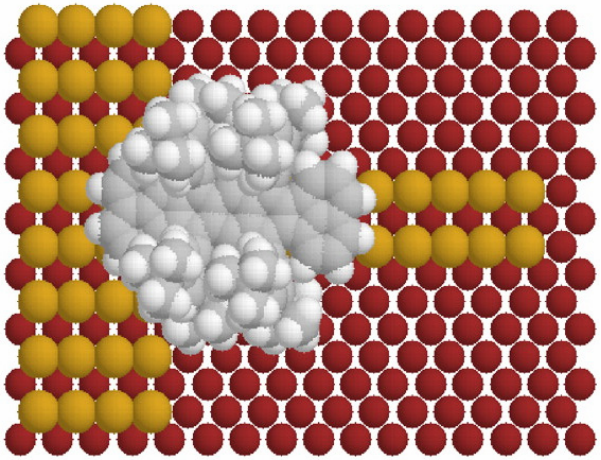
Cu(110):Formation of Nanostructures

Lander/Cu(110)



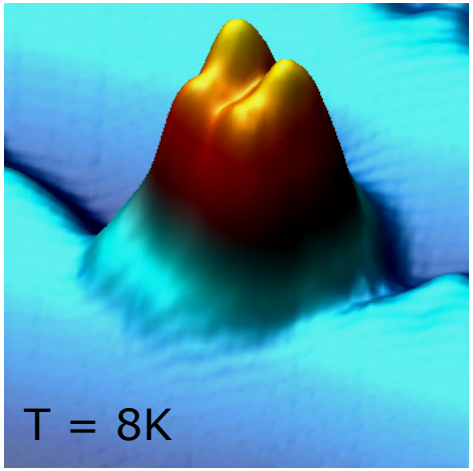
F. Rosei et al. Science 296, 328 (2002)

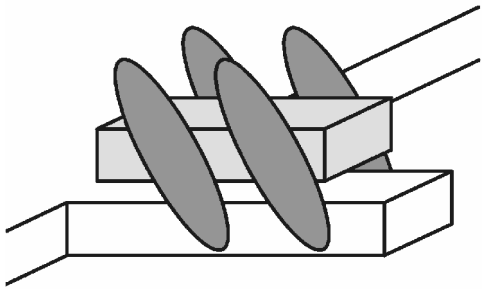
Adsorption of Lander molecules at Cu(110) step edges



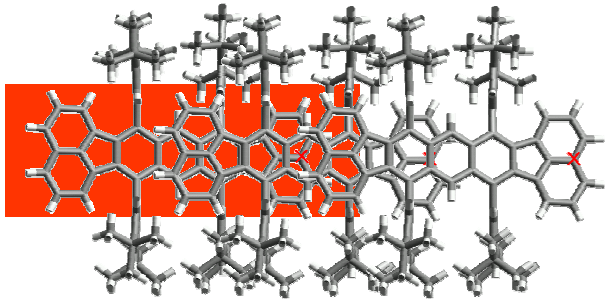
Selective Adsorption
Surface Restructuring

2-atoms wide rows

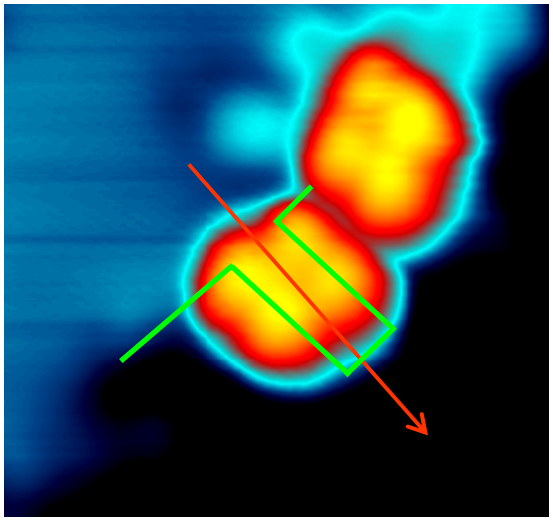


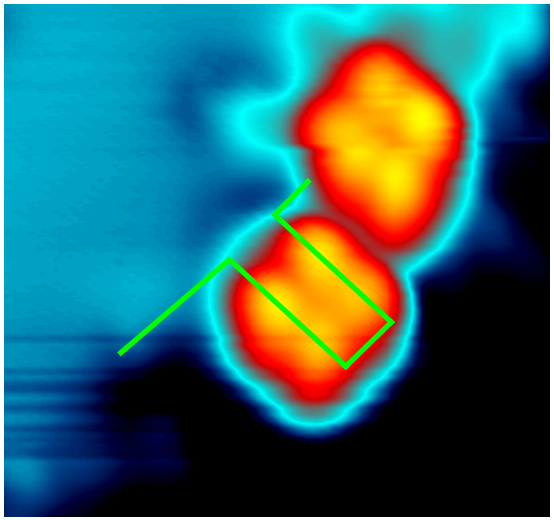


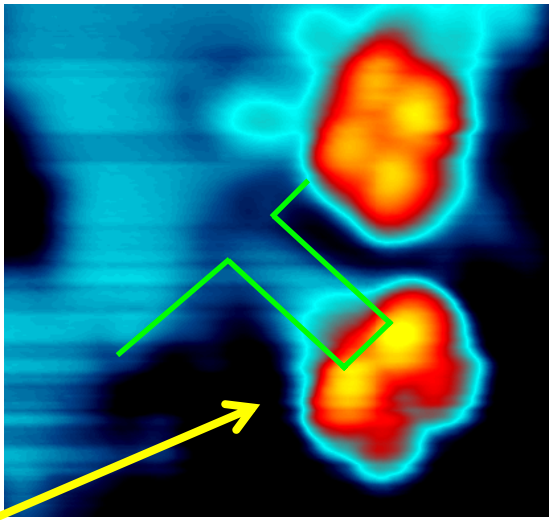
Idea:
Manipulation to contact



Motion along the Cu-Wire

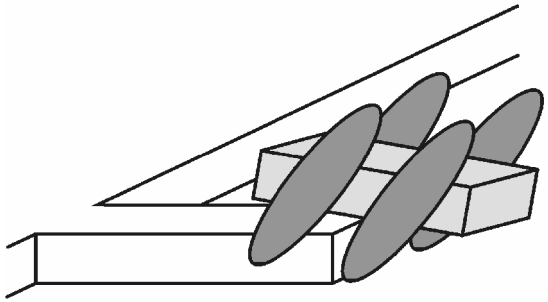


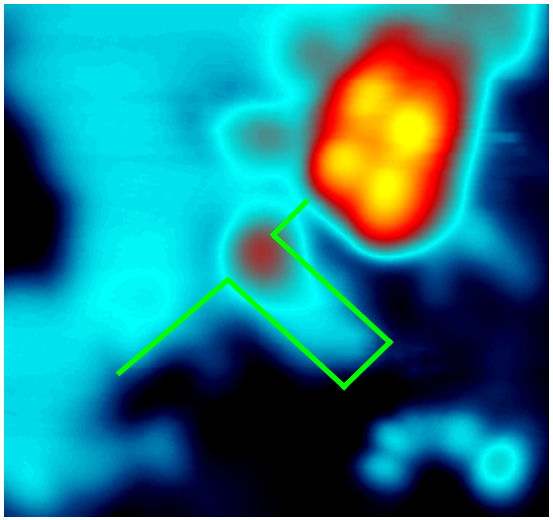




Manipulation: R=50 kΩ

The end naphthalene group is still in contact

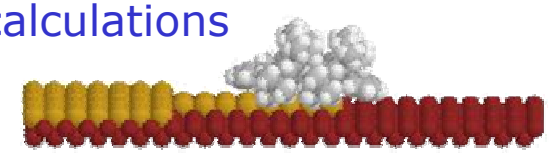


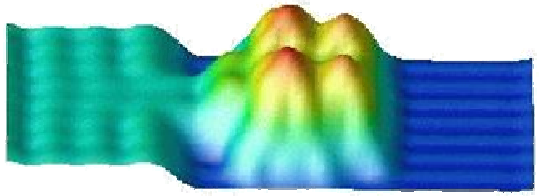


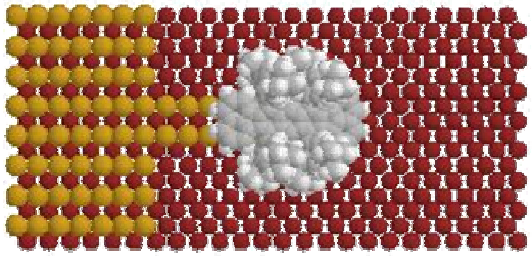
The molecular wire end is visible

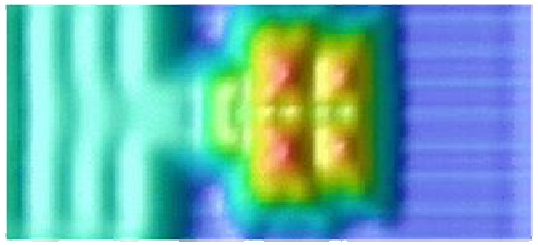
Contact position: theory

ESQC calculations



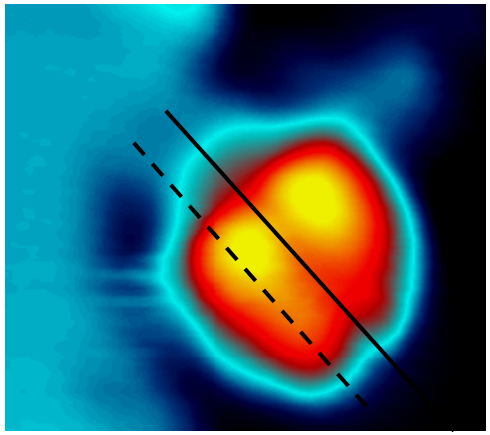


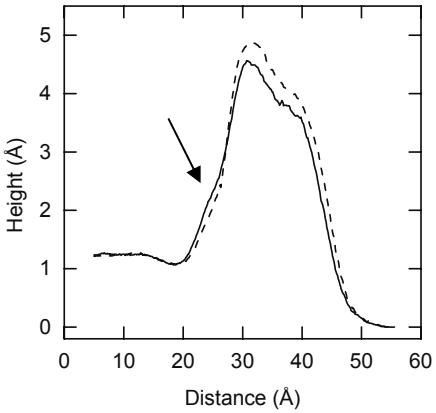




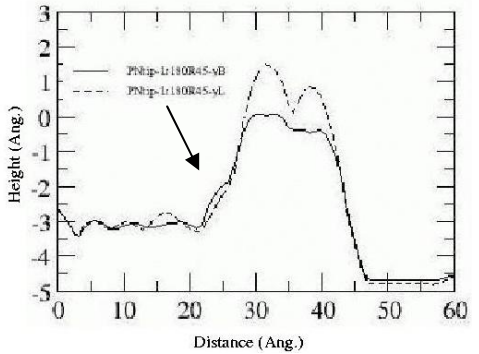
The contact point is visible

Experiment





Theory

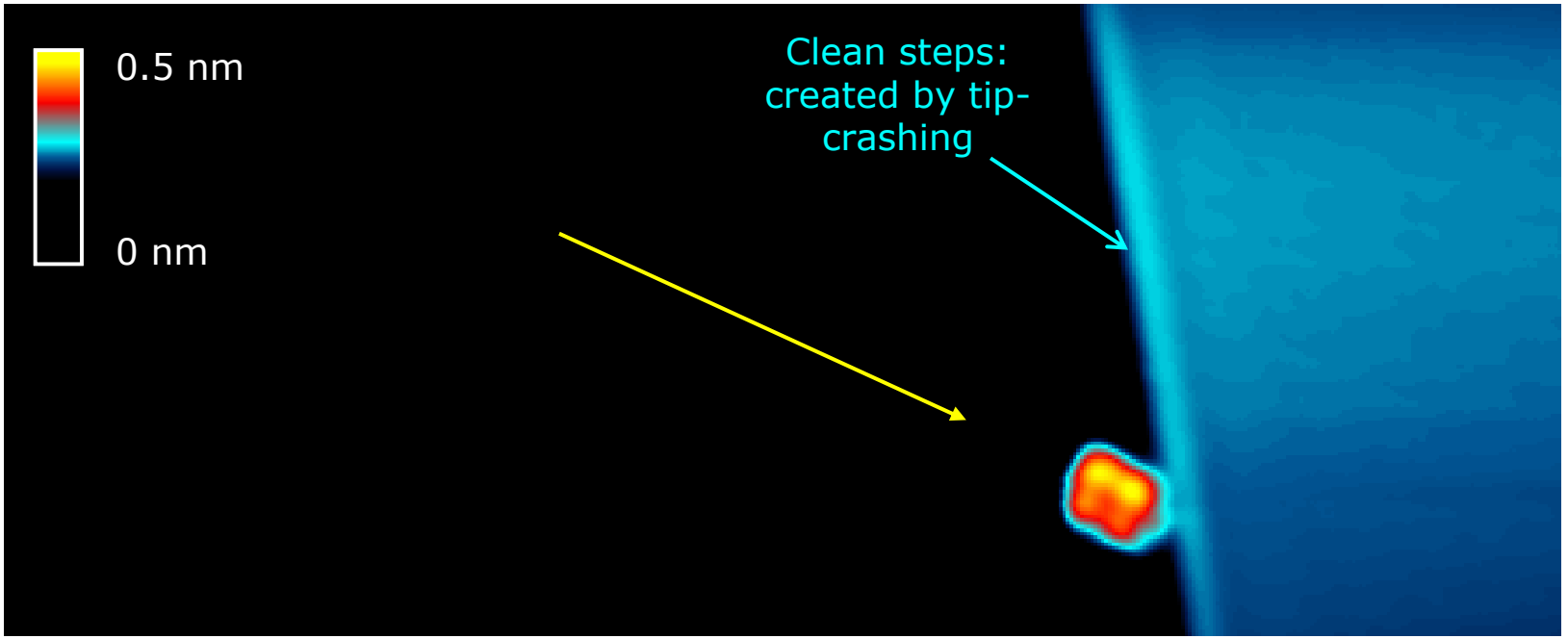


Apparent height of the contact: 20 pm

The complete wire is in electronic contact with the nanostructure.
The contact is visible only in this final position.

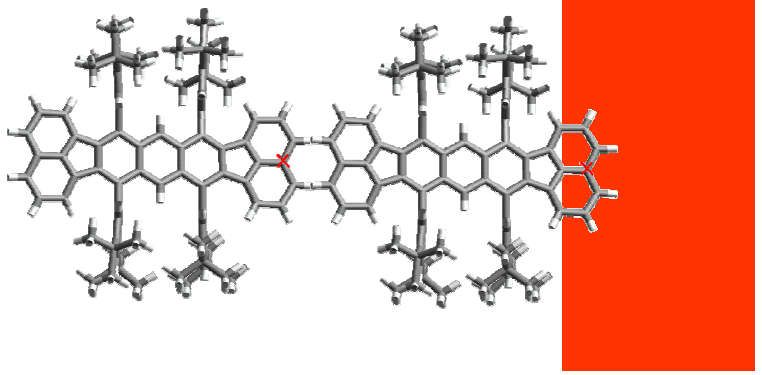
L. Grill, F. Moresco, P. Jiang, C. Joachim, A. Gourdon, K.-H. Rieder , Phys. Rev. B 69, 035416 (2004)

Contacting a Lander to a step edge: Cu(111)



Manipulation in constant height mode, z = 0.25 nm, image V = 0.8 V, I = 0.2 nA, T = 8 K

Lateral manipulation in the direction of a step



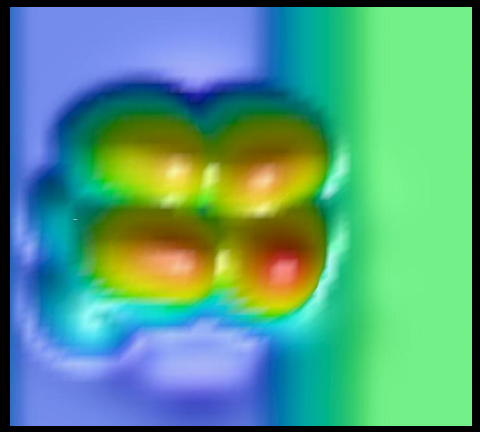
Connecting the legs to a step

The molecule can be manipulated to connect the legs to the step

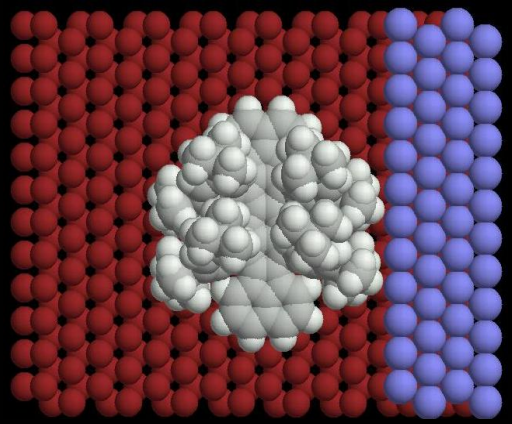
The board is parallel to the step edge

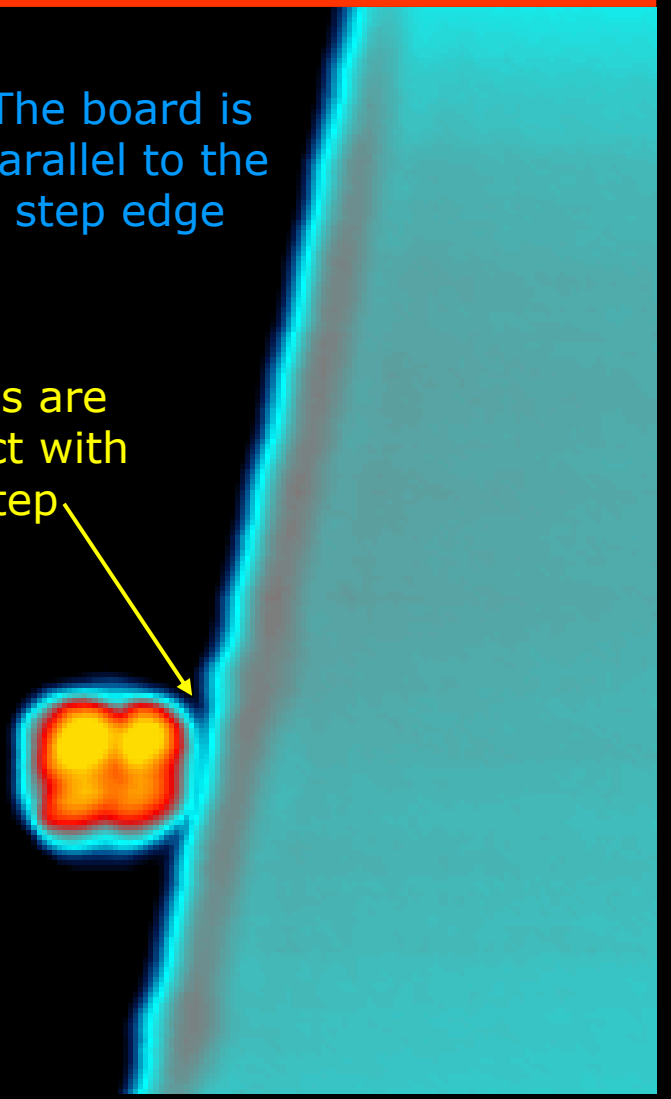
Two legs are in contact with the step

ESQC calculations



Model



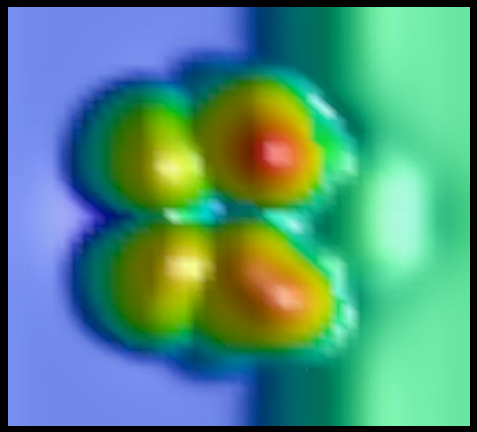


Contacting the board to the step

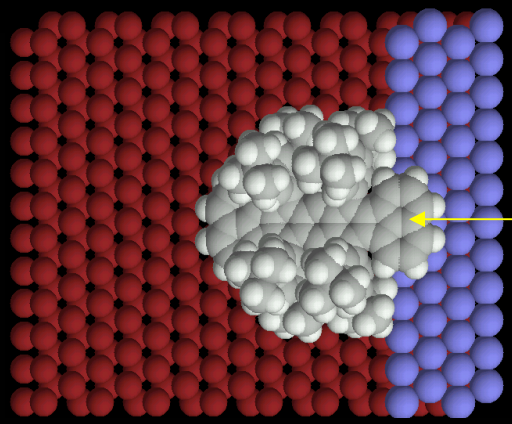
Contact position

Effect on the standing wave patterns

ESQC calculation

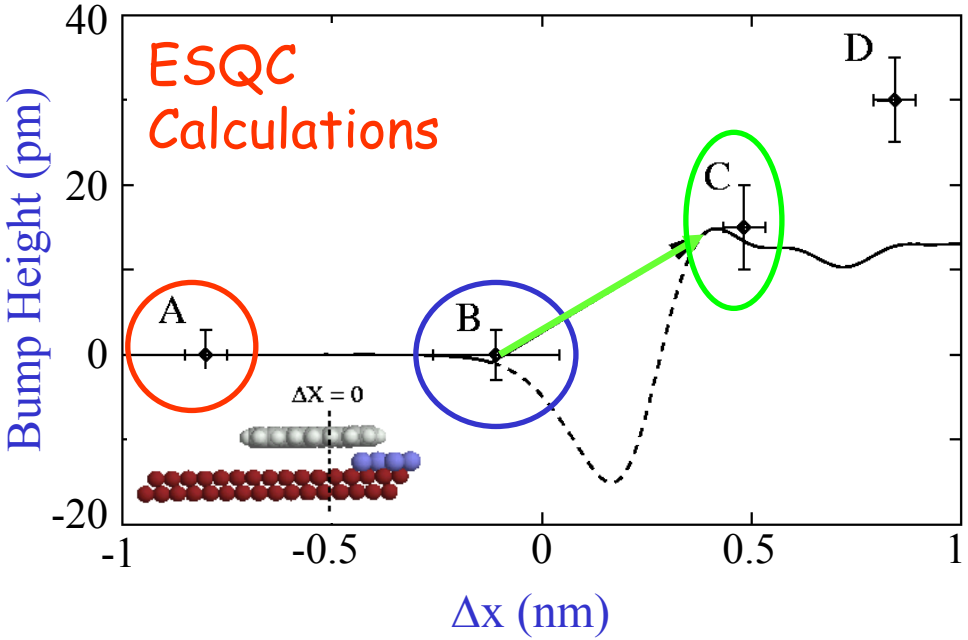


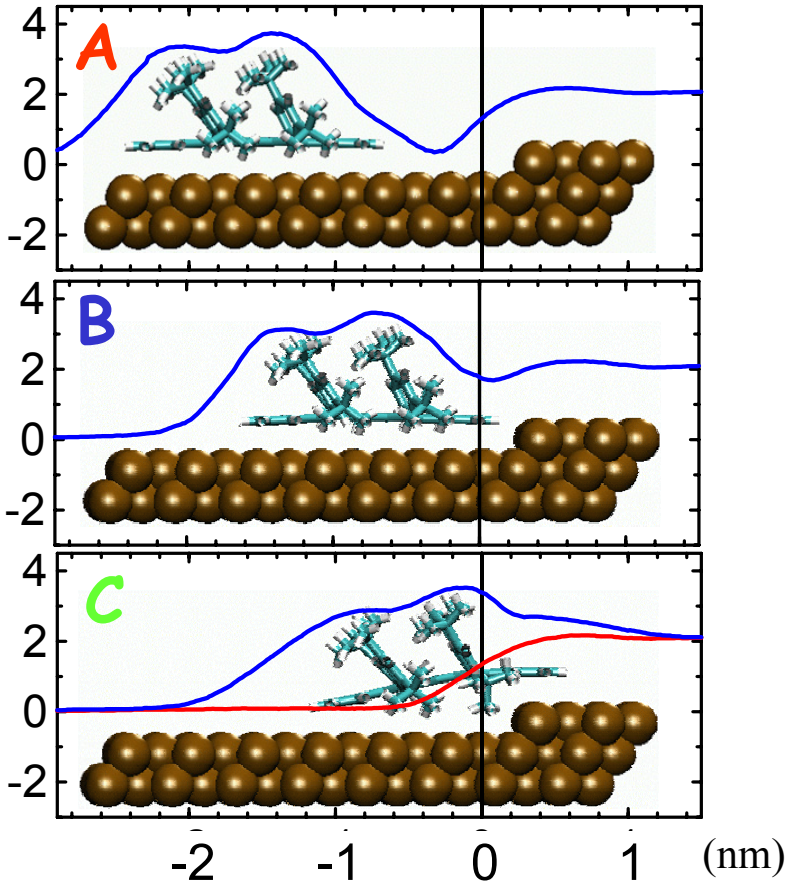
Model



The terminal naphthalene group of the wire is in contact with the step edge

The different stages of the contact

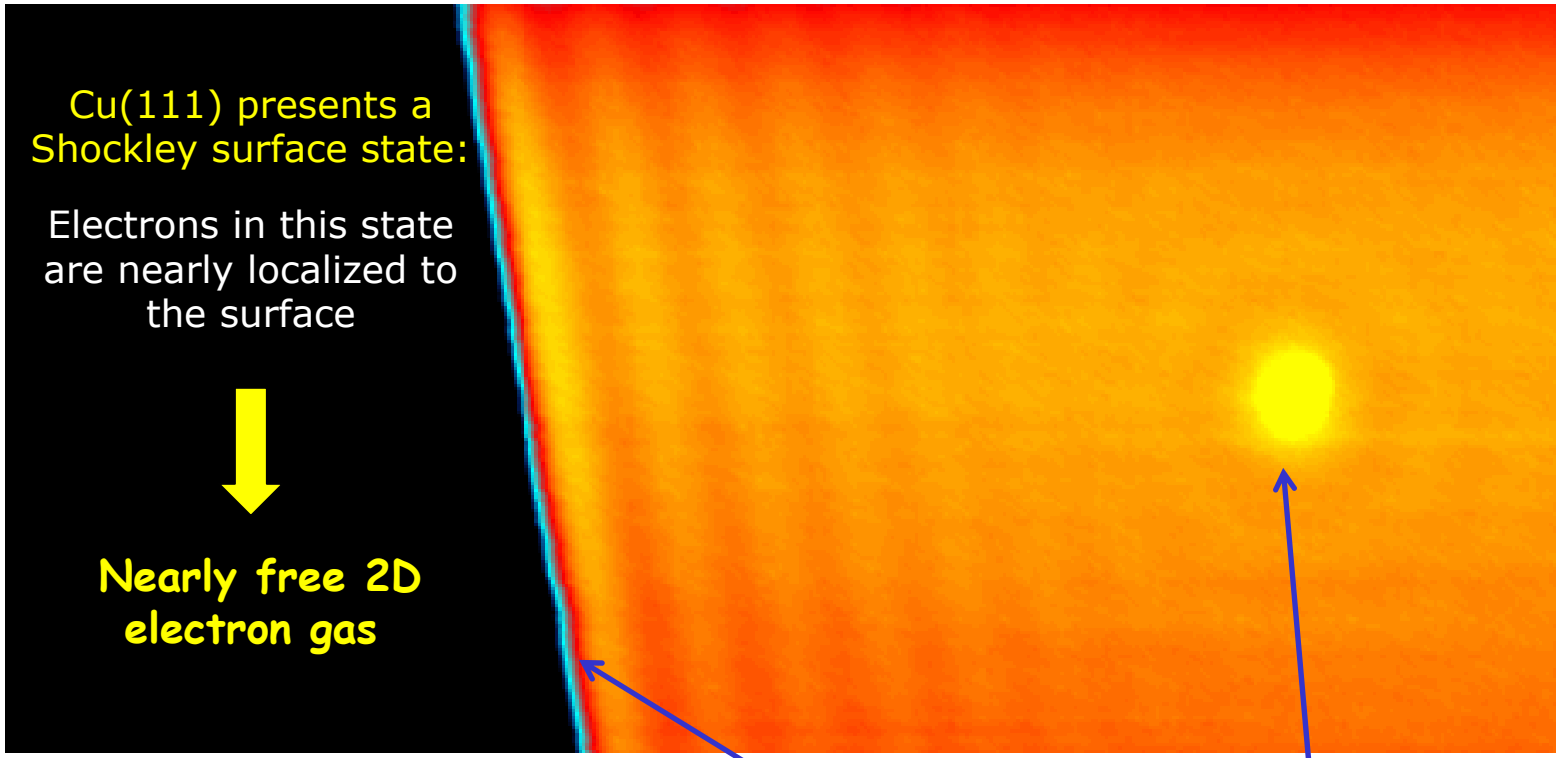




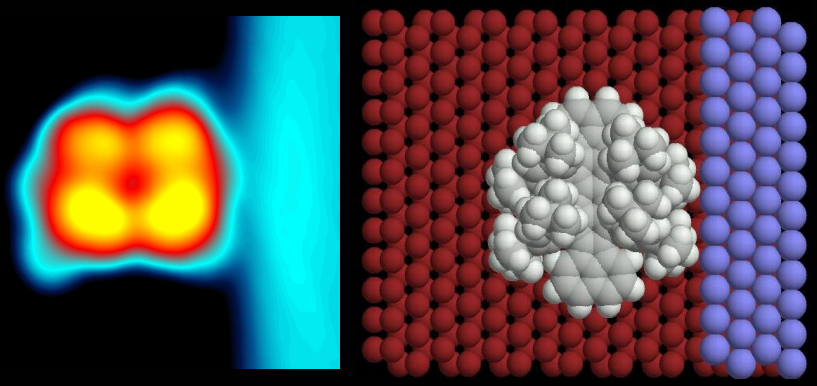
C: Electronic contact position. Maximum of the bump height.

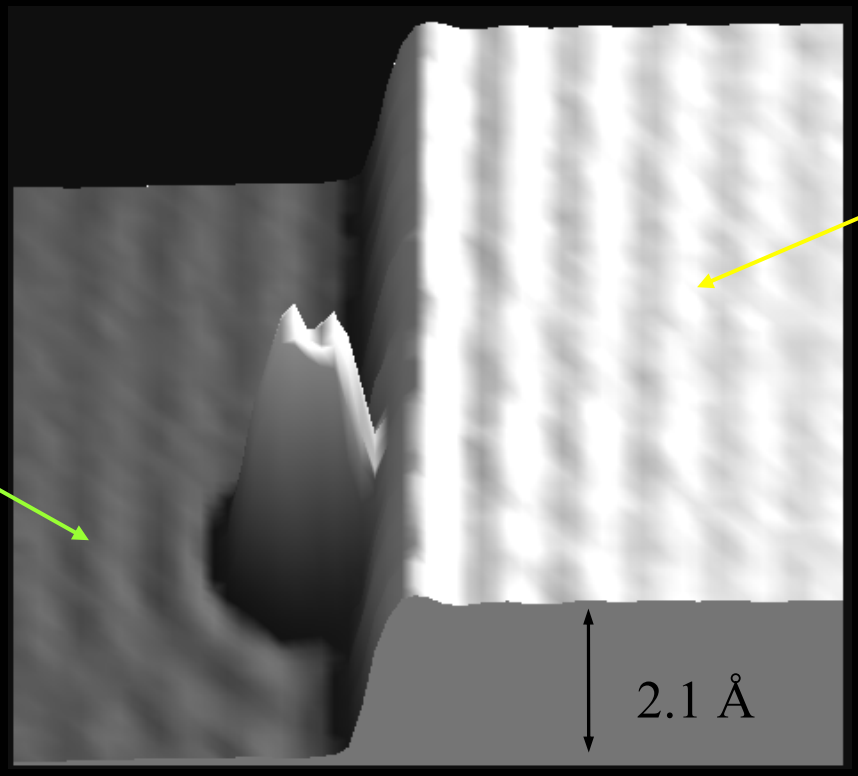
Apparent height at the contact: about 15 pm

Cu(111): standing wave patterns



Board parallel to the step

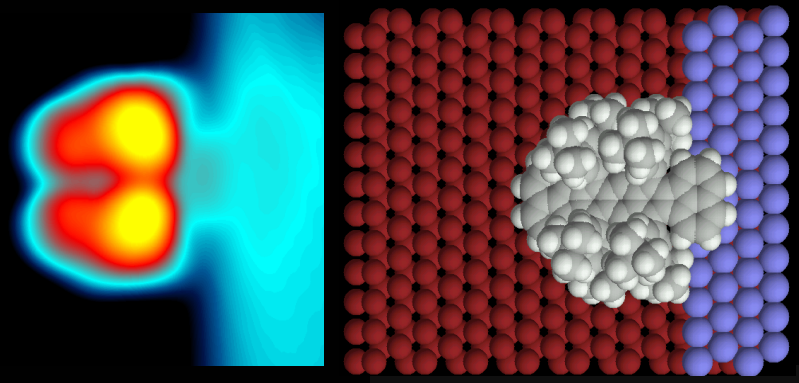


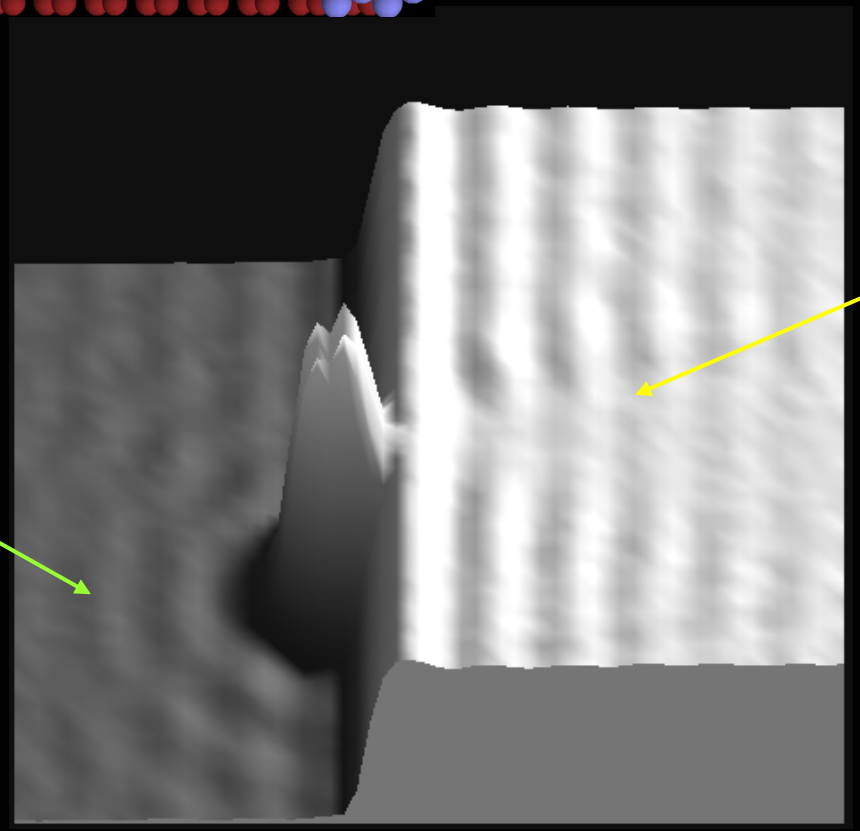


The molecule scatters surface state electrons of the lower terrace

The parallel patterns on the upper terrace are not influenced by the molecule

Board perpendicular to the step

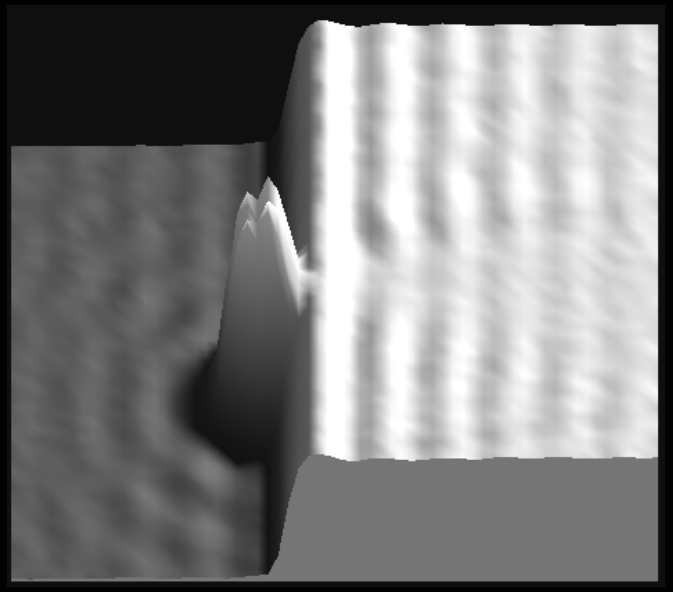


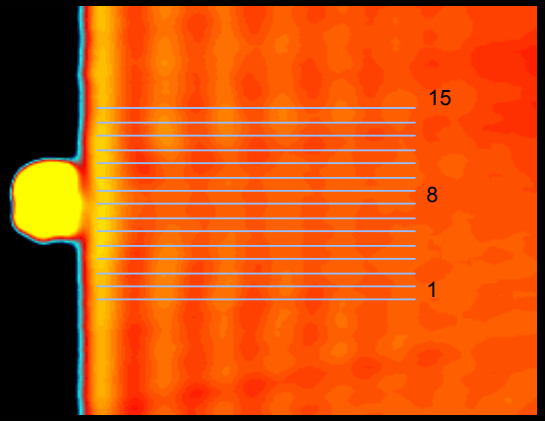


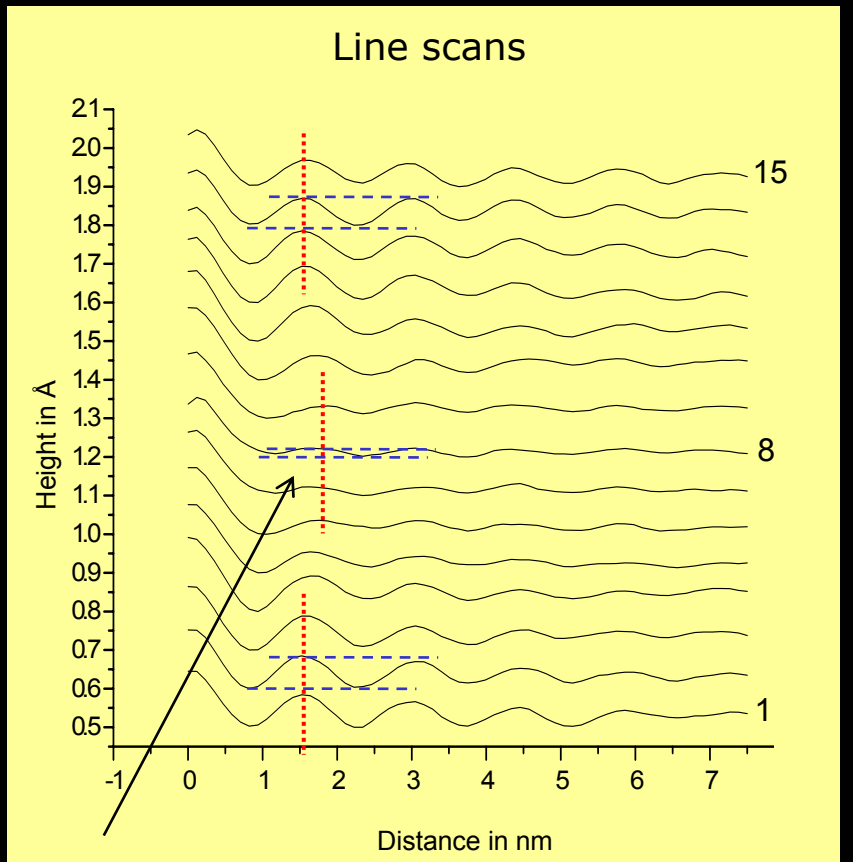
The wave amplitude is reduced at the contact location

The molecule scatters surface state electrons of the lower terrace

Influence of the contacted board





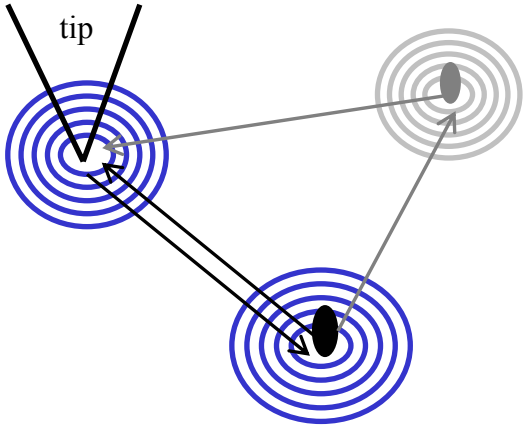


In the contact region:

Amplitude damped by factor 0.25±0.05

Phase shift by (2.0±0.5)Å or (24±6)°

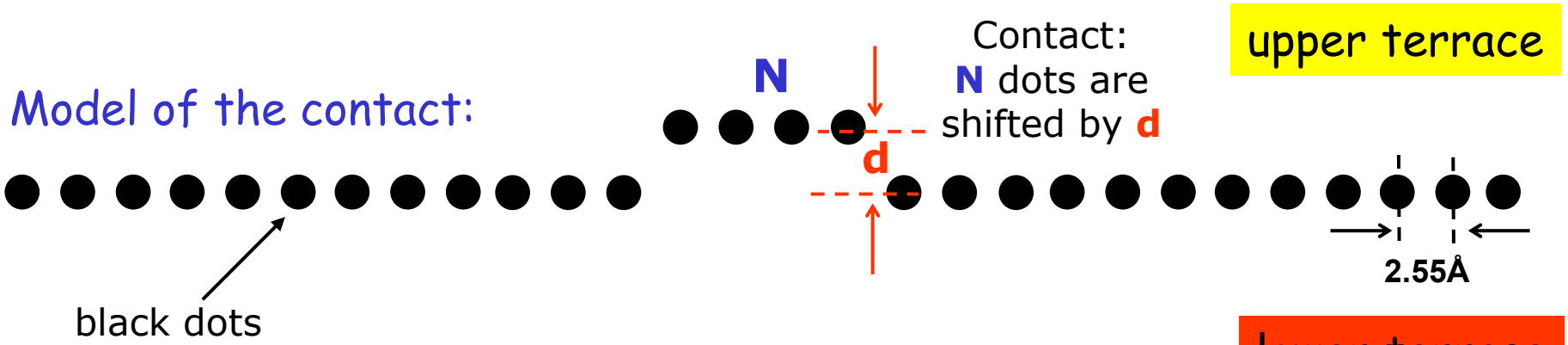
Single scattering calculations



- Electrons coming from the tip forms a circular wave
- The wave is scattered back from a defect to the tip
- Interference with the amplitude leaving the tip

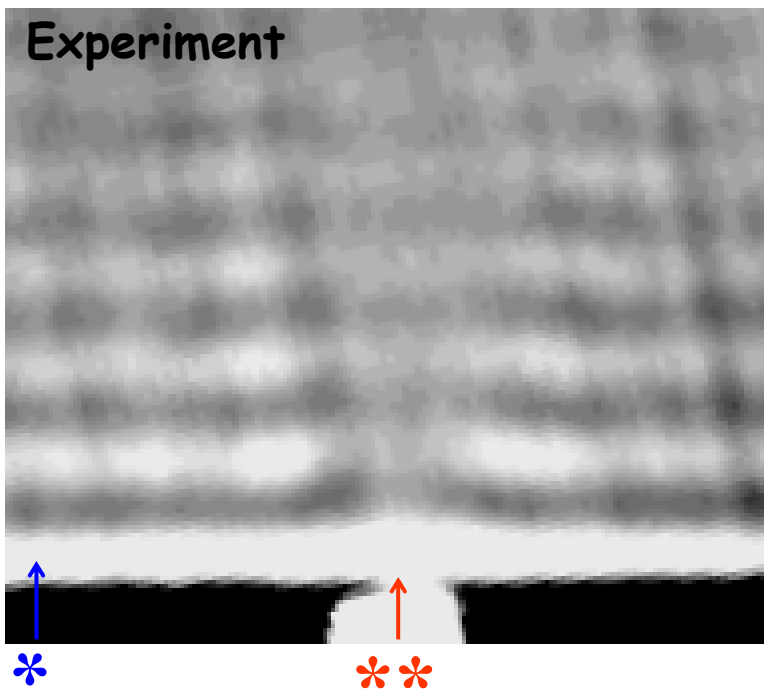
[Heller et al. Nature 296, 464 (1994)]

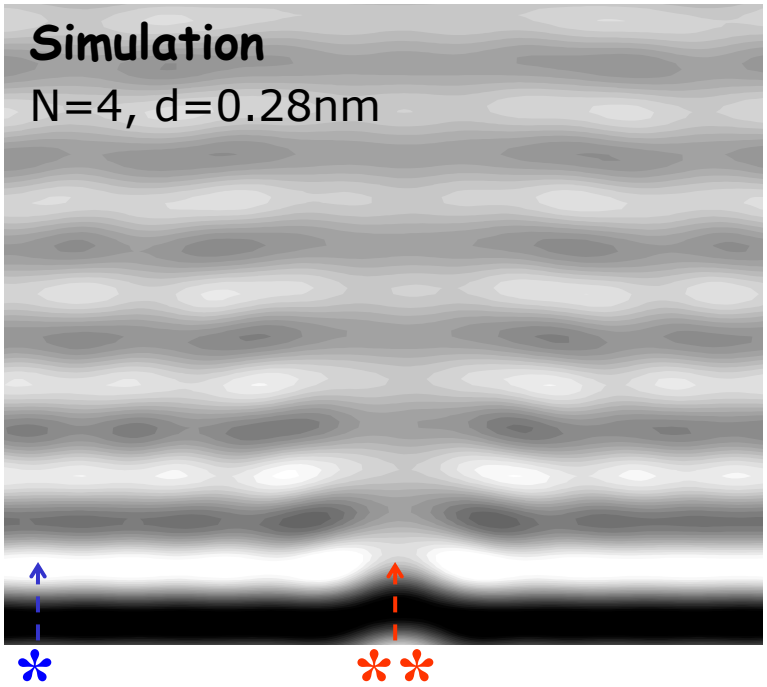
Model of the contact:

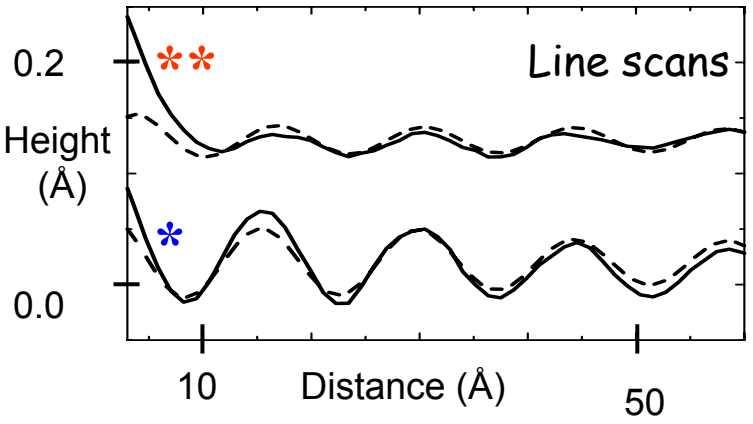


Best fit:
N=4 and d=0.28 nm

Single scattering calculations

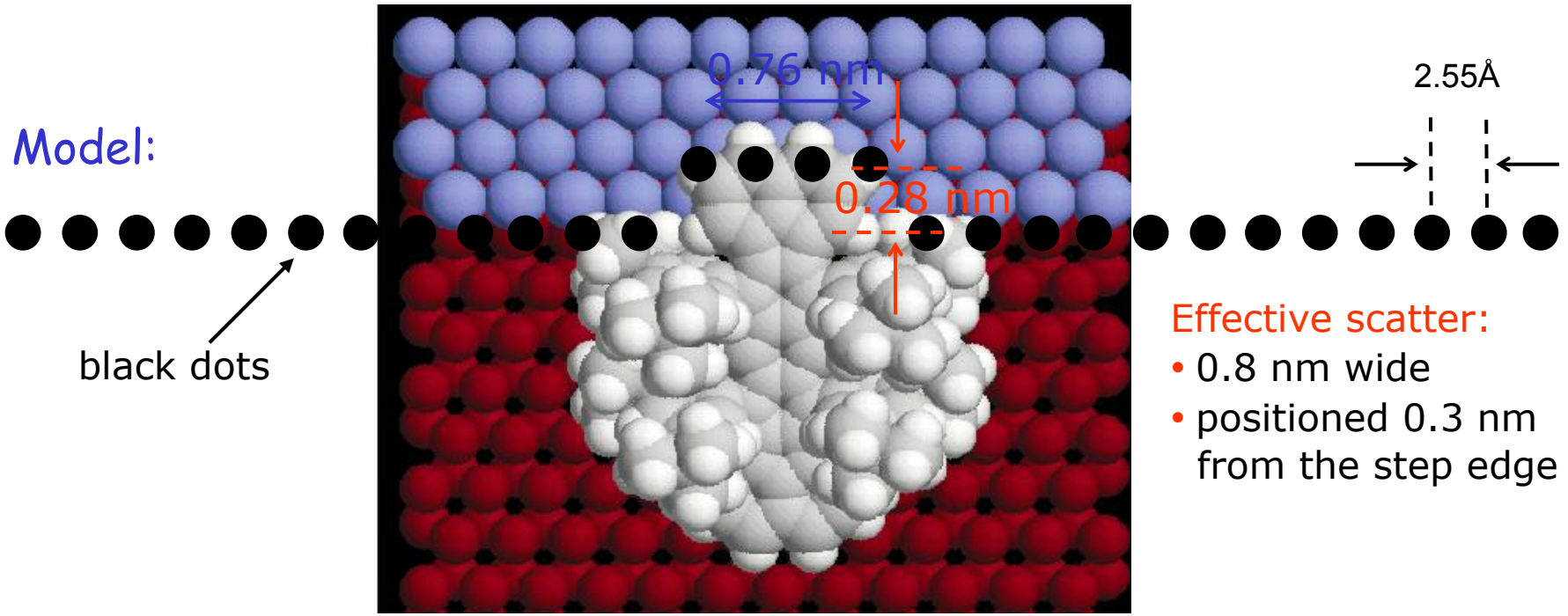






Very good agreement between experiment and model

Standing waves: comparison

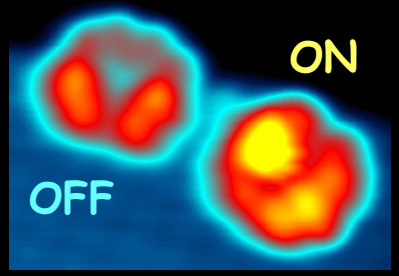


The model exactly reproduces the position of the end naphthalene group

The standing wave patterns are modified by the end naphthalene group building the contact

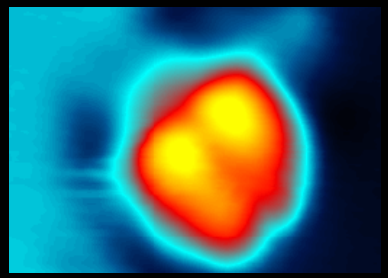
F. Moresco, L. Gross, M. Alemani, K.H. Rieder, H. Tang, A. Gourdon, C. Joachim, Phys. Rev. Lett. 91, 36601 (2003)

Summary



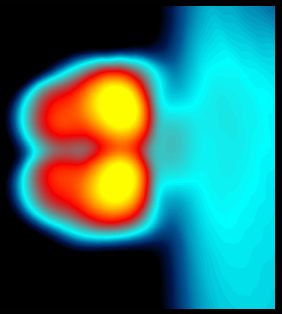
TBPP on Cu(211): molecular switch

- A single leg can be reversibly rotated
- The tunneling current depends on the orientation of the legs



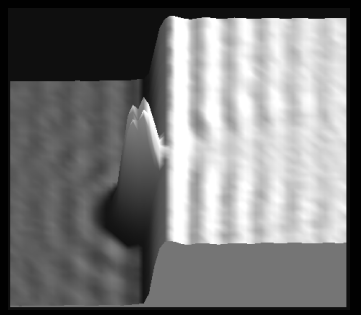
Cu(110) nanostructure

- Manipulation step by step
- Characterization of the contact



Cu(111) step edge

- Manipulation to contact
- Standing wave patterns modified by the contacted board



Founded by the EU program RTN "AMMIST" and Volkswagen Foundation project "Single Molecule Synthesis"