STM-Manipulation of Atoms and Molecules

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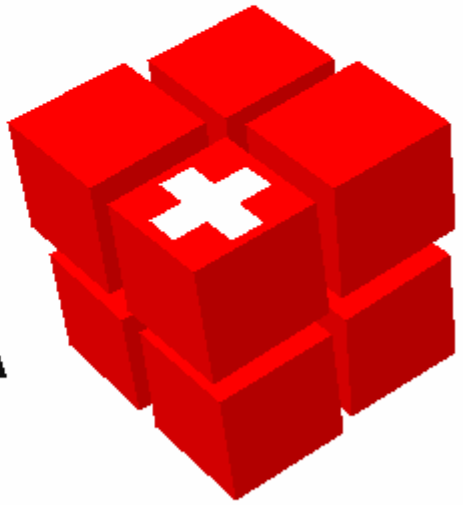
EMPA



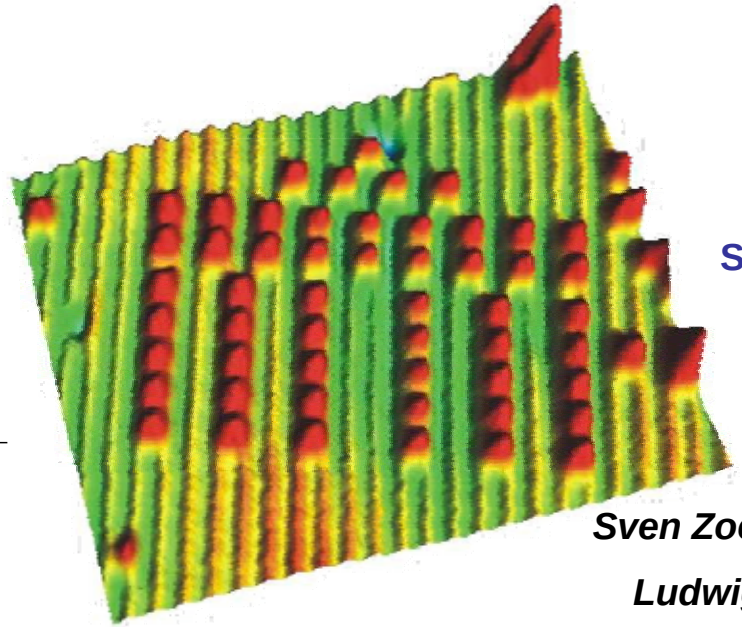
Materials Science and Technology

EMPA

STM-Manipulation of Atoms and Molecules

K.H. Rieder

Department of Physics, Free University of Berlin



Francesca Moresco

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Sven Zoephel DP Dr.

Ludwig Bartels Dr.

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Angelika Kuehnle DP

Kai Schaeffer DP

Bjoern Neu DP

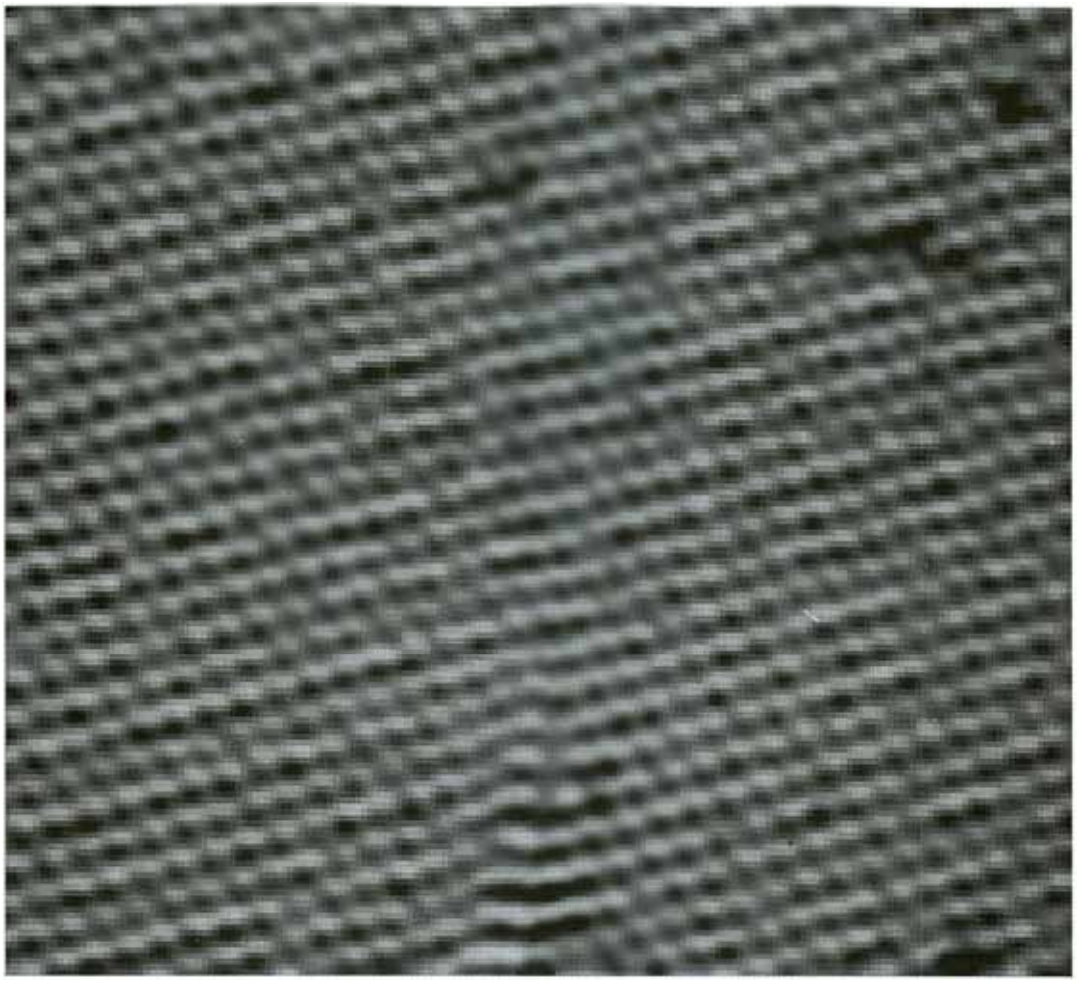
Jens Schulz DP Dr.

Jascha Repp DP Dr.

Andreas Riemann Dr.

Natalya Pertaya Dr.

Ag (111) with atomic resolution



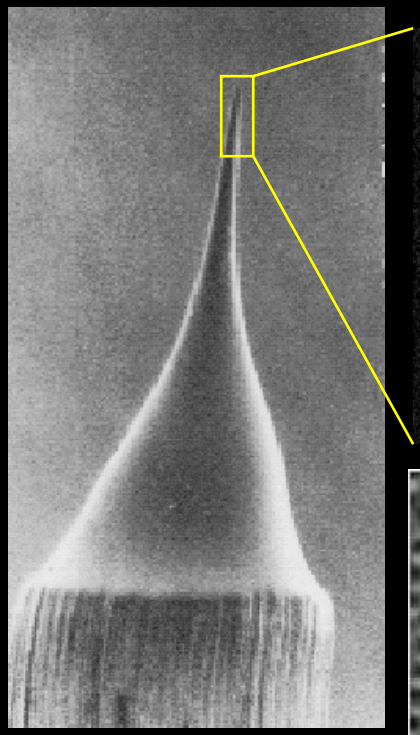
Nearest neighbour distance 2.89 A

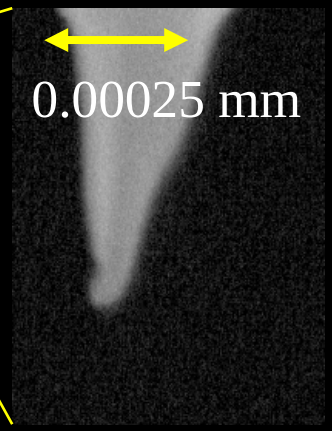
Corrugation amplitude 0.1 A

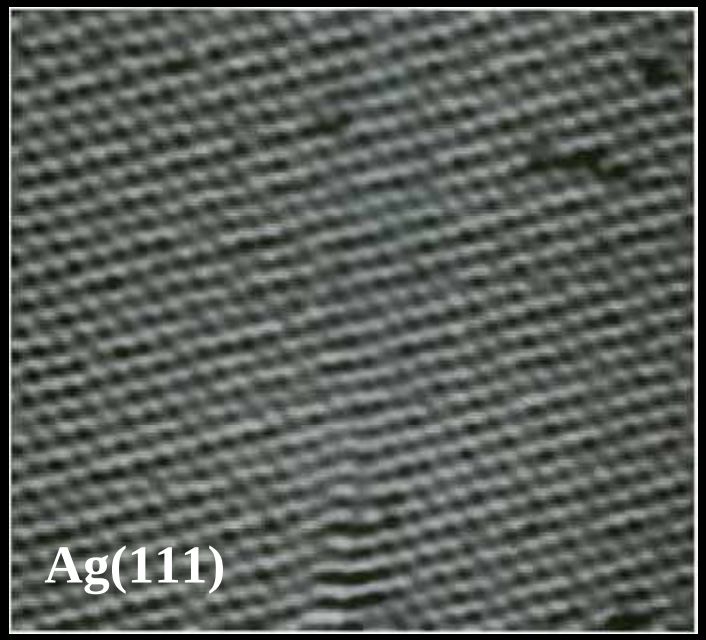
Screw dislocation

Height Resolution of STM

(courtesy of P.M.Koenraad/Techn. Univ.Eindhoven)



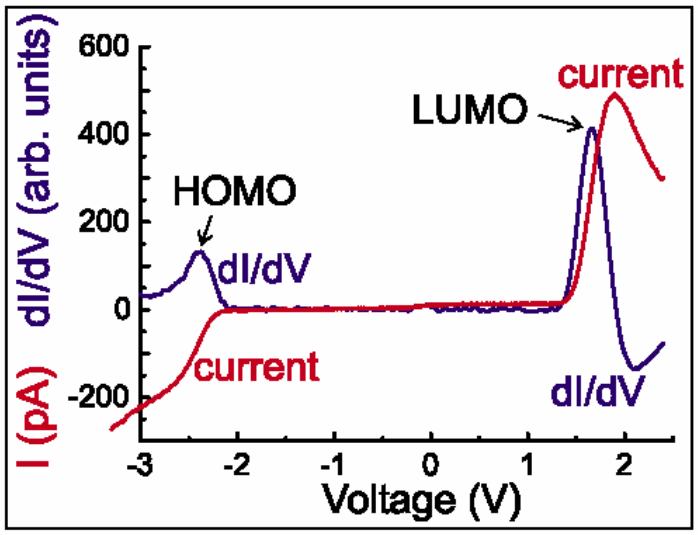




Distance of tip to surface is 1 nm = 0,000.001 mm while height regulation is accurate to 1 pm = 0,000.000.001 mm

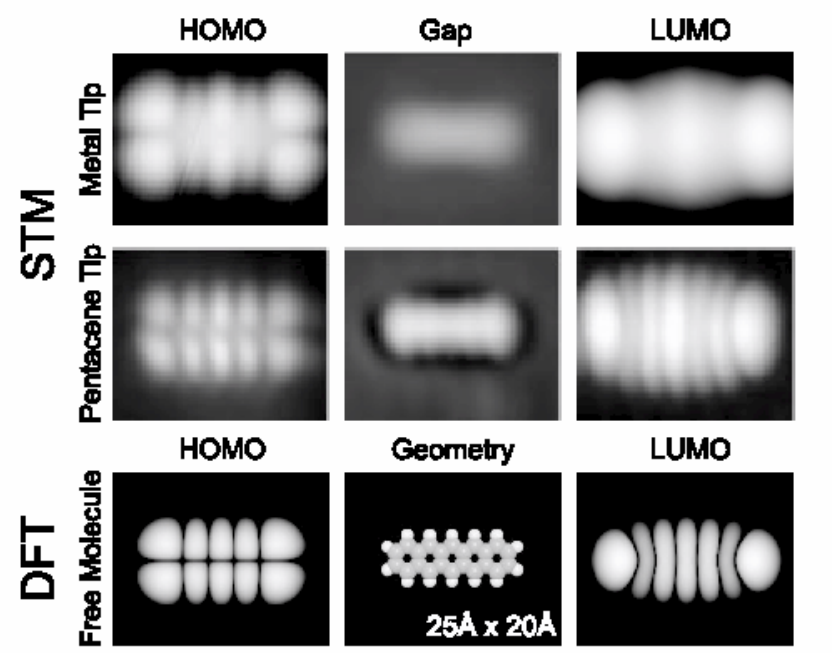
For an analogous height resolution using the Eiffel tower one must position it at 1 mm above the Champs Élysées and scan it with an accuracy of at least 0,001 mm.

Pentacene on 2ML NaCl(100)-Film on Cu(111)



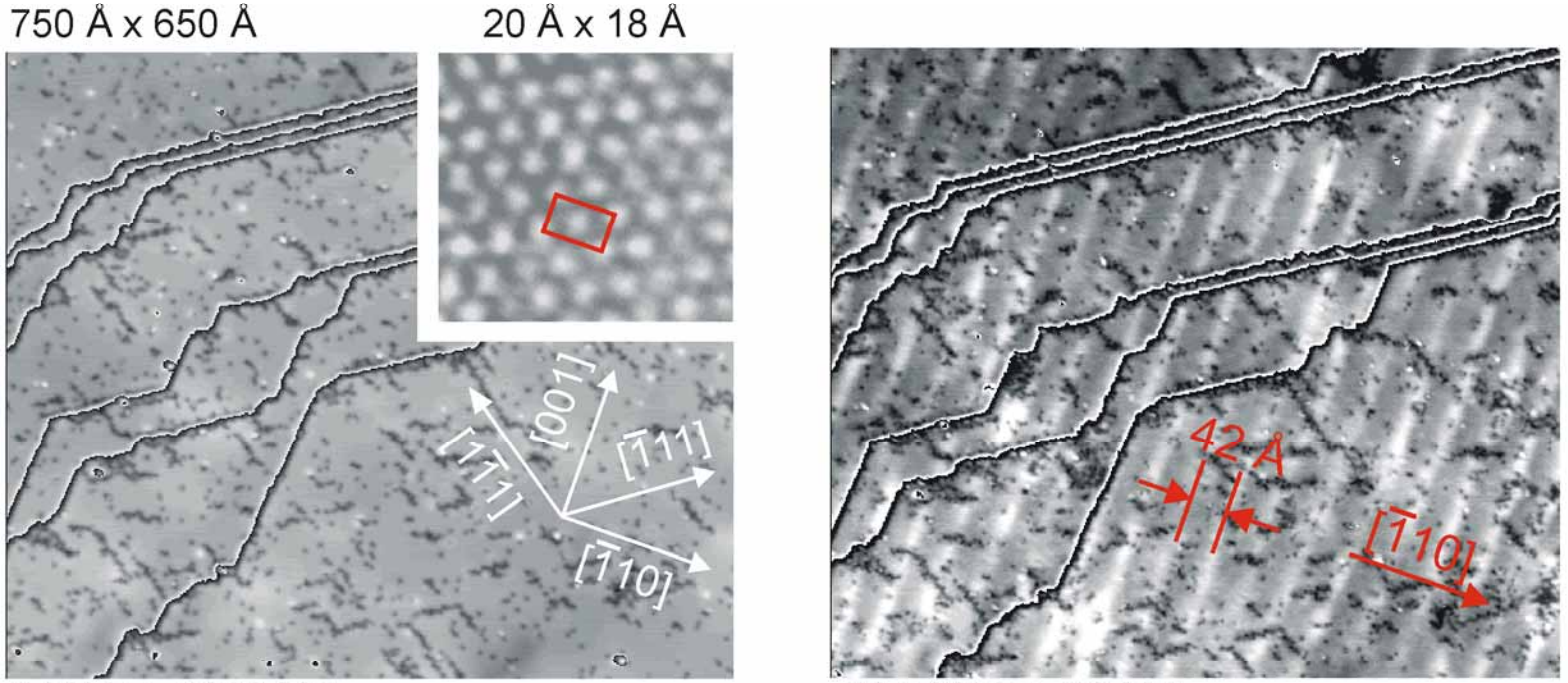
J. Repp, G. Meyer et al.,
Phys. Rev. Lett. 94, 026803
(2005)

dI/dV spectroscopy at pentacene center exhibits HOMO and LUMO peaks.



STM-images at voltages U in the gap region are relatively featureless (middle).
For U <-2.4 V they closely resemble the HOMO electron density (left).
For U >1.7V (right) the STM-images resemble the LUMO.
A pentacene molecule picked up to the tip enhances the spatial resolution.

Cr(110), STM at 6K



-1 V bias, 1000 MΩ

-10 mV bias, 10 MΩ

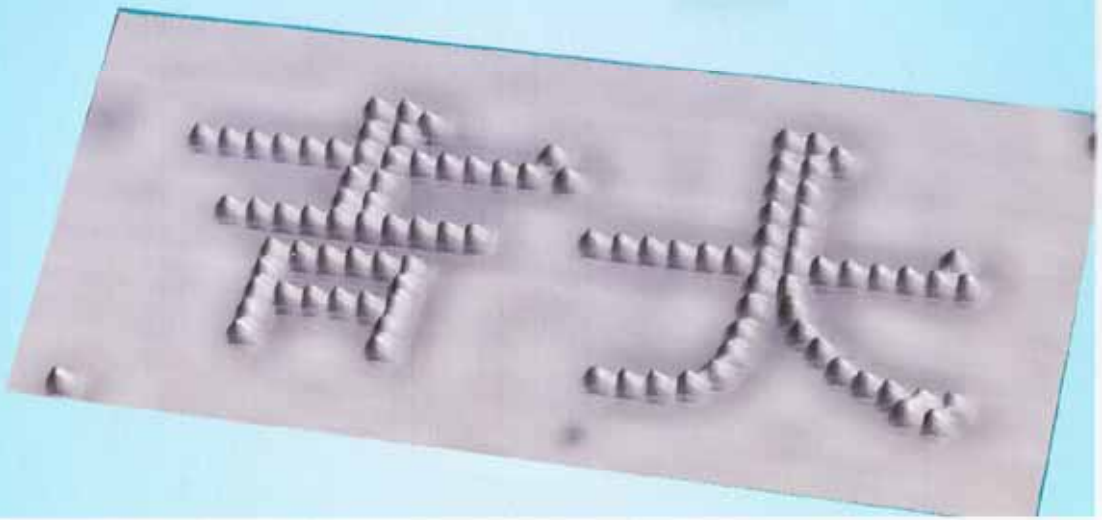
Braun, Fölsch, Meyer, Rieder, PRL **85**, 3500 (2000).

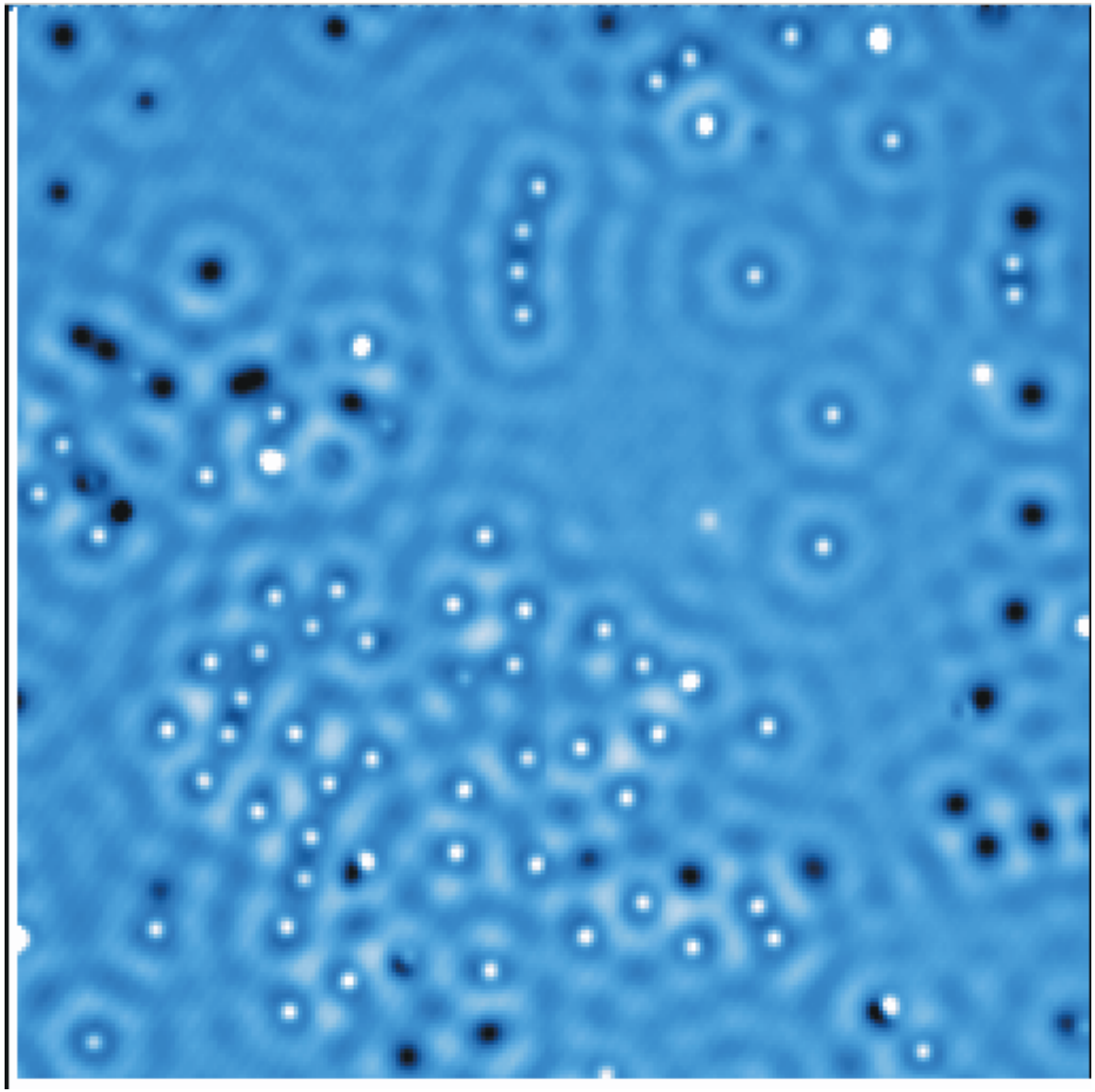
atomic manipulation

- 98 Ag atoms forming two chinese letters: Ji Jing

C. Gu[1], K.-F. Braun[2], K.H. Rieder[2]

[1] Ji Jing university, China
[2] Freie University, Berlin

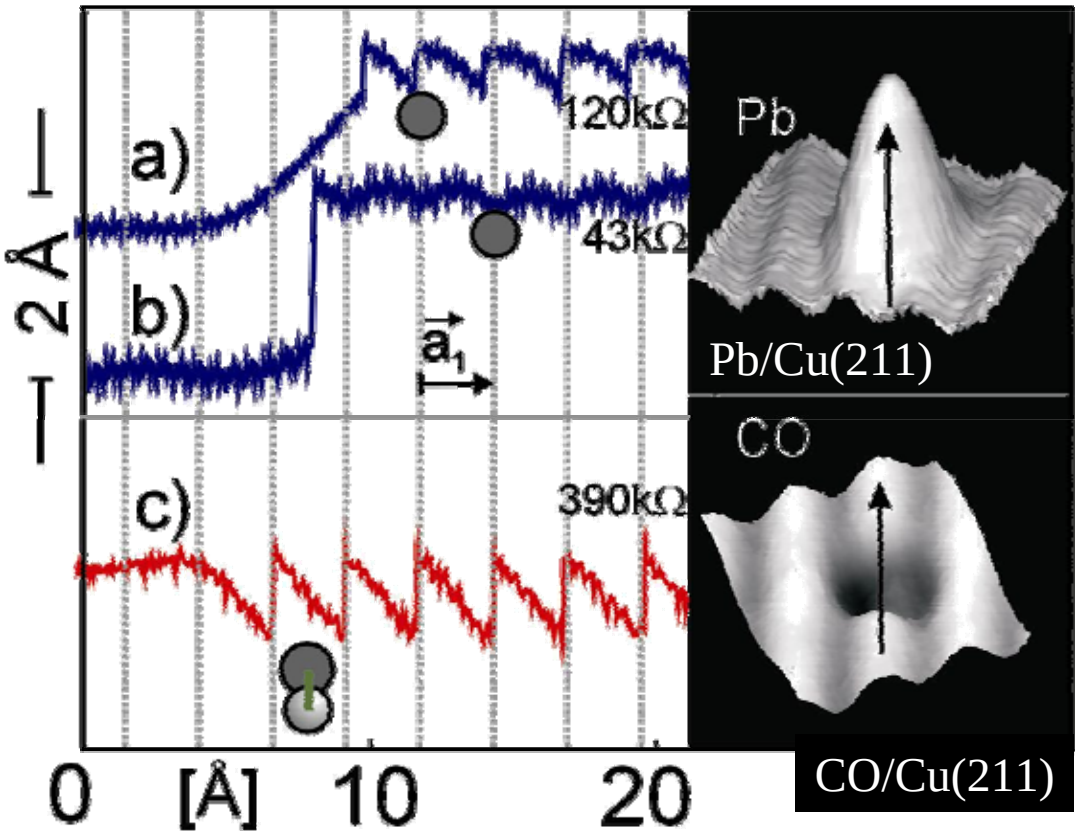




Lateral manipulation: Experiment

attractive force

repulsive force



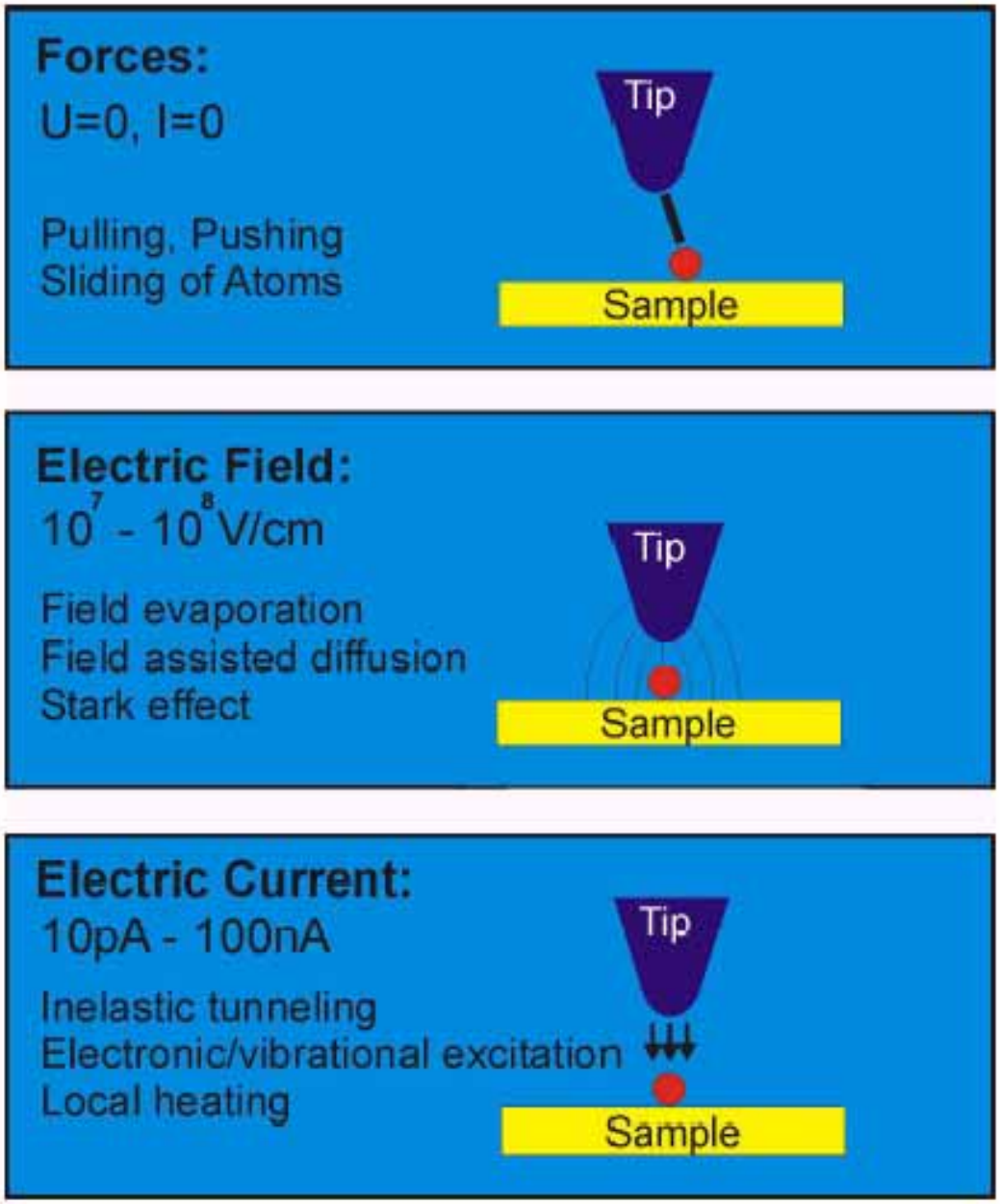
pulling

sliding

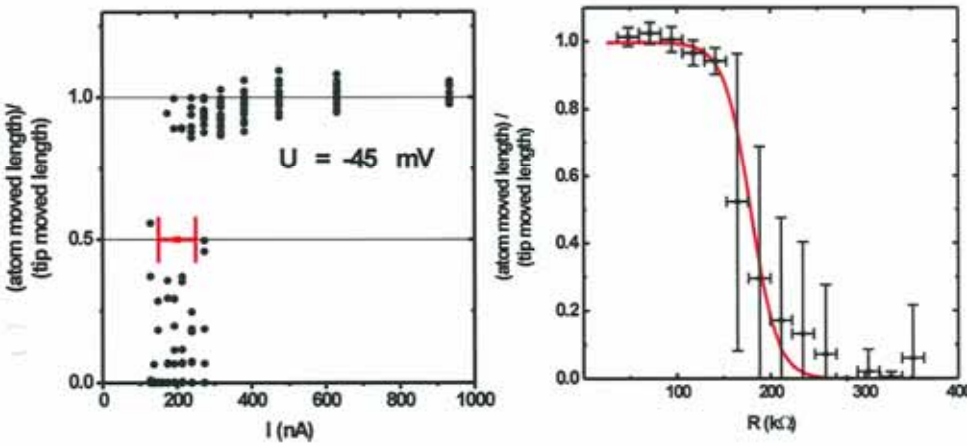
pushing

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

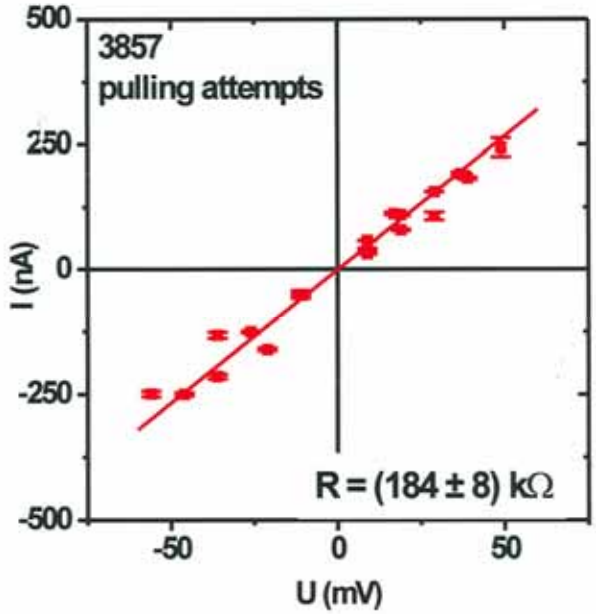
Basic tip-sample interaction mechanisms for atomic scale modifications of surfaces



Pulling of single Ag atoms on Ag(111) at 5 K



$$I \propto Ue^{-Kz}$$



S.-W. Hla, K.-F. Braun, K.-H. Rieder, PRB **67**, 201402(R) (2003).

Model calculations based on simple assumptions:

Adparticles move in combined potential of tip and surface.

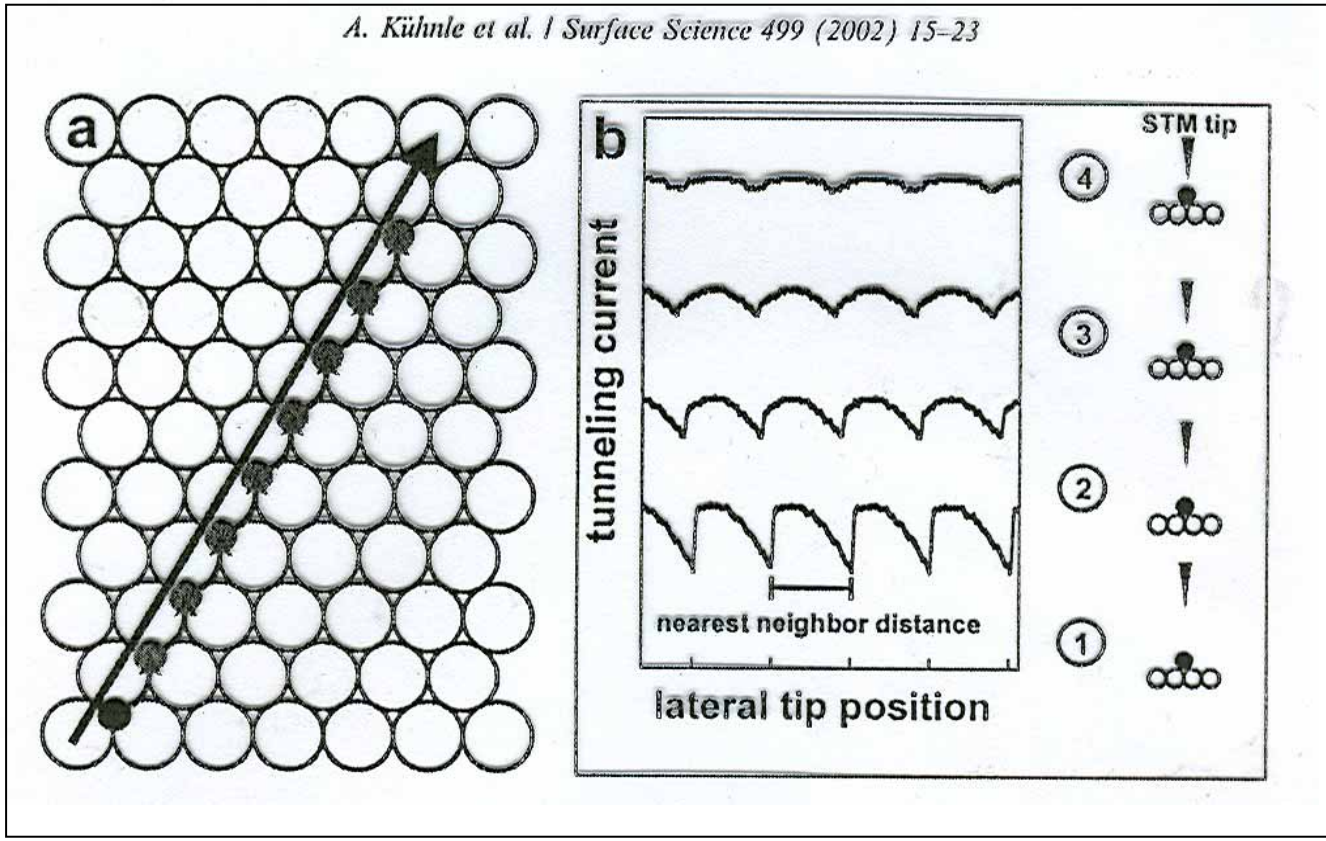
Surface potential related to electron density contour.

Tip-adparticle potential has Morse form.

Pathway of tip divided into small steps -

adparticle position calculated by searching

for closest energy minimum.

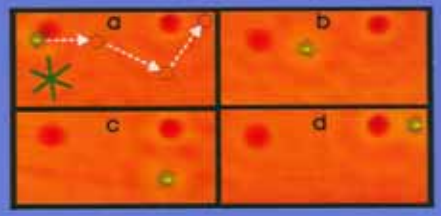


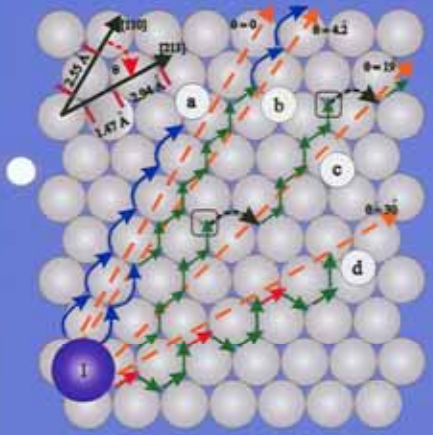
1-4

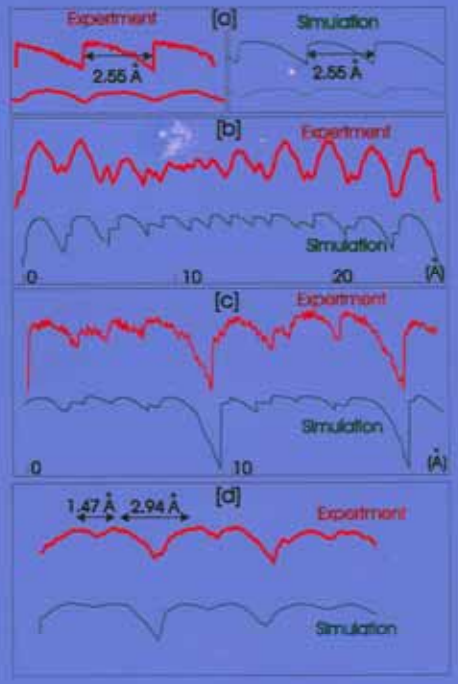
Transition from

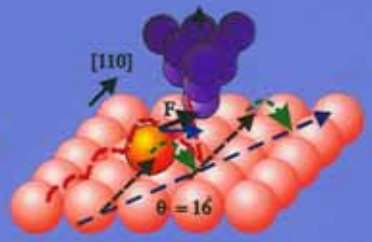
pulling to sliding

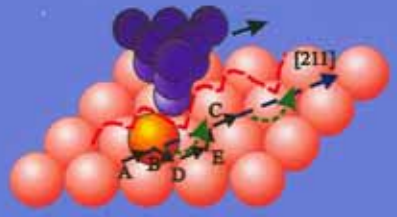
Detailed Atom Movement Mechanisms



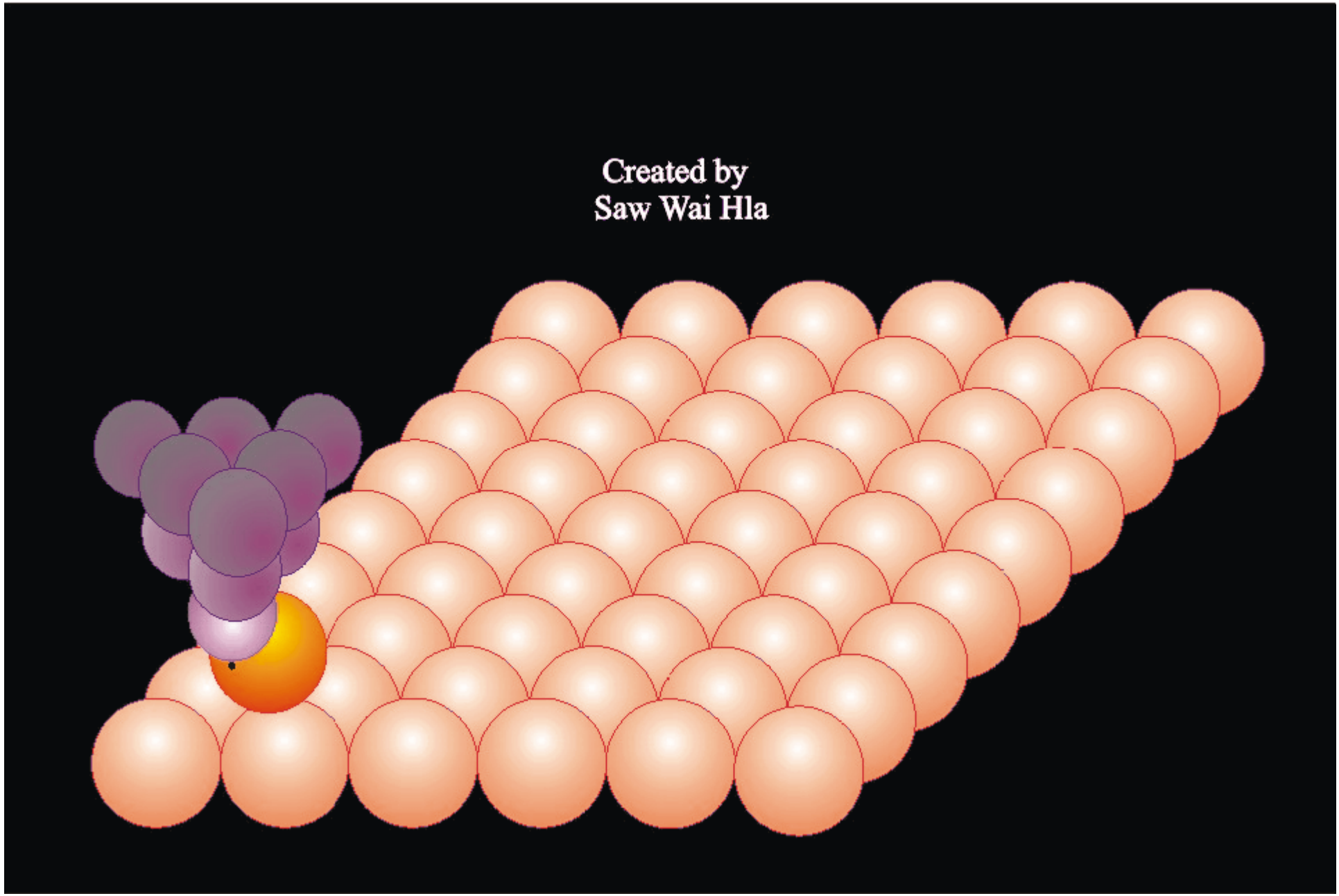


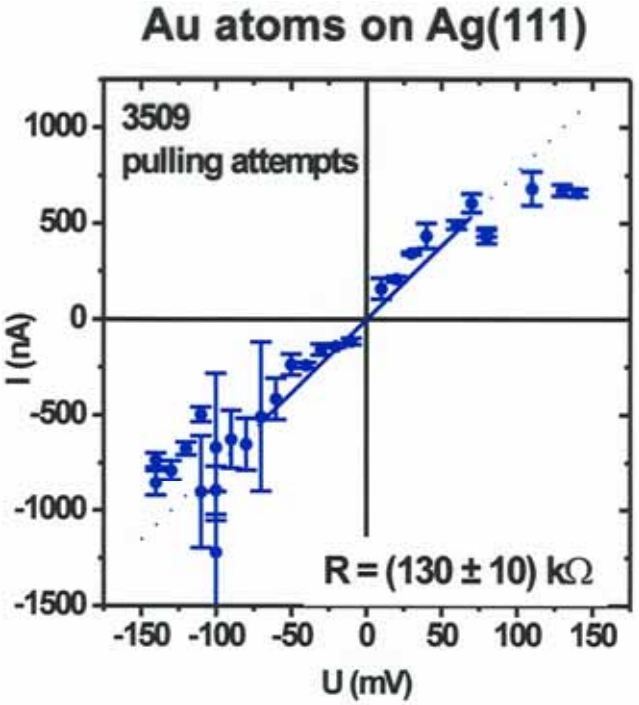






Saw-Wai Hla, Angelika Kuehnle, Gerhard Meyer, Karl-Heinz Rieder

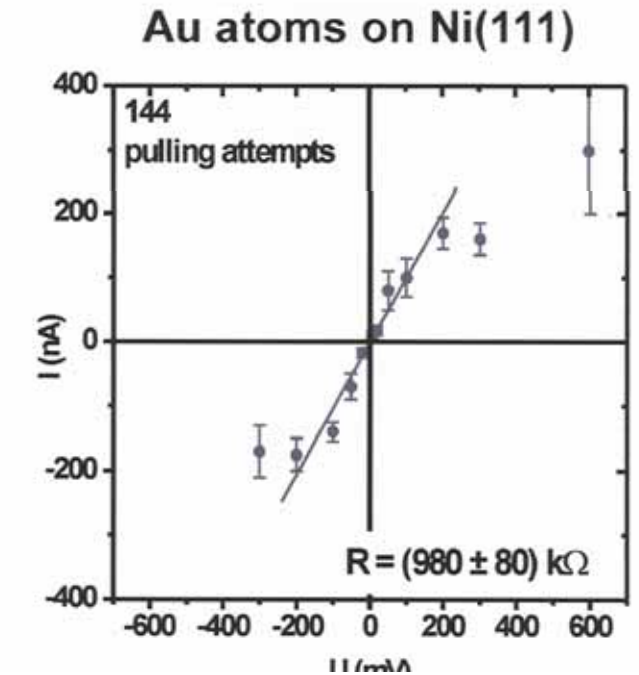

Created by
Saw Wai Hla



Joe Stroscio, Bob Celotta
(NIST,Washington DC)

„Autonomous atom assembly“

Science (2004)



K.F. Braun, S.W. Hla, N. Pertaya, H.W. Soe, C.F.J. Flipse and K.H. Rieder

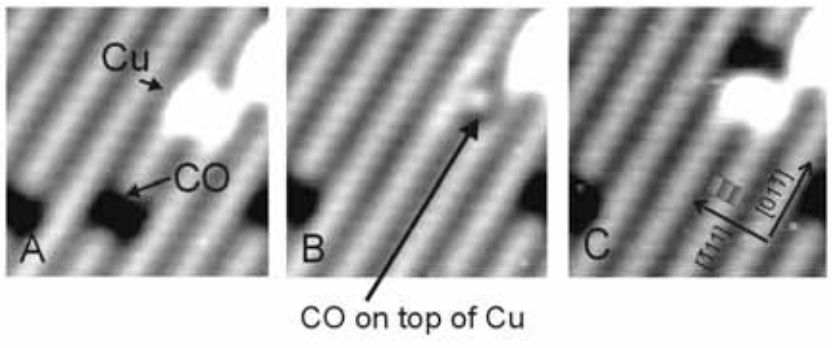
Proc. 12 th Int. Conf. on

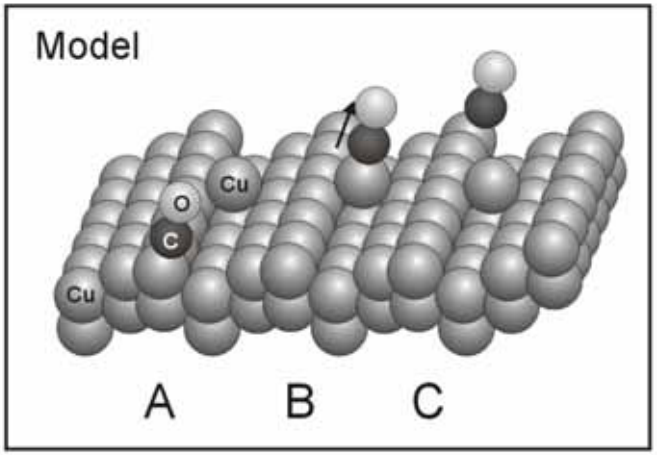
Scanning Tunneling Microscopy/Spectroscopy and Related Techniques

Eindhoven 2003

p.109

Positioning a single CO molecule on top of a single Cu atom





Results of lateral manipulation:

$R_{\perp}$ = 400kΩ, $R_{\parallel}$ = 270kΩ

Higher force necessary to remove a CO molecule from a single Cu atom

M. Gajdos, A. Eichler, J. Hafner, G. Meyer and K.H. Rieder:

CO-bonding energy to single Cu-atom at step edge ~0.1 eV larger than on step edge

Phys.Rev.B 71, 035402 (2005)

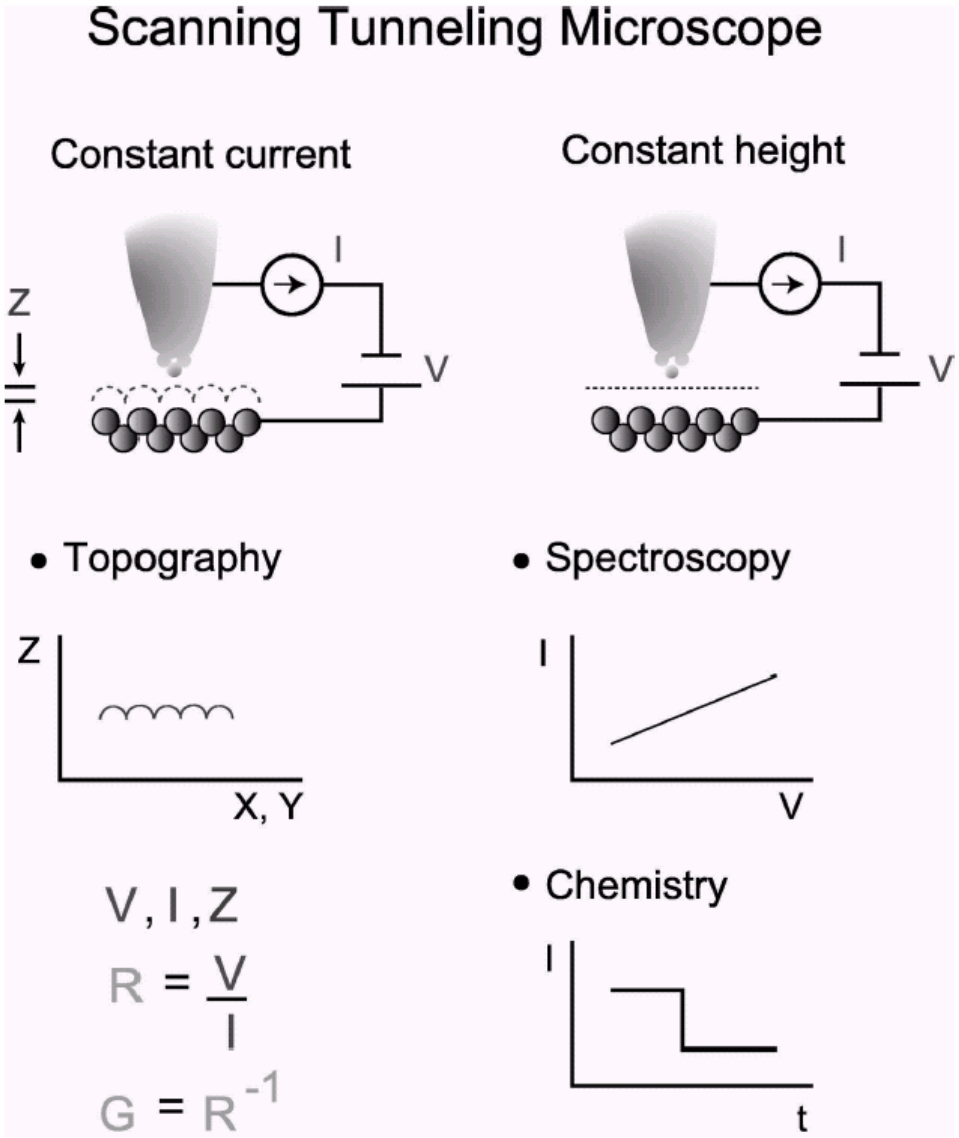
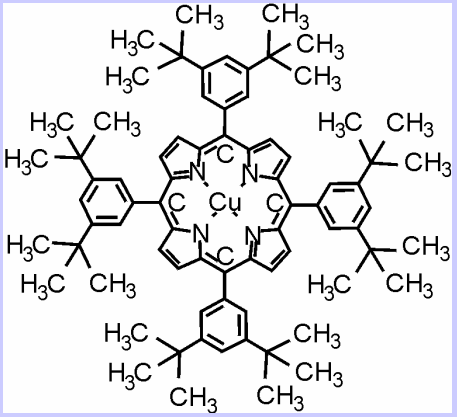


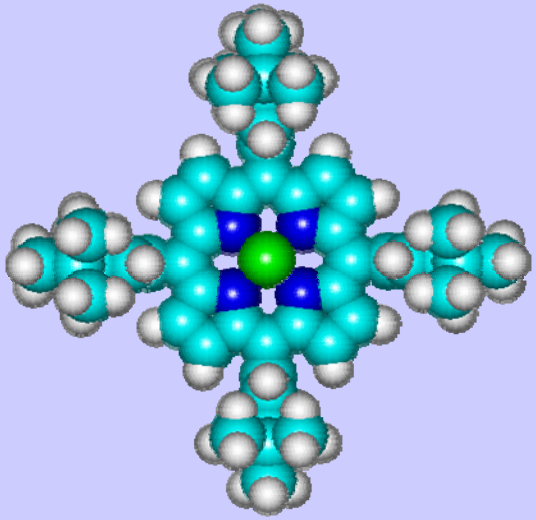
FIG. 2. Schematic showing the different operational modes of the STM. In the constant current (constant height) mode, the feedback remains on (off). With the tip fixed in the $x-y$ position and height (z), electronic and vibrational spectroscopy can be carried out by modulating and sweeping the bias voltage. By monitoring the time dependence of the current, motions of the molecule can be observed and quantitatively measured. With the homemade STM, the measured drifts with the feedback turned off are ~ 0.001 Å/min for the tip–sample separation and ~ 0.01 Å/min for the $x-y$ position. G is the conductance.

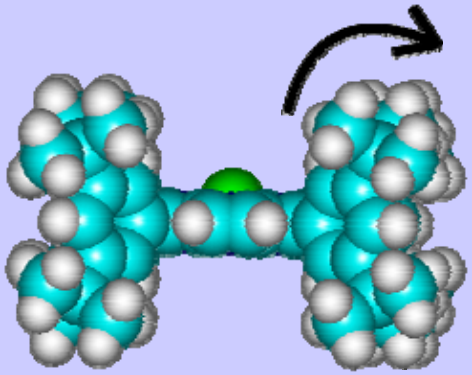
TBPP

Cu-tetra-3.5-di-tert-butyl-phenyl-porphyrin



Porphyrin-based molecule with four lateral TBP-groups

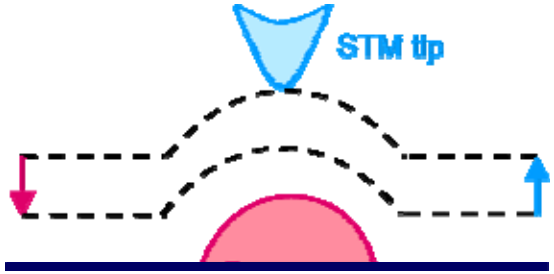




- In the gas phase the legs are oriented perpendicularly to the porphyrin ring
- The legs can rotate

Manipulating into parts of molecules

by means of the lateral manipulation technique

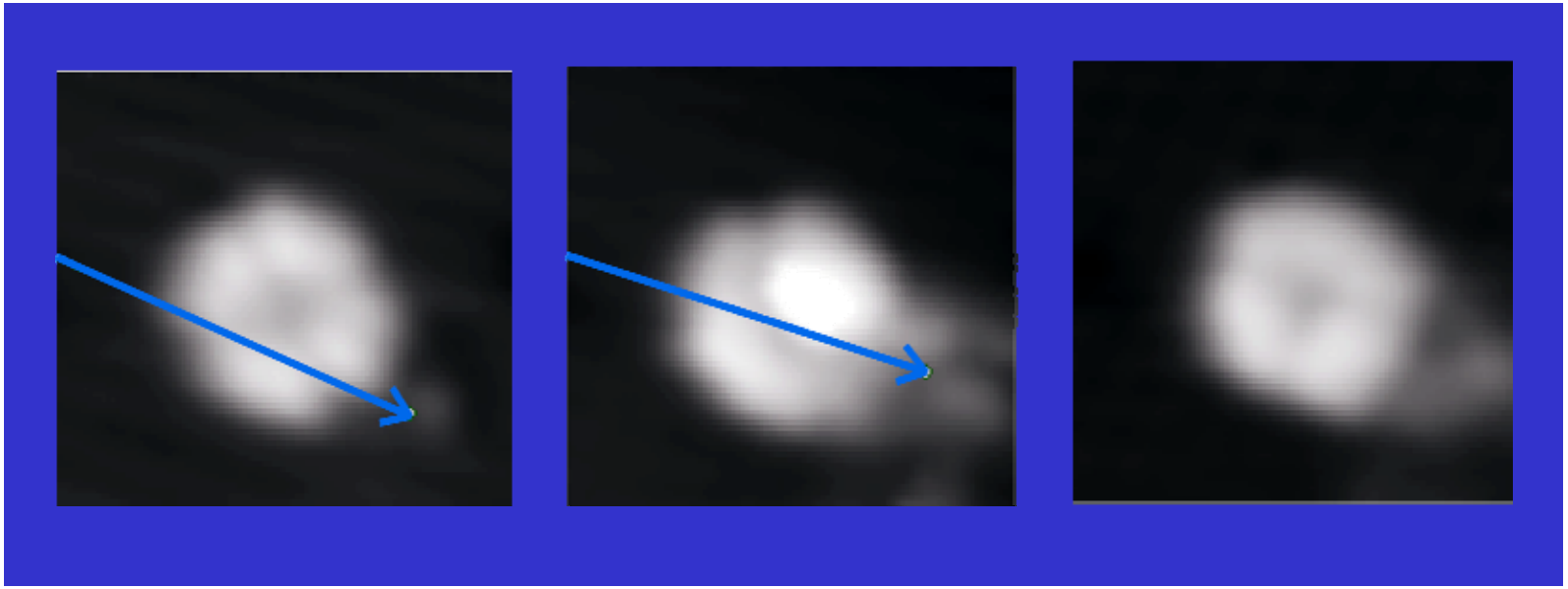


a single leg of TBPP can be **reversibly** rotated on Cu(211)

image: R = 7.5 x 10^8 Ohm

manipulation: R = 6 x 10^4 Ohm

V = 0.3 V, I = 4x10^{-10} A



the legs are flat

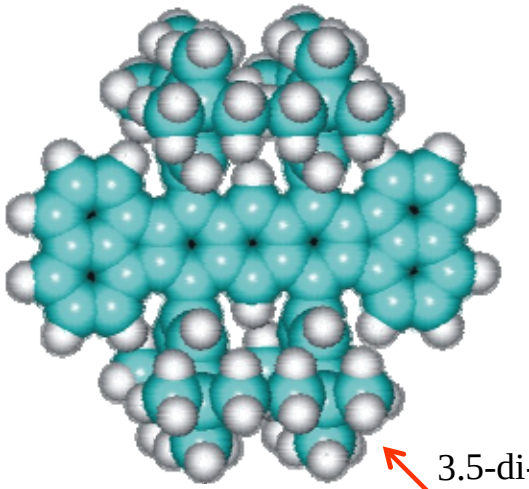
one leg is rotated

the leg is flat again

A molecular wire system

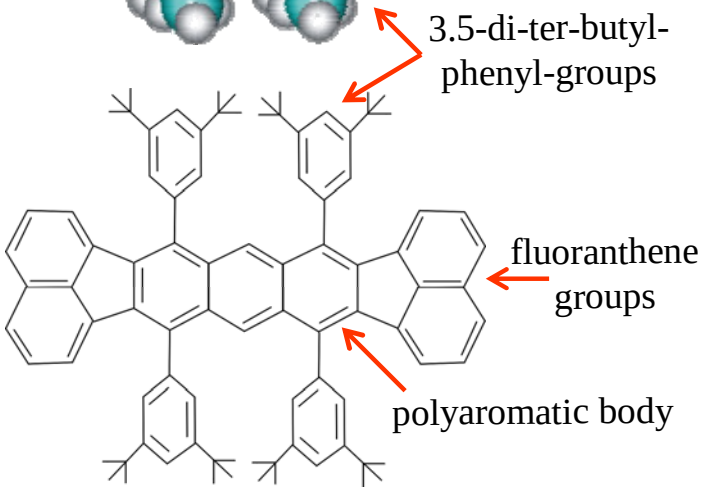
molecular-wire-board
with the same 4 lateral TBP-groups as TBPP

better conduction through the polyaromatic body



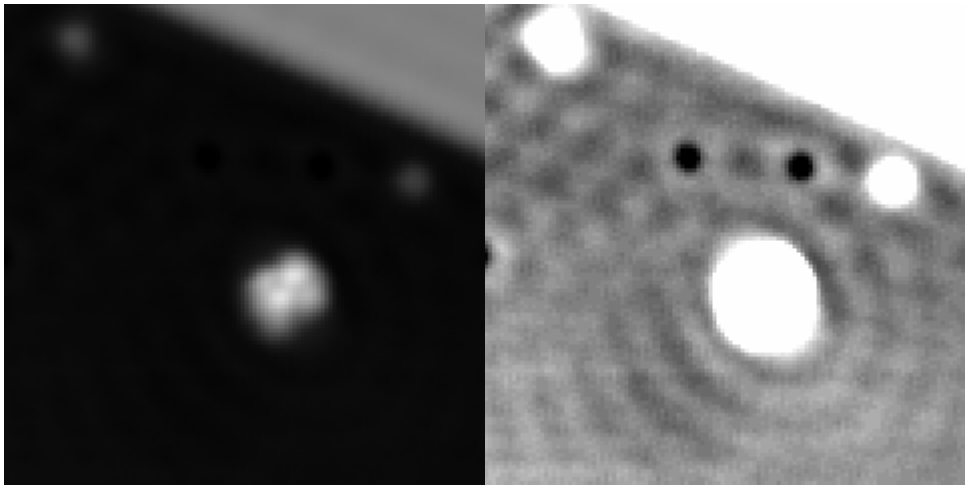
Lander ($C_{90}H_{98}$)

in the gas phase the legs are oriented perpendicular to the board



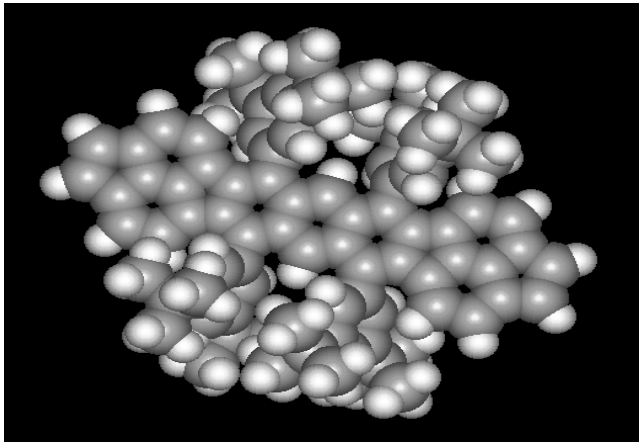
Standing wave patterns of Lander molecules

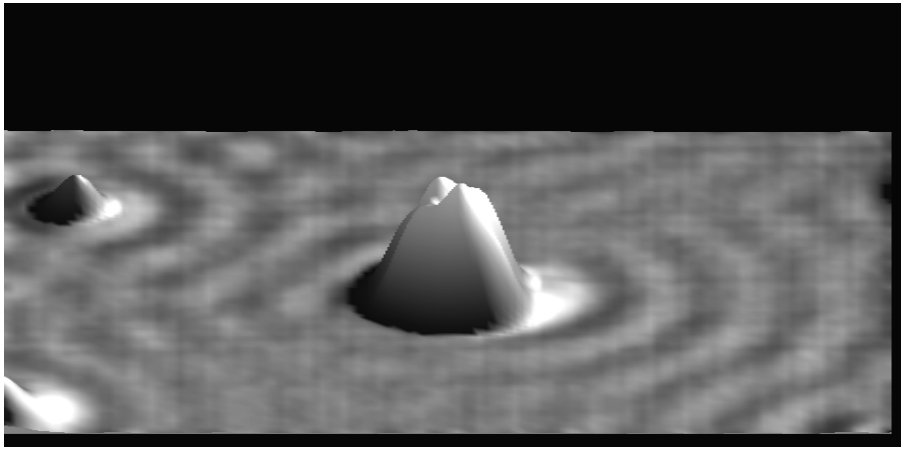
The Cu(111) surface exhibits Shockley surface states.
Standing wave patterns in the LDOS are accessible with STM



R-Lander
U=100mV, I=0.3nA,
size: (150Å)²

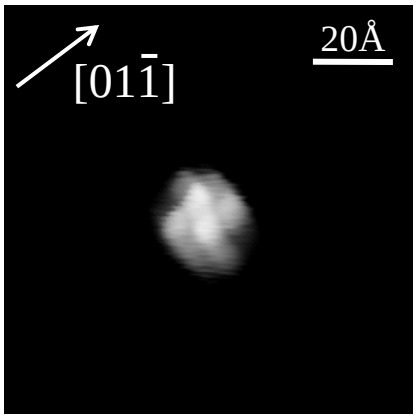
Same image,
increased contrast

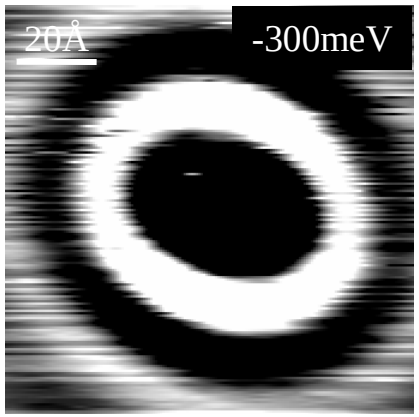


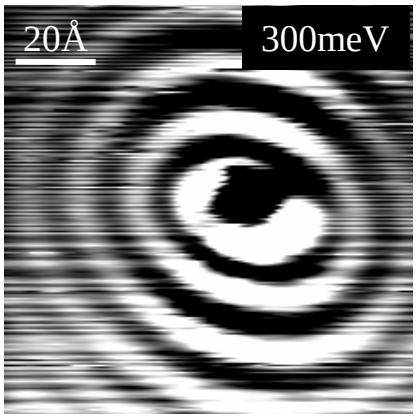


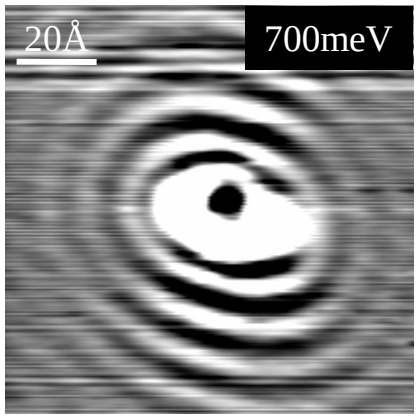
dI/dV maps

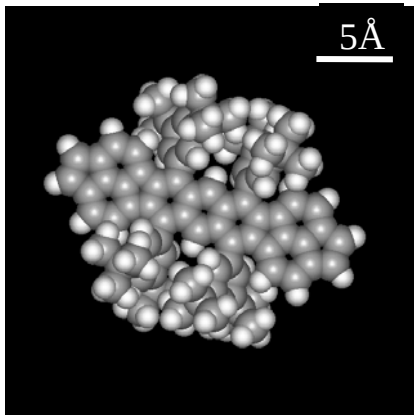
Spectroscopic images of differential conductance (dI/dV maps)
recorded in constant current mode,
with typical modulation frequency 500Hz and amplitude 10mV







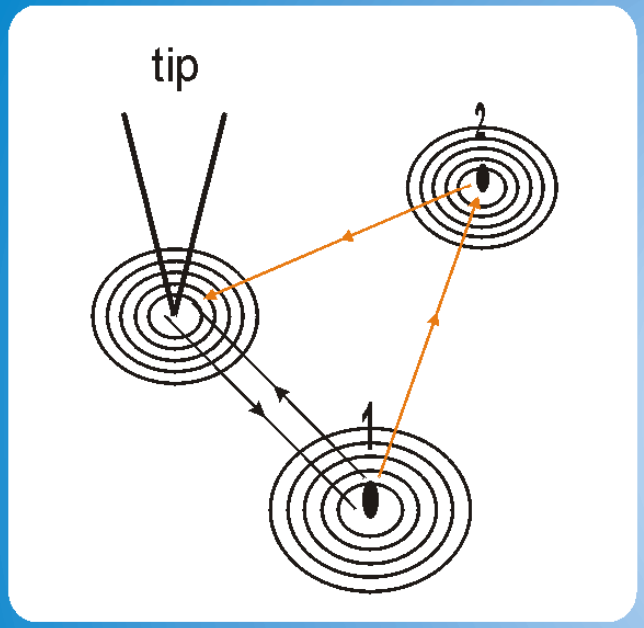




$$k(E) = \sqrt{\frac{2m^*(E - E_\Gamma)}{\hbar^2}}$$

Parabolic dispersion for Cu(111)
$m^* = 0.4m_e$ and $E_\Gamma = -420$meV

calculation of the wavepattern



- tip emits a circular wave: $a_T = H_0^{(1)}$
- point interaction yields s-wave phaseshift δ and

  absorption α: $a(r) = H_0^{(1)} \dfrac{\left(\alpha e^{2i\delta} - 1\right)}{2}$

- interference term after all scattering processes:

$$LDOS \propto \mathrm{Re}\left(\vec{a}_T \cdot \left[1 - \tilde{A}\right]^{-1} \cdot \vec{a}\right)$$

*[Heller et al., Nature **369**, 464 ('94) and thesis group Heller]*

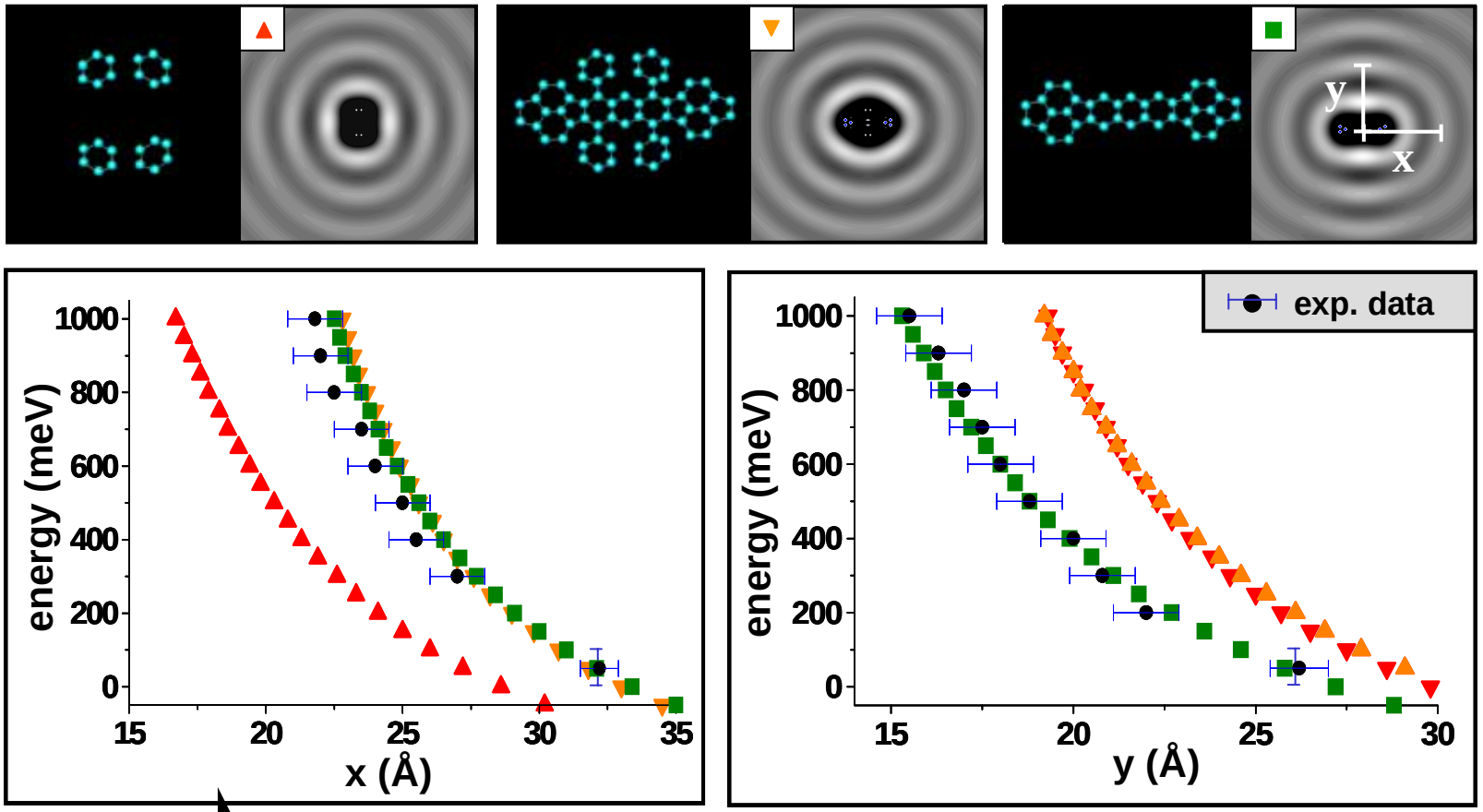
- inelastic scattering between adatoms:

  $e^{-x/L}$

  x length of the trajectory
  $L = \tau \cdot v$ phase relaxation length

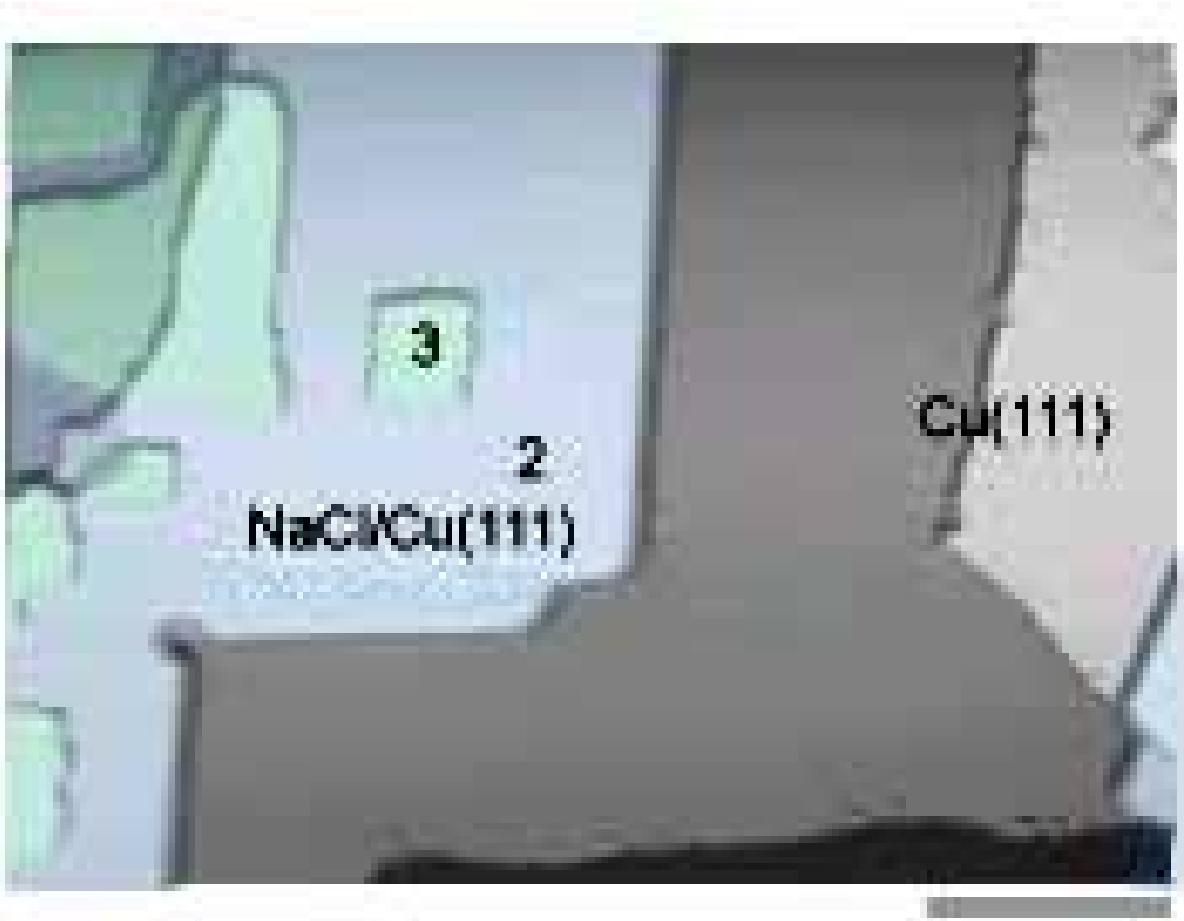
  v group velocity
  τ electron lifetime

Comparison of different model calculations



The molecular board is the predominant scattering centre of the surface state electrons

L.Gross, F.Moresco, L.Savio, A.Gourdon, C.Joachim, K.H. Rieder, Phys.Rev.Lett. 93, 056103 (2004)



NaCl on Cu(111): Large islands with sharp unpolar edges

Image size 2300x1600A, 230pA; -1.26V

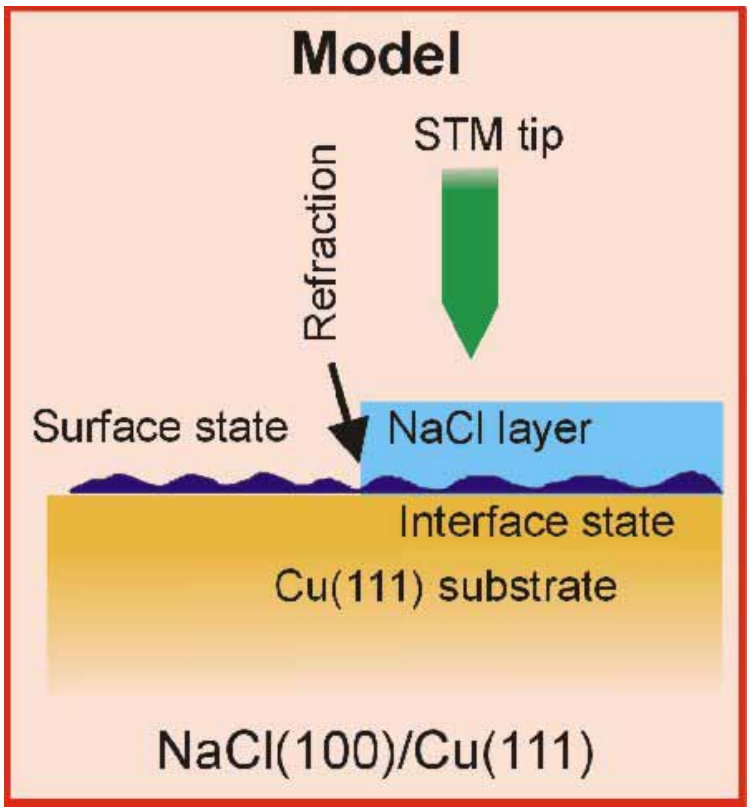
Jascha Repp, Gerhard Meyer and K.H. Rieder,

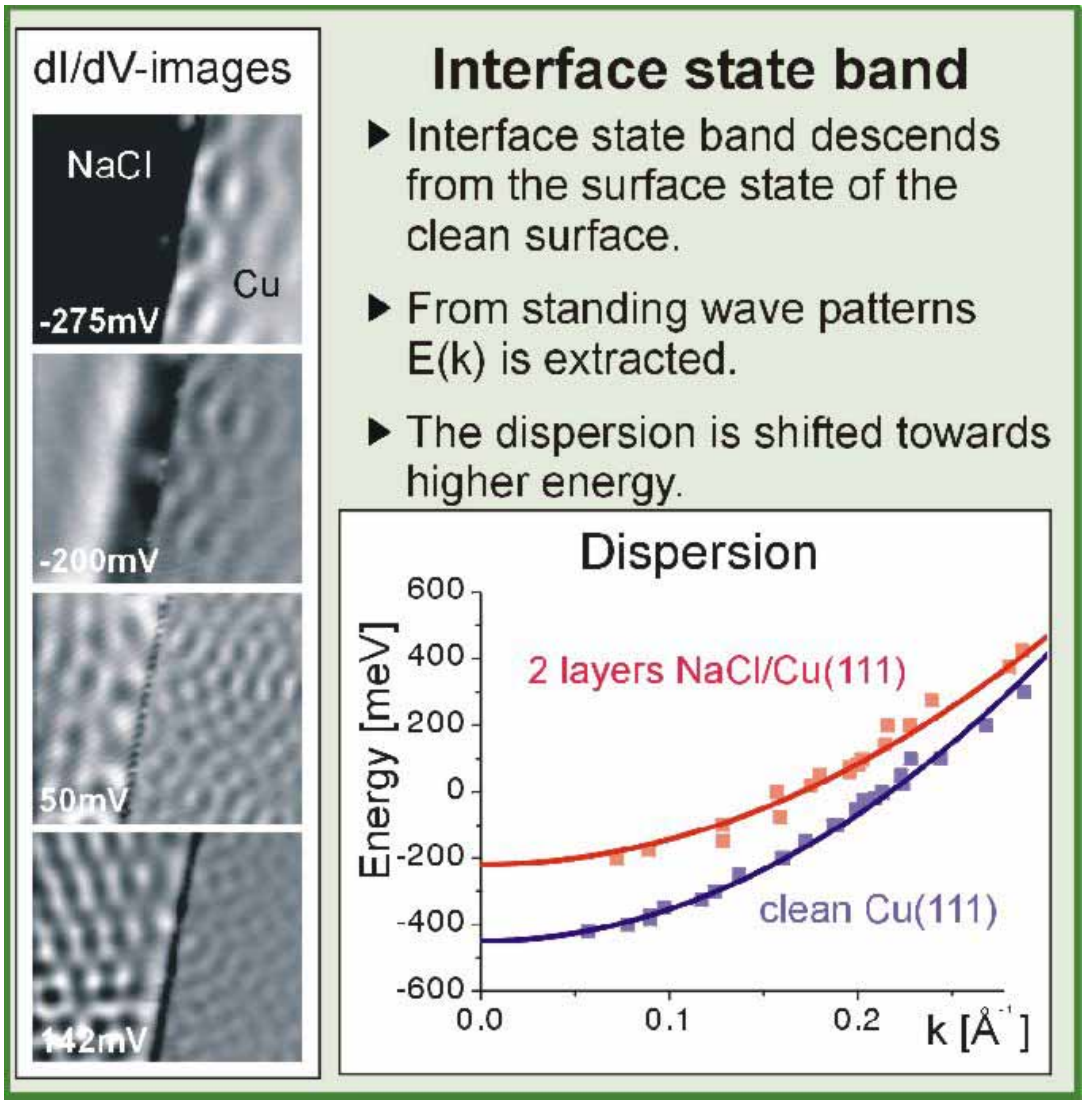
Phys. Rev. Lett. 92, 036803 (2004)

Interface state band and refraction: NaCl/Cu(111)

Phys. Rev. Lett. 92, 036803 (2004)

J. Repp,
G. Meyer,
K.-H. Rieder





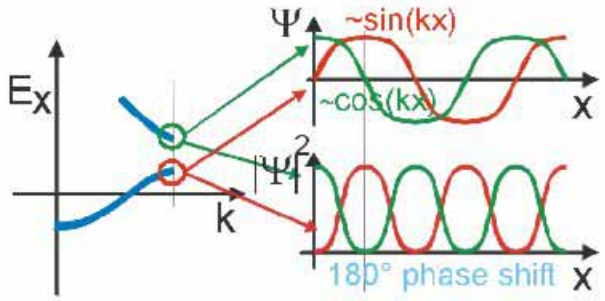
Band gap

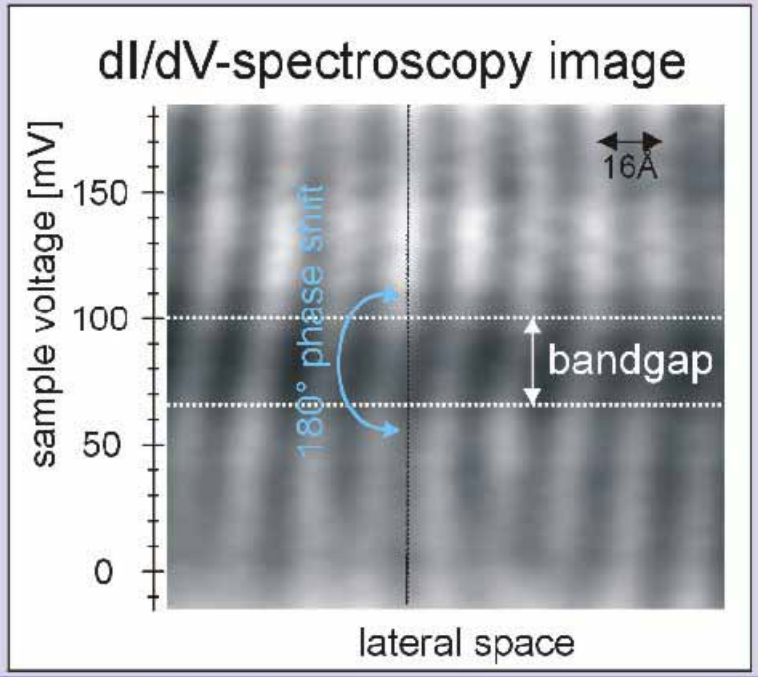
- Incomensurate growth causes Moiré patterns.
- This gives rise to a modulation of the electron potential and thereby creates a 1D bandgap in the 2D band.
- dI/dV images show the bandgap behavior.

NFE-model:

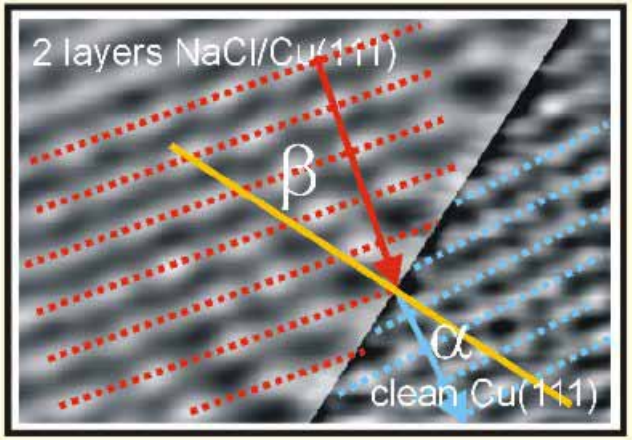
for $k_X = k_V/2$:

$$\Psi = \begin{cases} \sin(k_X x) \\ \cos(k_X x) \end{cases}$$





Refraction of surface electrons

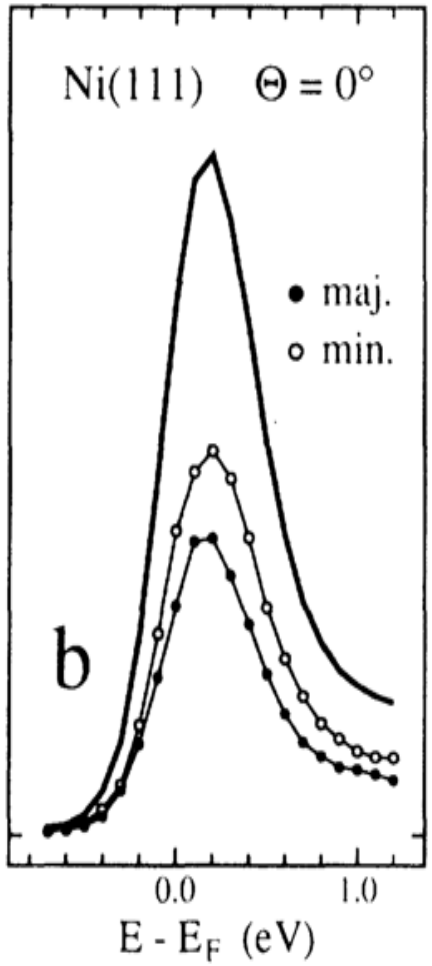


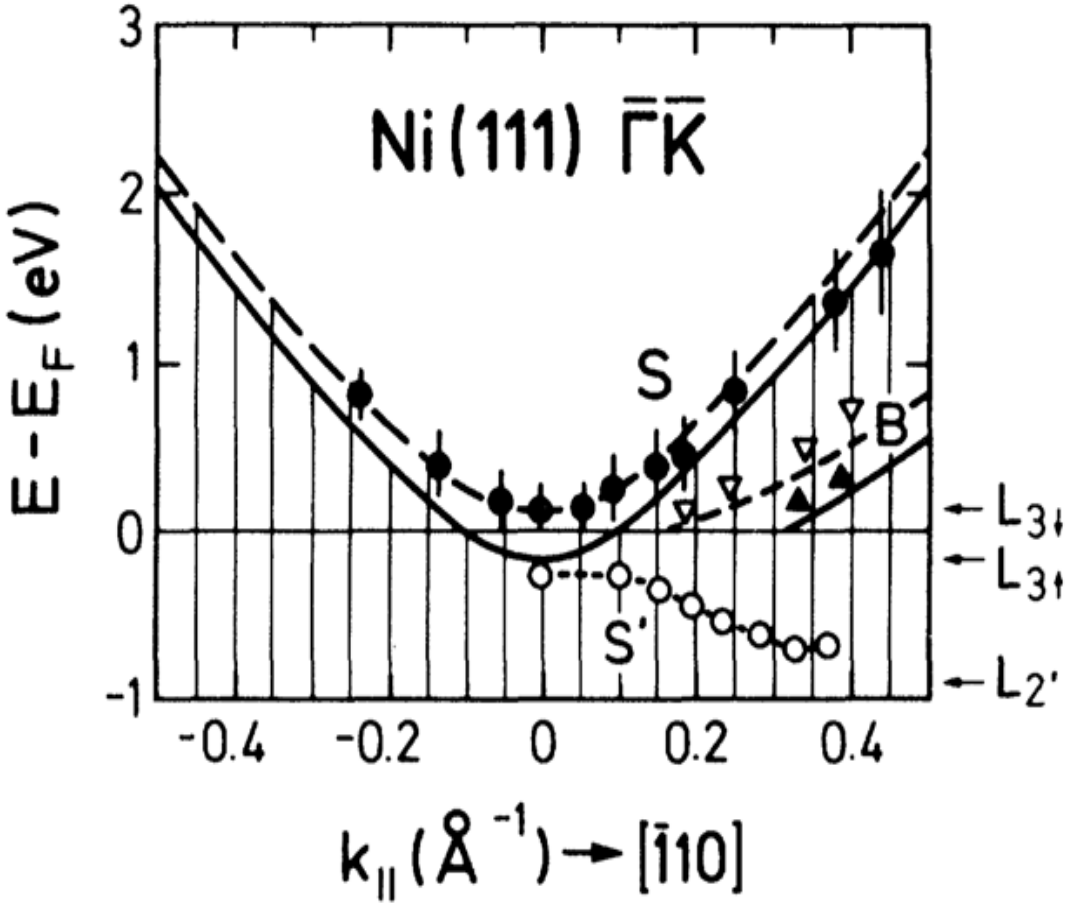
- Standing wave pattern on NaCl is due to the band gap.
- Also on the clean Cu near NaCl islands there is a strong wave pattern.
- These patterns at island edges obey Snell's refraction law.

Conservation of k_{II} → $\frac{\sin\alpha}{\sin\beta} = \frac{\lambda_1}{\lambda_2}$

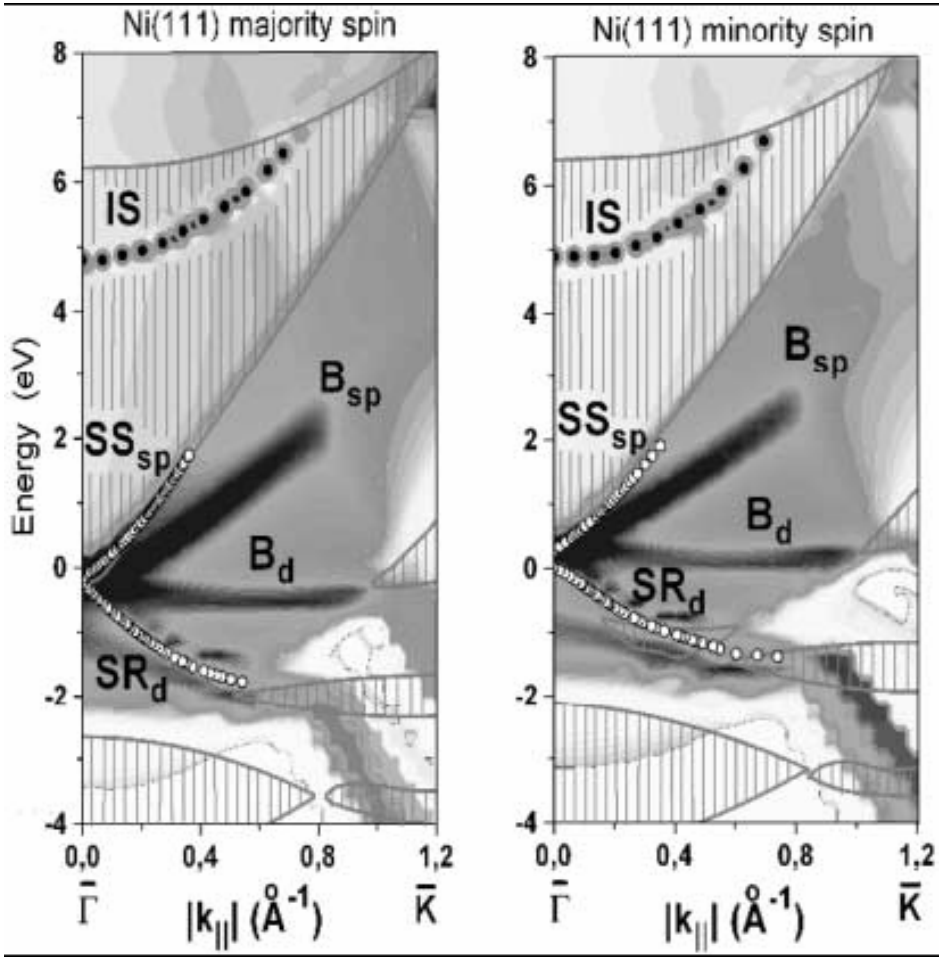
Spin-split surface state on Ni(111)?

Spin-resolved inverse photoemission from Ni(111):





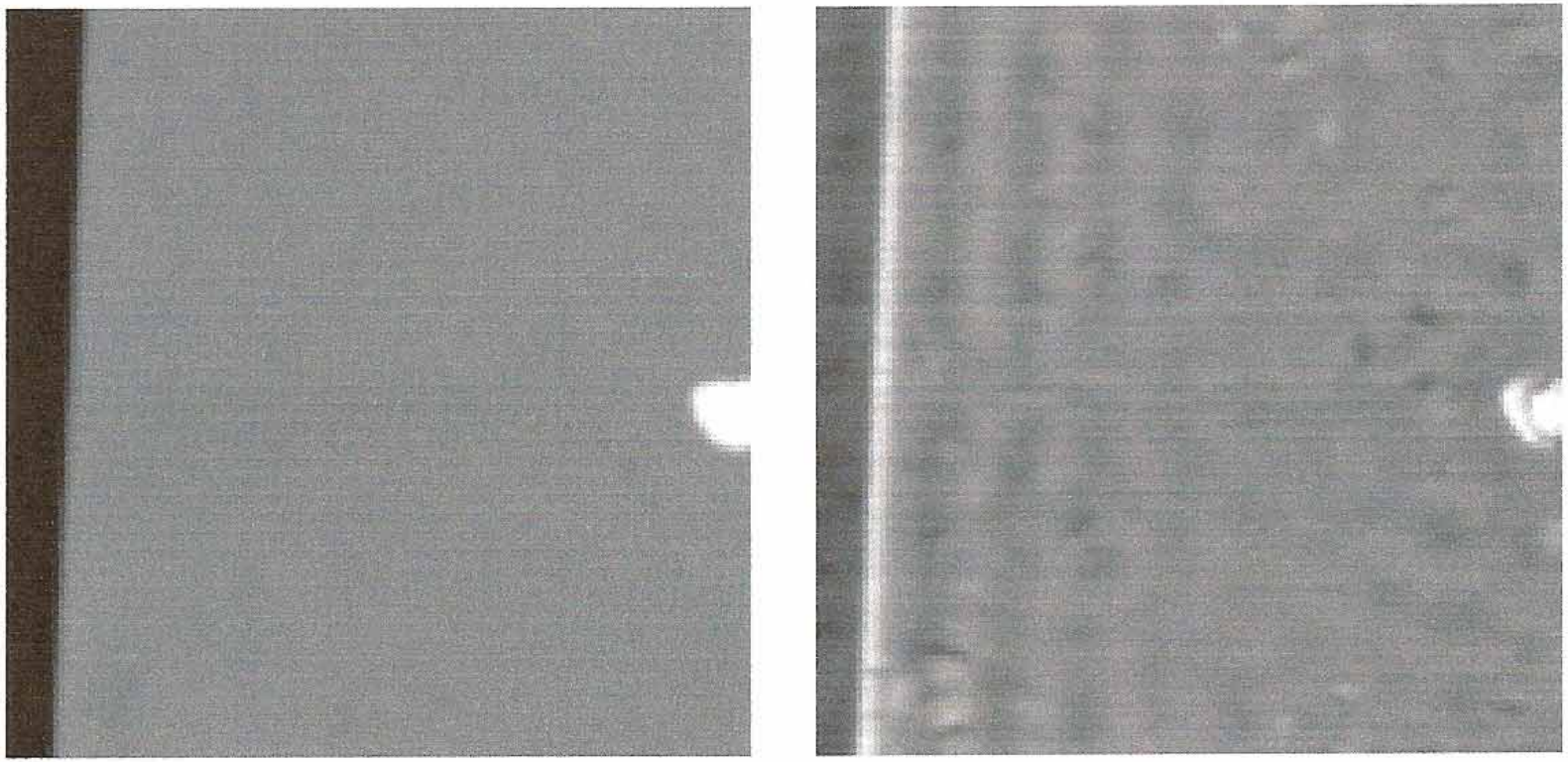
M. Donath, F. Passek, V. Dose, Phys. Rev. Lett. 70, 2802 (1993)



J. Braun, M. Donath, Europhys.Lett. 59, 592 (2002)

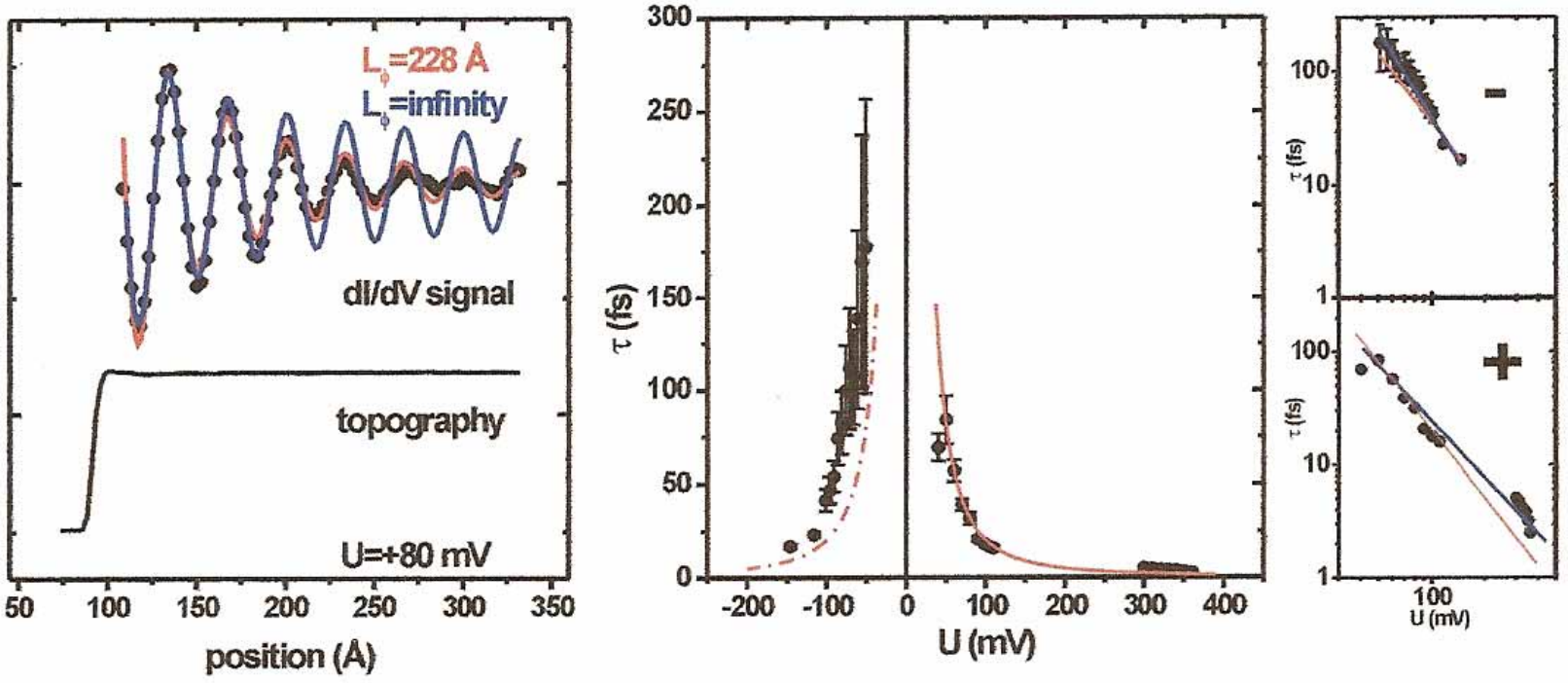
Ni(111)

Left: Topography of region with straight step edge.

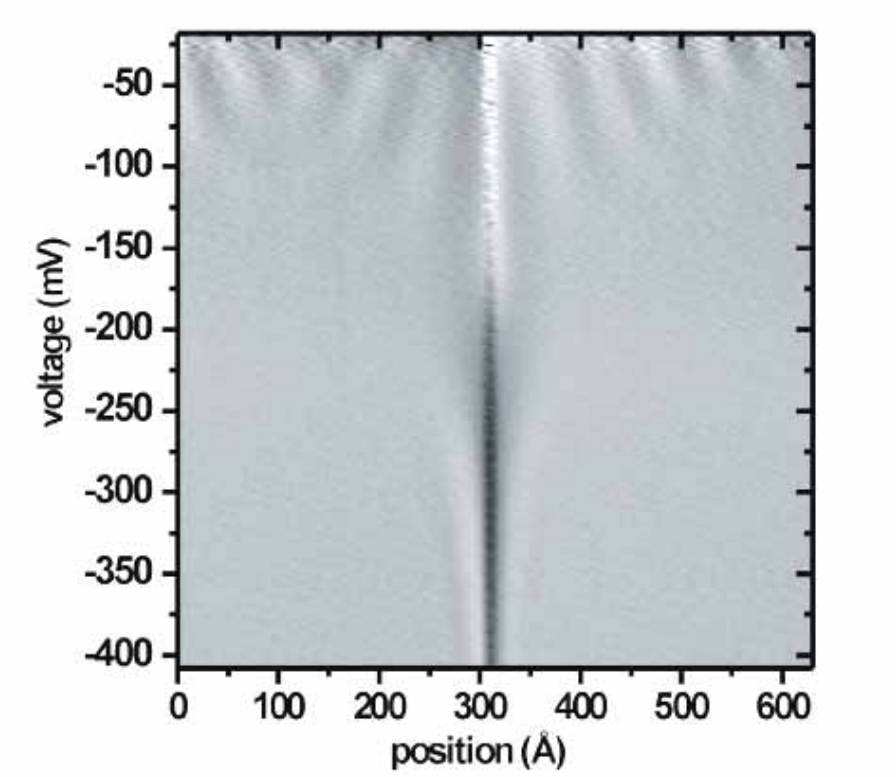


Right: dI/dV map showing standing wave pattern at step edge as well as adsorbates which appear as faint depressions (+80mV, 315x315 A).

Ni(111)


L_φ=228 Å
L_φ=infinity
dI/dV signal
topography
U=+80 mV
50 100 150 200 250 300 350
position (Å)
300 250 200 150 100 50 0
τ (fs)
-200 -100 0 100 200 300 400
U (mV)
100 10 1
τ (fs)
-
+
100
U (mV)

Ni(111)



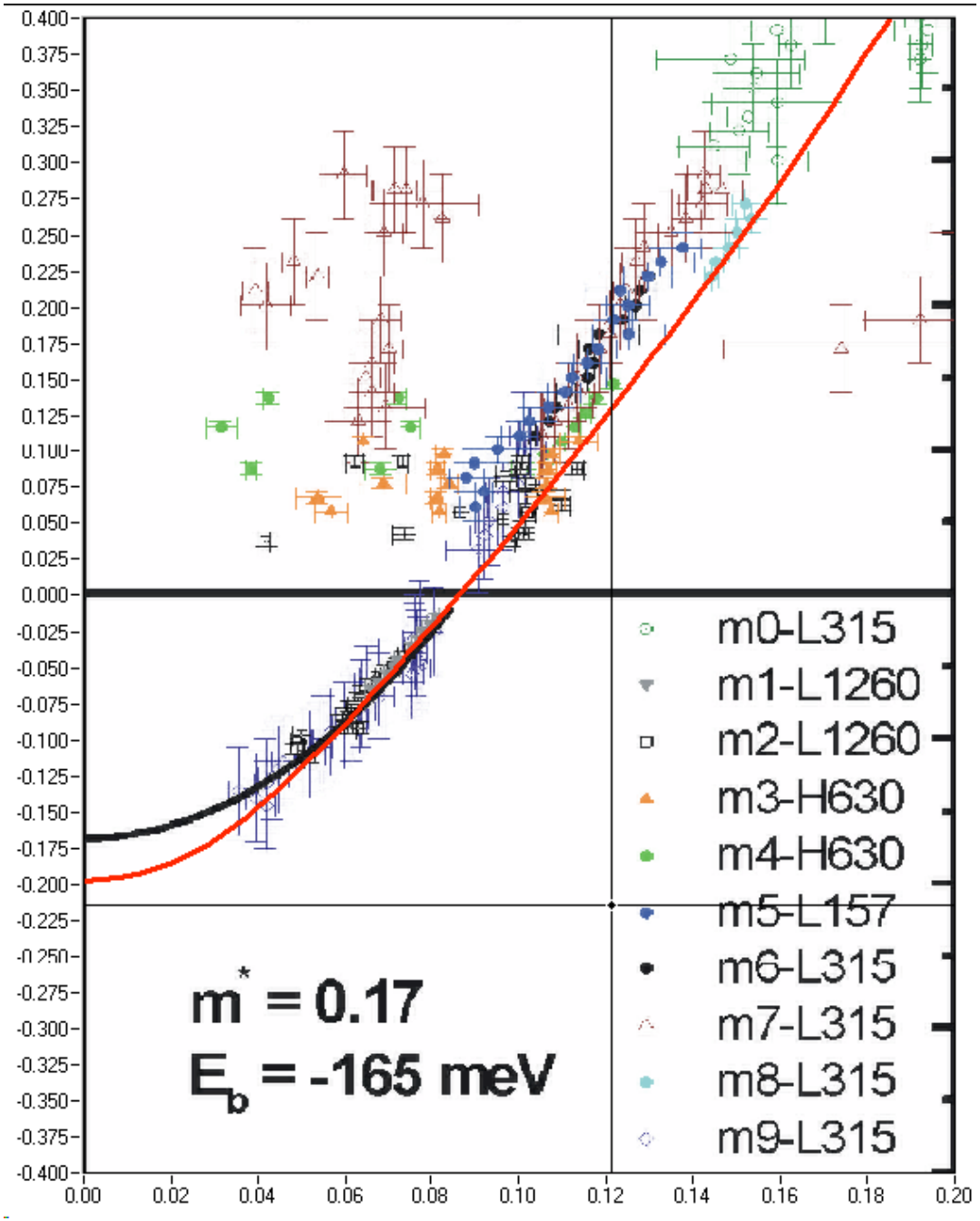
C.F.J. Flipse, K.-F. Braun, A. Grechnev, M.I. Katsnelson, A.I. Lichtenstein, K.H. Rieder, to be published

Ni(111)

Ni(111) surface sp-state dispersion (spin-up).

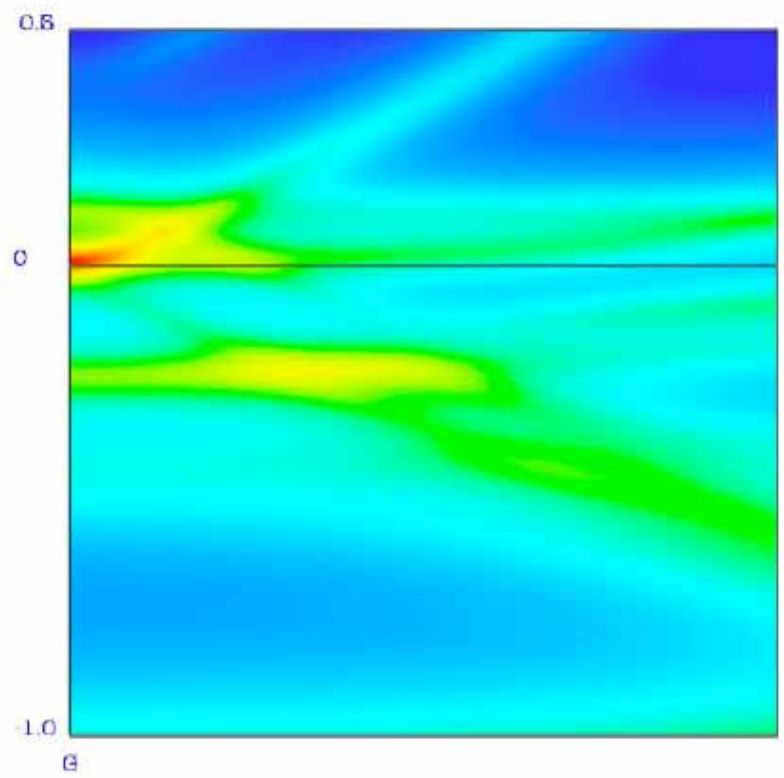
Different colours correspond to different data sets, solid black line is parabolic fit to the data at negative voltages. L low scatterer density, H higher scatterer density (Au atoms).

DMFT-calculated dispersion in red.

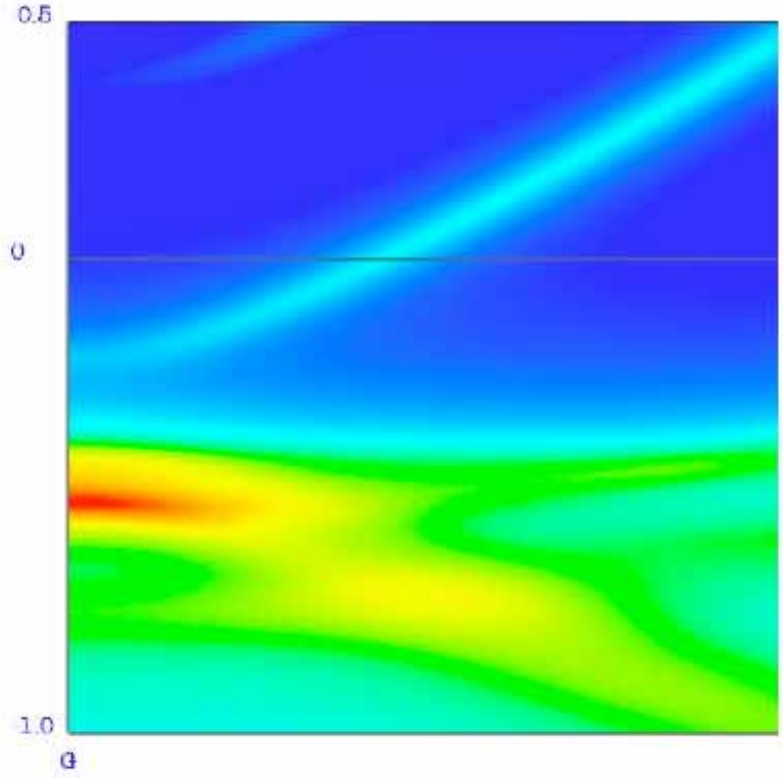


Ni(111)

Spin resolved DFT-calculations of surface states along Gamma-K



spin-down



spin-up

A.Grechnev, M.I. Katsnelson and A.I. Lichtenstein

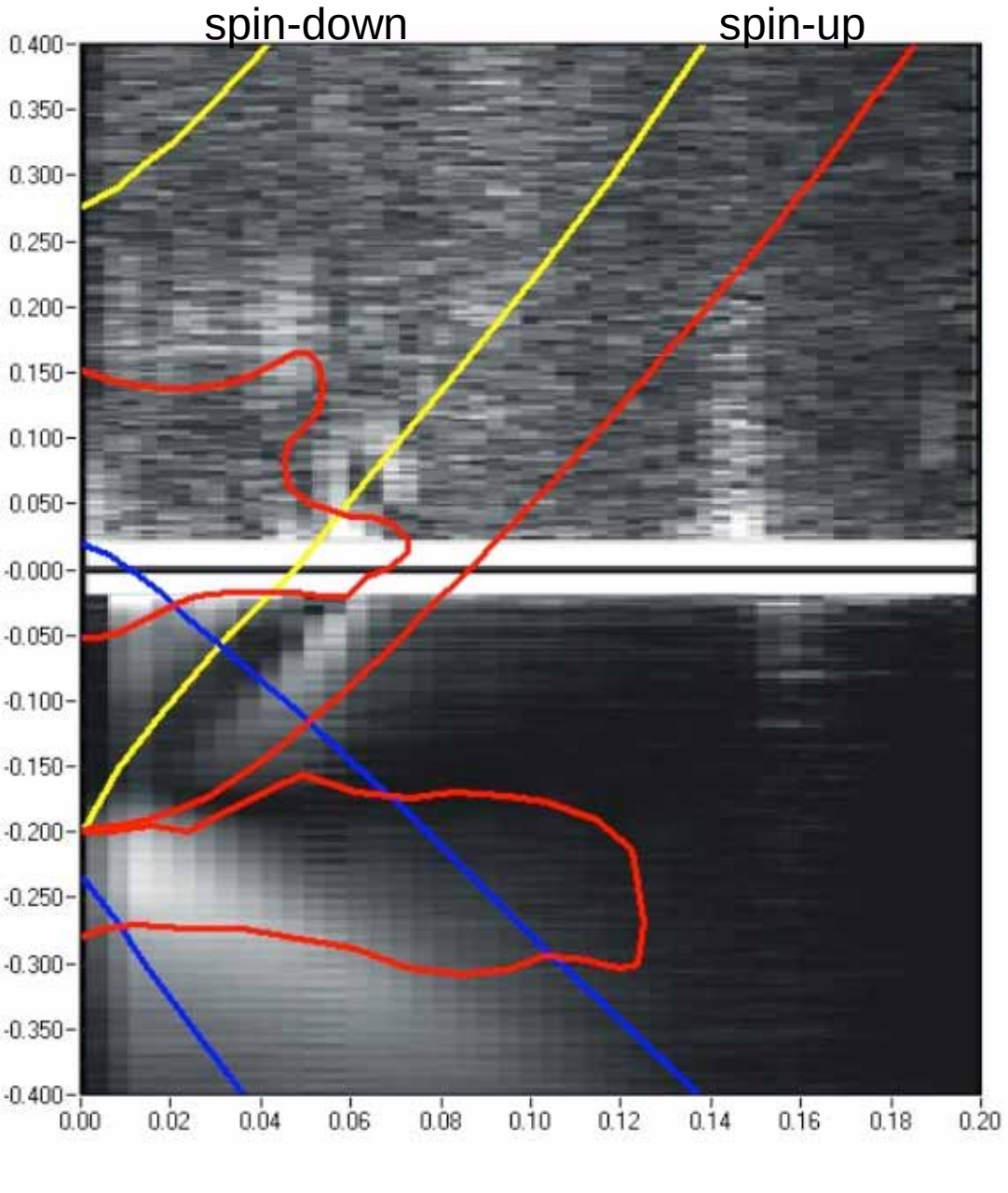
Ni(111)

experimental power spectra of dI/dV linescans and

theoretical results for surface electronic states

Braun & Donath (Europhys. Lett. 59, 592 (2002)
Yellow: sp-surface state
Blue: d-resonance

Red: DFT-Results for sp-surface state (spin-up) and d-resonance (spin-down) (Grechnev, Katsnelson &Lichtenstein)

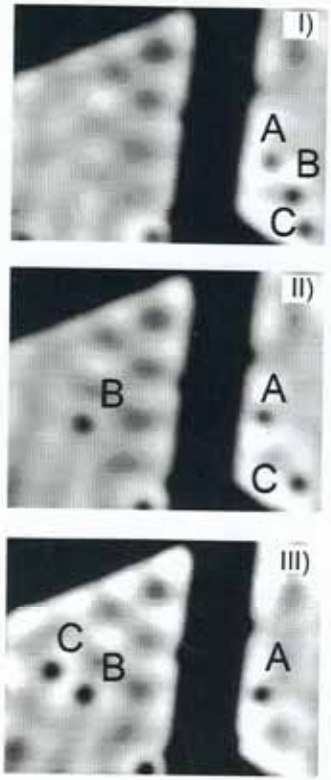


Parameters of the surface state dispersion on (111) noble metal surfaces in comparison to Ni.

The energy at the band bottom at T= 30K is from F. Reinert et al., Phys. Rev. B 63, 115415 (2001). RT values (a) from F. Baumberger et al., Phys. Rev. B 64, 195411 (2001) and (b) R. Paniago et al. Surf. Sci. 336, 113 (1995)

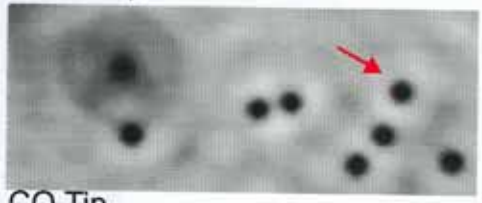
	$E_0 - E_F$ (eV)	m^*/m_e	$k_F(A^{-1})$
Cu	-0.435 (-0.391[a])	0.412	0.215
Au	-0.487 (-0.440[b])	0.255	0.167/0.192
Ag	-0.063 (-0.026[b])	0.397	0.080
Ni (spin-up)	-0.165	0.17	0.085

Vertical Manipulation of CO on Cu(111)



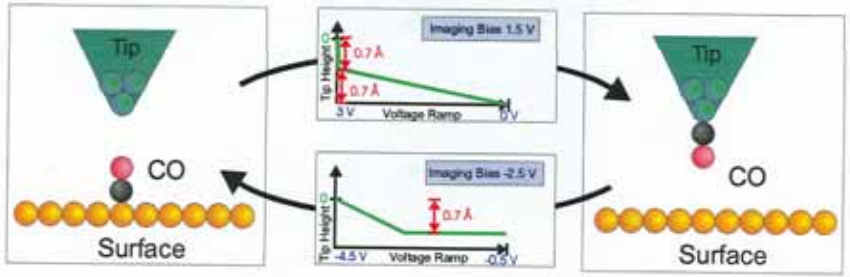
Transfer of single CO molecules from the right to the left terrace

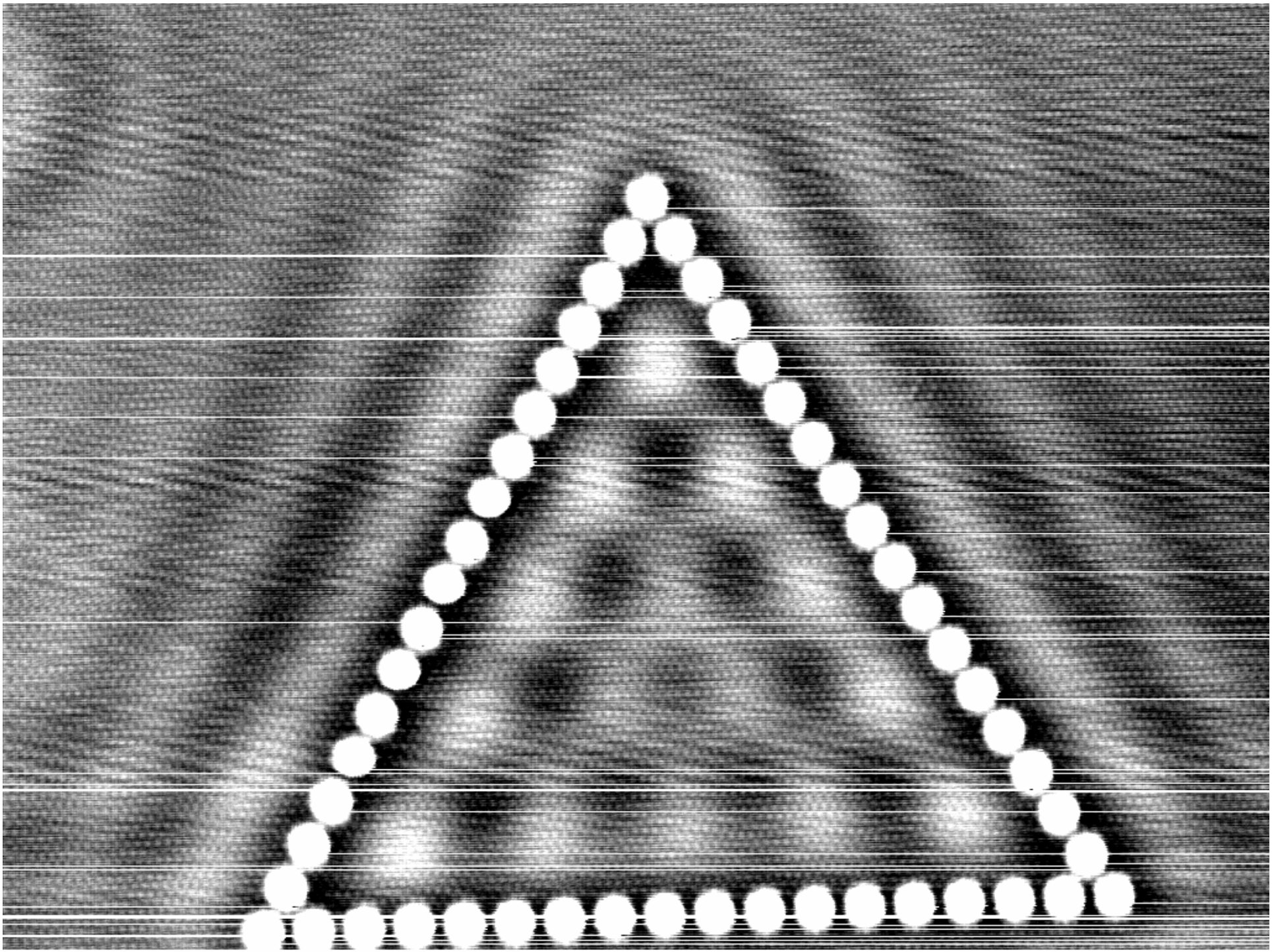
Metal Tip

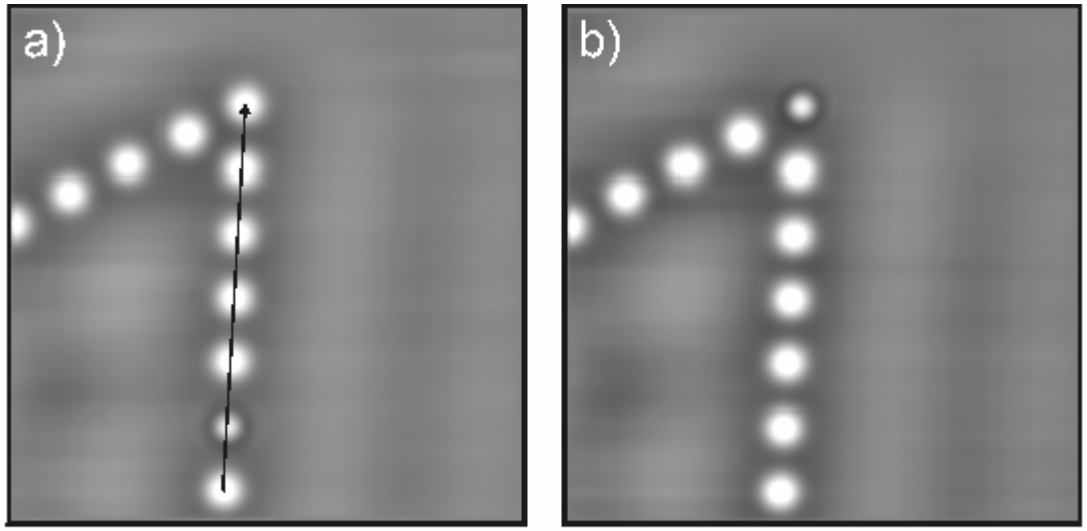


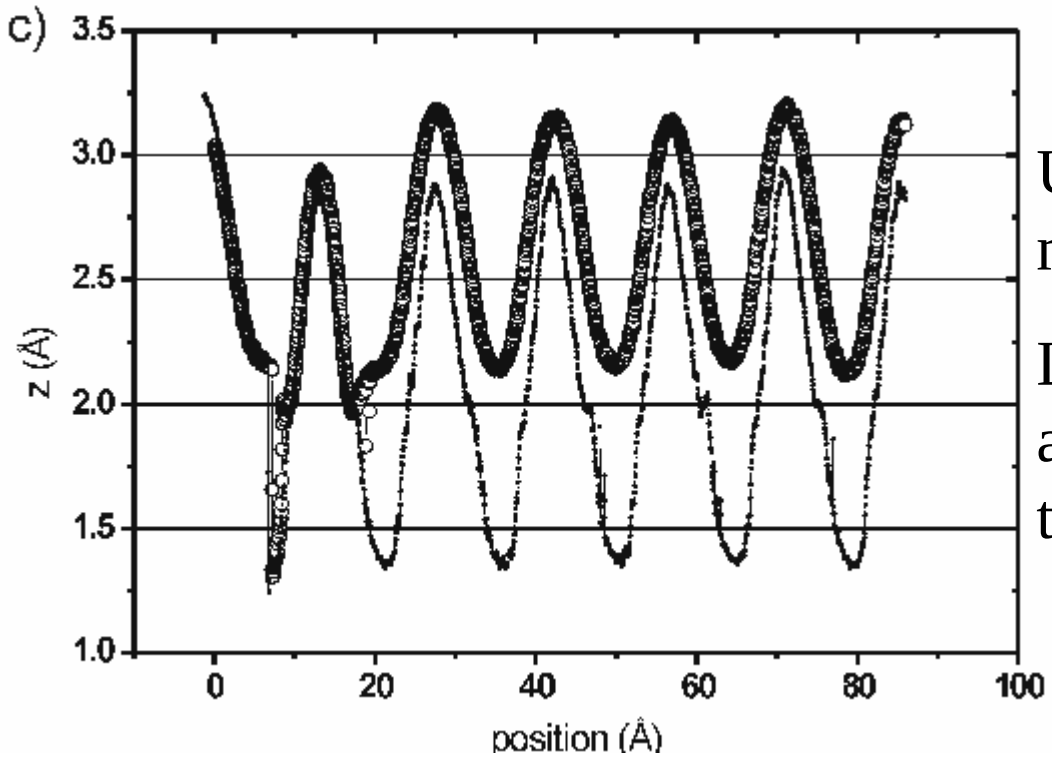
CO Tip

L. Bartels, G. Meyer, K. H. Rieder, Appl. Phys. Lett. **71**, 213 (1997)





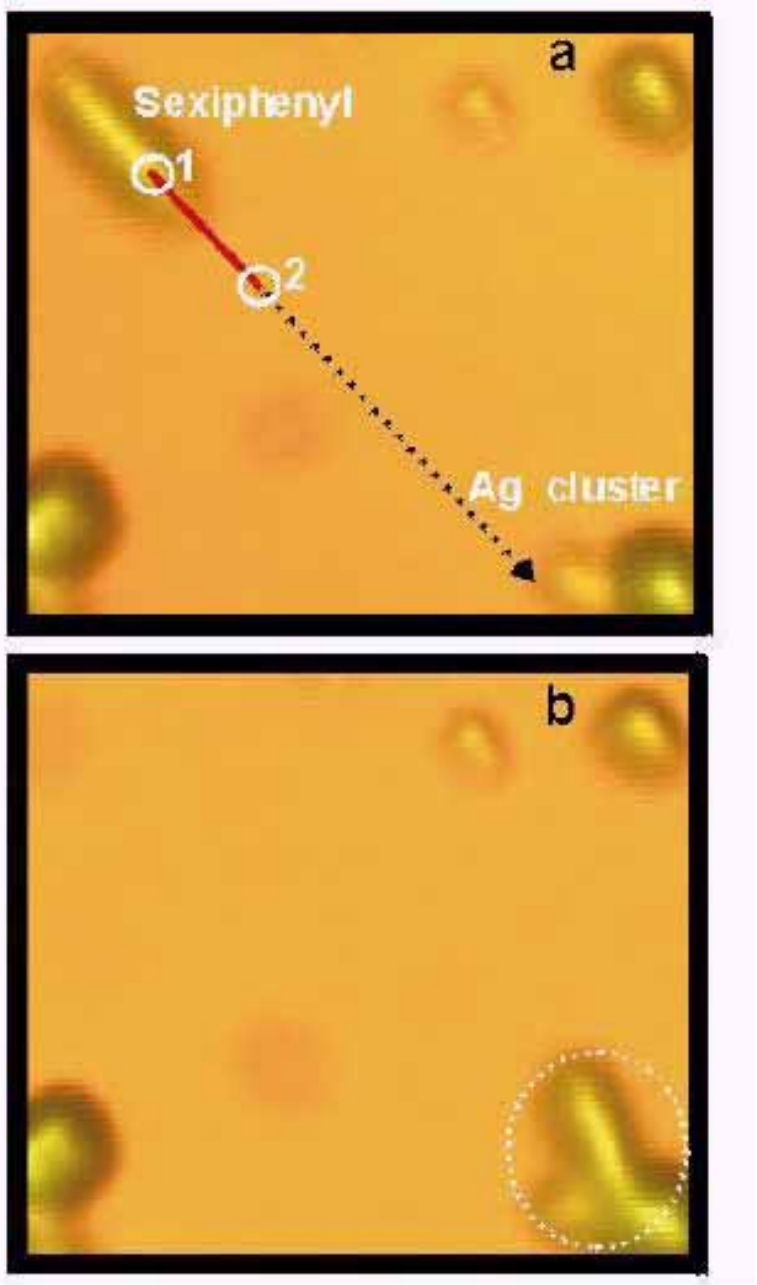




Upper curve: tip moves over adsorbate

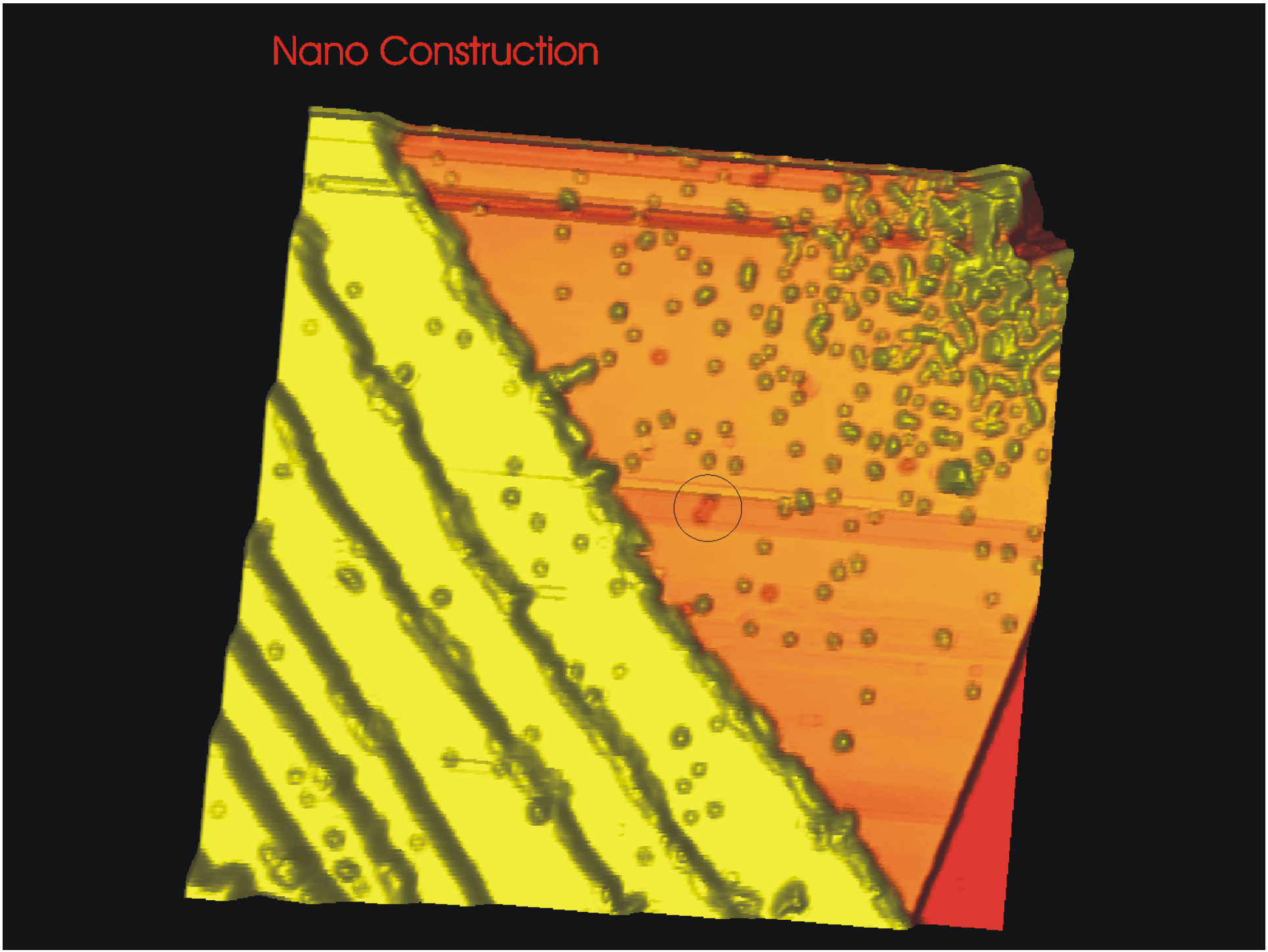
Lower curve: adsorbate moves with tip

K.H. Rieder et al., Philos. Transact. Roy. Soc. 362, 1207 (2004)



Molecule"shooting". (a) A sexiphenyl molecule at the upper left corner is dragged over 3.3 nm along the red line from location '1' to '2'. The molecule continues to travel further after withdrawing the tip and hits a silver cluster
located at the lower right corner 10 nm away from the initial position (b). The molecule´s final location deviates by ~2nm from the straight-line path indicated by the dashed arrow.
(Image: 11 nm x 9.5 nm,
shooting parameters: R_t= 1.5 *x* 10^5 Ω ,
V_t = 30 mV).

S.W. Hla, K.F. Braun, B.Wassermann and K.H. Rieder, Phys. Rev. Lett. 93, 208302 (2004)

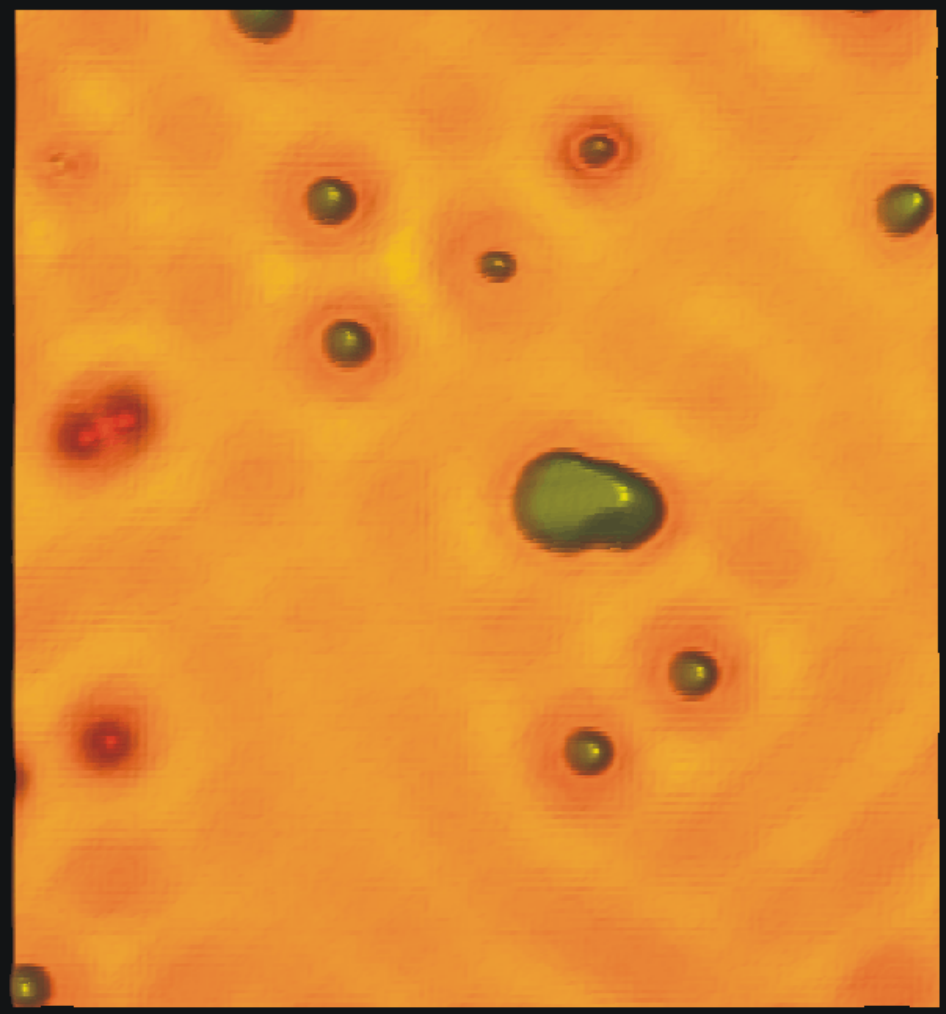

Nano Construction

Nano Construction

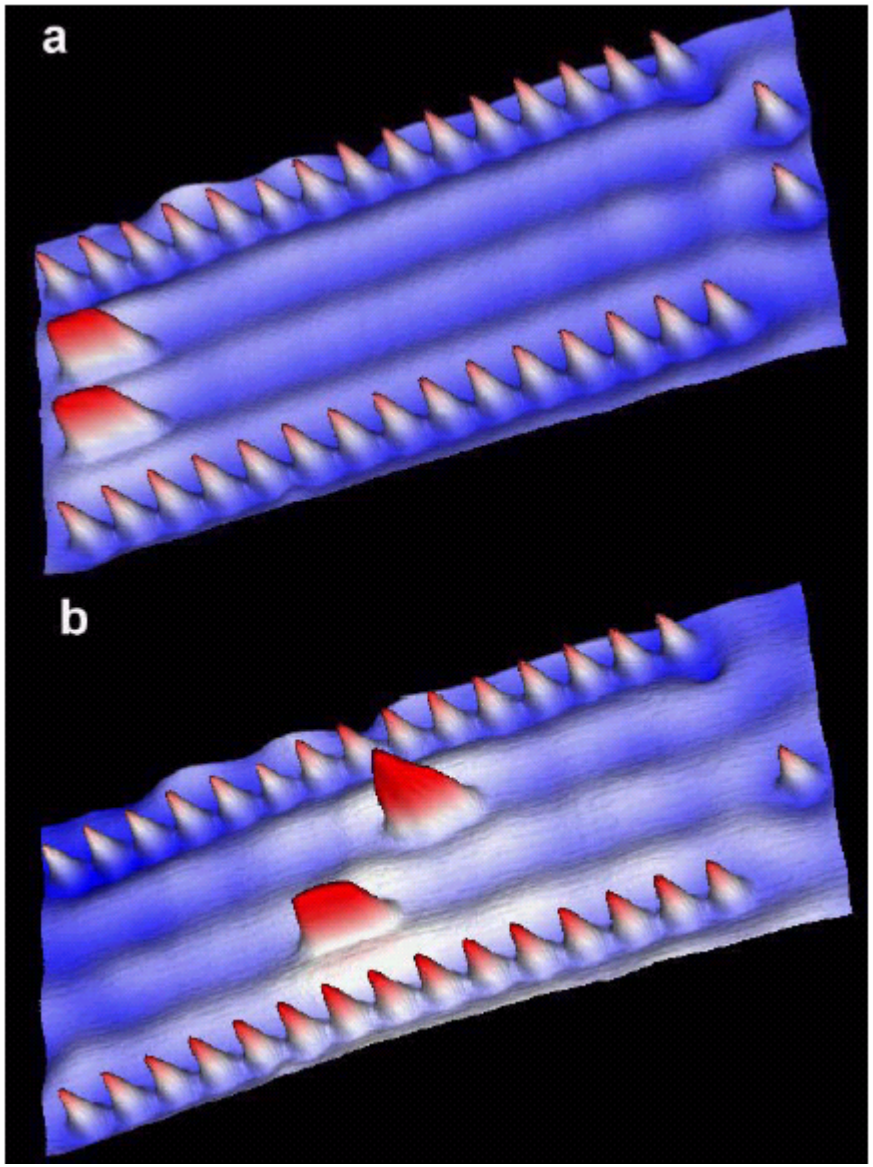
Saw-Wai Hla,

Kai-Felix Braun,

Karl-Heinz Rieder



Ag / Ag(111) at 6 K

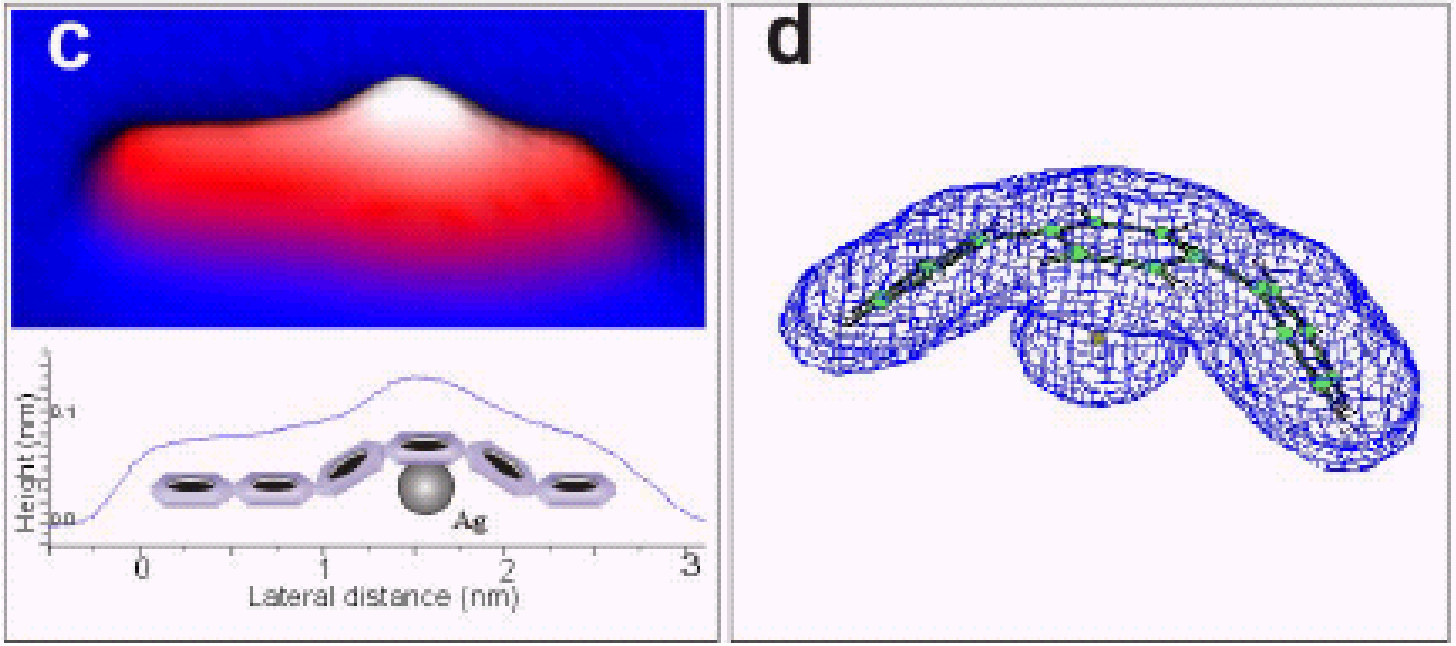


Nano-gun barrel

(a) Two sexiphenyl molecules (left end) are located inside the barrel. Two target silver atoms (right end) are positioned along the standing wave minimum in a straight-line path.

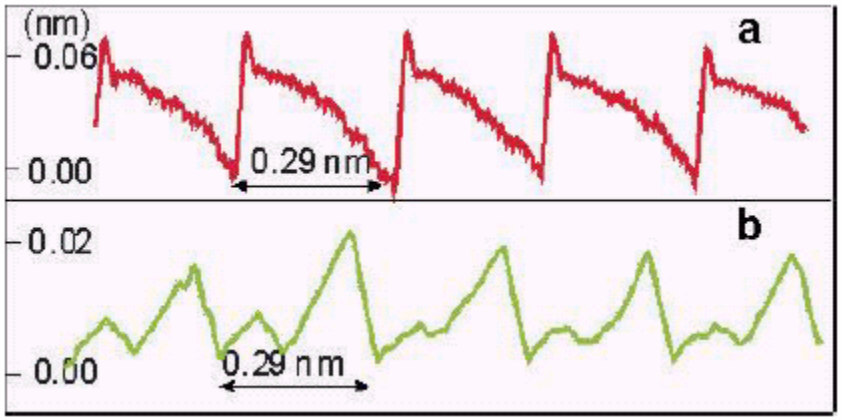
(b) Upon shooting the upper molecule towards the upper target atom a silver-sexiphenyl complex is formed. Both the complex and the lower sexiphenyl molecule are laterally moved with the STM-tip into the middle of the nano-barrel to ease visual comparison.

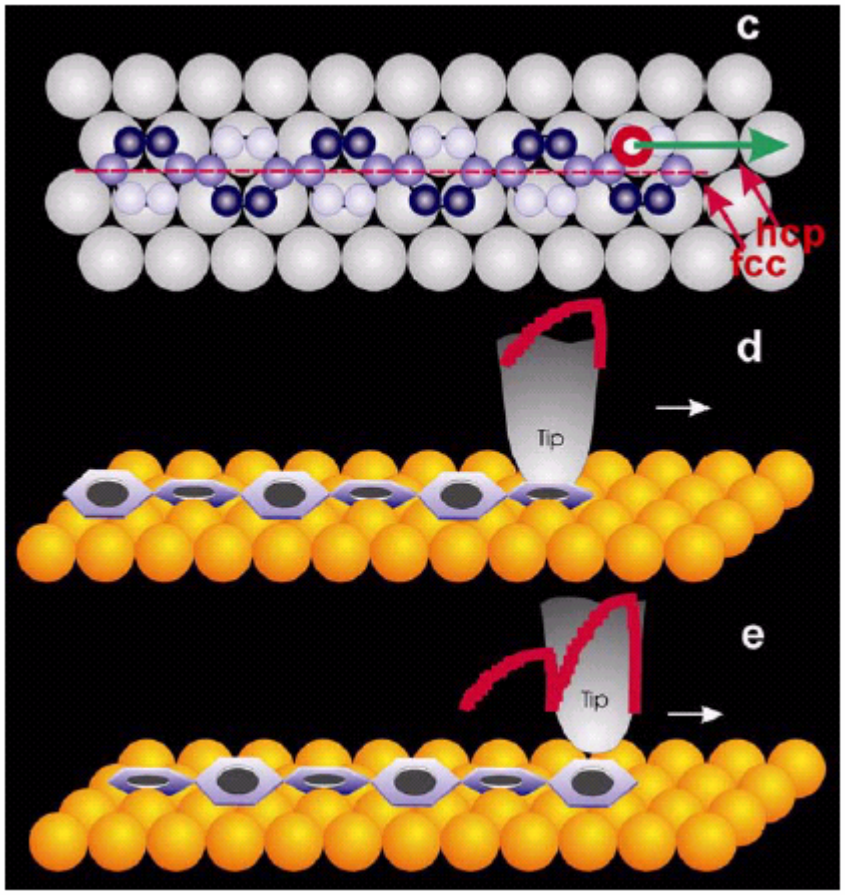
(Imaging parameters: V_t = 30 mV, I_t = 1.1 nA, 16 x 26 nm2).



(c) 3-D STM image of the silver-sexiphenyl complex and the corresponding tip-height profile. The determined silver position inside the complex is shown in the inset drawing.

(d) The computed silver-tarphenyl complex structure confirms bending of π-rings from the inter-ring joints to enclose the silver atom.





Manipulation experiments:

Typical STM pulling signal with single silver atom-distance jumps observed for lateral manipulation of **silver-sexiphenyl complex** (a).
Periodic low-high peak STM signal repeating at single silver atom distances observed for **bare sexiphenyl** lateral manipulation (b).
(c) illustrates **sexiphenyl adsorption geometry**. Red line indicates center axis of molecule; light and dark balls represent carbon atoms from the **up and down sites of π-rings**, respectively. Tip position - illustrated with redwhite circle - is shifted 0.1 nm to the side of the molecule axis in order to detect the up-down movement of the π-ring caused by **flipping between the two positions**. Tip is located 0.27 nm above the molecule and moved along the direction indicated by the green arrow. When **tip is in low-site of π-ring**, a **low-height manipulation signal** is observed (d);
higher height signal is obtained when tip is in up-site of the π-ring (e).
(Manipulation parameters: V_t =49 mV, R_t = 600 kΩ)

S.W. Hla, K.F. Braun, B.Wassermann and K.H. Rieder, Phys. Rev. Lett. 93, 208302 (2004)

VOLUME 84, NUMBER 26 PHYSICAL REVIEW LETTERS 26 JUNE 2000

Atomic Scale Engines: Cars and Wheels

Markus Porto, Michael Urbakh, and Joseph Klafter

[redacted]

The proposed engine consists in general of two parts: the supporting carrier and the moving object. Achieving motion of the engine is based on dynamical competition between the two intrinsic lengths of the carrier and the object. This competition is used to transform initially fed energy to directed motion. To exemplify the concept, we use below a *simple* model system of a chain in a periodic potential, namely, a Frenkel-Kontorova-type model [13].

1D model: Supporting carrier is surface with periodic potential $\Phi(x) = -\Phi_0 \cos(2\pi x/b)$

Moving object is chain of N identical particles at x_i with mass m with rest distance a_i.

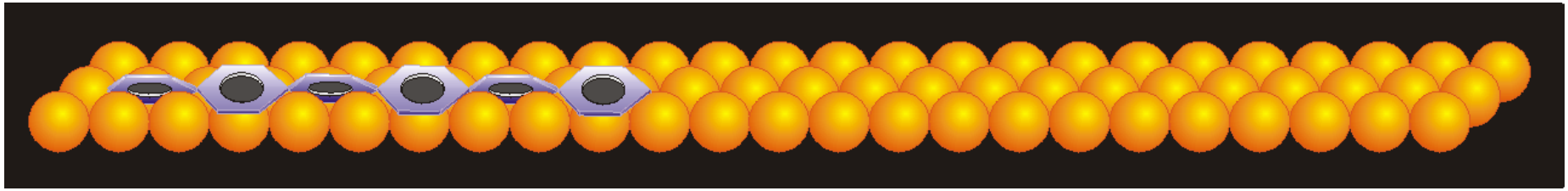
$$m\ddot{x}_i + \eta\dot{x}_i + \frac{\partial\Phi(x_i)}{\partial x_i} + \sum_{\delta_i} \frac{\partial\Psi(x_i - x_{i+\delta_i})}{\partial x_{i+\delta_i}} = 0 \qquad i = 1, \ldots, N$$

Second term describes friction between particles and surface (proportional to relative velocities).

Static interaction between particles and surface governed by surface potential with periodicity b.

Interparticle interaction is described by nearest neighbor harmonic forces.

If **energy is pumped** into the system in a specific manner that provides spatially and temporally correlated changes of the particle distances, the dynamical competition between the periodicity b and the rest lengths a_i can induce a **directed motion** of the chain.



Created by Saw-Wai Hla

Possibly *realization of an idea* of

Markus Porto, Michael Urbakh and Joseph Klafter:

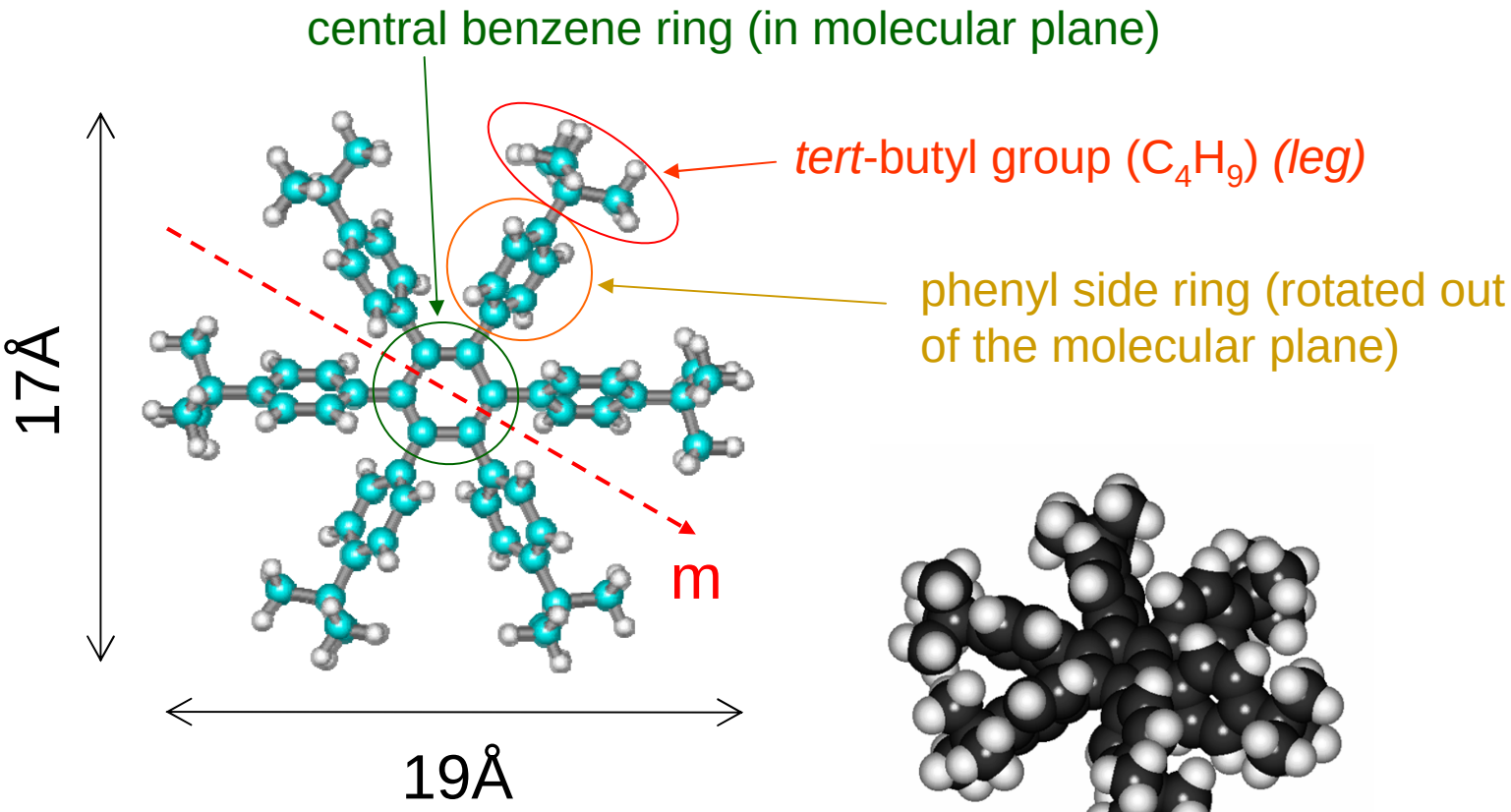
„Atomic Scale Engines: Cars and Wheels“

Phys. Rev. Lett. 84, 6058 (2000)

See also homepage of Prof. Markus Porto at University Frankfurt

Hexa-*tert*-butyl-hexaphenylbenzene

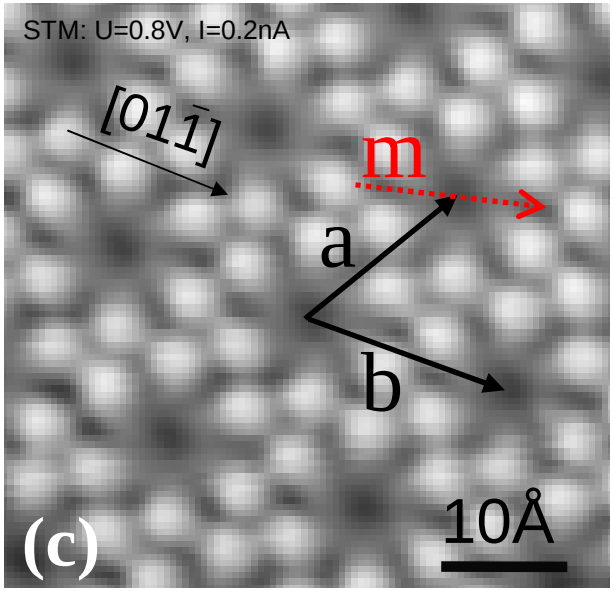
HB-HPB: $C_{42}H_{30}$

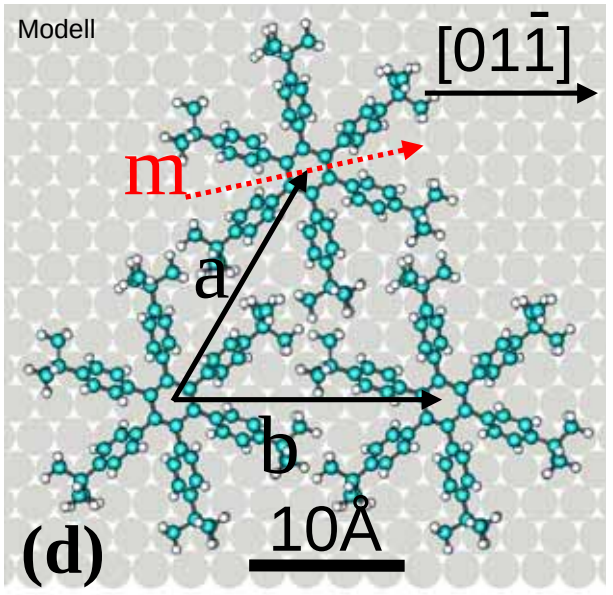


Synthesis: André Gourdon
CEMES-CNRS Toulouse

Tilt of side rings leads to a overall propeller shape of the molecule

Monolayer Structure





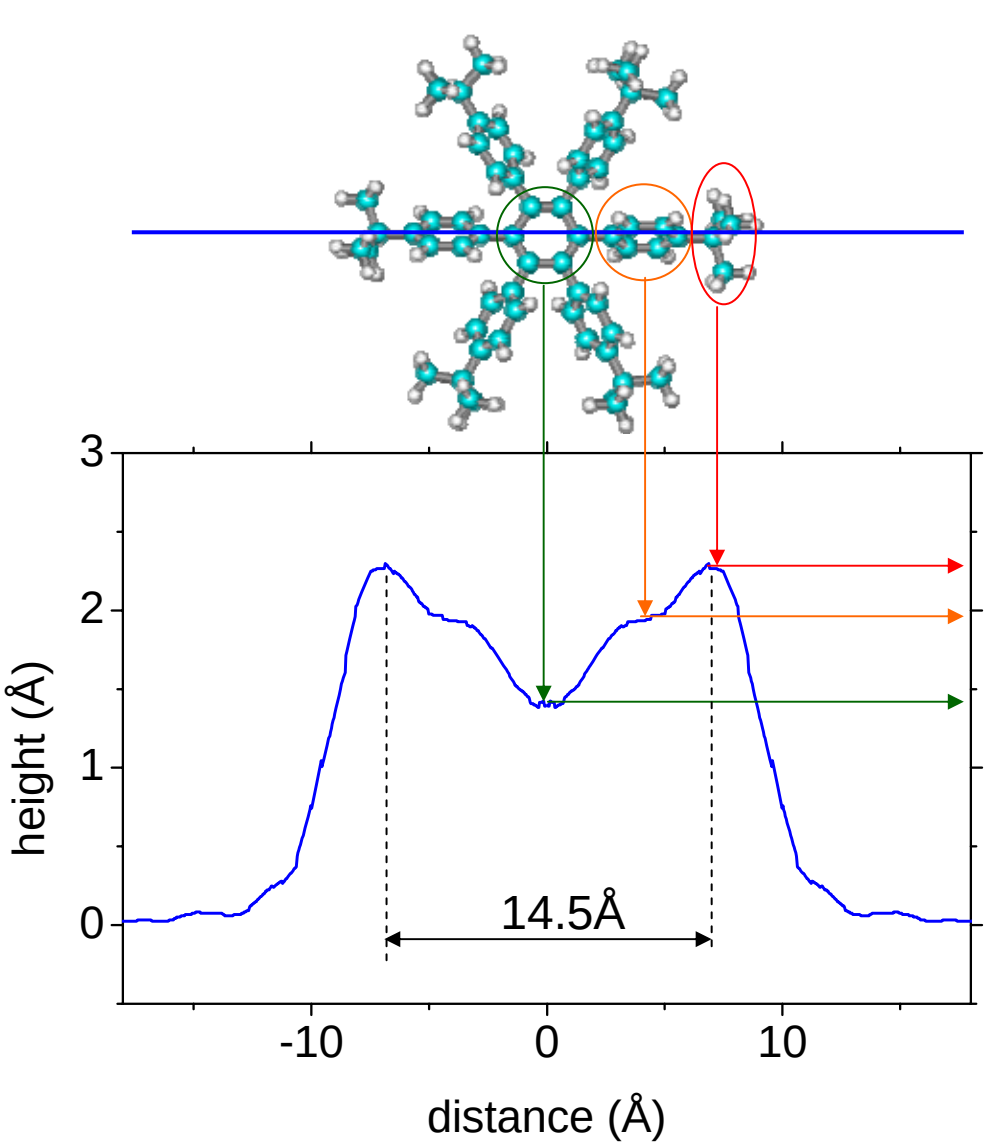
Structure matrix:

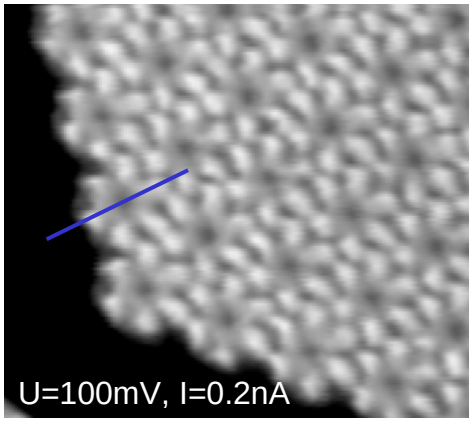
$$HB-HPB \begin{pmatrix} 7 & 0 \\ 0 & 7 \end{pmatrix} Cu(111)$$

Monolayer orientation (**b**, [01-1]): **0°**

Molecular orientation (**m**, [01-1]): **±11°**
(either +11° or -11° for all molecules in one molecular island)

Intramolecular Contrast





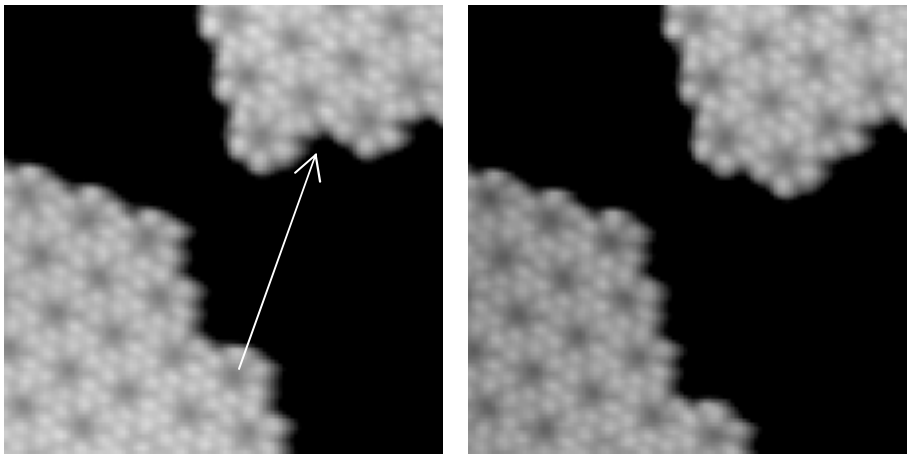
tert-butyl legs 2.3 Å

phenyl side rings 2.0 Å

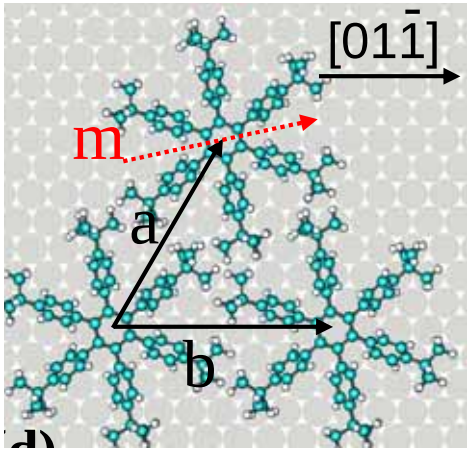
central benzene ring 1.4 Å

- STM distinguishes between different molecular parts
- Molecular orientation can be determined.

Manipulation between Molecular Islands



Manipulation in constant current mode: U=50mV, I=50nA



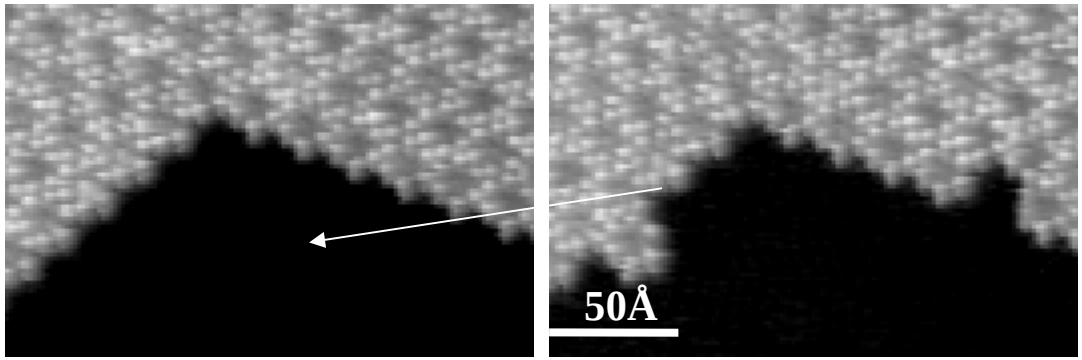
monolayer structure

Manipulation from the edge of one island to another island

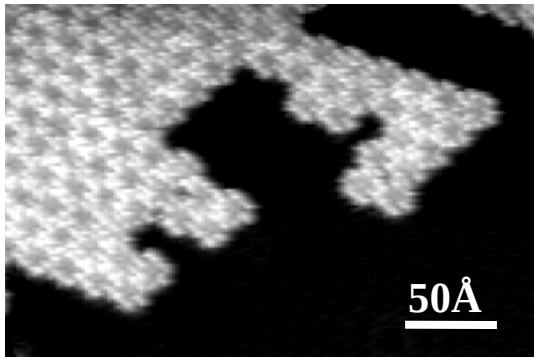
Molecule locks into monolayer structure at final position

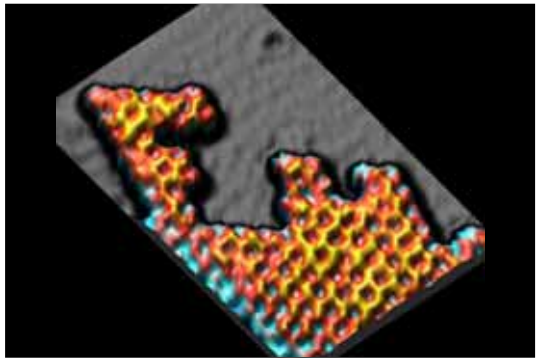
→ Final molecular position and orientation are precisely defined by the monolayer structure

Building Supramolecular Structures



Manipulation in constant current mode: U = 50mV, I = 10nA, R = 5MΩ



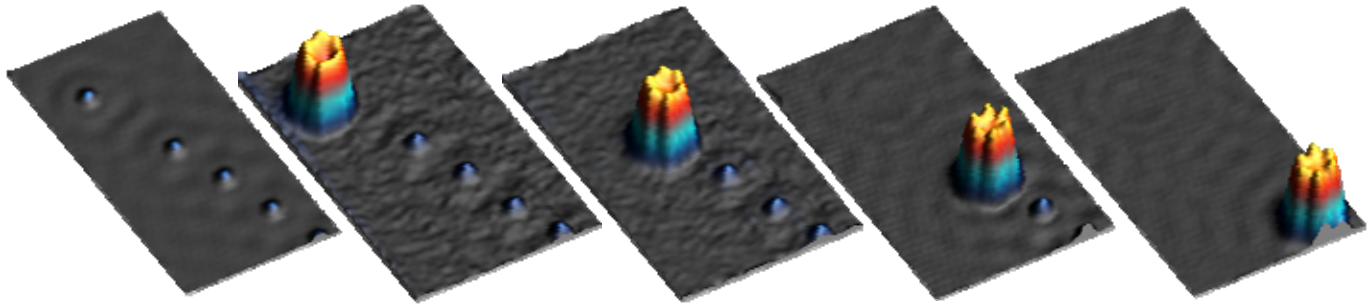


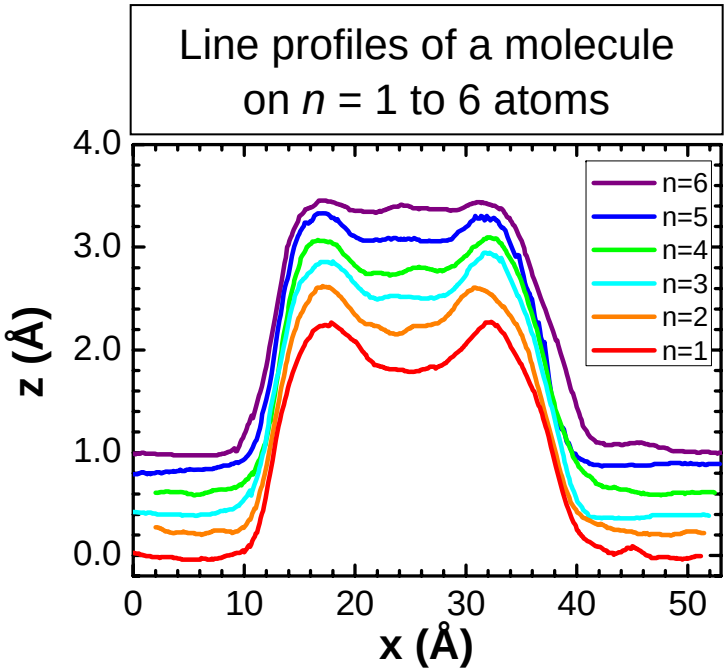
„La Linea“

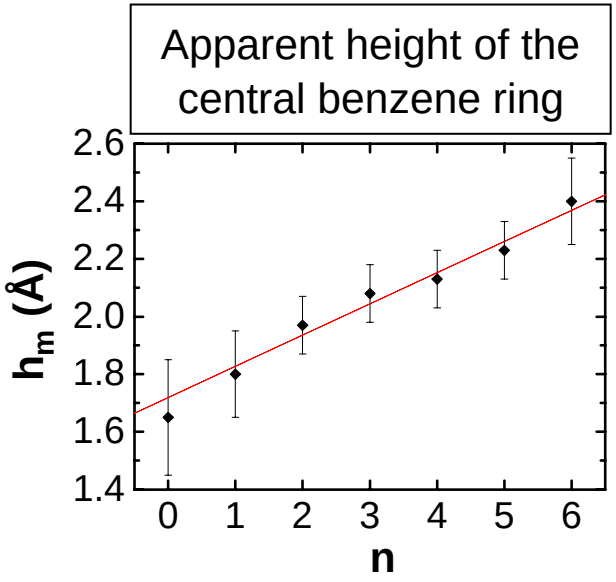
Osvaldo Cavandoli

FU written from 36 HB-HPB molecules, which are in registry with the (7x7) monolayer structure on Cu(111).

STM induced molecular manipulation and molecular self-ordering are combined to create well defined artificial molecular structures







- Apparent height of the molecular board h_m increases with n.
- Atoms are accumulated under the molecular board (“Molecular dumper truck”).

L.Gross, K.H. Rieder. F. Moresco et al., Nature Materials 4, 892 (2005)

Isomerization:

The geometrical structure

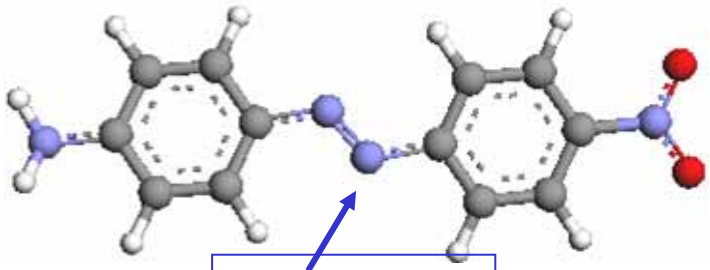
but not the composition of a compound is rearranged.

Disperse Orange 3

(Azobenzene derivate)

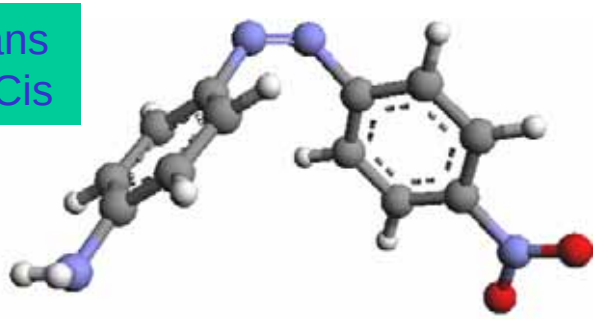
$NH_2C_6H_4N{=}NC_6H_4NO_2$

Amino- end groups Nitro-



"lone pair"

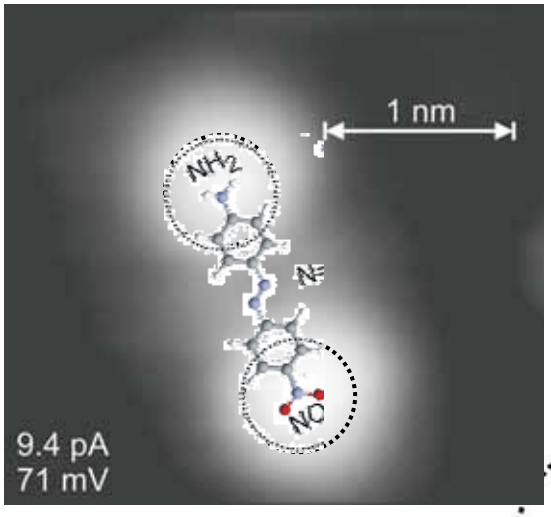
Trans
 Cis



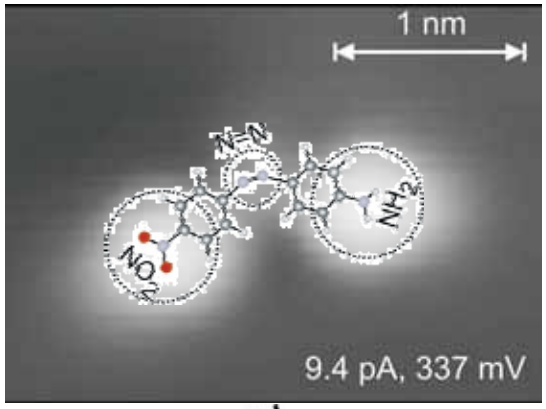
Conformational Cis-Trans-Isomerization of Azobenzene derivate:

Disperse Orange 3 ($NO_2C_6H_4N=NC_6H_4NH_2$) on Au(111))

Trans



Cis



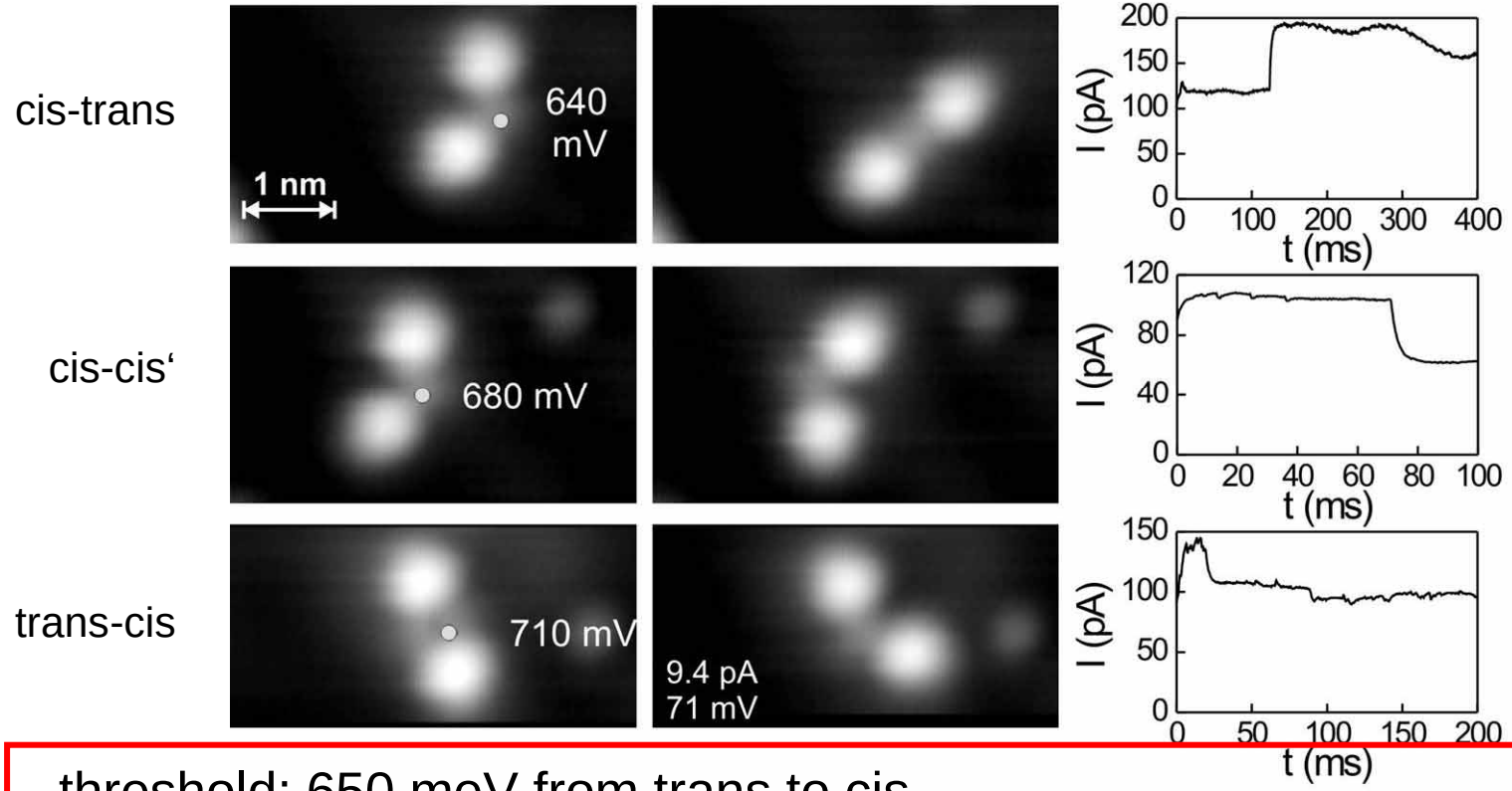
J.Henzl,
Michael Mehlhorn,
Heiko Gawronski,
K.H. Rieder and Karina Morgenstern: Angewandte Chemie Int. Ed. 45, 603 (2005)

planar adsorption geometry
with bond angle increased to 150°

Conformational Cis-Trans-Isomerization of Azobenzene

derivate: Disperse Orange 3 ($NO_2C_6H_4N=NC_6H_4NH_2$) on Au(111))

Injecting electrons into N=N bond

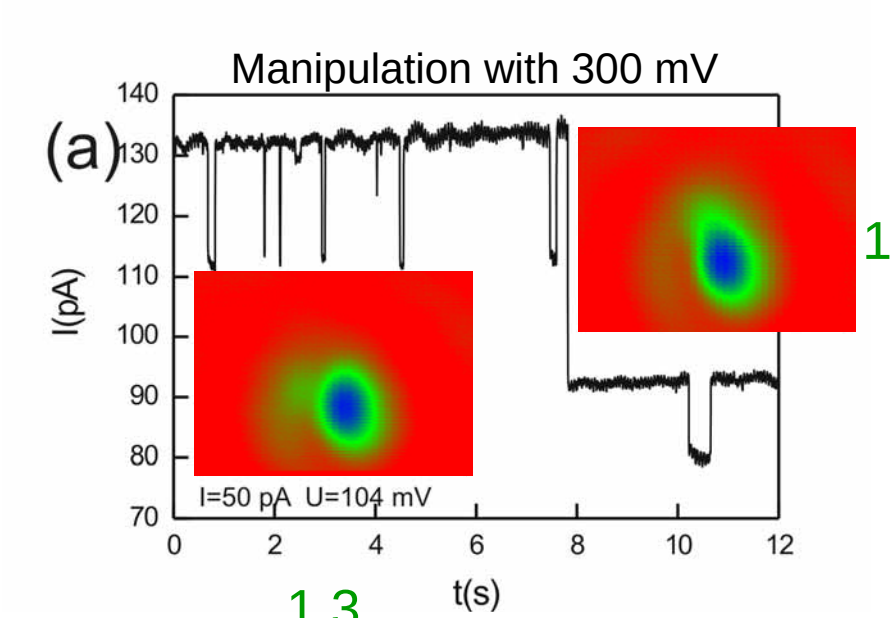


threshold: 650 meV from trans to cis

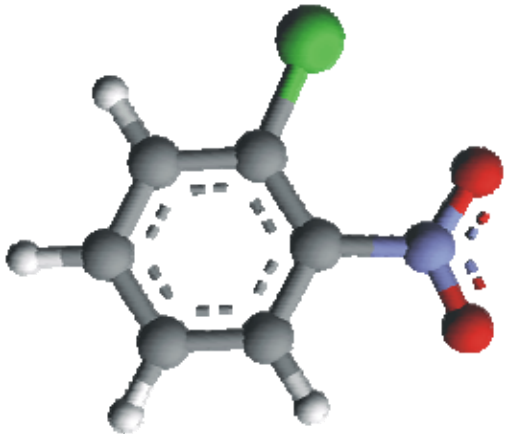
610 meV from cis to trans: far below optical switching energy

-> via excitation of vibrational modes

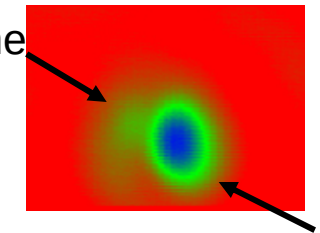
Configurational isomerization: $C_6H_4ClNO_2$ on Cu(111)



1,2

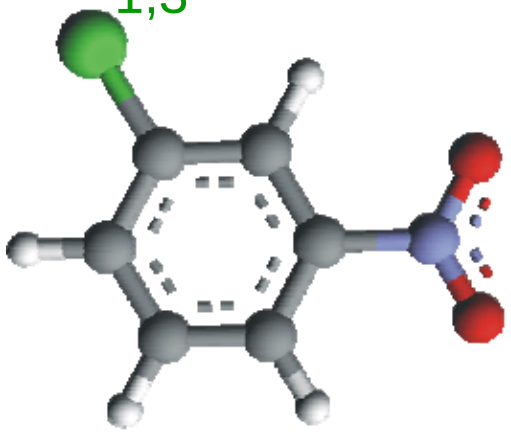


Chlorine



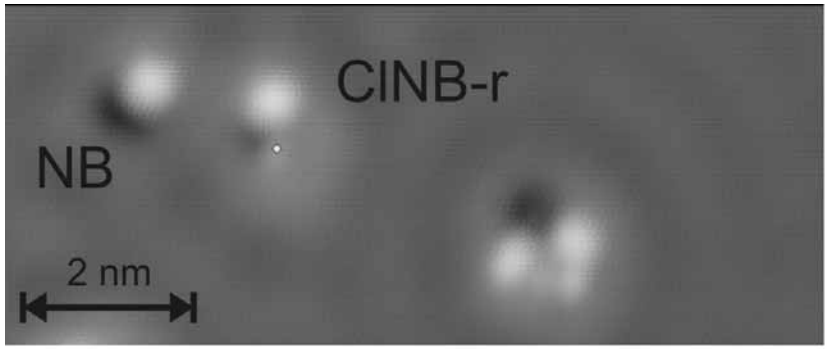
Nitro-group

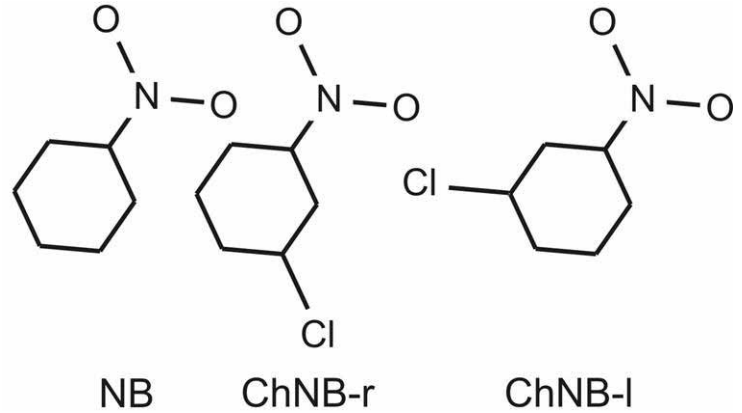
1,3

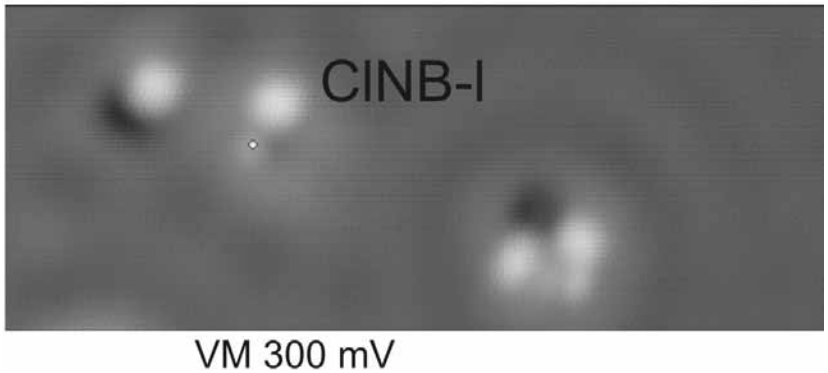


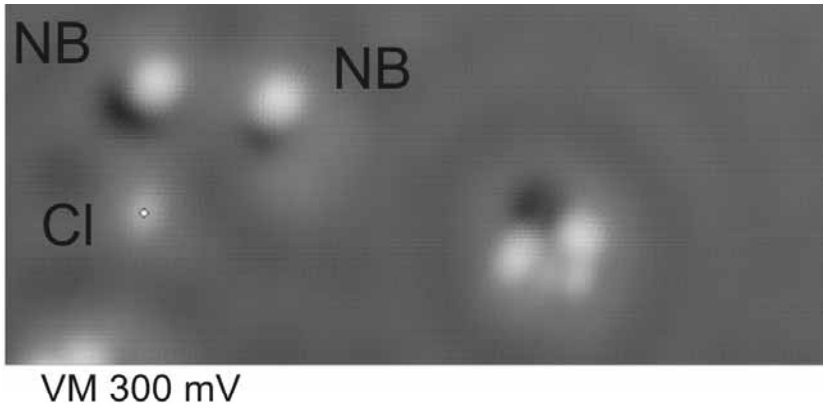
V. Simic-Milosevic, M. Mehlhorn, K.H. Rieder, J.Meyer and K. Morgenstern, to be published

Electron induced chemistry

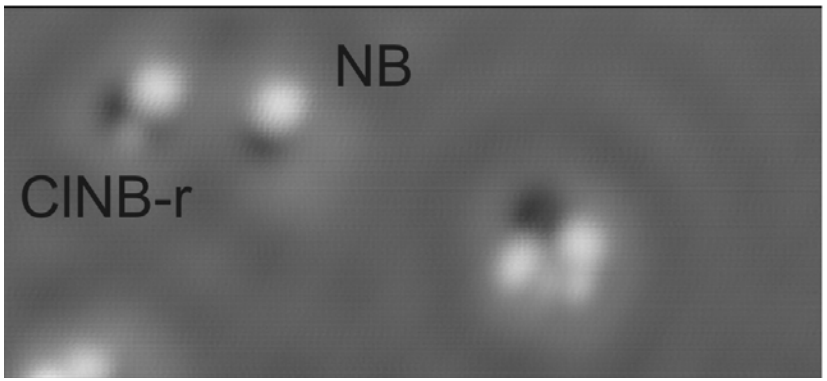




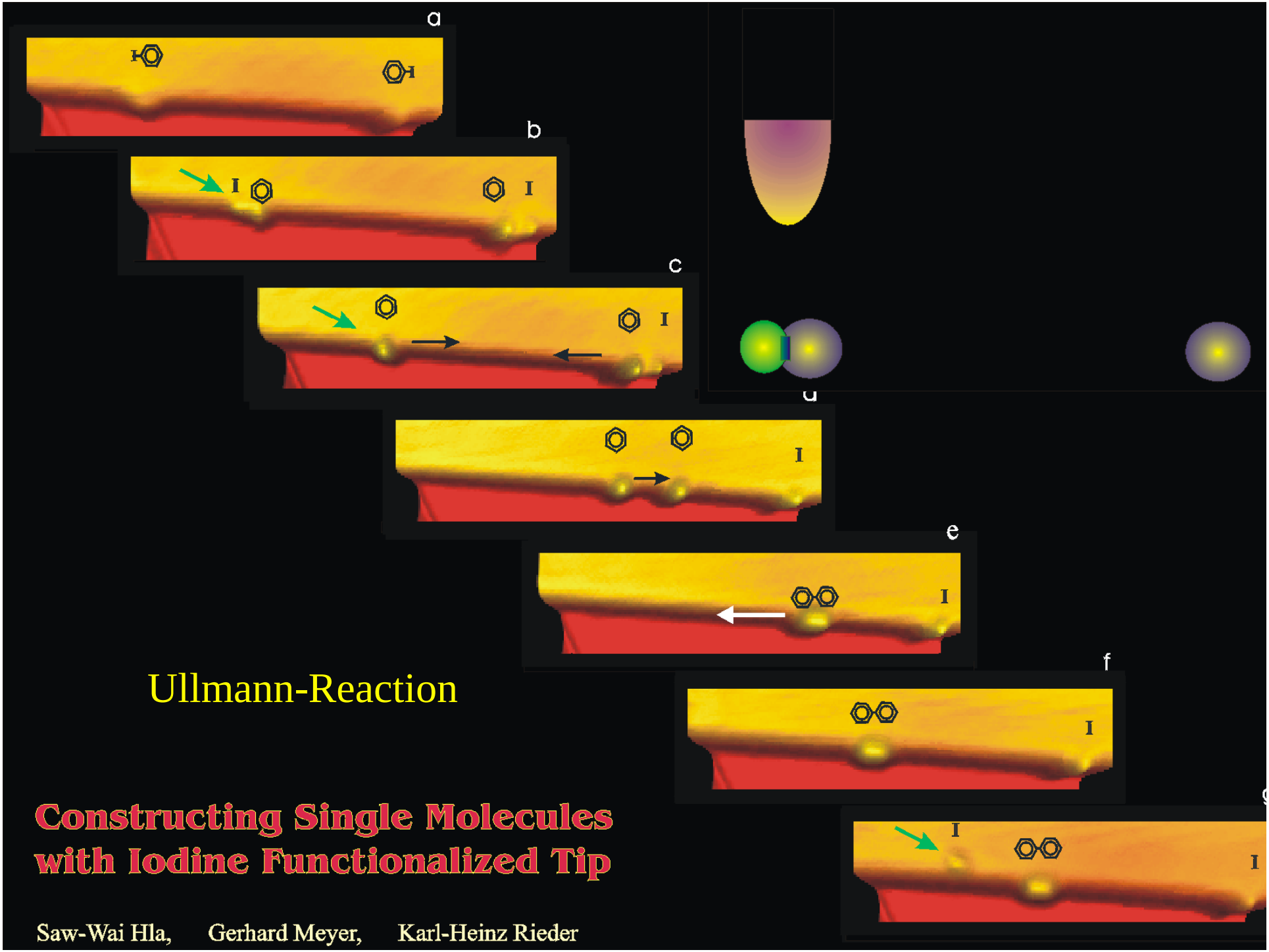




Changing the molecules chirality



Moving substitutional groups between molecules - ->



Constructing Single Molecules with Iodine Functionalized Tip

Saw-Wai Hla, Gerhard Meyer, Karl-Heinz Rieder

Summary

STM-Imaging: Atoms/ Charge density waves/ Molecular frontier orbitals

Spectroscopy: Standing surface state waves at steps and around molecules

Interface states between Cu(111) and NaCl-overlayer

Dispersion of surface states in Ni(111)

Manipulation: Artificial Nanostructures

Molecular „dumper truck“-> „Soft manipulation“

Molecular shooting – molecular engines?

Induction of a full chemical reaction

Isomerization (conformational and configurational)

Challenges and Chances

Artificial structures built with atoms and molecules with specific functions?

Molecular engines which can carry cargo?

Addressing molecular switches laterally?

Connecting molecules to electrical networks?

Performing all steps in parallel for many nets?

Connecting these networks to the macroscopic world?

.....

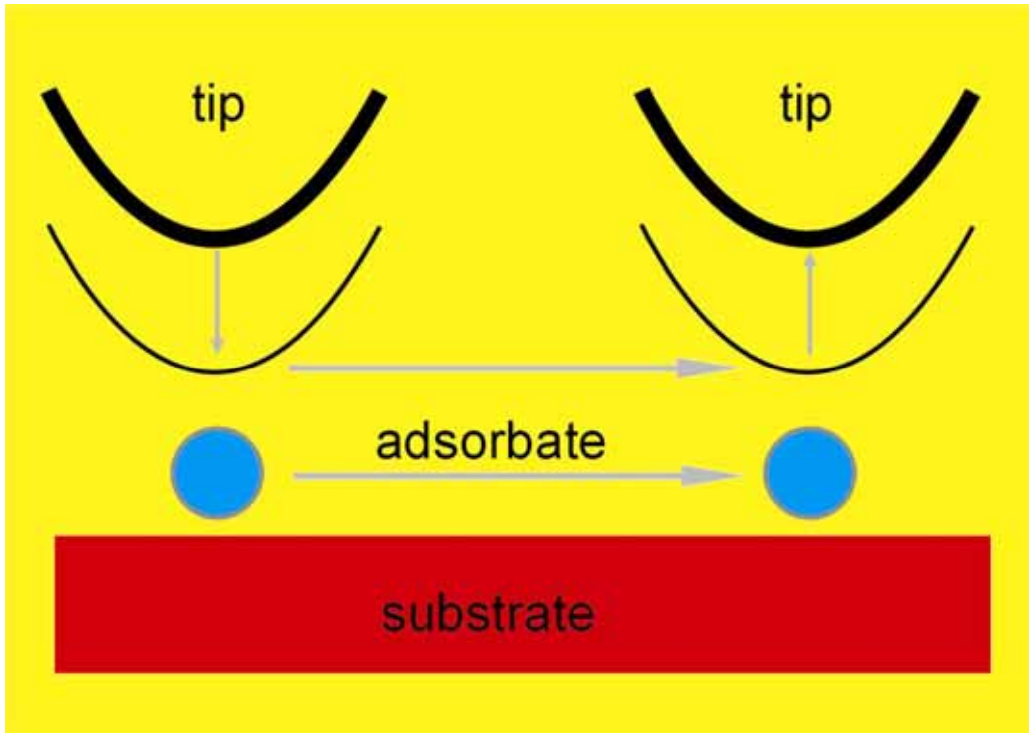
„Molecular tool box“

How to prepare tips with ultrahigh lateral and chemical resolution?

.....

? ? ?

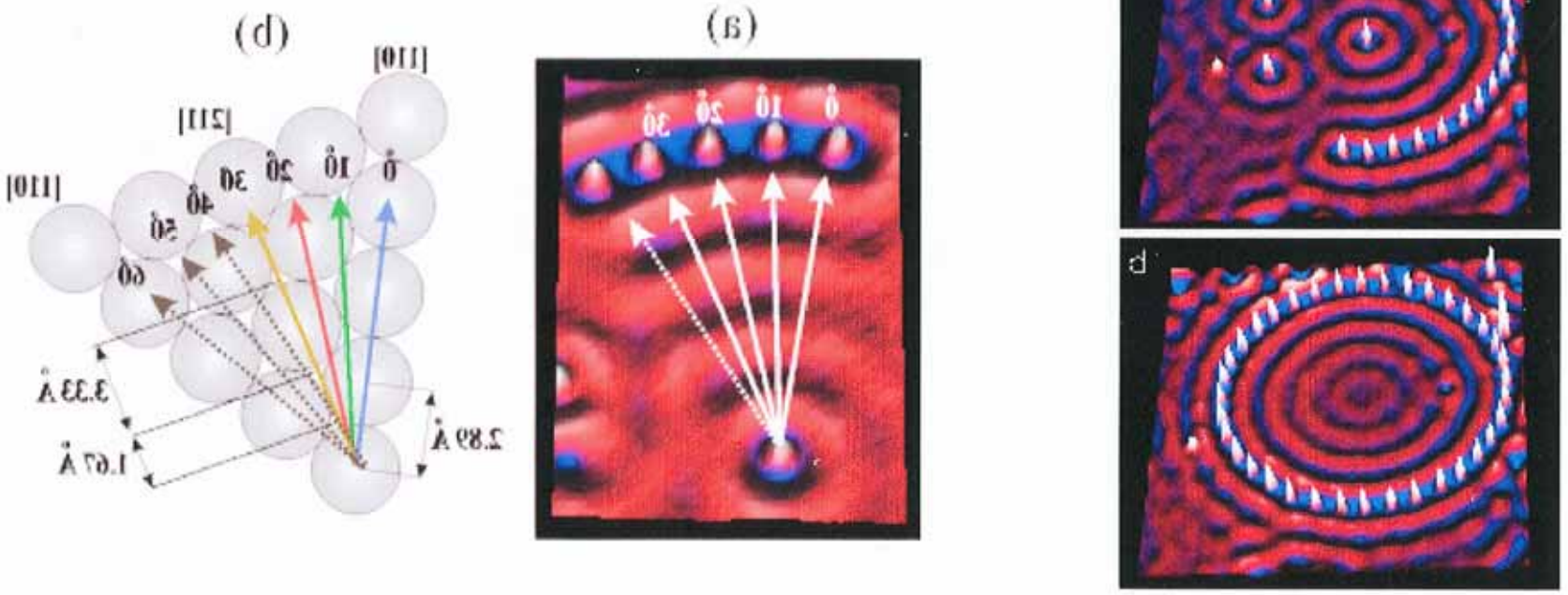
Manipulation with the STM tip



Van der Waals or chemical forces between tip and adsorbate

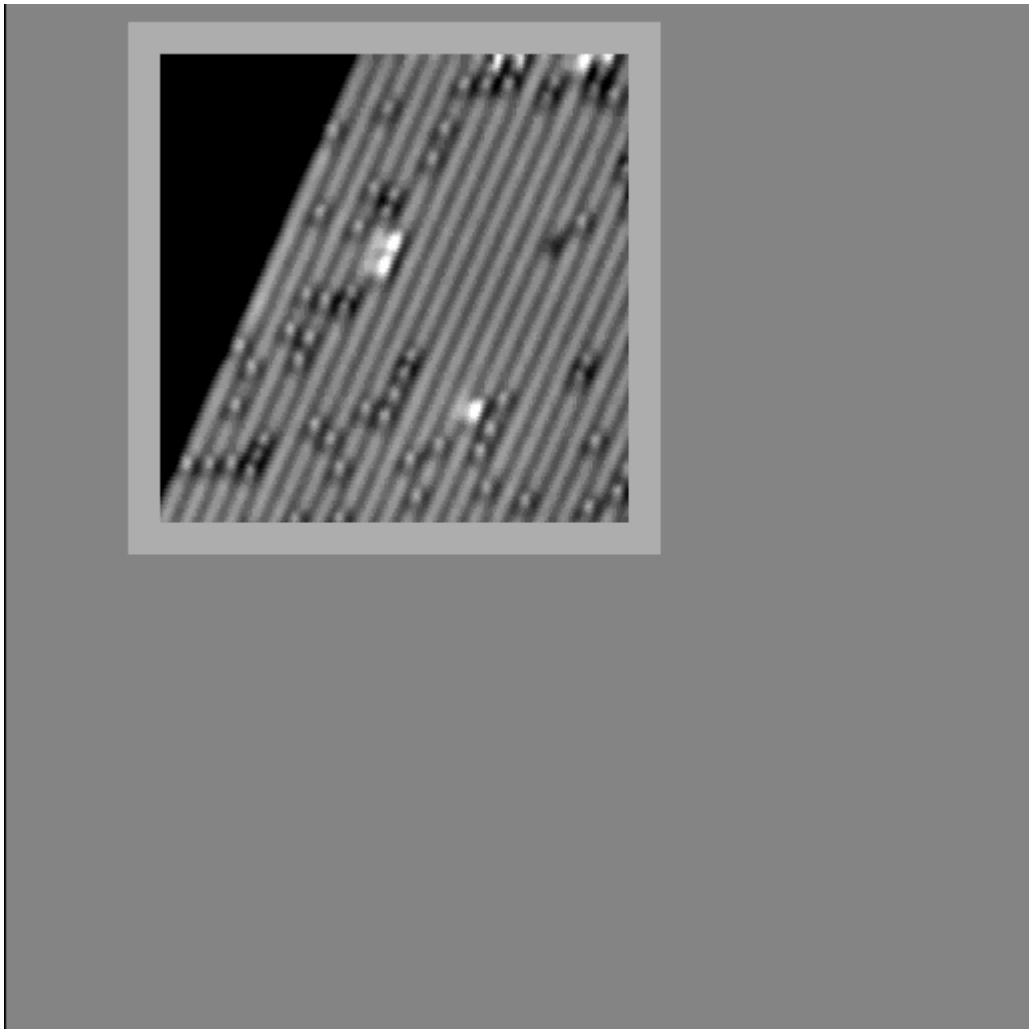
Lateral manipulation:

constant current or constant height modes



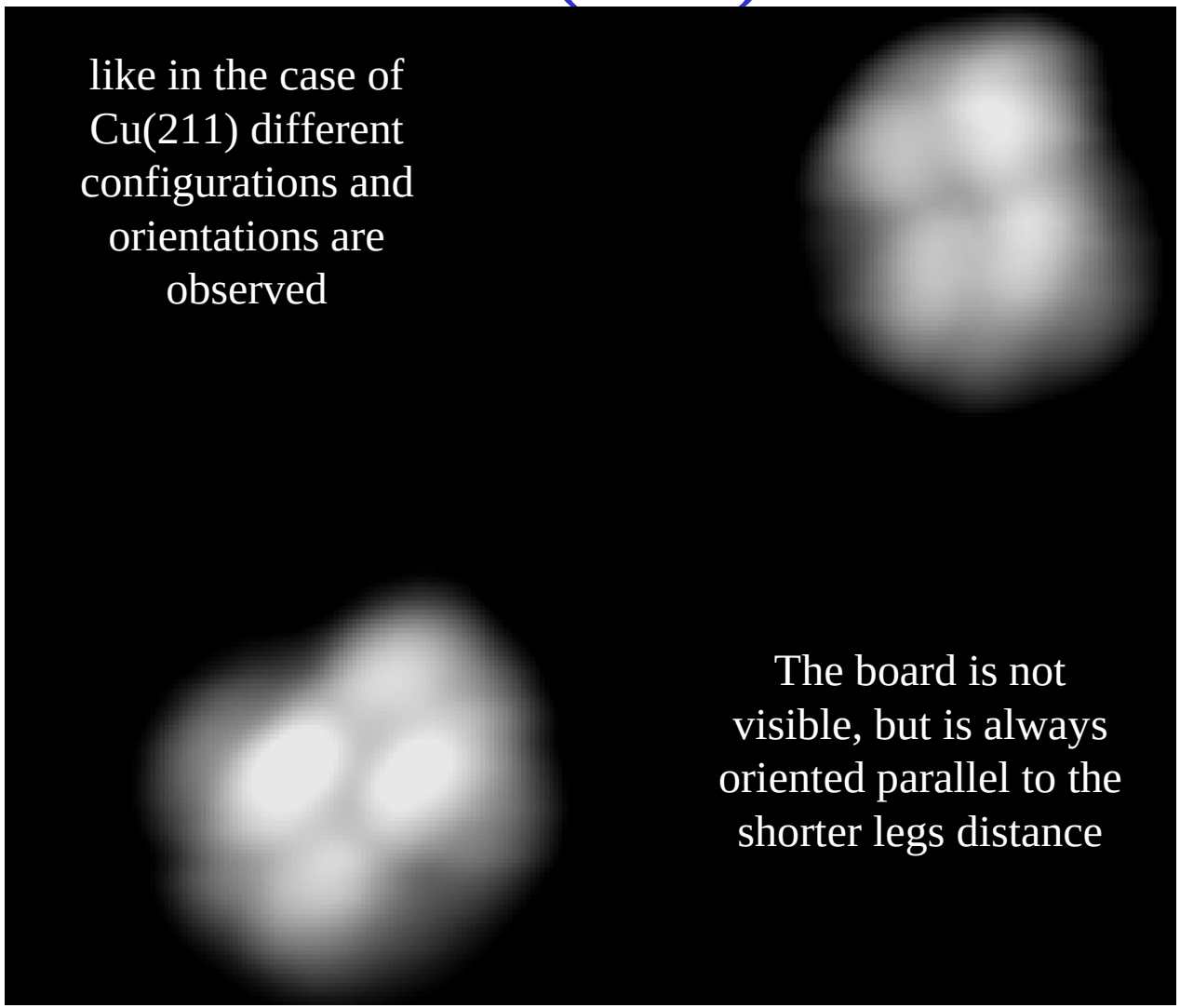
Saw-Wai Hla, K.-F. Braun and K.H. Rieder, Phys.Rev. B 67 201402 (R) (2003)

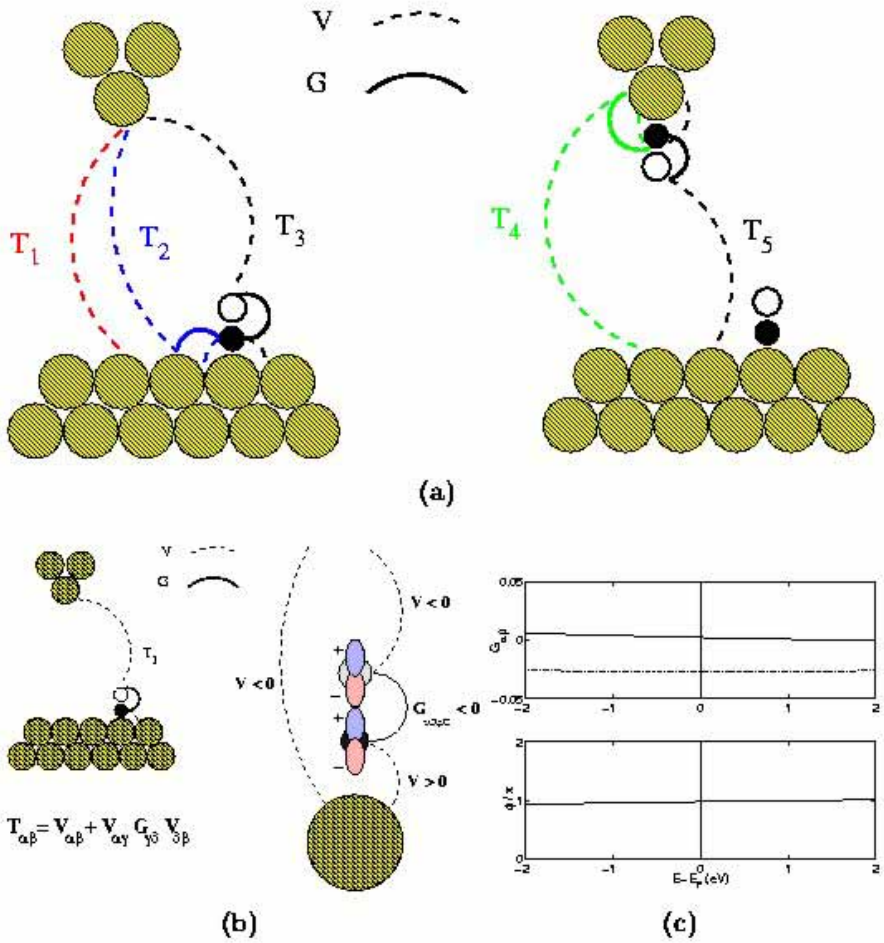
Lateral manipulation on atomic scale: CO/Cu(211)



Gerhard Meyer

Lander on Cu(111)





The five possible tunneling channels in the presence of an adsorbate molecule + a molecule at the apex of the tip (a). In the case of CO, the description, how the phase difference between through vacuum and through 3σ channel comes up (b). The phase of the Green's function relevant to 3σ tunneling (c).

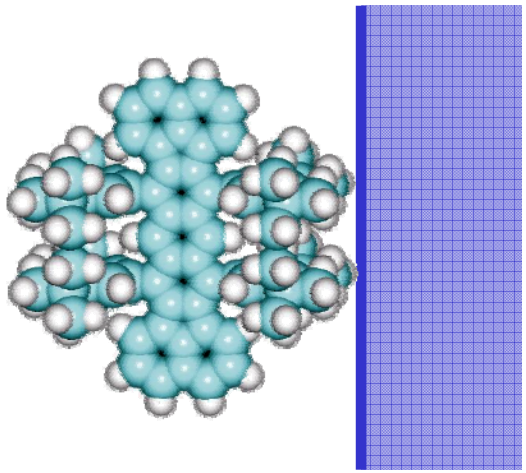
Jouko Nieminen and Eeva Niemi,

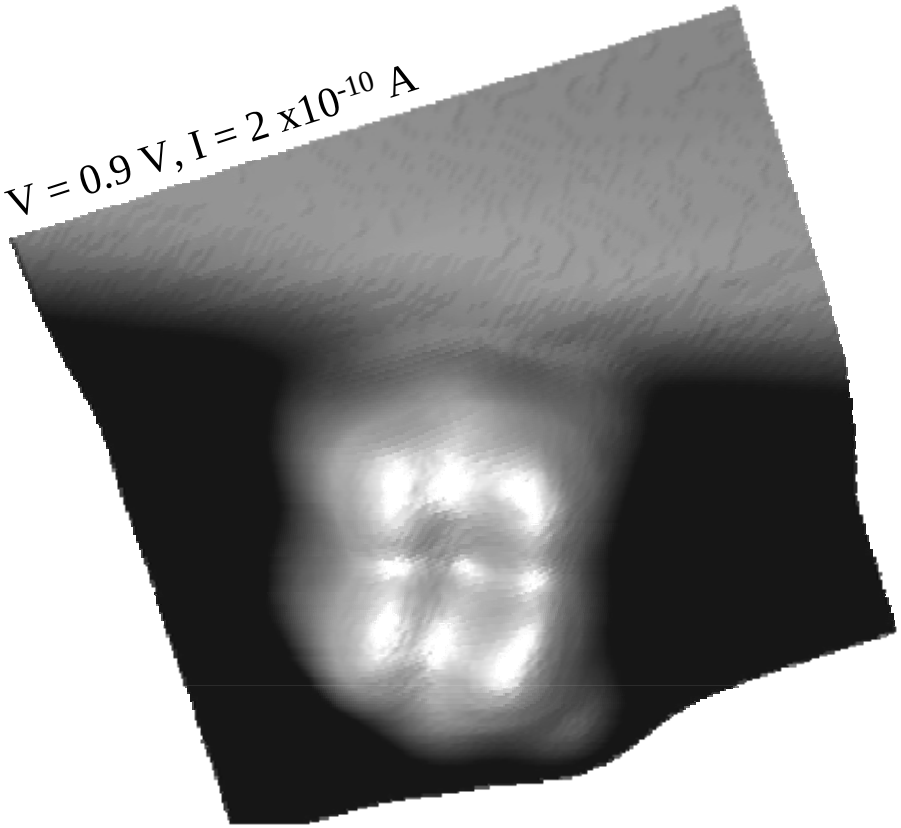
Tampere University of Technology, Finland.

Lander on Cu(111)

Manipulation to the step edge

with the board parallel to the step edge



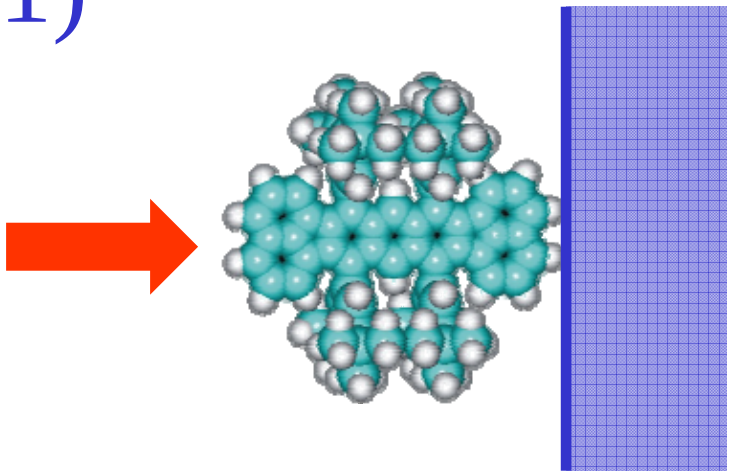


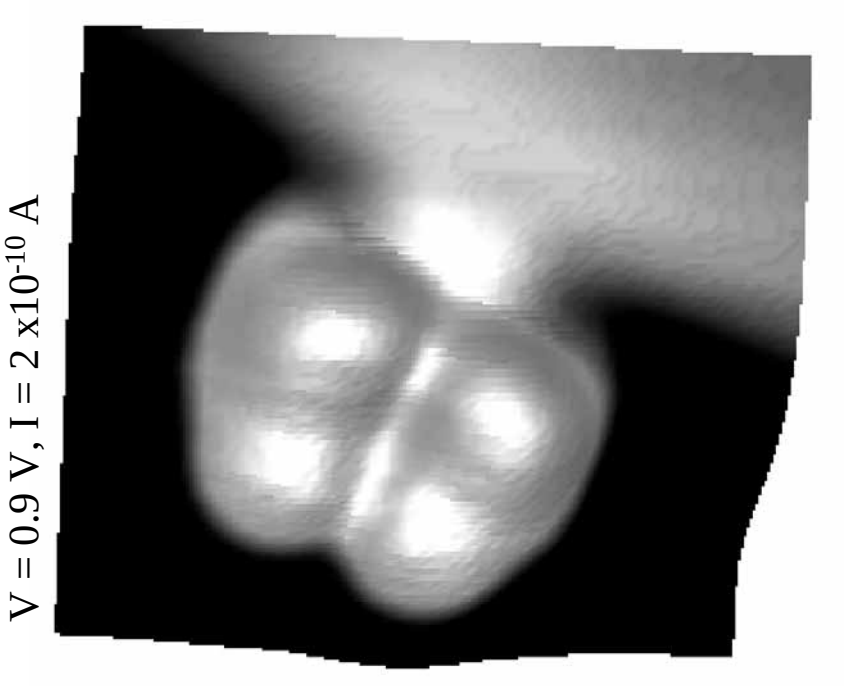
no contact point is visible

Lander on Cu(111)

Manipulation to the step edge

to bring the board in contact with the step



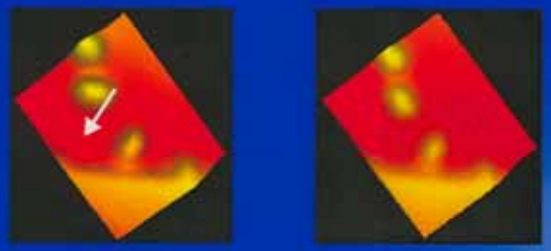


the molecule is pushed by lateral manipulation to contact the step edge

The termination of the central board becomes visible

RECOGNIZING MOLECULAR CONFORMATIONS DURING MANIPULATION WITH A STM TIP.

ROTATION BY USING TIP-MOLECULE FORCE



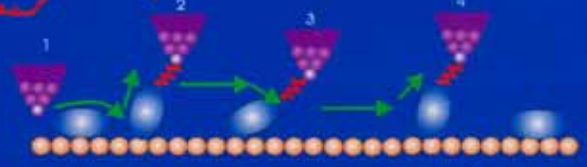
Tip height curve

$R_t = 2\ M\Omega$

LUMO OF DIIODOBENZENE

LATERAL MANIPULATION WITH AN UP-RIGHT POSITION

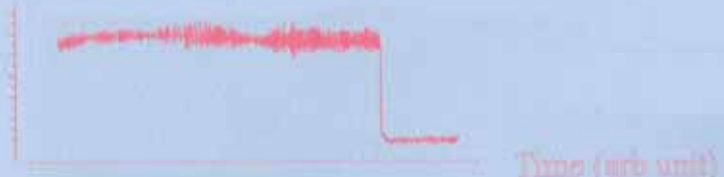
Tip height curve



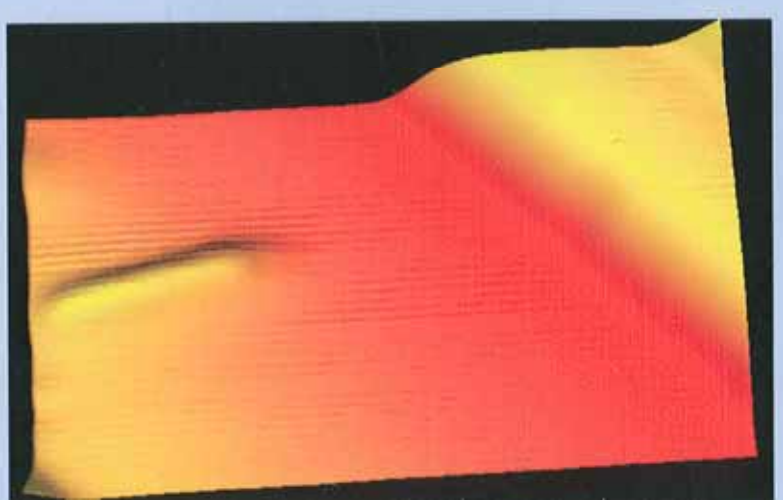
$R_t = 0.45\ M\Omega$

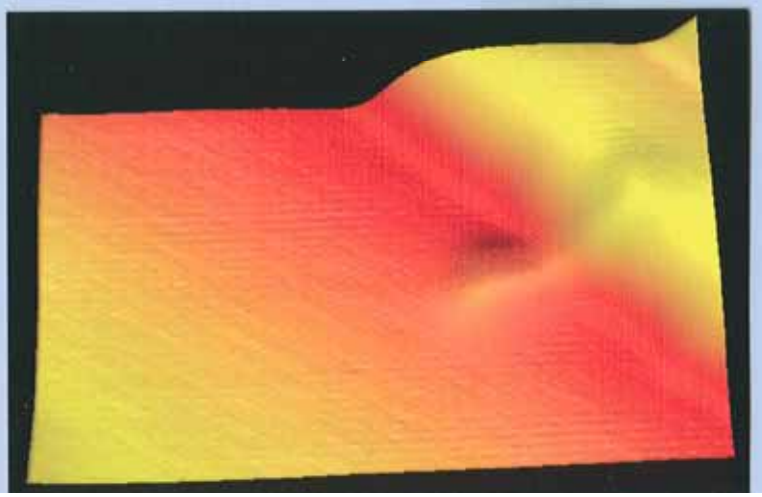
S.W. Hla, A. Kühnle, G. Meyer, K.-H. Rieder

Molecular Shooting



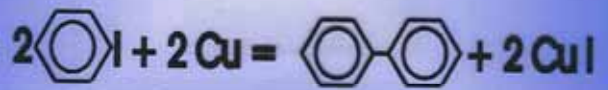
- Electrons with energies up to 1.8 eV are injected into the end pi-ring of Sexi-phenyl.
- Electron injection rate ~10^{10} electron/sec
- The inelastic excitation causes the molecule to slide across the Ag(111) surface.



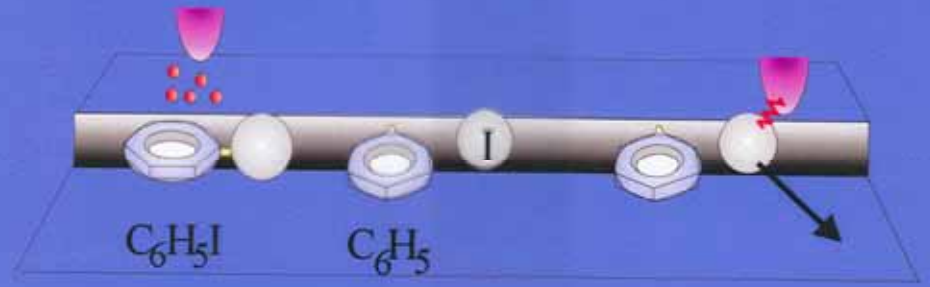


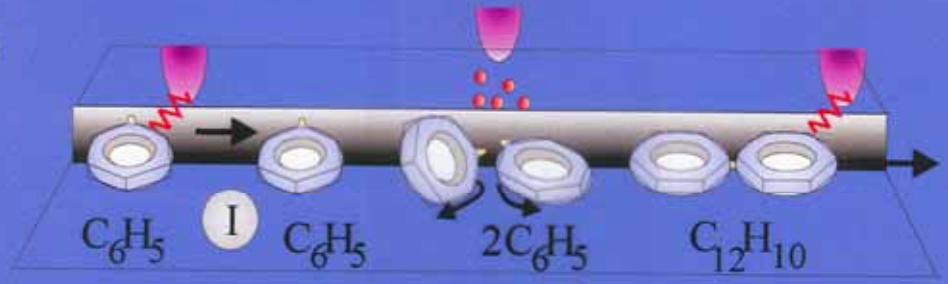
SINGLE MOLECULE ENGINEERING:

SYNTHESIS OF INDIVIDUAL BIPHENYL MOLECULES WITH AN STM TIP



Ullmann Reaction



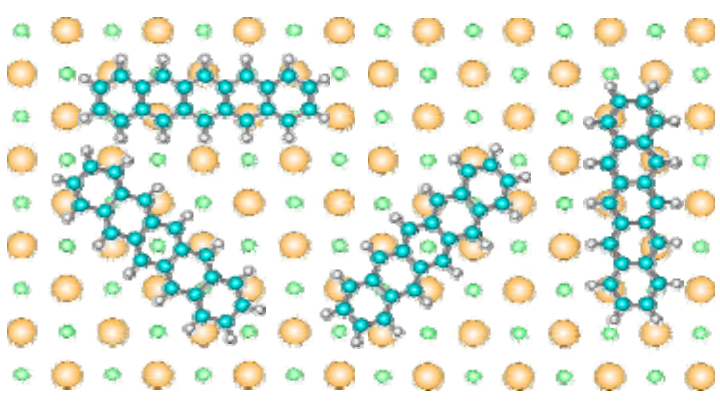


S.W. Hla, L. Bartels, G. Meyer, K.-H. Rieder

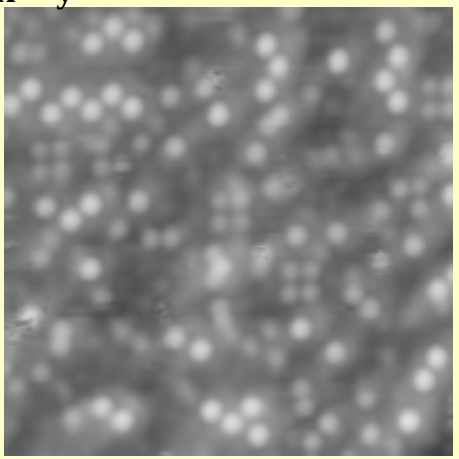
FB Physik, FU Berlin, Germany

Pentacene on a Vanadiumoxide Thin Film grown on $Cu_3Au(100)$

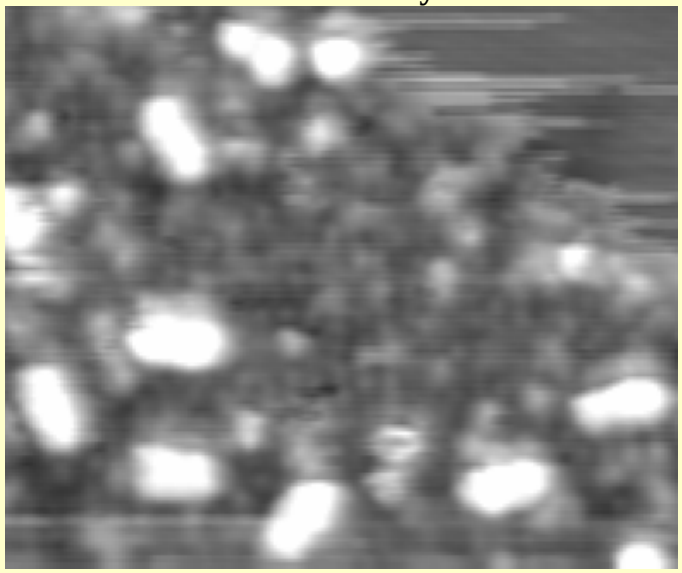
Molecule structure



V_xO_y disordered islands



Pentacene on V_xO_y



I=0.1nA, U=0.4V, T=7K, 108Å x 120Å

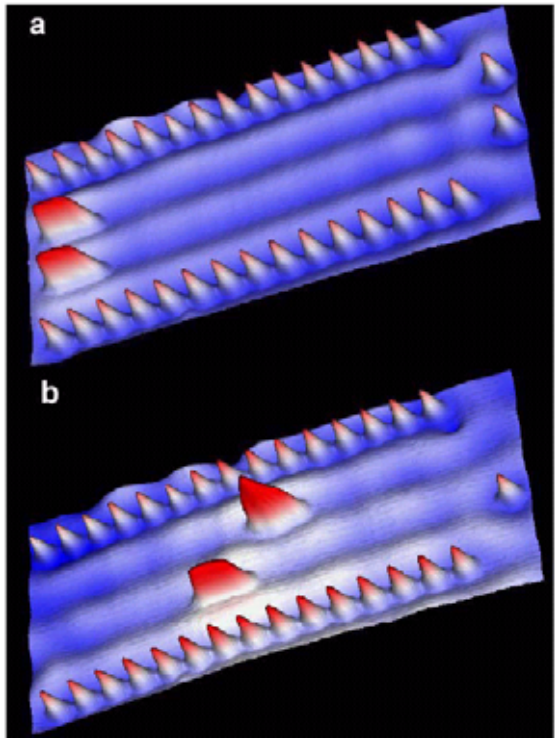
Pentacene image resembles HOMO electron density of free molecule

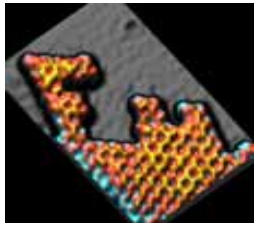
I=0.1nA, U= -1V, T=7K, 18Å x 15Å

M.Alemani, F. Moresco and K.H. Rieder, unpublished

Summary

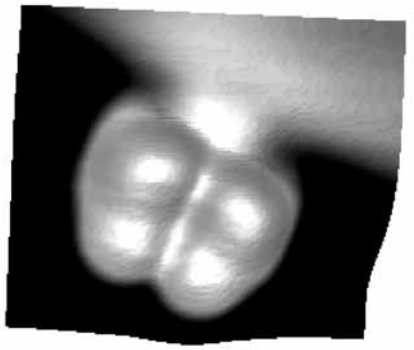
Building artificial nanostructures in an atom by atom and molecule by molecule way



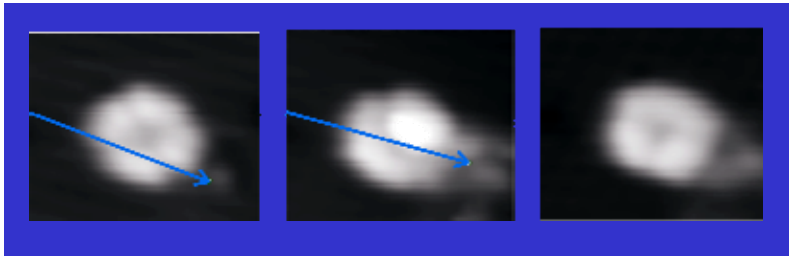


Molecular shooting: a possible atomic scale engine?

Making electrical contacts with atomic precision

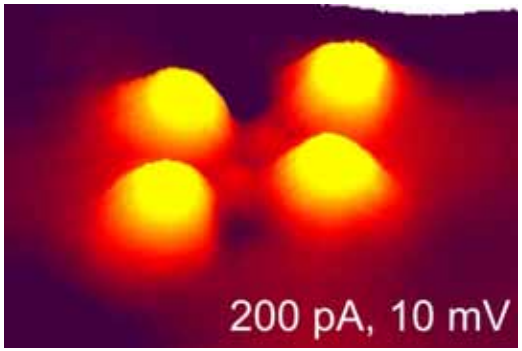


Switching molecules by mechanical and electron induced manipulation



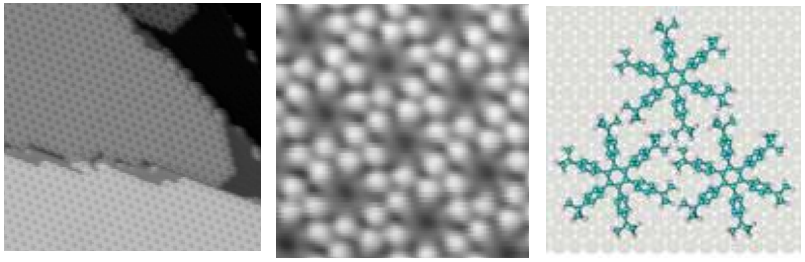
Vertical manipulation:

A route to chemical contrast?

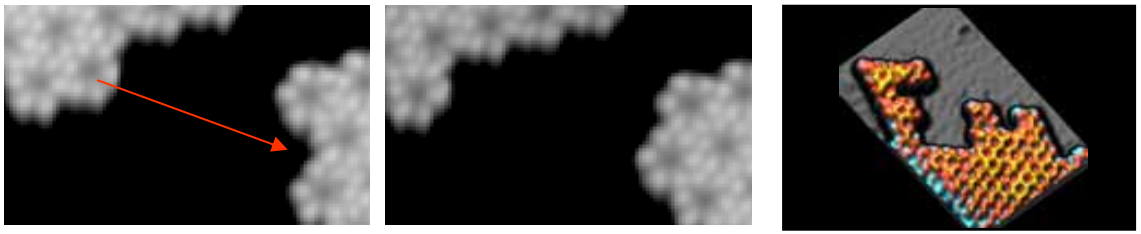


Conclusions: HB-HPB/Cu(111)

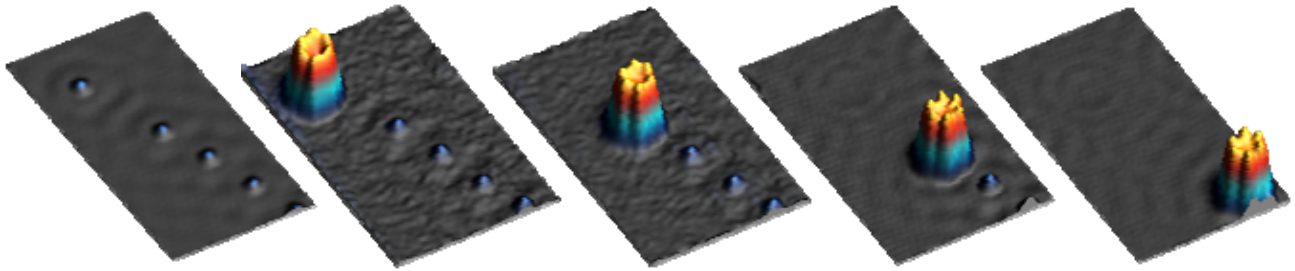
Characterization of monolayer structure and growth



Manipulation of monolayer structures

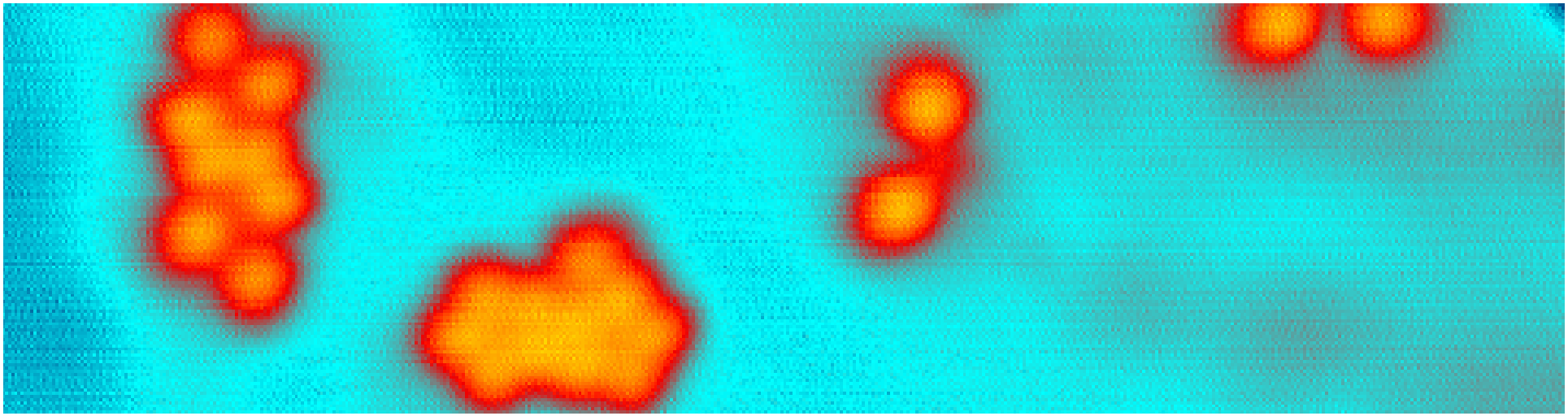


Manipulation of adatoms with molecules



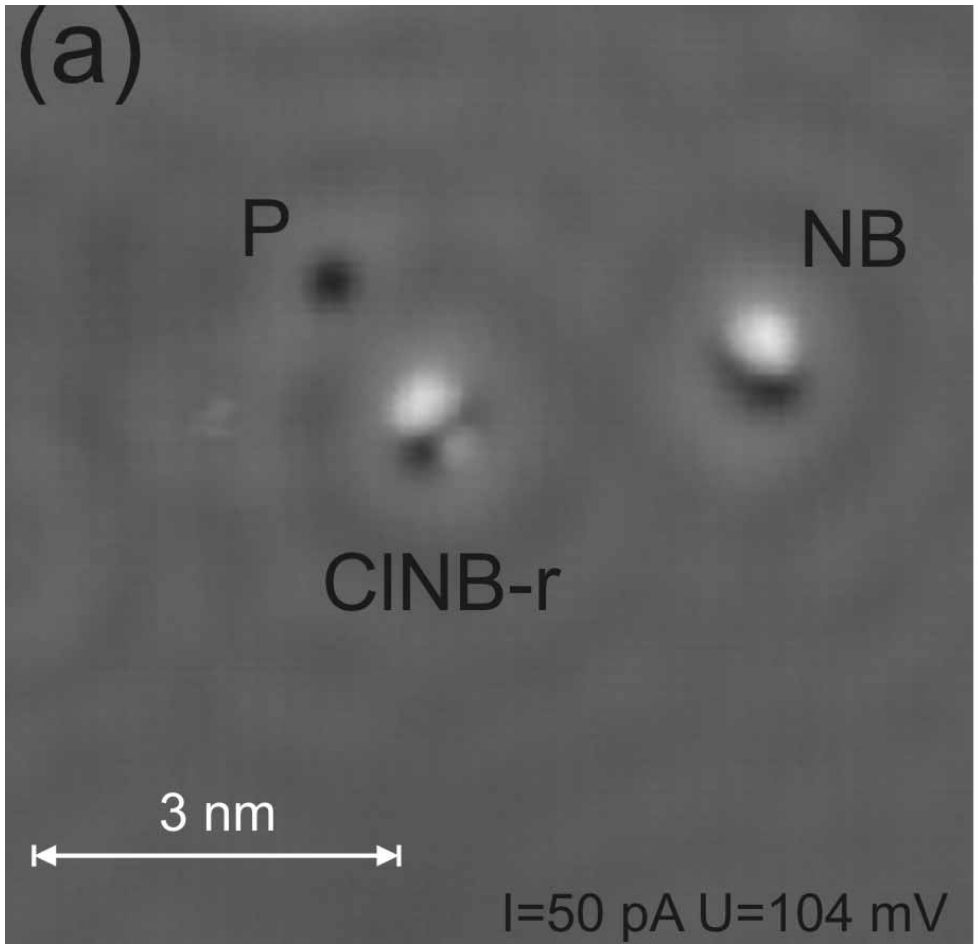
Cis-Trans-Isomerization of Azobenzene derivate: Disperse Orange 3 ($NO_2C_6H_4N=NC_6H_4NH_2$) on Au(111)

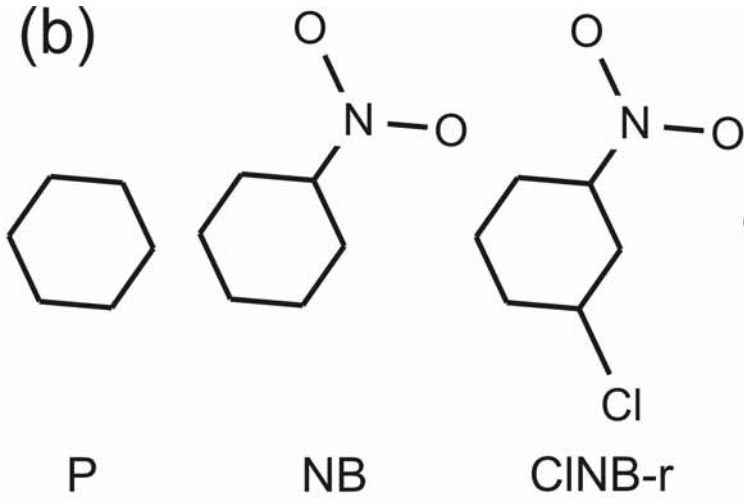
Injecting electrons into N=N bond with increasing energy 600 meV to 720 meV



induced diffusion
and conformational isomerization
(interconversion around single bonds)

1,3 Chloronitrobenzene on Cu(111)

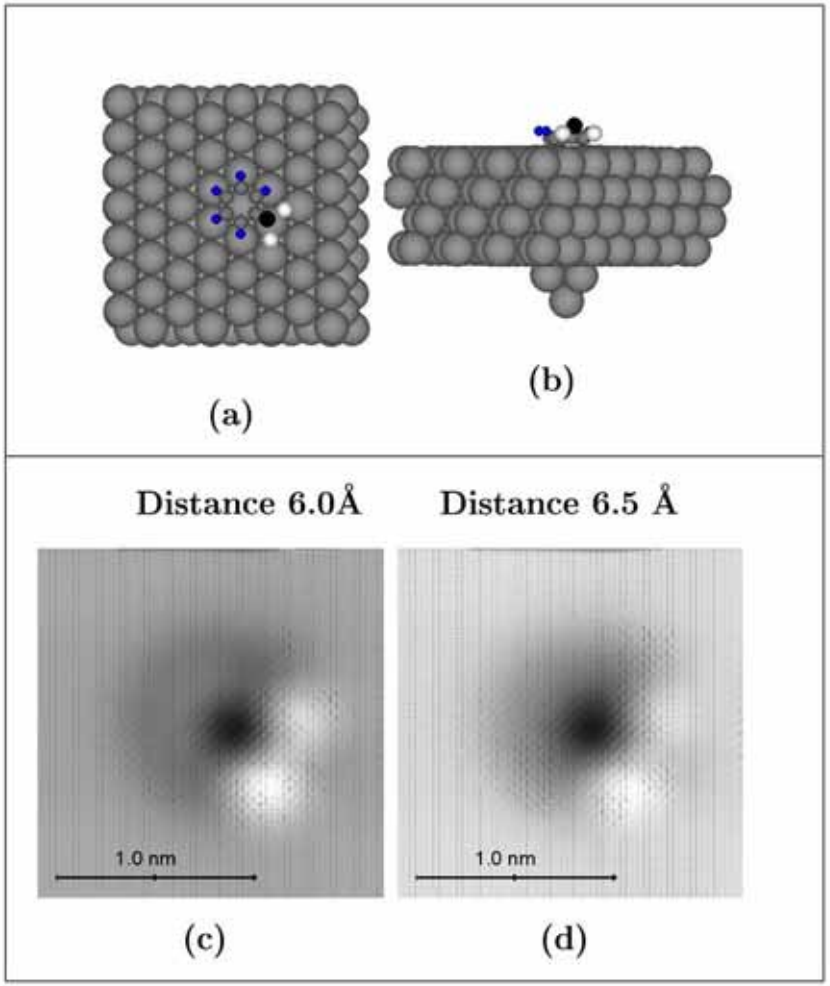




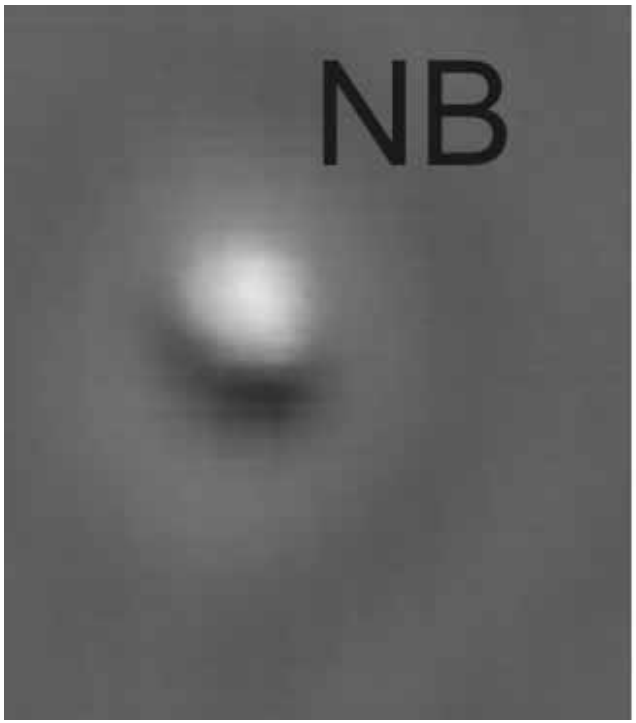
(Phenyl)

Nitrobenzene on Cu(111)

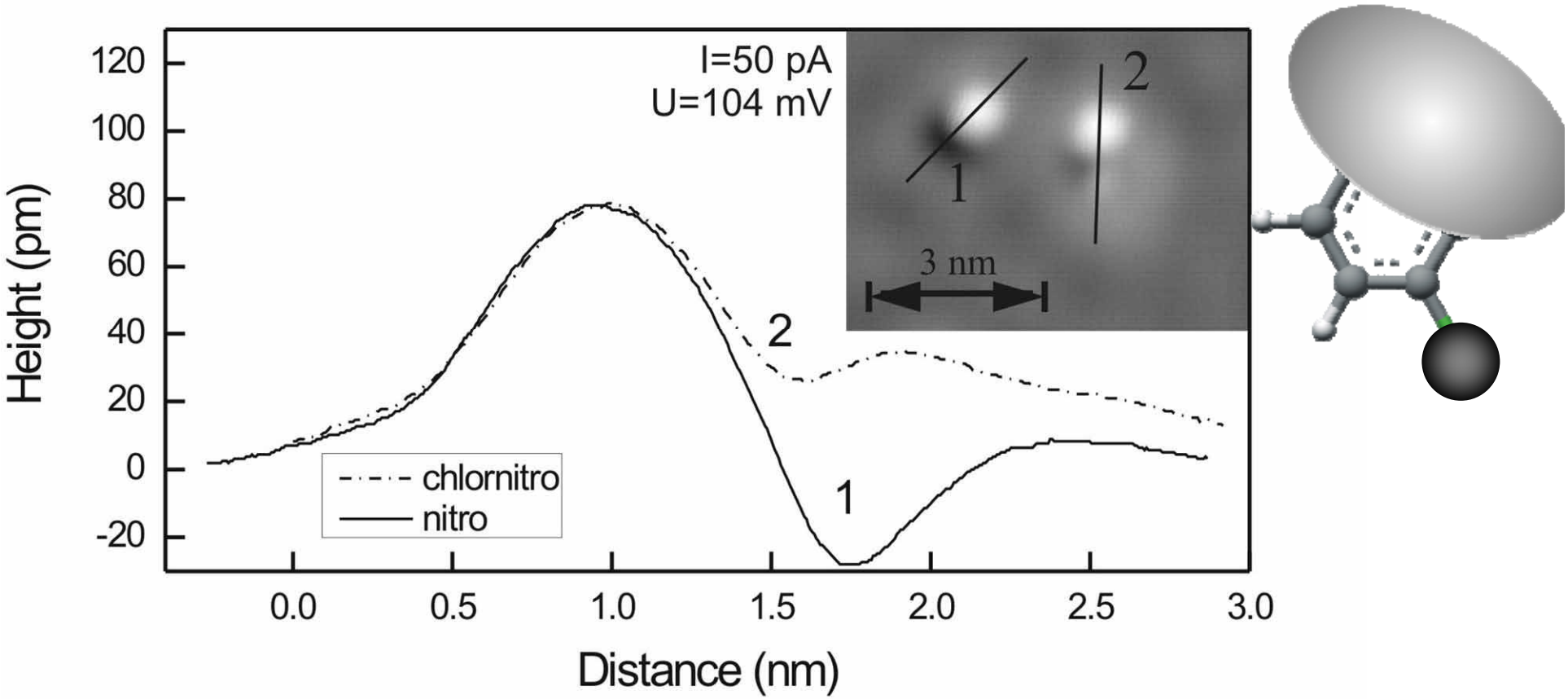
Calculation in 'tight-binding'
(J. Nieminen et al.)



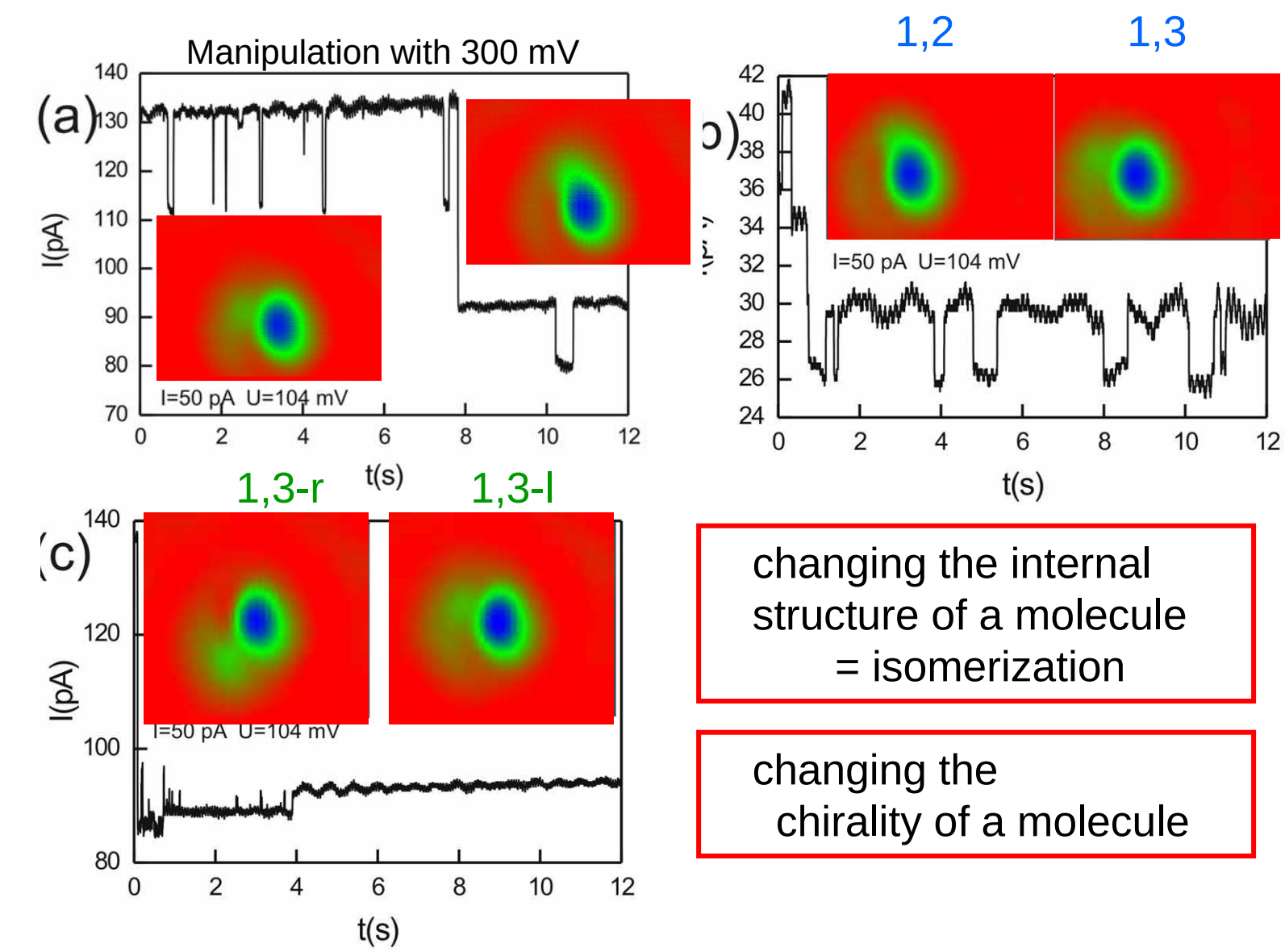
Experiment



$C_6H_4ClNO_2$ / $C_6H_4NO_2$ on Cu(111)

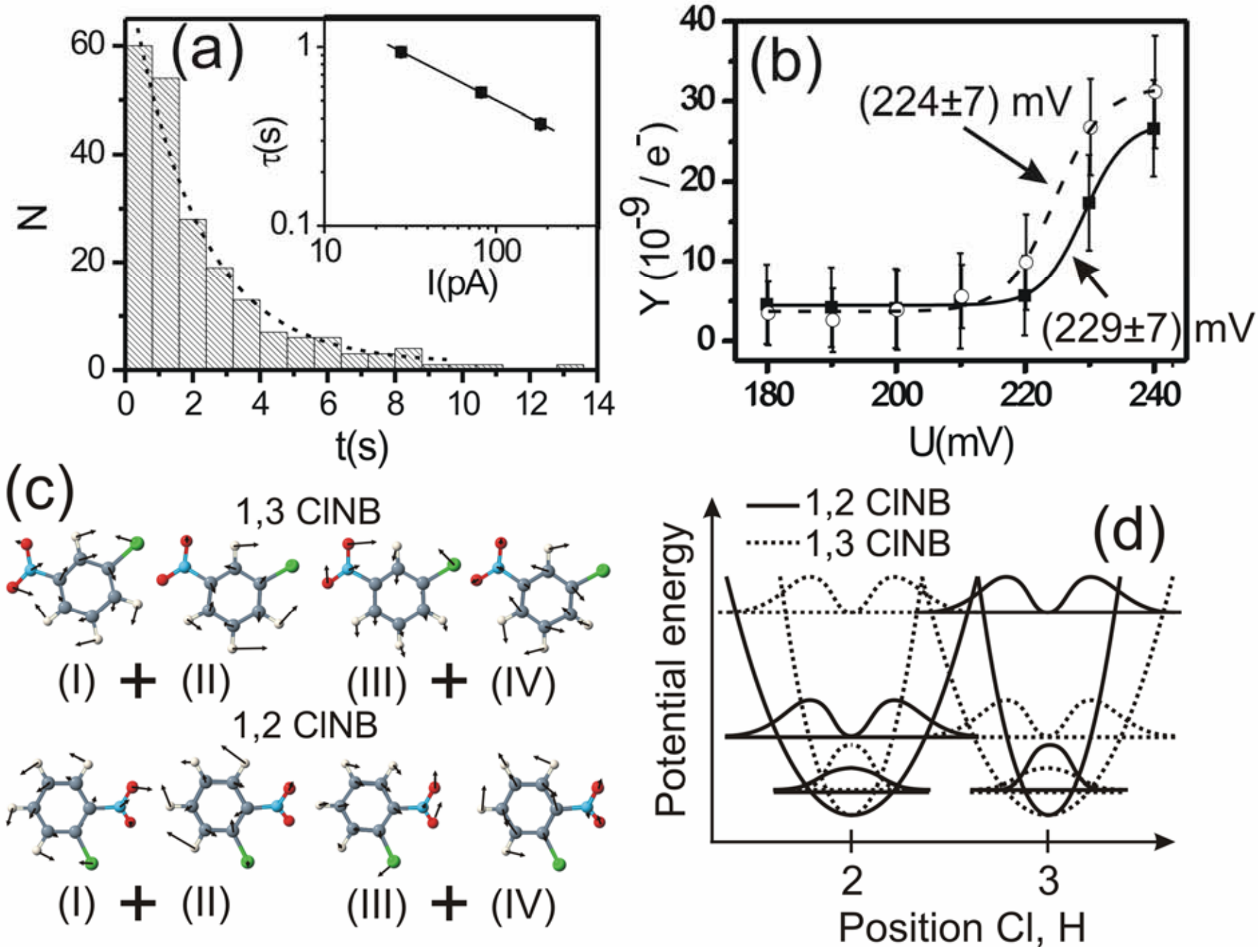


$C_6H_4ClNO_2$ on Cu(111)



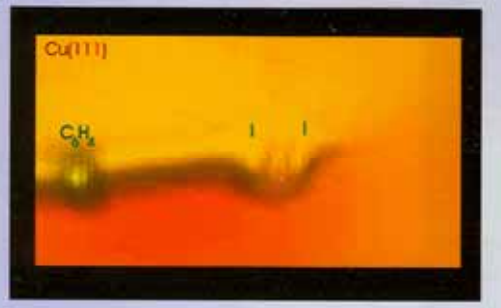
changing the internal structure of a molecule = isomerization

changing the chirality of a molecule

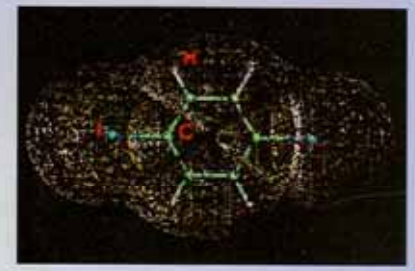

(a)
N
t(s)
τ(s)
I(pA)
(b)
Y (10^-9 / e^-)
U(mV)
(224±7) mV
(229±7) mV
(c)
1,3 ClNB
(I) + (II)
(III) + (IV)
1,2 ClNB
(I) + (II)
(III) + (IV)
(d)
1,2 ClNB
1,3 ClNB
Potential energy
Position Cl, H

Iodine Dissociation from Diiodobenzene with the STM Tip.

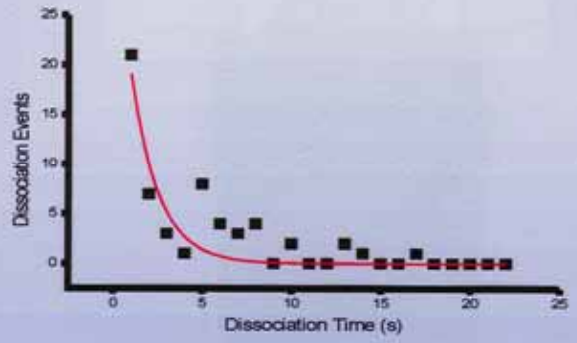
$C_6H_4I_2$



2.5 V, 1.33 nA



Lowest Unoccupied Molecular Orbitals (LUMO) of Diiodobenzene

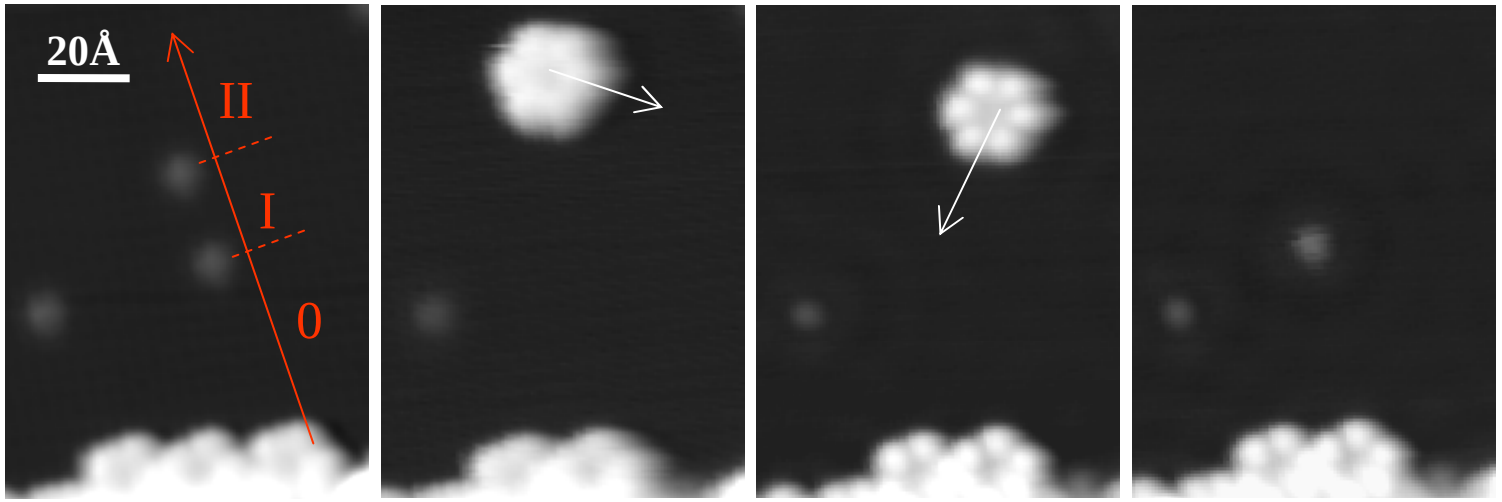


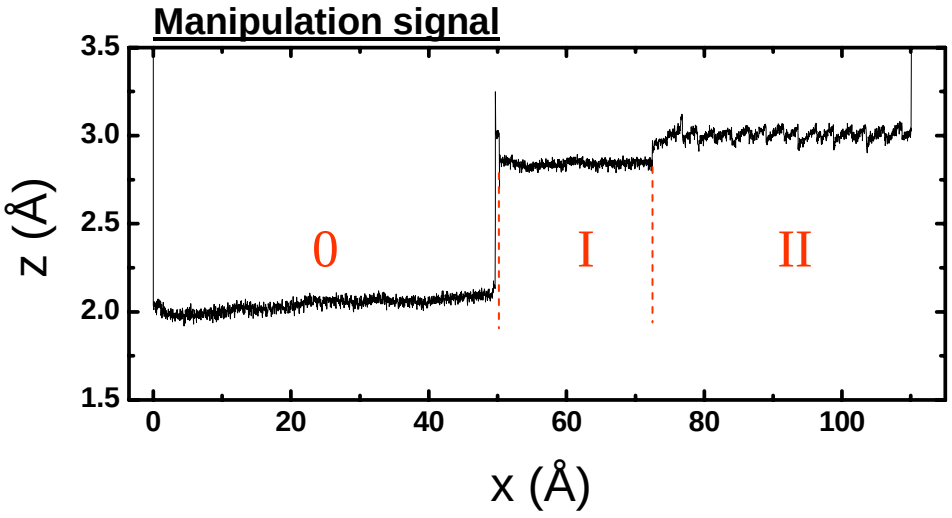
S.W. Hla, G. Meyer, K.H. Rieder

Releasing Adatoms on the Surface

Imaging:
I=0.2nA,
U=100mV

Manipulation:
I=40nA,
U=-30mV





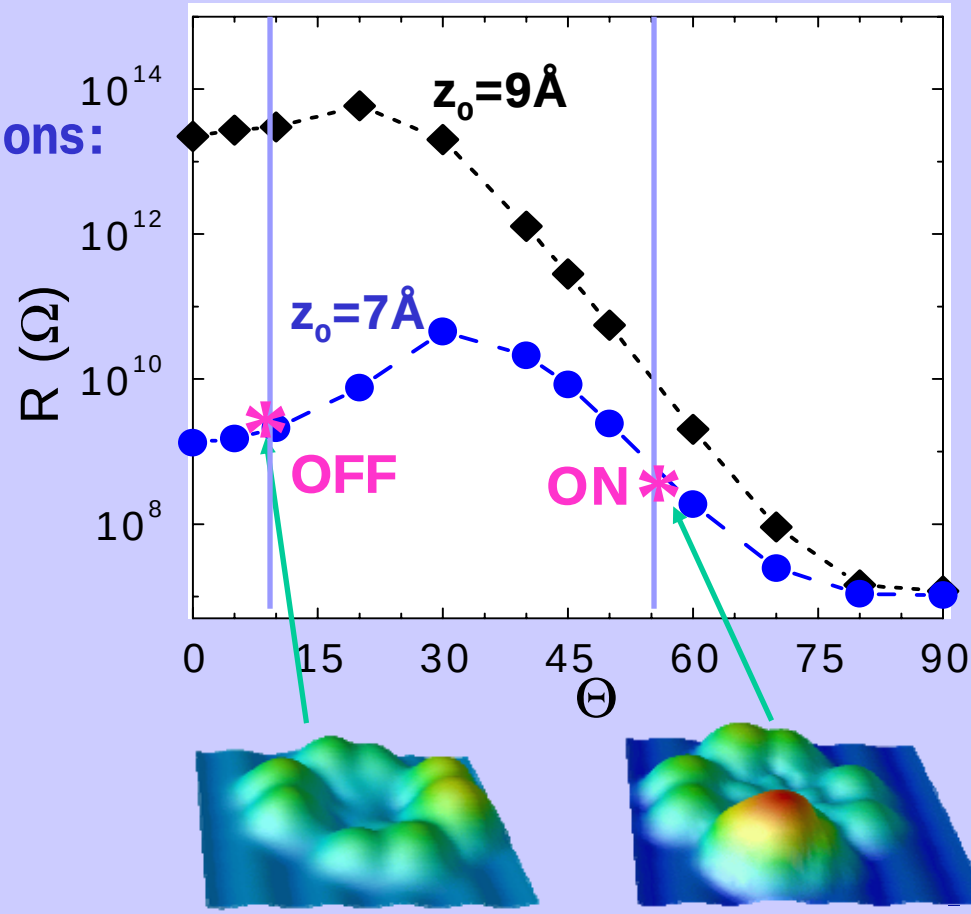
- Vertical manipulation of molecule releases atoms

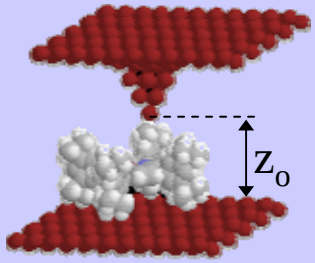
- After absorption of the 2nd atom the manipulation signal changes from sliding to pushing

Molecular switch: Theory

How does the resistance depend on
the leg‘s orientation?

ESQC calculations:

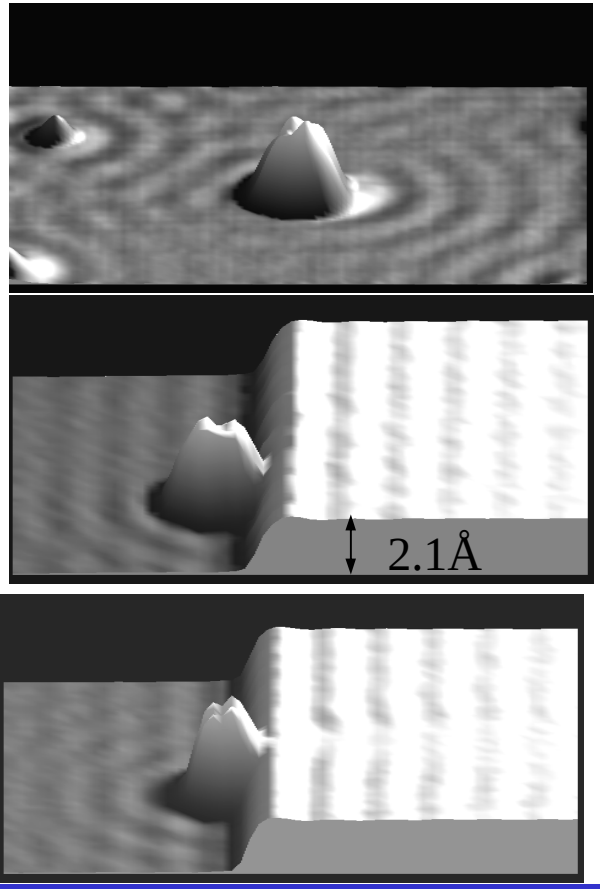




⇒**Initiated new Berlin Sonderforschungsbereich 658: Elementarprozesse in molekularen Schaltern an Oberflächen**

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

Probing the electronic contact with surface standing waves



molecule on a terrace:
elliptic standing wave patterns

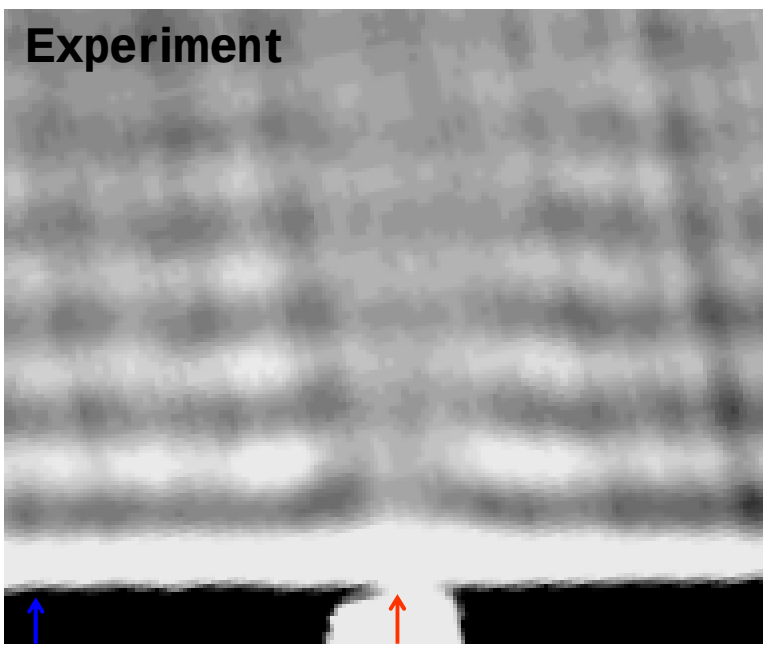
molecule contacted to a step edge with the board parallel to it:
the parallel patterns in the upper terrace are not perturbed by the molecule

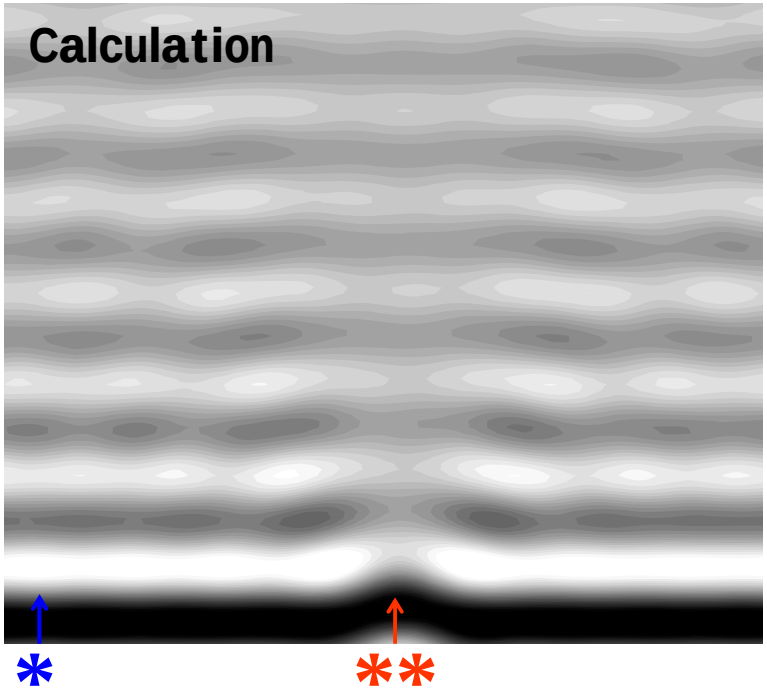
board of the molecule contacted to a step edge:
the standing wave patterns in the upper terrace are modified by the contact of the molecular wire

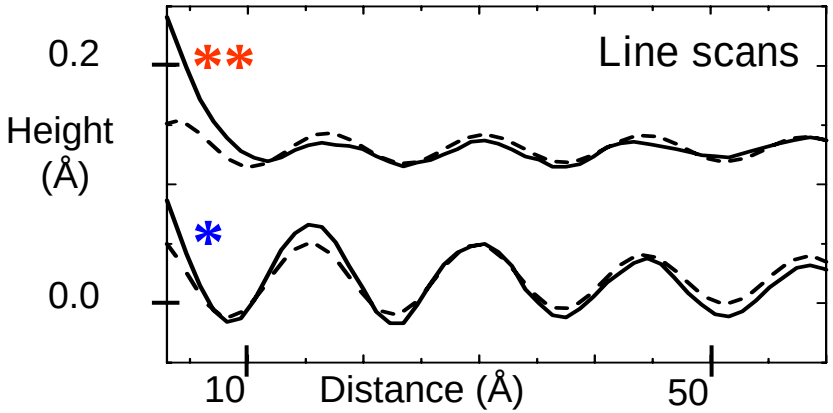
The standing waves due to the surface state electrons probe the electronic characteristics of the contact

F. Moresco, L. Gross, M. Alemani, K.H. Rieder, H. Tang, A. Gourdon, C. Joachim
Phys. Rev. Lett. 91, 036601 (2003)

Standing waves: calculations using Heller theory



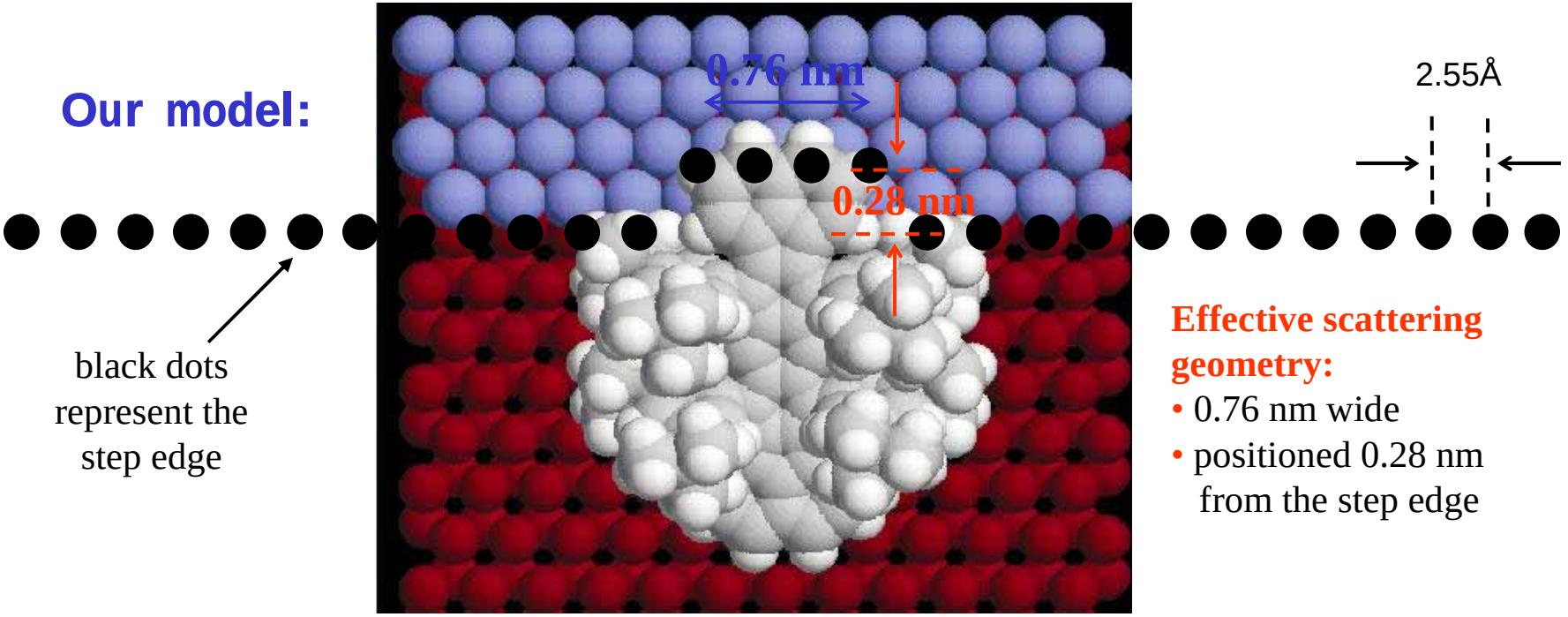




Very good agreement between experiment and model

Standing waves

Our model:



black dots represent the step edge

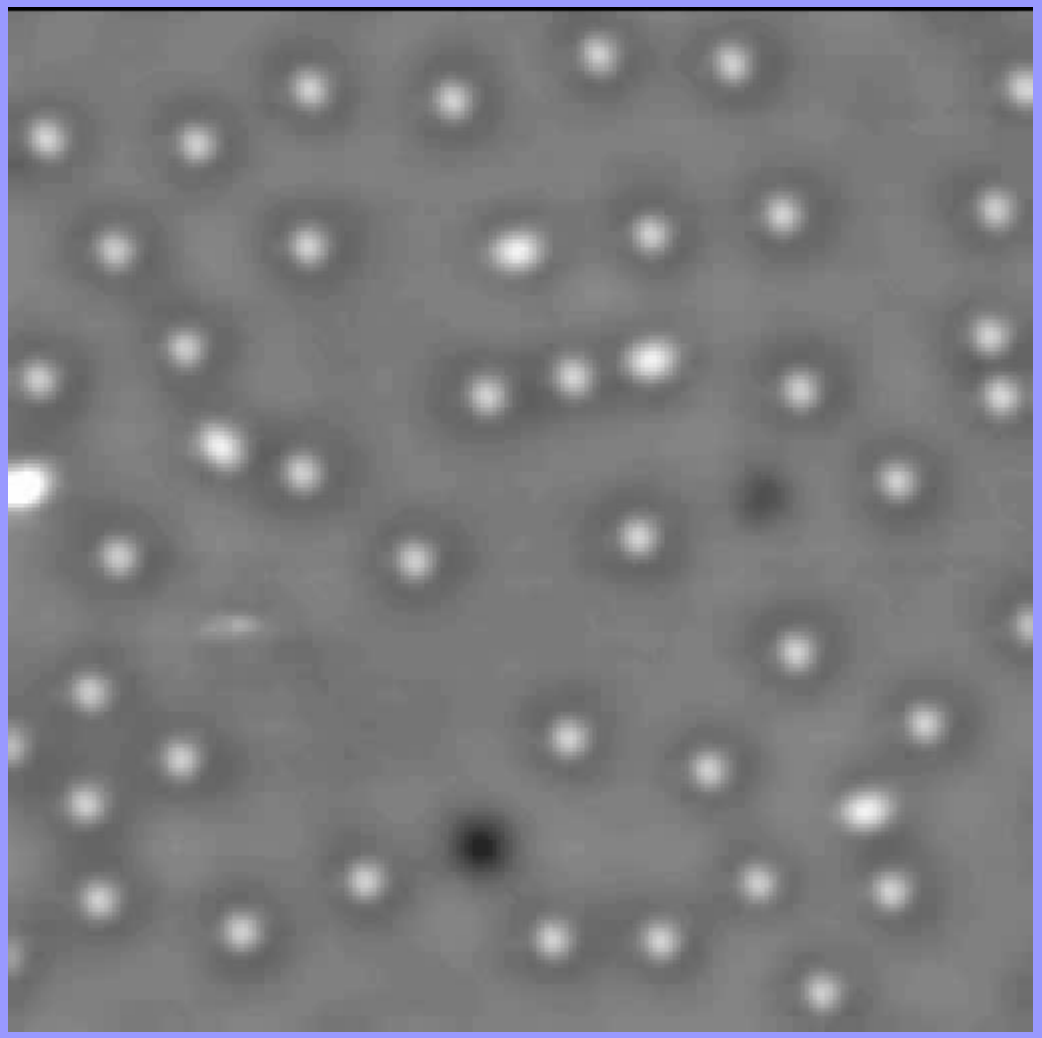
Effective scattering geometry:

- 0.76 nm wide
- positioned 0.28 nm from the step edge

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

Thermally induced motion of Cu-monomers and Cu-dimers on Ag(111)



Monomer diffusion mainly but not exclusively between fcc, influenced by the surface state

Dimer rotation between three eqivalent sites

K.Morgenstern, K.F. Braun and K.H. Rieder

Phys.Rev.Lett. 93 056102 (2004)

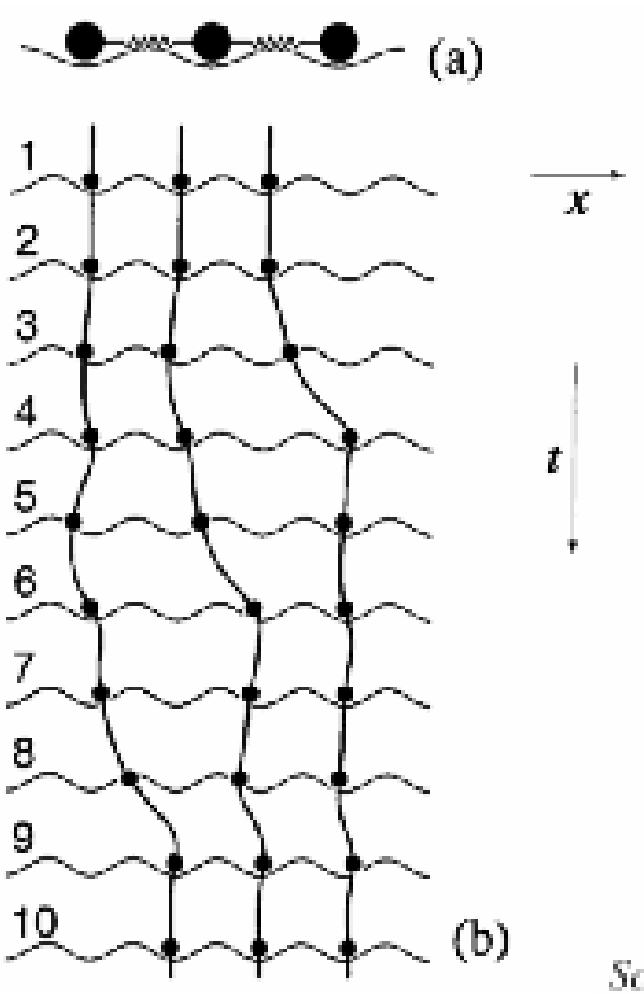
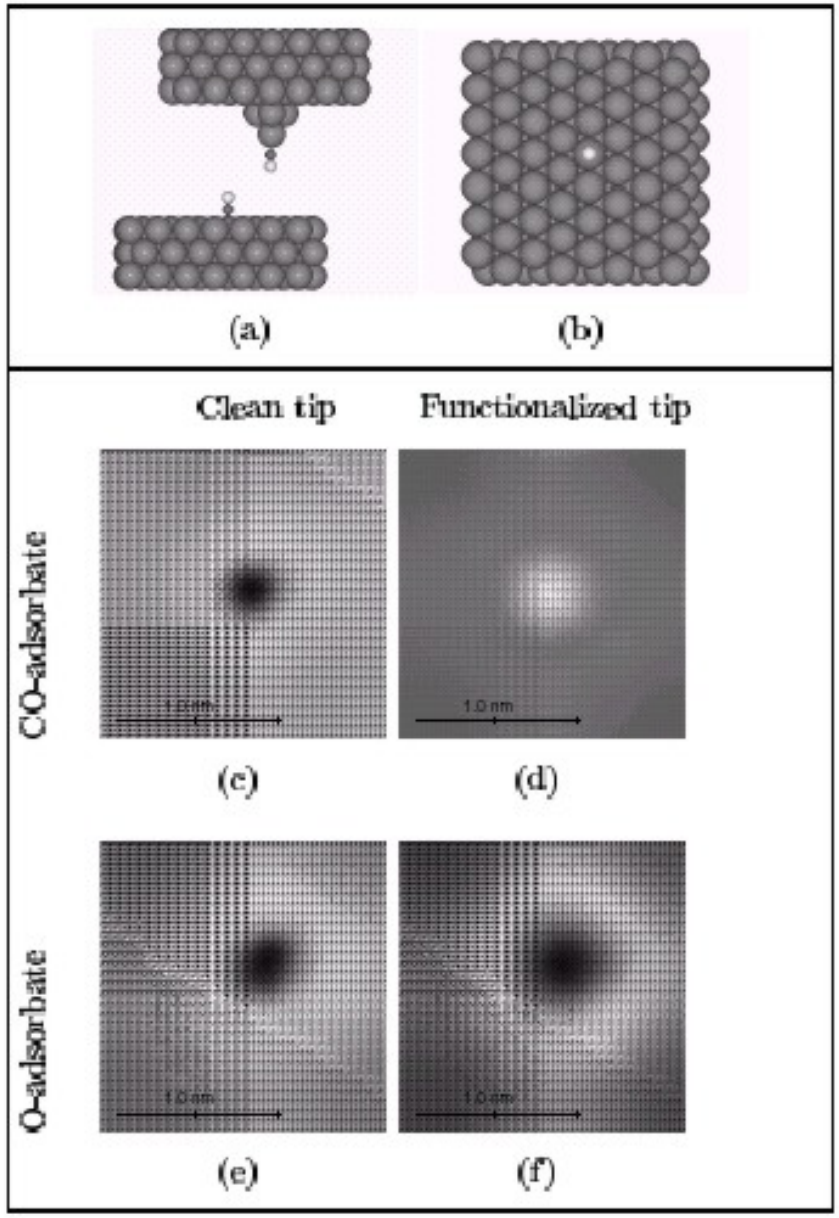


FIG. 1. (a) Sketch of the geometry of the example engine showing the surface potential $\Phi(x)$ and the chain with $N = 3$ particles. (b) Motion of the chain sketched in (a); the position x_i of the particles as a function of time t is shown. The large disks indicate the particles' position in relation to the surface potential in the ten numbered snapshots in time intervals of $(5b/2\pi)\sqrt{m/\Phi_0}$. The time $(25b/\pi)\sqrt{m/\Phi_0}$ of a full oscillation of $a_{i,i+s_i}(t)$ and hence of a single step of length b to the right is shown. The parameters are the misfit between the minimum rest length of the interparticle potential and the potential period $a/b = 11/10$, the dissipation constant $\eta = (16\pi/10b)\sqrt{\Phi_0 m}$, the interparticle potential strength $k = [(2\pi)/b]^2\Phi_0$, the driving frequency $\omega = (\pi/25b)\sqrt{\Phi_0/m}$, the wave vector $q = 1/5b$, the amplitude $c = 7/10$, and the peak width $s_0 = 4/10$.

Atomic Scale Engines: Cars and Wheels

Markus Porto, Michael Urbakh, and Joseph Klafter
School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

Phys. Rev. Lett. 84, 6058 (2000)



J.Nieminen, E.Niemi and
K.H.Rieder
Surf.Sci.Lett.552, 47 (2004)