STM-Manipulation of Atoms and Molecules

K.H. Rieder

Postprof at

Swiss Federal Laboratories for Materials Testing and Research, 8600 Duebendorf, Switzerland
Ag (111) with atomic resolution

Nearest neighbour distance 2.89 Å

Corrugation amplitude 0.1 Å

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.,

d$I$/d$V$ spectroscopy at pentacene center exhibits HOMO and LUMO peaks.

STM-images at voltages $U$ in the gap region are relatively featureless (middle).
For $U \leq -2.4$ V they closely resemble the HOMO electron density (left).
For $U > 1.7$V (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

atomic manipulation

98 Ag atoms forming two Chinese letters: Ji Jing

C. Gu¹, K.-F. Braun², K.H. Rieder²

¹ Ji Jing university, China
² Freie University, Berlin
Lateral manipulation: Experiment

Basic tip-sample interaction mechanisms for atomic scale modifications of surfaces
Pulling of single Ag atoms on Ag(111) at 5 K

\[ I \propto U e^{-\frac{R}{kT}} \]

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.

Transition from pulling to sliding
Proc. 12th Int. Conf. on Scanning Tunneling Microscopy/Spectroscopy and Related Techniques
Eindhoven 2003
p.109

Joe Stroscio, Bob Celotta (NIST, Washington DC)
„Autonomous atom assembly“
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

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

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 leads to a single leg of TBPP being reversibly rotated on Cu(211). Image: $R = 7.5 \times 10^8$ Ohm. Manipulation: $R = 6 \times 10^4$ Ohm. The legs are flat, one leg is rotated, the leg is flat again.
A molecular wire system

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

3.5-di-ter-butyl-phenyl-groups

fluoranthene groups

polyaromatic body
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 \( E_\Gamma = -420\text{meV} \)
calculation of the wavepattern

- tip emits a circular wave: \( a_T = H_0^{(1)} \)
- point interaction yields s-wave phaseshift \( \delta \) and absorption \( \alpha \): \( a(r) = H_0^{(1)} \left( \frac{\alpha e^{2i\delta} - 1}{2} \right) \)
- interference term after all scattering processes:
  \[
  LDOS \propto \text{Re} \left( \bar{\alpha}_T \cdot \left[ 1 - \bar{\mathcal{A}} \right] \cdot \bar{\alpha} \right)
  \]
  [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
  \( \tau \) electron lifetime
Comparison of different model calculations

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

NaCl on Cu(111): Large islands with sharp unpolar edges
Image size 2300x1600A, 230pA; -1.26V
Jascha Repp, Gerhard Meyer and K.H. Rieder,
Interface state band and refraction: NaCl/Cu(111)

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


Model

STM tip

Refraction

Surface state

NaCl layer

Interface state

Cu(111) substrate

NaCl(100)/Cu(111)

Interface state band

- Interface state band descends from the surface state of the clean surface.
- From standing wave patterns $E(k)$ is extracted.
- The dispersion is shifted towards higher energy.

dl/dV-images

NaCl

Cu

-275mV

-200mV

50mV

142mV

Dispersion

2 layers NaCl/Cu(111)
clean Cu(111)
**Band gap**

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

**NFE-model:**

\[
\psi(x) = \begin{cases} 
\sin(k_xx) & \text{for } k_x = k_y/2 \\
\cos(k_xx) & \text{for } k_x = 0
\end{cases}
\]

**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.

\[
\frac{\sin \alpha}{\sin \beta} = \frac{\lambda_1}{\lambda_2}
\]

Conservation of $k_{\parallel}$
Spin-split surface state on Ni(111)?

Spin-resolved inverse photoemission from Ni(111):

**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)
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) 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.

\[ m^* = 0.17 \]
\[ E_b = -165 \text{ meV} \]
Ni(111)

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

A.Grechnev, M.I. Katsnelson and A.I. Lichtenstein
Ni(111)

eperimental power spectra of dI/dV linescans and theoretical results for surface electronic states

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.


<table>
<thead>
<tr>
<th></th>
<th>E₀ − Eₐ (eV)</th>
<th>m*/mₑ</th>
<th>kₚ(A⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-0.435 (-0.391ᵃ)</td>
<td>0.412</td>
<td>0.215</td>
</tr>
<tr>
<td>Au</td>
<td>-0.487 (-0.440ᵇ)</td>
<td>0.255</td>
<td>0.167/0.192</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.063 (-0.026ᵇ)</td>
<td>0.397</td>
<td>0.080</td>
</tr>
<tr>
<td>Ni (spin-up)</td>
<td>-0.165</td>
<td>0.17</td>
<td>0.085</td>
</tr>
</tbody>
</table>
Vertical Manipulation of CO on Cu(111)

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

Upper curve: tip moves over adsorbate

Lower curve: adsorbate moves with tip

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: $R_t = 1.5 \times 10^5 \Omega$, $V_t = 30 \text{ mV}$).

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: $V_t = 30 \text{ mV}$, $I_t = 1.1 \text{ nA}$, $16 \times 26 \text{ nm}^2$).
(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: \( V_t = 49 \text{ mV}, R_t = 600 \text{ k}\Omega \))

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 \( a_i \).

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.
Possibly realization of an idea of

Markus Porto, Michael Urbakh and Joseph Klafter:
„Atomic Scale Engines: Cars and Wheels“

See also homepage of Prof. Markus Porto at University Frankfurt
Hexa-\textit{tert}-butyl-hexaphenylbenzene

HB-HPB: $\text{C}_{42}\text{H}_{30}$

central benzene ring (in molecular plane)

\textit{tert}-butyl group ($\text{C}_4\text{H}_9$) \textit{(leg)}

phenyl side ring (rotated out of the molecular plane)

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

Synthesis: André Gourdon
CEMES-CNRS Toulouse
Monolayer Structure

STM: $U=0.8\,V$, $I=0.2\,nA$

Structure matrix:

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

Monolayer orientation ($b$, [01-1]): $0^\circ$

Molecular orientation ($m$, [01-1]): $\pm 11^\circ$
(either $+11^\circ$ or $-11^\circ$ for all molecules in one molecular island)
Intramolecular Contrast

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

- tert-butyl legs 2.3 Å
- phenyl side rings 2.0 Å
- central benzene ring 1.4 Å
Manipulation between Molecular Islands

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

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”).

Isomerization:

The geometrical structure
but not the composition of a compound is rearranged.

Disperse Orange 3
(Azobenzene derivate)
\[
\text{NH}_2\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2
\]
Conformational Cis-Trans-Isomerization of Azobenzene derivate:
Disperse Orange 3 (NO$_2$C$_6$H$_4$N=NC$_6$H$_4$NH$_2$) on Au(111))

J. Henzl,
Michael Mehlhorn,
Heiko Gawronski,

Planar adsorption geometry with bond angle increased to 150°
Conformational Cis-Trans-Isomerization of Azobenzene derivate: Disperse Orange 3 (NO$_2$C$_6$H$_4$N=NC$_6$H$_4$NH$_2$) on Au(111))

Injecting electrons into N=N bond

<table>
<thead>
<tr>
<th>Conformation</th>
<th>Voltage (mV)</th>
<th>Current (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-trans</td>
<td>640</td>
<td>9.4</td>
</tr>
<tr>
<td>cis-cis'</td>
<td>680</td>
<td>71</td>
</tr>
<tr>
<td>trans-cis</td>
<td>710</td>
<td></td>
</tr>
</tbody>
</table>

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)

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

Moving substitutional groups between molecules

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

Lateral manipulation:
constant current or constant height modes

Van der Waals or chemical forces between tip and adsorbate
Lateral manipulation on atomic scale: CO/Cu(211)
Lander on Cu(111)

like in the case of Cu(211) different configurations and orientations are observed

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

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

lateral dimension: 25-30 Å
apparent height: 4 Å
The five possible tunneling channels in the presence of an adsorbed molecule at 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

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

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

$V = 0.9 \text{ V}, I = 2 \times 10^{-10} \text{ A}$
RECOGNIZING MOLECULAR CONFORMATIONS DURING MANIPULATION WITH A STM TIP.

ROTATION BY USING TIP-MOLECULE FORCE

LUMO OF DIIODOBENZENE

LATERAL MANIPULATION WITH AN UP-RIGHT POSITION

S.W. Hia, A. Kühne, G. Meyer, K.-H. Rieder
- Electrons with energies up to 1.8 eV are injected into the end pi-ring of Sexi-phenyl.
- Electron injection rate $\sim 10^{10}$ 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

$2(\text{I}) + 2\text{Cu} = (\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5) + 2\text{CuI}$

Ullmann Reaction

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

FU Physik, TU Berlin, Germany
Pentacene on a Vanadiumoxide Thin Film grown on Cu$_3$Au(100)

Molecule structure

Pentacene on V$_x$O$_y$

Pentacene image resembles HOMO electron density of free molecule

V$_x$O$_y$ disordered islands

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

Making electrical contacts with atomic precision

Molecular shooting: a possible atomic scale engine?

Switching molecules by mechanical and electron induced manipulation

Vertical manipulation: A route to chemical contrast?

200 pA, 10 mV
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 (NO₂C₆H₄N=NC₆H₄NH₂) 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)
Nitrobenzene on Cu(111)

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

Experiment

Distance 6.0 Å
Distance 6.5 Å

(c)  
(d)
$C_6H_4ClNO_2 / C_6H_4NO_2$ on Cu(111)
Changing the internal structure of a molecule = isomerization

C$_6$H$_4$ClNO$_2$ on Cu(111)

Manipulation with 300 mV

changing the chirality of a molecule

= isomerization

changing the chirality of a molecule
Iodine Dissociation from Dibromobenzene with the STM Tip.
Releasing Adatoms on the Surface

- 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:

\[ R (\Omega) \]

\[ \Theta \]

\[ z_o=9\text{Å} \]

\[ z_o=7\text{Å} \]

\[ \text{OFF} \quad \text{ON} \]

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

Standing waves: calculations using Heller theory

Very good agreement between experiment and model
Standing waves

Our model:

- Black dots represent the step edge.
- The model exactly reproduces the position of the end naphthalene group.

Effective scattering geometry:
- 0.76 nm wide
- Positioned 0.28 nm from the step edge

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 equivalent sites

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

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 $x(t)$ 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 $a_{i,\chi+\delta}(t)$ 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

J. Nieminen, E. Niemi and K. H. Rieder