Zurich Research Laboratory

Scanning Probe Microscopy of Adsorbates on Insulating Films:

From manipulation of the charge state to imaging of individual molecular orbitals and bond formation

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Dresden, June 2008

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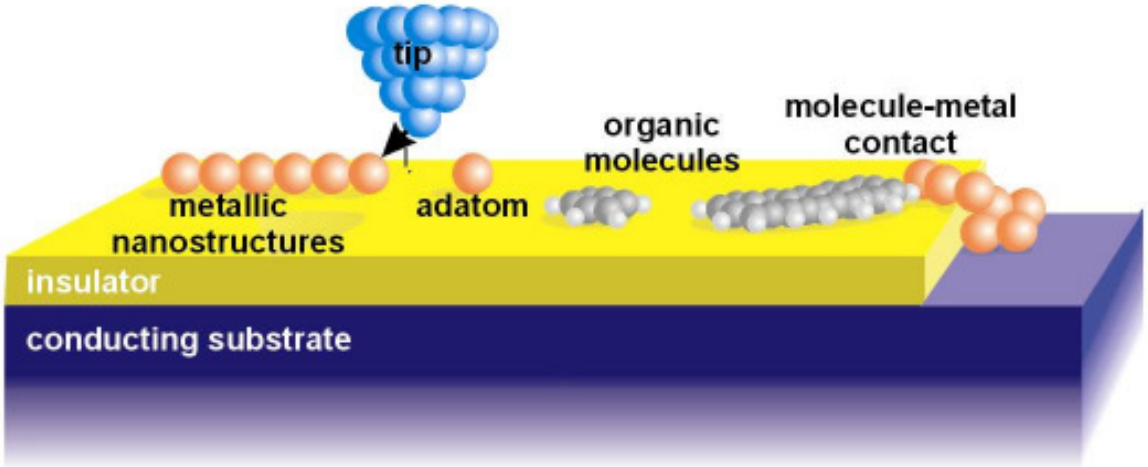
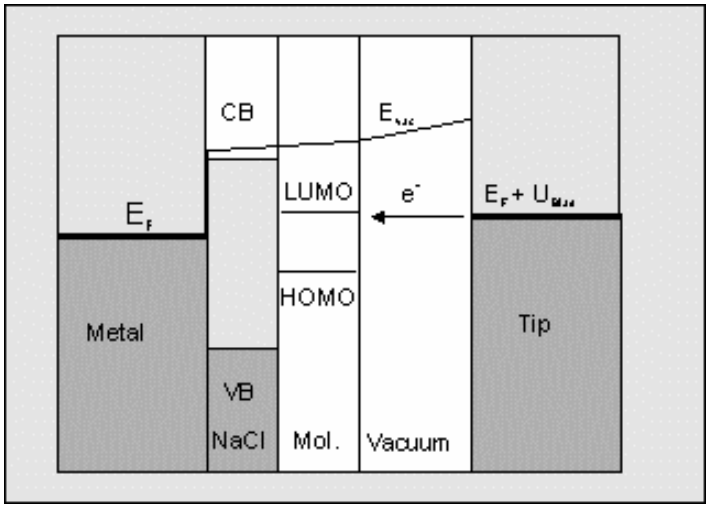
STM of adsorbates on ultrathin insulating films

Model:



Double Barrier Tunneling Junctio



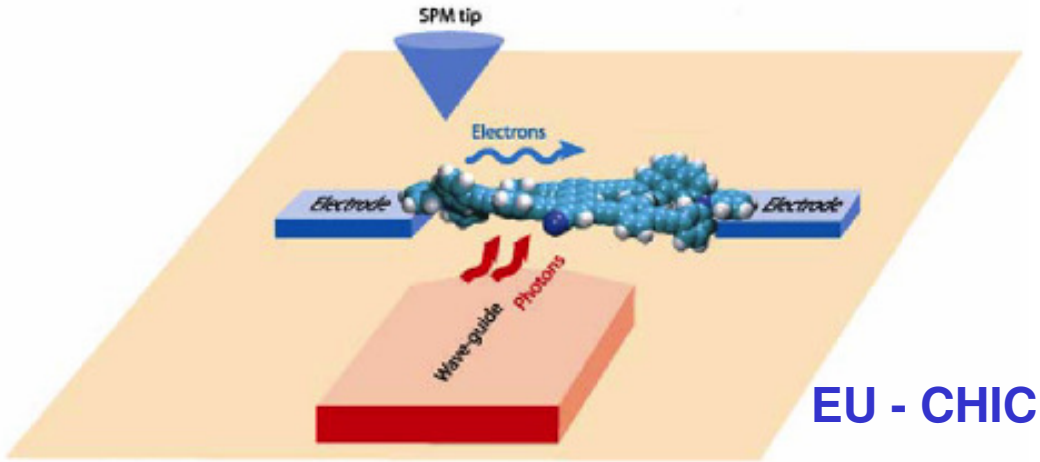
To study:

- Electronic properties of atoms/molecules
- Inelastic tunneling
- Catalytic processes on insulators
- Metallic nanostructures

Electrical transport through single molecules in a planar junction geometry

STM of atoms/molecules on insulating films:

An ideal technique to study electrical transport through single molecules in a planar junction geometry



EU - CHIC

Advantage:
Single molecule contributes, direct information/control on conformation, contact geometry well defined, several electrodes, assemblies of larger molecular systems

Instrumentation:

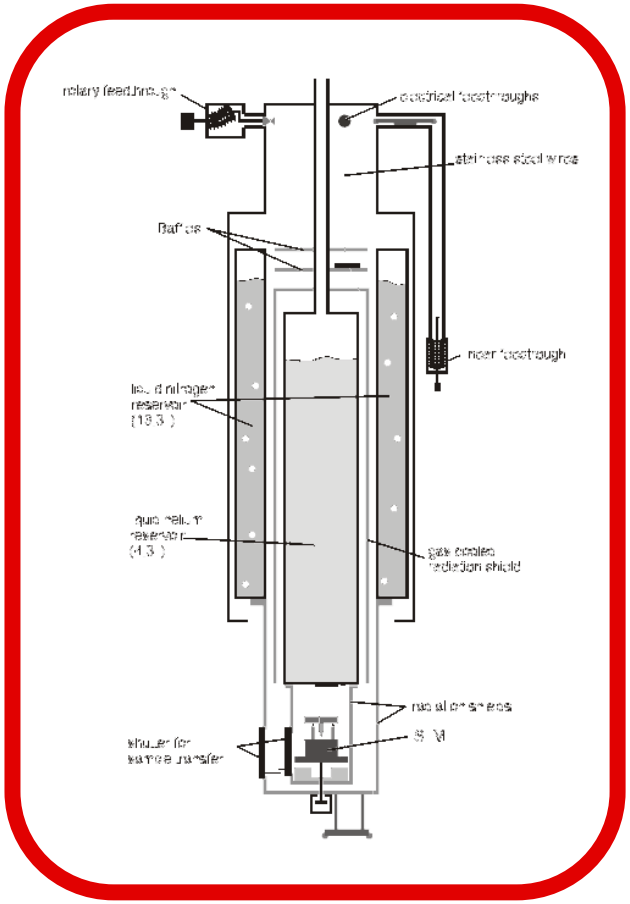
- Low Temperature STM/AFM

- NanoStencil

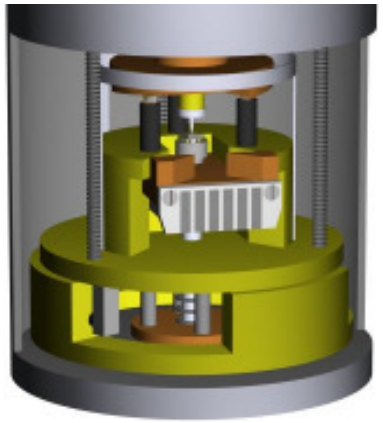
Low Temperature STM/AFM

Features:
-Temperature range: 4K - 300K
-Besocke 'Beetle' type scanner
-Tuning fork force sensor
-sample transfer
-optical access at low temp.
-atomic/molecular manipulation

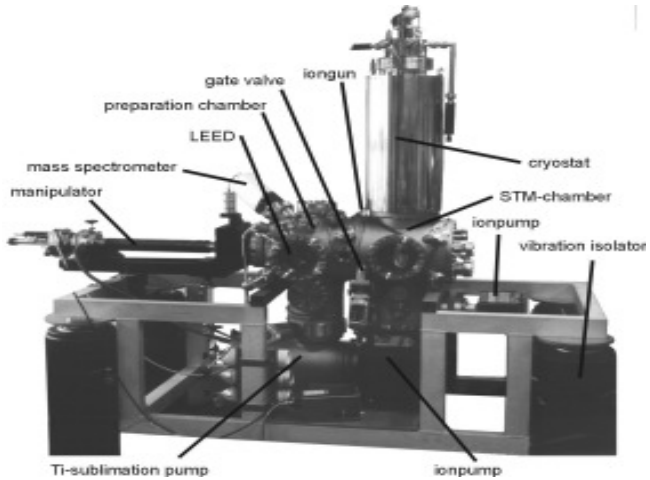
Cryostat



Scanner

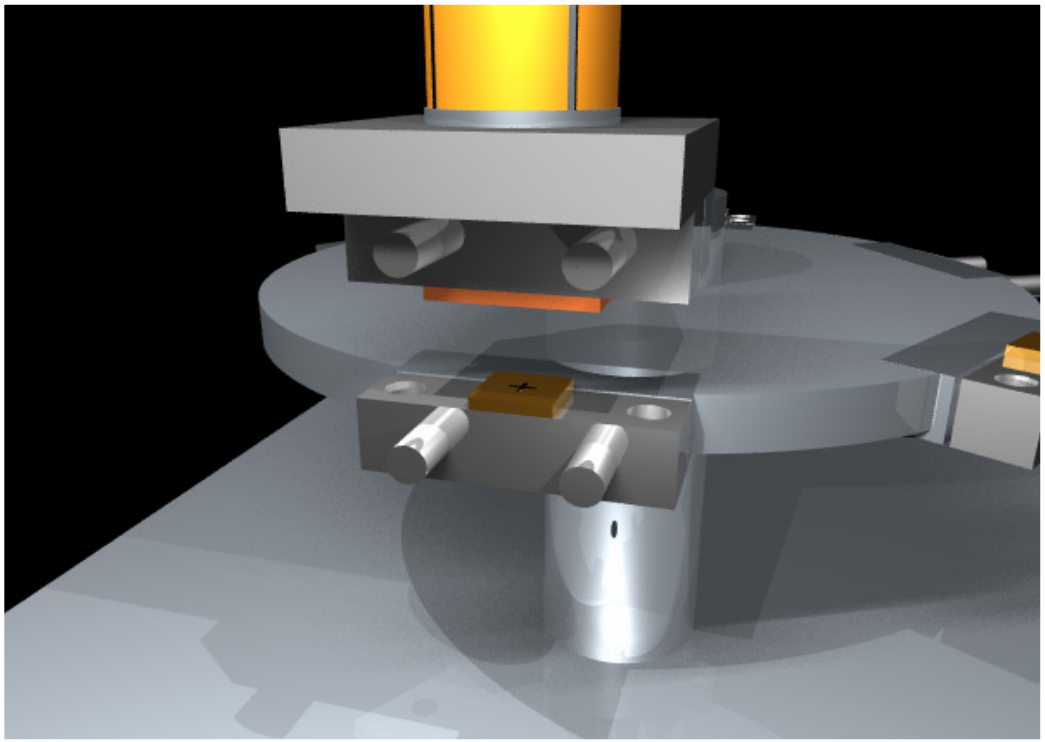


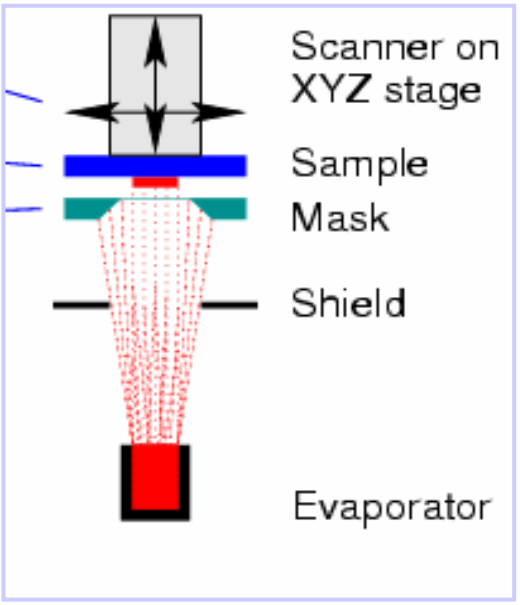
UHV - chamber



How to make macroscopic contacts: Nanostencil

- Shadow mask technique operated in UHV
- Integrated microscopy modes: AFM / DFM / STM

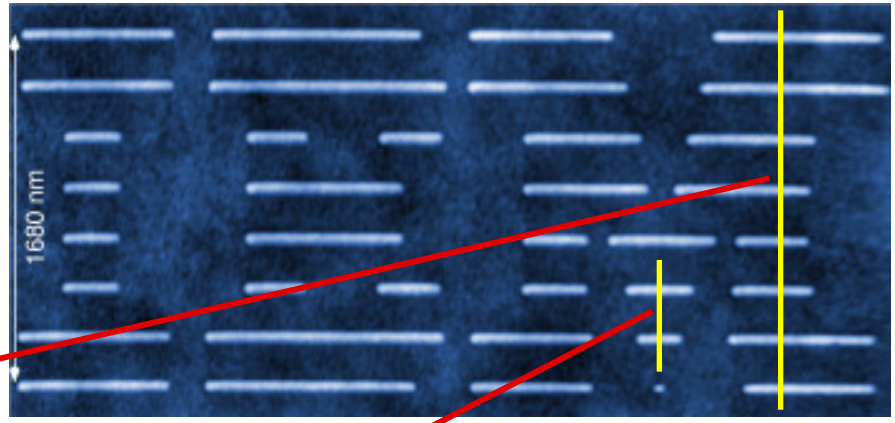


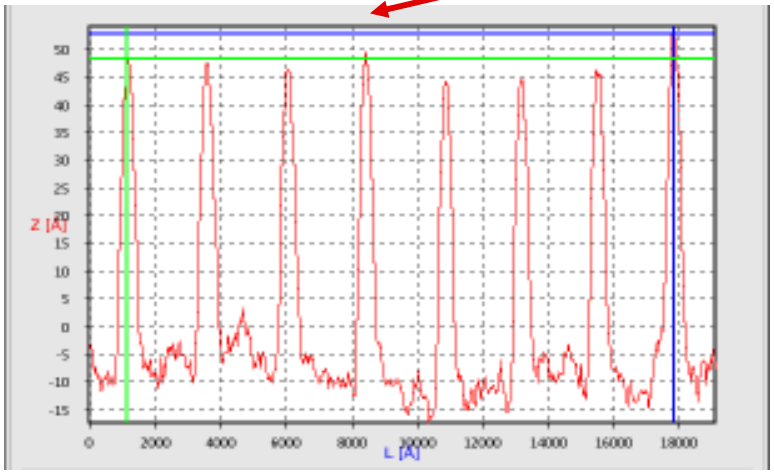


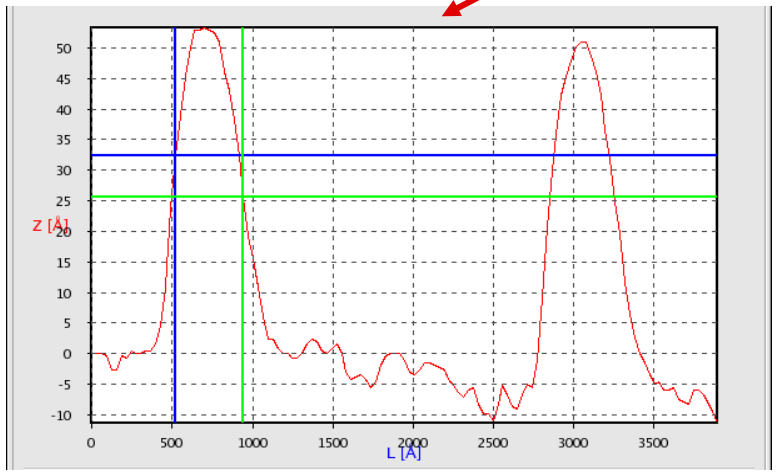
P. Zahl, M. Bammerlin, G. Meyer, R. R. Schlittler, Rev. Sci. Instrum. 76, 23707 (2005)

Nanostencil performance (static mode)

- static mode
- Cu on SiO_2
- deposited pattern imaged subsequently by in-situ AFM







- line width (FWHM): 40 nm

P. Zahl, M. Bammerlin, G. Meyer, R. R. Schlittler, Rev. Sci. Instrum. 76, 23707 (2005)

Ultrathin Insulating Films

Growth of ultrathin insulating films on metal surfaces:

Ionic crystals:

Oxides: MgO, TiO_2, SiO_2, Al_2O_3, ...

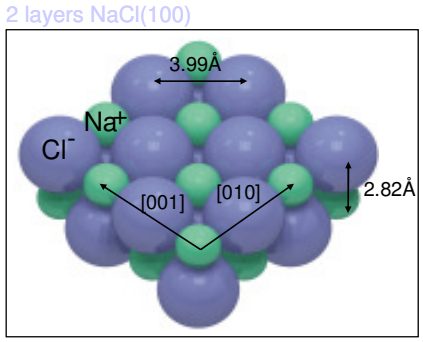
Fluorides: CaF_2, . . .

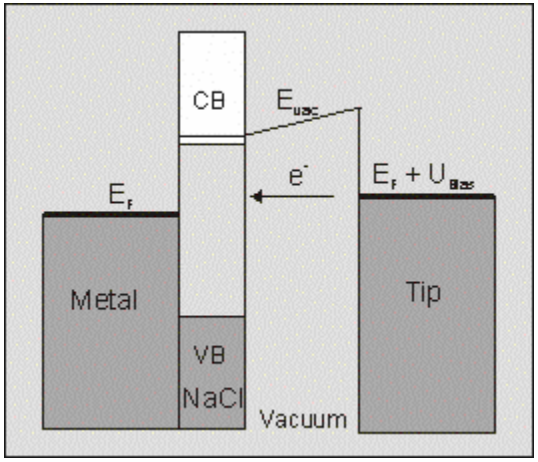
Halides: NaCl, KCl, LiF, . . .

(Covalent, Van der Waals: Diamond, C_{60}, Organic thin films)

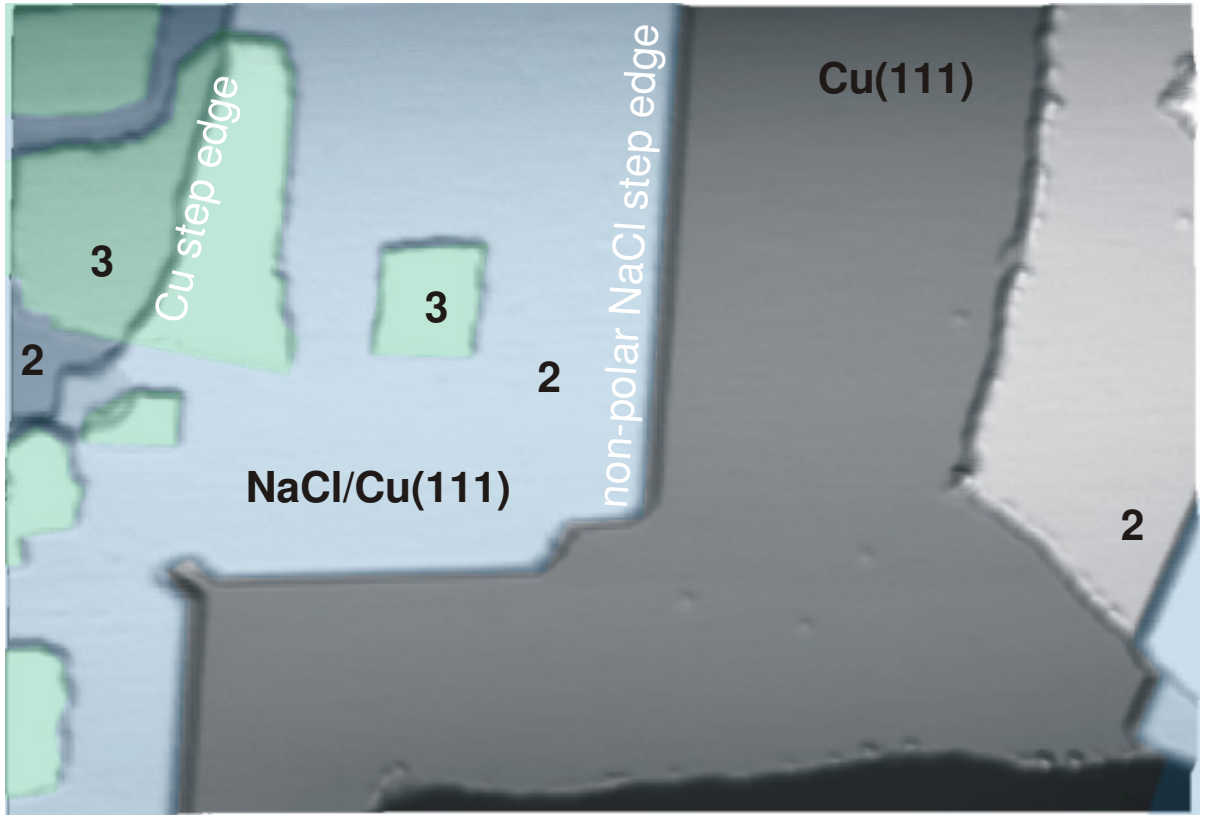
Properties of NaCl:

- Deposition of NaCl as molecules
- Growth temperatures < 600K
- Band gap: 8.9eV
- Simple unit cell
- Lattice constant: 0.565nm





NaCl/Cu(111): Growth



2300Å x 1600Å

-1.26V; 230pA

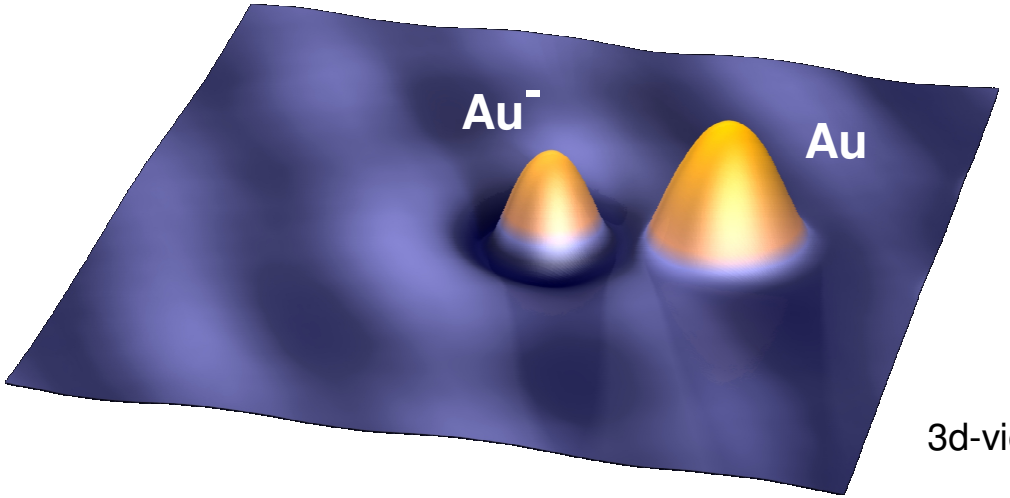
- $T_{\mathrm{Deposition}} = 320\,\mathrm{K}$
- μm-sized islands
- 2 layers minimum
- different rotational domains
- up to 4 layers can be imaged

Control of the charge state of single Au atoms

Au/NaCl/Cu(111): 'Switching' the charge state of individual Gold adatoms

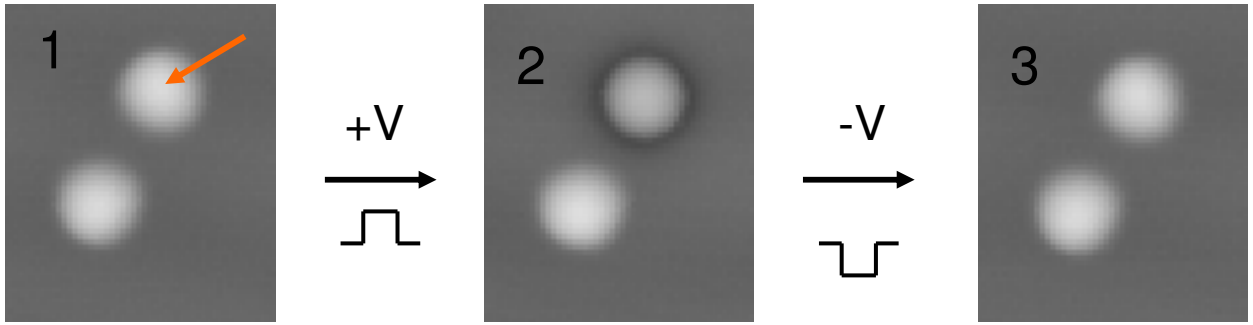
STM imaging:

Au anion has a 0.5Å
smaller apparent height and is
surrounded by a depression



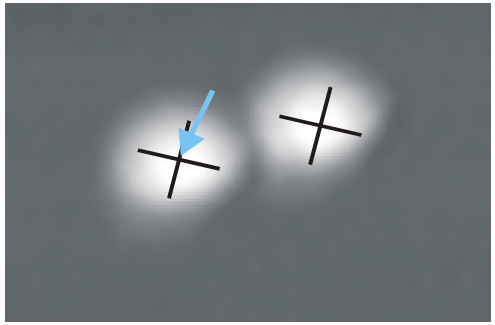
3d-view

'Switching' is reversible (using a voltage pulse with opposite polarity)

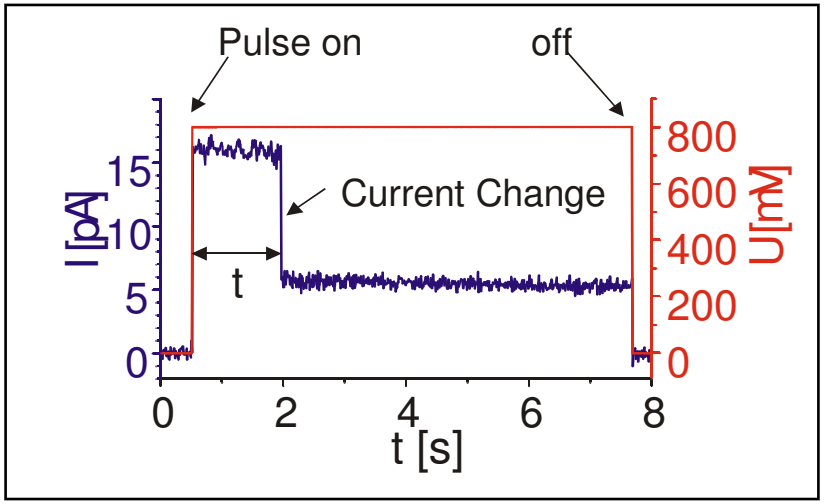


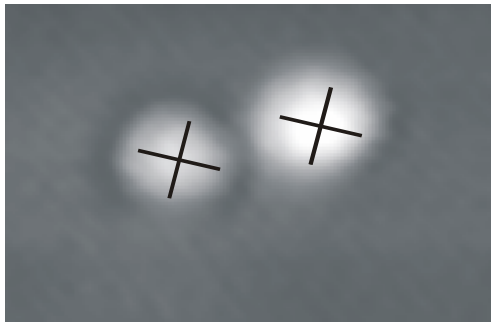
J. Repp, G. Meyer, F. Olsson, M. Persson, Science 305, 493 (2004)

Au/NaCl/Cu(111): 'Switching' of individual Au adatoms



42Å x 30Å 10pA; 500mV





Results:

- Au adatoms can be 'switched' by applying a positive (sample) voltage pulse

- Binding site does not change

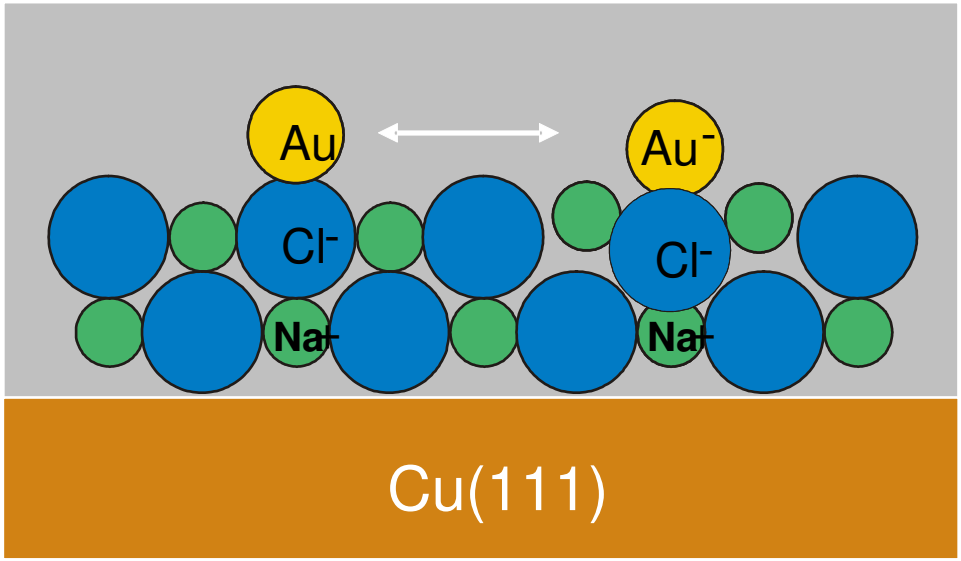
J. Repp, G. Meyer, F. Olsson, M. Persson, Science 305, 493 (2004)

Au/NaCl/Cu(111): Model: 'Switching' between different charge states

Model:

- Switching between differently charged states:

Au^0 <-> Au^-



Theory (DFT)
F. Olsson, M. Persson Chalmers Univ.

Two (meta)stable configurations:
Neutral and negatively charged Au adatom.

Large ionic relaxations of the NaCl stabilize the extra charge on the Au atom.

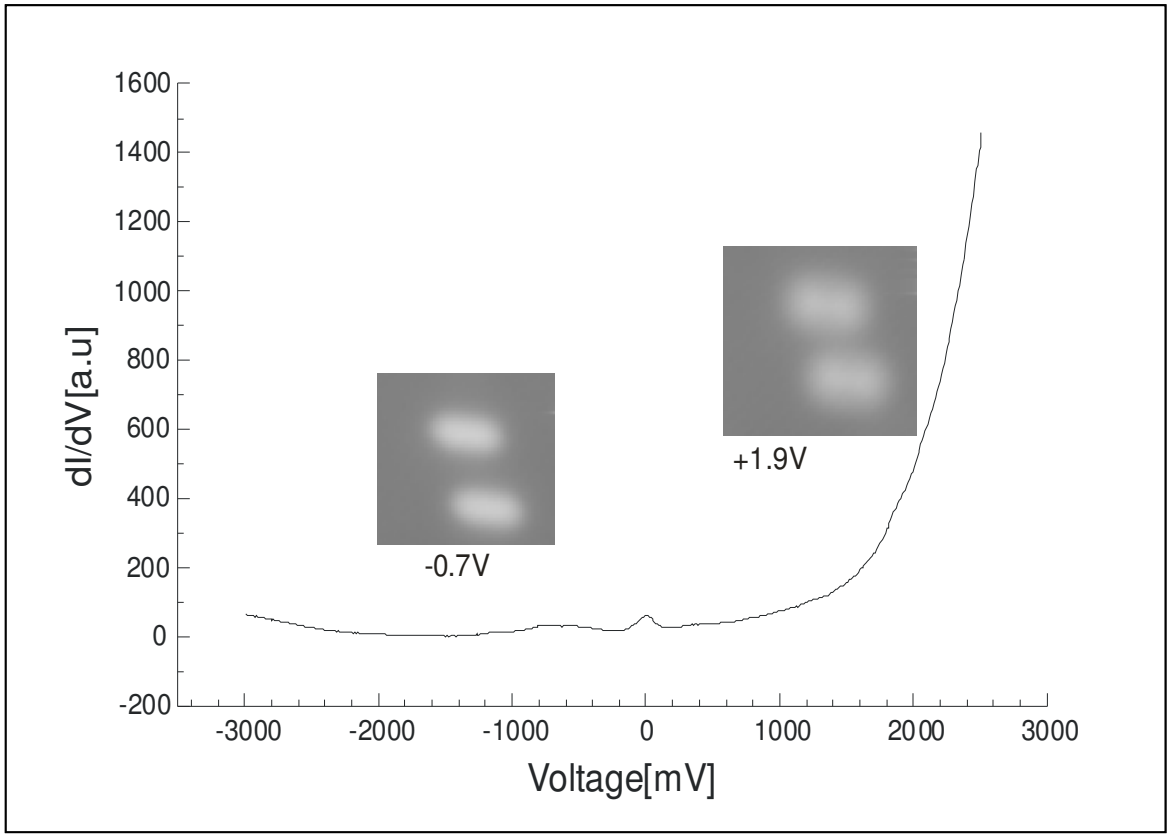
- Au^0 and Au^- have different chemical and magnetic properties

J. Repp, G. Meyer, F. Olsson, M. Persson, Science 305, 493 (2004)

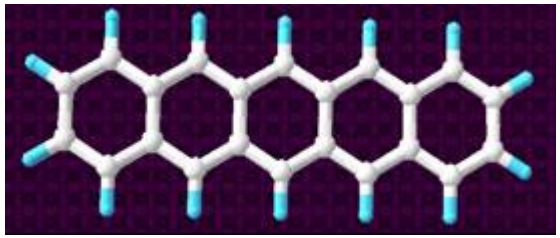
Single molecules on ultrathin insulating NaCl films

Molecules on metals: Pentacene/Cu(111)

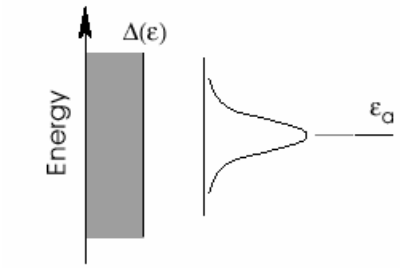
Voltage dependant imaging and local spectroscopy:



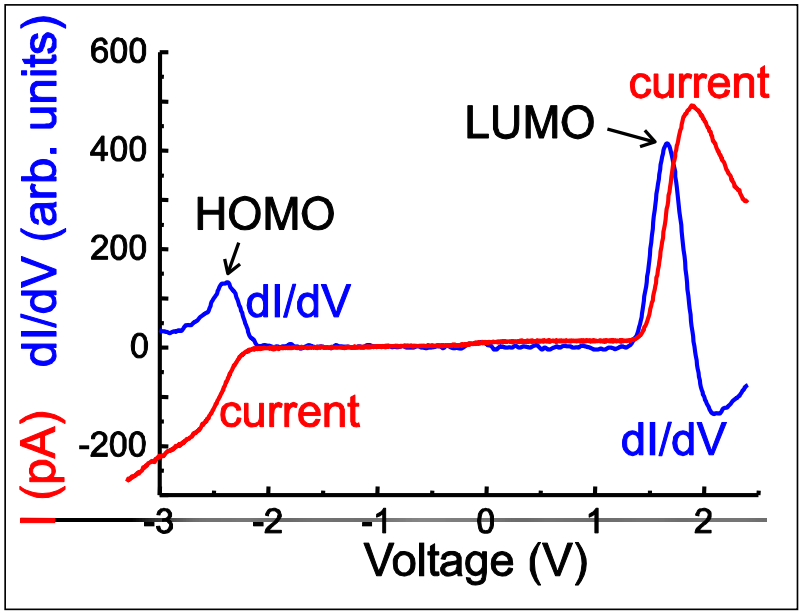
Pentacene:

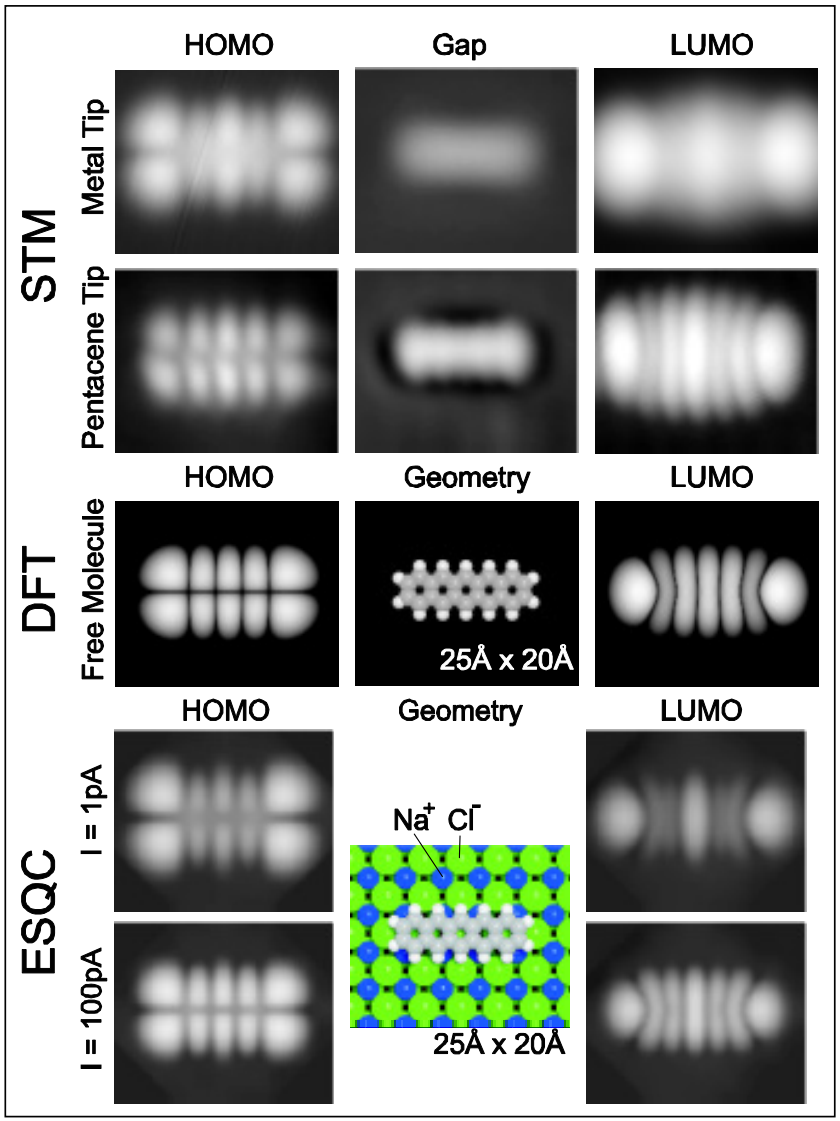


Molecules on metals:
Overlap with metal states results in a large energetic shift and broadening of molecular orbitals



Molecules on Insulators: Pentacene/2ML NaCl/Cu(111)





Molecules are electronically decoupled from the Substrate:

1. STM Images resemble closely the shape of the HOMO/LUMO of the free molecule

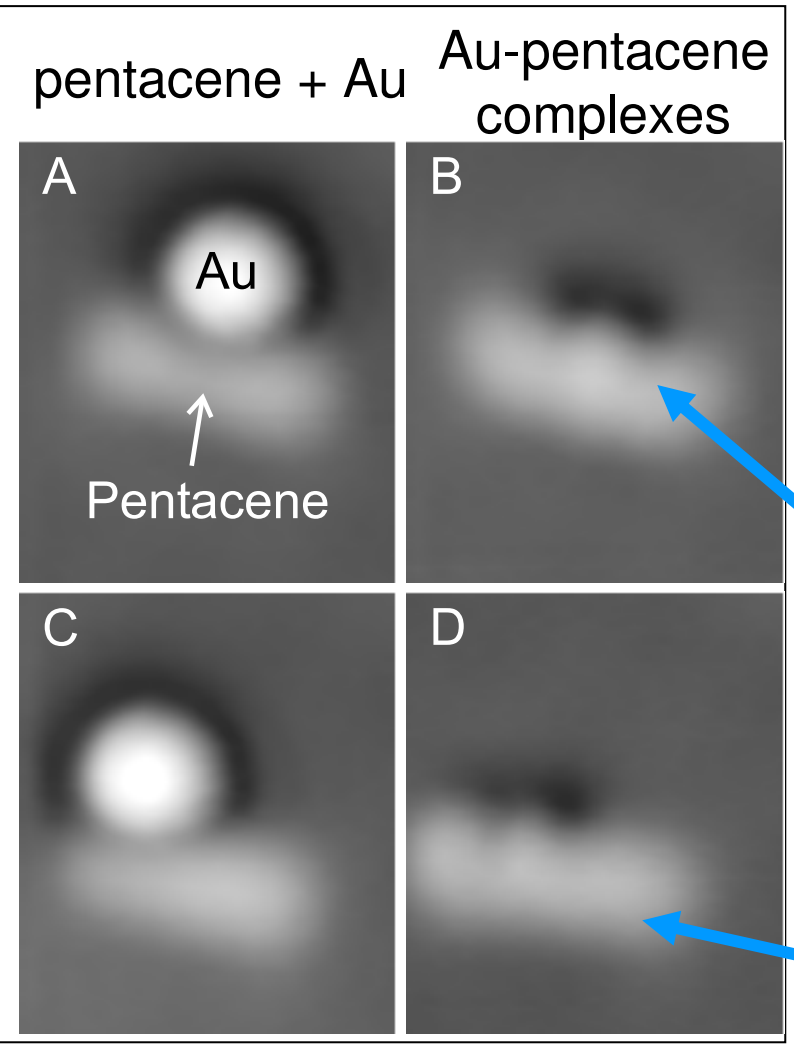
2. In STS well separated peaks

Phys. Rev. Lett. 94, 026803 (2005)

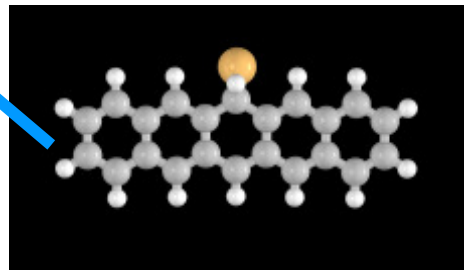
Formation of metal – molecule complexes:

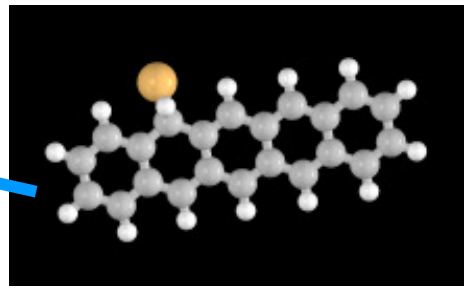
‘electrical contacting’

Bond formation between Au and pentacene

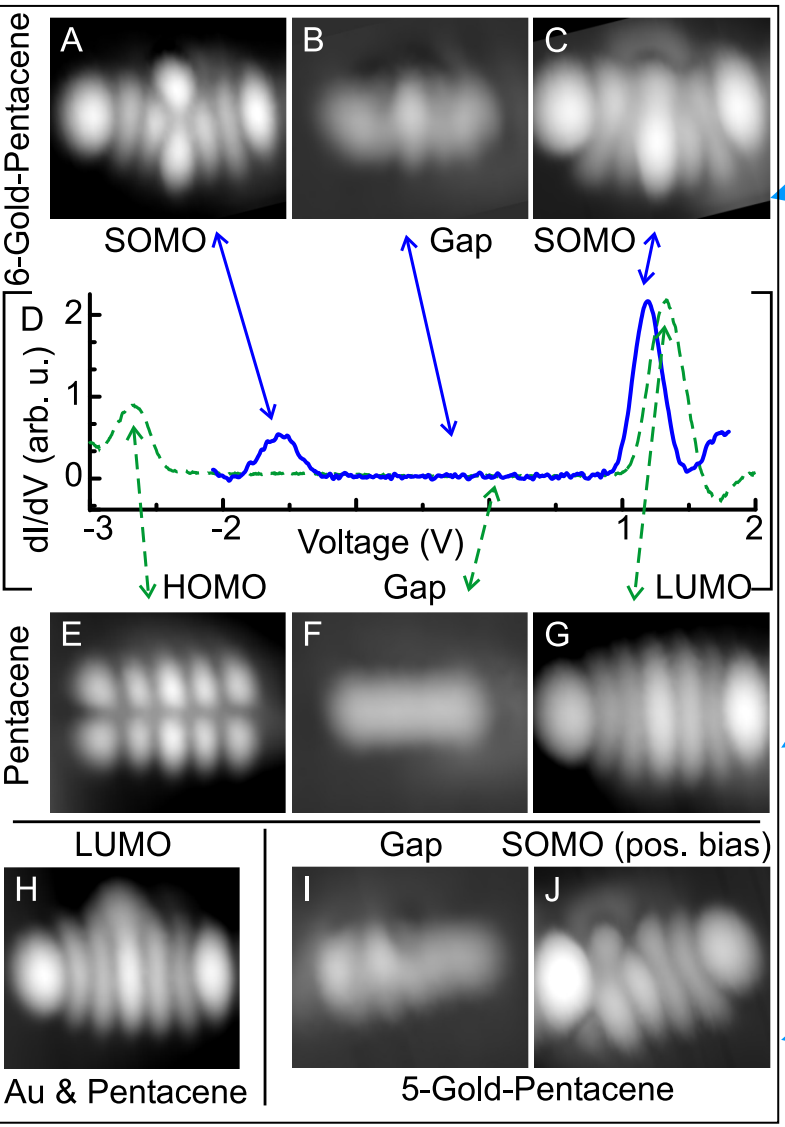


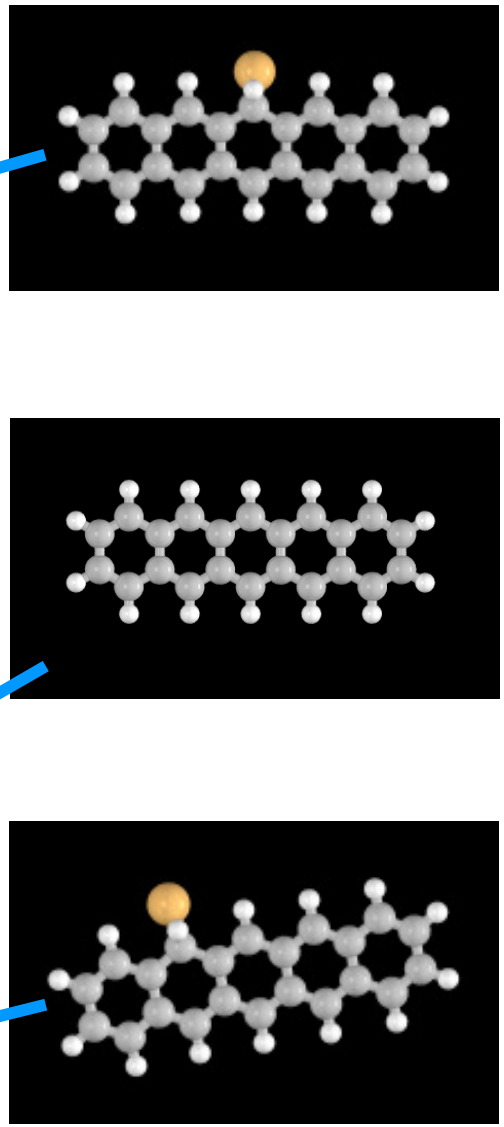
- Formation of a stable atom-molecule complex by atomic manipulation (single molecule chemistry by inelastic excitation).
- Different isomers can be created (5-gold-pentacene and 6-gold-pentacene)
- Bond formation is reversible
- dI/dV shows much smaller gap





Bias-dependent imaging of Au-pentacene



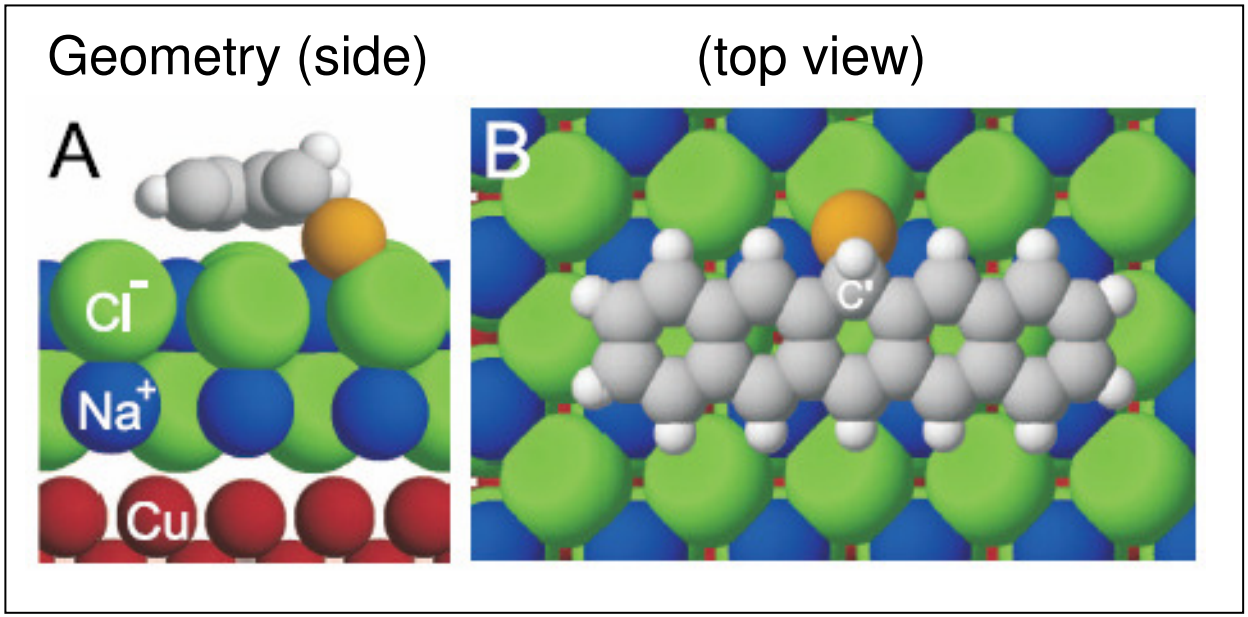


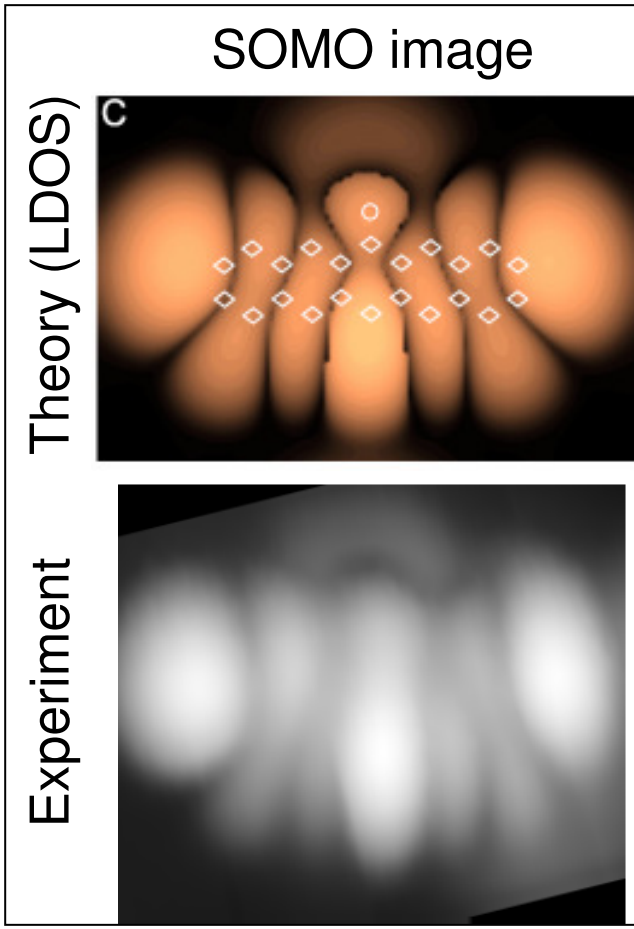
- Au-pentacene shows a much smaller gap region in $\mathrm{d}I/\mathrm{d}V$ than pentacene alone
- Singly occupied molecular orbitals (SOMO) appears at both voltage polarities
- SOMO exceeds over the whole complex $\rightarrow$ covalent bond
- Different isomers show different frontier orbitals

Theory:

DFT calculations: (Sami Paavilainen, Fredrik Olsson, Mats Persson)

- Corroborate experimental findings: Configuration, covalent bond, charge, SOMO
- New insights: geometrical structure, $sp^2 \rightarrow sp^3$ re-hybridization, apparent bending is purely an electronic effect

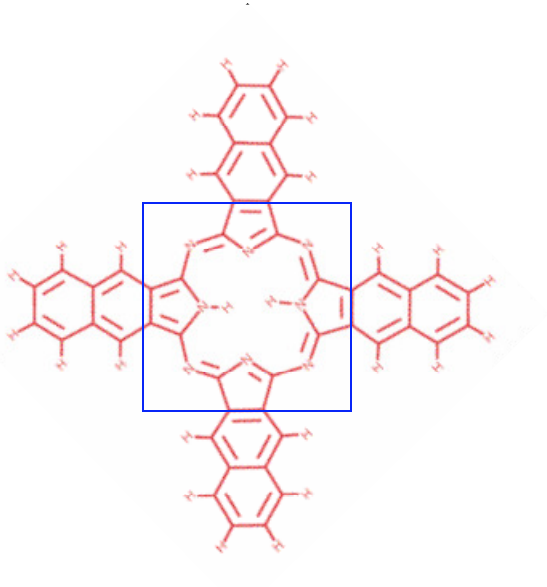




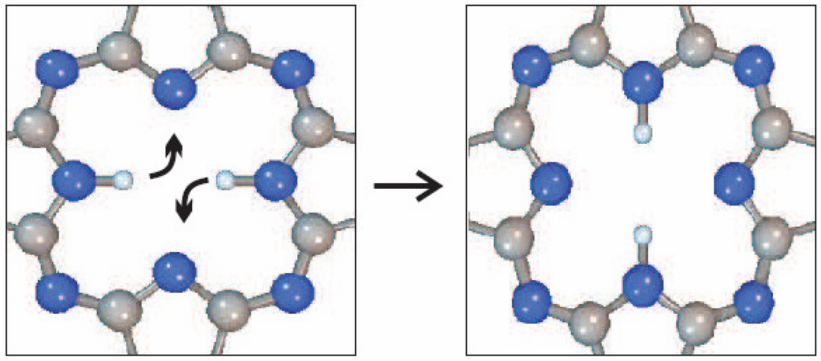
Planar Molecular Switches

A planar molecular switch:

Tunneling induced hydrogen tautomerization in free base naphthalocyanine



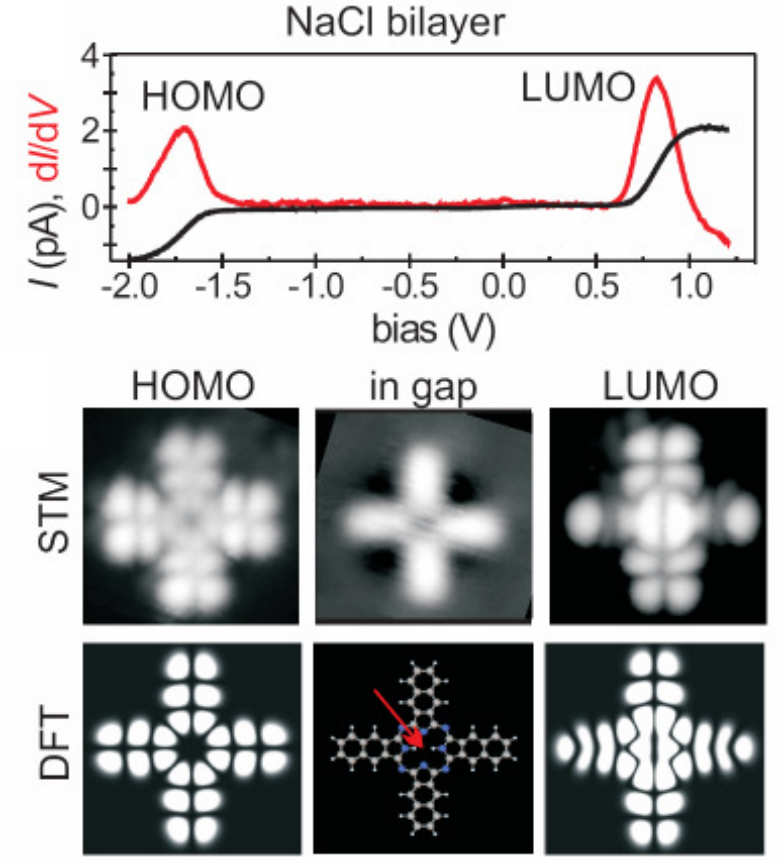
Naphthalocyanine



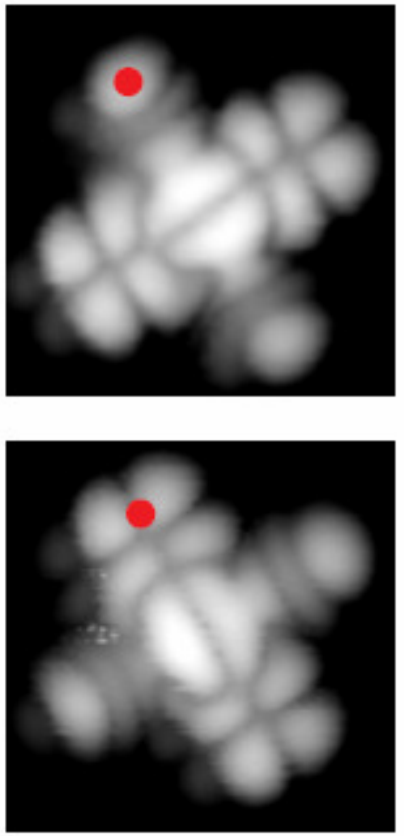
Model of the hydrogen transfer process

Advantages: Molecules are planar, switching between fully symmetric configurations, switching is reversible, switching confined to the inner part of the molecule, arrays of molecules easily formed by self assembly

Free Base Naphthalocyanine: Orbital Imaging

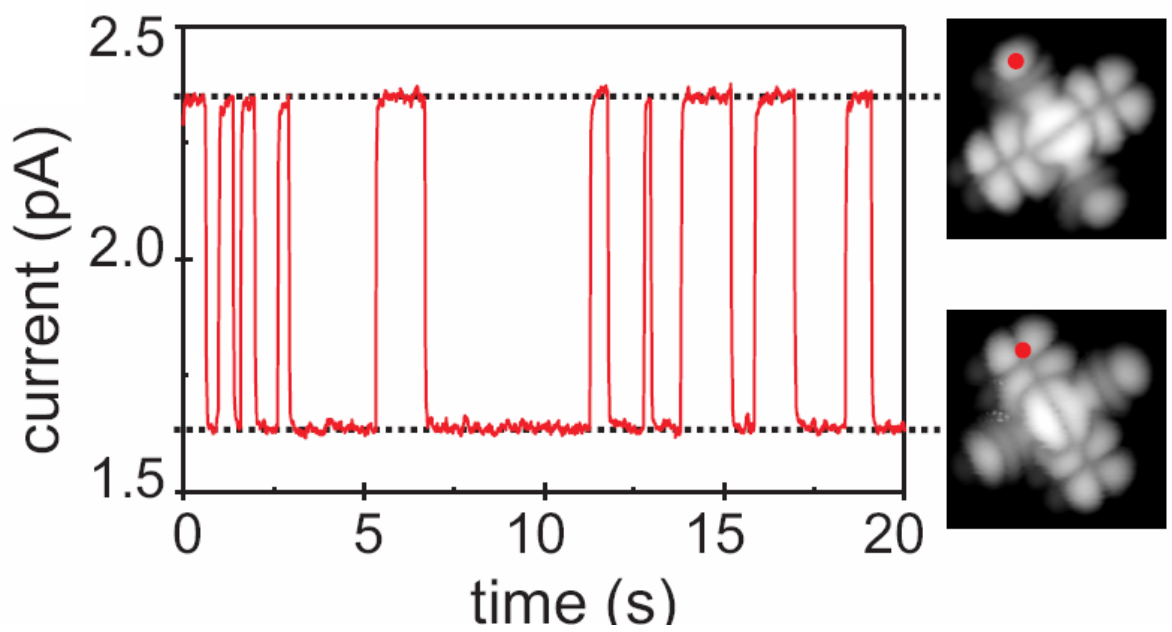


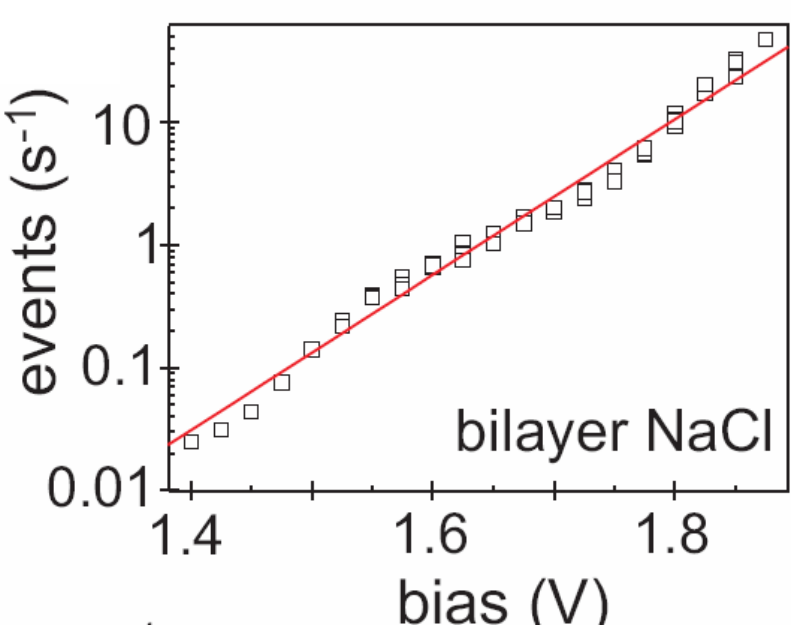
STS/STM of naphthalocyanine on 2MLNaCl/Cu(111)



Images of the LUMO before and after switching

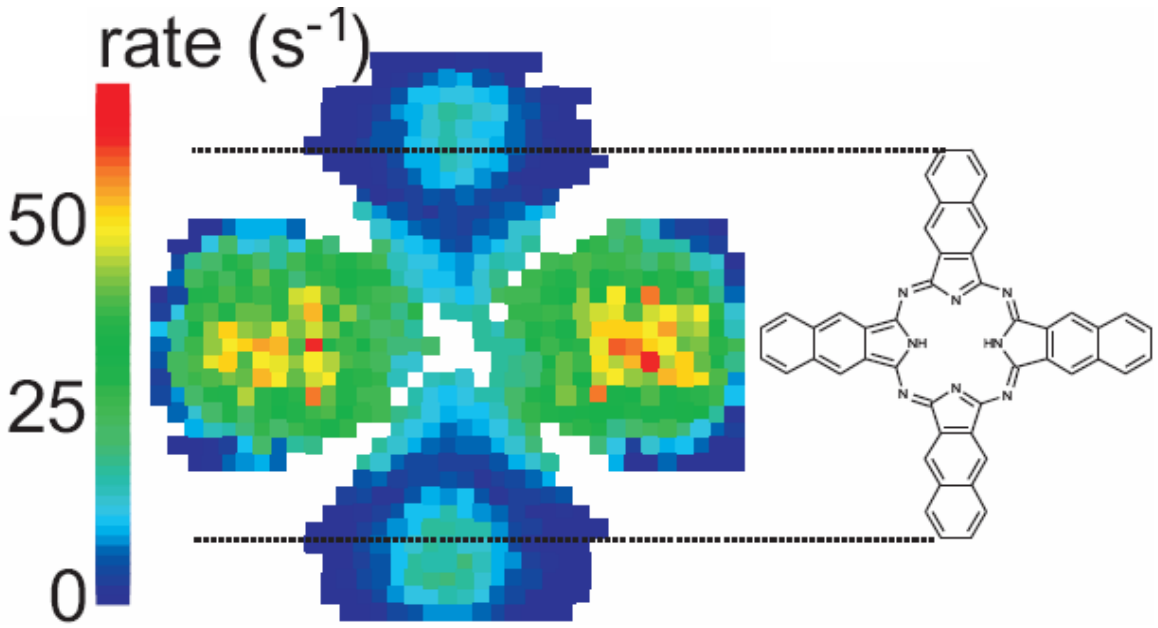
Details of the Current-Induced Switching Process





1. Switching rate increases exponentially with bias voltage

Details of the Current-Induced Switching Process

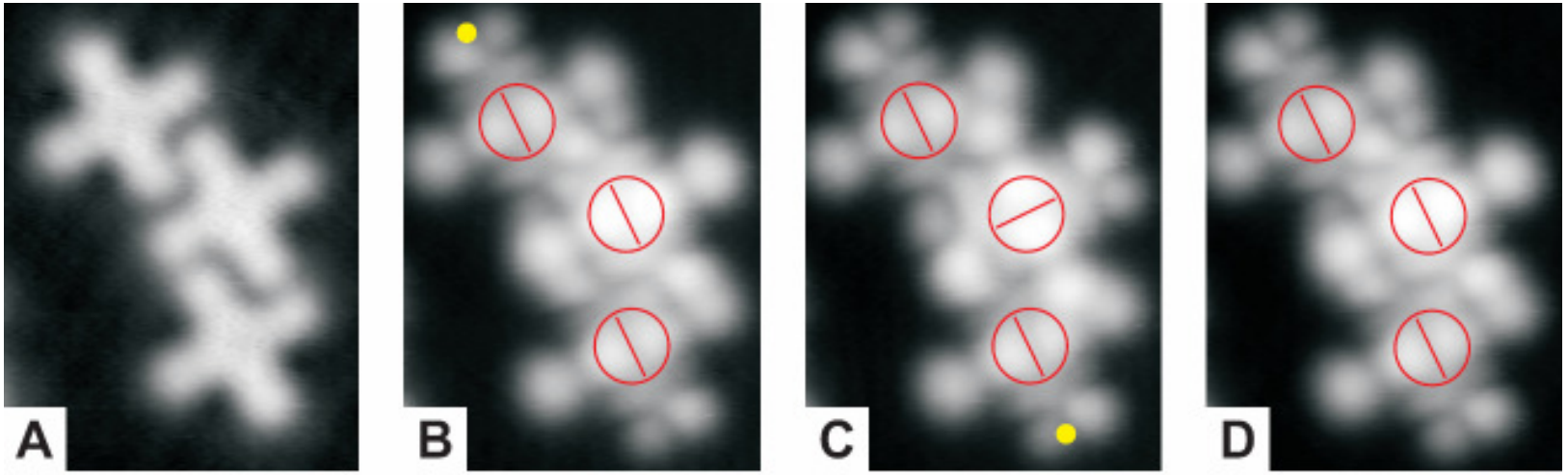


2. Highest switching rate with the tip far at the periphery of the molecule

3. Switching back and forth different by up to factor of 10

Switching induced through adjacent molecules

Arrays of molecules can be assembled by controlled manipulation or self assembly. Switching can be induced by electron injection into neighboring molecules.



A: in gap image 0.3V. B-D Current injection through top/bottom molecules induces switching of middle one

Support:

EU projects: AMMIST, CHIC, NANOSPECTRA, NANOMAN

NCCR Nanoscale Science

Coworker:

J. Repp, P. Liljeroth (LTSTM)

L. Gross, P. Zahl, R. R. Schlittler (Nanostencil)

Cooperation:

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