Zurich Research Laboratory

Scanning Probe Microscopy of Adsorbates on Insulating Films:

First Steps towards a modular molecular logic

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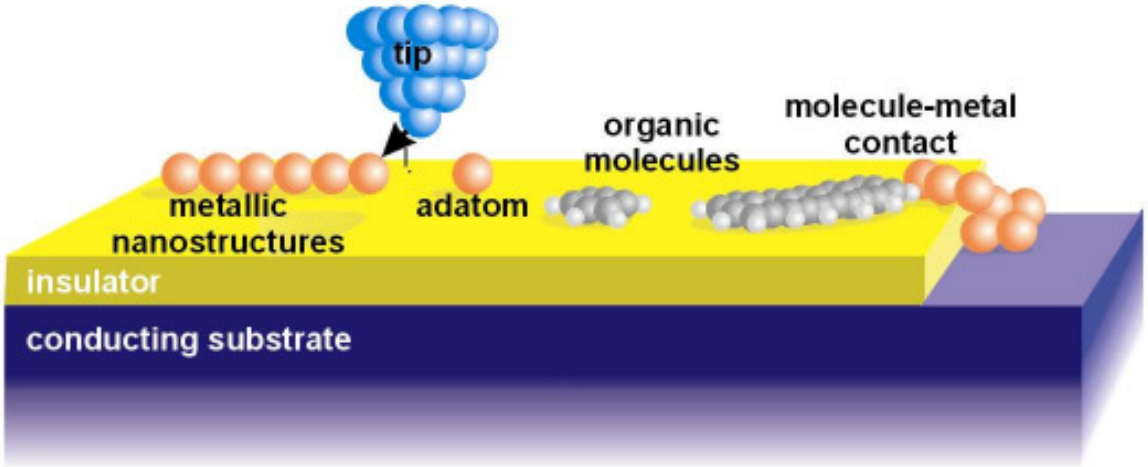
IBM Zurich Research Laboratory

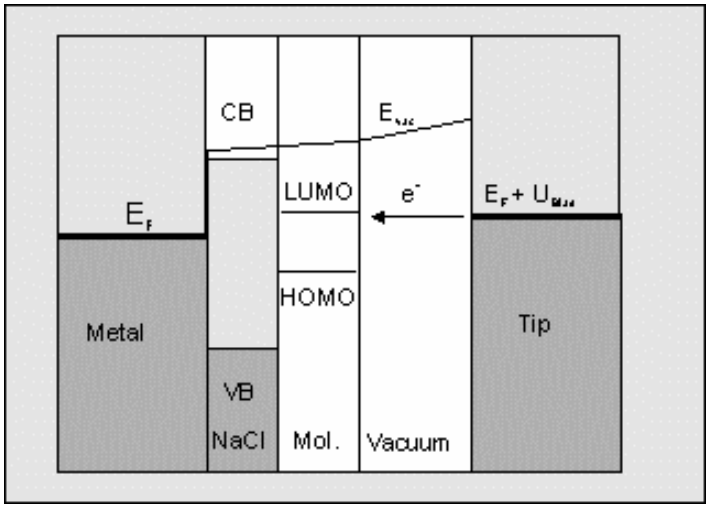
2nd EU FET cluster meeting Las Palmas, Nov. 14th 2007

STM of adsorbates on ultrathin insulating films

Model:



Double Barrier Tunneling Junctio



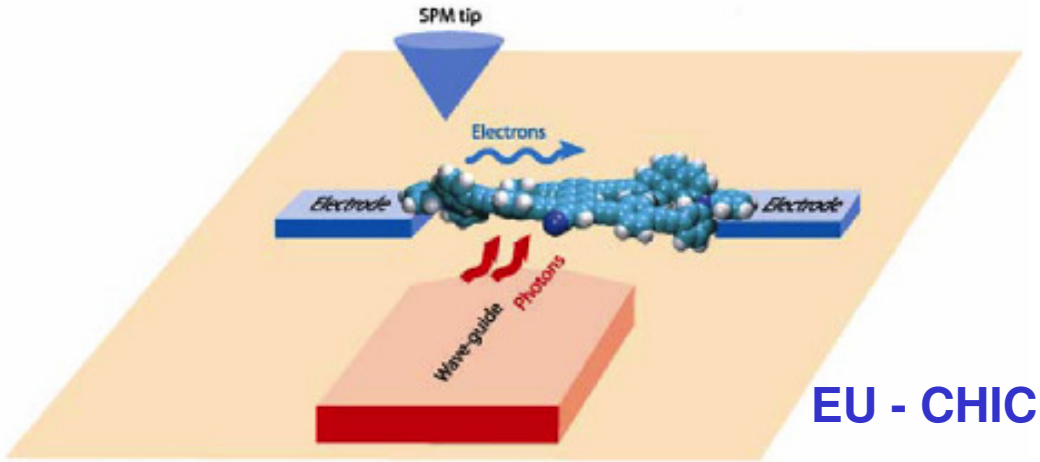
To study:

- 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

Ultrathin Insulating Films

Growth of ultrathin insulating films on metal surfaces:

Ionic crystals:

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

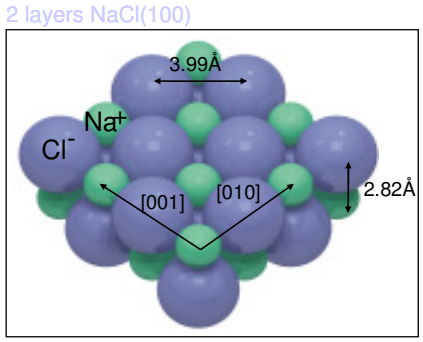
Fluorides: CaF_2, . . .

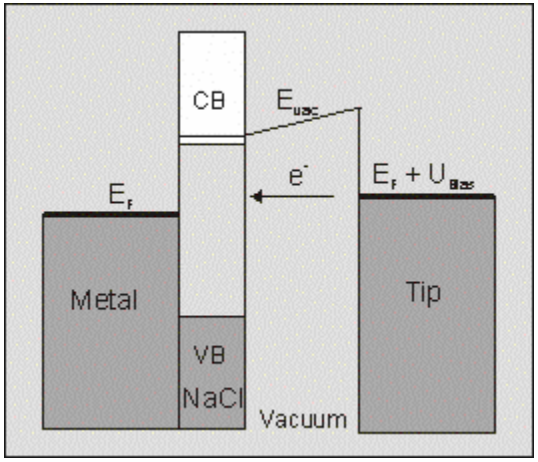
Halides: NaCl, KCl, LiF, . . .

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

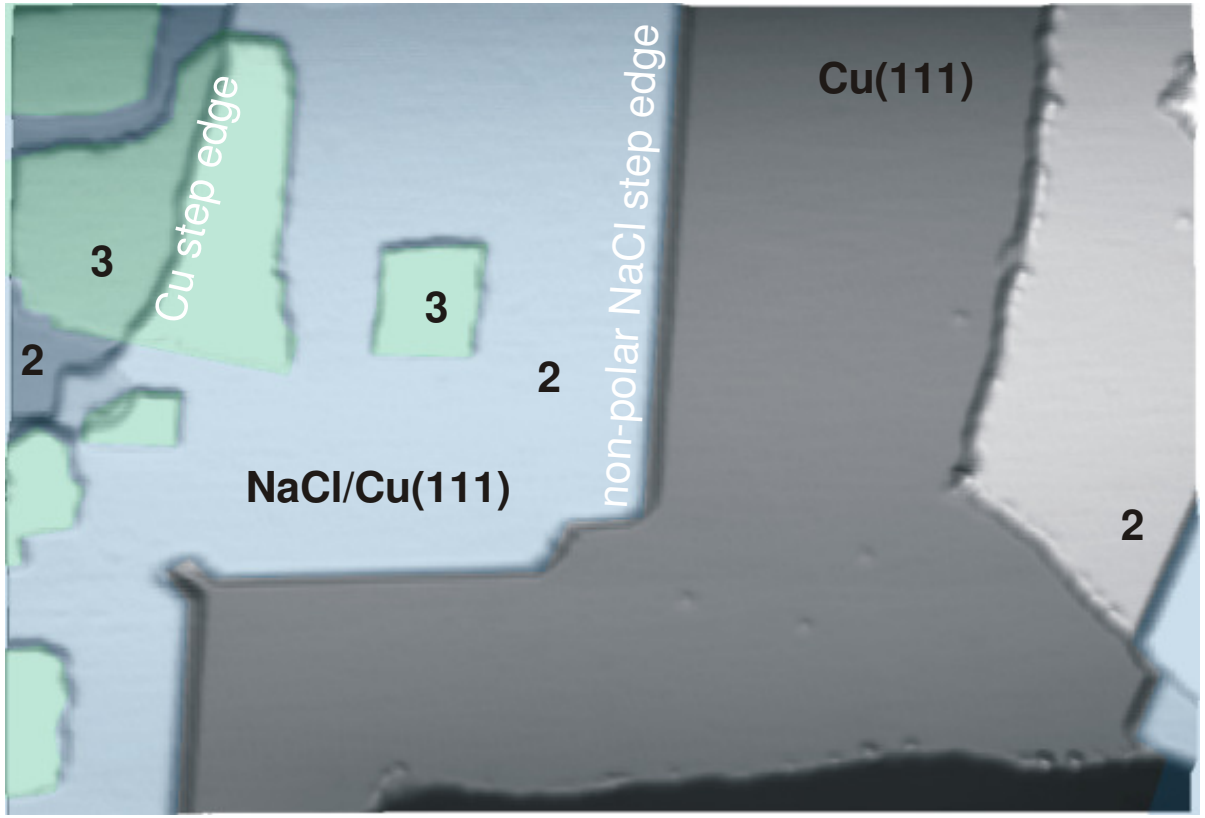
Properties of NaCl:

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





NaCl/Cu(111): Growth

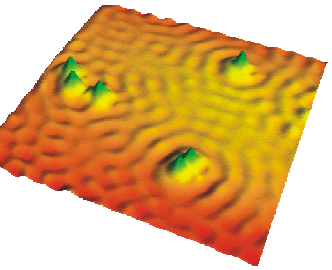


2300Å x 1600Å

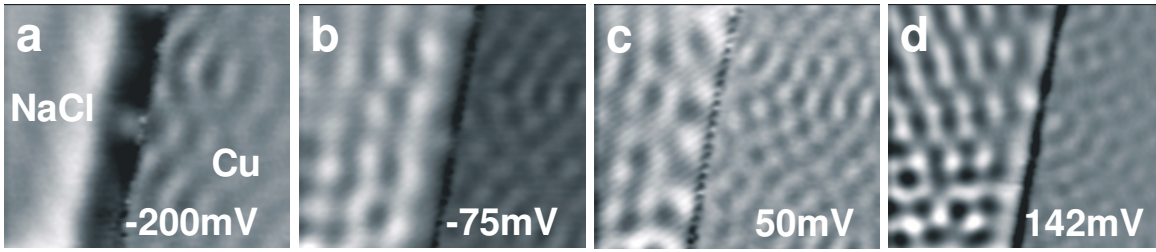
-1.26V; 230pA

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

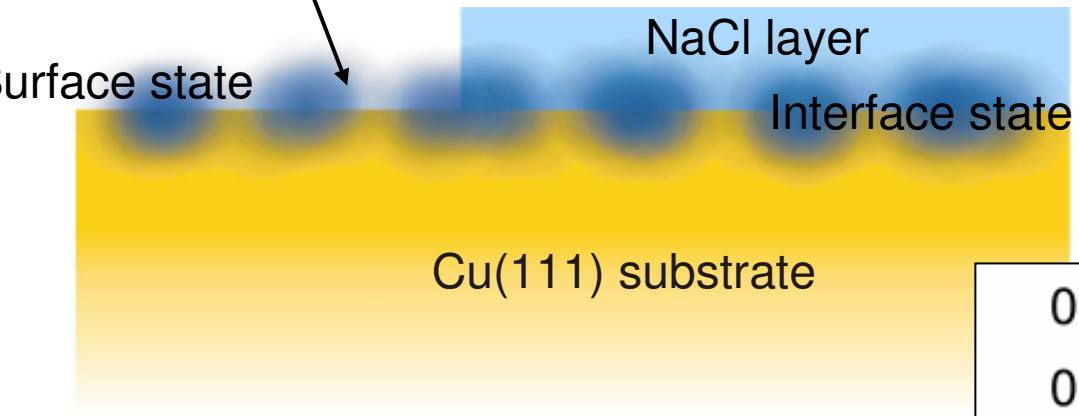
Interface states in NaCl/Cu(111)



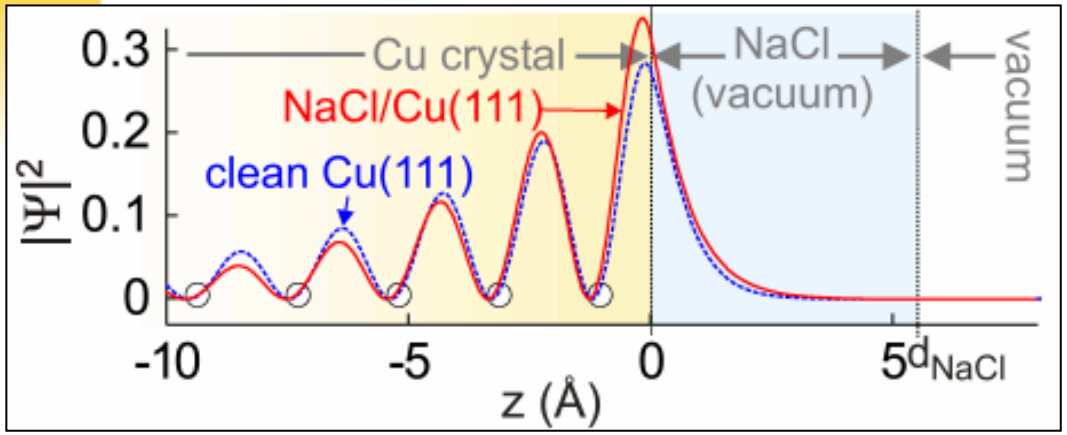
STM tip



Fermi wavelength of the interface state on NaCl/Cu(111 is larger: $\lambda_F = 38$ Å (clean Cu: $\lambda_F = 30$ Å)



Probability distribution:



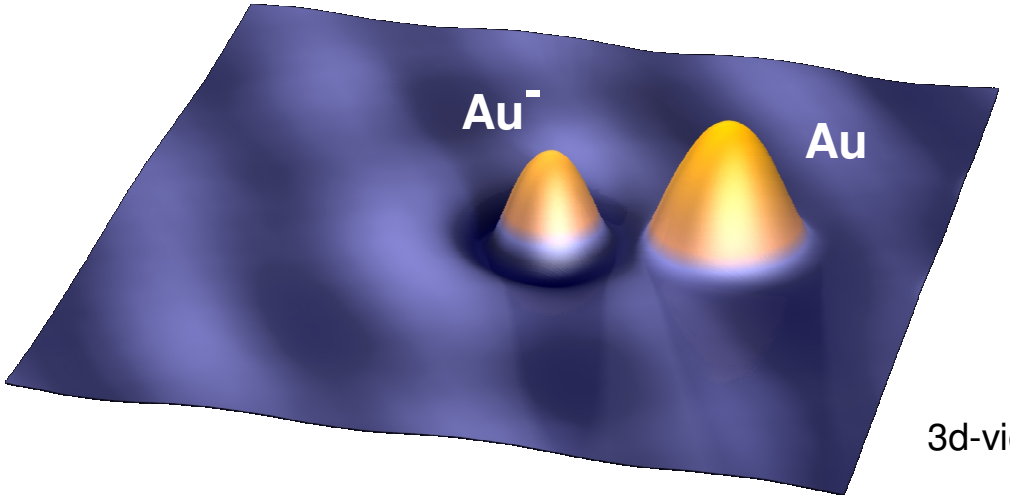
Phys. Rev. Lett. 92, 036803 (2004)

Control of the charge state of single Au atoms

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

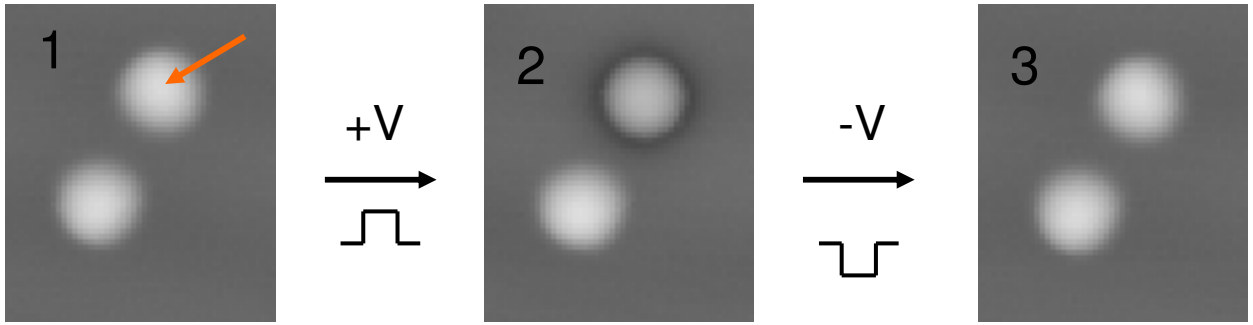
STM imaging:

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)

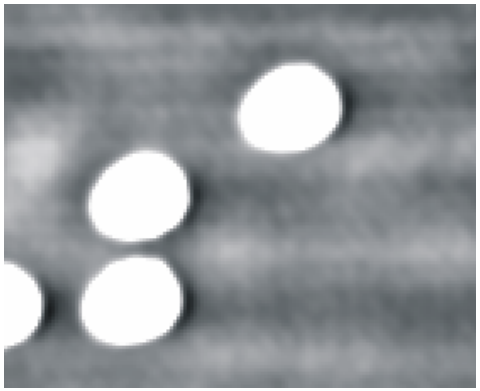


J. Repp, G. Meyer, F. Olsson, M. Persson, Science 305, 493 (2004)

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

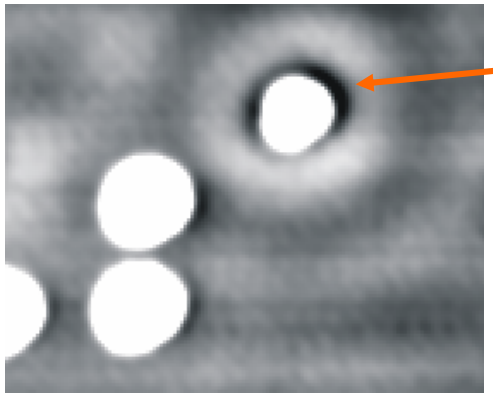
Further experimental results:

- 'Switched' Au atoms scatter electrons in the interface state



60Å × 55Å 940pA; 148mV

+V



'switched' Au adatom scatters interface electrons

- 'Switched' Au atoms have a repulsive interaction with negative biased STM tip

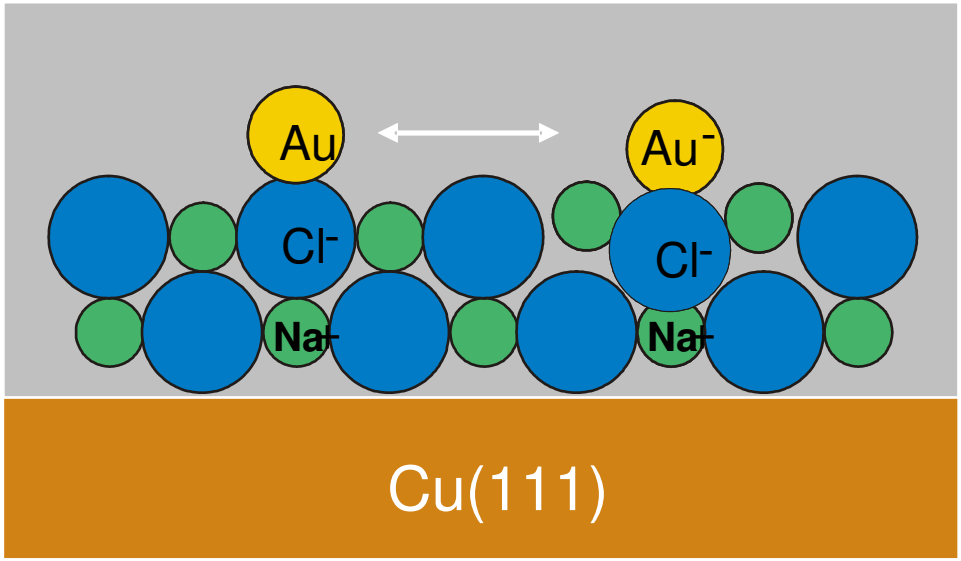
J. Repp, G. Meyer, F. Olsson, M. Persson, Science 305, 493 (2004)

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.

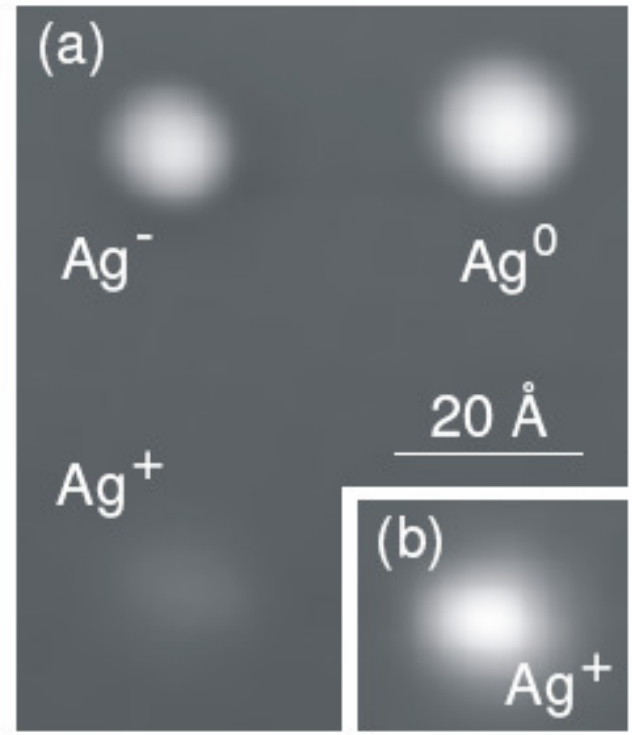
- Au^0 and Au^- have different chemical and magnetic properties

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

Multiple charge states of Ag atoms on ultrathin NaCl films

Ag atoms on 2 ML NaCl/Cu(100) can be switched between 3 different charge states:

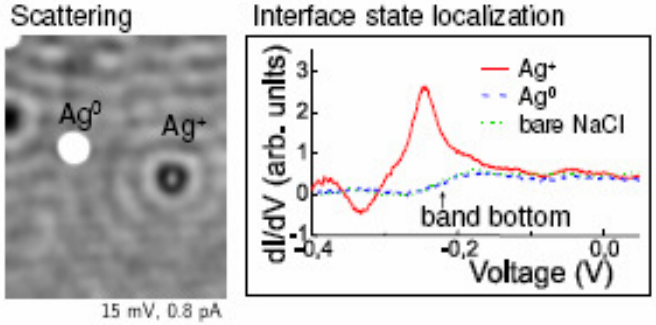
Ag^-: On top of Cl anion, Ag^0: On top of Cl anion, Ag^+: Bridge site ($[AgCl_2]^-$)



Ag/2ML NaCl/ Cu(100)

How to measure the positive charge ?

Ag / 2ML NaCl / Cu(111)



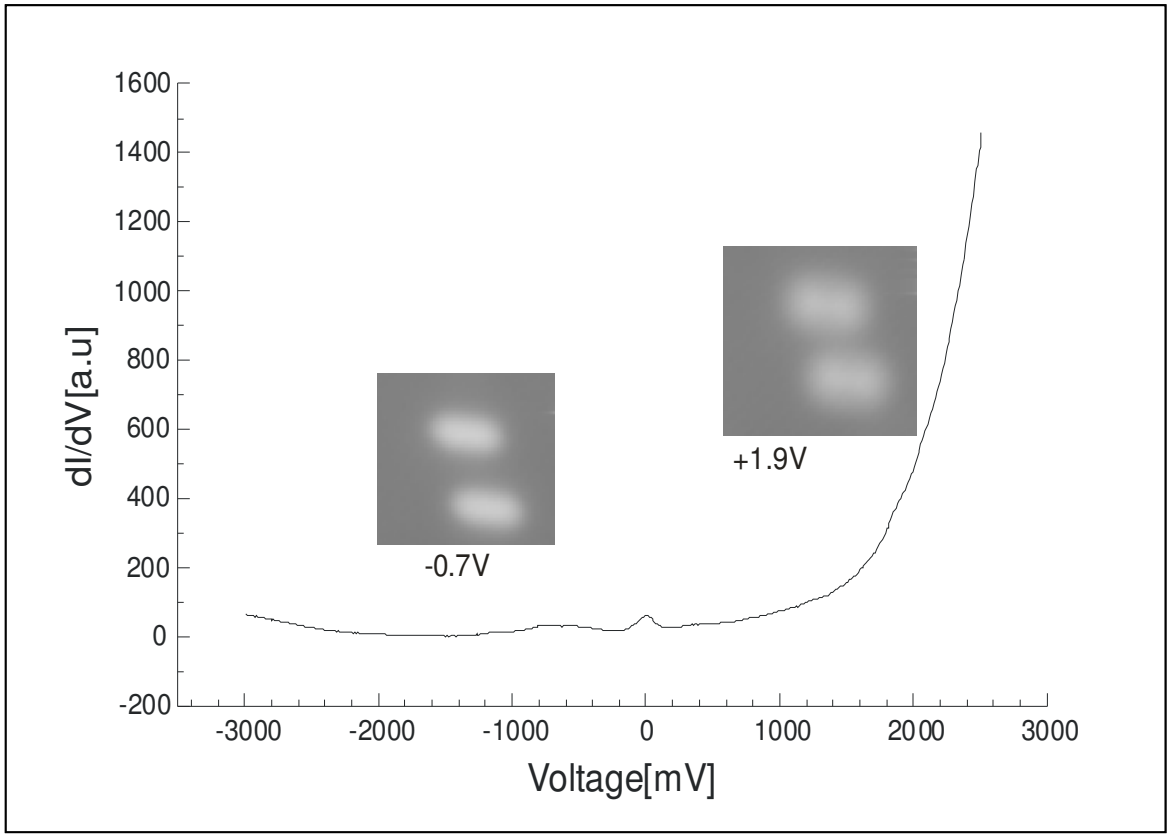
Ag^+ induces a localized bound state for interface electrons

F. E. Olsson, S. Paavilainen, M. Persson, J. Repp, G.Meyer Phys. Rev. Lett. 98, 176803 (2007)

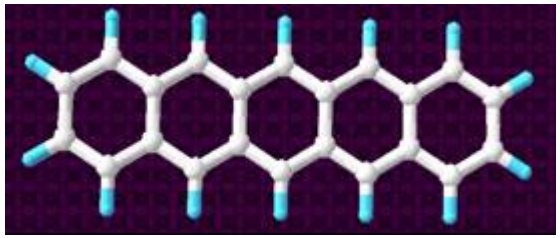
Single molecules on ultrathin insulating NaCl films

Molecules on metals: Pentacene/Cu(111)

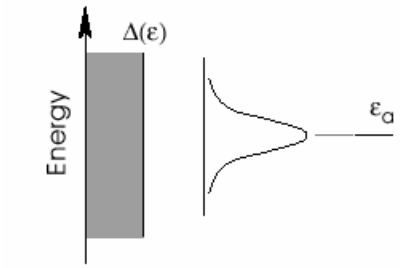
Voltage dependant imaging and local spectroscopy:



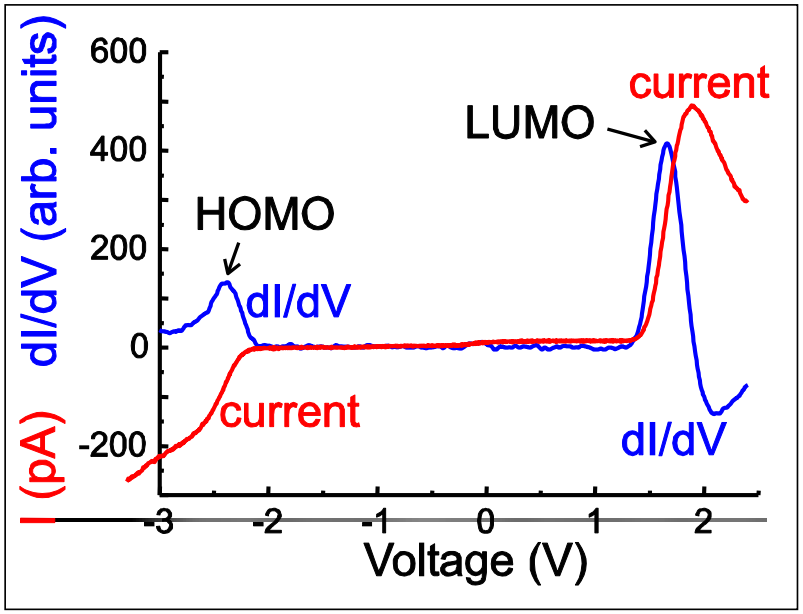
Pentacene:

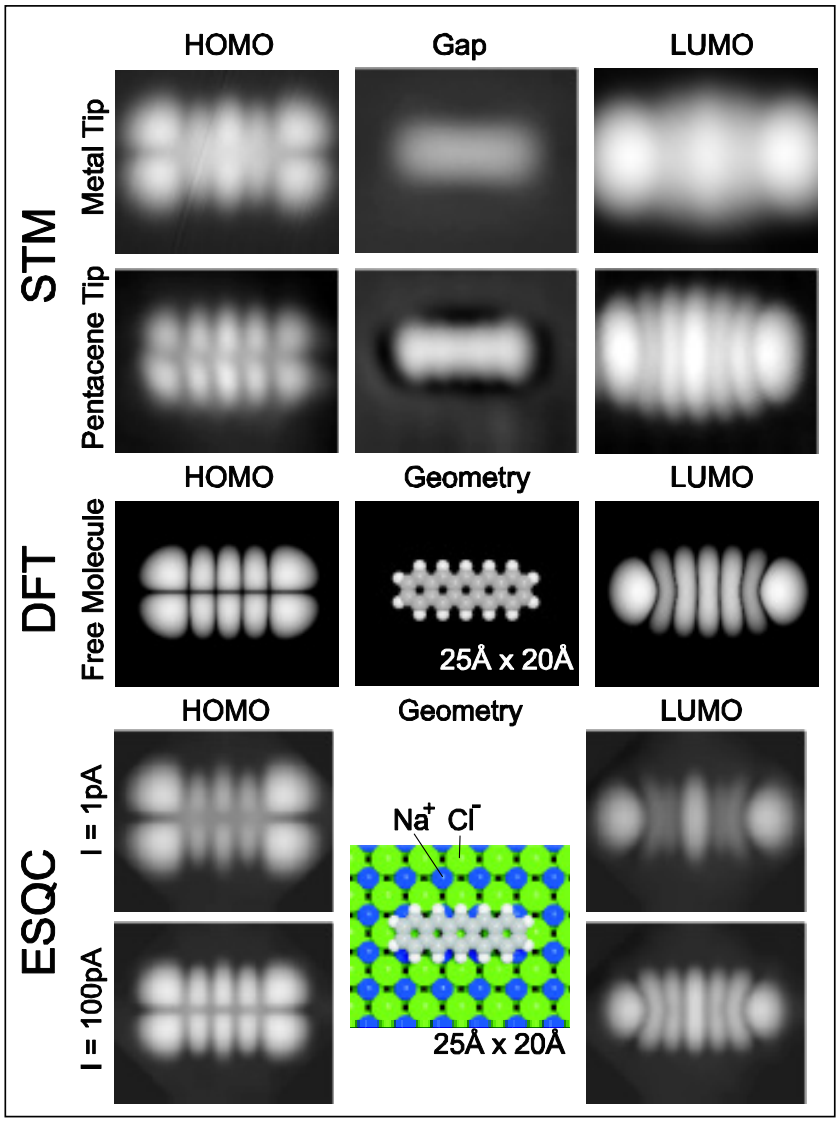


Molecules on metals:
Overlap with metal states results in a large energetic shift and broadening of molecular orbitals



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





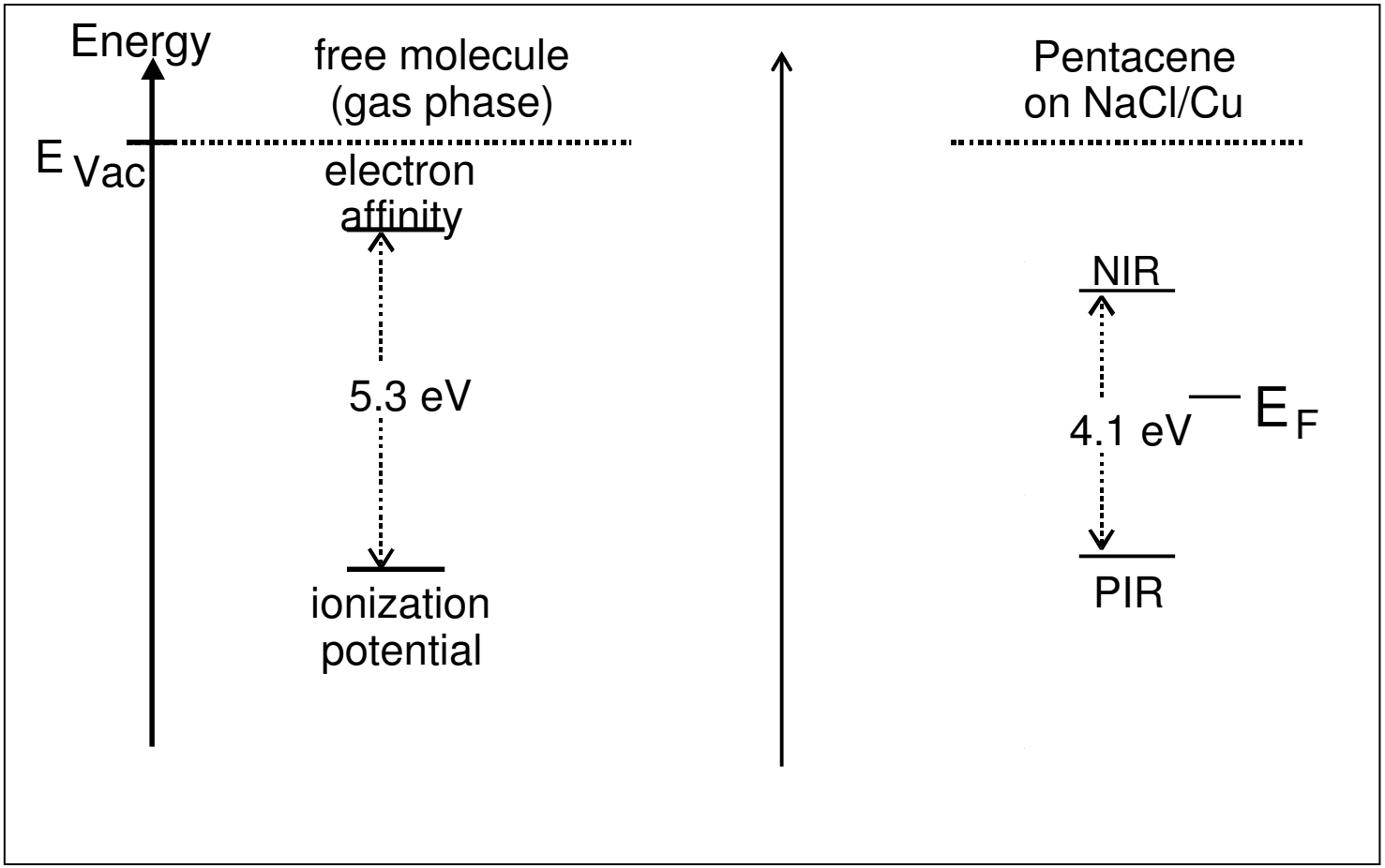
Molecules are electronically decoupled from the Substrate:

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)

Pentacene: Energy diagram

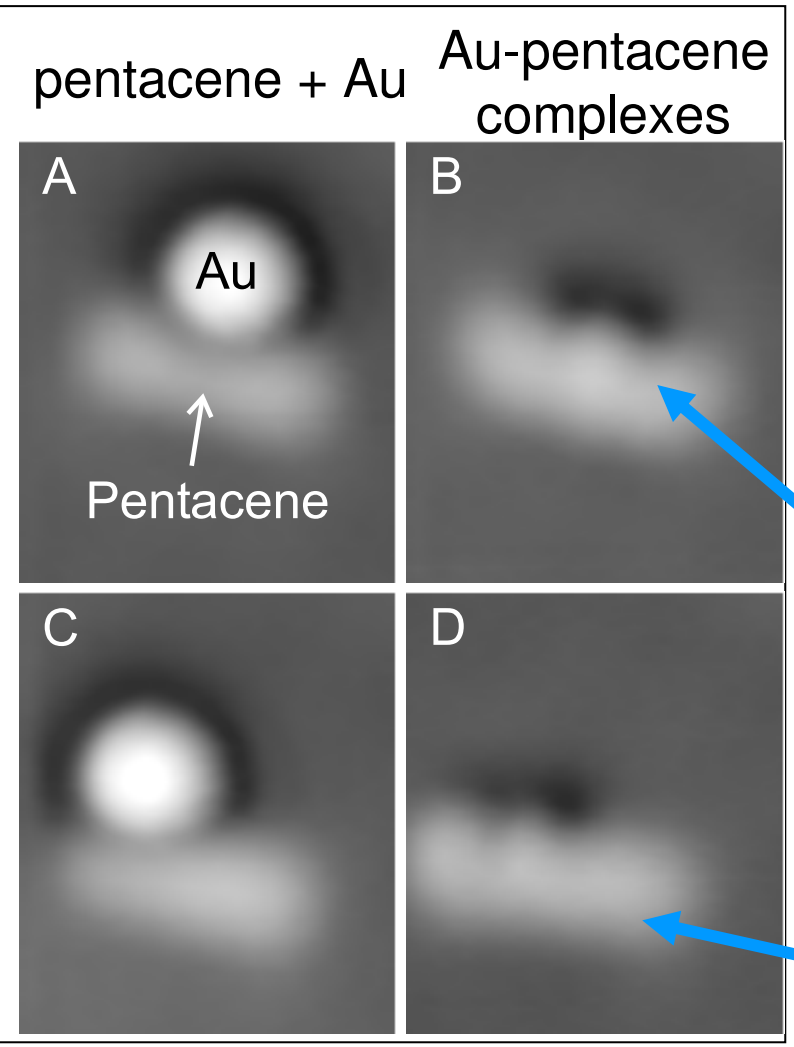


NIR: Negative Ion Resonance, PIR: Positive Ion Resonance

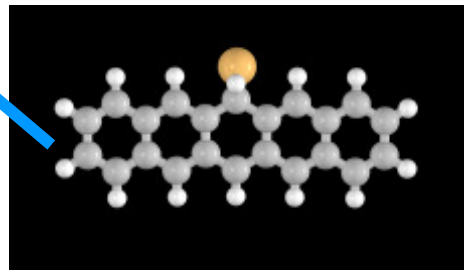
Formation of metal – molecule complexes:

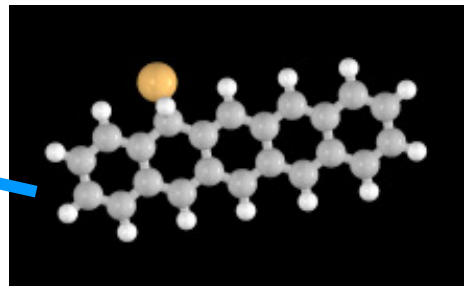
‘electrical contacting’

Bond formation between Au and pentacene

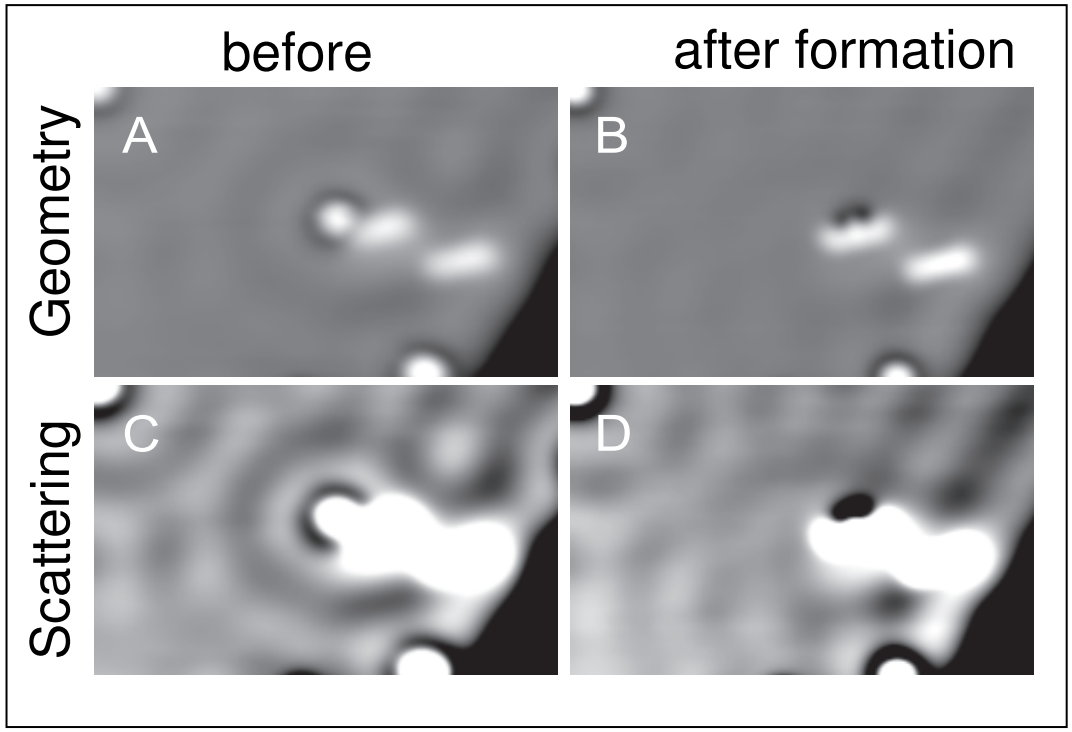


- Formation of a stable atom-molecule complex by atomic manipulation (single molecule chemistry by inelastic excitation).
- Different isomers can be created (5-gold-pentacene and 6-gold-pentacene)
- Bond formation is reversible
- dI/dV shows much smaller gap



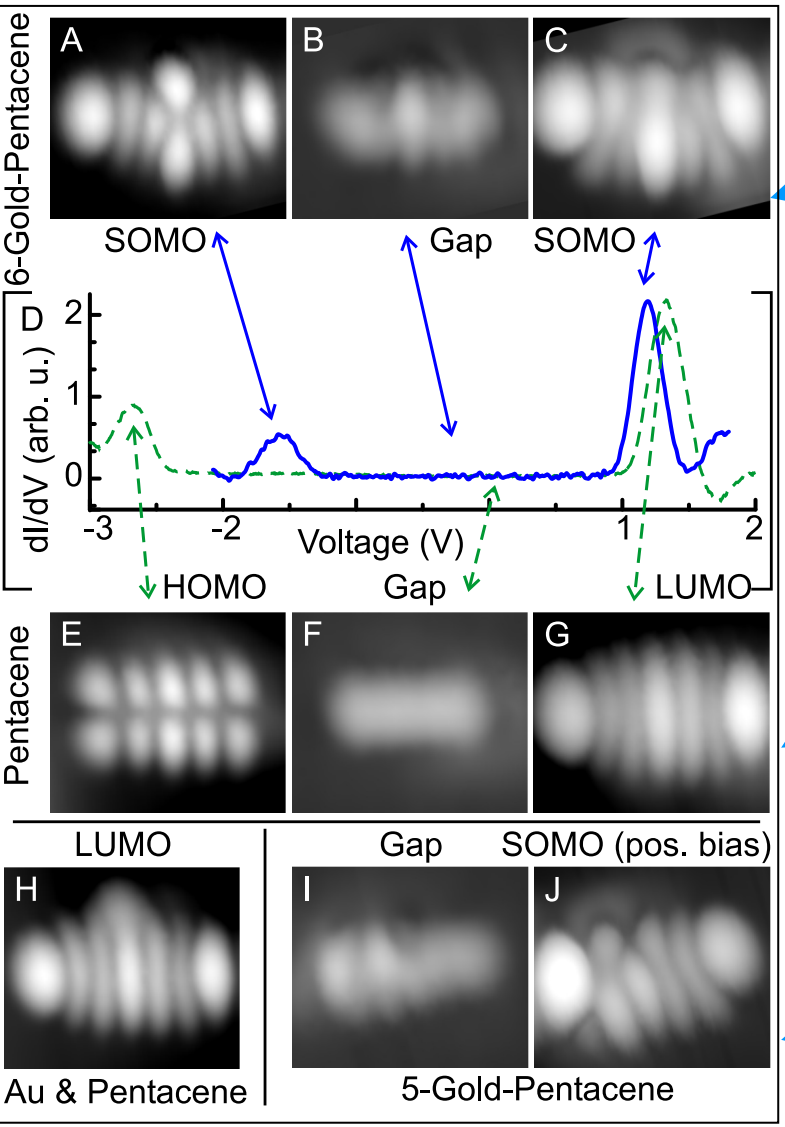


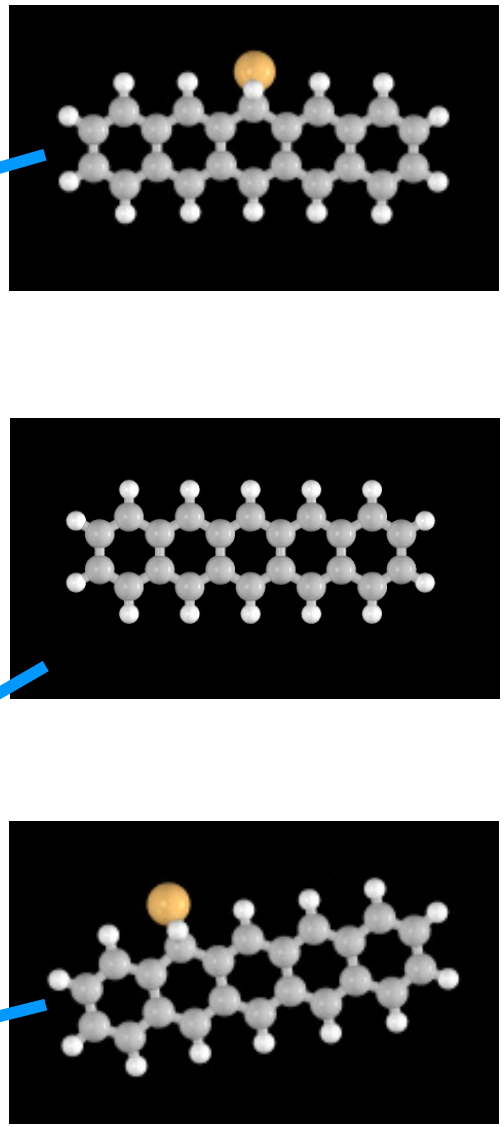
Charge determination of the Au-pentacene complex



- No strong scattering → Complex is neutral (as a whole)
- Number of electrons:
  Pentacene: even + Gold: odd = Complex: odd → Radical

Bias-dependent imaging of Au-pentacene



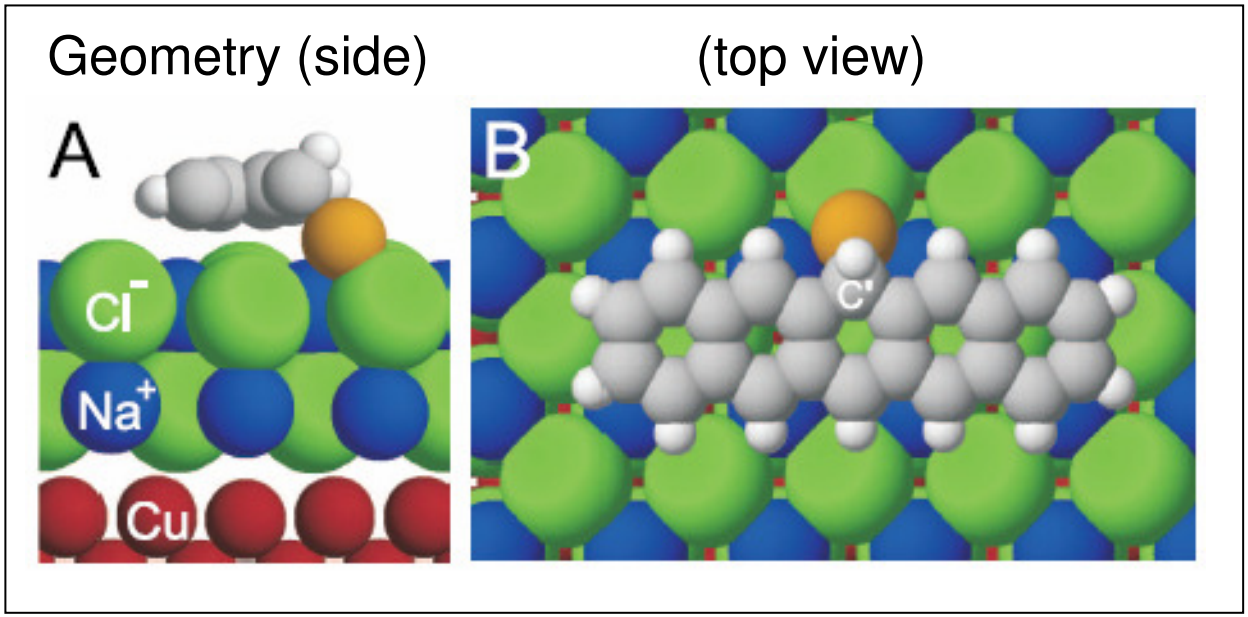


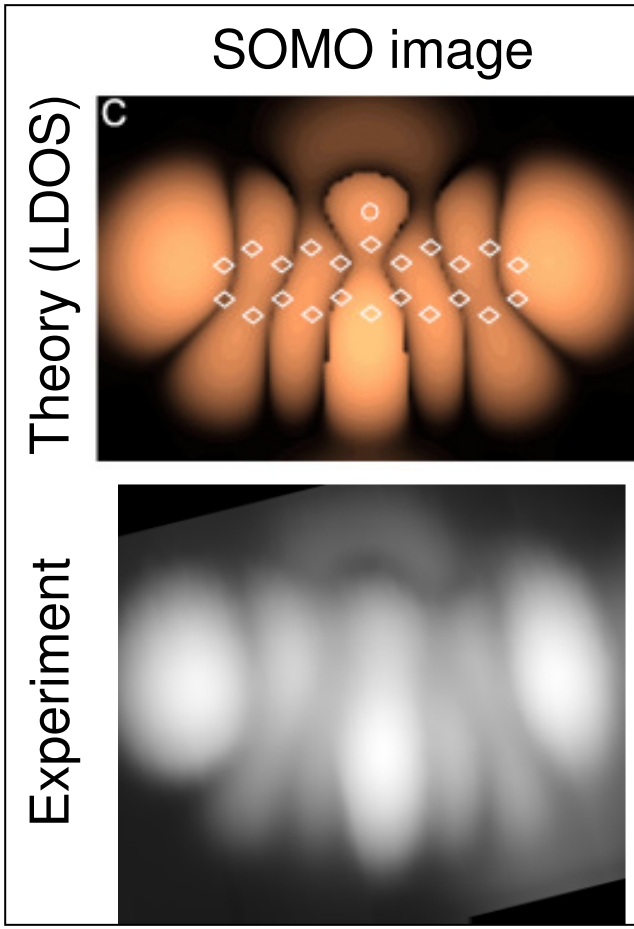
- Au-pentacene shows a much smaller gap region in $\mathrm{d}I/\mathrm{d}V$ than pentacene alone
- Singly occupied molecular orbitals (SOMO) appears at both voltage polarities
- SOMO exceeds over the whole complex $\rightarrow$ covalent bond
- Different isomers show different frontier orbitals

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

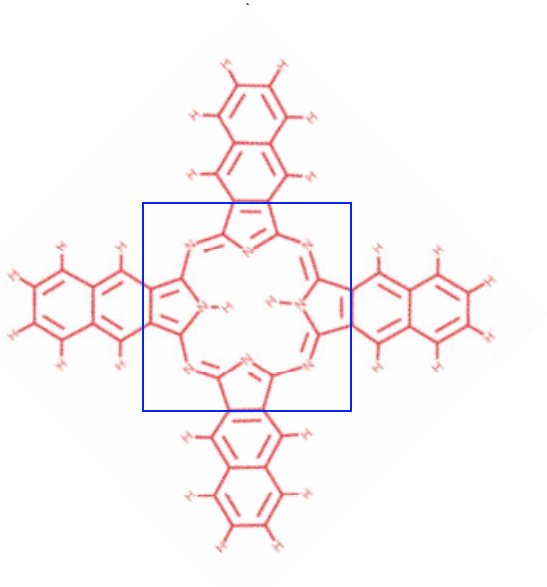




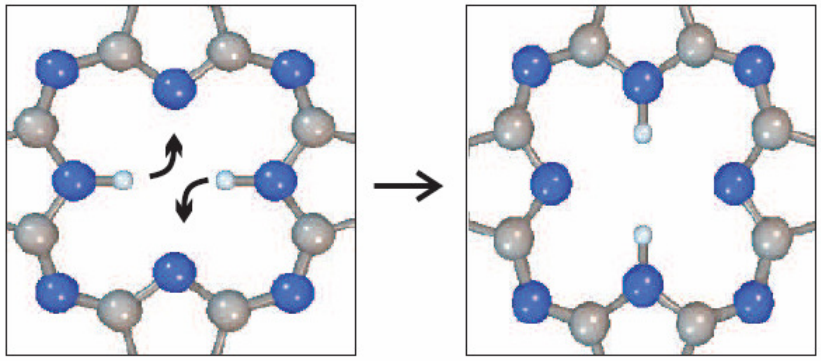
Planar Molecular Switches

A planar molecular switch:

Tunneling induced hydrogen tautomerization in free base naphthalocyanine



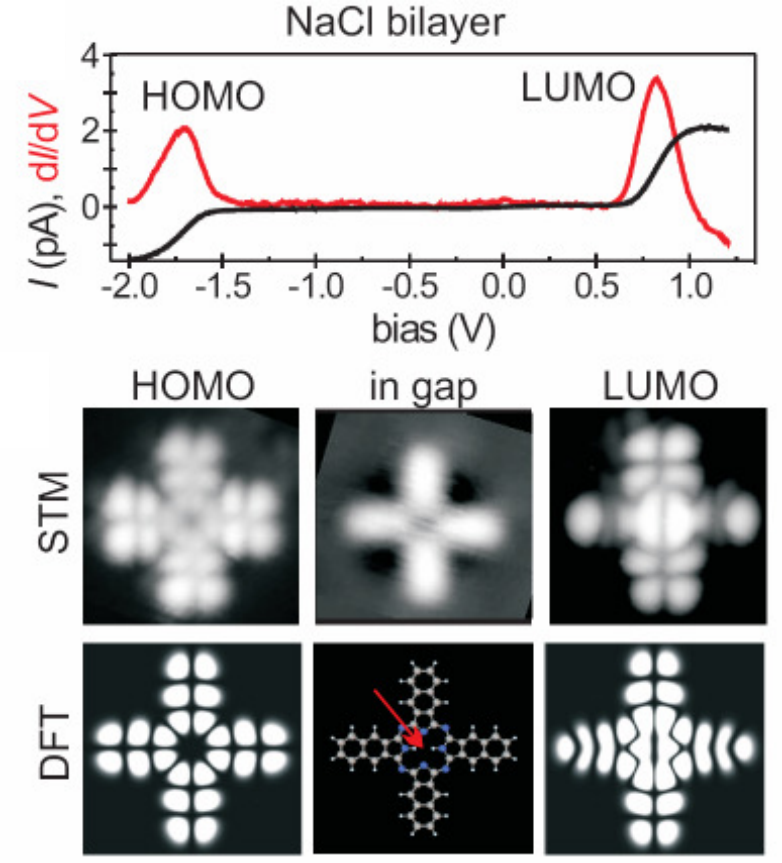
Naphthalocyanine



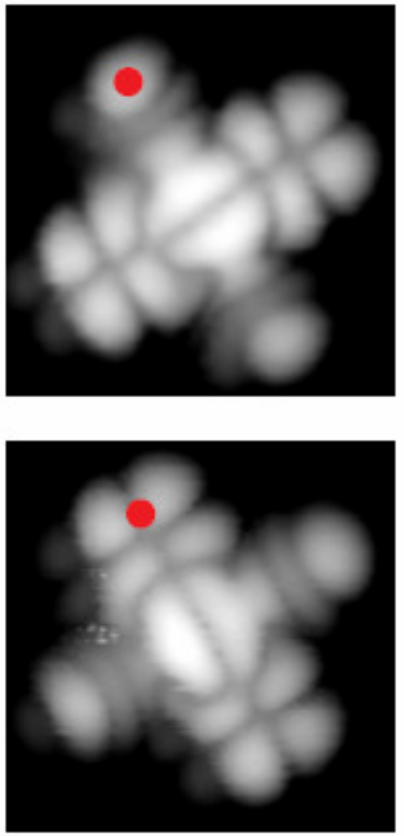
Model of the hydrogen transfer process

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

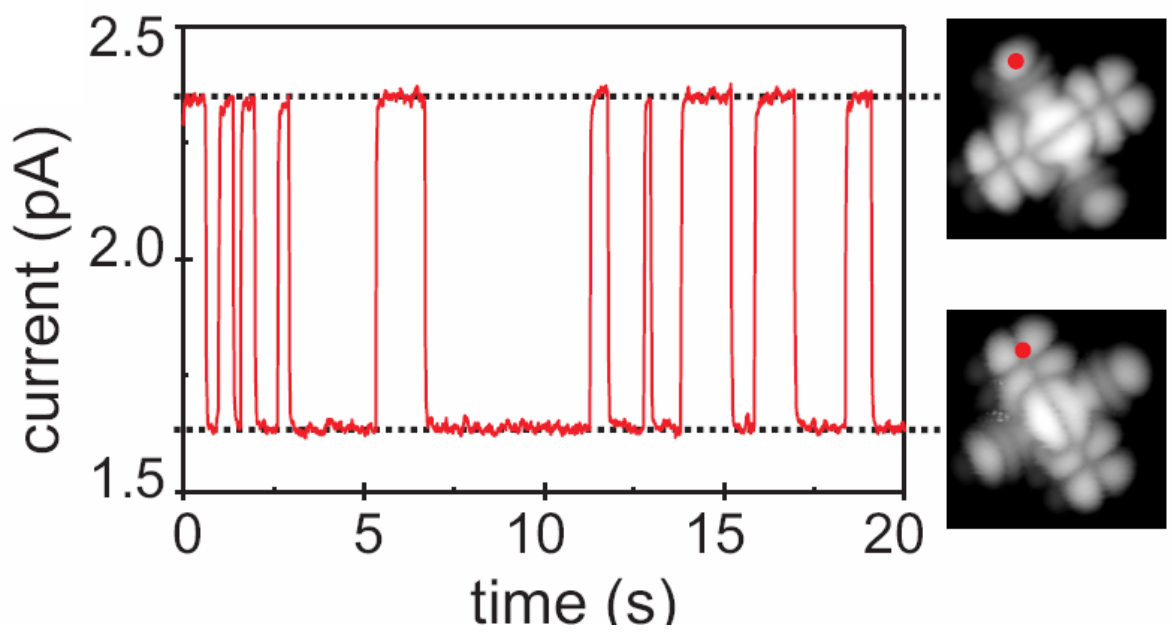


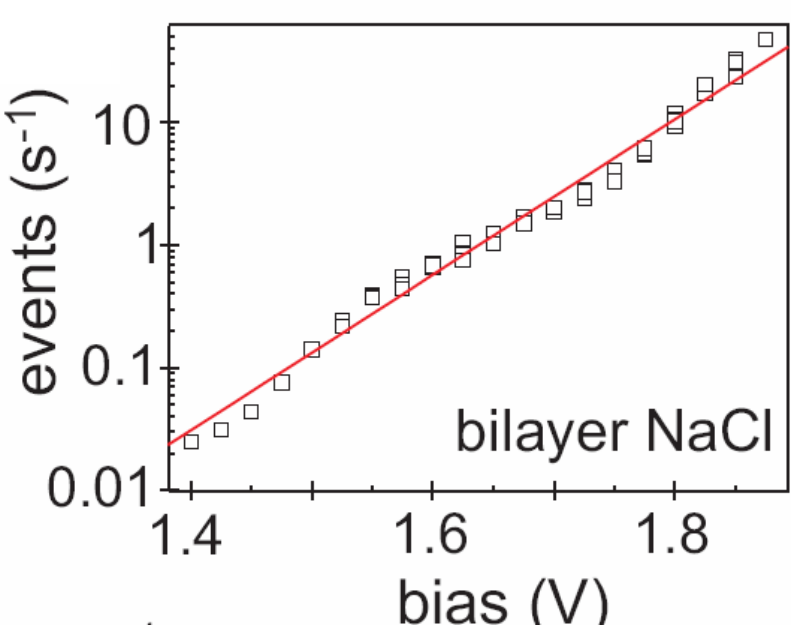
STS/STM of naphthalocyanine on 2MLNaCl/Cu(111)



Images of the LUMO before and after switching

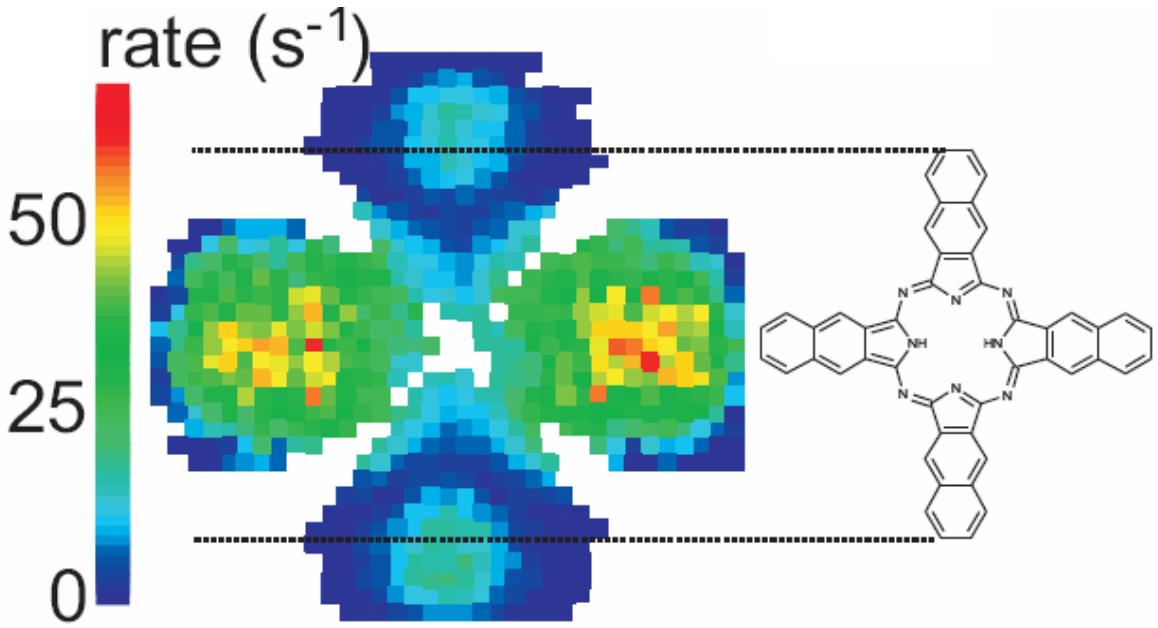
Details of the Current-Induced Switching Process





1. Switching rate increases exponentially with bias voltage

Details of the Current-Induced Switching Process

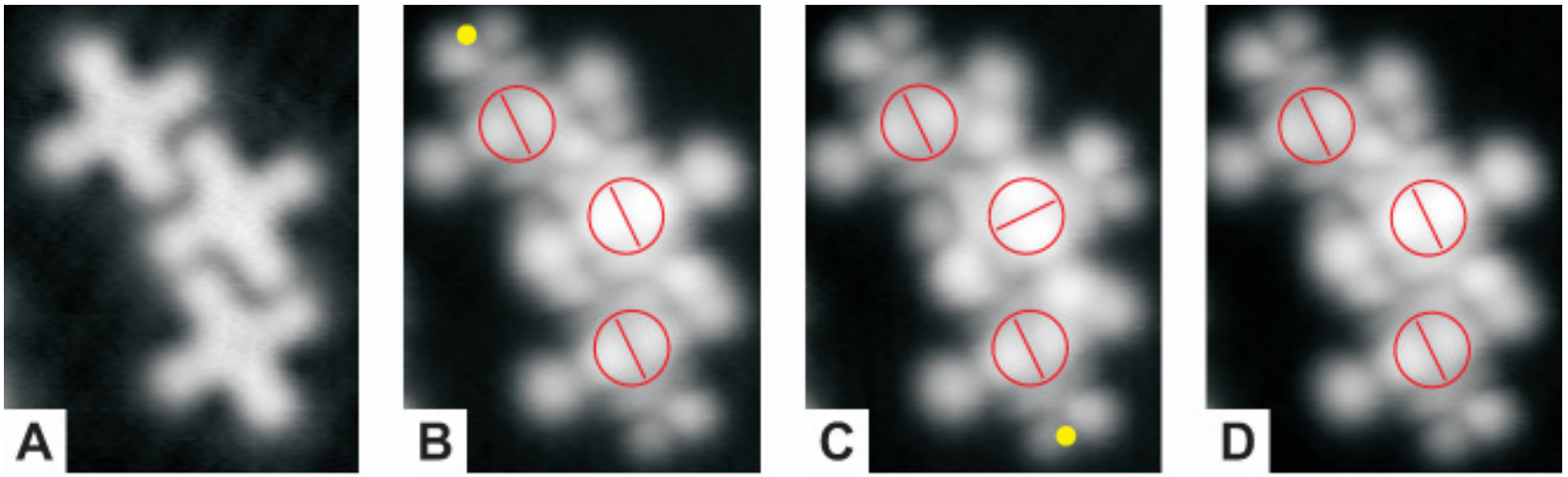


2. Highest switching rate with the tip far at the periphery of the molecule

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)

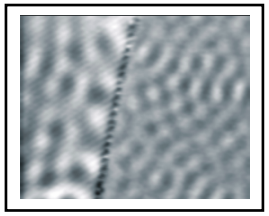
L. Gross, P. Zahl, R. R. Schlittler (Nanostencil)

Cooperation:

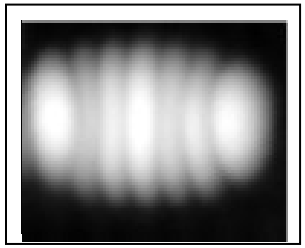
C. Joachim, A. Gourdon, S. Stojkovic CEMES Toulouse

M. Persson, F. Olsson, S. Paavilainen Chalmers University Goeteborg (Liverpool Univ.)

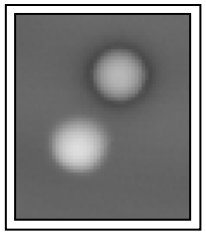
Summary:



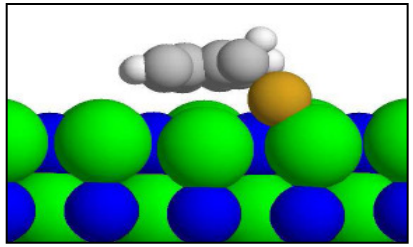
NaCl/Cu(111):
Interface state
as a probe for charges



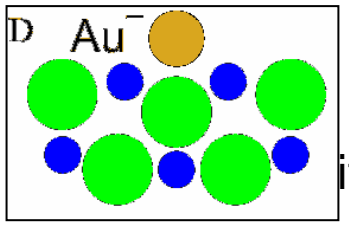
Molecules/NaCl:
Orbital imaging



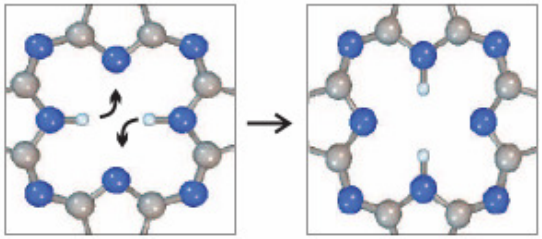
Au/NaCl(100):
Manipulation
of gold adatoms



Single-molecule chemistry,
doping,
contacting



Control of the charge state and
iffusion of Au(Ag)/NaCl



Planar **molecular switches**