Spin transport across single molecules

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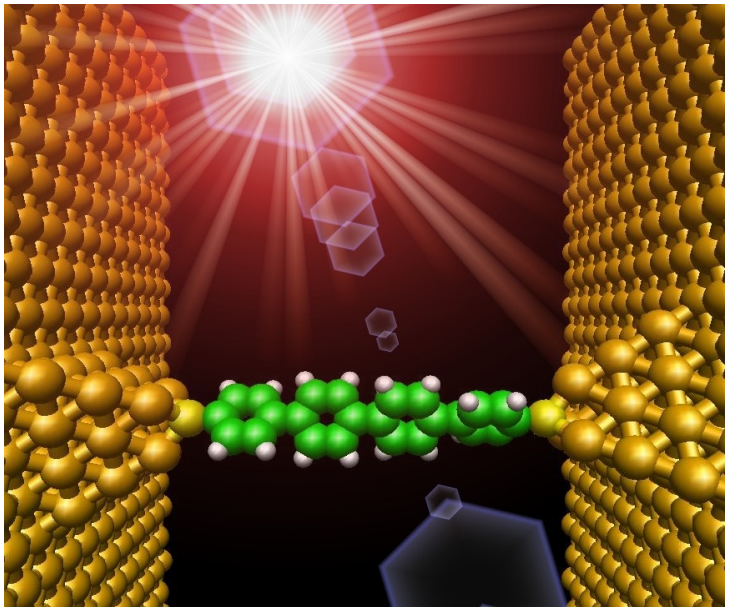
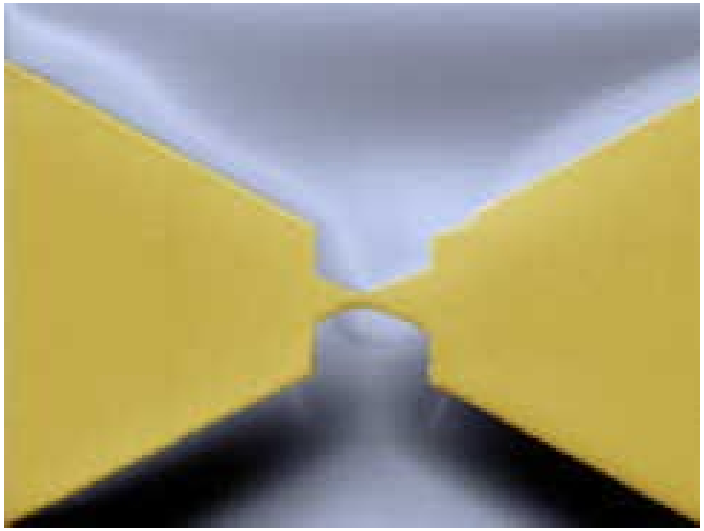
IPCMS



Alexander von Humboldt
Stiftung/Foundation

Contacting single molecules

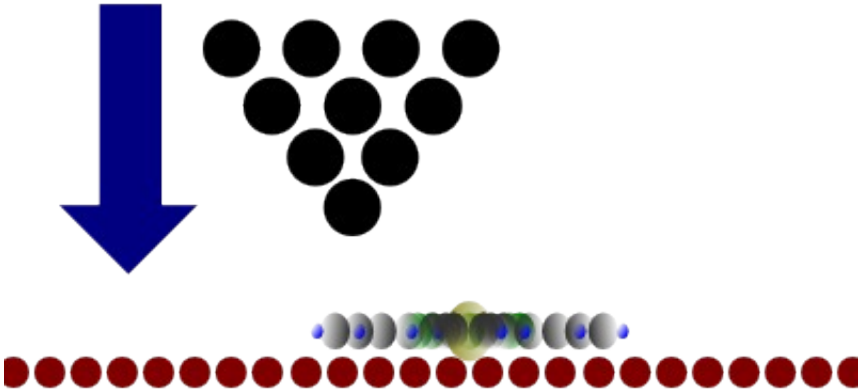
Break Junctions



- high stability
- simple approach
- contact geometry unknown
- “blind” technique
- most data is cast aside

see e.g. M.A. Reed et al. Science 278, 252 (´97).

Scanning Tunneling Microscope



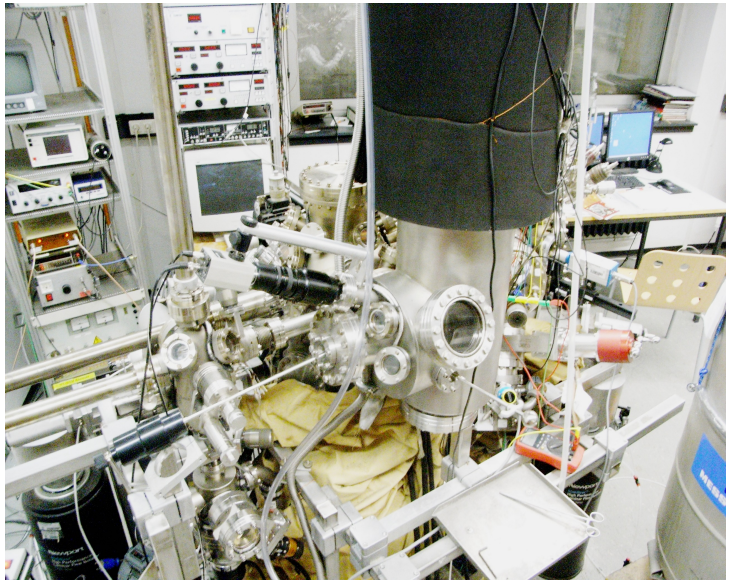
- well controlled contact geometry
- one electrode and molecule can be imaged
- high experimental effort
- limited stability

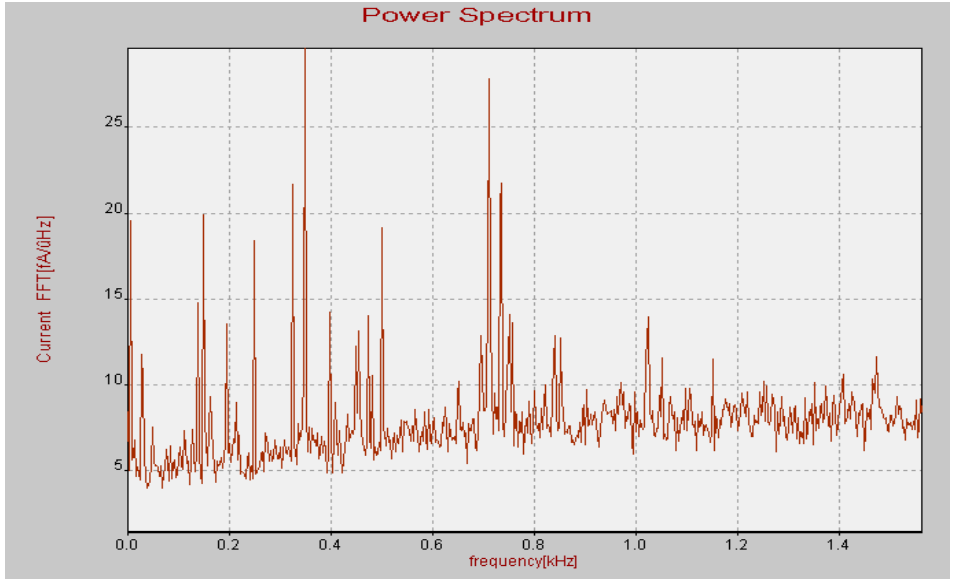
see e.g. R. Berndt et al. Phys. Rev. Lett. 98, 65502 (`07).

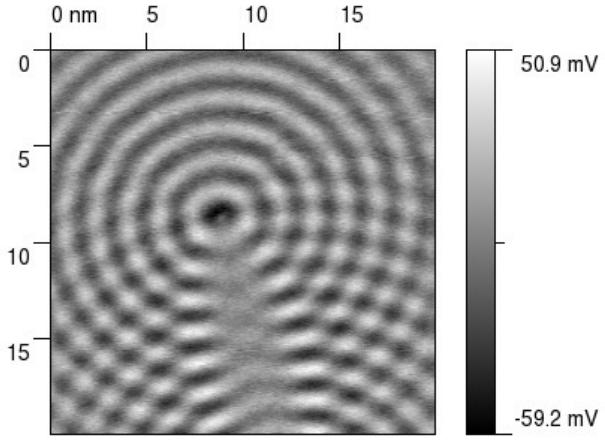
The experimental setup

Scanning Tunneling Microscope

Design of a 4K STM
Magnetic fields up to 1T







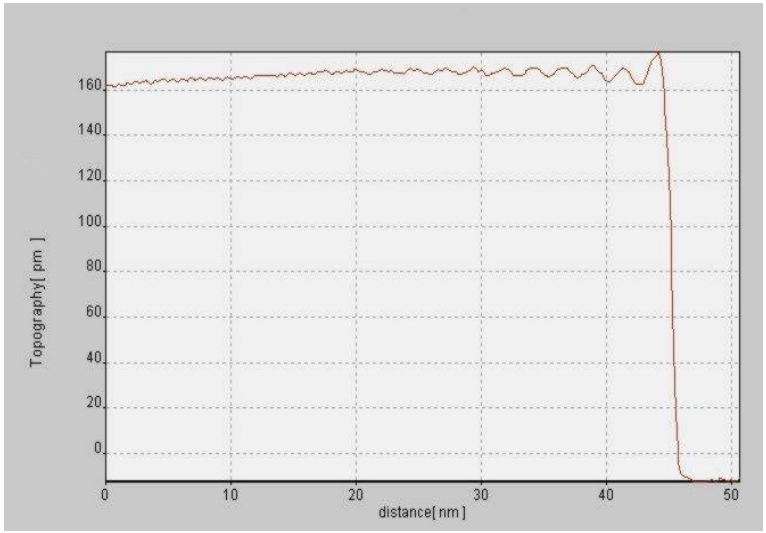
- low vibration
  <300fm rms
- low noise
  <8 fA/√Hz
- high bandwidth
  up to 500kHz

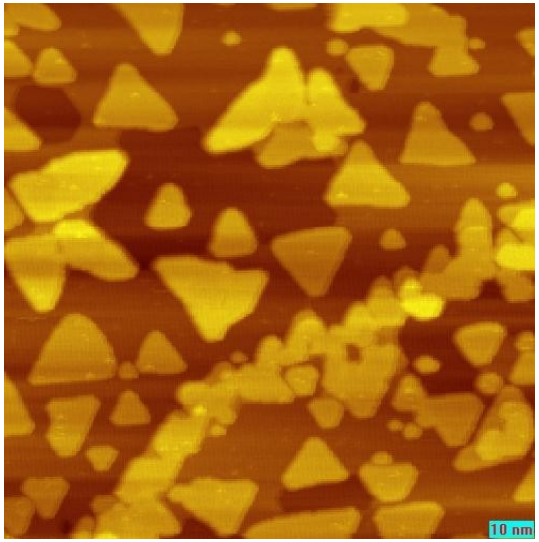
The substrate

Cu(111) and Co/Cu(111)

- Cu samples are cleaned in situ by Ar-sputtering and annealing
- Auger shows no contamination
- STM shows only very few adsorbates

- Co deposition by MBE
- Sub monolayer coverage results in double layer island formation

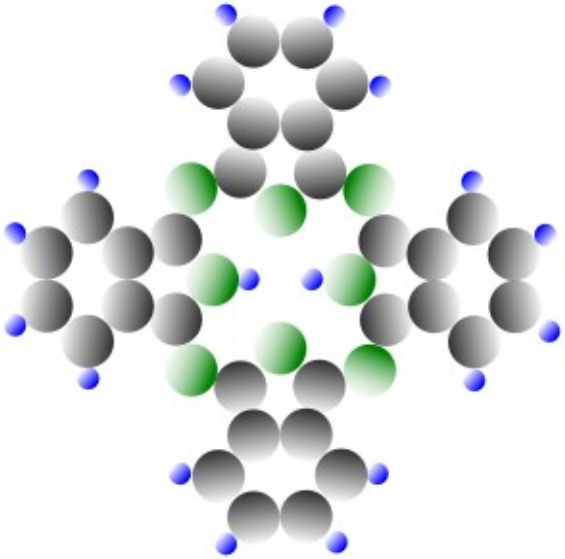




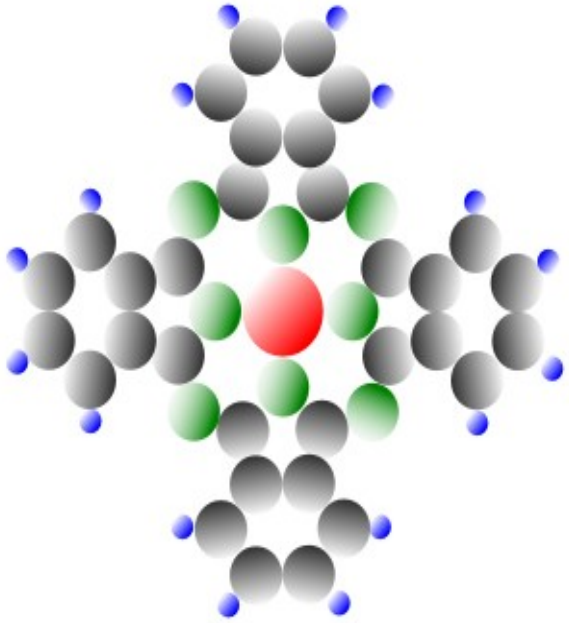
The molecules

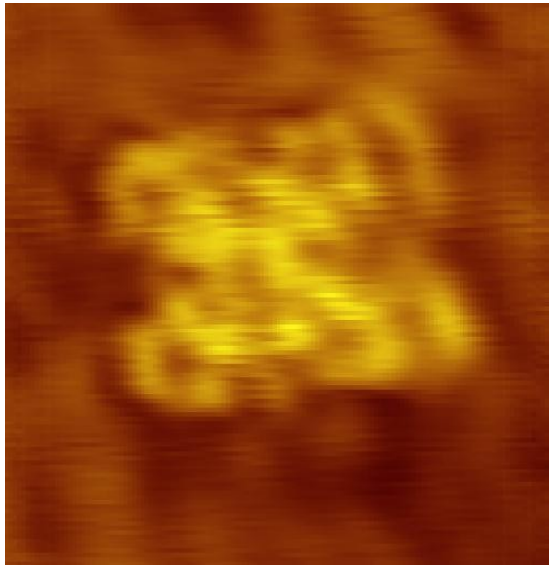
Metal-organic molecules

H_2Pc



CoPc

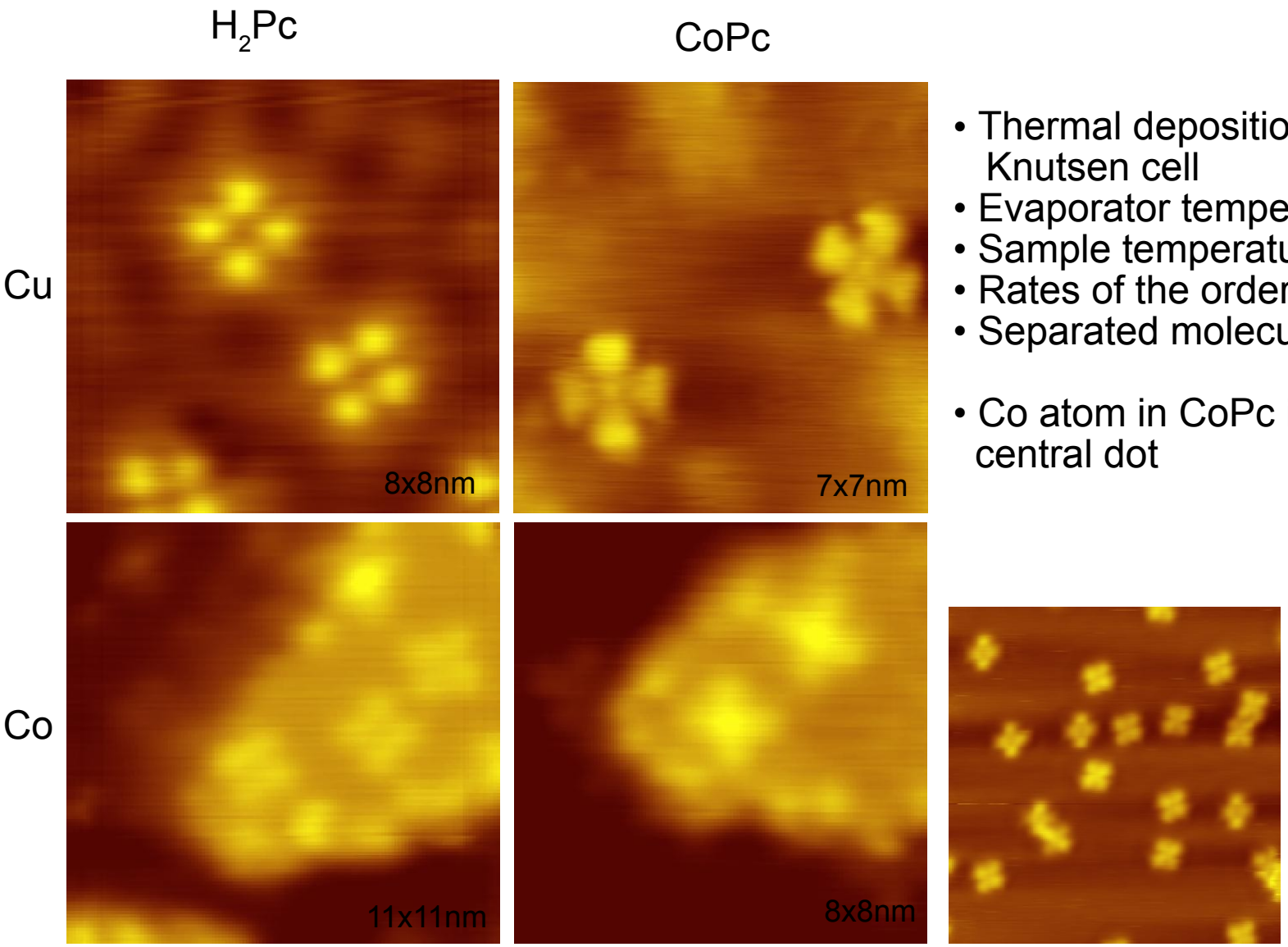




Phthalocyanine (Pc) molecules with central metal ion M

Preparation of MPc samples

MPc deposition on Cu(111) and Co/Cu(111)

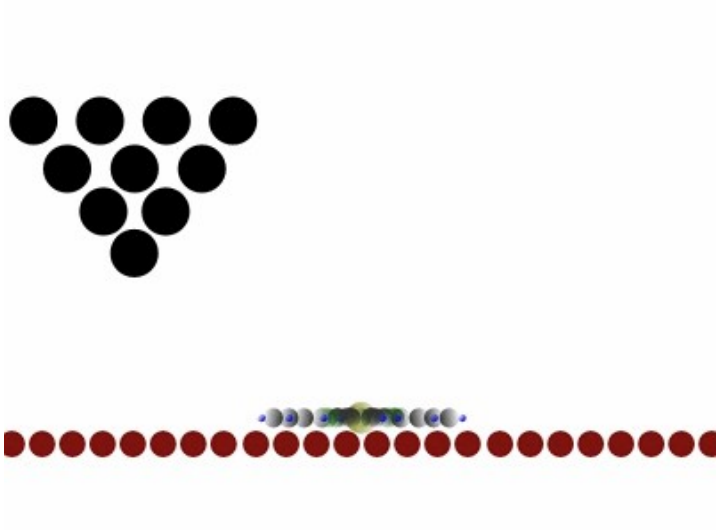


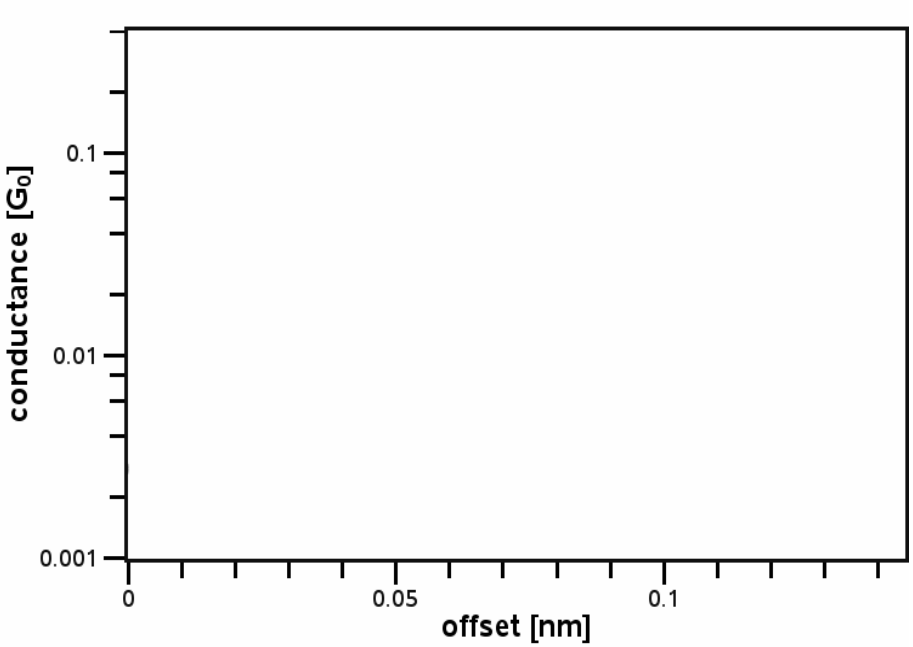
- Thermal deposition from a Knutsen cell
- Evaporator temperature of 250°C
- Sample temperature <300K
- Rates of the order of 0.1ML/min
- Separated molecules

- Co atom in CoPc is visible as central dot

Contacting single MPc molecules on Cu(111)

Jump to contact

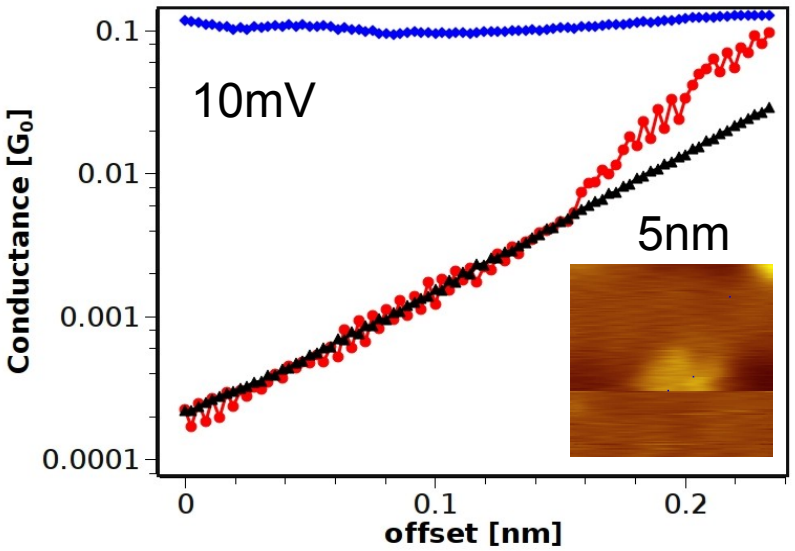




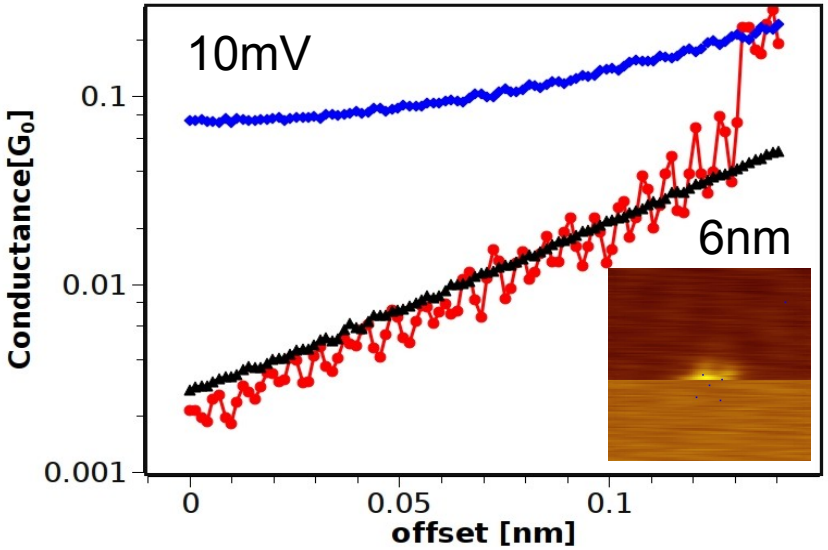
- Exponential increase of current upon approach to substrate.
- Tip approaches molecule.
- Part of molecule jumps to tip.
- Tip is retracted, molecule form bridge.
- Approach is repeated, but molecule keeps bond to tip and surface.

Contacting single MPc molecules on Cu(111)

H_2Pc



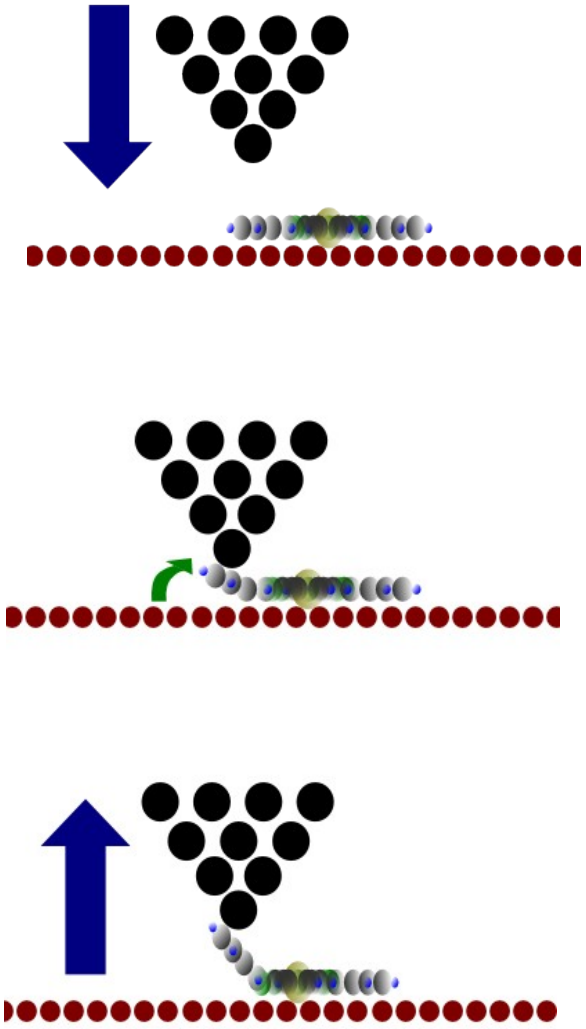
CoPc



- Relatively high conductance of ~0.1 G_0.
- When tip is moved away, molecule disappears (transferred to tip).
- Central metal atom has no influence on conductance.

Contacting single MPc molecules on Cu(111)

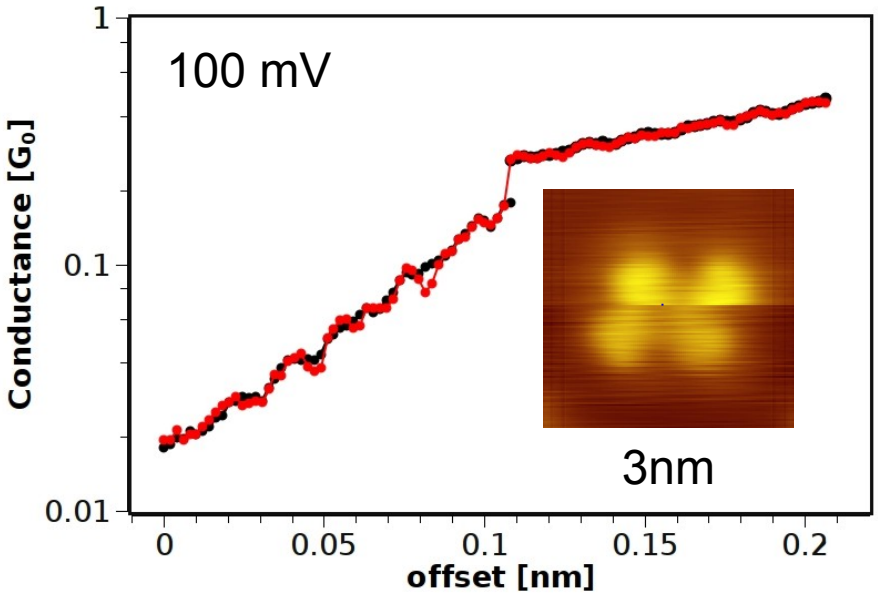
Jump to contact



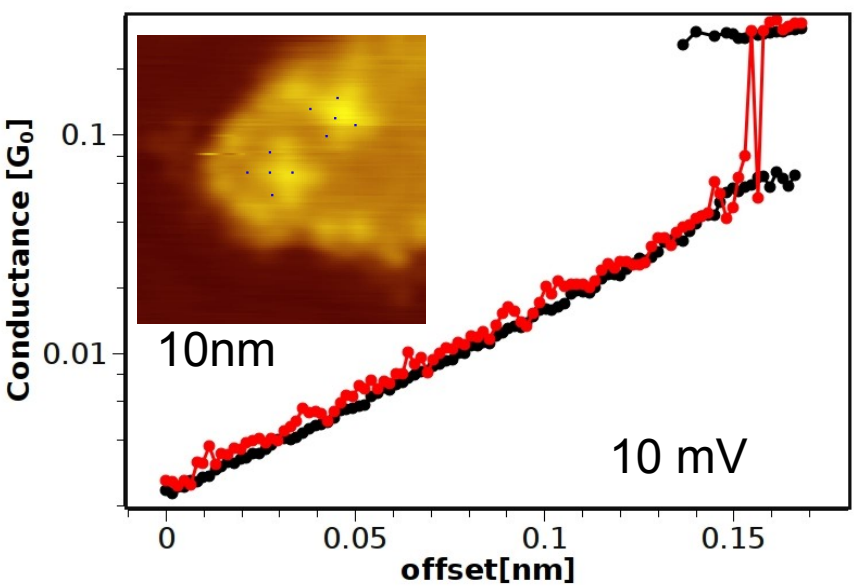
- Tip approaches molecule.
- Part of molecule jumps to tip.
- Tip is retracted, molecule forms bridge.
- Approach is repeated, but molecule keeps bond to tip and surface.
- Molecule is transferred to tip when tip is moved away.

Contacting single MPc molecules on Co/Cu(111)

H_2Pc



CoPc



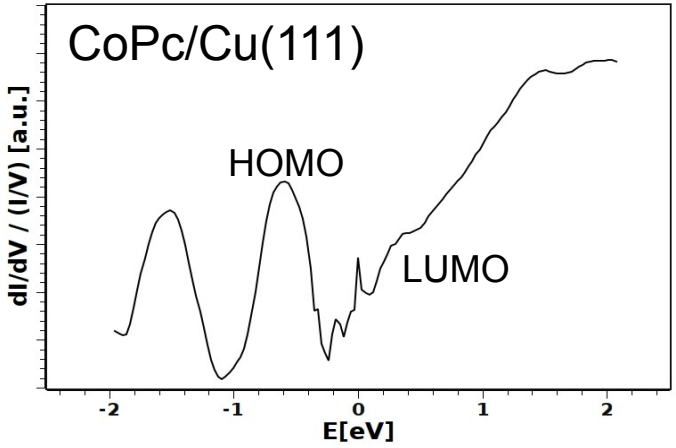
- Jump to contact but no transfer of the molecule to tip.
- Better sticking of the molecule to substrate.
- Conductance ~ 0.3 G_0

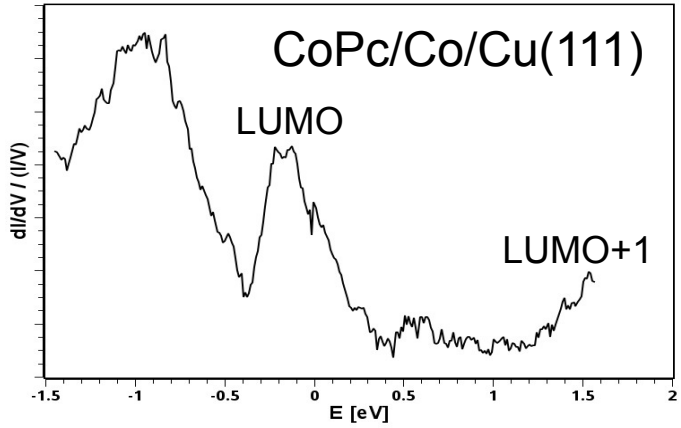
Takacs et al. Phys Rev B 78, 233404 (2008)

What is the origin of the different conductances?

Linear transport theory

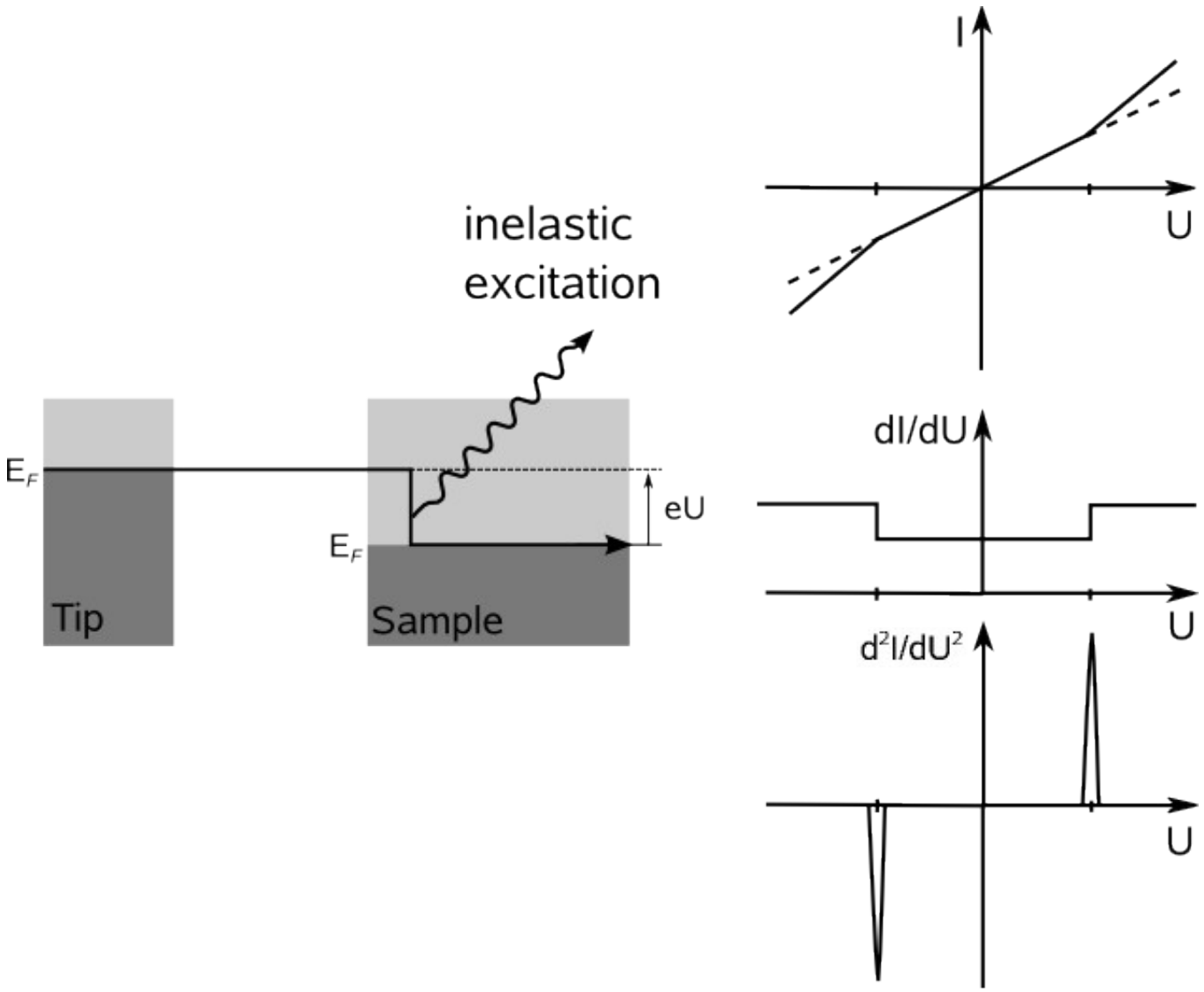
- Landauer-Büttiker : G (l)*T* (r)
- Density of states not much different for Co and Cu
- Transmission T of the molecule is altered by substrate?





- LDOS of the molecules is measured by Scanning Tunneling Spectroscopy (STS).
- LDOS is proportional to (dI/dV)/(I/V).
- HOMO of CoPc on Cu(111) is broadened but state hardly overlaps with Fermi edge. Physiosorbed molecule.
- Low conductance.
- HOMO shifts up towards Fermi edge on Co/Cu(111) due to charge transfer. Chemisorbed molecule.
- Higher conductance.

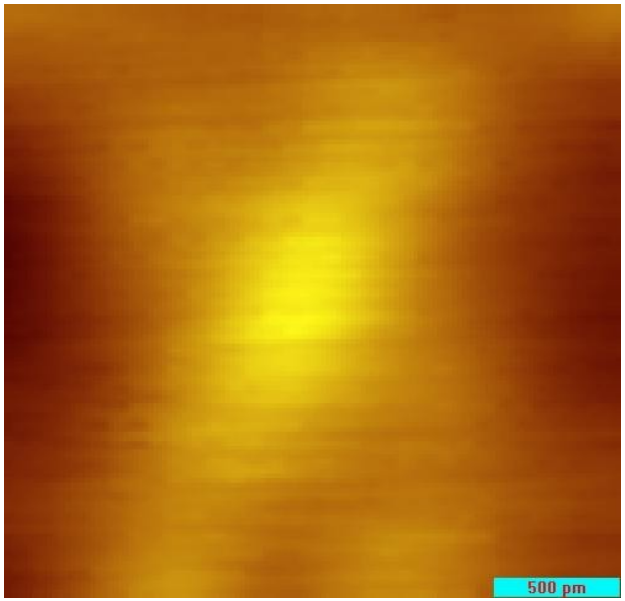
Inelastic tunneling spectroscopy



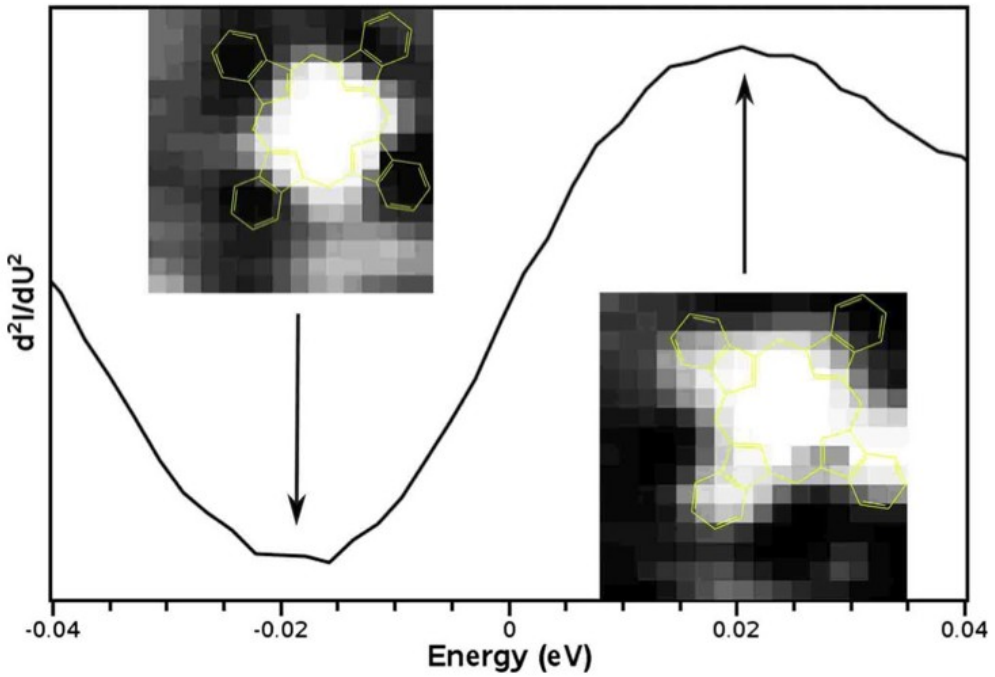
Mechanism of jump to contact

CoPc on Co

Topography



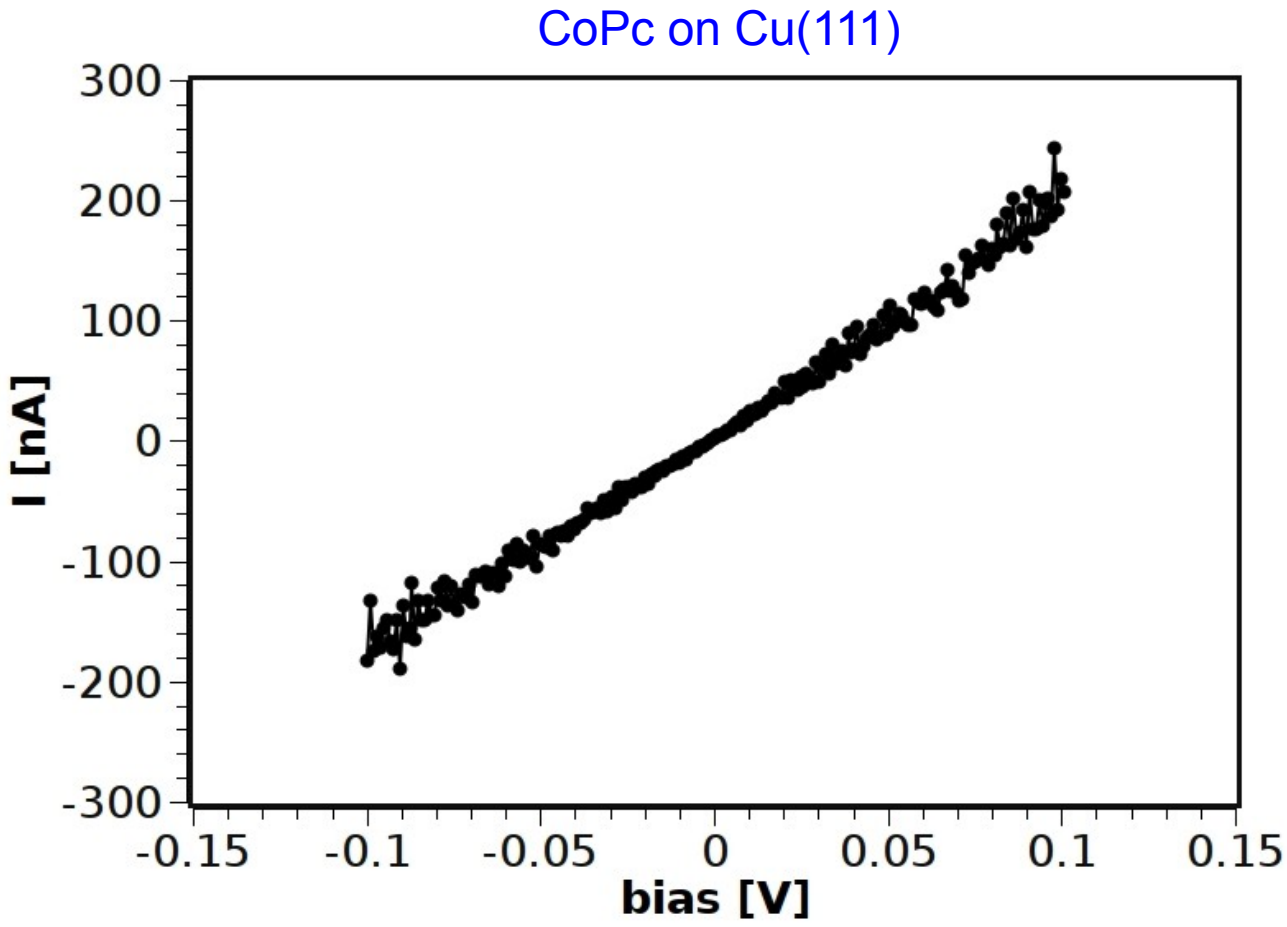
Spectroscopy



- On the lobes of the molecules, inelastic tunneling spectroscopy (d^2I/dU^2) shows an excitation at +-20mV, which can be interpreted as a molecular vibration.

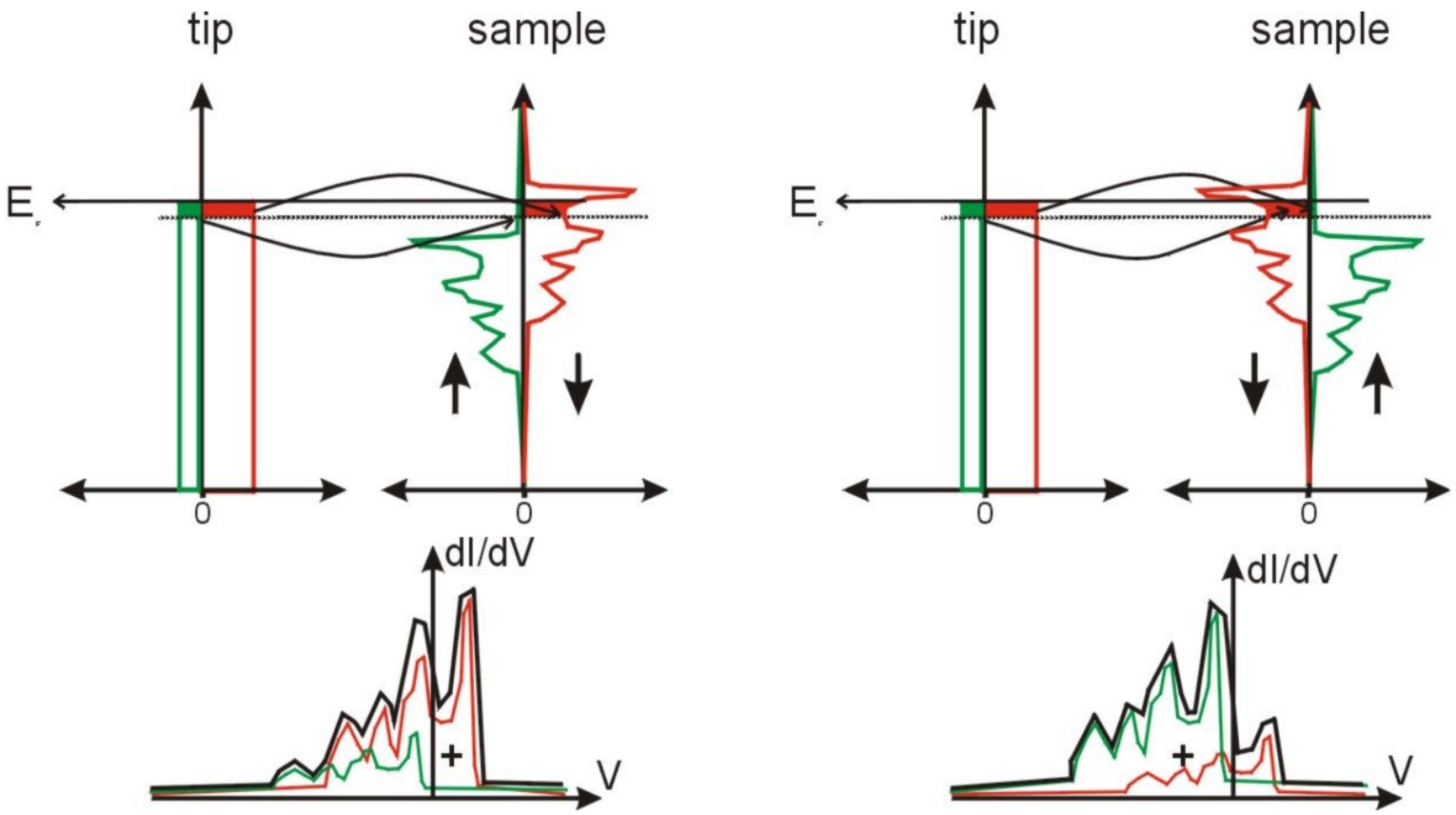
- This mode could be responsible for the jump to contact by lifting and bending of one of the side groups.

I(V) curves of single molecules



- For all combinations, the I(V) curves across single molecules are strictly linear within the accessible voltage range.
- Due to the high conduction, currents get very large even at low bias voltages.
- At currents near to a μA, the molecules disintegrate.

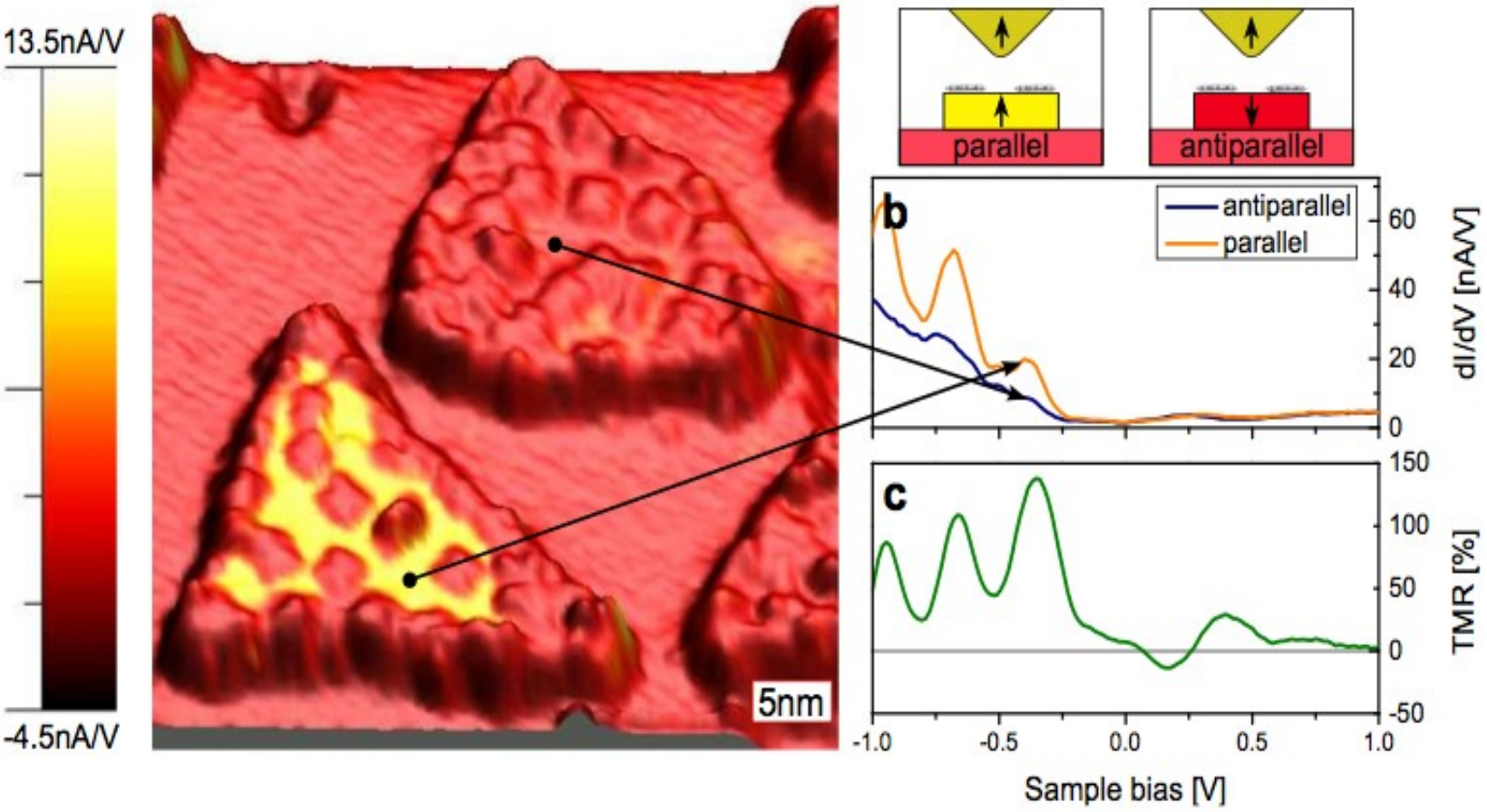
Spin-polarized STM



- Within Tersoff-Hamman Model tip states are s-electrons of constant DOS but with spin-polarization.
- As function of relative orientation of magnetization the measured dI/dV spectra are a weighted superposition of majority and minority LDOS of sample.
- Sample magnetization can be deduced from spectrum.

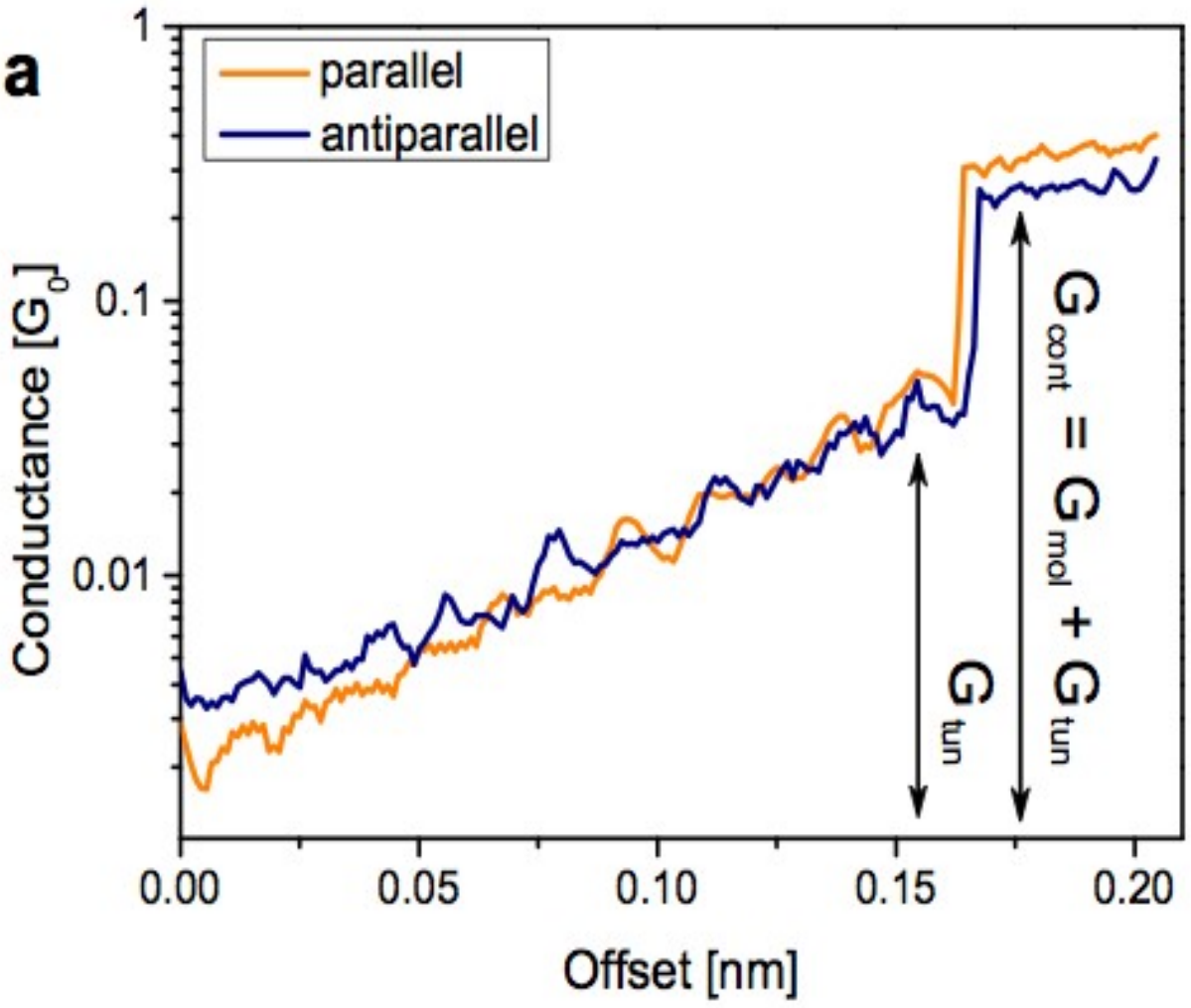
M. Bode et al. PRL 81, 4256 (1998)

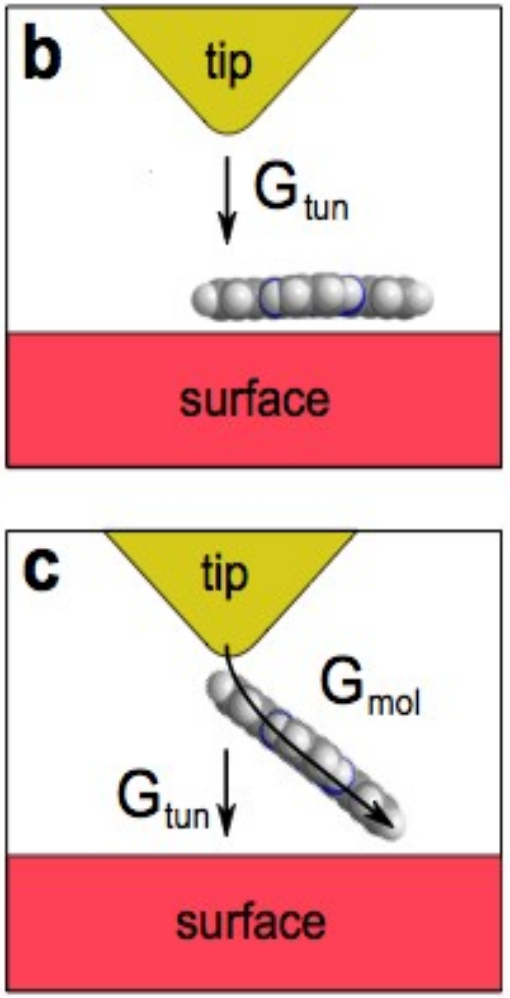
Spin-polarized STM of Co/Cu(111)



- Magnetization of the islands can be identified.
- Low TMR of only 5% near Fermi edge.

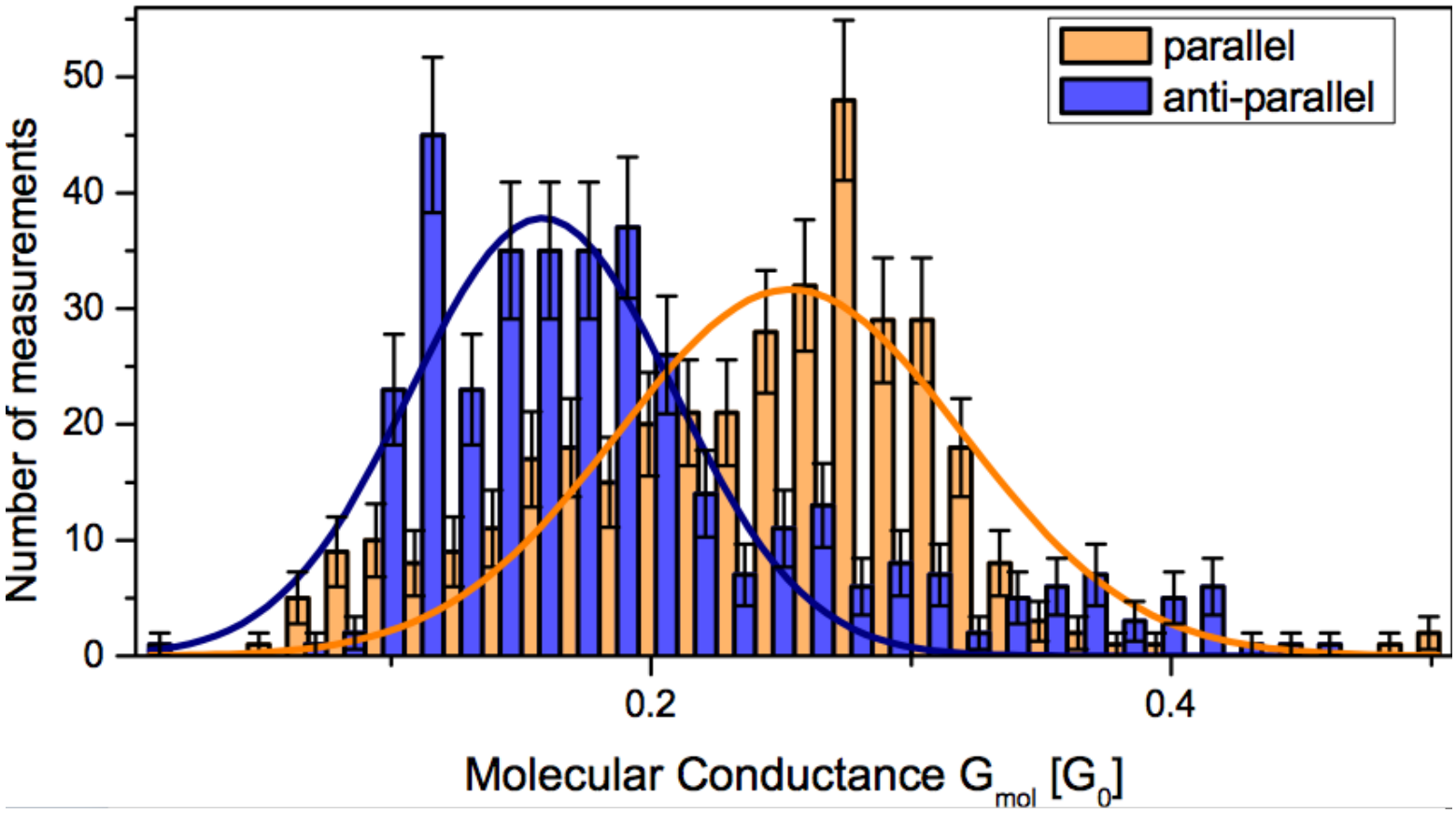
Spin-polarized transport across H_2Pc





- Different conductances for parallel and antiparallel alignment of magnetization.
- Separation into tunneling current and current across molecule.

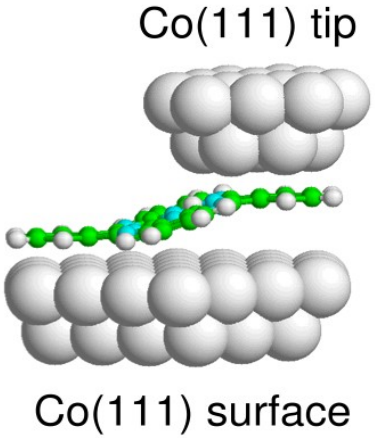
Spin-polarized transport across H_2Pc



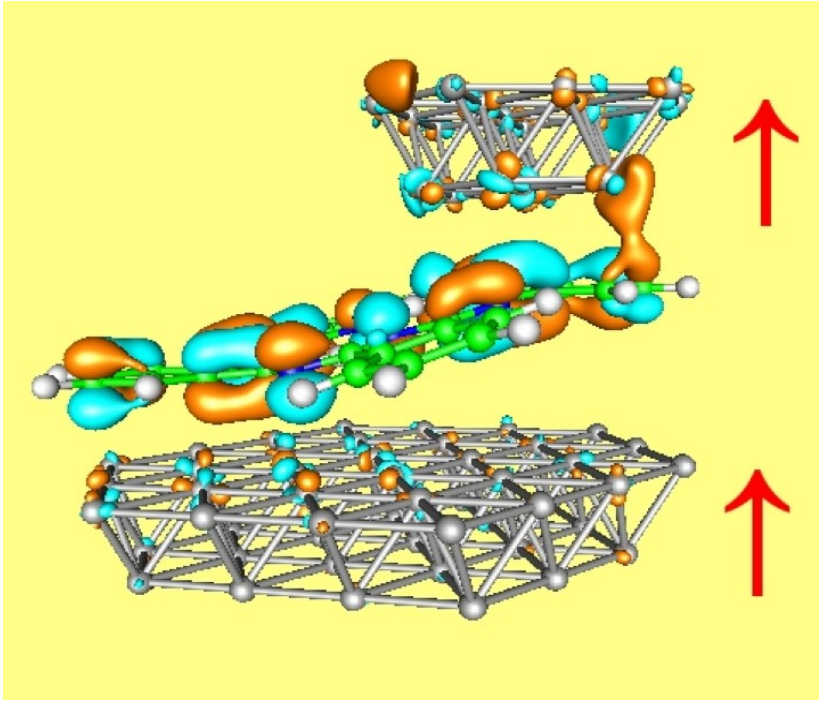
- Small scatter in conductance allows to determine GMR.
- GMR across molecule of 60±9% is much larger than TMR.

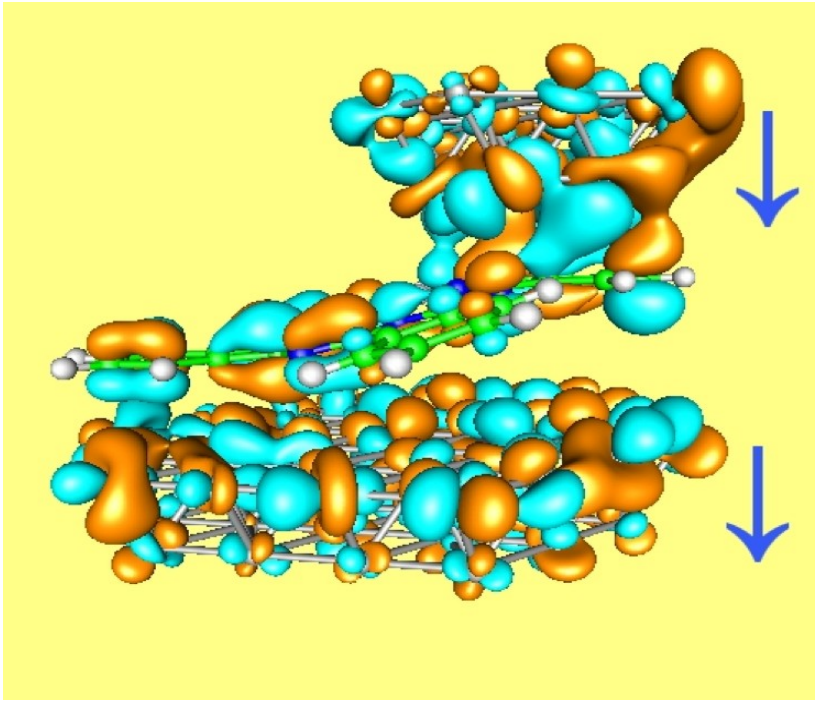
Schmaus et al. submitted

Spin-polarized transport calculations



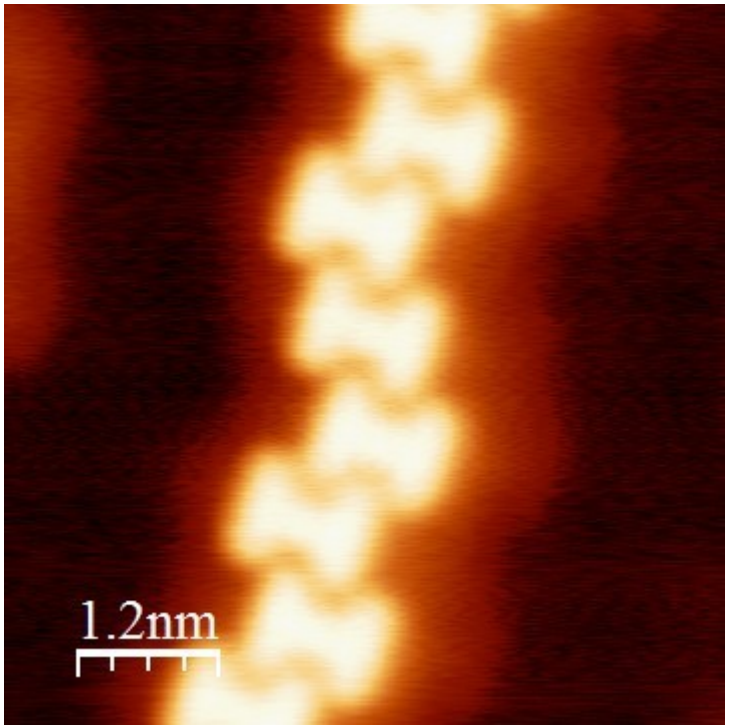
- Calculations in tunneling and contact geometry.
- HOMO strongly hybridizes with spin down Co dz-states.
- Much enhanced transmission across hybridized state.
- Calculated GMR of 65% in good agreement with experiments.





Current projects on molecular magnets

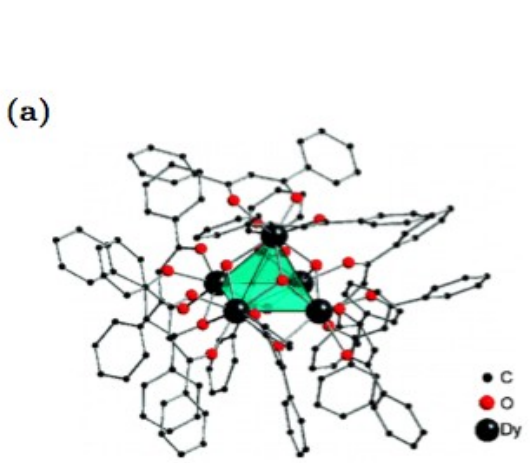
Chromium-acetylacetonate

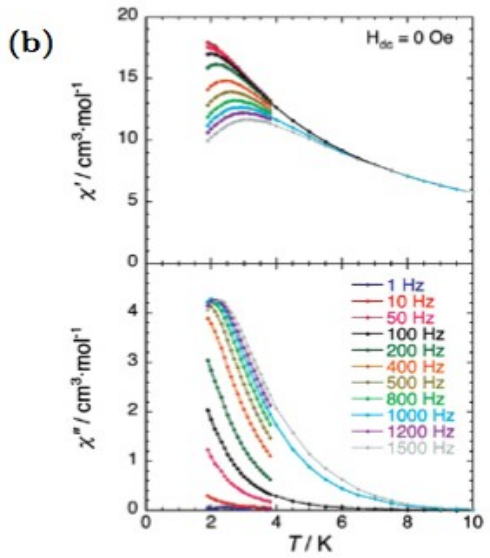


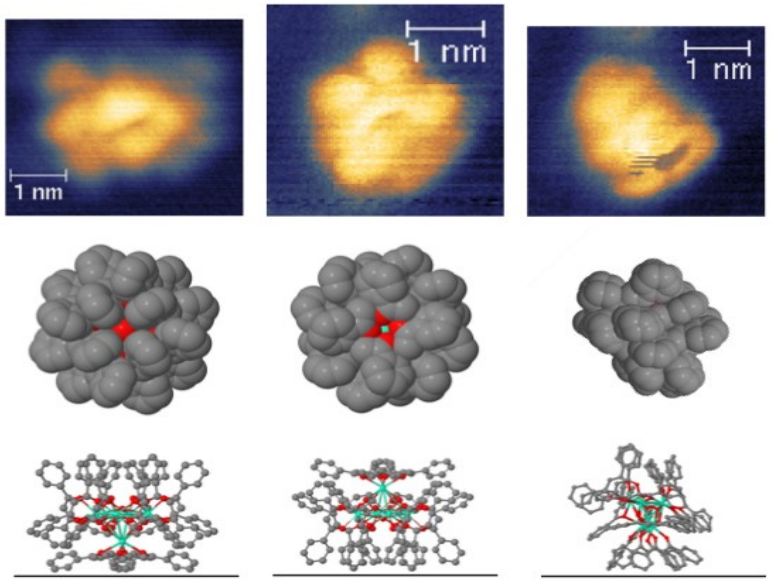
S=1/2 system leads to Kondo-effect on surfaces

Current projects on molecular magnets

Dy-5 single molecular magnets





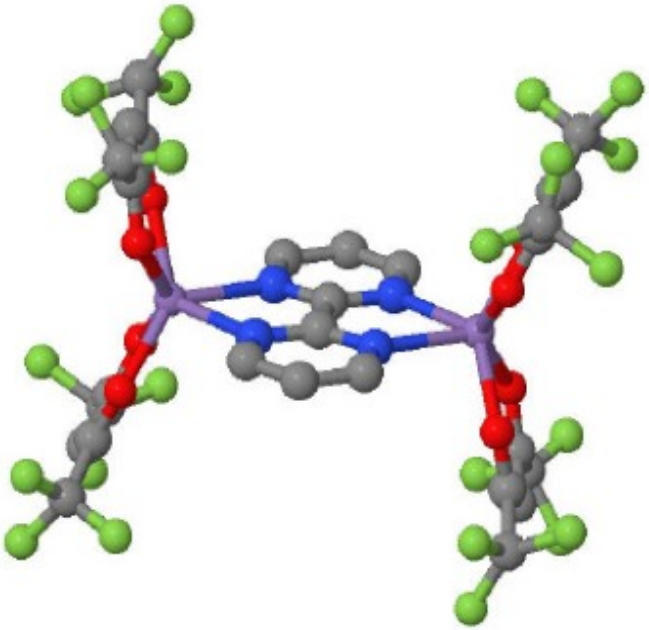


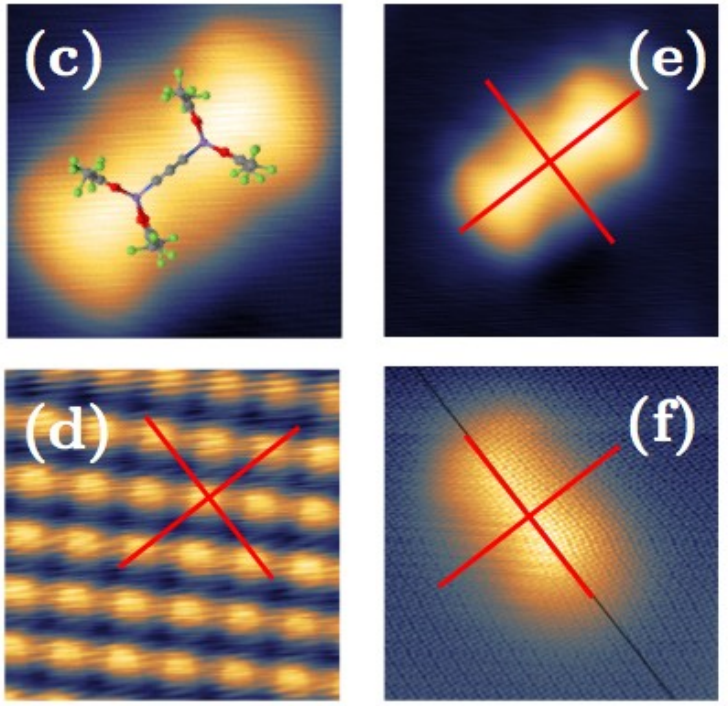
Evaporation by sublimation in UHV

In collaboration with AG Roesky, KIT

Current projects on molecular magnets

Mn_2 & Ni_2– antiferromagnetic dimers





Evaporation by sublimation in UHV

See poster of L. Zhang, M. Schackert ....

In collaboration with AG Ruben, KIT & IPCMS

Conclusions

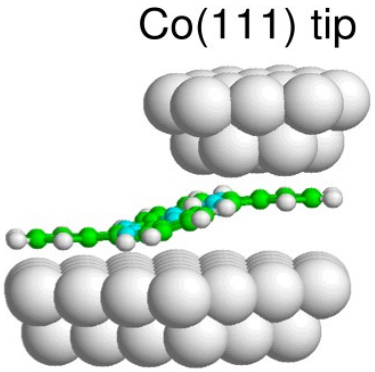
- Contacting single Pc molecules with STM tip
- Jump to contact allow to determine precisely the conductance
- Chemisorption on Co leads to charge transfer and HOMO at Fermi level

- Spin polarized transport measurements show high GRM of 60%
- Calculations confirm the high value based on hybridization of LUMO with Co minority states

First steps in molecular spintronics

Thank you for the attention!

Spin-polarized transport calculations



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