Diffusion and Anchoring of large Organic Molecules on Cu(110)

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Introduction

- **Large Organic Molecules:**

  Building Blocks in Nanoelectronics devices

  - Static behavior: anchoring and ordering on surfaces
  - Dynamic behavior (e.g. Diffusion on Metal Surfaces)

  Nanomechanics? Nanomachines?

- **Model systems in molecular electronics:**

  Two closely related molecules, DC and HtBDC

  - Conducting backbone (aromatic π - system)
  - Spacer legs (bulky aliphatic groups)
  - Diffusion studies

- **Investigation of molecule - surface interactions:**

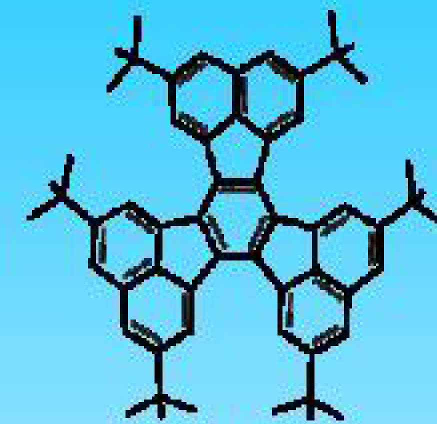
  "Lander" Molecules

  - influence of spacer groups
  - conformation of the molecules
  - effect of the surface (is the surface a staticcheckerboard)

Related Organic Molecules

- DC molecules on Cu(110)
  (Decacyclene): $C_{36}H_{18}$
  Disk – like aromatic molecule

A



B

- **HtBDC molecules on Cu(110)**
  (Hexa - *tert* - butyl Decacyclene): $C_{60}H_{66}$
  - Aromatic core (resembling DC)
  - six *tert* – butyl – groups (- C_4H_9) attached to the core

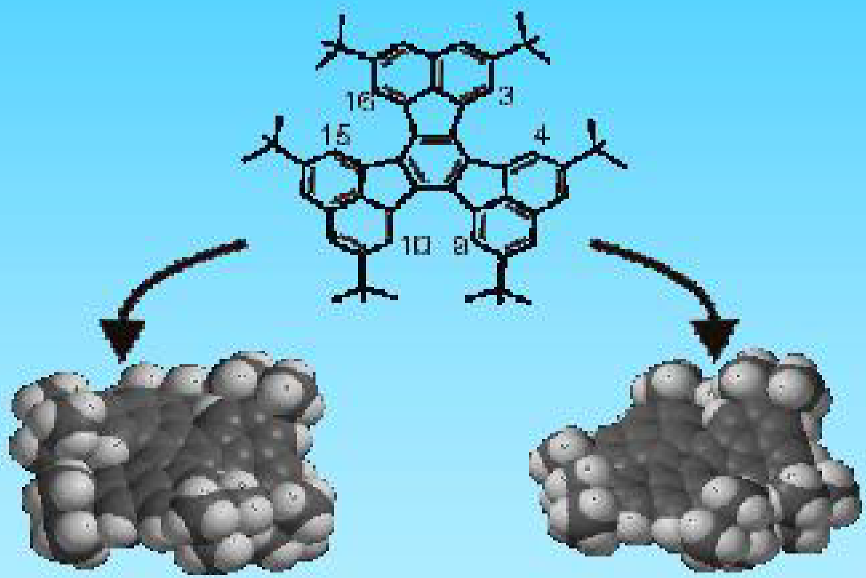
The groups act as spacers => separation of the π - system from the substrate

Previous Studies

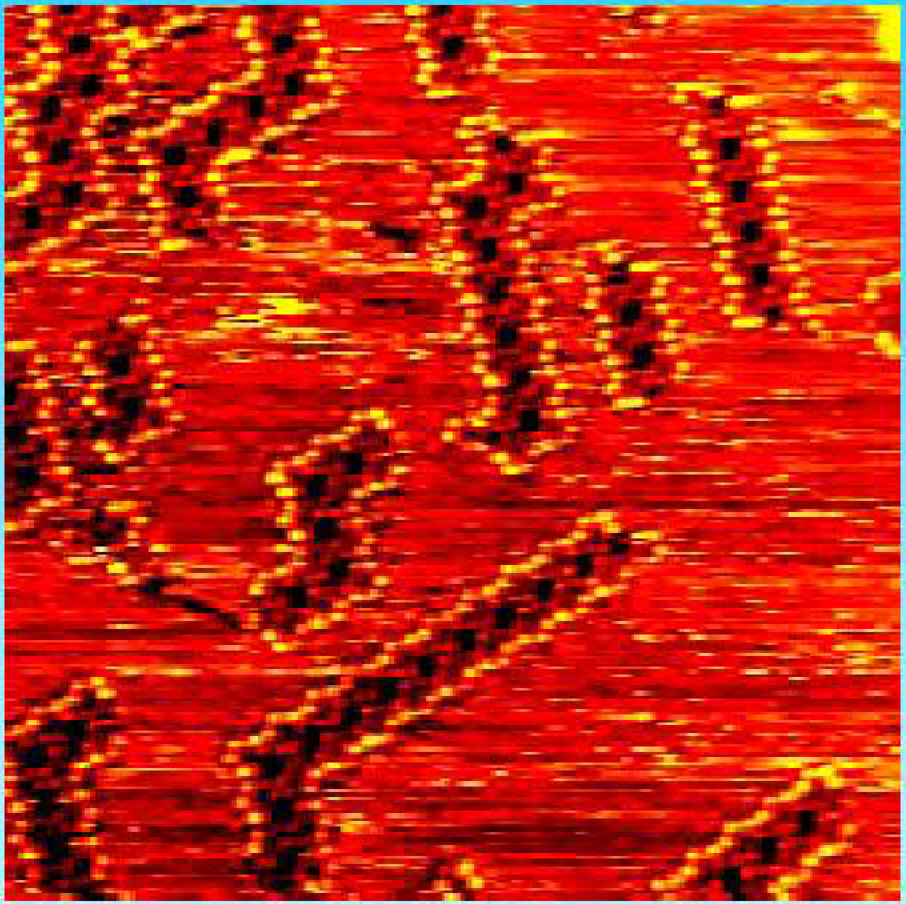
- **HtBDC on Cu(001):**
  - J.K. Gimzewski et al., *Science* **281** (1998) 531:
    - **Rotation of a Single Molecule Within a Supramolecular Bearing**
- **HtBDC on Cu(110):**
  - M. Schunack et al., *Phys. Rev. Lett.* **86** (2001) 456
    - **HtBDC molecules locally restructure the surface**
  - M. Schunack et al., *Angewandte Chemie* **40** (2001) 2623:
    - **The induced restructuring is chiral**
- **Diffusion Studies** (few on large organic molecules):
  - **PVBA on Pd(110)**, J. Weckesser et al., *J. of Chem. Phys.* **110** (1999) 5351
  - **C_{60} on Pd(110)**, J. Weckesser et al., *Phys. Rev. B* **64**, 161403 (2001)

HtBDC on Cu(110): Mobility at Room Temperature

Formation of double rows of molecules with zig – zag shape



propeller   boat



streaks from fast diffusing molecules (probably dragged by the tip)

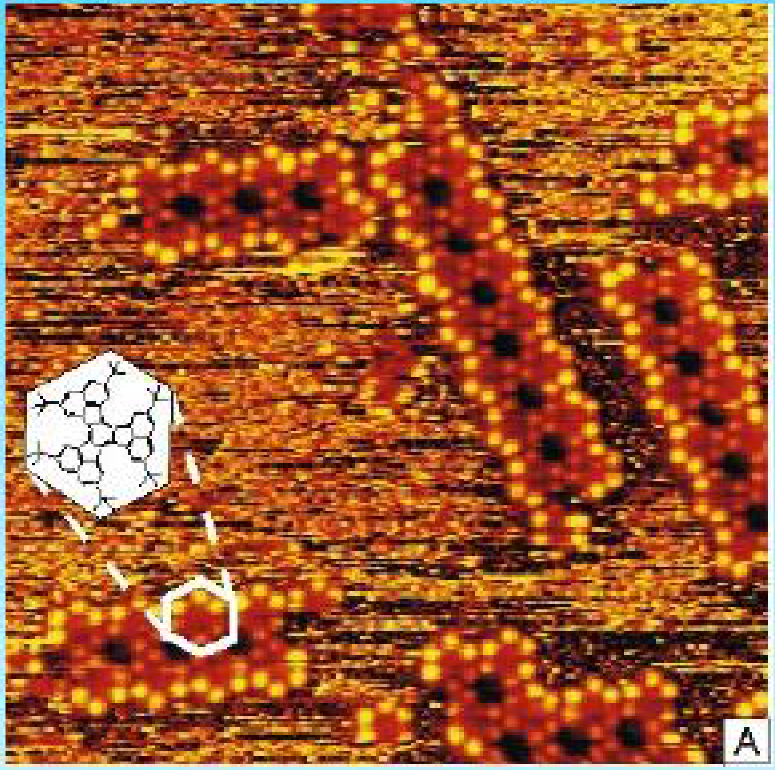
M. Schunack *et al.*, PRL **86**, 456 (2001)

HtBDC on Cu(110)

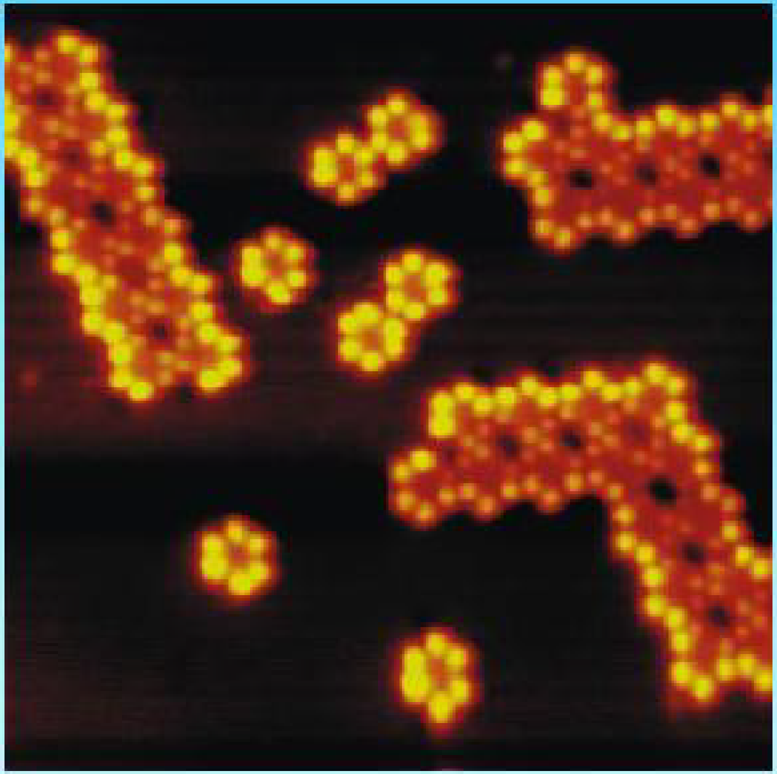
hexa-*tert*-butyl decacyclene ($C_{60}H_{66}$): deposition at RT

Molecules imaged as having 6 lobes = 6 spacer legs

RT **25 K**



200x200 Å²

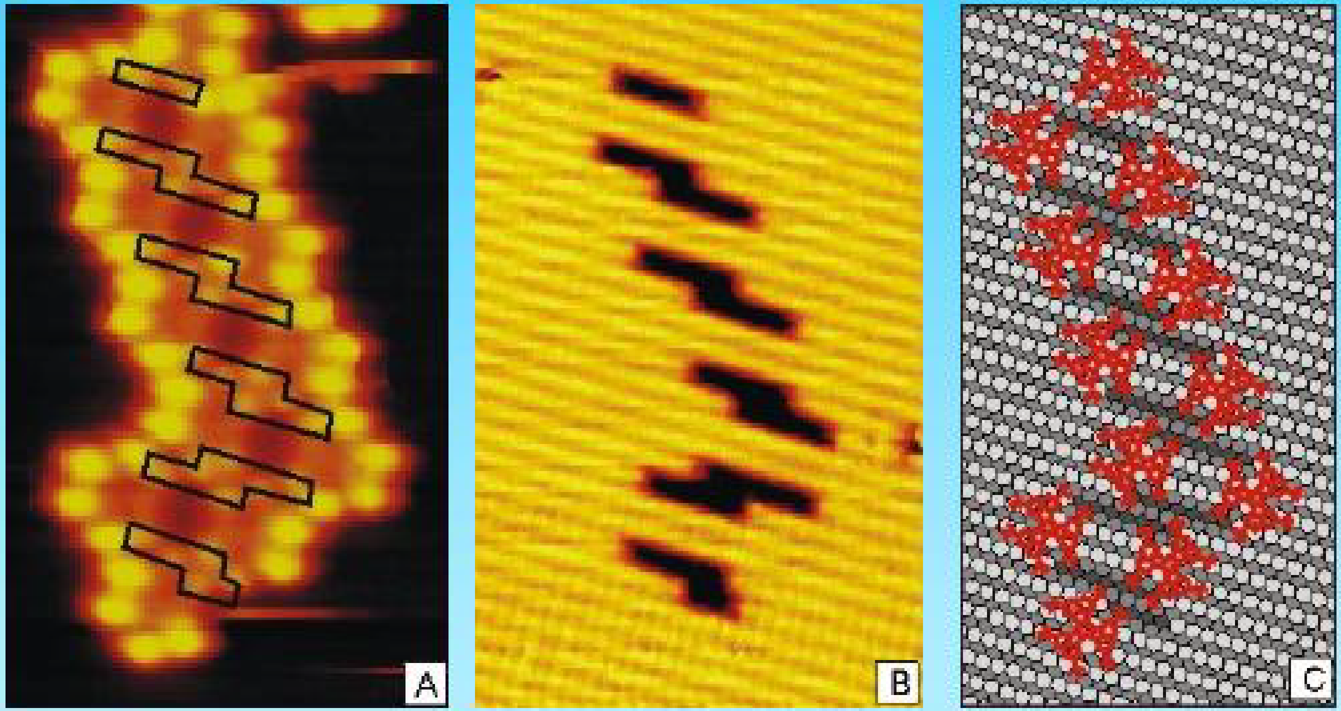


RT: Intermediate streaks from fast diffusing individual molecules

M. Schunack *et al.*, PRL **86**, 456 (2001)

Manipulation with STM

Pushing molecules aside at reduced tip-sample distance: Restructuring of the surface underneath the molecules



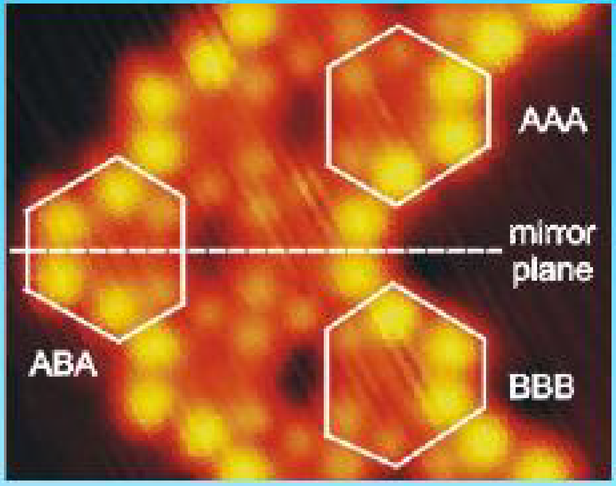
before — after — model

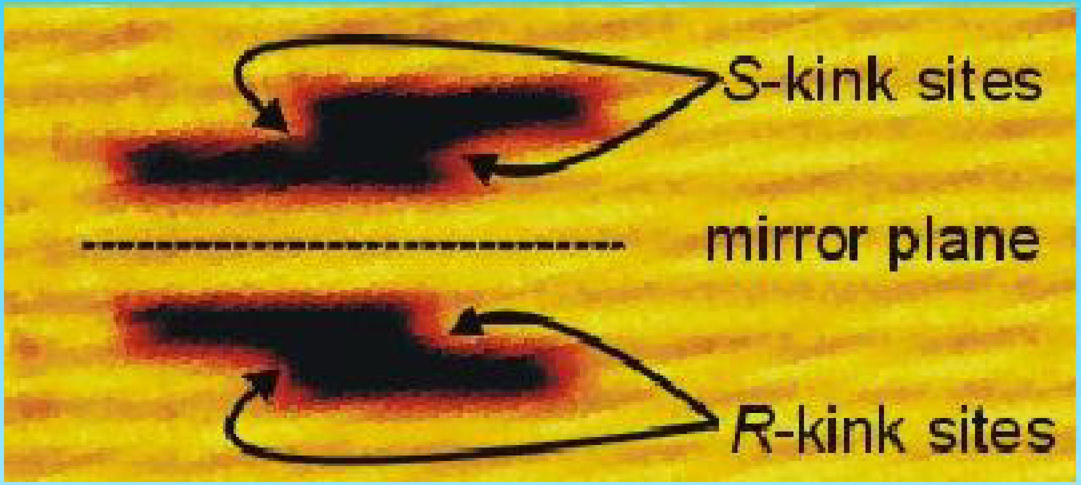
Adsorption of large organic molecules on metal surfaces can be associated with a disruption of the substrate

M. Schunack, *et al.*, PRL **86**, 456 (2001)

Chirality and Leg Conformation

Holes are chiral due to the presence of kink sites:





- **Chirality "imprinted" by chiral molecules**
- **Understanding of underlying processes may lead to new route for nanostructuring surfaces in a controlled manner**

M. Schunack et al., *Angewandte Chemie* **40** (2001) 2623

Experimental Set - up

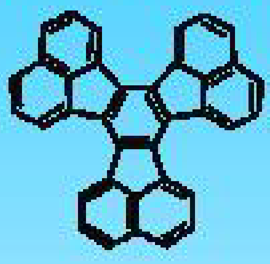
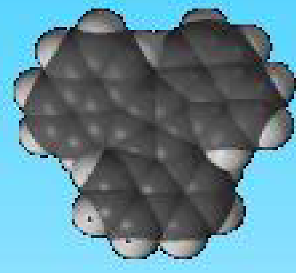
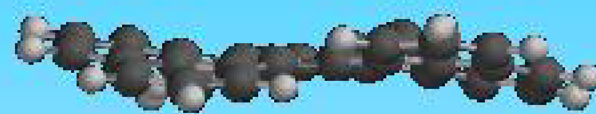
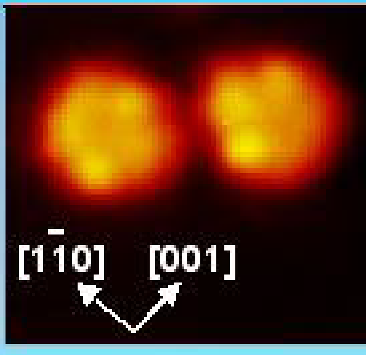
- UHV Chamber: $p < 1x10^{-10}$ mbar
- Standard Surface Science Techniques:
  - Auger Electron Spectroscopy
  - LEED
- Variable Temperature STM (100 – 400 K) – **fast scanning**
- Standard Sputtering / Annealing for preparing the Cu(110) surface
- Organic Molecular Beam Deposition (OMBD): crucible heated with a filament

Related organic molecules on Cu(110)

on Cu(110):
(50 × 50 Å²)

decacyclene (DC, $C_{36}H_{18}$): 220 - 250 K

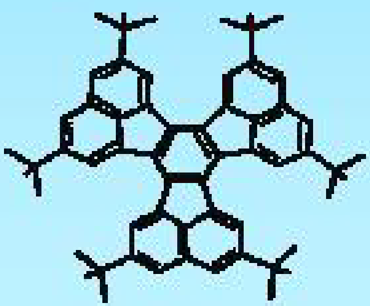
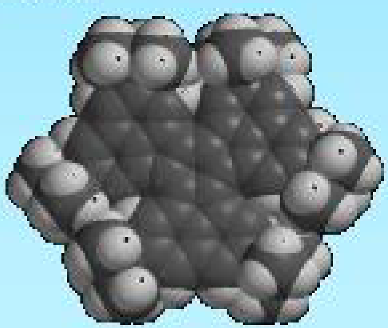
Cu(110) = RT, T_{powder} = 430 K

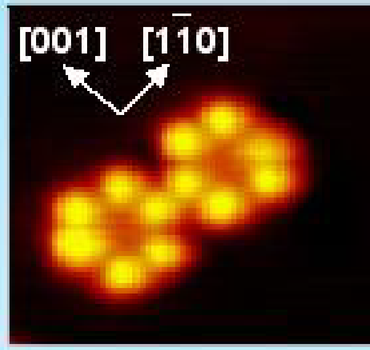





T = 96 K

hexa-(*tert*-butyl)decacyclene (HtBDC, $C_{60}H_{66}$): 170 - 200 K

Cu(110) < 250 K, T_{powder} = 450 K

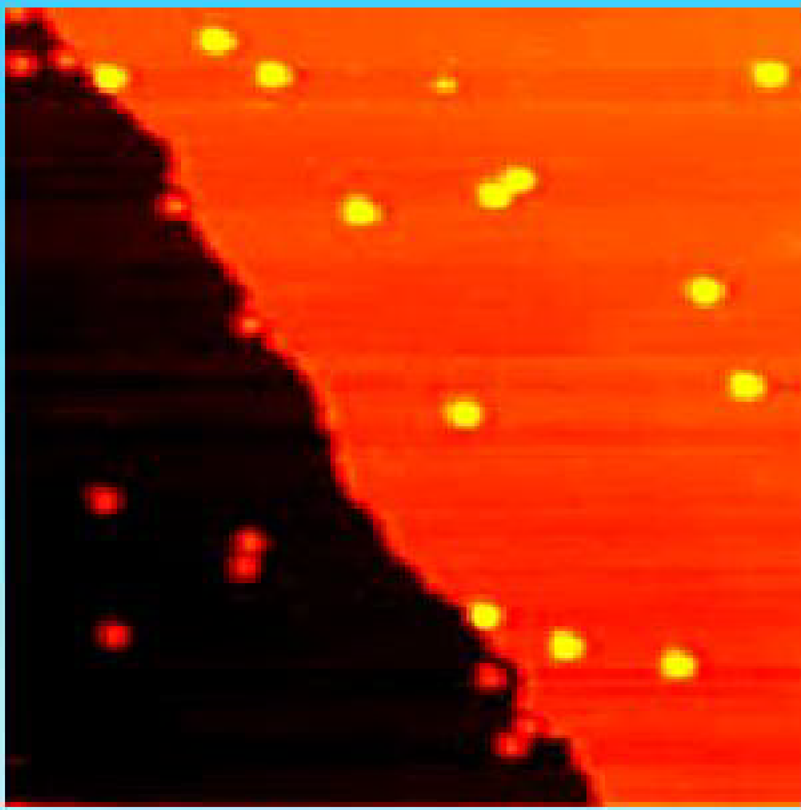


T = 25 K

spacers groups → separation of the π - system from the substrate

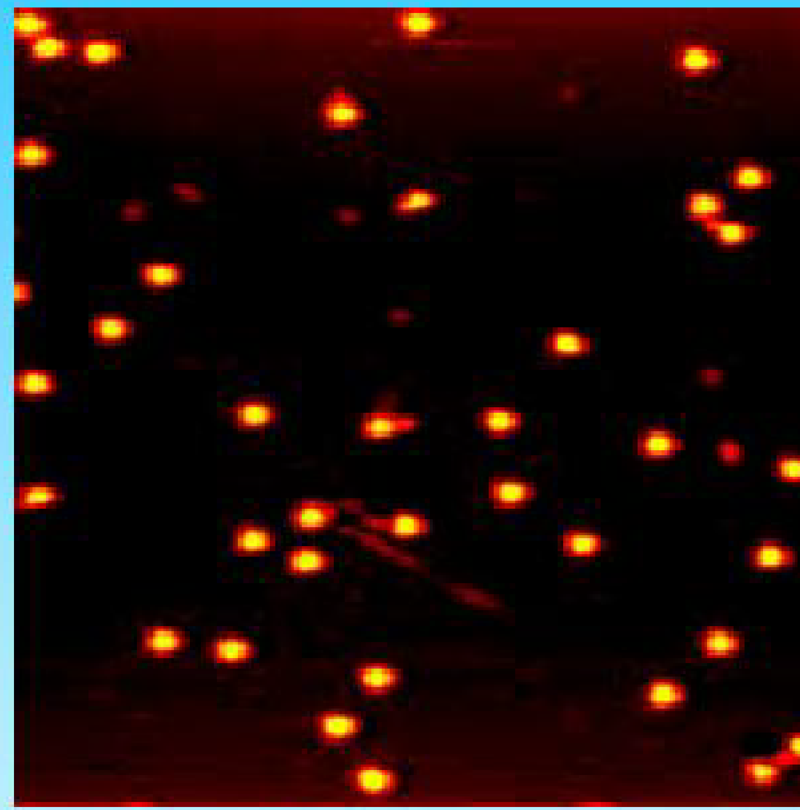
DC Movies

- 1 D Diffusion along the close packed direction [110] of Cu(110)

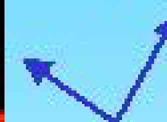


500x500 Å^2
T = 235 K

15 seconds
per image



500x500 Å^2
T = 251 K



<u>image size:</u>
compromise between good statistics and good resolution

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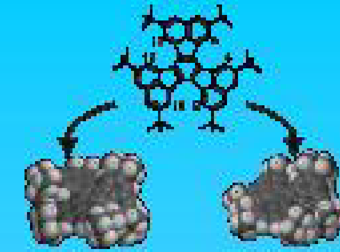
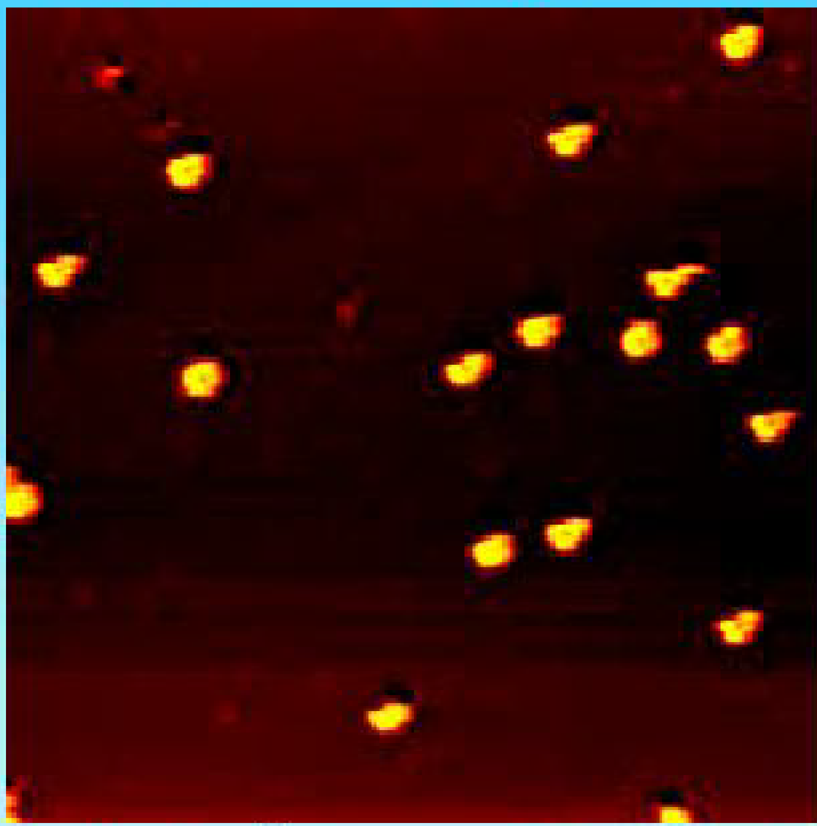
HtBDC Movies

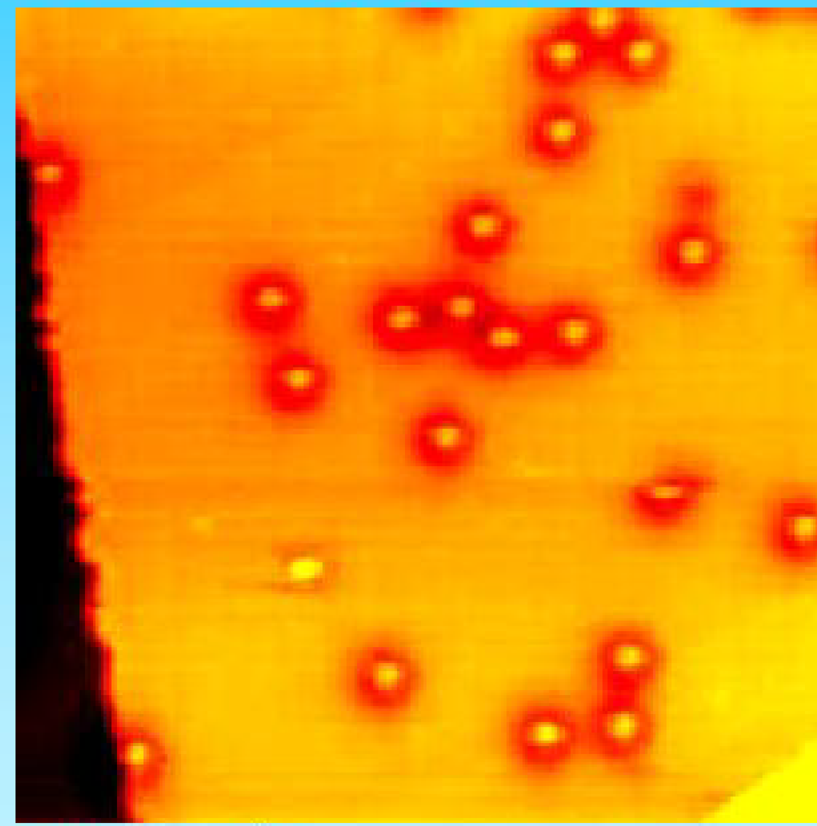


- 1 D Diffusion along the close packed direction [110] of Cu(110)



500x500 Å^2
T = 194 K

15 seconds
per image



500x500 Å^2
T = 203 K

V = - 1768 mV
I = - 0.61 nA

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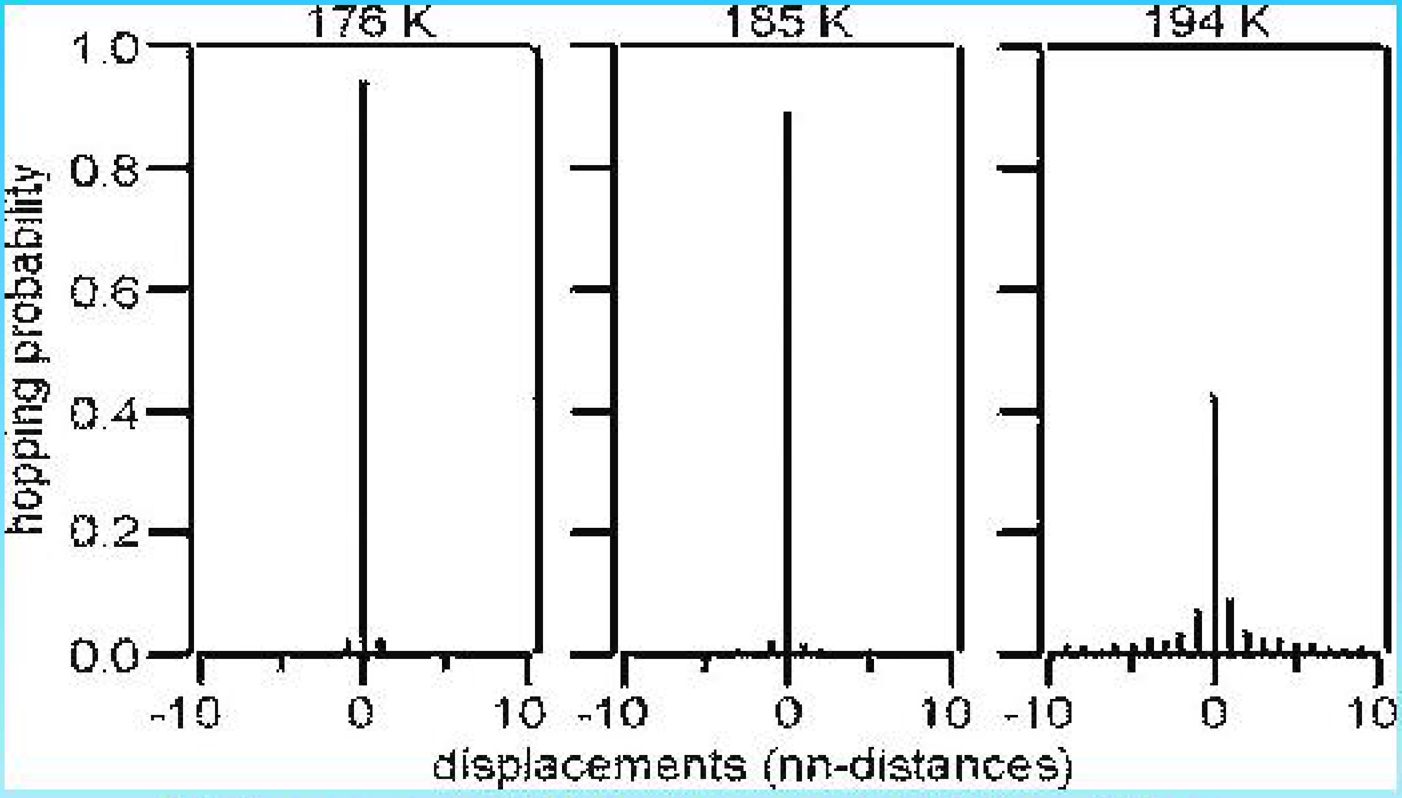
Diffusion Theory – Data Analysis

- "Tracer" Diffusion Coefficient:
  - $D = \langle(\Delta x)^2\rangle / 2t$ (1-d diffusion)
- Arrhenius behavior:
  - $D = D_0 \exp(-E_D/kT)$
- Hopping rate (measured directly):
  - $h = h_0 \exp(-E_D/kT)$
    - Hopping rate: counting the proportion of molecules that have not moved between two consecutive images:

$$P_0 = M / N = F(ht)$$

- Link:
  - $\langle(\Delta x)^2\rangle = \lambda^2 h t$, where λ is the 'jump length'

Hopping Histograms: HtBDC



Histograms of Hopping probability of the HtBDC Molecule: three different Temperatures

- Symmetric
- Mean value close to 0
=> No tip influence

• Controlled manipulations
  • DC: ≤ 100 M_
  • HtBDC: ≤ 500 M_

→ Values far below usual imaging conditions (about 5 G_)

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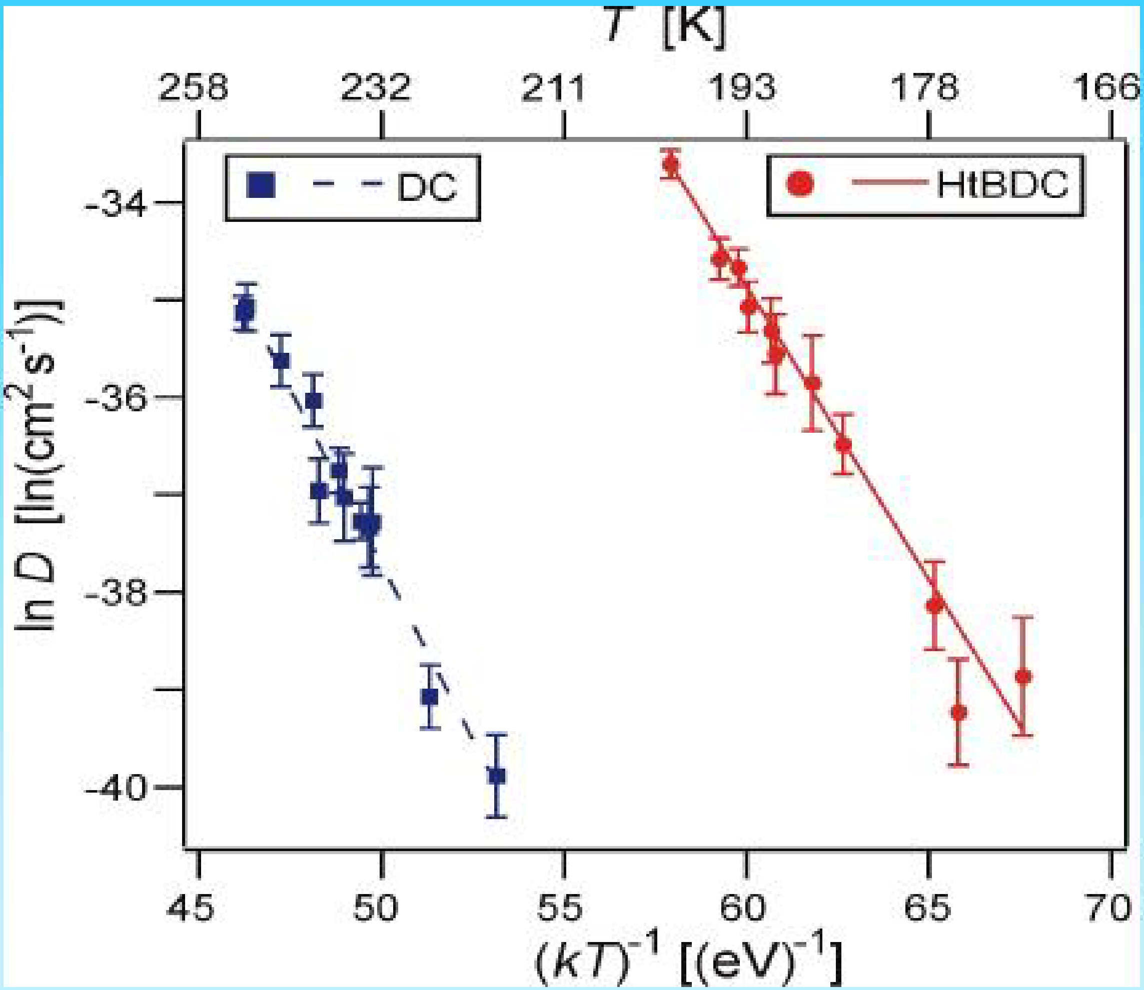
Arrhenius Plot - 1



First Method:

Analysis of Mean Square Displacement

$$D = D_0 \exp(-E_D/kT)$$

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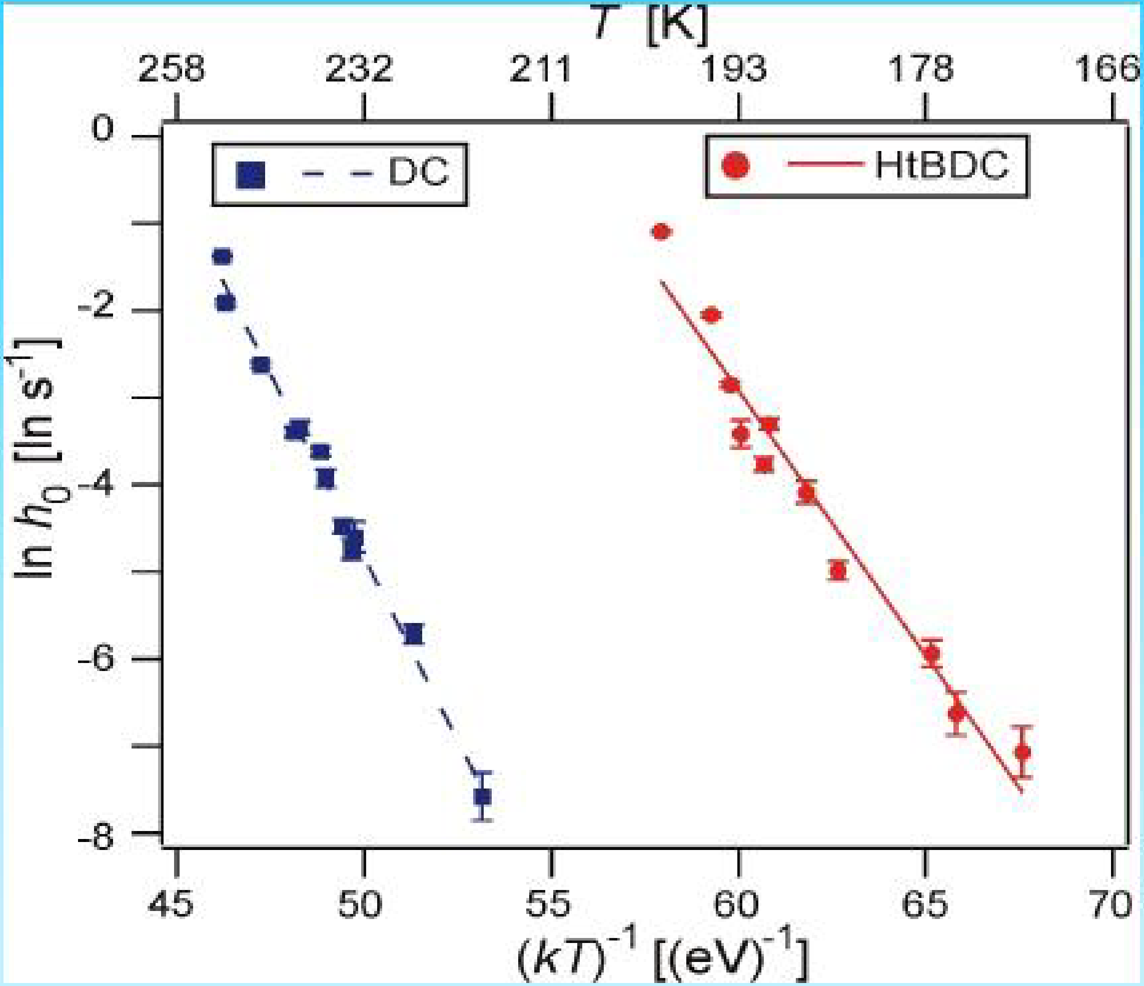
Arrhenius Plot - 2



Second Method:

Analysis of hopping rate

$$h = h_0 \exp(-E_D/kT)$$

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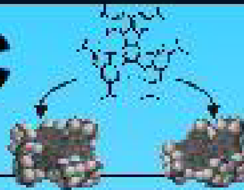
Comparison of Results

- Relevant parameters reported in table below:

	DC 		HtBDC 	
	$<(\Delta x)^2>$	hopping rate	$<(\Delta x)^2>$	hopping rate
E_D(eV)	0.76±0.07	0.78±0.03	0.60±0.04	0.61±0.04
$h_0(s^{-1})$	-	$10^{16.2 \pm 0.6}$	-	$10^{14.6 \pm 1.1}$
$D_0(cm^2s^{-1})$	$10^{-0.8 \pm 0.9}$	-	$10^{0.5 \pm 1.0}$	-

molecular structure: aromatic π-system binds stronger to surface

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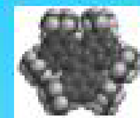
Discussion - jump length

new approach: $D = \_\ \lambda^2 h$

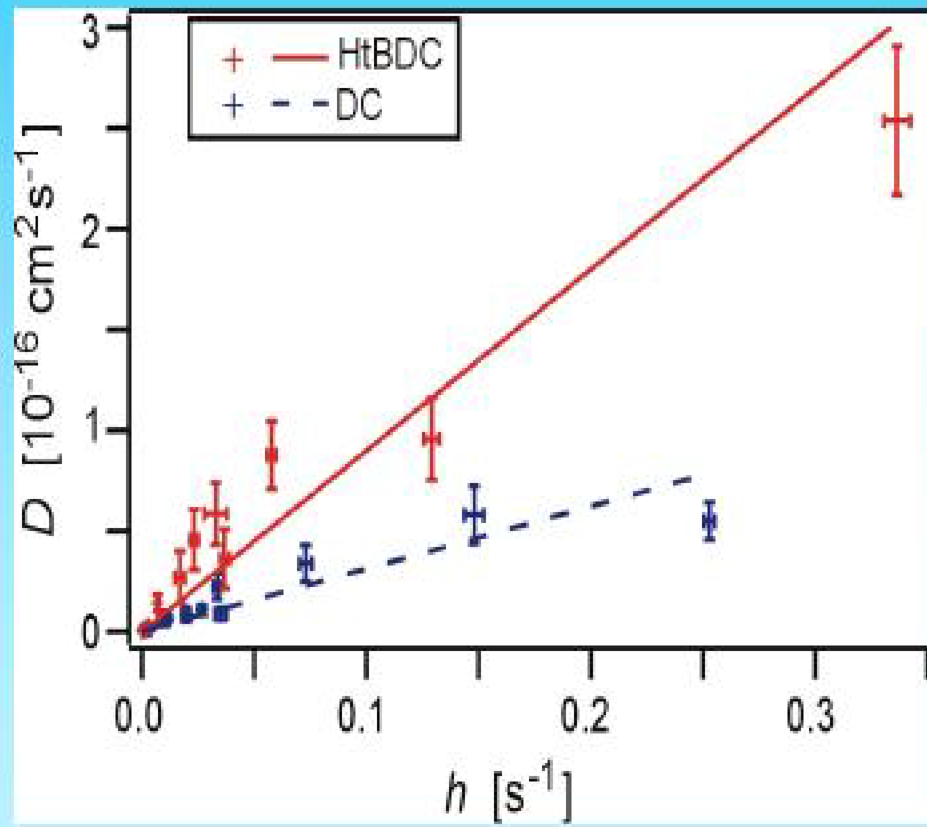
 DC: $\lambda = 7.9 \pm 0.4$ Å <  HtBDC: $\lambda = 13.4 \pm 0.6$ Å

- no jump length distribution required
- large RMS jumps treatable
- avoids huge error bars of prefactors

comparison: $D_0 = \_\ \lambda^2 h_0$

DC: $\lambda = 1 \pm 10$ Å;

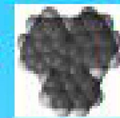
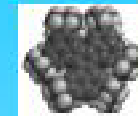
HtBDC: $\lambda = 13 \pm 13$ Å



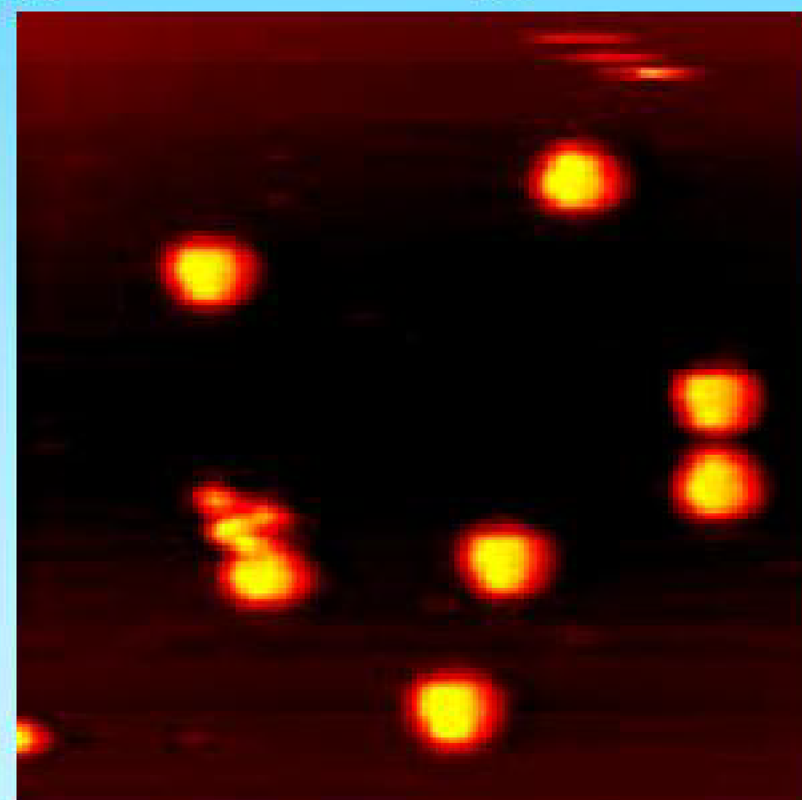
$\lambda_{metals} \ll \lambda_{molecules}$: low friction model, energy dissipation through internal modes

Discussion – prefactors 1

2 - 3 orders of magnitude above "standard" values

	"standard"	 DC	 HtBDC
h_0 (s^{-1})	10^{13}	$10^{16.2 \pm 0.6}$	$10^{14.6 \pm 1.1}$
D_0 ($cm^2 s^{-1}$)	10^{-3}	$10^{-0.8 \pm 0.9}$	$10^{0.5 \pm 1.0}$

When the resolution is sufficient, it is possible to observe rotation of single molecules, coupled to diffusion: this provides a reasonable explanation for the high prefactors observed



Discussion – prefactors 2

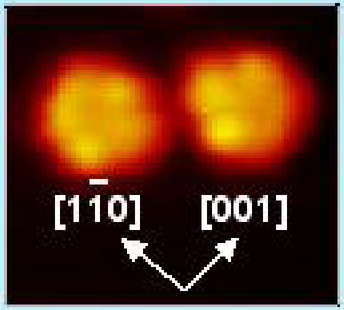
- $h_0 = \nu_0 \exp(S_D/k)$ and $D_0 = (\nu_0 \lambda^2/2) \exp(S_D/k)$
- $S_D \approx 0$ for metal – on – metal diffusion
- large molecules: $S_D > 0$

  (many internal degrees of freedom)

  - conformational changes over the diffusion path (e.g. rotation: rotational motion detectable on top of diffusion!)

DC

- long jumps: assumption of standard values not appropriate



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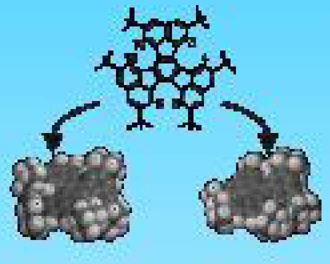
Conclusions – Part 1

- Comparison of Diffusion of related large organic molecules on Cu(110):

  - HtBDC – DC
  - Two methods for data analysis:
    - Mean square displacement
    - Hopping rate



Measurement of:

- Activation Energy: Higher for DC – stronger interaction with the substrate
- Prefactor: 2 – 3 orders of magnitude above standard values
- Attempt frequency

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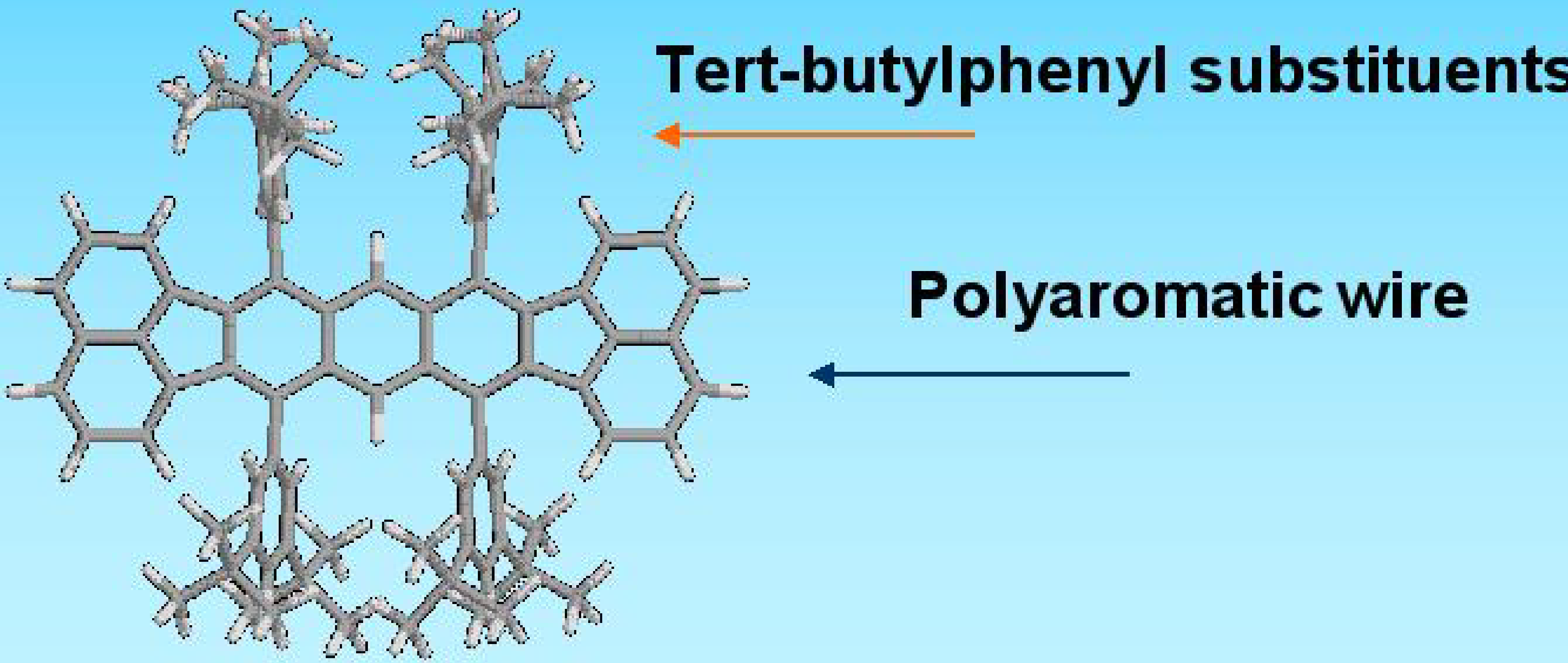
Part 2:
Anchoring of large molecules

- "Lander" Molecule on Cu(110):
  - 3,5-di-*tert*-butylphenyl: **$C_{90}H_{98}$**



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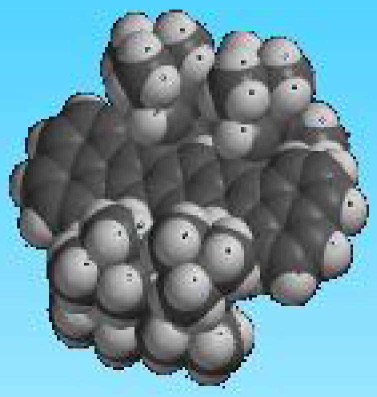
Molecular wire

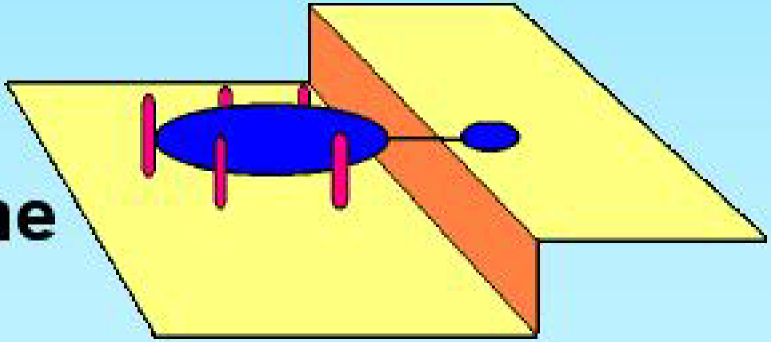
- **Properties:**
  - Conducting backbone

    (polyaromatic wire terminated by a fluoranthene group)
  - 4 spacer legs for "isolation" from the substrate

    (Tbp substituents)
  - Basic idea: interconnect the molecule to a step edge

Ball model





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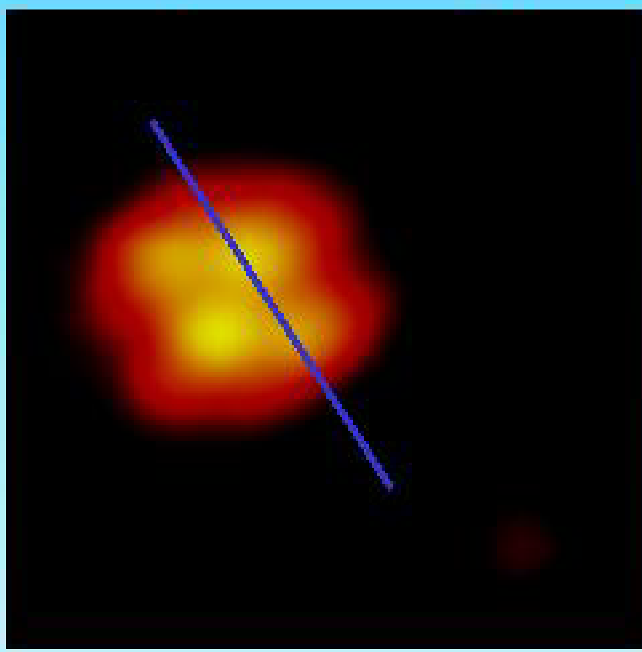
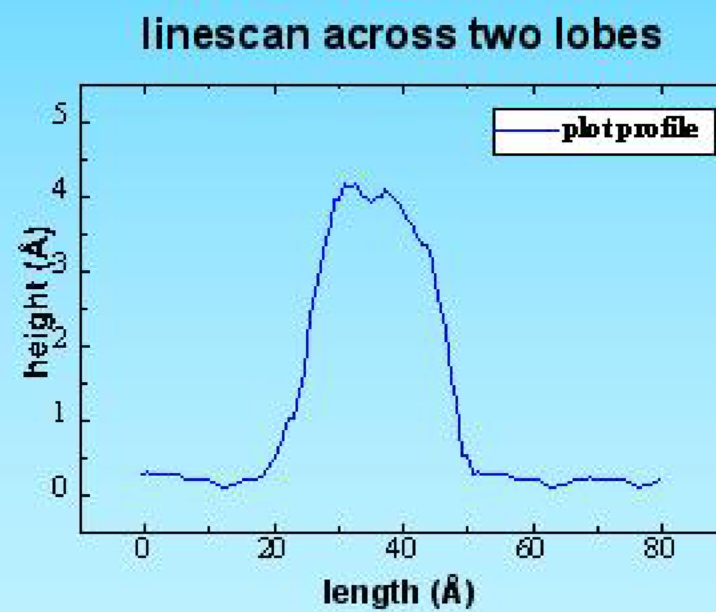
STM imaging of the Lander

- Imaged by STM as four lobes => four spacer legs
- Two possible conformations, rectangular or parallelogram - like



Lander on Cu(110)



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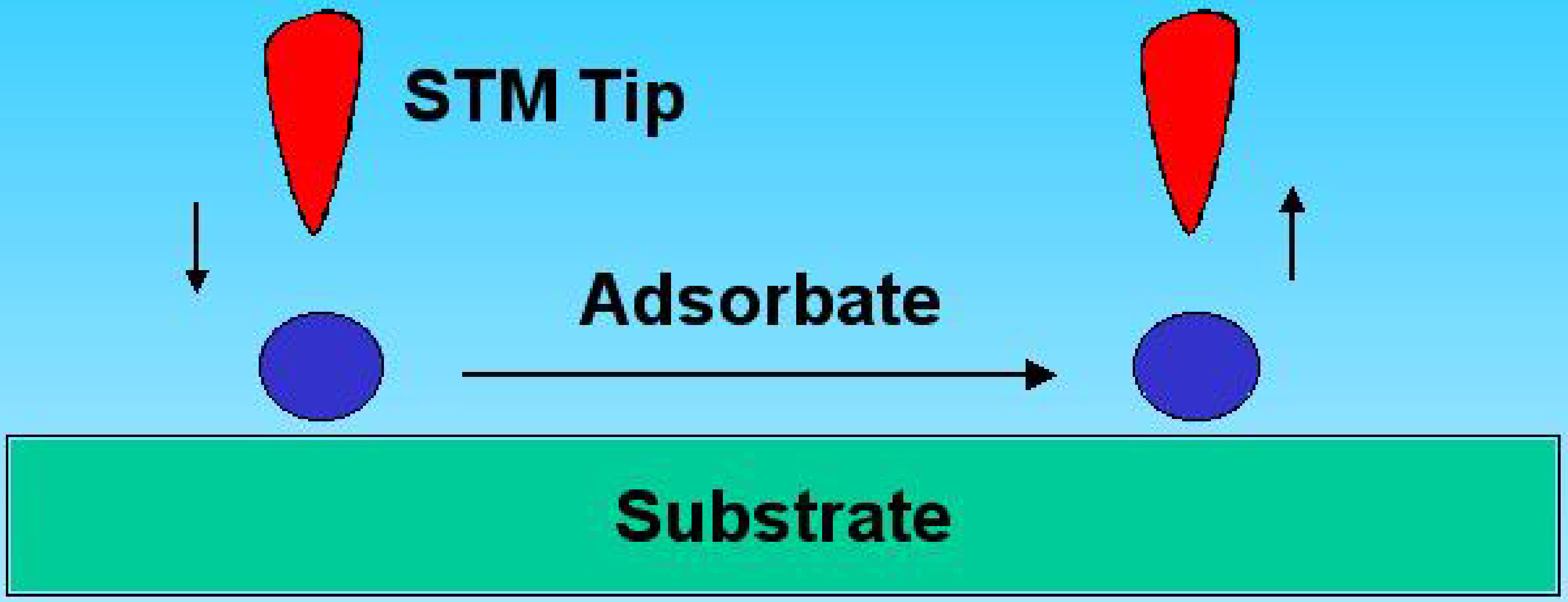
Previous studies

- **Lander molecule on Cu(100):**
  - Langlais et al., “Spatially resolved tunnelling along a molecular wire” *Phys. Rev. Lett.* **83** (1999) 2809
  - M. Magoga and C. Joachim, “Conductance of molecular wires connected or bonded in parallel”, *Phys. Rev. B* **59**, 16011 (1999)

Lateral manipulation of single atoms and molecules with the STM



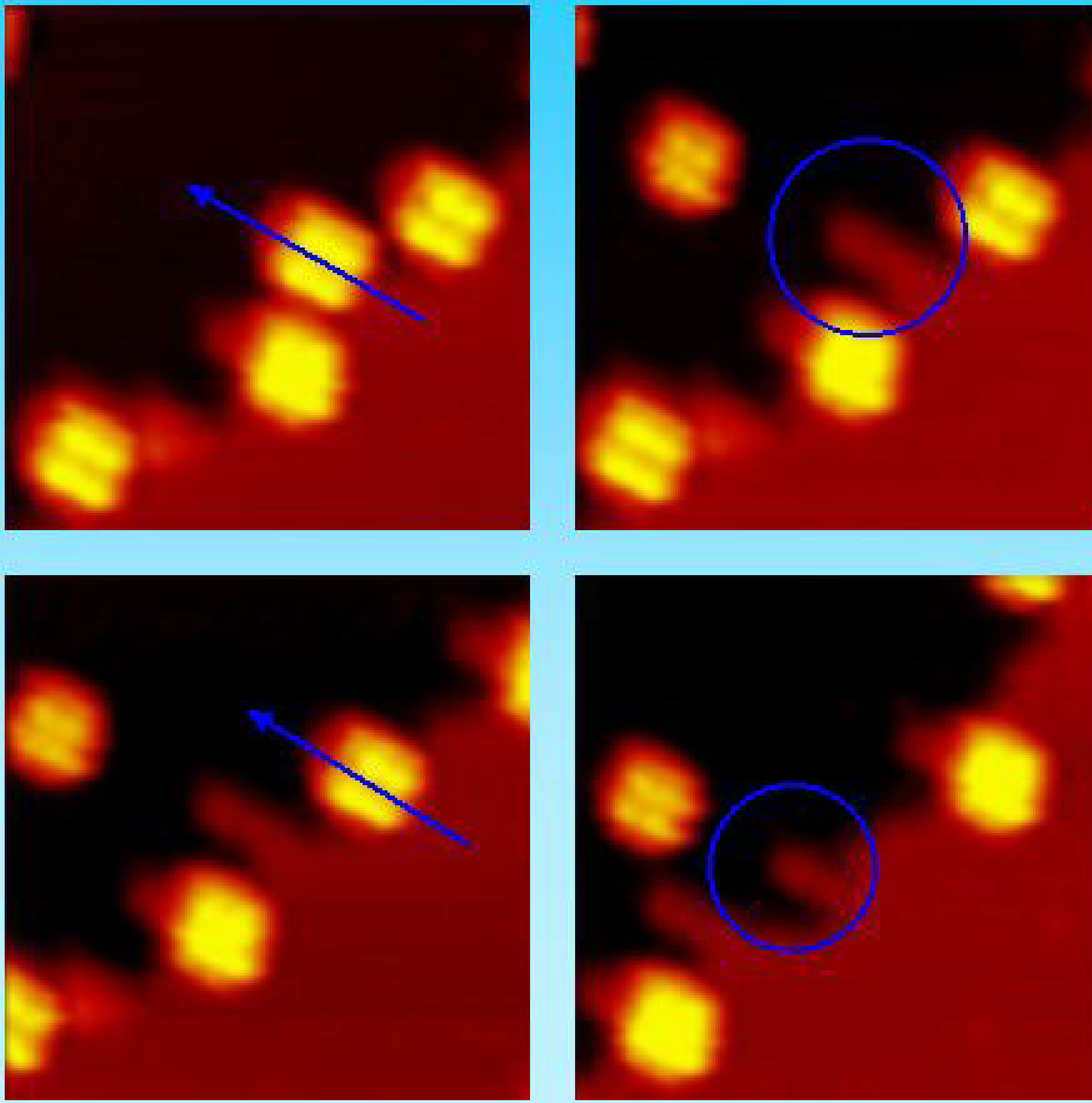
Constant current or constant height mode

Tunneling resistance V / I measures tip – sample separation:

$$I \sim V \exp(-2kz)$$

reducing the tunneling resistance means approaching the surface: stronger tip – surface interaction

Step Restructuring on Cu(110)



- **Deposition at room temperature submonolayer coverage:**
  decoration of step edges
- **Low temperature manipulations: the molecules are anchored to the step edge**

300 x 300 Å^2

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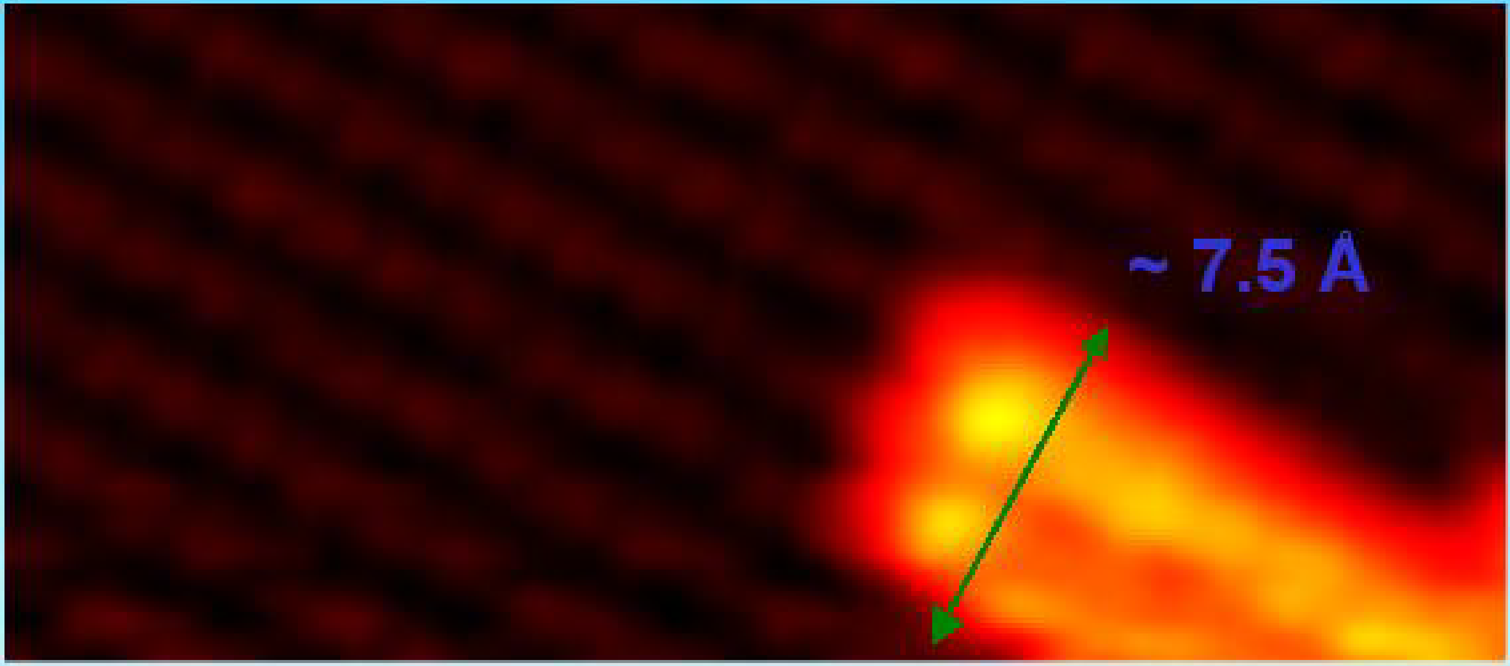
Step Restructuring

- Formation of a "nano – contact"
- The width of the nano – contact is 2 Cu atomic rows



Width: <x> = 7.5 ± 0.5 Å (~ 2 atoms)

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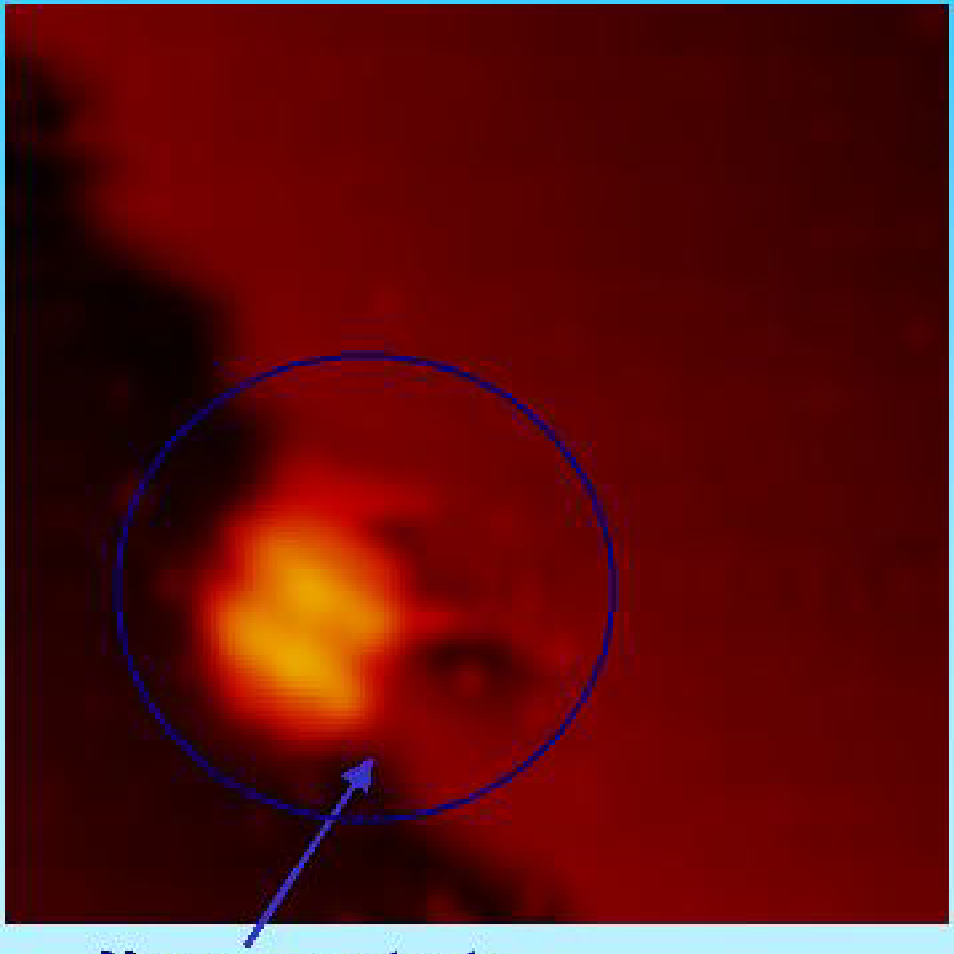
Controlled STM Manipulation

Using **controlled** STM **manipulation**, it is possible to slide a molecule until it just **barely** touches the edge of the nano – contact it has previously formed



Nano – contact:
to be shown by finding a signature, e.g. with tunneling spectroscopy

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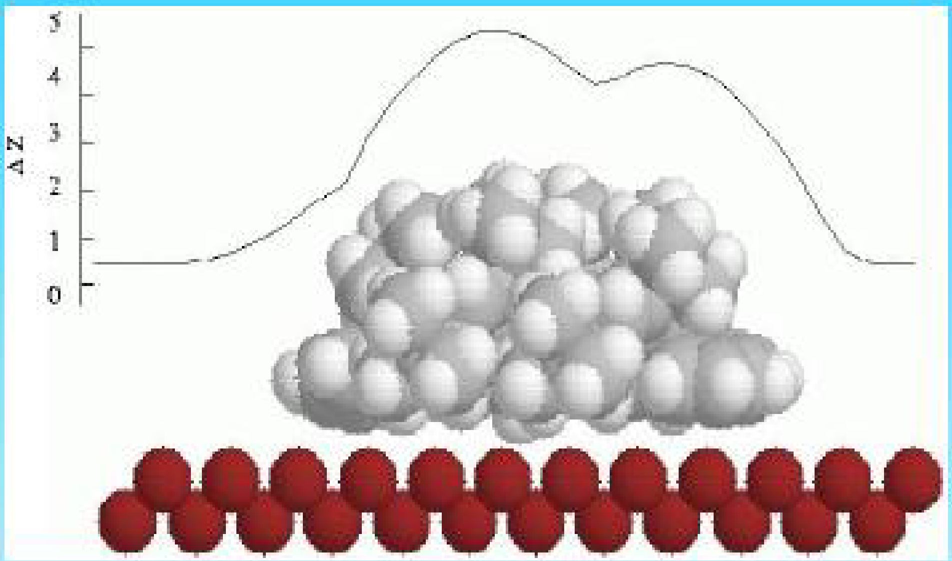
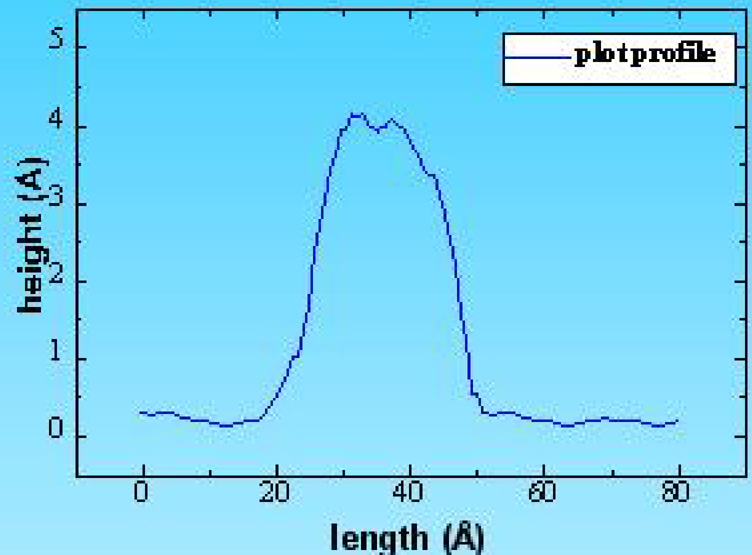
Theory vs. Experiment 1



calculated cross - section

linescan across two lobes



Experimental
Line - scan

Elastic Scattering Quantum Chemistry (ESQC) + Molecular Mechanics (MM2)

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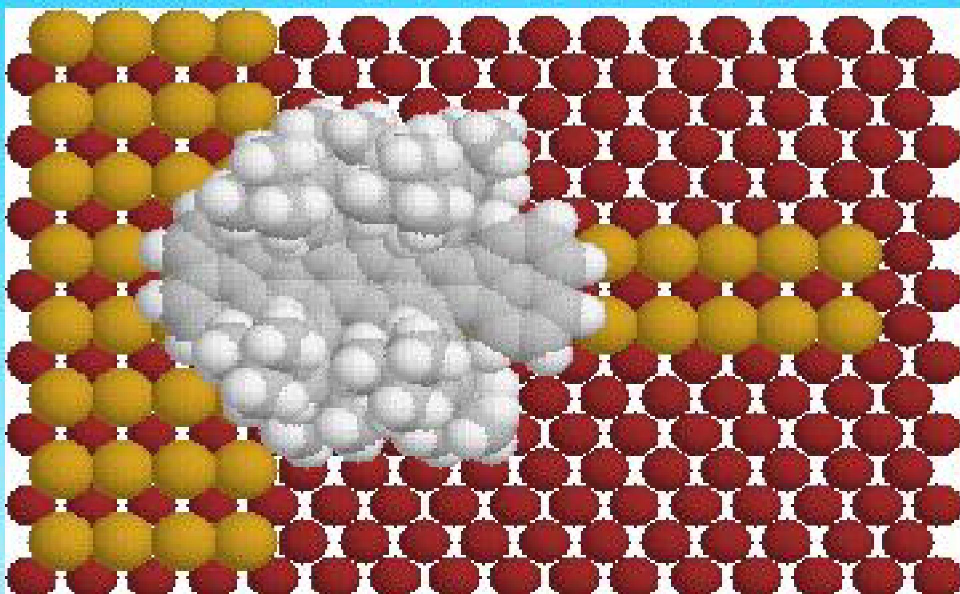
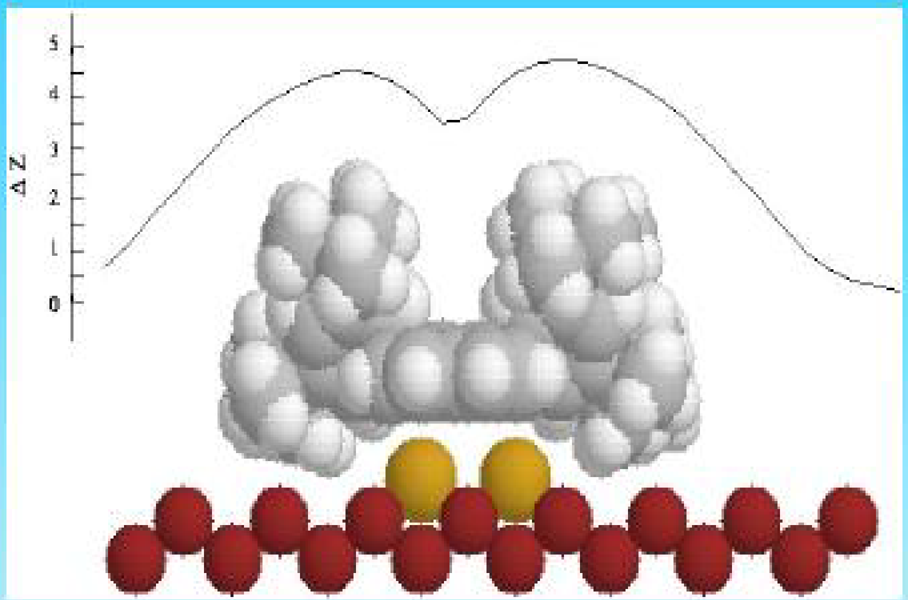
Theory vs. Experiment 2


conformation



calculated cross - section

The conformation of the Lander on the nano – contact has been successfully extracted

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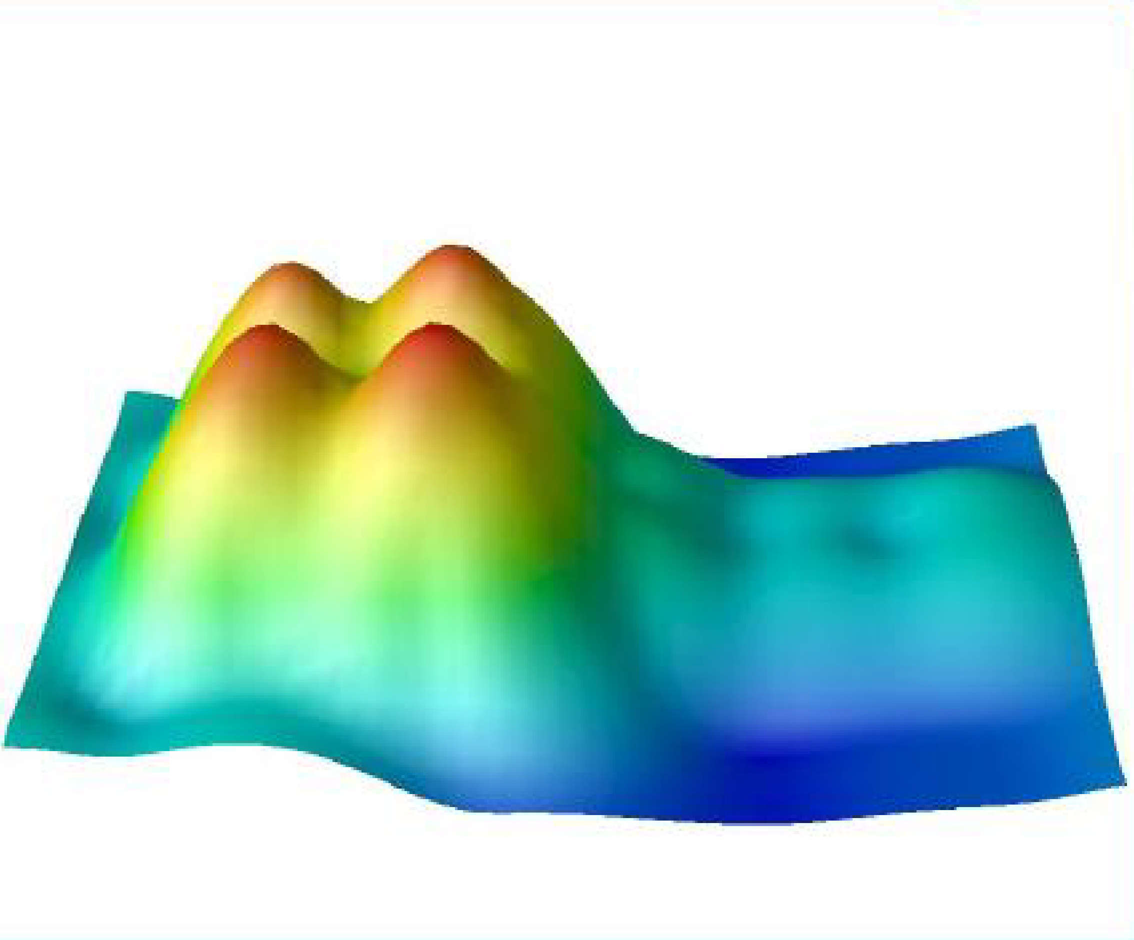
Theoretical Simulations

Simulated STM image



Molecule on Nano contact

tunneling parameters are the same as in experiments

Collaboration with P. Jiang and C. Joachim
(CNRS Toulouse)

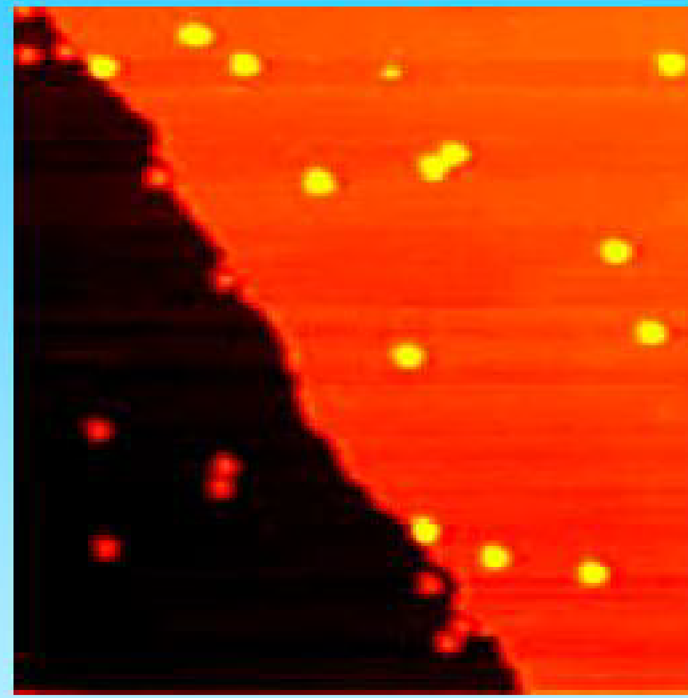
Thermally activated process

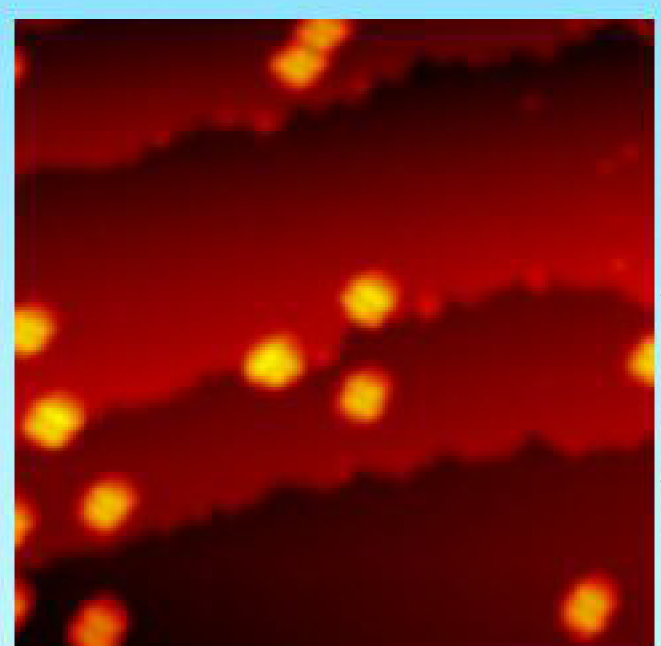
- Cu(110) **step edge fluctuates very rapidly even well below RT**

500x500 Å^2

T = 235 K

15 seconds per image





Upon deposition at low temperatures (about 150 K), no restructuring is found:

the process is thermally activated

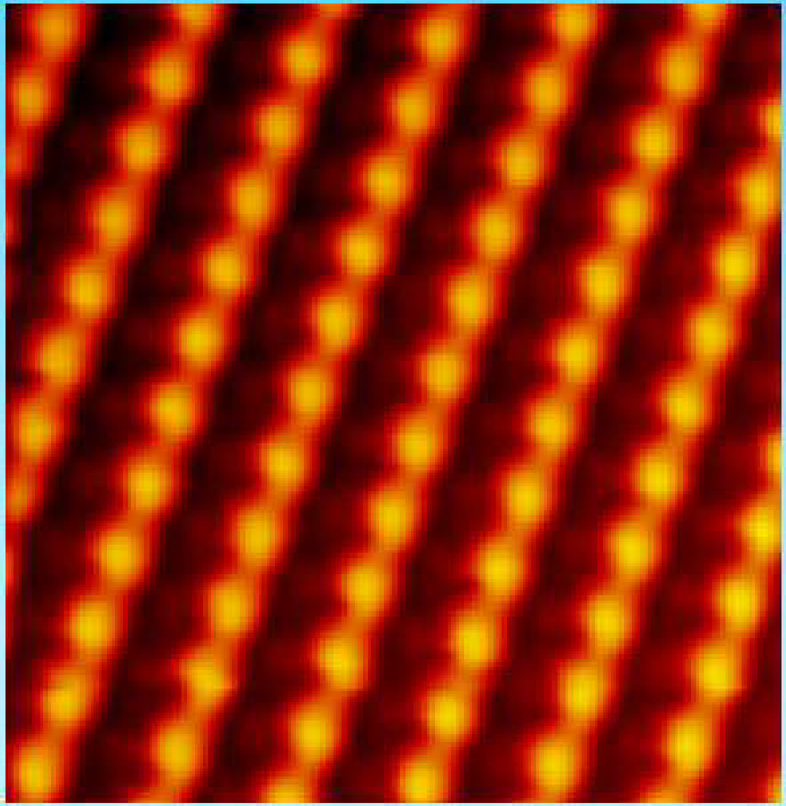
F. Rosei et al., in preparation

Conclusions – Part 2

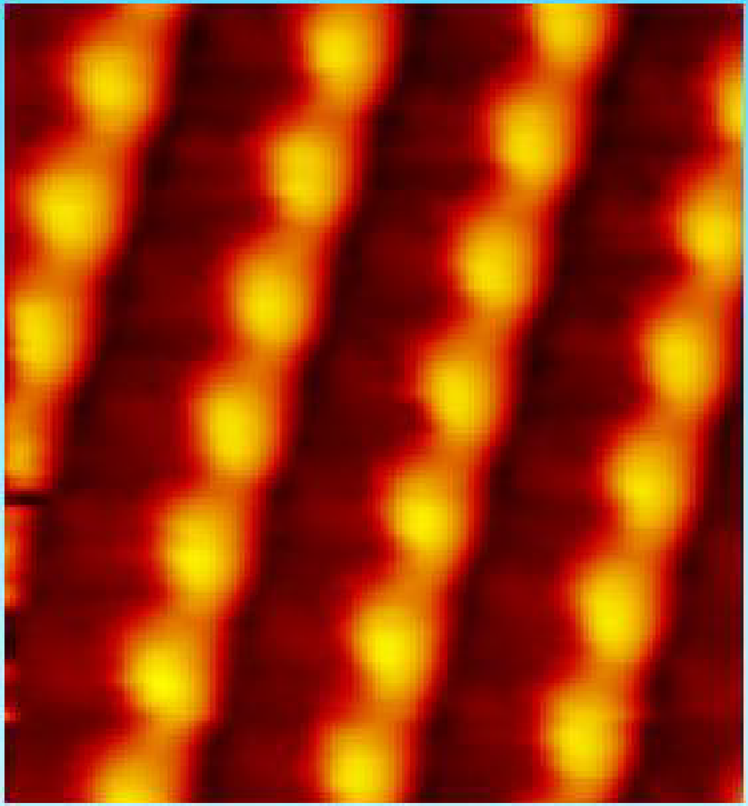
- The Lander Molecule is able to create its own nano-contact on Cu(110)
- The nano-contacts are formed by a thermally activated process
- The width of the nano - contacts is two Cu atomic rows
- Theoretical simulations (CNRS Toulouse) have been performed to extract the exact conformation of the molecule on the surface, and on the structure

Latest Results

O_2 chemisorption on Cu(110): partial 2x1 reconstruction (”patches”)



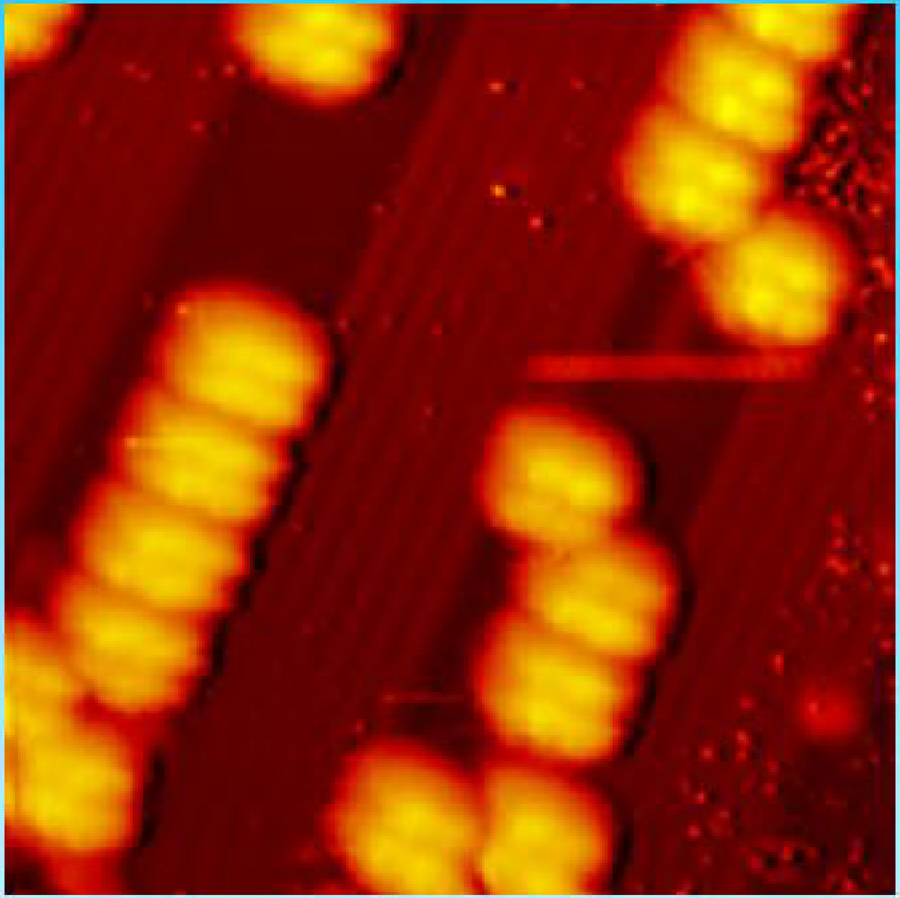
35x35 Å^2



20x20 Å^2

Nanopatterning Cu(110)

100x100 Å^2

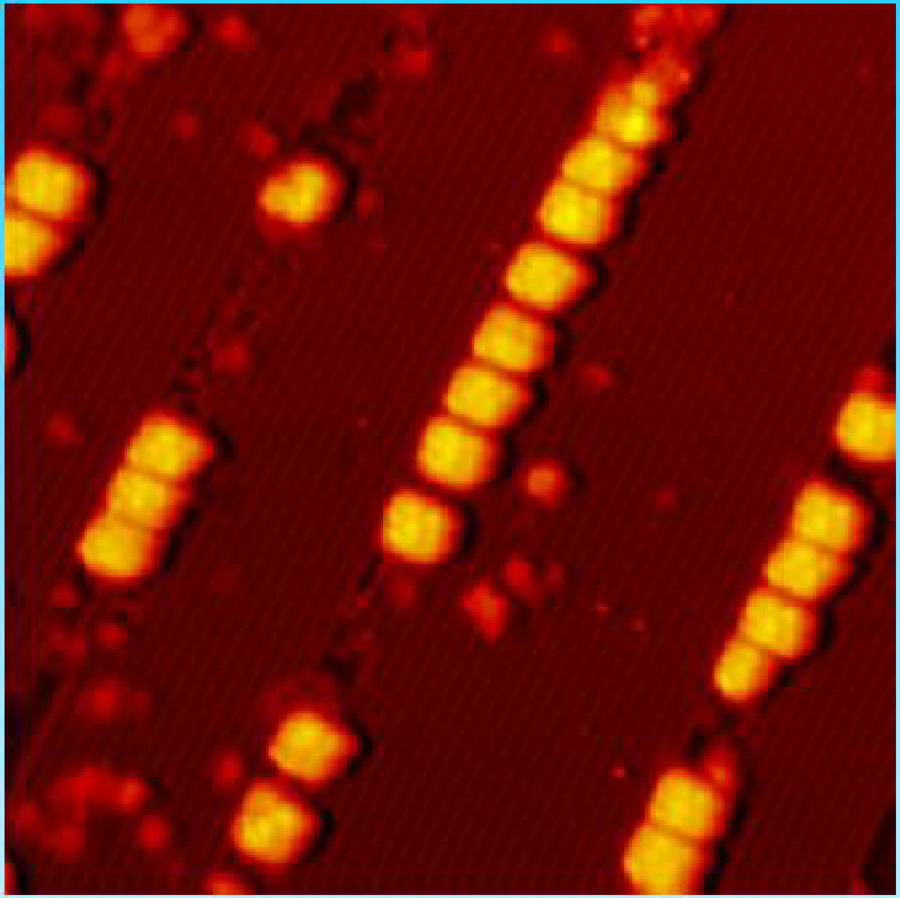


Lander molecules adsorb on bare Cu areas

It is possible to resolve the 2x1 structure along with the molecules

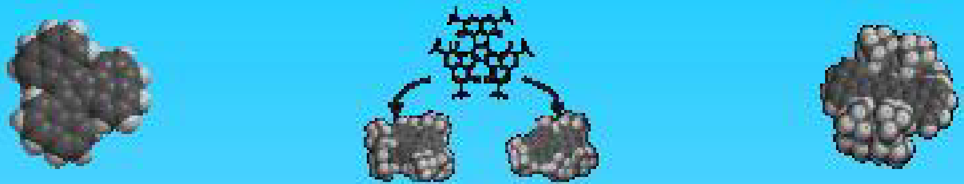
Nanopatterning 2

300x300 Å^2



the Lander adsorbs at the edge of the Cu / Cu-O interface, and it forms long rows of"molecular wires"

Acknowledgements



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