Numerical tools for local probe based methods: from imaging to single molecule manipulation

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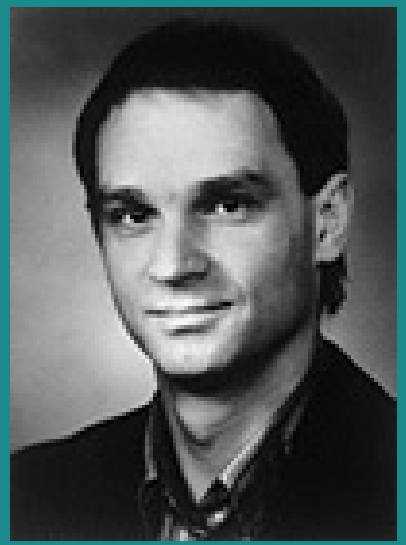
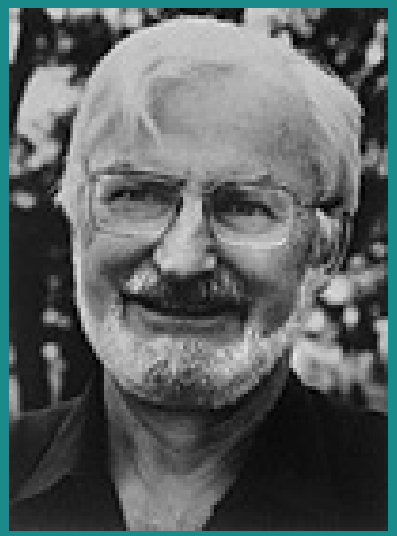
The beginning of the STM story...



Gerd Binnig



Heinrich Röhrer

IBM Zürich

Nobel Price 1986

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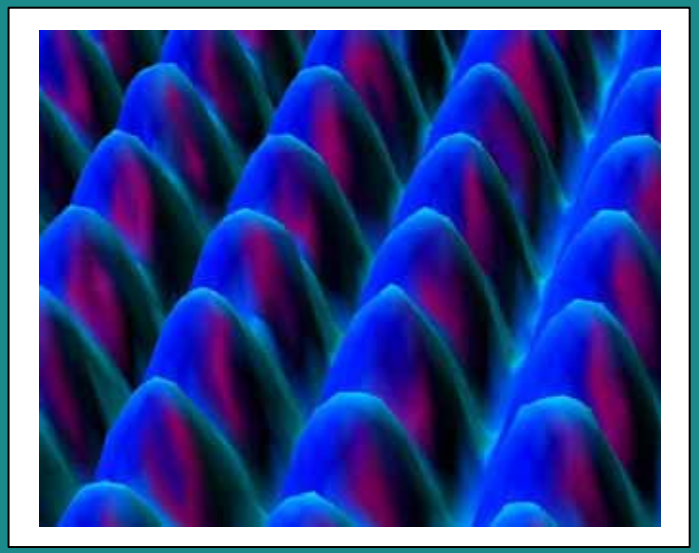
Some examples of STM images...

Metallic surfaces

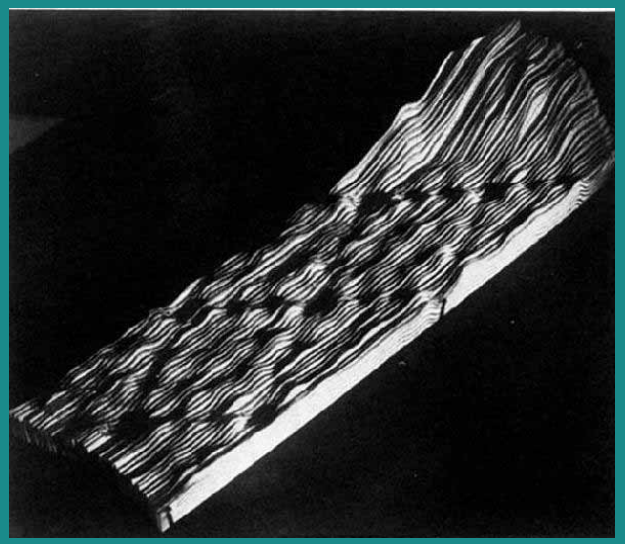


Ni(110)

Eigler, IBM Almaden

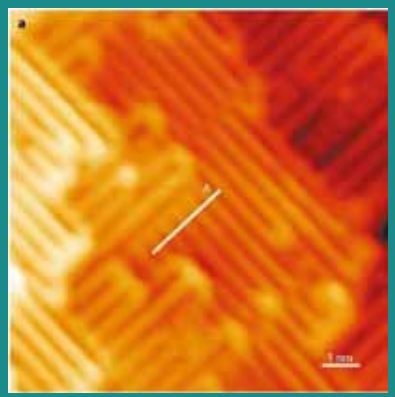
Semiconducting surfaces

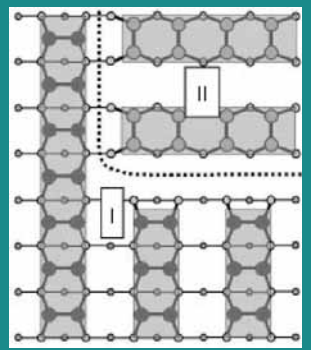
Si(111)-7x7

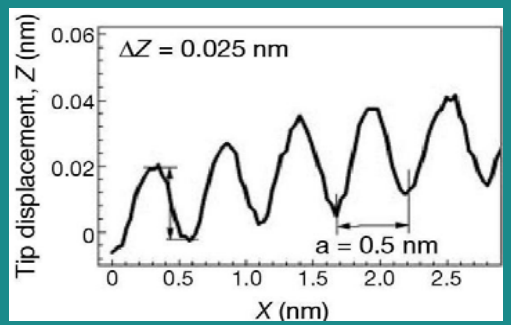


Binnig, Rohrer, *PRL* **50** 120 (1983)

Insulating surface: diamond







Dujardin, *Nature* **413** 616 (2001)

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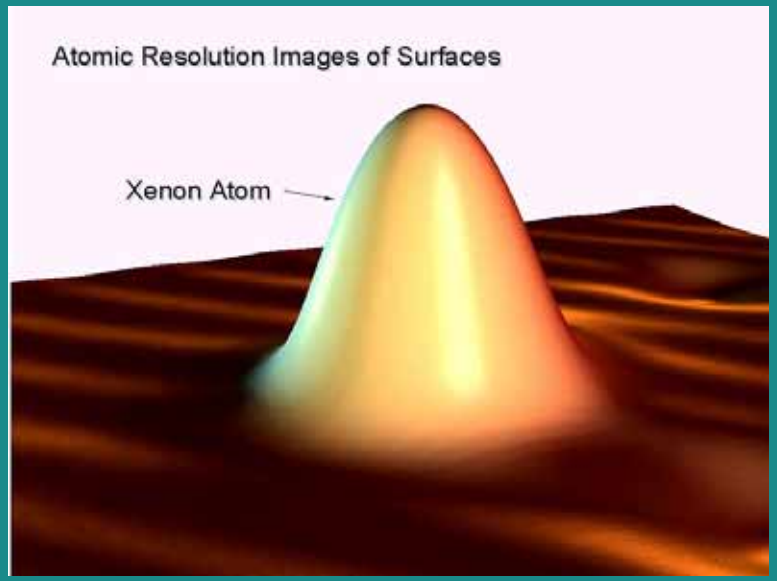
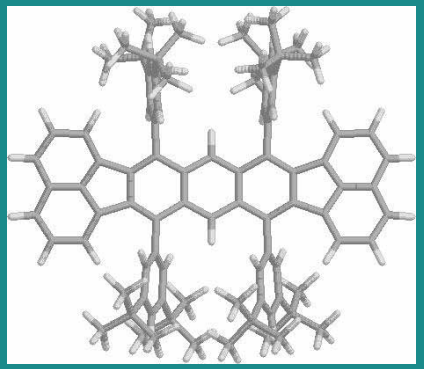
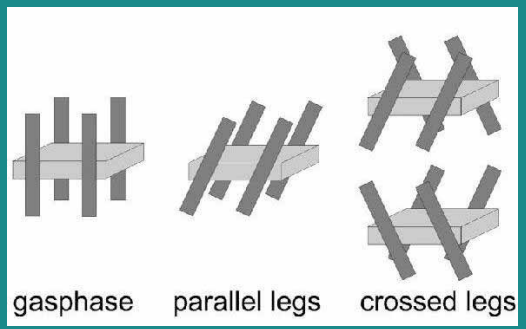
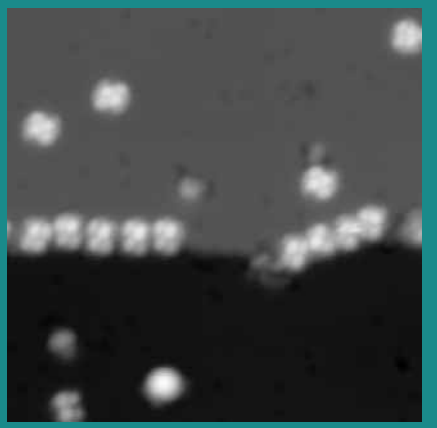
Some examples of STM images...



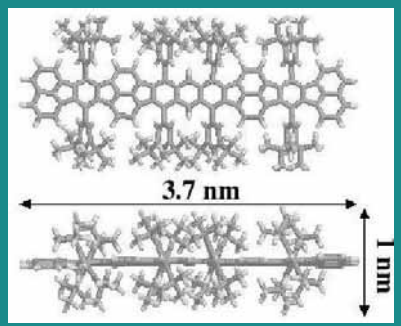
Eigler, IBM Almaden

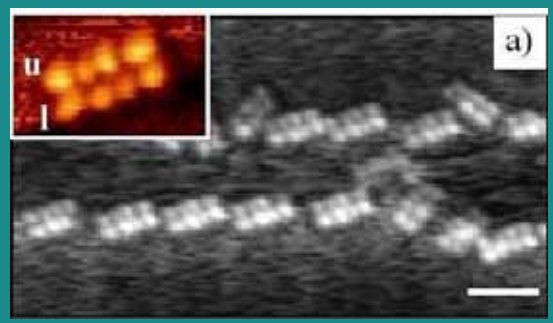






Berndt, Gourdon, Joachim
PRB **65** 233405 (2002)





Zambelli, Gauthier, Gourdon, Joachim, *PRB* **66** 075410 (2002)

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Need of simulations...

- Tersoff-Hamman's approximation
- Bardeen's approach (transfer Hamiltonian)
- Chen's approximation
- Scattering theory (Landauer-Bütticker approach)
- Keldysh-Green's function formalism (Nonequilibrium Green's function formalism)

Recent review

Jose Manuel Blanco, Fernando Flores and Rubén Pérez
Progress in Surface Science **81** 403 (2006)

Codes

TransSiesta, Fireball, Quantum Espresso, bSKAN, Tsukada's simulator, Cerda's code...

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ESQC-STM

Elastic Scattering Quantum Chemistry

Developed by C. Joachim and P. Sautet in 80'

Tunnelling of an electron: scattering event ~~gap: defect~~

Method models the tip-adsorbate-substrate system by a mono-electronic Hamiltonian (computed using Extended Hückel method)

Matrix representation: within the tight-binding approximation

Complete chemical description of the tip, adsorbate, surface

Full geometry of the tip, adsorbate, surface

Transmission coefficient *t(E)*

$$t = |\tau|^2 = \frac{1}{|F|^2} = \frac{1}{|\underline{\underline{T}}_{11}|^2}$$

Generalised Landauer formula

$$\frac{I}{V} = \frac{e^2}{\pi\hbar} t(E_F).$$

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ESQC-STM

Elastic Scattering Quantum Chemistry

Developed by C. Joachim and P. Sautet in 80'

More than 40 papers already published

Surfaces: metal, semiconductor, insulating films

Adsorbates: atoms, small and large molecules

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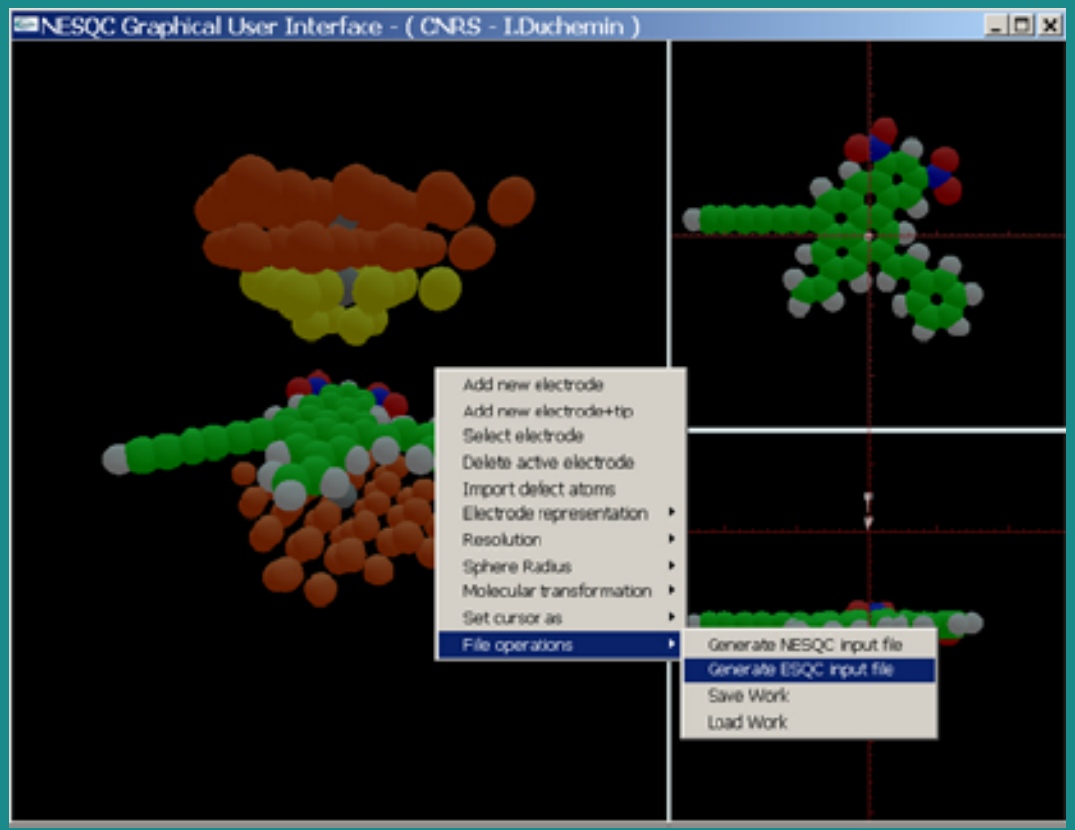
NESQC

N electrodes

ESQCGUI: OpenGl based application + Builder



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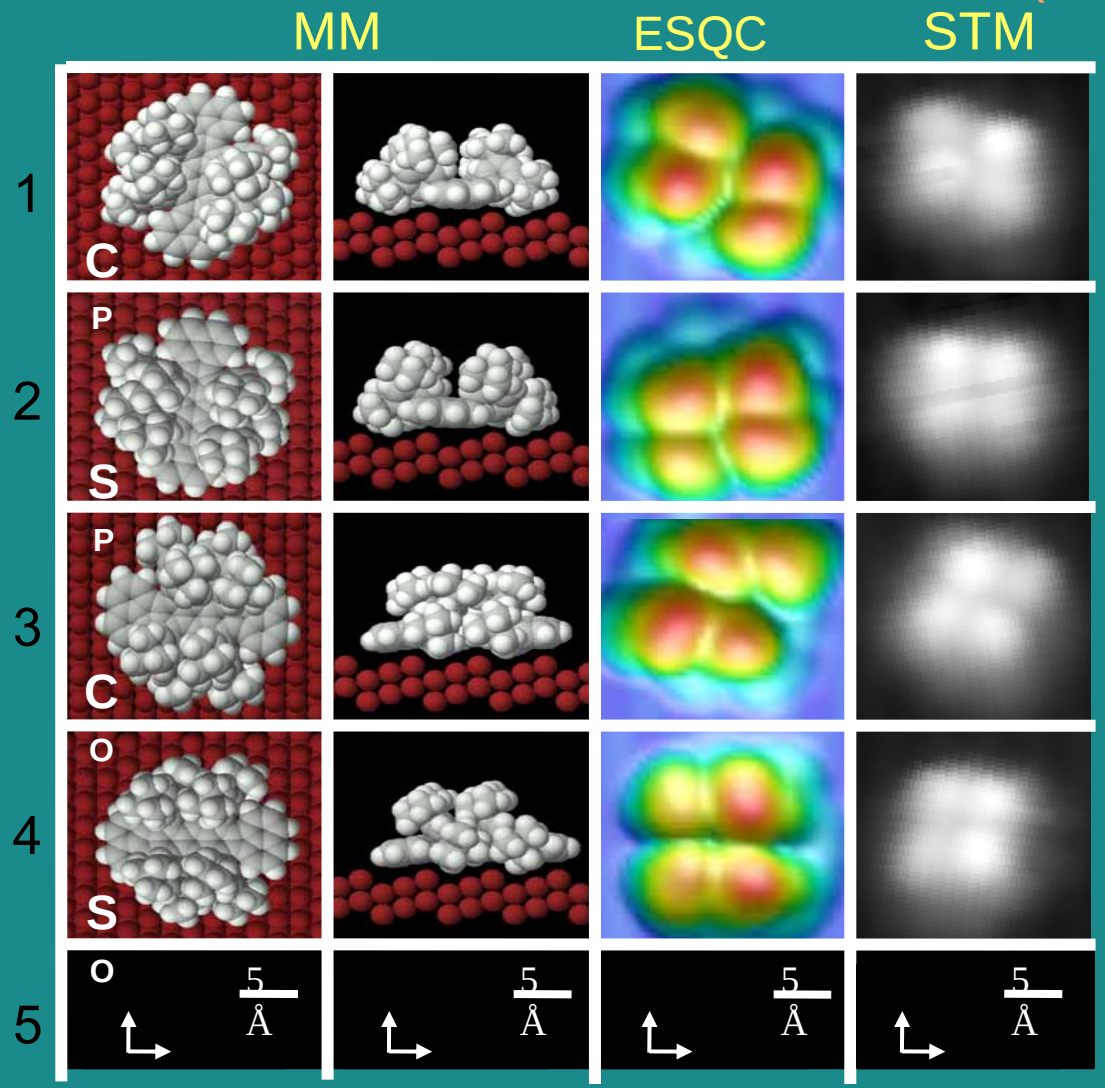
STM imaging

Lander molecule on Cu(211)



Chemical Physics Letters
428 (2006) 331–337

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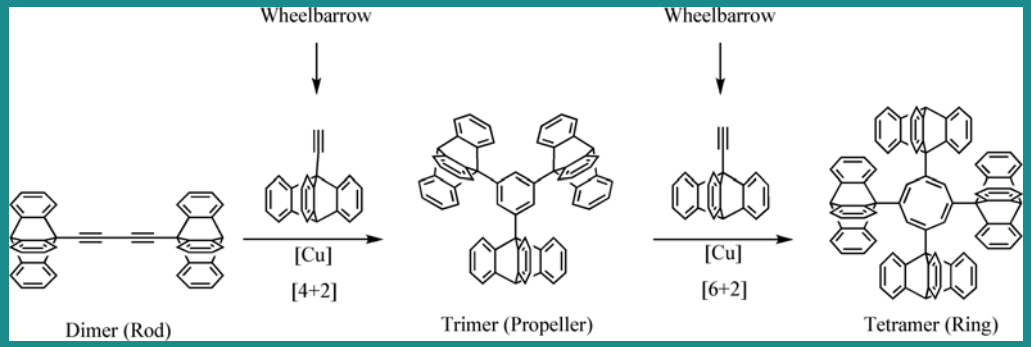
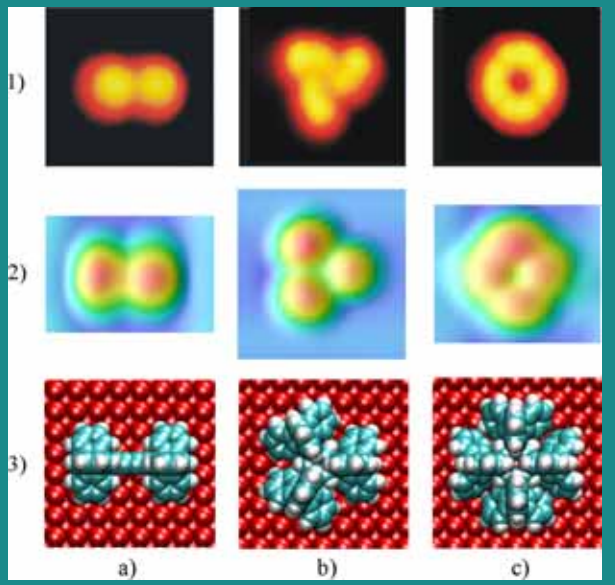
STM imaging

Molecular wheels *n*-mers on Cu(100)



Exp.

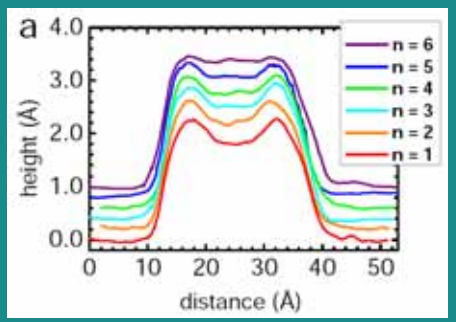
Calc.

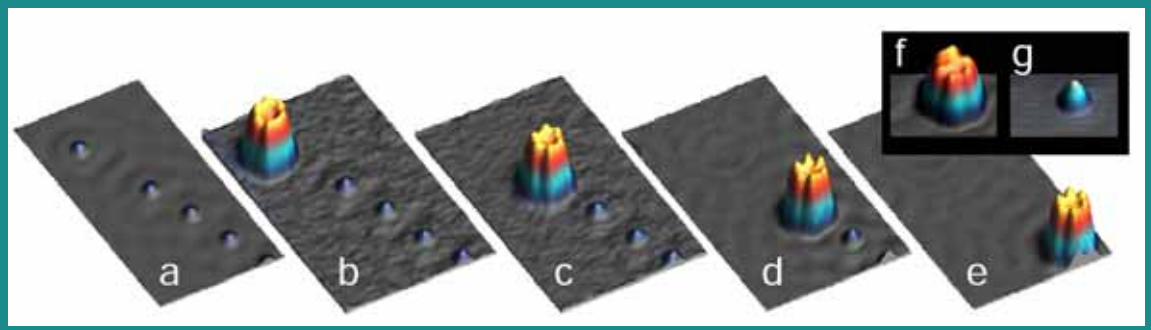


Chemical Physics Letters **431** (2006) 219–222

Hexa-*tert*-butyl-hexaphenylbenzene (HB-HPB, $C_{66}H_{78}$)

Calc.





Nature Materials **4**, 892 - 895 (2005)

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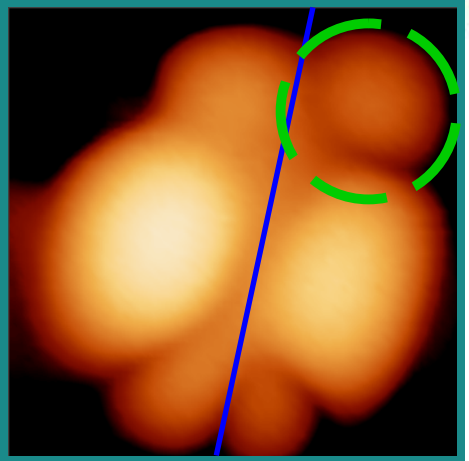
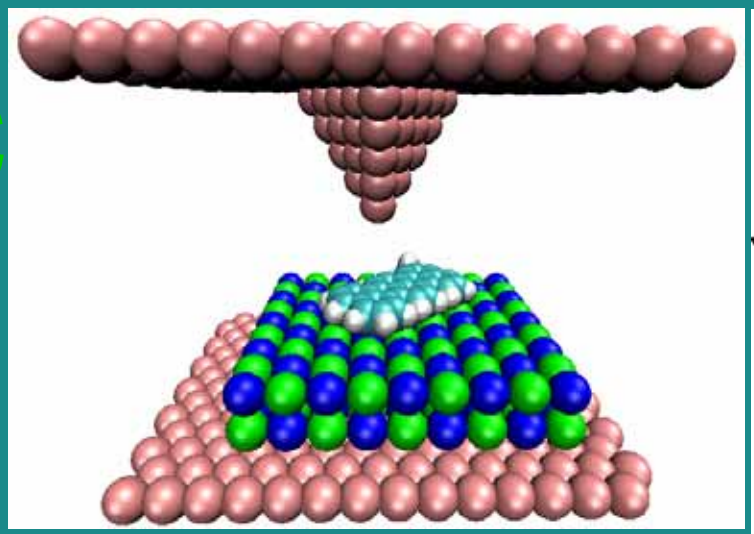
STM imaging

Methylterrylene on NaCl(100)/Cu(111)



2.3 nm

Experimental

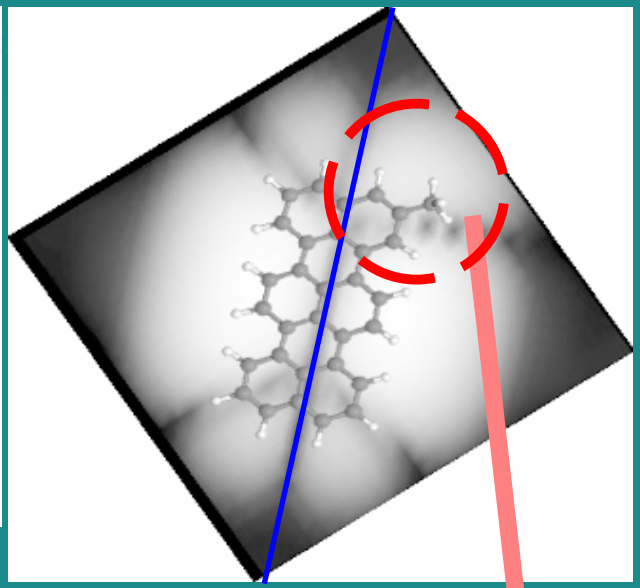


Model geometry of the

methylterrylene adsorbed on

2ML NaCl/Cu(111)

The NaCl – surface distance is 3.1 Å.



2.3 nm

Calculated

Methyl group

The methyl group of the adsorbed molecule is visualized in the STM image with a longer protuberance.

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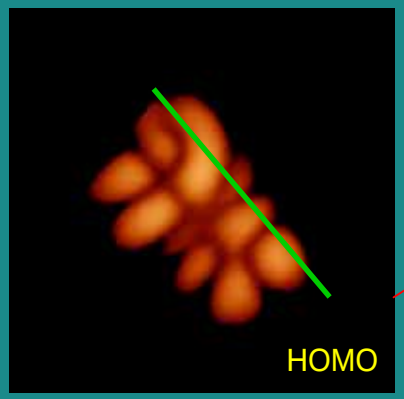
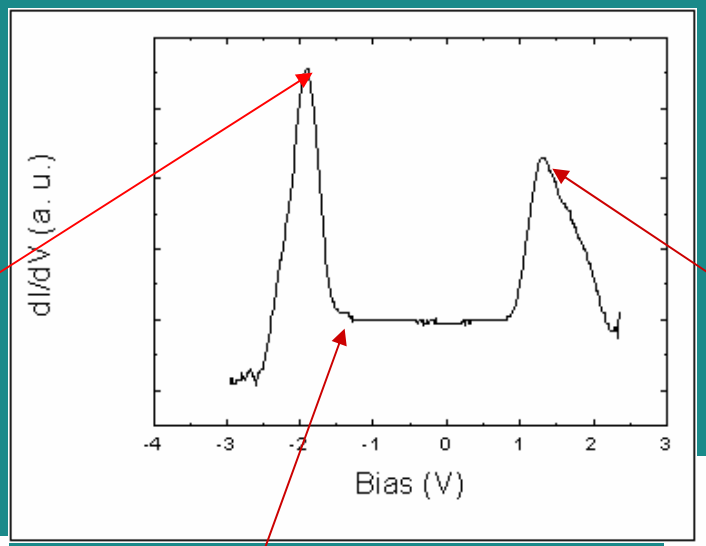
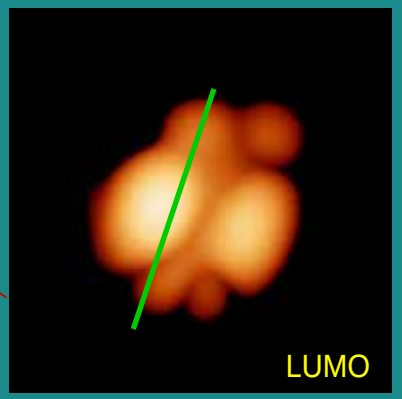
STM imaging

Methylterrylene on NaCl(100)/Cu(111)



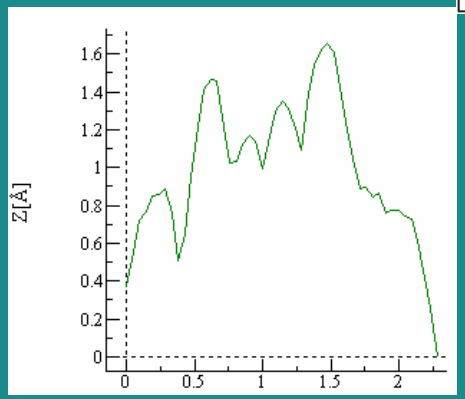
5nm x 6nm



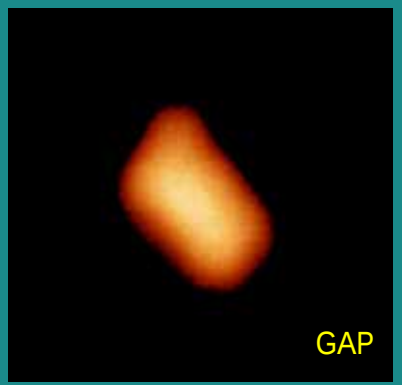


5nm x 6nm

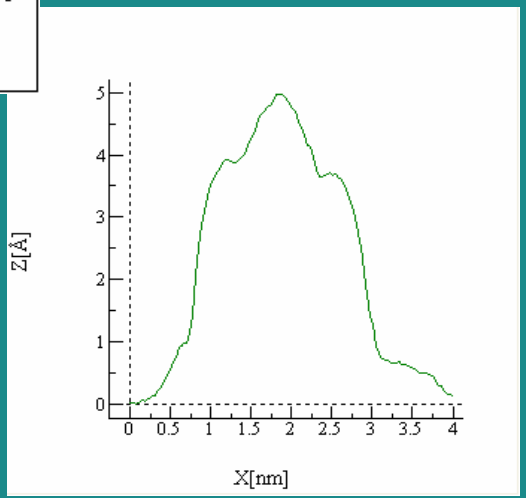
dI/dV Spectroscopy



Height 1.6 Å
Length 2.5 nm



5nm x 6nm



Height 5.5 Å
Length 2.6 nm

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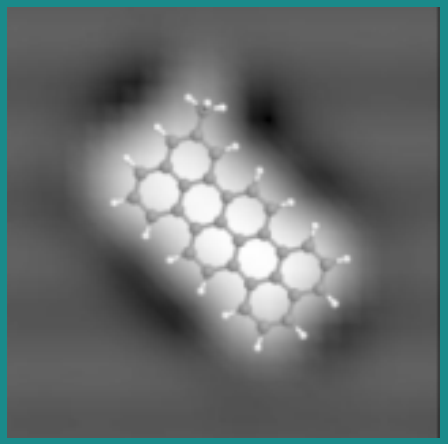
STM imaging

Methylterrylene on NaCl(100)/Cu(111)

2.3 nm

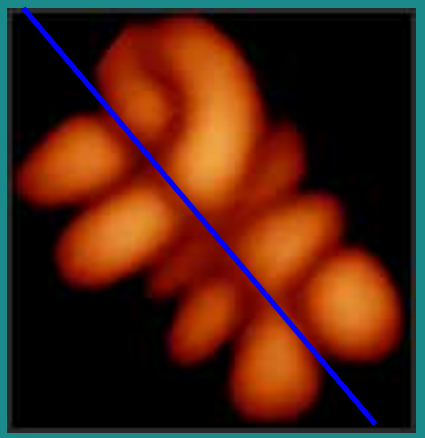
Experimental



GAP

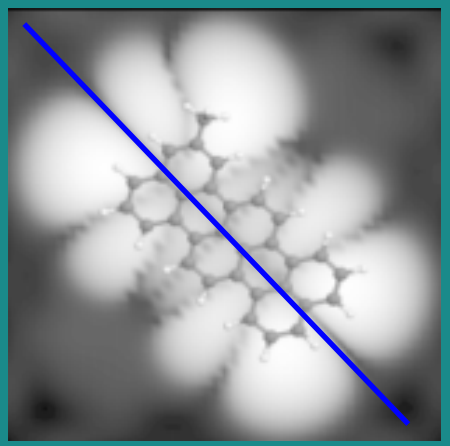
2.3 nm

Calculated



2.3 nm

Experimental



HOMO

2.3 nm

Calculated

The experimental nodes are reproduced by ESQC.
Presence of the methyl group breaks the symmetry of the image.
Hyperconjugaison of the methyl group.
For the gap, the image contrast ≅ geometrical dimension of the molecule.

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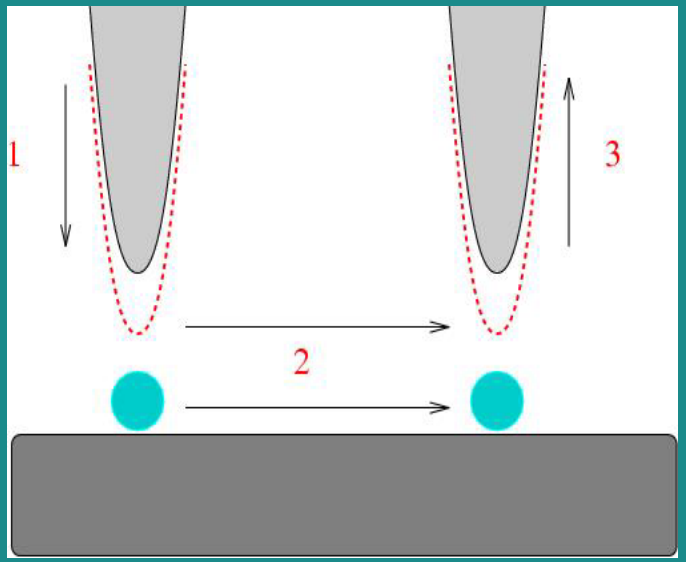
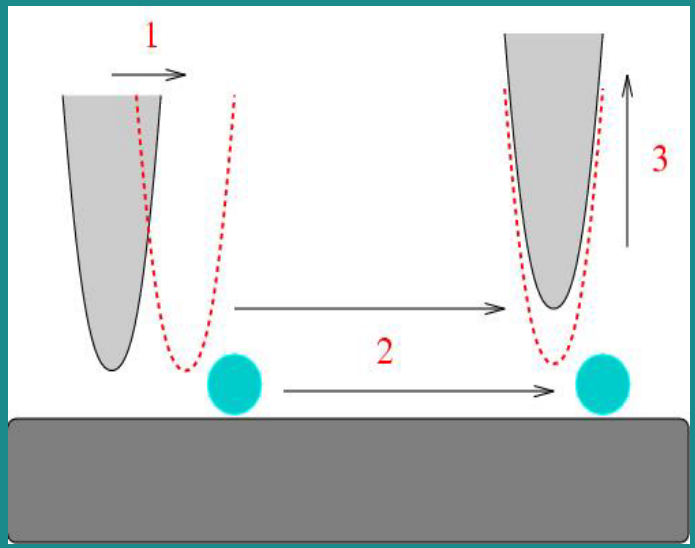
STM Manipulation

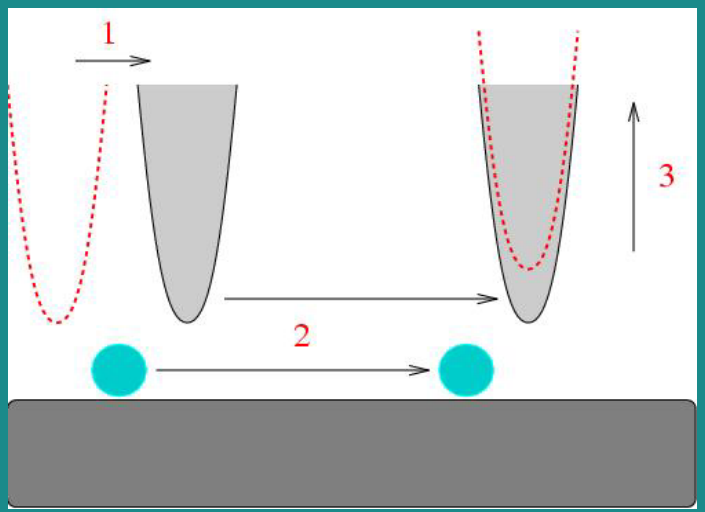
Controlled lateral manipulation



Sliding mode



Pushing mode



Pulling mode

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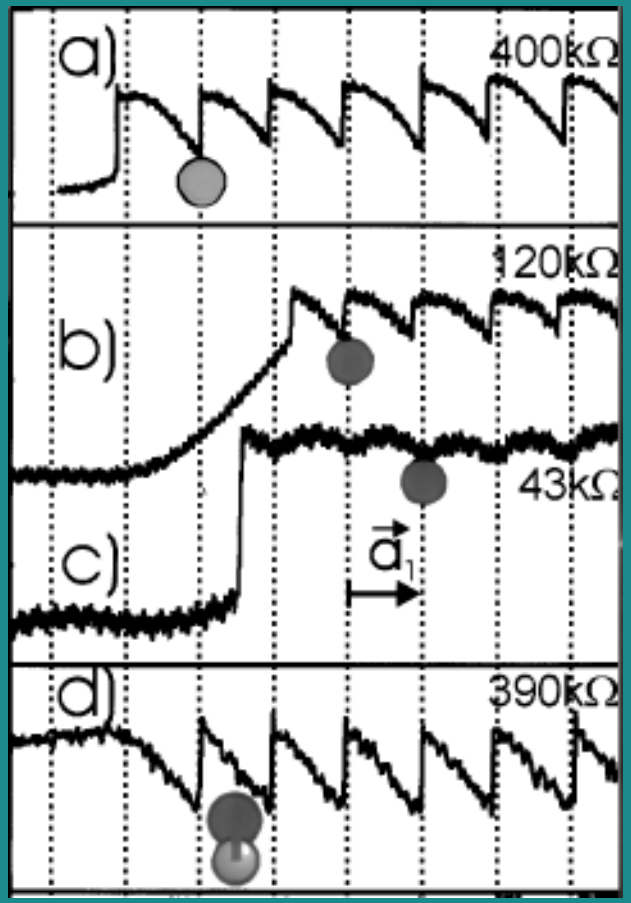
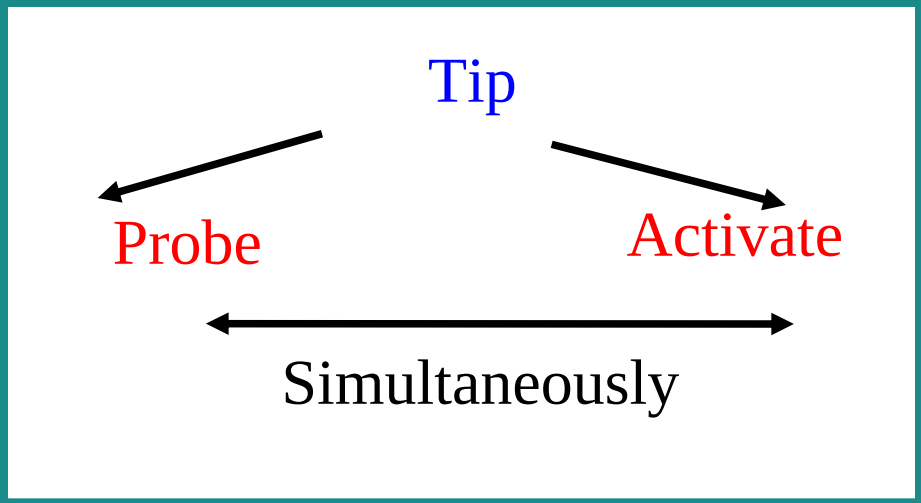
Lateral manipulation

How does the tip move the particle?



Study of the signal recorded during the manipulation process



Simulations to interpret the signatures

L. Bartels, G. Meyer, K.H. Rieder, Phys. Rev. Lett. 79, 697 (1997)

X. Bouju, C. Joachim, Ch. Girard, Phys. Rev. B 59, R7845 (1999)

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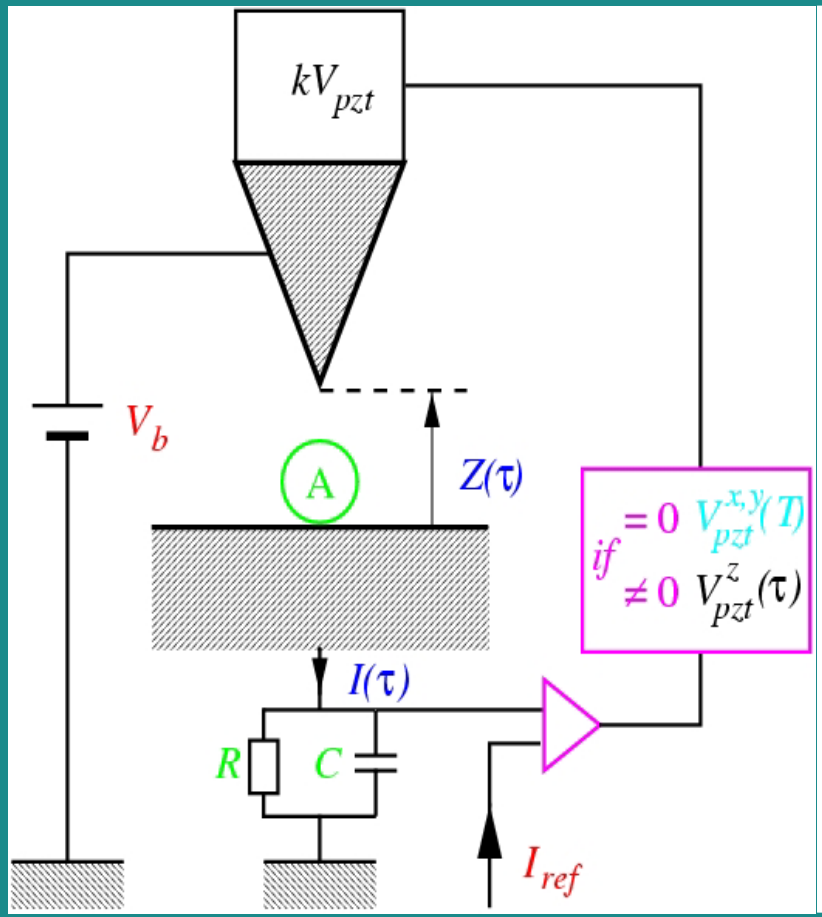
Virtual STM – Manipulation simulations at constant current

Tunnel jonction : Cu(110) / Xe / Cu [110]

Experimental setup

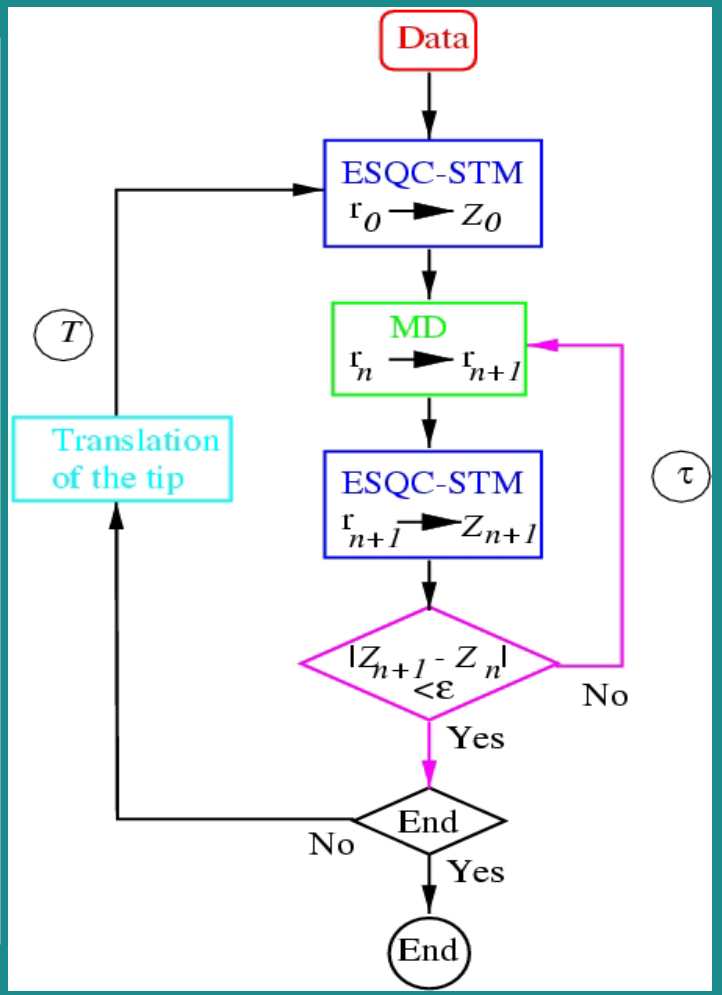


Electronic structure of the junction and tunnel current intensity

Molecular dynamics of adsorbates

STM feedback loop

Numerical STM



X. Bouju, C. Joachim, Ch. Girard, *Phys. Rev. B* **59**, R7845 (1999)
X. Bouju, C. Joachim, Ch. Girard, H. Tang, *Phys. Rev. B* **63**, 085415 (2001)

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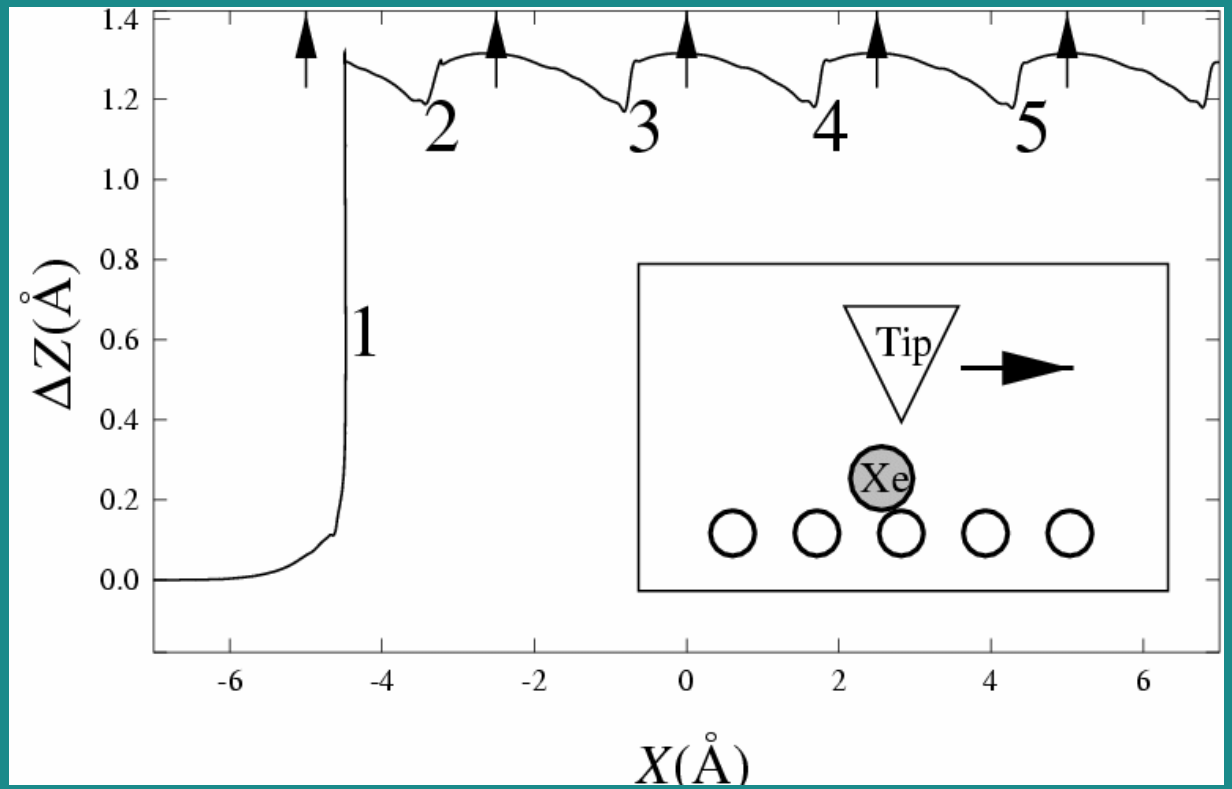
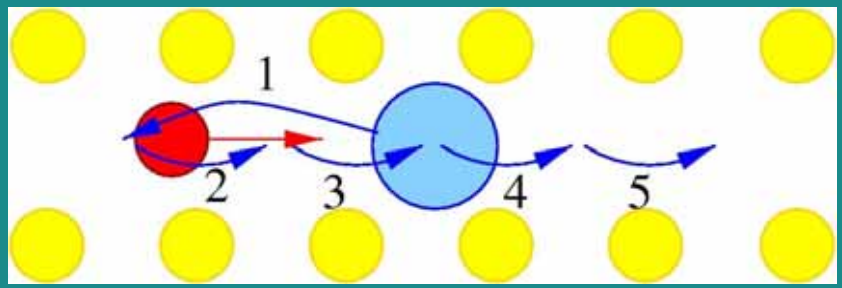
Induced displacements by lateral motion
Signatures of manipulation

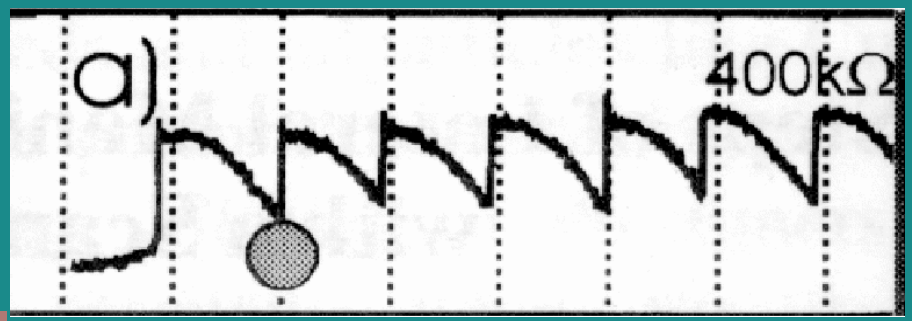


Atomic controlled manipulation

I = 1.9 nA

Pulling-sliding mode





Cu/Cu(211)
Bartels, Meyer, Rieder
Phys. Rev. Lett. **79**, 697 (1997)

X. Bouju, C. Joachim, Ch. Girard, *Phys. Rev. B* **59**, R7845 (1999)

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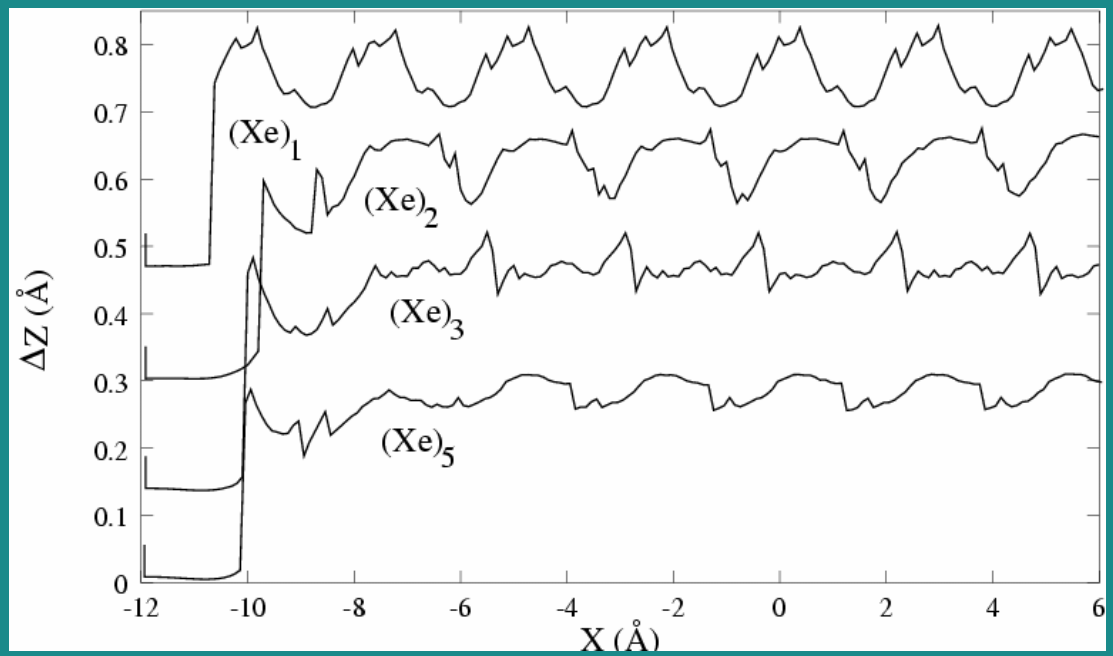
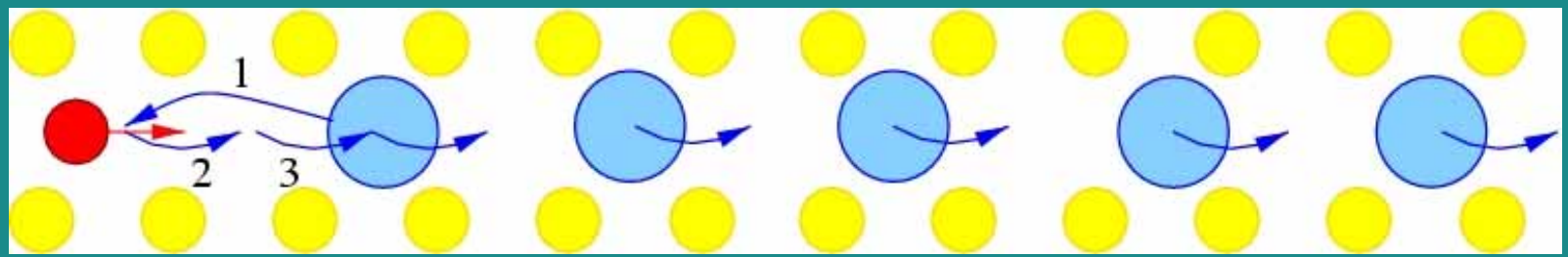
Induced displacements by lateral motion
Signatures of manipulation

Controlled manipulation of an atomic chain

I = 10.0 nA ***pushing mode***



- Linear $(Xe)_n$ chain.
- Stress and release cycle.
- Signatures ≅ nearest adsorbate of the tip.
- Signatures amplitude □ numerous degrees of freedom when *n* □.



X. Bouju, C. Joachim, Ch. Girard, H. Tang, *Phys. Rev. B* **63**, 085415 (2001)

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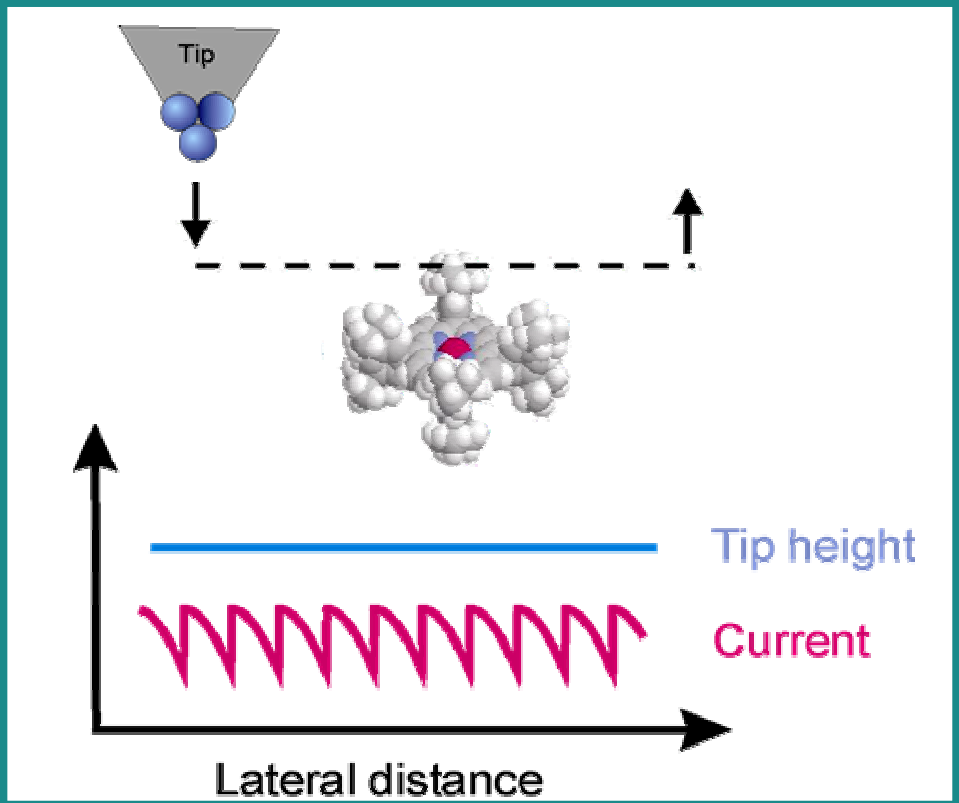
Lateral manipulation at constant height mode

Manipulation of complex molecules

Lateral motion of the molecule

Study of the intramolecular mechanics during the movement

Tunneling current:
information about the intramolecular conformational changes.

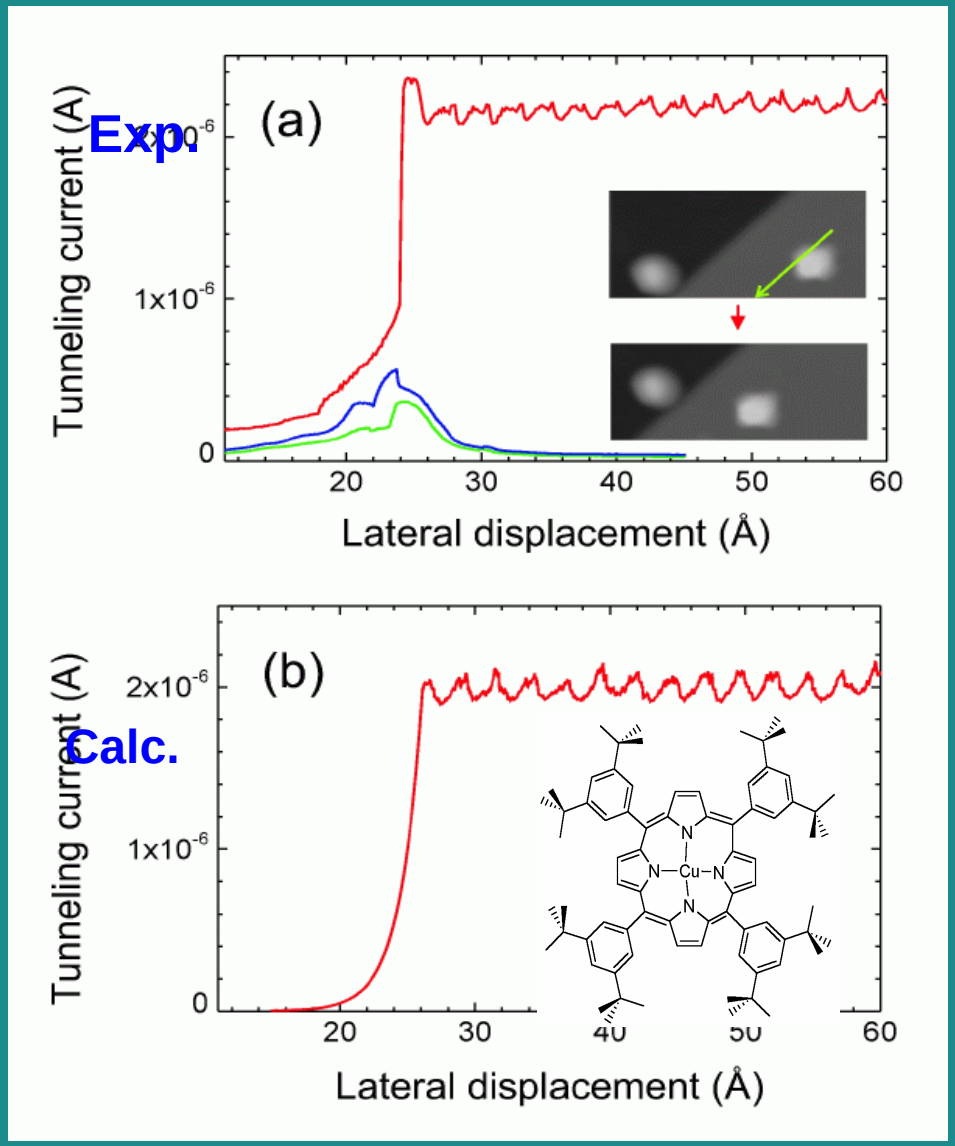


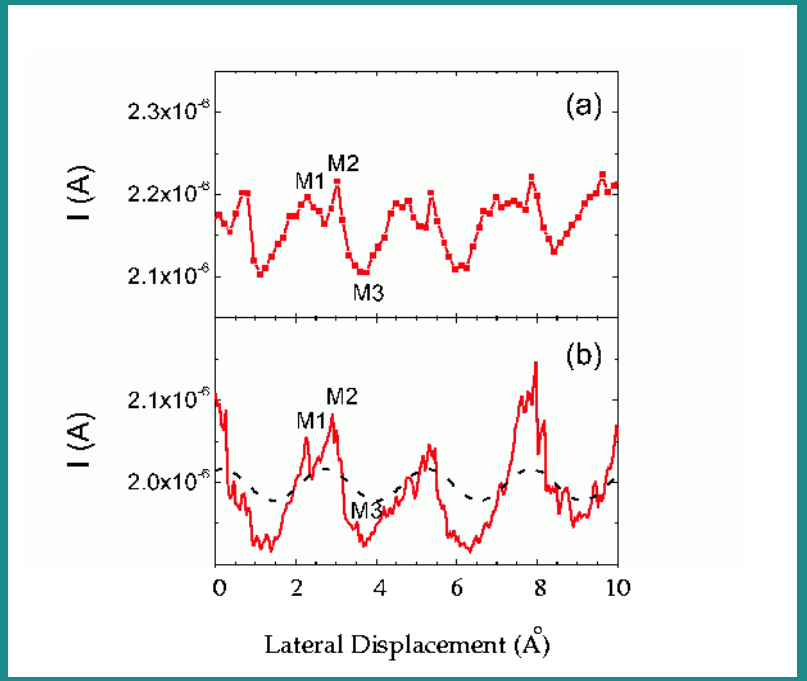
Pico-Inside

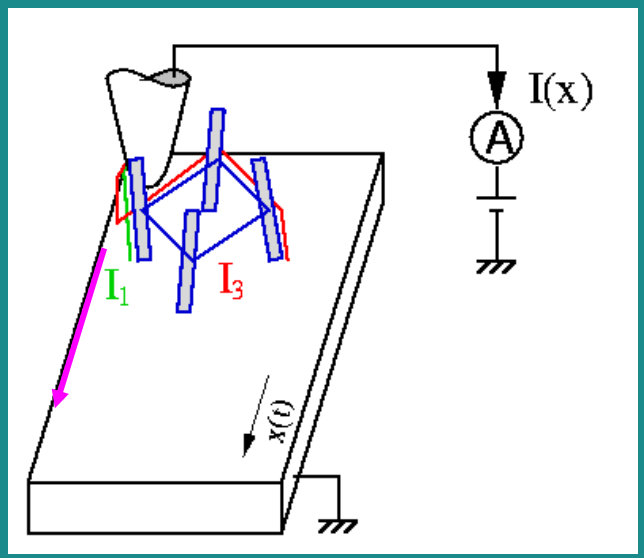
F. Moresco, G. Meyer, K.H. Rieder, H. Tang, A. Gourdon, C. Joachim, *Appl. Phys. Lett.* **78**, 306 (2001)

CEMES

Manipulation signal at constant height







F. Moresco *PRL* **87** 088302 (2001)

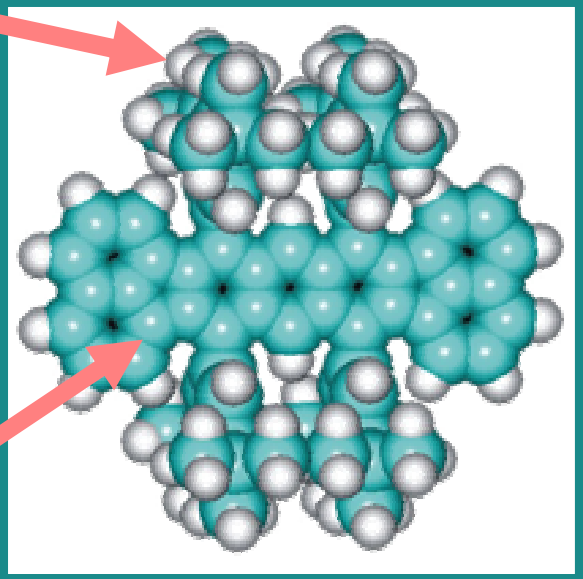
Lander molecule $C_{90}H_{98}$

The Mars lander
« Sojourner » (NASA)

In the gas phase the legs are oriented perpendicular to the board

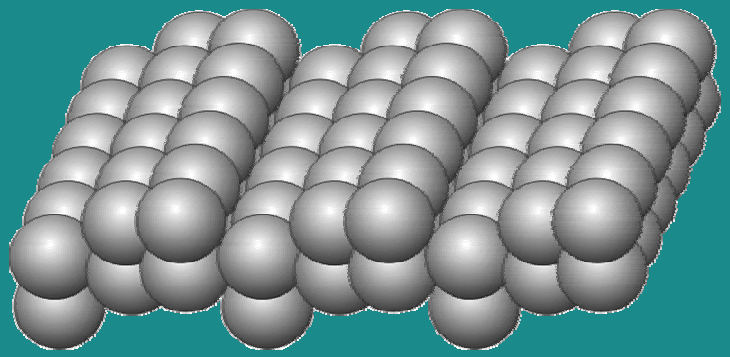
spacer legs
3.5-di-*tert*-butyl-phenyl-groups

polyaromatic board



+

Cu (211)



(111) facets **+** (100) steps

A. Gourdon *Eur. J. Org. Chem.*, 391 (1999)

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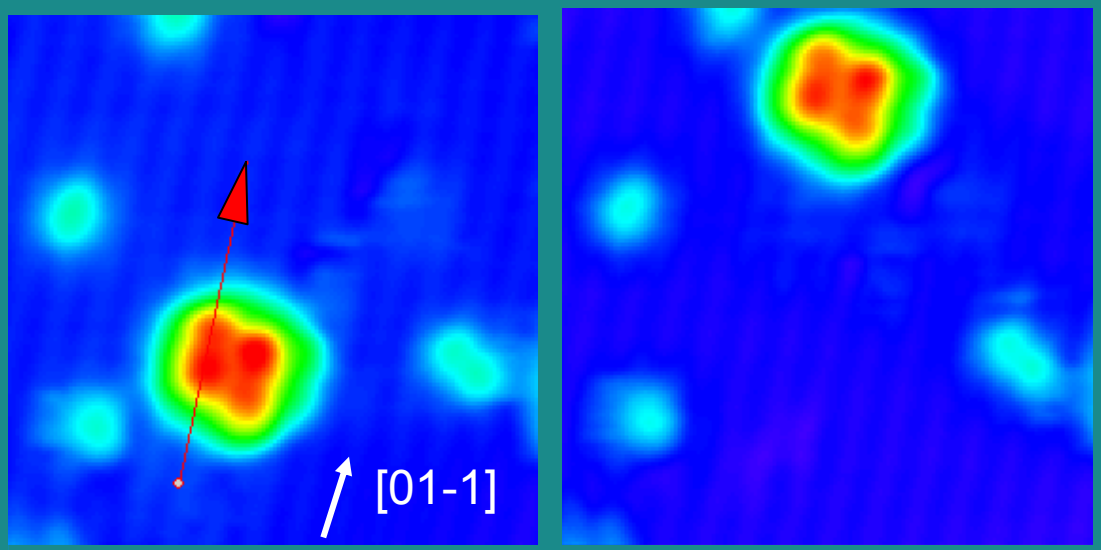
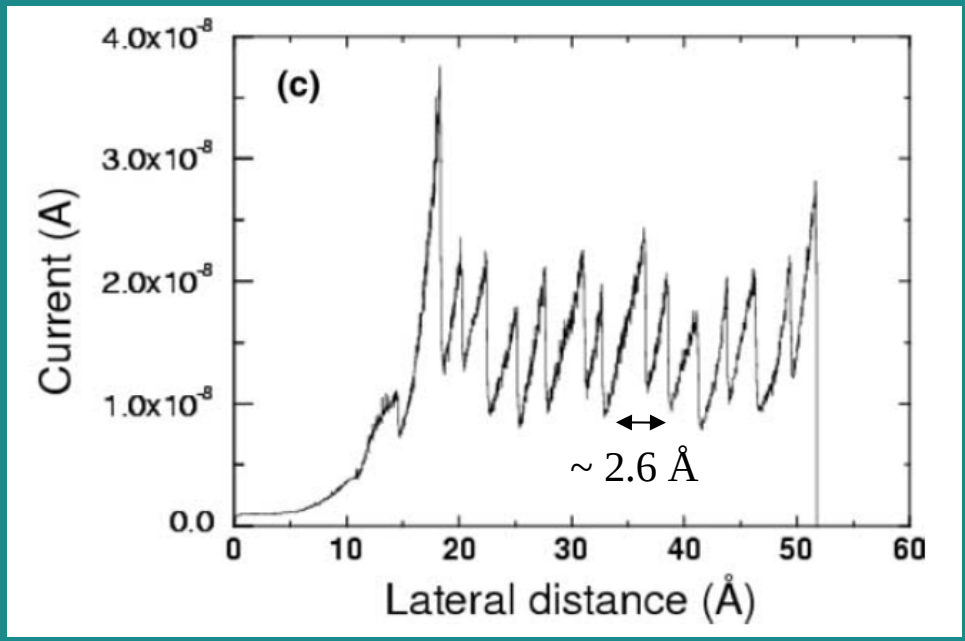
Manipulation parallel to the steps

Pushing on one leg





z = 5.6 Å V = 30 mV

Regular signal with the substrate periodicity (2.55 Å) in pushing mode.
The curves are reproducible.
An initial weaker peak is always observed.

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The STM junction: tip / molecule / surface

Lander on Cu(211)

Interaction

ab initio methods

semi-empirical methods

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CEMES

The STM junction: tip / molecule / surface

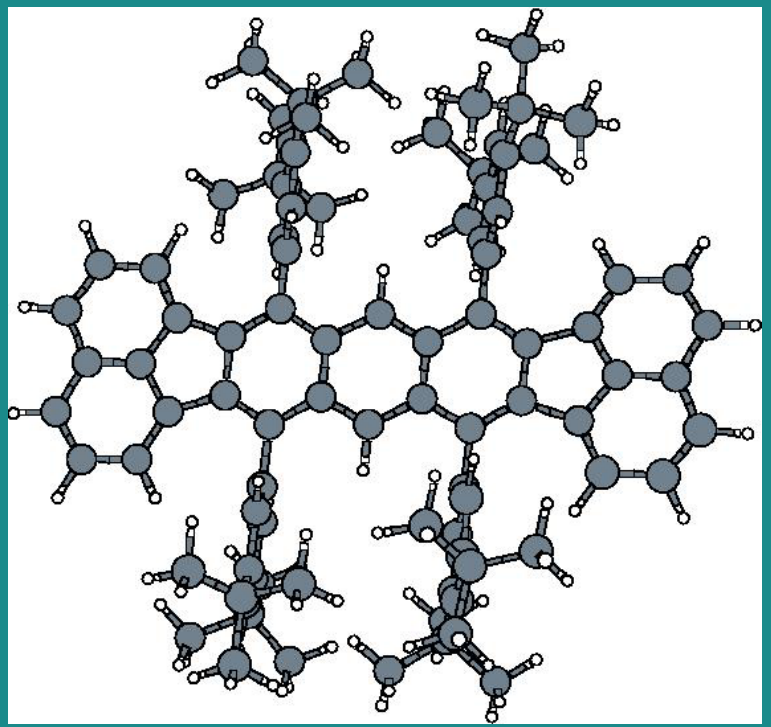
Lander on Cu(211)

Interaction

ab initio methods

- Lander : $C_{90}H_{98}$

188 atoms



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The STM junction: tip / molecule / surface

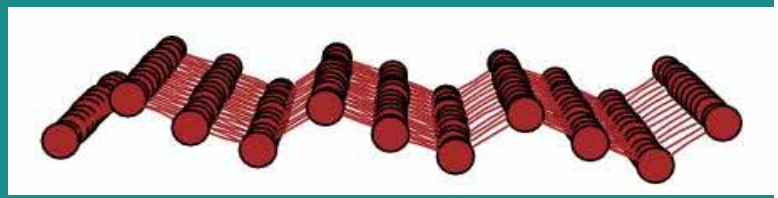
Lander on Cu(211)

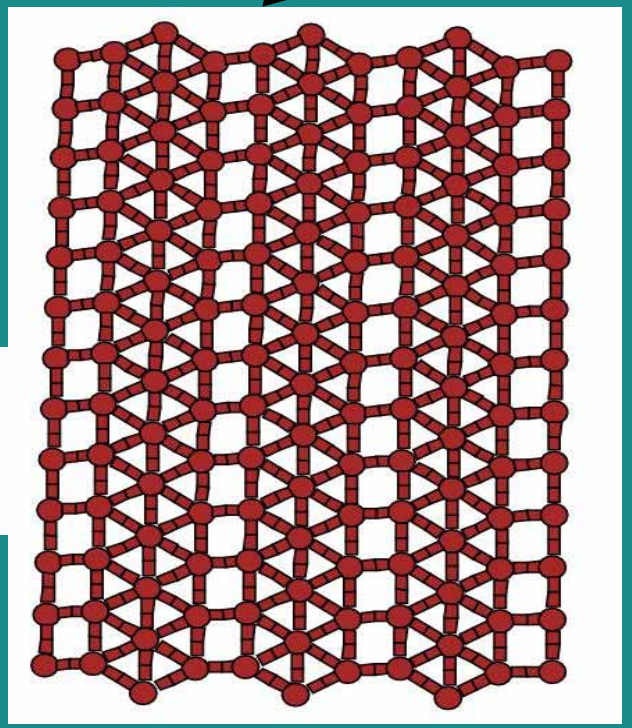
Interaction

ab initio methods

- Lander: 188 atoms
- Surface: (211)

146 atoms





The STM junction: tip / molecule / surface

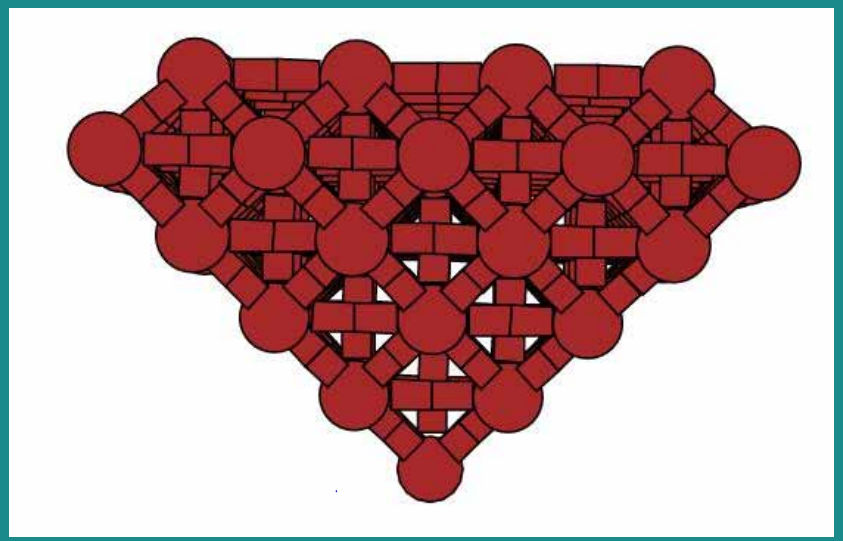
Lander on Cu(211)

Interaction

ab initio methods

- Lander: 188 atoms
- Surface: 146 atoms
- Tip: [110]

73 atoms



Pico-Inside

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The STM junction: tip / molecule / surface

Lander on Cu(211)

Interaction

ab initio methods

- Lander: 188 atoms
- Surface: 146 atoms
- Tip: 73 atoms

407 atoms

large # of degrees of freedom

Computing time versus needed precision?

The STM junction: tip / molecule / surface

Lander on Cu(211)

Interaction → semi-empirical methods

- Accurate for hydrocarbon molecules
- Molecule is physisorbed, weakly chemisorbed
- Fast and easy to handle

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Manipulation at constant height

Lander on Cu(211)

Mechanics: MM2 force field

STM: ESQC

Signature of manipulation

To extract useful information

To understand signatures of manipulation

Lateral step: each 0.05 Å

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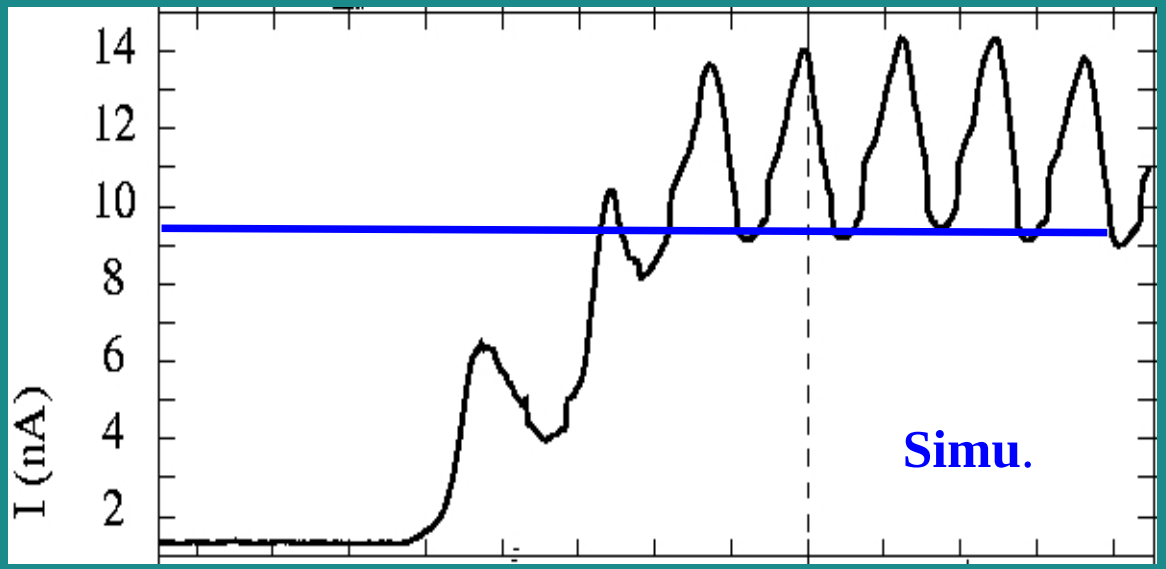
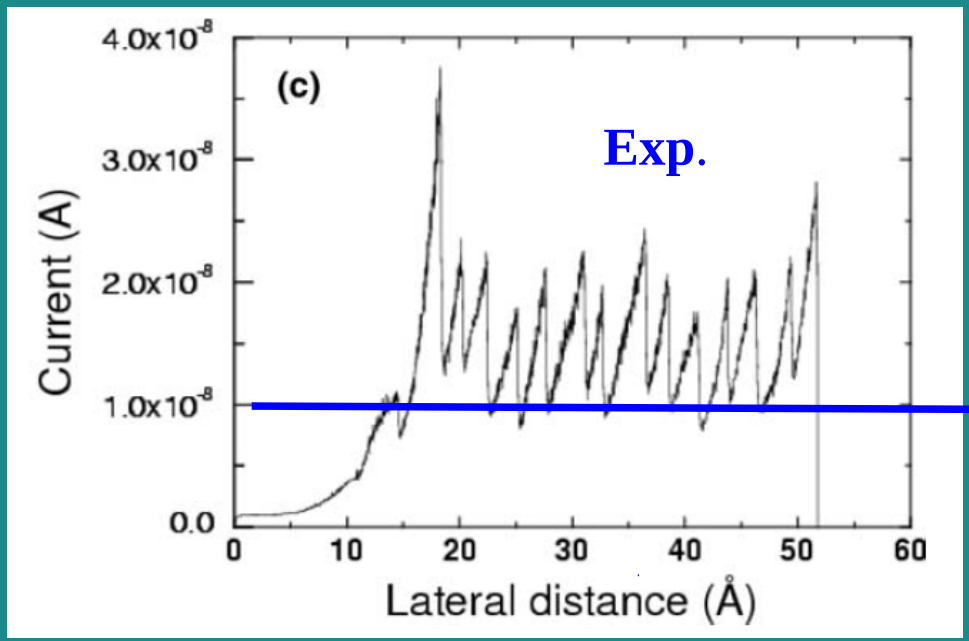
Signature of manipulation // to the rows



* same global charateristics of a pushing mechanism
* periodicity in the permanent regime
* shoulder in front of the signal
* initial peak recovered in the transitory regime



10 nA

M. Alemani *et al*. Chem. Phys. Lett. **402**, 180 (2005)

Pico-Inside

CEMES

The tip / molecule / surface junction

Interpretation of the full signal

↓

Decomposition to identify the tunnel channels and the part of the molecule contributing to it

↓

Keep the MM and deformation of the Lander

Pico-Inside

CEMES

The tip / molecule / surface junction

Interpretation of the full signal

↓

Decomposition to identify the tunnel channels and the part of the molecule contributing to it

↓

Keep the MM and deformation of the Lander

Modify the weight of the molecular orbitals, either on the legs or on the board

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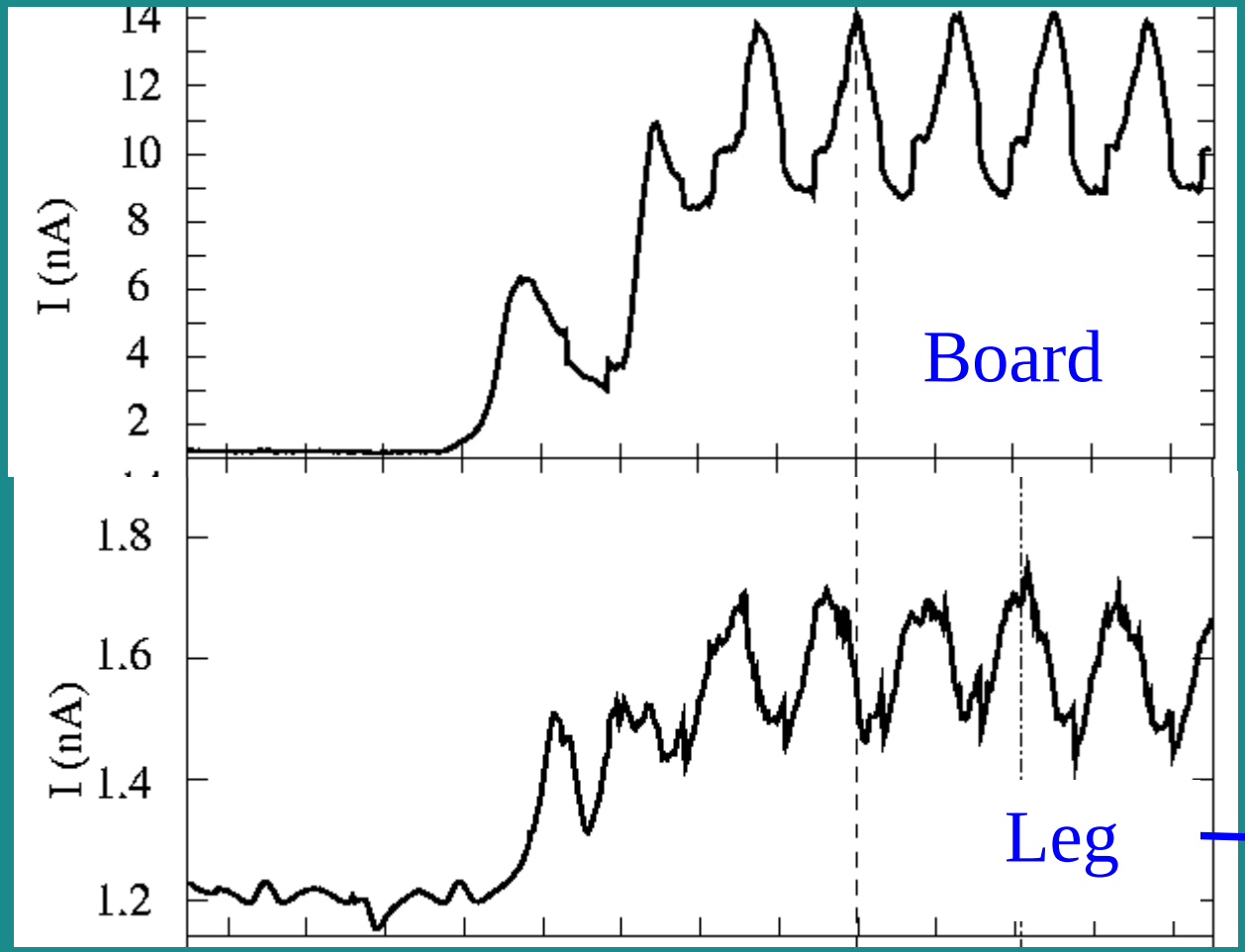
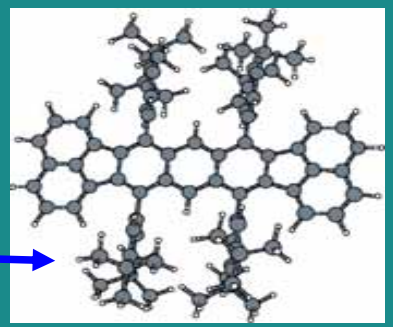
The tip / molecule / surface junction



Main signal

↓

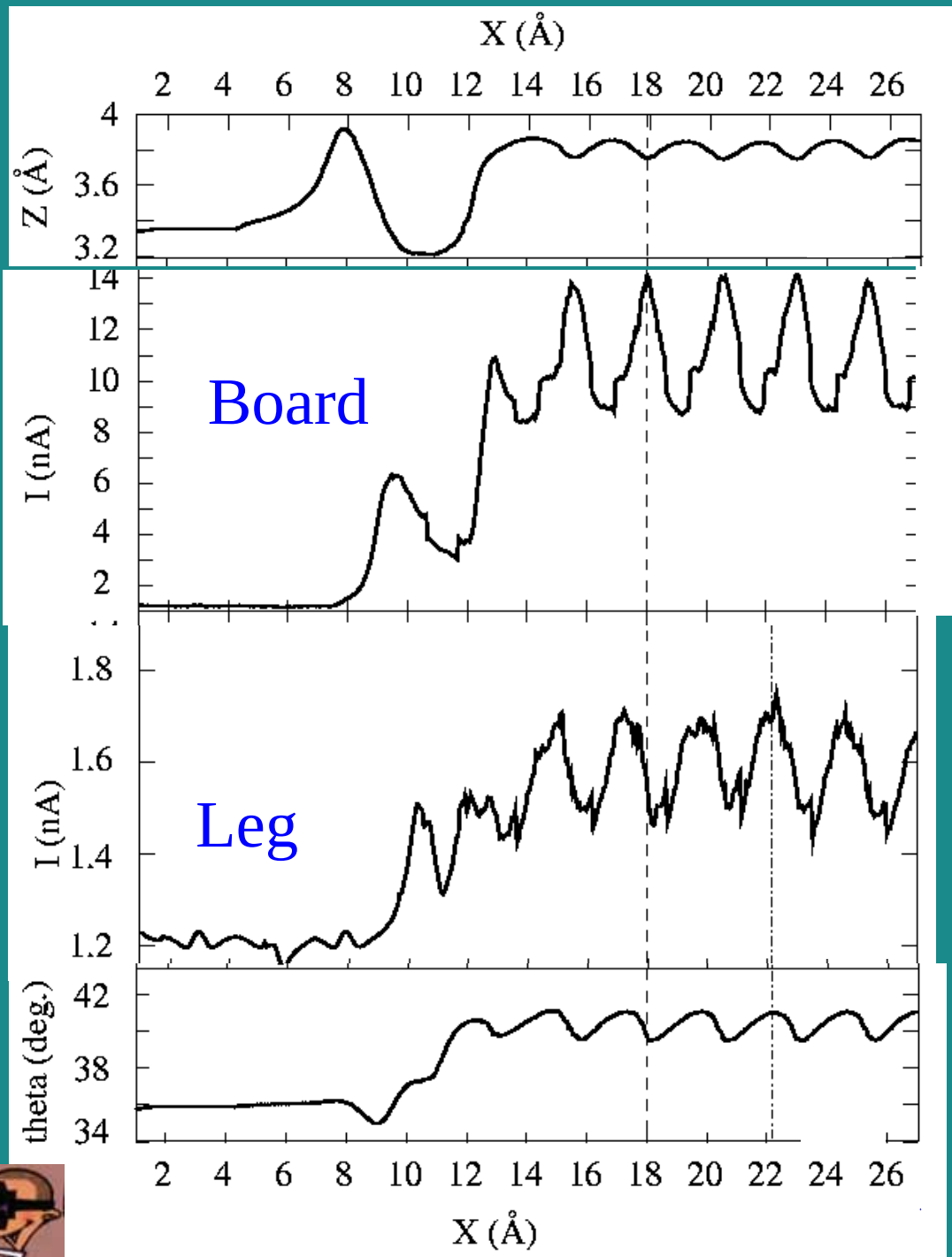
Board

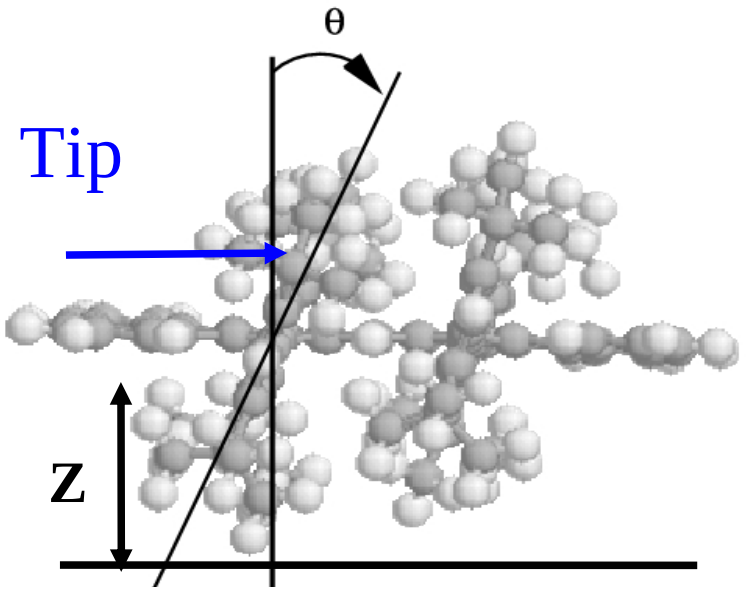


M. Alemani *et al*. Chem. Phys. Lett. **402**, 180 (2005)

Pico-Inside

CEMES





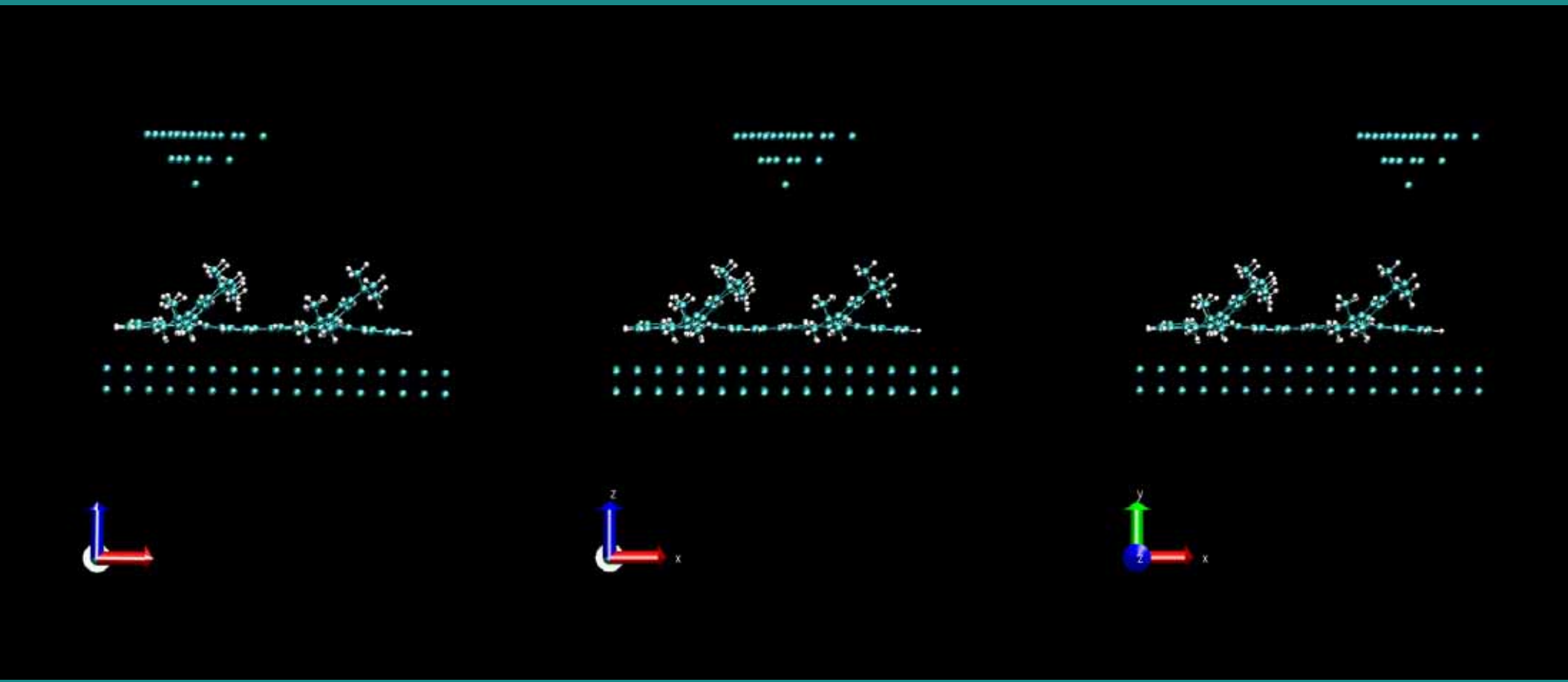
M. Alemani *et al*. Chem. Phys. Lett. **402**, 180 (2005)

Pico-Inside

CEMES

“Piezo”-chemistry or mechanical chemistry with a single molecule

Molecular creeping: Lander on Cu(110)

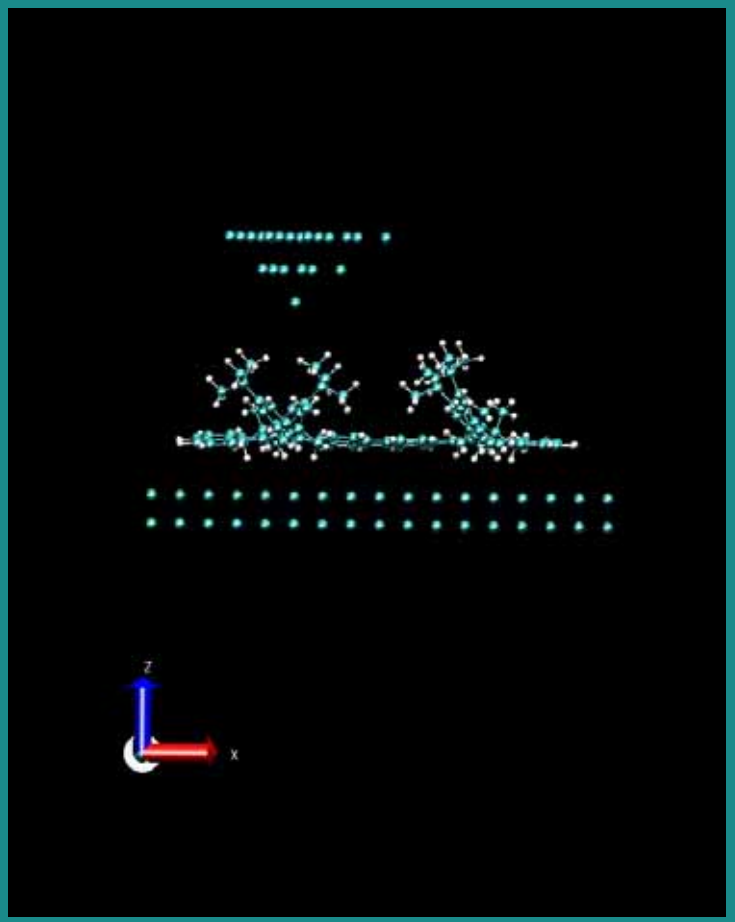


Pico-Inside

CEMES

“Piezo”-chemistry or mechanical chemistry with a single molecule

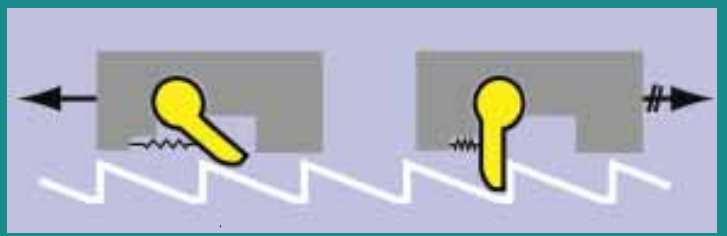
Molecular creeping: Lander on Cu(110)



Crossed legs: no manipulation occurs.

Legs play the role of a linear “ratchet and pawl” system, prohibiting the reverse motion.

Unidirectional motion



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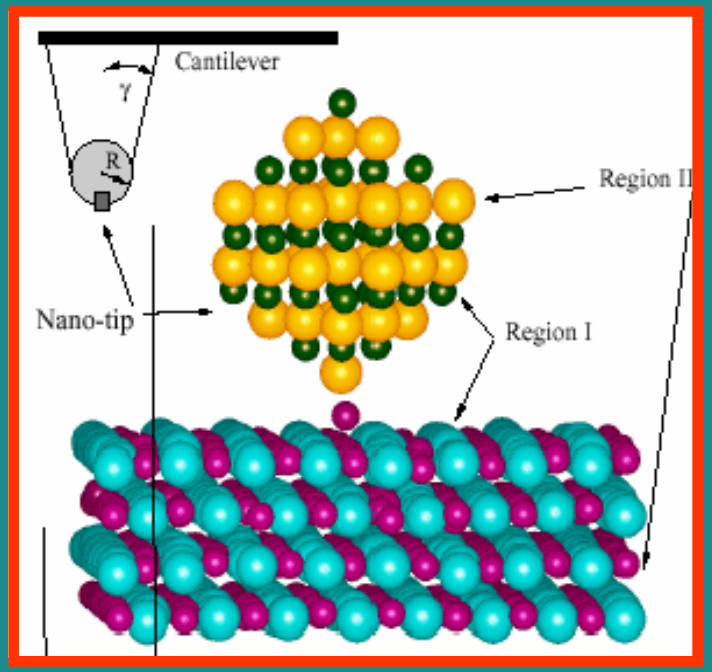
AFM imaging

Extensive calculations are required to determine the 3D force-field for the moving tip - usually interatomic potentials for surface-molecule-tip interaction are needed.

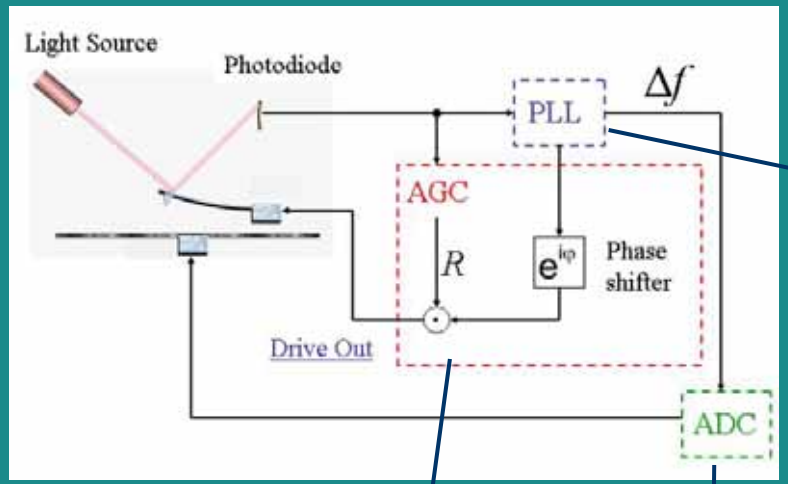
Frequency shift as a function of closest approach and lateral position is then calculated.



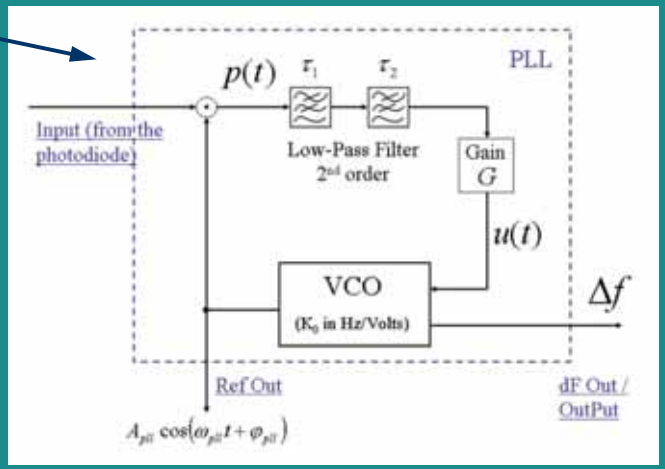
It is assumed that the instrumentation works ideally, the tip trajectory is periodic and that the tip-surface interaction is **conservative**

Imaging weakly adsorbed atoms and molecules presents new challenges since dynamical processes can occur during the imaging, making image interpretation difficult.

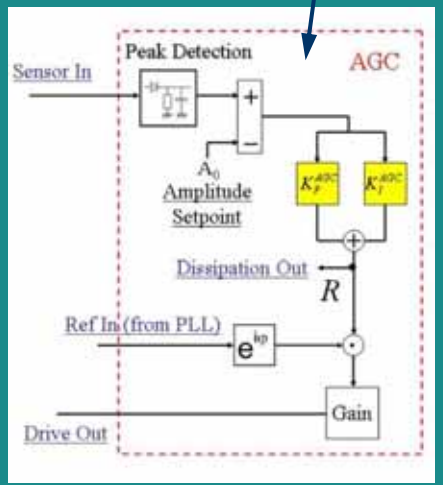
AFM imaging: virtual AFM

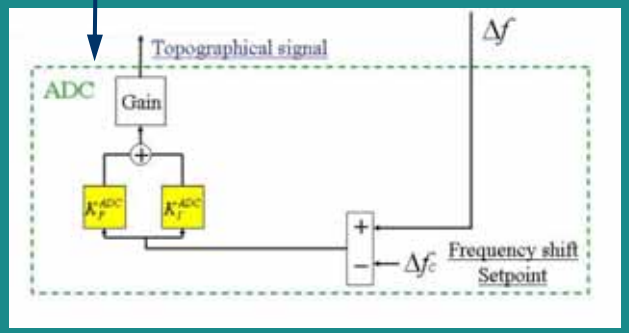


A complete, real time simulation of the entire NC-AFM experiment, including noise.



Developed in a collaboration of **Toulouse** (S. Gauthier), **KCL** (L. Kantorovich) and **UCL** (A. Shluger) groups.





The response of the cantilever and feedback control is realistically accounted for.

It is now possible to investigate and image real-time dynamical processes with a non-conservative tip-surface interaction - such as dissipation, diffusion and manipulation.

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AFM imaging

The following important questions should be addressed:

- **Can we resolve large molecules?**
- **Or, at least, obtain some sub-molecular resolution?**
- **Can we, at the same time, resolve the surface?**
- **And thus position the molecule correctly within the surface?**

These points can be illustrated by the following prototype systems:

C_{60} on the Si(001) surface

Defects on the MgO(001) surface

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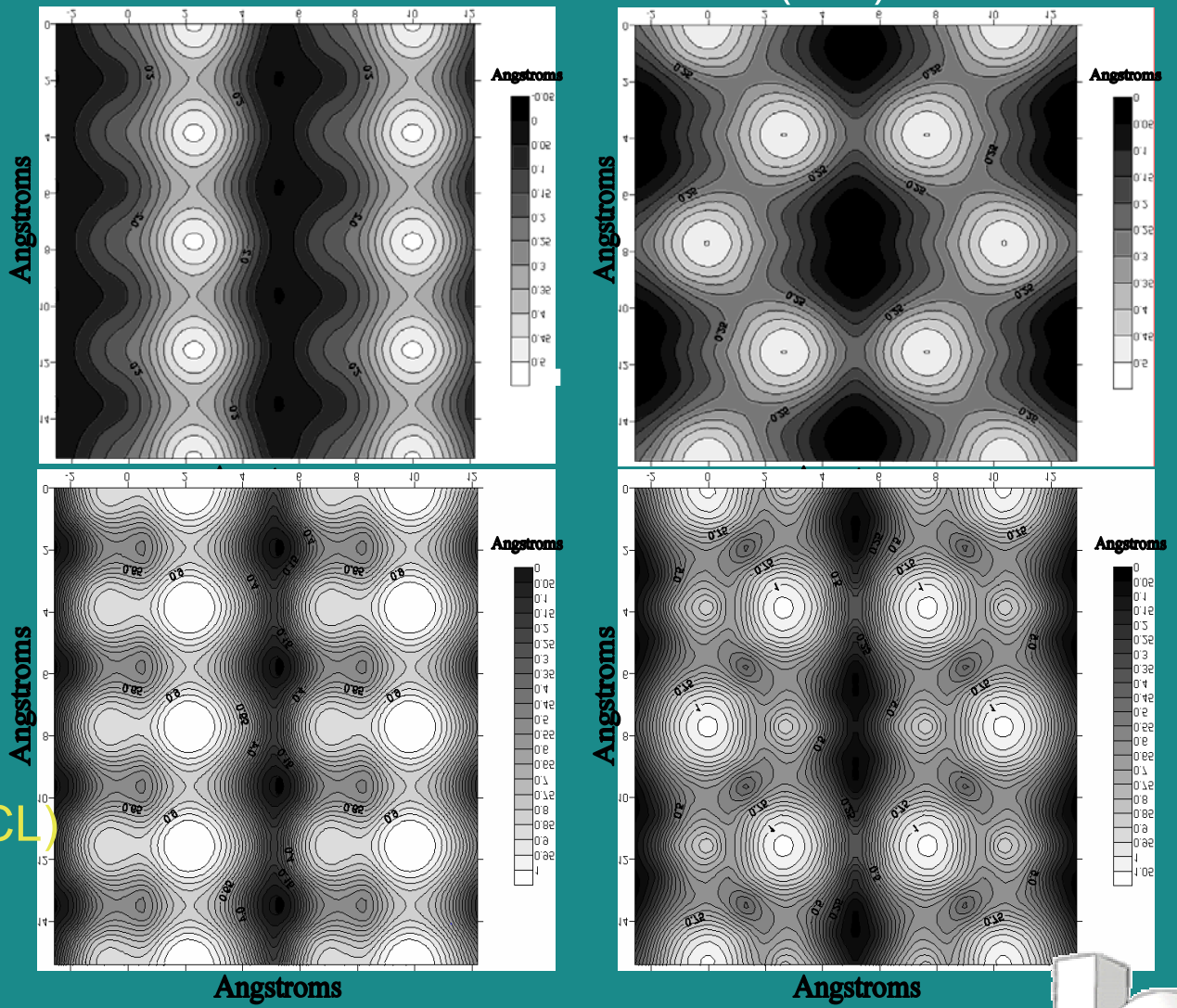
AFM imaging

Si(001) surface: both reconstructions are clearly recognised!

p(2x1) c(4x2)

Small frequency shift

Larger frequency shift



L. Kantorovich (KCL)

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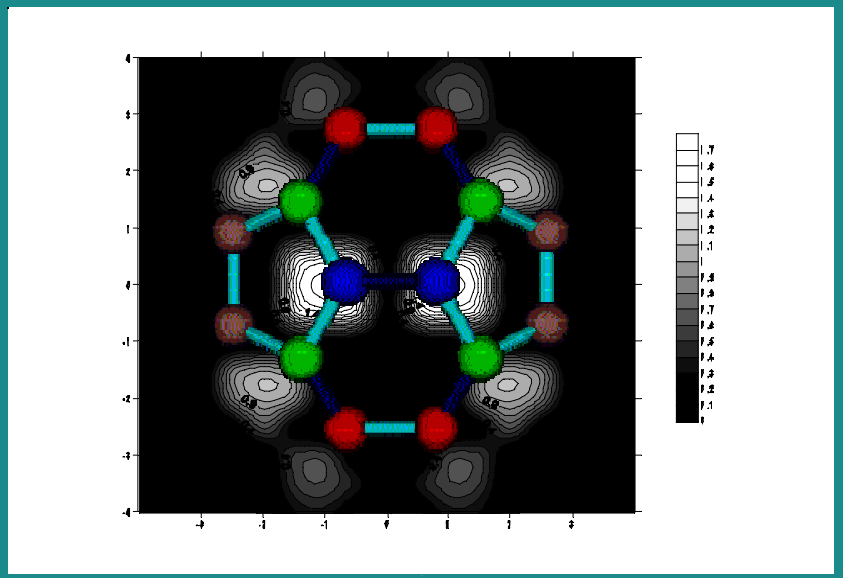
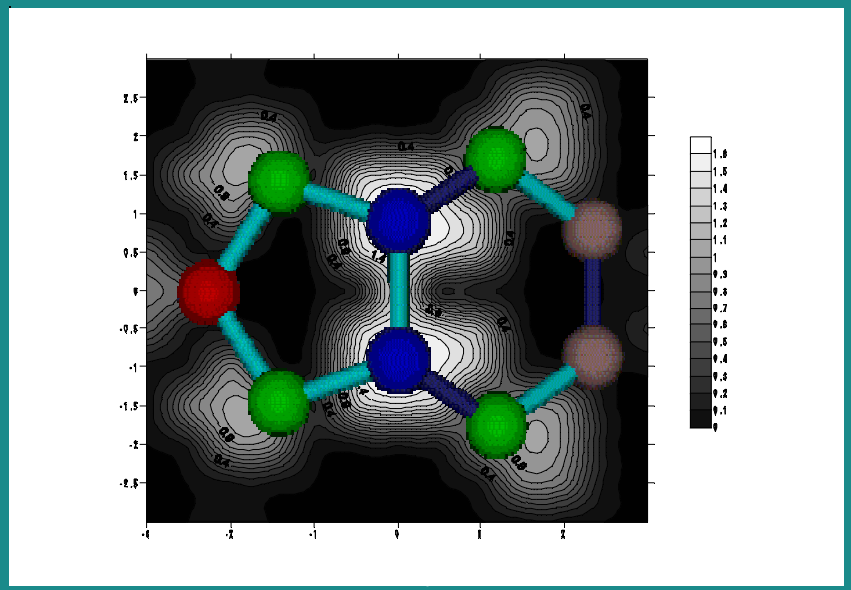
AFM imaging

C_{60} molecule: pentagons and hexagons can be seen!





- The same frequency shift can be used as for the Si(001) surface
- Therefore, both the molecule and the surface can be recognised
- Thus, as we know all possible adsorbed sites, we should be able to identify the particular configuration the molecules have in the NC-AFM images

L. Kantorovich (KCL)

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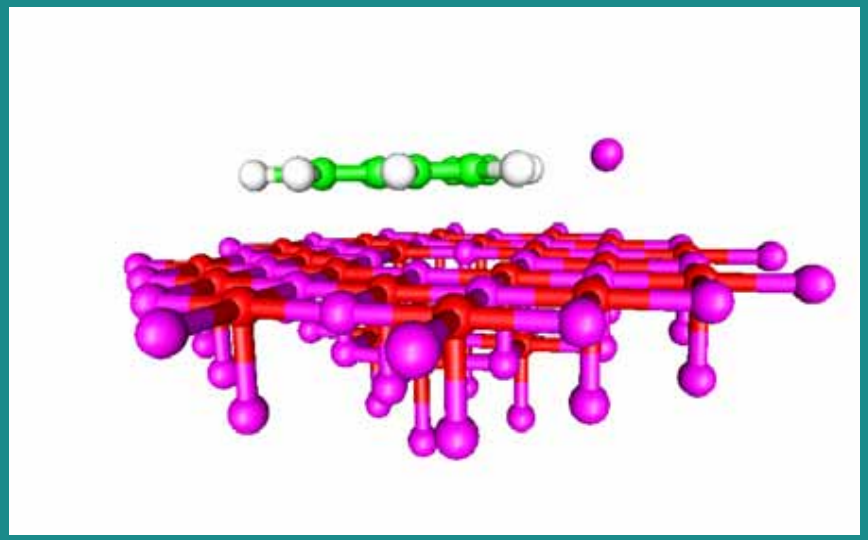
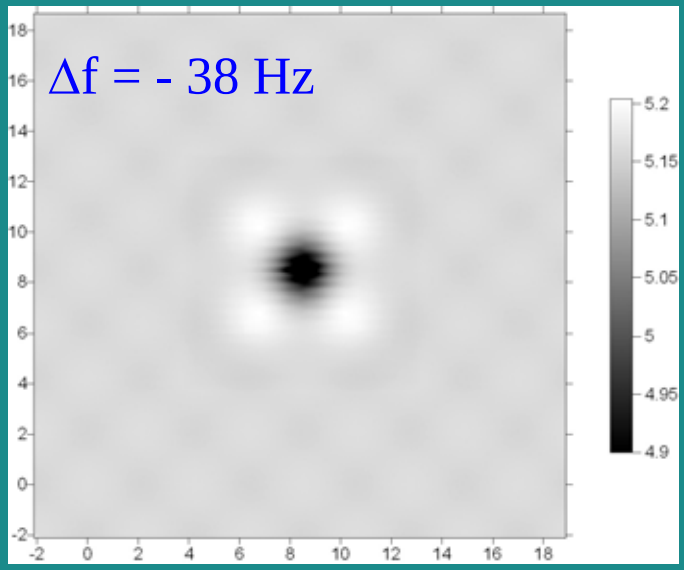
CEMES

AFM imaging

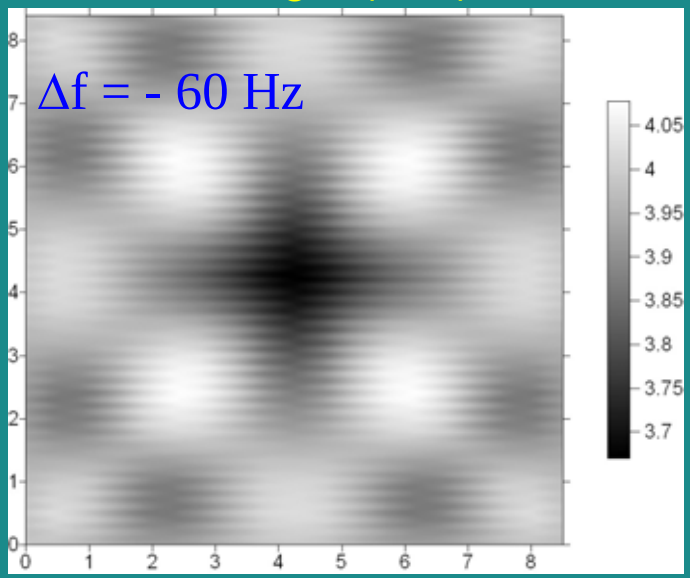
Defects on the MgO (001) surface

The electronic structure of a molecule adsorbed on the MgO surface can be modified by a +2 oxygen vacancy.





Pd on MgO (001)



+2 oxygen vacancy on MgO (001)

Also, metal atoms and clusters (such as Pd) will be required to form connections to the molecule.

We can image these defects and also (in theory) manipulate them laterally with the NC-AFM

A. Shluger (UCL)

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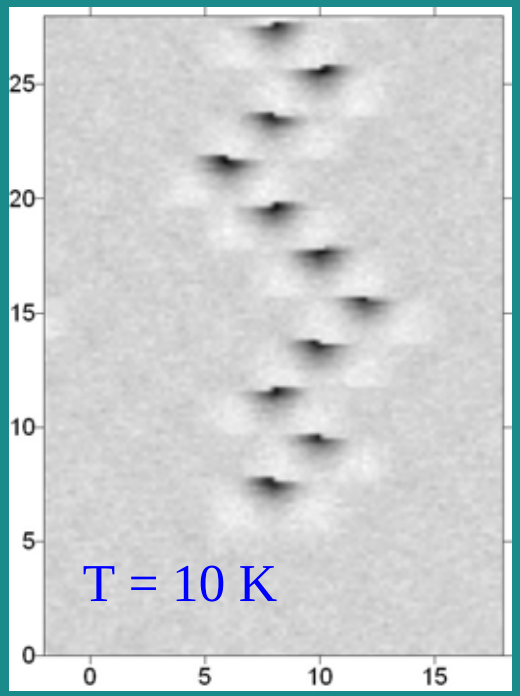
AFM imaging

Experimental Noise

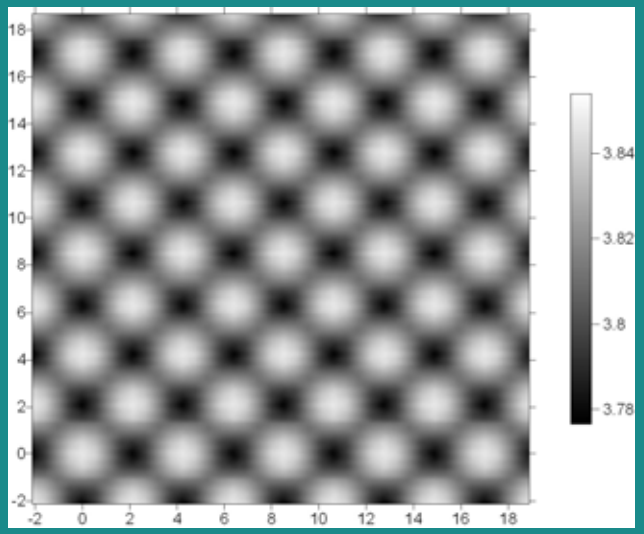
Realistic experimental noise can be added to the virtual instrument:

- Thermomechanical (cantilever) noise
- Photodetector shot noise
- Johnson noise in the electronics

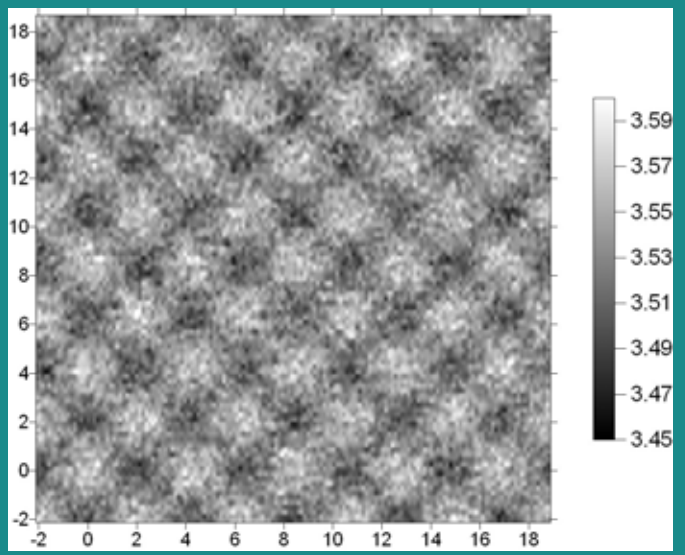


The addition of noise does not remove atomic resolution.

The noise affects the trajectory of the tip, however adatom manipulation is still possible.



MgO(001) - no noise



MgO(001) - with noise at 10 K

Implementation developed through Toulouse, KCL and UCL collaboration

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Conclusion

Exploiting the resources of a single molecule

Understanding the intrinsic mechanisms of a localized action

Controlling the motion of the molecule

Activating the functions for which the molecule has been designed

Necessary coupling of STM calculations and molecular mechanics/molecular dynamics

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Acknowledgements

Chemistry

Christophe Coudret, André Gourdon, Gwénaël Rapenne

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Kings College London, Lev Kantorovich

University College London, Alex Shluger

EC – FP5 projects AMMIST and CHIC

EC – FP6 STREP NANOMAN EC – FP6 IP Pico-Inside

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