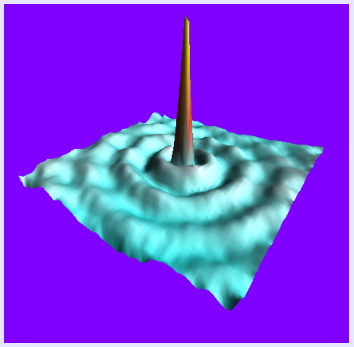
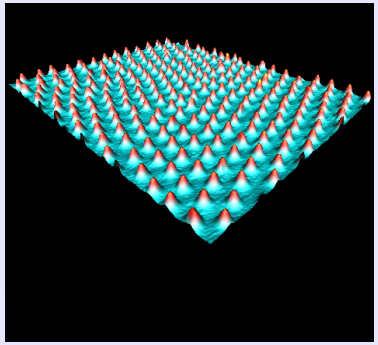
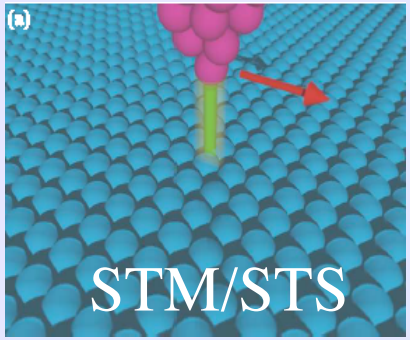
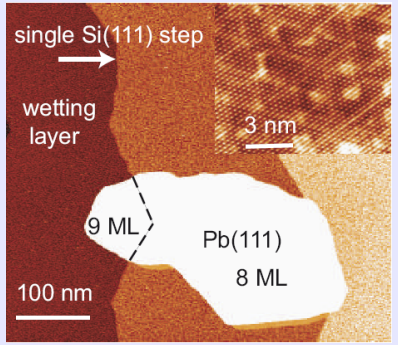
Tutorial: Fabrication and characterization of ordered atomic-scale structures: Necessary steps towards a future nanotechnology

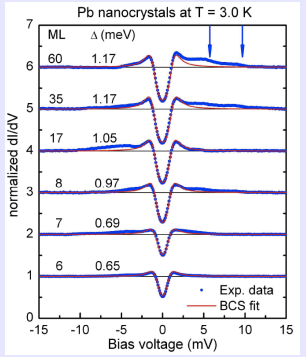




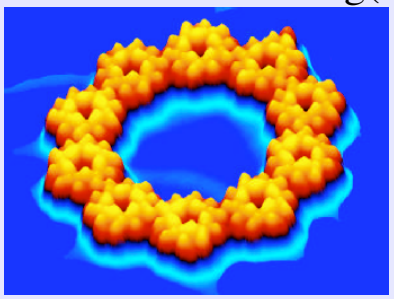
Ce/Ag(111)

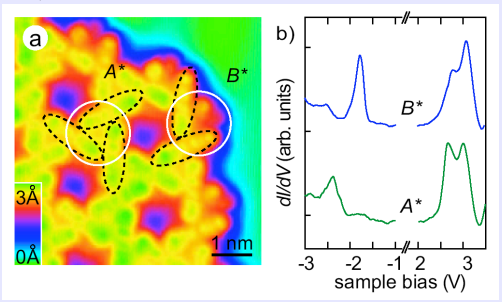




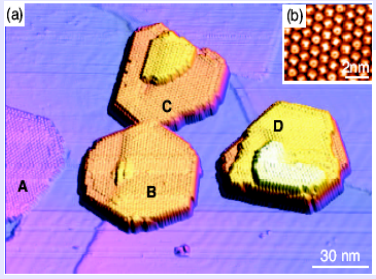


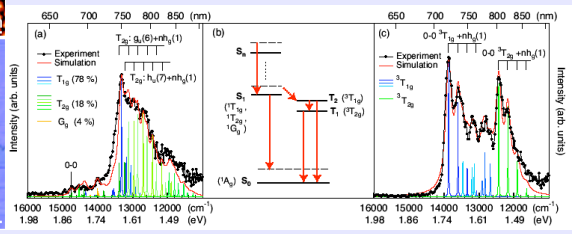
Pb(111)





Rubrene/Au(111)



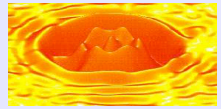


C_{60} NaCl/Au(111)

Wolf-Dieter Schneider

Institut de Physique de la Matière Condensée

Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland



Acknowledgements

Experiment
François Patthey
Marina Pivetta, Christophe Brun
Frédéric Rossel, I-Po Hong
Richard Berndt (Kiel), Robert Gaisch (Bern)
Fabien Silly (Groningen)
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Jiutao Li (Micron, USA)
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Elizabeta Ćavar (Argonne National Lab.)
Majed Chergui
Karina Morgenstern (Hannover)
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A. Baldereschi, M. Stengel, A. De Vita (London)
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Cédric Weber, Thierry Giamarchi (Geneva)
N. N. Negulyaev, V. S. Stepanyuk, L. Niebergall,
P. Bruno (MPI Halle, ESRF)
I. Yu. Sklyadneva, R. Heid, K. P. Bohnen (KIT)
P. M. Echenique, E. V. Chulkov (San Sebastian)

« There's Plenty of Room at the Bottom »

Richard P. Feynman's

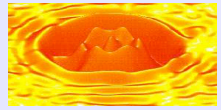
« Invitation to enter
a new field of physics »

…creation of nanostructures

atom by atom….

molecule by molecule….

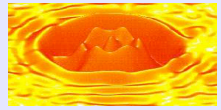
A talk given on December 29, 1959, at the annual meeting of the American Physical Society at Caltech, (Engineering and Science, Feb 1960, p. 22).



Definition

Self-assembly is the autonomous organisation
of
components
into
patterns or structures
without
human intervention

G. M. Whitesides, B. Grzybowski, Science **295**, 2418 (2002)



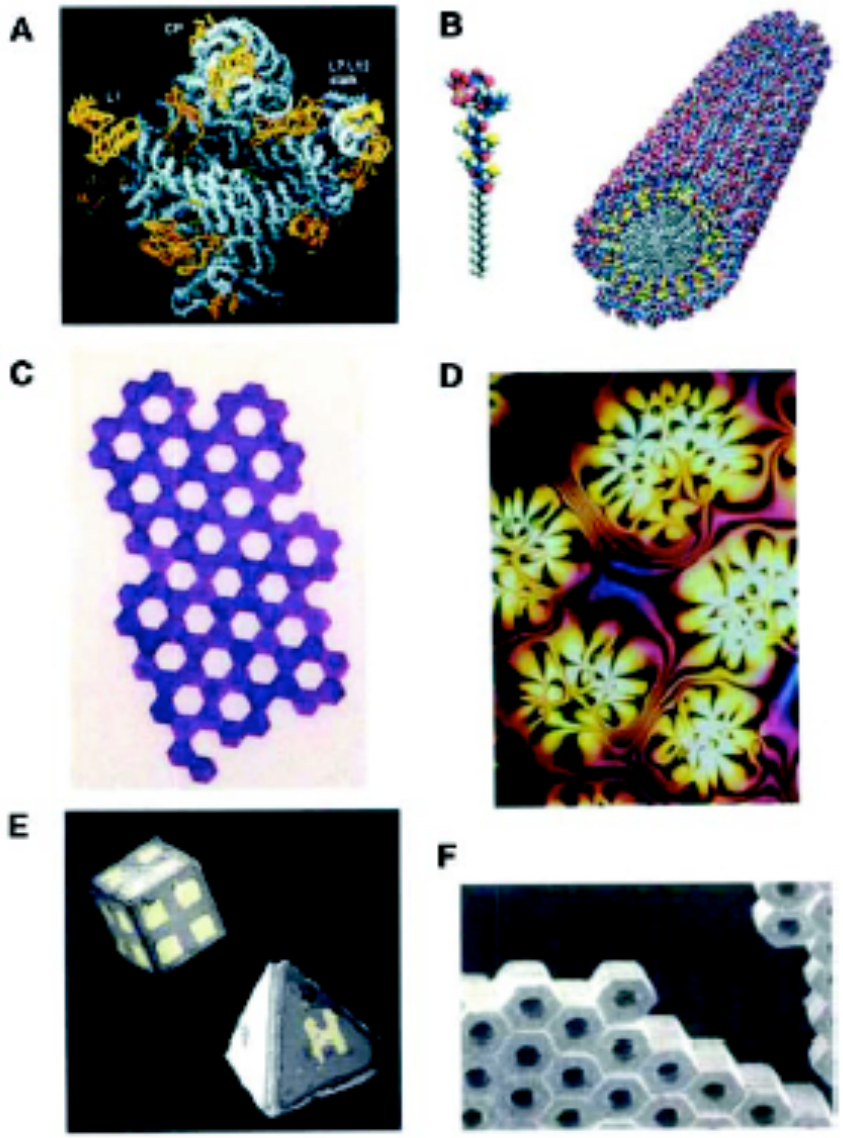
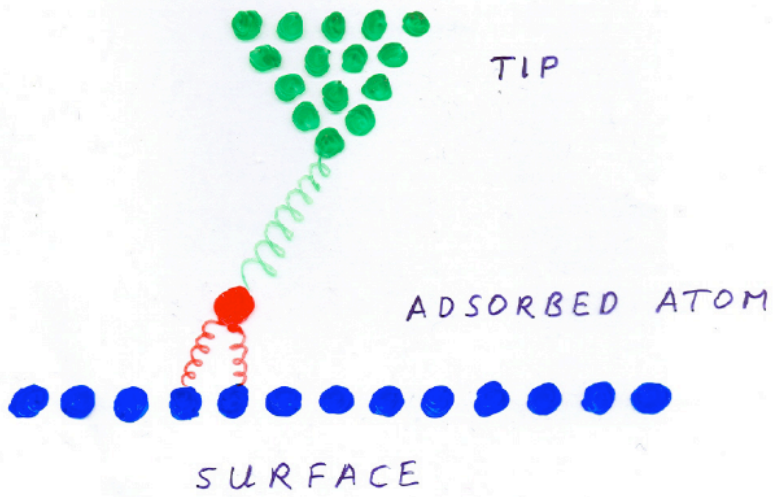


Fig. 1. Examples of static self-assembly. (A) Crystal structure of a ribosome. (B) Self-assembled peptide-amphiphile nanofibers. (C) An array of millimeter-sized polymeric plates assembled at a water/perfluorodecalin interface by capillary interactions. (D) Thin film of a nematic liquid crystal on an isotropic substrate. (E) Micrometer-sized metallic polyhedra folded from planar substrates. (F) A three-dimensional aggregate of micrometer plates assembled by capillary forces. [Image credits: (A) from (*24*); (B) from (*25*); (C) from (*26*); (D) from (*27*); (E) from (*28*); (F) from (*29*)]

Table 1. Examples of self-assembly (S, static, D, dynamic, T, templated, B, biological).

STM :

ADJUSTABLE BONDING



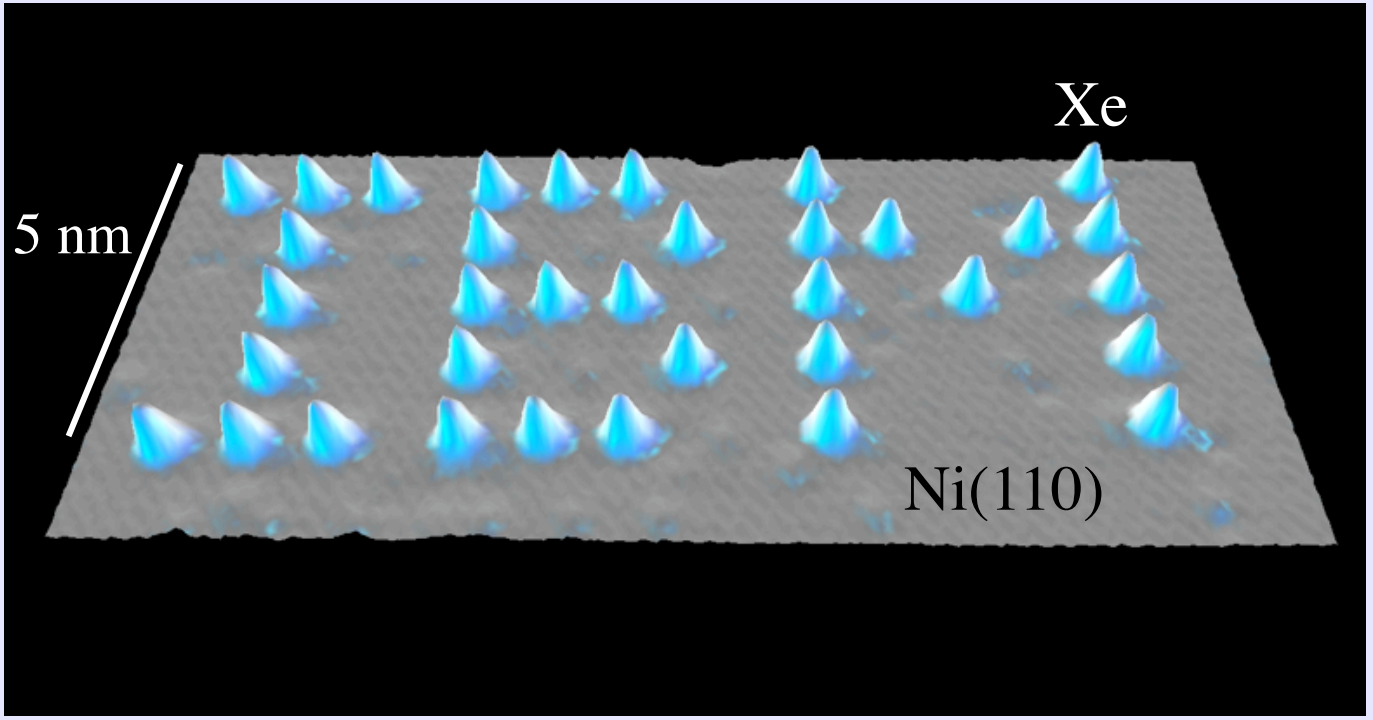
(D. M. EIGLER)

Positioning single atoms with a scanning tunnelling microscope

D. M. Eigler & E. K. Schweizer*

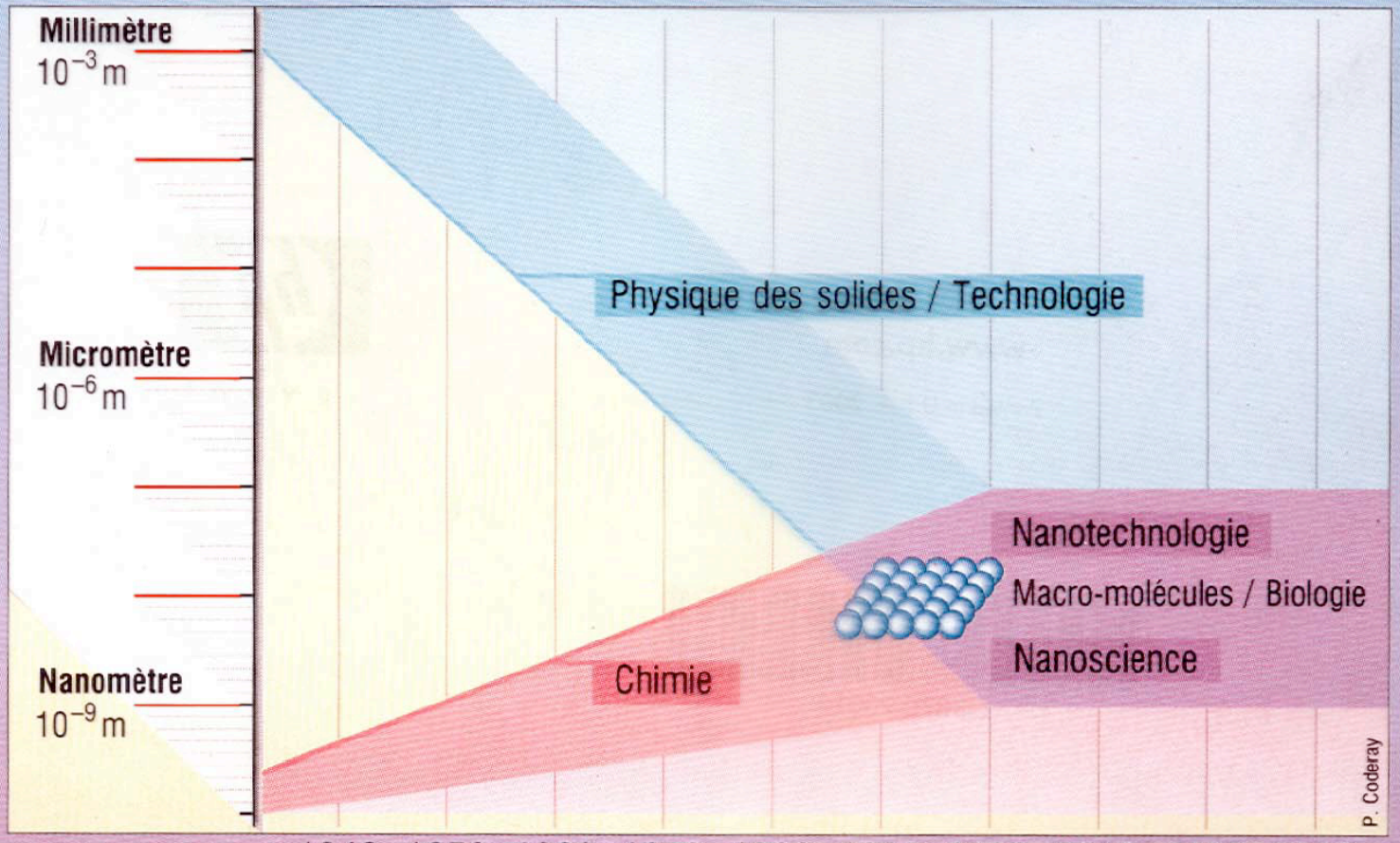
IBM Research Division, Almaden Research Center, 650 Harry Rd, San Jose, California 95120, USA

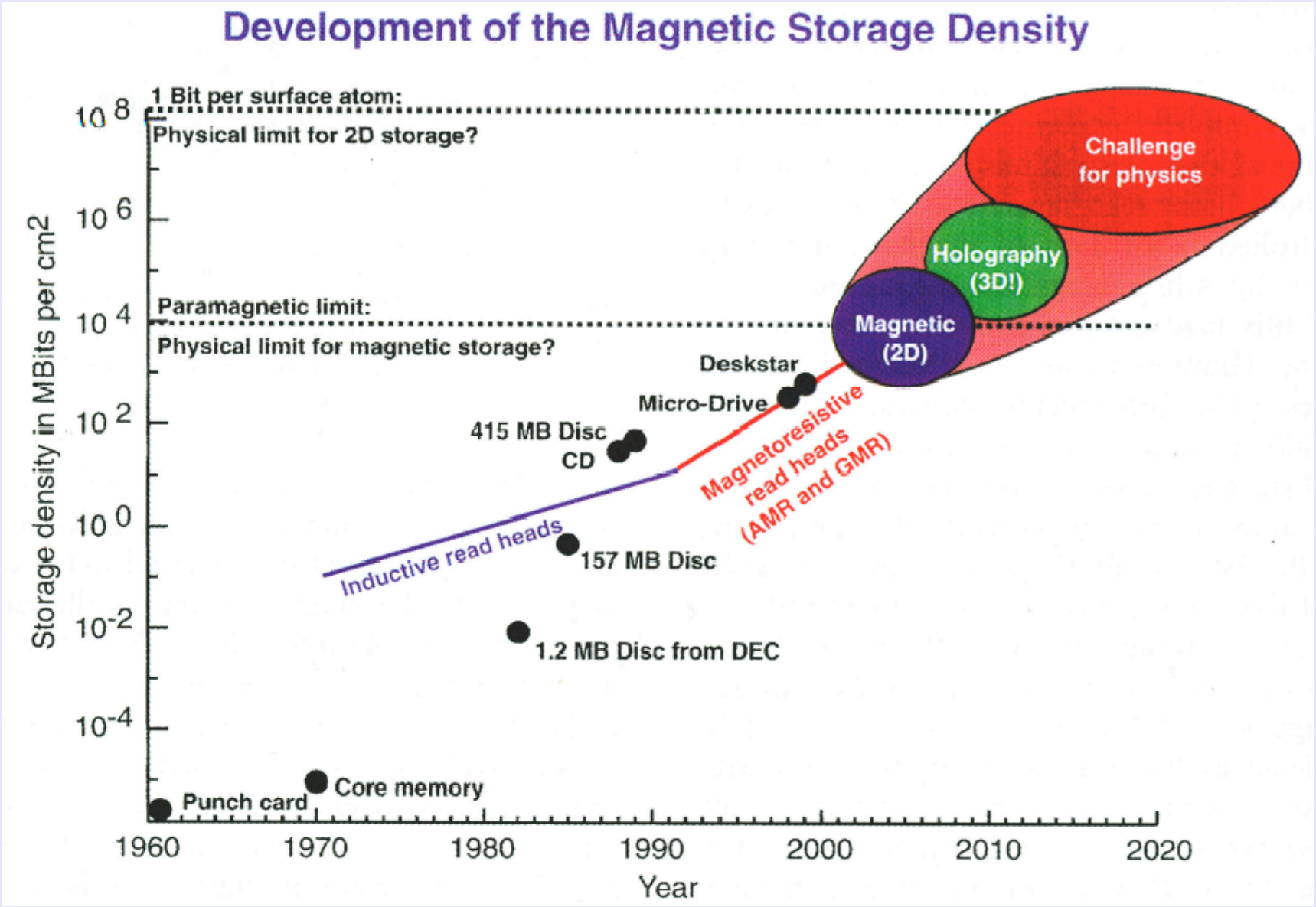
NATURE · VOL 344 · 5 APRIL 1990



LA NOUVELLE SYNTHÈSE

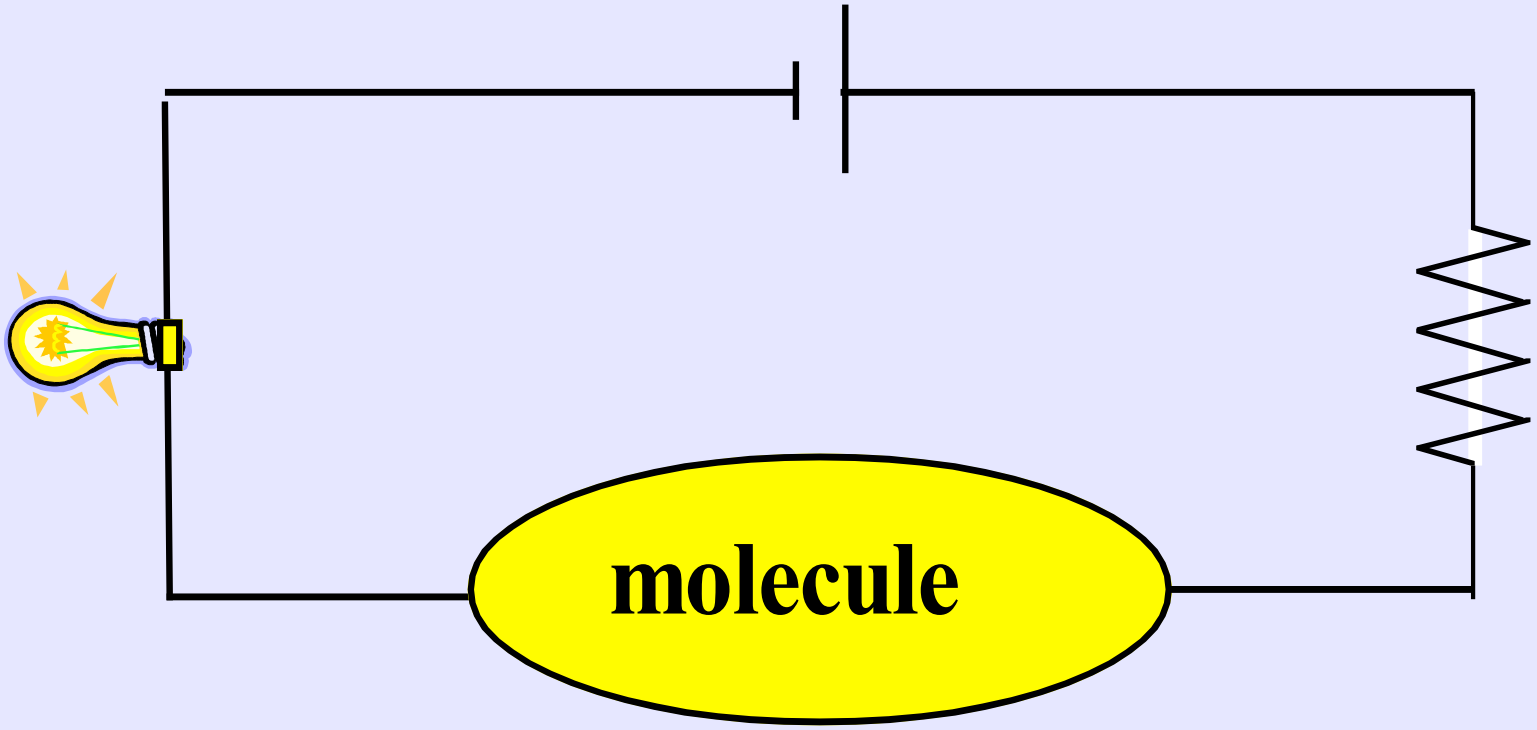
Dans la nouvelle ère de la «post-miniaturisation», différentes disciplines, dont la physique et la chimie, se rejoignent pour donner naissance à la nanoscience et à la nanotechnologie





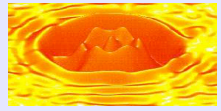
W. Eberhardt, Surf. Sci. **500**, 242 (2002)

Molecular conduction



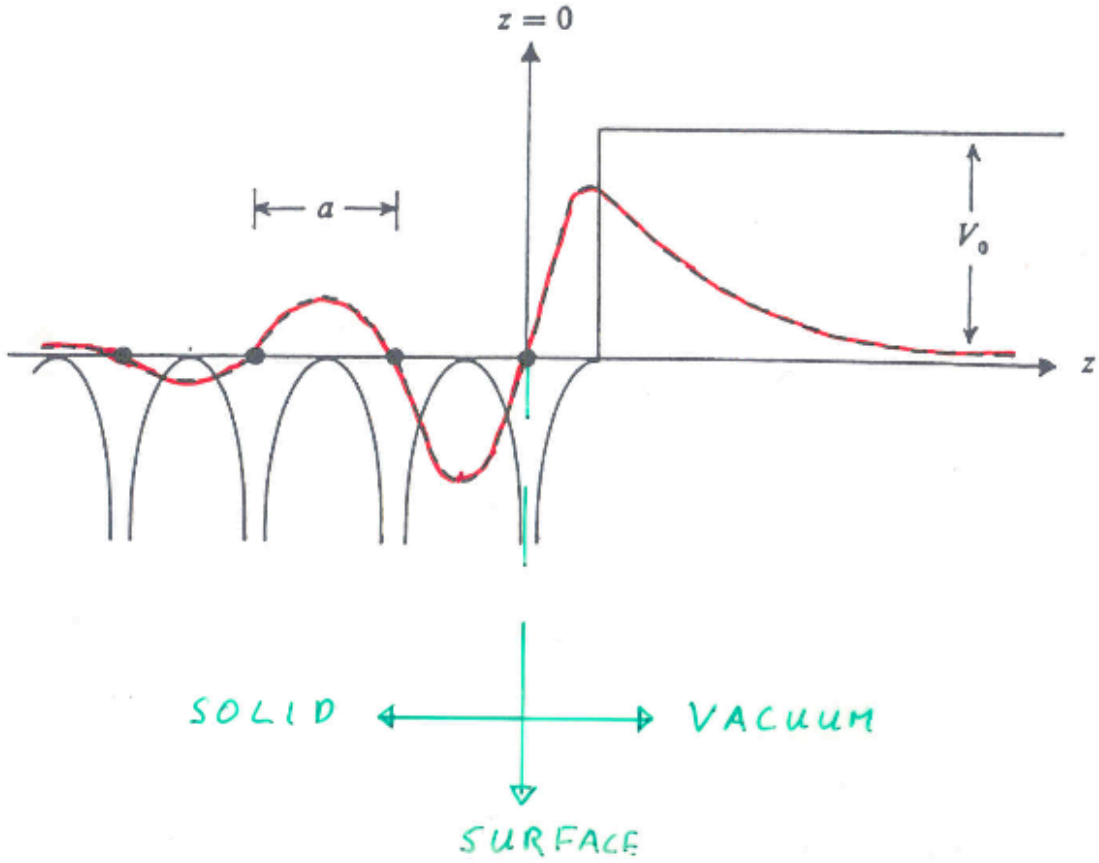
Courtesy of A. Nitzan

Surface state electrons « create » a two-dimensional adatom superlattice



Real part of a surface state electron wave function

Fig. 4.8. One-dimensional semi-infinite lattice model potential (solid curve) and an associated surface state (dashed curve). (ZANGWILL)



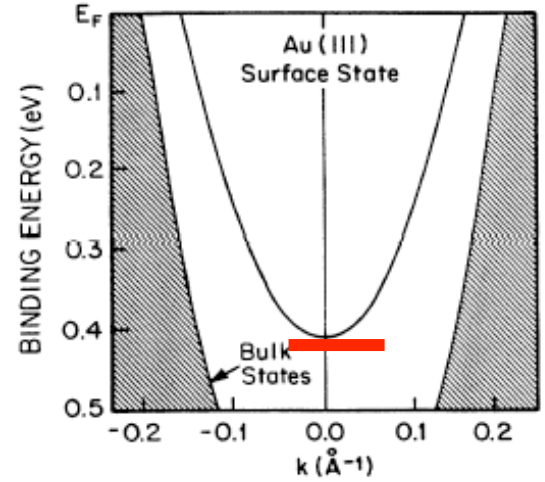
A. Zangwill, Physics at Surfaces

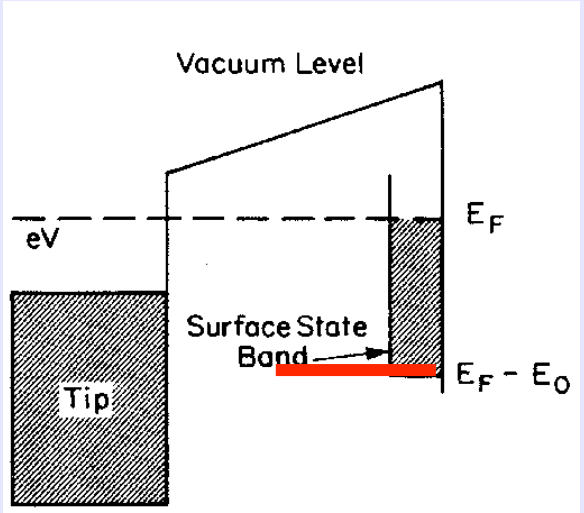
PHYSICAL REVIEW B VOLUME 43, NUMBER 5 15 FEBRUARY 1991-I

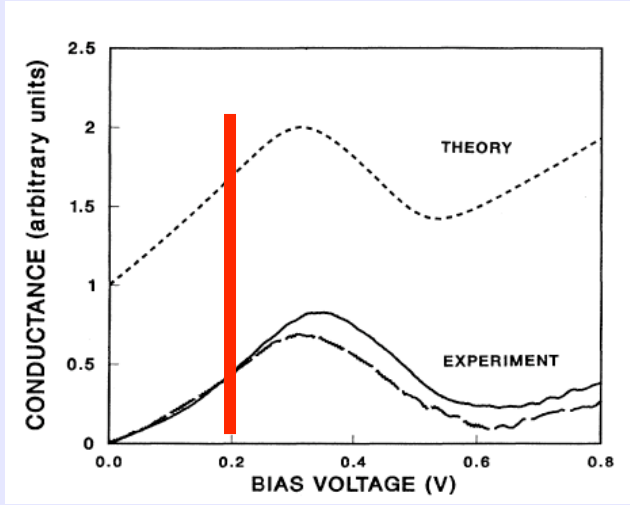
Theory of the local density of surface states on a metal: Comparison with scanning tunneling spectroscopy of a Au(111) surface

L. C. Davis, M. P. Everson, and R. C. Jaklevic
Research Staff, Ford Motor Company, Dearborn, Michigan 48121-2053

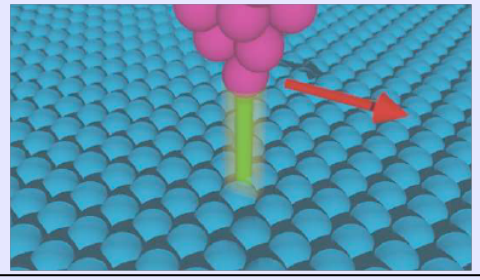
Weidian Shen
Science Division, Northeast Missouri State University, Kirksville, Missouri 63501
(Received 27 June 1990)







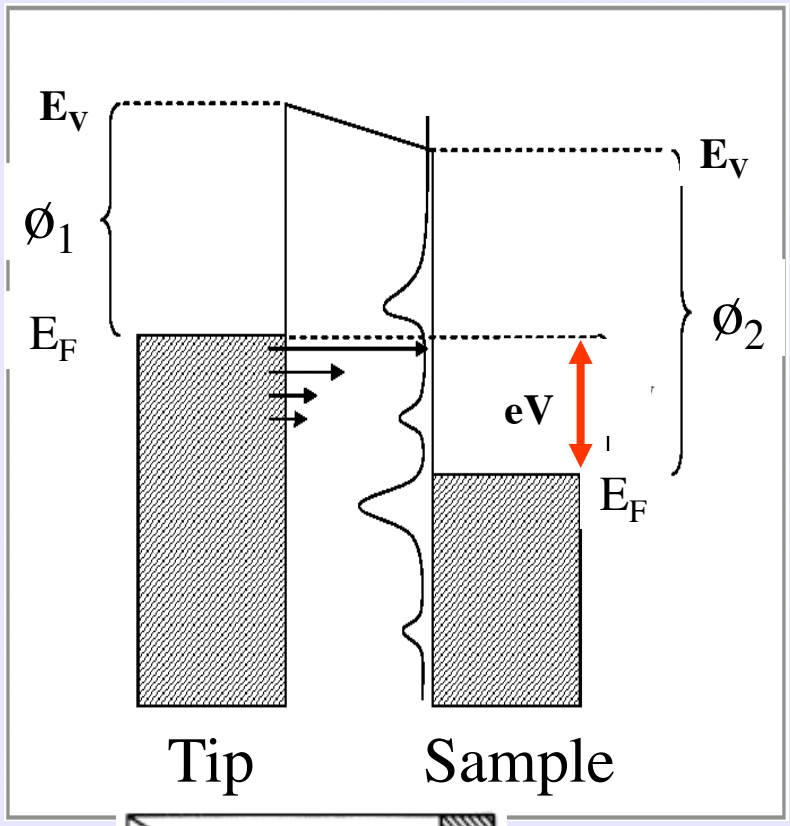
First STS observation

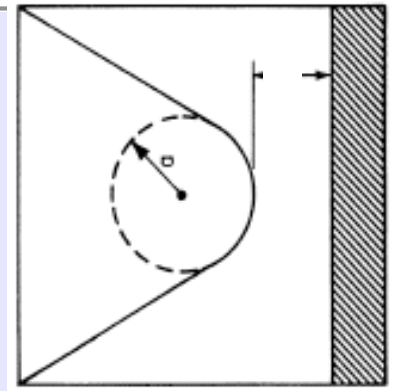


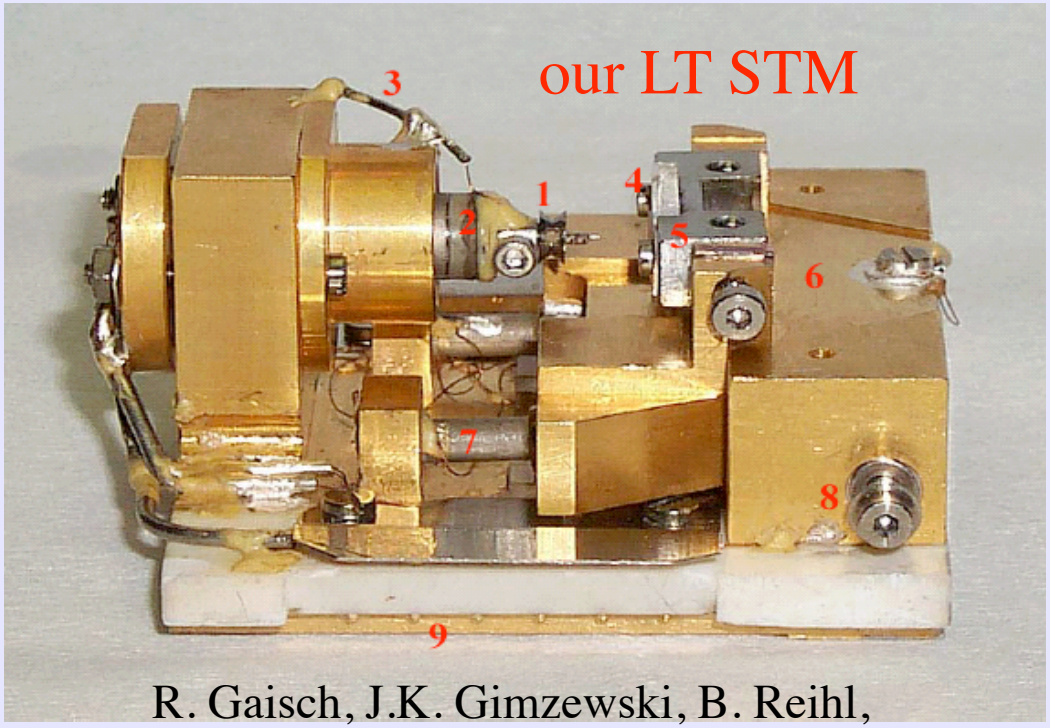
room temperature,

V_{mod} = 200 mV

Scanning probe methods: STM, STS



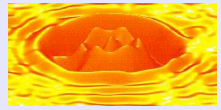




R. Gaisch, J.K. Gimzewski, B. Reihl, R.R. Schlittler, M. Tschudy, WDS, Ultramicroscopy **42 – 44**, 1621 (1992).

$$I(V) \propto \int_0^{eV} \rho_t(\pm eV \mp E)\, \rho_s(E)\, T(E, eV)\, dE$$

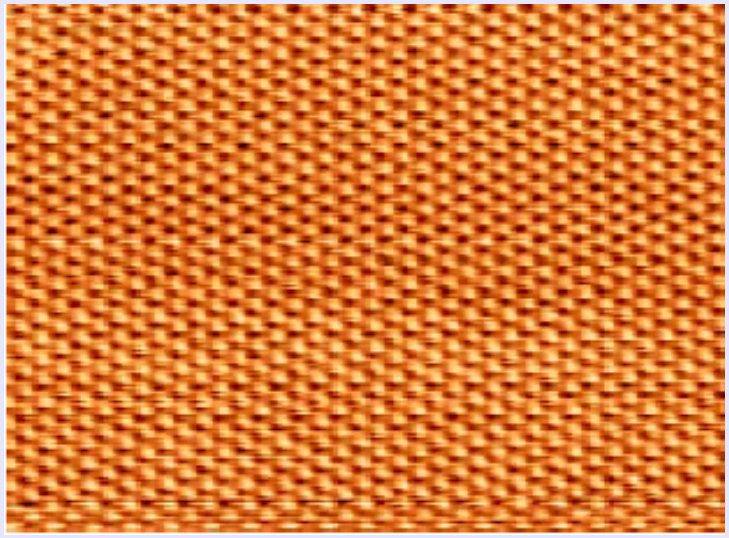
$$\frac{dI}{dV}(V) \propto e\, \rho_t(0)\, \rho_s(eV)\, T(eV, eV)$$



Ag(111) surfaces support an electron surface state band:

low density (~0.01 electron/surface atom), free 2D electron gas (2DEG).

On a defect-free surface, the 2DEG is *spatially uniform*

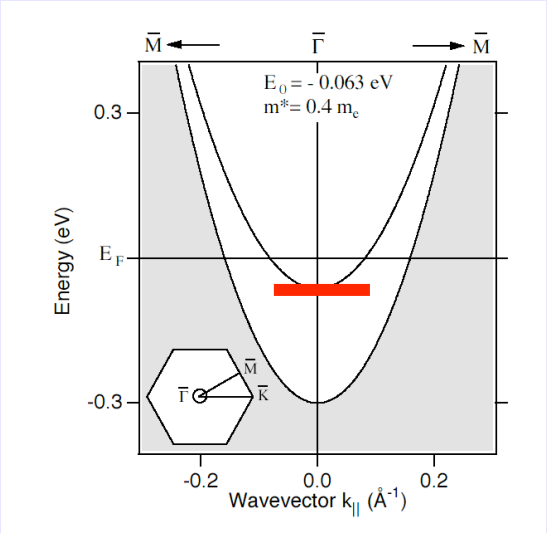


Ag(111) @ 4.8 K;

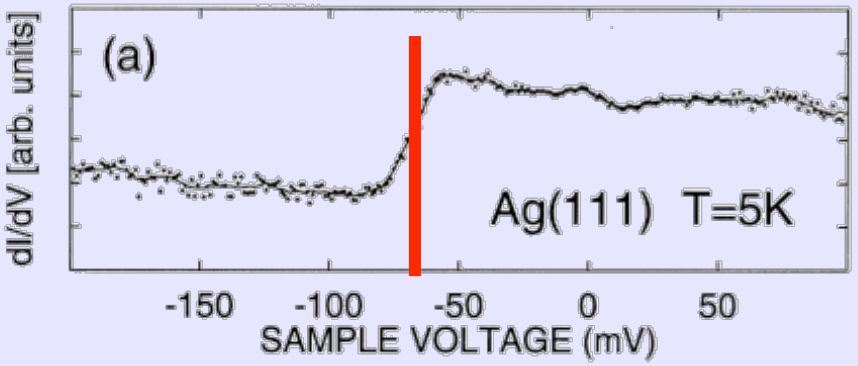
lattice constant $a = 0.29$ nm.

M. Pivetta, F. Silly, F. Patthey, J. P. Pelz,

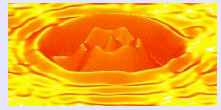
WDS, Phys. Rev B **67**, 193402 (2003)



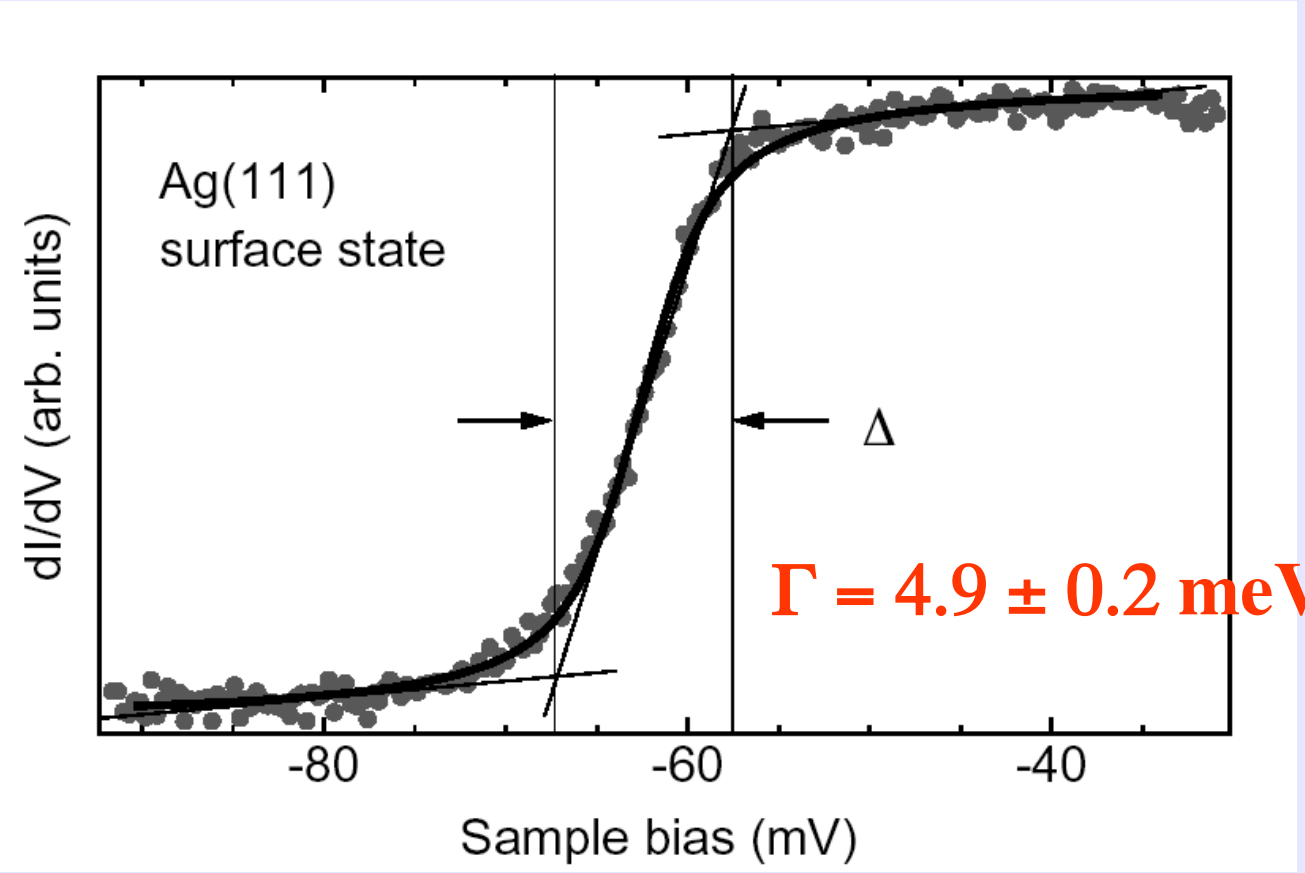
First lifetime determination with STS



J. Li, WDS, R. Berndt, O. R. Bryant, S. Crampin,
PRL **81**, 4464 (1998)

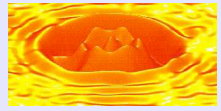


Lifetime width of surface state electrons on Ag(111)

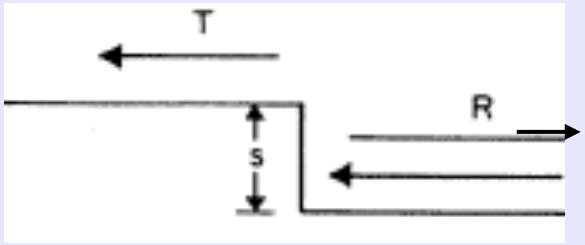


M. Pivetta, F. Silly, F. Patthey, J. P. Pelz, WDS, Phys. Rev B **67**, 193402 (2003)

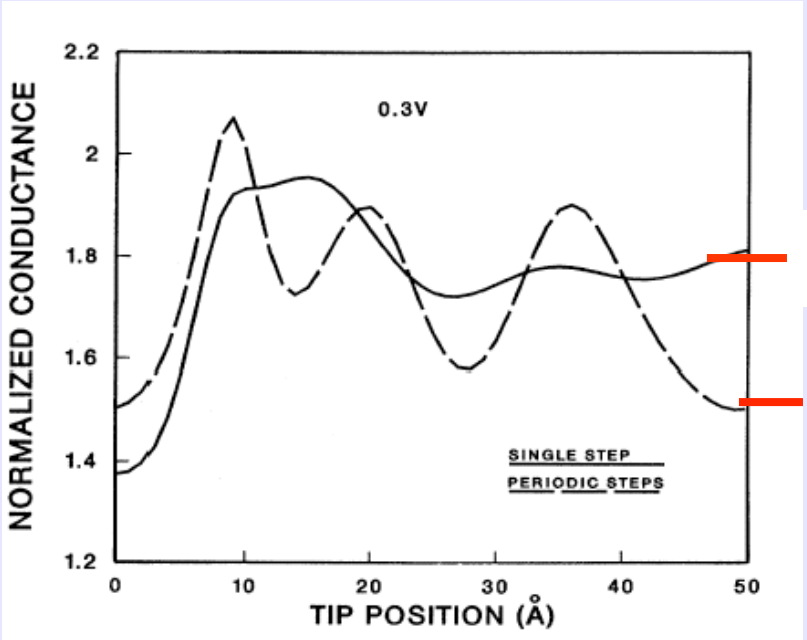
Electron confinement to nanoscale structures on Ag(111)



Scattering of surface state electrons at steps



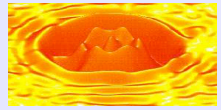
$$\psi(x) = \begin{cases} e^{-iqx} + Re^{iqx}, & x > 0 \\ Te^{-iqx}, & x < 0 \end{cases}$$



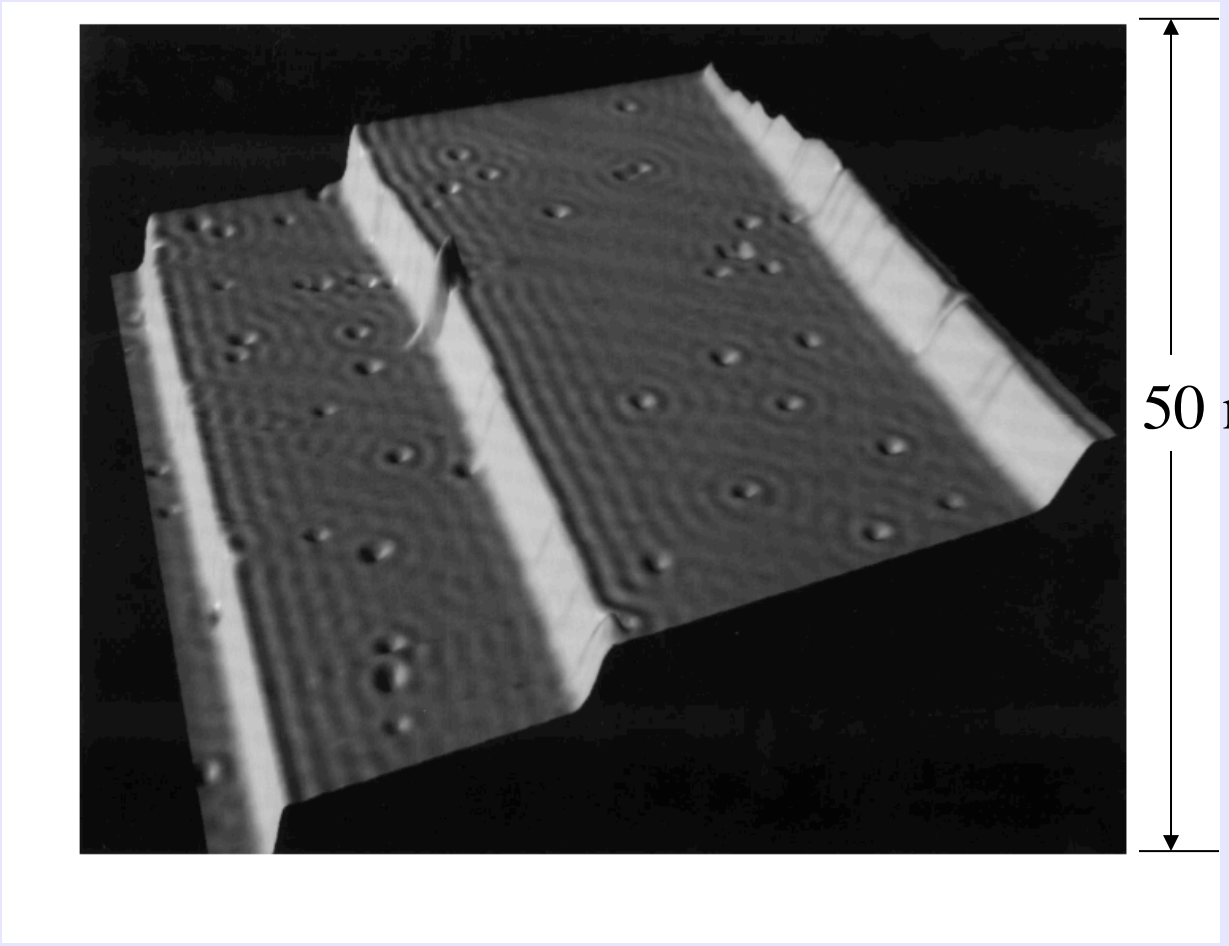
single step

periodic steps (confinement)

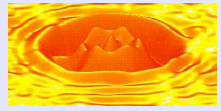
Prediction: L. C. Davis *et al.*, PRB **43**, 3821 (1991)



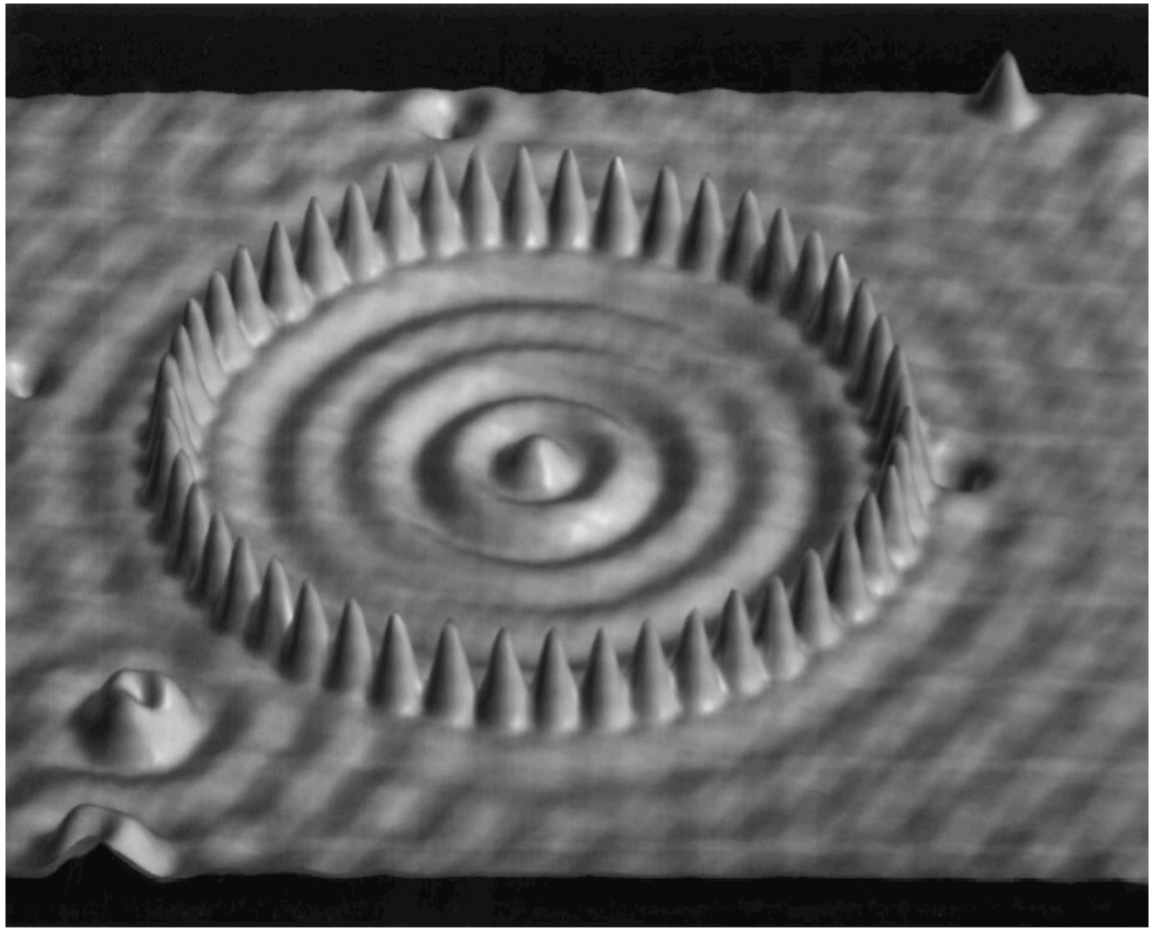
Electron standing waves on Cu(111) @ 5 K



M. F. Crommie, C. P. Lutz, D. M. Eigler, Nature **363**, 524 (1993)



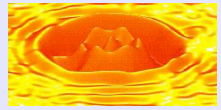
Electron standing waves in a quantum corral



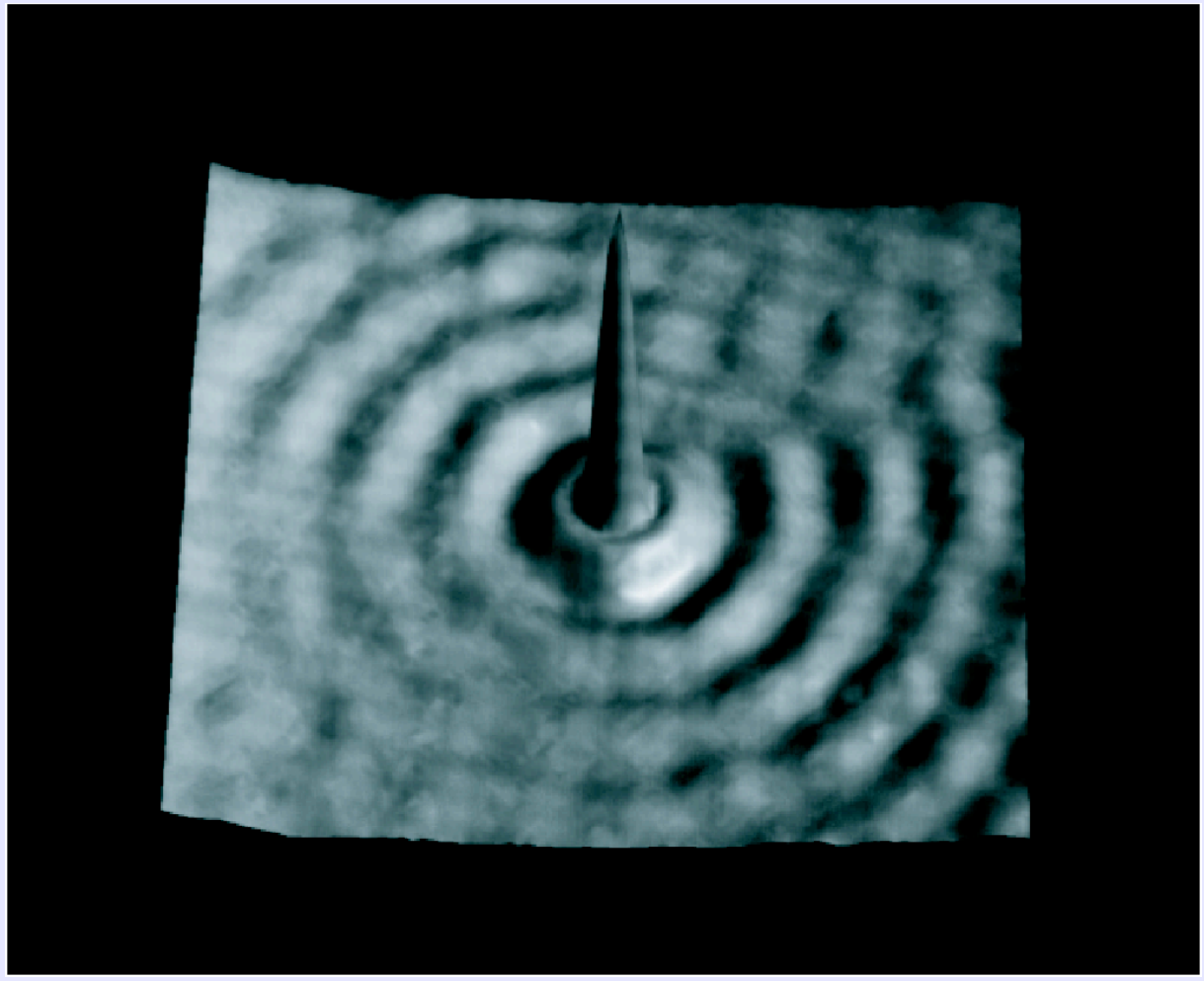
48 Fe atoms
on Cu(111)

Ø = 14.26 nm

M. F. Crommie, C. P. Lutz, D. M. Eigler, Science **262**, 218 (1993)



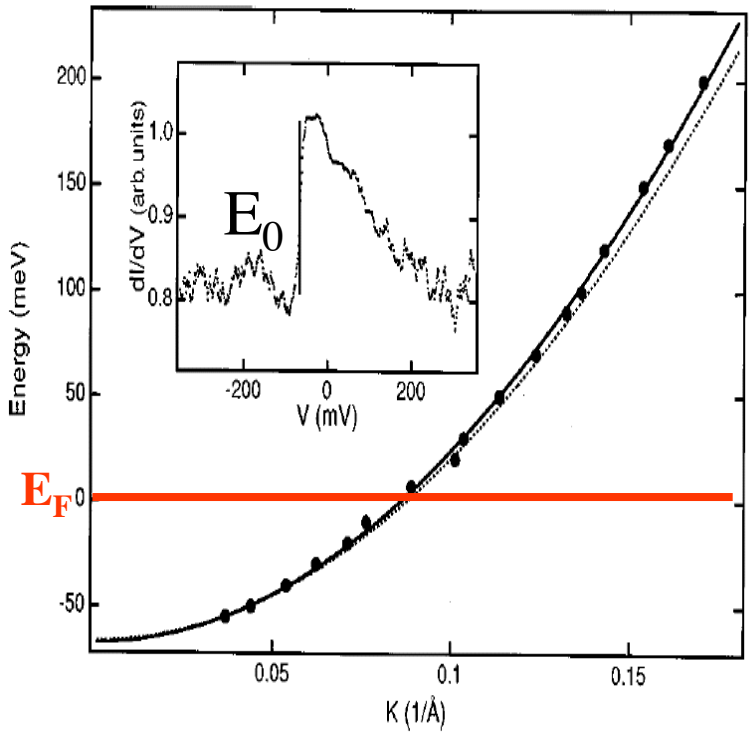
Electron standing waves: Fe atom on Cu(111)

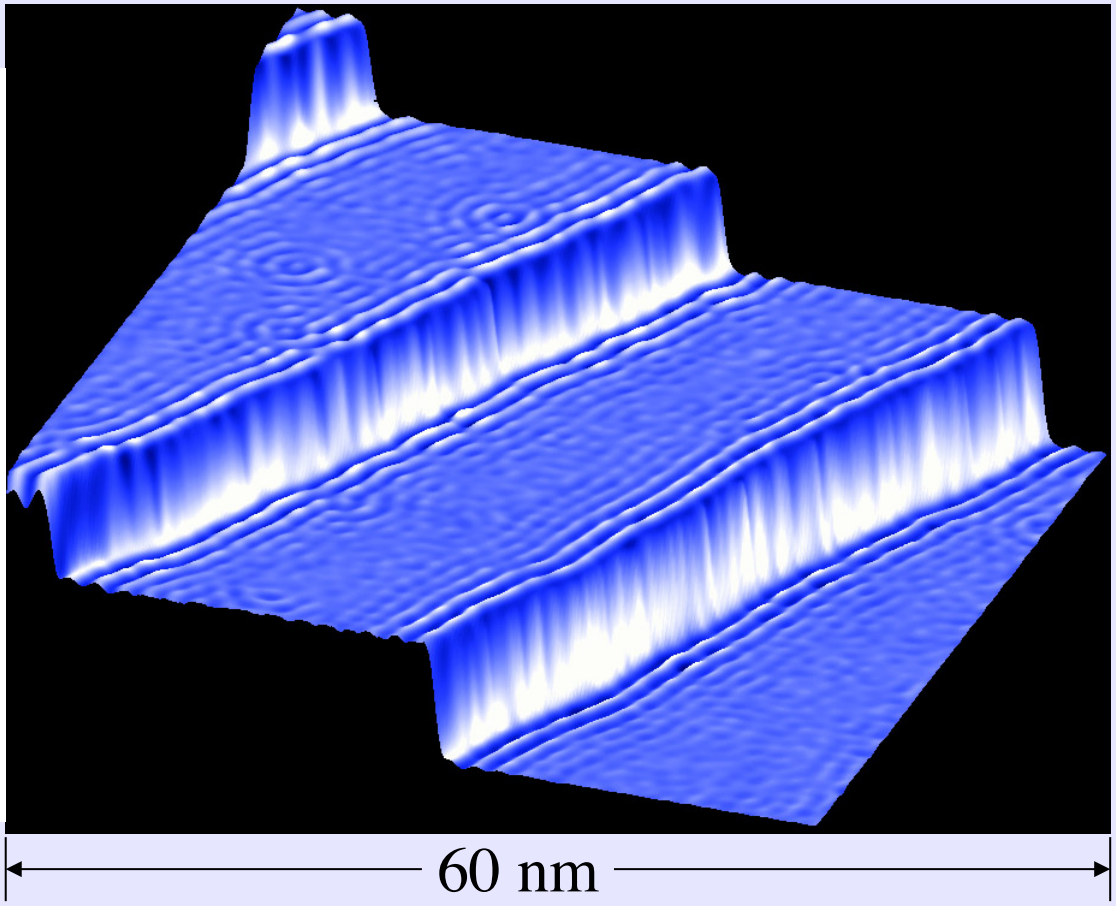


13 nm^2,
Fe/Cu(111)

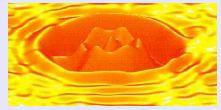
M. F. Crommie, C. P. Lutz, D. M. Eigler, Science **262**, 218 (1993)

Electron standing waves on Ag(111) @ 5 K





J. Li, R. Berndt, WDS, PRB **56**, 7656 (1997)



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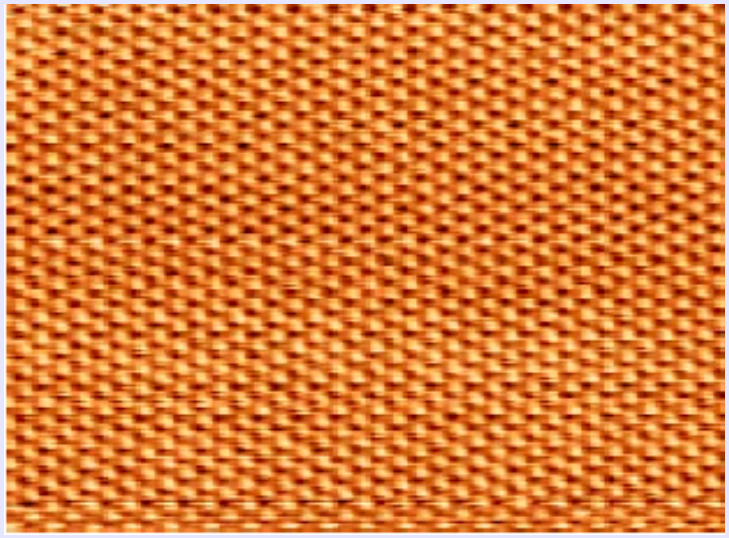
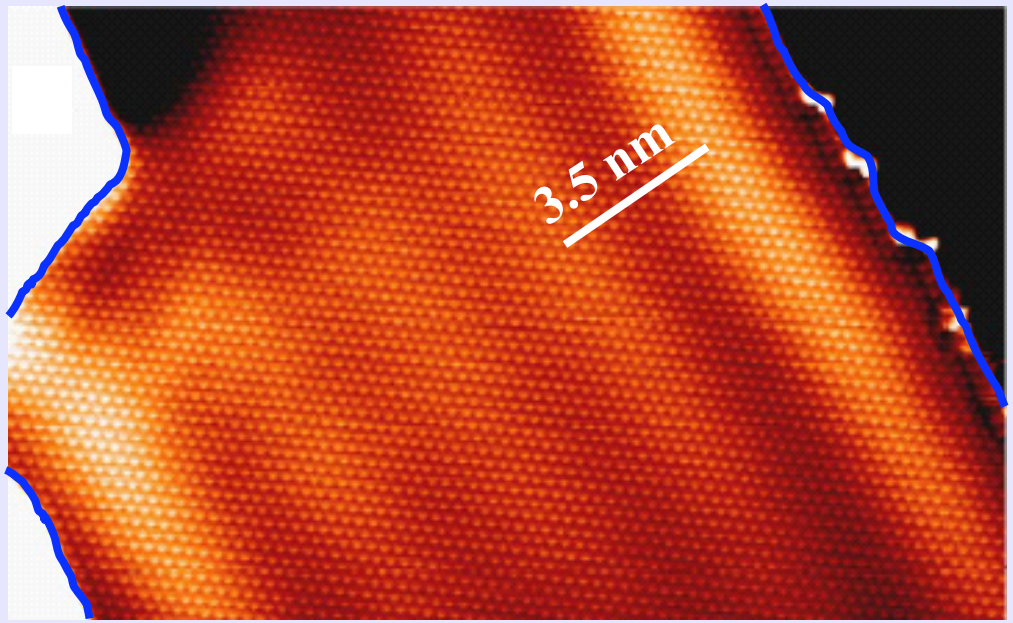


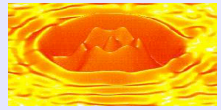
Ag(111) @ 4.8 K;
lattice constant $a = 0.29$ nm.

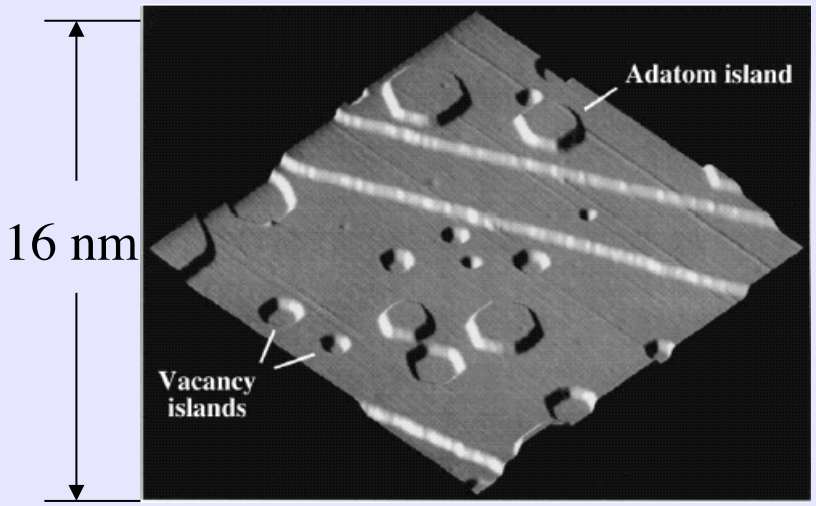
Surface steps: standing wave undulations, repeat distance at E_F ~$\lambda_F/2$.



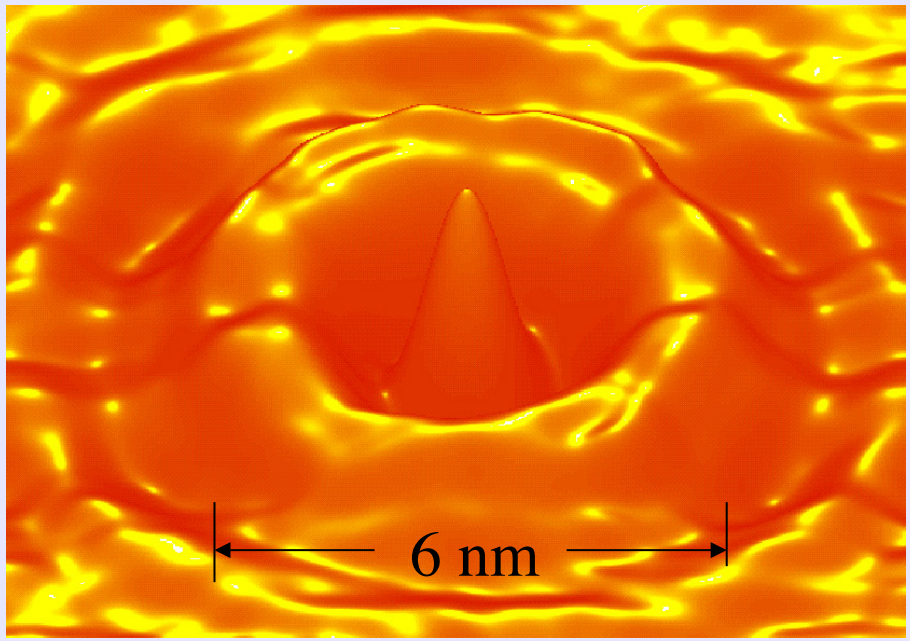
Ag(111) terrace between two surface steps (marked in blue). V_S= +6 mV, I_T = 1.8 nA

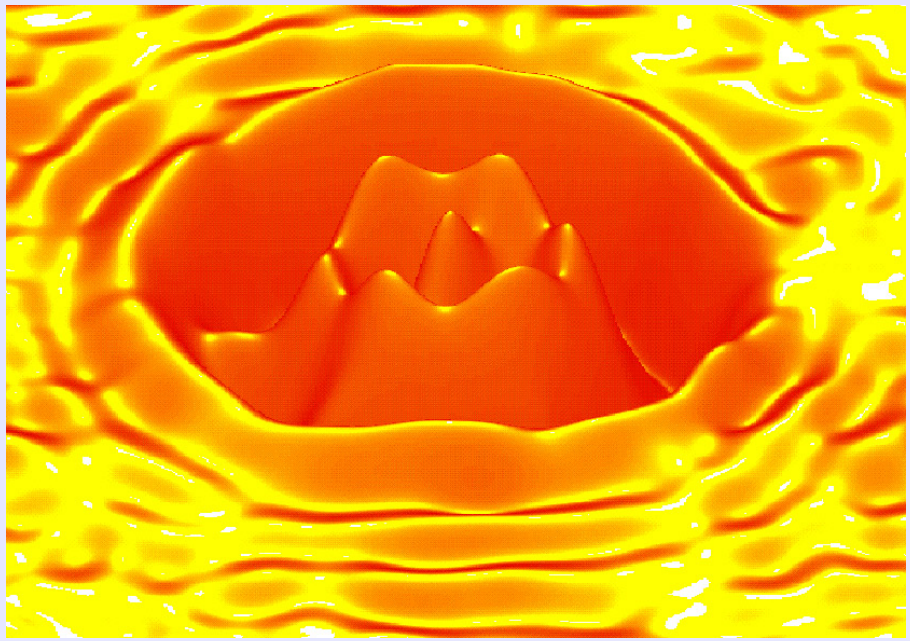
M. Pivetta, F. Silly, F. Patthey, J. P. Pelz, WDS, Phys. Rev B **67**, 193402 (2003)





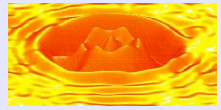
Electron confinement to nanoscale Ag islands: Ag(111)



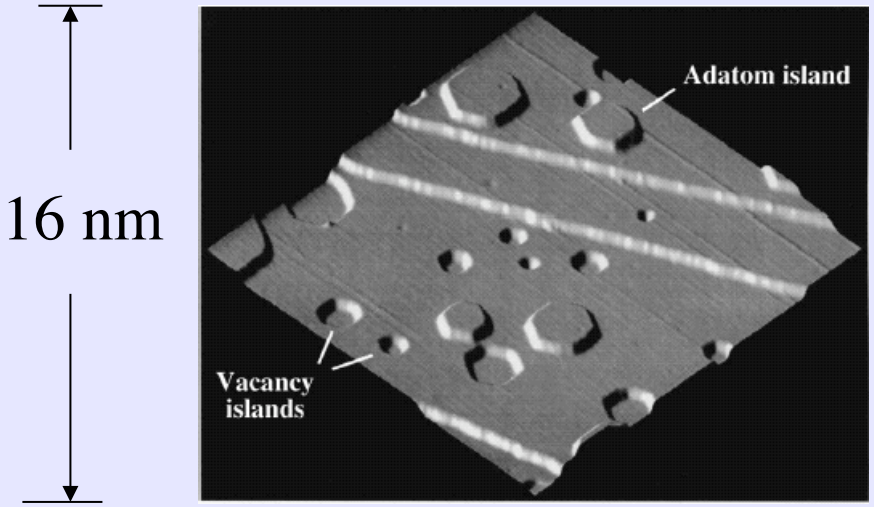


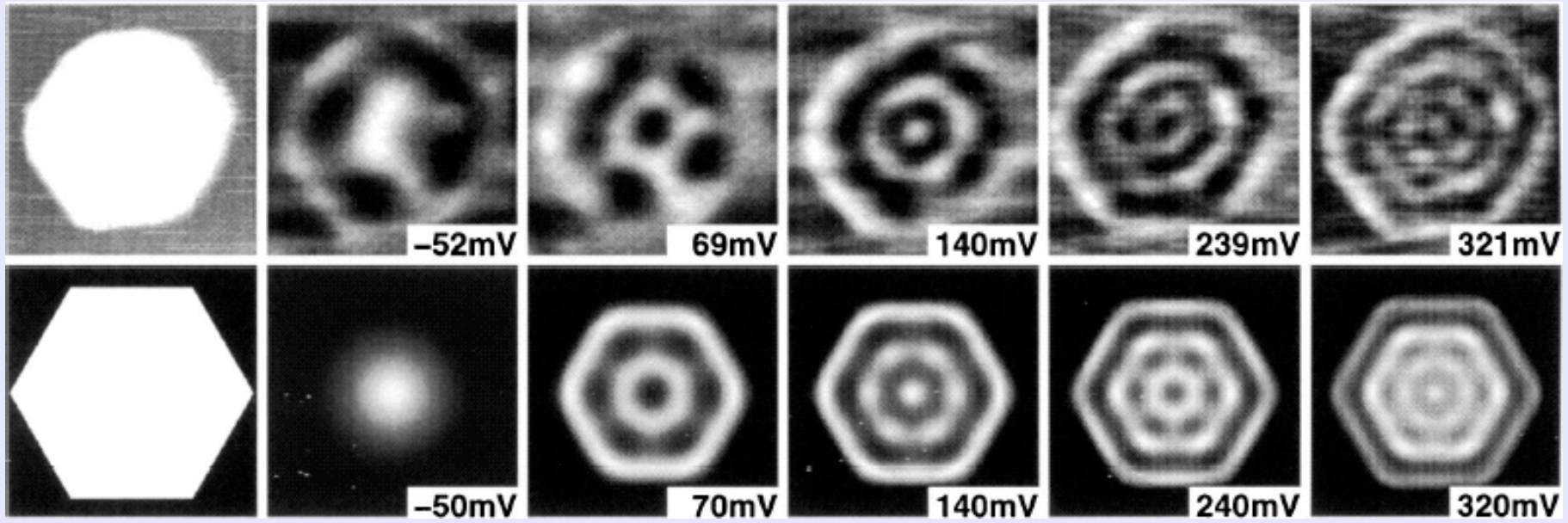
J. Li, PhD thesis, University of Lausanne (1997)

EPFL

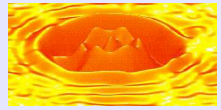


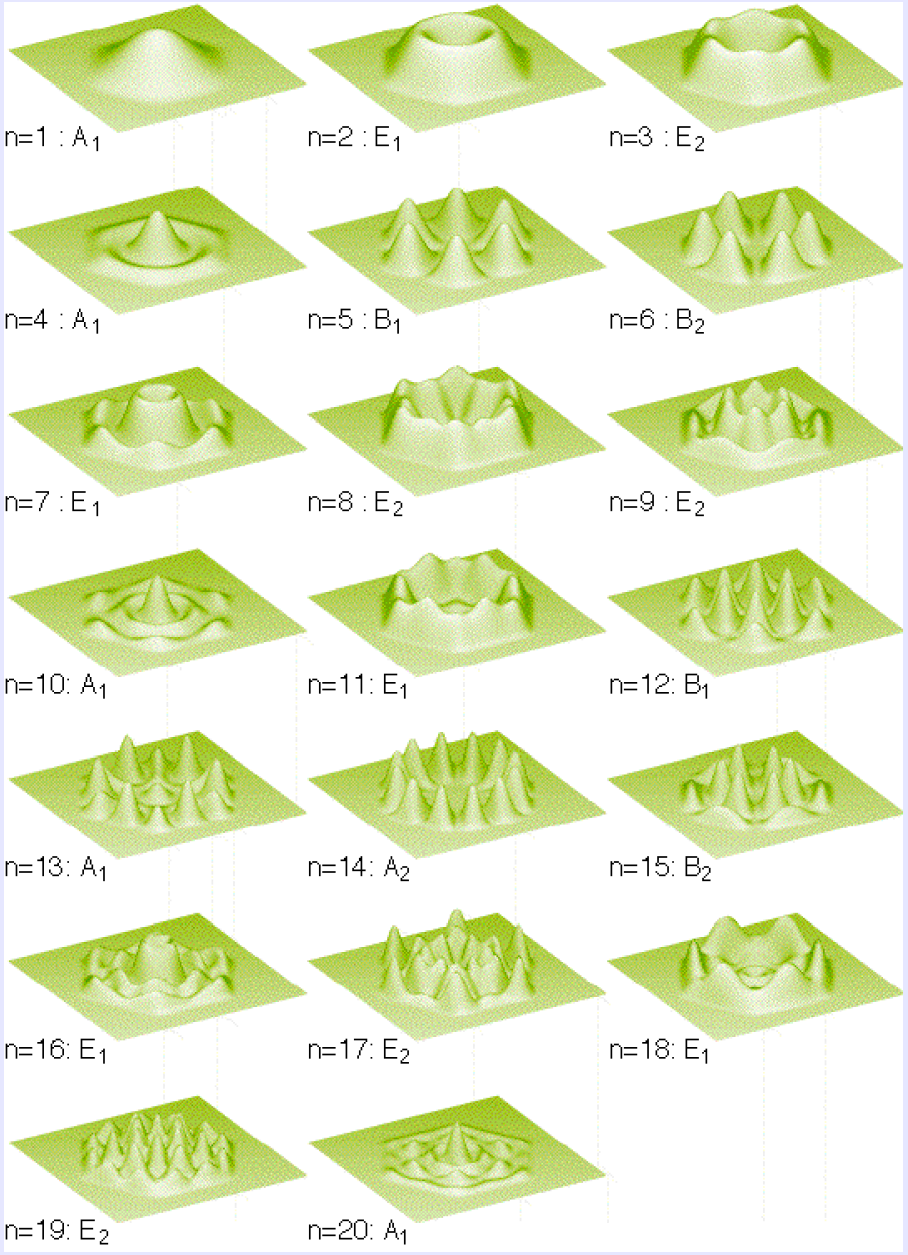
Electron confinement to Ag islands on Ag(111)





J. Li, WDS, R. Berndt, S. Crampin, PRL **80**, 3332 (1998)

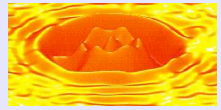




State densities of the lowest Eigenstates of a particle in a hexagonal box

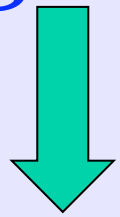
(S. Crampin)

J. Li, WDS, R. Berndt, S. Crampin, Surf. Sci. **422**, 95 (1999)

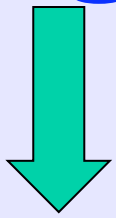


2D electron gas:

Scattering at adatoms



Standing waves



Interaction between adatoms

Long-range interaction between adatoms mediated by substrate electrons

Theory:

T. B. Grimley, Proc. Phys. Soc. **90**, 751 (1967).

T. L. Einstein and J. R. Schrieffer, Phys. Rev. B **7**, 3629 (1973).

➢ K. H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978).

➢ P. Hyldgaard and M. Persson, J. Phys.: Condens. Matter **12**, L13 (2000).

Experiments:

FIM

T. T. Tsong, Phys. Rev. Lett. **31**, 1207 (1973).

F. Watanabe and G. Ehrlich, Phys. Rev. Lett. **62**, 1146 (1989).

STM

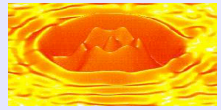
M. N. Kamna, S. J. Stranick, and P. S. Weiss, Science **274**, 119 (1996).

➢E. Wahlström, I. Ekvall, H. Olin, and L. Walldén,
Appl. Phys. A: Mater. Sci. Process. **A66**, S1107 (1998).

➢J. Repp, F. Moresco, G. Meyer, K. H. Rieder, P. Hyldgaard, and M. Persson,
Phys. Rev. Lett. **85**, 2981 (2000).

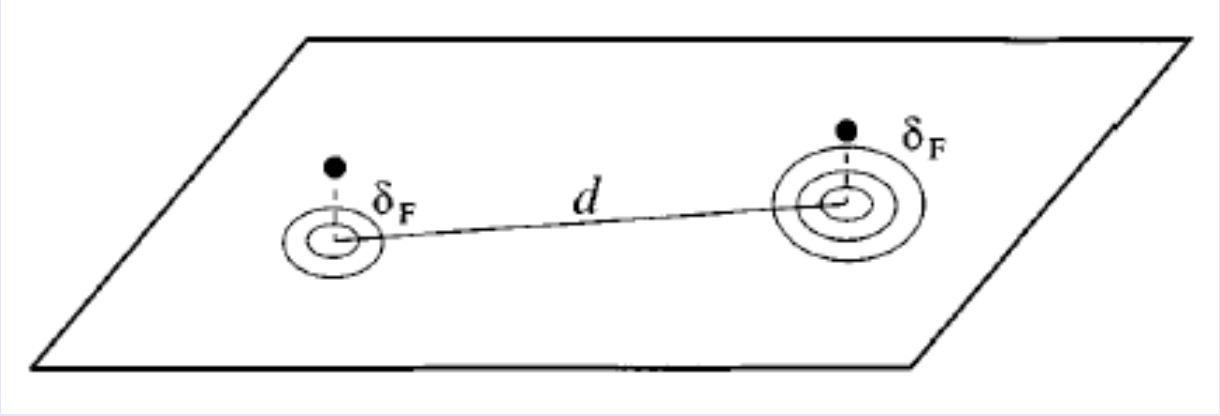
➢N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, and K. Kern,
Phys. Rev. B **65**, 115420 (2002).

But: No self-organisation of an adatom superlattice!

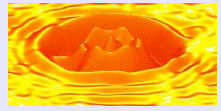


Indirect long-range oscillatory interactions between adsorbed atoms mediated by surface state electrons

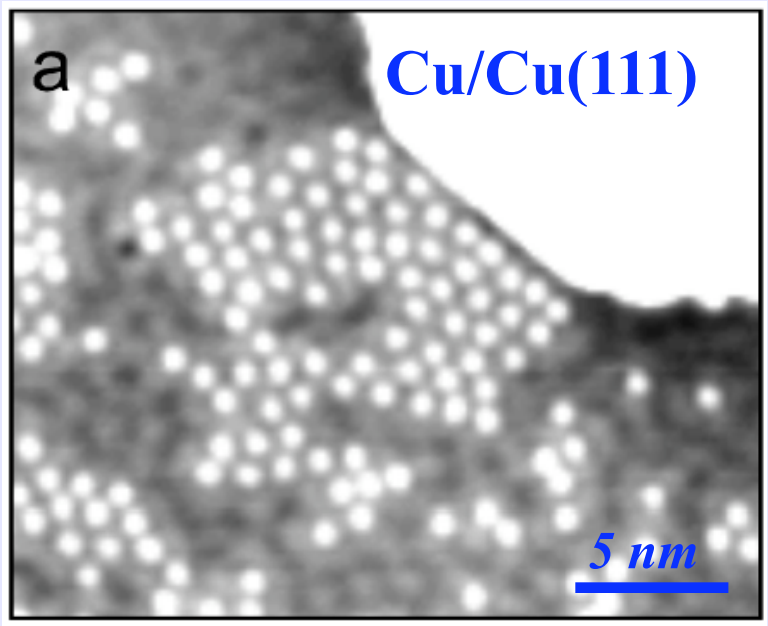
K. H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978)



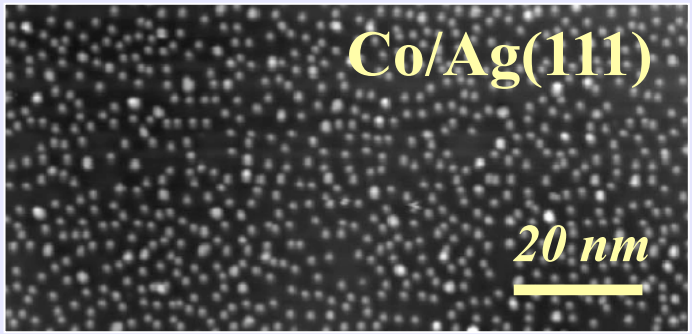
$$\Delta E_{int} \sim \cos(2k_F d + \delta_F)/d^2$$

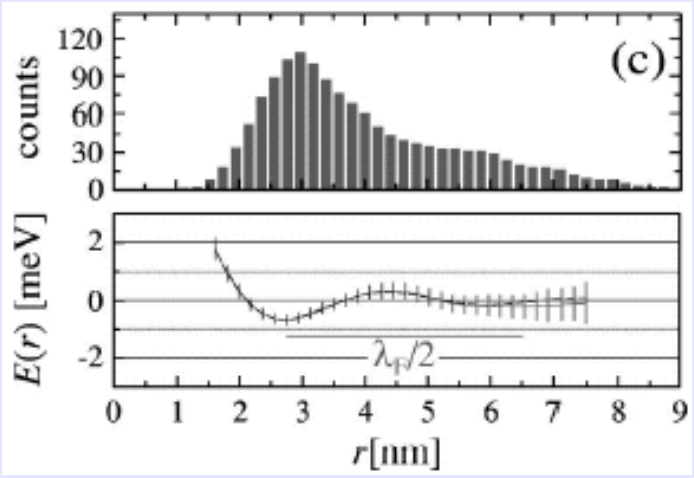


Experimental evidence of this adatom-adatom interaction:



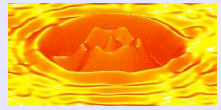
J. Repp, F. Moresco, G. Meyer, K.
H. Rieder, P. Hyldgaard,
M. Persson,
Phys. Rev. Lett. **85**, 2981(2000)



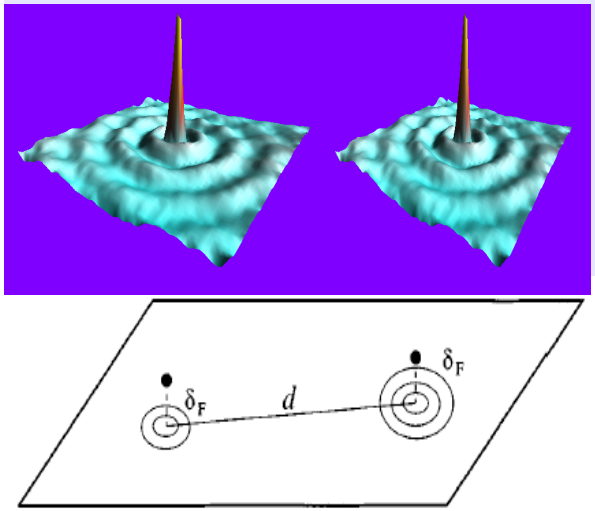


N. Knorr, H. Brune, M. Epple,
A. Hirstein, M. A. Schneider, K. Kern,
Phys. Rev. B **65**, 115420 (2002)

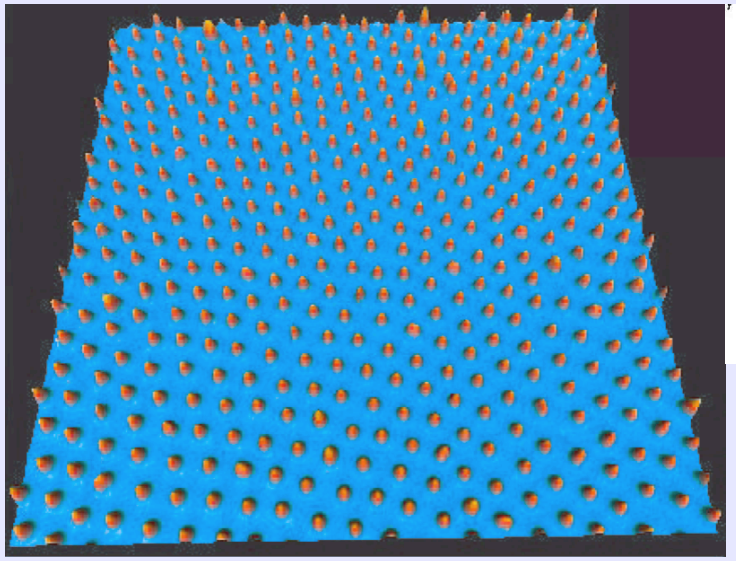
Spatial correlations and some local ordering observed, but attempts to create an extended adatom superlattice were not successful

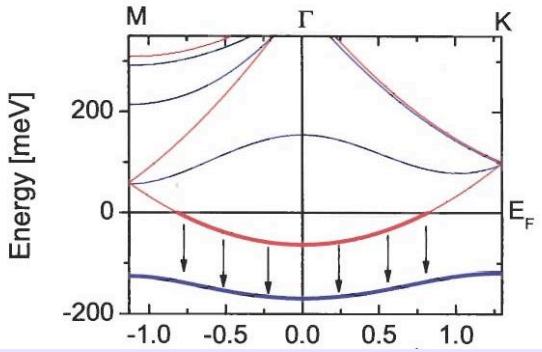


Self-Assembled Adatom Superlattice Created by Surface State Electrons: Ce on Ag(111)



$\Delta E_{int} \sim \cos(2k_F d + \delta_F)/d^2$





64 nm^2, 100mV, 10pA
T = 3.9 K

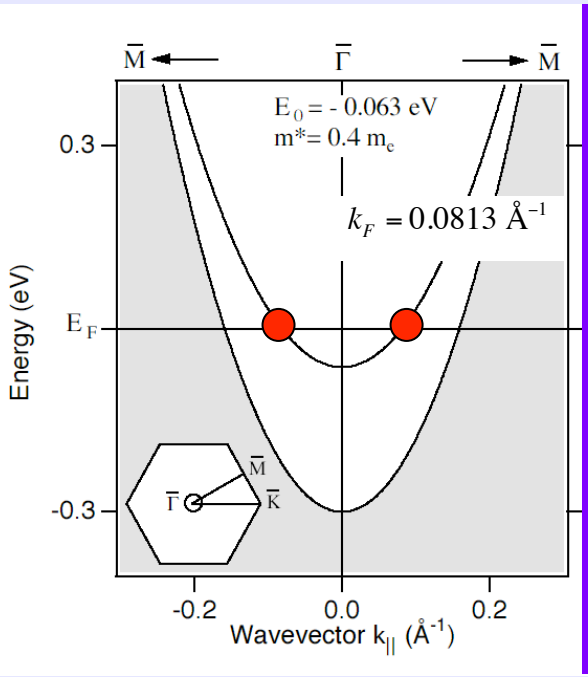
F. Silly, M. Ternes, M. Pivetta, F. Patthey, J. P. Pelz, WDS, Phys. Rev. Lett. **92**, 016101 (2004)

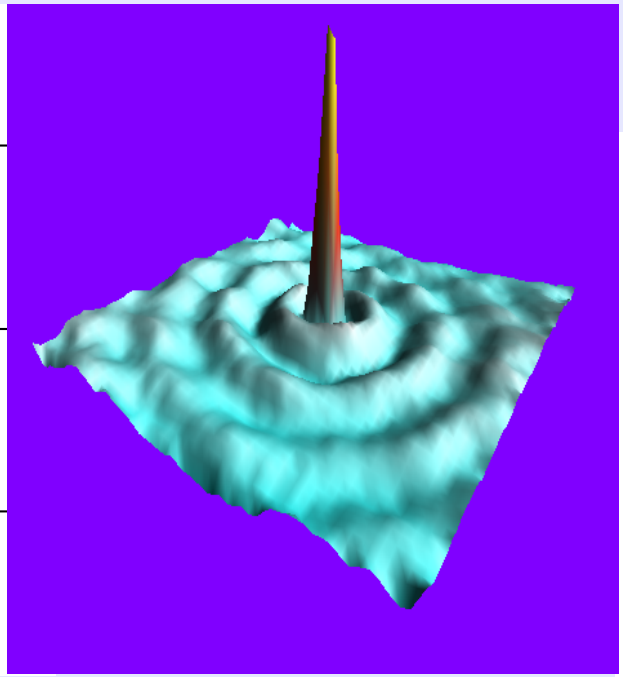
M. Ternes, M. Pivetta, F. Patthey, J. P. Pelz, C. Weber, Th. Giamarchi, F. Mila, WDS, Phys. Rev. Lett. **93**, 146805(2004)

EPFL

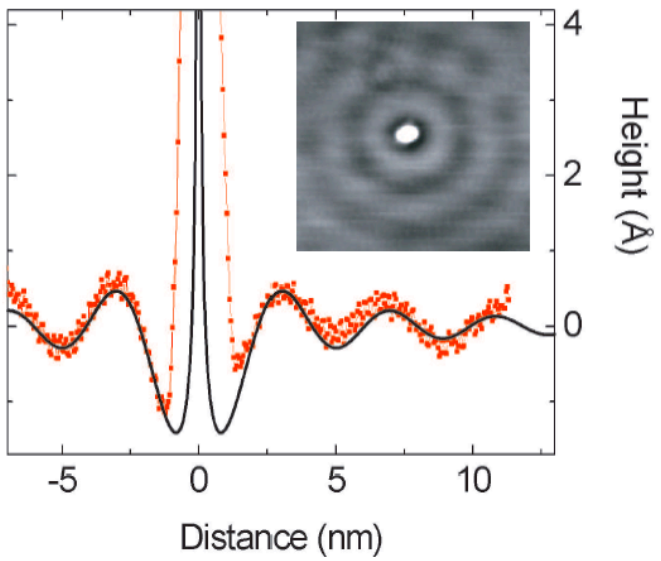
Standing wave pattern at a point defect: Ce on Ag(111)

Phase shift δ_0





210 Å x 210 Å
V = -3 mV, I = 19 pA
T = 3.9 K



$$\Delta D(r) \propto \frac{1}{k_F r}\left(\cos^2(k_F r - \frac{\pi}{4} + \delta_0) - \cos^2(k_F r - \frac{\pi}{4})\right)$$

$\Rightarrow$

$\lambda_F = 2\pi / k_F$

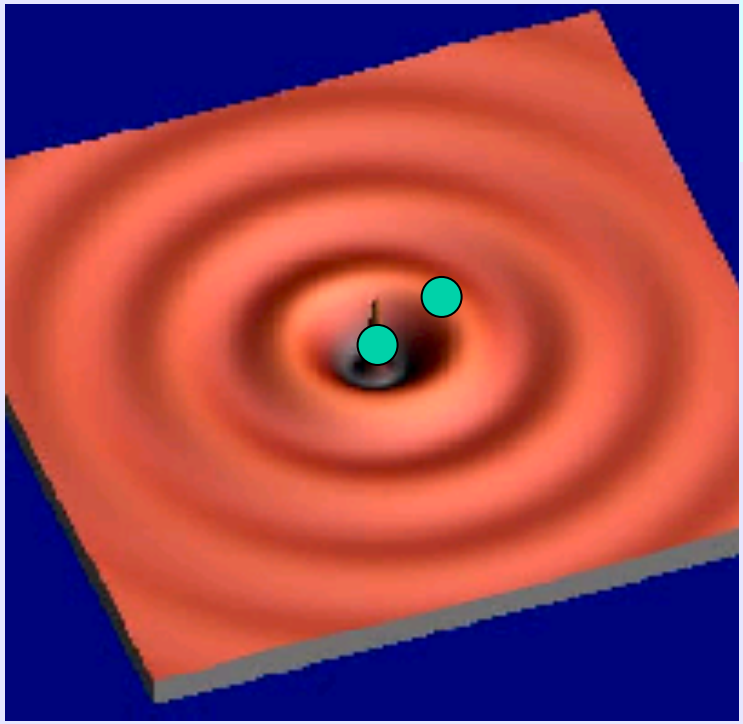
$\lambda_F / 2 = 3.8$ nm

$\delta_0 = (0.37 \pm 0.05)\pi$

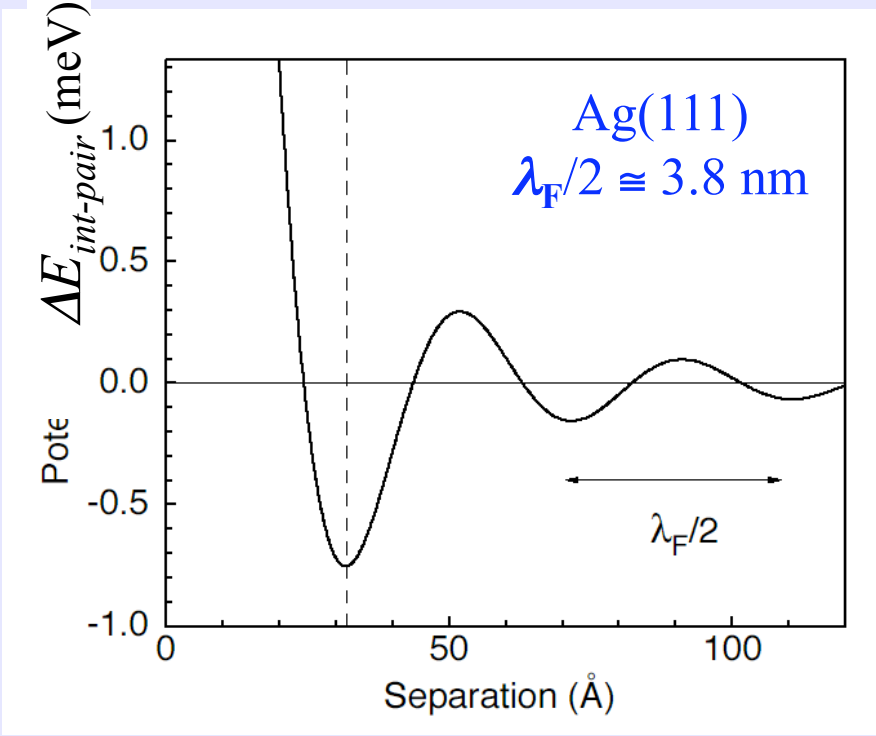
first maximum: 3.2 nm

Physical origin of interaction: 1st adatom creates ripples in 2DEG

Hyldgaard and Persson, J. Phys. Condens. Matter **12**, L13 (2000):



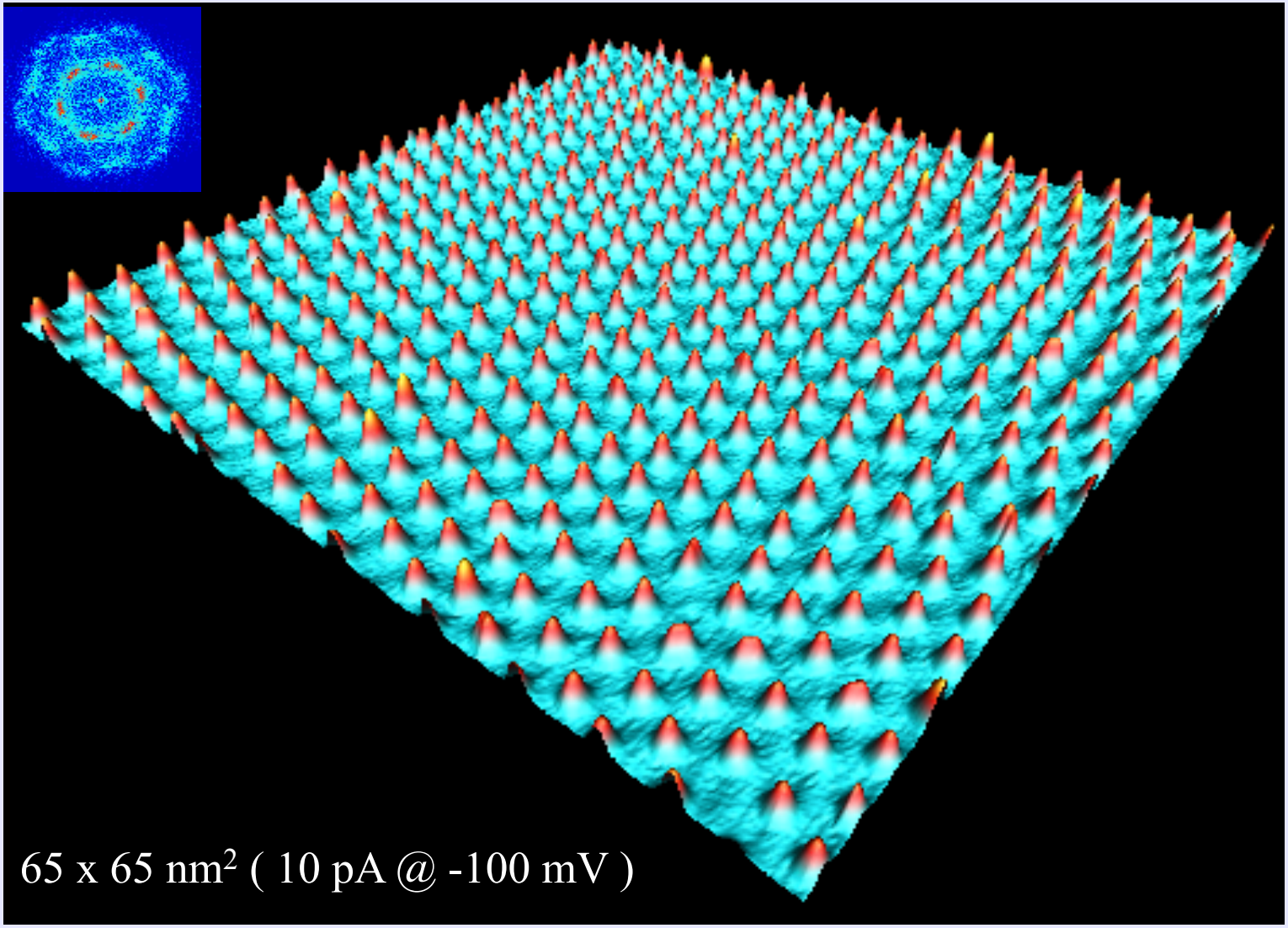
$$\Delta E_{\text{int}-pair}(d) \cong -AE_0\left(\frac{2\sin(\delta_0)}{\pi}\right)^2 \frac{\sin(2k_F d + 2\delta_0)}{(k_F d)^2}$$



2nd adatom has lowest energy at a "crest" (maximum electron density)

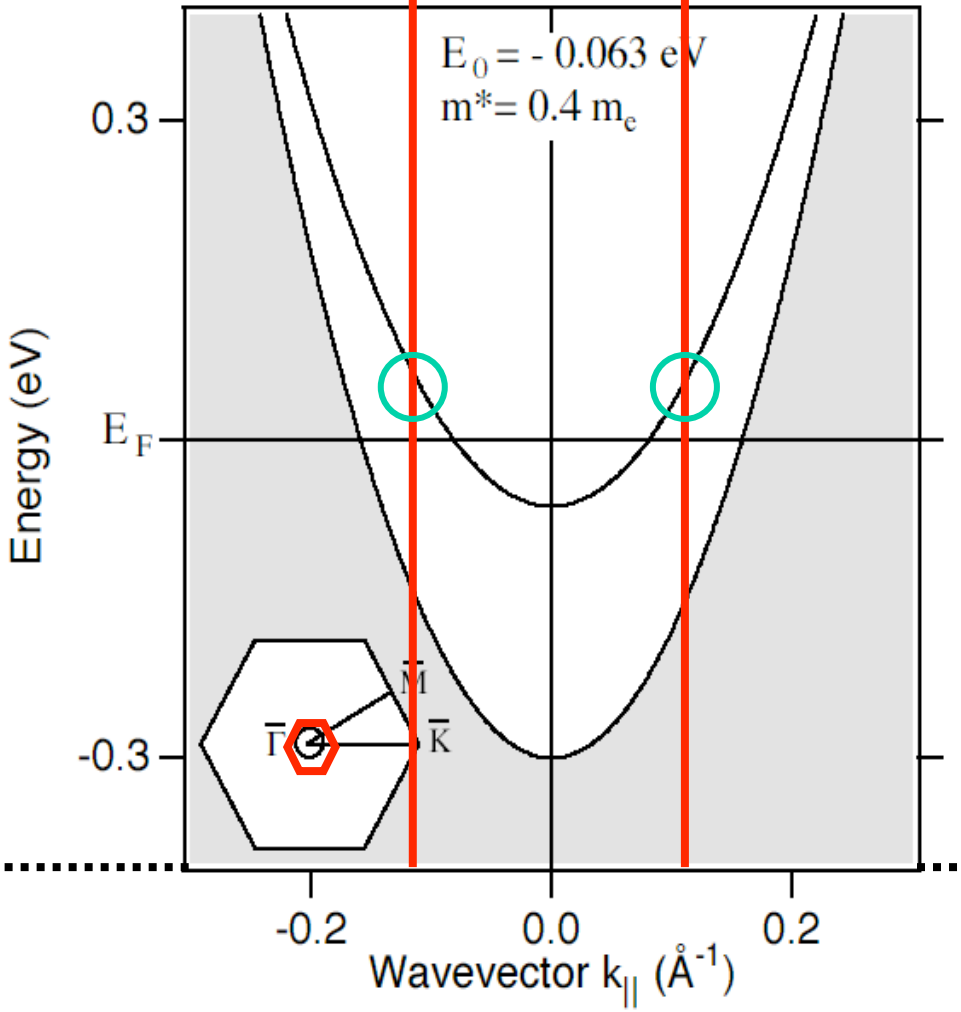
Cu(111) : $\lambda_F/2 \cong 1.4$ nm

Ce adatom superlattice at 3.9 K



Mini-Brillouin zone within Ag(111) surface Brillouin zone

M: 12,5 nm^{-1} ← $\bar{\Gamma}$ → K: 14,4 nm^{-1}

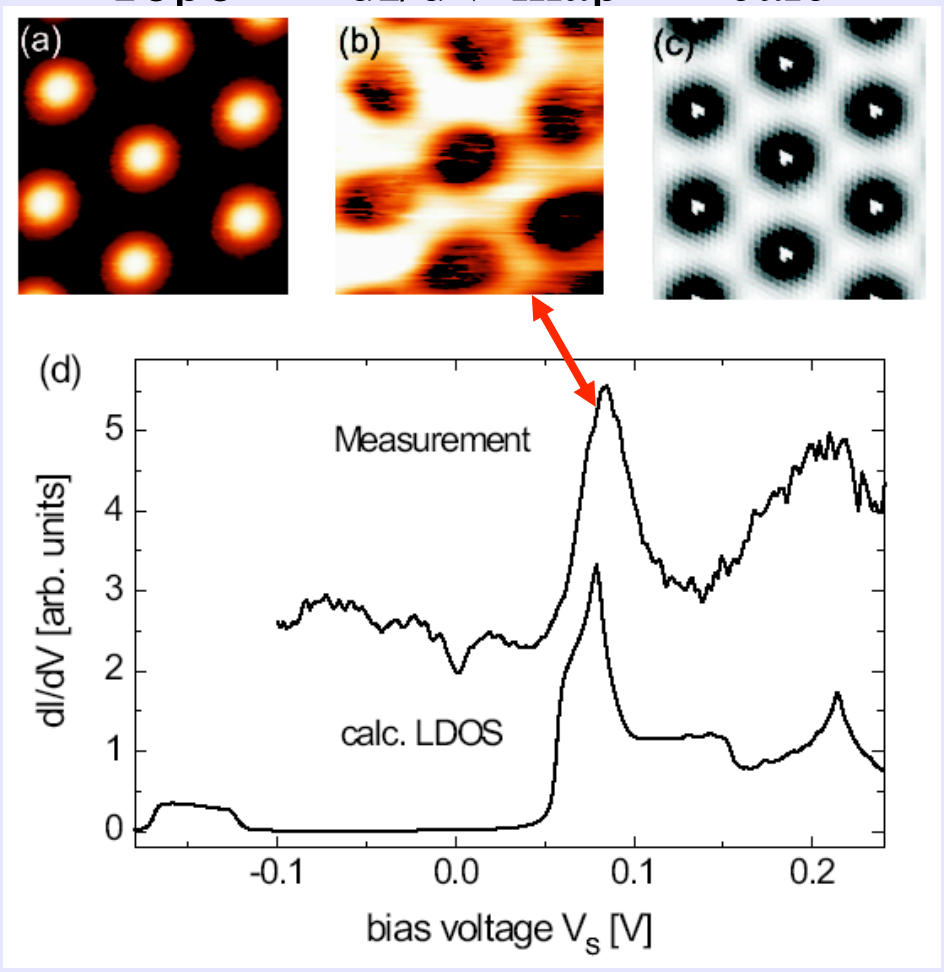


1.25 $Å^{-1}$ ..... 1.44 $Å^{-1}$

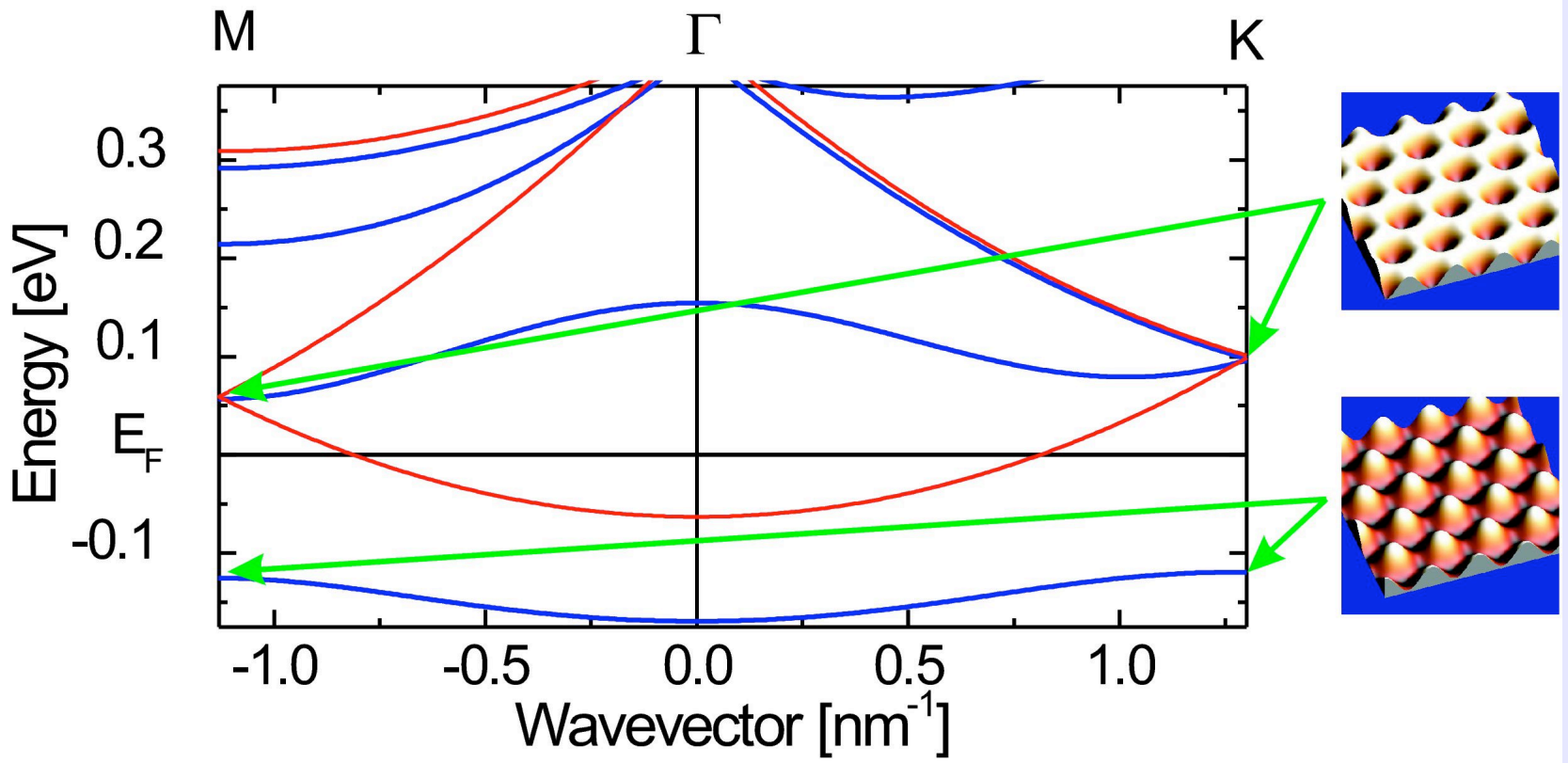
Electronic structure within the superlattice (d = 3.2 nm): Experiment and model

Topo dI/dV-map calc

7.5 x 7.5 nm^2

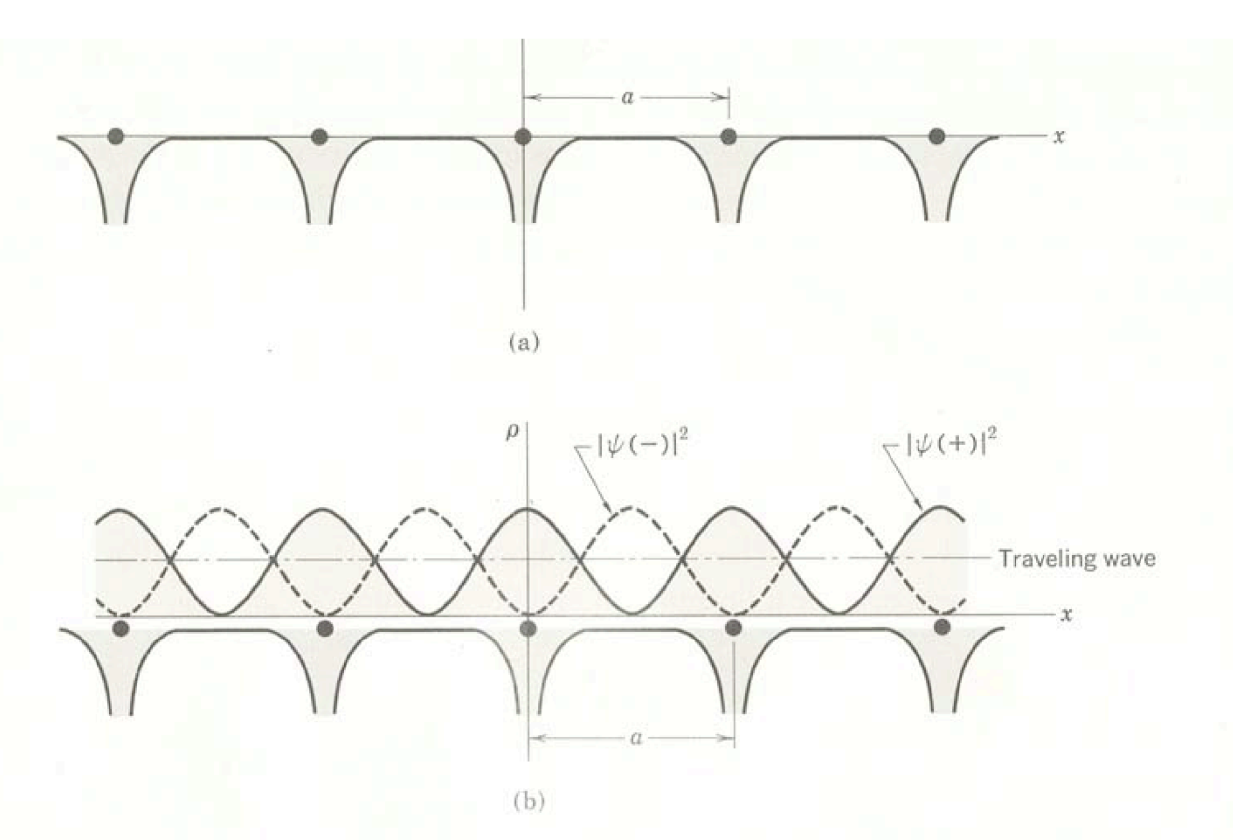


First Brillouin zone of the 2D superlattice



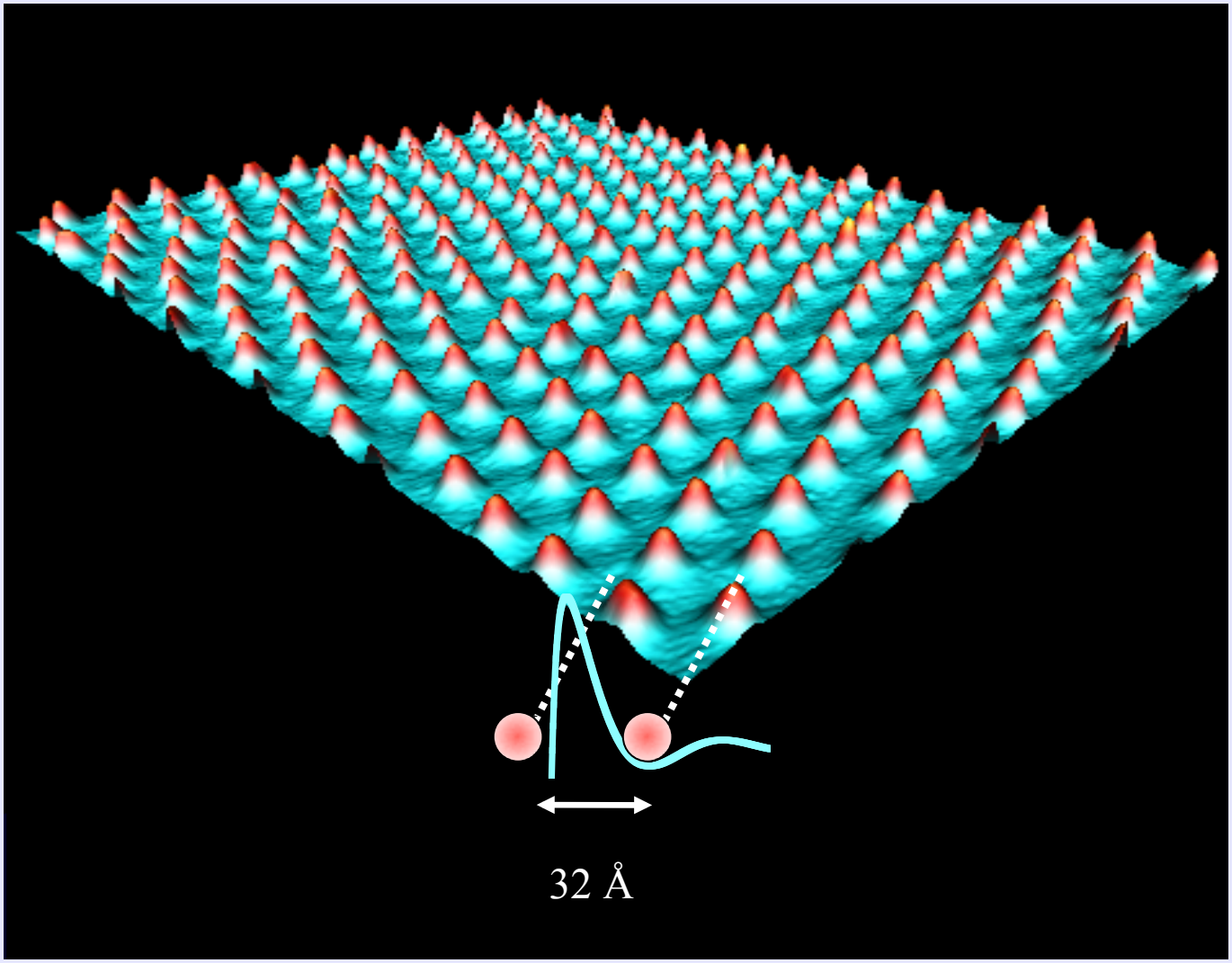
Interaction potential: Gaps open at high symmetry points

Origin of the energy gap



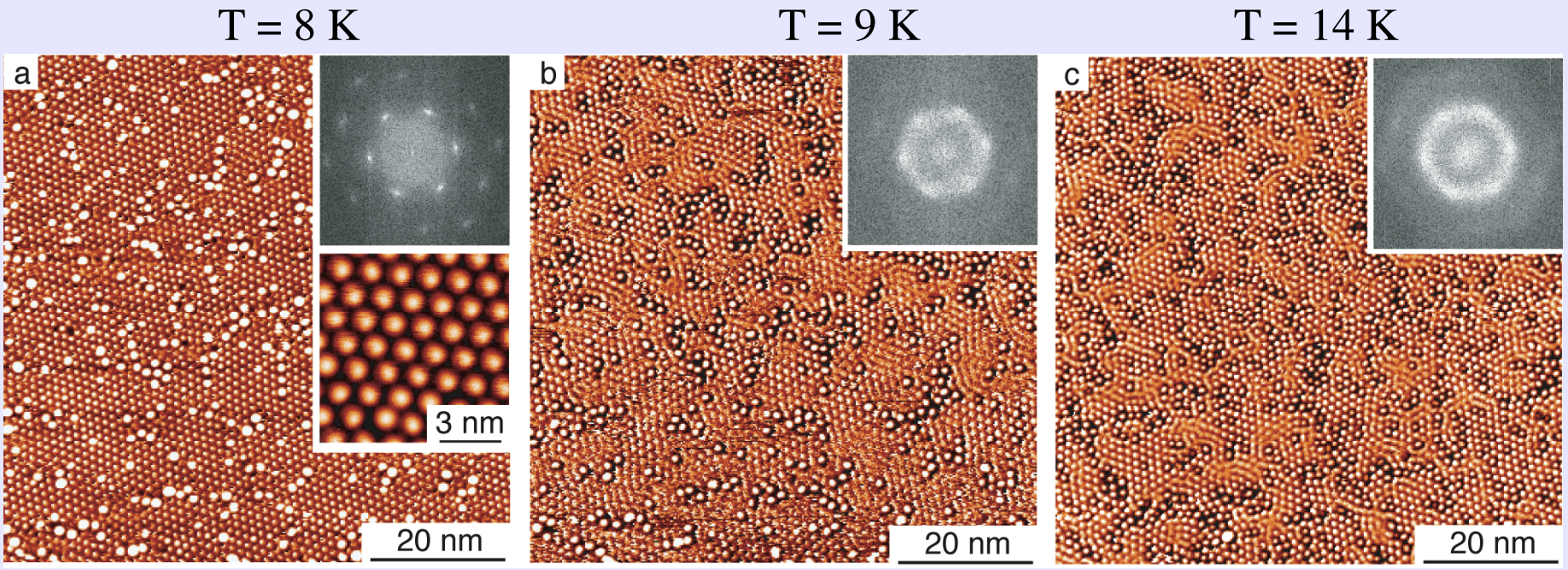
C. Kittel, Introduction to Solid State Physics, 4th Edition, J. Wiley (1971), p.298

2D superlattice of magnetic Ce adatoms on Ag(111): A Kondo lattice ?



M. Ternes, A. J. Heinrich, WDS, J. Phys.: Condens. Matter **21**, 053001 (2009)

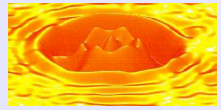
Melting of 2D adatom superlattices stabilized by long-range electronic interactions: Ce/Cu(111)



Ce nearest-neighbour distance: **1.4 nm**

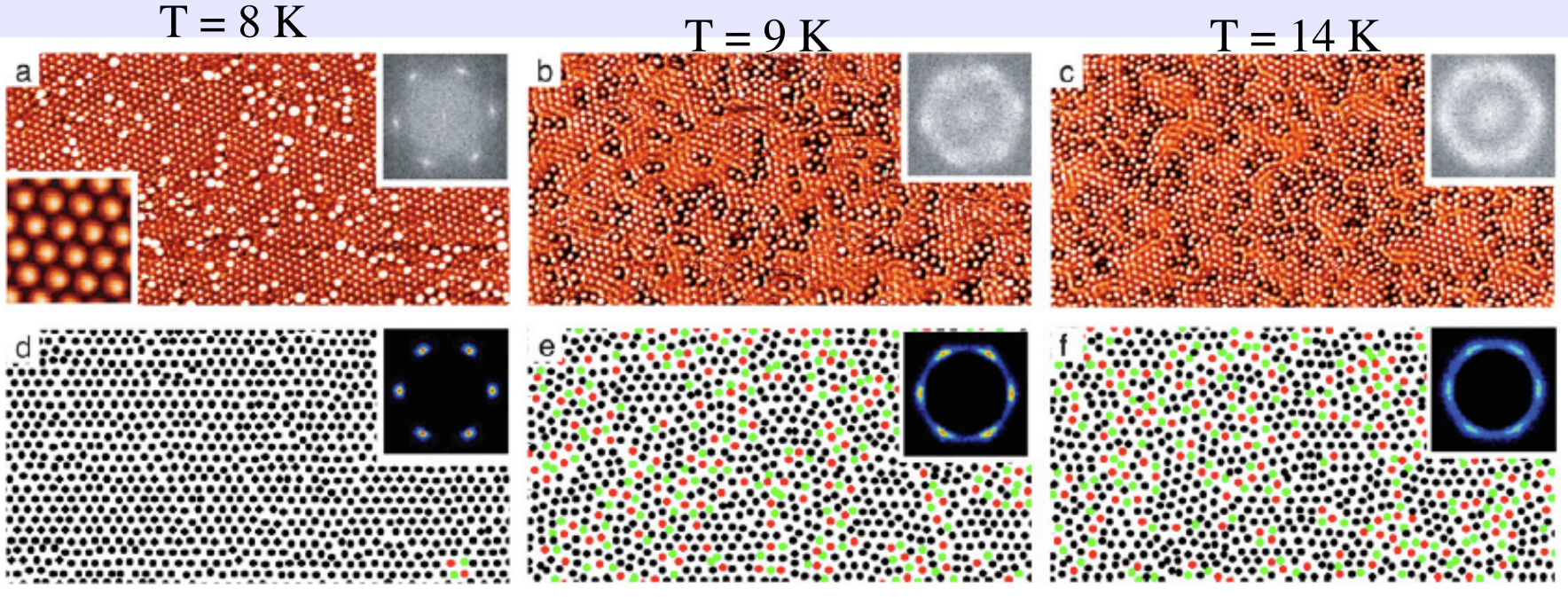
Fermi wave length of the surface state electrons on Cu(111): $\lambda_F/2 \cong 1.4$ nm

N. N. Negulyaev, S. Stepanyuk, L. Niebergall, P. Bruno,
M. Pivetta, M. Ternes, F. Patthey, WDS, PRL **102**, 246102 (2009)



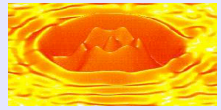
Melting of an adatom superlattice: Ce/Cu(111)

Experiment and theory



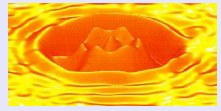
In the presence of a weak substrate potential, the superlattice melts by a direct transition from the solid to the liquid phase, as predicted by Kosterlitz, Thouless, Halperin and Nelson

N. N. Negulyaev, S. Stepanyuk, L. Niebergall, P. Bruno,
M. Pivetta, M. Ternes, F. Patthey, WDS, PRL **102**, 246102 (2009)

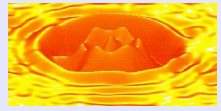


Creation, electronic structure, and melting of a two-dimensional adatom superlattice stabilized by long-range electronic interactions

M. Ternes, M. Pivetta, F. Patthey, WDS,
Progr. Surf. Sci., (December 2009)



Electron confinement to nanoscale structures: Quantum-size effects in Pb-islands on Si(111)



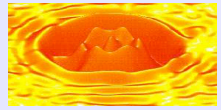
Pb/Si(111) ultrathin nanocrystals:

- **Electron dynamics of quantum well states**

I-Po Hong, C. Brun, F. Patthey, I. Yu. Sklyadneva, X. Zubizarreta, R. Heid, V. M. Silkin, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, WDS, PRB **80**, 081409 (2009) (RC)

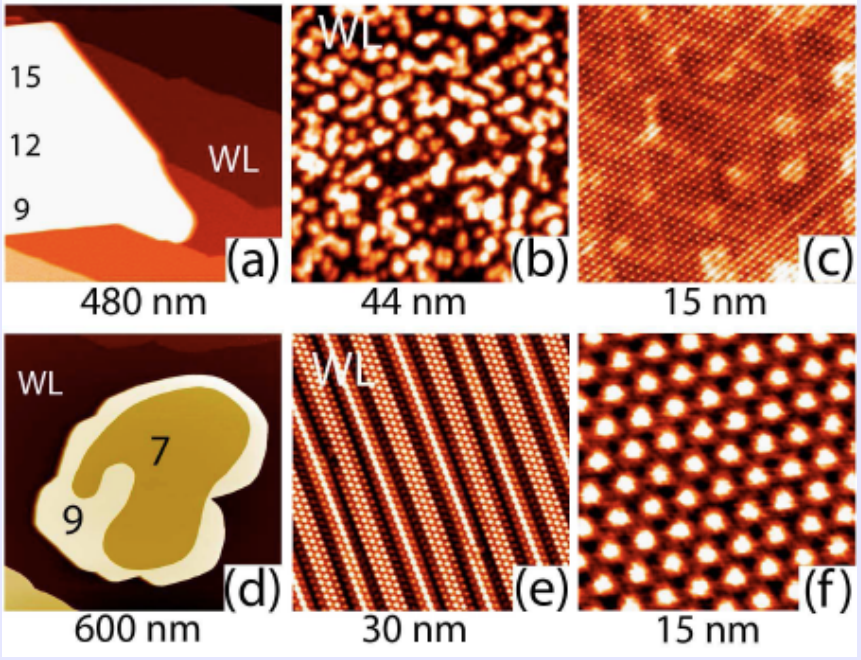
- **Reduction of the superconducting transition temperature**

C. Brun, I-Po Hong, F. Patthey, I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, WDS, Phys. Rev. Lett. **102**, 207002, (2009)

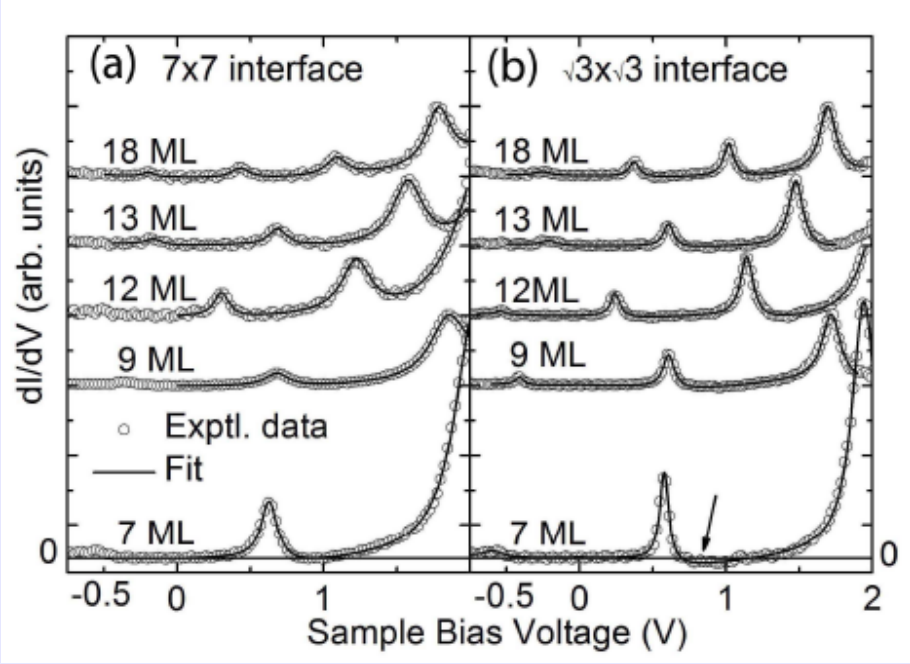


Quantum-well states

Pb/Si(111)7x7



disordered crystalline



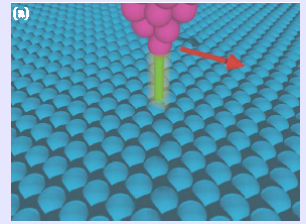
Pb/Pb-√3x √3/Si(111)

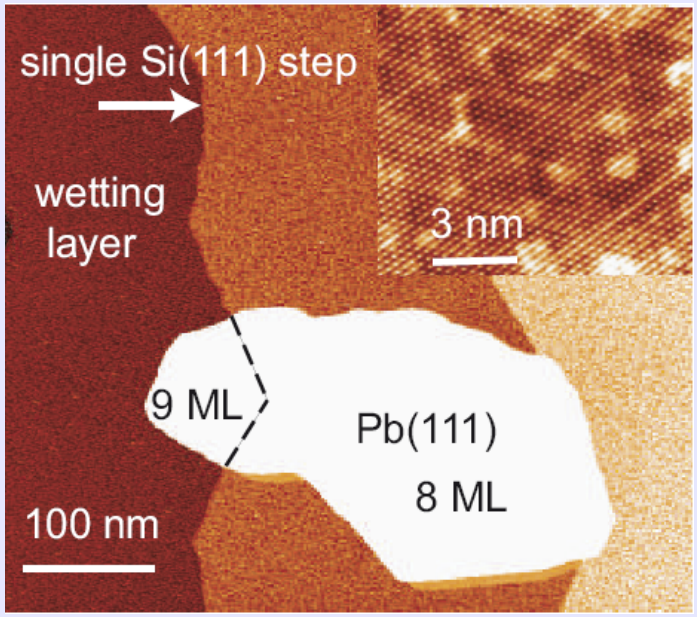
T = 5 K

I-Po Hong, C. Brun, F. Patthey, I. Yu. Sklyadneva, X. Zubizarreta, R. Heid, V. M. Silkin, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, WDS, PRB **80**, 081409 (2009) (RC)

EPFL

Reduction of the superconducting gap in ultrathin Pb islands

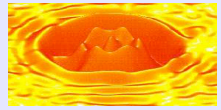




C. Brun, I-Po Hong, F. Patthey, I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, WDS,

(Lausanne, San Sebastian, Karlsruhe)

Phys. Rev. Lett. **102**, 207002, (2009)



Contradictory experimental results:

- Transport, magnetic susceptibility:

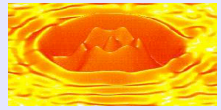
  T_c decreases

  with decreasing film thickness

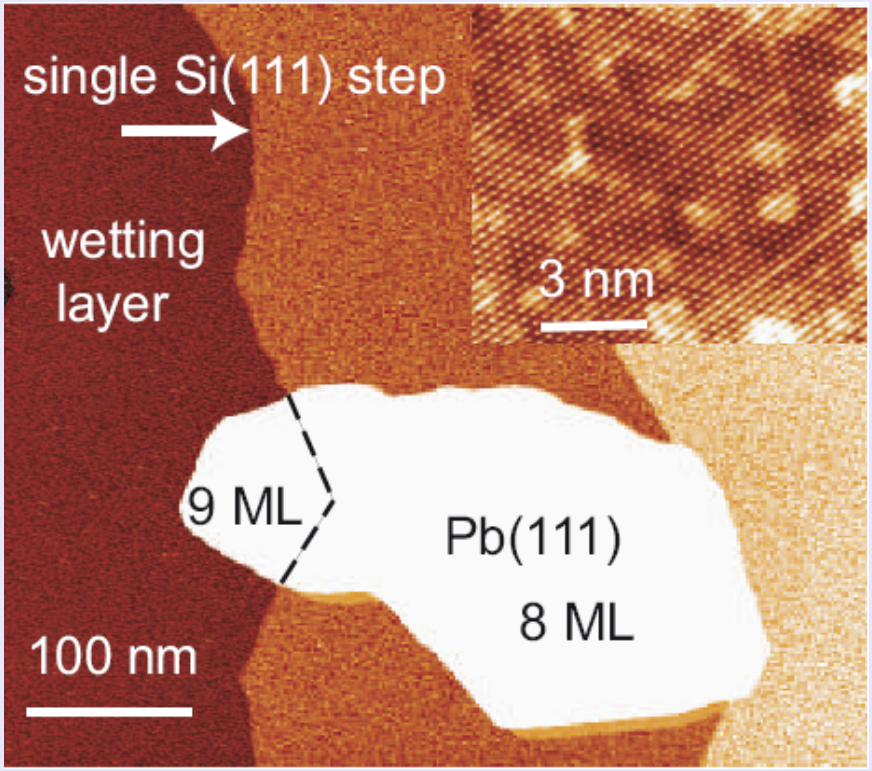
- STS:

  T_c stays constant

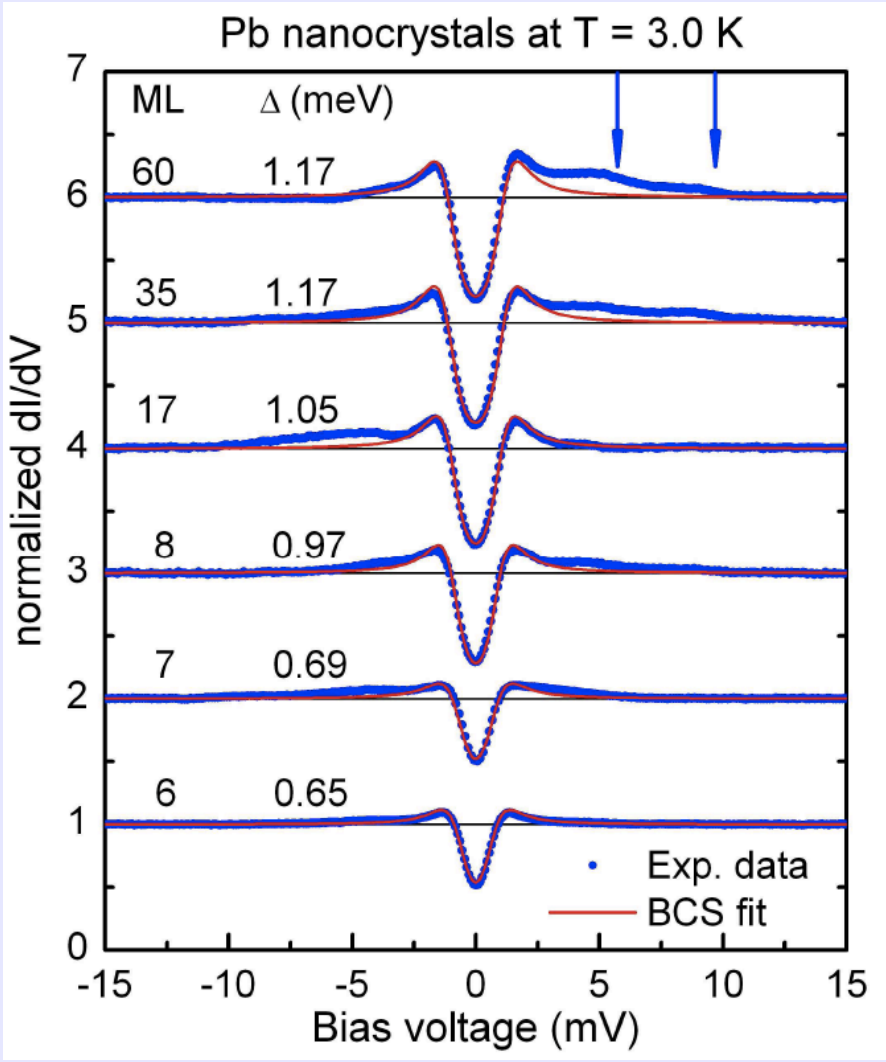
  with decreasing film thickness



Pb- islands: Thickness dependent dI/dV spectra



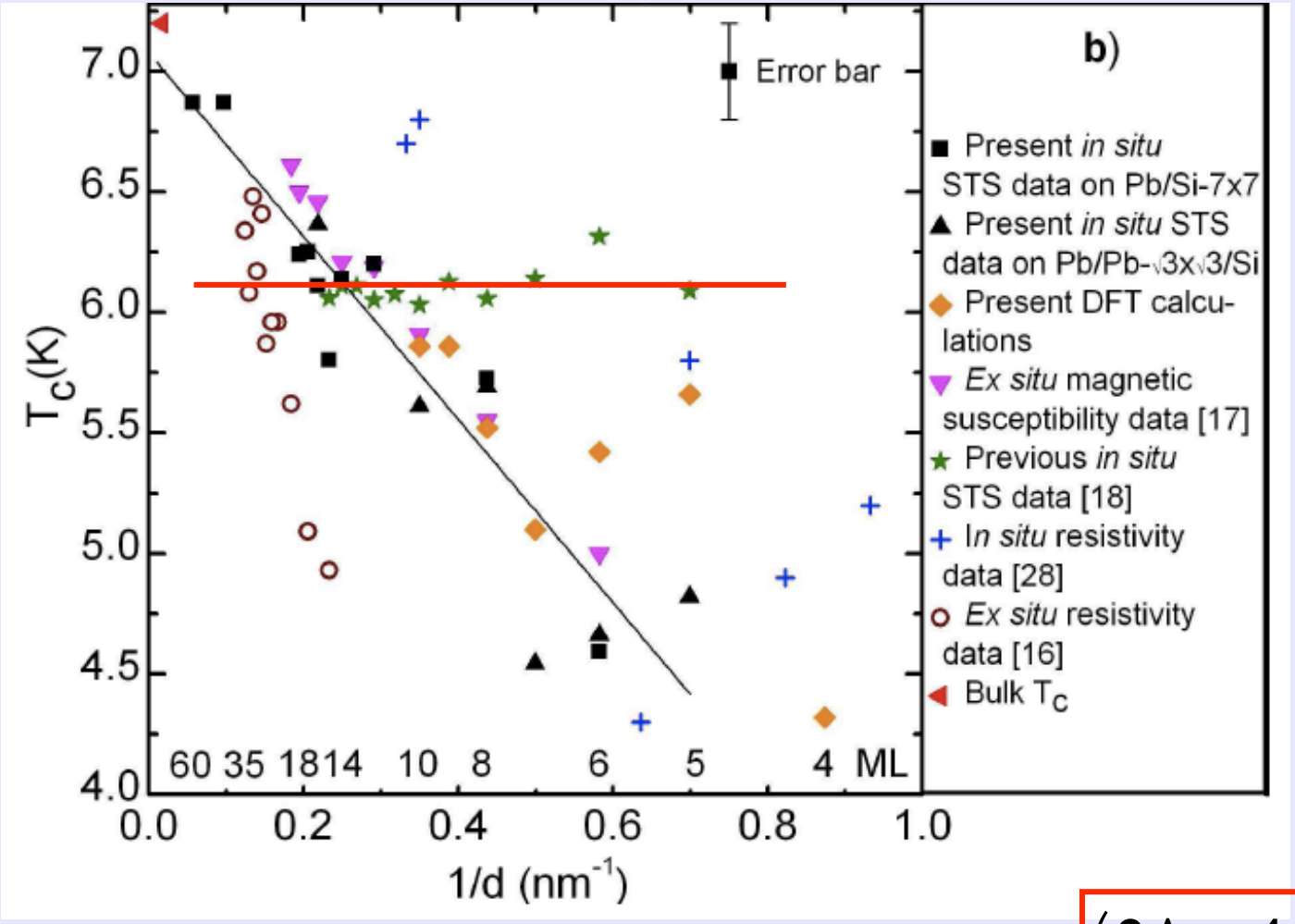
U = -1.0 V; I = 100 pA



C. Brun *et al*., PRL **102**, 207002 (2009)

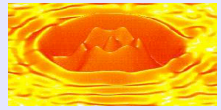
280 μV remaining RF noise

Comparison with literature and theory



Assumption: $\left(2\Delta = 4.19T_c\right)$

C. Brun *et al.*, PRL **102**, 207002 (2009)



Summary

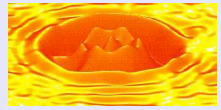
Pb/Si(111)

Study of large ($l > \xi_c$) atomically flat superconducting single crystal islands of atomic-layer defined thickness d

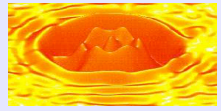
Critical temperature:

- **Reduction of $T_c(d)$ as function of 1/d**
- **DFT: λ reduction with decreasing d**

C. Brun, I-Po Hong, F. Patthey, I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, WDS, PRL **102**, 207002 (2009)



Self-assembly: Rubrene on Au(111)



Motivation

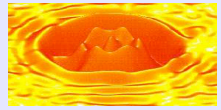
Rubrene

- *Semiconducting, fluorescent, chiral*

  (V. C. Sundar et al., Science **303**, *1644 (2004))*
- *Three-dimensional structure → decoupling*
- *No previous investigations at the nanoscale*

STM and STS

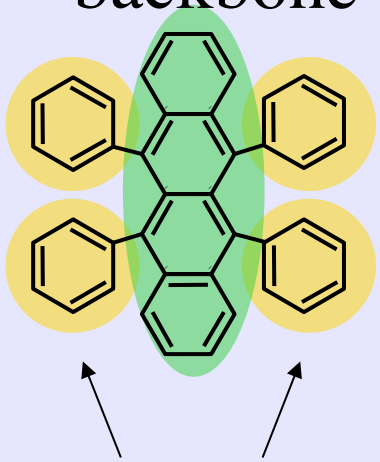
- *Local measurement: single molecules*
- *Simultaneous geometric and electronic analysis*
- *Manipulation experiments*



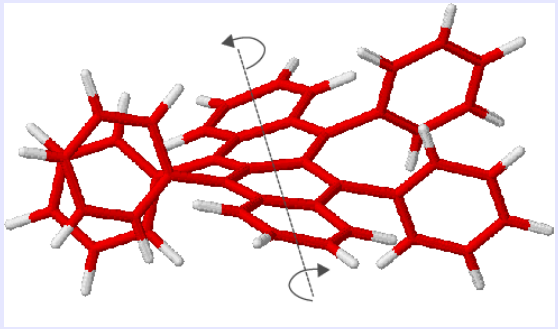
Rubrene

$C_{42}H_{28}$ / 5,6,11,12-tetraphenylnaphthacene

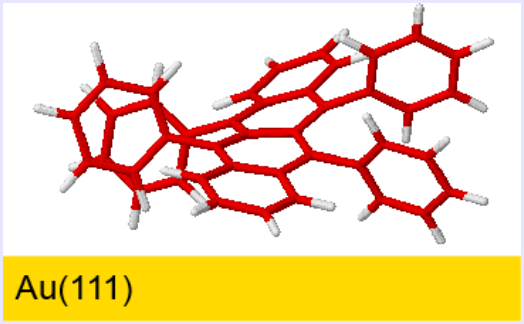
Tetracene backbone



Phenyl groups

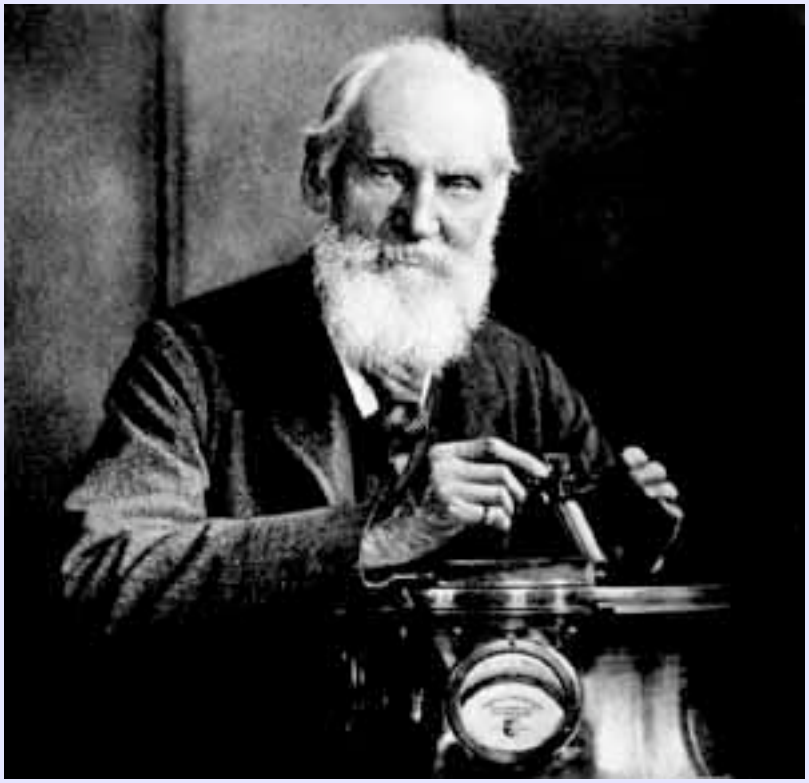


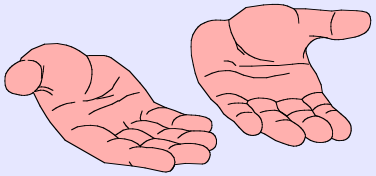
Chirality



Non-planar, chiral adsorption

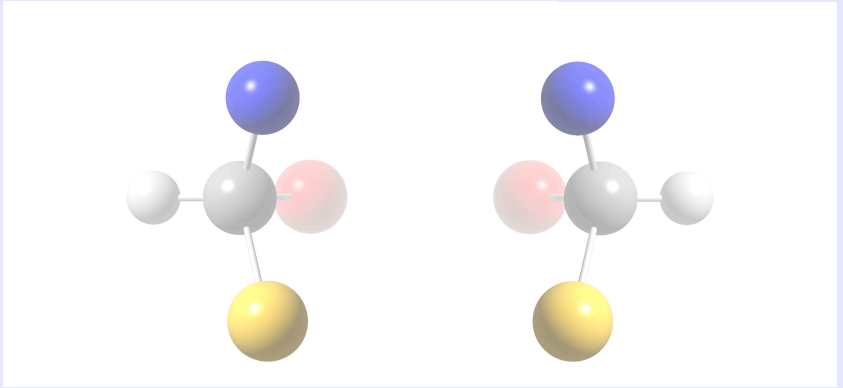
NEXAFS: D. Käfer et al., PRL ***95****, 166602 (2005)*





Chirality

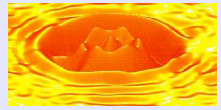
'CHIRAL' from the
Greek word for hands



Lord Kelvin, Baltimore Lectures, 1884

I call any geometrical figure, or group of points, *chiral*, and say that it has chirality, if its image in a plane mirror, ideally realised, cannot be brought to coincide with itself.

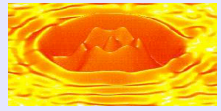
Courtesy of N. V. Richardson



Chirality

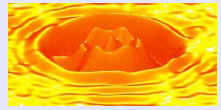
Why investigate the chirality of molecules on surfaces?

"Life" is very sensitive to chirality;
drugs, biosensors, biomaterials,
The origin of life…

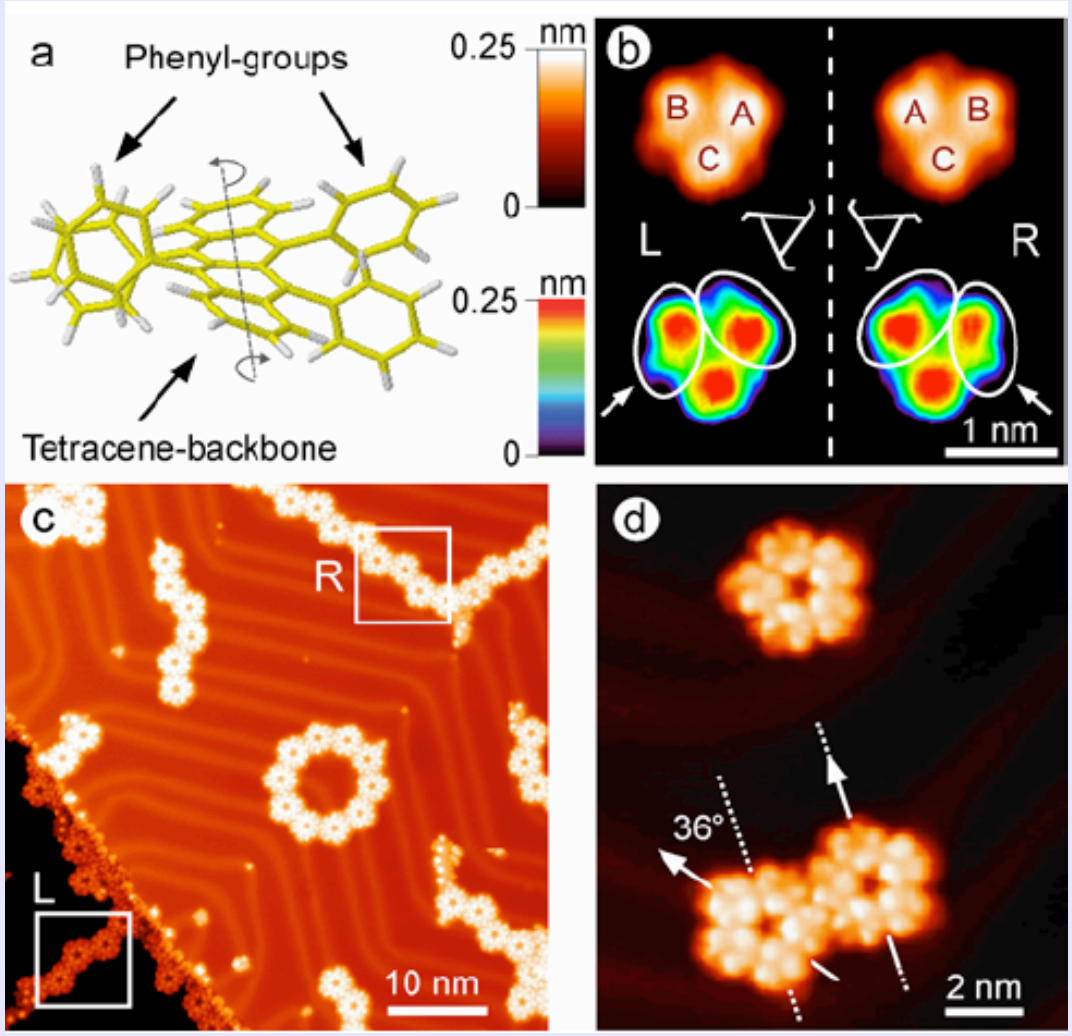


Motivation for a local investigation of chirality in two dimensions:

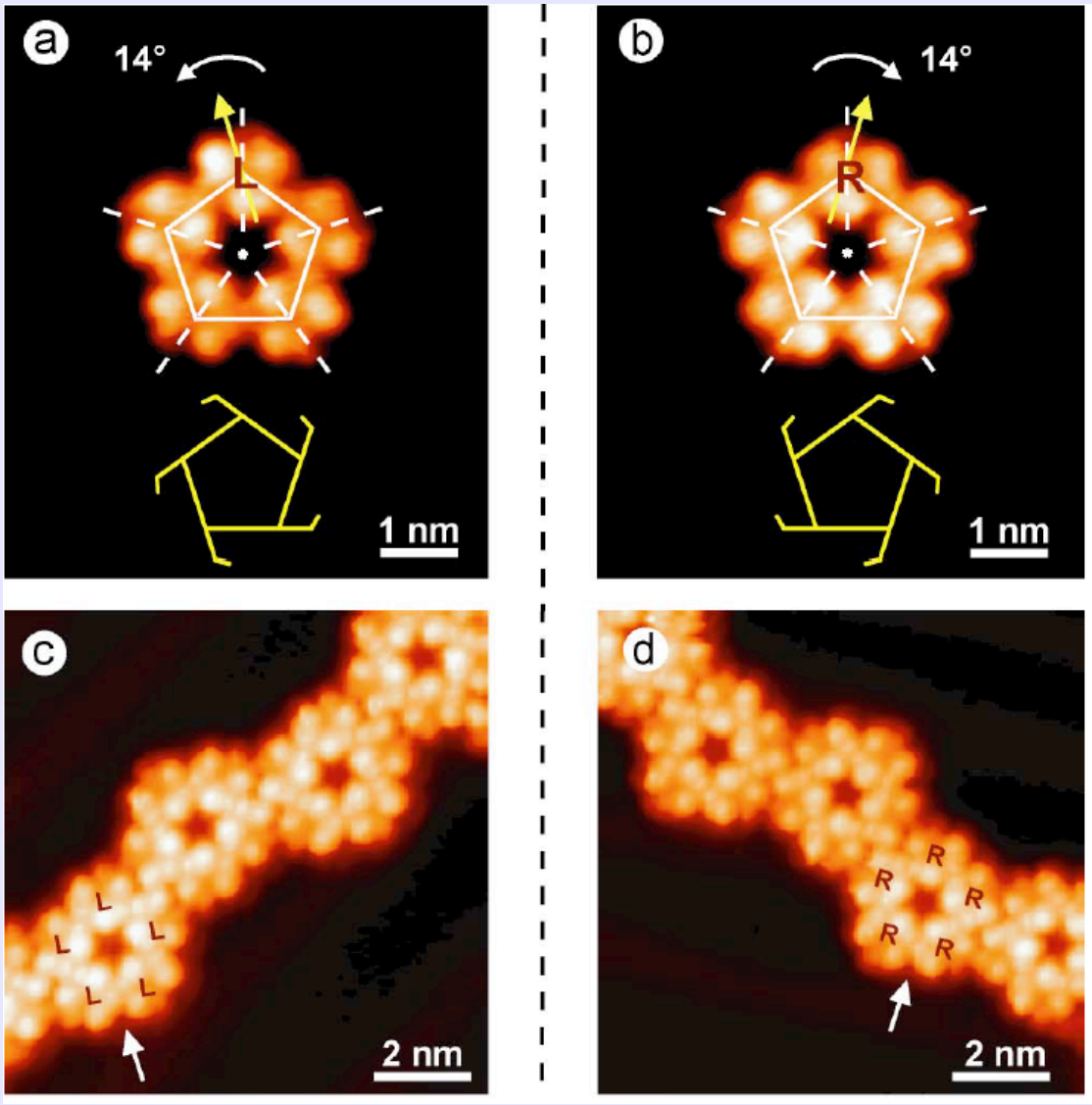
- Chiral Recognition: Chirality of Single Molecules and of Supermolecules
- Enantiomeric Separation on the Nanoscale
- Driving Force for Self-Assembly of Supramolecular Structures



Rubrene on Au(111)



M.-C. Blüm, E. Cavar, M. Pivetta, F. Patthey, WDS,
Angew. Chem. Int. Ed. **44**, 5334 (2005)



Rubrene on Au(111): Enantioselective self-assembly

M.-C. Blüm, E. Cavar, M. Pivetta, F. Patthey, WDS,
Angew. Chem. Int. Ed. **44**, 5334 (2005)

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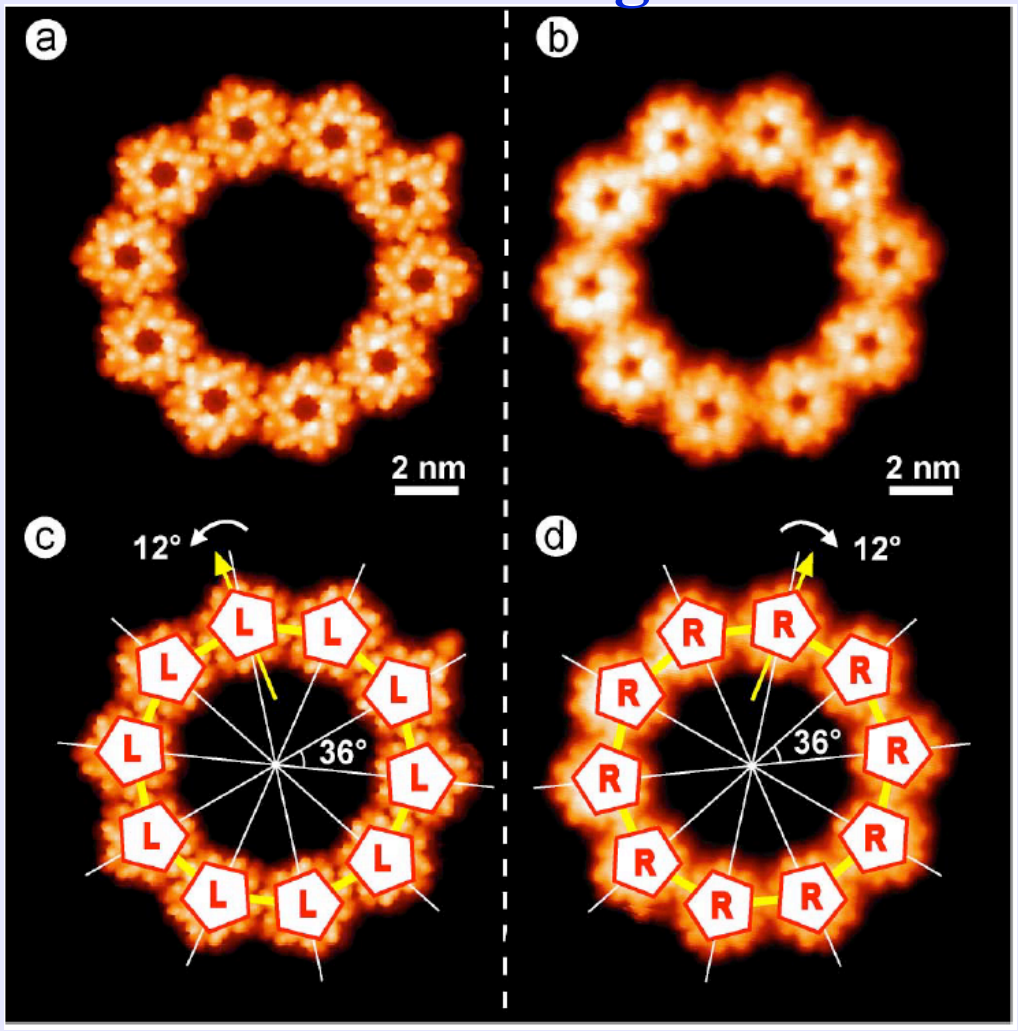
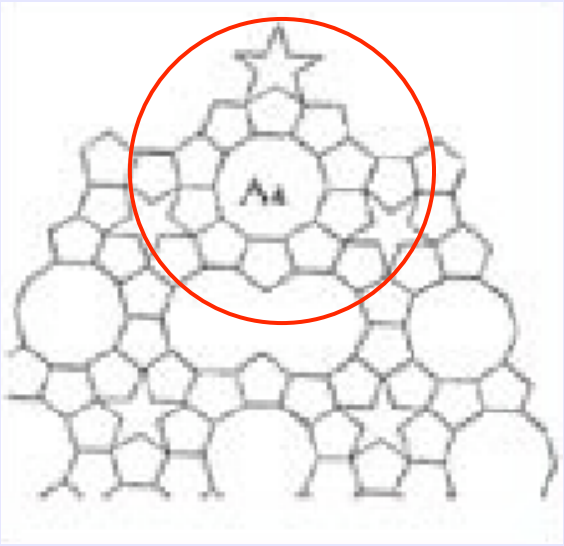
Left-handed Right-handed

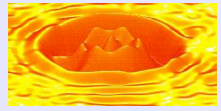


Rubrene on Au(111):
Formation of homochiral supramolecular decagons of pentagonal supermolecules (pentacontamer)

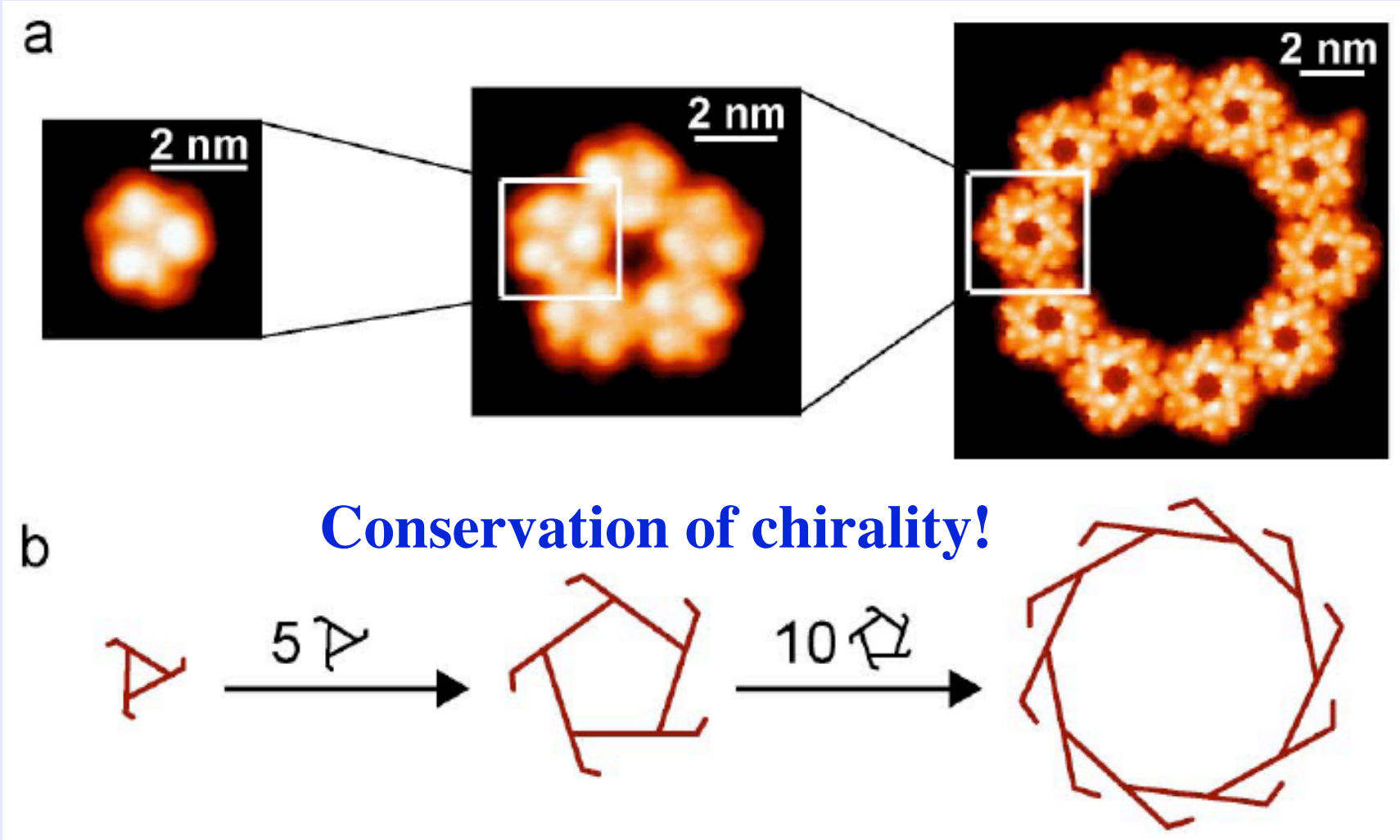


J. Kepler, Harmonices Mundi Libri V, 1619

M.-C. Blüm, E. Čavar, M. Pivetta, F. Patthey, WDS,
Angew. Chem. Int. Ed. **44**, 5334 (2005)



Rubrene on Au(111): 3 generations of nested self-assembly



M.-C. Blüm, E. Cavar, M. Pivetta, F. Patthey, WDS,
Angew. Chem. Int. Ed. **44**, 5334 (2005)

EPFL

nature

NATURE|Vol 442|10 August 2006

RESEARCH HIGHLIGHTS

JOURNAL CLUB

Rasmita Raval
University of Liverpool, UK

A surface scientist observes how self-seeking molecules build up asymmetry.

Nobel laureate Jean-Marie Lehn described supramolecular chemistry as 'molecular sociology'. Lehn, who won the 1987 chemistry prize for his work in this field, thus neatly encapsulated the concept of molecules congregating under the influence of multifarious intermolecular forces.

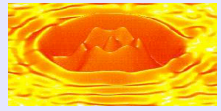
One guiding force, important in biology, is the property of chirality, or 'handedness'. Chiral molecules exist in two mirror-image forms that cannot be superimposed. Some of us try to capture in our work the ease with which biological systems can distinguish chiral molecules or create chirality in reactions.

As a first step, we study how chirality can propagate from molecules to larger, supramolecular structures. Wolf Dieter-Schneider and co-workers at the Swiss Federal Institute of Technology in Lausanne recently revealed a system of impressive complexity (M.-C. Blüm *et al. Angew. Chem. Int. Edn* **44**, 5334–5337; 2005).

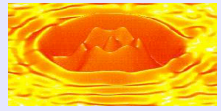
They used a scanning tunnelling microscope to image the structures formed by rubrene, a chiral molecule, on a gold surface. First it groups into pentagonal rings, resembling complex gearwheels. These wheels then link up into chains or form ten-membered rings. At each stage, intermolecular forces ensure that only molecules of the same chirality assemble together.

It is striking that an essentially simple molecule — rubrene ($C_{42}H_{28}$) is a small, buckled sheet of carbon rings — can create such intricate homochiral architectures spontaneously.

The separation of molecules by chirality is a process that must have emerged at our very beginning, as proteins assembled from chiral amino acids in the primordial soup. Thus we, as molecular sociologists, are mapping the very first steps in the evolution of complex matter.

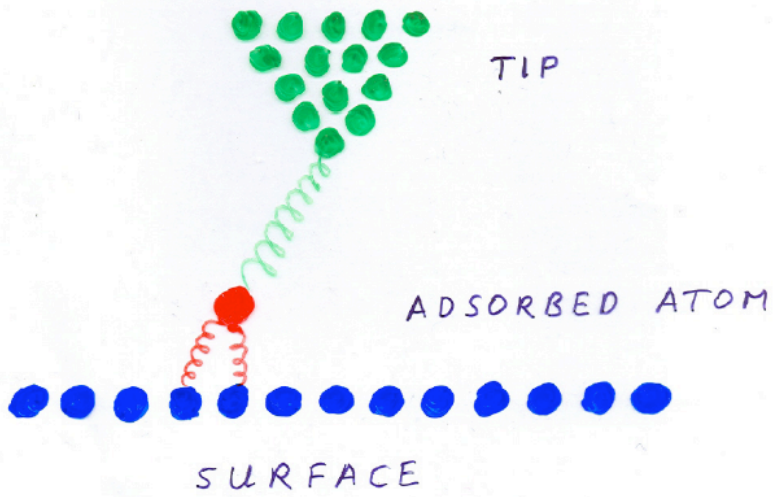


Manipulation of individual supermolecules



STM :

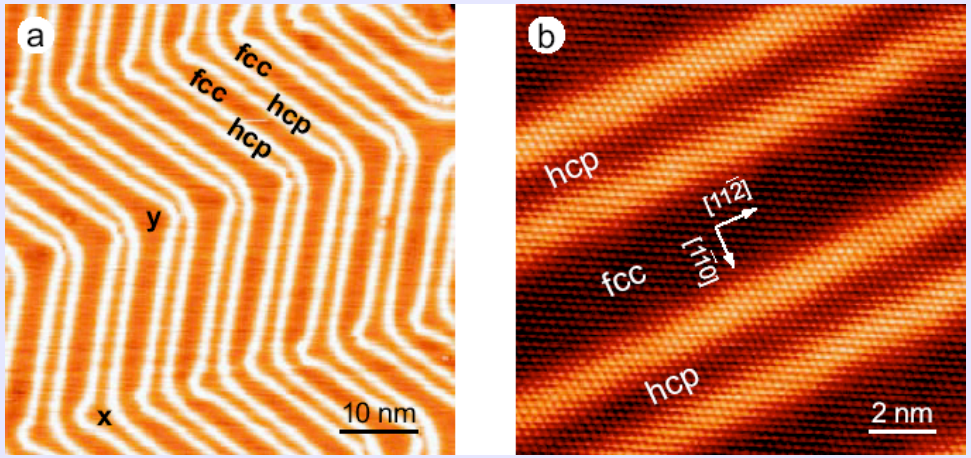
ADJUSTABLE BONDING

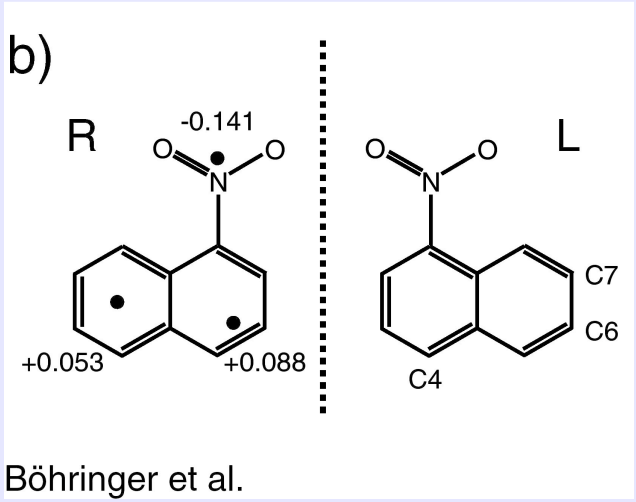


(D. M. EIGLER)

Reconstructed Au(111) surface + 1-nitronaphthalene: 2D chiral

(J. V. Barth et al., Phys. Rev. B **42,** 9307 (1990))





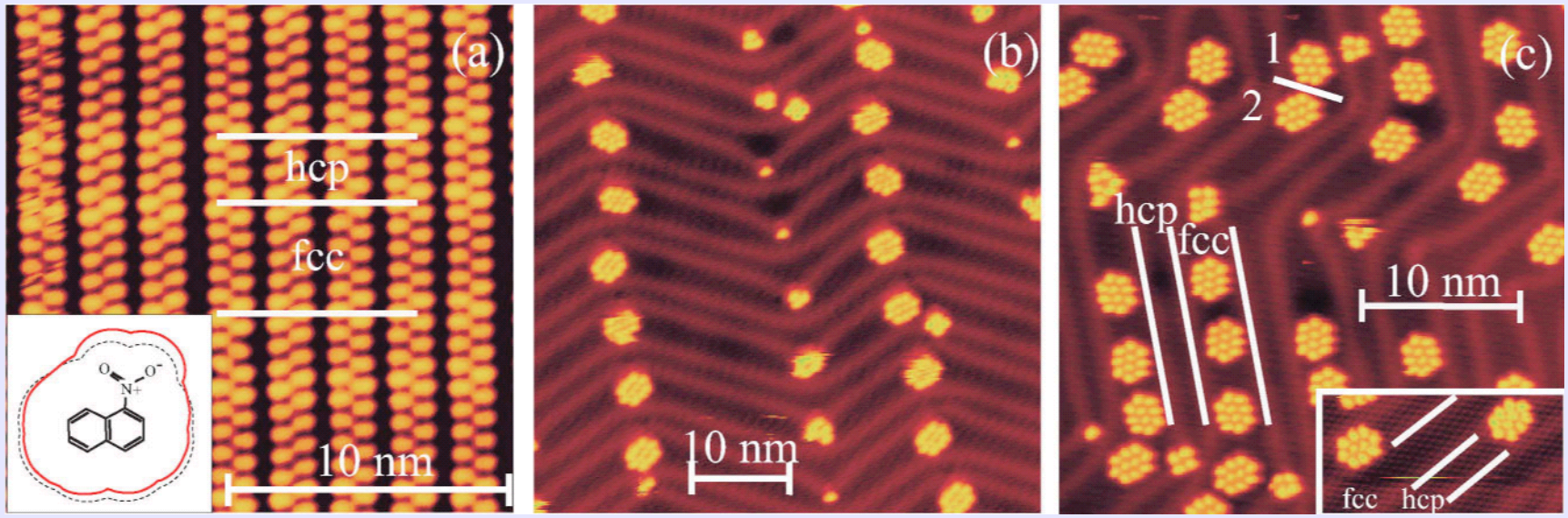
Böhringer et al.

The molecule and its mirror image cannot be superimposed by translation or rotation within the surface plane

M. Böhringer, K. Morgenstern, WDS, M. Wühn, Ch. Wöll, R. Berndt, Surf. Sci. **444**, 199 (2000)

Two-dimensional self-assembly of supramolecular chains & clusters

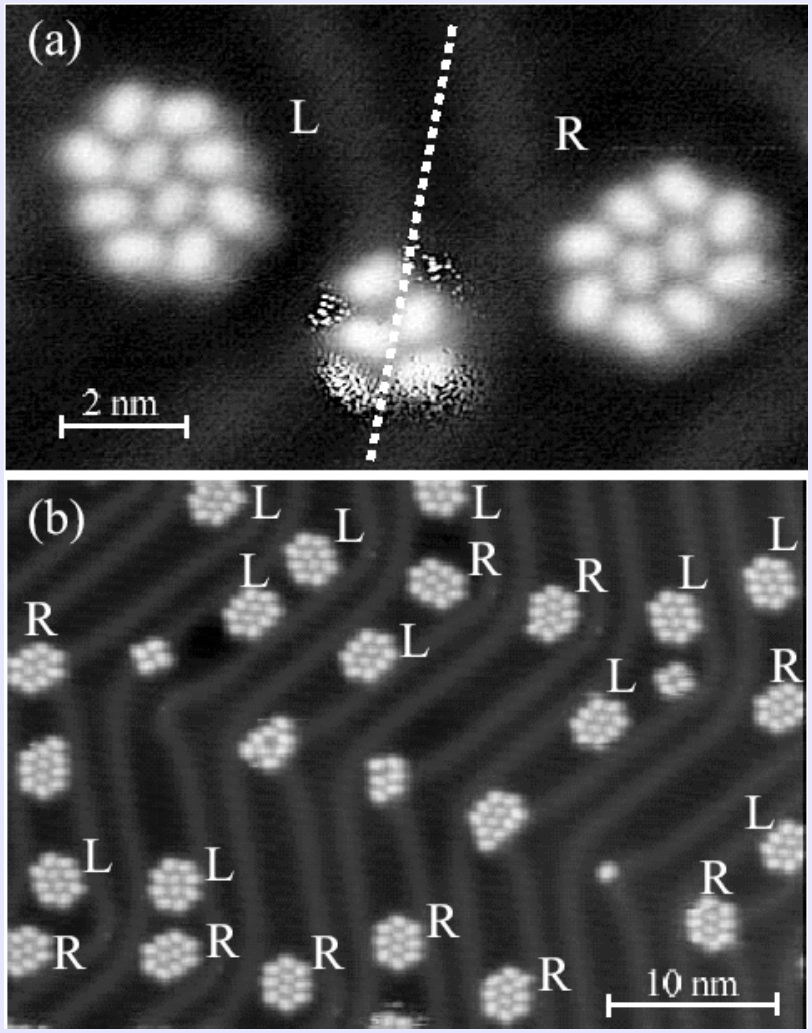
(1-Nitronaphthalene (1-NN))



M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

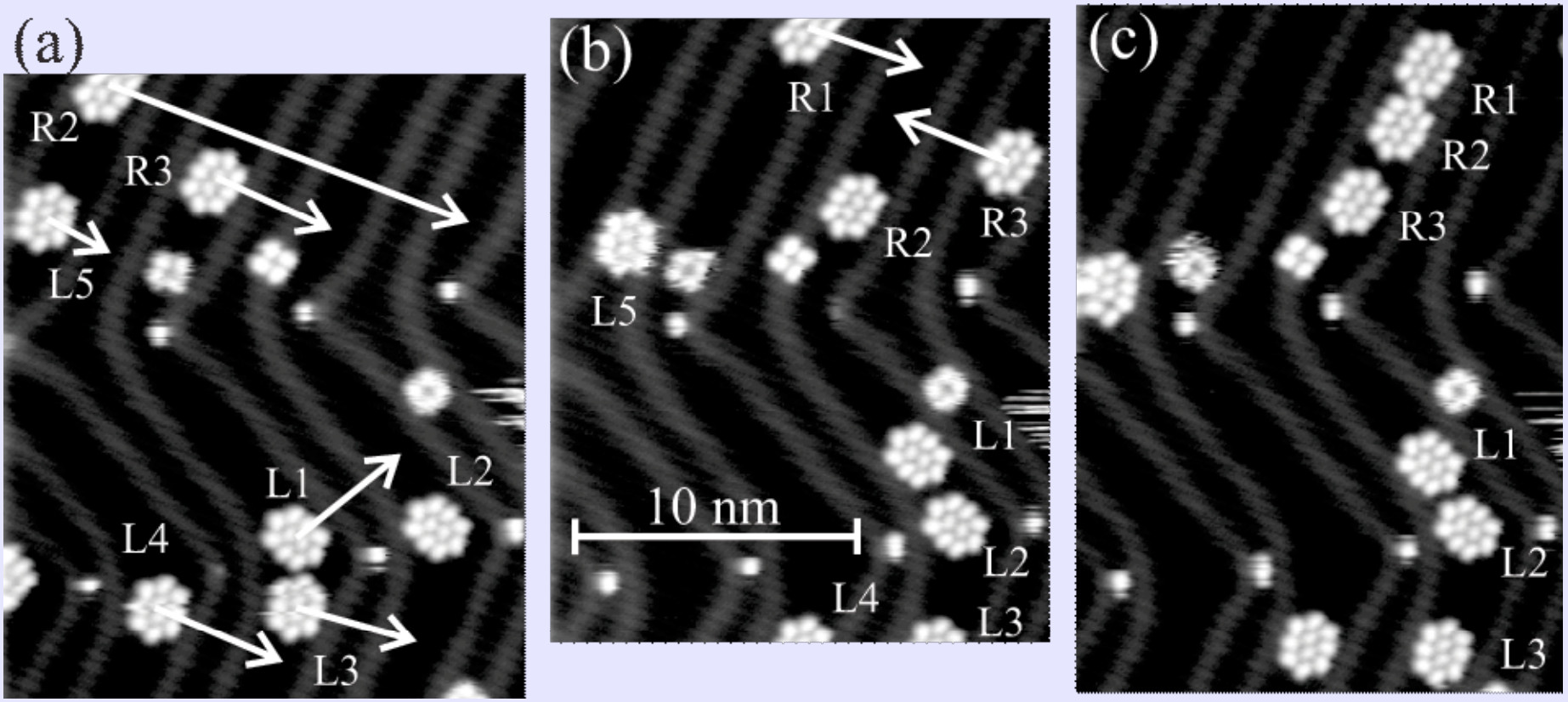
EPFL

Two-dimensional chiral 1-NN decamers

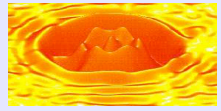


M. Böhringer, K. Morgenstern, WDS, R. Berndt,
Angew. Chem. Int. Ed. **38**, 821 (1999)

Separation of a racemic mixture: Pasteur's experiment on the nanoscale



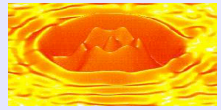
M. Böhringer, K. Morgenstern, WDS, R. Berndt, Angew. Chem. Int. Ed. **38**, 821 (1999)



STM tweezes chiral clusters apart

- Just as Louis Pasteur used a light microscope to guide his tweezers to separate sodium ammonium tartrate crystals in 1848, an STM is used both to image and separate chiral decameric clusters of 1-nitronaphthalene.

- This achievement adds separation of enantiomers to the previously developed SPM techniques of atomic-scale manipulation (Eigler), selective dissociation (Avouris), conformal analysis (Gimzewski), and chiral recognition (Wolkow), as part of the practice of nanochemistry.



Chirality on the Nanoscale:

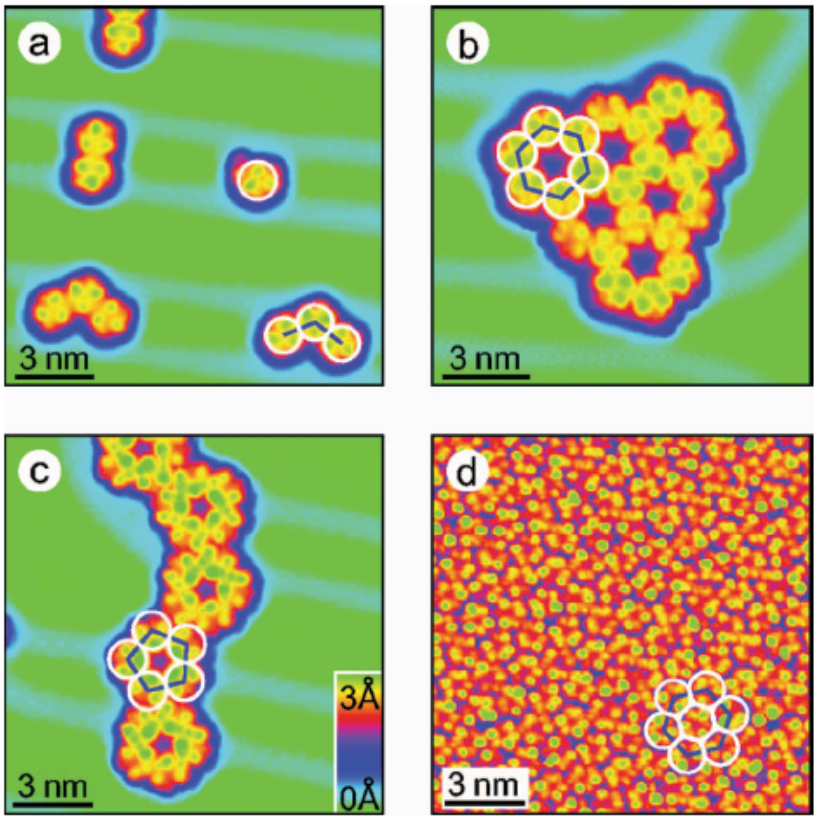
STM observations and modeling ➡

- Stability, chirality, and arrangement of 2D self-assembled supramolecular structures
- Chirality of single molecules and decamers
- Chiral phase transition in 2D

S. de Feyter, J. Barth, K. Kern, T. Yokoyama, R. Raval, F. Besenbacher, N. Richardson, K.-H. Ernst, R. Fasel, R. J. Behm, H. Hoster…and many others

EPFL

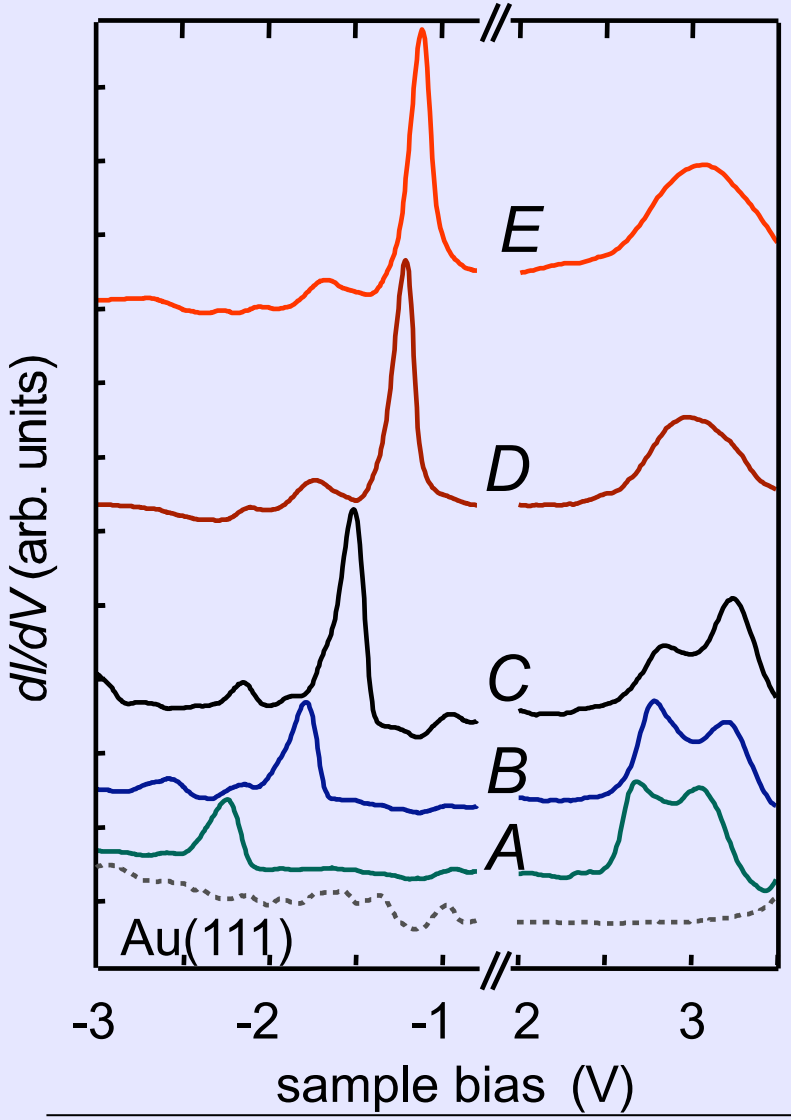
Rubrene conformations on Au(111)

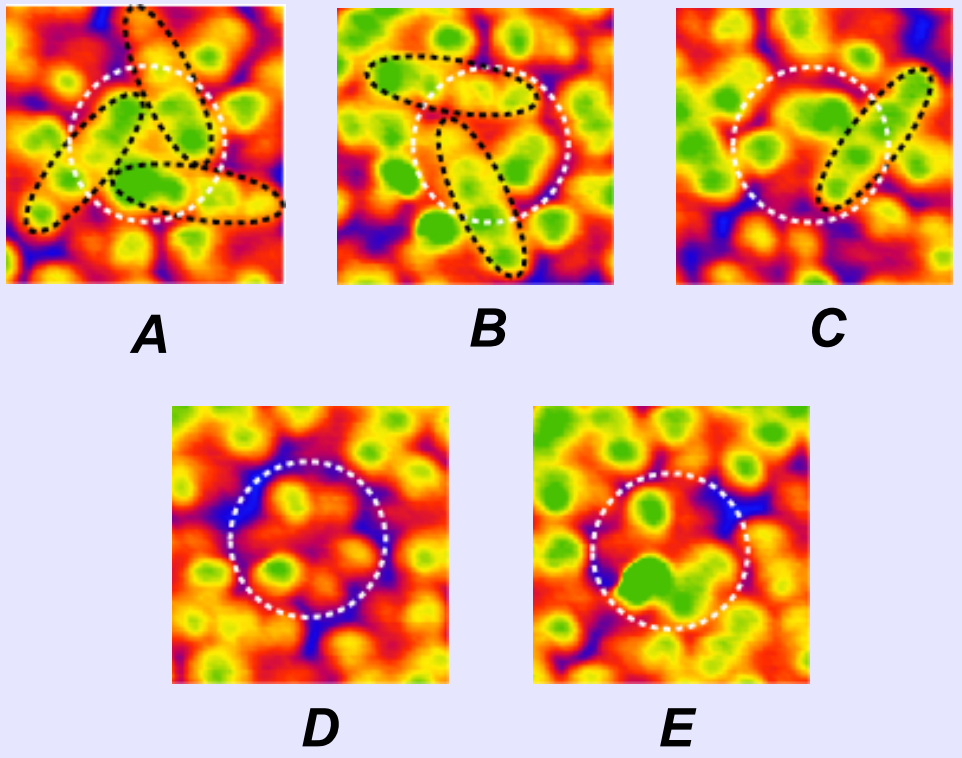


Different
adsorption conformations
for molecules
in different structures

M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)

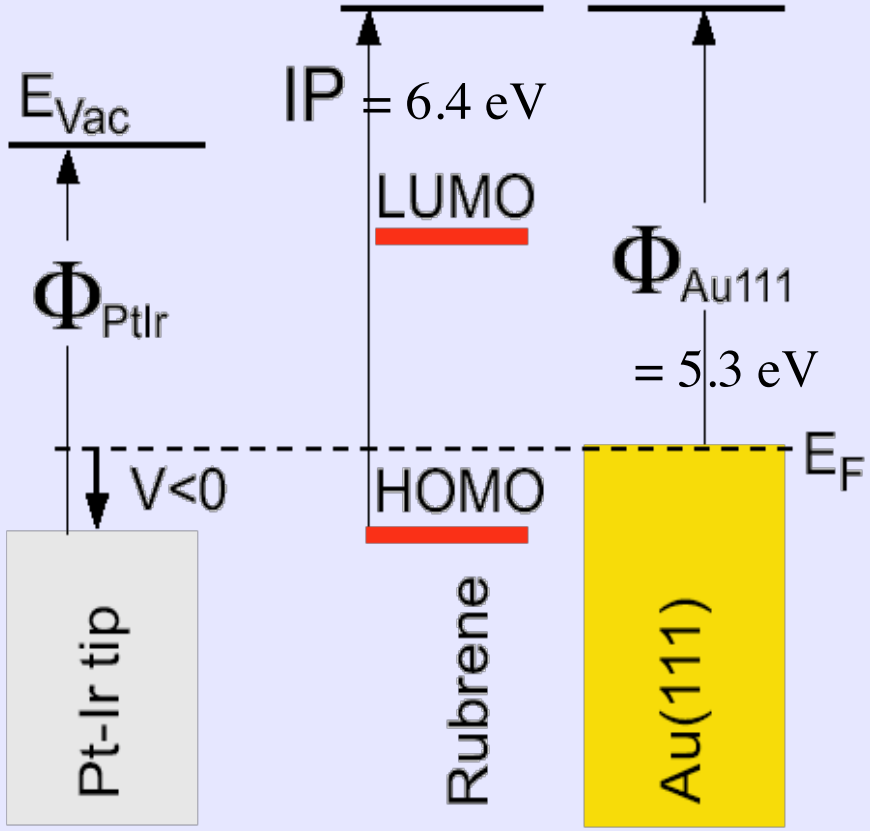
STS of Rubrene on Au(111): Different molecular conformations exhibit different electronic structure

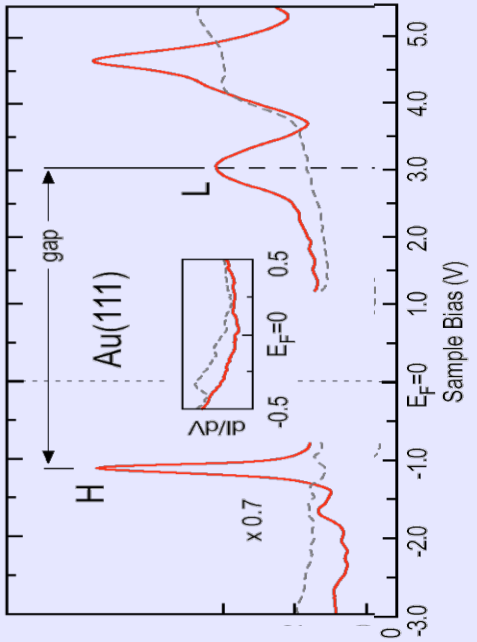




M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB**73**, 195409 (2006)

Experimentally deduced energy level diagram: Rubrene on Au(111)





M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB**73**, 195409 (2006)

Renormalization of Molecular Electronic Levels at Metal-Molecule Interfaces

J. B. Neaton,[1] Mark S. Hybertsen,[2] and Steven G. Louie[1,3]

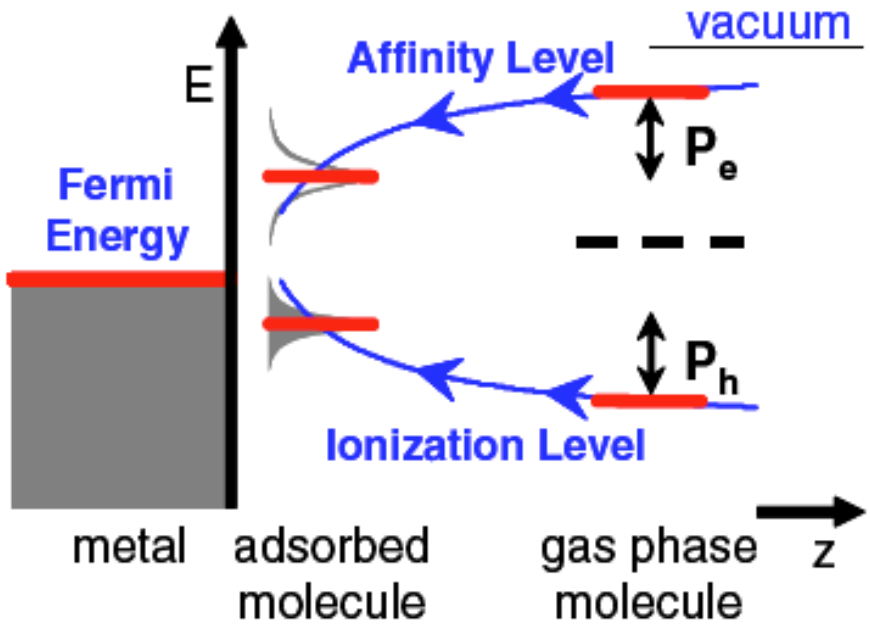
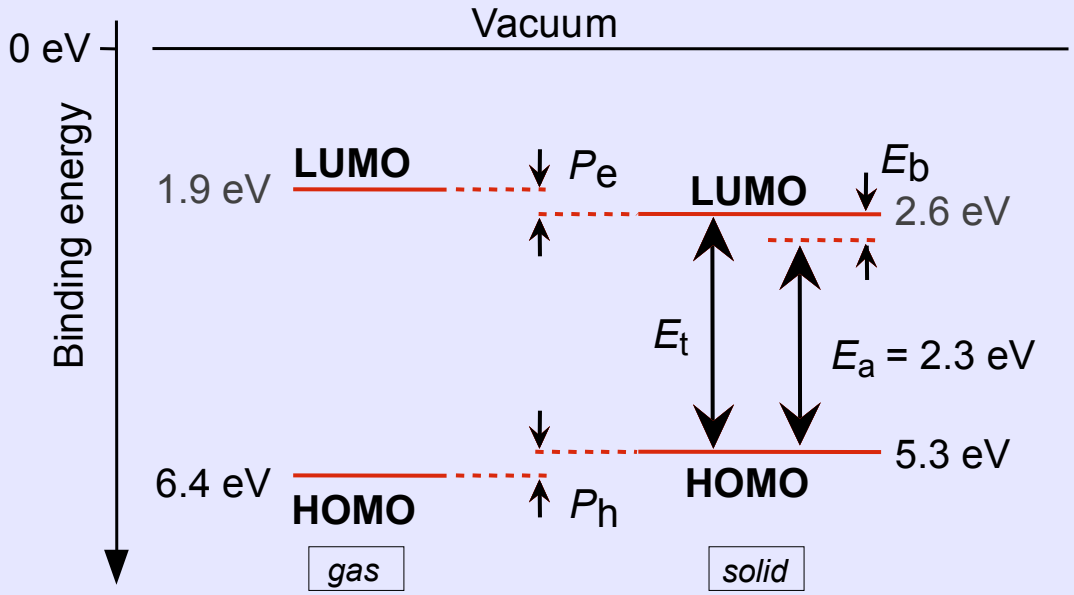


FIG. 1 (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.

Energy levels of Rubrene



	E_{HOMO}	E_{LUMO}	E_t
gas phase	6.4 eV	≈ 1.9 eV	≈ 4.5 eV
solid phase	5.3 eV	≈ 2.6 eV	≈ 2.7 eV

STS on Au(111):

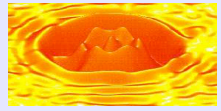
7.5 eV > E_{HOMO} > 6.4 eV

E_{LUMO}= 2.3 eV

?

4.1 eV < E_{gap} < 5.2 eV

M.-C. Blüm, PhD thesis, EPFL, Lausanne 2006



Proposal: Origin of the 1D self-assembly

The unusually large energy gaps of the STS spectra arise from the fact that the probed HOMO and LUMO states belong to positively charged and neutral adsorbates, respectively

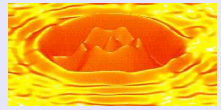
Interaction of rubrene pentagons

$$U_{2b}(r) = \xi \left[\left(\frac{\sigma}{r'} \right)^{12} - 2 \left(\frac{\sigma}{r'} \right)^{6} \right] + \frac{p^2}{2r^3}$$

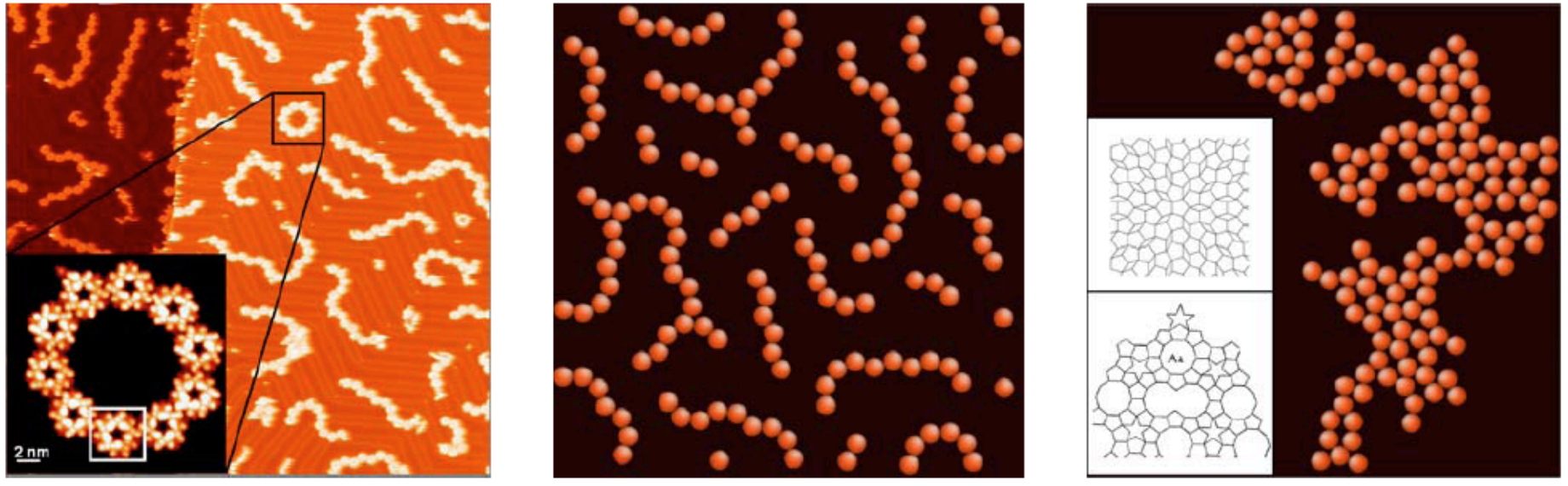
Lennard-Jones

Dipole-dipole repulsive term

G. Tomba, M. Stengel, WDS, A. Baldereschi, A. De Vita, submitted



Rubrene on Au(111): Self-assembly mediated by short-range attractive and long-range repulsive electrostatic interactions



No repulsive interaction

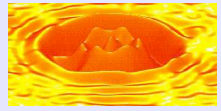
The regular decagon shape maximizes the relative distance between non-neighbouring pentagons

G. Tomba, M. Stengel, WDS, A. Baldereschi, A. De Vita, submitted

EPFL

Inelastic electron tunneling spectroscopy:

Optical spectroscopy and chemical identification at the nanoscale



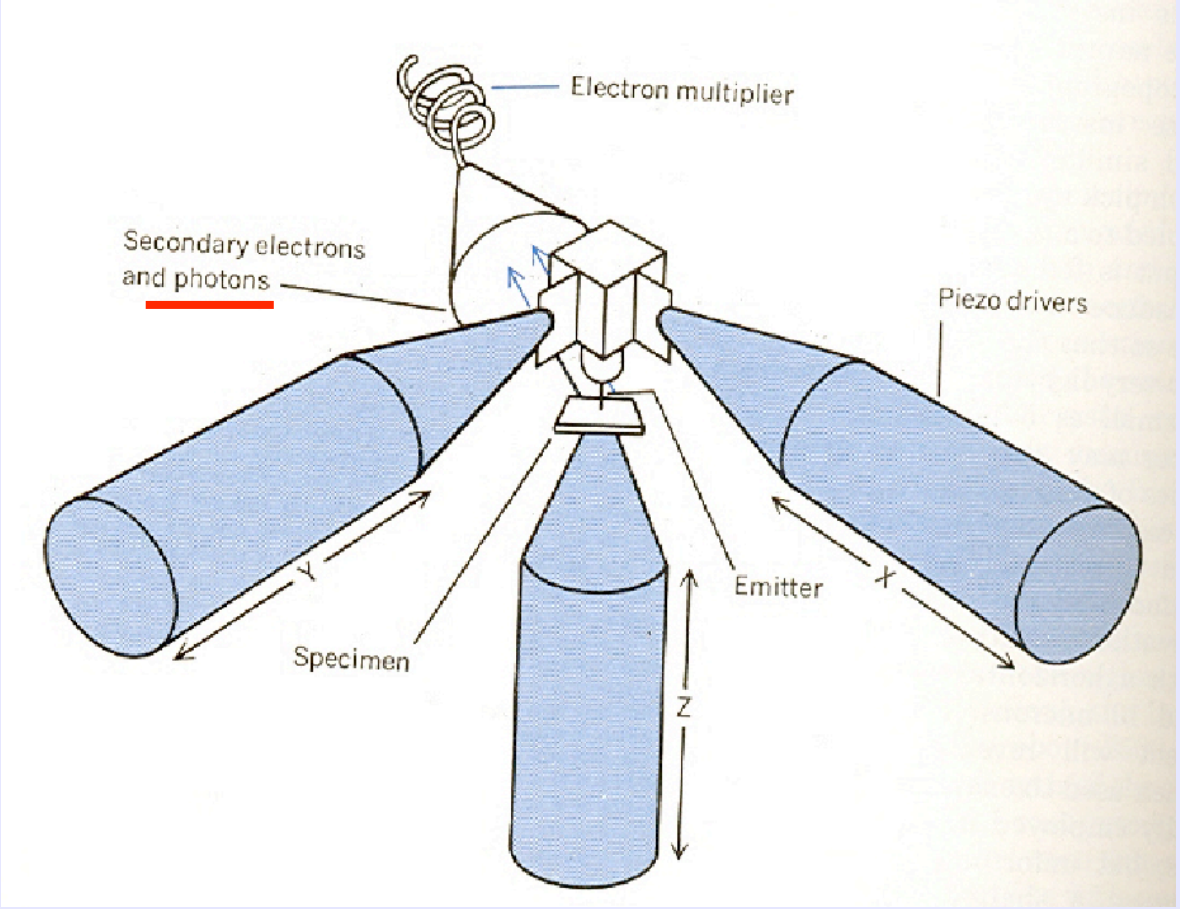
The Topografiner

Proposal:

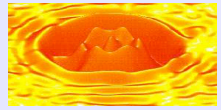
Chemical identification of a single atom, molecule, cluster….

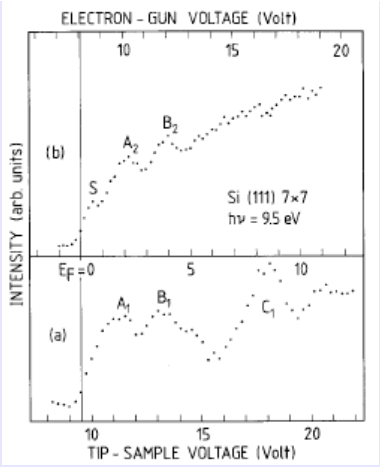
by analyzing the

induced local light emission



Russell D. Young, Physics Today, November **1971**, 42



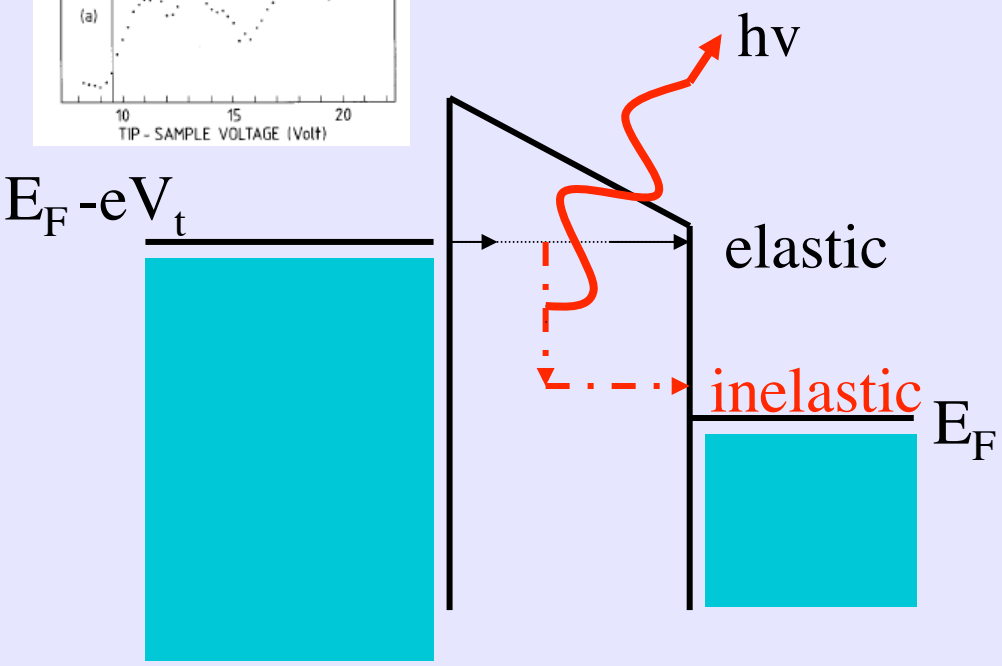


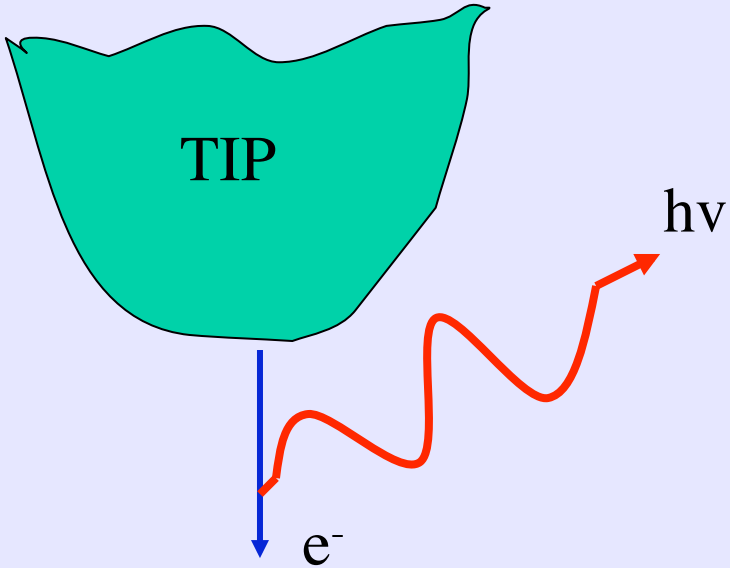
Photon emission with the scanning tunneling microscope

J.K. Gimzewski, B. Reihl, J.H. Coombs, and R.R. Schlittler
IBM Research Division, Zurich Research Laboratory, Rüschlikon, Switzerland

Received April 5, 1988

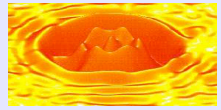
Z. Phys. B **72**, 497 (1988)



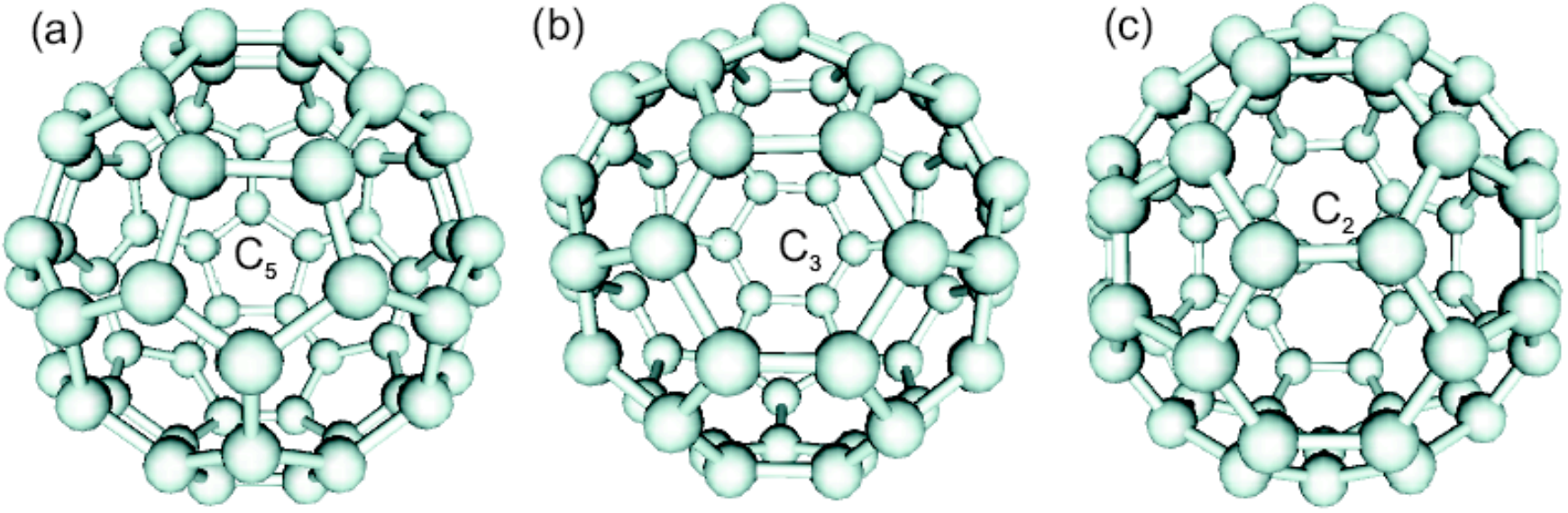


- Inelastic process
- P ≈ 10^{-4} photons/electron

Sample



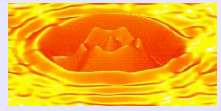
Symmetry operations of the regular truncated icosahedron: C_{60}



J. Menéndez and J. B. Page,

in Light Scattering in Solids VIII, ed. by M. Cardona and G. Güntherodt, Springer, Berlin, 2000

http://www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm

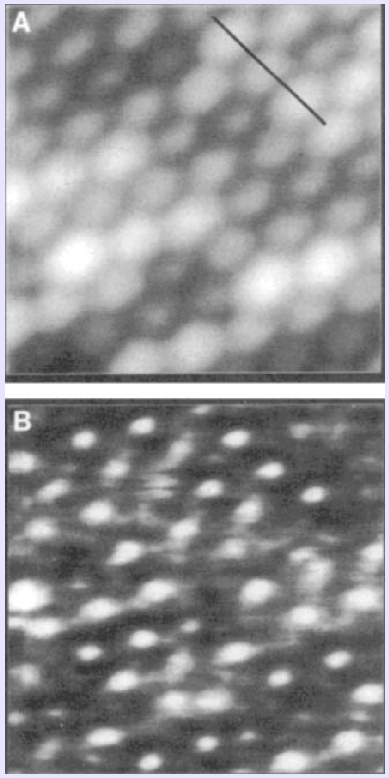


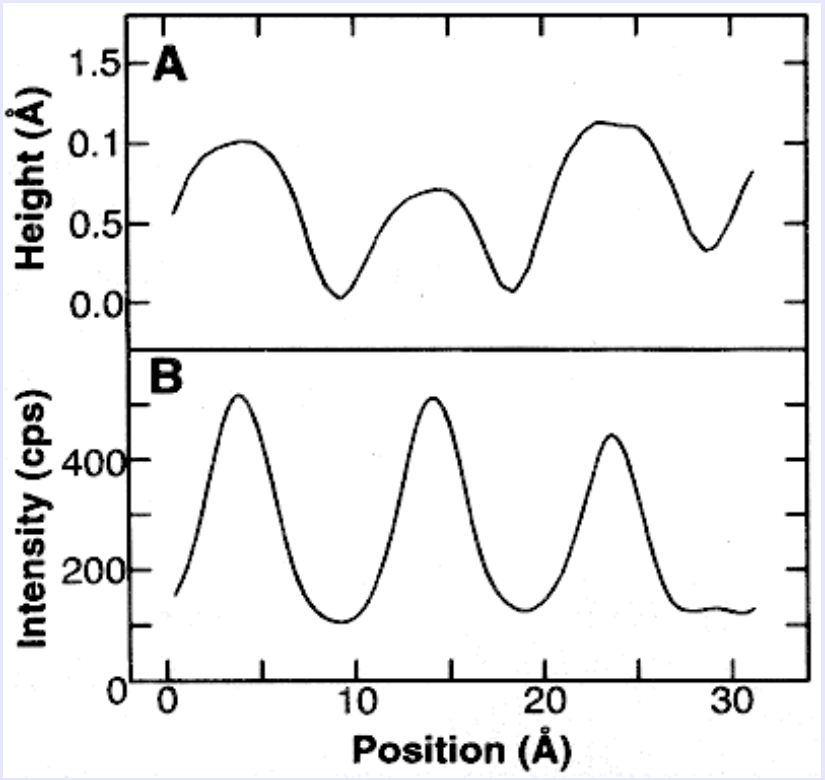
Photonemission: C_{60} on Au(110)

Topography

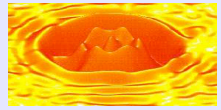
T = 50 K

Photon map

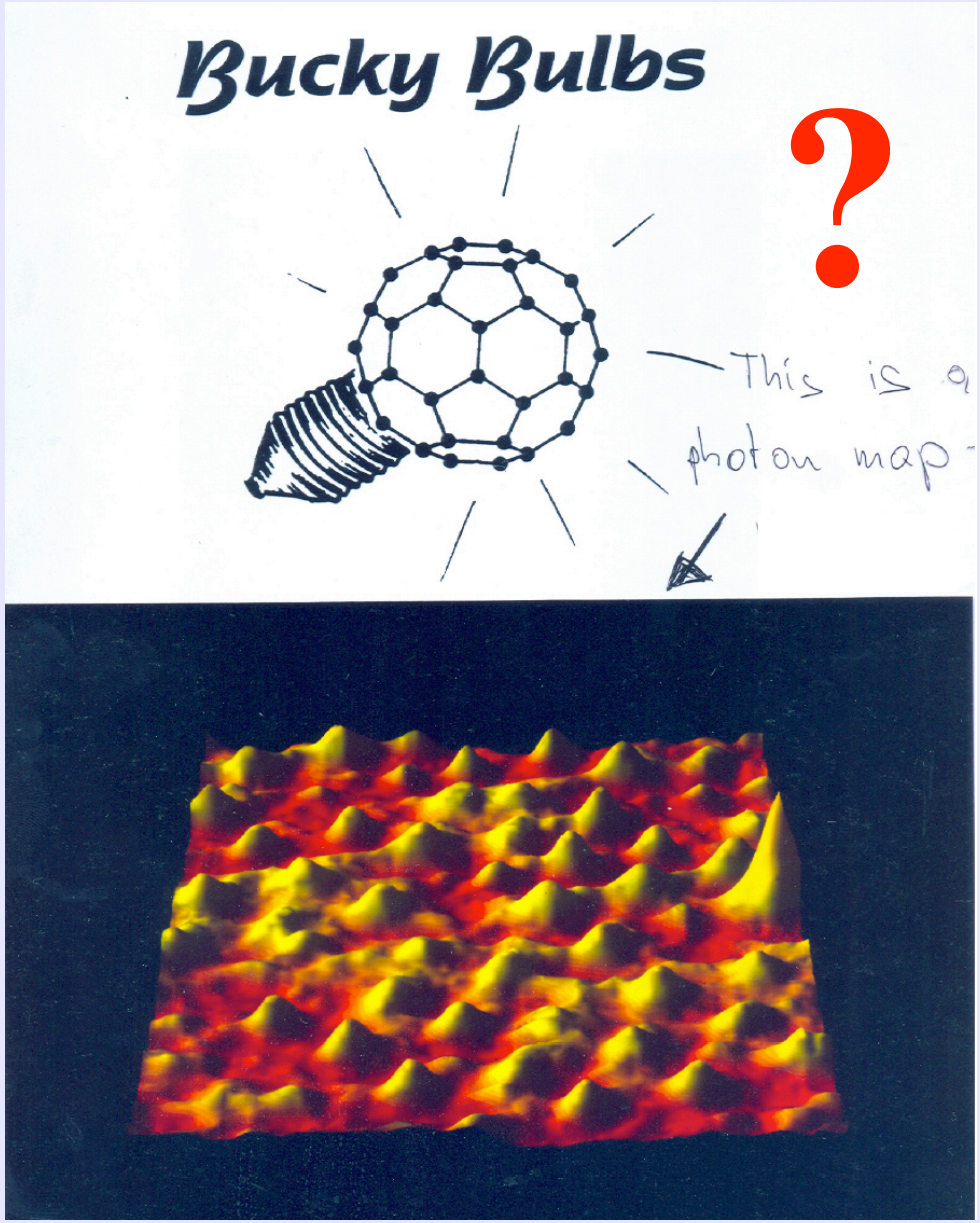




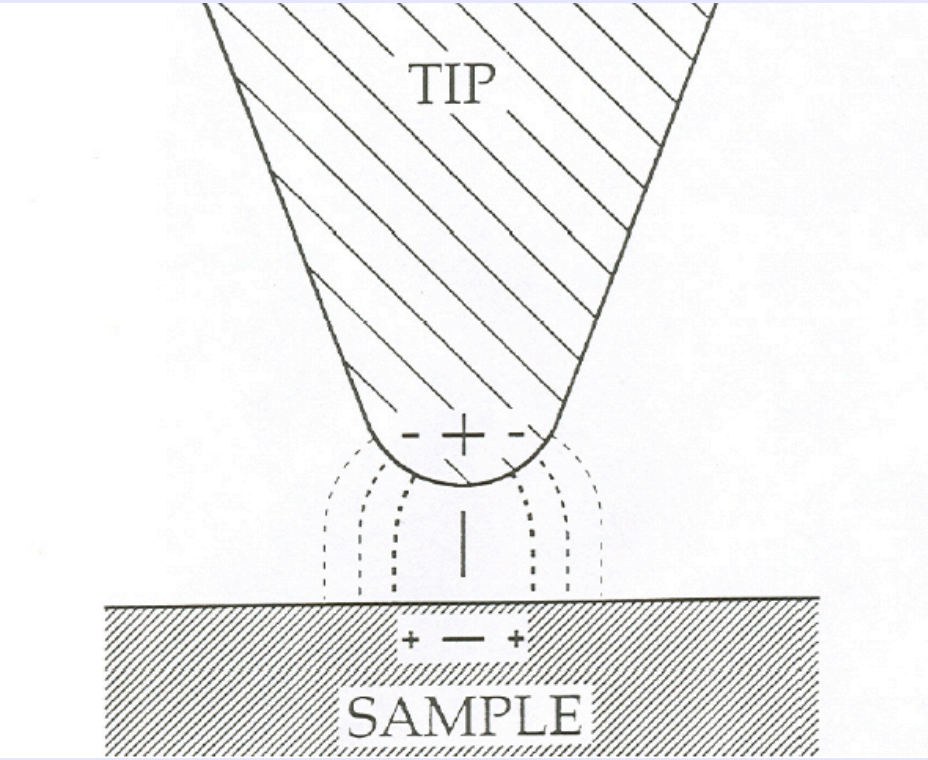
R. Berndt, R. Gaisch, J. K. Gimzewski, B. Reihl,
R. R. Schlittler, WDS, M. Tschudy, Science **262**, 1425 (1993)



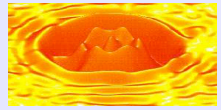
C_{60} on Au(110)



A snapshot of the energetically lowest tip-induced plasmon mode



R. Berndt, R. Gaisch, WDS,
J.K. Gimzewski, B. Reihl, R.R. Schlittler, M. Tschudy, Appl. Phys. A **57**, 513 (1993)



VOLUME 67, NUMBER 27 PHYSICAL REVIEW LETTERS 30 DECEMBER 1991

Inelastic Tunneling Excitation of Tip-Induced Plasmon Modes on Noble-Metal Surfaces

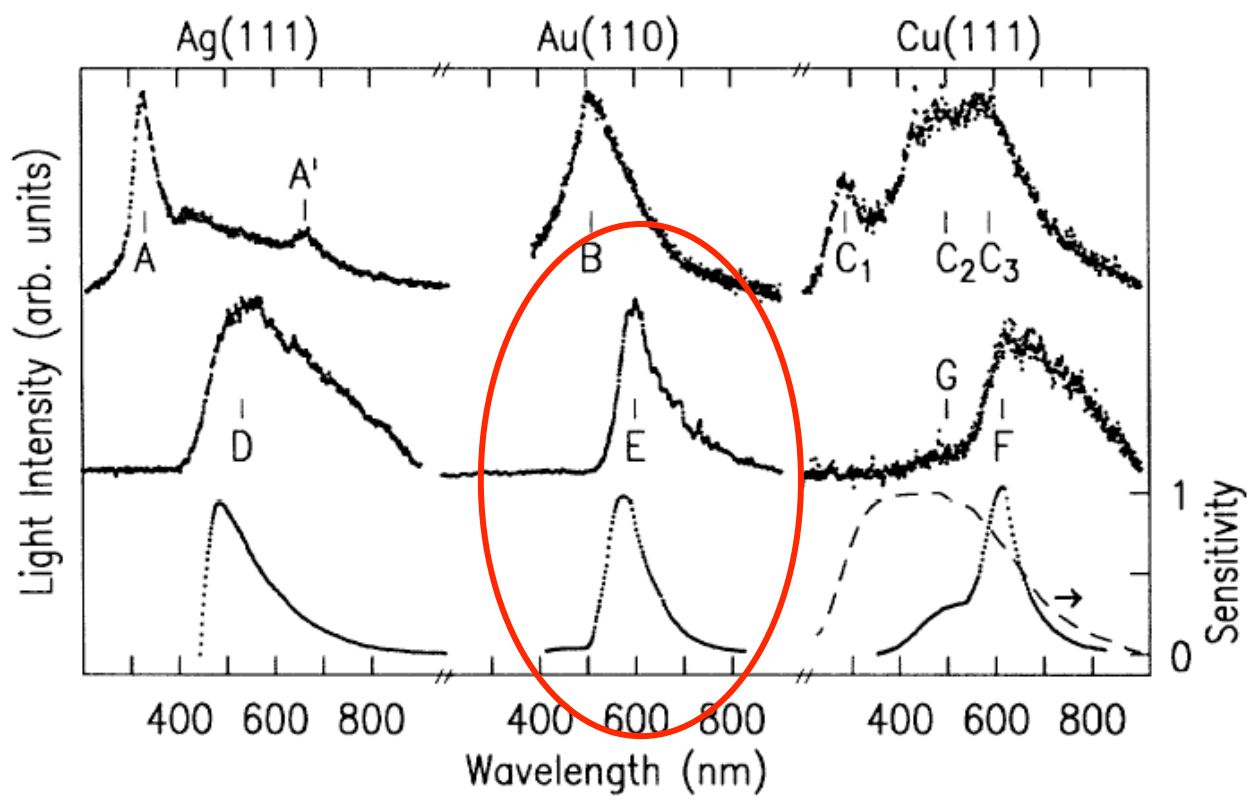
Richard Berndt and James K. Gimzewski
IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

Peter Johansson
Institute of Theoretical Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden
(Received 23 September 1991)

Field emission regime

Tunneling regime

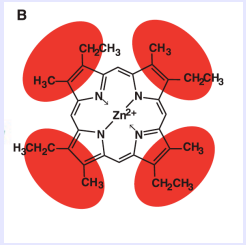
Theory

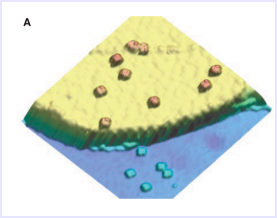


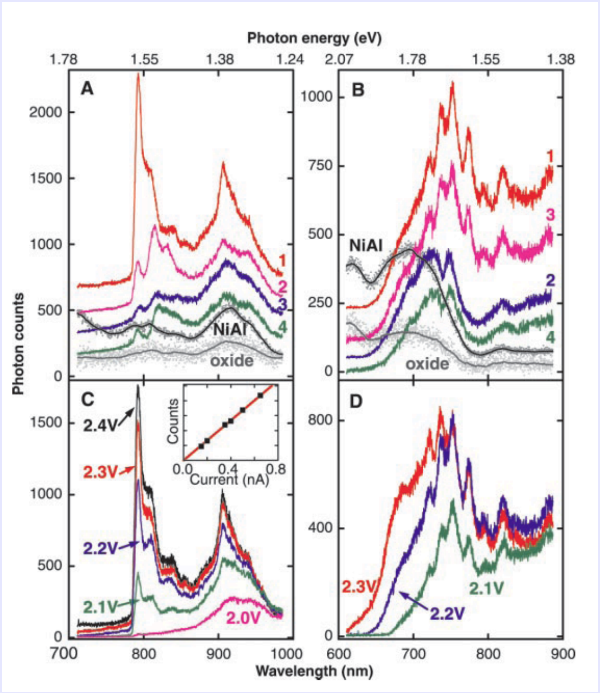
Decoupling the molecules from the metallic substrate: Ultrathin insulators

STM-induced light emission - luminescence from molecules

ZnEtiol / Al_2O_3 / NiAl(110)

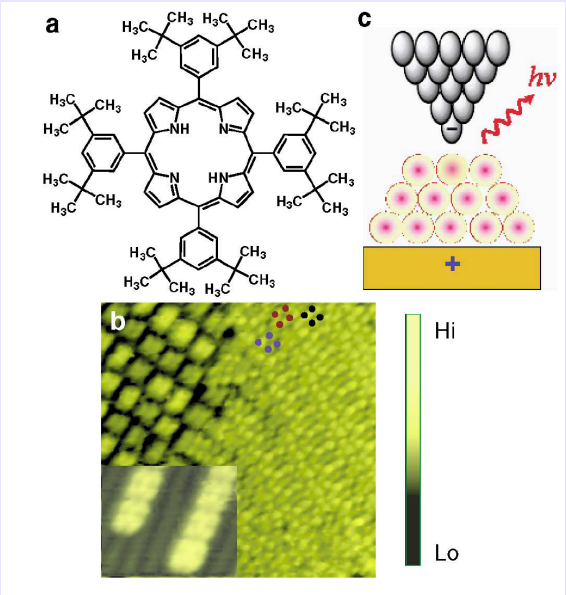


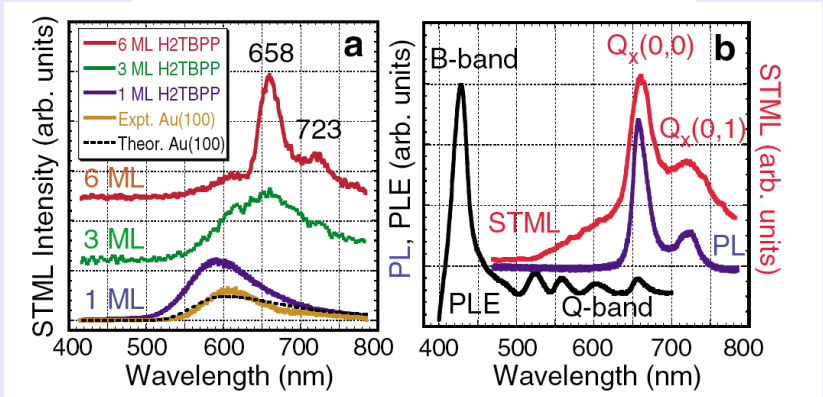




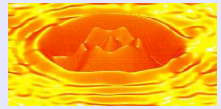
X. H. Qiu, G. V. Nazin, W. Ho, Science **299**, 542 (2003)

H_2TBPP/ Au(100) - multilayer

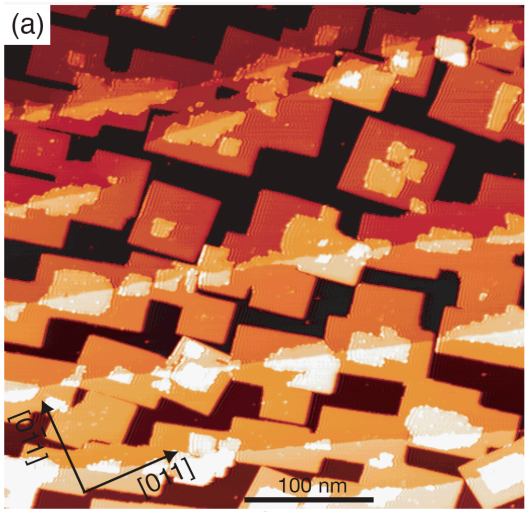




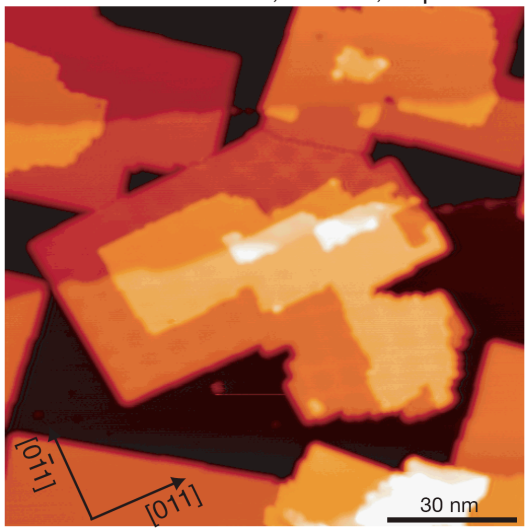
Z.-C. Dong, X.-L. Guo, A. Trifonov, P. S. Dorozhin, K. Miki, K. Kimura, S. Yokoyama, S. Mashiko, PRL **92**, 08601 (2004)



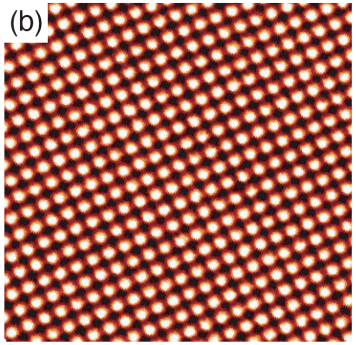
NaCl/Ag(100)



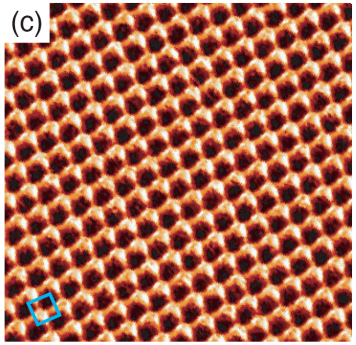
400 x 400 nm^2, +4.18V, 20pA



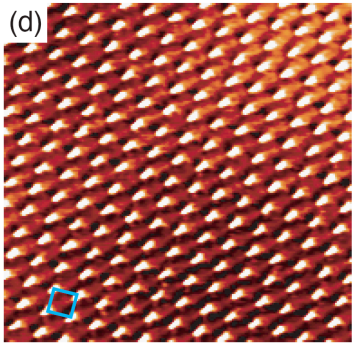
120 x 120 nm^2, +4.0V, 20pA



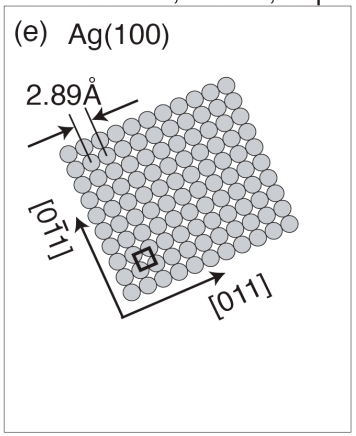
5.6 x 5.6 nm^2, -20mV, 50pA

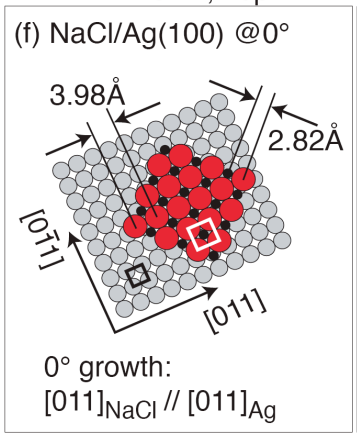


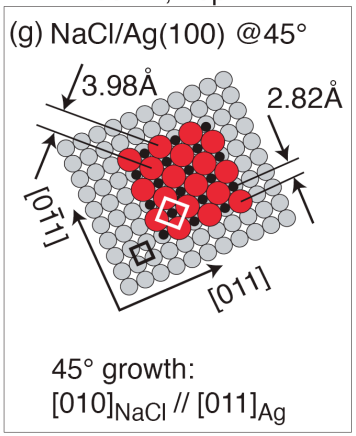
-110mV, 20pA



-100mV, 20pA

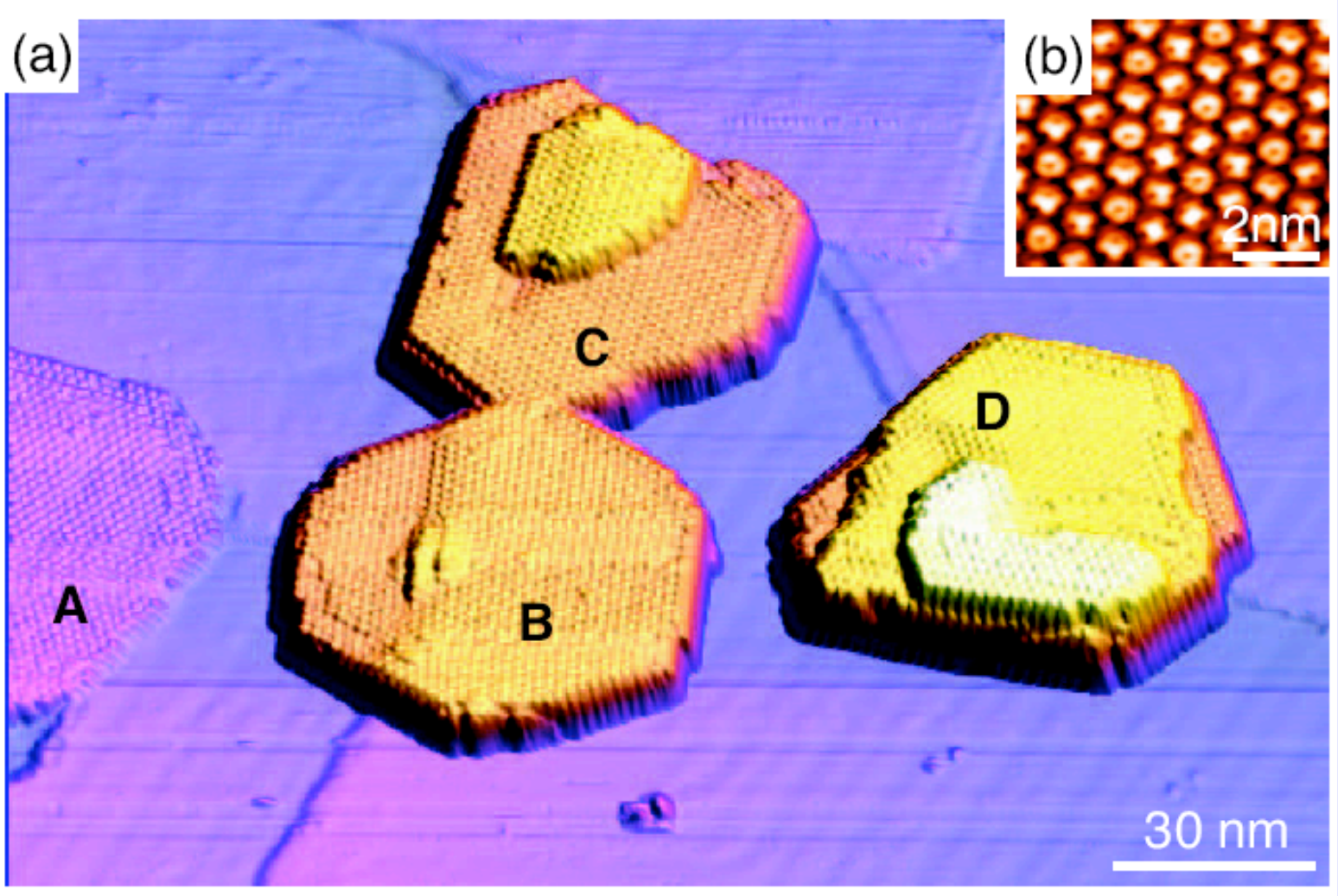




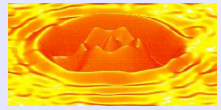


M. Pivetta, F. Patthey, WDS, M. Stengel, A. Baldereschi,
PRB **72**, 115404 (2005),
H.-C. Ploigt, C. Brun, M. Pivetta, F. Patthey, WDS,
PRB **76**, 195404 (2007)

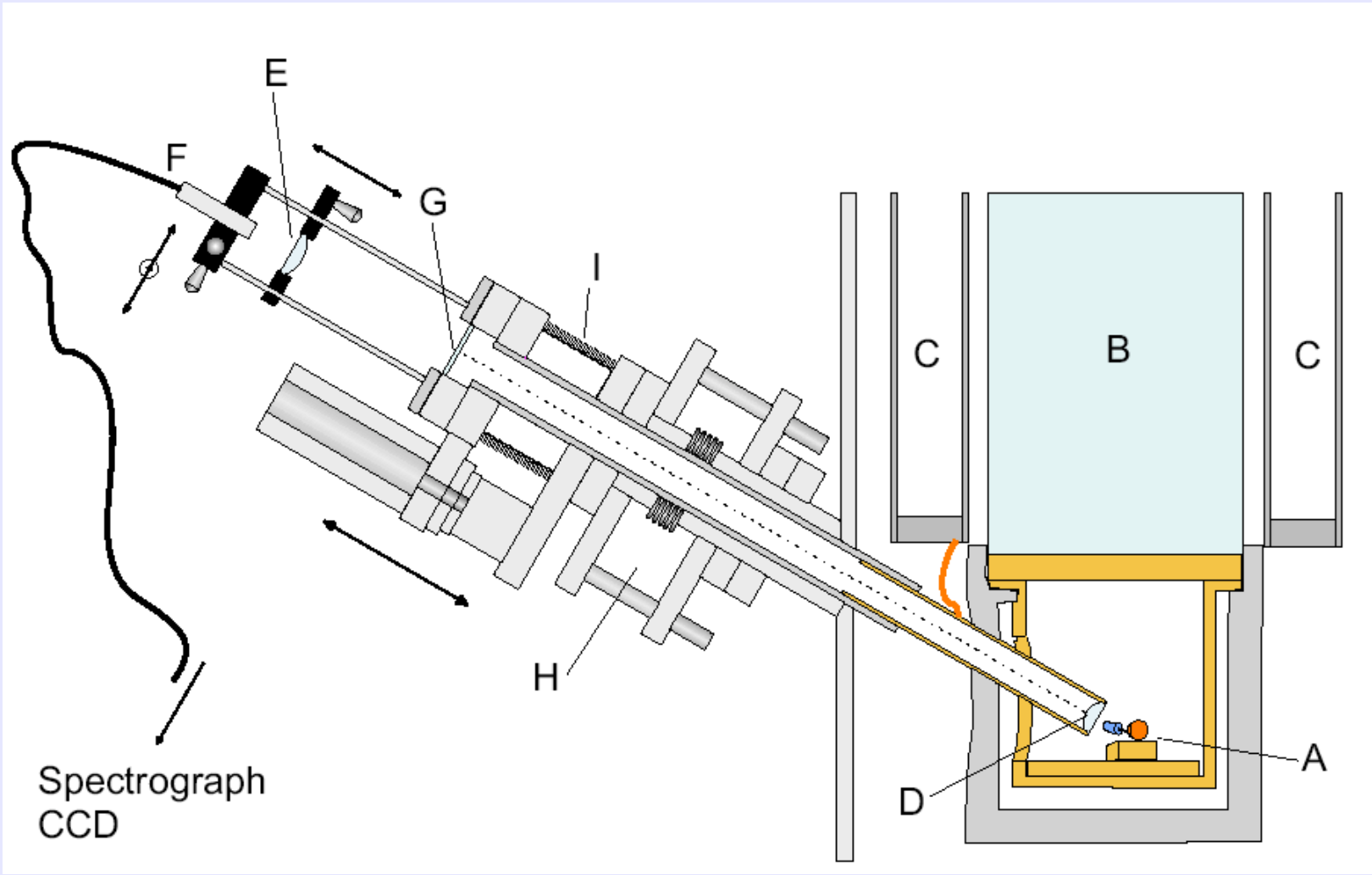
C_{60}/NaCl/Au(111): Growth of C_{60} nanocrystals



E. Ćavar, M.-C. Blüm, M. Pivetta, F. Patthey, M. Chergui, WDS, PRL **95**, 196102 (2005)

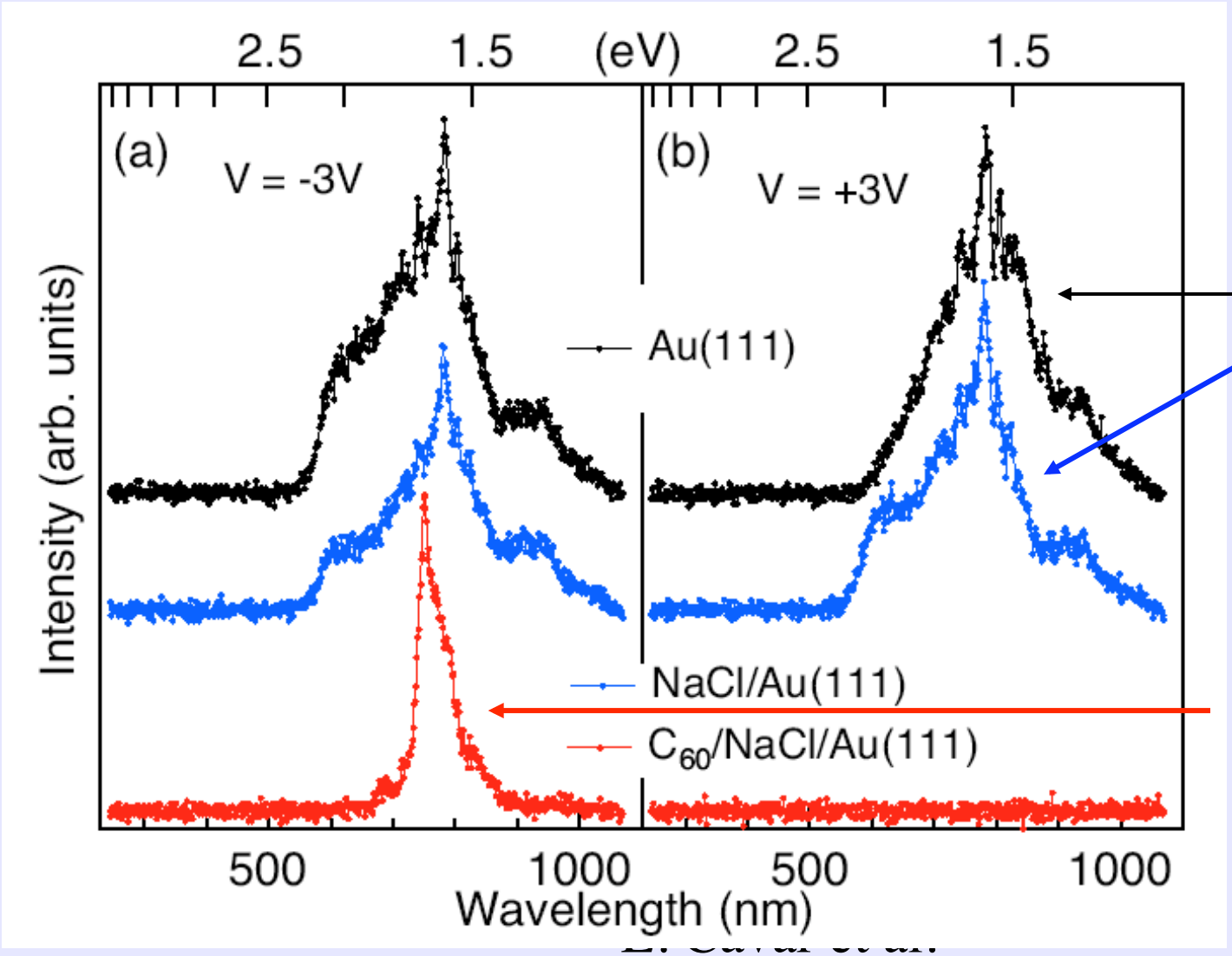


Eperimental setup



E. Ćavar, PhD thesis, EPFL, Lausanne (2005)

C_{60}/NaCl/Au(111): STM-induced luminescence



Decay of tip induced local surface plasmon on Au

(@ 50 K)

Luminescence

E. Ćavar, M.-C. Blüm, M. Pivetta, F. Patthey, M. Chergui, WDS, PRL **95**, 196102 (2005)

Table 4.1: Symmetry properties of vibrational modes in the C_{60} molecule (icosahedral symmetry.)

N_ω	a_g	t_{1g}	t_{2g}	g_g	h_g	a_u	t_{1u}	t_{2u}	g_u	h_u
46	2	3	4	6	8	1	4	5	6	7

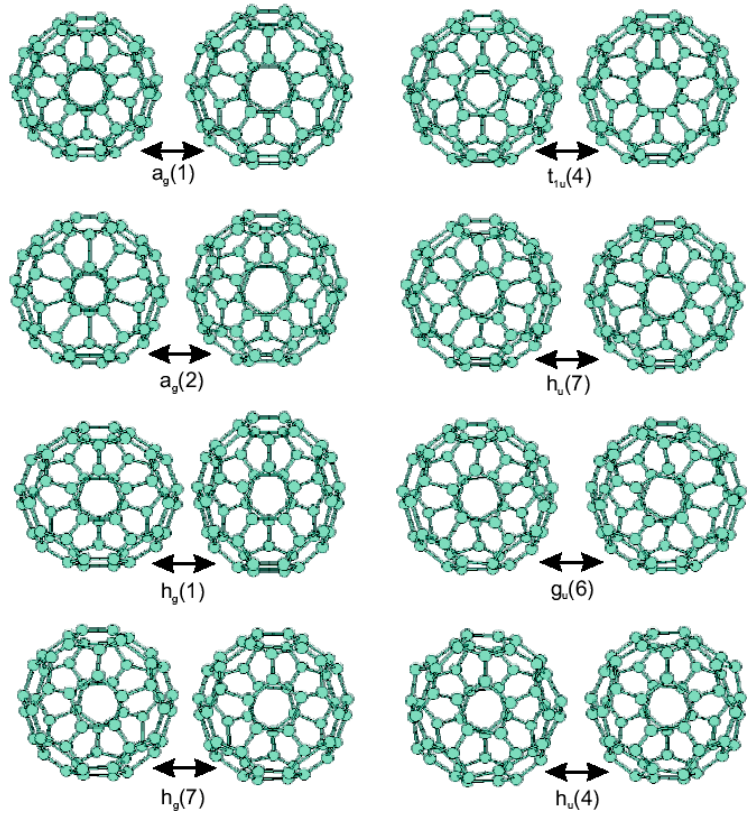
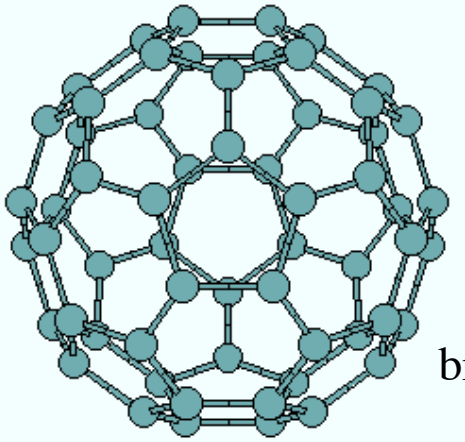


Figure 4.2: A schematic diagram of normal mode displacements (only some modes are shown). Left - even parity modes and right - odd parity modes. These are some of the vibrational modes we identified in luminescence spectra of C_{60} in the tunneling junction. These images are adapted from [113].



$a_g(1)$
496 cm^{-1}
breathing mode

E. Ćavar, PhD thesis,
EPFL, Lausanne (2005)

Vibrational modes of C_{60}
J. Menéndez and J. B. Page

STM-induced light emission

fluorescence **phosphorescence ?**

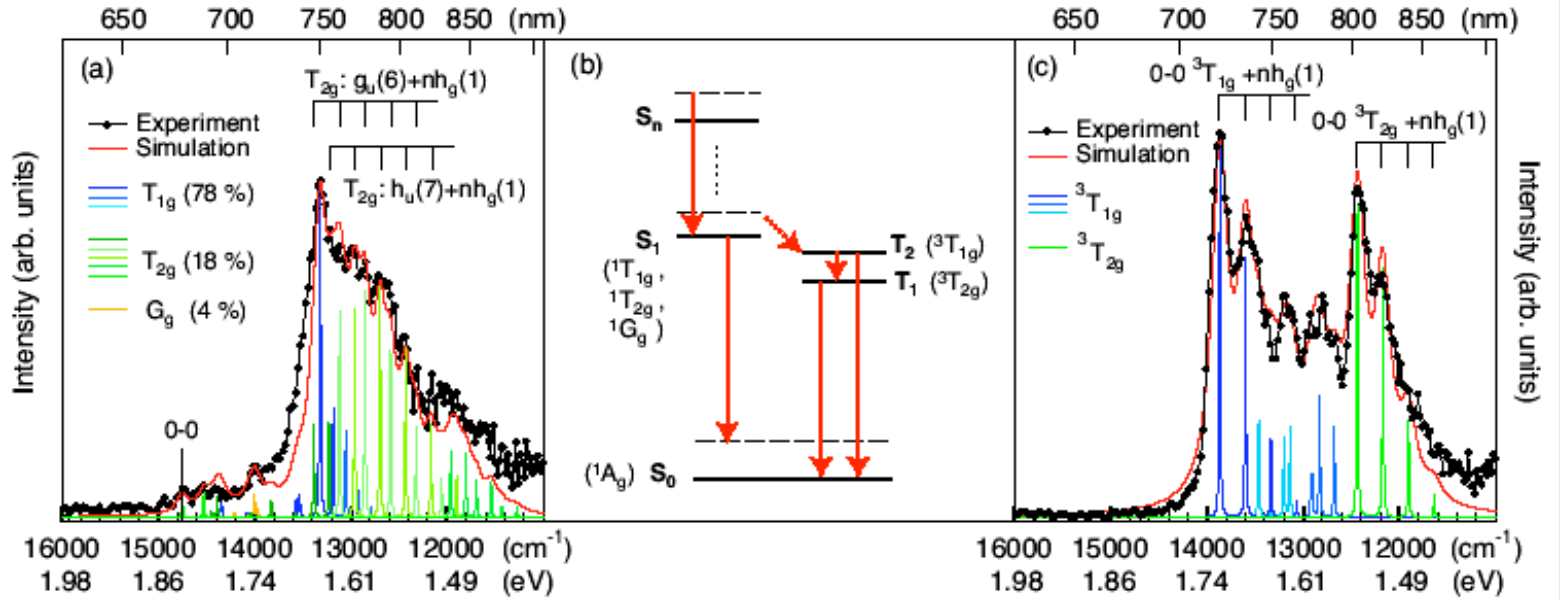
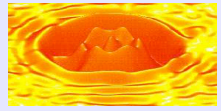


TABLE I: HT and JT active modes used in the simulation of the STM-induced light emission spectra shown in Fig. 4(a,c). For the most intense modes contributing to the spectra, the experimental frequencies [14, 27] are indicated in brackets.

Fluorescence: $S_0 \leftarrow S_1$		Phosphorescence: $S_0 \leftarrow T_1, T_2$	
S_1 (T_{1g})	HT: $t_{1u}(4)$ (1430 cm^{-1}), $h_u(7)$ (1566 cm^{-1}), $h_u(1)$, $h_u(3)$, $h_u(4)$, $t_{1u}(3)$, $h_u(5)$. JT: $h_g(7)$, $a_g(2)$, $h_g(1)$.	T_1 ($^3T_{2g}$)	JT: $h_g(1)$ (266 cm^{-1}).
S_1 (T_{2g})	HT: $g_u(6)$ (1410 cm^{-1}), $h_u(7)$ (1566 cm^{-1}), $g_u(1)$, $h_u(1)$, $g_u(4)$, $h_u(5)$. JT: $h_g(1)$ (266 cm^{-1}), $h_g(7)$, $a_g(2)$.	T_2 ($^3T_{1g}$)	HT: $t_{2u}(3)$ (1037 cm^{-1}), $h_u(1)$, $h_u(2)$, $h_u(4)$, $a_u(1)$, $g_u(4)$, $t_{1u}(3)$. JT: $h_g(1)$ (266 cm^{-1}).
S_1 (G_g)	HT: $h_u(4)$ (738 cm^{-1}), $h_u(2)$, $h_u(3)$, $g_u(3)$, $g_u(5)$, $t_{2u}(2)$.		

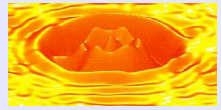


Fluorescence and phosphorescence (?) from individual (?) C_{60} molecules excited by local electron tunneling

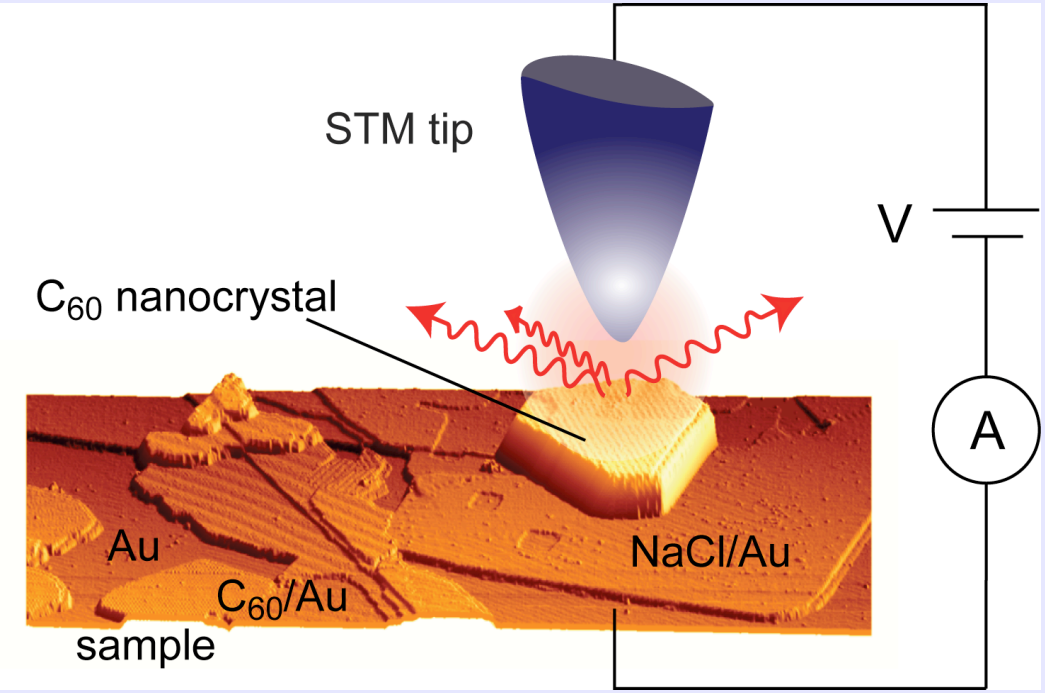
Three multilayered C_{60} nanocrystals self-assembled on an ultrathin NaCl film.

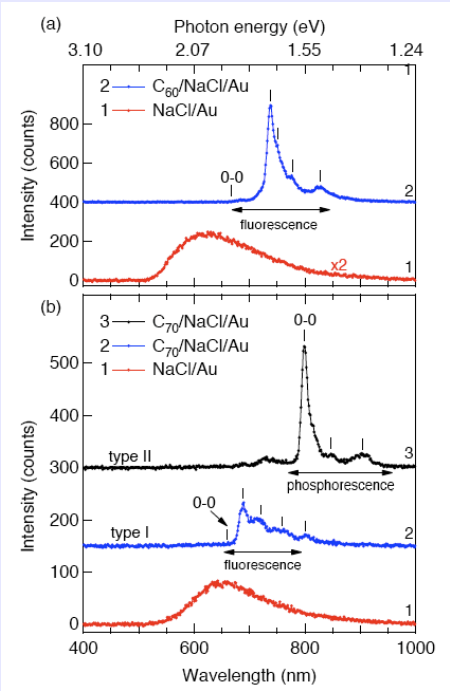
Luminescence induced by tunneling electrons can provide unambiguous chemical identification of individual (?) C_{60} molecules.

E. Ćavar, M.-C. Blüm, M. Pivetta, F. Patthey, M. Chergui, WDS, PRL **95**, 196102 (2005)



Light emission from STM tunneling junctions: The role of the localized surface plasmon C_{60} and C_{70} on NaCl/Au(111)



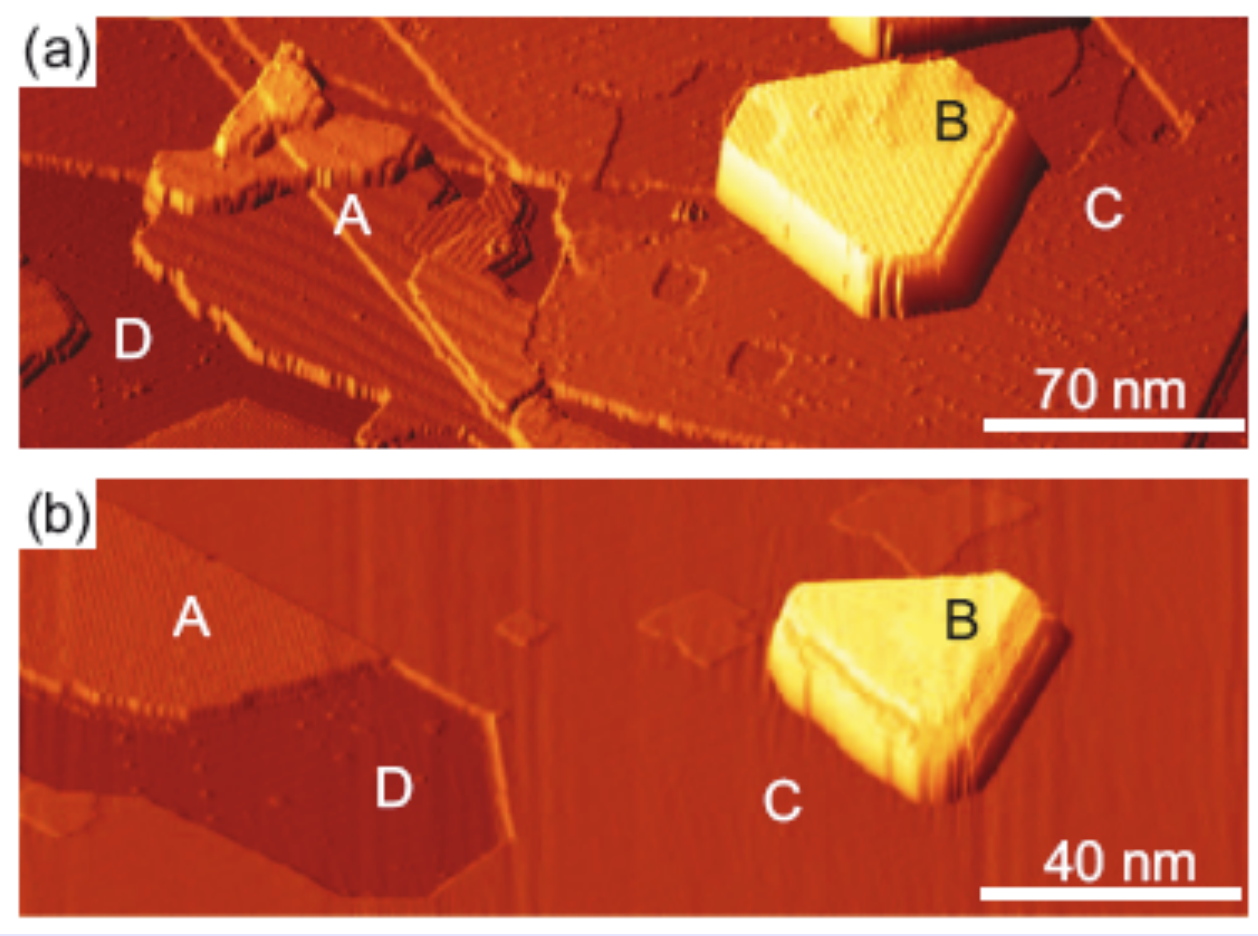


Frédéric Rossel, Marina Pivetta, François Patthey, WDS

Institut de Physique de la Matière Condensée

Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland

Fullerene nanocrystals on NaCl/Au(111)

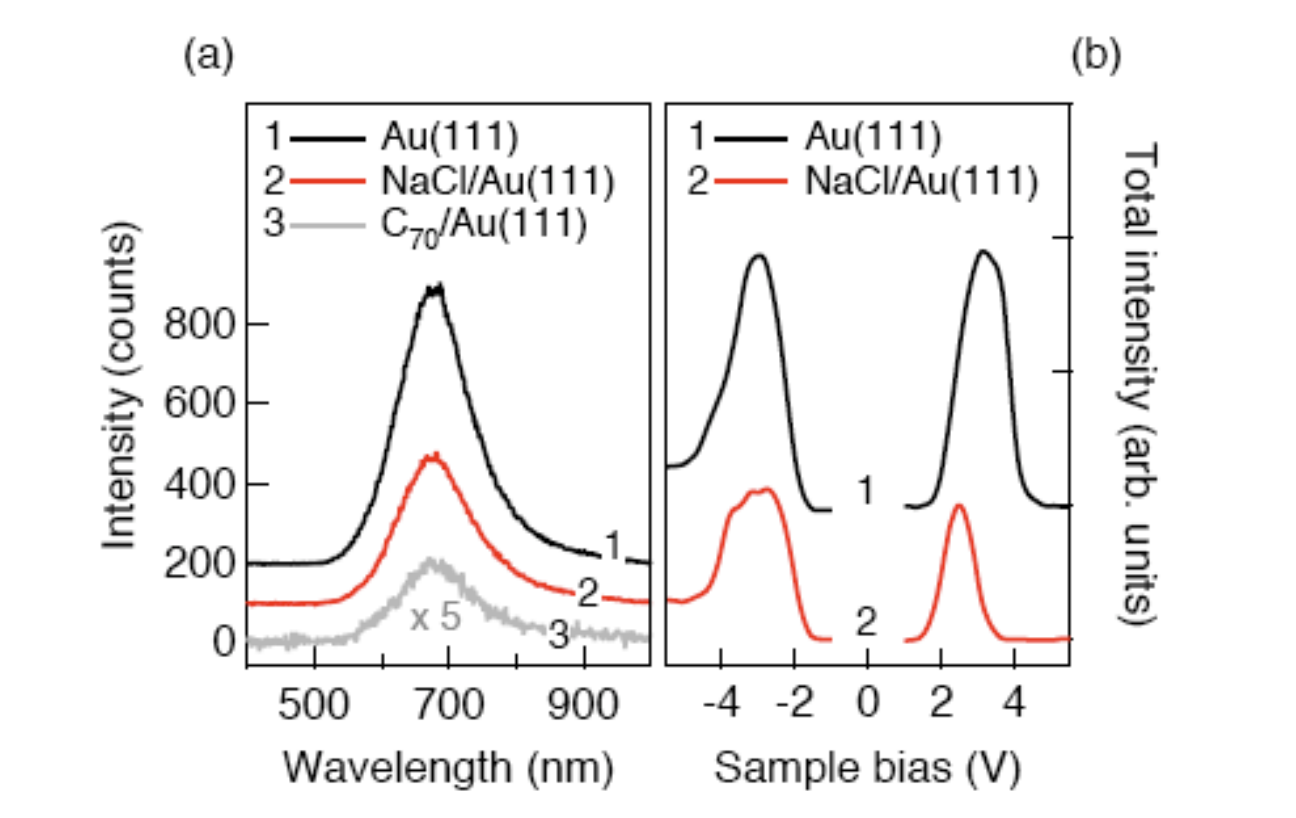


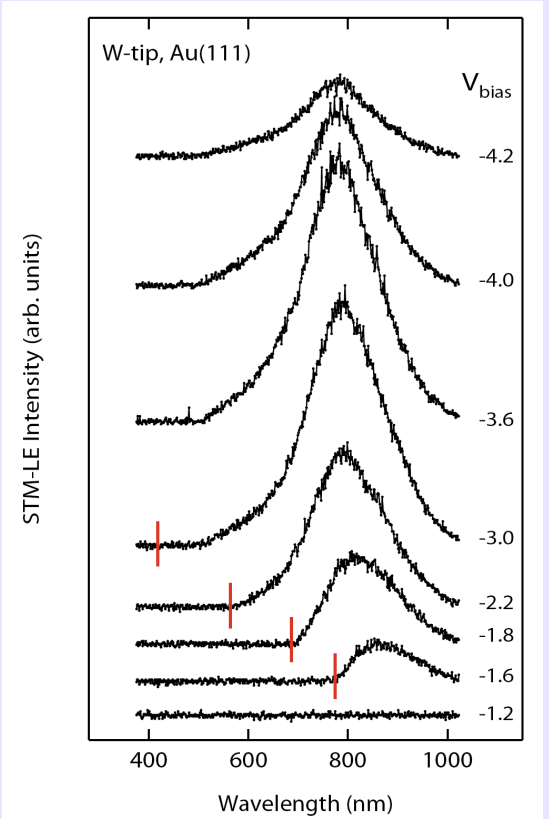
C_{60}

C_{70}

F. Rossel, M. Pivetta, F. Patthey, WDS, Optics Express **17**, 2714 (2009)

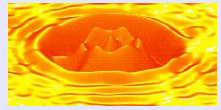
Plasmon-mediated light emission spectra

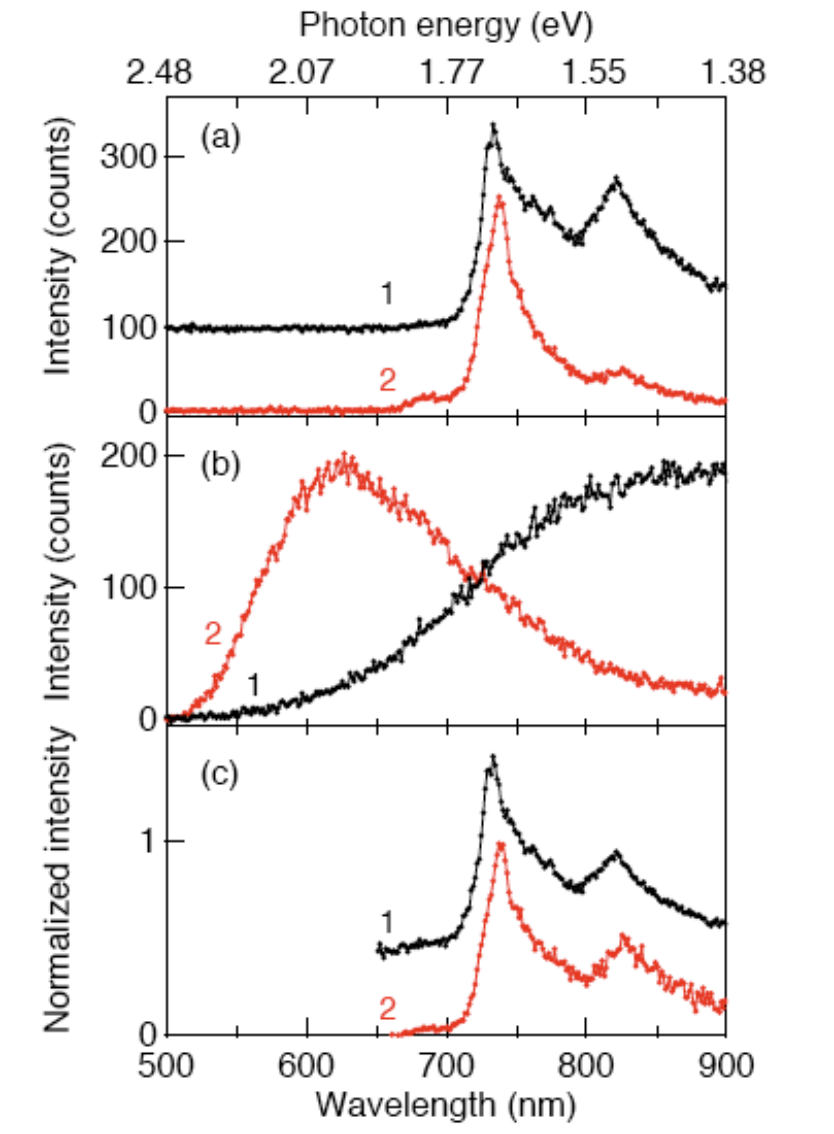




I = 2 nA, t = 60 s

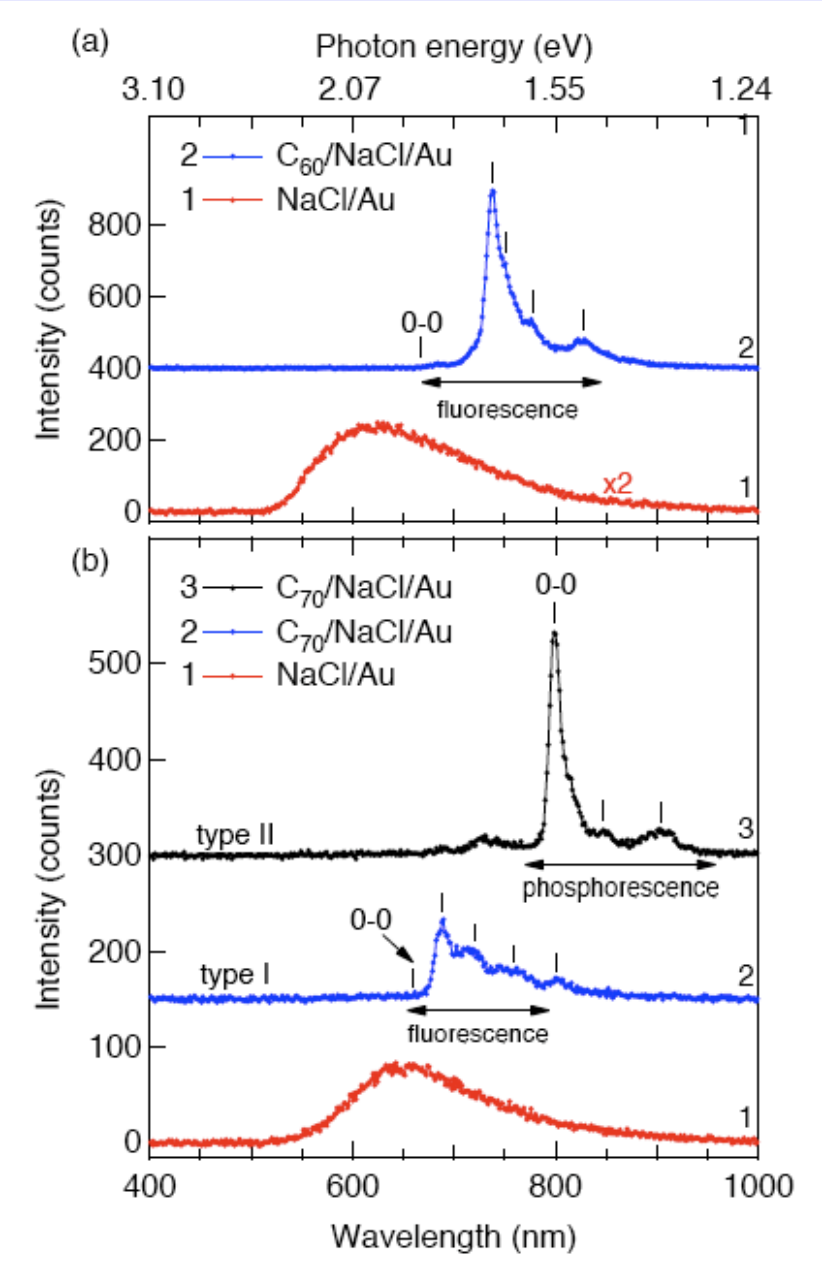
F. Rossel, M. Pivetta, F. Patthey, WDS, Optics Express **17**, 2714 (2009)





Plasmon induced enhancement of spectral stuctures at different energies

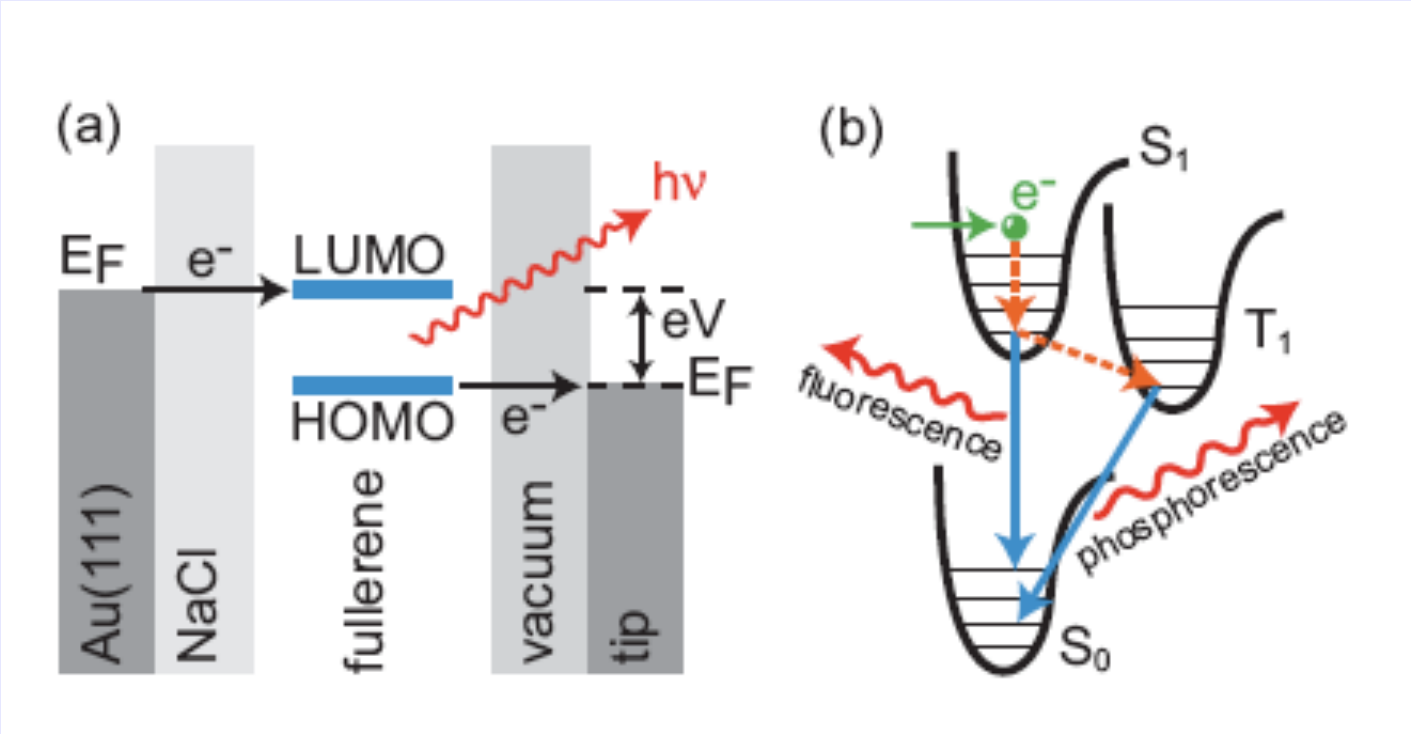
F. Rossel, M. Pivetta, F. Patthey, WDS, Optics Express **17**, 2714 (2009)



Plasmon enhanced luminescence from fullerene molecules excited by local electron tunneling

F. Rossel, M. Pivetta, F. Patthey, WDS,
Optics Express **17**, 2714 (2009)

Schematic energy diagram of a double barrier tunnel junction at negative bias voltage



F. Rossel, M. Pivetta, F. Patthey,WDS, Optics Express **17**, 2714 (2009)

What about the spatial resolution?

The ultimate challenge:

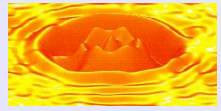
Can we observe and characterize

light emission

from

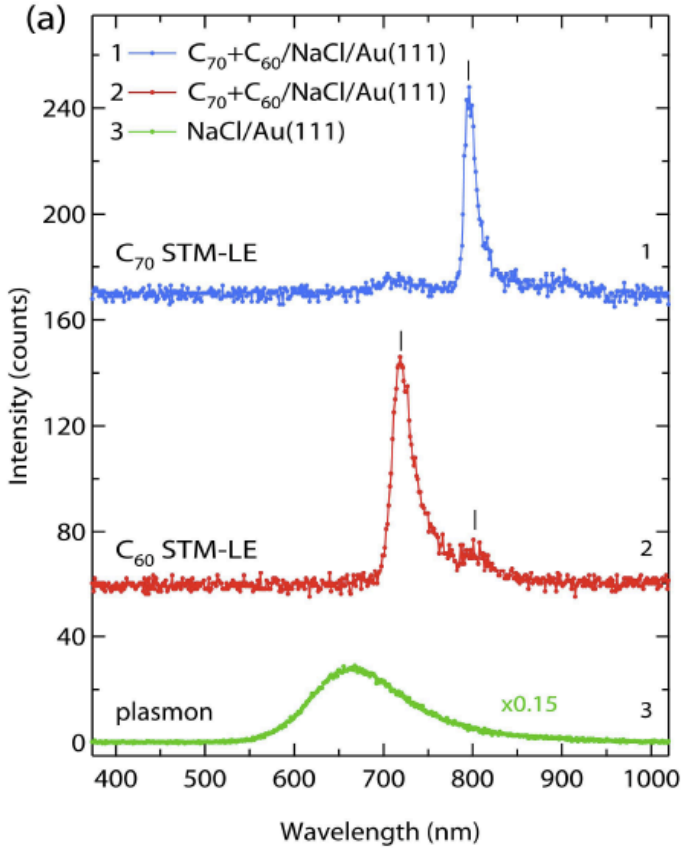
a single molecule

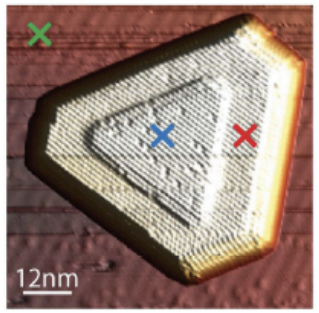
embedded within a surface layer of an ensemble?



STM-LE spectra from C_{70} island surrounded by C_{60} molecules on NaCl/Au(111)

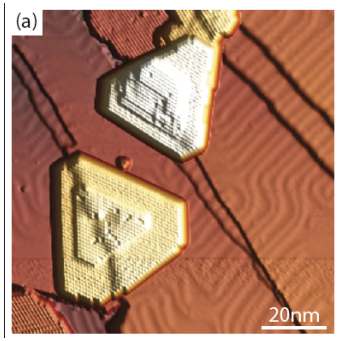
Light emission:
U = -3 V
I = 2 nA
t = 60 s

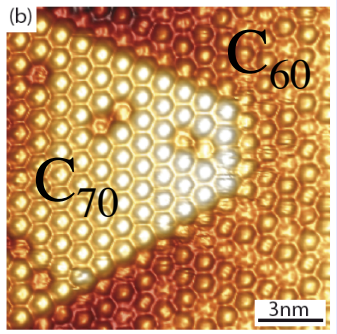




Topo:
U = -3 V
I = 0.02 nA
60 x 60 nm^2

Sequential evaporation





«lateral chemical resolution» ≈ 2 nm ≈ 2 molecules

F. Rossel, M. Pivetta, F. Patthey, A. P. Seitsonen, WDS, in preparation

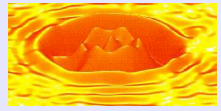
EPFL

Conclusions

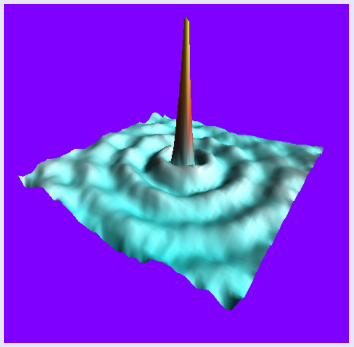
STM induced light emission:

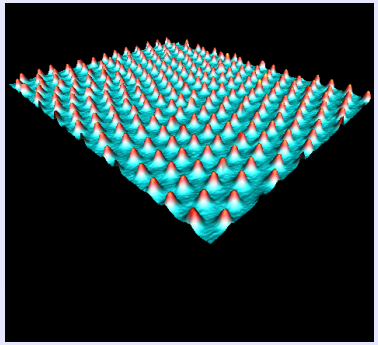
- Observation of luminescence from C_{60} and C_{70} molecules embedded within an ensemble

- Chemical identification via vibrational modes and electronic transitions

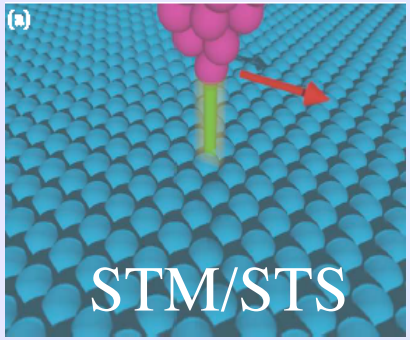


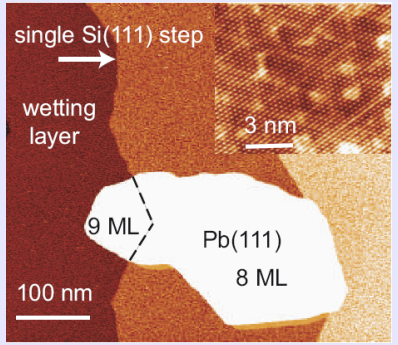
Tutorial: Fabrication and characterization of ordered atomic-scale structures: Necessary steps towards a future nanotechnology

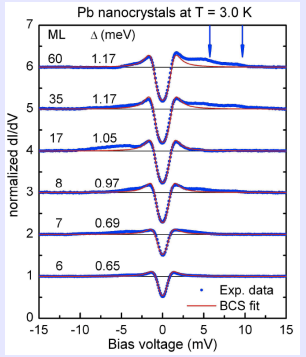




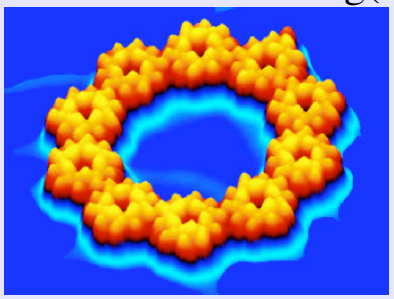
Ce/Ag(111)

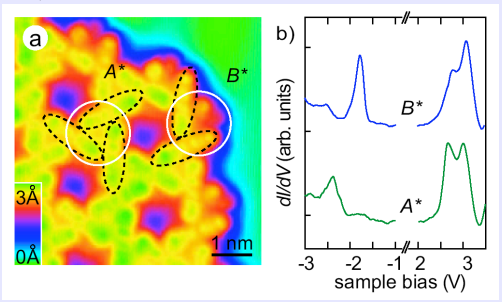




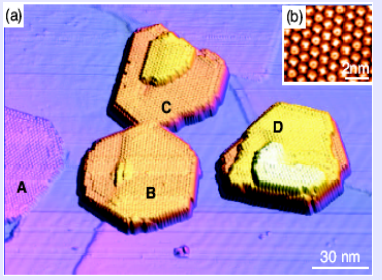


Pb(111)

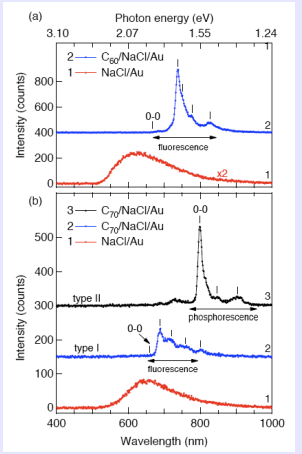




Rubrene/Au(111)



C_{60}/NaCl/Au(111)



C_{70}/NaCl/Au(111)

Wolf-Dieter Schneider

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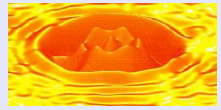
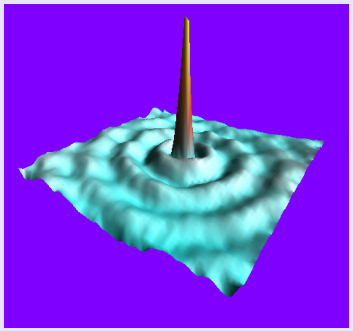
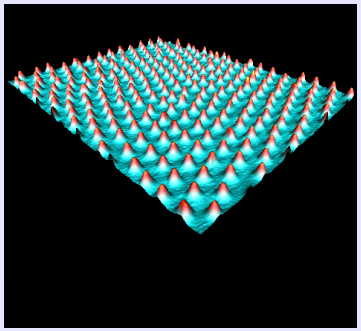
Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland



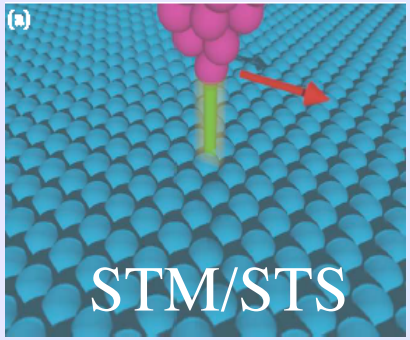
Thank you for your attention!

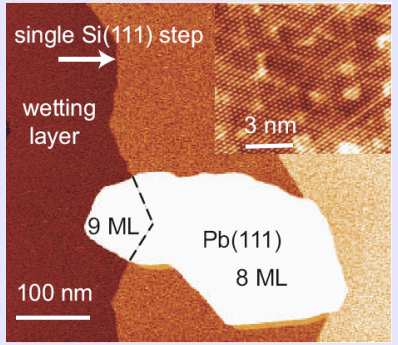
Fabrication and characterization of ordered atomic-scale structures

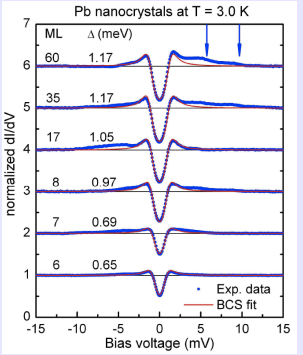




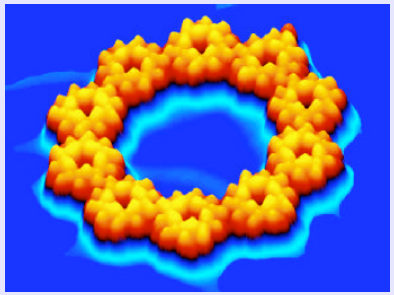
Ce/Ag(111)

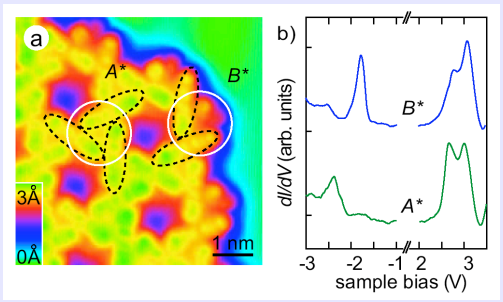






Pb(111)



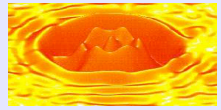


Rubrene/Au(111)

Wolf-Dieter Schneider

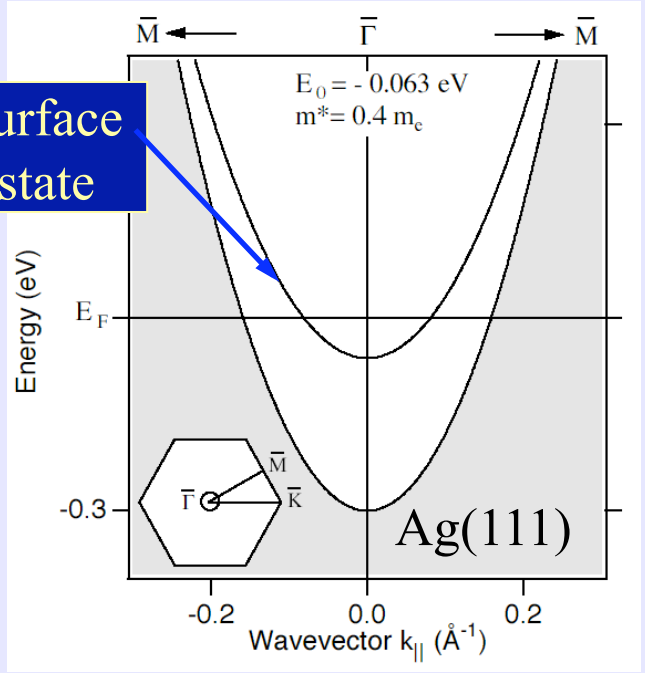
Institut de Physique de la Matière Condensée

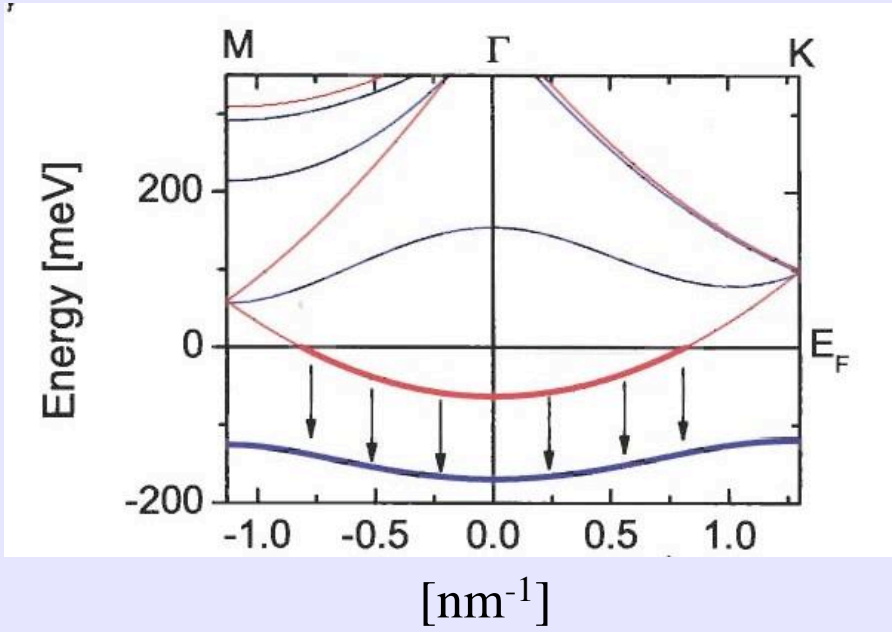
Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland



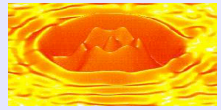
Electronic effects of superlattice on the surface-state 2DEG:

- the superlattice induces **band-structure** in the surface state band
- opens gap at Fermi level ⇒ **stabilizes the superlattice**
- directly observe effect of **local disorder** and **superlattice constant** on the surface state DOS



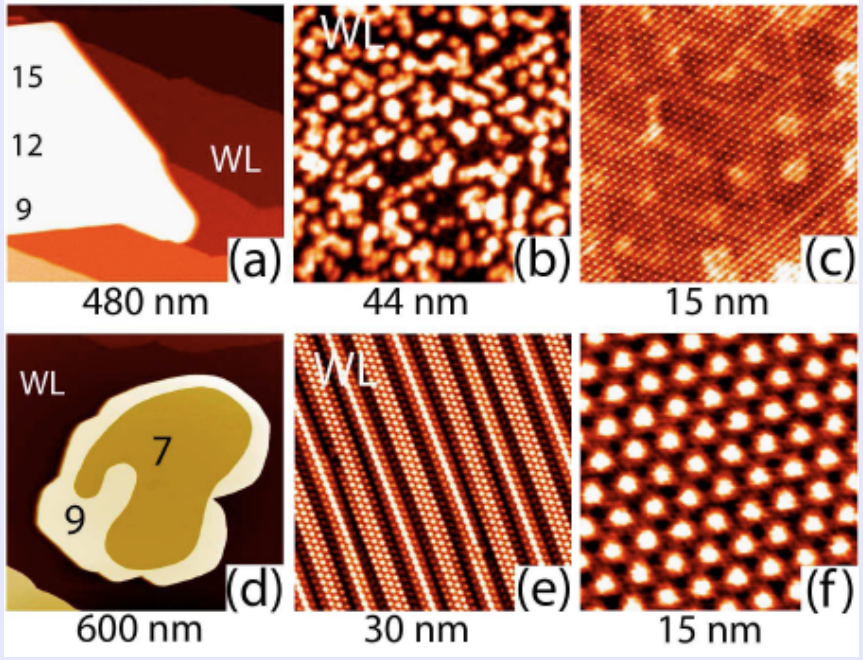


M. Ternes, C. Weber, M. Pivetta, F. Patthey, J. P. Pelz, Th. Giamarchi, F. Mila, WDS, PRL **93**,146805 (2004)



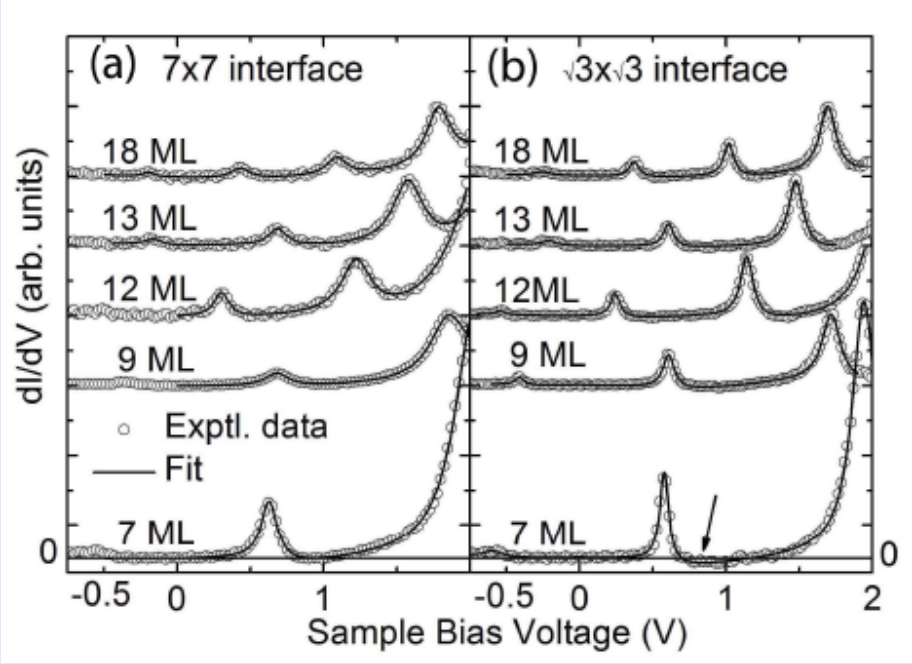
Quantum-well states

Pb/Si(111)7x7



Pb/Pb-√3x √3/Si(111)

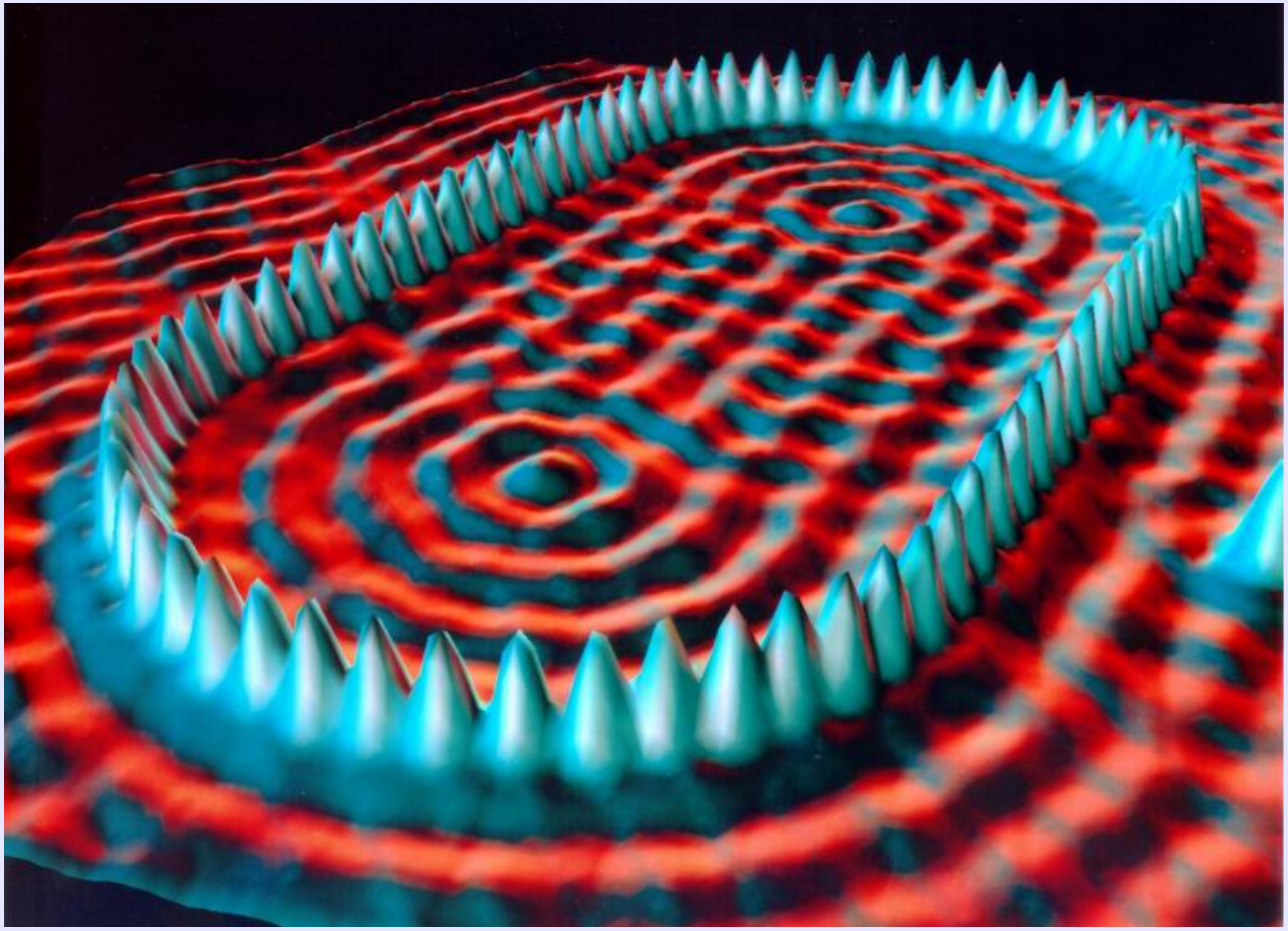
disordered crystalline



T = 5 K

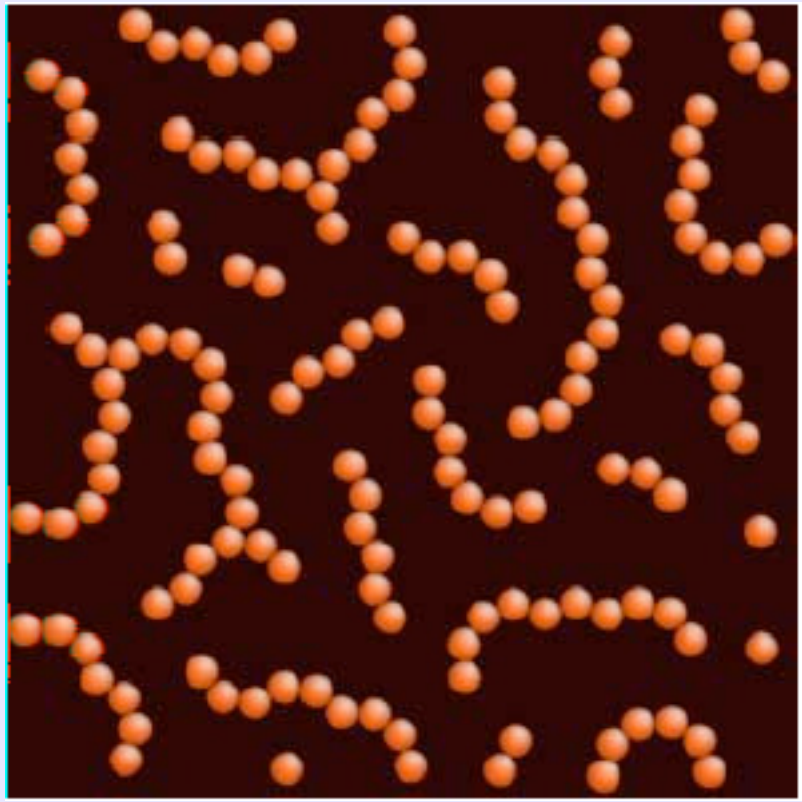
Ripples in the 2DEG from a Quantum Corral ~15 nm wide

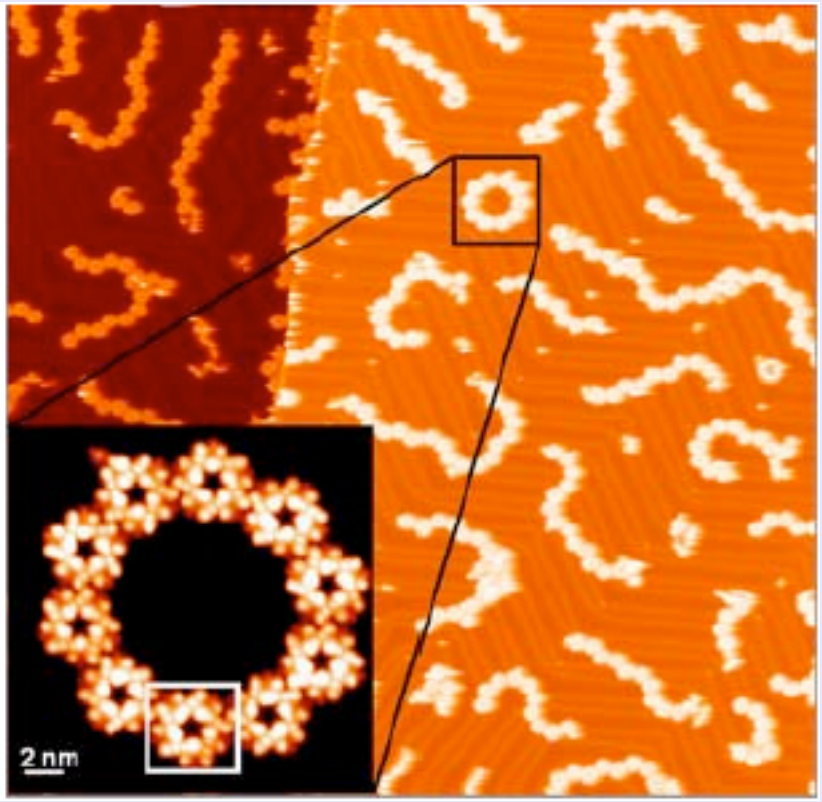
Fe atoms on a Cu(111) surface



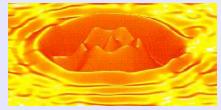
M. Crommie, C. Lutz, D. M. Eigler, Science **262**, 218 (1993)

Rubrene on Au(111): Self-assembly mediated by short-range attractive and long-range repulsive electrostatic interactions

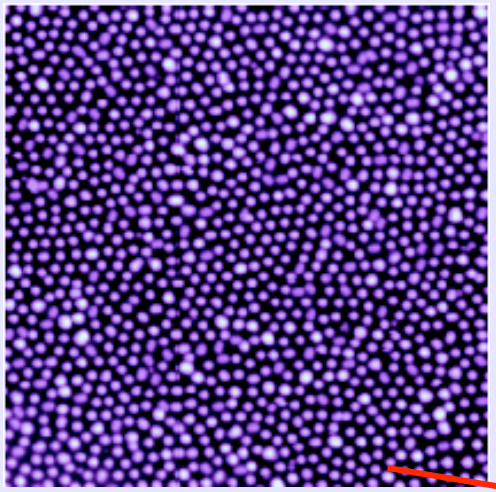


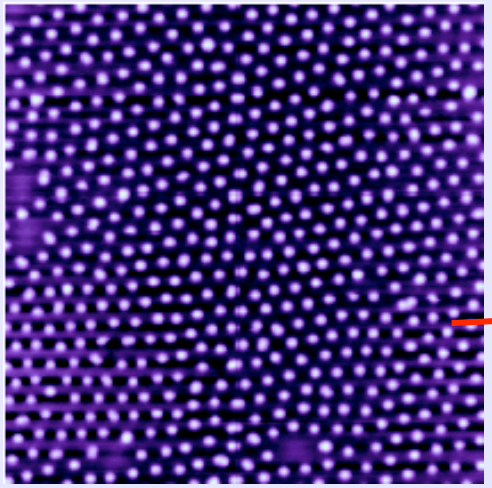


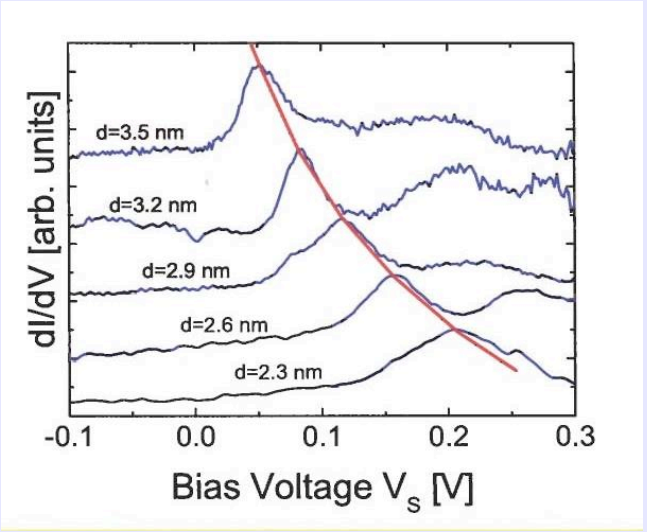
G. Tomba, M. Stengel, WDS, A. Baldereschi, A. De Vita, submitted

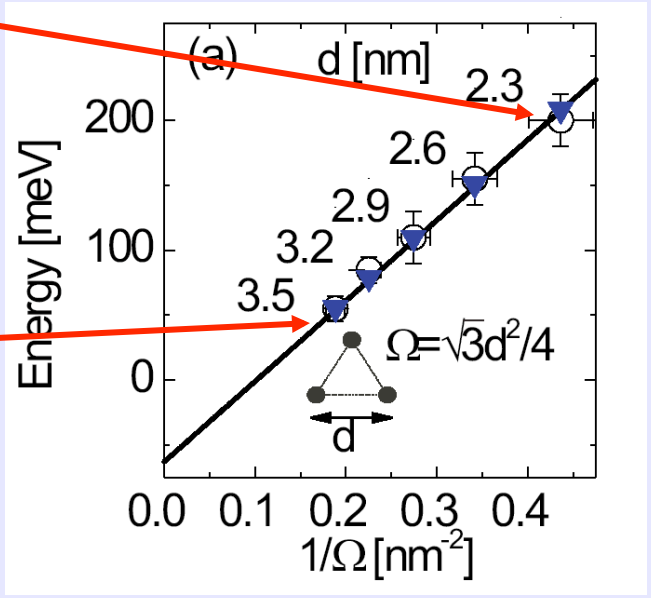


Quantum-size effect of Ce superlattices on Ag(111)









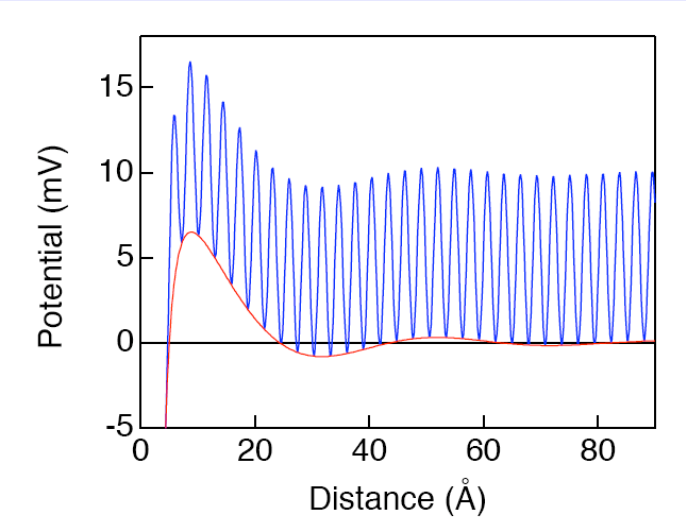
M. Ternes, M. Pivetta, F. Patthey, WDS, Prog. Surf. Sci., to be published

Requirements to create and observe a superlattice

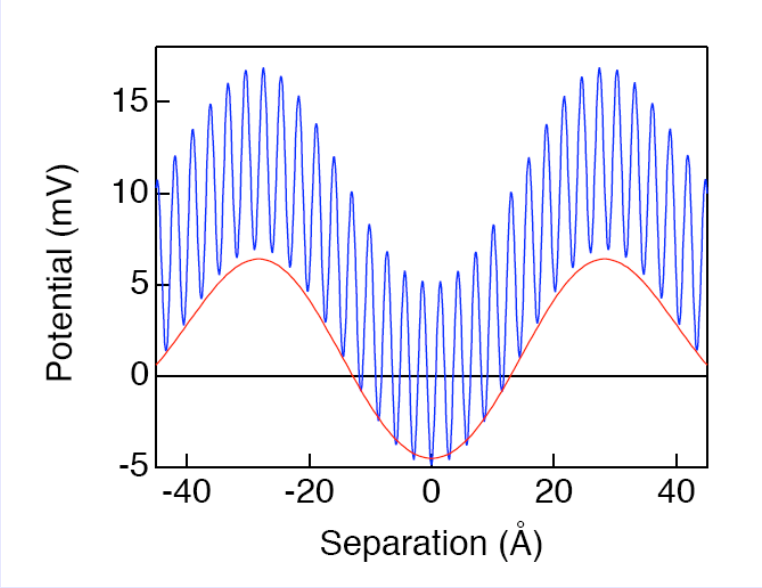
(1) The adatom diffusion barrier ΔE_{diff} cannot be too large compared to the interaction potential ΔE_{int}.

(2) ΔE_{int} increases with adatom coordination, $\Rightarrow$ more likely to find stable lattice at higher coverage.

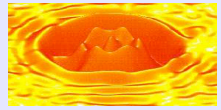
Ce/Ag(111) - pair potential



Ce/Ag(111) Hex-lattice potential



(3) If you find adatom with small ΔE_{diff} , must be able to go to low enough temperature to observe it!

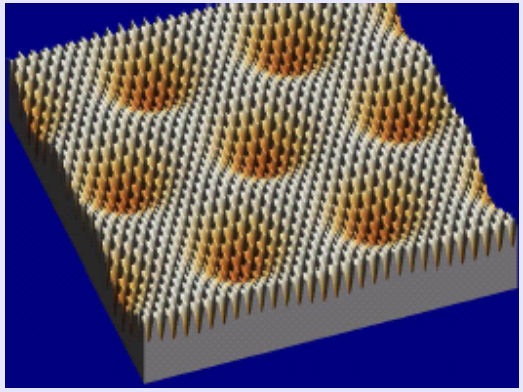


To summarize:

- **Self-assembly of a 2D hexagonal Ce superlattice mediated by Ag(111) surface state electrons**

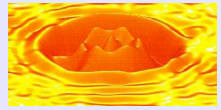
- **Analysis of the thermal motion of the Ce adatoms in their superlattice site**

- **Determination of the confining potential for the Ce adatoms in the superlattice**

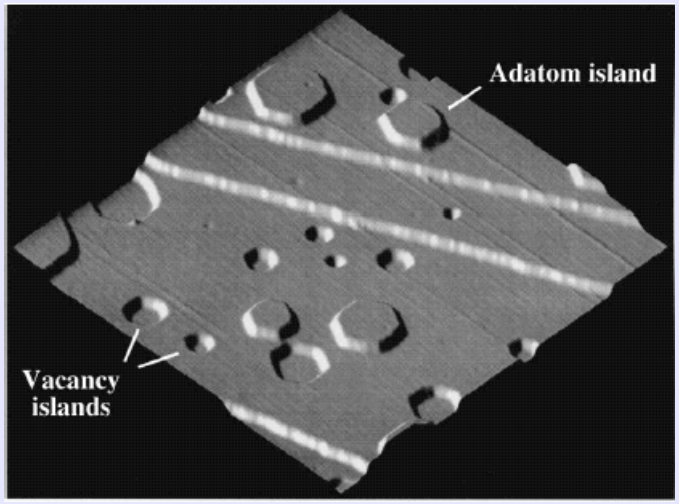


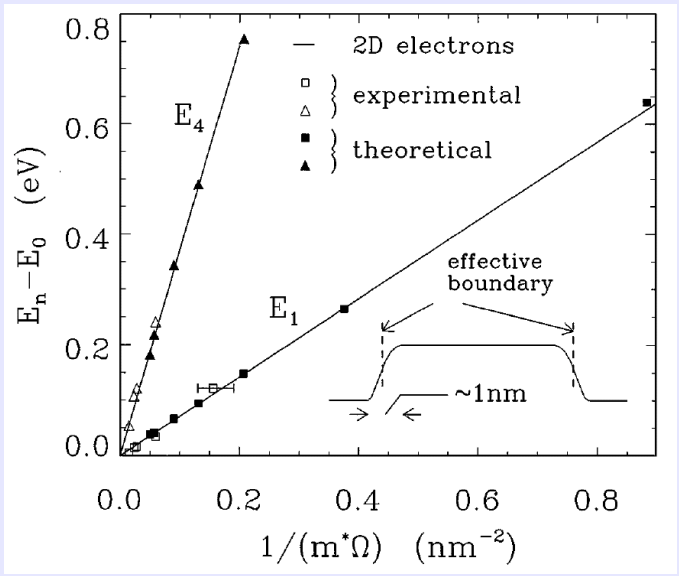
- **Stability of the superlattice:**
  Subtle balance between
  sample temperature,
  surface diffusion barrier,
  concentration-dependent adatom interaction potential.

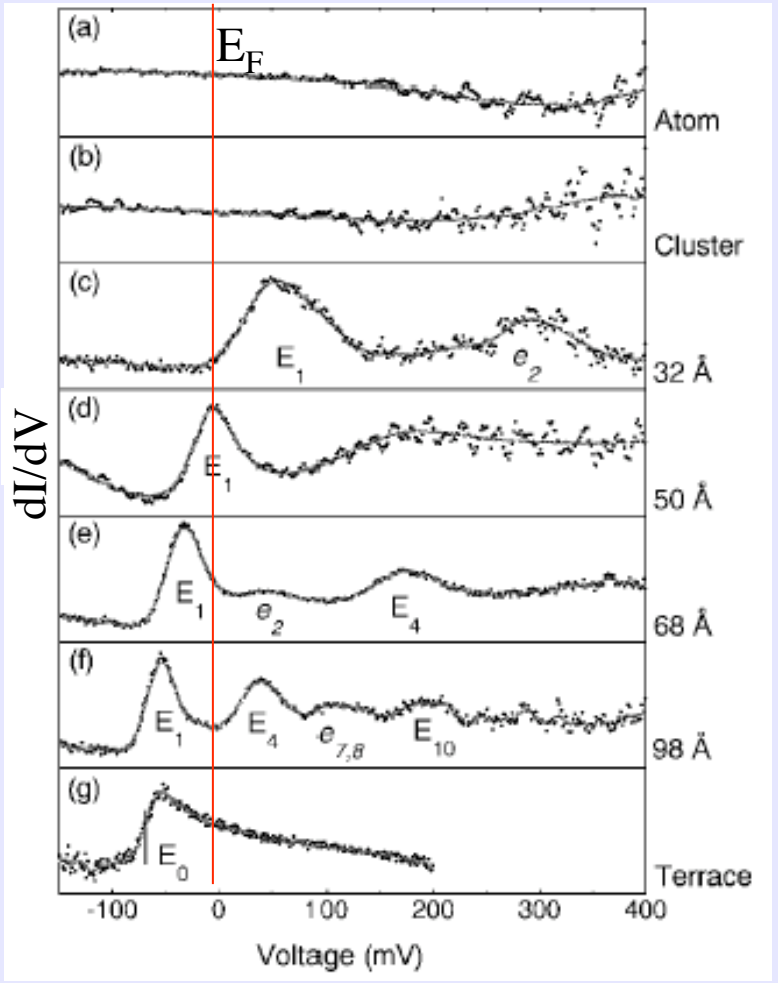
F. Silly, M. Pivetta, M. Ternes, F. Patthey, J. P. Pelz, WDS, PRL **92**, 016101 (2004)



Quantum size effect in Ag islands on Ag(111)







J. Li, WDS, R. Berndt, S. Crampin,
PRL **80**, 3332 (1998) & Surf. Sci. **422**, 95 (1999)

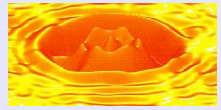
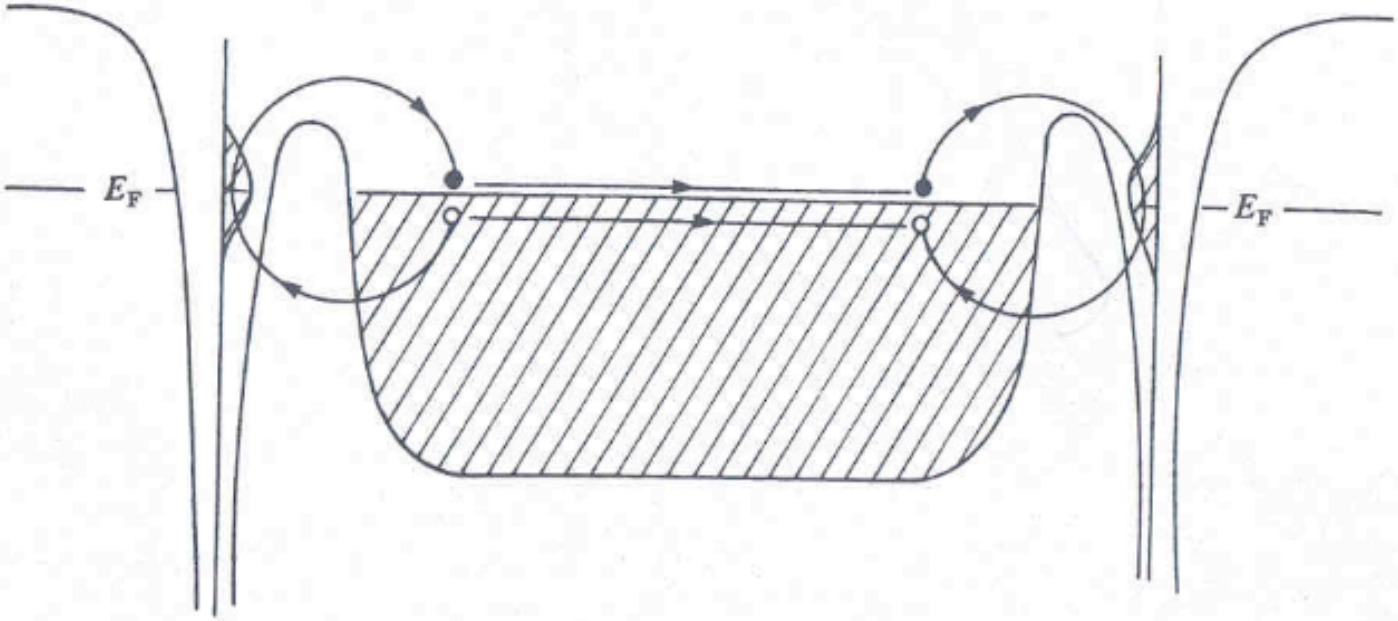
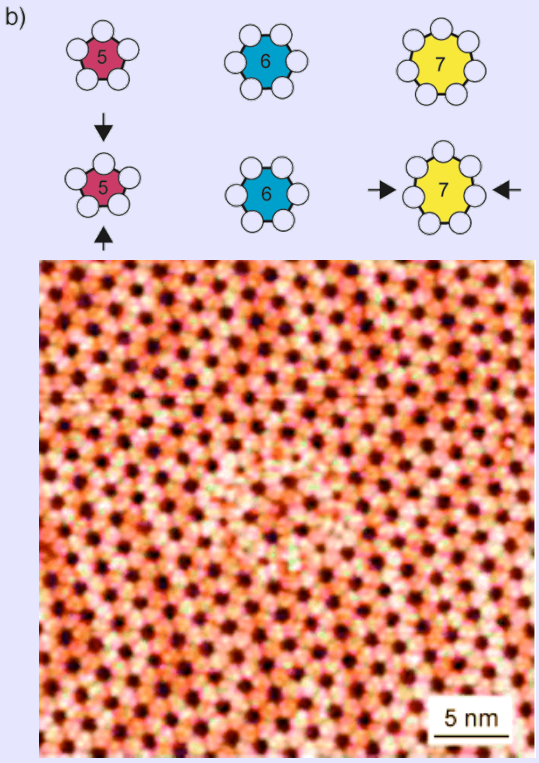


Fig. 11.18. Schematic view of the indirect electronic interaction between two adsorbates in the resonant level model.

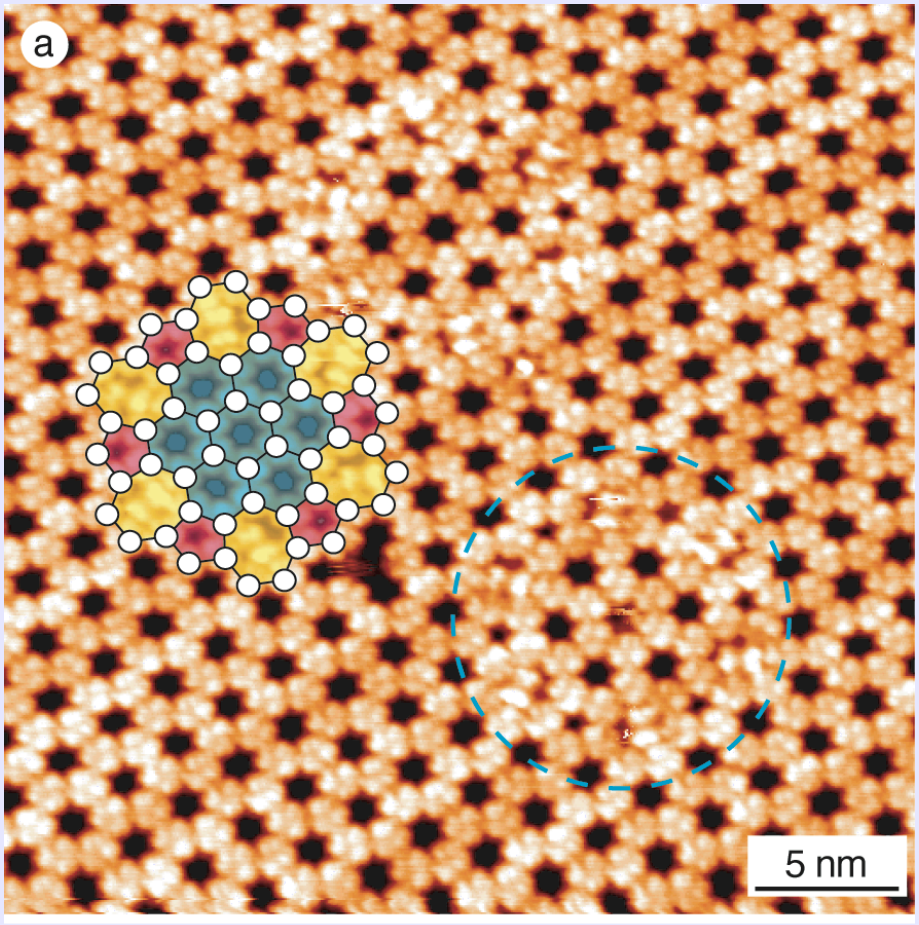


A. Zangwill, Physics at Surfaces

2D-tiling: Supramolecular rosettes embedded in a well-ordered honeycomb domain



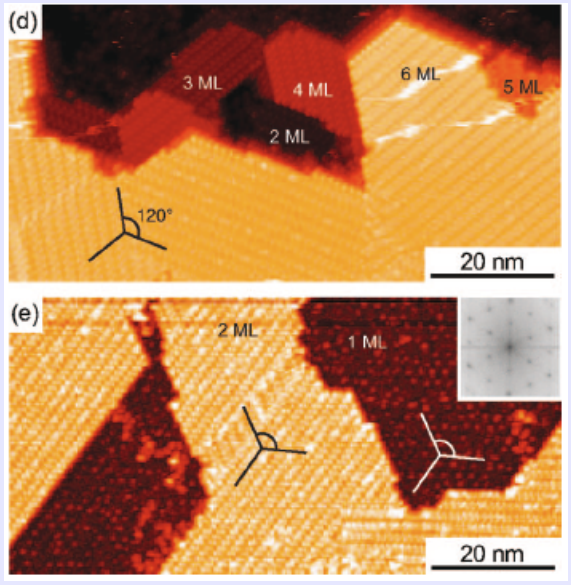
Circular singularities in extended honeycomb domains, formed by the replacement of a ring of twelve hexagons by six pentagon-heptagon pairs



M. Pivetta, M.-C. Blüm, F. Patthey, WDS, Angew. Chem. Int. Ed. **47**, 1076 (2008)

EPFL

3D-chirality transfer in Rubrene multilayer islands on Au(111)



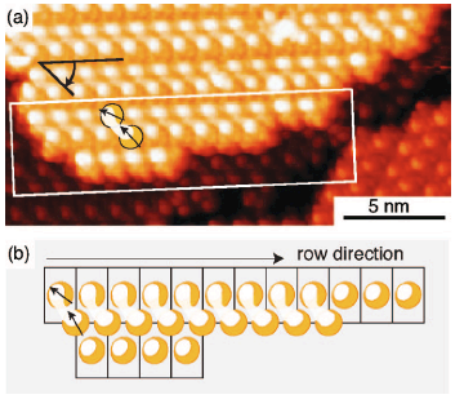


Figure 2. (a) STM image (22 nm × 11 nm) showing the detail of the twin-row structure and a layer edge. Different layers and domain orientations are visible. (b) Model reproducing the region of the uppermost layer of the island delimited by a white rectangle in a, sketched using the unit cell described in Figure 3b. A model of a molecular pair is superimposed on the STM data shown in a.

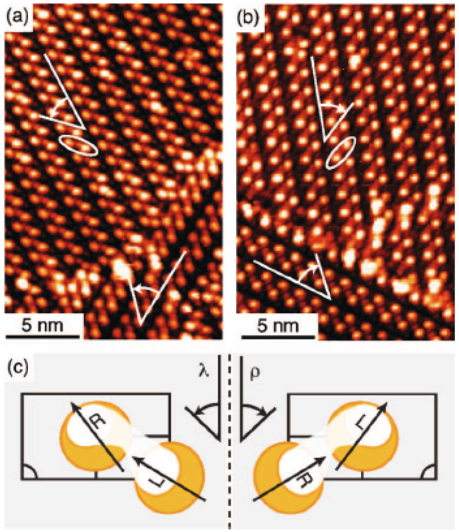
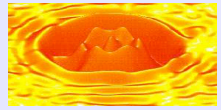
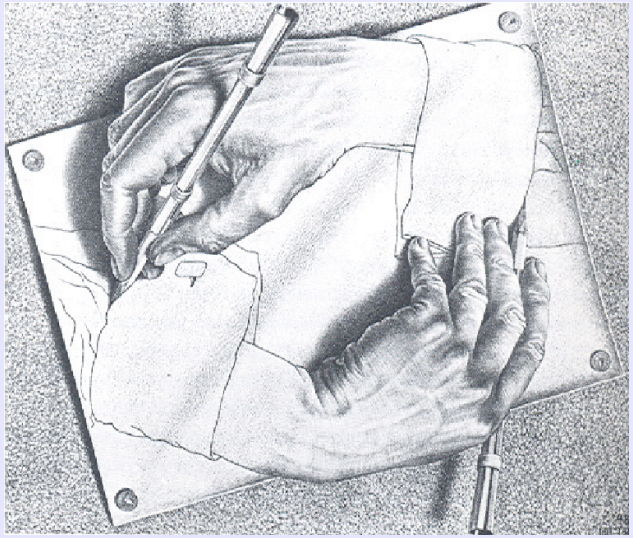


Figure 4. STM images (15 nm × 23 nm) acquired on two distinct rubrene islands demonstrating the island chirality: (a) left-handed domains; (b) right-handed domains. Each island is formed by domains of only one chirality. (c) Mirror unit cells for left-handed (λ) and right-handed (ρ) domains.

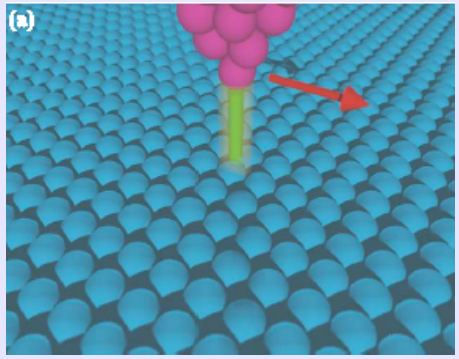
M. Pivetta, M.-C. Blüm, F. Patthey, WDS, J. Phys. Chem. B**113**, 4578 (2009)



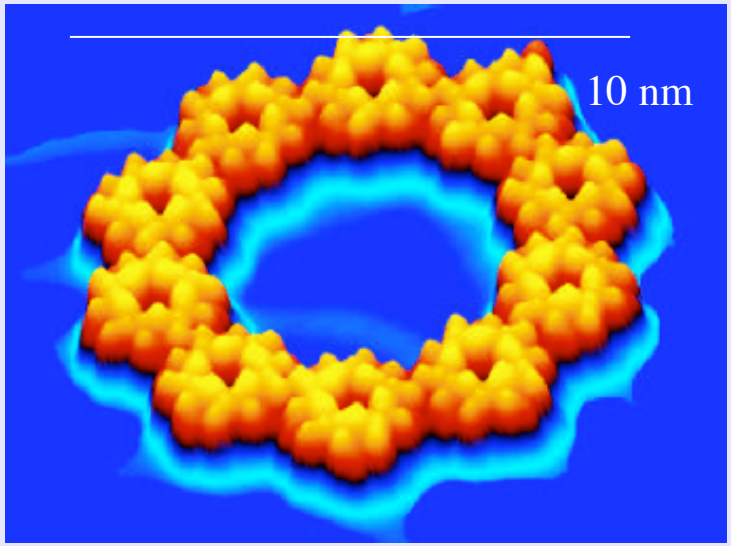
A Local View on Chirality



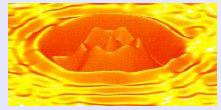
M. C. Escher, "Mains dessinant"
Lithographie (1948)



STM



Rubrene/Au(111):
Nested chiral supramolecular self-assembly



Identification:
White protusions =
individual
methyl groups

Determination of the absolute chirality of individual adsorbed molecules using the scanning tunnelling microscope

G. P. Lopinski, D. J. Moffatt, D. D. M. Wayner & R. A. Wolkow

Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, Canada K1A 0R6

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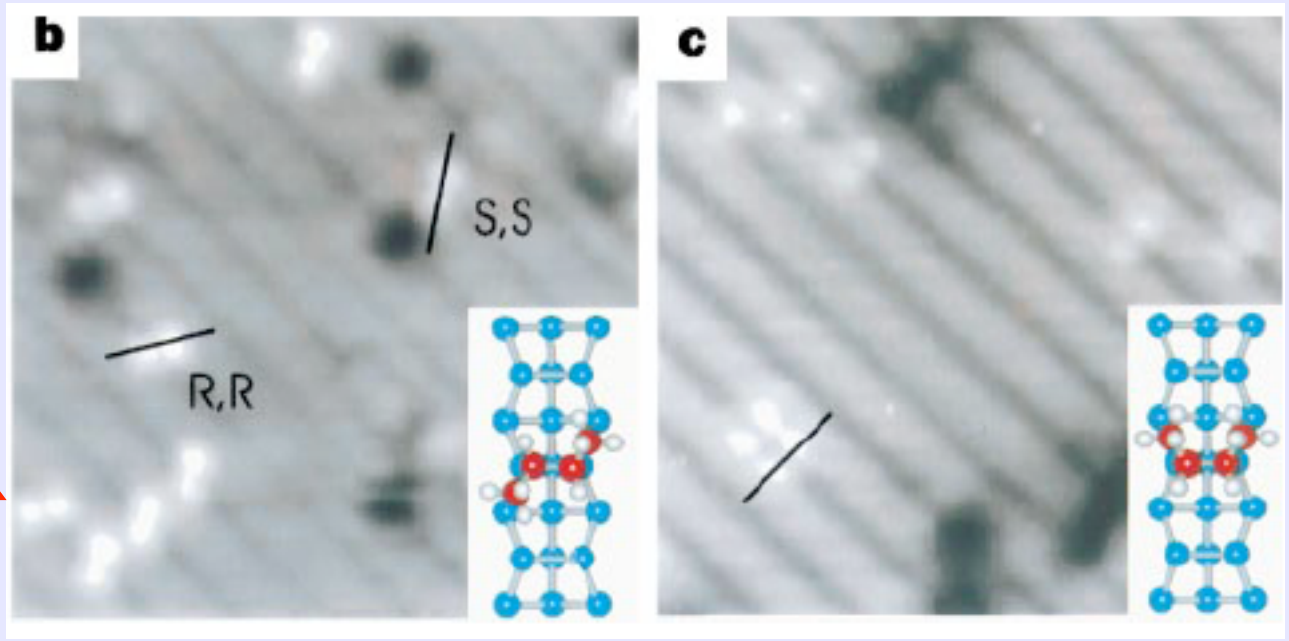
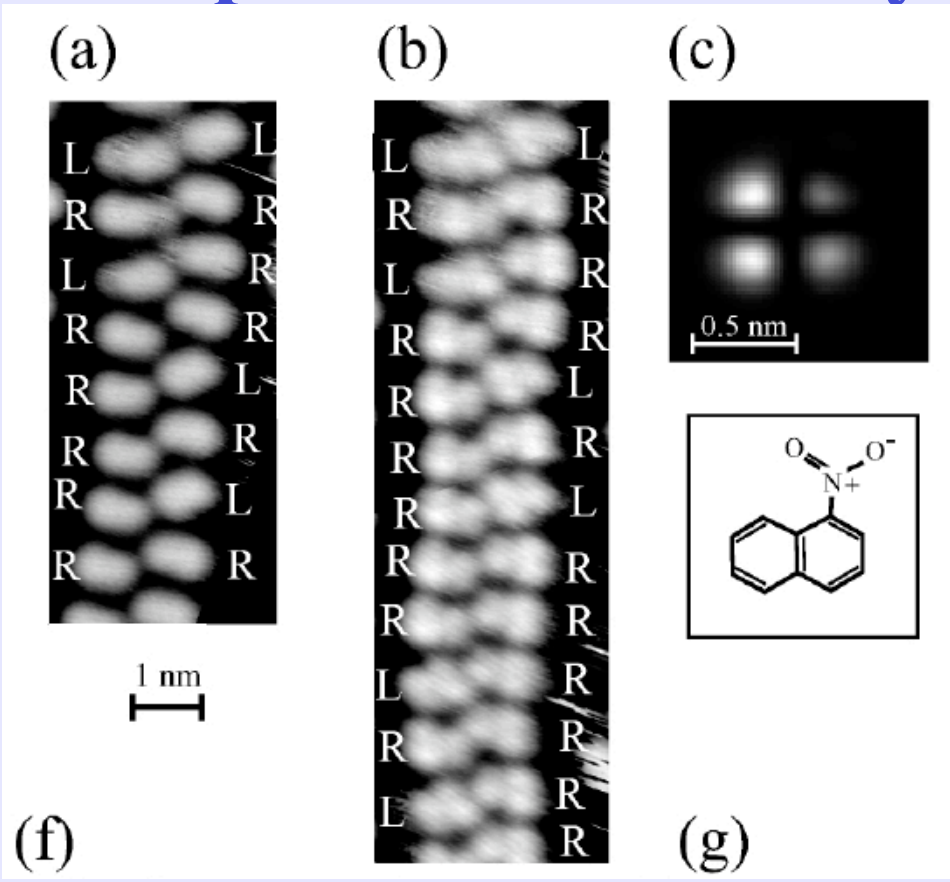


trans-2-butene *cis*-2-butene

Submolecular resolution of supramolecular chains: Comparison with theory



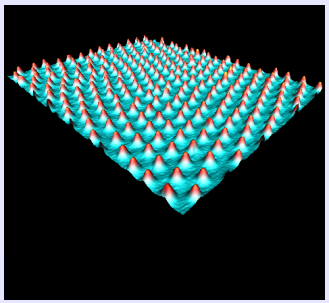
2D chirality

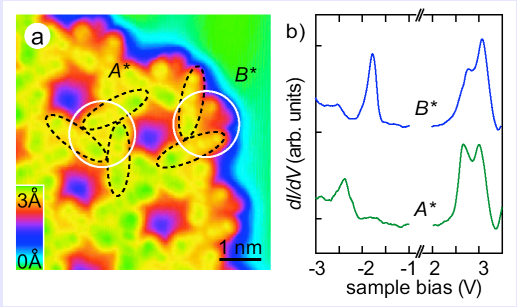
M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

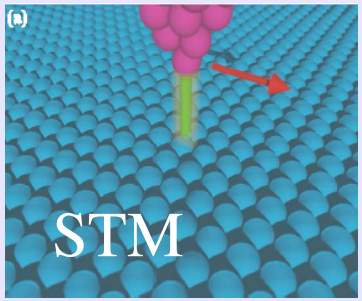
Spectroscopic manifestations of low-dimensional physics: A local view

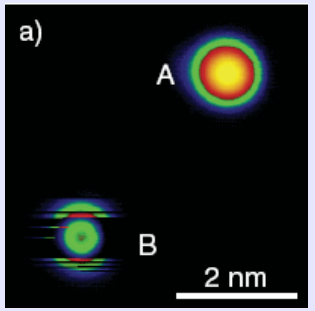
elastic tunneling

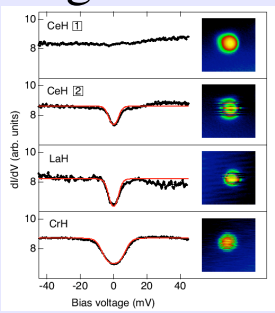
inelastic tunneling

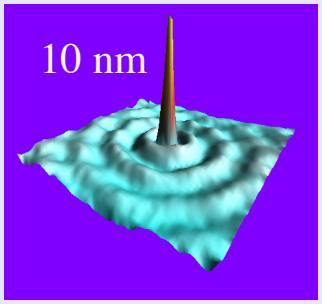


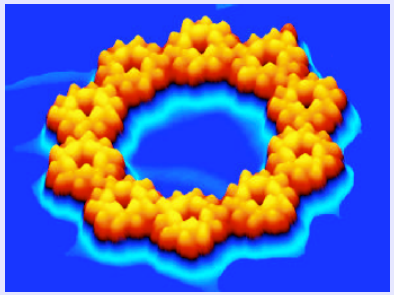


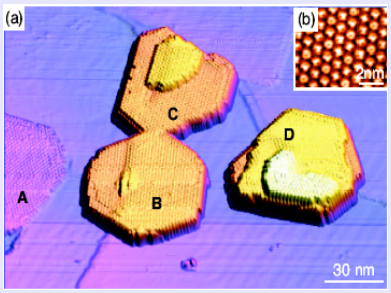


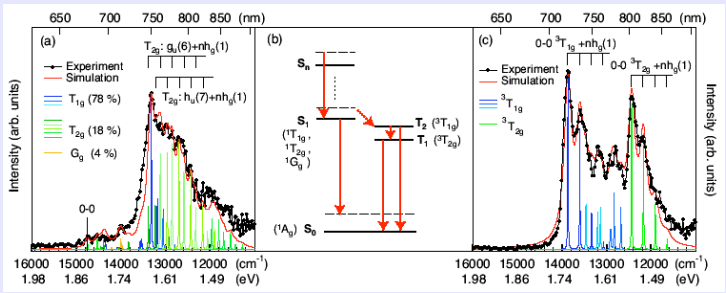










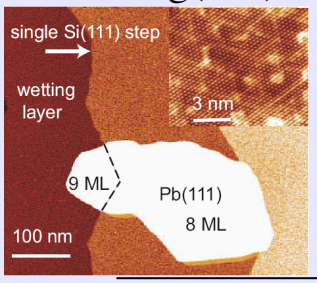


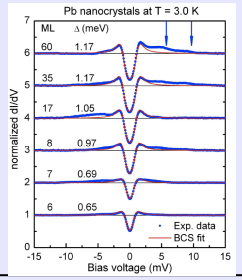
Ce/Ag(111)

Rubrene/Au(111)

C_{60}/NaCl/Au(111)

STM-induced luminescence from a single C_{60} molecule?

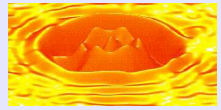




Wolf-Dieter Schneider

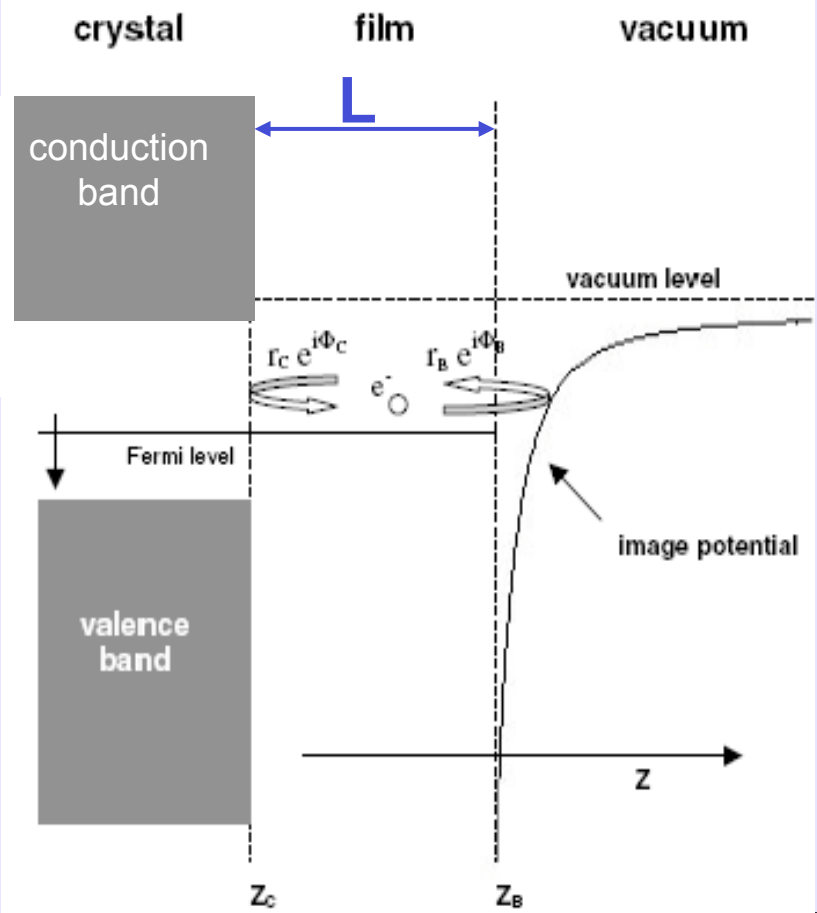
Institut de Physique de la Matière Condensée

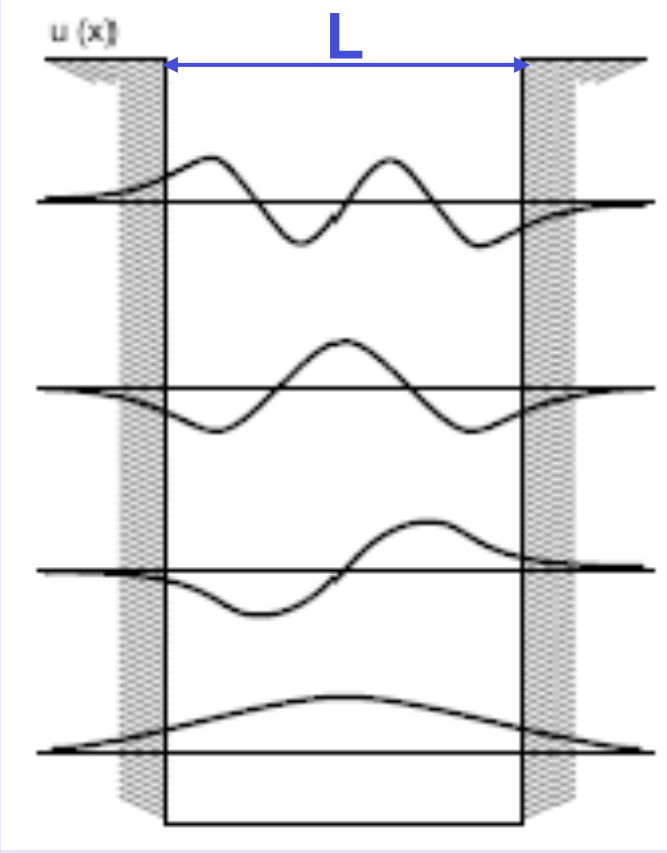
Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland



Quantum Well System

For metals: R. C. Jaklevic and J. Lambe PRB**12**,4146 (1975) (electron tunneling)
L. Wachs, A. P. Shapiro, T.C. Hsieh, T. C. Chiang, PRB **33**, 1460 (1986) (photoemission)
J. E. Ortega, F. J. Himpsel, PRL **69**, 844 (1992) (photoemission)
I. B. Altfeder, K. A. Matveev, D. M. Chen, PRL 78, 2815 (1997) (STM/STS)





$\lambda_n = 2L / n \quad ; \quad E_n = n^2h^2 / (8mL^2)$

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Electron Fringes on a Quantum Wedge

I. B. Altfeder,[1] K. A. Matveev,[1,2] and D. M. Chen[1]
[1]*The Rowland Institute for Science, Cambridge, Massachusetts 02142*
[2]*Department of Physics, Duke University, Durham, North Carolina 27708-0305*
(Received 11 October 1996)

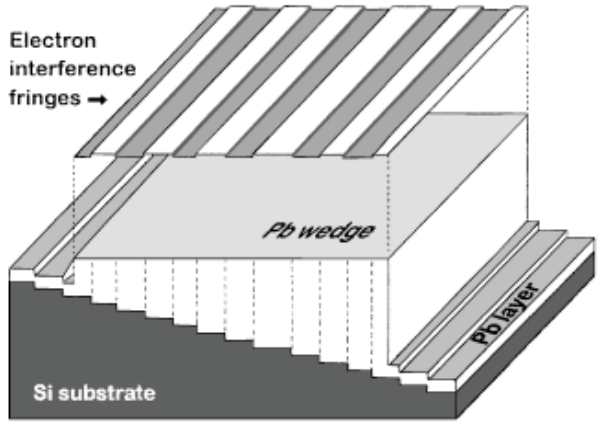
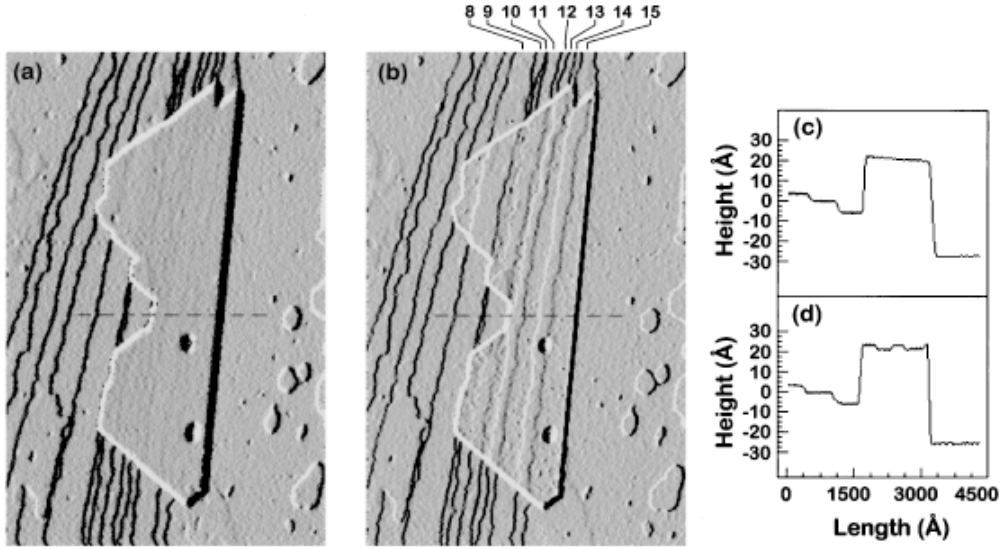


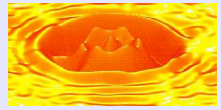
FIG. 2. Schematic of a quantum wedge on a stepped substrate. Electron interference fringes are shown above the wedge. Vertical scale is enlarged by a factor of 100.



U= 5V U= - 5V

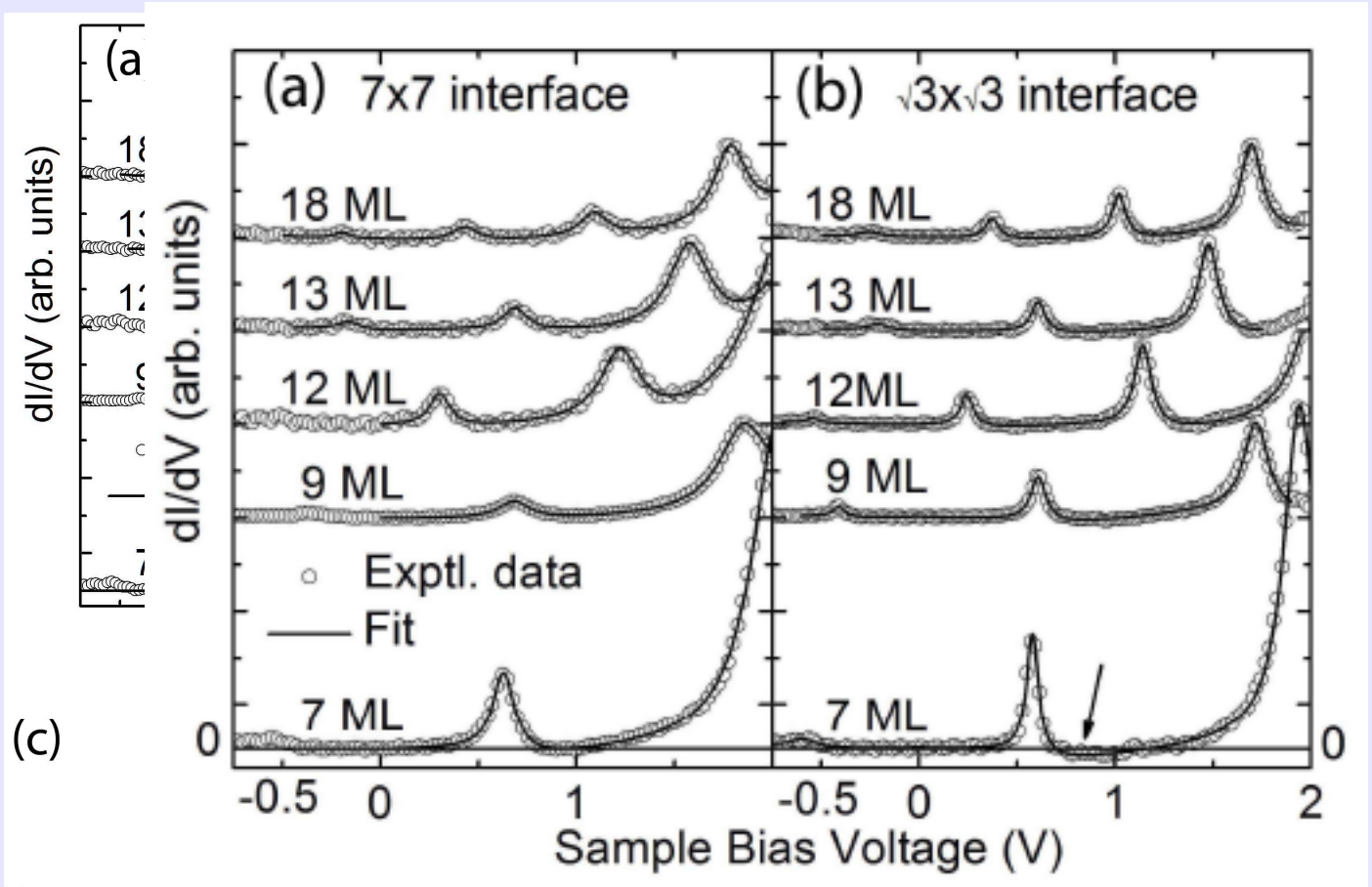
For subsurface noble gas bubbles in Al:
M. Schmid, W. Hebenstreit,
P. Varga, S. Crampin, PRL **76**, 2298 (1996)

Interference fringes!

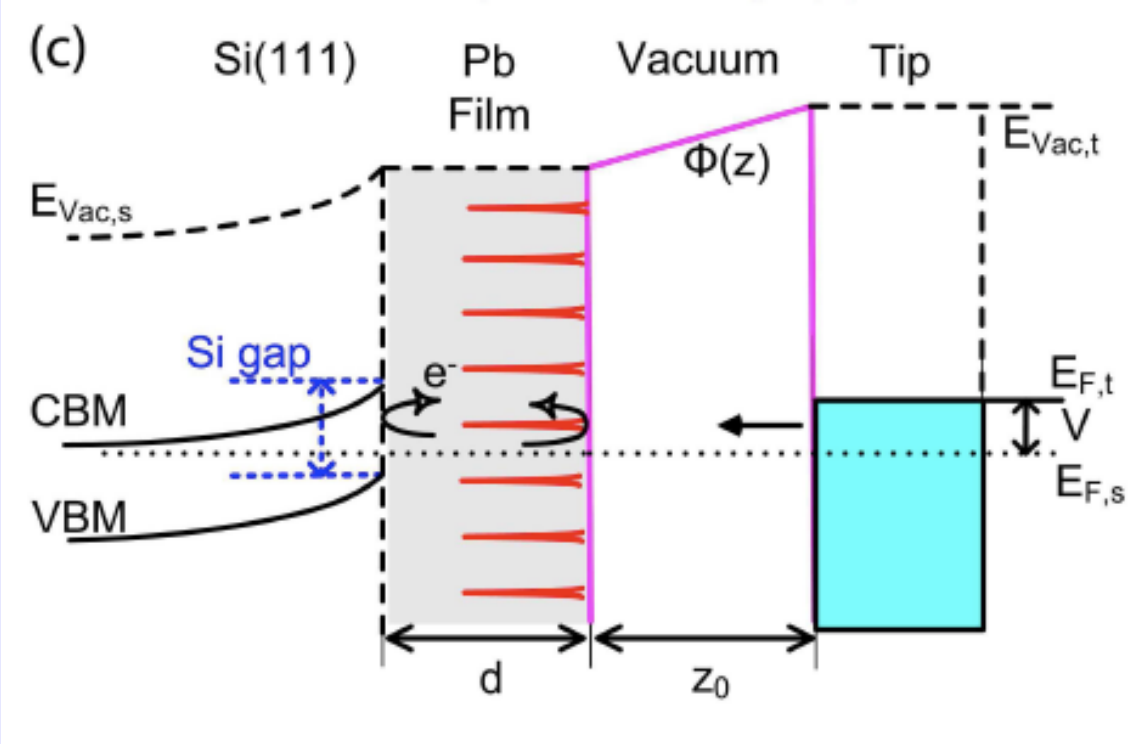


Pb: QWS on two different Pb/Si interfaces

disordered T=5 K **crystalline**



Schematic energy diagram of the tunnel junction



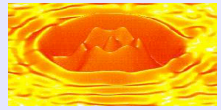
$$I_{WKB}(V)=\int_{-\infty}^{\infty}\Big[\rho_s(\epsilon)\rho_t(\epsilon-eV)[f(\epsilon)-f(\epsilon-eV)]\times exp\Big(-\frac{2}{\hbar}\int_0^{z_0}Re\Big\{\sqrt{2m[\Phi-\epsilon+(1-\frac{z}{z_0})eV]}\Big\}dz\Big)\Big]d\epsilon. \quad (1)$$

The non-zero conductance observed between the QWS peaks is modeled by an additional exponential term. The final fit function dI/dV is expressed as :

$$\frac{dI}{dV}(V)=\frac{dI_{WKB}(V)}{dV}+A\cdot(e^{V/b}-1). \quad (2)$$

$$\Gamma(T,E)=\Gamma_0+\Gamma_1(T)+\Gamma_2(E)$$

$$\tau(T,\ddot{E})=\hbar/\Gamma(T,E)$$



Summary

Pb/Si(111): Study of large atomically flat single nanocrystals of atomic-layer defined thickness on

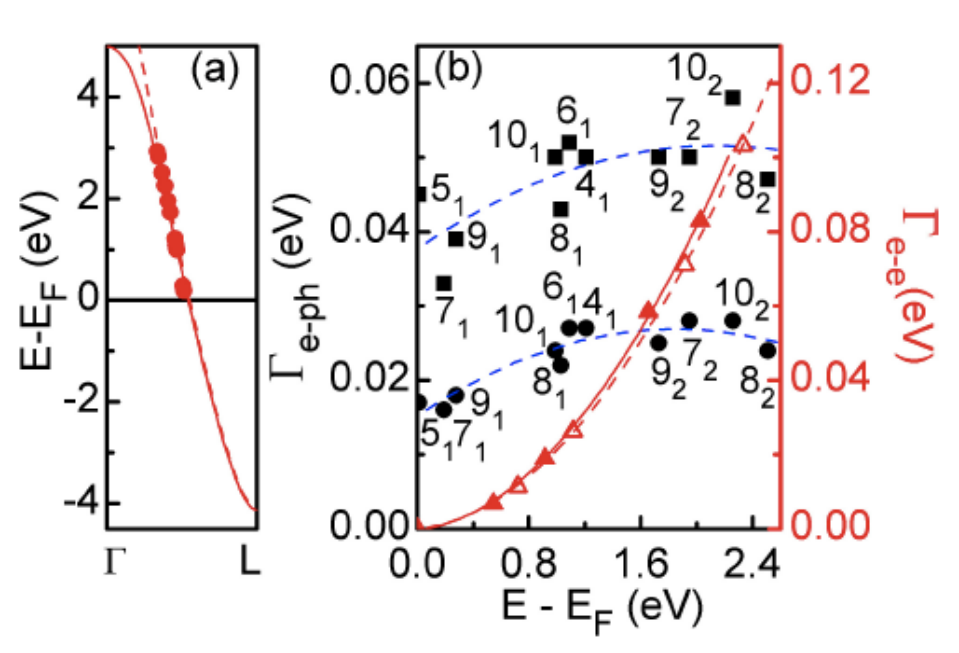
two different interfaces

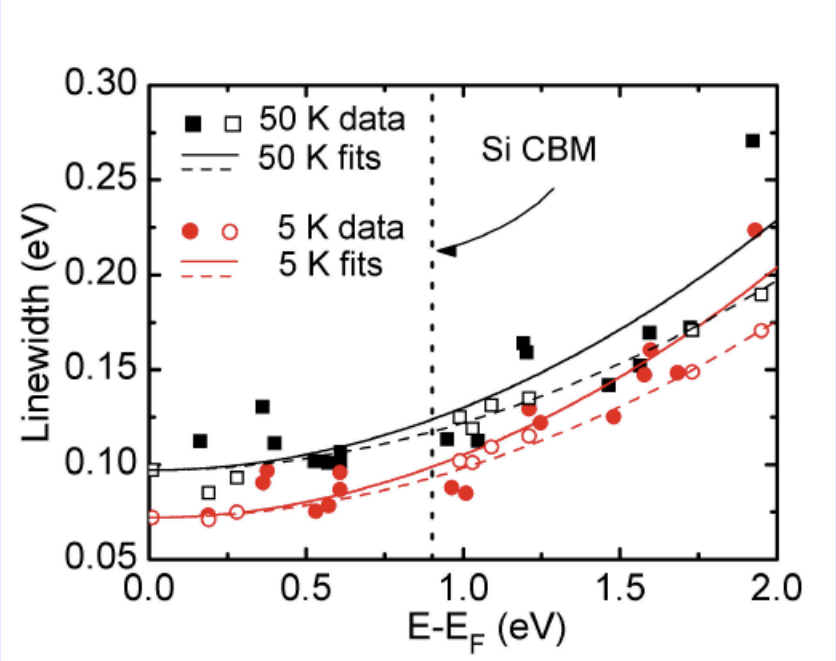
Lifetime analysis of unoccupied QWS (5-20 ML):

- lifetime at 1 eV: $\tau = 33$ meV (20 fs)
- e-e interaction in agreement with

  3D Fermi liquid theory: $2\beta = 0.033\ eV^{-1}$
- average e-ph contribution similar to bulk: $\lambda = 1.55$
- crystalline/disordered interface broadening: $\Gamma_0 \approx 90$ meV

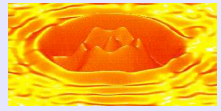
Lifetime of QWS on the crystalline interface





I-Po Hong, C. Brun, F. Patthey, I. Yu. Sklyadneva, X. Zubizarreta, R. Heid, V. M. Silkin, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, WDS, PRB **80**, 081409 (2009) (RC)

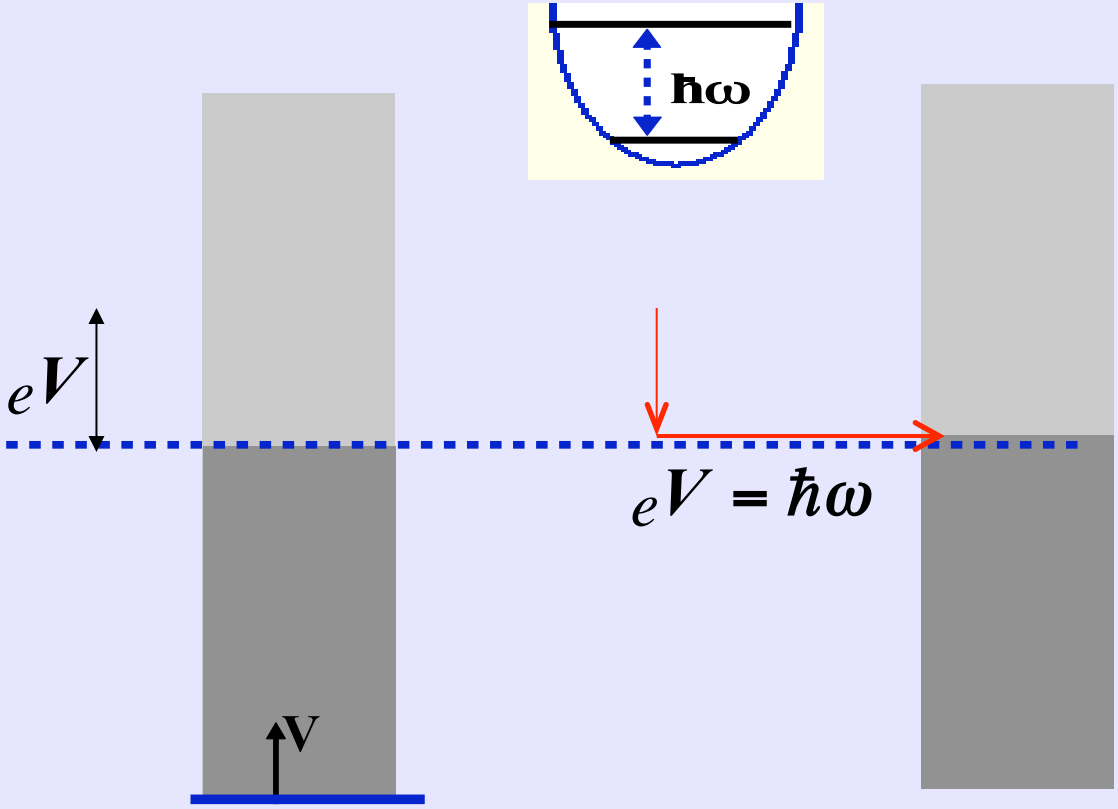
From elastic to inelastic tunneling processes



Inelastic electron tunneling spectroscopy (I):

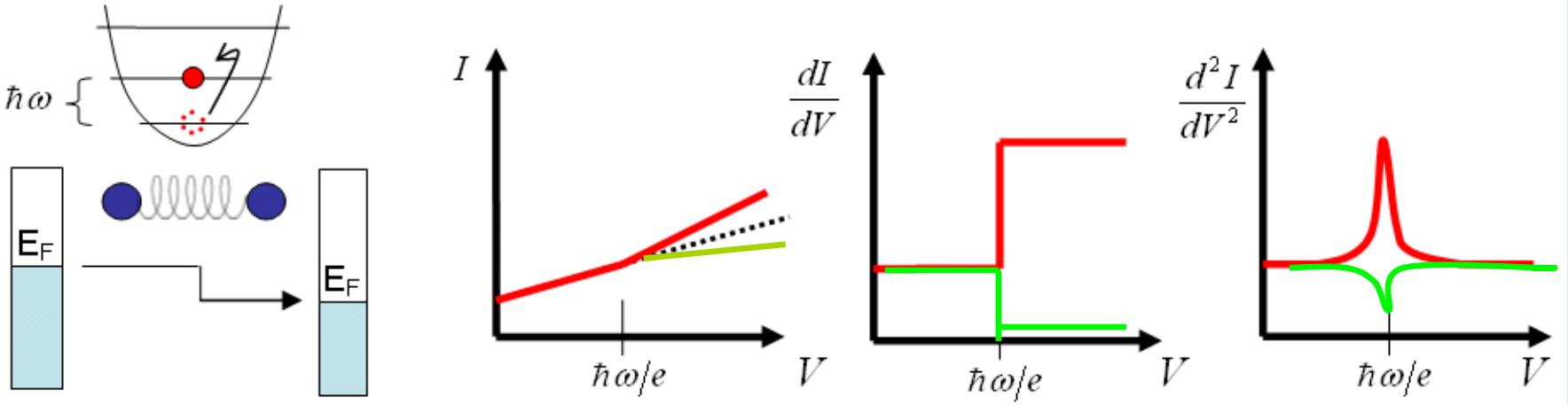
For planar tunnel junctions: R. C. Jaklevic and J. Lambe, Phys. Rev. Lett. **17**, 1139 (1966)

For STS: B. C. Stipe, M. A. Rezaei, and W. Ho, Science **280**, 1732 (1998)



Courtesy of A. Nitzan

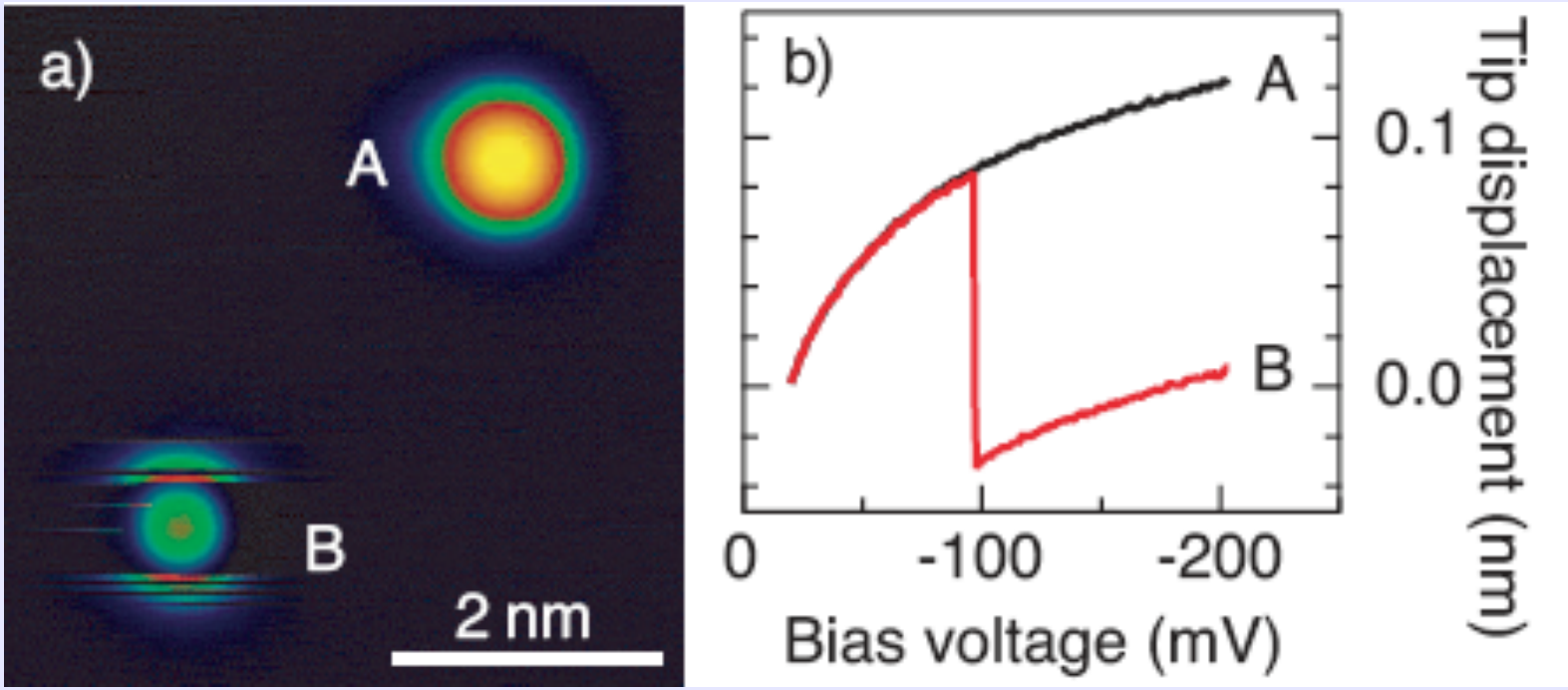
What is typically observed



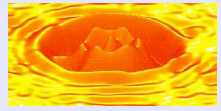
Negative signals possible too

Courtesy of A. Nitzan

A Ce adatom and a switching object on Ag(100)



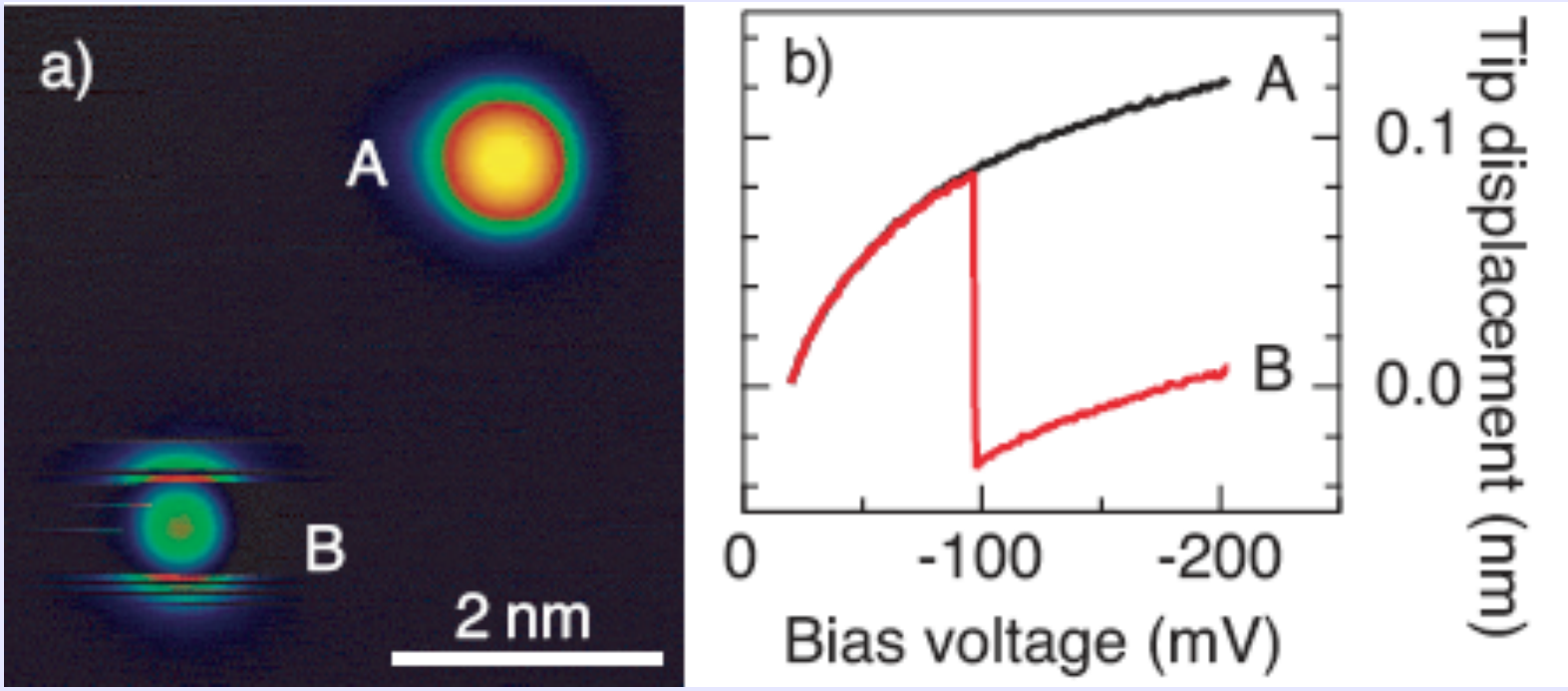
M. Pivetta, M. Ternes, F. Patthey, WDS, Phys. Rev. Lett. **99**, 126104 (2007)



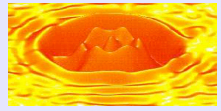
The number of switching objects increases with increasing hydrogen partial pressure:

Coadsorption of H

A Ce adatom and a switching CeH molecule on Ag(100)



M. Pivetta, M. Ternes, F. Patthey, WDS, Phys. Rev. Lett. **99**, 126104 (2007)

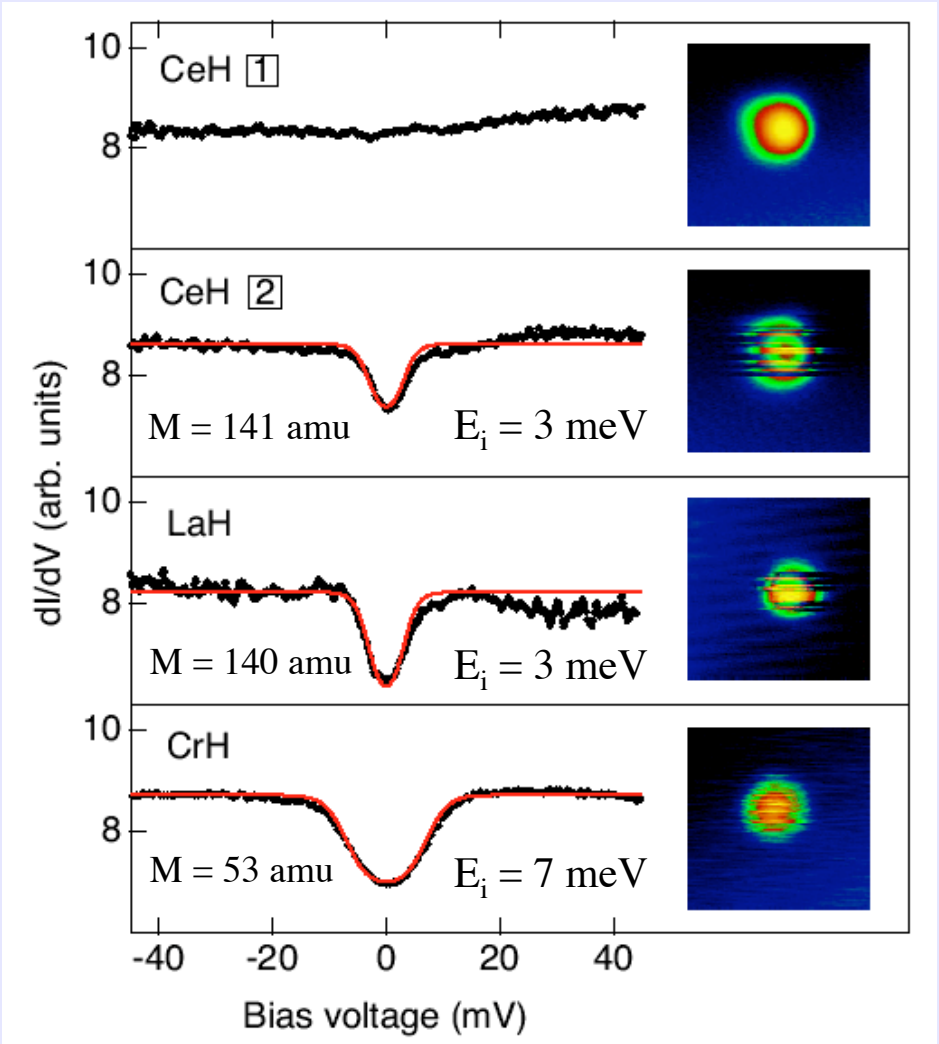


Vibrational excitations and STM topographies

simulation

$$\left.\frac{dI_T}{dV}\right|_{V_T} = \sigma_e + \sigma_i \left[F\left(\frac{-eV_T + E_i}{k_B T}\right) + F\left(\frac{eV_T + E_i}{k_B T}\right)\right]$$

J. Lambe and R. C. Jaklevic, Phys. Rev. **165**, 821 (1968).
A. Kogan, S. Amasha, D. Goldhaber-Gordon, G. Granger, M. A. Kastner, and H. Shtrikman, Phys. Rev. Lett. **93**, 166602 (2004).



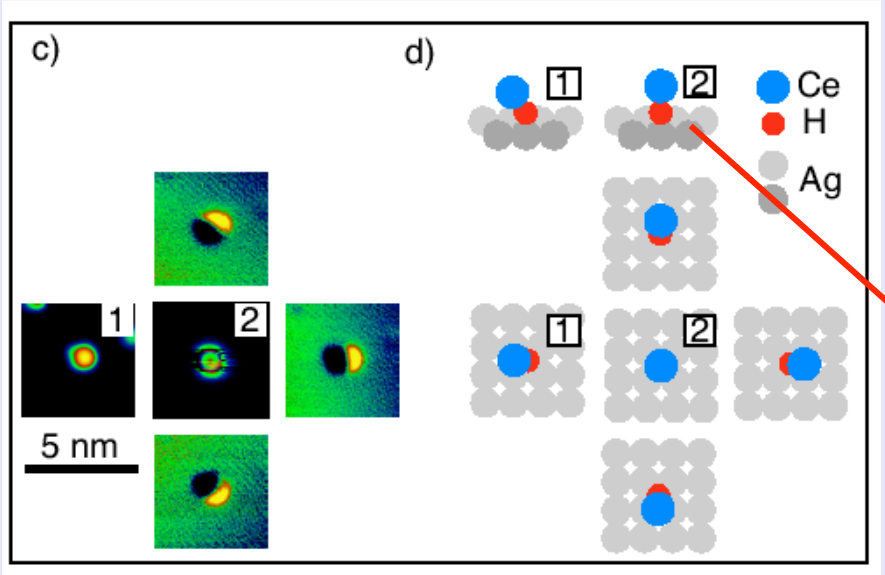
$E_i\,(M)^{1/2} = 35.6$

$E_i\,(M)^{1/2} = 35.5$

$E_i(M)^{1/2} = 50.9$

M. Pivetta, M. Ternes, F. Patthey, WDS, Phys. Rev. Lett. **99**, 126104 (2007)

CeH on Ag(100)



Experiment:
4 equivalent configurations for CeH in its large state

Ball model:
CeH/Ag(100) in its small (2) and large (1) state

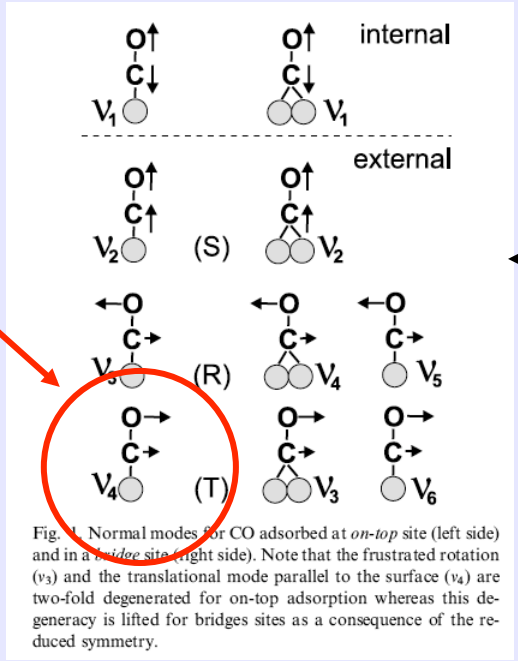


Fig. 1. Normal modes for CO adsorbed at *on-top* site (left side) and in a *bridge* site (right side). Note that the frustrated rotation (ν_3) and the translational mode parallel to the surface (ν_4) are two-fold degenerated for on-top adsorption whereas this degeneracy is lifted for bridges sites as a consequence of the reduced symmetry.

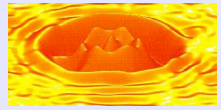
> 200 meV
(for LaH)

←G. Witte, Surf. Sci. **502**, 405 (2002)

< 5 meV

Frustrated translational mode parallel to the surface

M. Pivetta, M. Ternes, F. Patthey, WDS, Phys. Rev. Lett. **99**, 126104 (2007)



Origin of the spectroscopic feature:

- **Not a Kondo resonance**:
  Also present for LaH (no occupied 4f states)

- **Not a spin-flip excitation**:
  The molecules are in direct contact with a metallic surface
  (A. J. Heinrich, J. A. Gupta, C. P. Lutz, D. M. Eigler, Science **306**, 466 (2004))

- **A very low-lying vibrational excitation**:
  A frustrated translational mode
  where the molecule vibrates parallel to the surface plane

  M. Pivetta, M. Ternes, F. Patthey, WDS, Phys. Rev. Lett. **99**, 126104 (2007)

Other Hydrogen induced phenomena:

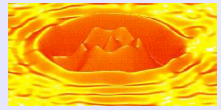
Vibrational excitations of H_2: J. C. Gupta, C. P. Lutz, A. J. Heinrich, D. M. Eigler, PRB **71**, 115416 (2005)

Mobile H-atoms on Rh((100): C. Klein, A. Eichler, E. L. D. Hebenstreit, G. Pauer, R. Koller, A. Winkler, M. Schmid, P. Varga, PRL **90**. 176101 (2003)

Giant spin-polarization: W. A. Hofer, K. Palotás, S. Rusponi, T. Cren, H. Brune, PRL 100, 026806 (2008)

Ultra-high geometrical resolution on adsorbed molecules:

R. Temirov, S. Soubatch, O. Neucheva, A. C. Lassise, F. S. Tautz, NJP **10**, 053012 (2008)

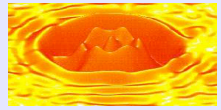


Intermolecular interactions

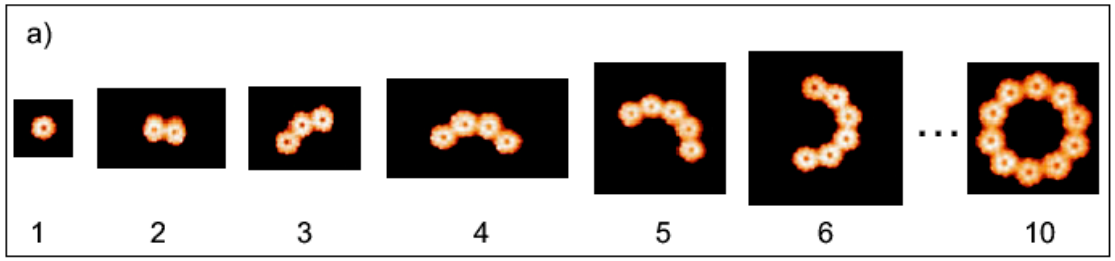
dipole-dipole[a]	quadr.-quadr.[a]	vdW[b]	XH$\cdots$Y[c]	XH$\cdots\pi$[d]	$\pi\cdots\pi$[e]
$\propto r^{-3}$	$\propto r^{-5}$	$\propto r^{-6}$	X-H $\rightarrow$ Y	(X-H) $\perp$ π-system	$\pi \parallel \pi$-system

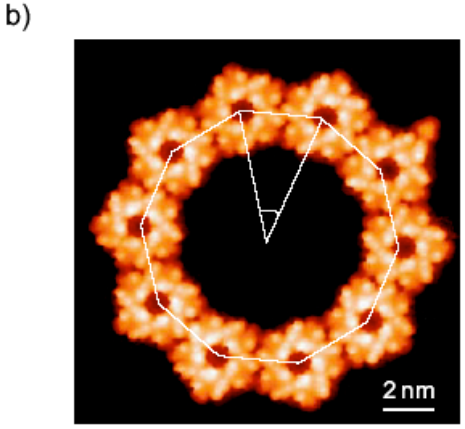
Table 3.1: Attractive intermolecular forces and the dependence of their interaction potential on the distance *r* or the orientation of essential parts of the molecules.
[a] Maximal electrostatic interaction energy between permanent dipoles and quadrupoles.
[b] Van der Waals interaction due to the attraction between fluctuating dipoles.
[c] Hydrogen bonds between an X-H group (X,Y=F, N, O) pointing to an Y.
[d] Weak hydrogen bonds between an X-H group (X=N, O, C) and a π system.
[e] Interaction between π systems.

M.-C. Blüm, PhD thesis, EPFL Lausanne, 2006



From a pentagonal supermolecule to a supramolecular decagon





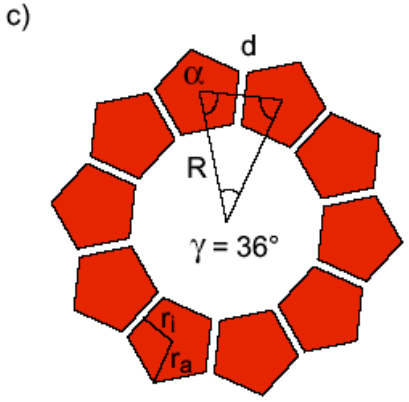
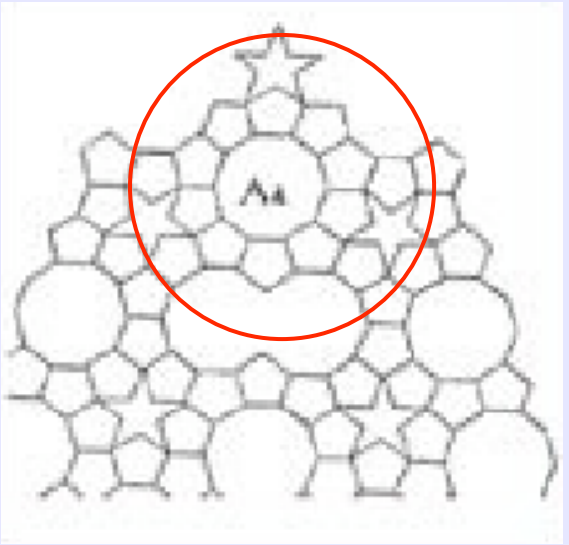


Figure 4.3: a) STM images showing the construction of a supramolecular decamer of pentagonal supermolecules. b) STM image of a closed structure forming a regular decagon (as indicated by the white line). c) Geometry of a regular decagon with γ =36°, α =72° and the values of the supramolecular decagon shown in (a): d=3.0±0.1 nm and R=5.0±0.1 nm.

M.-C. Blüm, PhD thesis, EPFL Lausanne, 2006



J. Kepler,
Harmonices Mundi Libri V, 1619

Tunneling conductance

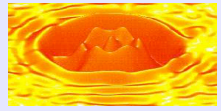
between

a normal metal and a superconductor

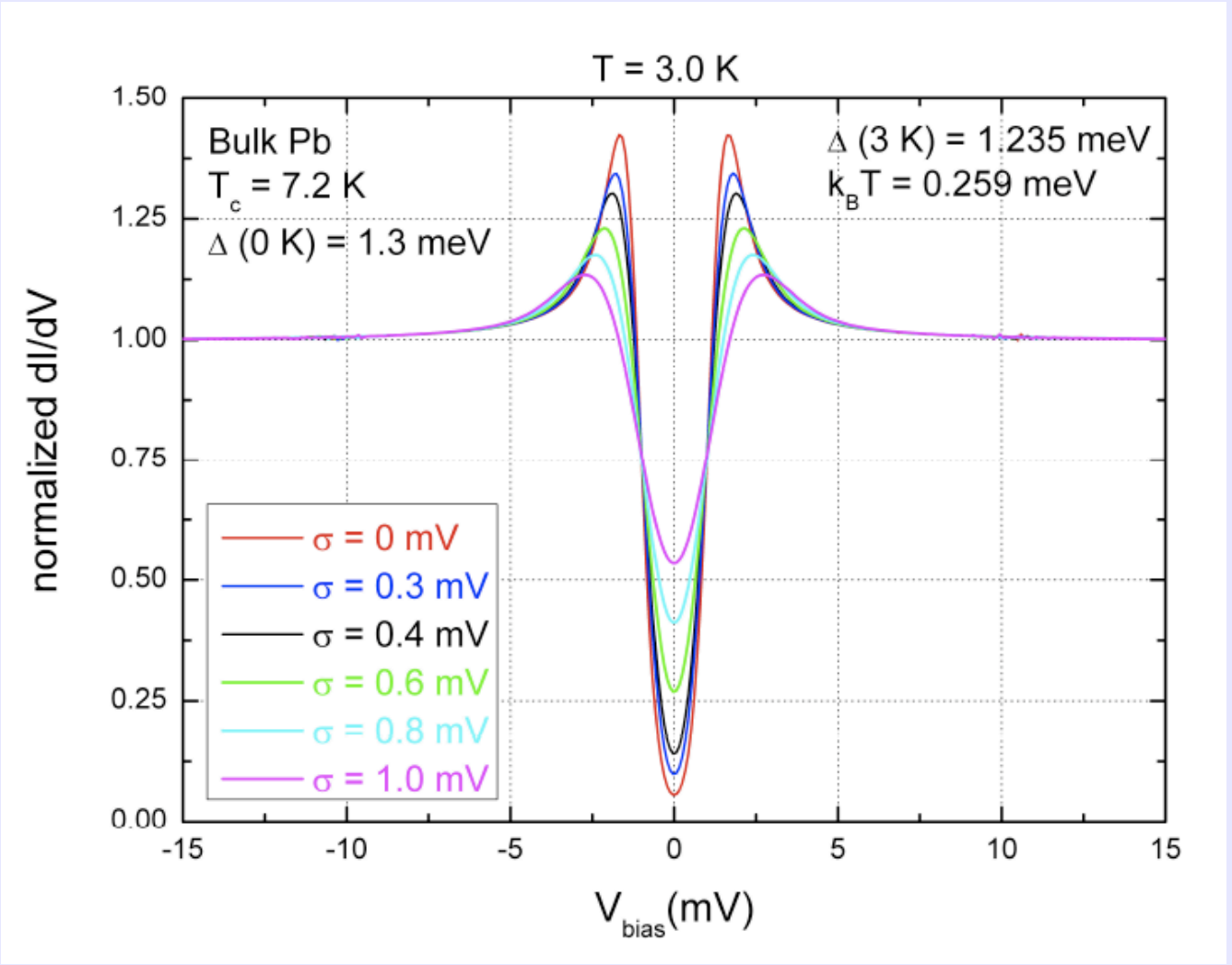
$$\frac{dI}{dV}(V) = -G_{nn} \int_{-\infty}^{\infty} \frac{\rho_s(\epsilon)}{N(0)} \times f'(\epsilon - eV) d\epsilon \qquad (1)$$

where $f'(\epsilon)$ is the derivative of the Fermi function, G_{nn} is the ohmic conductance of the junction, and

$$\frac{\rho_s(\epsilon)}{N(0)} = \frac{|\epsilon|}{\sqrt{\epsilon^2 - \Delta^2}}, \qquad (2)$$

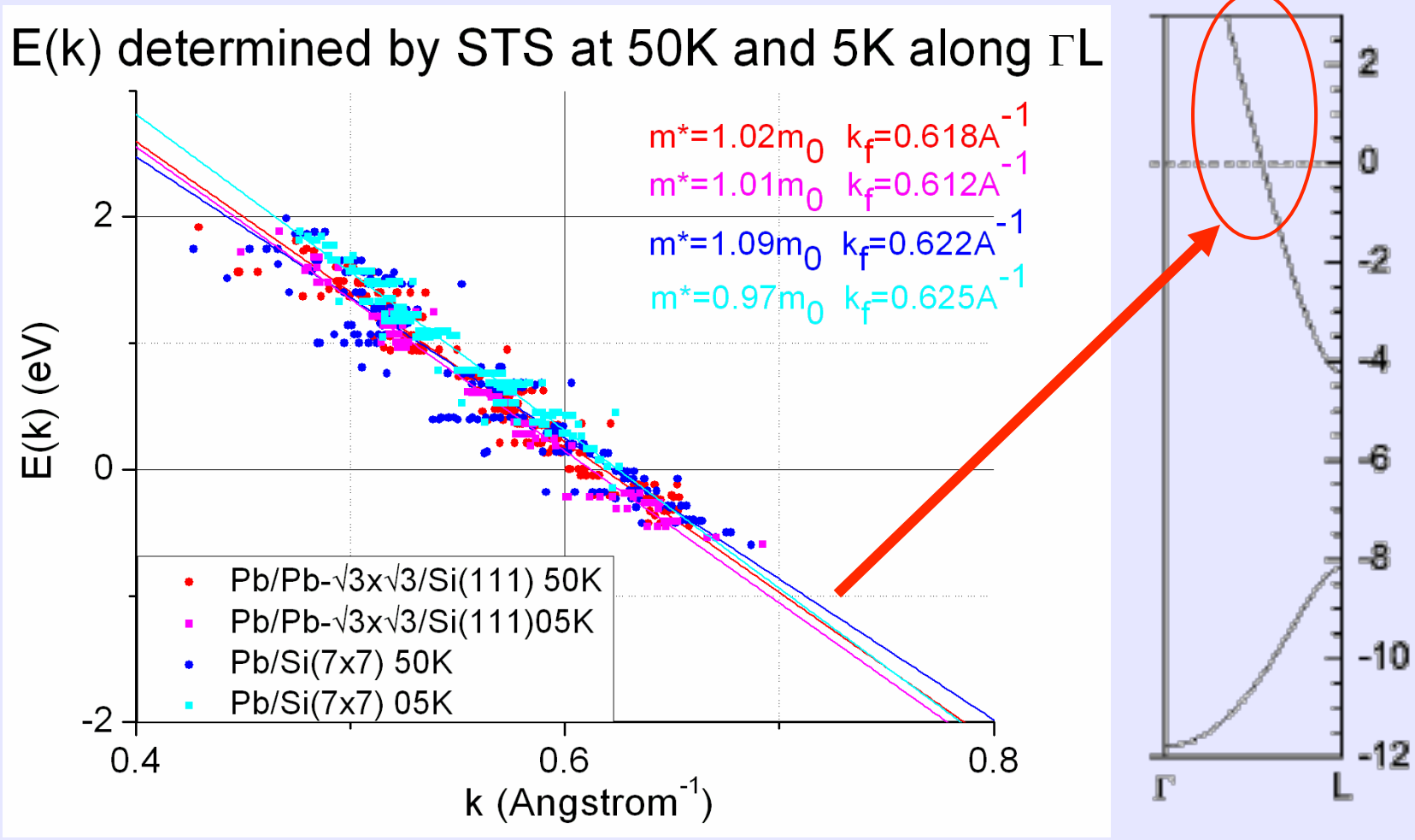


Influence of RF noise on the quasiparticle gap



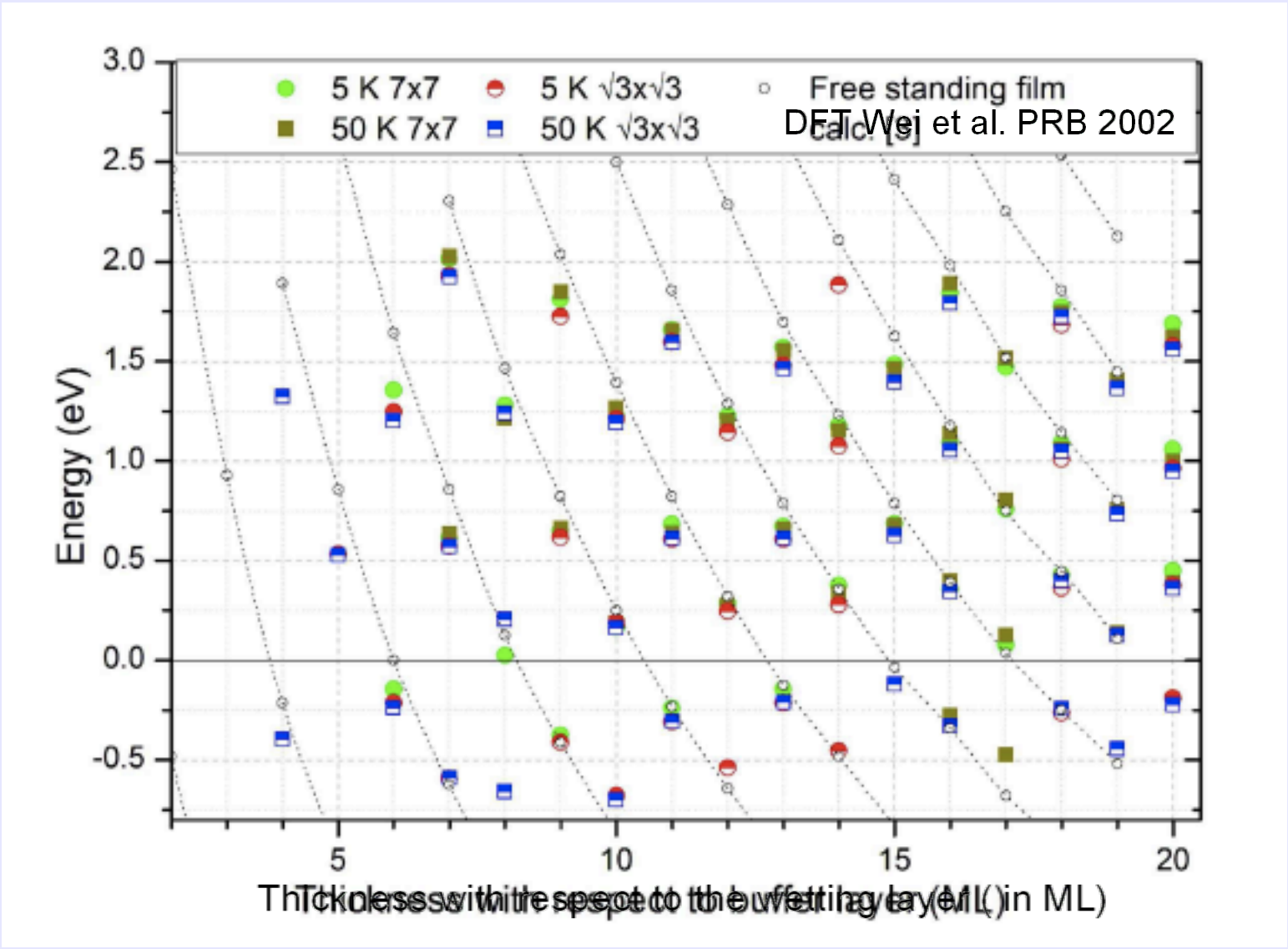
C. Brun *et al*.

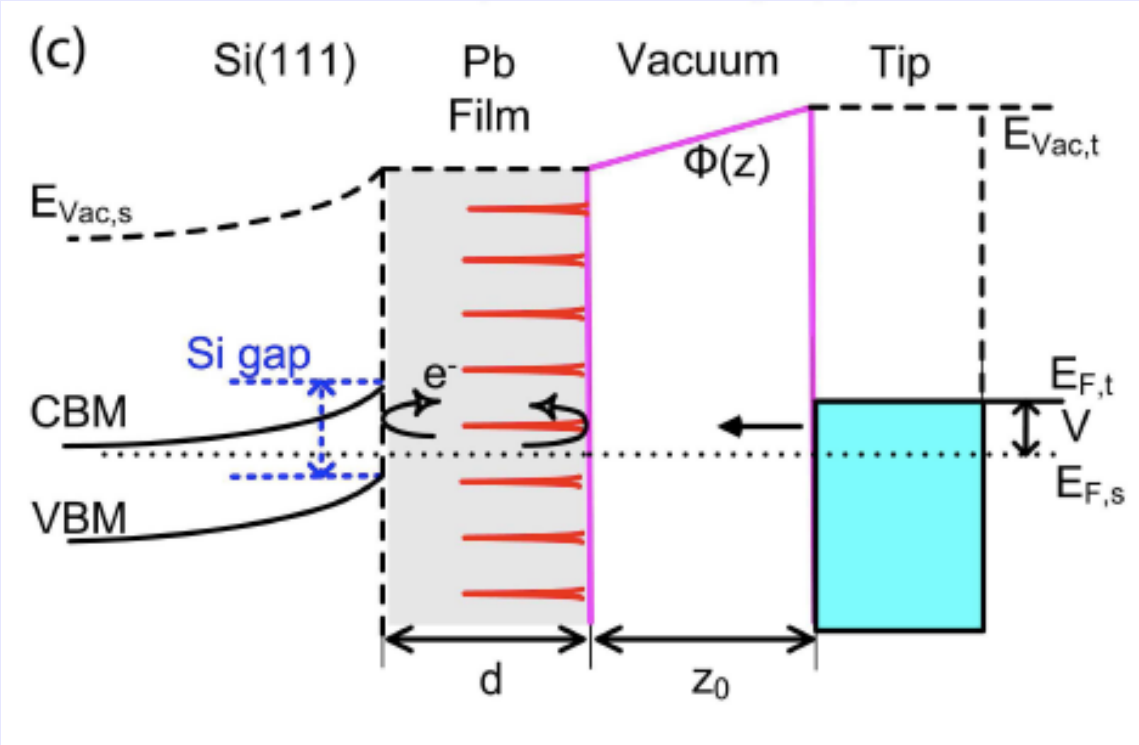
Pb band dispersion from QWS energies



Very good agreement with ARPES (Zhang *et al*. PRL 2005) and De Haas-Van Alphen measurements (Anderson *et al*. PR 1965, Jalochowski *et al*. PRB 1992)

QWS in Pb/Si(111): Comparison Experiment - Theory





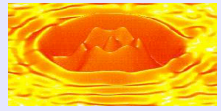
$$I_{WKB}(V)=\int_{-\infty}^{\infty}\Big[\rho_s(\epsilon)\rho_t(\epsilon-eV)[f(\epsilon)-f(\epsilon-eV)]\times$$
$$exp\Big(-\frac{2}{\hbar}\int_0^{z_0} Re\Big\{\sqrt{2m[\Phi-\epsilon+(1-\frac{z}{z_0})eV]}\Big\}dz\Big)\Big]d\epsilon. \quad (1)$$

The non-zero conductance observed between the QWS peaks is modeled by an additional exponential term. The final fit function dI/dV is expressed as :

$$\frac{dI}{dV}(V)=\frac{dI_{WKB}(V)}{dV}+A\cdot(e^{V/b}-1). \quad (2)$$

$$\Gamma(T,E)=\Gamma_0+\Gamma_1(T)+\Gamma_2(E)$$

$$\tau(T,\ddot{E})=\hbar/\Gamma(T,E)$$



The intrinsic linewidth Γ is obtained from the fitted linewidth W as follows [23] : J. J. Paggel et al., Science **283**, 1709 (1999)

$$W = \Gamma\eta \frac{1 - Rexp(-1/\eta)}{R^{1/2}exp[-1/(2\eta)]}, \quad with \ \eta = \frac{\ell}{d}. \qquad (3)$$

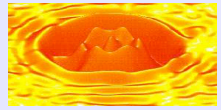
$$\Gamma(T, E) = \Gamma_0 + \Gamma_1(T) + \Gamma_2(E),$$
$$with \ \Gamma_2(E) = 2\beta(E - E_F)^2, \qquad (4)$$

with d the film thickness, R the reflectivity of the barriers for the confined electrons, ℓ the mean free path of the electron

T : temperature
E : energy
Γ_0:interface and defect scattering, k-broadening
Γ_1: electron-phonon interaction
Γ_2: electron-electron interaction
2β:parabolic Fermi liquid parameter

The total quasiparticle lifetime is given by

$\tau = h/(2\pi\Gamma)$



STM probes enantio-selective processes at surfaces at the single-molecule level

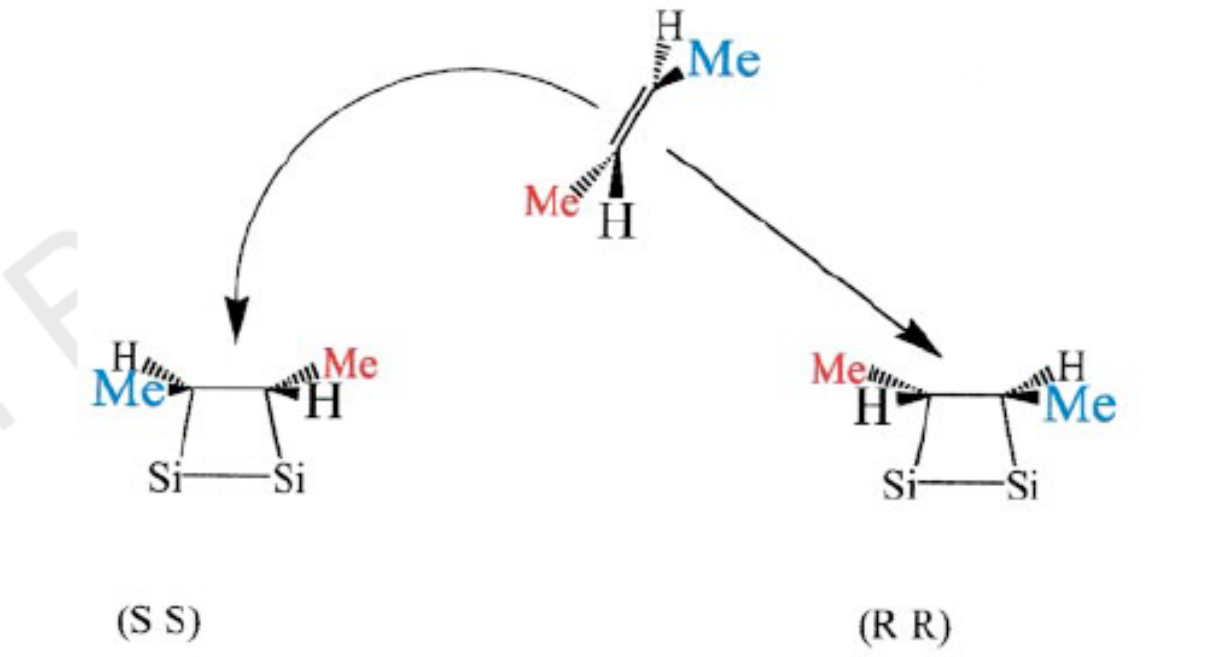
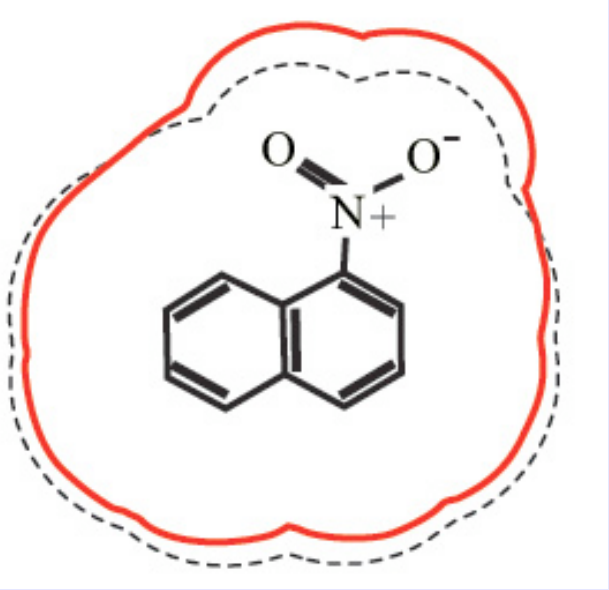


Figure 2 The planar *trans*-2-butene molecule has two distinct faces. Reaction at the *Si* face leads to the *SS* structure shown at the left, whereas reaction at the *Re* face leads to the *RR* structure at the right. Although indistinguishable using optical and other spectroscopic techniques, the individual enantiomers are clearly identified by STM.

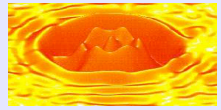
G. P. Lopinski, D. J. Moffat, D. D. M. Wayner, R. A. Wolkow, Nature **392**, 909 (1998)

Theory



1-NitroNaphthalene (1-NN)

- Assumptions:
  - ✓ molecules are planar rigid units
  - ✓ physisorbed at 0.35 nm parallel to surface
  - ✓ steric repulsion
  - ✓ electrostatic interaction screened by metallic substrate
  - ✓ neglect atomistic detail of the substrate
- ab-initio electrostatic potential from Density Functional Calculation
  - ✓ atomic point charges which best fit potential outside exclusion area
- Molecular Dynamics



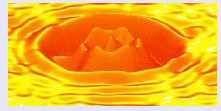
Conclusions

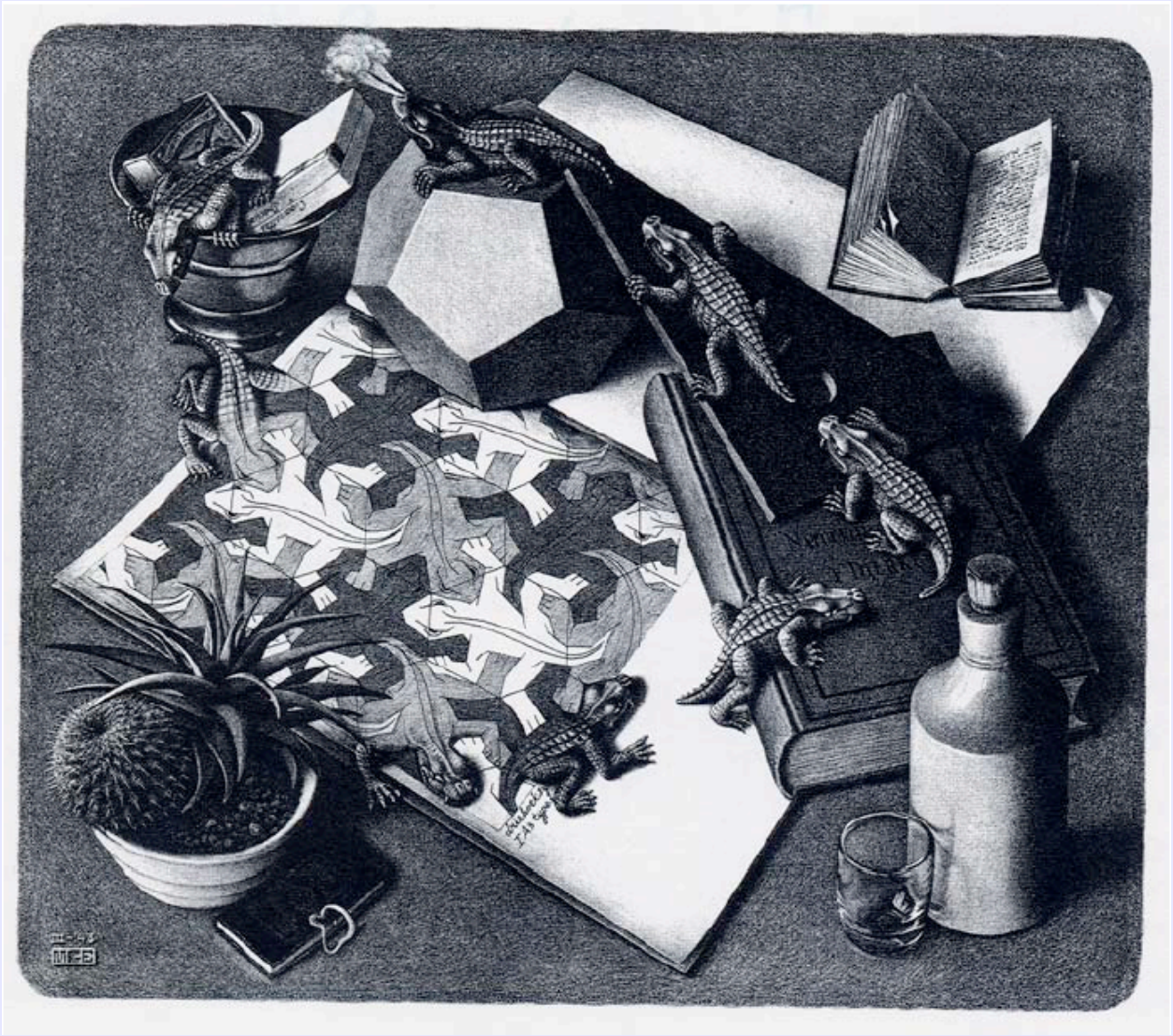
STM observations and modeling ⇨

- Stability, chirality, and arrangement of 2D self-assembled supramolecular structures
- Chirality of single molecules and decamers

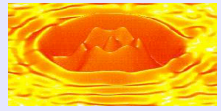
Conservation of chirality in a hierarchical supramolecular self-assembly of pentagonal symmetry: Rubrene on Au(111)

M.-C. Blüm, E. Cavar, M. Pivetta, F. Patthey, WDS,
Angew. Chem. Int. Ed. **44**, 5334 (2005)





M. C. Escher, *Reptiles*, Lithographie (1943)



Non-planar, chiral adsorption of Rubrene on Au(111)

PRL 95, 166602 (2005) PHYSICAL REVIEW LETTERS week ending 14 OCTOBER 2005

Role of Molecular Conformations in Rubrene Thin Film Growth

D. Käfer, L. Ruppel, G. Witte, and Ch. Wöll
Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780 Bochum, Germany
(Received 27 May 2005; published 11 October 2005)

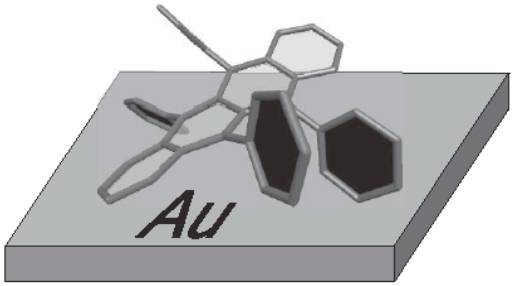
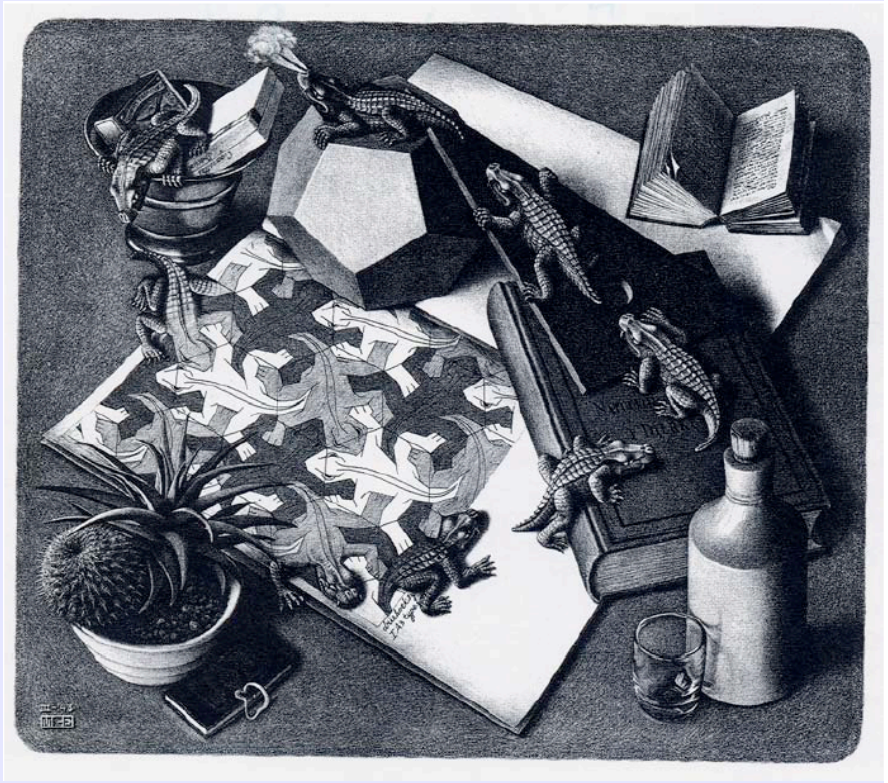


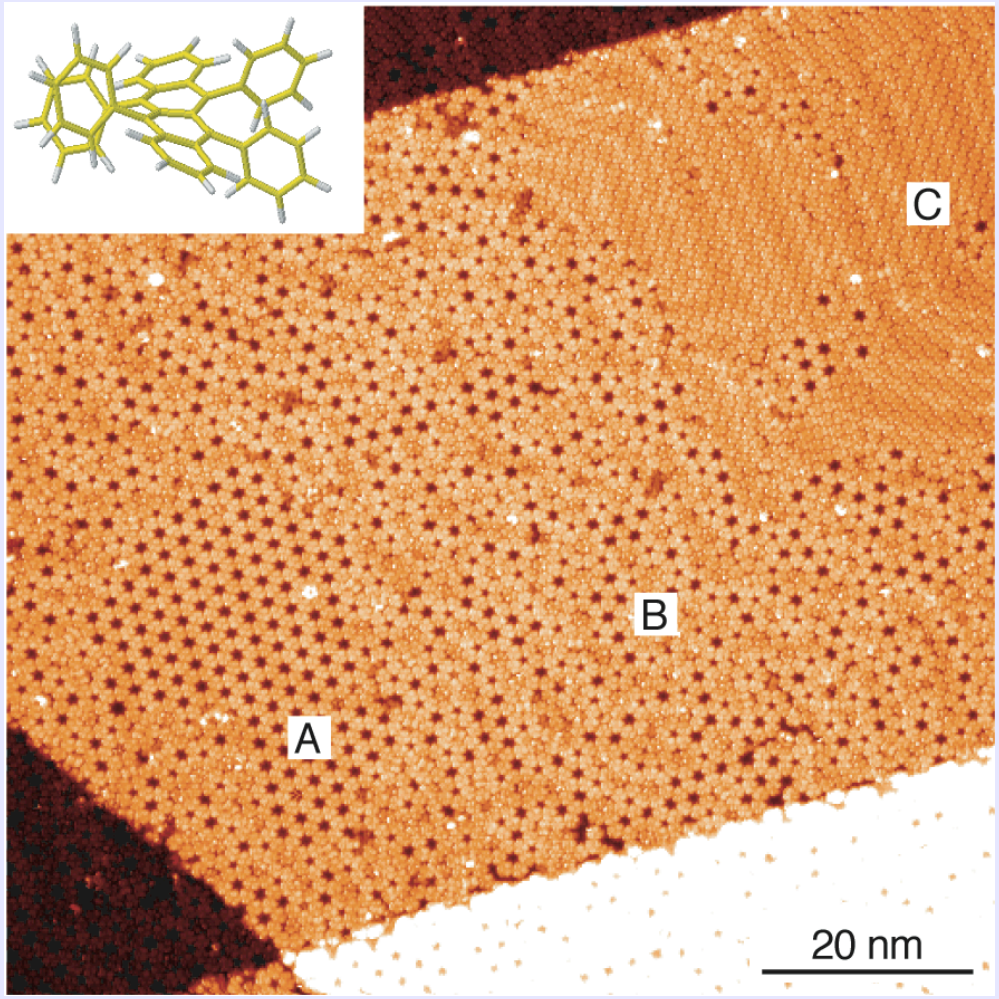
FIG. 4. Schematic representation of the molecular orientation and geometry of rubrene in the thin films grown on gold.



M. C. Escher, *Reptiles*, Lithographie (1943)

Rubrene on Au(111)

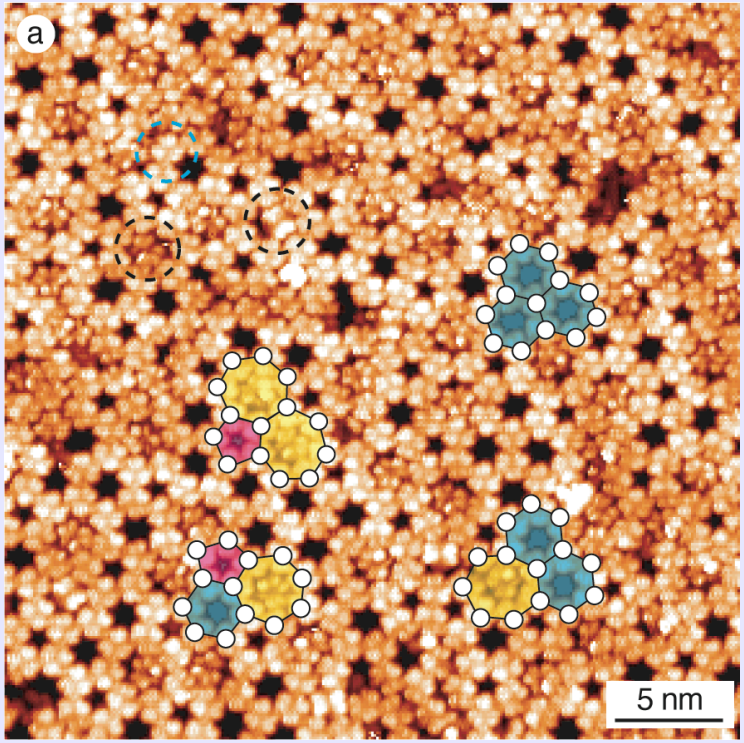
Domains with different densities and degrees of order

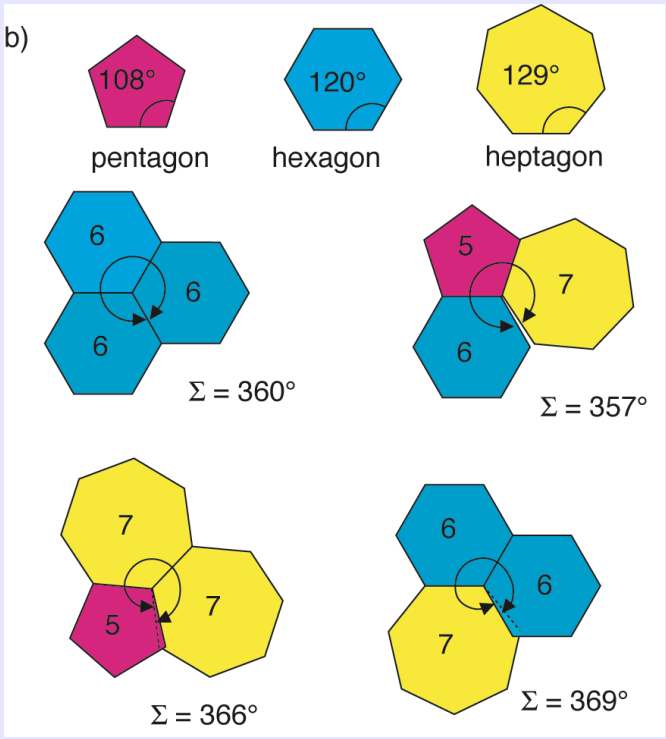


M. Pivetta, M.-C. Blüm, F. Patthey, WDS, Angew. Chem. Int. Ed. **47**, 1076 (2008)

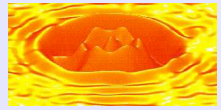
2D non-periodic tiling with pentagons, hexagons, and filled heptagons.

Schematic representation of the assembly of pentagons, hexagons, and heptagons, resulting in three configurations close to the case of an ideal honeycomb arrangement



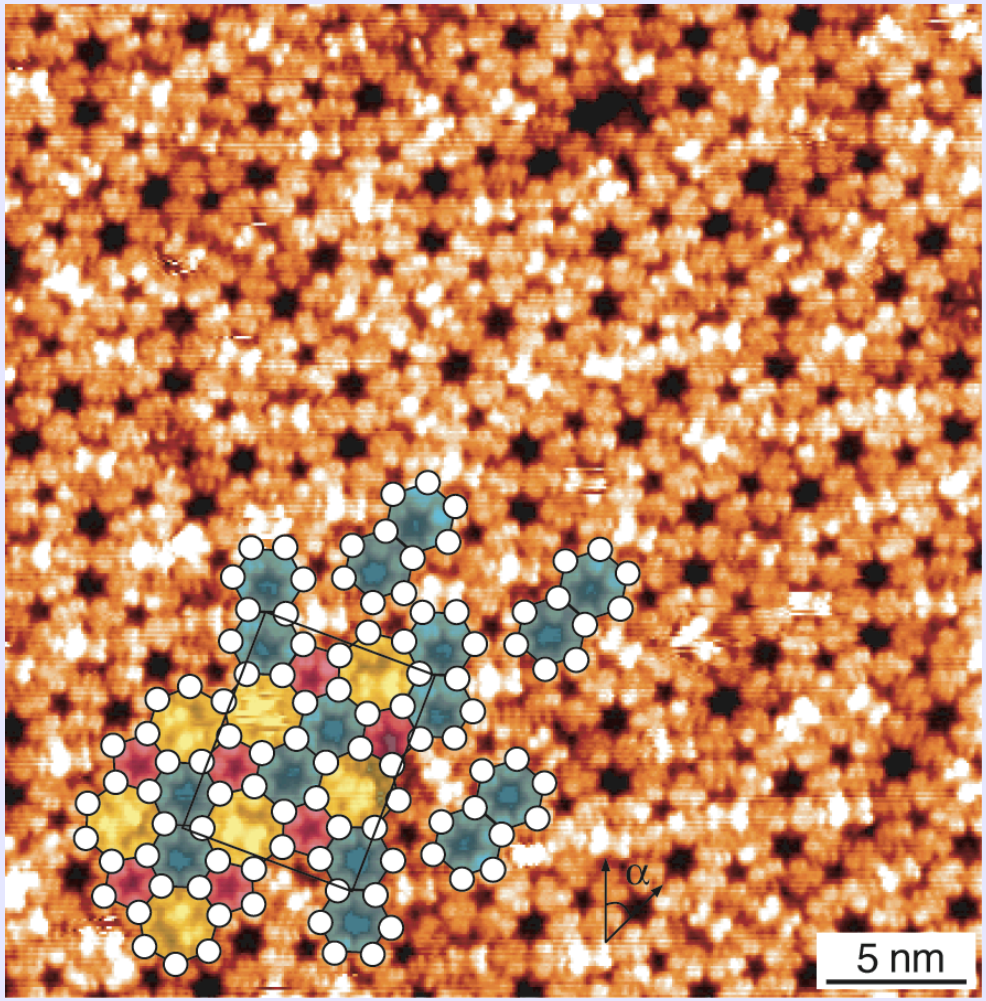


M. Pivetta, M.-C. Blüm, F. Patthey, WDS, Angew. Chem. Int. Ed. **47**, 1076 (2008)



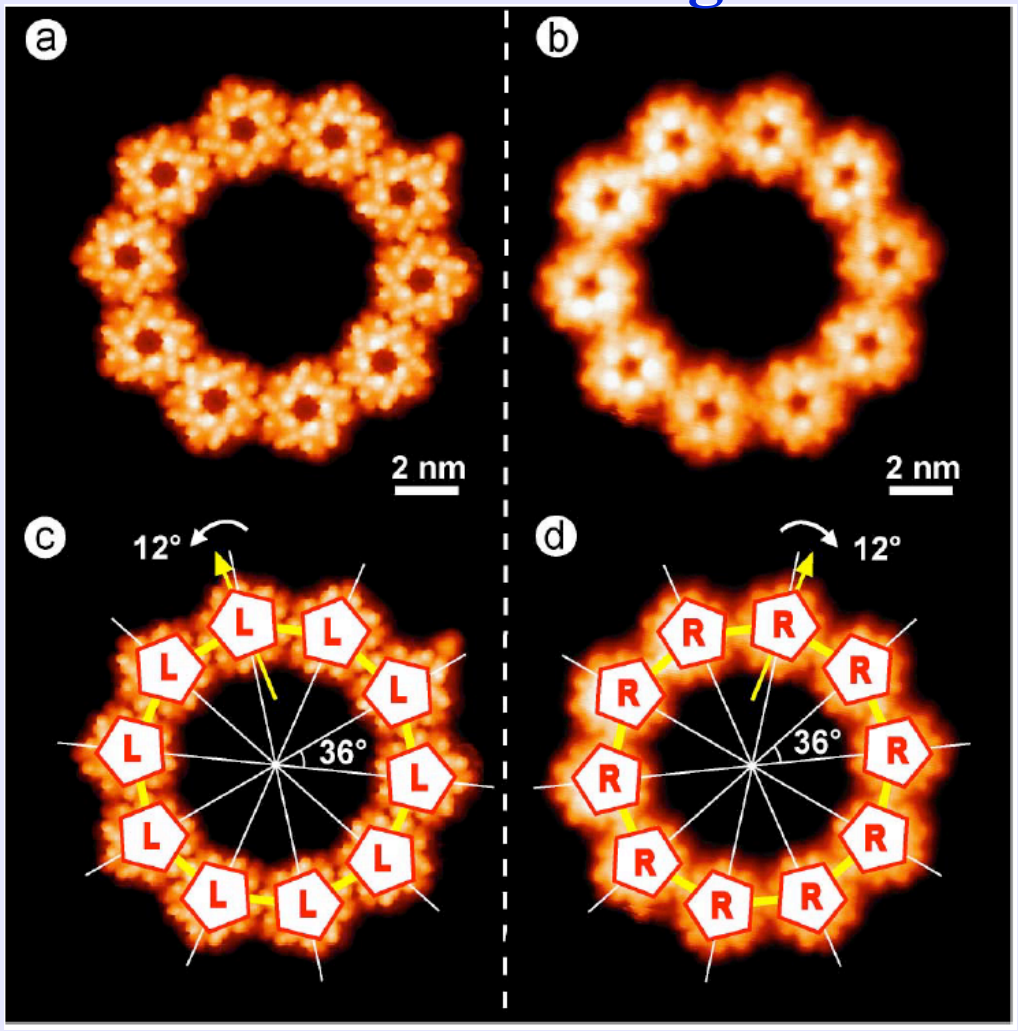
2D periodic tiling
with pentagons, hexagons, and filled heptagons.

A possible unit cell:



M. Pivetta, M.-C. Blüm, F. Patthey, WDS, Angew. Chem. Int. Ed. **47**, 1076 (2008)

Left-handed **Right-handed**



Rubrene on Au(111):

Formation of homochiral supramolecular decagons of pentagonal supermolecules

M.-C. Blüm, E. Cavar, M. Pivetta, F. Patthey, WDS,
Angew. Chem. Int. Ed. **44**, 5334 (2005)

Docking sites and supramolecular chains

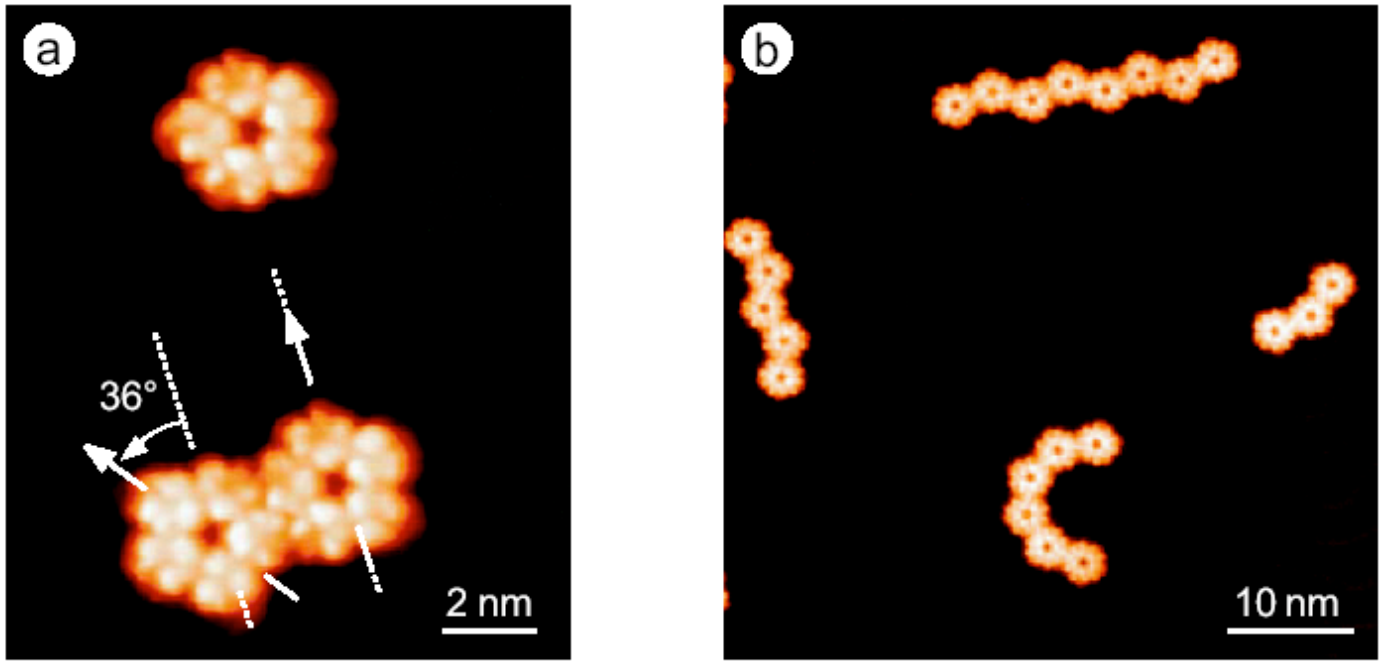
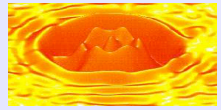


Figure 4.1: a) STM image of an individual pentagonal supermolecule and a dimer of pentagons which is formed by a rotation of 36° of one of the supermolecules with respect to the other. b) STM image showing different results of a self-assembly into pentagonal chains.

M.-C. Blüm, PhD thesis, EPFL Lausanne, 2006



Schematic representation of the interlocking mechanism leading to a supramolecular decagon. Probability: $(1/2)^7 \approx 1\%$

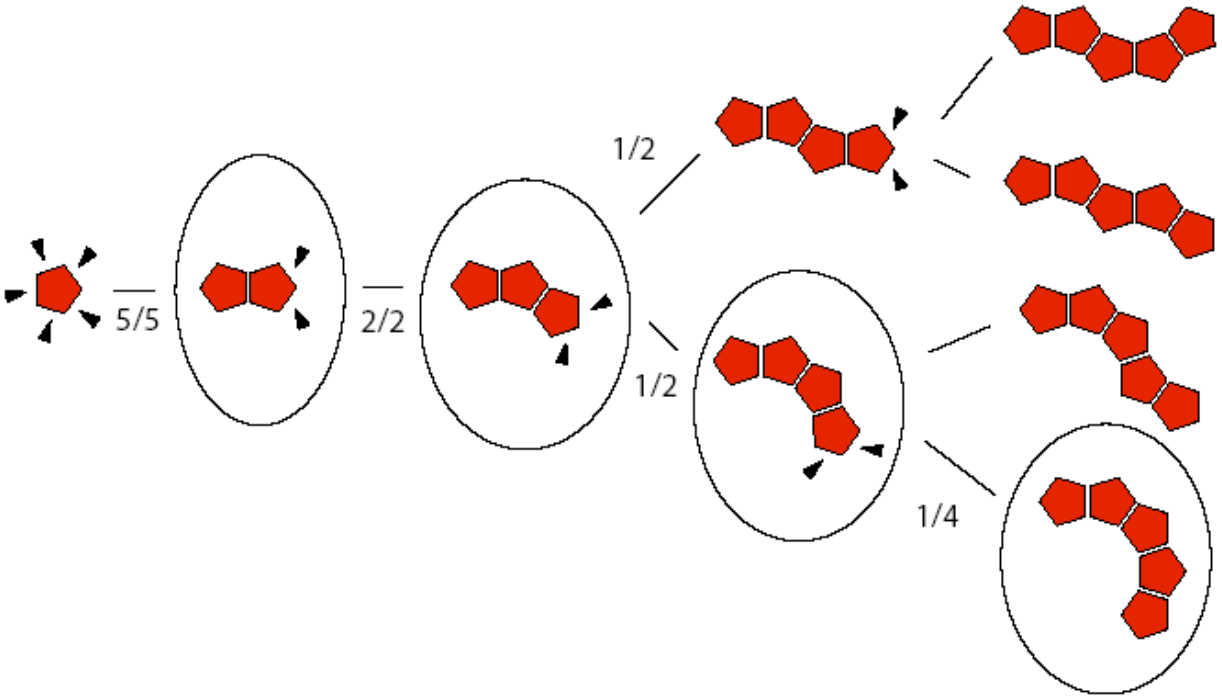
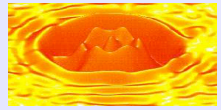


Figure 4.2: Schematic representation of the interlocking mechanism leading to the formation of differently shaped pentagonal chains. From the second pentagon on, each pentagon at the end of the chain offers two possible bonding sites (indicated by the black triangles) for an additional supermolecule. The choice between two possibilities results in a branching of the assembly from the tetramer on, favoring the creation of zigzag chains compared to the circular assembly.

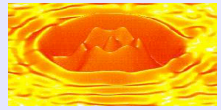
M.-C. Blüm, PhD thesis, EPFL Lausanne, 2006



Chirality on the Nanoscale: Rubrene

STM observations ⇨

- Nested 2D self-assembly of chiral molecules into cyclic supramolecular structures
- Spontaneous chiral resolution of a racemate into disjoint homochiral architectures
- Evolution of chiral recognition processes on the molecular and supramolecular level
- Exemplification of the working principle of basic processes in nature



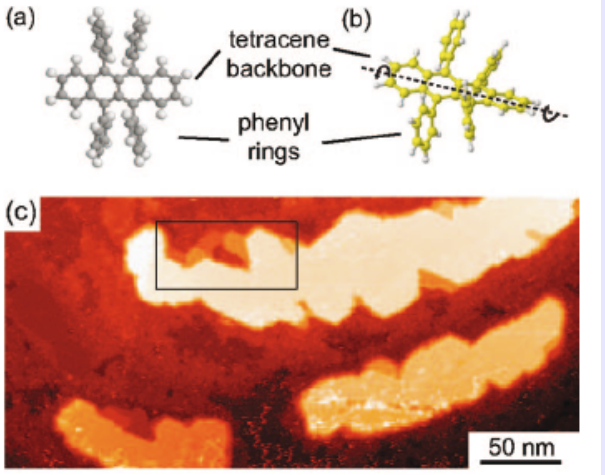
Three-Dimensional Chirality Transfer in Rubrene Multilayer Islands on Au(111)

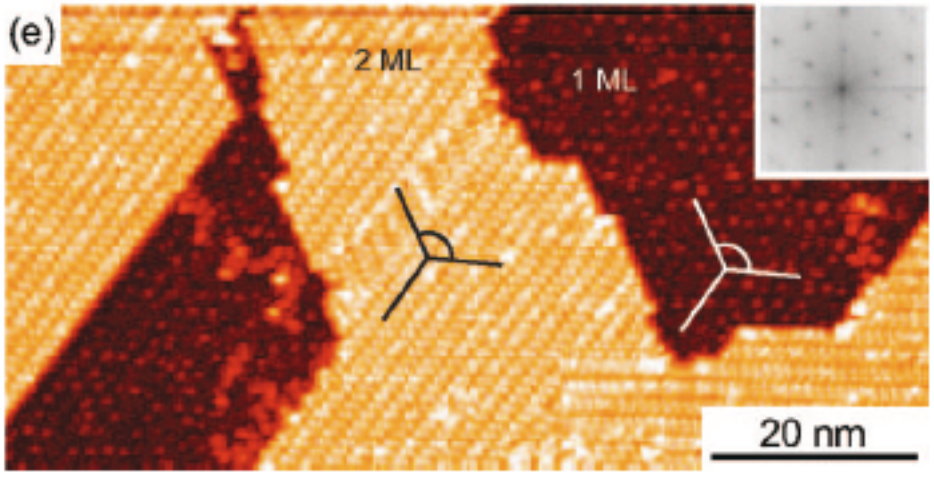
Marina Pivetta,* Marie-Christine Blüm,‡ François Patthey, and Wolf-Dieter Schneider

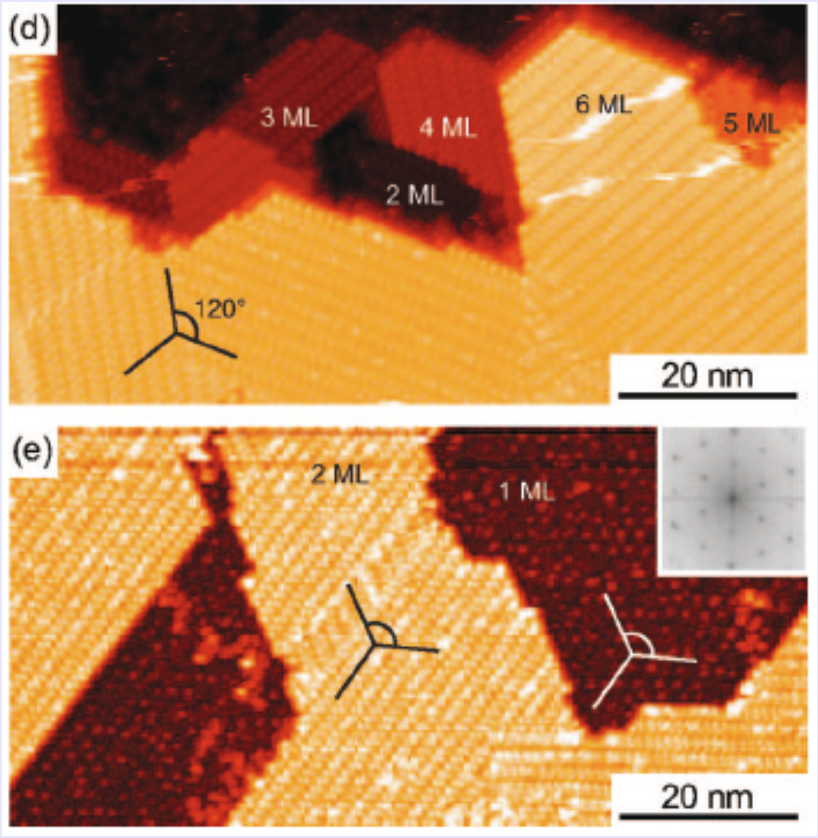
Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut de Physique de la Matière Condensée CH-1015 Lausanne, Switzerland

Received: November 26, 2008; Revised Manuscript Received: January 19, 2009

The growth of rubrene ($C_{42}H_{28}$, 5,6,11,12-tetraphenylnaphthacene) multilayer islands up to a thickness of six layers on a Au(111) surface has been investigated by scanning tunneling microscopy. The molecules self-organize in parallel twin rows, forming mirror domains of defined local structural chirality. Each layer is composed of twin-row domains of the same structural handedness rotated by 120° with respect to each other. Moreover, this structural chirality is transferred to all successive layers in the island, resulting in the formation of three-dimensional objects having a defined structural chirality. The centered rectangular surface unit cell differs from the one characteristic for the single-crystal orthorhombic phase.







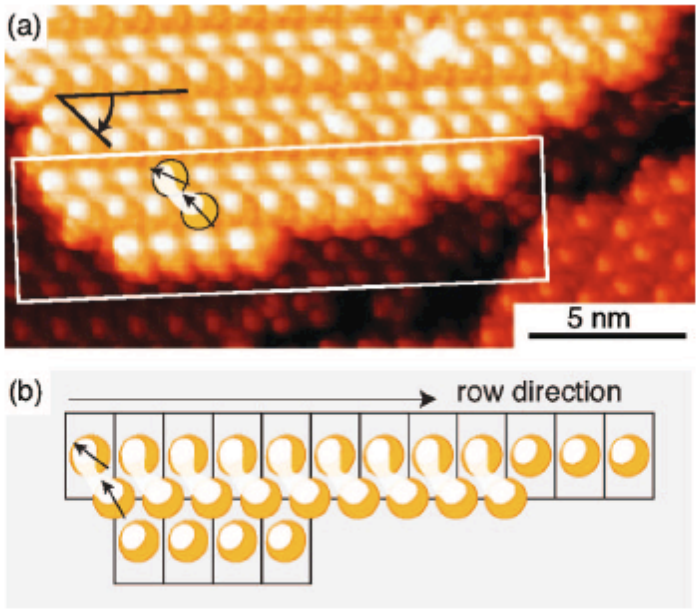
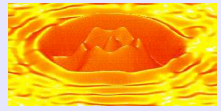
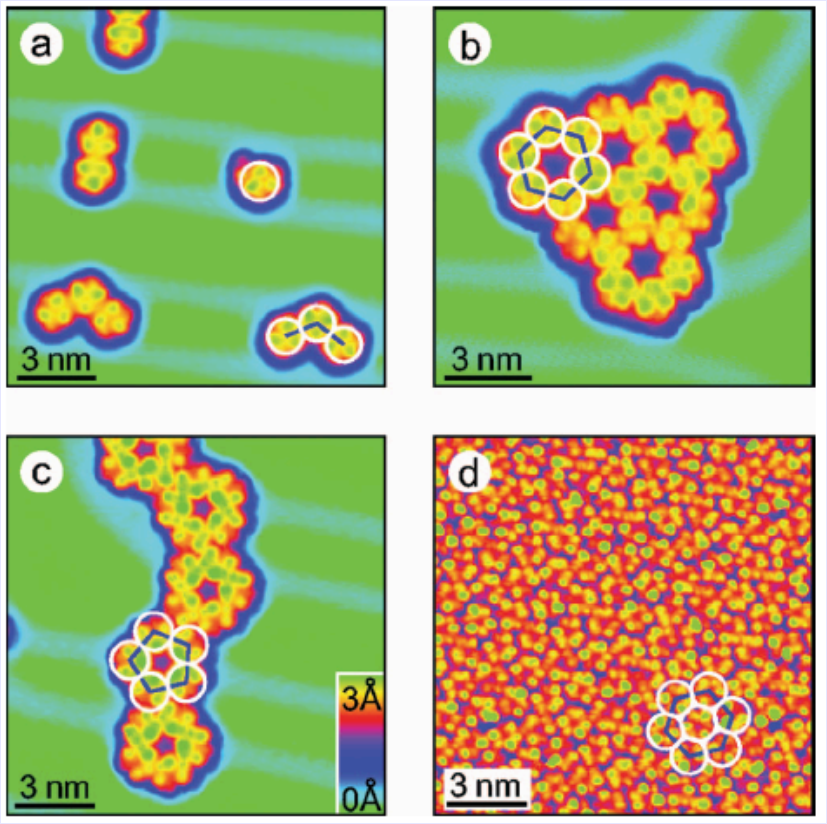


Figure 2. (a) STM image (22 nm × 11 nm) showing the detail of the twin-row structure and a layer edge. Different layers and domain orientations are visible. (b) Model reproducing the region of the uppermost layer of the island delimited by a white rectangle in a, sketched using the unit cell described in Figure 3b. A model of a molecular pair is superimposed on the STM data shown in a.

Modifying the conformation and the electronic structure of individual molecules and of supermolecules



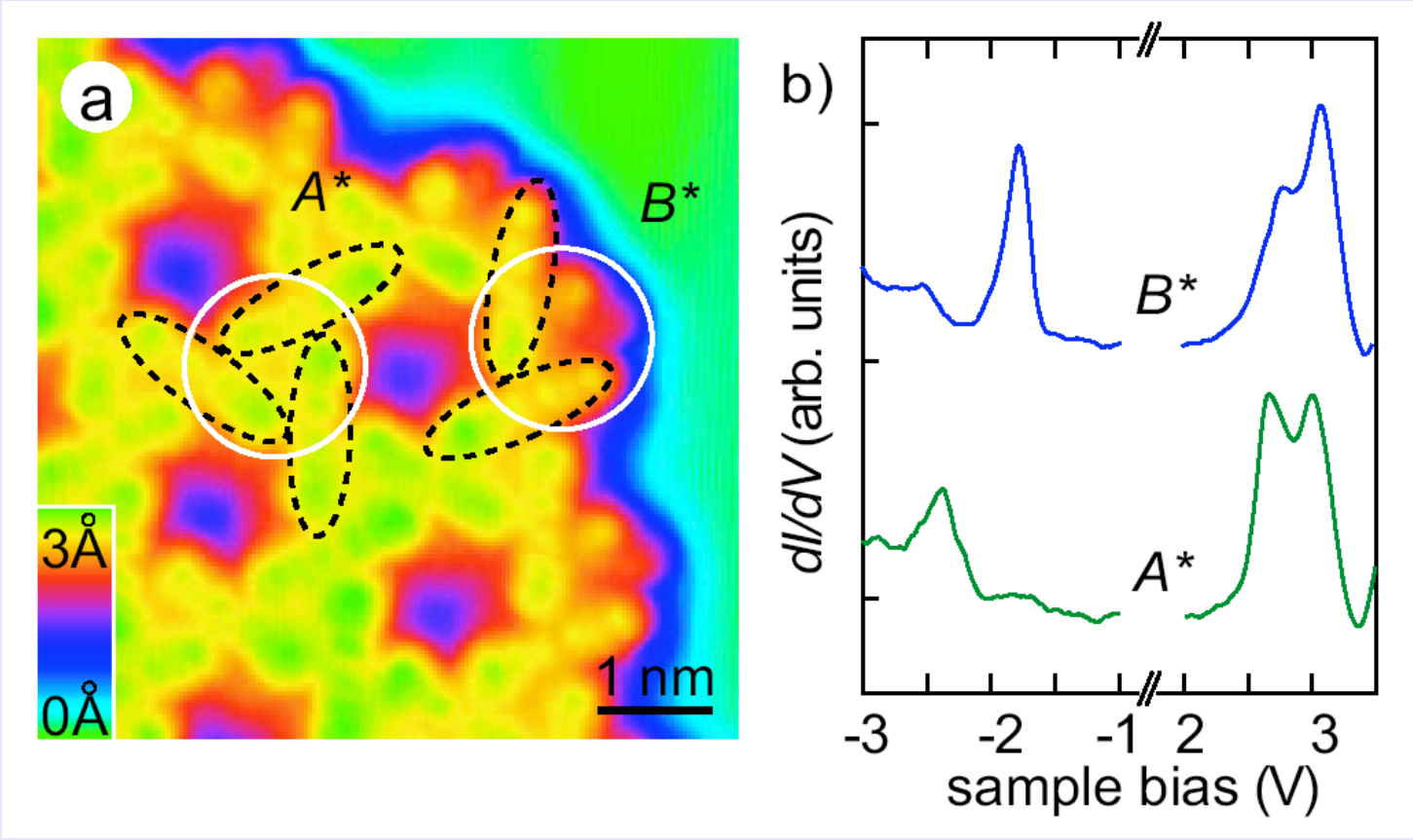
Rubrene conformations on Au(111)



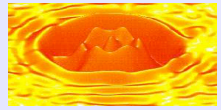
Different
adsorption conformations
for molecules
in different structures

M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)

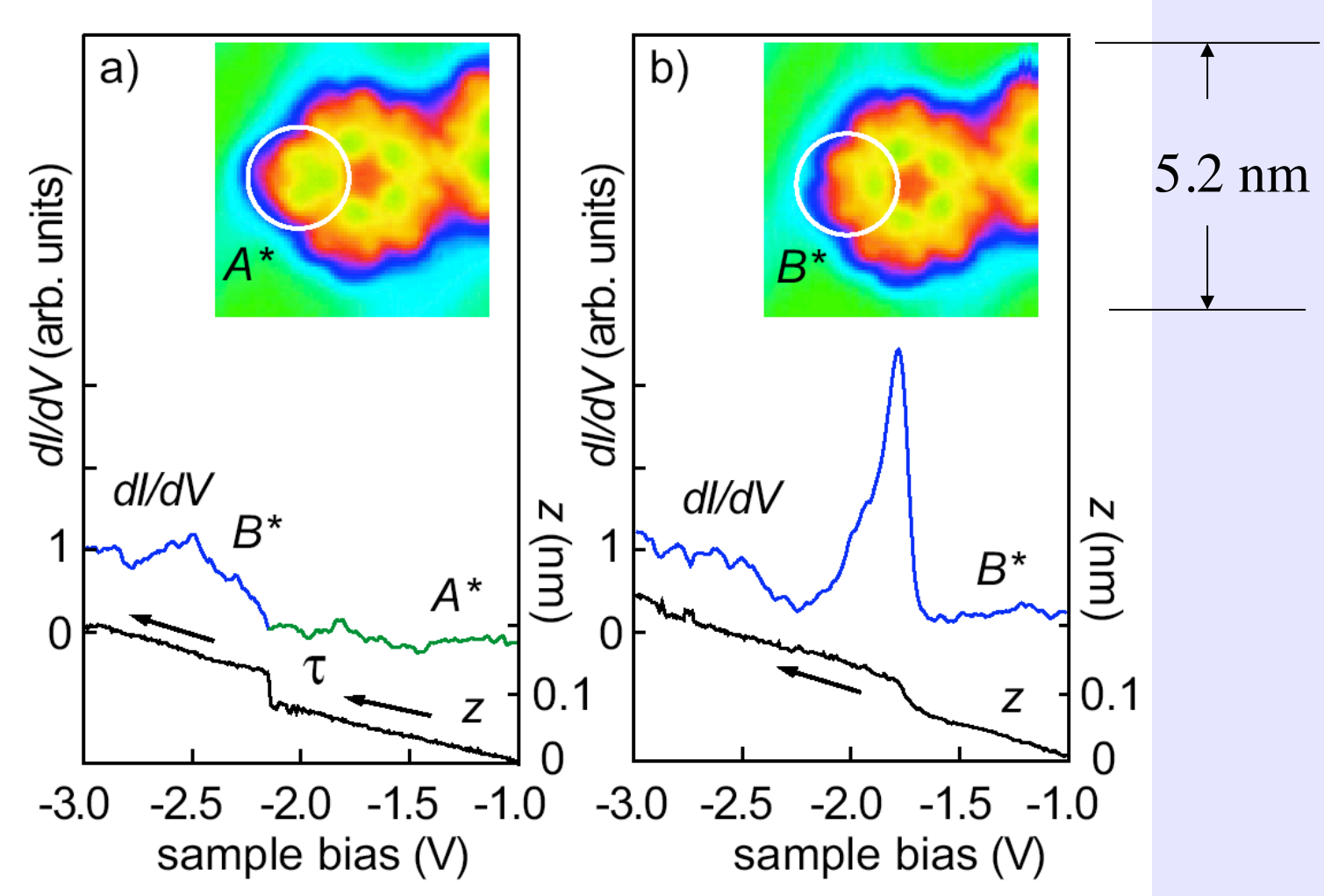
Small honeycomb islets reveal two different conformations with different electronic structure



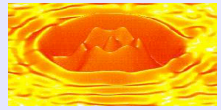
M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)



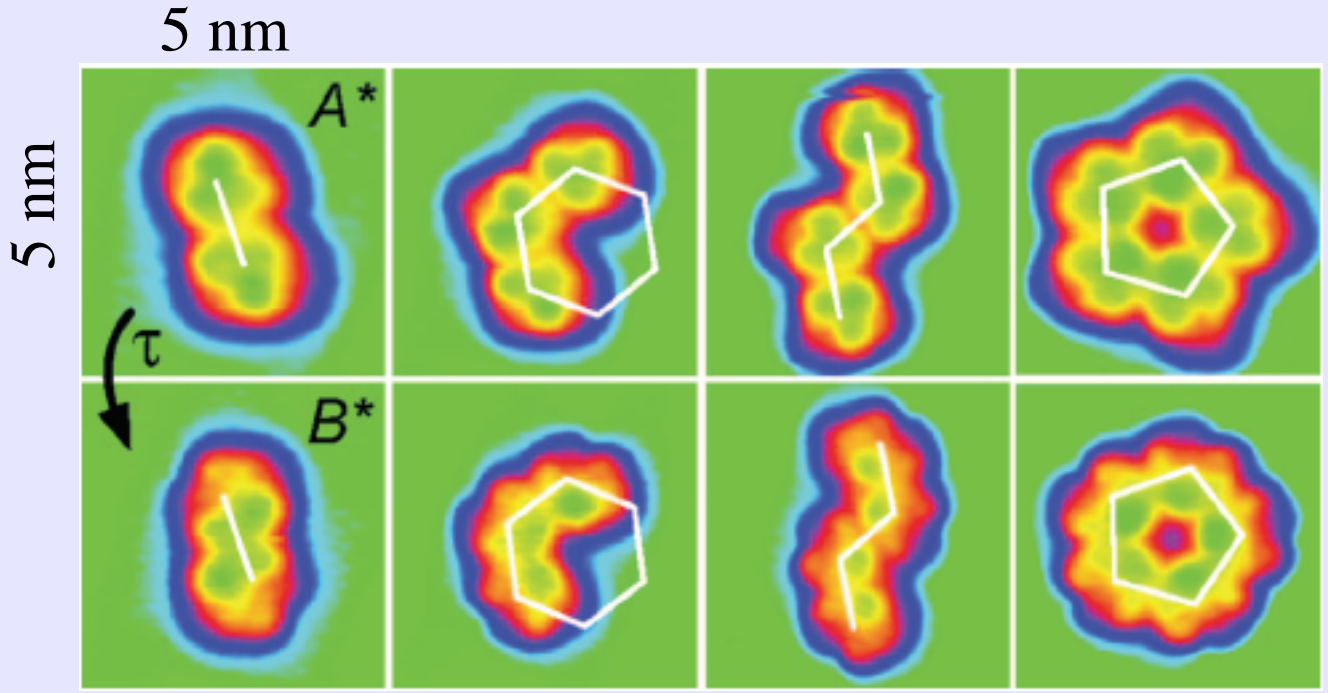
Tip-induced switching of the conformation of a rubrene molecule



M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)

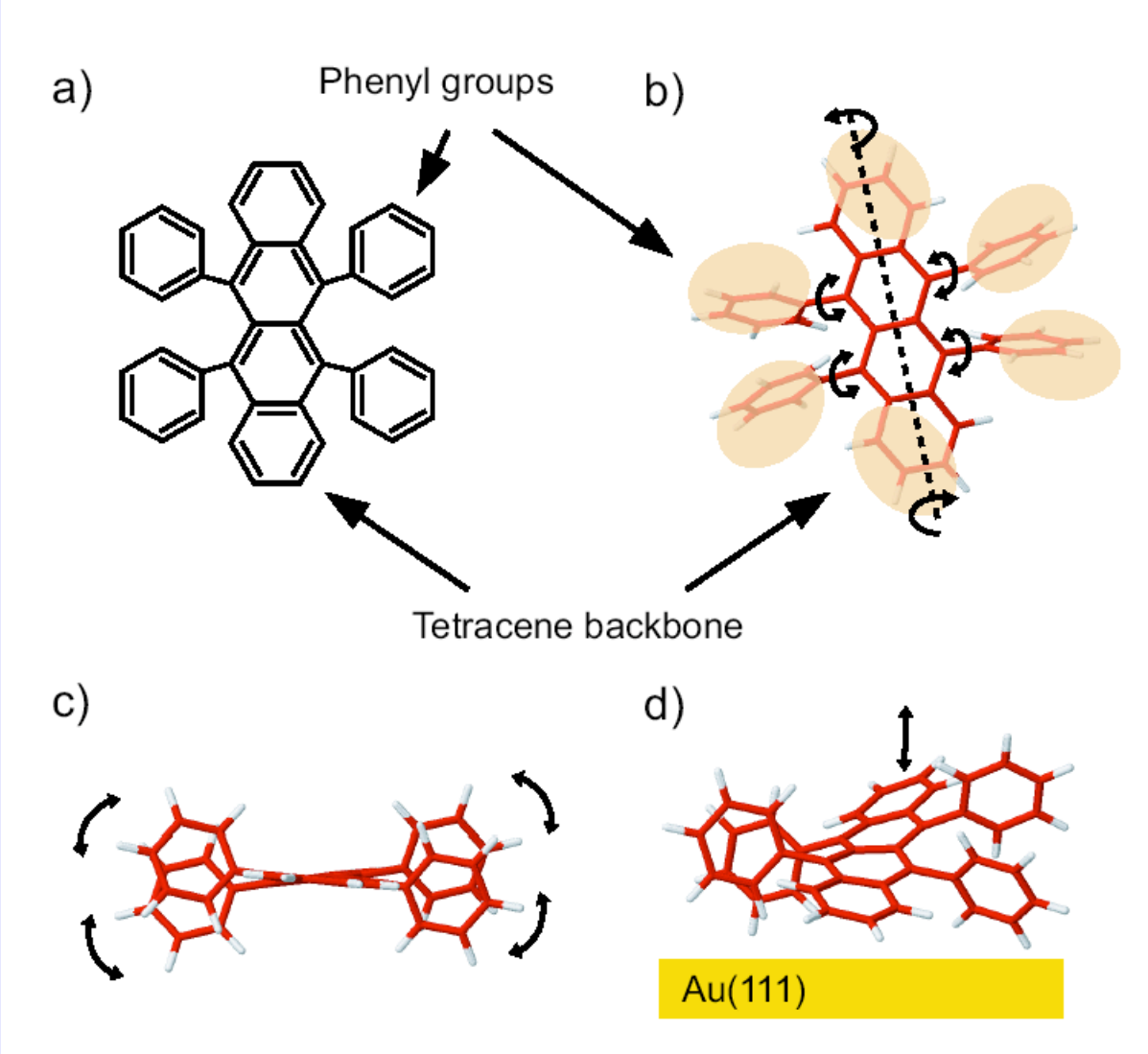


Tip-induced switching of the conformation of a supramolecular dimer, trimer, tetramer, and pentamer of rubrene on Au(111)



M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)

Chemical structure and 3D representations of rubrene

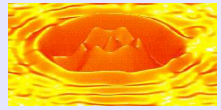


STM and STS on rubrene:

- Observation of different conformers revealing individual HOMO energies

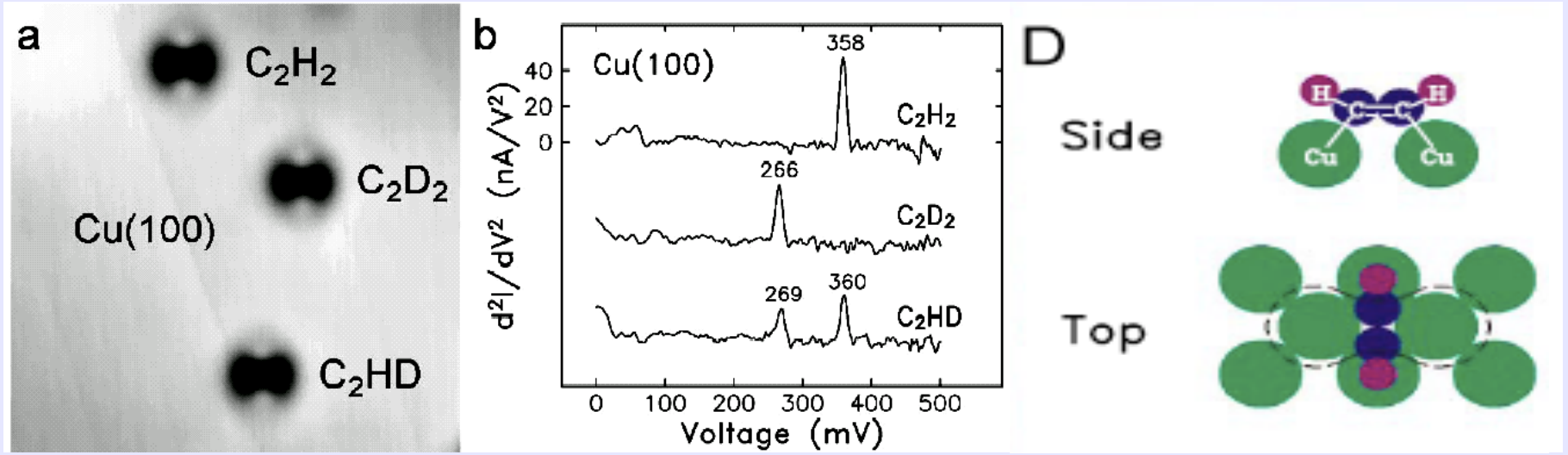
- Switching locally the conformation and the electronic structure of single molecules and small supermolecules

M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)



Single-Molecule Vibrational Spectroscopy and Microscopy:

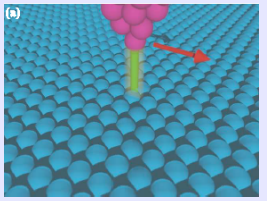
Three acetylene isotopes on Cu(100) at 8 K



56 Å x 56 Å,
$U_t = 50$ mV, $I_t = 1$nA

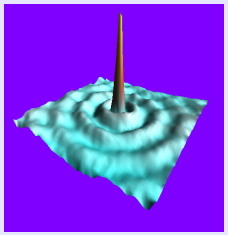
B. C. Stipe, M. A. Rezaei, W. Ho, Science **280**, 1732 (1998) & PRL **82**, 1724 (1999)

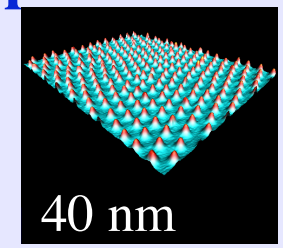
Science at the Nanoscale

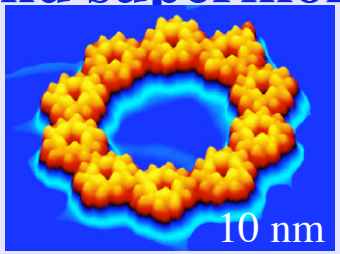


Part I: **Introduction to scanning probe methods**

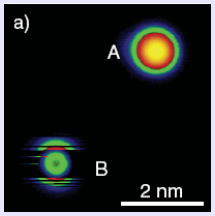
Part II: **Case Studies: Two-dimensional self-assembly of adatom superlattices and supermolecules**

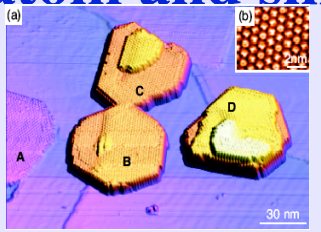


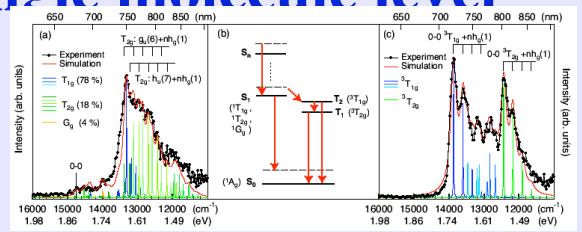




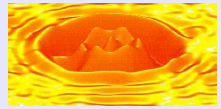
Part III: **Electron and optical spectroscopy at the single atom and single molecule level**





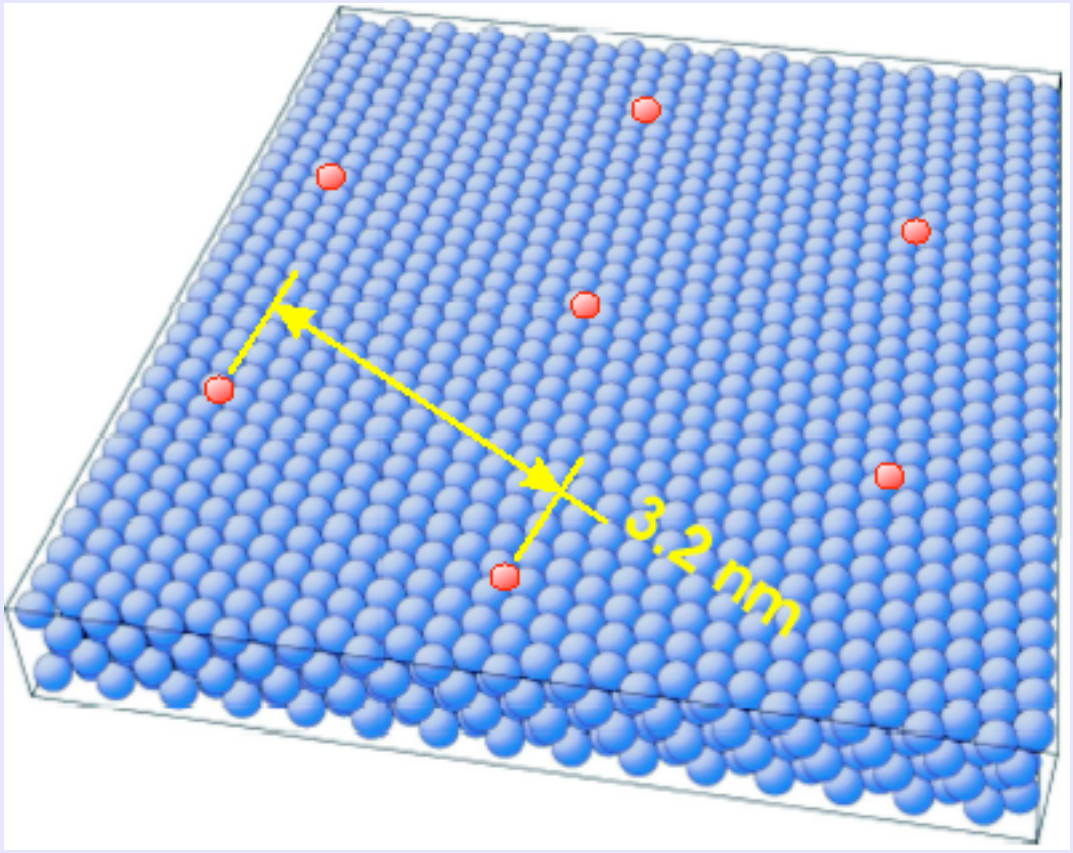


Wolf-Dieter Schneider
Institut de Physique des Nanostructures
Ecole **P**olytechnique **F**édérale de **L**ausanne, Switzerland

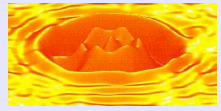


Now it’s really enough!

Ce adatom superlattice on Ag(111)
(1 % of a ML)



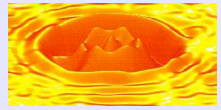
Ce-Ce adatom distance: 3.2 nm ⟺ 11 Ag atoms



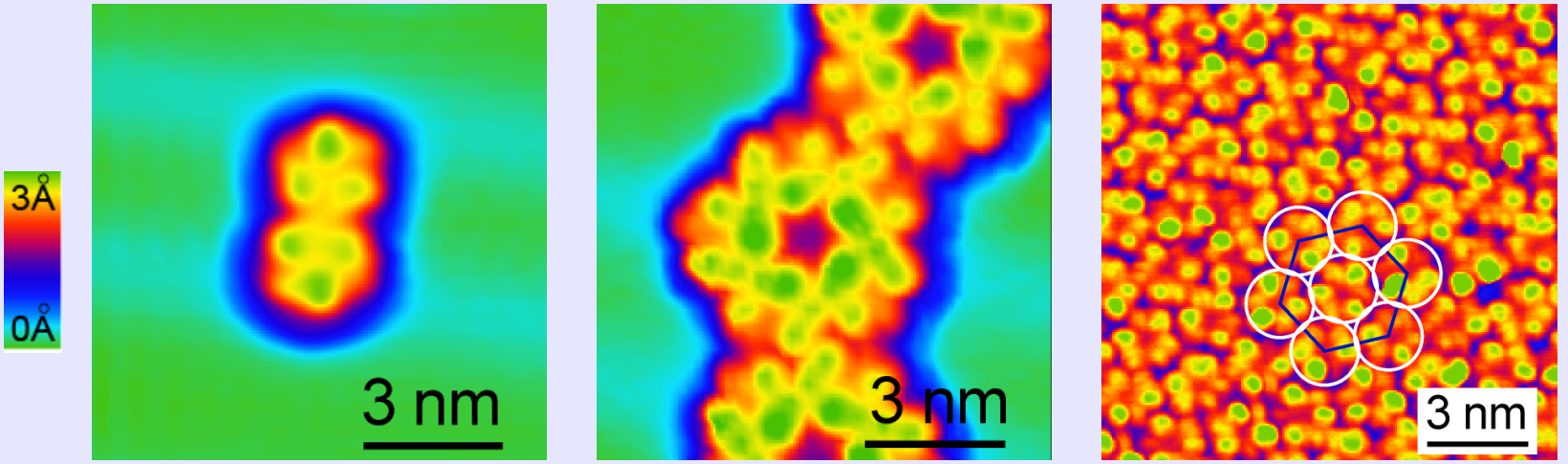
Possible future research directions

- try to detect FM or AFM interactions in superlattice of magnetic atoms. *This will likely require even lower temperatures (< 1 K).*
- investigate superlattice-forming properties on noble metal and semiconductor surfaces supporting surface states.
- explore superlattice "tuneablility," via adatom concentration, alternate substrates.

Example: Ce /Ag(111) with superlattice spacing from 2.3nm – 3.5nm have been observed by varying the amount of deposited Ce.
[Silly, Pivetta, Ternes, Patthey, Pelz, WDS, *New J. Phys.* **6**, *16 (2004).*]

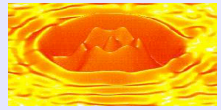


Rubrene conformations on Au(111)

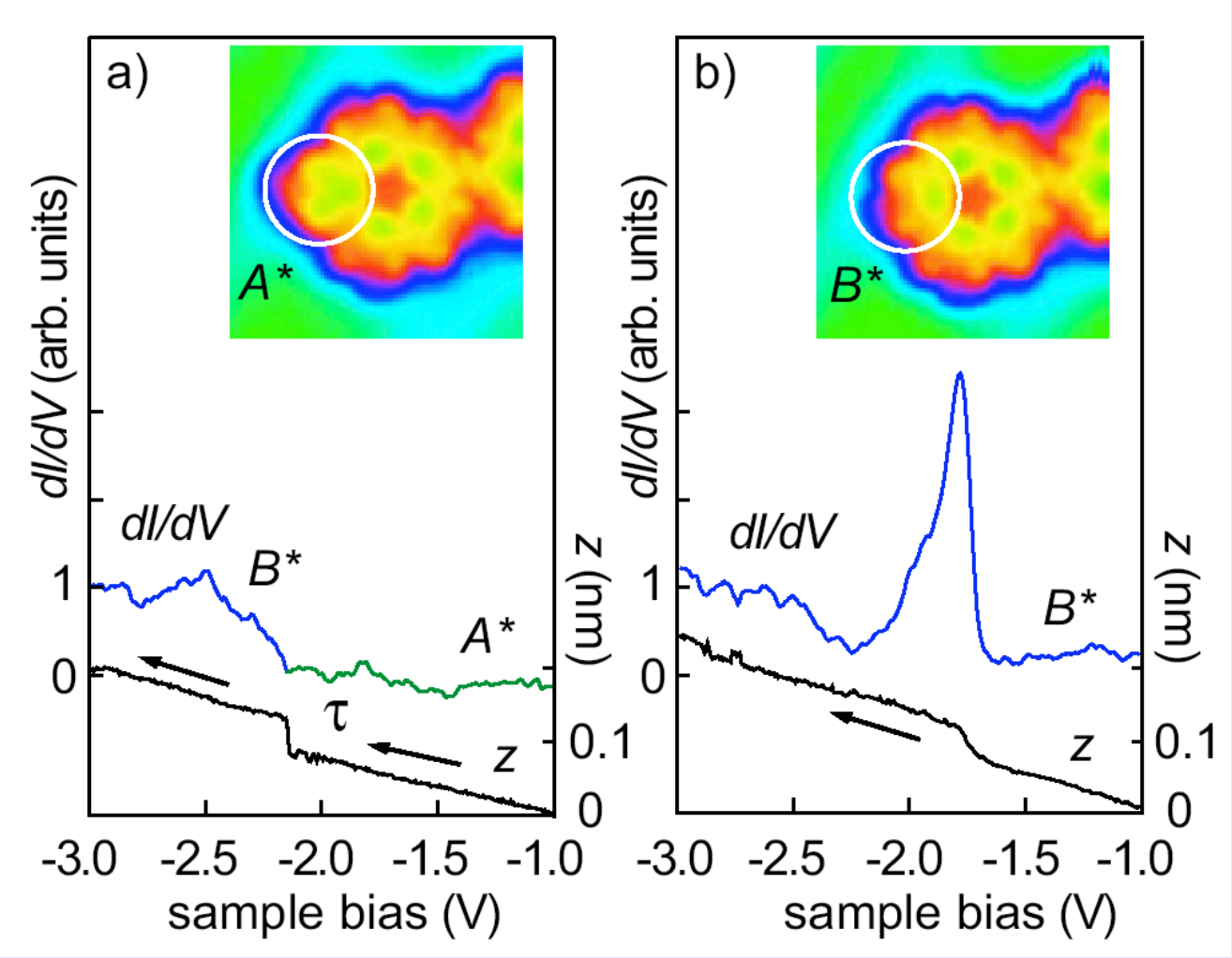


- Different adsorption conformations for molecules in different structures

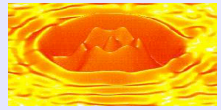
M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)



Tip-induced switching of the conformation of a rubrene molecule



M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)

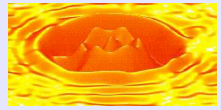


Conclusions

STM and STS on rubrene:

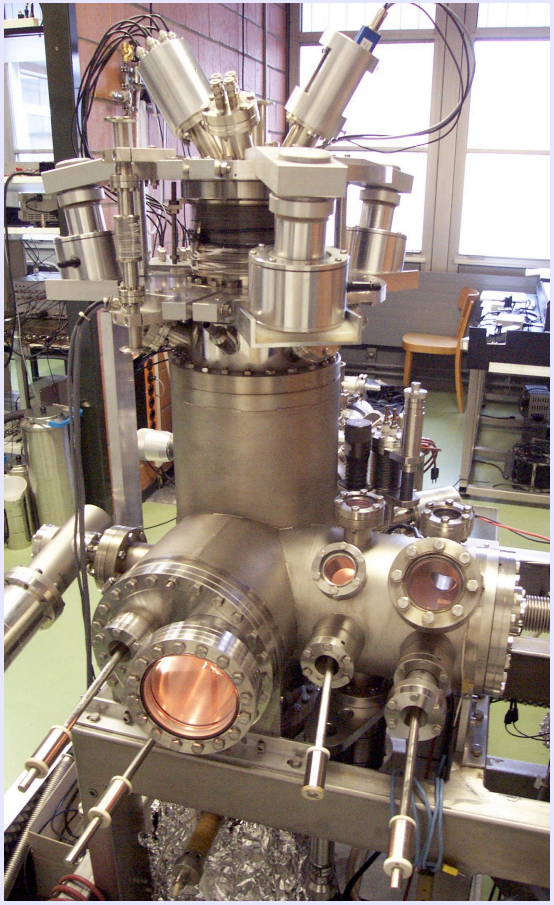
- Observation of different conformers revealing individual HOMO energies
- Switching locally the conformation and the electronic structure of single molecules and small islets

M.-C. Blüm, M. Pivetta, F. Patthey, WDS, PRB **73**, 195409 (2006)

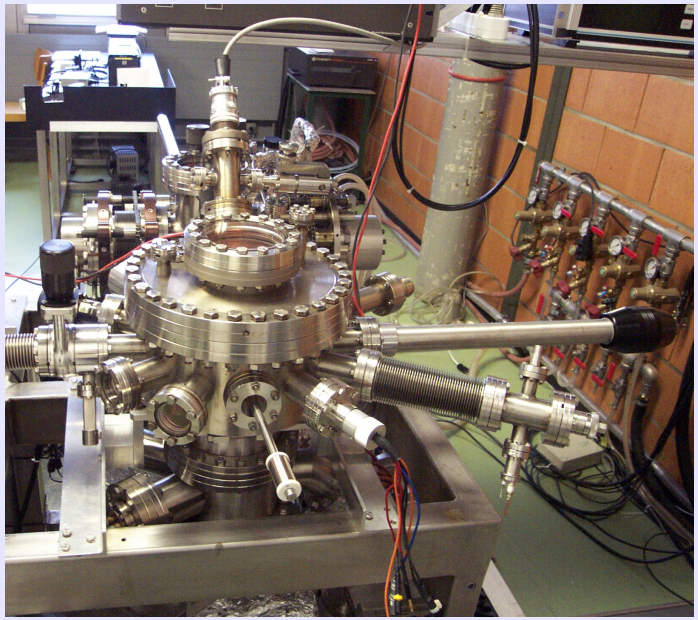


Low-temperature STM (50 K, 4.8 K, 3.9 K)

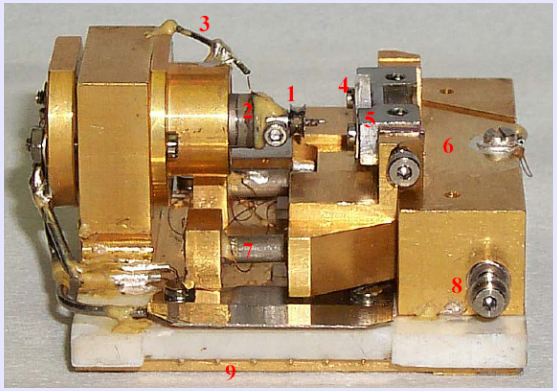
STM chamber

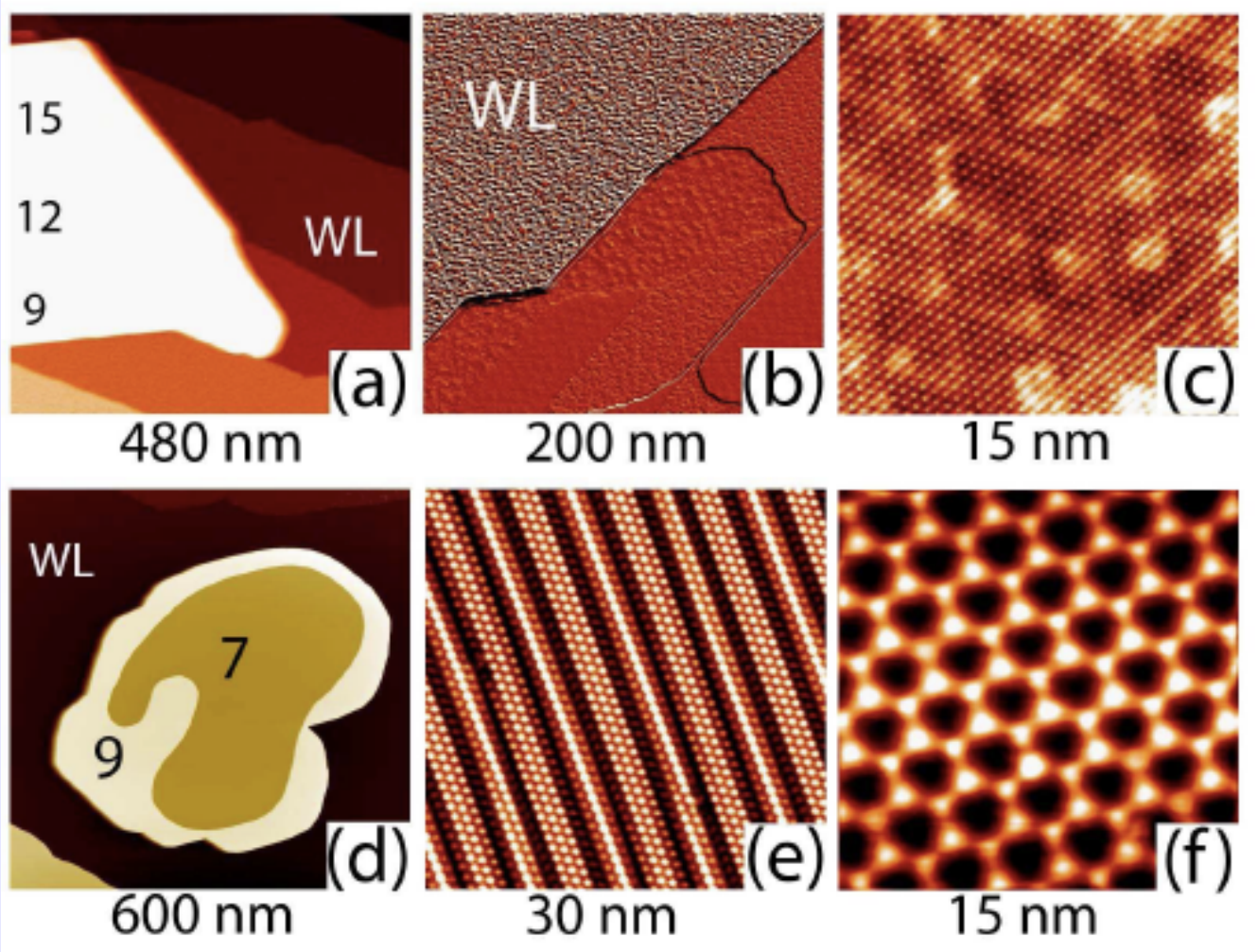


Preparation chamber



STM head




15
12
9
WL
(a)
480 nm
WL
(b)
200 nm
(c)
15 nm
WL
7
9
(d)
600 nm
(e)
30 nm
(f)
15 nm

Adatom Self-Organization Induced by Quantum Confinement of Surface Electrons

V. S. Stepanyuk,[1,*] N. N. Negulyaev,[2] L. Niebergall,[1] R. C. Longo,[3] and P. Bruno[1]

[1]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

[2]*Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany*

[3]*Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain*

(Received 26 May 2006; published 2 November 2006)

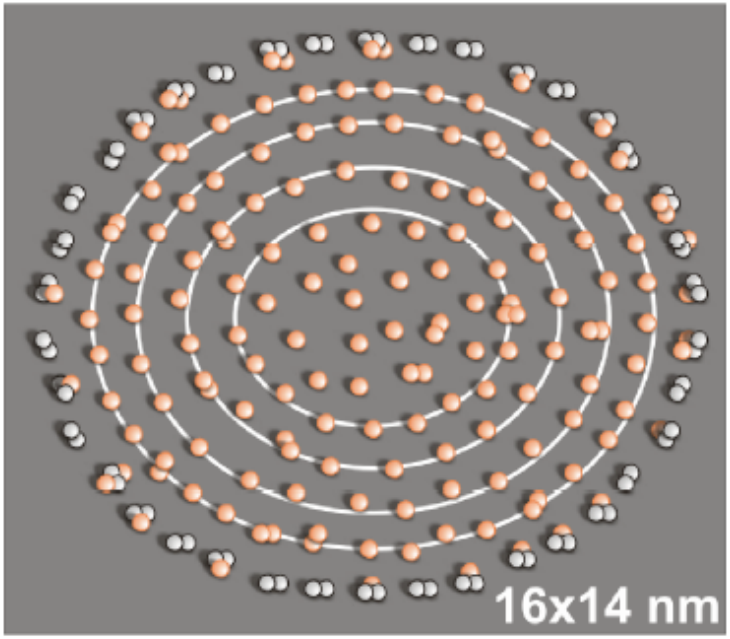


FIG. 4 (color). Self-organization of Co adatoms inside the Co corral made of Co dimers (white balls) on Cu(111). The temperature of the system is 13 K, Co adatom coverage is 0.06 monolayers, and Co adatoms were deposited simultaneously.

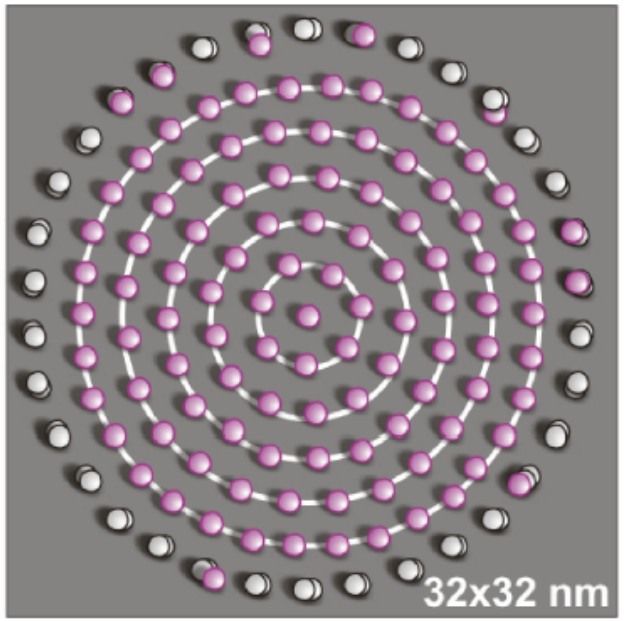
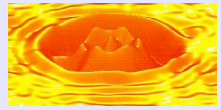
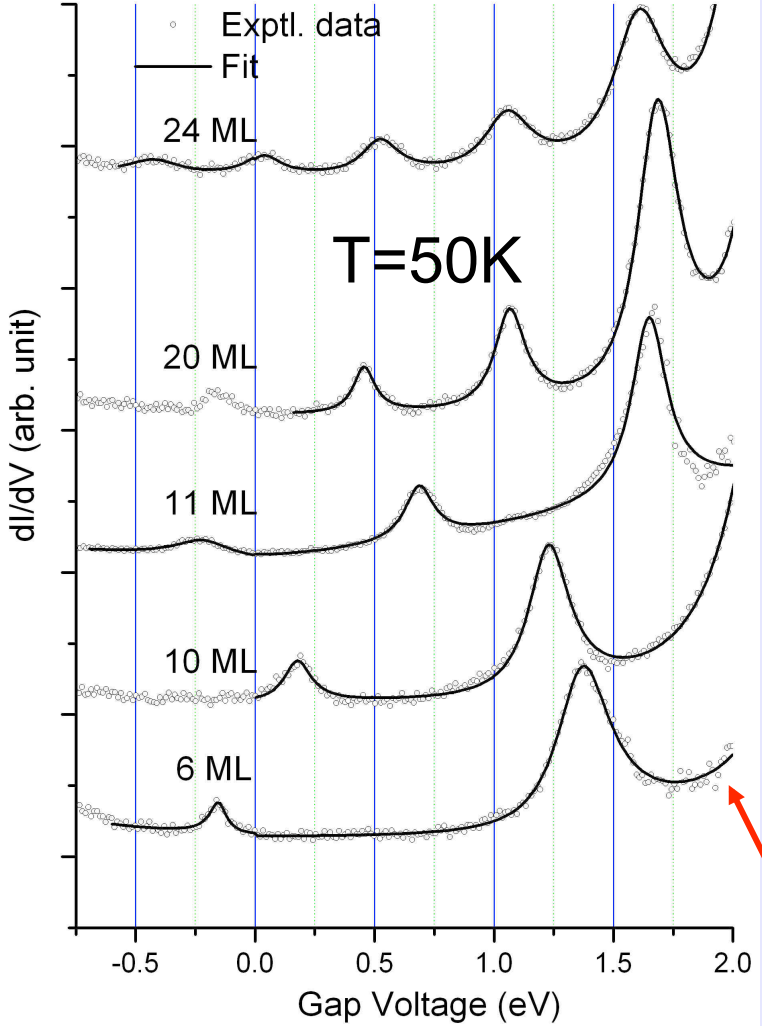


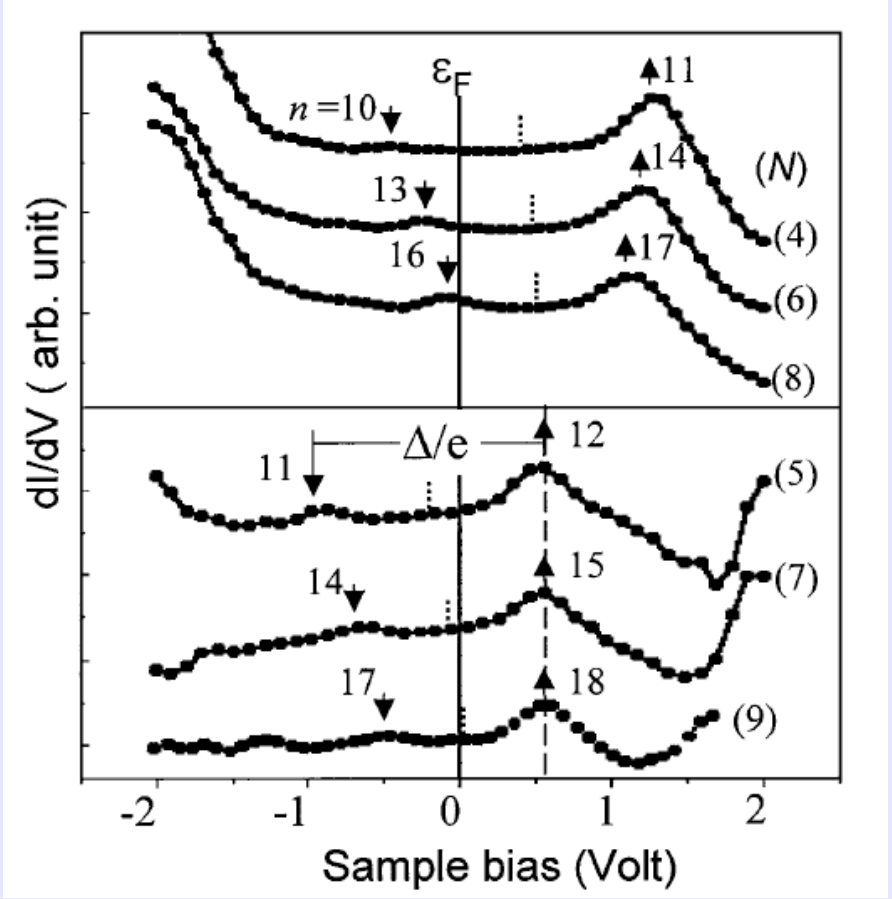
FIG. 5 (color). "Quantum onion": Self-assembly of Ce adatoms inside the Ce corral (semiaxis $a = 150$ Å; eccentricity $\varepsilon = 0$) made of Ce dimers on Ag(111). Temperature of the system is 4 K, Ce adatom coverage is 0.01 monolayers, and Ce adatoms were deposited simultaneously.



STS on Pb/Si(111)7x7 nanocrystals



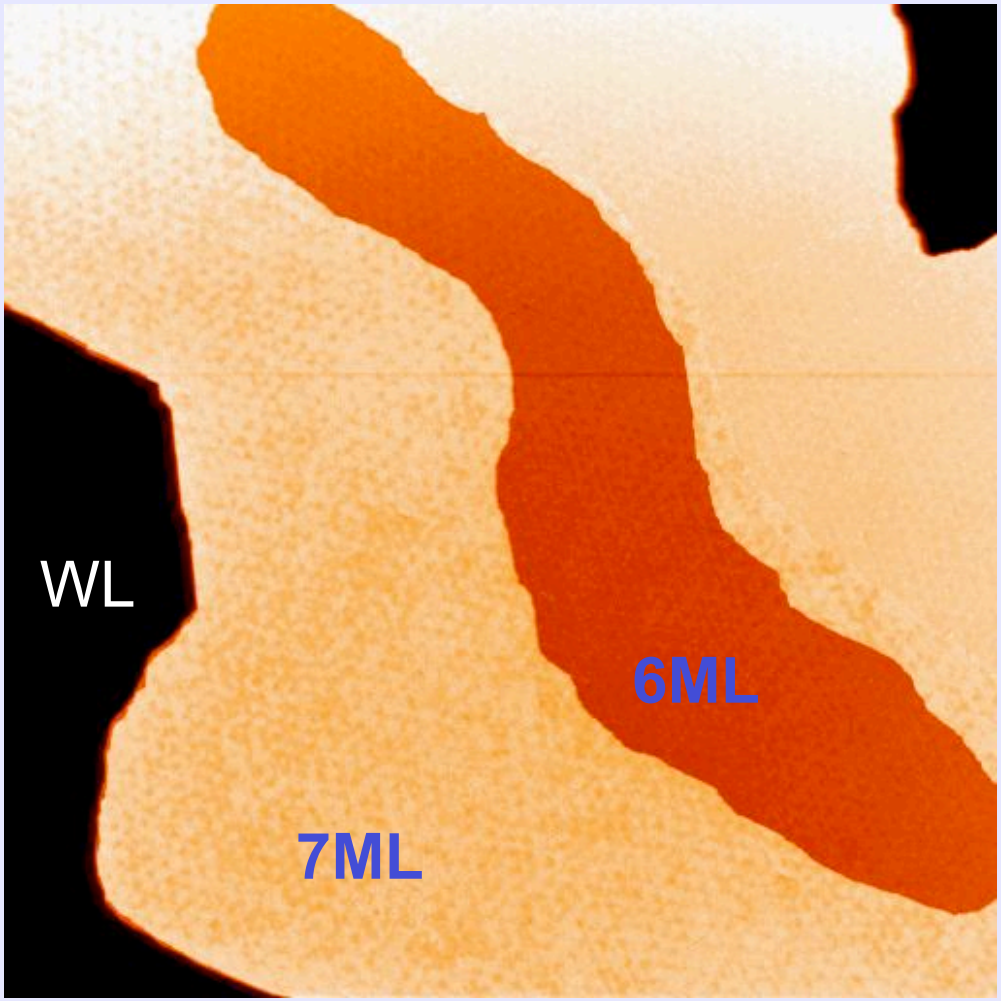
dI/dV spectra of QWS



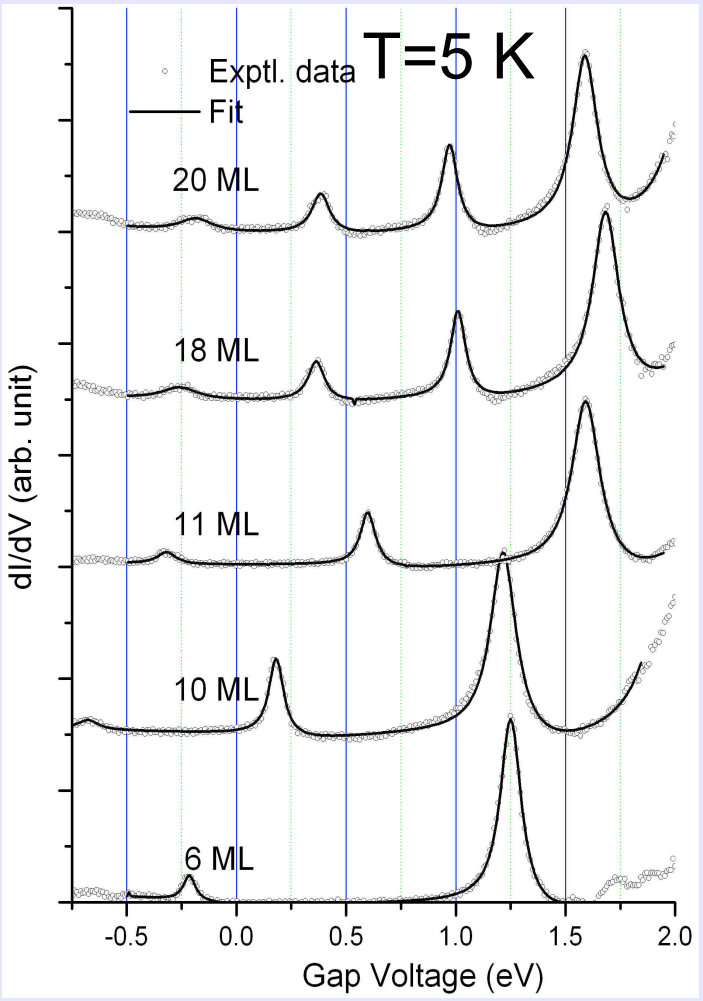
Our analysis (full lines) follows:

Altfeder *et al.*, PRL **78**, 2815 (1997)

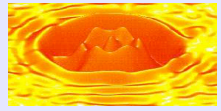
Quantum Well States: Pb/Pb-√3x √3/Si(111)



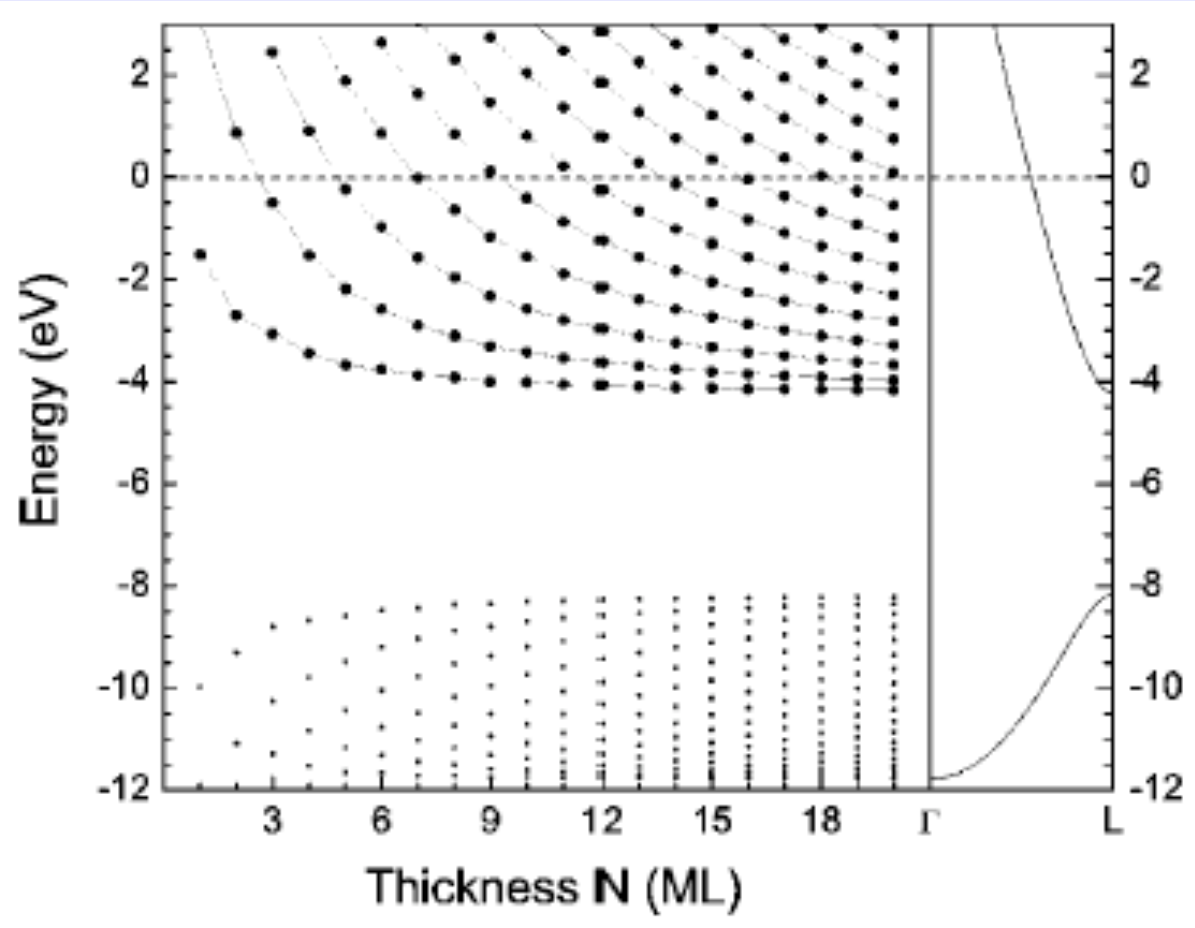
750x750nm^2



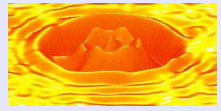
dI/dV spectra of QWS



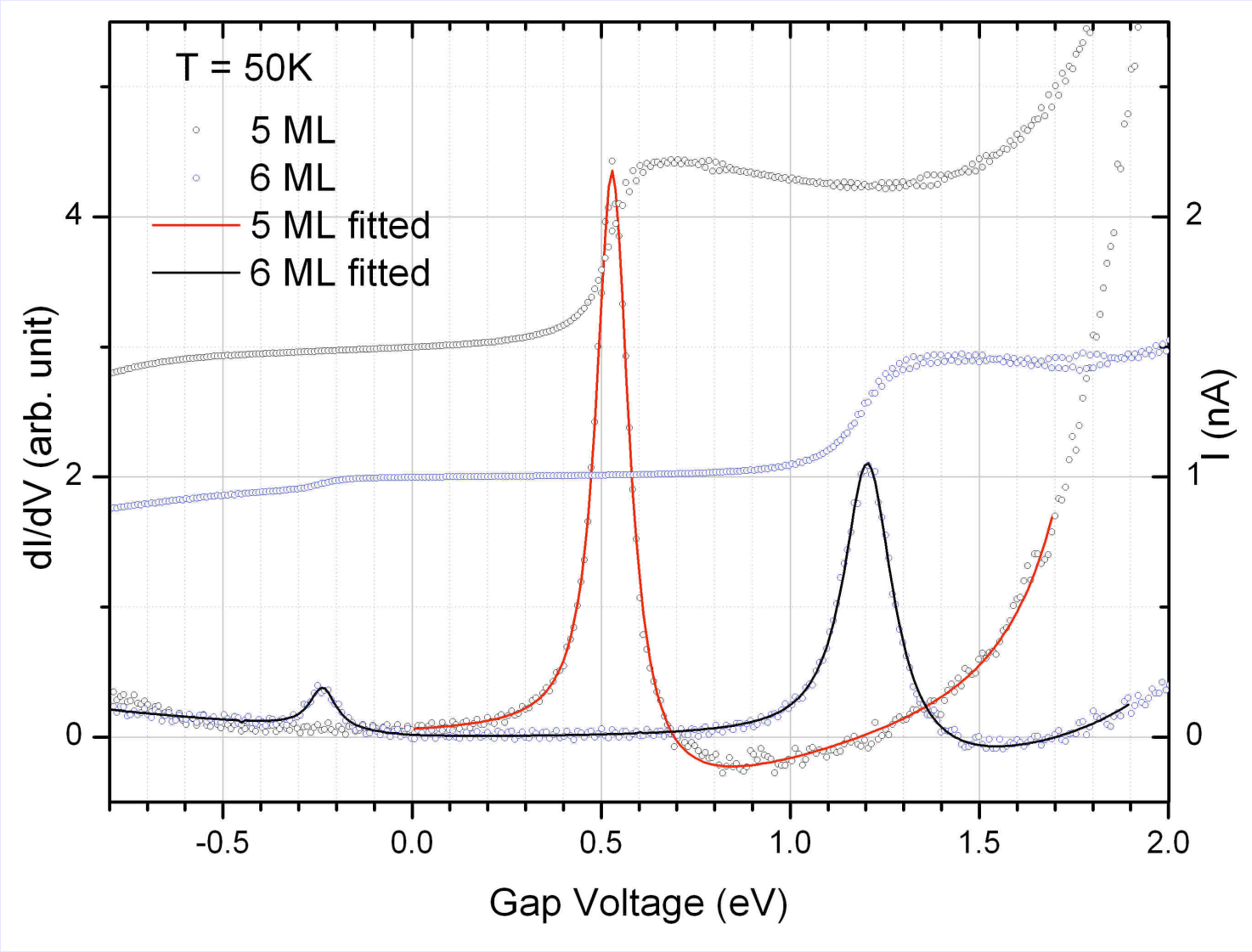
Theory of quantum size effects in thin Pb(111) films (free standing films)



Ab initio DFT calculations: C. M. Wei and M. Y. Chou PRB **66**, 233402 (2002)



QWS in STS: Pb/Pb-√3x √3/Si(111)



Motivation

- **Since the 1960's interest for Quantum Size Effects in thin films on superconductivity**

  Theory: $T_c(d) > T_c(bulk)$ - Blatt and Thompson, PRL 1963

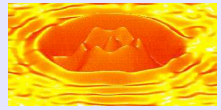
  Experiment (resistivity measurements on disordered films of granular structure, superconducting properties determined by the grains):

  Strongin *et al*. J. Appl. Phys. 1968, Komnik *et al*. JETP 1970

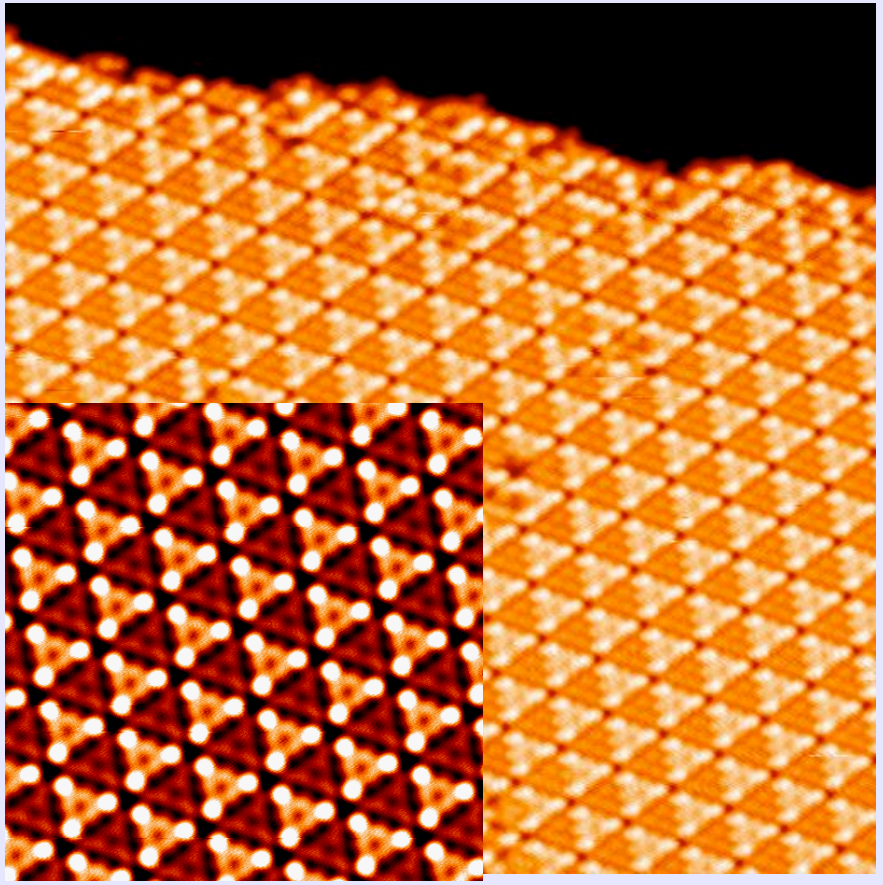
- **Until recently, lack of clean and uniform thin film systems to study intrinsic thickness dependent superconducting properties**

  Goldman and Markovic, Phys. Today 1998,

  Chiang, Science 2004



STM: Si(111)-7x7 at 4.6 K



320 x 320nm²

40 x 40nm²

U = -2.5 V, I = 20 pA

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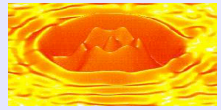
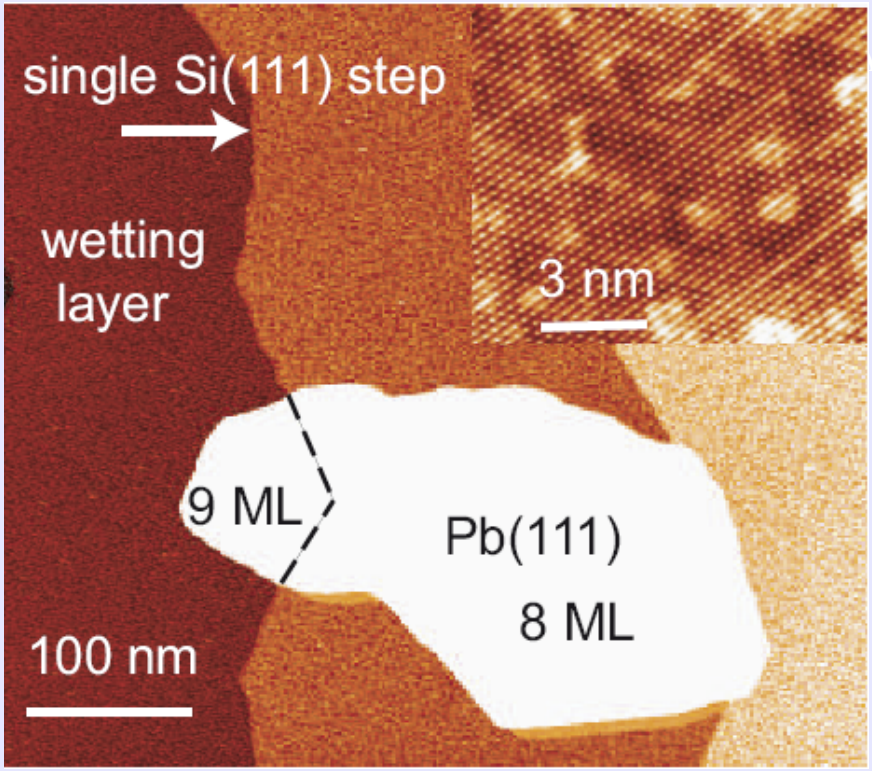
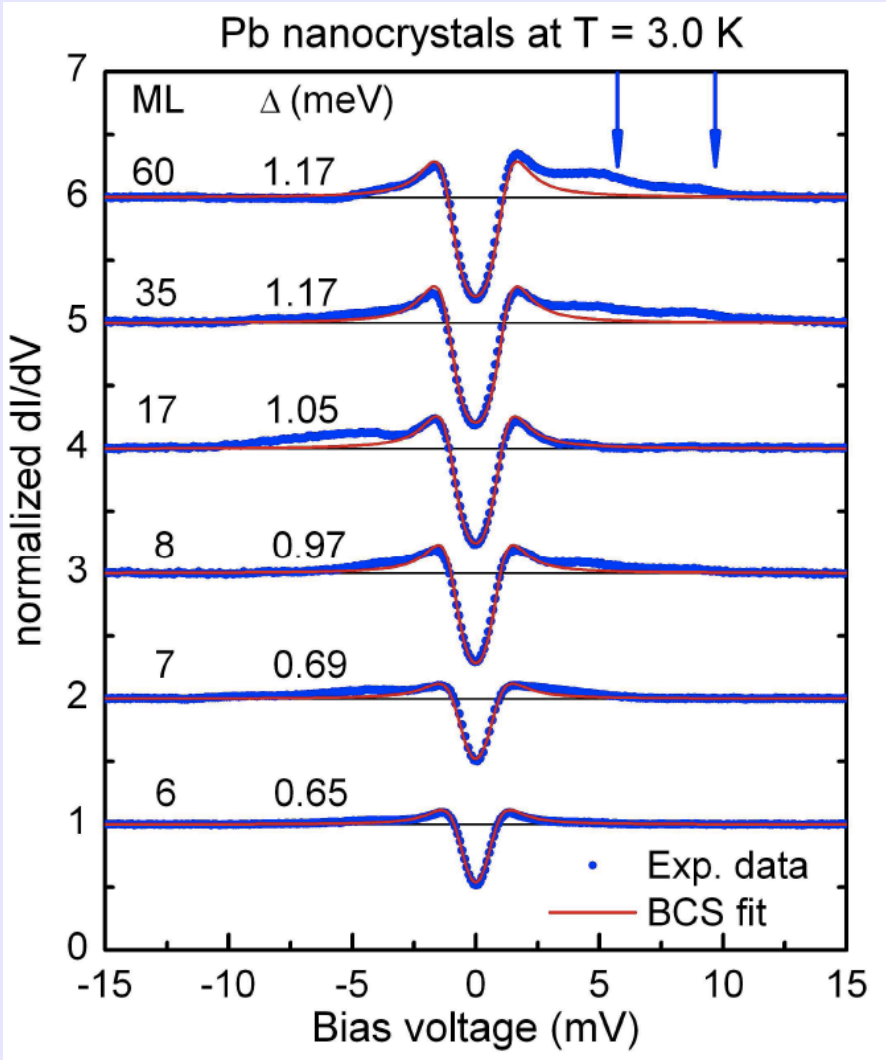


Pb- islands: Thickness dependent dI/dV spectra



U = -1.0 V; I = 100 pA



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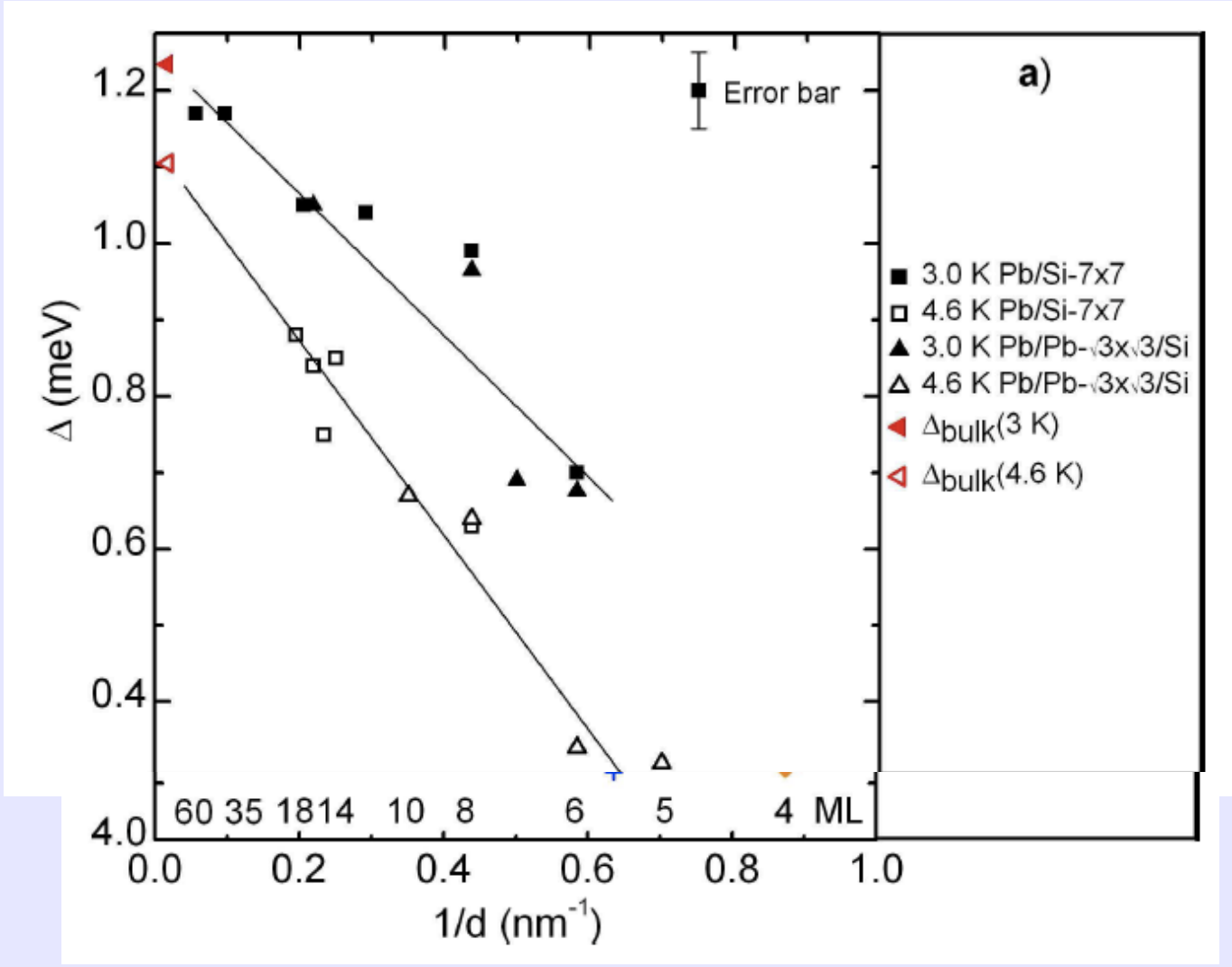
STS results: Energy gap Δ on "large" islands ($L > \xi_c$)



Δ: no observable dependence on the specific interface

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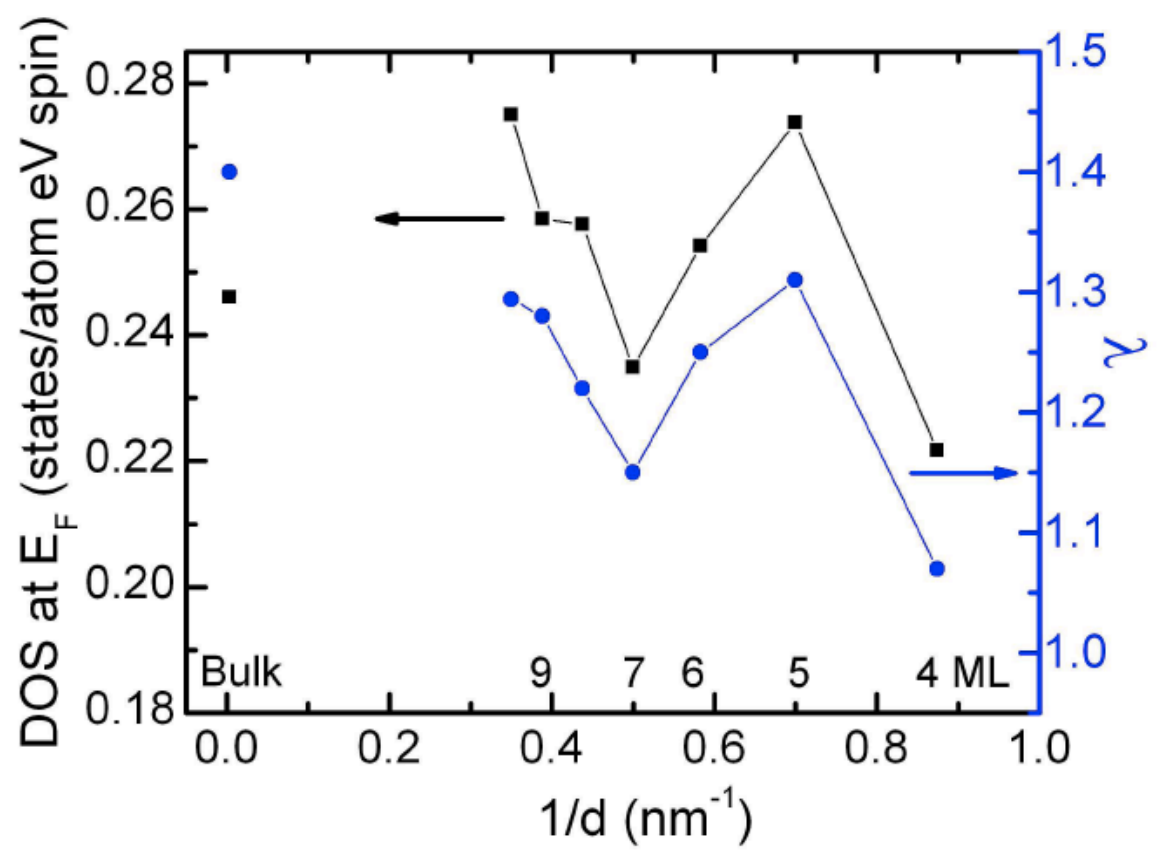
Ab initio DFT calculations of electronic properties and electron-phonon coupling in Pb thin films



McMillan : $T_c = \frac{\Theta_D}{1.45} \times exp[-\frac{1.04(1+\lambda)}{\lambda-\mu^*-(1+0.62\lambda)}]$

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