STM spectroscopy (STS)

$$\frac{dI}{dV} = \frac{4\pi e^2}{\hbar} \rho_S(E_F + eV, r)\rho_T(E_F)\left|M\right|^2$$

Basic concepts of STS. With the feedback circuit open the variation of the tunneling current due to the application of a small oscillating voltage (10-20 mV) is acquired as a function of the tunneling bias V. Recording these values as a function of position (x,y) generates a map of the local density of states (assuming that the density of states of the tip not changes during the measurements)

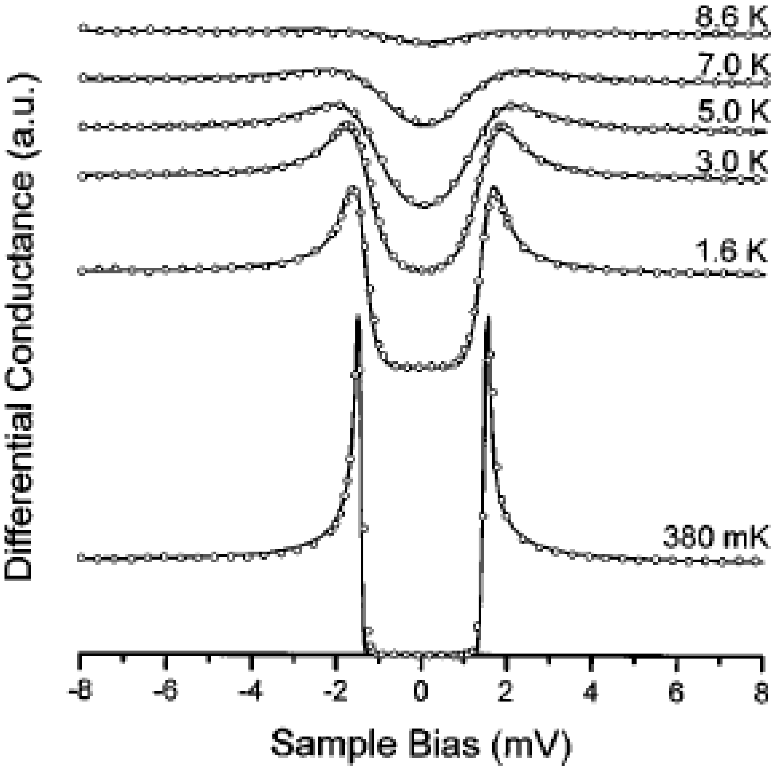
For example: Niobium tip on Au surface

Superconducting LDOS

$$\rho_S = \rho(0)\frac{\left|V\right|}{\sqrt{V^2 - \Delta^2}} \qquad \left|V\right| > \Delta$$

Electrons can scatter only if the energy change is larger than Δ

$$\rho_S = 0 \qquad \left|V\right| < \Delta$$

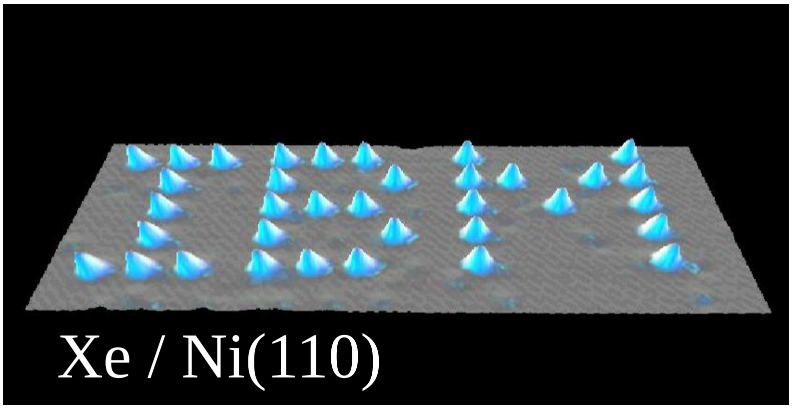


— BCS DOS fit
with Δ_{Nb}=1.47 meV

Nb is superconducting at temperature < 10 K

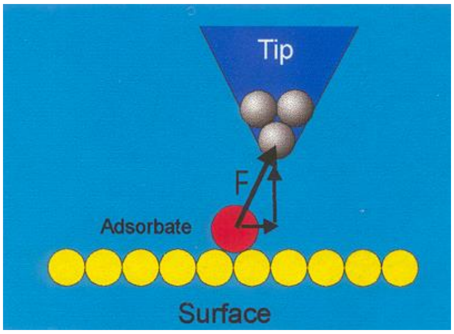
Pan, et al., APL 73, 2992 (1998)

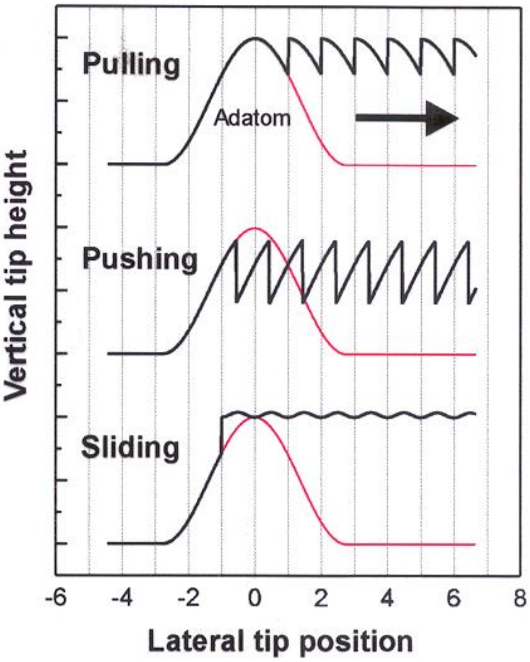
Atom manipulation



D. Eigler & E. Schweizer,
Nature **344**, 524 (1990)

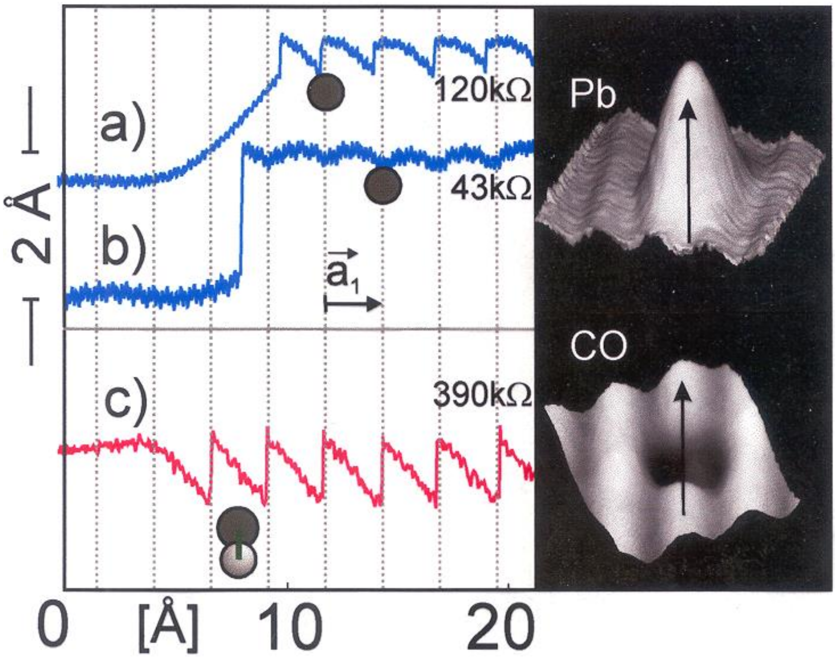
Model:





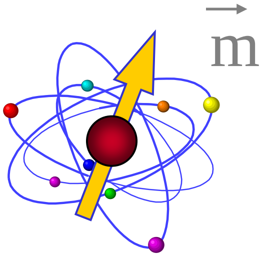
G.Meyer, *et al*. Applied Physics A
68, 125 (1999)

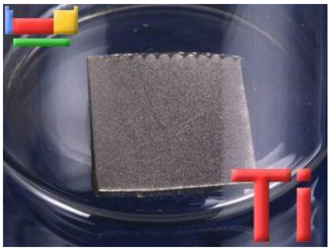
Experiment:



First the tip is approached close to the adsorbate by reducing the tunneling resistance and then, at constant tunneling current, moves parallel to the surface, with the atom following the tip.
The steps in the tip height clearly indicate a discontinuous movement of the atom, meaning the atom is jumping from one adsorption site to the next.

Electronic properties of nano-objects

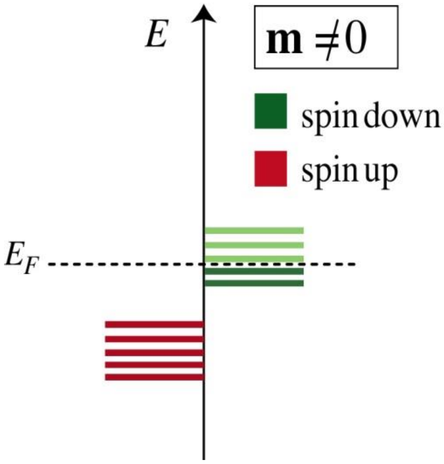


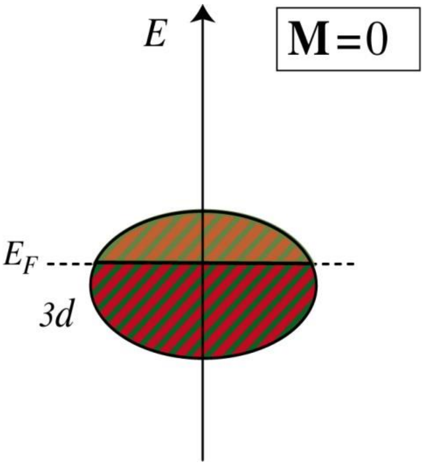


Band formation

atom

bulk



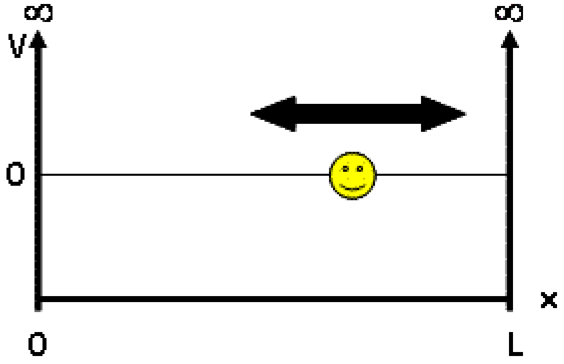


-Discrete energy levels
-Electrons localized at the atom site

-Continuous energy levels
-Electrons delocalized

Where is the frontier ?
Does the frontier depend on the chemical element ?

Confined electrons: “Particle in a box”

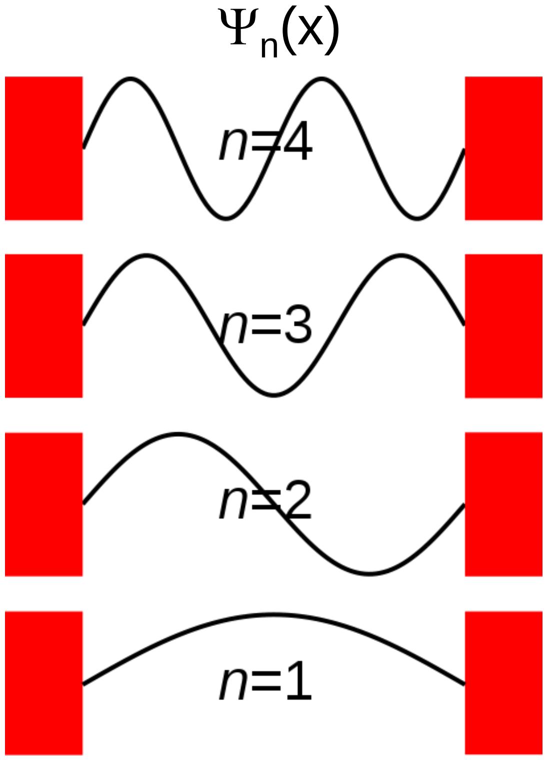


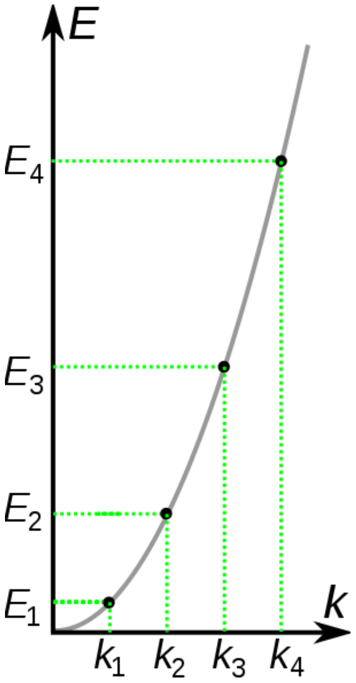
The potential energy is *0 inside the box* (V=0 for 0<x<L) and *goes to infinity at the walls of the box* (V=∞ for x<0 or x>L).

$$-\frac{h^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2}+V(x)\Psi(x)=E\Psi(x) \quad \Longrightarrow$$

$$\Psi_n(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$

$$E_n=\frac{n^2h^2}{8mL^2}$$



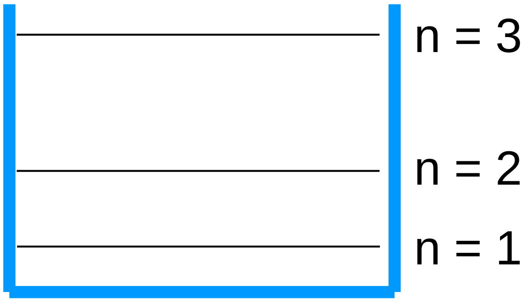


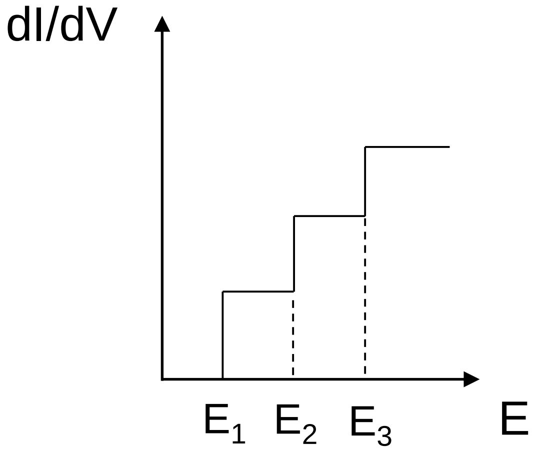
The energy of a particle in a box (black circles) and a free particle (grey line) both depend upon wavenumber in the same way. However, the particle in a box may only have certain, discrete energy levels.

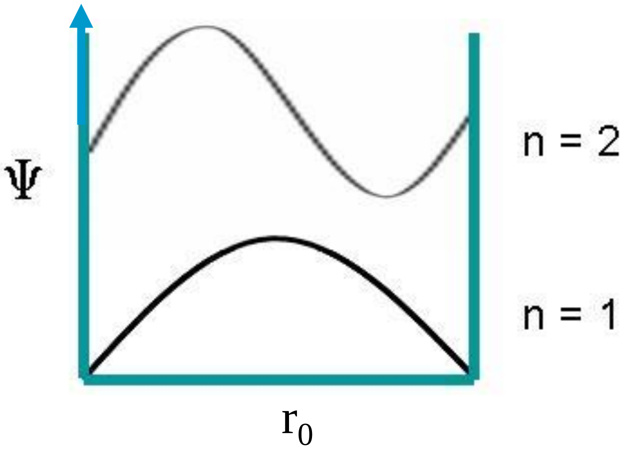
$$\frac{dI}{dV} = \frac{4\pi e^2}{\hbar} \rho_S (E_F + eV, r) \rho_T (E_F) |M|^2$$

STS: the measured *dI/dV* signal (conductivity) is high, when the sample bias matches one of the energy levels.

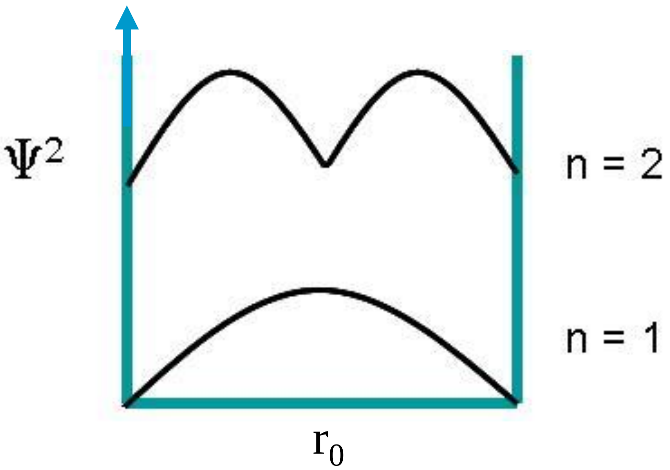
$$E_n = \frac{n^2 h^2}{8mL^2}$$







The wavefunction for a particle in a box at the n=1 and n=2 energy levels



$$\rho_s(E, \vec{r}_0) \propto \Psi_n(r_0)^2$$

$$E = E_n$$

1D electron band in a wire of 20 Au atoms

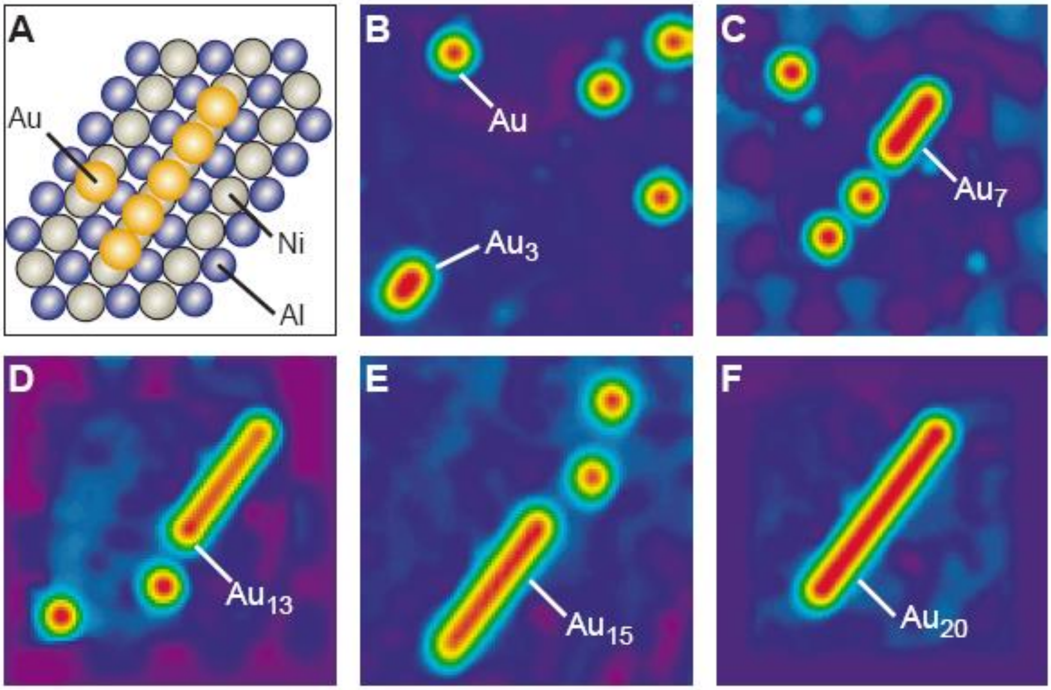
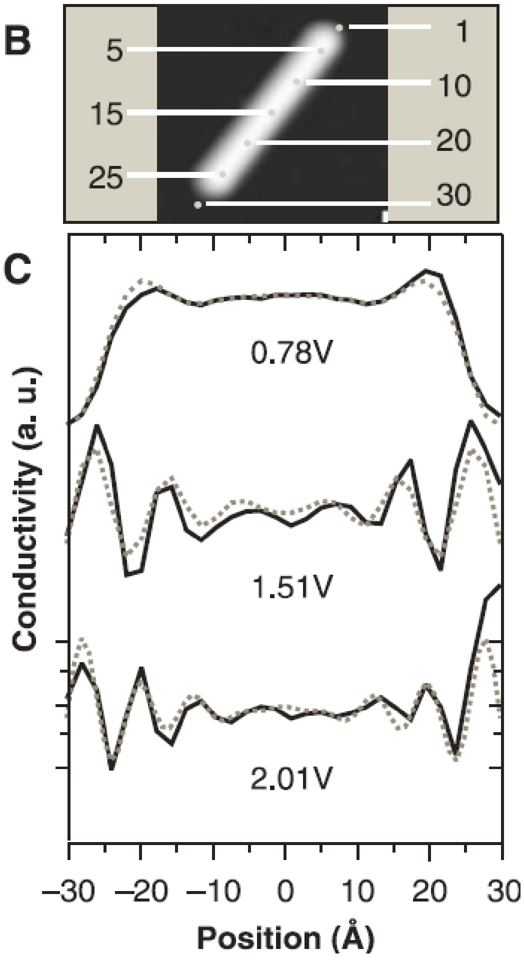
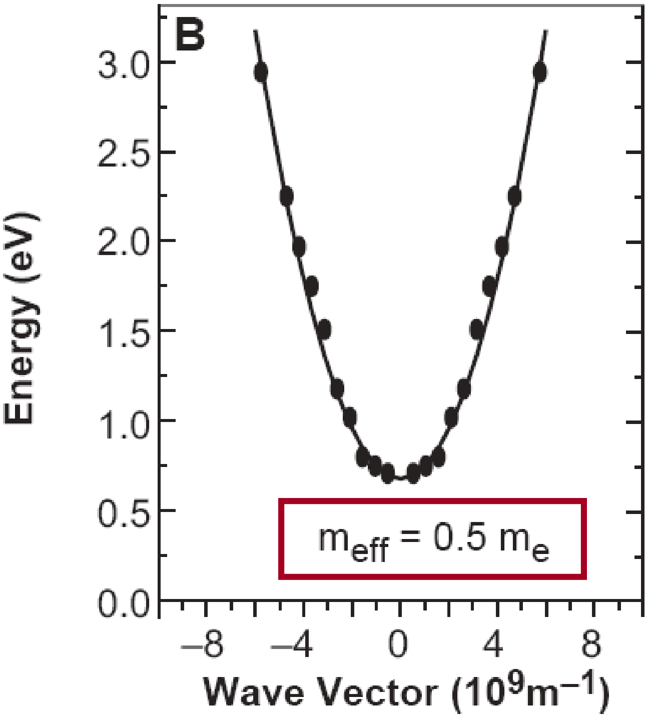


Fig. 1. (**A**) Structure model of a Au_5 chain and a Au atom on NiAl(110). (**B** to **F**) STM topographic images showing intermediate stages of building a Au_{20} chain. Single Au atoms were manipulated with the STM tip and attached on both sides to the chain (image sizes 95 Å by 95 Å, V_{sample} = 2.1 V, I = 1 nA).

$$E_n = \frac{n^2 h^2}{8mL^2}$$





Nilius et al., Science **297**, 1853 (2002).

Assembling 20 Au atoms to a linear chain results in the formation of a 1D electron band from a single Au atomic orbital.

Does the frontier depend on the chemical element ?

Energy spectrum depends on the chemical element via m_{eff}

$$E_n = \frac{n^2 h^2}{8 m_{eff} L^2}$$

$$E_2 - E_1 = \frac{3h^2}{8 m_{eff} L^2}$$

$m_e = 9.1\ 10^{-31}$Kg; $m_{eff} = 0.5\ m_e$;
$h = 6.6\ 10^{-34}$ J s

For the previous Au chains (L about 6nm) we get E_2-E_1 = 60 meV

To observe E_2-E_1 you need E_2-E_1 >> kT

At room temperature kT = 25.8 meV

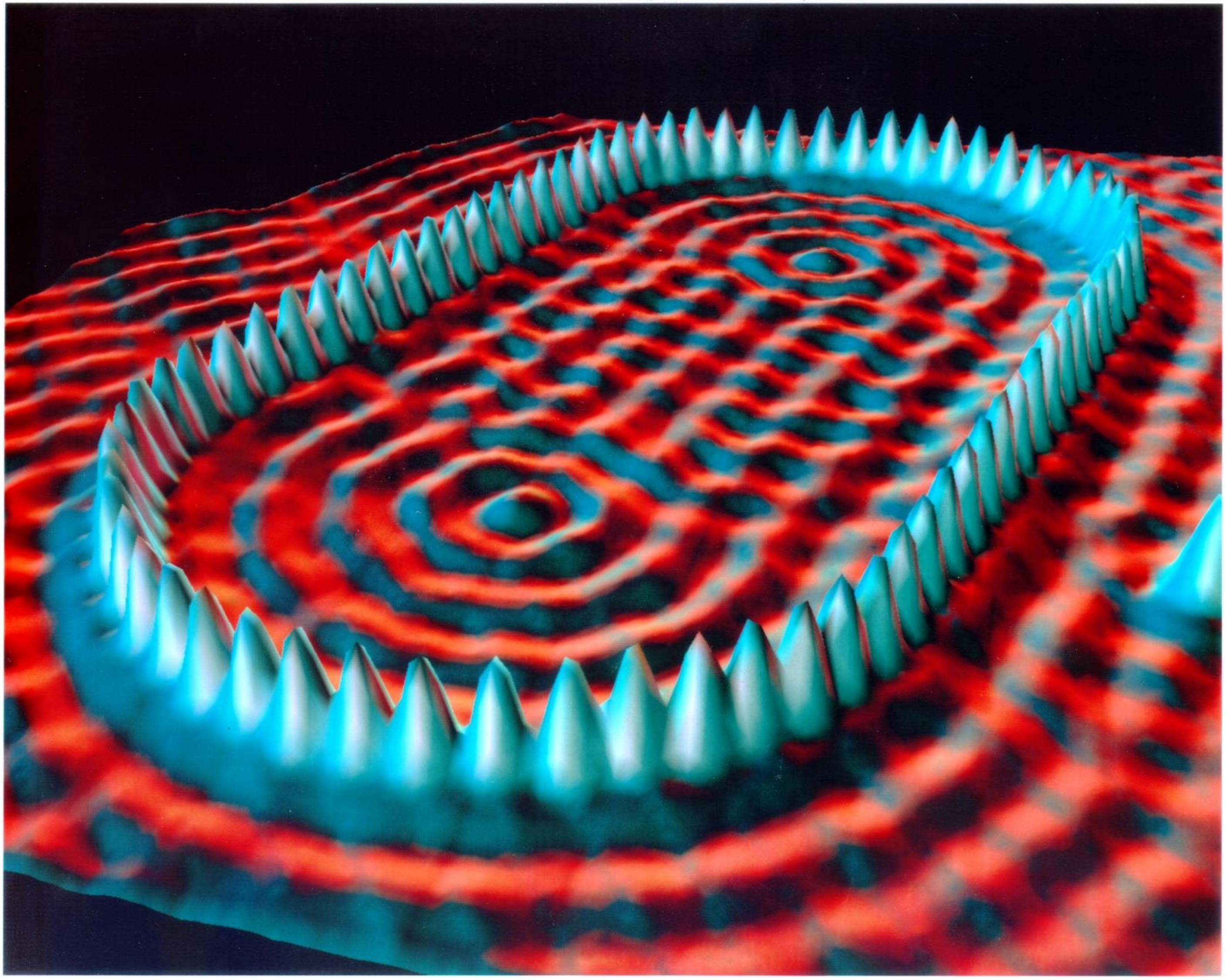
What happens if we replace gold atoms with a semiconductor ?

	III-V
GaAs	0.067 m_e
InSb	0.013 m_e

m_{eff} is reduced => L can be larger => the quantum world starts at larger sizes for semiconductors (tens of nanometers) in respect to metals (nanometers)

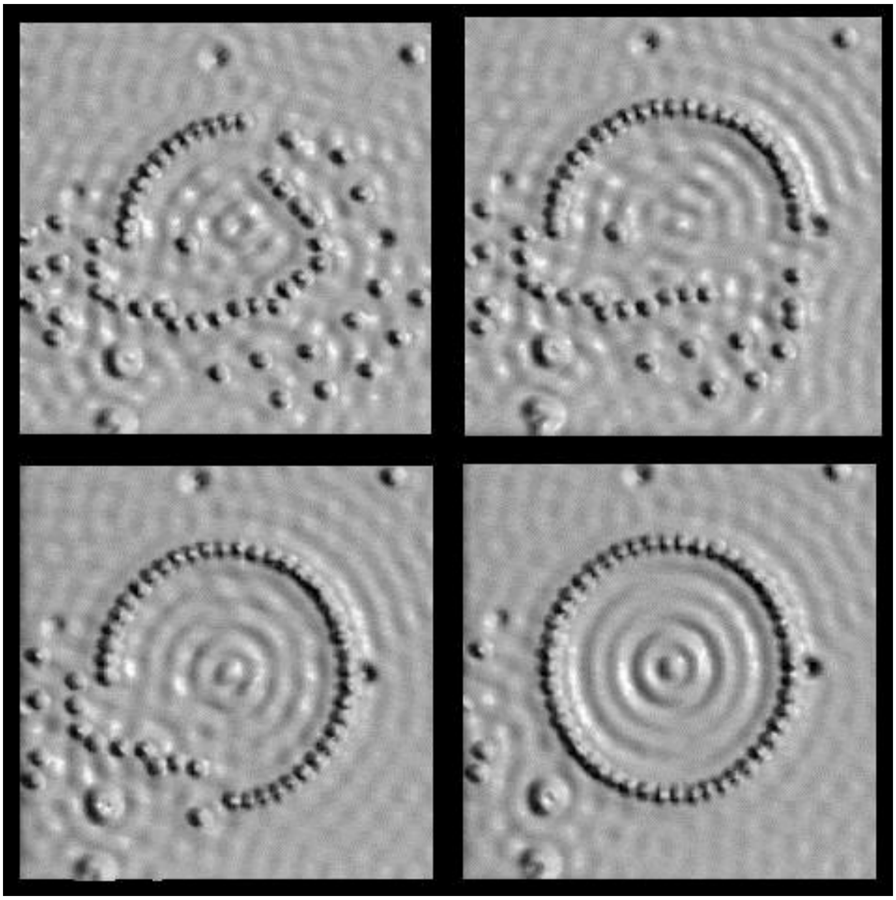
Quantum corral

Fe on Cu(111)

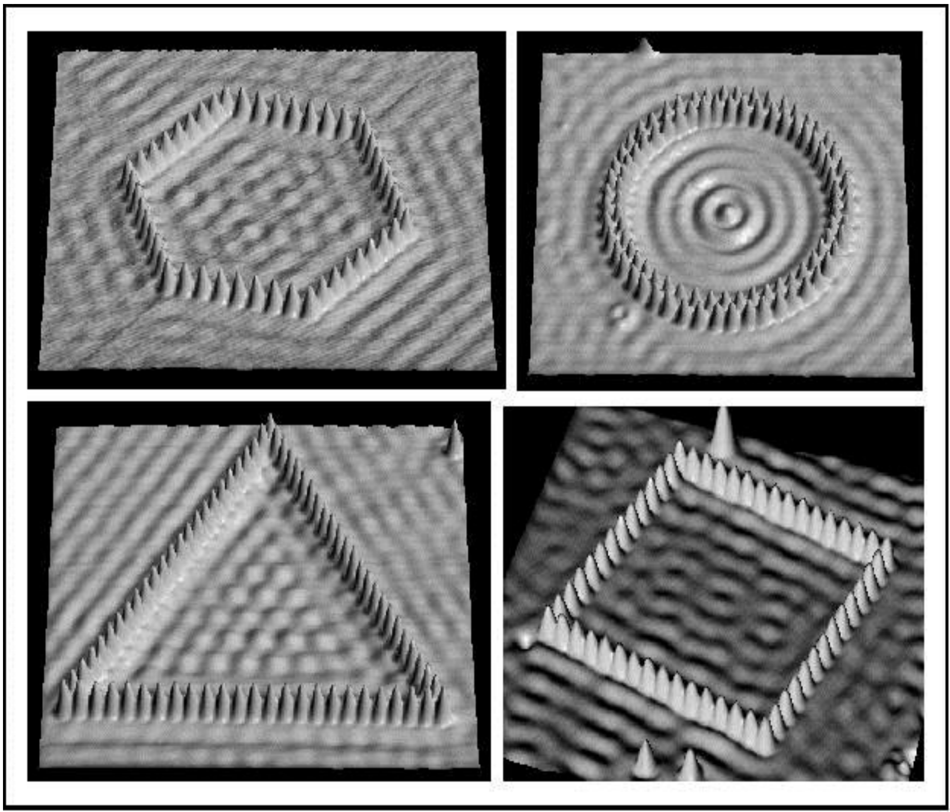


http://www.almaden.ibm.com/vis/
stm/corral.html

Quantum corral



Fe on Cu(111)

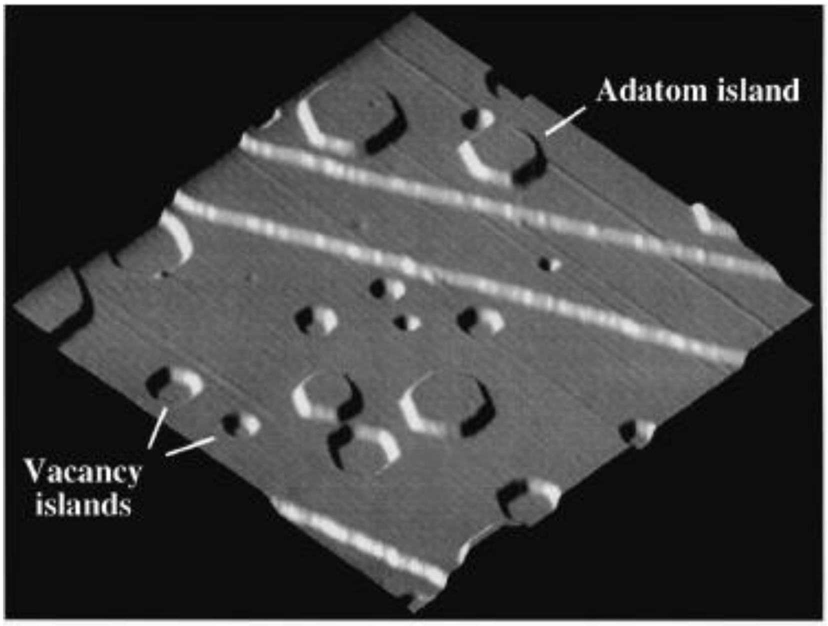


http://www.almaden.ibm.com/vis/stm/corral.html

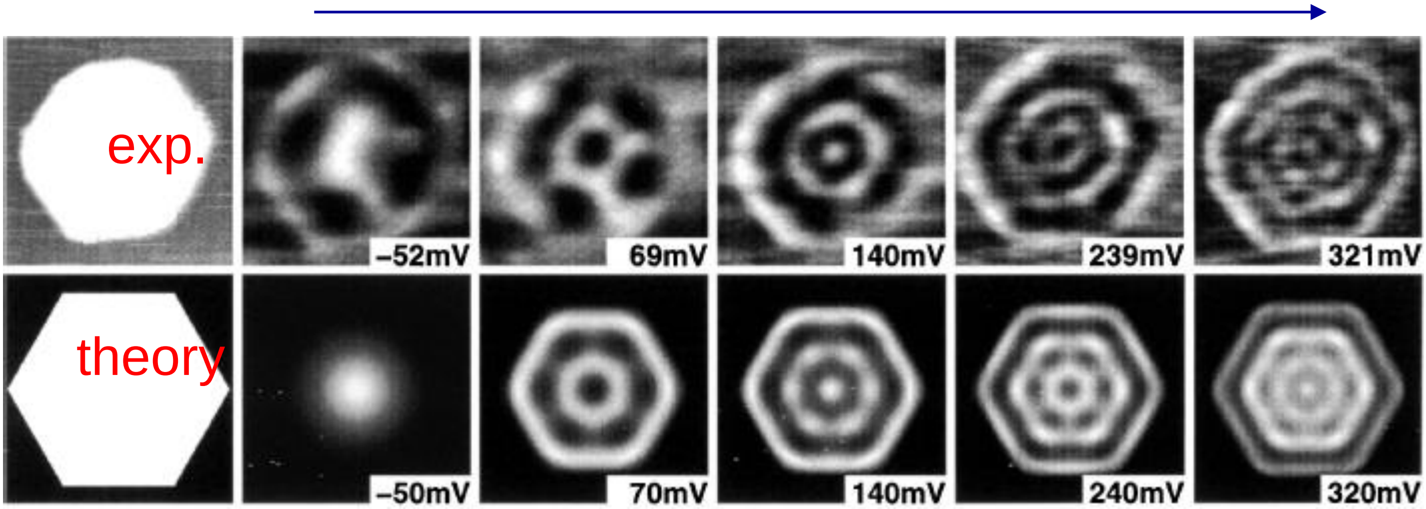
2D quantum box

Ag islands on Ag(111)

topography



dI/dV



Li et al., Phys. Rev. Lett. **80**, 3332 (1998).

Electrons in a crystal

Bulk electrons move in the weak crystalline periodic potential and thus they are described by plane waves

$$\psi(r) = u_k\, e^{i\vec{k}\vec{r}}$$

At surface the periodicity is broken in one spatial direction

Assume: a) the surface is described by an infinite energy wall
b) the wall is perpendicular to the z axis (z // crystallographic direction)

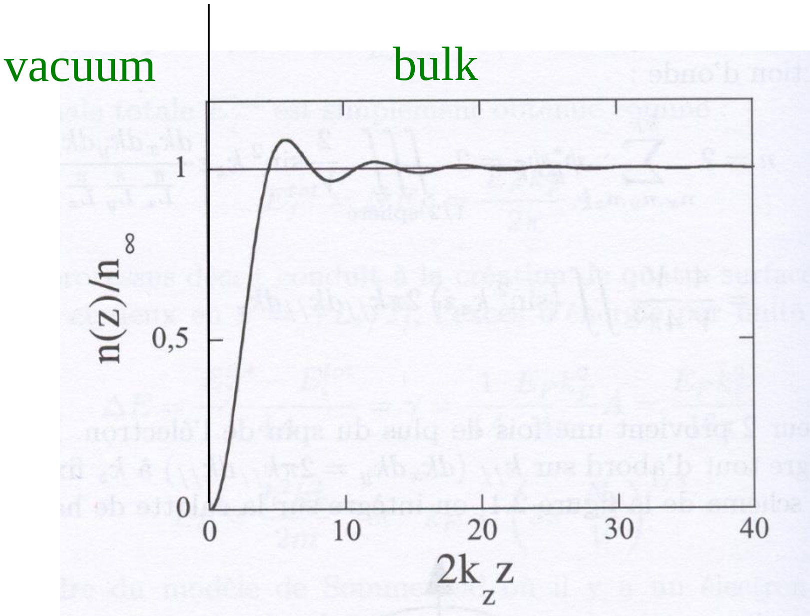
Assuming Born-von Karman periodic boundary conditions:

$$\psi(r) = \sqrt{\frac{2}{V}}\, e^{i\vec{k}_{//}\vec{r}} \sin k_z z \qquad k_z = \frac{n\pi}{L_z}$$

The electronic density is given by:

$$n = \sum_{n_x n_y n_z}^{k_F} \psi(r)\psi^*(r) = 2\iiint \frac{2}{V}\sin^2 k_z z \,\frac{dk_x dk_y dk_z}{\frac{\pi}{L_x}\,\frac{\pi}{L_y}\,\frac{\pi}{L_z}} =$$

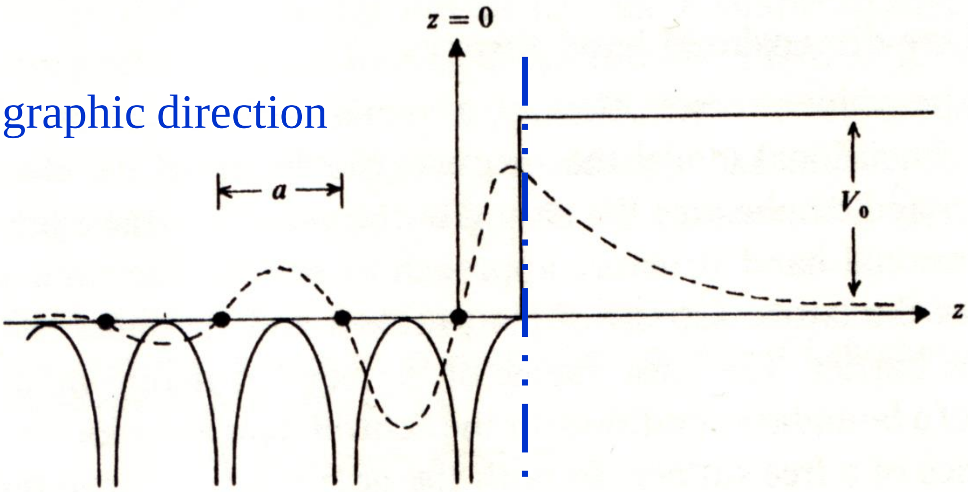
$$\frac{k_F^3}{3\pi^2}\left(1-3\,\frac{\sin(2k_F z)-(2k_F z)\cos(2k_F z)}{(2k_F z)^3}\right)$$



No electrons at surface

Surface states

z // crystallographic direction



$V(z) = -2V_g \cos(gz)$

$V(z) = V_0$

At surface the crystal periodicity is broken in one spatial direction

$$\psi(r) = e^{i\vec{k}_{//}\vec{r}}[Ae^{ikz} + Be^{i(k-g)z}]$$

Solution of the Schrodinger equations

$$\psi(r) = e^{i\vec{k}_{//}\vec{r}} e^{-iqz} \cos(\frac{g}{2}z + \delta) \qquad z < \frac{a}{2}$$

$$\psi(r) = e^{i\vec{k}_{//}\vec{r}} e^{-pz} \qquad z > \frac{a}{2}$$

$$p = \sqrt{2m(V_0 - E)/\hbar}$$

Perpendicular to the surface:

vacuum (z > a/2): evanescent wave exponentially decreasing with z

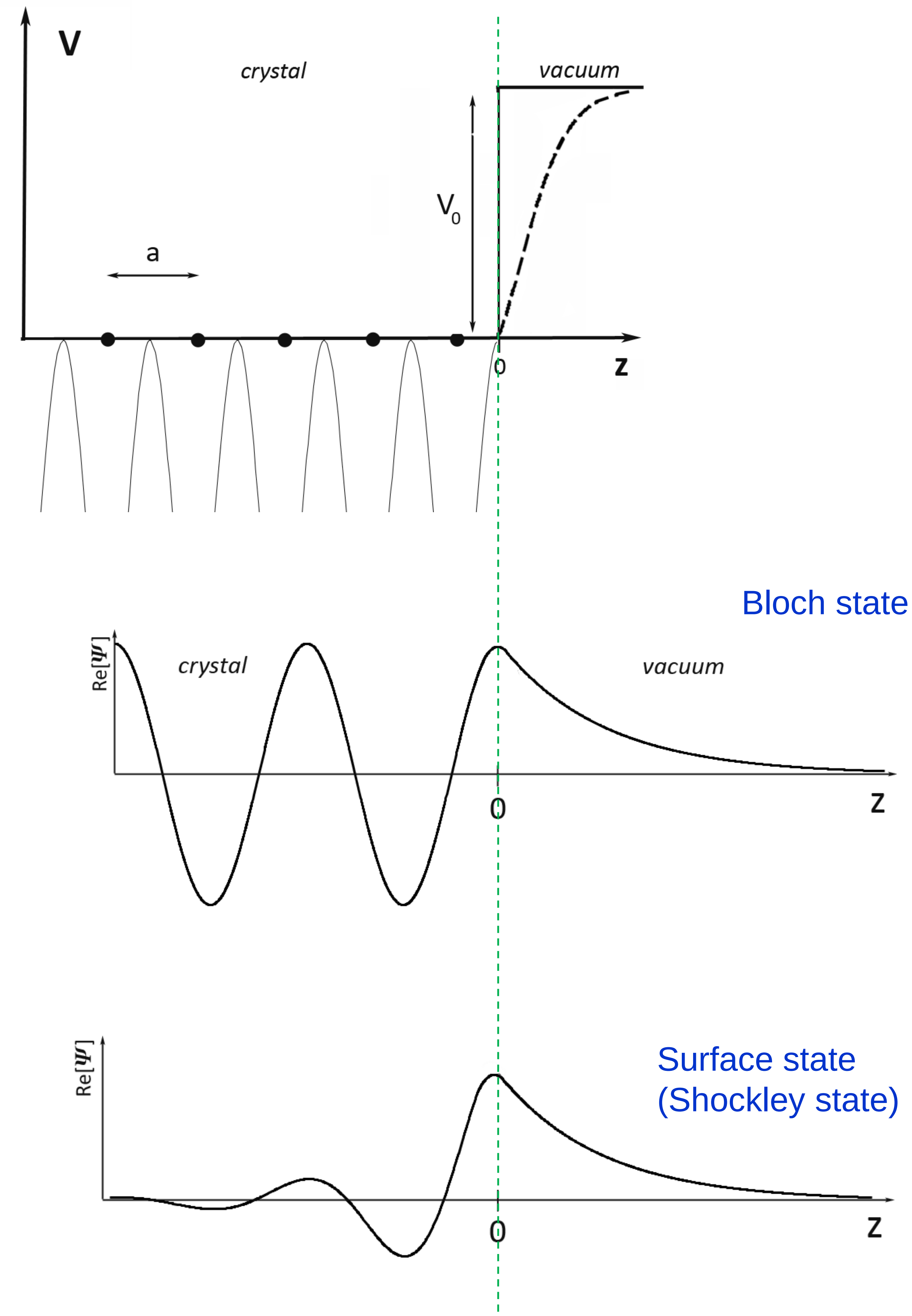
Crystal (z < a/2):

q real -> Bloch function for quasi free electrons

q imaginary -> standing wave exponentially decreasing with z

Parallel to the surface: plane wave for quasi free electrons

Ψ(r) (with q imaginary) describe states which behave like free electron parallel to the surface and which are localized at surface due to the exponential decreasing in both z directions.

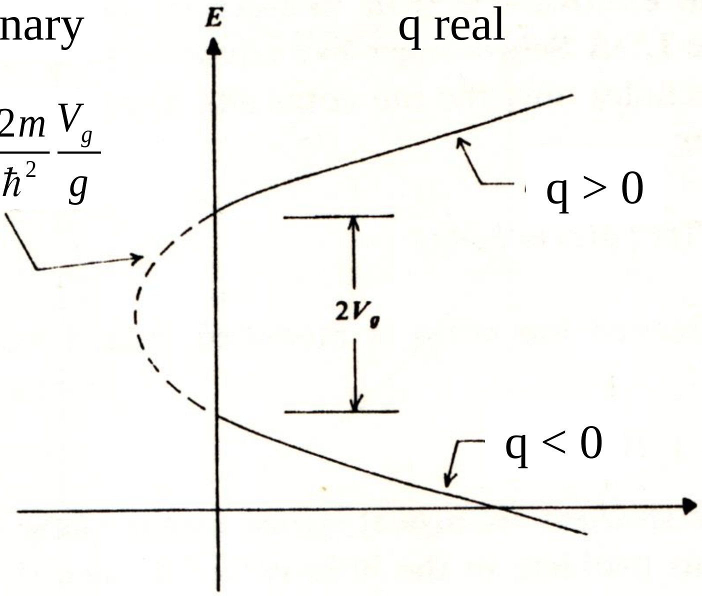

V
crystal
vacuum
V_0
a
0
z
Bloch state
Re[Ψ]
crystal
vacuum
0
z
Surface state
(Shockley state)
Re[Ψ]
0
z

Surface state energy spectrum

The case of a linear chain

$$E(q^2) = -V_0 + \frac{\hbar^2}{2m}[(\frac{g}{2})^2 + q^2] \pm \sqrt{V_g{}^2 + (\frac{\hbar^2}{2m})^2 g^2 q^2}$$

$$q = k - \frac{g}{2}$$



q imaginary

q real

$0 < |q| < \frac{2m}{\hbar^2}\frac{V_g}{g}$

q > 0

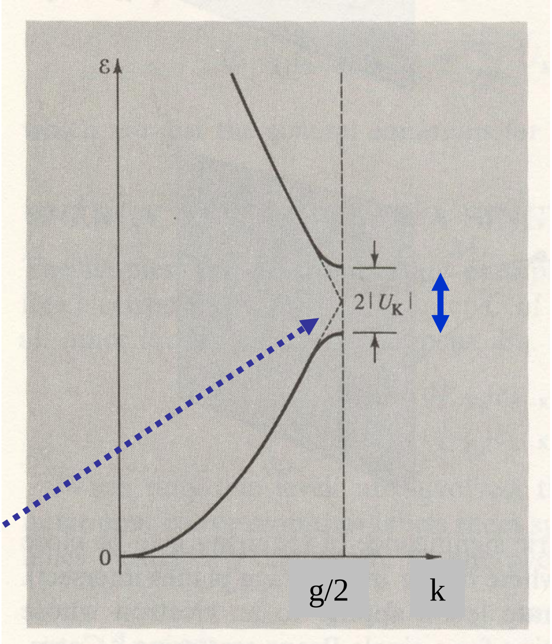
q < 0

$q^2 = (k-g/2)^2$

In an infinite chain (-∞<z<∞) imaginary values of q give exponentially increasing wave function.

$$\psi(r) = e^{i\vec{k}_{//}\vec{r}}[Ae^{ikz} + Be^{i(k-g)z}]$$

Forbidden values generating an energy gap.
This is not the case for a finite chain



The states corresponding to imaginary q are localized in a bulk energy gap and they are localized at surface (see the wave function Ψ(r))

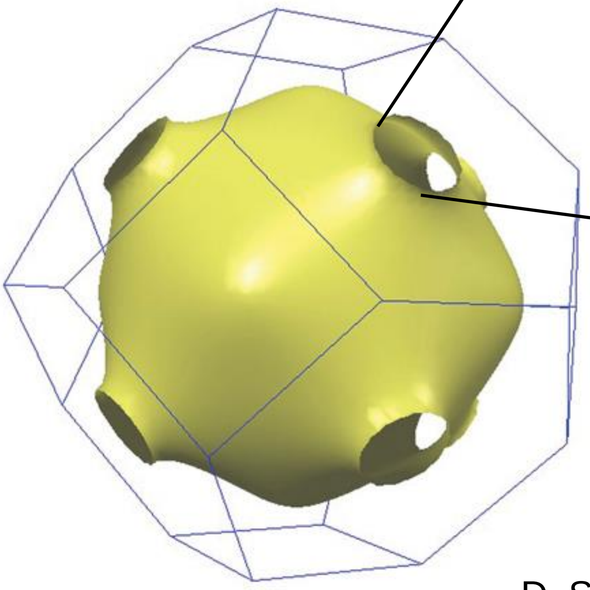
Why surface states are observed on the (111) noble metal surfaces?

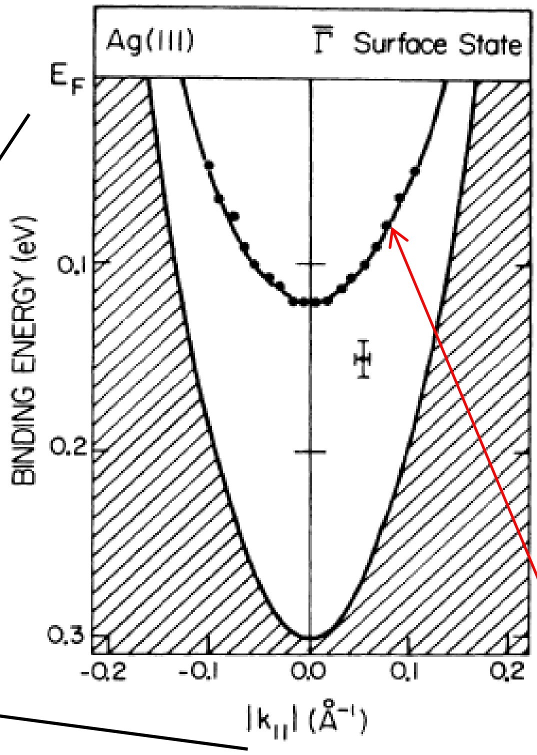
Free electron gas -> in the reciprocal space they uniformly occupy a sphere of radius $k_F = 3\pi^2$ n (n is the electron density)

No way to observe surface states since they are mixed with bulk states

Noble metals

Deviation from the ideal case of a sphere. There is a gap in the bulk states close to the normal to the (111) surface at the Fermi level





Surface states

D. Shoenberg (1962) http://www.jstor.org/stable/73177

Friedel oscillations of 2D electrons scattered by surface steps

Reflection by a step edge

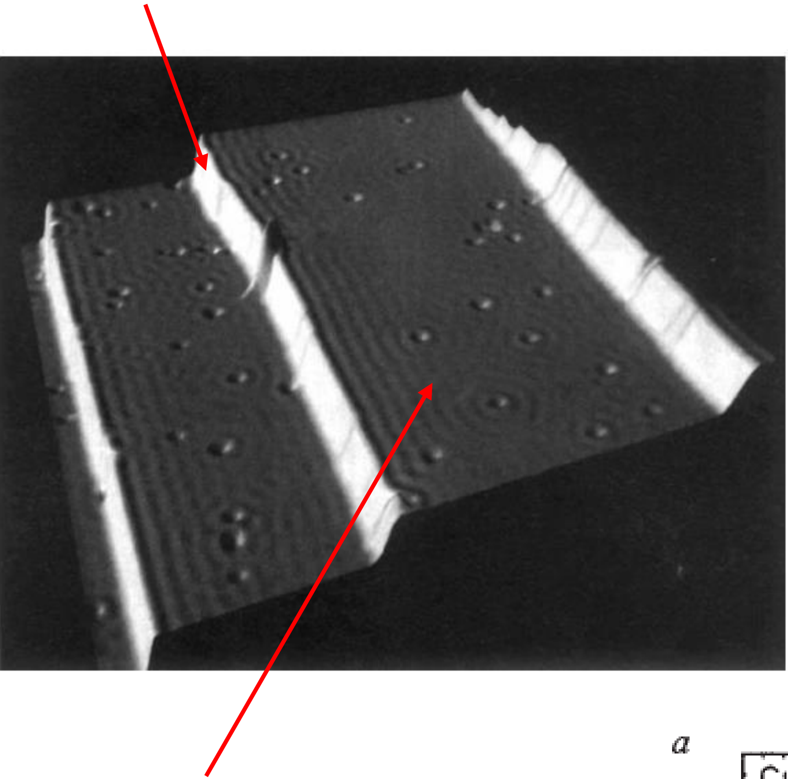
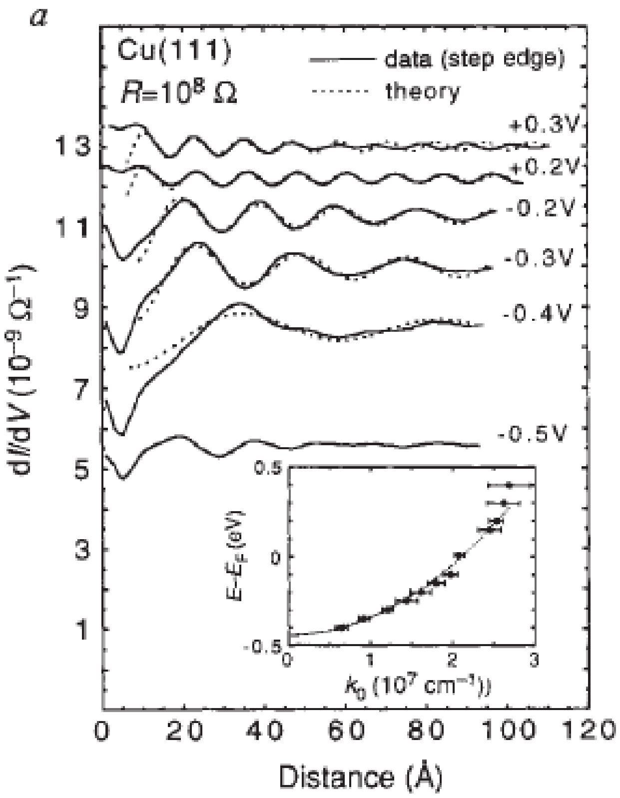


FIG. 1 Constant-current 500 Å × 500 Å image of the Cu(111) surface (V=0.1 V, I=1.0 nA). Three monatomic steps and about 50 point defects are visible. Spatial oscillations with a periodicity of ~15 Å are clearly evident. The vertical scale has been greatly exaggerated to display the spatial oscillations more clearly.

T = 4.5 K -> k_BT= 0.4 meV

Scattering by a point defect

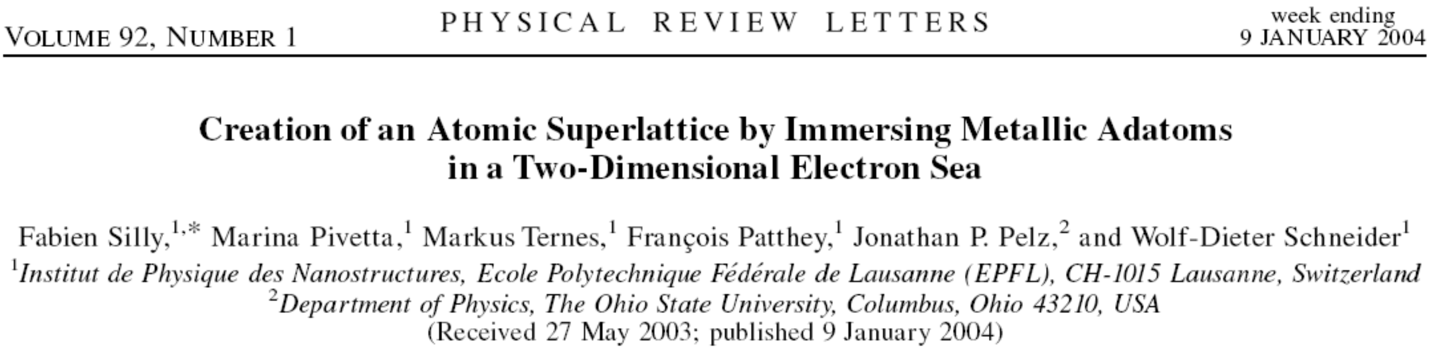


The periodicity of the oscillations gives the wave vector k -> we can measure E *vs* k

Decrease in the surface LDOS for E<-0.45 eV (bottom of the surface state band)

M. F. Crommie, Nature **363** (1993) 524.

FIG. 2 *a*, Solid lines: spatial dependence of dI/dV, measured as a function of distance (along upper terrace) from step edge at different bias voltages. Zero distance corresponds to the lower edge of the step.



VOLUME 92, NUMBER 1 PHYSICAL REVIEW LETTERS week ending 9 JANUARY 2004

Creation of an Atomic Superlattice by Immersing Metallic Adatoms in a Two-Dimensional Electron Sea

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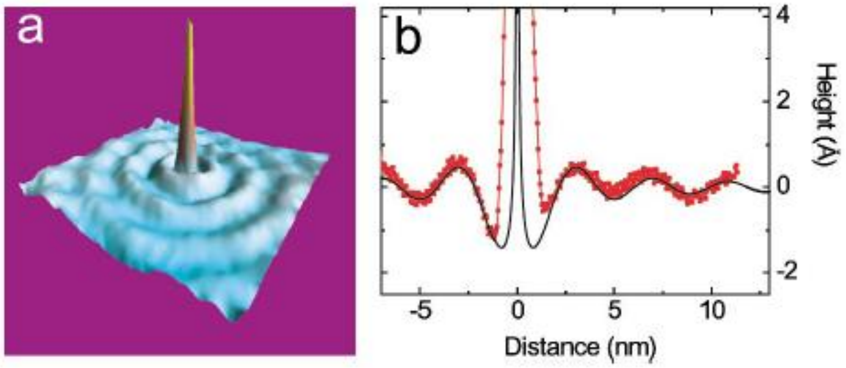
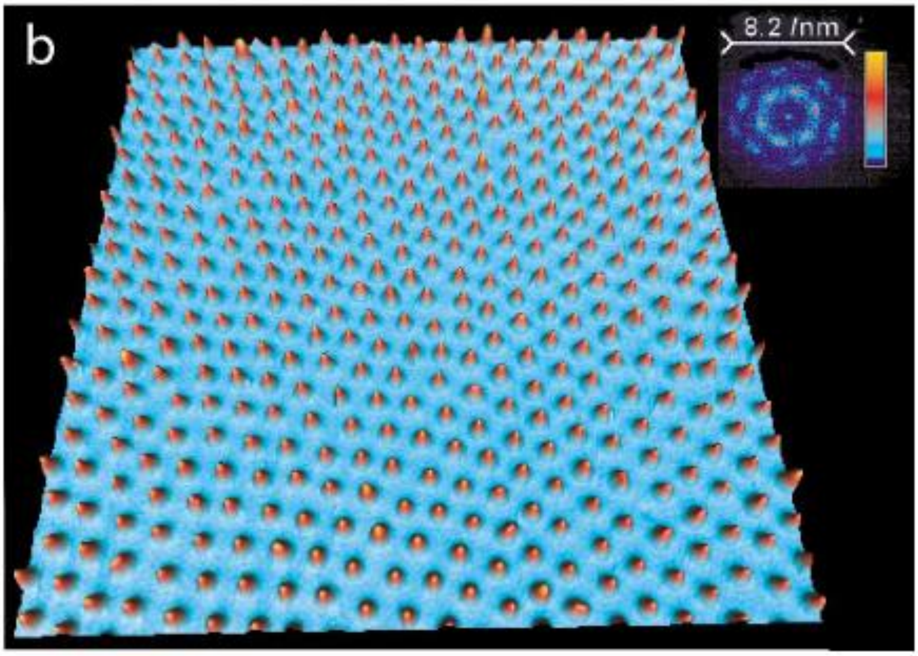
(Received 27 May 2003; published 9 January 2004)



(a) The 21 x 21 nm^2 3D STM image of a standing-wave pattern around an isolated Ce adatom on Ag(111) at 3.9 K (*Us*=3 mV, *Is*=19 pA).
(b) Dotted line: topographic profile as a function of distance from a single Ce adatom.

The interaction of surface state electrons with Ce adatoms determines the formation of a superlattice



The 3D STM image at **3.9 K** (64 x 64 nm^2; *Us* =100 mV, *Is* =10 pA): Ce adatoms (red), Ag(111) (blue).

Nanoscale Tunable Reduction of Graphene Oxide for Graphene Electronics

SCIENCE VOL 328 11 JUNE 2010 1373

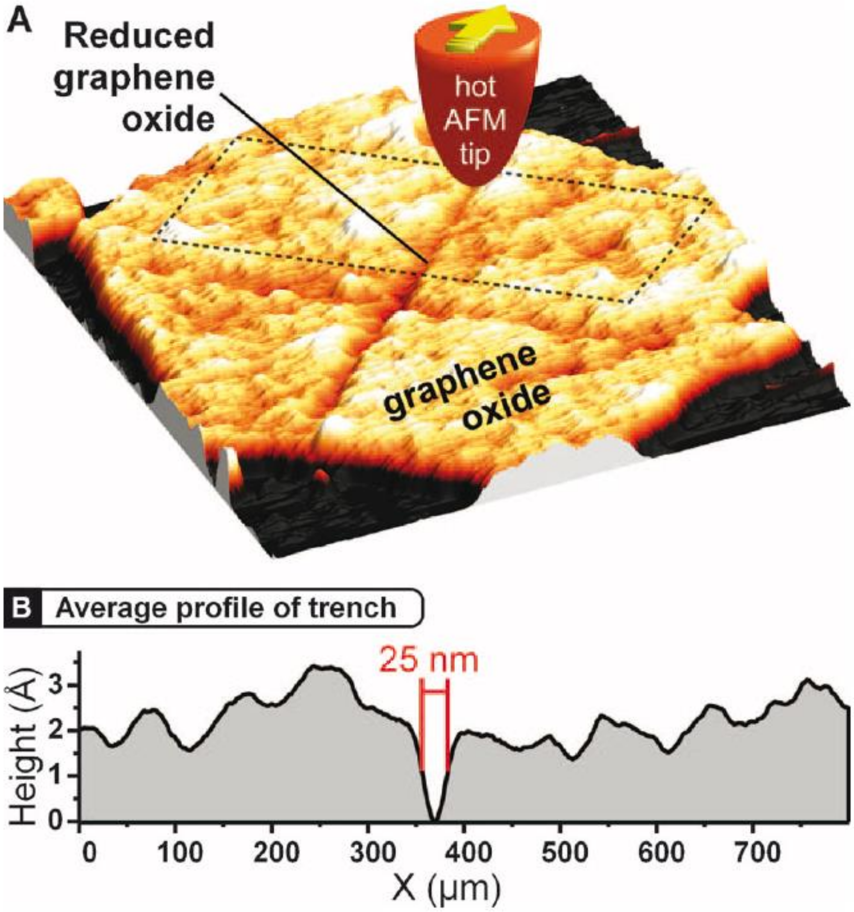
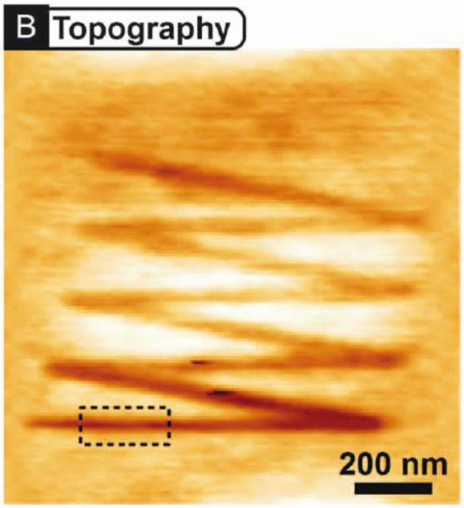


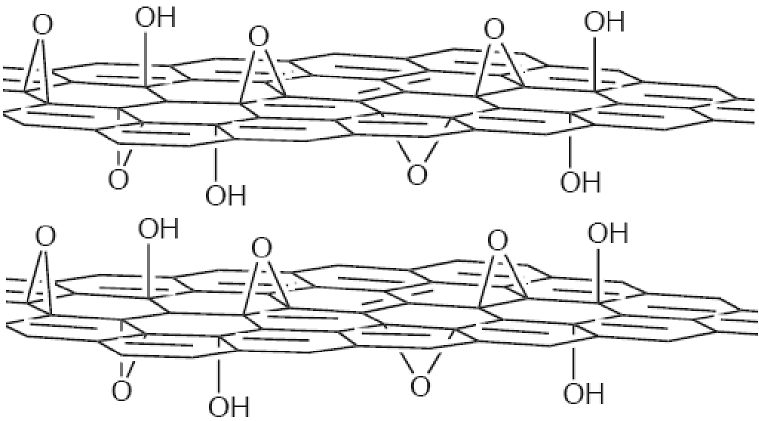
Fig. 1. Local thermal reduction of a single-layered graphene oxide flake. (**A**) Topography of a cross shape of reduced GO formed after an AFM tip heats the contact to 330°C scanned across the GO sheet at 2 μm/s. (**B**) The averaged profile of the trench outlined in (A) shows that the width (FWHM) of the line can be as narrow as 25 nm.

Cross

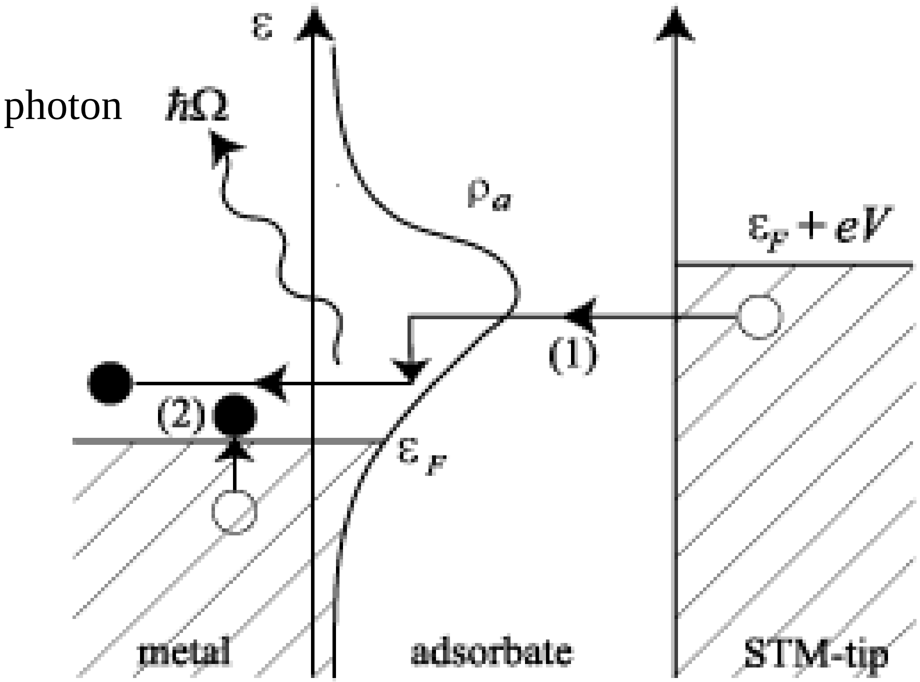
zig-zag



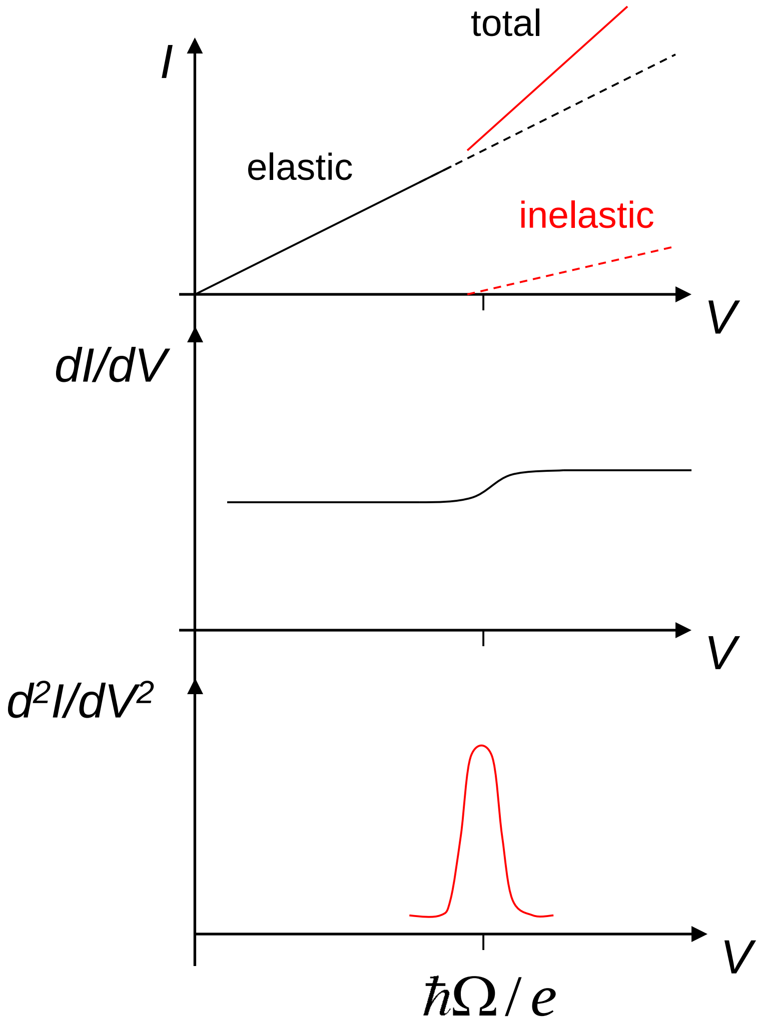
Graphene oxide (GO) schema



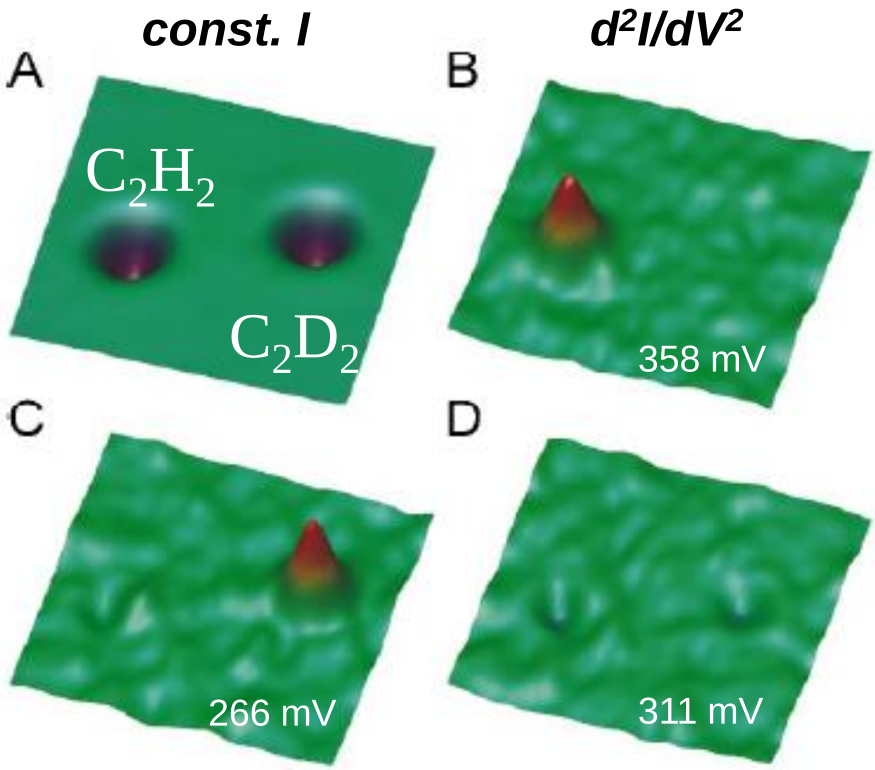
Single molecule chemistry: Inelastic tunneling spectroscopy

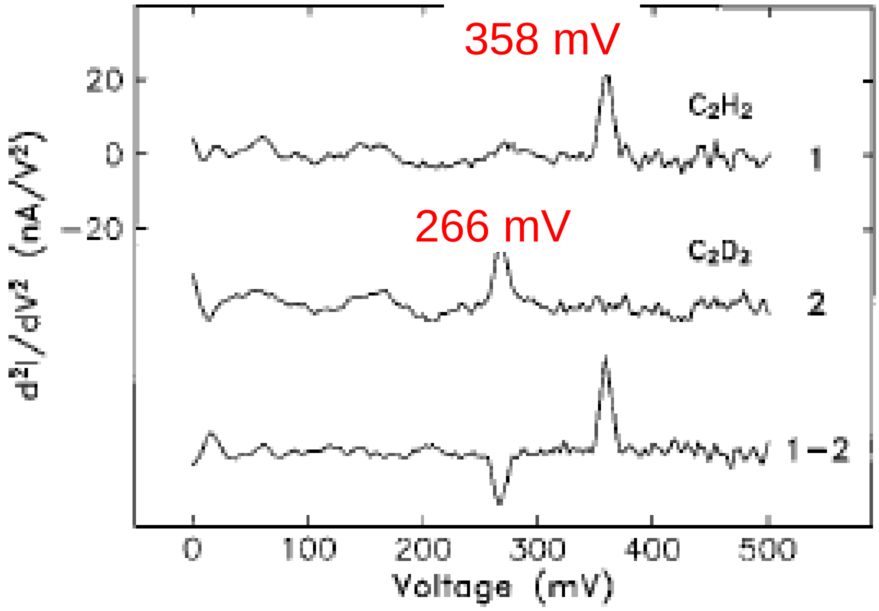


The tunneling electron excite a vibrational mode of the adsorbate and a photon is emitted (inelastic process)



Single-molecule vibrational microscopy: chemical contrast

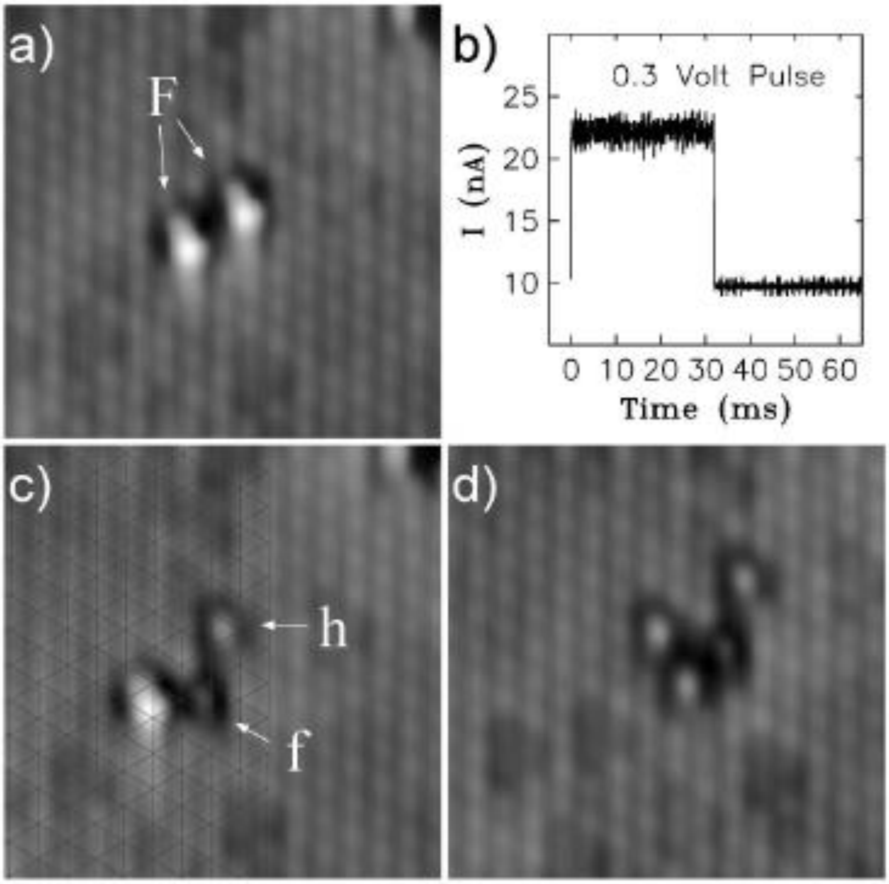




B. C. Stipe, *et al.* Phys. Rev. Lett **82**, 1724 (1999)

Single-Molecule Dissociation by Tunneling Electrons

O_2 molecules on Pt(111) surface

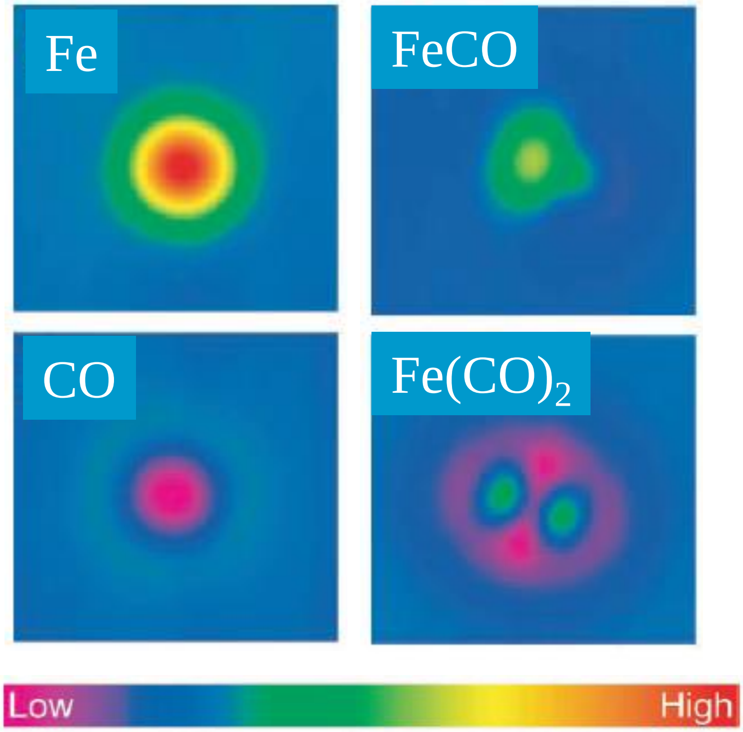


(a) STM image of two adjacent pear shaped O_2 molecules on fcc sites. (b) Current during a 0.3 V pulse over the molecule on the right showing the moment of dissociation (step at t , 30 ms). (c) After pulse image with a grid fit to the platinum lattice showing one oxygen atom on an fcc and one on an hcp site along with the unperturbed neighboring molecule on an fcc site. (d) STM image taken after a second pulse with the tip centered over the molecule showing two additional oxygen atoms on hcp sites. Raw data images scanned at 25 mV sample bias and 5 nA tunneling current.

B. C. Stipe, *et al*. Phys. Rev. Lett **78**, 4410 (1997)

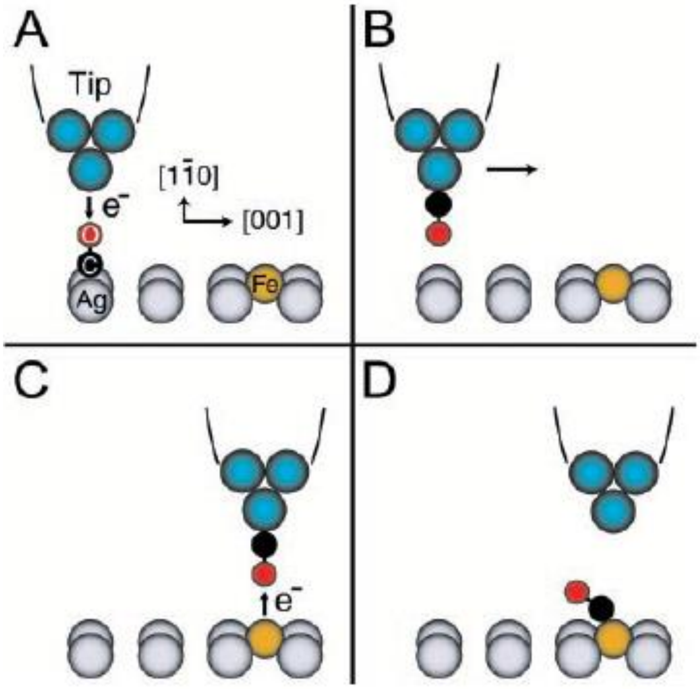
Single-Bond Formation with a Scanning Tunneling Microscope

1) Molecule recognition



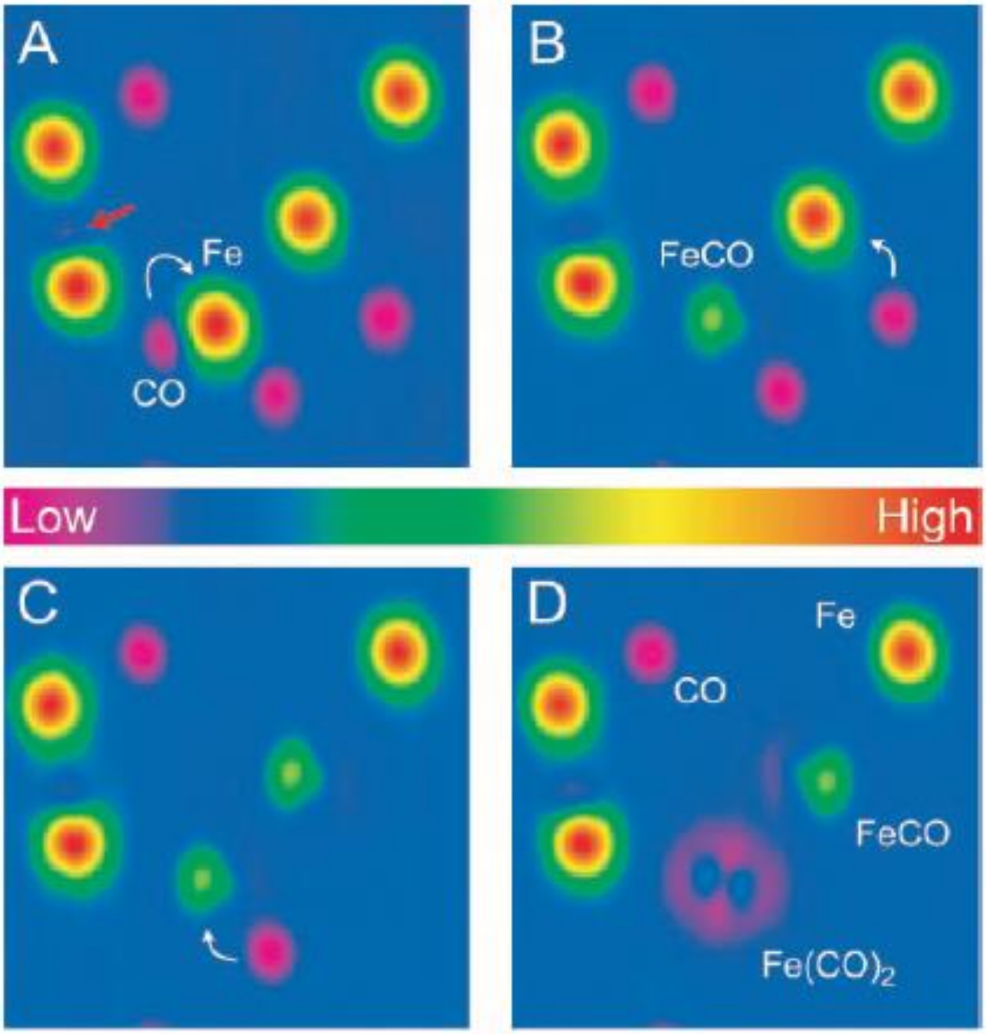
2.5 nm by 2.5 nm STM topographic images recorded at 70-mV bias and 0.1 nA

2) Molecule displacement



(**A**) The tip is positioned over a single CO molecule to induce the detachment of CO from Ag and its bonding to the tip. Because CO forms a bond predominantly through the carbon, a 180° rotation of the CO occurs in the transfer. (**B**) The tip with the attached single CO molecule is translated and positioned over an Fe atom. (**C**) The bias voltage and the flow of electrons are reversed, inducing the transfer of CO from the tip to the Fe. (**D**) A single Fe-CO bond is formed.

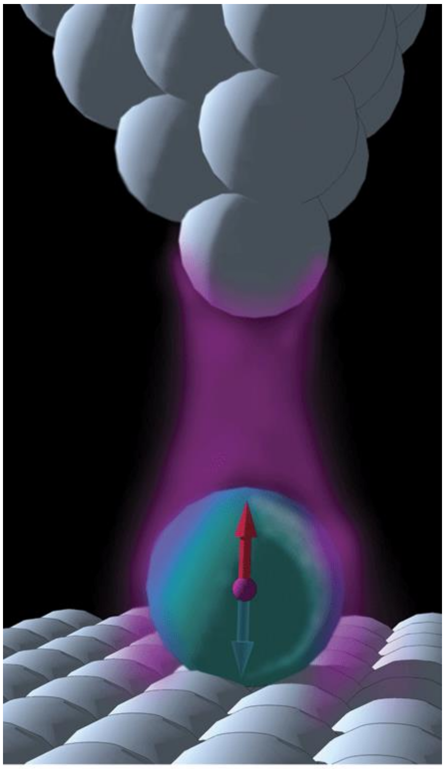
Single-Bond Formation with a Scanning Tunneling Microscope



A sequence of STM topographical images recorded at 70- mV bias, 0.1-nA tunneling current, and 13 K to show the formation of Fe-CO bond. The size of each image is 6.3 nm by 6.3 nm. Fe atoms image as protrusions and CO molecules as depressions. The white arrows indicate the pair of adsorbed species involved in each bond formation step. (**A**) Five Fe atoms and five CO molecules are adsorbed in this area of the Ag(110) surface. One CO is very close to an Fe atom (indicated by the red arrow). (**B**) A CO molecule has been manipulated and bonded to an Fe atom to form Fe(CO). (**C**) Another Fe(CO) is formed by binding CO to a second Fe atom. (**D**) An additional CO has been bonded to Fe(CO) to form Fe(CO)2. A 180° flip is observed for the remaining Fe(CO).

H. J. Lee, *et al*. Science **286**, 1719 (1999)

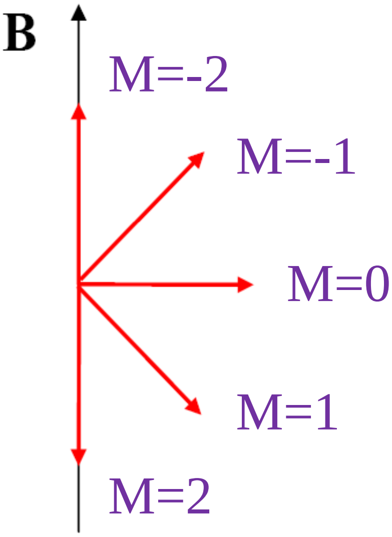
Spin-flip excitation by means of STM



M. Bode, Science **309**, 423 (2004)

J=2

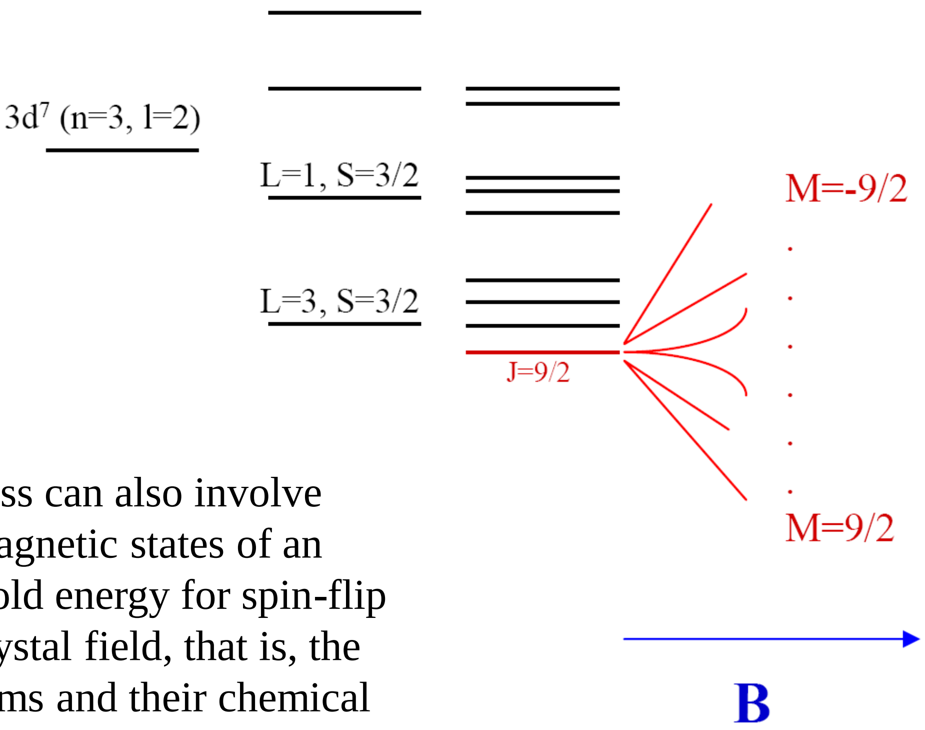
M=-2,..,2



$$E = -m_J B = -g_J M \mu_B B$$

$$\Delta E = g\,\mu_B B \Delta M = g\,\mu_B B$$

Co: $3d^7\,4s^2$

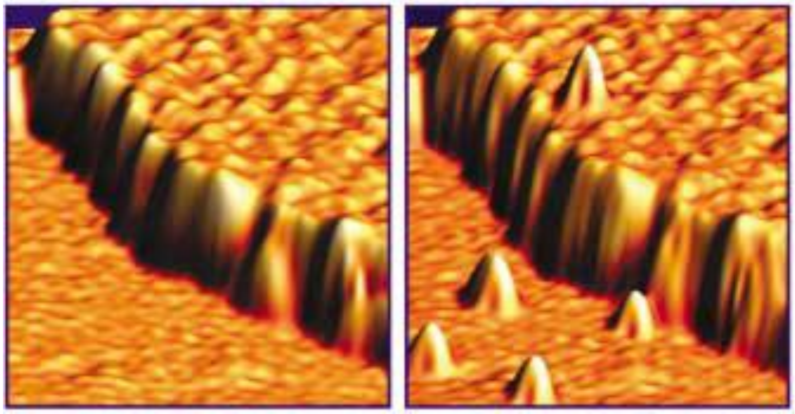


An inelastic tunneling process can also involve energy transfer to excited magnetic states of an atom (spin-flip). The threshold energy for spin-flip processes depends on the crystal field, that is, the coordination of adjacent atoms and their chemical composition, and the magnetic field.

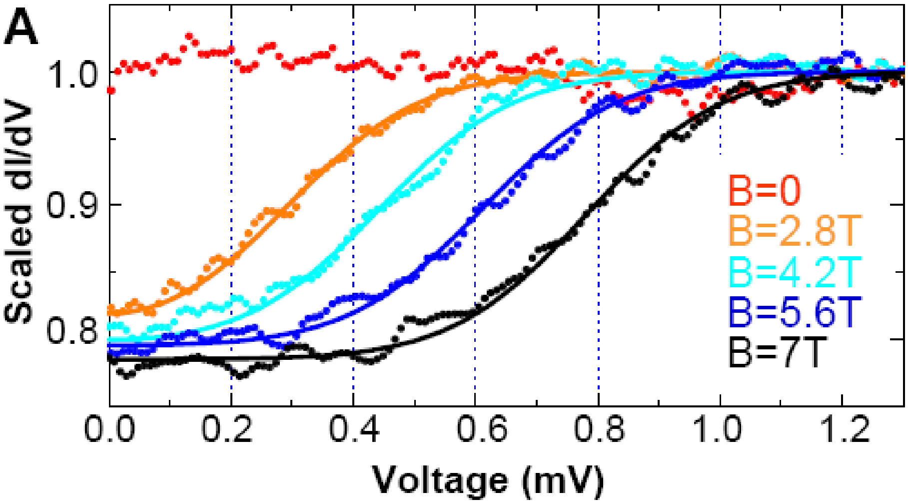
Spin-flip excitation by means of STM

T = 0.6 K

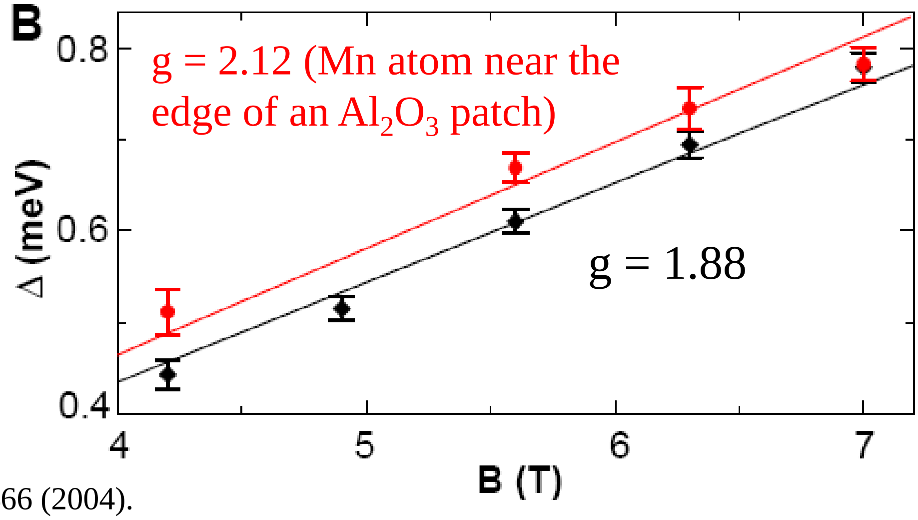
$Mn/Al_2O_3/Ni_3Al(111)$



Shift of the spin-flip conductance step with magnetic field



$$\Delta E = g\ \mu_B B$$



g = 2.12 (Mn atom near the edge of an Al_2O_3 patch)

g = 1.88

A.J. Heinrich *et al.*, Science **306**, 466 (2004).

Controlling the magnetism of a molecule through its chemical bonding

The STM is used to partially dehydrogenate the molecule

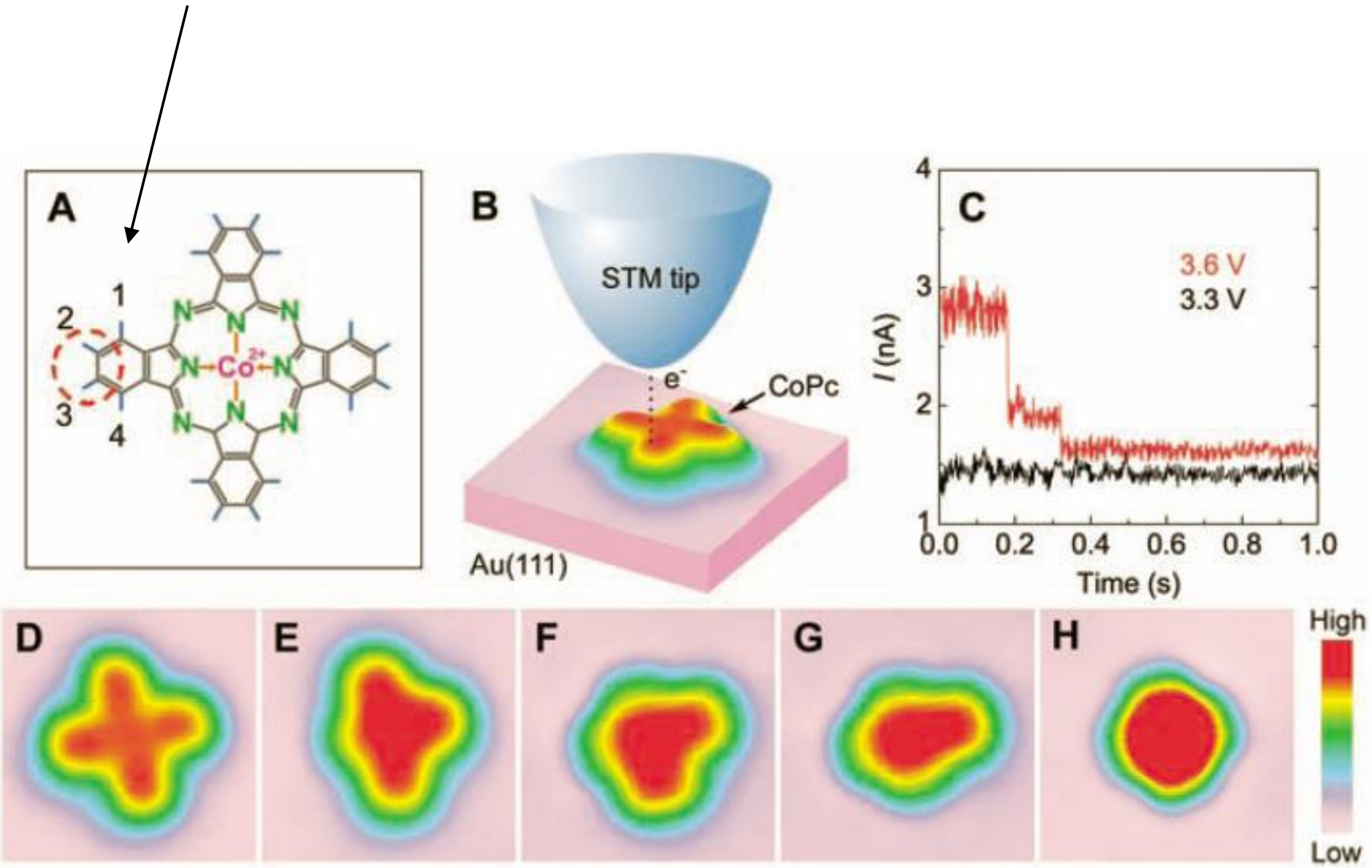
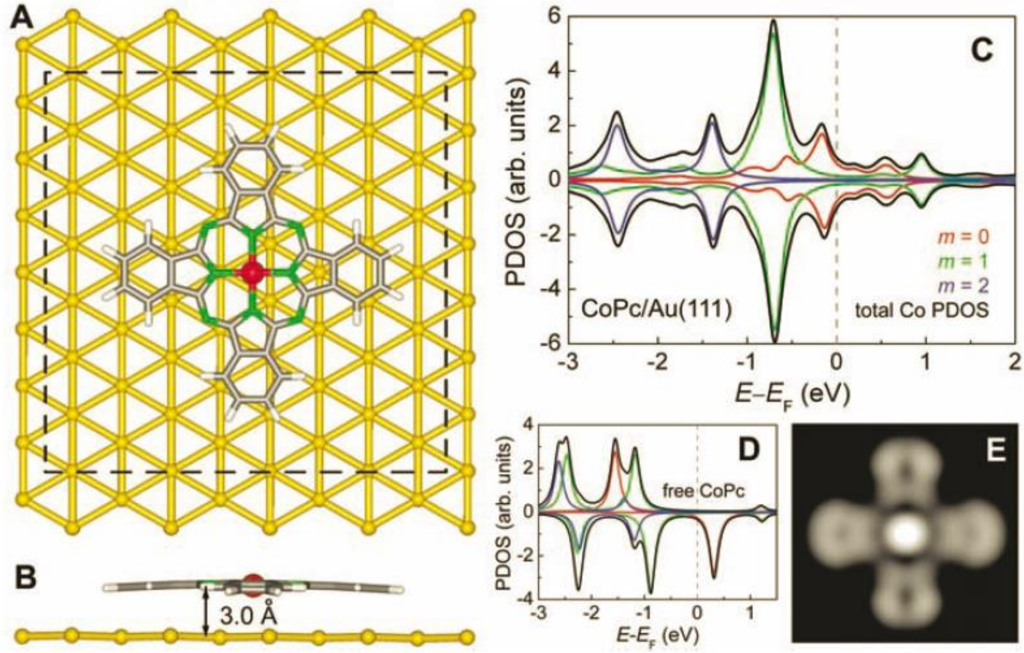


Fig. 1. STM tip–induced dehydrogenation of a single CoPc molecule. **(A)** Structural formula of the CoPc. Hydrogen atoms 2 and 3 of one lobe were dissociated in our experiments. **(B)** Diagram of the dehydrogenation induced by the STM current. **(C)** Current versus time during two different voltage pulses on the brink of one lobe. Black and red lines correspond to 3.3 V and 3.6 V, respectively. **(D to H)** STM images of a single CoPc molecule during each step of the dehydrogenation process, from (D) an intact CoPc to (H) d-CoPc. Image area, 25 Å by 25 Å. The color scale represents apparent heights, ranging from 0 Å (low) to 2.7 Å (high).

A. Zhao, *et al*. Science **309**, 1542 (2005)

Non magnetic

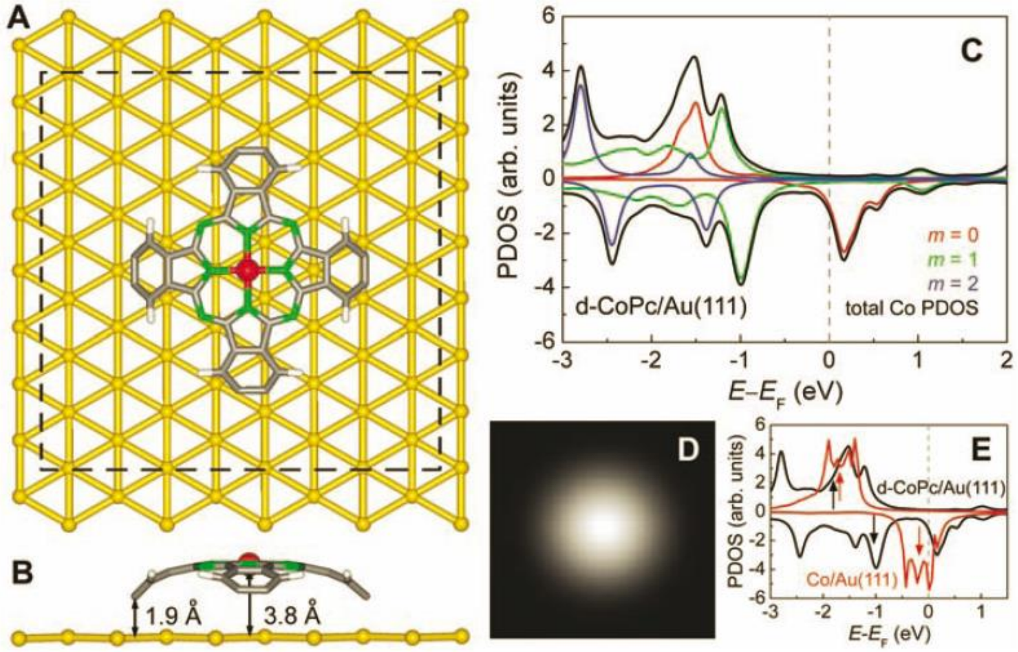


Spin up

Spin down

Fig. 3. The geometric and electronic structures of CoPc on Au(111). (**A** and **B**) Top and side views, respectively, of the optimized computational model for the CoPc/Au(111) adsorption system. The dashed line represents the unit cell, which contains 56 Au atoms per layer. (**C**) The PDOS of the Co atom in a CoPc molecule on a Au(111) surface. The black line is the total PDOS; the red, green, and blue lines represent its $m = 0$, $|m| = 1$, and $|m| = 2$ components, respectively. E, electron energy. (**D**) The PDOS of the Co atom in a free CoPc molecule is shown. (**E**) The simulated STM image of CoPc/Au(111). arb., arbitrary.

Magnetic



Spin up

Spin down

Fig. 4. The geometric and electronic structures of d-CoPc on Au(111). (**A** and **B**) Top and side views, respectively, of the optimized structure model for the d-CoPc/Au(111) adsorption system. The dashed line stands for the unit cell. (**C**) The PDOS of the Co atom in a d-CoPc molecule on a Au(111) surface. The black line is the total PDOS; the red, green, and blue lines represent its $m = 0$, $|m| = 1$, and $|m| = 2$ components, respectively. (**D**) The simulated STM image of d-CoPc/Au(111). (**E**) Comparison of the total PDOS of an isolated Co atom on a hollow site of a Au(111) surface with that of a d-CoPc molecule on Au(111). Arrows indicate the energy positions of the spin-polarized PDOS centroids of the Co atom.