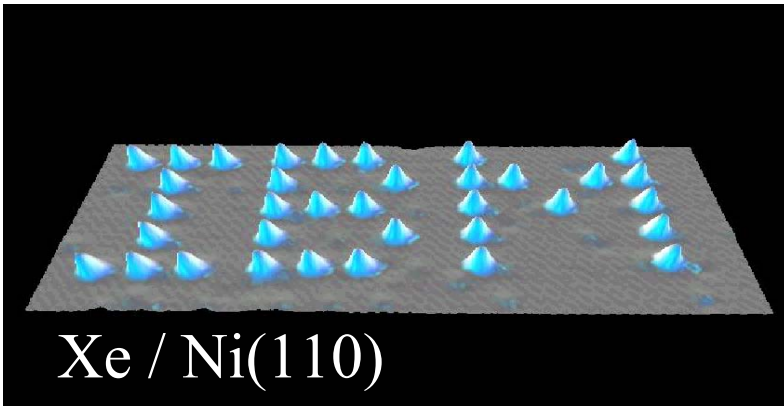


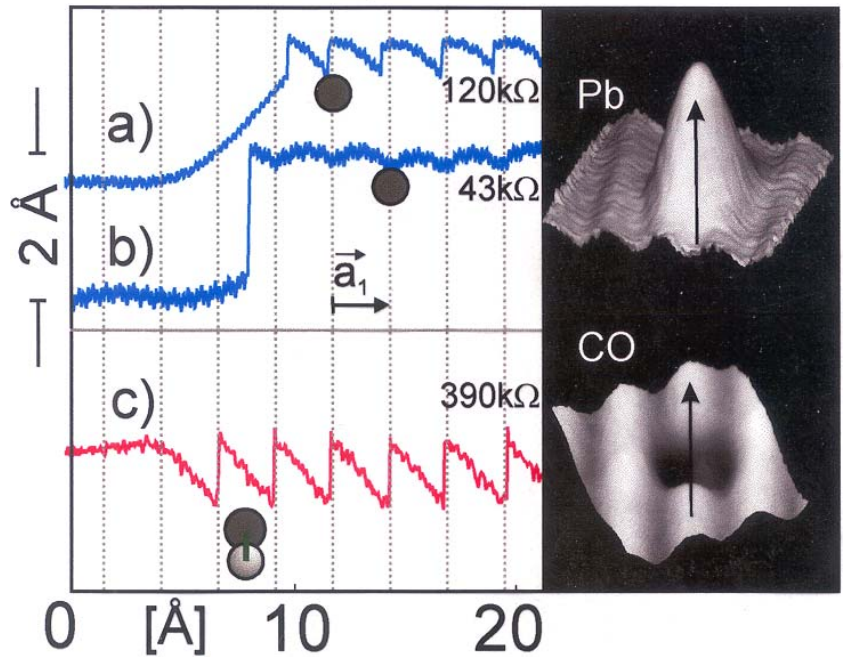
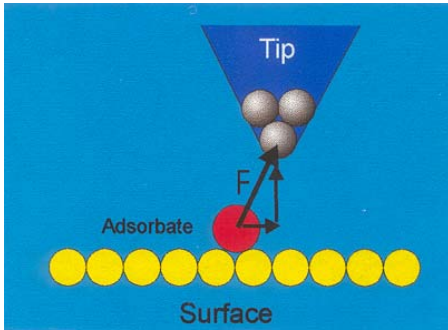
2) Atom manipulation



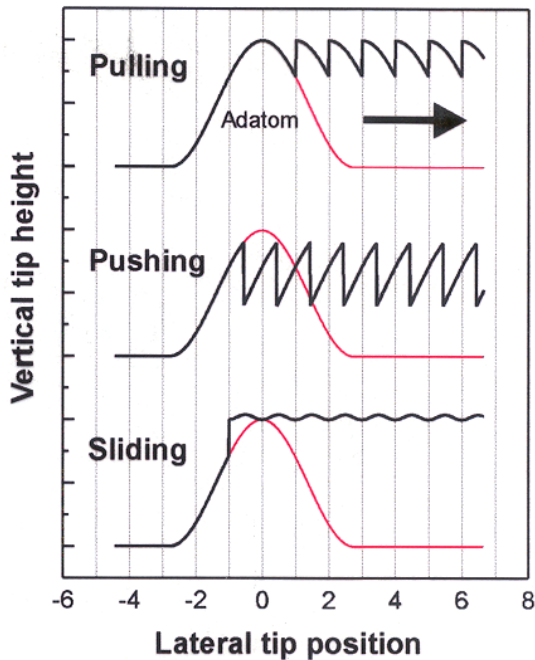
D. Eigler & E. Schweizer,
Nature **344**, 524 (1990)

Model:

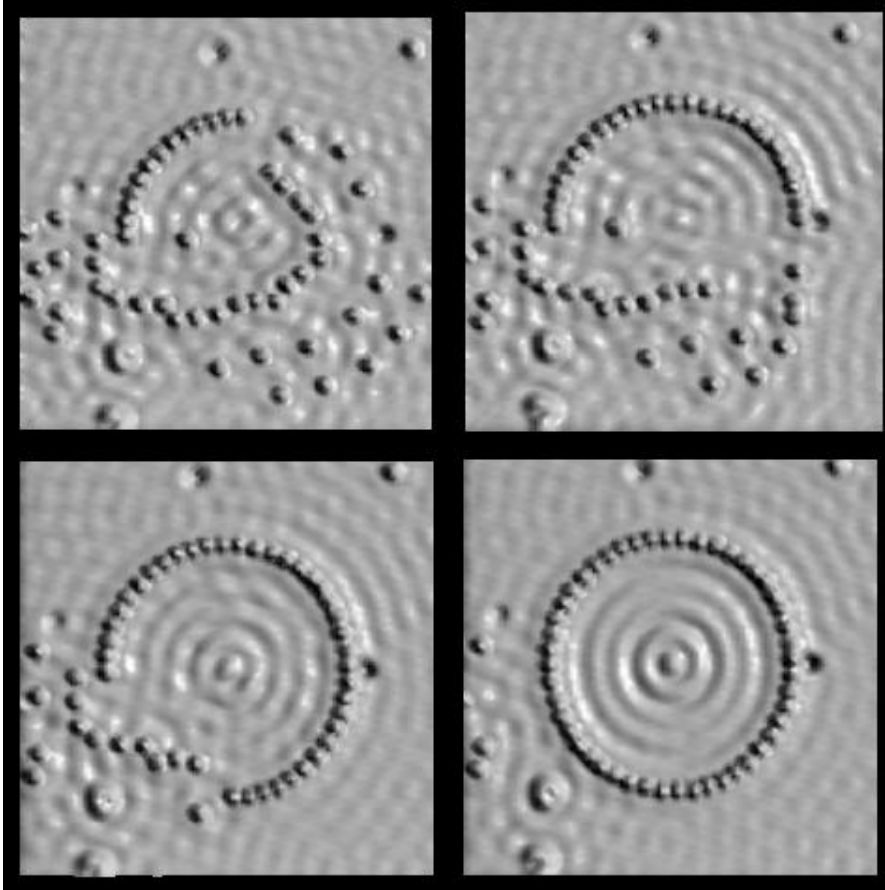
Experiment:



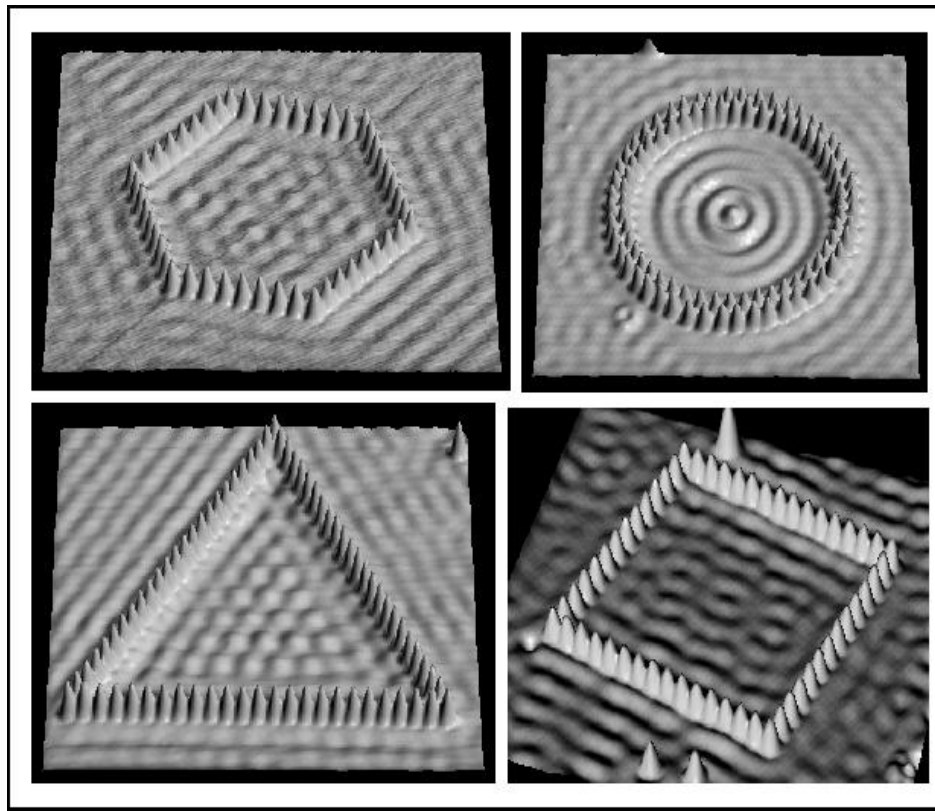
First the tip is approached close to the adsorbate by reducing the tunneling resistance and then, at constant tunneling current, moves parallel to the surface, with the atom following the tip. The steps in the tip height clearly indicate a discontinuous movement of the atom, meaning the atom is jumping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



Quantum corral



Fe on Cu(111)



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

3) STM spectroscopy (STS)

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

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)

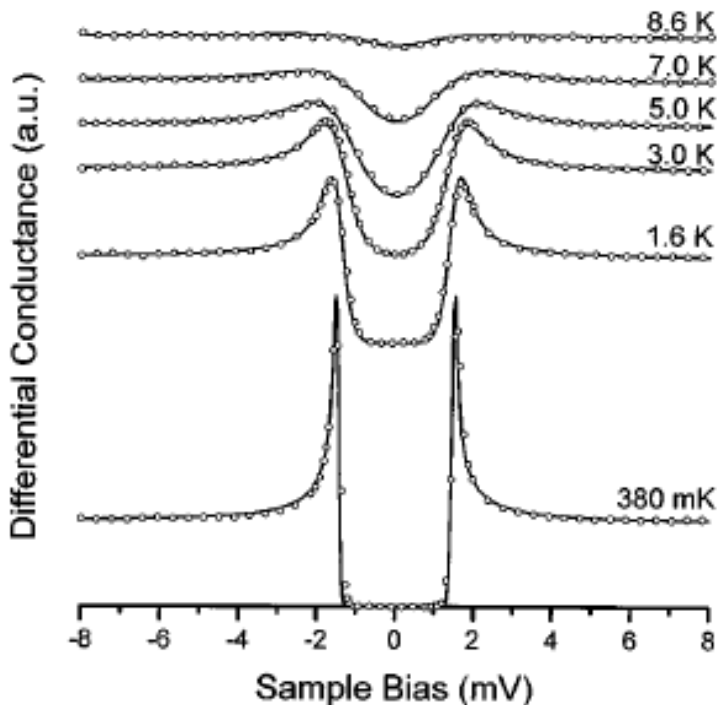
For example: Niobium tip on Au surface

Superconducting LDOS

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

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

$$\rho_S = 0 \quad |V| < \Delta$$



— BCS DOS fit
with $\Delta_{\text{Nb}} = 1.47$ meV

Nb is superconducting at temperature < 10 K

Electrons in a crystal

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

$$\psi(\mathbf{r}) = u_{\mathbf{k}} e^{i\vec{k}\vec{r}}$$

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)

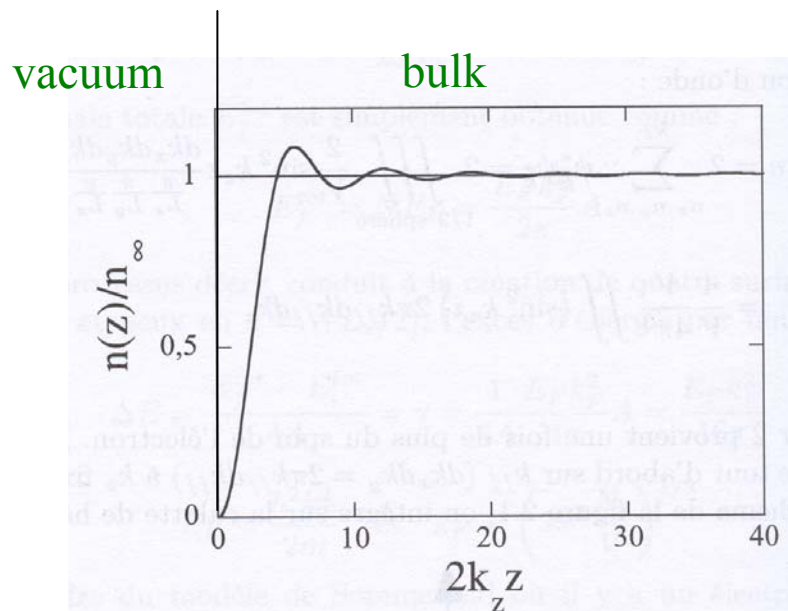
Assuming Born-von Karman periodic boundary conditions, the electrons are described by:

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

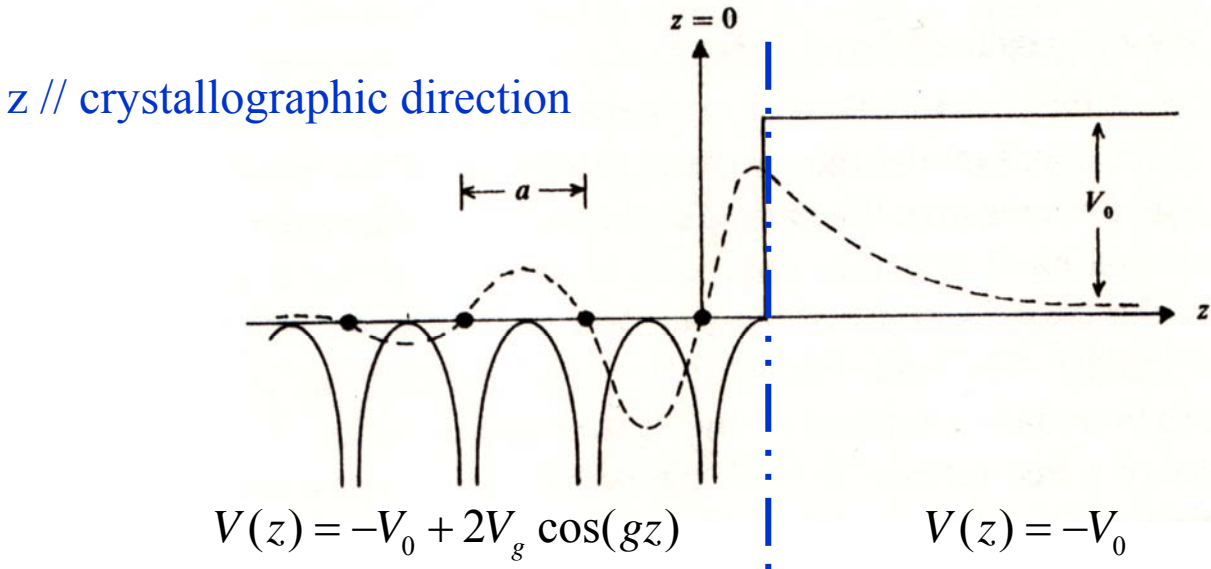
The electronic density is given by:

$$n = \sum_{n_x n_y n_z}^{k_F} \psi(\mathbf{r}) \psi^*(\mathbf{r}) = 2 \iiint \frac{2}{V} \sin^2 k_z z \frac{dk_x}{\pi} \frac{dk_y}{\pi} \frac{dk_z}{\pi} = \frac{k_F^3}{3\pi^2} \left(1 - 3 \frac{\sin(2k_F z) - (2k_F z) \cos(2k_F z)}{(2k_F z)^3} \right)$$

No electrons at surface



Surface states



At surface the crystal periodicity is broken in one spatial direction

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

Solution of the Schrodinger equations

$$\psi(\mathbf{r}) = e^{i\vec{k}_{\parallel}\vec{r}} e^{-iqz} \cos\left(\frac{g}{2}z + \delta\right) \quad z < \frac{a}{2}$$

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

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

q real \rightarrow usual Bloch function for quasi free electrons

q imaginary \rightarrow Direction perpendicular to the surface

In vacuum: evanescent wave exponentially decreasing with z

In crystal: standing wave exponentially decreasing with z

Direction parallel to the surface: plane wave for quasi free electrons

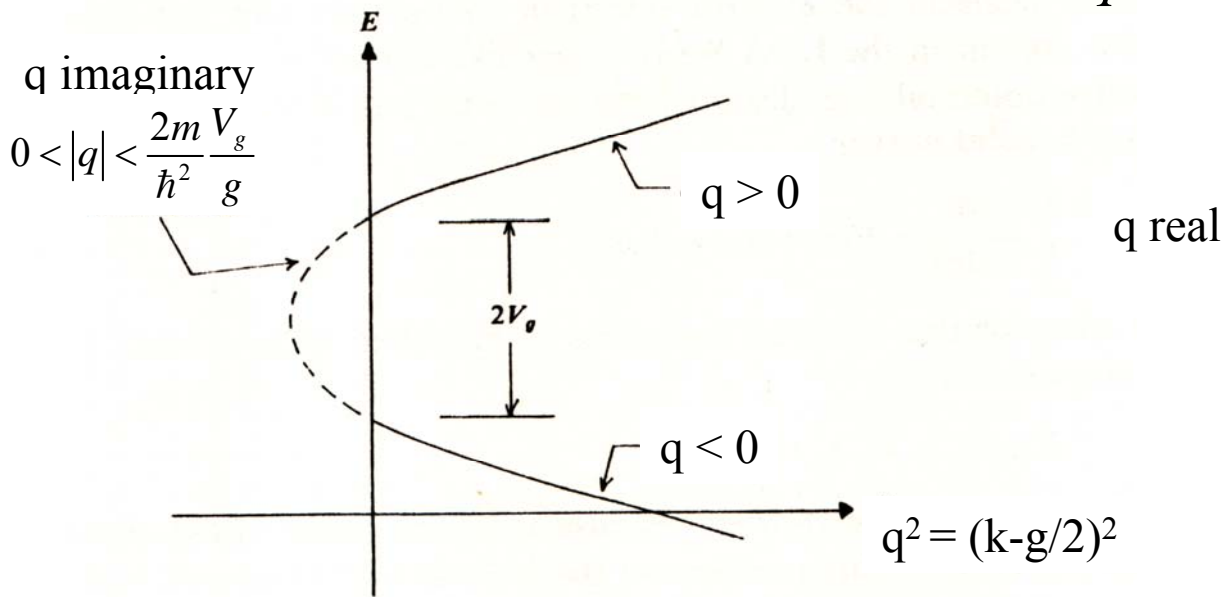
$\Psi(\mathbf{r})$ (with q imaginary) describe states which behave like free electron parallel to the surface and which are localized at surface due to the exponential decreasing in both z directions.

Surface state energy spectrum

The case of a linear chain

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

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

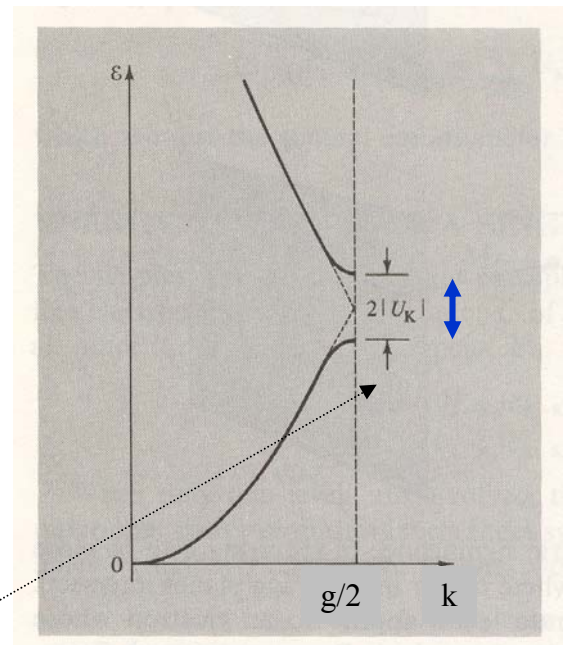


In an infinite chain imaginary values of q give exponentially increasing wave function.

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

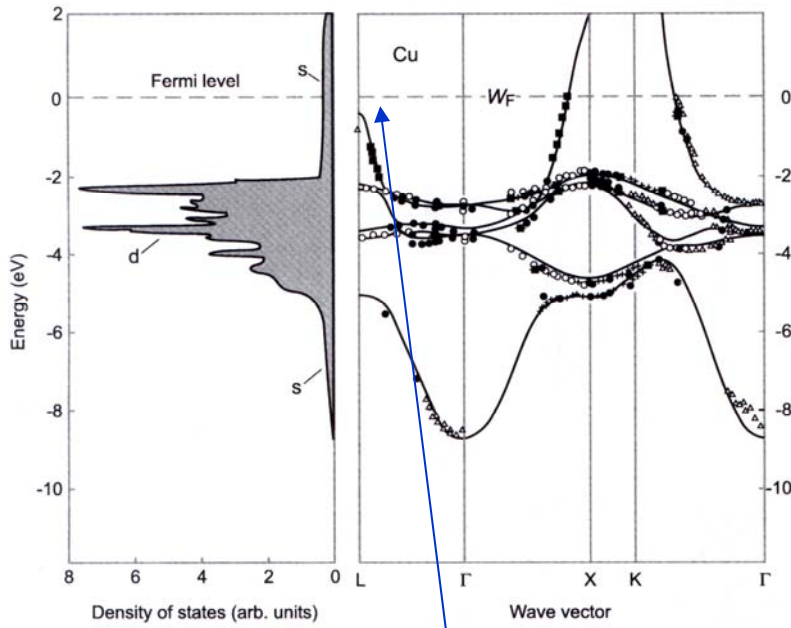
Forbidden values generating an energy gap.

This is not the case for a finite chain

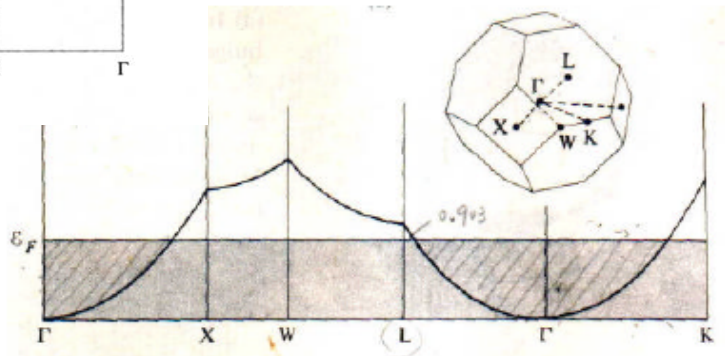


The states corresponding to imaginary q are localized in a bulk energy gap and they are localized at surface (see the wave function $\Psi(r)$)

Surface states in metals

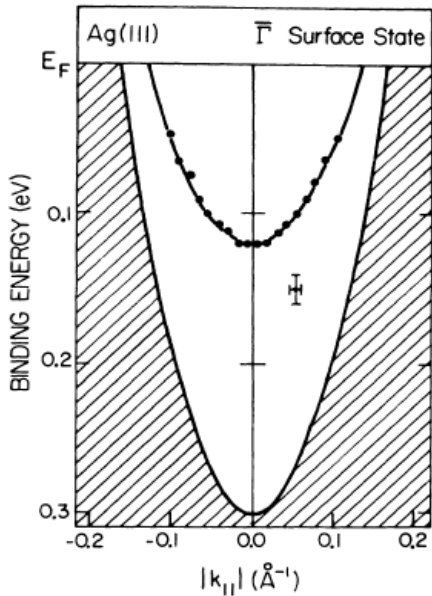
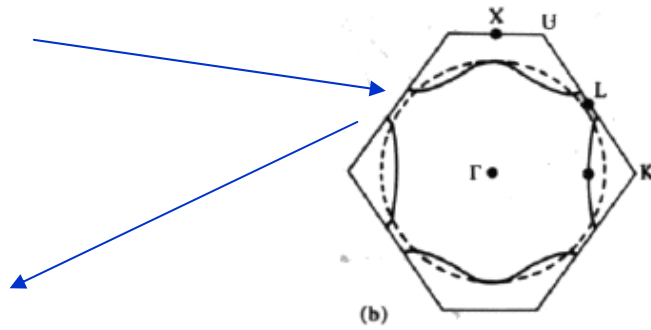


Fermi surface of copper



Gap in the bulk density of states at the Brillouin zone (due to the interaction with the crystal field) where the surface state can exist

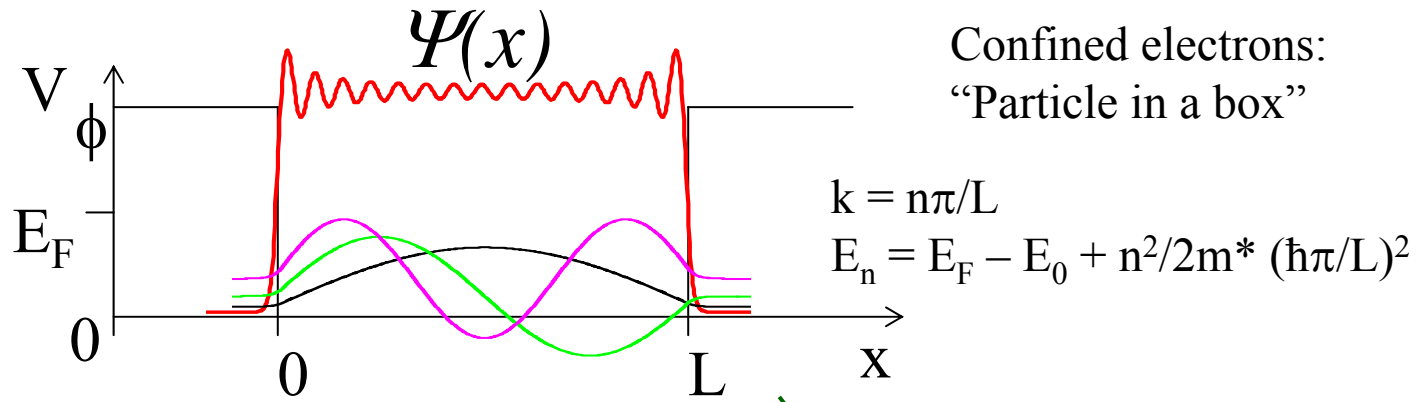
● Fermi surface (a cross section)



Material	Binding-energy E_0	effective mass m^*
Cu(111)	-0.390 eV	0.4
Ag(111)	-0.065 eV	0.4
Au(111)	-0.41 eV	0.3

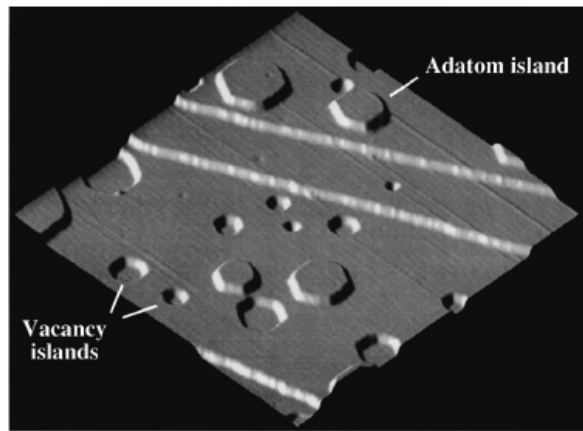
Surface-confined electrons constitute a 2D electron gas

STS on metal surfaces



$$\rho(x) = \Psi(x)\Psi(x)^*$$

topography

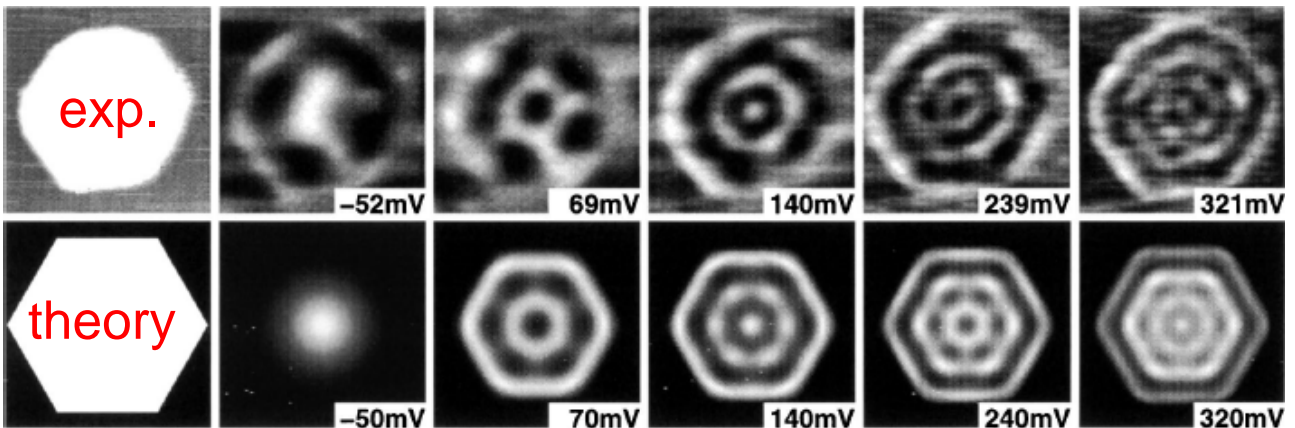


Ag/Ag(111)

$$\rho_s(E, \vec{r}_0) = \frac{1}{V} \sum_{E_s = E_F - eV}^{E_F} |\psi_s(\vec{r}_0)|^2 \delta(E - E_s)$$

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

dI/dV



Friedel oscillations of 2D electrons scattered by surface steps

Reflection by a step edge

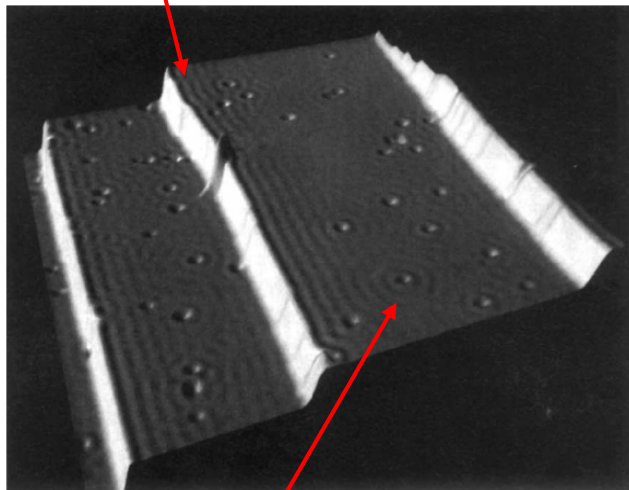


FIG. 1 Constant-current $500 \text{ \AA} \times 500 \text{ \AA}$ image of the Cu(111) surface ($V=0.1 \text{ V}$, $I=1.0 \text{ nA}$). Three monatomic steps and about 50 point defects are visible. Spatial oscillations with a periodicity of $\sim 15 \text{ \AA}$ are clearly evident. The vertical scale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

Scattering by a point defect

$$T = 4.5 \text{ K} \rightarrow k_B T = 0.4 \text{ meV}$$

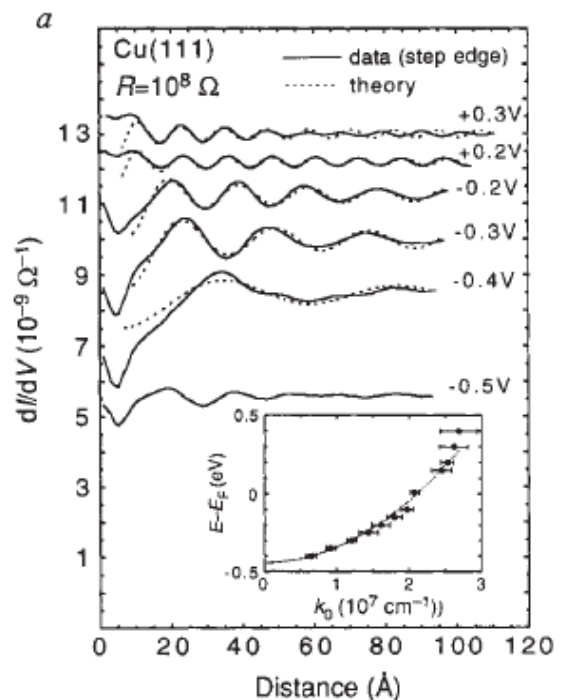


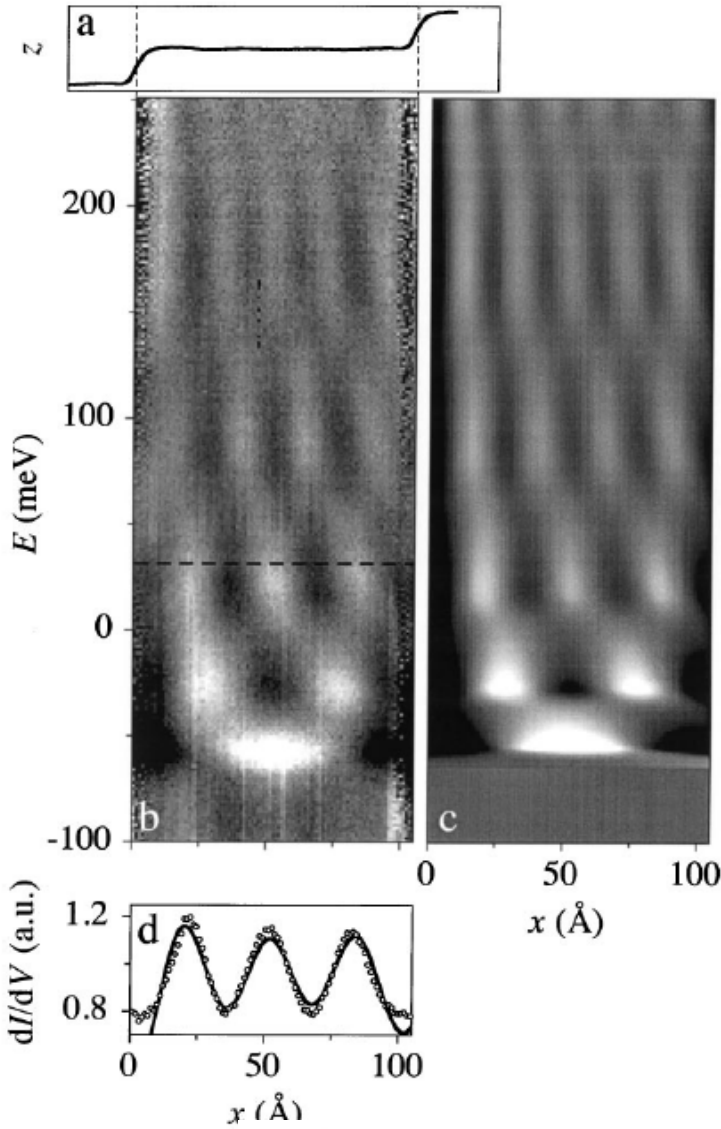
FIG. 2 a, Solid lines: spatial dependence of dI/dV , measured as a function of distance (along upper terrace) from step edge at different bias voltages. Zero distance corresponds to the lower edge of the step.

Decrease in the surface LDOS
for $E < -0.45 \text{ eV}$ (bottom of
the surface state band)

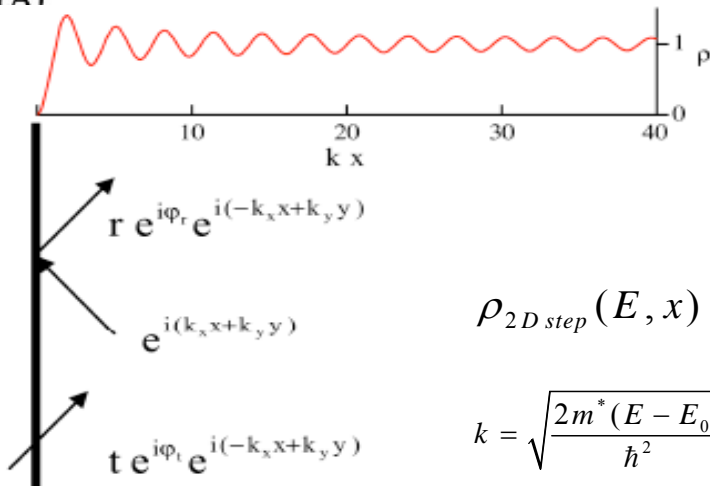
Ag(111) surface state electrons confined by two atomically parallel step edges.

L. Burgi, Phys. Rev. Lett. **81** (1998) 5370

$T = 5 \text{ K} \rightarrow k_B T = 0.4 \text{ meV}$



(a) Constant current line scan over 104 \AA wide asymmetric resonator taken at $V = 115 \text{ mV}$ and $I = 1 \text{ nA}$.
 (b) Corresponding differential conductance map.
 (c) Model $\rho(E, x)$
 (d) A constant energy cut of (b) at $E = 31.5 \text{ meV}$ (see dashed line) is plotted as open circles.



$$\rho_{2D \text{ step}}(E, x) = \frac{m^*}{\pi \hbar^2} (1 - r J_0(2kx))$$

$$k = \sqrt{\frac{2m^*(E - E_0)}{\hbar^2}}$$

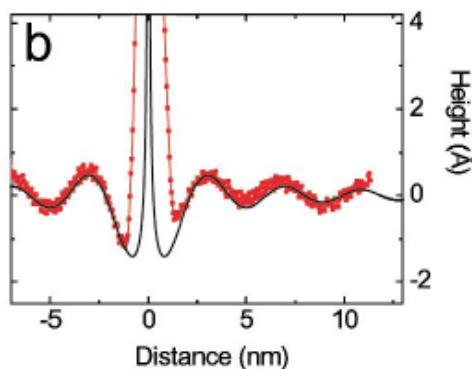
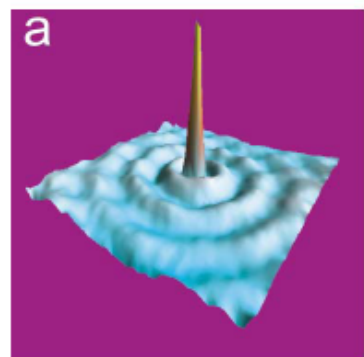
Creation of an Atomic Superlattice by Immersing Metallic Adatoms in a Two-Dimensional Electron Sea

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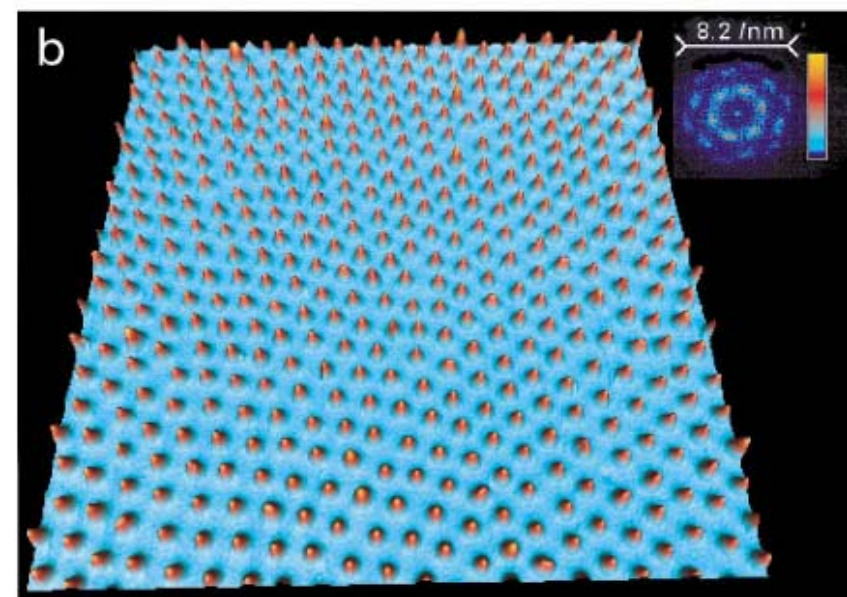
(Received 27 May 2003; published 9 January 2004)



(a) The $21 \times 21 \text{ nm}^2$ 3D STM image of a standing-wave pattern around an isolated Ce adatom on Ag(111) at 3.9 K ($U_s=3 \text{ mV}$, $I_s=19 \text{ pA}$).

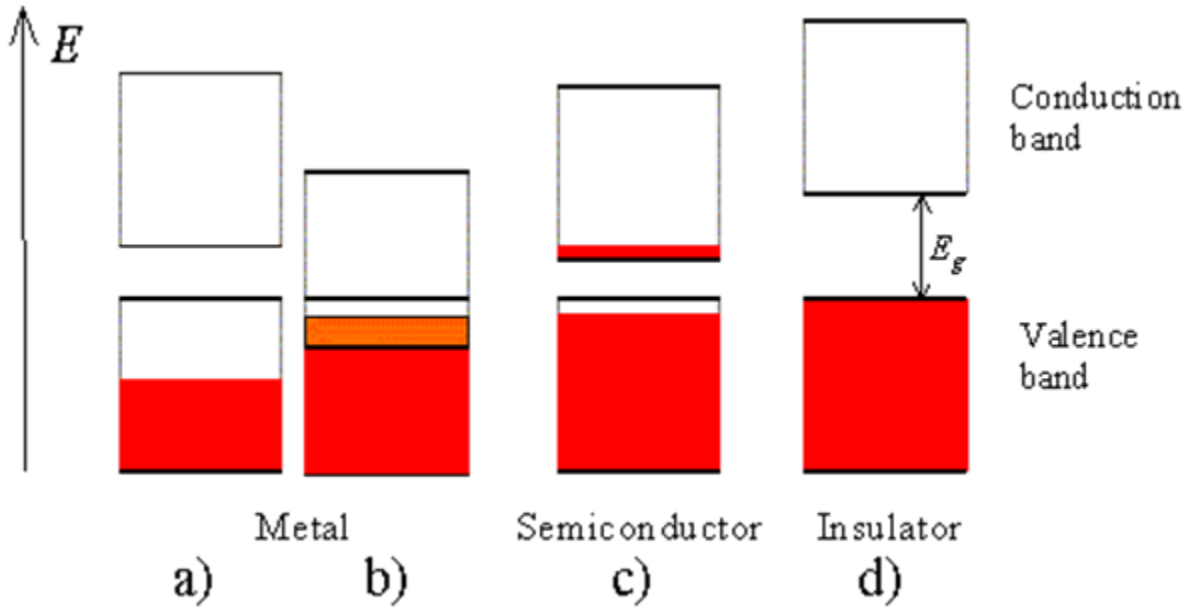
(b) Dotted line: topographic profile as a function of distance from a single Ce adatom.

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



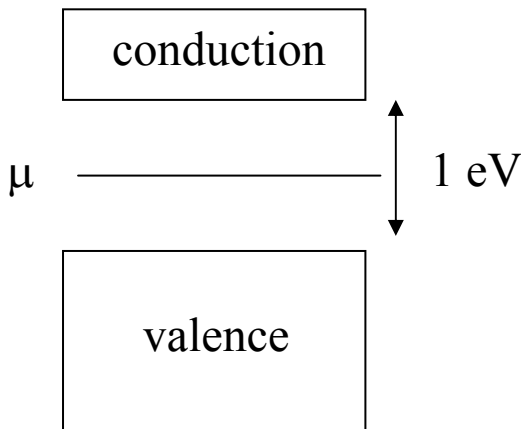
The 3D STM image at 3.9 K ($64 \times 64 \text{ nm}^2$; $U_s=100 \text{ mV}$, $I_s=10 \text{ pA}$): Ce adatoms (red), Ag(111) (blue).

Energy band diagram

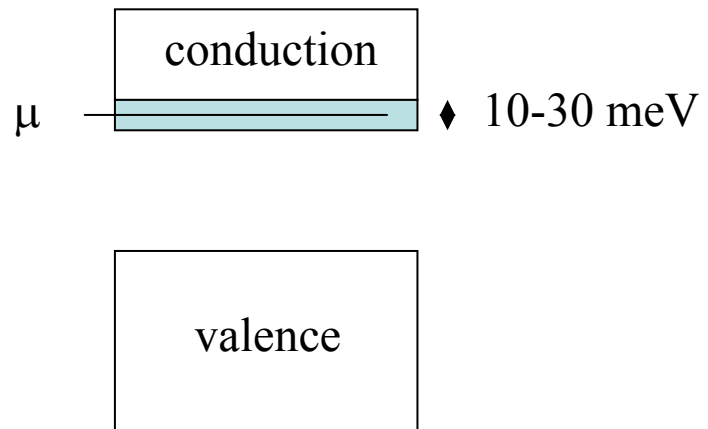


Possible energy band diagrams of a crystal. Shown are **a)** a half filled band, **b)** two overlapping bands, **c)** an almost full band separated by a small bandgap from an almost empty band and **d)** a full band and an empty band separated by a large bandgap

semiconductor



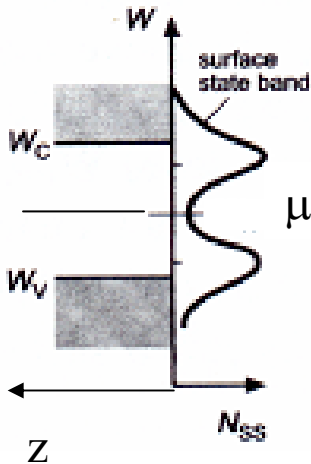
n-doped semiconductor



In intrinsic semiconductor the chemical potential μ sits in the forbidden gap. Doping shift the chemical potential closer to one of the two bands

Surface states in a semiconductor

Intrinsic semiconductor

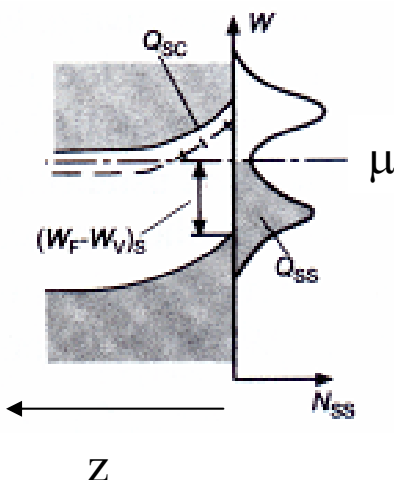


Because both the conduction and valence band are occupied surface states are allowed in correspondence of both bands.

For symmetric conduction and valence band also the surface states bands are symmetric)

Surface state band: affects the density of states at the sample surface: increase of the number of carriers (electrons and holes) at the crystal surface

n-doped semiconductor

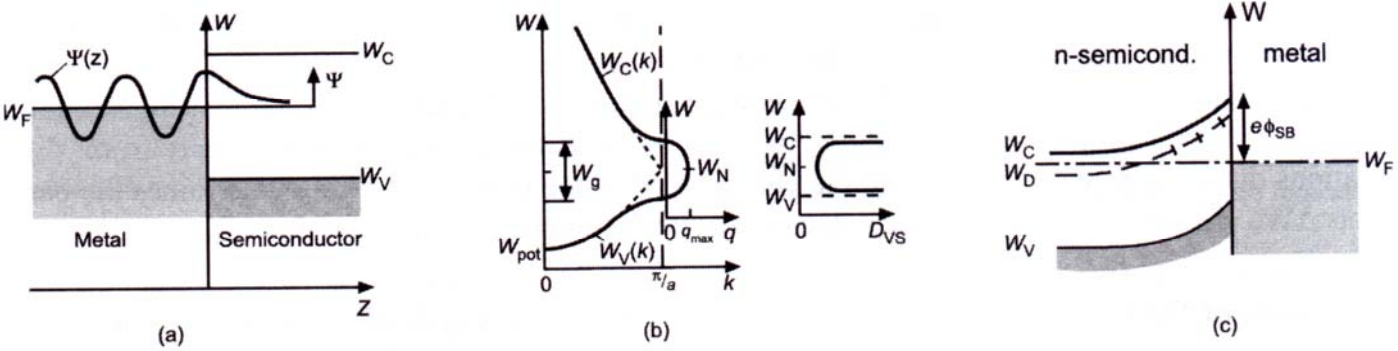


The chemical potential in the bulk and within the band of surface states has to be the same -> **band bending**

Interface states

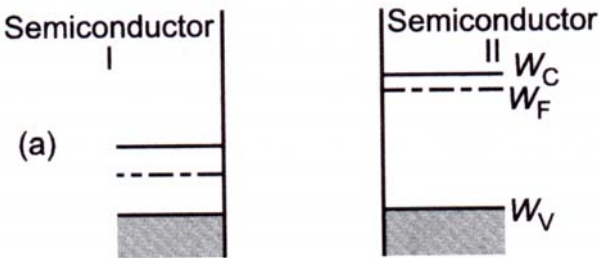
At the interface between two materials electrons can find an energy barrier (equivalent to the work function to escape in the vacuum)

metal-semiconductor junction

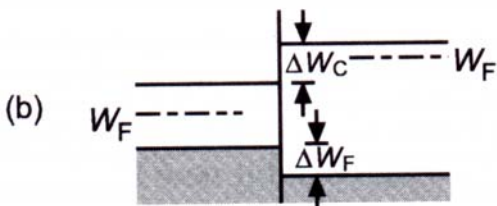


$e\Phi_{SB}$ = Schottky barrier: electron can flow through the junction only if a voltage $V = e\Phi_{SB}$ is applied

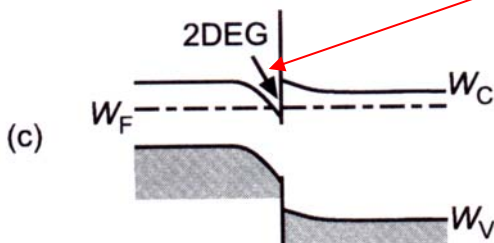
semiconductor-semiconductor junction



Semiconductor I moderately n-doped
Semiconductor II highly n-doped

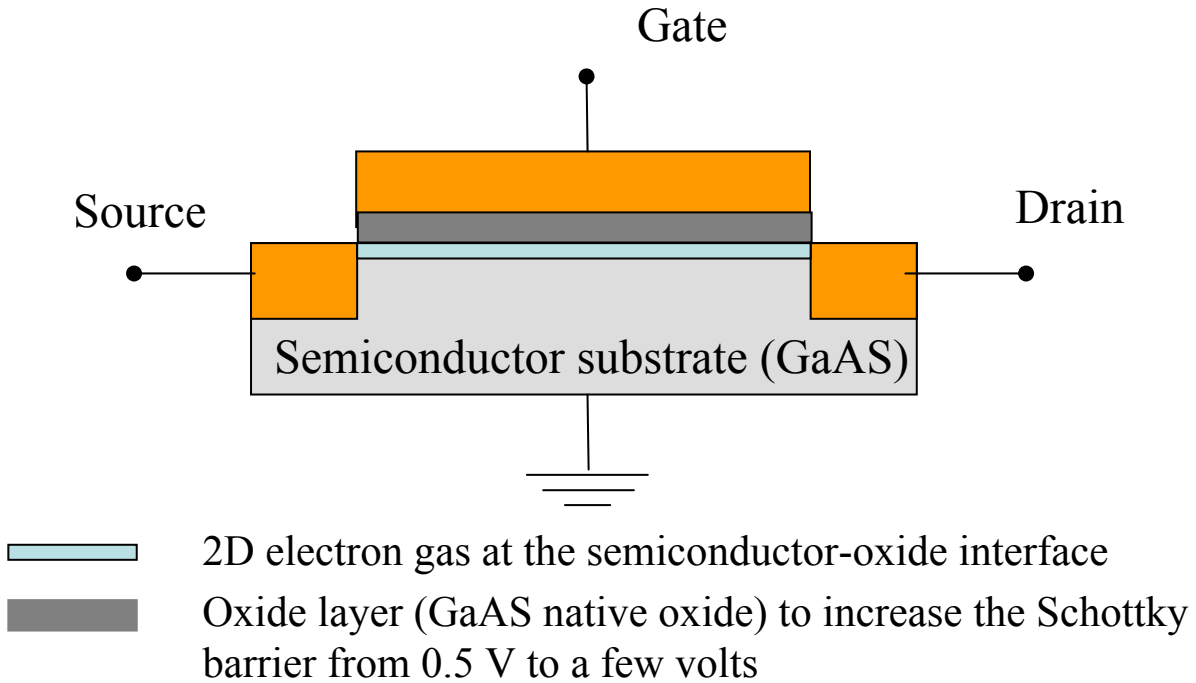


Quasi two-dimensional electron gas confined within a layer of thickness 1-2 nm

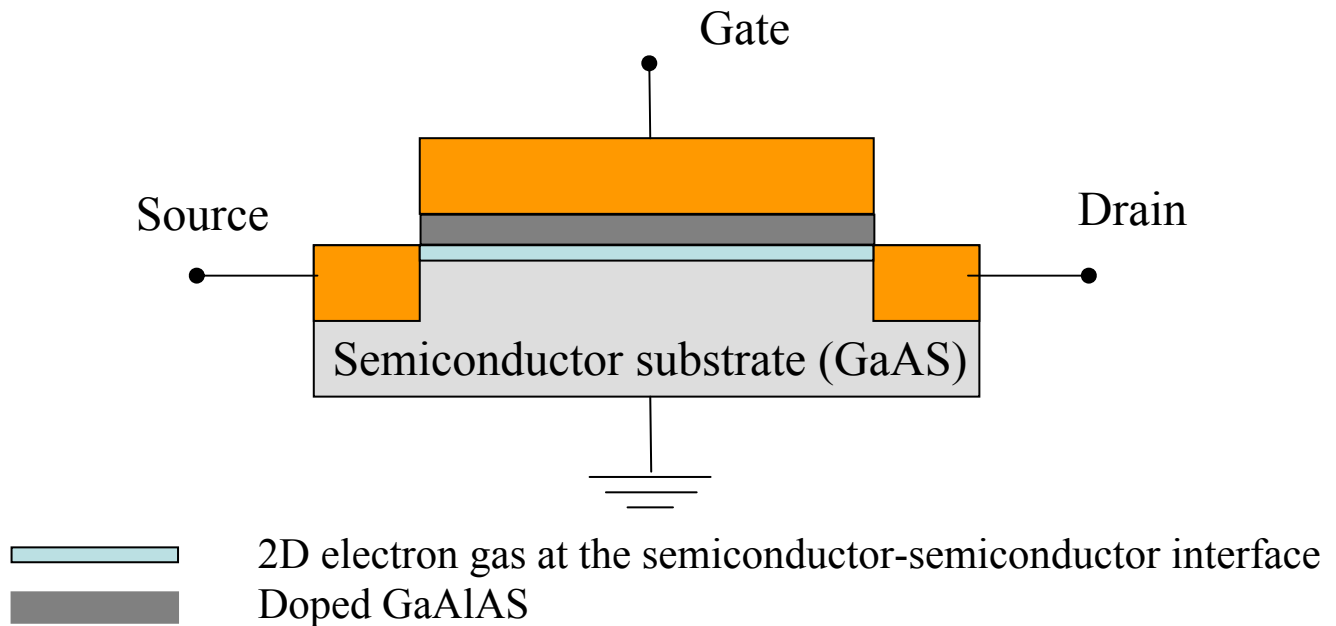


The effect of this junction is to create a very thin layer where the Fermi level is above the conduction band

MOSFET: metal oxide semiconductor field effect transistor

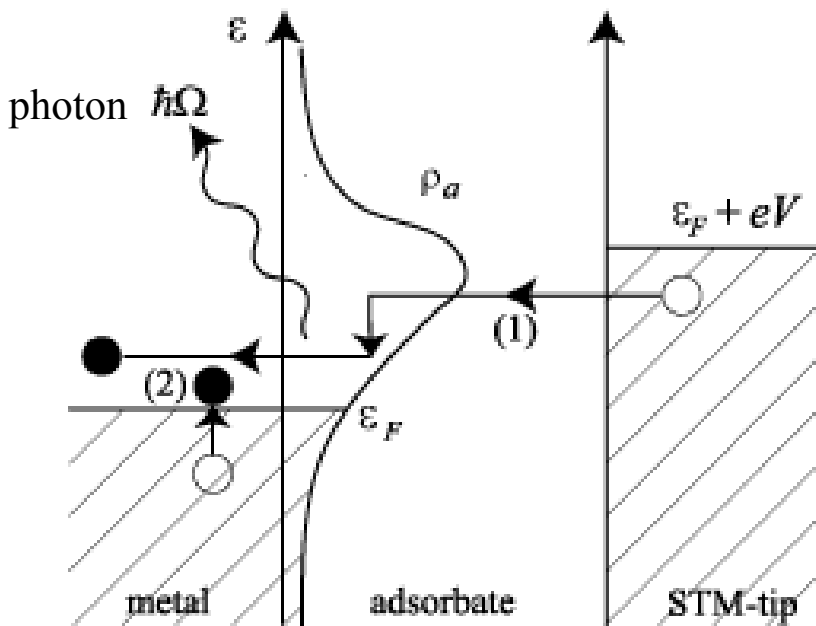


HEMT: High electron mobility transistor

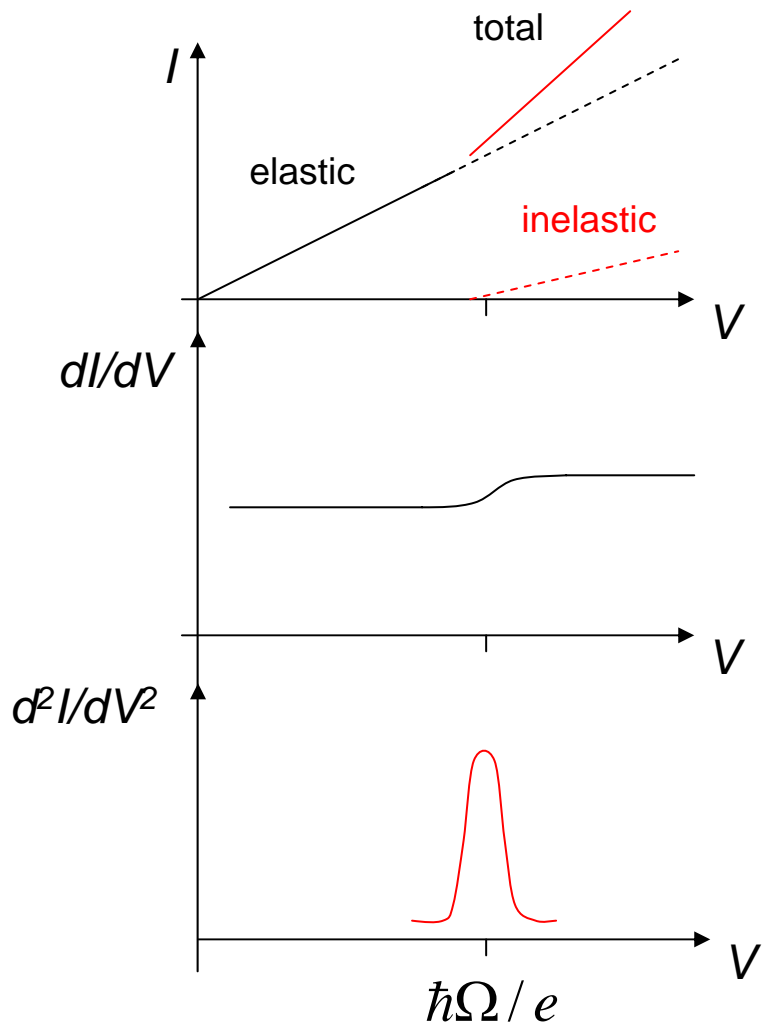


The gate voltage is used to control the number of carriers in the 2D channel (opens or closes the 2D channel by shifting the respective bands)

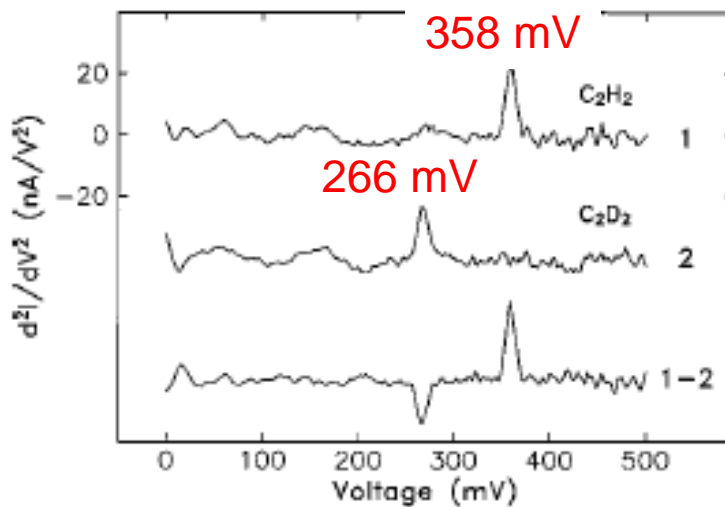
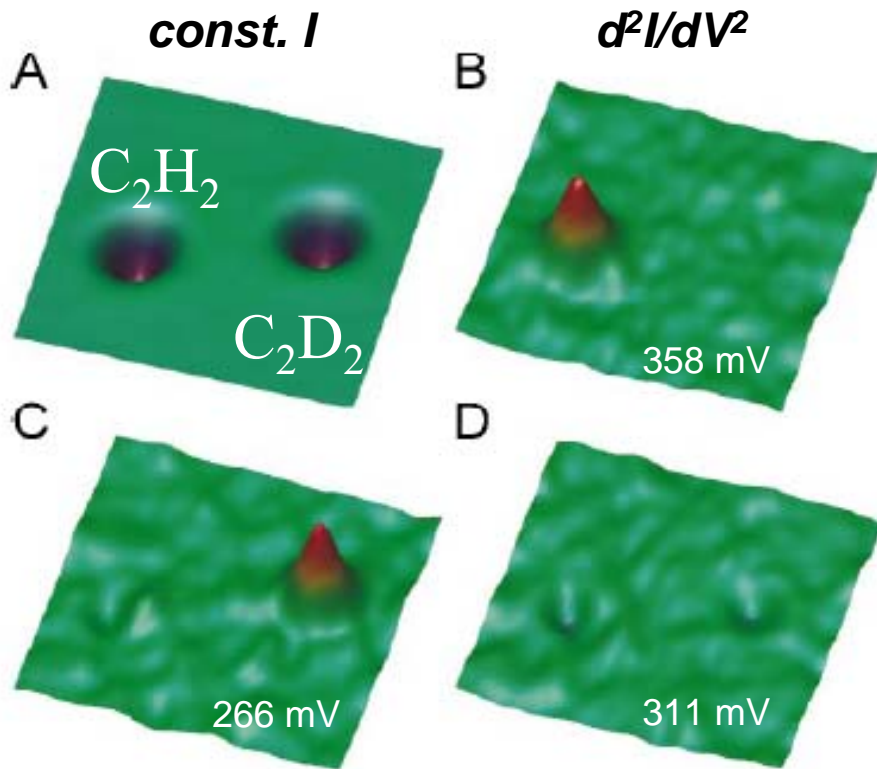
4) Inelastic tunneling spectroscopy



The tunneling electron excite an electron of the adsorbate

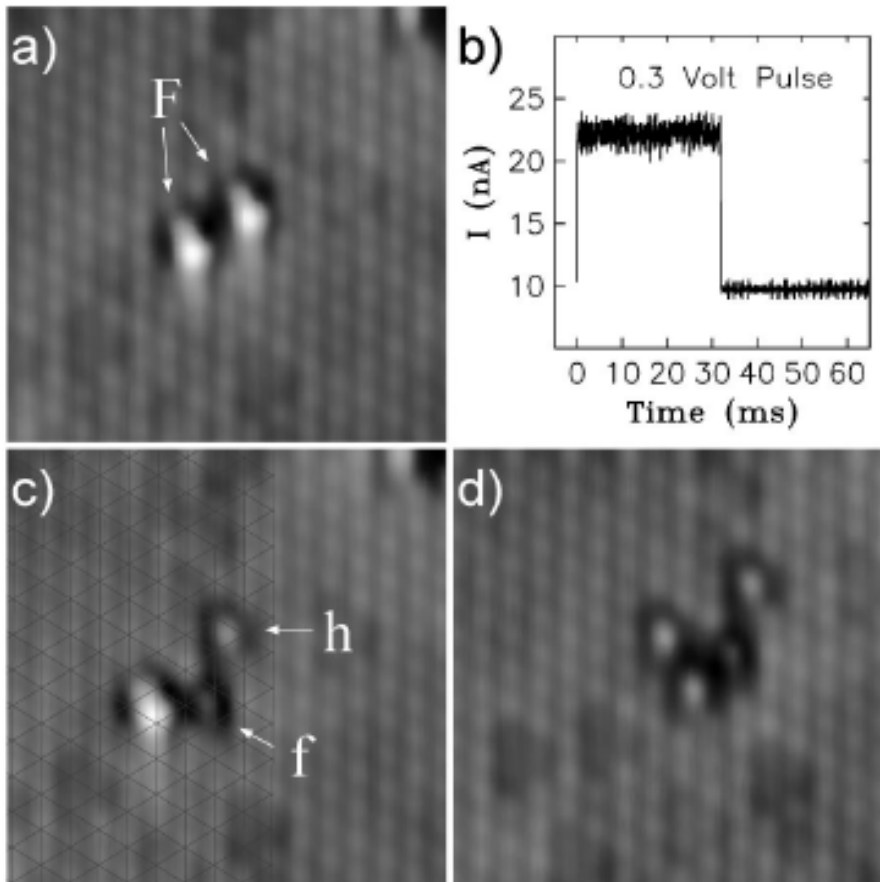


Single-molecule vibrational microscopy: chemical contrast



Single-Molecule Dissociation by Tunneling Electrons

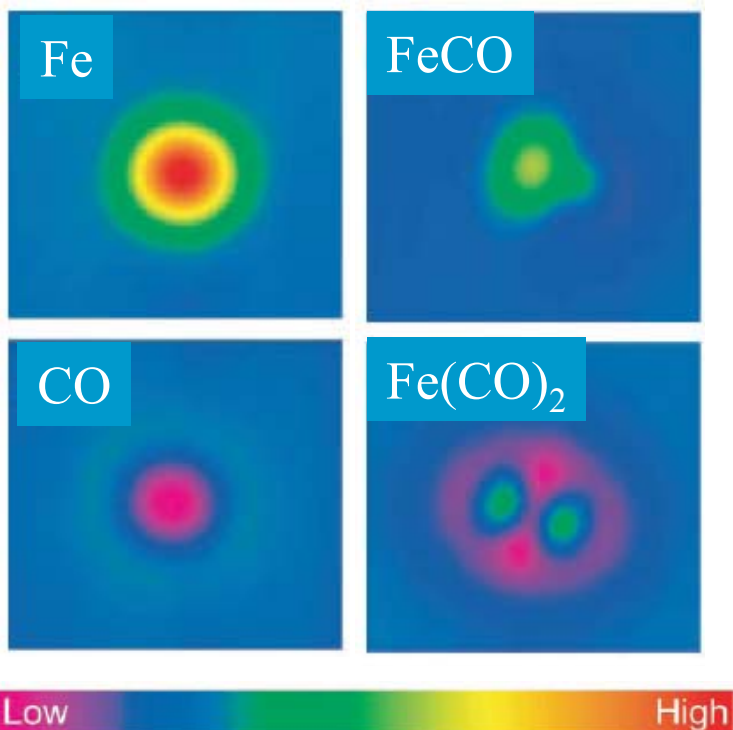
O₂ molecules on Pt(111) surface



(a) STM image of two adjacent pear shaped O₂ 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.

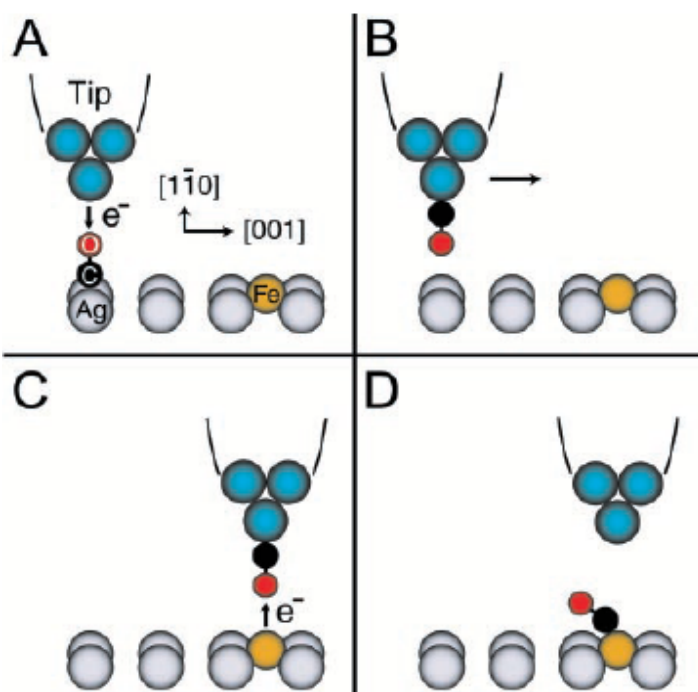
Single-Bond Formation with a Scanning Tunneling Microscope

1) Molecule recognition



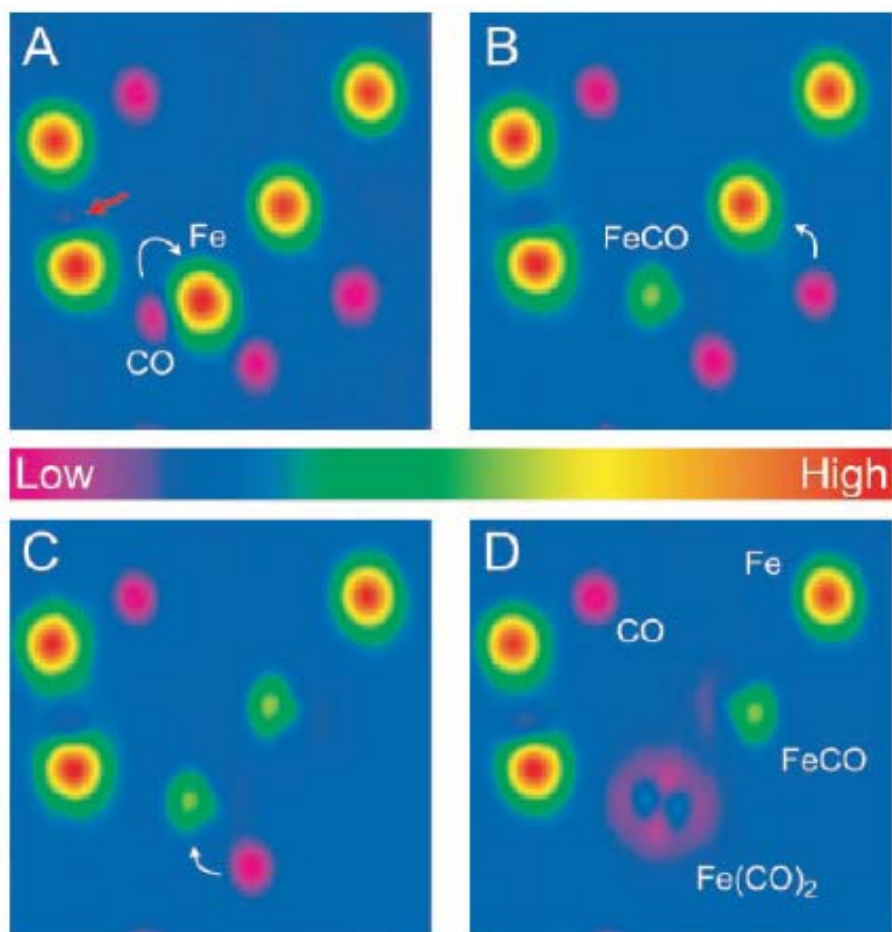
2.5 nm by 2.5 nm STM
topographic images recorded at
70-mV bias and 0.1 nA

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).