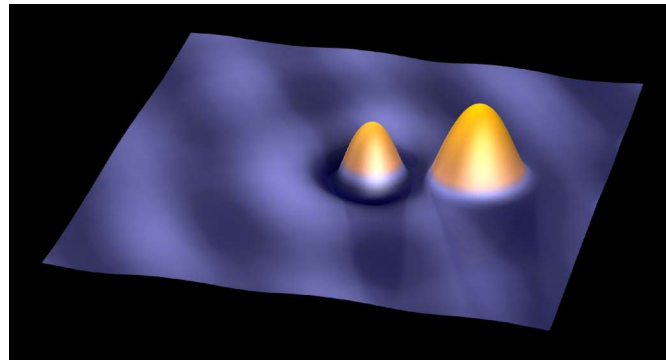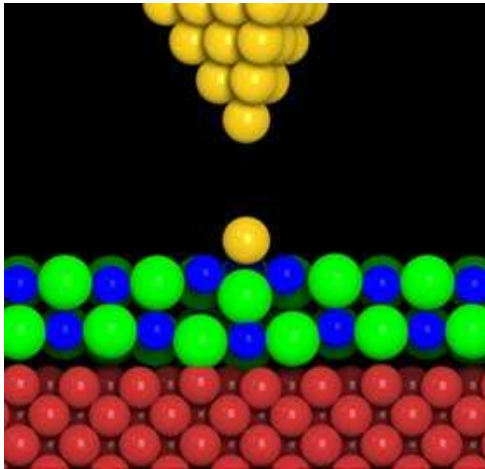# Theory of Control of Matter on the Atomic Scale

Mats Persson,

*Dept. of Applied Physics, Chalmers, Göteborg, SWEDEN*

Introduction and Outline

- The ultimate limit of engineering materials involves control of matter on the atomic scale : imaging, characterization and manipulation by scanning tunneling microscope (STM)
  - Example of molecular device (nanomachine)
- To fully exploit these unique capabilities of the STM one needs theory and modelling
  - STM images
  - Vibrational inelastic tunneling
  - Charge control of adatoms

Example of Molecular Nanomachine:
Three-Input Sorter*

12nm

17 nm
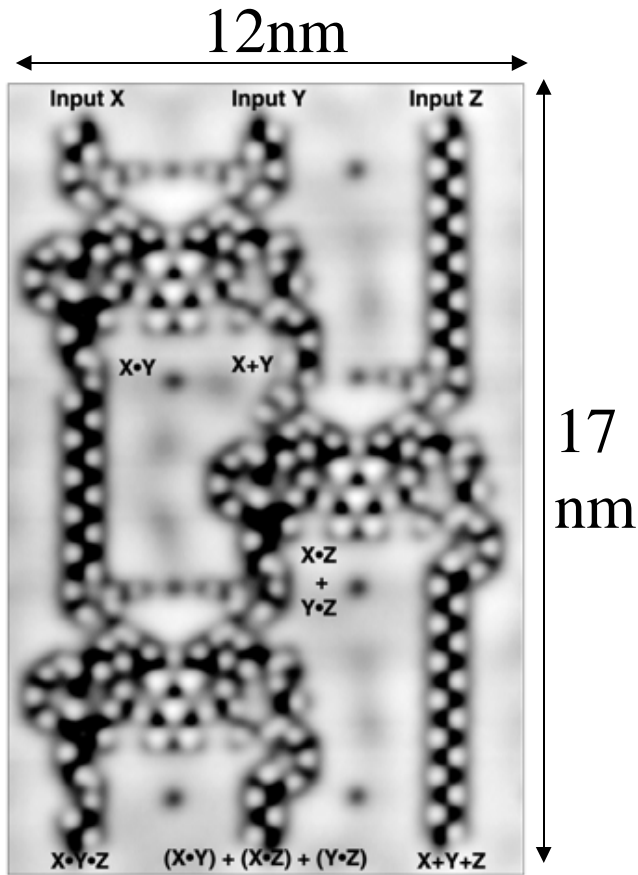
Function by molecular cascades of 512 CO molecules on Cu(111)
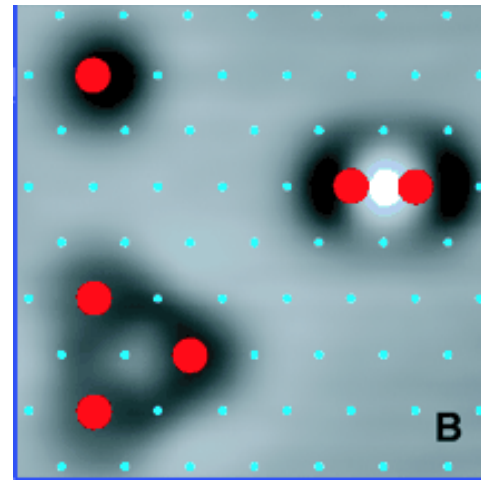
* Heinrich *et al.,* Science **298**, 1381 (2002)

Scanning Tunneling Microscope: Control of Matter on the Atomic Scale
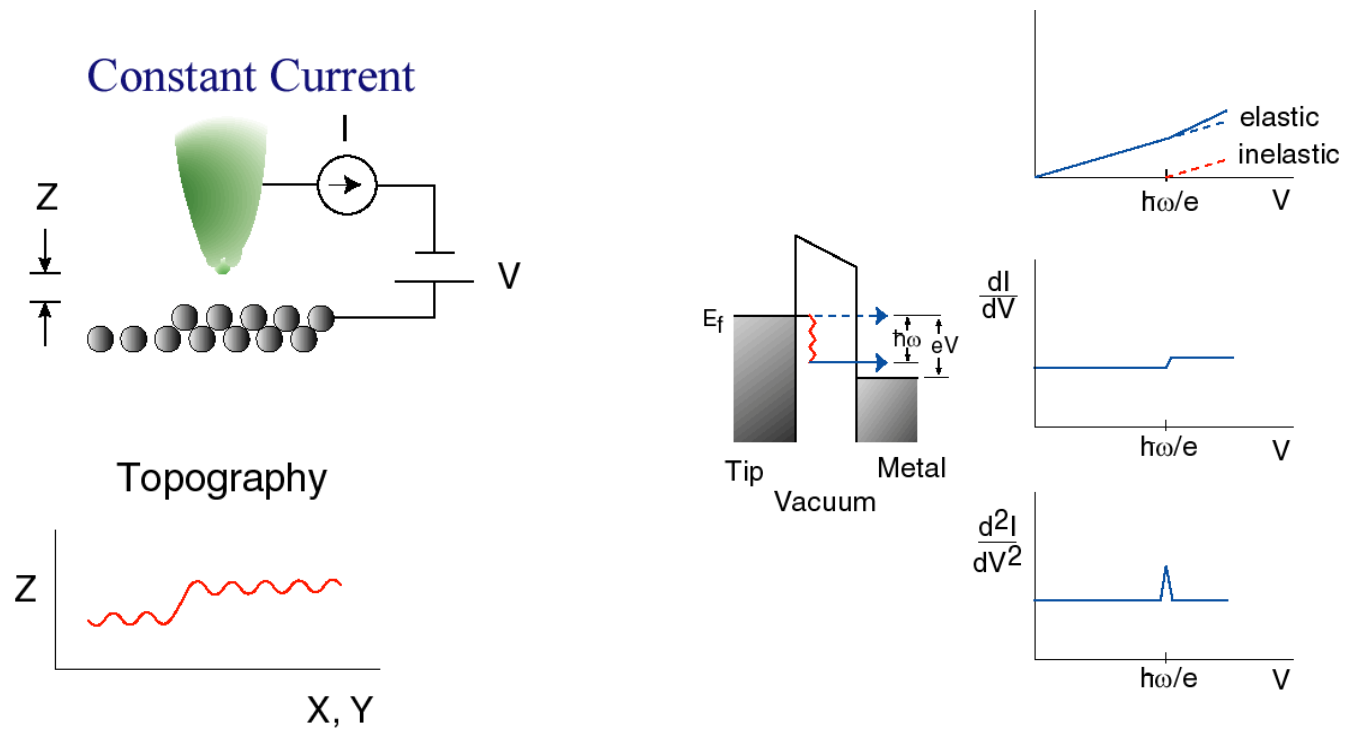
"The Three Pillars"

Imaging (1983)   Characterization (1998)

Manipulation (1990)

From analysis and synthesis of *ensembles* of atoms to *single* atoms: *paradigm shift in (surface) science*

Elastic and Inelastic Electron Tunneling

Binnig & Rohrer, (1983)

Vibrations:
Stipe, Rezaei, & Ho, (1998)

Theoretical and Computational Challenges

- Calculation of geometric and electronic structure of several hundreds of atoms in low symmetry configurations with useful accuracy and predictive power: density functional theory calculations

- Theory and modelling of elastic and inelastic electron tunneling

Density Functional Theory

- The total energy, E_{tot}, of the electrons and all ground state properties determined by the electron density $n(\boldsymbol{r})$ by minimizing:

$$E_{tot} = T_0[n] + E_{Coulomb}[n] + E_{XC}[n]$$

- All complicated exchange and correlation effects hidden in $E_{XC}[n]$

- Development of good approximations in the 90s for $E_{XC}[n]$ with useful accuracy and predictive power: Generalized gradient approx.

Walter Kohn ~ 1964, Nobel prize in Chemistry, 1998

Density Functional Calculations

- Numerical solution of non-linear Kohn-Sham equations obtained from minimization of $E_0[n]$:

$$\left| \frac{\hbar^2}{2m}\nabla^2 + \varphi_{Coulomb}(n) + v_{XC}(n) \right| \psi_i(r) = \varepsilon_i \psi_i(r)$$

$$n(r) = \sum_{\varepsilon_i < \varepsilon_F} |\psi_i(r)|^2$$

- Efficient algorithms and methods developed in the 90s so that   large systems can be handled
    - *e.g.* Plane wave basis set, FFT, and super cell geometry
    - Iterative diagonalisation methods for lowest lying states
    - Effective valence-ion core potentials

- Exponential development of computer power

"First Pillar"

Characterization

Imaging

Manipulation
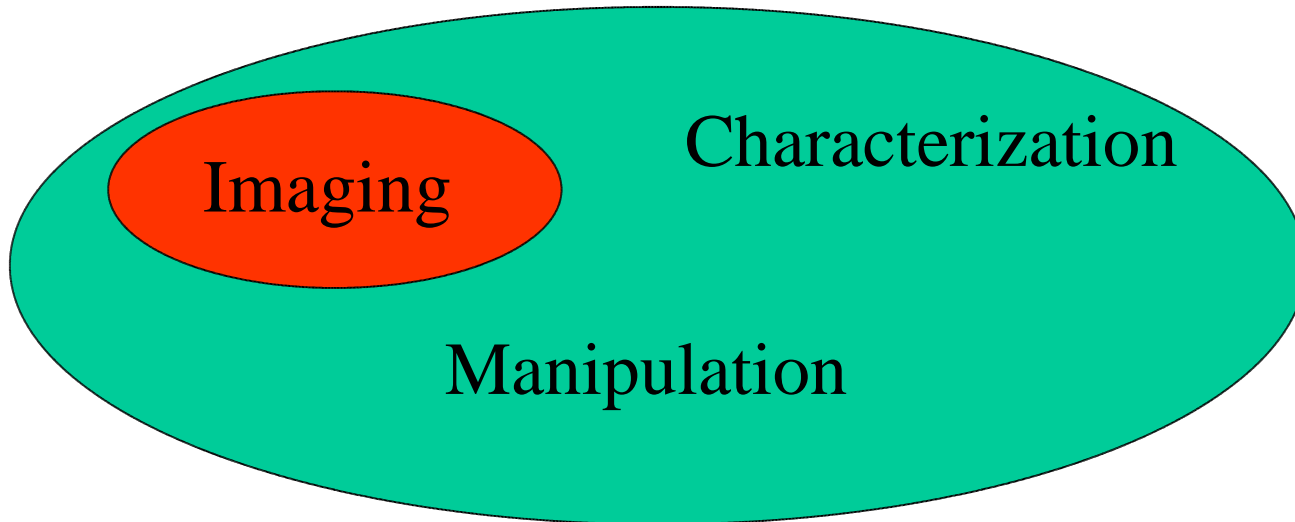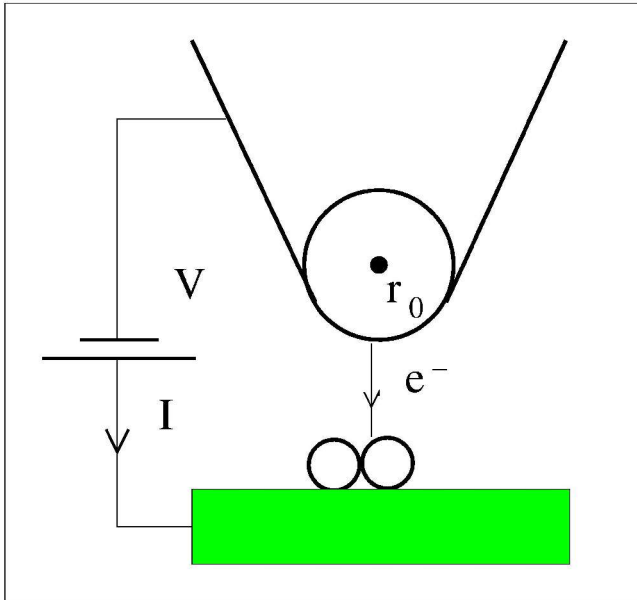
Example: STM images of O_2/Ag(110)*

(CO-functionalized tip)
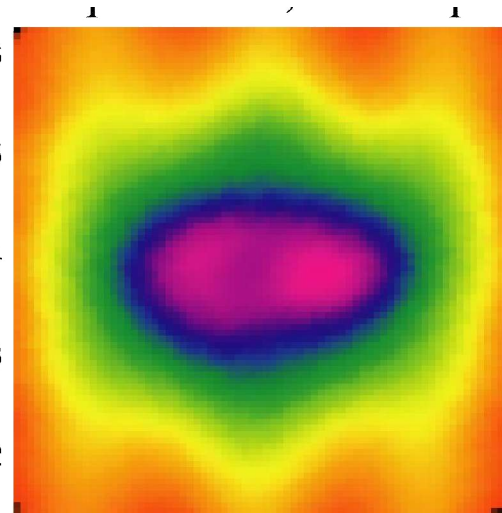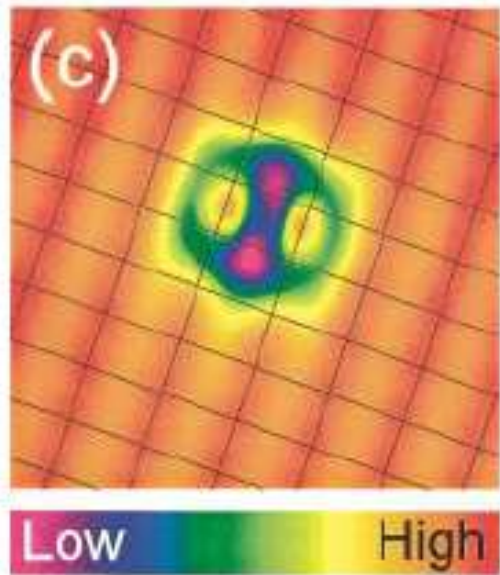
What kind of information is contained in the STM image ?

_____

* Hahn, Lee, and Ho, Phys. Rev. Lett. **85**, 1914 (2000)

Theory: STM and LDOS images

Tersoff-Hamann approx. (1983):

(Bardeen approx. & spherical wave)

$$\frac{dI}{dV} \propto \rho \qquad (r_0, \varepsilon_F + eV)$$

Local density of one-electron states

One-electron approximation (Kohn-Sham states) for LDOS:

$$\rho \qquad (r_0, \varepsilon_F) = \sum_0 |\langle r_0|\psi_0\rangle|^2 \delta(\varepsilon_0 - \varepsilon_F)$$

$\langle r_0|\psi_0\rangle$ one-electron wavefunction with energy ε_0

(In principle, excited state property)

Density functional theory calculations

Iterative solution of a $N \times N_k$ non-linear Schrödinger (Kohn-Sham) equations for $2N$ valence electrons in a planewave basis set of size N_{pw} in a super cell geometry sampled by N_k
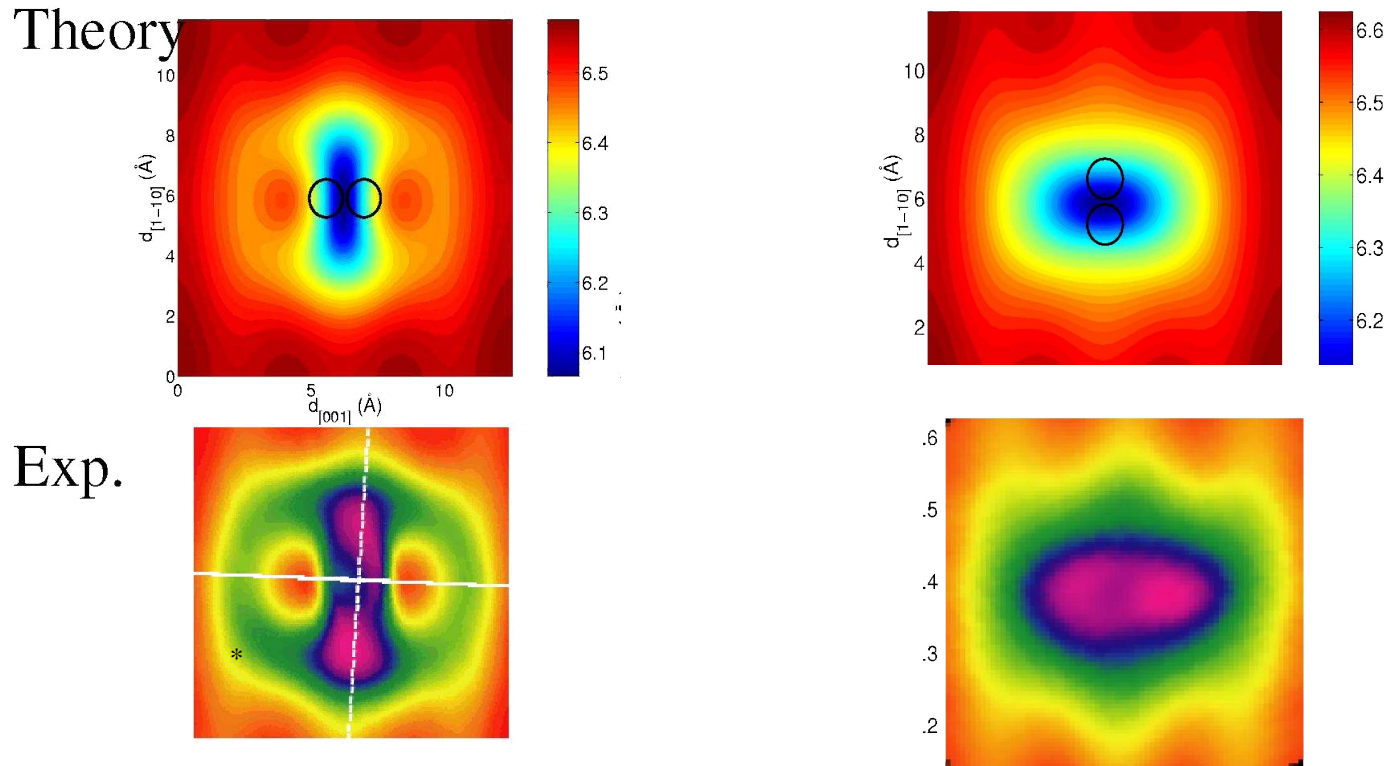
Typical size: ~100 atoms, $N \sim 500$, $N_{pw} \sim 20{,}000$ and $N_k \sim 5$ gives about 5×10^7 degrees of freedom
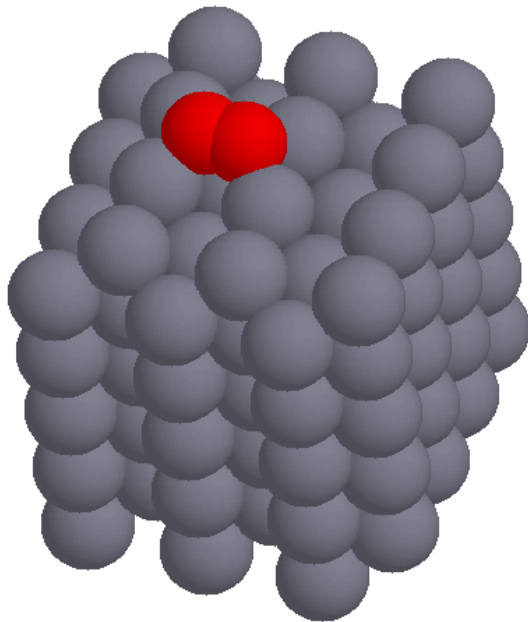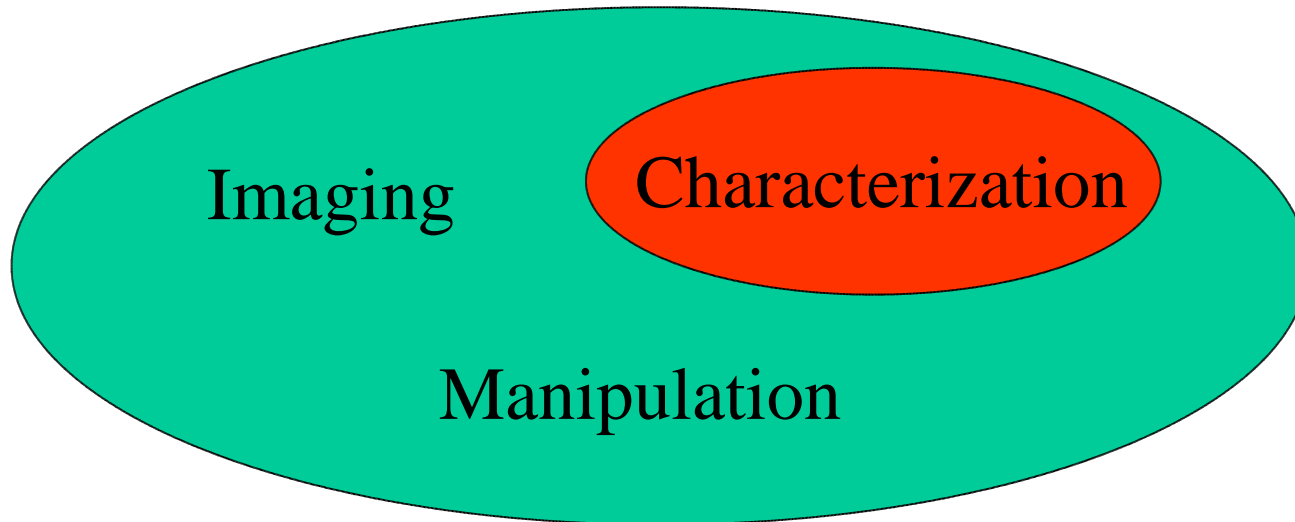

Total energy, force and electronic structure calculations:
- Geometric optimization
- Energitics: Barriers, ….
- Vibrational frequencies
- One-electron (Kohn-Sham) wave functions

LDOS vs. STM images: O_2/Ag(110)

Theory

Exp.

Protrusions derive from an anti-bonding molecular state and not from the nuclear positions
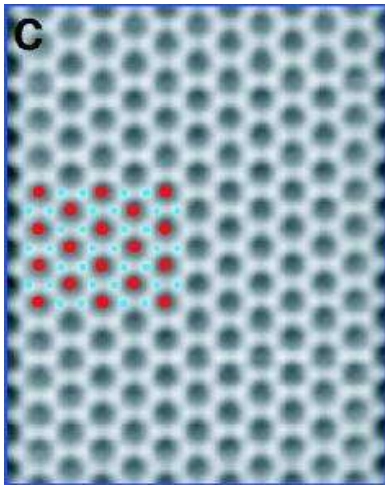
"Second Pillar"
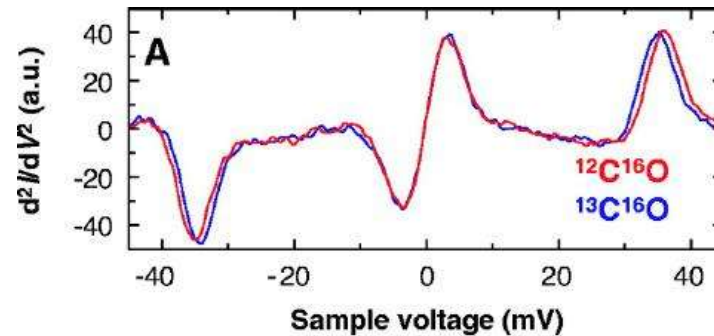
Imaging

Characterization

Manipulation

- Electron Spectroscopy by Elastic Tunneling
- Vibrational Spectroscopy and Microscopy by Inelastic Electron Tunneling

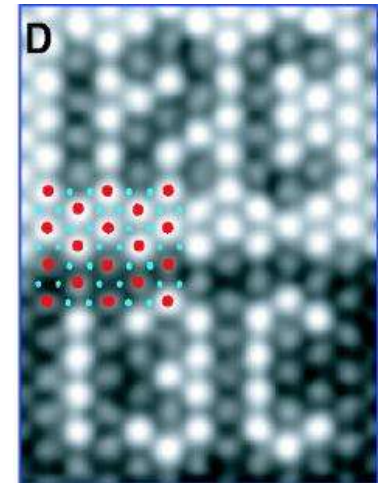# Inelastic Electron Tunneling from an Ordered CO Structure on Cu(111)*

STM image

Vibrational Spectroscopy
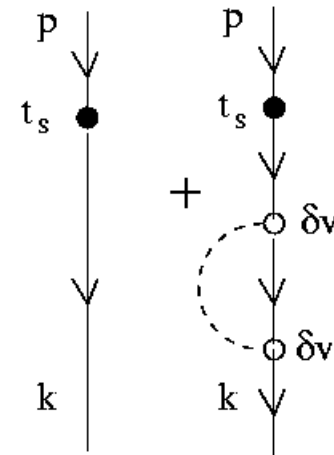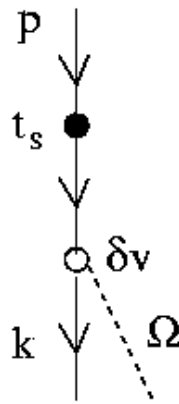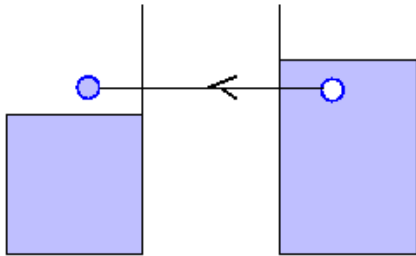
Vibrational Microscopy

* Heinrich, Lutz, Gupta & Eigler, Science **298**, 138 (2002)

Generalized Tersoff-Hamann Approx. for IET

Going beyond the Born-Oppenheimer approx.

Inelastic channel   Elastic channel

Fermi exclusion principle in final states and intermediate states results in a threshold at bias $V = h\Omega/e$ for both elastic and inelastic tunneling

$$\frac{dI}{dV} \propto \rho \left(r_0, \varepsilon_F + eV \right)$$

LDOS of electrons interacting with vibration

IET-LDOS intensities*

IET signal:

$$\frac{d^2 I}{dV^2} / \frac{dI}{dV} \approx n_{tot}(r_0)\, \delta(V - \hbar\Omega/e)$$

Broadened by temperature (Fermi level smearing), modulation voltage, and vibrational lifetime

Spatially dependent parameters:

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*Lorente & Persson, Phys. Rev. Lett. **85**, 2997 (2000)

# Density Functional Calculations:

PW-PAW-GGA (VASP)
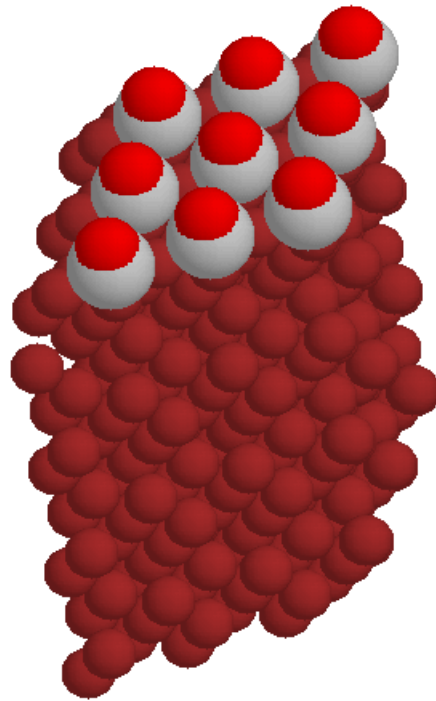
IET intensities

Mode(deg.)	η_{tot} (%)	η_{inel}(%)	η_{el}(%)	$\hbar\Omega$ (meV)
FT(2)	11.8	12.2	-0.3	3.7 (4) [a]
FR(2)	15.6 (~8)	16.8	-0.9	34 (35 [a], 36 [b])
M	0.6 (ND)	0.7	-0.2	42 (43) [b]
I	0.4* (1.5)	0.5	-0.1	253 (258) [b]

ND: Not detected; (a) IETS data; (b) IRAS data

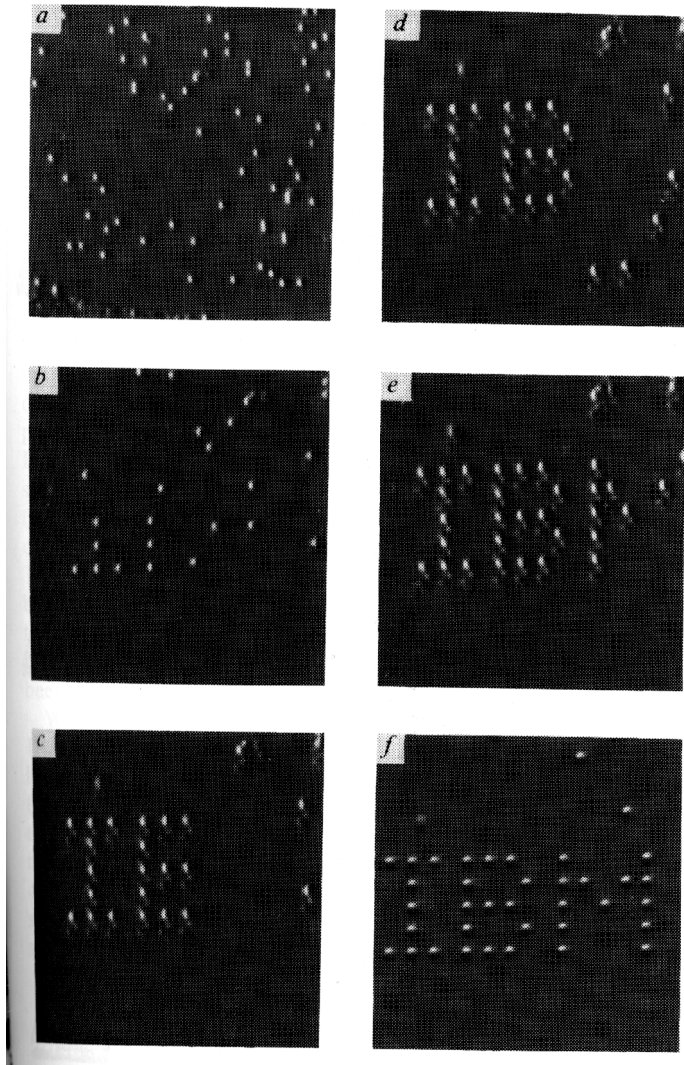Explains why only two vibrational modes (FT&FR) are strong and observed

*I mode "dipole" excited not fully included in the theory

"Third Pillar"

Imaging   Characterization
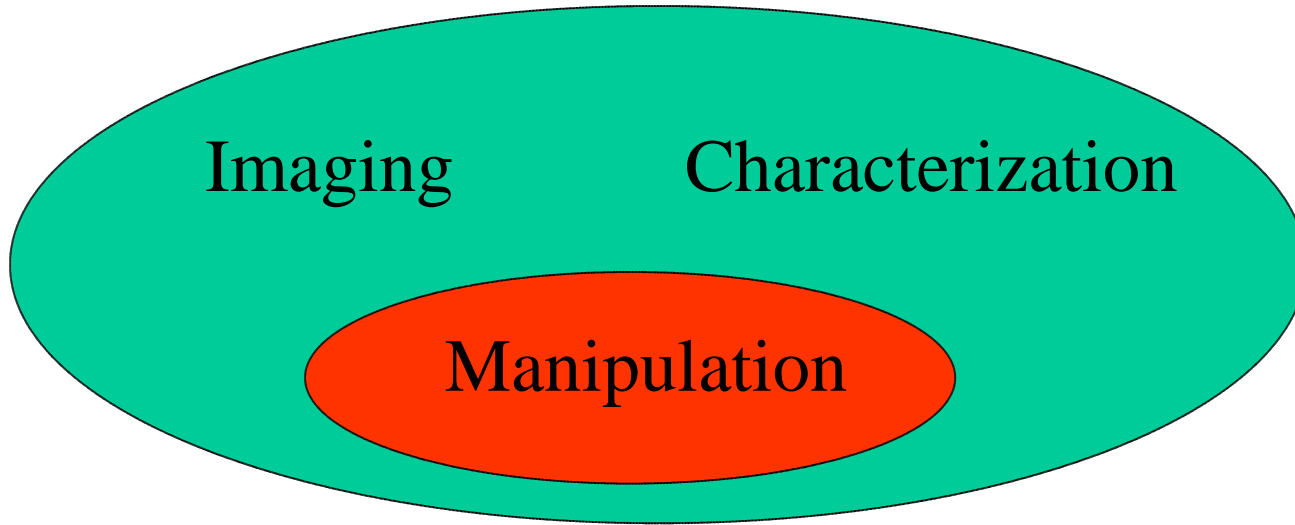
Manipulation

- Direct tip-surface interaction either by electric field or chemical interactions
- Bond making and breaking by IET
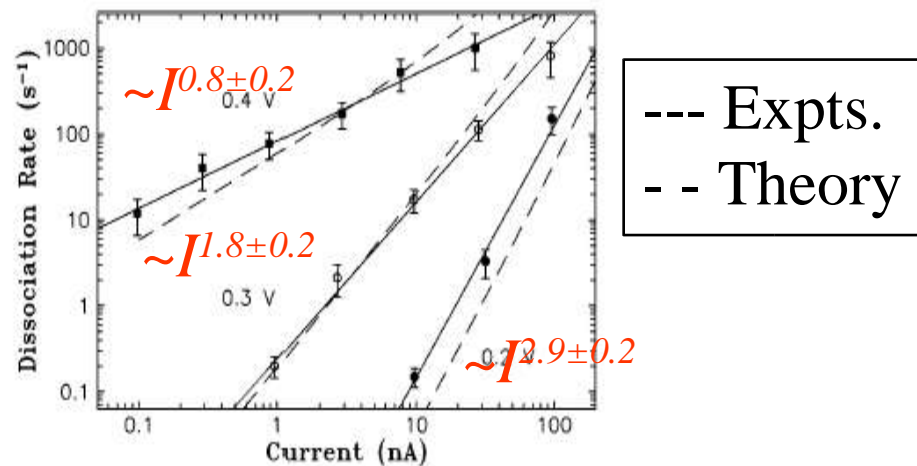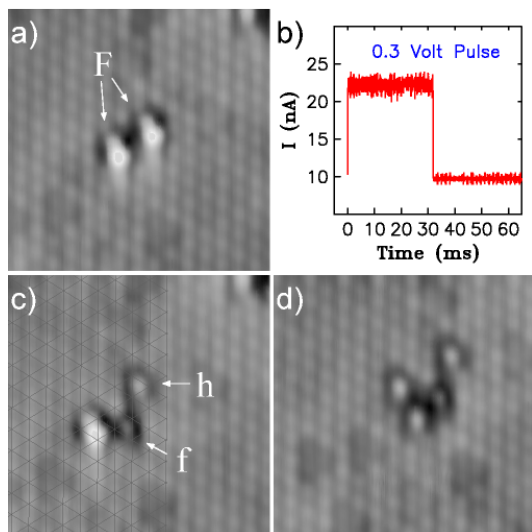- Charge control by IET

First Controlled Atomic Manipulation*

- Xe atoms adsorbed on Ni(110) at 4K
- Xe adatoms dragged by direct tip surface interaction around in a controlled manner

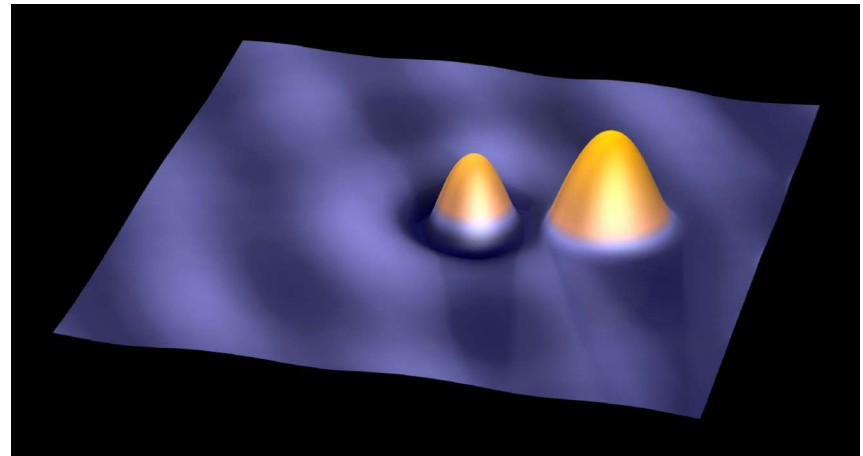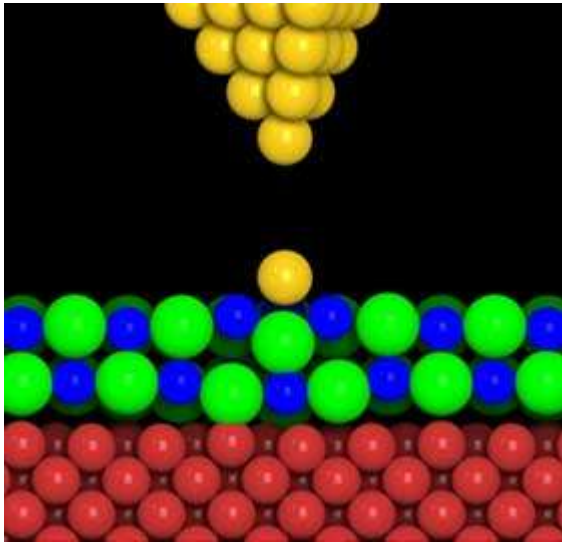*Eigler&Schweizer, Nature **344** 524 (1990)

Single Molecule Chemistry: O_2 on Pt(111)*

--- Expts.
- - Theory

Inelastic electron tunneling mechanism

*Stipe, Rezaei, Ho, Gao, Lundqvist & Persson, Phys. Rev. Lett. **97**, 4410 (1997)
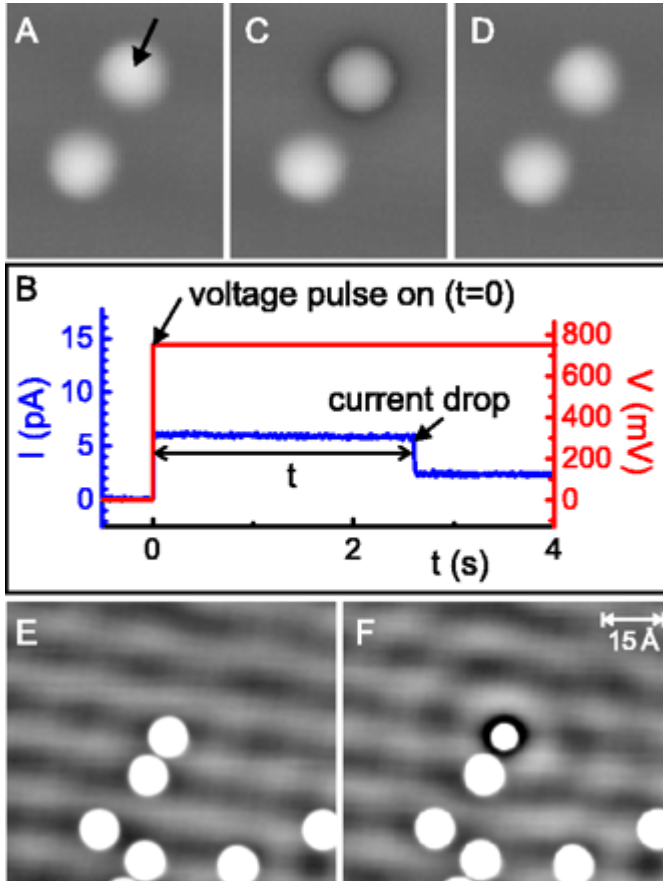
Charge State Control of Single Gold Adatoms*

Single Au atom on an insulating NaCl bilayer supported by a Cu surface

_____

*Repp, Meyer, Olsson, & Persson, Science **305**, 493 (2004)

# Manipulation of Au adatom by a Voltage/Current Pulse

- Shape of STM image changed *reversibly* by voltage pulse and tunneling current

- Manipulated adatom scatter interface state with no bound states and is repelled by positive sample bias =>
  Negatively Charged !?

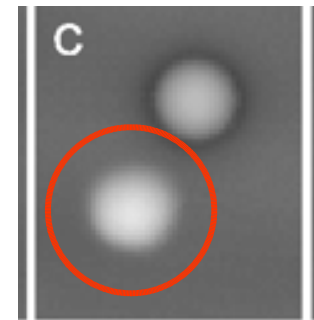- Both states are stable and have different diffusion coefficients

Au atom on NaCl bilayer supported by a Cu(111) surface

Physical Origin of Charge Bistability ?

Density functional theory calculations: Au atom on a NaCl bilayer supported by a Cu(100) surface (177 atoms)
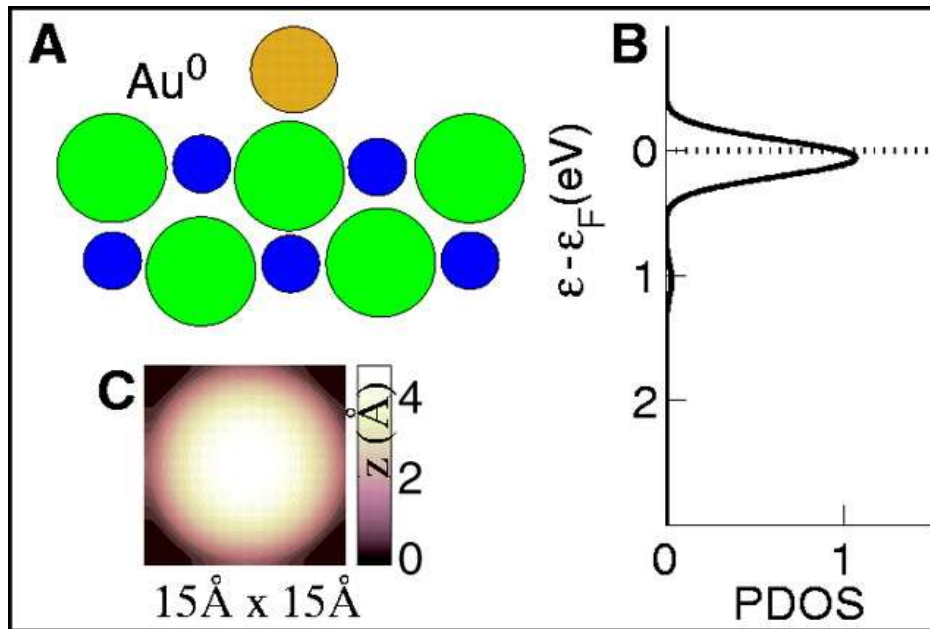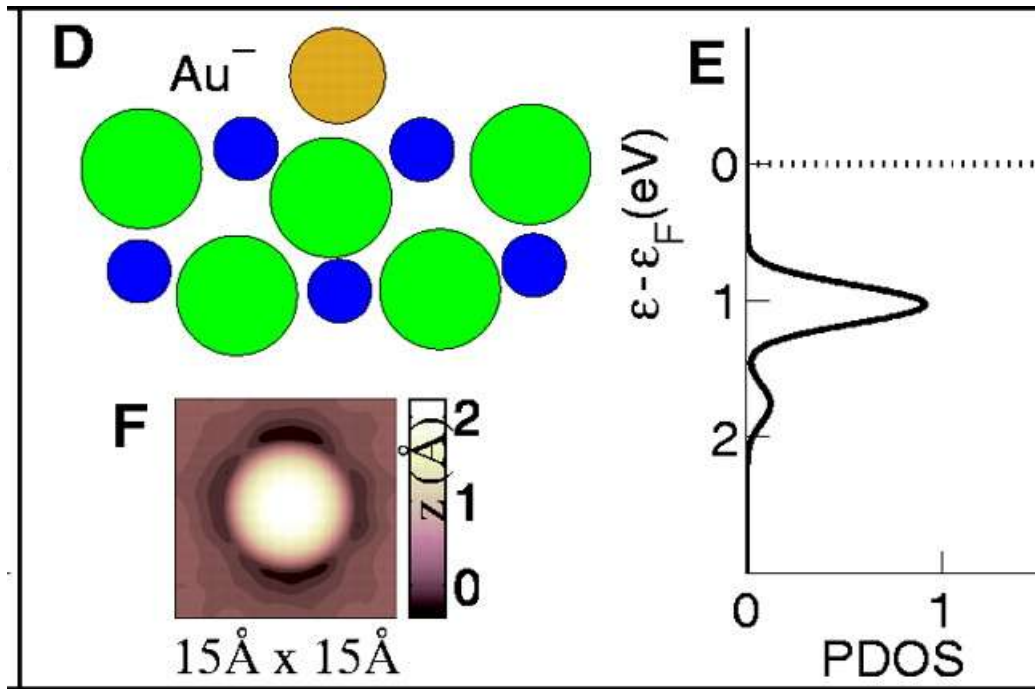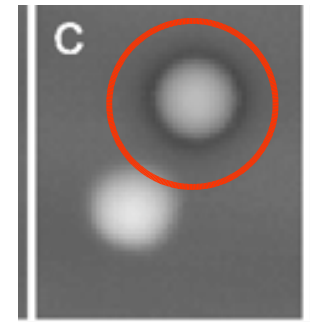

Original Au state

- Nearly half-filled 6*s* resonance*
- LDOS image in qualitative but not quantitative agreement with STM image

_____

*Broadening artificial and not resolved in the calculation

Manipulated Au state

- Fully occupied 6*s* resonance*
- Large ionic relaxations key mechanism behind stabilization of negative Au ion
- LDOS image in quantitative agreement with STM image

_____

*Broadening artificial and not resolved in the calculation
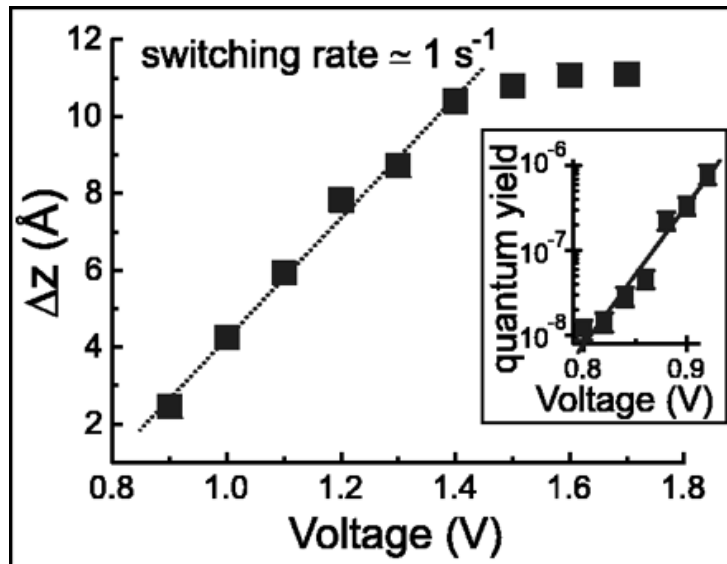
Origin of large ionic relaxations ?

Alkali-halides such as NaCl and also other polar materials have a large ionic polarizability: $\varepsilon_0 - \varepsilon_\infty$

Material	ε_0	ε_∞
NaCl	5.9	2.0
NaBr	6.3	2.6
LiI	16.9	3.8
α-Al$_2$O$_3$	11.6	3.1

- So NaCl is not unique !
- Is the Au atom unique ?

Mechanism behind charge state control ?

Δz is the tip-retraction distance to keep a switching rate ~1/s

- Yield saturates at 1.4V bias
- Simple estimate of tunneling current suggests a saturation yield of order unity: one switching event per tunneling electron !!

Tunneling electron attachment to a negative Au ion resonance a ~1.4 eV !

Nature of the negative Au ion resonance ?

- Negative ion resonances poorly described by the unoccupied Kohn-Sham states of the neutral adatom.
- "poor man's" description: U coulomb interaction term
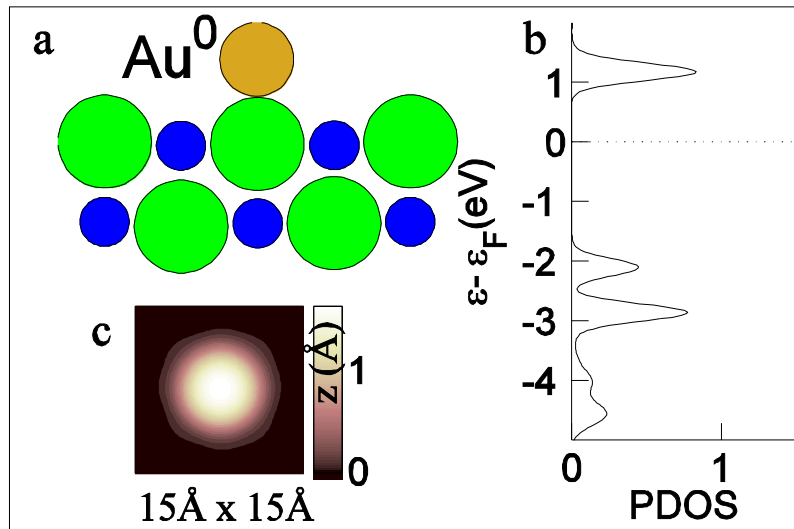
- Negative ion resonance at ~1.1 eV derives from Au atom affinity level, which is unusually large
- STM image in quantitative agreement

Concluding Remarks

- The fiction of controlling matter at the atomic scale is becoming a reality -- molecular devices (nanomachines) for catalysis, sensors, computing, etc

- Theory play an important role in developing new concepts and physical understanding through large scale computer simulations and simple modeling:
  - STM images
  - Single molecule vibrational spectroscopy by inelastic electron tunneling
  - Charge state control

Acknowledgments

Theory:

Nicolas Lorente, *U. de Paul Sabatier, Toulouse*

Fredrik Olsson and Sami Paavilainen, *Chalmers/GU*

Experiments:

Wilson Ho, *UC Irvine*
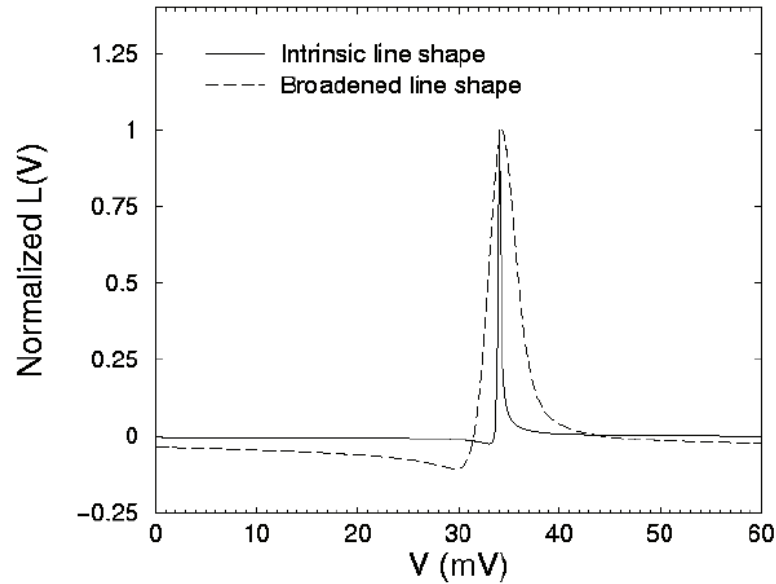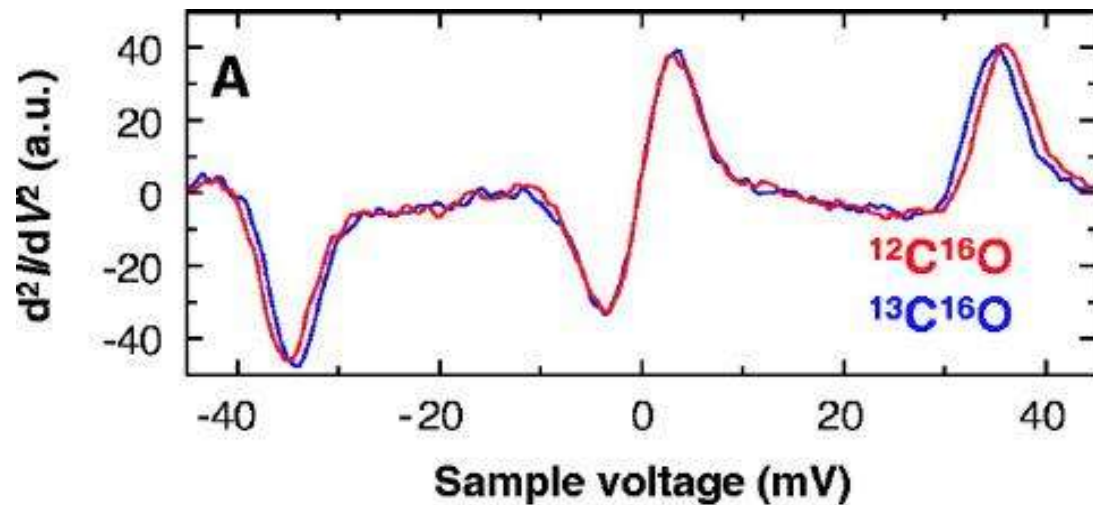
Jascha Repp and Gerhard Meyer; *IBM Zurich*

Funding:

Simulated IET Spectrum of FR mode

$\gamma_{eh} = \gamma$
Modulation $1mV_{RMS}$
and $T = 5K*$

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*A. Heinrich (private communication)