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Scanning Probe Microscopy

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*

Department of Materials Science and Engineering, Northwestern University

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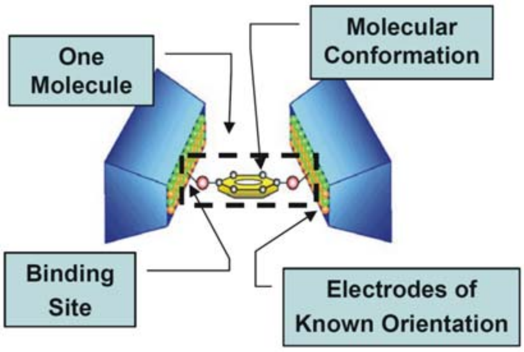
An Ideal Experiment for Probing Molecular Conduction



M. C. Hersam, *et al.*, *MRS Bulletin*, **29**, 385 (2004).

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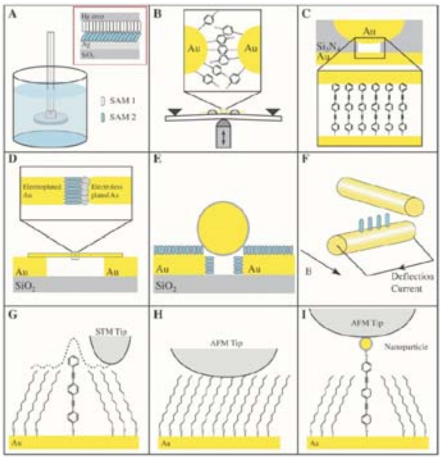
Real Experimental Strategies for Probing Molecular Conduction



B. A. Mantooth, *et al.*, *Proc. IEEE*, **91**, 1785 (2003).

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The Scanning Tunneling Microscope (STM)

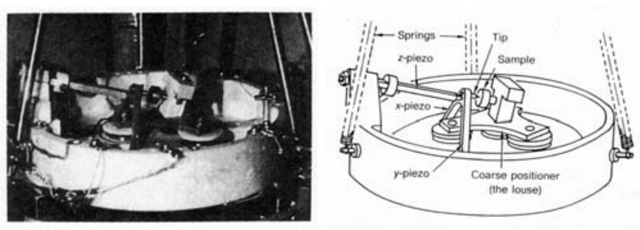

Plate 2. A humble gadget that shocked the science community. Upper, a photograph of an earlier version of the scanning tunneling microscope that enabled real-space imaging of the Si(111)-7×7 structure. Lower, a schematic of it. See Binnig and Rohrer (1982). Original photograph courtesy of Ch. Gerber.

- STM invented by Gerd Binnig and Heinrich Rohrer in 1982
- Led to Nobel Prize in Physics, 1986

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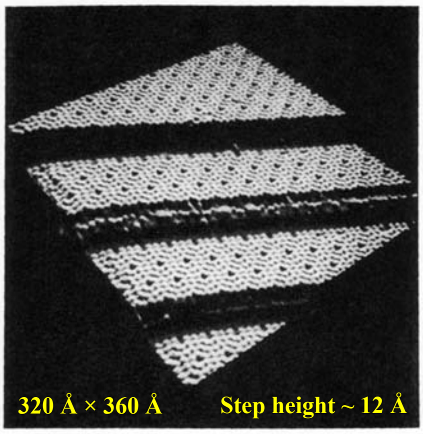
Si(111)-7×7: "Stairway to Heaven"



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Scanning Tunneling Microscope Schematic

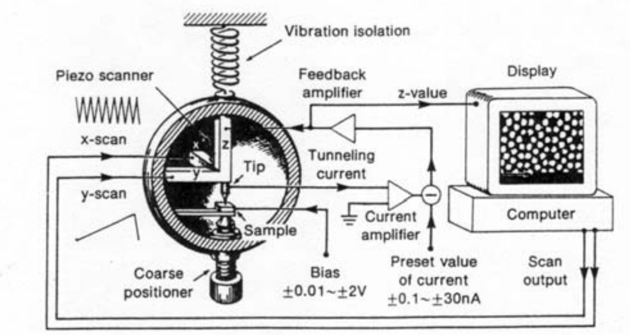

Fig. 1.1. Schematic diagram of the scanning tunneling microscope.

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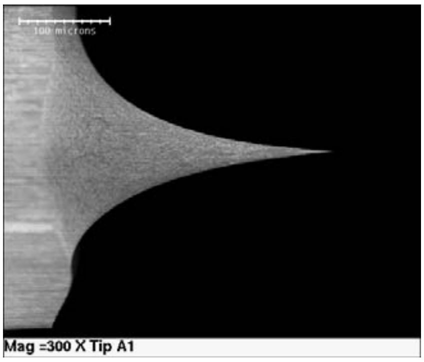
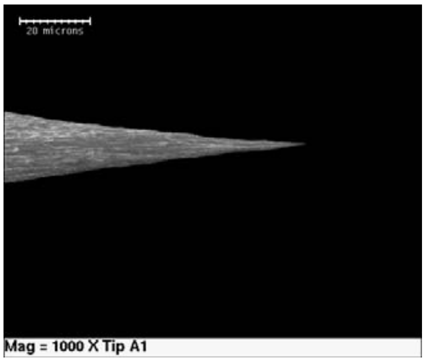
Tungsten STM Tip





- Electrochemically etched using NaOH
- Ideally, the tip is atomically sharp

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One-Dimensional Tunnel Junction

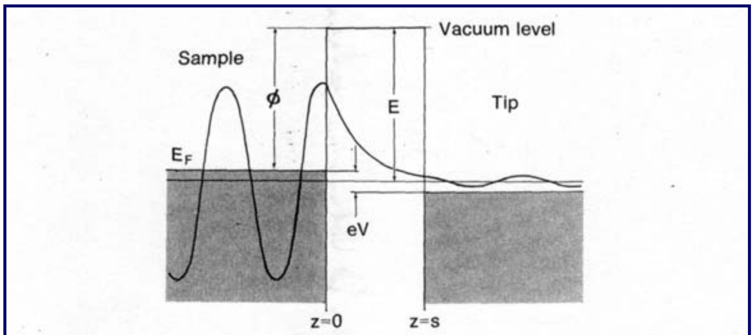

Fig. 1.4. A one-dimensional metal–vacuum–metal tunneling junction. The sample, left, and the tip, right, are modeled as semi-infinite pieces of free-electron metal.

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Tunneling Current – Approach #1

Assume metal-vacuum-metal junction, solve Schrödinger Equation:

$$I \propto V\rho_s e^{-2kW}, \text{ where } k = \frac{\sqrt{2m\phi}}{\hbar} = 0.51\sqrt{\varphi(eV)}\ \text{Å}^{-1}$$

I = tunneling current
V = tip-sample voltage
ρ_s = local density of states of sample
W = width of barrier

Typically, $\varphi \sim 4$ eV → $k \sim 1$ Å^{-1}

→ Current decays by $e^2 \sim 7.4$ times per Å

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Bardeen Tunneling Theory

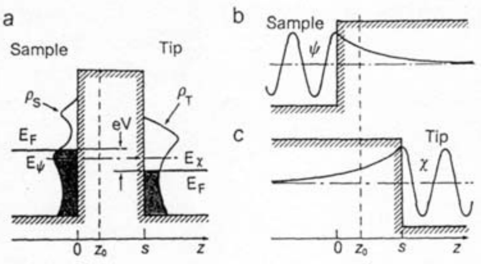

Fig. 1.20. The Bardeen approach to tunneling theory. Instead of solving the Schrödinger equation for the coupled system, a, Bardeen (1960) makes clever use of perturbation theory. Starting with two free subsystems, b and c, the tunneling current is calculated through the overlap of the wavefunctions of free systems using the *Fermi golden rule*.

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Tunneling Current – Approach #2

Consider overlap of wavefunctions from either side of barrier:

Using Fermi's Golden Rule (assuming kT << energy resolution of the measurement),

sample — tip

$$I \propto \int_0^{eV} \rho_s(E_F - eV + \varepsilon)\rho_t(E_F + \varepsilon)d\varepsilon$$

For a free electron metal tip, ρ_t is constant:

$$\frac{dI}{dV} \propto \rho_s(E_F - eV)$$ → STM Spectroscopy

Atomic Force Microscopy (AFM)

- Invented at Stanford by Binnig and Quate in 1986
- Bring tip-mounted micromachined cantilever into contact or close proximity of the surface
- "Atomic forces" deflect cantilever and is detected with laser deflection into a position sensitive photodiode
- Cantilever deflection is control signal for the feedback loop
- AFM can be done on "any surface" (i.e., conductive, insulating, semiconducting, biological, etc.) in "any environment" (i.e., air, vacuum, liquid, etc.)

Force Detection with Optical Beam Deflection

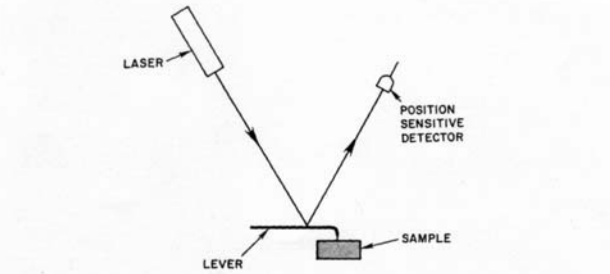

Fig. 15.7. Detection of cantilever deflection by optical beam deflection. A light beam, typically from a solid-state laser, is reflected by the top surface of the cantilever. The cantilever is vacuum deposited with gold, which reflects red light almost perfectly. The deflection of the mechanical cantilever deflects the optical beam, thus changing the proportion of light falling on the two halves of the split photodiode. The difference of the signals from the two halves of the photodiode is detected. (Reproduced from Meyer and Amer, 1988, with permission.)

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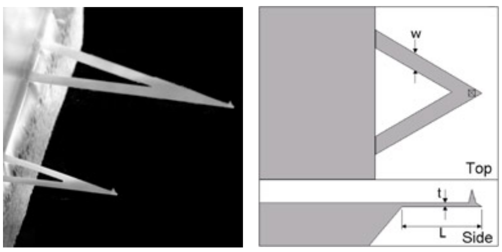
Atomic Force Microscope Cantilevers

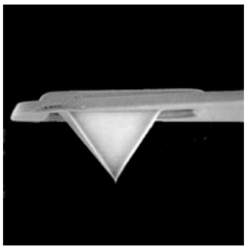


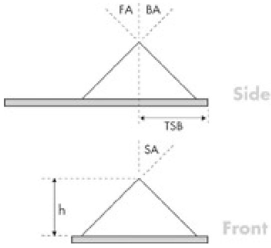
L = 100 µm
w = 20 µm
t = 0.5 µm

- Fabricated using conventional microfabrication procedures
- Backside coated with an optically reflective material (e.g., Au)

https://www.veecoprobes.com/

Atomic Force Microscope Tips





h = 3 μm
Angles = 35º

- Typical radius of curvature is ~ 10 nm
- Tips are often coated with conductive materials, magnetic materials, low wear materials, or organic/biological molecules.

https://www.veecoprobes.com/

Fluid Cell for Atomic Force Microscopy

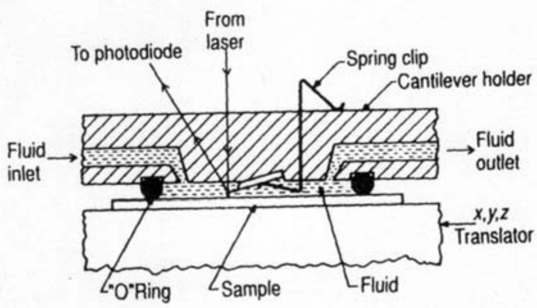


Fig. 15.10. Fluid cell for AFM study of electrochemistry. (Reproduced from Manne et al., 1991, with permission.)

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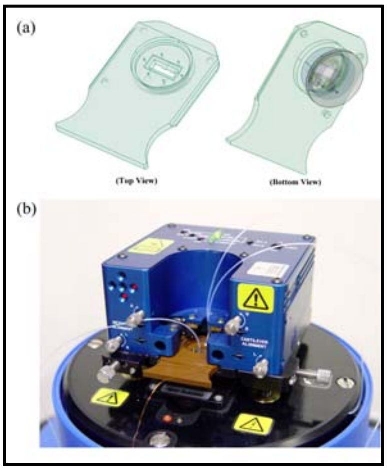
AFM Photographs

Thermomicroscopes
CP Research AFM



Custom Liquid Cell

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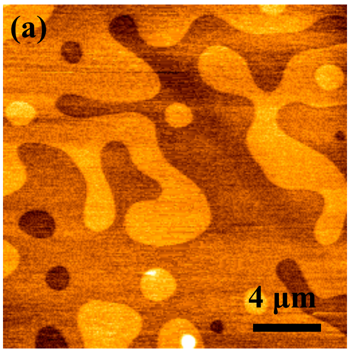
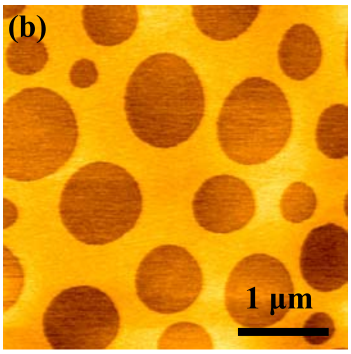
AFM Images of Hematite





- Measured atomic step height of 2.2 Å
- Vertical spatial resolution of ~0.1 Å in air.

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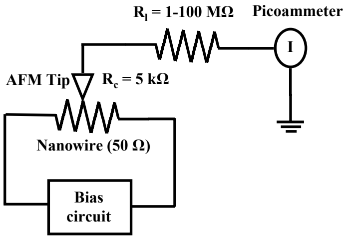
Contact Mode AFM Potentiometry

Experimental setup:



Resolution requirements:

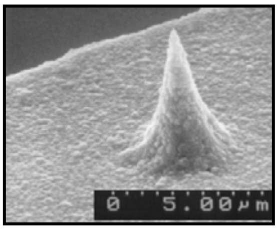
To analyze nanowire failure,

- Spatial resolution < 10 nm
- Voltage sensitivity < 100 µV

Requirements of AFM tip:

- Conductive tip with small R_c (kΩ range).
- Low R_c must be sustained after extensive scanning in contact mode.

Conductive diamond coated Si tips provide R_c = 5 kΩ with low wear at a repulsive force of 0.54 µN.



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Noncontact vs. Contact AFM Potentiometry

Noncontact mode: | **Contact mode:** | **Contact mode:**

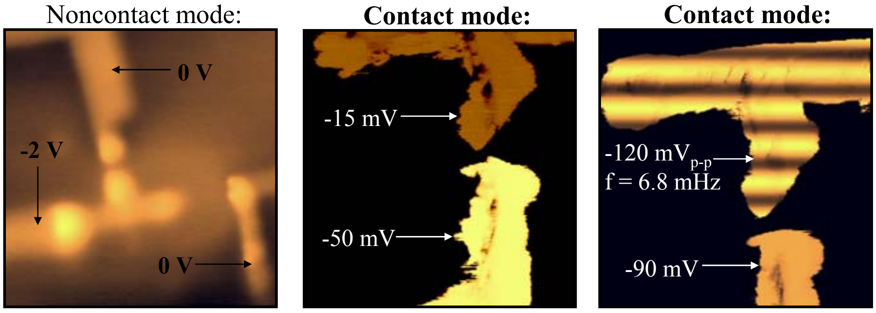

Image size = (1000 nm)^2 | Image size = (500 nm)^2 | Image size = (500 nm)^2

- Noncontact mode AFM potentiometry possesses **~50 mV** potential sensitivity and **~50 nm** spatial resolution.
- Contact mode AFM potentiometry possesses **~1 µV** potential sensitivity, **~5 nm** spatial resolution, and **~0.01 ms** time response.

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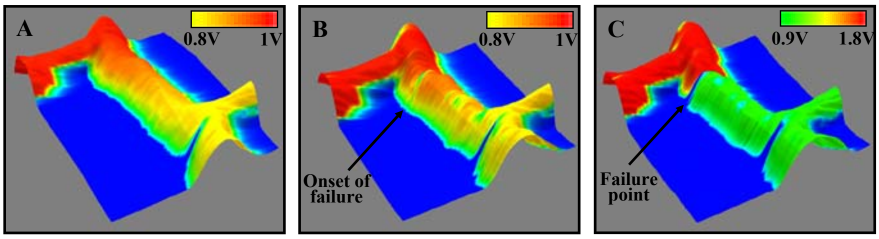
AFM Potentiometry of Nanowire Failure

Evolution of nanowire failure:



Contact mode AFM potentiometry images: Wire width = 60 nm

(Breakdown current density = 3.75×10^{12} A/m^2).

M. C. Hersam, *et al.*, *Appl. Phys. Lett.*, **72**, 915 (1998).

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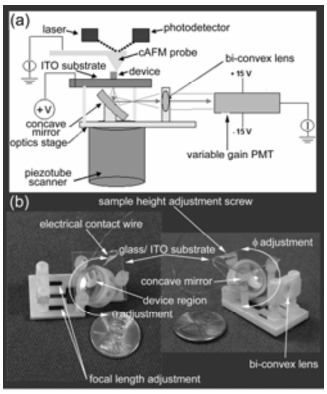
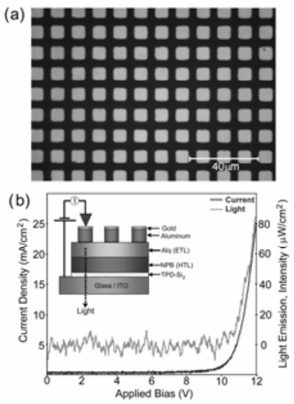
Atomic Force Electroluminescence Microscopy





L. S. C. Pingree, *et al.*, *Appl. Phys. Lett.*, **85**, 344 (2004).

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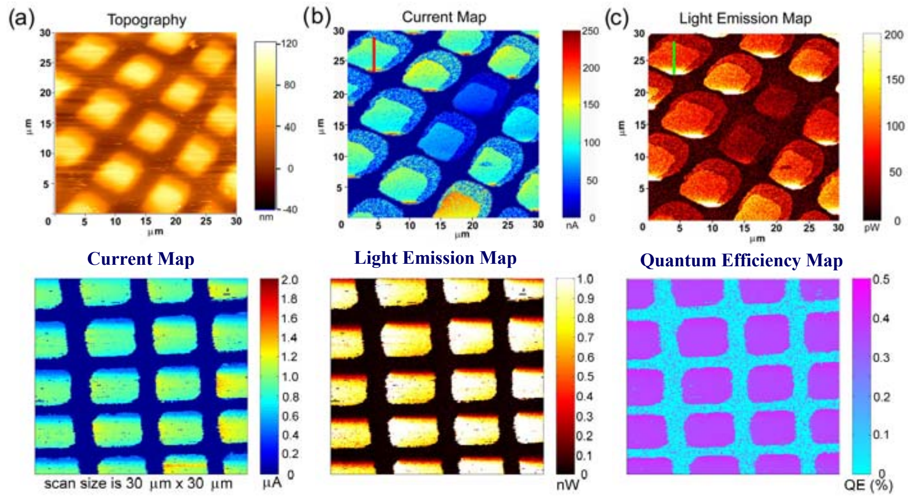
AFEM on Organic LED Arrays



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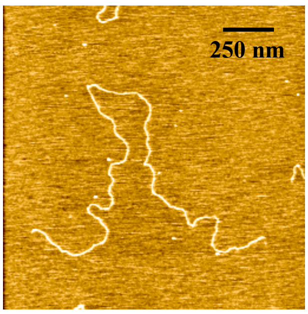
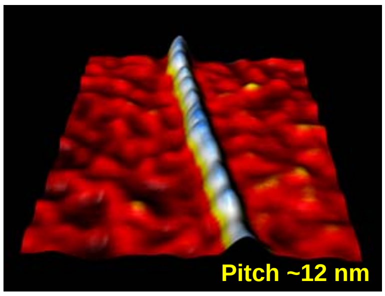
"Single Molecule Imaging" with Ambient AFM

DNA Molecules



DNA Wrapped SWNTs



Typical ambient AFM resolution is ~10 nm as opposed to atomic resolution for STM → STM is typically the technique of choice for intramolecular spatial resolution imaging

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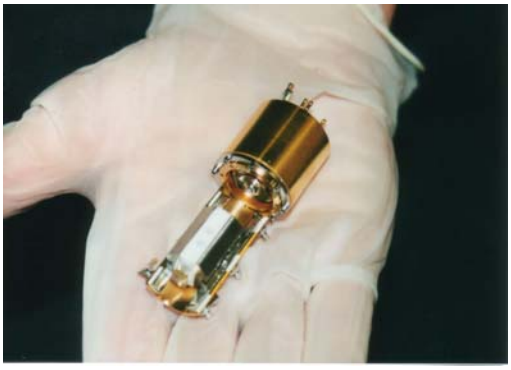
Example Ultra-high Vacuum (UHV) STM Design



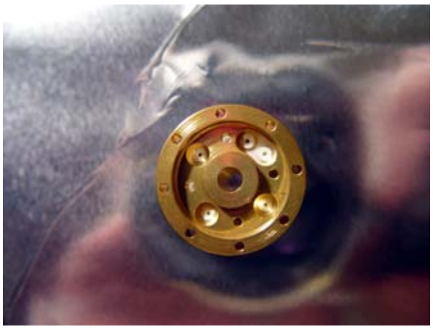
- Homebuilt STM in the Hersam lab at Northwestern University
- STM is a modified Lyding scanner

Scanner Construction: Piezotubes

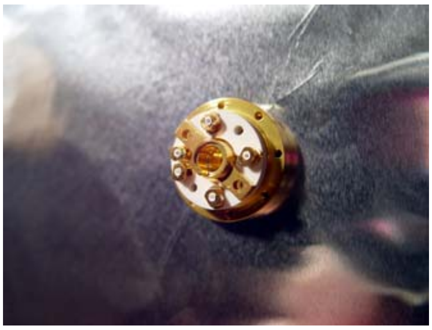
Outer tube:
0.650" OD
0.570" ID
0.750" Long

Inner tube:
0.375" OD
0.315" ID
0.750" Long

Scanner Construction: Base Plug



Front View



Rear View

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Scanner Construction: Piezotubes Soldered into Base Plug

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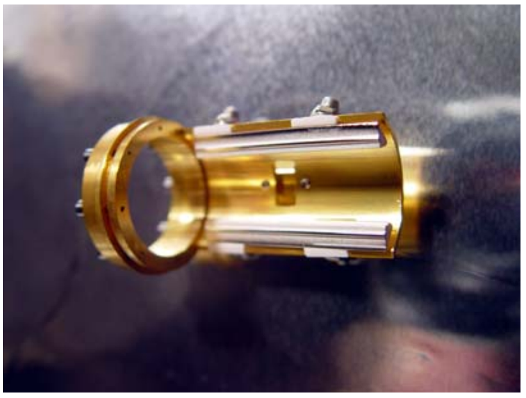
Scanner Construction: Course Translation Platform



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Scanner Construction: Course Translation Platform Soldered onto Outer Piezotube

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Scanner Construction: End Cap Positioned onto Inner Piezotube

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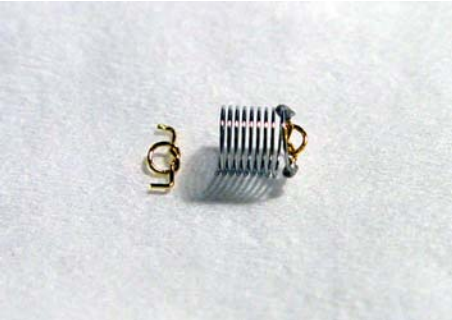
Scanner Construction: Tip Contact Assembly



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Scanner Construction: Full Tip Assembly


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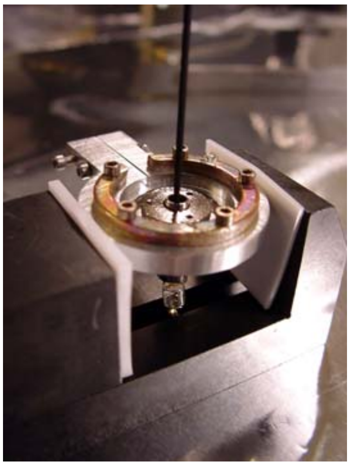
Scanner Construction: Adjusting Clamping Force on Sapphire Washer and Soldering into Inner Piezotube End Cap



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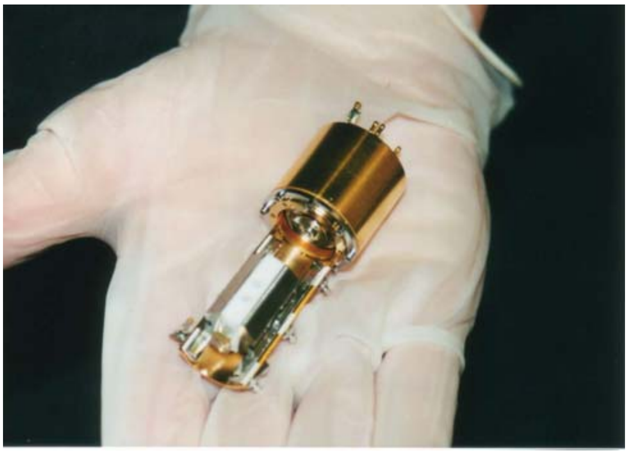
Scanner Complete



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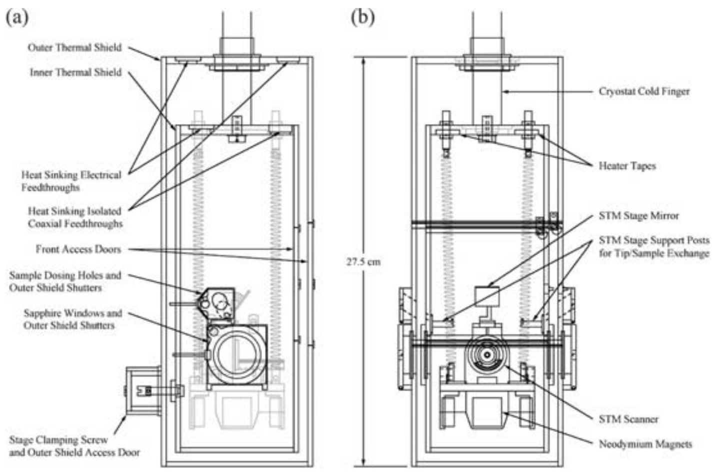
Cryogenic Variable Temperature UHV STM



E. T. Foley, *et al.*, *Rev. Sci. Instrum.*, **75**, 5280 (2004).

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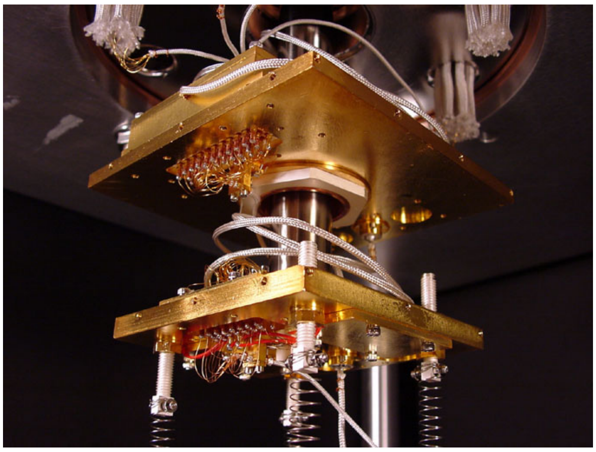
Vibration Isolation

Detail of Roof Plate



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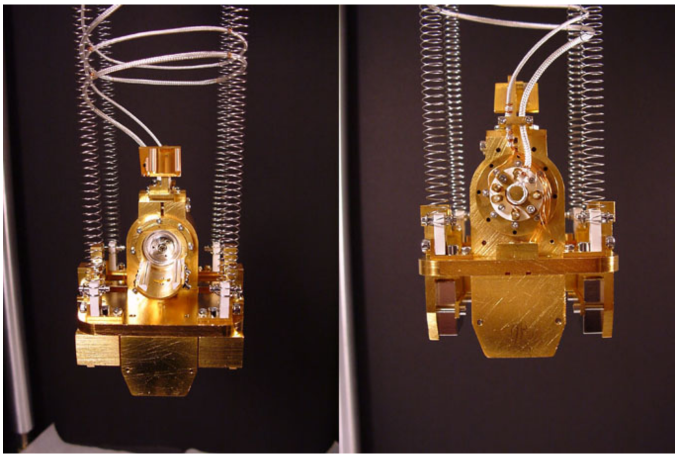
Detail of STM Stage



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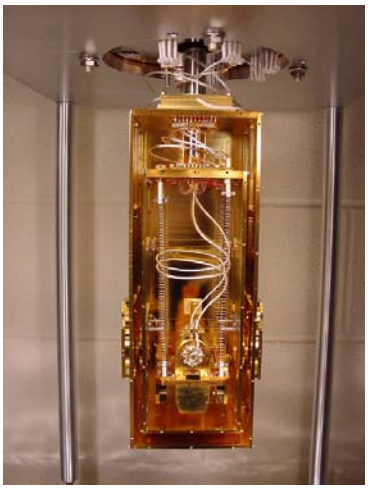
Thermal Shields with Back Panel Removed



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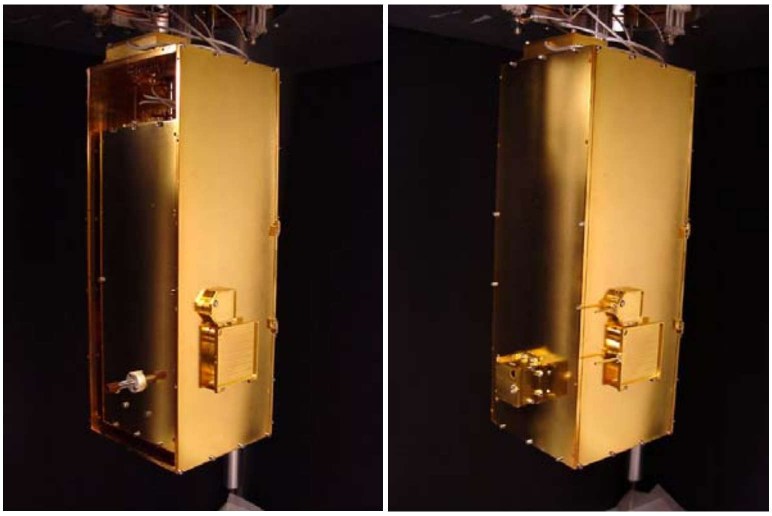
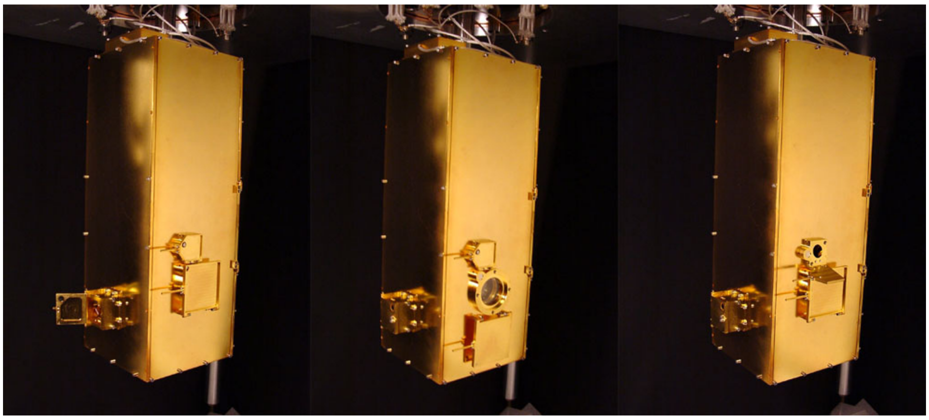
Stage Locking Screw for Cooldown



Rear Door and Shutter Action



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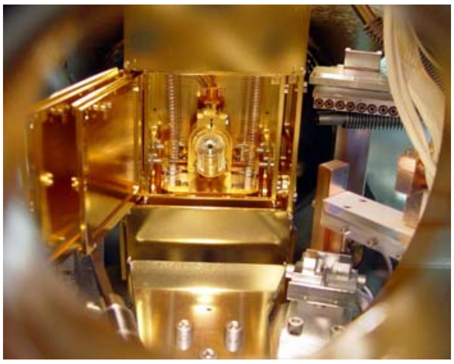
Front Doors Open for STM Access



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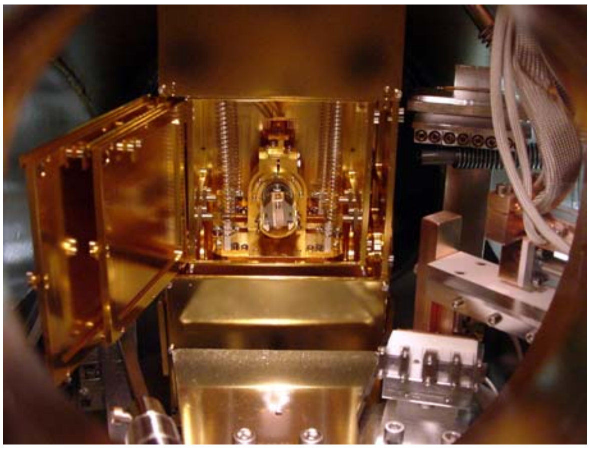
Sample and Probe Mounted for Scanning



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Mirror Allows for Top-Down View of Tip-Sample Junction

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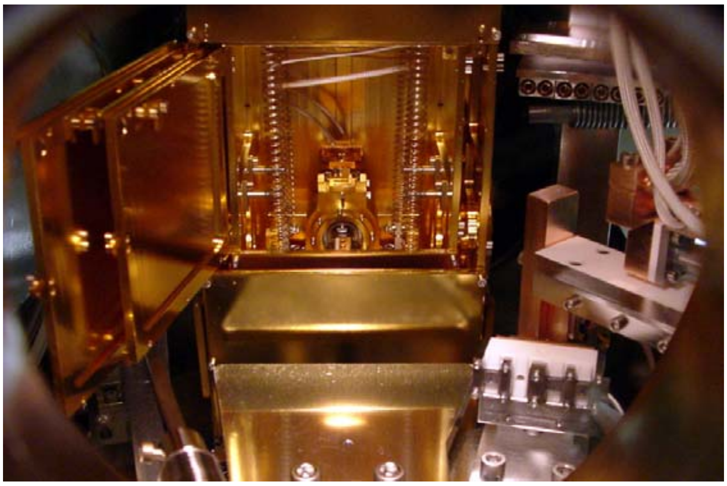
STM Suspended for Scanning



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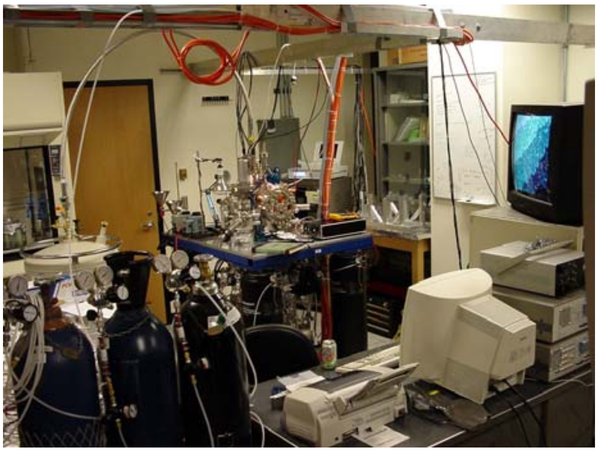
UHV Chamber and Liquid Helium Dewar



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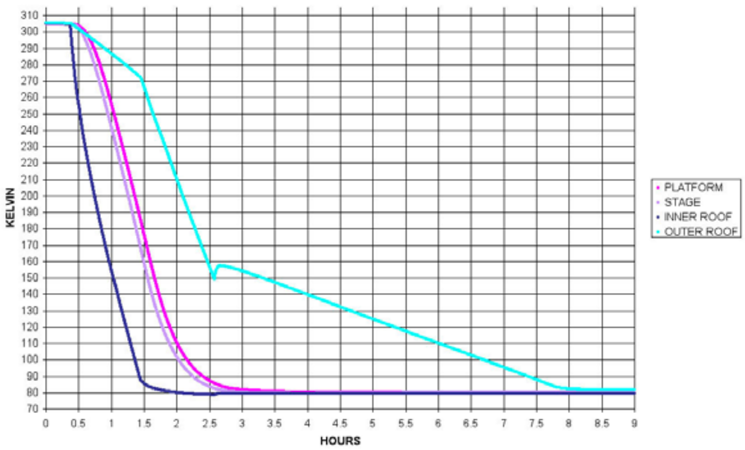
Cooling with Liquid Nitrogen



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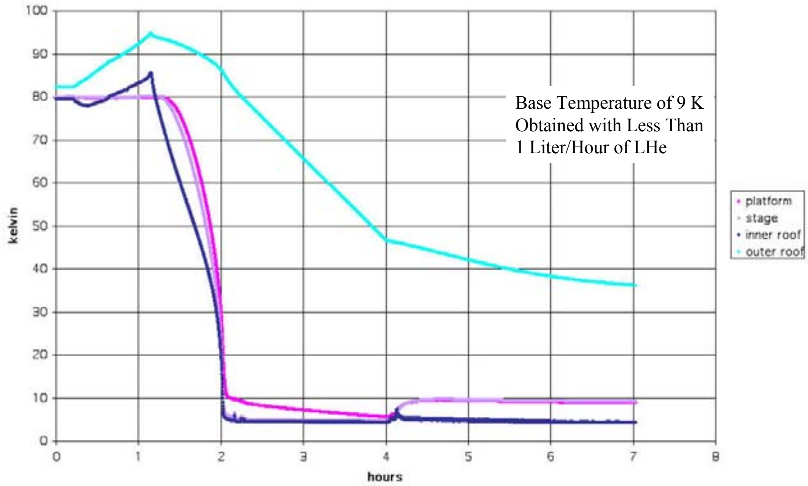
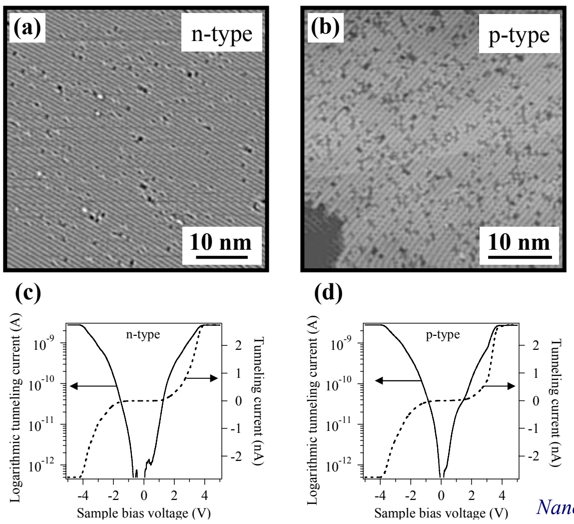
Cooling with Liquid Helium



Degenerately Doped Si(100) Surfaces

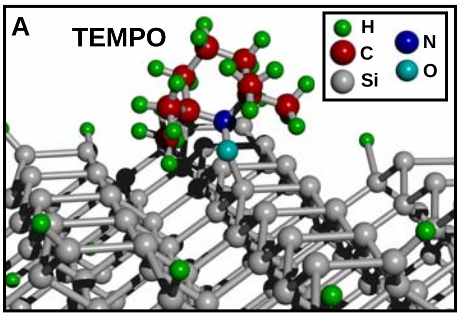


N. P. Guisinger, *et al.*, *Nanotechology*, **15**, S452 (2004).

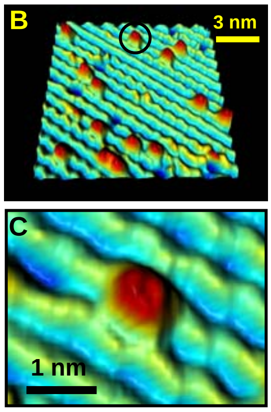
TEMPO on the Si(100)-2×1 Surface

N. P. Guisinger, *et al.*, *Nano Lett.*, **4**, 55 (2004).

TEMPO:
(2,2,6,6-tetramethyl-1-piperidinyloxy)



DFT Optimized Geometry (Hyper Chem Release 7)



Individual TEMPO molecules are probed with the STM

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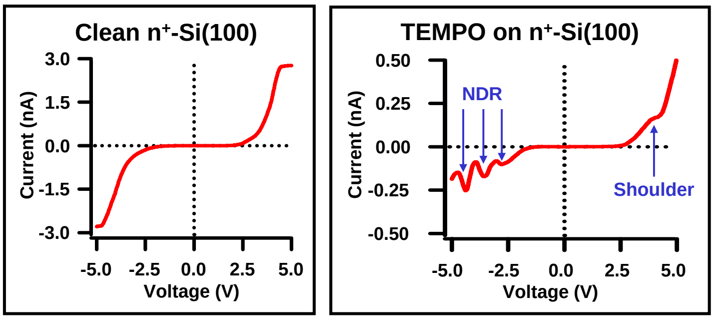
I-V Curve for TEMPO on n^+-Si(100)

N. P. Guisinger, *et al.*, *Nano Lett.*, **4**, 55 (2004).



- NDR events are only observed at negative sample bias.
- Shoulder is only observed at positive sample bias.
- NDR bias values depend sensitively on tip-sample spacing
- NDR is observed in both bias sweep directions

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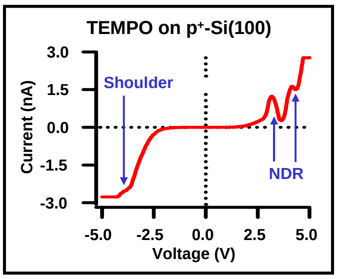
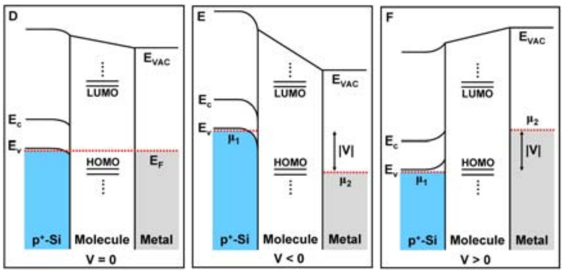
I-V Curve for TEMPO on p^+-Si(100)

N. P. Guisinger, *et al.*, *Nano Lett.*, **4**, 55 (2004).

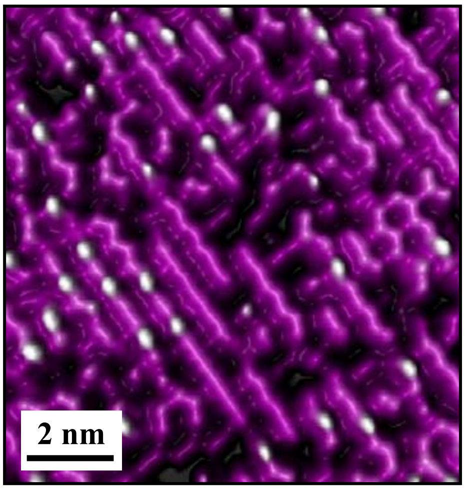




Equilibrium **Shoulder** **NDR**

- Qualitatively similar behavior to TEMPO on n^+-Si(100) except opposite polarity.
- Orbital energy shift may be due to charge transfer with the substrate.

Si(100) Dosed with Cyclopentene at 80 K



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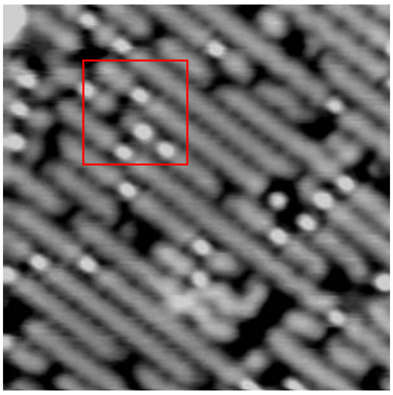
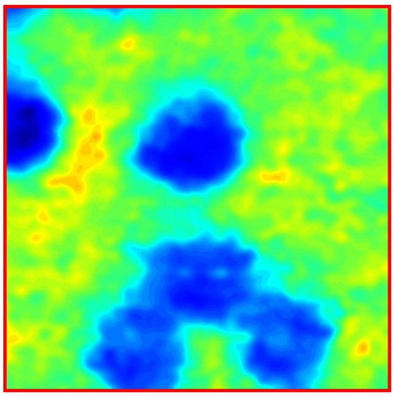
dI/dV Imaging of Cyclopentene on Si(100) at 80 K



150 Å x 150 Å, -2.15 V, 0.1 nA



dI/dV Map at -2.8 V

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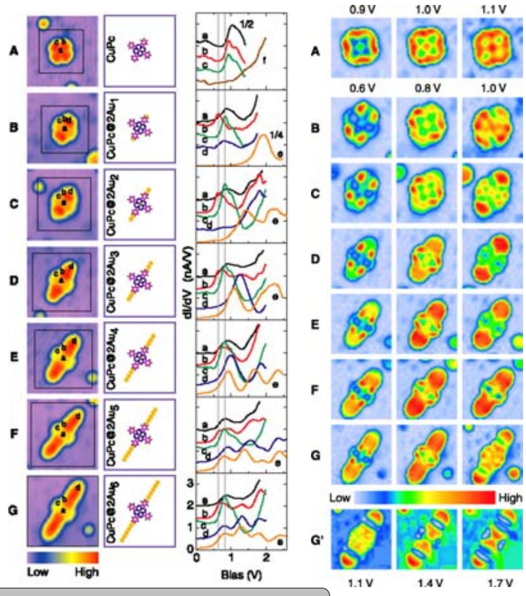
STM Spectroscopy: CuPc and Au Nanoelectrodes on NiAl(110)



G. V. Nazin, *et al.*, *Science*, **302**, 77 (2003).

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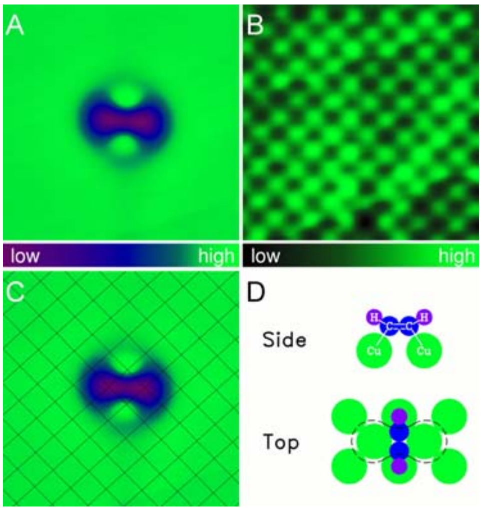
C_2H_2 on Cu(100)



B. C. Stipe, *et al.*,
Science, **280**, 1732 (1998).

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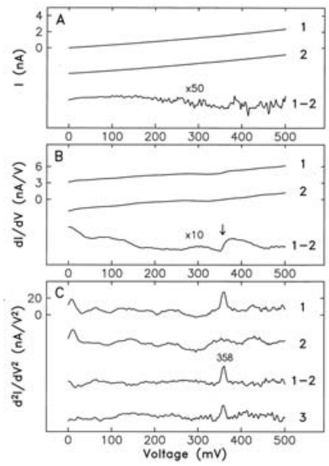
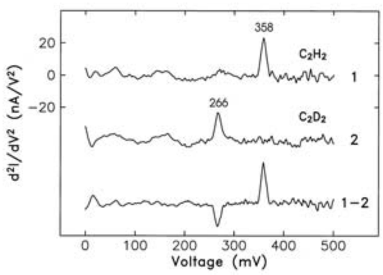
Inelastic Electron Tunneling Spectroscopy





B. C. Stipe, *et al.*,
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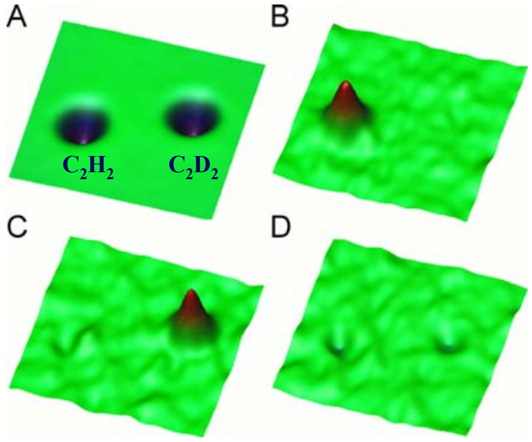
Spatial Maps of d^2I/dV^2

Topo

d^2I/dV^2 @ 358 mV



d^2I/dV^2 @ 266 mV

d^2I/dV^2 @ 311 mV

B. C. Stipe, *et al.*, *Science*, **280**, 1732 (1998).

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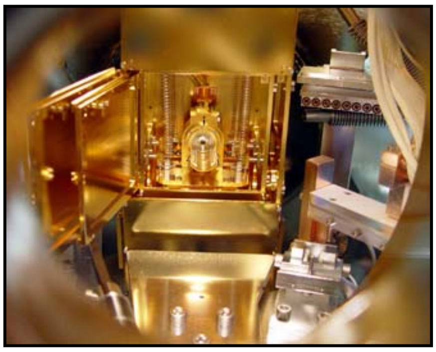
Tip Enhanced Raman Spectroscopy



- TERS is an alternative strategy for single molecule vibrational spectroscopy
- UHV TERS is currently being constructed at Northwestern University.

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