The Interior of Single Molecules

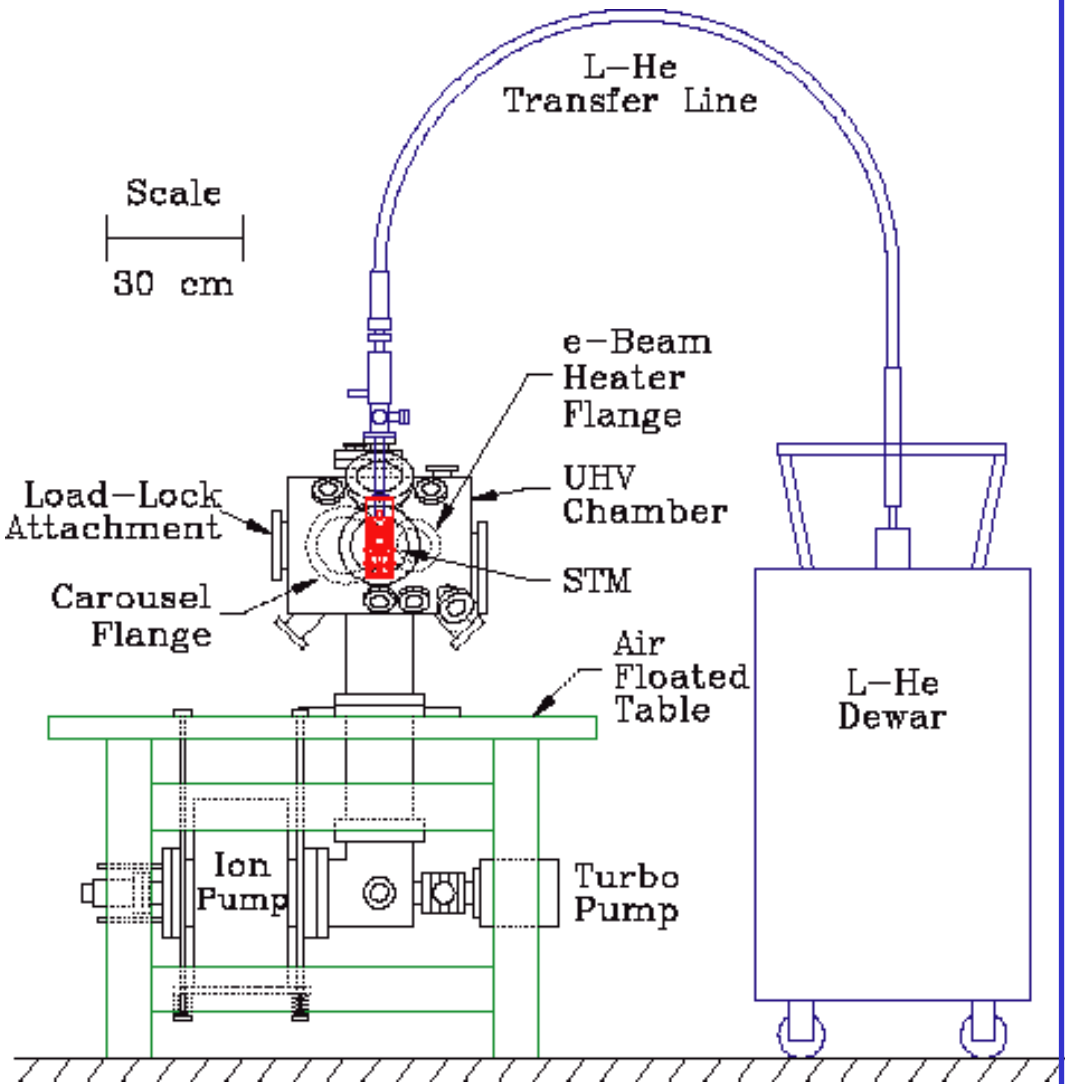
Wilson Ho
University of California, Irvine

Single Molecule Chemistry with STM

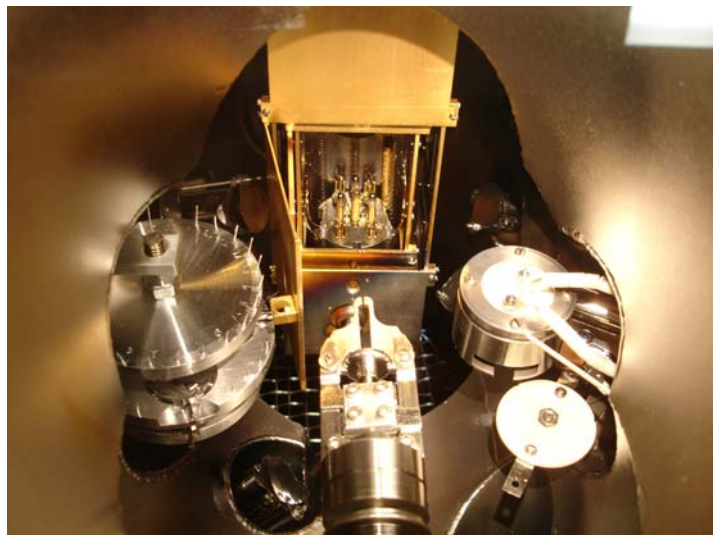
Starting from the bottom: the individual atoms

- Understanding their properties, interactions, assembly, and function – STATIC
- How molecules transform, stimulated by heat, photons,electrons – DYNAMICS
- Control of Chemical Interactions to obtain novel composition, structure, and function

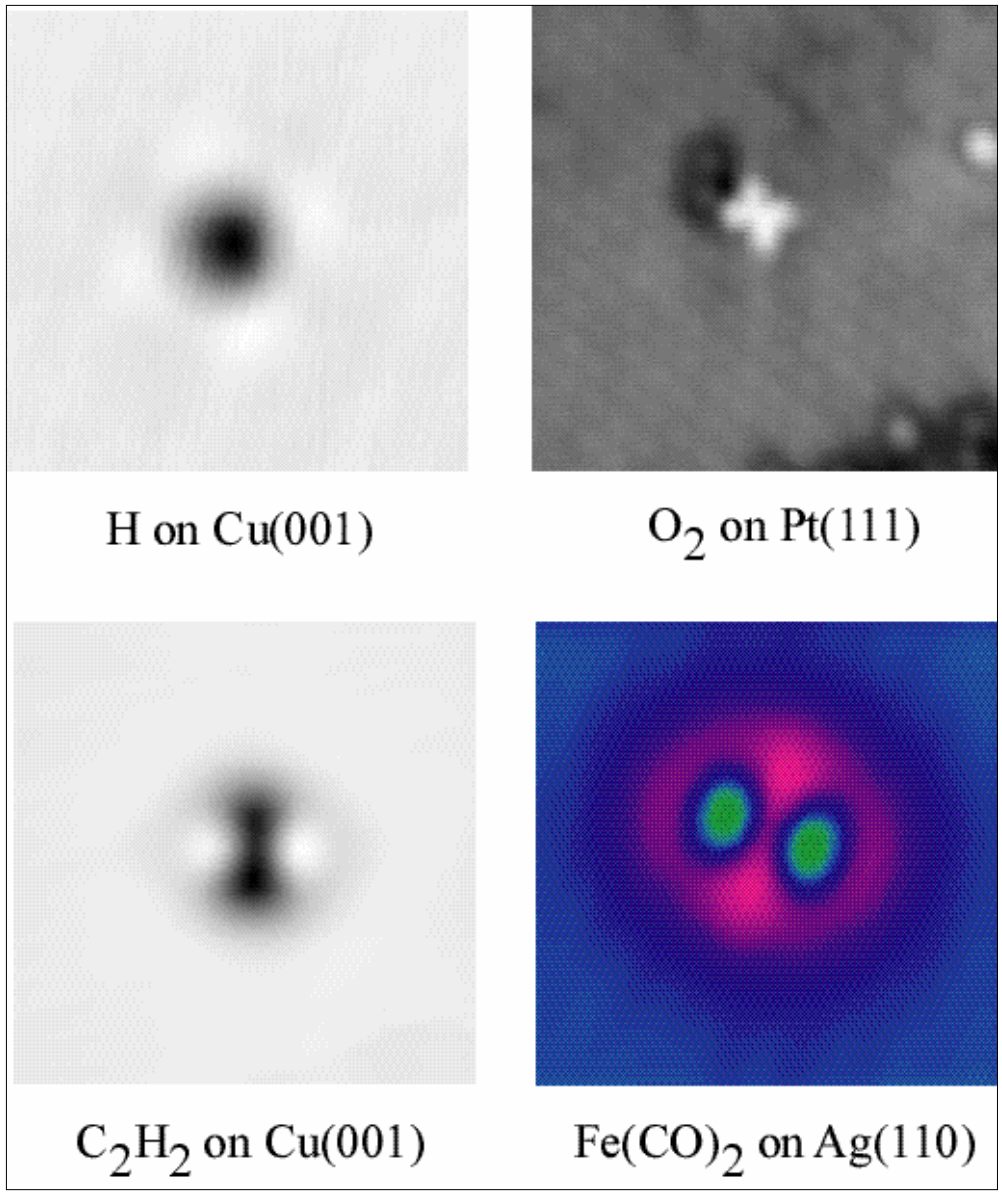
STM Apparatus



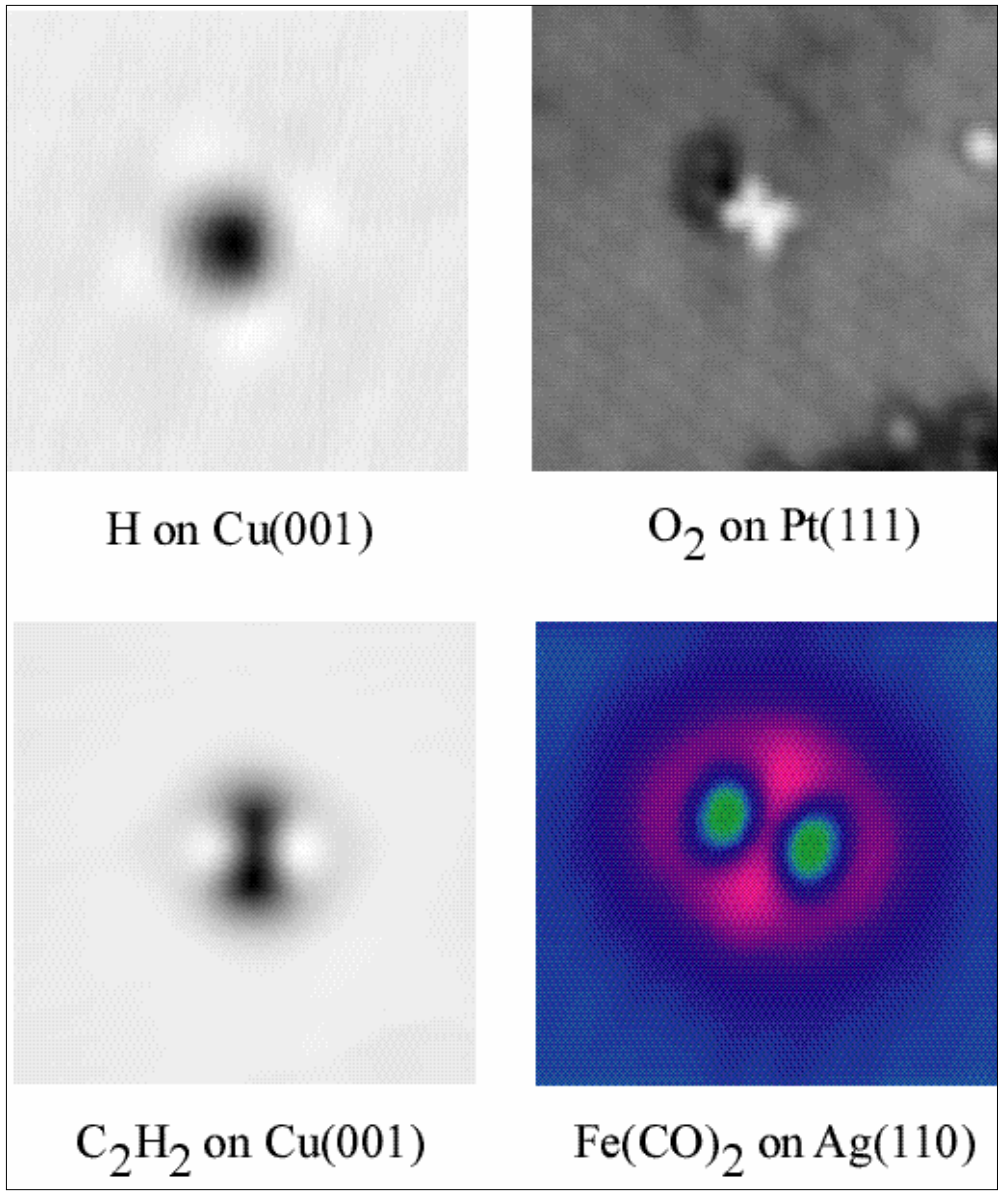
Low temperature (10 K) ultrahigh vacuum STM



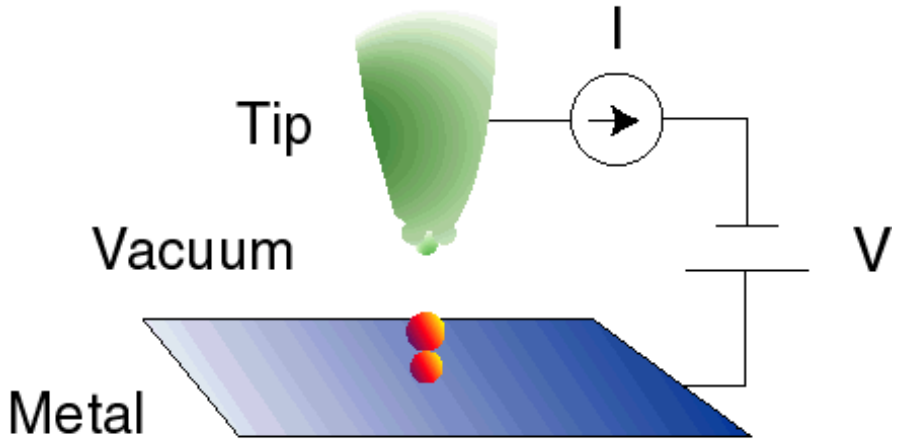
Visualization of Single Molecules

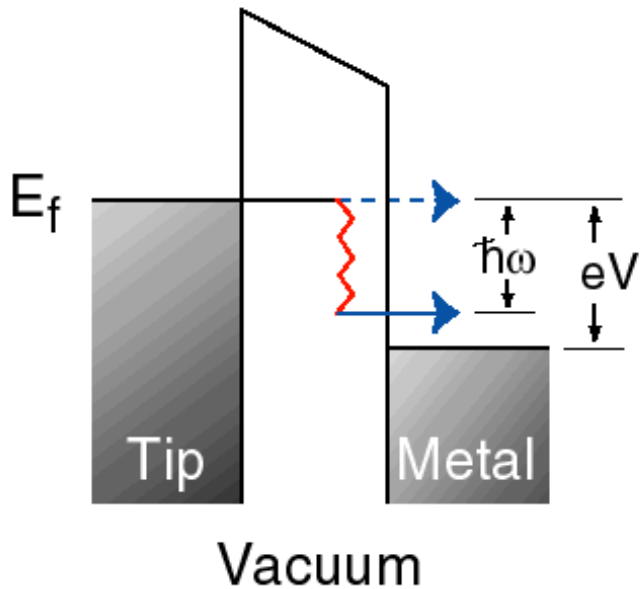


Visualization of Single Molecules

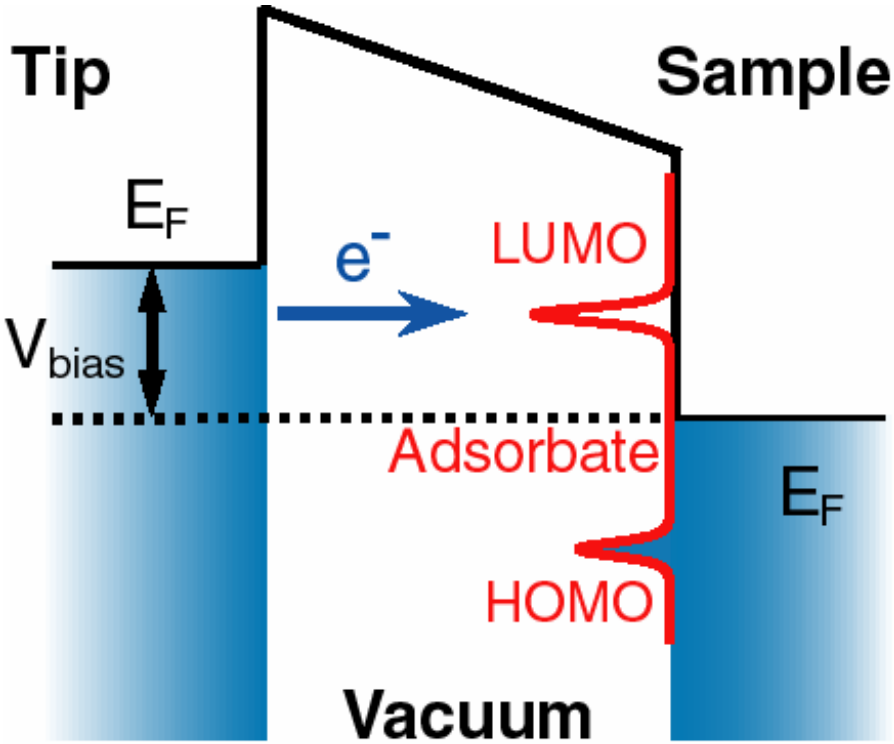


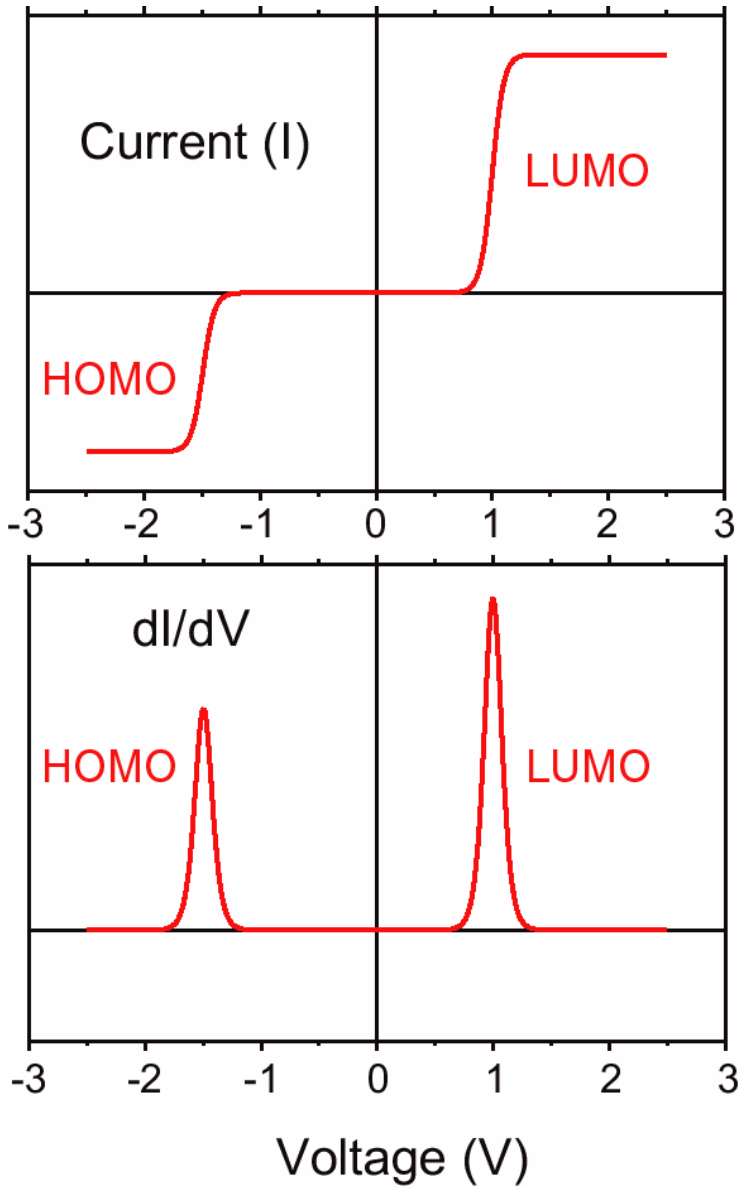
Elastic vs. Inelastic Tunneling



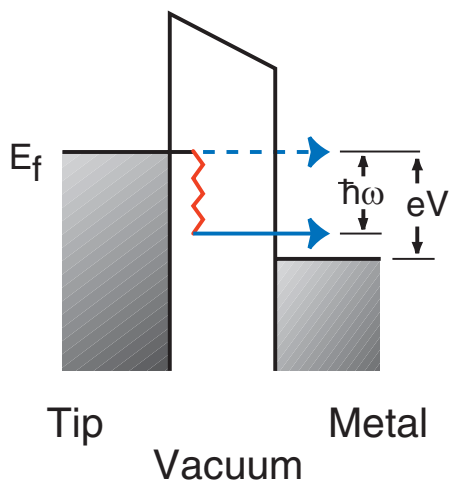


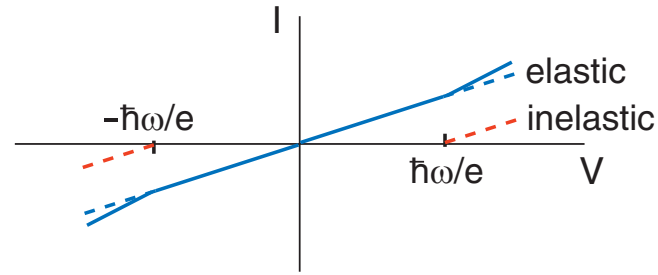
Atomic Scale Electronic Spectroscopy

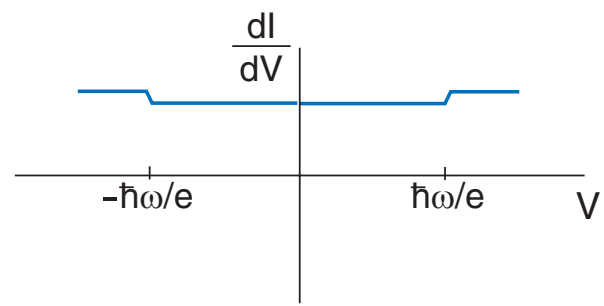


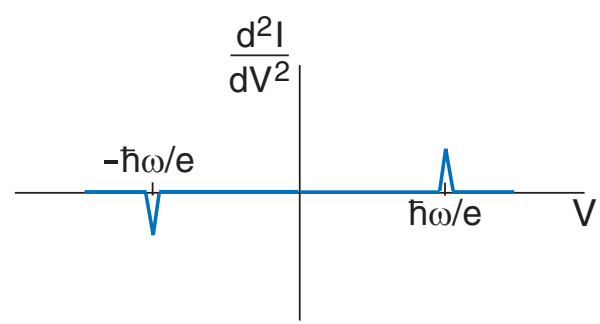


STM
Inelastic Electron Tunneling Spectroscopy

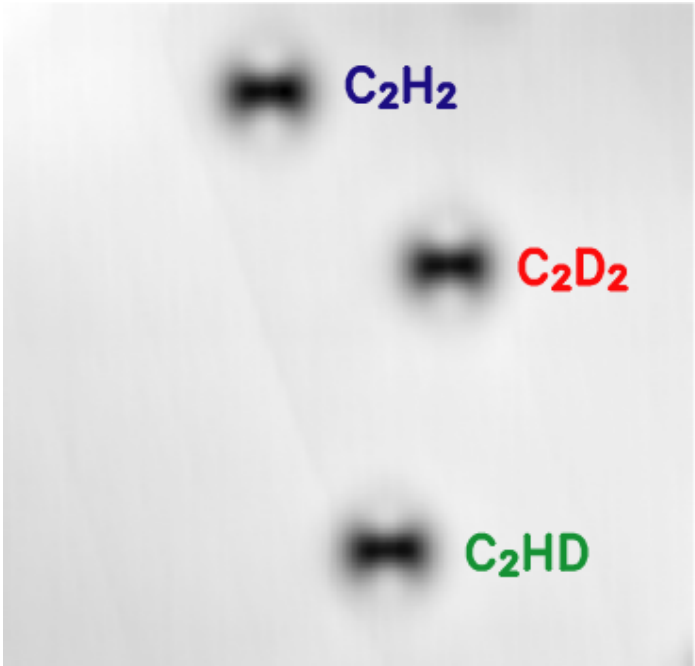


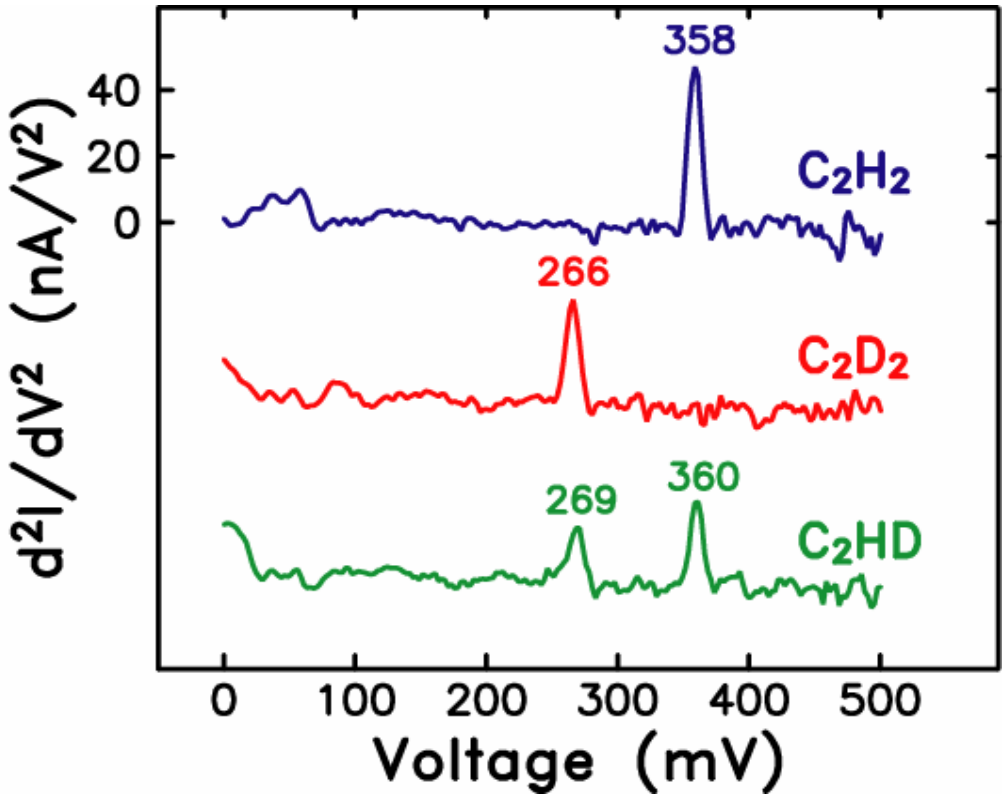




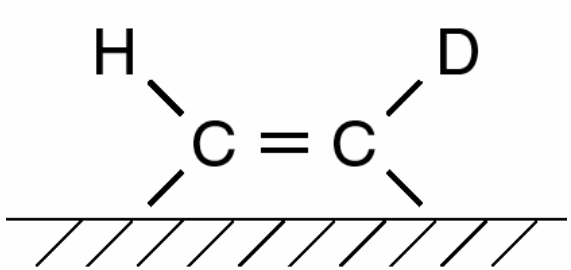


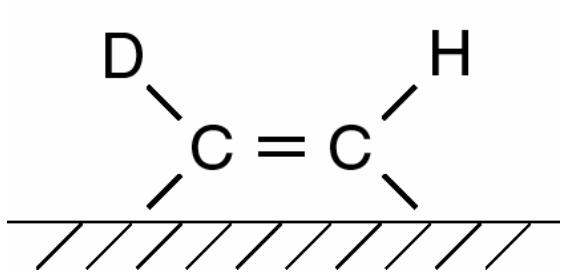
Chemical Identification: Single Acetylene Molecules on Cu(100)

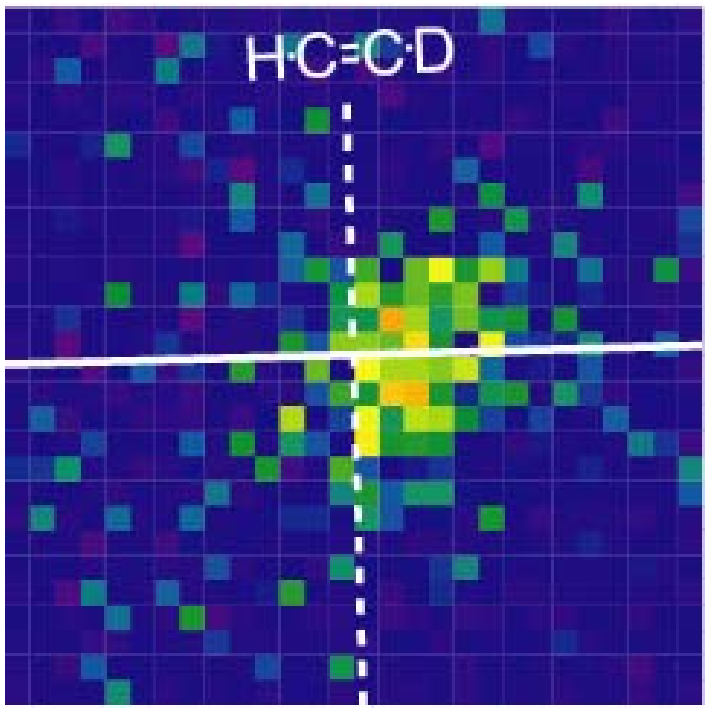


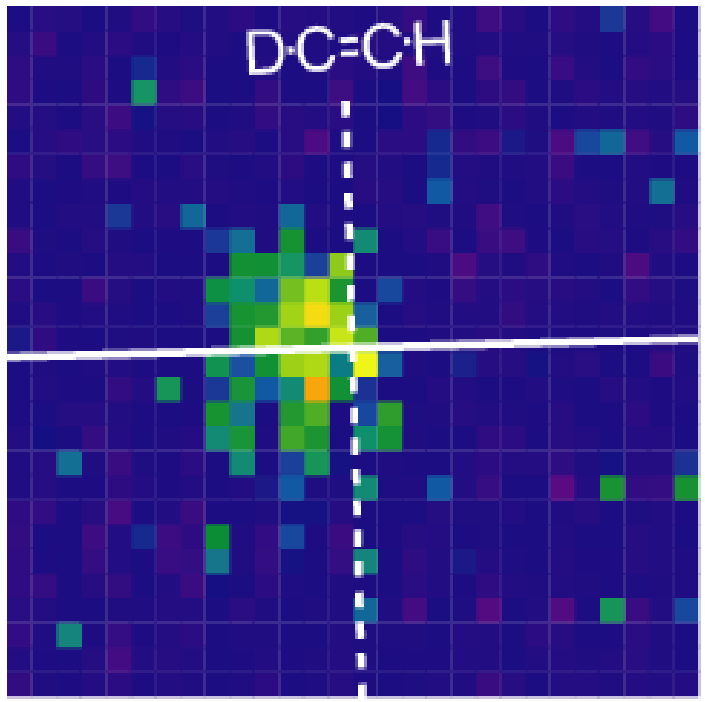


Inside Single Acetylene

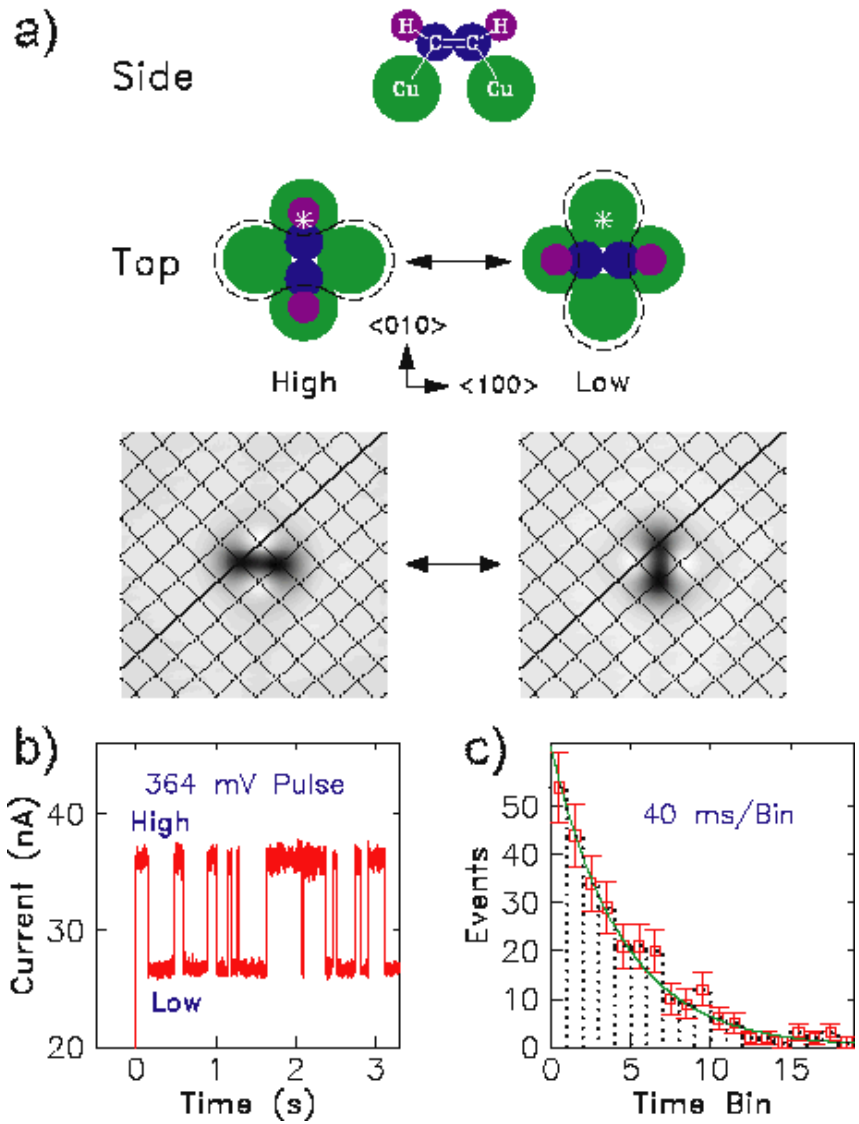




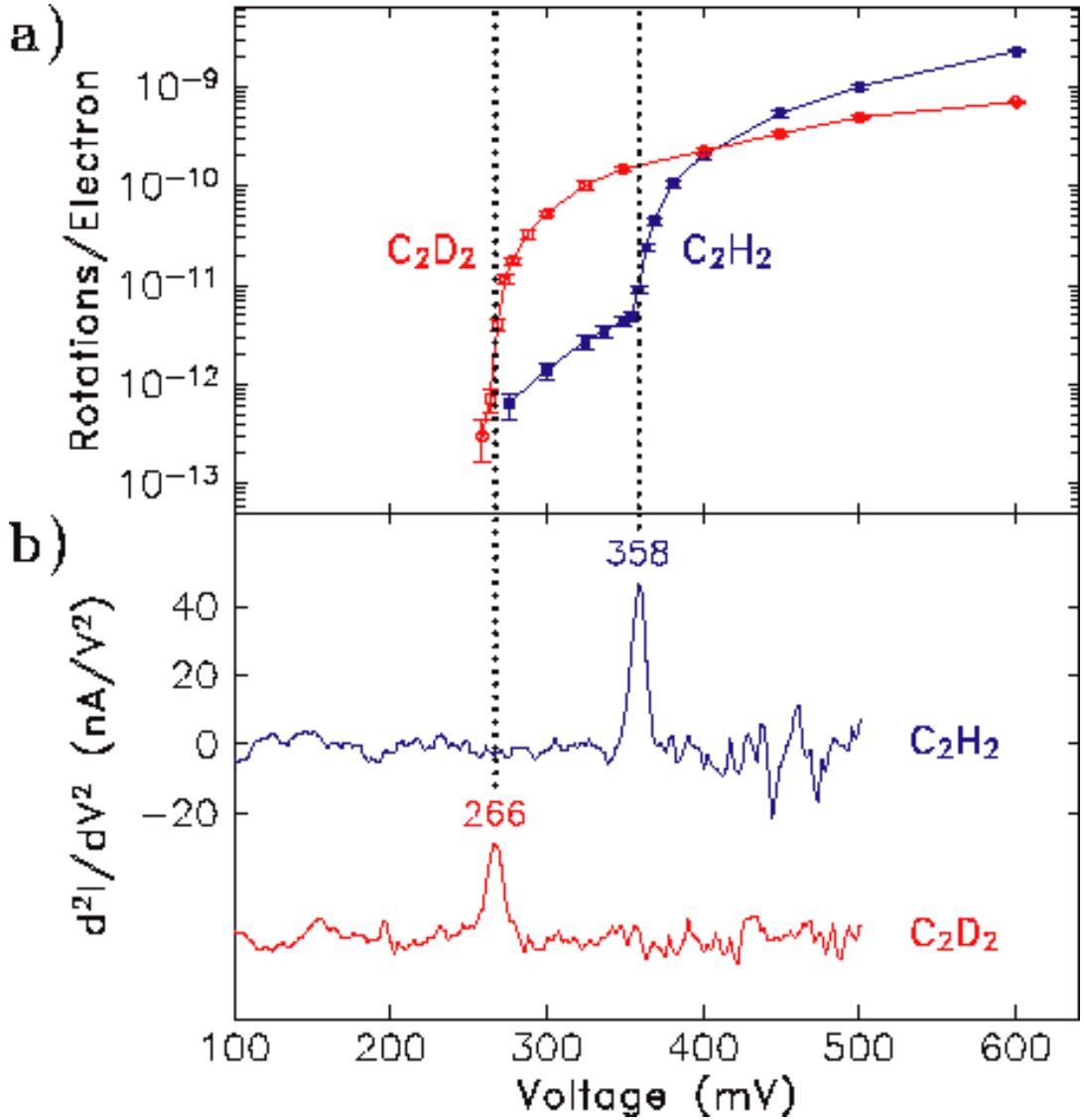




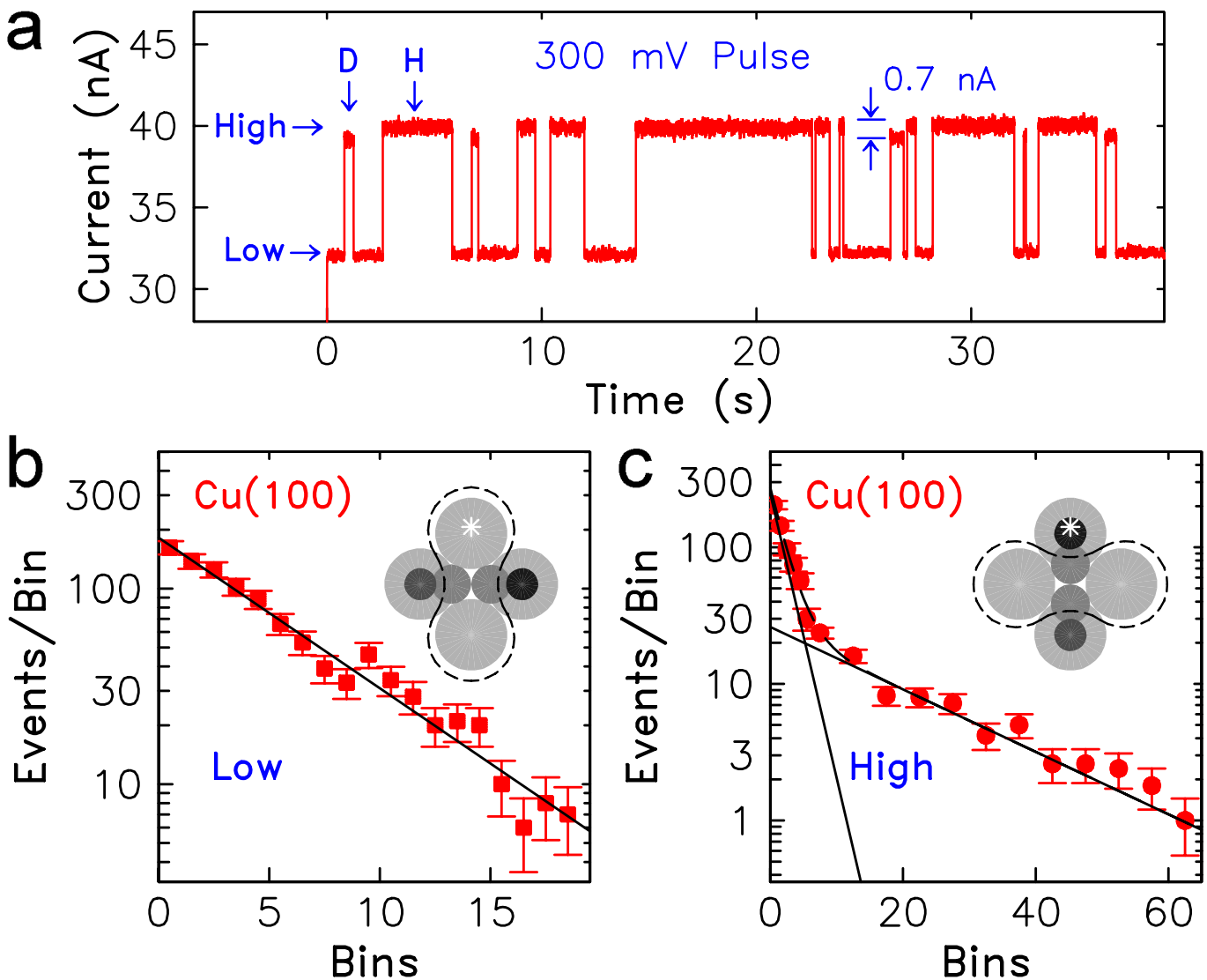
Single Molecule Rotation: Acetylene on Cu(001)



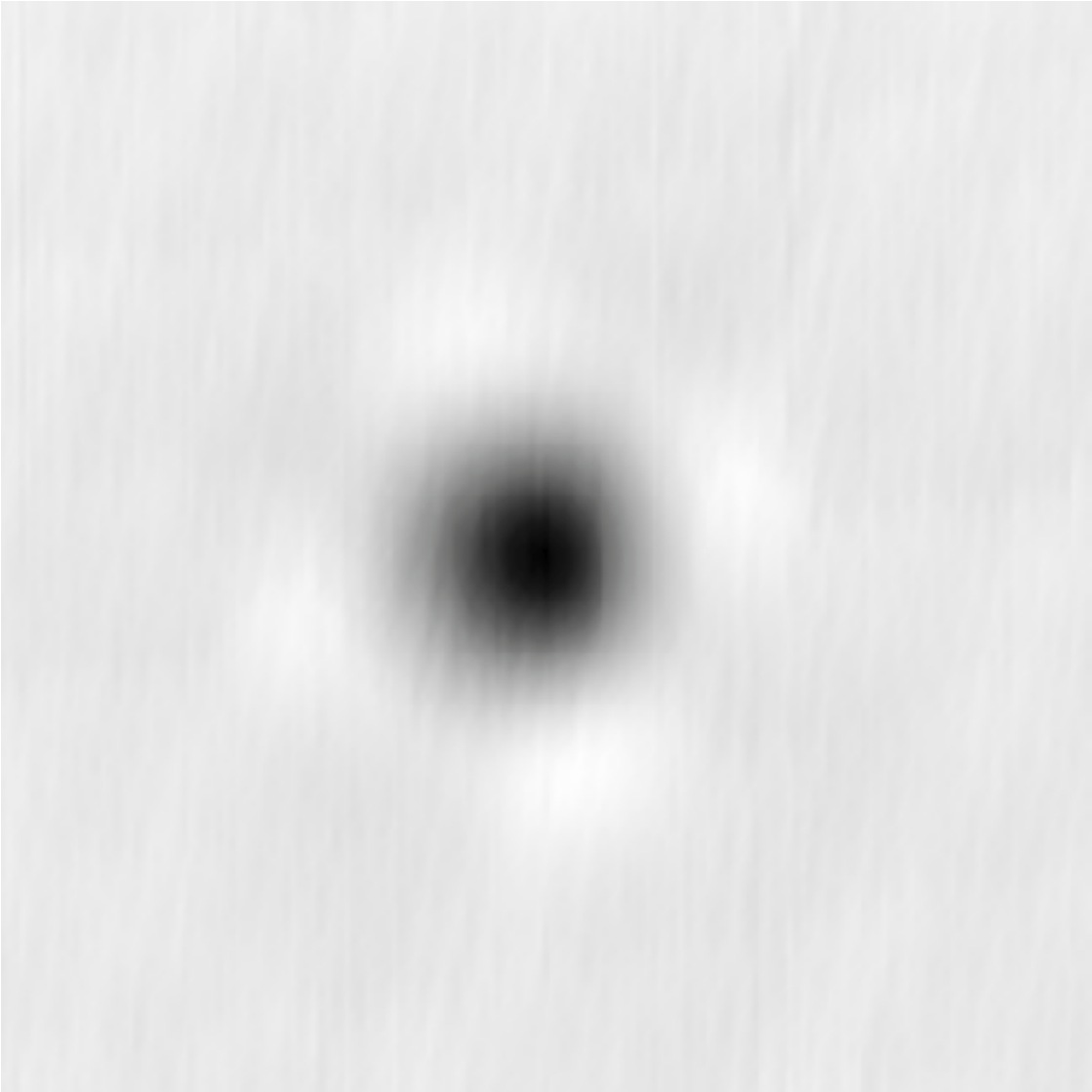
Vibration-Rotation Coupling
Acetylene on Cu(001)



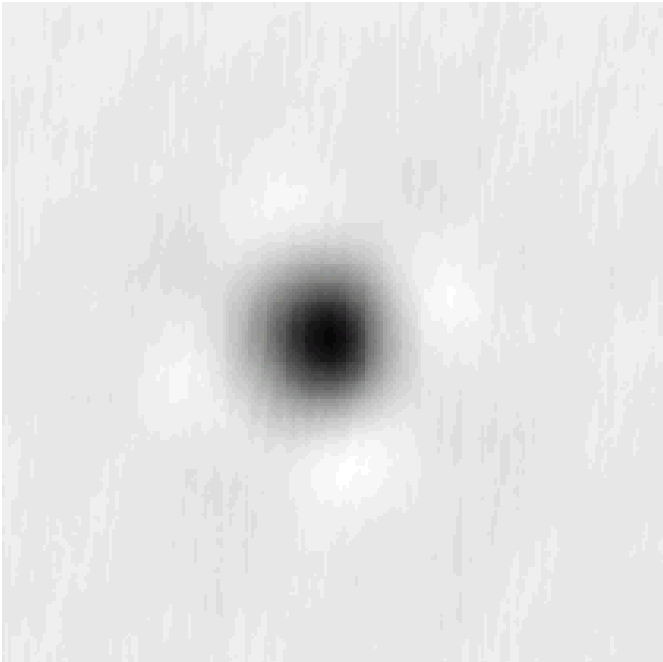
C_2HD Rotation on Cu(001)



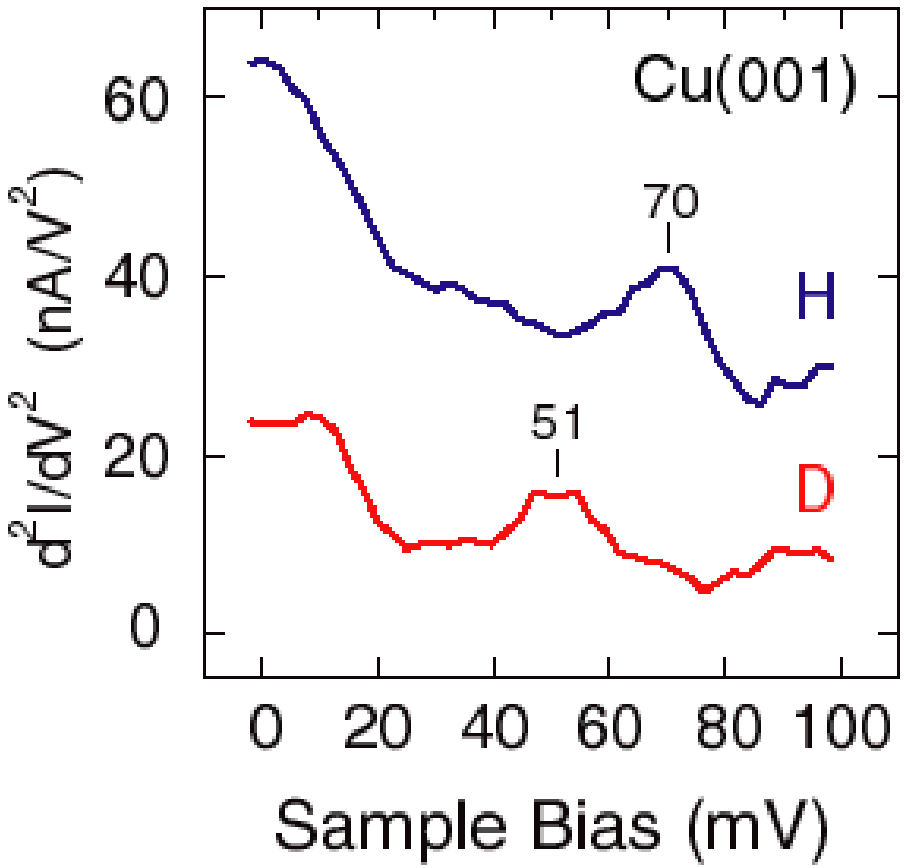
H Atom

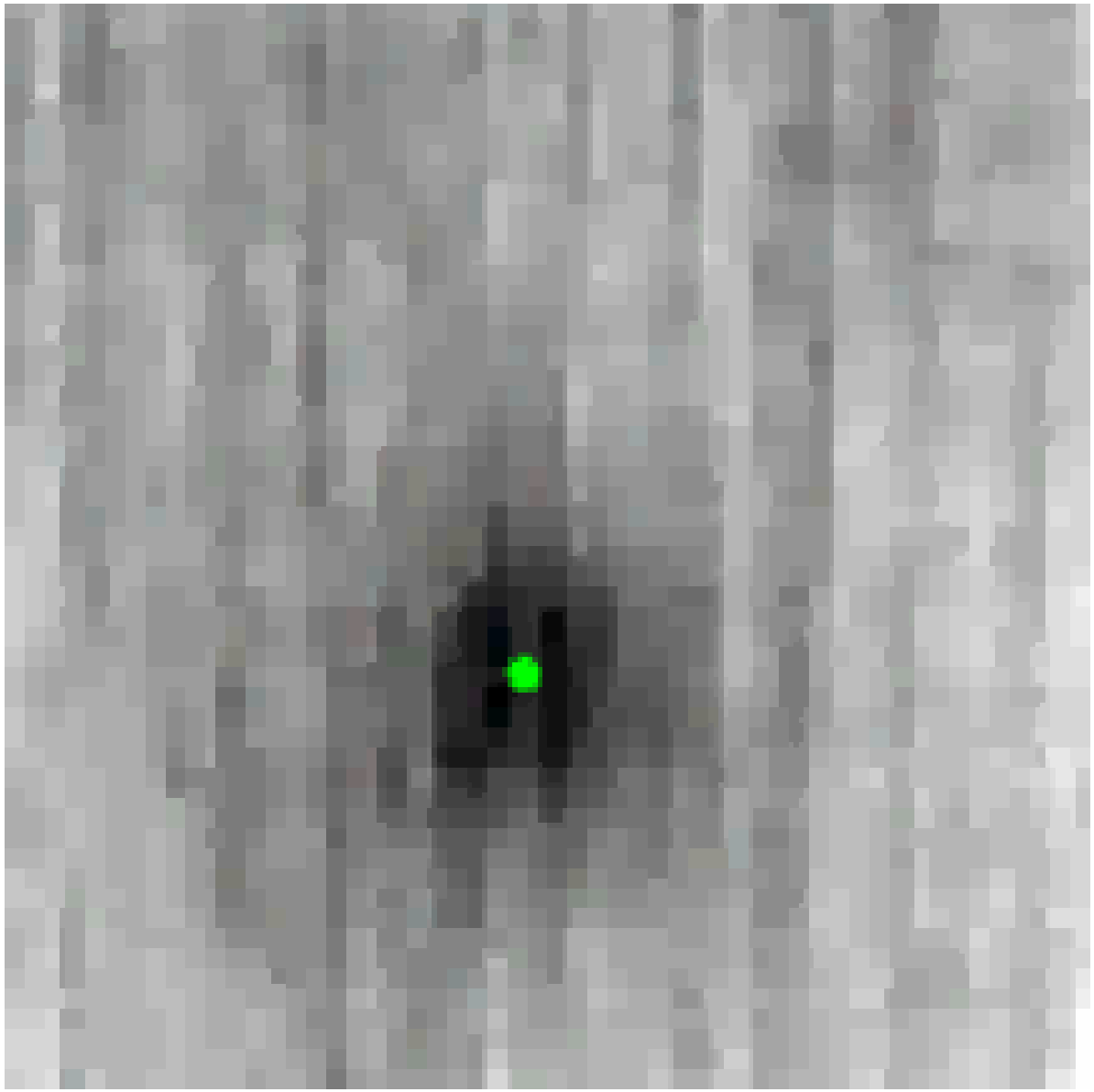


Single H Atom

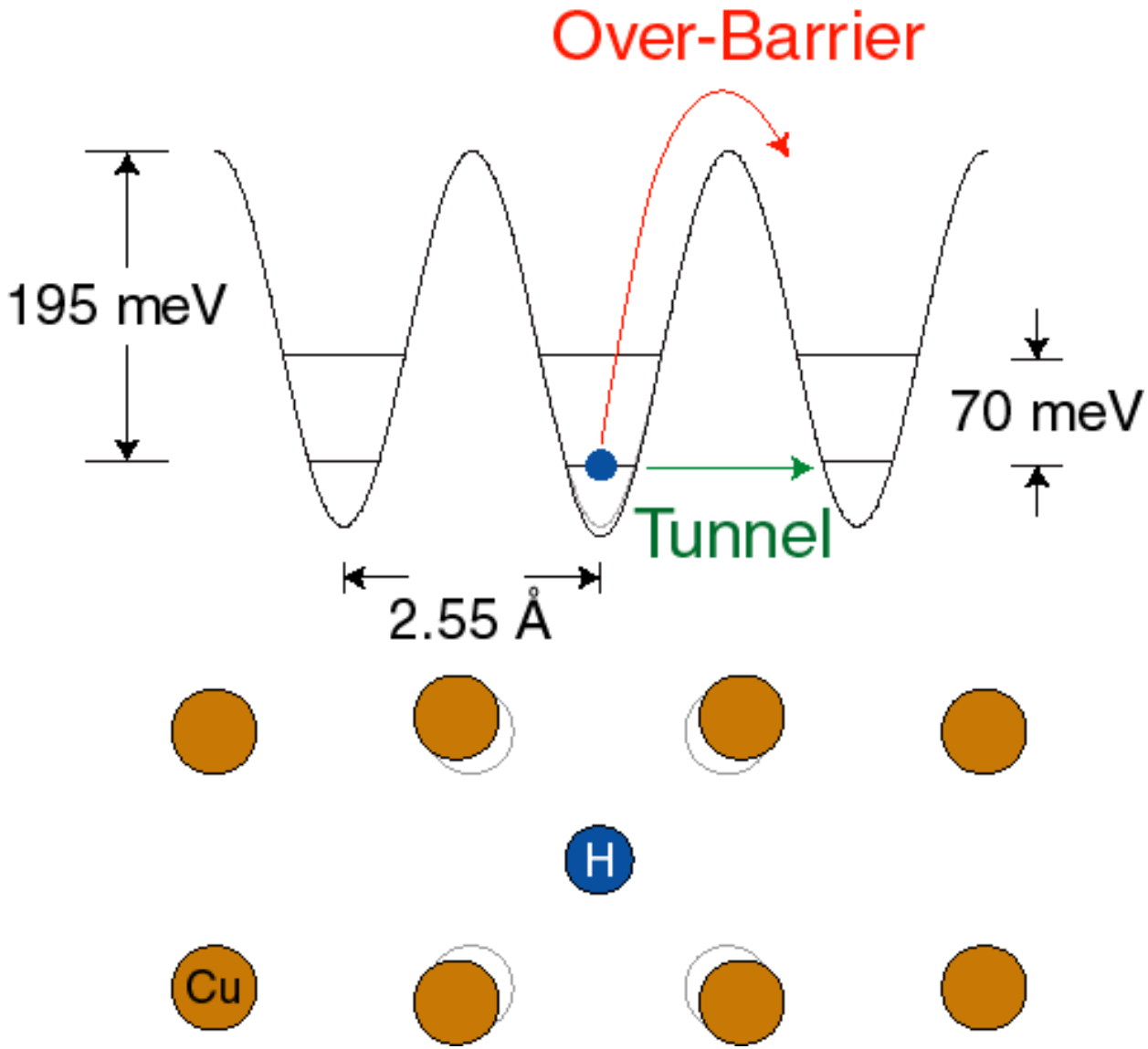


15 x 15 Å^2

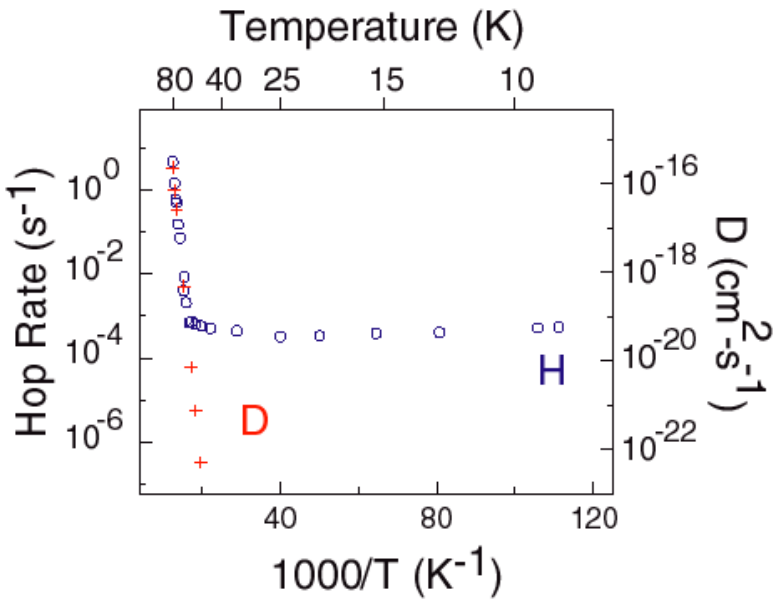


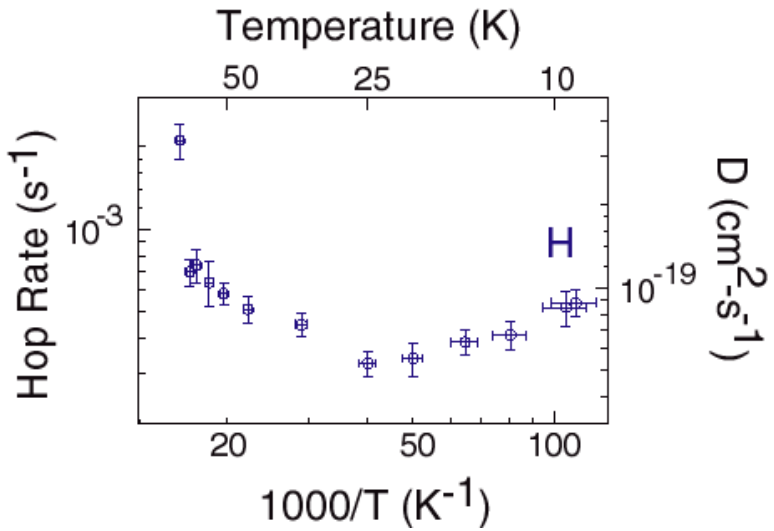


Over-Barrier vs. Tunneling

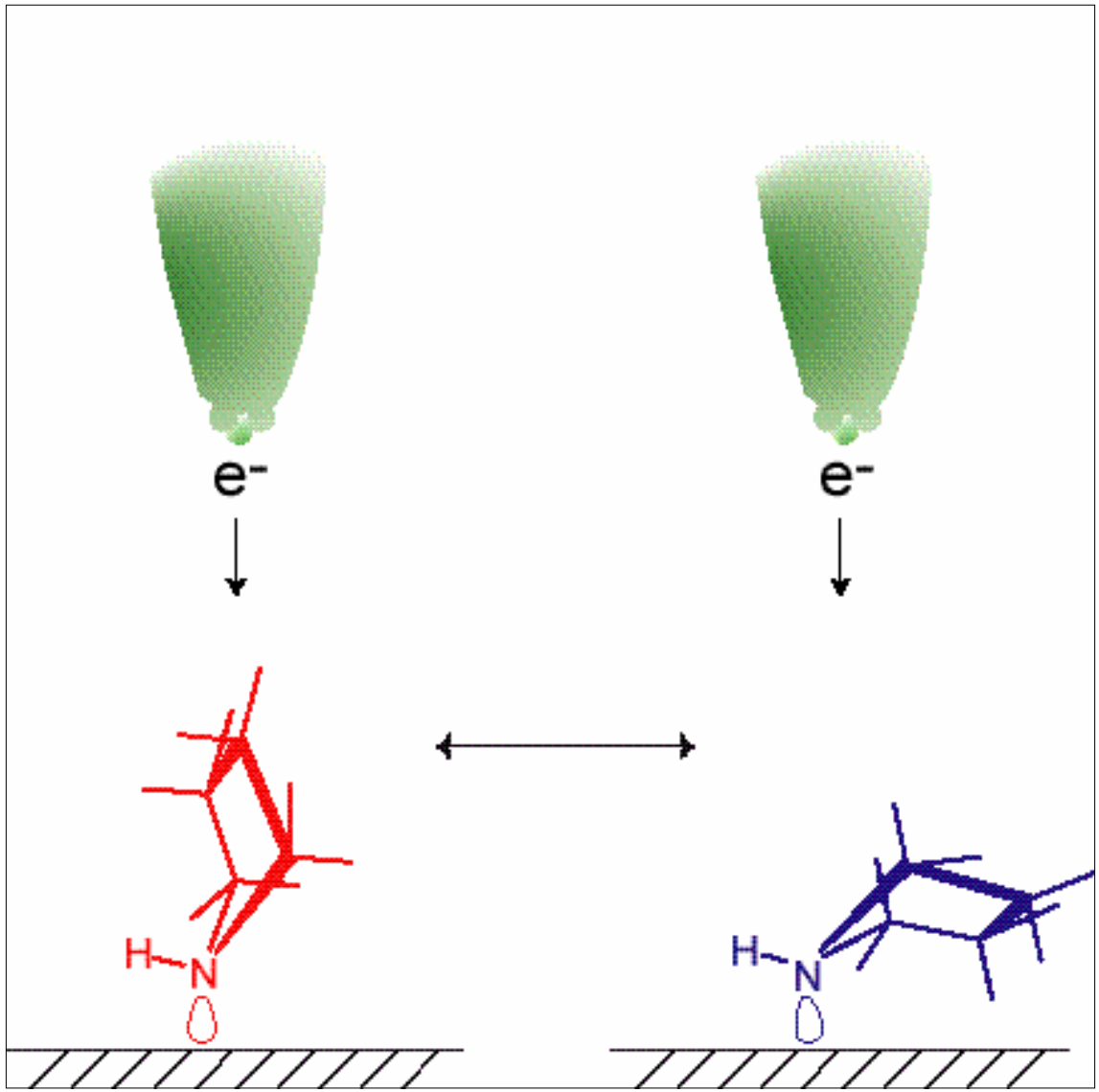


Hydrogen Atom Diffusion

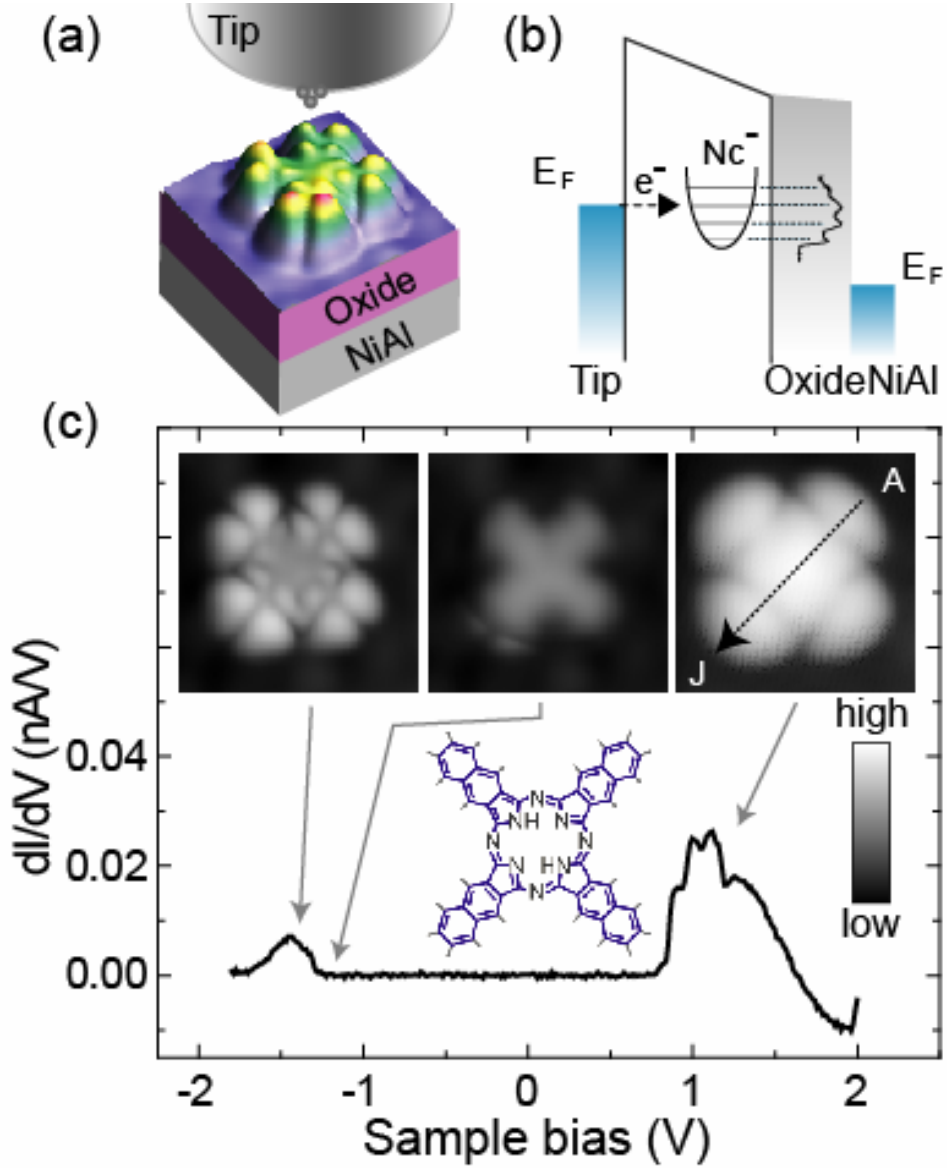




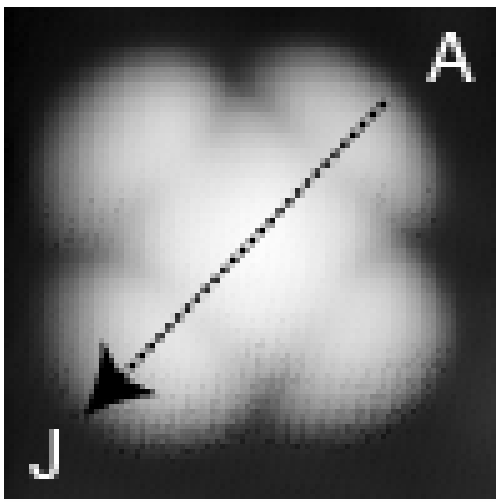
STM Induced Conformation Change

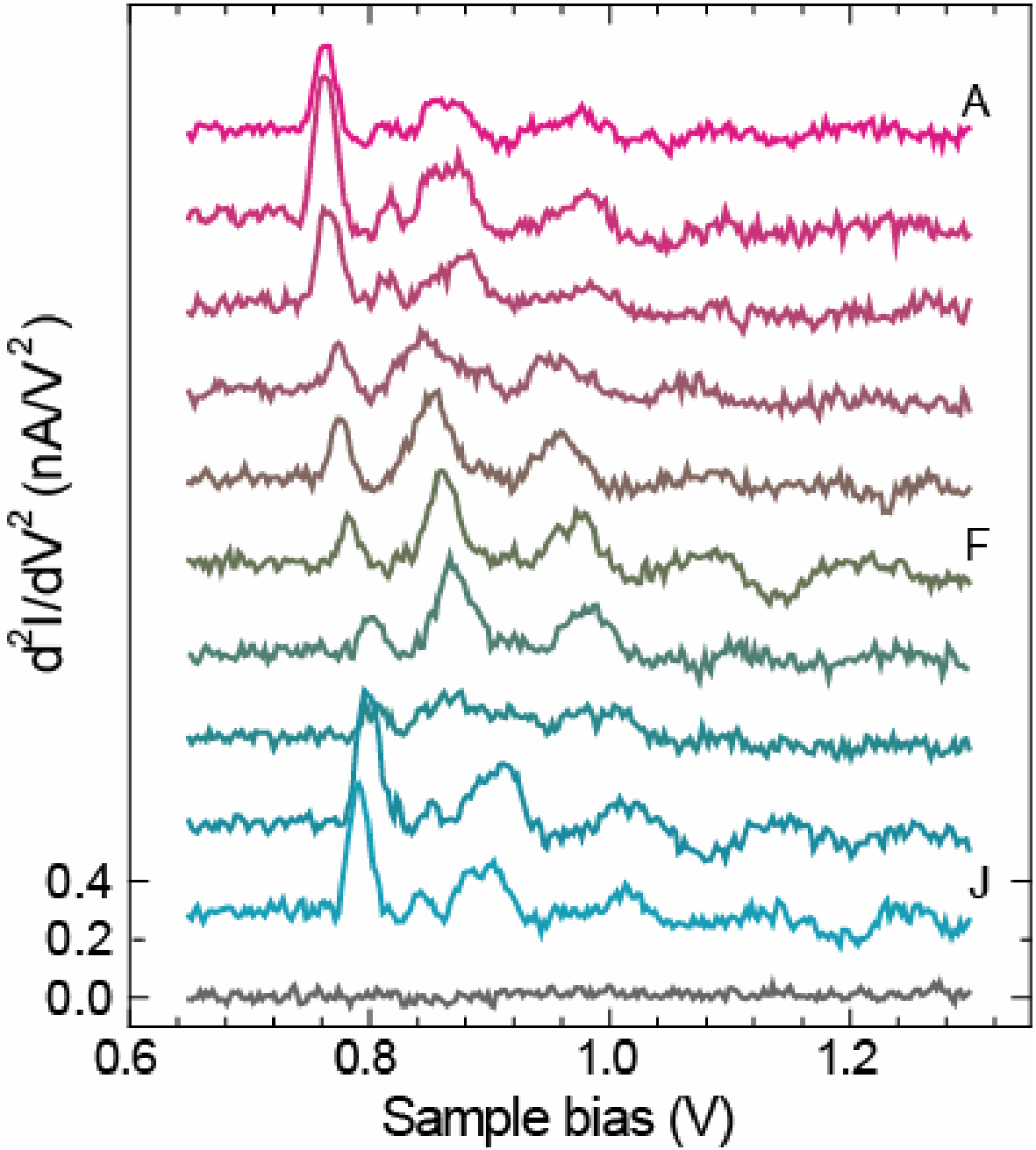


Vibronic States: Naphthalocyanine

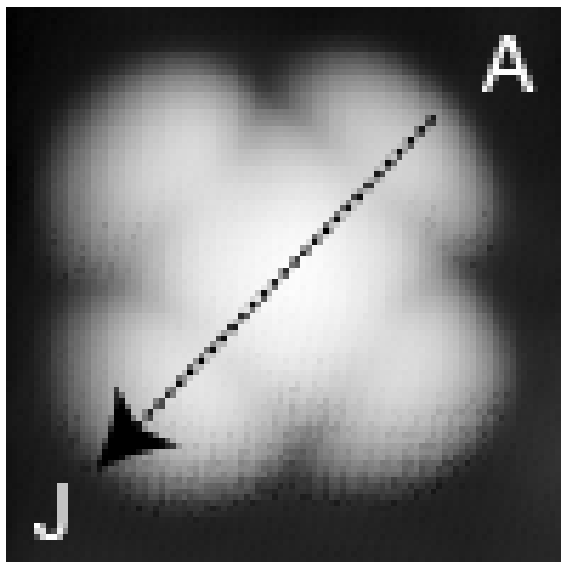


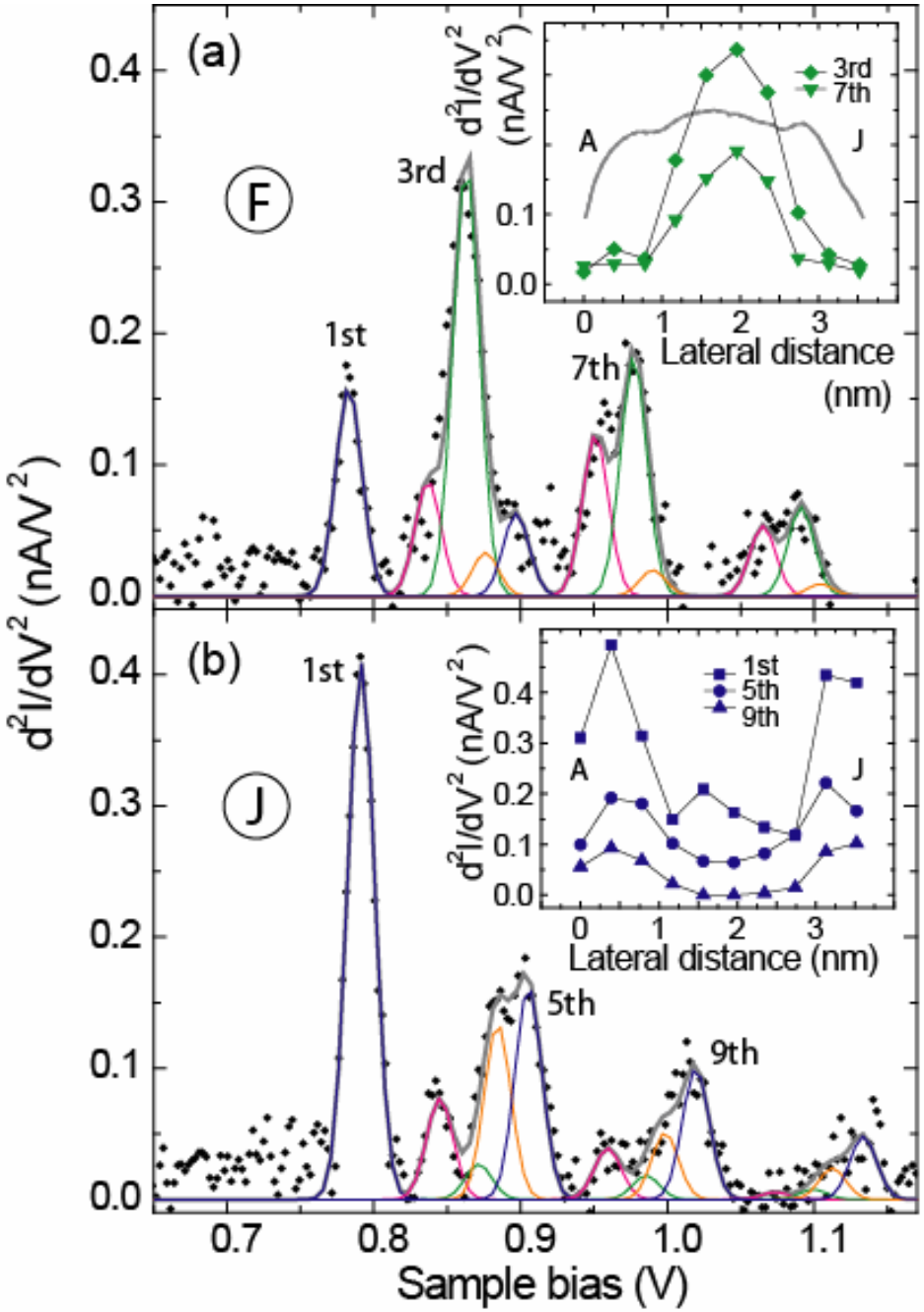
Spatially Resolved Vibronic Spectroscopy



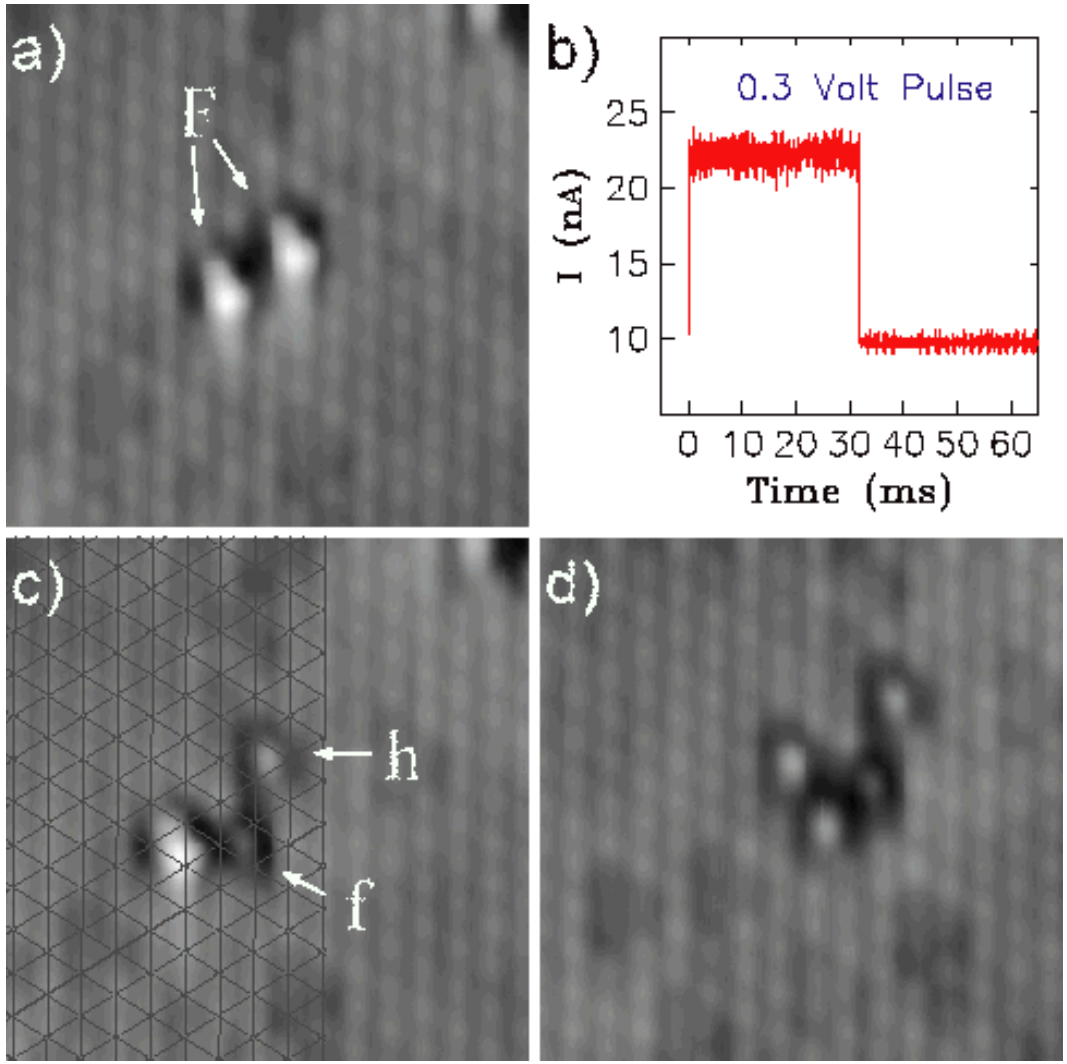


Spatial Dependence of Electron-Vibronic Coupling

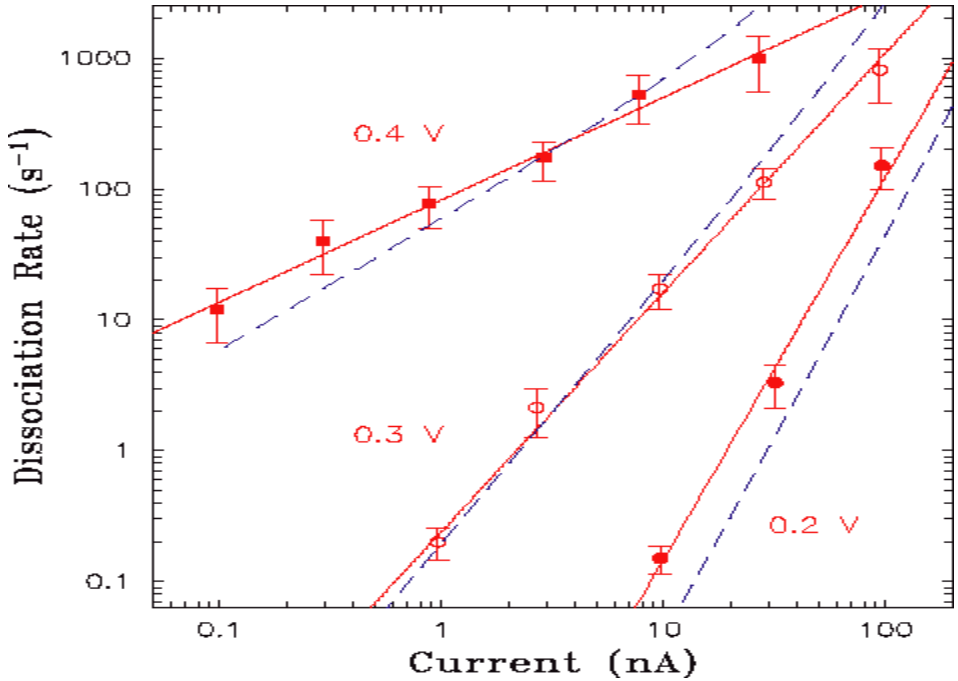


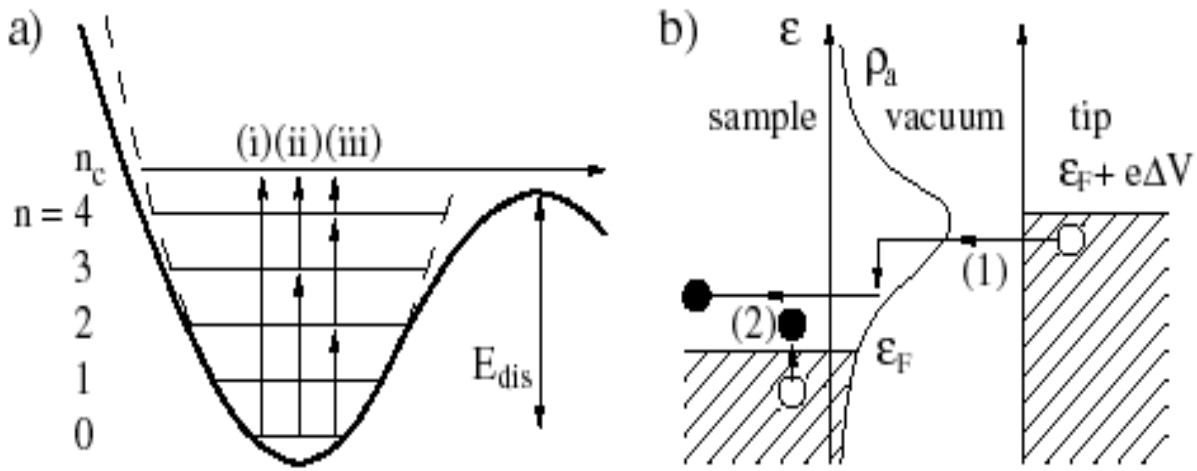


Single O_2 Dissociation by Tunneling Electrons

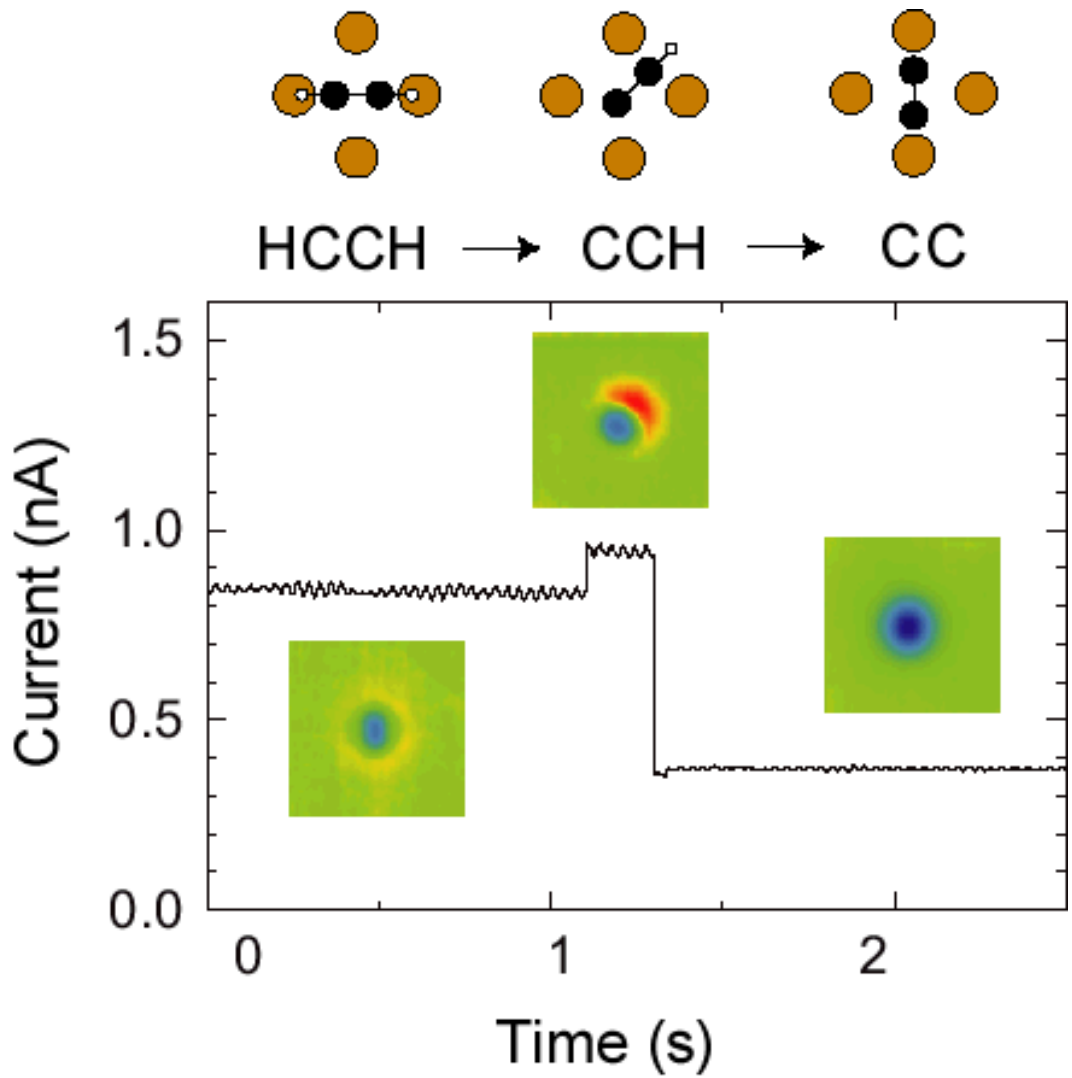


Single O_2 Dissociation

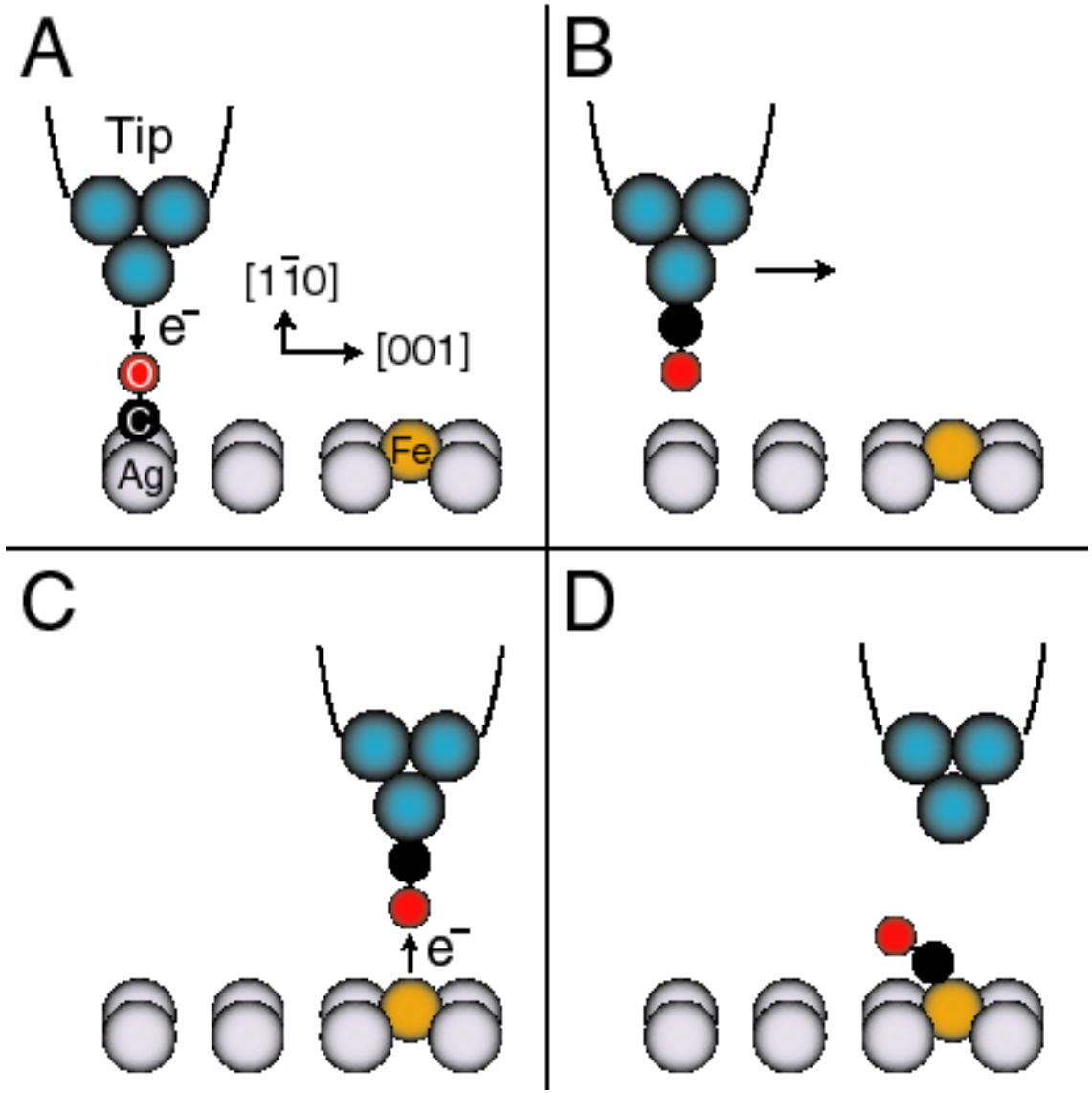




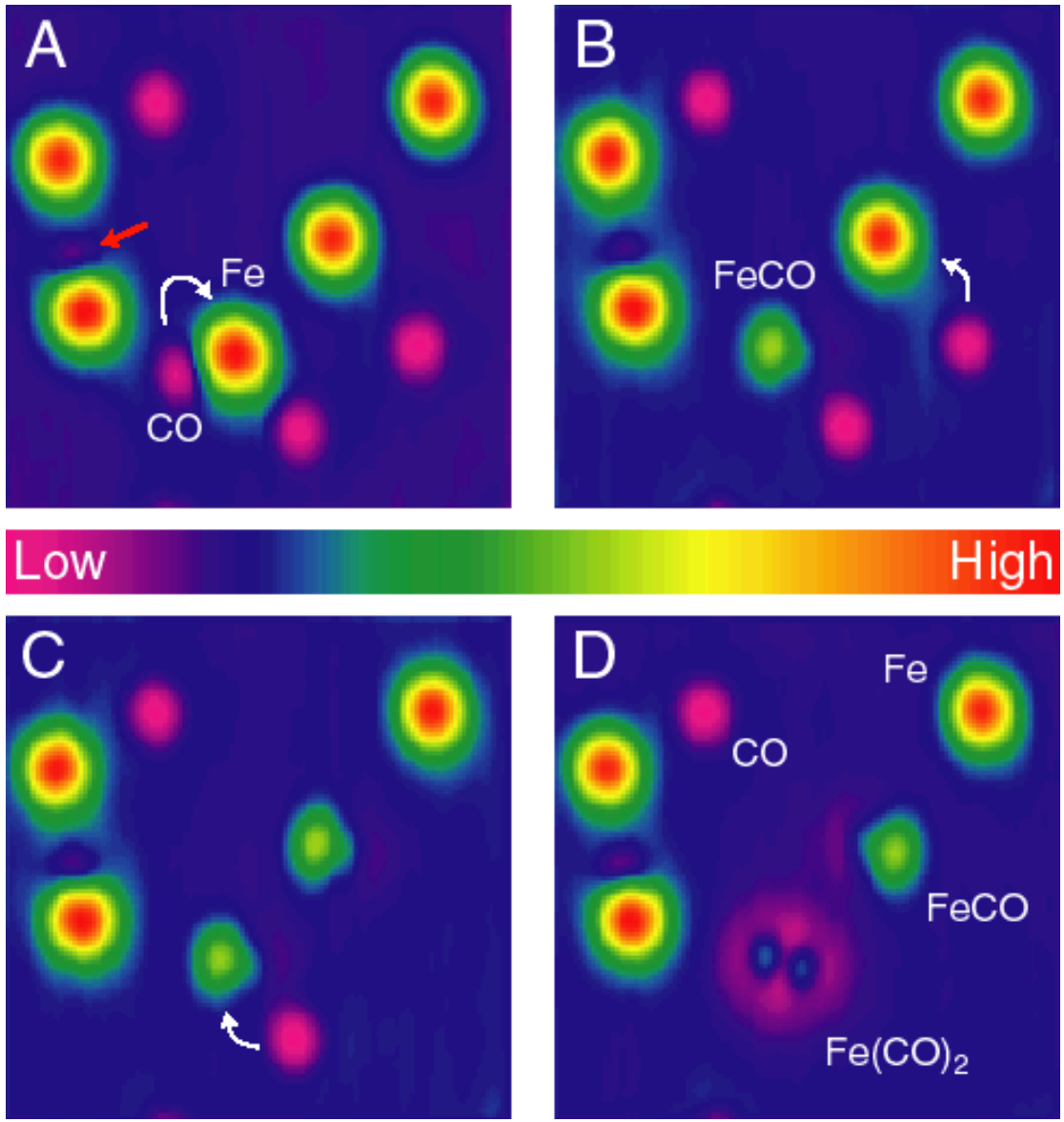
Single Bond Dissociation: Acetylene on Cu(001) @ 9 K



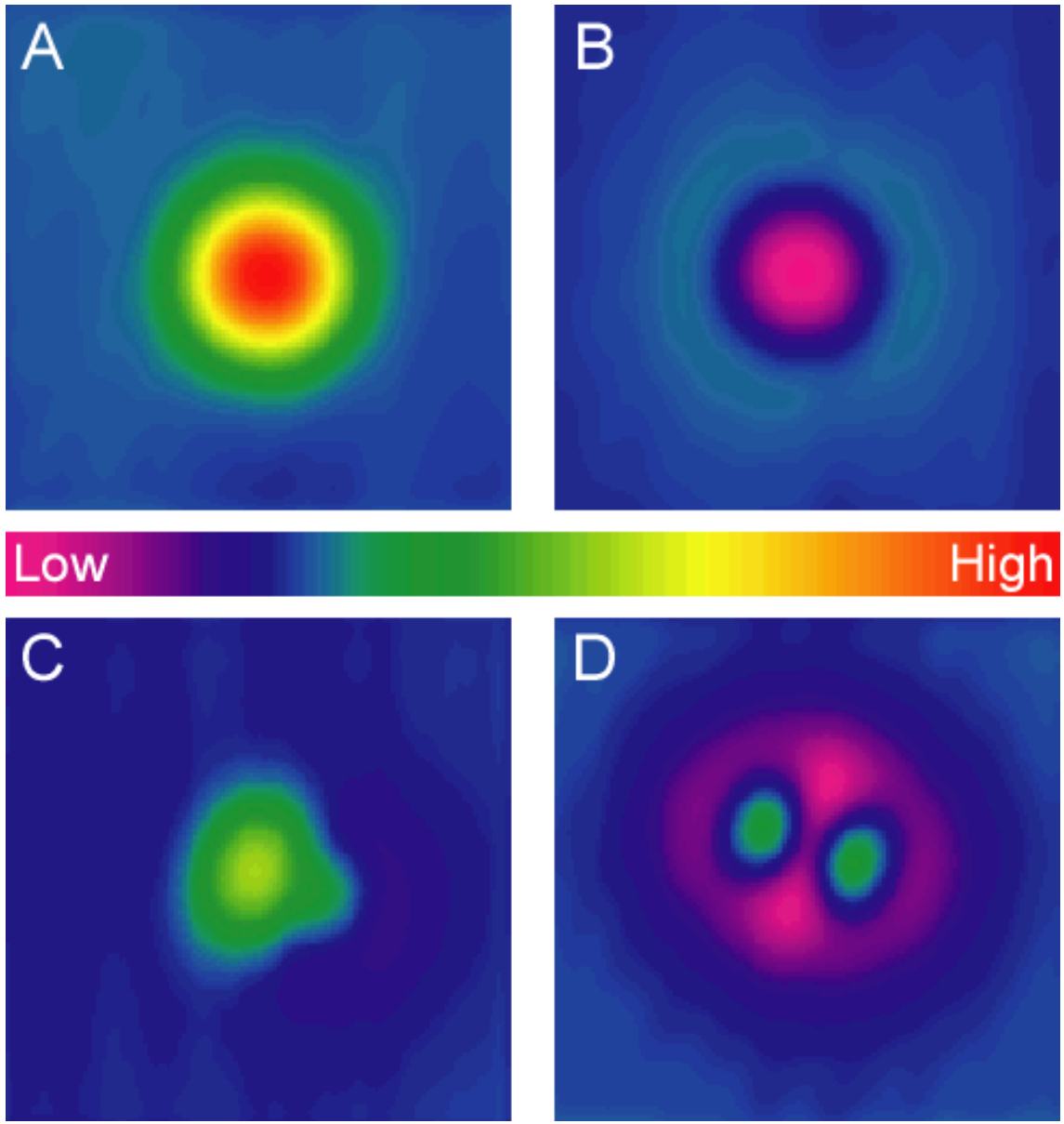
Making a Molecule



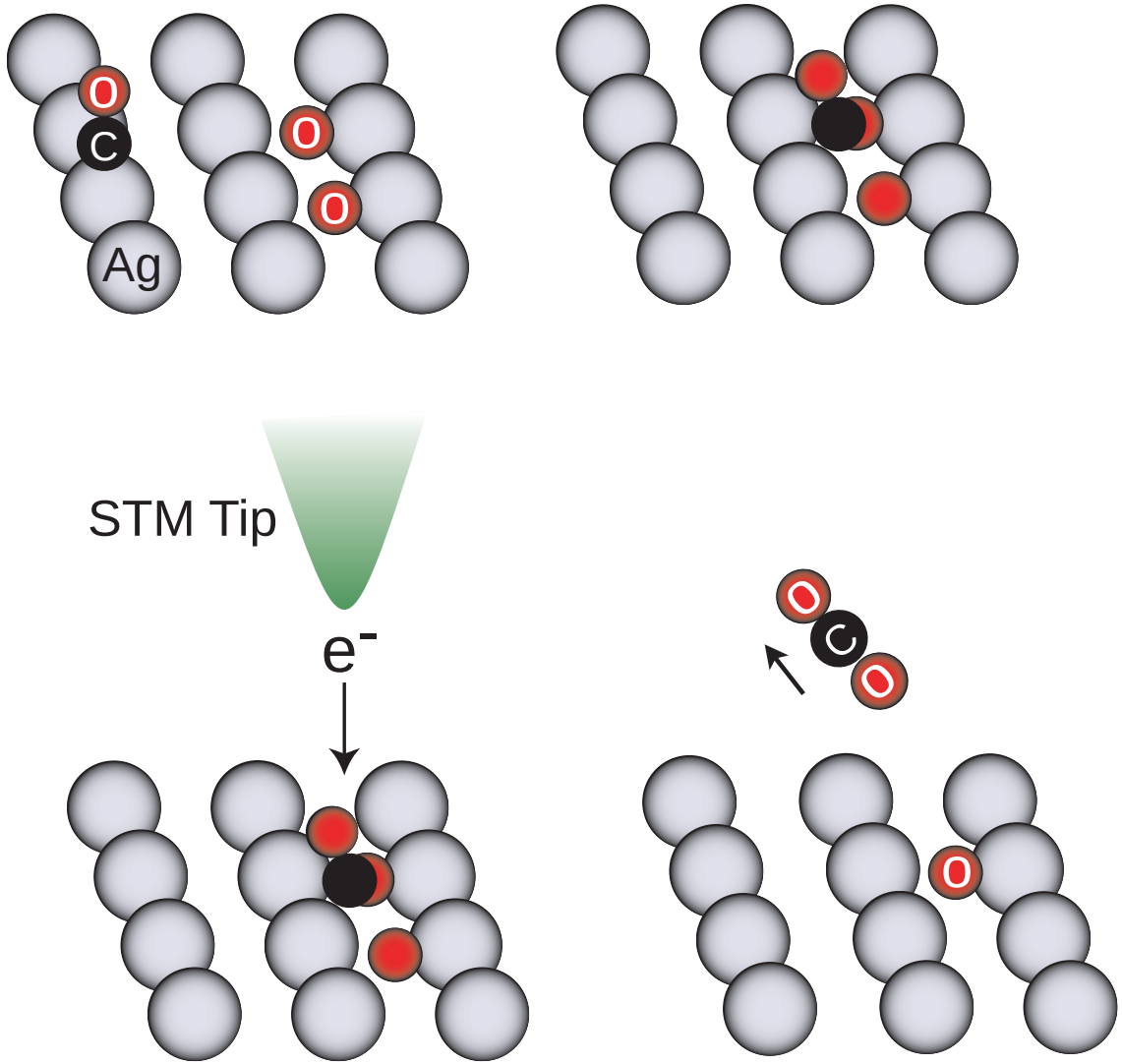
Making Molecules One by One



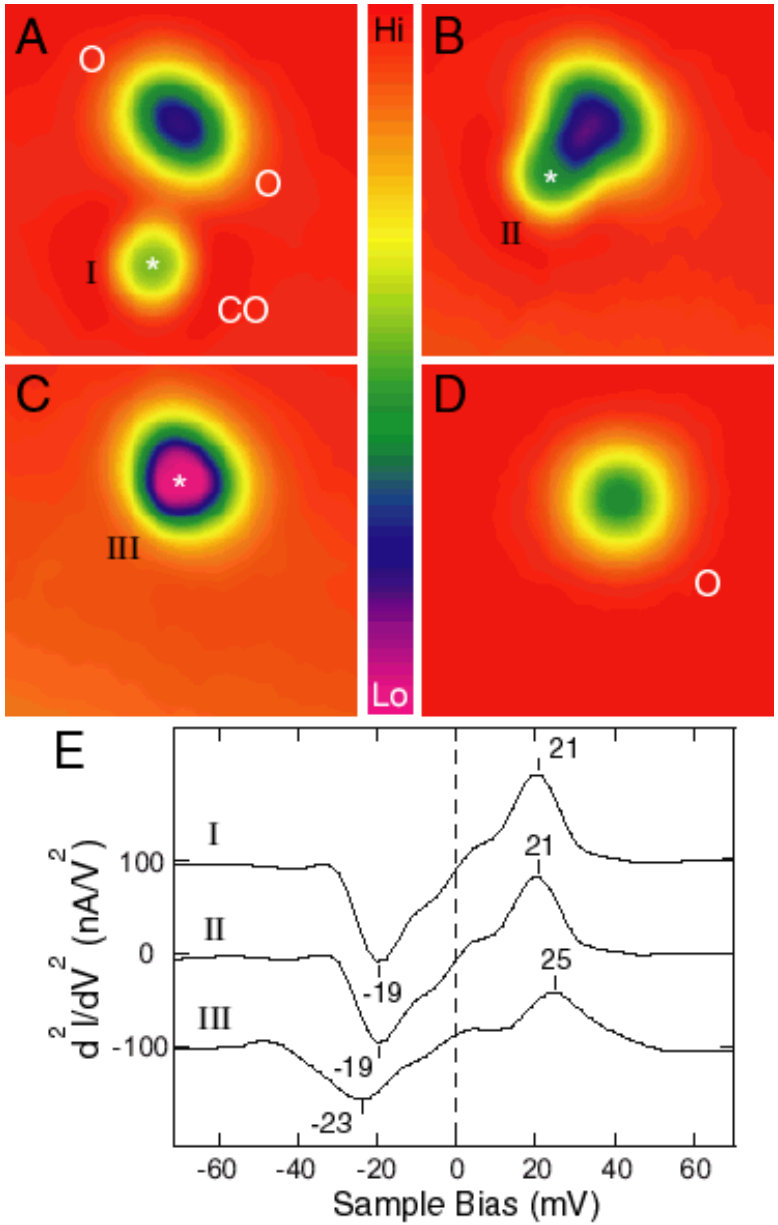
Singles: Close-Up View



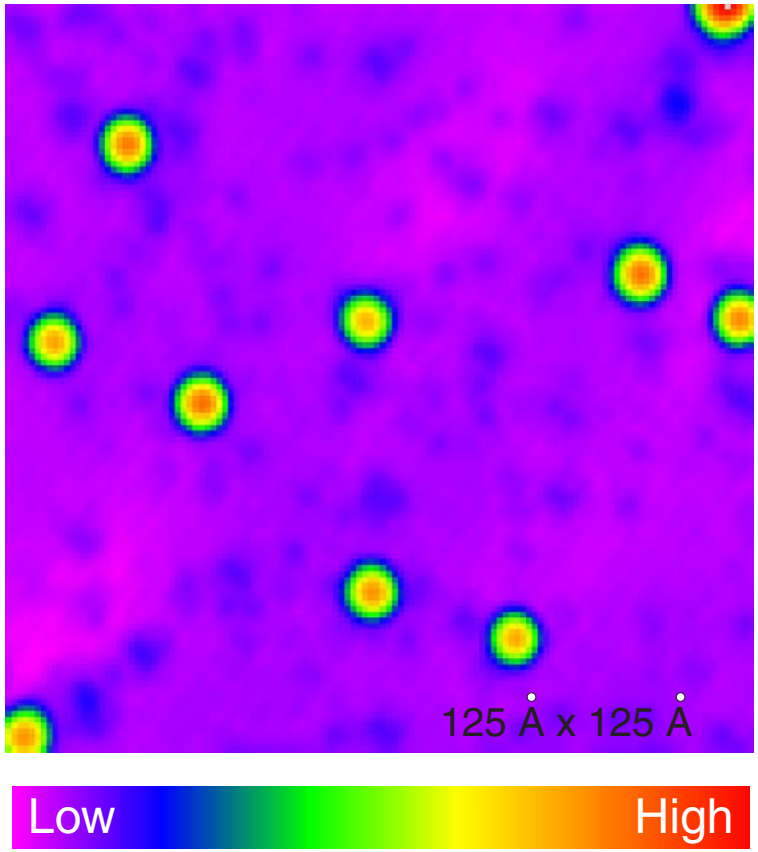
Single Molecule Oxidation

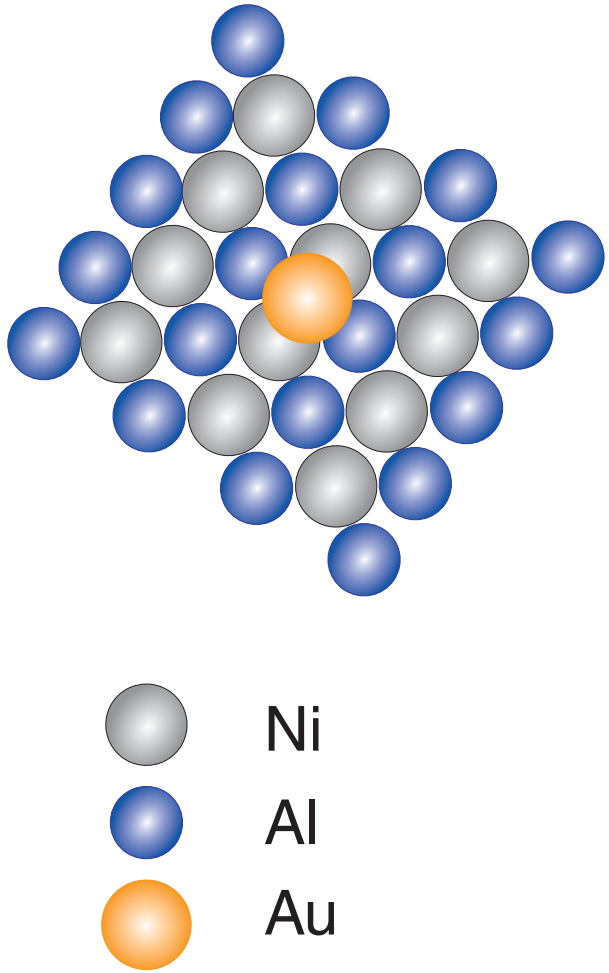


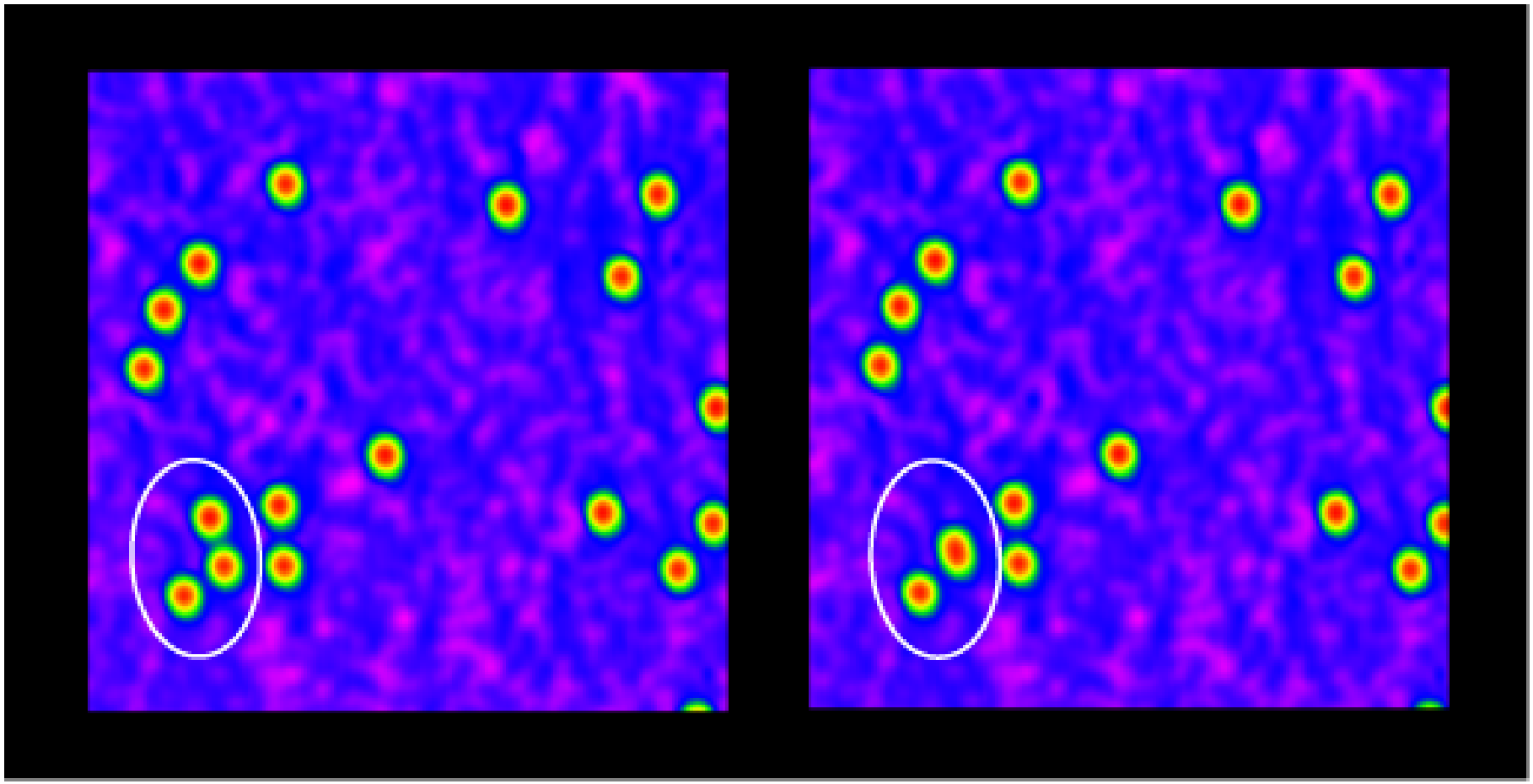
How Close is Close?



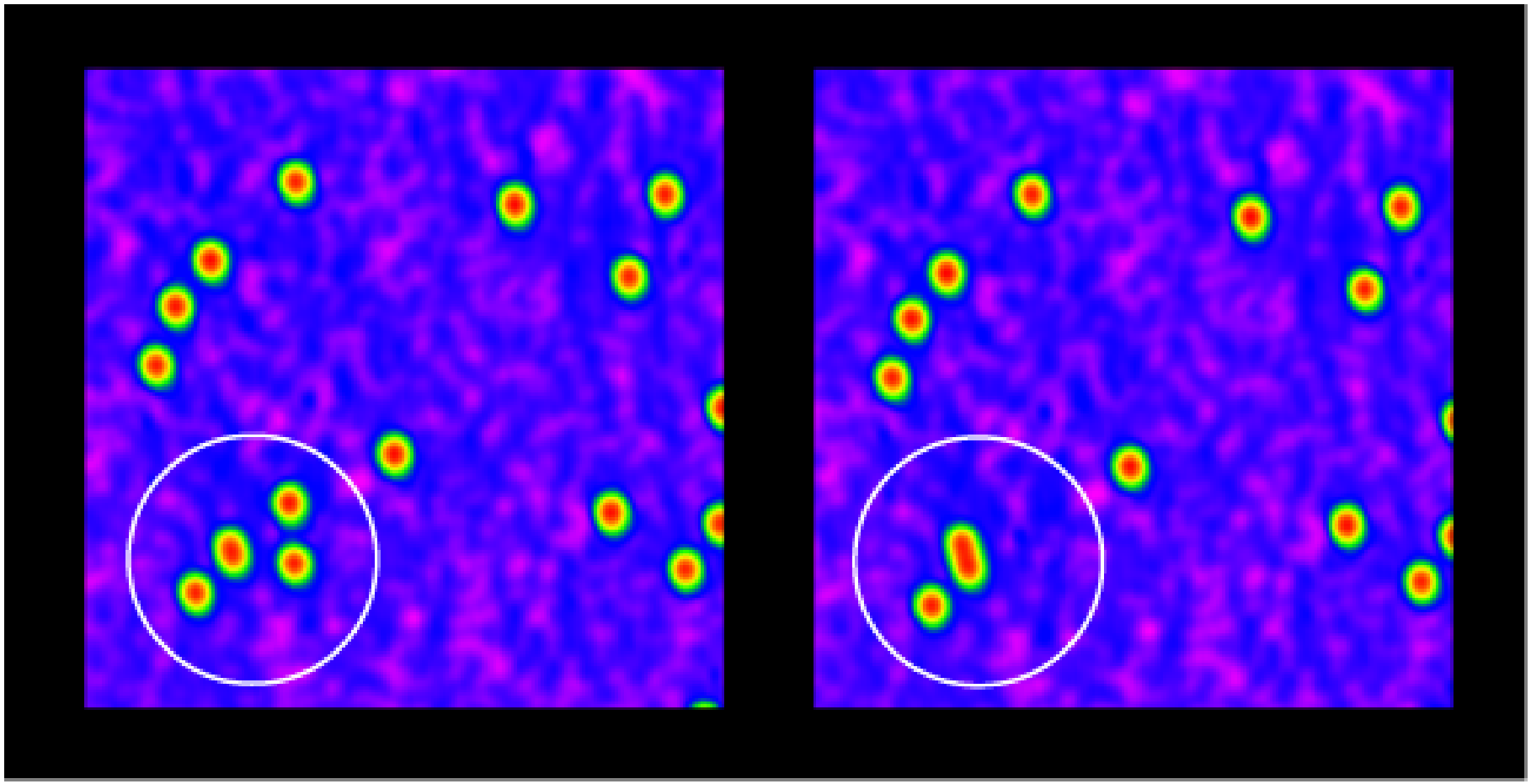
Single Gold Atoms on NiAl(110)



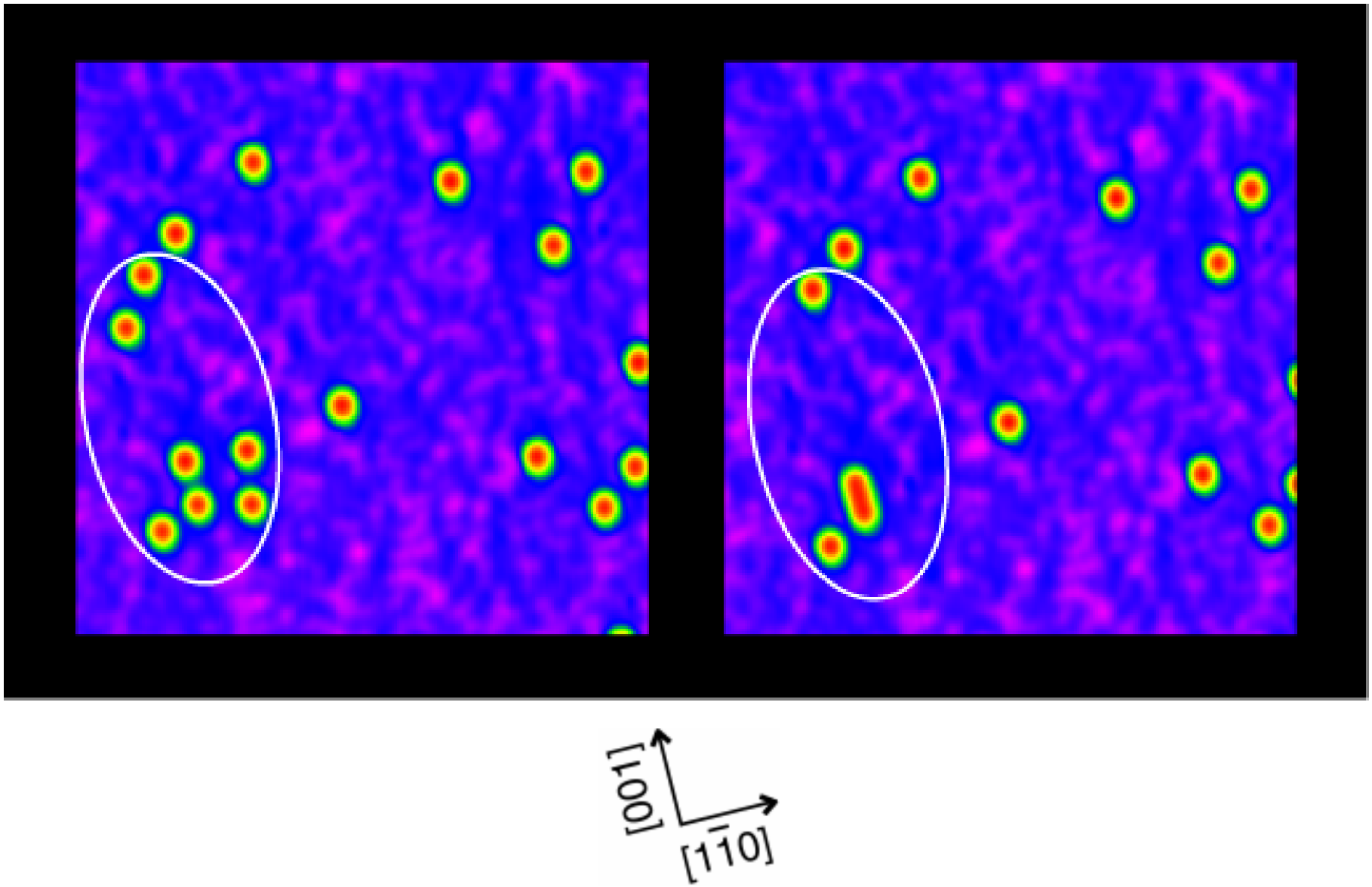




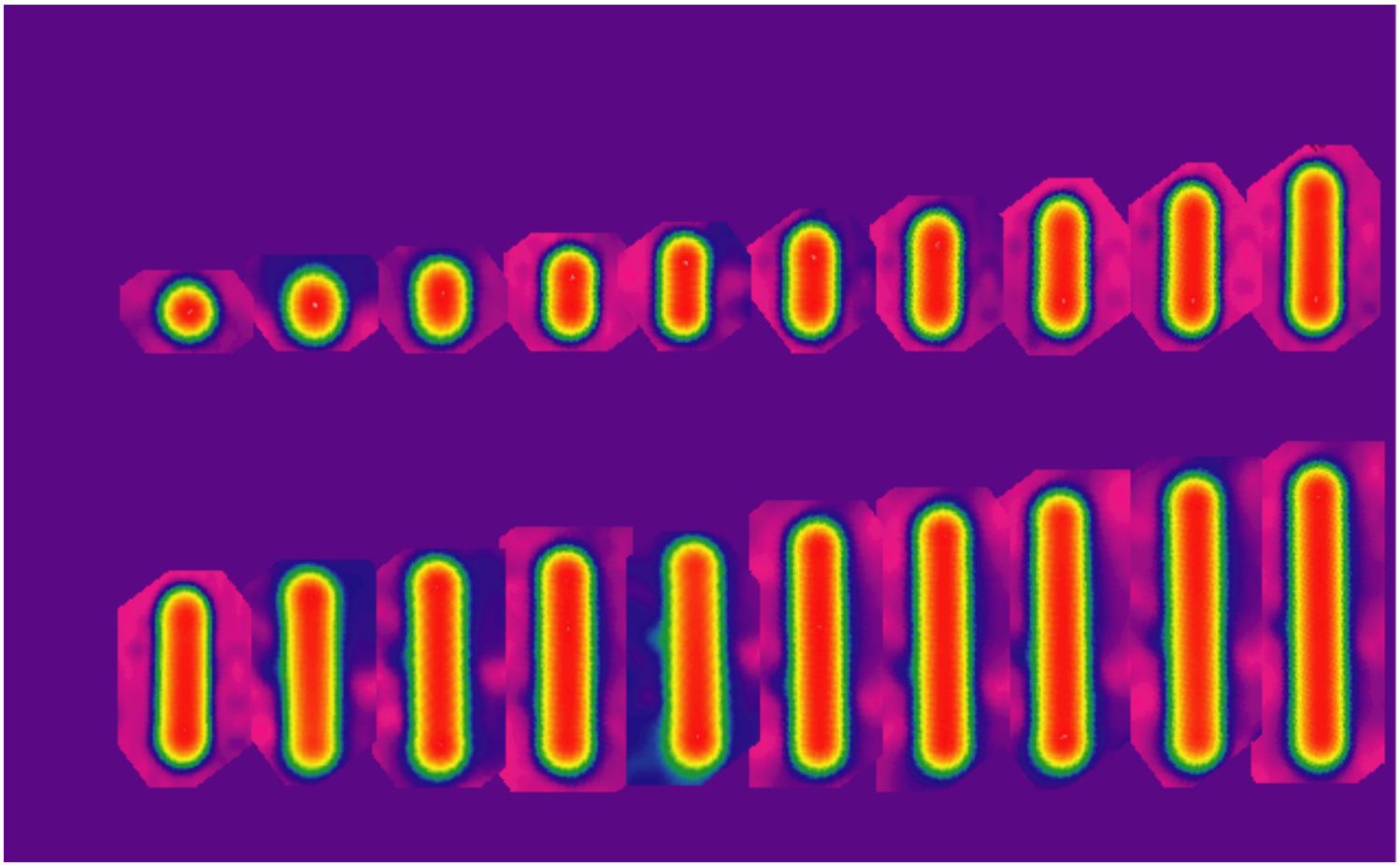
19 x 19 nm



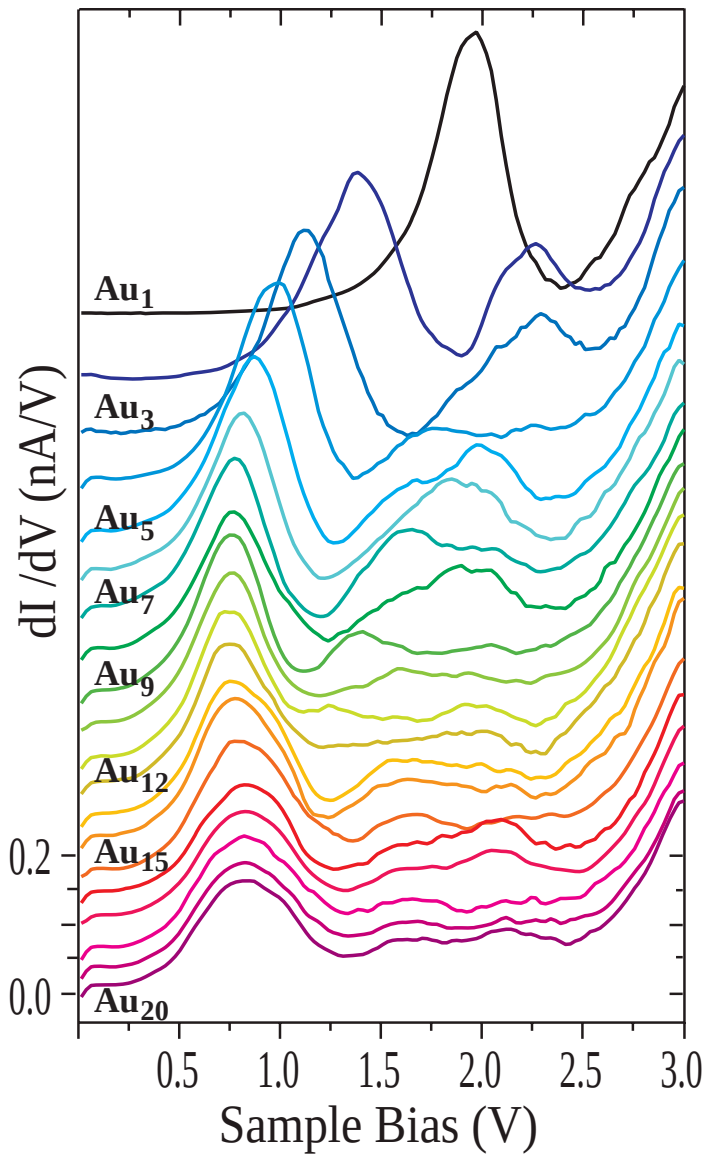
19 x 19 nm


[001]
[1$\bar{1}$0]

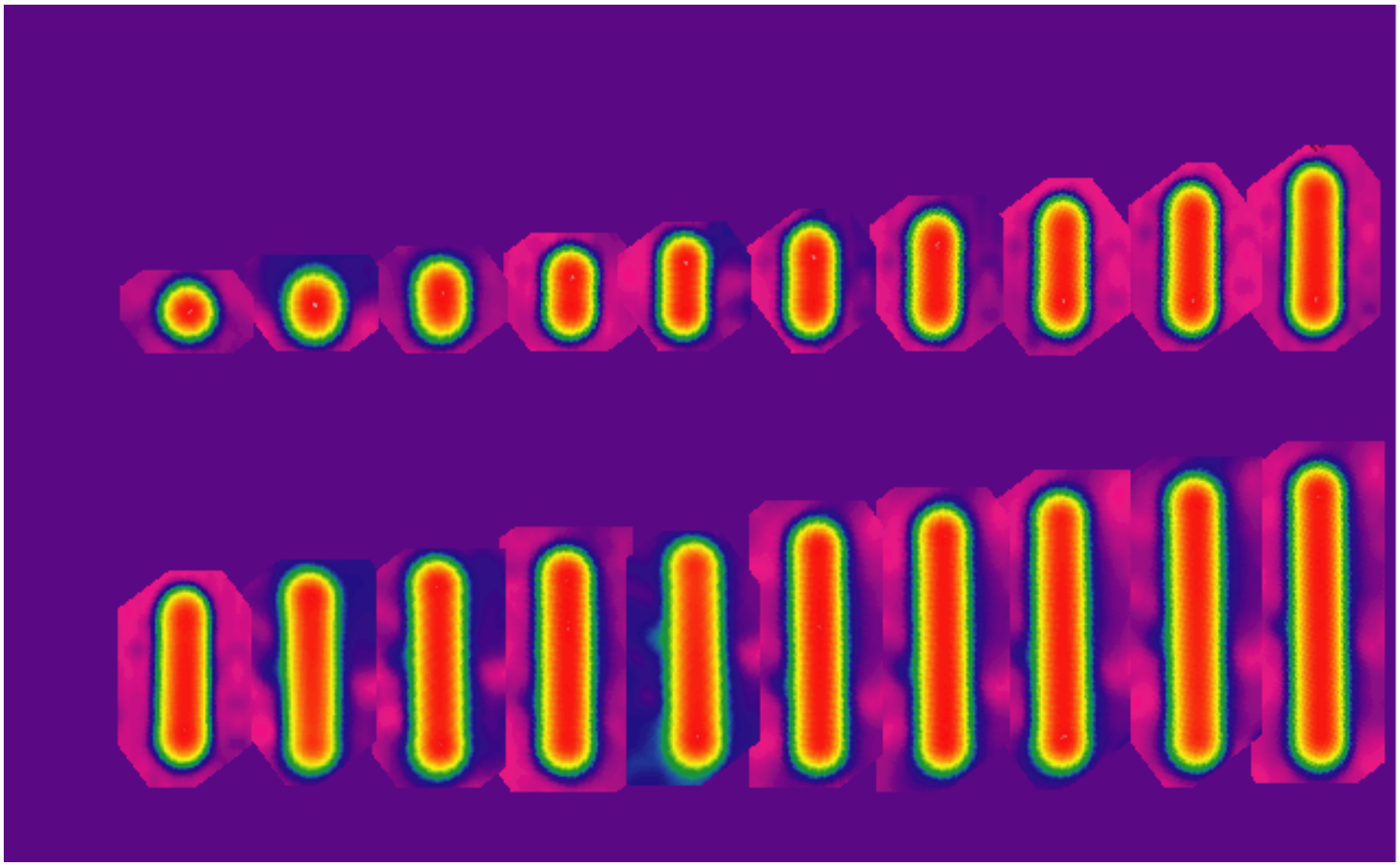
Gold Chains: 1 to 20 Atoms



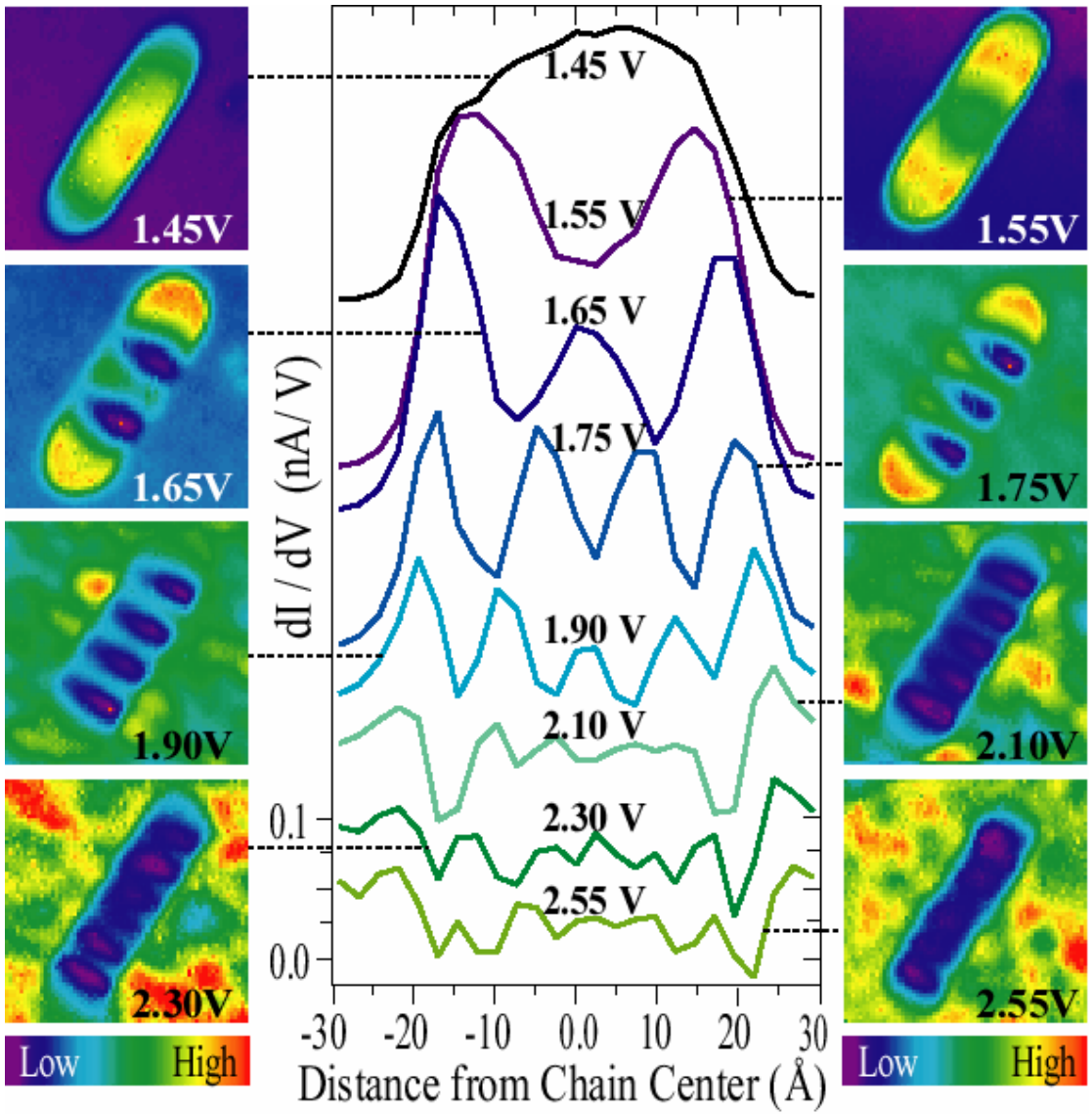
Electronic Spectra of 1 to 20-Atom Au Chains

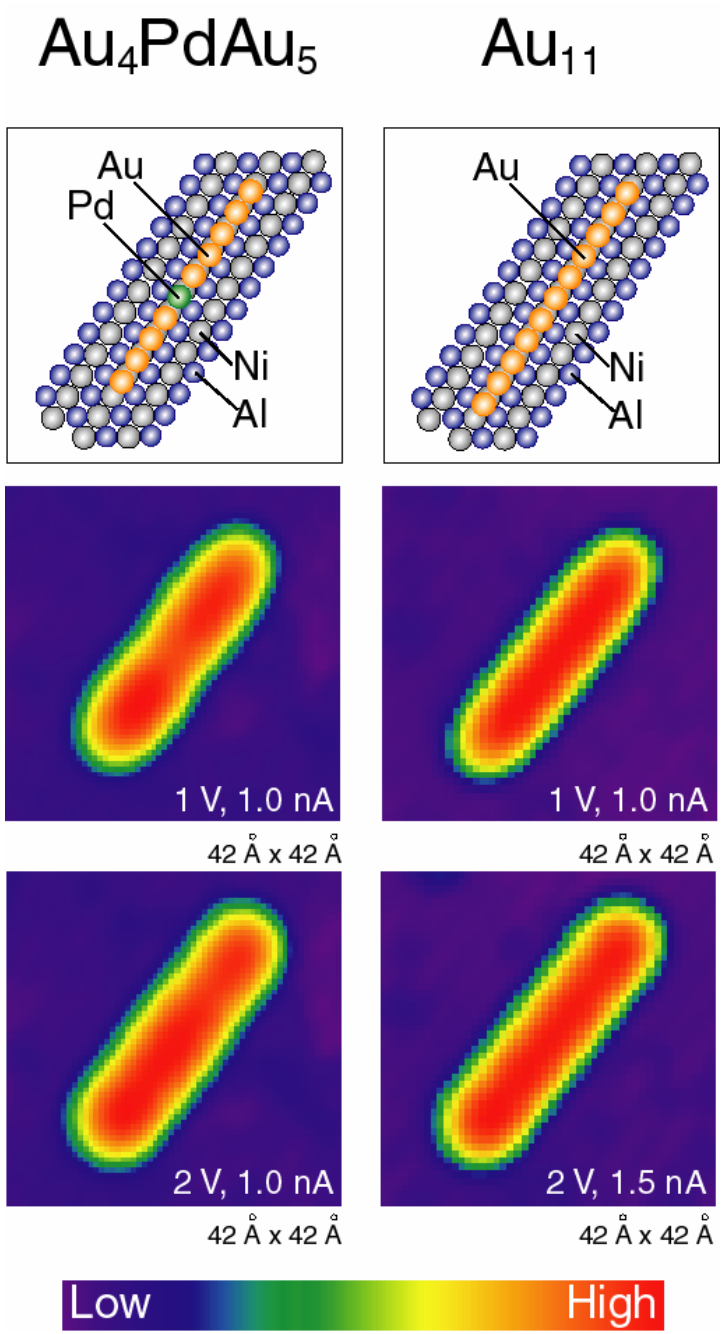


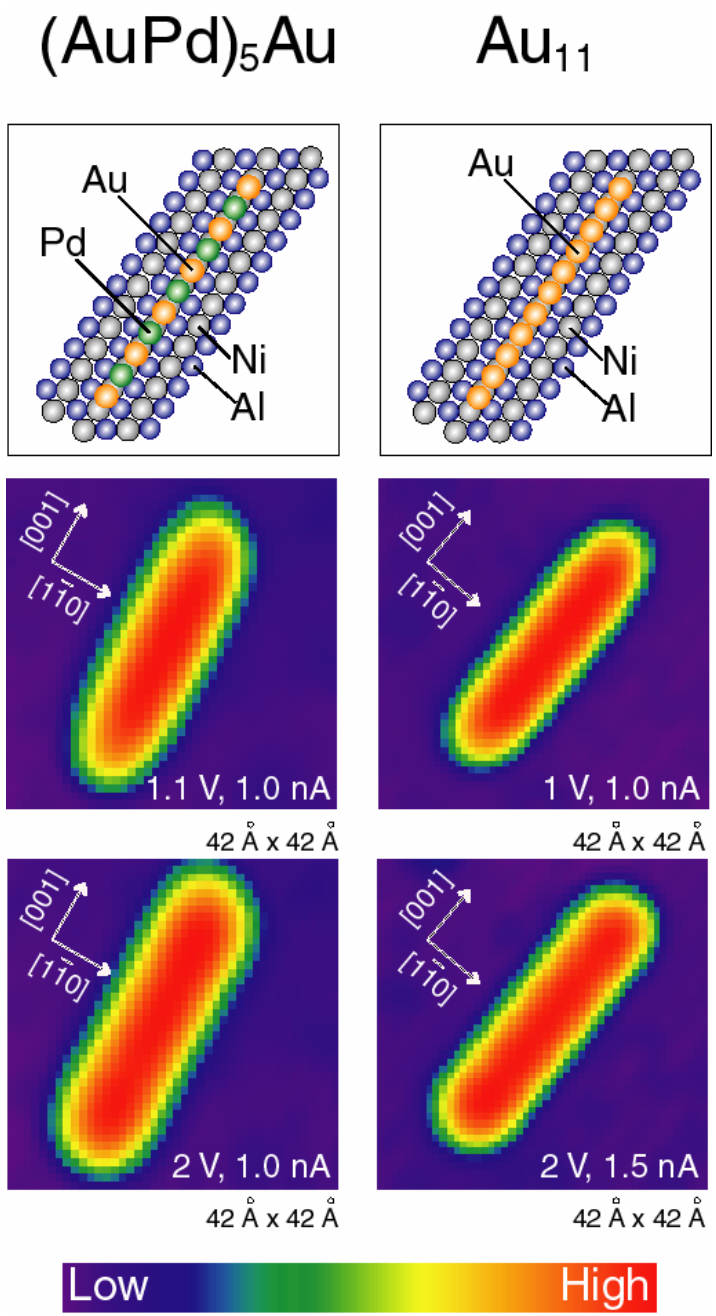
Gold Chains: 1 to 20 Atoms



Pd_{20} Chain

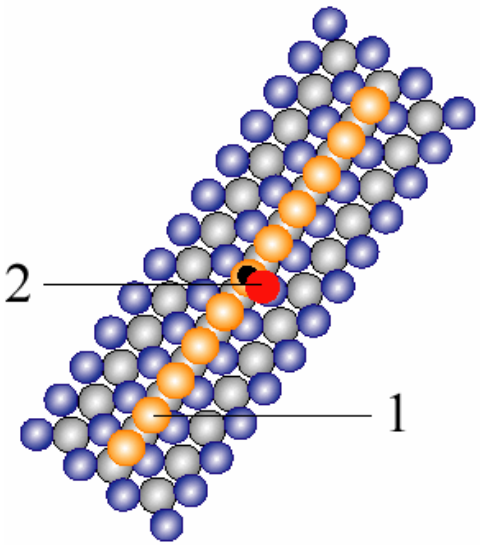

1.45V
1.65V
1.90V
2.30V
1.55V
1.75V
2.10V
2.55V
Low
High
1.45 V
1.55 V
1.65 V
1.75 V
1.90 V
2.10 V
2.30 V
2.55 V
dI / dV (nA/ V)
0.1
0.0
-30
-20
-10
0.0
10
20
30
Distance from Chain Center (Å)

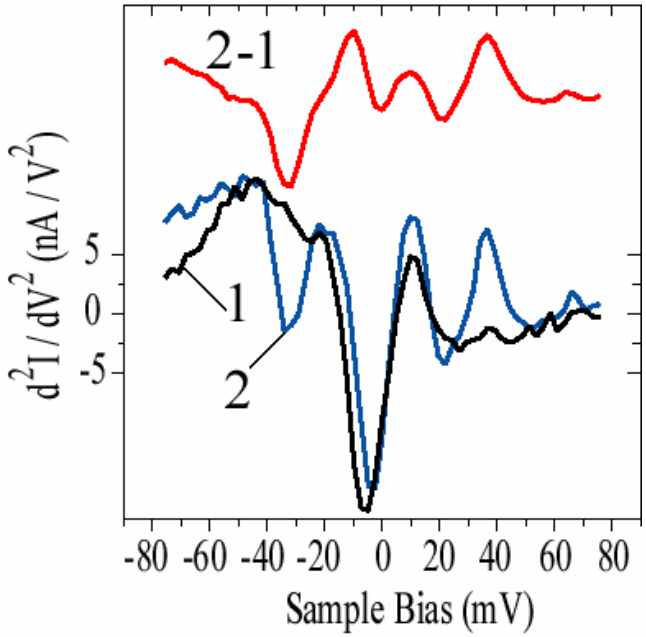

Au_4PdAu_5
Au_{11}
Au
Pd
Ni
Al
Au
Ni
Al
1 V, 1.0 nA
42 Å x 42 Å
1 V, 1.0 nA
42 Å x 42 Å
2 V, 1.0 nA
42 Å x 42 Å
2 V, 1.5 nA
42 Å x 42 Å
Low
High

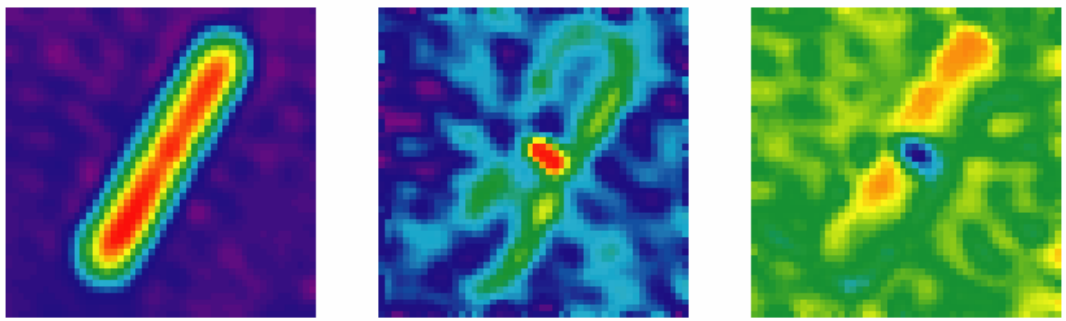

(AuPd)5Au
Au11
Au
Pd
Ni
Al
Au
Ni
Al
[001]
[1$\bar{1}$0]
1.1 V, 1.0 nA
42 Å x 42 Å
[001]
[1$\bar{1}$0]
1 V, 1.0 nA
42 Å x 42 Å
[001]
[1$\bar{1}$0]
2 V, 1.0 nA
42 Å x 42 Å
[001]
[1$\bar{1}$0]
2 V, 1.5 nA
42 Å x 42 Å
Low
High

Single CO Adsorption on 11-Atom Au Chain

Au_5 - AuCO-Au_5

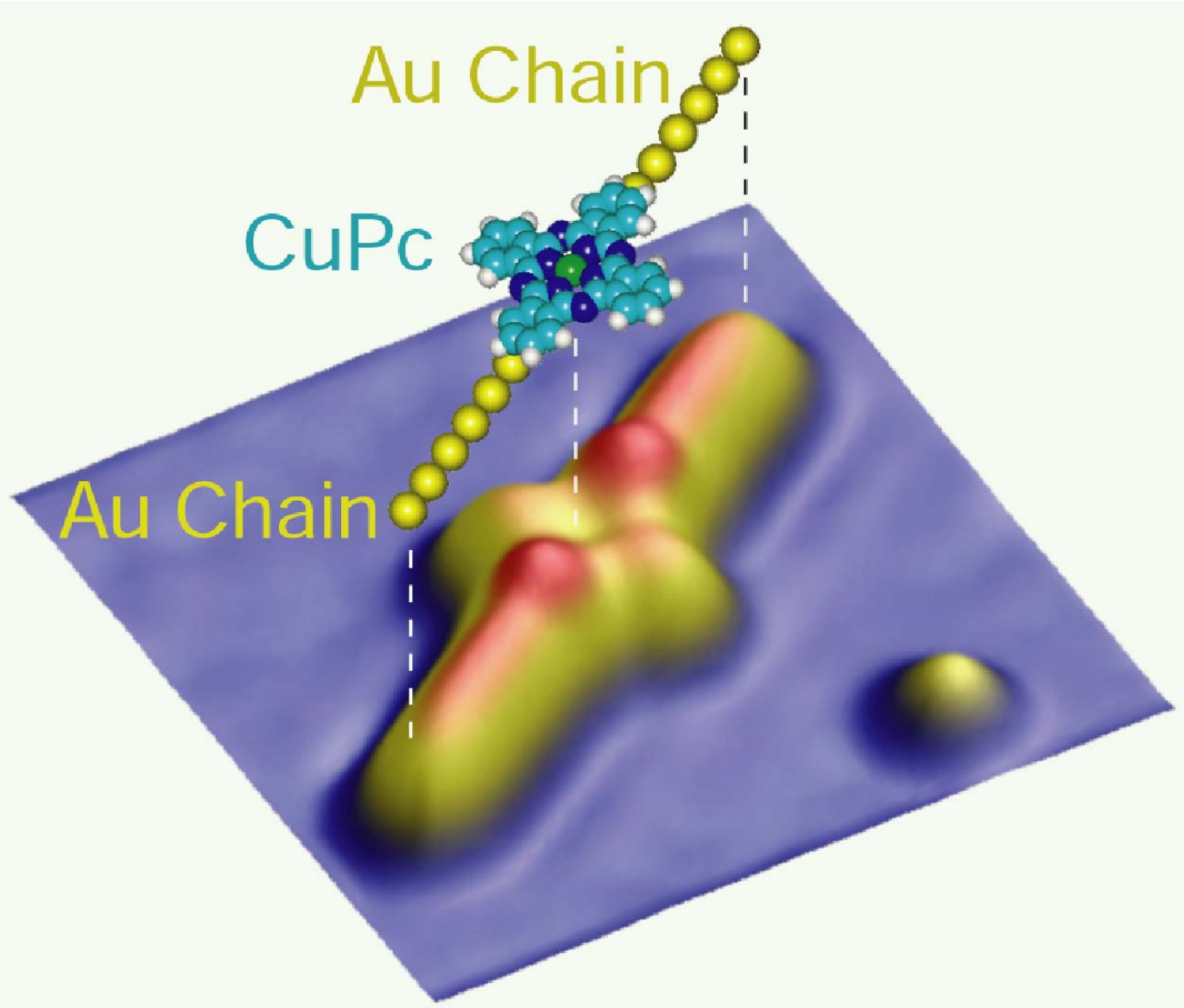




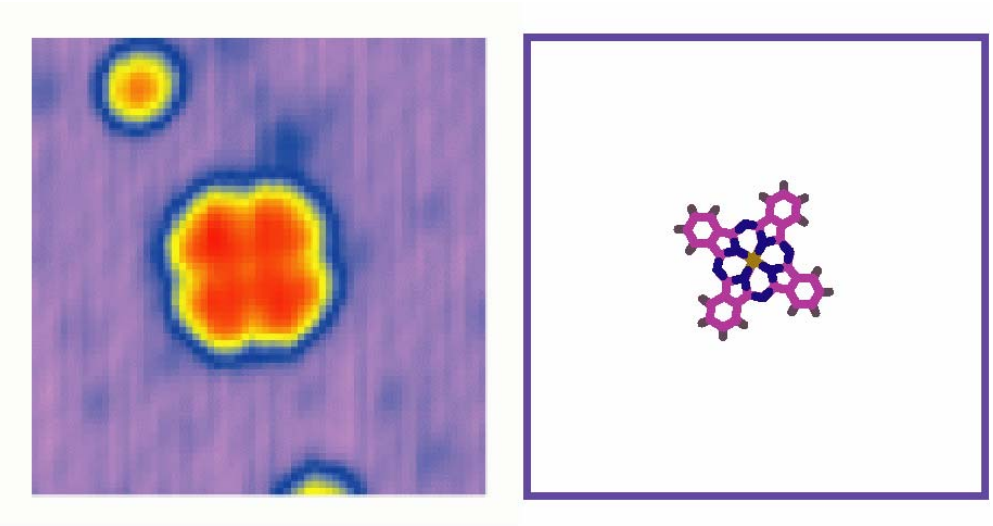


Topography +36 mV -36 mV

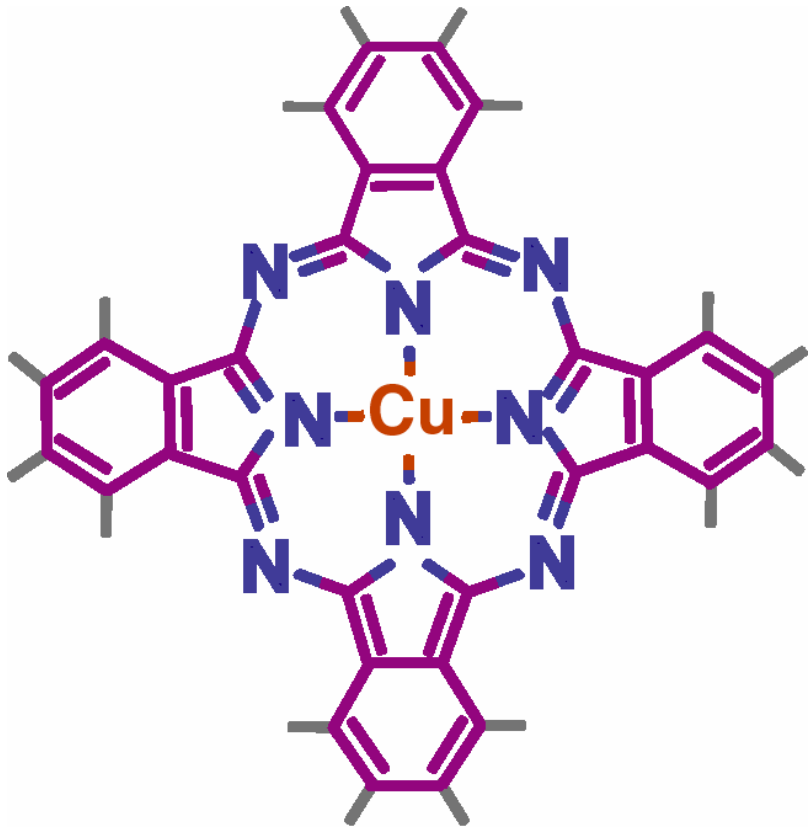
CuPc@2Au$_6$



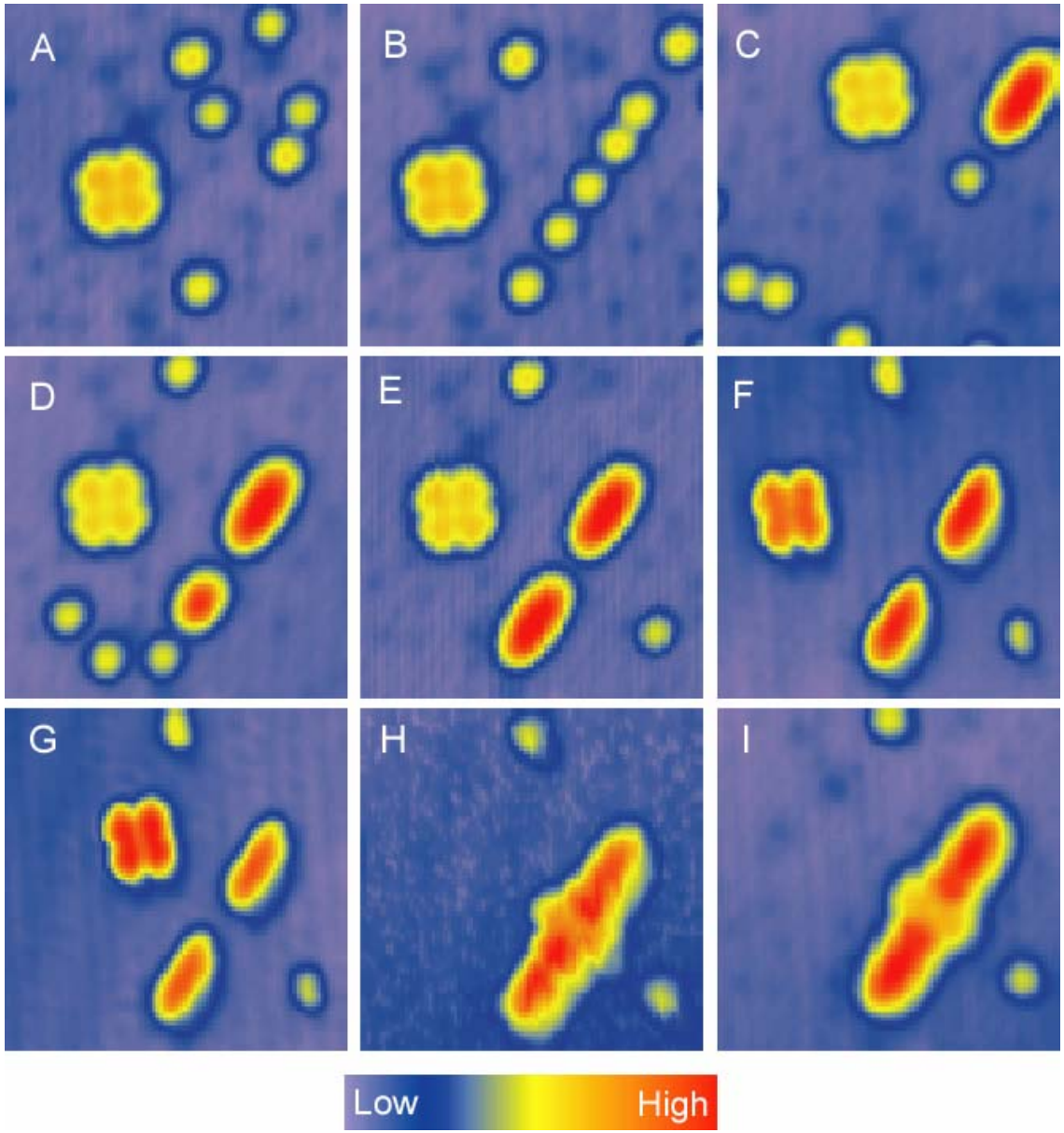
Structure of CuPc



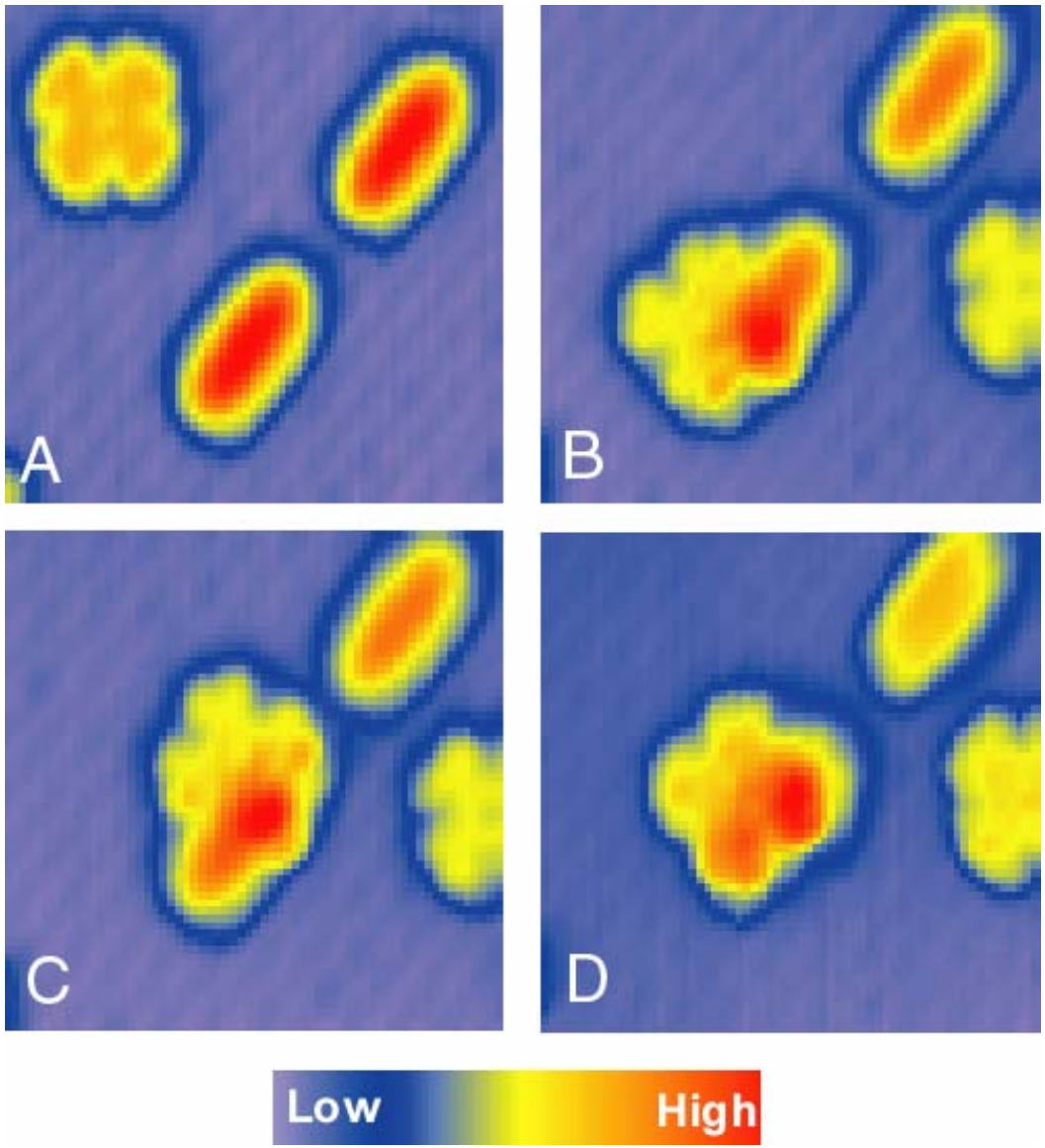
CuPc



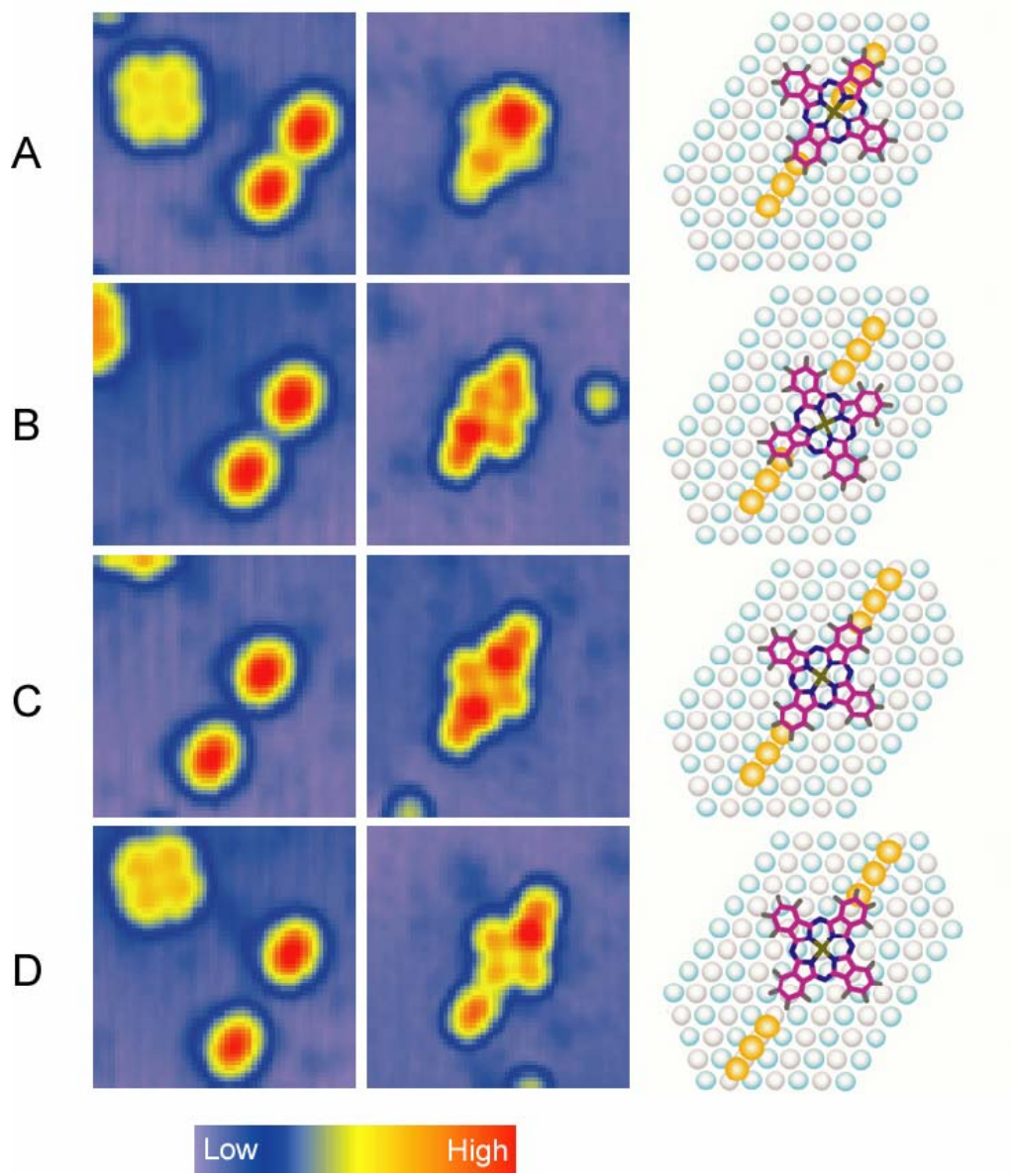
Assembly of CuPc@2Au$_6$



Missed Trajectory



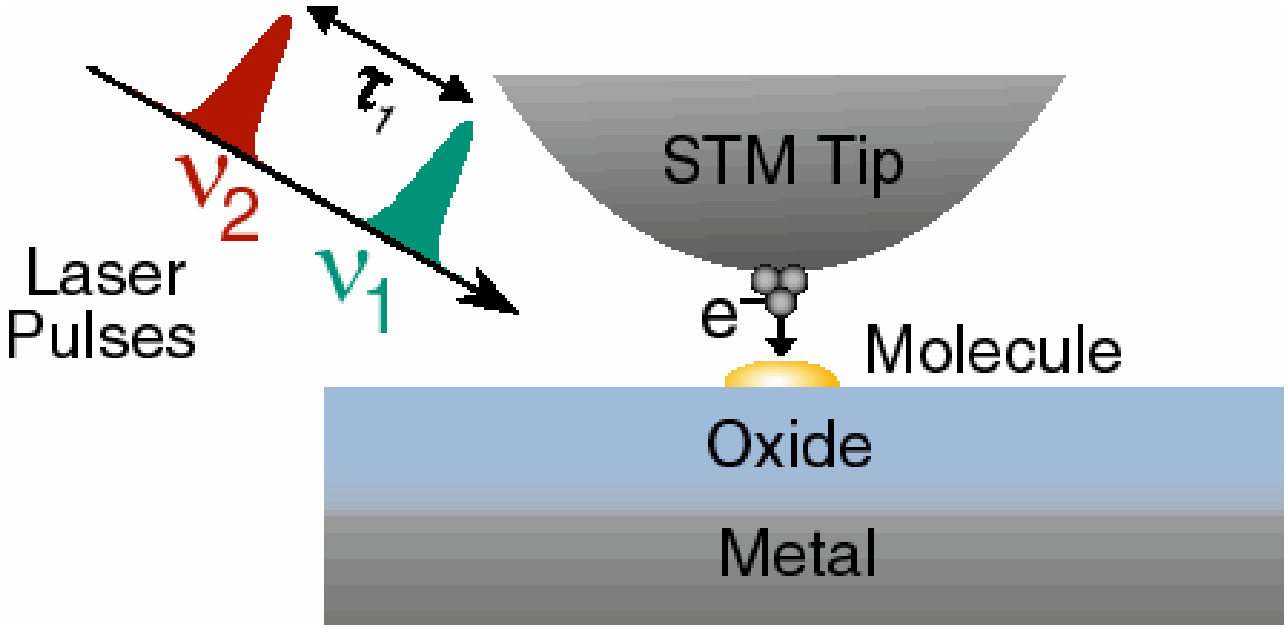
The Right Gap for Molecular Bridge



Acknowledgment

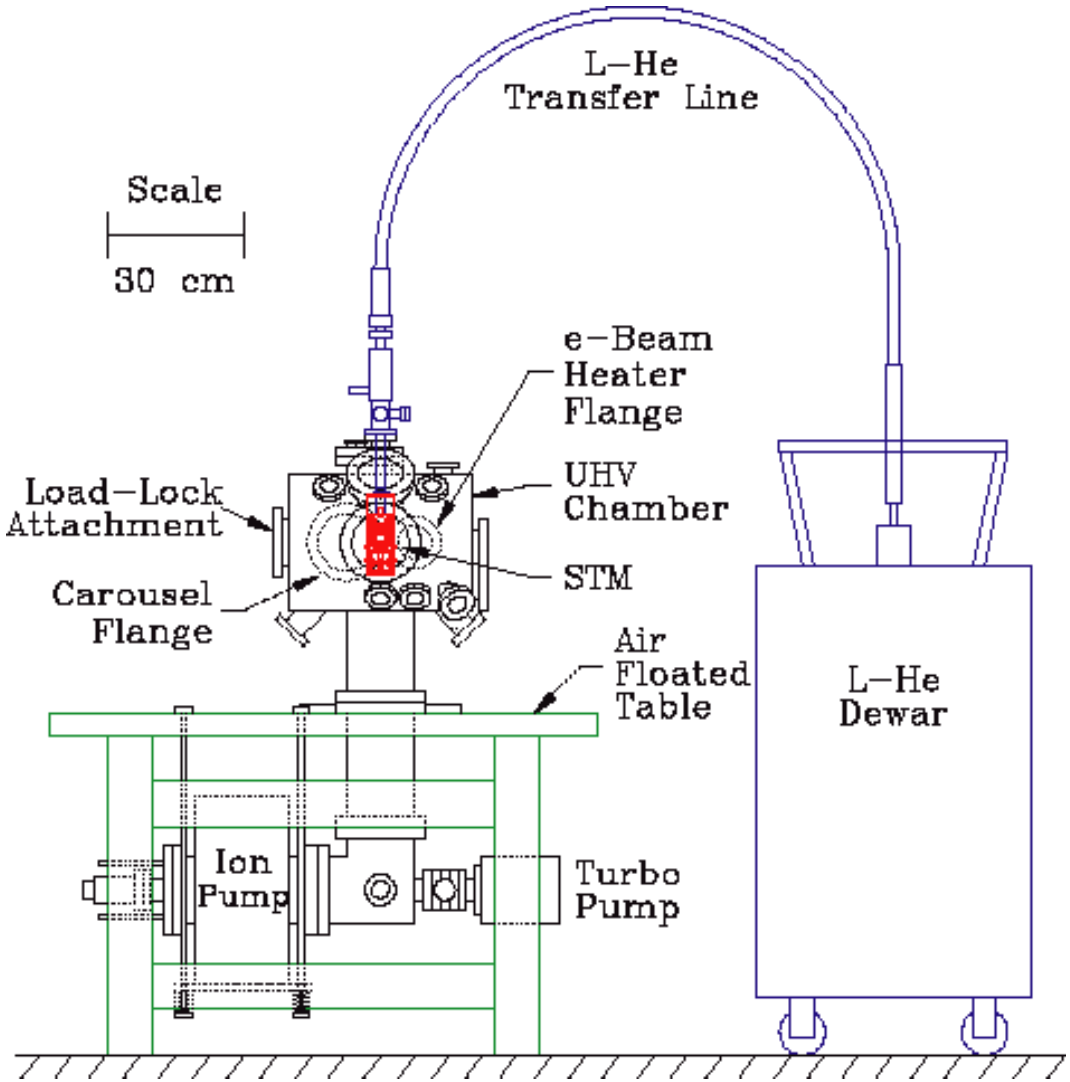
Past	***Present***
Xi Chen	Chi Chen
Jennifer Gaudioso	Ungdon Ham
Jae Ryang Hahn	Kiyeo Kim
Martin Janson	Markus Lackinger
Lincoln Lauhon	Gary Mikaelian
Hyojune Lee	George Nazin
Joonhee Lee	Freddy Toledo
Ning Liu	Xiuwen Tu
Niklas Nilius	Shiwei Wu
Naoki Ogawa	
Nilay Pradhan	
Xiaohui Qiu	
Mohammad Rezaei	
Christophe Silien	
Barry Stipe	
Mitch Wallis	
Nicolas Lorente	Shiwu Gao
	Mats Persson

Ultrafast Optical Spectroscopy with Spatial Resolution of the STM

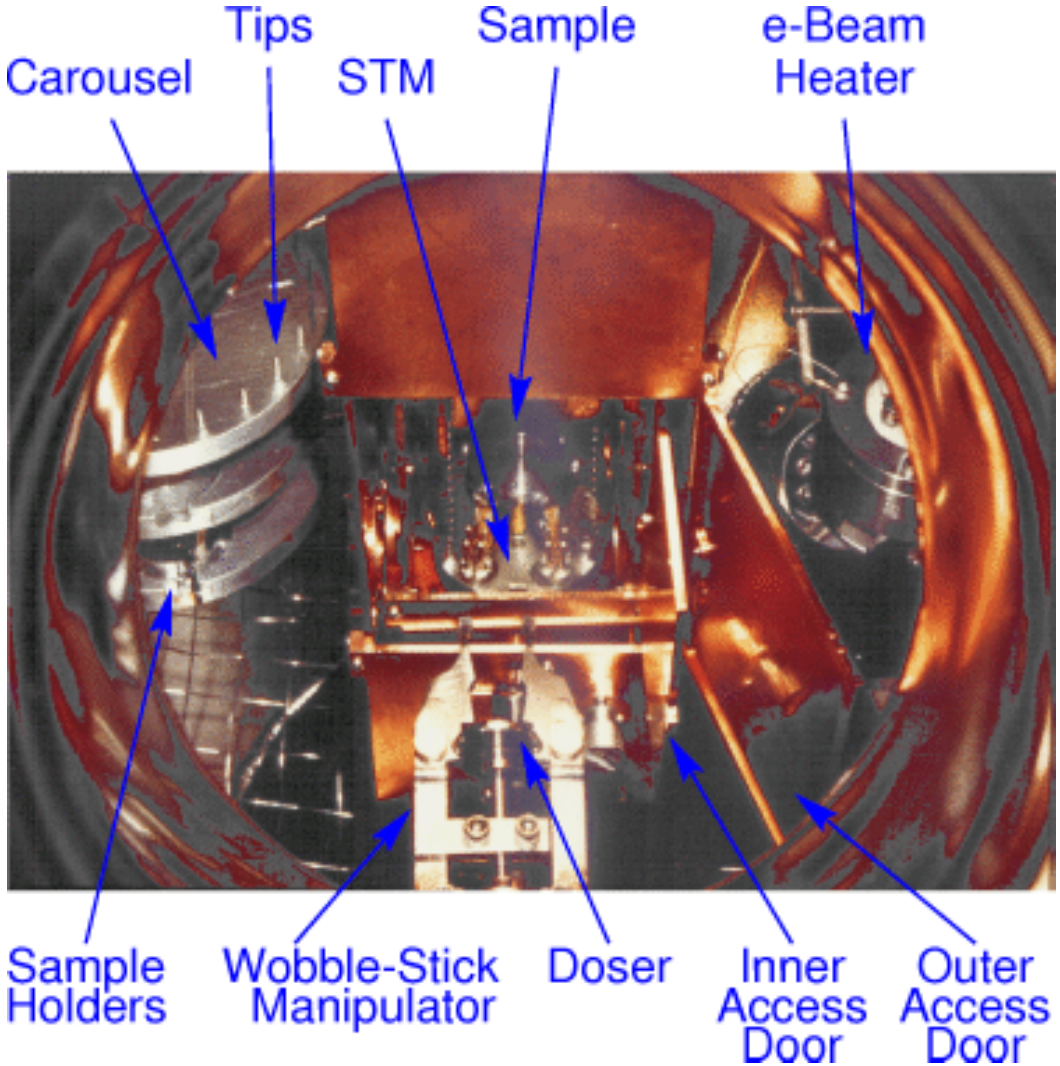


- Femtosecond Lasers:
  Chemistry at the Temporal Limit
- Scanning Tunneling Microscopes:
  Chemistry at the Spatial Limit

STM Apparatus



STM in Vacuum



50,000,000× Magnification

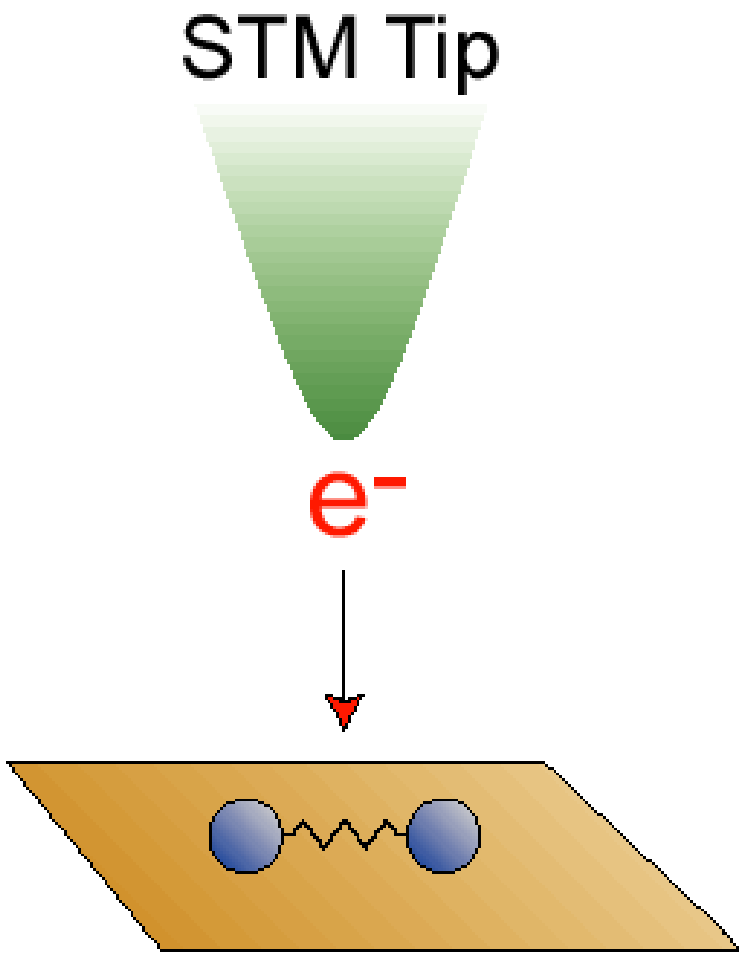
Galileo, 1992
3,900,000 Miles

Reines Hall
UC Irvine

The Interior of Single Molecules

- Single Molecule Vibrations and Dynamics
- Synthesis One by One
- Atomic Scale Optical Phenomena

Single Molecule Chemistry with the STM

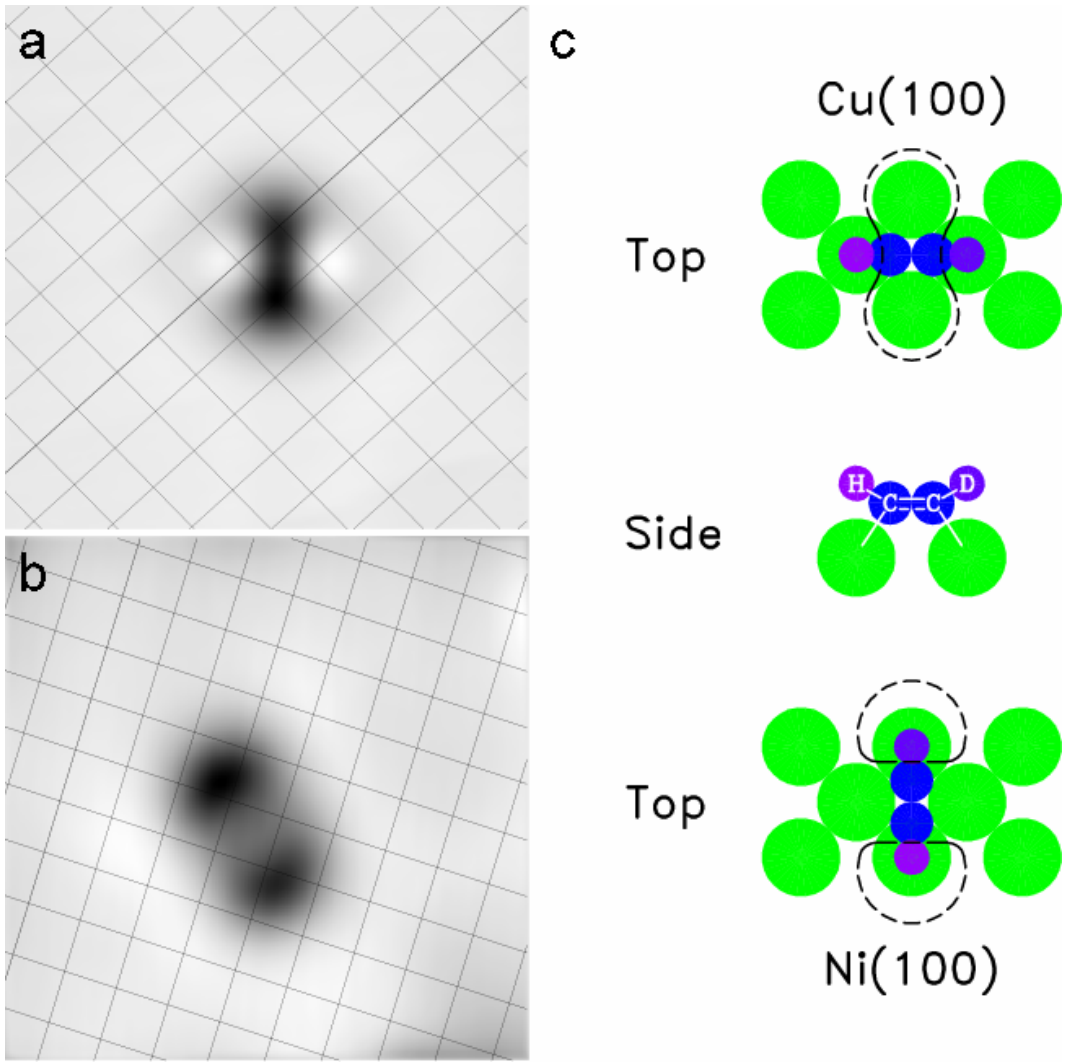


- Direct Visualization and Control of Chemistry
- Electrons Couple to Nuclear Motions
- Spatially Localized I-V Curves and Excitations
- Real Space Mapping

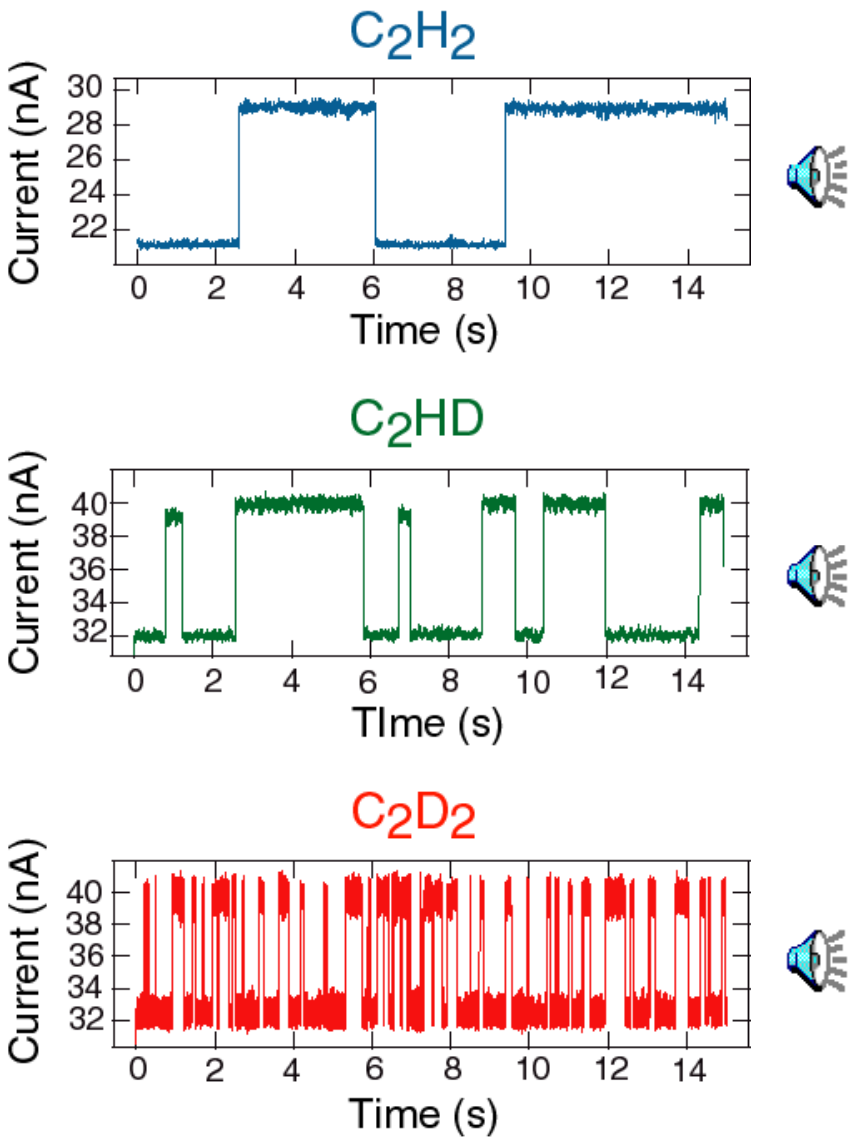
Single Molecule Vibrational Spectroscopy

- Inelastic Electron Tunneling Spectroscopy (IETS)
- Vibronic Spectroscopy
- Vibrationally Resolved Fluorescence
- RF Induced Rectification Current

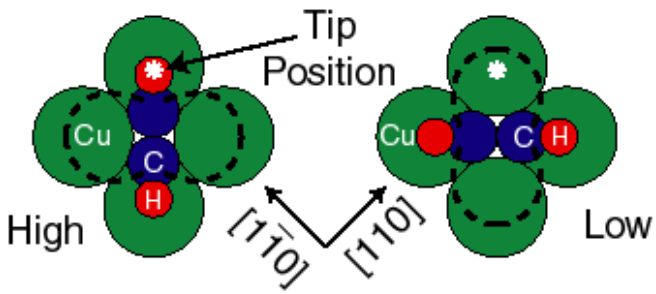
Structural Determination

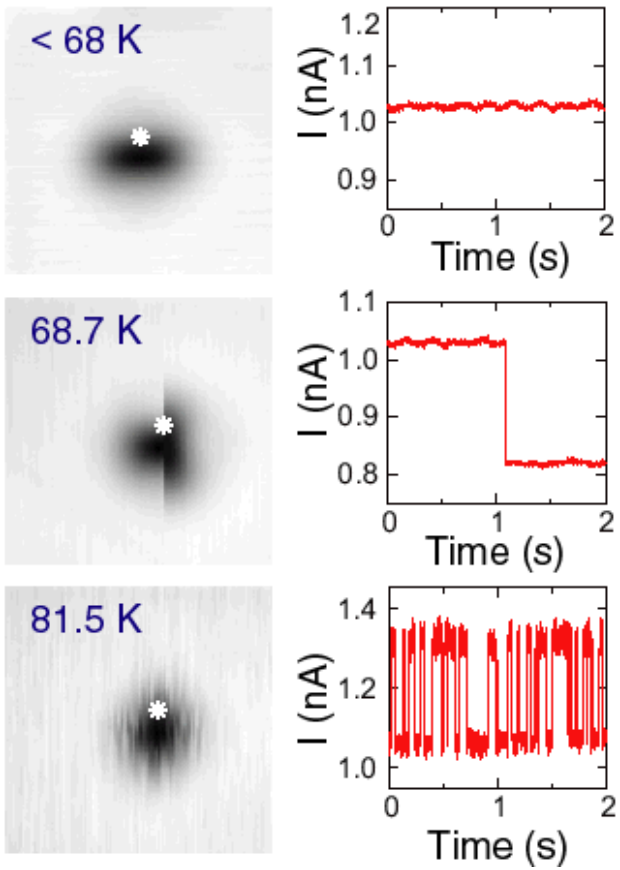


Molecular Rotation: Acetylene on Cu(001) @ 8 K

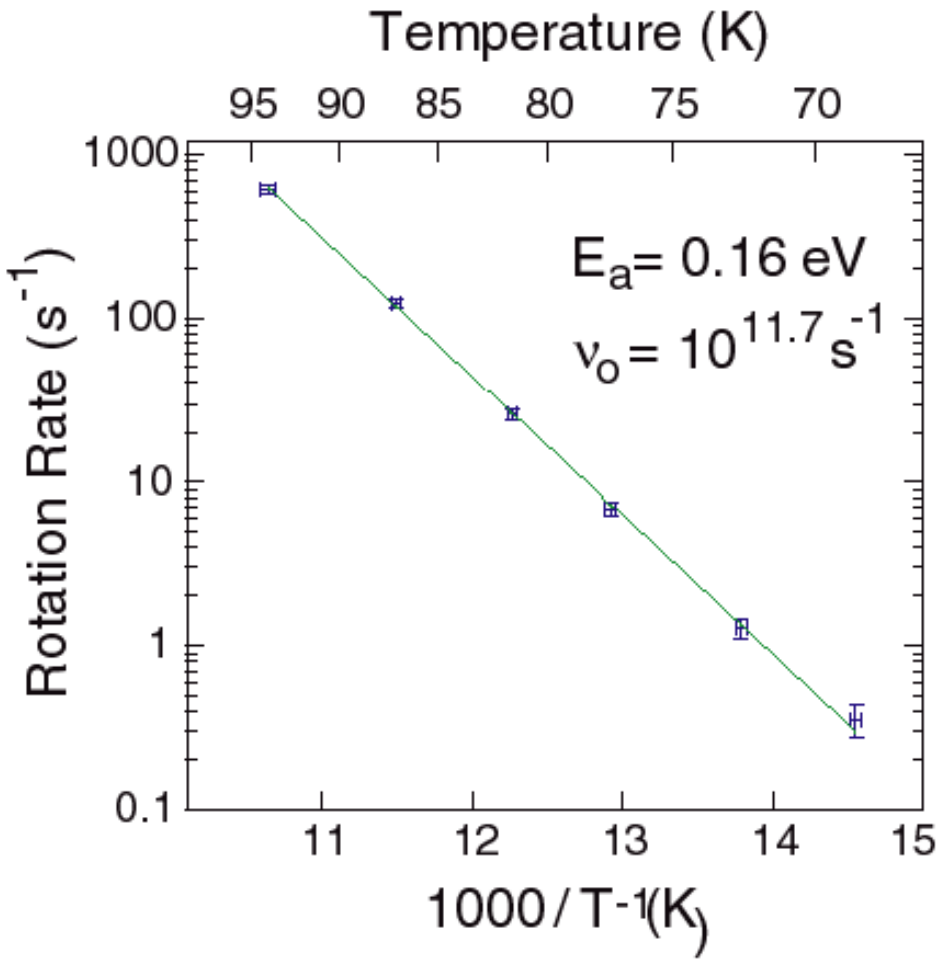


Acetylene Thermal Rotation





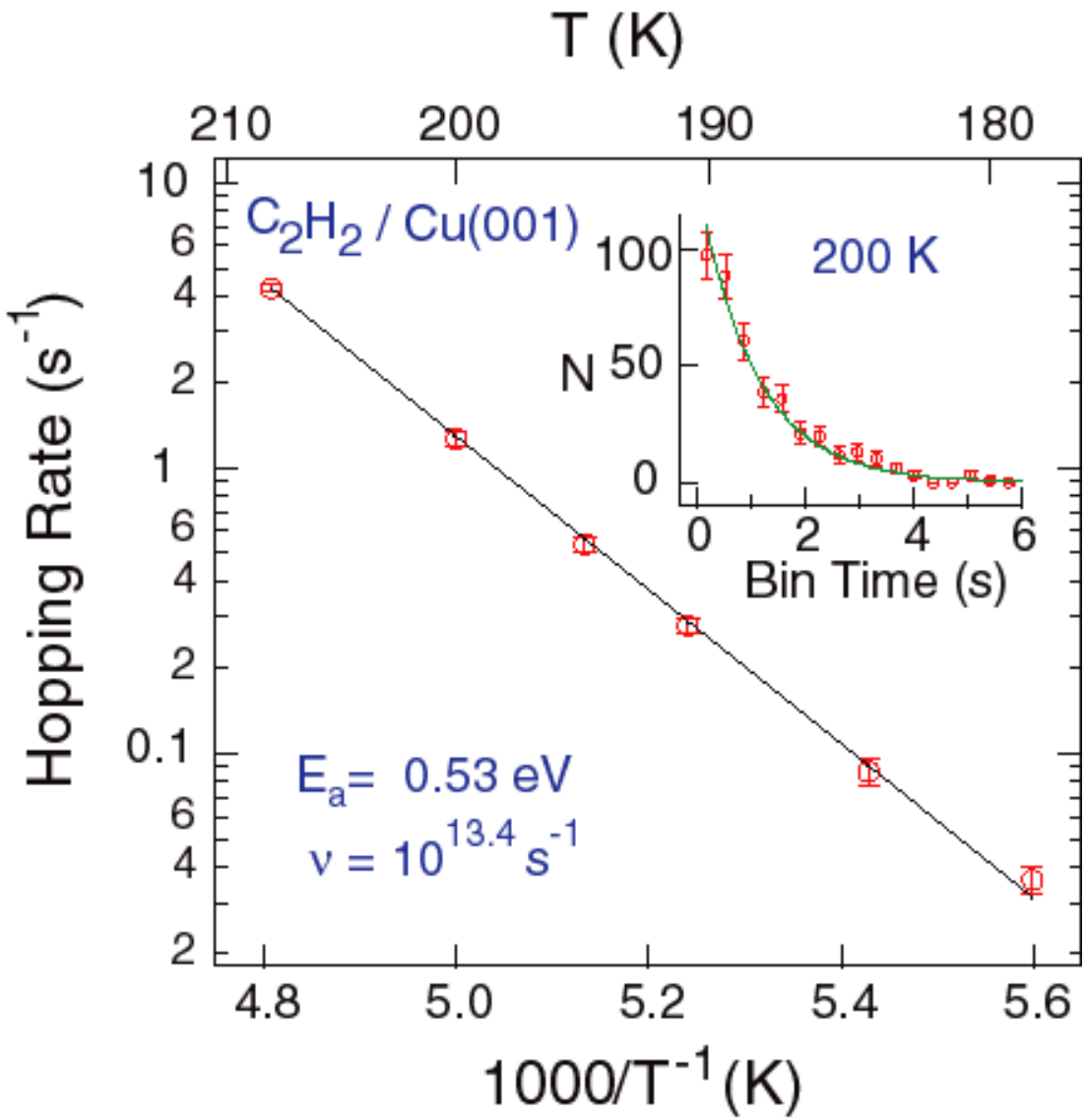
Acetylene Thermal Rotation Rate



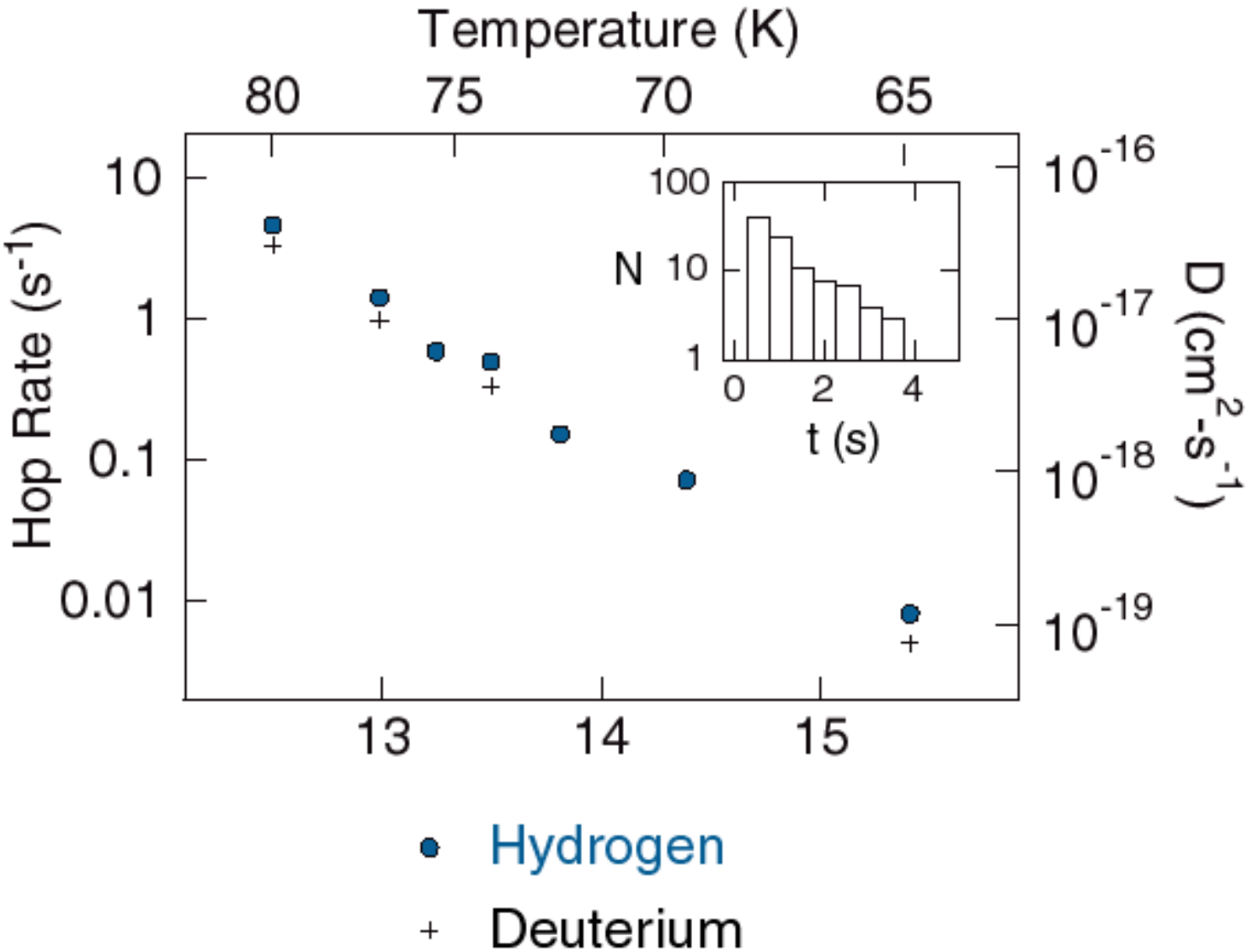
$$\text{rate} = \nu_o \exp(-E_a/kT)$$

$$\ln(\text{rate}) = \ln \nu_o - E_a/kT$$

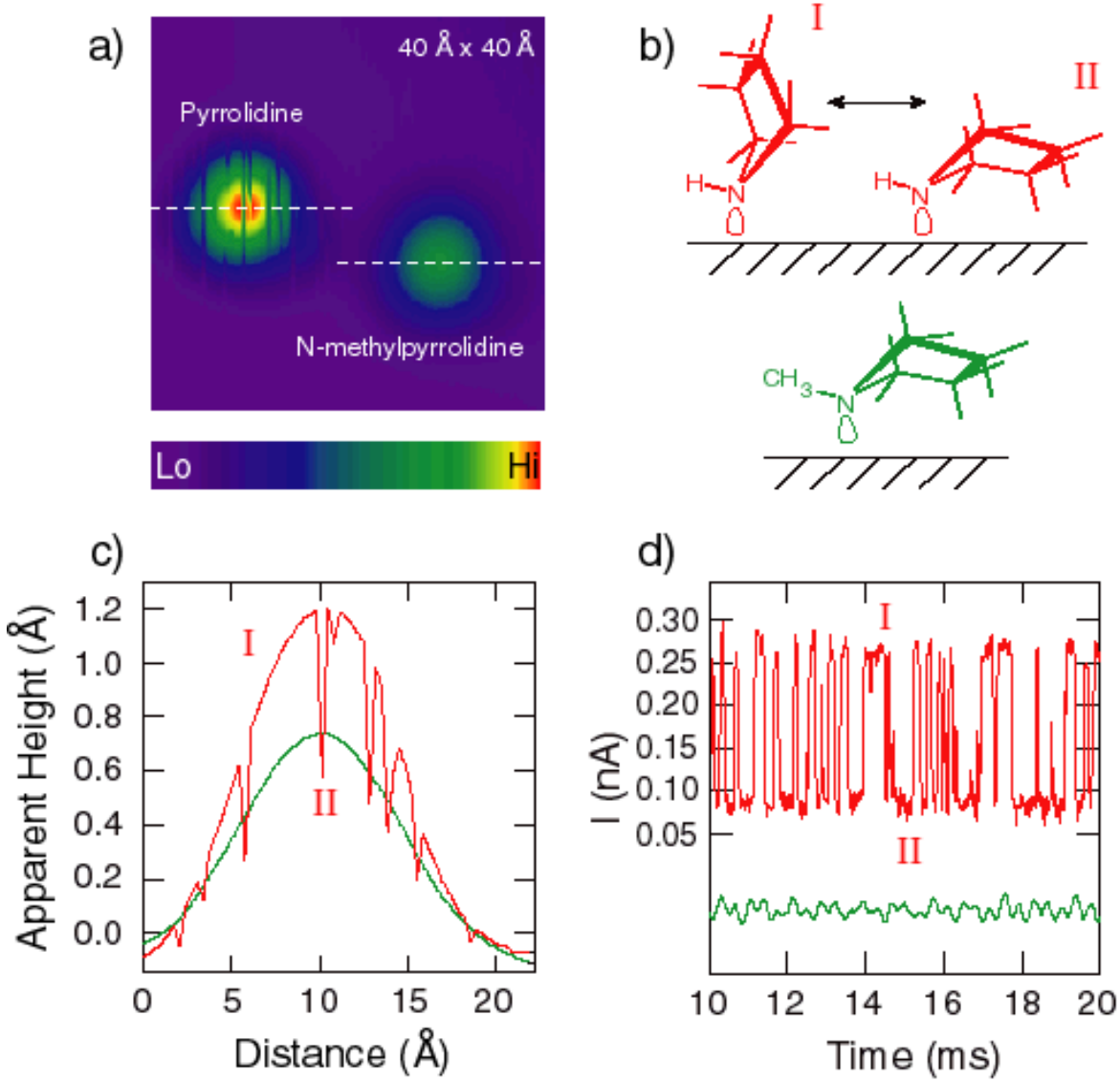
Acetylene Thermal Hopping Rate



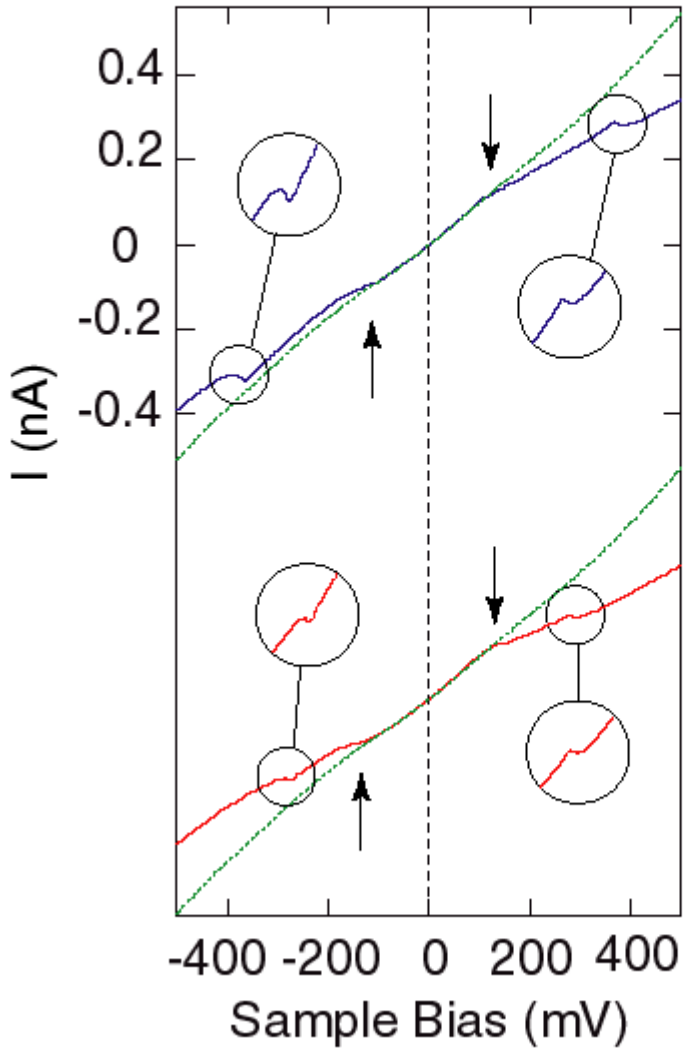
Single Atom Thermal Diffusion

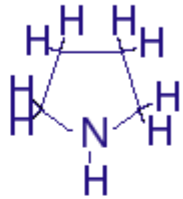


Conformation Suppression

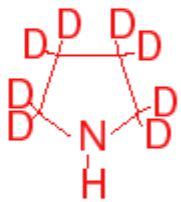


Vibrationally-Mediated Negative Differential Resistance





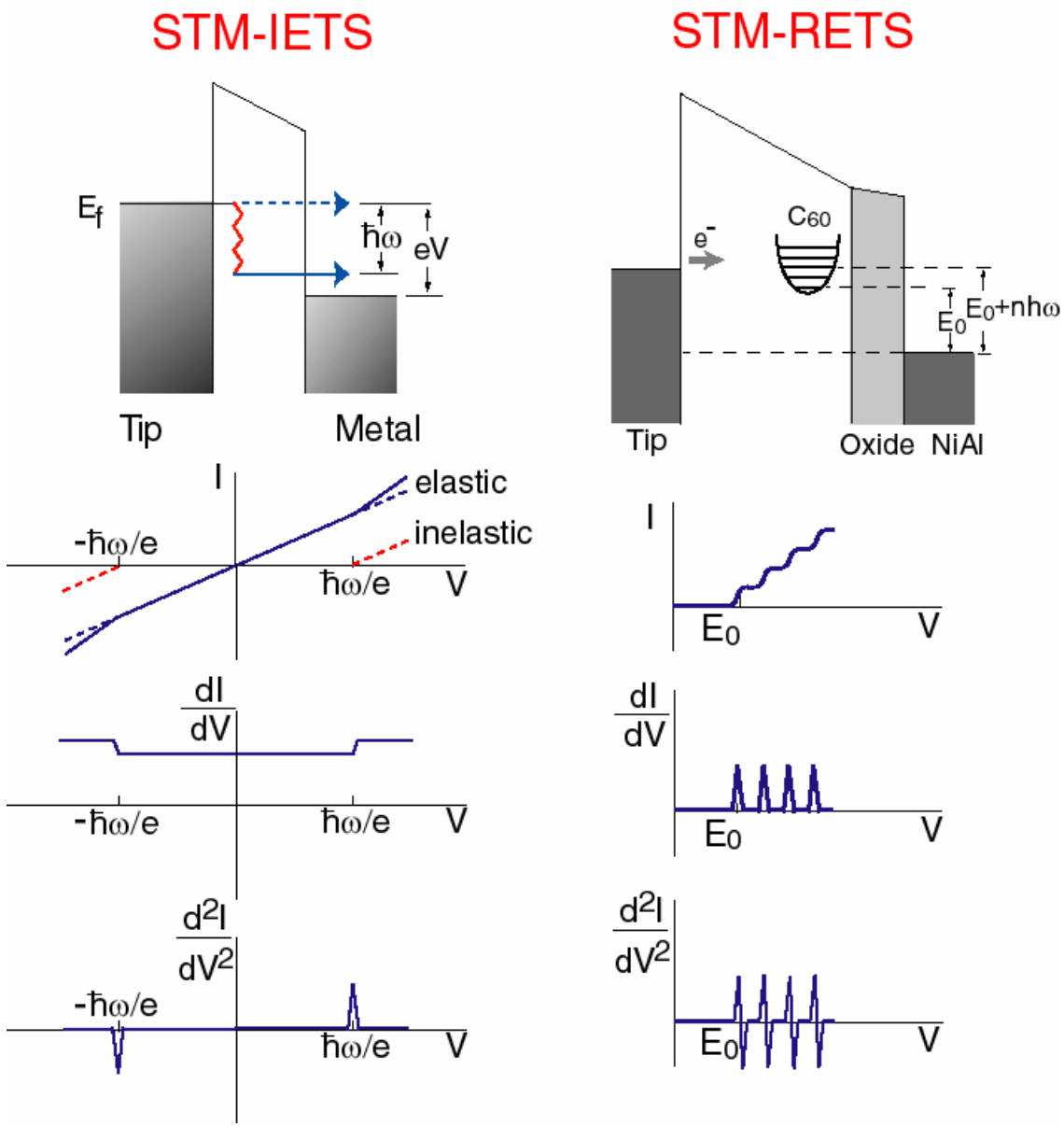
Pyrrolidine-h_9



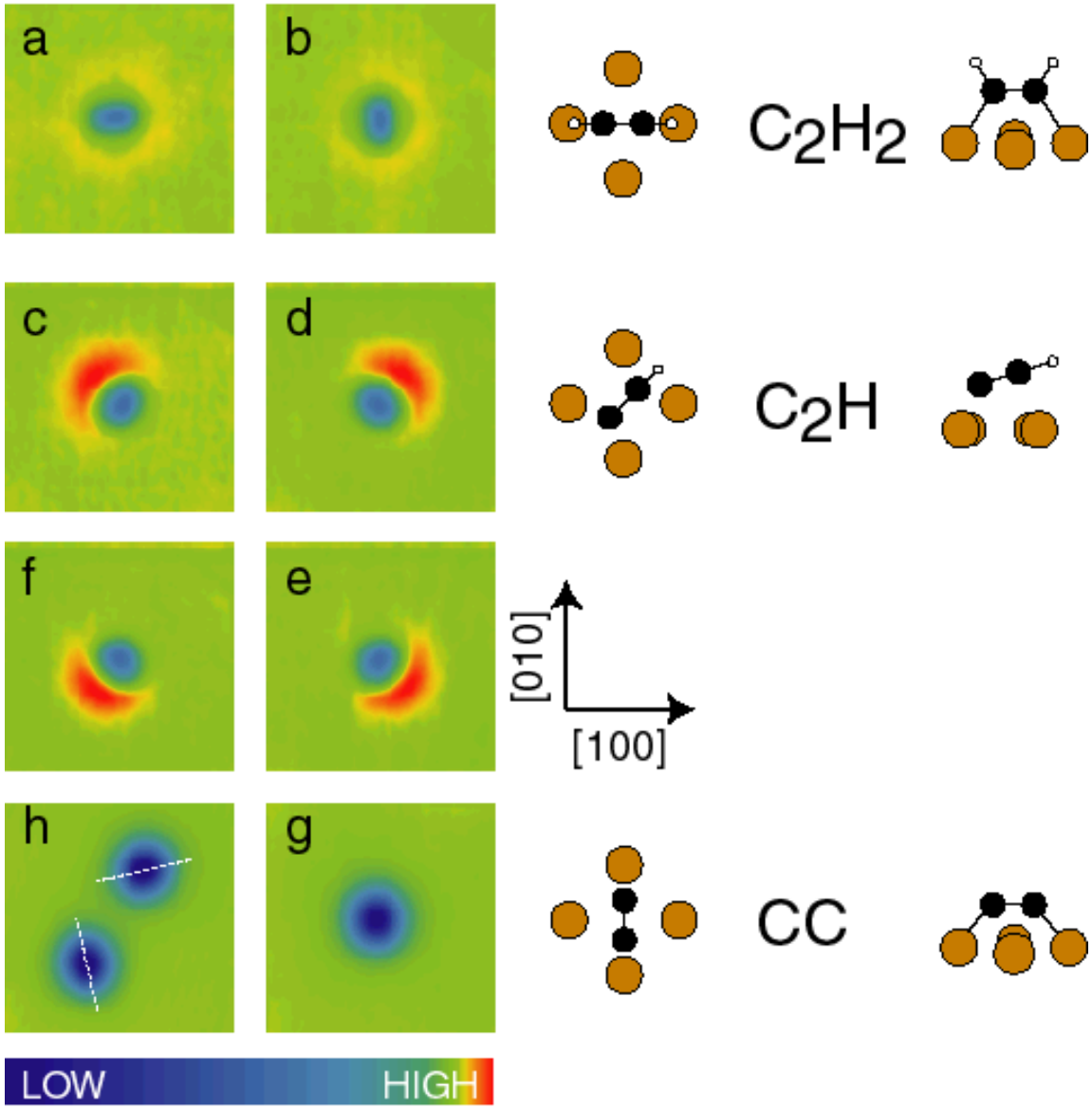
Pyrrolidine-d_8

Cu(001)

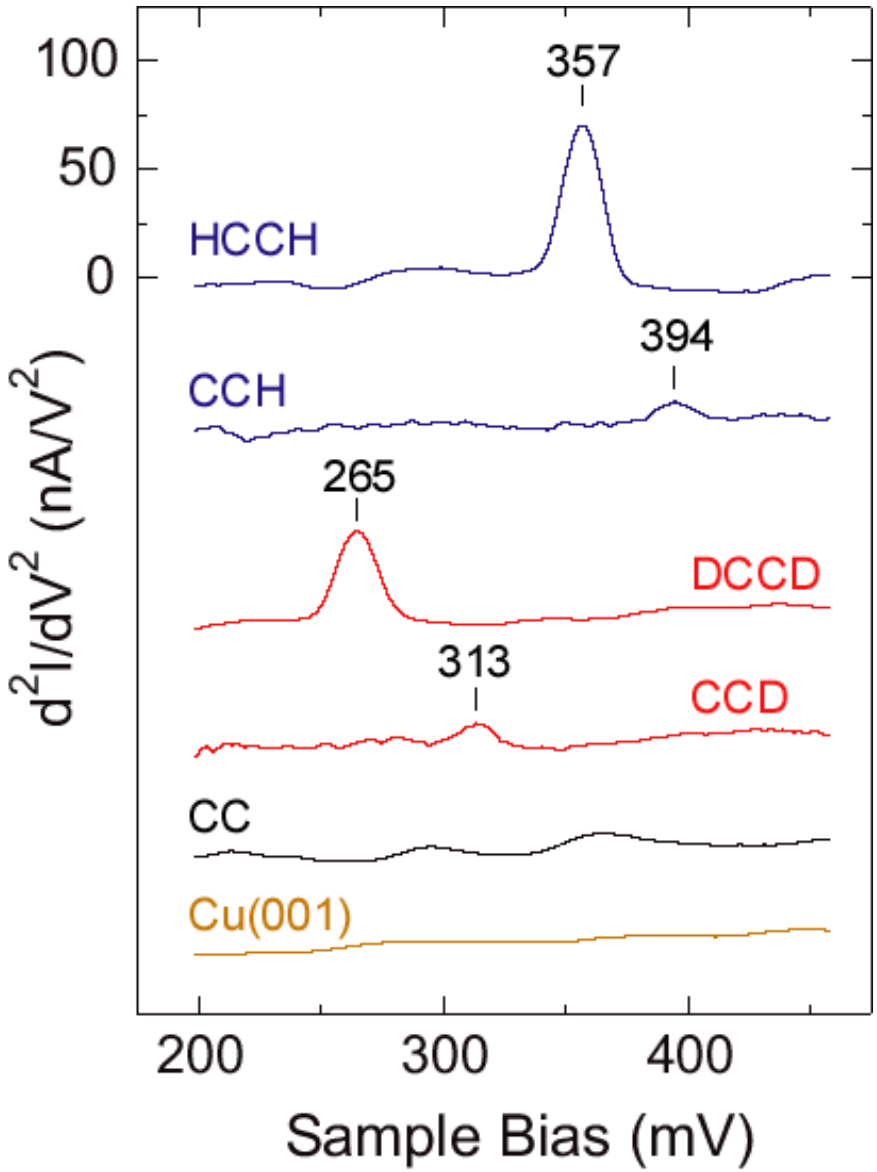
Inelastic Vibrational vs. Vibronic Spectroscopy



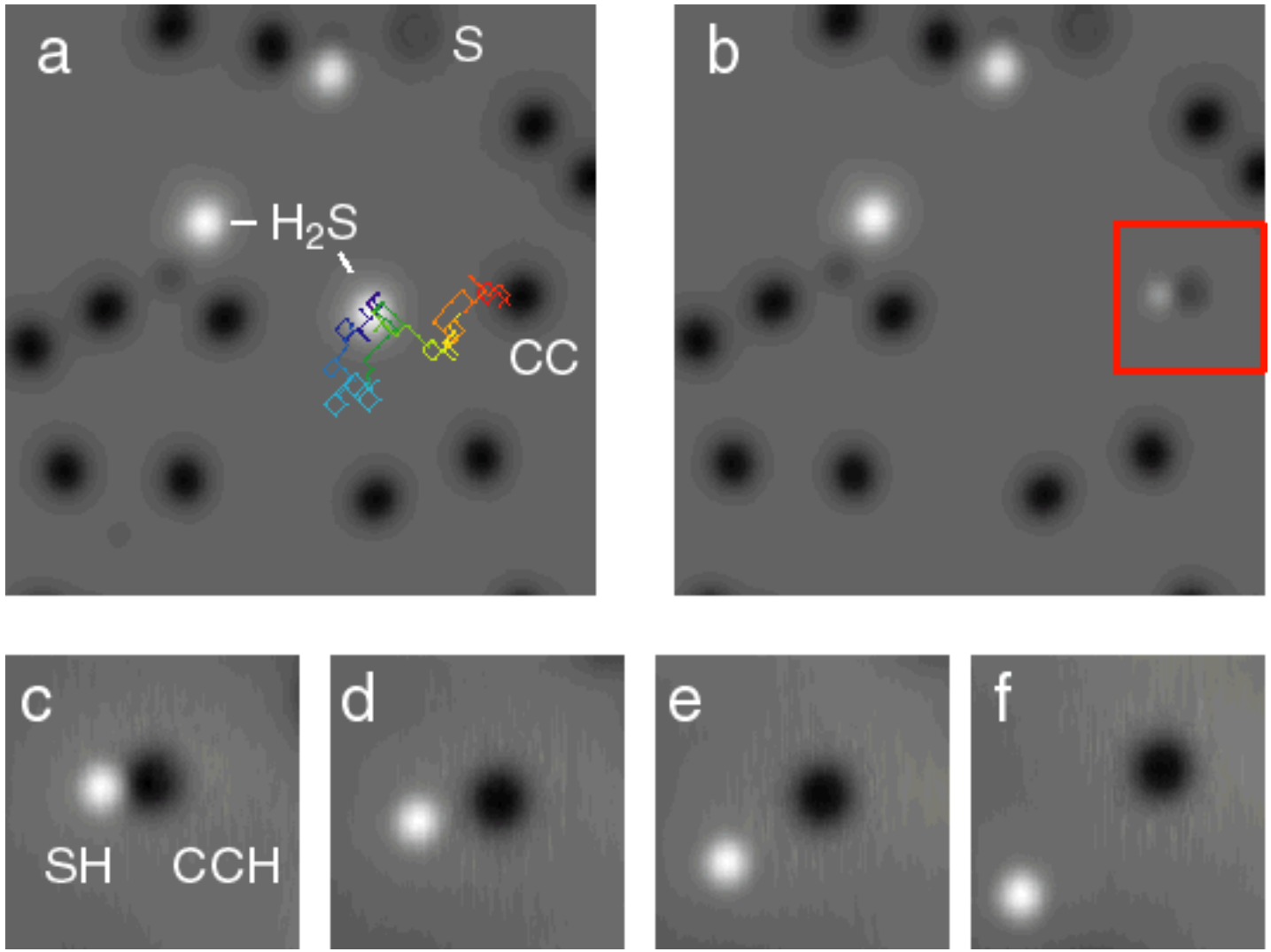
Rotational Analysis



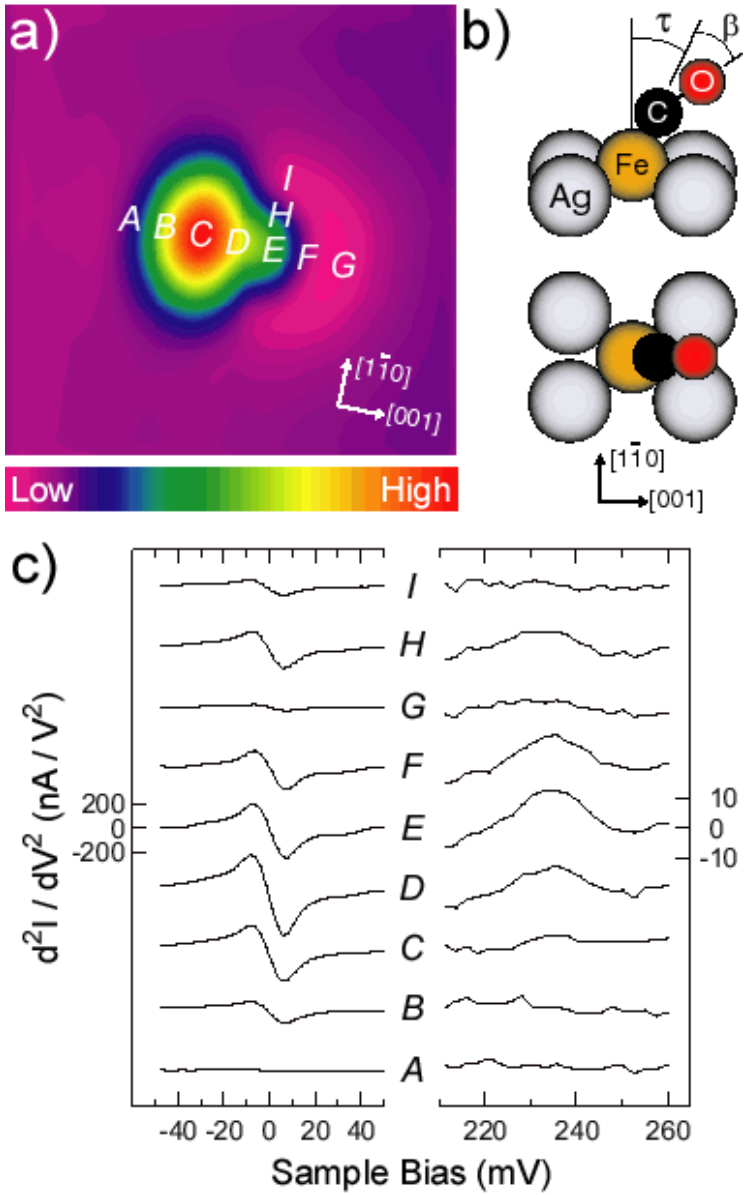
Vibrational Analysis



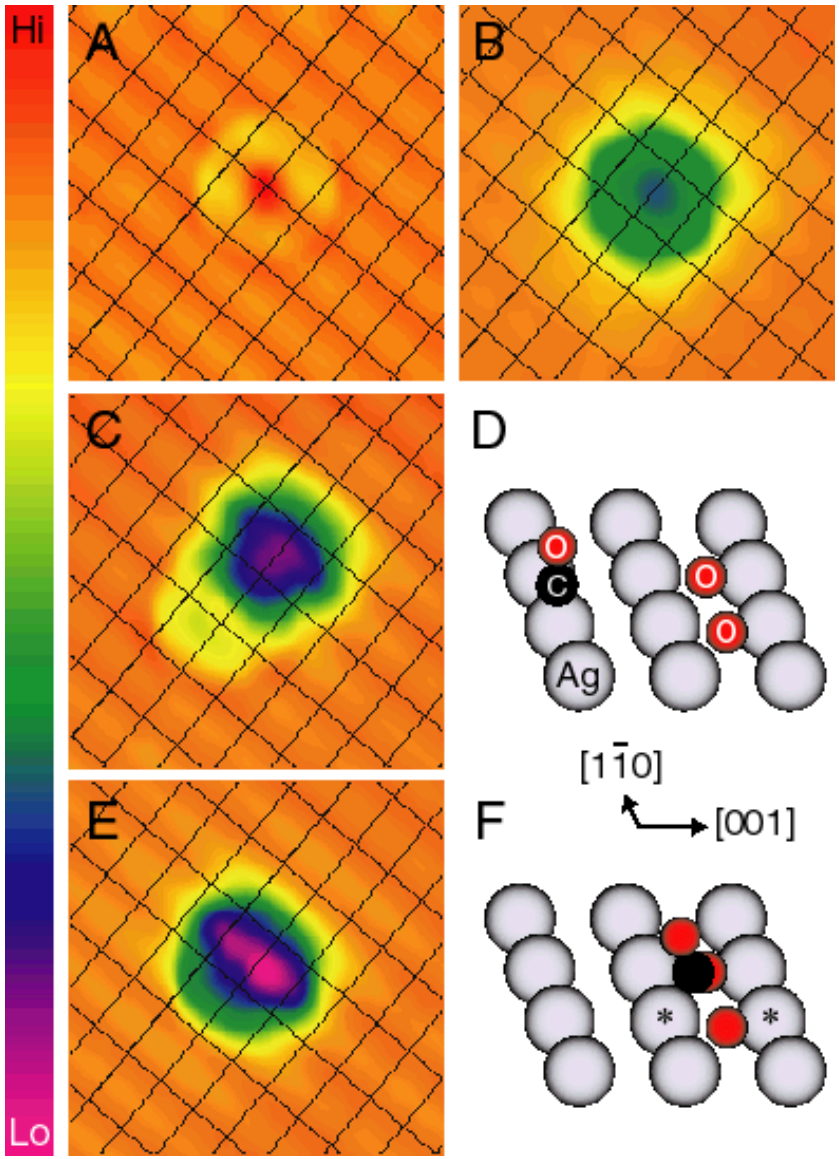
$H_2S + CC \rightarrow SH + CCH$
Cu(001) @ 9 K



Sub-Å Vibrational Spectroscopy

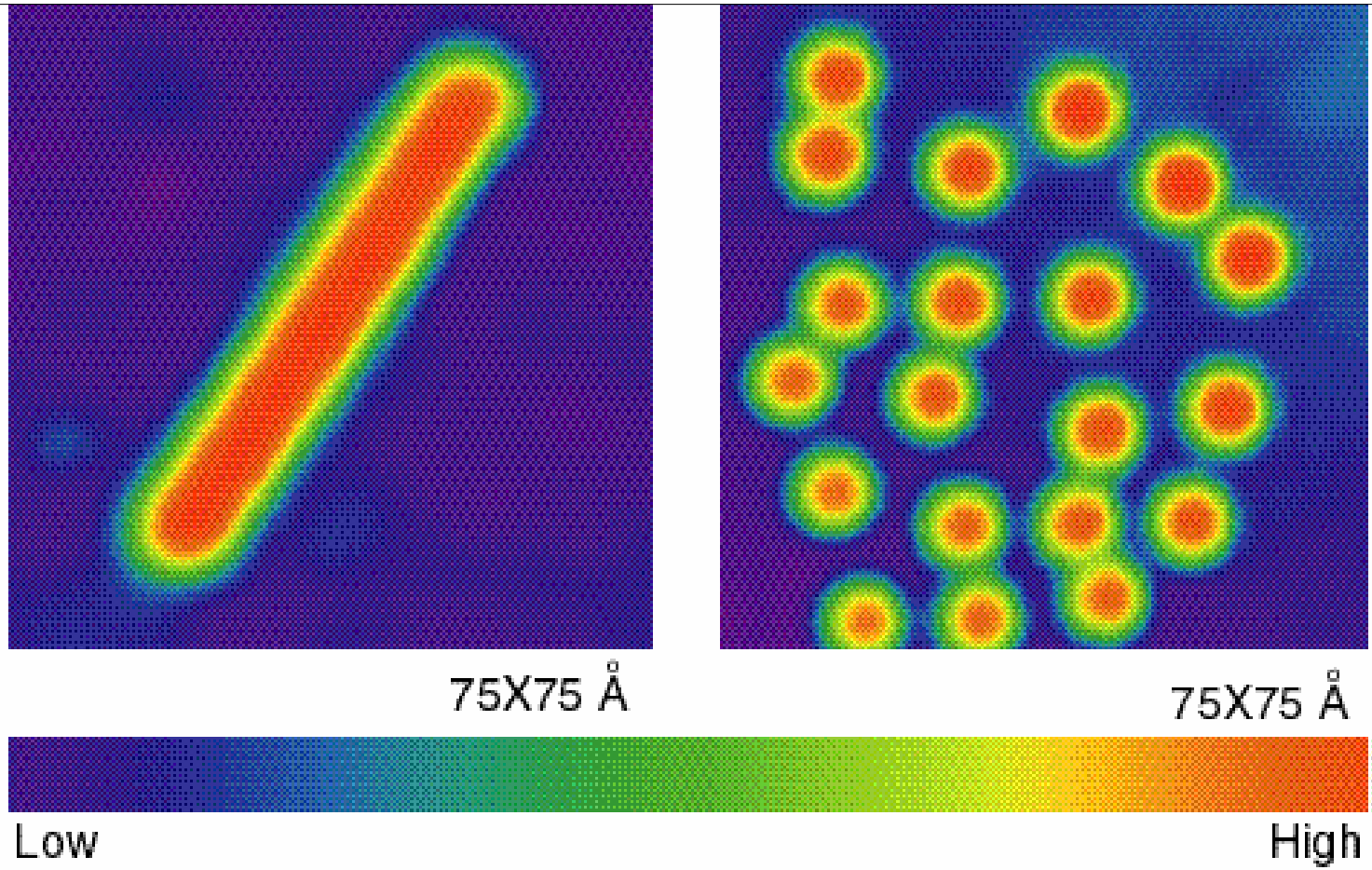


$CO + 2O \rightarrow CO_2 + O$

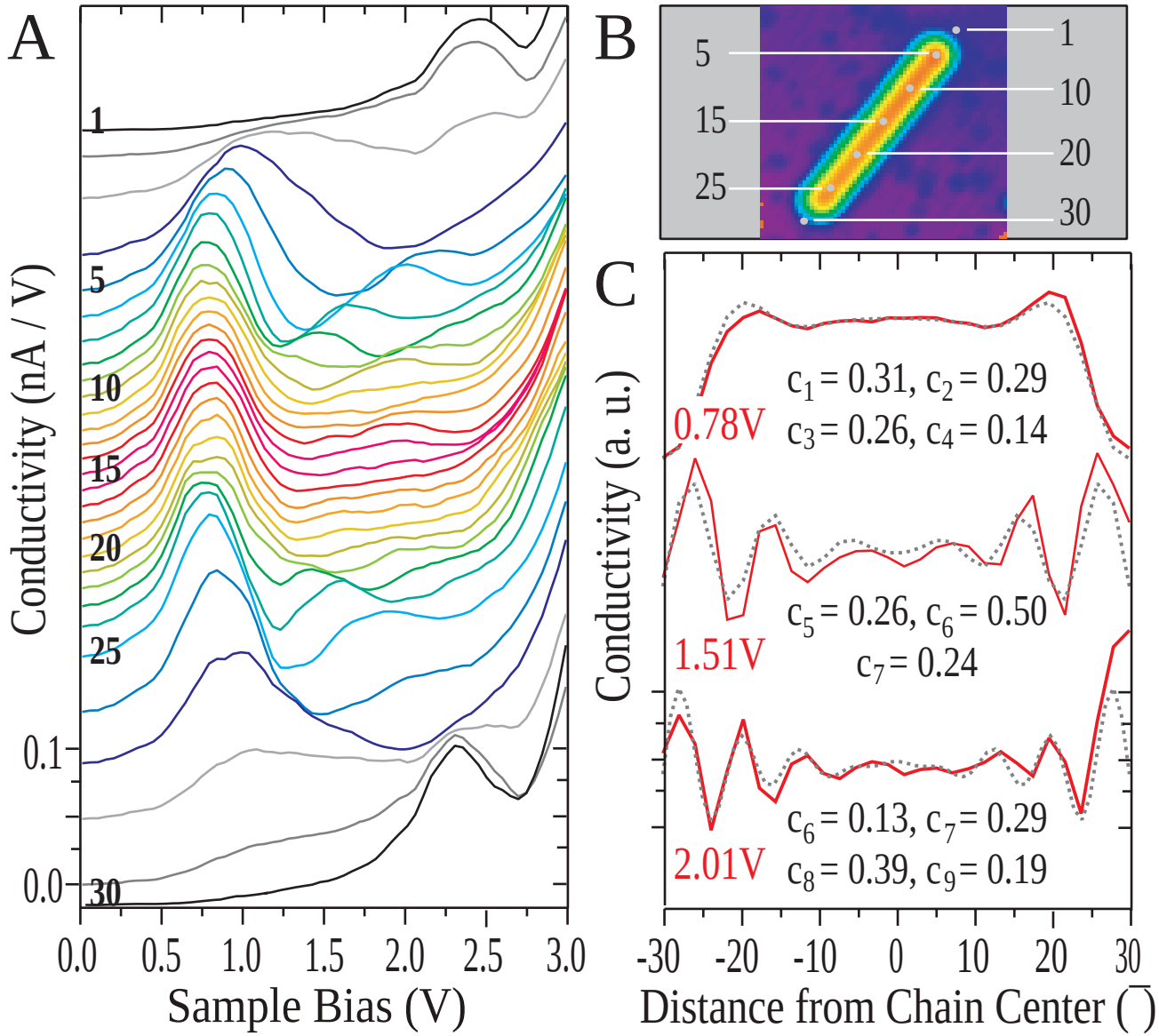


20-Atom Au Chain

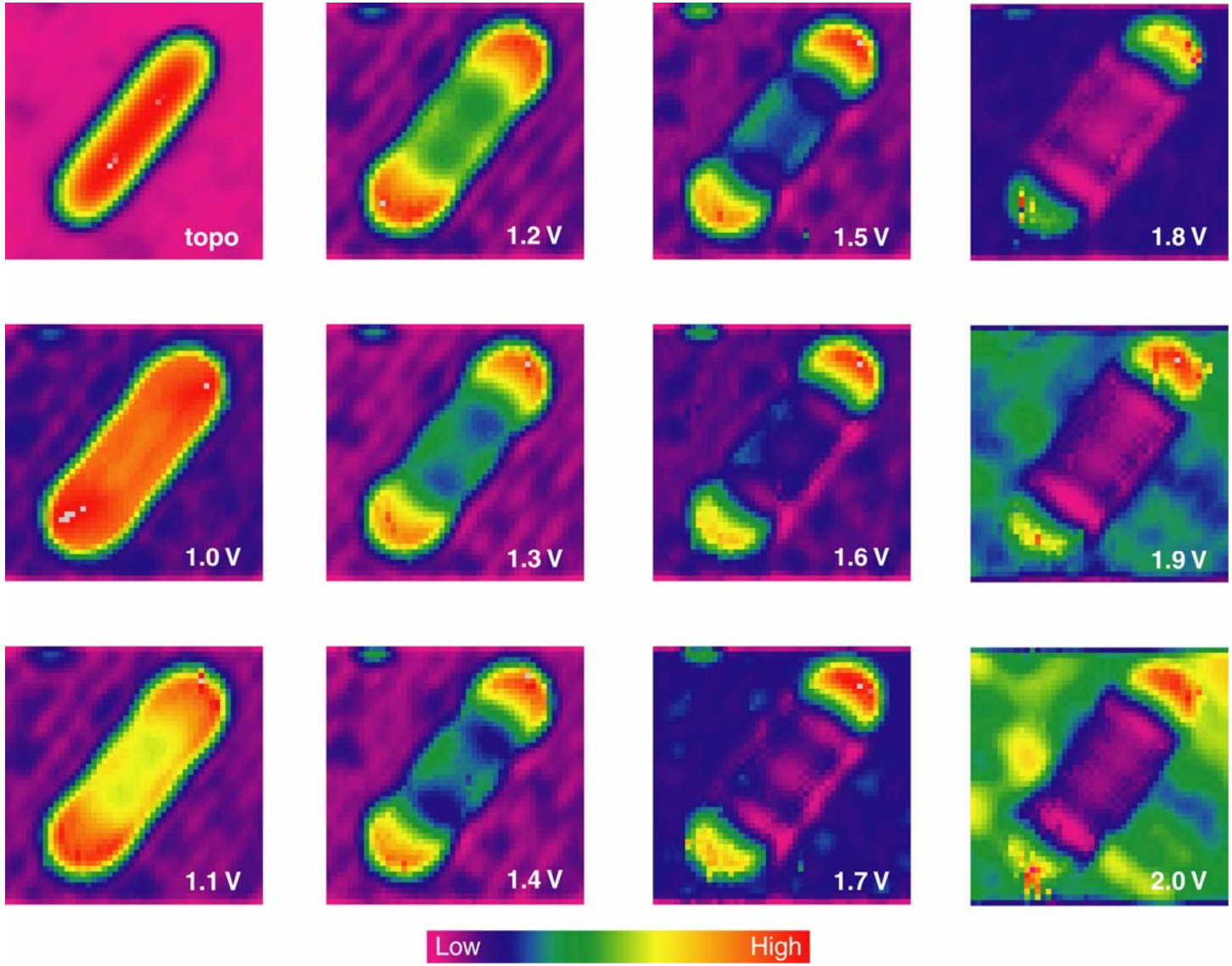
Assembled **Disassembled**



Au_{20}: Spatially Resolved Spectra

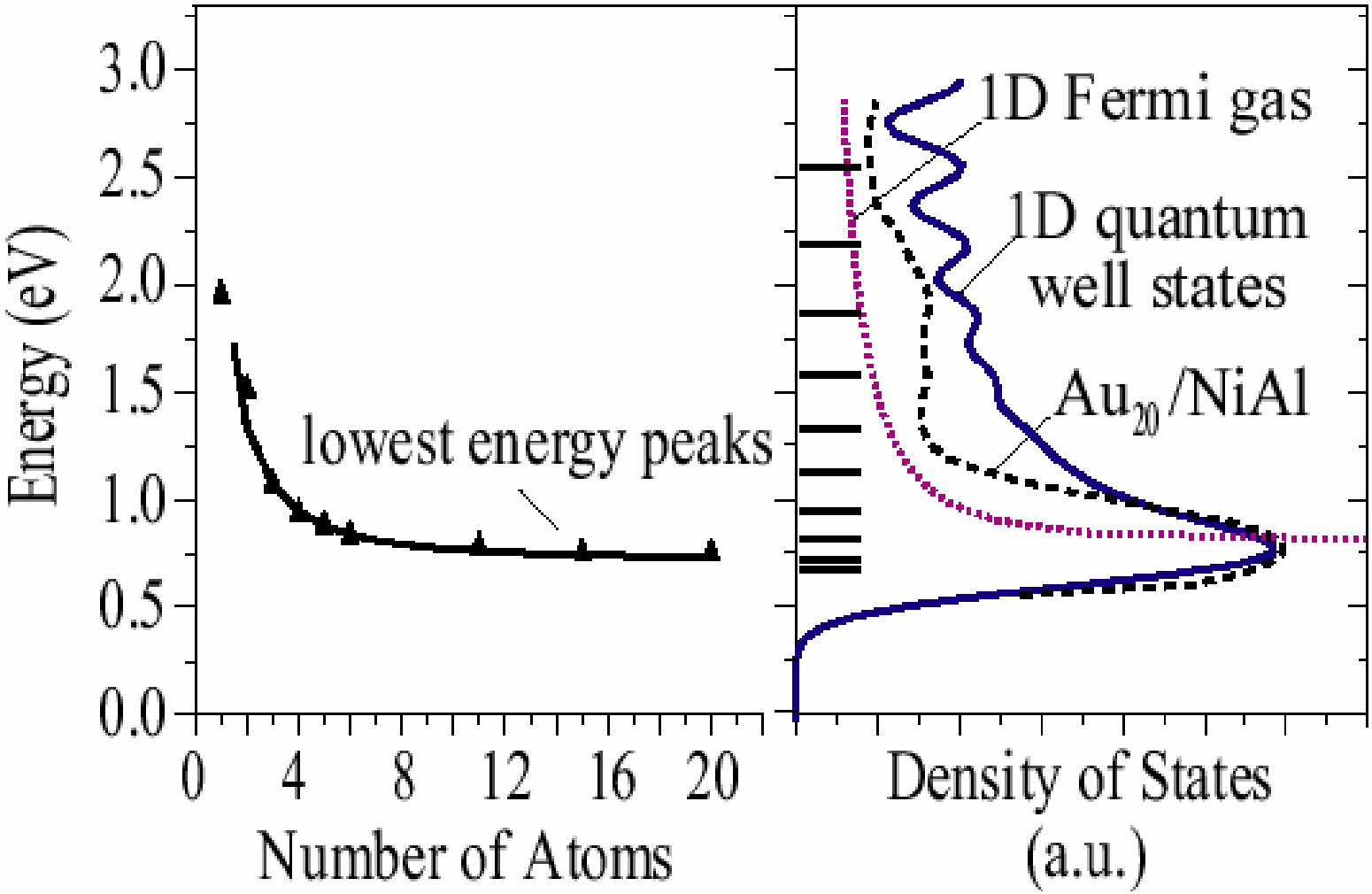


Electron Density of States of 11-Atoms Au Chain



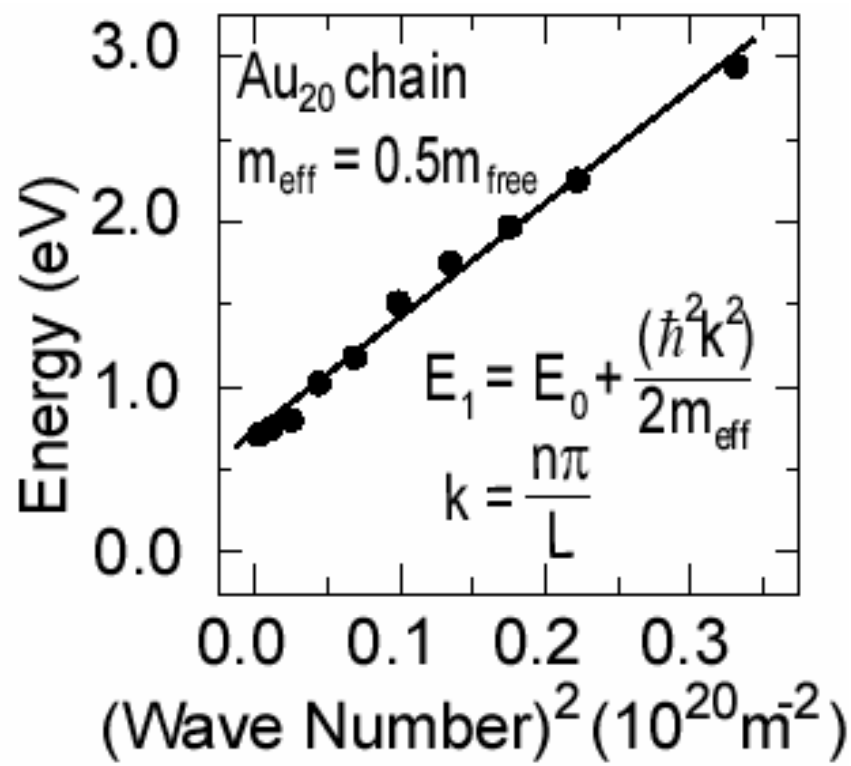
Au Chains: 1-D Particle-in-a-Box

$E \sim 1 / L^2$ $\rho \sim 1 / E^{1/2}$

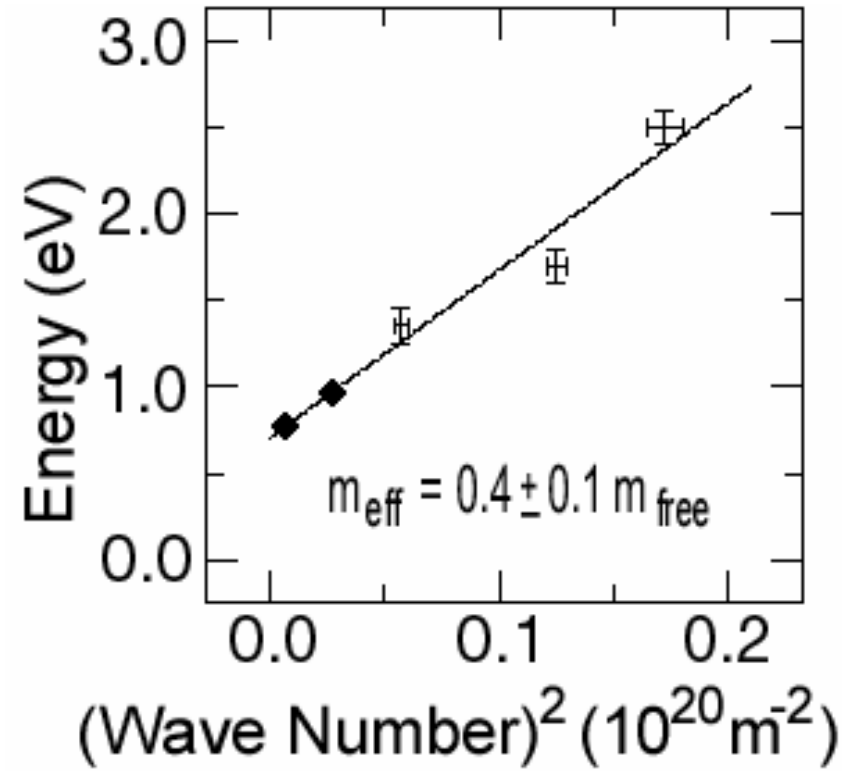


Au Chains – Energy Dispersion

Au_{20}



Au_{11}



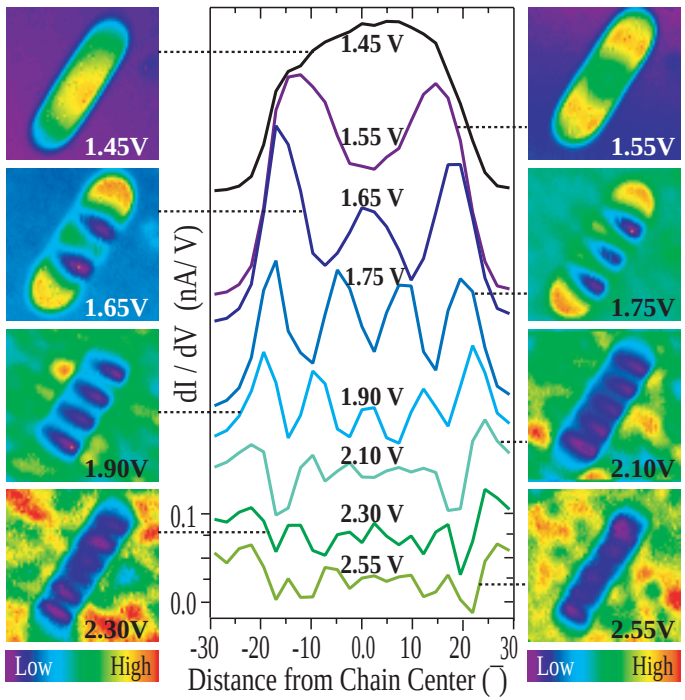
Physics 238C

Spring 2003

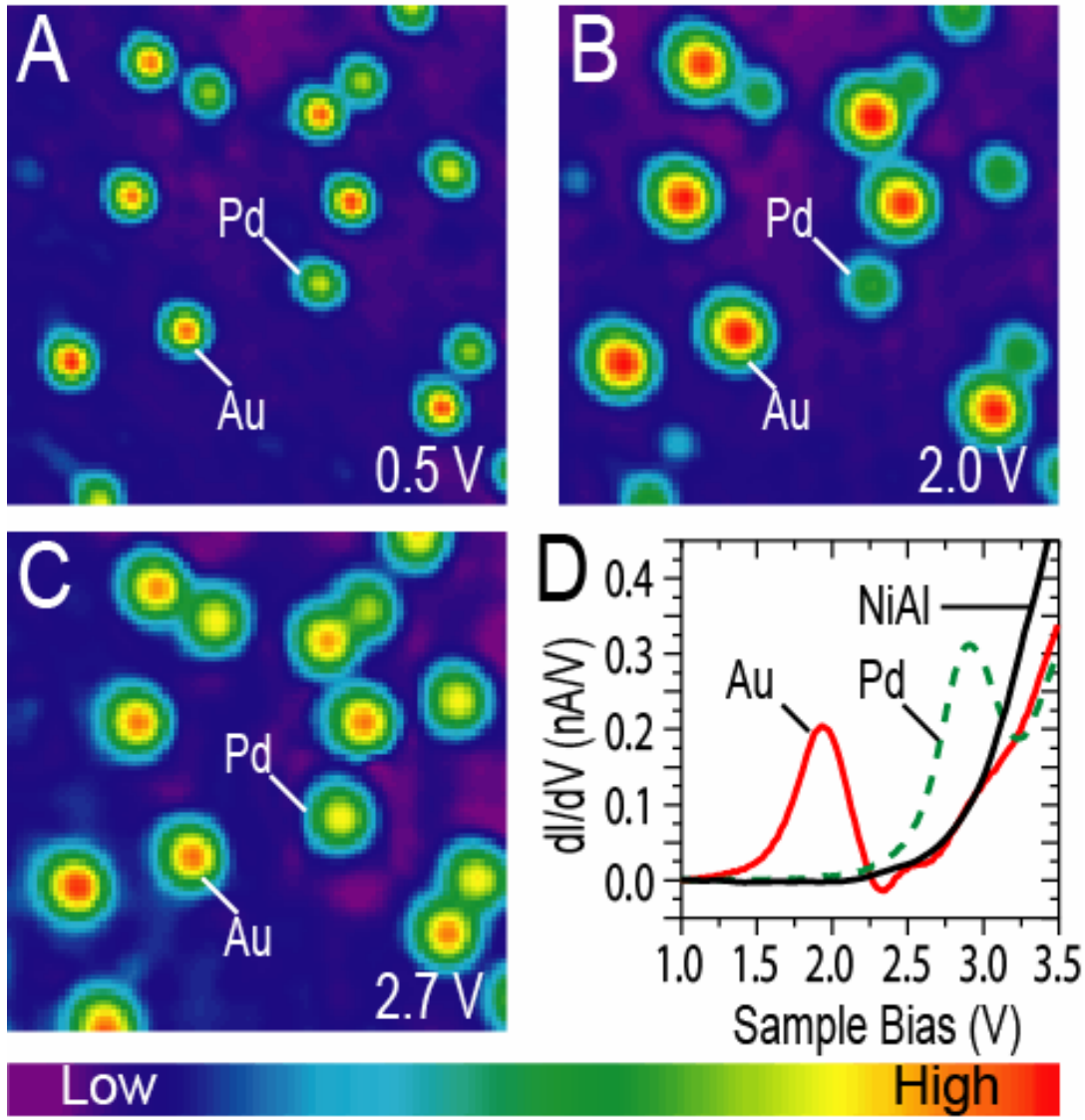
(Due Thursday, May 1, 2003)

The figure below shows standing wave patterns observed in an atomic chain assembled from 20 Pd atoms using a scanning tunneling microscope to manipulate individual Pd atoms on a NiAl(110) surface at 12 K. The NiAl(110) surface provides a one-dimensional template for the chain. The standing wave patterns are the electronic density of states which are proportional to the differential conductance (dI/dV) measured by the scanning tunneling microscope. Each image is a display of the spatial distribution of the dI/dV intensity. To generate each image, the tip is scanned over the displayed area and dI/dV signal is recorded at each point. The curves in the middle of the figure show cross sectional plots of the dI/dV intensity along the chain from the images. The voltages correspond to the sample bias and when multiplied by the magnitude of the electron charge give the energies of the standing wave states.

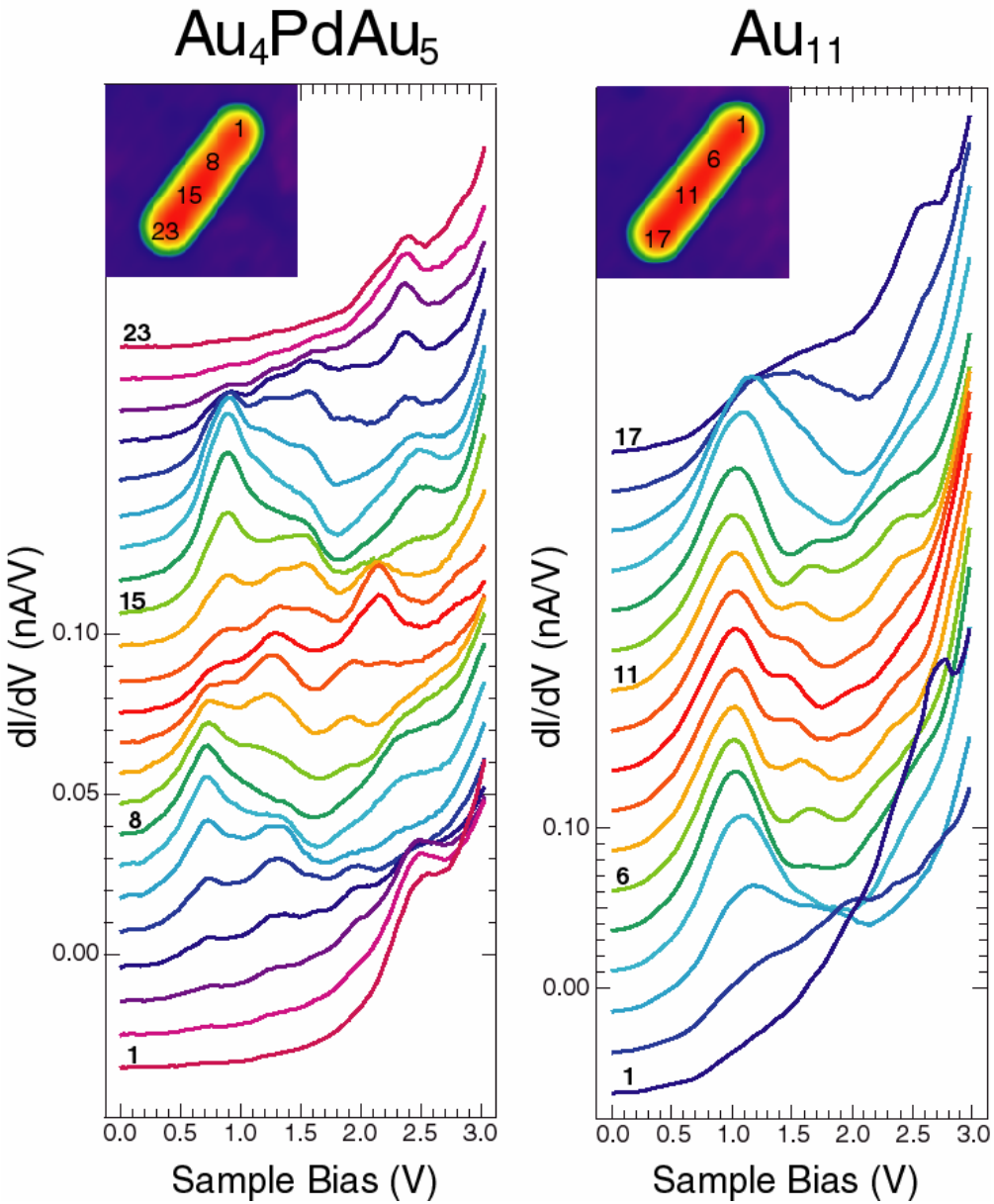
(a) Calculate the wavelength for each state observed.
(b) Obtain the energies and wave vectors for the states observed.
(c) Obtain and plot the wavefunctions for the states observed.
(d) Plot the dispersion relation (i.e. E vs. k) for the chain.
(e) Calculate the effective mass of an electron in the chain.
(f) Compare and discuss your results with a particle in a one-dimensional box.
(g) Discuss any discrepancies of your results with those of particle in a one-dimensional box.



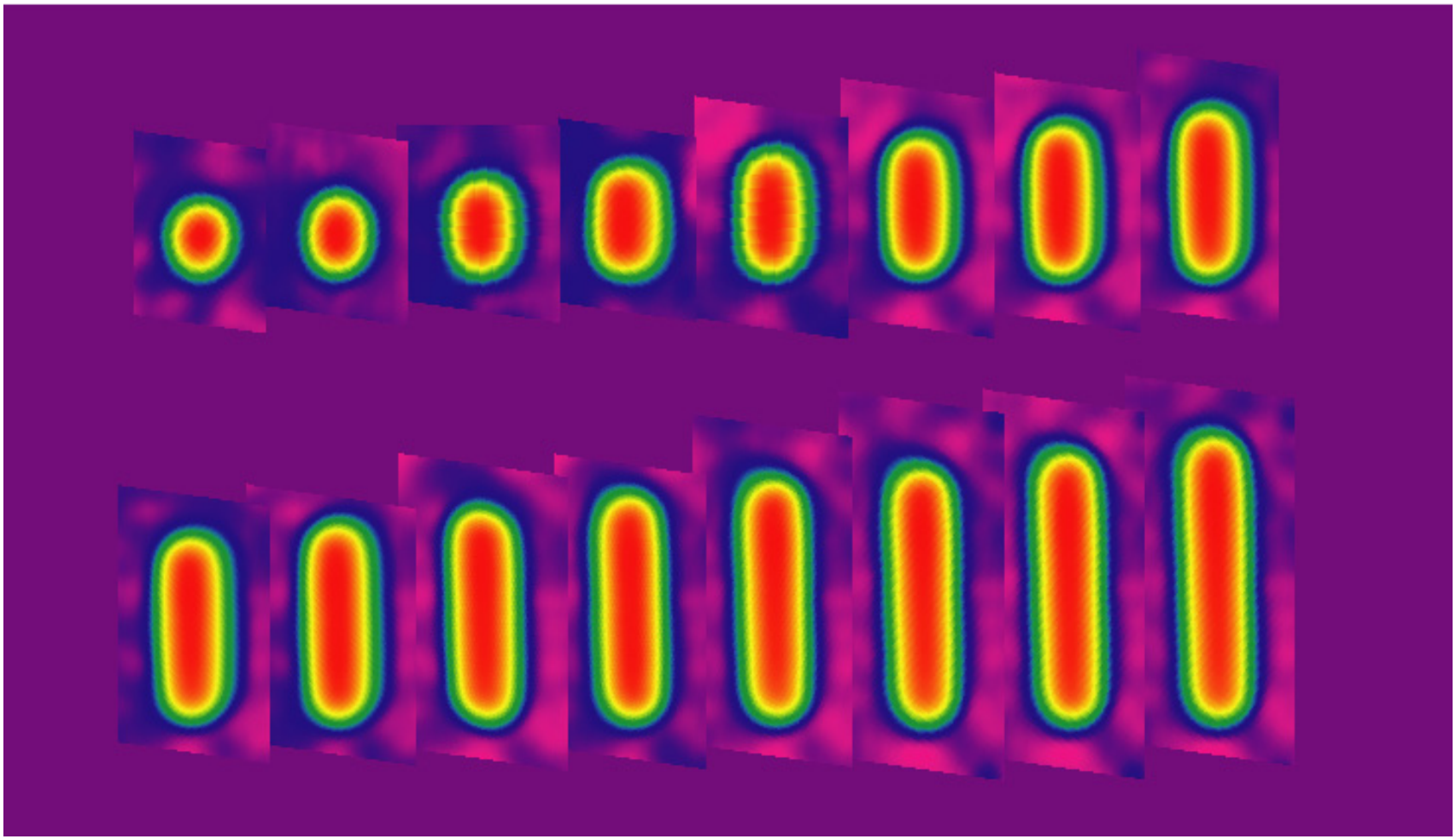
Au vs. Pd Atoms



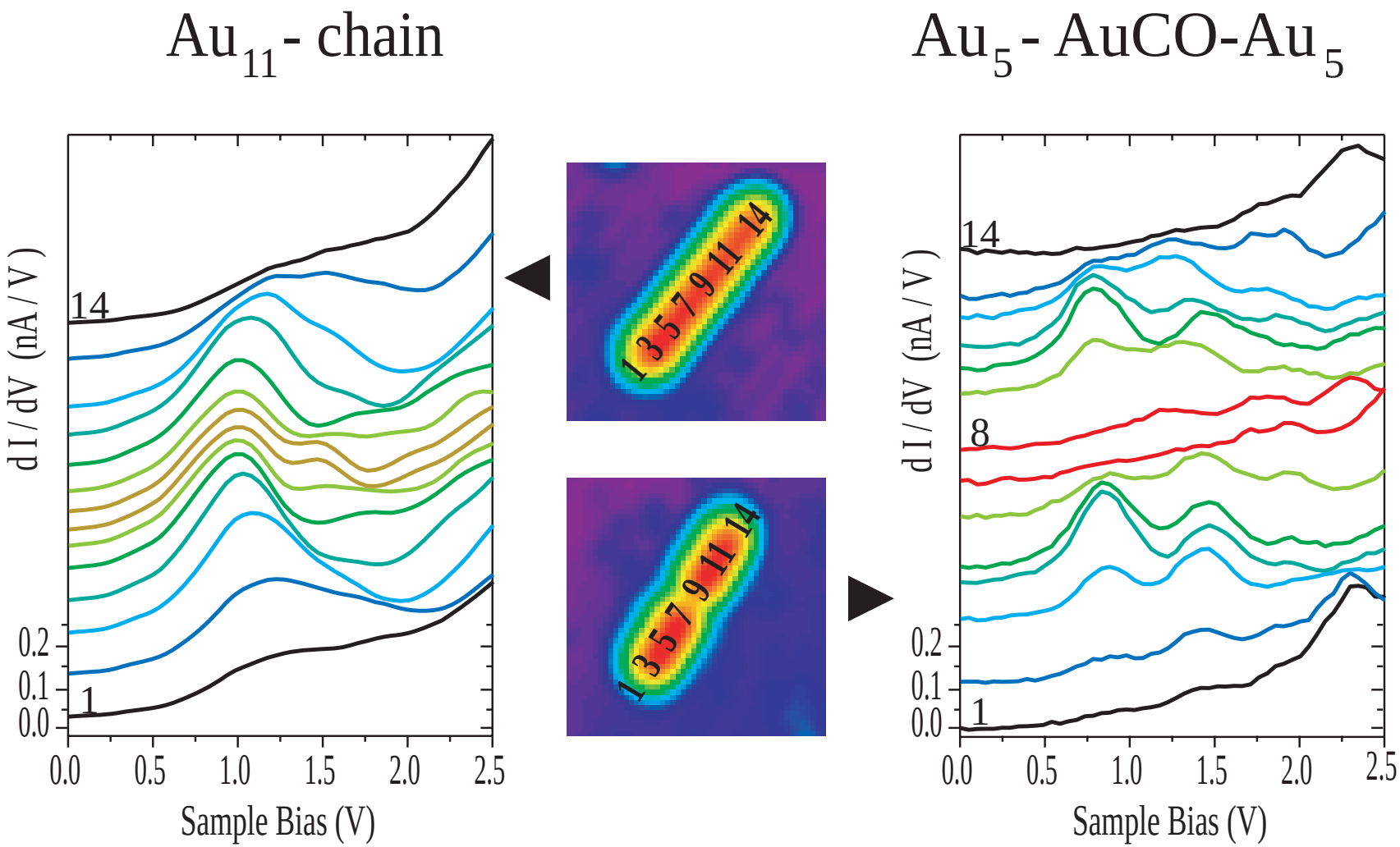
dI/dV Mapping



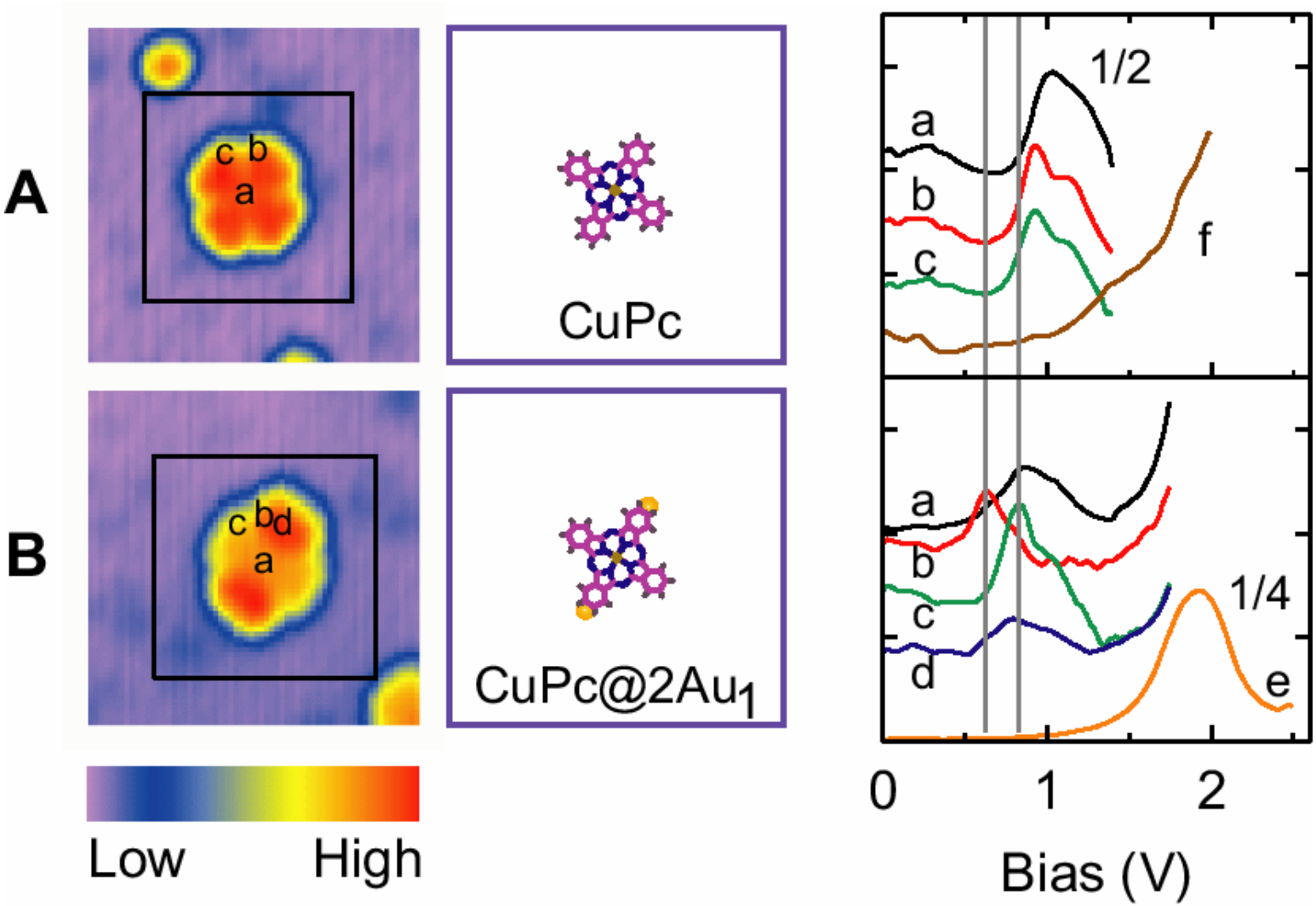
Mn Chains: 1 to 16 Atoms



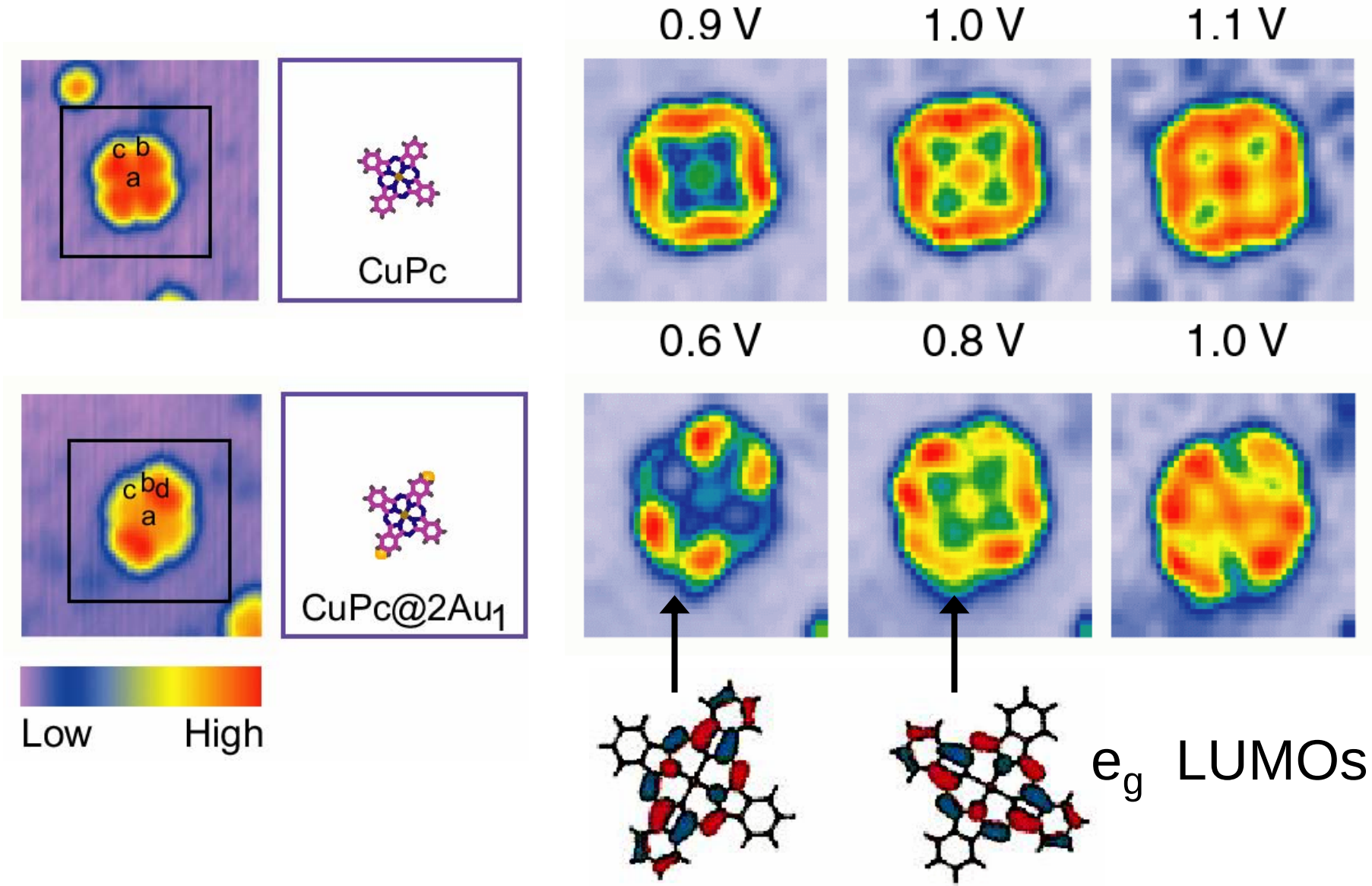
Au_{11}-Au_{11}CO: Spectral Mapping



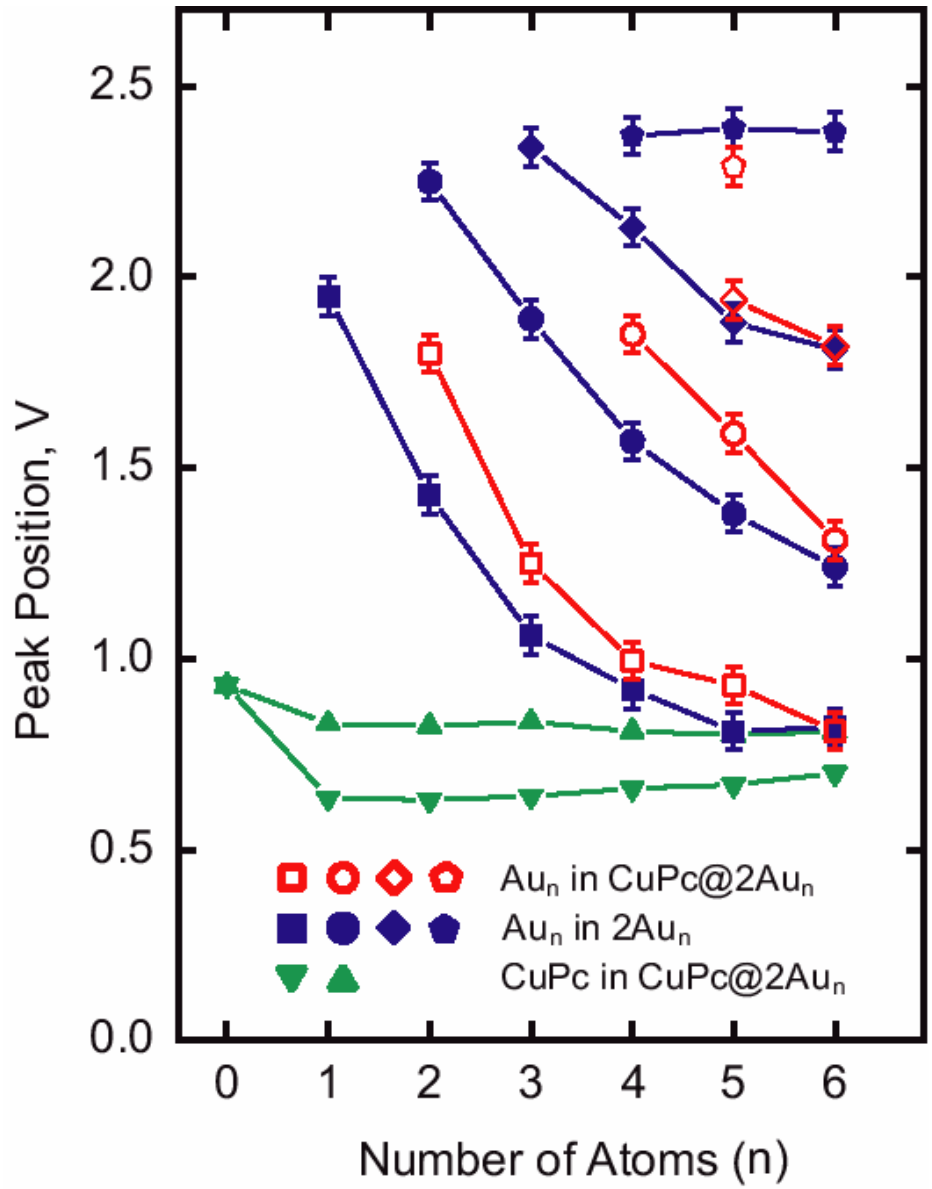
Perturbation of CuPc states by the Au atoms



DOS maps for CuPc and CuPc@2Au$_1$



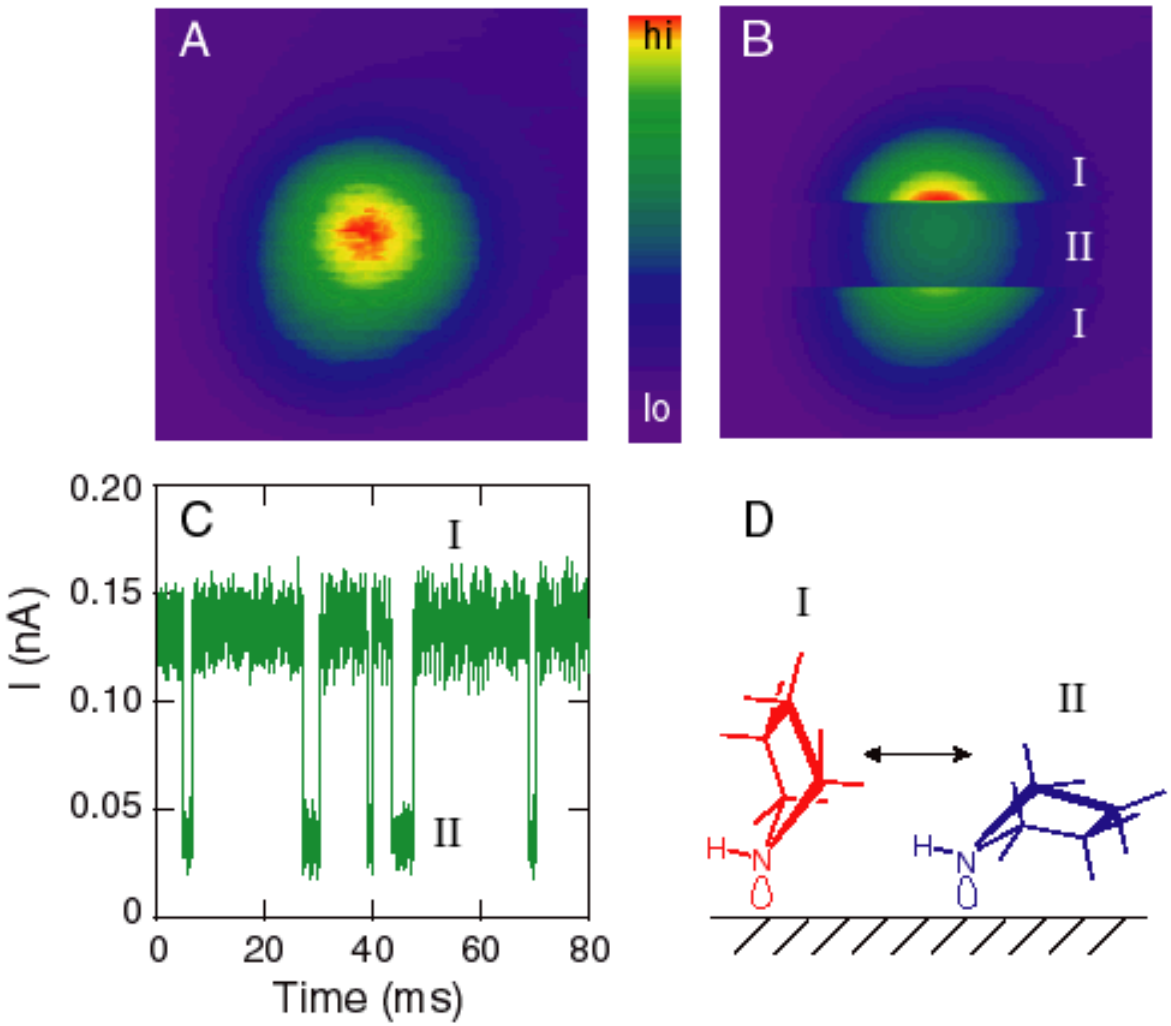
Tuning of Electronic States



The Interior of Single Molecules

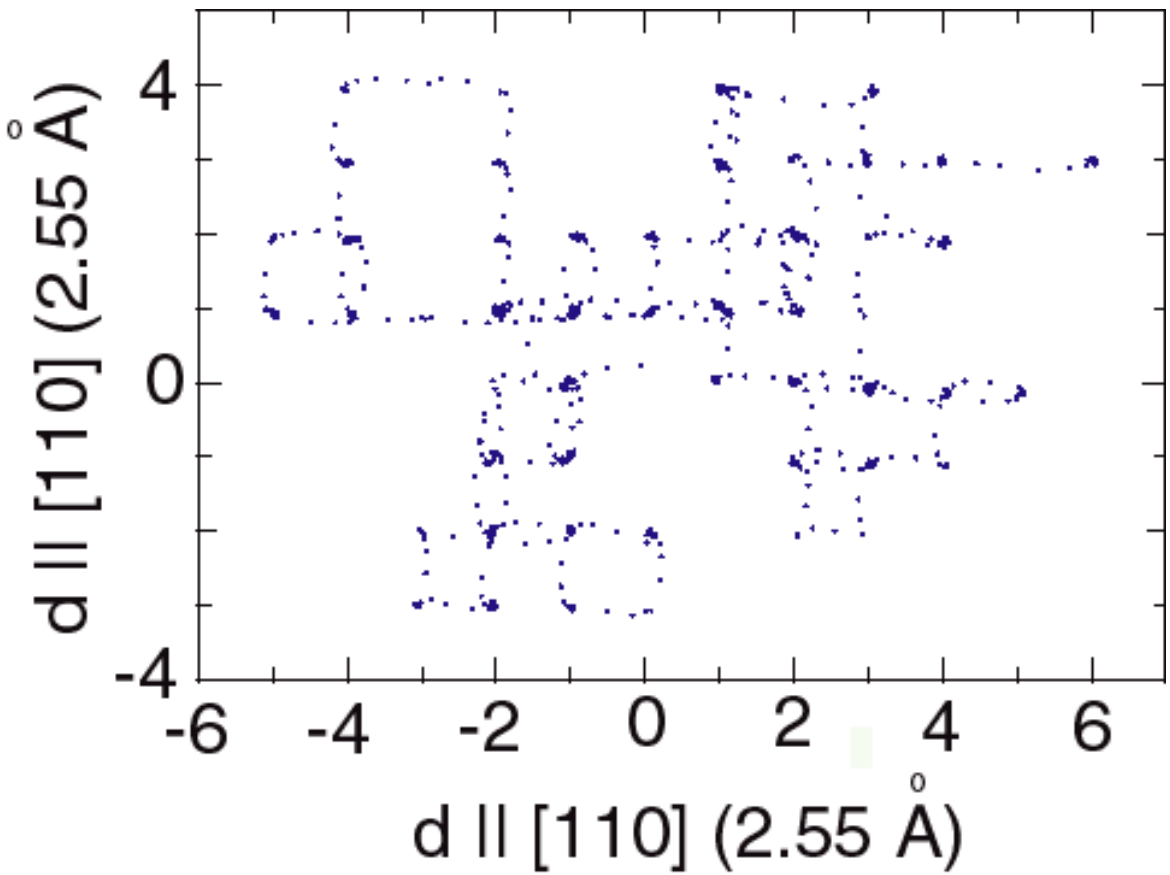
- **Single Molecule Vibrations and Dynamics**
- **Synthesis One by One**
- **Atomic Scale Optical Phenomena**

Two Conformations of Pyrrolidine on Cu(001)

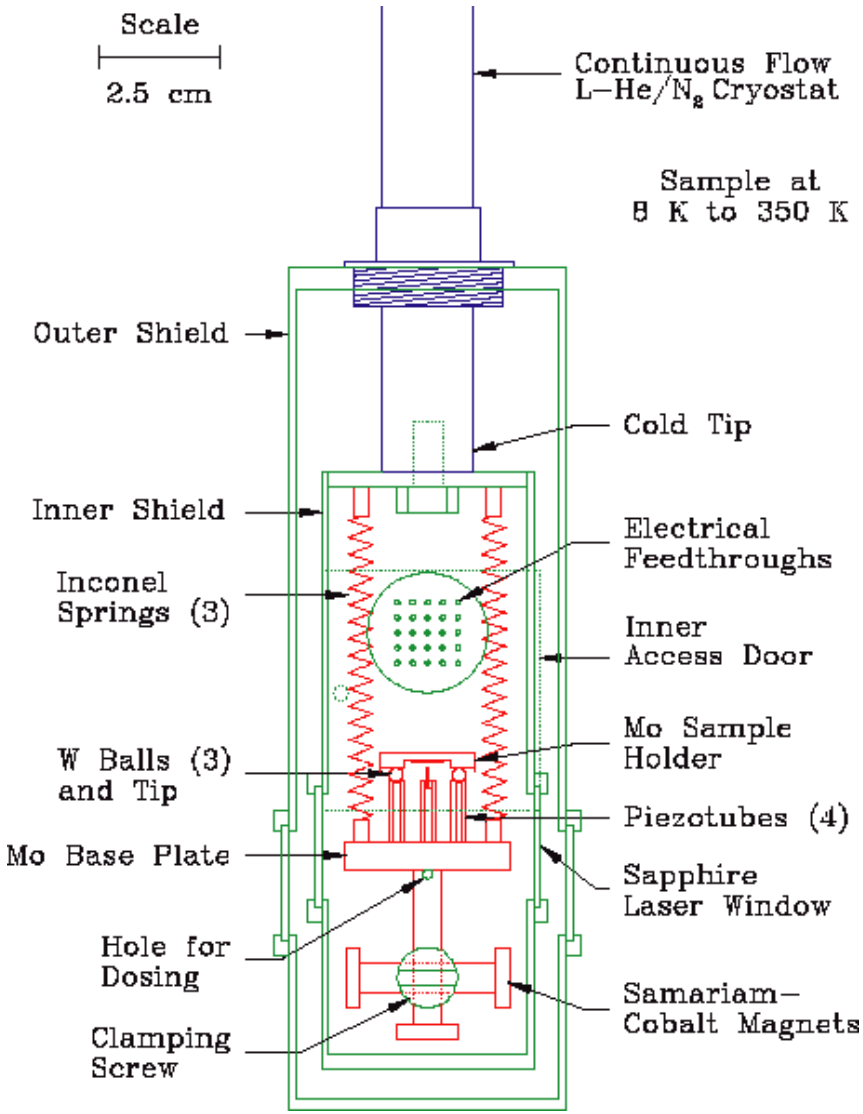


Thermal Diffusion

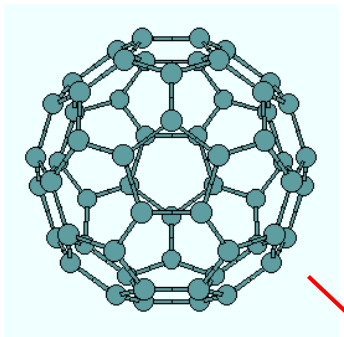
Acetylene on Cu(001) at 200 K



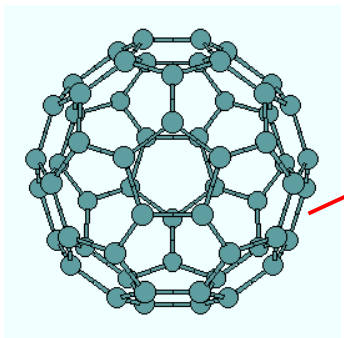
Scanning Tunneling Microscope



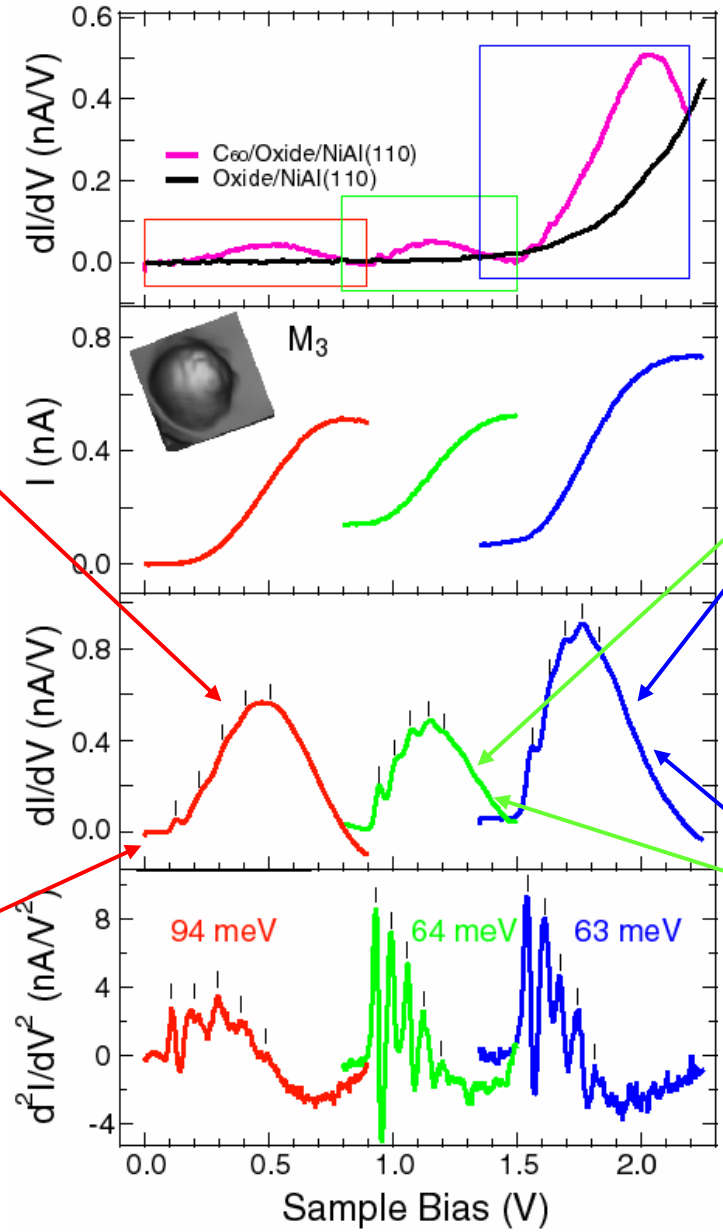
Vibronic States – C_{60} on Al_2O_3

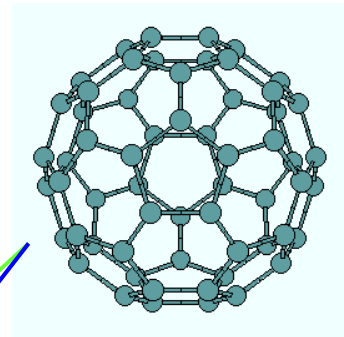


$H_g(\omega_3)$ ~ 88.1 meV

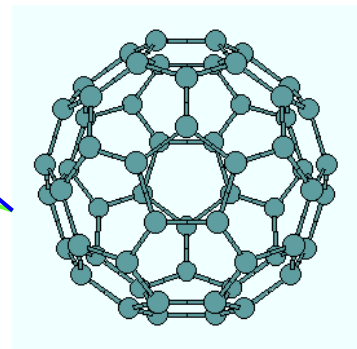


$H_g(\omega_4)$ ~ 96.1 meV





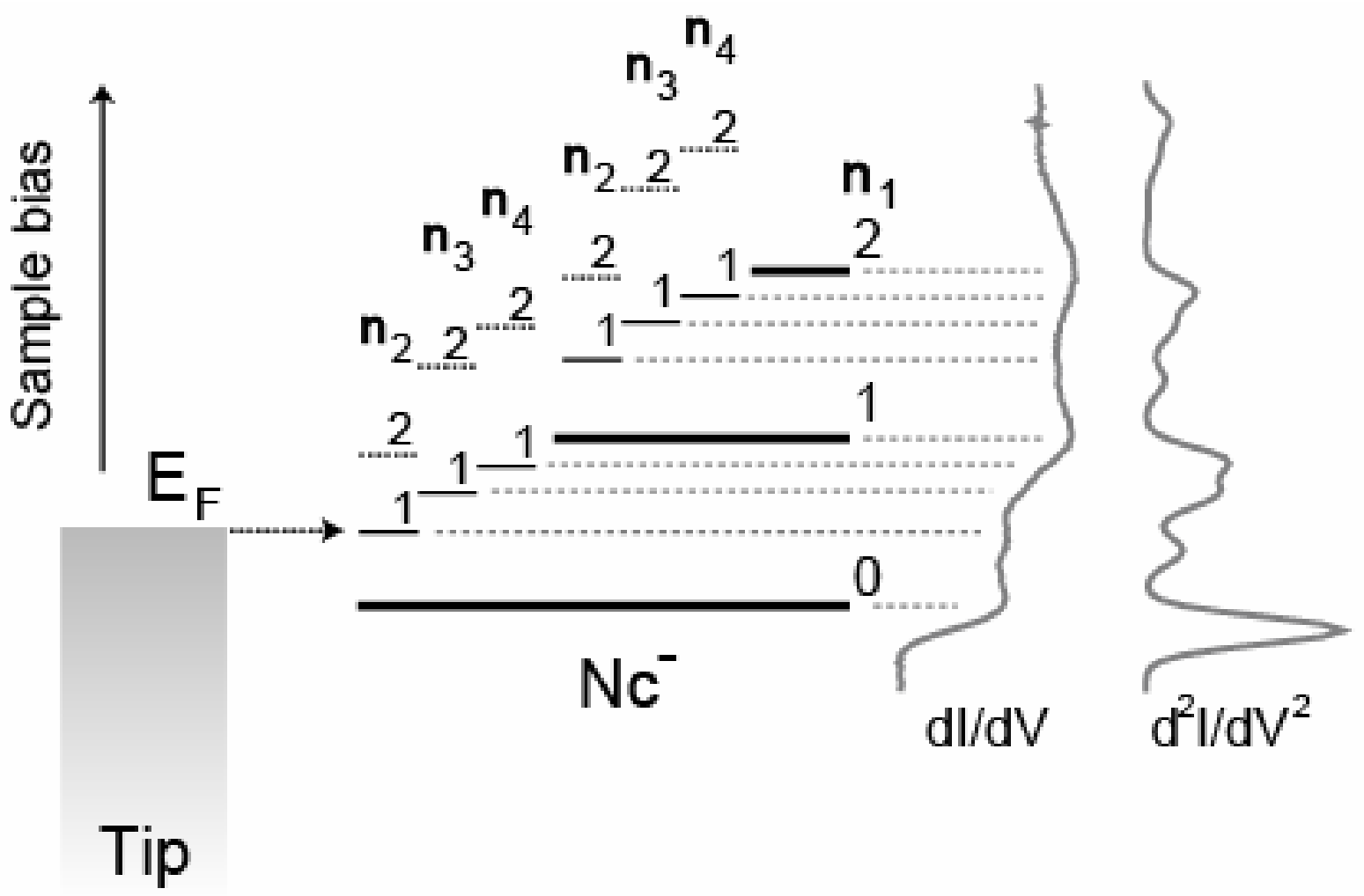
$H_g(\omega_2)$ ~ 53.6 meV



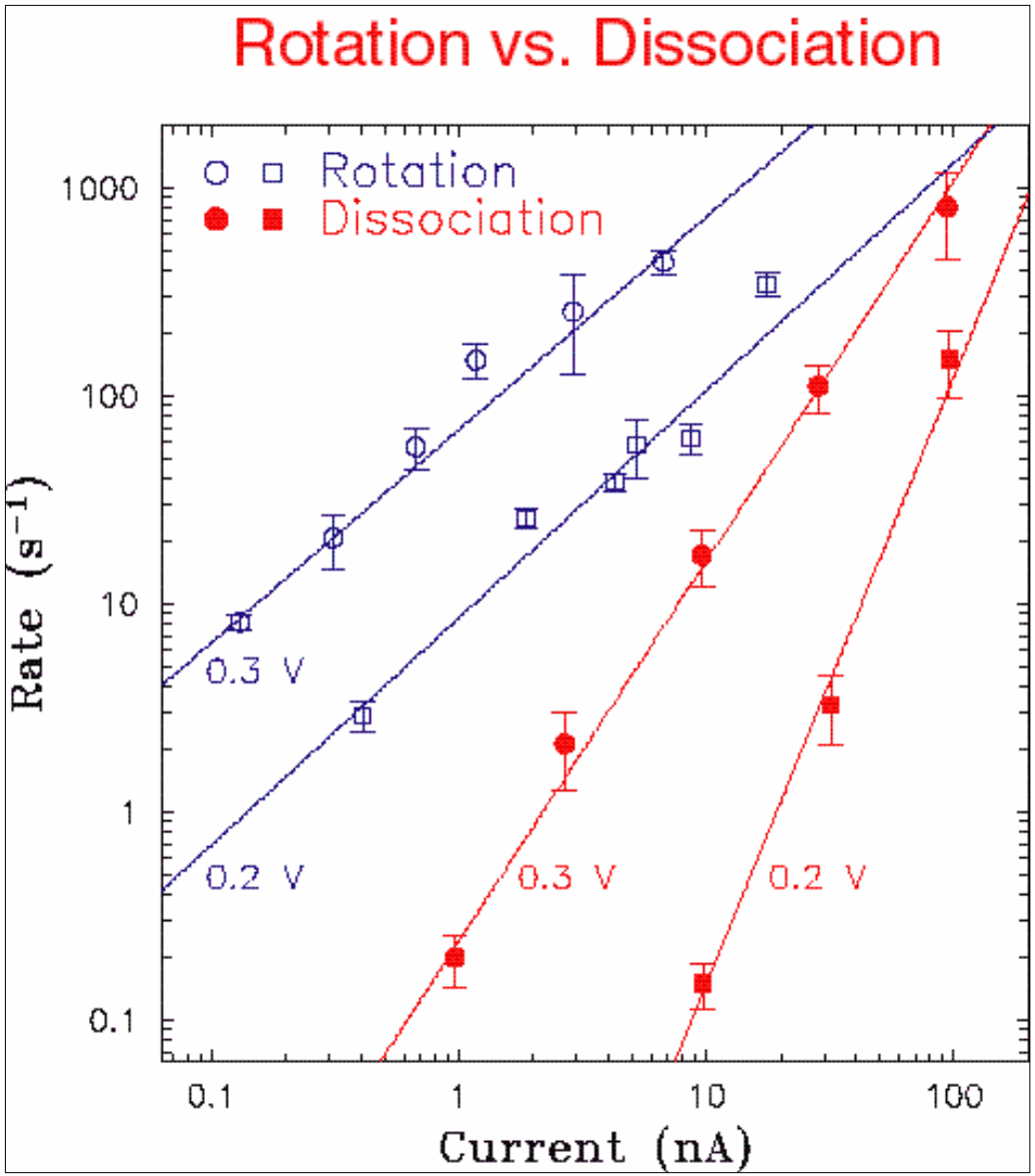
$A_g(\omega_1)$ ~ 61.7 meV

Animations courtesy: John Page, Ariz. State. Univ. http://www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm

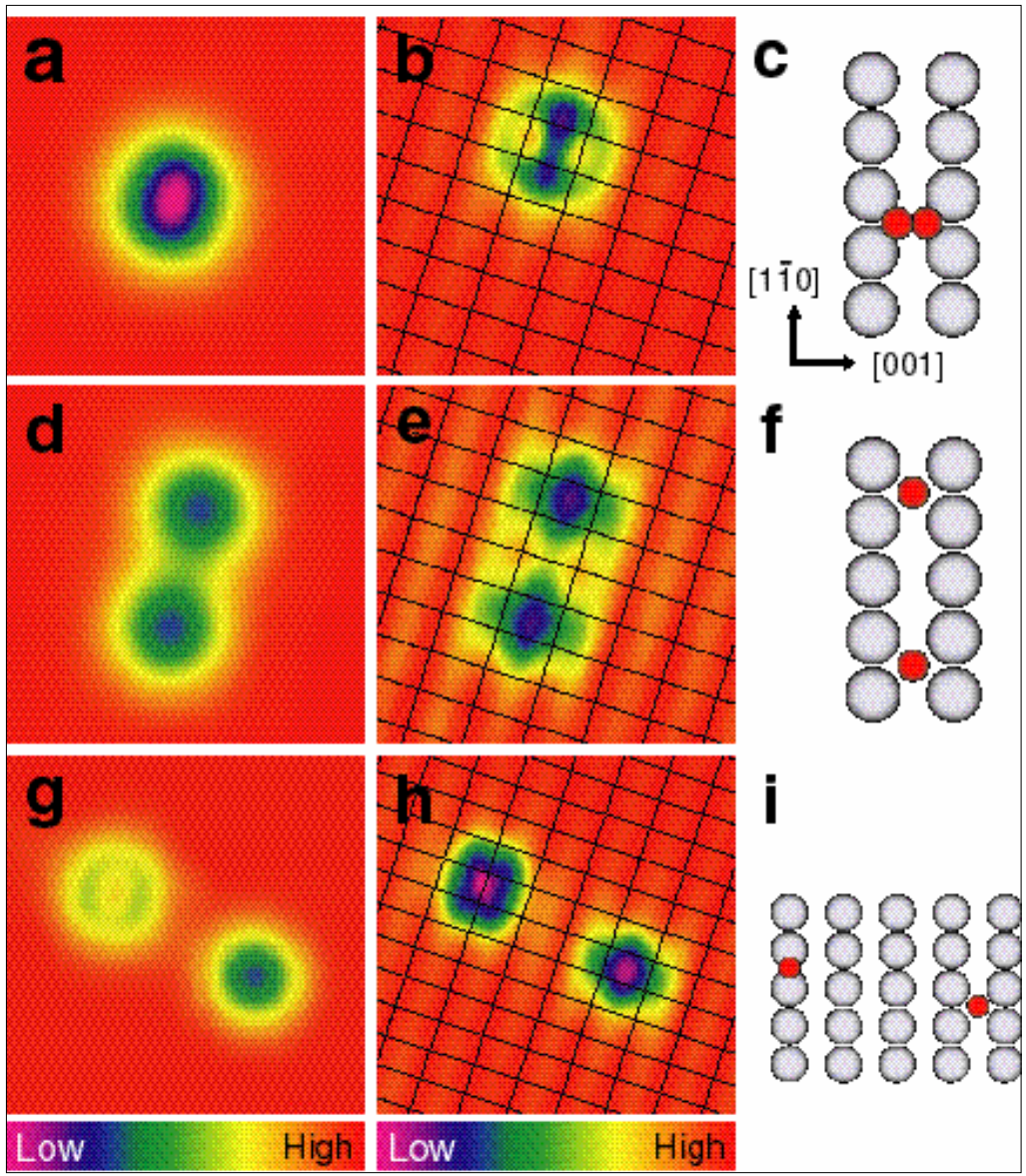
Vibronic Progression on Progression



O_2 on Pt(111)


Rotation vs. Dissociation
Rotation
Dissociation
0.3 V
0.2 V
0.3 V
0.2 V
1000
100
10
1
0.1
Rate (s⁻¹)
0.1
1
10
100
Current (nA)

Orbital Specific Chemistry



Acknowledgment

Jennifer Gaudioso
Jae Ryang Hahn
Lincoln Lauhon
Mohammad Rezaei
Barry Stipe

Xi Chen
Hyojune Lee
George Nazin
Niklas Nilius
Xiaohui Qiu
Mitch Wallis

Shiwu Gao
Nicolas Lorente
Mats Persson

STM Capabilities

- Imaging
- Manipulation
- Spectroscopy
- Modification

Single Molecule Chemistry

- Single Molecule Motions and Dynamic
- Synthesis of Single Molecules and Metallic Structures
- Electromagnetic Response of Single Molecules

Single Molecule Virtues

- Free from Environmental Effects & Intermolecular Interactions
  - → molecular motions

- Sensitive to Energetic Inhomogeneity & Local Potentials
  - → bond energies
  - → vibrational frequencies
  - → molecular structures

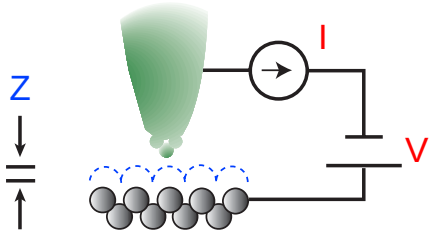
- Elimination of Ensemble Averaging
  - → rotational motion
  - → conformational transformation
  - → chemical purity

- Control of Intermolecular Interactions
  - → bimolecular reactions
  - → complex formation

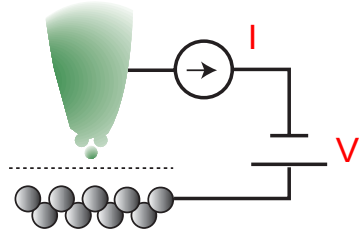
- Elucidation of Structural Factor
  - → molecular conductivity
  - → light emission
  - → chemical reactivity

Scanning Tunneling Microscope

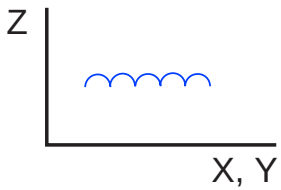
Constant current



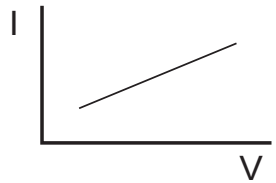
Constant height



- Topography



- Spectroscopy

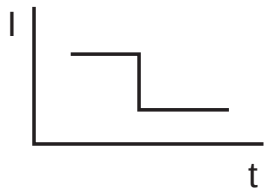


V, I, Z

$$R = \frac{V}{I}$$

$$G = R^{-1}$$

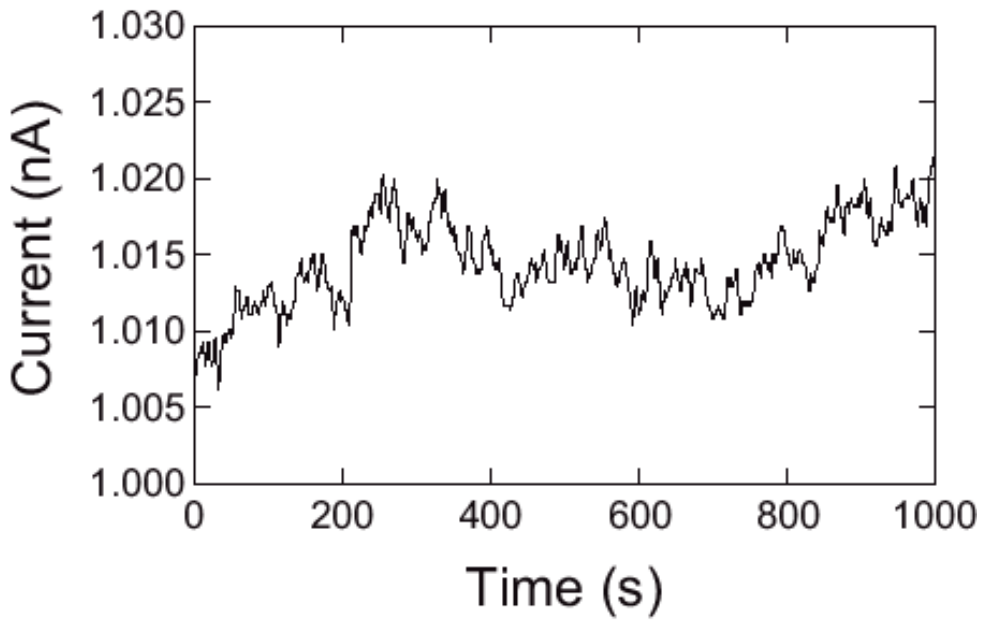
- Chemistry



STM-IETS Requirement

Junction Stability

Feedback Off

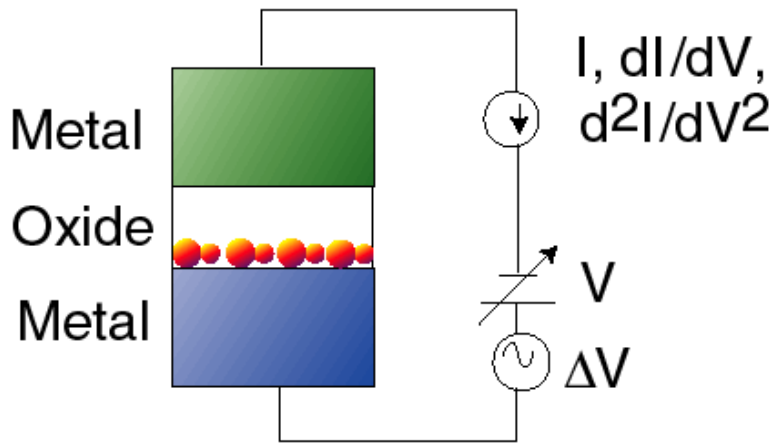


$\Delta Z \sim 0.005$ Å $\longrightarrow$ $\Delta I \sim 0.01$ nA

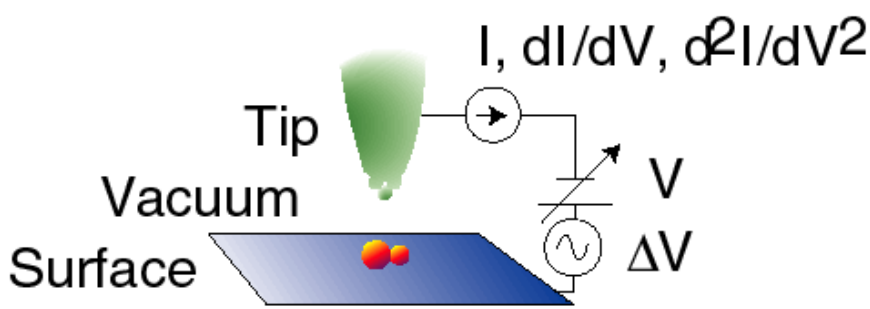
Drift ~ 0.001 Å-min^{-1}

Inelastic Electron Tunneling Spectroscopy (IETS)

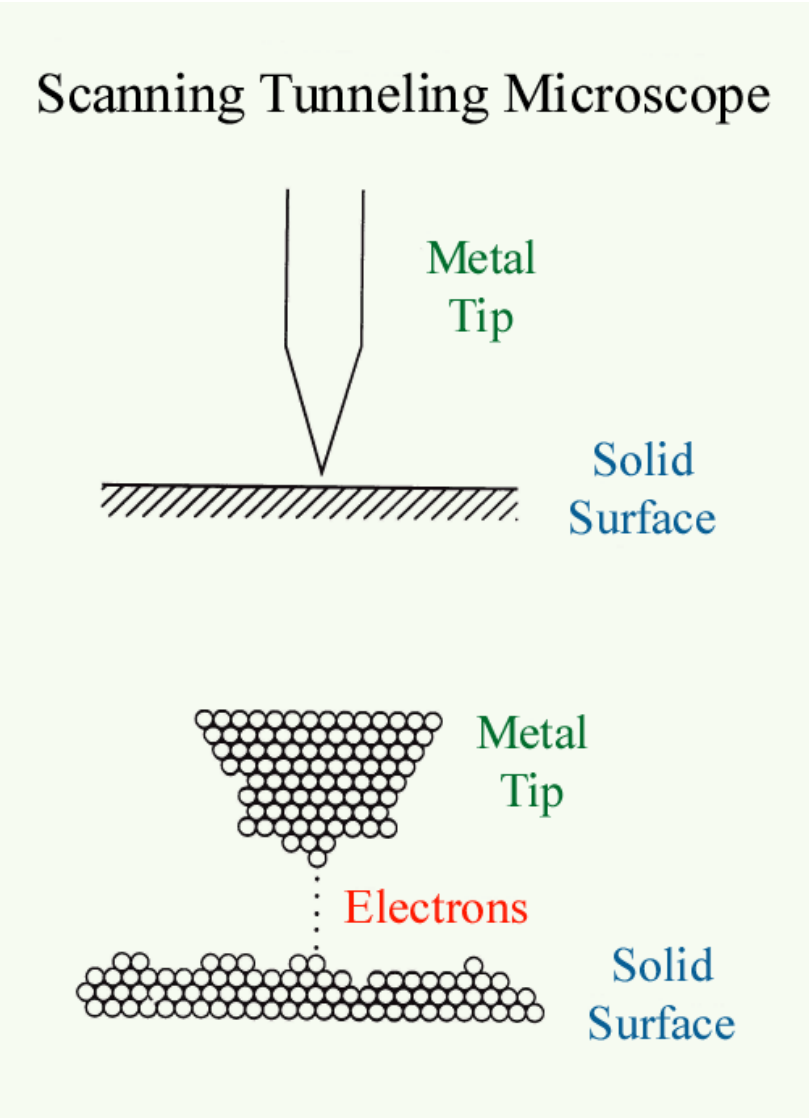
Conventional IETS: ~10^9 molecules

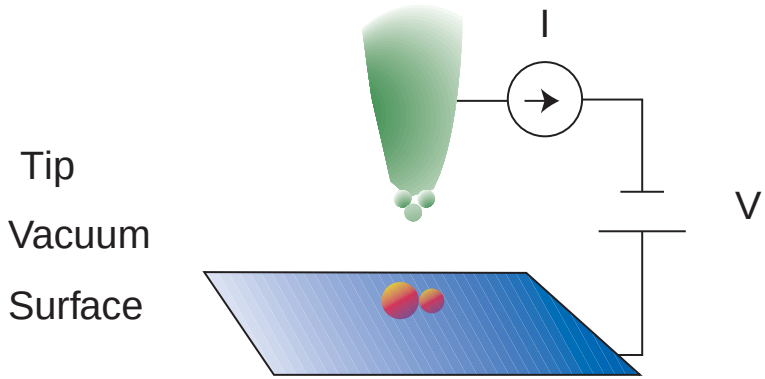


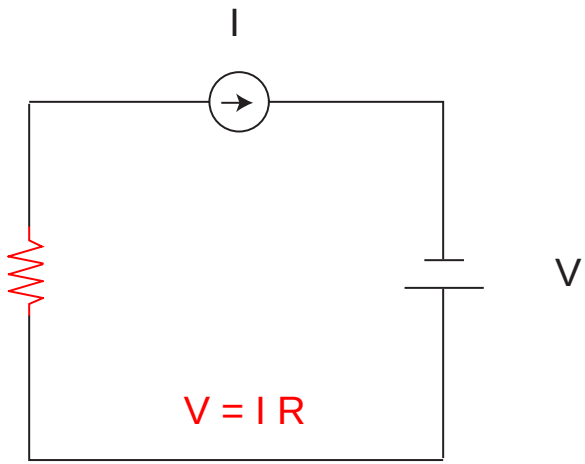
STM-IETS: 1 molecule



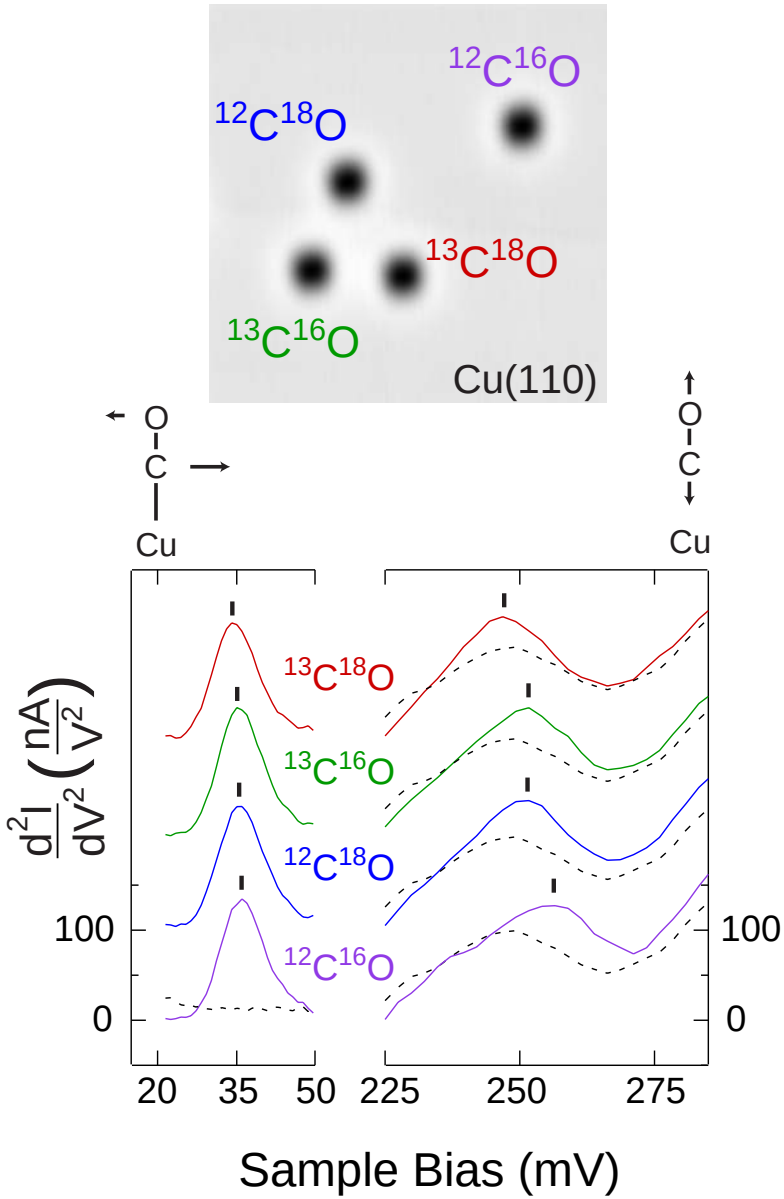
Scanning Tunneling Microscope (STM)



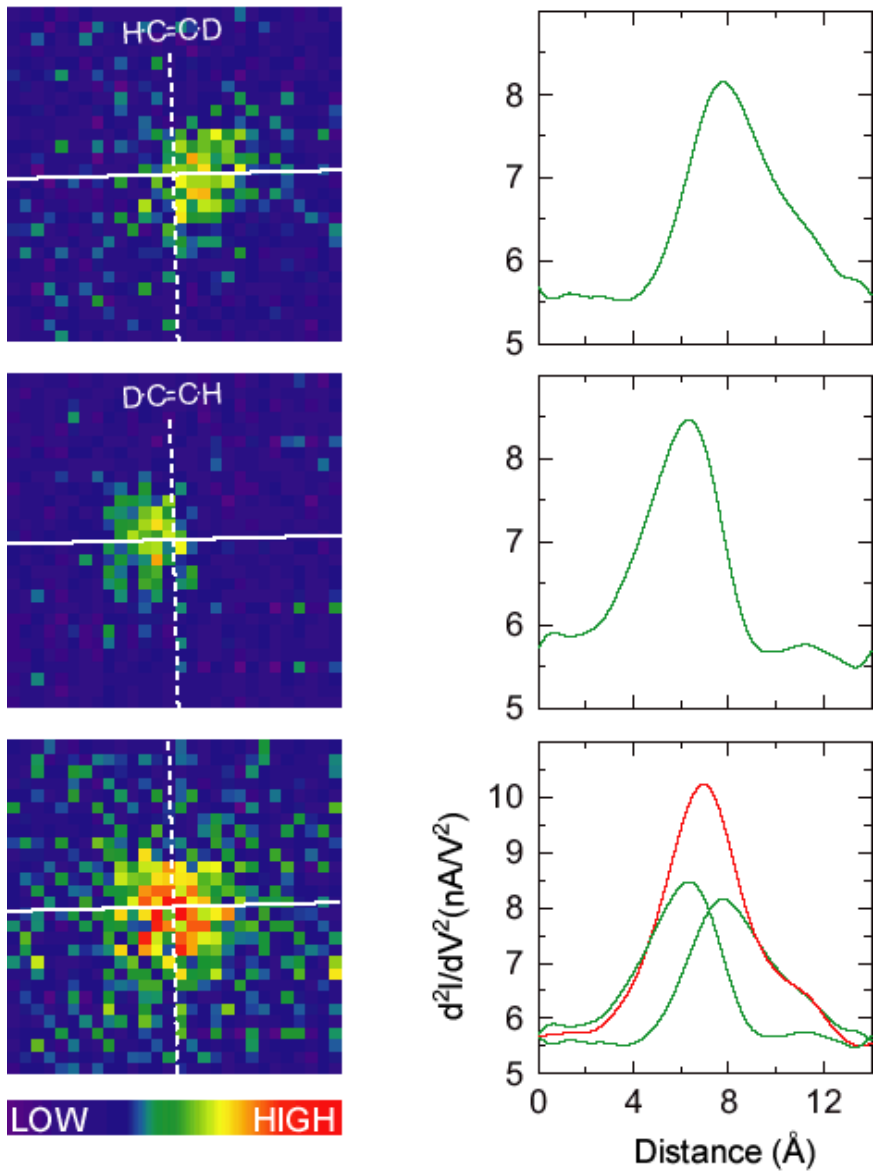




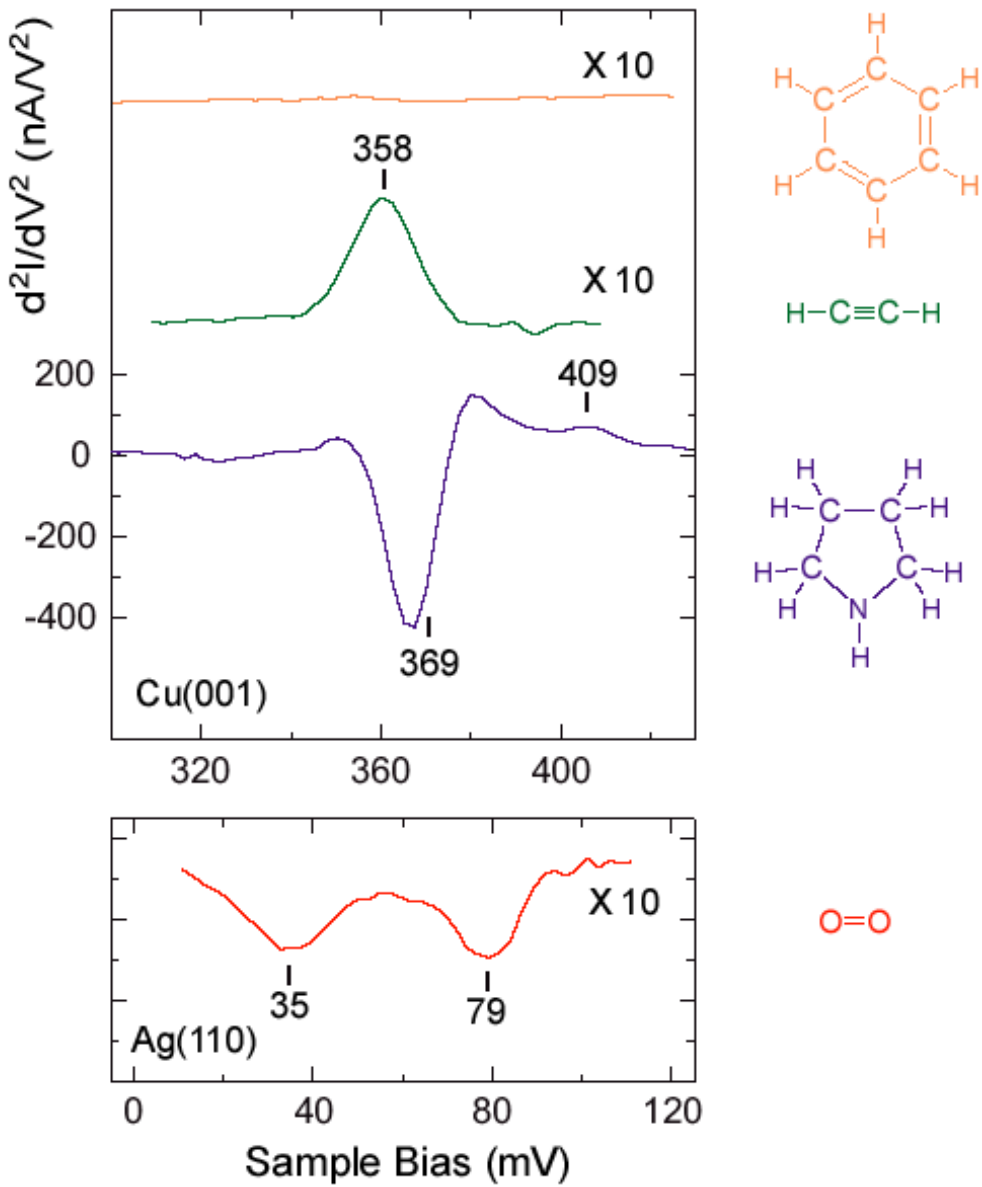
STM-IETS: CO on Cu(110)



Mapping a Single Bond

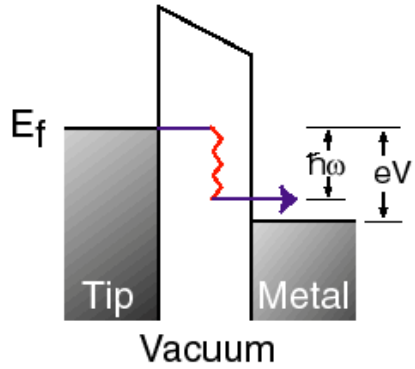


STM-IETS Lineshape

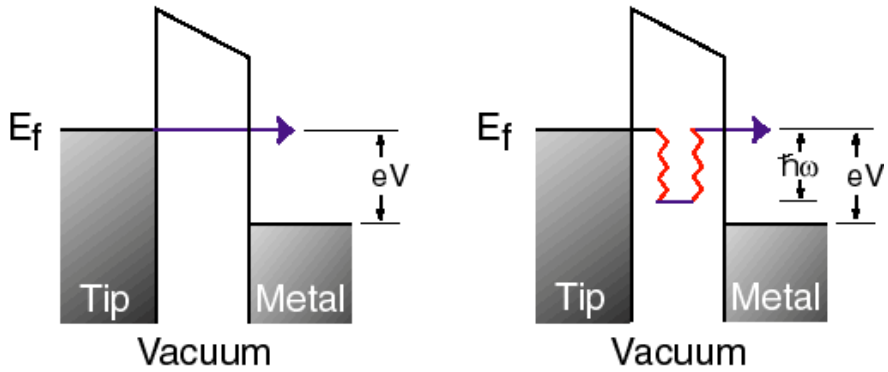


STM-IETS

Inelastic Tunneling

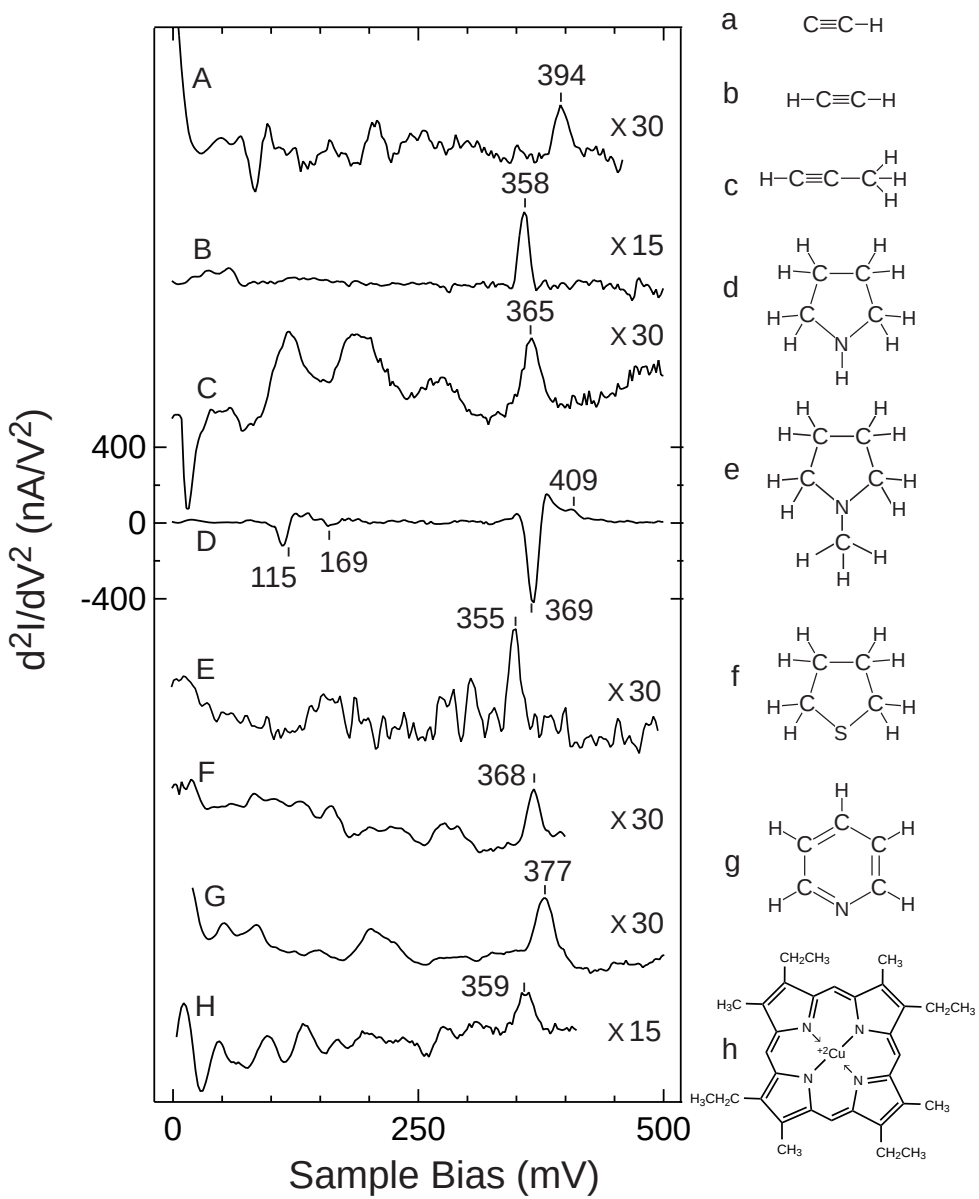


Elastic Tunneling

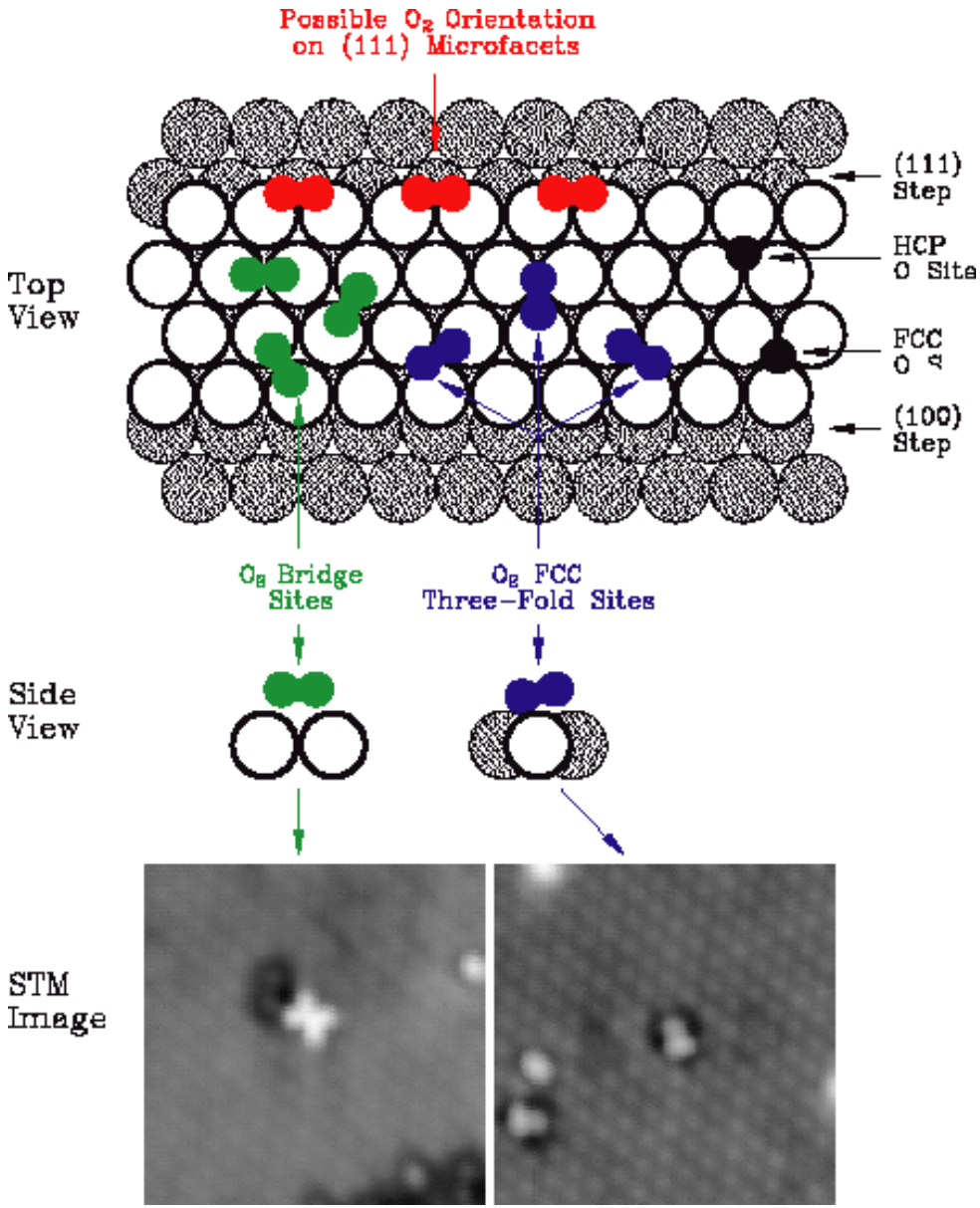


$$I_{tot} = I_{el} + I_{inel}$$

STM-IETS: Hydrocarbons

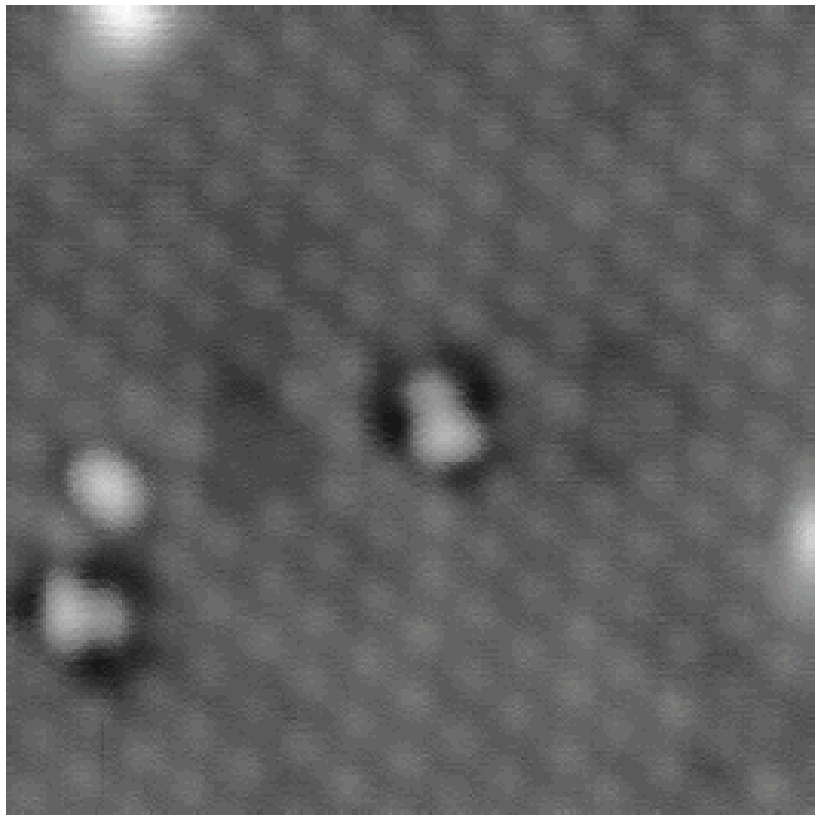


Oxygen on Pt(111)



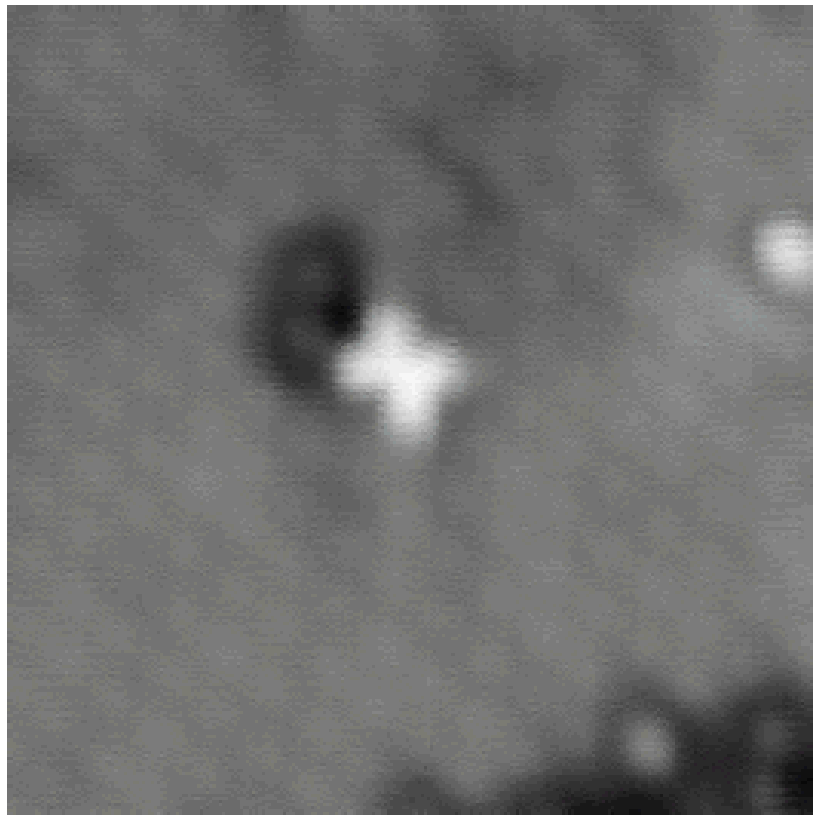
Molecular Oxygen on Pt(111)

"Pear"



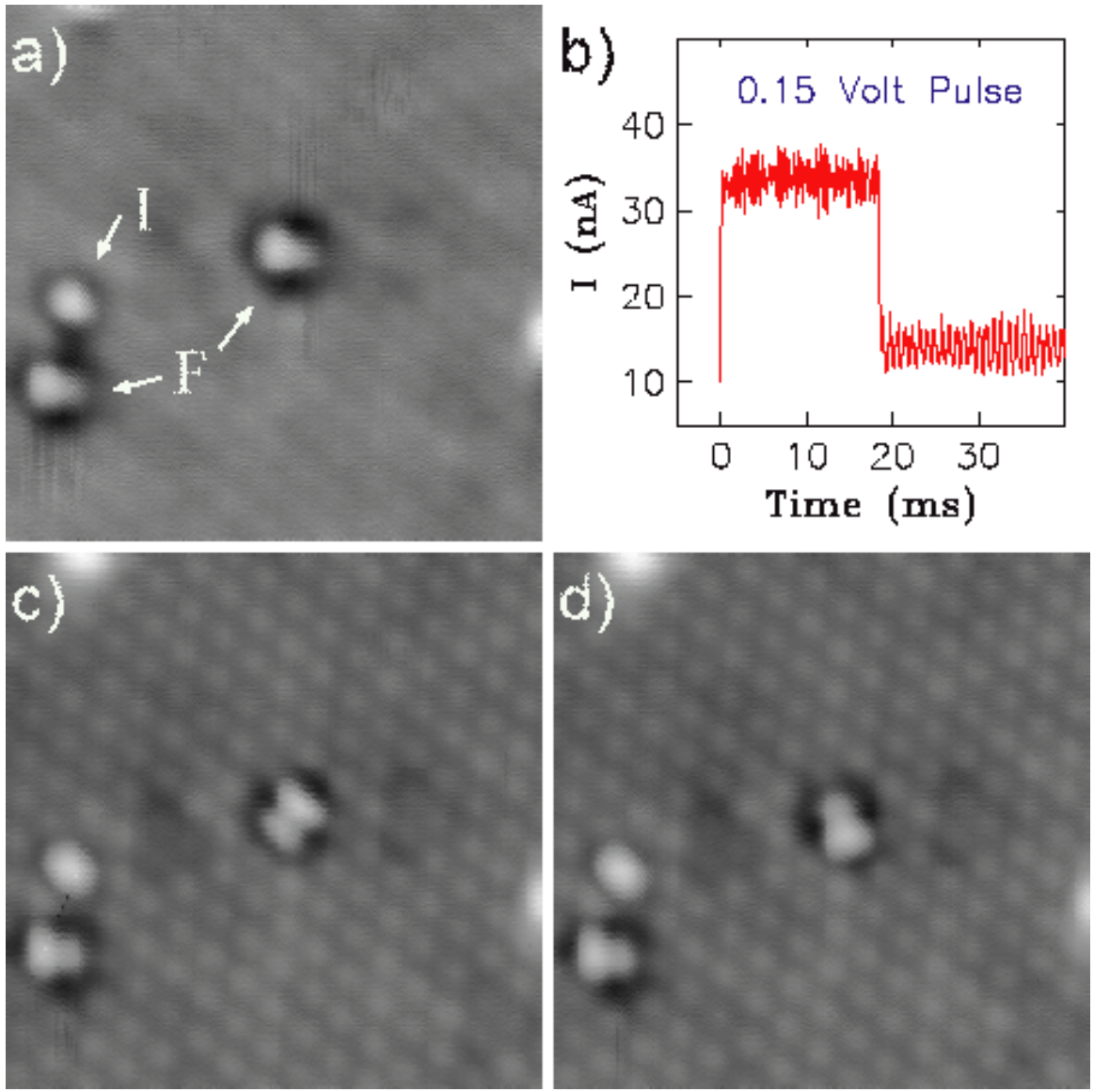
FCC Three-Fold Site

"Clover"

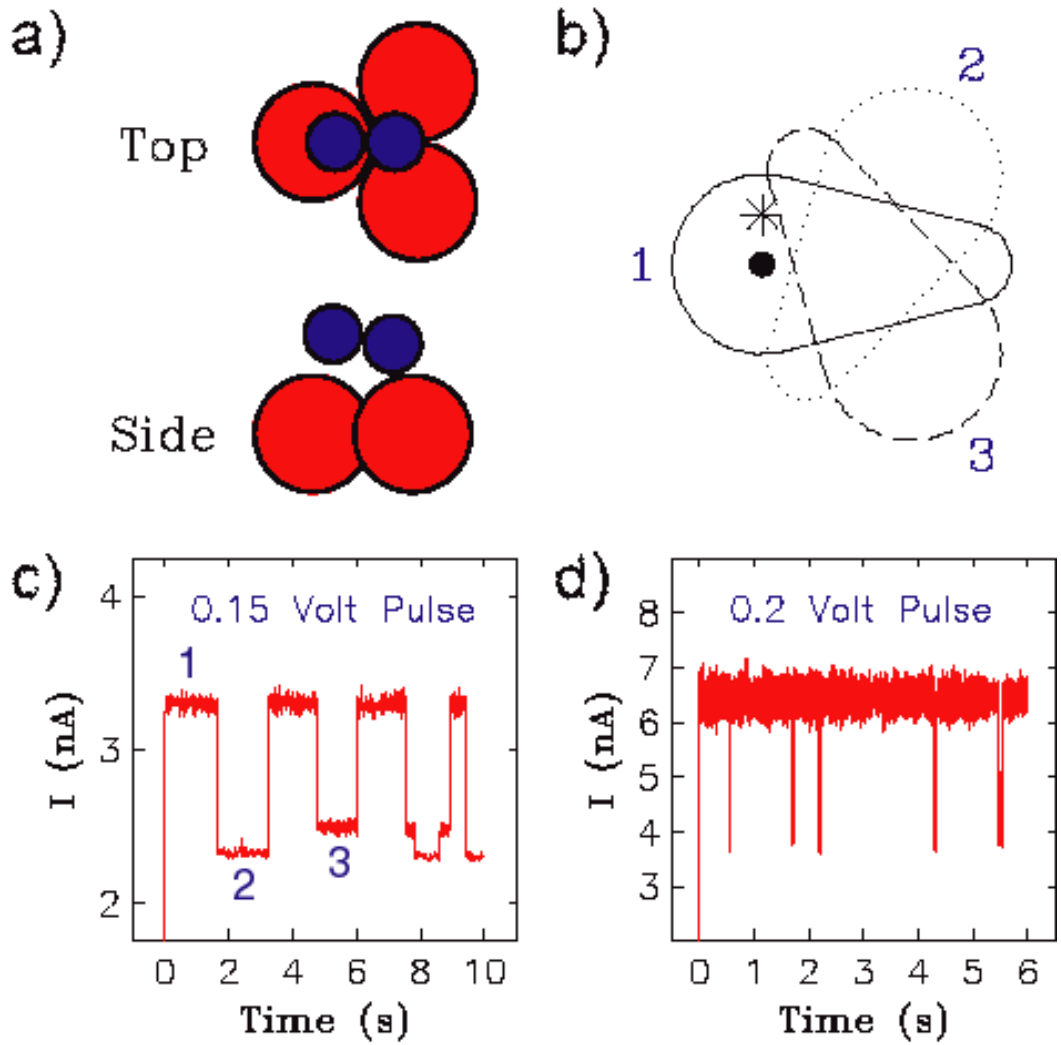


Bridge Site

Rotation of Oxygen on Pt(111)



Monitoring Oxygen Rotation

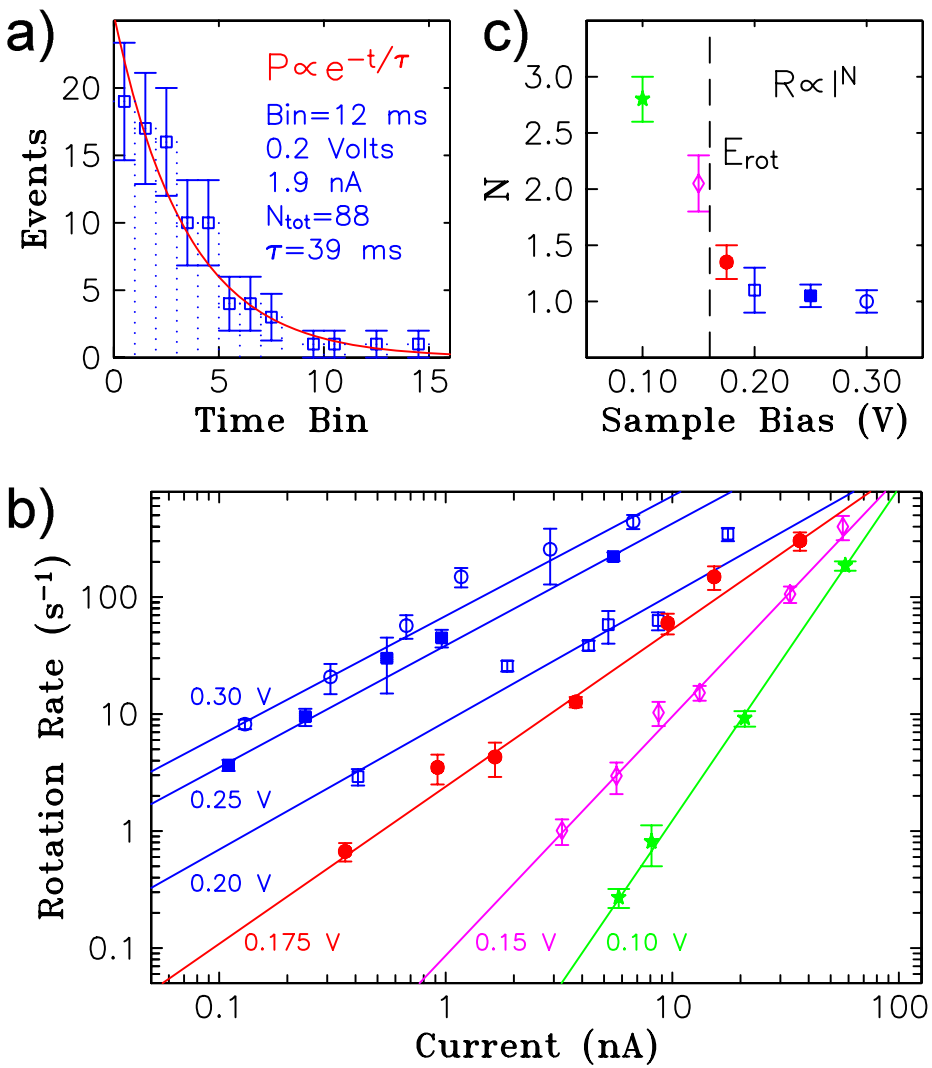


Oxygen Molecule Isolated

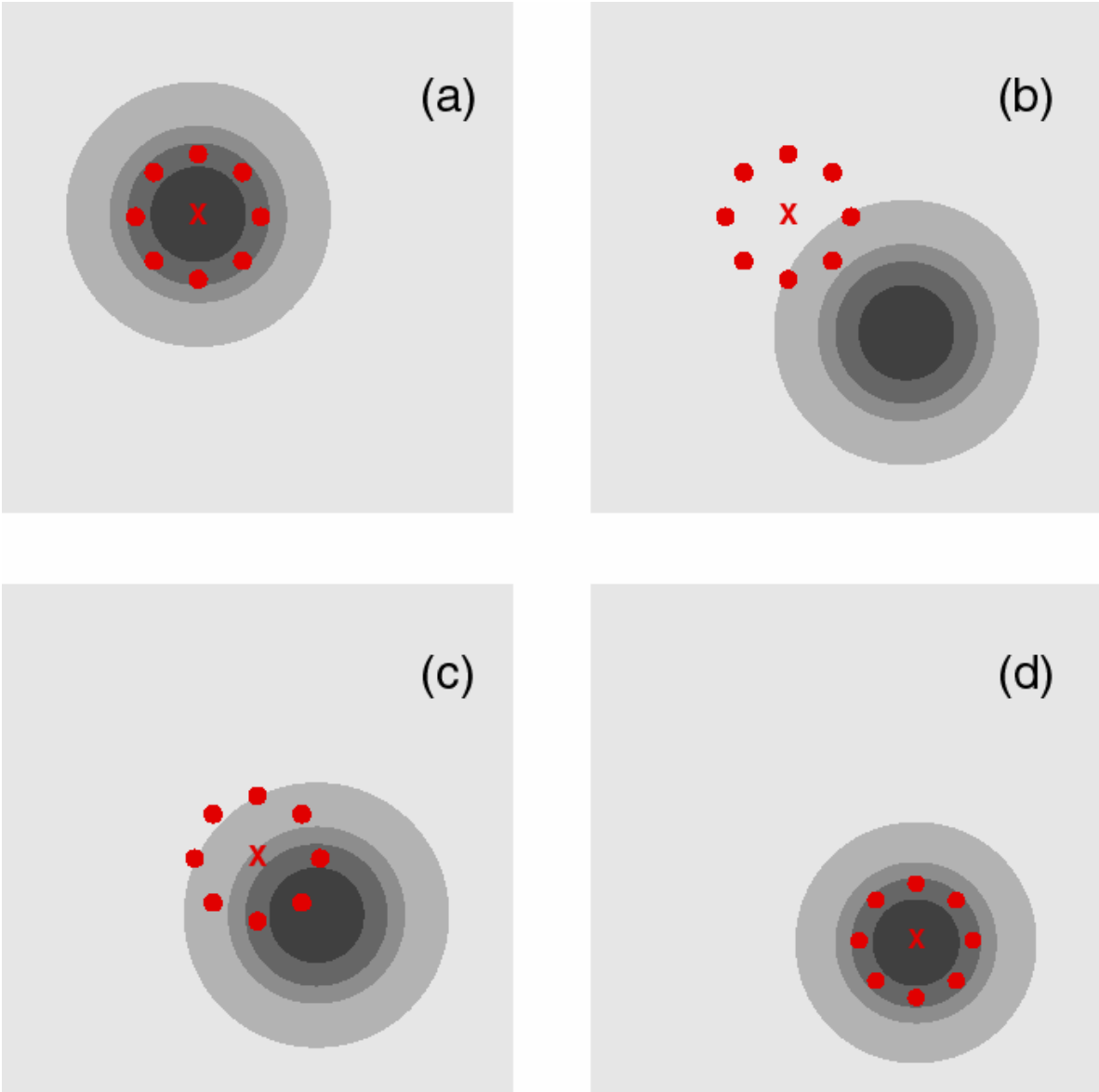
Oxygen Molecule Next to Defect

O_2 Rotation on Pt(111)

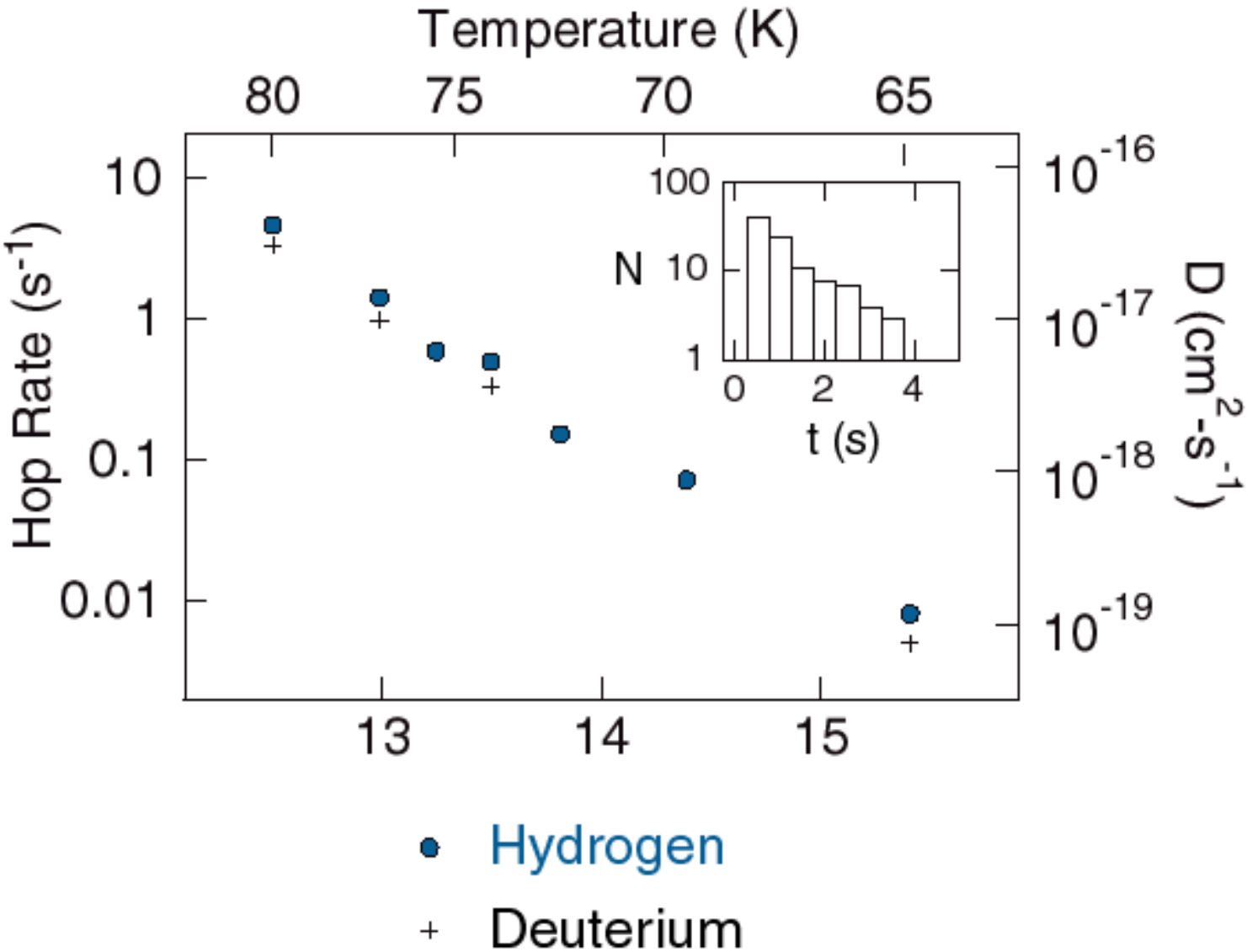
Single Molecule Rotation Rates



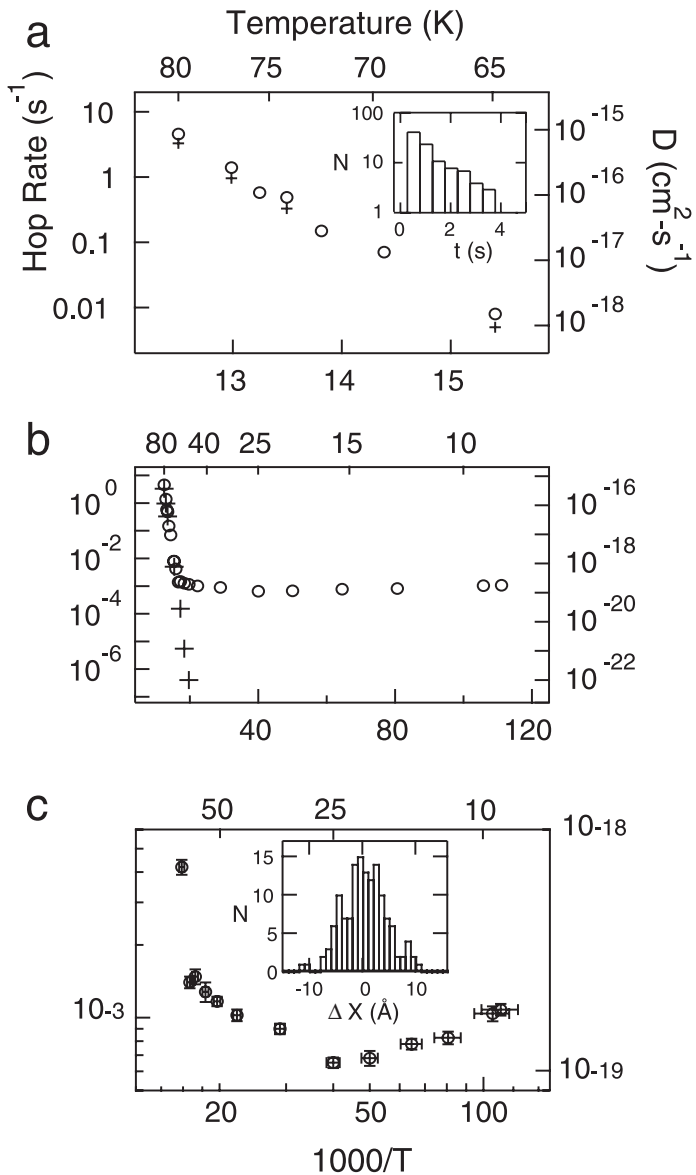
Single Atom/Molecule Tracking



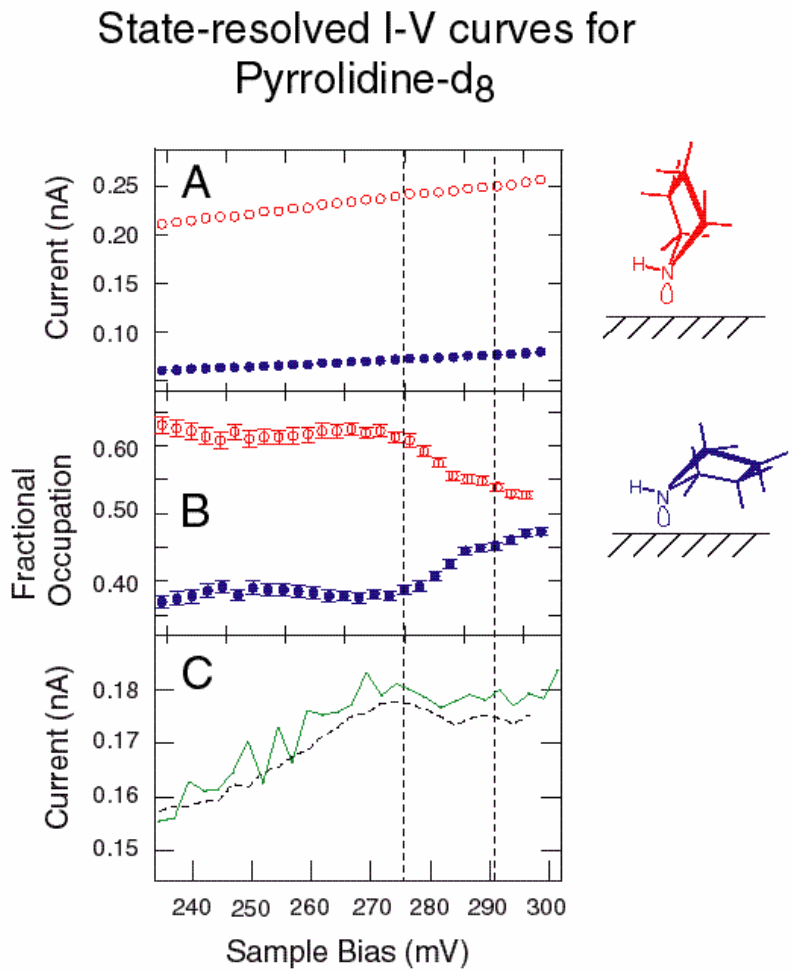
Single Atom Thermal Diffusion



H & D Diffusion on Cu(001)

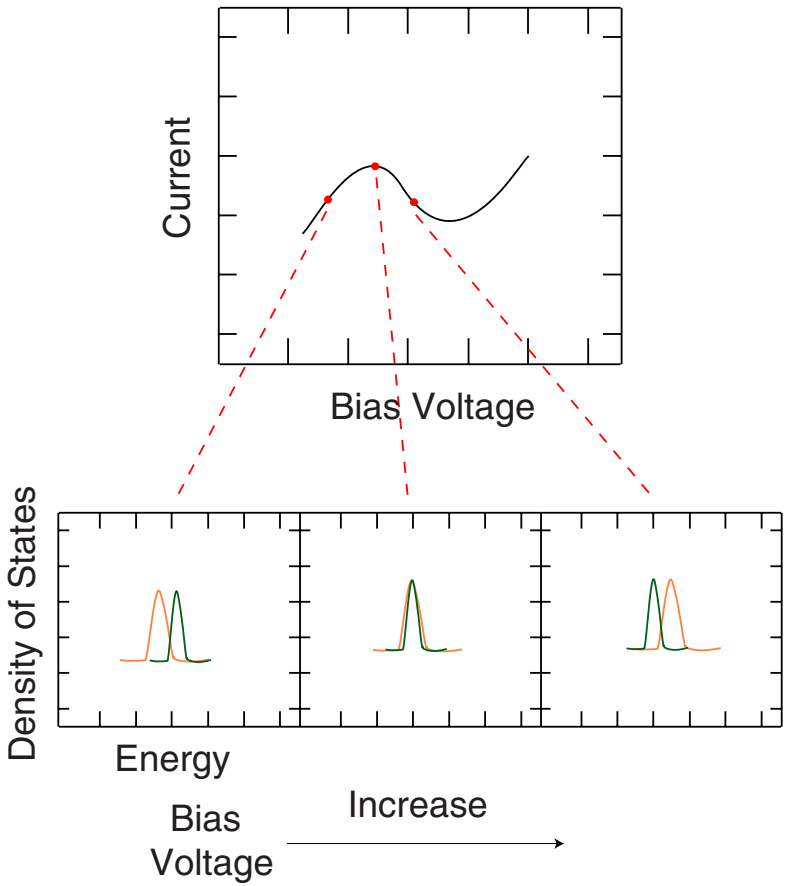


NDR: Population Analysis

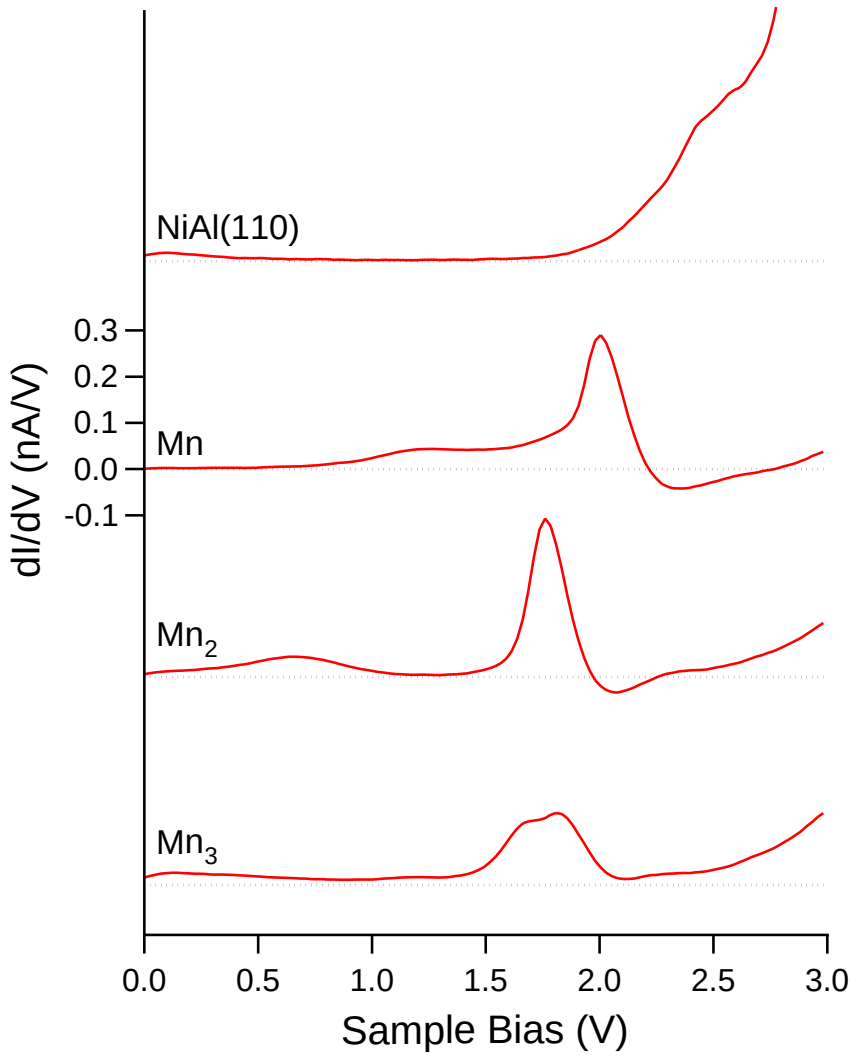


NDR: Electronic Origin

Conventional NDR:
An Electronic Mechanism

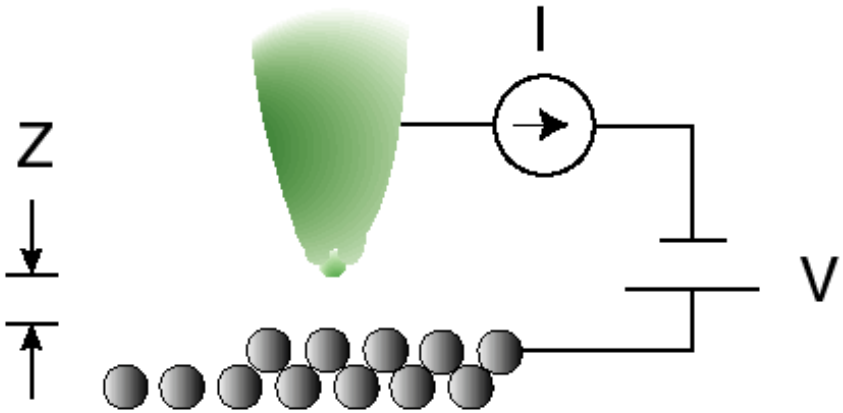


Single Atom NDR

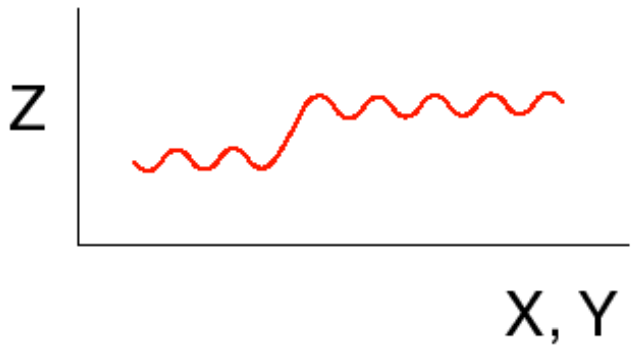


STM Imaging

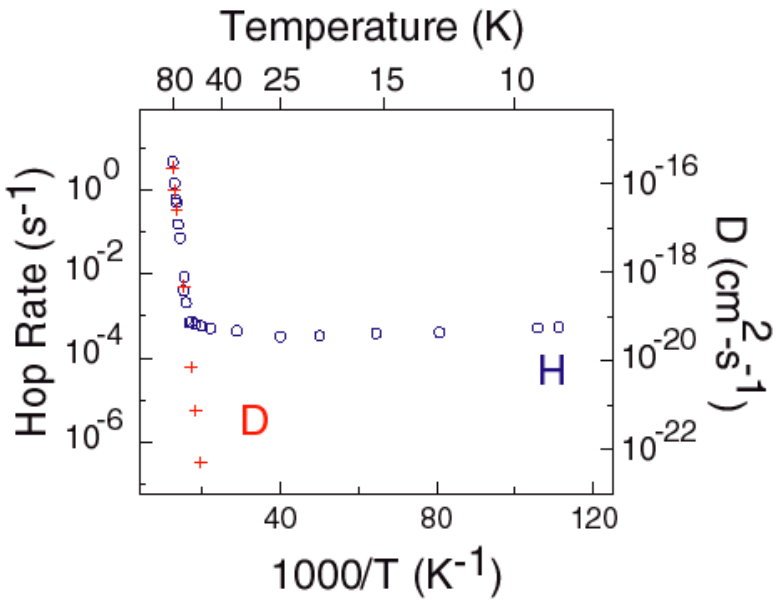
Constant Current

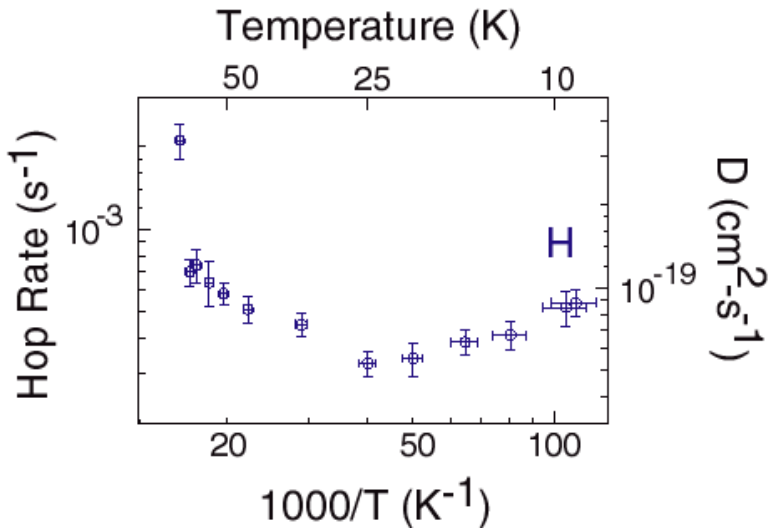


Topography



Hydrogen Atom Diffusion





Vibronic Spectroscopy – C_{60}/Al_2O_3