Atomic Scale Coupling of Electromagnetic Radiation to Single Molecules

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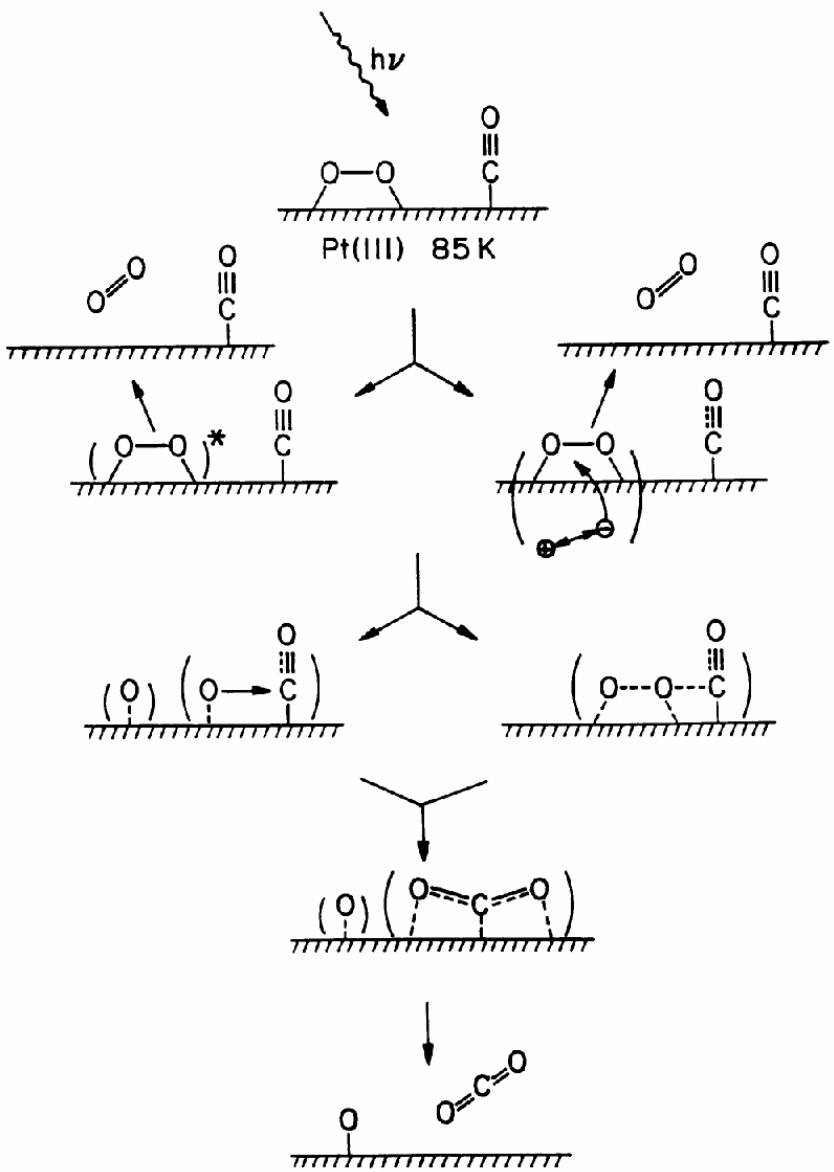
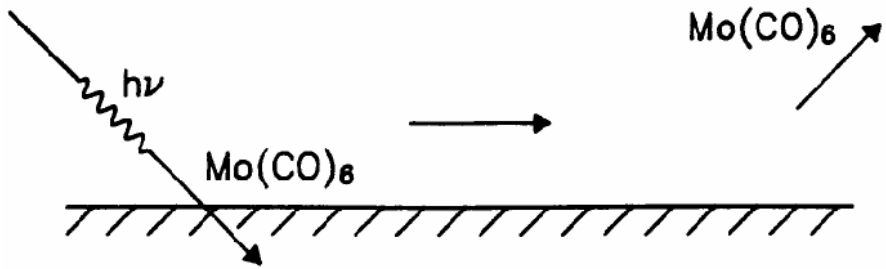
Surface Photochemistry

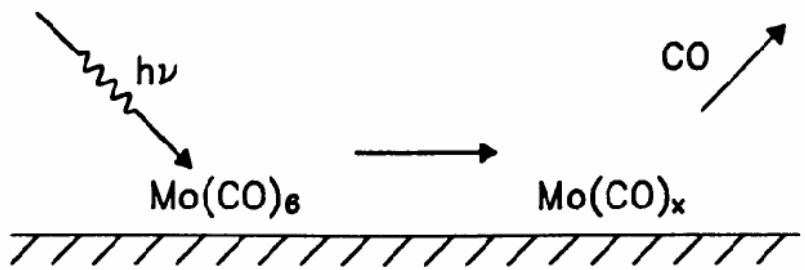


Mechanisms of Photo–Induced Reactions
$Mo(CO)_6$ on Si(111)7×7

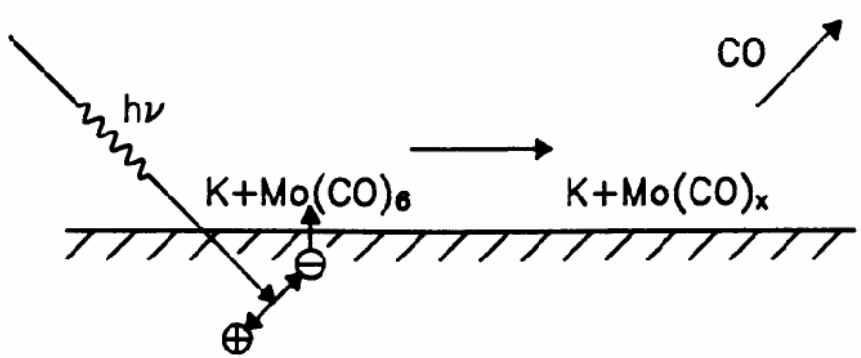
1) Desorption via Substrate Heating



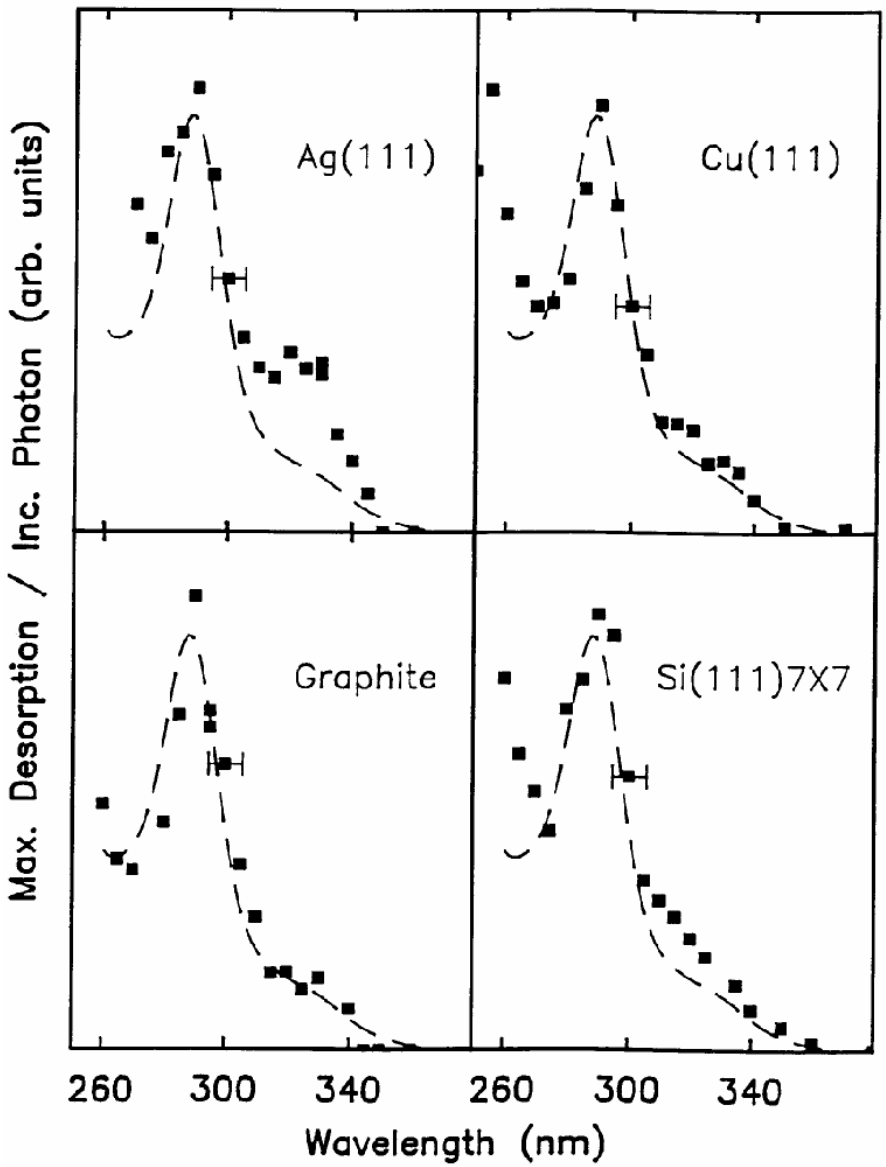
2) Dissociation via Adsorbate Excitation



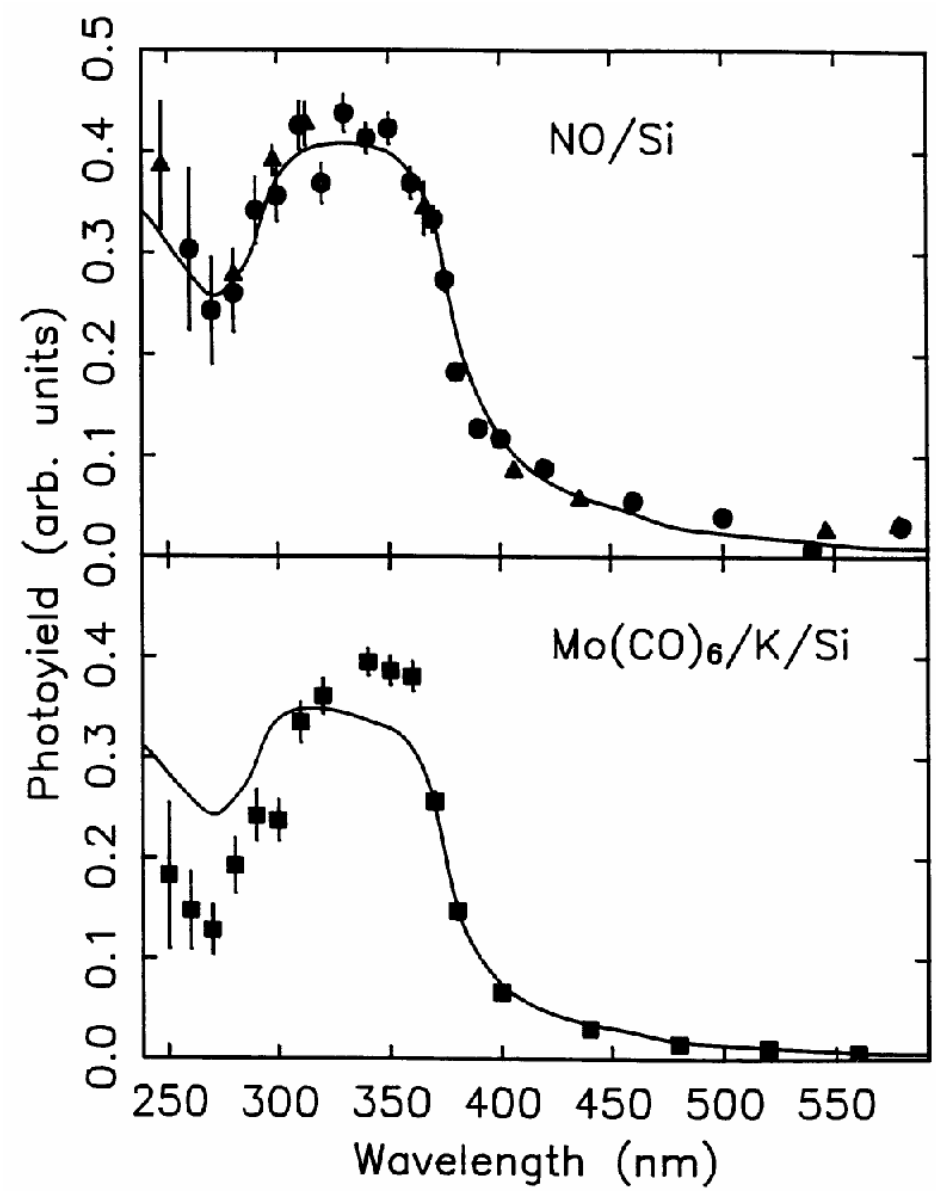
3) K–Induced Electron Attachment Dissociation



Direct Adsorbate Excitation



Photoelectron Mechanism

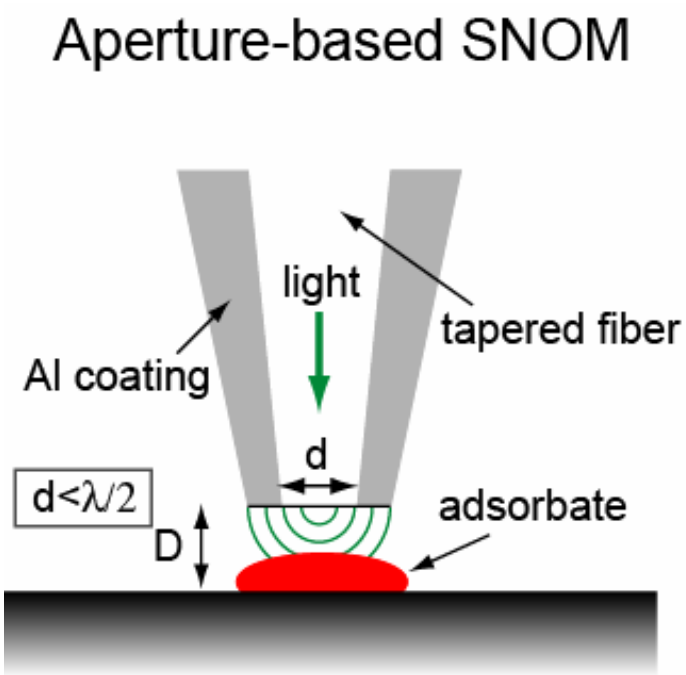


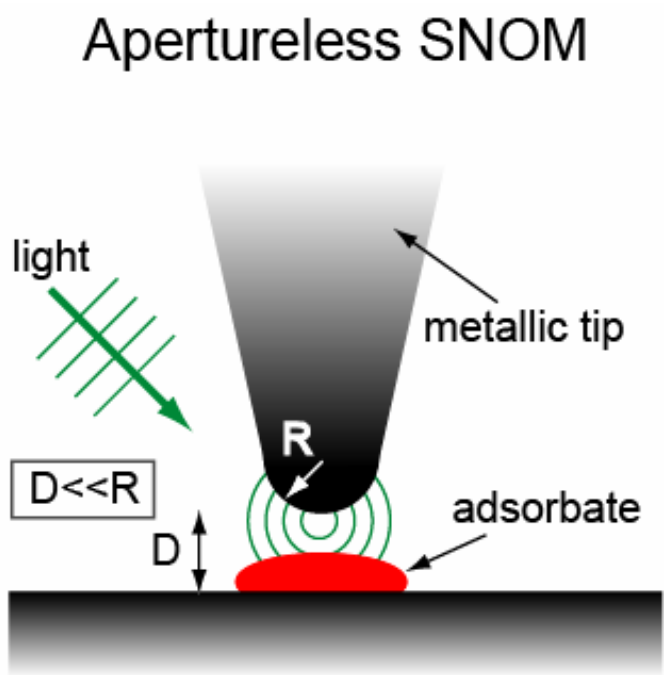
Objective

How to achieve atomic scale resolution in probing matter with electromagnetic radiation?

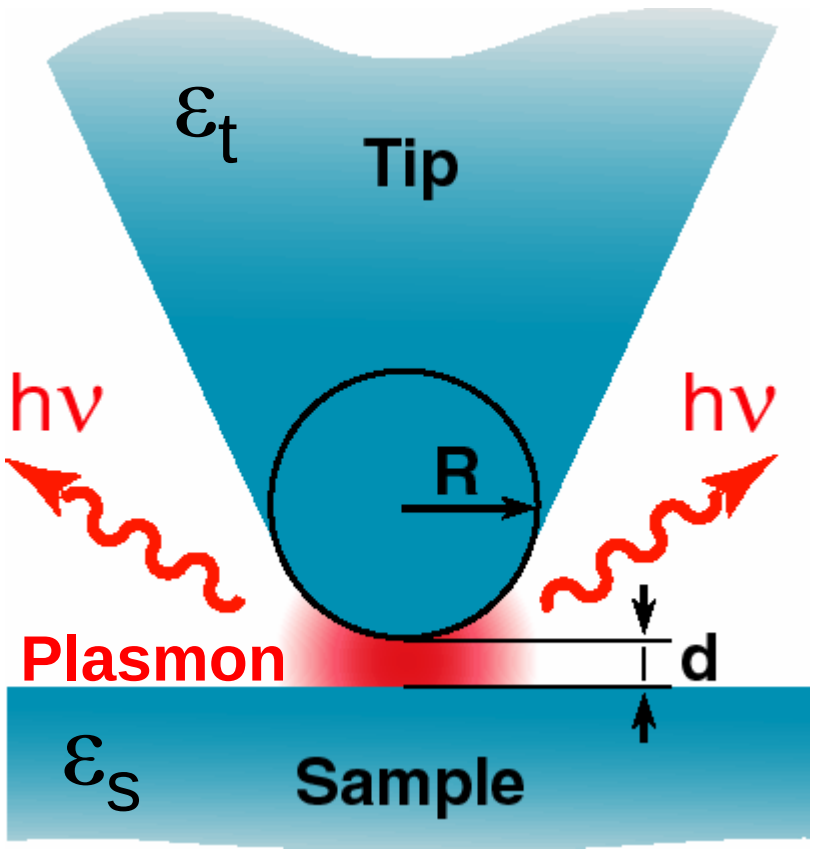
- **Spectroscopy**
- **Optical Phenomena**

Resolution of Optical Spectroscopy



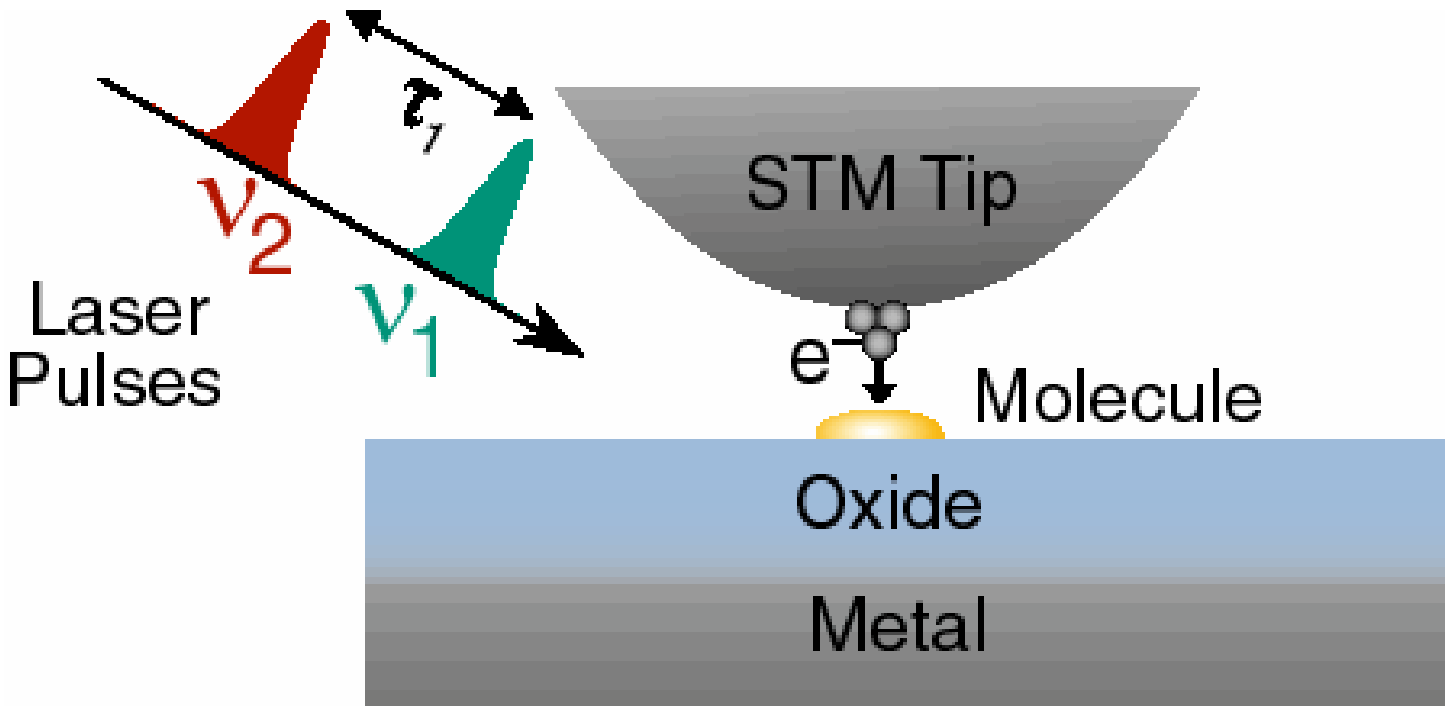


Tip-Induced Plasmon Modes

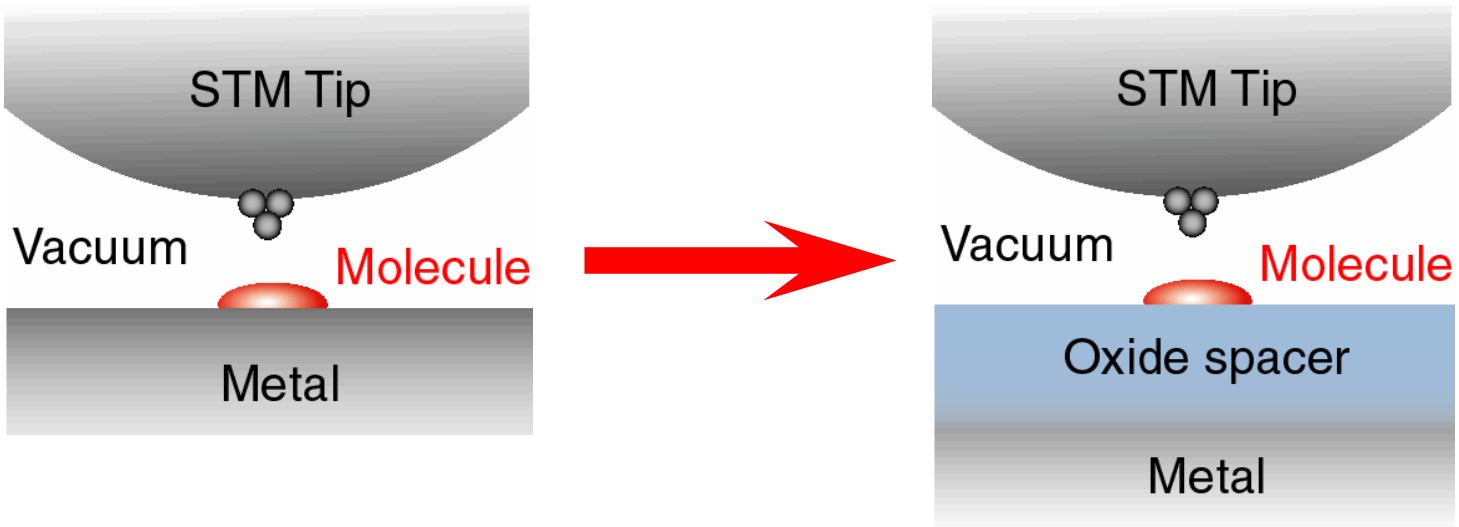


Plasmon "size" : $\sqrt{dR}$

Combination of Electromagnetic Radiation With Spatial Resolution of the STM

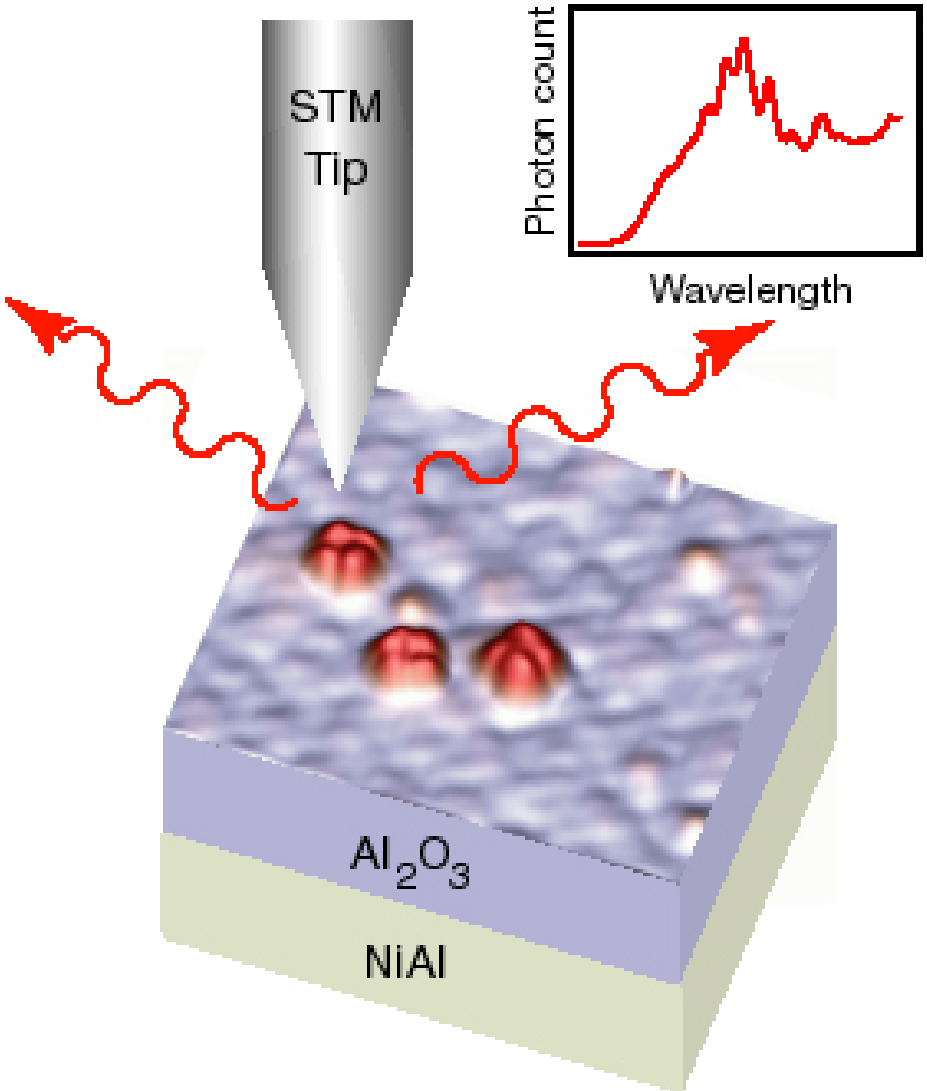


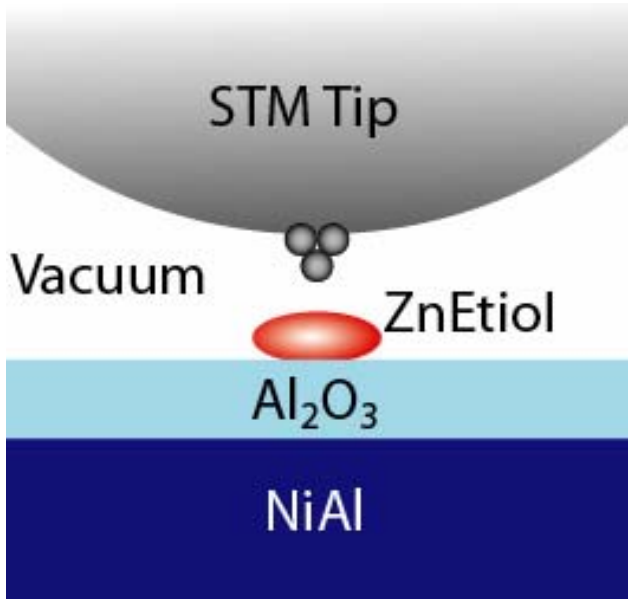
Molecules in Double Barrier Junctions



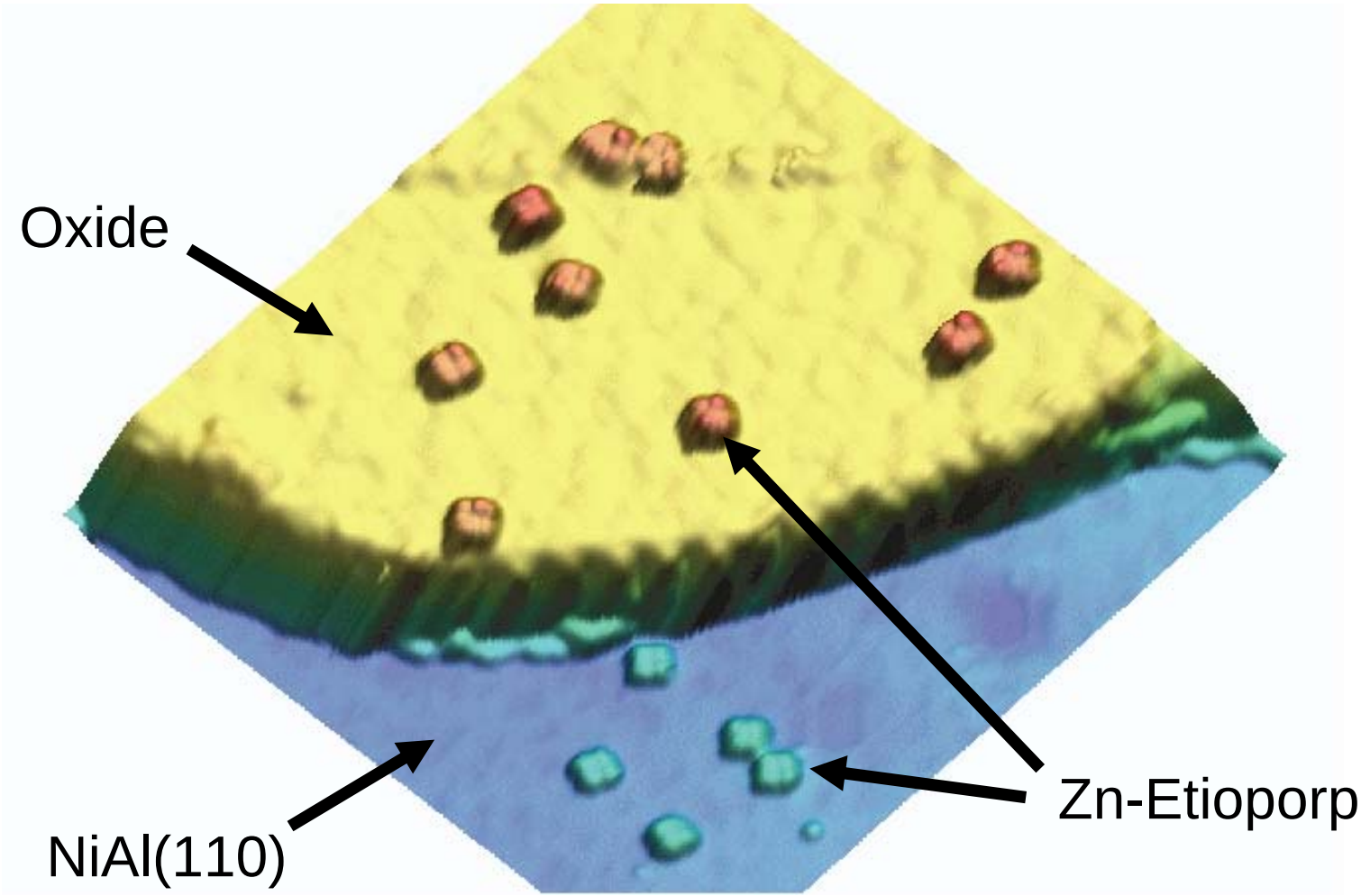
- The oxide film spacer increases the lifetime of the transient charged molecular state created after electron injection/withdrawal.

Single Molecule Electroluminescence

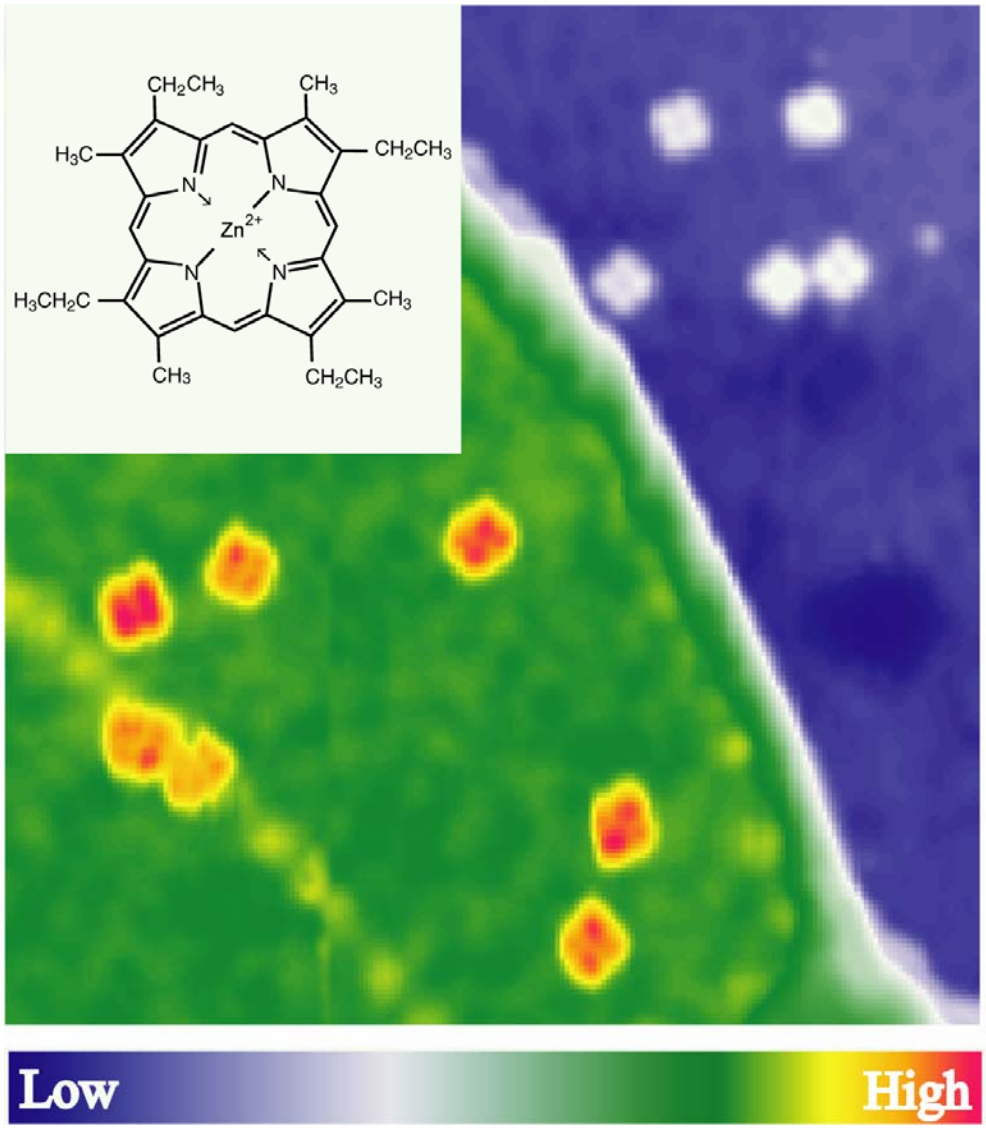




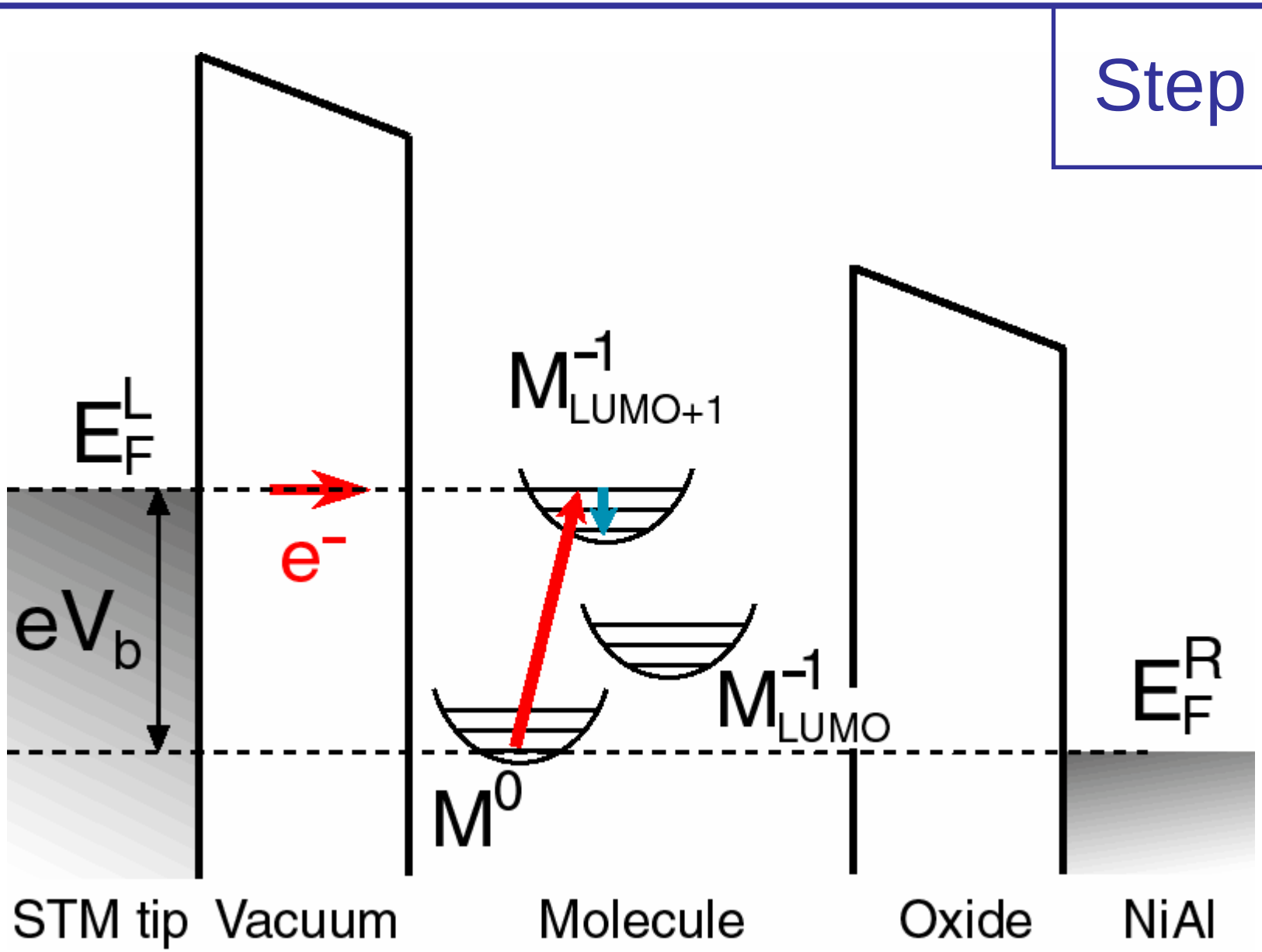
Photon Emission from Single Molecules: Zn-Etioporphyrin on Partially Oxidized NiAl(110)



Zn(II) Etioporphyrin on Al_2O_3 & NiAl(110)

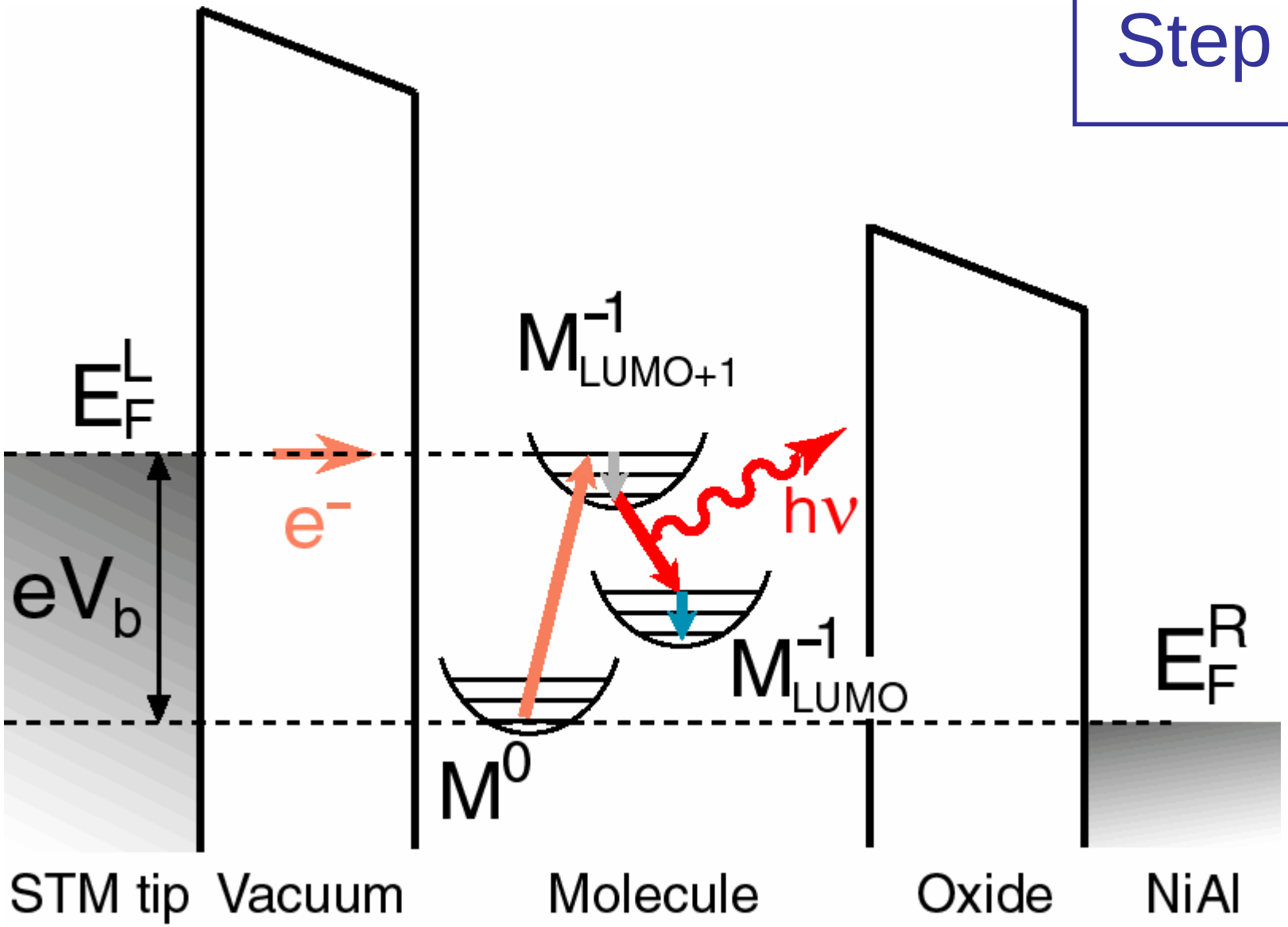


Mechanism of STM-induced Electroluminescence :



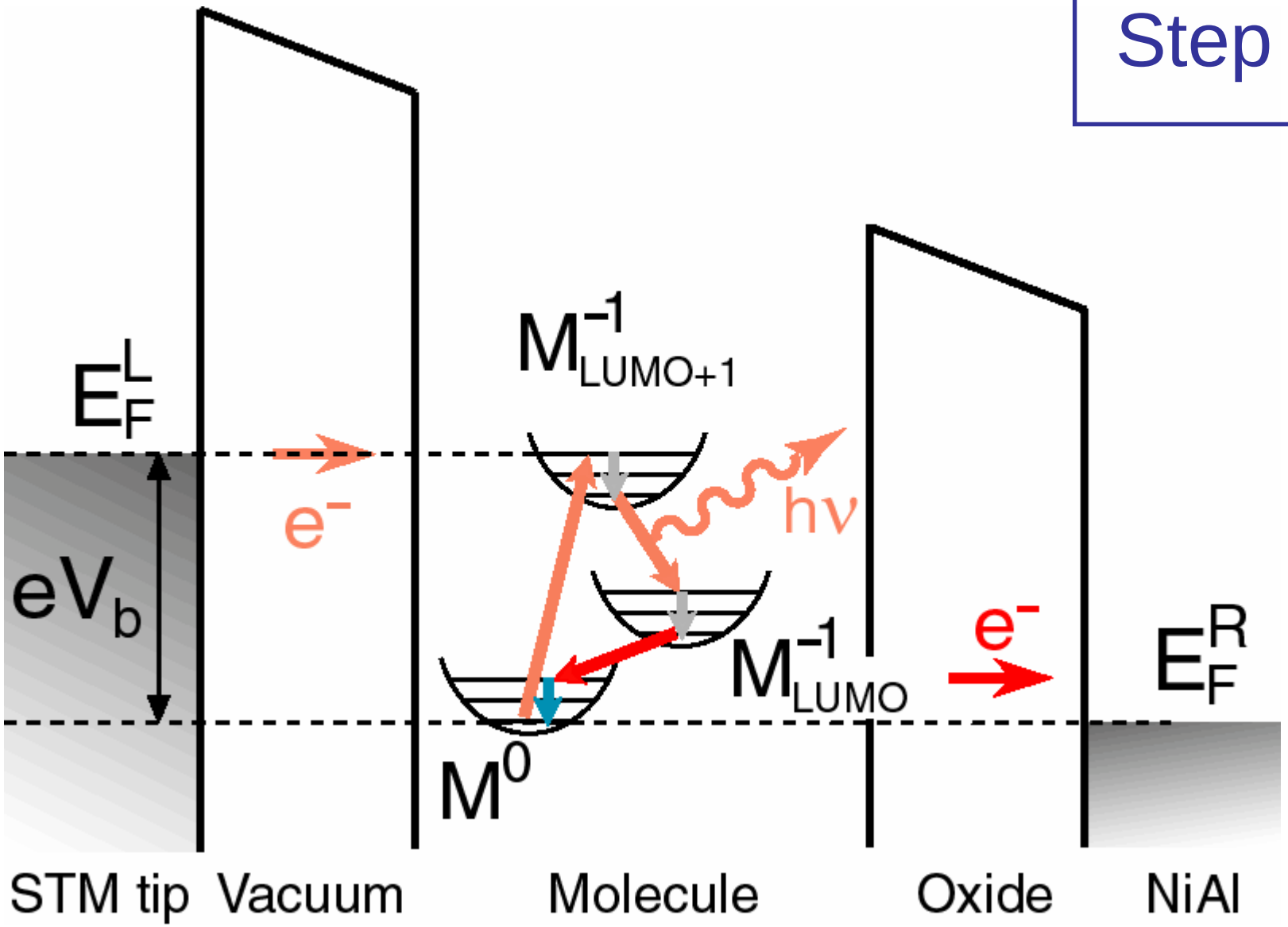
Mechanism of STM-induced Electroluminescence :

Step 2

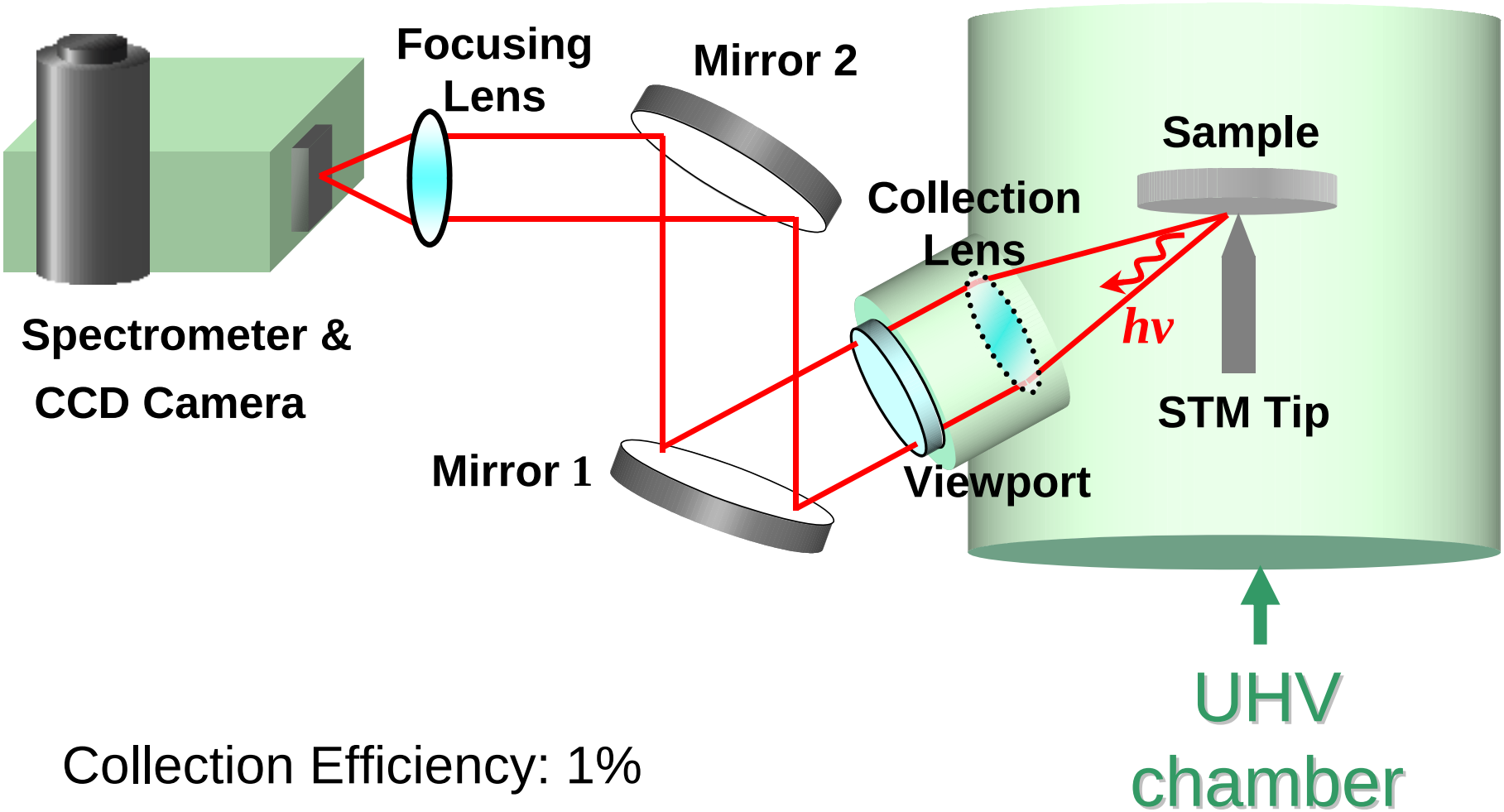


Mechanism of STM-induced Electroluminescence :

Step 3

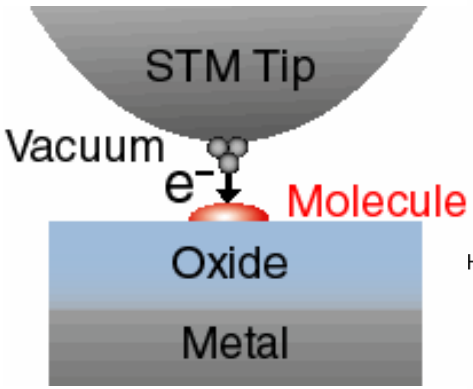


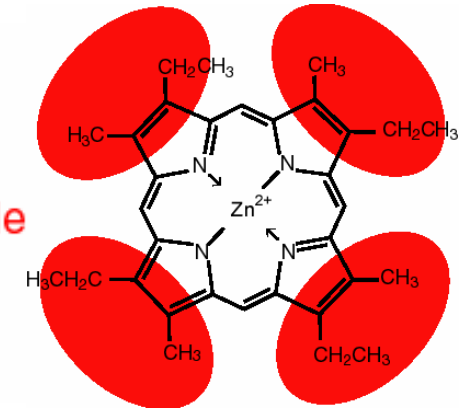
Light collection setup (electroluminescence)

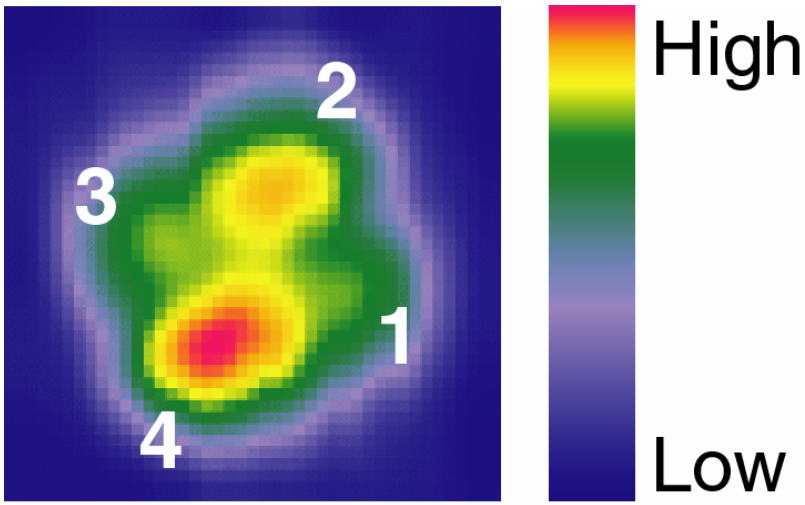


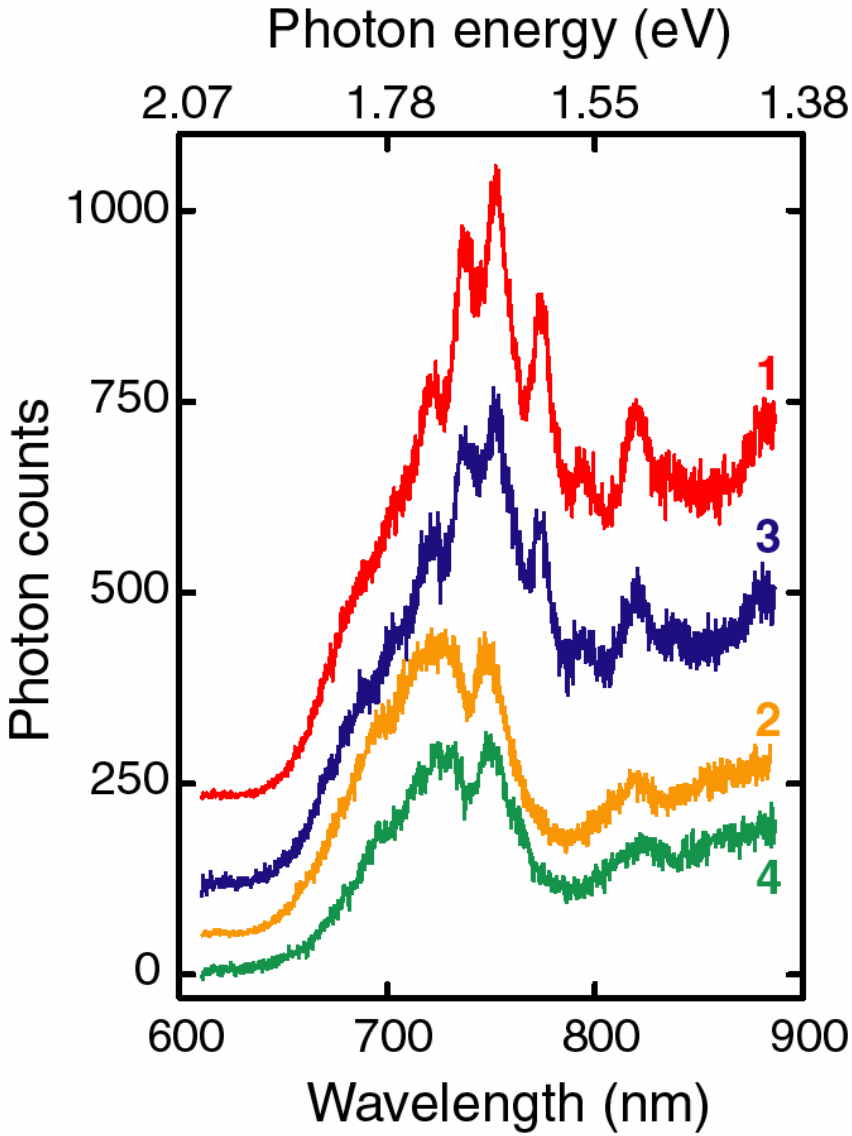
Collection Efficiency: 1%

Photon Emission From Molecules on Oxide Films

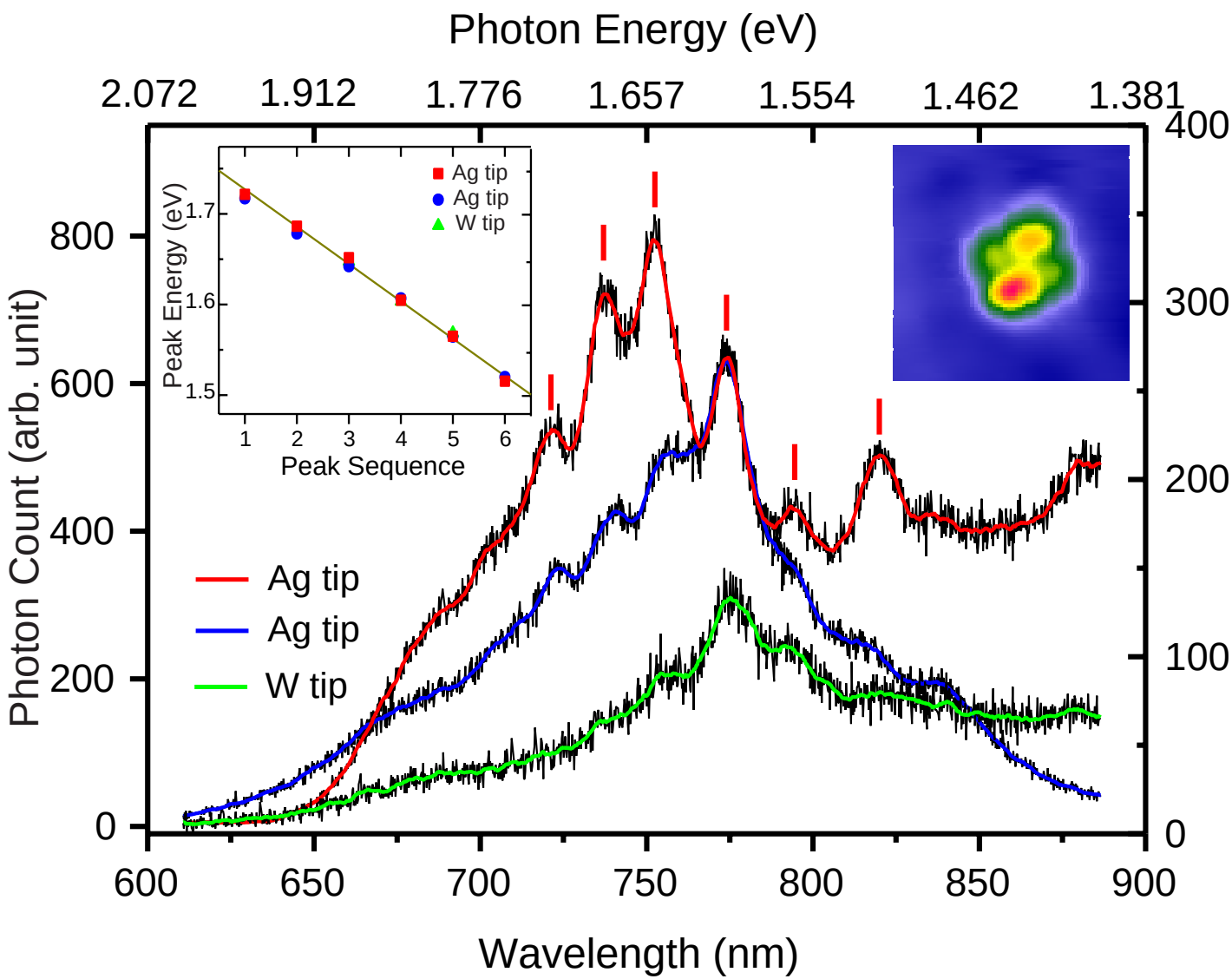




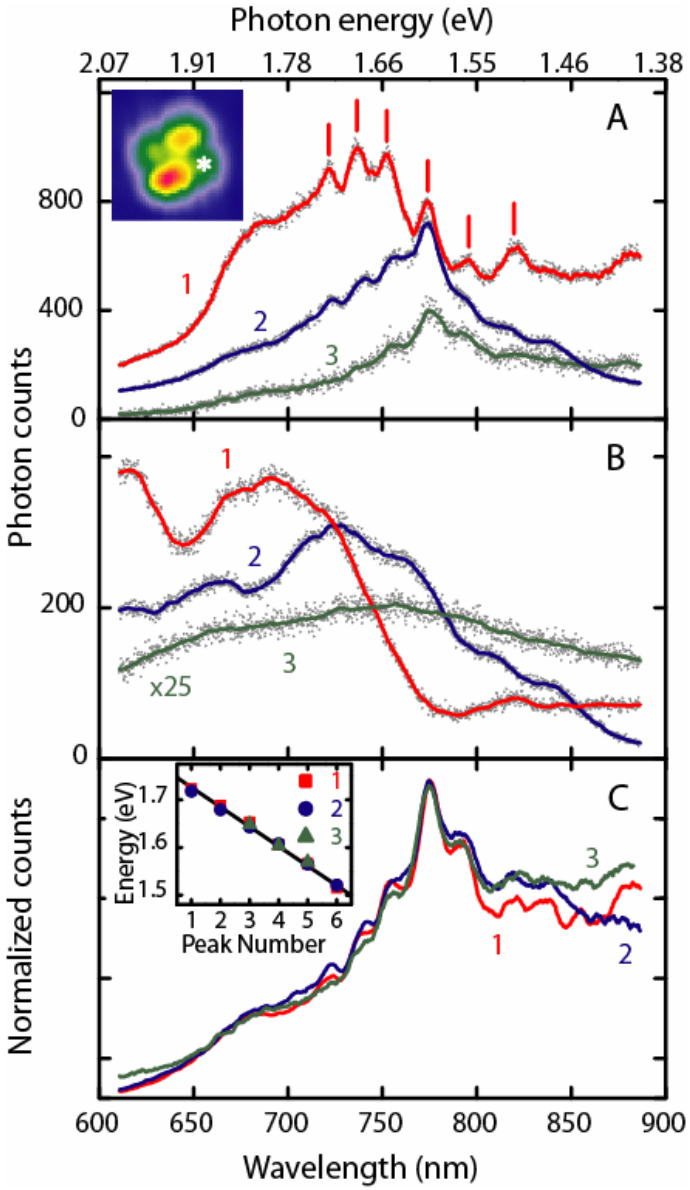




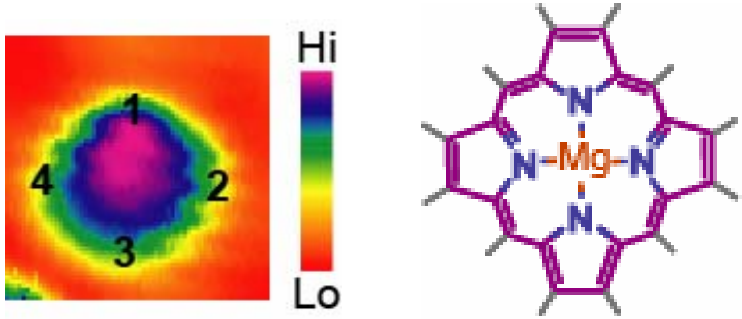
TIF – Ag vs. W Tips

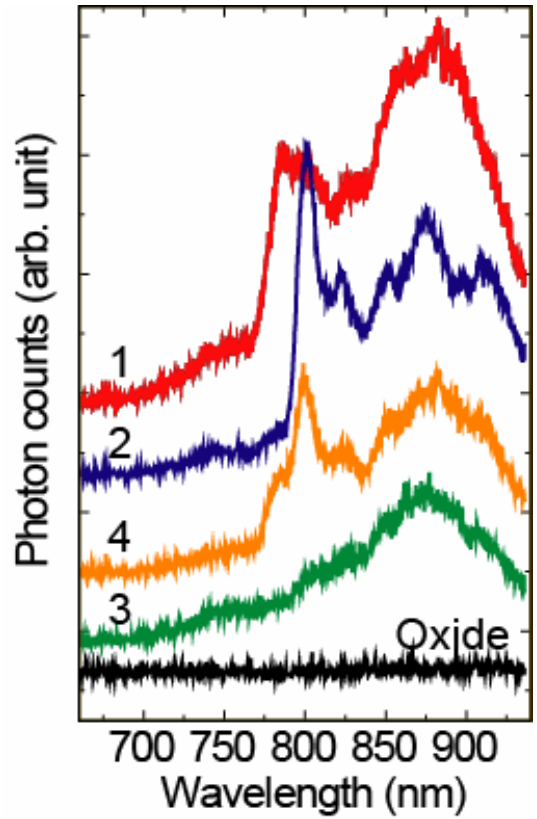


Tunneling Electron Induced Single Molecule Fluorescence: Zn-Etioporphyrin

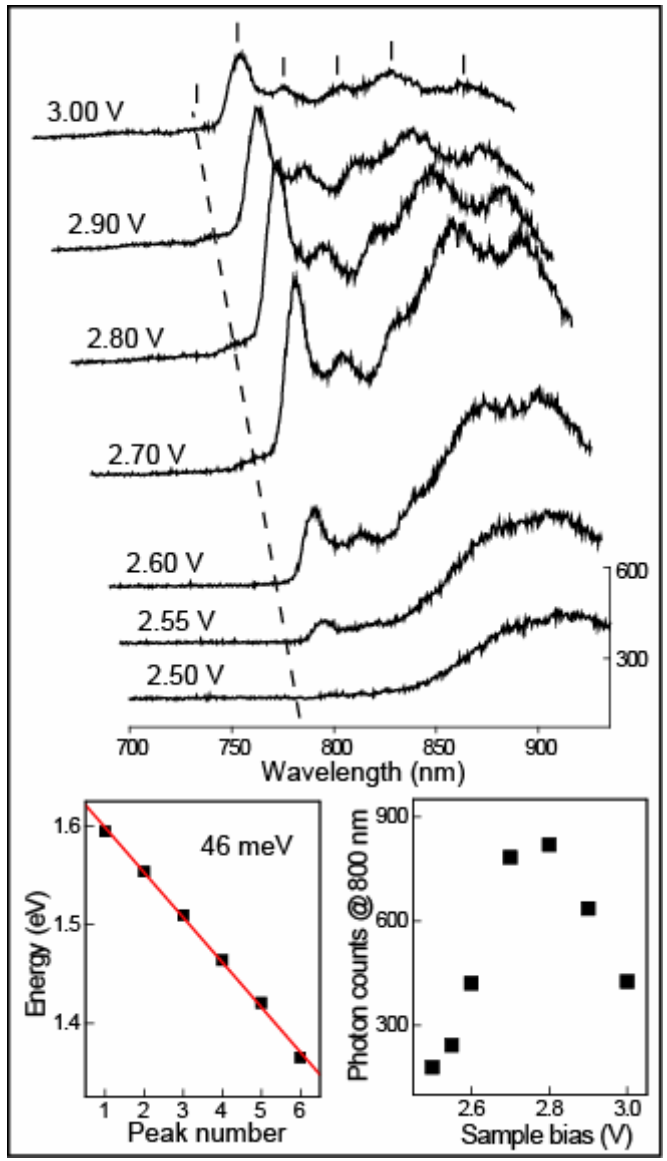


Spatial Dependence of Single Molecule Fluorescence

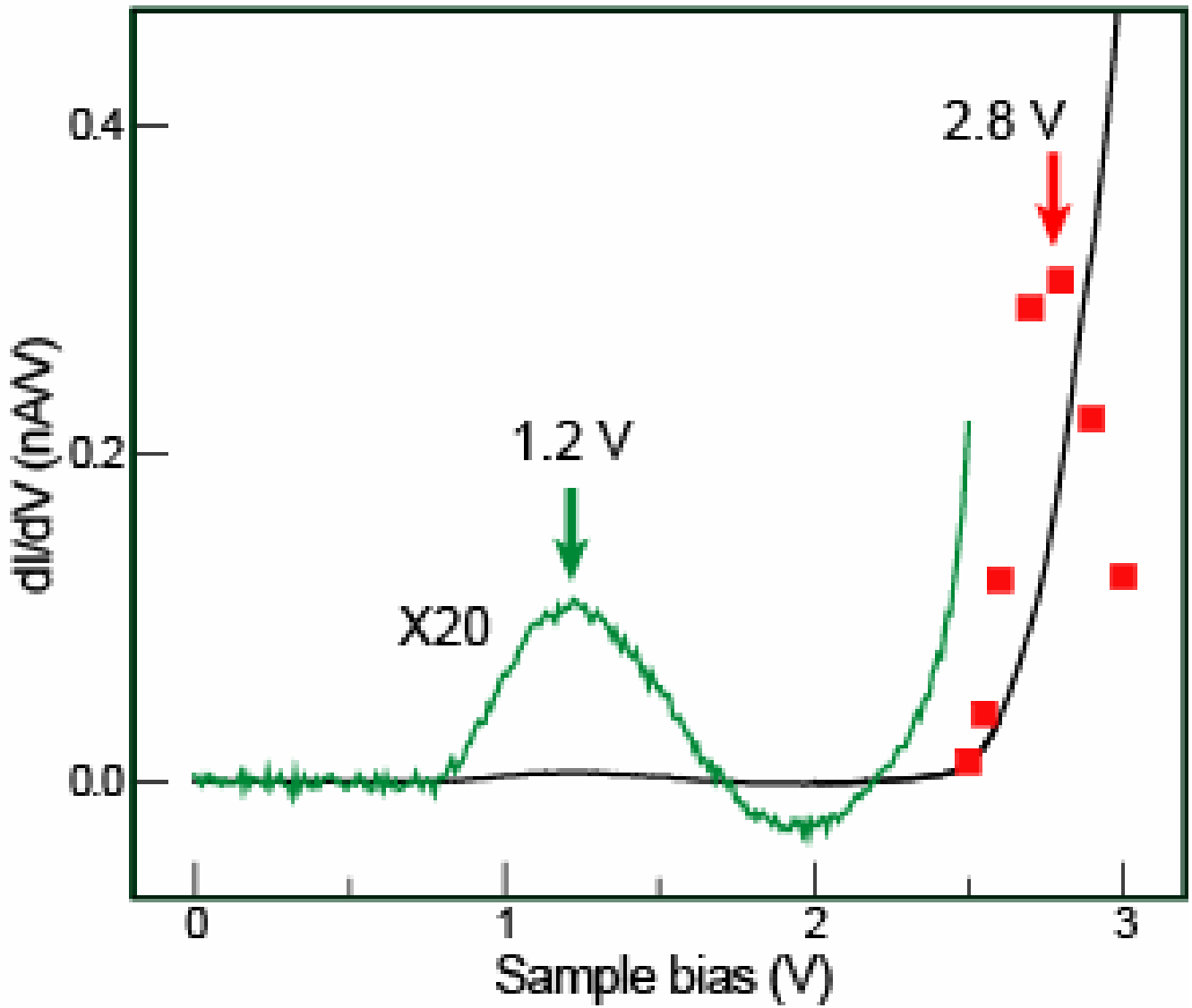




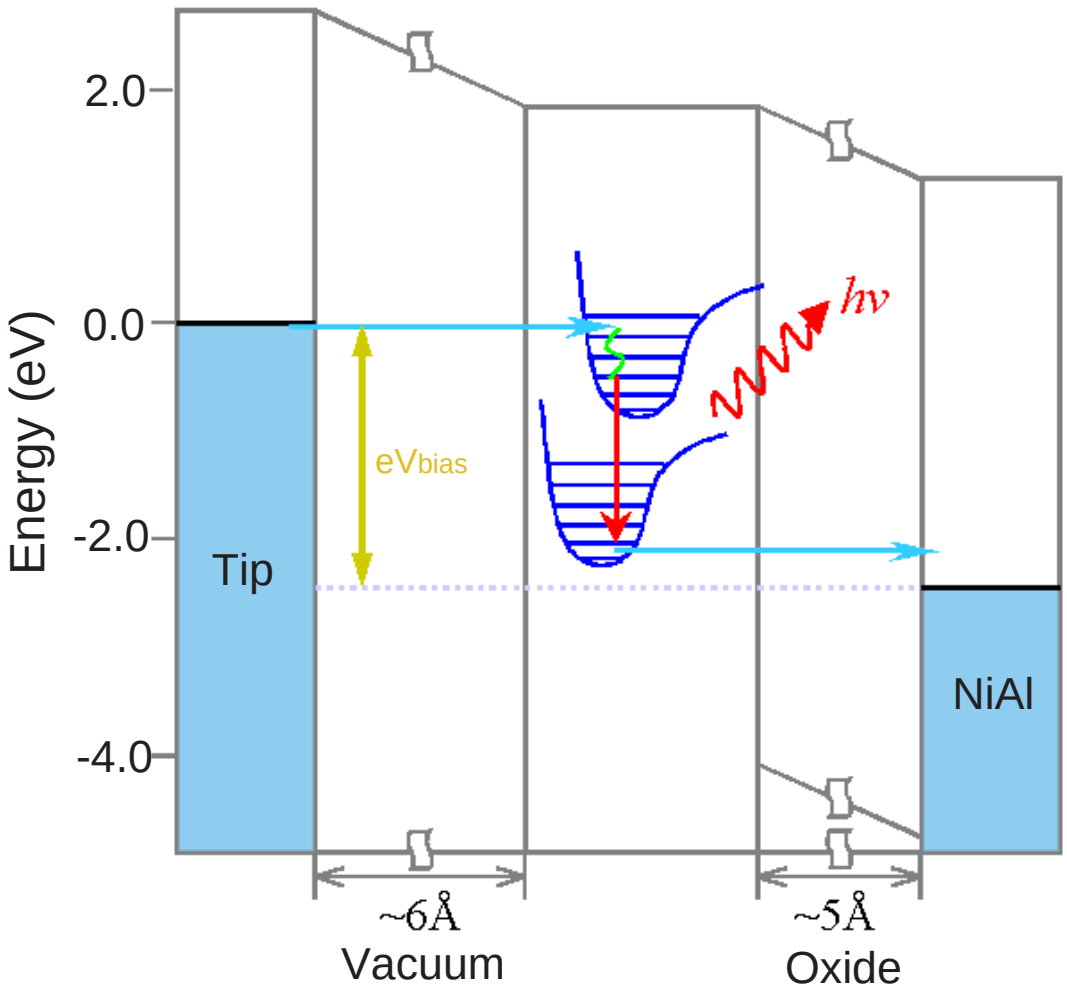
Tunneling Electron Induced Single Molecule Fluorescence



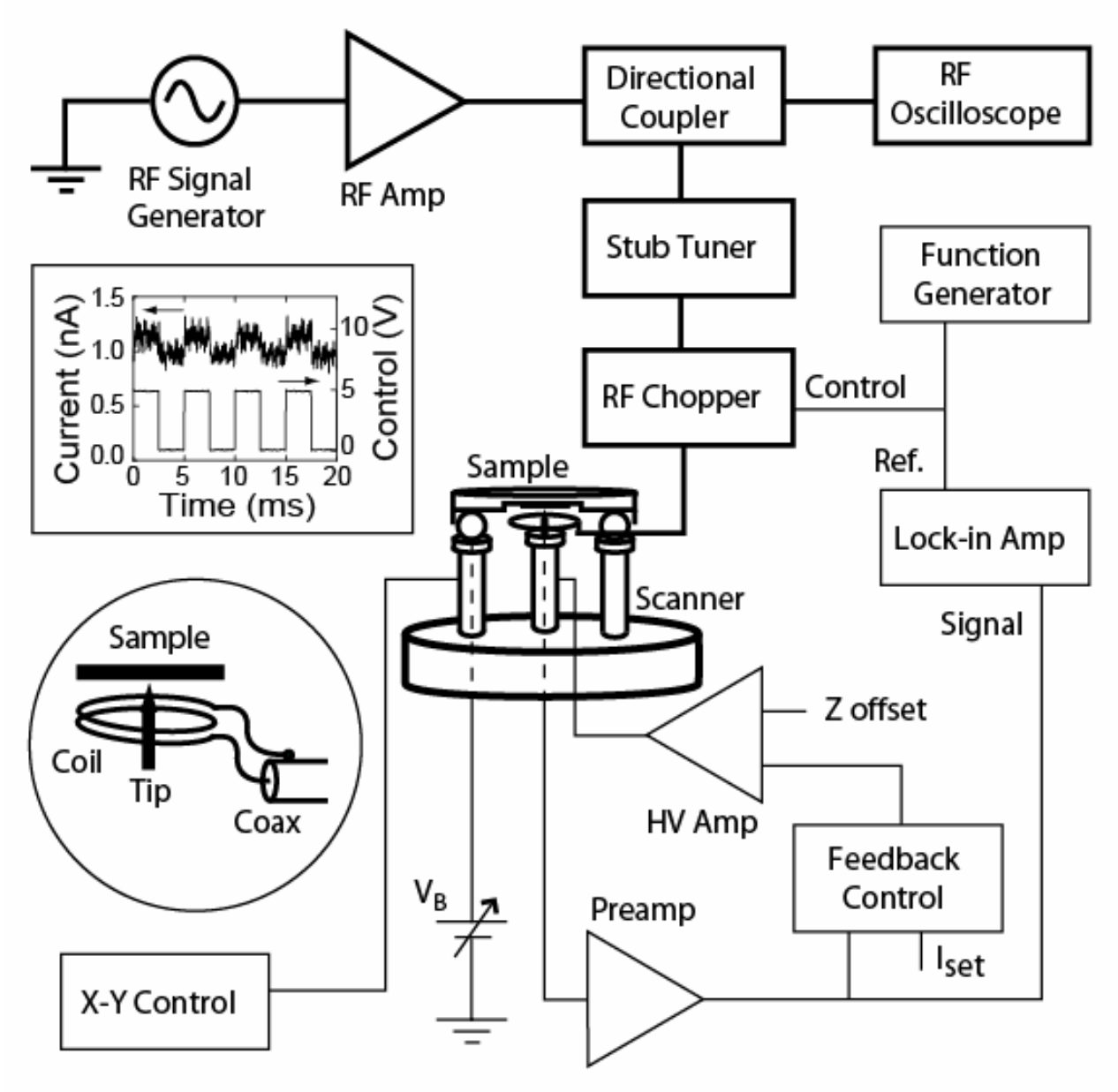
LUMO & LUMO + 1: MgP

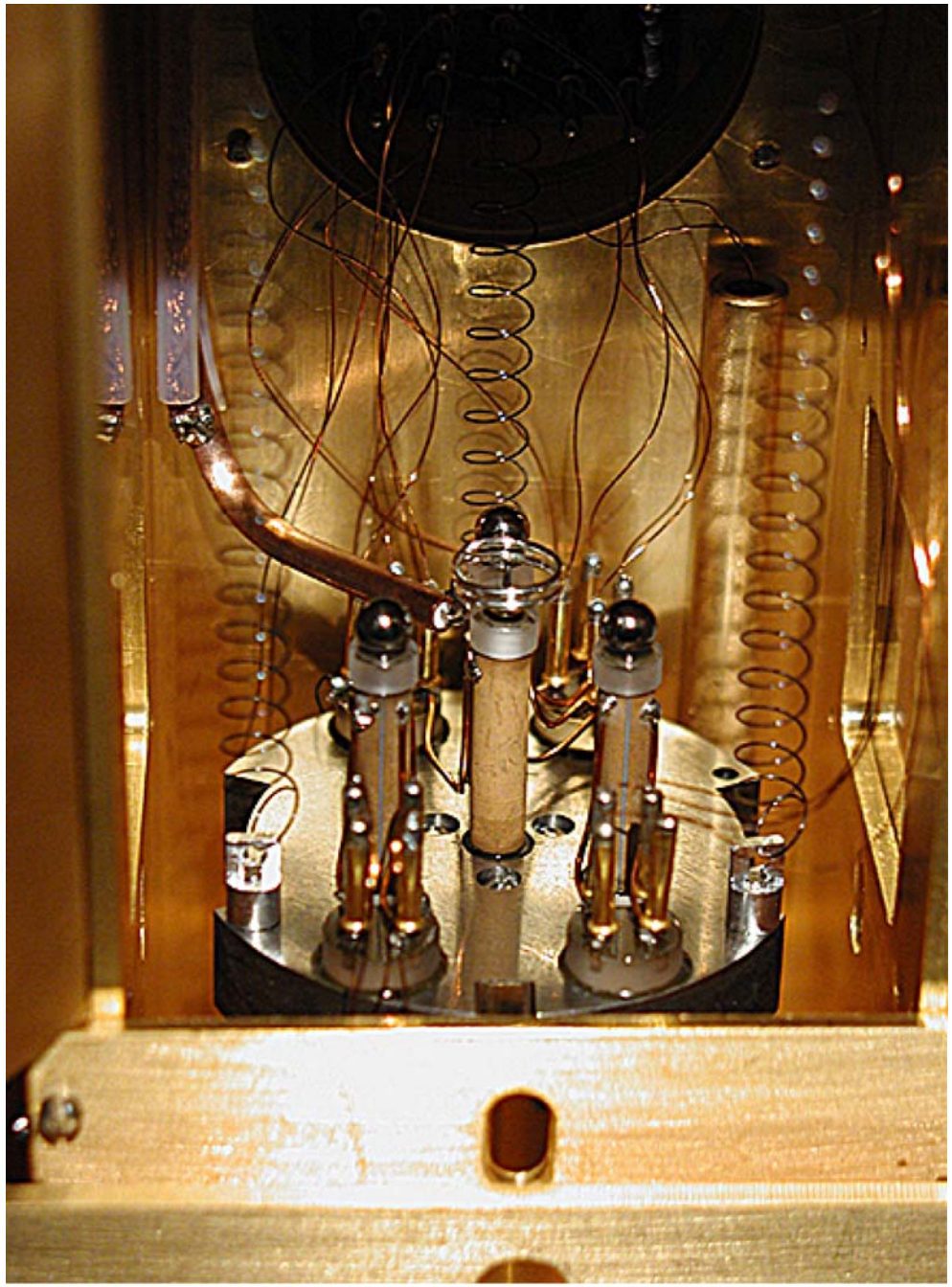


TIF Mechanism

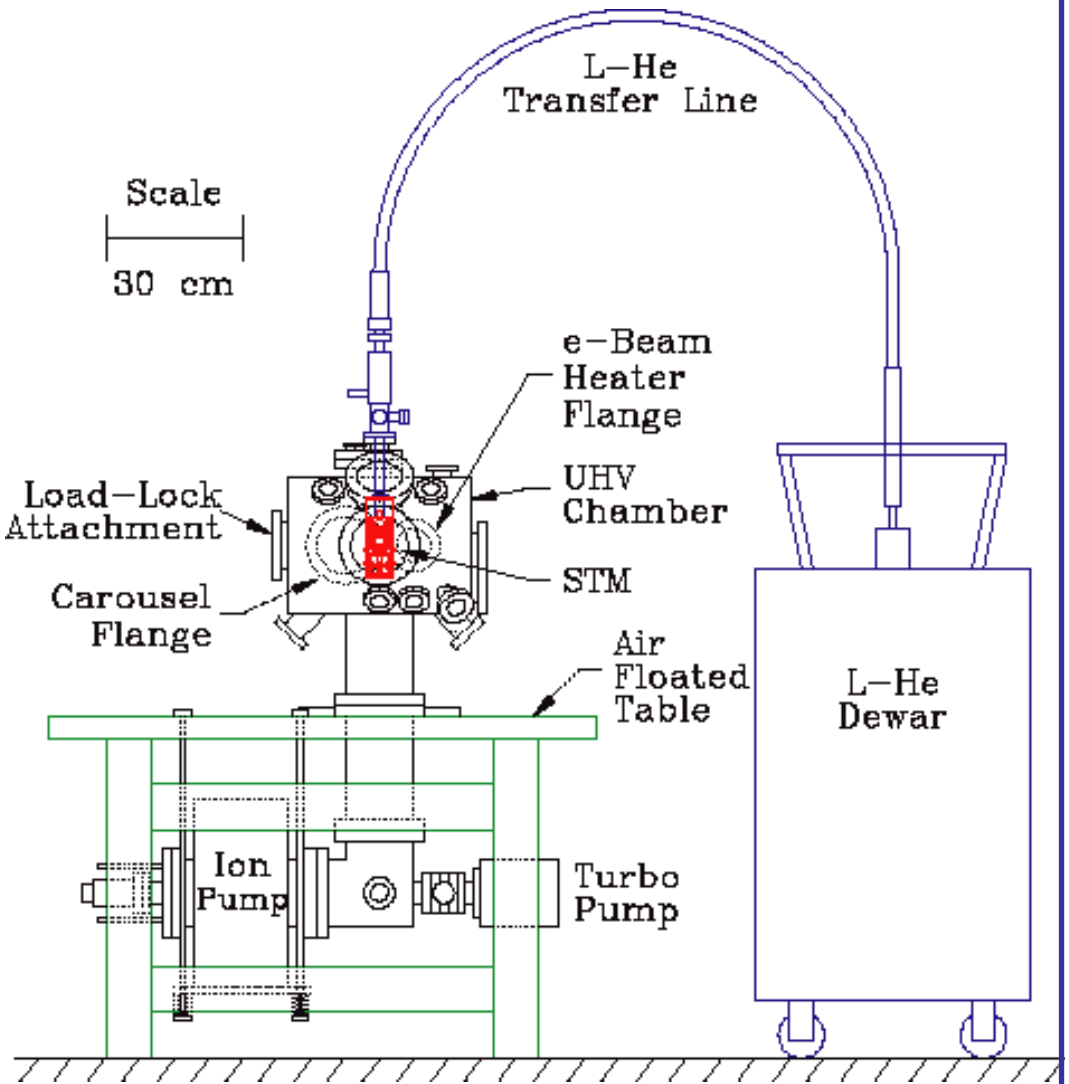


RF Induced Rectification Current

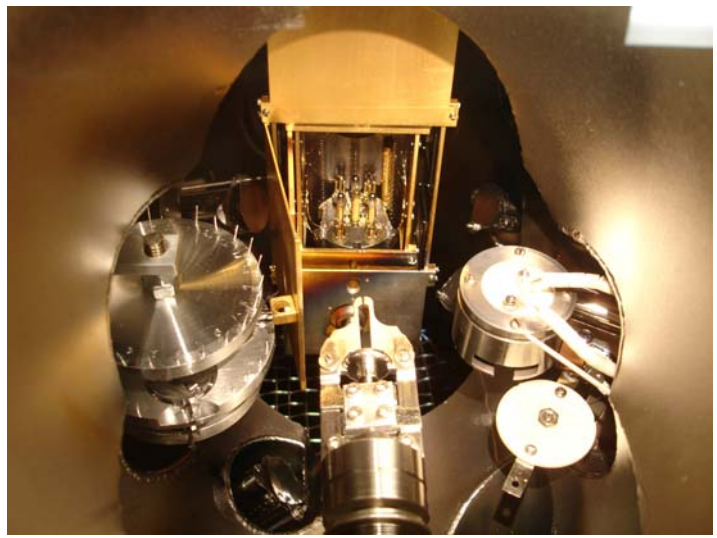




STM Apparatus



Low temperature (10 K) ultrahigh vacuum STM



Origin of Rectification Current

$$V = V_B + \sqrt{2}V_J \cos(\omega t)$$

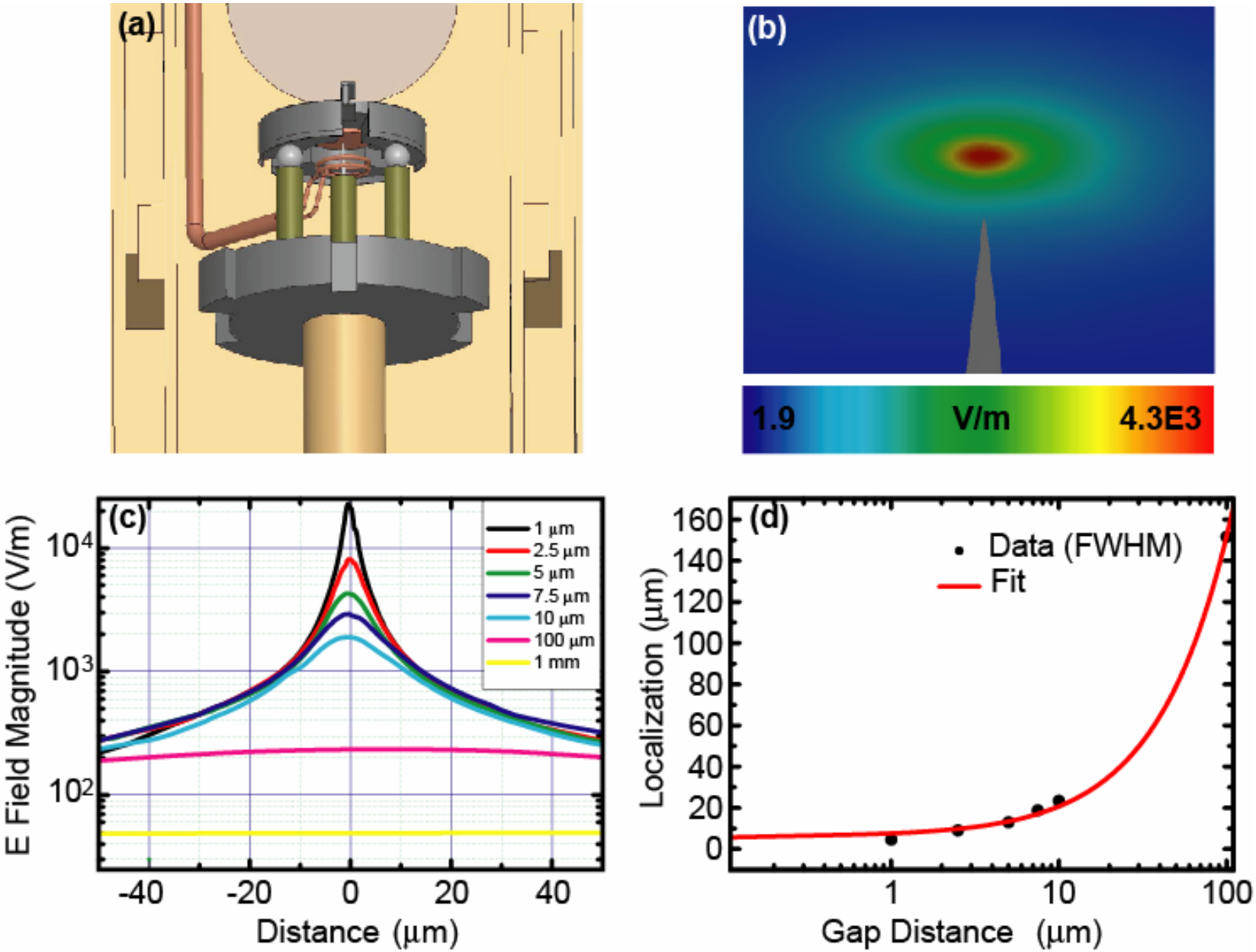
$$I(V) = I_0(V_B) + \left.\frac{dI}{dV}\right|_{V_B} \sqrt{2}V_J \cos(\omega t) + \left.\frac{d^2 I}{dV^2}\right|_{V_B} V_J{}^2 \cos^2(\omega t) + \cdots$$

$$I(V) = I_0(V_B) + \left.\frac{dI}{dV}\right|_{V_B} \sqrt{2}V_J \cos(\omega t) + \left.\frac{d^2 I}{dV^2}\right|_{V_B} V_J{}^2 \frac{1+\cos(2\omega t)}{2} + \ldots$$

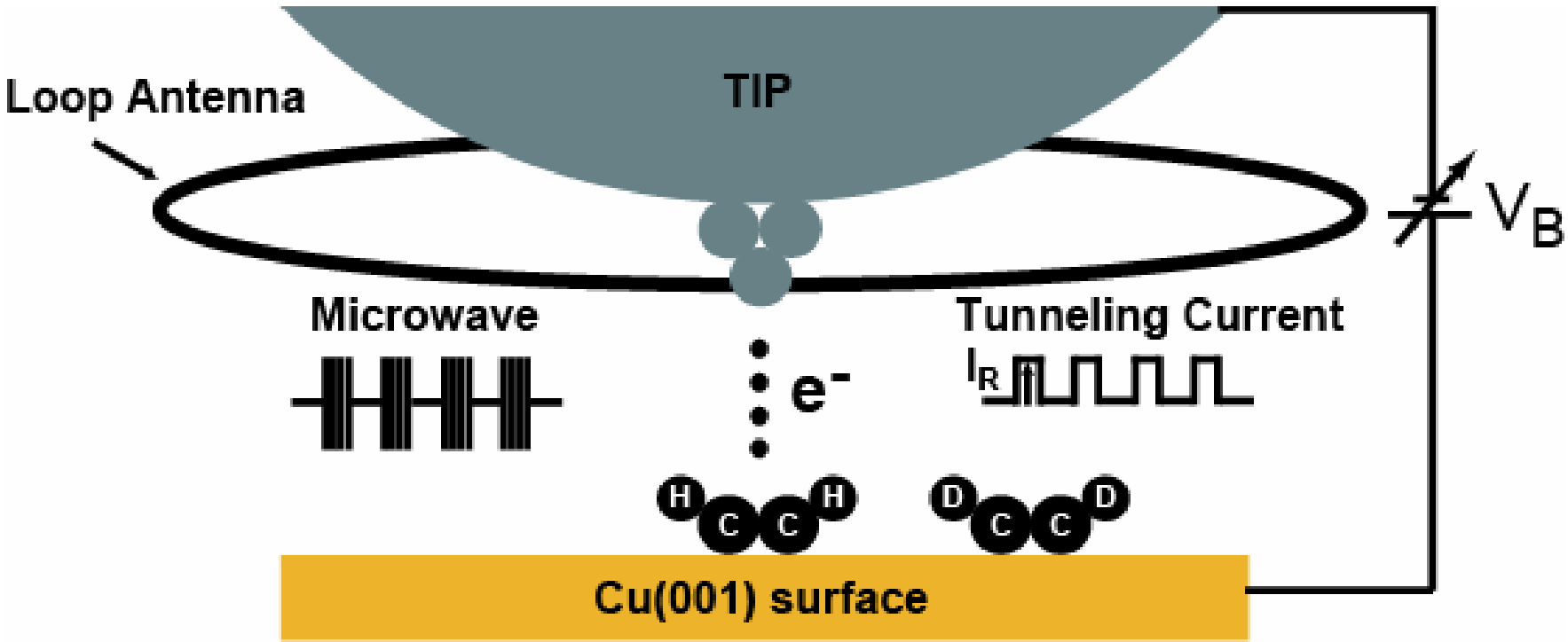
$$I_{dc}(V_B, V_J) = I_0(V_B) + I_R(V_B, V_J) = I_0(V_B) + \frac{1}{2} V_J{}^2 \left.\frac{d^2 I}{dV^2}\right|_{V_B} + \cdots$$

$$I_R(V_B, V_J) \approx \frac{1}{2} V_J{}^2 \left.\frac{d^2 I}{dV^2}\right|_{V_B}$$

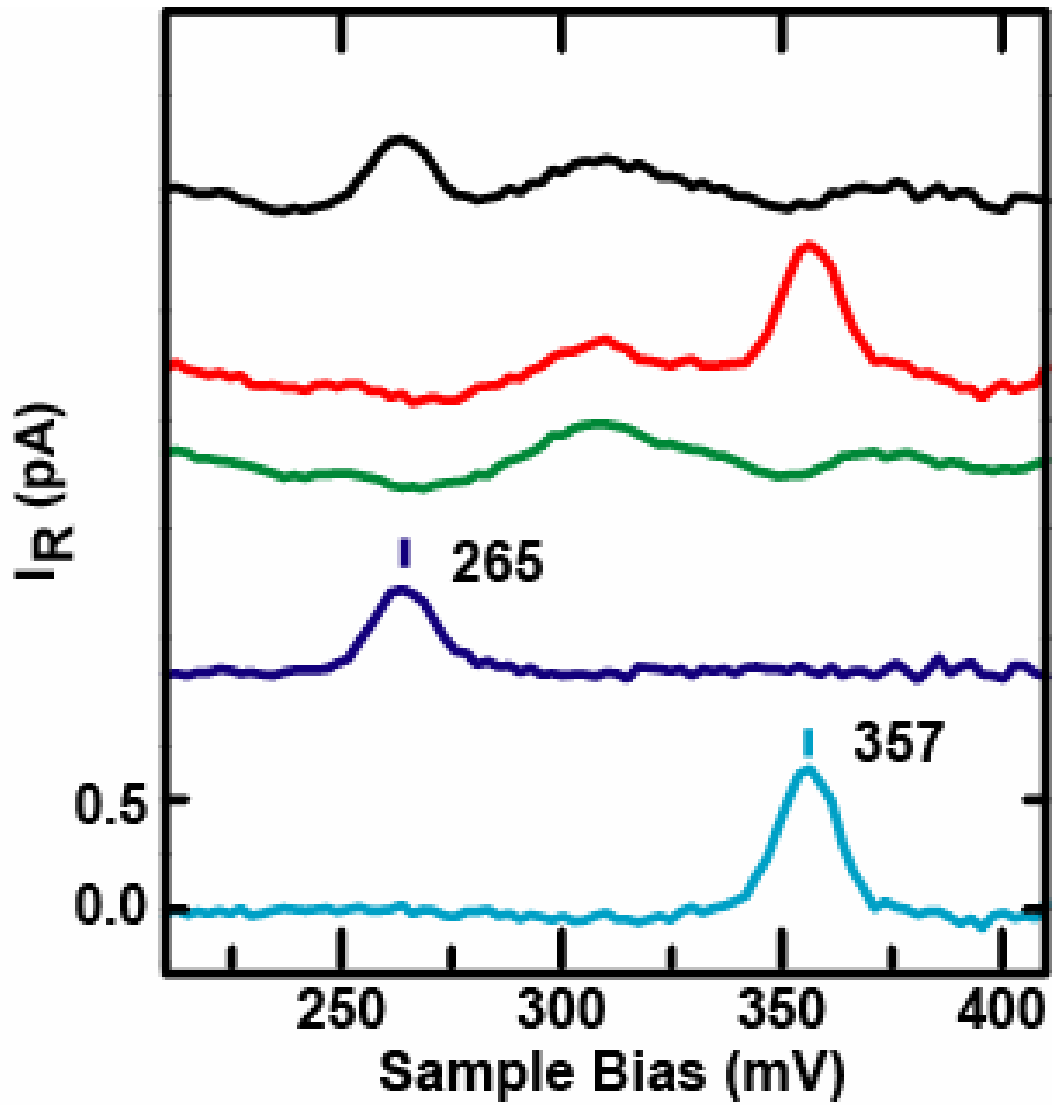
Spatial Localization of RF Field



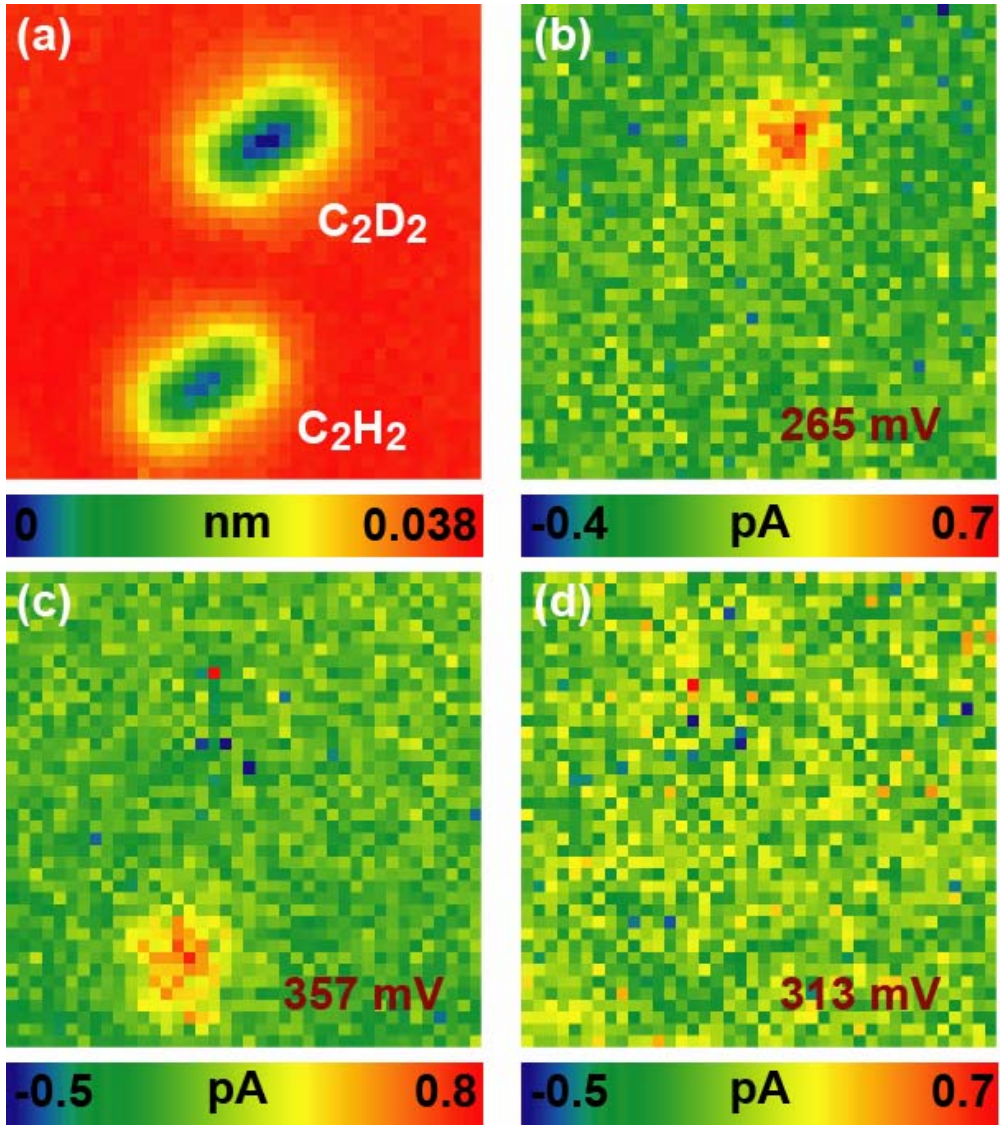
Double Modulation
Vibrational Rectification



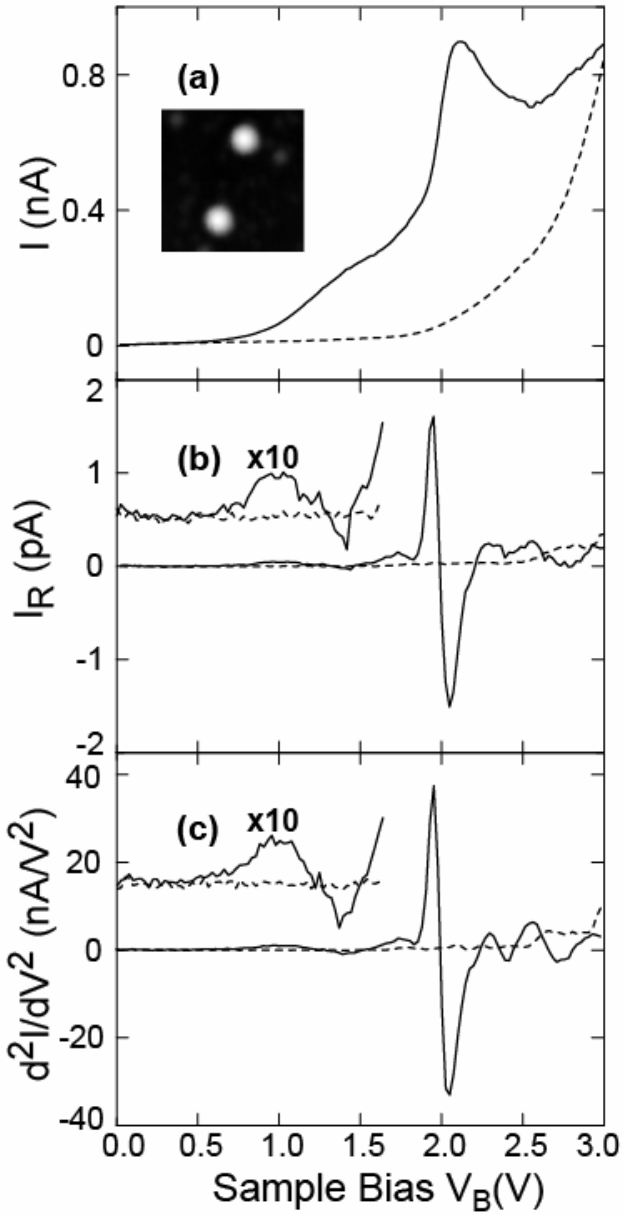
Vibrational Rectification Current: C_2D_2 and C_2H_2 on Cu(001)



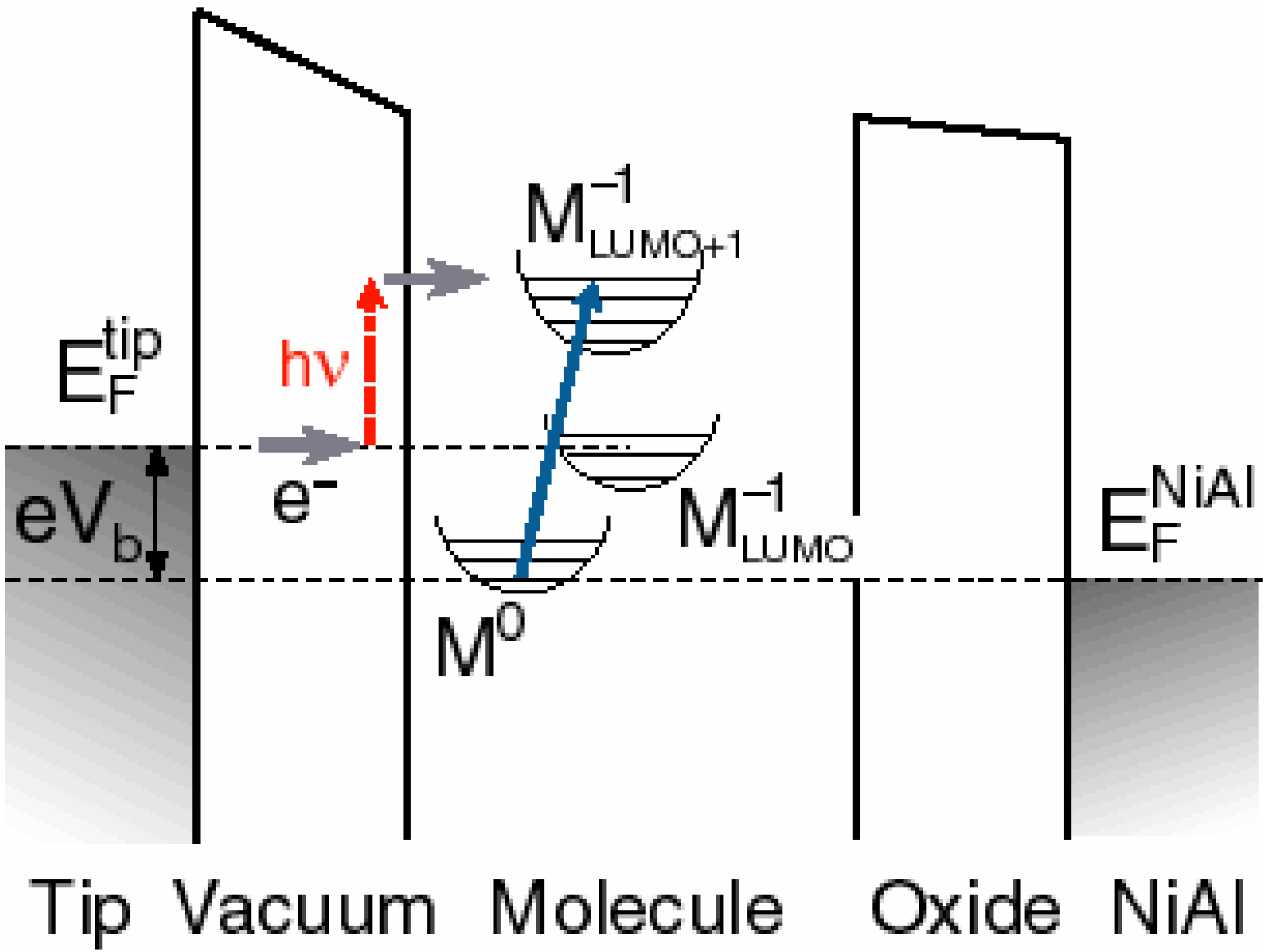
Vibrational Rectification Microscopy: C_2D_2 and C_2H_2 on Cu(001)



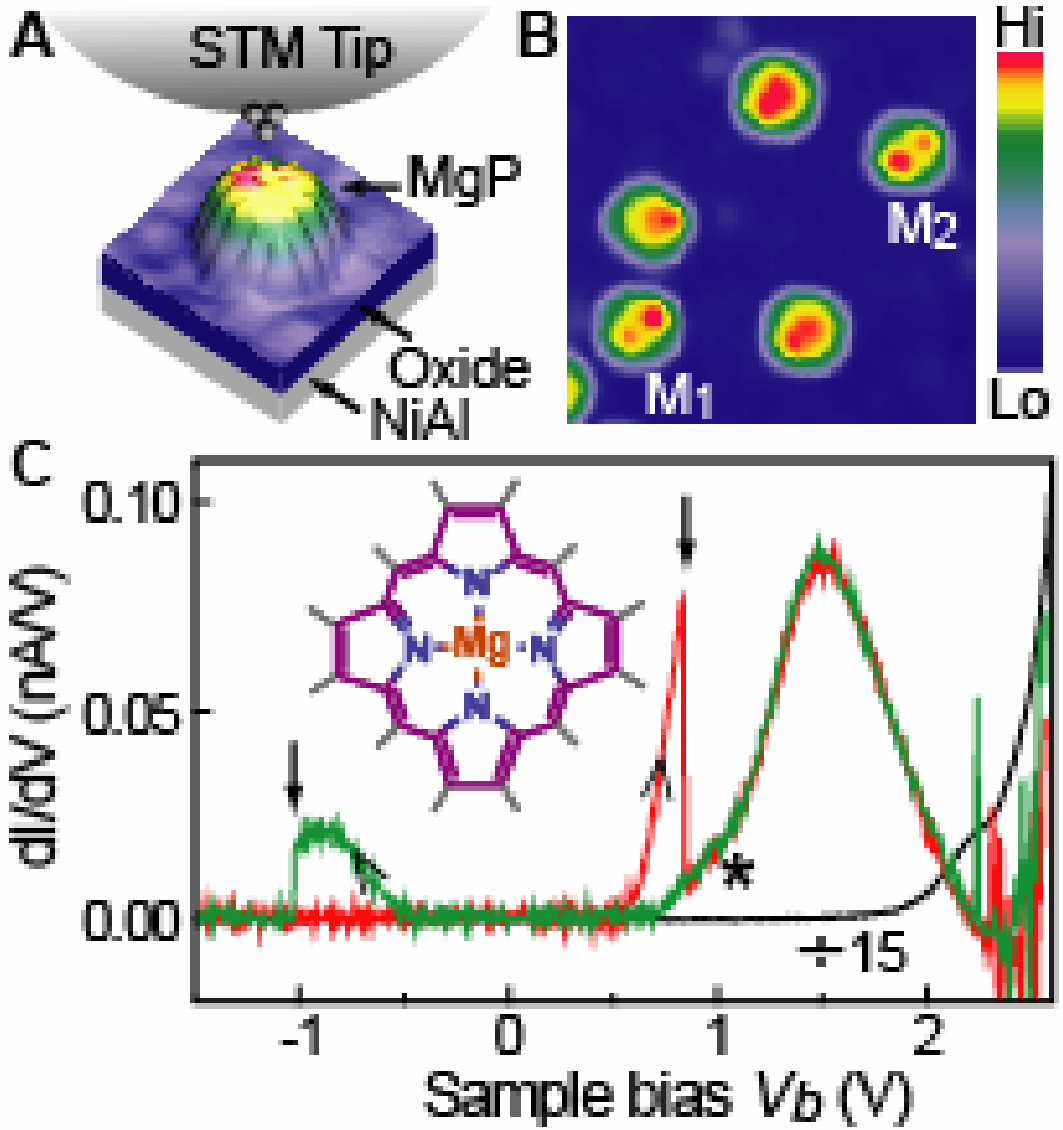
Rectification of Single Mn Atom



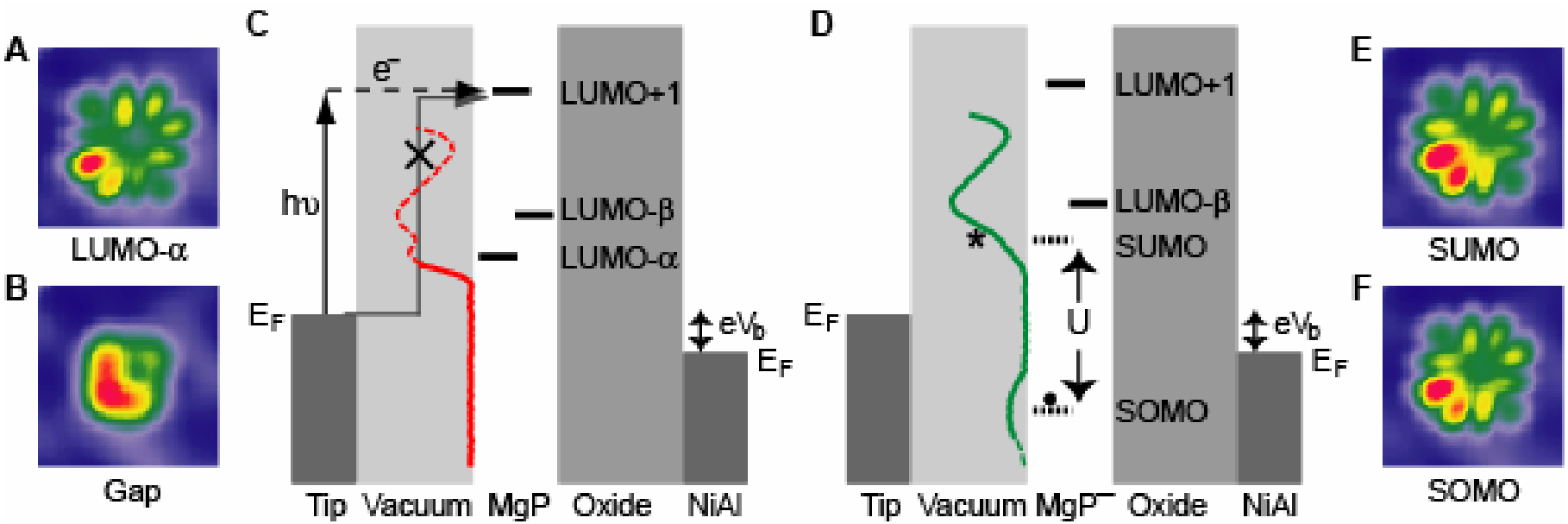
Photon Induced Tunneling



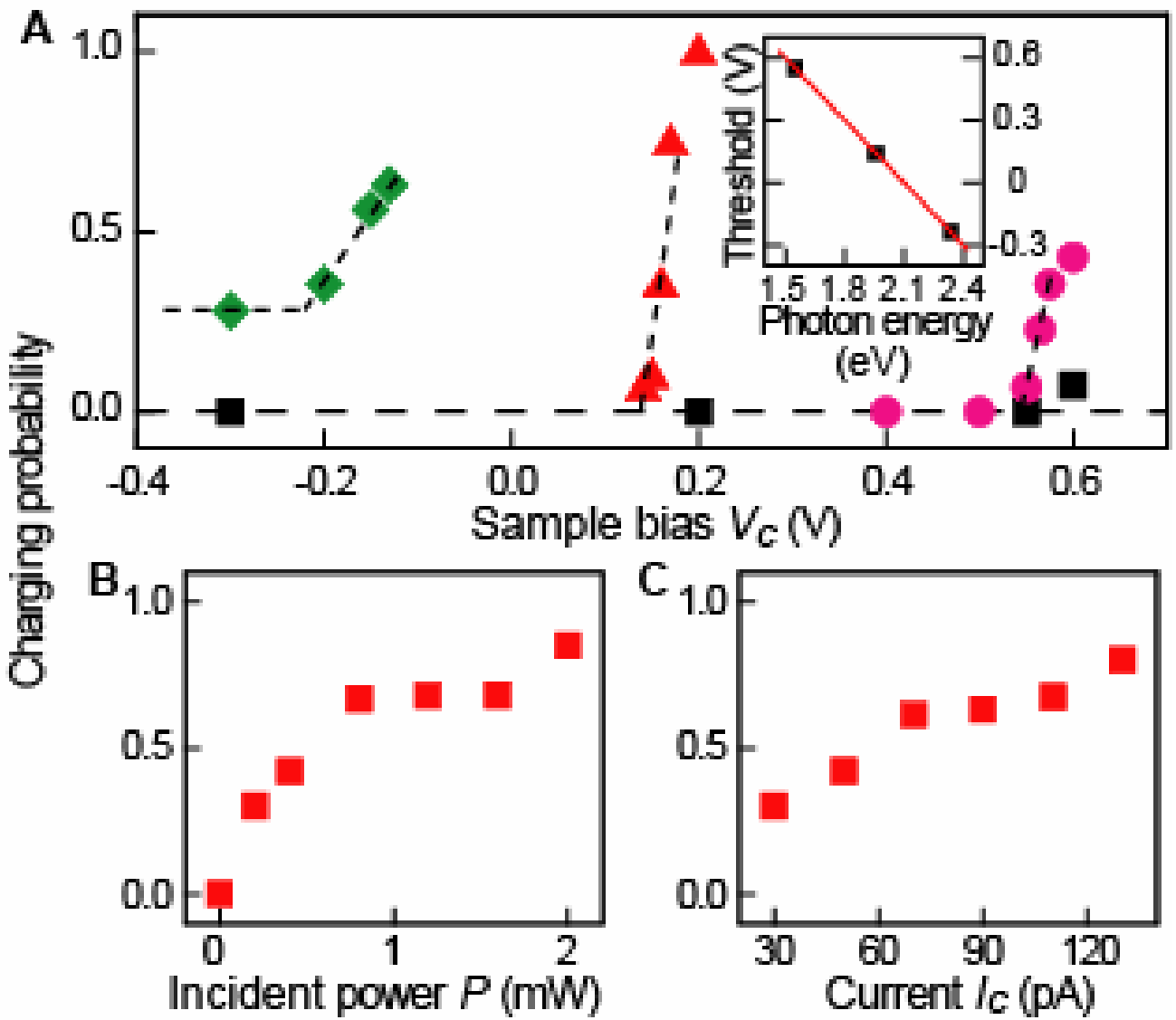
Single Molecule Electron Transfer



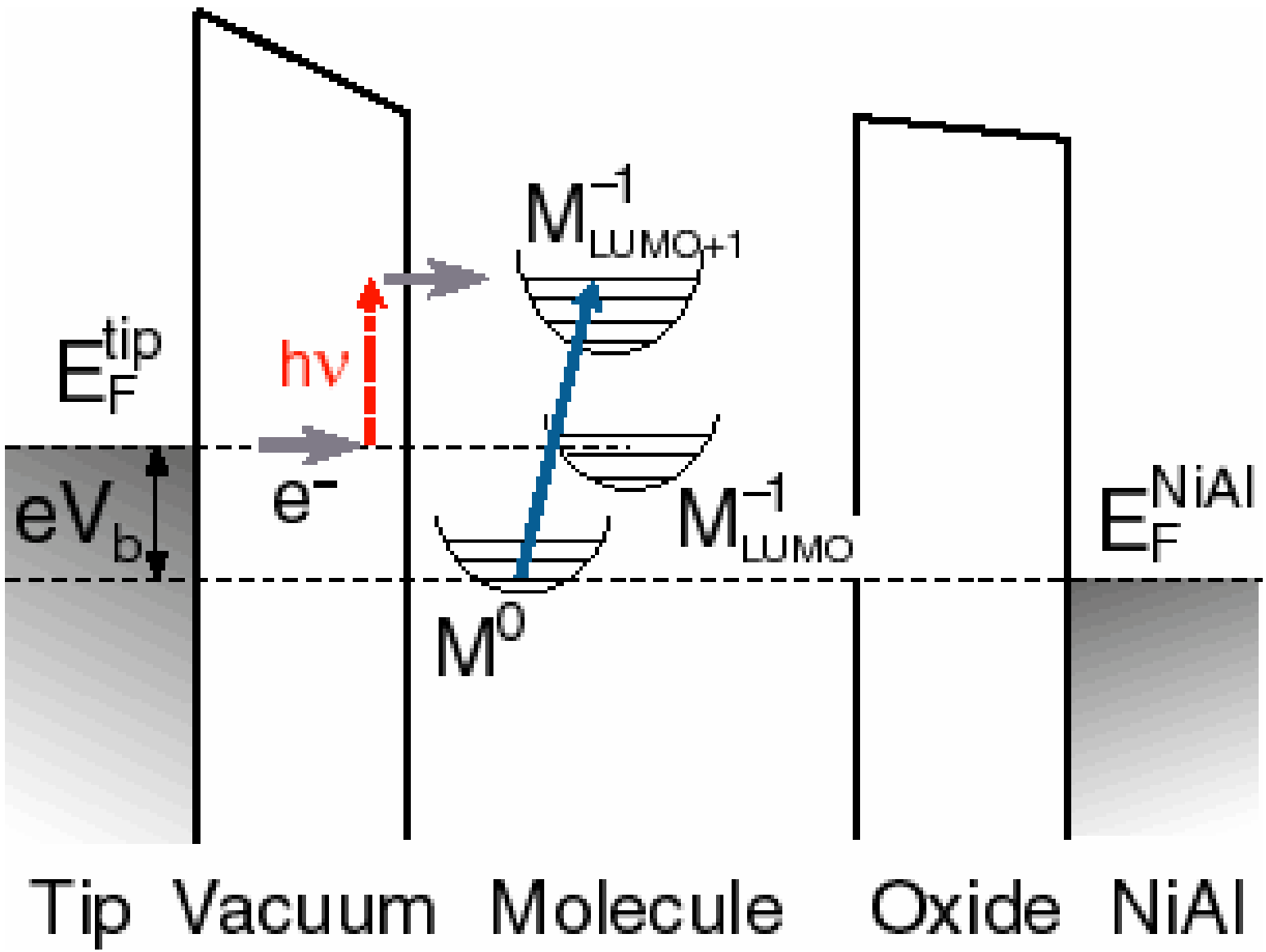
Mechanism of Photon-Induced Electron Transfer to a Single Molecule



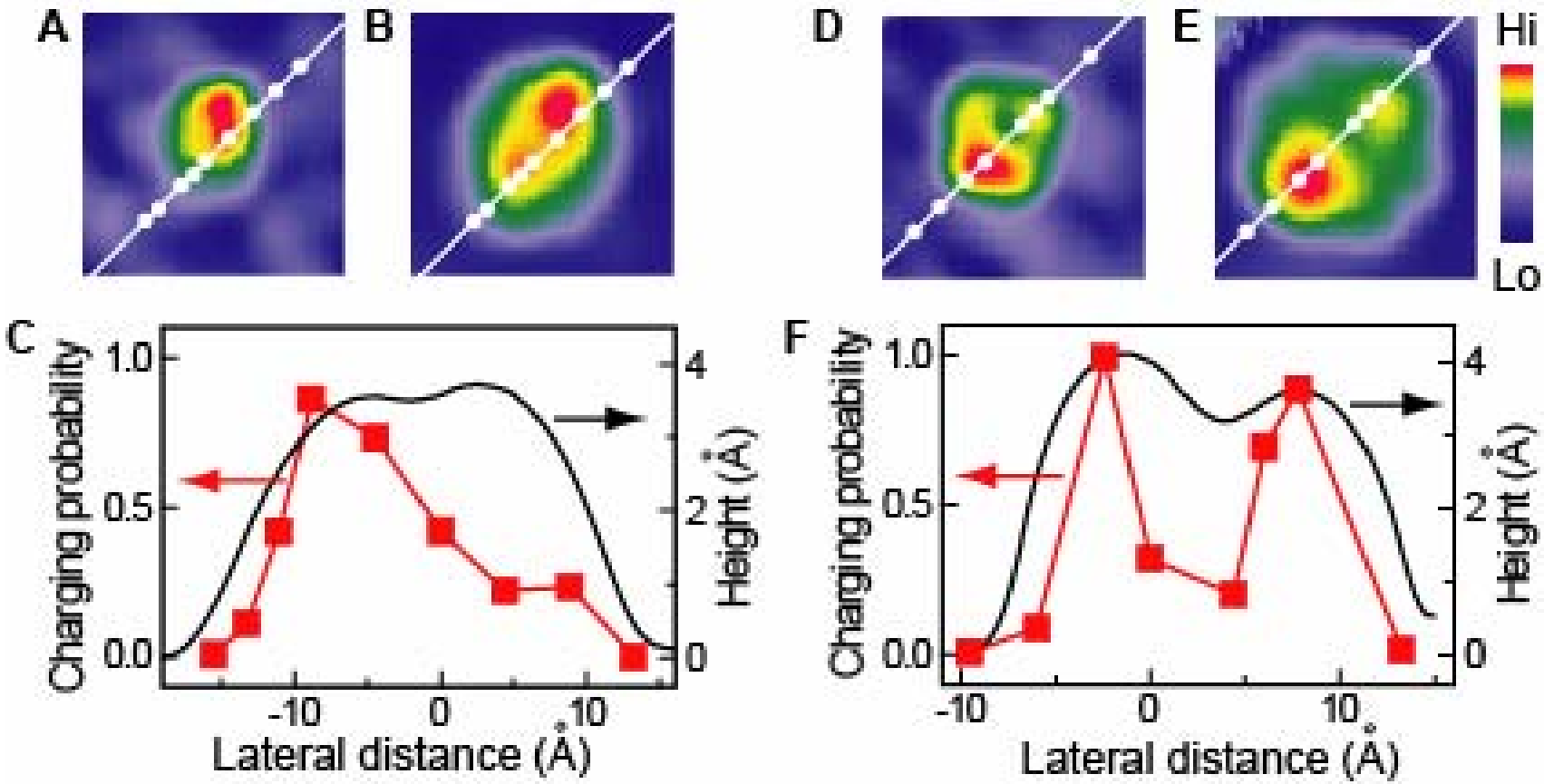
Photon-Induced Electron Transfer Threshold



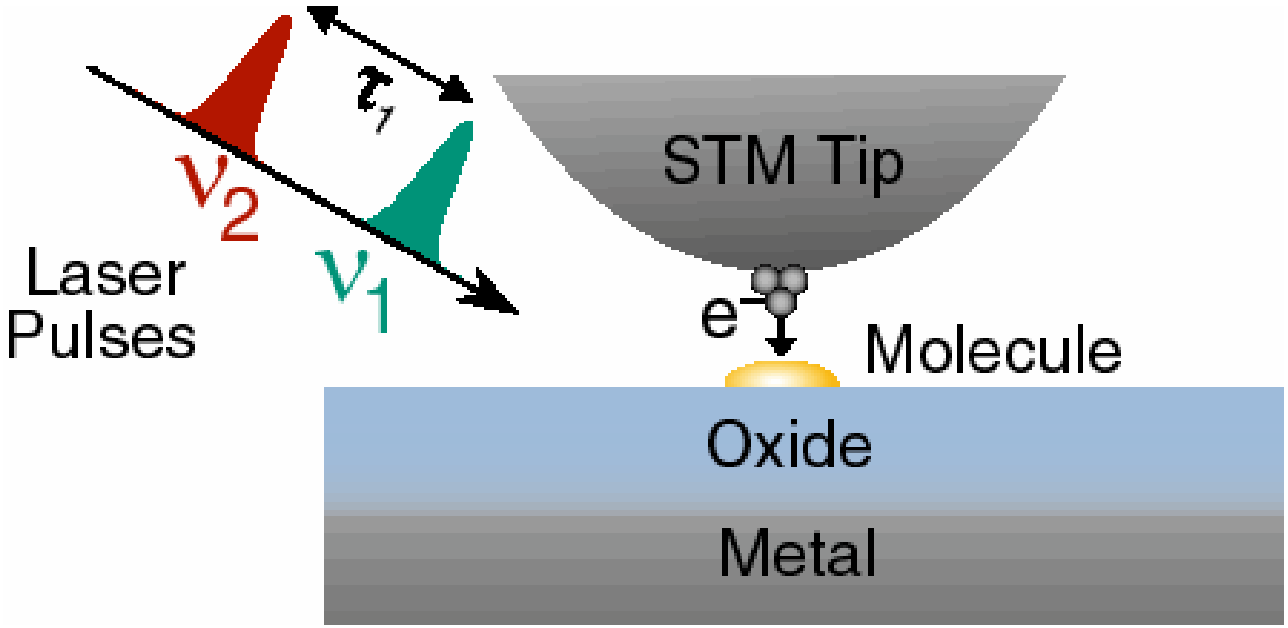
Photon Induced Tunneling



Spatial Variations of Electron Transfer within a Single Molecule



Ultrafast Optical Spectroscopy with Spatial Resolution of the STM



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

Acknowledgment

Past

Xi Chen
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Nilay Pradhan
Xiaohui Qiu
Mohammad Rezaei
Christophe Silien
Barry Stipe
Mitch Wallis

Nicolas Lorente

Present

Chi Chen
Ungdon Ham
Kiyeo Kim
Markus Lackinger
Gary Mikaelian
George Nazin
Freddy Toledo
Xiuwen Tu
Shiwei Wu

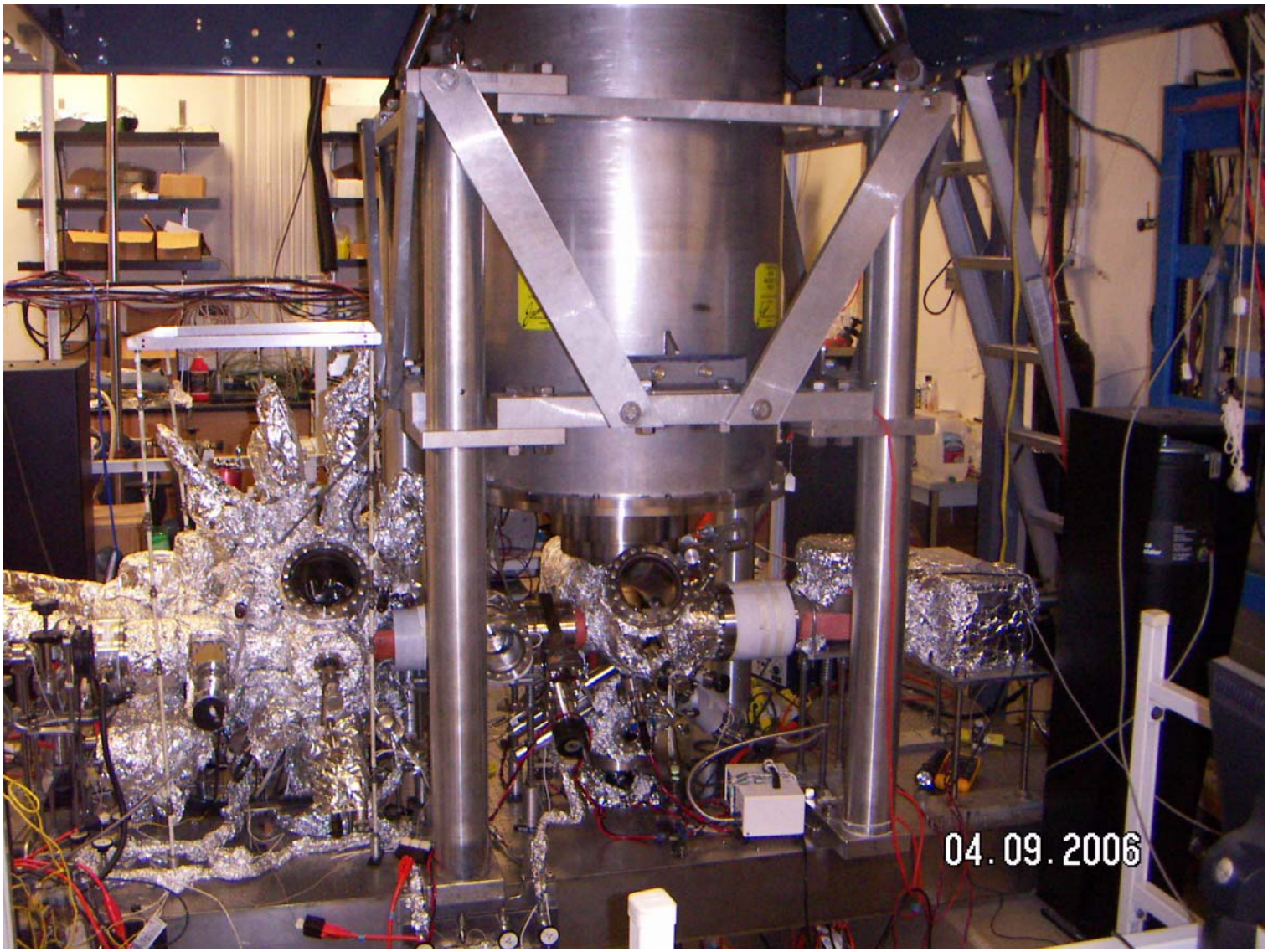
Shiwu Gao
Mats Persson

Prospects

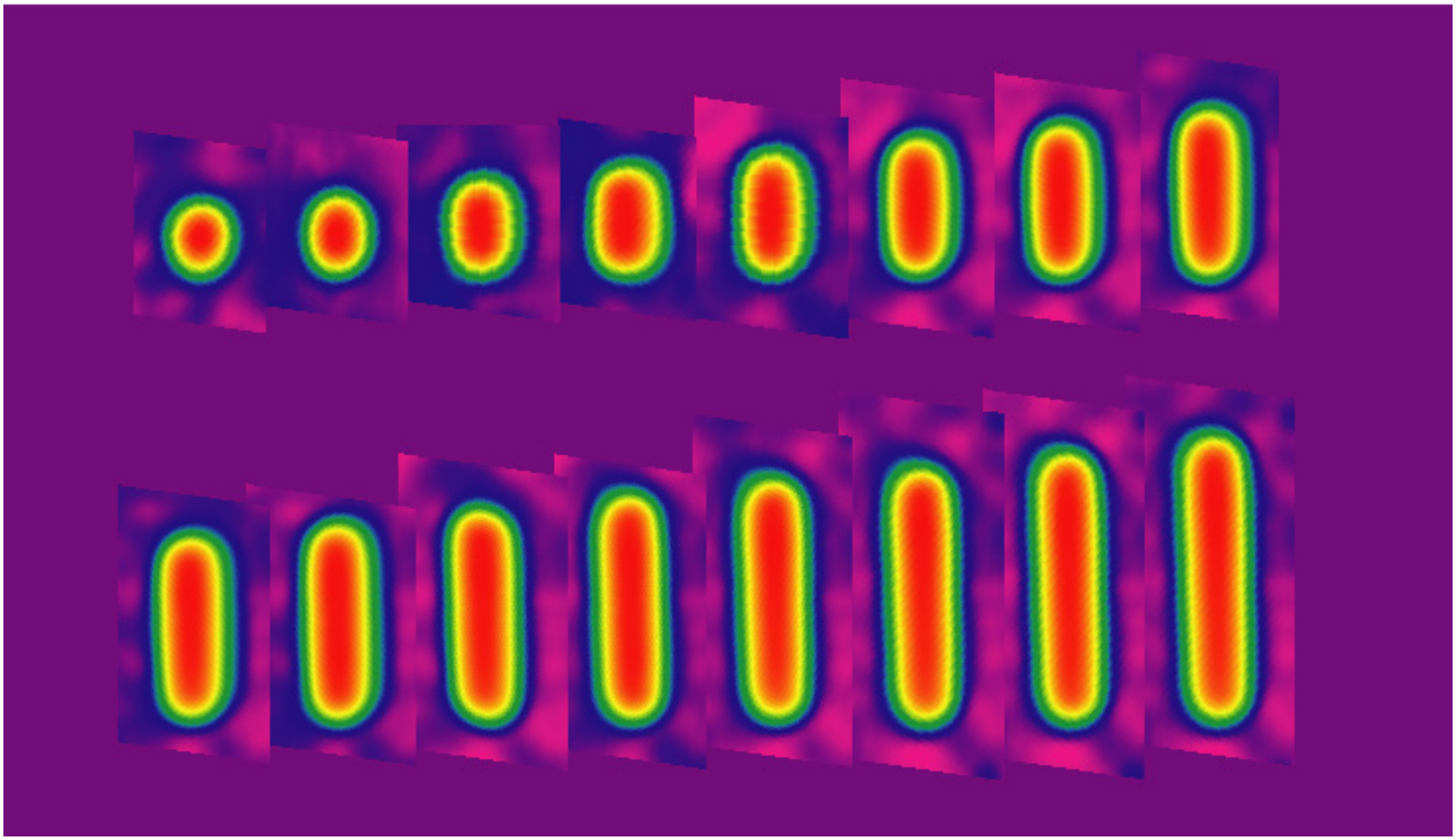
Instrumentation Development

- **Electron Spin**
  - **microwave-RF excitation**
  - **T ≈ sub-K, B ≈ 10 Tesla Zeeman spectroscopy**
  - **spin interactions: Kondo, nanomagnetism**
- **Laser-STM**
  - **simultaneous spatial + temporal limits 1 Å – 10 fs**
  - **sub-molecular photochemistry, non-linear optics**
- **Non-Vacuum Environment**
  - **biological systems**

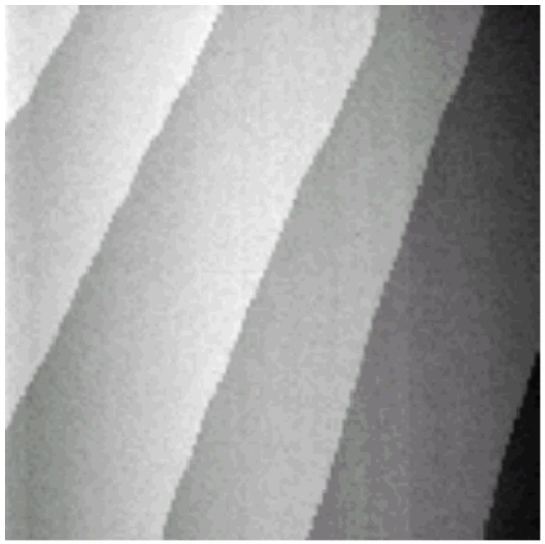
< 1 K, 9 Tesla UHV STM



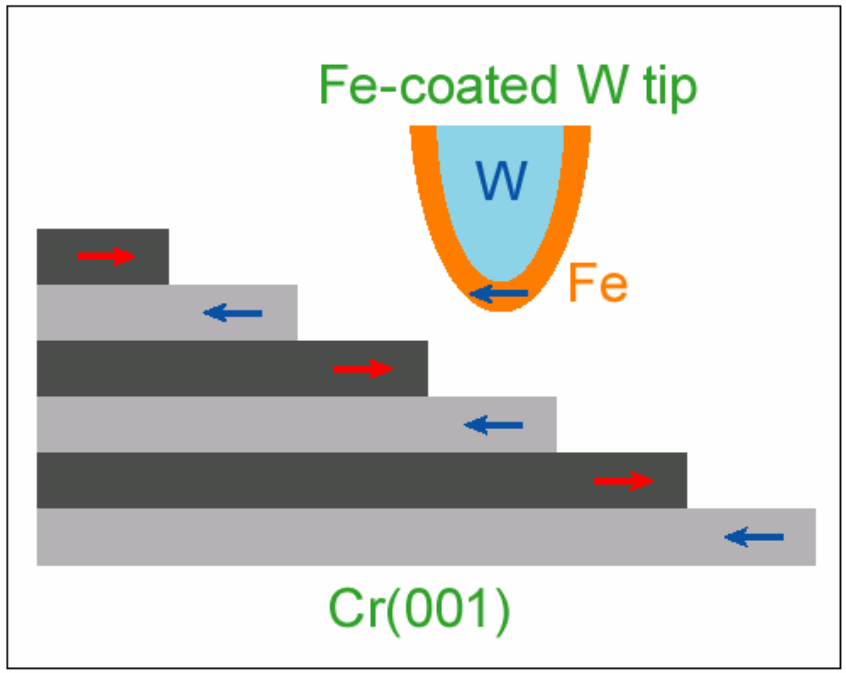
Mn Chains: 1 to 16 Atoms

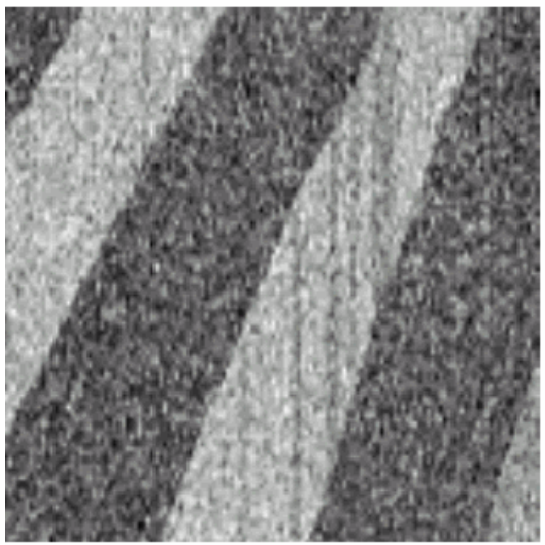


Spin-Dependent Tunneling



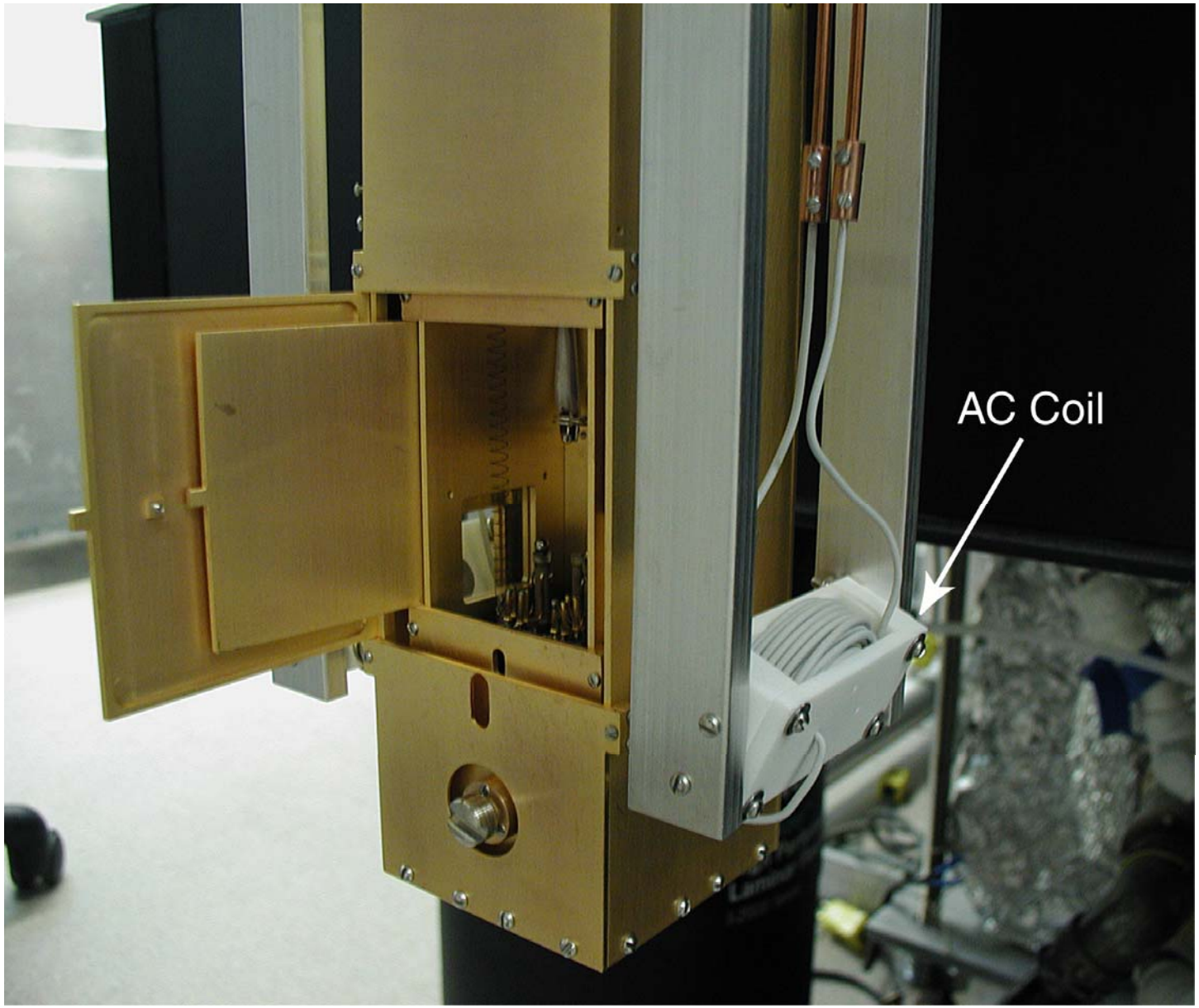
Topography

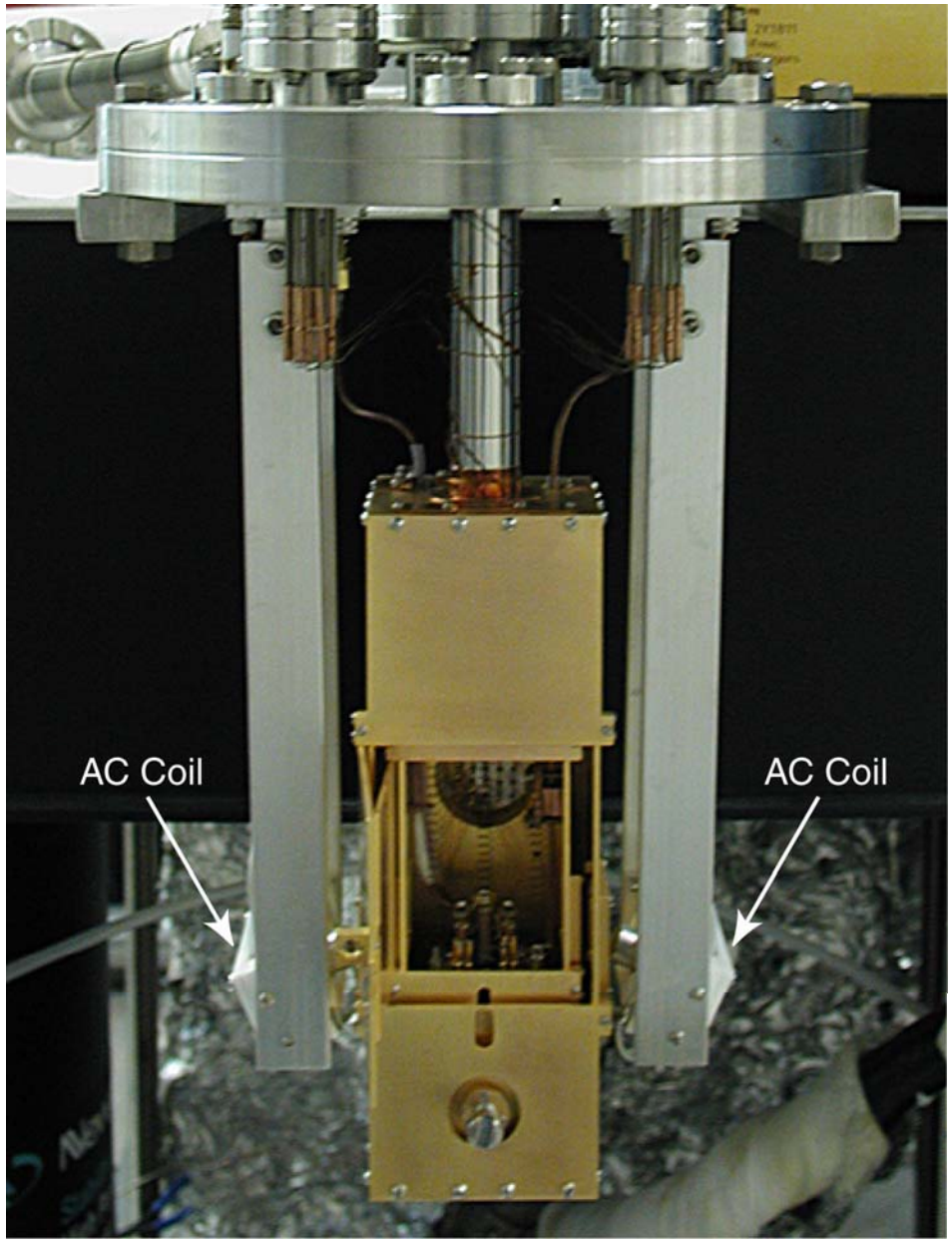


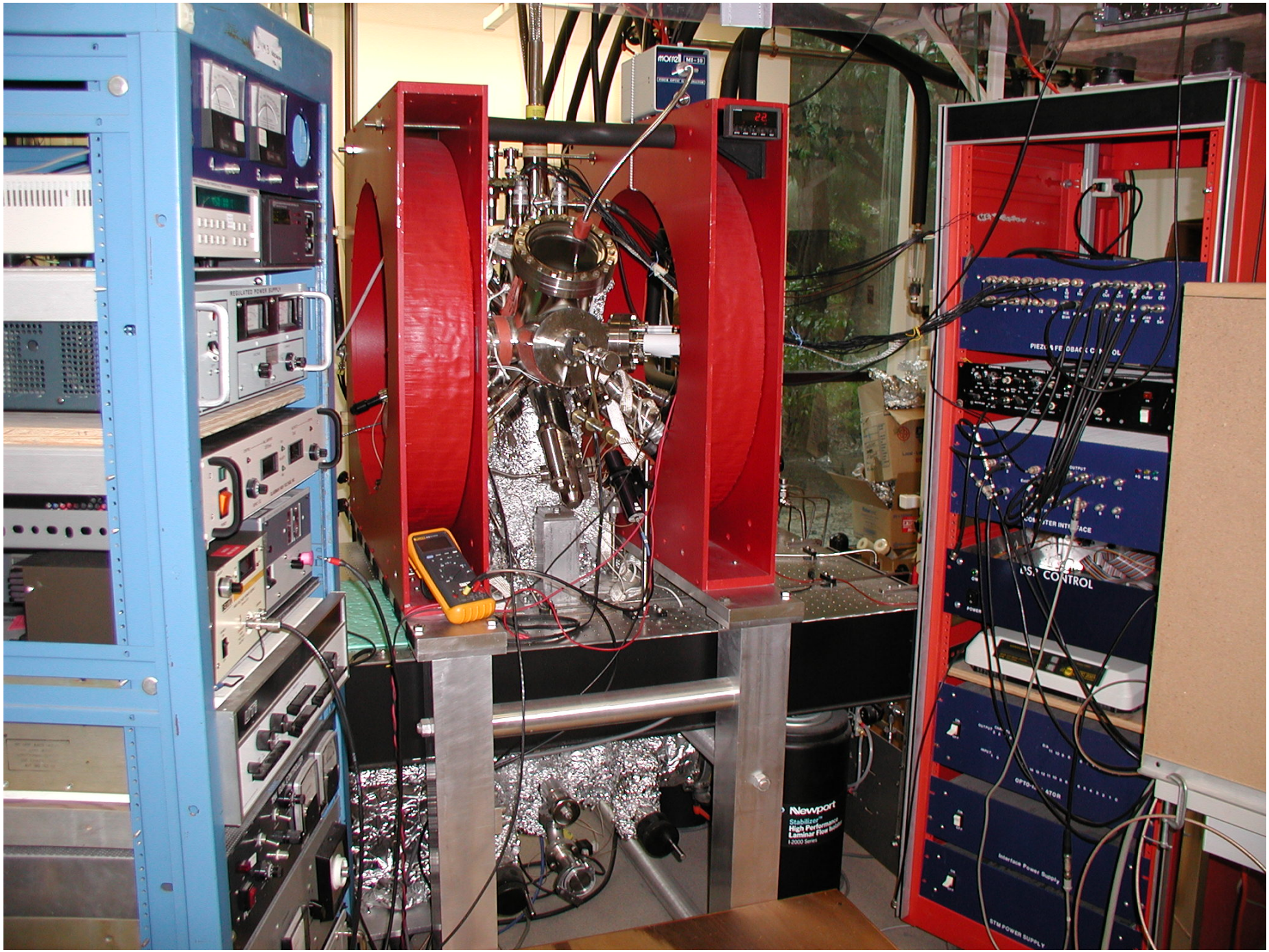


dI/dV microscopy

400 nm x 400 nm


AC Coil


AC Coil
AC Coil


Newport
Stabilizer
High Performance
Laminar Flow Isolator
I-2000 Series
Interface Power Supply
STM POWER SUPPLY

Acknowledgment

Past

Jennifer Gaudioso
Jae Ryang Hahn
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Joonhee Lee
Ning Liu
Niklas Nilius
Nilay Pradhan
Xiaohui Qiu
Mohammad Rezaei
Christophe Silien
Barry Stipe
Mitch Wallis

Nicolas Lorente

Present

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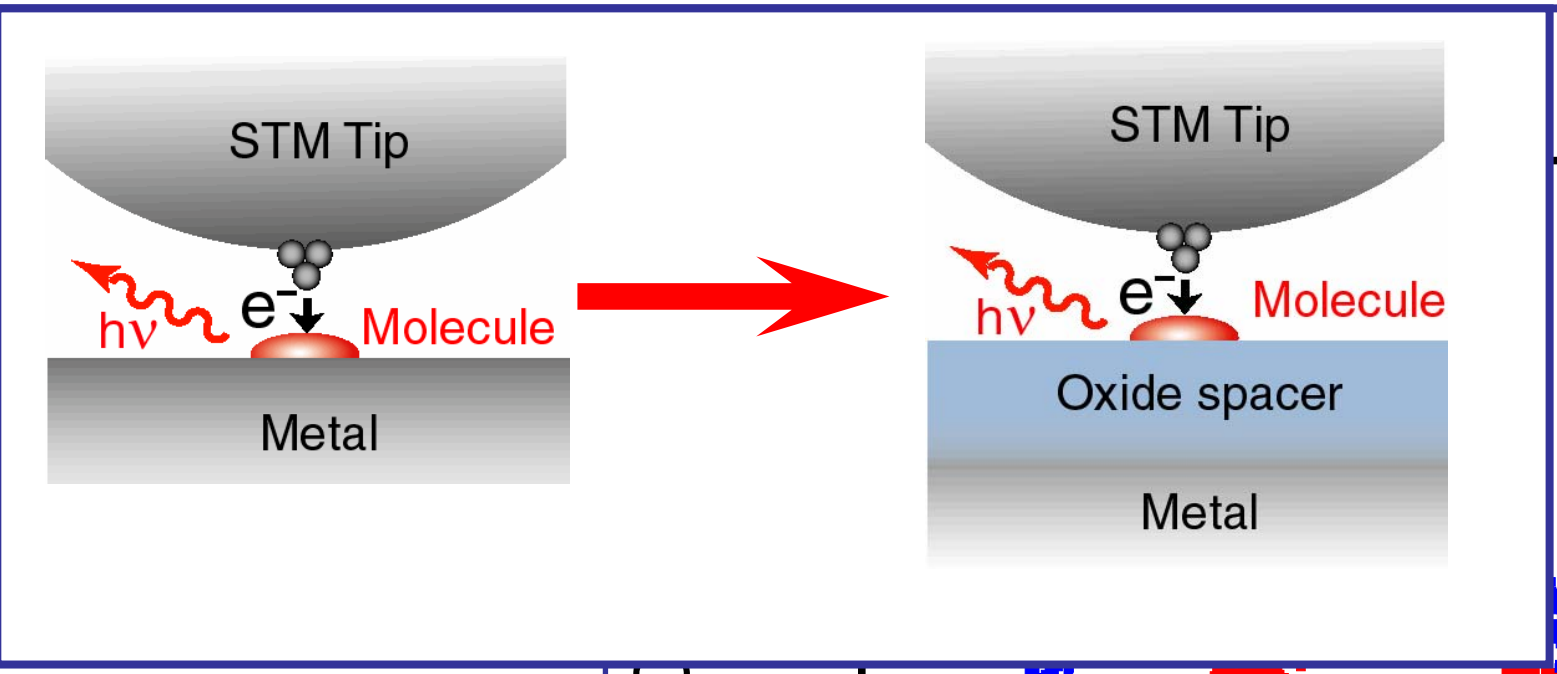
Xi Chen
Ungdon Ham
Martin Janson
John Karnes
Kiyeo Kim
Markus Lackinger
Gary Mikaelian
George Nazin
Naoki Ogawa
Xiuwen Tu
Shiwei Wu

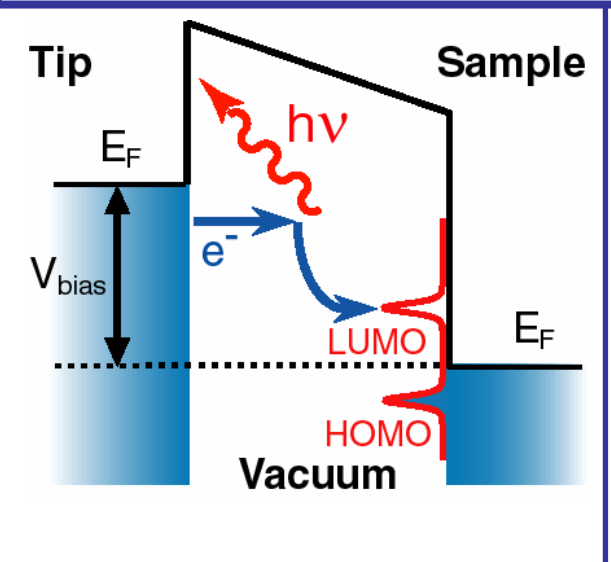
Shiwu Gao
Mats Persson

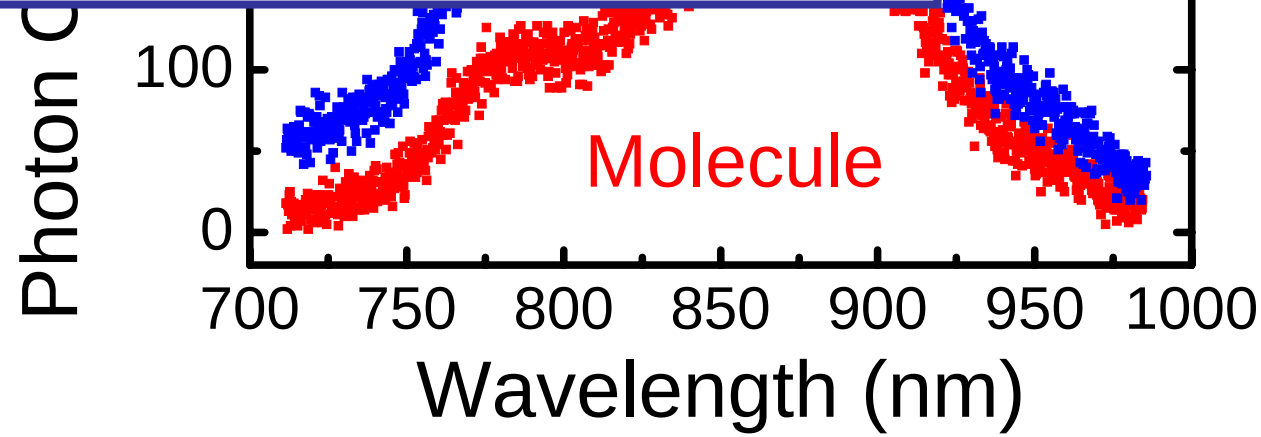
Atomic Scale Photochemistry

Wilson Ho
University of California, Irvine

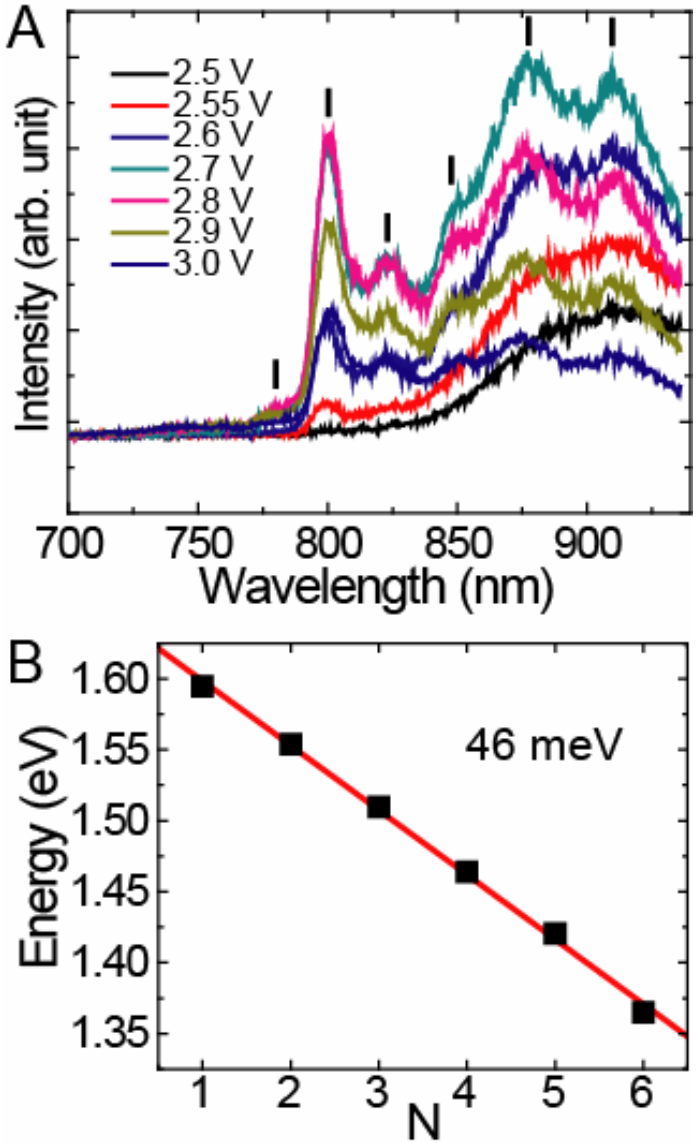
Photon Emission from molecules on metal surfaces



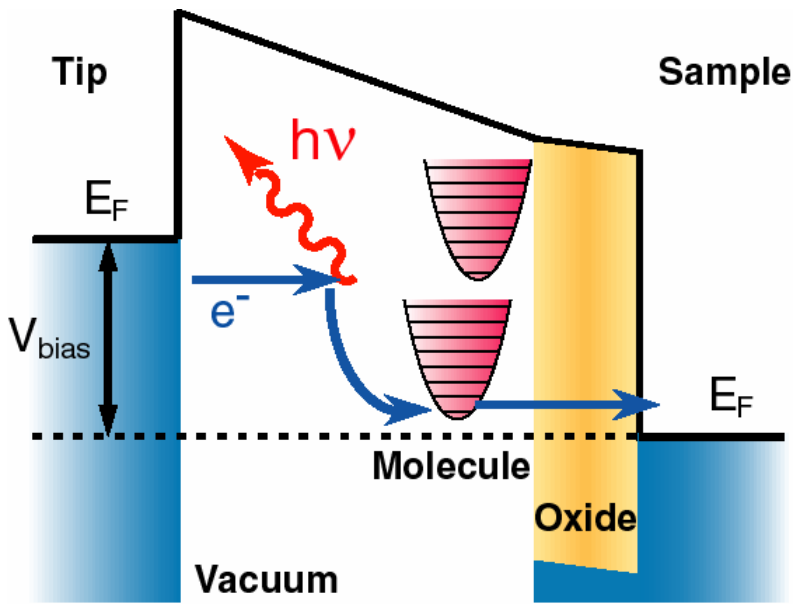




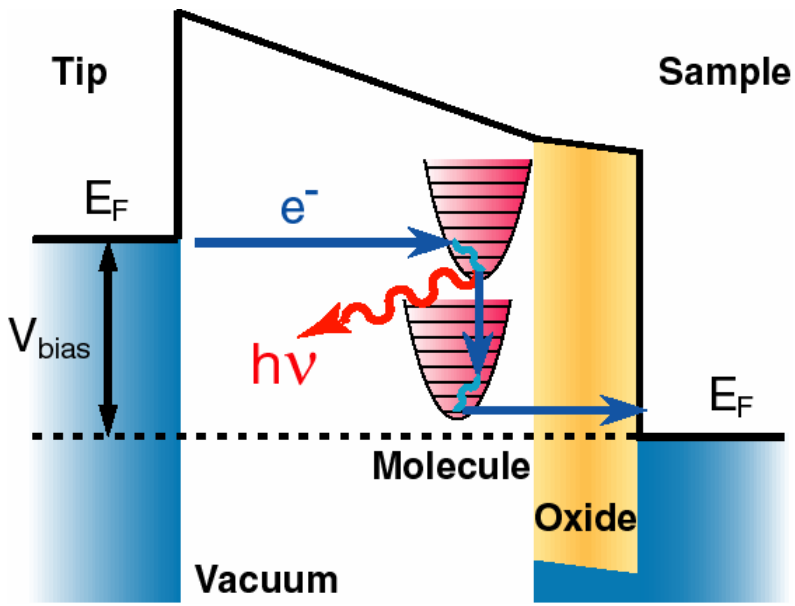
Tunneling Electron Induced Single Molecule Fluorescence



IET vs. Single Molecule Fluorescence:

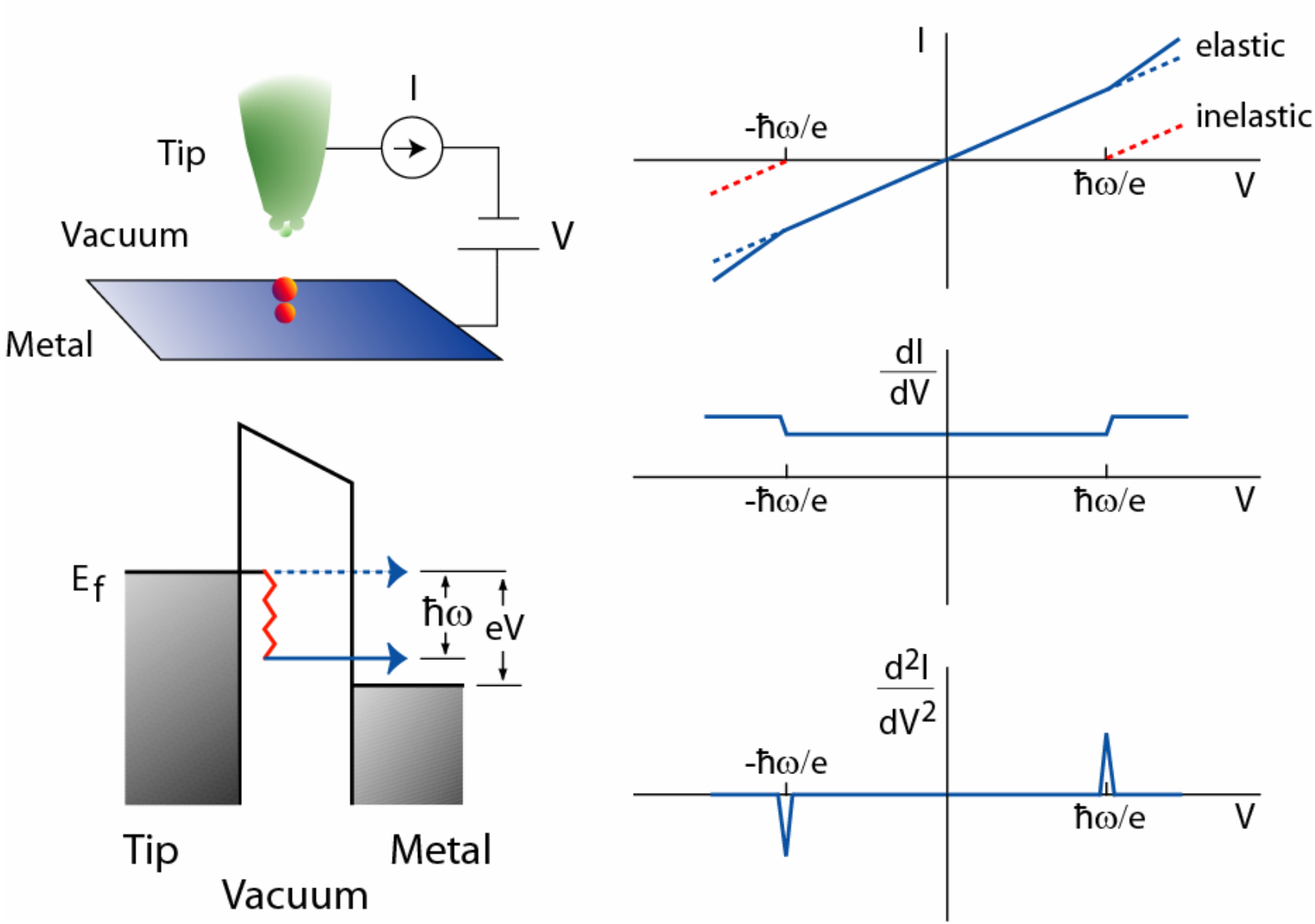


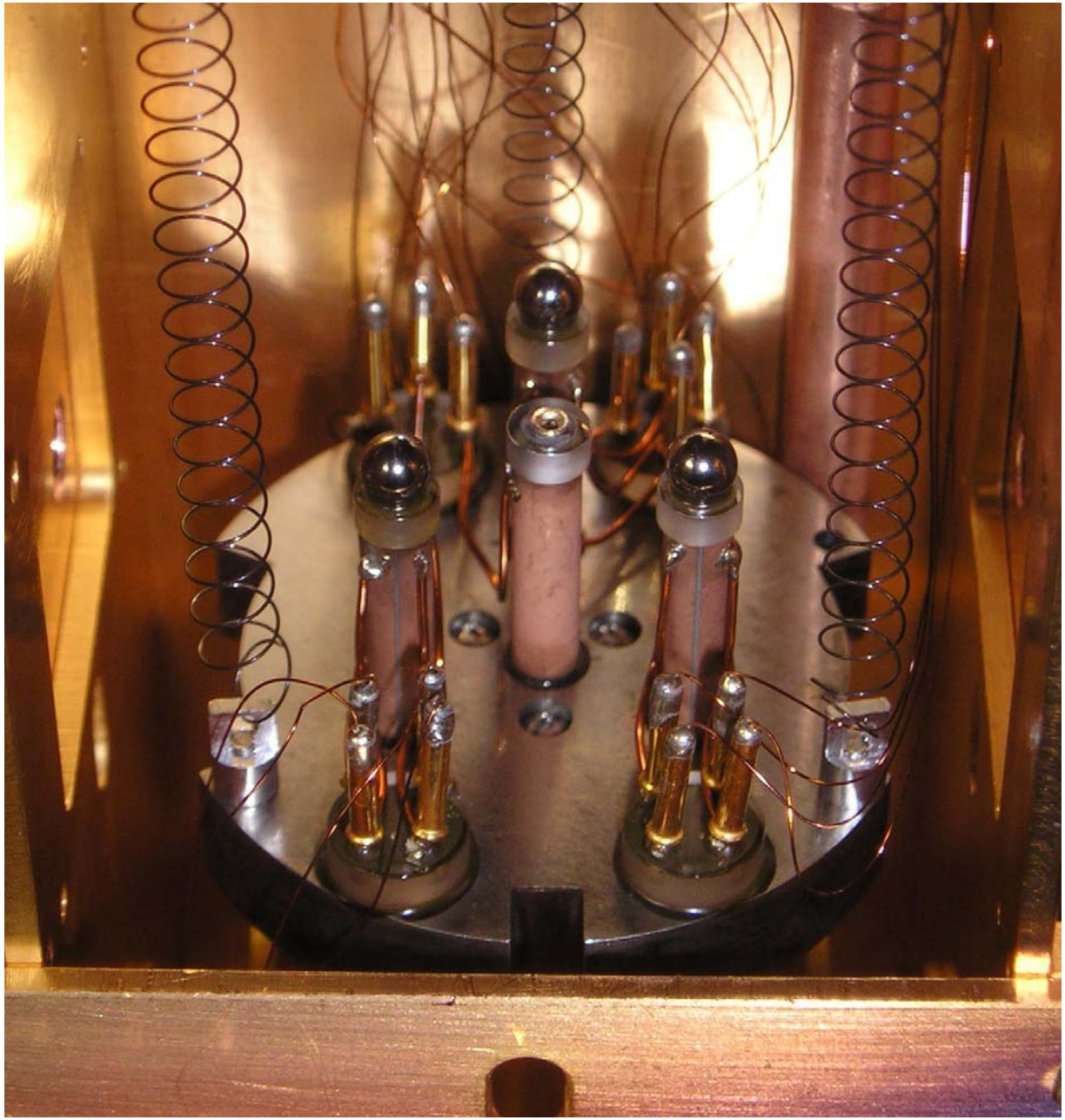
Inelastic Electron Tunneling



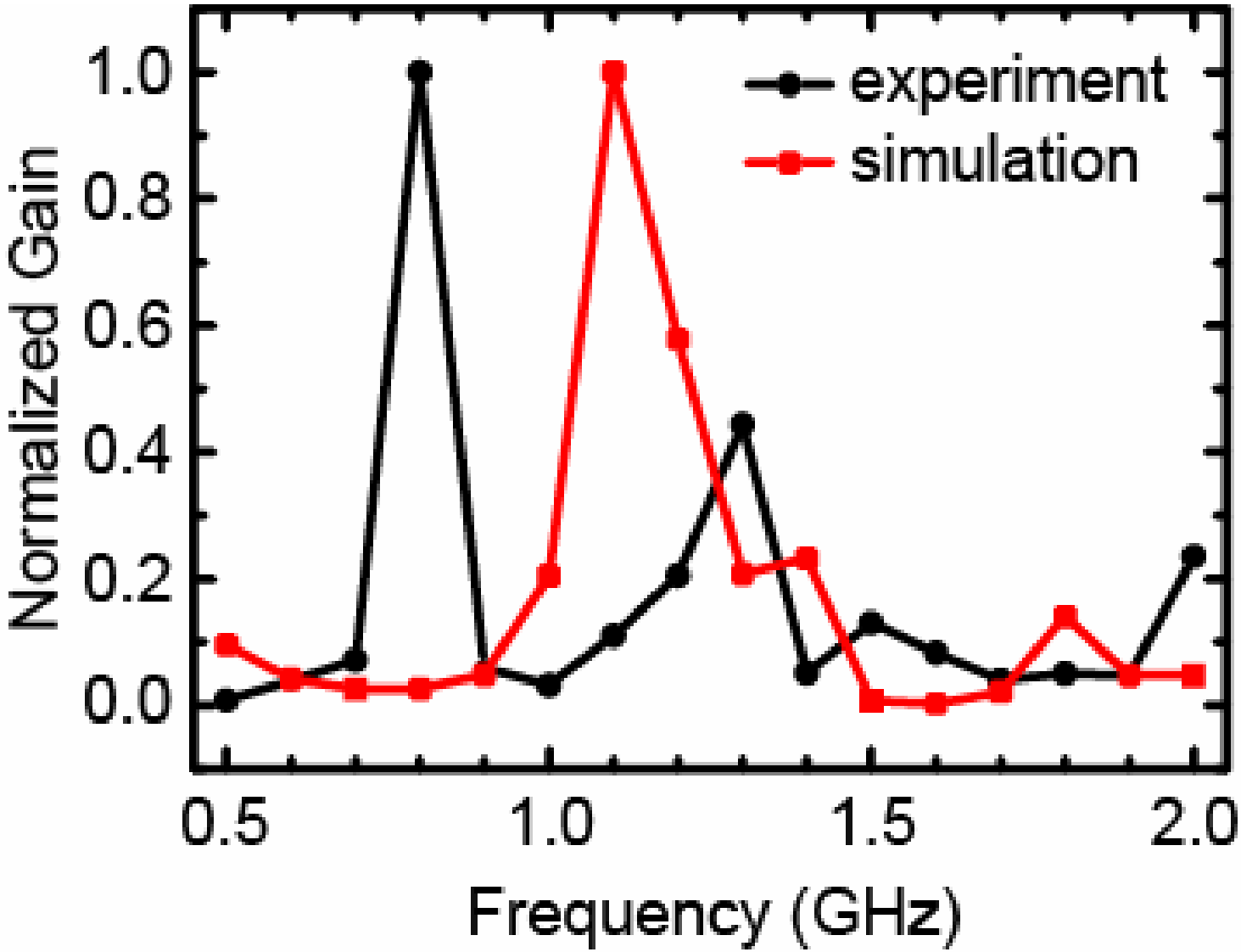
Fluorescence

Inelastic Electron Tunneling Spectroscopy (STM-IETS)

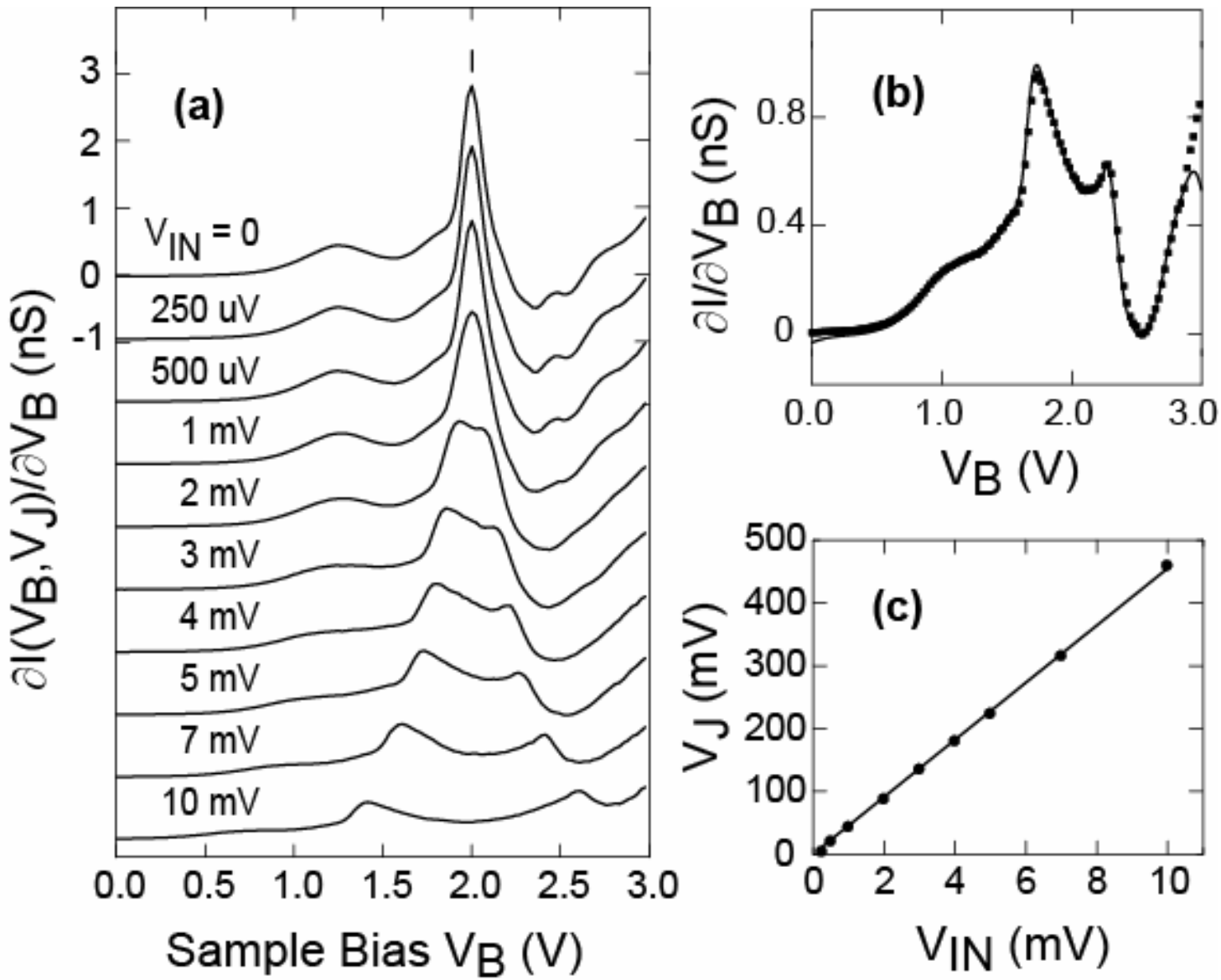




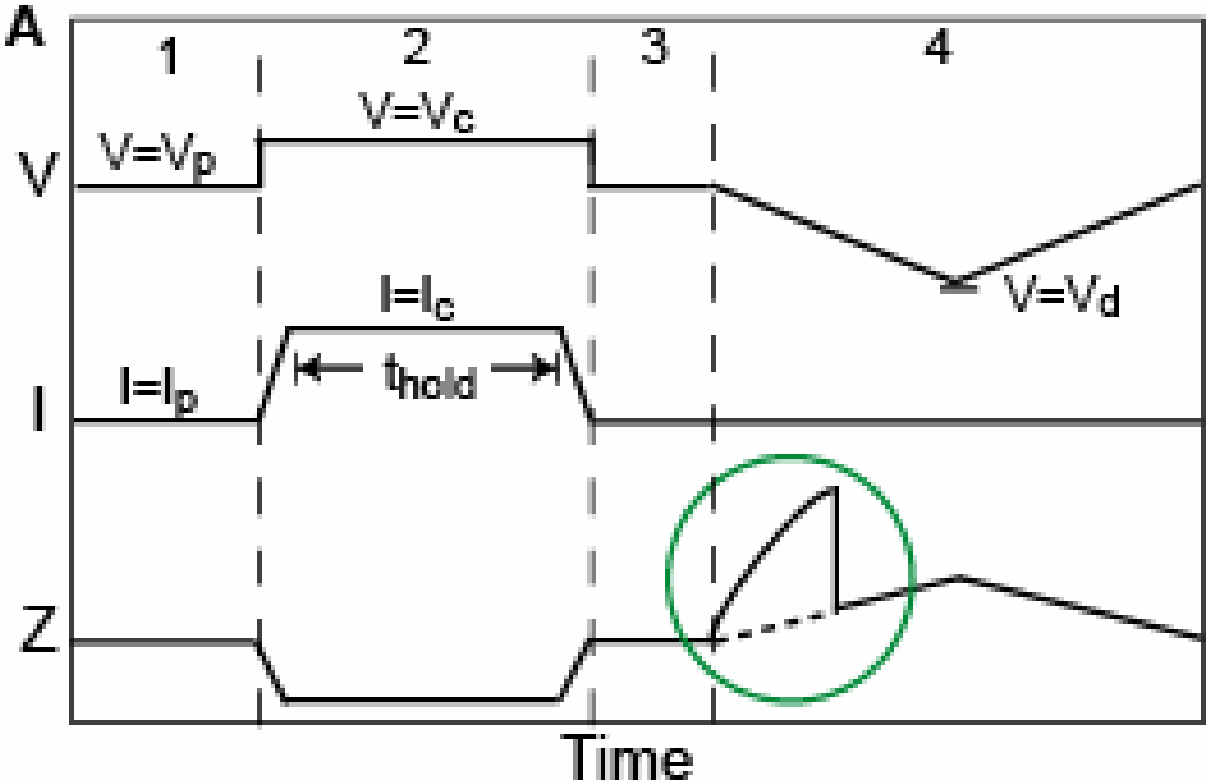
Frequency Dependence of RF Voltage Across Junction

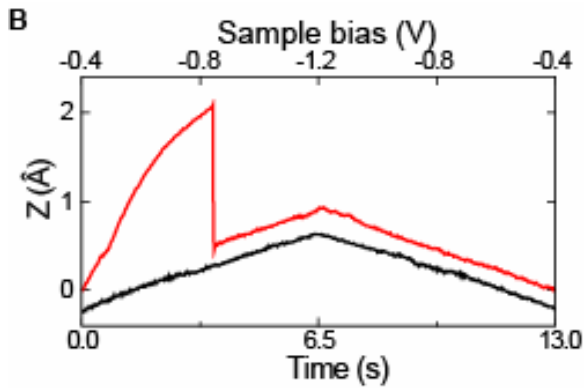


RF Voltage Across STM Junction: V_J

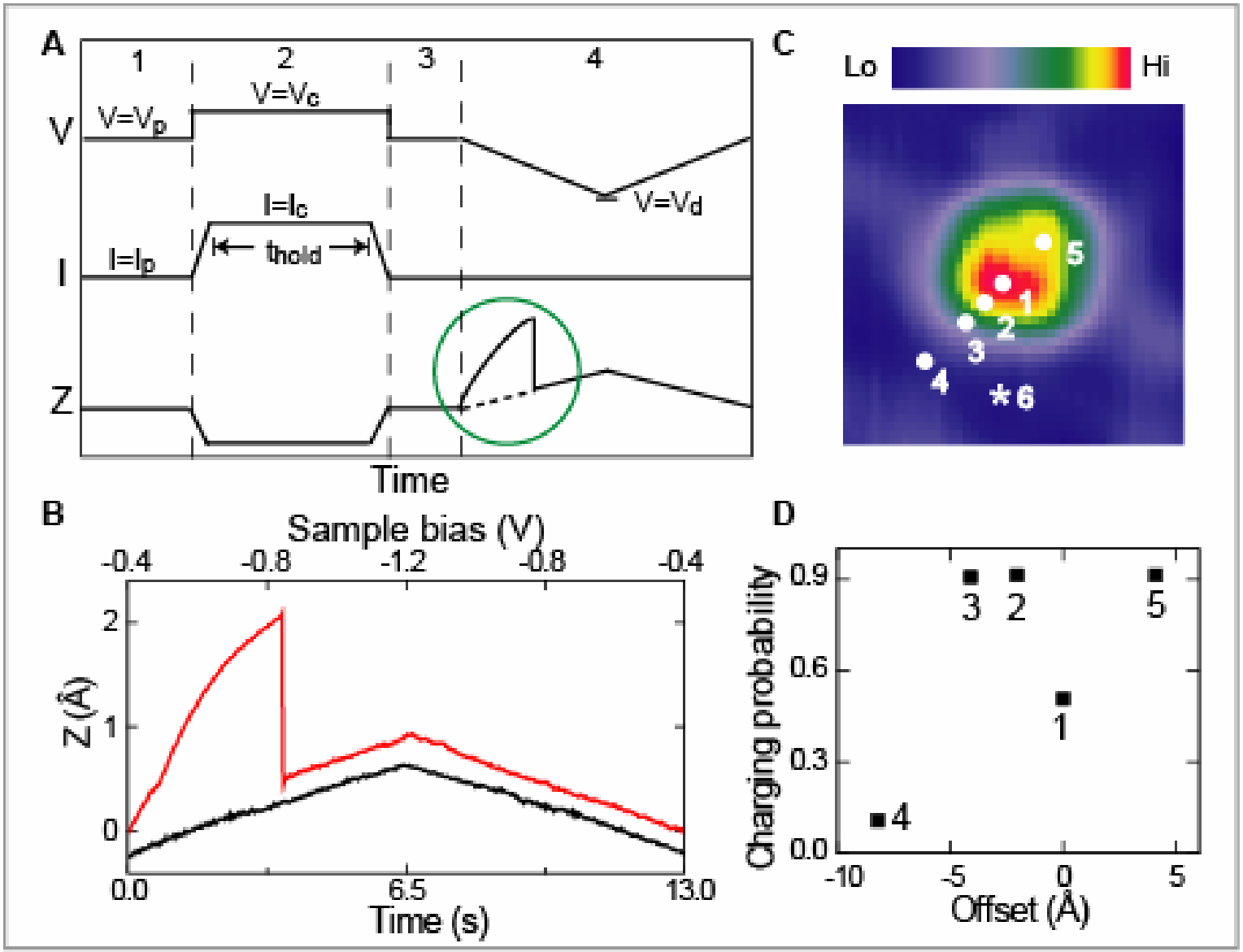


Monitoring Photon-Induced Electron Transfer in a Single Molecule



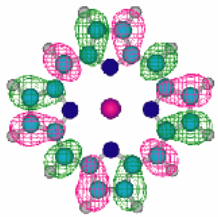


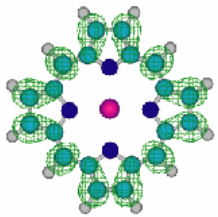
Single Molecule Photon Induced Electron Transfer with Sub-Molecular Spatial Resolution



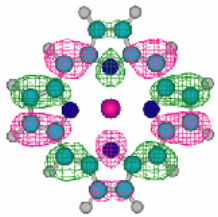
Mg-Porphine Orbitals

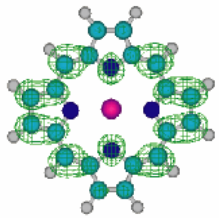
LUMO+2
-1.46 eV

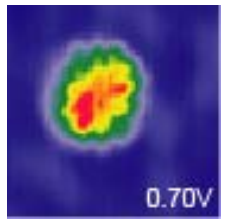




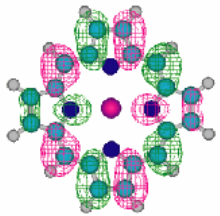
LUMO+1
-2.84 eV

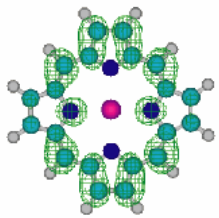


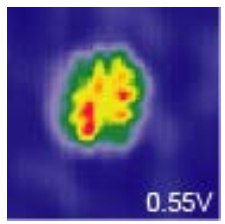


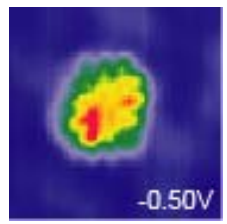


LUMO
-2.84 eV

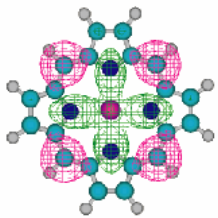


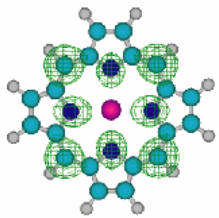




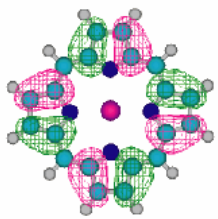


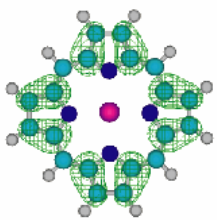
HOMO
-4.84 eV



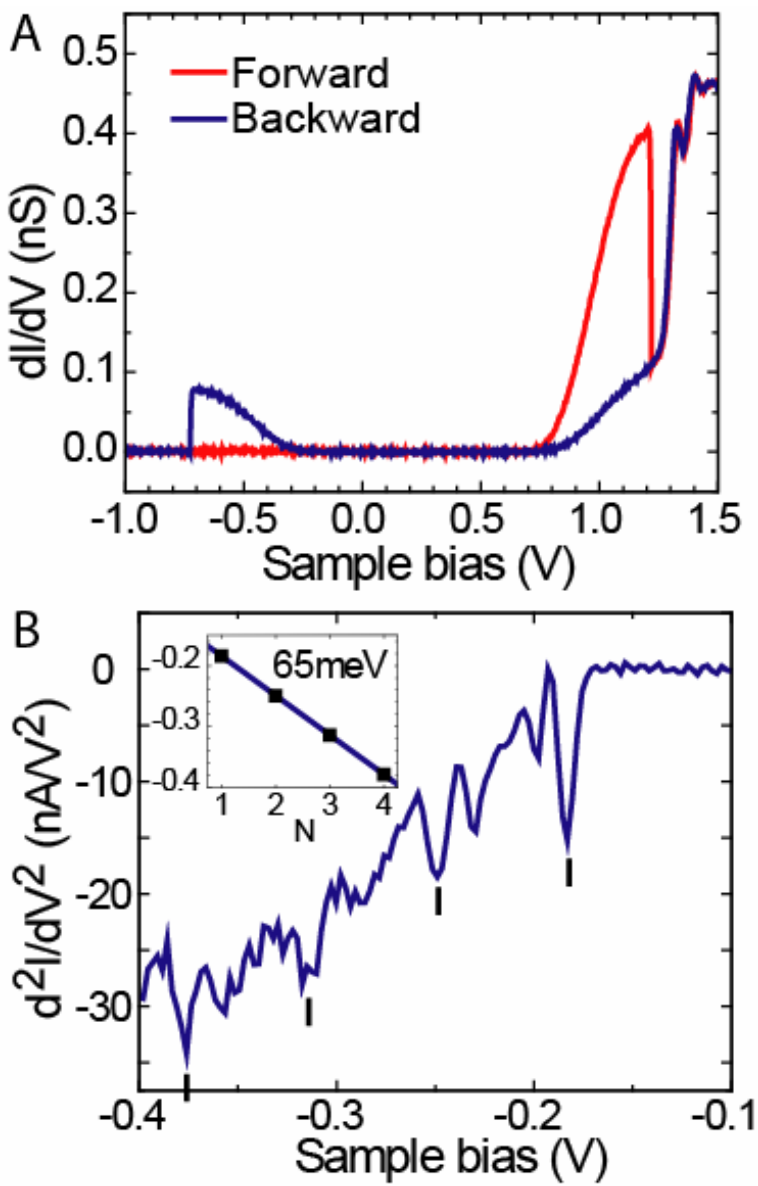


HOMO-1
-5.52 eV

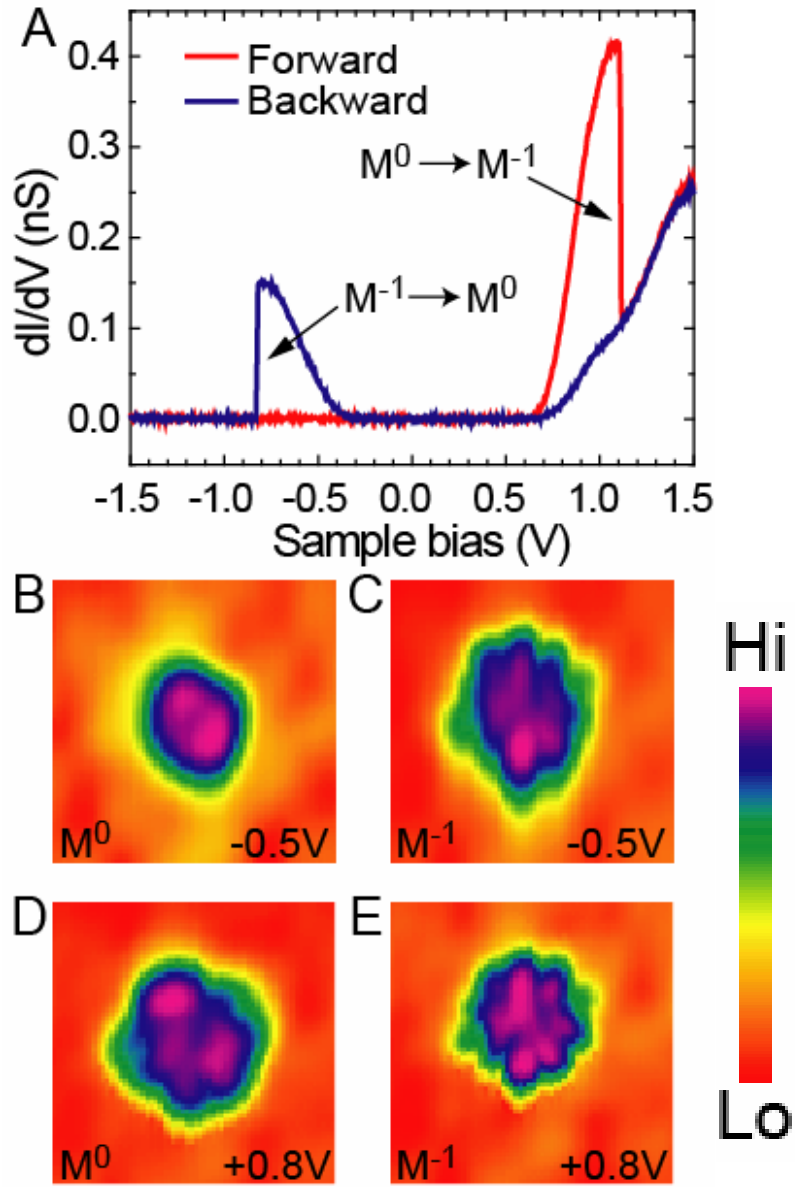




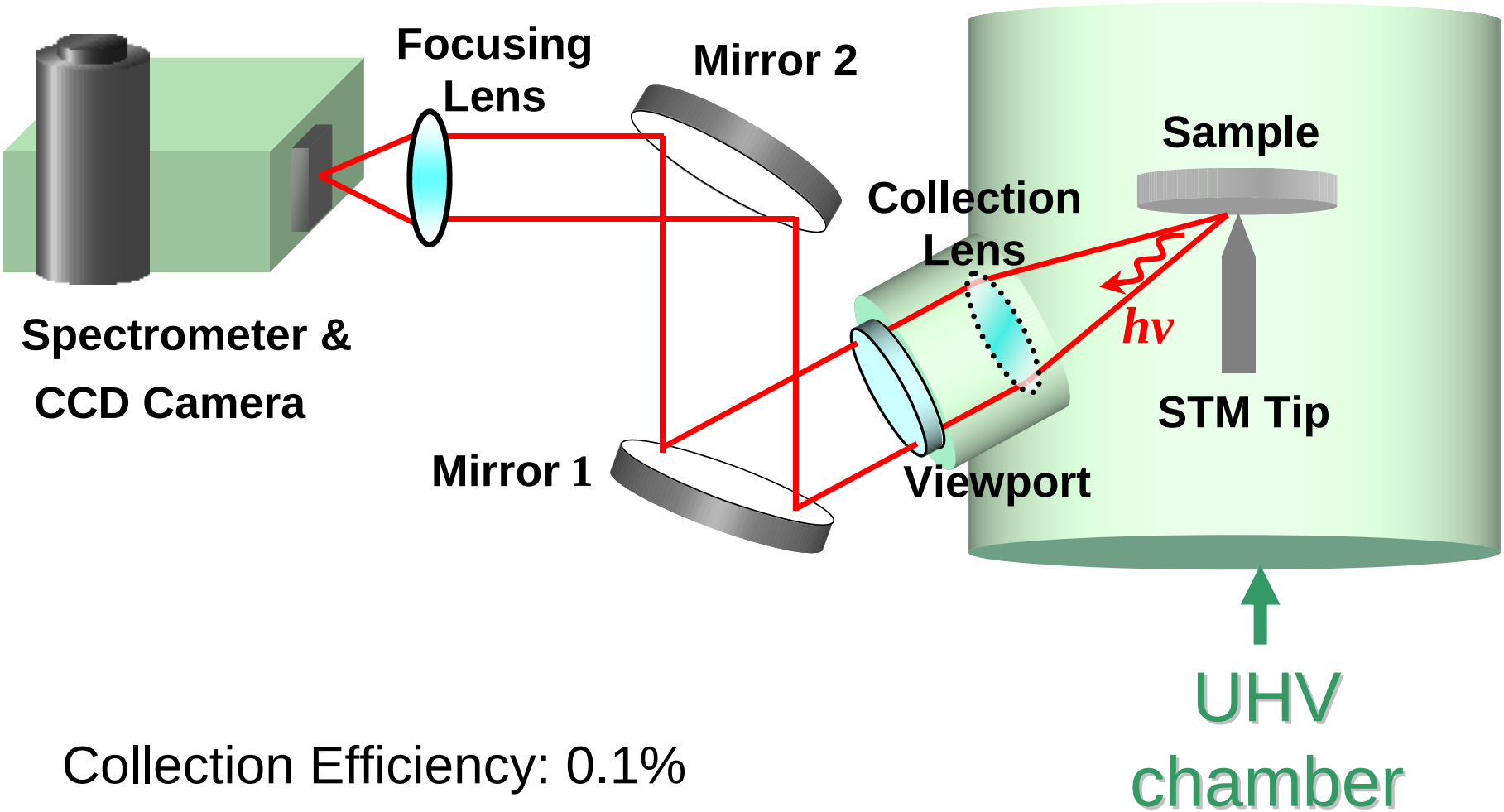
Single Molecule Vibronic States: MgP



Neutral and Charged States: MgP

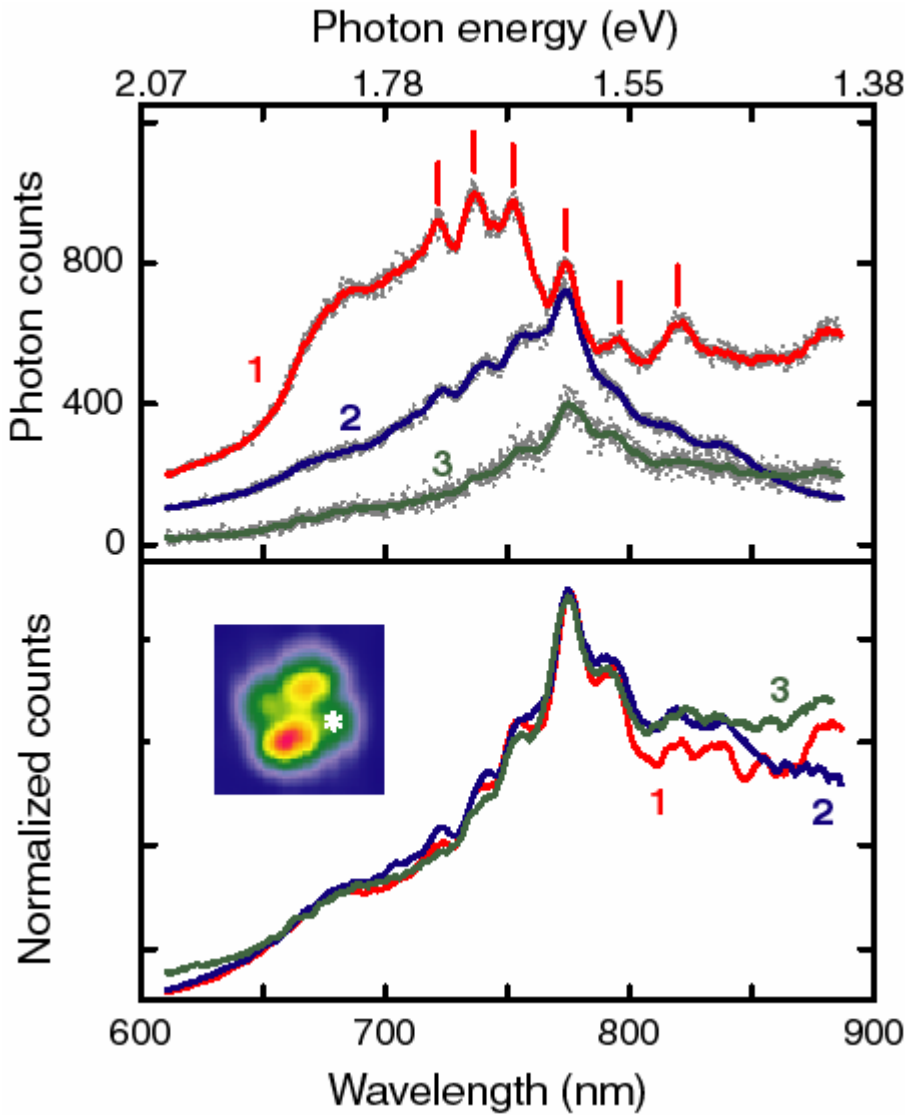


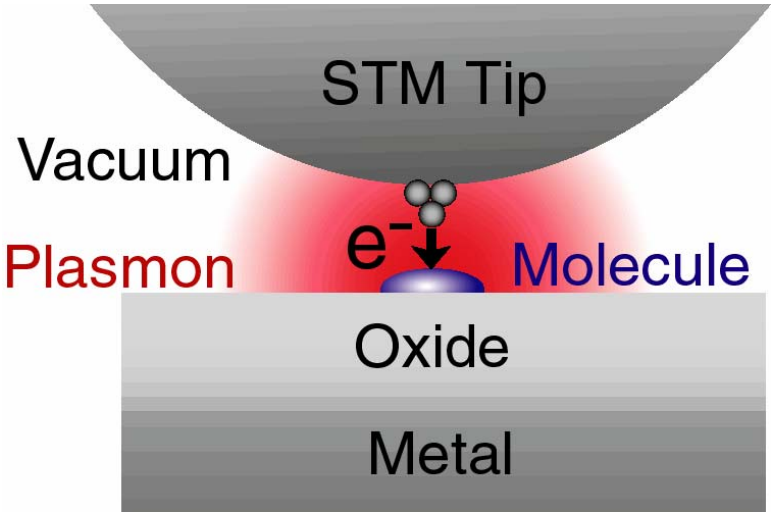
Experimental Setup



Collection Efficiency: 0.1%

Plasmon modes in the STM junction





Double Modulation Spectroscopy

Modulate RF Signal at ω_c

$$f(t) = \frac{4}{\pi} \sum_{n=1,3,5...}^{\infty} \frac{1}{n} \sin(n\omega_C t)$$ (Square Wave –1 to +1 at ω_c)

$$f(t) = \frac{2}{\pi} \sum_{n=1,3,5...}^{\infty} \frac{1}{n} \sin(n\omega_C t) + \frac{1}{2}$$ (Square Wave 0 to +1 at ω_c)

$$I(t) = I_0(V_B) + I_R \cdot \left(\frac{2}{\pi} \sum_{n=1,3,5\cdots}^{\infty} \frac{1}{n} \sin(n\omega_C t) + \frac{1}{2} \right)$$ (Modulated Current)

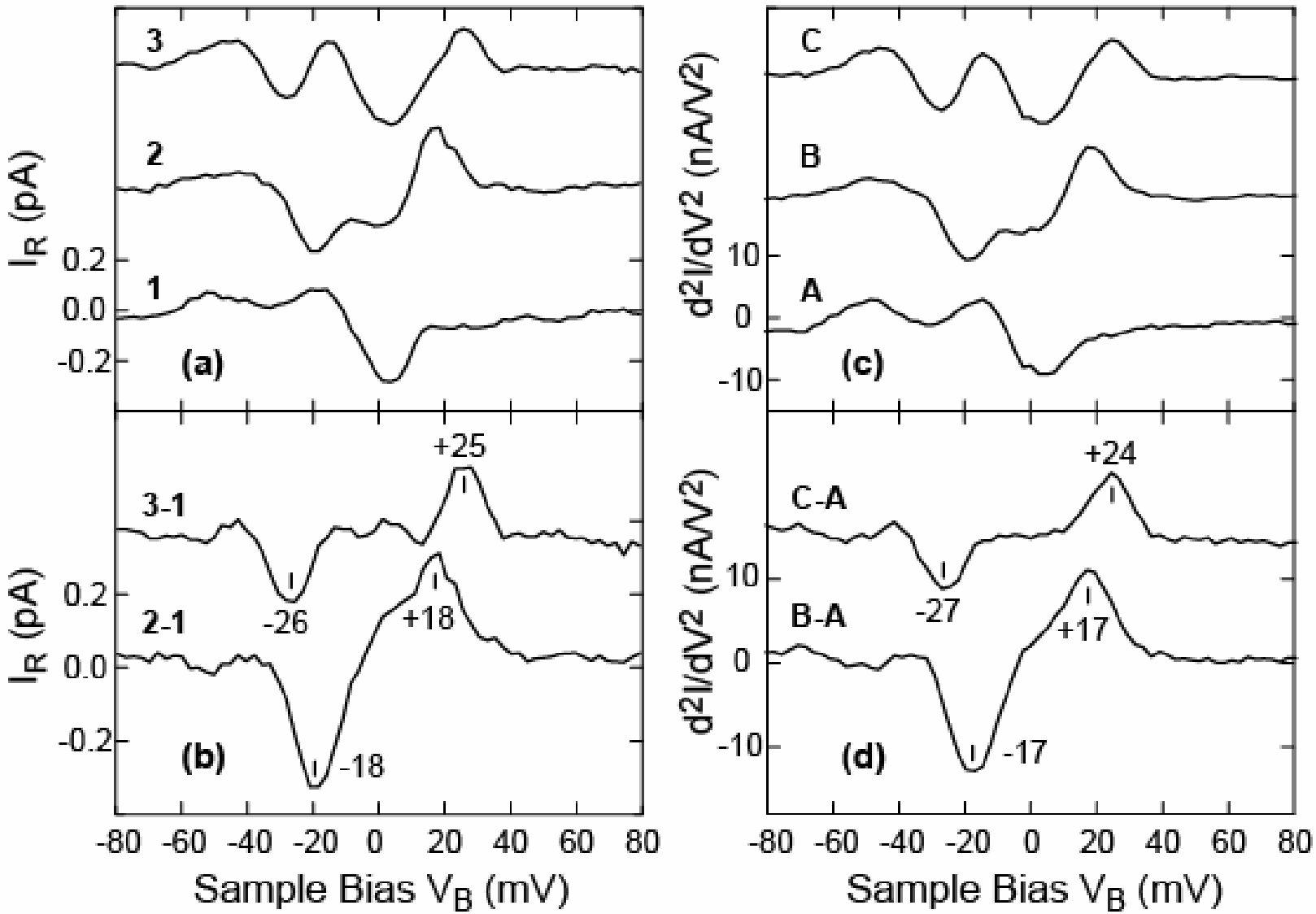
$$I_1(t) = I_R \cdot \left(\frac{2}{\pi} \sin(\omega_C t) \right)$$ (First Harmonic Signal)

$$X_1(RMS) = I_R \times \frac{2}{\pi} \times \frac{1}{\sqrt{2}}$$ (First Harmonic rms Amplitude)

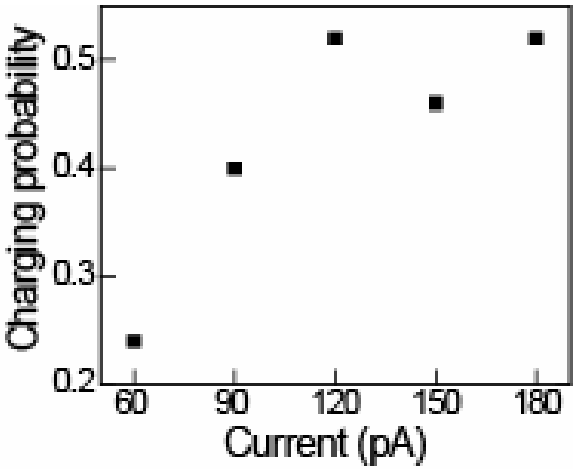
$$I_R = \frac{\pi}{\sqrt{2}} \times X_1$$ (Absolute Rectification Current)

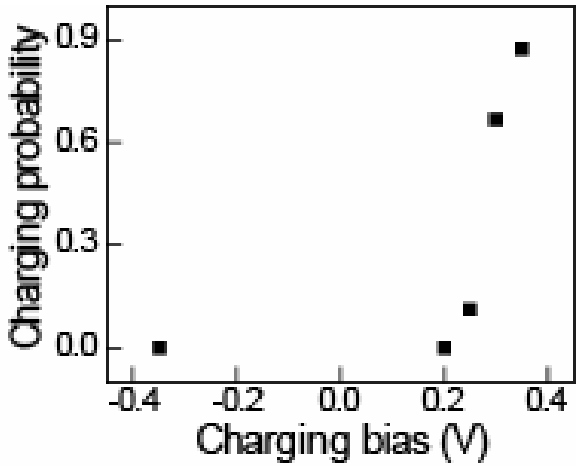
Lock-in Sensitivity: 1 nA/1 V $I_R \sim 1$ pA $I_0(V_B) \sim 1$ nA

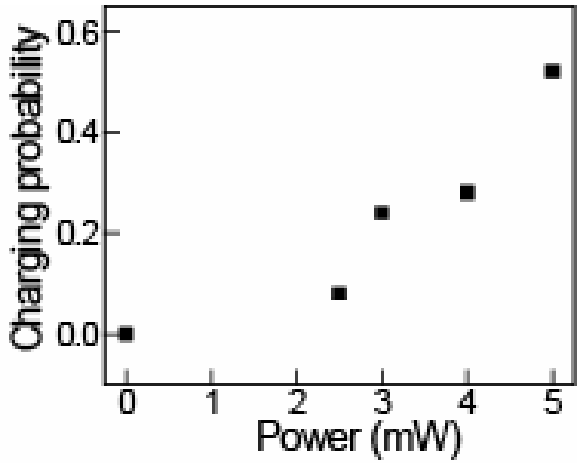
Vibrational Rectification: Single $^{12}C^{16}O$ & $^{13}C^{18}O$



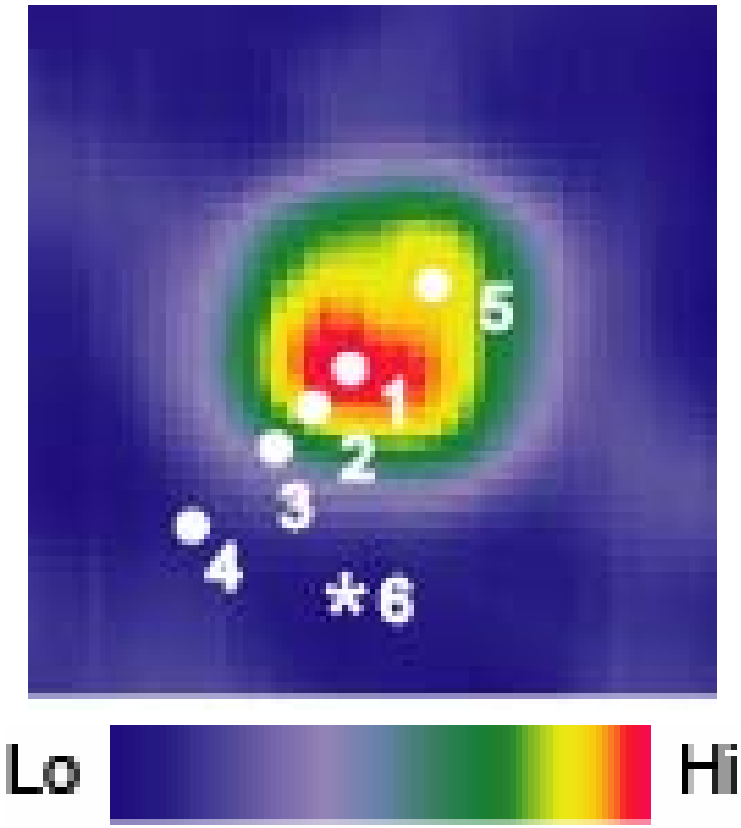
Single Molecule Photon Induced Electron Transfer

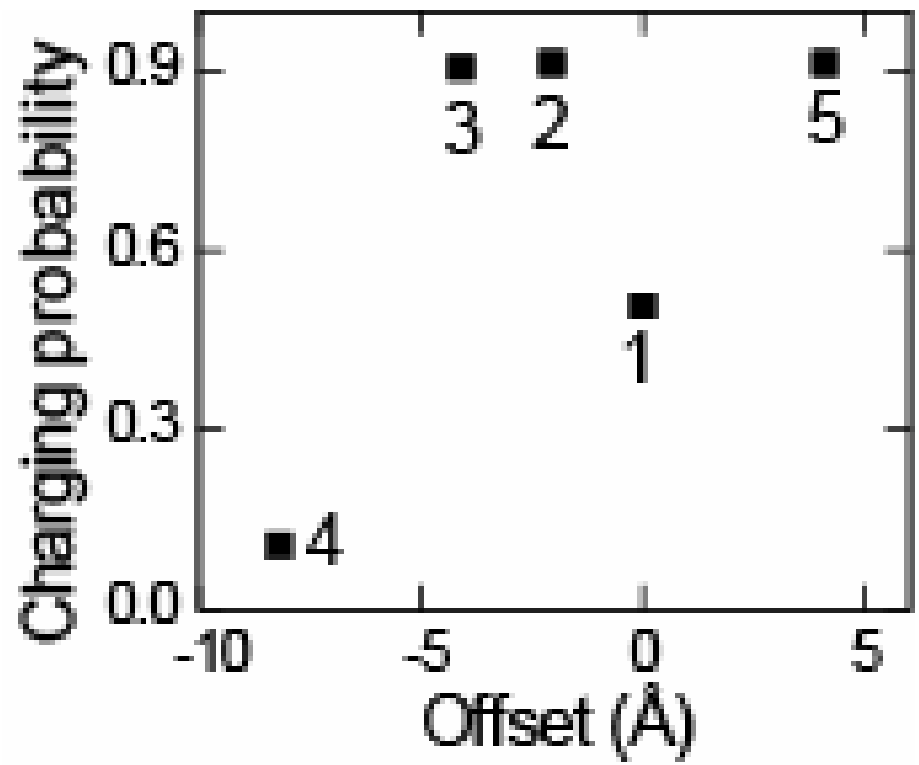




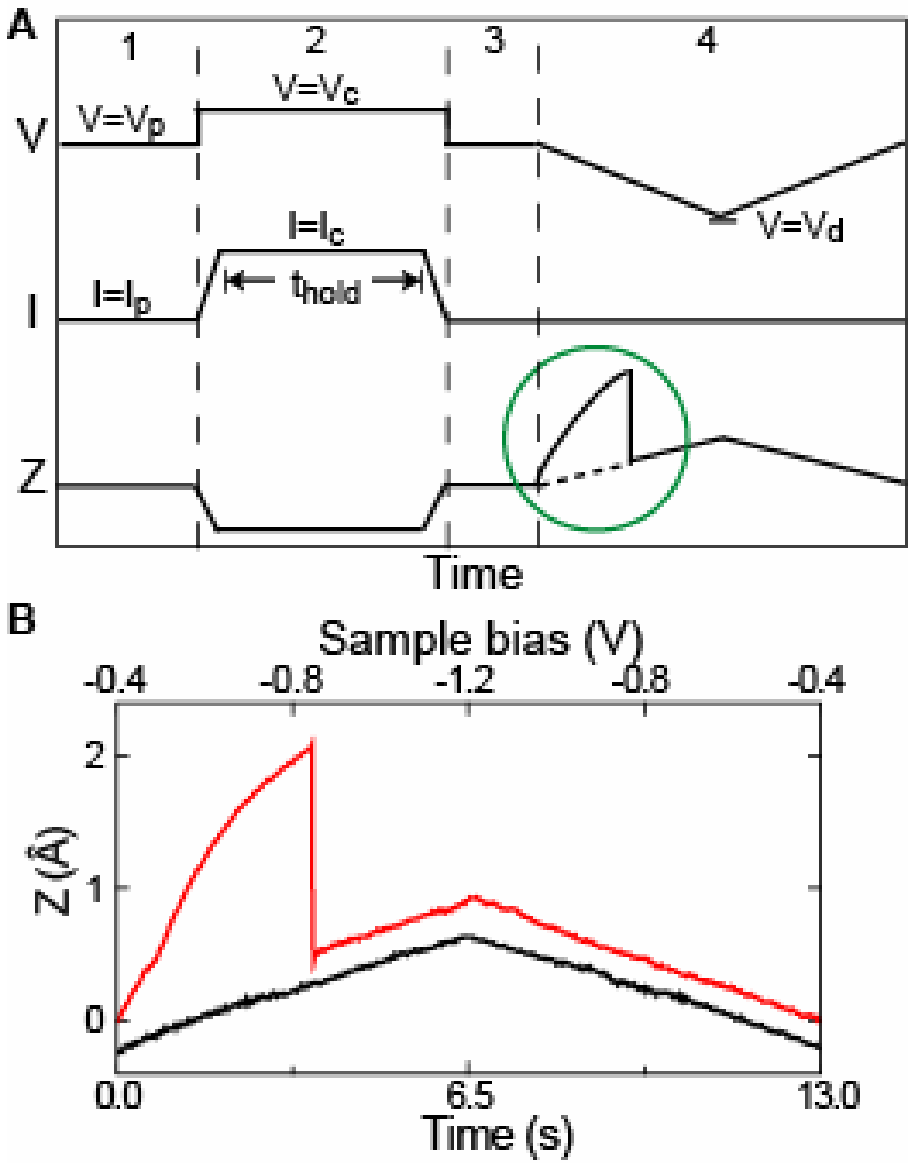


Single Molecule Photon Induced Electron Transfer with Sub-Molecular Spatial Resolution





Monitoring Photon-Induced Electron Transfer in a Single Molecule



Single Molecule Electron Transfer