The Interior of Single Molecules

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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

- H on Cu(001)
- O$_2$ on Pt(111)
- C$_2$H$_2$ on Cu(001)
- Fe(CO)$_2$ on Ag(110)
Visualization of Single Molecules

- H on Cu(001)
- O$_2$ on Pt(111)
- C$_2$H$_2$ on Cu(001)
- Fe(CO)$_2$ on Ag(110)
Elastic vs. Inelastic Tunneling
Atomic Scale Electronic Spectroscopy

Tip $V_{\text{bias}}$ $E_F$ Sample $e^-$ LUMO

Vacuum Adsorbate HOMO

Current (I)

$dl/dV$

Voltage (V)
STM
Inelastic Electron Tunneling Spectroscopy

\[
\begin{align*}
    \frac{dI}{dV} & \quad \text{elastic inelastic} \\
    \frac{d^2I}{dV^2} & \quad \text{elastic inelastic}
\end{align*}
\]
Chemical Identification: Single Acetylene Molecules on Cu(100)
Inside Single Acetylene
Single Molecule Rotation: Acetylene on Cu(001)

a) Side View

Tap View: High and Low states

b) Current vs. Time

364 mV Pulse

High and Low Currents

c) Events vs. Time Bin

40 ms/Bin
Vibration-Rotation Coupling
Acetylene on Cu(001)

\[ \text{Rotations/Electron} \]

\[ d^2I/dV^2 \text{ (nA/V$^2$)} \]

\[ \text{Voltage (mV)} \]

\[ C_2D_2, C_2H_2 \]

\[ 358, 266 \]
C$_2$HD Rotation on Cu(001)

(a) Current (nA) versus Time (s)

(b) Events/Bin versus Bins for Cu(100) Low

(c) Events/Bin versus Bins for Cu(100) High
H Atom
Single H Atom

15 x 15 Å²

$\frac{d^2I}{dV^2}$ (nA/V²)

Sample Bias (mV)
Single H Diffusion
Over-Barrier vs. Tunneling

Over-Barrier

Tunnel

195 meV

70 meV

2.55 Å
Hydrogen Atom Diffusion
STM Induced Conformation Change
Vibronic States: Naphthalocyanine
Spatially Resolved Vibronic Spectroscopy
Spatial Dependence of Electron-Vibronic Coupling
Single $\text{O}_2$ Dissociation by Tunneling Electrons
Single $O_2$ Dissociation
Single Bond Dissociation:
Acetylene on Cu(001) @ 9 K
Making a Molecule

A

Tip

O

C

Ag

e\(^-\)

[1\bar{1}0]

[001]

B

C

D

Fe

\uparrow e^-
Making Molecules One by One
Singles: Close-Up View
Single Molecule Oxidation
How Close is Close?
Single Gold Atoms on NiAl(110)
Gold Chains: 1 to 20 Atoms
Electronic Spectra of 1 to 20-Atom Au Chains
Gold Chains: 1 to 20 Atoms
Pd$_{20}$ Chain
Single CO Adsorption on 11-Atom Au Chain

\[ \text{Au}_5 - \text{AuCO-Au}_5 \]

Topography

+36 mV

-36 mV
CuPc@2Au$_6$
Structure of CuPc
Assembly of CuPc@2Au₆
Missed Trajectory
The Right Gap for Molecular Bridge

A

B

C

D
# Acknowledgment

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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

[C2H2]

[C2HD]

[C2D2]
Acetylene Thermal Rotation

< 68 K

68.7 K

81.5 K
Acetylene Thermal Rotation Rate

![Graph showing the relationship between temperature and rotation rate, with the equation rate = \( v_o \exp(-E_a/kT) \) and \( n_{o} = 10^{11.7} \text{s}^{-1} \) and \( E_a = 0.16 \text{ eV} \).]
Acetylene Thermal Hopping Rate

$E_a = 0.53 \text{ eV}$

$v = 10^{13.4} \text{ s}^{-1}$
Single Atom Thermal Diffusion
Conformation Suppression
Vibrationally-Mediated Negative Differential Resistance

Pyrrolidine-hg

Pyrrolidine-dg

Cu(001)
Inelastic Vibrational vs. Vibronic Spectroscopy
Rotational Analysis

(a) (b) $C_2H_2$

(c) (d) $C_2H$

(e) (f) (g) (h) CC

LOW  HIGH

[010]
[100]
Vibrational Analysis

The diagram shows the vibrational analysis of different molecules. The graph plots the second derivative of the current (d²I/dV²) in nA/V² against the sample bias in mV. Peaks at 357, 394, 265, 313, and 200 mV correspond to different molecules labeled HCCH, CCH, DCCD, CCD, and Cu(001), respectively.
$\text{H}_2\text{S} + \text{CC} \rightarrow \text{SH} + \text{CCH}$

Cu(001) @ 9 K
Sub-Å Vibrational Spectroscopy
\[ \text{CO} + 2\text{O} \rightarrow \text{CO}_2 + \text{O} \]
20-Atom Au Chain

Assembled

Disassembled

75x75 Å

Low

High
Au$_{20}$: Spatially Resolved Spectra

![Graph showing spatially resolved spectra with conductivity on the y-axis and sample bias on the x-axis. The graph includes multiple curves each labeled with different samples and their respective conductivities.]

- Sample 1: $c_1 = 0.31, c_2 = 0.29$
- Sample 2: $c_3 = 0.26, c_4 = 0.14$
- Sample 3: $c_5 = 0.26, c_6 = 0.50$
- Sample 4: $c_7 = 0.24$
- Sample 5: $c_6 = 0.13, c_7 = 0.29$
- Sample 6: $c_8 = 0.39, c_9 = 0.19$
Electron Density of States of 11-Atoms Au Chain
Au Chains: 1-D Particle-in-a-Box

\[ E \sim \frac{1}{L^2} \]

\[ \rho \sim \frac{1}{E^{1/2}} \]
Au Chains – Energy Dispersion

\[ \text{Au}_{20} \quad \text{Au}_{11} \]

**Au\textsubscript{20} Chain**

- \( m_{\text{eff}} = 0.5m_{\text{free}} \)
- \( E_1 = E_0 + \frac{\hbar^2 k^2}{2m_{\text{eff}}} \)
- \( k = \frac{n\pi}{L} \)

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<th>(Wave Number)(^2) ( \times 10^{20} \text{ m}^{-2} )</th>
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**Au\textsubscript{11} Chain**

- \( m_{\text{eff}} = 0.4 \pm 0.1 m_{\text{free}} \)

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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

[A images showing spatial distribution of Au and Pd atoms at different voltages.

B graph showing the derivative of current (dI/dV) with sample bias voltage, with curves for Au and Pd labeled.]
dl/dV Mapping

Au$_4$PdAu$_5$  

Au$_{11}$
Mn Chains: 1 to 16 Atoms
Au₁₁-Au₁₁CO: Spectral Mapping

Au₁₁ - chain

Au₅ - AuCO-Au₅
Perturbation of CuPc states by the Au atoms
DOS maps for CuPc and CuPc@2Au$_1$

---

**CuPc**

- Low
- High

**CuPc@2Au$_1$**

- Low
- High

Voltage levels:

- 0.9 V
- 1.0 V
- 1.1 V
- 0.6 V
- 0.8 V
- 1.0 V

Annotations:

- $e_g$
- LUMOs
Tuning of Electronic States

![Graph showing the tuning of electronic states with the number of atoms (n) on the x-axis and peak position (V) on the y-axis. The graph includes data points for Au\textsubscript{n} in CuPc@2Au\textsubscript{n}, Au\textsubscript{n} in 2Au\textsubscript{n}, and CuPc in CuPc@2Au\textsubscript{n}.]
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

- Scale: 2.5 cm
- Continuous Flow L-He/N$_2$ Cryostat
- Sample at 8 K to 350 K
- Outer Shield
- Inner Shield
- Inconel Springs (3)
- W Balls (3) and Tip
- Mo Base Plate
- Hole for Dosing
- Clamping Screw
- Cold Tip
- Electrical Feedthroughs
- Inner Access Door
- Mo Sample Holder
- Piezotubes (4)
- Sapphire Laser Window
- Samarium–Cobalt Magnets
Vibronic States – $\text{C}_6\text{O}$ on $\text{Al}_2\text{O}_3$

$H_g(\omega_3) \sim 88.1 \text{ meV}$

$H_g(\omega_2) \sim 53.6 \text{ meV}$

$H_g(\omega_4) \sim 96.1 \text{ meV}$

$A_g(\omega_1) \sim 61.7 \text{ meV}$

Animations courtesy: John Page, Ariz. State. Univ. [http://www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm](http://www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm)
Vibronic Progression on Progression
O$_2$ on Pt(111)
Orbital Specific Chemistry
Acknowledgment

Jennifer Gaudioso          Xi Chen
Jae Ryang Hahn             Hyojune Lee
Lincoln Lauhon             George Nazin
Mohammad Rezaei            Niklas Nilius
Barry Stipe                Xiaohui Qiu
                            Mitch Wallis

Shiwu Gao
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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**

\[ I \]

**Constant height**

\[ I \]

- **Topography**

\[ I \]

- **Spectroscopy**

\[ I \]

- **Chemistry**

\[ I \]

\[ V, I, Z \]

\[ R = \frac{V}{I} \]

\[ G = R^{-1} \]
STM-IETS Requirement

Junction Stability
Feedback Off

\[ \Delta Z \sim 0.005 \text{ Å} \quad \rightarrow \quad \Delta I \sim 0.01 \text{ nA} \]

Drift \sim 0.001 \text{ Å-min}^{-1}
Inelastic Electron Tunneling Spectroscopy (IETS)

Conventional IETS: $\sim 10^9$ molecules

STM-IETS: 1 molecule
Scanning Tunneling Microscope (STM)

- **Metal Tip**
- **Vacuum Surface**
- **Solid Surface**

The diagram shows an electron tunneling from the metal tip to the solid surface through a vacuum space.

The equation $V = I \cdot R$ represents the relationship between voltage ($V$), current ($I$), and resistance ($R$) in an electrical circuit.

The setup includes a tip, vacuum space, and a solid surface, illustrating the principles of electron tunneling in a Scanning Tunneling Microscope.
STM-IETS: CO on Cu(110)
Mapping a Single Bond
STM-IETS Lineshape

- **Cu(001)**
  - $d^2I/dV^2$ (nA/V^2)
  - Peaks at 369 mV and 409 mV

- **Ag(110)**
  - Peaks at 35 mV and 79 mV

Chemical structures:
- $H\equiv C\equiv C\equiv H$
- $H\equiv C\equiv C\equiv H$
- $O\equiv O$
STM-IETS

Inelastic Tunneling

Elastic Tunneling

\[ I_{\text{tot}} = I_{\text{el}} + I_{\text{inel}} \]
STM-IETS: Hydrocarbons

Sample Bias (mV)

d\text{d}^2I/dV^2 (nA/V^2)

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Chemical Structures:

1. C\equiv C-H
2. H-C\equiv C-H
3. H-C\equiv C-H
4. H-C\equiv C-H
5. H-C\equiv C-H
6. H-C\equiv C-H
7. H-C\equiv C-H
8. H-C\equiv C-H
Oxygen on Pt(111)

Possible $O_2$ Orientation on (111) Microfacets

Top View

(111) Step
HCP O Site
FCC O Site
(100) Step

$O_2$ Bridge Sites
$O_2$ FCC Three-Fold Sites

Side View

STM Image
Molecular Oxygen on Pt(111)

"Pear"

FCC Three-Fold Site

"Clover"

Bridge Site
Rotation of Oxygen on Pt(111)
Monitoring Oxygen Rotation

(a) Top and Side views of an oxygen molecule.

(b) Diagram showing oxygen molecule orientations.

(c) Graph showing current (I) over time (s) for an oxygen molecule isolated with 0.15 Volt Pulse.

(d) Graph showing current (I) over time (s) for an oxygen molecule next to a defect with 0.2 Volt Pulse.

Oxygen Molecule Isolated

Oxygen Molecule Next to Defect
O$_2$ Rotation on Pt(111)

Single Molecule Rotation Rates

(a) $P \propto e^{-t/\tau}$
- Bin = 12 ms
- 0.2 Volts
- 1.9 nA
- $N_{tot} = 88$
- $\tau = 39$ ms

(b) Graph showing rotation rate vs. current.

(c) Graph showing $R \propto I^N$
Single Atom/Molecule Tracking

(a) 

(b) 

(c) 

(d)
Single Atom Thermal Diffusion
H & D Diffusion on Cu(001)
NDR: Population Analysis

State-resolved I-V curves for Pyrrolidine-$d_8$

A

B

C

Sample Bias (mV)
NDR: Electronic Origin

Conventional NDR: An Electronic Mechanism

- Current
- Density of States
- Energy
- Bias Voltage
- Increase

Bias Voltage

Increase
Single Atom NDR

![Graph showing dI/dV vs Sample Bias (V) for NiAl(110), Mn, Mn$_2$, and Mn$_3$.](image)
Hydrogen Atom Diffusion

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**Figure 1:**
- **Top Graph:**
  - Temperature (K) on the x-axis.
  - Hop Rate (s⁻¹) on the y-axis.
  - Data points for H and D are shown.

- **Bottom Graph:**
  - Temperature (K) on the x-axis.
  - Hop Rate (s⁻¹) on the y-axis.
  - Data points for H are shown.
Vibronic Spectroscopy – C$_{60}$/Al$_2$O$_3$