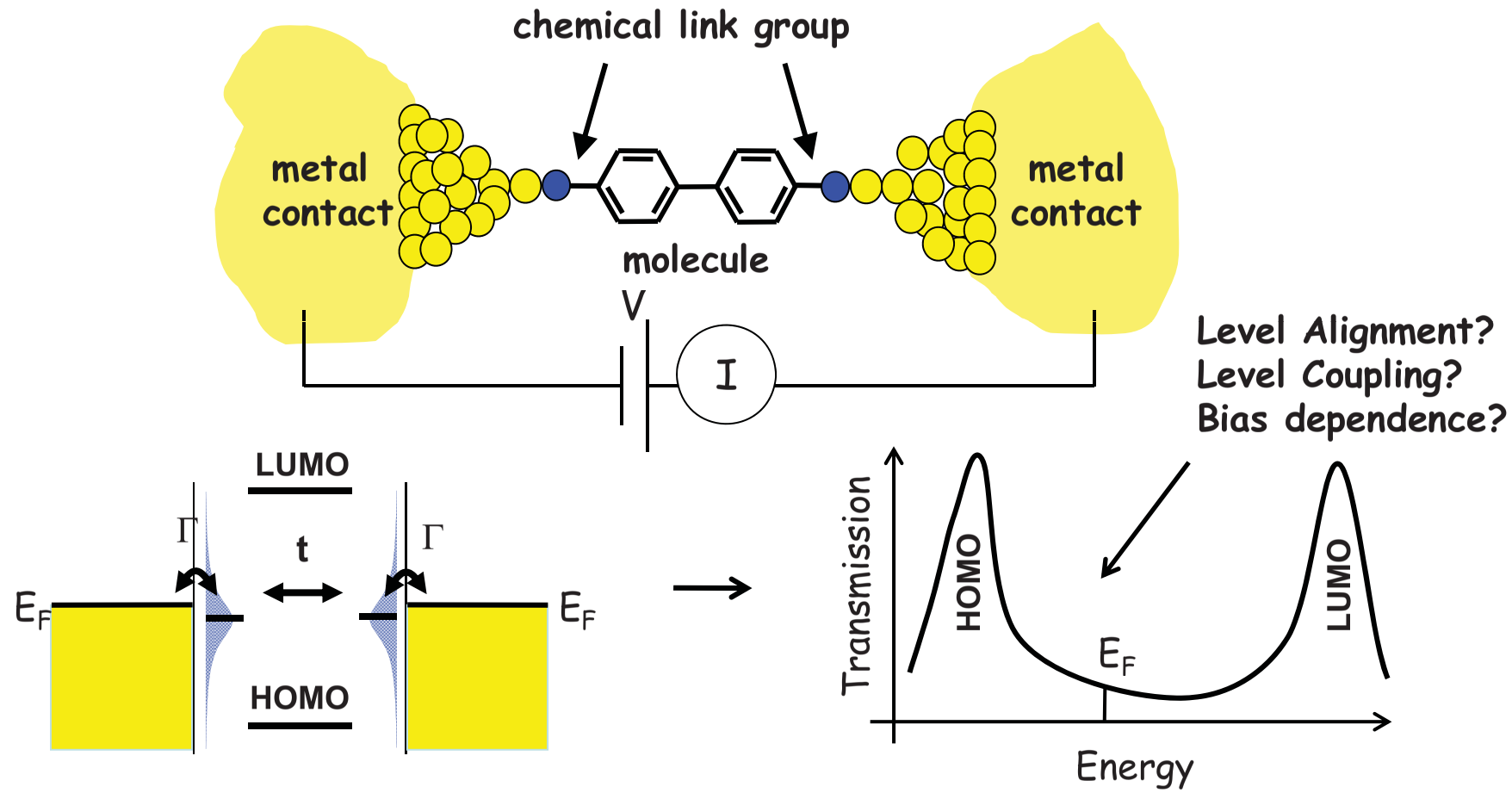
Mechanics and Electronics of Single Molecule Circuits

Latha Venkataraman
Dept. of Applied Physics
Columbia University

Funding from:
- NSF-NSEC Program
- NYSTAR
- Packard Foundation
- ACS-PRF Fund
- NSF-Career
- DOE-EFRC

Anatomy of a Single Molecule Device



- How can we create such single molecule devices and measure transport?
- What are key parameters that control transport?
- How can we get transport functionality from chemistry?

Outline

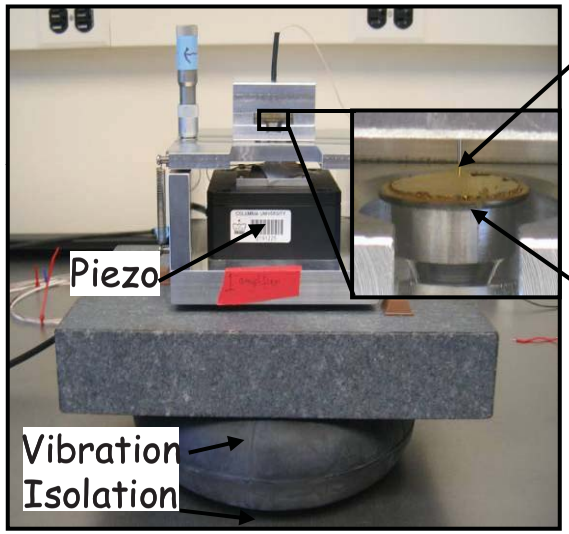
1. Experimental Method

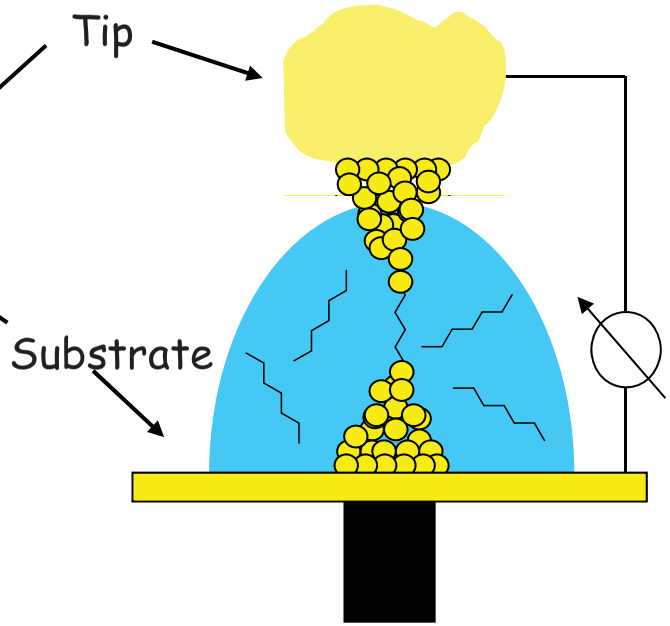
2. Conductance Measurements with Amines

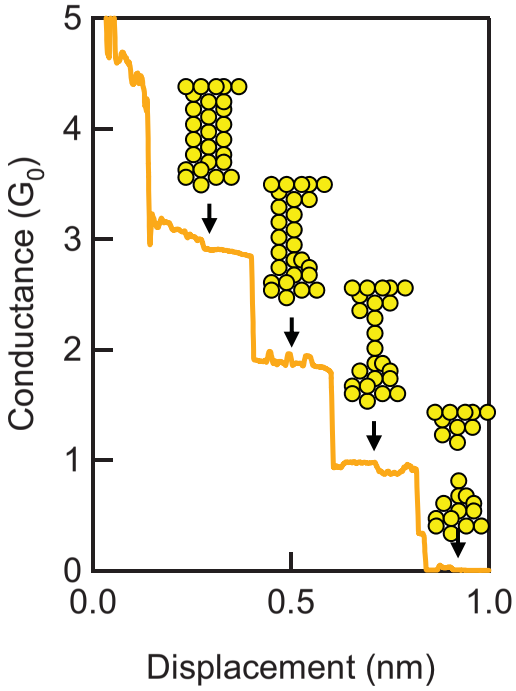
3. Conductance & Mechanics: Switching in Bipyridine

Experimental Method

STM based mechanically controlled break junction





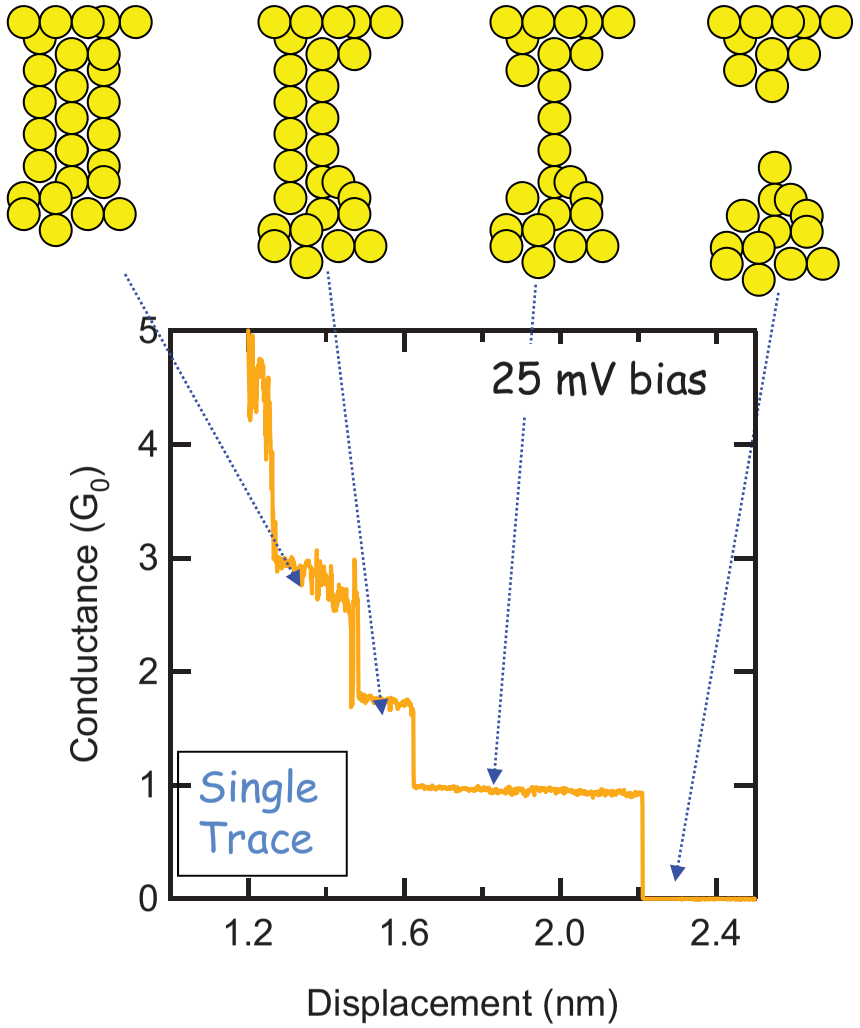


Key Points:
- Good vibration and acoustic isolation
- Low voltage noise for piezo
- Clean substrate & high purity solvents

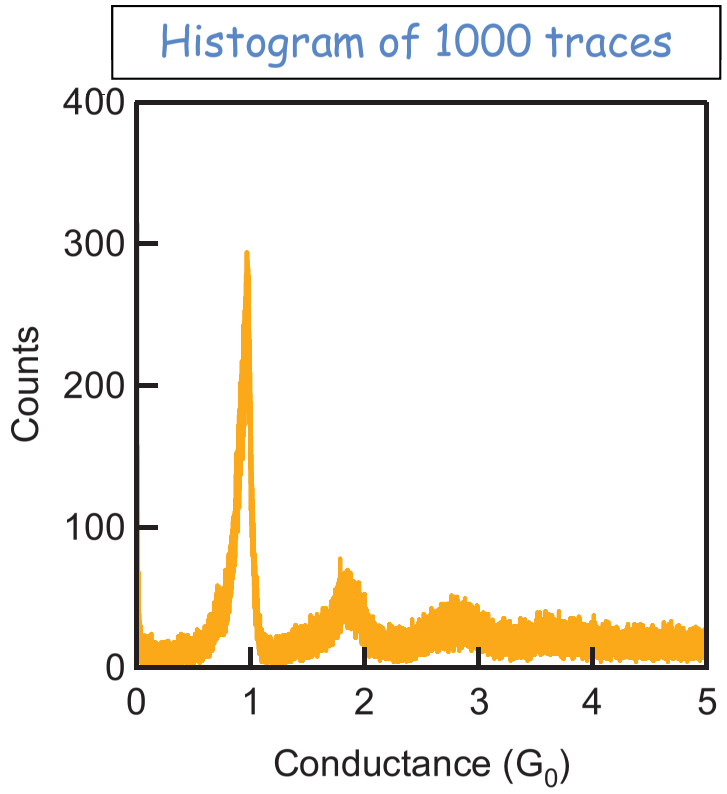
Advantages:
- Statistics
- Same platform for different molecules
- Variable Environment

Based on Xu & Tao, Science 2003

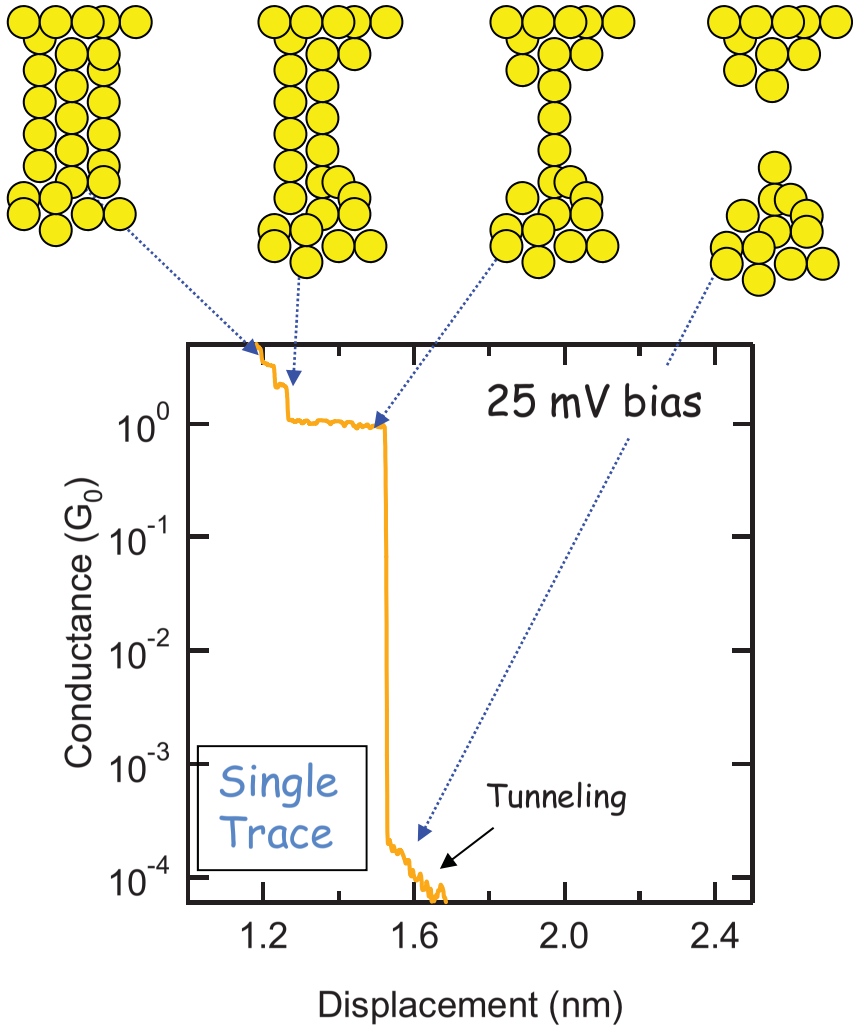
Breaking A Gold Contact



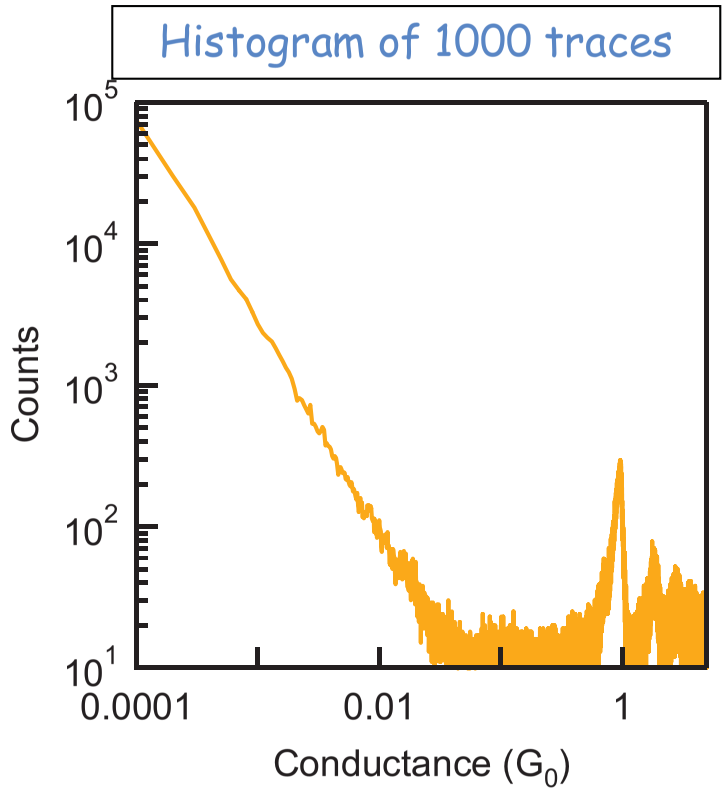
Conductance peaks visible at multiples of $G_o = 2e^2/h$



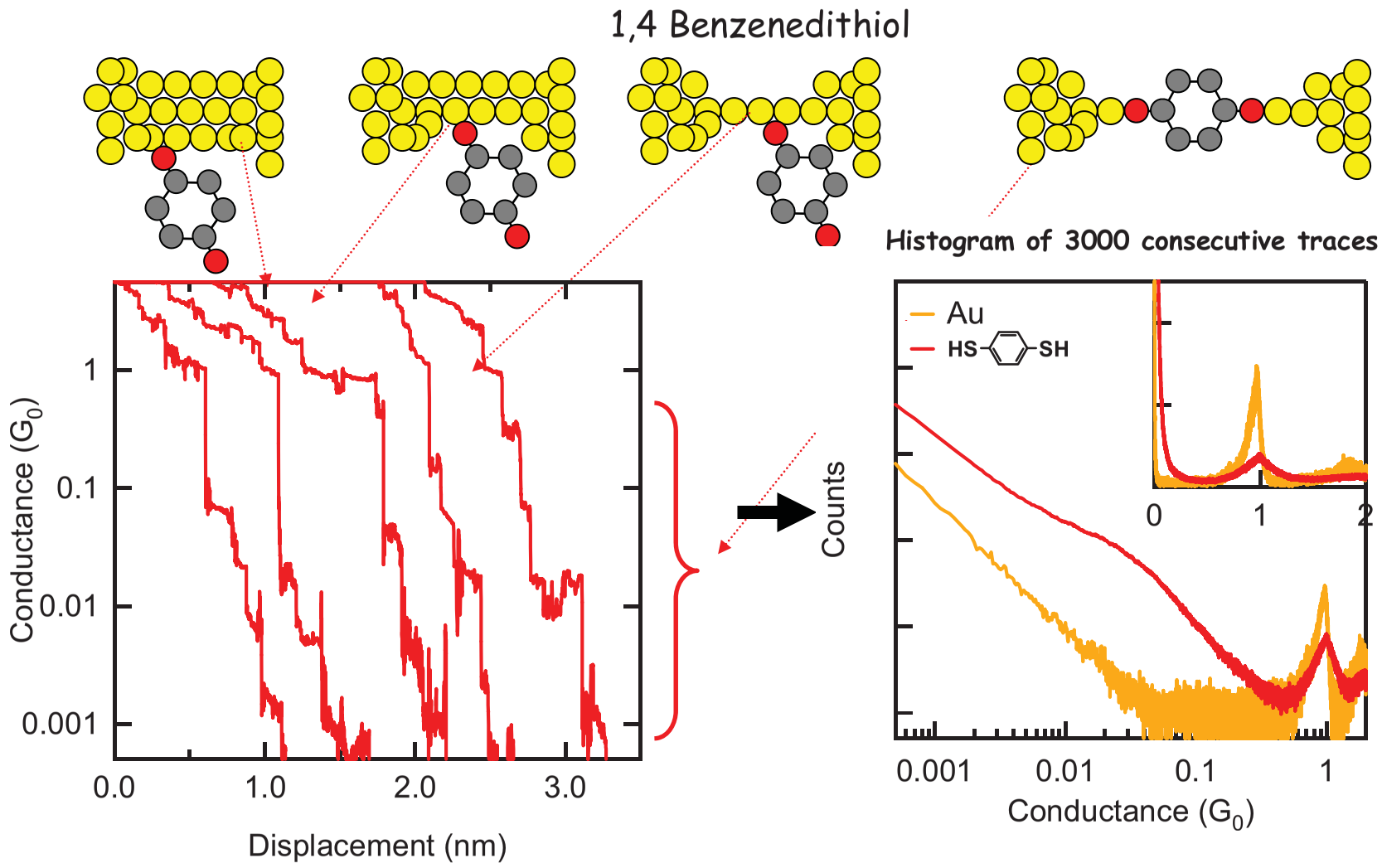
Data on a Log Scale



Conductance peaks visible at multiples of $G_o = 2e^2/h$



Adding Thiolated Molecules



Steps visible over large conductance range.

(Ulrich et al, J. Phys. Chem. B 2006)

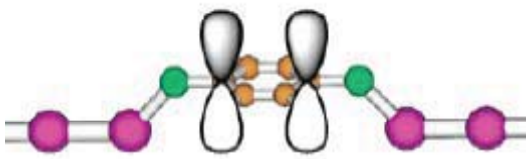
Thiols Links: Not Reproducible

Conductance depends on geometric details

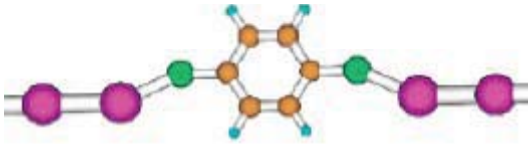
Thiols – bind to hollow, bridge, and atop site
Each configuration has different conductance

→ **Look for alternate links**

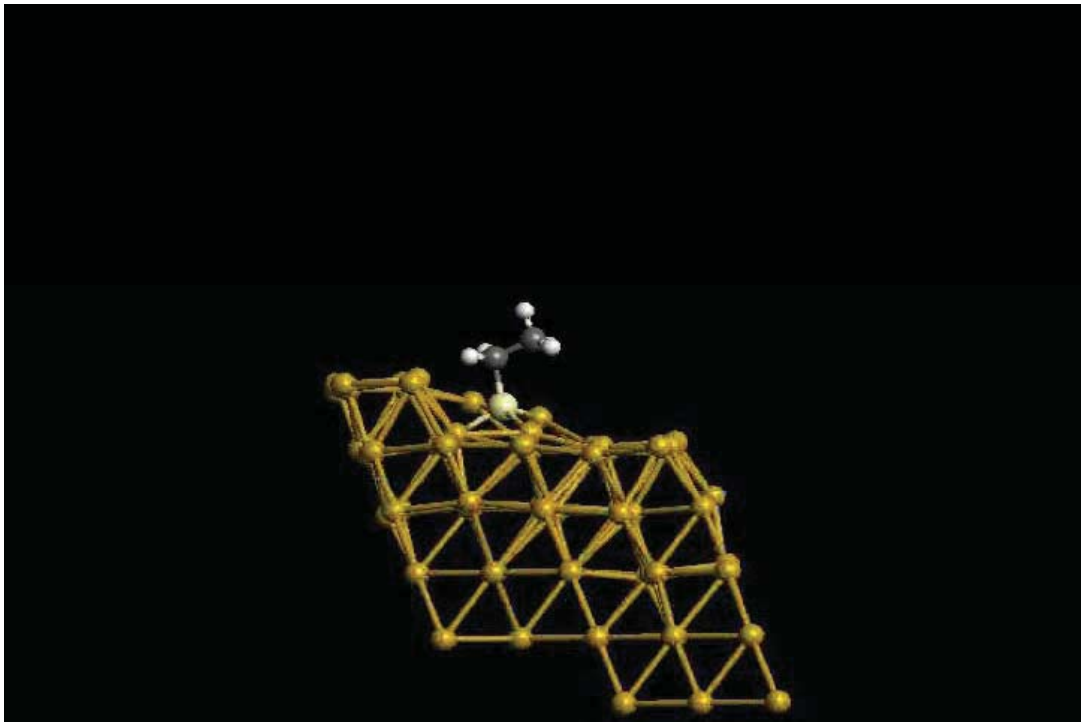
$G = 7 \times 10^{-5}\ G_0$



$G = 2 \times 10^{-8}\ G_0$



(H. Basch, Ratner et al., Nanoletters 2005)



(D. Kruger, H. Fuchs, Parrinello et al, PRL 2002)

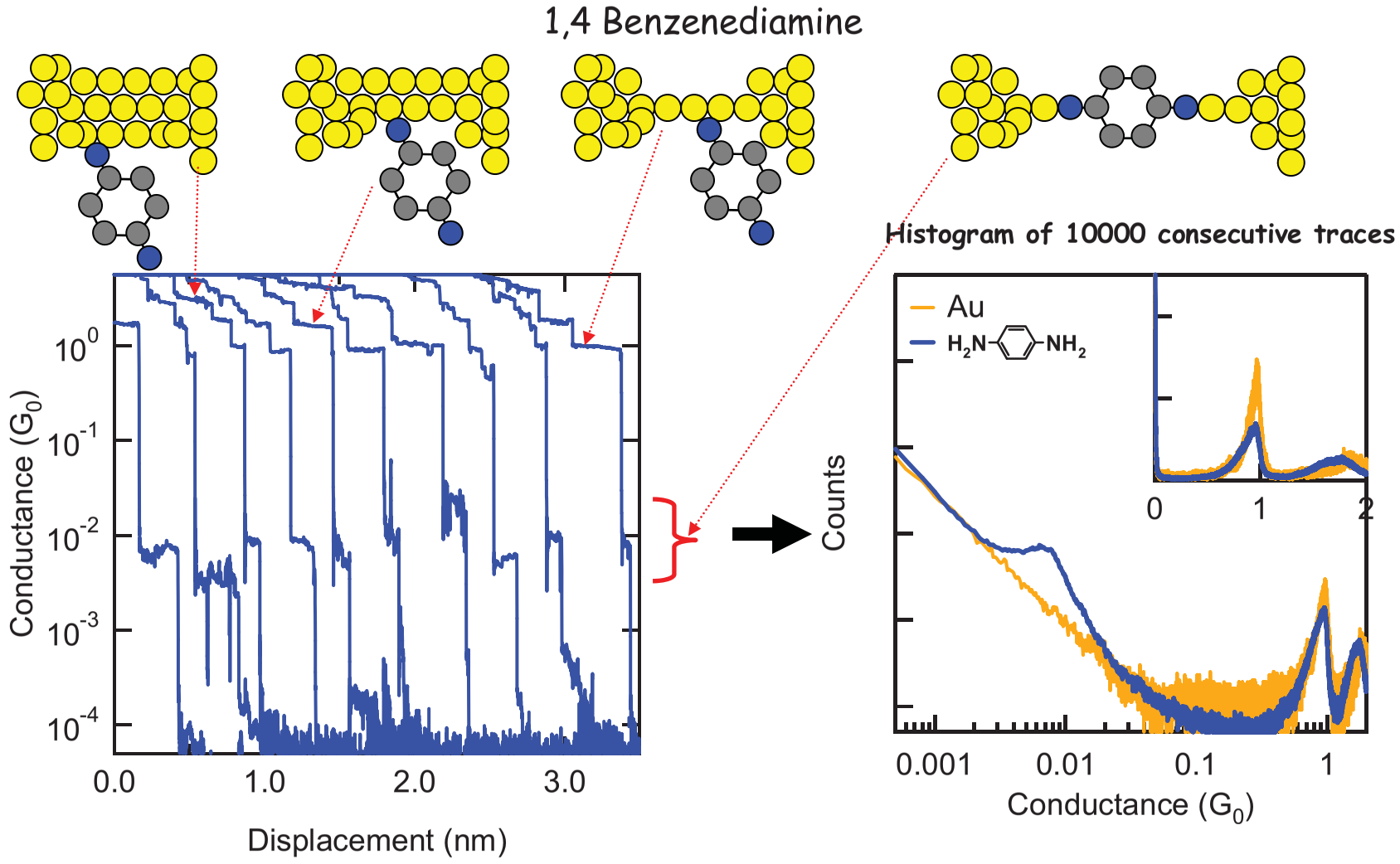
Outline

1. Experimental Method

2. Conductance Measurements with Amines

3. Conductance & Mechanics: Switching in Bipyridine

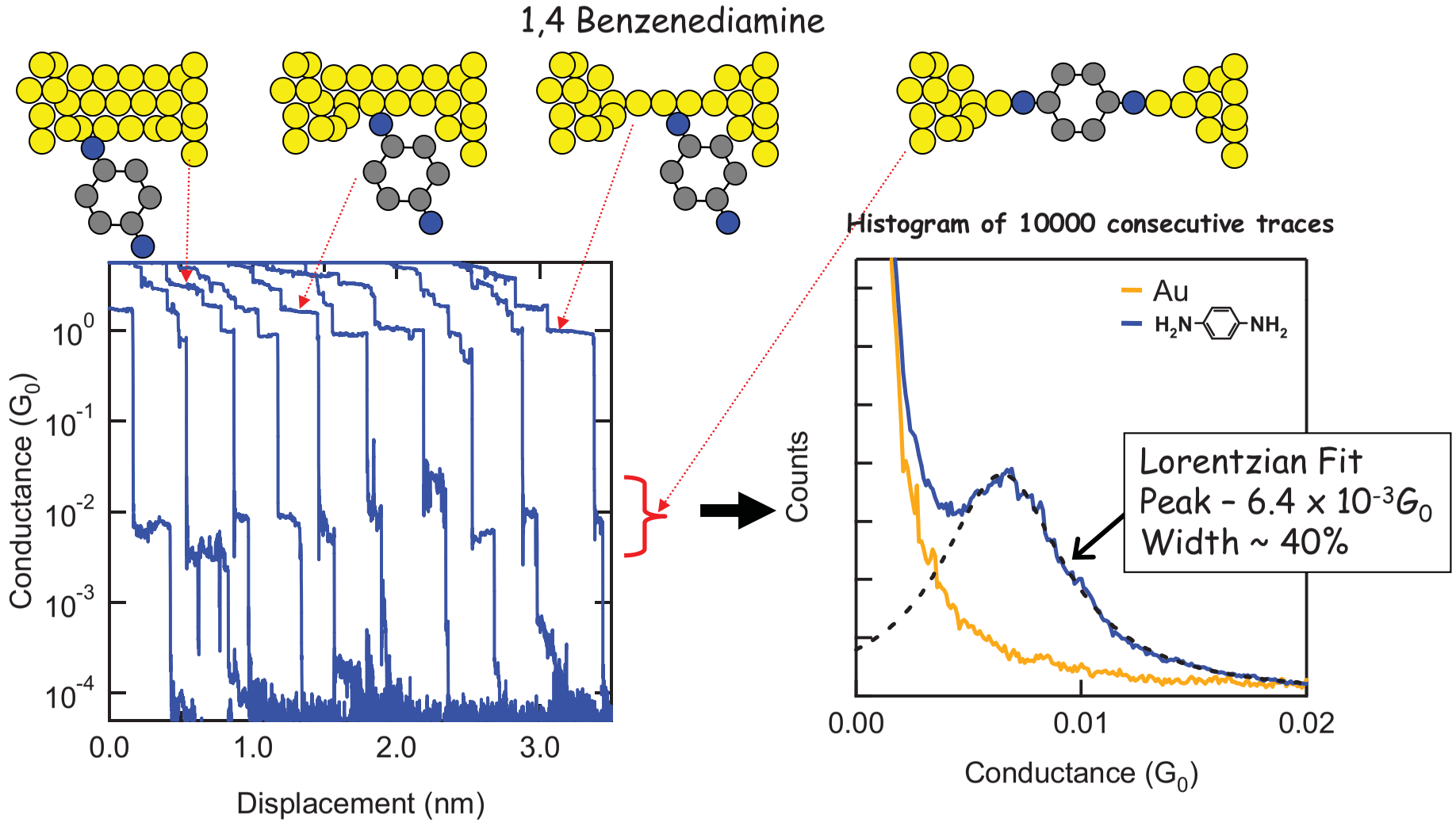
Amines (NH_2): An Ideal Link



Steps visible over a very limited range!

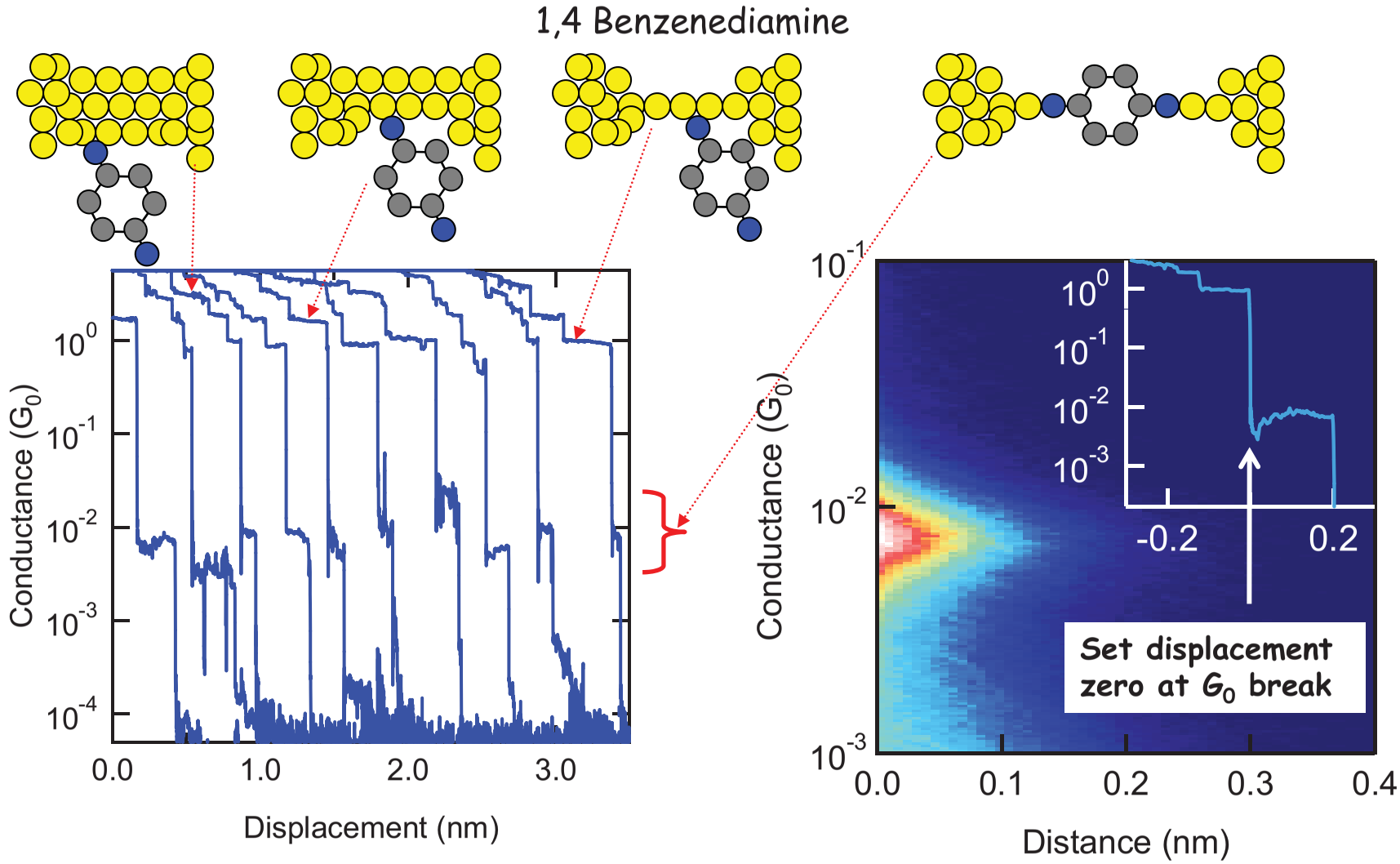
(L. Venkataraman et al, Nano Letters 2006)

Amines (NH_2): An Ideal Link

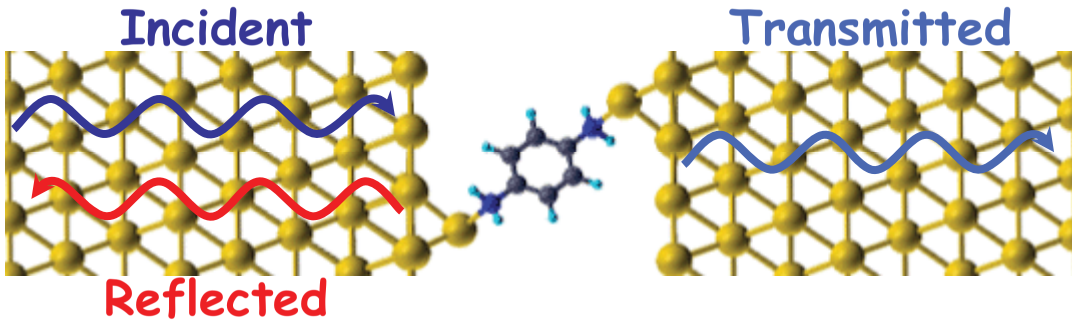


Steps visible over a very limited range!

Looking at Data in Using 2 Axes

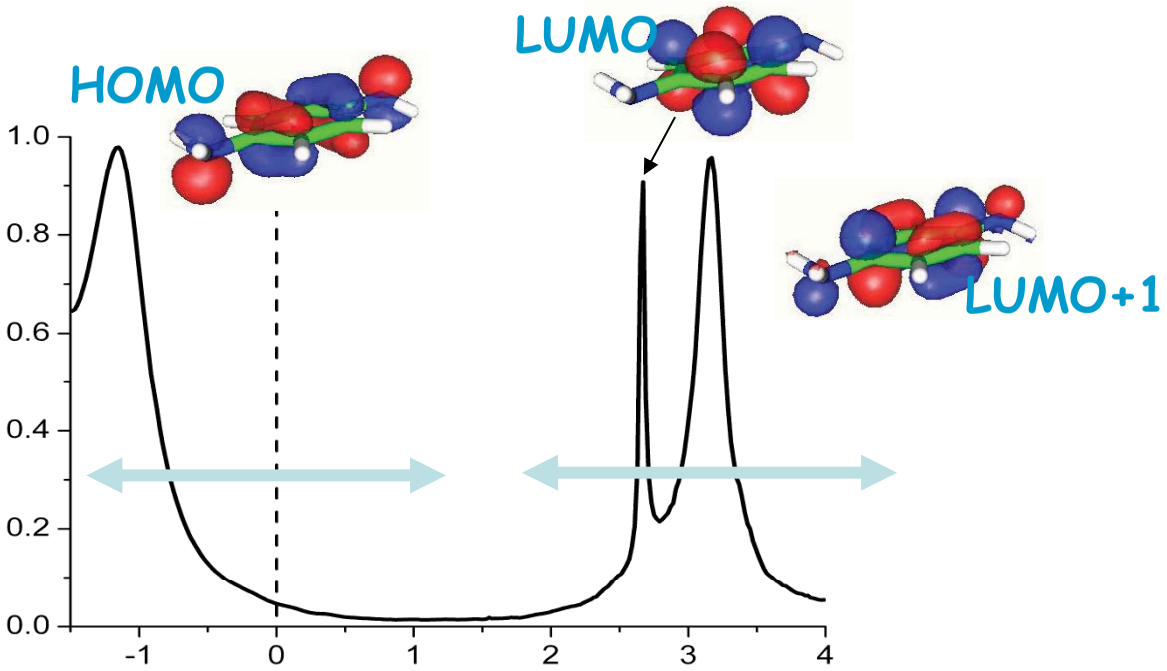


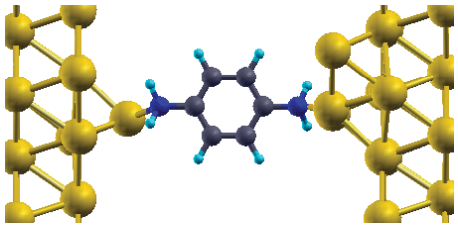
Single Molecule Junctions: Scattering Theory



Conductance from transmission using the Landauer formula:

$$G = \frac{2e^2}{h} T(E_F)$$



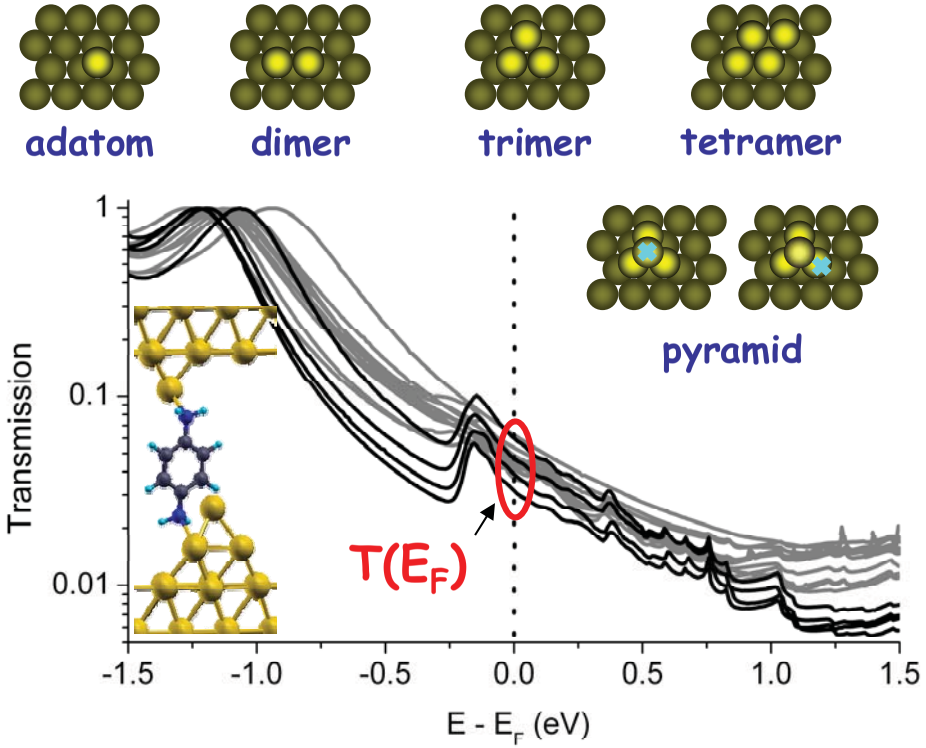


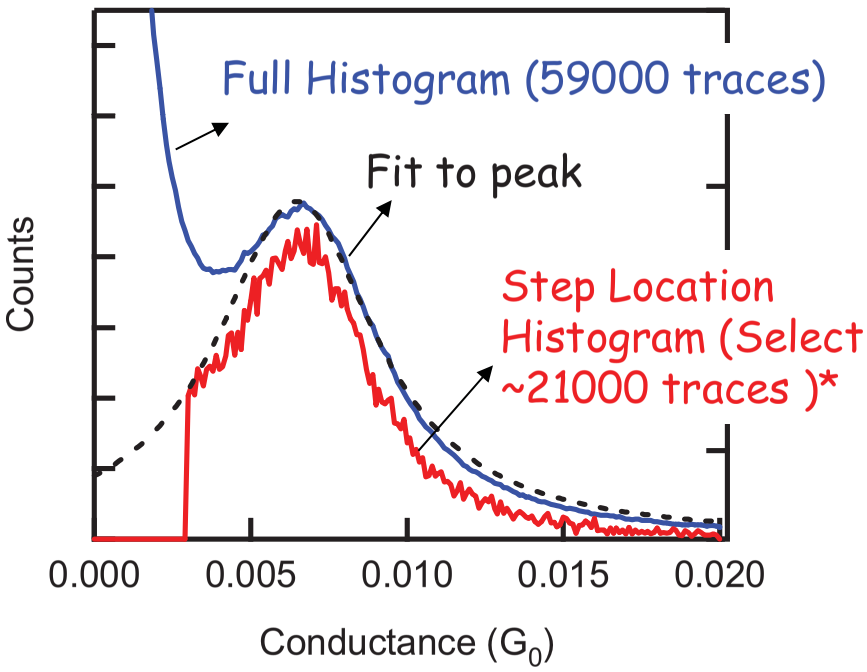
(Quek, Venkataraman, Choi, Louie, Hybertsen & Neaton, Nano Letters, 2007)

Comparison of Theory & Experiment

Theory:
- 15 different junction geometries analyzed
- Calculated conductance: 0.046 G_0
- Distribution width ~ 30 %

Experiment:
- 59000 conductance traces analyzed
- Measured peak position .0064 G_0
- Distribution width ~ 40 %



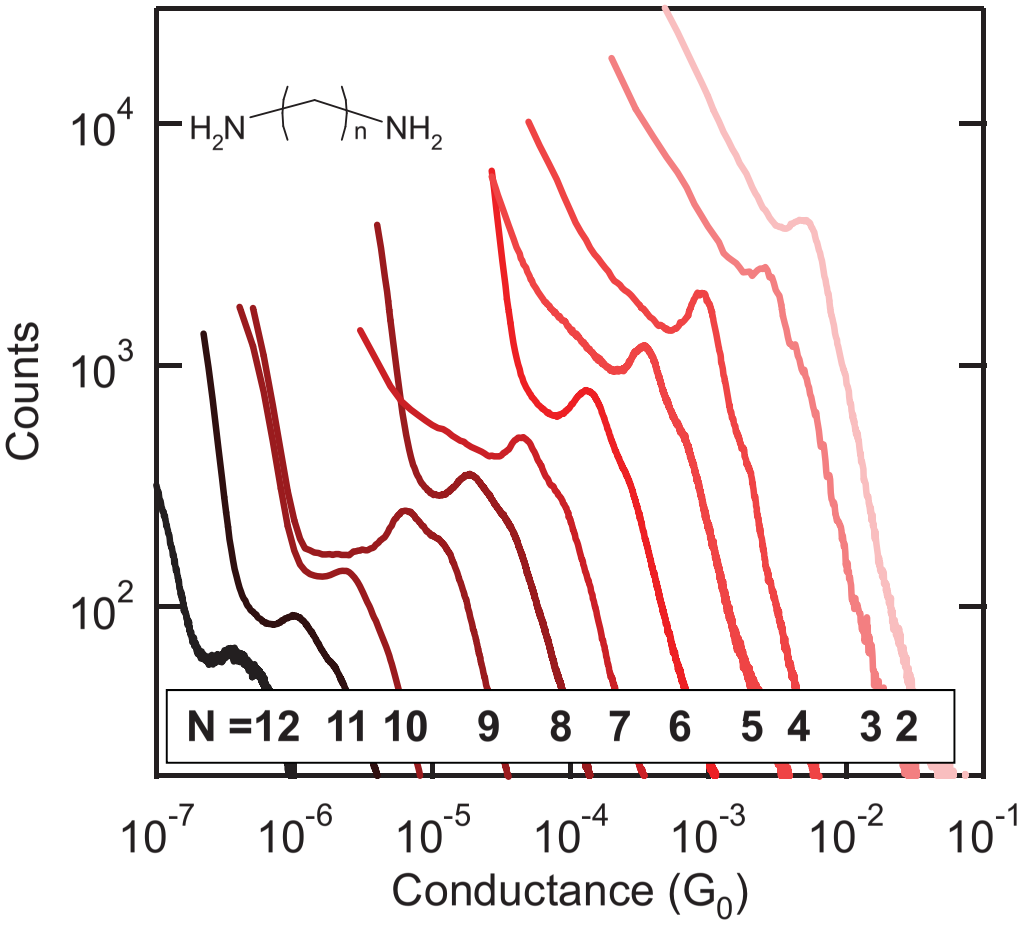


* Traces selected using automated algorithm

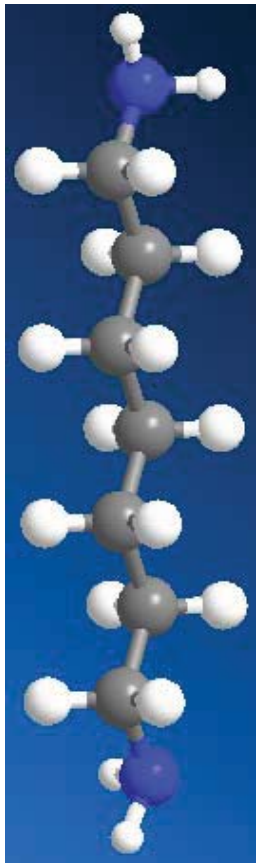
Self-energy & image corrections are missing

(Quek, Venkataraman, Choi, Louie, Hybertsen & Neaton, Nano Letters, 2007)

Conductance of Alkanes



Data offset vertically for clarity

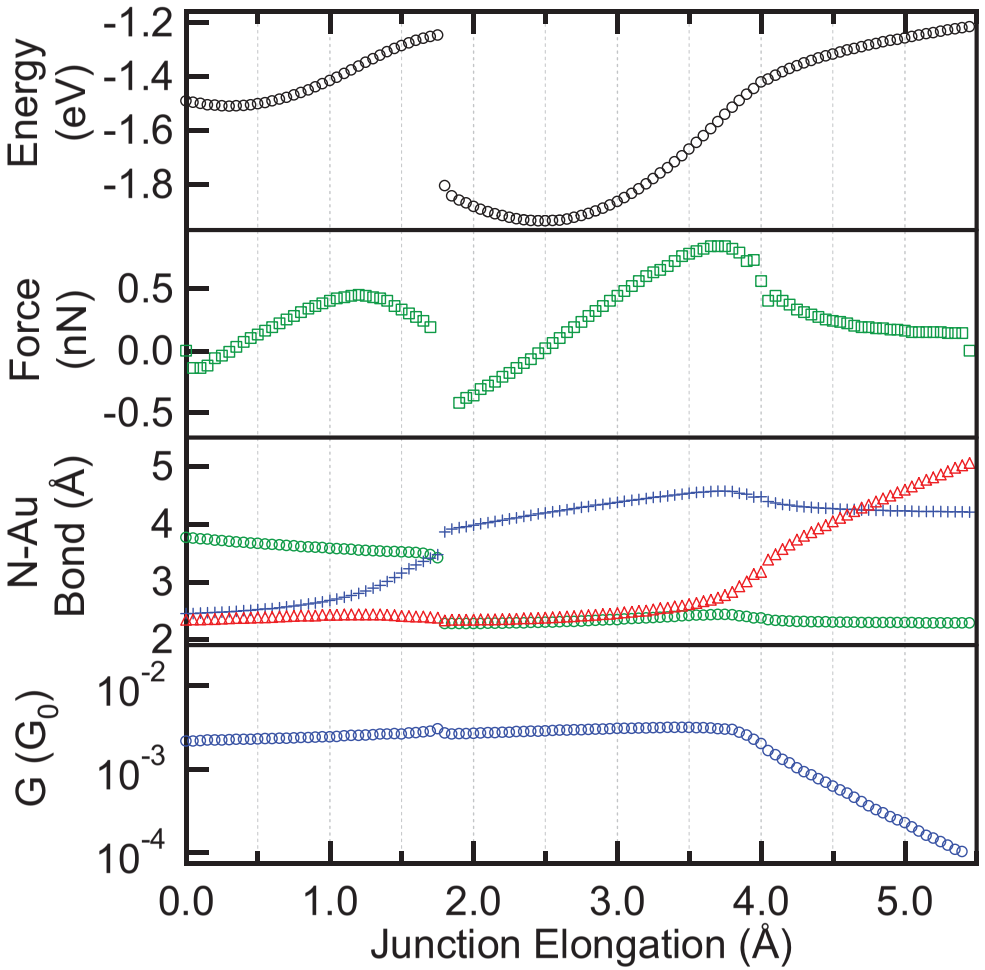


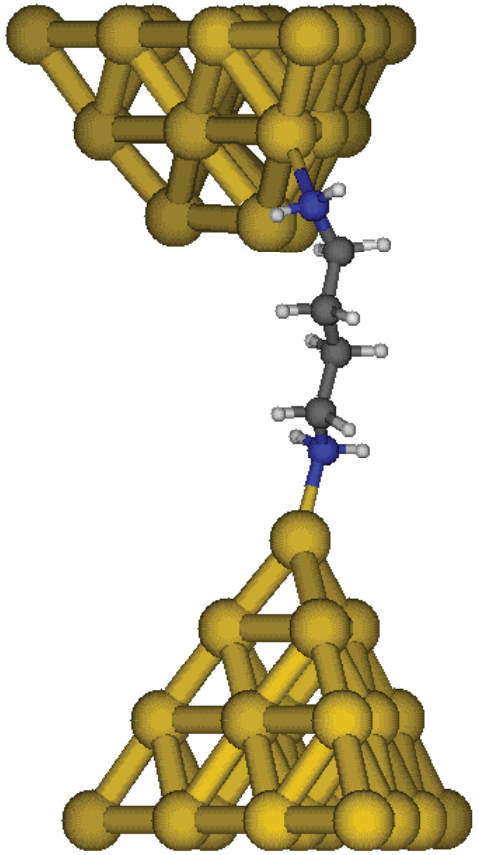
Alkane with 7 Carbon atoms and Amine groups on the two ends

(L.Venkataraman et al, Nano Letters 2006,
M. Hybertsen et al, J. Phys. Cond. Matter 2008)

Detailed Look at 1 Junction

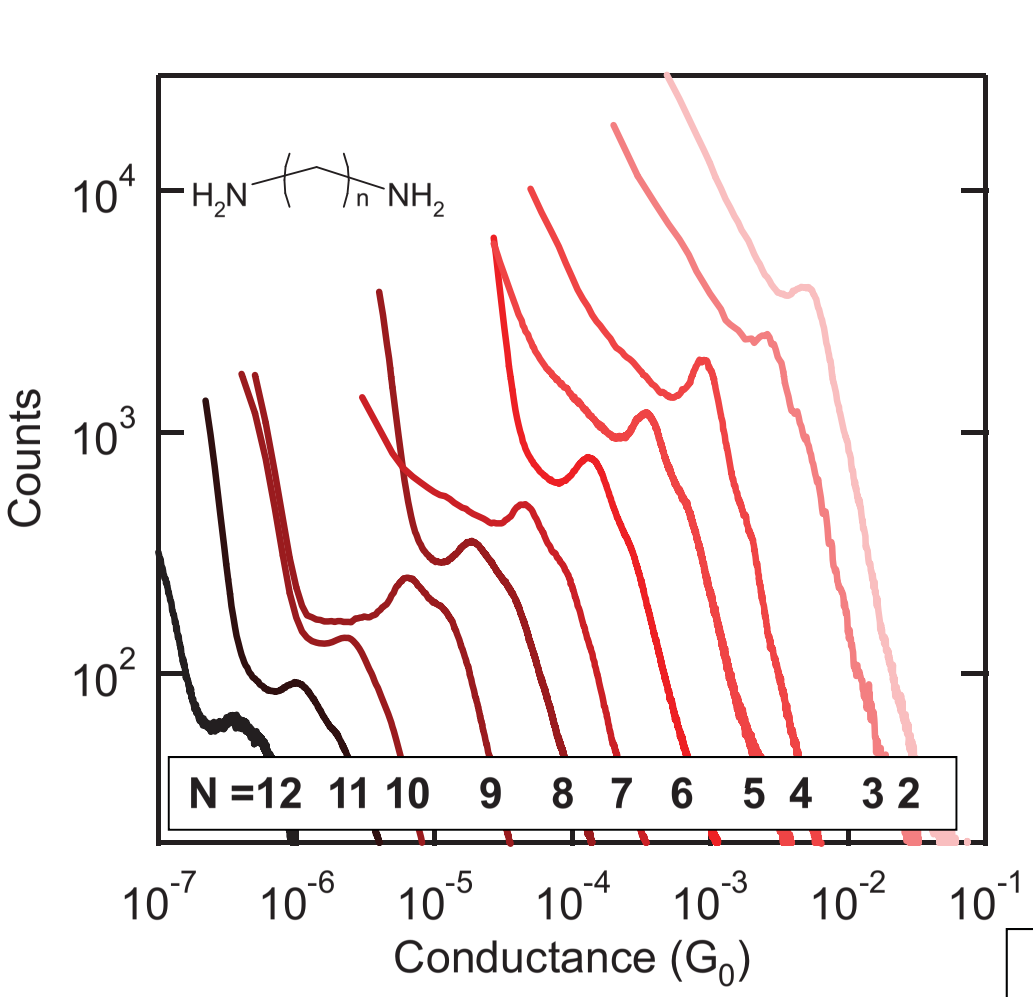
Butanediamine bonded to apex on bottom
and to an edge atom on the top



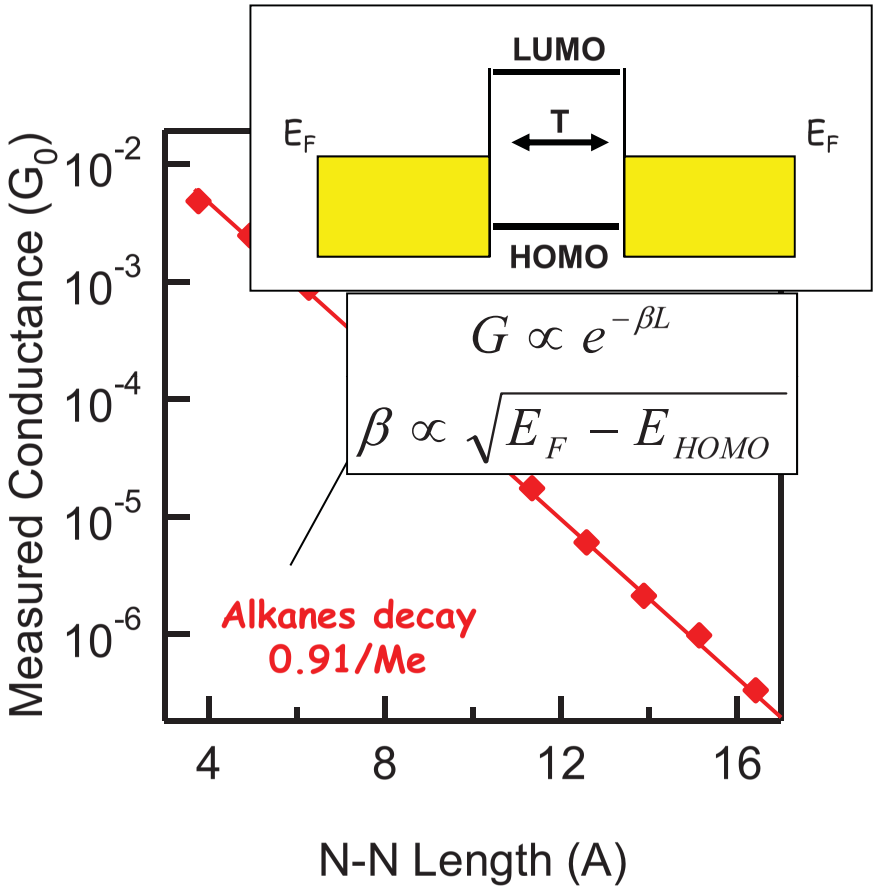


(Kamenetska, Koentopp, Hybertsen, L.V. PRL 2009)

Conductance vs Length



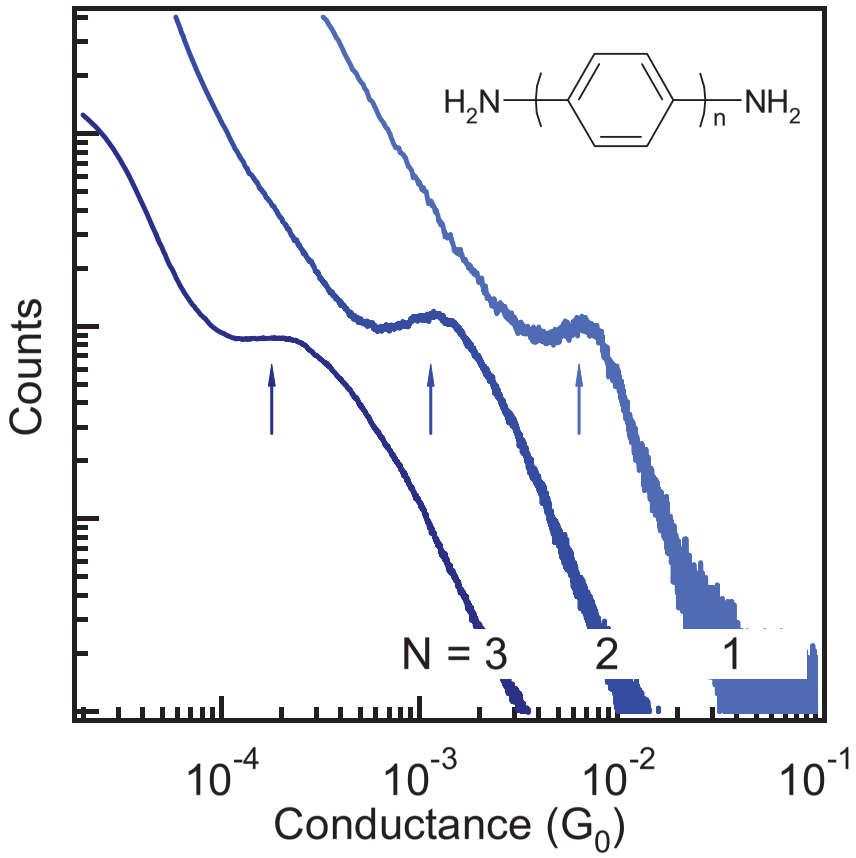
Data offset vertically for clarity



Direct evidence for non-resonant tunneling

(L.Venkataraman et al, Nano Letters 2006,
M. Hybertsen et al, J. Phys. Cond. Matter 2008)

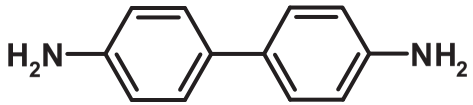
Conductance of Polyphenyls



Data offset vertically for clarity

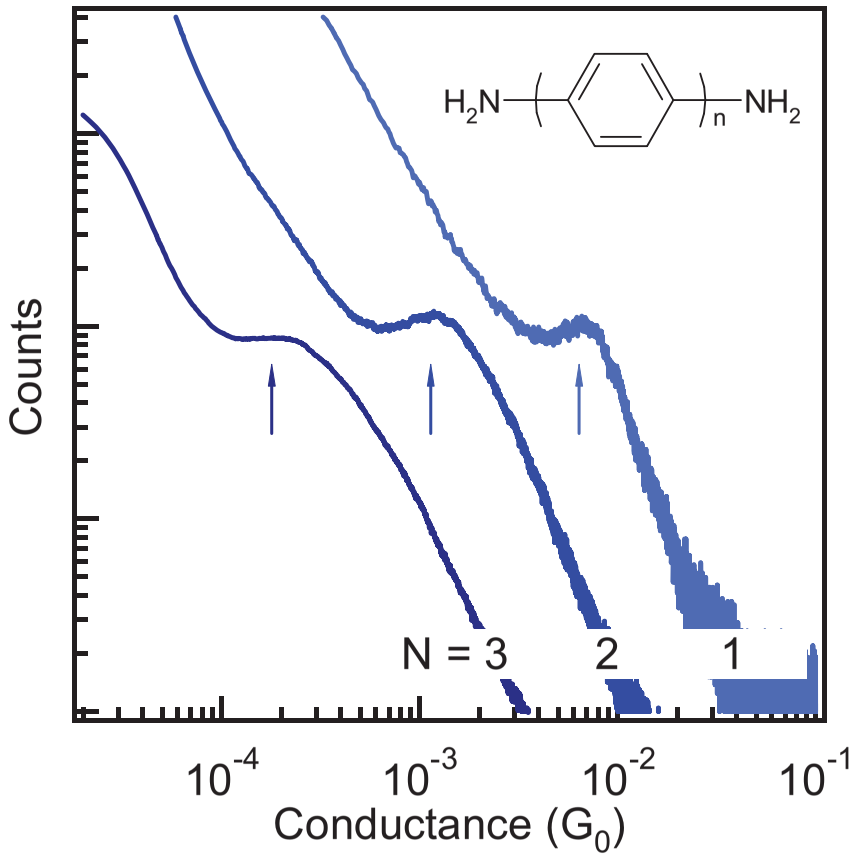
N: Phenyl Chains Attempted

1 

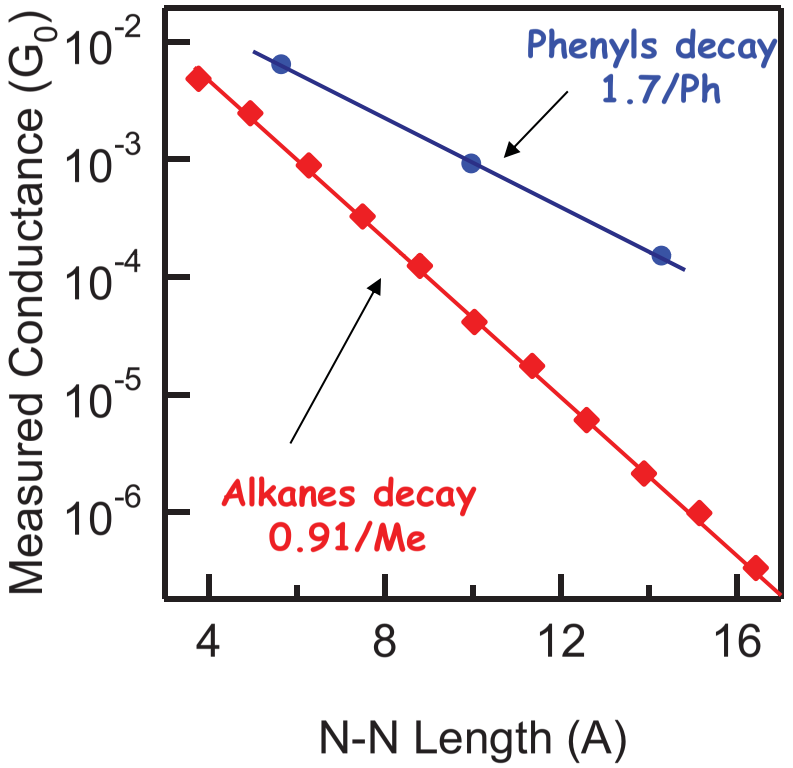
2 

3 

Conductance vs Length



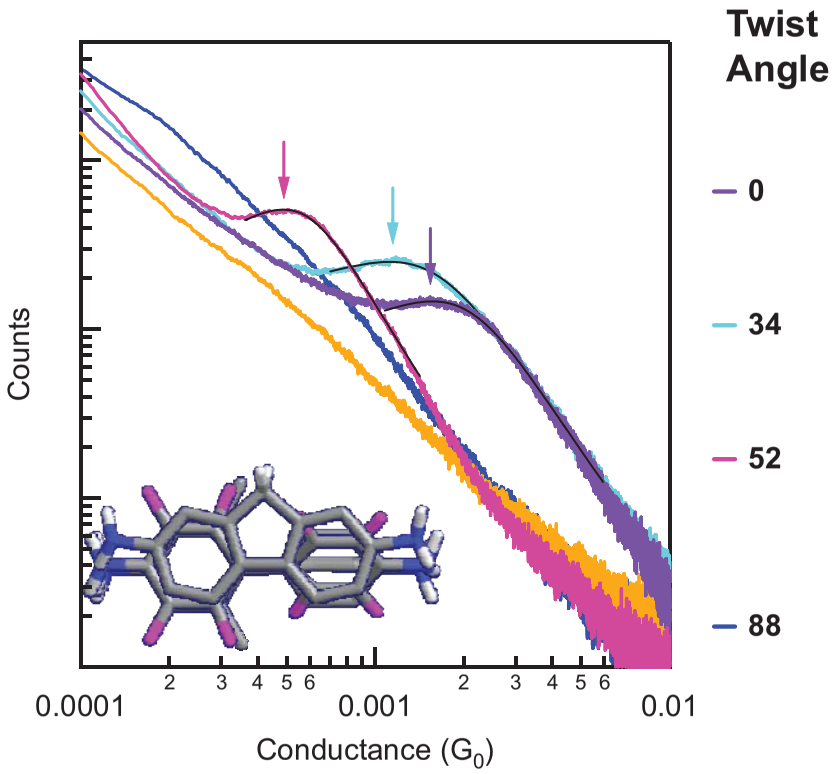
Data offset vertically for clarity

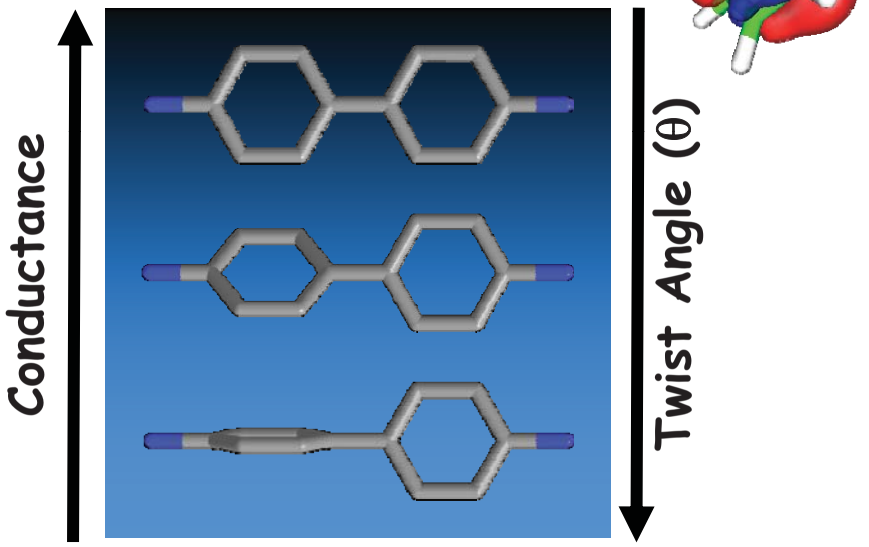


- Conjugated better than saturated
- We are measuring single molecule conductance.

What Can We Learn With Amine Links?

A Study of Biphenyls: Conductance vs Conformation



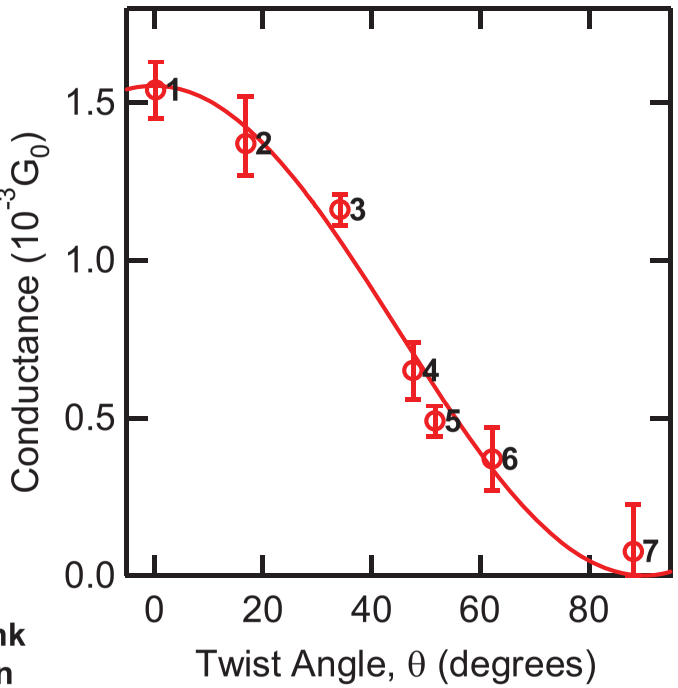


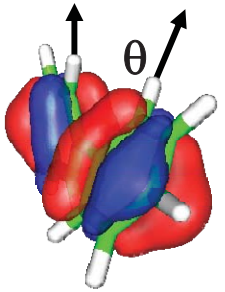
Twist Angle are from calculations

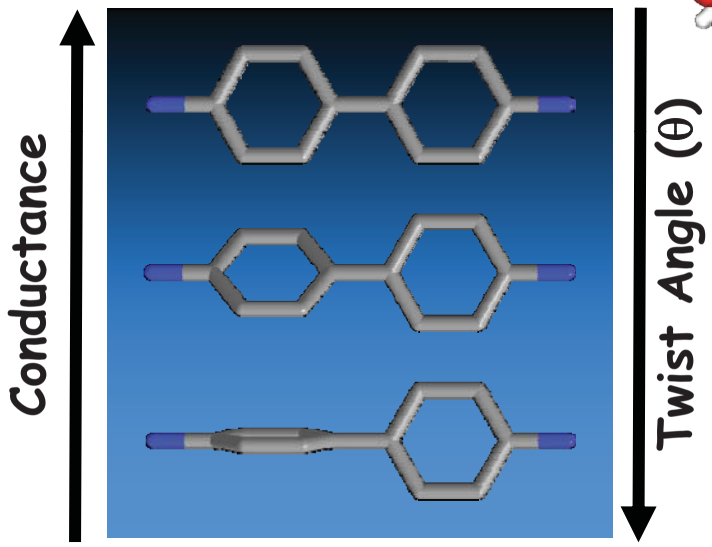
(L. Venkataraman, J. Klare, M. Hybertsen, C. Nuckolls, M. Steigerwald, Nature 2006)

What Can We Learn With Amine Links?

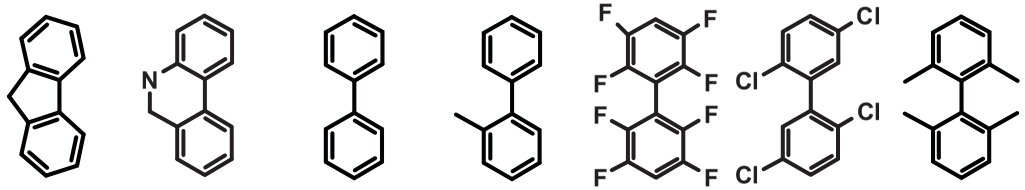
A Study of Biphenyls: Conductance vs Conformation







Amine Link not shown

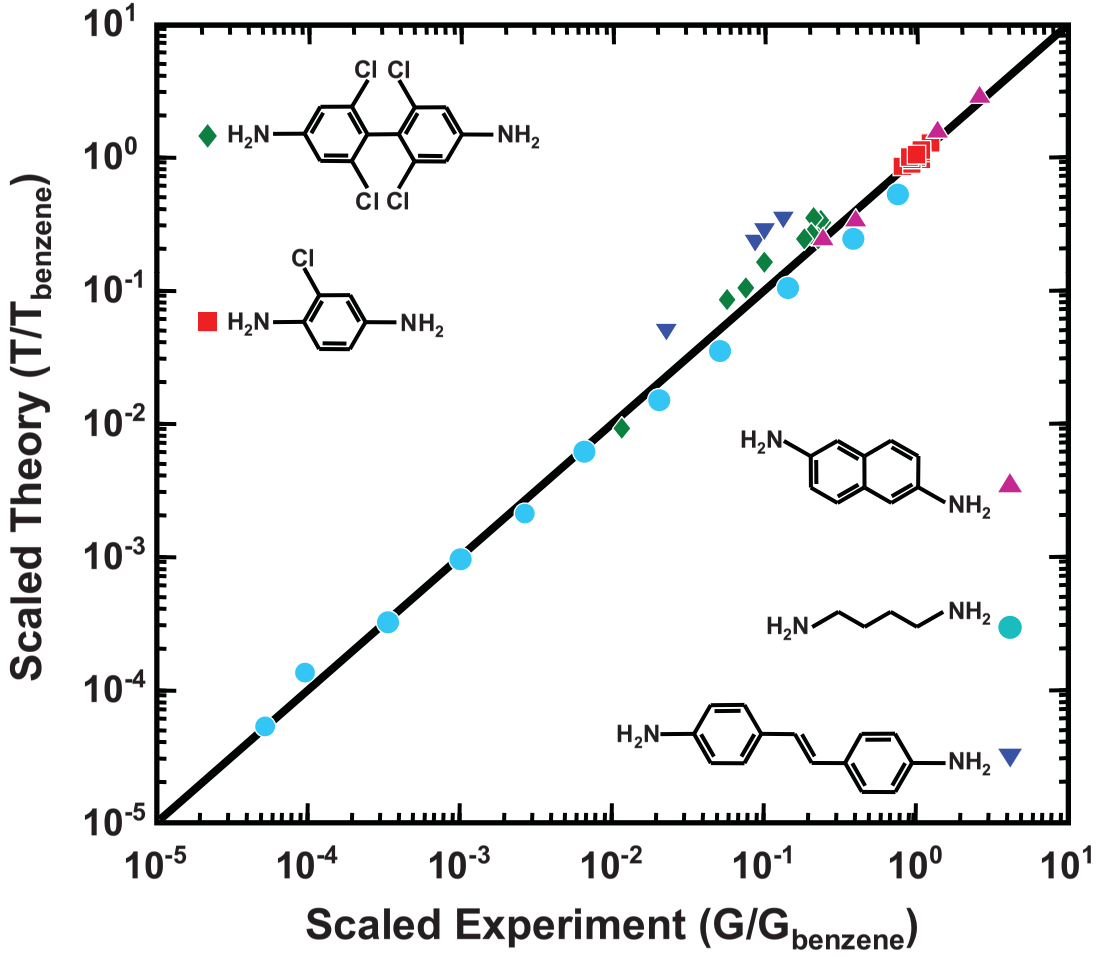


Cosine square dependence measured

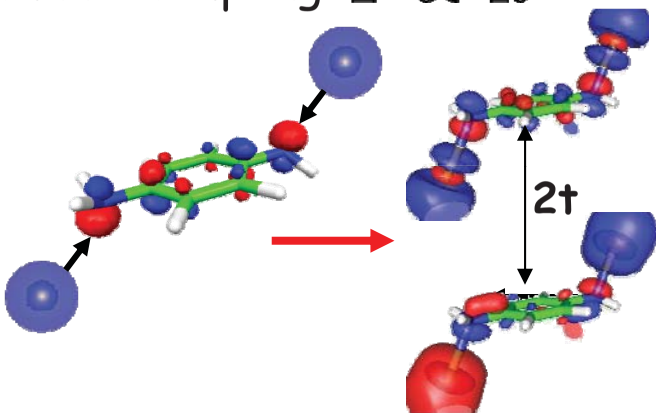
(L. Venkataraman, J. Klare, M. Hybertsen, C. Nuckolls, M. Steigerwald, Nature 2006)

Structure-Conductance Relation

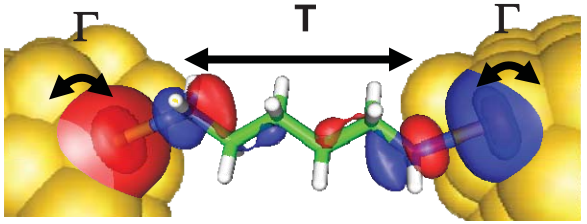
Calculated tunnel coupling vs measured conductance



Use an Au_1 cluster to obtain tunnel coupling $T \propto 4t^2$



Trends show that G is roughly the same for all molecules



41 molecules shown here

M. Hybertsen et al, J. Phys. Cond. Matter 2008

Outline

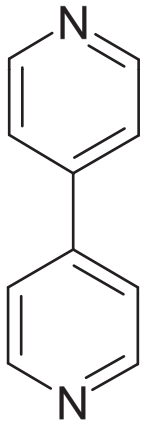
1. Experimental Method

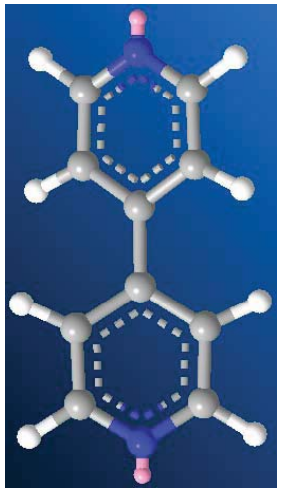
2. Conductance Measurements with Amines

3. Conductance & Mechanics: Switching in Bipyridine

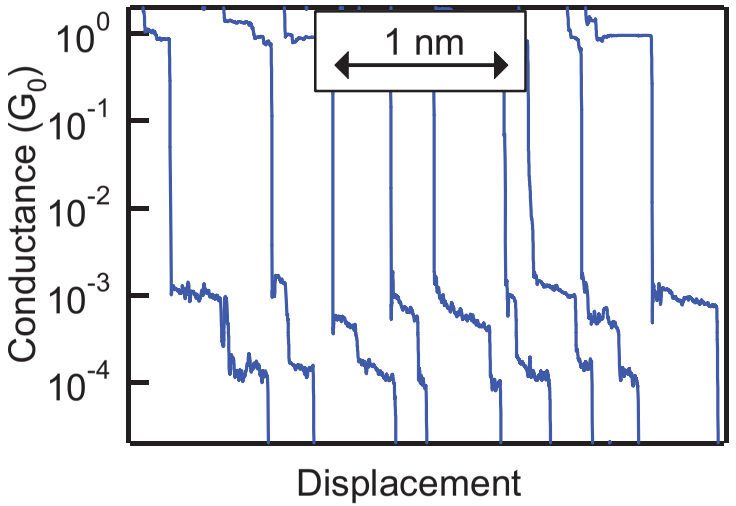
Functionality From a Molecule?

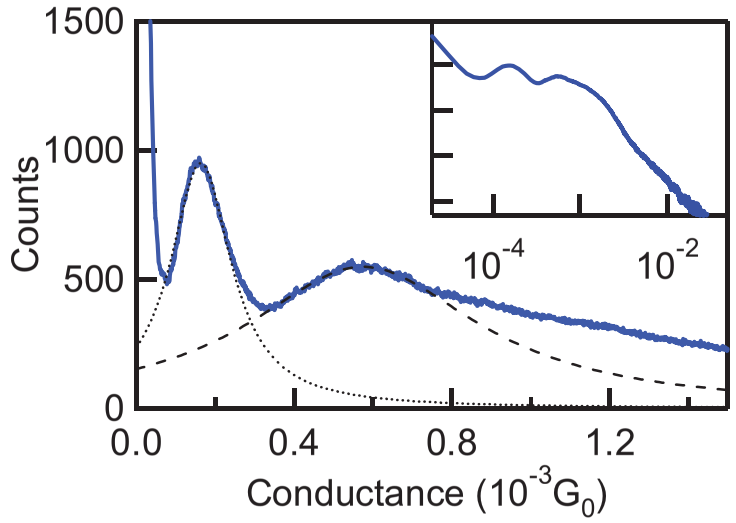
Bipyridine:
A Variation on the Amine





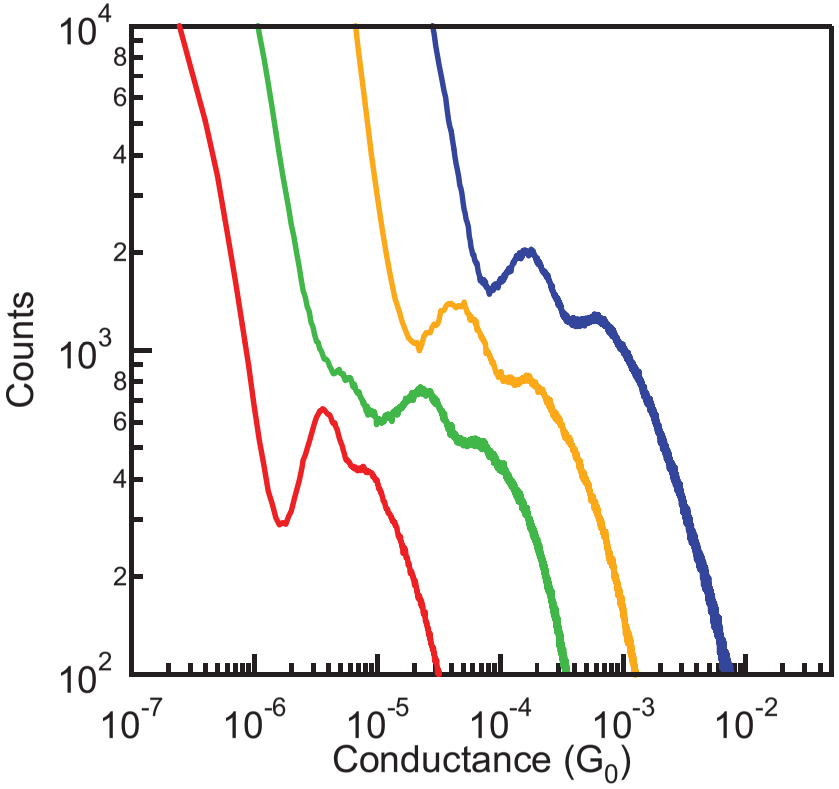
One molecule with two conducting states

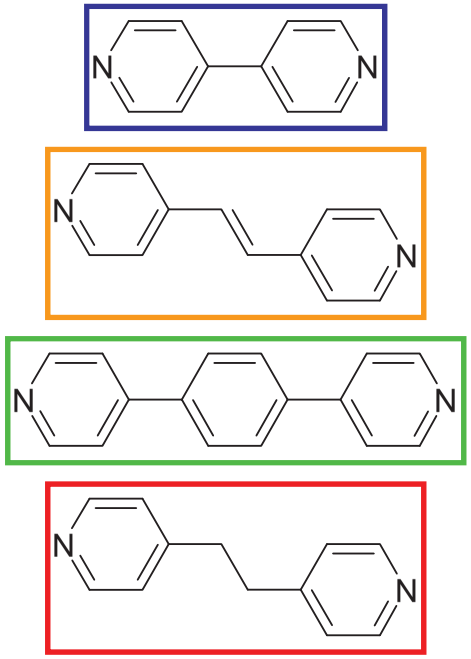




(Quek, Kamenetska et al, Nature Nanotechnology 2009)

Are The Two Peaks Due To Pyridine Link?





Bipyridine

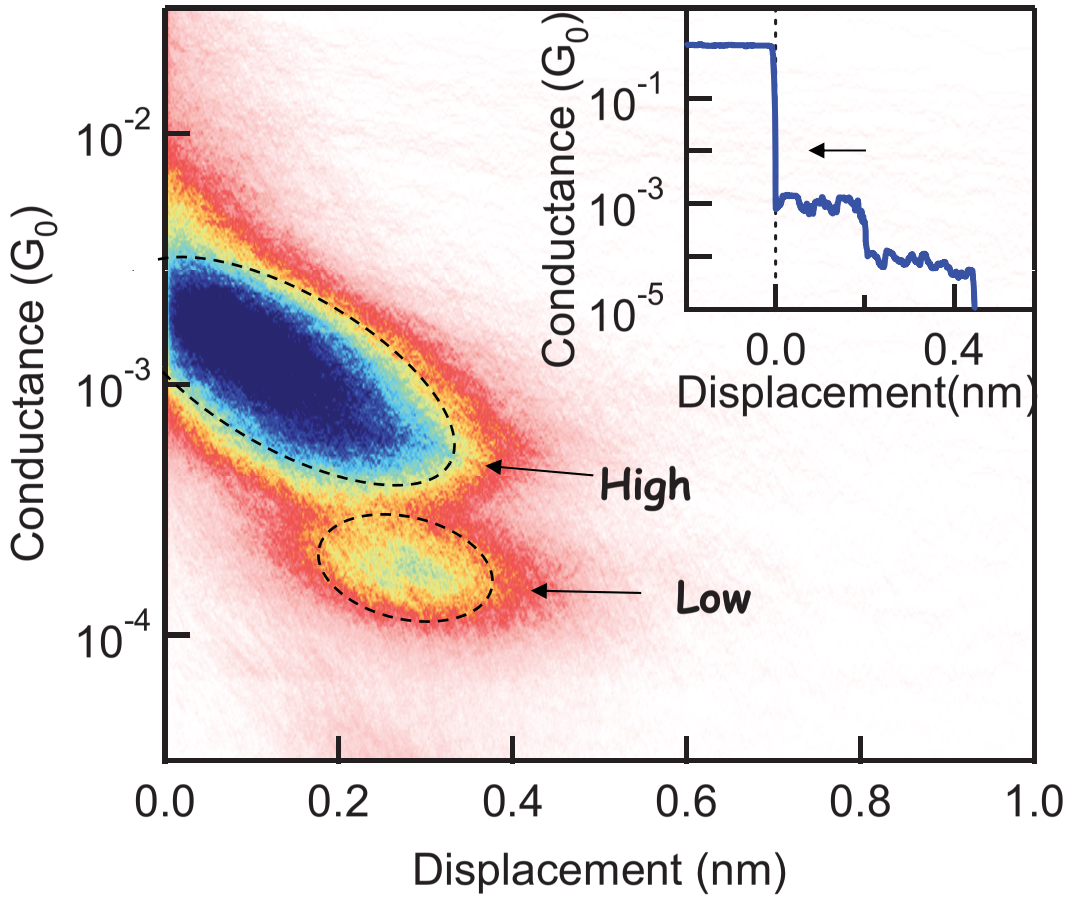
Pyridine-Ethylene-Pyridine

Terpyridine

Pyridine-Ethane-Pyridine

Yes, two conducting states are due to the pyridine link.

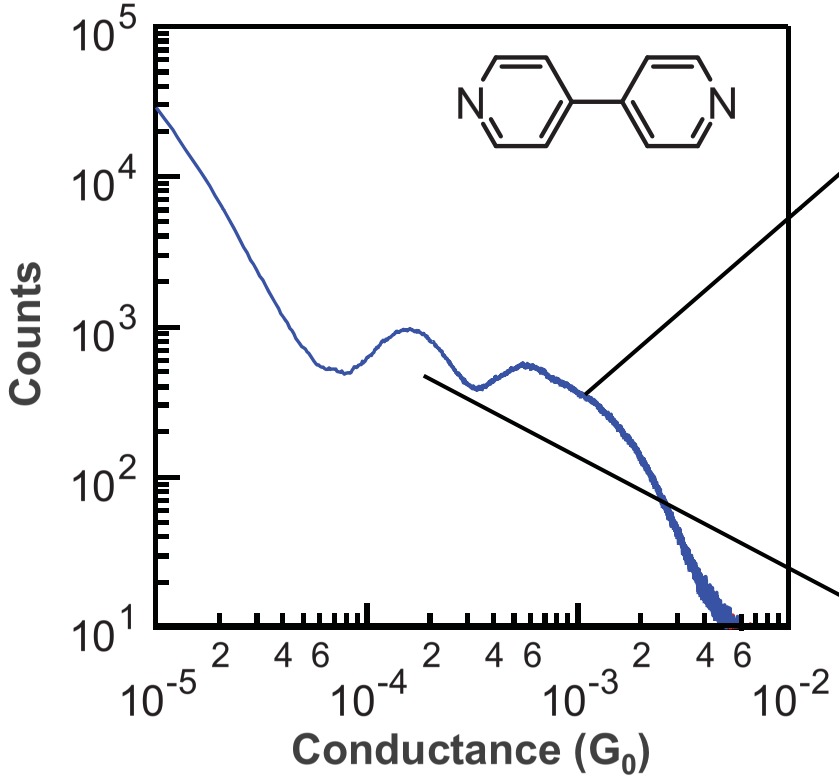
2D Histograms from Bipyridine Data

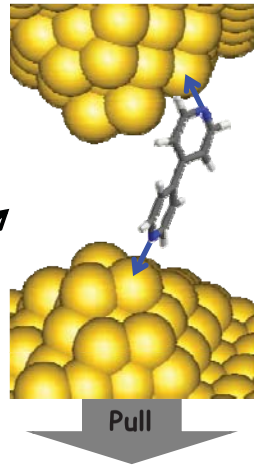


Low conductance follows high conductance on junction elongation

(Quek, Kamenetska et al, Nature Nanotechnology 2009)

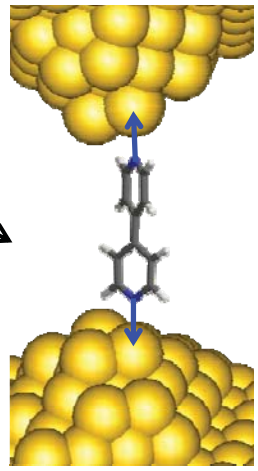
Hypothesis: Two Contact Geometries





Junction forms with C-N-Au angle smaller than 180 degrees.

Au is better coupled to the molecular π-system, giving a higher conductance

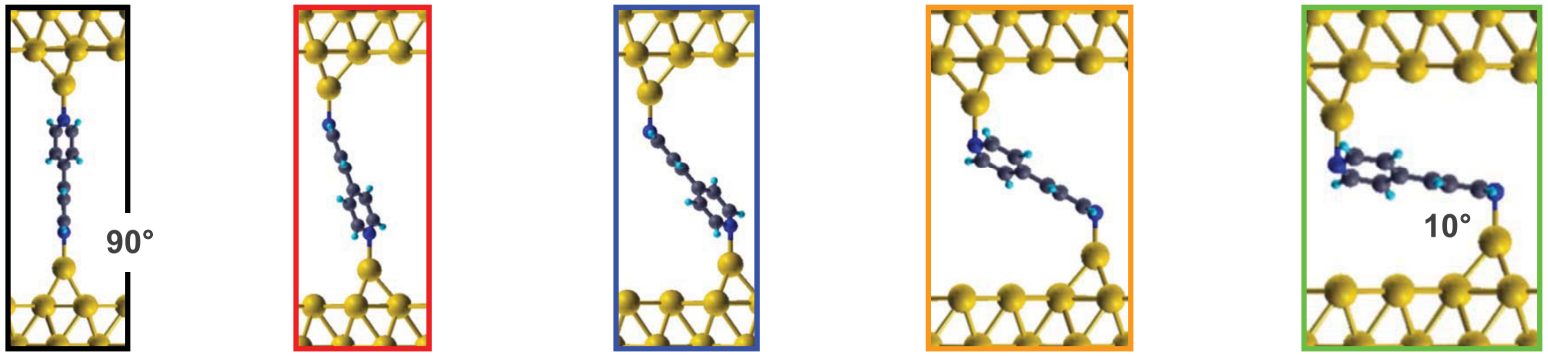


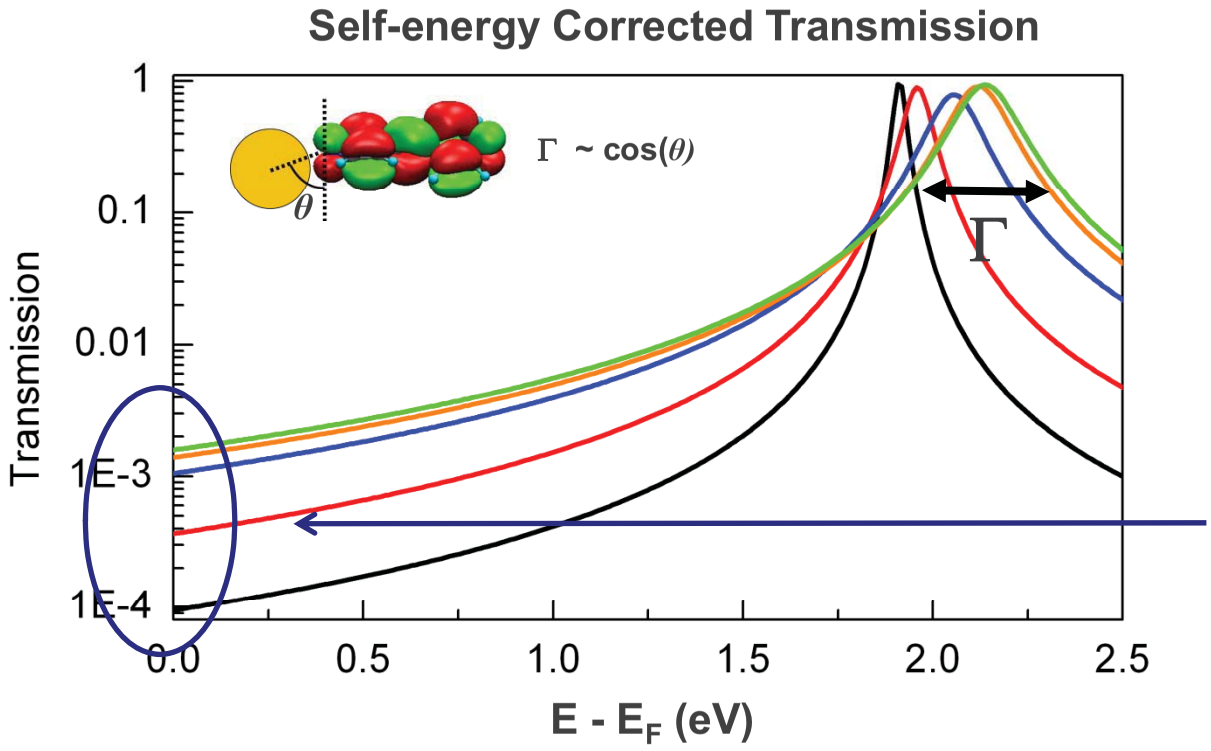
On pulling, molecule becomes vertical in the junction.

Au is not well coupled to the molecular π-system. This results in a lower conductance

(Quek, Kamenetska et al, Nature Nanotechnology 2009)

BiPy Transmission Sensitive to Geometry



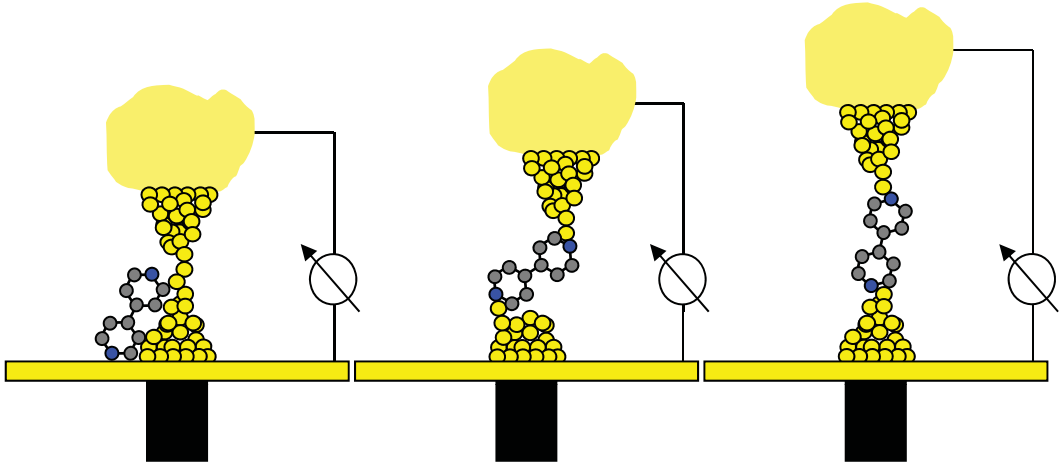


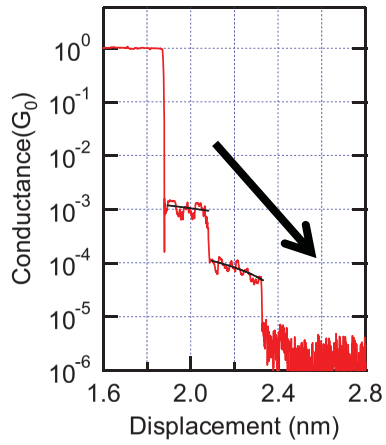
- LUMO dominates $T(E_F)$
- Large correction (~ 1 eV)
- Coupling of pi system to Au enhanced w/ angle (w/ modest binding energy cost)
- Conductance increases by 10x, covers 'Low G' & 'High G' expt'l range

(Quek, Kamenetska et al, Nature Nanotechnology 2009)

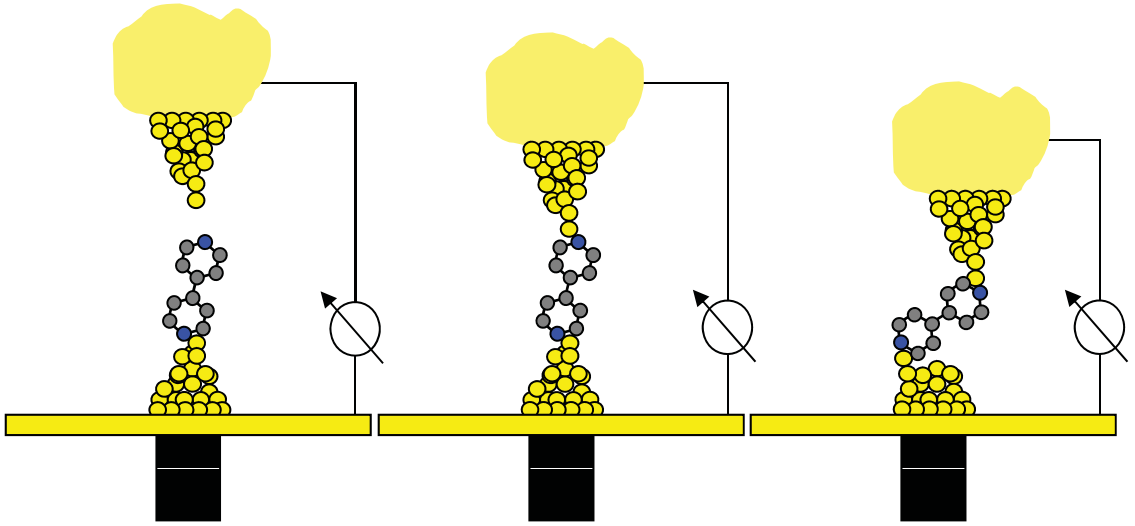
Two Types of Measurements

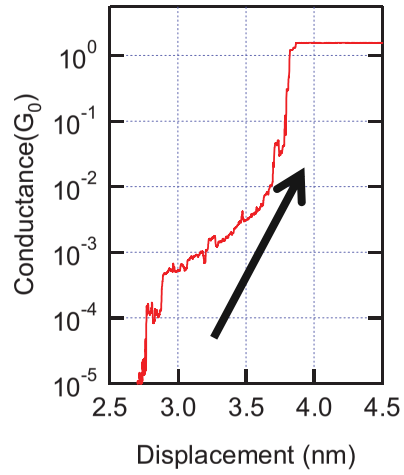
Pulling





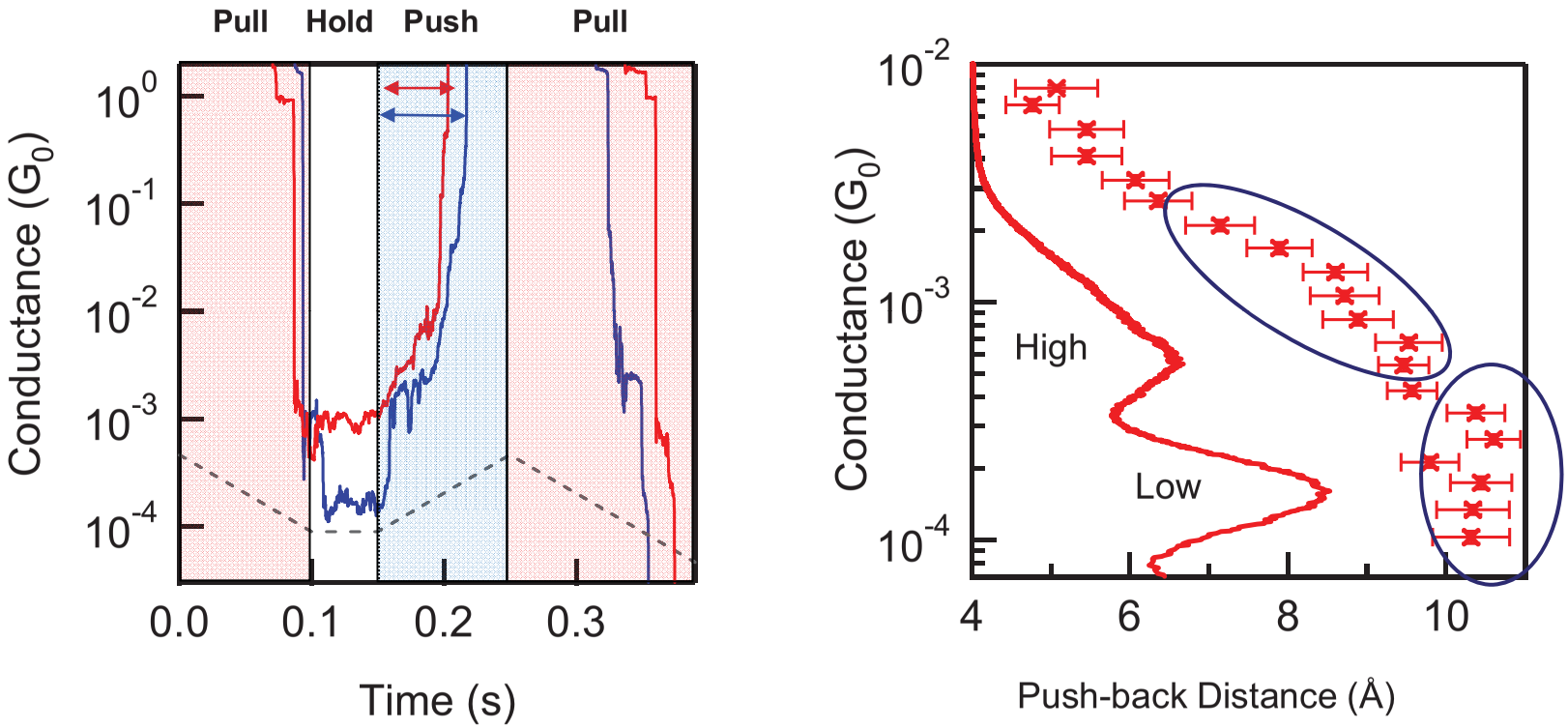
Pushing





(Quek, Kamenetska et al, Nature Nanotechnology 2009)

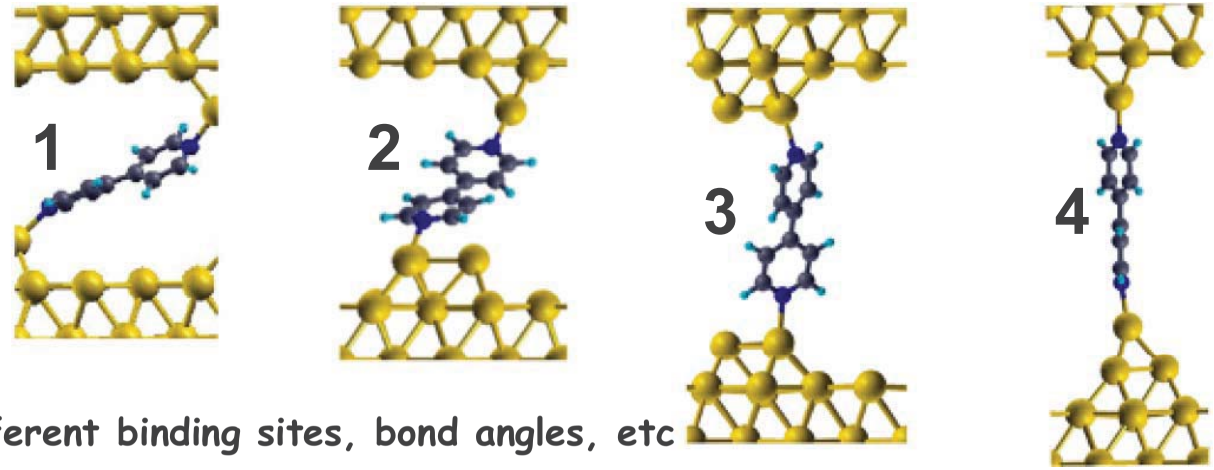
Au-Au Separation & Conductance



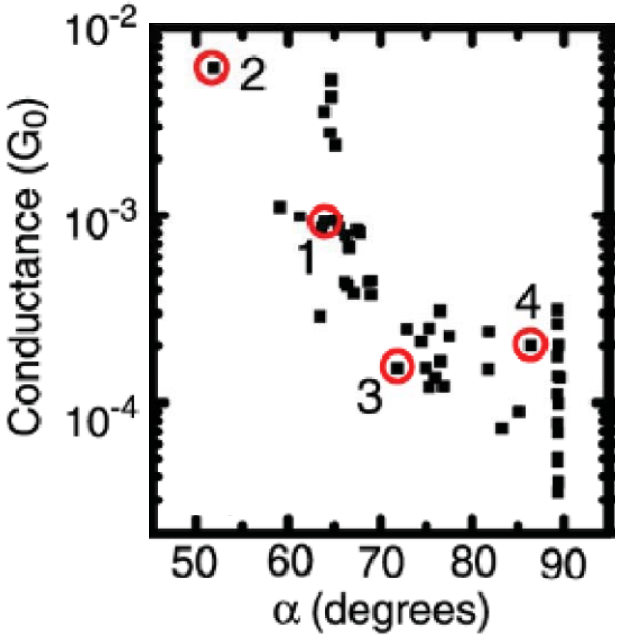
Pull – push – pull a molecular junction. Use the "push-back" distance to correlate Au electrode separation to junction conductance.

(Quek, Kamenetska et al, Nature Nanotechnology 2009)

Structure-Conductance: 55 Junctions



Different binding sites, bond angles, etc



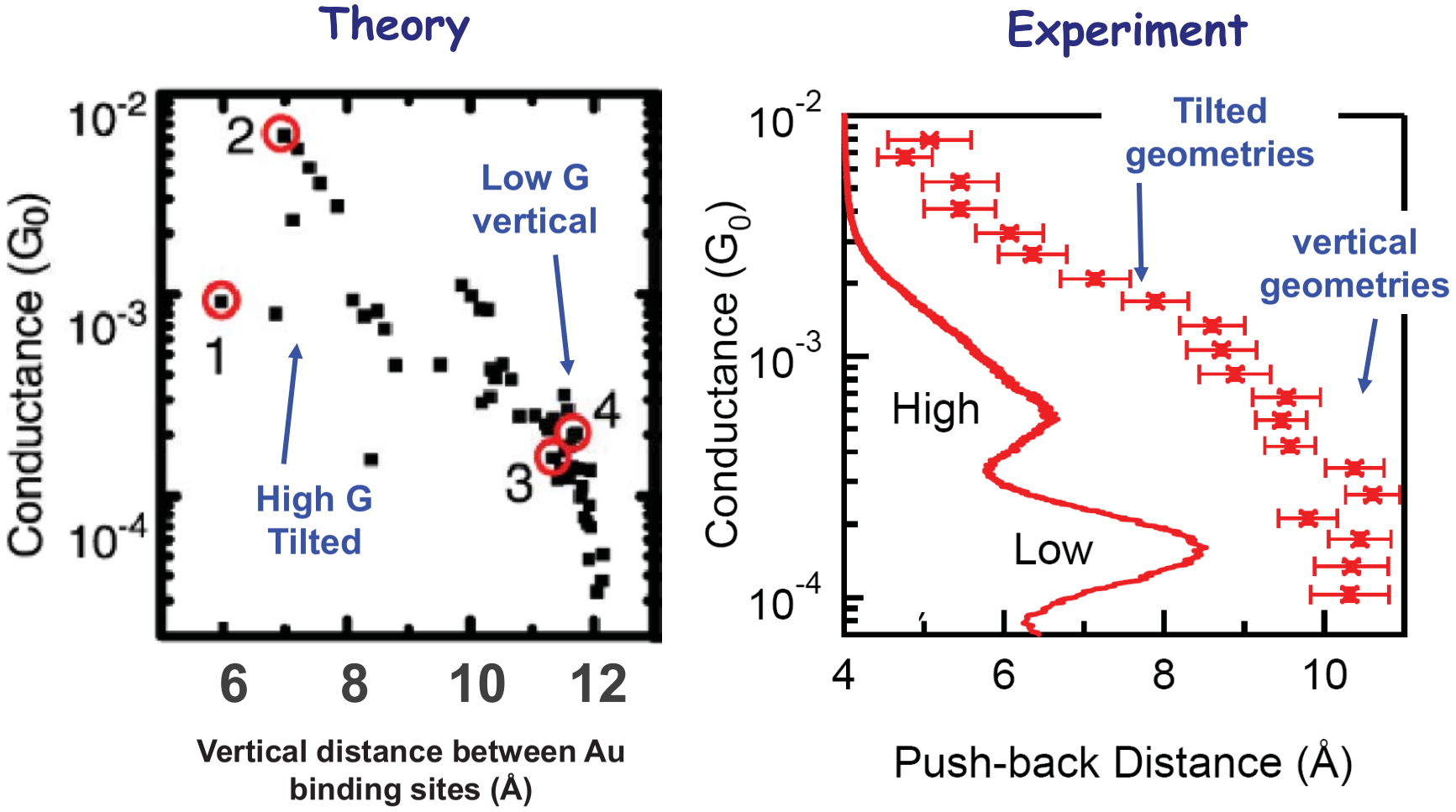
Experimental Conductance Range

'High G' (5.4×10^{-4} G_0)

'Low G' (1.6×10^{-4} G_0)

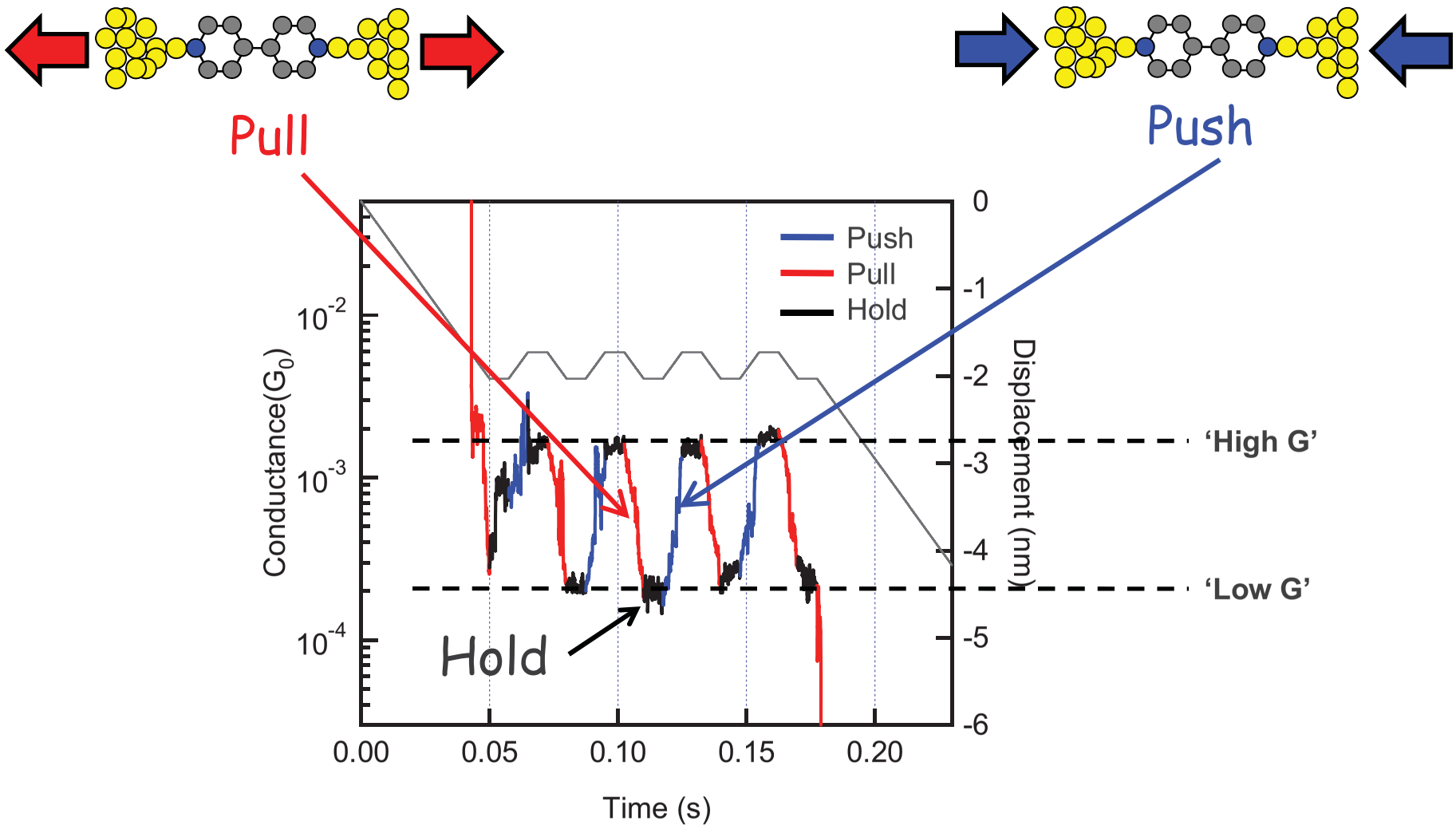
(Quek, Kamenetska et al, Nature Nanotechnology 2009)

Quantitative Comparison: Theory & Exp.



(Quek, Kamenetska et al, Nature Nanotechnology 2009)

Reversible, controllable mechanical switching!



Toggle between low & high G by mechanical manipulation

(Quek, Kamenetska et al, Nature Nanotechnology 2009)

Conclusions & Open Questions

1. We can measure low bias transport accurately using amine-linked molecules.

2. Measurements agree with "corrected" DFTcalculations.

3. We show some functionality from molecular devices, achieved due to changes at the contact.

4. Open questions relating to theory:
   a) Understanding bias dependent transport measurements
   b) Correlating mechanics to transport
   c) Understand level alignment in molecular systems

Thanks

Funding

NSEC – NSF/NYSTAR
NSF- Career
Columbia – RISE
ACS-Petroleum Research Fund
Packard Foundation
DOE-EFRC





Chemistry:
Jennifer Klare
Young Suk Park
Adam Whalley
Colin Nuckolls
Mike Steigerwald
Severin Schneebeli
Rachid Skouta
Ronald Breslow

Applied Physics:
Masha Kamenetska
Michael Frei
Jonathan Widawsky
Sriharsha Aradhya
Valla Fatemi

Theory:
Jeffrey Neaton
Su Ying Quek
Mark Hybertsen
Max Koentopp
Hector Vazquez