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**Third Stig Lundqvist Conference on
Advancing Frontiers of Condensed Matter Physics:**

"Fundamental Interactions and Excitations in Confined Systems"

11 - 15 August 2003

Single Molecule Electronics

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Tempe, AZ 85287-1504
U.S.A.**

Single Molecule Electronics

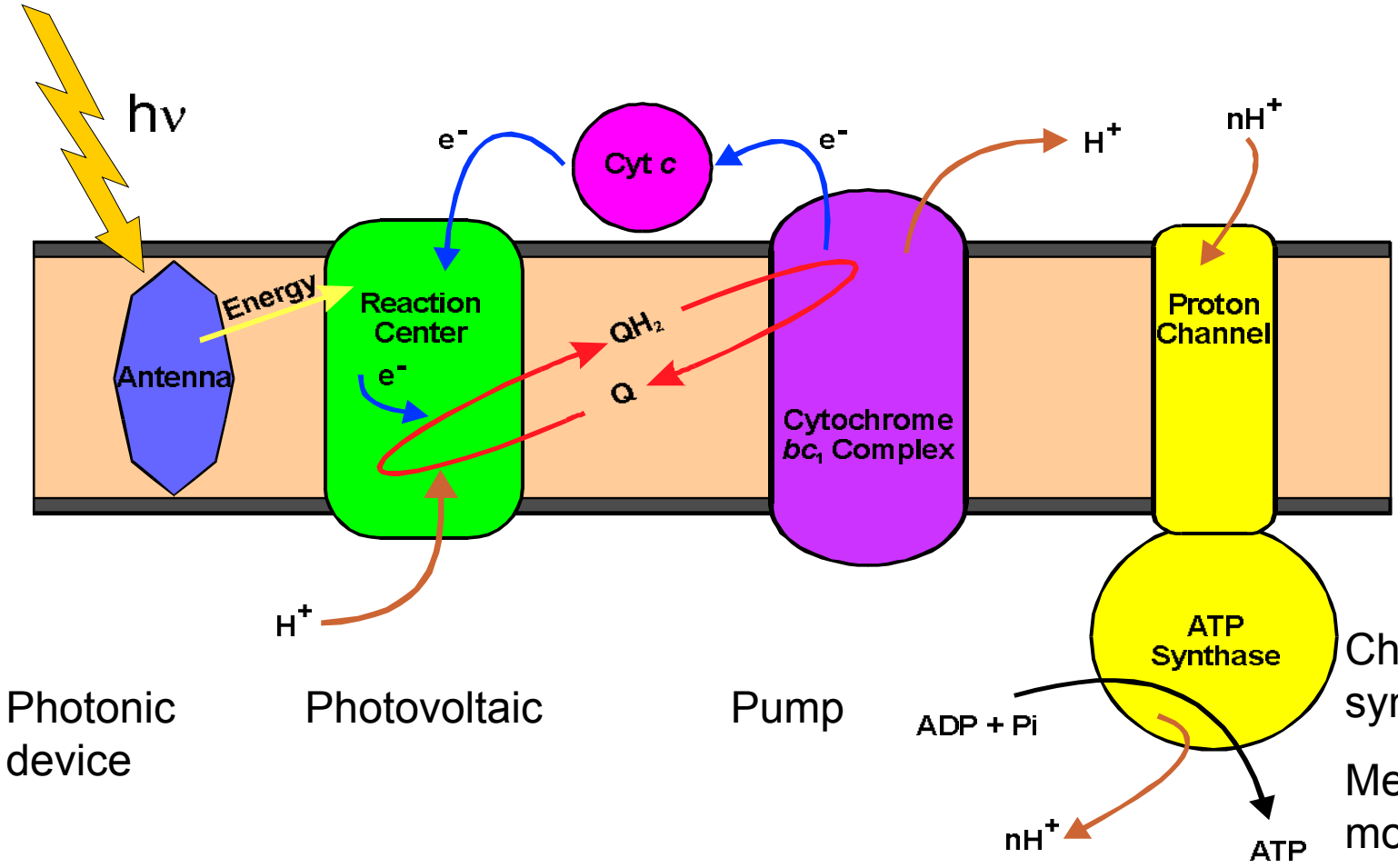
Stuart.Lindsay@asu.edu

1. Motivation and background
2. Bonded contacts to single alkane molecules
3. Quantitative agreement and Coulomb Blockading
4. Stochastic switching and labile bonds
5. More complex molecules

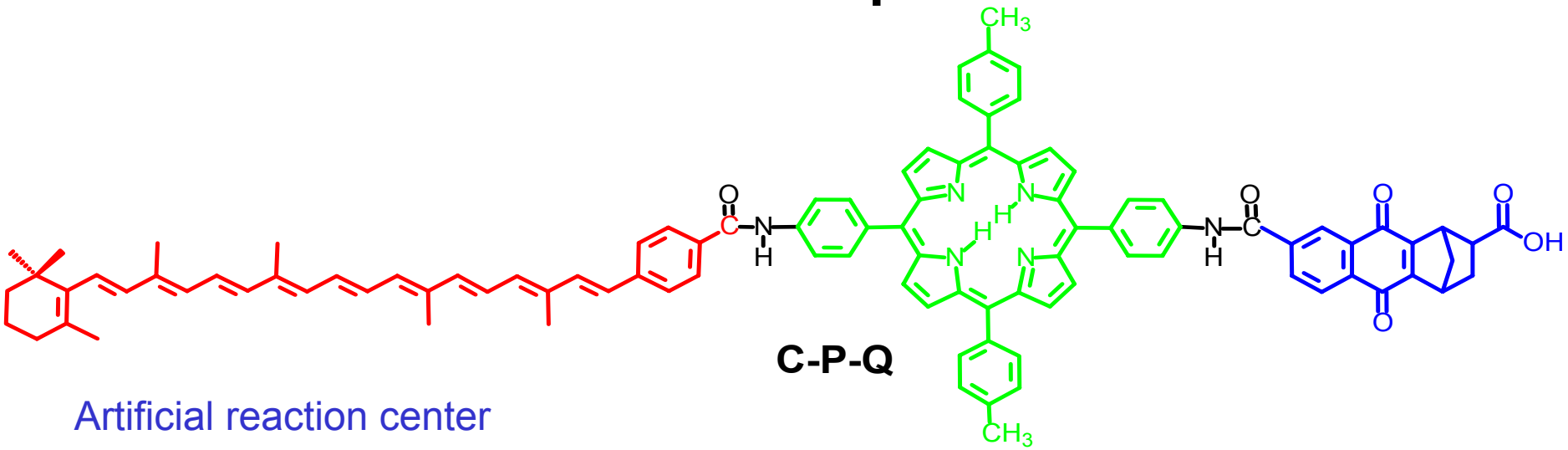
Photosynthesis and single molecule electronics

The ASU-Physics-Chemistry-Engineering-Motorola group:

How Bacterial Photosynthesis Works

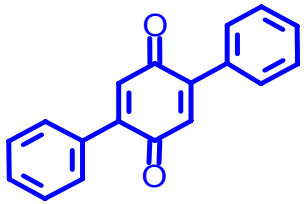


Components of the Artificial Proton Pump



C-P-Q

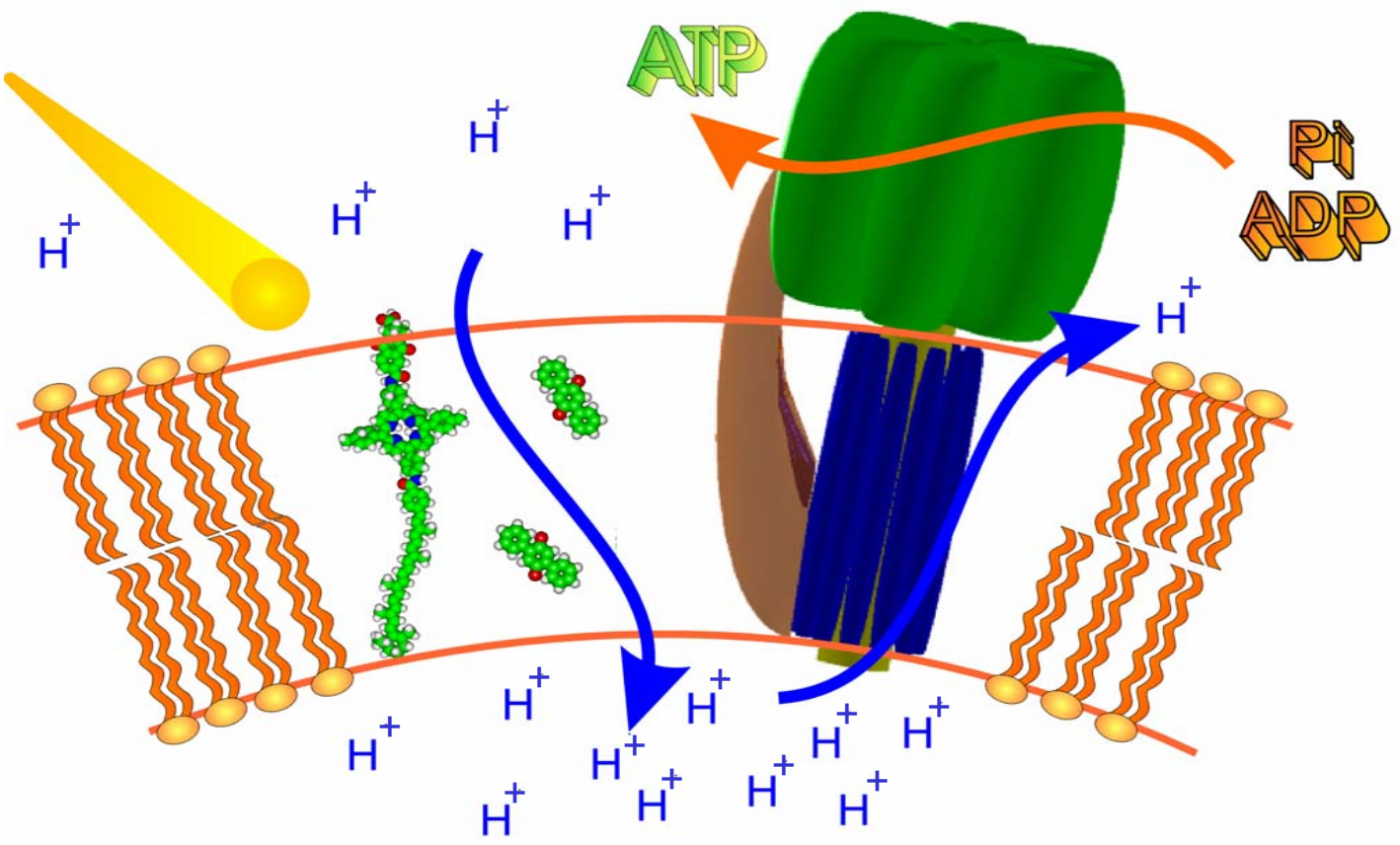
Artificial reaction center



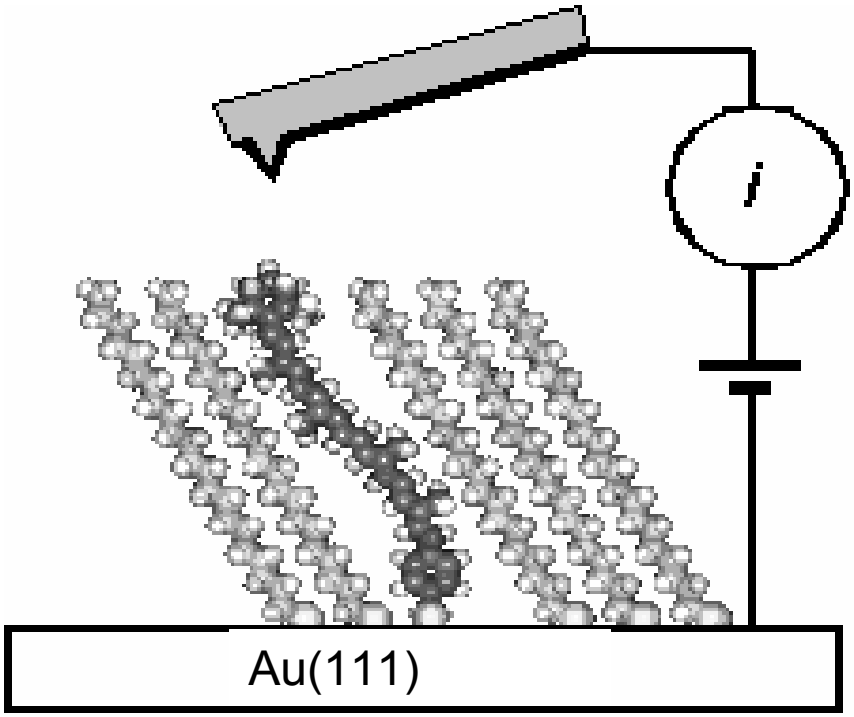
Qs

Proton shuttle quinone

Artificial Biological Power Plant



Conducting AFM of reaction center components (J. Phys. Chem B**103**, 4006, 1999)



- Pt coated cantilever
- 1V/nA, 0.01pA/√Hz noise
- N_2 Environment
- Image in freshly distilled toluene

The Grim Truth:

- Poor reproducibility
- Only the poorest contact with theory: How many molecules? Contacts to the molecules? Position of Fermi Level?…
- Decanethiols/gold 10^{5} - $10^{21}\Omega$

The molecule-metal contact problem

Many Few-Molecule-Devices have been made but measurements/theories generally do not agree:

For example, DNA is:

AN INSULATOR *(D. Dunlap et al. PNAS **90**, 7652, 1993)*

A SEMICONDUCTOR *(D. Porath et al, Nature **403**, 635, 2000)*

A CONDUCTOR *(Fink and Schoenberger, Nature **398**, 407,1999)*

A SUPERCONDUCTOR *(A.Y. Kasumov et al. Science **291**, 280, 2001)*

Can we measure the electronic properties of a single simple molecule
in a well-defined environment?

Can we understand the results?

2. Theoretical Definitions

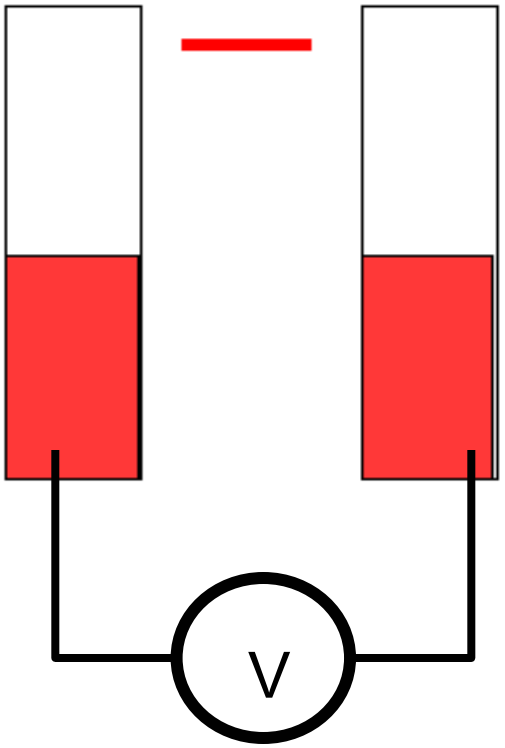
1. Simple Barrier Model
2. Greens Function approach
3. Transport involving redox centers

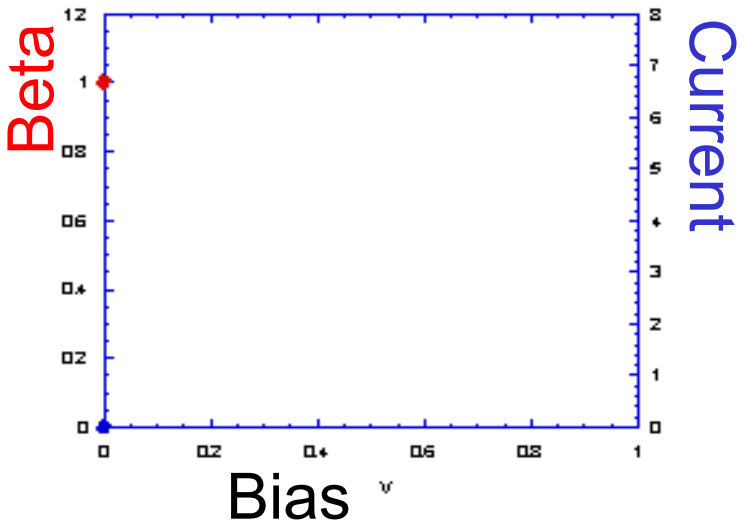
β(V) and I(V) are related:

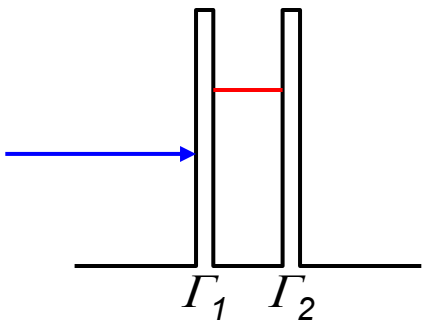
$$\beta \propto 2\sqrt{\frac{2m^*}{\hbar^2}\left(E-\frac{V}{2}\right)}$$

$$I = \frac{V}{h/2ne^2}\exp\left(-2\left[\sqrt{\frac{2m^*}{\hbar^2}\left(E \pm V/2\right)}\right]x\right)$$

Current and β for *E*=5eV

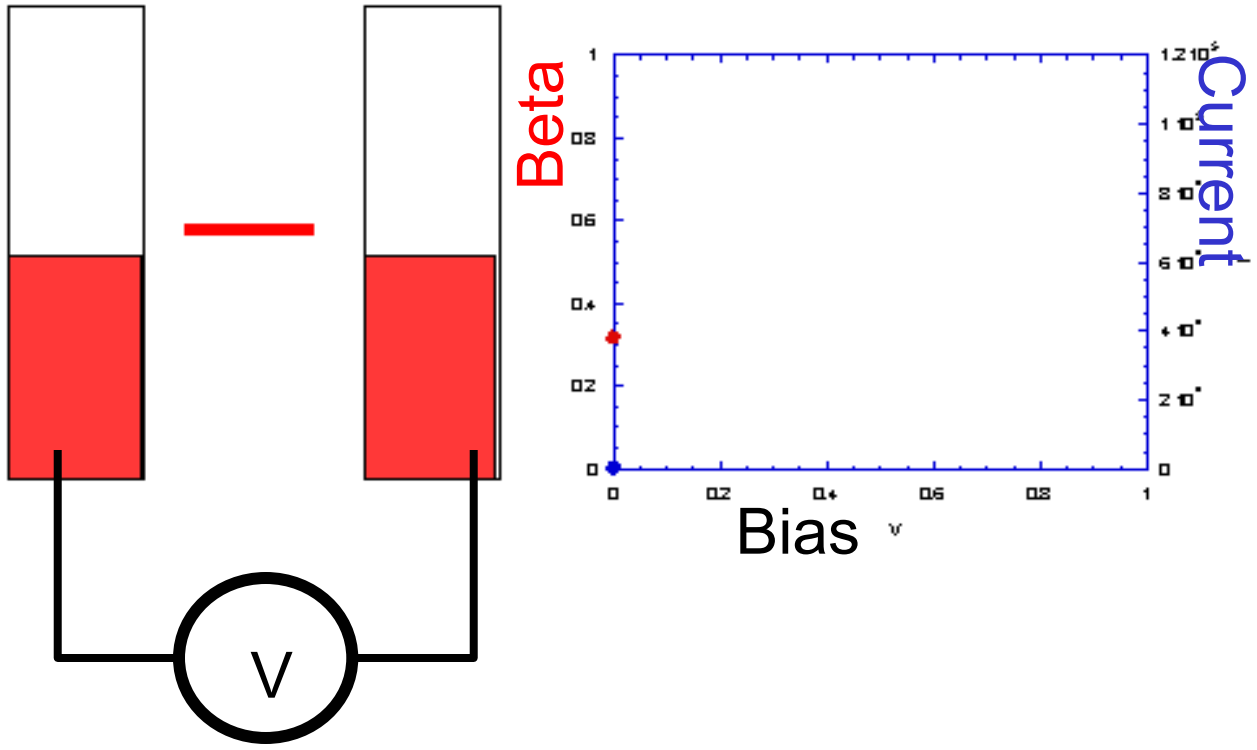






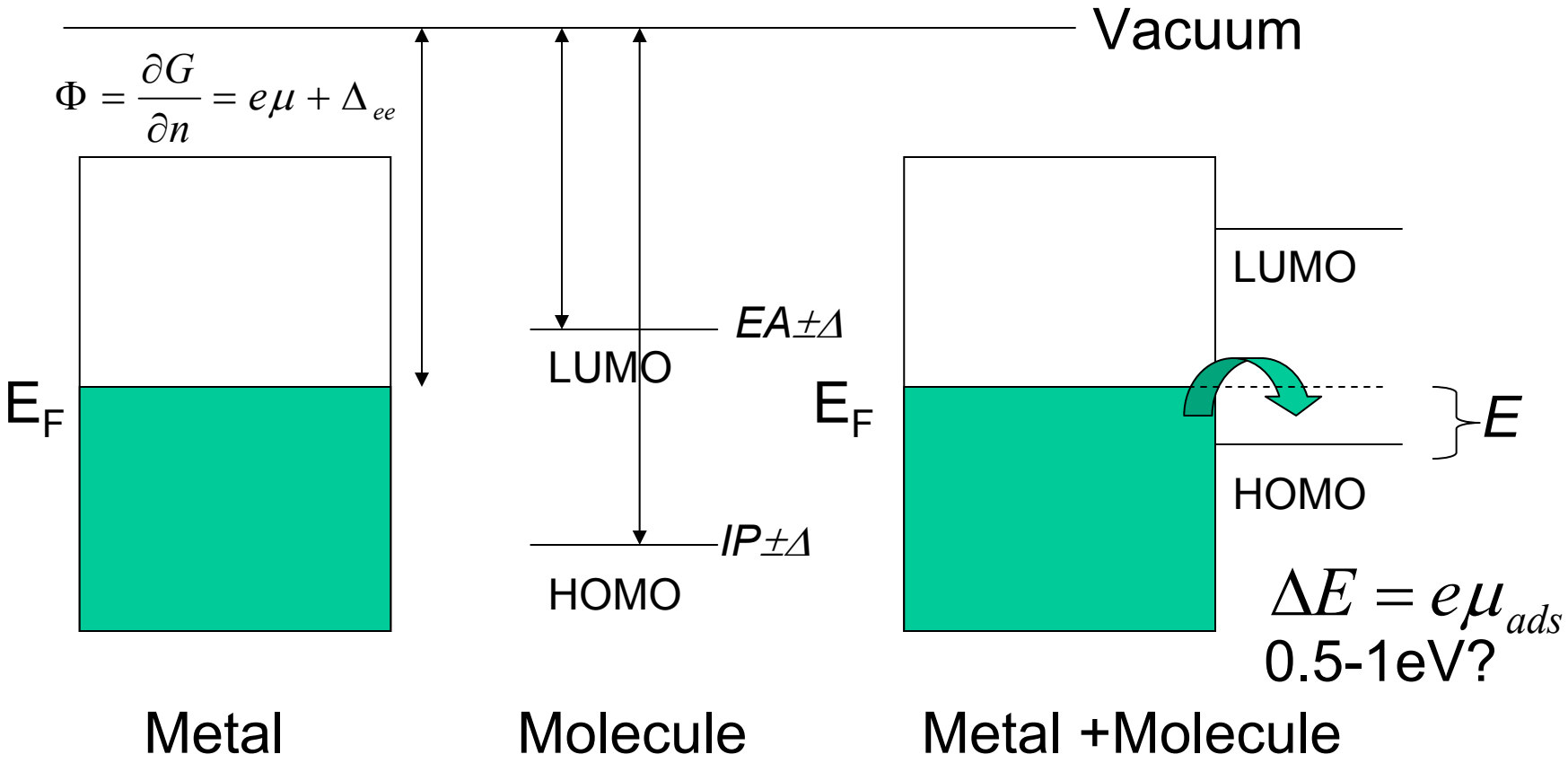
Model maps onto simple result for thin barriers, $\Gamma_1 \Gamma_2$

Current and β for *E*=0.5eV



Models Vs. Reality

Where is E_F?



In the absence of chemistry, ΔE tends to be half gap

Models Vs. Reality

Contacts

$$I(V) = \frac{2e^2}{h} \int T(E,V)\left[f(E - eV/2) - f(E + eV/2) \right]$$

System Green functions

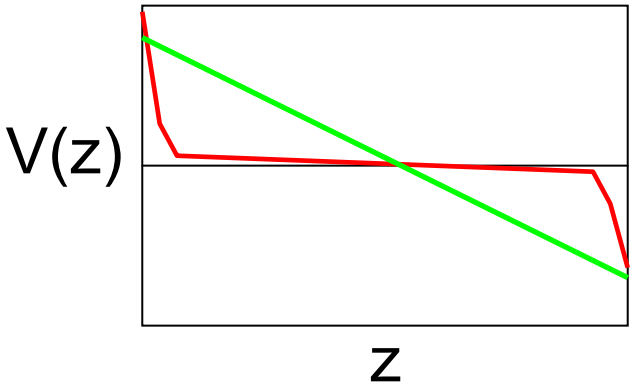
$$T(E,V) = tr\left(\Gamma_L \left(E - {eV}/{2} \right) G_M(E) \Gamma_R \left(E + {eV}/{2} \right) G_M^*(E) \right)$$

Electrode couplings

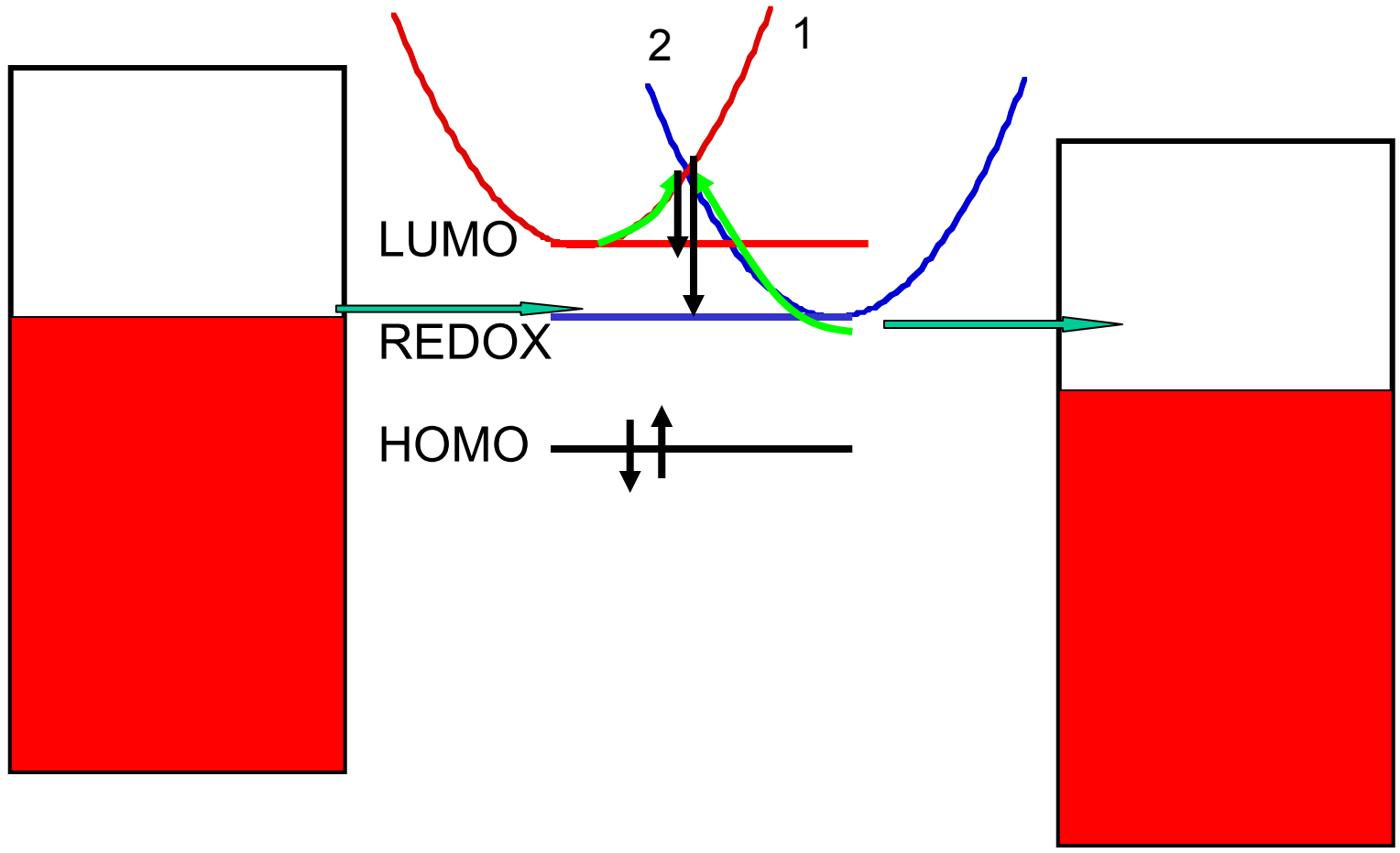
Exponentially sensitive to geometry

Models Vs. Reality

- Potential distribution not an issue for symmetric structures
- One electron approach ? Seems to work well for tunneling



Transport via redox center – role of thermal fluctuations

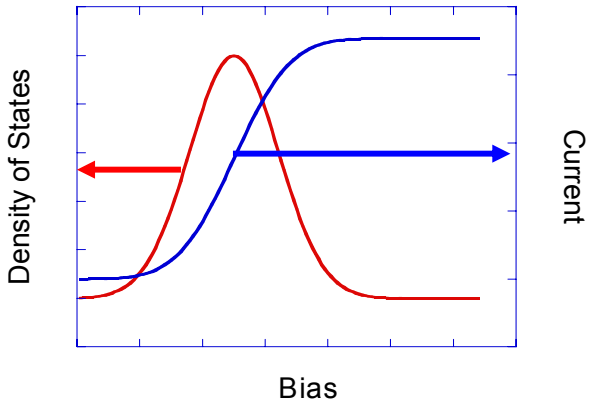


Environmental fluctuations lower transport barrier

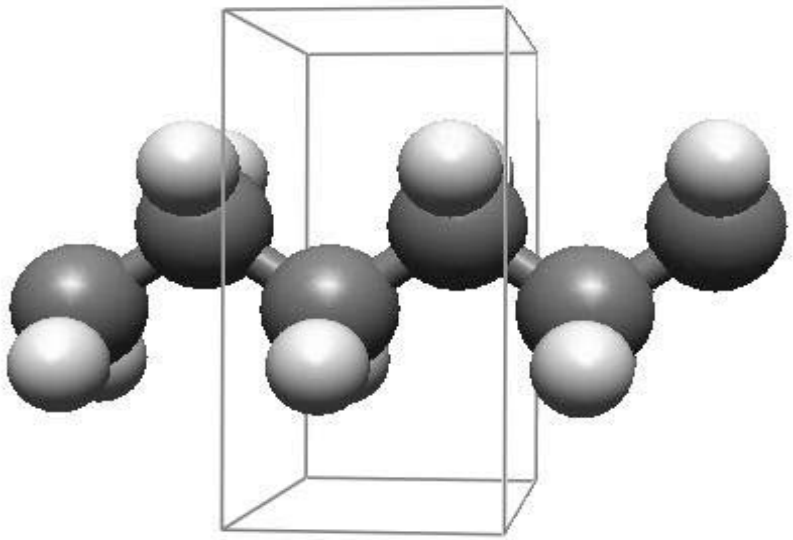
Transport via redox center – contribution to current

I-V determined by integrated DOS:

$$D_{OX} \approx \exp - \frac{\left(\lambda - E_0 - eV/2\right)^2}{4\lambda kT}$$



N-alkanes as a simple test case



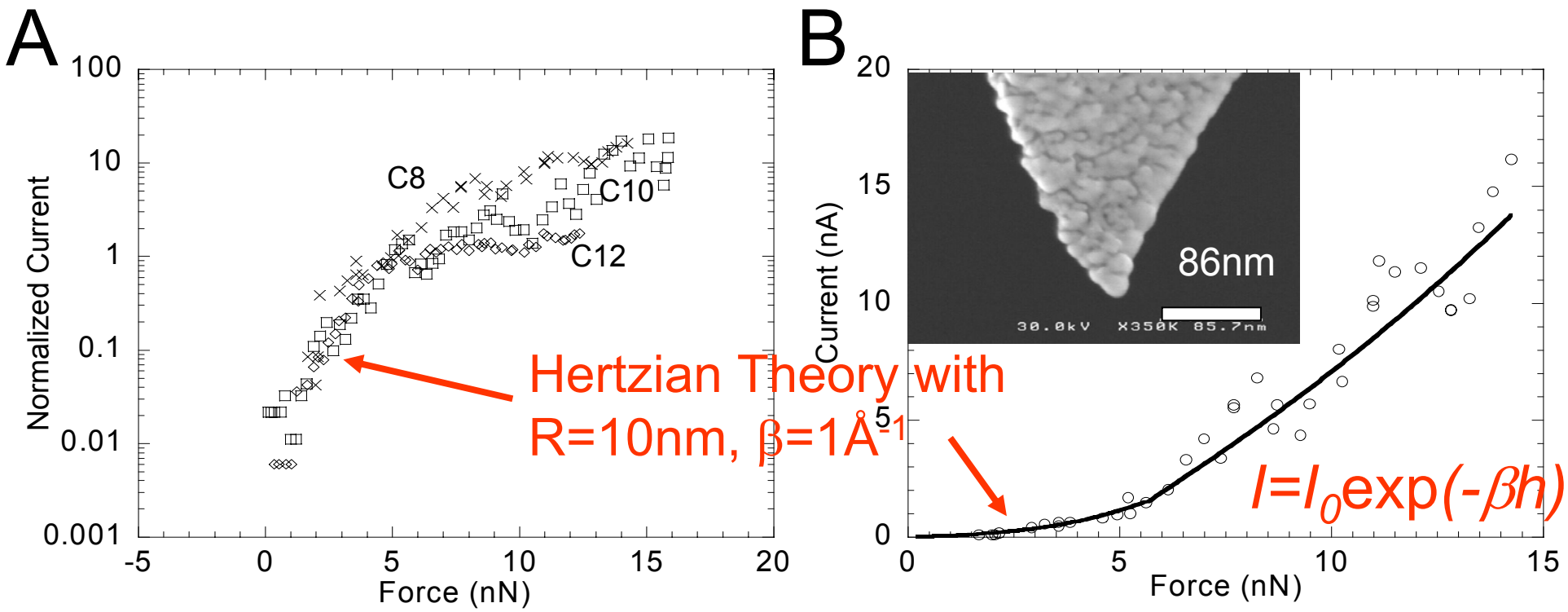
- *Well studied on electrochemical electrode surfaces*

Tunneling checklist
(mechanical contact)

Nanotechnology, ***13*** *5-14 (2002), Ultramicroscopy* ***92****, 67 2002*

- Exponential decay of current with distance 
- I(V) and β(V) should track X
- β(V) and β(0) should agree X
- Magnitude of I predicted by transport calculations? XX
- *Note effect of stress…..*

Contact force – Tunneling rate explained by film thickness

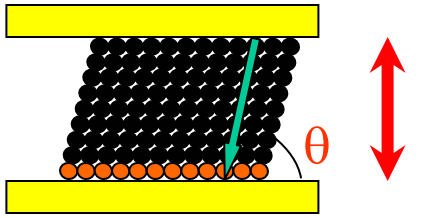


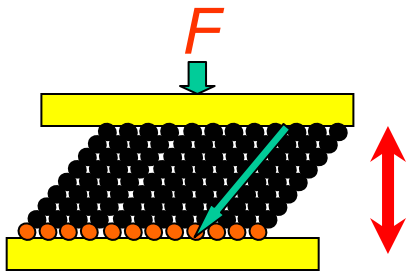
Result implies chain to chain tunneling

Stress dependence of tunneling

*Monolayers distort by tilting, 2 modes of transport (Slowinski et al.JACS **119** 11910)*

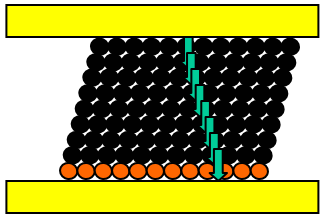
THROUGH BOND

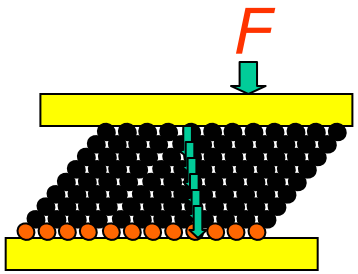




I≠F(h)

CHAIN TO CHAIN





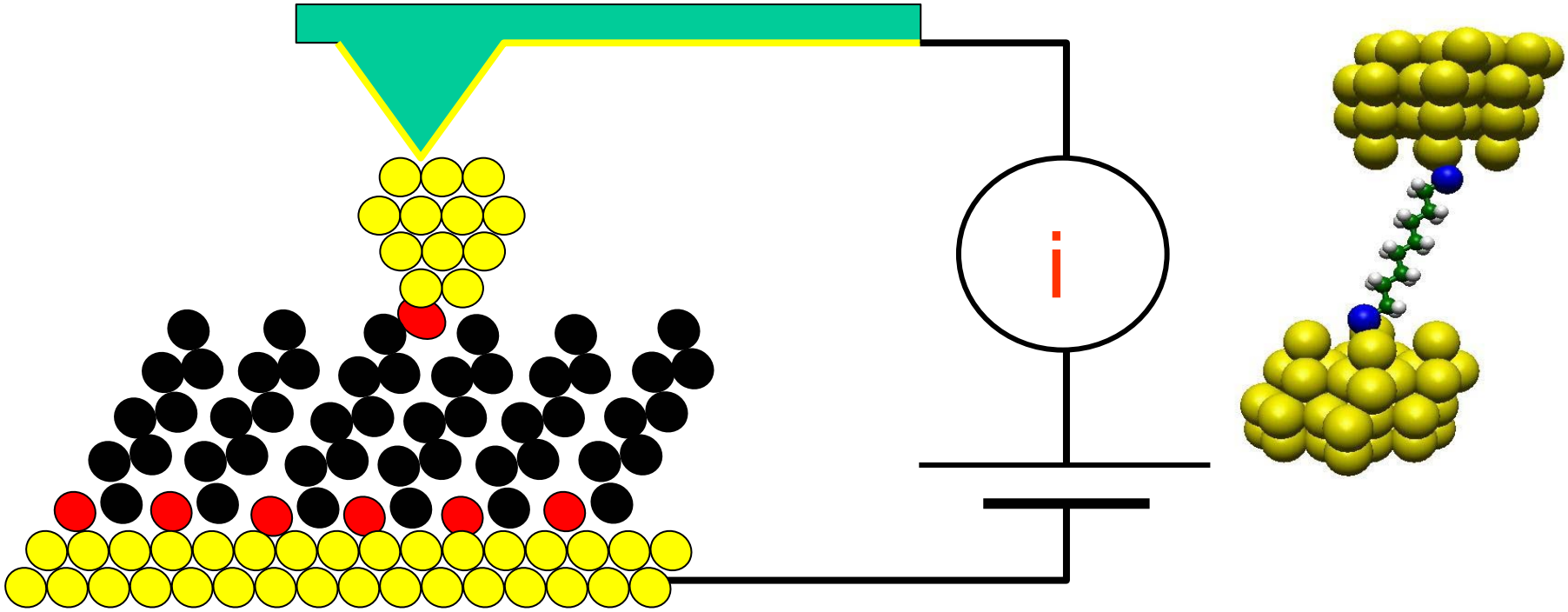
I=F(h)

Bonded Contacts

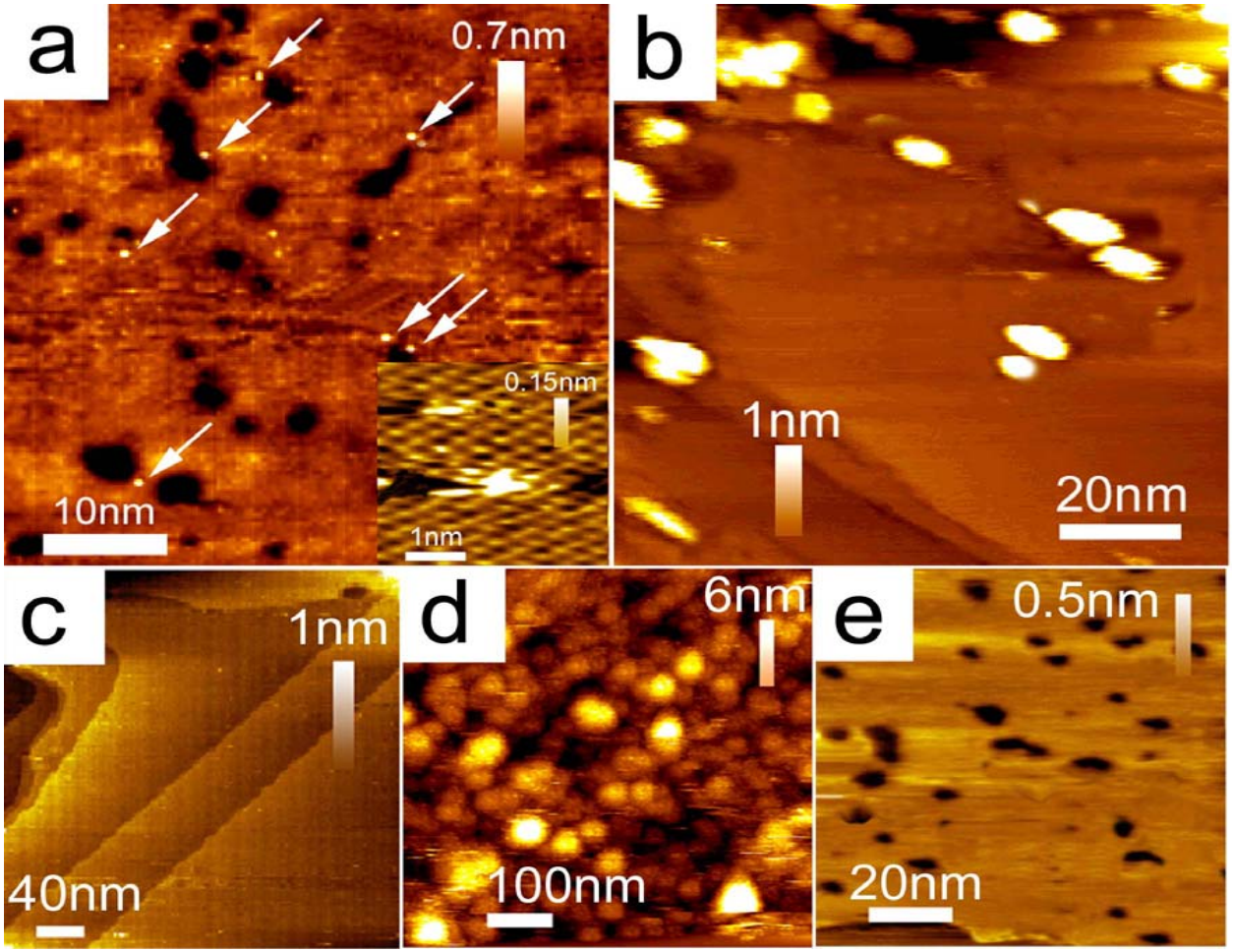
(Science **294**, 571, 2001)

A simple recipe for good contacts

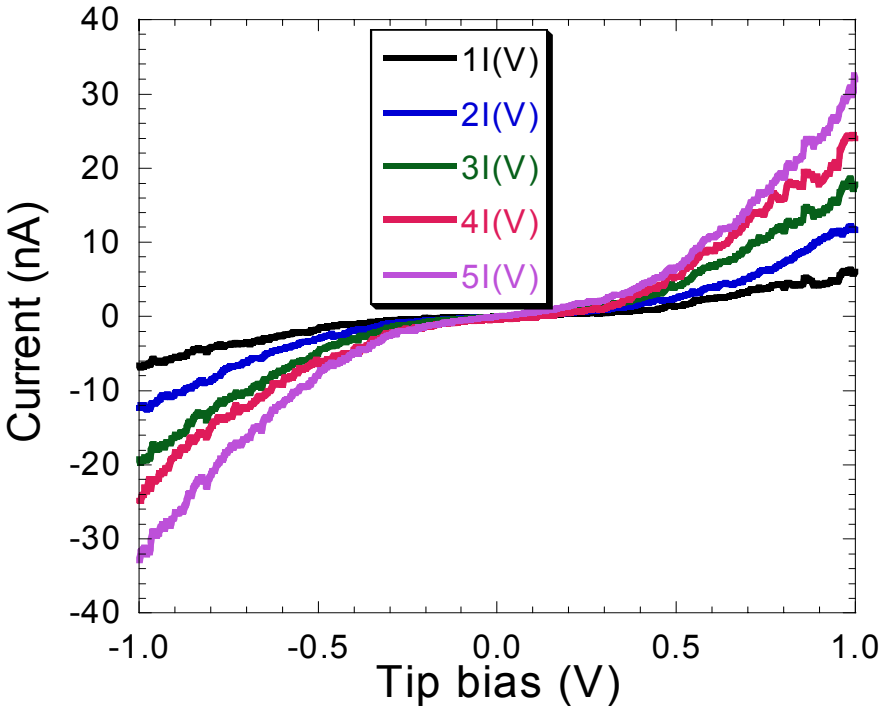
– bonds at each end

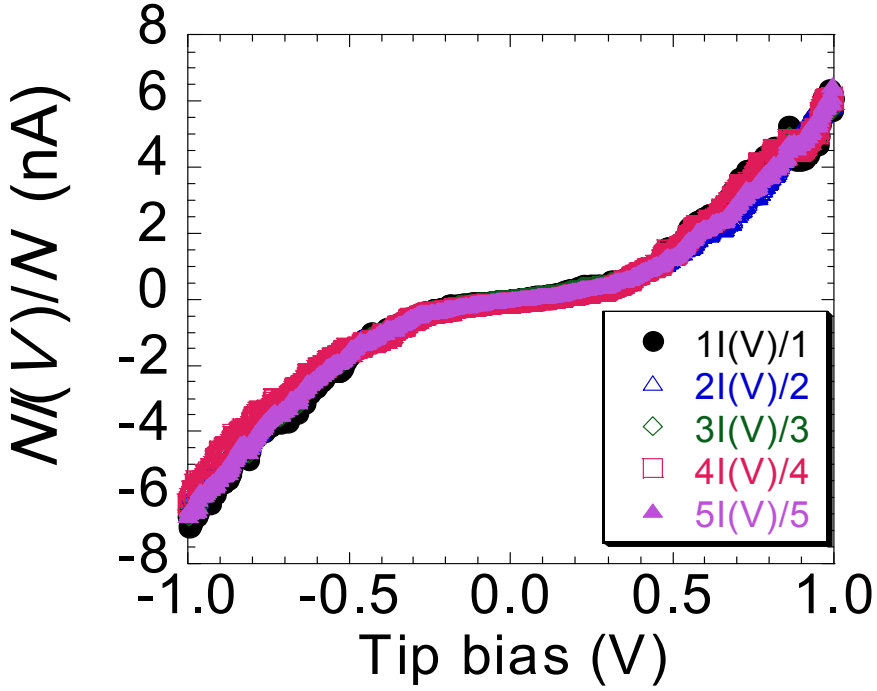


Alkanedithiols – STM Images

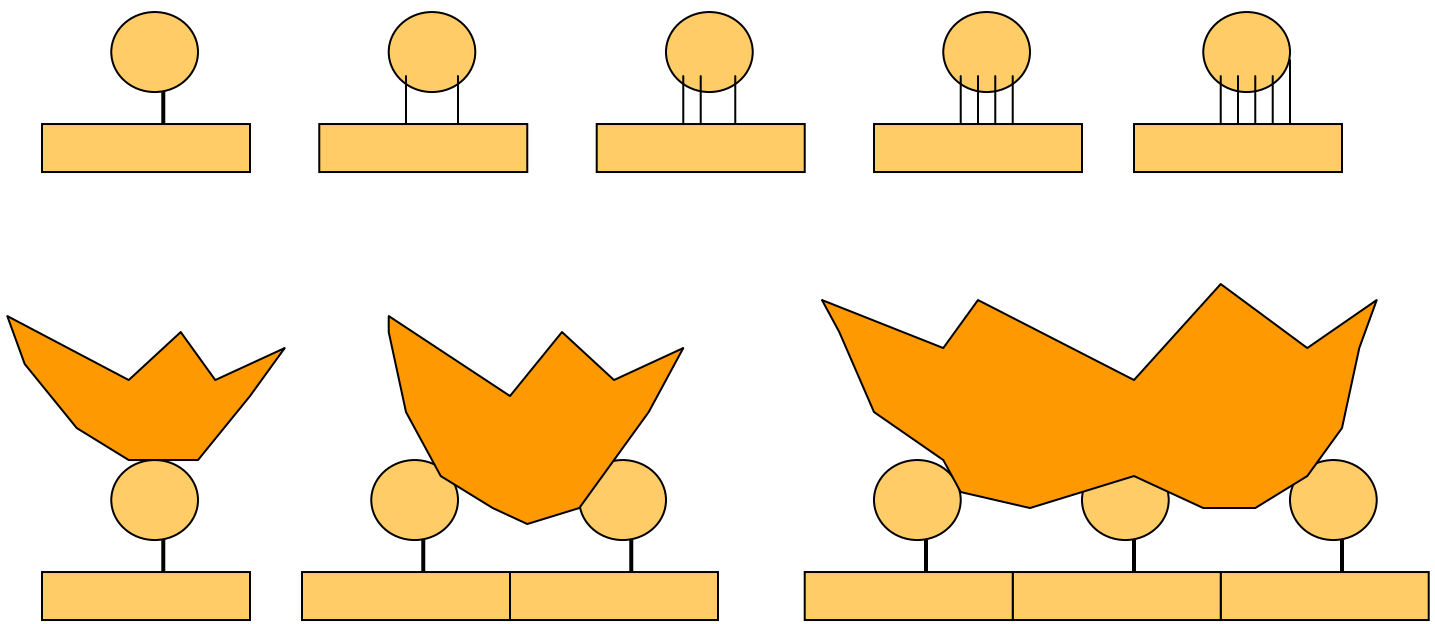


IV-Curves are integral multiples

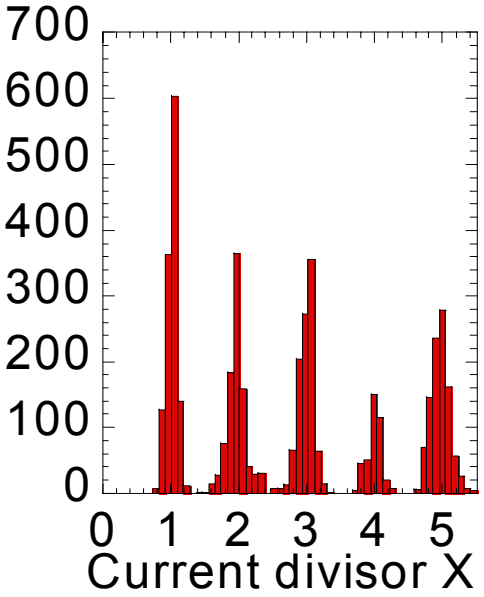




Two Models…….



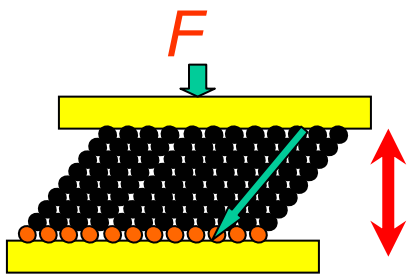
Histogram of curve multipliers



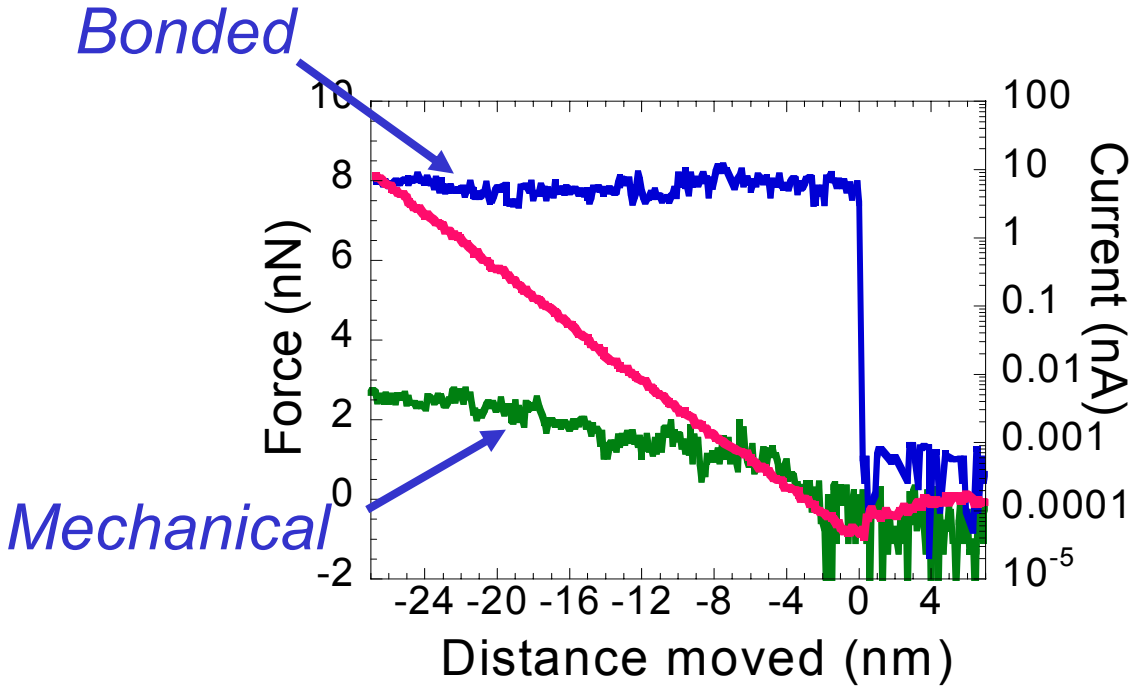
- Find X such that variance from curve to curve is minimized
- Over 1000 curves for n=1

IV-Curves of bonded molecules not very stress dependent!

Current not stress-dependent – through bond?

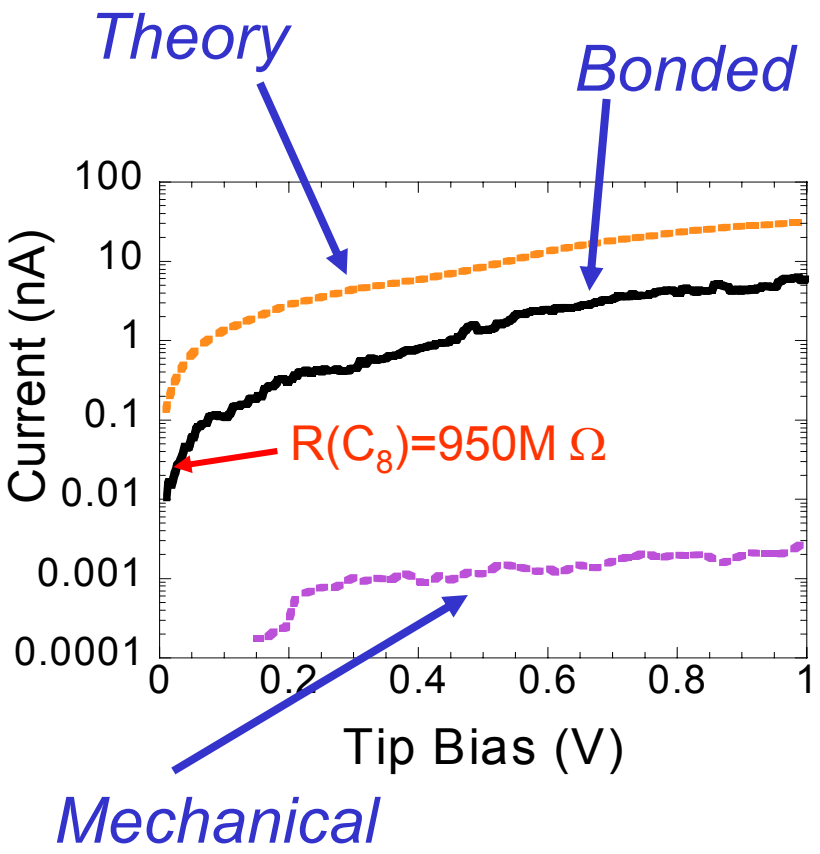


I≠F(h)



*(Nanotechnology **13** 5-14, 2002)*

I is closer to theory for bonded molecules



Comparison with electrochemistry:

$$R = \frac{k_B T}{e^2 K(E_A = 0)}$$

$$K(E_A = 0) = \frac{K}{\exp\left[-\frac{E_A}{k_B T}\right]}$$

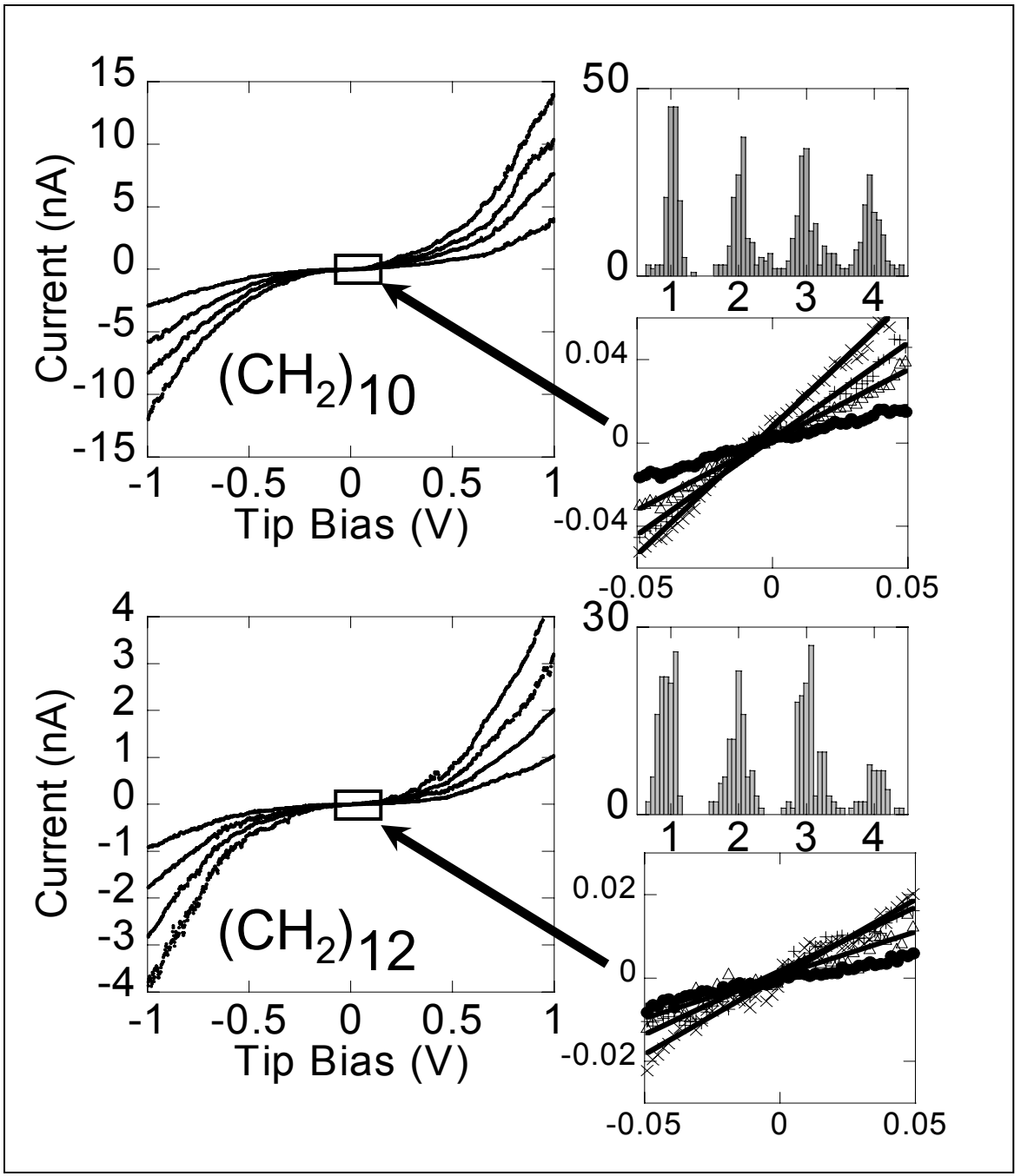
K=10^5s^{-1}, E_A=21kJ/m,
R(C_8)=300M Ω

More chain lengths give β(V)

(J. Phys. Chem. B **106** 8609-8614, 2002)

$$I = I_0 \exp[-\beta(v) z]$$

- Also measure Ohmic region carefully to get β(0)

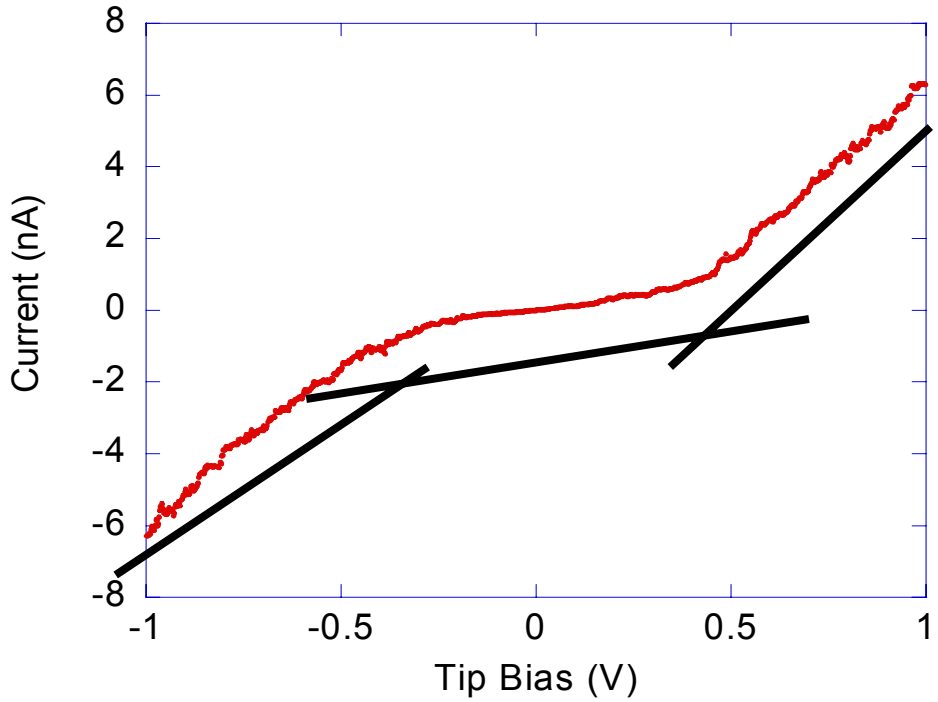


Can we understand our data?

Summary

- Get I(V) reproducibly
- Independent of stress – *through bond*
- I-V close to theory (but still 6x too small)
- Shape is subtly different from theory
- Apparent β too small (ca. 0.6) and too bias dependent

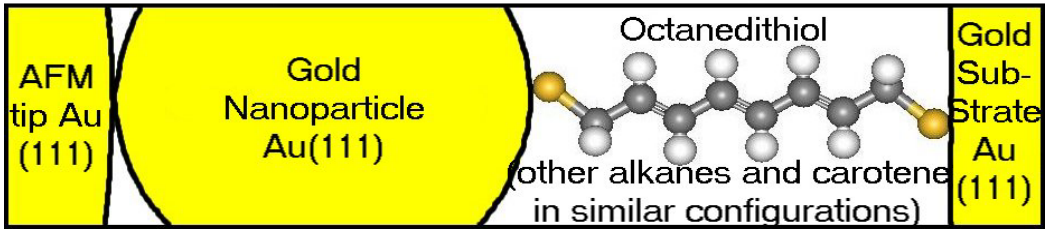
I-V Doesn't fit tunneling

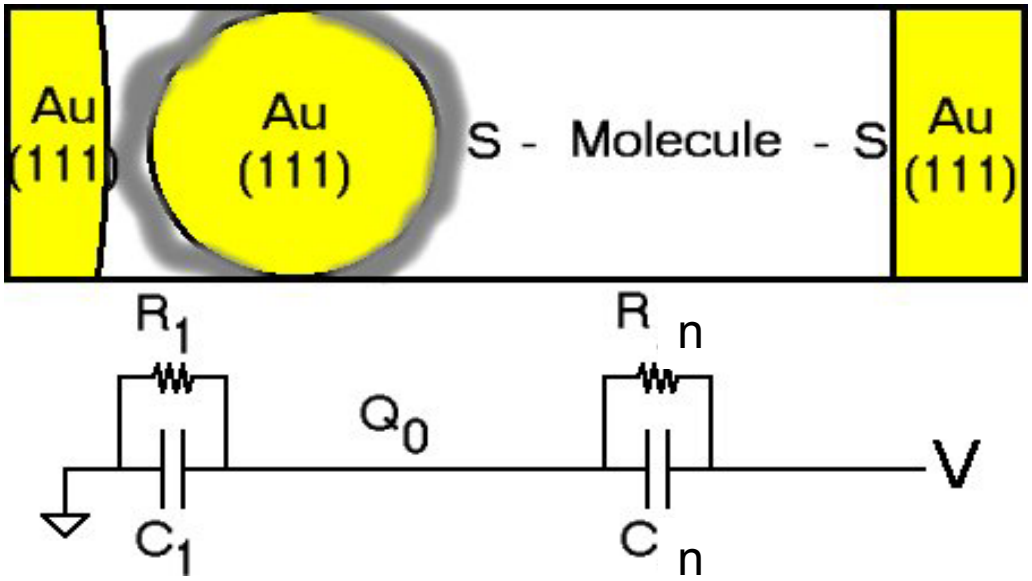


What if the top contact is not so good?

Coulomb Blockade?

Coulomb Blockade: Quantized charge transfer





$R_1 >> h/2e^2$

$\Rightarrow$ Coulomb Blockade

Double Junction Model

A. E. Hanna and M. Tinkham, Phys. Rev. B, 44, (1991), 5919-5922.

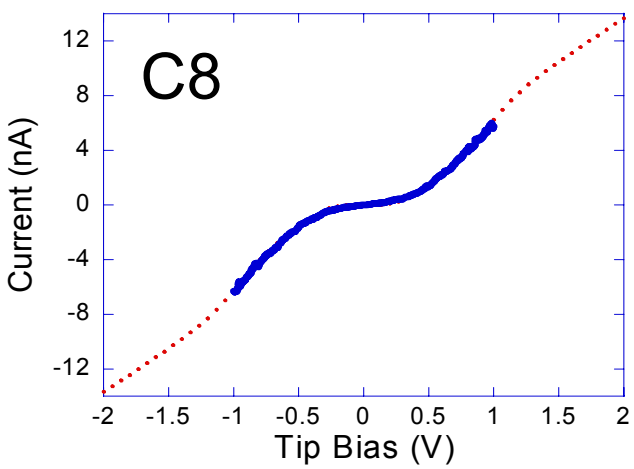
5 Parameters

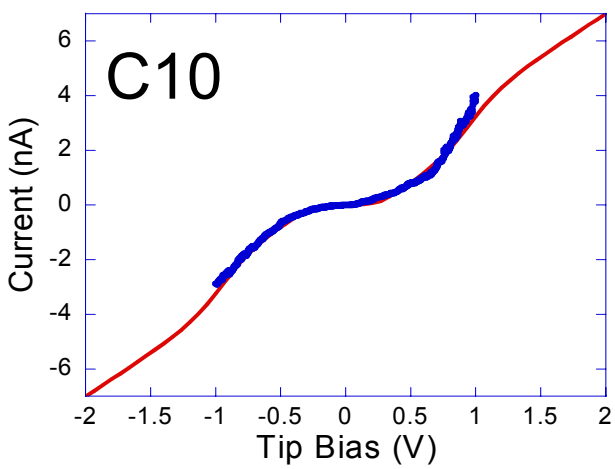
R_1, R_2, C_1, C_2, Q_0

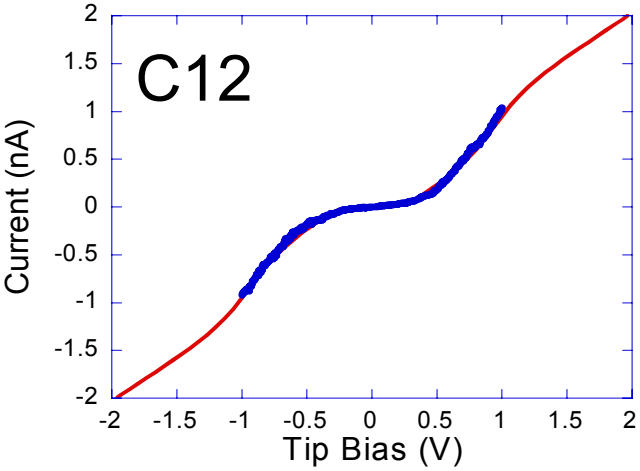
Symmetry $\Rightarrow Q_0 = 0$

Solve subject to integral charge transfer, with thermal hopping at 300K

Best Fits:







r_1 = 1MΩ

c_1 = 0.318aF

(from fitting C8)

r_8 = 128.36MΩ

r_{10} = 252MΩ

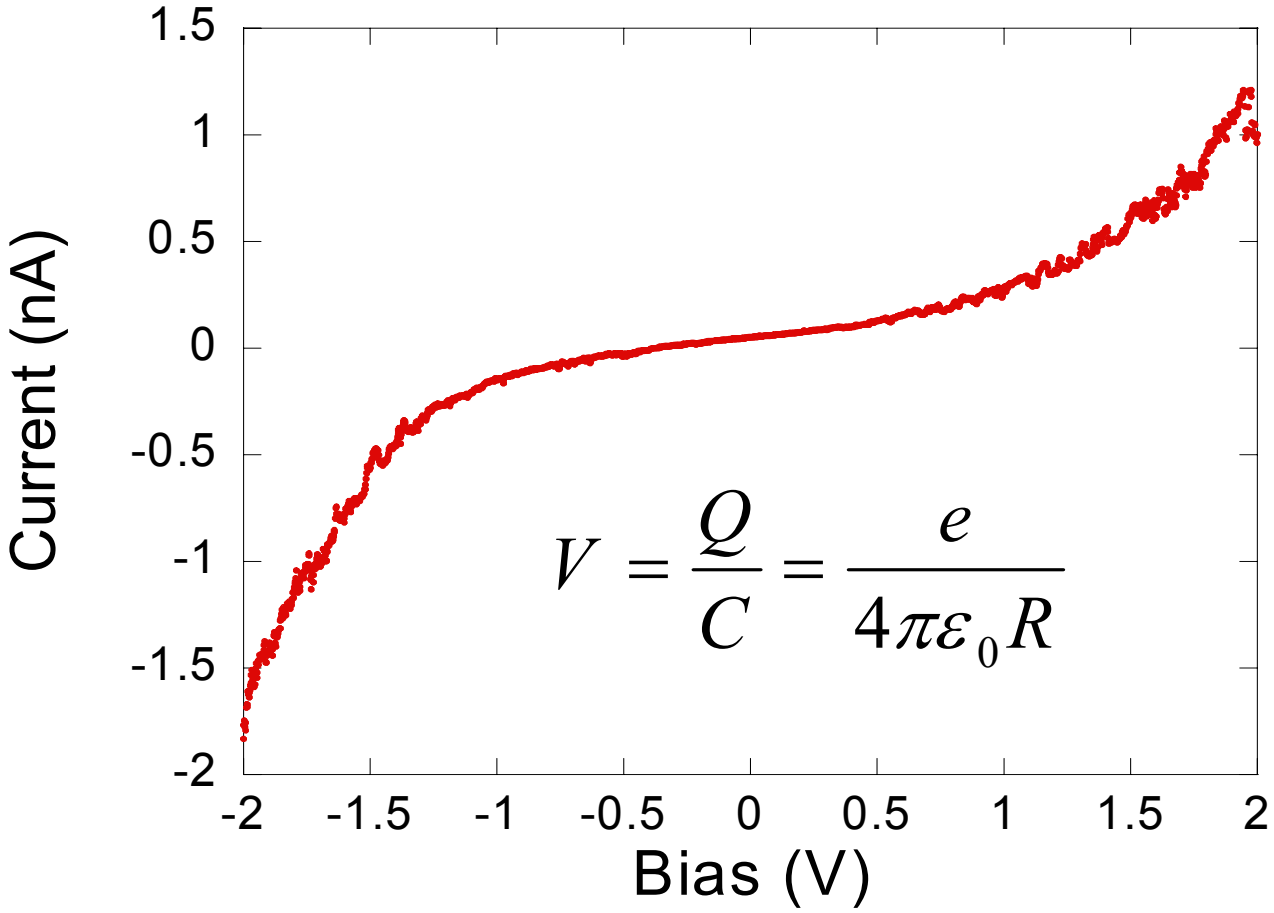
r_{12} = 875MΩ

(c_1, r_1 fixed)

C8=c10 =c12= 0.085aF

(Theory=0.08aF)

Halve the sphere size (0.7nm):



Double the blockade range!

(note that this accounts for anomalous beta too)

Coulomb Blockading

Summary

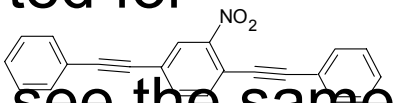
- Fit I-V curves
- Fixes beta problem
- Correct size dependence
- What about molecular levels of gold nanoparticles? Use bigger gold contacts.

Stochastic Switching

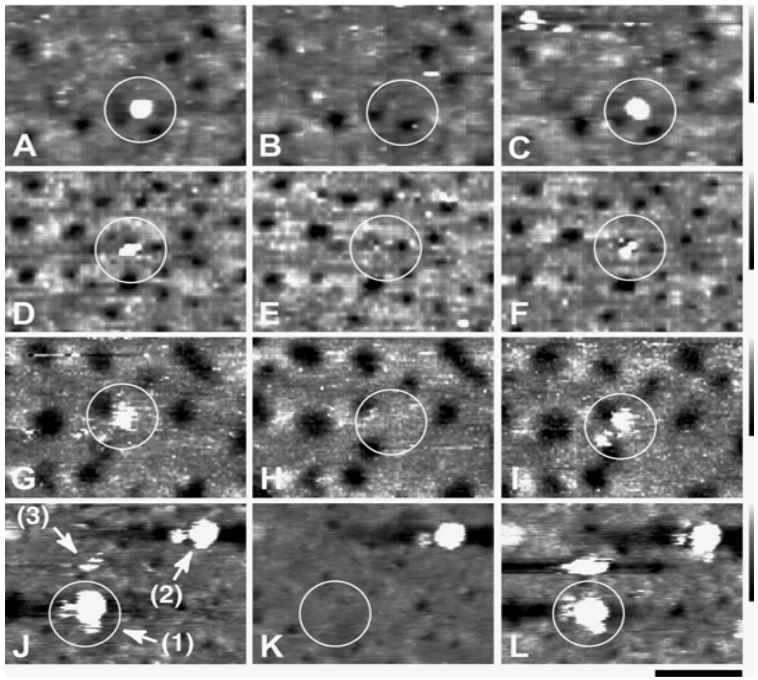
- First reported in phenylene-ethylenene NDR molecules (Donhauser et al. Science **292**, 2303, 2001)
- Thought to be related to conformational changes associated with NDR

Single Molecule Bonding Fluctuations (Science **300** 1413, 2002)

- "Stochastic switching" reported for

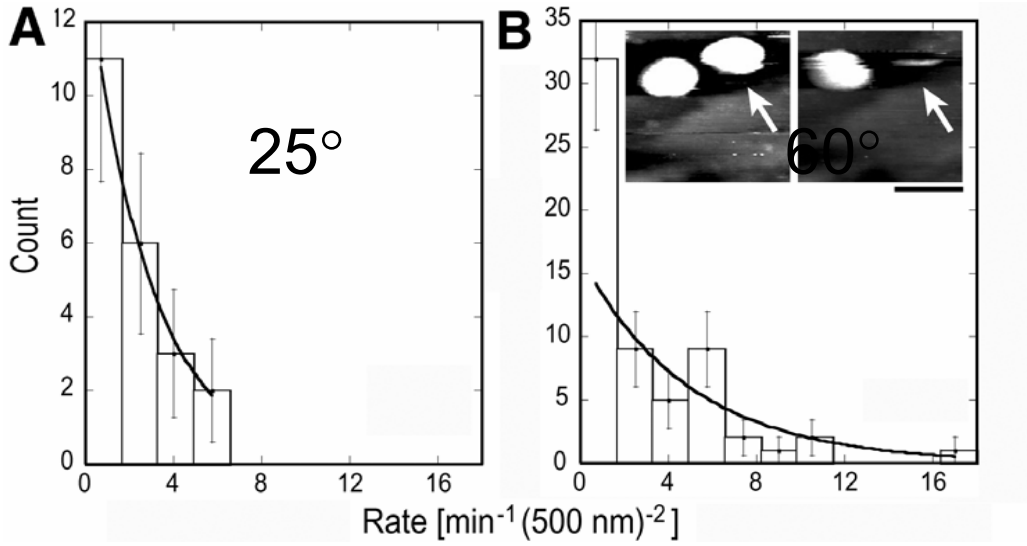


- We see the same effect in alkane dithiols
- Significant switching with gold sphere attached



Single Molecule Bonding Fluctuations

- Cannot internal electronic changes
- Cannot be top ‘dipping’ into film
- Cannot be bond to sphere breaking
- Rate increases at annealing temperature
- Fluctuations of lower bond



Stochastic Switching

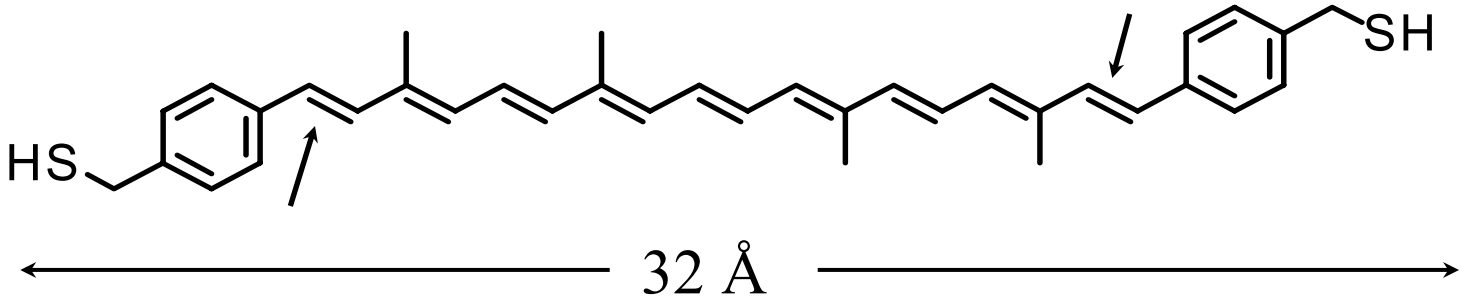
- Gold is probably not the right metal to use
- Not compatible with CMOS anyway

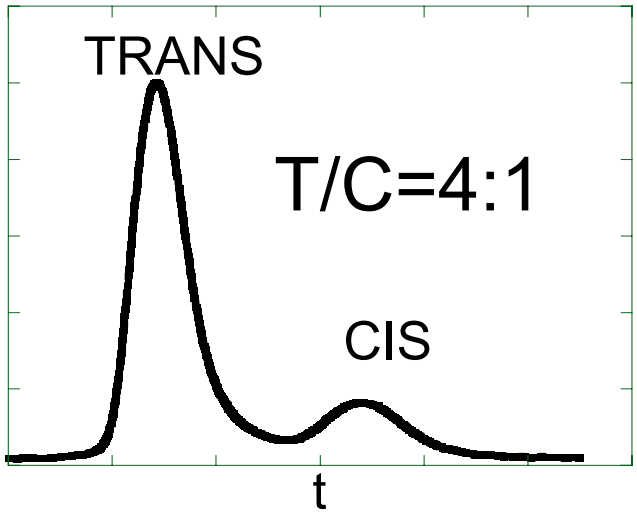
More Complex Molecules

- Carotenoids (J. Phys. Chem. B, 107, 6162-6169 (2003))

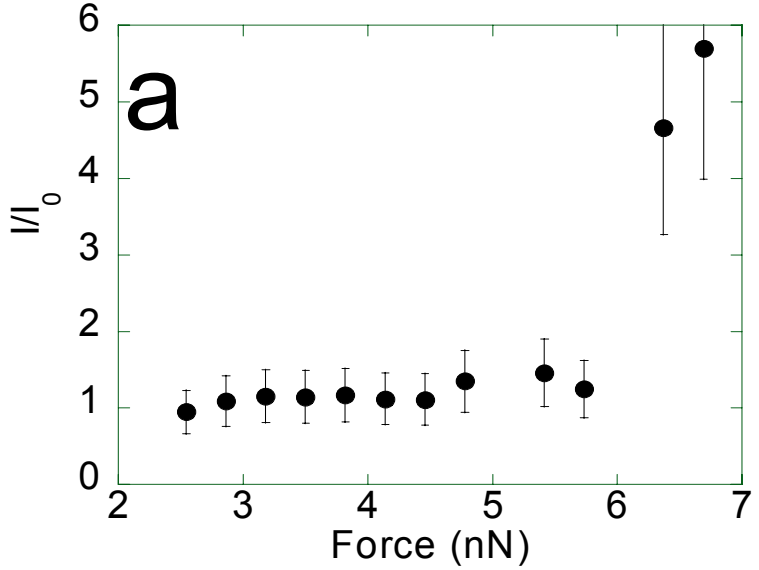
- PET-NDR molecules (Applied Physics Letters **81** 3043-3045 (2002))

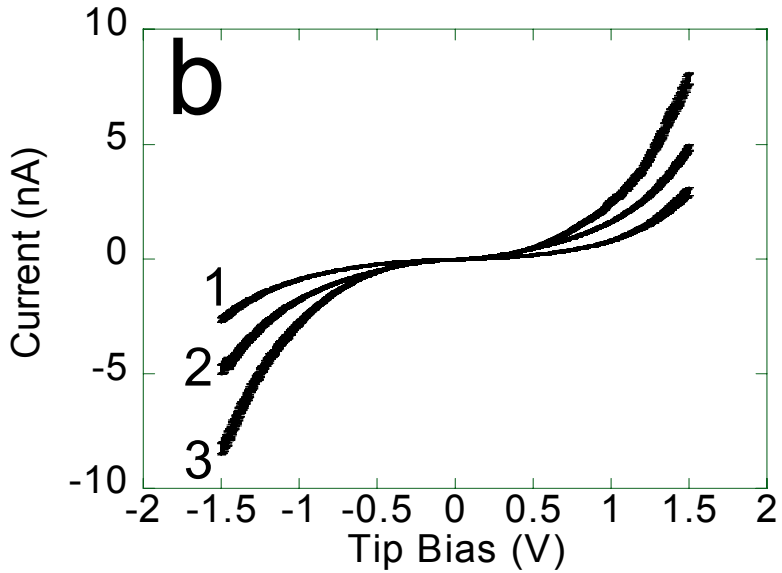
Caroteniod

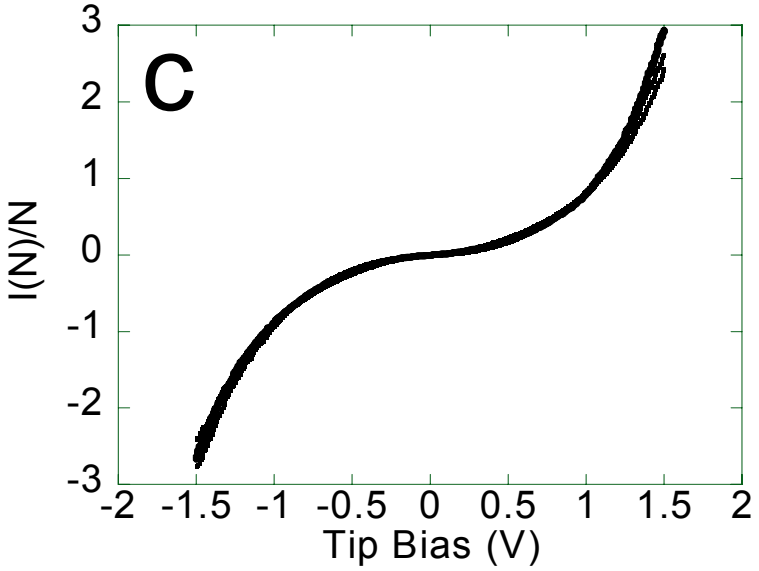


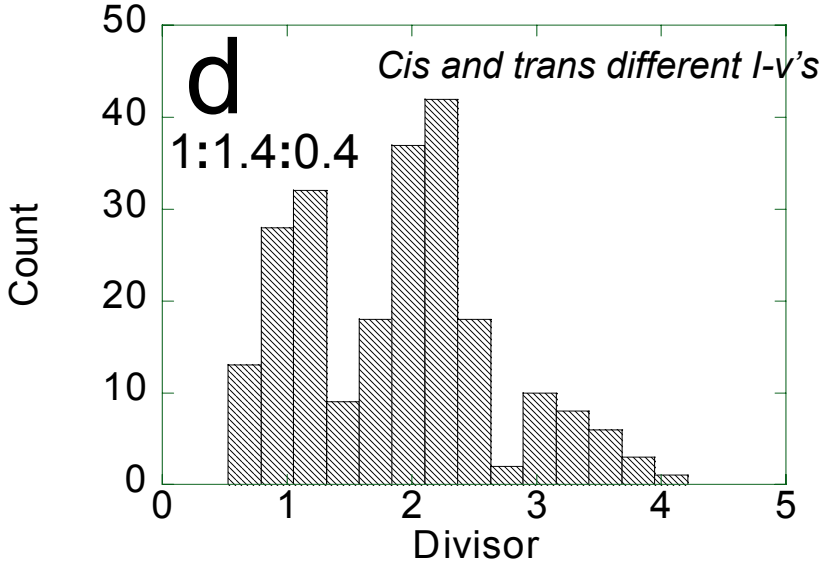


Current vs. force





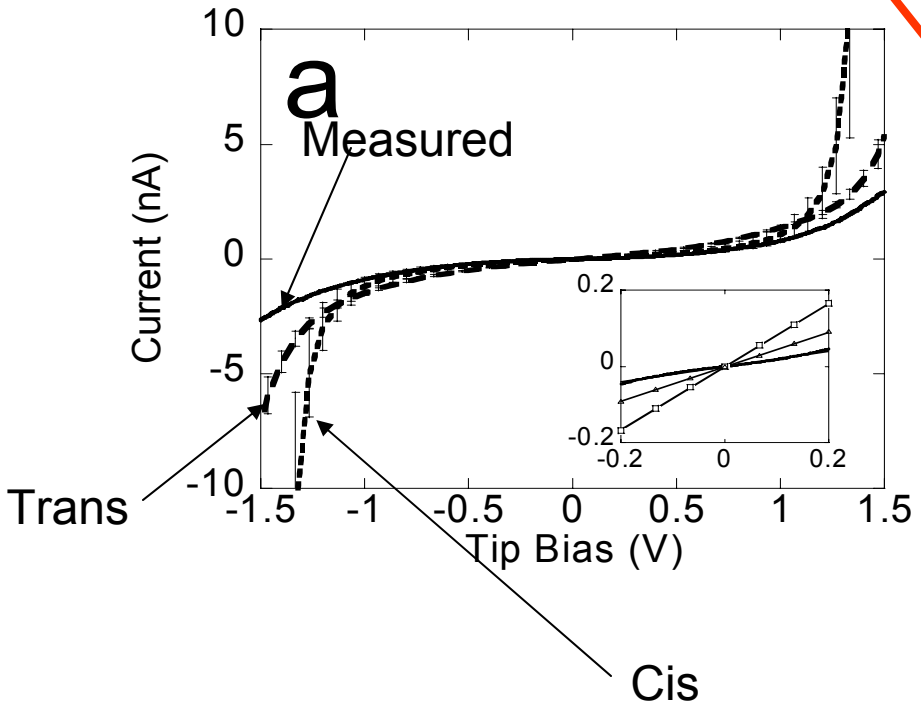


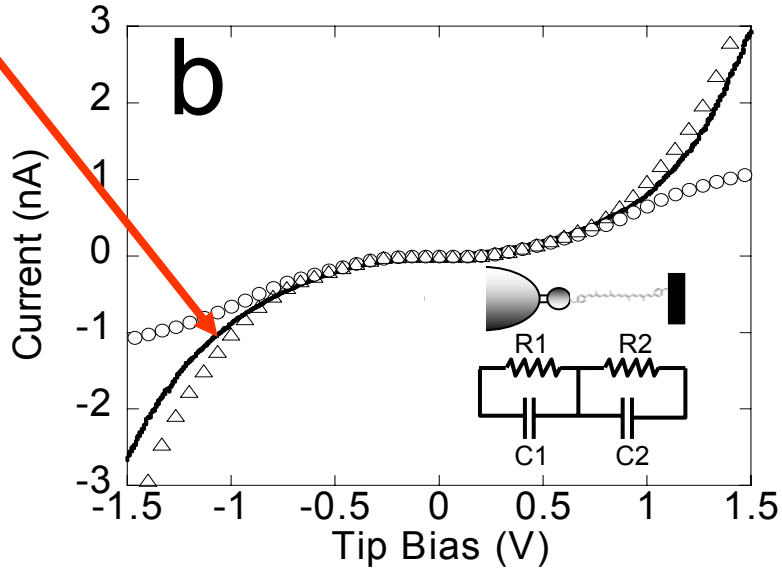


N=1 Curve

I-V curves and histograms

No free parameters!



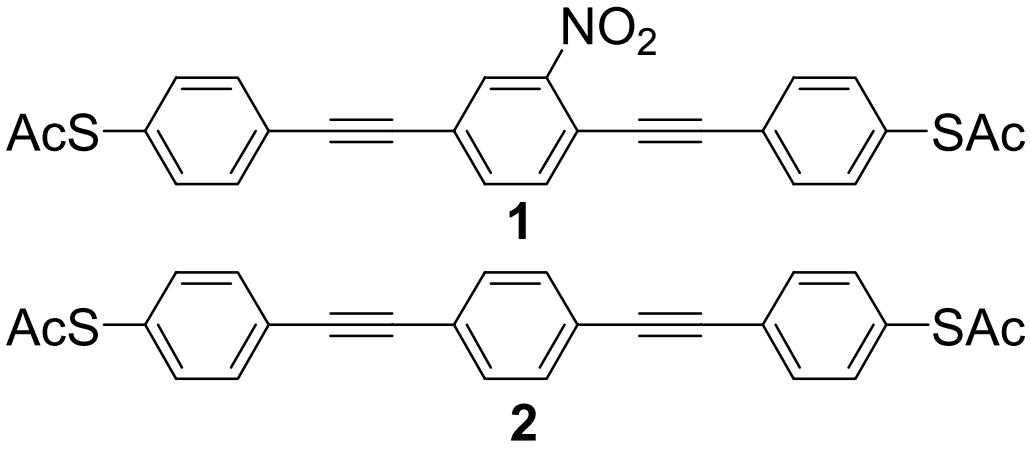


Error bars show range owing to possible orientations

Circles: Coulomb Blockade model with gold ball parameters from alkane expts and R from calculation.

Triangles: As adjusted for non-linearity of I-v curve

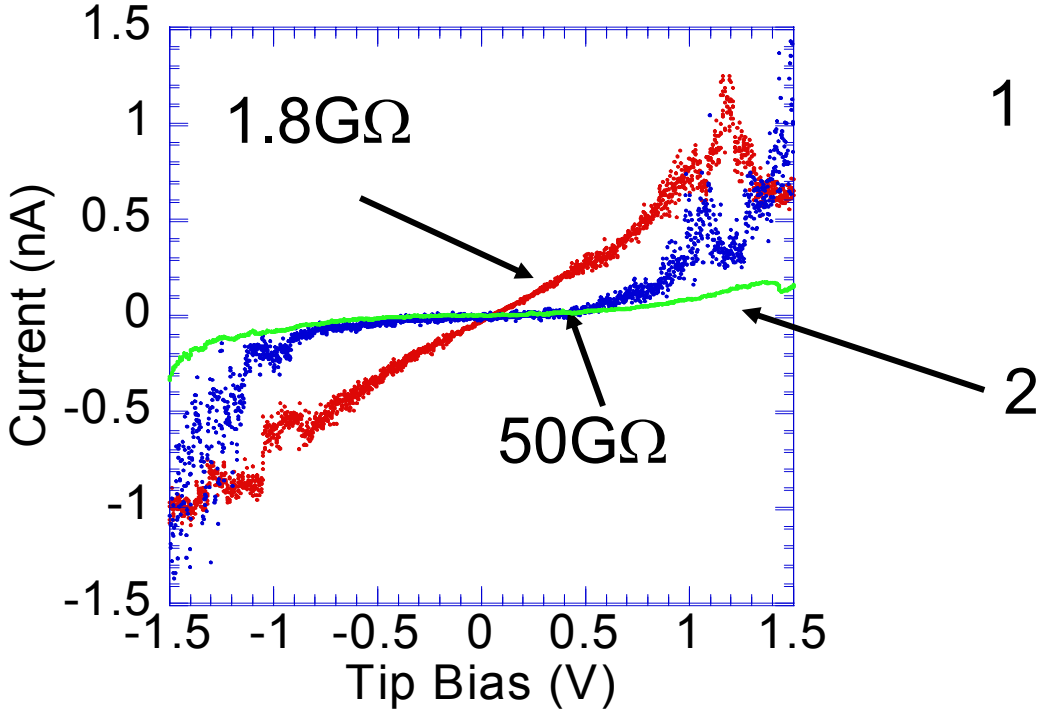
Phenylene-ethylynene Oligomers

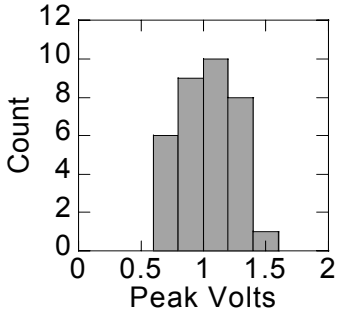


1 = 1-nitro-2,5-di(phenylethynyl-4′-thioacetyl)benzene

2 = 2,5-di(phenylethynyl-4′-thioacetyl)benzene

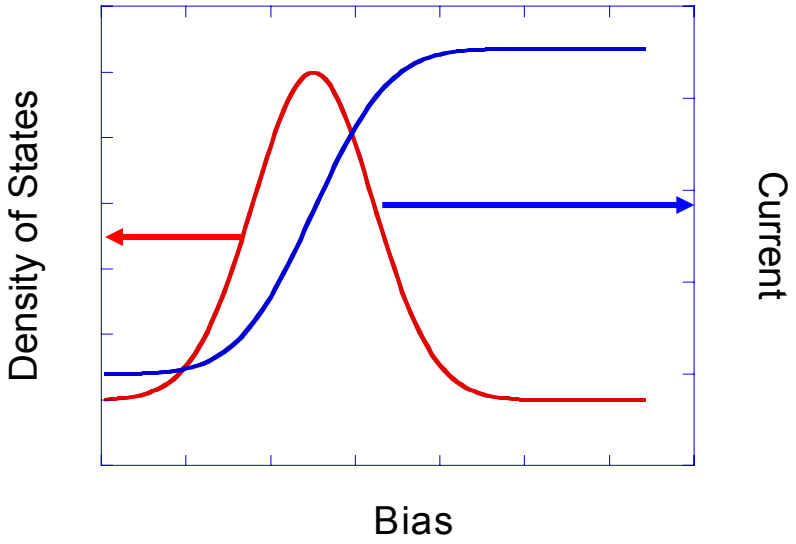
NDR Molecules one at a time:





Origin of NDR peak?

Expected



- Nitro group implies redox chemistry
- Non reversible
- Environmentally-mediated chemistry (thio-reduction)?

Summary

1. Bonded system with large ‘contact pads’ gives reproducible results, probably because of small AFM-nanoparticle resistance
2. In some situations, single molecule curves can be identified unambiguously
3. Bonded system gives correct order of current, in contrast to large disagreement in the case of mechanical contacts
4. Both apparent Beta discrepancy and residual magnitude of current discrepancy accounted for Coulomb Blockade surface ‘fluctuate’
5. Both apparent Beta discrepancy and residual magnitude of current discrepancy accounted for Coulomb Blockade
6. Contacts on Au surface ‘fluctuate’
7. Carotene current well accounted for by tunneling, despite ease of oxidation
8. NDR molecules show small redox-related peak on tunneling background. ‘Irreversible’ electrochemistry?
9. *Fabricating Nanogaps???*

ACKNOWLEGEMENTS

ASU PHYSICS

X.D. Cui

O.F. Sankey

J. Tomfohr

J. Li

G. Ramachandran

ASU Chemistry

A.L. Moore

T. A. Moore

J. D. Gust

X. Zarate

A. Primak

Y. Terazano

Motorola

G. Harris

L. Nagahara