νανο

THANKS

Ale Troisi

Alex Xue

Michael Galperin

Emily Weiss

NNI-NCN

Mark Lundstrom

Supriyo Datta

Vladi Mujica

Abe Nitzan

NSF, DoD MURI, NASA, DARPA

MOLECULAR ELECTRONIC DEVICE CONCEPTS

1987

David N. Beratan *California Institute of Technology*

I. What's Wrong with Silicon?
II. What Are Molecular Devices?
III. How Big Are Molecular Devices?
IV. How Is Molecular Information Manipulated?
V. What Molecular Devices Are Possible?
VI. Does the Field of Molecular Electronics Exist?

GLOSSARY

Molecular electronics: A field comprised of a diverse collection of scientists with the goal of creating electronic elements or other functional devices based on relatively small molecules.

I. What's Wrong with Silicon?

ELECTRONIQUE MOLECULAIRE

LE JOURNAL DU GROUPEMENT DE RECHERCHE N° 5609 DU CNRS

N°2, décembre 1990 - Editeurs : C. Joachim‡ et S. Palacin*

‡C.N.R.S. 29, rue Jeanne Marvig, B.P. 4347 - 31055 TOULOUSE CEDEX
*SCM, Bât 125 CEN Saclay 91191 GIF SUR YVETTE CEDEX

C'EST QUOI CE JOURNAL ?

2001

BREAKTHROUGH OF THE YEAR:

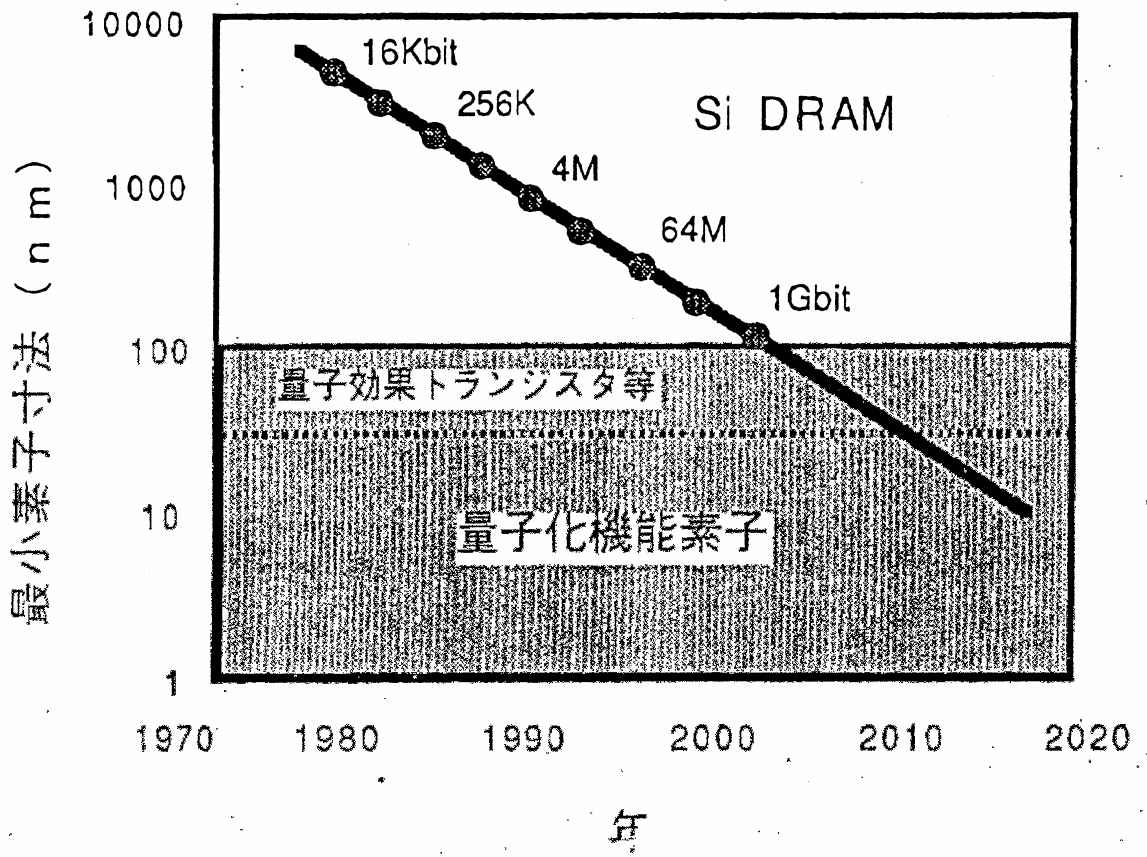
Molecules Get Wired

Robert F. Service

Why molecular electronics?

Size
Tunability
Recognition, Assembly
Dynamical stereochemistry

MOORE-SAN's LAW



1）微細化限界

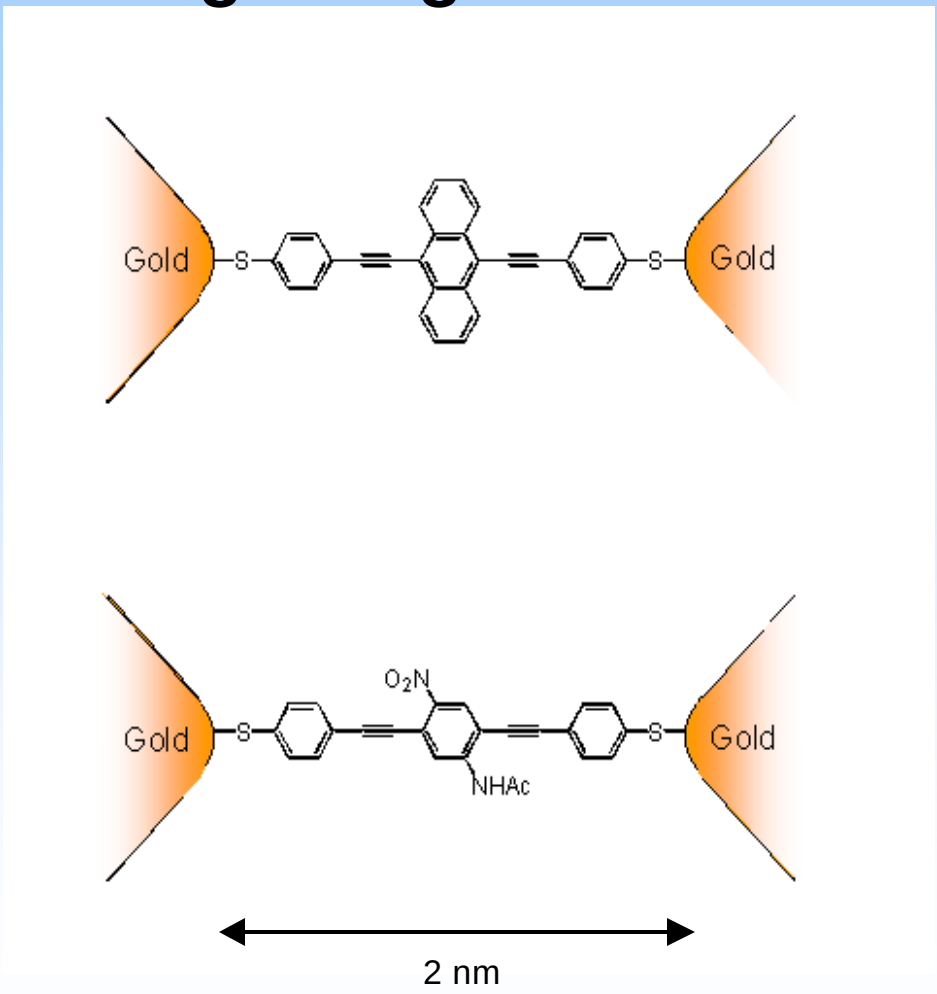
2）デバイス限界
ex. トンネルリーク

3）集積化限界
ex. 配線遅延

Why molecular electronics?

Size
Tunability
Recognition, Assembly
Dynamical stereochemistry

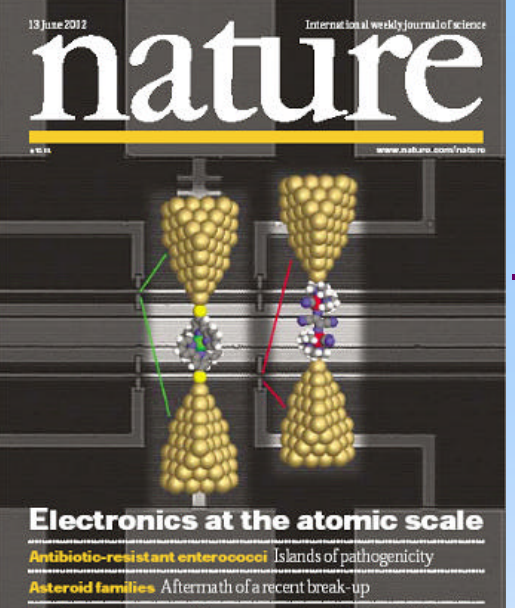
How does current flow through single molecules?



Symmetric molecule

Asymmetric molecule

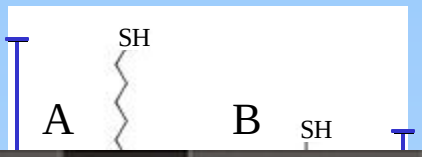
H. Weber et al



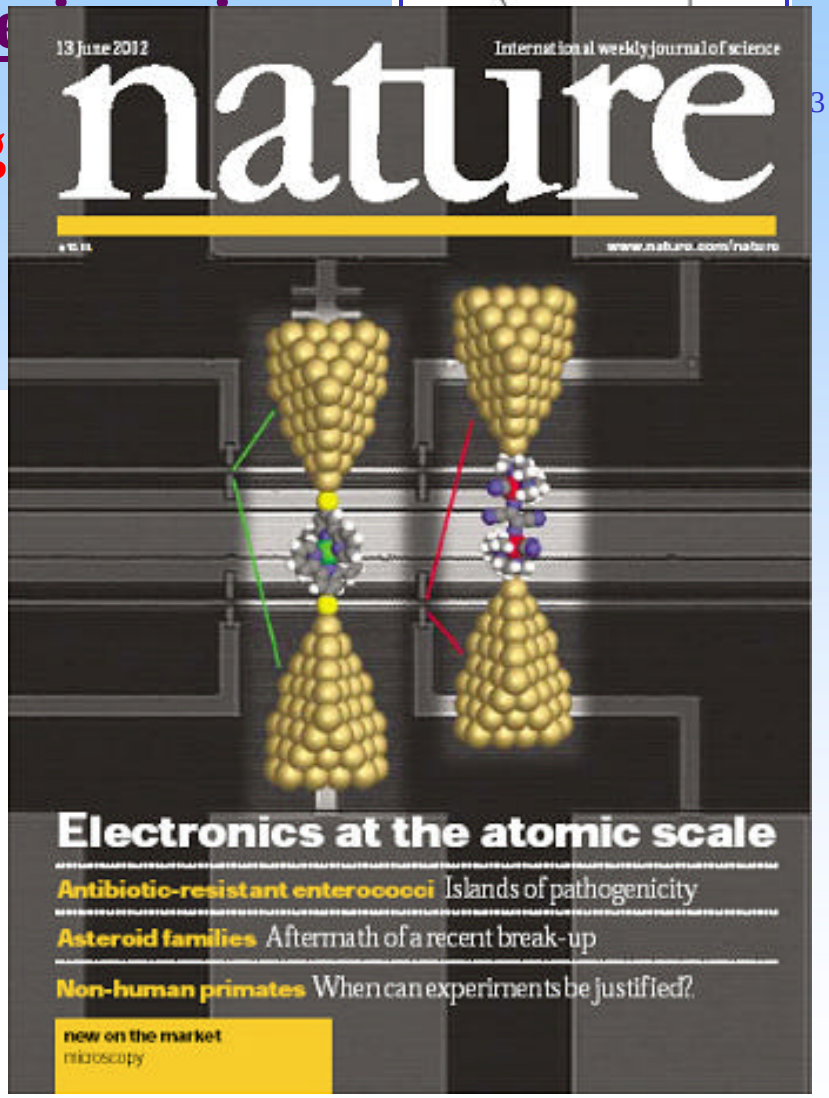
GATED

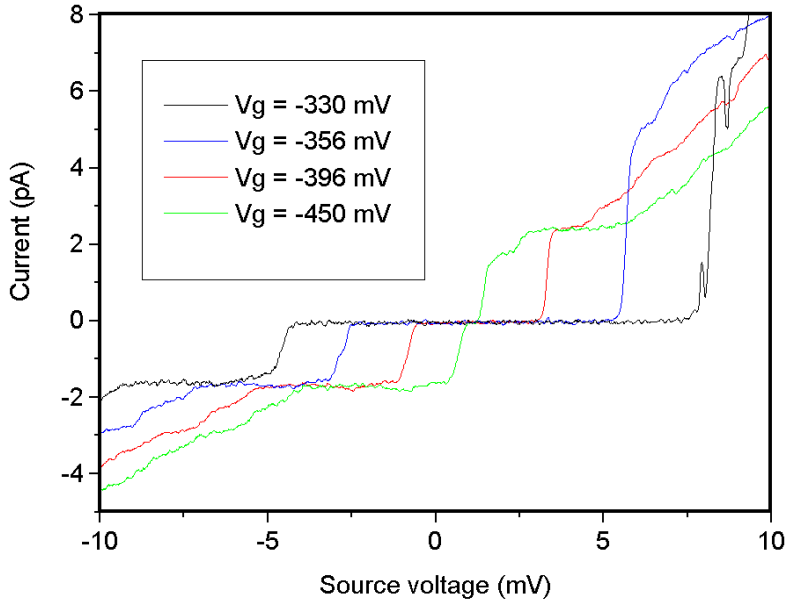
Single wire

Cornell g



3 Å

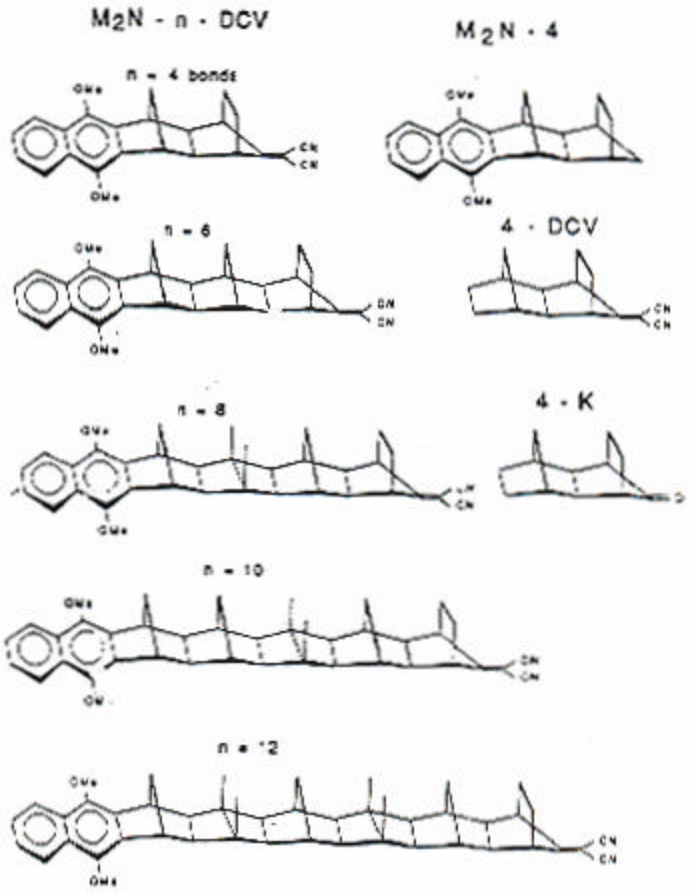




Coulomb blockade (long wire)

Paddon-Row, Hush, Verhoeven et.al.

Chart I

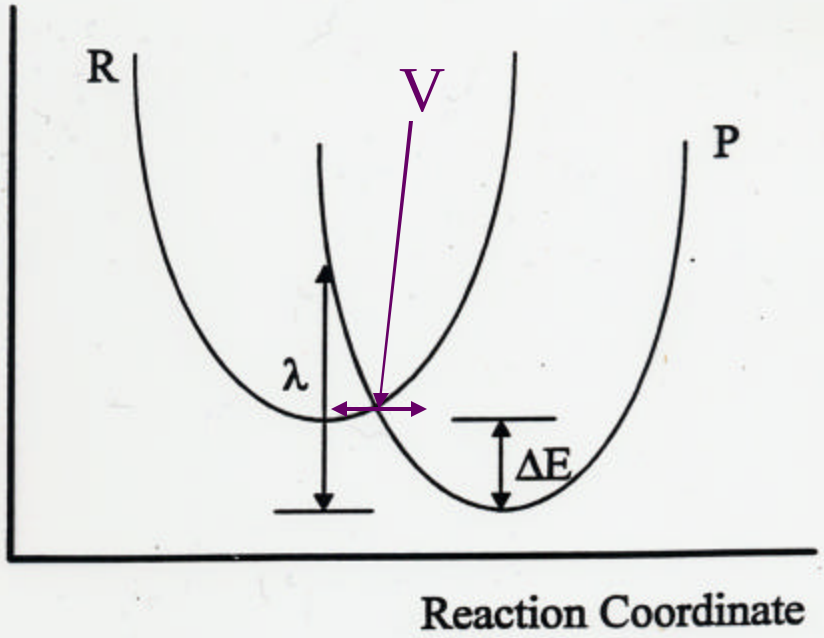


(B) having 4, 6, 8, 10, or 12 saturated bonds. Photoexcitation of these molecules provided evidence for rapid electron transfer[29-32]

$$D^*\text{-}B\text{-}A \rightarrow D^+\text{-}B\text{-}A^- \quad (2)$$

Distance dependent Donor/Bridge/Acceptor electron transfer

Nonadiabatic Electron Transfer

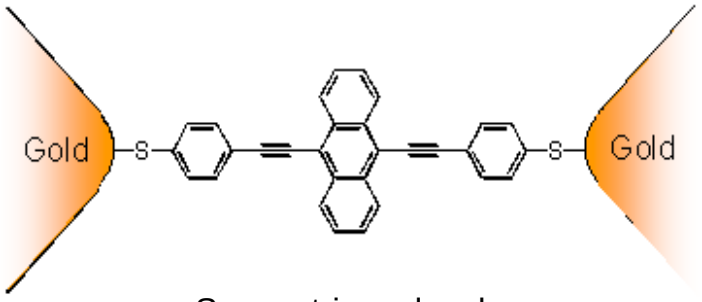


$$k = \frac{2\pi}{\hbar} V^2 \left(DWFC \right)$$

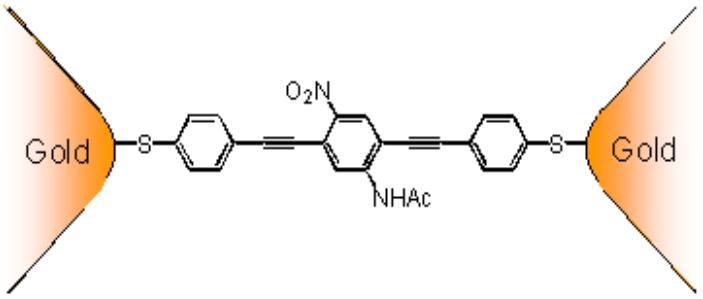
Vibronic Continuum

Marcus, Hush, Jortner

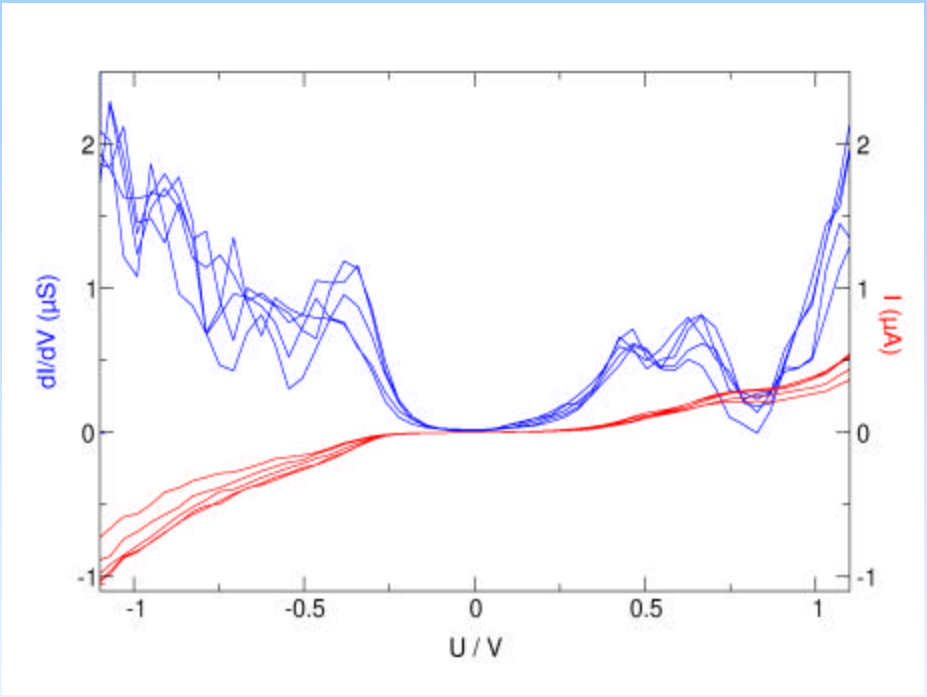
How does current flow through single molecules?



Symmetric molecule



Asymmetric molecule



2 nm

Single molecule break junctions

H. Weber et al
Karlsruhe

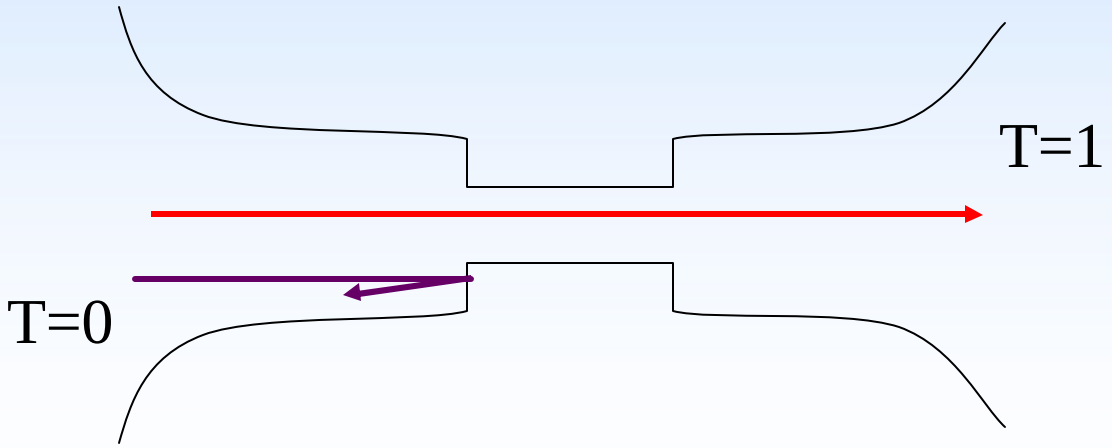
Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

- **NEGF Formulation**
- **Simple Tunneling Transport**
- **Geometry Modulation**
- **Weak vibronic coupling**
- **Strong vibronic coupling**

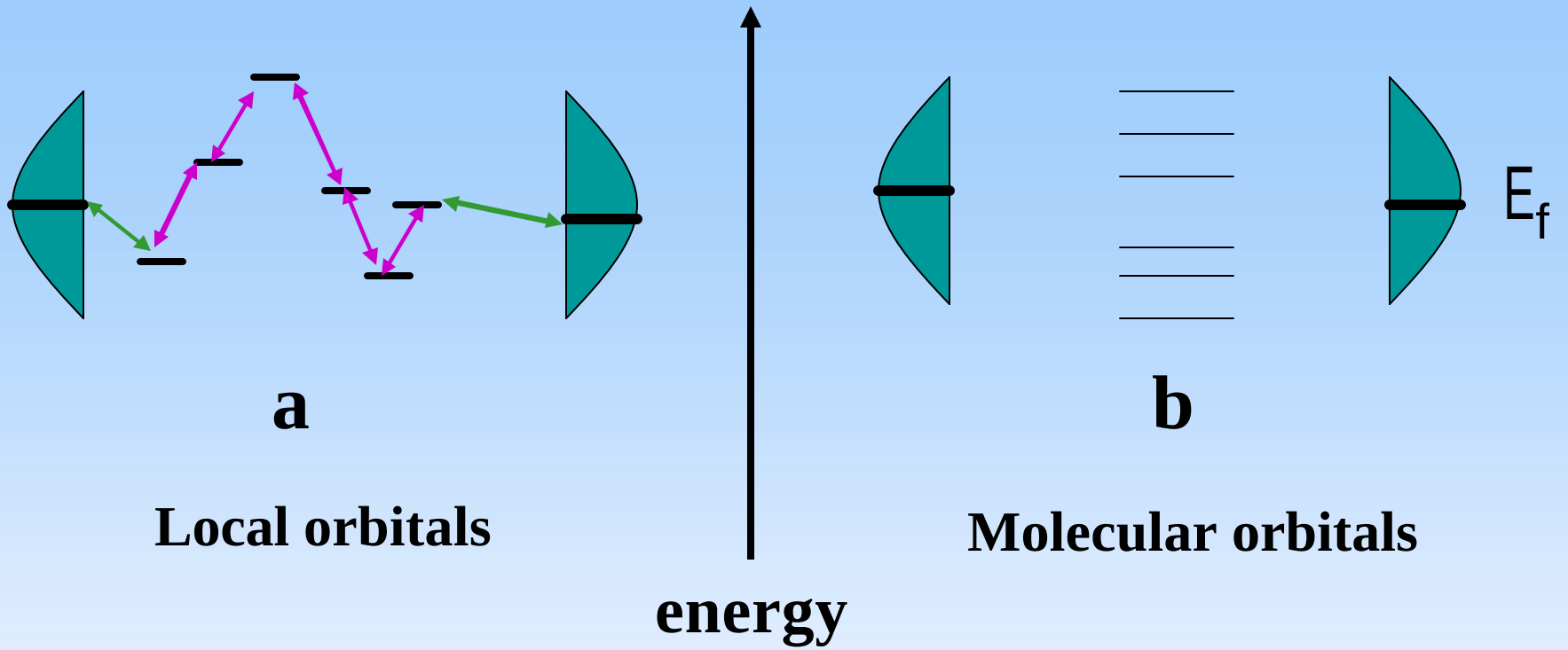
Landauer-Imry Coherent Conductance

$$g = \frac{e^2}{h} \sum_i T_{ii}$$

T_{ii}= transition probability in the i^{th} transverse channel



"Conductance is scattering"



Metals mix with molecular states

Landauer-Imry Conductance for Tunneling Circuits

conductance

propagator

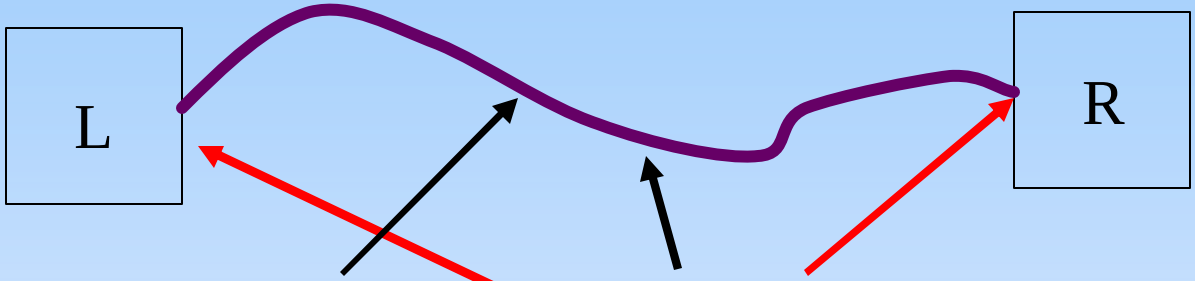
$$g(E) \propto \Gamma_1 \Gamma_N \, | \, G^r_{1N}(E) \, |^2$$

Spectral density (mixing) at molecular ends

first, Nth sites on molecule

Meir/Wingreen, Datta,……

Design Possibilities – Molecule



$$g(V) = g_0 \int Tr\{G(V)\Gamma(V)G^{+}\Gamma\}\{Fermi\ factor\}$$

$$G_{i,j} = \sum_{l,MO} \langle u_i | j_l \rangle \langle j_l | u_j \rangle / [E - e_l]$$

Good Conduction:

- **if the molecule has delocalized MO's, the numerator is big**
- **if the MO's are close to the Fermi level, the denominator is small**

Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

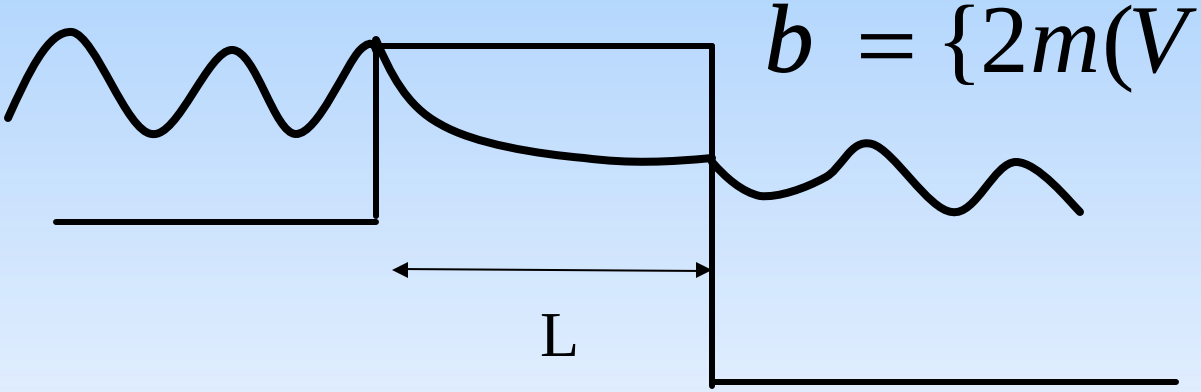
- **NEGF Formulation**
- **Simple Tunneling Transport**
- **Geometry Modulation**
- **Weak vibronic coupling**
- **Strong vibronic coupling**

Distance Dependence - Purely Electronic

$$k = k_0 \exp(-bL)$$

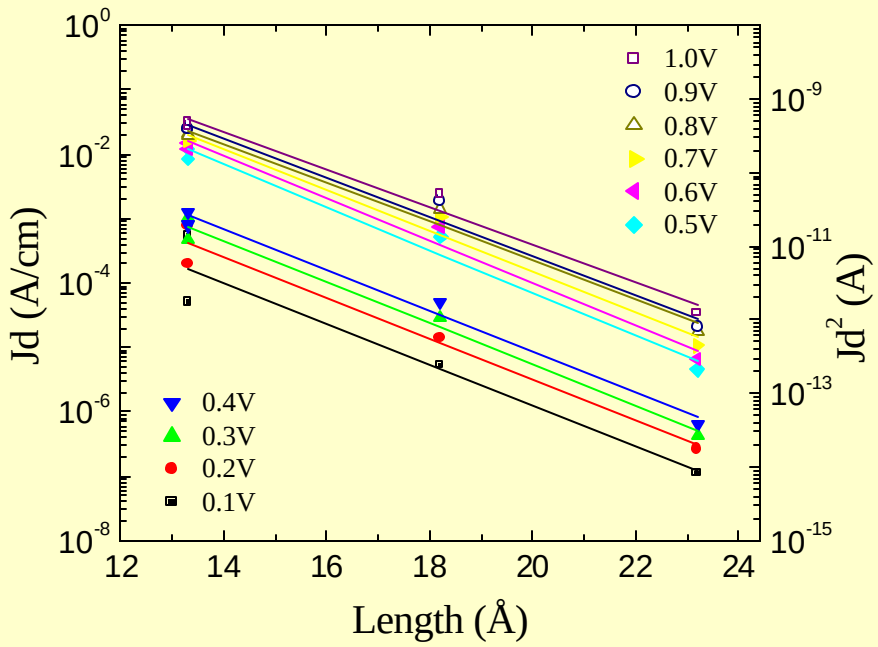
Barrier tunneling

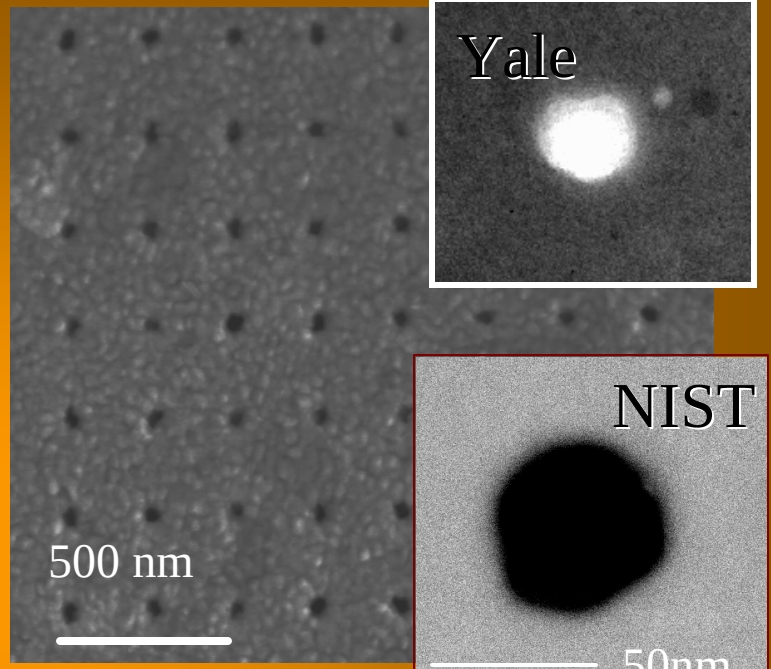
$$b = \{2m(V - E)\}^{1/2}$$

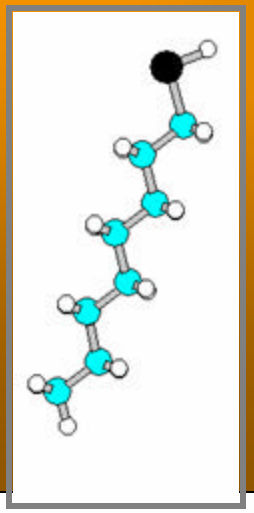


Alkanethiol distance Dependence

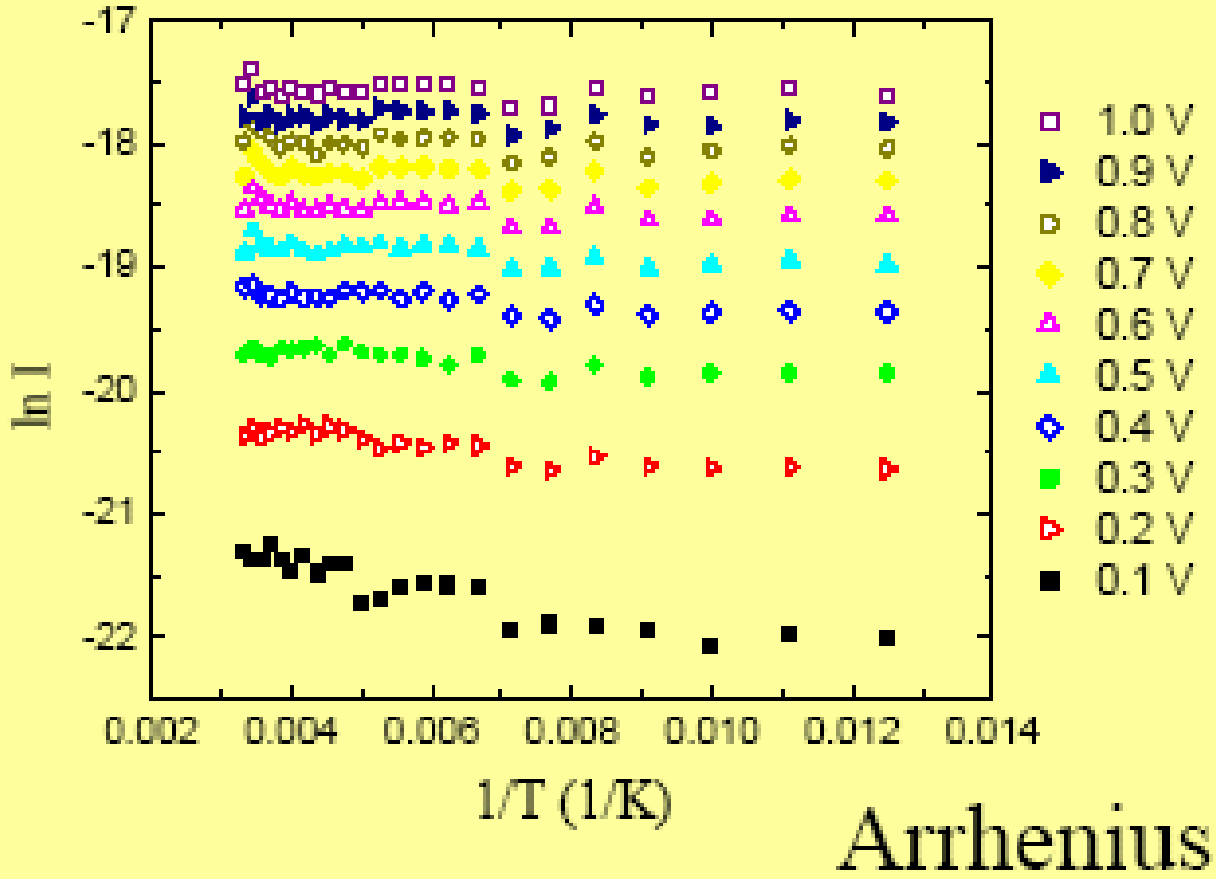
Reed , 2003







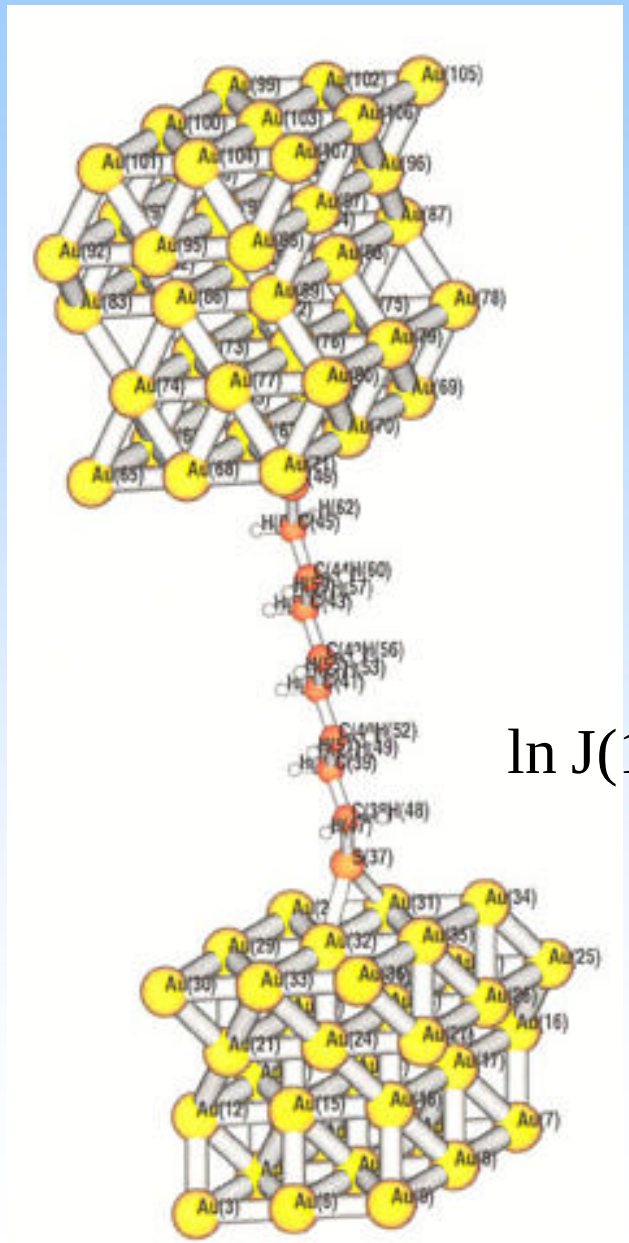
Octanethiol (C8)
Dodecanethiol (C12)
Hexadecanethiol (C16)



T- independent (tunneling)

Reproducible transport in alkanethiols (Reed, 2003)

Dithioalkane calculations with Transiesta code (DFT + NEGF)

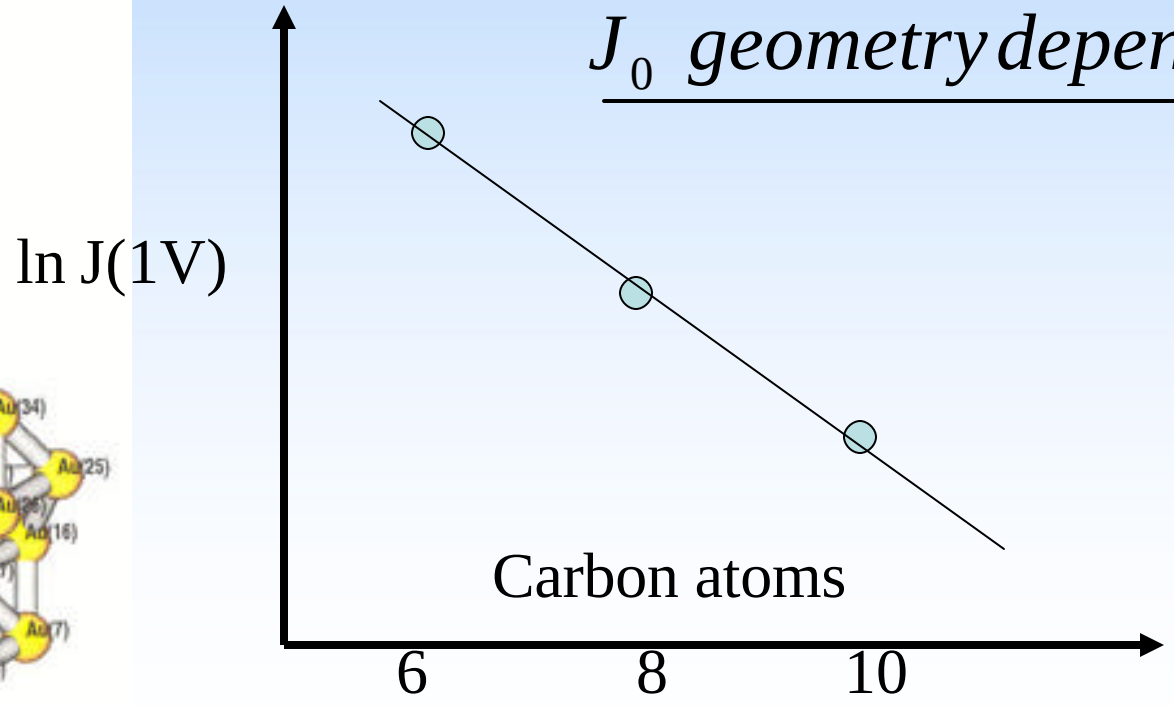


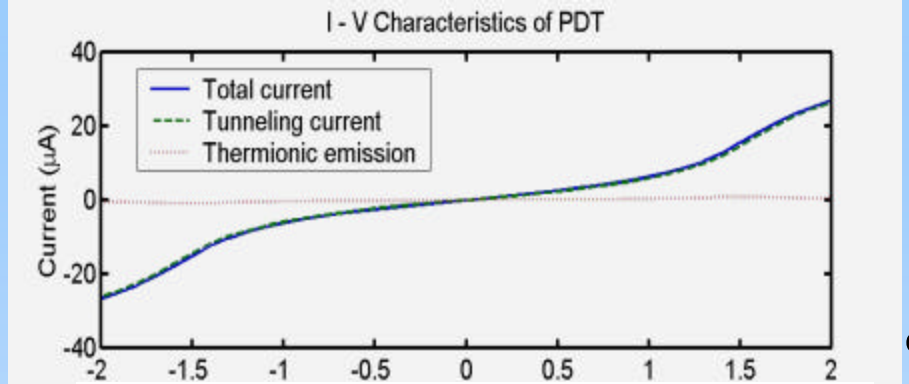
$$J = J_0 \exp(-b\,r)$$

$$b = 0.63/Angstrom$$

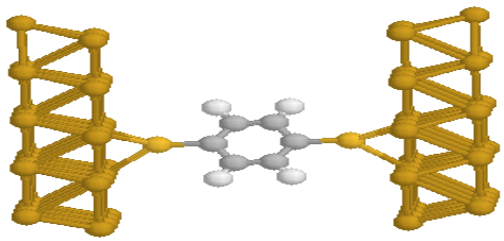
Expt. 0.60/Angstrom

J_0 *geometry dependent*



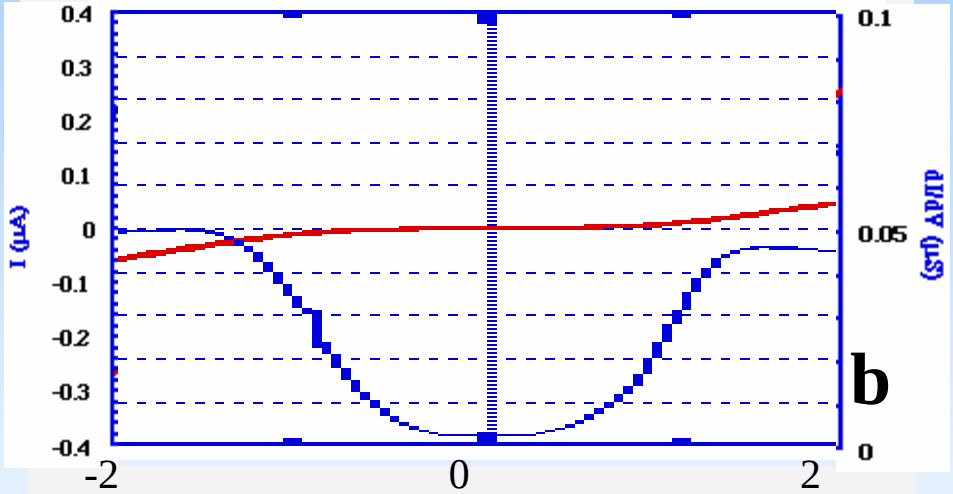


a

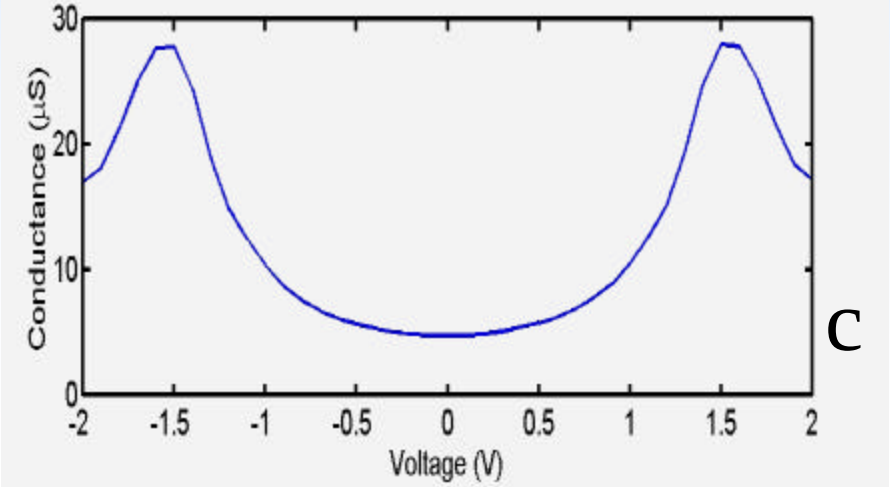


d

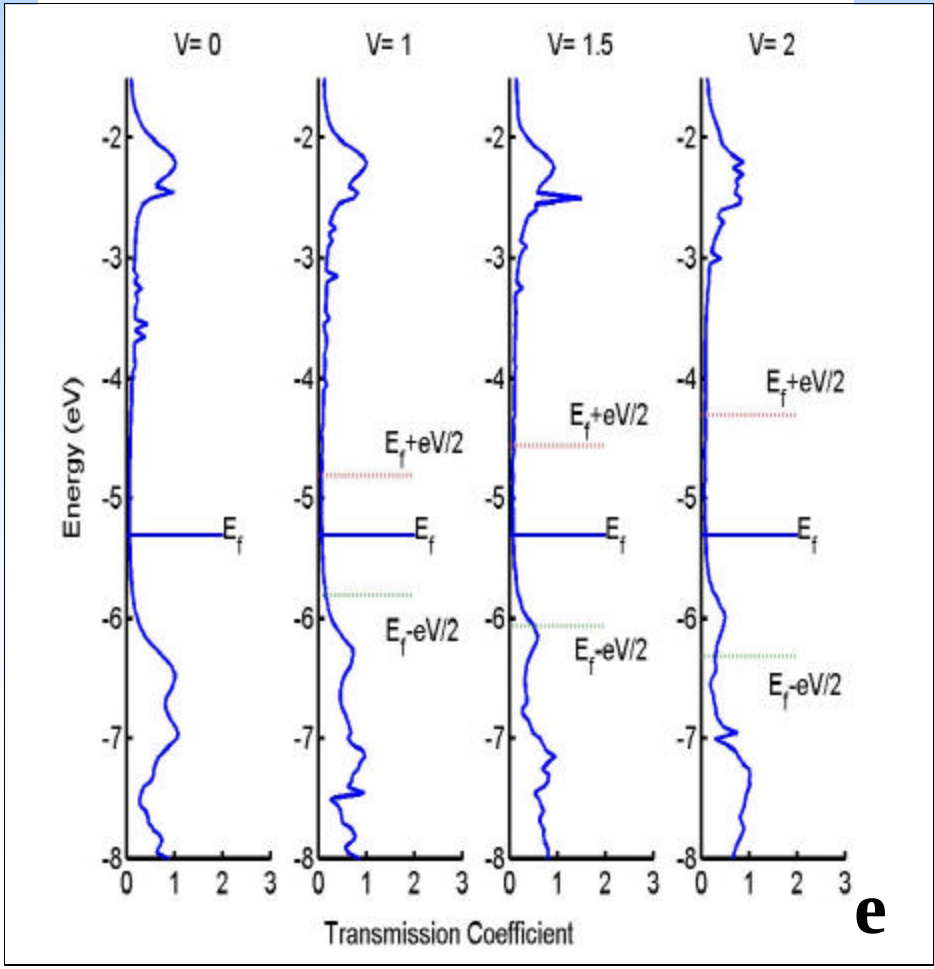
Transmission Property



b

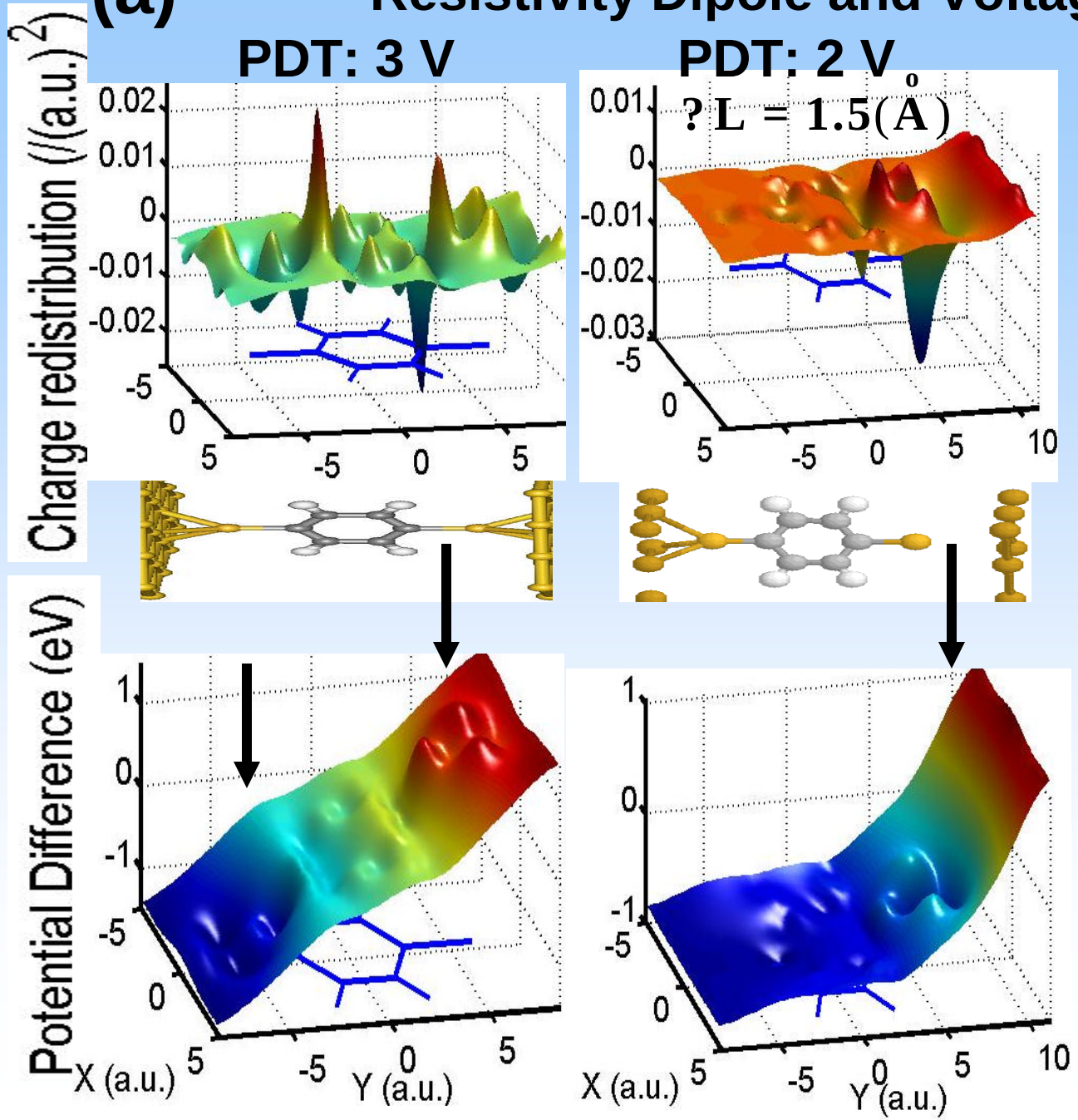


c



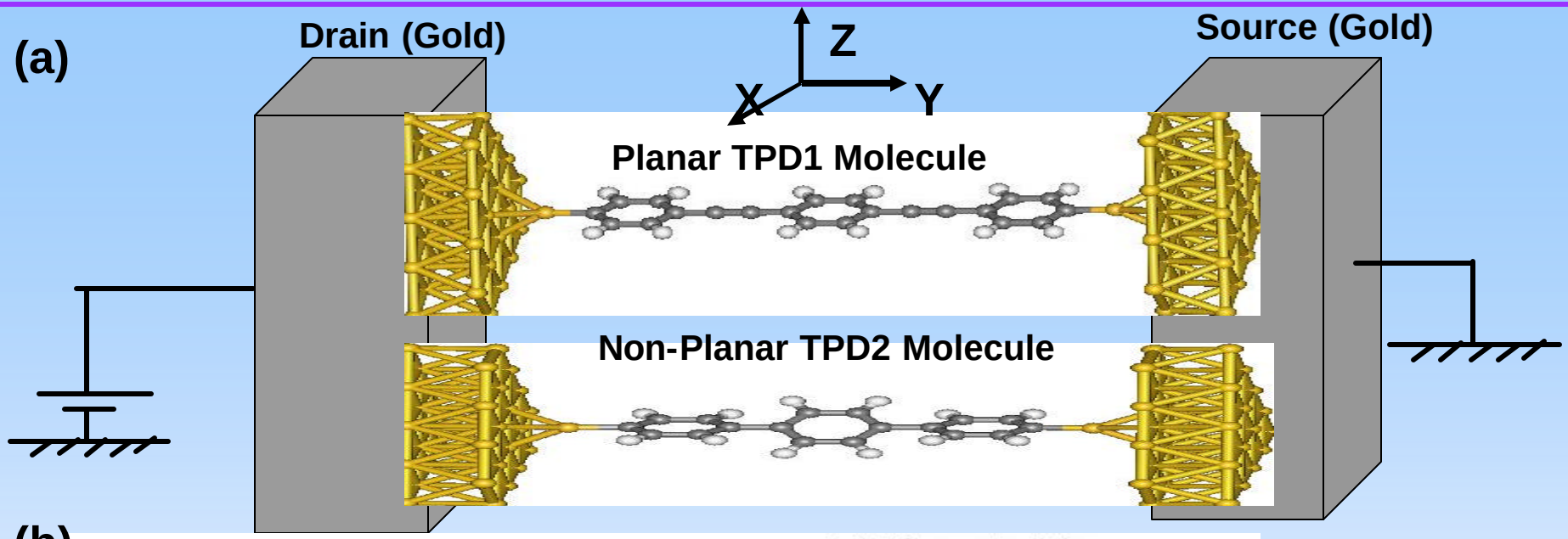
e

(a) Resistivity Dipole and Voltage Drop



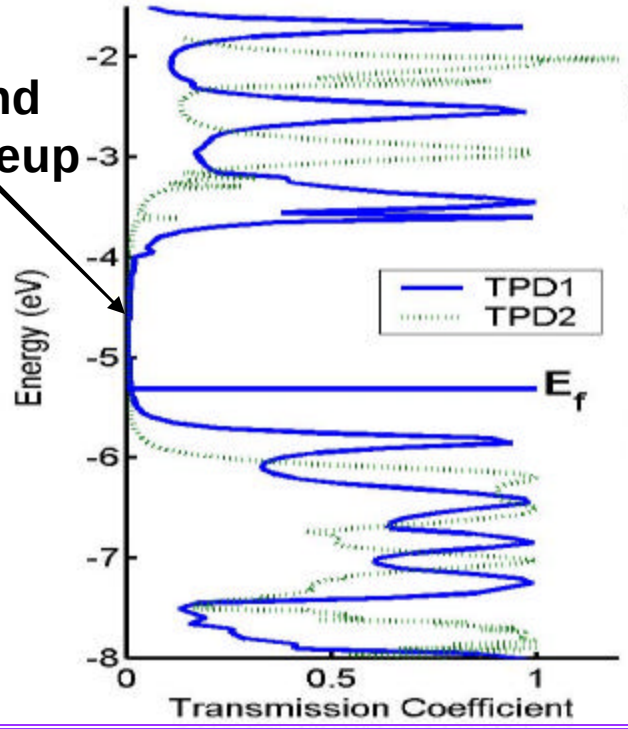
Change in flow density from pathway blockage

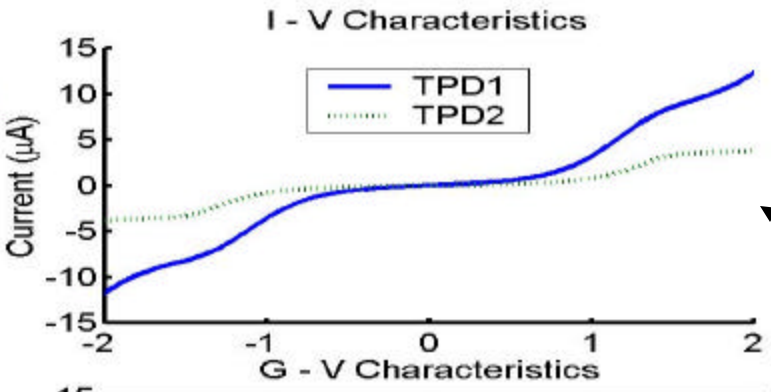
(a)

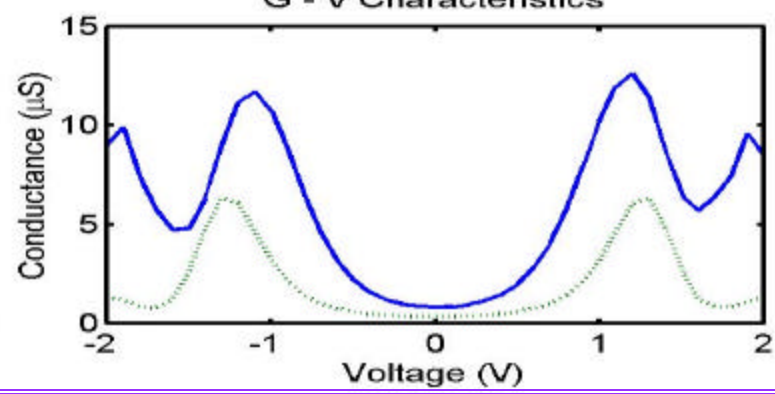


(b)

Band Lineup





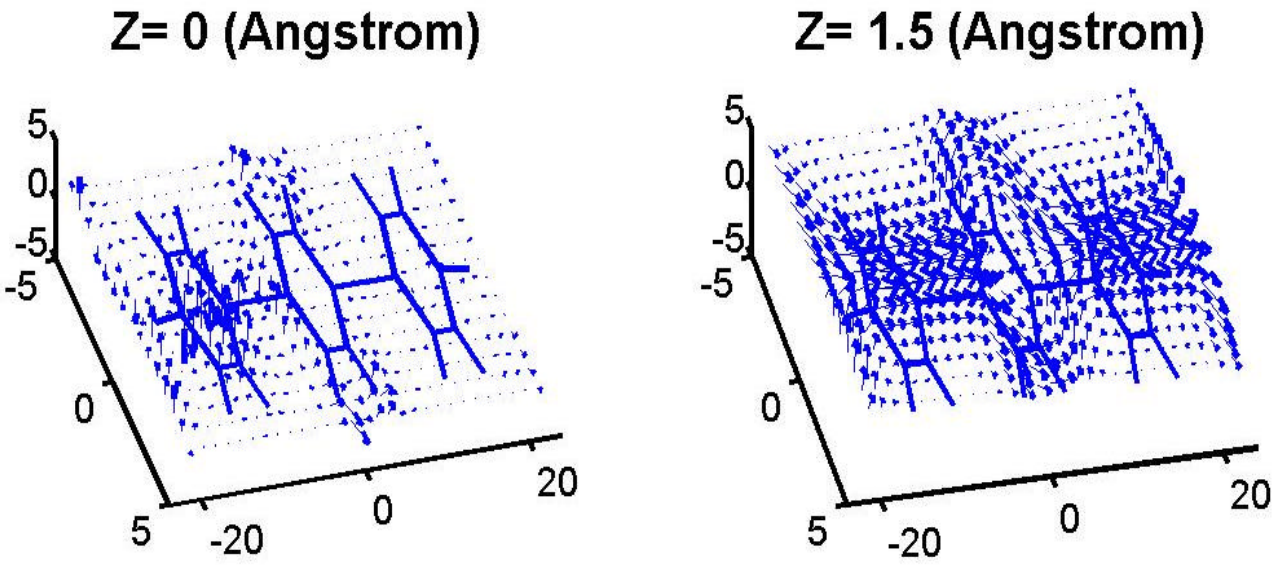


Similar I-V/G-V Characteristics

Current Flows Along the Internal Structure of Molecule

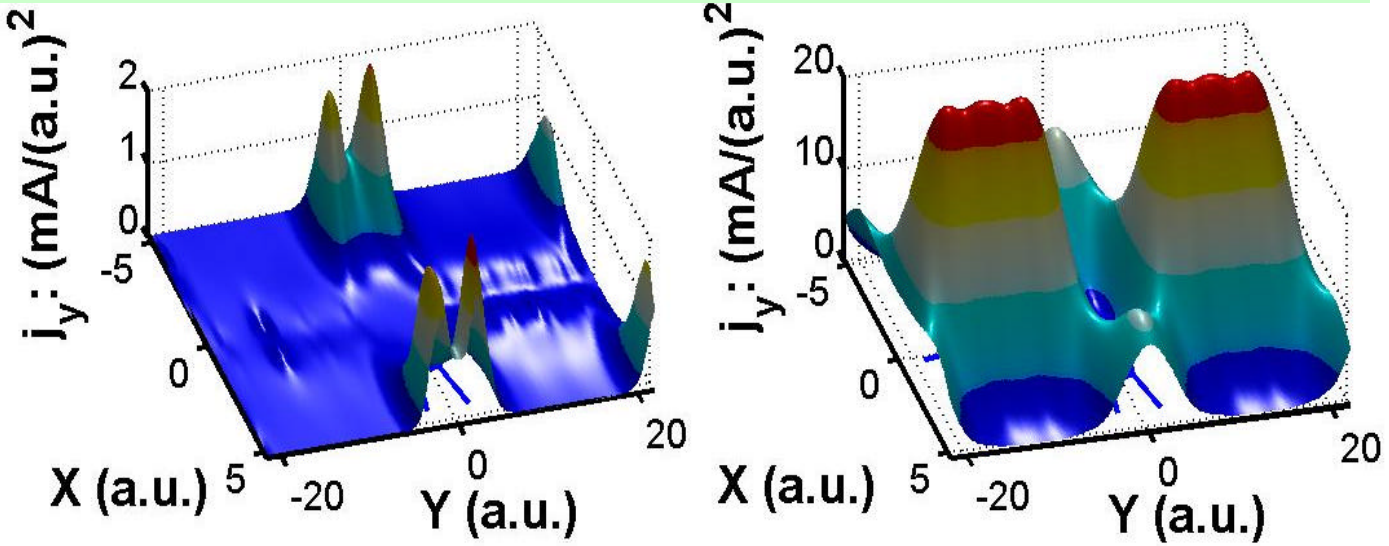
Direction of Current

XY Plane: Benzene Rings



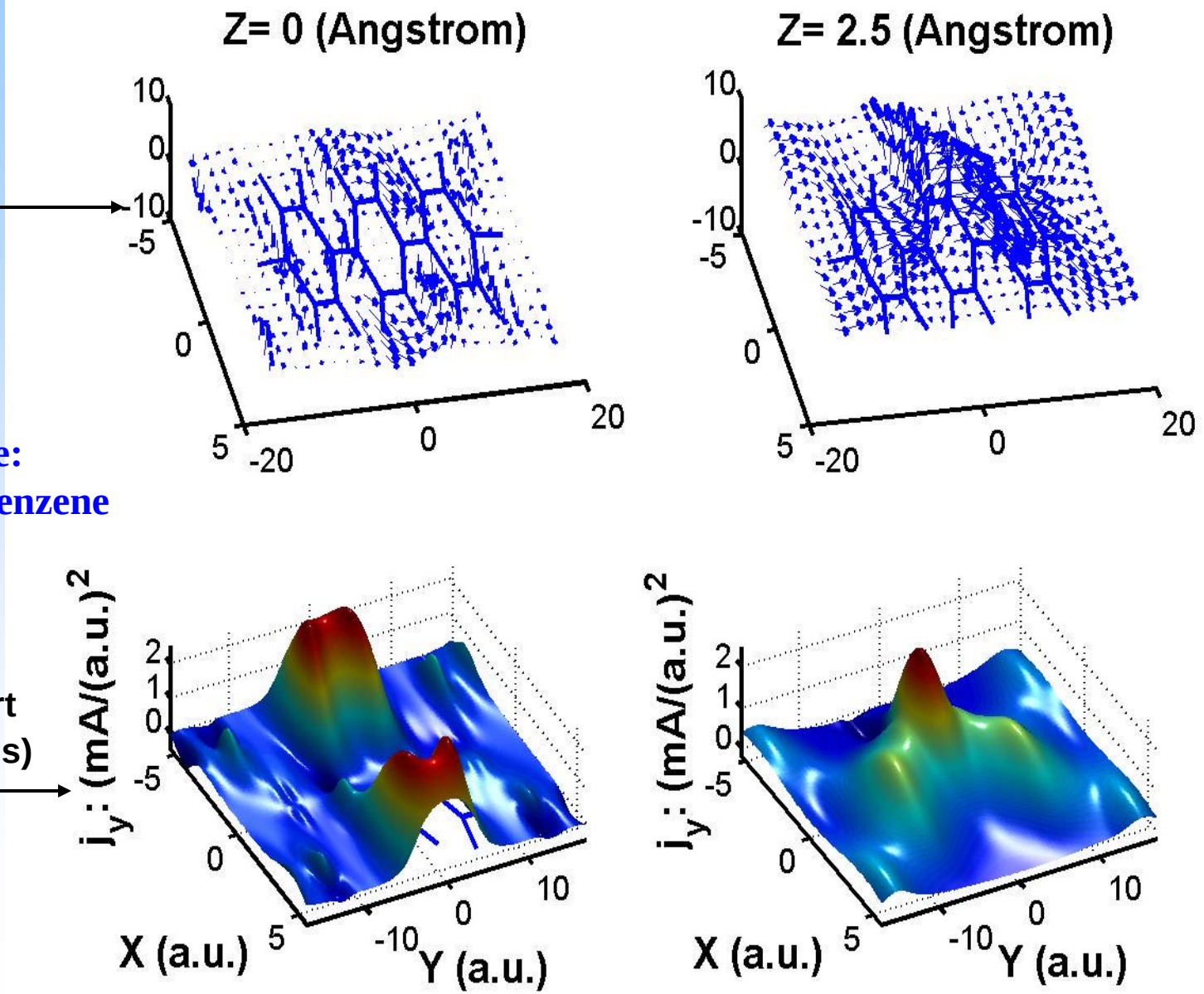
Current Flow Pattern in Planar Terphenyl Dithiol (TPD1) Molecule

Current Component Along Transport Direction (Y-axis)



Current Flow Pattern in Non-Planar Terphenyl Dithiol (TPD2) Molecule

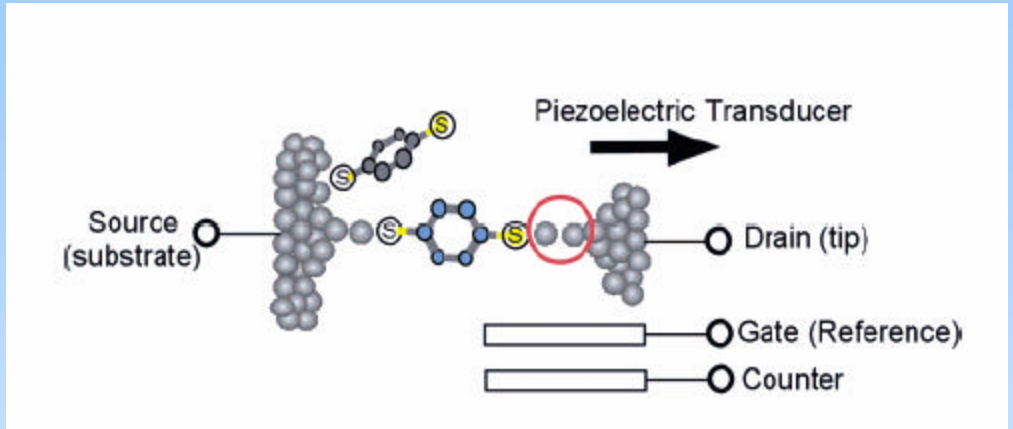
Direction of Current

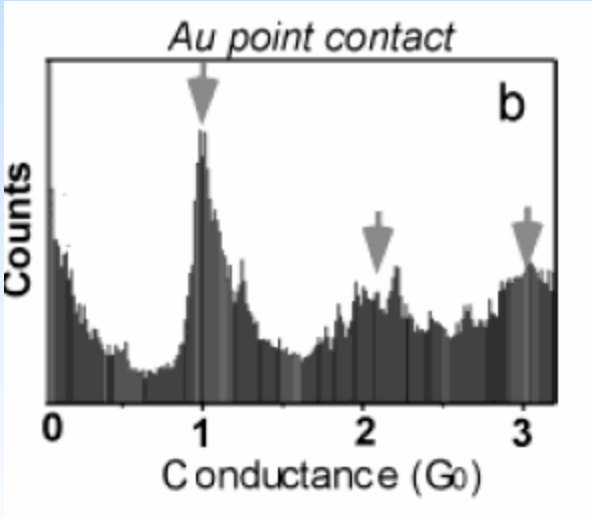


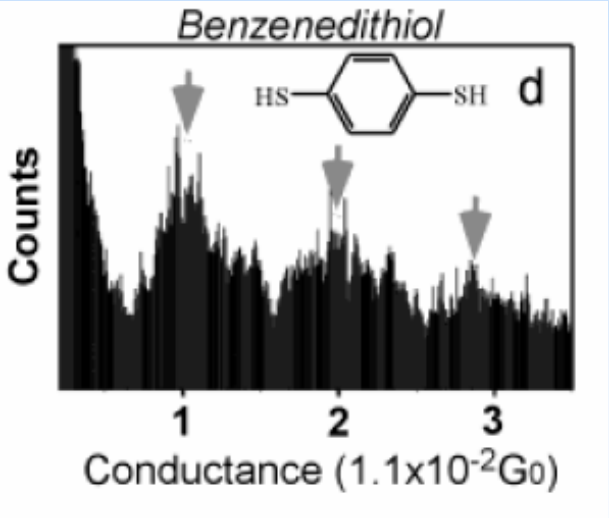
Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

- **NEGF Formulation**
- **Simple Tunneling Transport**
- **Geometry Modulation**
- **Weak vibronic coupling**
- **Strong vibronic coupling**

Electrochemical Measurement of Single-Molecule Conductance



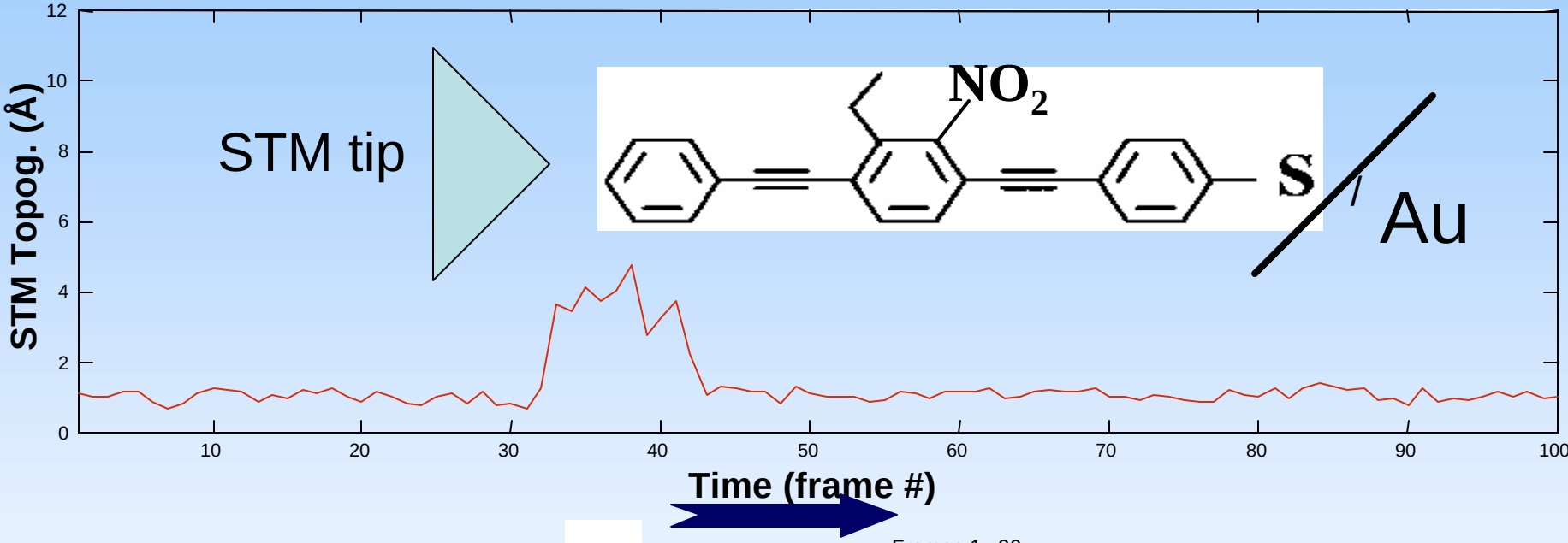


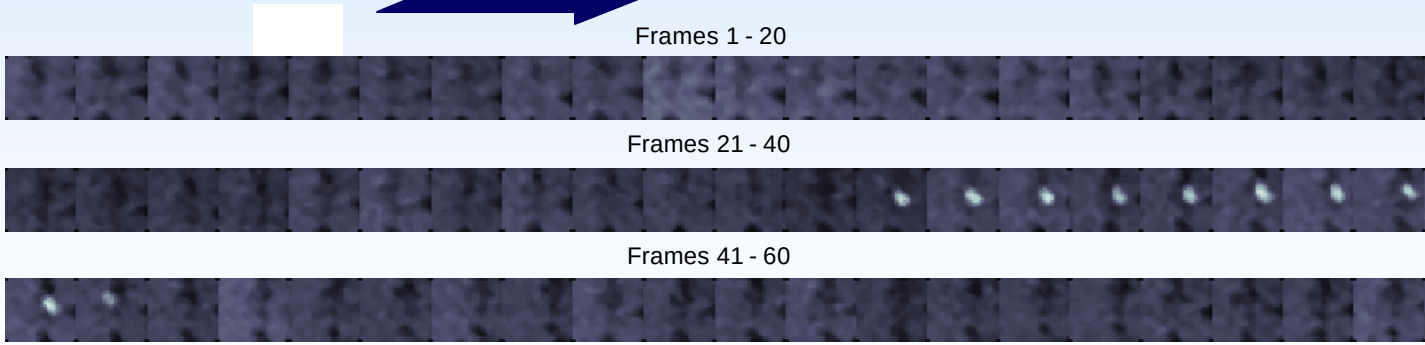


- **Gold contacts indeed quantized**
- **Molecule conducts 100 times less well**
- **Big fluctuations**

N. J. Tao, Nanolett. 2005

Dynamical conductance fluctuations





$V_{sample} = {}^{+}1.4$ V

I = 0.2 pA

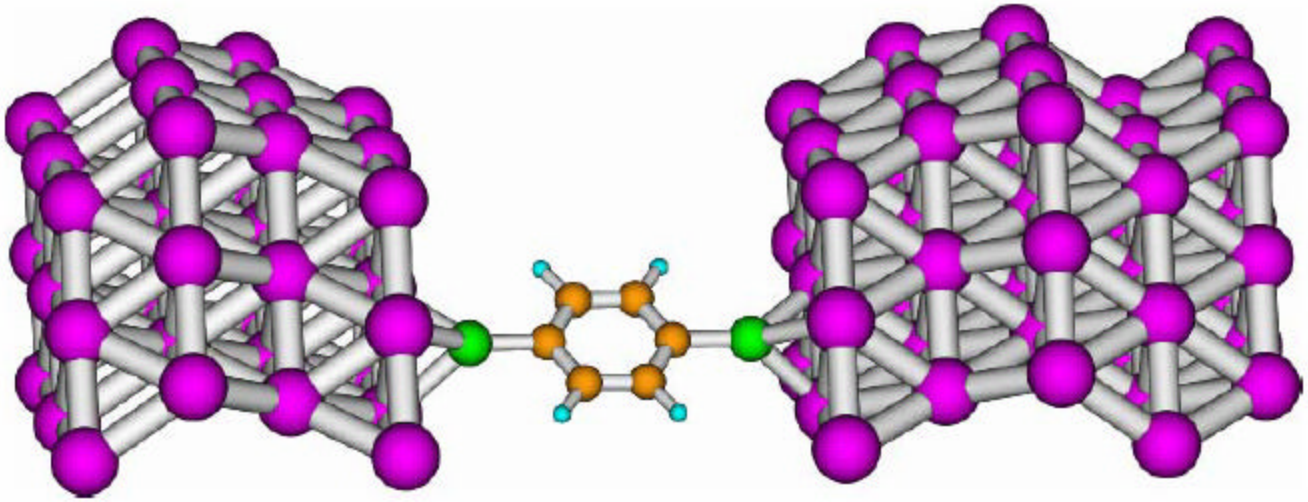
3 min/frame

Mantooth, Donhauser, Kelly &Weiss

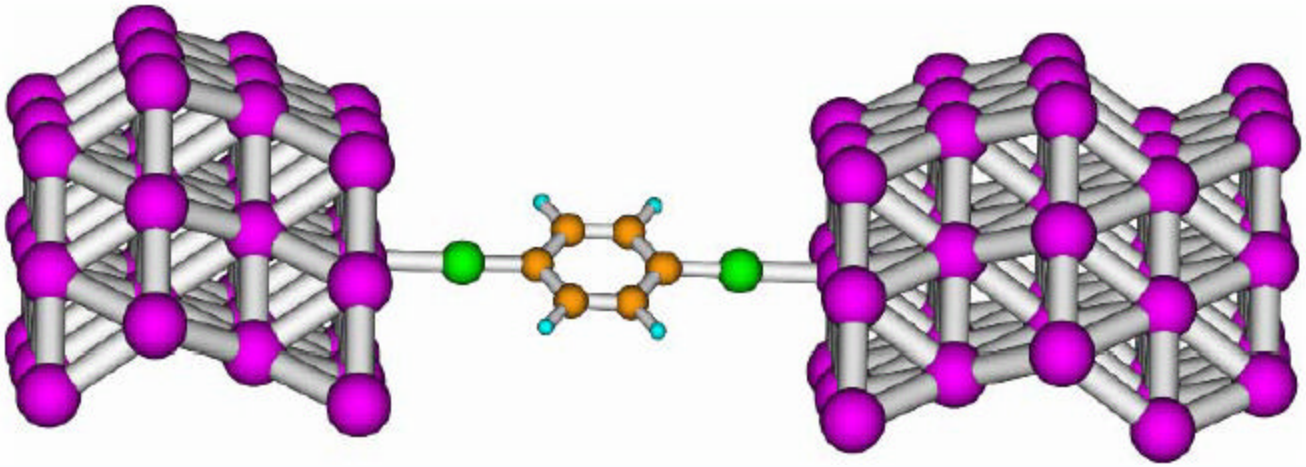
Review of Scientific Instruments 73, 313 (2002)

Different local thio coordination

(A)

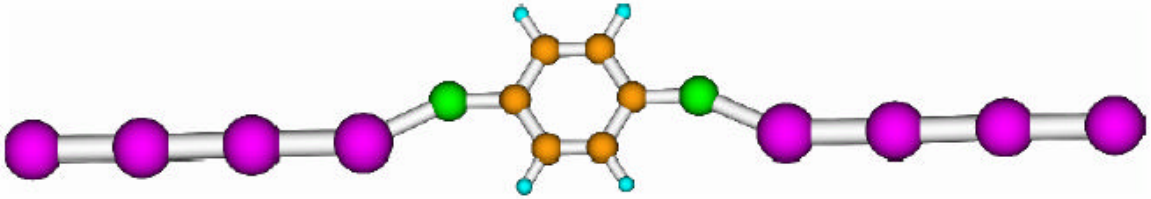


(B)

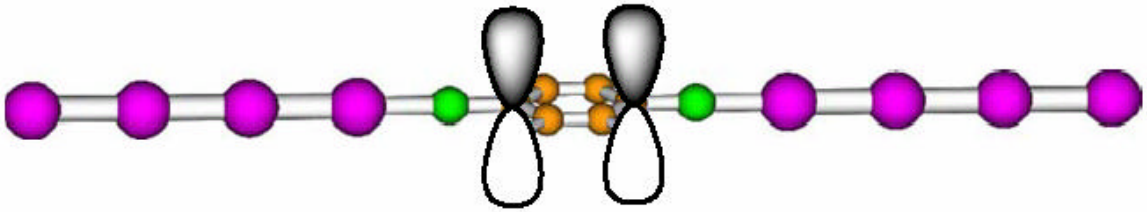


g(atop)/g(FCC) = 2.4

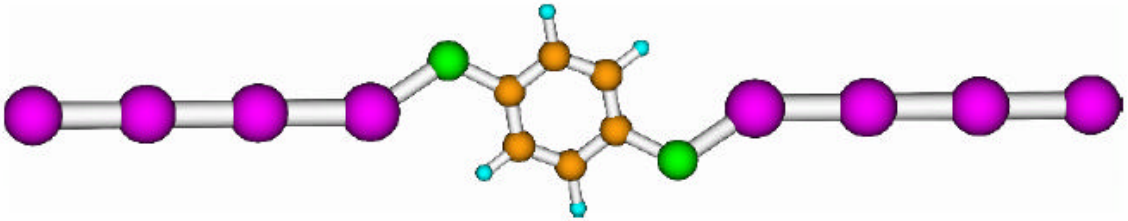
(A) $g = 2.1*10^{-8}$ S



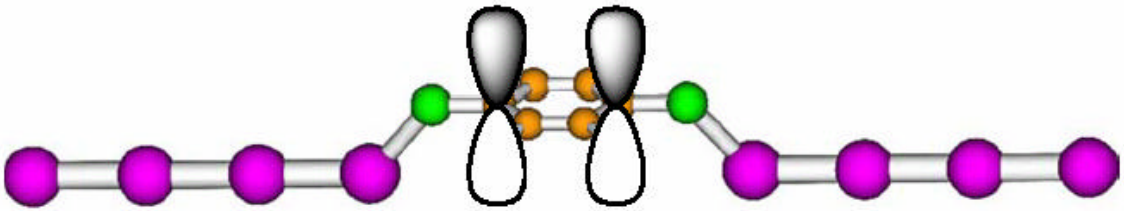
(B) $g = 2.6*10^{-8}$ S



(C) $g = 4.9*10^{-6}$ S



(D) $g = 7.0*10^{-5}$ S



Very sensitive to symmetry

Nano Lett. 2005

Single-molecule studies highlight conformational heterogeneity in the early folding steps of a large ribozyme

Zheng Xie*†, Narayanan Srividya‡, Tobin R. Sosnick†‡, Tao Pan‡, and Norbert F. Scherer*†§

†Institute for Biophysical Dynamics and Departments of ‡Biochemistry and Molecular Biology and *Chemistry, University of Chicago, Chicago, IL 60637

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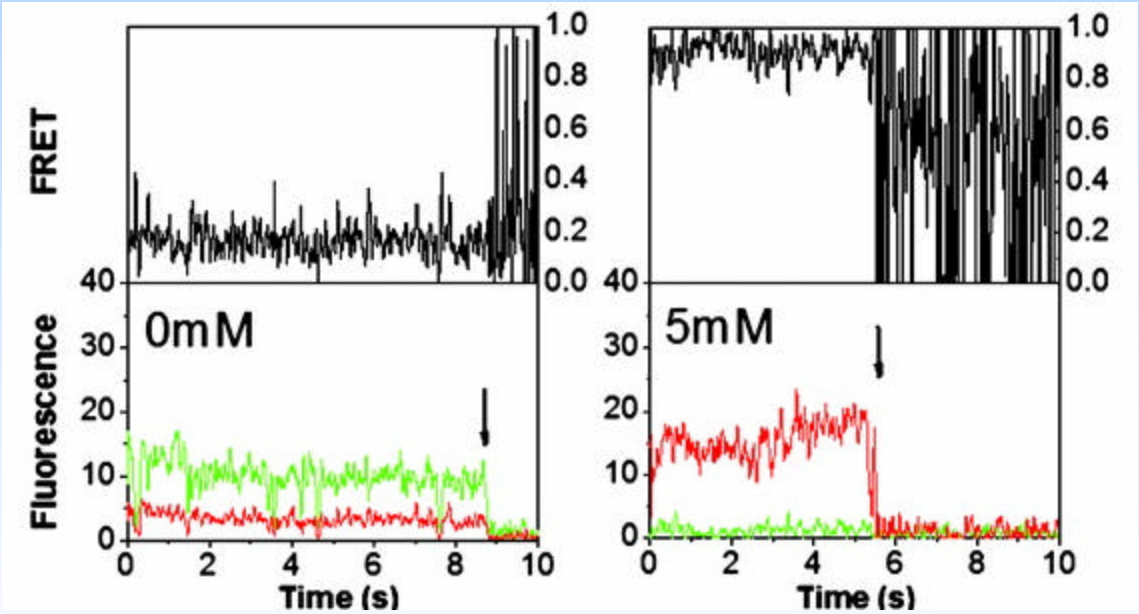


Complex inter- and intra-class dynamics are observed for the equilibrium conformational fluctuations of the C-domain of P RNA.
Subpopulations undergo different structural interconversions on the seconds time scale.

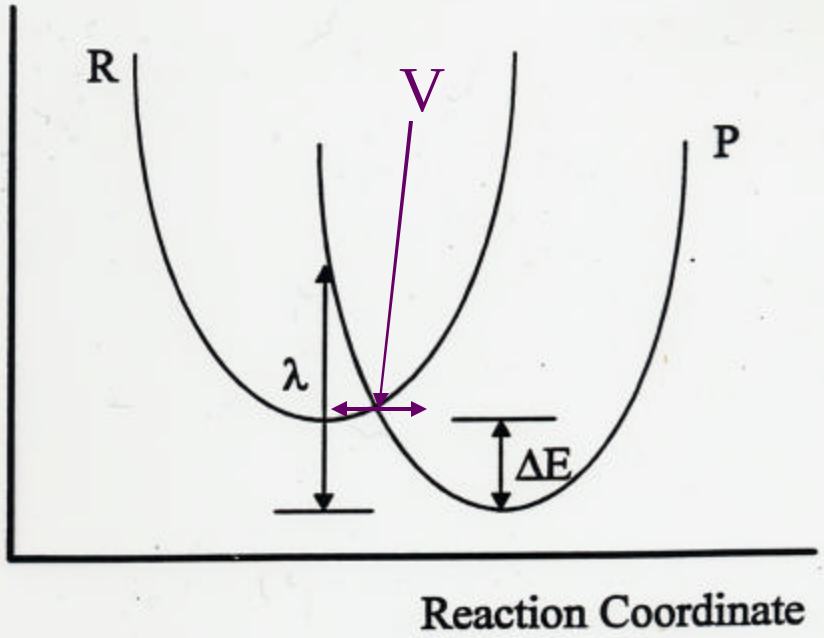
Conductance Fluctuations?

- multiple stable sites, low barriers
- conductance changes with site symmetry
- characteristic of Lewis bonding like Au/thiol
- reminiscent of single-molecule spectra
- characteristic of nanoscale phenomenon (exacerbated on soft metal interfaces)

Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

- **NEGF Formulation**
- **Simple Tunneling Transport**
- **Geometry Modulation**
- **Weak vibronic coupling**
- **Strong vibronic coupling**

Nonadiabatic Electron Transfer

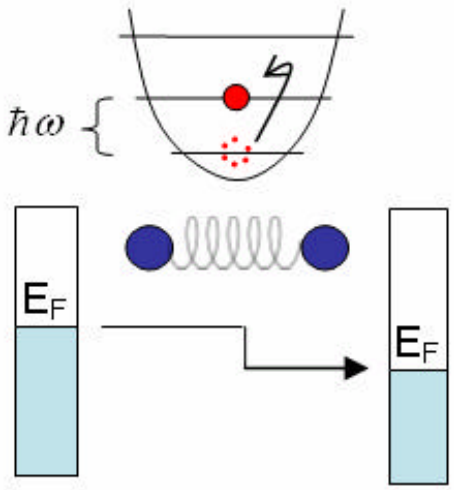


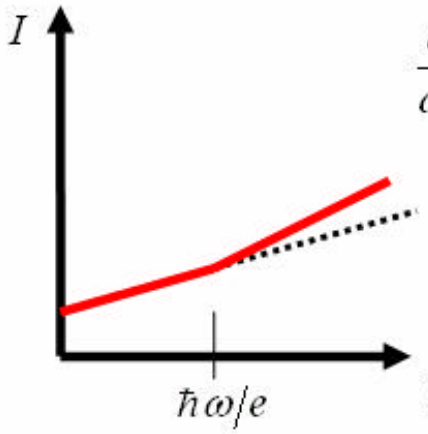
$$k = \frac{2\pi}{\hbar} V^2 \left(DWFC \right)$$

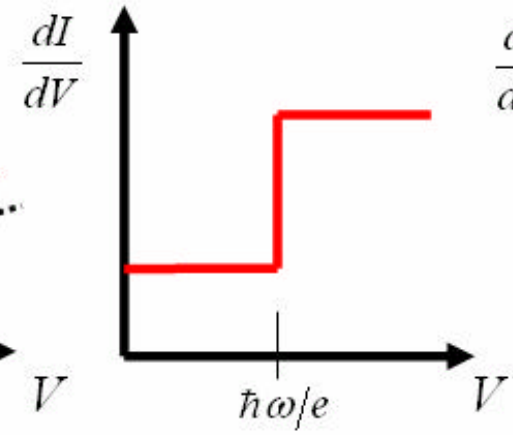
Vibronic Continuum

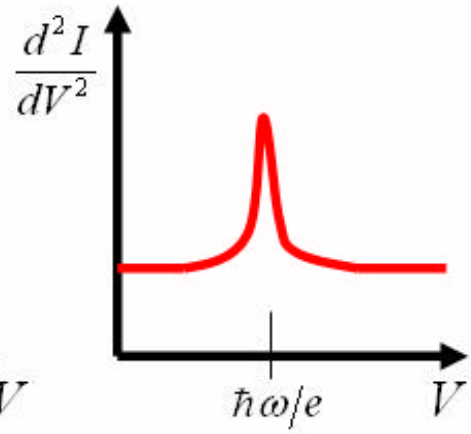
Marcus, Hush, Jortner

IETS SCHEMATIC



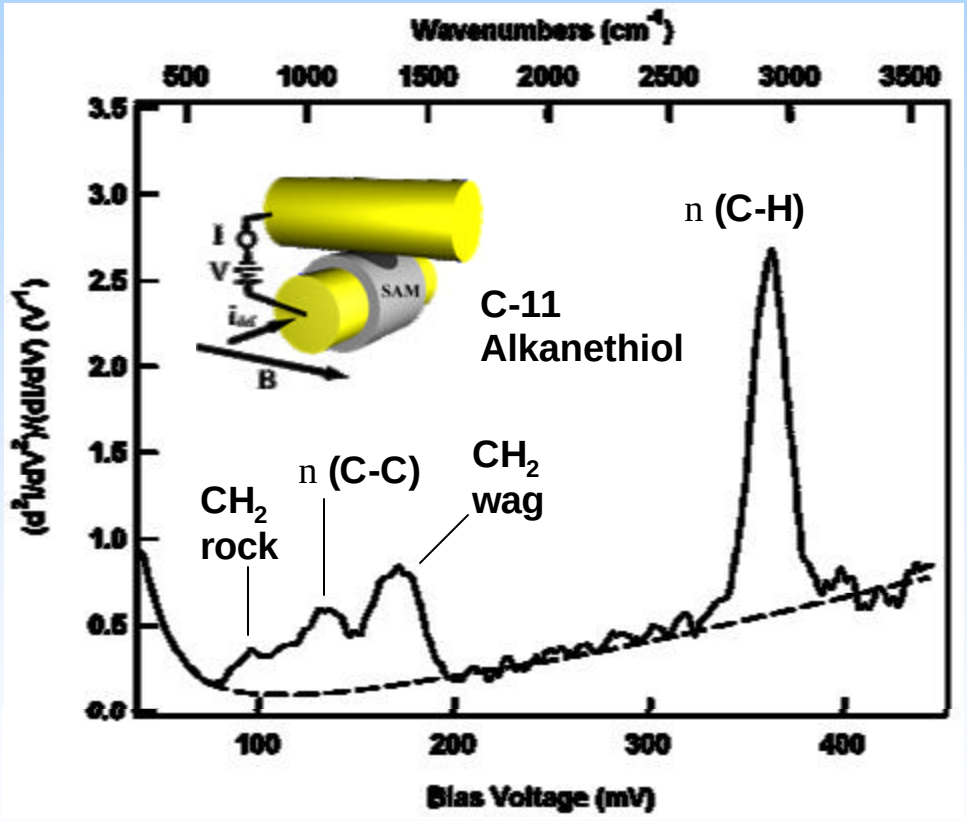


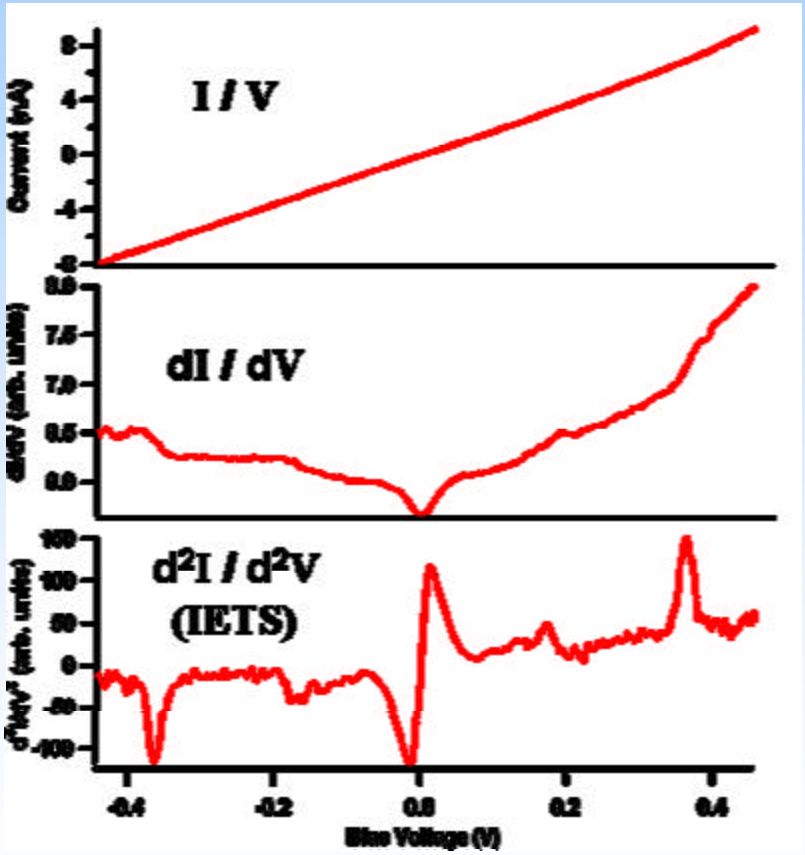




IETS Measurements using Crossed-Wire Junctions

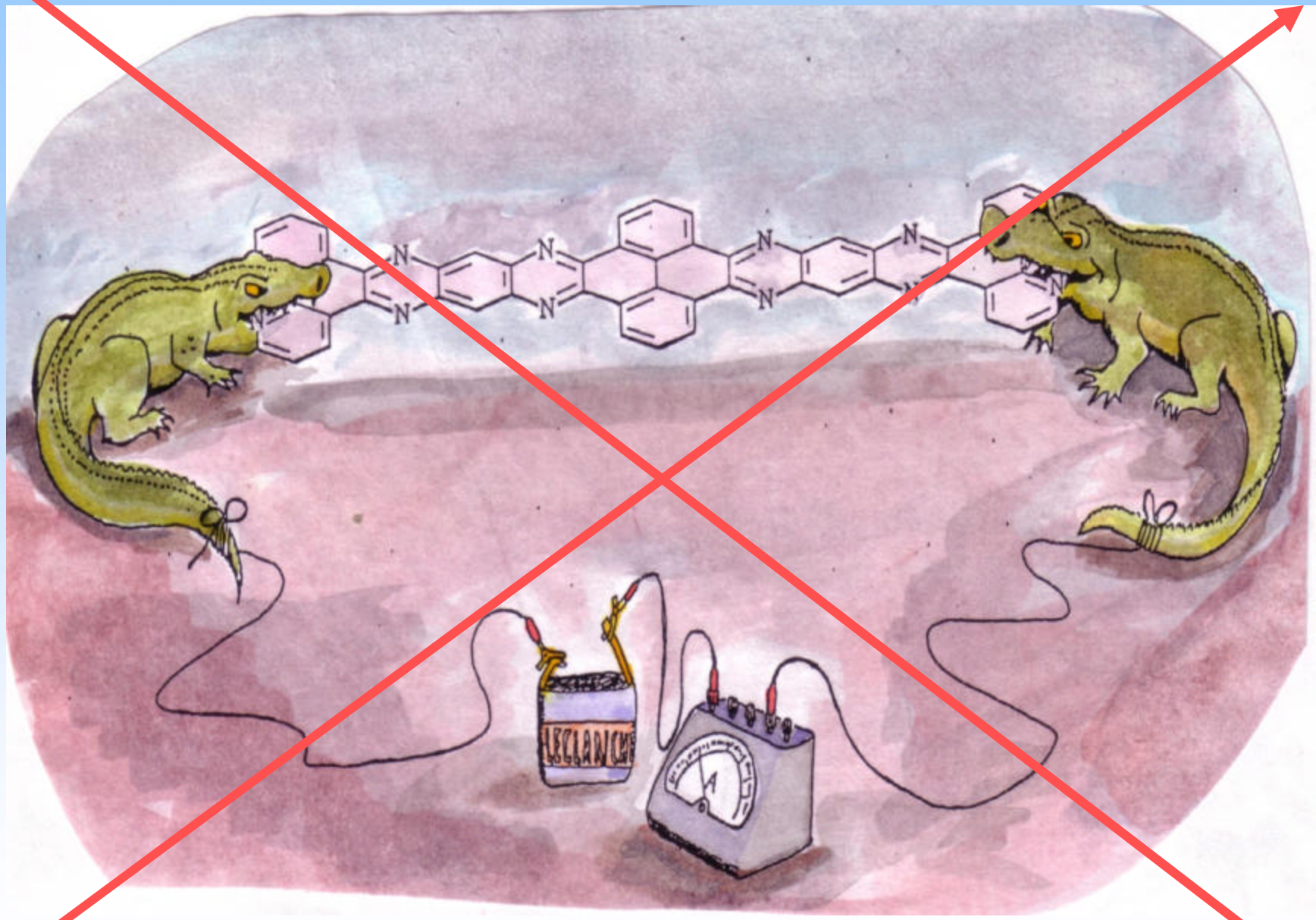
Observed IETS peaks are primarily longitudinal vibrations of the molecules comprising the molecular junction.





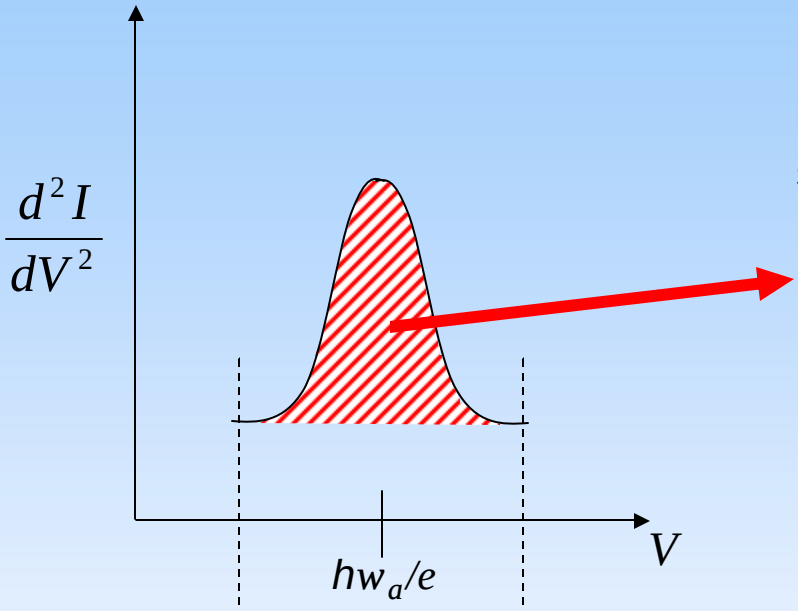
Vibronic Contributions to Charge Transport Across Molecular Junctions

J. Kushmerick et al. *Nano Letters* **2004**, *4*, 639.



@ C. Coudret (CNRS-1992)

Simulation of IETS spectra (basic equations)



Normal mode α produces a peak in the IETS spectra at $V=hw_a/e$ with integrated intensity:

$$W_a = g_c \mathrm{Tr}(\mathrm{G}^{\mathrm{L}}(E_F)\mathbf{G}^{\alpha}(E_F)\mathrm{G}^{\mathrm{R}}(E_F)\mathbf{G}^{\alpha}(E_F)^{+})$$

The matrix elements of $\mathbf{G}^{\alpha}$ are Green's function derivatives with respect to the normal modes

$$G_{ij}^{a} = \frac{\sqrt{2}}{2}\left(\frac{\P G_{ij}(E,\{Q\})}{\P Q_a}\right)_{Q_a=0}$$

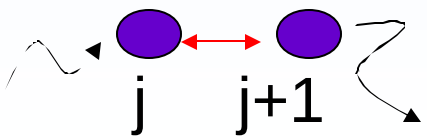
Can then get the IETS spectral peaks from DFT calculations:

The IETS can be seen as a pathway sum:

Interface terms

$$W^a = g_c \sum_{\substack{m\in L \\ n\in R}} \Gamma^L_{mm}(E)\Gamma^R_{nn}(E)\frac{1}{2}\left|\sum_{path\ P}\left[\frac{\P G^P_{mn}(E)}{\P Q^a}\right]\right|^2$$

$$\frac{\P G_{1N}(E)}{\P Q_a} = \text{Pathway sum}$$

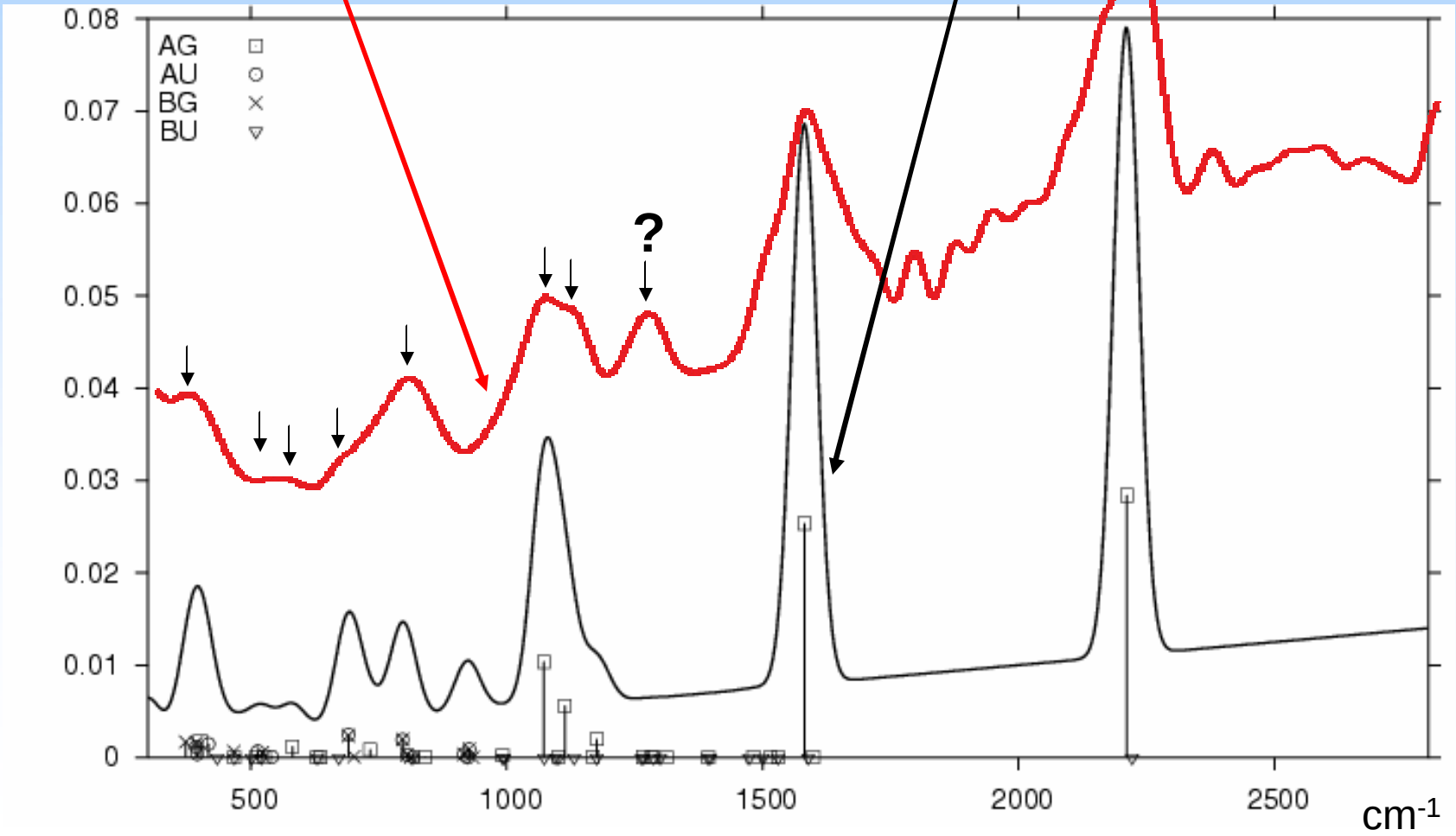


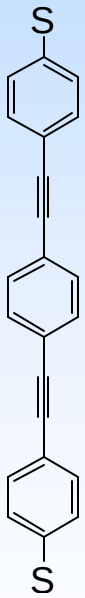
$$= \sum_{paths\ P}\left[\sum_{j=1,M} G^P_{1P(j)}(E)\frac{\P V_{P(j),P(j+1)}(Q)}{\P Q_a} G^P_{P(j+1)N}(E)\right]$$

HIGH RESOLUTION EXPERIMENTAL SPECTRA OF OPE

COMPARED WITH THE CALCULATION

Dominated by symmetric modes

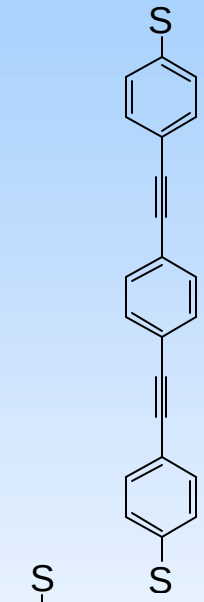


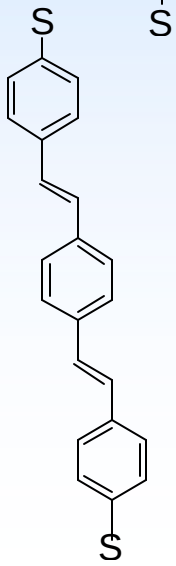


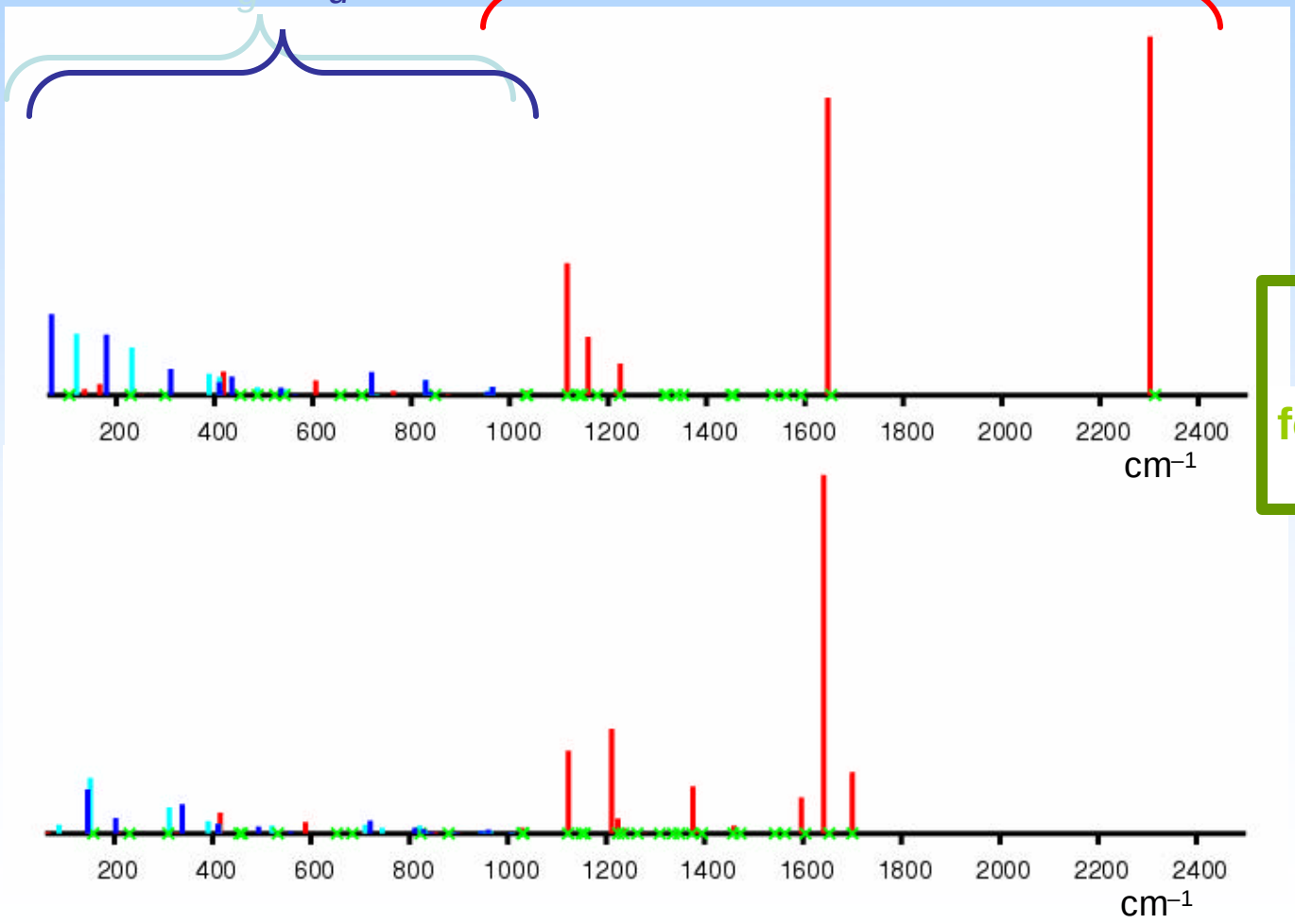
PROPENSITY RULES (C_{2h} conjugated molecules):

out-of-plane modes
(mixed π–σ tunneling)

in plane stretching
& bending modes
(all π tunneling)







b_u
forbidden
(all σ)

From Group Theoretical Analysis of the Perturbation formula for IETS

some rules for the spectra:

1. **For single chain type molecules, only totally symmetric vibrations seen**

2. **Stronger IETS signals from vibrations along active transport paths (side chain vibrations less significant)**

3. **Multiple binding at electrodes changes the relative IETS intensities (**s/p)

Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

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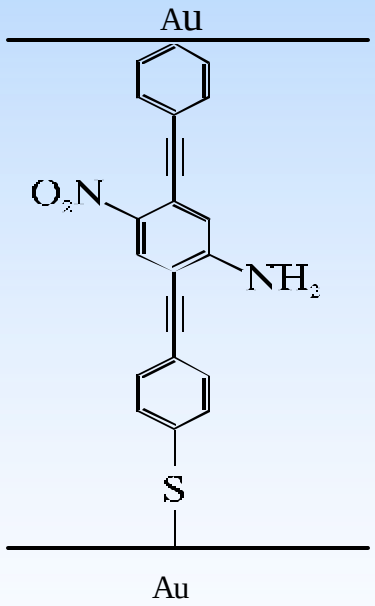
- **Strong vibronic coupling**

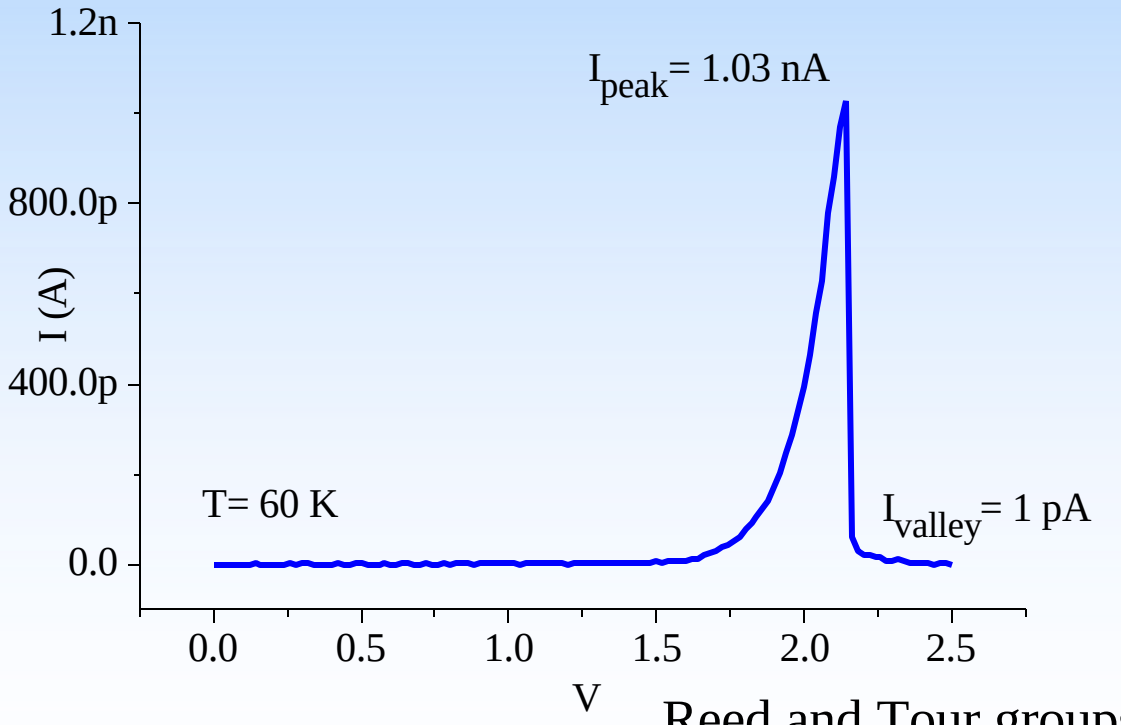
What about vibronic coupling, the heart of electron transfer ?

Now, stronger coupling

MOLECULAR CIRCUITS – BEYOND SIMPLE CONDUCTANCE

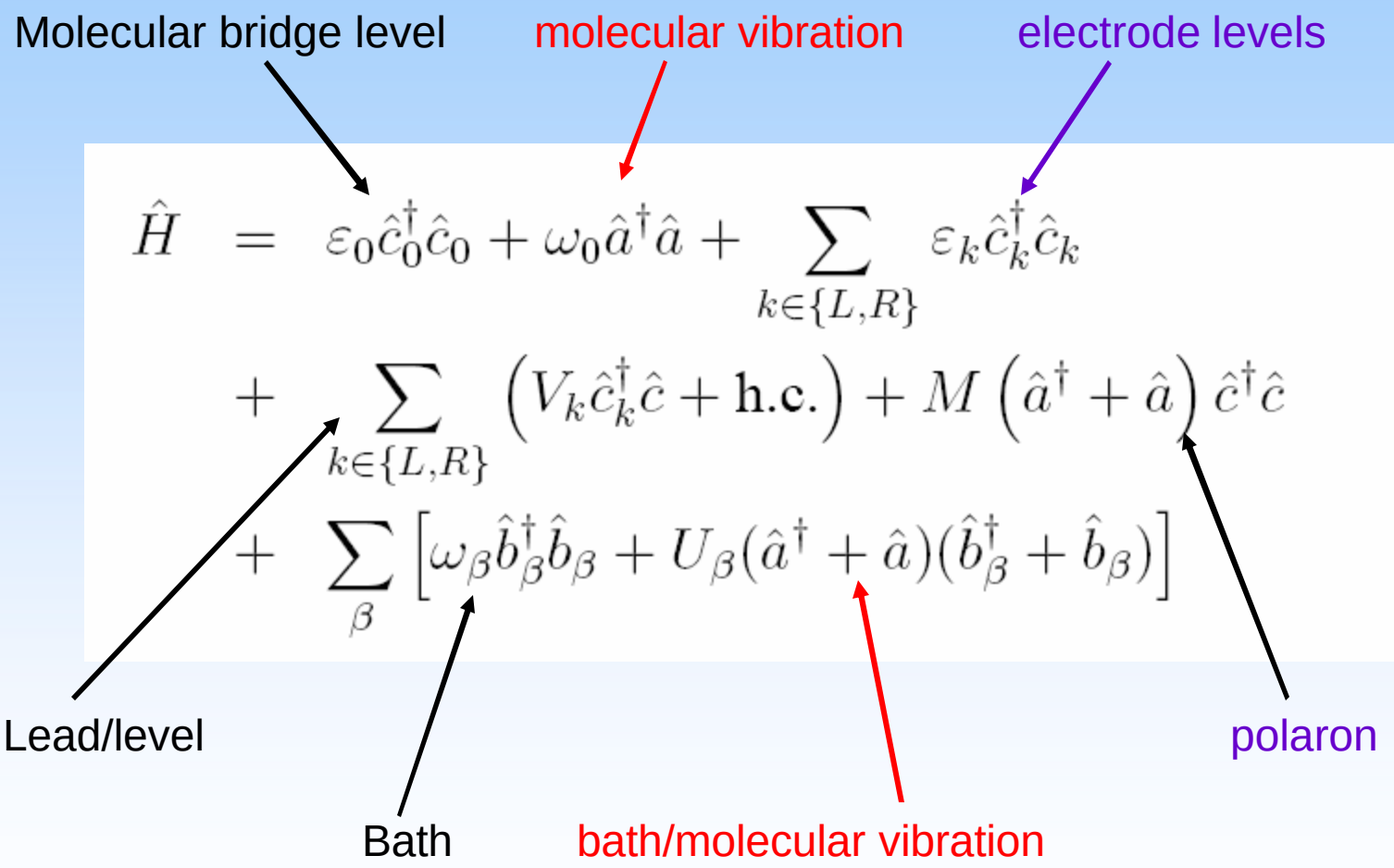
rectifiers, negative differential resistance circuits, molecular transistors, recognition conductance modulation





Reed and Tour groups, NDR response

Polaron model for treating hysteresis in junctions

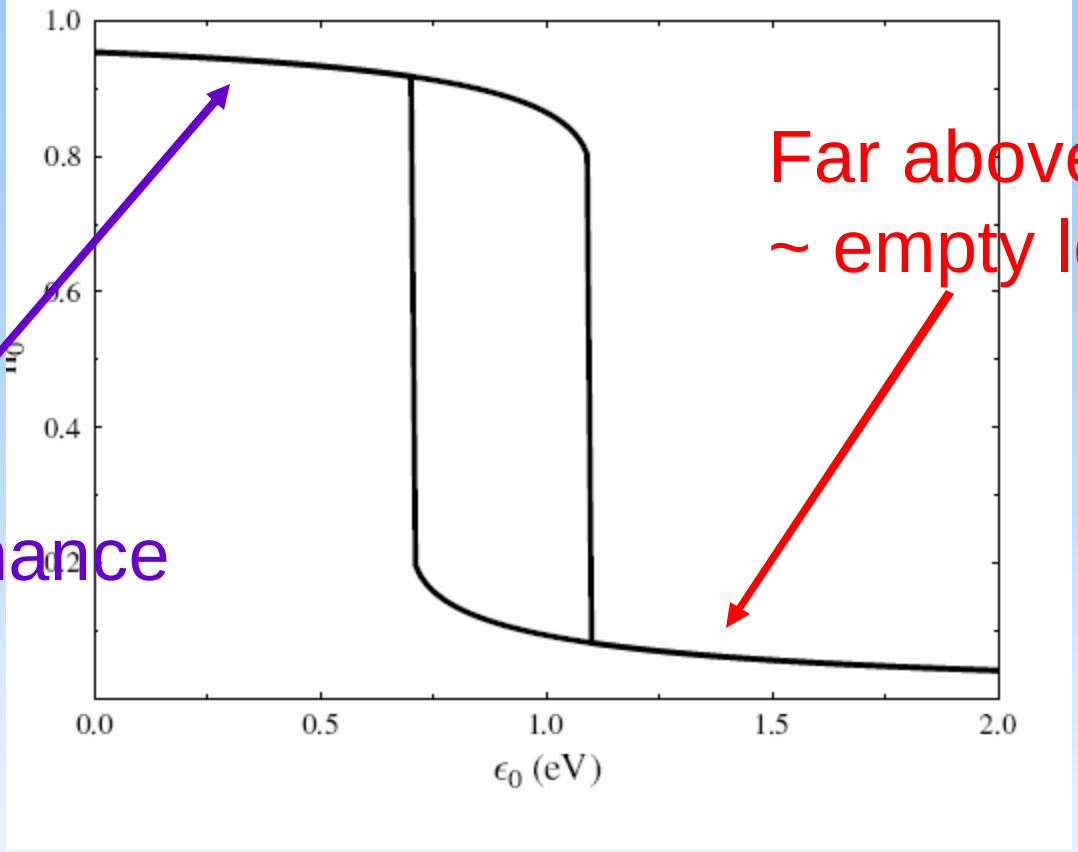


Born- Oppenheimer separation

$$\hat{H}_{el} = \tilde{\varepsilon}_0(n_0)\hat{c}^\dagger\hat{c} + \sum_{k\in\{L,R\}} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_{k\in\{L,R\}} \left(V_k \hat{c}_k^\dagger \hat{c} + \text{h.c.}\right)$$

$$\tilde{\varepsilon}_0(n_0) = \varepsilon_0 - 2\varepsilon_{reorg} n_0$$

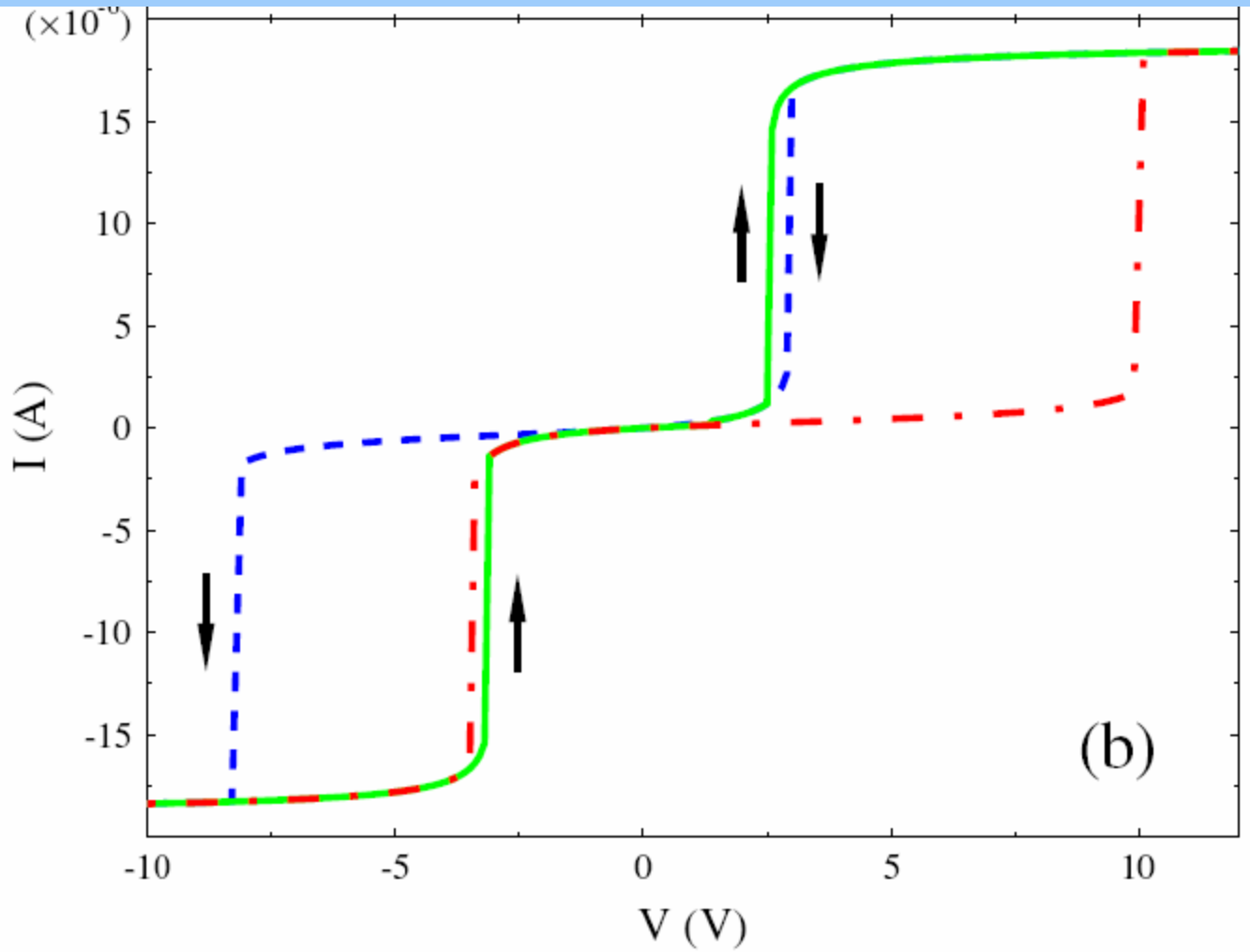
$$\varepsilon_{reorg} = M^2 \frac{\omega_0}{\omega_0^2 + (\gamma/2)^2}$$



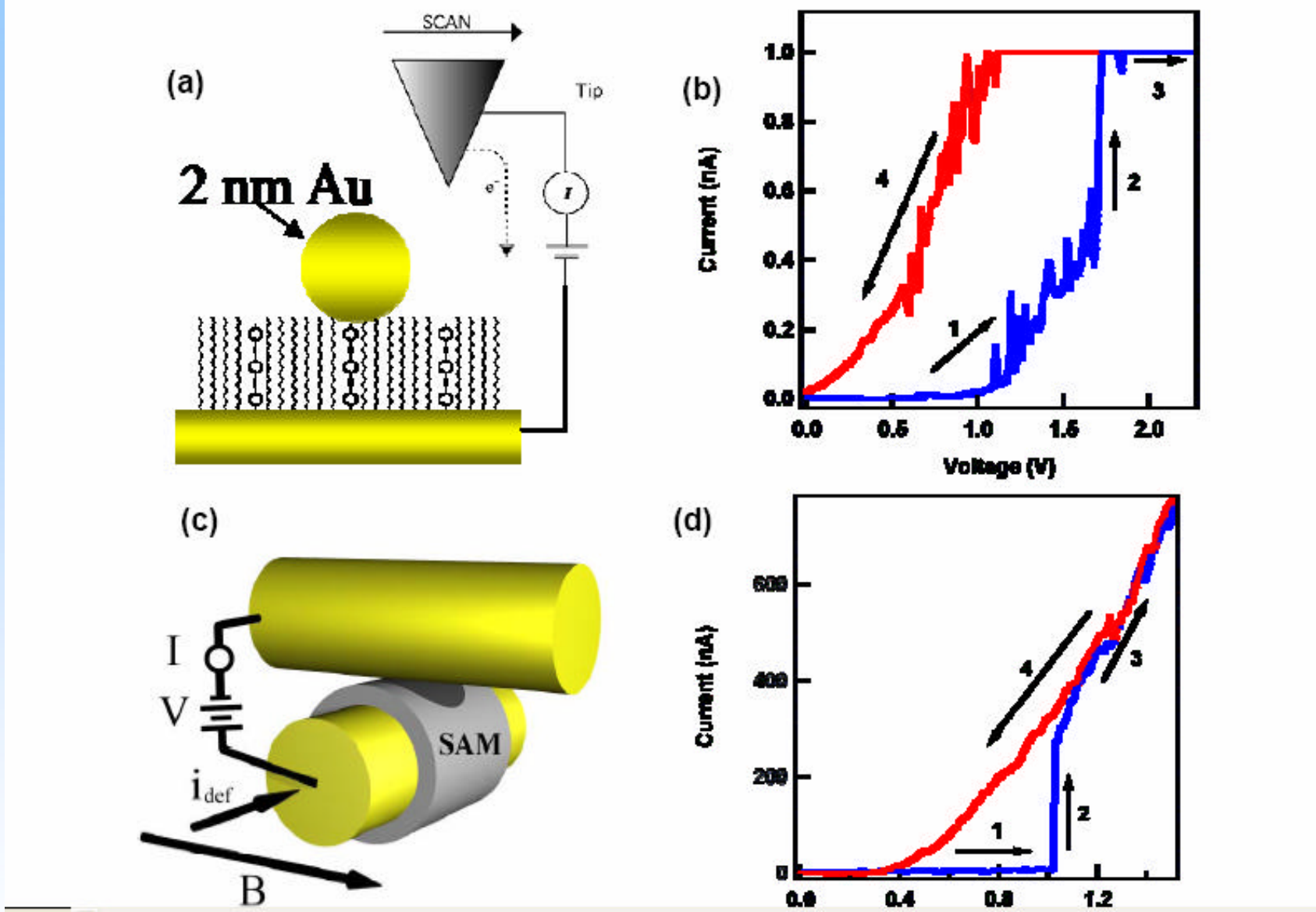
Near resonance
~ full level

Far above resonance
~ empty level

In the energy window, there is a bistable structure:
as an electron localizes on the molecule, its polaron energy can drop out of the conductance window

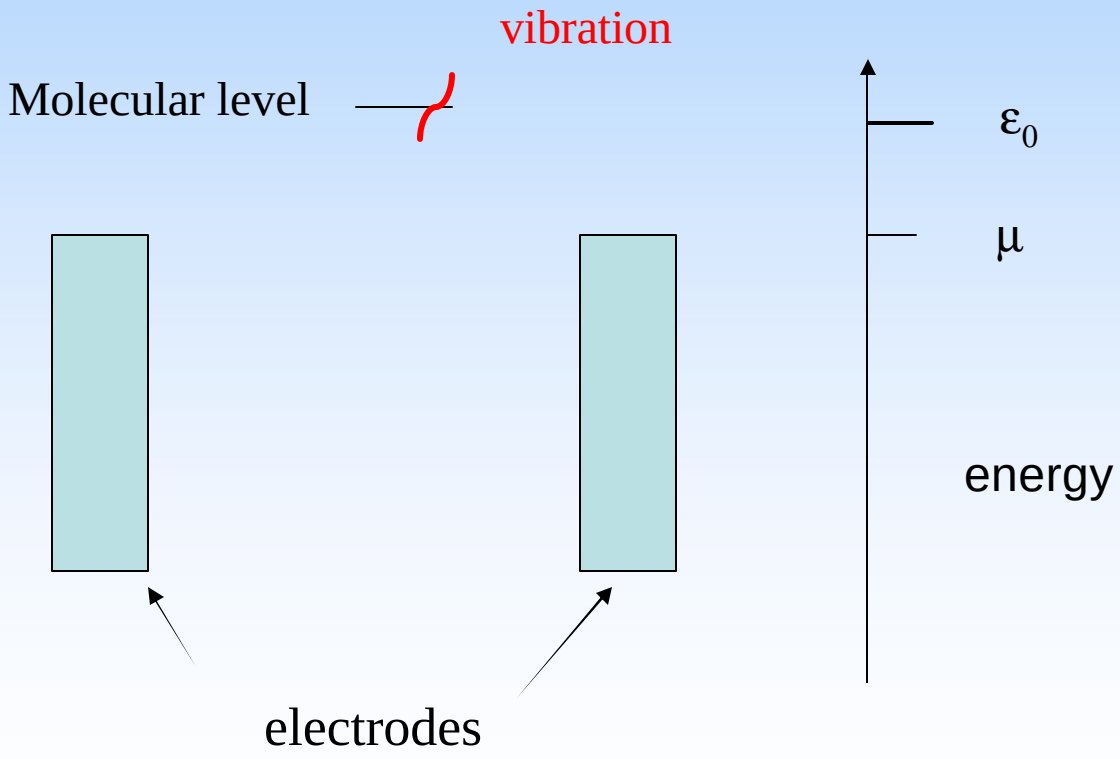


Hysteresis from vibronic coupling

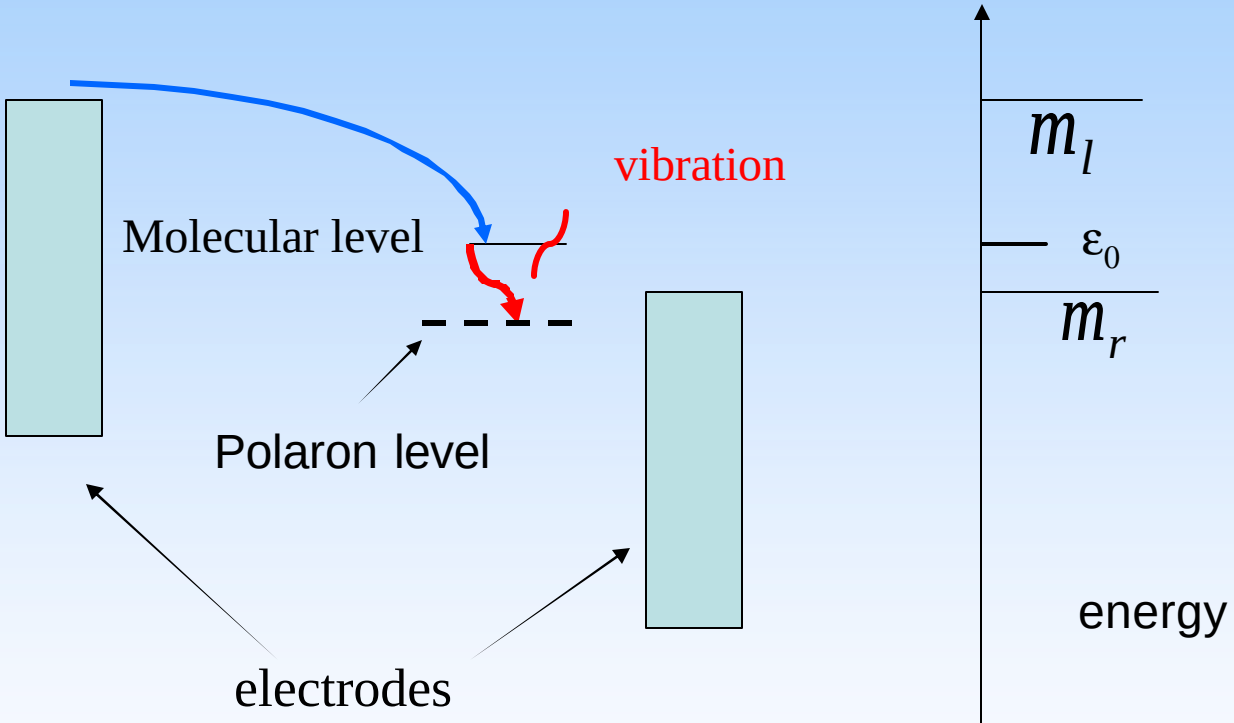


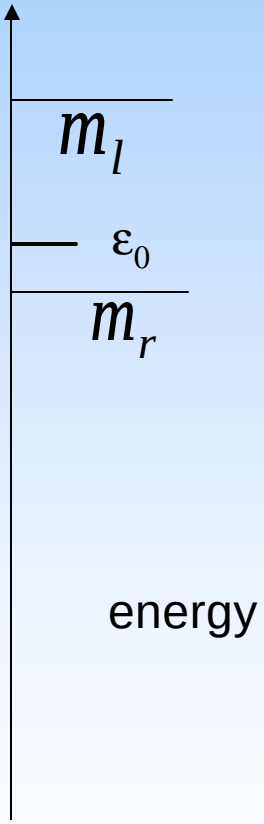
Shashidhar et. al. 2005

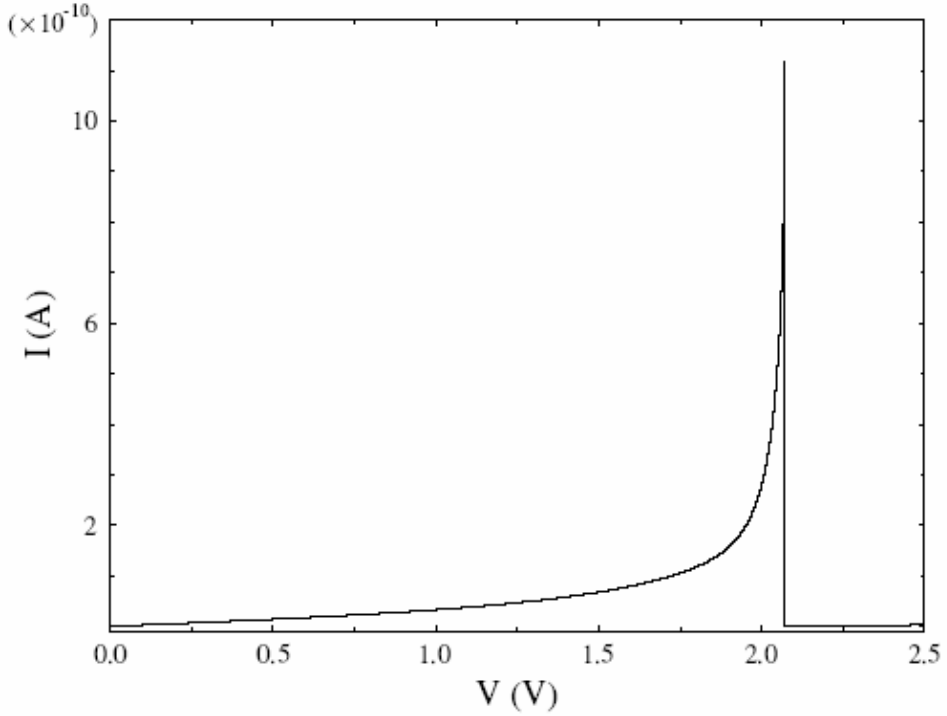
Polaron model for treating hysteresis in junctions



Polaron formation under bias







Computed NDR behavior

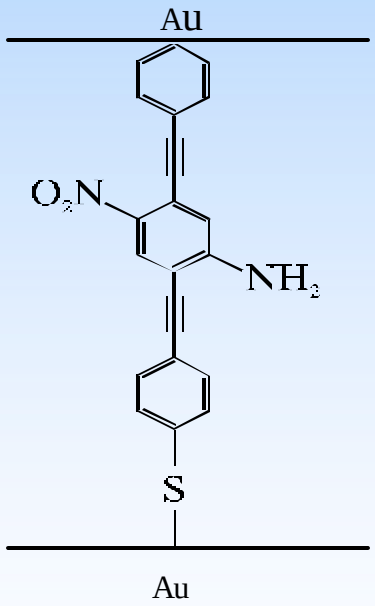
$$I_{peak} / I_{valley} = 487$$

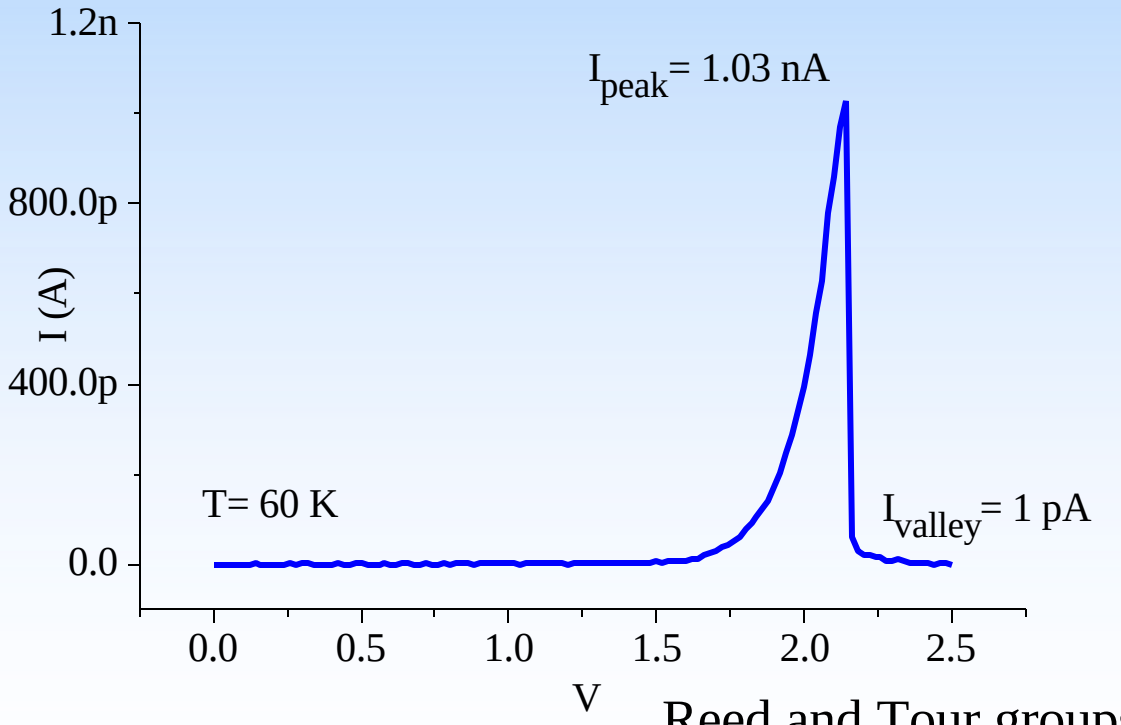
Polaron model of nonequilibrium response

Requires redox active species

MOLECULAR CIRCUITS – BEYOND SIMPLE CONDUCTANCE

rectifiers, negative differential resistance circuits, molecular transistors, recognition conductance modulation



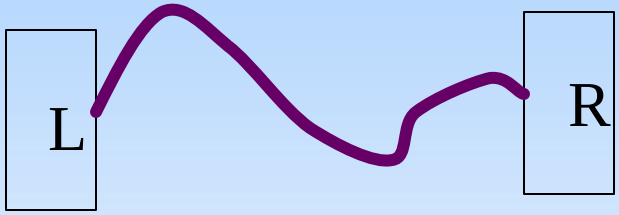


Reed and Tour groups, NDR response

Molecular wires and Electron transfer?

Molecular wires and Electron transfer?

Wire junction



electron tunneling
Electrode sink
Electrode interface
Landauer approach

Conductance

ET

D-B-A

electron tunneling
vibronic sink
Donor,acceptor,bridge
Marcus formula

Rate constant

Rate constant and conductance are proportional (Nitzan)

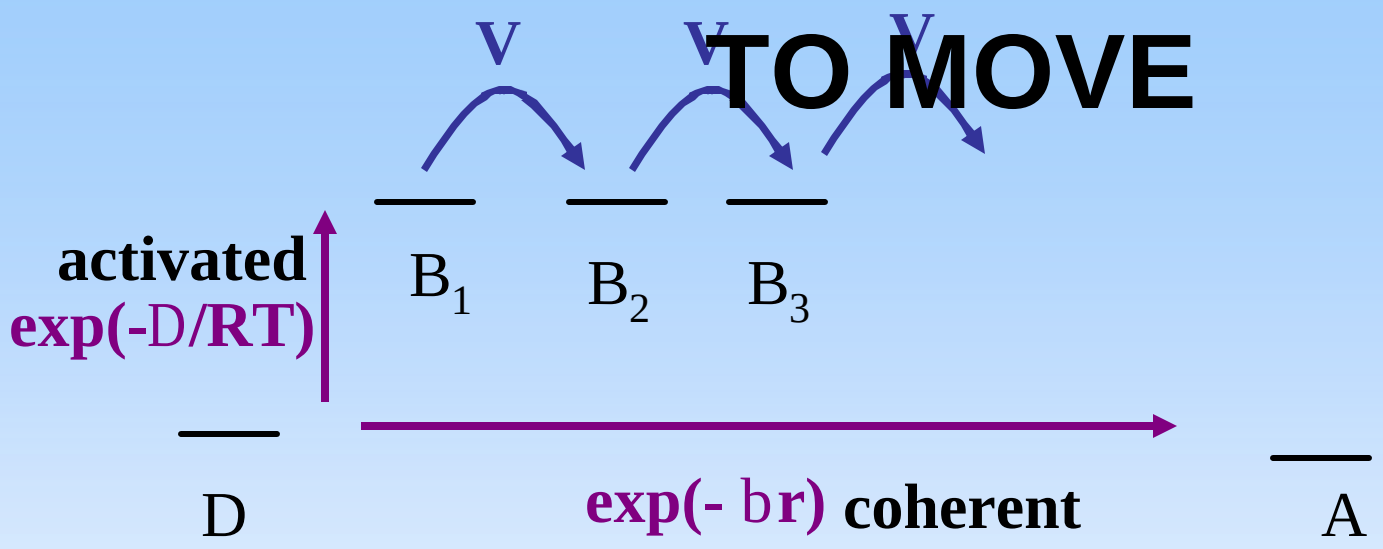
ET-conductance relationship

$$k_{ET} = \frac{2\pi}{\hbar} T_{DA}^2 \rho_{FC}$$

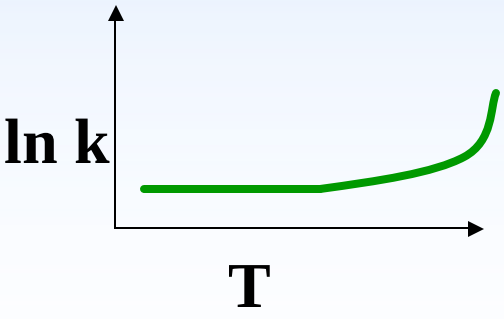
$$g = \frac{2\pi e^2}{\hbar} T_{DA}^2 \rho_D \rho_A$$

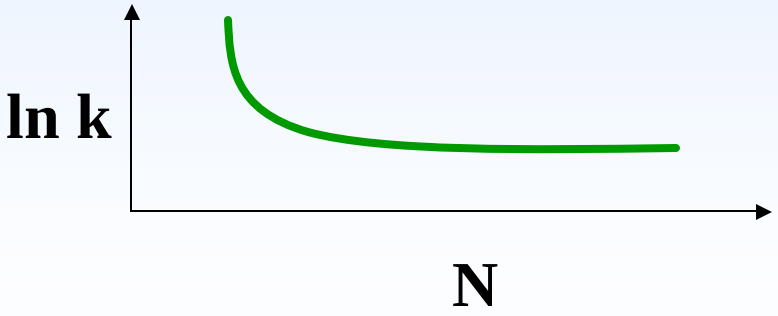
Similar dependence of effective coupling on molecular parameters if Factorization electrode-wire holds.

PAY SOME EXPONENTIAL COST TO MOVE



$$k_{tot} = k_{coherent} + k_{activated}$$





*in molecular systems

It follow from the NMR example
(using complicated theory that I
would be delighted to discuss)

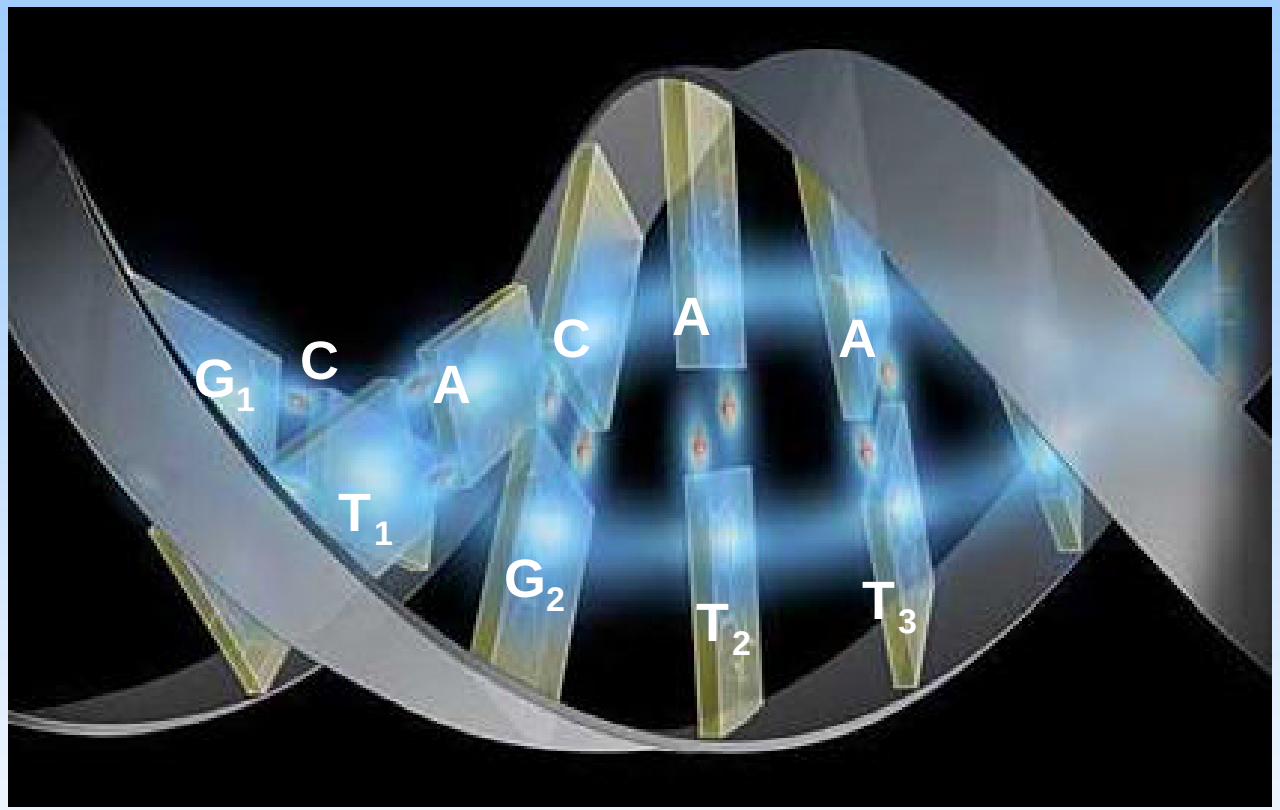
That there are **two mechanisms**

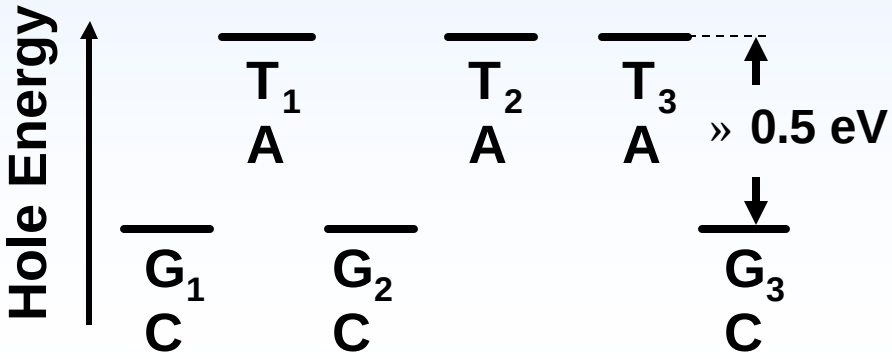
$$k = k_{coherent} + k_{incoherent}$$

$$k_{coherent} \approx \exp(-b\,r)$$ ← **For short and cold chains**

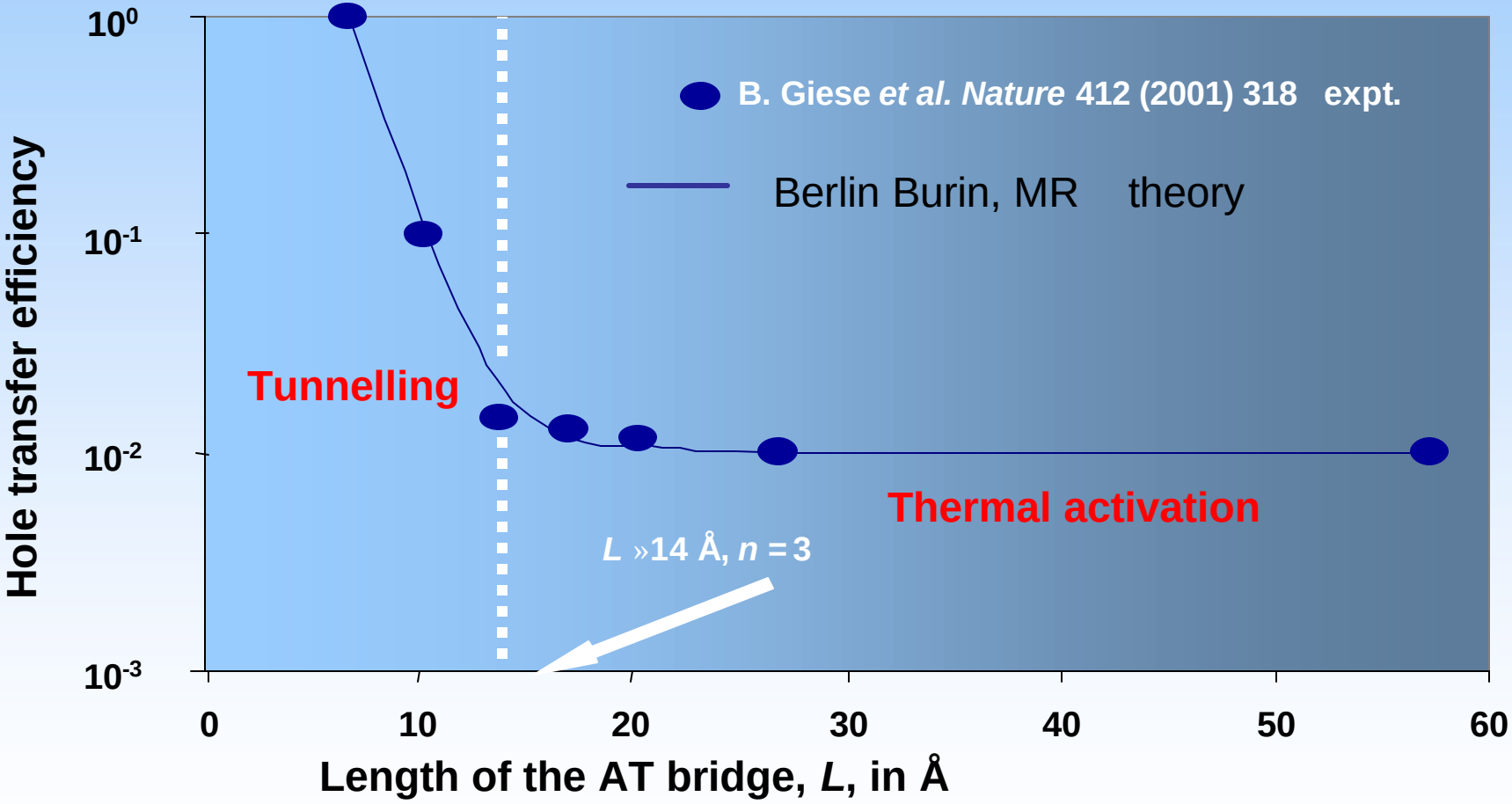
$$k_{incoherent} \approx 1/(a + br)$$ ← **For long and hot chains**

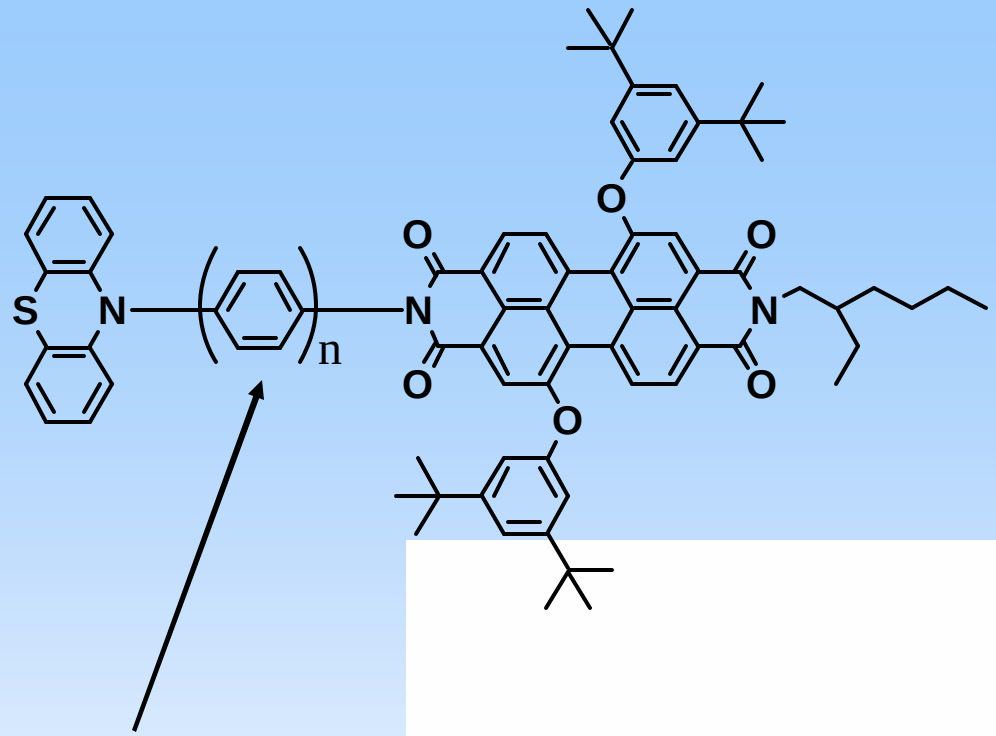
GC ⟶ GC Hopping in DNA



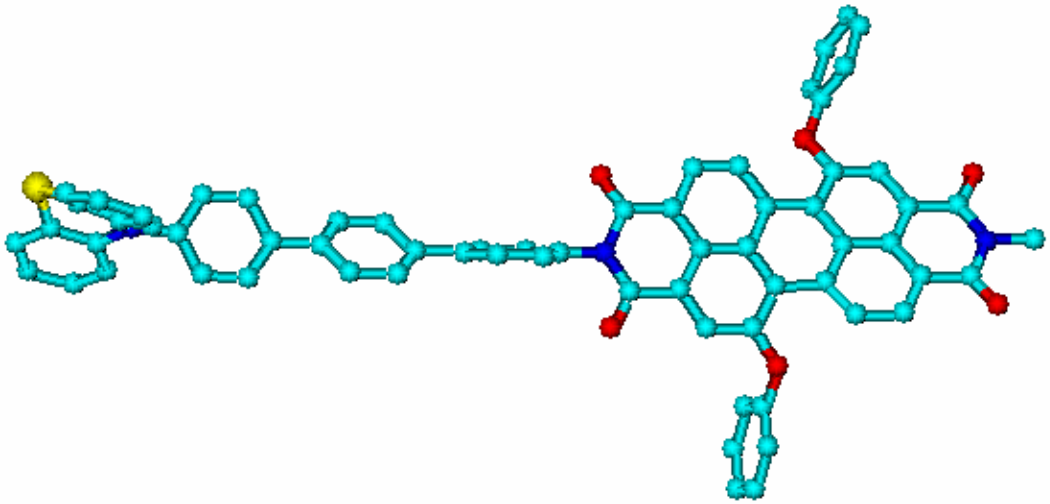


DNA electron transfer – mechanistic turnover





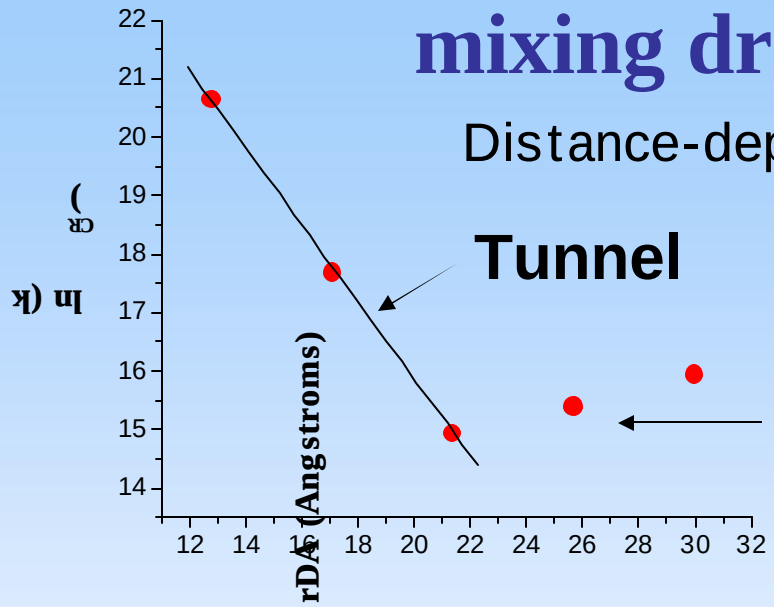
Variable length bridge



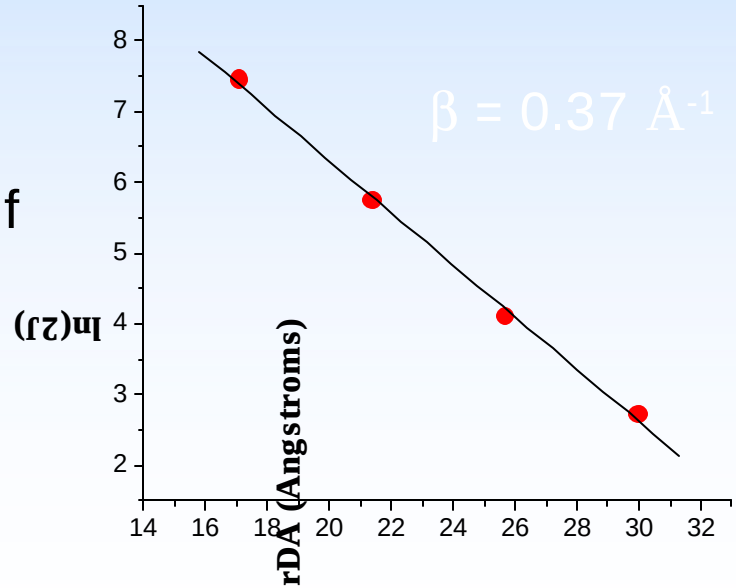
DFT (B3LYP, 6-31G**) geometry-optimized structures

Rates change mechanism, mixing drops exponentially

Distance-dependence of charge recombination



Distance-dependence of electronic interaction



Devices??

In pictures: Nanotechnology - Building from the bottom up

Little bits

The cosmetics industry already puts nano-particles in lotions, creams and shampoos.

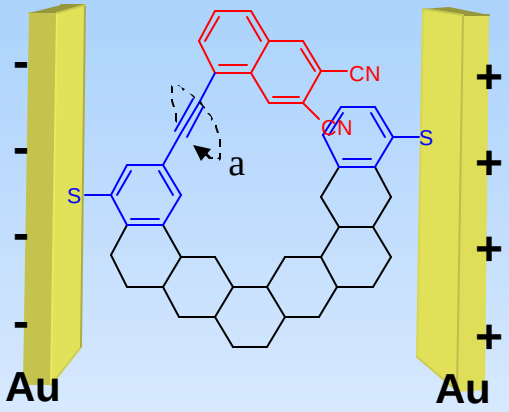
Nano-sized zinc oxide particles are used in suncreams.

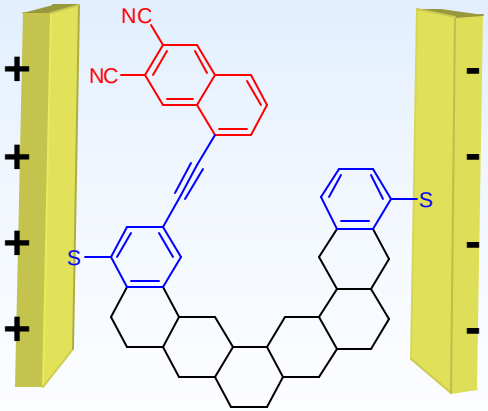
The particles are particularly good at absorbing ultra-violet rays, but make the lotion transparent and smooth instead of sticky and white.

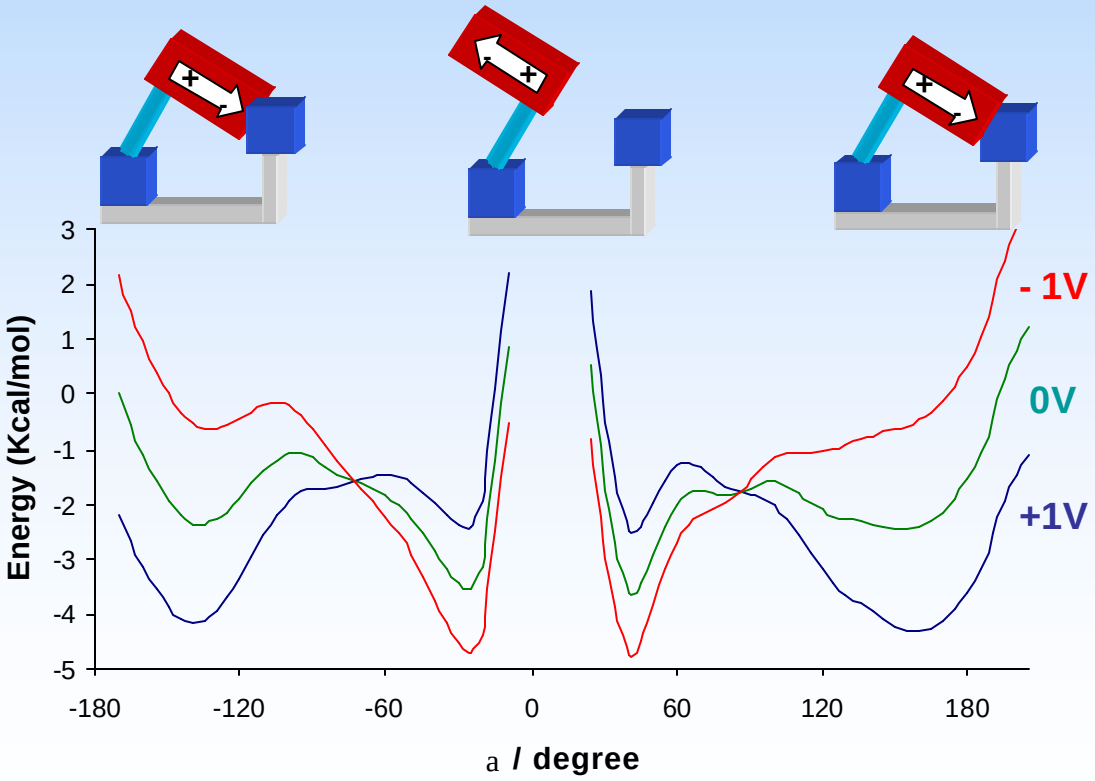
Devices??

A rectifier based on *intra*-molecular structural changes

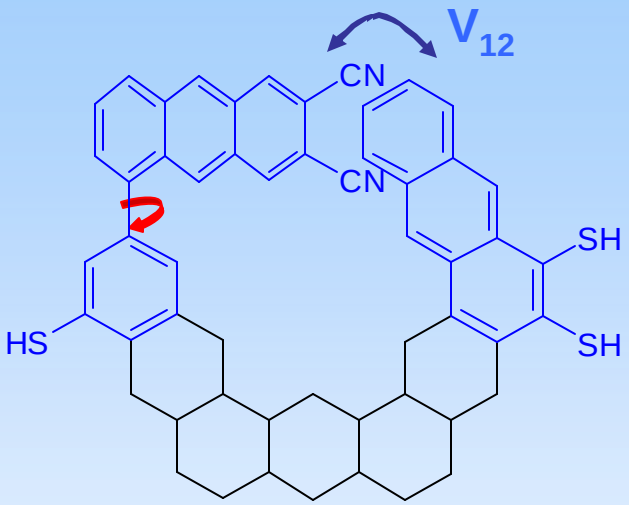
(a device minimally dependent on the metal-molecule contact)

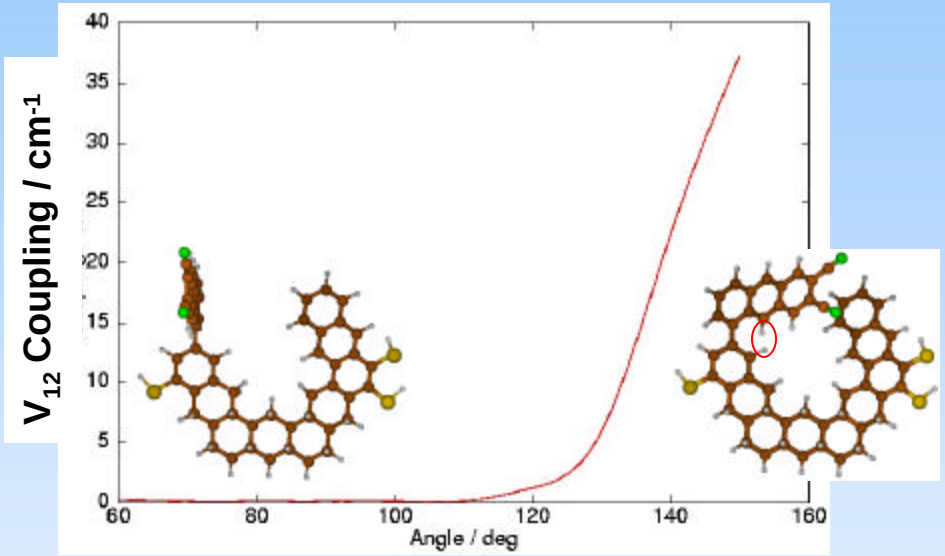


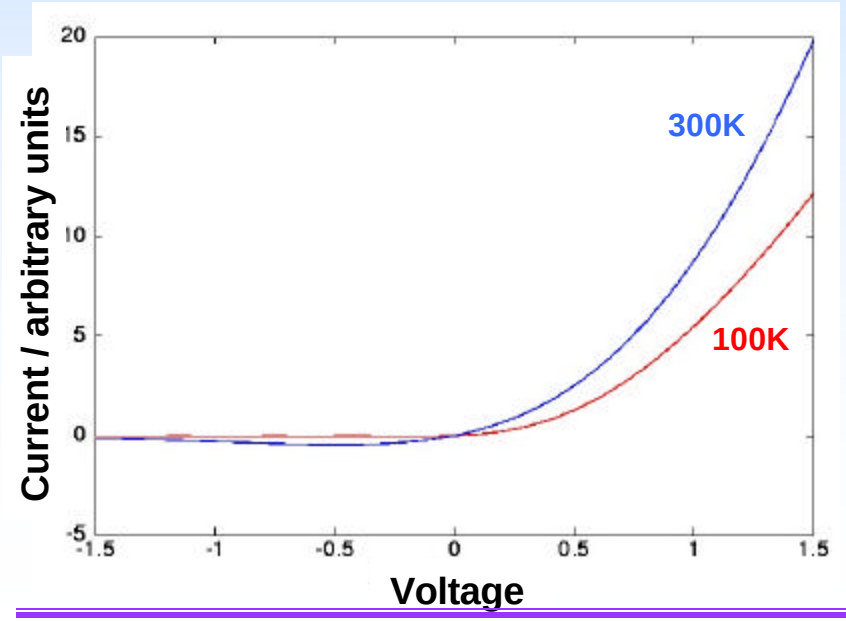




A SYSTEM WITH ONLY THROUGH-SPACE COUPLING AND VERY HIGH ON/OFF CONDUCTANCE RATIO







Giant Rectification/switch,
With two electrodes
From control of

stereochemistry

Troisi and MR, 2003

“Prediction is very difficult,

Especially of the future ”

attributed to Niels Bohr

MOLECULAR ELECTRONIC DEVICE CONCEPTS

1987

David N. Beratan *California Institute of Technology*

I. What's Wrong with Silicon?
II. What Are Molecular Devices?
III. How Big Are Molecular Devices?
IV. How Is Molecular Information Manipulated?
V. What Molecular Devices Are Possible?
VI. Does the Field of Molecular Electronics Exist?

Yes!

GLOSSARY

Molecular electronics: A field comprised of a diverse collection of scientists with the goal of creating electronic elements or other functional devices based on relatively small molecules.

I. What's Wrong with Silicon?

Questions & Answers