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ICTP 40th Anniversary

SMR 1564 - 40

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
24 May - 11 June 2004

MOLECULAR ELECTRONICS: Switching, Dynamics and Control

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These are preliminary lecture notes, intended only for distribution to participants.

TRANSPORT IN MOLECULAR JUNCTIONS

Trieste 2004

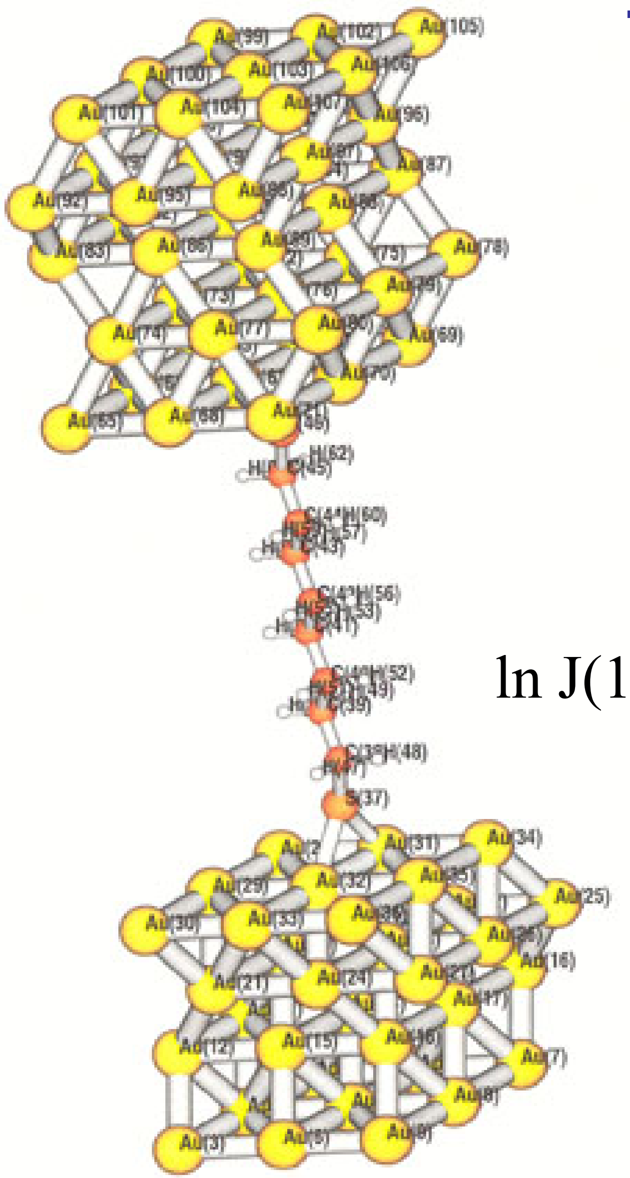
Outline:

SOME GENERALITIES
LANDAUER AND KELDYSH PICTURES
MOLECULAR ELECTRONICS CHALLENGES

ELECTRON TRANSFER AND ELECTRON CONDUCTANCE
CHARGE BUILDUP AT JUNCTIONS - INTERFACES
VOLTAGE ENGINEERING

MECHANISMS: INCOHERENCE
TUNNELING TIMES
DNA AND MECHANISMS
DYNAMICS AND SWITCHING

Dithioalkane calculations with Transiesta code (DFT + NEGF)

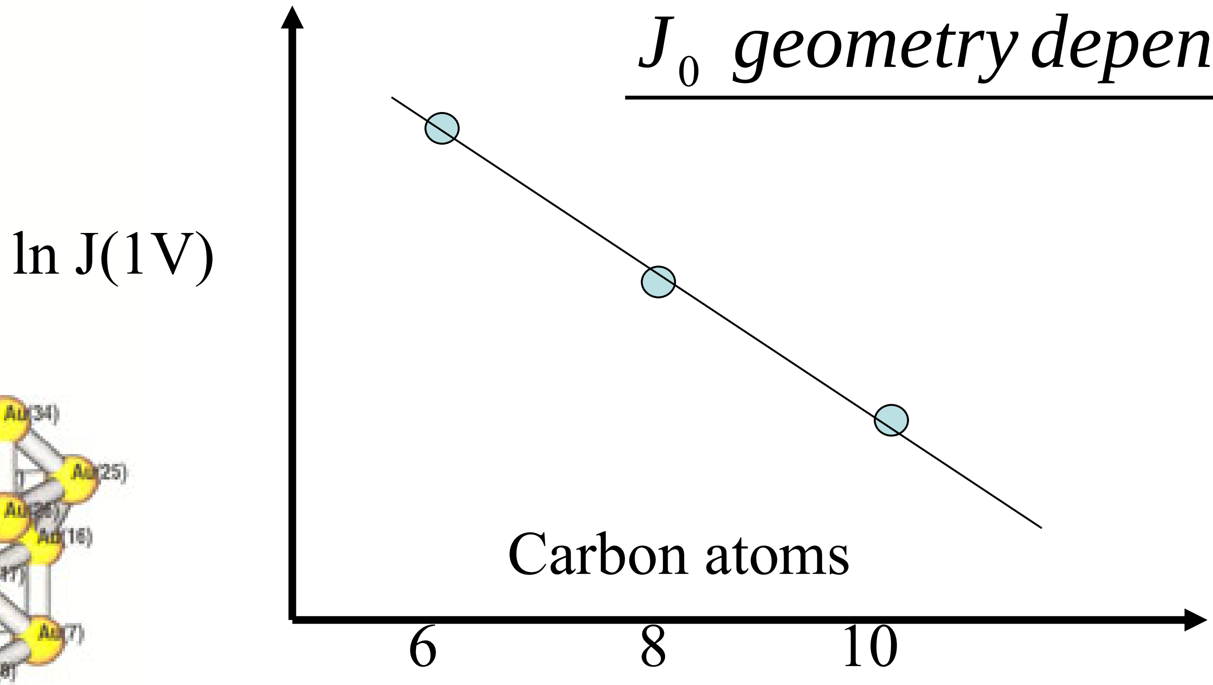


$$J = J_0 \exp(-\beta r)$$

$$\beta = 0.63 / Angstrom$$

Expt. 0.60/Angstrom

J_0 *geometry dependent*



Molecular Wire Junctions:
Some Mechanisms and Transport Behaviors

- **NEGF Formulation**

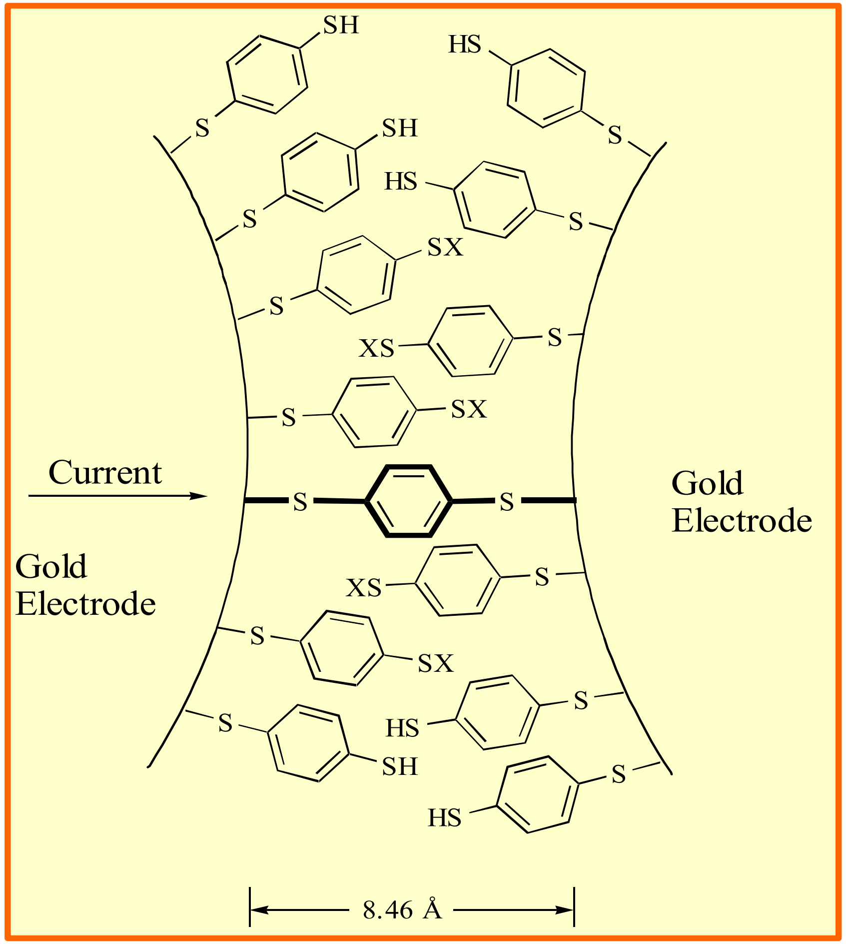
- **Simple Tunneling Transport**

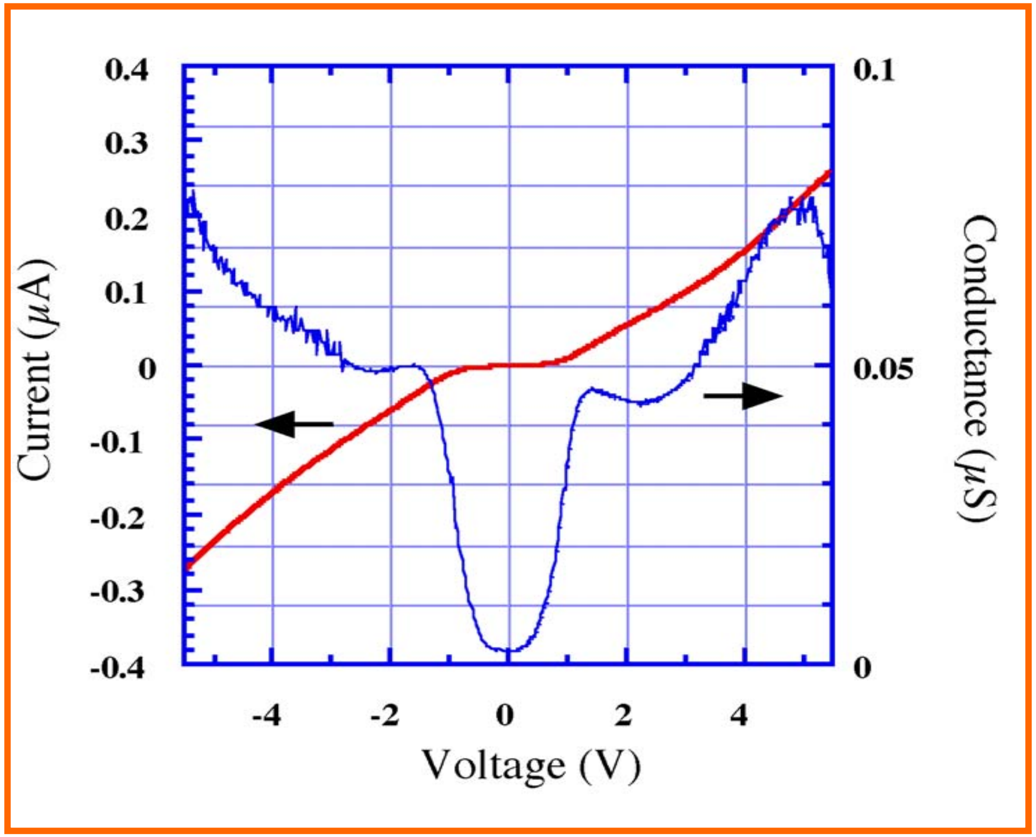
- **Incoherent Transport**

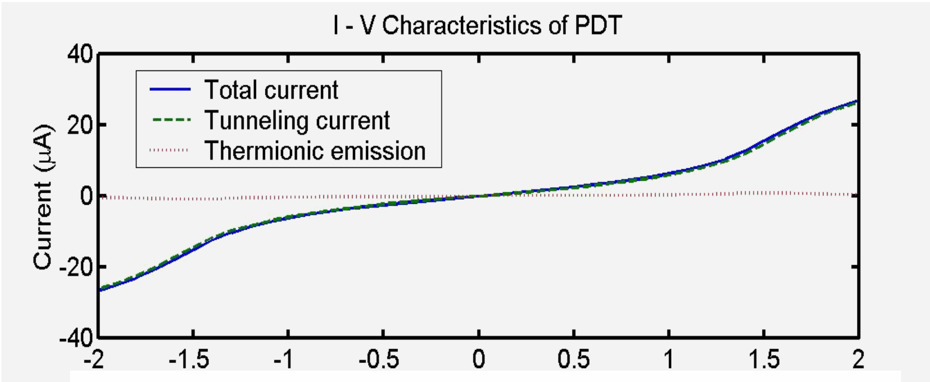
- **<u>Geometry Modulation</u>**

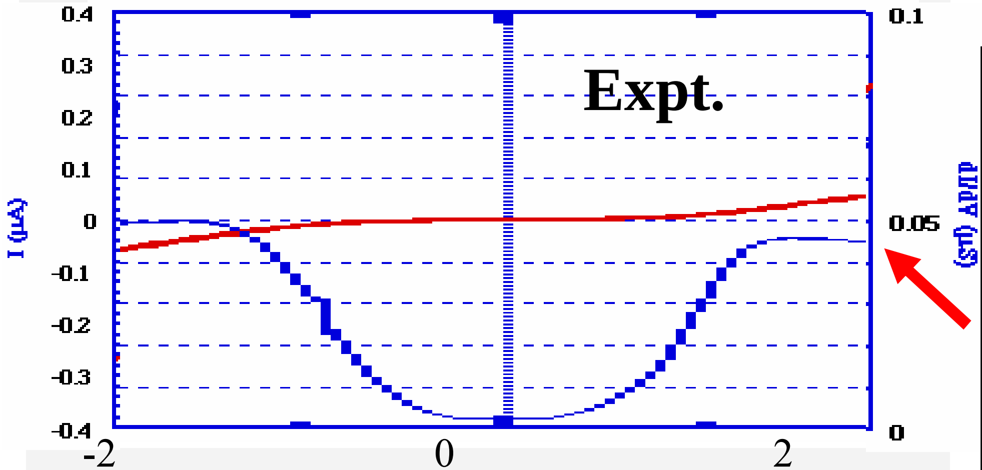
Non – Ohmic transport

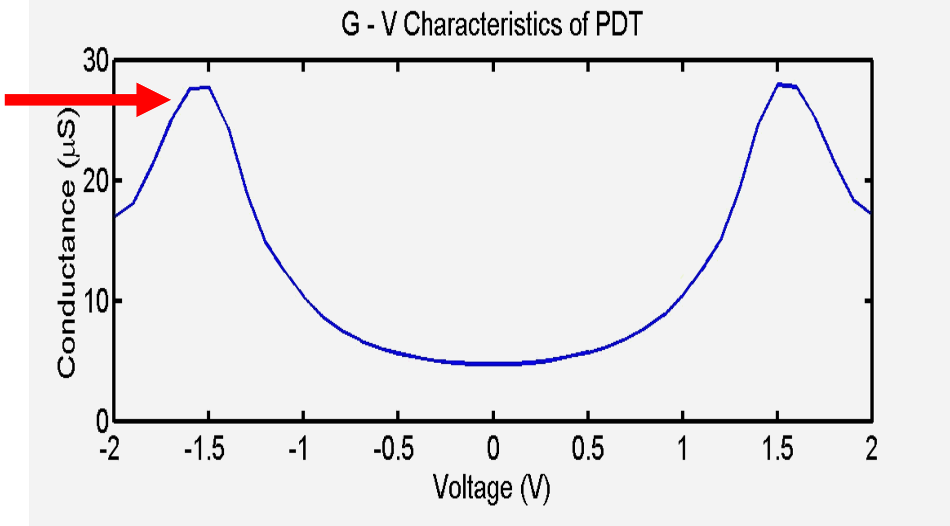
Reed group,
Break junction

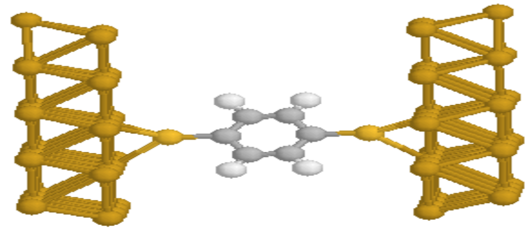




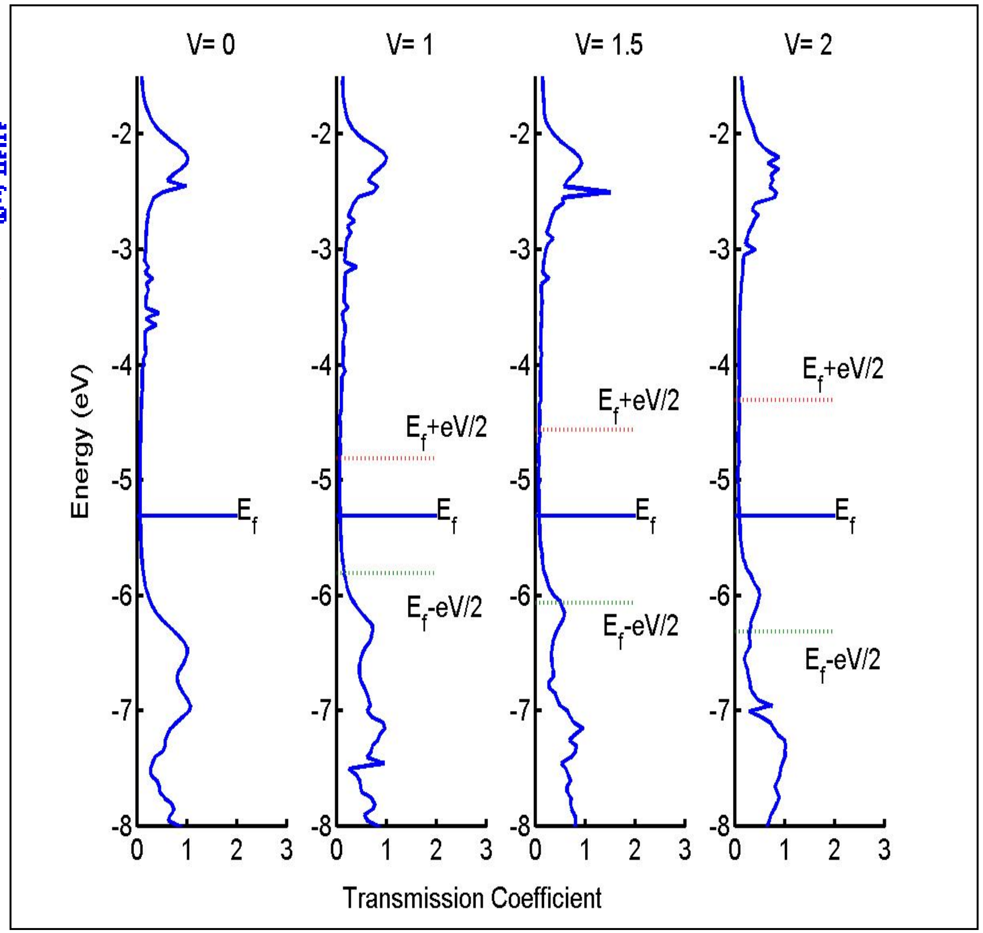








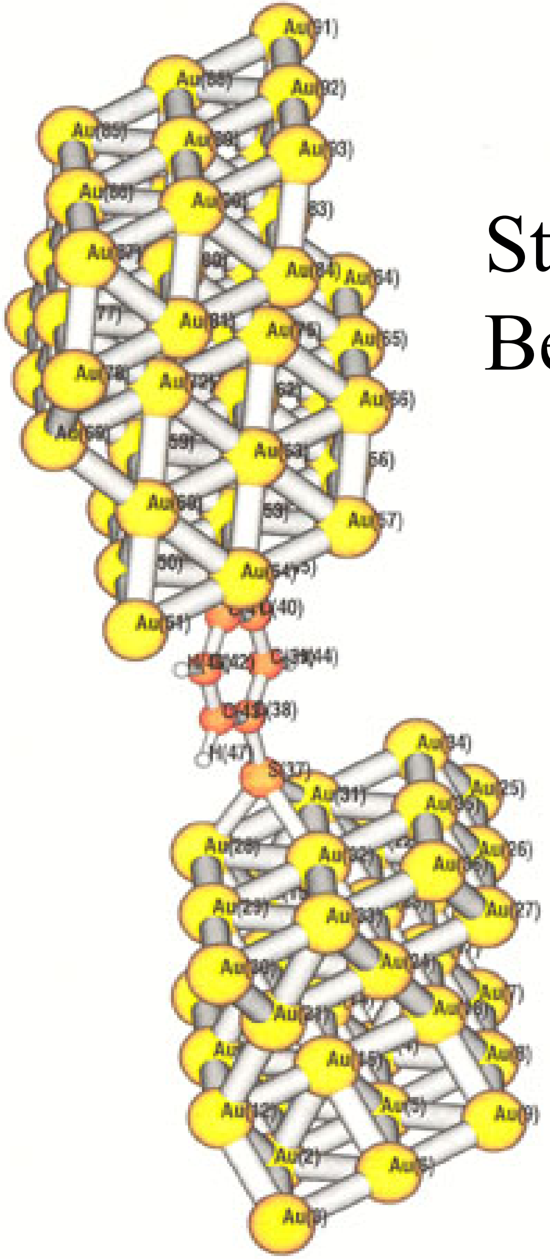
Transmission Property



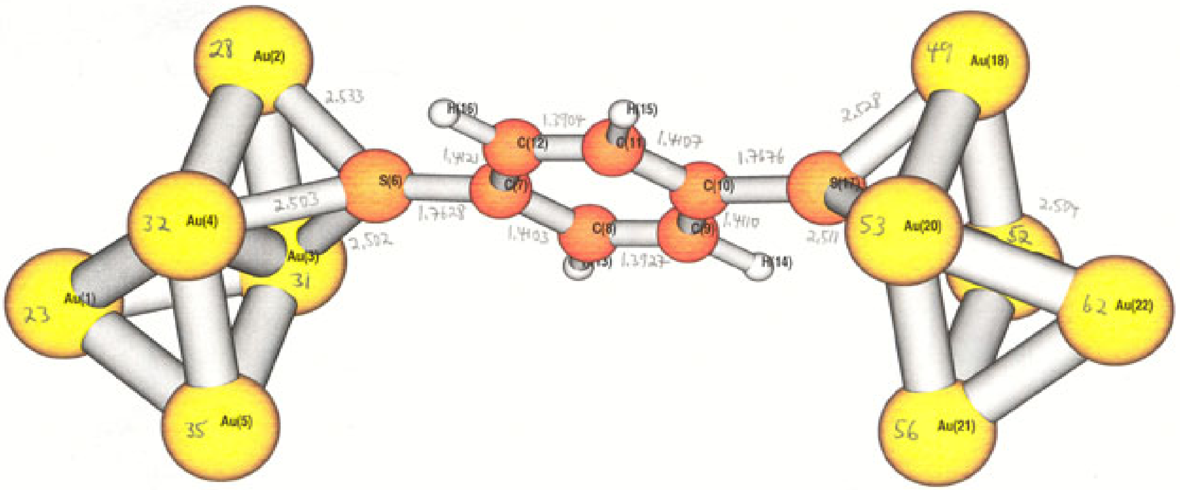
Technically:

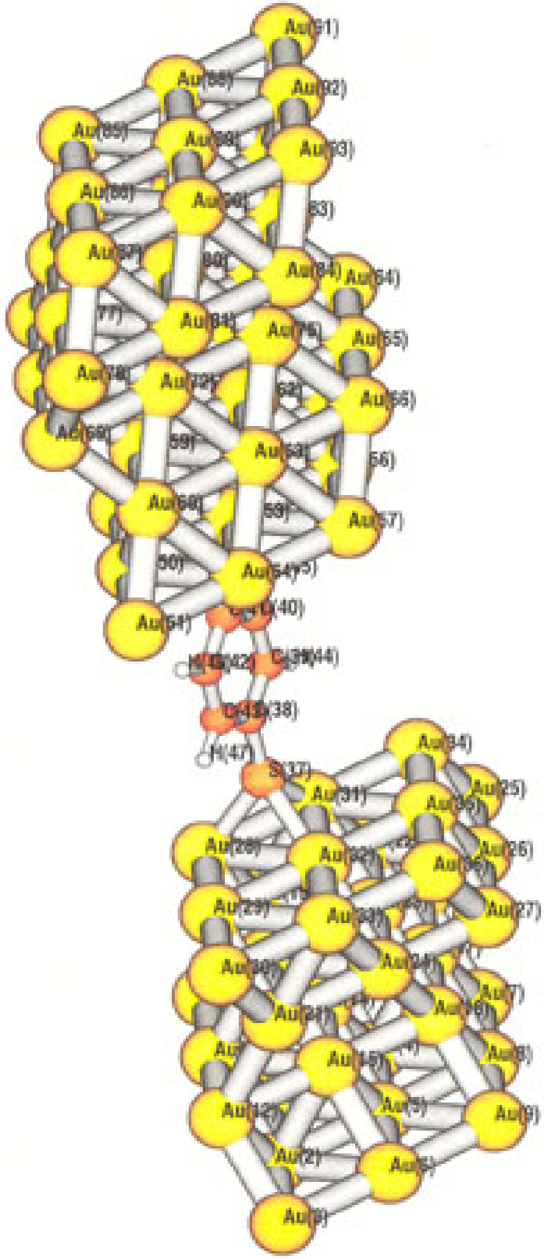
PW 91 DFT calculation
Soft pseudopotentials
Extended basis on molecule
Optimized molecular geometry
Non-equilibrium Green function for bulk

default junction geometry
truncated gold basis set



Standard Test Case (Reed, 1997)
Benzenedithiol /Gold Break Junction

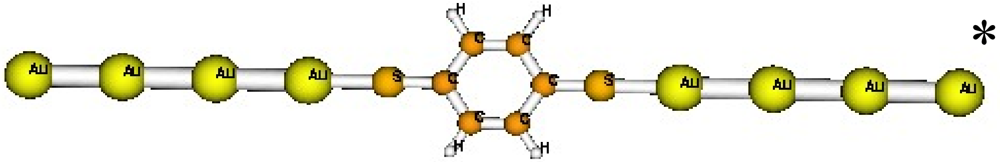




Biggish cluster, 3D
Shows conductance fluctuations:
g(atop)/g(FCC) = 2.4

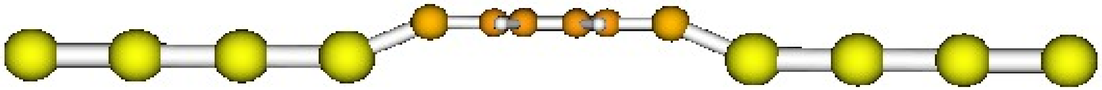
Geometric Change Effect on Transport

Current(A) at V=1.0V



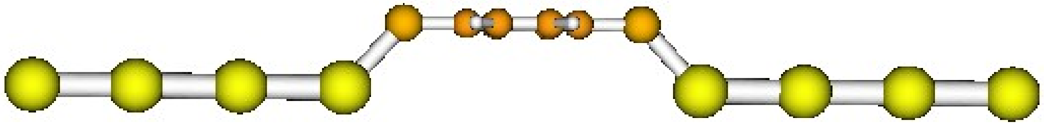
**

2.6×10^{-8}



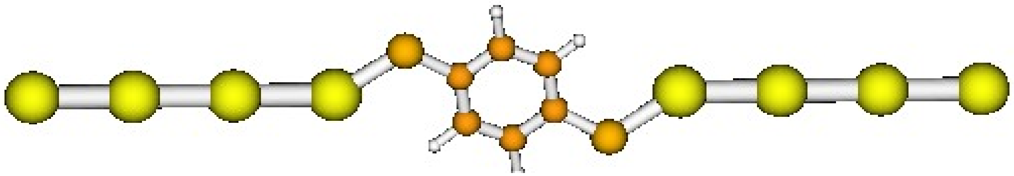
pi mix

2.2×10^{-5}



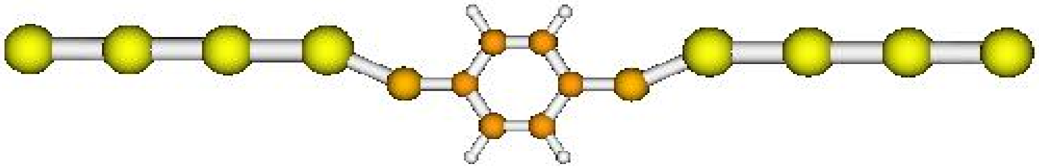
pi mix

7.0×10^{-5}



**

4.9×10^{-6}

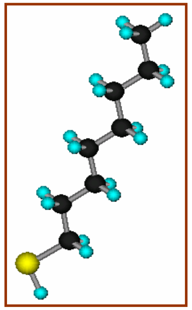


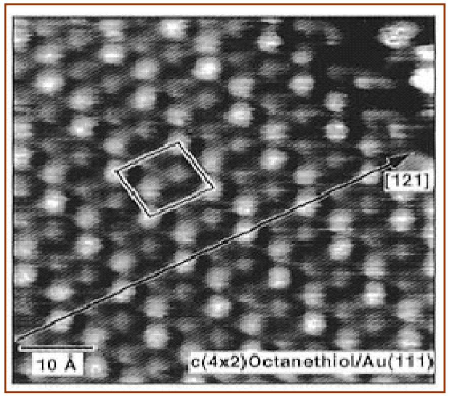
2.1×10^{-8}

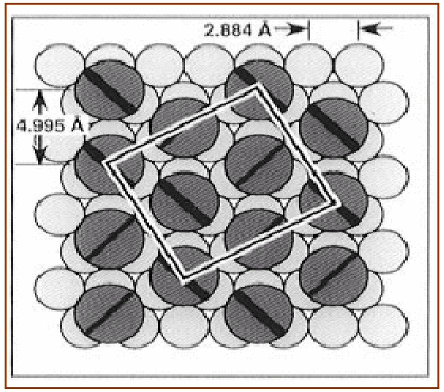
** optimized structure

SAMs on Au(111)-STM Images

Octanethiol



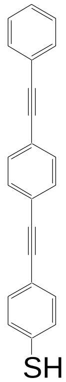


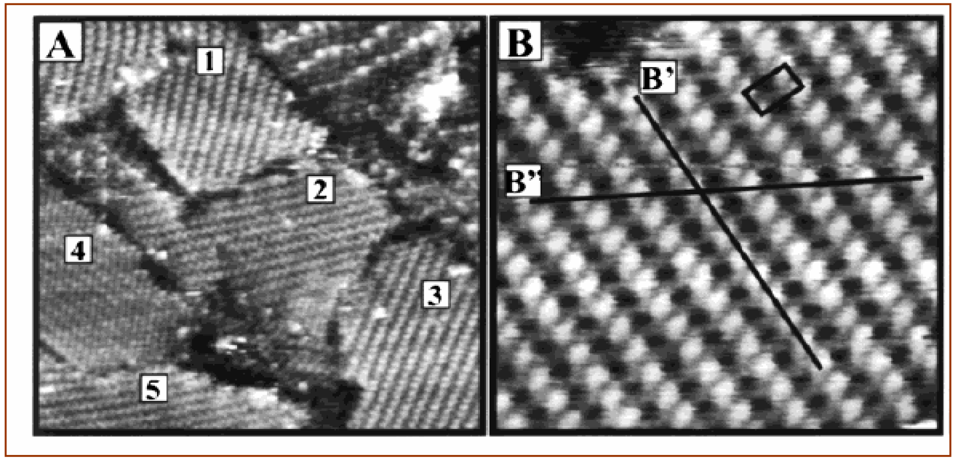


Octanethiol/Au(111)

Poirier, Chem. Rev. 97, 1117 (1997)

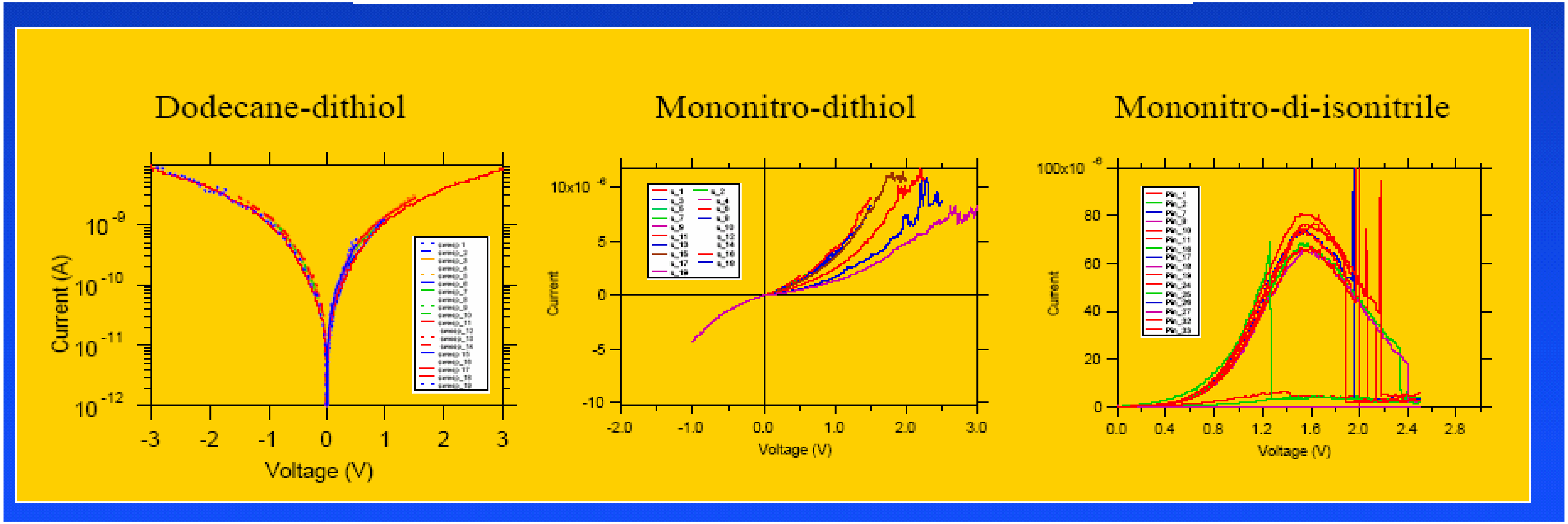
4-[4'-(phenylethynyl)-phenylethynyl]-benzenethiol





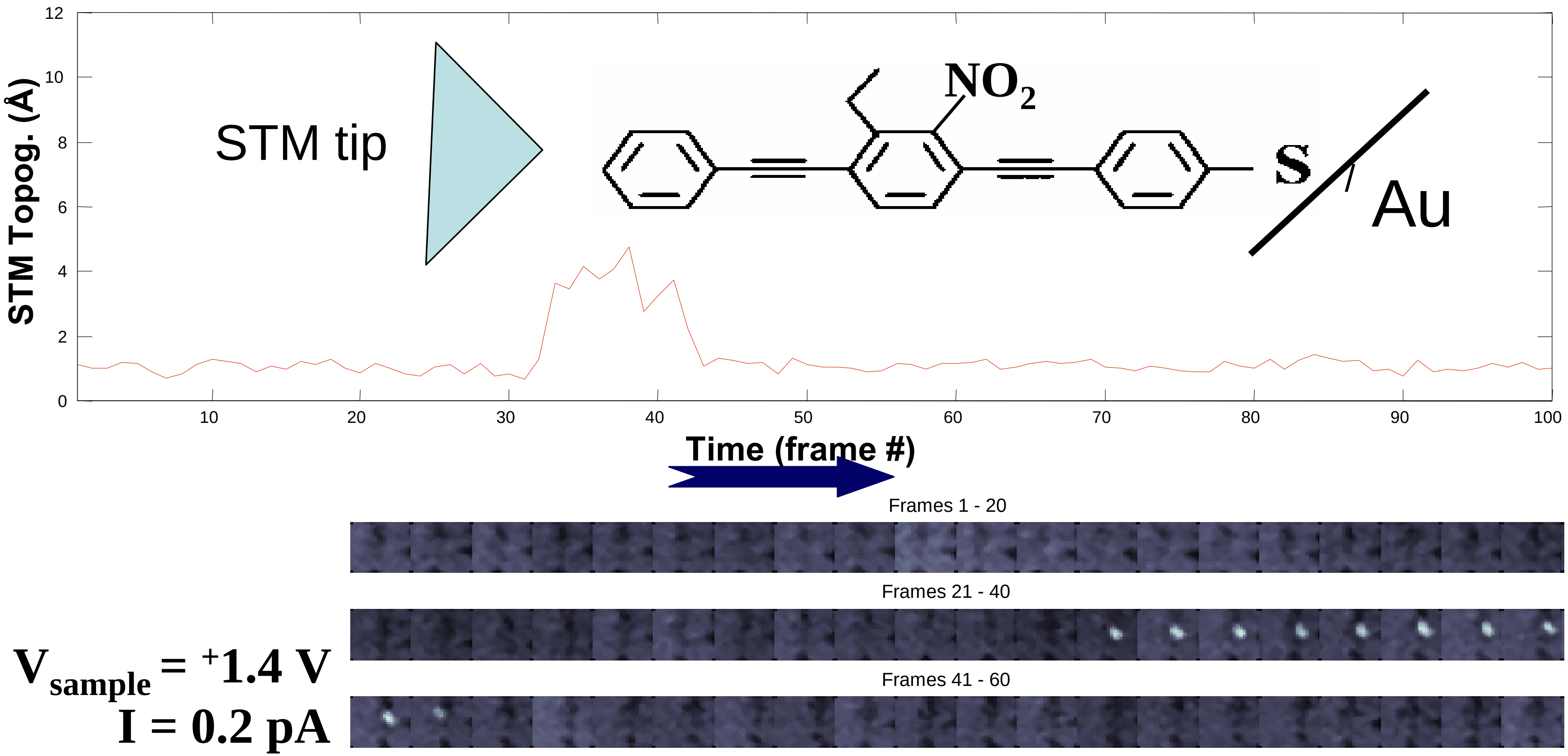
Arenethiol/Au(111)

Yang et al, J. Phys. Chem. B 104, 9059 (2000))



Reproducibility ok in alkanethiols, poor in aromatics (Reed, 2003)

Dynamical conductance fluctuations
How many molecules are required for switching? 1.



$V_{sample} = {}^{+}1.4$ V
I = 0.2 pA
3 min/frame

Mantooth, Donhauser, Kelly &Weiss
***Review of Scientific Instruments* <u>73</u>, 313 (2002)**

Conductance Fluctuations?

- multiple stable sites, low barriers
- conductance changes with site symmetry
- characteristic of Lewis bonding like Au/thiol

Thiol/Gold Interfaces??

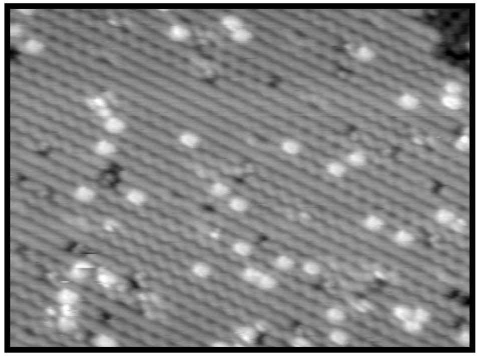
- Schottky barriers from charge flow
- Fluid geometry from Lewis binding
- Sigma/pi problems
- Relatively poor spectral density

- Facile and general structure formation

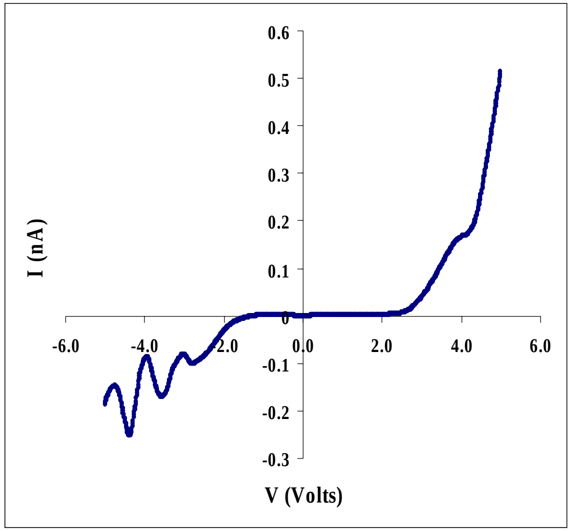
ALTERNATIVES?

- BETTER LEWIS BINDING (ISOCYANIDE/Pt)
- COVALENT BINDING AT SEMICONDUCTORS

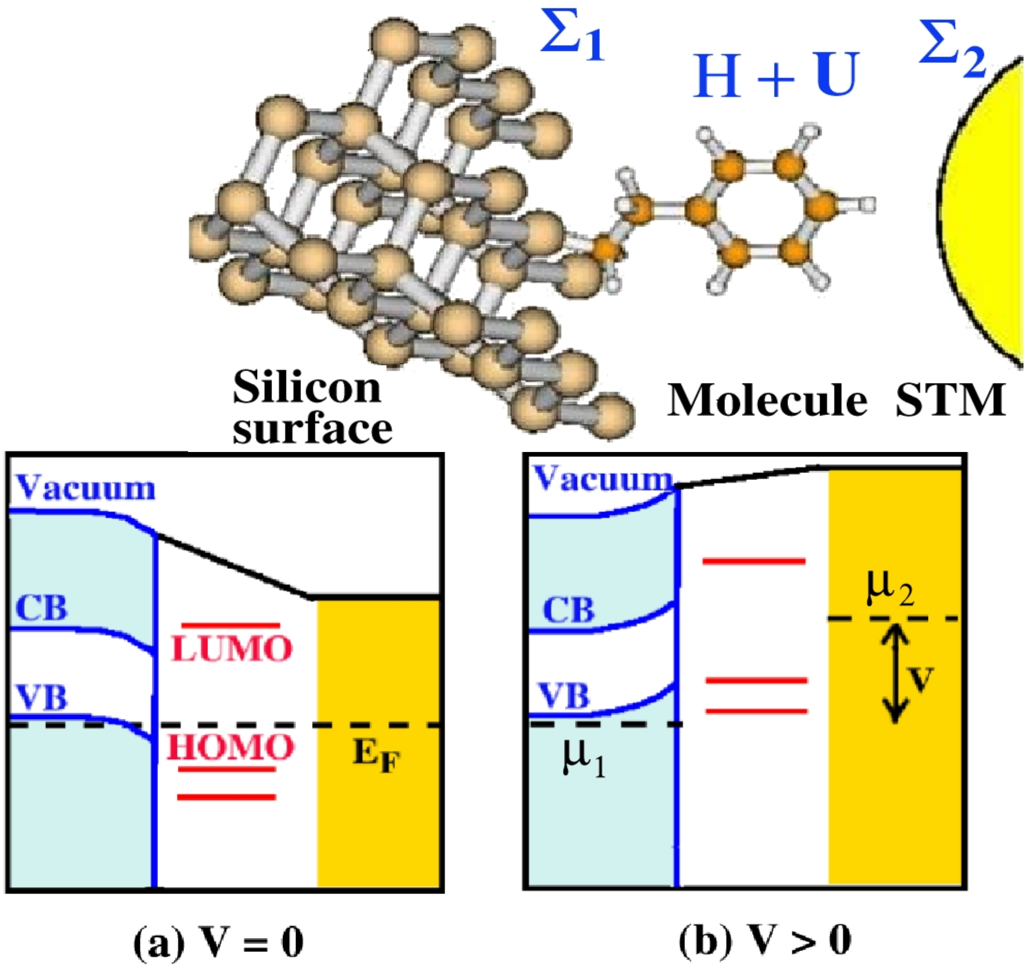
Covalent attachment NDR



20 nm × 20 nm, -2 V, 0.1 nA

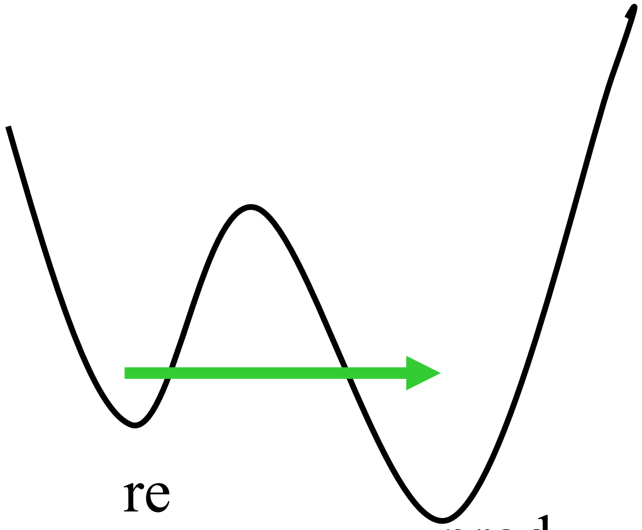


I-V Curve of Individual TEMPO Molecule on ***Clean Si(100)***



Hersam, NanoLetters 2004

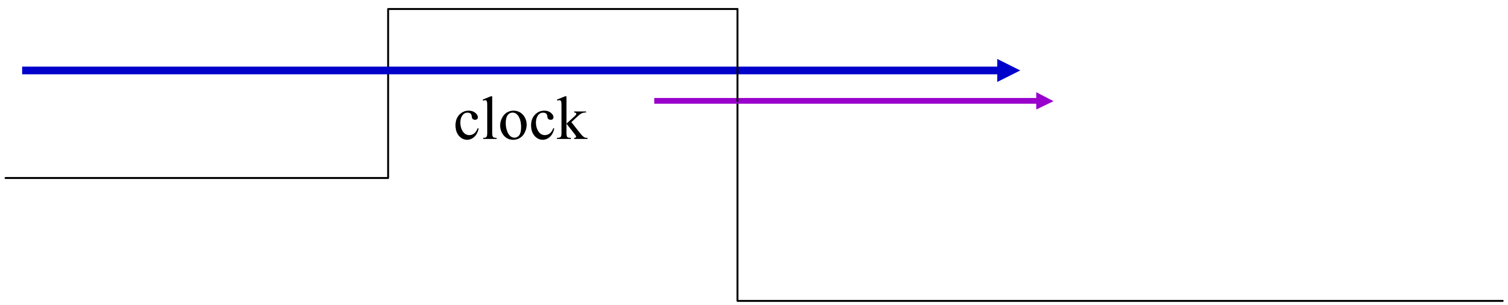
Tunneling Time



Rate time $= k_{ET}^{-1} \approx 10^{-13} - 10^{-8}$ sec

Tunneling time??

Landauer Buttiker Time



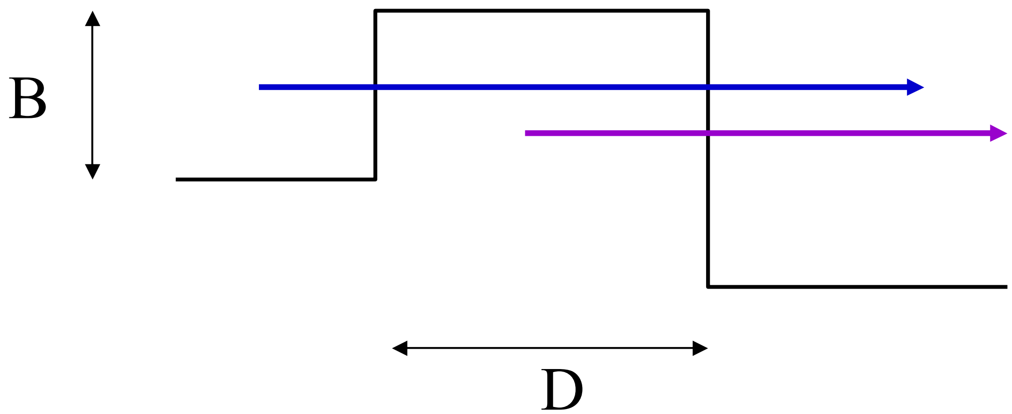
Clock frequency = f

At resonance, the ratio

Maximizes, and

$$f = 2\pi / \tau_{LB}$$

Landauer Buttiker Time

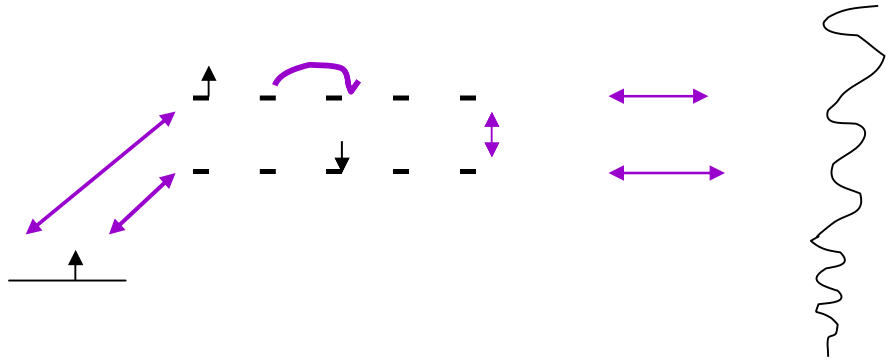


$$\tau_{LB} = D * \sqrt{m / 2(B - E)}$$

As B increases, LB time drops,
Rate time increases

How to generalize this to rate problems??

Model for tunnel time



t = 0 : electron in $(0, \uparrow)$

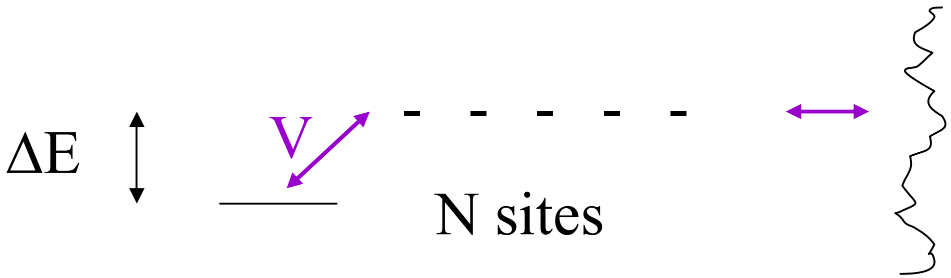
$R = P[\downarrow]/(P[\uparrow] + P[\downarrow])$

R can index tunneling time

some complicated arithmetic suggests:

The equivalent of the Landauer/Buttiker time (for superexchange system)

$$\tau_T = \hbar N / \Delta E$$



NOTE:

tunnel time looks like uncertainty time

tunnel time linear in N

tunnel time independent of V

Landauer-Buttiker Contact Time For Wires

$$\tau_{LB} = N\hbar / (gap)$$

So: big gaps, short wires (alkanes) give attosecond times, weak vibronic coupling, Coherent ,T-independent tunneling transport

Other times also enter

Wilkie, Nitzan, Jortner, MR

Molecular Wire Junctions:
Some Mechanisms and Transport Behaviors

- **NEGF Formulation**
- **Simple Tunneling Transport**
- **<u>Incoherent Transport</u>**
- **Geometry Modulation**

Landauer-Buttiker Contact Time For Wires

$$\tau_{LB} = N\hbar / (gap)$$

So: small gaps, long wires (aromatics)
give times approaching nuclear motion
suggesting nuclear coupling, dephasing,
transition to activated motion

Other times also enter

Wilkie, Nitzan, Jortner, MRr

Molecular Wire Junctions:
Some Mechanisms and Transport Behaviors

- **NEGF Formulation**

- **Simple Tunneling Transport**

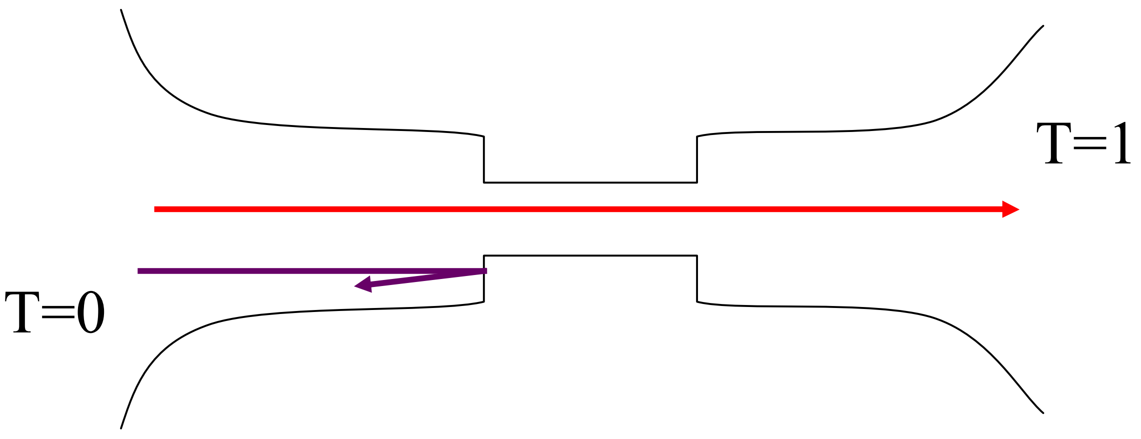
- **<u>Incoherent Transport</u>**

- **Geometry Modulation**

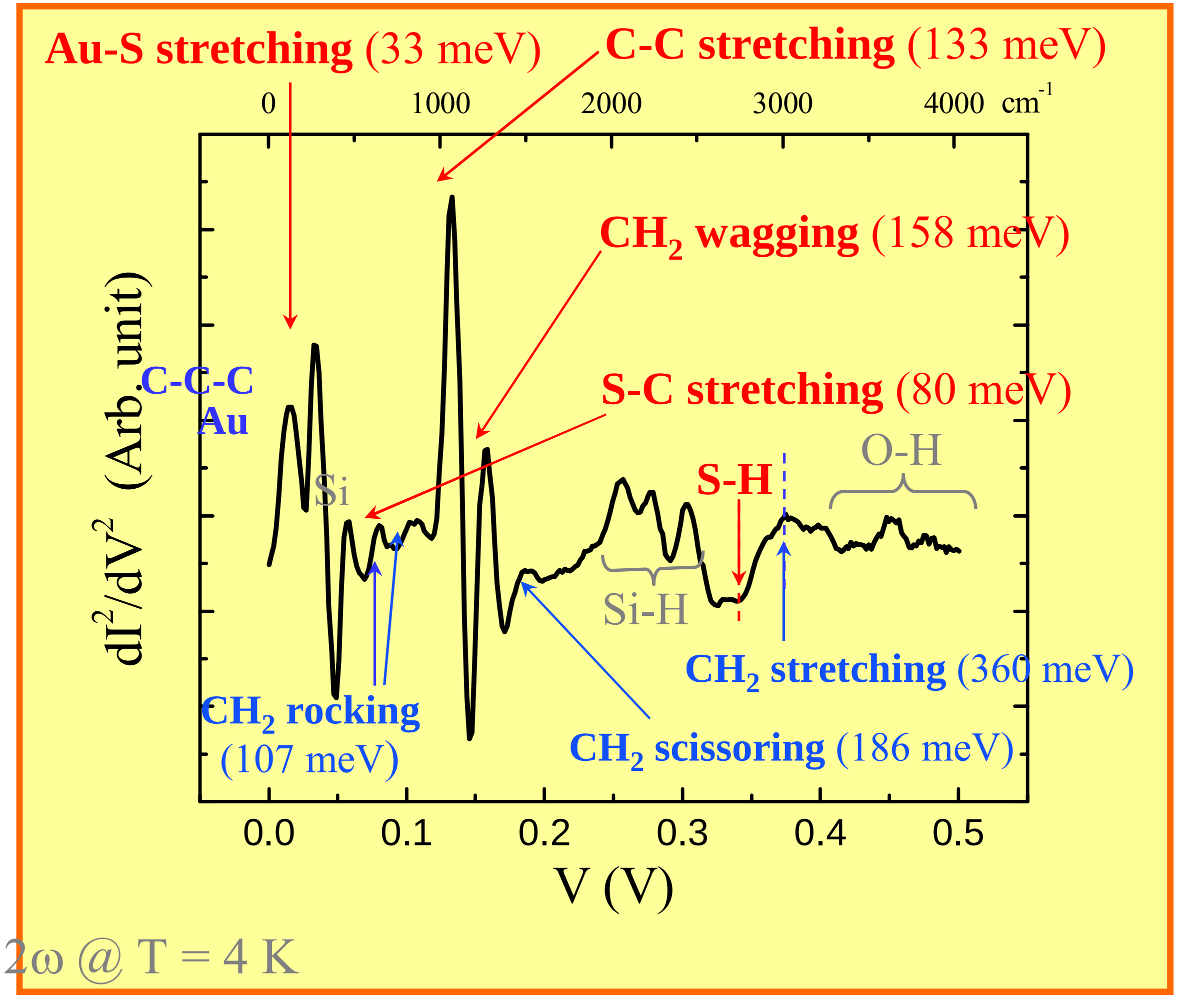
I. Landauer Coherent Conductance

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

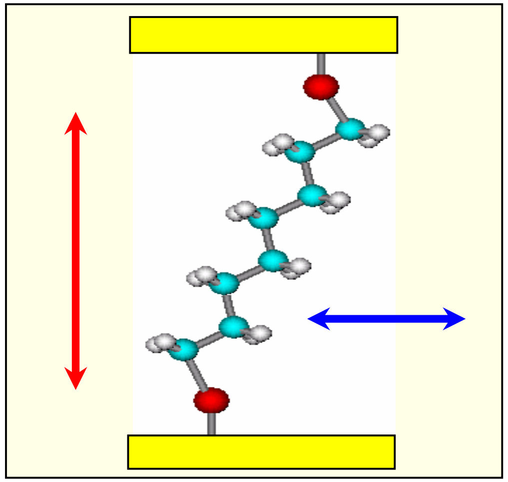
T_{ii} = transition probability in the i^{th} transverse channel

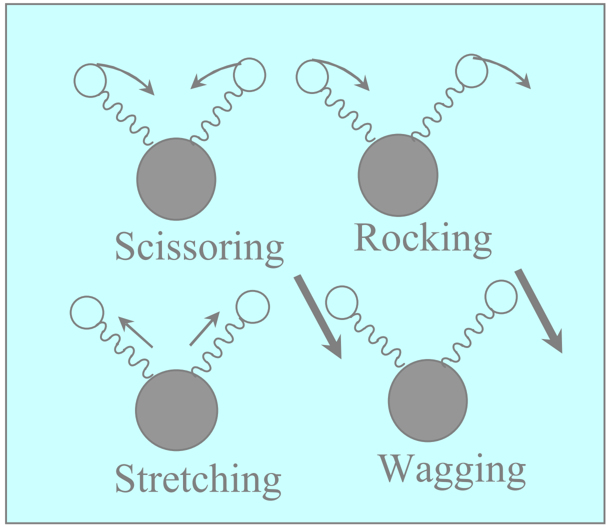


Inelastic electron tunneling spectroscopy on SAMs



Wang *et. al*, NanoLetters (in press)





Hamiltonian for electrons and vibrations

$$\hat{H}_0 = \sum_{k \in L,R} \varepsilon_k^{L,R} \hat{d}_k^+ \hat{d}_k + \sum_{i,j} t_{ij} \hat{c}_i^+ \hat{c}_j + \sum_m \omega_m^{bath} \hat{b}_m^+ \hat{b}_m + \sum_k \omega_k \hat{a}_k^+ \hat{a}_k$$

leads electrons — molecule electrons — vibrons — phonons

Couplings and interactions are represented by the Hamiltonian

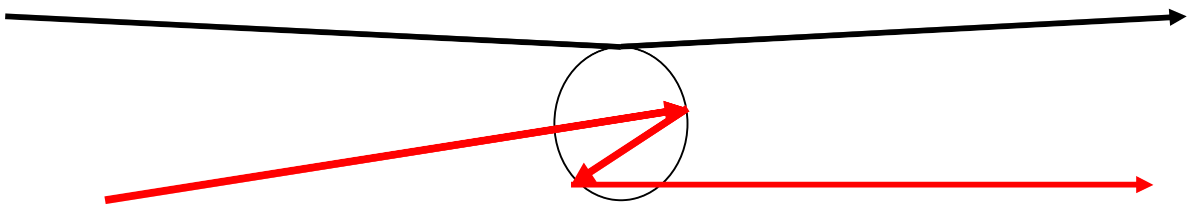
$$\hat{H}_1 = \sum_{k \in L,R;i} \left(V_{ki} \hat{d}_k^+ \hat{c}_i + h.c. \right) + \sum_i V_{ij}^{ext} \hat{c}_i^+ \hat{c}_j + \sum_{k,m} U_m^k \hat{A}_k \hat{B}_m + \sum_{k,i} M_i^k \hat{A}_k \hat{c}_i^+ \hat{c}_i + \frac{1}{2} \sum_{i_1,i_2,i_3,i_4} V_{i_3 i_4}^{i_1 i_2} \hat{c}_{i_1}^+ \hat{c}_{i_2}^+ \hat{c}_{i_4} \hat{c}_{i_3}$$

$$\hat{A}_k = \hat{a}_k^+ + \hat{a}_k \qquad \hat{B}_m = \hat{b}_m^+ + \hat{b}_m$$

Green function in composite system:

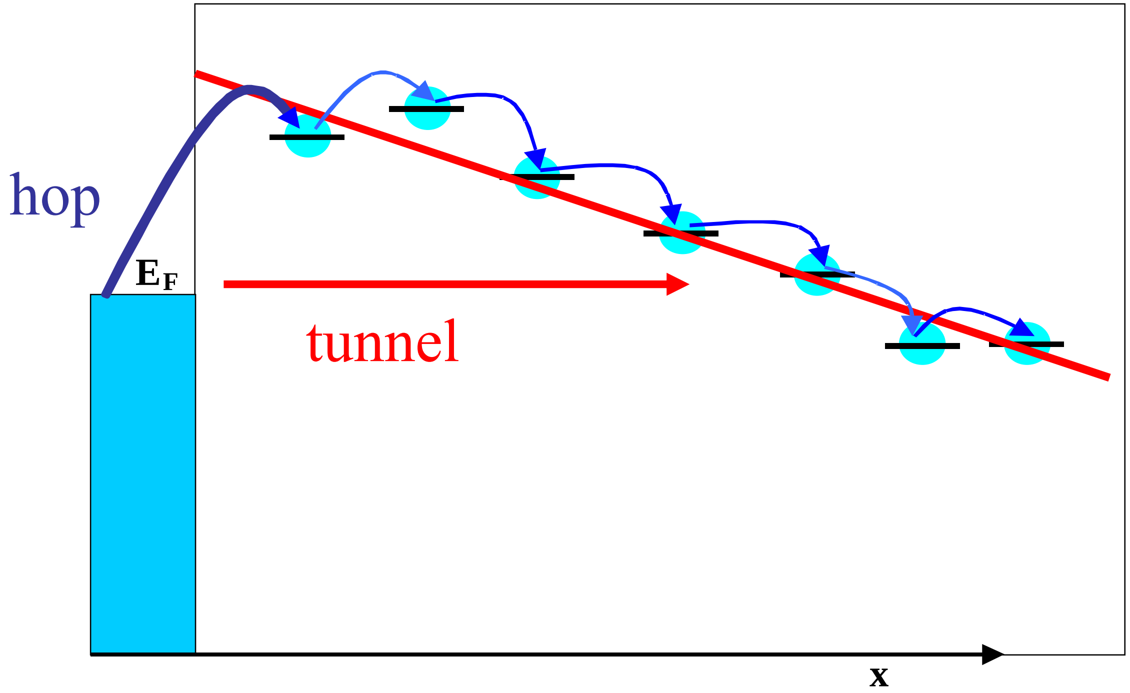
$$G(\tau,\tau') = G_0(\tau,\tau') + \int_c d\tau_1 \int_c d\tau_2 \; G_0(\tau,\tau_1)\Sigma(\tau_1,\tau_2)G(\tau_2,\tau')$$

$$\Sigma\left(\tau_1,\tau_2\right) = \Sigma^{ext} + \Sigma^{L} + \Sigma^{R} + \Sigma^{ph}$$



Electron/vibron coupling can be elastic or inelastic

Moving over and through the Injection Barrier



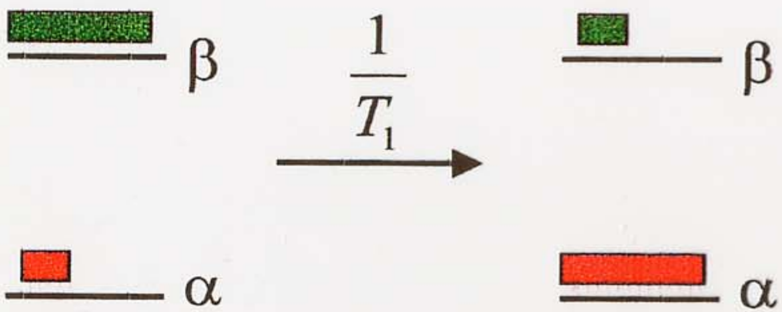
Expect to tunnel for short, cold junctions

hop for long, hot junctions

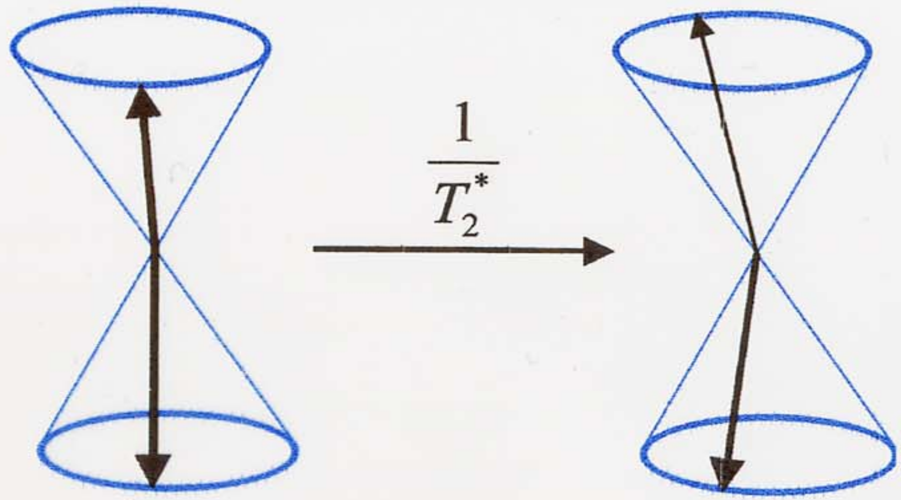
System-Bath Coupling -- Concepts from NMR

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$

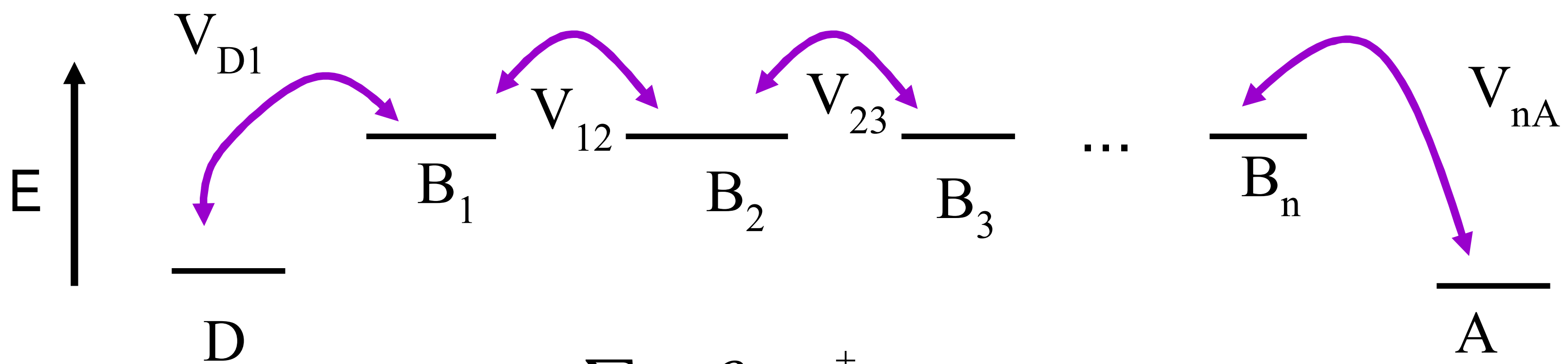
Longitudinal Relaxation



Transverse Relaxation



Time Dependence - Purely Electronic



$$H = \sum_{ij} \beta_{ij} a_i^+ a_j$$

$$\langle a_i^+ a_j \rangle = \rho_{ji}$$

$$\langle \frac{d}{dt}(a_i^+ a_j) \rangle = i[H, a_i^+ a_j]$$

$$\boxed{\frac{d}{dt}\rho_{ji} = i\sum_n \{\rho_{jn}\beta_{ni} - \beta_{jn}\rho_{ni}\}}$$

Multiple Oscillations

Density Matrix formalism

Used for systems with partial information

$$\rho_{ii} = \; populations$$

$$\rho_{ij} = coherences$$

$$d\rho / dt = \mathrm{i}[\mathrm{H}, \rho] + \mathrm{d}\rho/\mathrm{dt})_{\;\mathrm{diss}}$$

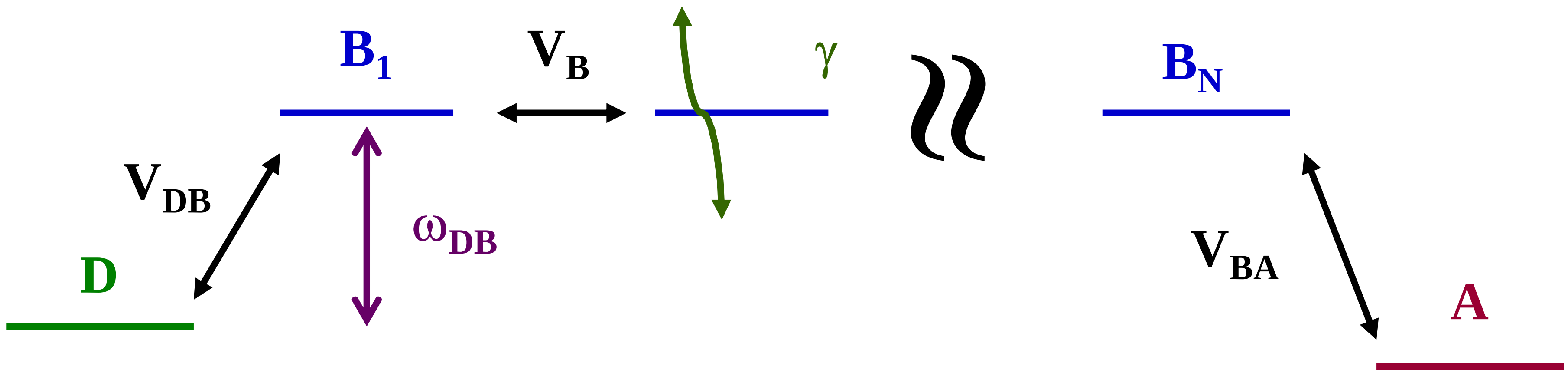
Time Dependence - Addd Vibronic Couplings, Dephasings

$$\frac{d\rho_{ij}}{dt} = i\,[\rho, H\,] + \frac{d\rho_{ij}}{dt}\,)_{diss}$$

$$Bloch:^{-}\quad \frac{d\rho_{ij}}{dt}\,)_{diss} = \quad \rho_{ij}\,(1-\delta_{ij})/T_2 + \delta_{ij}\rho_{ij}/T_1$$

Damped oscillations ⟶ **rate processes**

Steady-State Density Matrix Theory of Bridge Assisted ET



Equations:

$$\dot{\rho} = -\frac{i}{\hbar}\left[\mathbf{H}_S, \rho\right] + \mathbf{L}_D$$

$$\dot{\rho} = \mathbf{A} \cdot \rho + \mathbf{C}$$

$$\rho^{SS} = \mathbf{A}^{-1} \cdot \mathbf{C}$$

$$\mathrm{RATE}_{ET,SS} = \frac{C}{\rho^{SS}_{DD}}$$

Mathematica Results:

$\omega > V, \kappa > \gamma$

$$k_{ET} = \frac{4V^{2N+2}}{\kappa\omega^{2N}} + \gamma\left(\frac{V}{\omega}\right)^2$$

$\gamma > \omega, \kappa, V$

$$k_{ET} = \frac{2V^2}{N\gamma}$$

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

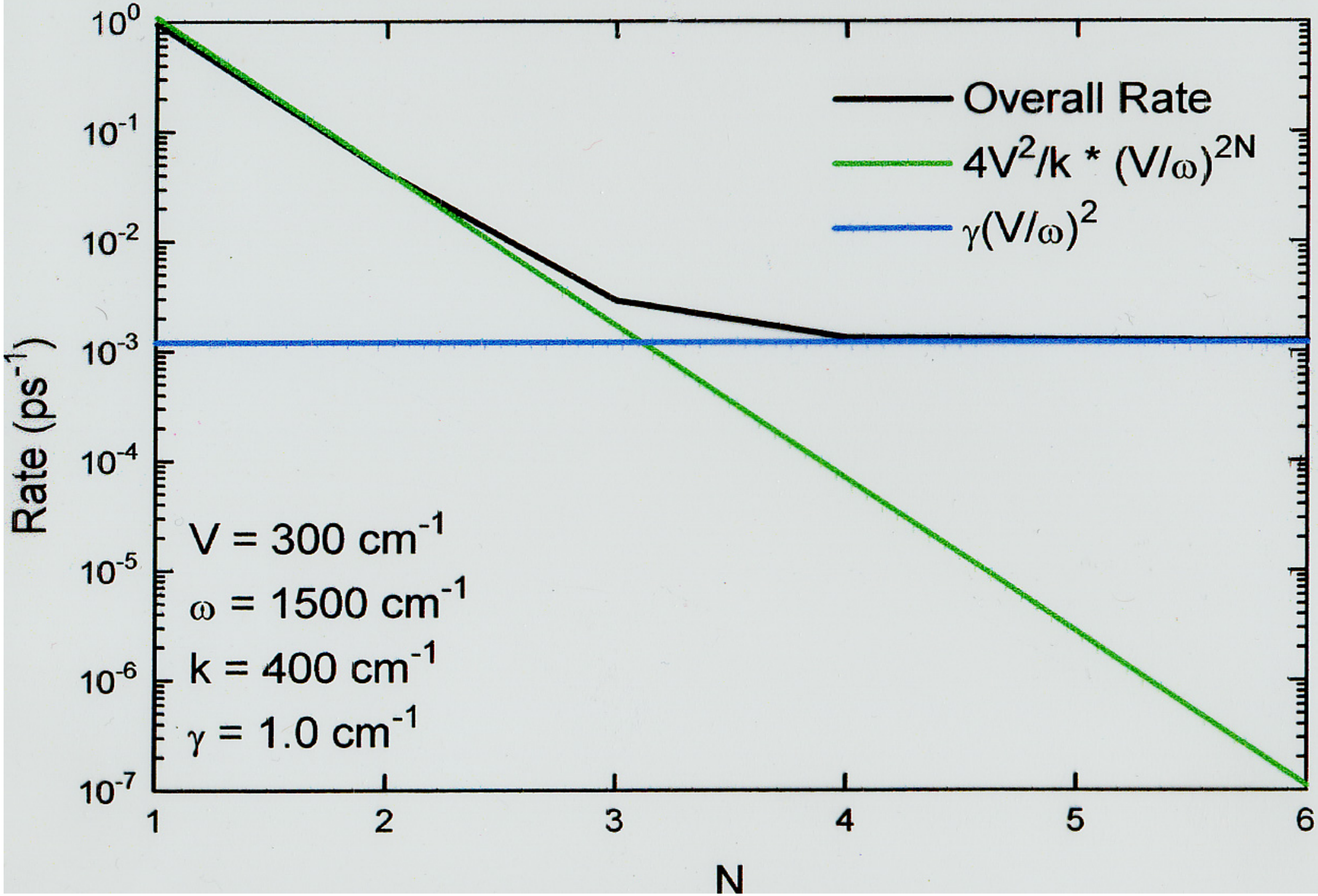
That there are **two mechanisms**

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

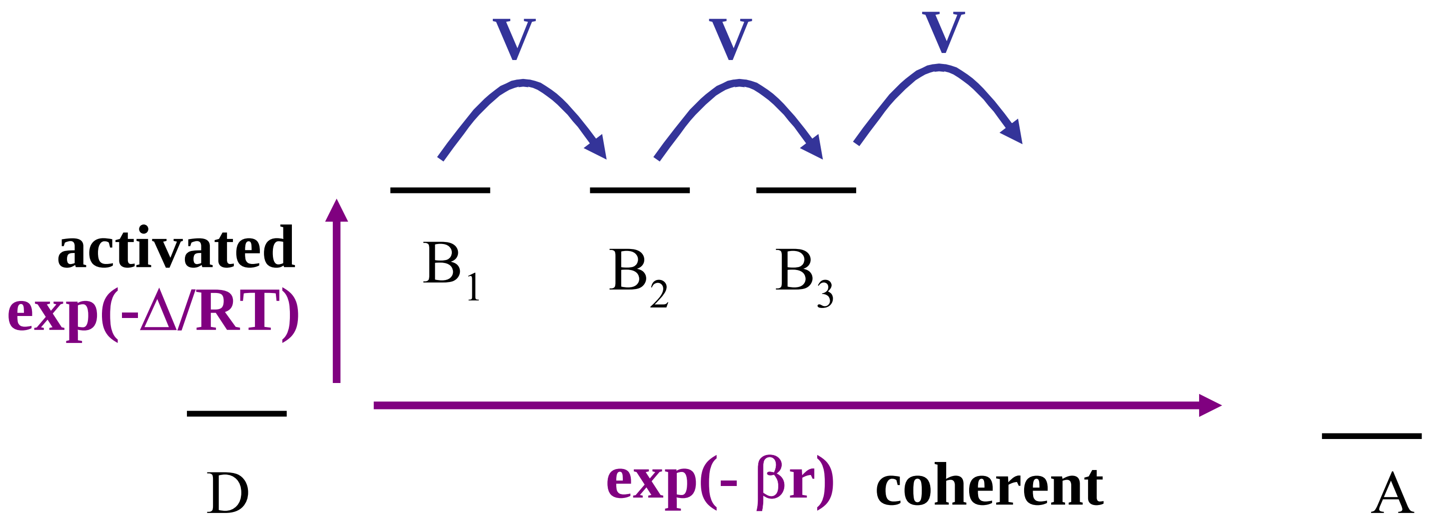
$$k_{coherent} \approx \exp(-\beta r)$$ ← **For short and cold chains**

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

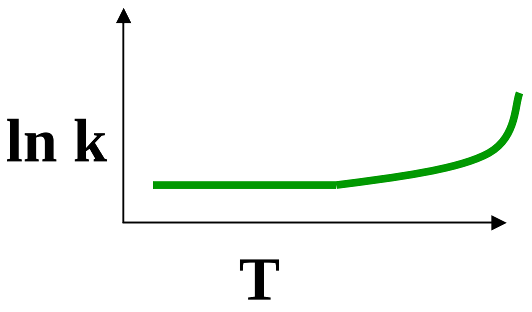
Total Rate Has Two Contributions

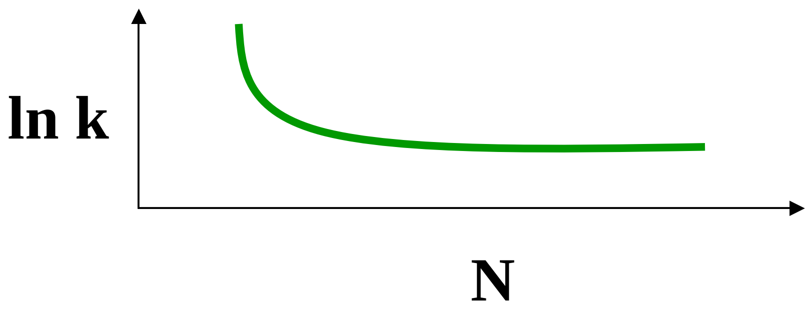


PAY SOME EXPONENTIAL COST TO MOVE*

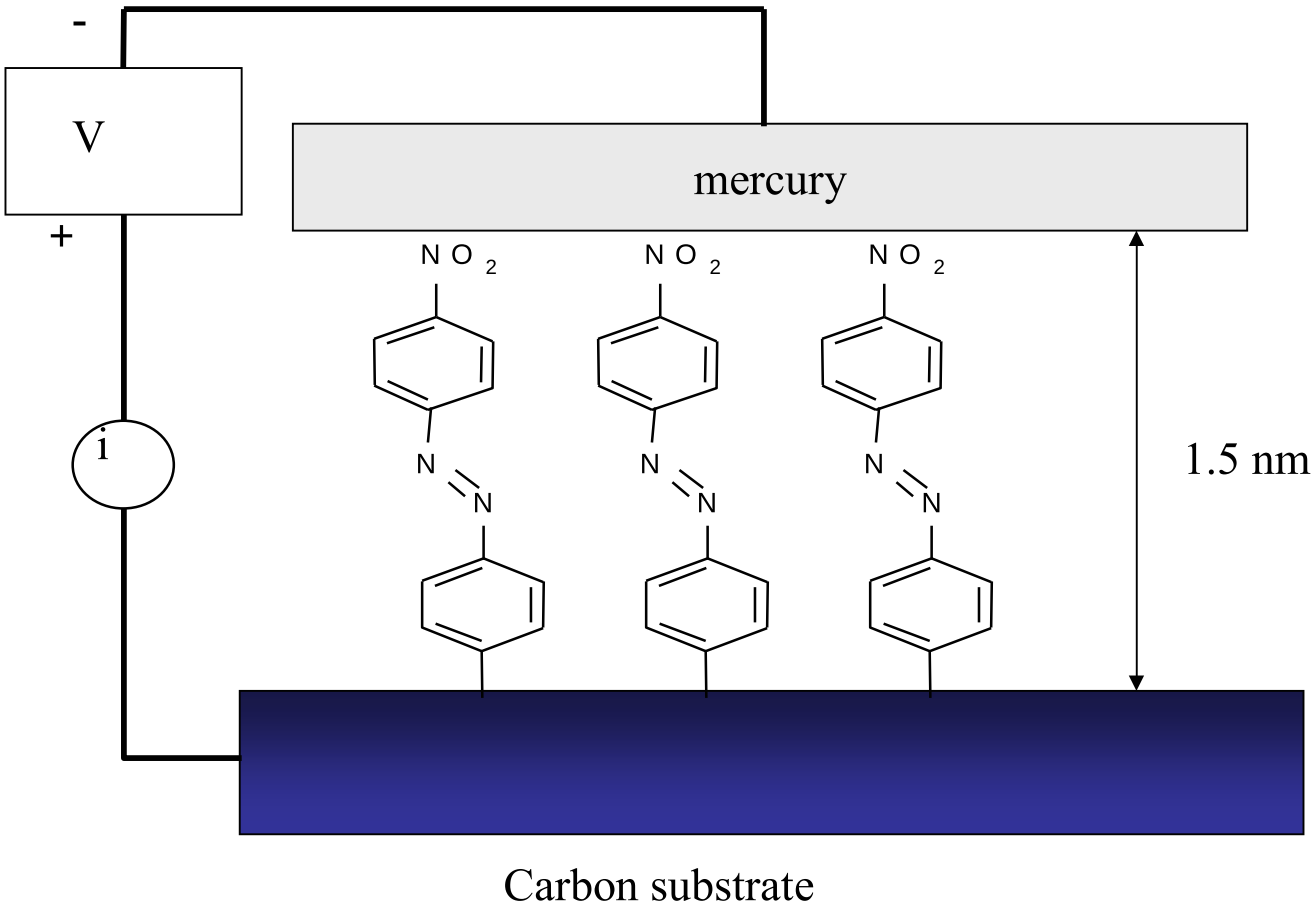


$$k_{tot} = k_{coherent} + k_{activated}$$





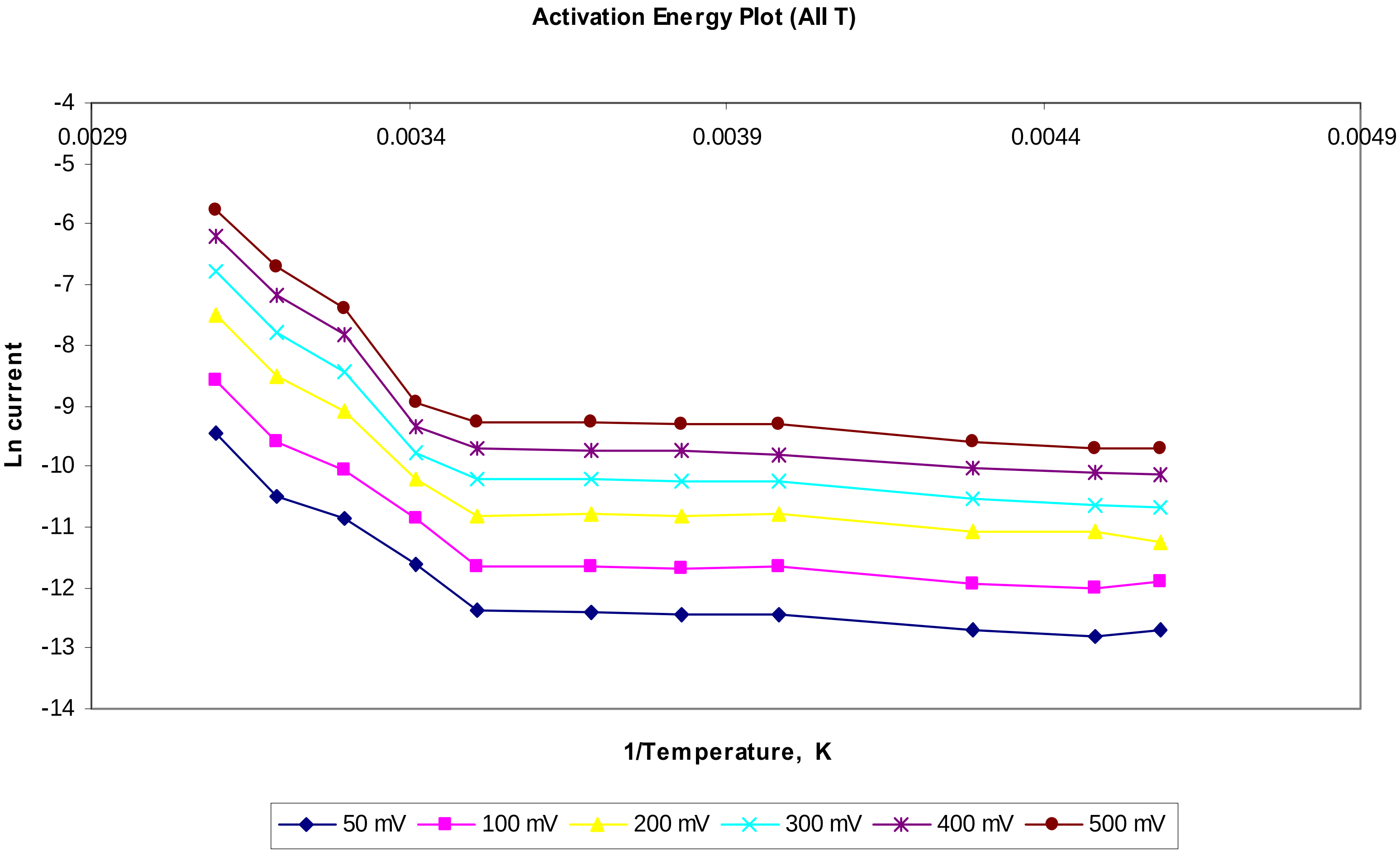
*in molecular systems



McCreery and Collaborators. Note :

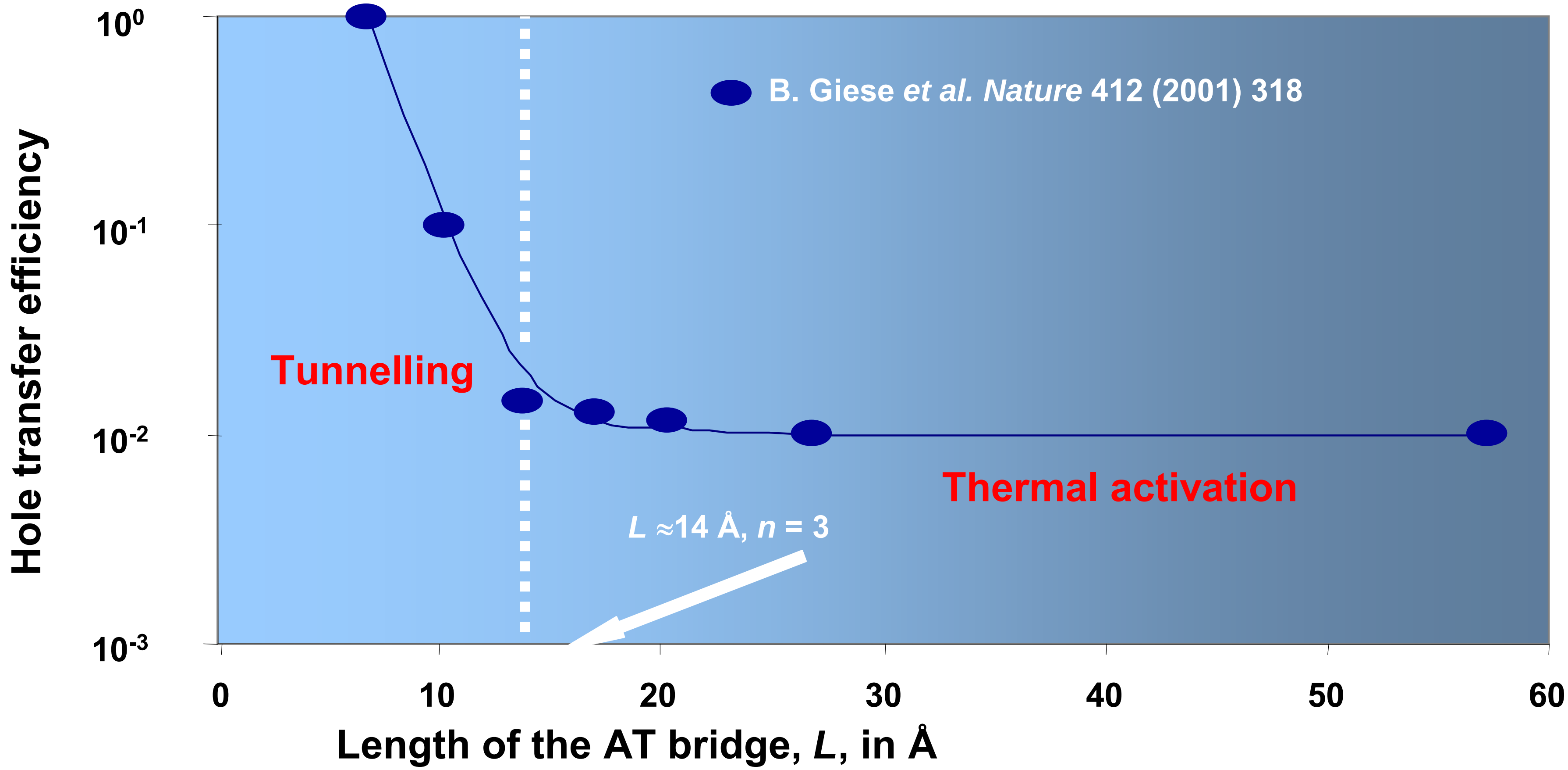
- **Covalent binding**
- **Semiconductor electrode**

Carbon electrode junctions using Polyphenylenes show thermal turnover

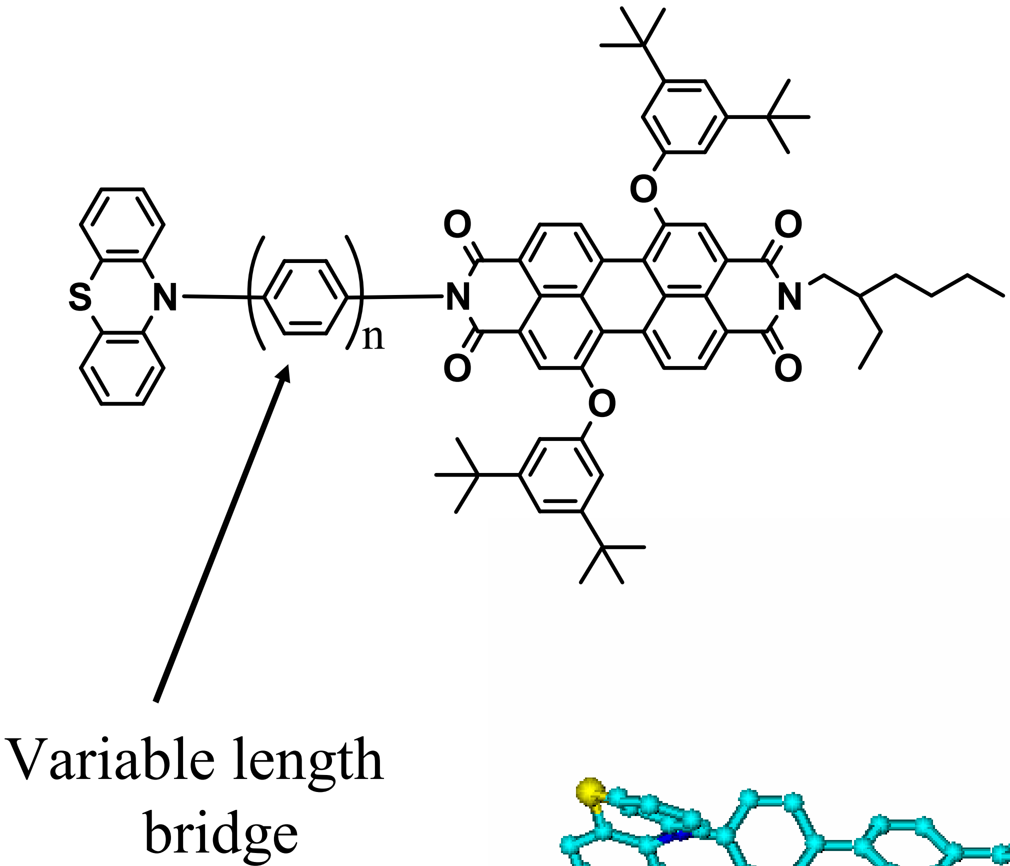


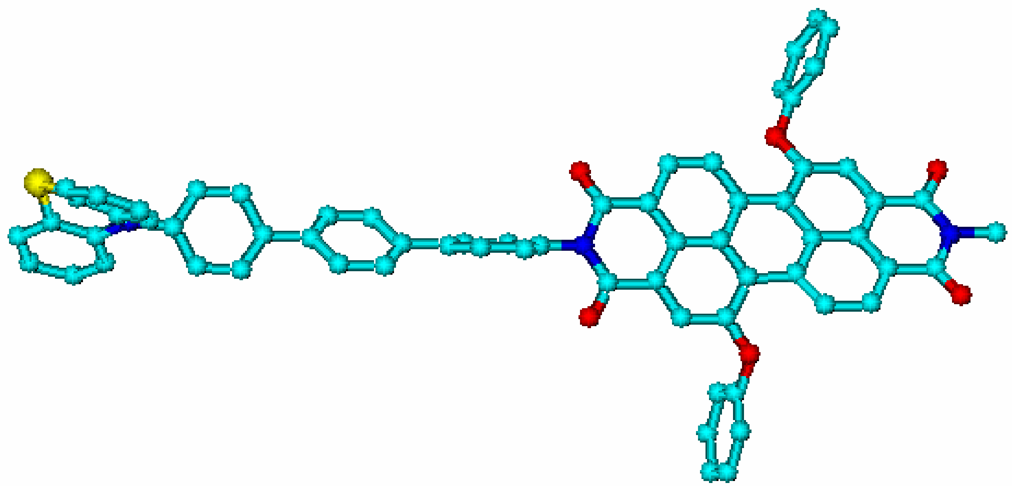
McCreery et.al., 2003

DNA electron transfer – mechanistic turnover



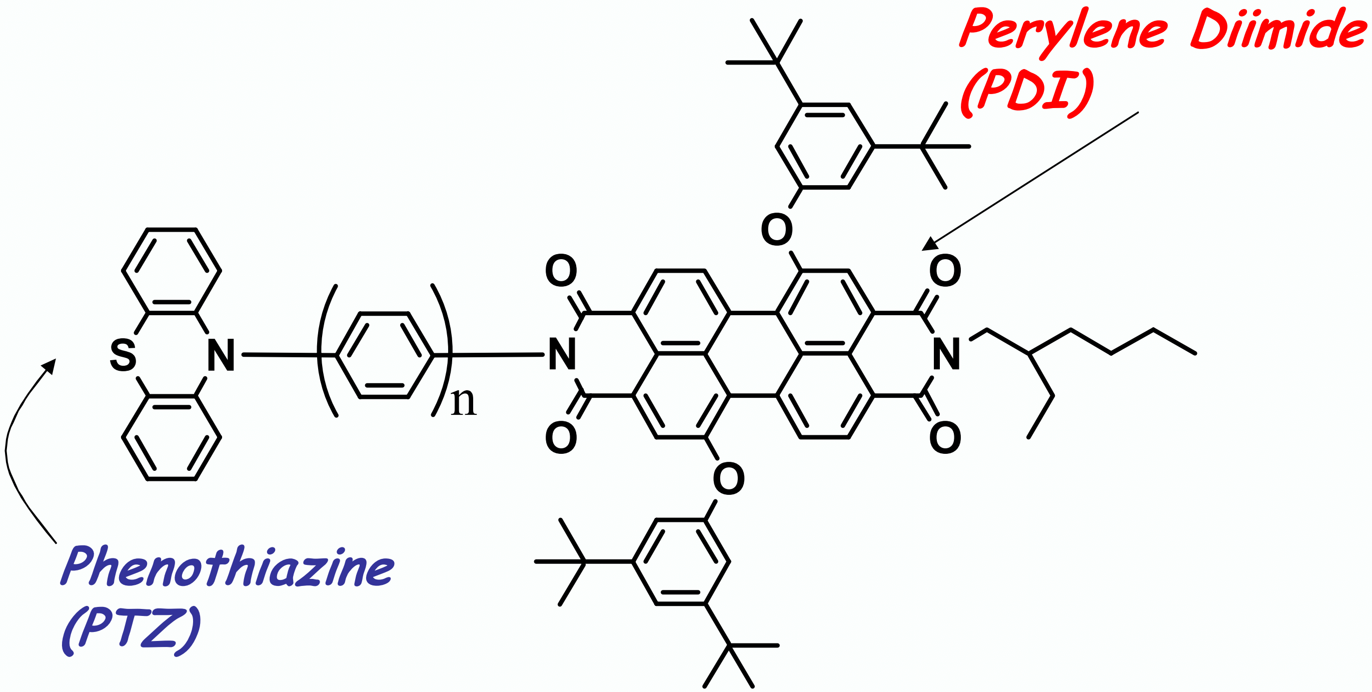
Berlin Burin, MR





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

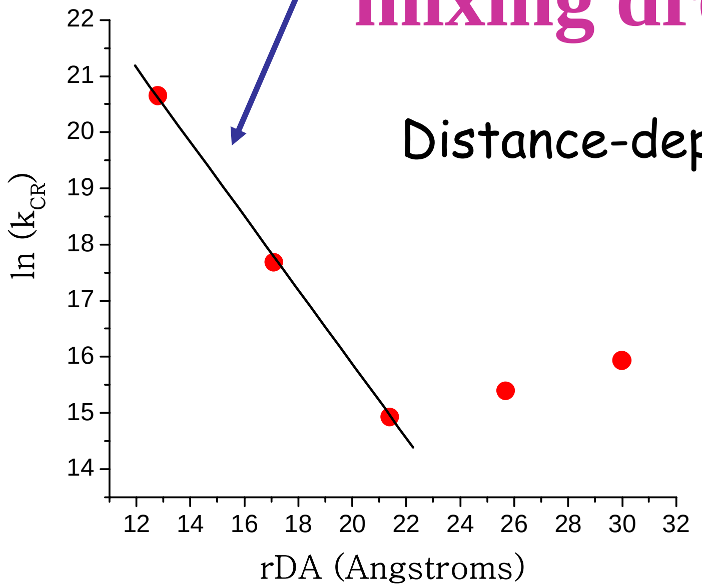
Intramolecular rates do the same turnover in mechanism



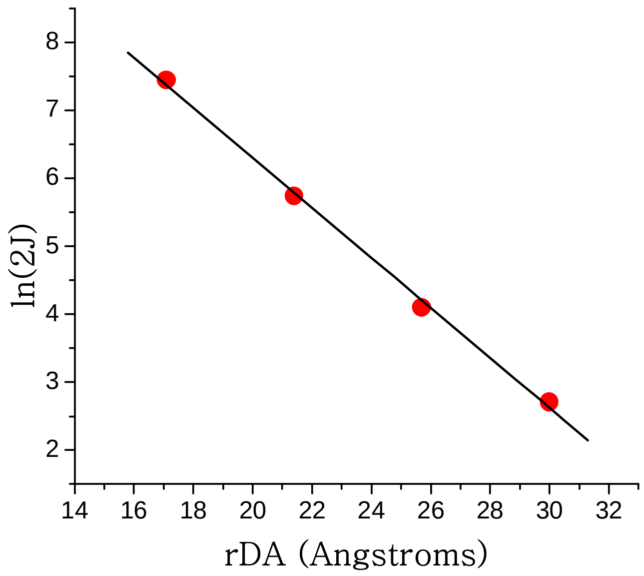
Donor/ridge/acceptor photoexcited ET

Weiss, Wasielewski

Rates change mechanism, mixing drops exponentially



Distance-dependence of charge recombination

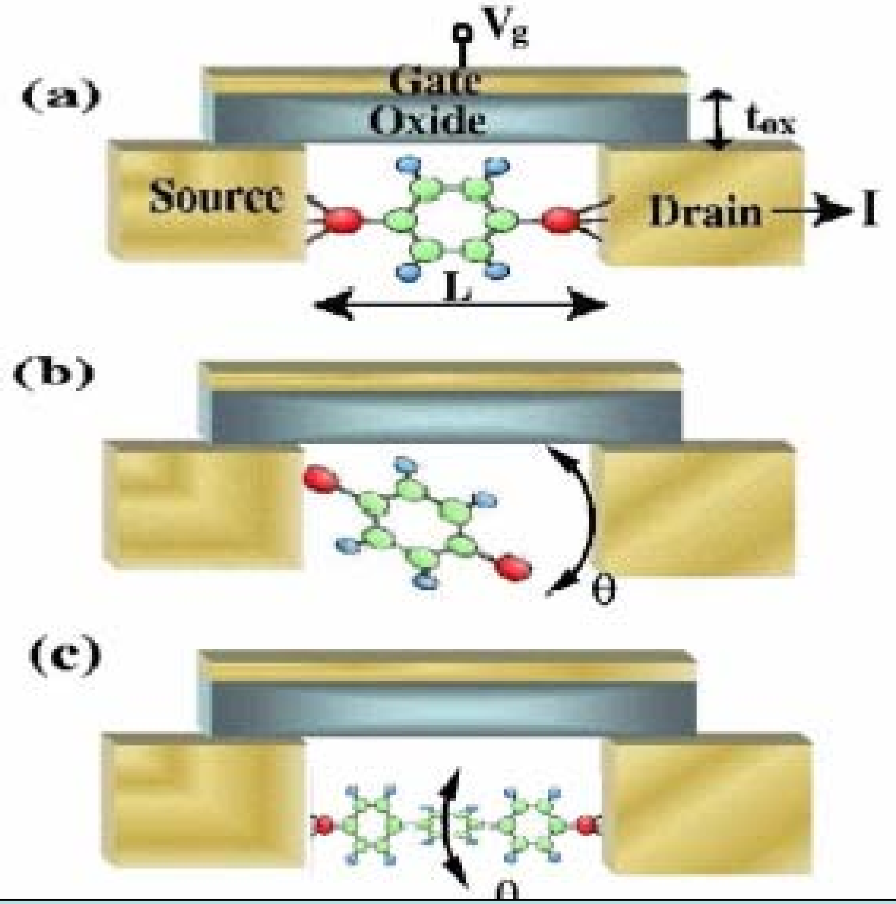


Distance-dependence of electronic interaction

Devices??

Molecular Switch?

Gate switching?



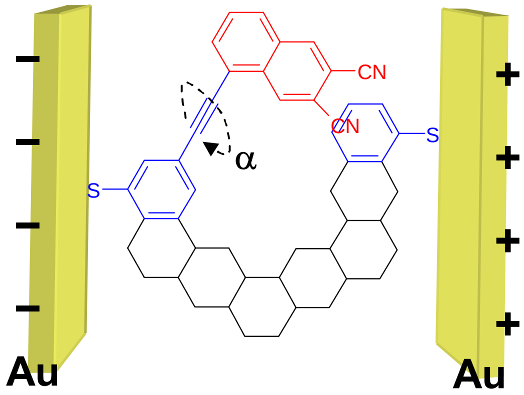
For effective gating, the gate oxide thickness
Must be thinner than the source/drain length

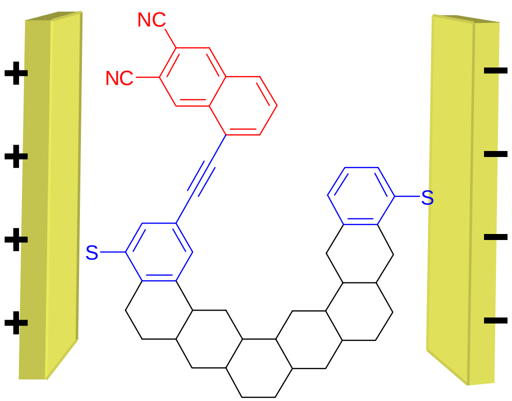
<u>**This is tough with a short molecule!**</u>

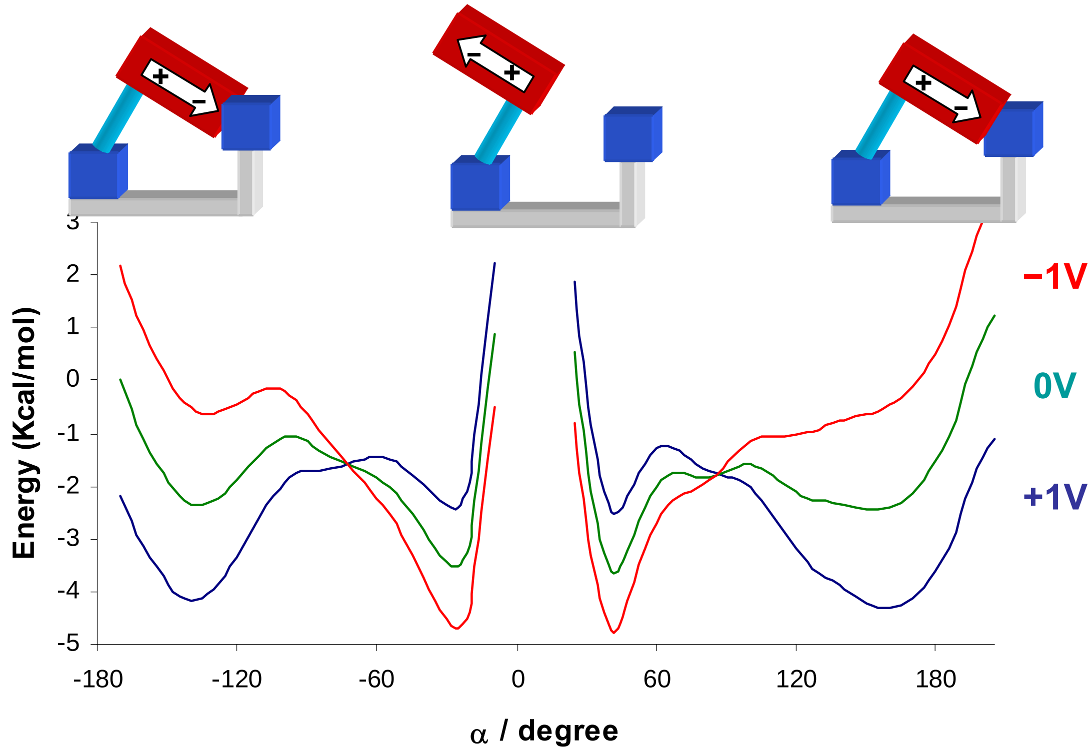
Datta, Ghosh

A rectifier based on *intra*-molecular structural changes

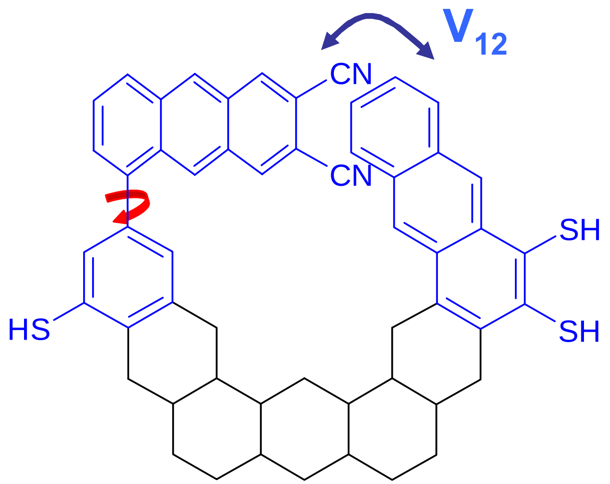
(a device minimally dependent on the metal-molecule contact)

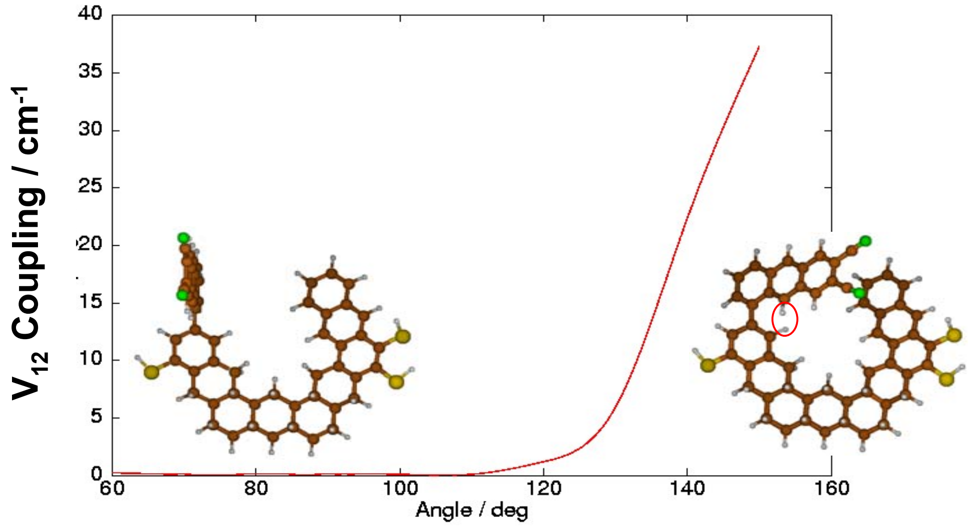


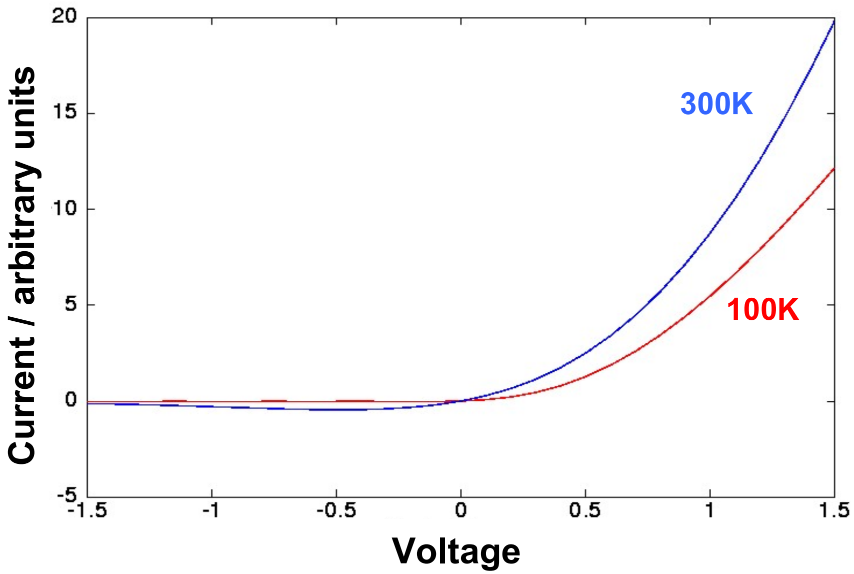




A SYSTEM WITH ONLY ONE THROUGH-SPACE COUPLING AND VERY HIGH ON/OFF CONDUCTANCE RATIO







Giant Rectification/switch,
With two electrodes
From control of
stereochemistry

Troisi and MR, 2003

Devices??

NANOCOMPOSITES IN TENNIS BALLS LOCK IN AIR, BUILD BETTER BOUNCE

Jan. 29, 2002 – When the first round of the Davis Cup gets under way Feb. 8, nanotechnology will be working, literally, within the game.

TENNIS RACKETS

CONTENDER / ACTIV

PASSION
Top-of-the-line

- VS Nanotube™ Power
- VS Nanotube™ Drive
- VS NCT Power
- VS NCT Drive
- VS NCT Control

All products Contender / Activ

COMPETITOR / PRO

COMPETITION
Performance objectives

- Pure Power Zylon™ used 360°
- Pure Drive Zylon™ used 360°
- Pure Control Zylon™ used 360°
- Pure Drive Team
- Pure Control Team

All products Competitor/Pro

CHALLENGER

RECREATION
Priority on enjoyment

- Soft Power
- Soft Drive
- Contest Serie 1
- Contest Serie 2
- Classic Ti

All products Challenger

JUNIOR

A range designed to allow the progressive learning of junior players.

- Pure Drive Zylon™ used 360° Jr
- Pure Junior
- Roddick Junior 145
- Roddick Junior 140
- Ballfighter

VS Nanotube™ Power

Power thanks to a larger sweetspot.

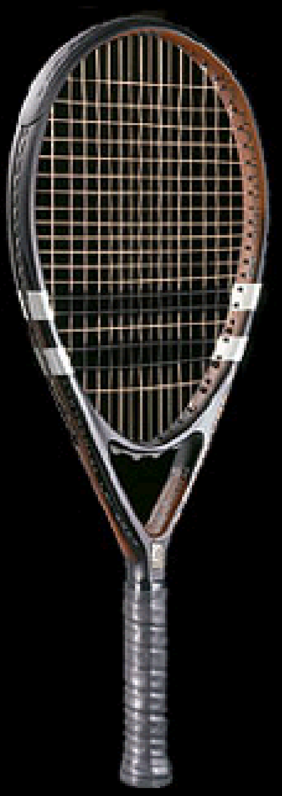
WOOFER DUAL

- Carbon Nanotube™ Stabilizers increases torque (+50%) and flex (+20%) resistance.
- Dual Woofer, 5 times more shock absorbing than conventional grommet.

PASSION | COMPETITION | RECREATION

Power — Control

HeadSize	750 cm² / 116 sq.in
Weight	245 gr / 8.6 oz
Composition	Carbon Nanotube™/ High modulus graphite
Grip	Air Touch Grip

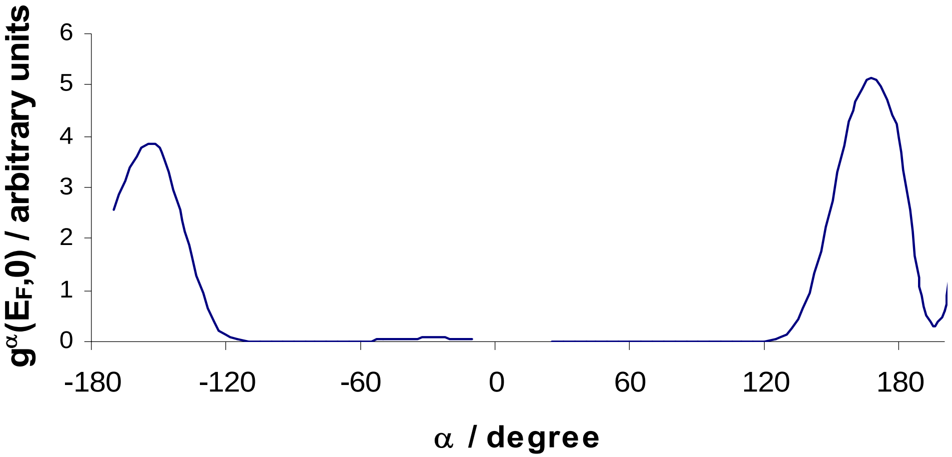


thanks

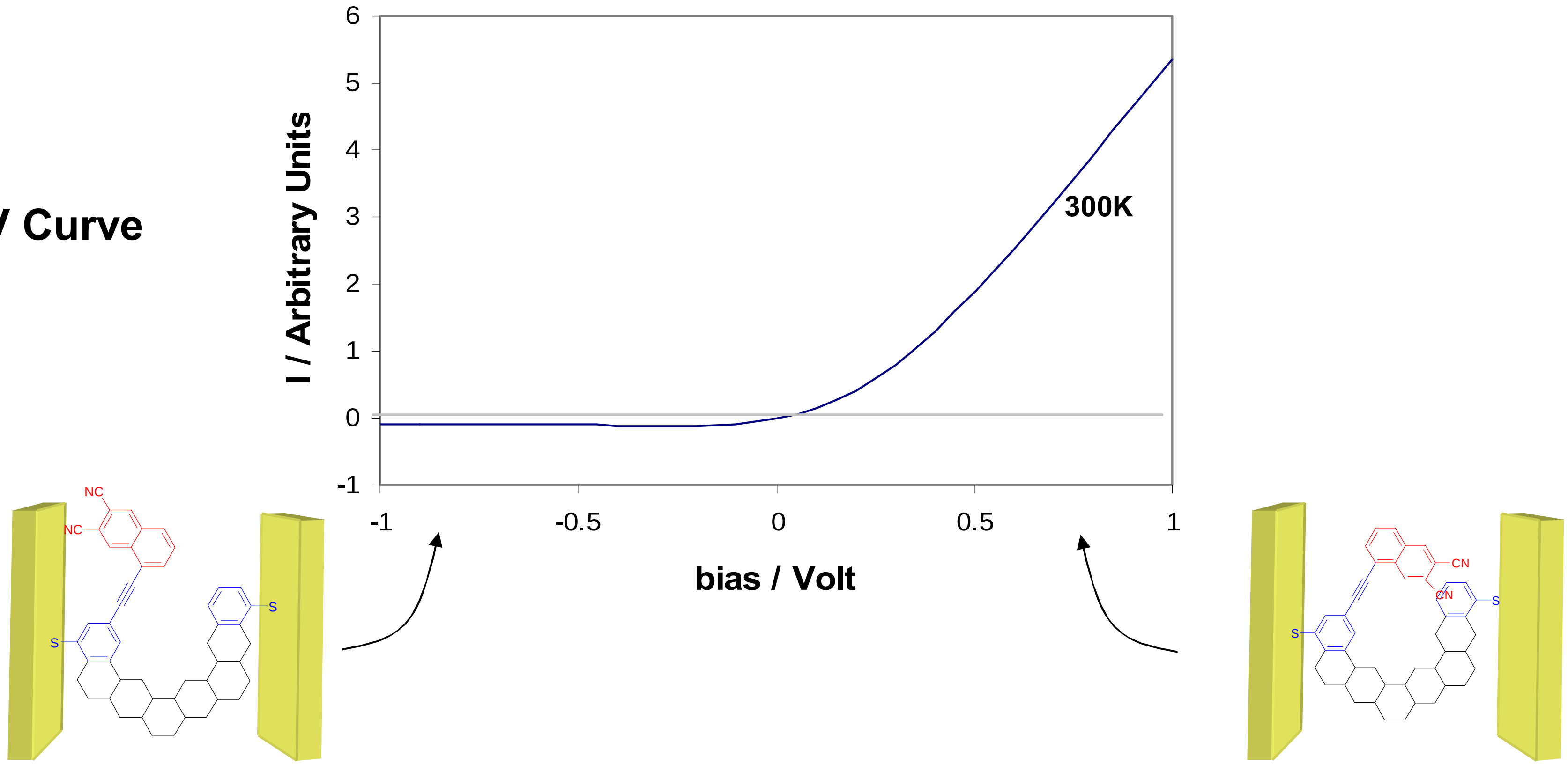
- <u>ICTP and the organizers</u>
- **Emily Weiss**
- **Abe Nitzan, Alex Xue, Misha Galperin**
- **Bill Davis**
- **Alessandro Troisi**
- **Mike Wasielewski**
- **Vladi Mujica**

ALL THE PARTICIPANTS!!

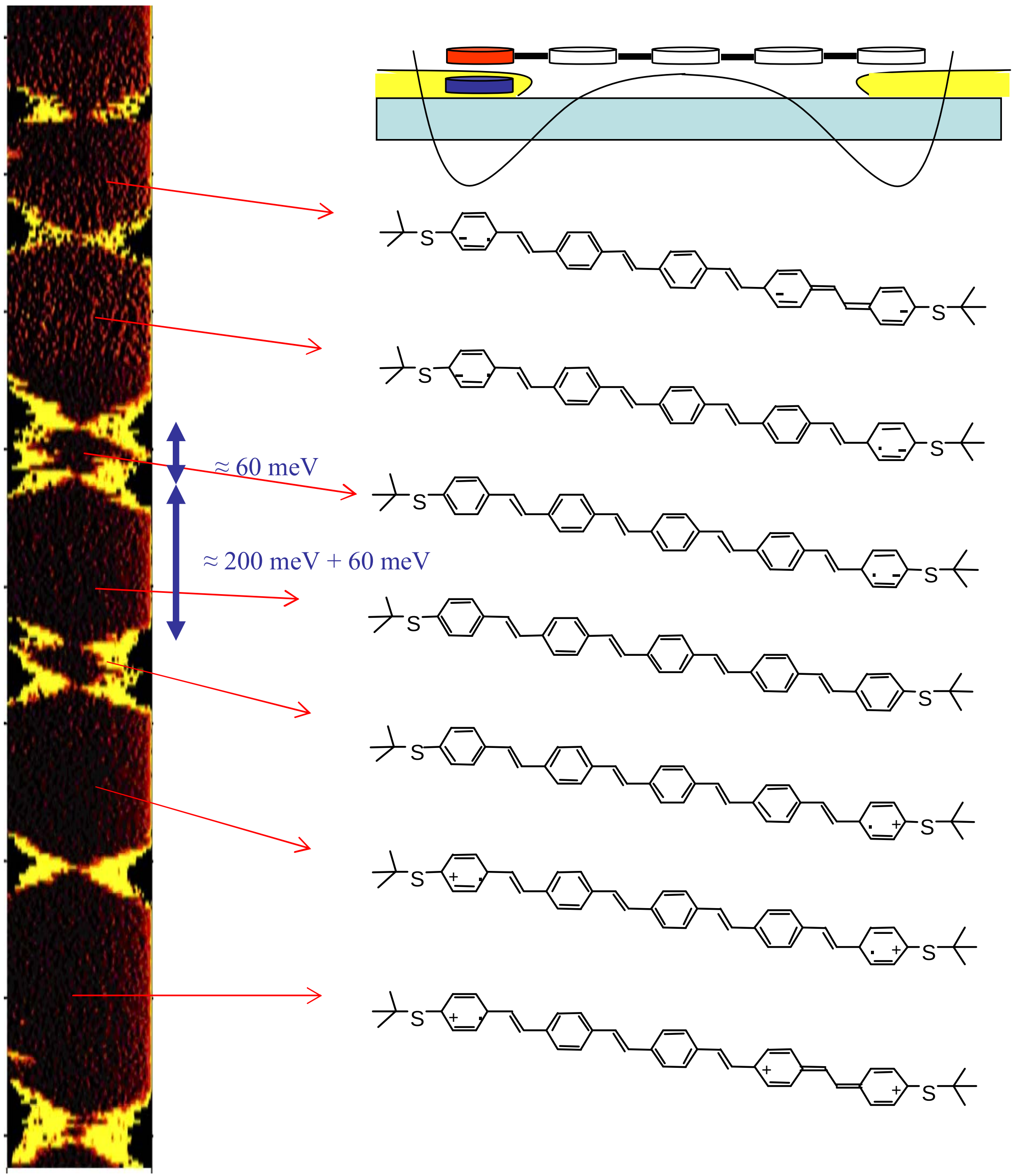
Conductance



I/V Curve

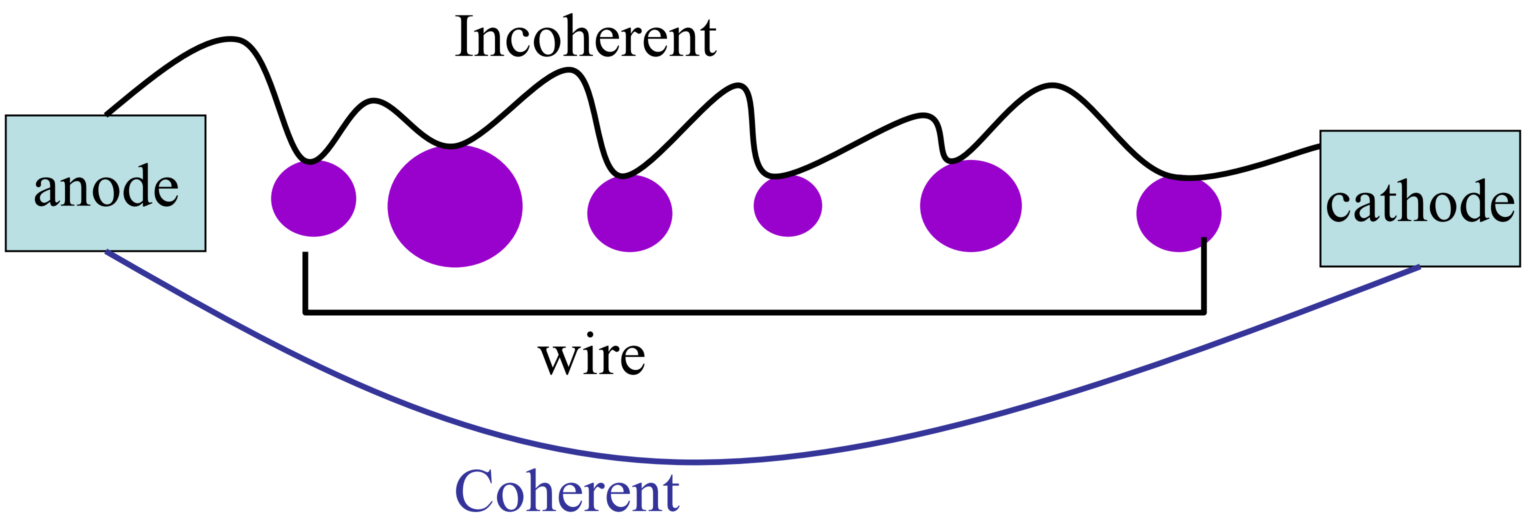


Multiple Charging steps!



Bjornholm et.al 2003

Molecular Wire Interconnects: Transport Regimes



Rigorously: $g = g_{coherent} + g_{incoherent}$

$g_{incoherent} \approx 1/(A + B * length)$ dissipation in electrodes, wire

$g_{coherent} \approx \exp(-\beta * length)$ dissipation in electrodes

ET-conductance relationship

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

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

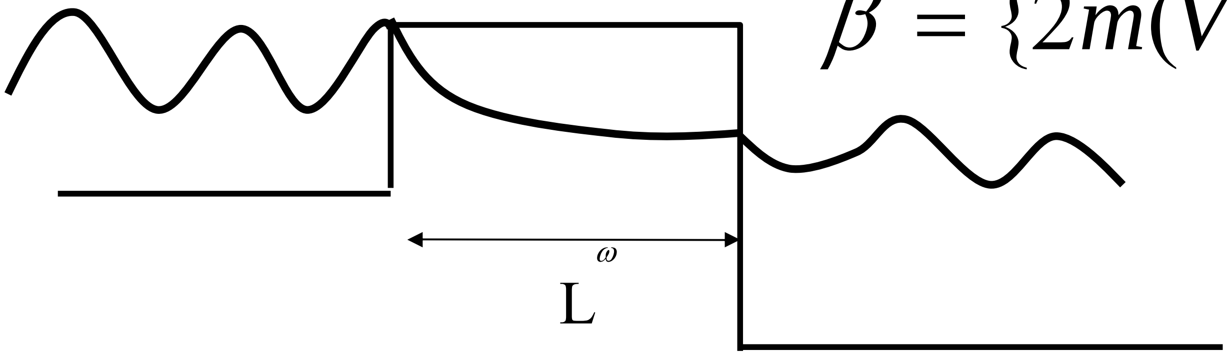
Similar dependence of effective coupling on molecular parameters if Factorization electrode-wire holds.

Distance Dependence - Purely Electronic

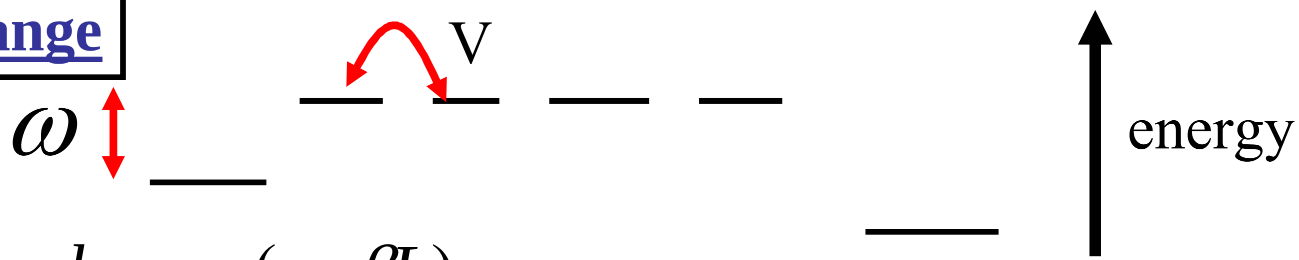
$$k = k_0 \exp(-\beta L)$$

Barrier tunneling

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



Superexchange



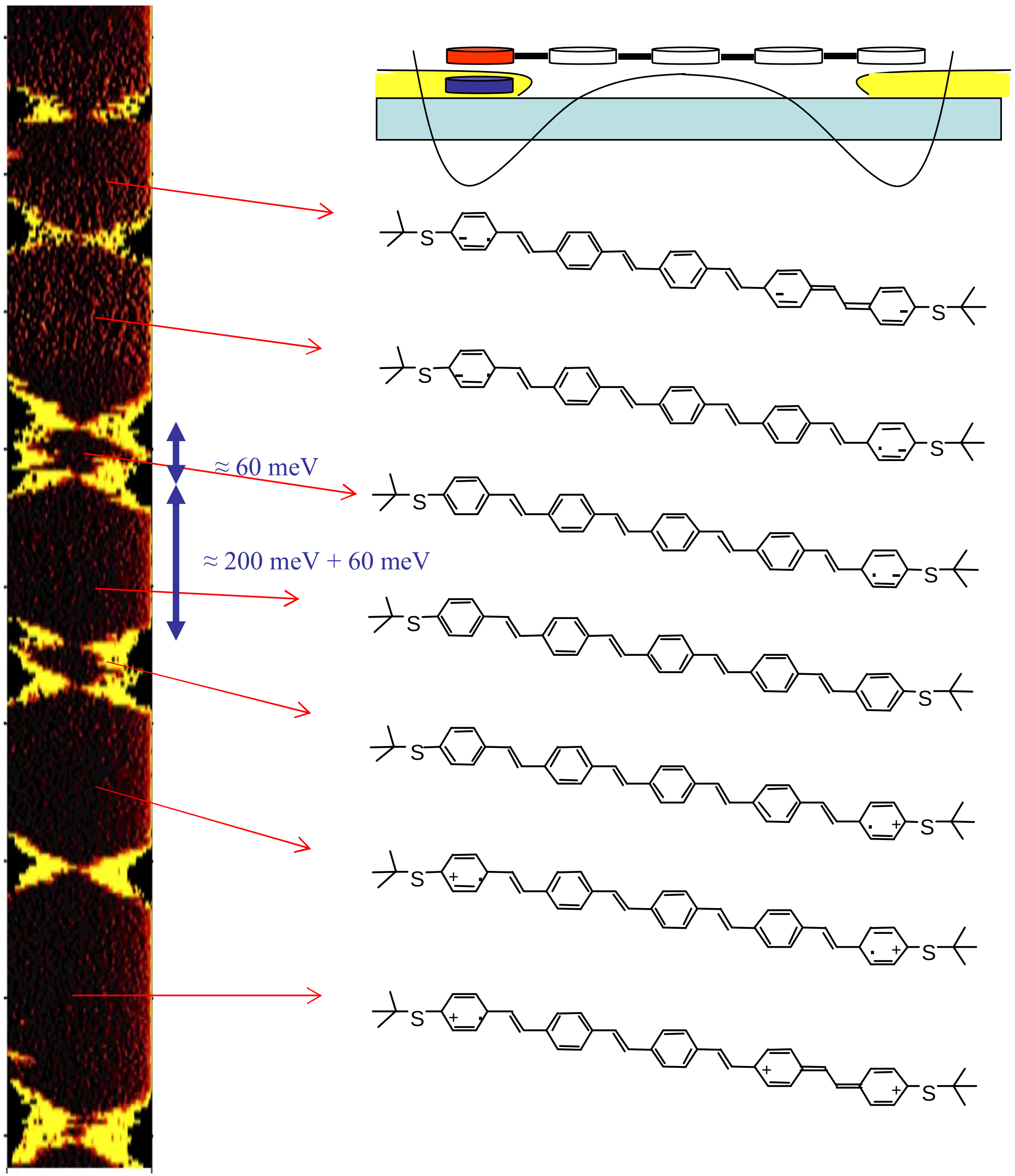
$$k = k_0 \exp(-\beta L)$$

$$\beta = \frac{2}{R_0} \ln(\omega / V) \qquad (\omega / V \langle\langle 1)$$

Table 1 Bridge length dependence of the transmission rate

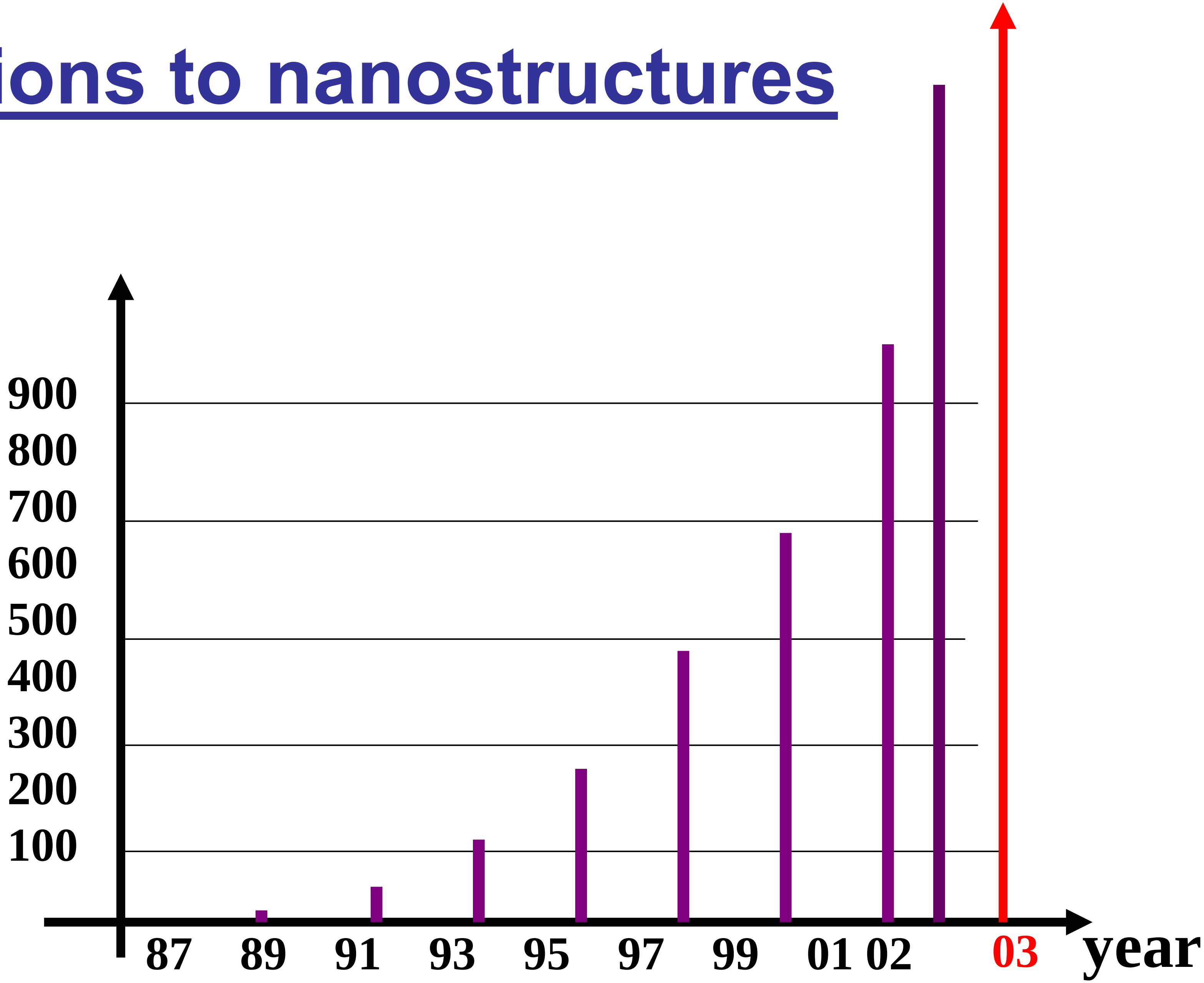
Physical Process	**Bridge length (*N*) dependence**	
Super exchange (*small N, large $\Delta E/V$, large $\Delta E/k_BT$*)	$e^{-\beta N}$	$\beta = 2\ln(V/\Delta E)$
Steady state hopping (*large N, small $\Delta E/V$, small $\Delta E/k_BT$*)	N^{-1}	
Non-directional hopping (*large N, small $\Delta E/V$, small $\Delta E/k_BT$*)	N^{-2}	
Intermediate range (*intermediate N, small $\Delta E/V$*)	$\left(k_{up}^{-1} + k_{diff}^{-1} N\right)^{-1}$	$k_{up} \sim \left(V^2\kappa/\Delta E^2\right)e^{-\Delta E/k_BT}$ $k_{diff} \sim \left(4V^2/\kappa\right)e^{-\Delta E/k_BT}$ (Markovian case)
Steady state hopping + competing loss at every bridge site	$e^{-\alpha N}$	$\alpha = \sqrt{\Gamma_B(\Gamma_B+\kappa)}/2V$ (Markovian case)

Multiple Charging steps!

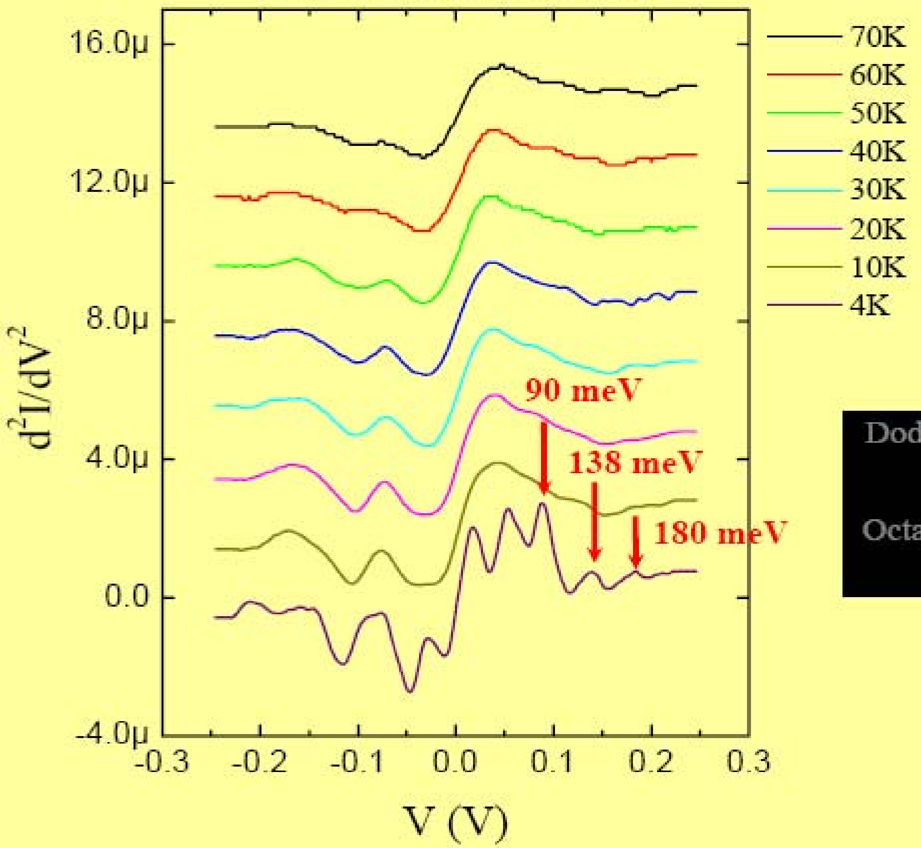


Bjornholm et.al 2003

Citations to nanostructures

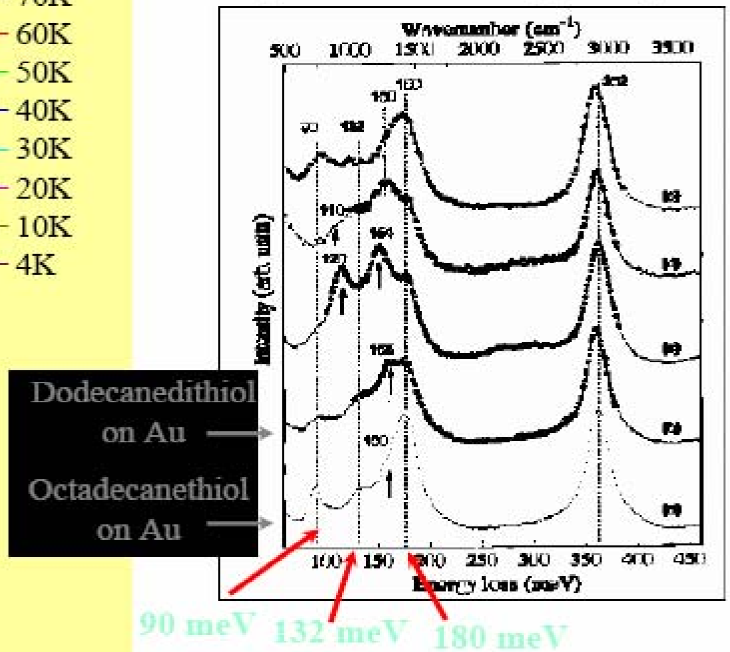


Temperature-dependent IETS data on dodecanethiol



HREELS Data

(High res. electron energy loss spectra)



Duwez, et al. Langmuir ***16****, 6569 (2000)*

- *180 meV: CH_2 scissoring mode and CH_3 symmetric bending mode*
- *132 meV: C-C stretching mode*
- *90 meV: Rocking mode of the CH_2*