Computational Modeling of Molecular Electronics

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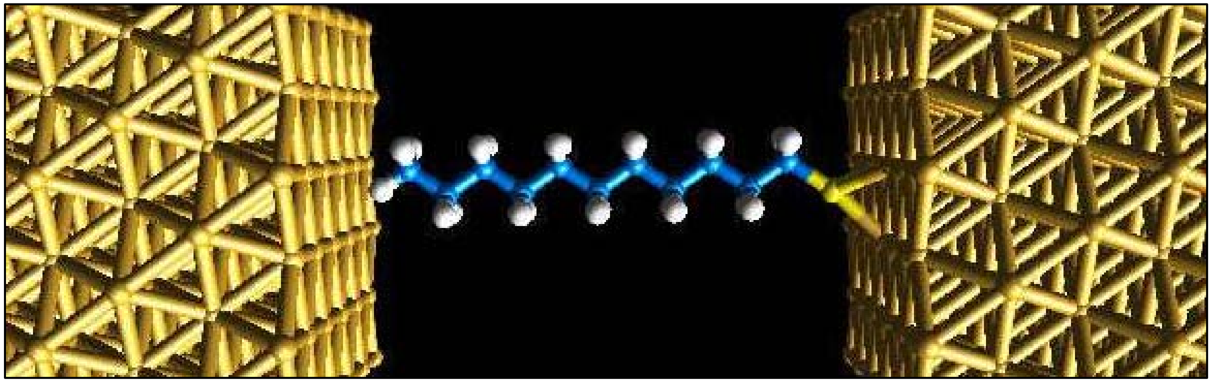


May 9, 2007

Outline:

1. Introduction

    Why molecular electronics?

2. Comparison with experiments

    Oligophenylene thiol and Alkanethiol molecular wires

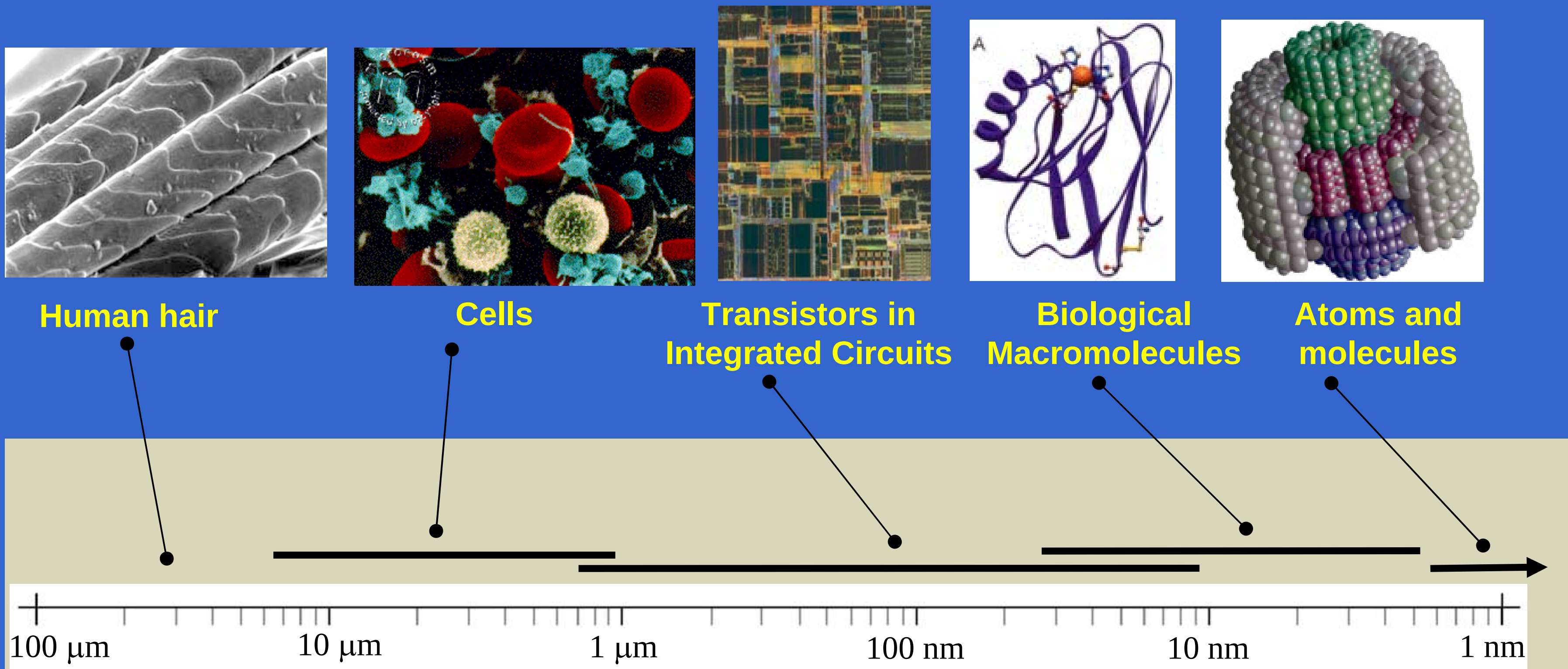
3. The gating efficiency of single-molecule transistors

4. A current-driven molecular machine

5. Desorption of molecules from silicon surface

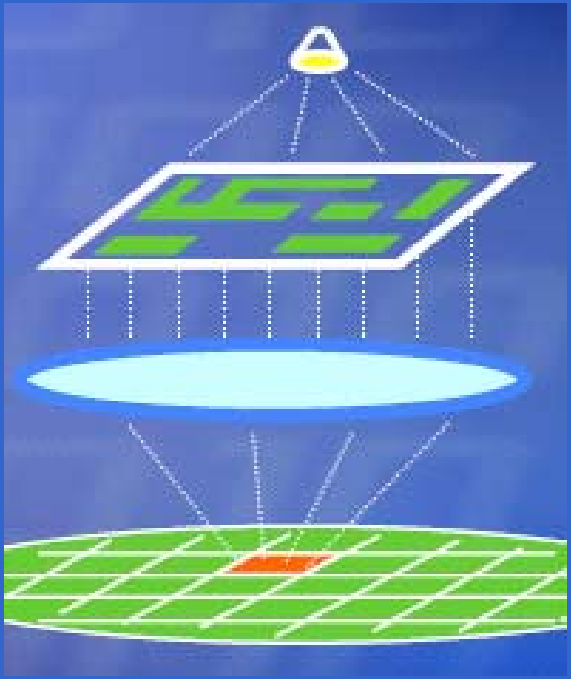
6. Summary

1. Introduction:



Nanotechnology: works at the atomic, molecular and supra-molecular levels, at the **0.1 – 100 nm scale**, with **fundamentally new properties.**

What’s the problem?



Physical limit:
Diffraction of light.

Economical limitation:
Too expensive.

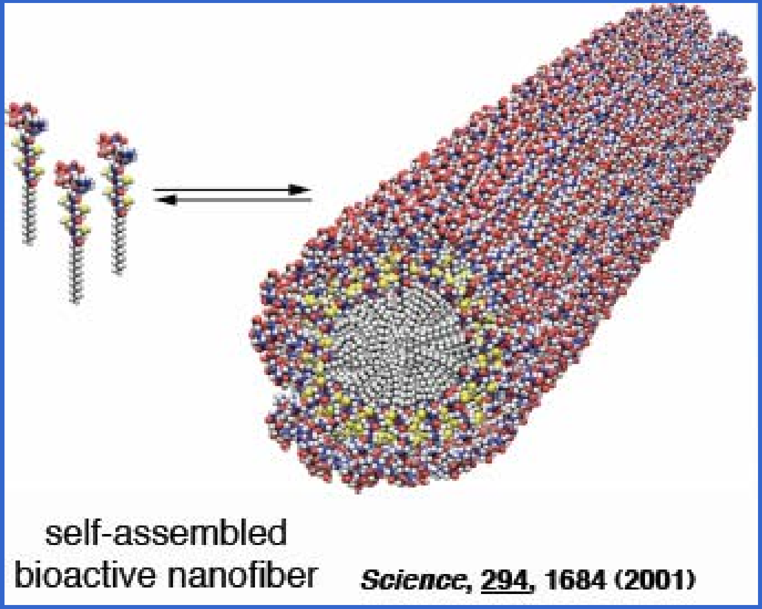
Molecular electronics: A solution

The main idea: use molecules to create analogues of today's IC chips.

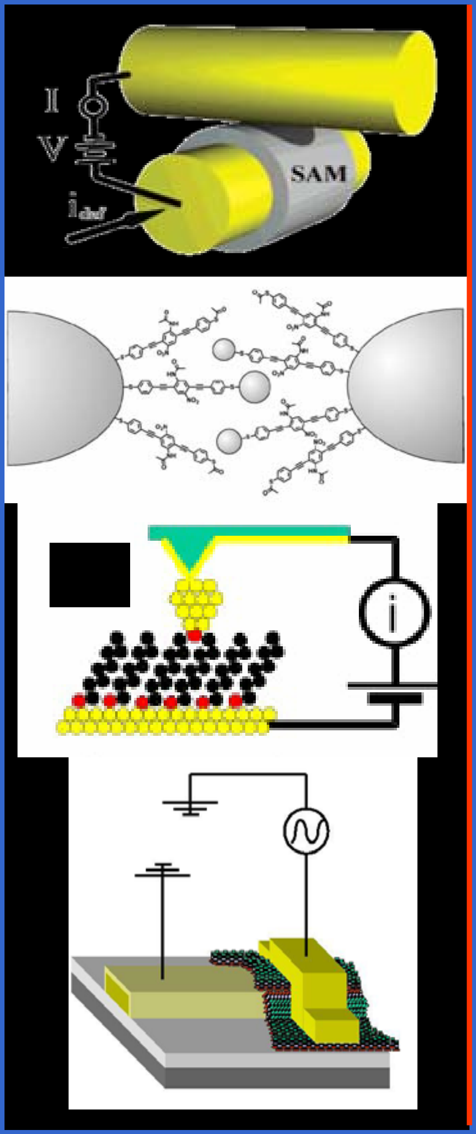
Because molecules are small and can form structures by self-assembly.

Aviram & Ratner, (1974).

For example ..



Some experiments



J.G. Kushmerick
NanoLetters ‘03

H.B. Weber
APL ‘03

S.M. Lindsay
Science ‘03

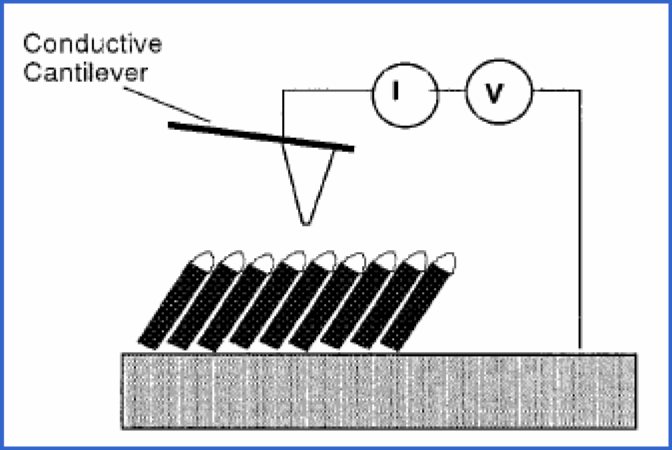
D. Stewart
NanoLetters ‘04

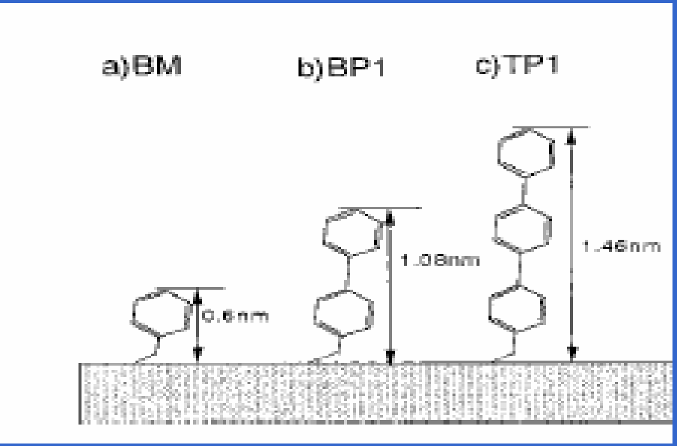
But, there is a big problem:

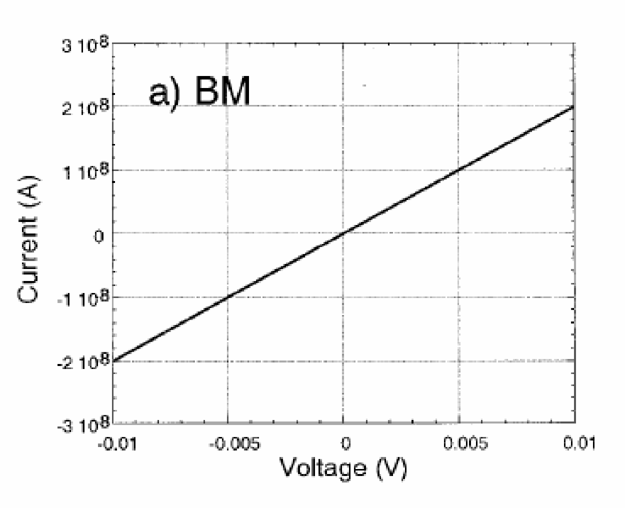
Most experimental data can not be reproduced by other groups!

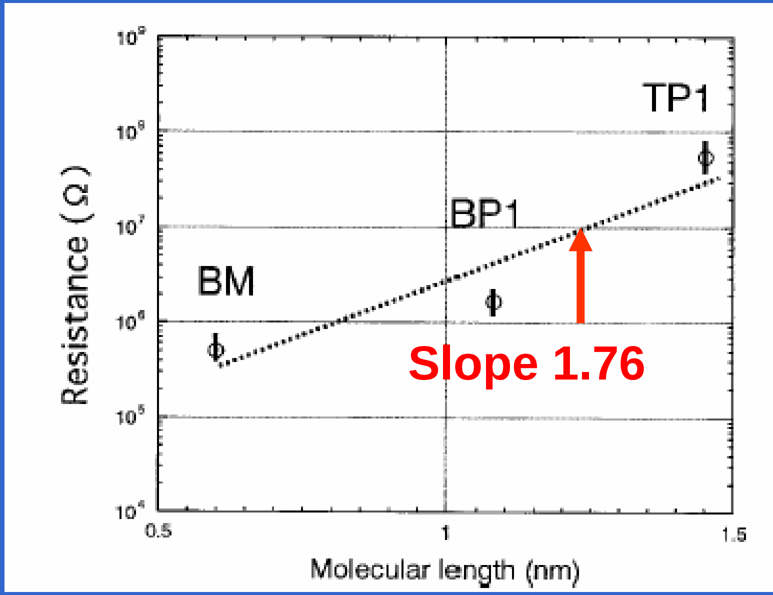
Except….

Resistance of Oligophenylene thiol molecular wires



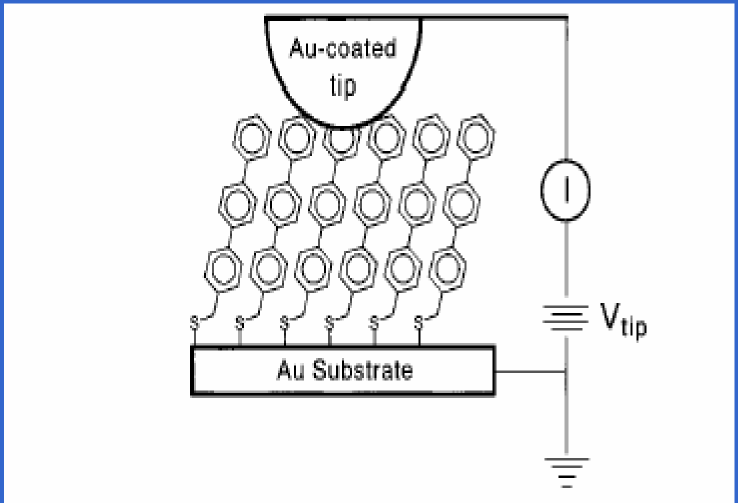


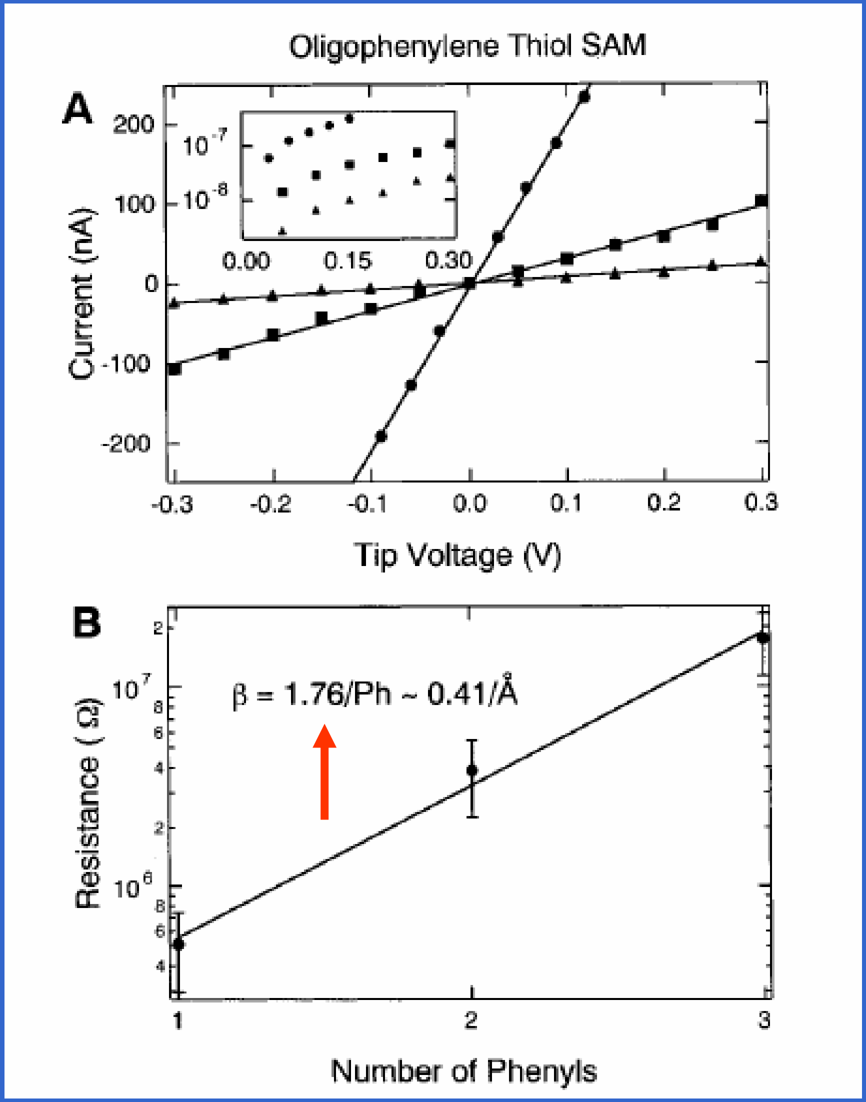




T. Ishida et al., J. Phys. Chem. B 106, 5886 (2002)

Another independent experiment from a different lab:
D. J. Wold et al. J. Phys. Chem. B, 106, 2813, (2002)





Very similar numbers were obtained as those of Ishida's!

It will be nice, if the properties can be understood and predicted by computational modeling!

Science and Economics

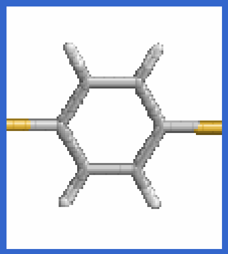
Can we simulate these experimental data from first principles?

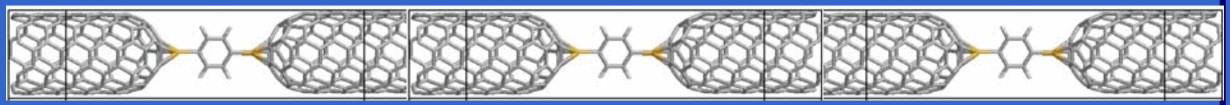
How to calculate current?

$$I(V_b) = \frac{2e^2}{h}\int_{-\infty}^{+\infty} T(E,V_b)\left(f_l - f_r\right)dE$$

Real space DFT plus Keldysh Green's functions: Taylor, Guo, Wang, PRB 63, 245407(2001)-----McGill-Device-CALculator (McDCAL); Brandbyge, et al, PRB 65, 165401(2002)---Transiesta.

Conventional Density Functional Theory (DFT) solves two kinds of problems:





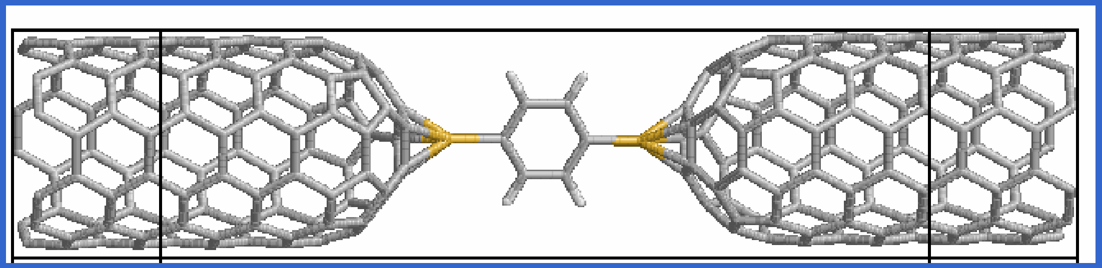
Periodic systems

VASP

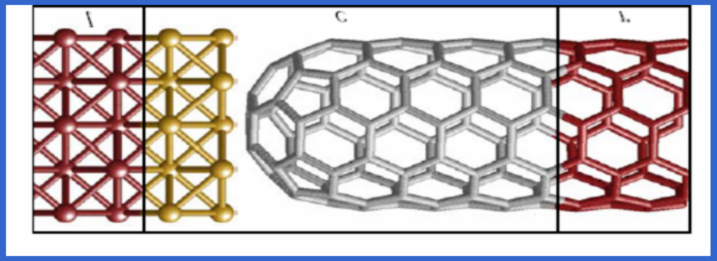
Finite isolated system

Gaussian-03

Quantum transport:

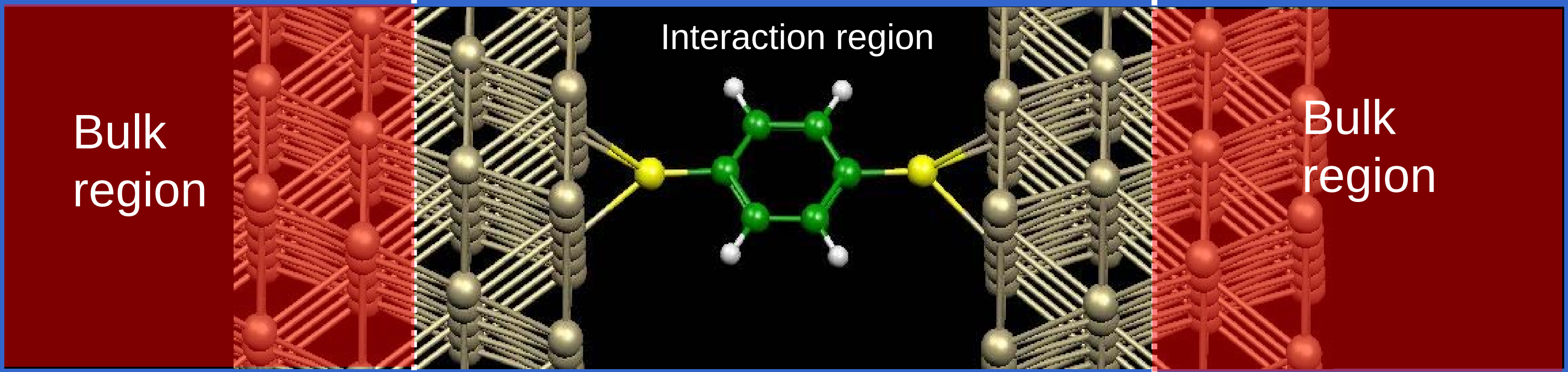


A device is neither finite nor periodic, and is in non-equilibrium



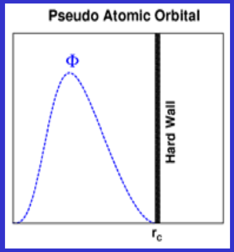
McDcal

Computational modeling



Electronic structure

- Density Functional Theory
- LCAO
- Pseudopotentials



ρ

H

Nonequilibrium physics

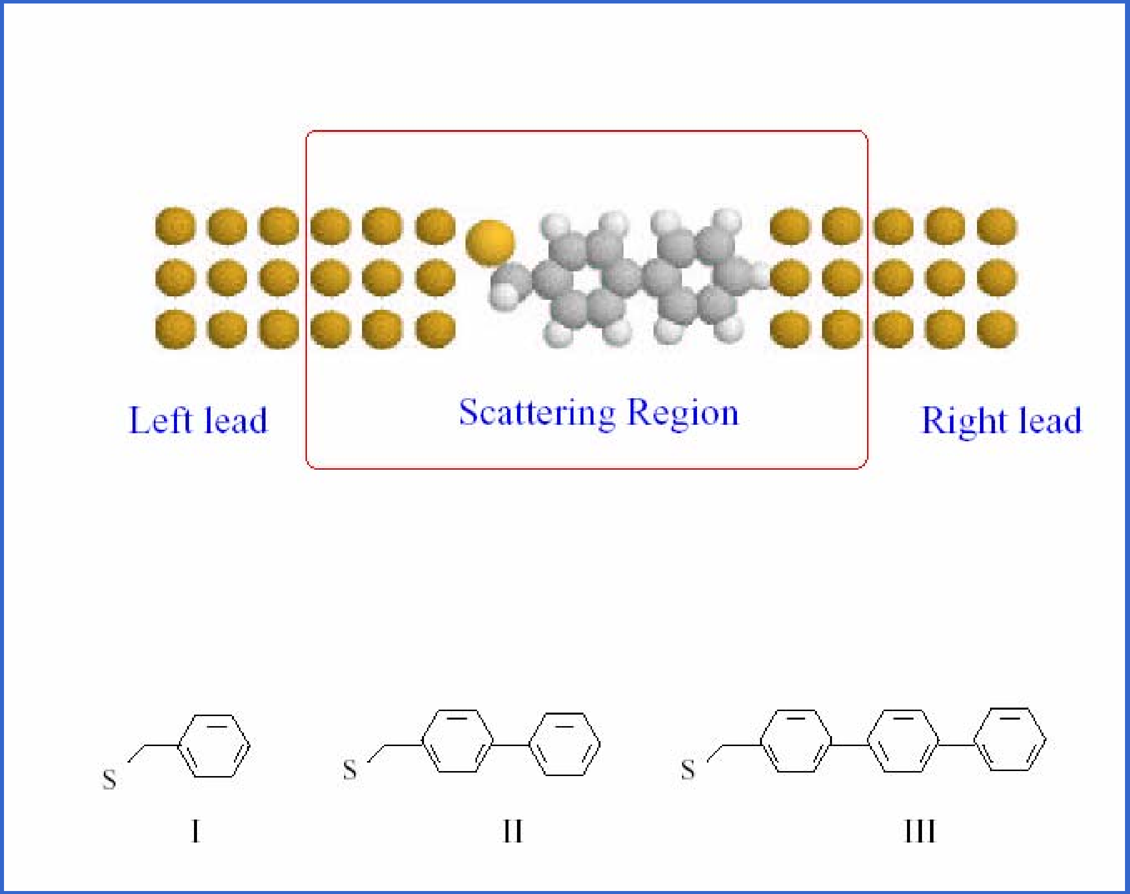
- Full description of electrodes using ab initio self-energies
- Non-equilibrium electron distribution using NEGF

- Calculation of electron current

2. Comparison with experiments:

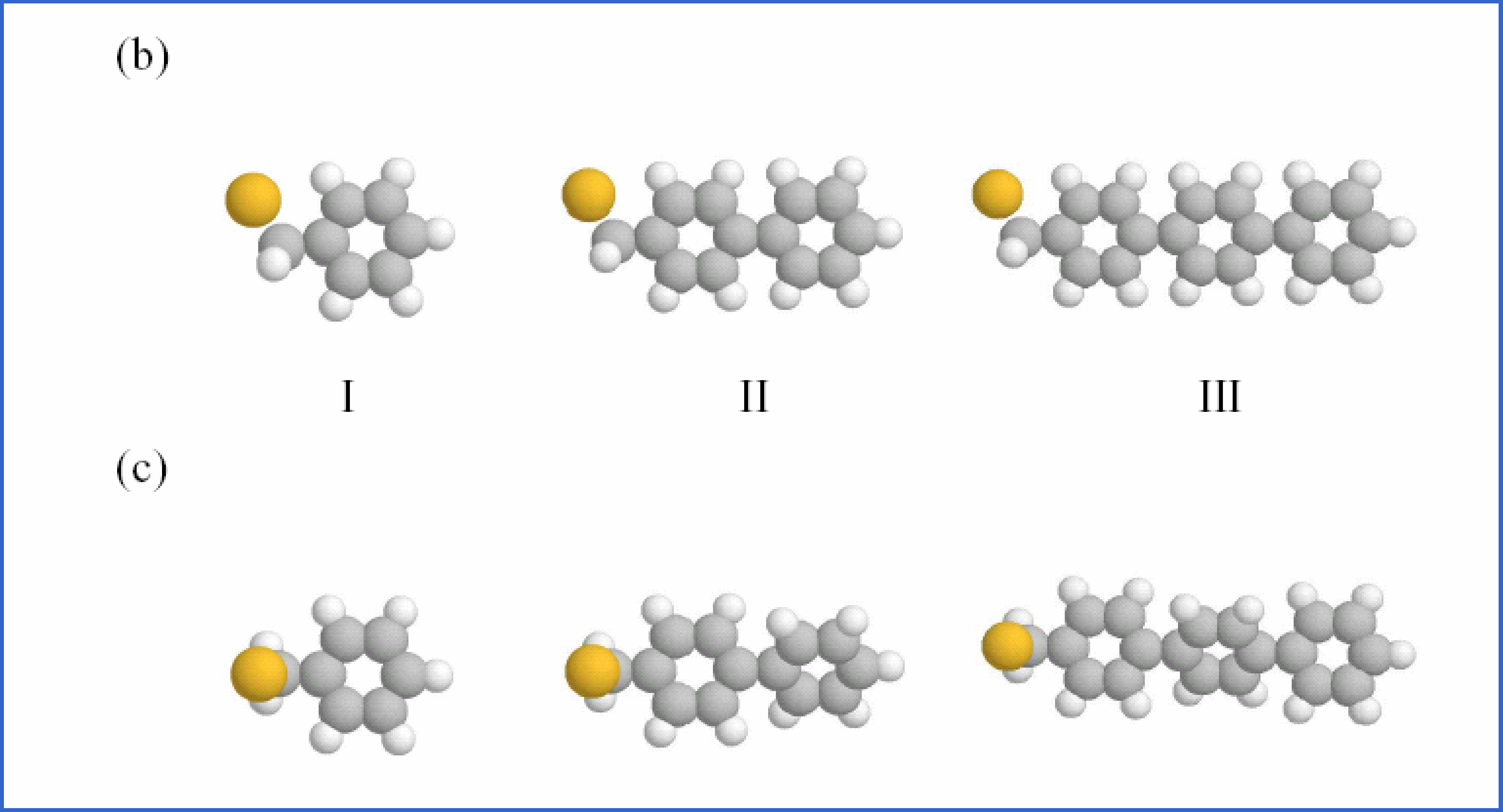
(1). Oligophenylene thiol molecular wires

Our model:

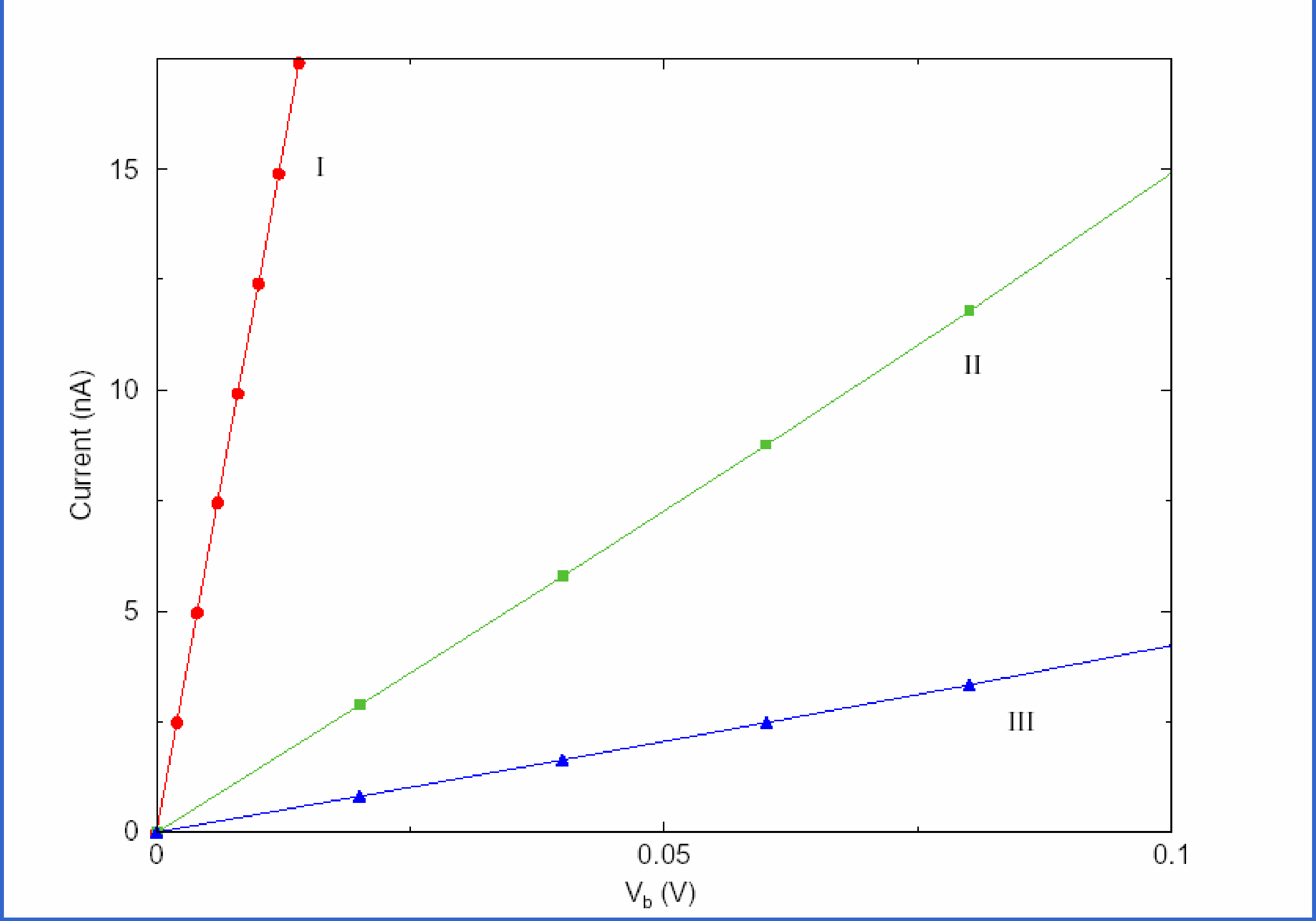


Kaun, Larade and Guo, PRB 67, 121411(R) (2003)

Planar vs rotated conformations:

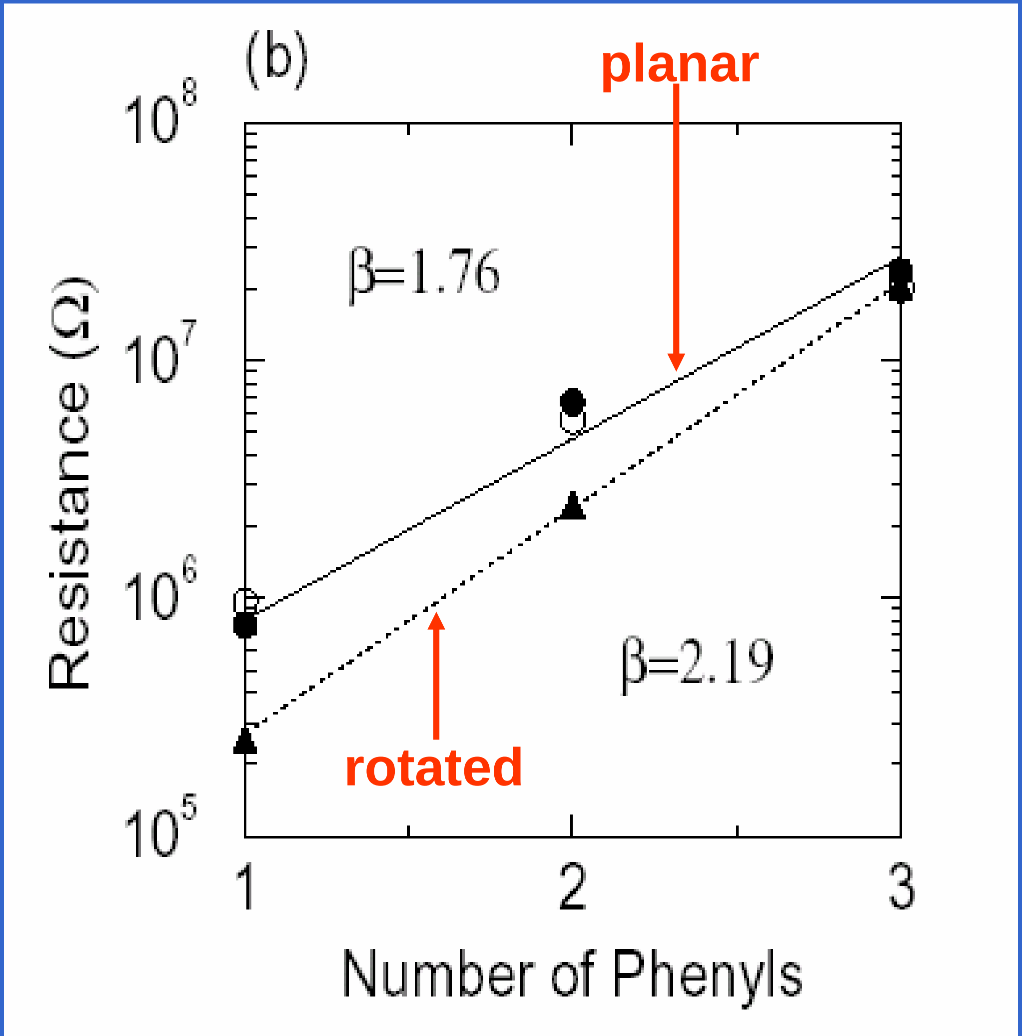


I-V curve for planar wire: linear and within a factor of 3 to experimental data



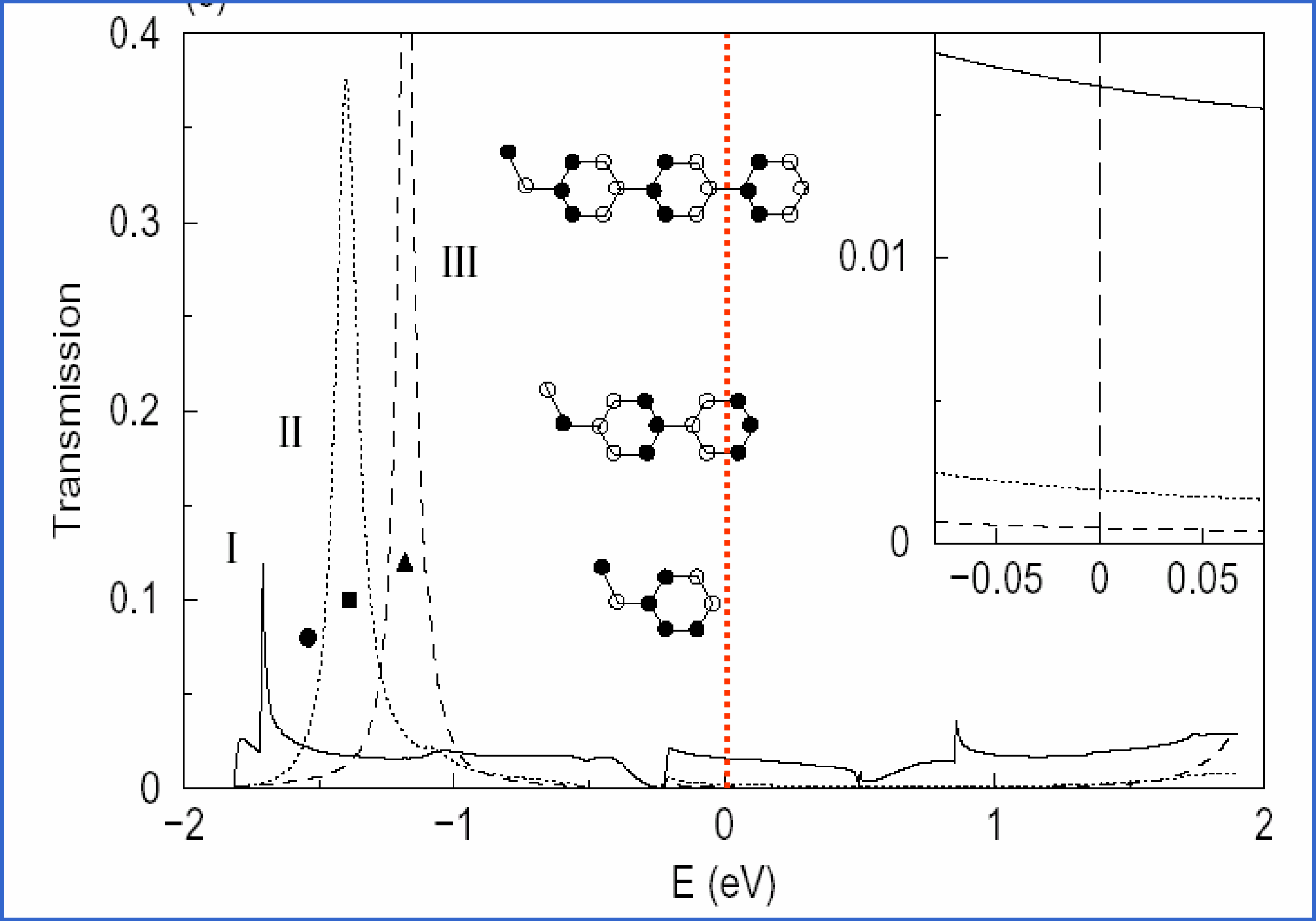
Experimental range:

1.7 and 2.2.



Rotated molecules have small resistance ?

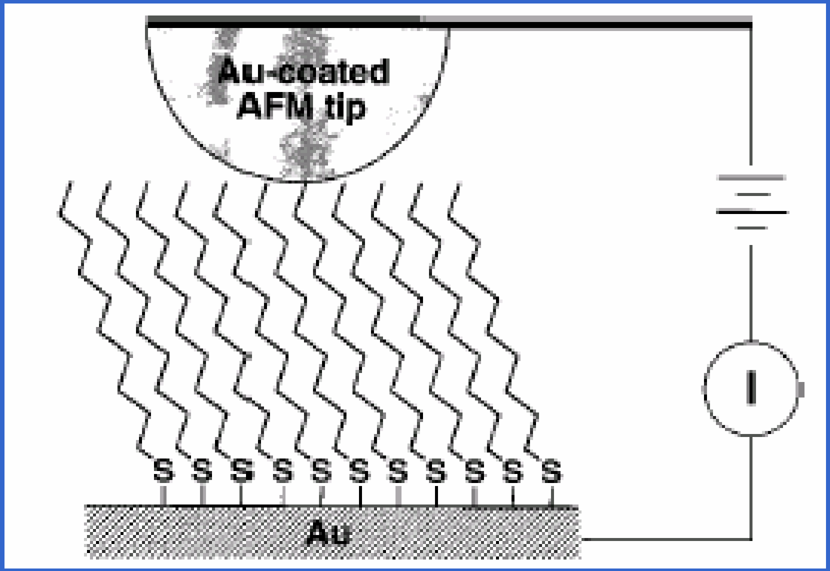
It is a non-resonant conduction: consistent with an exponential increase of resistance.

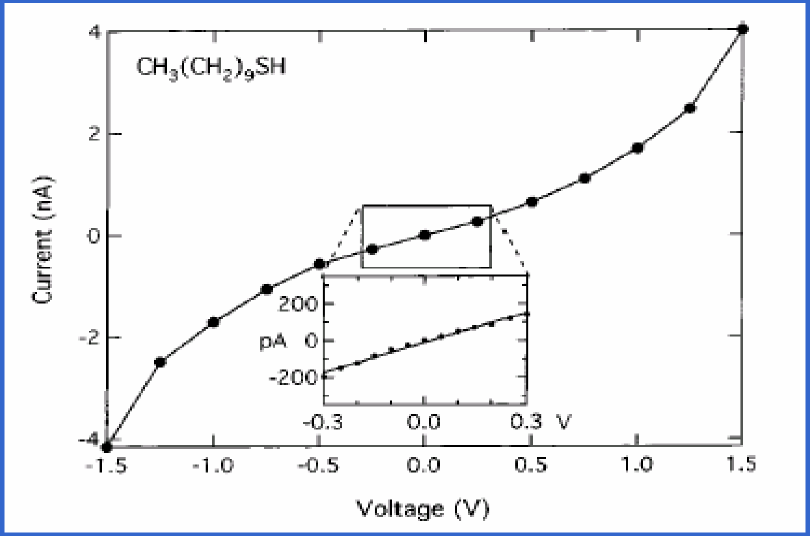


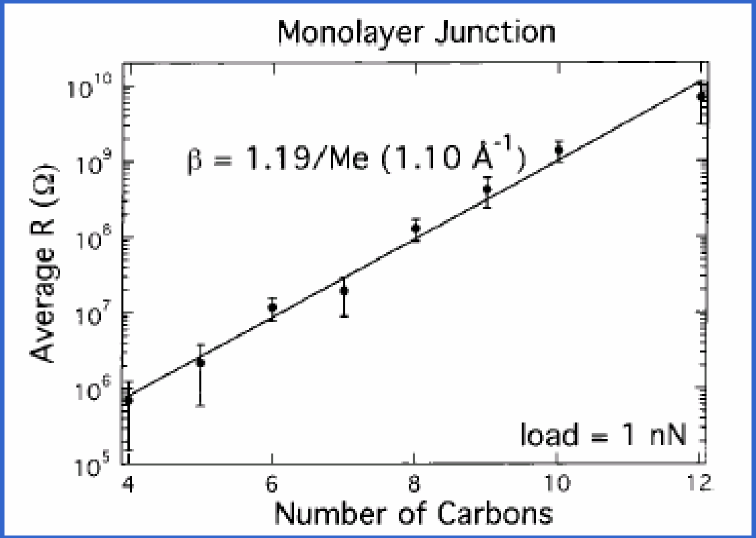
A large resistance device is easier to have repeatable data.

A SAM measurement: Alkanethiol molecular wires.

Wold and Frisbie, JACS 123, 5549 (2001)







Rather similar results from other groups: M. Reed et al (2003); Lindsay et al, Nanotechnology, 13, 5 (2002).

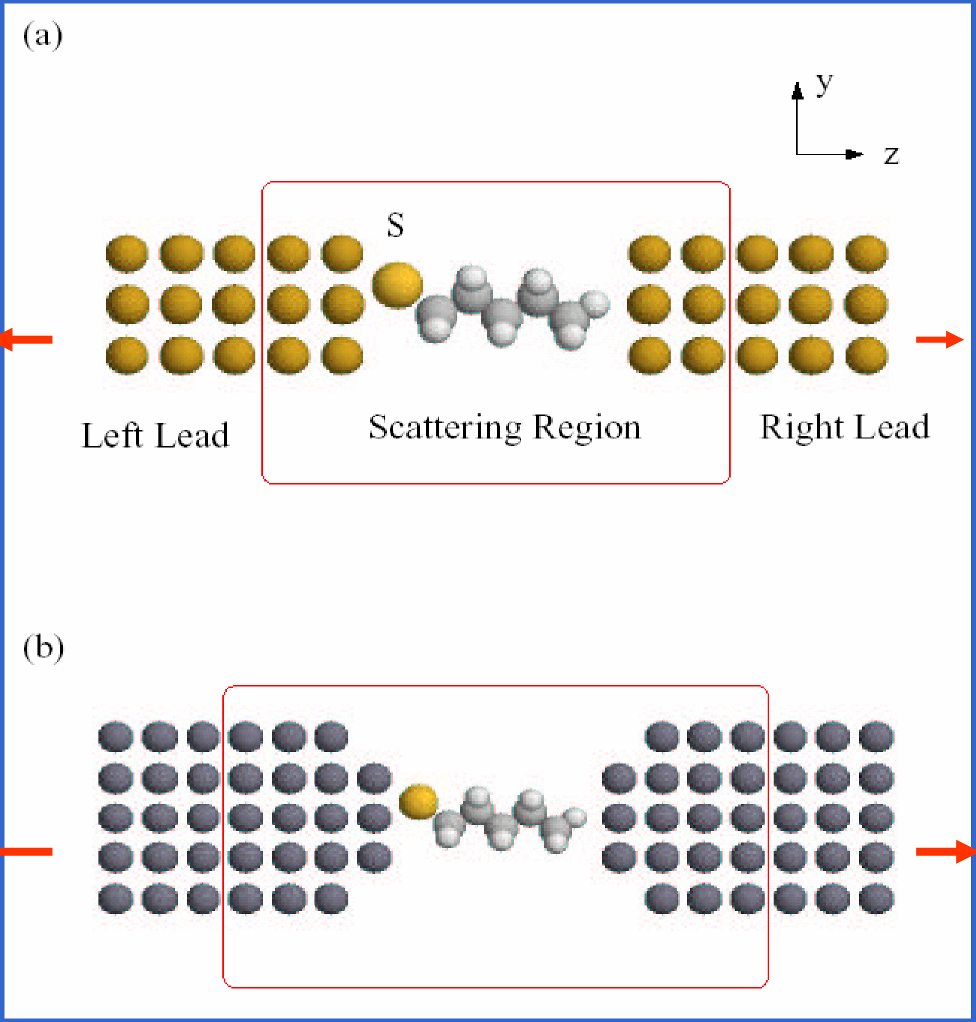
2. Comparison with experiments:

(2). Alkanethiol molecular wires

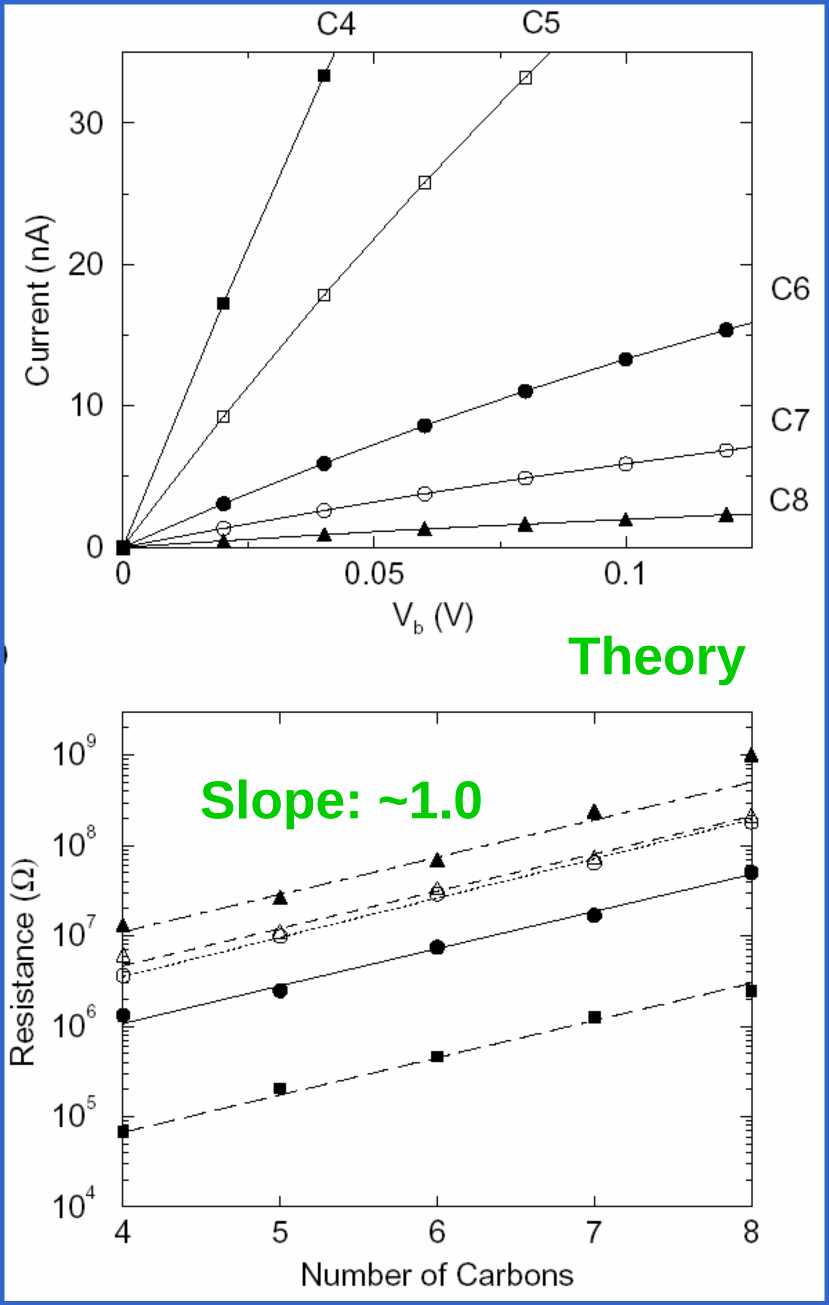
Our model:

Au electrodes

Al electrodes

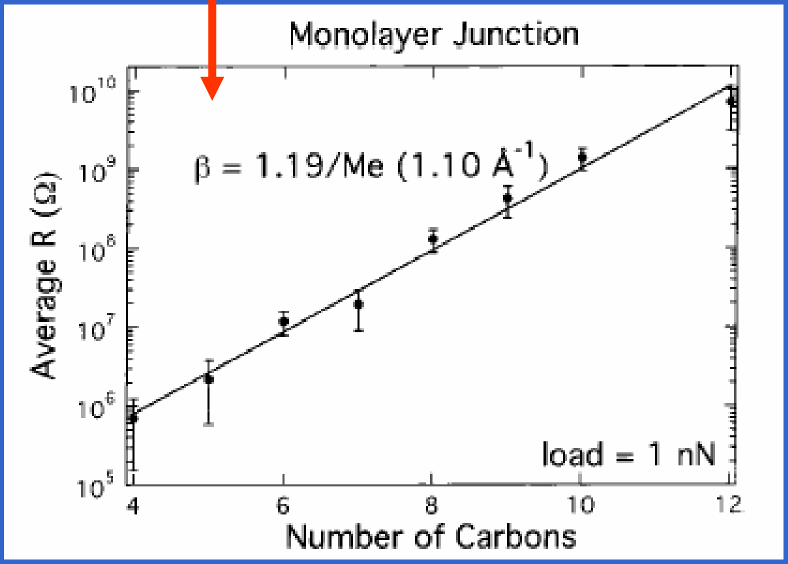


Kaun & Guo, NanoLetters 3, 1521 (2003)



Quantitative agreement with measurements

Experimental: average slope is close to 1



From alkanethiol to alkanedithiol

- Our calculation: still shows $R_n = R_o \exp(\beta n)$;
- Our calculated beta is still about 1.0;
- Our R_o is smaller than that of alkanethiol by about a factor of 18.

Experiments so far:

1. Cui et al, J. Chem. Phys. 106, 8069 (2002): $\beta = 0.57$

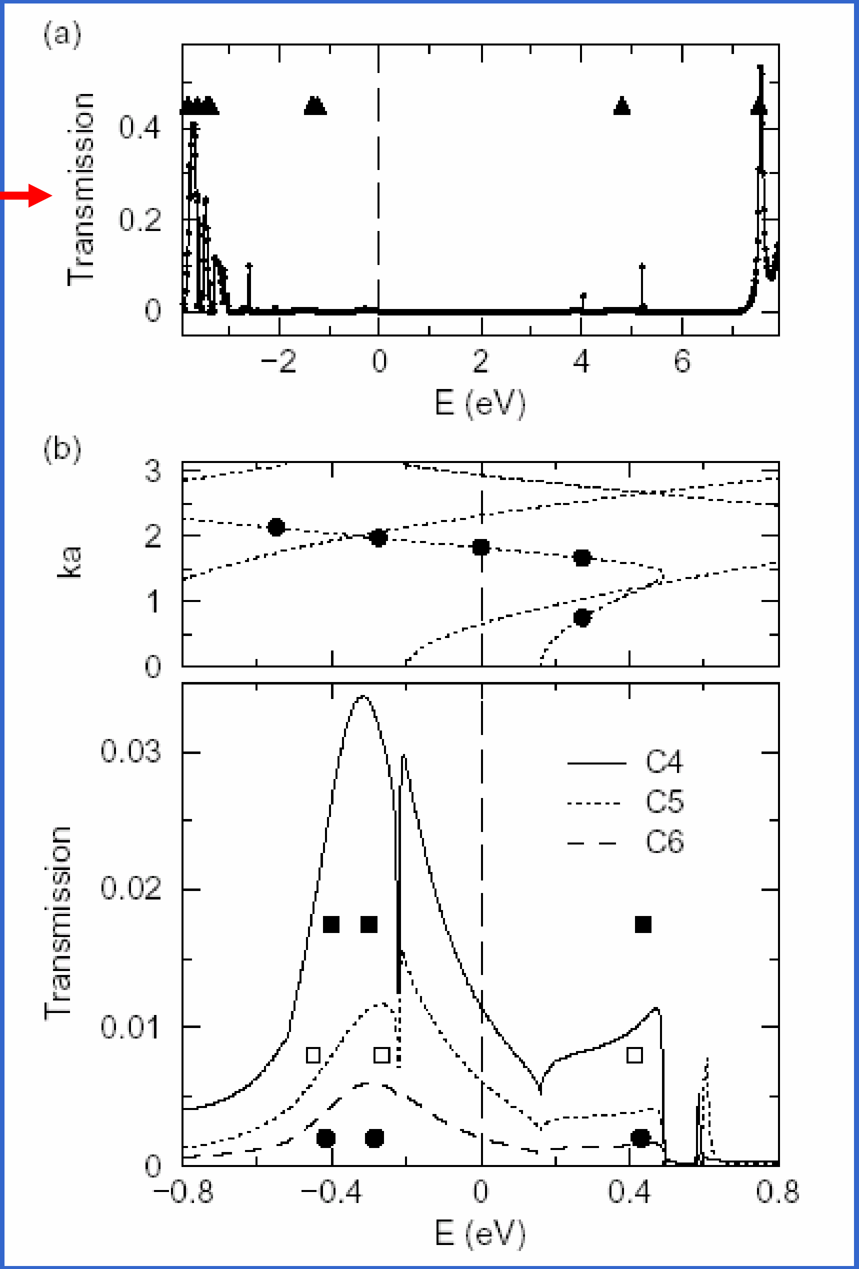
2. Engellkes et al (Frisbie lab) (2003):

   Xu and Tao, Science (2003):

   Lee and Reed, J. Phys. Chem (2004):

$\beta = 1.05$

Alkane has a large HOMO-LUMO gap, ~10eV. The Fermi level is inside the gap, but closer to HOMO.



There is a tiny feature near Fermi level which determines the resistance.

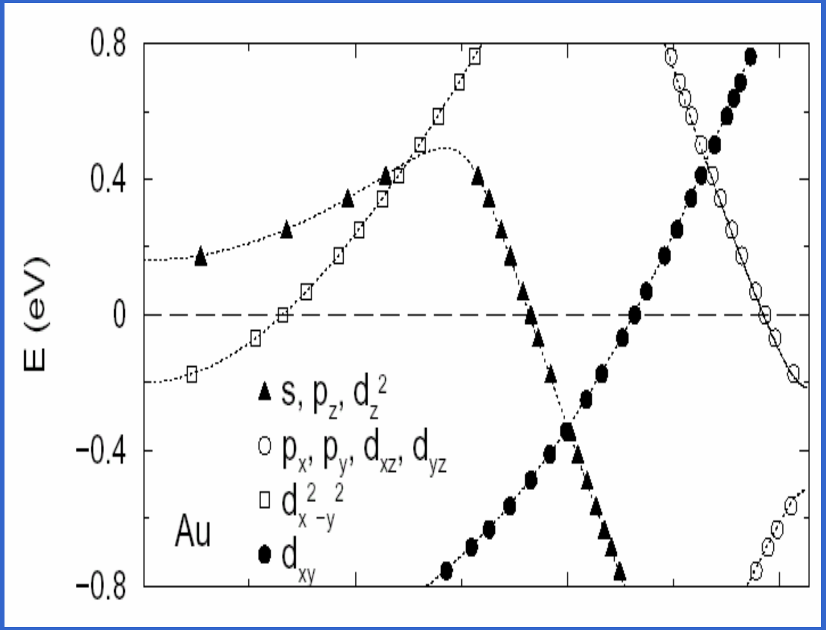
Why certain incoming bands conduct better than others?

LCAO basis set:

$$\Psi = \sum_{\upsilon,I} c_{\upsilon}^{I} \phi_{\upsilon}(r-R_{I})$$

Projection: $$P_{\upsilon} = \sum_{K} \langle \phi_{\upsilon}(r-R_{K}) | \Psi \rangle$$

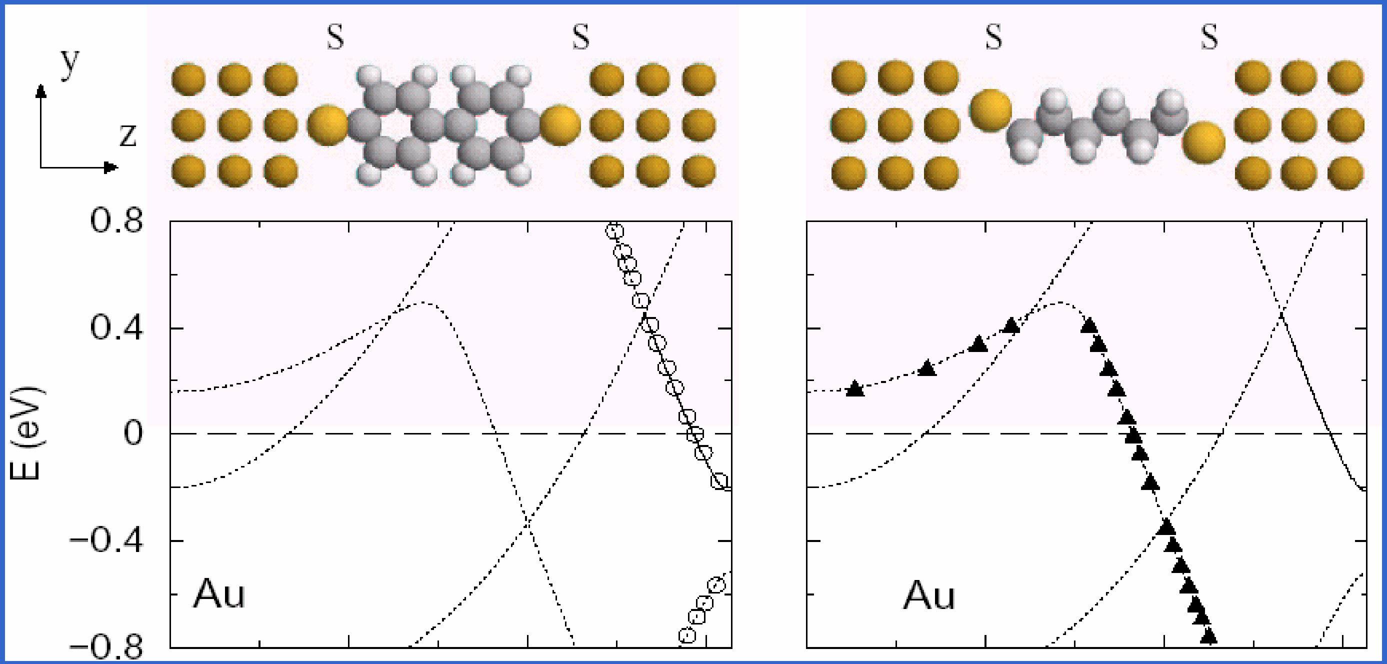
By projecting the Bloch eigenstate to each orbital, we can obtain the character of each band.



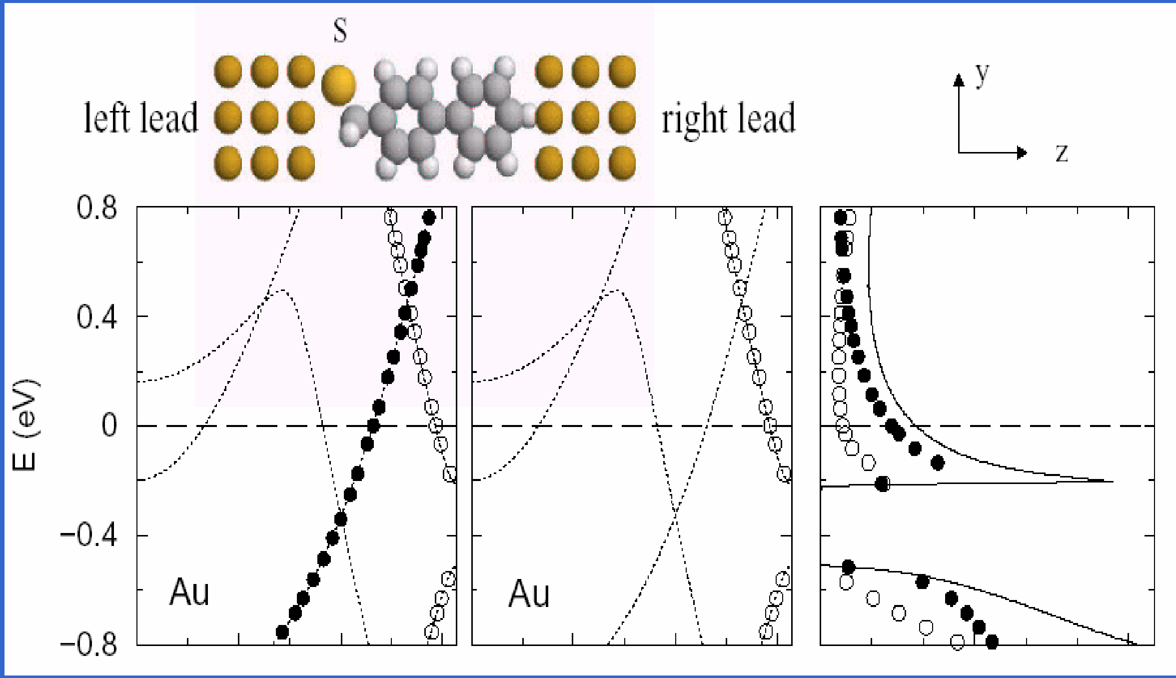
Kaun, et al, PRB, 70, 195309 (2004)

For biphenyl dithiol (pi orbital), the major conducting band has Px character.

For alkanedithiol (sigma orbital), the major conducting band has s and Pz character.

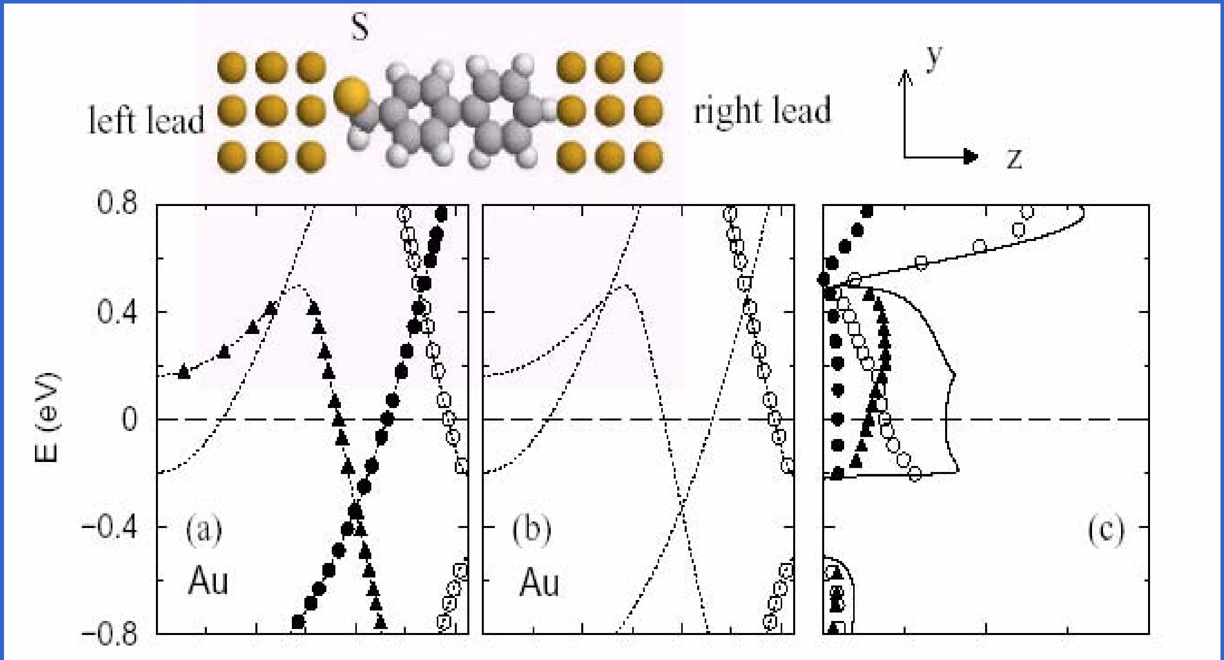


For biphenyl methanethiol, there are two bands conducting for the left lead but only one band conducting for the right lead.



By adding different end groups, one can couple different conducting band to the molecule.

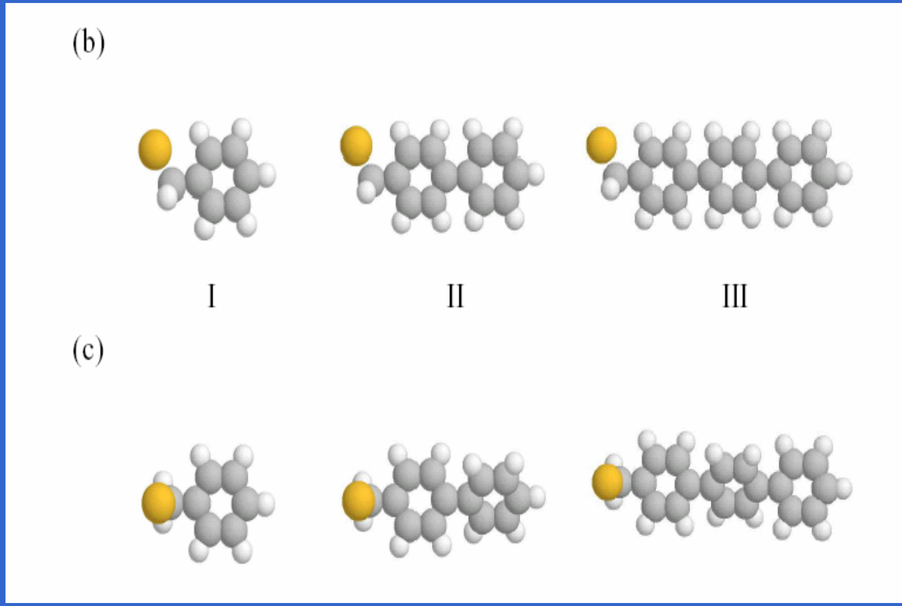
For rotated biphenyl methanethiol, there are three bands conducting for the left lead

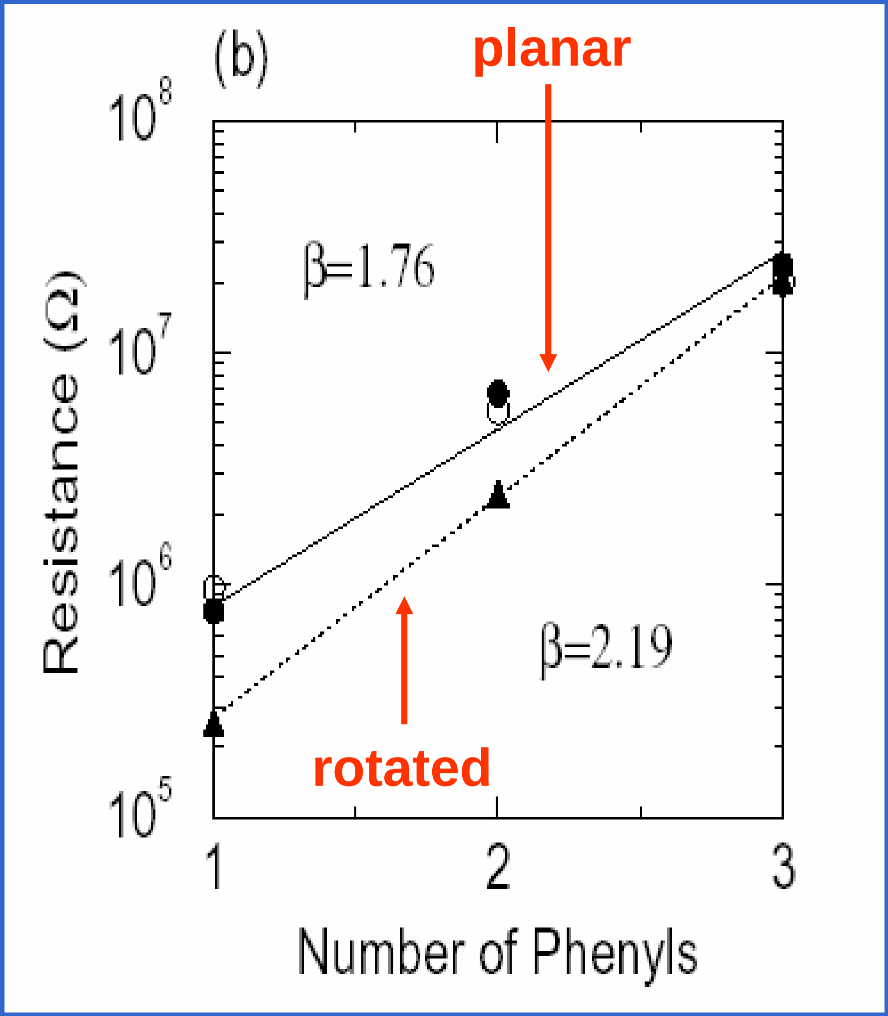


Experimental range:

1.7 and 2.2.

D. J. Wold et al. J. Phys. Chem. B, (2002)





Kaun, Larade, and Guo, PRB 67, 121411 (2003)

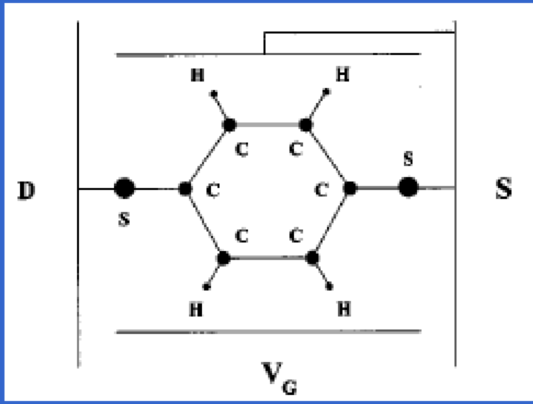
3. The Gating Efficiency of Single-Molecule Transistors

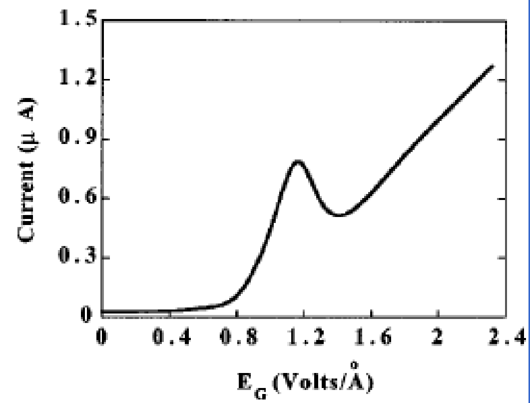
Transistors are a key component in IC chips.

Kaun and Seideman, Journal of Computational and Theoretical Nanoscience 3, 951 (2006)

Molecular transistors

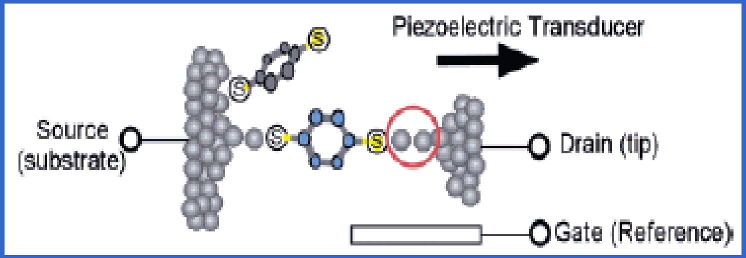
Theory





Di Ventra et al, APL 76, 3448 (2000).

Experiment

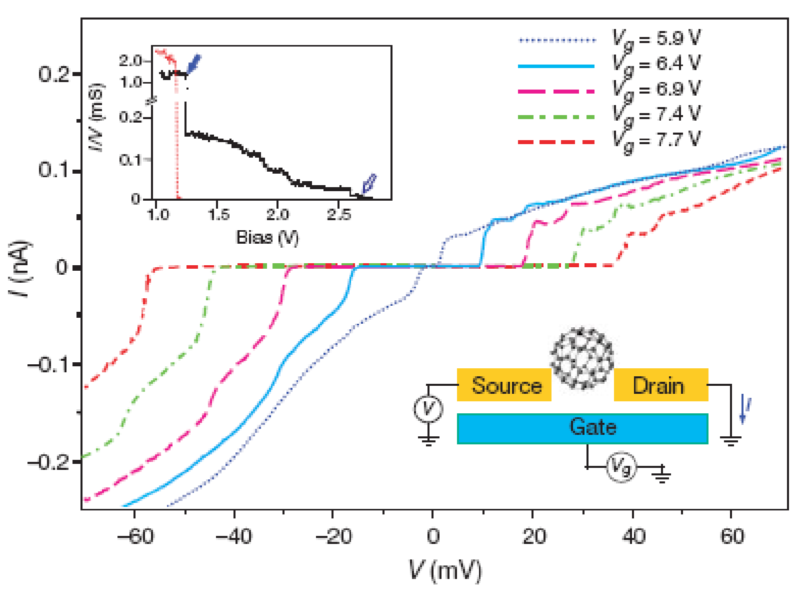


Tao et al, Nano Lett 4, 267 (2004).

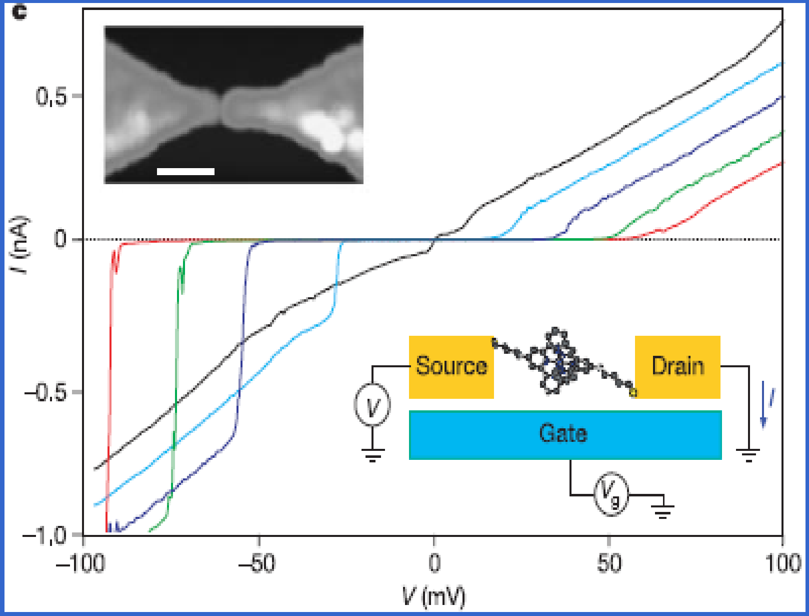
No pronounced gate effect has been found in such devices

Dekker et al, Nano Lett 3, 113 (2003); Ek et al, Nano Lett 3, 119 (2003).

By contrast, robust gate effects have been observed in …



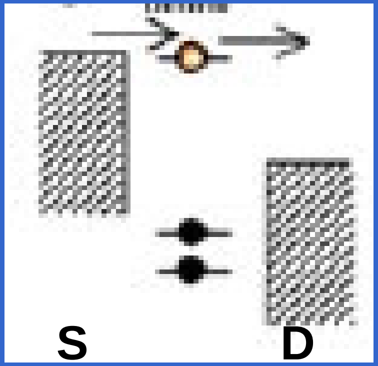
Park et al., Nature 407, 57 (2000)

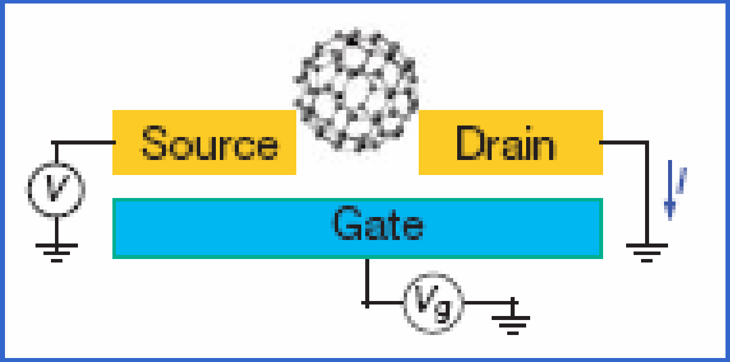


Ralph et al., Nature 417, 722 (2002)

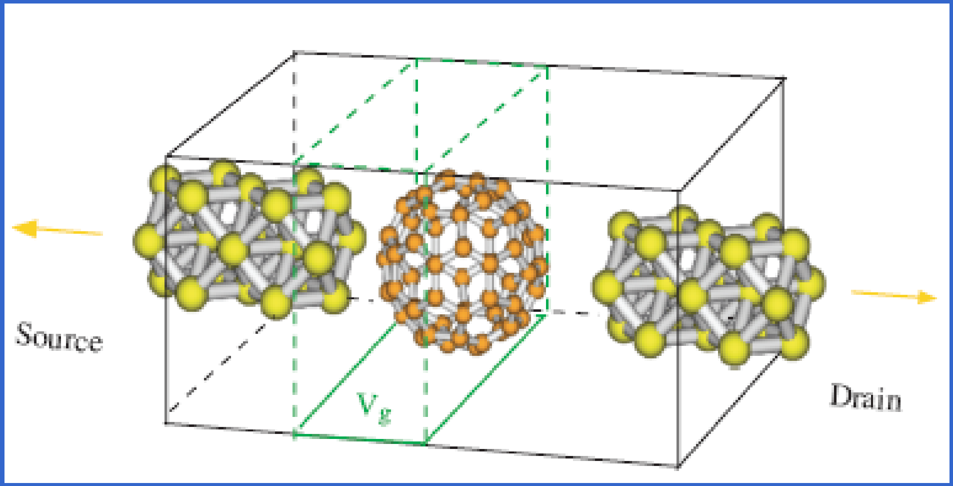
and other molecular junctions.

The qualitative difference may result from their different coupling to the Fermi level.

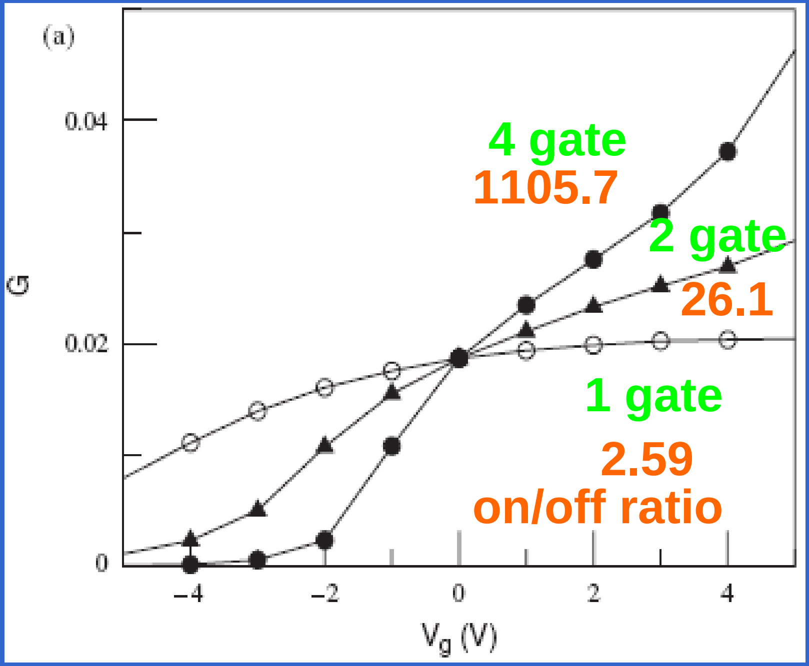




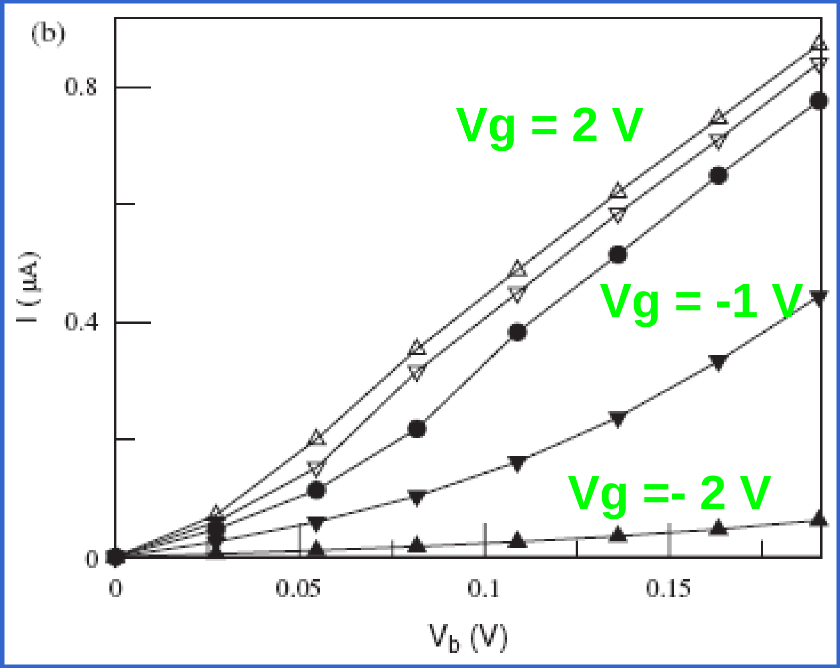
Our model:



Source
V_g
Drain

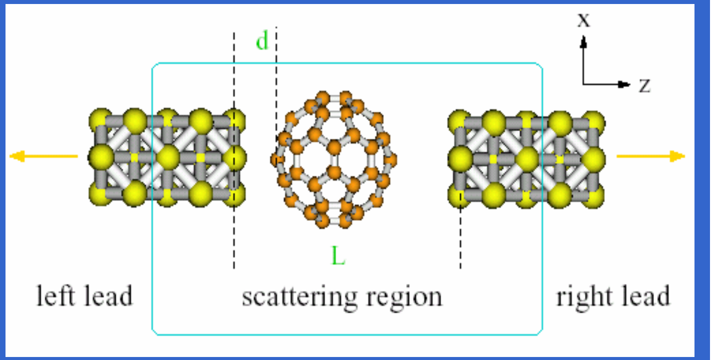


(a)
G
0.04
0.02
0
−4
−2
0
2
4
V_g (V)
4 gate
1105.7
2 gate
26.1
1 gate
2.59
on/off ratio

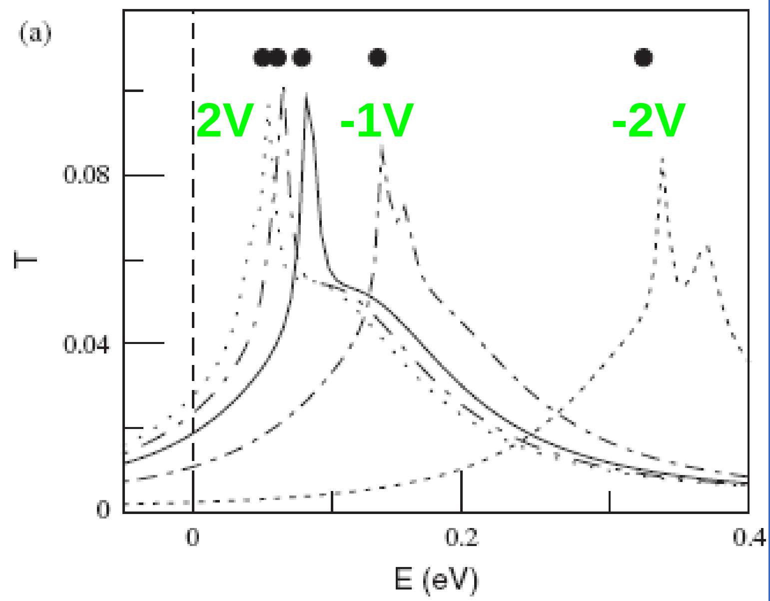


(b)
I (μA)
0.8
0.4
0
0
0.05
0.1
0.15
V_b (V)
Vg = 2 V
Vg = -1 V
Vg =- 2 V

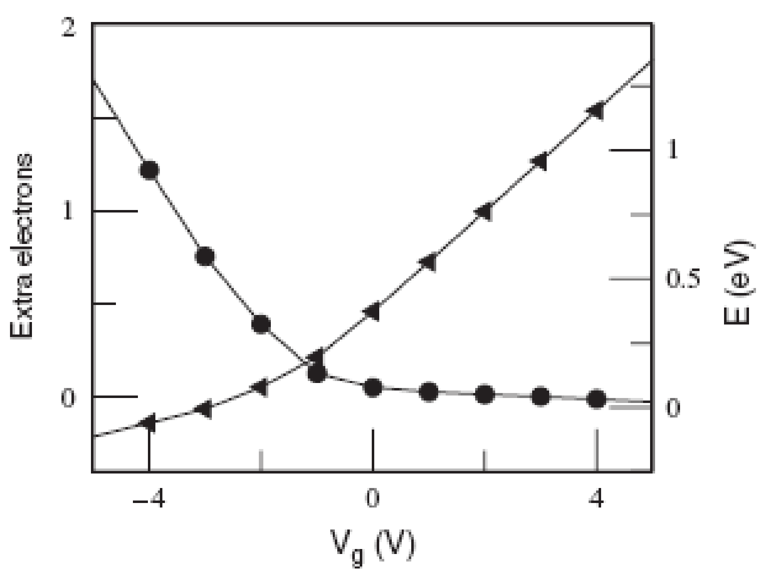
Asymmetric long-gap:



L = 26.42



The extra electrons on the molecule



The resonance orbital energy

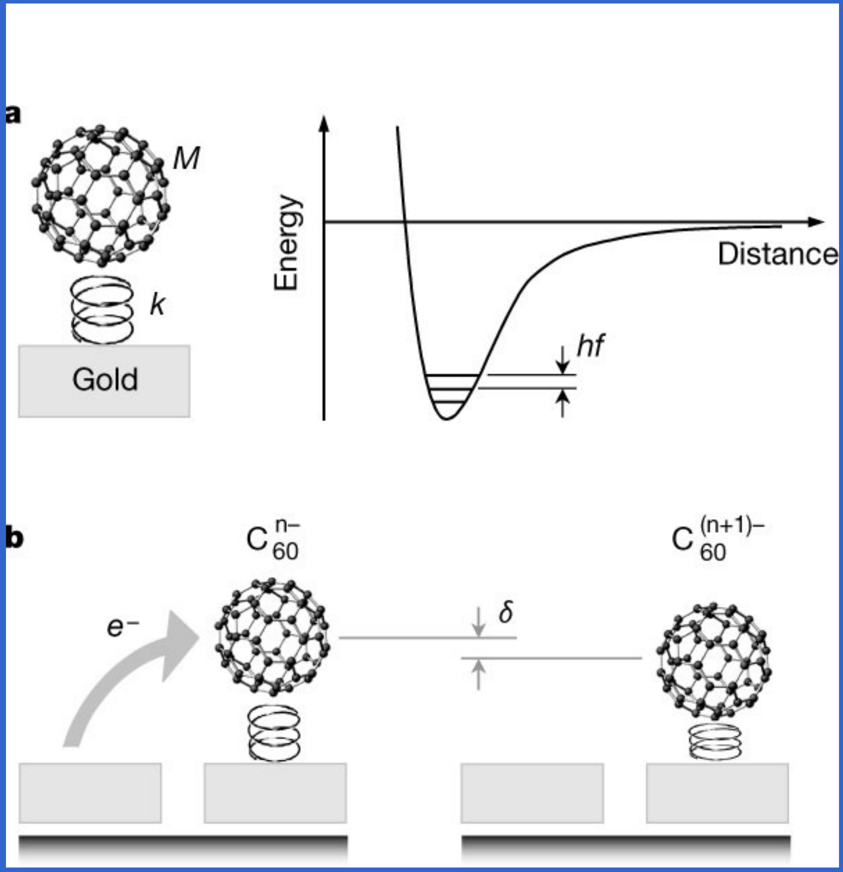
4. A current-driven molecular machine

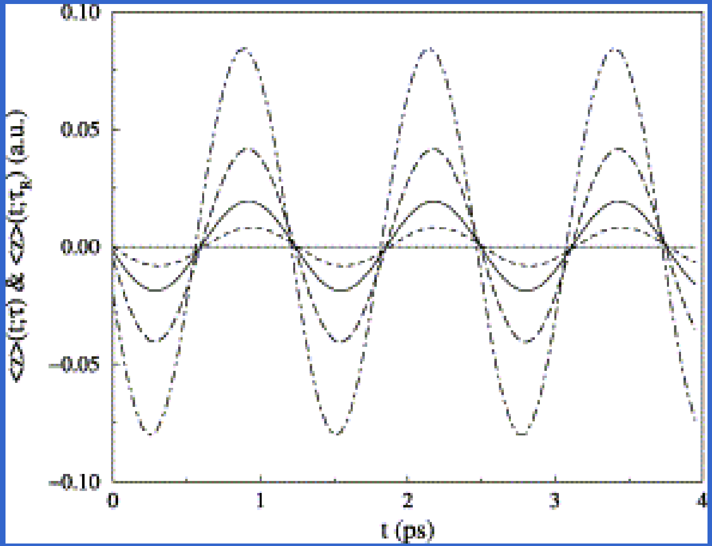
Conventional molecular machines are driven as an ensemble, by external light or chemistry, for example.

These machines are difficult to control.

A current-driven molecular machine can be addressed individually.

Current-driven dynamics:





Predictions from calculations

T. Seideman, et al, Chem. Phys. (2002)

<Z> ⟵ the lifetime of resonance

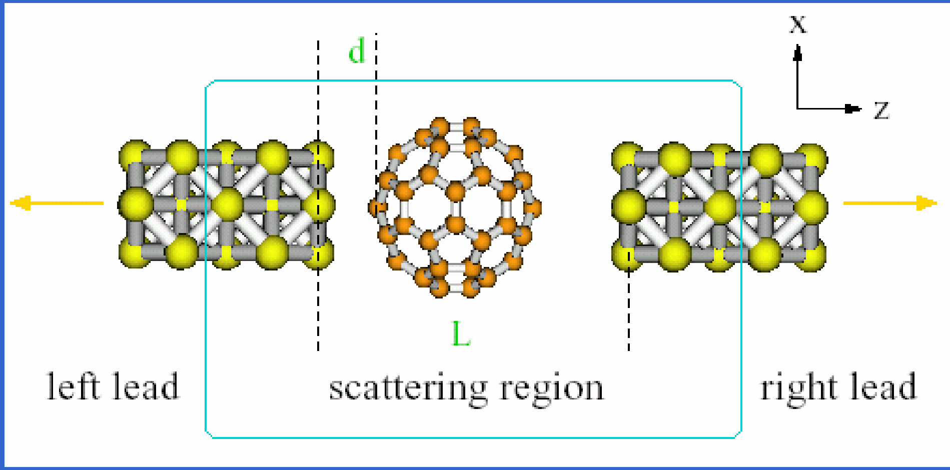
f ⟵ the C_{60} mass

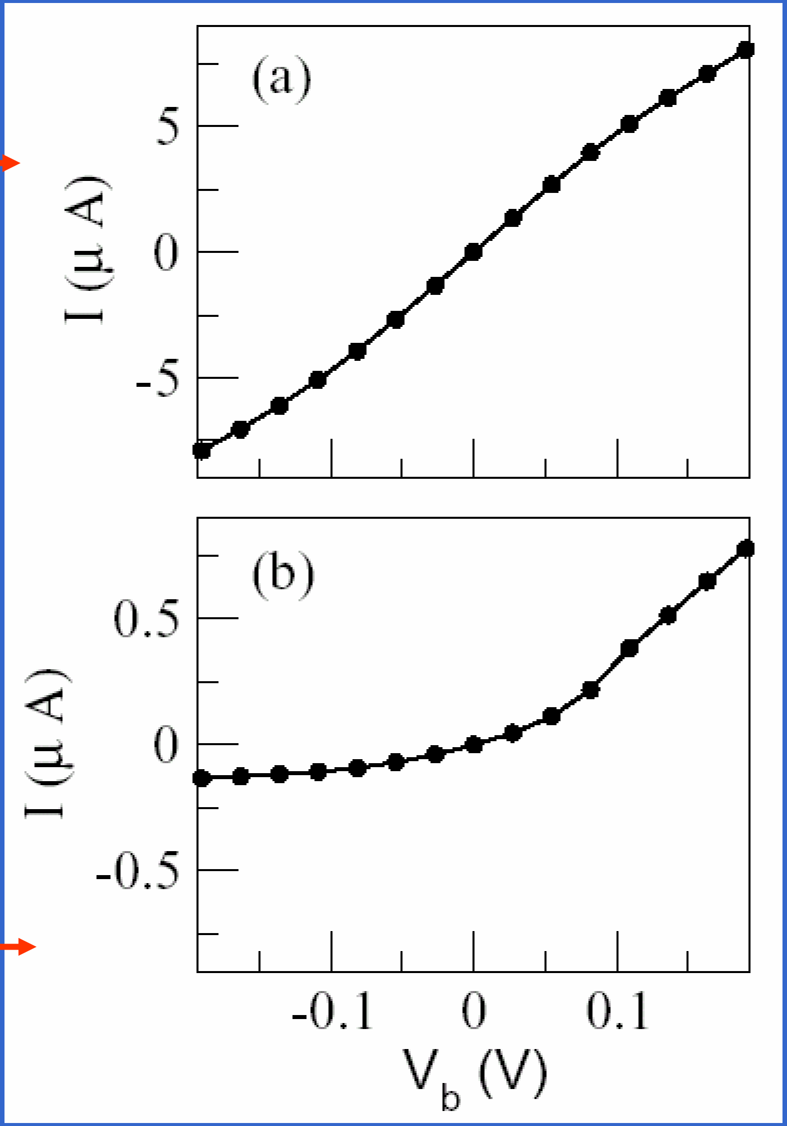
The bouncing Bucky ball

H. Park, et al, Nature (2000)

Our model:

Symmetric coupling

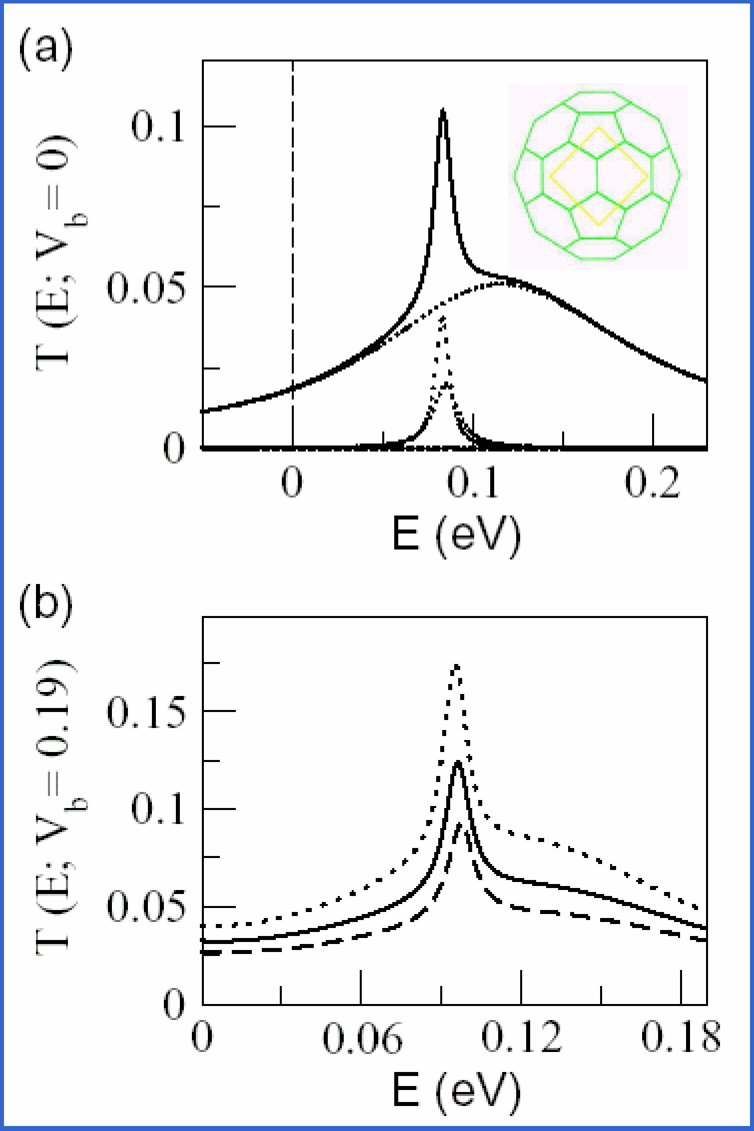




Asymmetric coupling

(L = 26.42 a.u.)

Transmission spectra:

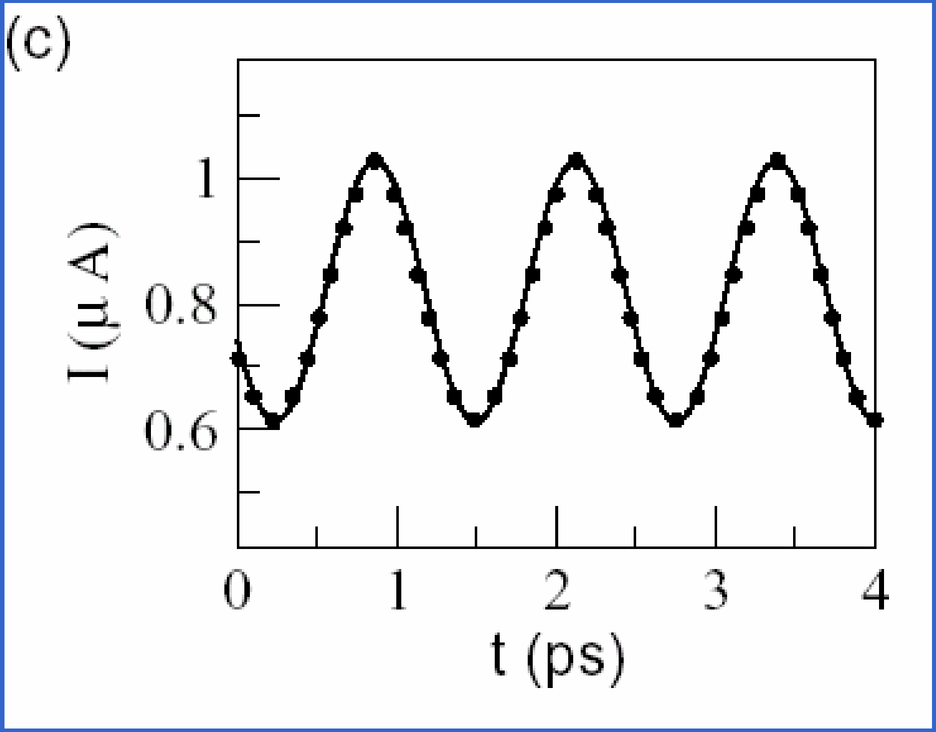


Three channels

One induces the motion; the other probes it.

Different locations

Current oscillates as the molecule vibrates



The ac/dc ratio, the power output efficiency, is 0.26 (L = 26.42 a.u.)

Kaun and Seideman, PRL 94, 226801 (2005)

Applications:

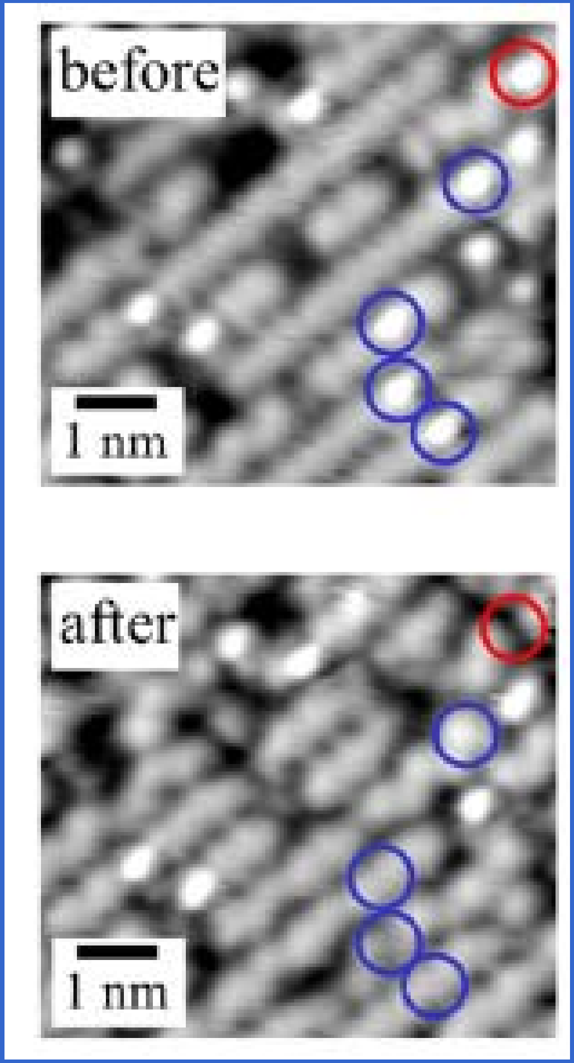
- A nanoscale generator of a radiation field, thus a THz optoelectronic device.
- A miniature mass spectrometry.
- The direct, time-domain probing of the current-driven dynamics in nanojunctions.

5. Desorption of molecules from silicon:

Molecular electronic devices + conventional silicon microelectronics.

The stability of organic molecules on semiconductors must be established.

Desorption of cyclopentene from Si(100)



A saturated molecule

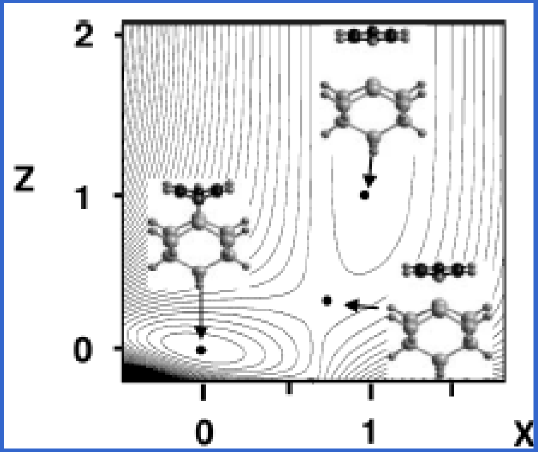
-2V, 0.1 nA

Elevated sample bias
(threshold voltage: -2.5 and 3.5)

-2V, 0.1 nA

N. L. Yoder, et al., PRL 97, 187601 (2006)

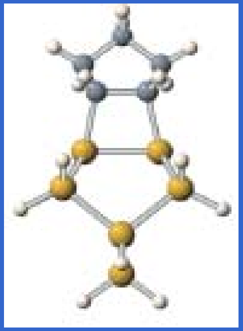
Previous studies: benzene bound to Si(100) with π -orbital character



Low-lying ionic resonances

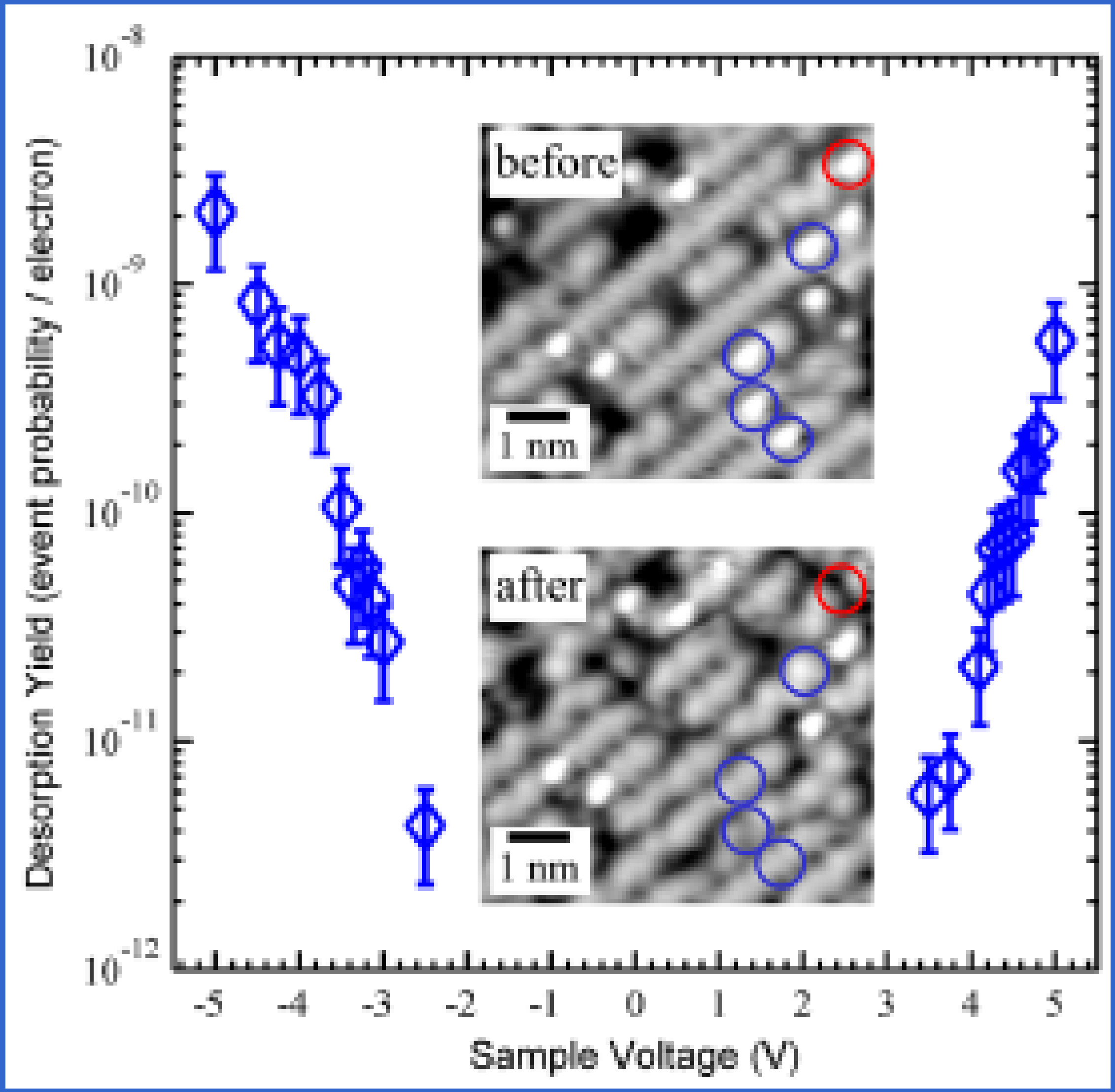
S. Alavi, et al., PRL 85, 5372 (2000).

Cyclopentene on Si(100):



A saturated molecule

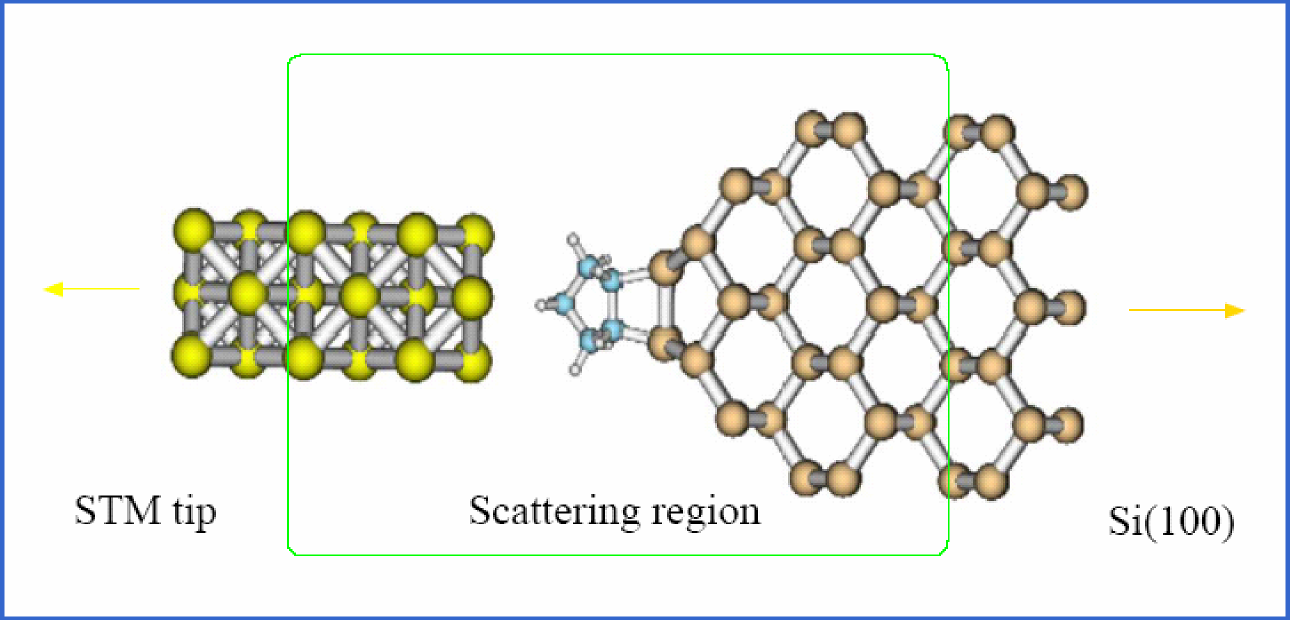
Why threshold voltages is so small (-2.5 V and 3.5 V)?



The yield is a factor of 500-1000 lower than for benzene/Si(100) or chlorobenzene/Si(111).

A new avenue for desorption dynamics!

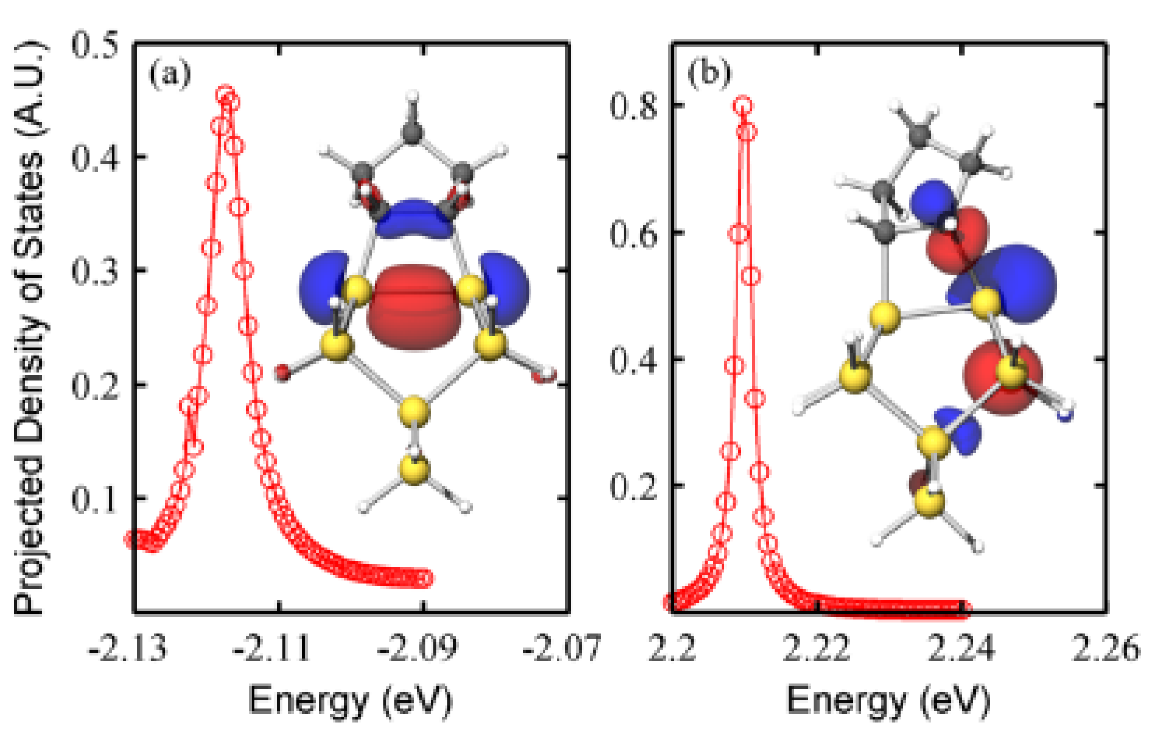
Our model:



	HOMO	LUMO
Cyclopentene	-2.49	6.90
Cyclopentene+Si	-2.00	2.95

Hybridization introduces new state into the gap

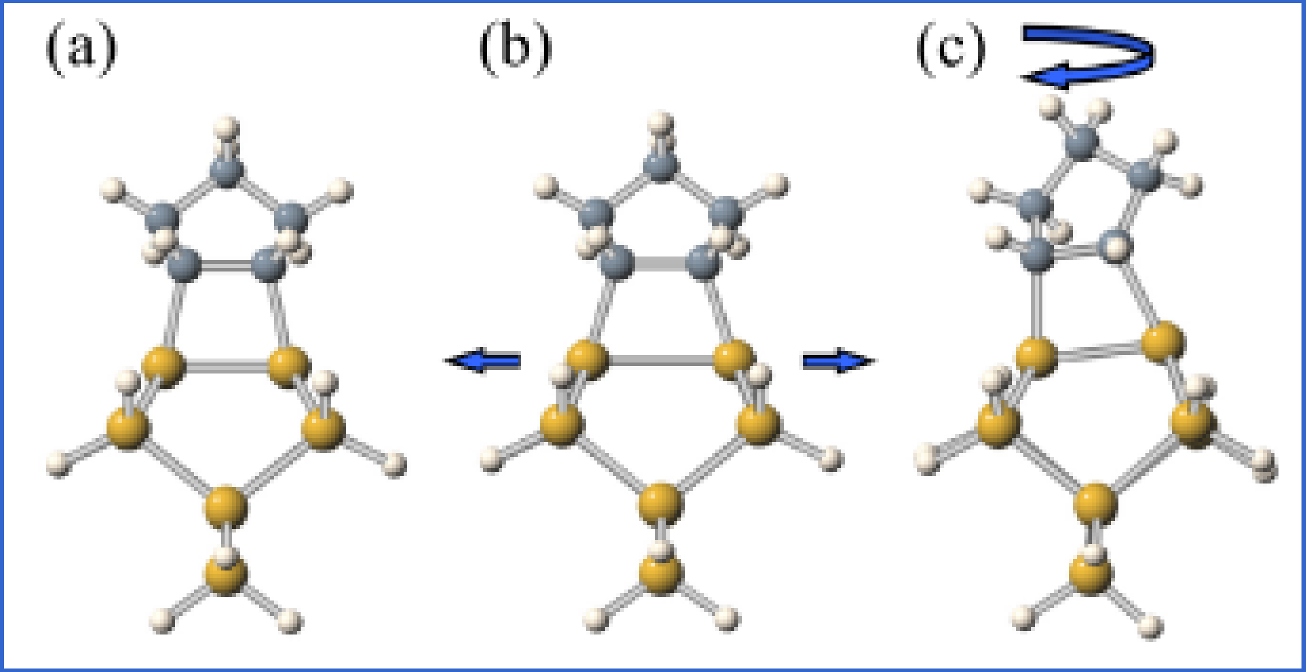
PDOS peaks and the localized orbitals:



The positive ion lifetime 94 fs

The negative ion lifetime 257 fs

Geometries of cyclopentene on a Si9H12 cluster:



Neutral molecule | **Positive molecule** | **Negative molecule**

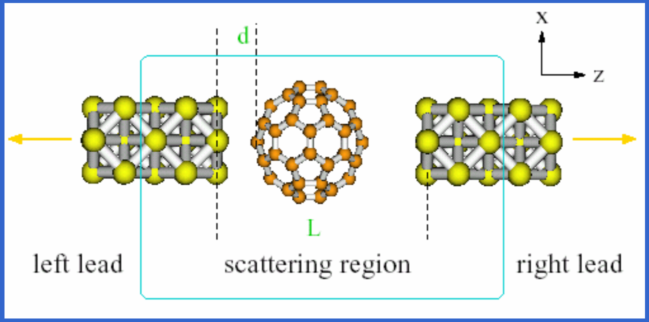
6. Sumary:

- Quantitative consistency with experimental data on the value of beta.
- The Gating Efficiency of SMT depends on the gate geometry and on the contact coupling.
- Current-driven dynamics can produce oscillating current in molecular junctions.
- New desorption pathways are found in a molecule/silicon system.

Outlook:

- A general physical picture for molecular electronics.
- New forms of molecular machines.
- Spintronics.

Different contact couplings:



Asymmetric short-gap

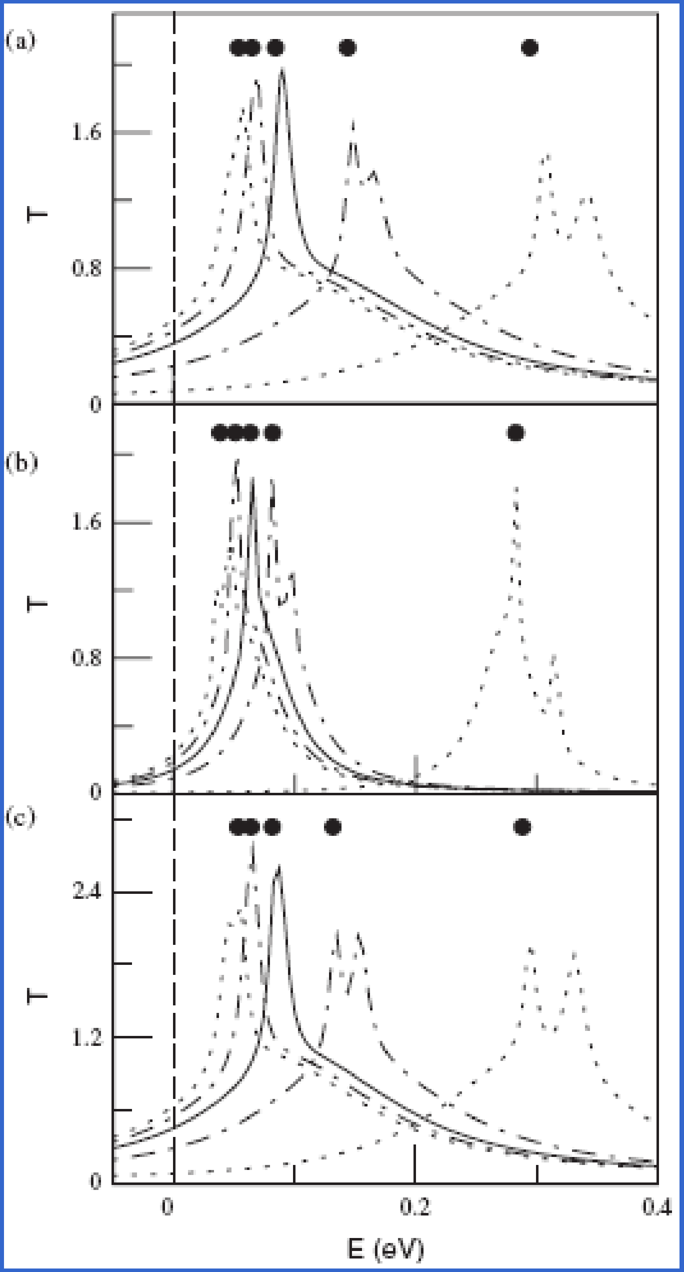
L = 24.42

Symmetric long-gap

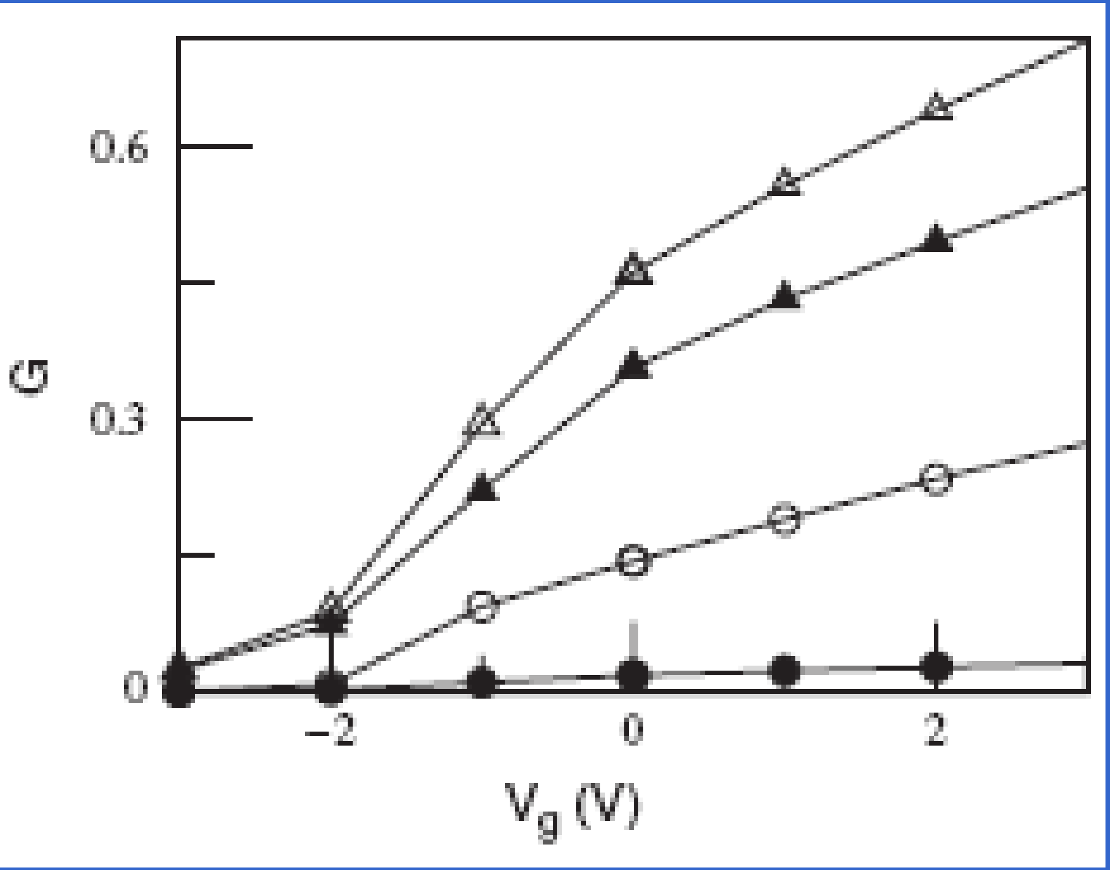
L = 26.42

Symmetric short-gap

L = 24.42



Our results



Symmetric short-gap		
28.3	0.47	
Asymmetric short-gap		
23.1	0.48	
Symmetric long-gap		
294.2	0.43	
Asymmetric long-gap		
56.7	0.46	
on/off ratio	excess electrons	

Transmission spectra at different molecular orientations

An alternative route to generate the time-modulated current