

First Lecture

- Interesting electronic properties of Molecules \Rightarrow Chemical structure

Molecular Wires

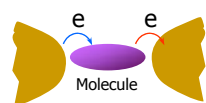
Switches and storage elements

Diodes

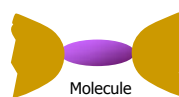
working principles proved in solution
(without electrodes)

- Transport mechanisms are determined by Metal-molecule coupling Γ

Weak coupling regime



Strong coupling regime



M. F. Goffman



Second Lecture

- Interesting electronic properties of Molecules \Rightarrow Chemical structure

②

Molecular Wires

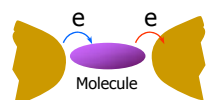
Switches and storage elements

Diodes

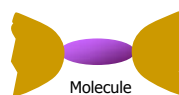
working principles proved in solution
(without electrodes)

- Transport mechanisms are determined by Metal-molecule coupling Γ

Weak coupling regime



Strong coupling regime



①

Qualitative Picture
S. Datta, Purdue University

③

Final Remarks

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Molecular Conduction: Qualitative Picture

Two Basic Ingredients:

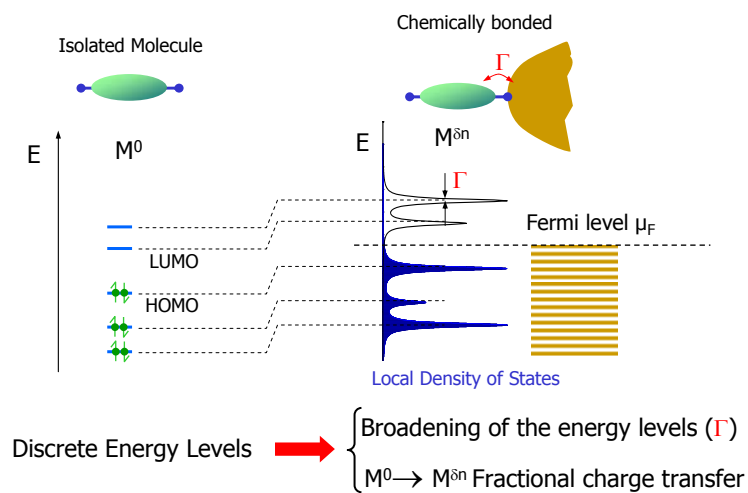
[Energy Diagram](#) showing the molecular levels relative to the electrochemical potential of electrodes

[Potential Profile](#) across the molecule due to the applied bias.

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Strong Coupling to Metallic Electrodes (Γ)



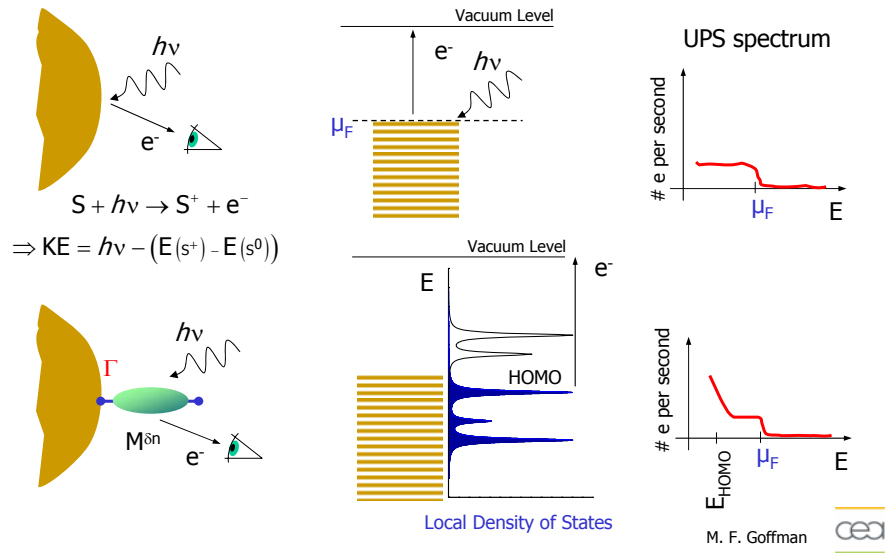
Which is the location μ_F with respect to HOMO-LUMO levels?

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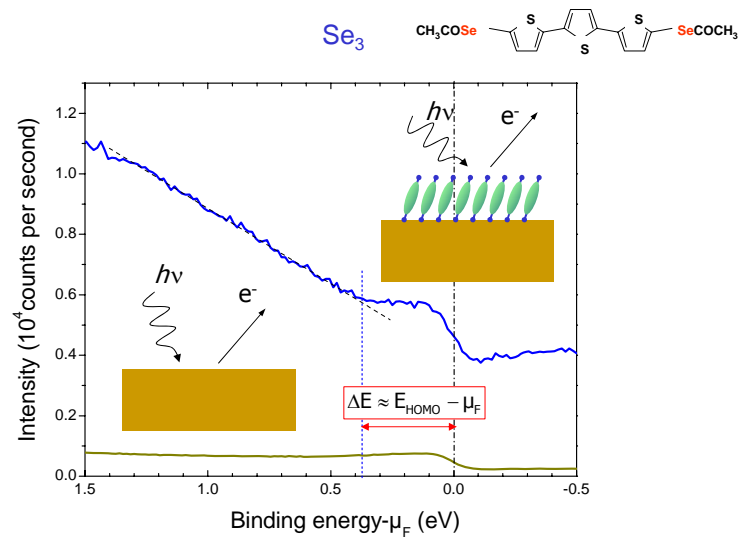


Location of the Fermi Energy

UPS Experiments (UV Photo Electron Spectroscopy)

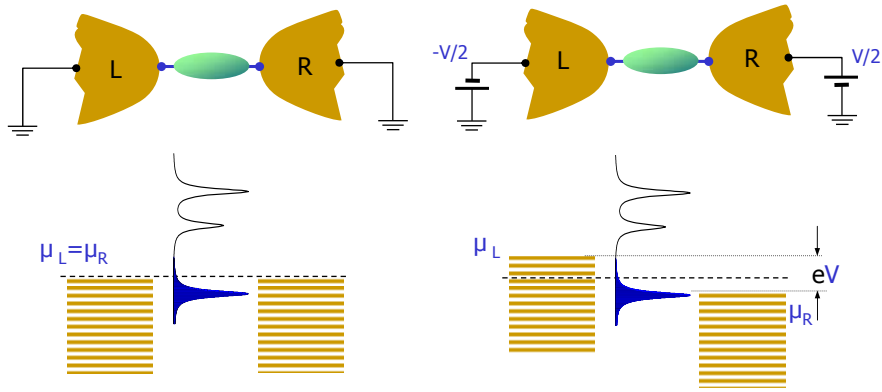


UPS Experiment on Self-assembled Monolayer on Au



Energy Diagram

At equilibrium ($V=0$)



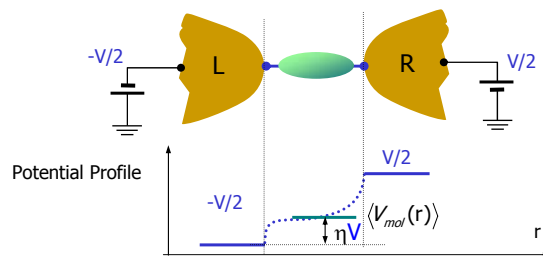
But how are μ_L and μ_R disposed with respect to the molecular levels?

⇒ Potential profile inside the molecule

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Potential Profile



To the lowest approximation Molecular Levels shift "rigidly" by $e\langle V_{mol}(r) \rangle$

Let us denote this average potential as:

$$\langle \Delta V_{mol}(r) \rangle = -V/2 + \eta V \quad \text{with } 0 \leq \eta \leq 1$$

Taking the molecular levels as our reference, the electrochemical potential of electrodes are shifted by

$$\mu_L = \mu_F - \eta eV \quad \mu_R = \mu_F + (1 - \eta) eV$$

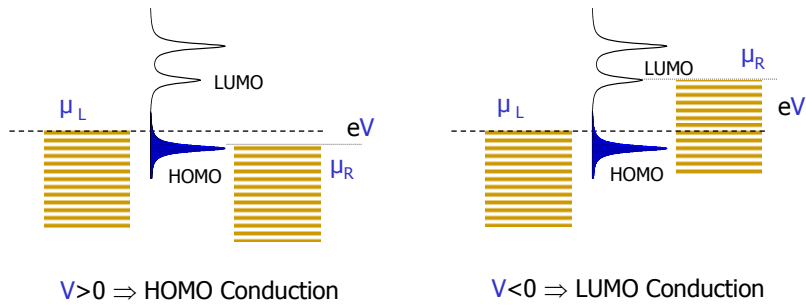
This voltage division factor has a profound effect on Current-Voltage Characteristics

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Energy Level Diagram ($\eta=0$)

$\eta=0 \Rightarrow$ Molecular levels remain fixed to μ_L



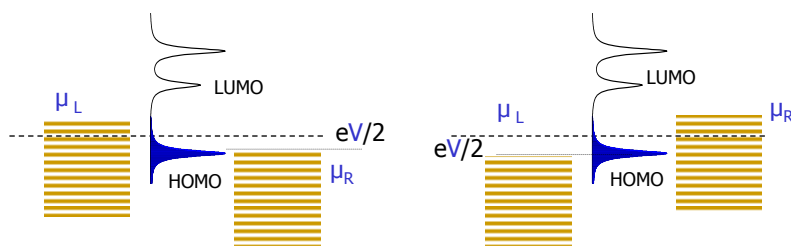
I-V Characteristics can look asymmetric
Positive branch ($V > 0$) and Negative branch ($V < 0$) involve different Molecular levels

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Energy Level Diagram ($\eta=1/2$)

$\eta=1/2 \Rightarrow$ Molecular levels shift with respect to μ_L by half the applied bias



Conduction takes place through the nearest molecular level
(HOMO in this case) for either bias polarity.

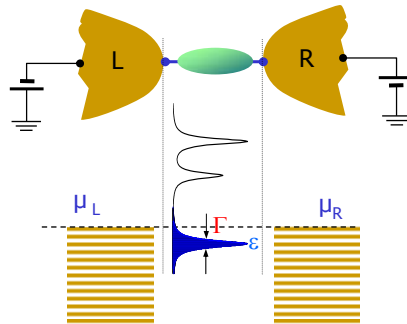
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Toy Model

Toy Model: single level ε (HOMO or LUMO) that incorporates relevant ingredients:

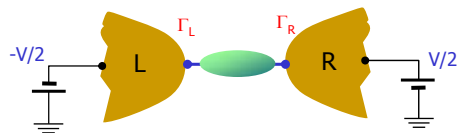
- (1) Location of ε with respect to μ_F
- (2) Broadening Γ_L, Γ_R due to contacts ($\Gamma = \Gamma_L + \Gamma_R$)
- (3) Potential Profile



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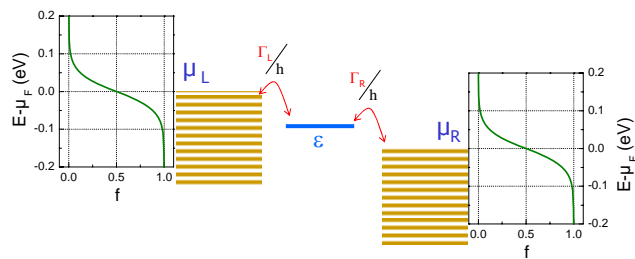


Discrete One-Level Model



$$f(\varepsilon) = \frac{1}{1 + e^{\varepsilon/k_B T}}$$

Fermi function



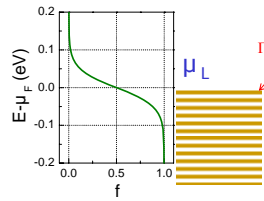
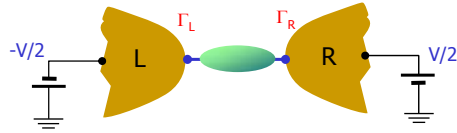
Current as a "balancing act"

$$f(\varepsilon - \mu_L) < \langle N \rangle < f(\varepsilon - \mu_R)$$

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Discrete One-Level Model



$$\text{Outflow}_L = \frac{\Gamma_L}{h} \langle N \rangle \left(\frac{1 - f(\epsilon - \mu_L)}{4} \right)_{\text{available states}}$$

$$\text{Inflow}_L = \frac{\Gamma_L}{h} \cdot f(\epsilon - \mu_L) \left(\frac{1 - \langle N \rangle}{4} \right)_{\text{available states}}$$

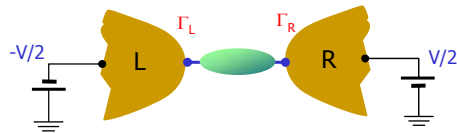
The net flux across left junction will be

$$I_L = e(\text{Inflow}_L - \text{Outflow}_L) = e \frac{\Gamma_L}{h} (\langle N \rangle - f(\epsilon - \mu_L))$$

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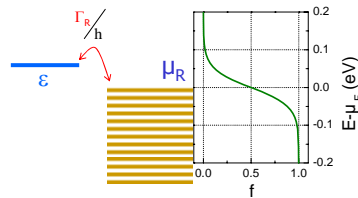


Discrete One-Level Model



The net flux across right junction will be

$$I_R = e \frac{\Gamma_R}{h} (\langle N \rangle - f(\epsilon - \mu_R))$$



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Discrete One-Level Model

At the steady state $I_L + I_R = 0$ (no charge accumulation in the molecule)

$$I_R + I_L = e \frac{\Gamma_R}{h} (\langle N \rangle - f(\epsilon - \mu_R)) + e \frac{\Gamma_L}{h} (\langle N \rangle - f(\epsilon - \mu_L)) = 0$$

$$\langle N \rangle = \frac{\Gamma_L f(\epsilon - \mu_L) + \Gamma_R f(\epsilon - \mu_R)}{\Gamma_L + \Gamma_R}$$

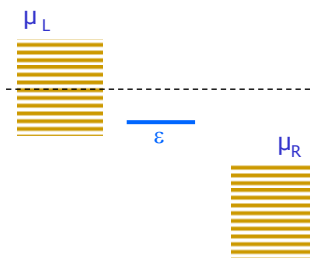
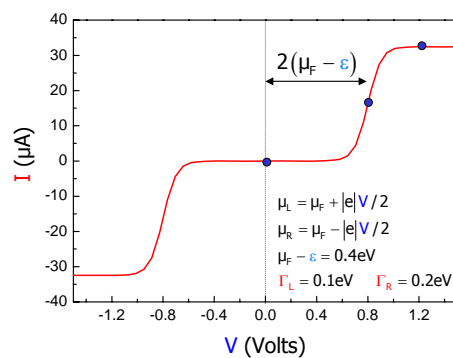
The current through the metal-molecule-metal structure will be

$$I = I_R = -I_L = \frac{e}{h} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (f(\epsilon - \mu_L) - f(\epsilon - \mu_R))$$

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One-level Model: Current (I) vs. Voltage (V)



$$I = \frac{e}{h} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (f(\epsilon - \mu_L) - f(\epsilon - \mu_R))$$

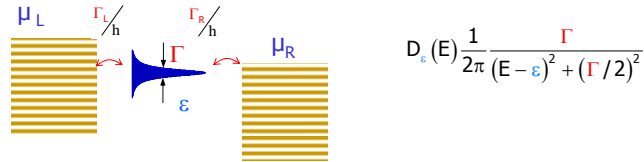
Let us take into account Broadening Γ of the level

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Broadening Γ

We replace the discrete level by a Lorentzian density of states:



$$D_{\epsilon}(E) = \frac{1}{2\pi} \frac{\Gamma}{(E - \epsilon)^2 + (\Gamma/2)^2}$$

Expression of the current will be modified

$$I = \frac{e}{h} \int_{-\infty}^{\infty} D_{\epsilon}(E) \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} [f(E - \mu_L) - f(E - \mu_R)] dE$$

We could write in the Landauer-Büttiker form

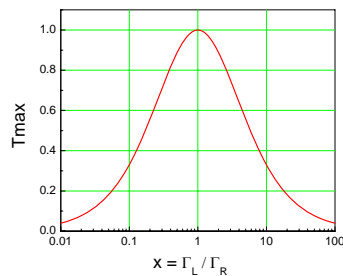
$$I = \frac{e}{2\pi h} \int_{-\infty}^{\infty} T(E) [f(E - \mu_L) - f(E - \mu_R)] dE \quad \text{where } T(E) = 2\pi D_{\epsilon}(E) \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R}$$

What is the maximum conductance of a single level molecule?

Conductance Quantum

$$T(E) = 2\pi D_{\epsilon}(E) \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} = \frac{\Gamma_L \Gamma_R}{(E - \epsilon)^2 + (\Gamma_L + \Gamma_R)^2 / 4}$$

$$T_{\max} = T(E = \epsilon) = \frac{4\Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)^2} = \frac{4}{x + 1/x + 2} \quad \text{with } x = \Gamma_L / \Gamma_R$$

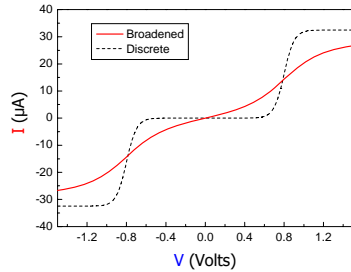


$$G_{\max} = \frac{e^2}{h} T_{\max} \approx 1 / 25.8 k\Omega$$

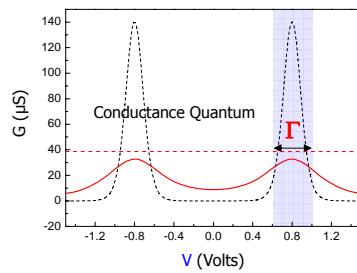
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One-level Model: Current (I) vs. Voltage (V)



$$\begin{aligned}\mu_L &= \mu_F + |e|V/2 \\ \mu_R &= \mu_F - |e|V/2 \\ \mu_F - \epsilon &= 0.4\text{eV} \\ \Gamma_L &= 0.2\text{eV} \quad \Gamma_R = 0.1\text{eV}\end{aligned}$$



Next: Potential Profile

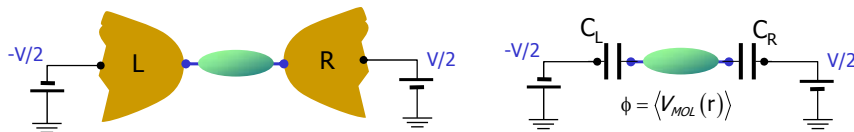
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Potential Profile

The potential profile $V_{MOL}(r)$ will be obtained by solving

$$\vec{\nabla} \cdot (\epsilon_r \vec{\nabla} V_{MOL}(r)) = e\Delta n / \epsilon_0 \quad \text{Poisson's Equation}$$



A solution can be visualized in terms of a capacitance circuit model:

$$e\Delta n = C_L \cdot (\phi + V/2) + C_R \cdot (\phi - V/2)$$

$\Delta n = N - f(\epsilon - \mu_F)$: change in the number of electrons @ equilibrium

The potential U that raises the position of the level is

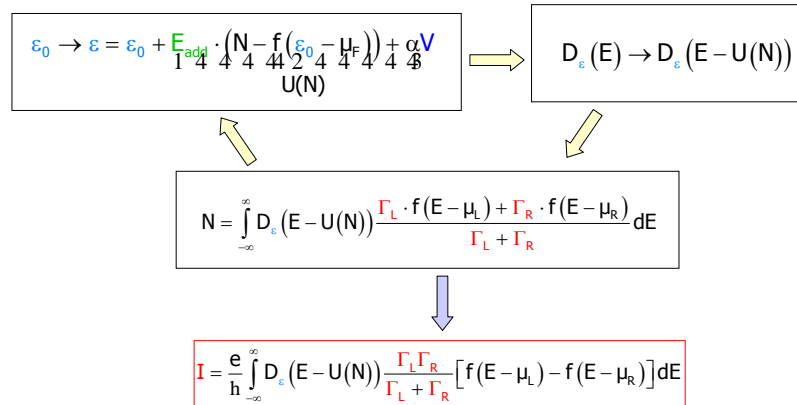
$$U = e\phi = \frac{e^2}{C} \Delta n + \frac{C_R - C_L}{C} \cdot eV$$

Charging Energy E_{add}

Solution of $\vec{\nabla} \cdot (\epsilon_r \vec{\nabla} V_{MOL}(r)) = 0$

Self Consistent Solution

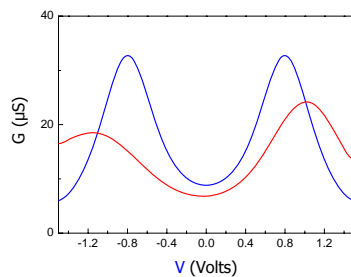
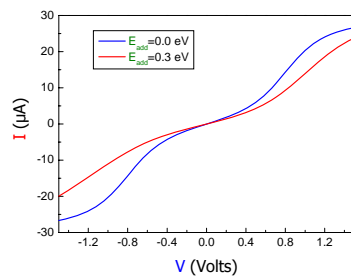
Iterative Procedure for calculating N and U self-consistently



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One-level Model: Current (I) vs. Voltage (V)

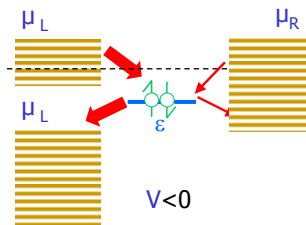


IV asymmetric



Coupling asymmetry + charging

$$\Gamma_L = 0.2\text{eV} \quad \Gamma_R = 0.1\text{eV}$$



Positively charges the molecule

⇒ shift ϵ down

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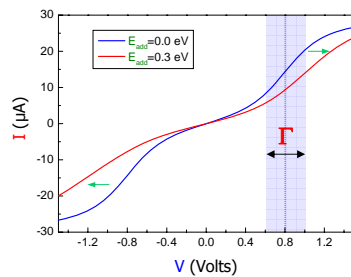
Summary

When Γ : E_{add} transport can be described using a "self-consistent field" method

Asymmetric IVs \Rightarrow asymmetric coupling + charging effect (E_{add})
even if transport is associated with a single level (symmetric molecule)

HOMO conduction \Rightarrow I is lower for positive bias on the stronger contact

LUMO conduction \Rightarrow I is higher for positive bias on the stronger contact



- I increases when ϵ is crossed at $V \sim 2(\mu_F - \epsilon)$
- I increases over a voltage width $\Gamma + k_B T$
- I dragged out by charging E_{add}

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Realistic Models

Non-Equilibrium Green's Function (NEGF) Formalism

Let us rewrite the previous eq. in terms of a Green Function $G(E)$

$$G(E) = \frac{1}{E - \epsilon + i\Gamma/2}$$

Then the density of states will be proportional to the so called Spectral function defined as

$$A(E) = i(G(E) - G(E)^\dagger) \Rightarrow D(E) = \frac{A(E)}{2\pi}$$

The mean number of excess electrons N and the current can be written as

$$N = \frac{2}{2\pi} \int_{-\infty}^{\infty} dE \left(|G(E)|^2 \Gamma_1 \cdot f(E - \mu_1) + |G(E)|^2 \Gamma_2 \cdot f(E - \mu_2) \right)$$

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \Gamma_1 \Gamma_2 |G(E)|^2 (f(E - \mu_1) - f(E - \mu_2))$$

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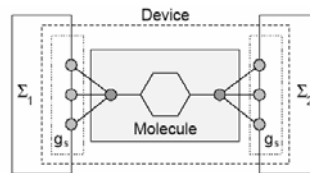


NEGF Formalism

For a multilevel Molecule (n levels) all quantities are replaced by a corresponding matrix (n x n)

ε	\rightarrow [H]	Hamiltonian Matrix
Γ	\rightarrow [Γ]	Broadening Matrix
D(E)	\rightarrow [A(E)/2 π]	Spectral Function
N	\rightarrow [ρ]	Density Matrix
U	\rightarrow [U]	Self-consistent Potential

$$G(E) = \frac{1}{E - \varepsilon + i\Gamma/2} \longrightarrow G(E) = \frac{1}{E[S] - [H] - [\Sigma]} \quad \Gamma = i[\Sigma - \Sigma^\dagger]$$



H : Molecule + surface atoms

Σ : Coupling to bulk contacts

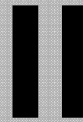
U : appropriate functional

A pedagogical tutorial: S. Datta, Nanotechnology 15, S433 (2004).

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Pause



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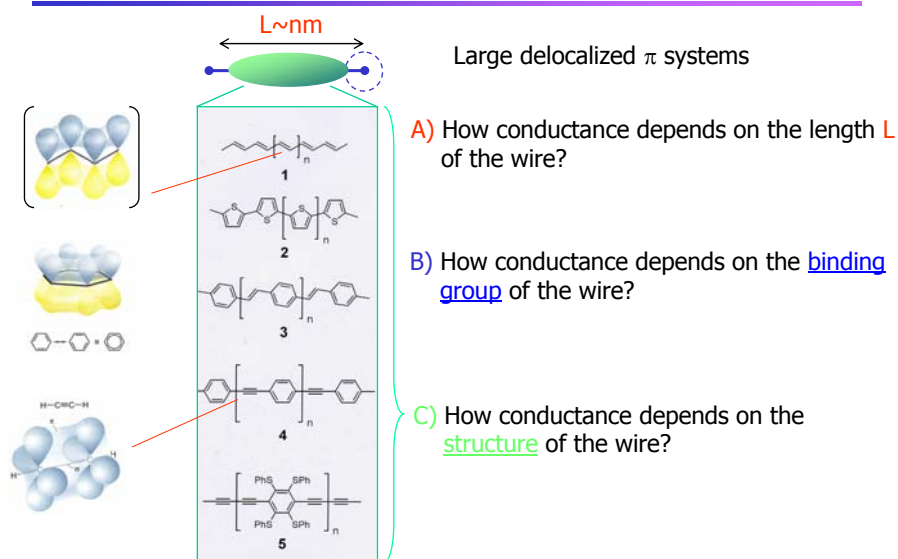
Experiments on Molecular Wires

Well coupled to electrodes (at least one of them)

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Molecular Wires



Conductance is a property of the Metal-Molecule-Metal structure

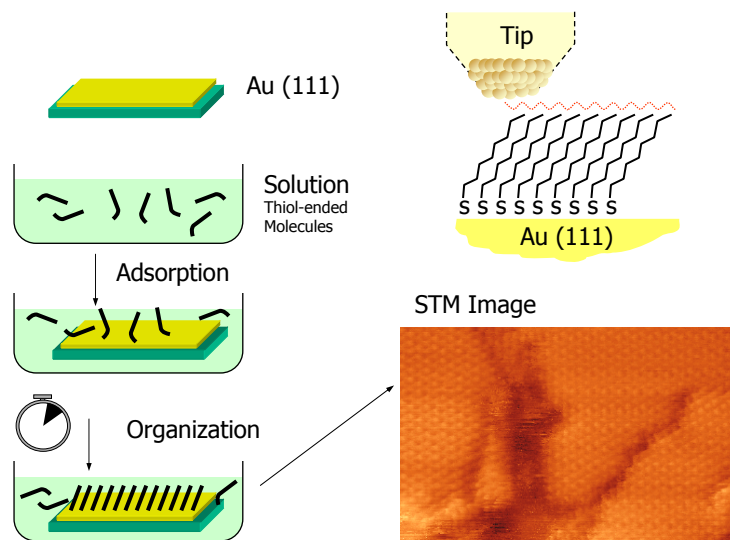
How one can measure transport properties of molecular wires?

- 1) STM: Scanning Tunneling Microscope
- 2) Break-junctions
 - Mechanically controlled
 - Electromigration-induced
- 3) Shadow evaporation on Self-assembled Monolayers (SAMs)

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MBE: Molecular "Beaker" Epitaxy



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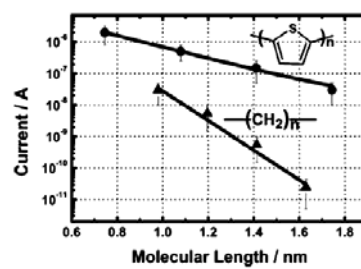
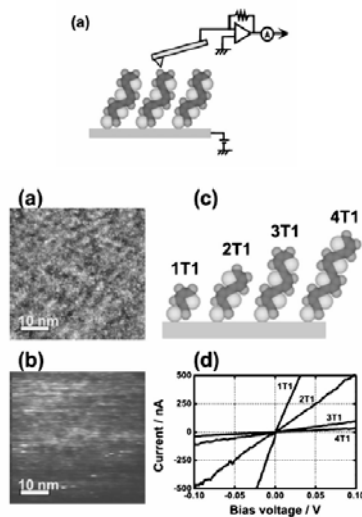
A) How conductance depends on L?

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Conductive AFM on Self-Assembled Monolayers

Sakaguchi et al., APL 2001



Measured

$\gamma = 0.41 \text{ \AA}^{-1}$ for oligothiophene
 $\gamma = 1.08 \text{ \AA}^{-1}$ for alkanethiol

Theory

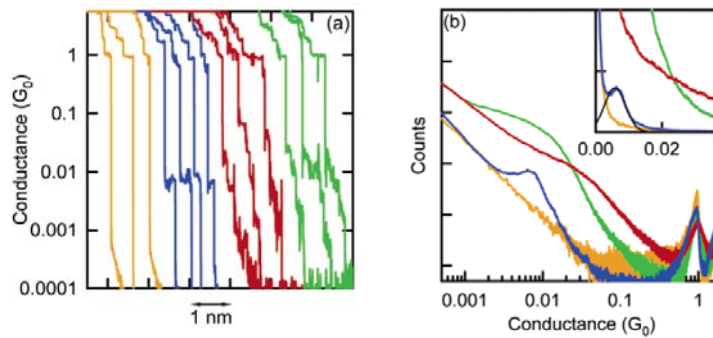
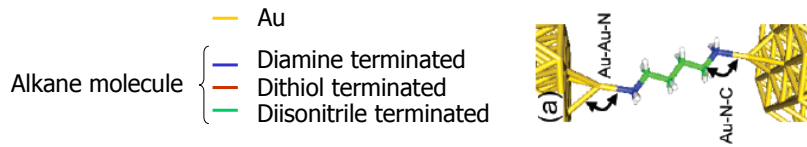
$\gamma = 0.33 \text{ \AA}^{-1}$ for oligothiophene
 $\gamma = 1.0 \text{ \AA}^{-1}$ for alkanethiol

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Single Molecule Measurements : statistical approach

L Venkataraman *et al.*, NanoLett. 6, 458,(2006)



DFT calculations support the scenario of the junction shown.

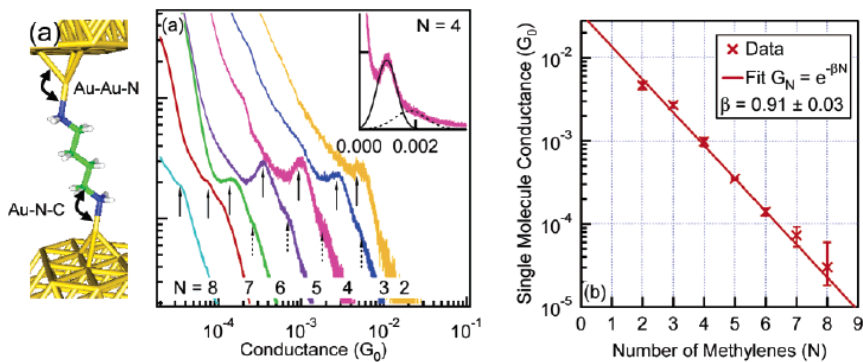
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Single Molecule Measurements : statistical approach

L Venkataraman *et al.*, NanoLett. 6, 458,(2006)

Amino-terminated molecules: alkane diamine



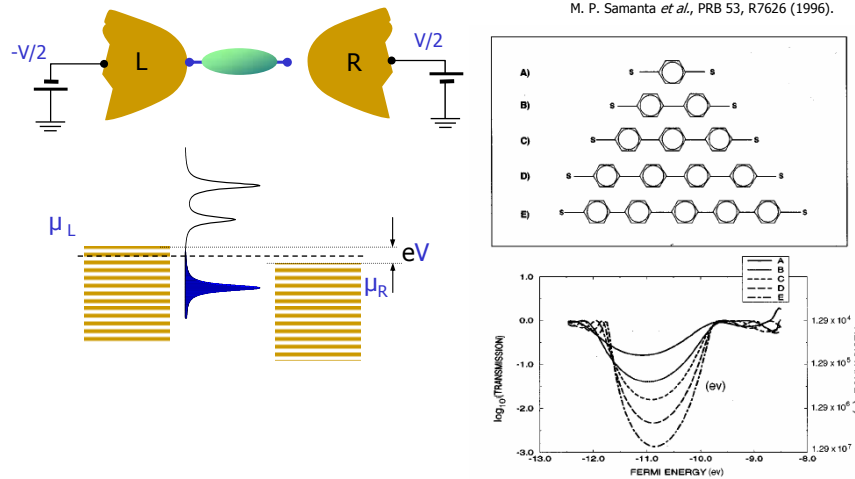
DFT calculations support the scenario of the junction shown.

The exponential behavior \Rightarrow histogram peak \equiv single molecule conductance

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Explanation



At low voltages μ_F is far from HOMO and/or LUMO \Rightarrow Tunneling Transmission

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B) How conductance depends on the binding group of the molecular wire?

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Influence of the binding group of electroactive molecules



Theoretical studies

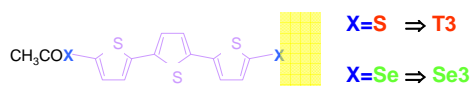
Conductance of molecular wires: Influence of molecule-electrode binding. S.N. Yaliraki, M. Kemp, and M.A. Ratner, J. Am. Chem. Soc. **121**(14), 3428 (1999)



Molecular alligator clips for single molecule electronics. Studies of group 16 and isonitriles interfaced with Au contacts. J.M. Seminario, A.G. Zacarias, and J.M. Tour J. Am. Chem. Soc. **121**(2), 411 (1999)



Experiments are needed

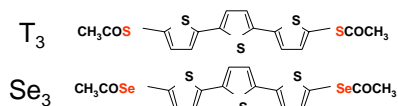


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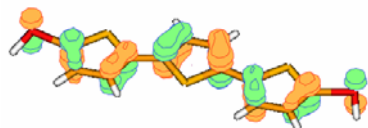
Influence of the binding group: Se vs S

Investigation of T3 and Se3



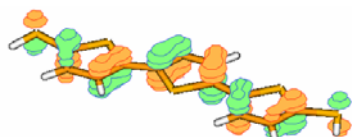
“Identical” HOMOs

quite similar IPs



Se3

6.50 eV



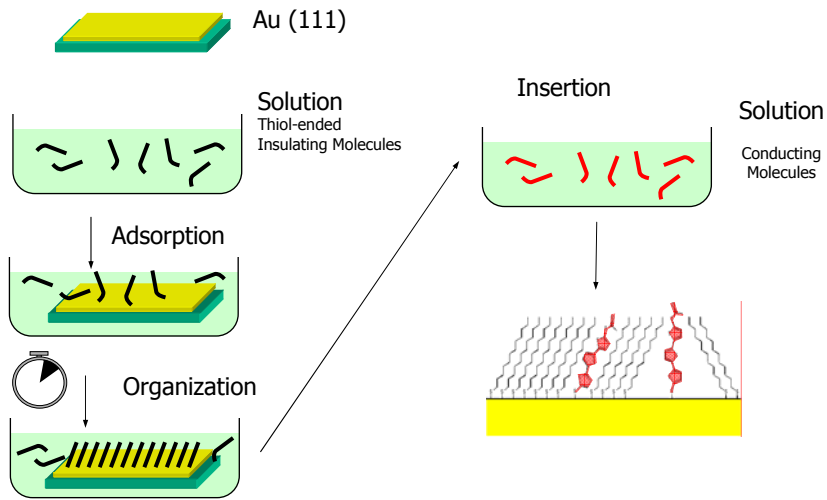
T3

6.52 eV

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Sample Preparation

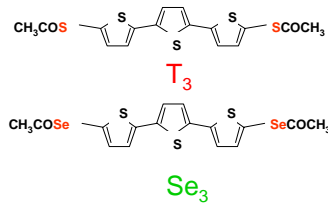
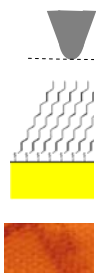


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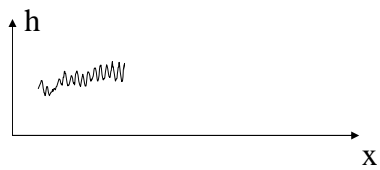


Molecular structure - transport properties relationship

STM tip



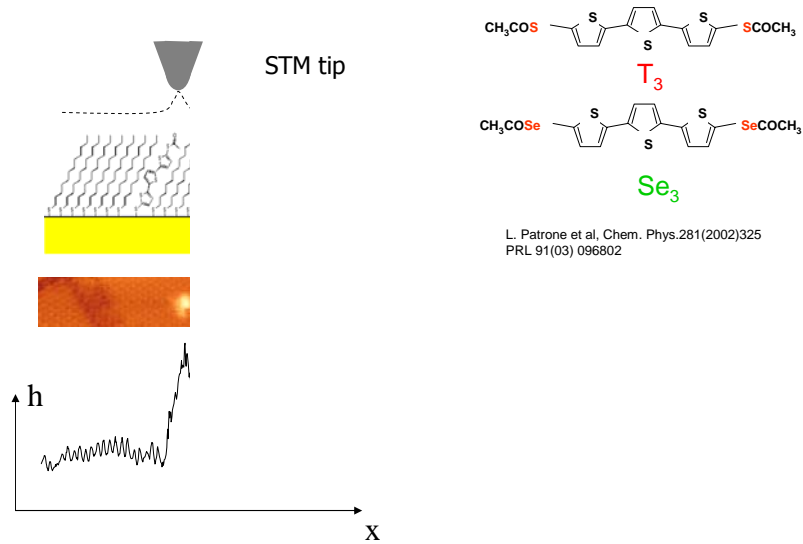
L. Patrone et al, Chem. Phys. 281 (2002) 325
PRL 91(03) 096802



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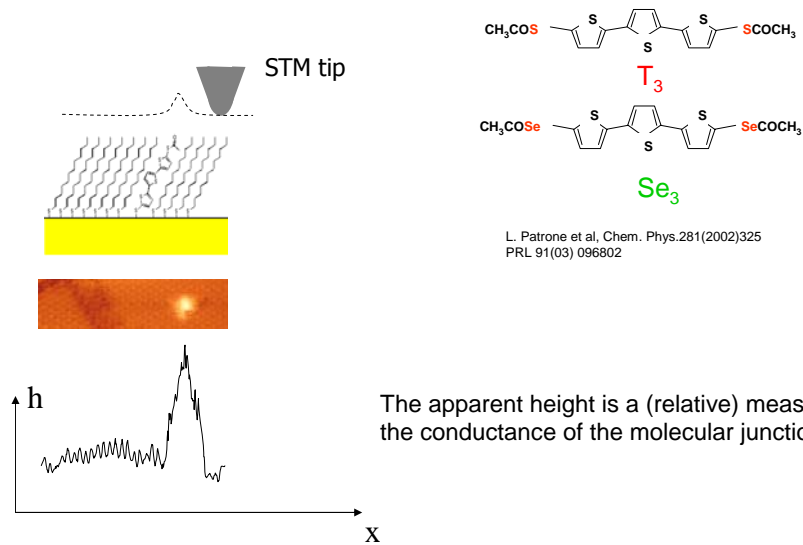
Molecular structure - transport properties relationship



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Molecular structure - transport properties relationship

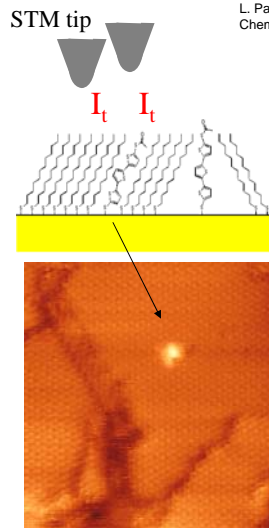


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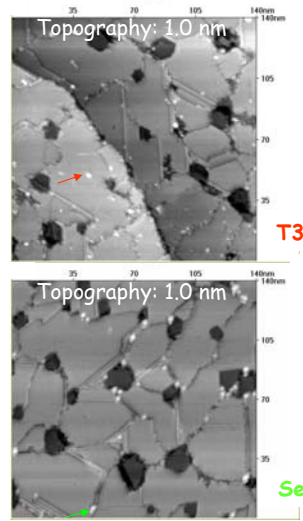


S vs Se: Experimental comparison

STM on T3 and Se3 Molecules inserted in a dodecanethiol Matrix



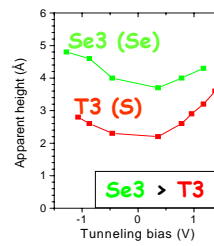
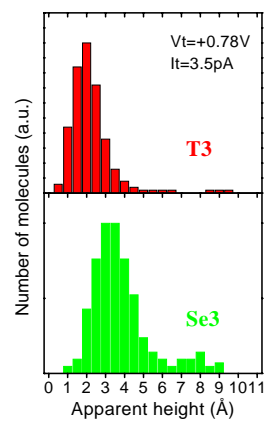
L. Patrone et al.
Chem. Phys. 281(2002)325



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S vs Se: Experimental comparison

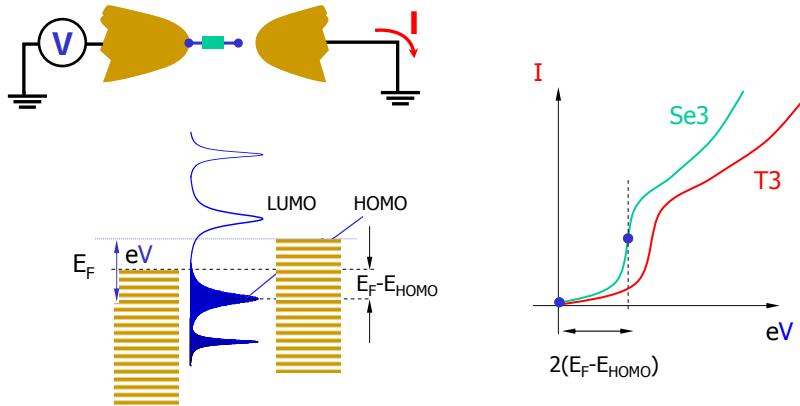


Se give rise to a more efficient transport than S

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Current-Voltage characteristic



Position of the HOMO level/ Fermi level

$$(E_F - E_{HOMO}) : T3 > (E_F - E_{HOMO}) : Se3$$

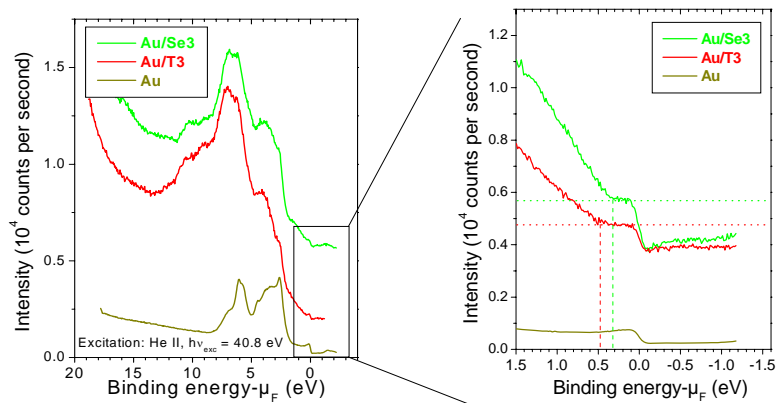
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Position of the HOMO / Fermi level

UPS (UV Photoelectron Spectroscopy)

1 monolayer adsorbed onto gold



$$T3 : E_F - E_{HOMO} > Se3 : E_F - E_{HOMO}$$

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C) How conductance depends on the structure of the wire?

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C) Comparison of backbone conductance

Table 1. Molecular Structures, Calculated HOMO–LUMO Gap (E_g), Calculated (G_{calc}) and Measured (G_{meas}) Relative Junction Conductance at 0.5 V

compound	molecular structure	E_g (eV) ^a	G_{calc} ^b	G_{meas} ^c
C12	<chem>AcS(CH2)12SAc</chem>	7.11	1	1
OPE	<chem>AcS-C6H4-C6H4-C6H4-SAc</chem>	3.51	10	15
OPV	<chem>AcS-C6H4-C6H2(OBu)2-C6H4-SAc</chem>	3.12	78	46

^a E_g is the HOMO–LUMO gap calculated from density-functional theory at the B3LYP/6-31G* level. ^b Junction conductance (1/V) at 0.5 V normalized to the conductance of the C12 junction.

Kushmeric, Ratner et al JACS 2003

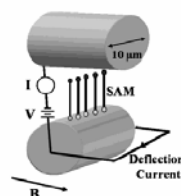
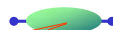


Figure 1. Schematic representation of the crossed-wire tunnel junction (not to scale). All measurements were made in a nitrogen purged Faraday cage at room temperature.

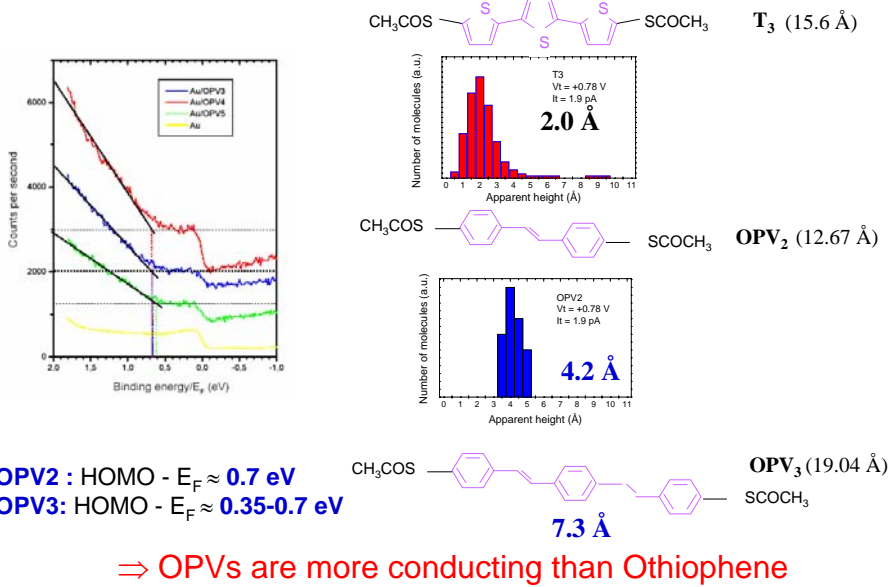
OPV > OPE

OPV vs Othiophene?

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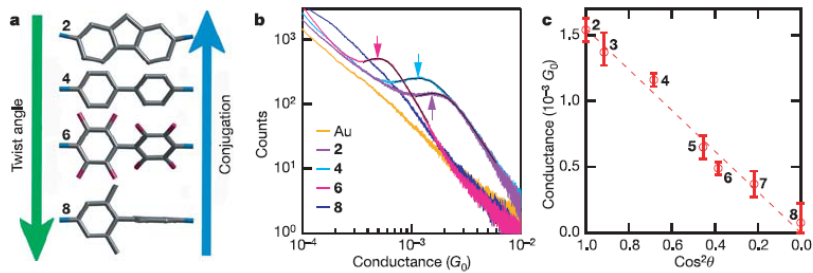
C) Influence of the conjugated body: T3 vs OPVn



Single Molecule Measurements : statistical approach

Biphenyl junction conductance as a function of molecular twist angle.

L Venkataraman *et al.*, Science 442, 904(2006)



The conductance for the series decreases with increasing twist angle in agreement with theoretical calculation



Which is the IV characteristic of a Metal-single molecule-Metal device?

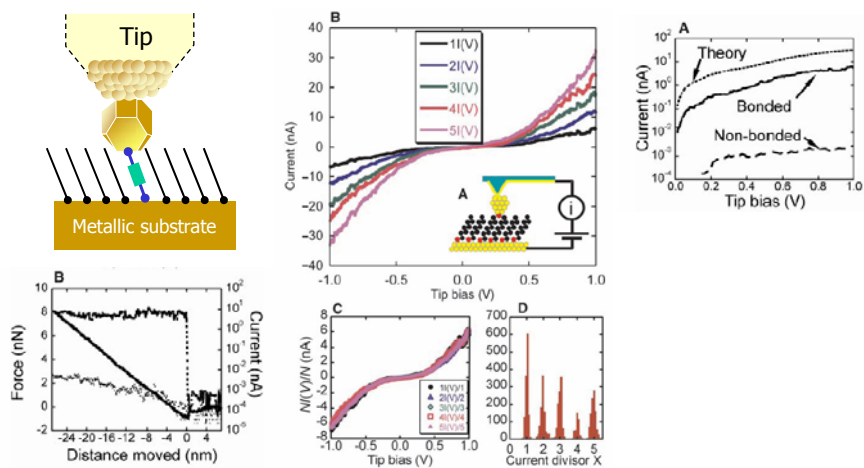
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Single Molecule Measurements

Conducting AFM on Alkanedithiol on a alkanethiol matrix

X.D. Cui et al., Science 2001.

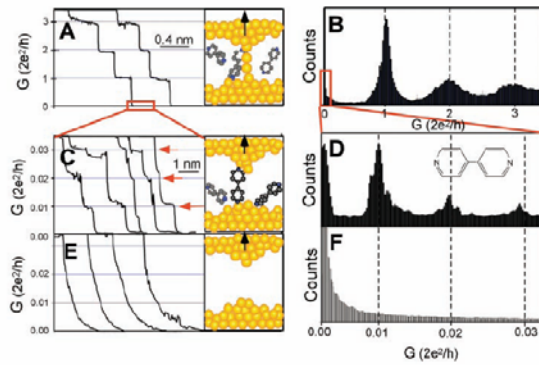


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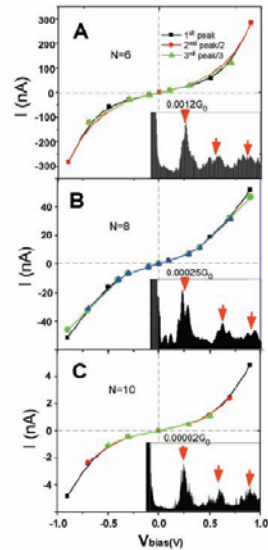


Single Molecule Measurements : statistical approach

Conductance histograms with STM N. J. Tao, Science 2003.
 Room temperature & molecules in solution (1mM)



The conductance of the most probable structure can be estimated



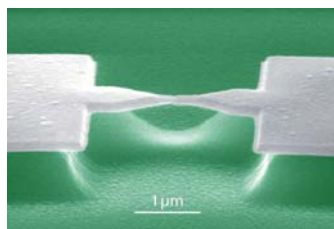
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Contacting Single Molecules

Mechanically Controlled break-junctions

J. M. van Ruitenbeek et al Rev. Sci. Instrum. 67 (1995) 108

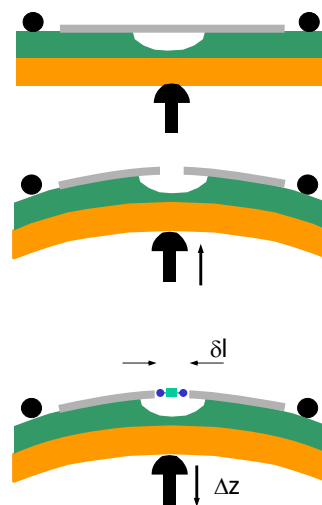


Advantages

- High stability
- accuracy $\delta l / \Delta z \sim 10^{-5}$
- Freshly exposed metal surfaces

Drawbacks

- No image of contacted molecules
- No gating

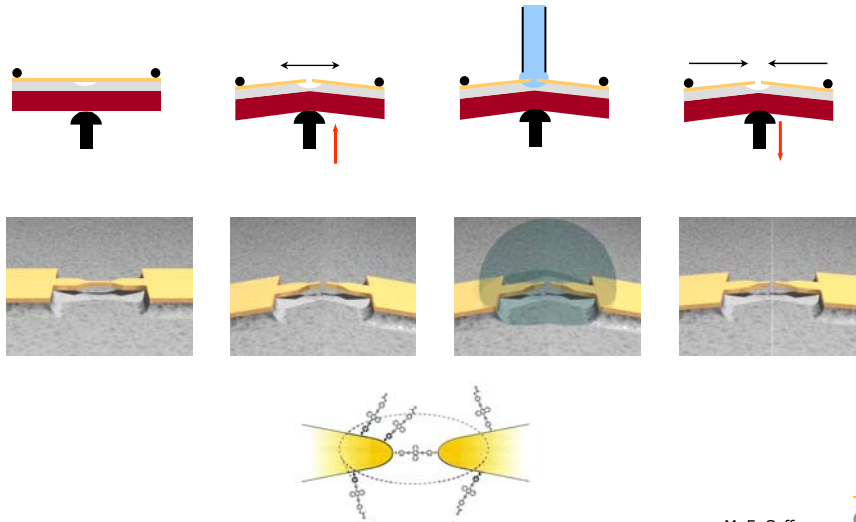


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Mechanically Controlled break-junctions (MCBJs)

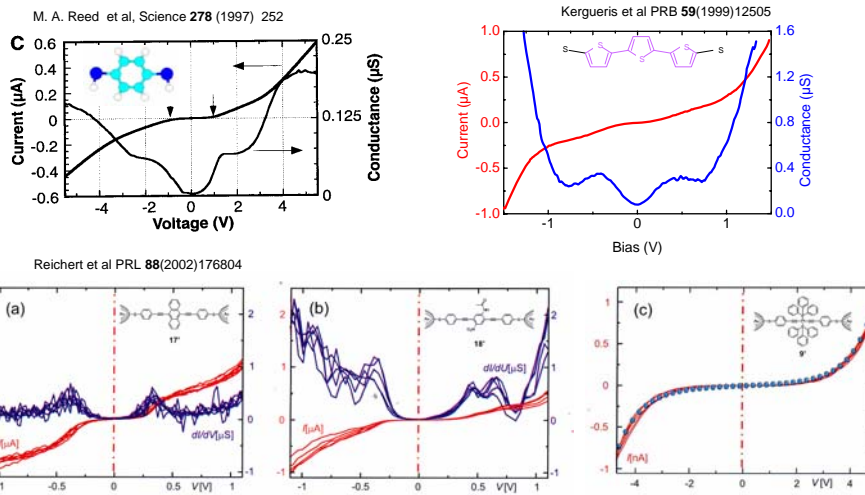
Experimental procedure



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MCBJs Results on Different Molecules (@300K)



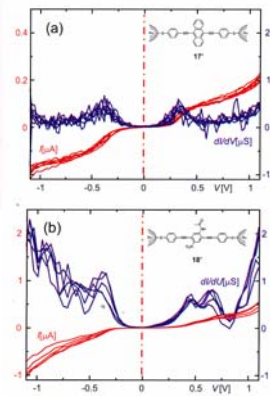
Single Molecule IV characteristics ?

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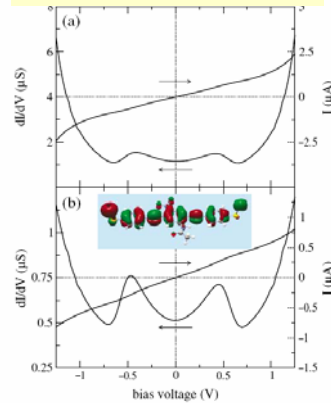
Probably Yes

- "Lock-in" behavior
- Similar molecules (length, binding groups) with different spatial symmetry gives corresponding behavior on IVs
- modeling consistent with a single molecule



J. Heurich *et al.*, PRL 88, 256803 (2002).

NEGF Formalism calculation



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Conclusions for Molecular Wires

At low Voltage Bias

$$G = \left. \frac{\partial I}{\partial V} \right|_{V \rightarrow 0} = G_{\text{Contact}} e^{-\gamma L}$$

- Exponential dependence on L is confirmed.
- The role of the **binding group** has been decoupled from that of the rest of the molecule:
 - Se yields a better molecule-metal coupling efficiency than S since the Fermi level is nearer to the HOMO level.
- Phenylene-Vinylene (OPV) is more efficient than thiophene as **backbone**.

IVs

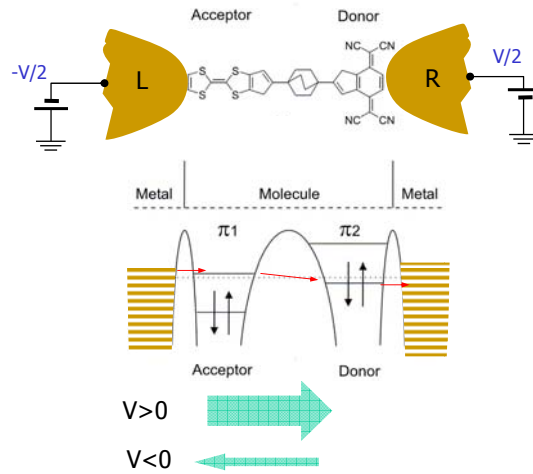
Single Molecule IV characteristics can be measured.
Qualitative agreement between experiments and theory

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2. Diodes

Aviram & Ratner Theoretical Proposal (1974)



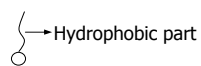
Rectifying behavior: expected from asymmetry of the D-A structure

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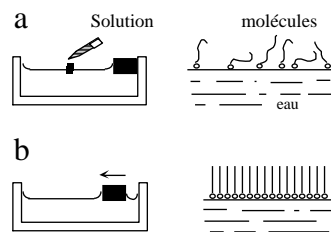


The Langmuir-Blodgett technique

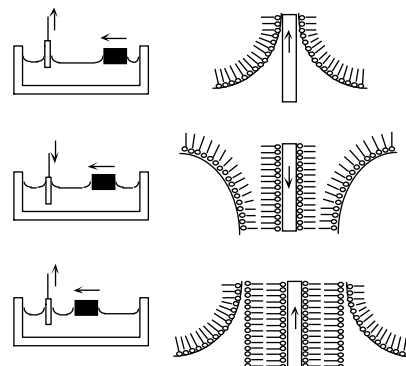
Special design of the molecule



Single Molecular Film formation



Transfer to a solid substrate



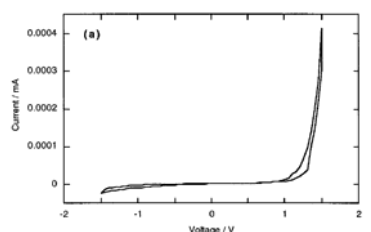
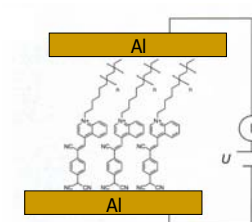
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2. Diodes

Experimental Realization

Metzger *et al.*, JACS 119, 10455 (1997).



Some differences

Aviram & Ratner

Metzger et al

Spacer: σ -saturated

Spacer: π -conjugated

aliphatic chain (donor side)

Is Rectification due to the Aviram & Ratner mechanism ?

Answer: No!

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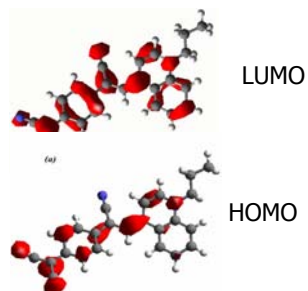
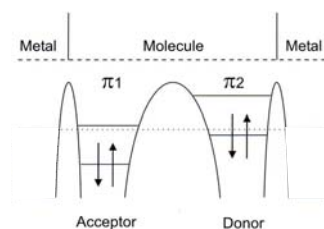
Which is the Rectification Mechanism

Aviram & Ratner
Spacer: σ -saturated

Metzger et al
Spacer: π -conjugated



Donor and Acceptor molecular orbitals remain localized



DFT calculation: HOMO and LUMO delocalized

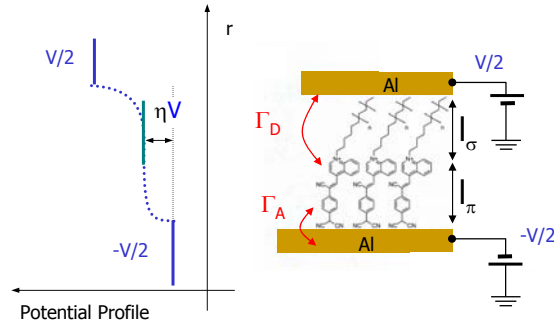
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Rectification Mechanism: Asymmetric Coupling

Metzger *et al.*, JACS 119, 10455 (1997).

aliphatic chain (donor side) $\Rightarrow \Gamma_D = \Gamma_A$



As a first approximation $\eta = \frac{1}{2 \left(1 + \frac{\epsilon_\pi l_\sigma}{\epsilon_\sigma l_\pi} \right)} : 0.1$

Asymmetric Coupling can be used for fabricating Diodes.

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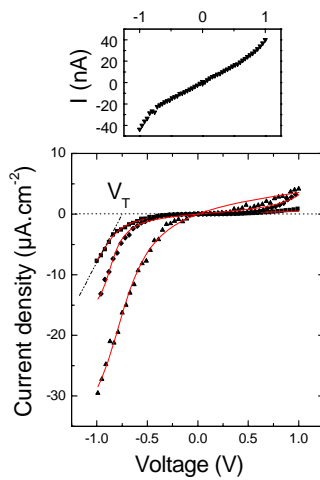


Using asymmetric coupling for Diode function

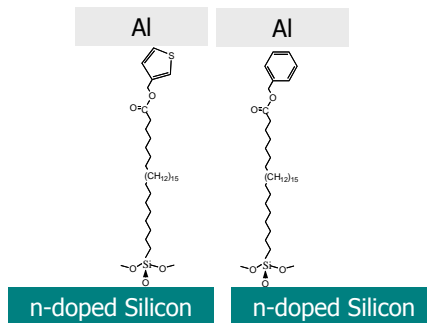
N. Lenfant *et al.*, Nanoletters 3, 741 (2003).

Two step fabrication:

Self-assembly of alkyl chains
π-conjugated groups



Control measurement on Alkyl chains

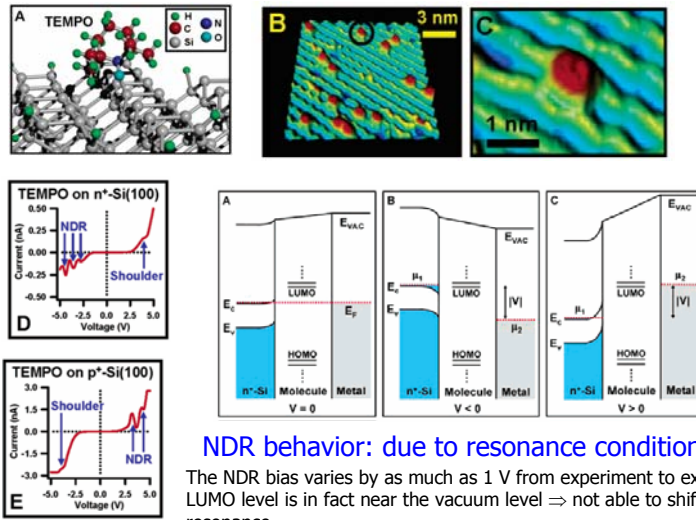


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2. Diodes and NDR

N. P. Guisinger *et al.*, Nanoletters 4, 55 (2004)



NDR behavior: due to resonance conditions

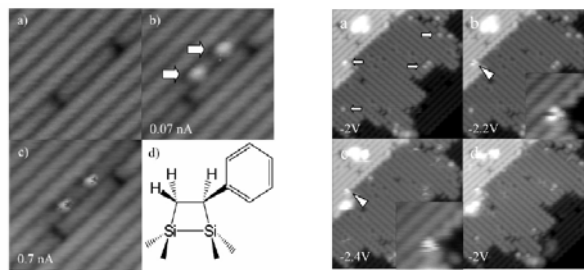
The NDR bias varies by as much as 1 V from experiment to experiment
LUMO level is in fact near the vacuum level \Rightarrow not able to shift into resonance

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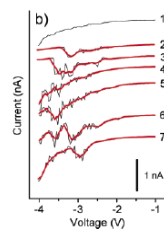


Origin of NDR

J. L. Pitters and R. A. Wolkow, Nanolett. 6, 390 (2006)



Increasing the tunneling current or the voltage produces structural changes



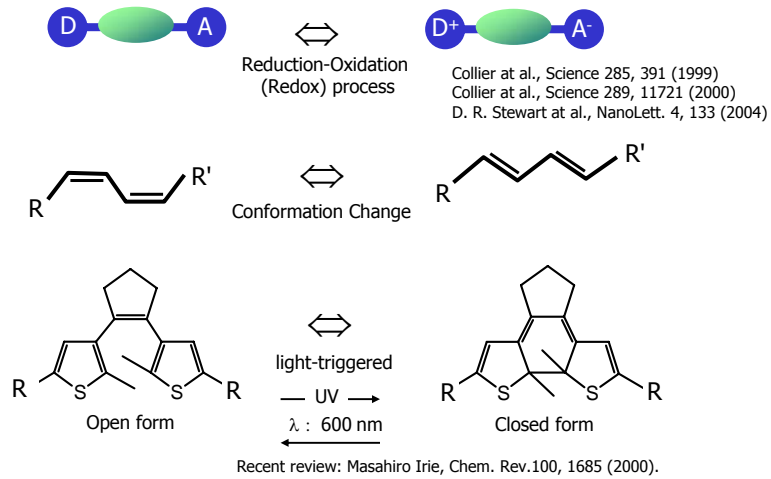
IV spectroscopy shows NDR-like peaks due to Molecular arrangements

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3. Switches

At least two different stable states \Leftrightarrow different conductance (high /low)



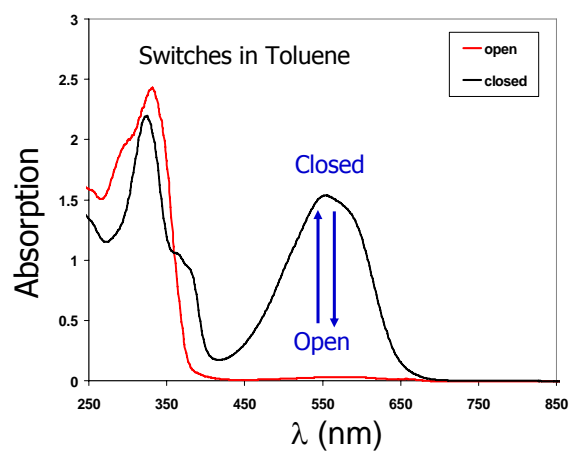
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Light-triggered Switches

Typically

Courtesy of D. Dulić and S.J. van der Molen



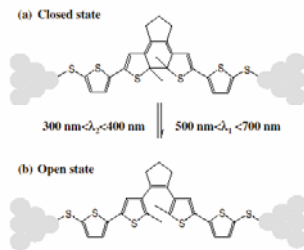
Does it work in a solid state device ?

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Breakjunction experiment

D. Dulić *et al.*, PRL 91,207402 (2003).

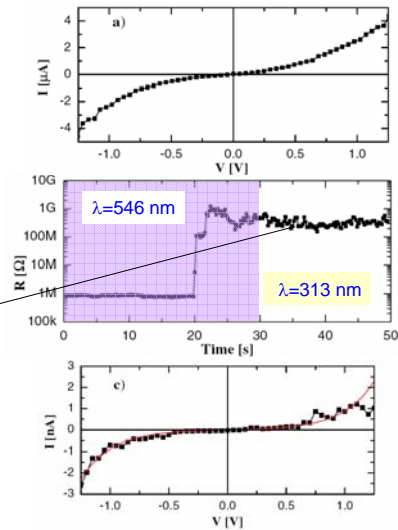


No switching back !?

One way Photochromism

Why closing is questioned?

OPEN QUESTION



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Final Remarks

- Conductance properties of single molecules can be probed. However reproducibility and stability remains a challenge.
- More experiments are needed in order to refine theory and more theoretical calculation are needed to design interesting experiments (feedback!).
- Molecular Diodes can be obtained using asymmetric coupling.
- Molecular Electronics on silicon can be a way of fabricating hybrid devices taking profit of the powerful infrastructure of the silicon-based IC industry \rightarrow Resonant tunneling devices.
- Light Triggered switches are promising molecules. Tuning of the coupling between the active part and the electrodes are needed to get reversible operation.

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