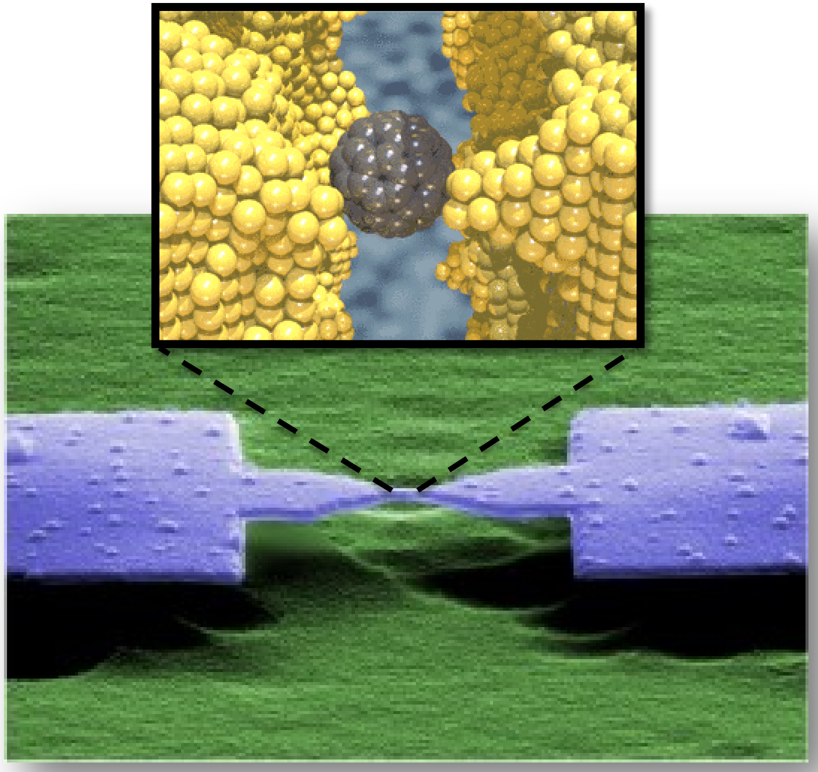
Chapter 7.2: Coherent transport through molecular junctions



7.2.1 Identifying the transport mechanism

How to identify experimentally the transport mechanism?

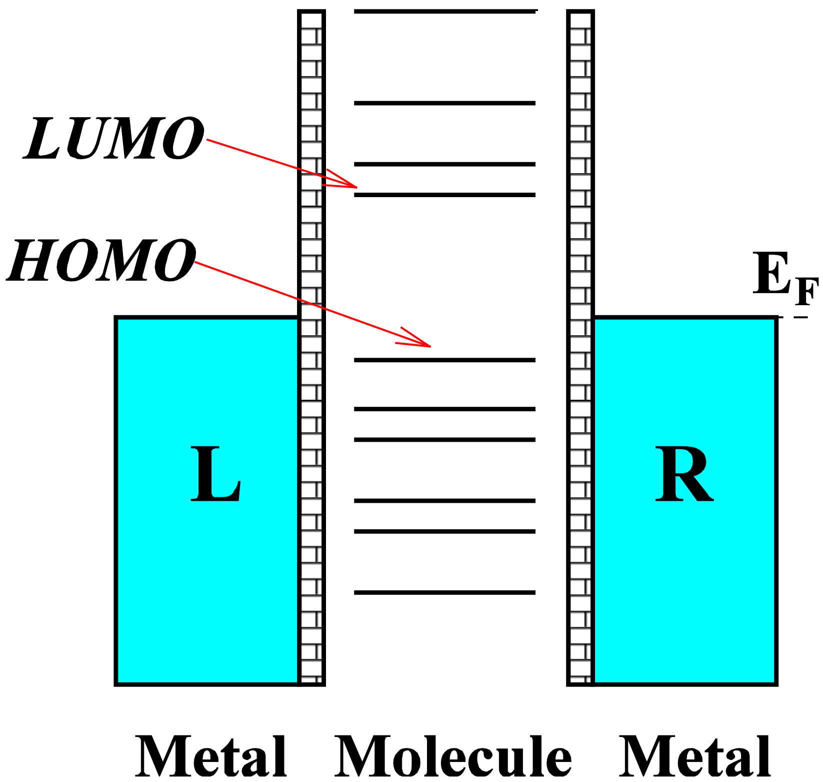
- Shape of I-Vs.
- Temperature dependence of I-Vs.
- Gate dependence of I-Vs.

Table 11.1 Possible conduction mechanisms. Here, J is the current density, V is the bias voltage, φ_B is the barrier height, d is the barrier length and T the temperature.

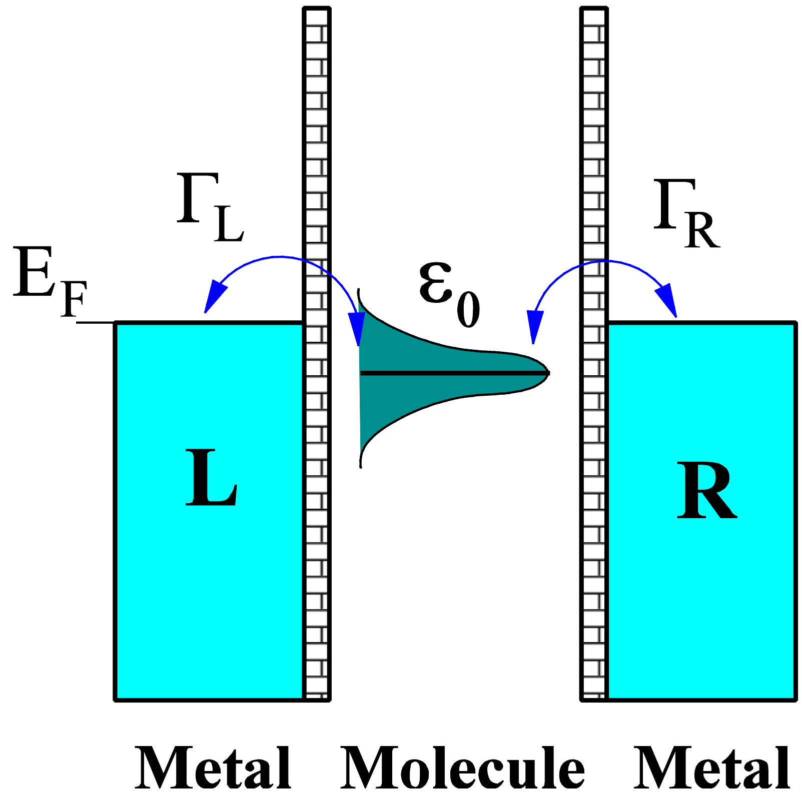
Conduction mechanism	**Characteristic behavior**	**Temperature dependence**	**Voltage dependence**
Direct tunneling	$J \sim V \exp\left(-\frac{2d}{\hbar}\sqrt{2m\varphi_B}\right)$	none	$J \sim V$
Fowler-Nordheim tunneling	$J \sim V^2 \exp\left(-\frac{4d\sqrt{2m}\varphi_B^{3/2}}{3q\hbar V}\right)$	none	$\ln(\frac{J}{V^2}) \sim \frac{1}{V}$
Thermionic emission	$J \sim T^2 \exp\left(-\frac{\varphi_B - q\sqrt{qV/4\pi\epsilon d}}{k_B T}\right)$	$\ln\left(\frac{J}{T^2}\right) \sim \frac{1}{T}$	$\ln(J) \sim V^{1/2}$
Hopping conduction	$J \sim V \exp\left(-\frac{\varphi_B}{k_B T}\right)$	$\ln\left(\frac{J}{V}\right) \sim \frac{1}{T}$	$J \sim V$

7.2.2 Some lessons from the single-level model

Often the transport through a molecular junction is dominated by a single molecular orbital. Those situations can be described with the **single-level model (sometimes also called resonant tunneling model)**. But for molecular junctions, the transport is typically off-resonant, as compared to atomic contacts.



(Multi-level model)

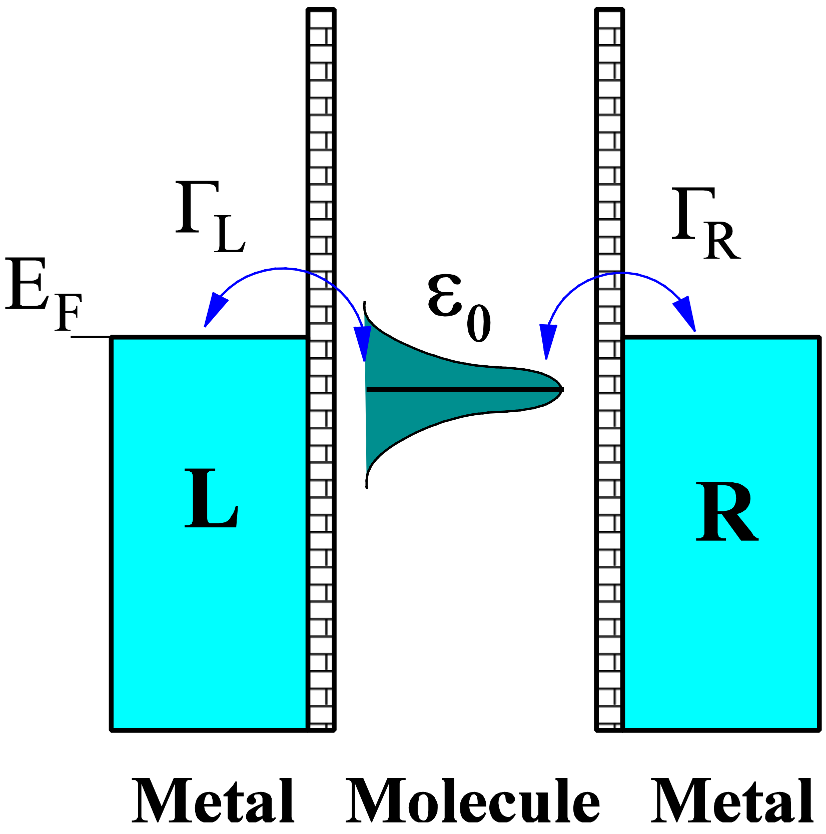


(Single-level model)

7.2.2 Some lessons from the single-level model

Landauer formula:

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



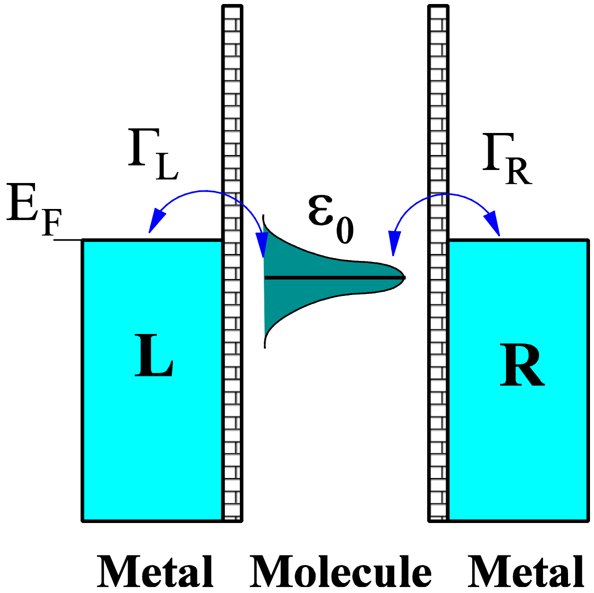
$$T(E,V)=\frac{4\Gamma_L\Gamma_R}{[E-\varepsilon_0(V)]^2+[\Gamma_L+\Gamma_R]^2}$$

[Breit-Wigner formula]

$$\begin{cases} \varepsilon_0 = \text{level position} \\ \Gamma_L+\Gamma_R = \text{level width} \end{cases}$$

7.2.2 Some lessons from the single-level model

❑ **Derivation of the Breit-Wigner formula for the transmission through a single electronic level from the general expression of the transmission.**



- Hamiltonian: $H_{CC} = \varepsilon_0$
- Self-energies: $\Sigma^a_{L,R} = i\Gamma_{L,R} = (\Sigma^r_{L,R})^*$
- Scattering rates: $\Gamma_{L,R} = \mathrm{Im}(\Sigma^a_{L,R})$
- Green's functions:

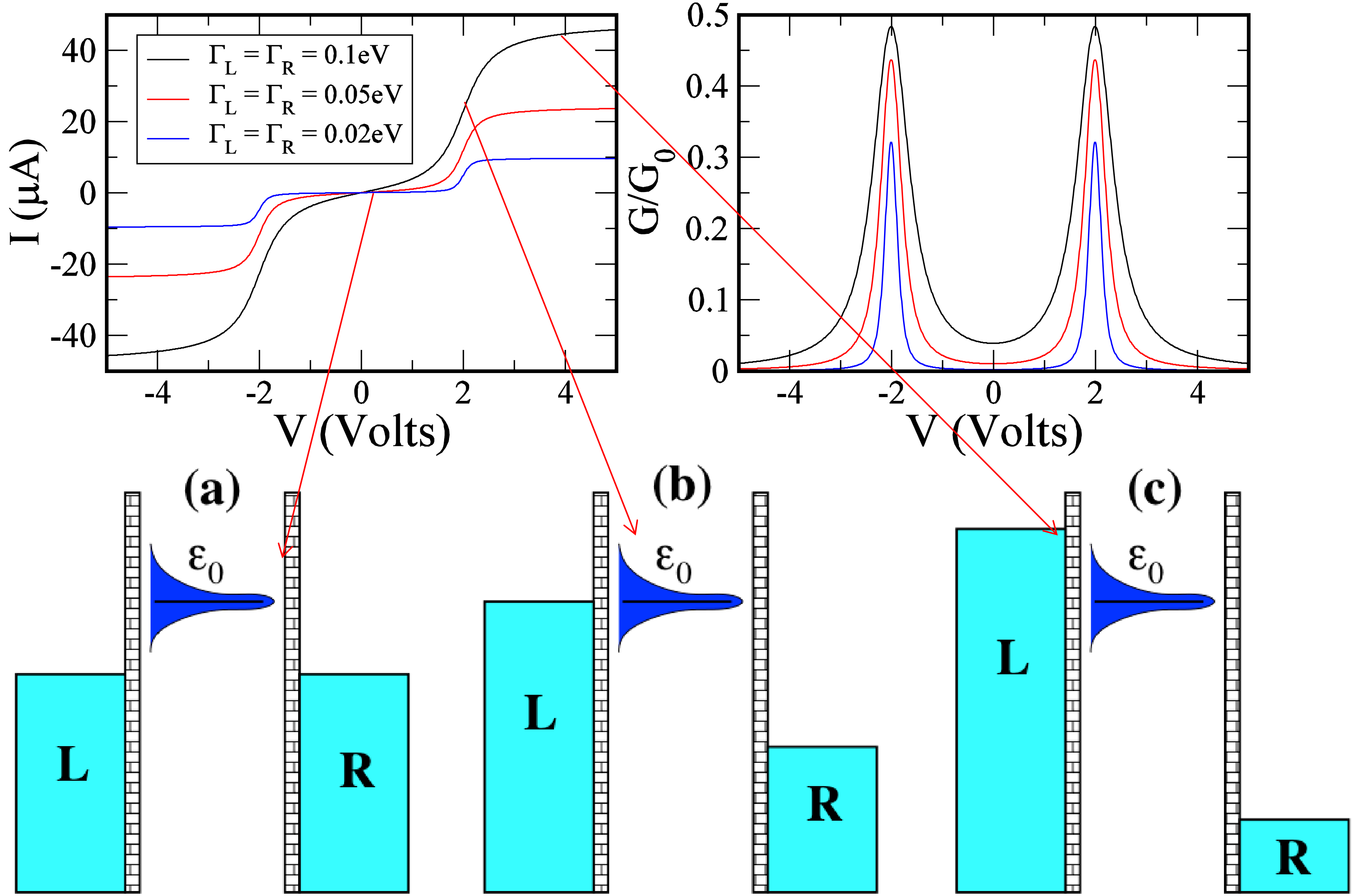
$$G^{r,a}_{CC}(E) = \left[(E \pm i\eta)1 - H_{CC} - \Sigma^{r,a}_L - \Sigma^{r,a}_R\right]^{-1}$$

Transmission (Breit-Wigner formula)

$$T(E) = 4\mathrm{Tr}\left[\Gamma_L(E)G^r_{CC}(E)\Gamma_R(E)G^a_{CC}(E)\right] = \frac{4\Gamma_L\Gamma_R}{(E-\varepsilon_0)^2 + (\Gamma_L+\Gamma_R)^2}$$

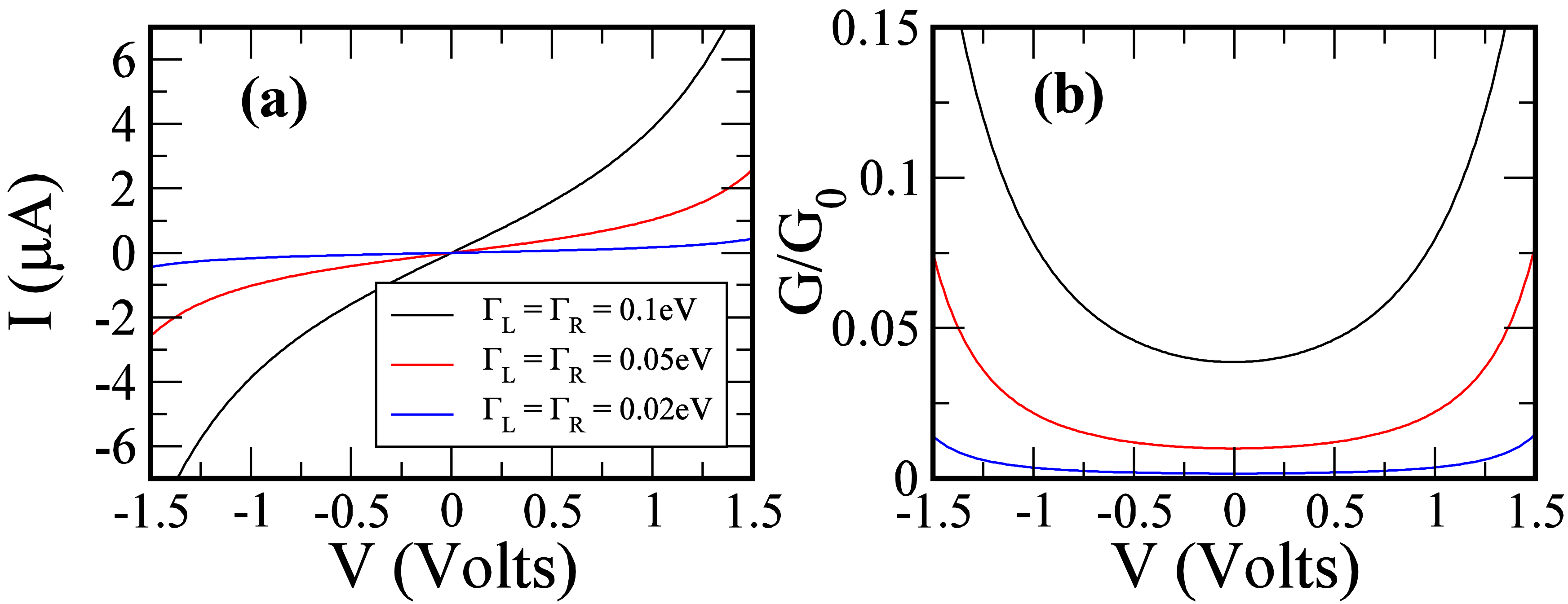
7.2.2.1 Shape of the I-V curves

$\varepsilon_0 = 1\text{eV}; k_BT = 0.025\text{ eV}$ (room temperature)



7.2.2.2 Molecular contacts as tunnel junctions

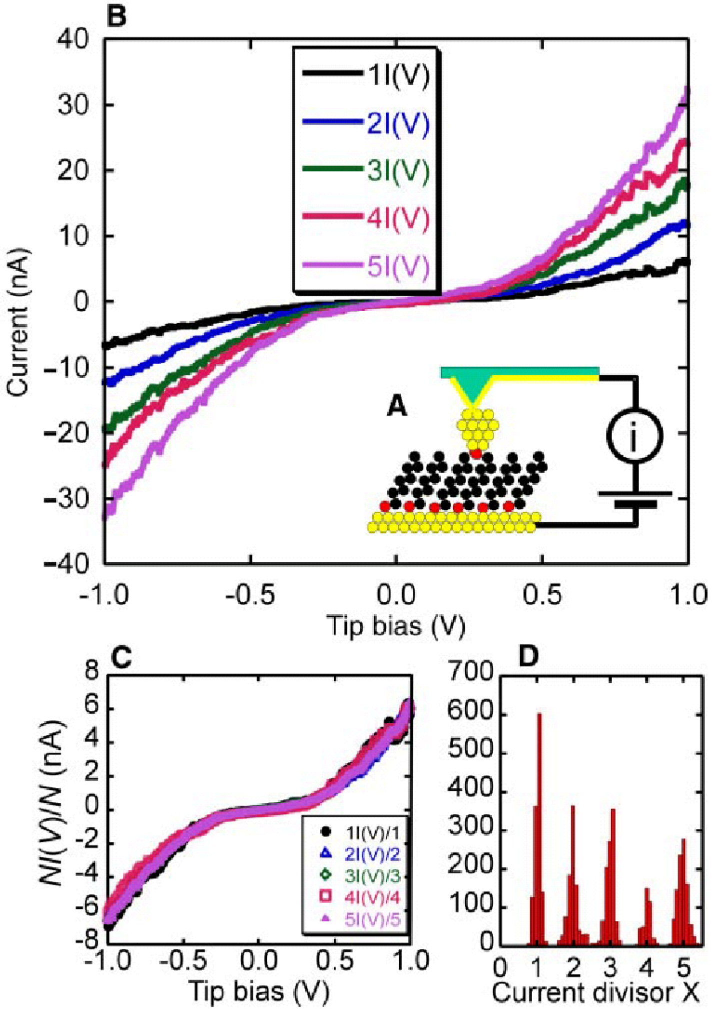
Low bias region : $|eV| << |\varepsilon_0|$



Low-bias expansion: $I(V) \approx AV + BV^3 \Rightarrow G(V) \approx A + 3BV^2$

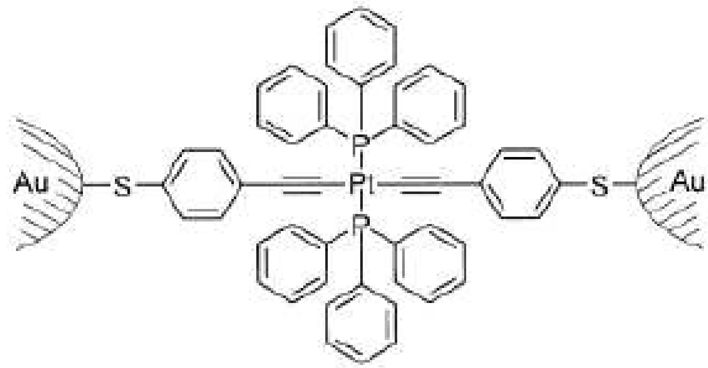
7.2.2.2 Molecular contacts as tunnel junctions

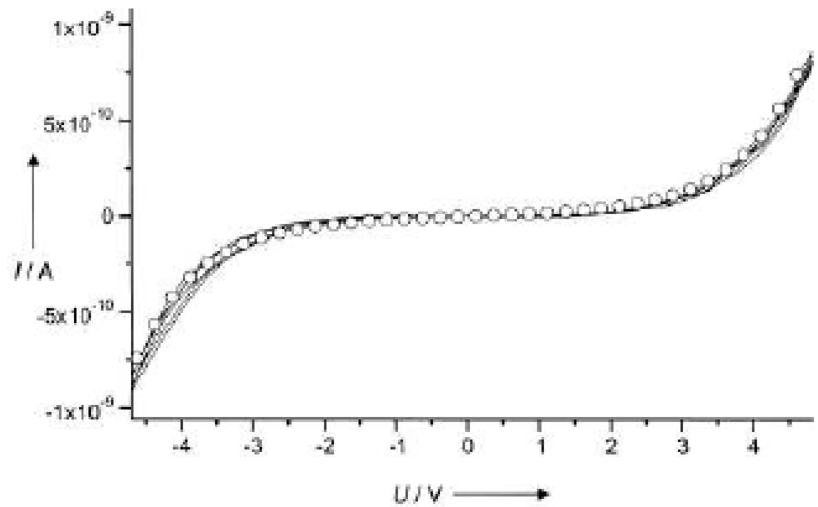
Cui et al. (Lindsay's group), Science ***294****, 571 (2001)*



A *trans*-Platinum(II) Complex as a Single-Molecule Insulator**

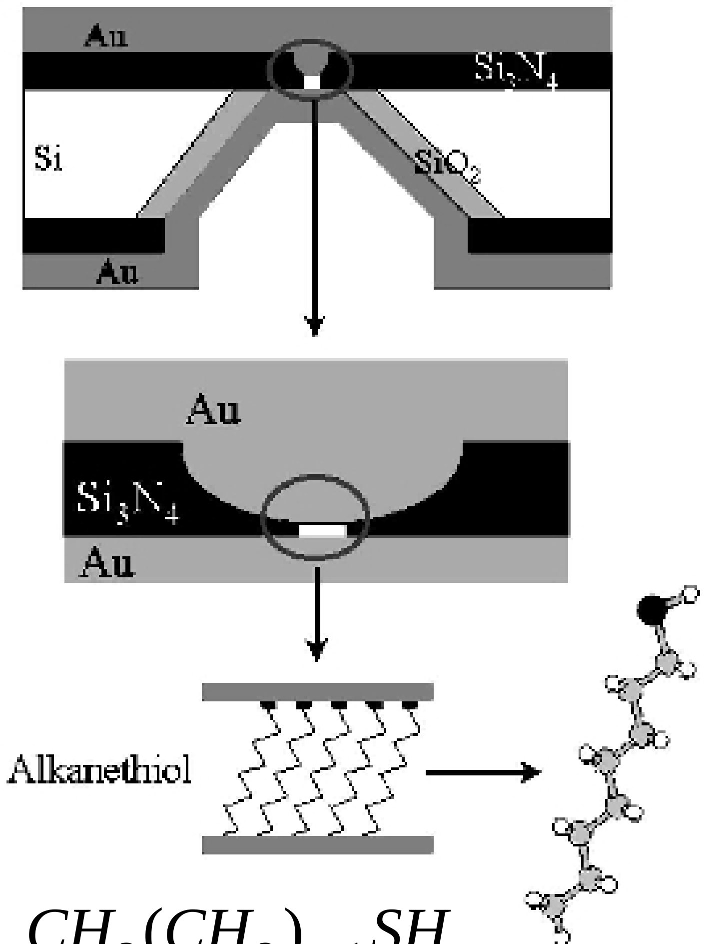
Marcel Mayor,* Carsten von Hänisch, Heiko B. Weber,* Joachim Reichert, and Detlef Beckmann





7.2.2.3 Temperature dependence of the current

Wang, Lee and Reed,
PRB 68, 035416 (2003)



$$CH_3(CH_2)_{n-1}SH$$

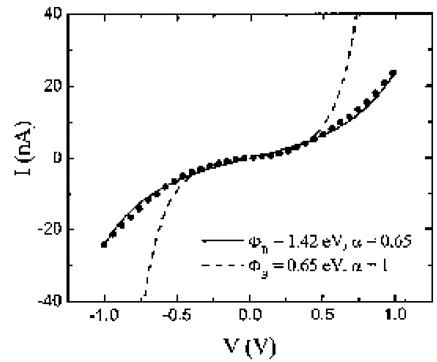
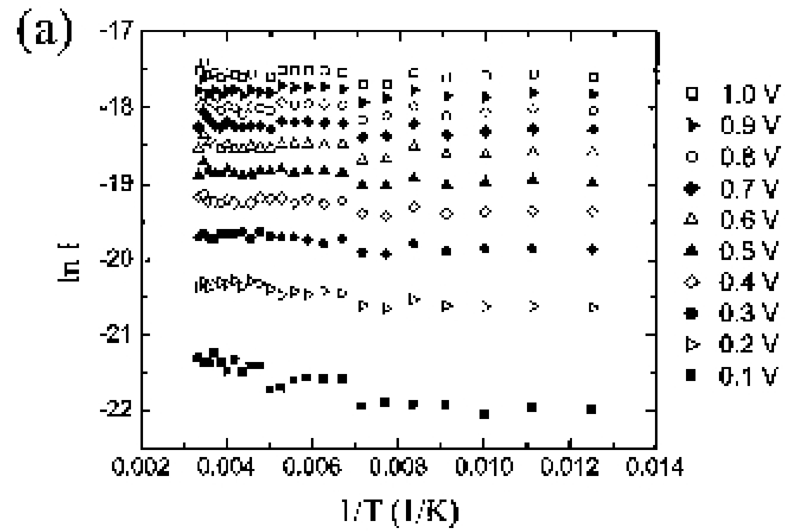


FIG. 5. Measured C12 $I(V)$ data (circular symbols) is compared with calculation (solid curve) using the optimum fitting parameters of $\Phi_B = 1.42$ eV and $\alpha = 0.65$. The calculated $I(V)$ from a simple rectangular model ($\alpha = 1$) with $\Phi_B = 0.65$ eV is also shown as the dashed curve.

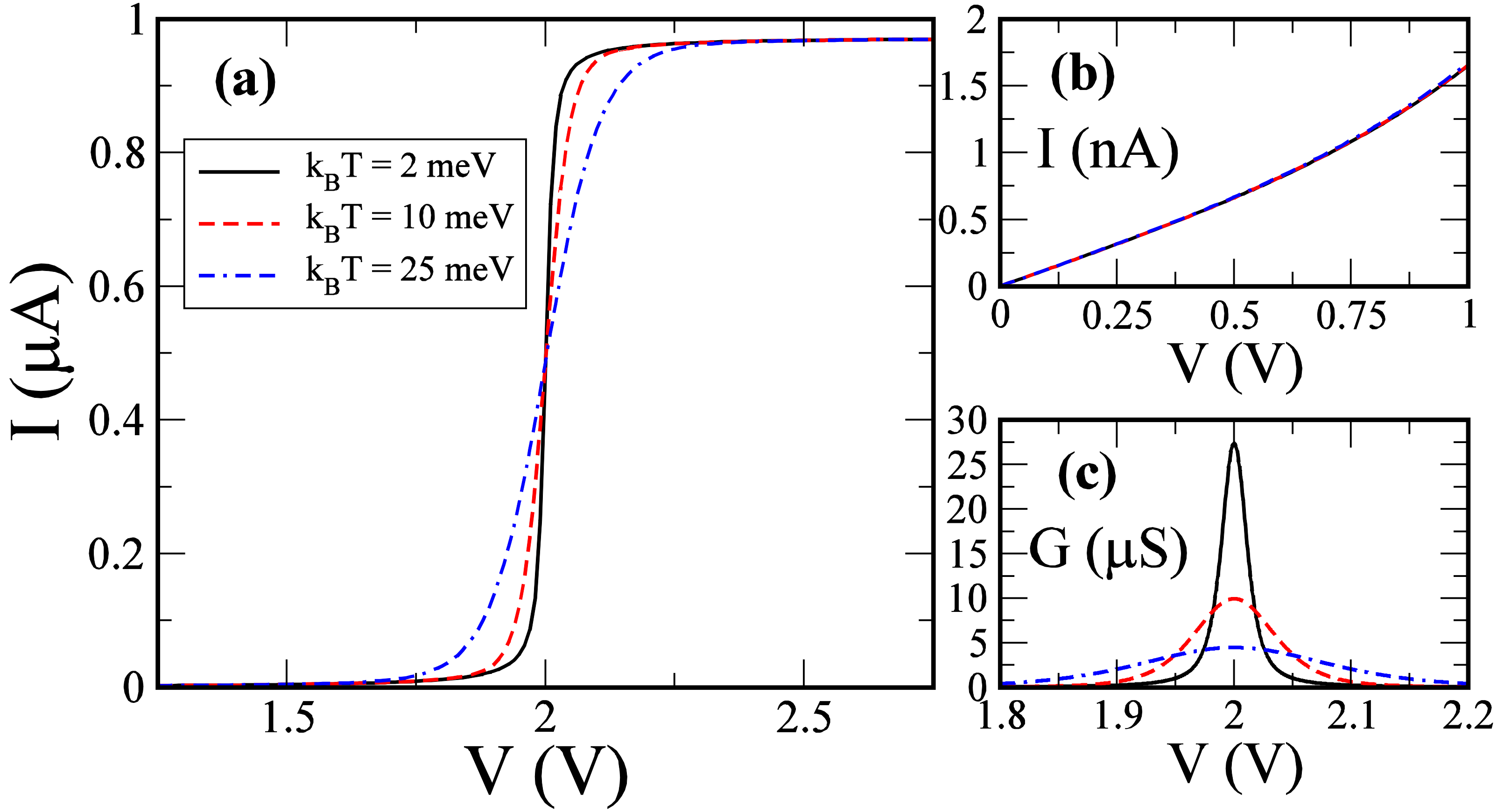
Voltage dependence:
Again a tunnel junction!

Current independent of the temperature



7.2.2.3 Temperature dependence of the current

$$\varepsilon_0 = 1\,\mathrm{eV}; \Gamma_L = \Gamma_R = 2\,\mathrm{meV}$$



- Off-resonant transport → T independent
- On-resonant transport → T dependent (as long as kT > Γ)

7.2.2.3 Temperature dependence of the current

General expression for the temperature-dependent conductance with the Fermi function *f*.

$$G(T) = \frac{2e^2}{h} \int_{-\infty}^{\infty} dE \tau(E) \left(-\frac{\partial f}{\partial E} \right)$$

Within the single-level model, the temperature dependence of the linear conductance is given by:

$$G(T) = \left(\frac{2e^2}{h} \right) \frac{1}{4k_B T} \int_{-\infty}^{\infty} dE \left[\frac{4\Gamma_L \Gamma_R}{(E-\varepsilon_0)^2 + (\Gamma_L + \Gamma_R)^2} \right] \frac{1}{\cosh^2(\beta E/2)}; \quad \beta = k_B T$$

- Off-resonant tunneling: $(|\varepsilon_0| >> \Gamma, k_B T)$

$$\boxed{G(T) = \left(\frac{2e^2}{h} \right) \frac{4\Gamma_L \Gamma_R}{\varepsilon_0^2}}$$

(temperature-independent)

- Weak coupling regime: $(\Gamma << k_B T)$

$$\boxed{G(T) = \left(\frac{2e^2}{h} \right) \frac{\pi \Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{1}{k_B T \cosh^2(\beta \varepsilon_0 / 2)}}$$

7.2.2.4 Symmetry of the I-V curves

"Molecular rectifiers"

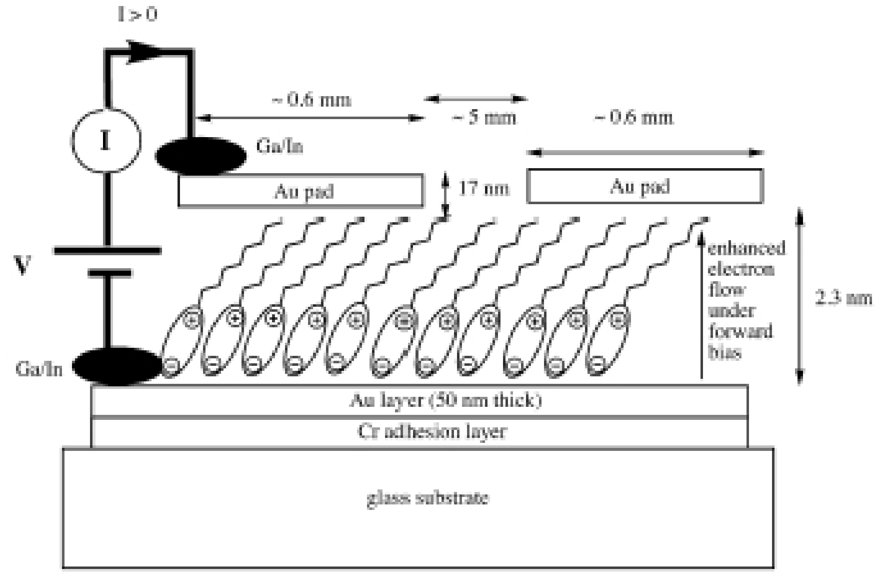
Arieh Aviram and Mark A. Ratner

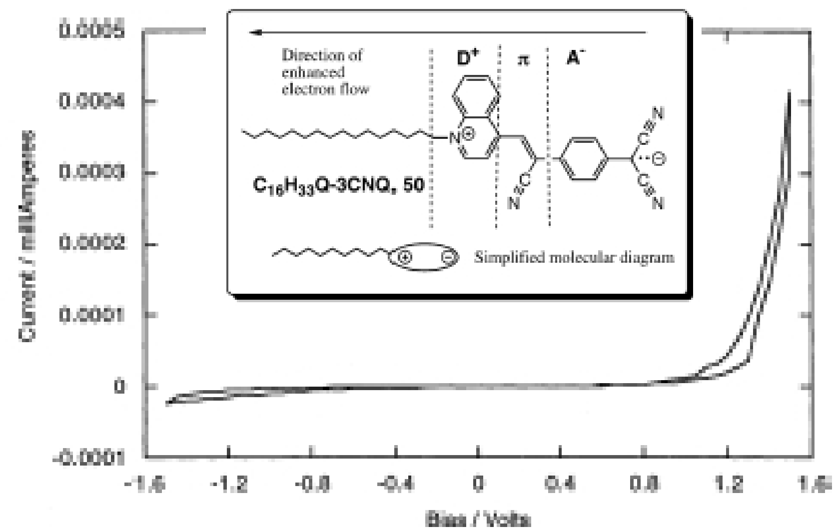
(Chem. Phys. Lett., 1974)

"The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor pi system and an acceptor pi system, separated by a sigma-bonded (methylene) tunneling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear."

(... 23 years later)

R. Metzger et al., JACS 1997

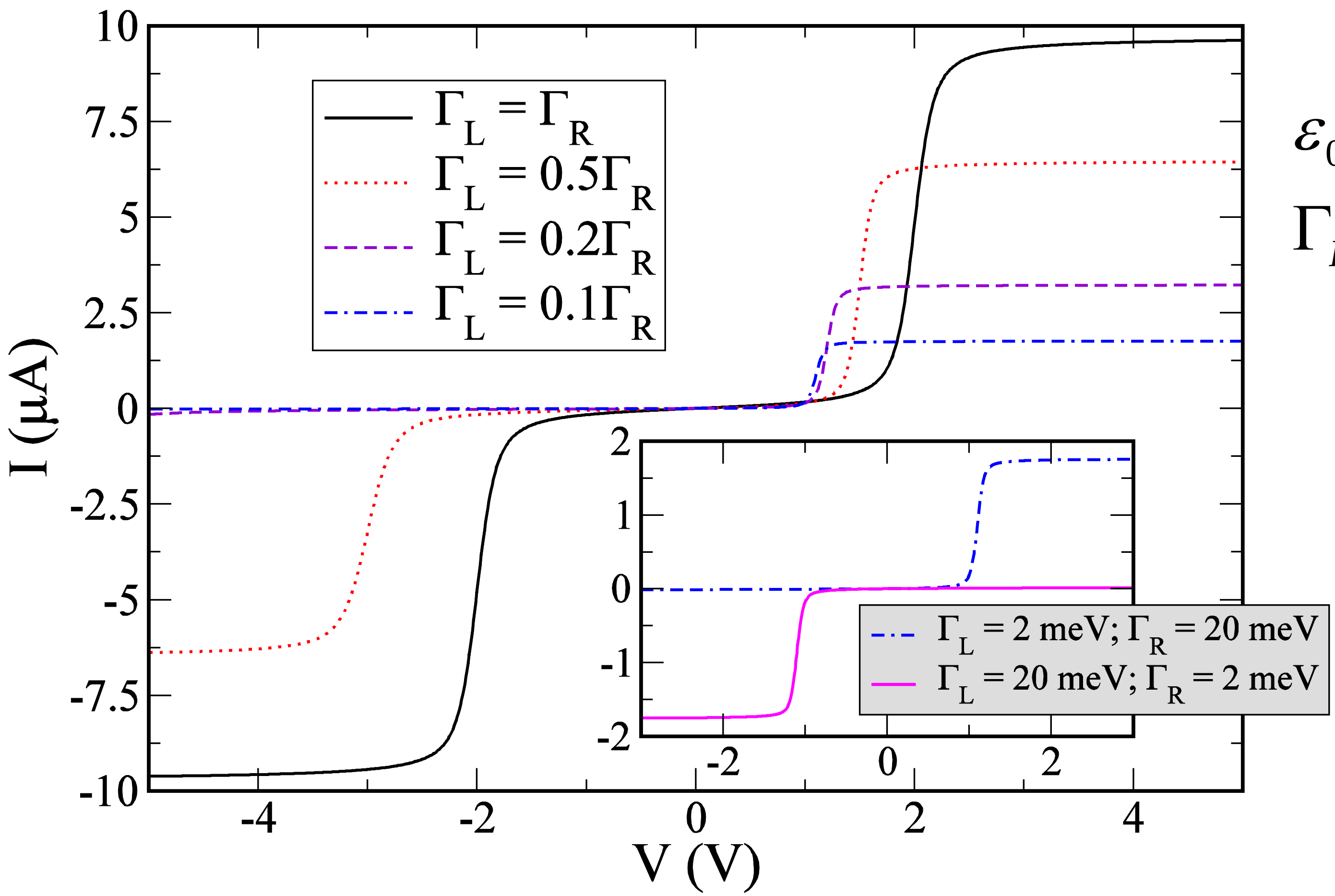




7.2.2.4 Symmetry of the I-V curves

Single-level model: asymmetric coupling

$$\varepsilon_0(V) = \varepsilon_0 + \left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R}\right)\frac{eV}{2}$$



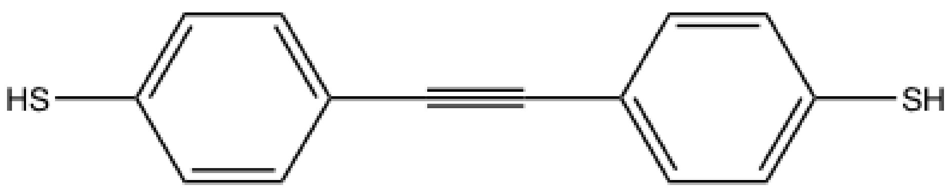
$\varepsilon_0 = 1\,\mathrm{eV}$

$\Gamma_R = 20\,\mathrm{meV}$

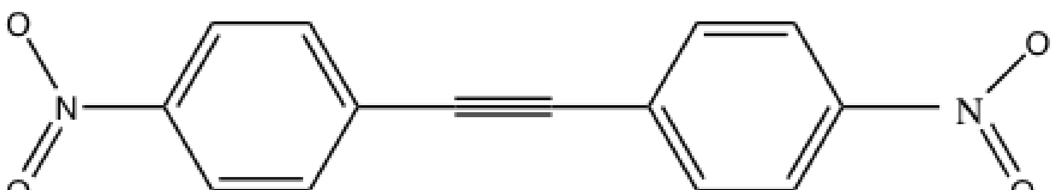
7.2.2.5 The resonant tunneling model at work

L.A. Zotti, T. Kirchner, JCC, F. Pauly, T. Huhn, E. Scheer, A. Erbe, Small **6**, *1529 (2010).*

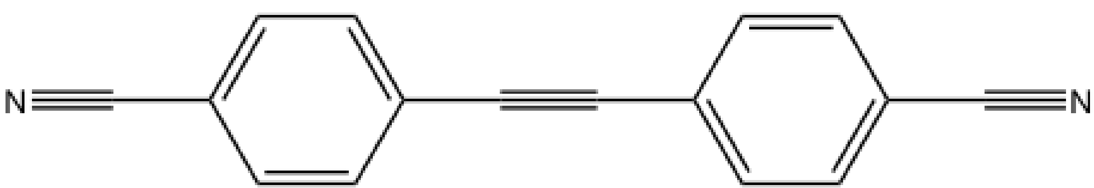
- Basic molecule: Bis-tolane
- Conjugated => conductive
- Change of linker groups



BTT: Bis-thiotolane



BNT: Bis-nitrotolane

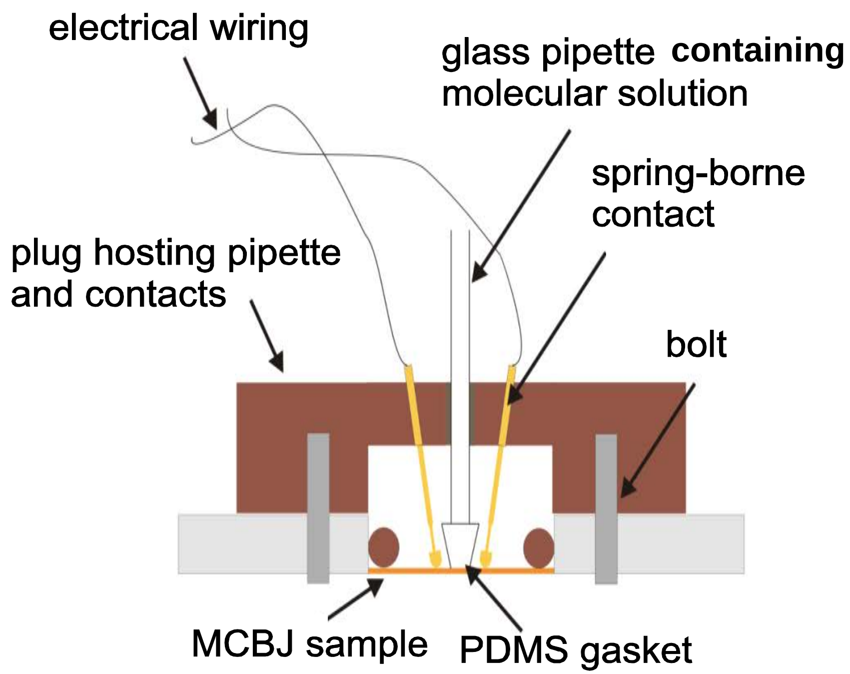


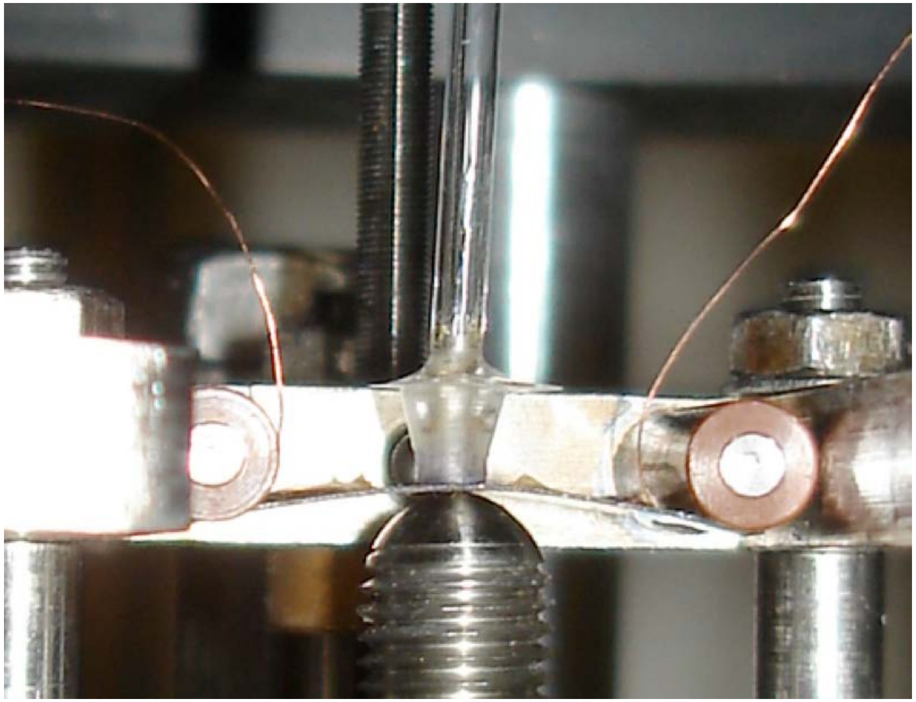
BCT: Bis-cyanotolane

7.2.2.5 The resonant tunneling model at work

L.A. Zotti, T. Kirchner, JCC, F. Pauly, T. Huhn, E. Scheer, A. Erbe, Small **6**, *1529 (2010).*

Characterization of molecules in liquid environment





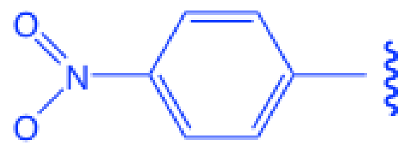
See also: L. Grüter et al., Small **1**, 1067 (2005)

7.2.2.5 The resonant tunneling model at work

L.A. Zotti, T. Kirchner, JCC, F. Pauly, T. Huhn, E. Scheer, A. Erbe, Small ***6***, *1529 (2010).*

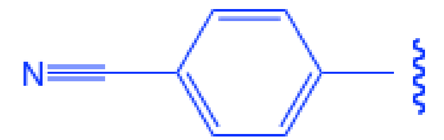
IV curves with various linkers

Nitro

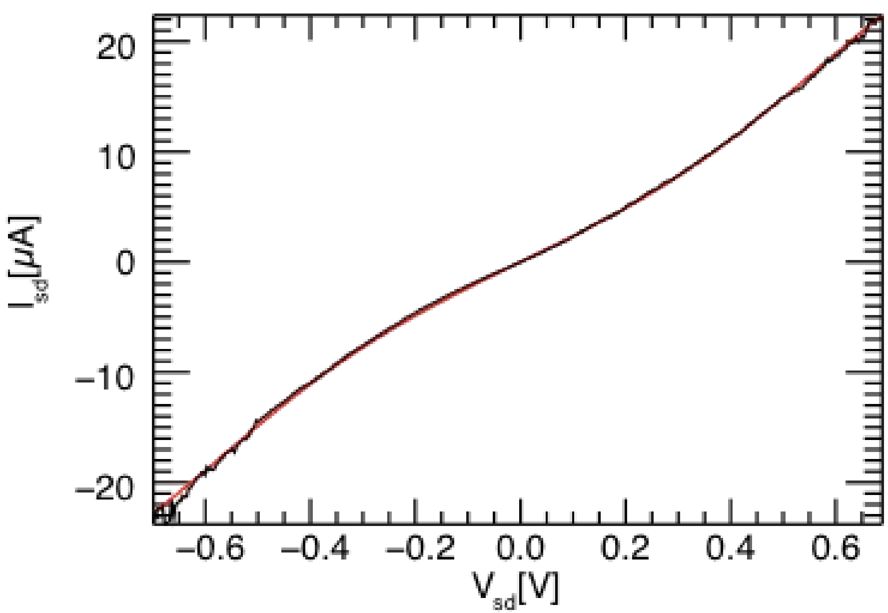


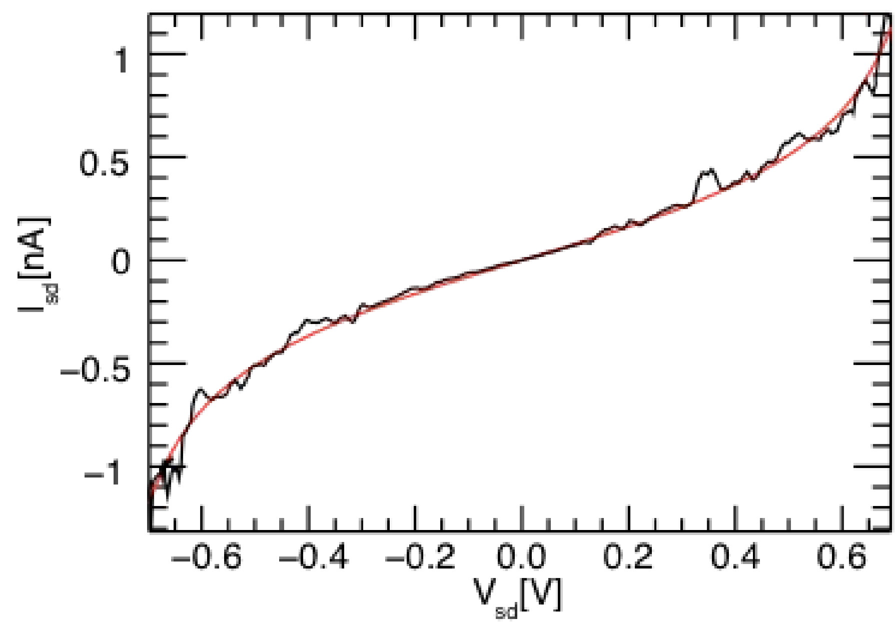
$$\Gamma_L = \Gamma_R = 0.094\text{eV}$$
$$E_0 = 0.29\text{eV}$$

Cyano



$$\Gamma_L = \Gamma_R = 0.85\text{meV}$$
$$E_0 = 0.54\text{eV}$$



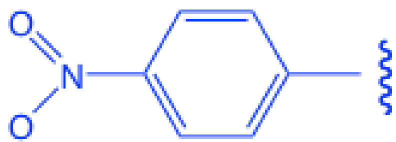


7.2.2.5 The resonant tunneling model at work

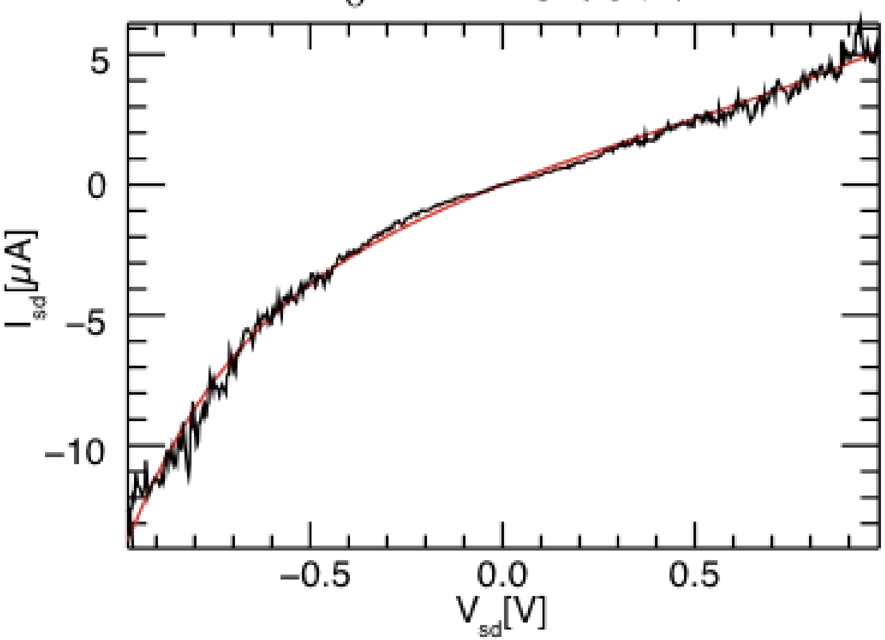
L.A. Zotti, T. Kirchner, JCC, F. Pauly, T. Huhn, E. Scheer, A. Erbe, Small **6**, *1529 (2010).*

Asymmetric coupling

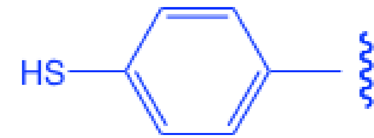
Nitro



$$
\begin{aligned}
\Gamma_L &= 0.13\mathrm{eV} \\
\Gamma_R &= 0.09\mathrm{eV} \\
E_0 &= 0.79\mathrm{eV}
\end{aligned}
$$

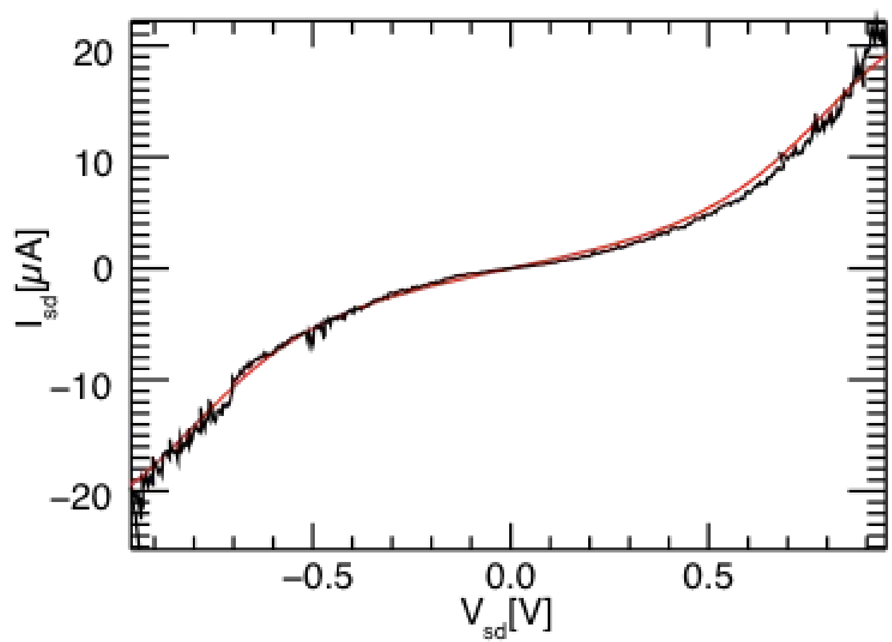


Comparison to thiol



✓ symmetric curves

$$
\begin{aligned}
\Gamma_L = \Gamma_R &= 0.065\mathrm{eV} \\
E_0 &= 0.4\mathrm{eV}
\end{aligned}
$$

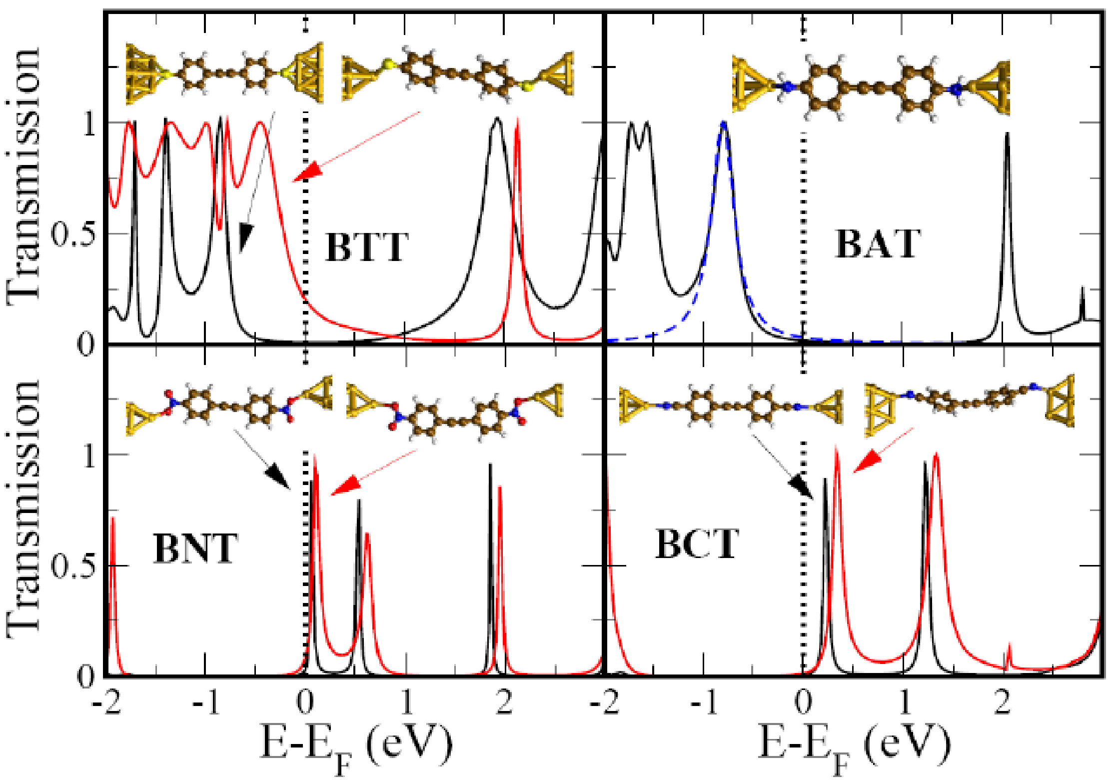


7.2.2.5 The resonant tunneling model at work

L.A. Zotti, T. Kirchner, JCC, F. Pauly, T. Huhn, E. Scheer, A. Erbe, Small **6**, *1529 (2010).*

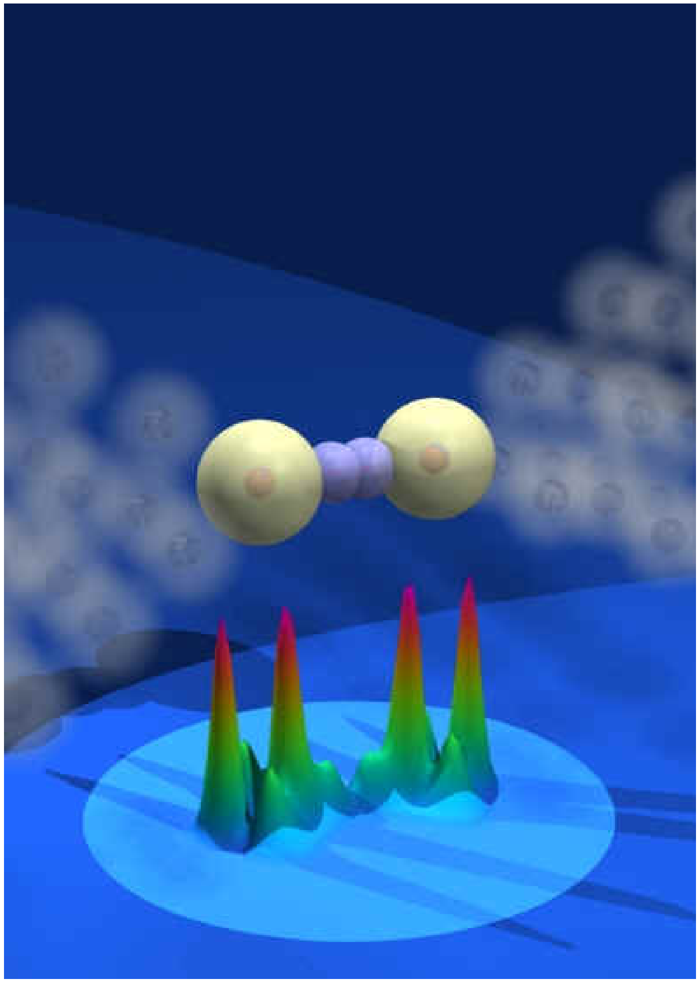
Transmission function of molecular junctions

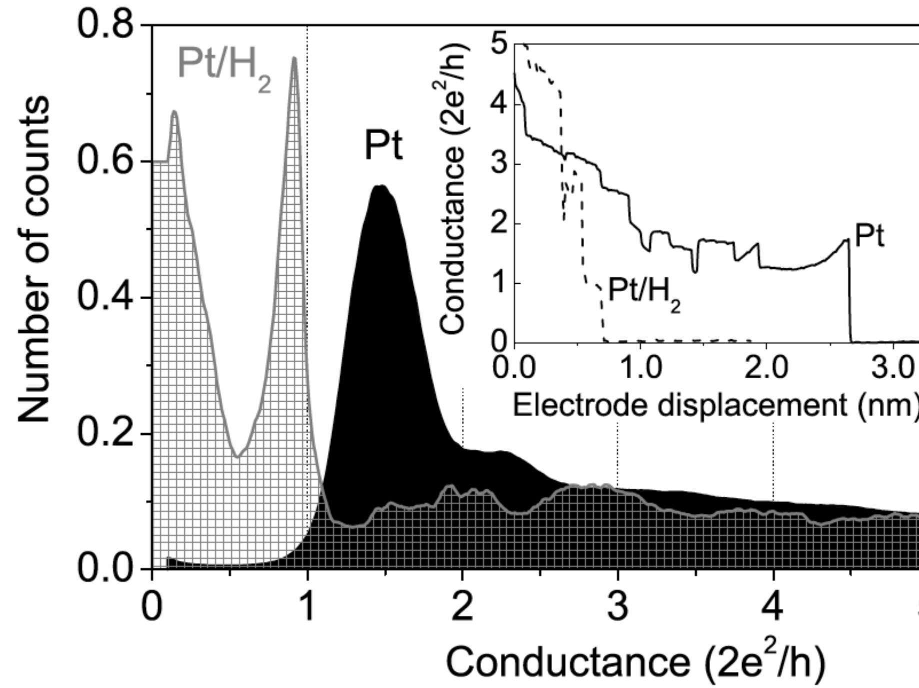
- Quantum chemistry & DFT
- Approximation to single Lorentzian valid
- Linkers determine nature of transport
- BTT & BAT: HOMO
- BNT & BCT: LUMO



7.2.3 Two-level model: Conductance of a hydrogen molecule

R.H.M. Smit, Y. Noat, C. Untiedt, N.D. Lang, M.C. van Hemert, J.M. van Ruitenbeek, Nature ***419****, 906 (2002)*

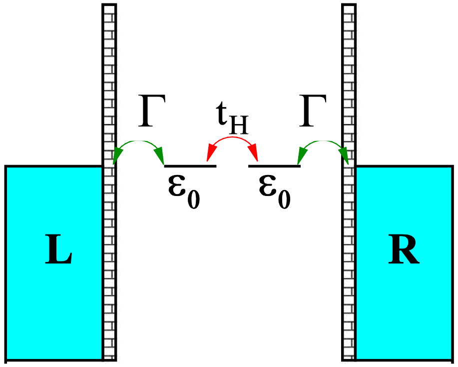




- The hydrogen molecule forms a stable bridge between Pt electrodes.
- The conductance is $G \sim G_0$ and it is largely dominated by a single conduction channel.

7.2.3 Two-level model

- **Derivation of the expression of the transmission through a hydrogen molecule.**



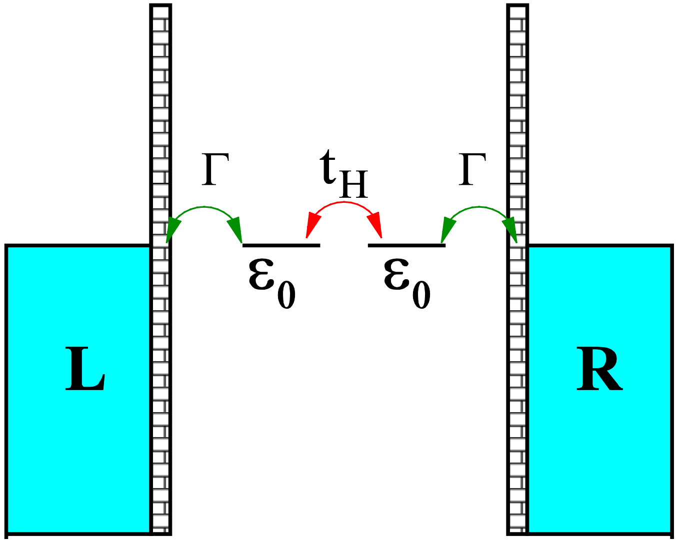
- Hamiltonian: $H_{CC} = \begin{pmatrix} \varepsilon_0 & t_H \\ t_H & \varepsilon_0 \end{pmatrix}$
- Self-energies: $\Sigma_L^a = \begin{pmatrix} i\Gamma_L & 0 \\ 0 & 0 \end{pmatrix}$; $\Sigma_R^a = \begin{pmatrix} 0 & 0 \\ 0 & i\Gamma_R \end{pmatrix}$
- Scattering rates: $\Gamma_{L,R} = \mathrm{Im}(\Sigma_{L,R}^a)$
- Green's functions: $G_{CC}^{r,a}(E) = \left[(E \pm i\eta)1 - H_{CC} - \Sigma_L^{r,a} - \Sigma_R^{r,a}\right]^{-1}$

Transmission

$$T(E) = 4\mathrm{Tr}\left[\Gamma_L(E)G_{CC}^r(E)\Gamma_R(E)G_{CC}^a(E)\right] = \frac{4\Gamma^2 t_H^2}{[(E-\varepsilon_+)^2+\Gamma^2][(E-\varepsilon_-)^2+\Gamma^2]}$$

where $\varepsilon_\pm = \varepsilon_0 \pm t_H$ (bonding and anti-bonding states).

7.2.3 Two-level model

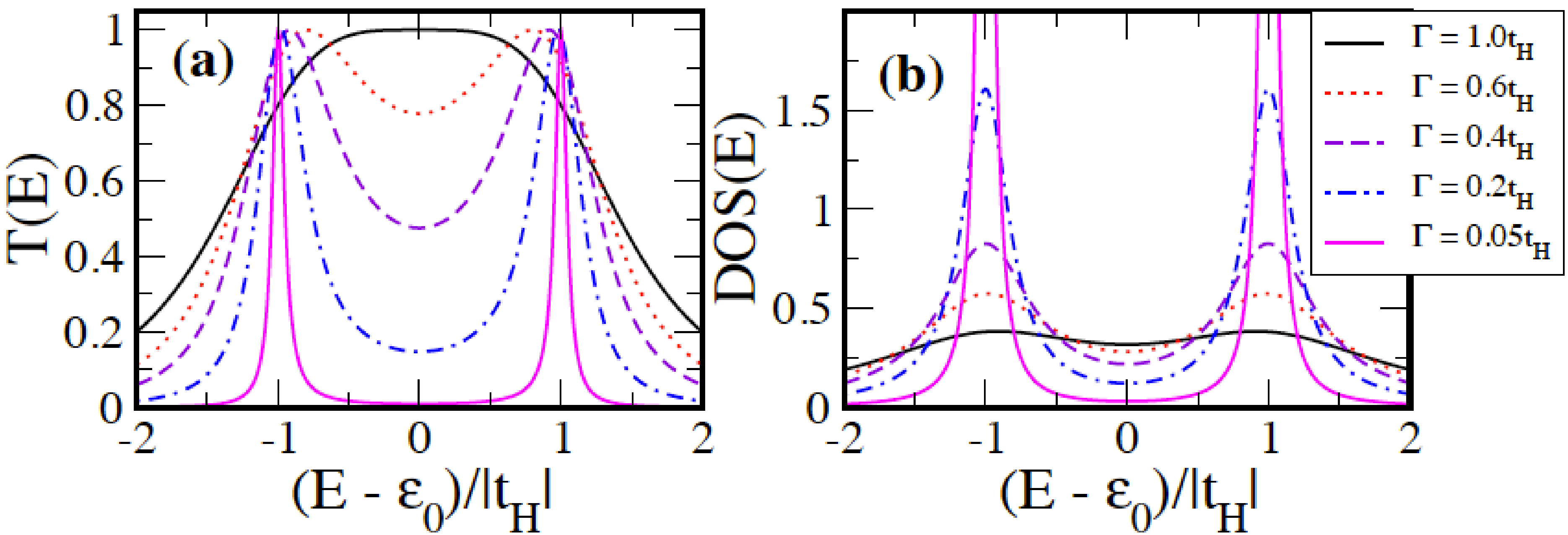


Bonding and antibonding states:

$$\varepsilon_{\pm} = \varepsilon_0 \pm t_H$$

Transmission:

$$T(E) = \frac{4\Gamma^2 t_H^2}{[(E-\varepsilon_+)^2+\Gamma^2][(E-\varepsilon_-)^2+\Gamma^2]}$$

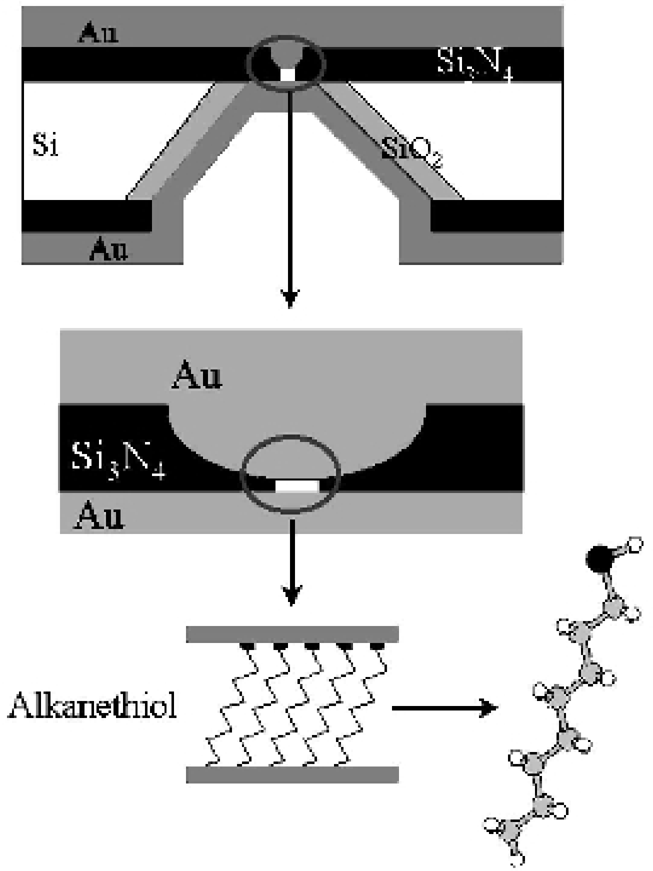


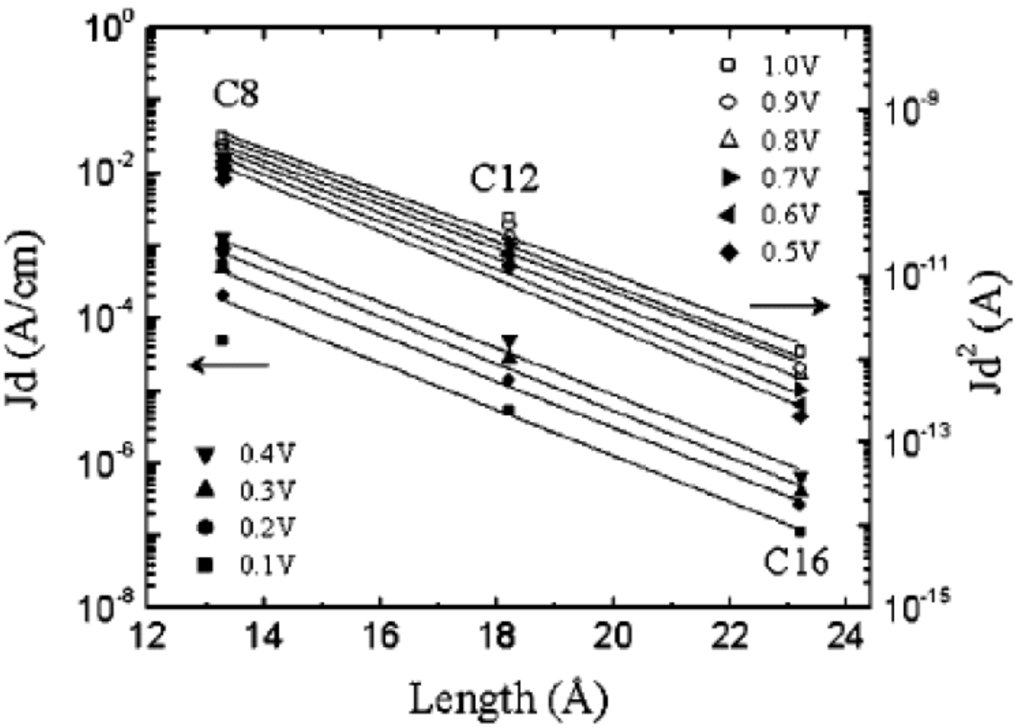
7.2.4 Length dependence of conductance

Wang, Lee and Reed,
Phys. Rev. B 68, 035416 (2003)

The conductance often decays exponentially with the length of the molecule

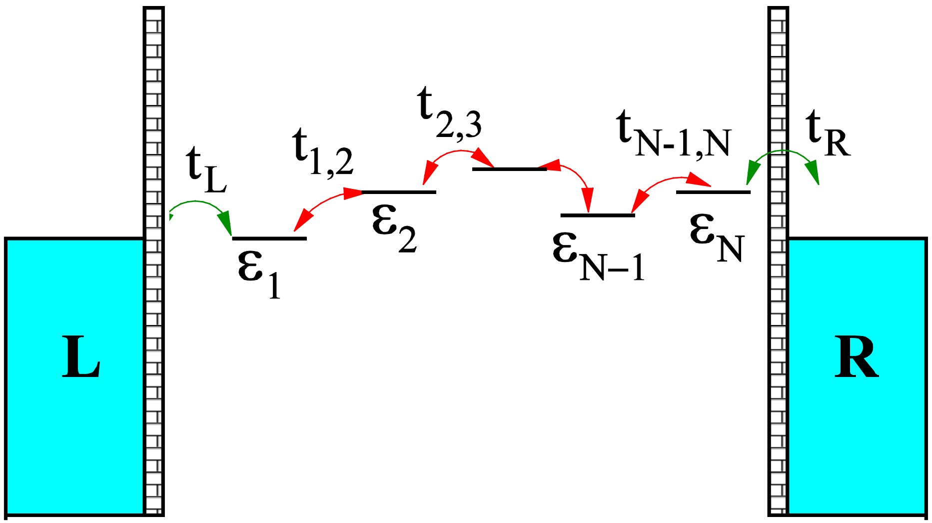
$$G = G_0 e^{-\beta d}$$





Typical values of β range from 2-4 nm^{-1} for conjugated molecules to 8-12 nm^{-1} for non-aromatic compounds.

7.2.4 Length dependence of conductance



$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} dE\,T(E,V)\left[f_L - f_R\right]$$

$$G = \frac{2e^2}{h}T(E_F)$$

$$T(E) = 4\Gamma_L\Gamma_R\left|G_{1N}(E)\right|^2$$

Off-resonant tunneling: $\max(t_{i,i+1}) << \min(|E-\varepsilon_i|) \Rightarrow G_{1N} \approx \frac{1}{E-\varepsilon_N}\prod_{i=1}^{N-1}\frac{t_{i,i+1}}{E-\varepsilon_i}$

homogeneous bridge: $t_{i,i+1} = t$ and $\varepsilon_i = \varepsilon$

$$\Rightarrow T(E) \approx \frac{4\Gamma_L\Gamma_R}{|t|^2}\left|\frac{t}{E-\varepsilon}\right|^{2N} \propto e^{-\beta(E)L}$$

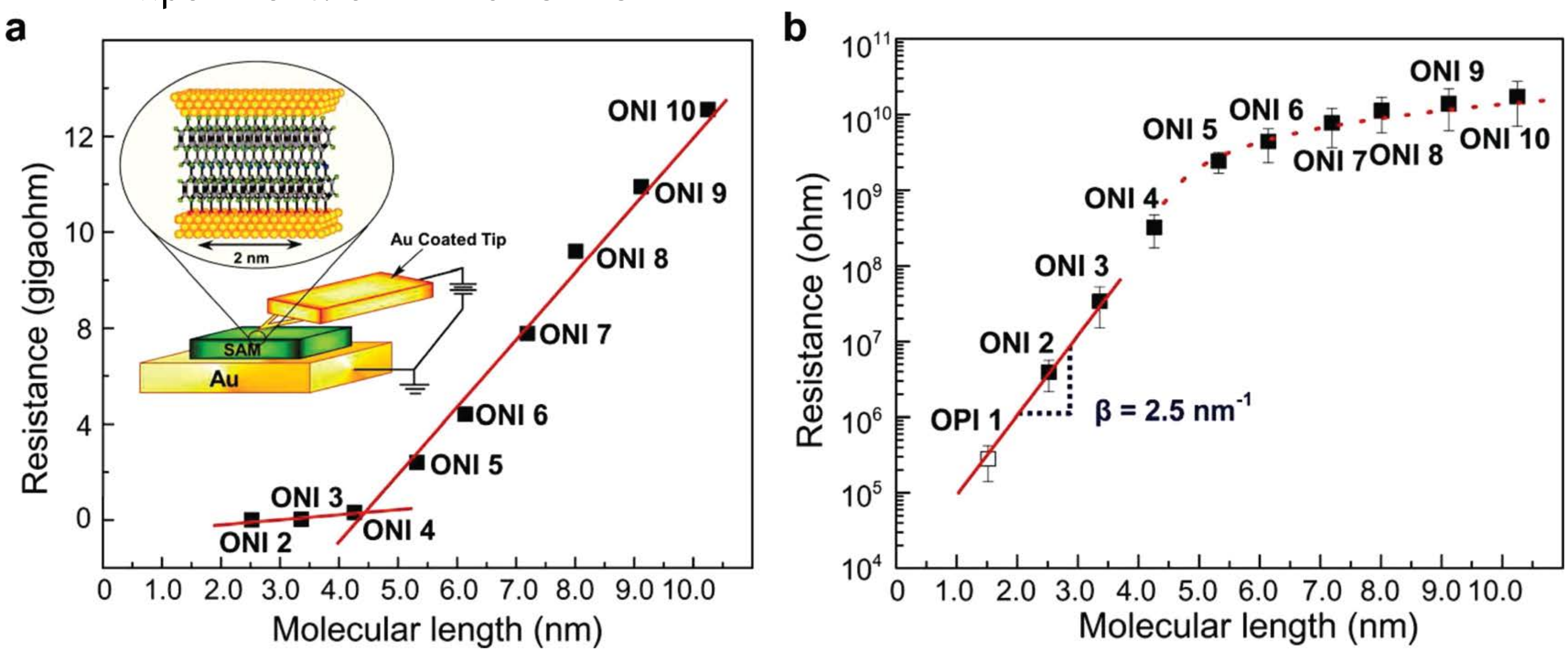
$$\beta(E) = \frac{2}{a}\ln\left|\frac{E-\varepsilon}{t}\right|$$

a* = lattice constant; *Na* = *L

7.2.4 Transition to hopping transport

Y. S. H. Choi, C. Risko, M. C. Ruiz Delgado, B.S. Kim, J.-L. Brédas, C. D. Frisbie , J. Am. Chem. Soc. 132, 4358 (2010)

Experiment: CP-AFM on SAMS



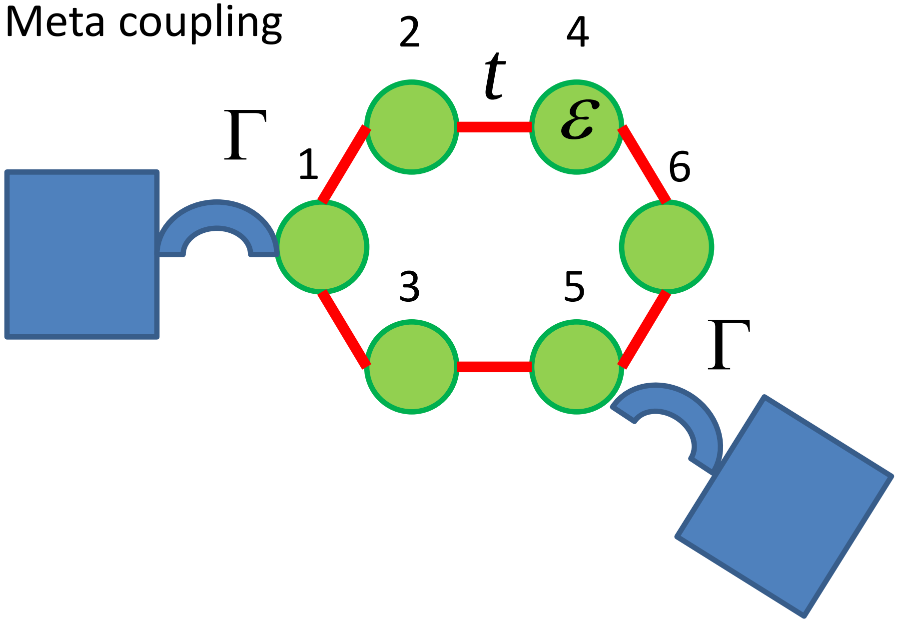
Non-resonant tunneling:
$G=G_{0c}\, e^{-\beta N}$ (at linear response)
β given by level alignment and conjugation

Hopping: linear length dependence as in Ohm‘s law

Observation: Transition from exponential length dependence to linear one

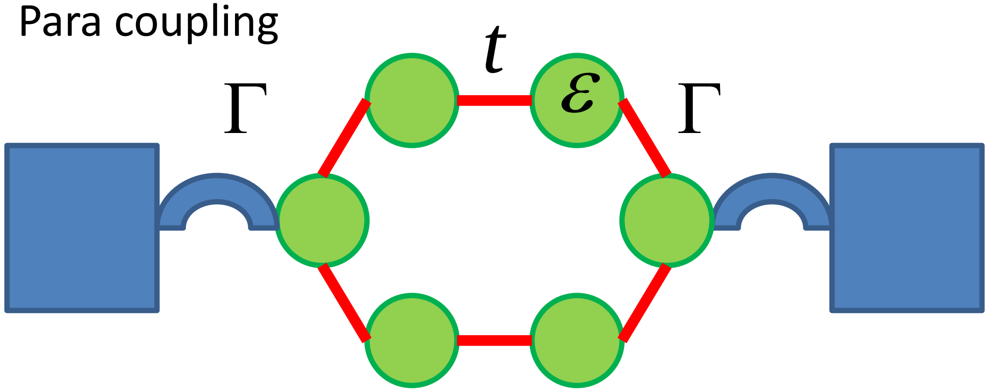
7.2.5 Destructive quantum interference

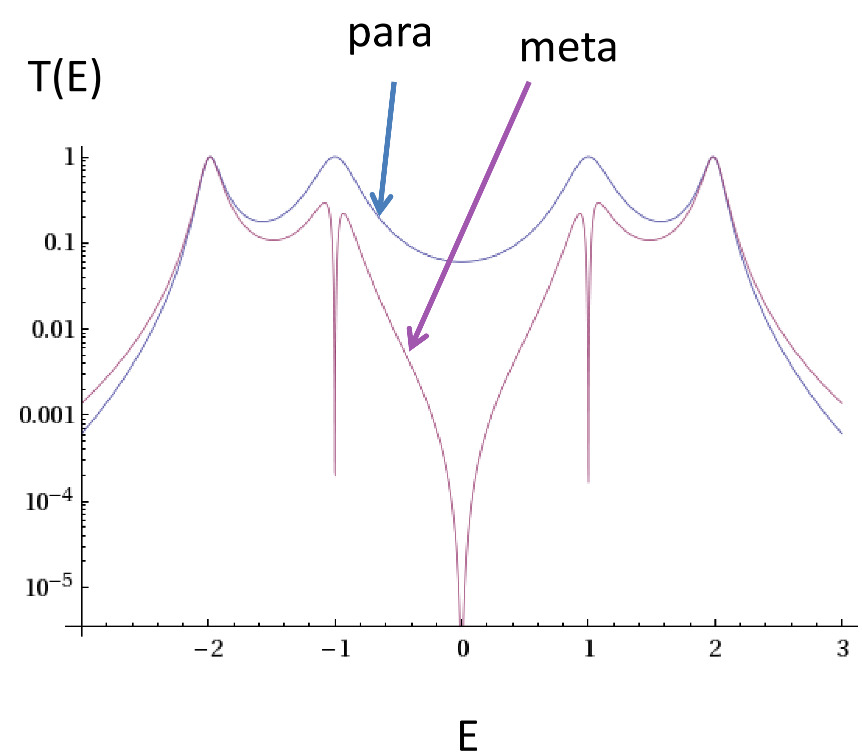
Meta coupling



$$H = \begin{pmatrix} \varepsilon & t & t & 0 & 0 & 0 \\ t & \varepsilon & 0 & t & 0 & 0 \\ t & 0 & \varepsilon & 0 & t & 0 \\ 0 & t & 0 & \varepsilon & 0 & t \\ 0 & 0 & t & 0 & \varepsilon & t \\ 0 & 0 & 0 & t & t & \varepsilon \end{pmatrix}$$

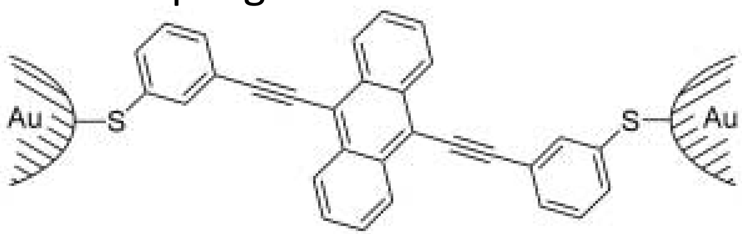
Para coupling





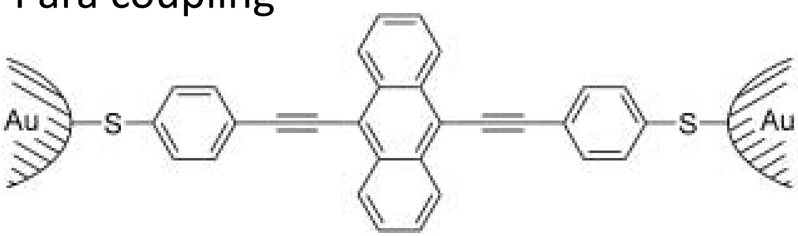
7.2.5 Destructive quantum interference

Meta coupling



1'

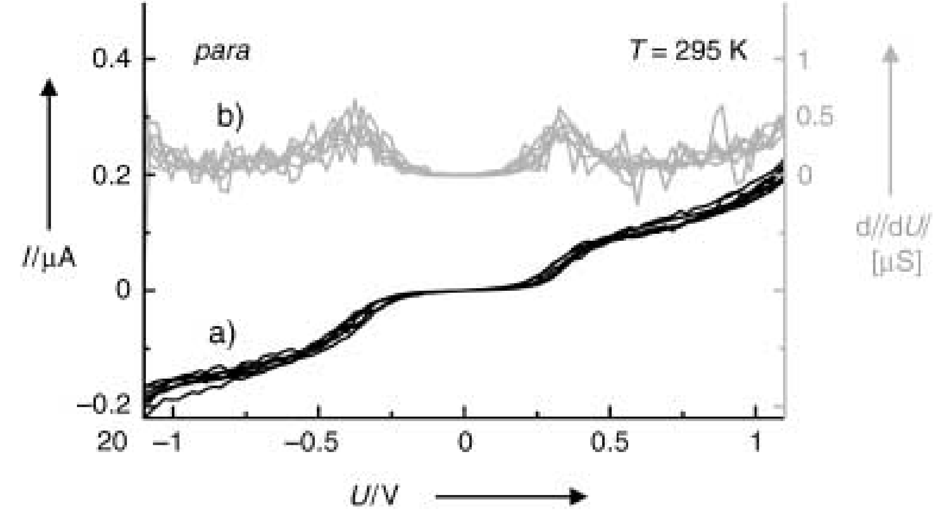
Para coupling

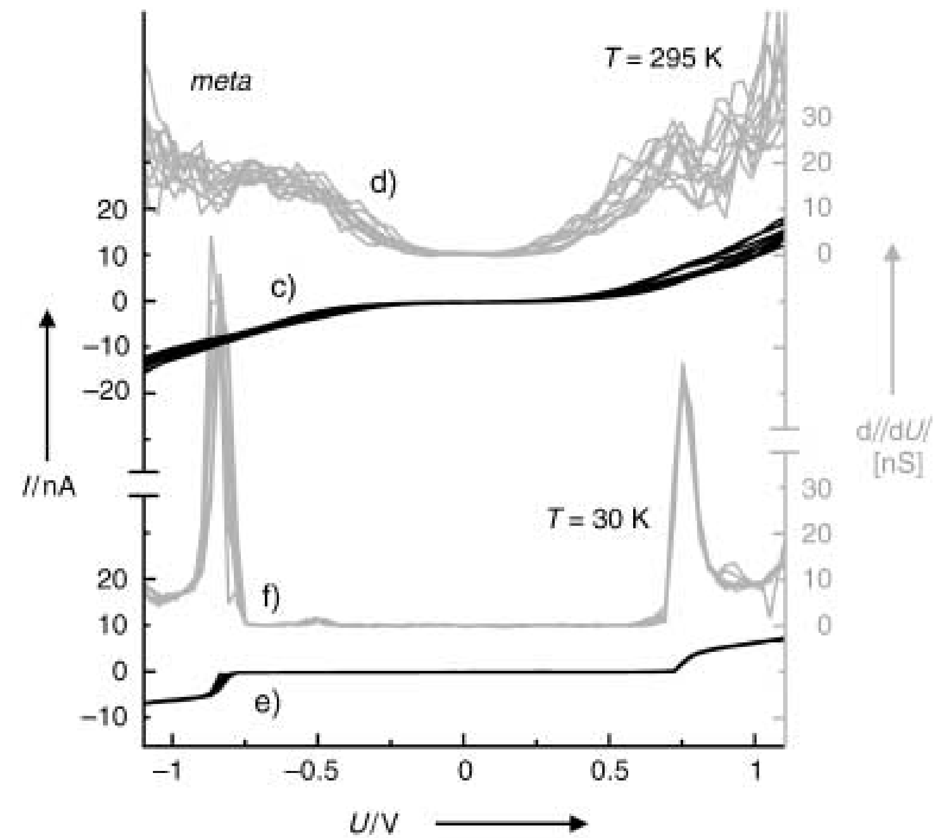


2'

- Suppression of current in meta (1') as compared to para (2') coupling

M. Mayor M et al., Angew. Chem. Int. Ed. **42**, 5834 (2003)





7.2.5 Destructive quantum interference

Recent measurements of conductance and force:
S. V. Aradhya et al., Nano Lett. 12, 1643 (2012)

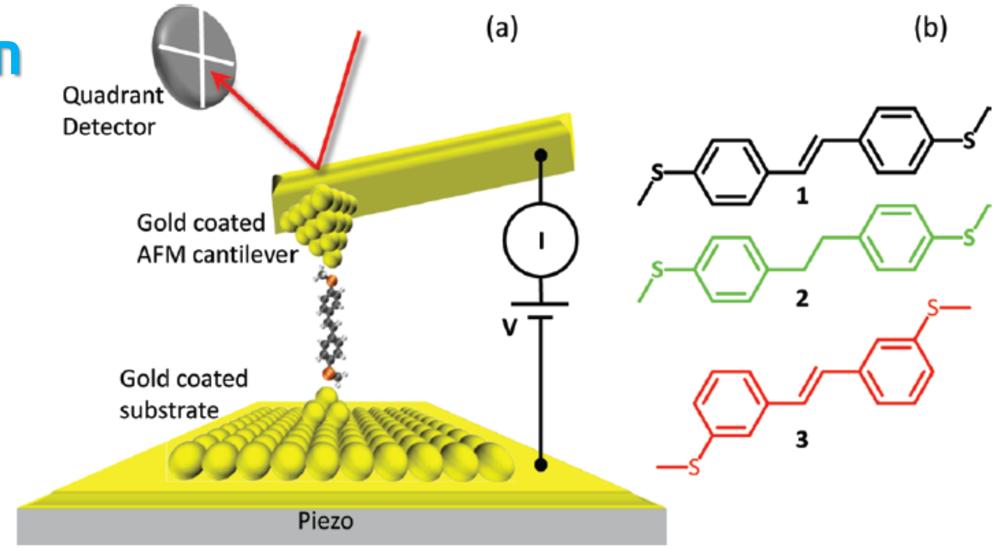


Figure 1. (a) Schematic of AFM apparatus and (b) chemical structures of molecules **1**–**3**.

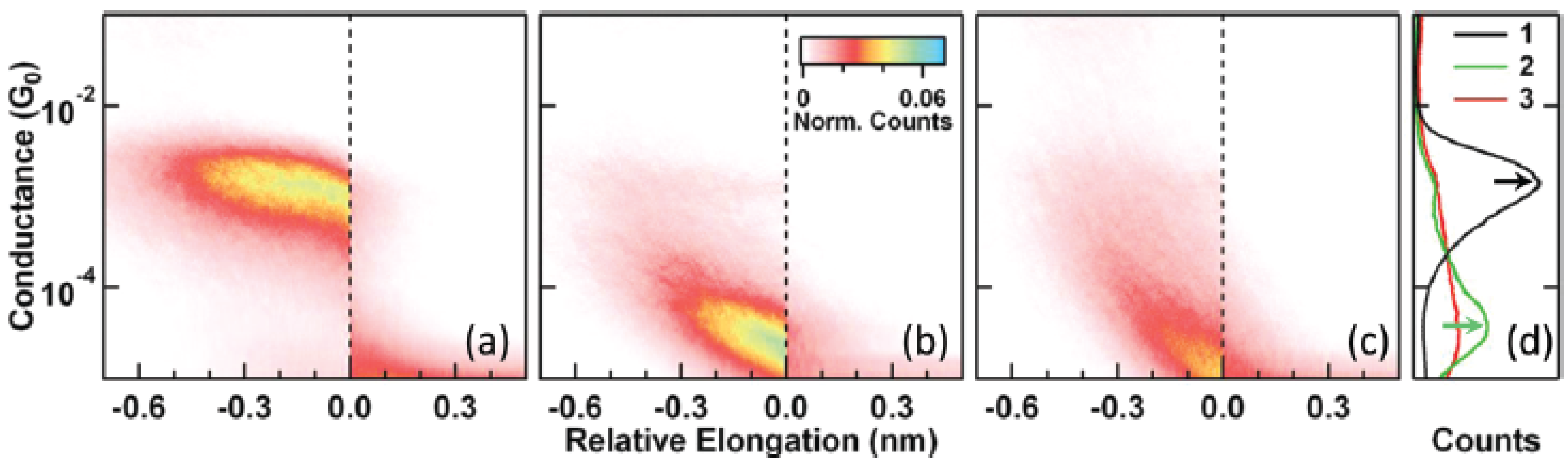
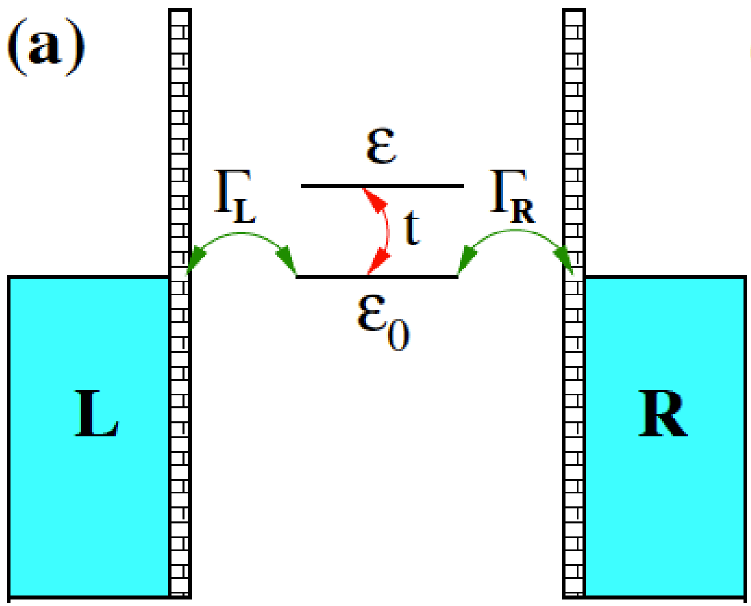
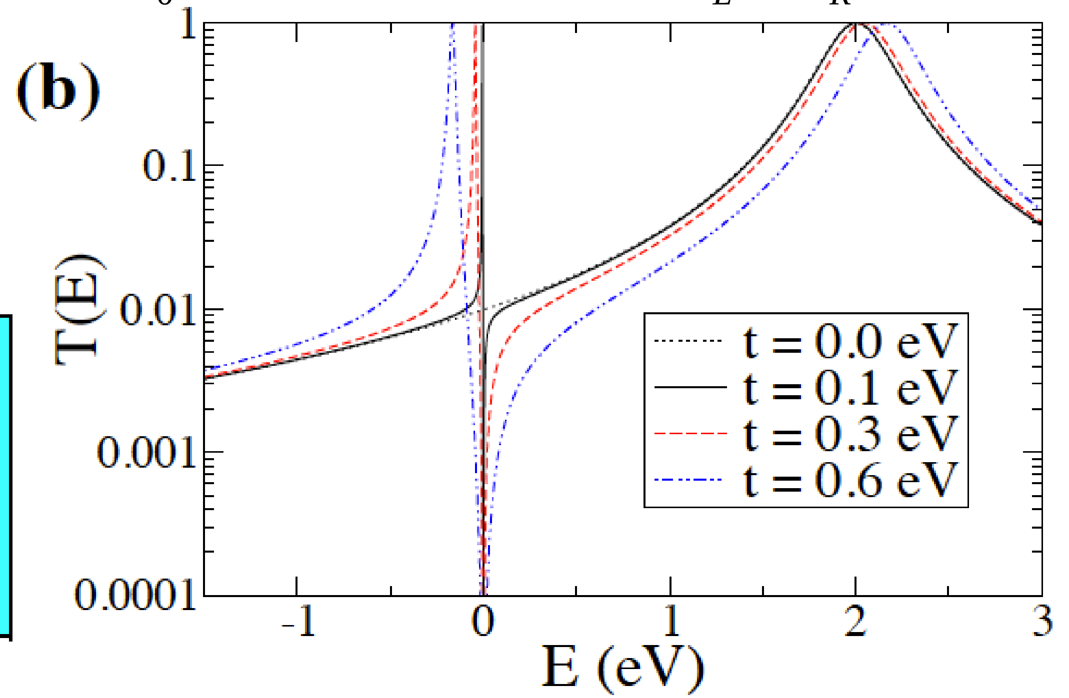


Figure 3. Displacement-preserving 2D conductance histograms (a, b, c) for **1**, **2**, and **3**, respectively, and profiles of conductance before rupture (d). The histograms represent more than 85% of the 7000 measured traces that show a significant force event beyond Au rupture in each case. The abrupt jump in conductance at the displacement origin (dashed vertical lines provided as a visual guide) for **1** and **2** shows that bond rupture coincides with conductance drops. Arrows indicate the most frequently measured conductance value from the conductance profiles of **1** and **2**.

7.2.7 Fano resonances



$$\varepsilon_0 = 2 \text{ eV};\ \varepsilon = 0.0 \text{ eV};\ \Gamma_L = \Gamma_R = 0.1 \text{ eV}$$



$$T(E) = \frac{4\Gamma_L \Gamma_R}{\left(E - \varepsilon_0 - \dfrac{t^2}{E - \varepsilon}\right)^2 + \left(\Gamma_L + \Gamma_R\right)^2}$$

- Anti-resonance (vanishing transmission):

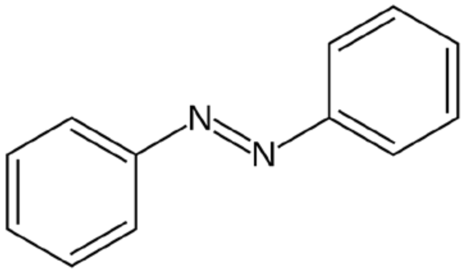
$$E = \varepsilon$$

- Transmission maxima:

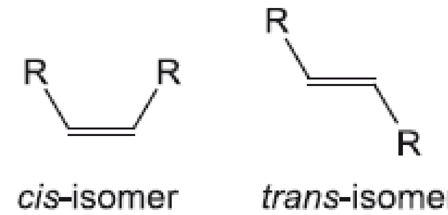
$$E = \varepsilon_\pm = \frac{1}{2}\left\{(\varepsilon + \varepsilon_0) \pm \sqrt{(\varepsilon - \varepsilon_0)^2 + 4t^2}\right\}$$

7.2.7 Fano resonances: Experiments

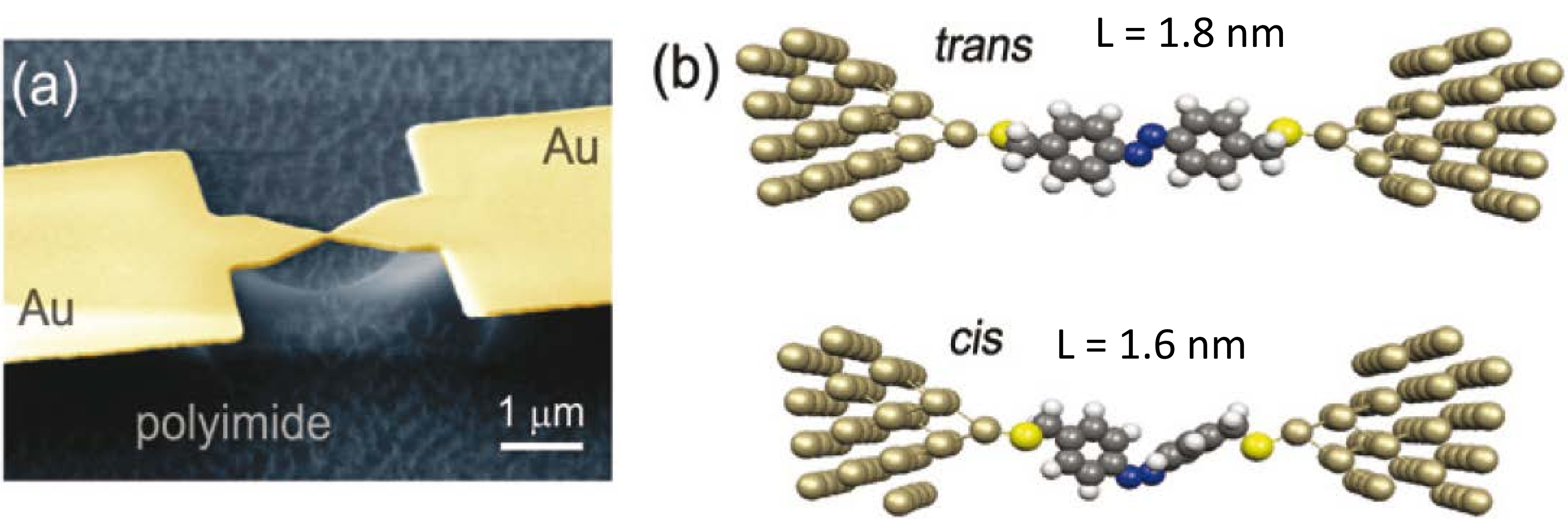
Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)



Azobenzene



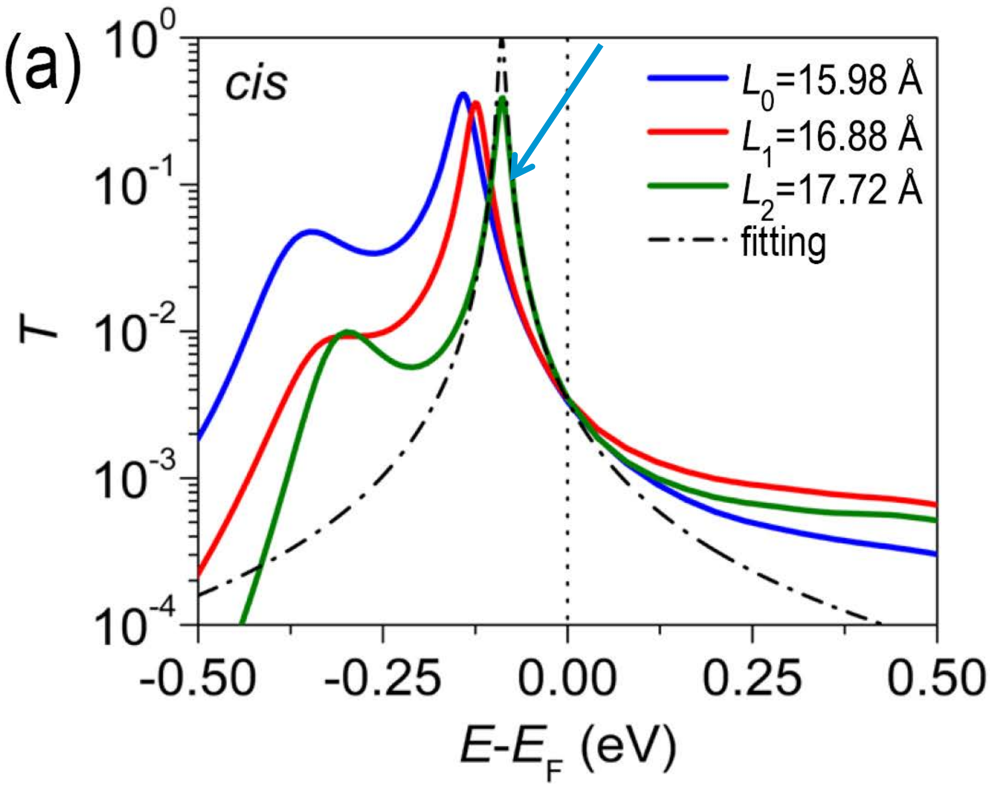
Decoupling of switching core by CH_2 group



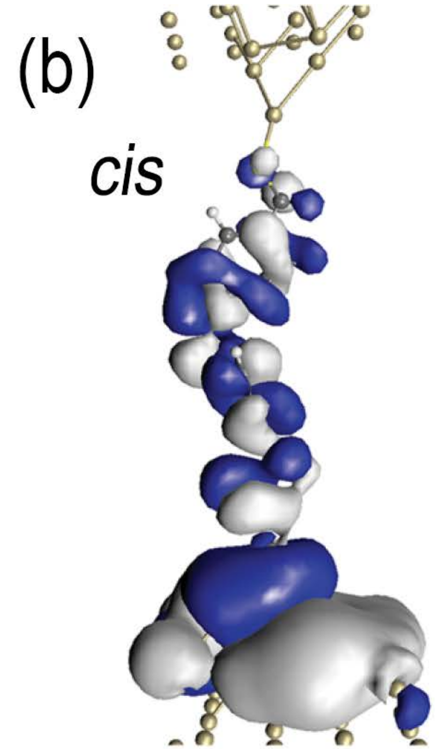
7.2.7 Fano resonances: Experiments

Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)

Transmission function



cis conformation

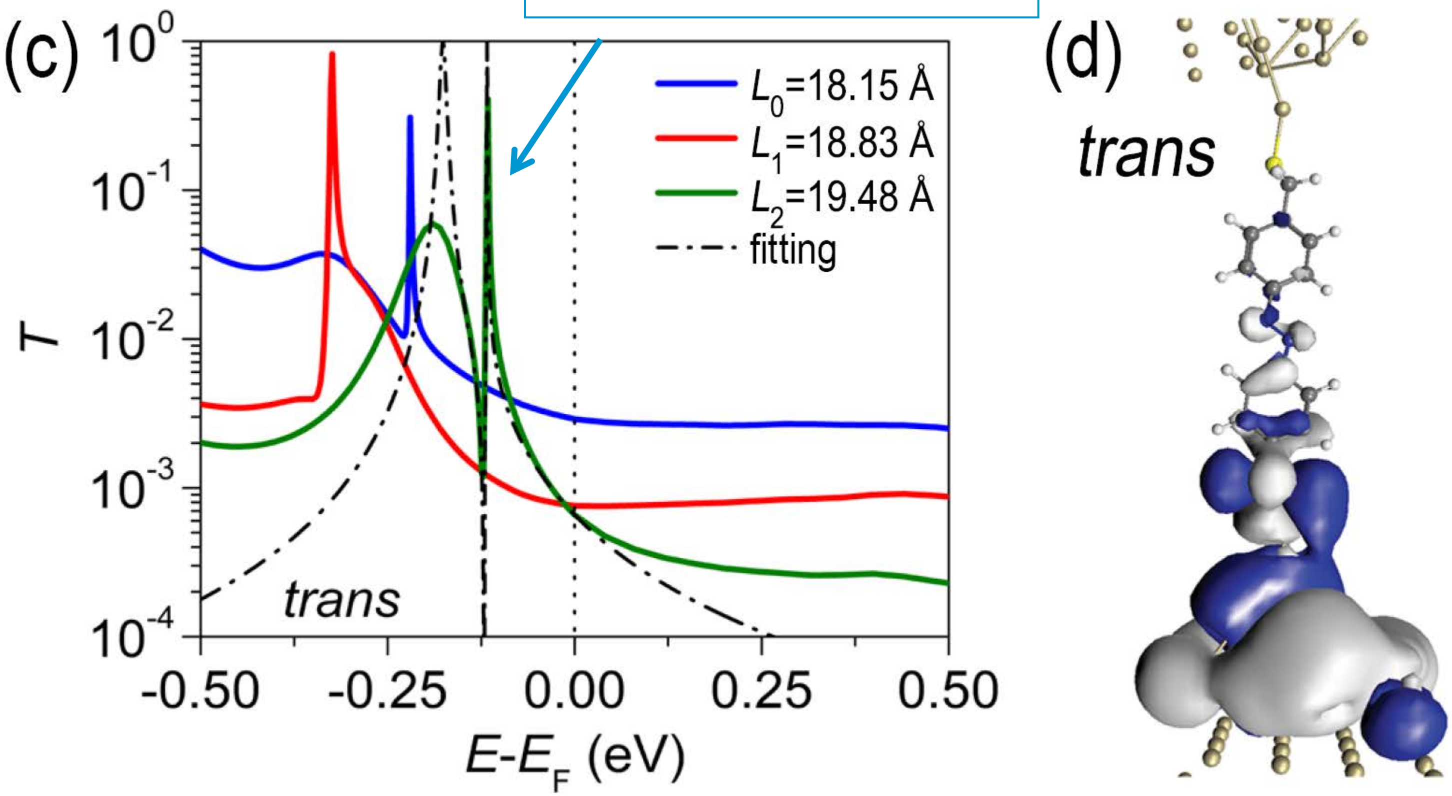


HOMO

7.2.7 Fano resonances: Experiments

Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)

HOMO localized at N-N



trans conformation

HOMO-1