Theoretical modeling and simulation of electron-phonon scattering processes in molecular electronic devices

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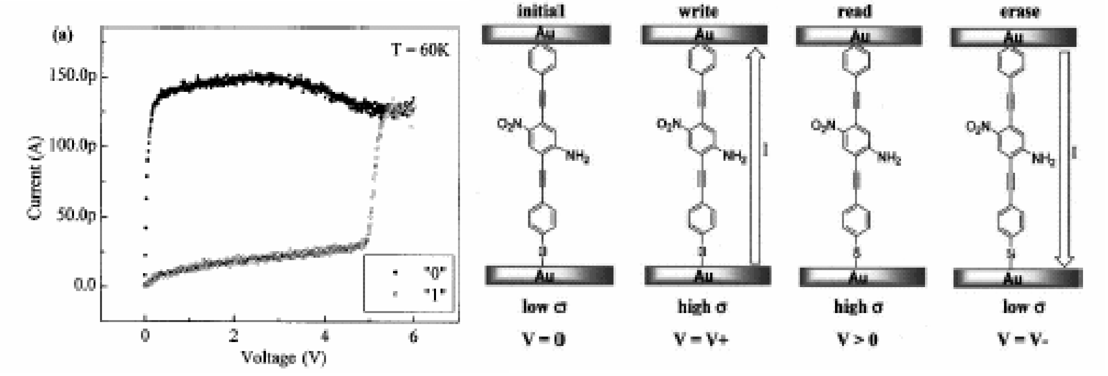
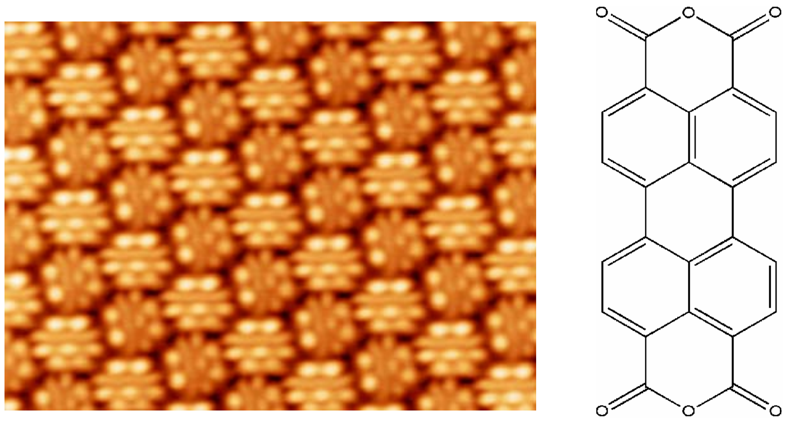
Molecular Electronics

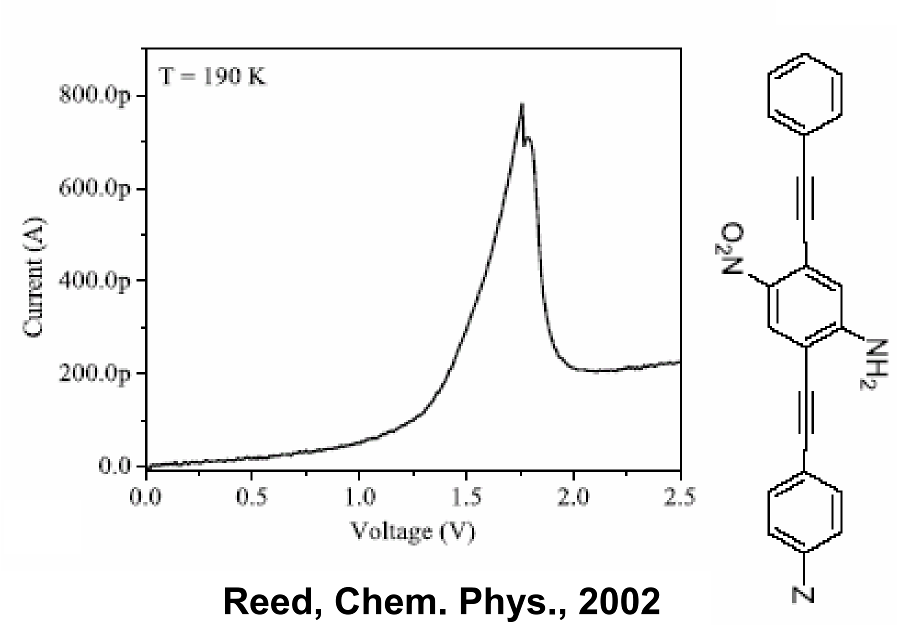


Reed, APL, 2002

- A single molecule or a single layer of molecules used as electronic switch
- Self-Assembling properties
- New electronic features

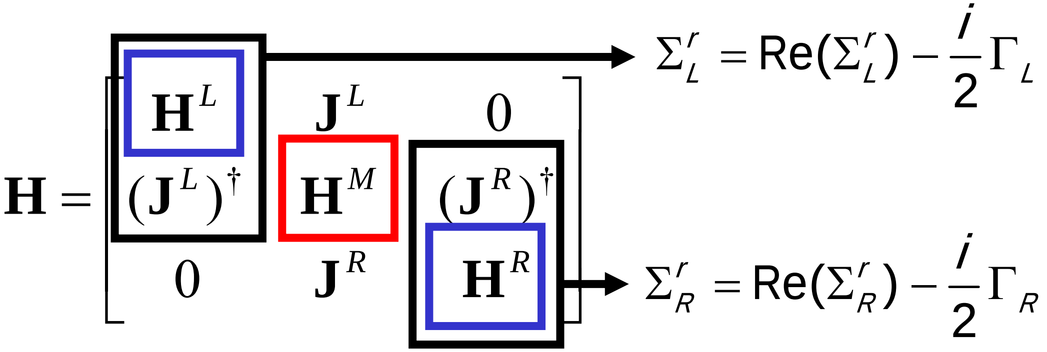


Tautz group, Jacobs Bremen University



Reed, Chem. Phys., 2002

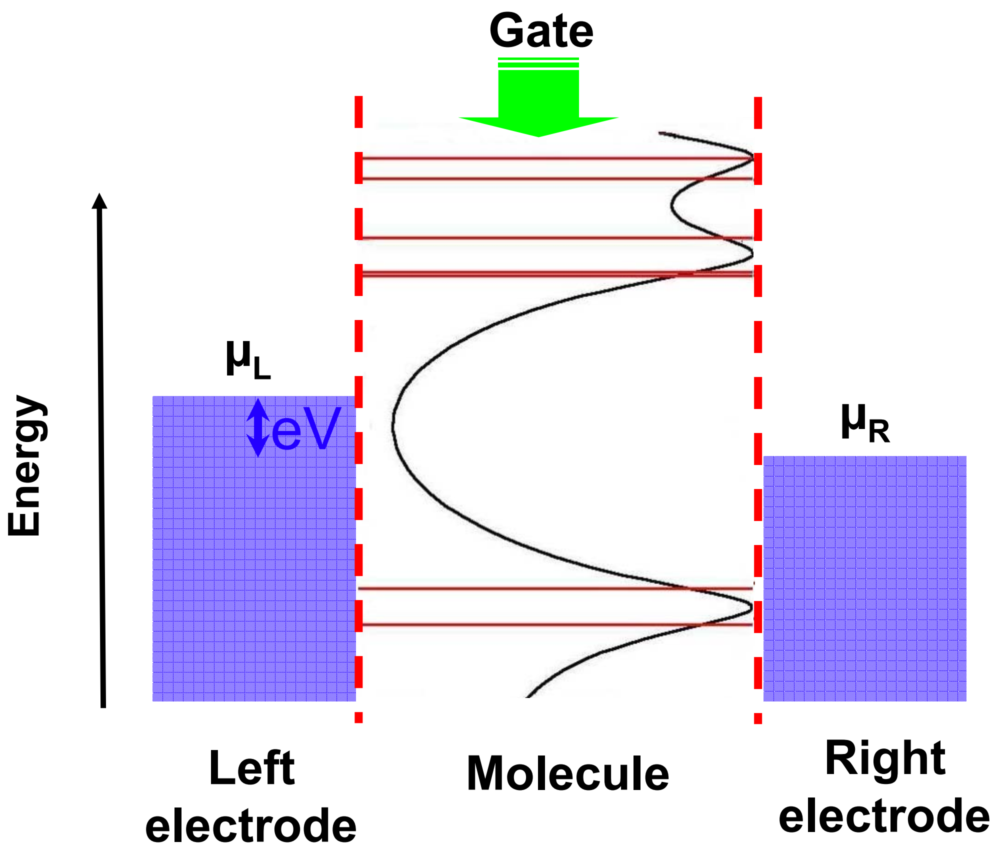
Molecular Electronics: Basic Concepts

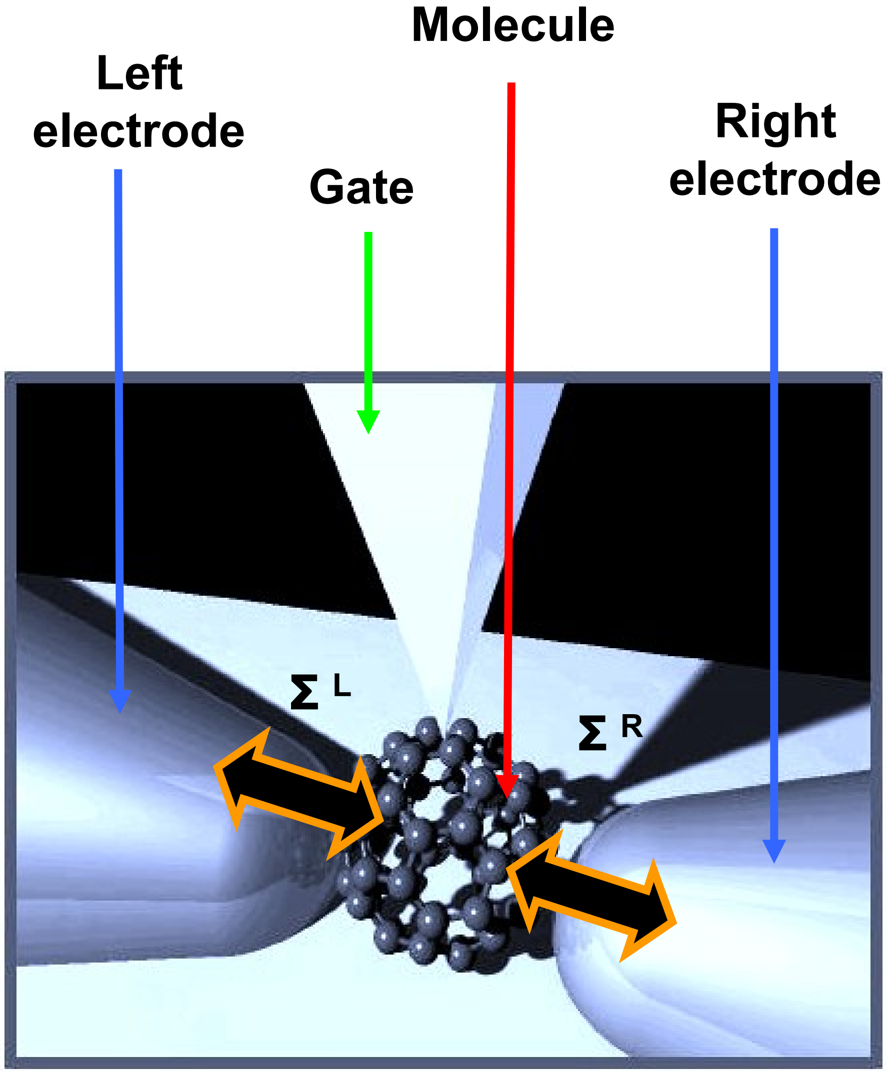


$$\mathbf{H} = \begin{bmatrix} \boxed{\mathbf{H}^L} & \mathbf{J}^L & 0 \\ (\mathbf{J}^L)^\dagger & \boxed{\mathbf{H}^M} & (\mathbf{J}^R)^\dagger \\ 0 & \mathbf{J}^R & \boxed{\mathbf{H}^R} \end{bmatrix}$$

$$\Sigma_L^r = \mathrm{Re}(\Sigma_L^r) - \frac{i}{2}\Gamma_L$$

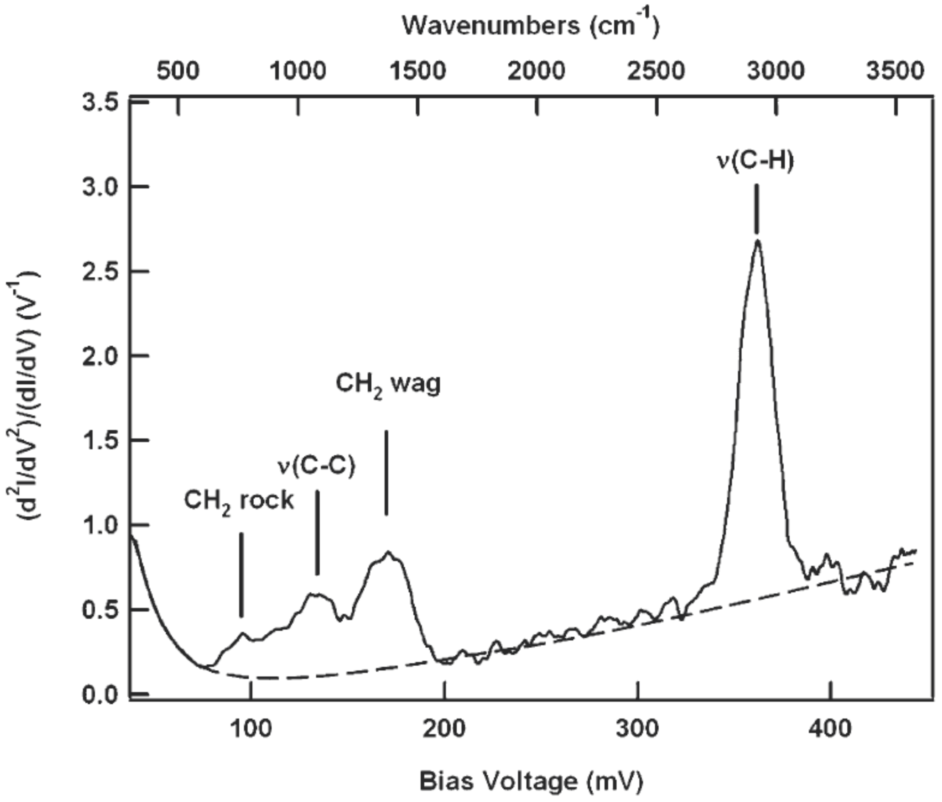
$$\Sigma_R^r = \mathrm{Re}(\Sigma_R^r) - \frac{i}{2}\Gamma_R$$

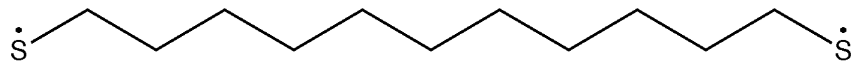




Dissipation in Molecular Electronics Experiments

Inelastic Electron Tunneling Spectroscopy

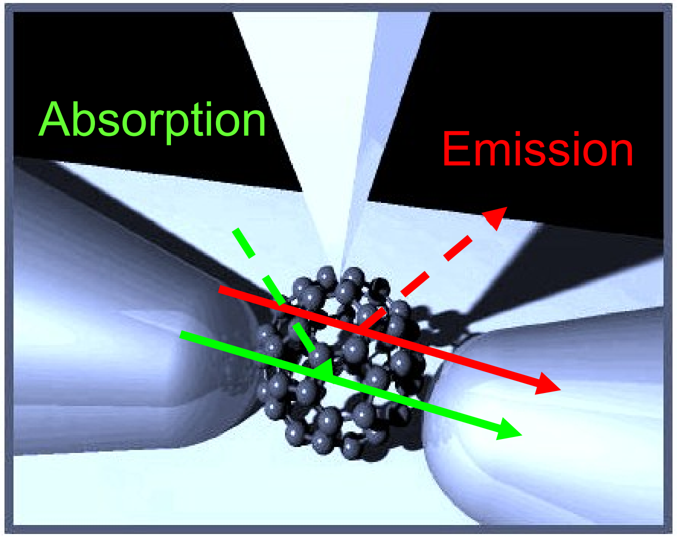




Kushmerick, Lazorcik, Patterson & Shashidhar
Nano Lett. (2004) **4** (4) 639

- Other experiments related to inelastic processes (Negative differential resistance, shot noise, etc.)
- Stability of the device

Electron-phonon coupling: M^{α}



Non-equilibrium Green’s Function: Computational Scheme

Electron propagator

$$G^{r}(E) = [E - H_{M} - \Sigma_{L}^{r} - \Sigma_{R}^{r} - \Sigma_{ph}^{r}]^{-1}$$

Electron in(out)-scattering functions

$$\Sigma^{<(>)} = \Sigma_{L}^{<(>)} + \Sigma_{R}^{<(>)} + \Sigma_{ph}^{<(>)}$$

Kinetic equation for the electronic correlation

$$G^{<(>)}(E) = G^{r}(E)\Sigma^{<(>)}(E)G^{a}(E)$$

Current: Meir-Wingreen Equation

$$I = \frac{2e}{h}\int_{-\infty}^{+\infty} Tr[\Sigma_{L}^{<}G^{>} - \Sigma_{L}^{>}G^{<}]dE$$

Electron-Phonon Couplings

$$\hat{H} + \delta\hat{H} = \sum_{\mu} \varepsilon_{\mu} c_{\mu}^{\dagger} c_{\mu} + \sum_{\mu,\nu} \sum_{\alpha} M_{\mu\nu}^{\alpha} c_{\mu}^{\dagger} c_{\nu} (a_{\alpha}^{+} + a_{\alpha})$$

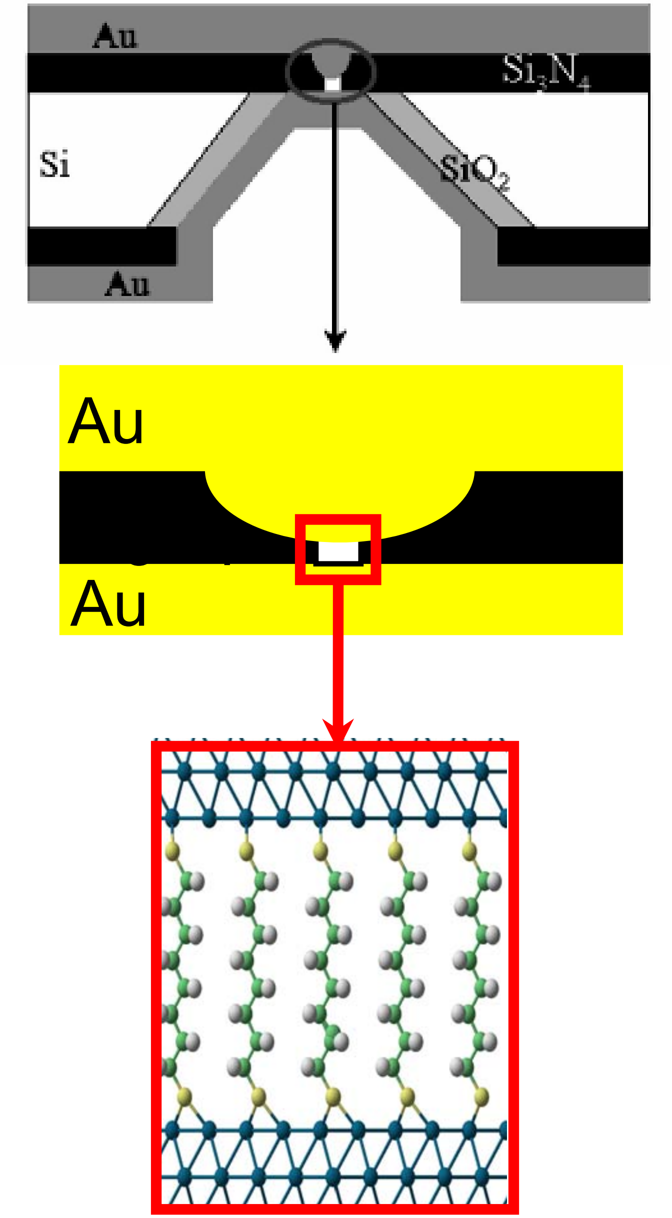
The electron-phonon coupling Hamiltonian is derived by expanding to first order the TB-Hamiltonian with respect to the atomic positions.

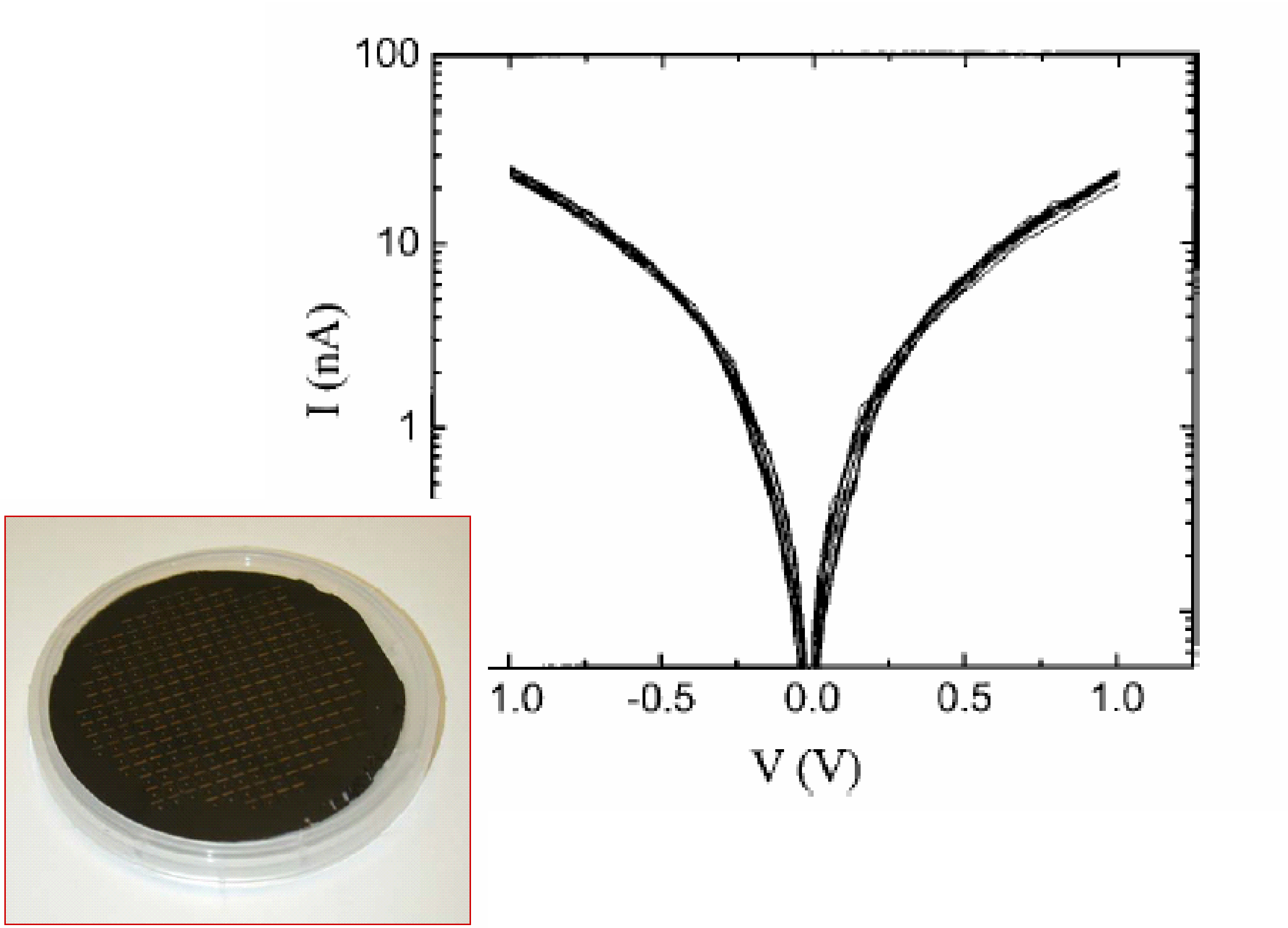
$$M_{\mu\nu}^{\alpha} = \sum_{l,\beta} \sqrt{\frac{\hbar}{2\omega_{\alpha} m_{l}}} \left\langle \mu \left| \frac{\partial \hat{H}}{\partial Q_{l,\beta}} \right| \nu \right\rangle_{Q=0} e_{l,\beta}^{\alpha}$$

Electron phonon self-energy, Born approximation:

$$\Sigma_{ph}^{<,>}(E) = \frac{i}{2\pi} \sum_{\alpha} \int dE' M^{\alpha} G^{<,>}(E - E') M^{\alpha} D_{\alpha}^{<,>}(E')$$

Nanopores

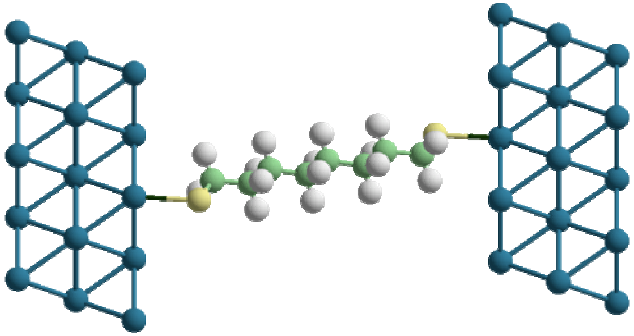




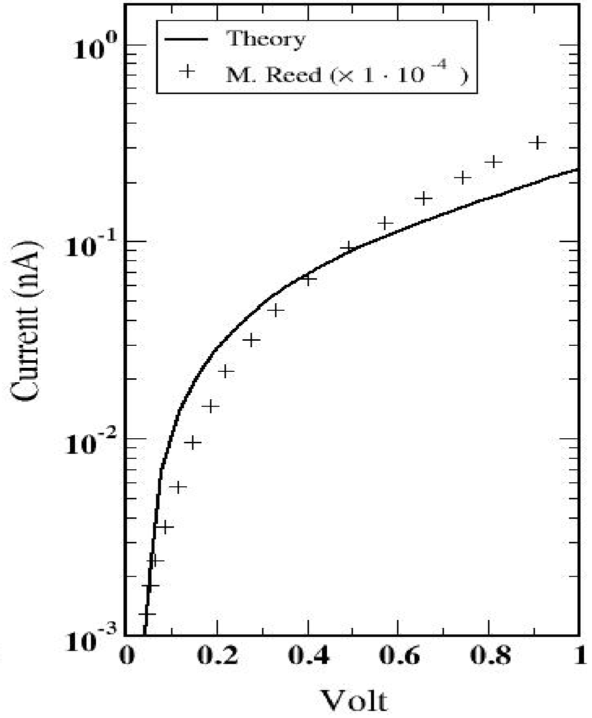
Wang, Lee, Reed, *Phys. Rev. B* **68** 035416 (2003)

I-V and Dissipation in Octane-di-Thiols on Gold: Simulations

Pecchia, Di Carlo, **Gagliardi**, *et al*, *Nano Lett.* **4** 2109 (2005)



I-V characteristic

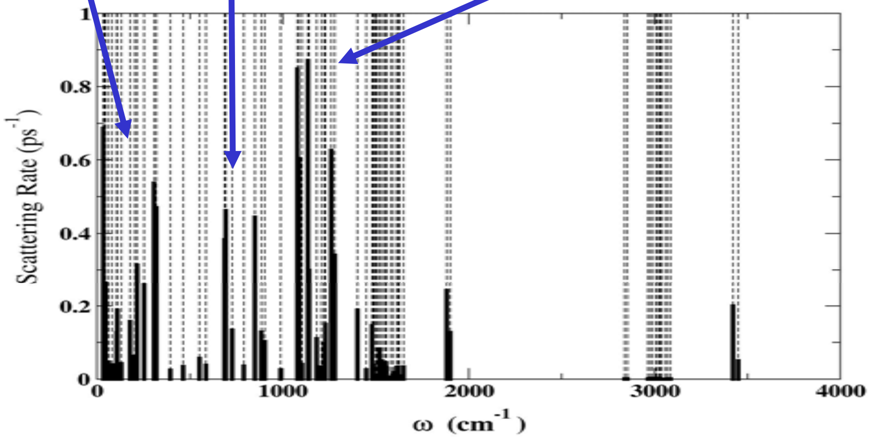


Many Modes

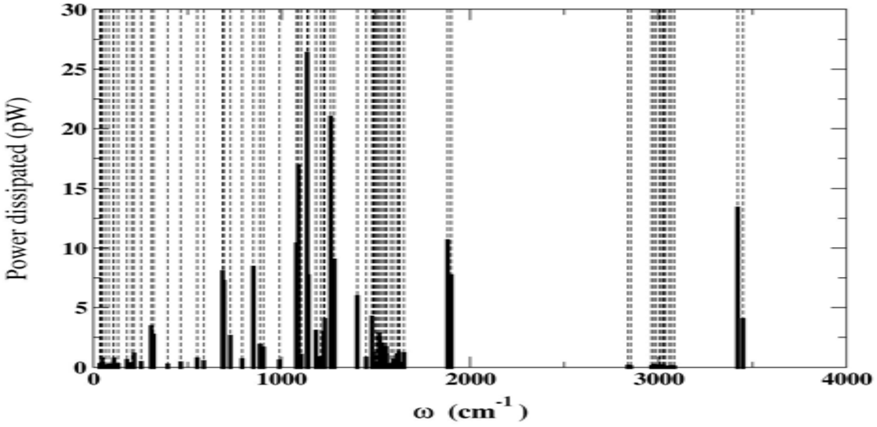
C-S Modes

C-C Modes

Scattering rate

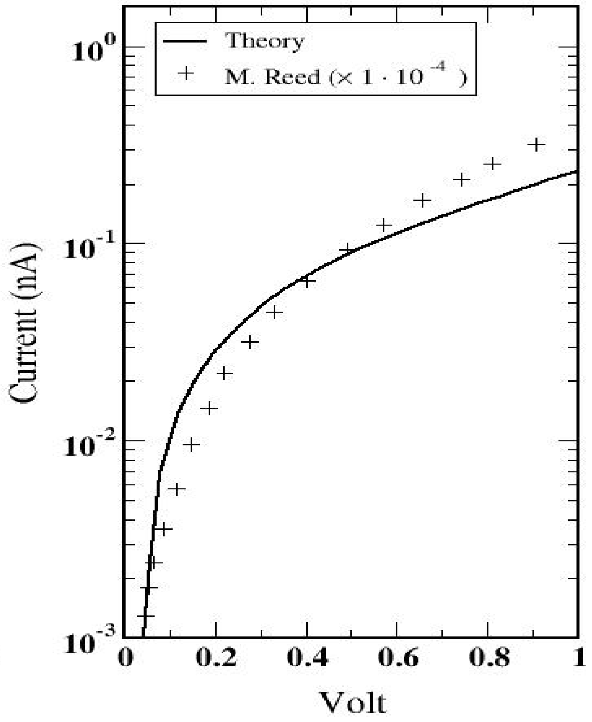


Power released in each mode



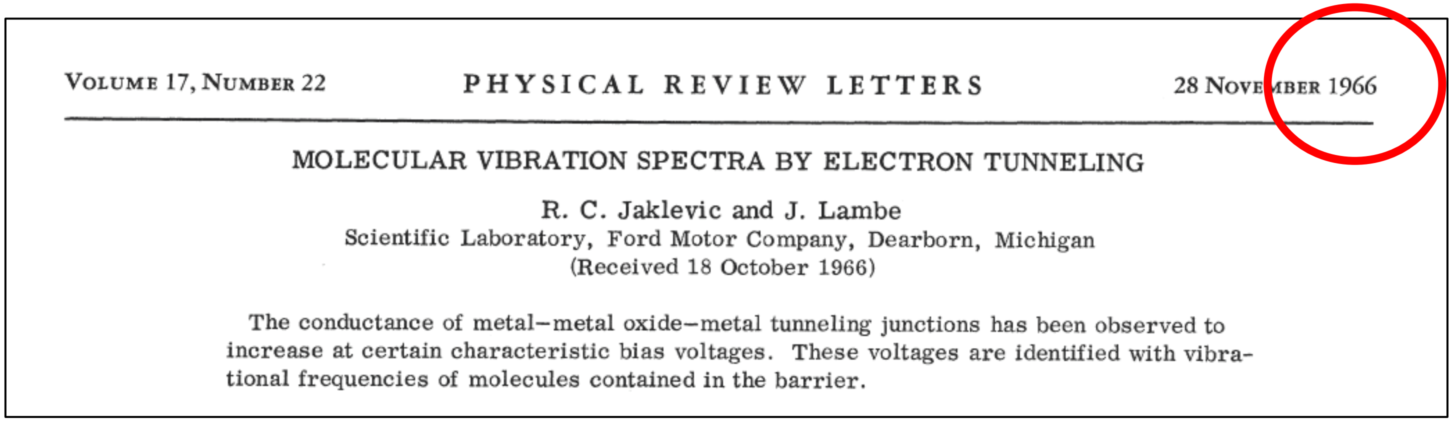
Problem

How we can really test our simulation for the inelastic current with experiments?



Current versus voltage characteristics are usually totally useless in this regard and Landauer-Büttiker formalism is in many cases already enough to describe the magnitude of the current

Solution: Inelastic Electron Tunneling Spectroscopy (IETS)

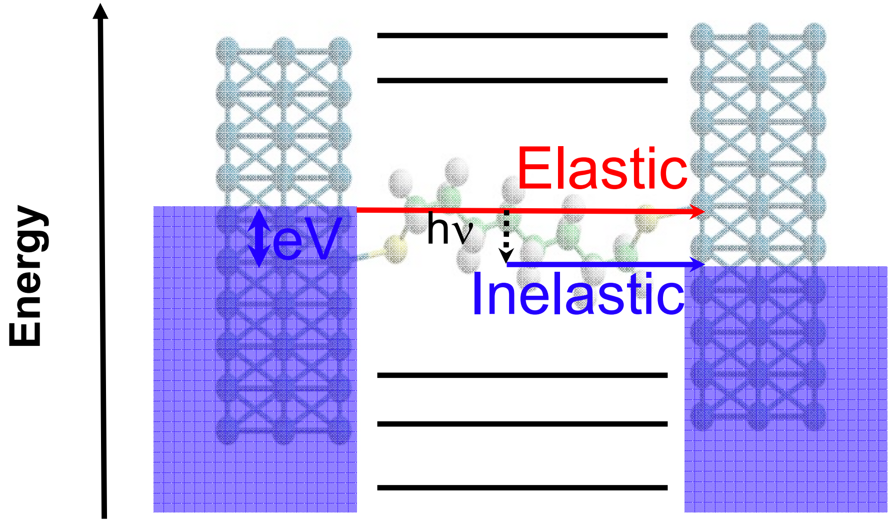


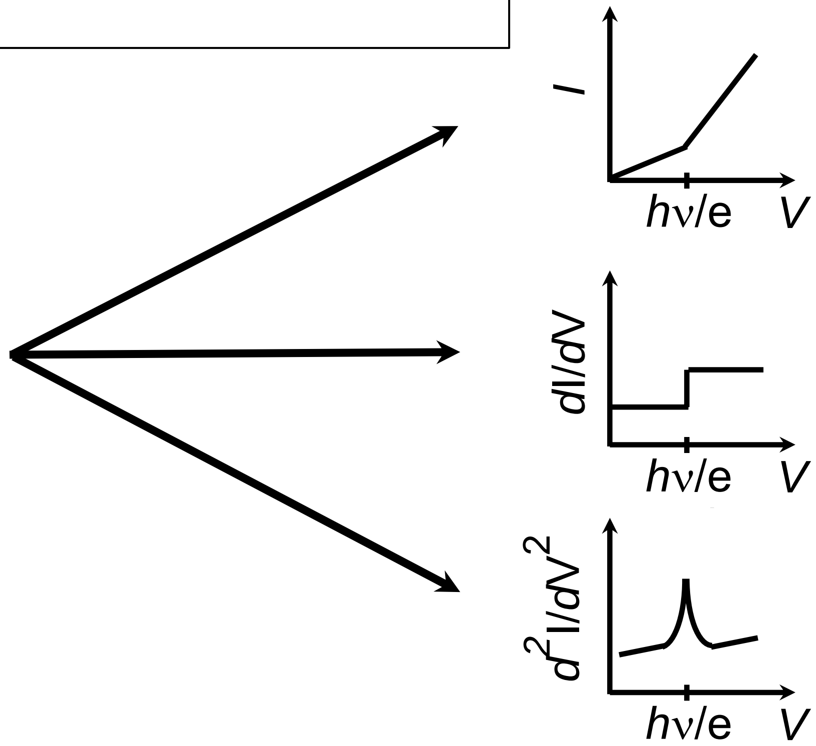
VOLUME 17, NUMBER 22 PHYSICAL REVIEW LETTERS 28 NOVEMBER 1966

MOLECULAR VIBRATION SPECTRA BY ELECTRON TUNNELING

R. C. Jaklevic and J. Lambe
Scientific Laboratory, Ford Motor Company, Dearborn, Michigan
(Received 18 October 1966)

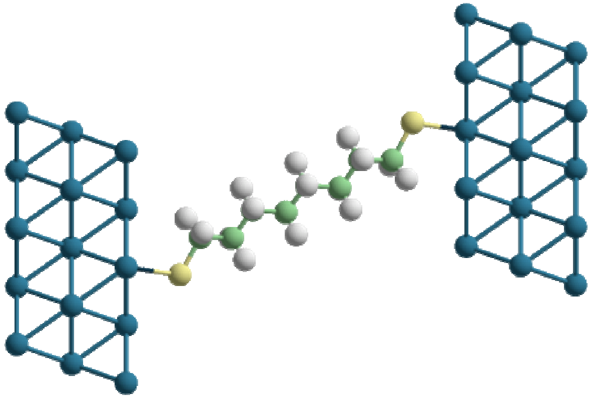
The conductance of metal–metal oxide–metal tunneling junctions has been observed to increase at certain characteristic bias voltages. These voltages are identified with vibrational frequencies of molecules contained in the barrier.



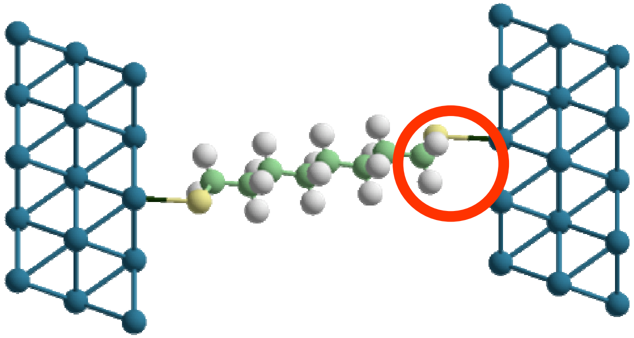


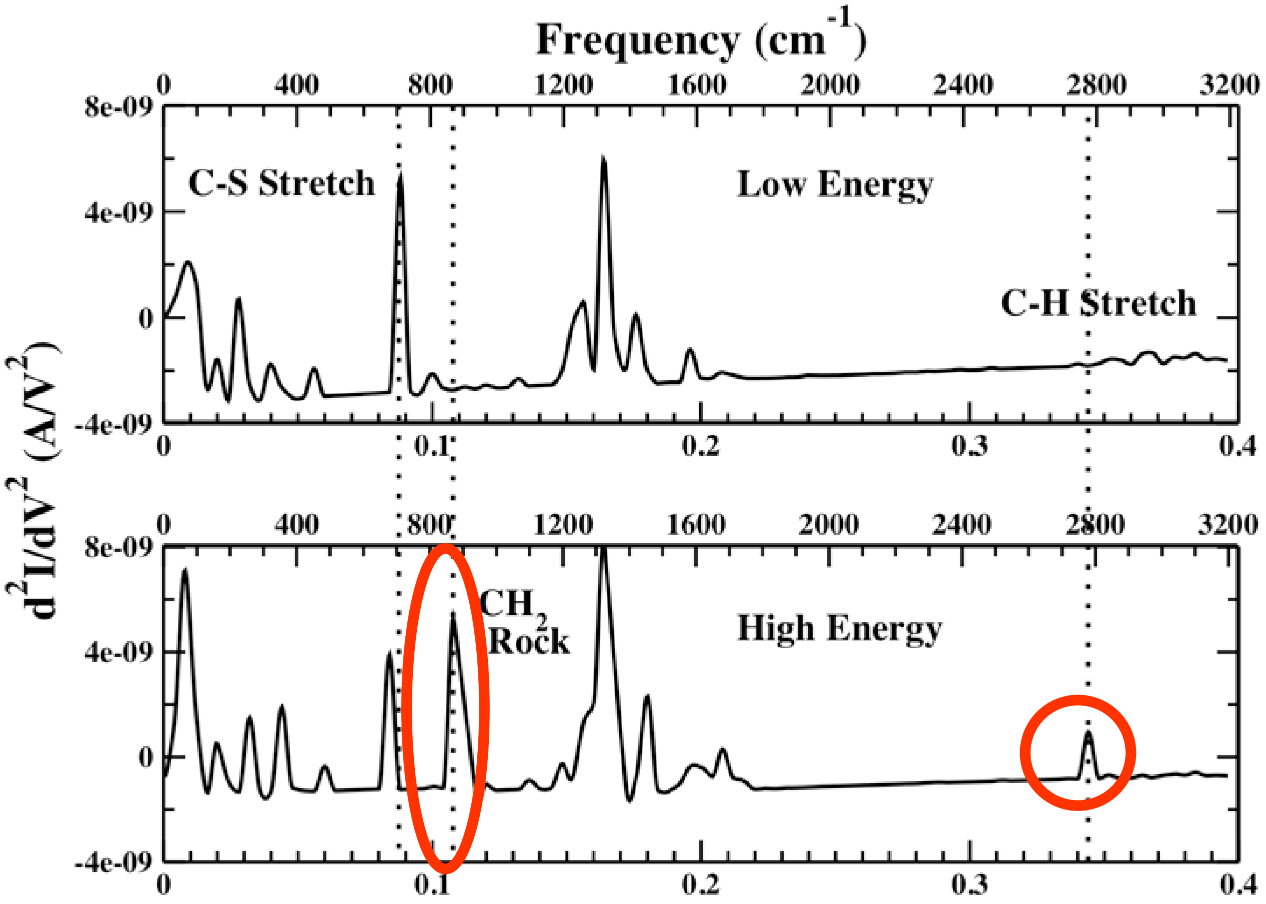
Effect of the Geometry to the Spectrum

lower energy



higher energy

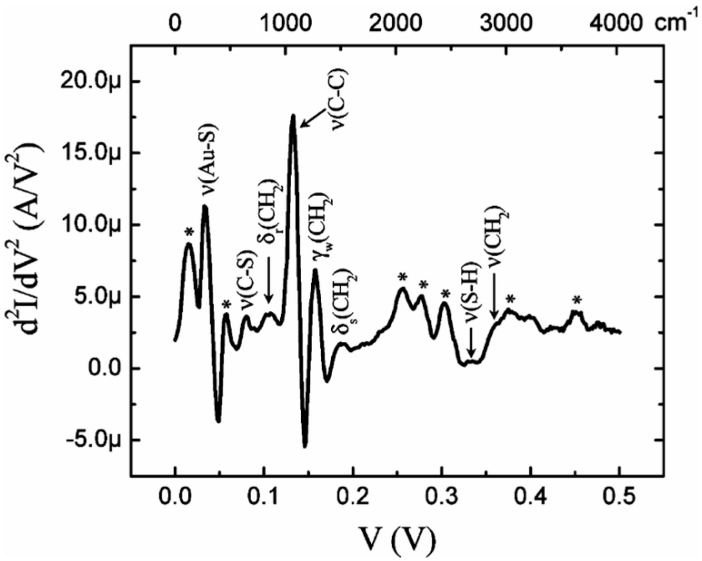


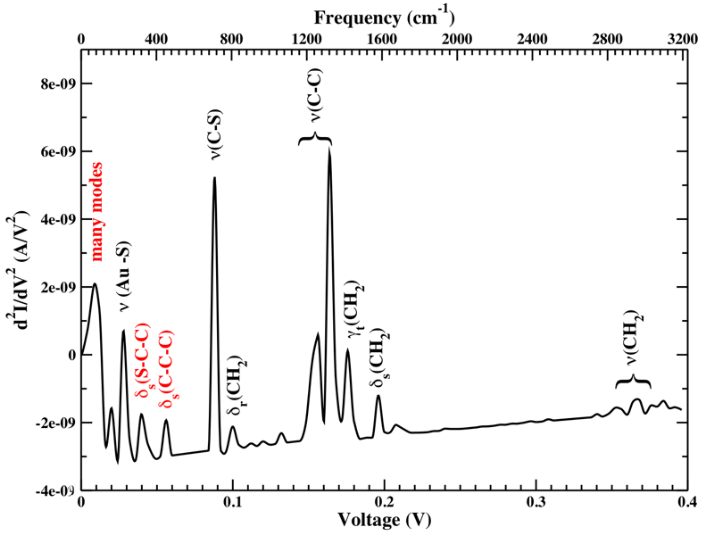


Solomon, **Gagliardi**, Pecchia, Frauenheim, Di Carlo, Hush, Reimers *JCP* **124** 094704 (2006)

Problem

- **Qualitative agreement (most relevant modes), far off quantitative**





Wang, Lee, Kretzschmar, Reed
Nano Lett. (2004) **4** (4) 643

Solomon, **Gagliardi**, Pecchia, Frauenheim, Di Carlo, Hush, Reimers *JCP* **124** 094704 (2006)

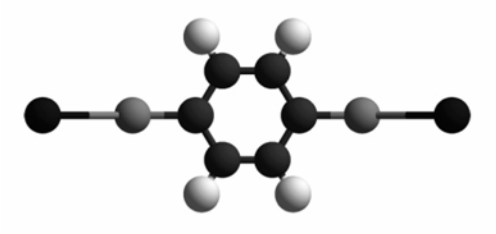
- **How to define which are the most relevant modes? Selection rules?**

Selection Rules in IETS: Propensity Rules

In IETS there are no hard selection rules because the symmetry of the molecule is reduced:

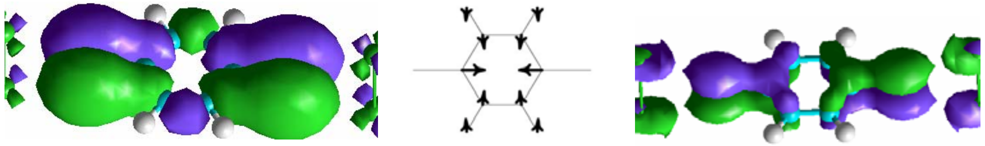
- distortion of the molecule between the contacts
- internal symmetry of the contacts

There are selection preferences called "propensity rules". The definition of them requires two steps:



1) The definition of an **approximated symmetry point group** for the molecule between the contacts

$\alpha_1 \otimes \alpha_2 \otimes \alpha_3 =$ Totally symmetric

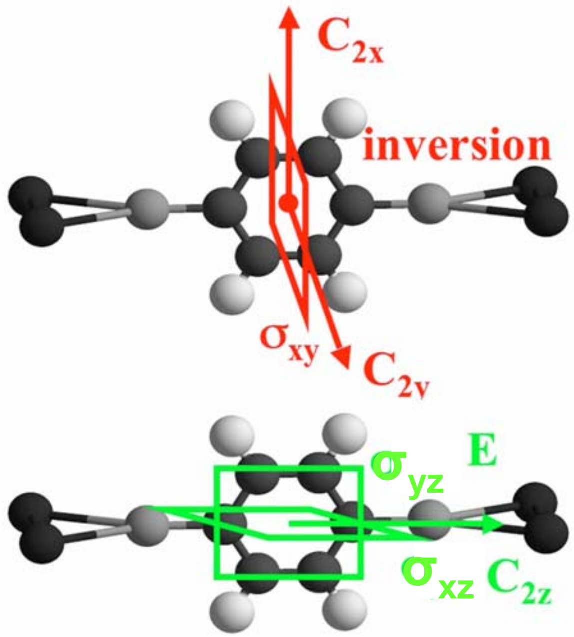


2) The definition of a set of generalized molecular orbitals to which apply the symmetry: **"channels"**

Point Group of the Device: Molecular Conductance Point Group

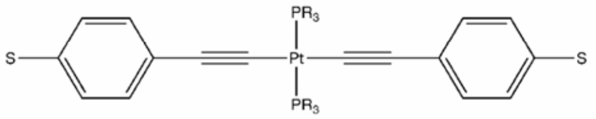
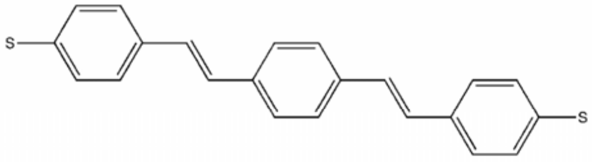
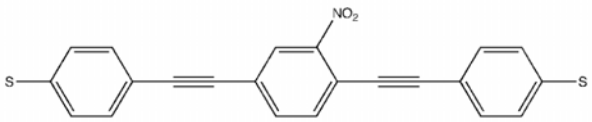
- **$G^{<,>}$** commute with all molecular point-group symmetry operators;
- **Σ_L** and also **Σ_R** only commute with operators that do not interchange the electrodes;

Benzene-di thiol molecule (BDT) on bridge site on gold



Lost operators:

- axes C_{2x} and C_{2y},
- inversion,
- Plane σ_{xy}

Au—Au—Au—Au	$D_{\infty h} \rightarrow C_{\infty v}$
	$D_{2h} \rightarrow C_{2v}$
	$D_{2h} \rightarrow C_{2v}$
	$\sim D_{2h}{}^{*} \rightarrow \sim C_{2v}$
 even alkane	$C_{2h} \rightarrow C_s$
	$C_{2h} \rightarrow C_s$
 odd alkane	$C_{2v} \rightarrow C_s$
	$C_s \rightarrow C_s$

Solomon, **Gagliardi**, Pecchia, Frauenheim, Di Carlo, Reimers, Hush *JCP* **125** (2006) 184702

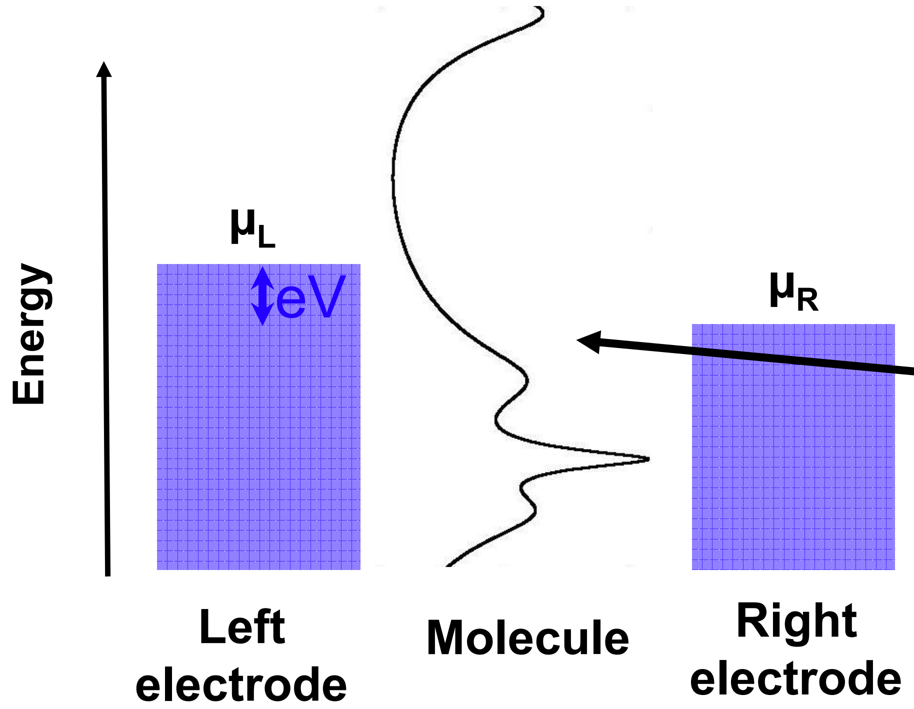
The Definition of A-channels

$$I(V) = I_{el} + I_{inel} = \frac{2e}{h}\int_{\mu_R}^{\mu_L} Tr[g(E)]dE + \sum_{\alpha}\frac{2e}{h}\int_{\mu_R+\omega_\alpha}^{\mu_L} Tr[\sigma_\alpha(E)]dE$$

$$g(E) = \Gamma_L G^r \Gamma_R G^a$$

$$\sigma_\alpha(E) = \underbrace{G^a \Gamma_L G^r}_{} M^\alpha \underbrace{G^r \Gamma_R G^a}_{} M^\alpha$$

$$\sigma_\alpha(E) = (A^L)^* M^\alpha A^R M^\alpha$$



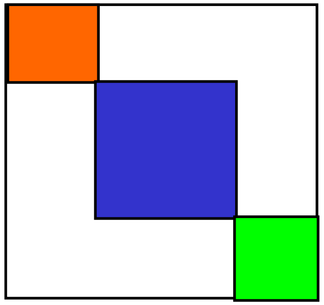
$$DOS(E) \propto A^L(E) + A^R(E)$$

Gagliardi, Solomon, Pecchia, Frauenheim, Di Carlo, Hush, Reimers *PRB* **75** 174306 (2007)

Systematic Approach to Find Propensity Rules

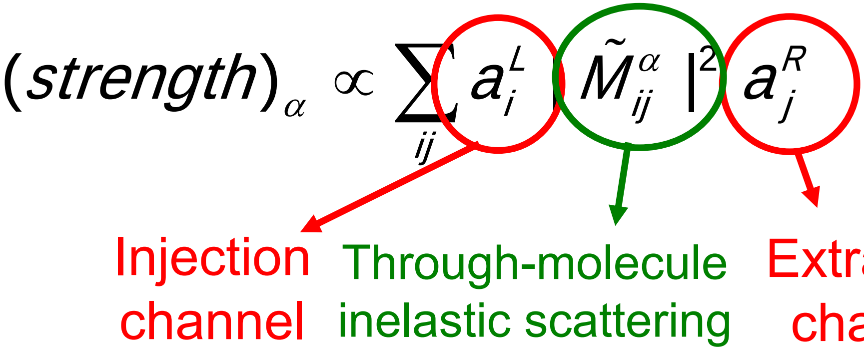
- Define the molecular conductance point group for the molecule in the junction
- Rotate the A matrices in the symmetry adapted basis

$A^{L,R} \rightarrow$



- Diagonalize the A matrices and transform the electron-phonon coupling matrices

$$(strength)_\alpha \propto Tr[\sigma_\alpha] = Tr[(A^L)^* M^\alpha A^R M^\alpha] \rightarrow \sum_{ij} a_i^L \mid \tilde{M}_{ij}^\alpha \mid^2 a_j^R$$



$$(strength)_\alpha \propto \sum_{ij} a_i^L \mid \tilde{M}_{ij}^\alpha \mid^2 a_j^R$$

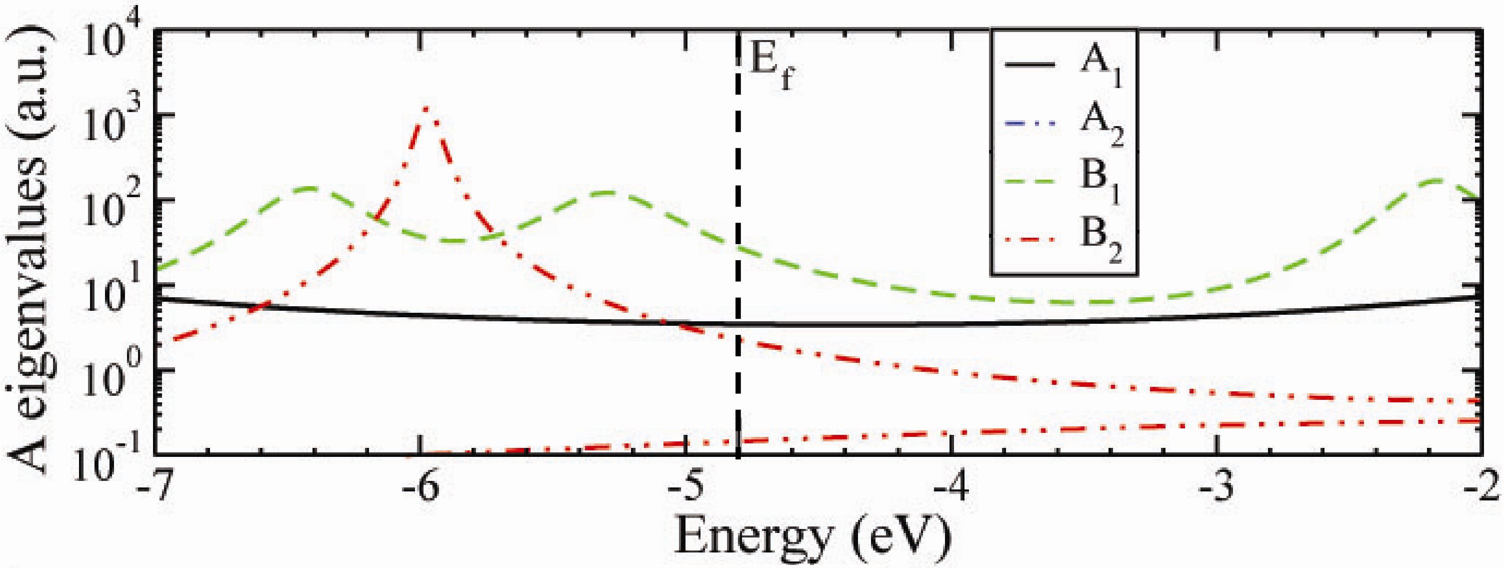
Injection channel

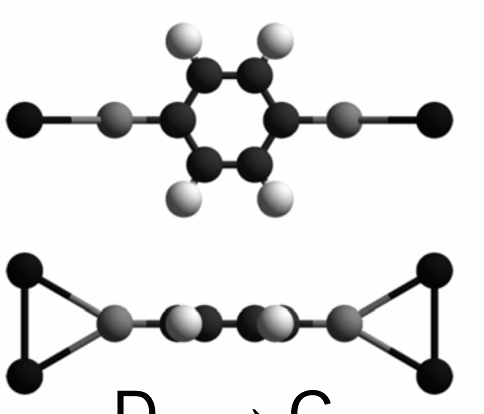
Through-molecule inelastic scattering

Extraction channel

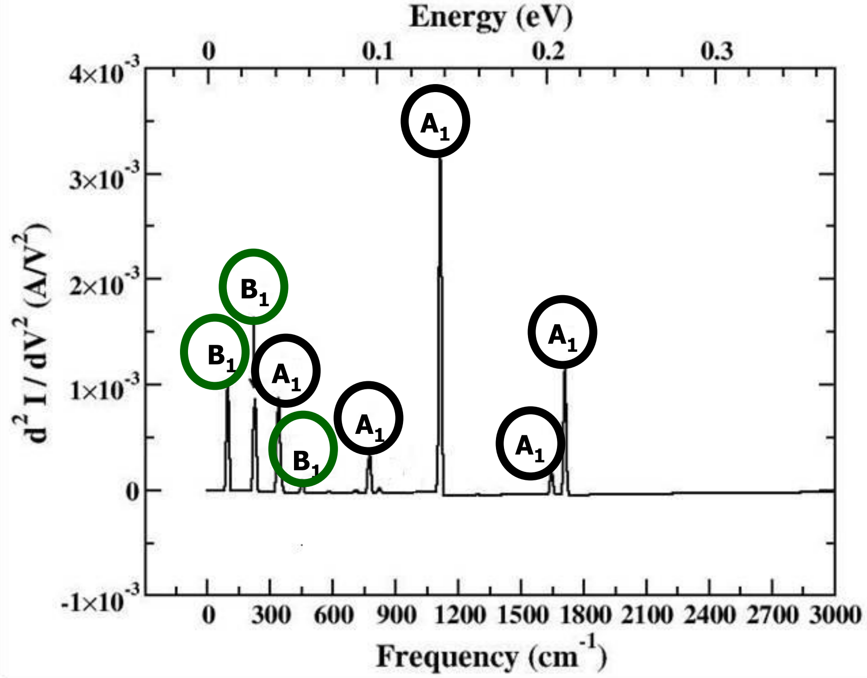
Totally symmetric = $\alpha_1 \otimes \alpha_2 \otimes \alpha_3$

Propensity Rules in Benzene di Thiols





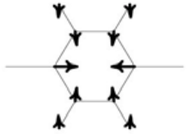
$D_{2h} \rightarrow C_{2v}$



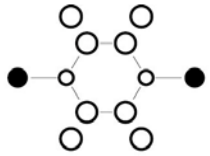
There are few dominant channels with representation **A_1** and **B_1**:

$$\sum_{ij} a_i^L \,|\, M_{ij}^{\alpha} \,|^2\, a_j^R$$

$$A_1 = B_1 \otimes A_1 \otimes B_1$$



$$A_1 = A_1 \otimes B_1 \otimes B_1$$



Conclusions

- My work was focused on the development of a code to describe dissipation in molecular electronic devices.
- The code was used to investigate dissipation in nanopore devices and simulate IETS measurements.
- Molecular symmetry can be used to provide a qualitative description of single-molecule conductivity: molecular conductance point group.
- A generalized set of molecular orbitals for transport has been developed and integrated in the code: channels.
- This has permitted the systematic investigation of propensity rules in IETS.

Channels and Canonical Molecular Orbitals