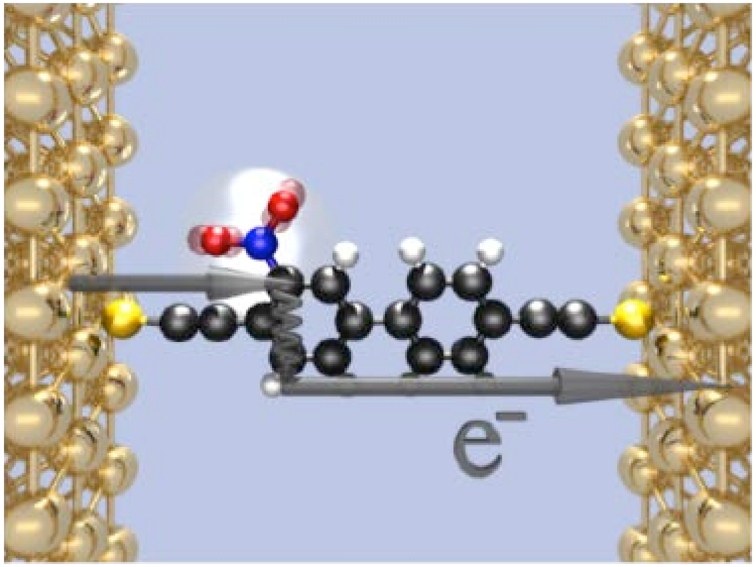
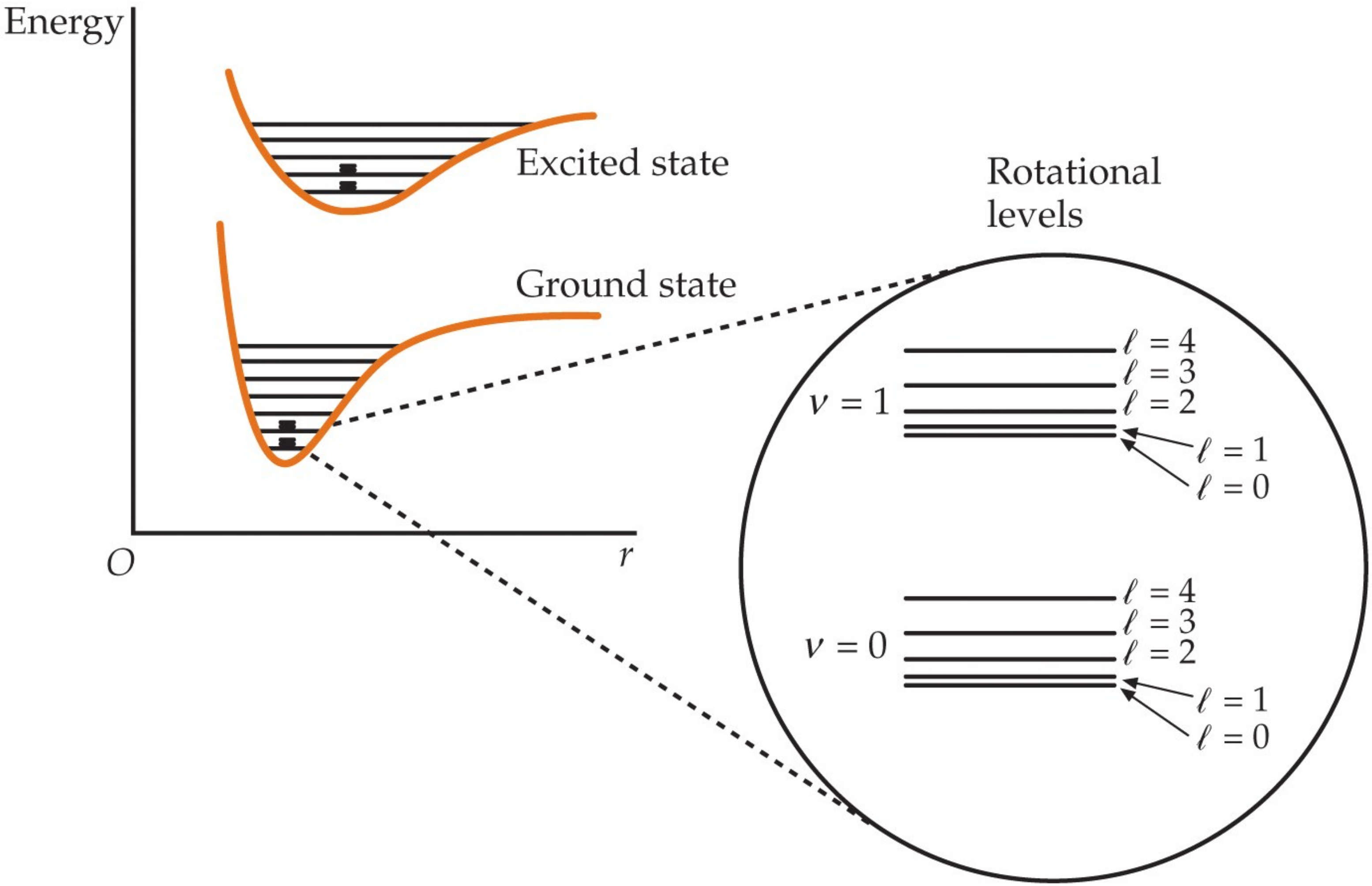
Chapter 9: Vibrationally-induced inelastic current



Main Reference: *Chapter 16 of Cuevas & Scheer*

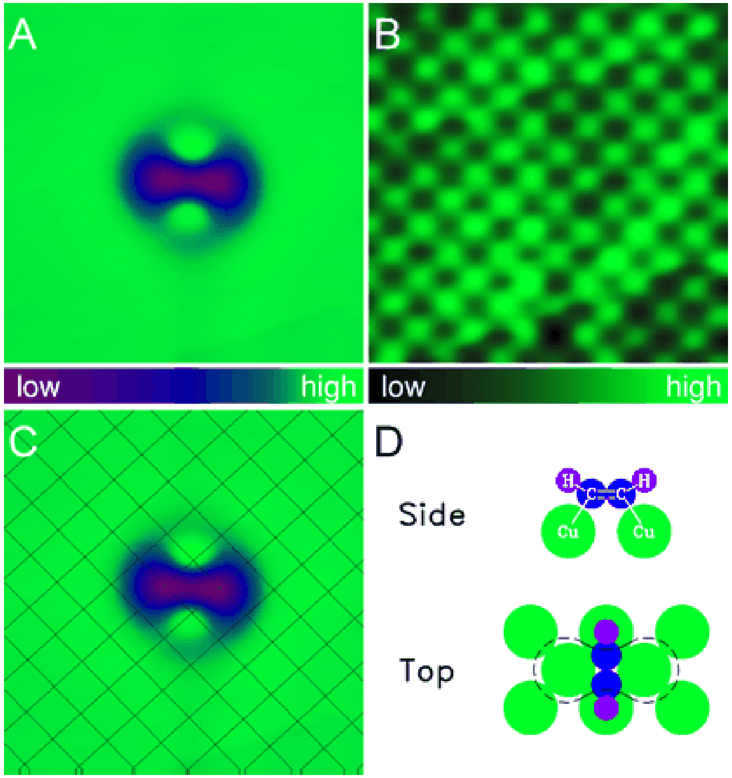
9.0 Molecular vibrational modes: a reminder

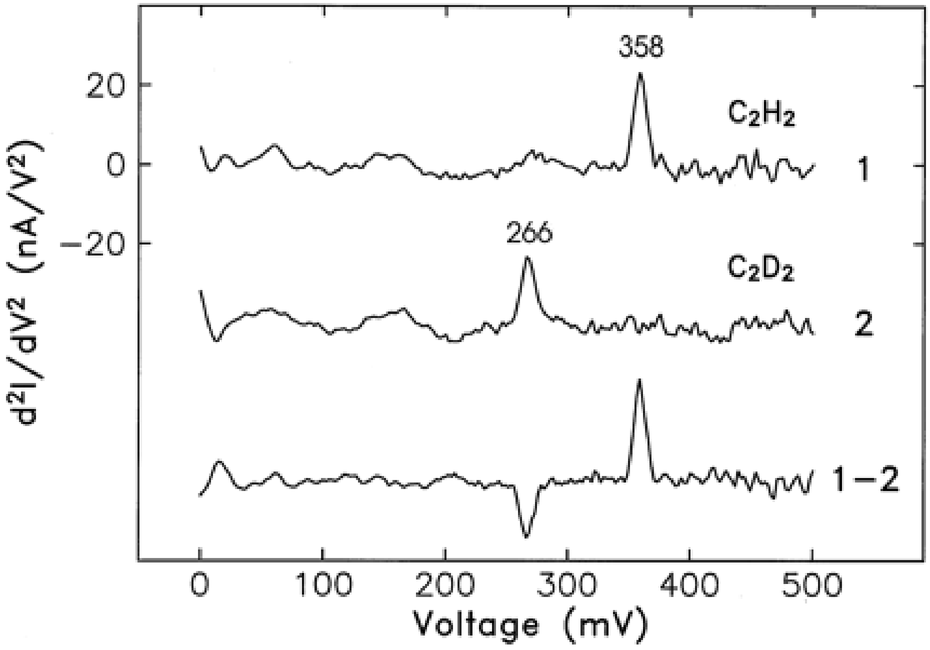
Molecular spectra: electronic states + vibrational modes + rotational levels.



9.1 Experimental signatures: Inelastic electron tunneling spectroscopy (IETS)

*B.C. Stipe, M.A. Rezaei, and W. Ho, Science **280**, 1732 (1998).*

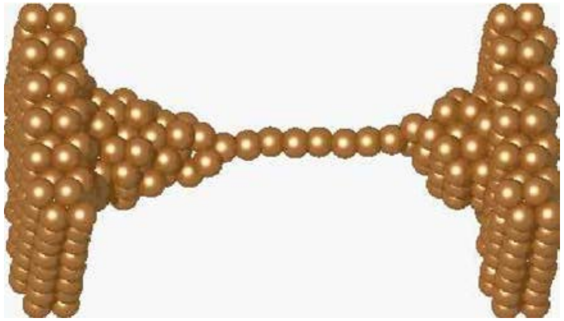


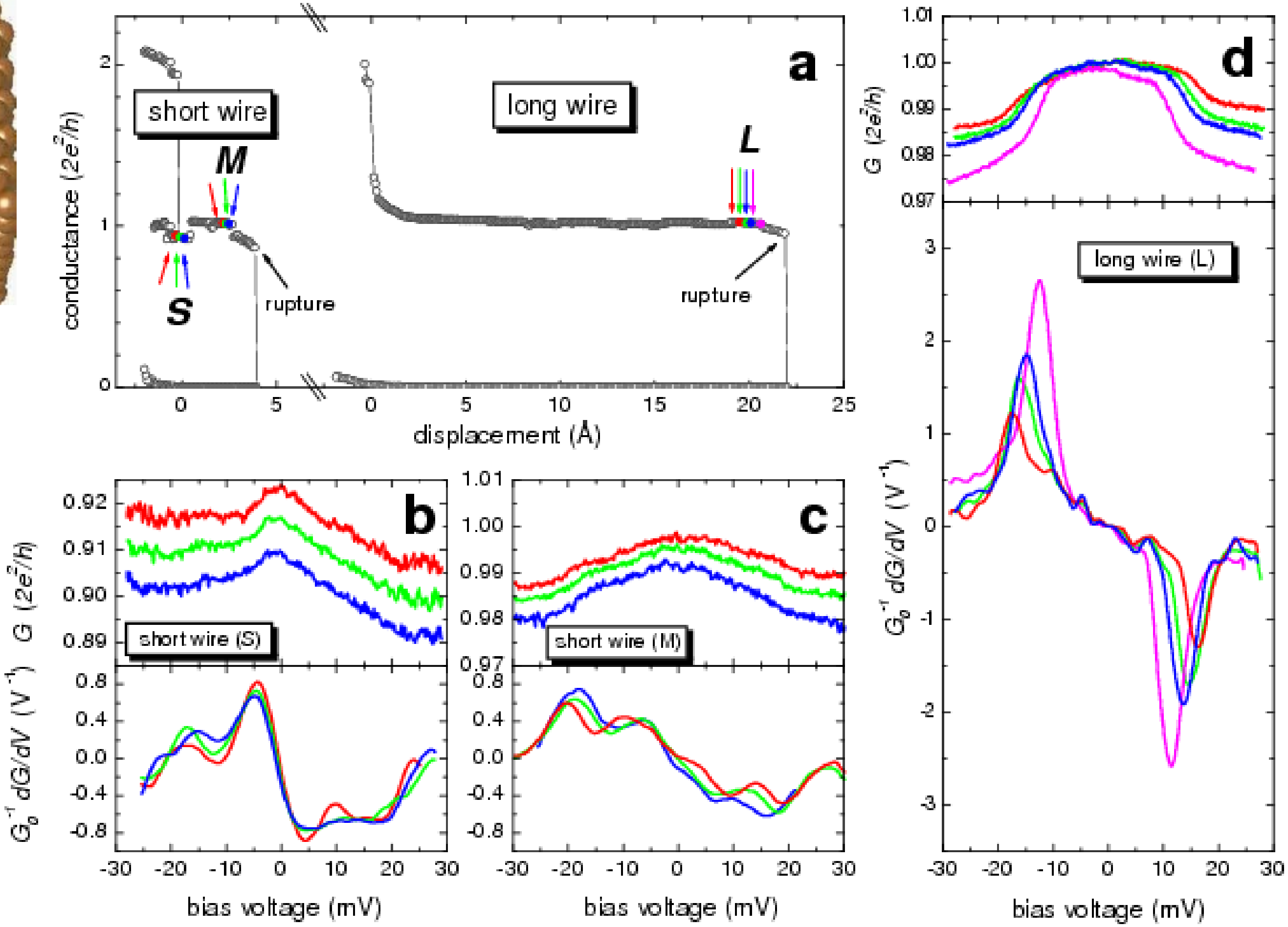


Example: STM study of acetylene (C_2H_2) on Cu(100).

9.1 Experimental signatures: Point contact spectroscopy (PCS) of gold chains

N. Agraït, C. Untiedt, G. Rubio-Bollinger, S. Vieira, Phys. Rev. Lett. 88, 216803 (2002).

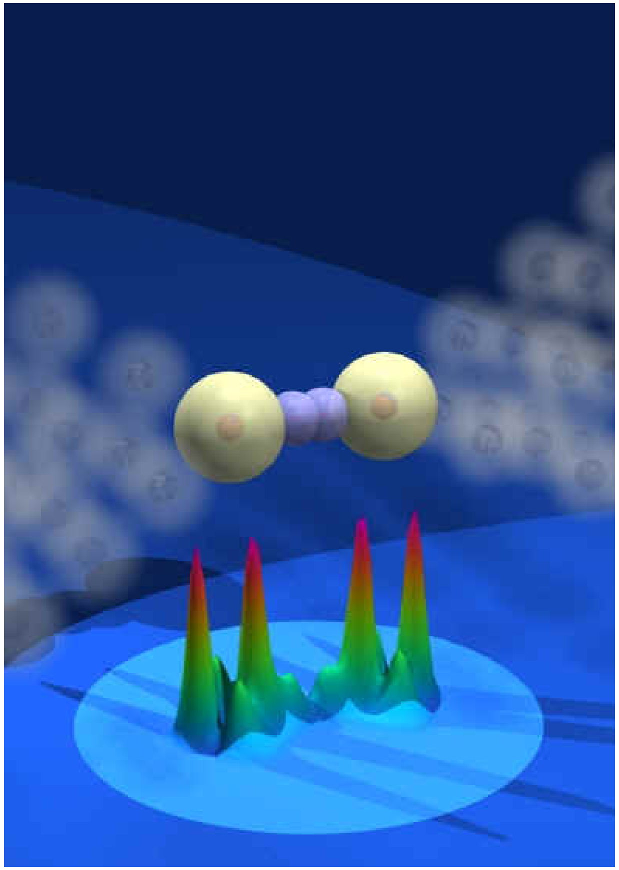


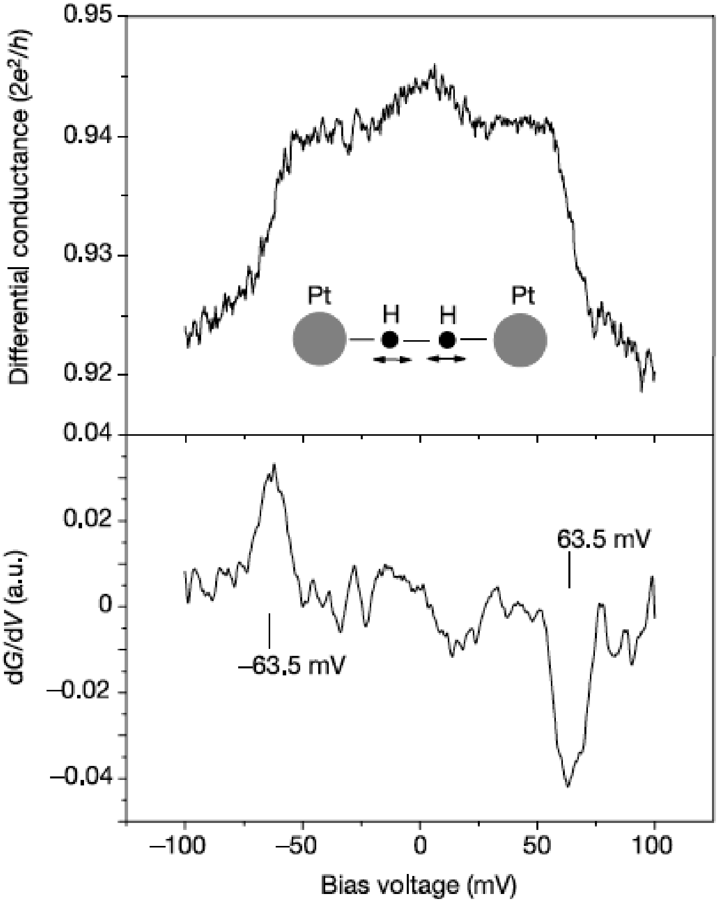


STM study in the contact regime between tip and substrate

9.1 Experimental signatures: Point contact spectroscopy (PCS) of Pt-H_2-Pt junctions

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

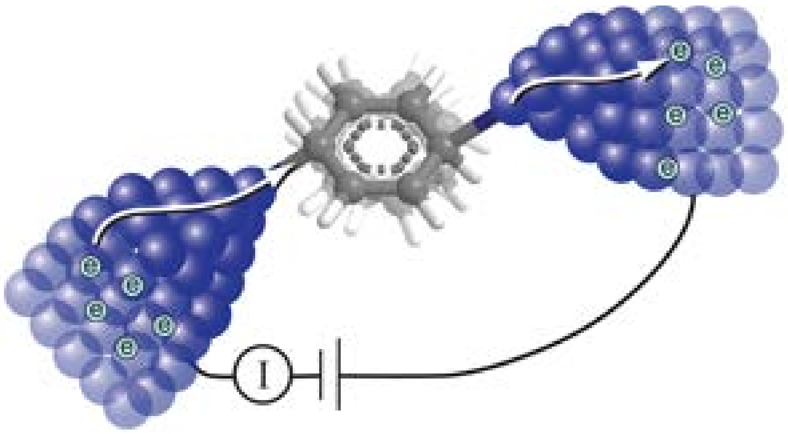


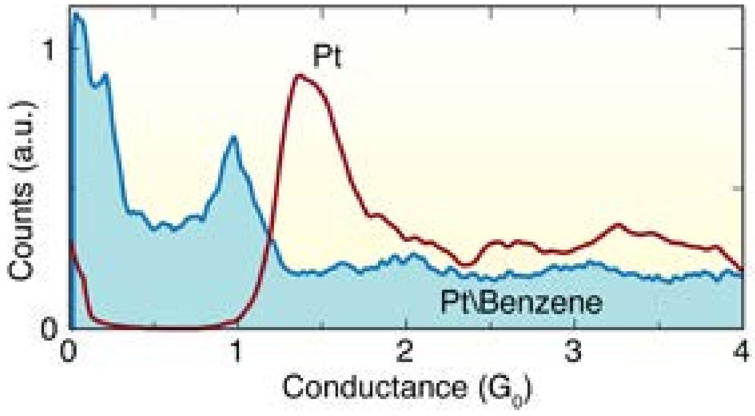


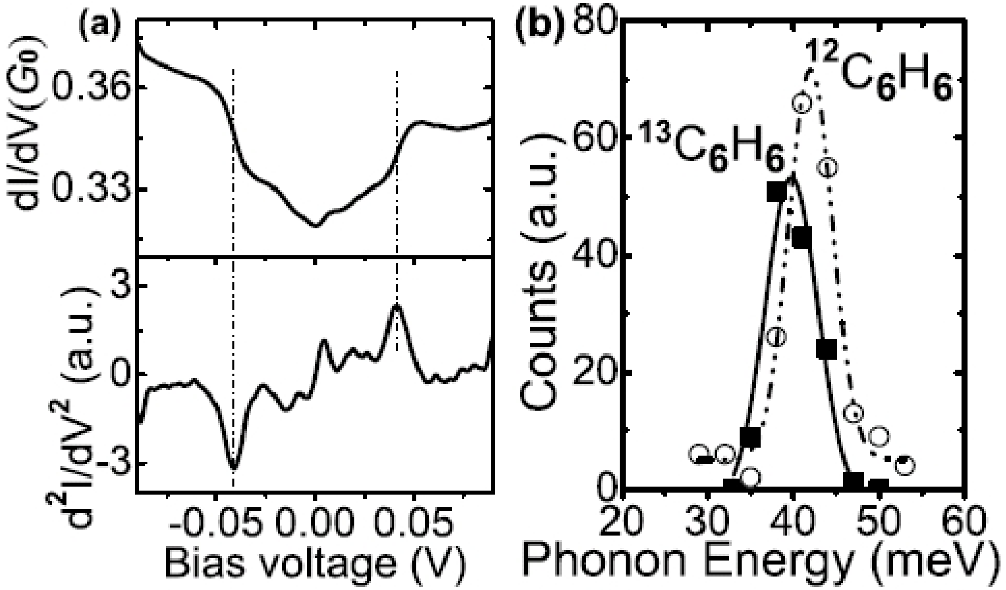
Measurement of the conductance of a hydrogen molecule between Pt leads with the break-junction technique

9.1 Experimental signatures: Pt-benzene-Pt junctions

M. Kiguchi, O. Tal, S. Wohlthat, F. Pauly, M. Krieger, D. Djukic, J.C. Cuevas, and J.M. van Ruitenbeek Phys. Rev. Lett. ***101****, 046801 (2008)*







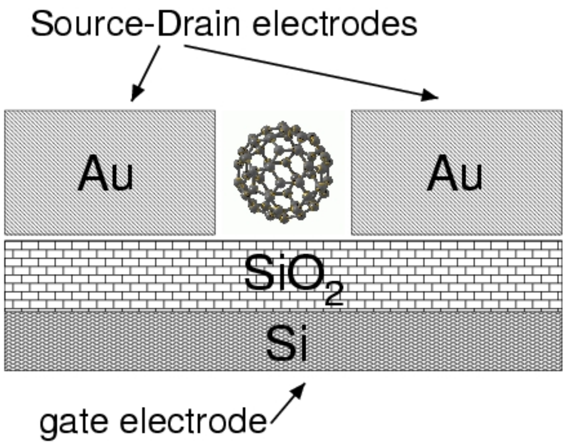
Signature of the vibration modes:

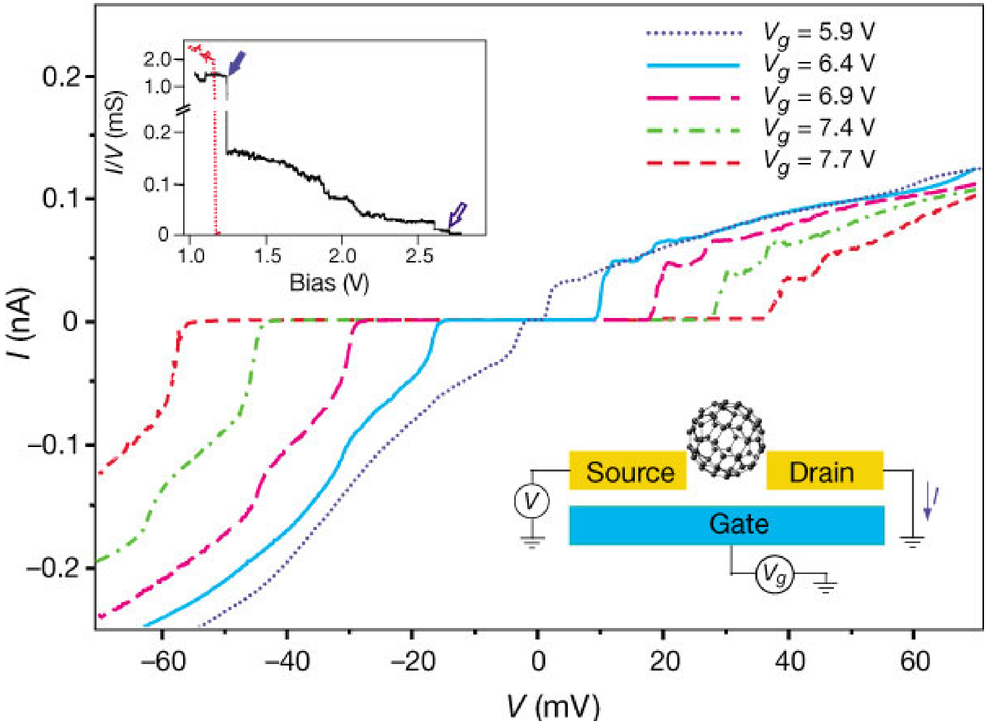
step up in the conductance.

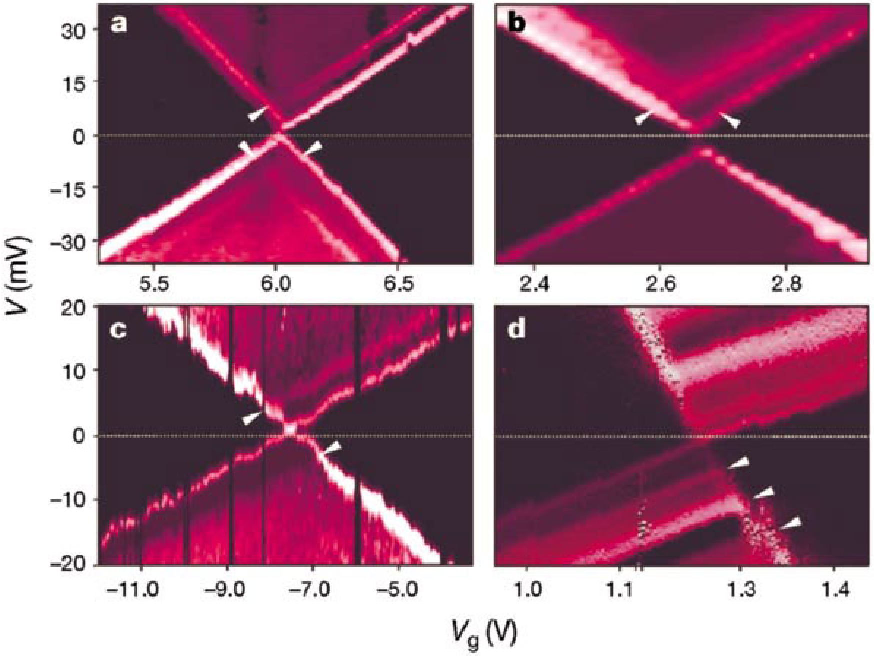
9.1 Experimental signatures: Resonant inelastic electron tunneling (RIETS) in a molecular transistor

Nanomechanical oscillations in a single-C_{60} transistor

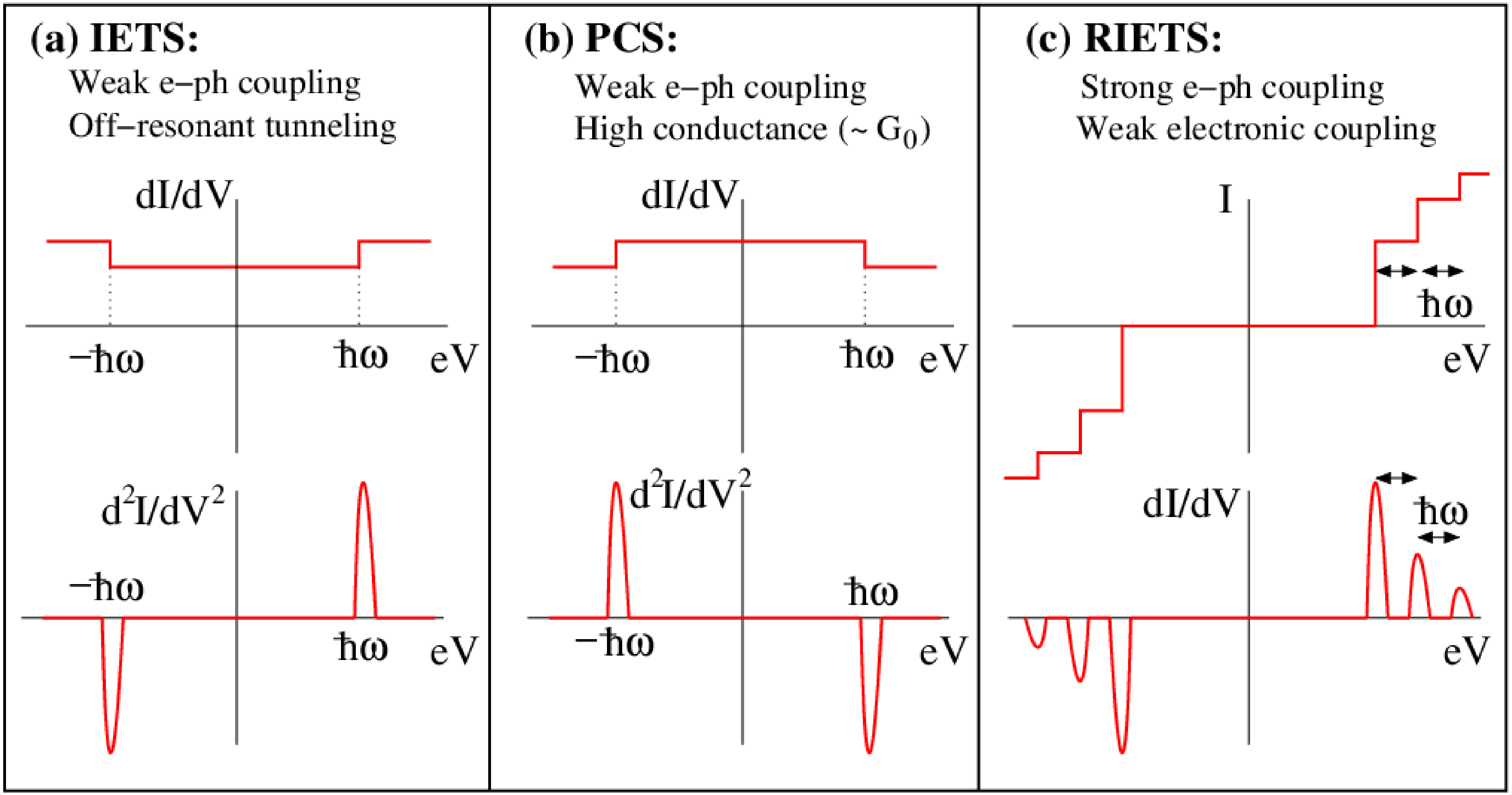
Park et al., Nature **407**, 57 (2000)







9.1 Signatures of vibrational modes: Summary

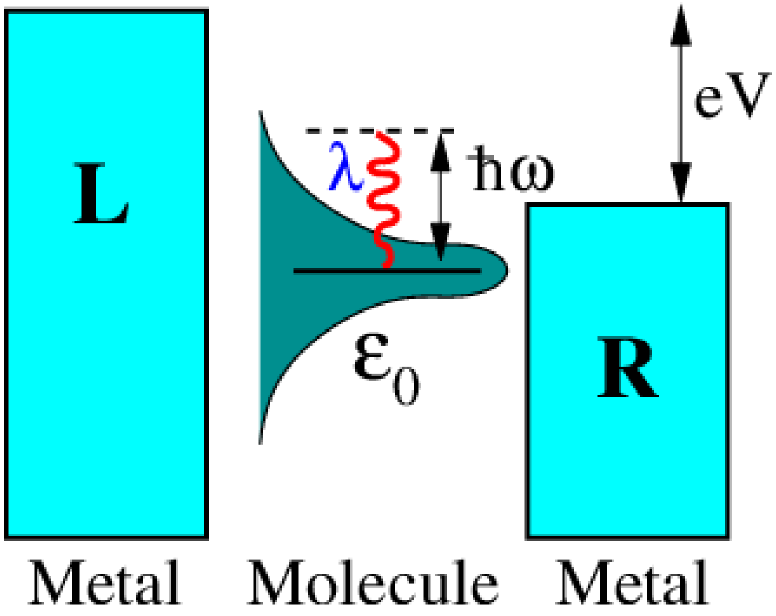


(a) IETS:
Weak e–ph coupling
Off–resonant tunneling

(b) PCS:
Weak e–ph coupling
High conductance (~ G_0)

(c) RIETS:
Strong e–ph coupling
Weak electronic coupling

9.2 Weak e-ph coupling regime: a single-phonon model



$$H = H_e + \hbar\omega(b^\dagger b + 1/2) + \lambda d^\dagger d(b^\dagger + b)$$

Electrons — Phonons — E-ph coupling

λ = electron-phonon coupling constant

ħω = energy of the vibration mode

$$I = I_{elastic} + I_{inelastic}$$

[Keldysh formalism]

$$I_{el} = \frac{2e}{h}\int dE\, 4\Gamma_L\Gamma_R \left|G^r(E)\right|^2 (f_L - f_R); \quad I_{in} = \frac{2e}{h}(2i\Gamma_L)\int dE \left|G^r(E)\right|^2 \left[\Sigma^{-+} f_L + \Sigma^{+-}(1 - f_L)\right]$$

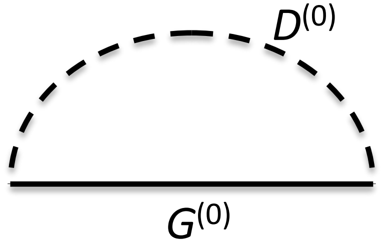
Need of approximations:

Weak e-ph interaction

→ lowest-order perturbation theory (LOE)

$$(\lambda << \sqrt{\Delta E^2 + \Gamma^2})$$

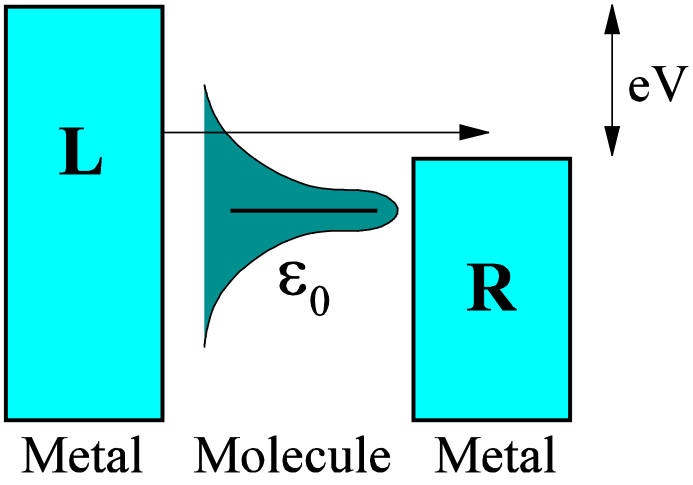
$\Sigma =$



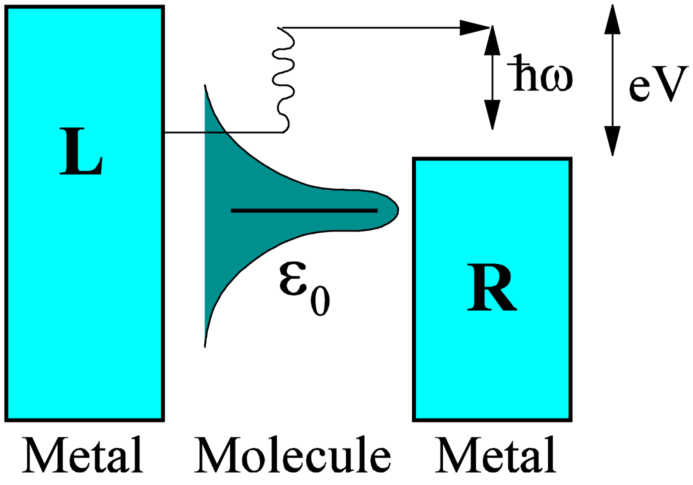
$\propto \lambda^2$

9.2 Weak e-ph interaction: tunneling processes

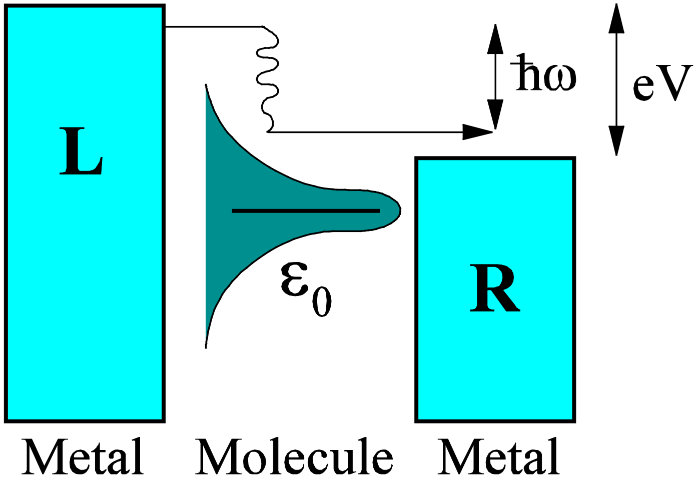
(a) Elastic process



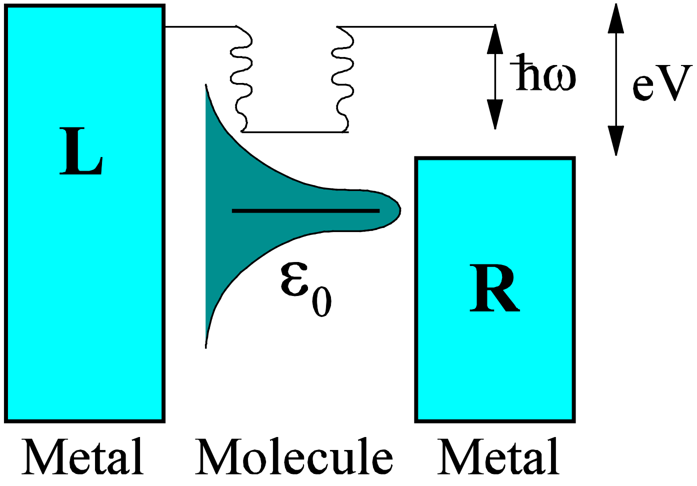
(b) Phonon absorption



(c) Phonon emission

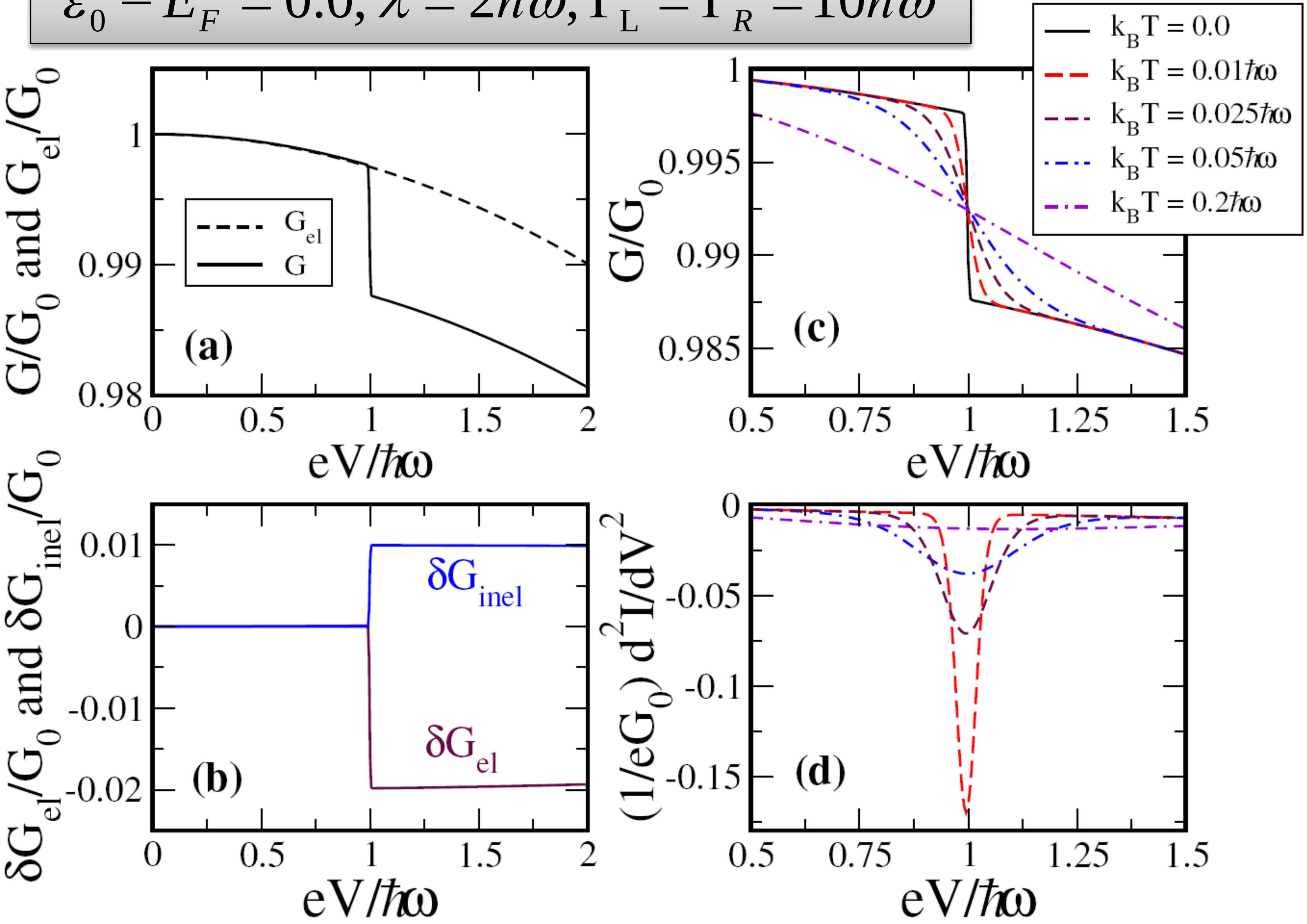


(d) Elastic correction



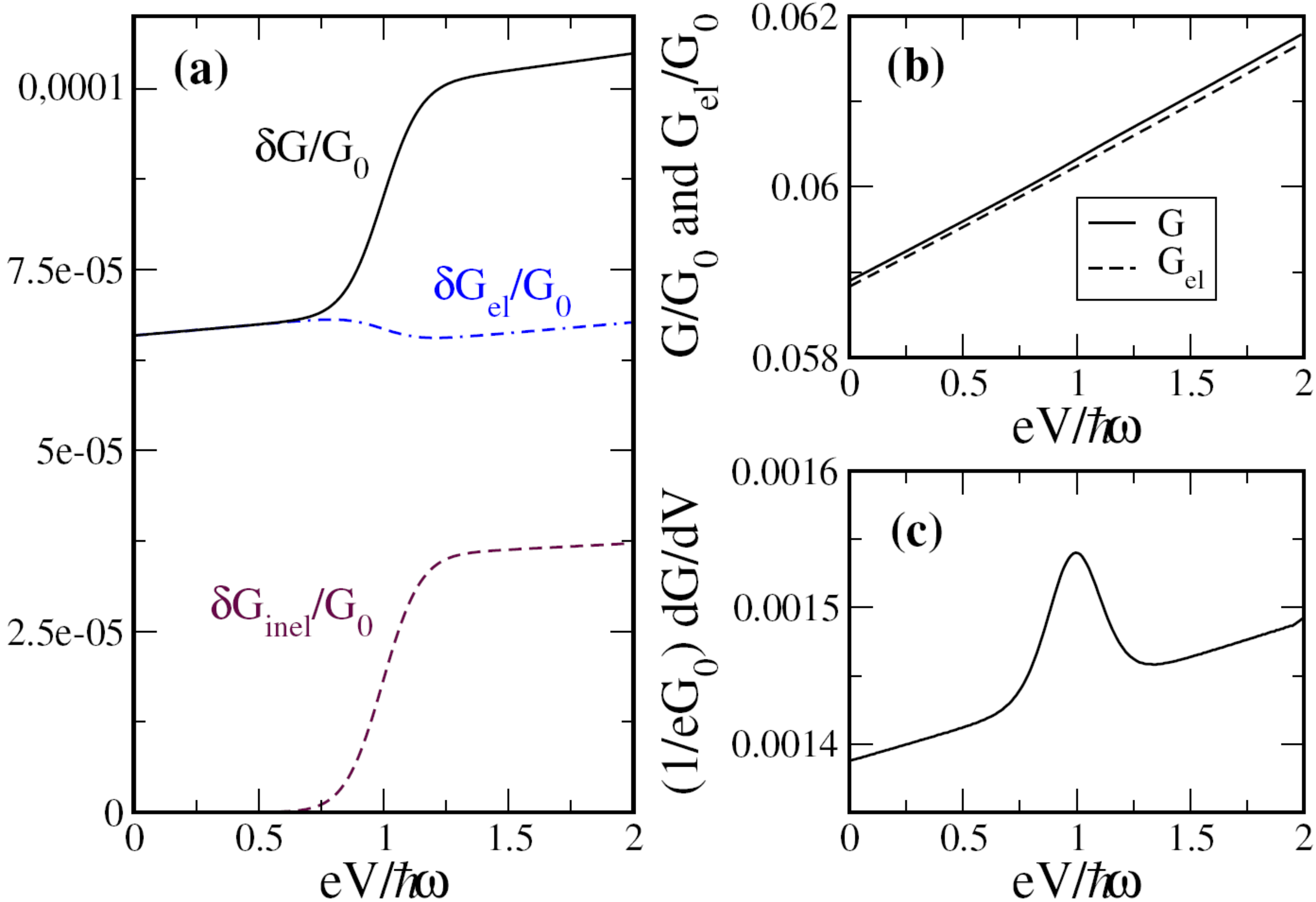
9.2 Simple model: high-transparency limit

$$\varepsilon_0 - E_F = 0.0; \lambda = 2\hbar\omega; \Gamma_{\mathrm{L}} = \Gamma_R = 10\hbar\omega$$



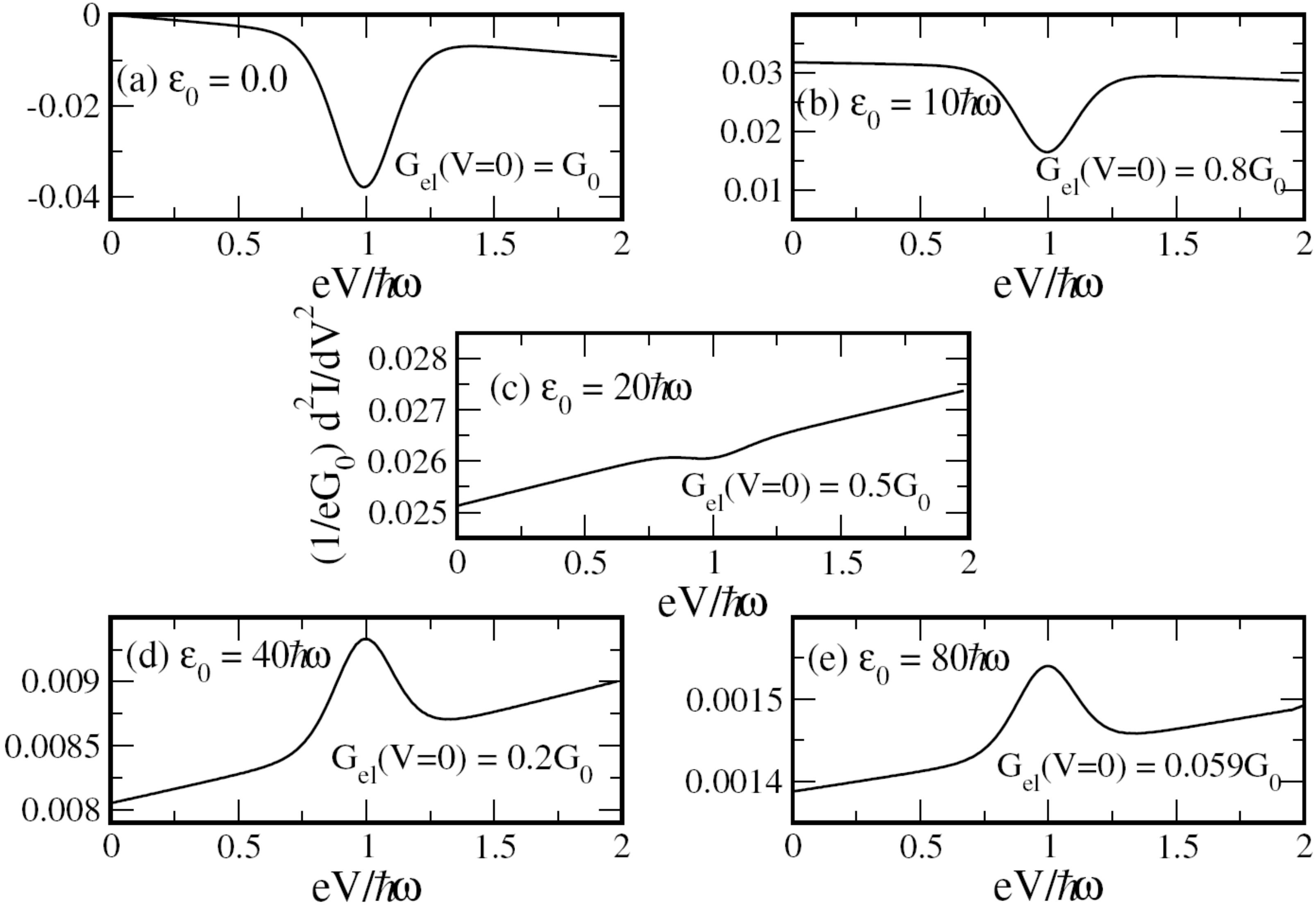
9.2 Simple model: low-transparency limit

$$\varepsilon_0 - E_F = 80\hbar\omega; \lambda = 2\hbar\omega; \Gamma_L = \Gamma_R = 10\hbar\omega; k_B T = 0.05\hbar\omega$$



9.2 Simple model: PCS-IETS crossover

$$\lambda = 2\hbar\omega; \Gamma_L = \Gamma_R = 10\hbar\omega; k_B T = 0.05\hbar\omega$$



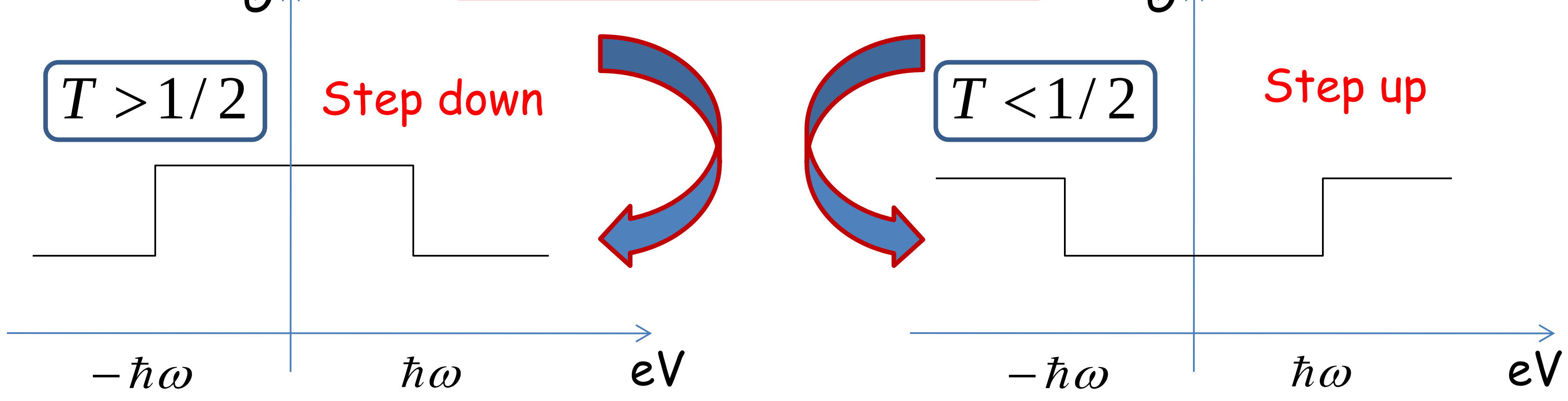
9.2 Simple model: arbitrary transparency

M. Paulsson, T. Frederiksen, and M. Brandbyge, Phys. Rev. B ***72****, 201101 (2005).*
L. de la Vega, A. Martin-Rodero, N. Agraït, and A. Levy Yeyati, Phys. Rev. B ***73****,075428 (2006).*

- Neglect the energy dependence of the elastic transmission.
- Symmetric contact: $\Gamma = \Gamma_L = \Gamma_R$
- Transmission $T = \Gamma^2 |G|^2$

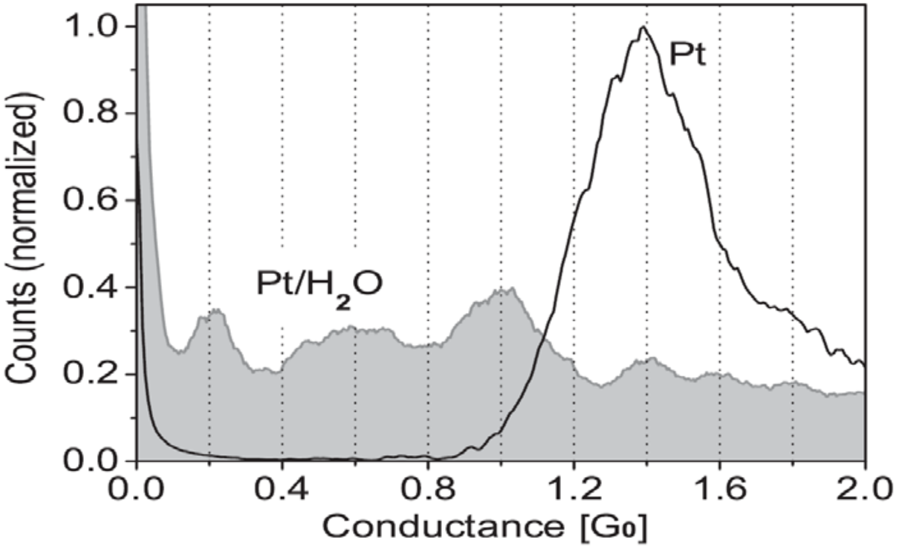
The inelastic correction to the conductance step at low temperatures is given by

$$\boxed{\delta G_{\mathrm{step}} = \frac{\lambda^2}{4\Gamma^2} T^2 (1-2T)}$$



14.2 Confirmation of the simple model: transport through water molecules

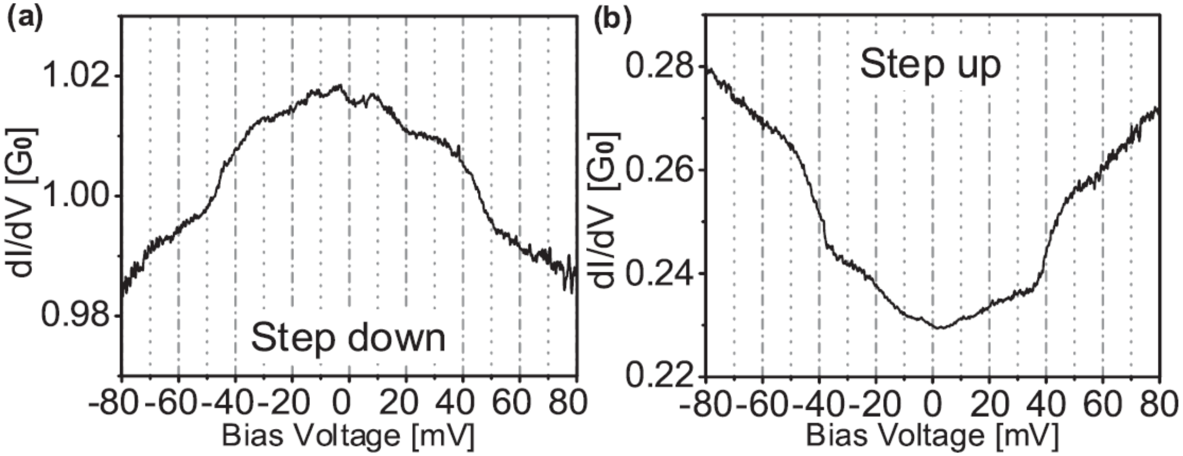
O. Tal, M. Krieger, B. Leerink, and J.M. van Ruitenbeek, Phys. Rev. Lett. ***100****, 196804 (2008)*



Pt-water-Pt junctions:

Conductance histogram

Inelastic electron tunneling spectroscopy



14.2 Inelastic transport method

$$H = H_e + H_{vib} + H_{e-vib}$$

$$H_e = \sum_{i,j} d_i^\dagger H_{ij} d_j \qquad H_{vib} = \sum_{\alpha} \hbar\omega_\alpha b_\alpha^\dagger b_\alpha \qquad H_{e-vib} = \sum_{i,j}\sum_{\alpha} d_i^\dagger \lambda_{ij}^\alpha d_j \left(b_\alpha^\dagger + b_\alpha\right)$$

$$\lambda_{ij}^\alpha = \sqrt{\frac{\hbar}{2\omega_\alpha}} \sum_{k,\mu} \langle i | \nabla_{k\mu} H_e \big|_{\vec{Q}=0} | j \rangle A_{k\mu,\alpha}$$

→ Implementation in TURBOMOLE by M. Bürkle using density functional perturbation theory (DFPT)

→ “analytical” derivatives

14.2 Lowest order expansion of current in e-vib coupling

$$I = I_{el}^0 + \delta I_{el}^0 + I_{inel}$$

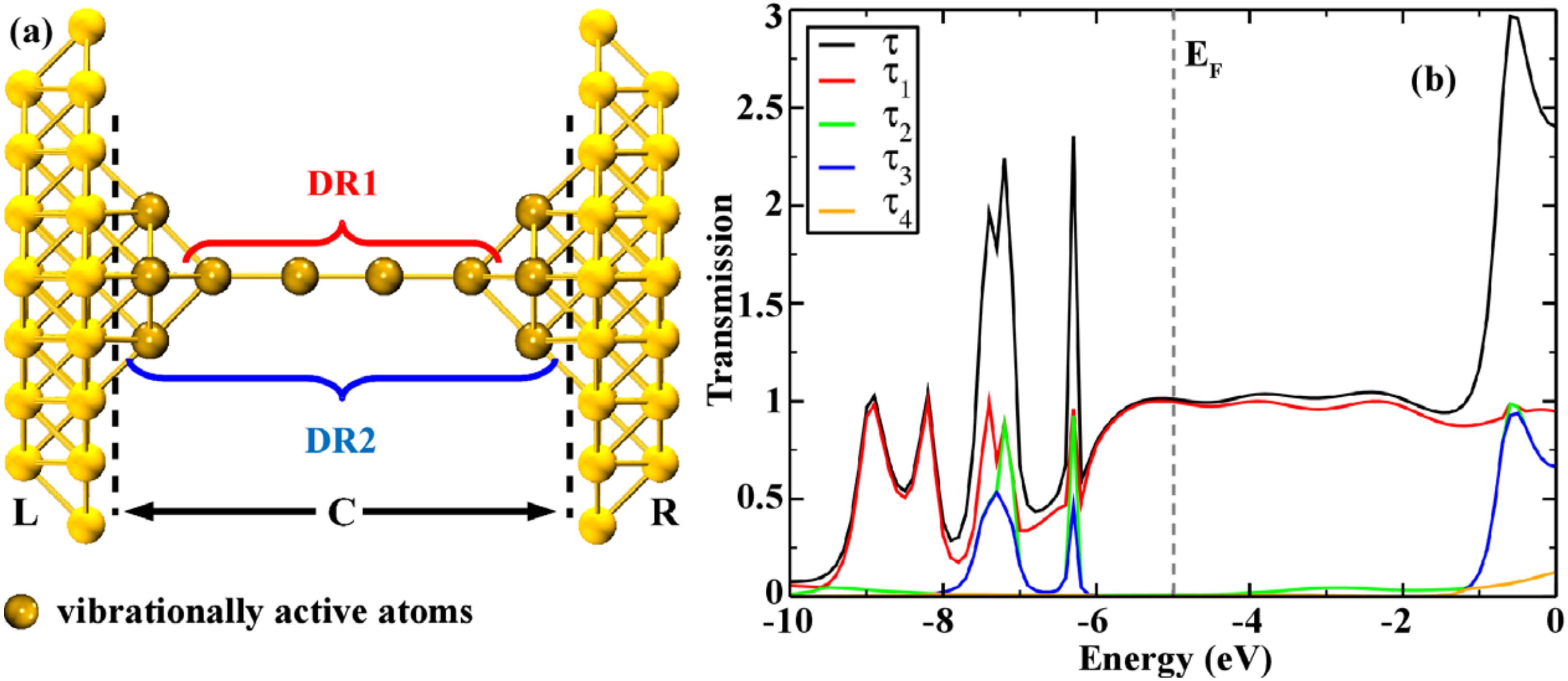
$$I_{el}^0 = \frac{2e}{h} \int \mathrm{d}E \,\mathrm{Tr}[\boldsymbol{G}^r \boldsymbol{\Gamma}_L \boldsymbol{G}^a \boldsymbol{\Gamma}_R] \left(f_L - f_R \right)$$

$$\delta I_{el}^0 = \frac{4e}{h} \int \mathrm{d}E \,\mathrm{Re}\,\mathrm{Tr}[\boldsymbol{\Gamma}_L \boldsymbol{G}^r \boldsymbol{\Sigma}^r_{e\text{-vib}} \boldsymbol{G}^r \boldsymbol{\Gamma}_R \boldsymbol{G}^a] \left(f_L - f_R \right)$$

$$I_{inel} = -\mathrm{i} \frac{2e}{h} \int \mathrm{d}E \,\mathrm{Tr}\left\{ \boldsymbol{G}^a \boldsymbol{\Gamma}_L \boldsymbol{G}^r \left[\left(f_L - 1 \right) \Sigma^<_{e\text{-vib}} - f_L \Sigma^>_{e\text{-vib}} \right] \right\}$$

Transport theory: J. K. Viljas, J. C. Cuevas, F. Pauly, and M. Häfner, Phys. Rev. B 72, 245415 (2005)
M. Bürkle et al., Phys. Status Solidi B 250, 2468 (2013)

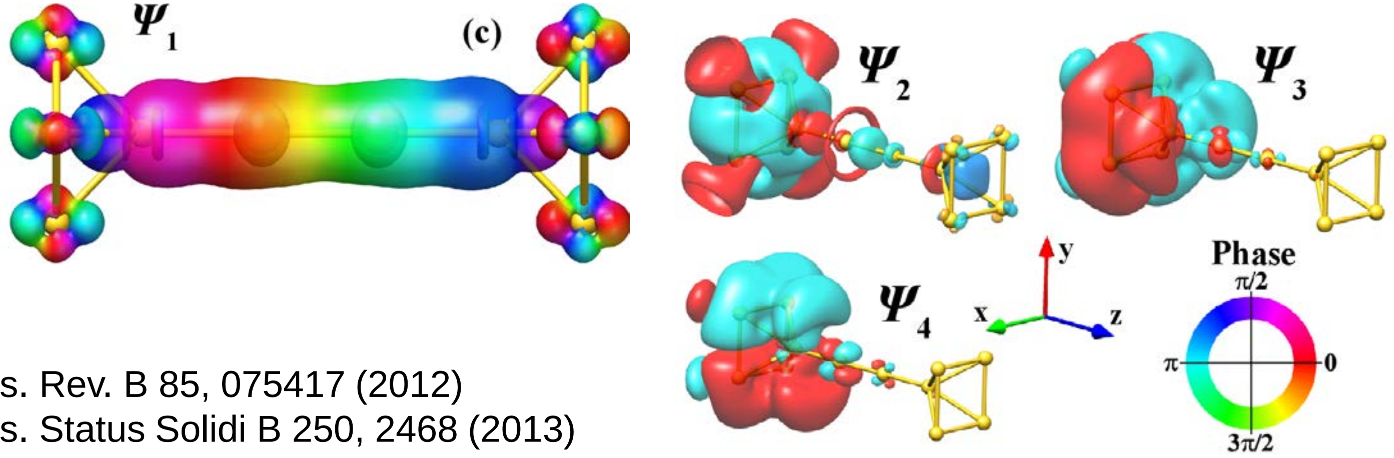
9.2 Selection rules for vibrational interactions



$$\tau_1 = 0.996$$

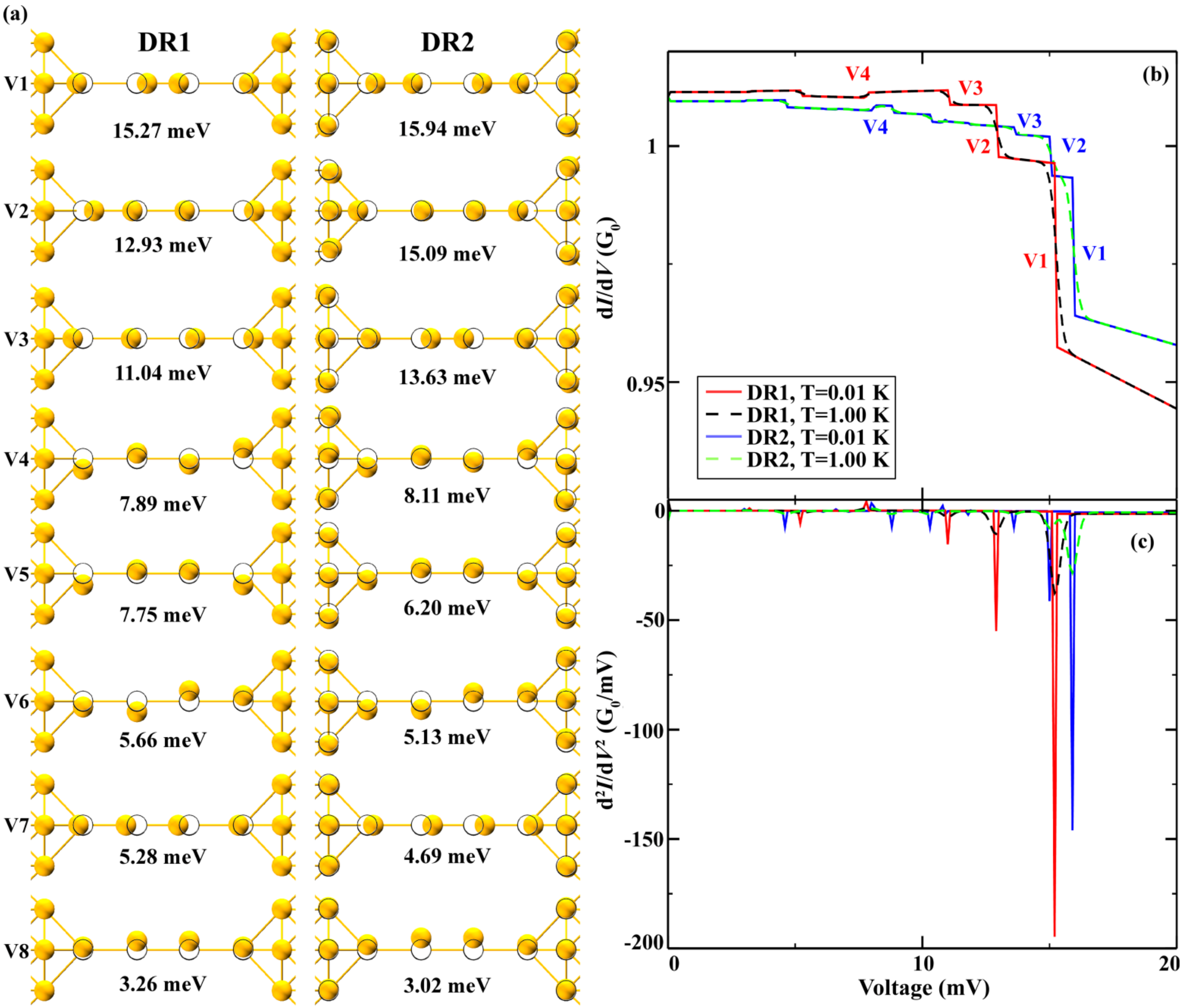
$$\tau_2 = 0.009$$

$$\tau_3 = \tau_4 = 0.003$$



M. Bürkle et al., Phys. Rev. B 85, 075417 (2012)
M. Bürkle et al., Phys. Status Solidi B 250, 2468 (2013)

9.2 Selection rules for vibrational interactions



M. Bürkle *et al.*,
Phys. Status Solidi
B 250, 2468 (2013)

9.3 Intermediate e-ph coupling regime: resonant phonon emission

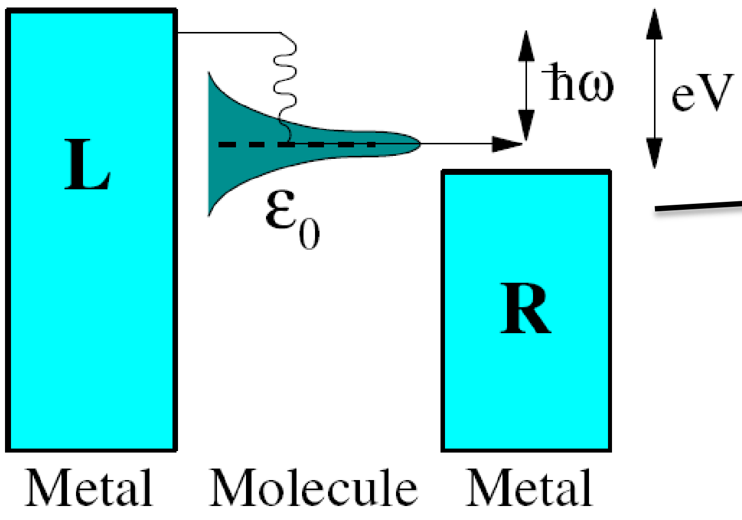
See for instance M. Galperin, A. Nitzan, M.A. Ratner, Phys. Rev. B ***73****, 045314 (2006)*

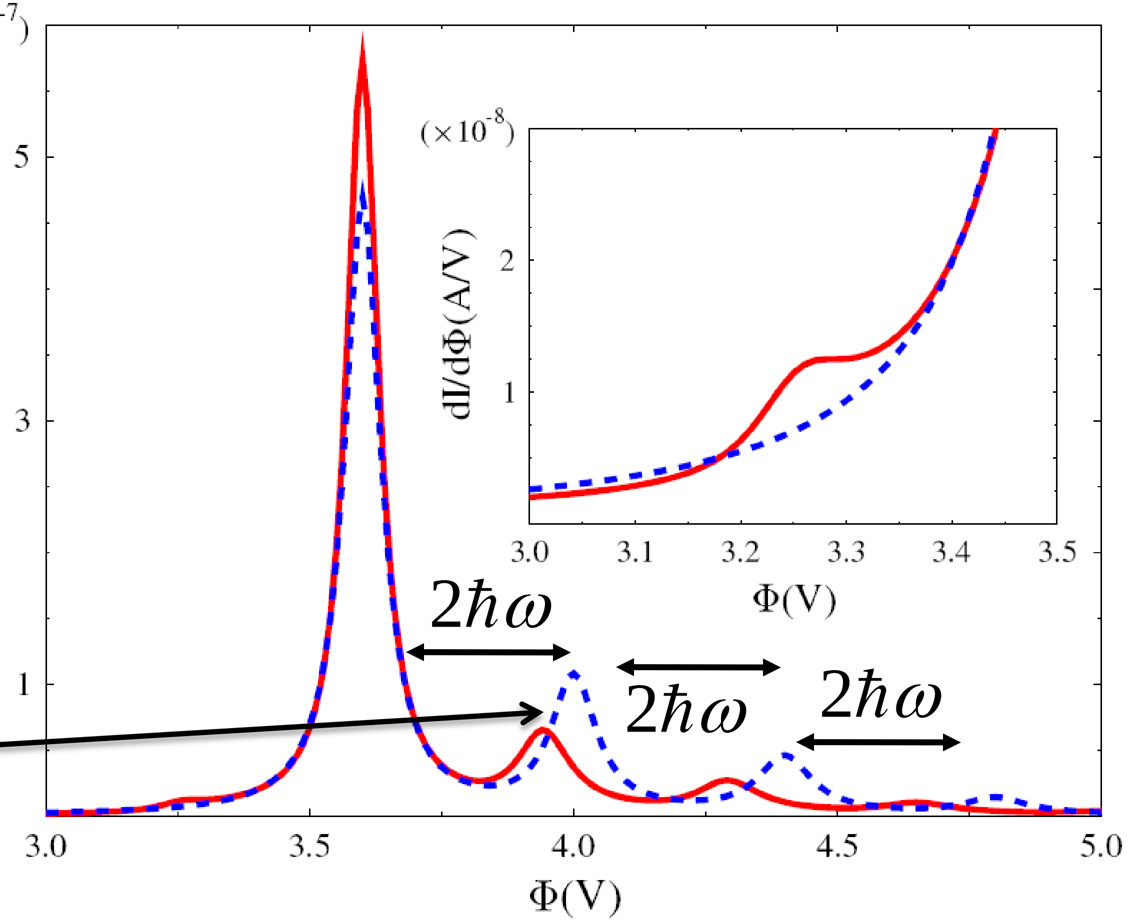
Theoretical method:

Equation of motion

$$(\lambda \approx \sqrt{\Delta E^2 + \Gamma^2})$$

(a) Resonant phonon emission

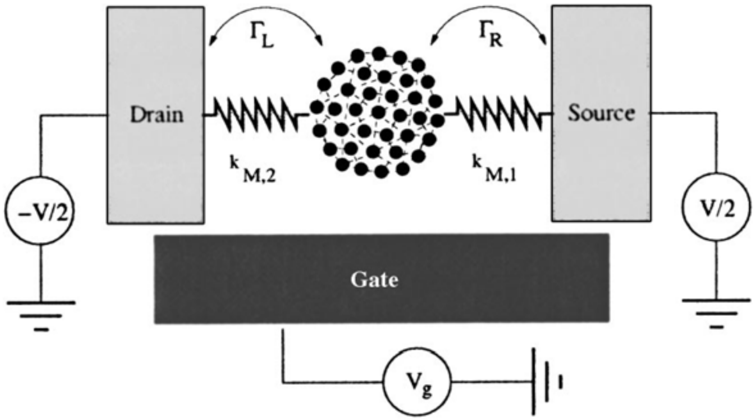




$$\lambda = 0.01\,\text{eV};\ \Gamma_L = \Gamma_R = 0.02\,\text{eV};\ \varepsilon_0 = 2\,\text{eV};$$

$$T = 10\,\text{K};\ \hbar\omega = 0.2\,\text{eV}$$

9.4 Strong e-ph coupling regime: phonon sidebands



Rate equations: $\lambda \gg \sqrt{\Delta E^2 + \Gamma^2}$

$$\begin{pmatrix} -2\Gamma_{10} & \Gamma_{01} & \Gamma_{01} \\ \Gamma_{10} & -\Gamma_{01} & 0 \\ \Gamma_{10} & 0 & -\Gamma_{01} \end{pmatrix} \begin{pmatrix} P_0 \\ P_\uparrow \\ P_\downarrow \end{pmatrix} = 0$$

*See for instance S. Braig and K. Flensberg, PRB **68**, 205324 (2003)*