INELASTIC EFFECTS IN MOLECULAR CONDUCTION

REGENSBURG 2004

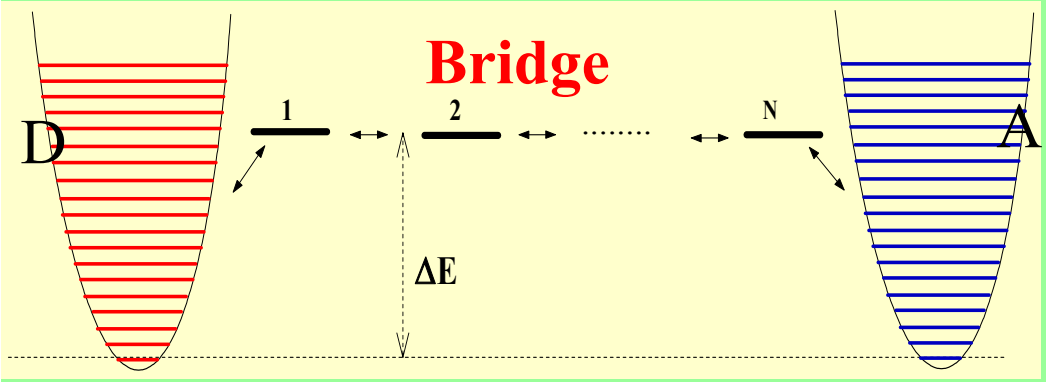
Thanks

I. Benjamin, A. Burin, G. Cuniberti, B. Davis, D. Evans, M. Galperin, H. Grabert, P. Hänggi, G. Ingold, J. Jortner, S. Kohler, R. Kosloff, J. Lehmann, M. Majda, A. Mosyak, V. Mujica, R. Naaman, U. Peskin, M. Ratner, D. Segal, T. Seideman, H. Tal-Ezer

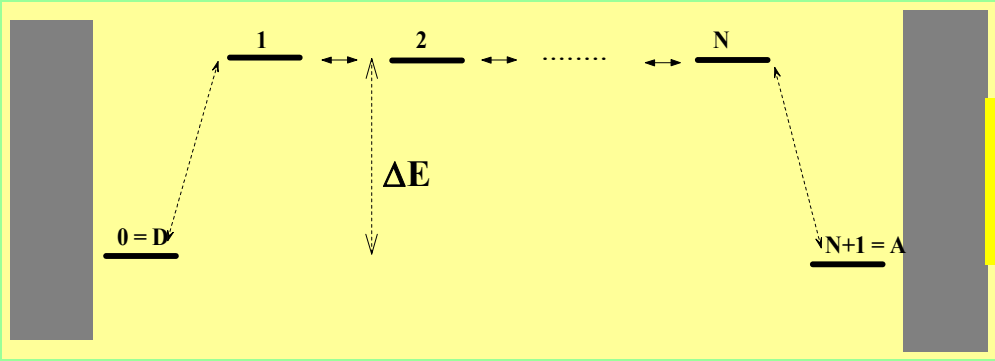
Barrier dynamics effects on electron transmission through molecular wires and layers

- ?Using frozen configurations in transmission calculations?
- Relevant timescales
- Inelastic contributions to the tunneling current
- Dephasing and activation - transition from coherent transmission to activated hopping
- Heating of current carrying molecular wires
- Inelastic tunneling spectroscopy

Electron transfer/transmission



$$k_{D\to A} = \frac{2\pi}{\hbar}\left|V_{D1}V_{NA}\right|^2 \left|G_{1N}(E_D)\right|^2 \mathcal{F}$$

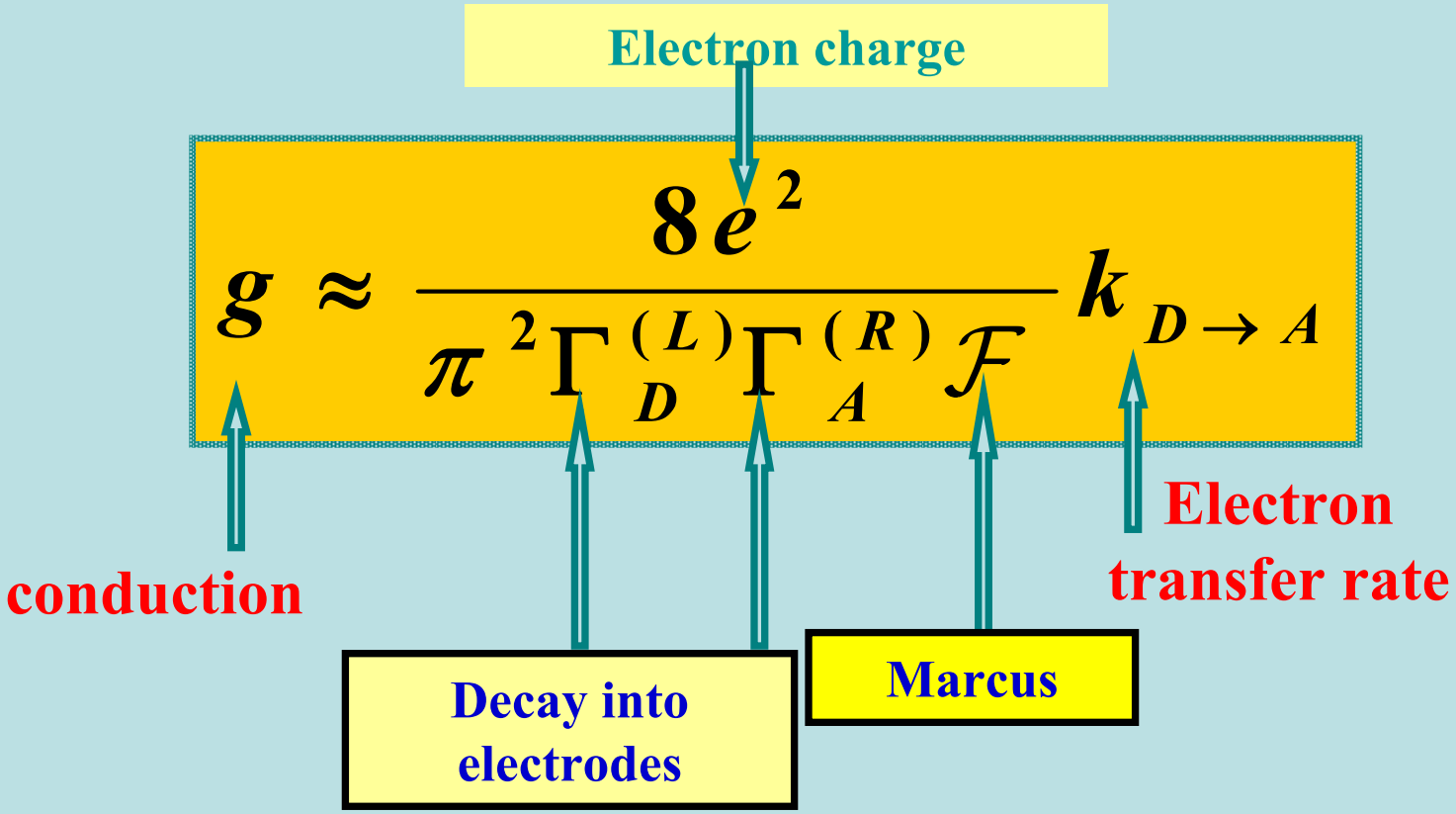


$$g(E) = \frac{e^2}{\pi\hbar}\left|G_{DA}(E)\right|^2 \Gamma_D^{(L)}(E)\Gamma_A^{(R)}(E)$$

$$G_{DA}(E) = \frac{V_{D1}V_{NA}}{\left(E - E_D - \Sigma_D^{(L)}(E)\right)\left(E - E_A - \Sigma_A^{(R)}(E)\right)} G_{1N}(E)$$

$$\approx -\frac{V_{D1}V_{NA}}{\left[(1/2)\Gamma_D^{(L)}\right]\left[(1/2)\Gamma_A^{(R)}\right]} G_{1N}(E)$$

A relation between g and k



AN, J. Phys. Chem. A 105, 2677(2001)

A relation between g and k

$$g \approx \frac{8e^2}{\pi^2 \Gamma_D^{(L)} \Gamma_A^{(R)} \mathcal{F}} k_{D \to A}$$

$$\mathcal{F} = \left(\sqrt{4\pi\lambda k_B T}\right)^{-1} \exp\left(-\lambda / 4k_B T\right)$$

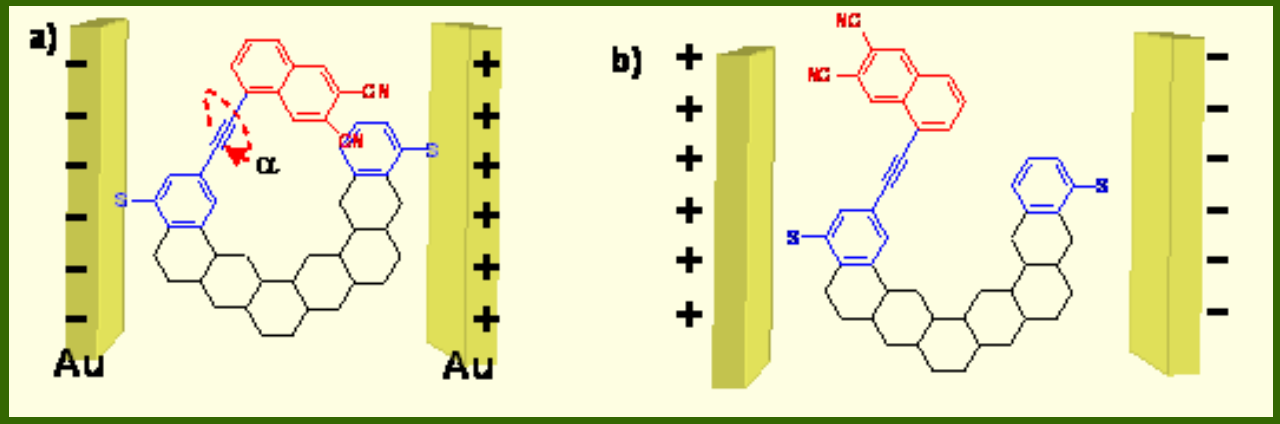
$\lambda \approx 0.5\text{eV}$ $\qquad \Gamma_D^{(L)} = \Gamma_A^{(R)} \approx 0.5\,eV$

$$g \sim \left(e^2 / \pi\hbar\right)\left(10^{-13} k_{D \to A}(s^{-1})\right)$$

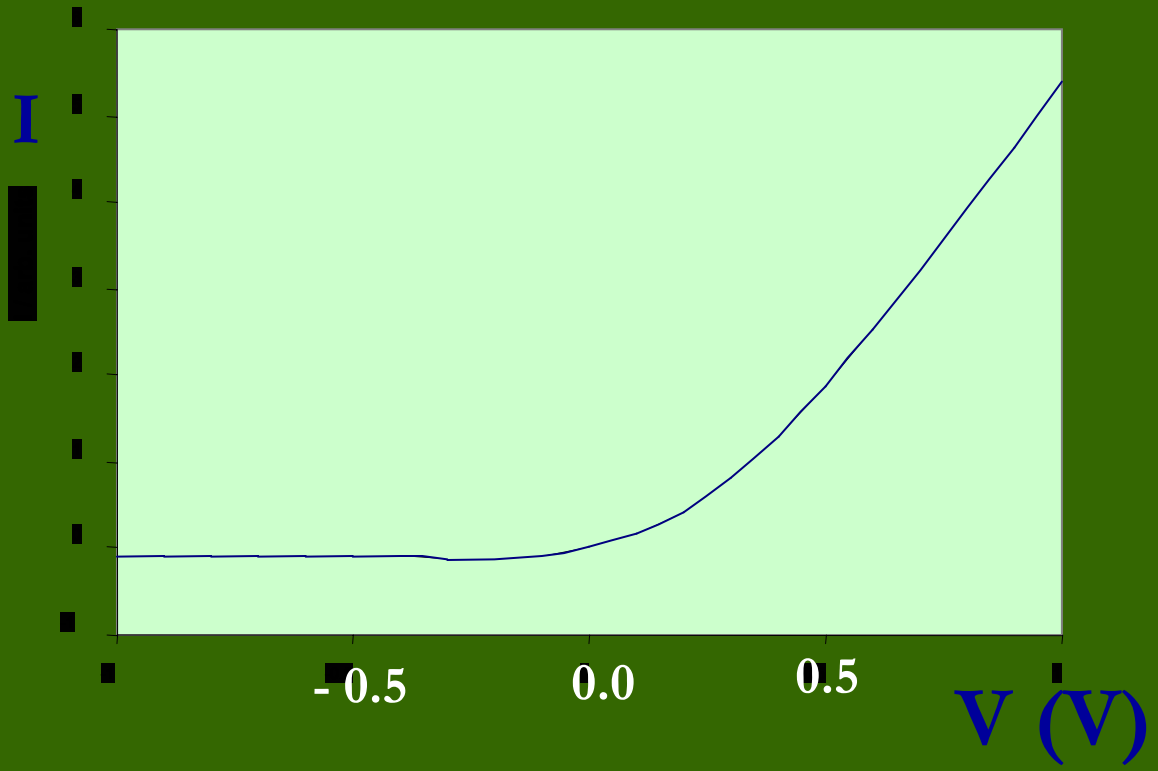
$$\cong \left[10^{-17} k_{D \to A}(s^{-1})\right] \Omega^{-1}$$

Comparing conduction to rates
(M. Newton, 2003)

alkane bridge[a] ($X(CH_2)_{n-2}$)	g (Ω^{1-})[b]	$5 \times 10^{-19} k_{et}$/DOS[c] (eq 2.23)
$n = 8$	$(10.3 \pm 0.5) \times 10^{-10}$	2×10^{-8}
$n = 10$	$(3.5 \pm 0.2) \times 10^{-10}$	$(2 \pm 1) \times 10^{-9}$
$n = 12$	$(1.2 \pm 0.1) \times 10^{-10}$	$(2 \pm 1) \times 10^{-10}$



Ratner and Troisi, 2004



Barrier dynamics effects on electron transmission through molecular wires and layers

- ?Using frozen configurations in transmission calculations?
- Relevant timescales
- Inelastic contributions to the tunneling current
- Dephasing and activation - transition from coherent transmission to activated hopping
- Heating of current carrying molecular wires
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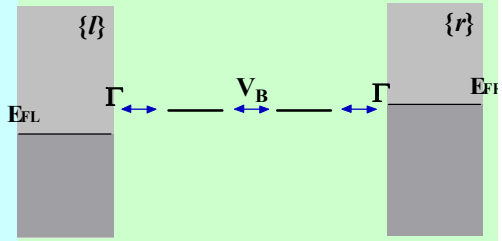
ENERGY PARAMETERS:

ΔE (energy gap) ; V_B (intersite coupling, bandwidth) ; Γ (coupling of edge sites to leads); U (charging energy); λ (reorganization energy - interaction with environment); $k_B T$ (thermal energy), $e\Phi$ (voltage drop)



TIME SCALES:

Traversal time

energy relaxation time

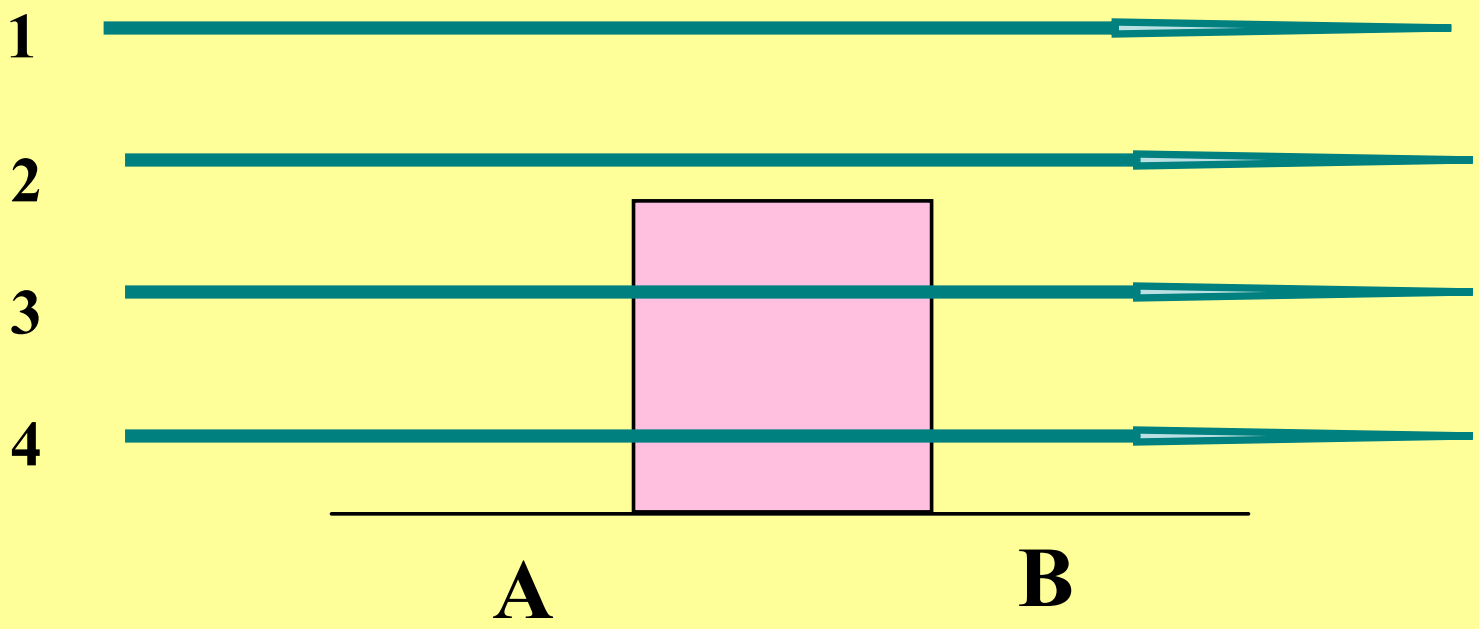
dephasing time

environmental correlation time

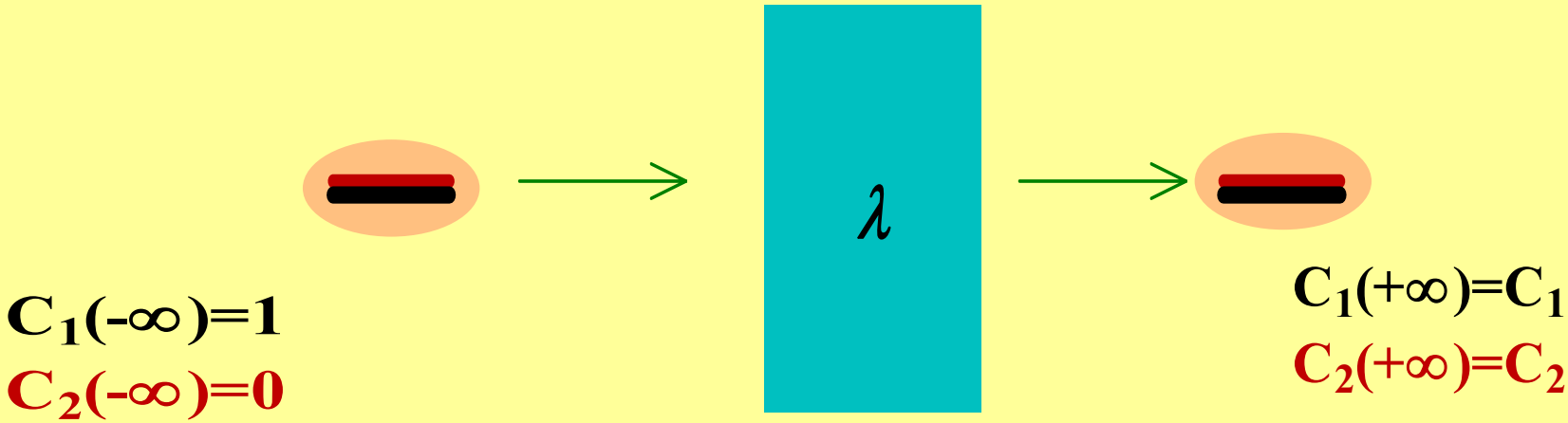
hopping time

lifetime of electron on edge site

Traversal time for tunneling?

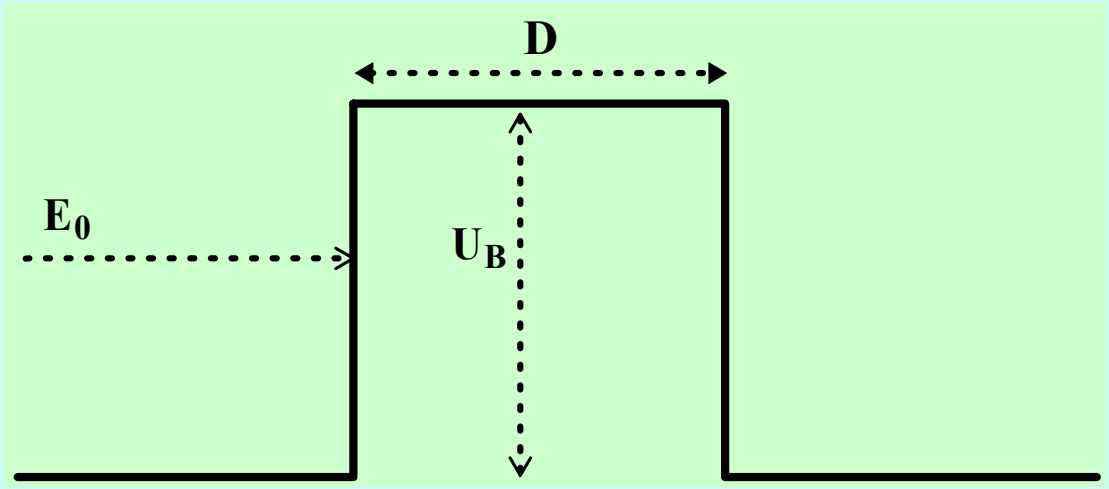


Traversal Time

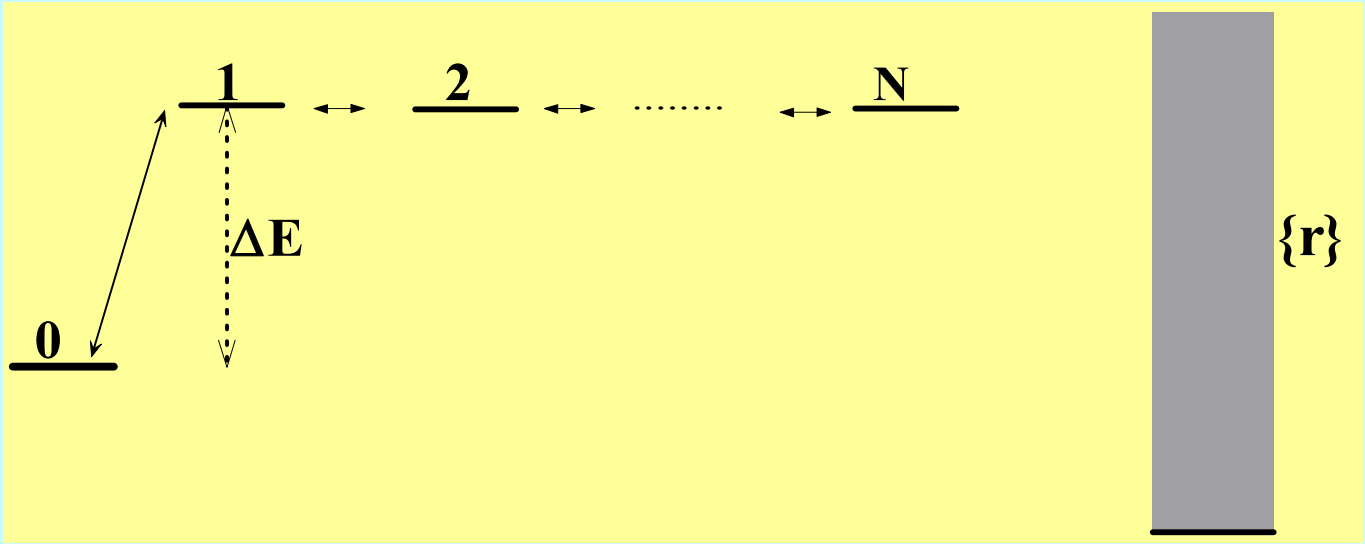


$$\tau = \lim_{\lambda \to 0} \left(\frac{\hbar}{|\lambda|} \left| \frac{c_2}{c_1} \right| \right)$$

"Tunnelling Times"



$$\tau = \sqrt{\frac{m}{2(U_B - E_0)}} D$$



$$\tau = \frac{\hbar N}{\Delta E}$$

Estimates

$$\tau = \sqrt{\frac{m}{2(U_B - E_0)}} D \qquad \sim 0.2\text{fs}$$

$$\tau = \frac{\hbar N}{\Delta E} \qquad \sim 2\ \text{fs}$$

For: D=10A (N=2-3)

U_B-E = ΔE~1eV

$m=m_e$

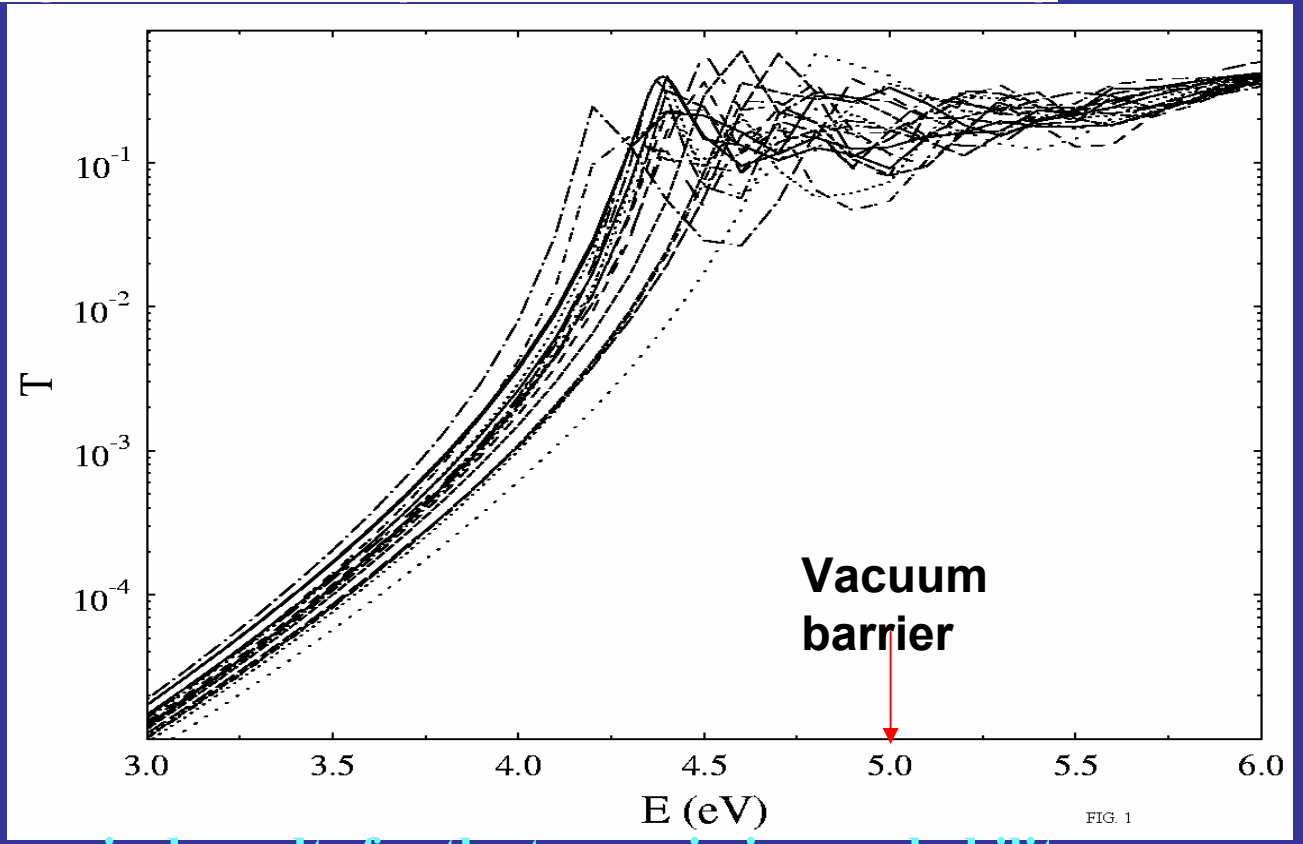
For resonance transmission same expression applies except that ΔE becomes the bandwidth

Notes:

- **Both time estimates are considerably shorter than vibrational period**
- **Potential problem: Near resonance these times become longer**

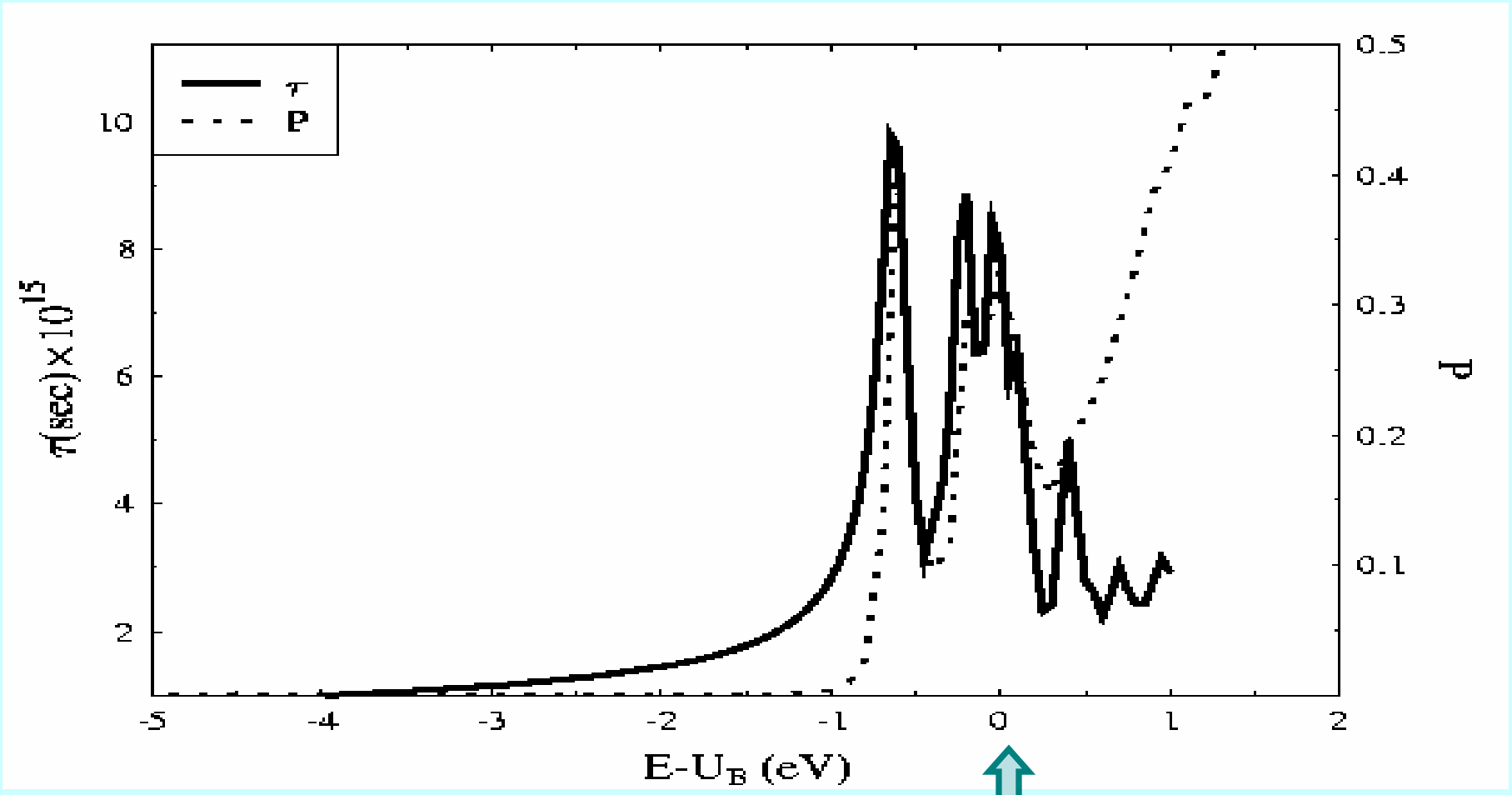
Transmission through several water configurations (equilibrium, 300K)

Galperin, AN & Benjamin, J. Phys. Chem., **106**, 10790-96 (2002)



1. A compilation of numerical results for the transmission probability as a function of incident electron energy, obtained for 20 water configurations sampled from an equilibrium trajectory (300K) of water between two planar parallel Pt(100) planes separated by 10Å. The vacuum is 5eV and the resonance structure seen in the range of 1eV below it varies strongly between any two configurations. Image potential effects are disregarded in this calculation.

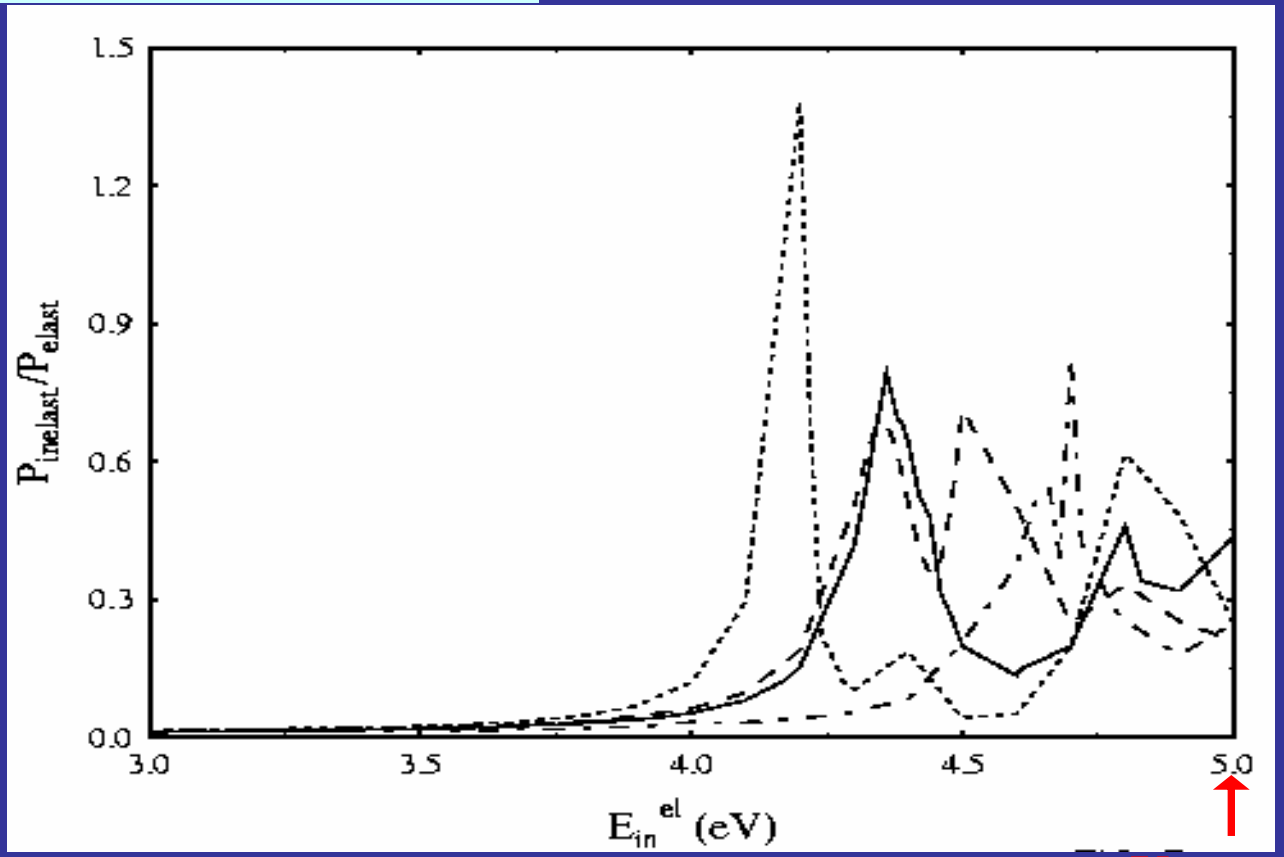
Water: Tunneling time and transmission probability



Galperin, AN, Peskin J. Chem. Phys. 114, 9205-08 (2001)

$$T_{L\to R}(E',E)=\gamma_L\bar{G}^r(E)\gamma_R\bar{G}^a(E)\delta(E-E')$$

$$+MG^r(E)\gamma_L G^a(E)M^\dagger\bar{G}^a(E')\gamma_R\bar{G}^r(E')$$
$$\times\left[N_0\delta(E-E'+\omega_0)+(N_0+1)\delta(E-E'-\omega_0)\right]$$



The ratio between the inelastic (integrated over all transmitted energies) and elastic components of the transmission probability calculated for different instantaneous structures of a water layer consisting of 3 monolayers of water molecules confined between two Pt(100) surfaces.

Vacuum barrier

Galperin & AN, J. Chem. Phys. **115**, 2681 (2001)

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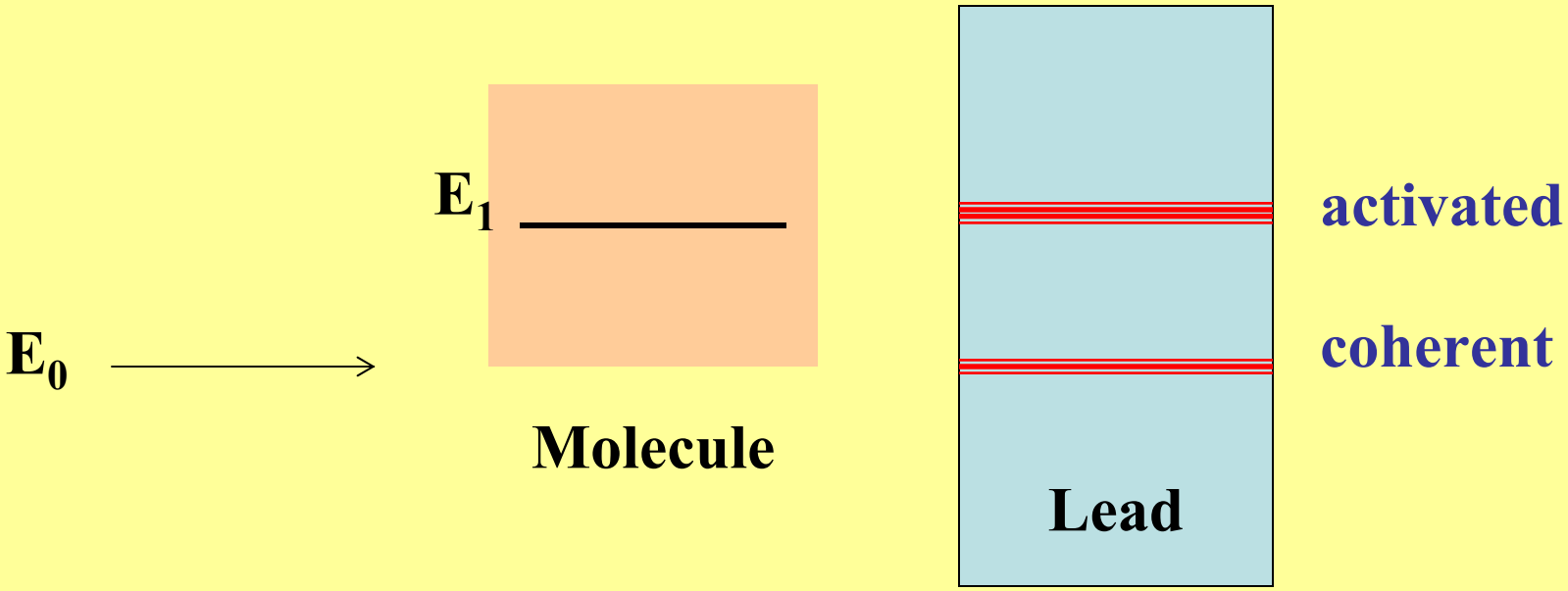
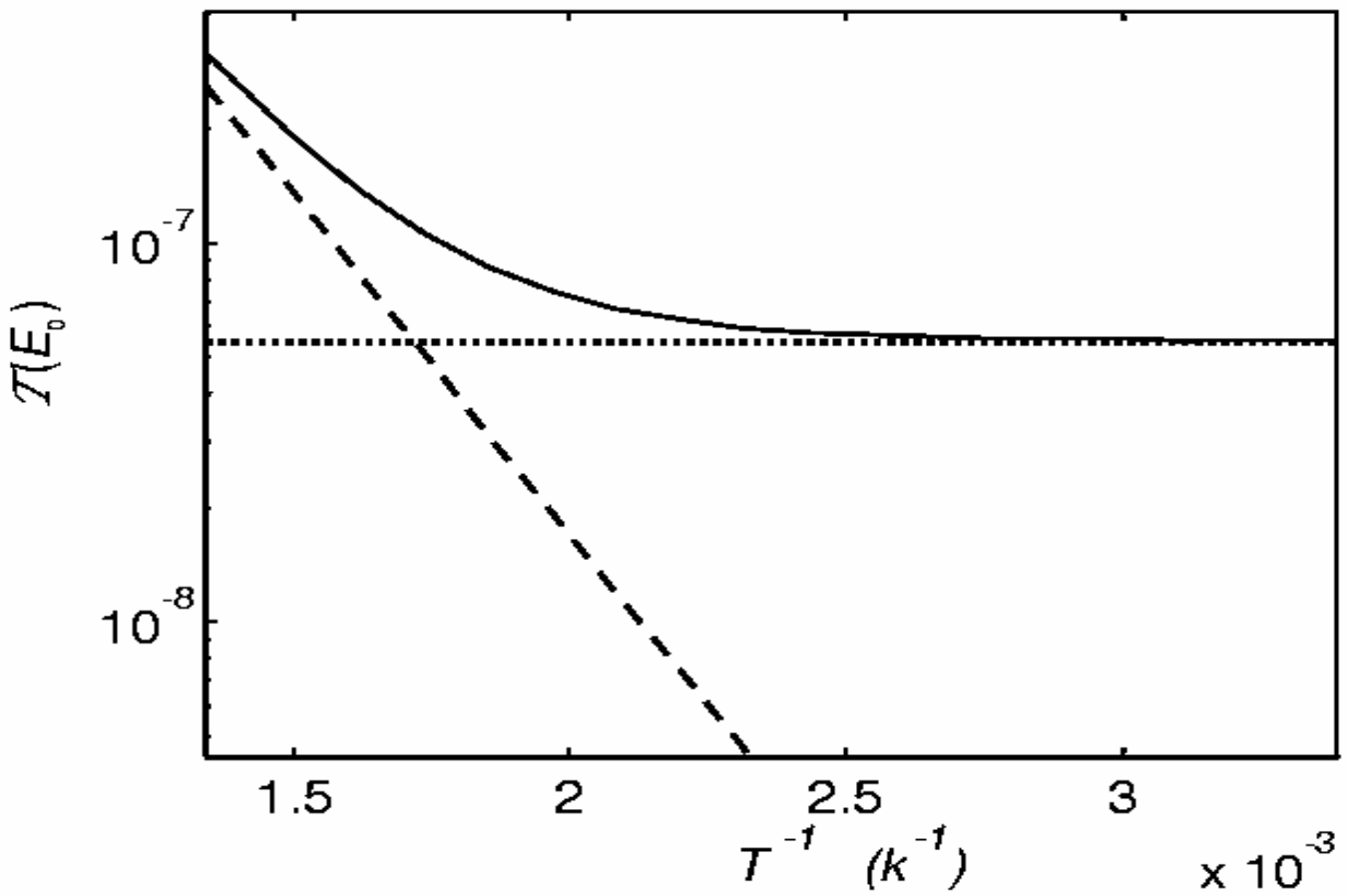
Coupling to thermal environment



- **Energy resolved transmission:**

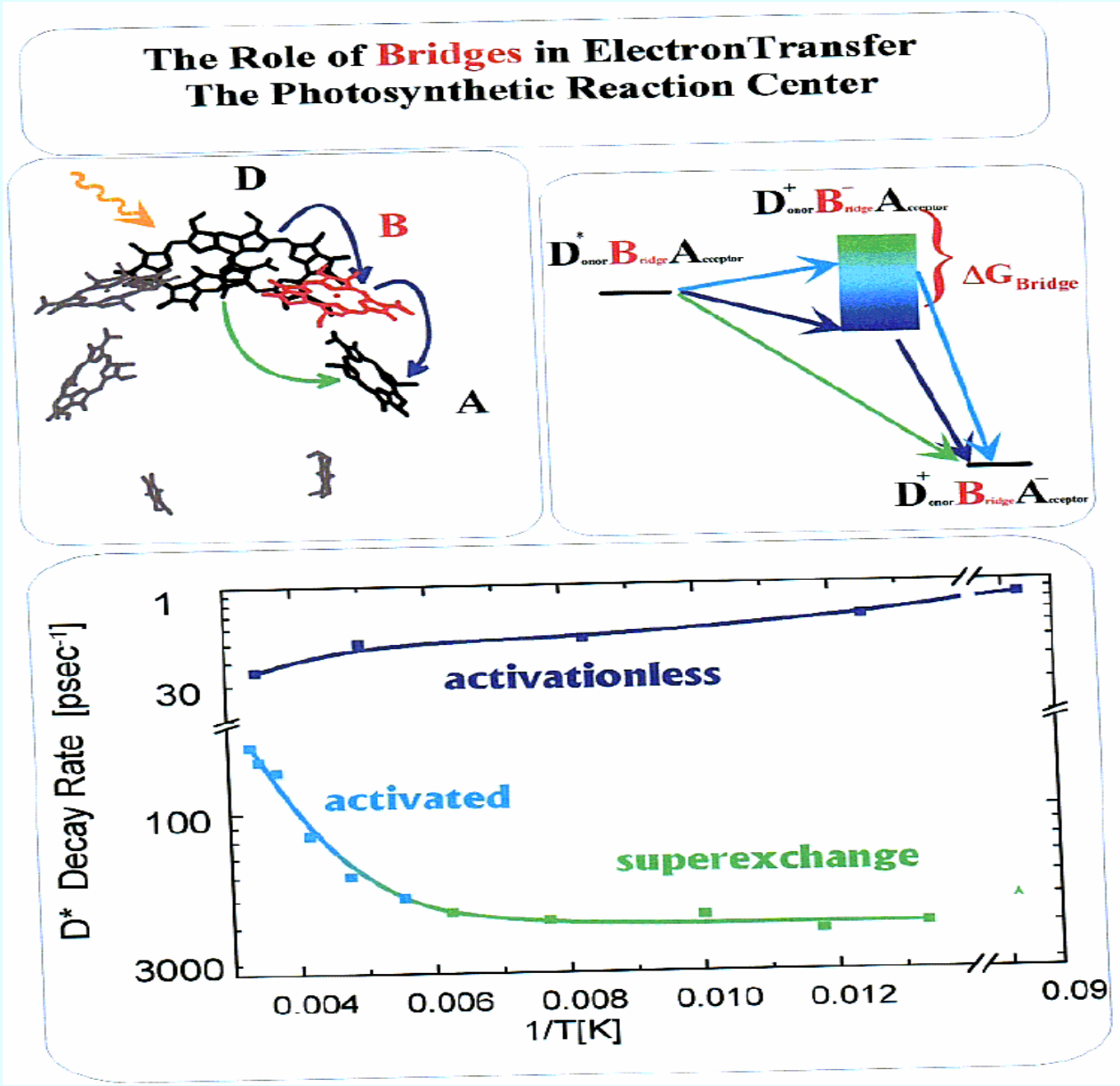
$$\mathcal{T}(E_0, E) = \frac{\Gamma_{1L}\Gamma_{1R}}{(E_1 - E_0)^2 + (\Gamma_1/2)^2}\left[\delta(E_0 - E) + \frac{(\kappa/2\pi)e^{-\beta(E_1 - E_0)}}{(E_1 - E)^2 + (\Gamma_1/2)^2}\right]$$

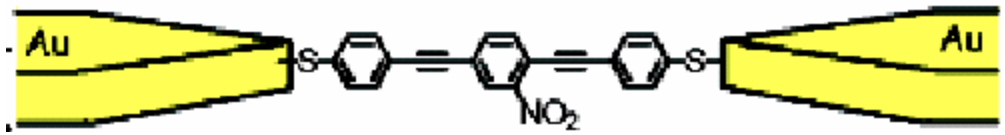
Dependence on temperature

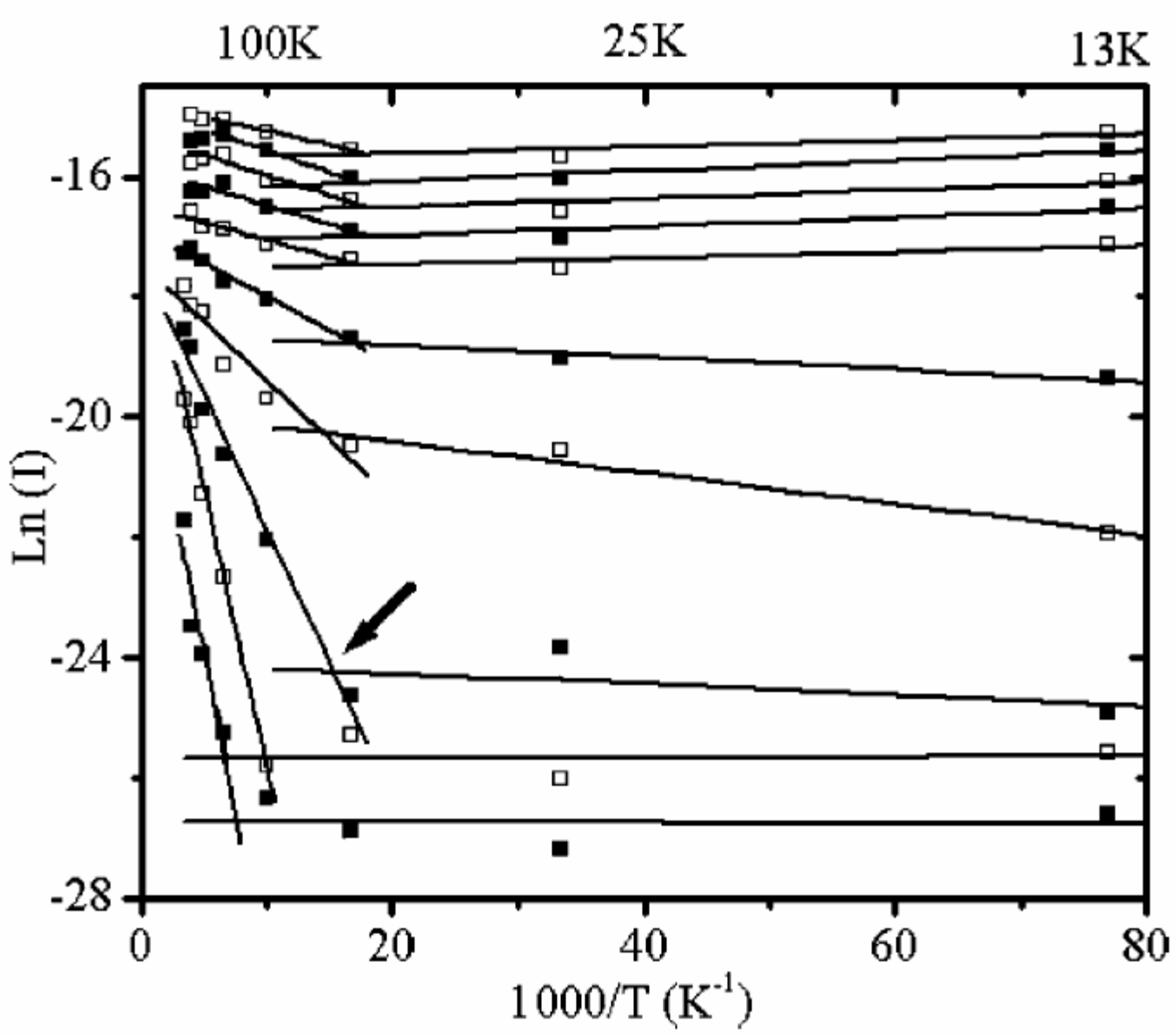


The integrated elastic (dotted line) and activated (dashed line) components of the transmission, and the total transmission probability (full line) displayed as function of inverse temperature. Parameters are as in Fig. 3.

The photosythetic reaction center

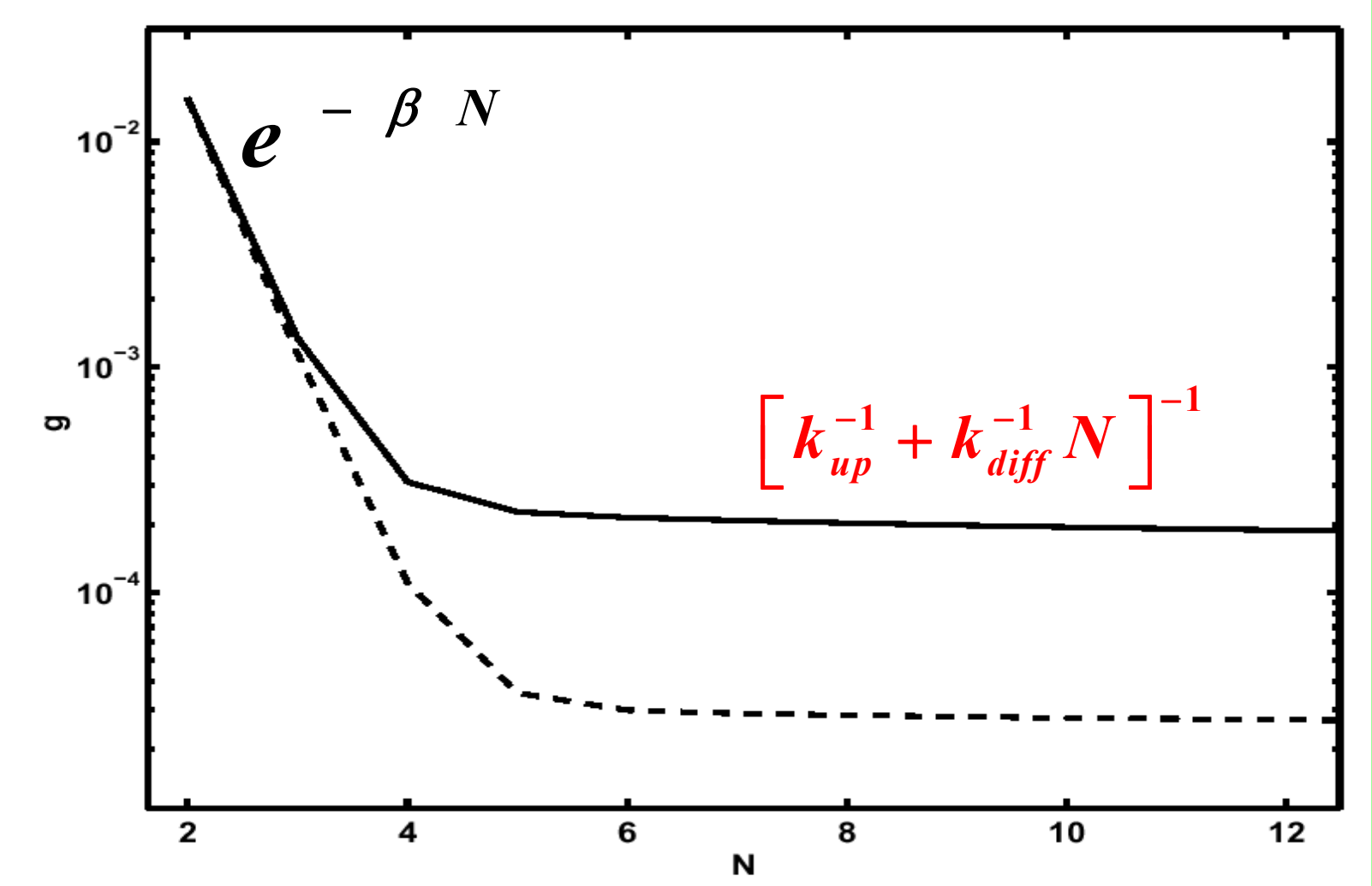




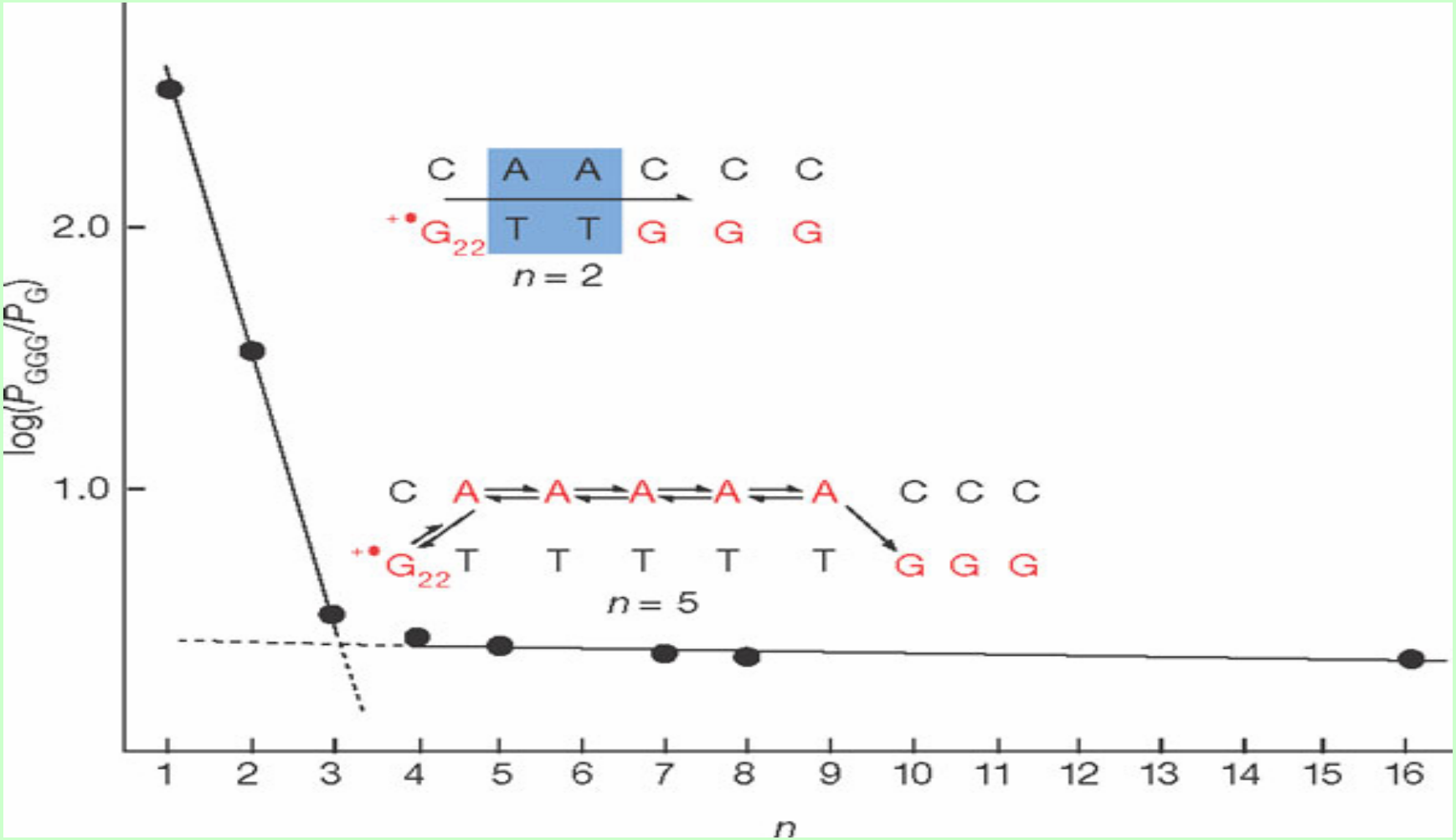


Selzer et al, JACS (2003)

Dependence on bridge length



DNA (Giese et al 2001)



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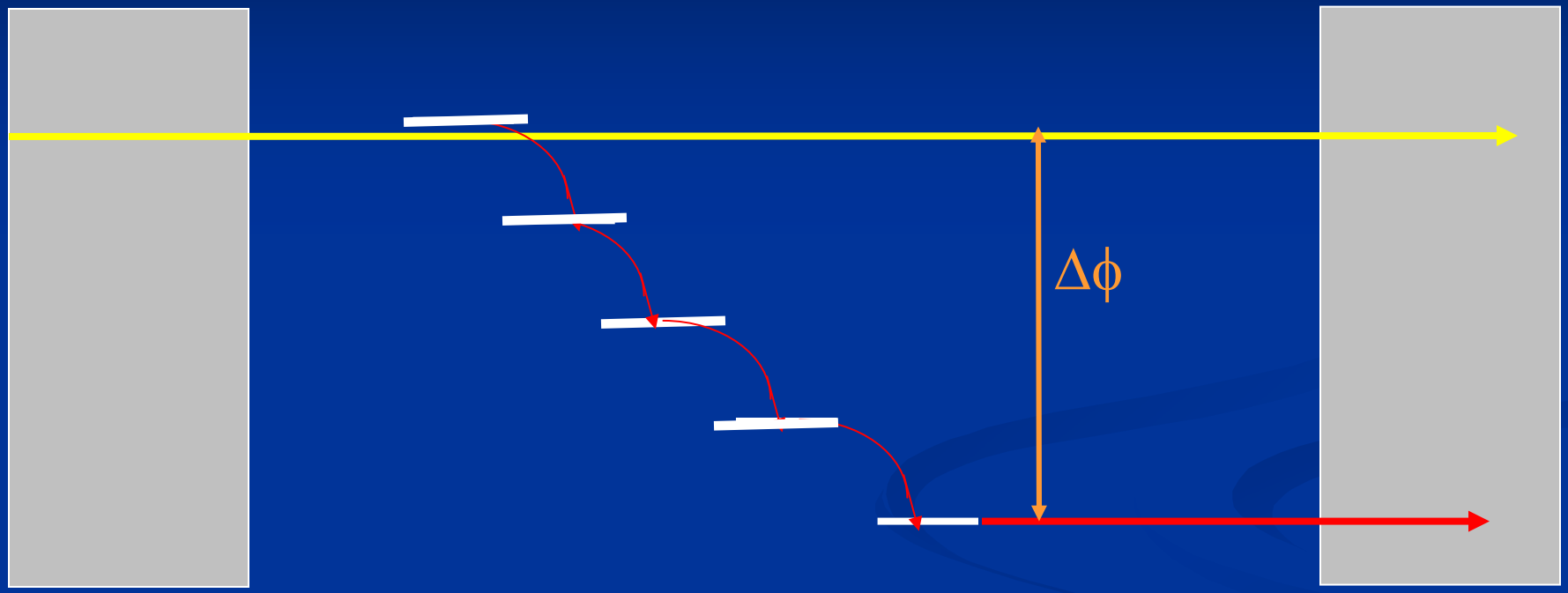
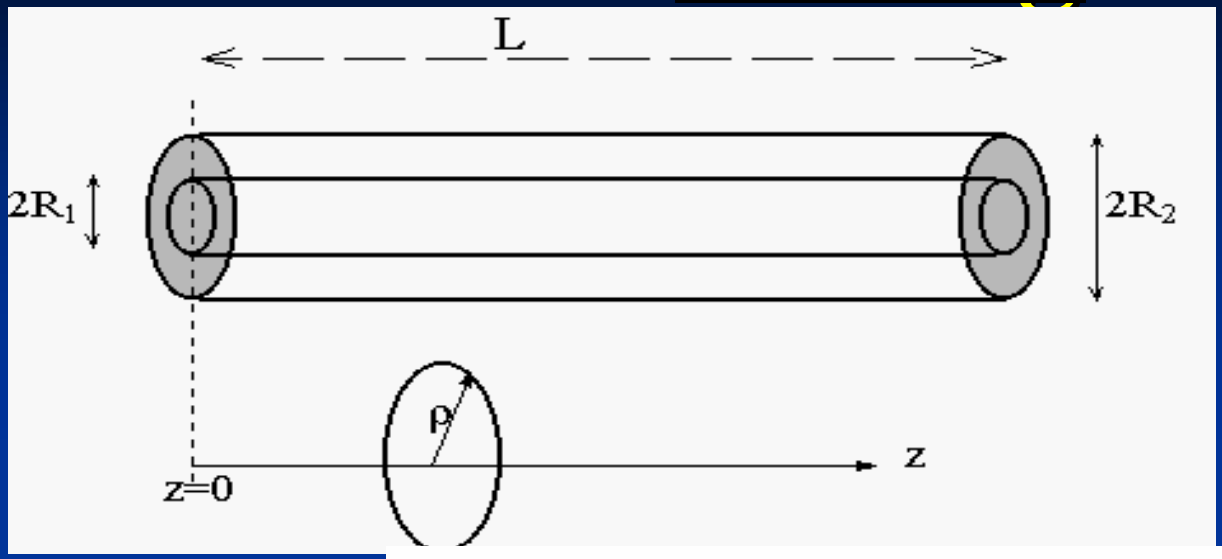
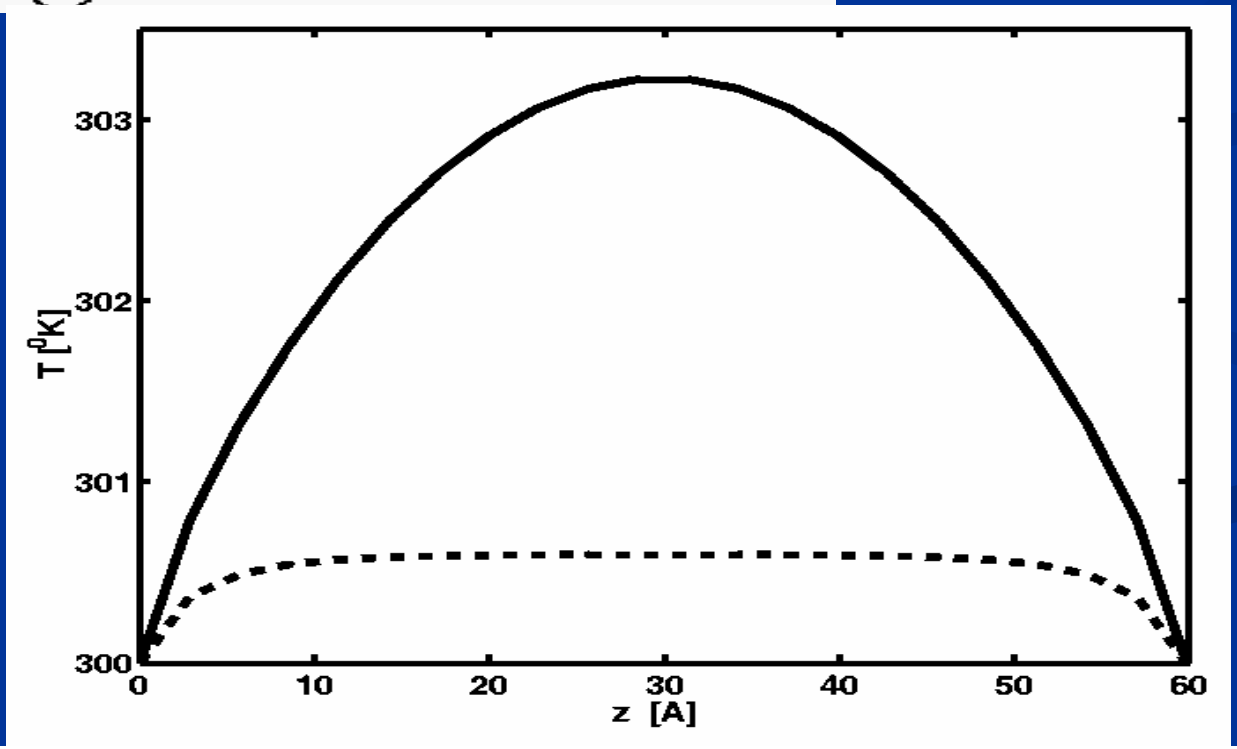
Elastic transmission vs. maximum heat generation:



Heating





The quantum heat flux

$$I_h = \int \mathcal{T}(\omega)\left[n_L(\omega) - n_R(\omega)\right]\omega d\omega$$

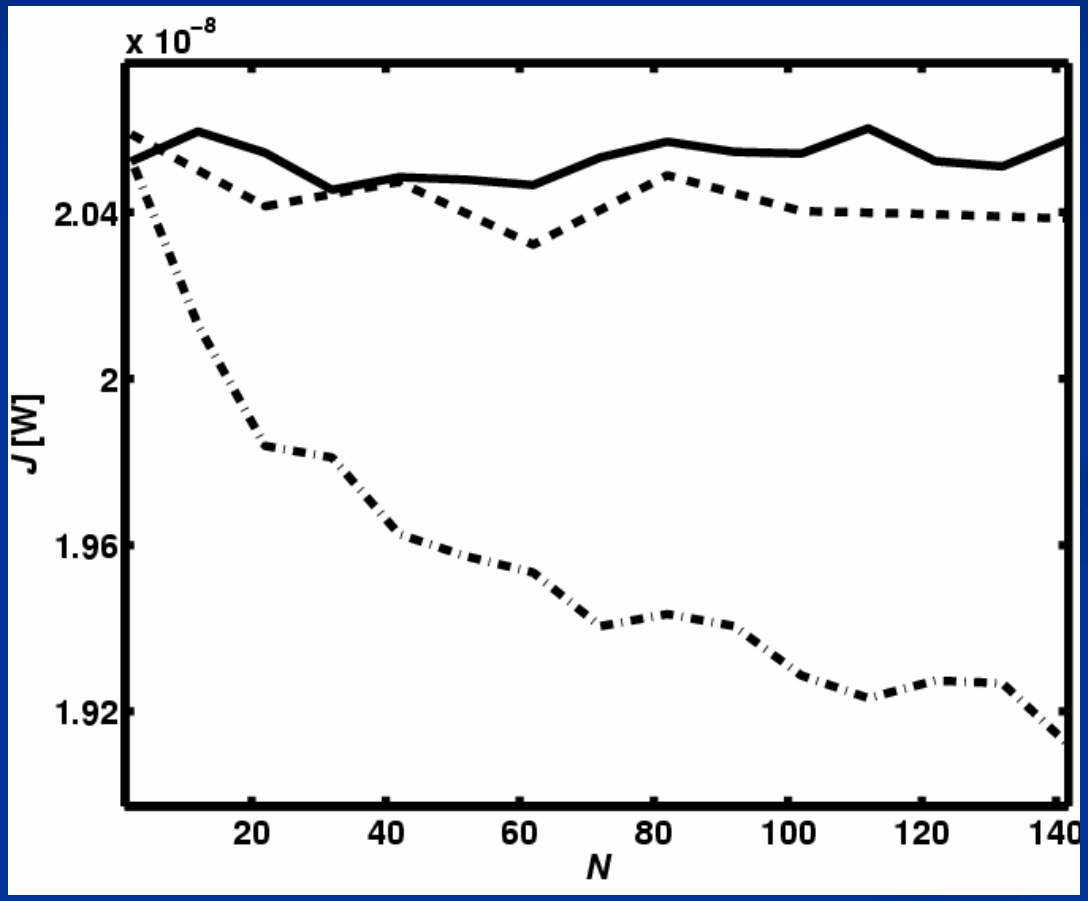
Transmission coefficient at frequency ω

Bose Einstein populations for left and right baths.

With Dvira Segal and Peter Hanggi

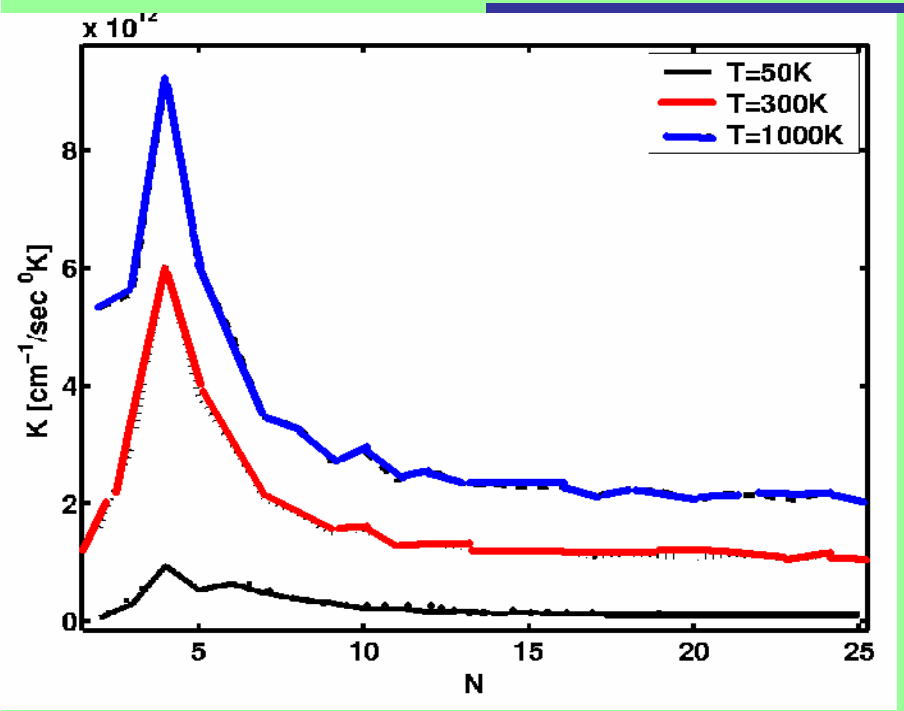
J. Chem. Phys. **119**, 6840-6855 (2003)

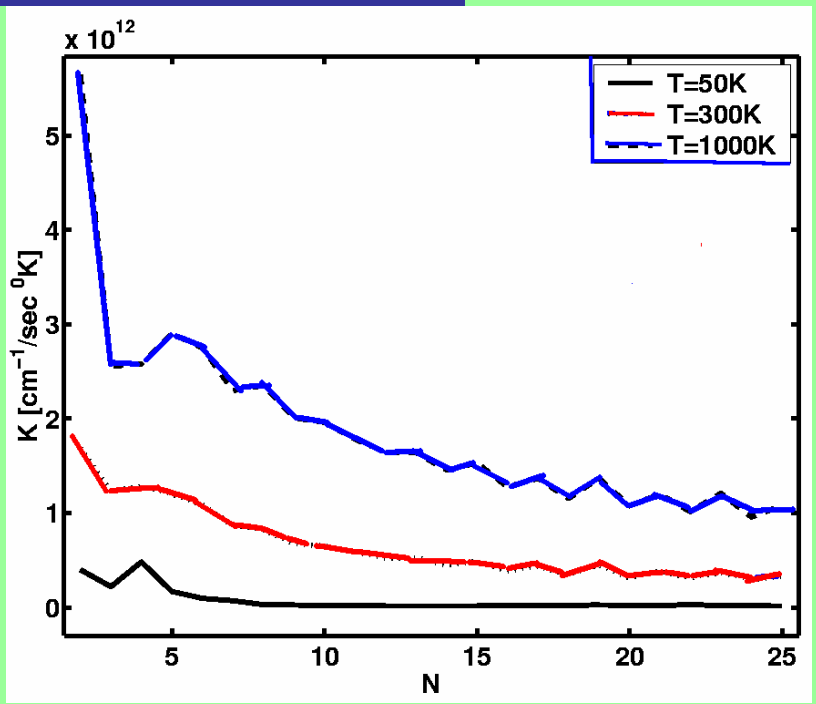
Anharmonicity effects



Heat current vs. chain length from classical simulations. Full line: harmonic chain; dashed line: anharmonic chain using the alkane force field parameters; dash-dotted line: anharmonic chain with unphysically large (x 30) anharmonicity

Heat conduction in alkanes of different chain length

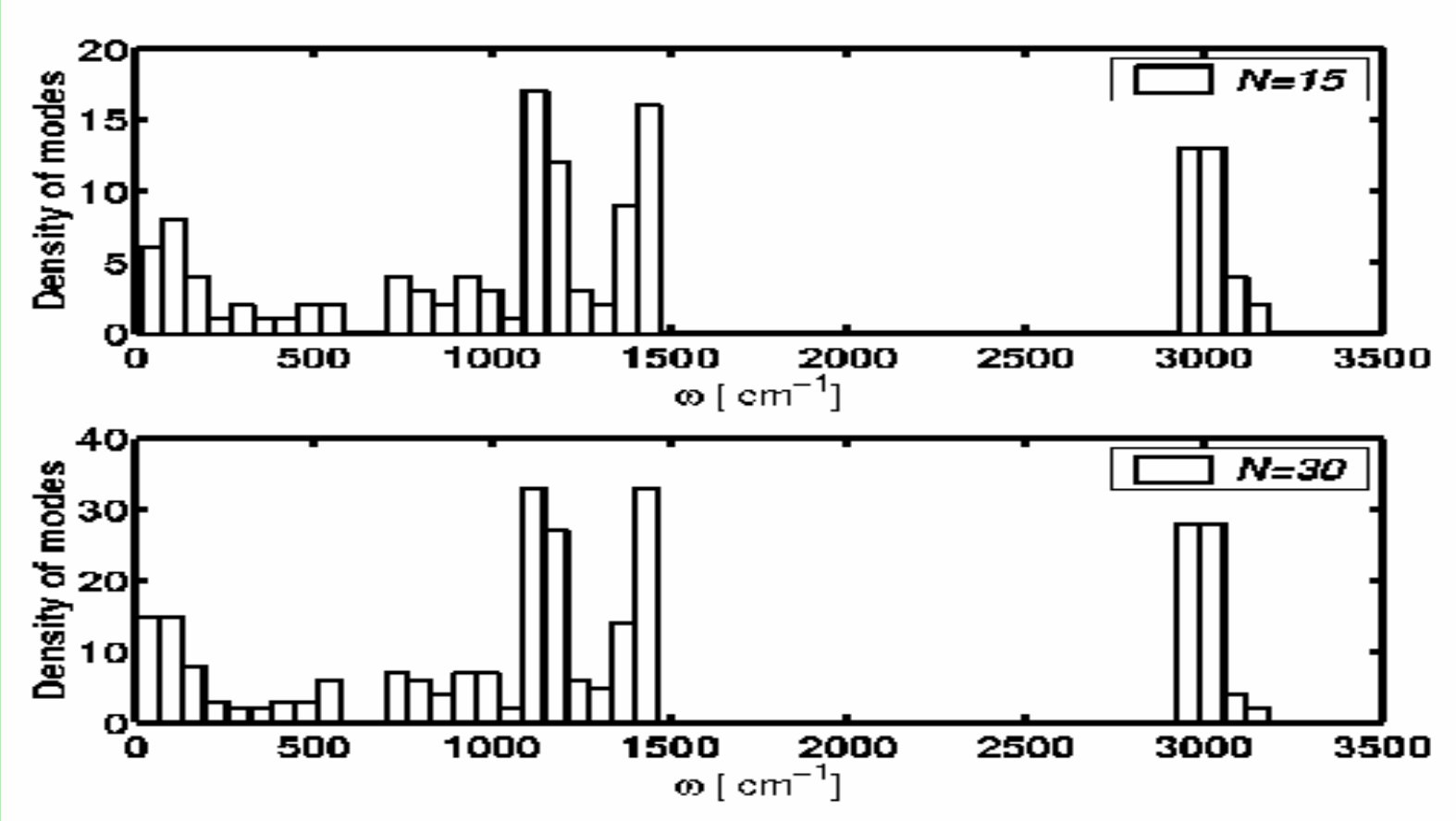




The thermal conductance vs. the chain length for Alkanes, ω_c=400 cm^{-1} , V_L=V_R=50 cm^{-2}. Black: T=50K; Red: T=300K; Blue: T=1000K

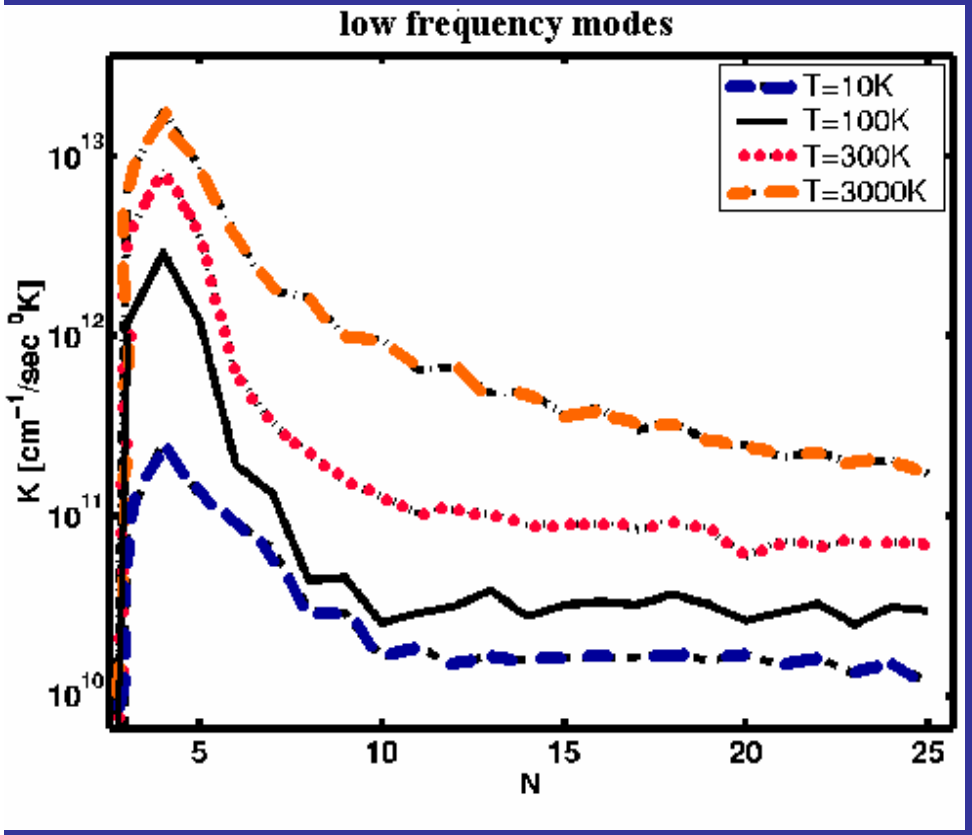
ω_c=400 cm^{-1} , V_L=V_R=200 cm^{-2}. Black: T=50K; Red: T=300K; Blue: T=1000K.

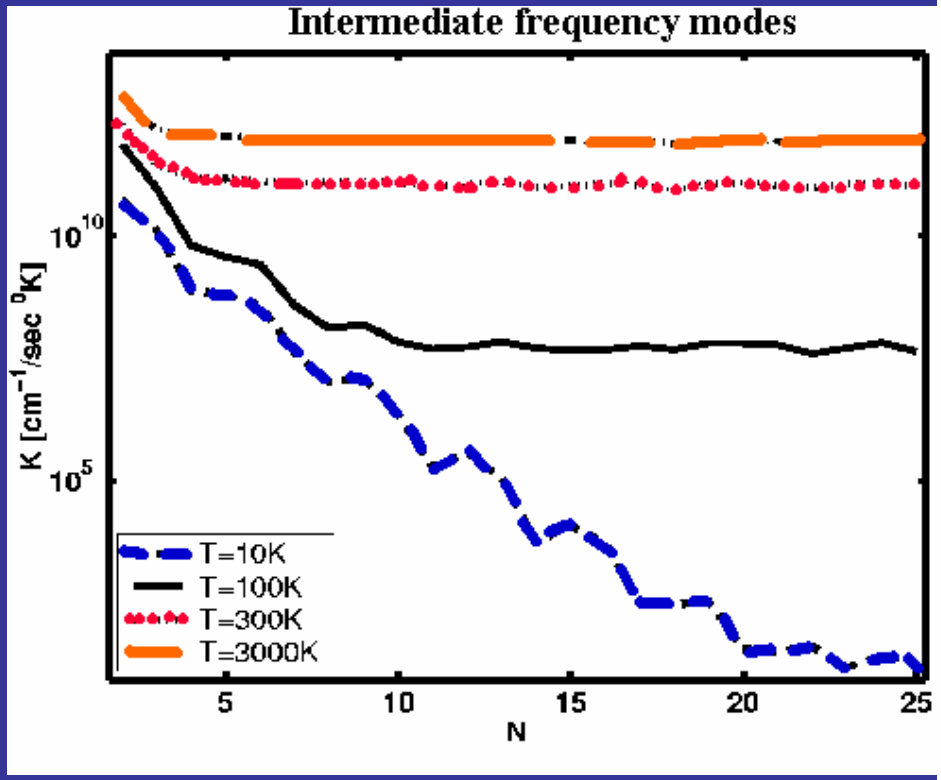
Density of normal modes in alkanes



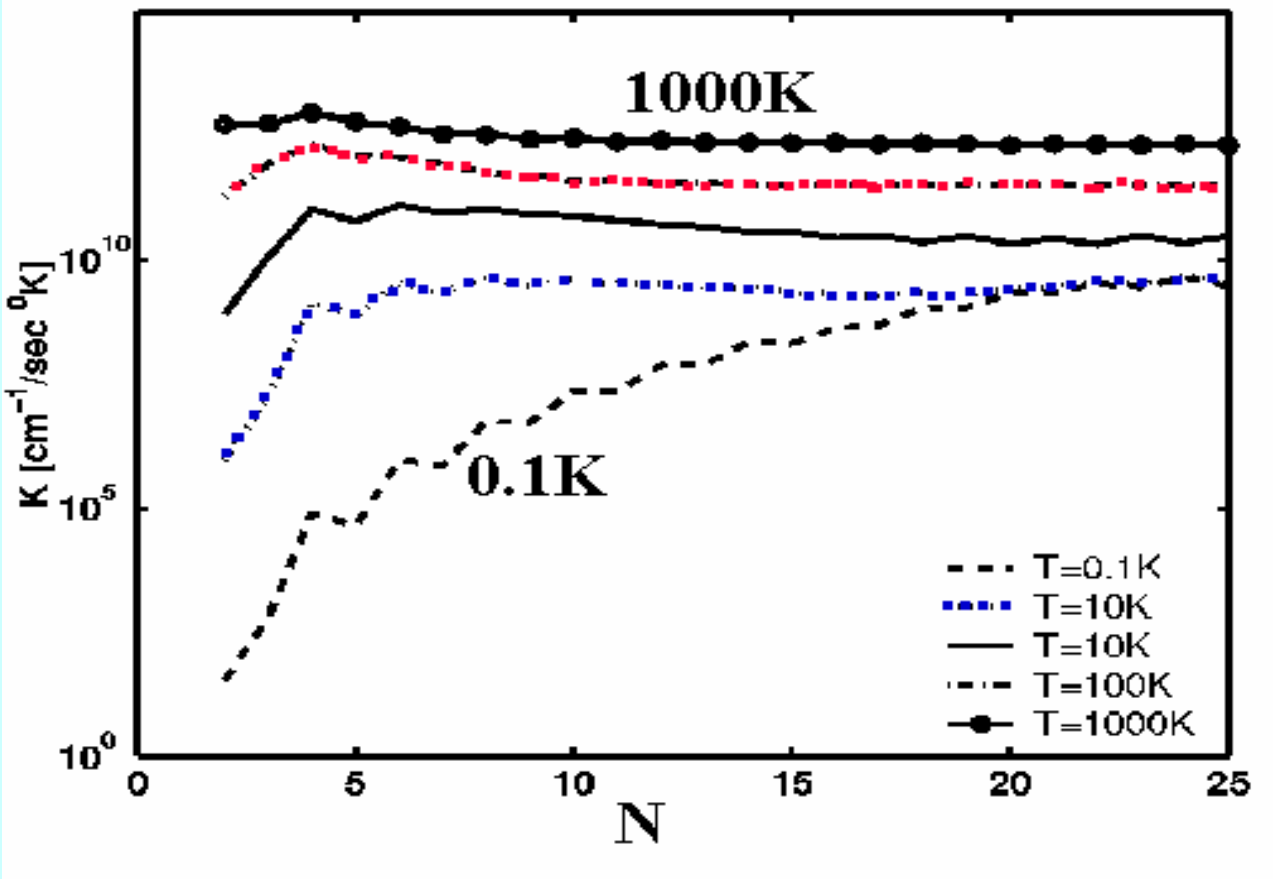
Low frequency group: 0-600cm^{-1};
Intermediate frequency group: 700-1500cm^{-1}
High frequency group: 2900-3200cm^{-1}

Heat conduction by the lower frequency groups

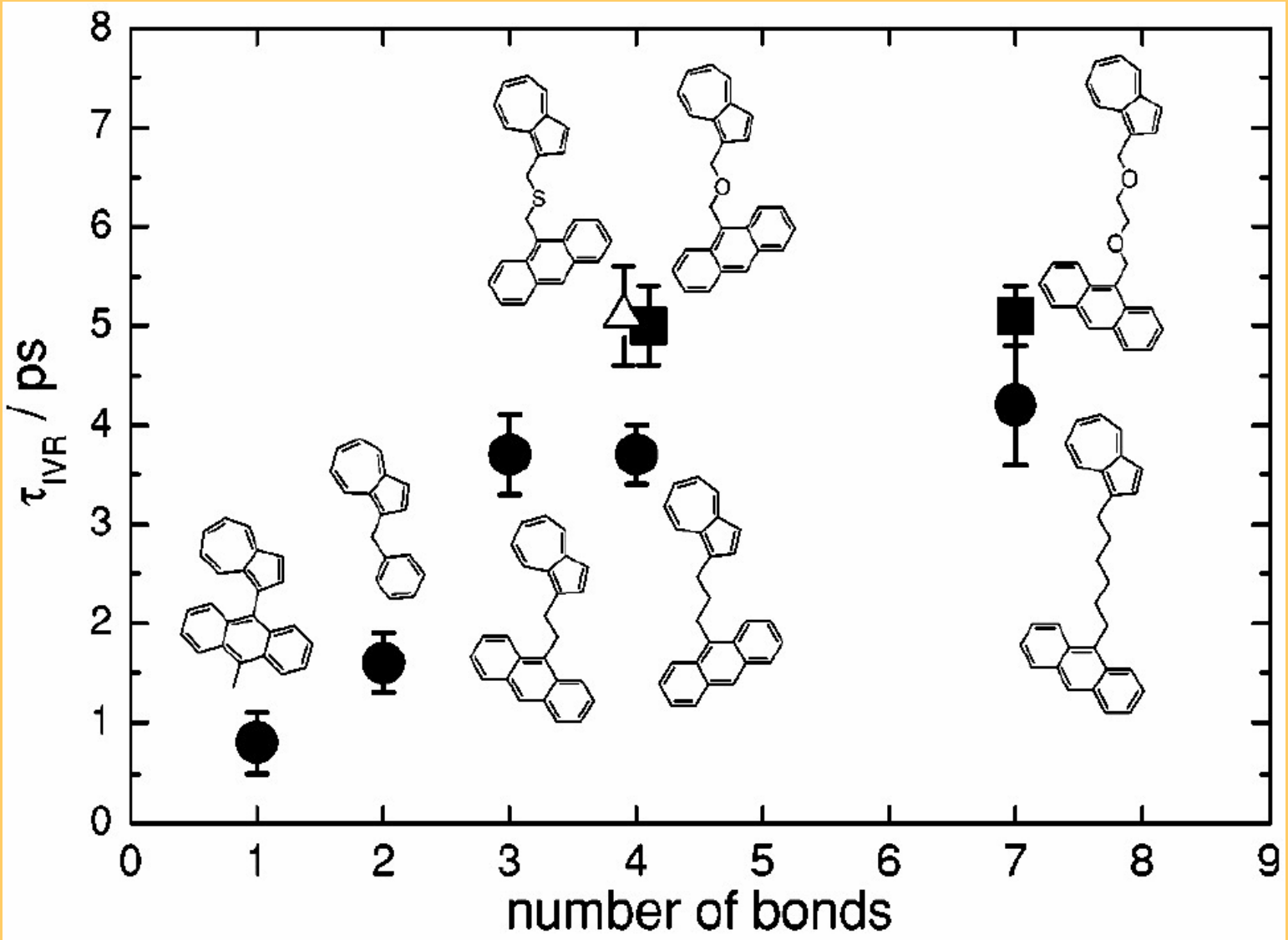




Thermal conduction vs. alkane chain length



Dashed line: T=0.1K; Blue dotted line: T=1K; Full line: T=10K; Red- dotted line: T=100K; Line with circles: T=1000K. ω_c=400 cm^{-1} ,V_L=V_R=50 cm^{-2}.



D.Schwarzer, P.Kutne, C.Schroeder and J.Troe, J. Chem. Phys., 2004

Intramolecular vibrational energy redistribution in bridged azulene-anthracene compounds:Ballistic energy transport through molecular chains

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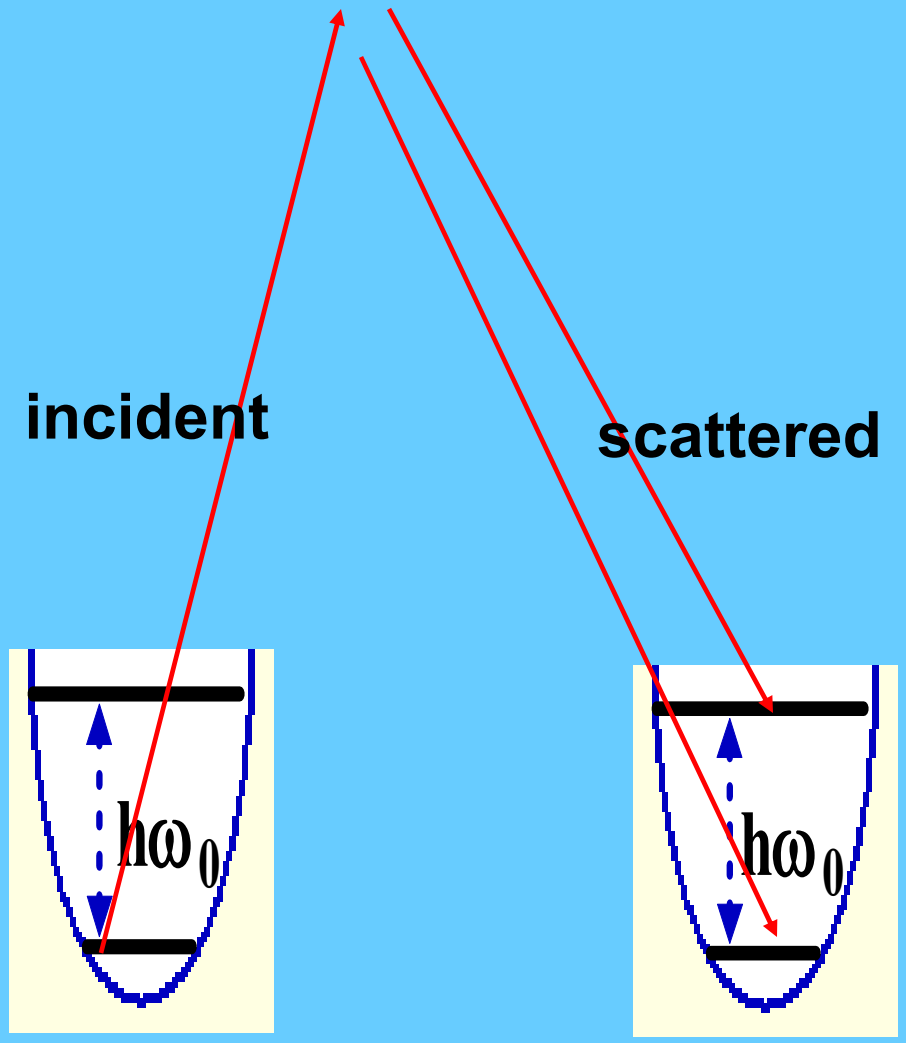
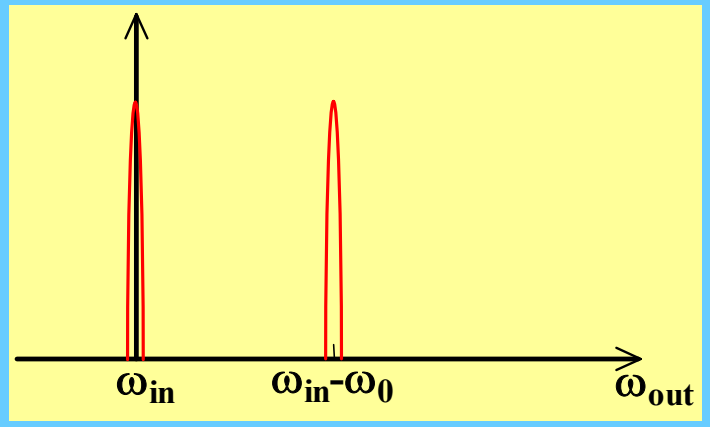
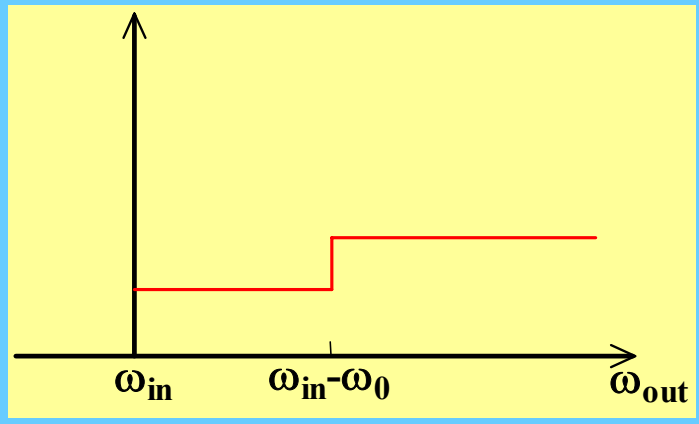
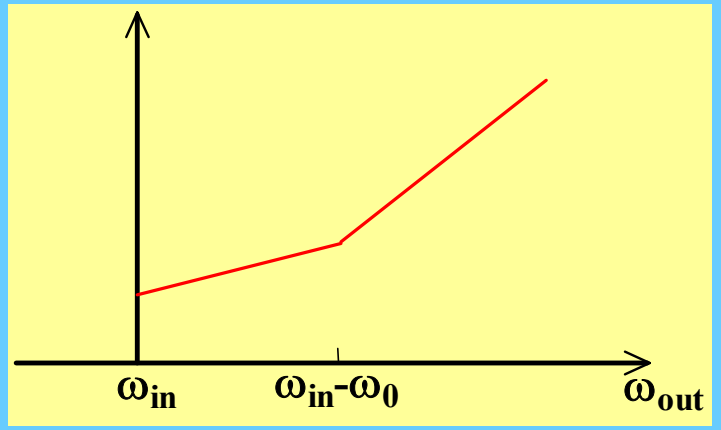
Light Scattering

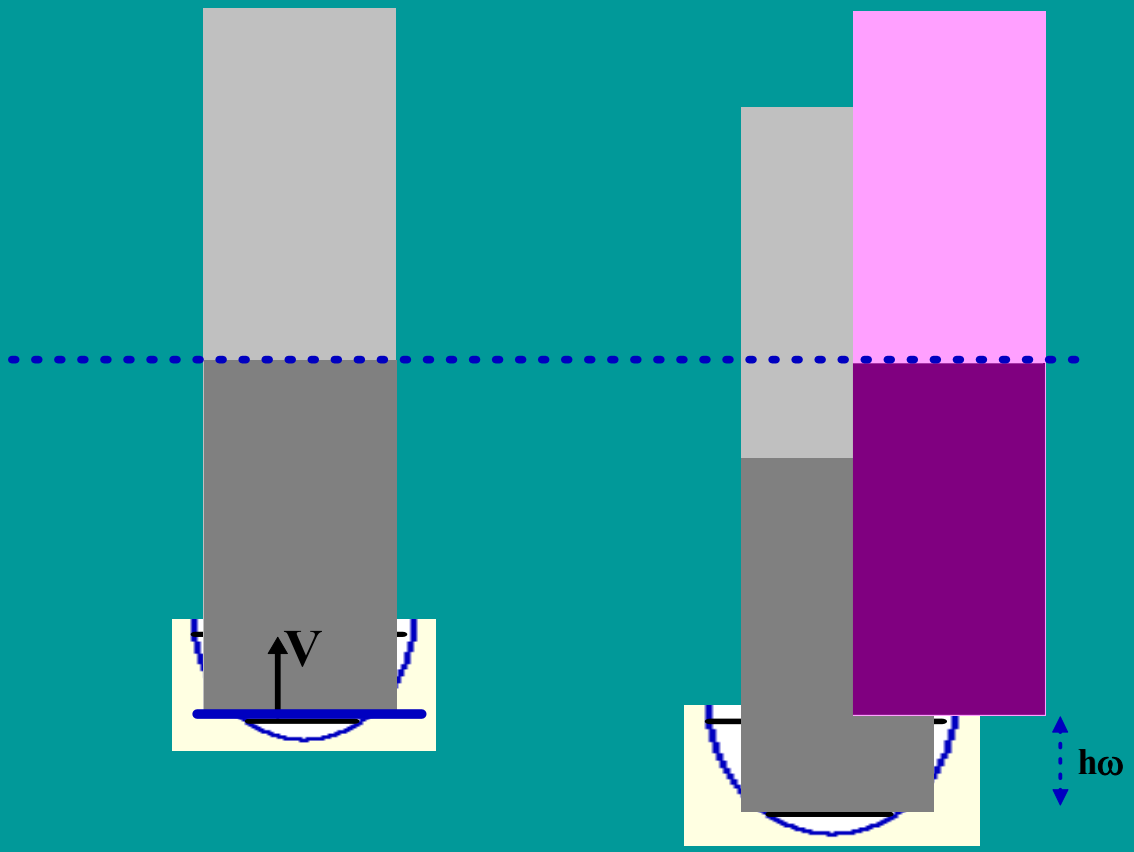






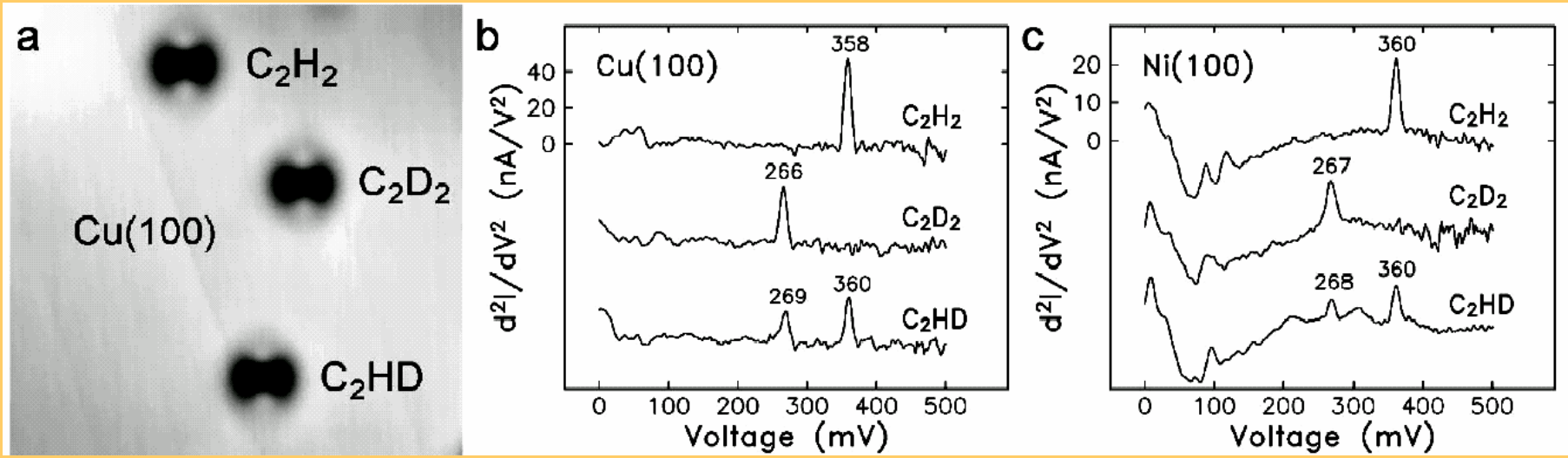


INELSTIC ELECTRON TUNNELING SPECTROSCOPY



Localization of Inelastic Tunneling and the Determination of Atomic-Scale Structure with Chemical Specificity

B.C.Stipe, M.A.Rezaei and W. Ho, PRL, 82, 1724 (1999)

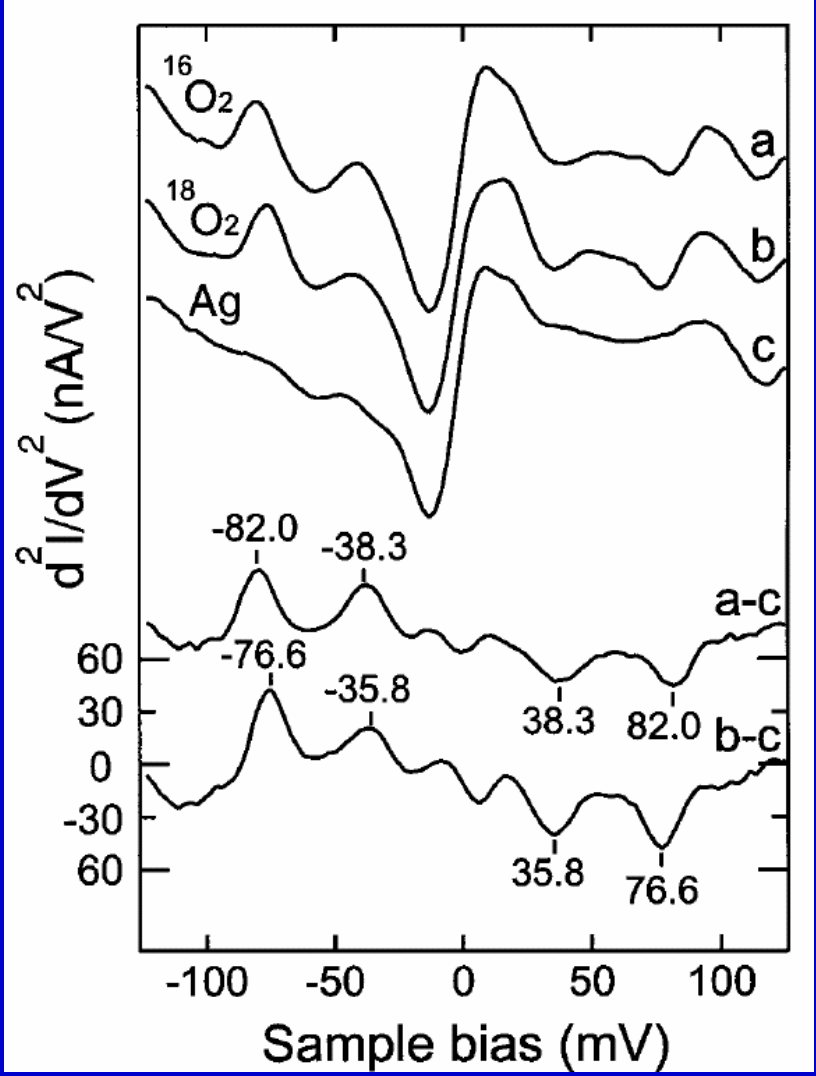


STM image (a) and single-molecule vibrational spectra (b) of three acetylene isotopes on Cu(100) at 8 K. The vibrational spectra on Ni(100)are shown in (c). The imaged area in (a), 56Å x 56Å, was scanned at 50 mV sample bias and 1nA tunneling current

Recall: van Ruitenbeek et al (Pt/H_2)- dips

Electronic Resonance and Symmetry in Single-Molecule Inelastic Electron Tunneling

J.R.Hahn,H.J.Lee,and W.Ho, PRL 85, 1914 (2000)

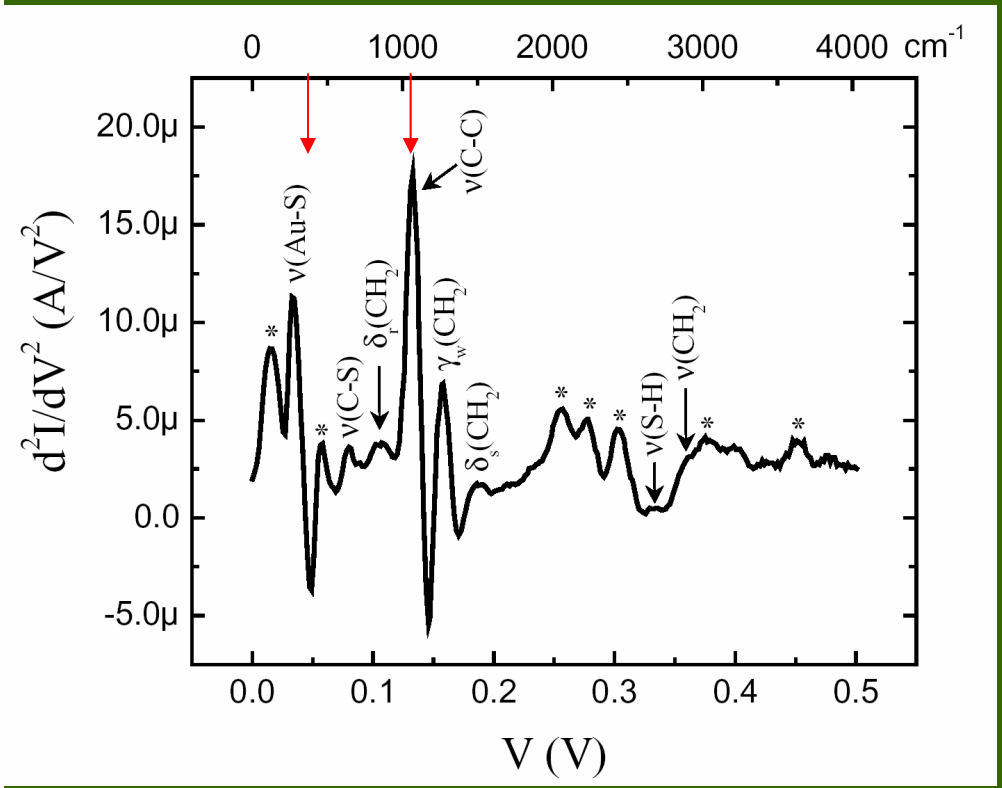


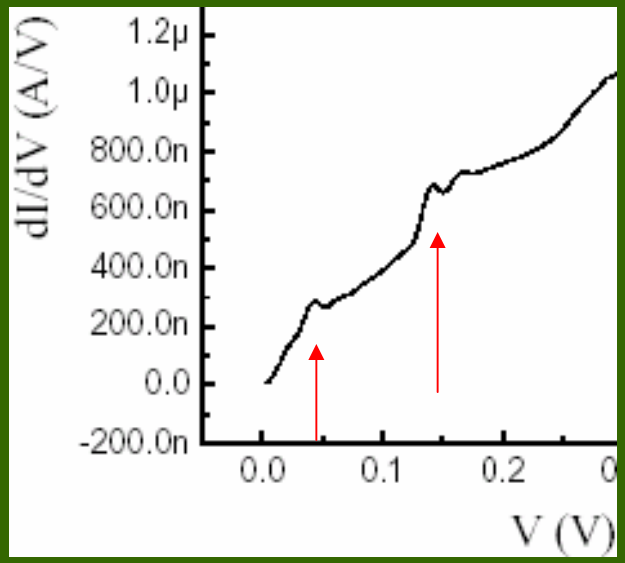
Single molecule vibrational spectra obtained by STM-IETS for $^{16}O_2$ (curve a),$^{18}O_2$ (curve b), and the clean Ag(110)surface (curve c).The O2 spectra were taken over a position 1.6 Å from the molecular center along the [001] axis.

The feature at 82.0 (76.6)meV for $^{16}O_2$ ($^{18}O_2$) is assigned to the O-O stretch vibration, in close agreement with the values of 80 meV for 16O2 obtained by EELS.
The symmetric O2 -Ag stretch (30 meV for 16O2) was not observed.The vibrational feature at 38.3 (35.8)meV for $^{16}O_2$ ($^{18}O_2$)is attributed to the antisymmetric O_2 -Ag stretch vibration.

Inelastic Electron Tunneling Spectroscopy of Alkanedithiol Self-Assembled Monolayers

W. Wang, T. Lee, I. Kretzschmar and M. A. Reed (Yale, 2004)

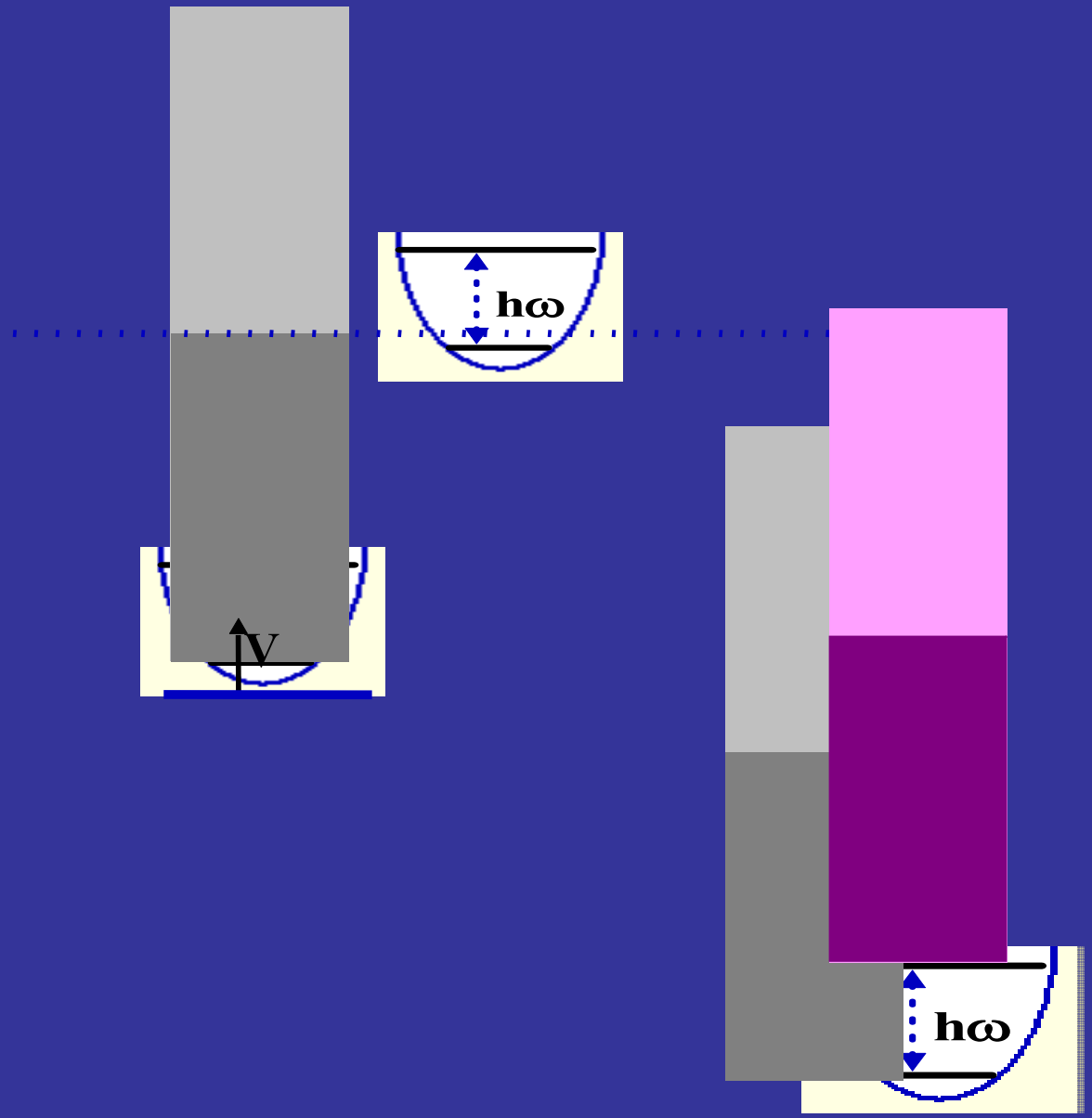




Inelastic electron tunneling spectra of C8 dithiol SAM obtained from lock-in second harmonic measurements with an AC modulation of 8.7 mV (RMS value) at a frequency of 503 Hz (T =4.2 K).Peaks labeled *are most probably background due to the encasing Si3N4

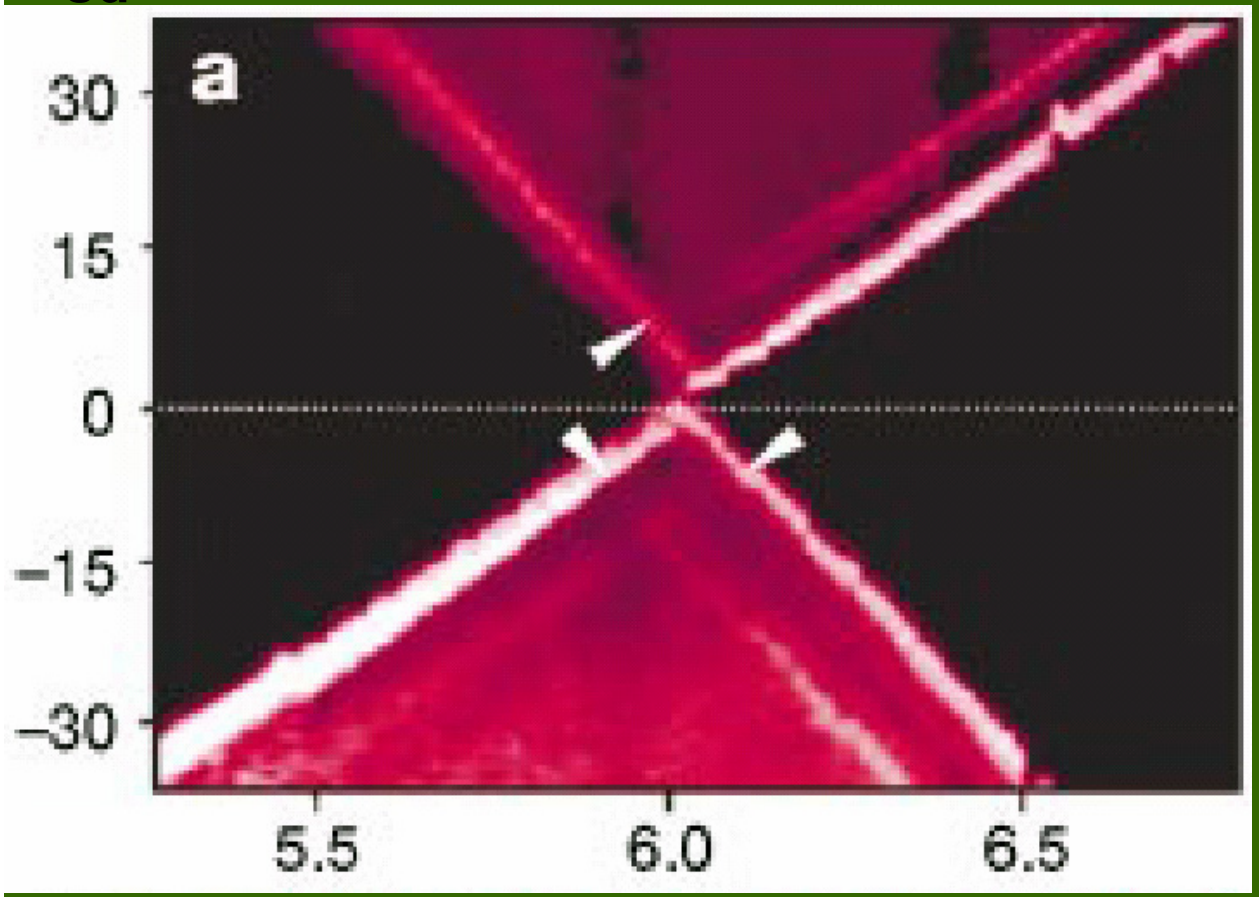
Nano letters, in press

INELSTIC RESONANCE ELECTRON TUNNELING SPECTROSCOPY



Nanomechanical oscillations in a single C_{60} transistor

H. Park, J. Park, A.K.L. Lim, E.H. Anderson, A. P. Alivisatos and P. L. McEuen [NATURE, 407, 57 (2000)]

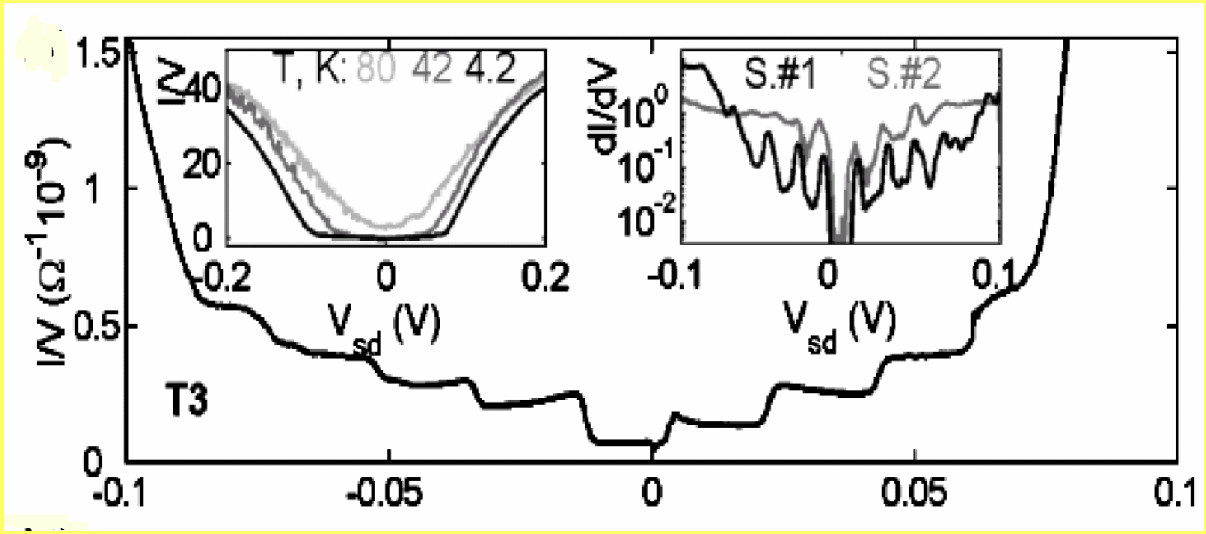


Two-dimensional differential conductance (∂I/∂V)plots as a function of the bias voltage (V) and the gate voltage (Vg). The dark triangular regions correspond to the conductance gap, and the bright lines represent peaks in the differential conductance.

Conductance of Small Molecular Junctions

N.B.Zhitenev, H.Meng and Z.Bao

PRL 88, 226801 (2002)

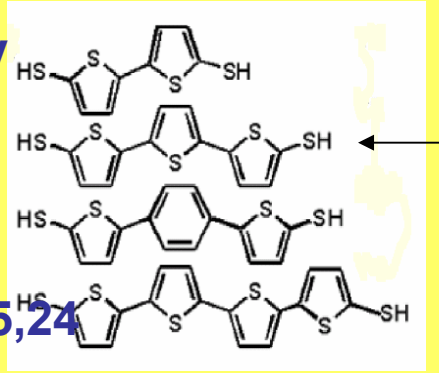


38mV

22

125

35,45,24



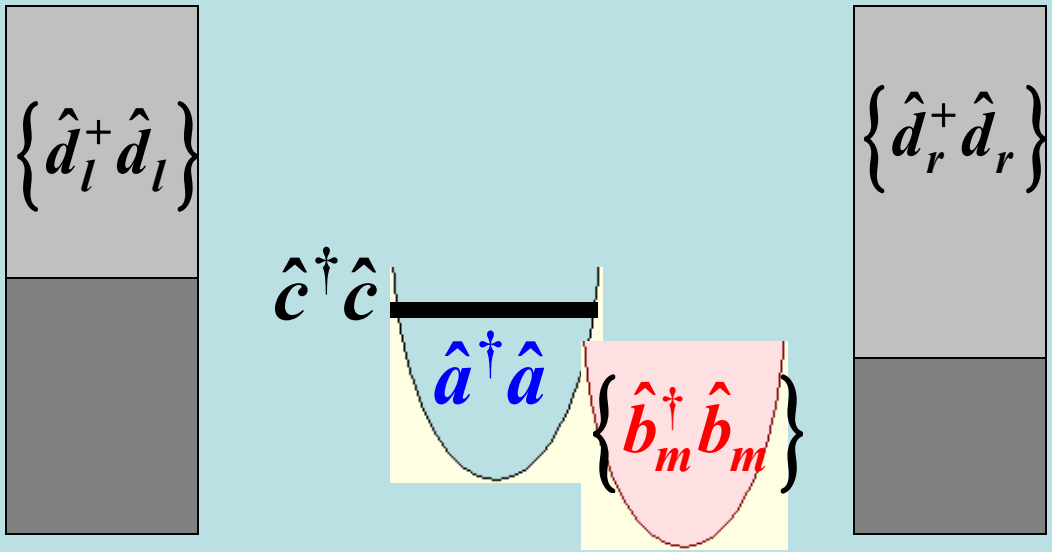
Conductance of the T3 sample as a function of source-drain bias at *T* =4.2 K. The steps in conductance are spaced by 22 mV.
Left inset: conductance vs source-drain bias curves taken at different temperatures for the T3 sample (the room temperature curve is not shown because of large switching noise).
Right inset: differential conductance vs source-drain bias measured for two different T3 samples at *T* = 4.2 K.

MODEL

$$\hat{H}_0 = \varepsilon_0 \hat{c}^\dagger \hat{c} + \sum_{k \in L,R} \varepsilon_k^{L,R} \hat{d}_k^\dagger \hat{d}_k + \omega_0 \hat{a}^\dagger \hat{a} + \sum_m \omega_m \hat{b}_m^\dagger \hat{b}_m$$

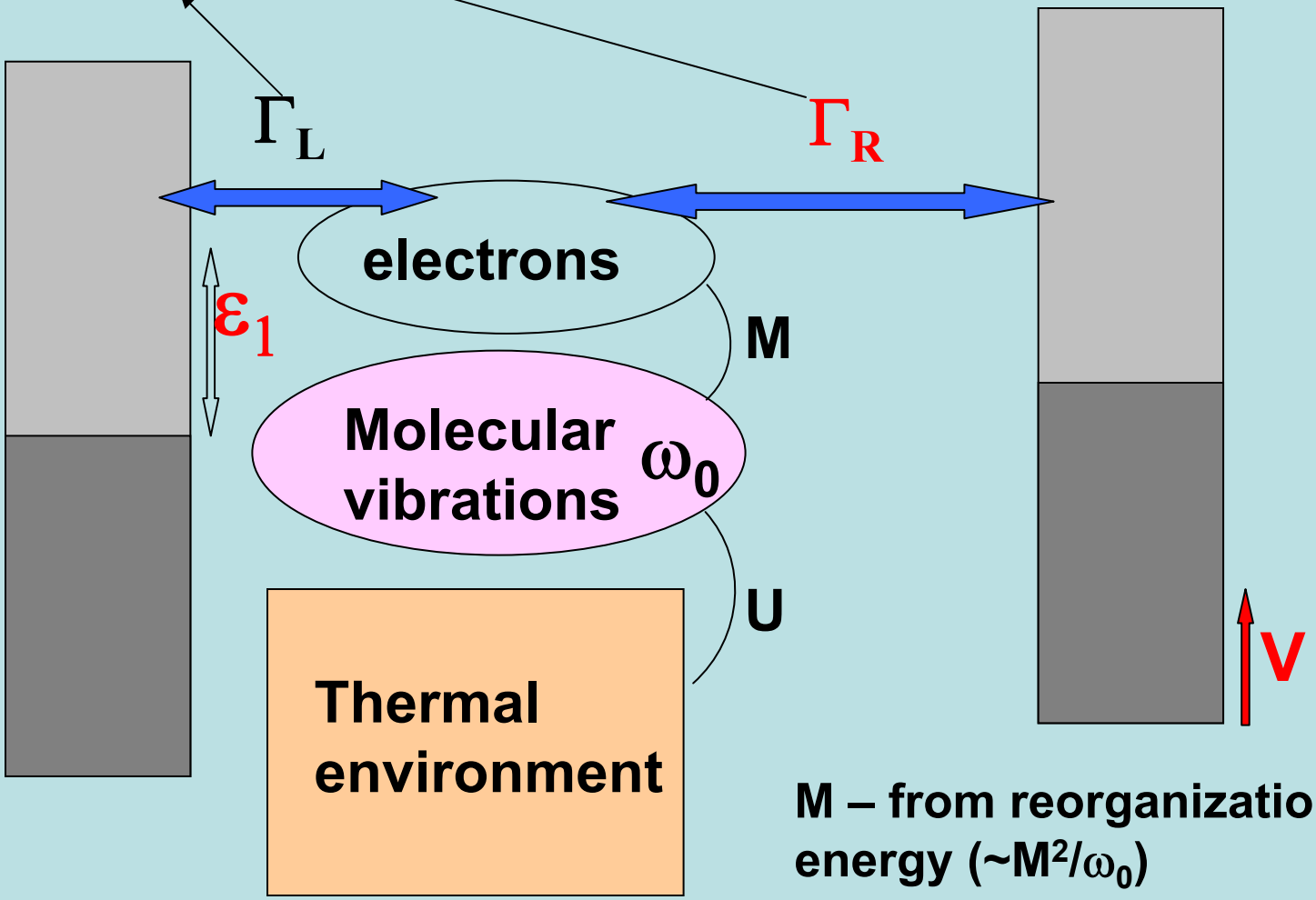
$$\hat{H}_1 = \sum_{k \in L,R} \left(V_{ki} \hat{d}_k^\dagger \hat{c} + h.c. \right) + \sum_m U_m \hat{A} \hat{B}_m + M \hat{A} \hat{c}^\dagger \hat{c}$$

$$\hat{A} = \hat{a}^\dagger + \hat{a} \; ; \quad \hat{B} = \hat{b}^\dagger + \hat{b}$$



Parameters

Constant in the wide band approximation



M – from reorganization energy ($\sim M^2/\omega_0$)

U – from vibrational relaxation rates

NEGF

$$G_{n,n'}^{\ r}(t,t') = -i\Theta(t-t')\left\langle\left\{a_n(t), a_{n'}^{\ \dagger}(t')\right\}\right\rangle$$

$$G_{n,n'}^{\ a}(t,t') = i\Theta(t'-t)\left\langle\left\{a_n(t), a_{n'}^{\ \dagger}(t')\right\}\right\rangle$$

({ }=anticommutator)

$$G_{n,n'}^{\ <}(t,t') = +i\left\langle a_{n'}^{\ \dagger}(t')a_n(t)\right\rangle$$

$$G_{n,n'}^{\ >}(t,t') = -i\left\langle a_n(t)a_{n'}^{\ \dagger}(t')\right\rangle$$

$$G^r(\omega) = G_0^r(\omega) + G^r(\omega)\Sigma^r(\omega)G_0^r(\omega)$$

$$G^a(\omega) = G_0^a(\omega) + G^a(\omega)\Sigma^a(\omega)G_0^a(\omega)$$

$$G^> = G^r\Sigma^>G^a$$

$$G^< = G^r\Sigma^<G^a$$

$$\Sigma_{ph}^r(E) = iM^2\int\frac{d\omega}{2\pi}\Big[D^<(\omega)G^r(E-\omega) + D^<(\omega)G^<(E-\omega) + D^r(\omega)G^r(E-\omega)\Big]$$

$$\Sigma_{ph}^<(E) = iM^2\int\frac{d\omega}{2\pi}D^<(\omega)G^<(E-\omega)$$

$$G_{jj'}^{0,r}(\omega) = \delta_{jj'}\frac{1}{\omega-\varepsilon_j+i\eta}$$

$$G_{jj'}^{0,a}(\omega) = \delta_{jj'}\frac{1}{\omega-\varepsilon_j-i\eta}$$

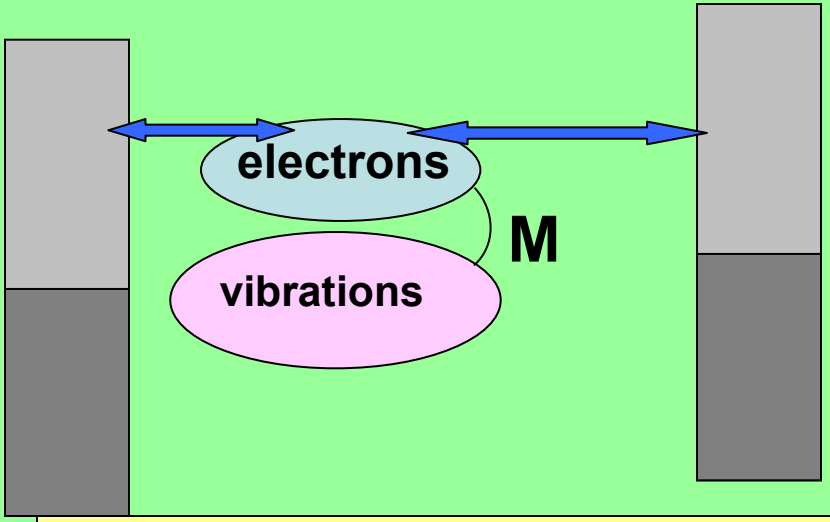
$$\rho_j(E) = -\frac{1}{\pi}\mathrm{Im}\,G_{jj}^r(E)$$

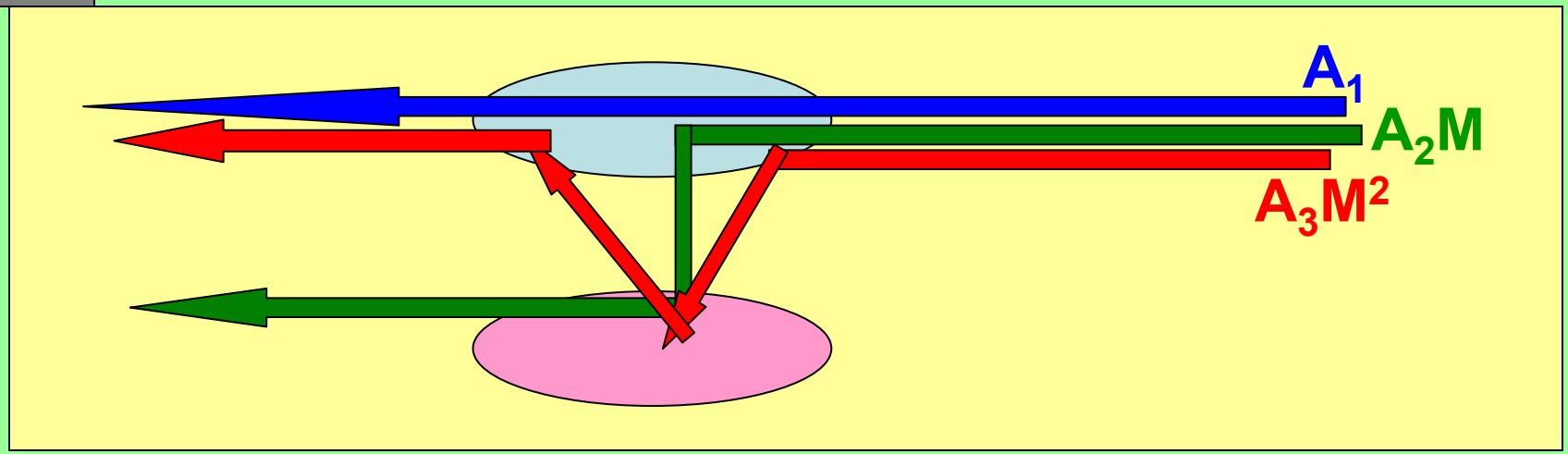
$$n_j(E) = \frac{1}{2\pi}\mathrm{Im}\,G_{jj}^<(E)$$

$$G_{j,j'}^{0,<}(\omega) = \delta_{j,j'}2\pi i f(\varepsilon_j)\delta(\omega-\varepsilon_j)$$

$$G_{j,j'}^{0,>}(\omega) = -\delta_{j,j'}2\pi i\Big[1-f(\varepsilon_j)\Big]\delta(\omega-\varepsilon_j)$$

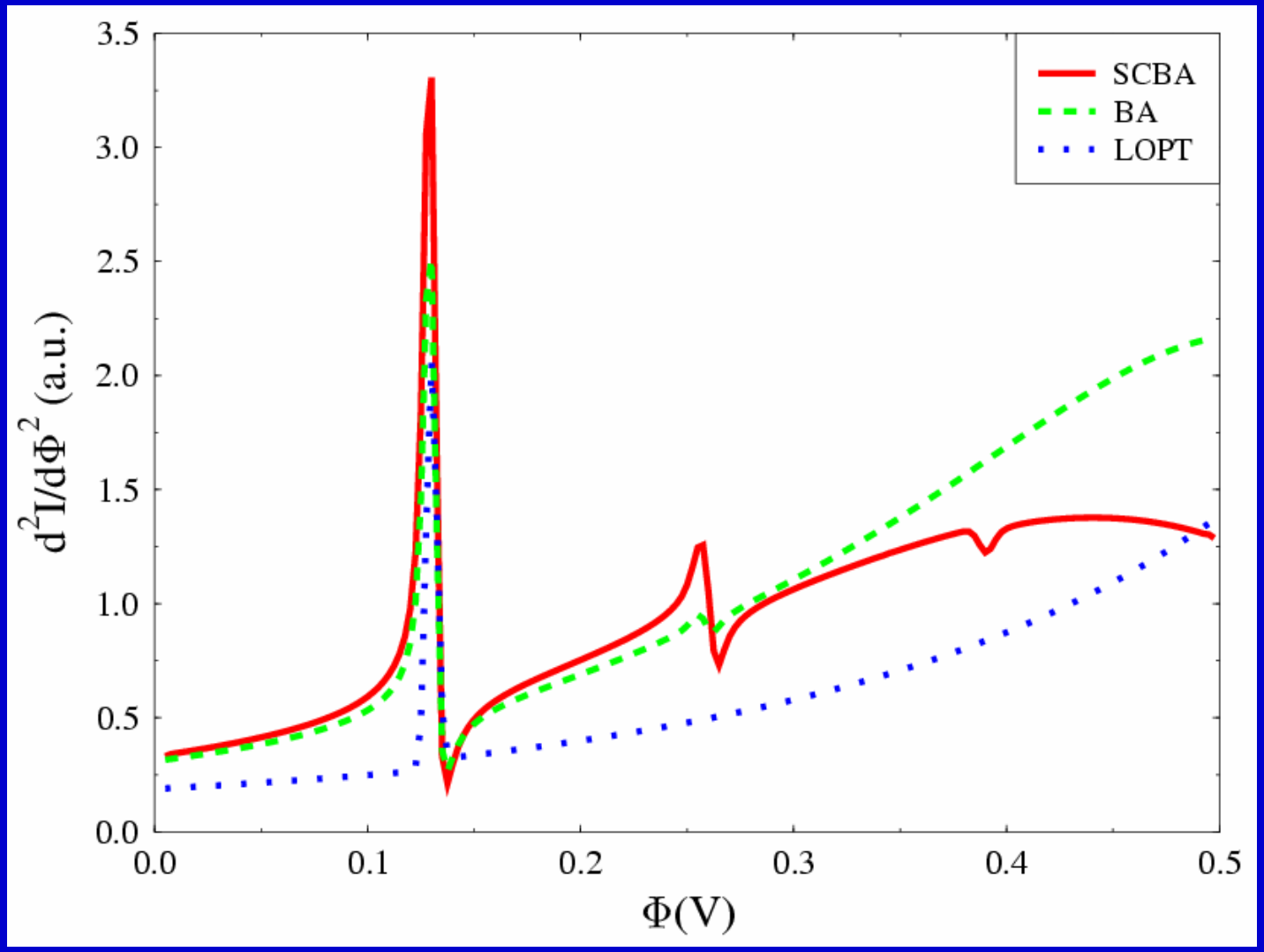
$$I = \frac{q}{\hbar}\int\frac{dE}{2\pi}Tr\Big[\Sigma^<(E)G^>(E) - \Sigma^>(E)G^<(E)\Big]$$

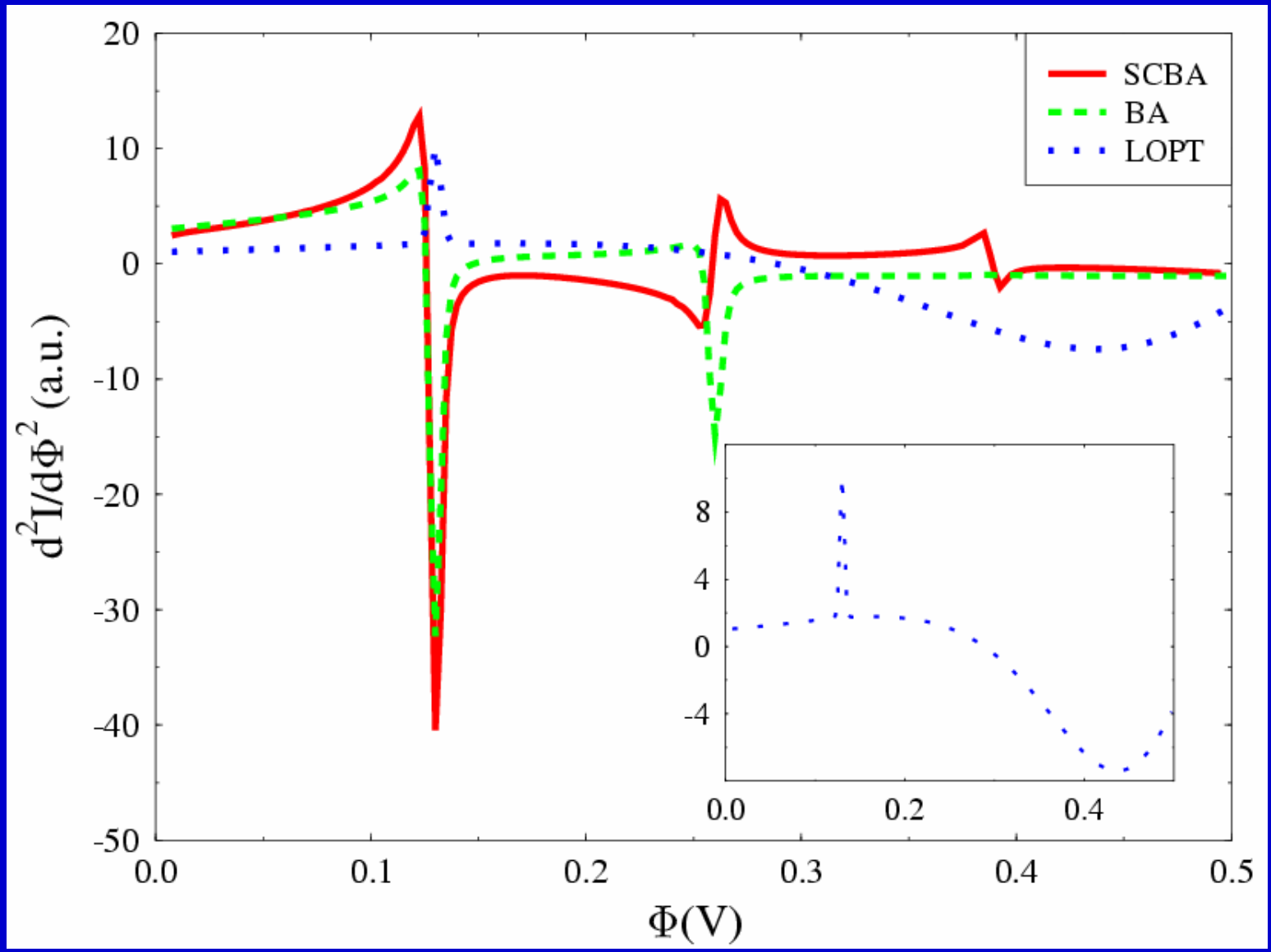




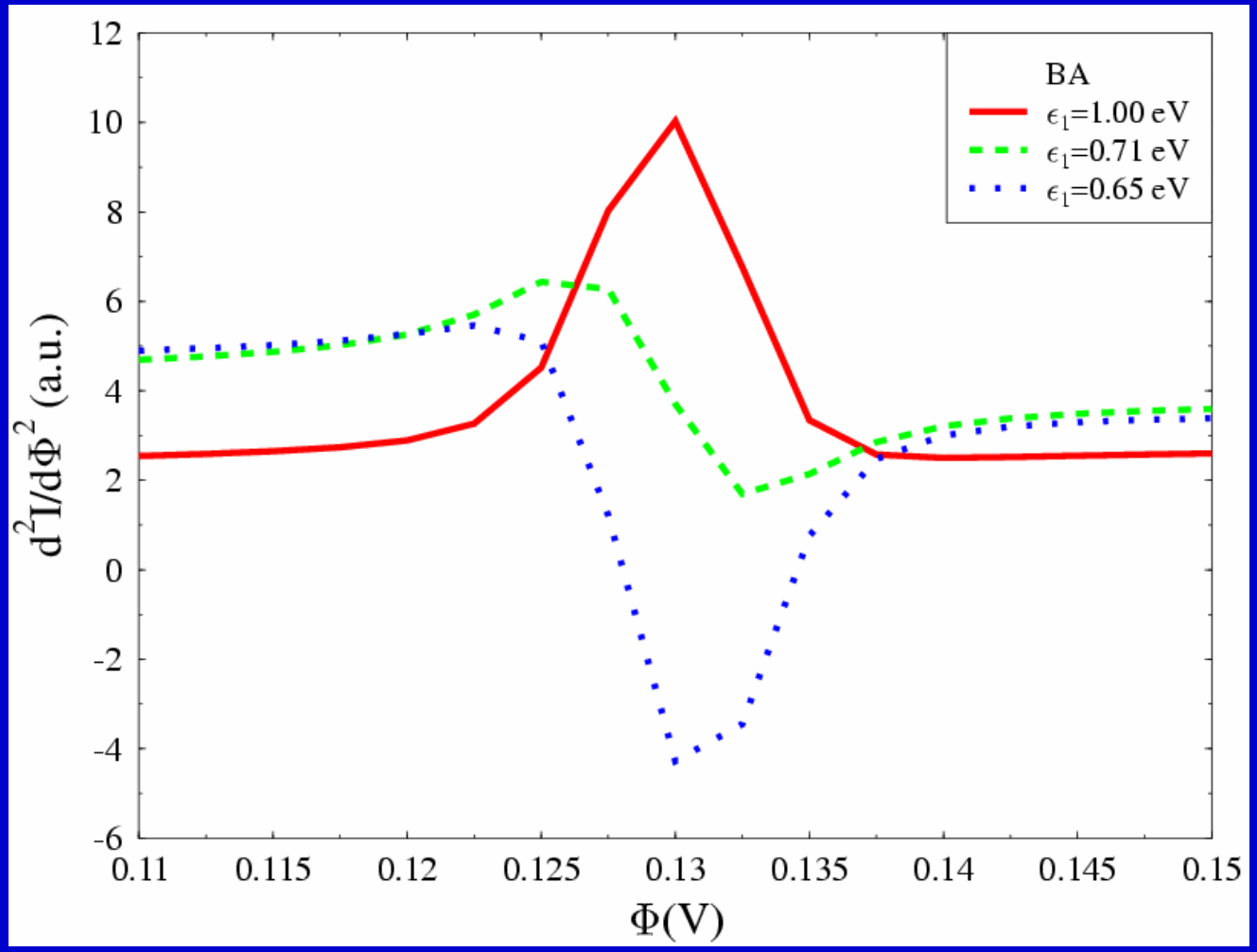
$$\left(A_1 + A_2 M + A_3 M^2\right)^2 = A_1^{\,2} + M^2\left(A_2^{\,2} + A_1 A_3\right)$$

elastic inelastic elastic

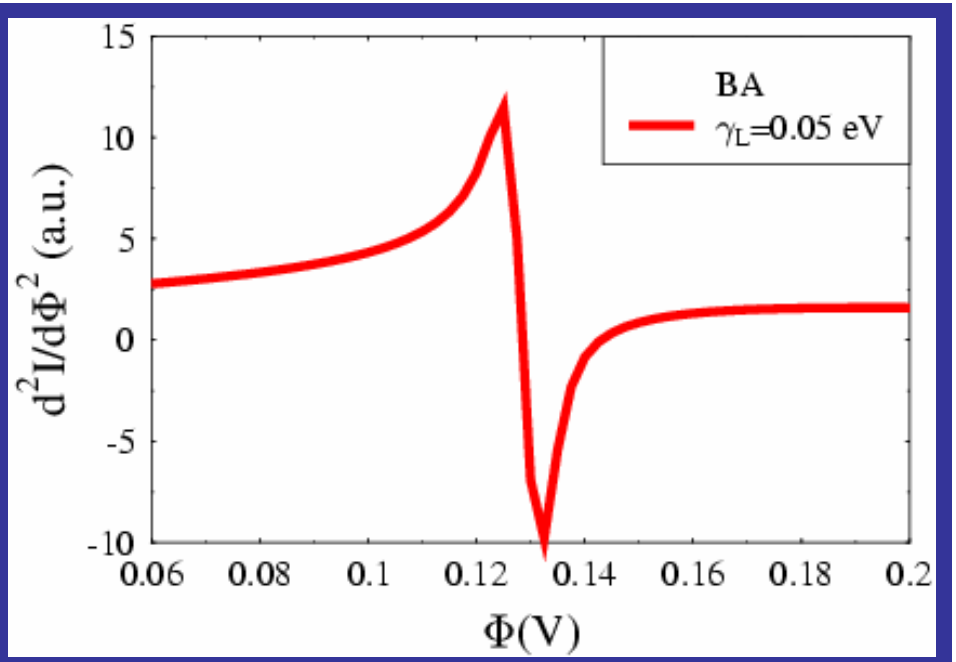

SCBA
BA
LOPT
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.1
0.2
0.3
0.4
0.5
d²I/dΦ² (a.u.)
Φ(V)

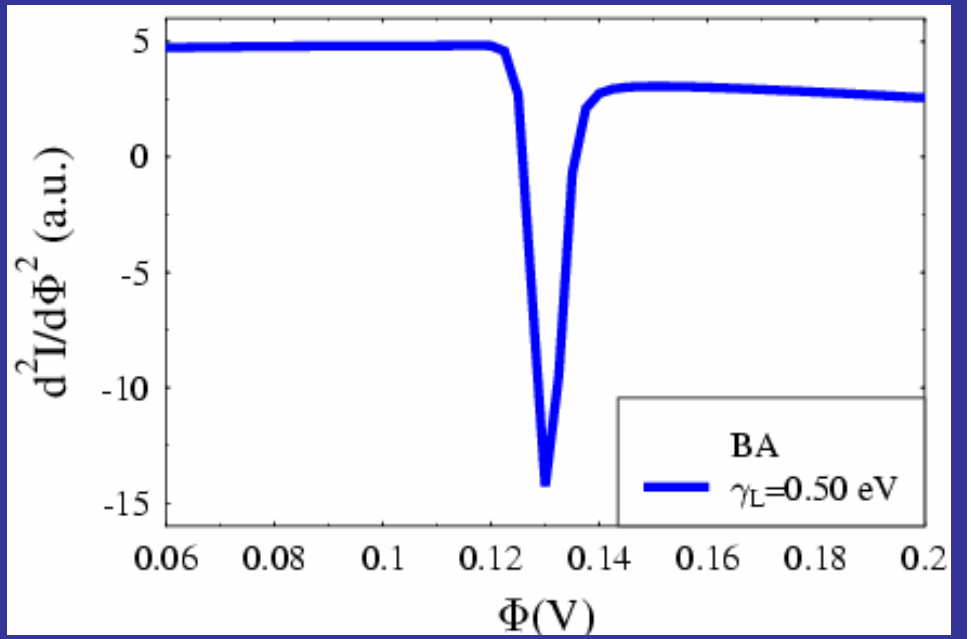

SCBA
BA
LOPT
20
10
0
-10
-20
-30
-40
-50
0.0
0.1
0.2
0.3
0.4
0.5
$d^2I/d\Phi^2$ (a.u.)
Φ(V)
8
4
0
-4
0.0
0.2
0.4

Changing position of molecular resonance:

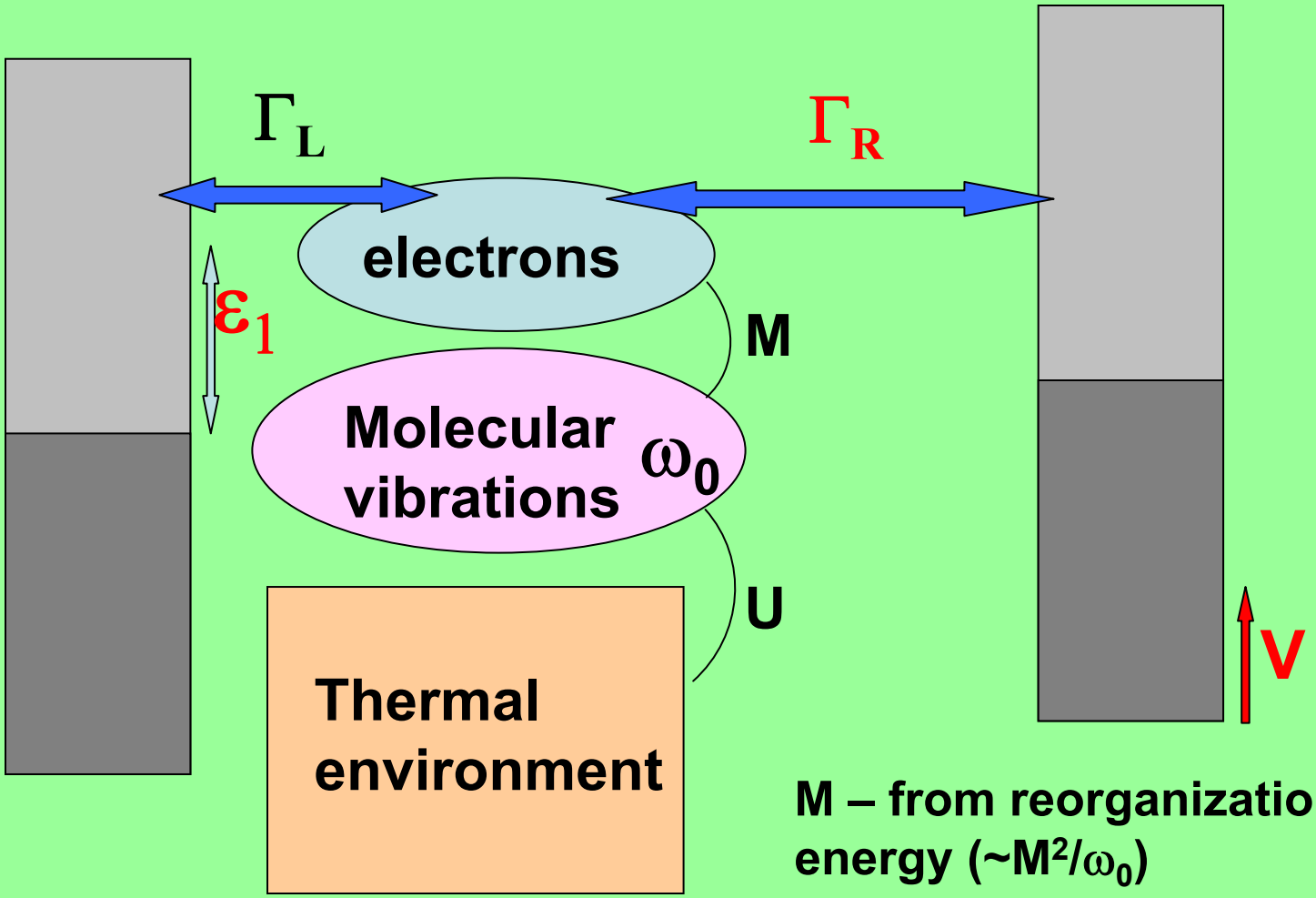


Changing tip-molecule distance





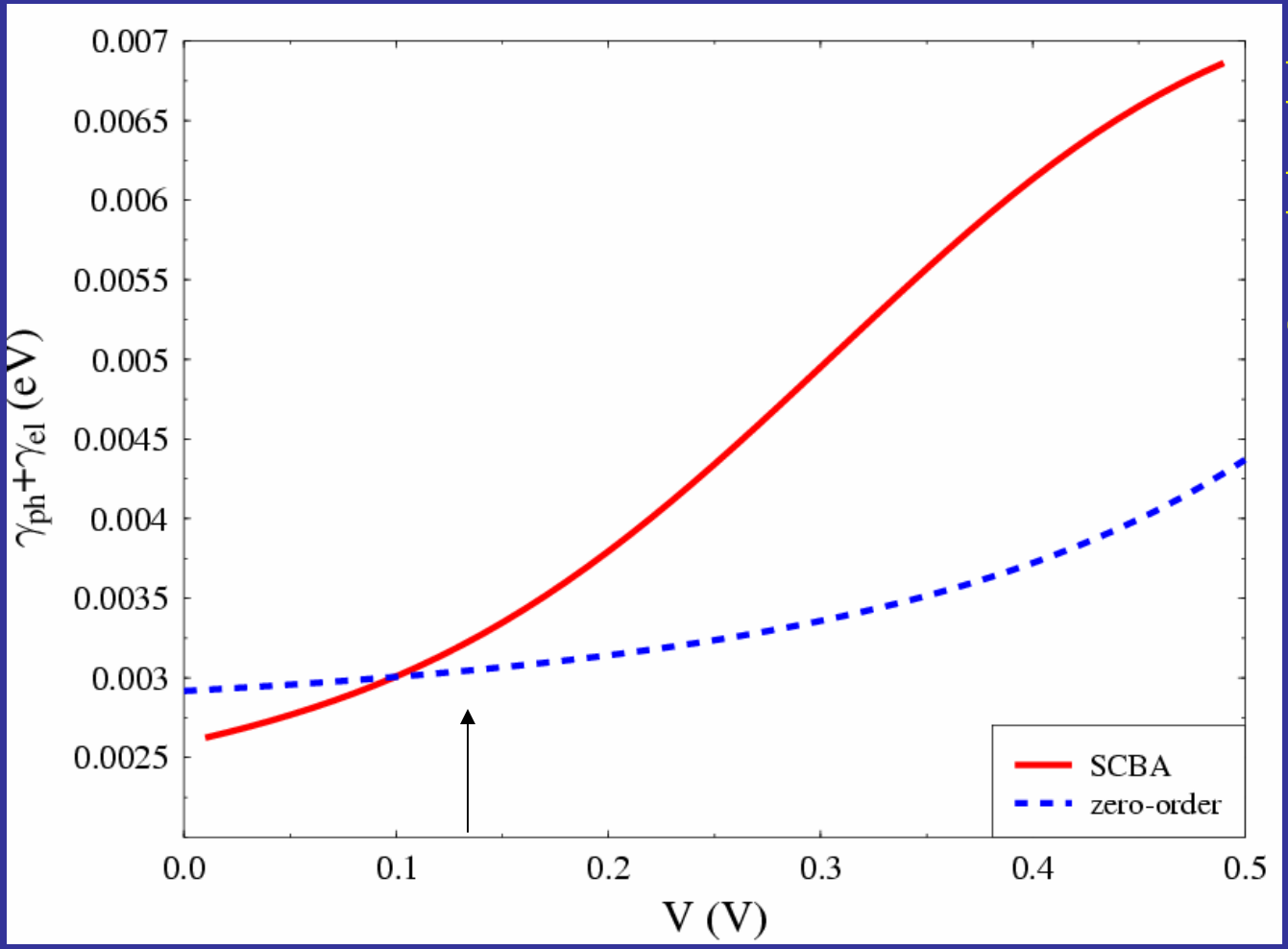
IETS (intrinsic?) linewidth



M – from reorganization energy (~M^2/ω_0)

U – from vibrational relaxation rates

IETS linewidth



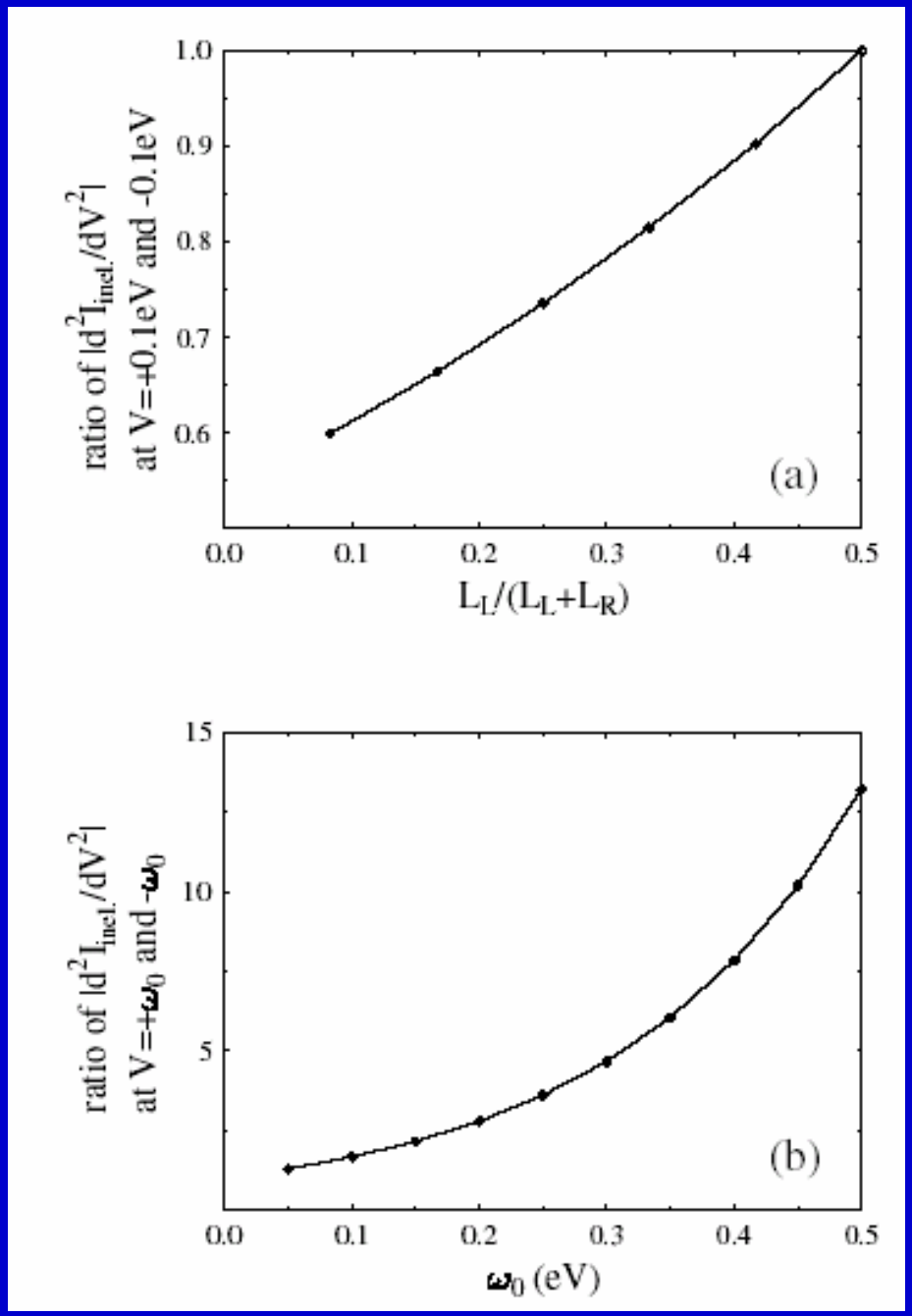
ε_1=1eV

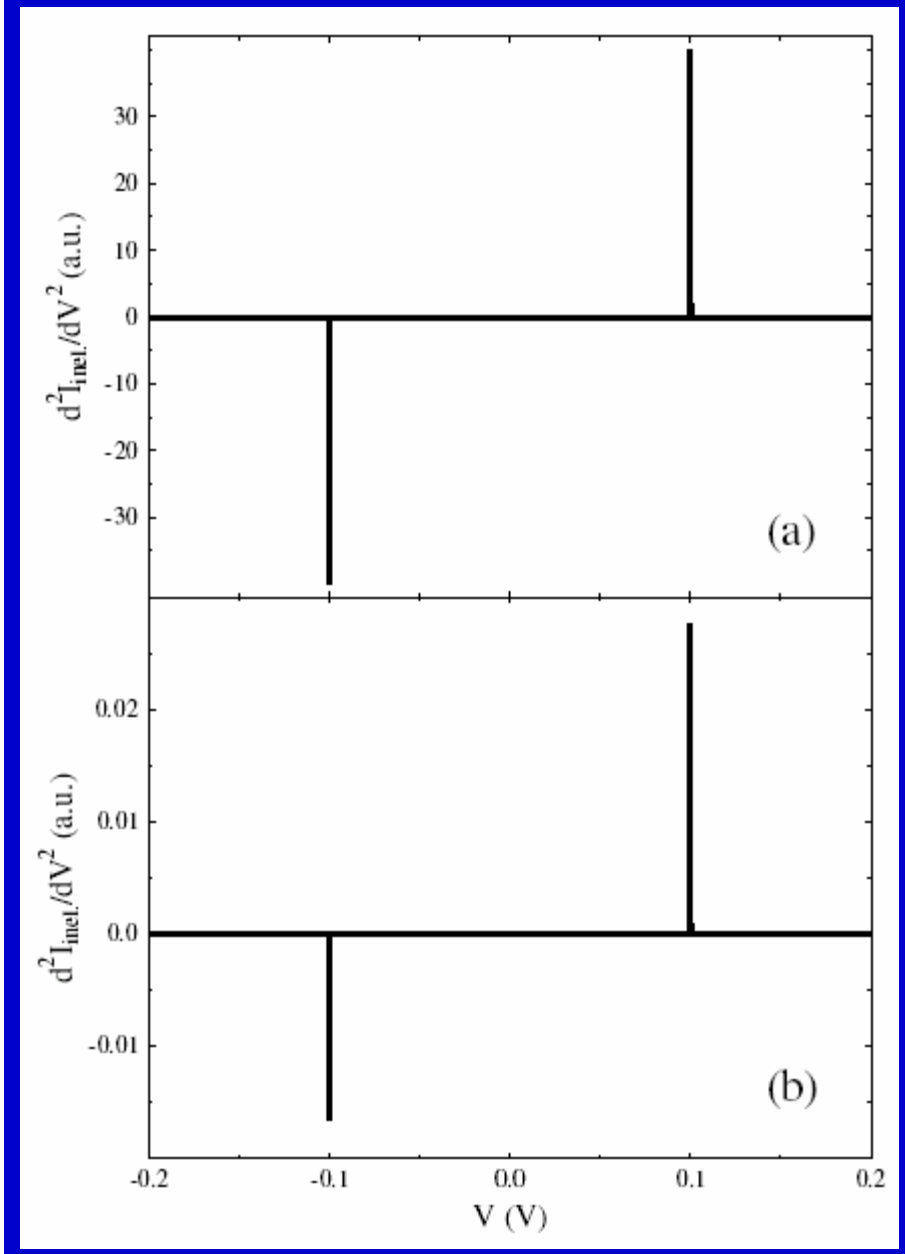
Γ_L=0.5eV

Γ_R=0.05eV

ω_0=0.13eV

M^2/ω_0=0.7eV


ratio of $|d^2I_{inel.}/dV^2|$ at V=+0.1eV and -0.1eV
1.0
0.9
0.8
0.7
0.6
(a)
0.0
0.1
0.2
0.3
0.4
0.5
$L_L/(L_L+L_R)$
ratio of $|d^2I_{inel.}/dV^2|$ at V=+ω_0 and -ω_0
15
10
5
(b)
0.0
0.1
0.2
0.3
0.4
0.5
ω_0 (eV)


$d^2I_{inel.}/dV^2$ (a.u.)
30
20
10
0
-10
-20
-30
(a)
$d^2I_{inel.}/dV^2$ (a.u.)
0.02
0.01
0.0
-0.01
(b)
-0.2
-0.1
0.0
0.1
0.2
V (V)

SUMMARY

- ?Using frozen configurations in transmission calculations?
- Relevant timescales
- Inelastic contributions to the tunneling current
- Dephasing and activation - transition from coherent transmission to activated hopping
- Heating of current carrying molecular wires
- Inelastic tunneling spectroscopy

Conclusions

- IETS: Peaks or dips in 2nd I/V derivative and their shapes – depend on parametrs. In particular, the position of the electronic resonance and its coupling to an STM lead can be controlled.
- While perturbation theory can qualitatively predict such results, it may fail quantitatively in a way that impact the qualitative observation: It may predict peaks instead of dips and it misses overtones.
- Satellite peaks may be observed in 1st I/V derivative if electronic resonance is narrow enough.
- "Intrinsic" linewidth in IETS may be due to broadening of phonon peaks due to coupling to metal electrons
- Asymmetry indicates geometry