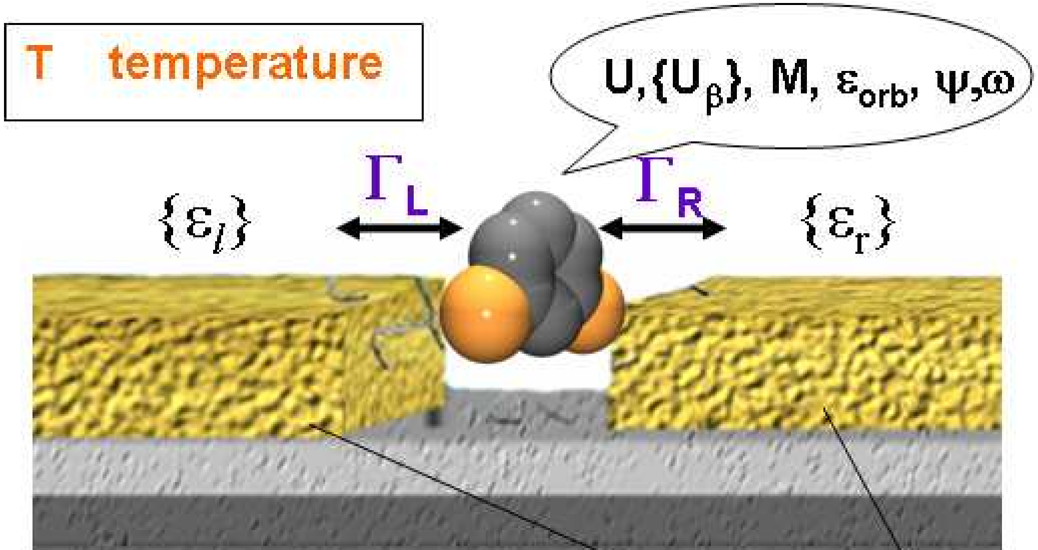
Transport and optical response of molecular junctions

UCSD July 20-21, 2009

Michael Galperin

University of California at San Diego

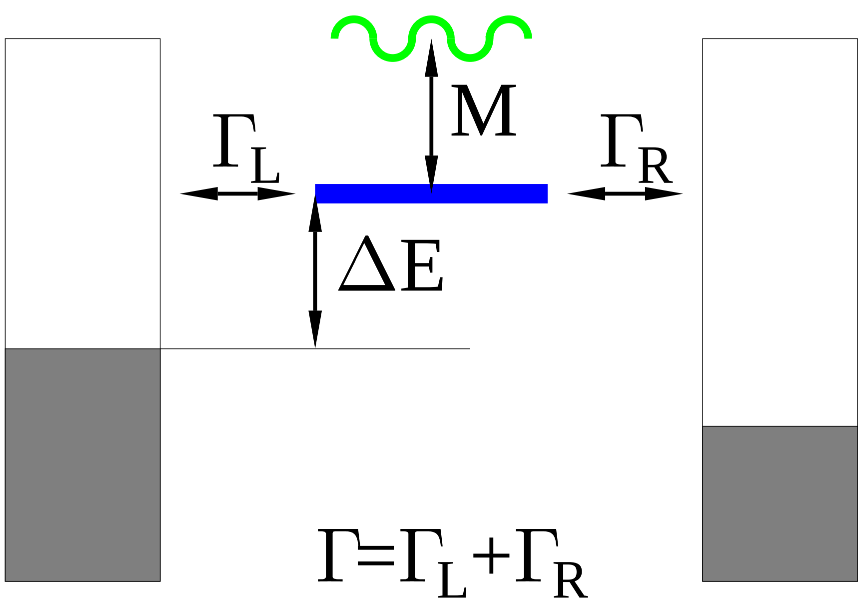
Introduction



ε_k band states in electrode
U electron repulsion on molecule
$\{U_\beta\}$ coupling to external bath modes
M vibronic coupling on molecule
ε_{orb} molecular orbital energies
ψ molecular orbitals
ω molecular vibrational frequency
Γ spectral density (electron-lead coupling
E_{FK} (K=L,R) Fermi energies
Φ bias potential

Introduction

- Timescale $\longrightarrow$ BO
- Energy scale



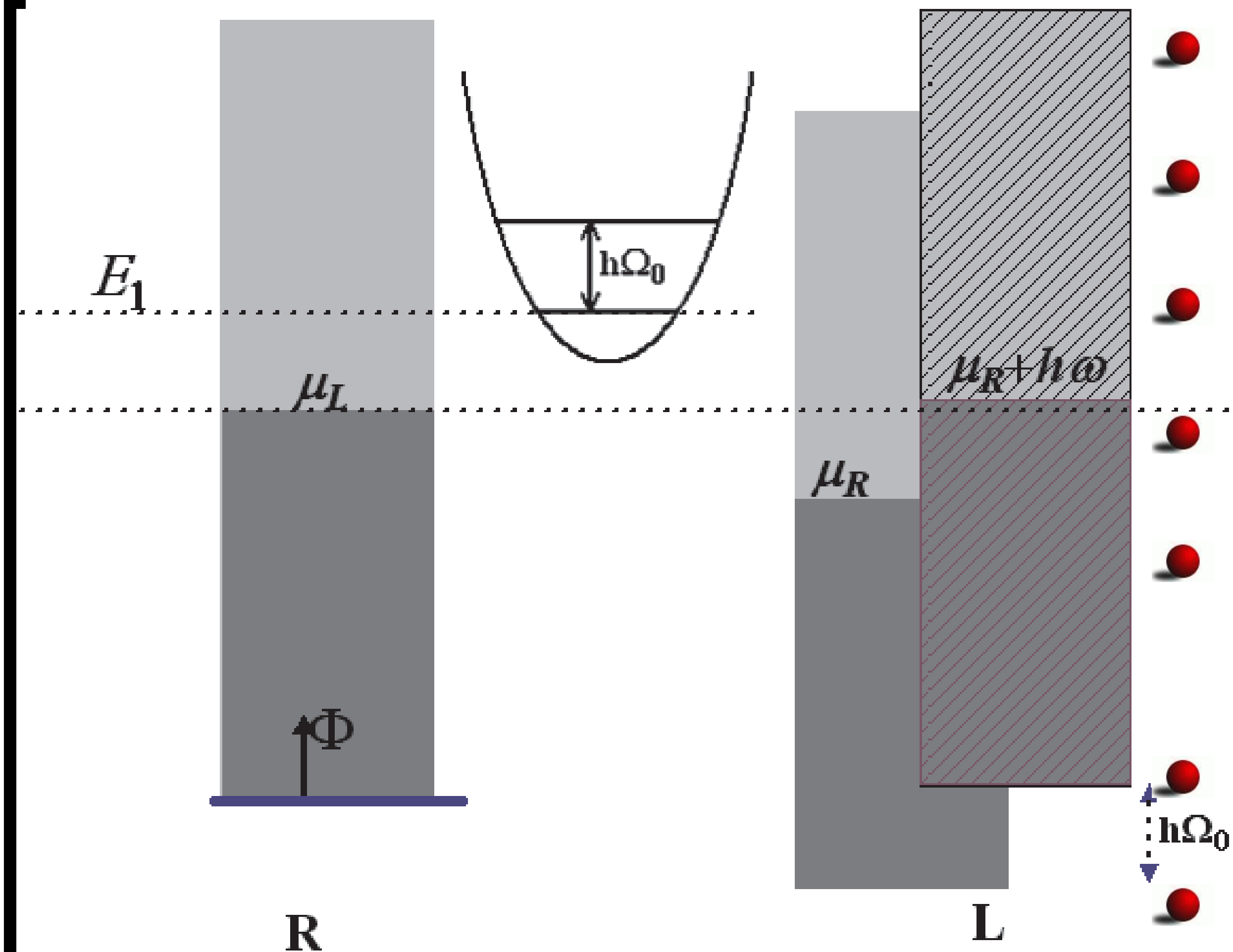
Weak el-ph coupling

$$M \ll \sqrt{\Delta E^2 + (\Gamma/2)^2}$$

Moderately strong el-ph coupling

$$M \geq \sqrt{\Delta E^2 + (\Gamma/2)^2}$$

Introduction

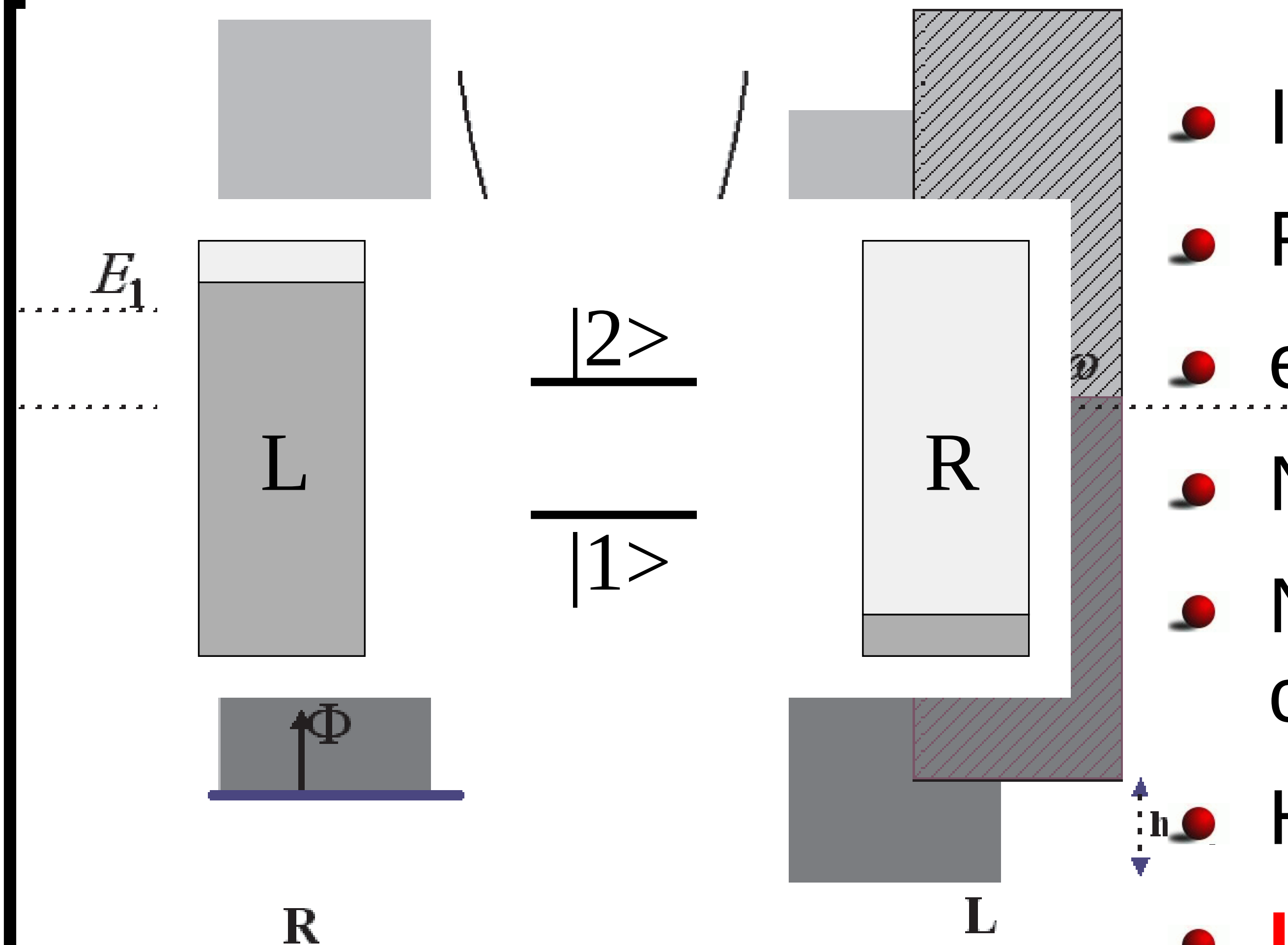


- IETS
- RIETS
- e-e interaction
- Noise
- Non-linear conductance
- Heating
- Light-matter interaction

J. Phys.: Condens. Matter **19**, 103201 (2007)

Science **319**, 1056 (2008).

Introduction



- IETS
- RIETS
- e-e interaction
- Noise
- Non-linear conductance
- Heating
- **Light-matter interaction**

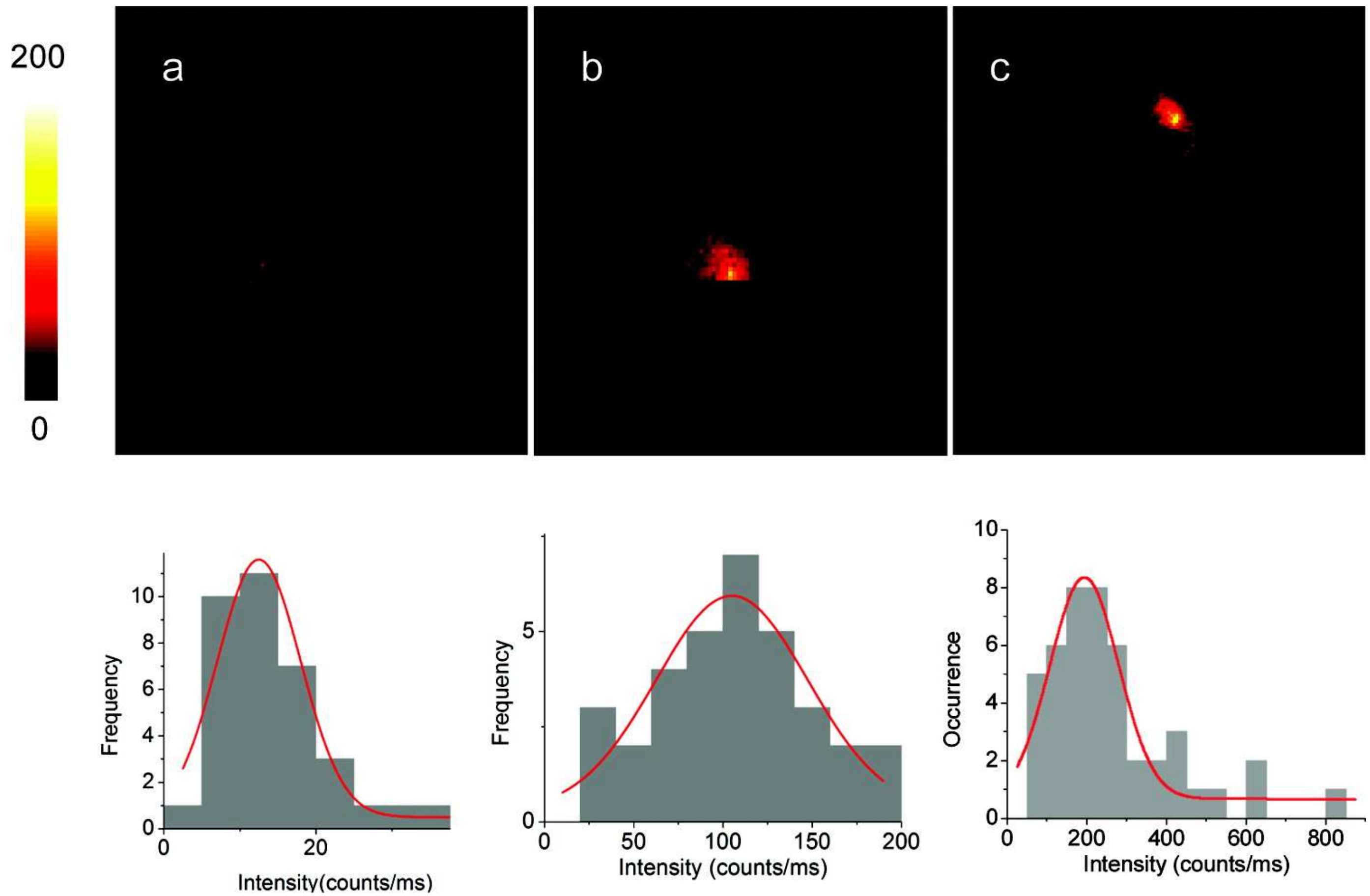
Phys. Rev. Lett. **95**, 206802 (2005)

J. Chem. Phys. **124**, 234709 (2006)

Nano Lett. **9**, 758 (2009)

Experiments

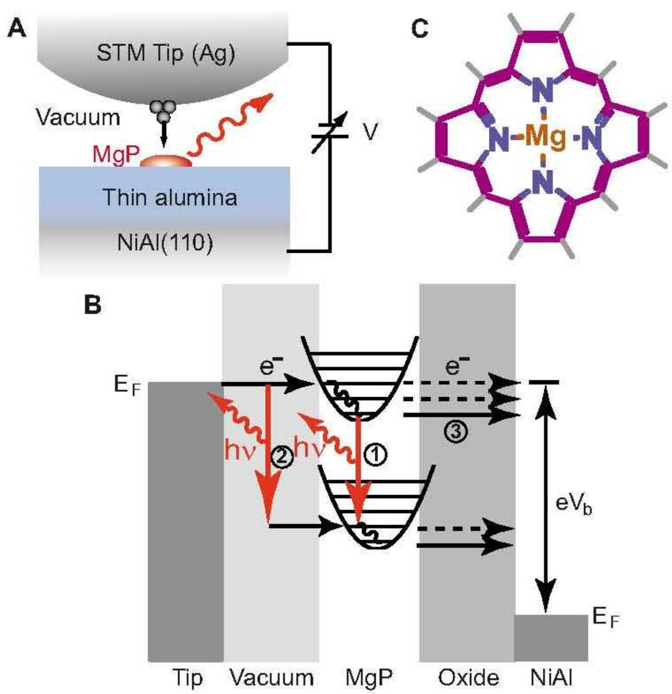
Metal enhanced fluorescence (Cy5 on Ag)

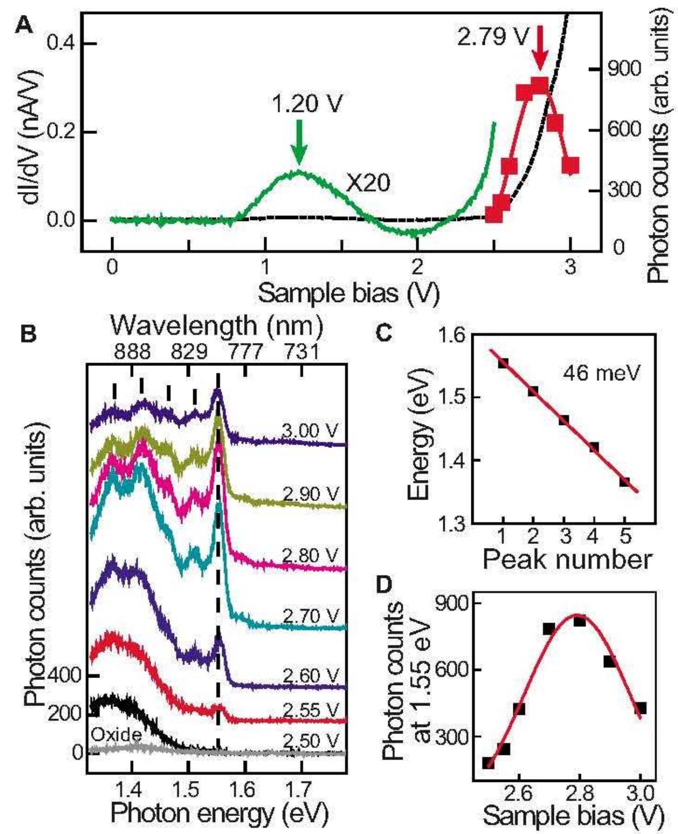


J.Zhang et al. *Nano Lett.* **7**, 2101 (2007)

Experiments

Intramolecular photon emission in STM

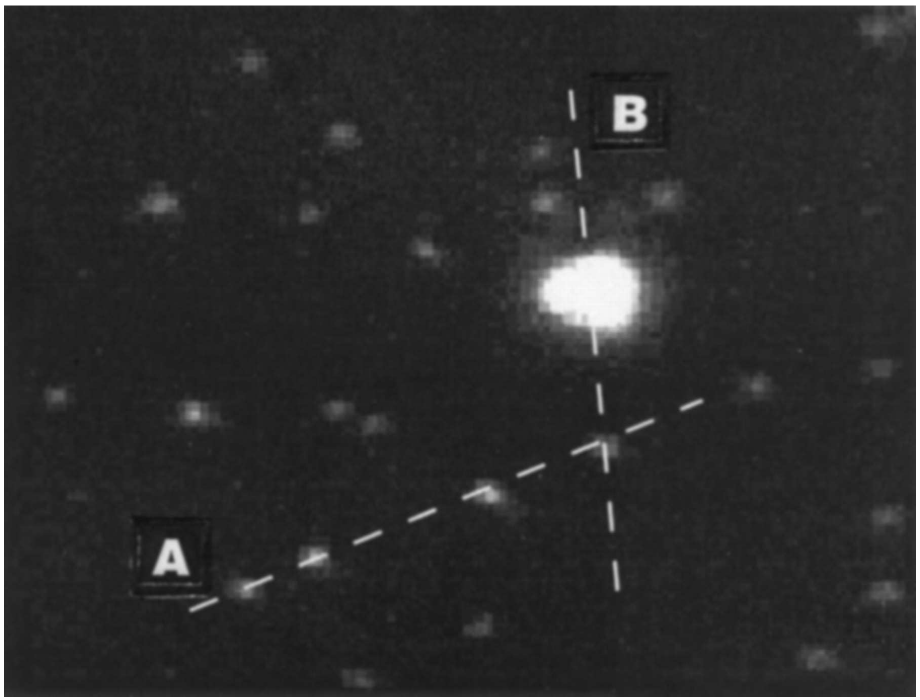


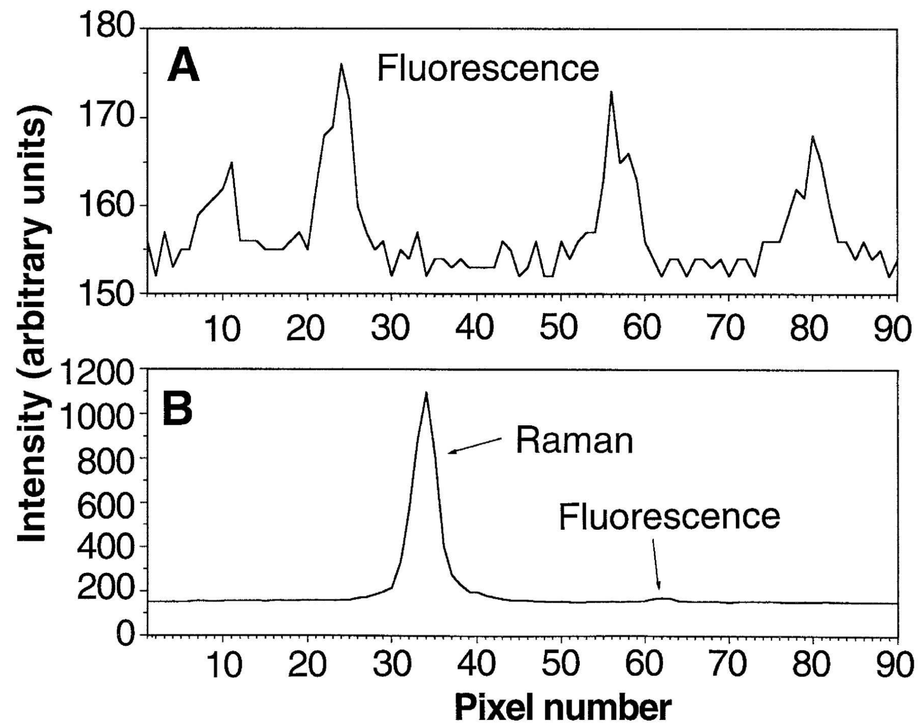


S.W.Wu et al. *Phys. Rev. B* **77**, 205430 (2008)

Experiments

SERS of molecules on nanoparticles

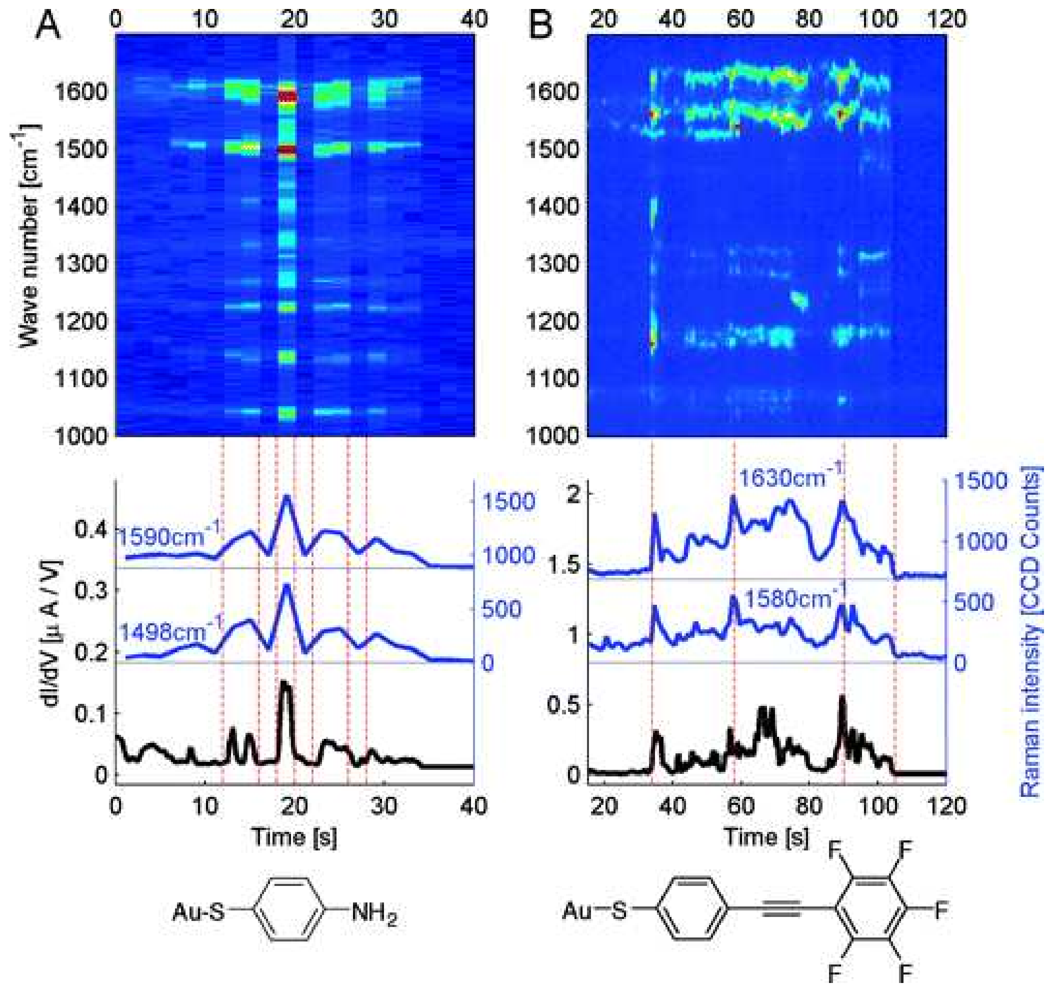




S.Nie and S.R.Emory. *Science* **275**, 1102 (1997)

Experiments

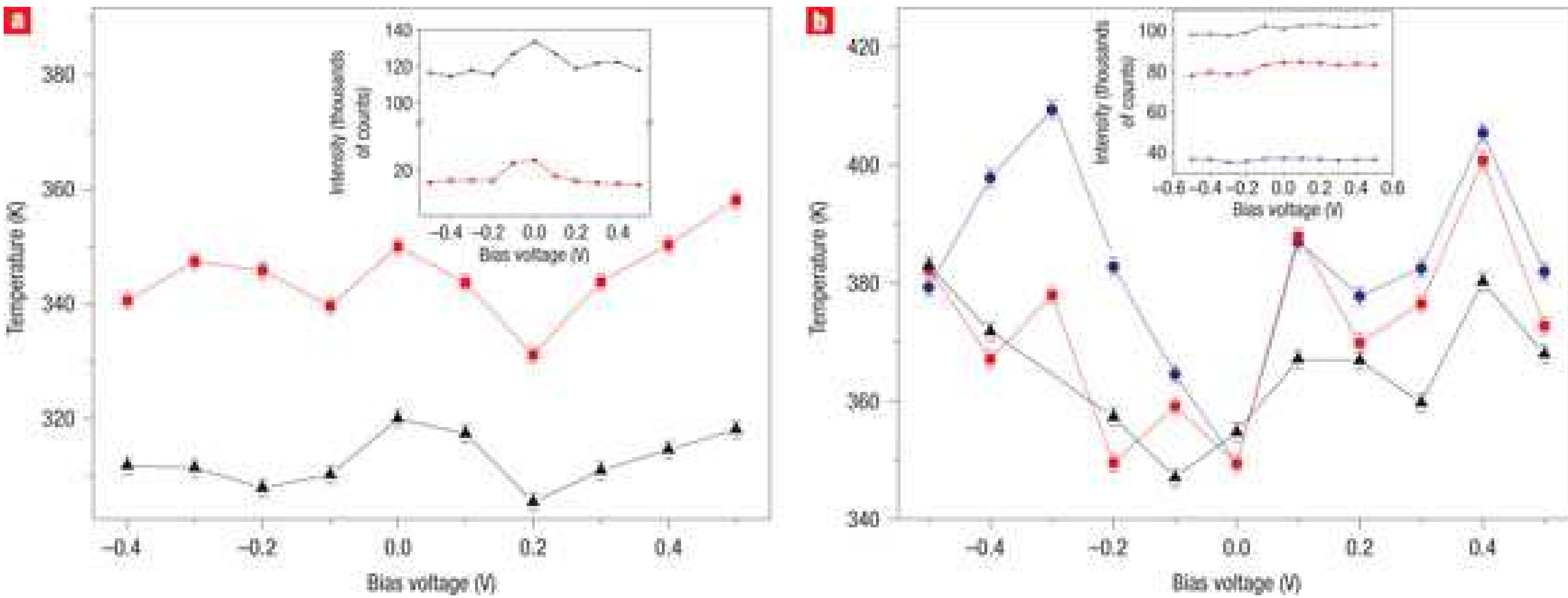
Simultaneous Raman and conduction



D.R.Ward et al. *Nano Lett.* **8**, 919 (2008)

Experiments

Heating detected by Raman



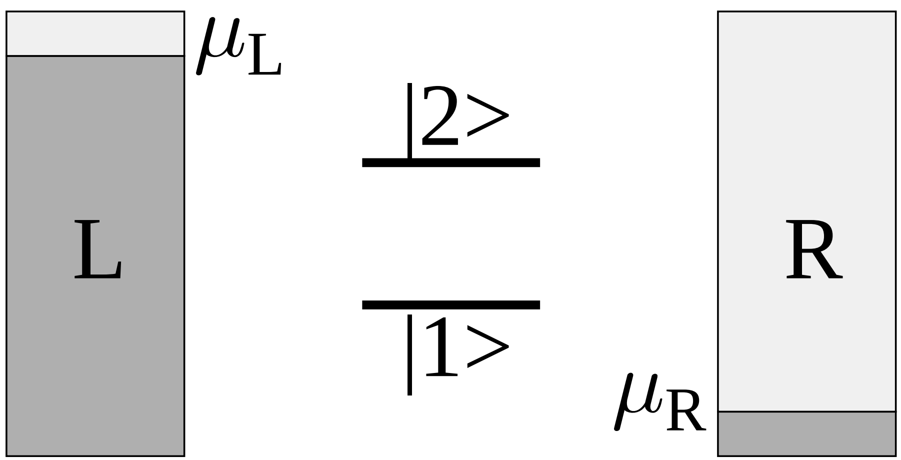
Z.Ioffe et al. *Nature Nanotechnology* **3**, 727 (2008)

HOMO-LUMO model

- Absorption line shape of molecule in biased junction
- Light induced current in molecular junction
- Fluorescence from current carrying molecular bridge
- Current from electronic excitations in the leads
- Raman spectroscopy of biased junctions

Phys. Rev. Lett. **95**, 206802 (2005); **96**, 166803 (2006)
J. Chem. Phys. **124**, 234709 (2006); **128**, 124705 (2008)
Nano Lett. **9**, 758 (2009); *J. Chem. Phys.* **130**, 144109 (2009)

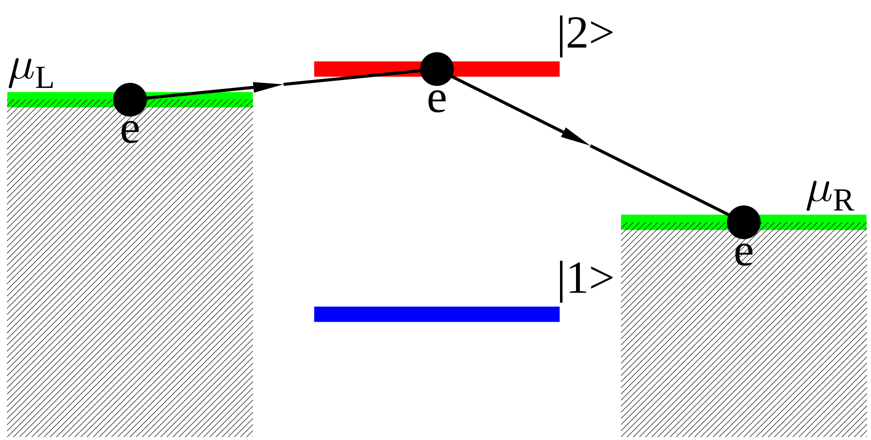
HOMO-LUMO model



Fluxes considered

- electronic current through the molecule
- energy flow between the molecule and electron-hole excitations in the leads
- incident or emitted photon flux

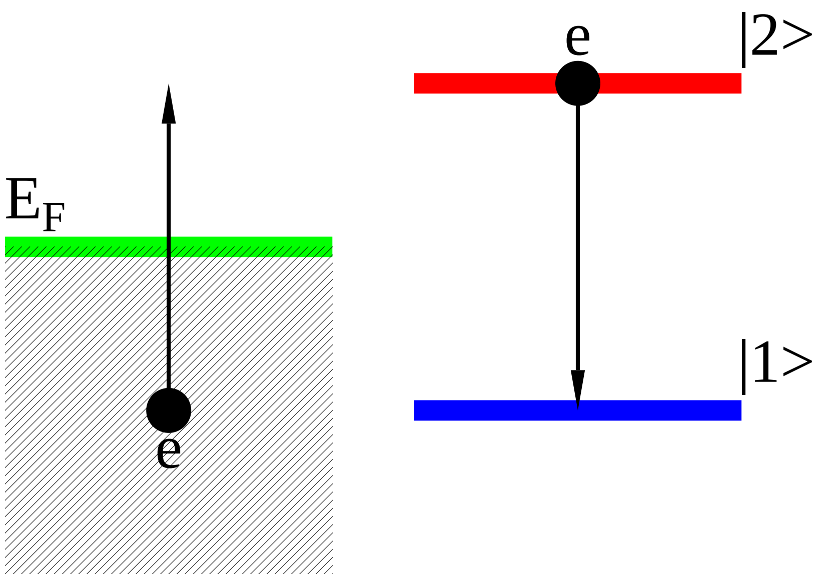
HOMO-LUMO model



Fluxes considered

- electronic current through the molecule
- energy flow between the molecule and electron-hole excitations in the leads
- incident or emitted photon flux

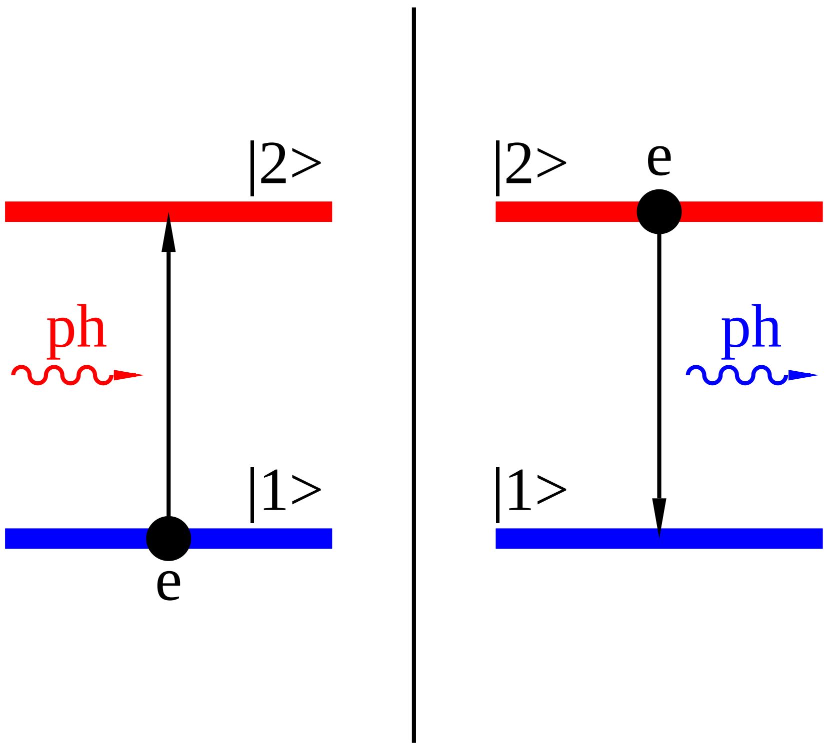
HOMO-LUMO model



Fluxes considered

- electronic current through the molecule
- energy flow between the molecule and electron-hole excitations in the leads
- incident or emitted photon flux

HOMO-LUMO model



Fluxes considered

- electronic current through the molecule
- energy flow between the molecule and electron-hole excitations in the leads
- incident or emitted photon flux

HOMO-LUMO model

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\hat{H}_0 = \sum_{m=1,2} \varepsilon_m \hat{c}_m^\dagger \hat{c}_m + \sum_{k\in\{L,R\}} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \hbar \sum_\alpha \omega_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha$$

$$\hat{V} = \hat{V}_M + \hat{V}_N + \hat{V}_P$$

$$\hat{V}_M = \sum_{K=L,R} \sum_{m=1,2;k\in K} \left(V_{km}^{(MK)} \hat{c}_k^\dagger \hat{c}_m + \text{H.c.} \right)$$

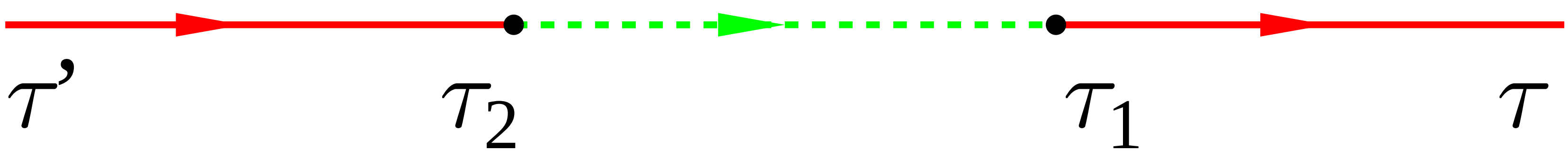
$$\hat{V}_N = \sum_{K=L,R} \sum_{k\neq k'\in K} \left(V_{kk'}^{(NK)} \hat{c}_k^\dagger \hat{c}_{k'} \hat{c}_2^\dagger \hat{c}_1 + \text{H.c.} \right)$$

$$\hat{V}_P = \sum_\alpha \left(V_\alpha^{(P)} \hat{a}_\alpha \hat{c}_2^\dagger \hat{c}_1 + \text{H.c.} \right)$$

HOMO-LUMO model

SE due to electron tunneling

$$\Sigma_{MK,mm'}(\tau_1,\tau_2) = \sum_{k\in K} V_{mk}^{(MK)} g_k(\tau_1,\tau_2) V_{km'}^{(MK)}$$



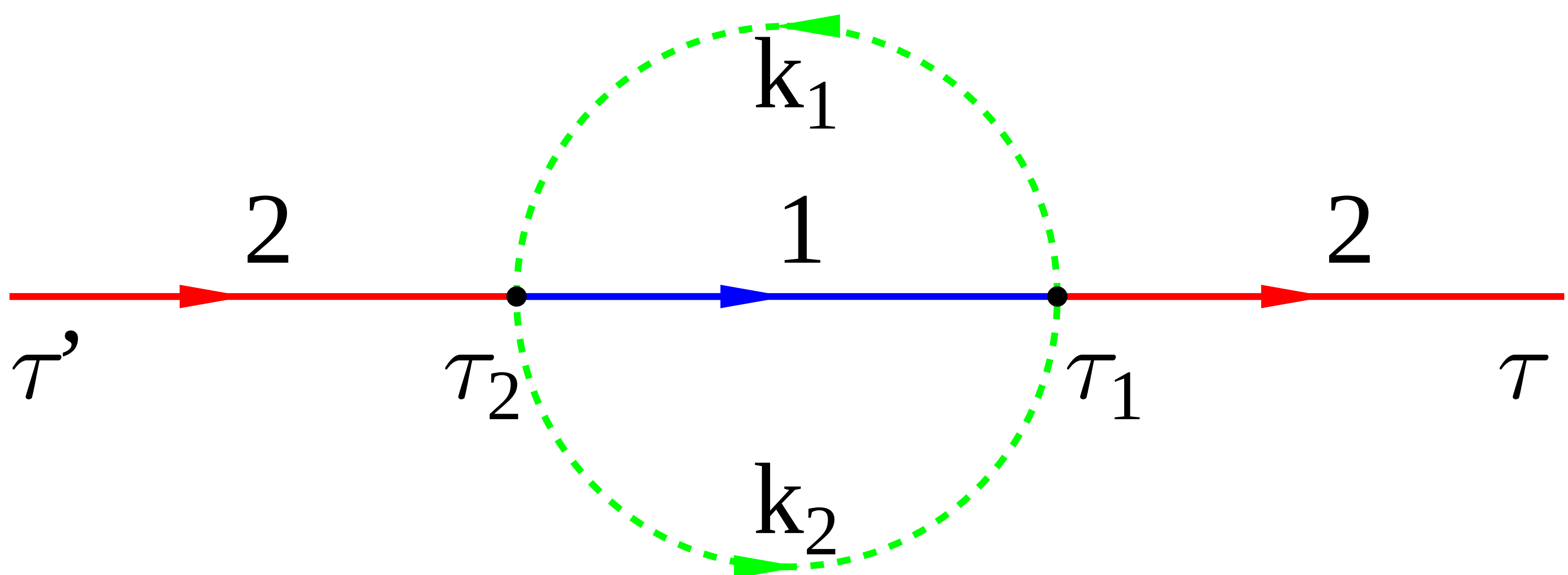
projections (WBL and no mixing)

$$\begin{aligned}
\Sigma^r_{MK,mm'} &= -i\delta_{mm'}\Gamma_{MK,m}/2 \\
\Sigma^<_{MK,mm'}(E) &= i\delta_{mm'} f_K(E)\Gamma_{MK,m} \\
\Sigma^>_{MK,mm'}(E) &= -i\delta_{mm'}[1-f_K(E)]\Gamma_{MK,m}
\end{aligned}$$

HOMO-LUMO model

SE due to e-h excitations in the contacts

$$\Sigma_{NK}(\tau_1,\tau_2) = \sum_{k\neq k'\in K} \left|V_{kk'}^{(NK)}\right|^2 g_k(\tau_2,\tau_1) g_{k'}(\tau_1,\tau_2) \times \begin{bmatrix} G_{22}(\tau_1,\tau_2) & 0 \\ 0 & G_{11}(\tau_1,\tau_2) \end{bmatrix}$$



HOMO-LUMO model

Projections

$$\Sigma^{<}_{NK,mm}(E) = \int \frac{d\omega}{2\pi} \, B_{NK}(\omega, \mu_K) \, G^{<}_{\bar{m}\bar{m}}(E+\omega)$$

$$\Sigma^{>}_{NK,mm}(E) = \int \frac{d\omega}{2\pi} \, B_{NK}(\omega, \mu_K) \, G^{>}_{\bar{m}\bar{m}}(E-\omega)$$

with

$$B_{NK}(\omega, \mu_K) = 2\pi \int dE \sum_{k \neq k' \in K} \left| V^{(NK)}_{kk'} \right|^2$$

$$\times \delta(E - \varepsilon_k)\delta(E + \omega - \varepsilon_{k'}) f_K(E)[1 - f_K(E+\omega)]$$

$$\equiv 2\pi \left| V^{(NK)} \right|^2 \rho^{e-h}_K(\omega)$$

HOMO-LUMO model

Simplified version when $\varepsilon_{21} \gg \Gamma_{1,2}$

$$\Sigma^{<}_{NK} = iB_{NK} \begin{bmatrix} n_2 & 0 \\ 0 & 0 \end{bmatrix}$$

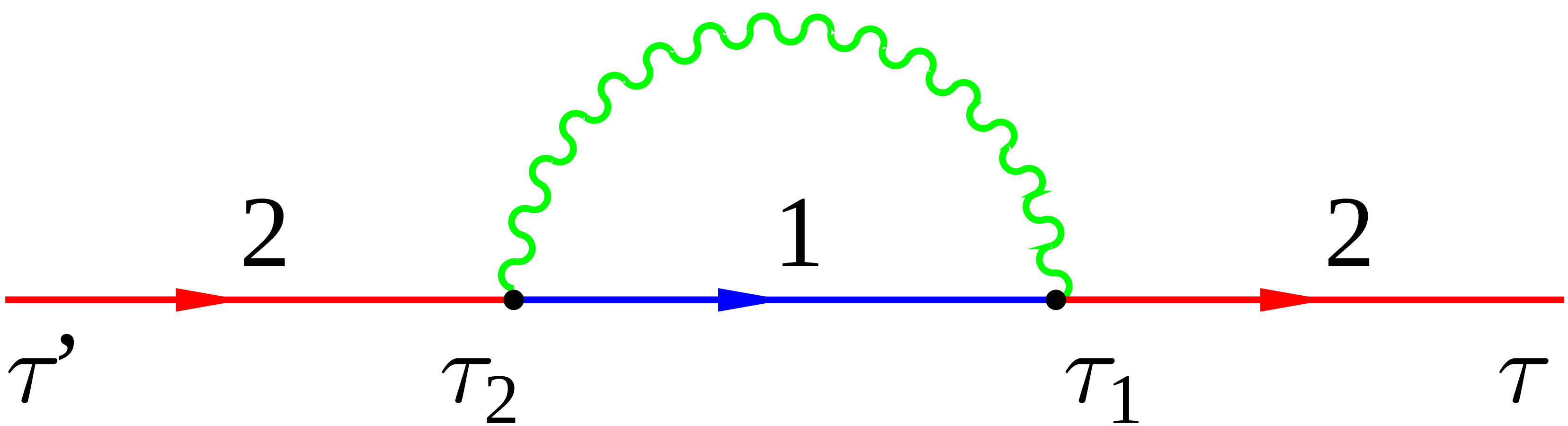
$$\Sigma^{>}_{NK} = -iB_{NK} \begin{bmatrix} 0 & 0 \\ 0 & 1 - n_1 \end{bmatrix}$$

where $B_{NK} = B_{NK}(\varepsilon_{21})$

HOMO-LUMO model

SE due to coupling to photon field

$$\Sigma_P(\tau_1,\tau_2) = i\sum_\alpha \left|V_\alpha^{(P)}\right|^2$$
$$\times \begin{bmatrix} F_\alpha(\tau_2,\tau_1)G_{22}(\tau_1,\tau_2) & 0 \\ 0 & F_\alpha(\tau_1,\tau_2)G_{11}(\tau_1,\tau_2) \end{bmatrix}$$



HOMO-LUMO model

$$\Sigma_P^<(E) = \sum_\alpha \left| V_\alpha^{(P)} \right|^2 \times \begin{bmatrix} (1+N_\alpha)G_{22}^<(E+\omega_\alpha) & 0 \\ 0 & N_\alpha G_{11}^<(E-\omega_\alpha) \end{bmatrix}$$

$$\Sigma_P^>(E) = \sum_\alpha \left| V_\alpha^{(P)} \right|^2 \times \begin{bmatrix} N_\alpha G_{22}^>(E+\omega_\alpha) & 0 \\ 0 & (1+N_\alpha)G_{11}^>(E-\omega_\alpha) \end{bmatrix}$$

$N_0 = 1$ for pumping mode (*absorption flux*)

$N_\alpha = 0$ for absorbing modes (*fluorescence*)

HOMO-LUMO model

Simplified version for emission flux when $\varepsilon_{21} \gg \Gamma_{1,2}$

$$\Sigma_P^< = i\gamma_P(\varepsilon_{21}) \begin{bmatrix} n_2 & 0 \\ 0 & 0 \end{bmatrix}$$

$$\Sigma_P^> = -i\gamma_P(\varepsilon_{21}) \begin{bmatrix} 0 & 0 \\ 0 & 1 - n_1 \end{bmatrix}$$

where $\gamma_P(\omega) = 2\pi \sum_\alpha \left| V_\alpha^{(P)} \right|^2 \delta(\omega - \omega_\alpha)$

Flux expression

$$I_B = \int_{-\infty}^{+\infty} \frac{dE}{2\pi\hbar} \mathrm{Tr} \left[\Sigma_B{}^{<}(E)\, G^{>}(E) - \Sigma_B{}^{>}(E)\, G^{<}(E) \right]$$

with $B0 = \ldots$

- $P0, 22$ or minus $P0, 11$ *for absorption flux*
- ML or minus MR for *current* through the junction
- $P, 11$ or minus $P, 22$ for *fluorescence*

Absorption line shape

General expression

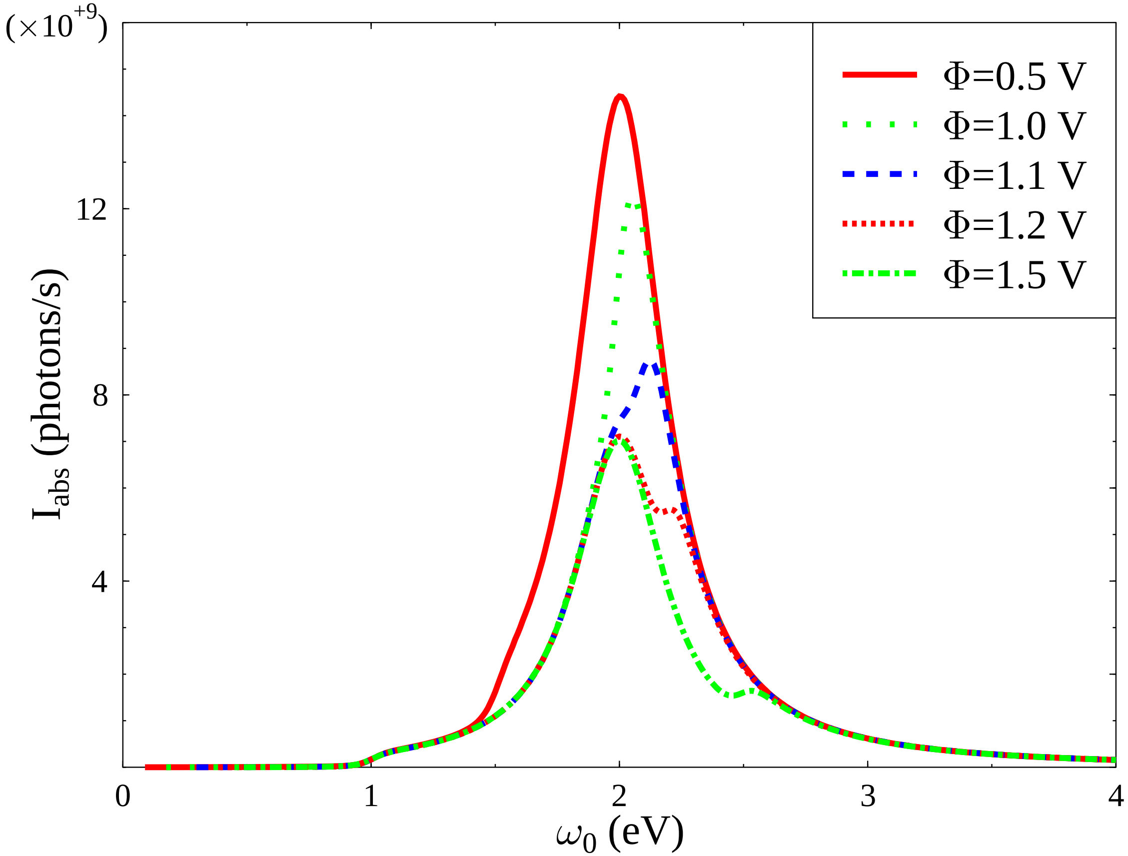
$$I_{abs}(\omega_0) = \int_{-\infty}^{+\infty} \frac{dE}{2\pi\hbar} \left[\Sigma^{<}_{P0,22}(E)\, G^{>}_{22}(E) - \Sigma^{>}_{P0,22}(E)\, G^{<}_{22}(E)\right]$$

Simplified version (Lorentzian)

- $\varepsilon_1 \ll \mu_{L,R} \ll \varepsilon_2$ (low bias)
- coupling to the photon field is weak
- $\Gamma_{1,2} \ll \varepsilon_{21}, |\varepsilon_{1,2} - E_F|$

$$I_{abs}(\omega_0) = \frac{\left|V_0^{(P)}\right|^2}{\hbar} \frac{\Gamma}{(\varepsilon_2 - \omega_0 - \varepsilon_1)^2 + (\Gamma/2)^2} \times \frac{\Gamma_{M,1}\Gamma_{M,2}}{\Gamma_1\Gamma_2}$$

Absorption line shape



$\varepsilon_{21} = 2$ eV

$\gamma_P = 10^{-6}$ eV

$T = 300$ K

$B_{NL} = B_{NR} = 0.1$ eV

$\Gamma_{ML/R,1} = 0.01$ eV

$\Gamma_{ML/R,2} = 0.2$ eV

partial population of LUMO (HOMO) distortes the Lorentzian shape

Light induced current

- Radiation field in resonance with the molecular optical transition
- Molecules with strong charge-transfer transitions
  - DMEANS (4-Dimethylamino-4'-nitrostilbene) 7D (ground) $\rightarrow$ 31D (first excited singlet)
  - all-trans Retinal in Poly-methyl methacrylate films 6.6D $\rightarrow$ 19.8D (^1B_u electronic state)
  - 40Å $CdSe$ nanocrystals 0D $\rightarrow$ 32D (first excited state)

If optical charge transfer is parallel to the wire axis

optical pumping $\rightarrow$ charge flow between the two leads

Light induced current

General expression

$$I_{sd} = \int_{-\infty}^{+\infty} \frac{dE}{2\pi\hbar} \mathrm{Tr}\left[\Sigma_{ML}^{<}(E)\, G^{>}(E) - \Sigma_{ML}^{>}(E)\, G^{<}(E)\right]$$

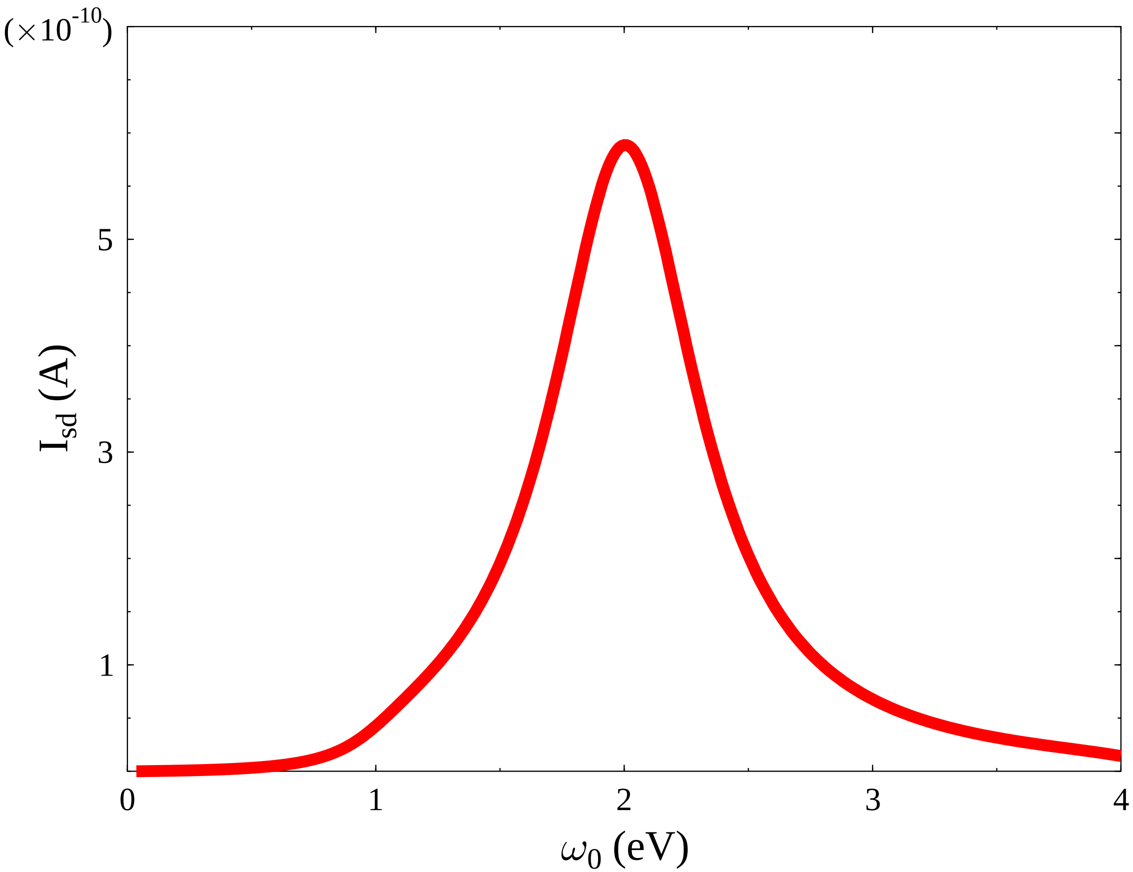
Simplified version ($\omega_0 \sim \varepsilon_{21}$, $\Phi = 0$, $\Gamma_{1,2} \ll \varepsilon_{21}$)

$$I_{sd} = \frac{|V_0^{(P)}|^2}{\hbar} \frac{\Gamma}{\left(\varepsilon_2 - \omega_0 - \varepsilon_1\right)^2 + \left(\Gamma/2\right)^2} \frac{\Gamma_{ML,1}\Gamma_{MR,2} - \Gamma_{ML,2}\Gamma_{MR,1}}{\Gamma_1\Gamma_2}$$

The yield of the effect

$$Y_c = \left(\frac{I_{sd}}{I_{abs}}\right)_{\Phi=0} = \frac{\Gamma_{ML,1}\Gamma_{MR,2} - \Gamma_{ML,2}\Gamma_{MR,1}}{\Gamma_{M,1}\Gamma_{M,2}}$$

Light induced current



$\Phi = 0$

$\varepsilon_{21} = 2$ eV

$\gamma_P = 10^{-6}$ eV

$T = 300$ K

$B_{NL} = B_{NR} = 0.1$ eV

$\Gamma_{ML/R,1} = 0.2$ eV

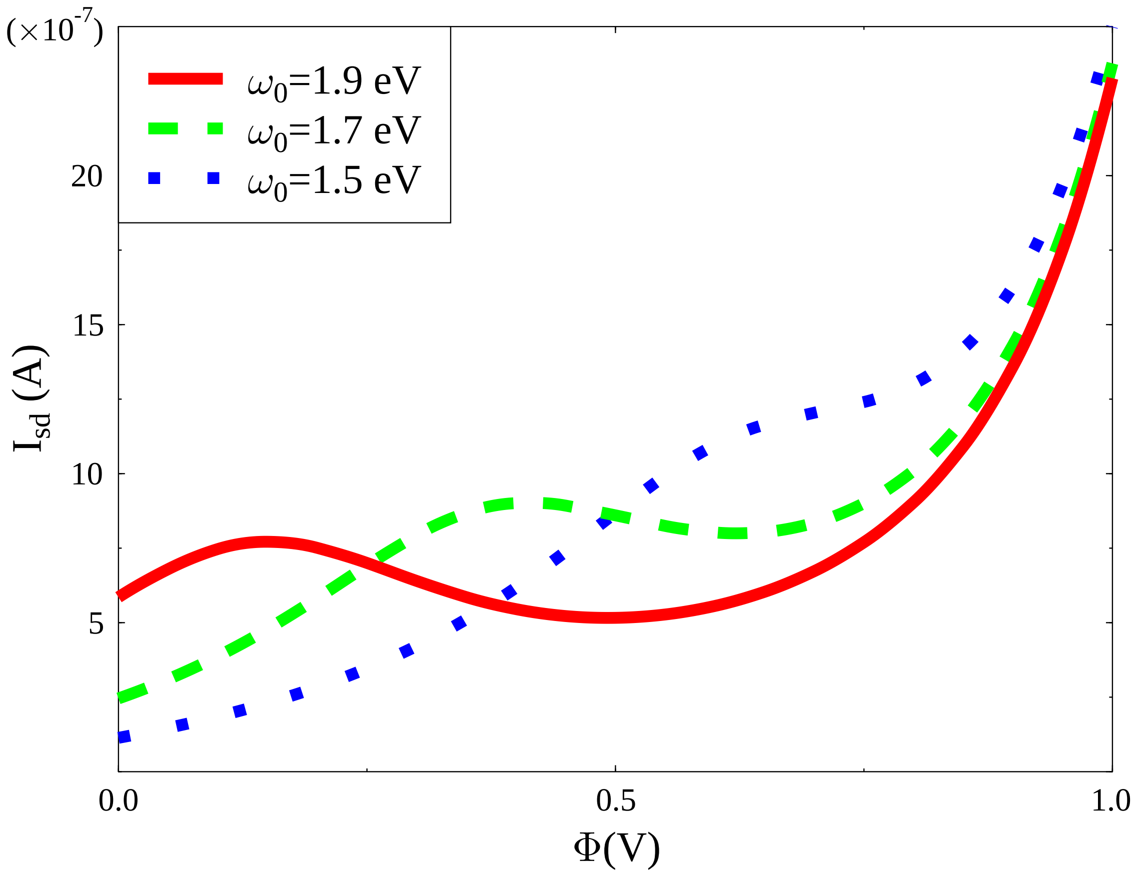
$\Gamma_{ML,2} = 0.02$ eV

$\Gamma_{MR,2} = 0.3$ eV

$V_0^{(P)} = 10^{-3}$ eV

peak at the HOM0-LUMO gap frequency

Light induced current



$\Phi = 0$

$\varepsilon_{21} = 2$ eV

$\gamma_P = 10^{-6}$ eV

$T = 300$ K

$B_{NL} = B_{NR} = 0.1$ eV

$\Gamma_{ML,1/MR,2} = 0.2$ eV

$\Gamma_{ML,2/MR,1} = 0.02$ eV

$V_0^{(P)} = 0.02$ eV

If the level position is pinned to the contact to which it is coupled stronger $\rightarrow$ NDR

Fluorescence

Light emission from STM junctions

- e excites *surface plasmon* which later emits
- *time-dependent potential* of a tunneling e $\longrightarrow$ electronic excitation of the molecule $\longrightarrow$ fluorescence
- *current carrying situation* with excited state formed with a finite probability $\longrightarrow$ photon emission. . .

Fluorescence

Frequency resolved spectrum

$$I'_{em}(\omega) = \rho_P(\omega) \int_{-\infty}^{+\infty} \frac{dE}{2\pi\hbar} \left[\Sigma^{<}_{P,11}(E,\omega)\, G^{>}_{11}(E) - \Sigma^{>}_{P,11}(E,\omega)\, G^{<}_{11}(E)\right]$$

Overall emission intensity

$$\begin{aligned} I^{tot}_{em} &= \int_0^{\infty} d\omega\, I'_{em}(\omega) \\ &= \int_{-\infty}^{+\infty} \frac{dE}{2\pi\hbar} \left[\Sigma^{<}_{P,11}(E)\, G^{>}_{11}(E) - \Sigma^{>}_{P,11}(E)\, G^{<}_{11}(E)\right] \end{aligned}$$

Fluorescence

When coupling to radiation field is weak and $\Gamma_{1,2} \ll \varepsilon_{21}$

$$
\begin{aligned}
I'_{em}(\omega) &= \frac{\gamma_P(\omega)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \\
&\quad \left[\frac{f_L(E+\omega)\Gamma_{ML,2} + f_R(E+\omega)\Gamma_{MR,2}}{(E+\omega-\varepsilon_2)^2 + (\Gamma_2/2)^2} \right. \\
&\quad \left. \times \frac{[1-f_L(E)]\Gamma_{ML,1} + [1-f_R(E)]\Gamma_{MR,1}}{(E-\varepsilon_1)^2 + (\Gamma_1/2)^2} \right]
\end{aligned}
$$

$$
I_{em}^{tot} = \frac{\gamma_P(\varepsilon_{21})}{\hbar} n_2 \left[1 - n_1\right]
$$

Fluorescence

When in addition $\mu_L \gg \varepsilon_2 > \varepsilon_1 \gg \mu_R$

$$I_{em}^{tot} = \frac{\gamma_P}{\hbar} \frac{\Gamma_{ML,2}\Gamma_{MR,1}}{\Gamma_1 \Gamma_2}$$

Also in this case

$$I_{sd} = \frac{1}{\hbar} \sum_{m=1,2} \frac{\Gamma_{ML,m}\Gamma_{MR,m}}{\Gamma_m} + \frac{B_N + \gamma_P}{\hbar} \frac{\Gamma_{ML,2}\Gamma_{MR,1}}{\Gamma_1 \Gamma_2}$$

So that the yield

$$Y_{em} = \frac{I_{em}^{tot}}{I_{sd}} = \frac{\gamma_P}{\frac{\Gamma_{MR,2}}{\Gamma_{MR,1}}\Gamma_1 + \frac{\Gamma_{ML,1}}{\Gamma_{ML,2}}\Gamma_2 + B_N + \gamma_P}$$

Fluorescence

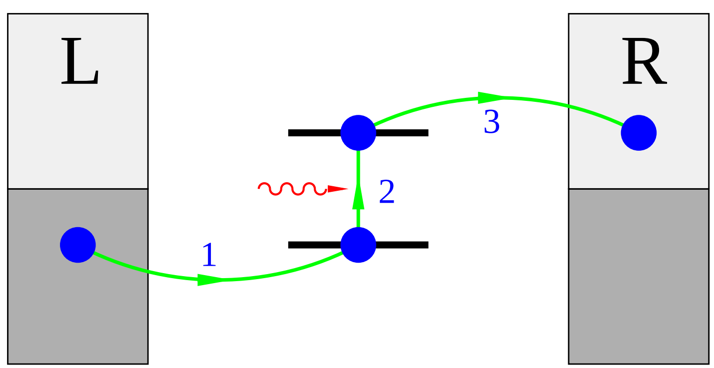
Conditions for the higher yield here

$$\Gamma_{MR,2} < \Gamma_{MR,1} \qquad \Gamma_{ML,1} < \Gamma_{ML,2}$$

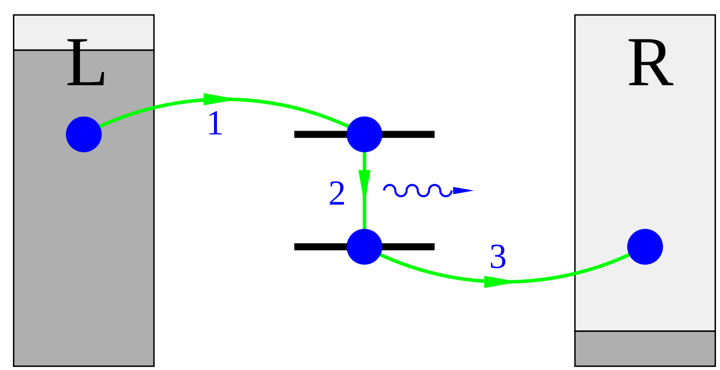
are *opposite* to the light induced case

$$\Gamma_{ML,1}\Gamma_{MR,2} > \Gamma_{ML,2}\Gamma_{MR,1}$$

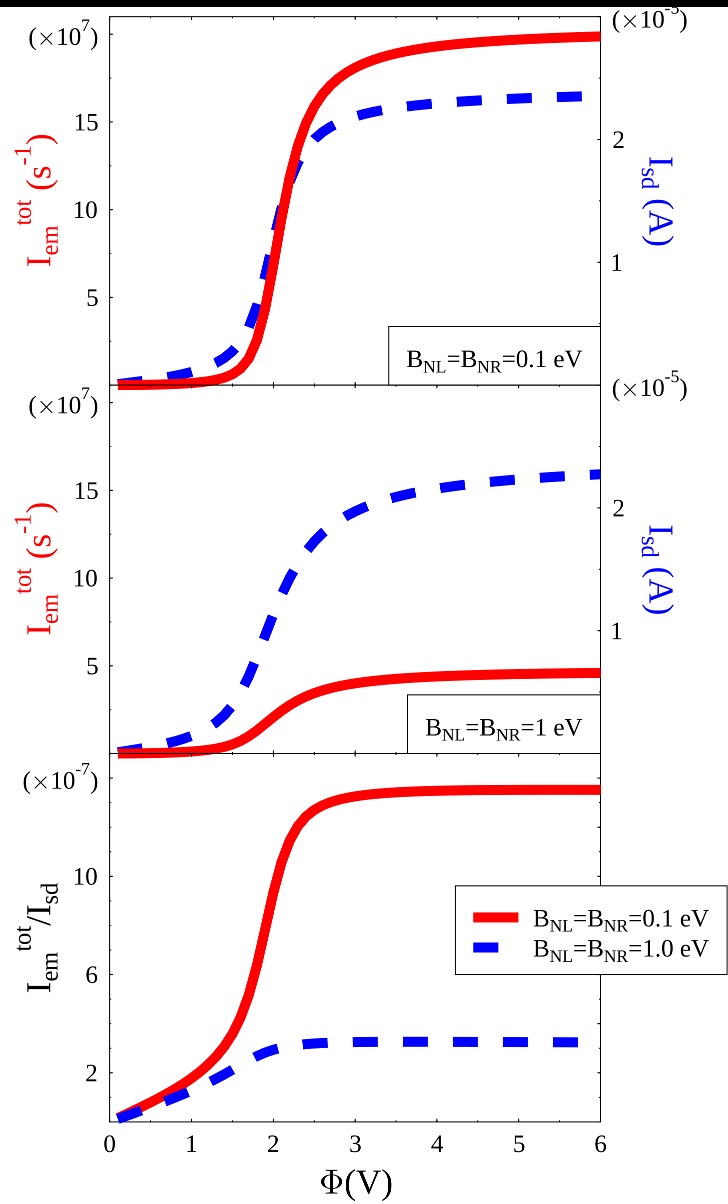
Light induced current



Fluorescence



Fluorescence



$T = 300$ K

$\varepsilon_{21} = 2$ eV

$\Gamma_{MK,m} = 0.1$ eV

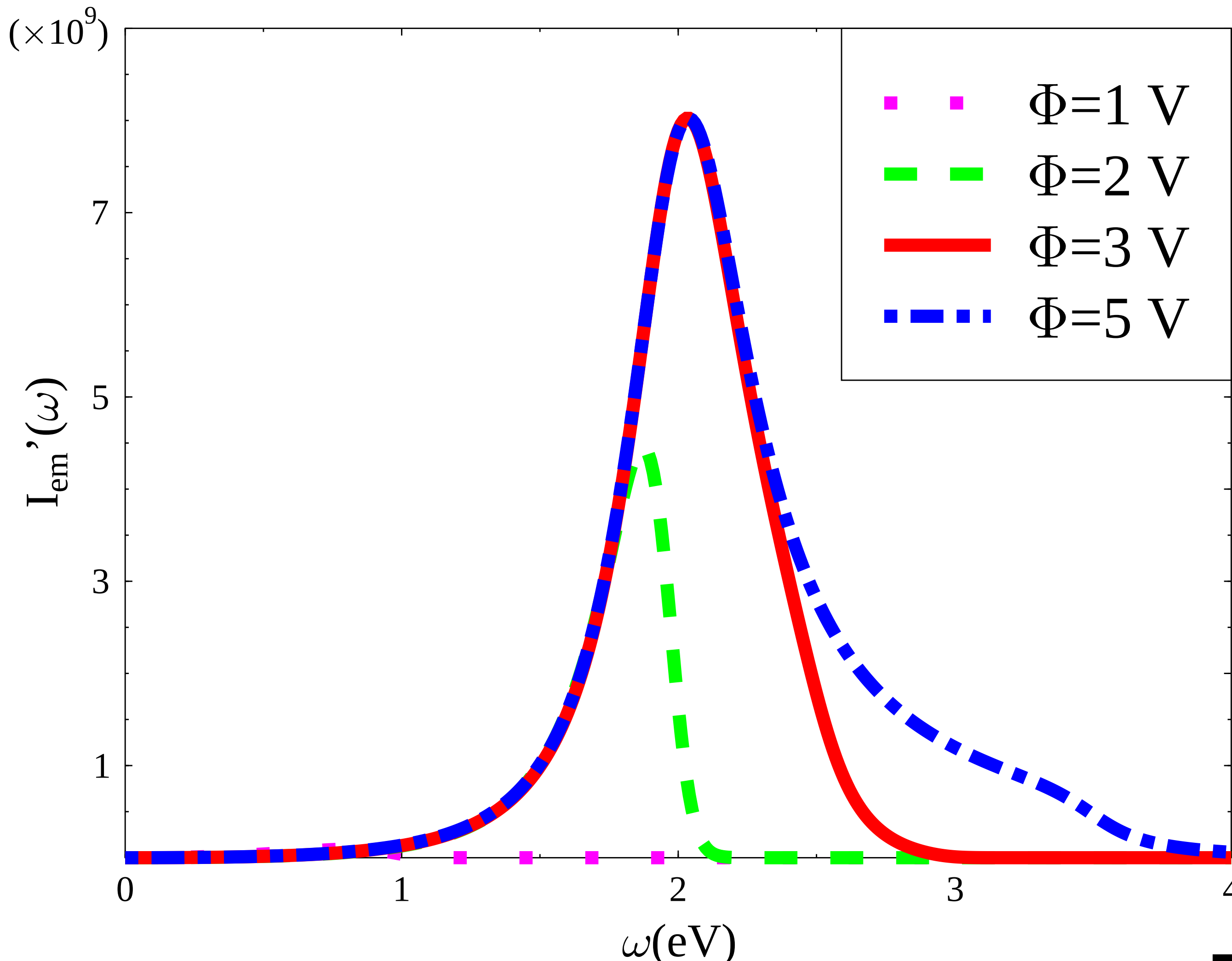
$\gamma_P = 10^{-6}$ eV

$B_{NL} = B_{NR} = 0.1$ eV

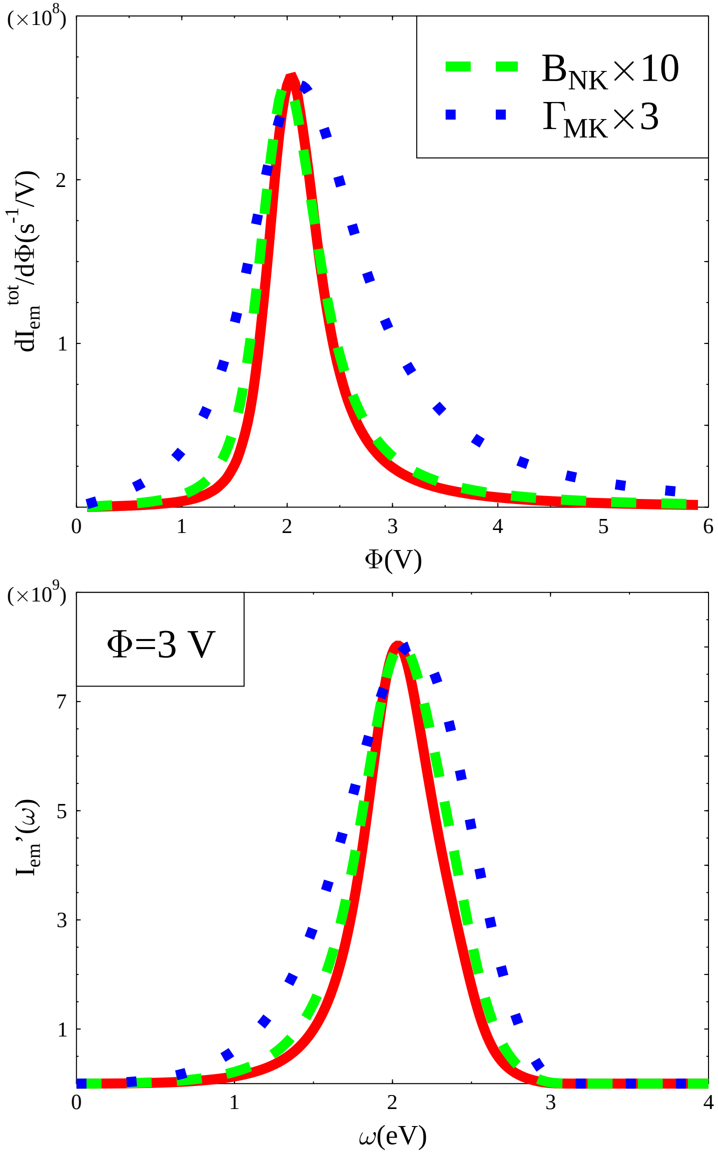
emission and
e-h excitations
compete for the same
LUMO $\rightarrow$ HOMO transition

Fluorescence

Fermi population features in the lineshape



Fluorescence



Linewidth is more sensitive to Γ_{MK} than B_N since

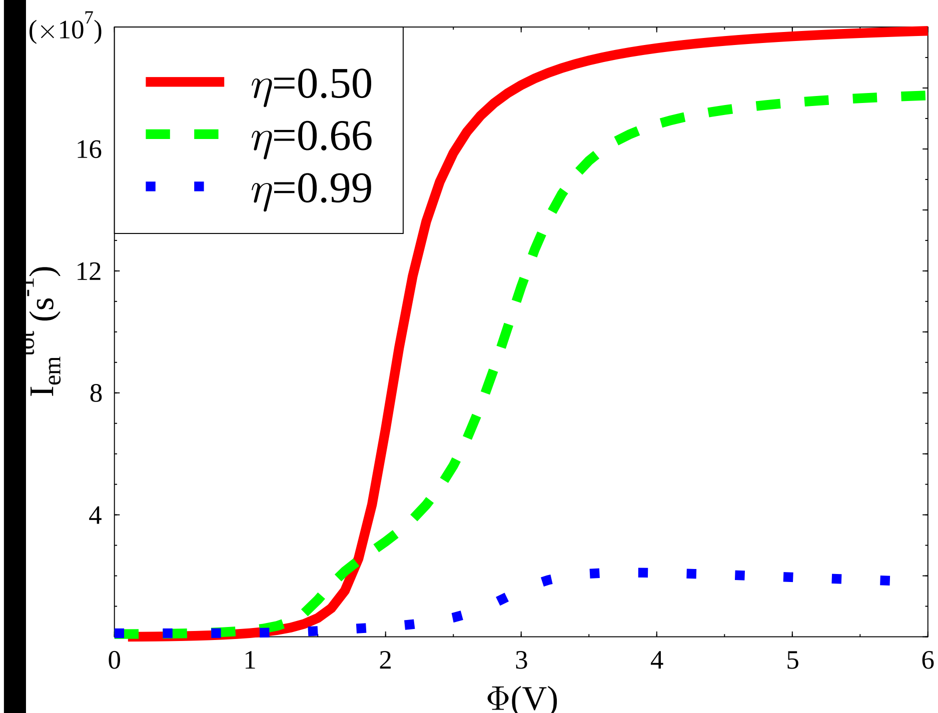
$$\Gamma_{N,1} = B_N n_2$$
$$\Gamma_{N,2} = B_N[1 - n_1]$$

while

$$[1 - n_1], n_2 \ll 1$$

for low bias

Fluorescence

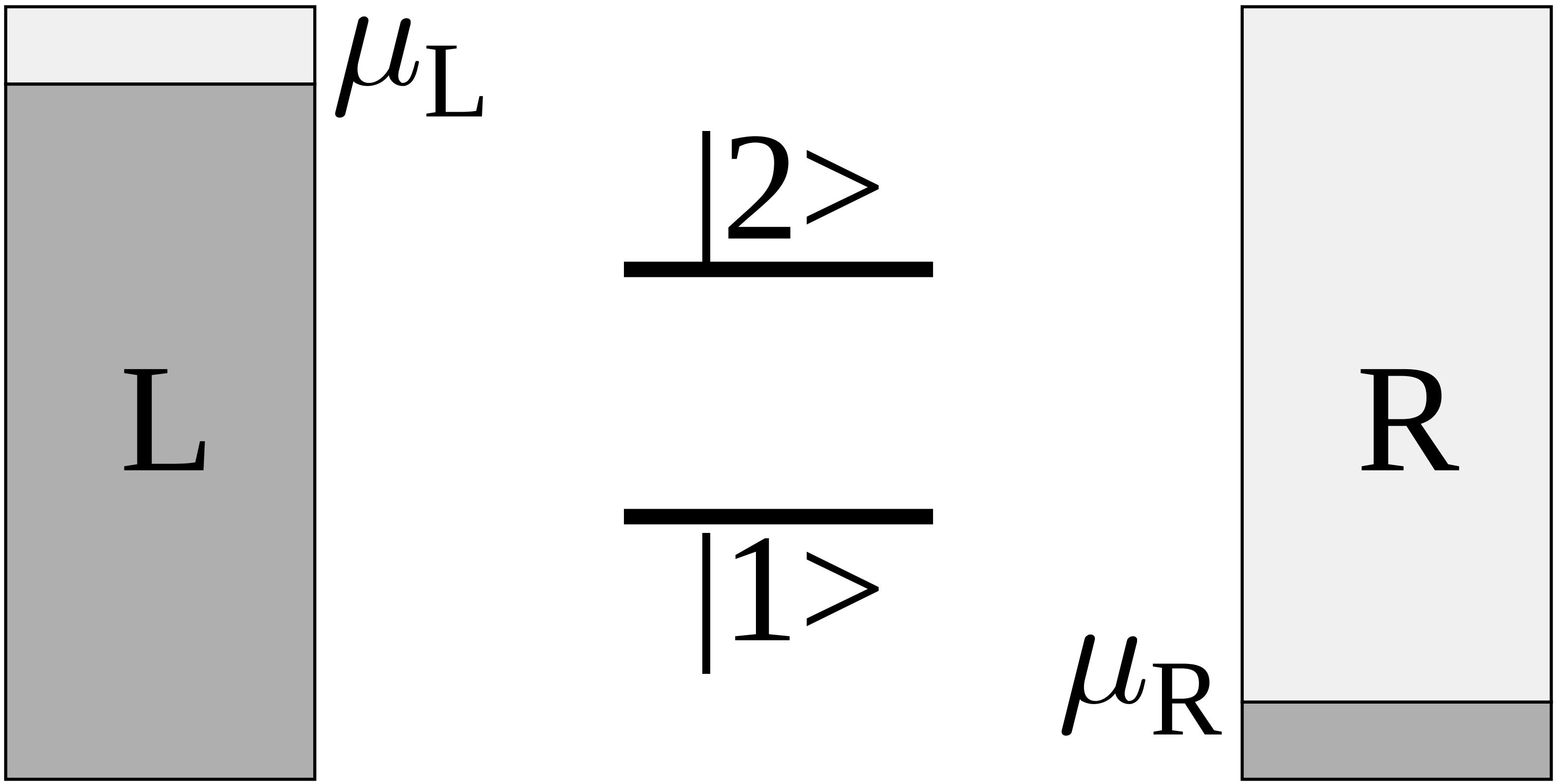


- $\eta = \Phi_L/\Phi = \Gamma_{MR,m}/\Gamma_m = B_{NR}/B_N$
- $\eta \to 1$ no emission (either LUMO is empty or HOMO is full)
- **Fluorescence in STM** Φ should fall at the molecule-substrate interface

Spacers reduce energy losses into substrate (B_N)

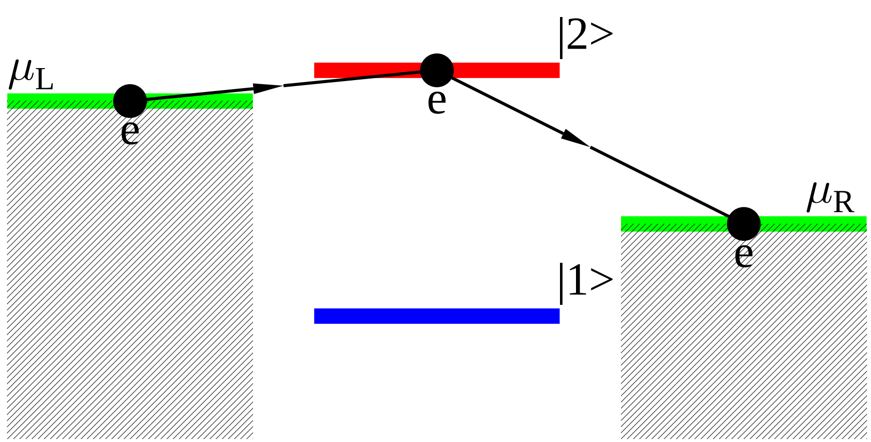
But enable light emission at the molecule

Current from e-h excitations



MG, A.Nitzan, M.A.Ratner, *PRL* **96**, 166803 (2006)

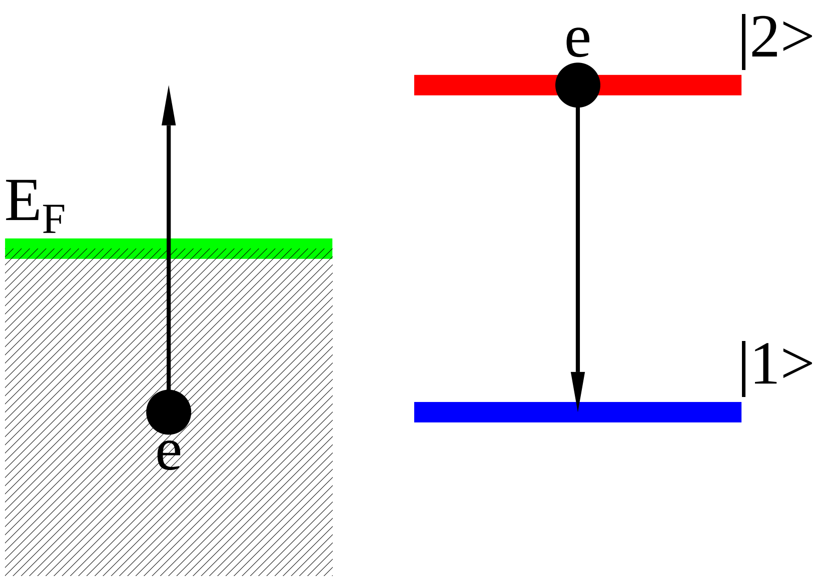
Current from e-h excitations



Fluxes considered

- electronic current through the molecule
- energy flow between the molecule and electron-hole excitations in the leads

Current from e-h excitations



Fluxes considered

- electronic current through the molecule
- energy flow between the molecule and electron-hole excitations in the leads

Current from e-h excitations

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\hat{H}_0 = \sum_{m=1,2} \varepsilon_m \hat{c}_m^\dagger \hat{c}_m + \sum_{k\in\{L,R\}} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k$$

$$\hat{V} = \hat{V}_M + \hat{V}_N$$

$$\hat{V}_M = \sum_{K=L,R} \sum_{m=1,2;k\in K} \left(V_{km}^{(MK)} \hat{c}_k^\dagger \hat{c}_m + \text{H.c.} \right)$$

$$\hat{V}_N = \sum_{K=L,R} \sum_{k\neq k'\in K} \left(V_{kk'}^{(NK)} \hat{c}_k^\dagger \hat{c}_{k'} \hat{c}_2^\dagger \hat{c}_1 + \text{H.c.} \right)$$

Current from e-h excitations

$$I_{sd} = I_{sd}^{L} + I_{sd}^{e-h}$$

$$I_{sd}^{L} = \frac{e}{\hbar}\int_{-\infty}^{+\infty}\frac{dE}{2\pi}\sum_{m=1,2}\Gamma_m^{(ML)}G_{mm}^{r}(E)\Gamma_m^{(MR)}G_{mm}^{a}(E) \times [f_L(E) - f_R(E)]$$

$$I_{sd}^{e-h} = \frac{e}{\hbar}B\left[n_2^{(ML)}\left(\frac{\Gamma_1^{(MR)}}{\Gamma_1} - n_1^{(MR)}\right) - n_2^{(MR)}\left(\frac{\Gamma_1^{(ML)}}{\Gamma_1} - n_1^{(ML)}\right)\right]$$

$\Gamma_m^{(MK)} \ll \varepsilon_{21}$ is assumed in the last

Current from e-h excitations

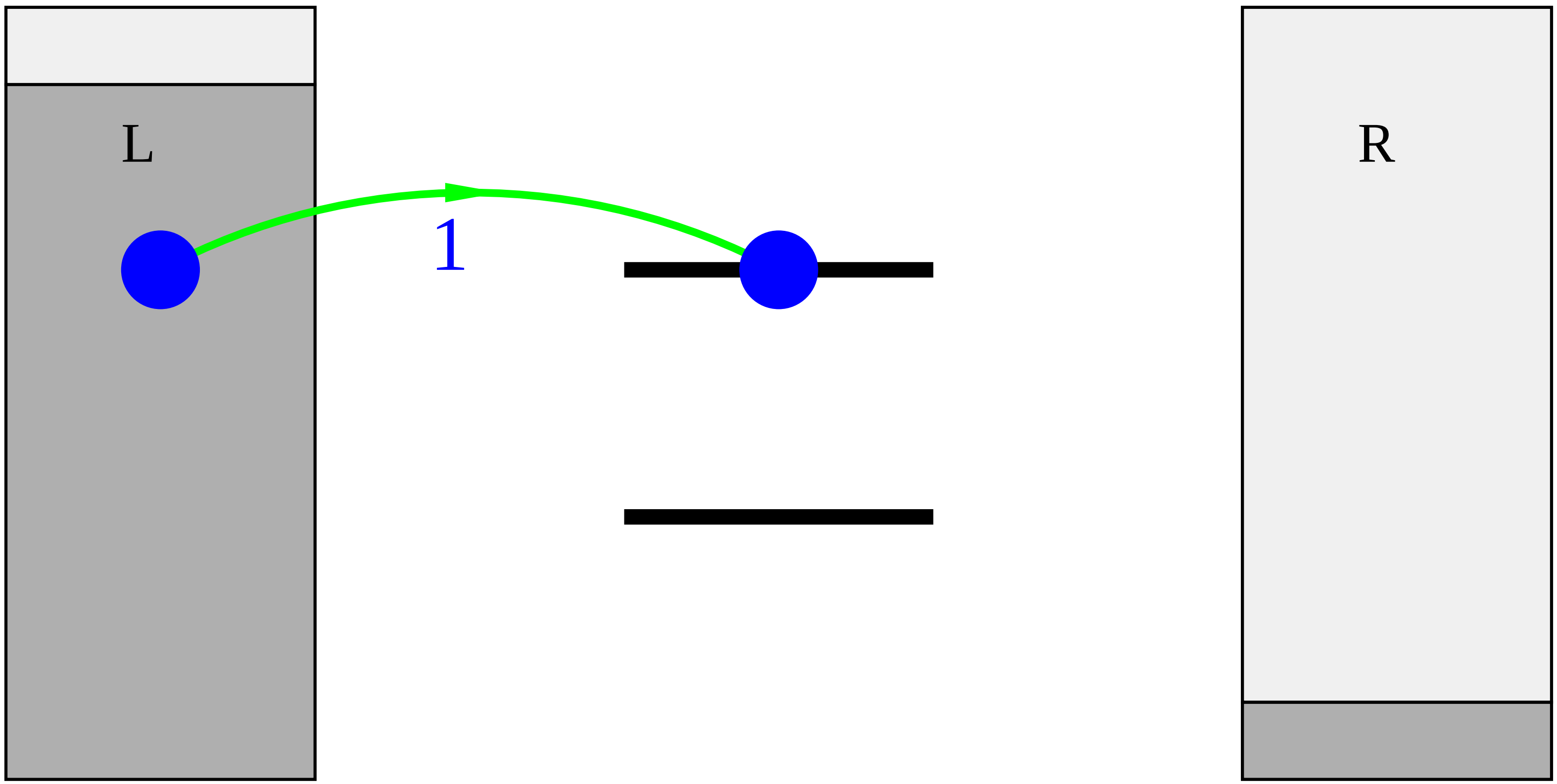
For strong bias (e.g. $\mu_R \ll \varepsilon_1 < \varepsilon_2 \ll \mu_L$)

$$I_{sd}^{L} = \frac{e}{\hbar} \sum_{m=1,2} \frac{\Gamma_m^{(ML)} \Gamma_m^{(MR)}}{\Gamma_m} \mathrm{sgn}(\mu_L - \mu_R)$$

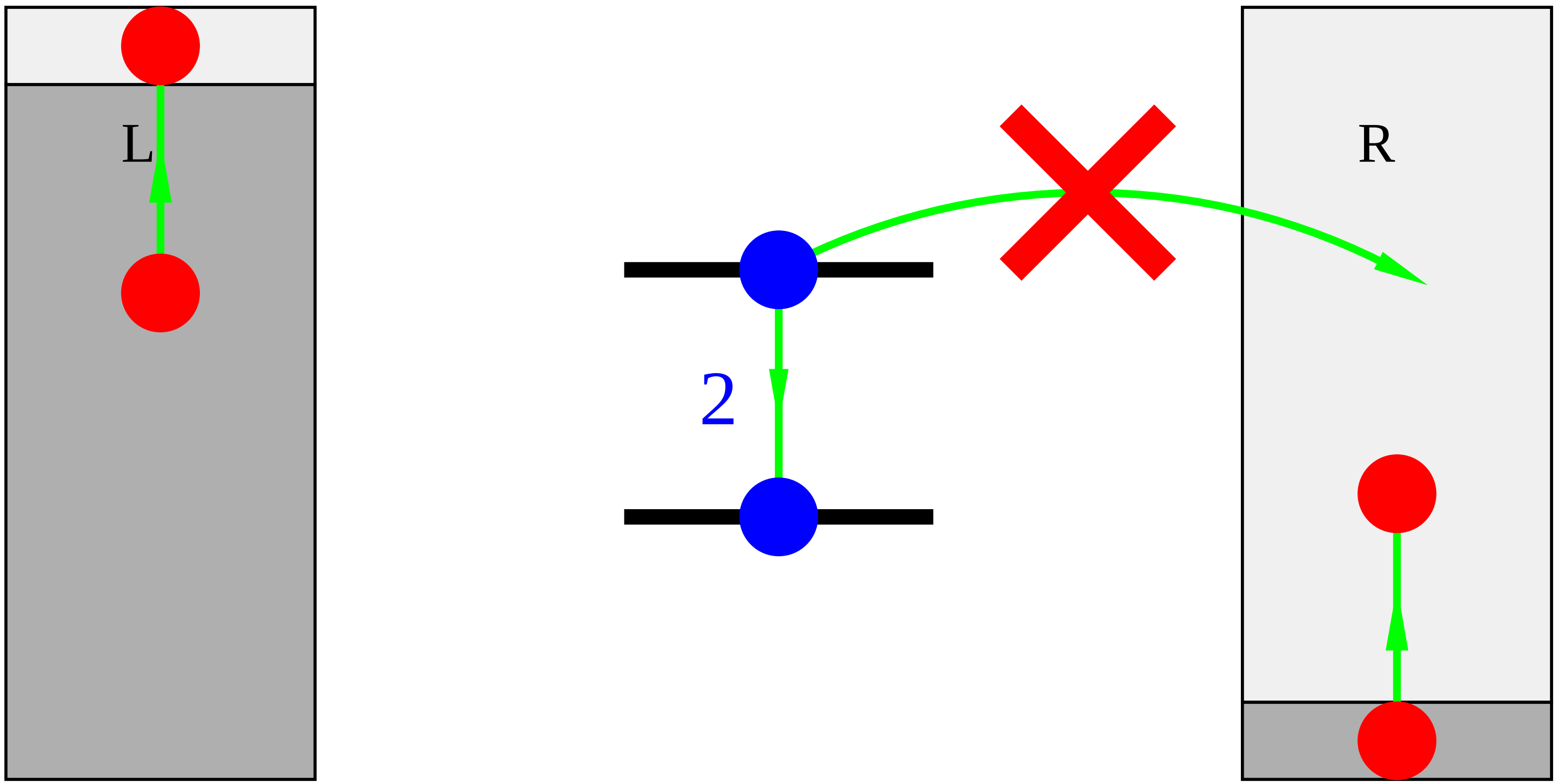
$$I_{sd}^{e-h} = \frac{e}{\hbar} B \times$$

$$\left[\frac{\Gamma_2^{(ML)} \Gamma_1^{(MR)}}{\Gamma_1 \Gamma_2} \theta(\mu_L - \mu_R) - \frac{\Gamma_1^{(ML)} \Gamma_2^{(MR)}}{\Gamma_1 \Gamma_2} \theta(\mu_R - \mu_L) \right]$$

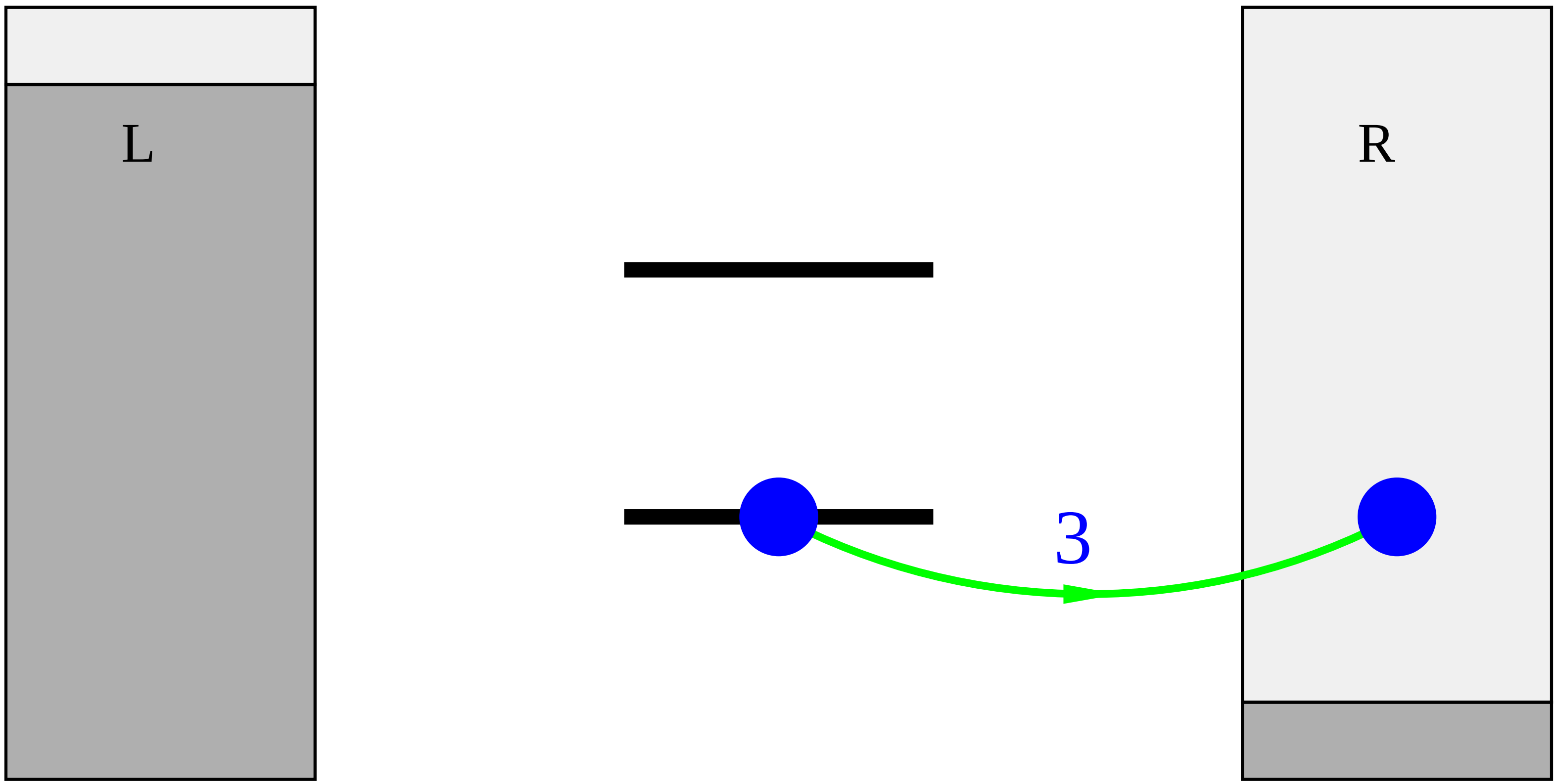
Current from e-h excitations



Current from e-h excitations



Current from e-h excitations



Current from e-h excitations

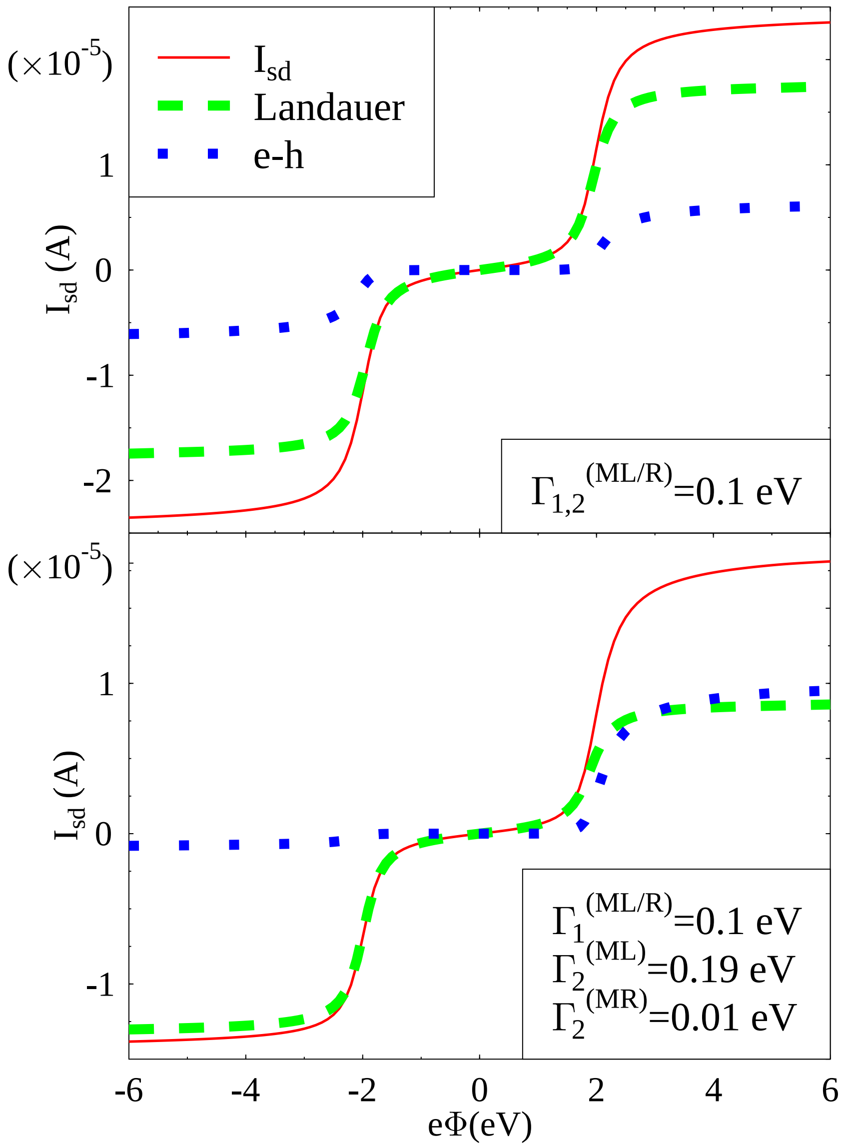
Molecules with strong charge-transfer transitions

- DMEANS (4-Dimethylamino-4'-nitrostilbene)
  7D (ground) $\rightarrow$ 31D (first excited singlet)
- all-trans Retinal in Poly-methyl methacrylate films
  6.6D $\rightarrow$ 19.8D (^1B_u electronic state)
- 40Å $CdSe$ nanocrystals 0D $\rightarrow$ 32D (first excited state)

If charge transfer is parallel to the wire axis

e-h excitation $\rightarrow$ charge flow

Current from e-h excitations



$T = 300$ K

$\varepsilon_1 = 0$ eV

$\varepsilon_2 = 2$ eV

$\Gamma_{1,2}^{(M)} = 0.2$ eV

in asymmetric case e-h is significant

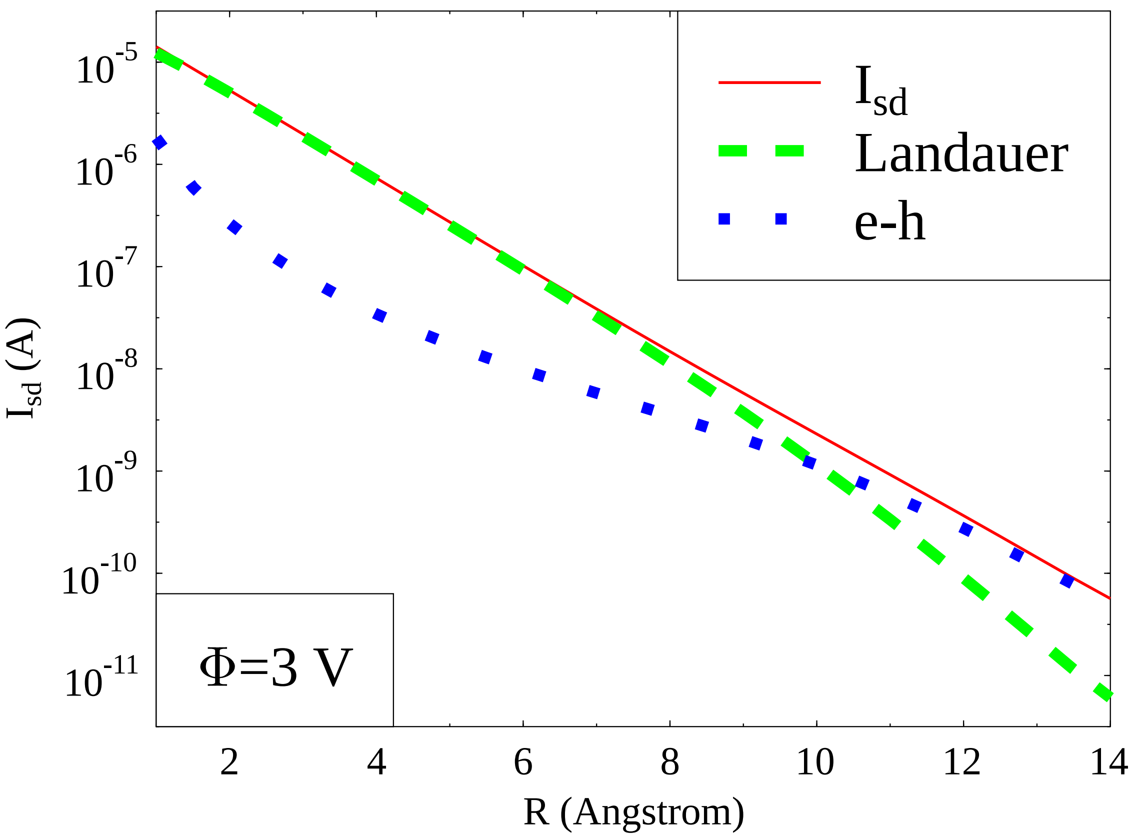
Current from e-h excitations

Distance dependence

$$\Gamma_m^{(MK)} = A_m^{(MK)} \exp\left[-\alpha_m^{(MK)} R\right]$$

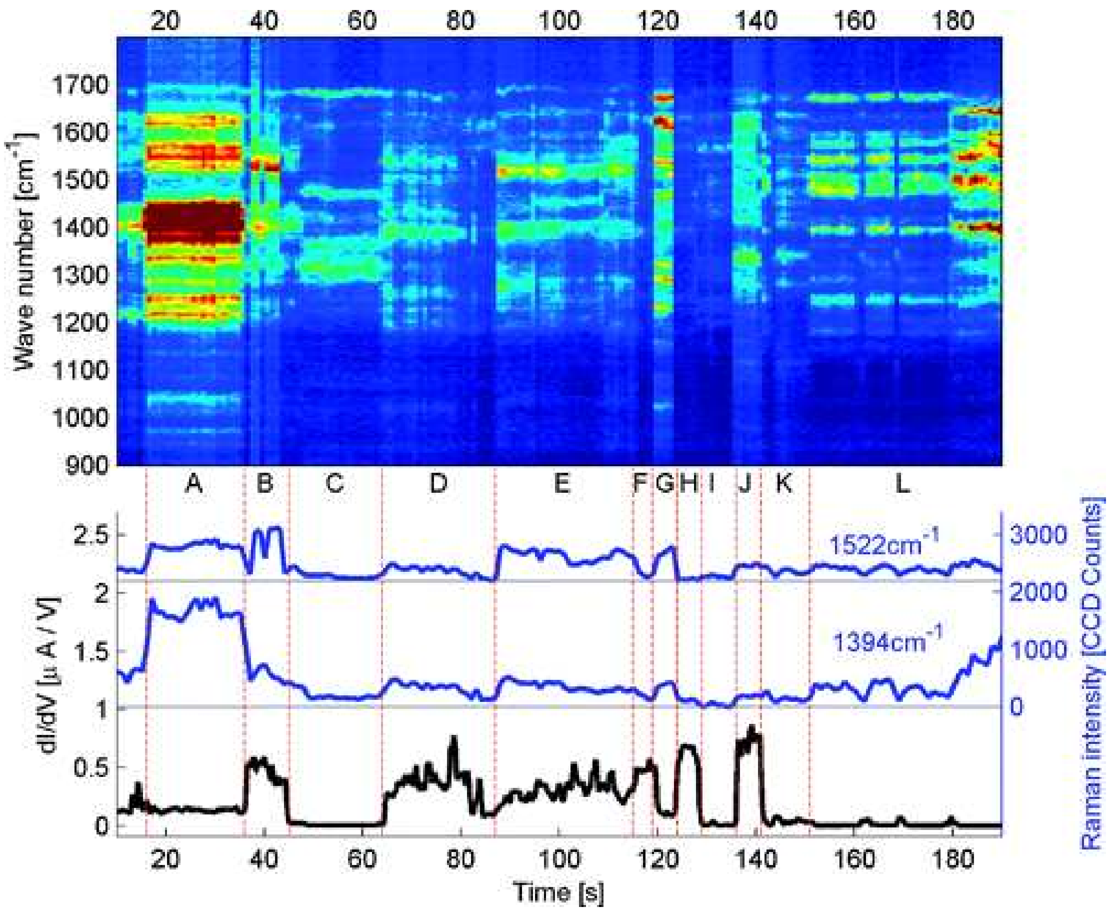
$$B^{(K)} = \beta^{(K)}/R^3$$

Current from e-h excitations



$$A_1^{(ML/R)} = 0.27 \text{ eV}$$
$$A_2^{(ML)} = 0.52 \text{ eV}$$
$$A_2^{(MR)} = 0.027 \text{ eV}$$
$$\alpha_m^{(MK)} = 1 \text{ Å}^{-1}$$
$$\beta^{(K)} = 0.01 \text{ eV}$$

Raman Spectroscopy



D.R.Ward et al. *Nano Lett.* **8**, 919 (2008)

Model

$$\hat{H} = \hat{H}_0 + \hat{V}^{(e-v)} + \hat{V}^{(et)} + \hat{V}^{(v-b)} + \hat{V}^{(e-h)} + \hat{V}^{(e-p)}$$

- $\hat{V}^{(e-v)}$ electron-vibration interaction
- $\hat{V}^{(et)}$ electron transfer
- $\hat{V}^{(v-b)}$ thermalization of vibration
- $\hat{V}^{(e-h)}$ energy transfer
- $\hat{V}^{(e-p)}$ coupling to radiation field

Nano Lett. **9**, 758 (2009); *J. Chem. Phys.* **130**, 144109 (2009)

Model

$$\hat{H}_0 = \sum_{m=1,2} \varepsilon_m \hat{d}_m^\dagger \hat{d}_m + \omega_v \hat{b}_v^\dagger \hat{b}_v + \sum_{k\in L,R} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k$$

$$+ \sum_\beta \omega_\beta \hat{b}_\beta^\dagger \hat{b}_\beta + \sum_\alpha \nu_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha$$

$$\hat{V}^{(e-v)} = \sum_{m=1,2} V_m^{(e-v)} \hat{Q}_v \hat{d}_m^\dagger \hat{d}_m$$

$$\hat{V}^{(et)} = \sum_{K=L,R} \sum_{k\in K;m} \left(V_{km}^{(et)} \hat{c}_k^\dagger \hat{d}_m + V_{mk}^{(et)} \hat{d}_m^\dagger \hat{c}_k \right)$$

$$\hat{V}^{(v-b)} = \sum_\beta U_\beta^{(v-b)} \hat{Q}_v \hat{Q}_\beta$$

$$\hat{V}^{(e-h)} = \sum_{k_1\neq k_2} \left(V_{k_1 k_2}^{(e-h)} \hat{d}_1^\dagger \hat{d}_2 \hat{c}_{k_1}^\dagger \hat{c}_{k_2} + \text{H.c.} \right)$$

Model

Coupling to the laser field

$$\hat{V}^{(e-p)} = \sum_{\alpha} \left[U_{\alpha}^{(e-p)} \hat{d}_1^{\dagger} \hat{d}_2 \hat{a}_{\alpha} + \overset{*}{U}{}_{\alpha}^{(e-p)} \hat{a}_{\alpha}^{\dagger} \hat{d}_2^{\dagger} \hat{d}_1 \right]$$

$$+ \sum_{\alpha} \sum_{k \in \{L,R\}} \sum_{m=1,2} \left[V_{km}^{\alpha} \hat{c}_k^{\dagger} \hat{d}_m + V_{mk}^{\alpha} \hat{d}_m^{\dagger} \hat{c}_k \right]$$

$$\times \left(\hat{a}_{\alpha} + \hat{a}_{\alpha}^{\dagger} \right)$$

Model

Introducing excitation operators

$$\hat{D} \equiv \hat{d}_1^\dagger \hat{d}_2 \quad \hat{D}_{mk} \equiv \hat{d}_m^\dagger \hat{c}_k \quad m = 1, 2 \; k \in \{L, R\}$$

and after small polaron transformation

$$\hat{V}^{(e-p)} = \sum_\alpha \left\{ \hat{a}_\alpha^\dagger \hat{O}_\alpha + \hat{O}_\alpha^\dagger \hat{a}_\alpha \right\}$$

$$\hat{O}_\alpha = \overset{*}{U}{}_\alpha^{(e-p)} \hat{D} \hat{X}$$

$$+ \sum_{k \in \{L,R\}} \left[V_{1k}^\alpha \hat{D}_{1k} \hat{X}_1^\dagger + V_{k2}^\alpha \hat{D}_{k2} \hat{X}_2 + V_{k1}^\alpha \hat{D}_{k1} \hat{X}_1 + V_{2k}^\alpha \hat{D}_{2k} \hat{X}_2^\dagger \right]$$

$$\equiv \hat{O}_\alpha^{(M)} + \hat{O}_\alpha^{(1)} + \hat{O}_\alpha^{(2)} + \hat{O}_\alpha^{(3)} + \hat{O}_\alpha^{(4)}$$

Raman flux

Photon flux from mode α into the system

$$J_\alpha(t) \equiv -\frac{d}{dt} < \hat{a}^\dagger_\alpha(t)\hat{a}_\alpha(t) >$$

$$= -\int_{-\infty}^{t} dt' \, [F^<_\alpha(t,t')\,\mathcal{G}^>_\alpha(t',t) + \mathcal{G}^>_\alpha(t,t')\,F^<_\alpha(t',t)$$

$$-F^>_\alpha(t,t')\,\mathcal{G}^<_\alpha(t',t) - \mathcal{G}^<_\alpha(t,t')\,F^>_\alpha(t',t)]$$

$$F_\alpha(\tau,\tau') = -\,i < T_c\,\hat{a}_\alpha(\tau)\,\hat{a}^\dagger_\alpha(\tau') >$$

$$\mathcal{G}_\alpha(\tau,\tau') = -\,i < T_c\,\hat{O}_\alpha(\tau)\,\hat{O}^\dagger_\alpha(\tau') >$$

Raman flux

Scattering-theory on the Keldysh contour

- One pumping mode i
- Empty final modes $\{f\}$

Steady-state photon flux to a final mode f

$$J_f = \int_{-\infty}^{+\infty} d(t-t')\, F_f^{>}(t'-t)\, \mathcal{G}_f^{<}(t-t')$$

Raman flux

2^{nd} **order perturbation for** $\mathcal{G}_f^<(t-t')$

in coupling to the initial mode i

$$J_{i\to f} = \int_{-\infty}^{+\infty} d(t-t') \int_c d\tau_1 \int_c d\tau_2\, F_f^>(t'-t)\, F_i(\tau_1,\tau_2)$$
$$\times < T_c\, \hat{O}_f^\dagger(t')\, \hat{O}_f(t)\, \hat{O}_i^\dagger(\tau_1)\, \hat{O}_i(\tau_2) >$$

we have $5^4 = 625$ channels *(different $\hat{O}$)*

we have $3 \times 3 = 9$ diagrams *(positions of t_1 and t_2)*

Raman flux

Choice of diagrams on the Keldysh contour

- i is pumping mode populated by one photon

$$F_i^{<}(t_1 - t_2) = -ie^{-i\nu_i(t_1 - t_2)}$$

- f are accepting modes not populated

$$F_f^{>}(t' - t) = -ie^{-i\nu_f(t' - t)}$$

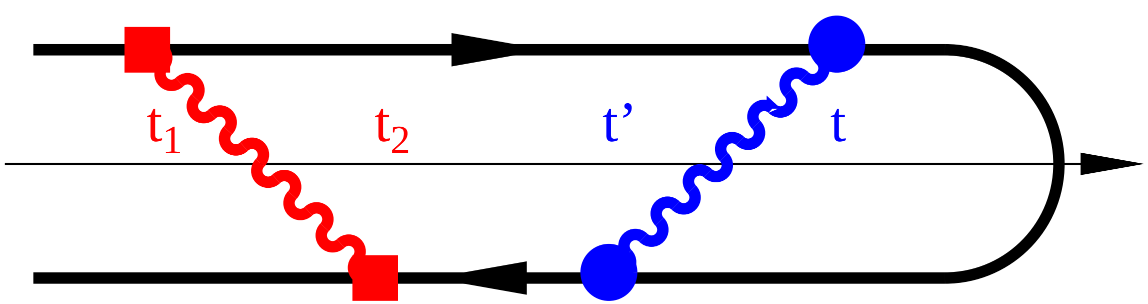
- **only rates are of interest**

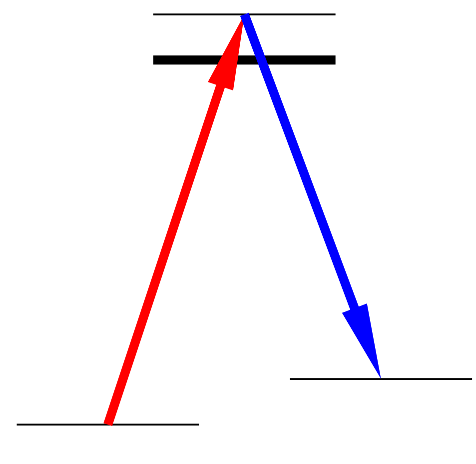
Raman flux

$$J_{i\to f}^{(nR)} = \int_{-\infty}^{+\infty} d(t-t') \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t'} dt_2$$

$$e^{-i\nu_i(t_1-t_2)}\, e^{i\nu_f(t-t')}$$

$$< \hat{O}_i(t_2)\, \hat{O}_f^\dagger(t')\, \hat{O}_f(t)\, \hat{O}_i^\dagger(t_1) >$$



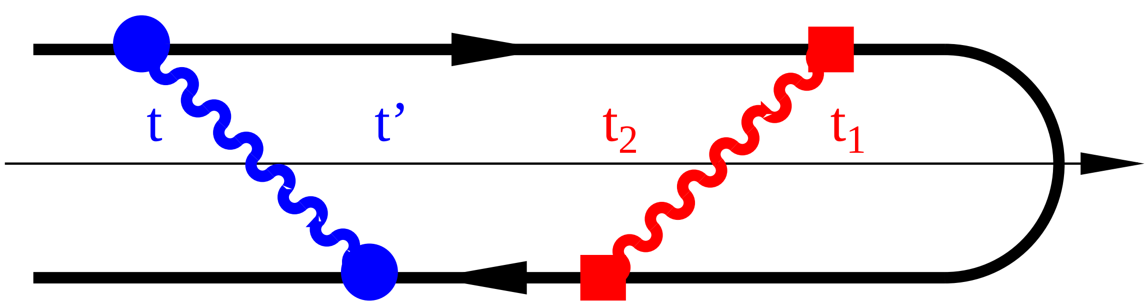


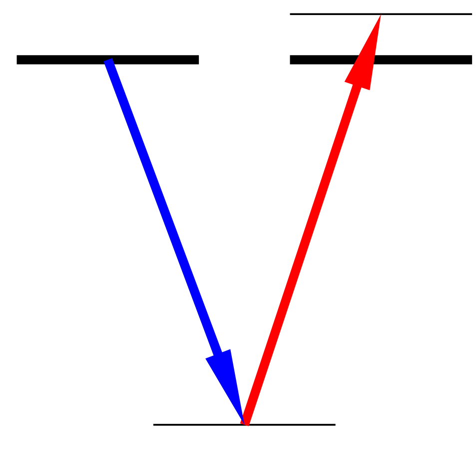
Raman flux

$$J^{(iR)}_{i\to f} = \int_{-\infty}^{+\infty} d(t-t') \int_{t}^{+\infty} dt_1 \int_{t'}^{+\infty} dt_2$$

$$e^{-i\nu_i(t_1-t_2)}\, e^{i\nu_f(t-t')}$$

$$< \hat{O}_f^\dagger(t')\, \hat{O}_i(t_2)\, \hat{O}_i^\dagger(t_1)\, \hat{O}_f(t) >$$



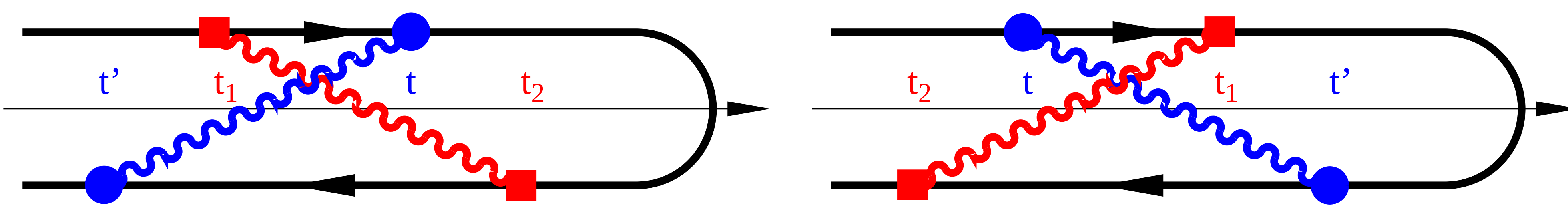


Raman flux

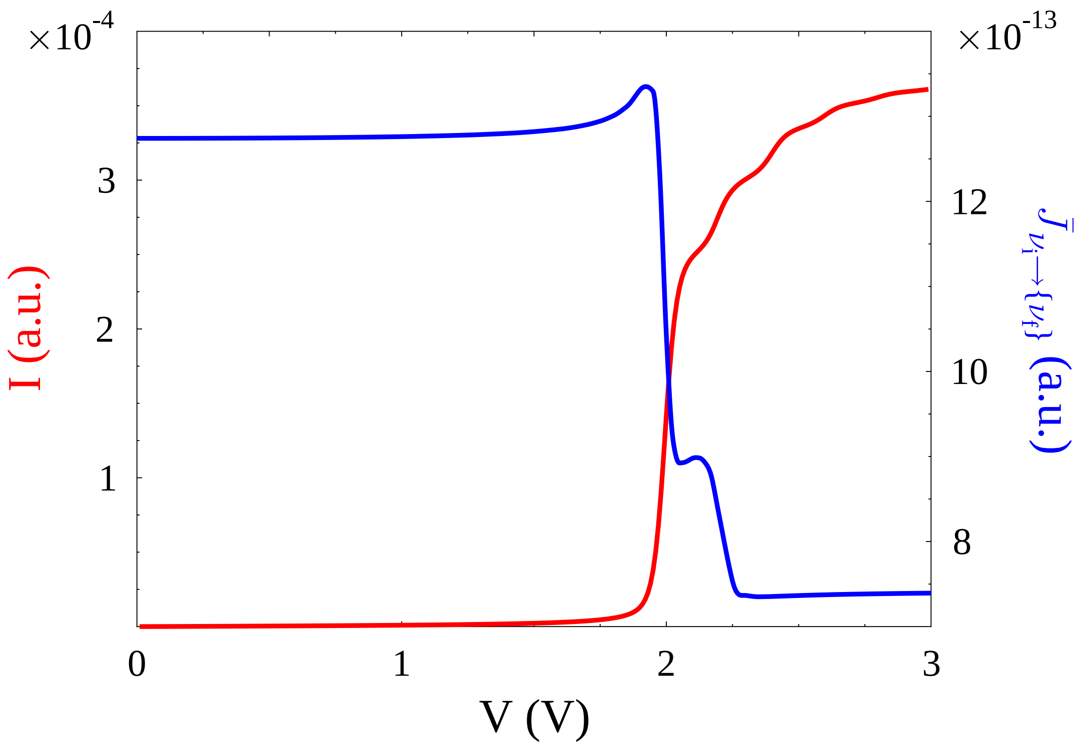
$$J^{(intR)}_{i\to f} = \int_{-\infty}^{+\infty} d(t-t') \int_{-\infty}^{t} dt_1 \int_{t'}^{+\infty} dt_2$$

$$2\mathrm{Re}\left[e^{-i\nu_i(t_1-t_2)}\, e^{i\nu_f(t-t')} \right.$$

$$\left. < \hat{O}^{\dagger}_{f}(t')\, \hat{O}_i(t_2)\, \hat{O}_f(t)\, \hat{O}^{\dagger}_{i}(t_1) > \right]$$



Molecular Raman



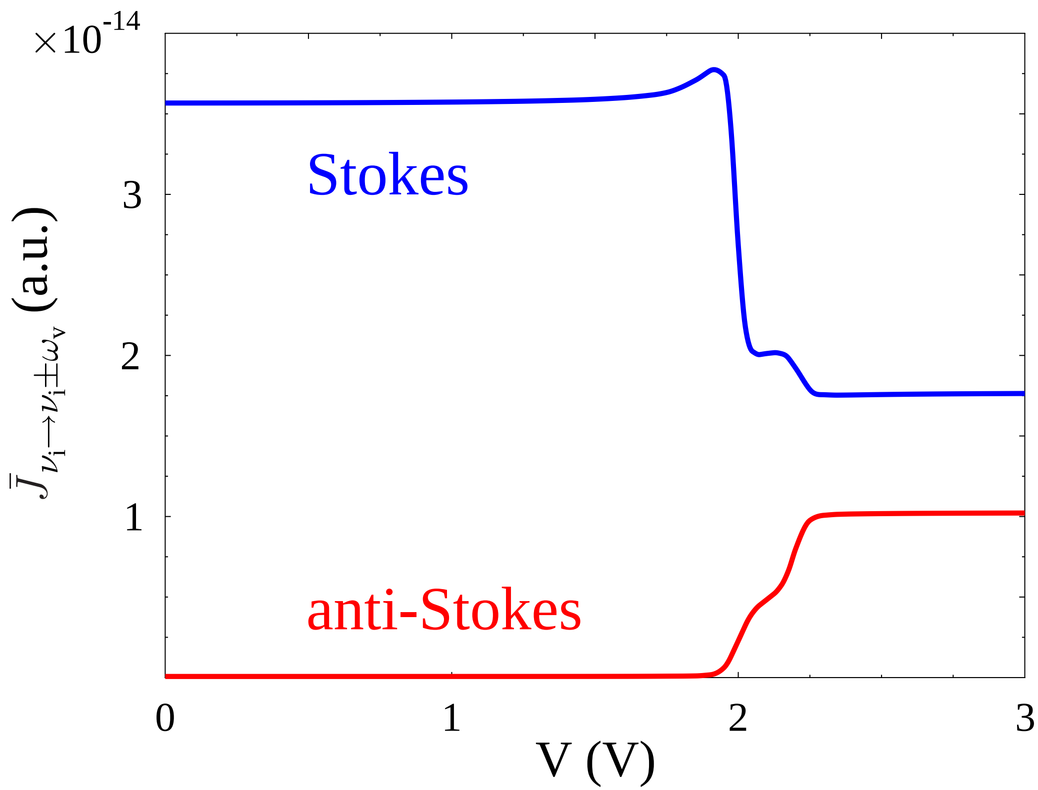
$\epsilon_2 - \epsilon_1 = 2$ eV

normal Raman $\sim n_1(1 - n_2) \Rightarrow 1 \rightarrow \frac{1}{4}$

inverse Raman $\sim n_2(1 - n_1) \Rightarrow 0 \rightarrow \frac{1}{4}$

total Raman $1 \rightarrow \frac{1}{2}$

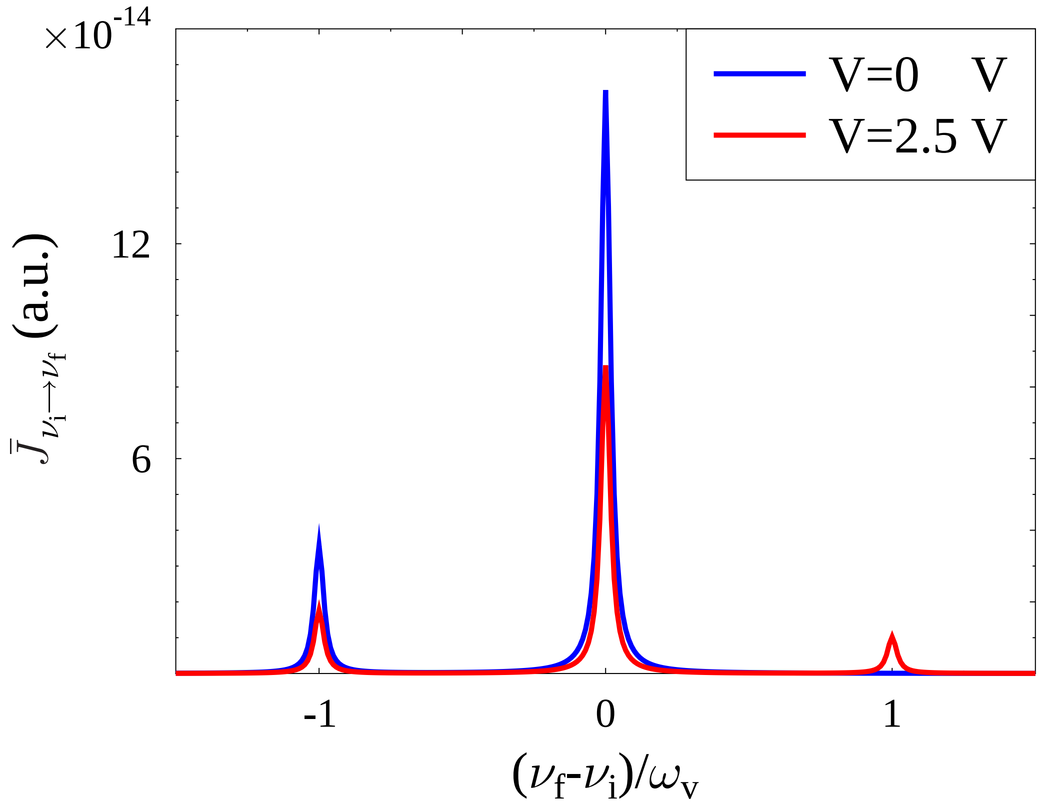
Molecular Raman



$\epsilon_2 - \epsilon_1 = 2$ eV

junction heating $\rightarrow$ increase in anti-Stokes

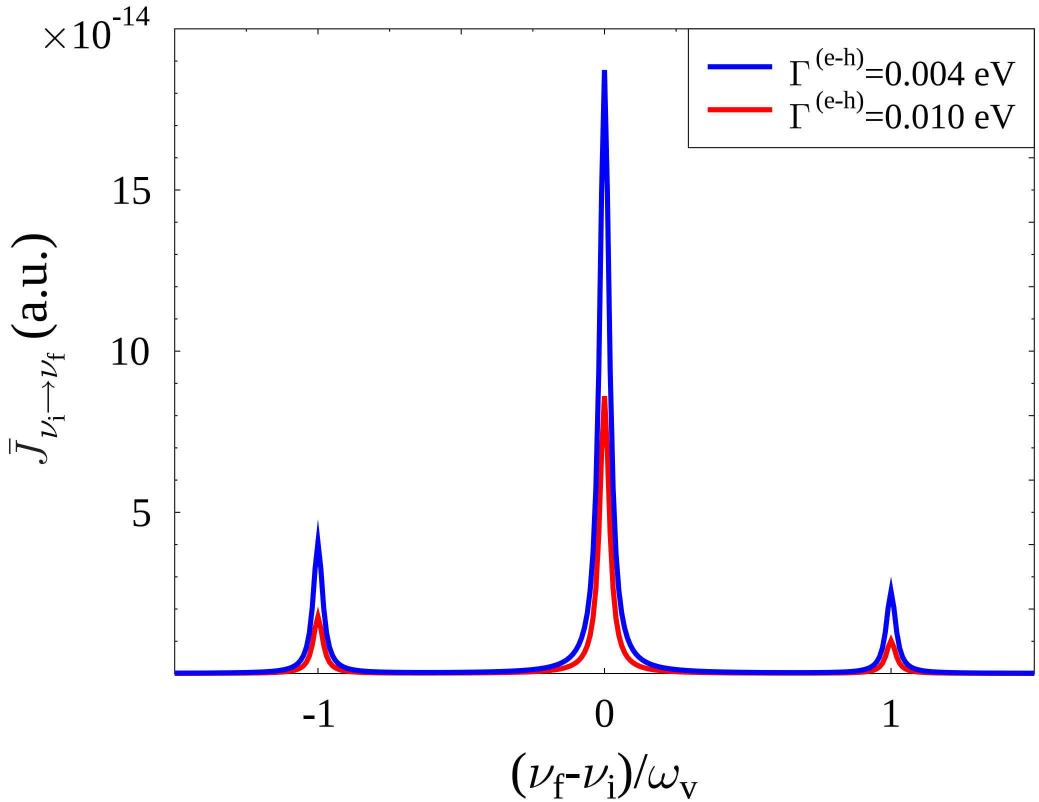
Molecular Raman



$$\epsilon_2 - \epsilon_1 = 2 \text{ eV}$$

$$\nu_i = \epsilon_2 - \epsilon_1$$

Molecular Raman

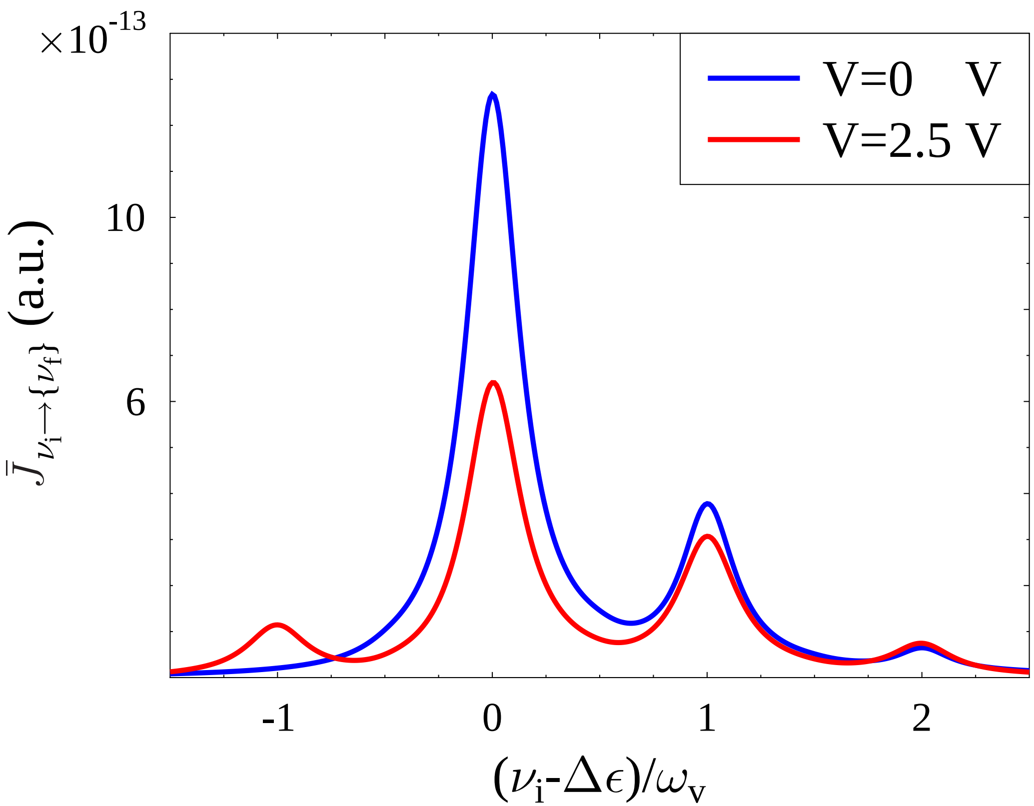


$$\epsilon_2 - \epsilon_1 = 2 \text{ eV}$$

$$\nu_i = \epsilon_2 - \epsilon_1$$

e-h excitations compete with Raman

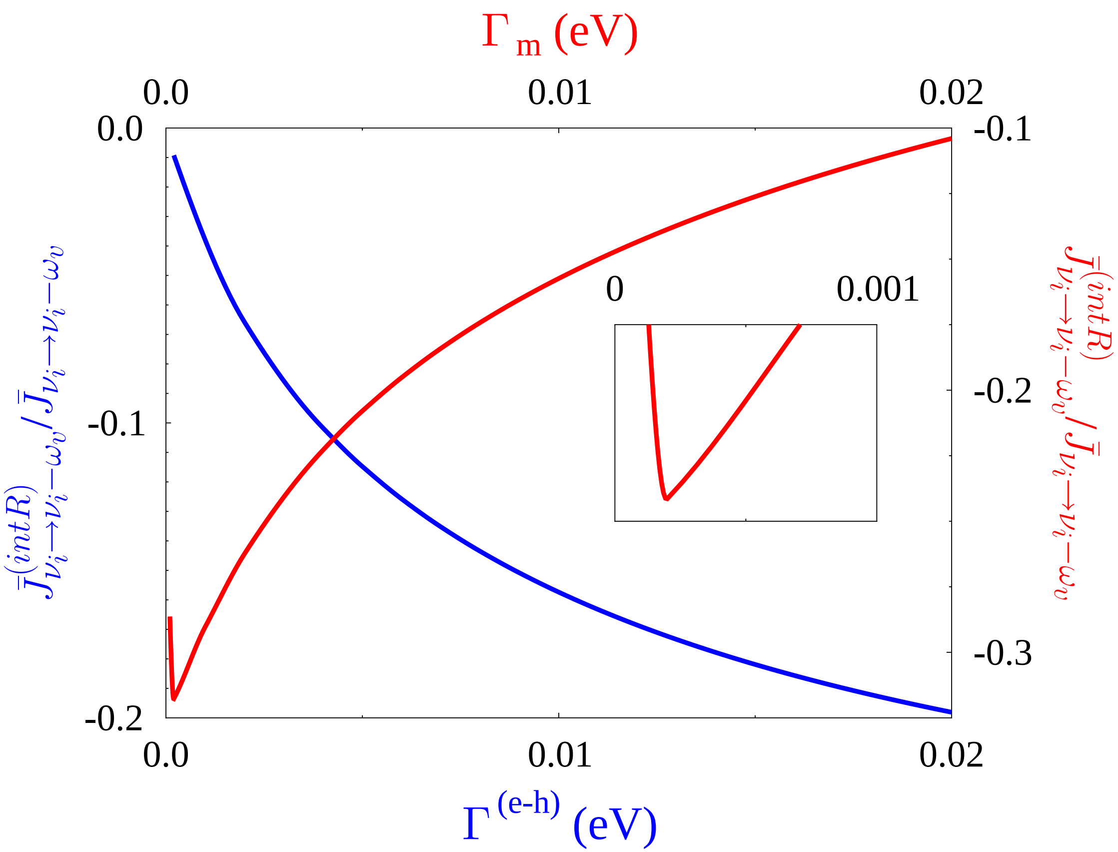
Molecular Raman



$\epsilon_2 - \epsilon_1 = 2$ eV

heating $\longrightarrow$ anti-Stokes

Molecular Raman

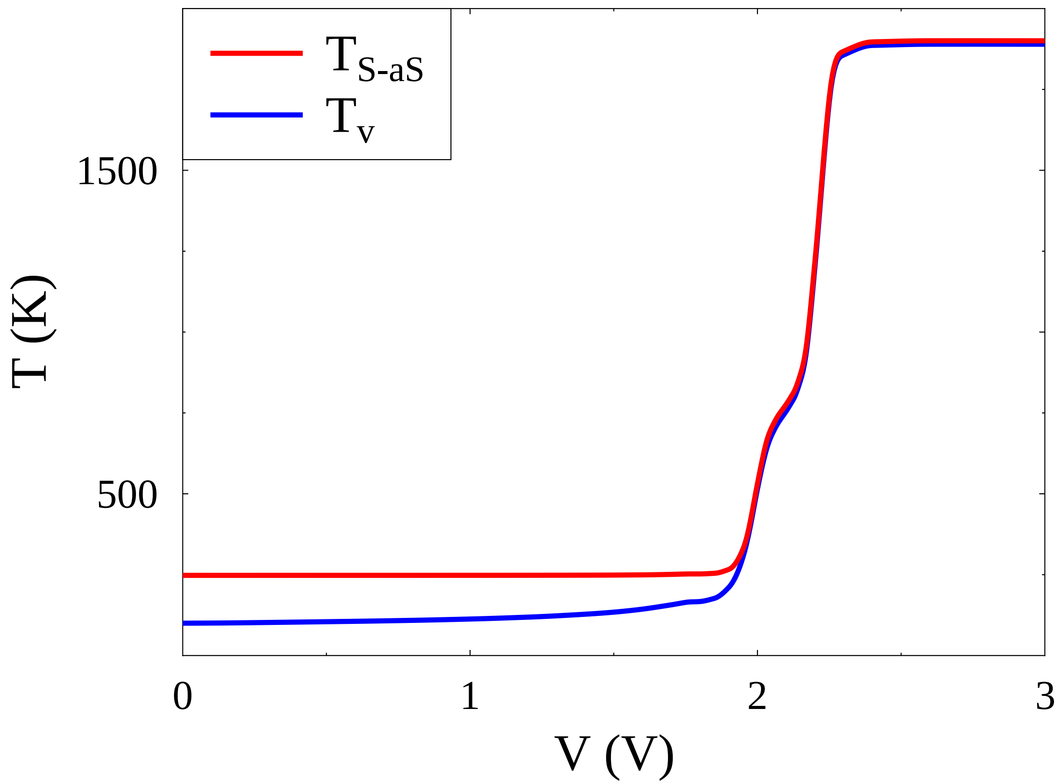


$$\nu_f = \nu_i - \omega_v$$

2 slits experiment?

$\Gamma^{(e-h)}$ is responsible for switching

Molecular Raman

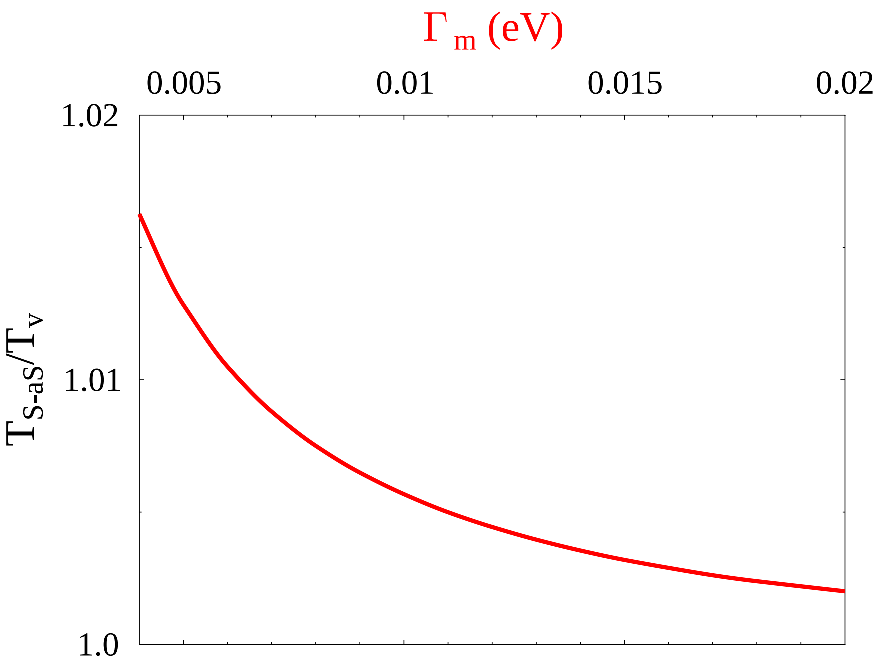


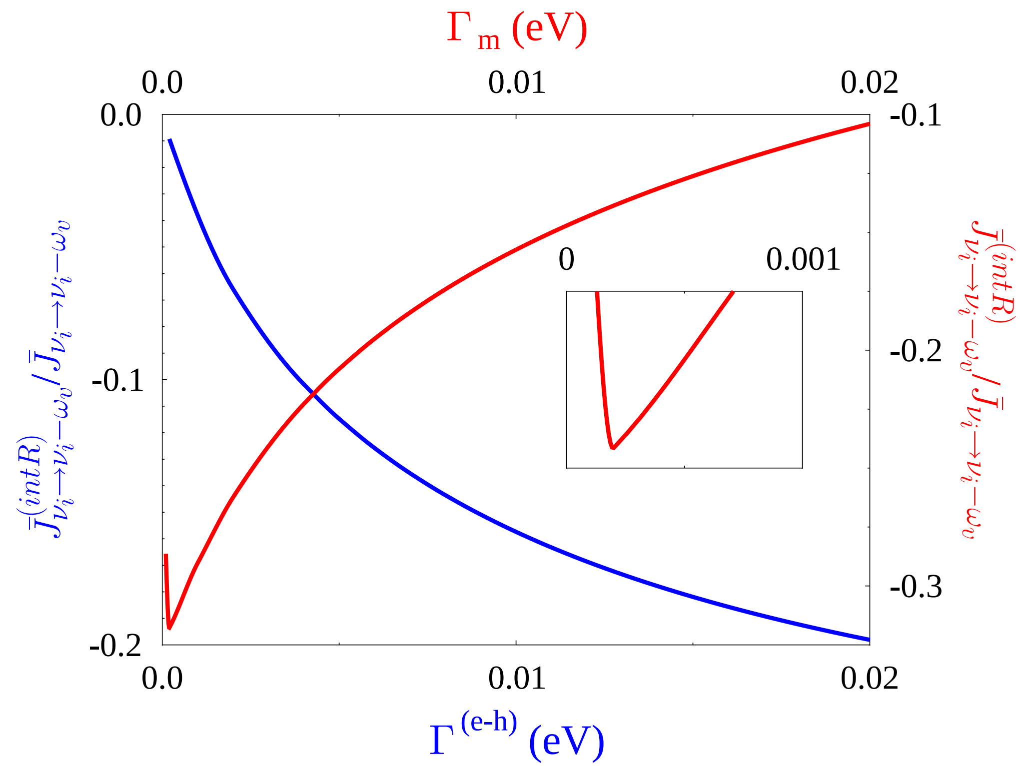
$$T_{S-aS} =$$

$$\omega_v / \ln \frac{\bar{J}_{\nu_i \to \nu_i - \omega_v}}{\bar{J}_{\nu_i \to \nu_i + \omega_v}}$$

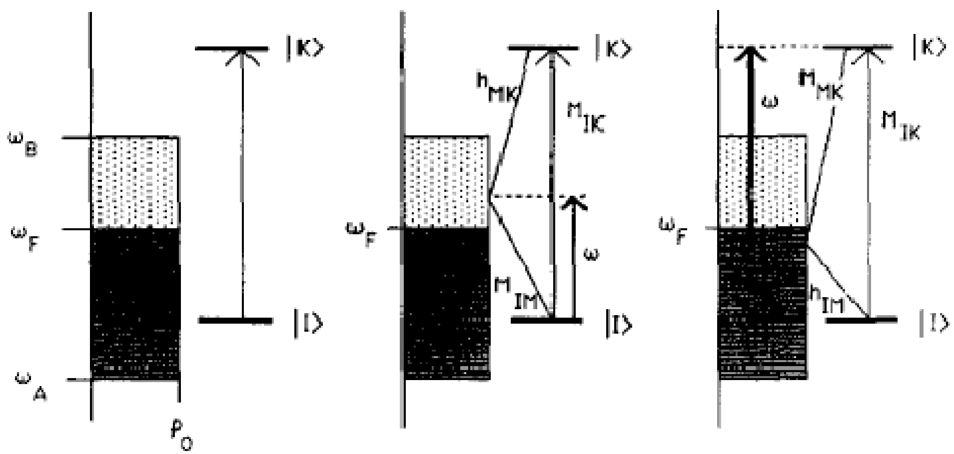
at low V anti-Stokes disappears

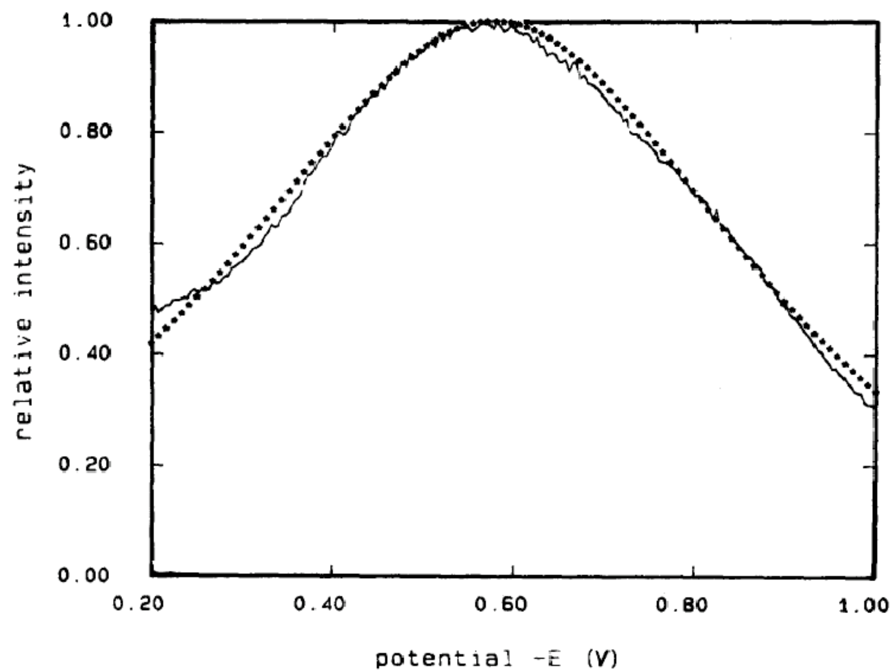
Molecular Raman





Metal-to-Molecule





J.R.Lombardi et al. JCP **84**, 4174 (1986)

Metal-to-Molecule

Origin of the (metal-to-molecule) peak

$$\int \frac{dE_1}{2\pi} \int \frac{dE_2}{2\pi} \sum_{K=L,R} \frac{S_2^{(K)<}(E_1)\, G_2^{>}(E_2)}{\nu_i + E_1 + \omega_v v_{in} - E_2 - \omega_v v' + i\Gamma^{(e-h)}/2}$$

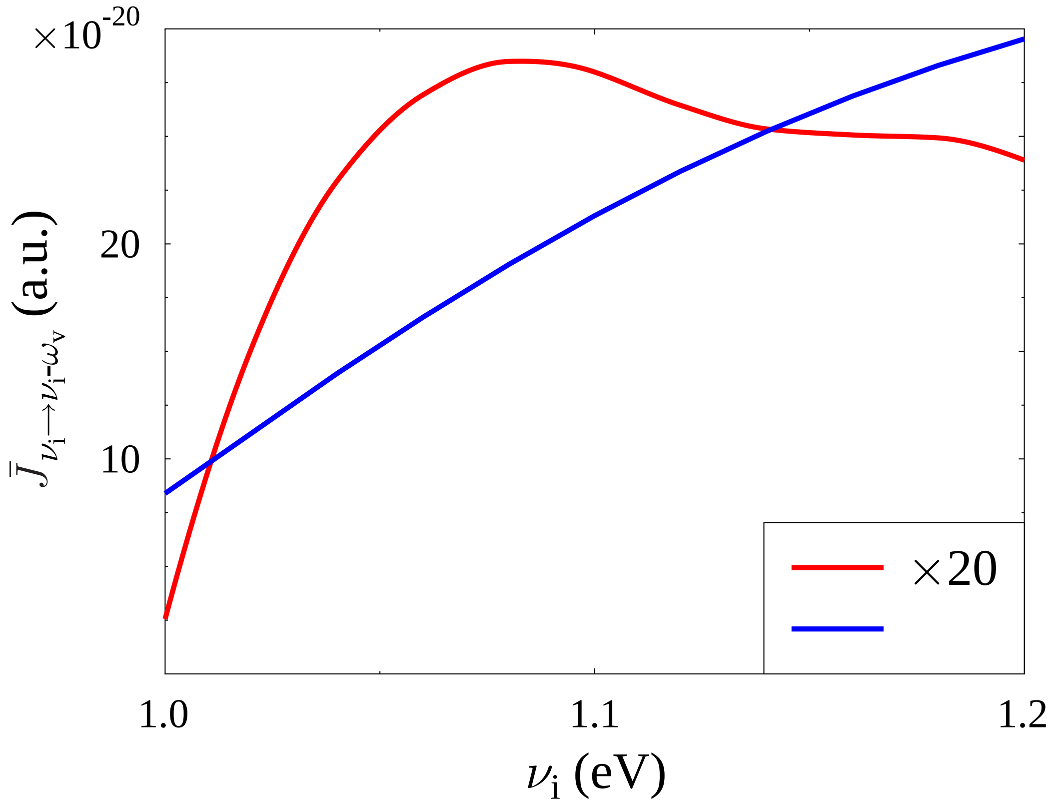
At $\mu_L = \mu_R = E_F$ and for $T \to 0$ integral on E_1 yields

$$\ln \frac{\sqrt{\left(E_F - E_2 + \omega_v(v_{in} - v') + \nu_i\right)^2 + \left(\Gamma^{(e-h)}/2\right)^2}}{D}$$

where D is leads half-bandwidth. This gives a peak at

$$\nu_i = E_2 - E_F - \omega_v(v_{in} - v')$$

Metal-to-Molecule

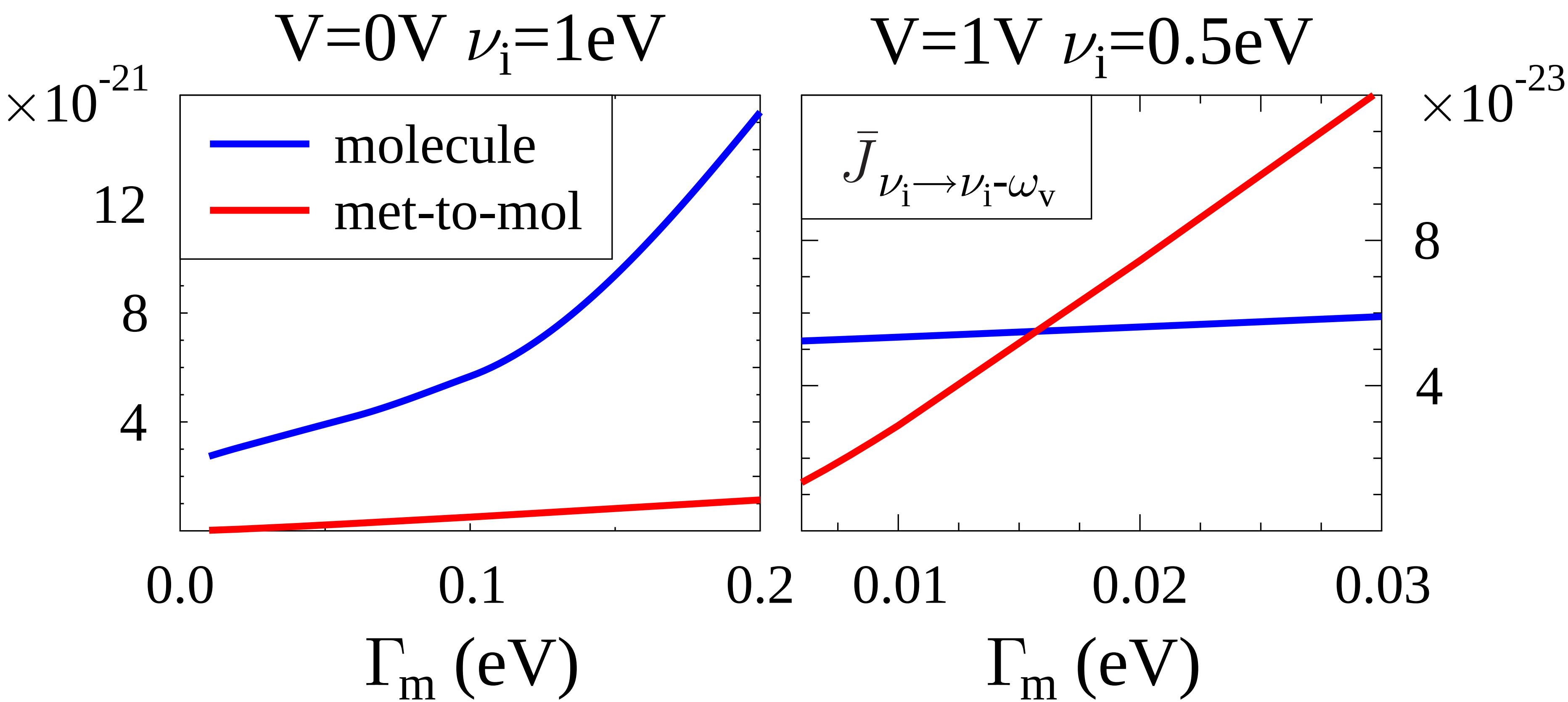


$\varepsilon_2 - E_F = 1$ eV

$\nu_f = \nu_i - \omega_v$

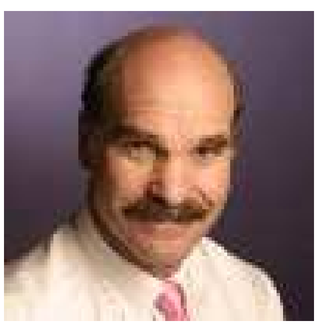
increase in Γ_2 eliminates the peak

Metal-to-Molecule



Thanks!

Prof. Abraham Nitzan
Tel Aviv University



Prof. Mark A. Ratner
Northwestern University

NORTHWESTERN UNIVERSITY

Thanks!

Thank You!

Funding:

UCSD Startup Fund

UC Academic Senate Research Grant