Laser–Induced Control of Condensed Phase Electron Transfer

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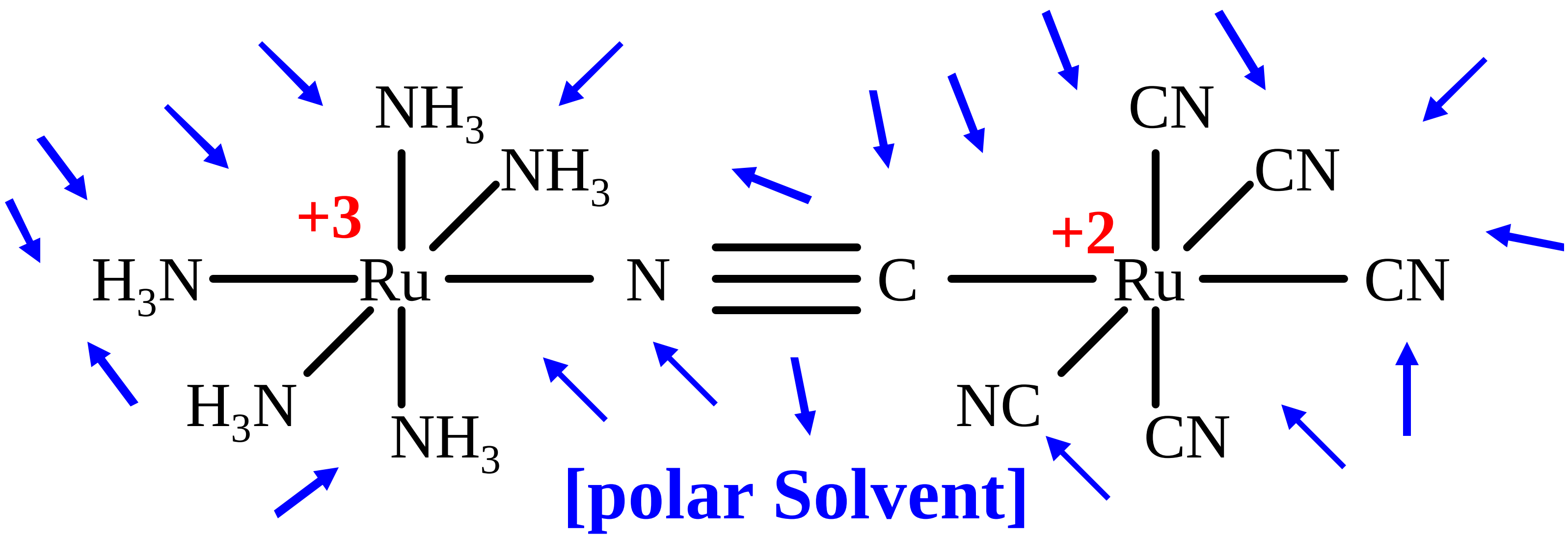
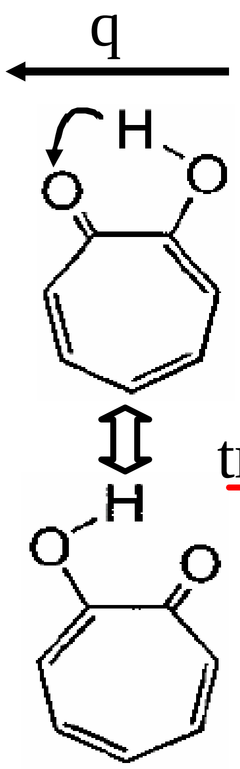
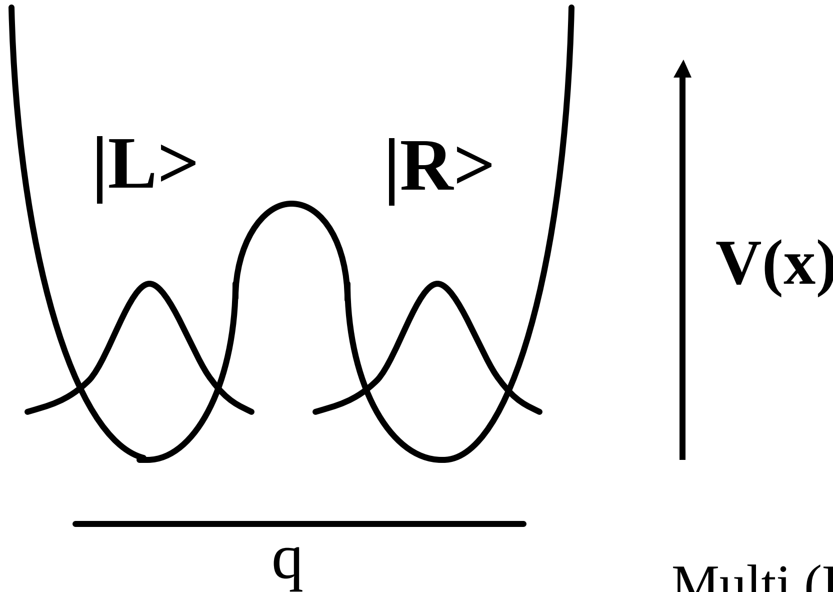


Tunneling in A 2-State System

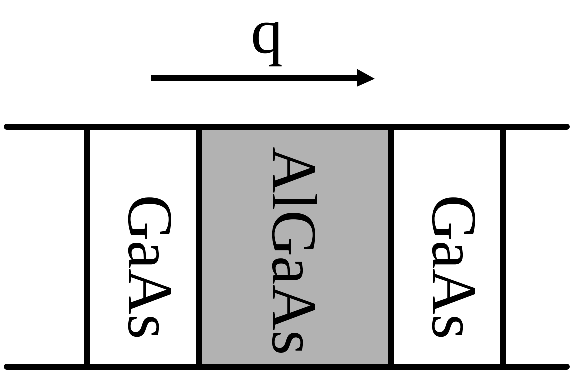


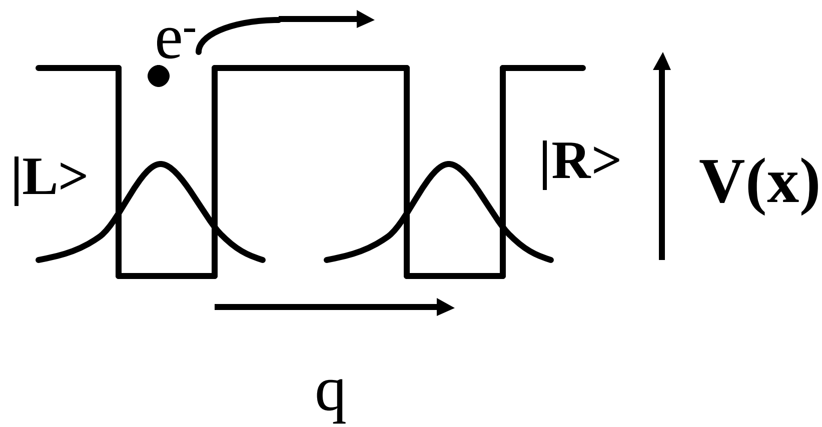
tropolone



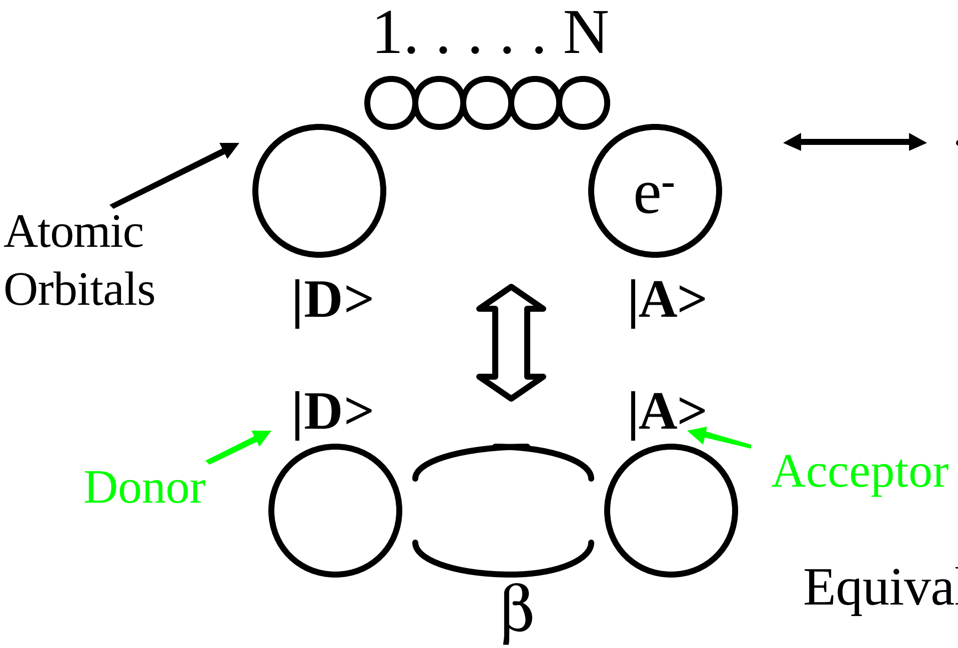
Proton Transfer

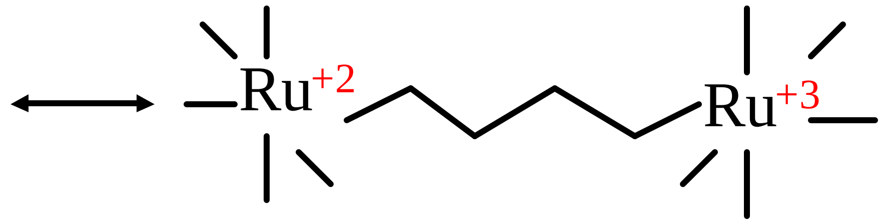
Multi (Double) Quantum Well Structure





Electron Transport In Solids





Molecular Electron Transfer

Equivalent 2-state model

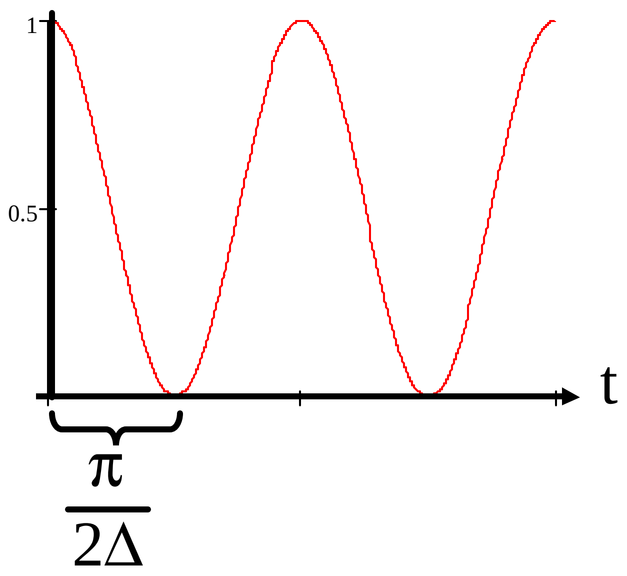
For any of these systems: $|\Psi(t)\rangle = c_D(t)\,|D\rangle + c_A(t)\,|A\rangle$

where $$\begin{pmatrix} H_{AA} & H_{AD} \\ H_{DA} & H_{DD} \end{pmatrix} \begin{pmatrix} c_A \\ c_D \end{pmatrix} = i\cancelto{1}{\hbar}\,\frac{d}{dt} \begin{pmatrix} c_A \\ c_D \end{pmatrix}$$

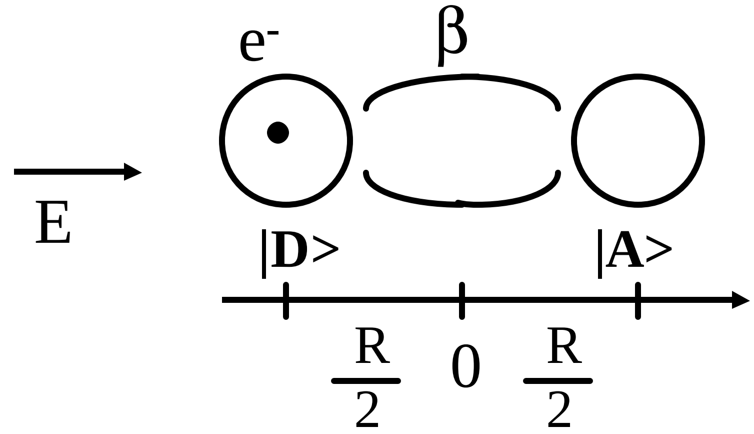
For a Symmetric Tunneling System: $H_{AA} = H_{DD} = 0$; $H_{AD} =$ $H_{AD} = \Delta\ (< 0)$

Given initial preparation in |D>, for a symmetric system:

$$P_D(t) = 1 - P_A(t) = \boxed{\cos^2(\Delta t)} =$$



Now, apply an electric field



Q: How does this modify the Hamiltonian??

A: It modifies the site energies according to " $-\vec{\mu} \cdot \vec{E}$ "

$$\text{Thus: } \left[\underset{\approx}{H}\right] = \begin{pmatrix} H_{AA} & \Delta \\ \Delta & H_{DD} \end{pmatrix} - E \begin{pmatrix} \overbrace{e_o R/2}^{\textbf{Permanent dipole moment of A}} & 0 \\ 0 & -e_o R/2 \end{pmatrix}$$

Analysis in the case of time-dependent $E(t) = E_o \cos\omega_o t$

Consider first the symmetric case:

$$i\frac{d}{dt}\begin{pmatrix} c_A \\ c_D \end{pmatrix} = \left[\begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} - \underset{\substack{\uparrow \\ \text{Permanent dipole moment difference}}}{\mu} E_o \cos\omega_o t \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \begin{pmatrix} c_A \\ c_D \end{pmatrix}$$

Letting: $c_A(t) = e^{\,i\ a \sin\omega_o t}\, c_A^I(t)$; $c_D(t) = e^{\,i\ a \sin\omega_o t}\, c_D^I(t)$

Where: $a = \dfrac{\mu E_o}{(\hbar)\omega_o}$ [**N.B.:** $\mu\int_0^t E_o \cos\omega_o t' dt' = \dfrac{\mu E_o}{\omega_o}\sin\omega_o t$]

Thus, Interaction Picture S.E. reads:

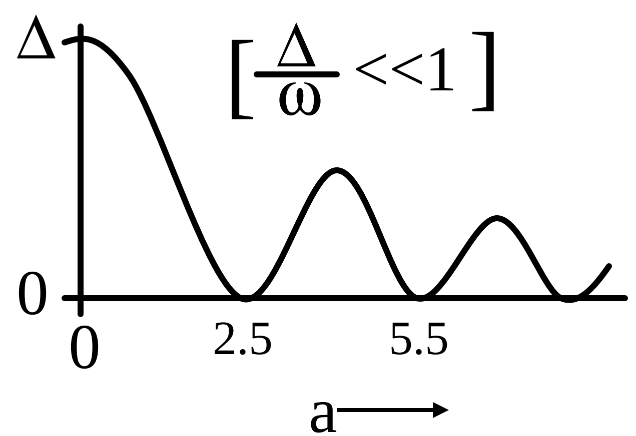
$$i\frac{d}{dt}\begin{pmatrix} c_A^I \\ c_D^I \end{pmatrix} = \begin{bmatrix} 0 & e^{-2i\ a \sin\omega_o t}\,\Delta \\ e^{2i\ a \sin\omega_o t}\,\Delta & 0 \end{bmatrix} \begin{pmatrix} c_A^I \\ c_D^I \end{pmatrix}$$

Now note: $e^{i\,b\sin\omega t} = \sum_{m=-\infty}^{\infty} J_m(b)\, e^{i\,m\omega t}$

So: $\Delta\, e^{2i\,a\sin\omega_o t} = \Delta \sum_{m=-\infty}^{\infty} J_m(2a)\, e^{i\,m\omega_o t}$

$$\underset{\underline{\underline{\text{RWA}}}}{\cong} \boxed{\Delta\cdot J_o(2a)} \quad , \quad \text{for } \Delta/\omega_o << 1$$

Thus, the shuttle frequency is renormalized to $\Delta\left|J_o(2a)\right|$



NB: Trapping or localization occurs at certain E_o values!

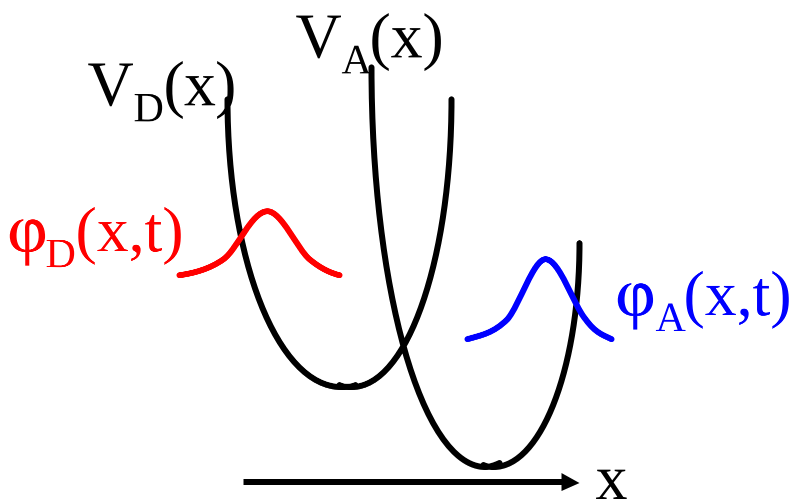
[Grossman - Hänggi, Dakhnovskii – Metiu]

Add coupling to a condensed phase environment

$$\hat{H} = \hat{T}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + \begin{bmatrix}V_D(x) & \Delta\\ \Delta & V_A(x)\end{bmatrix} - \underbrace{\mu E_o \cos\omega_o t \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}}_{\text{Field couples only to 2-level system}}$$

Nuclear coordinate kinetic energy

Nuclear coordinate

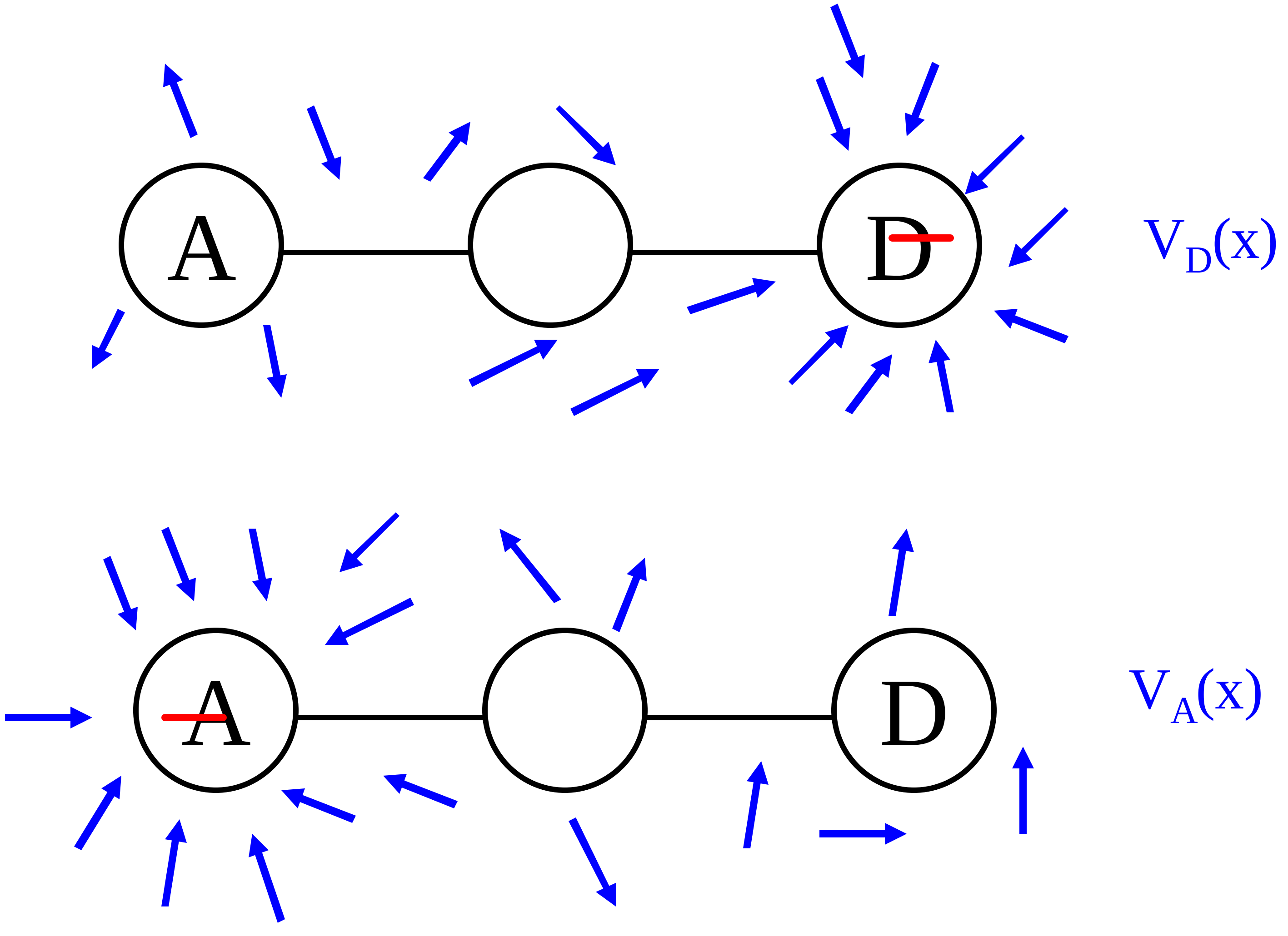


Now:

$$\left[\begin{pmatrix} T+V_D(x) & \Delta \\ \Delta & T+V_A(x) \end{pmatrix} - \mu E_o \cos\omega_o t \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] \begin{pmatrix} \varphi_D(x,t) \\ \varphi_A(x,t) \end{pmatrix}$$

$$= i\frac{d}{dt}\begin{pmatrix} \varphi_D(x,t) \\ \varphi_A(x,t) \end{pmatrix}$$

Construction of (Diabatic) Potential Energy functions for Polar ET Systems:



A few features of classical Nonadiabatic ET Theory [Marcus, Levich-Doganadze…]

$$\hat{H} = \begin{bmatrix} \hat{T}+V_1(x) & \Delta \\ \Delta & \hat{T}+V_2(x) \end{bmatrix}$$

Hamiltonian

non-adiabatic coupling matrix element

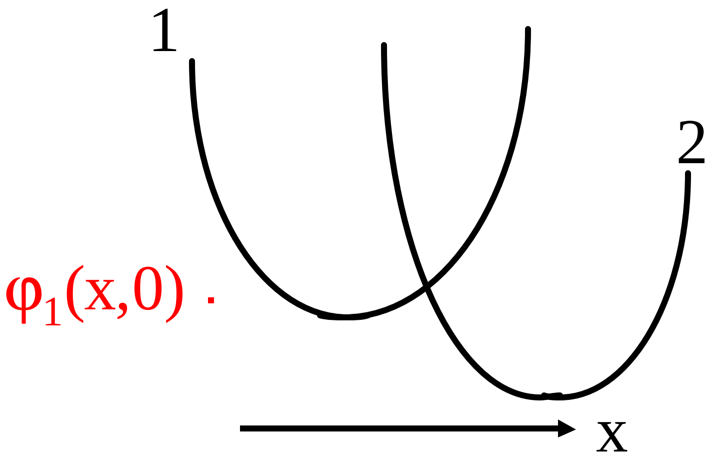
kinetic E of nuclear coordinates

(diabatic) nuclear coord. potential for electronic state 2

$$|\Psi(t)> = \begin{bmatrix} \varphi_1(x,t) \\ \varphi_2(x,t) \end{bmatrix}$$

States

Given initial preparation in electronic state 1 (and assuming nuclear coordinates are equilibrated on $V_1(x)$)



Then, $P_2(t)$ = fraction of molecules
in electronic state 2

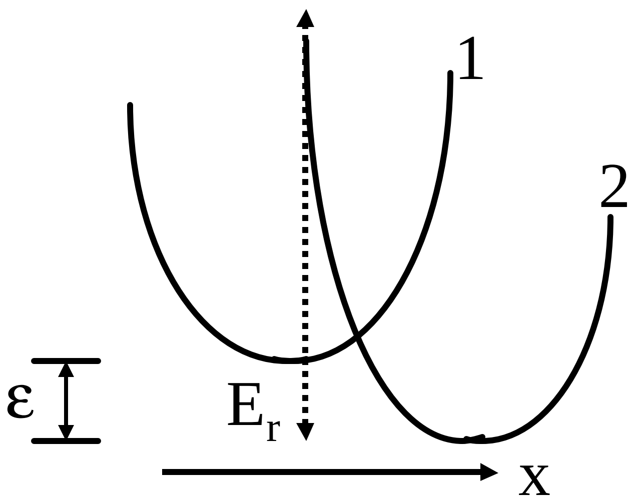
$$= \langle \varphi_2(x,t) | \varphi_2(x,t) \rangle \cong k_{1\to 2}t$$

where $k_{1\to 2}$ = (Golden Rule) rate constant

In classical Marcus (Levich-Doganadze) theory, $k_{1\rightarrow 2}$ is determined by 3 molecular parameters: $\boxed{\Delta, E_r, \varepsilon}$

$$k_{1\rightarrow 2} = \Delta^2 \left(\frac{\pi}{E_r kT}\right)^{1/2} e^{-(E_r - \varepsilon)^2/4E_r k_B T}$$

w/ E_r = “Reorganization Energy” ; e **= “Reaction Heat”**



For the “backwards” Reaction: $$k_{2\rightarrow 1} = \Delta^2 \left(\frac{\pi}{E_r kT}\right)^{1/2} e^{-(E_r + \varepsilon)^2/4E_r k_B T}$$

To obtain electronic state populations at arbitrary times, solve kinetic ["Master"] Eqns.:

$$dP_1(t)/dt = - k_{1\rightarrow 2}P_1(t) + k_{2\rightarrow 1}P_2(t)$$

$$dP_2(t)/dt = k_{1\rightarrow 2}P_1(t) - k_{2\rightarrow 1}P_2(t)$$

Note that long-time asymptotic ["Equilibrium"] distributions are then given by:

$$K_{eq} = \frac{P_2(\infty)}{P_1(\infty)} = \frac{k_{1\rightarrow 2}}{k_{2\rightarrow 1}} = e^{e/k_BT}$$

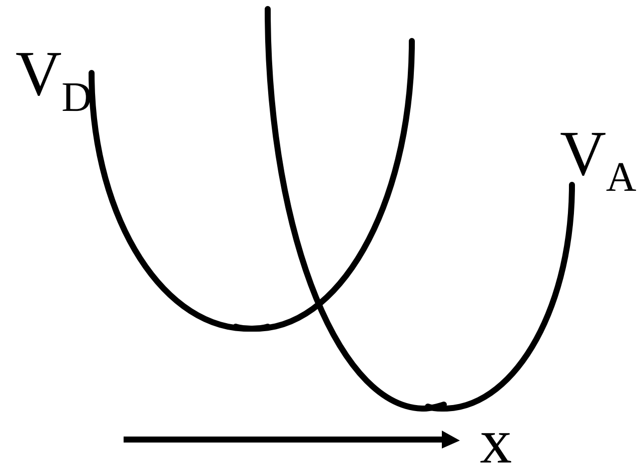
for Marcus formula rate constants

N.B. Marcus theory for nonadiabatic ET reactions works experimentally.

See: Closs & Miller, Science 240, 440 (1988)

Control of Rate Constants in Polar Electronic Transfer Reactions Via an Applied cw Electric Field

The Hamiltonian is:



$$\hat{H} = \begin{bmatrix} \hat{h}_D & 0 \\ 0 & \hat{h}_A \end{bmatrix} + \begin{bmatrix} 0 & \Delta \\ \Delta & 0 \end{bmatrix} + \mu_{12} E_o \cos\omega_o t \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

The forward rate constant is: [Y. Dakhnovskii, J. Chem. Phys. 100, 6492 (1994)

$$k_{D\rightarrow A} = \Delta^2 \sum_{m=-\infty}^{\infty} J_m^2(a) \cdot \frac{\mathrm{Re}}{\pi} \int_0^{\infty} dt\, e^{\,i\,\mathbf{mW_o t}}\ \mathrm{tr}\,\{\hat{\rho}_\beta^D\, e^{-i\,\hat{h}_A t}\, e^{\,i\,\hat{h}_D t}\}$$

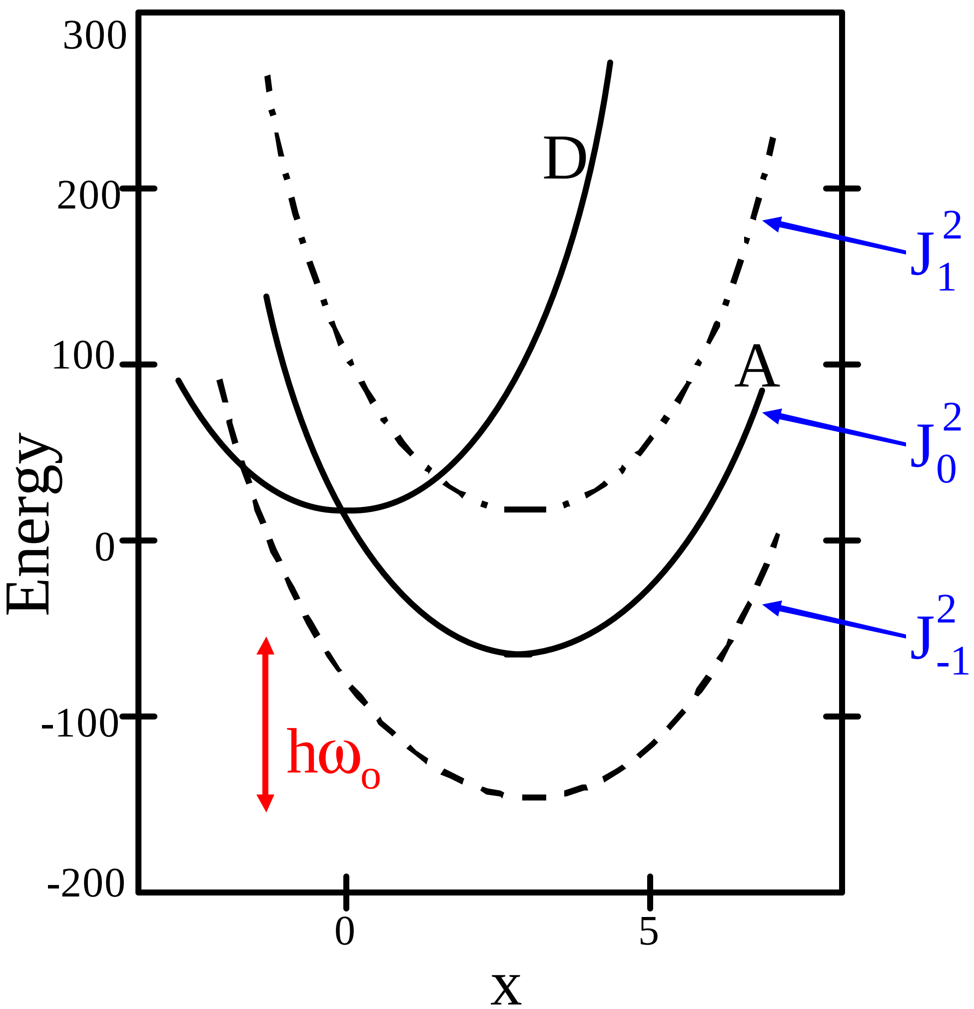
$$a = 2\,\mu_{12}\, E_o / h\omega_o$$

$$k_{\substack{D\rightarrow A \\ A\rightarrow D}} = \frac{\Delta^2}{4}\left(\frac{\pi}{E_r kT}\right)^{1/2} \sum_{m=-\infty}^{\infty} J_m^2(2\mu_{12}E_o/h\omega_o) \bullet$$

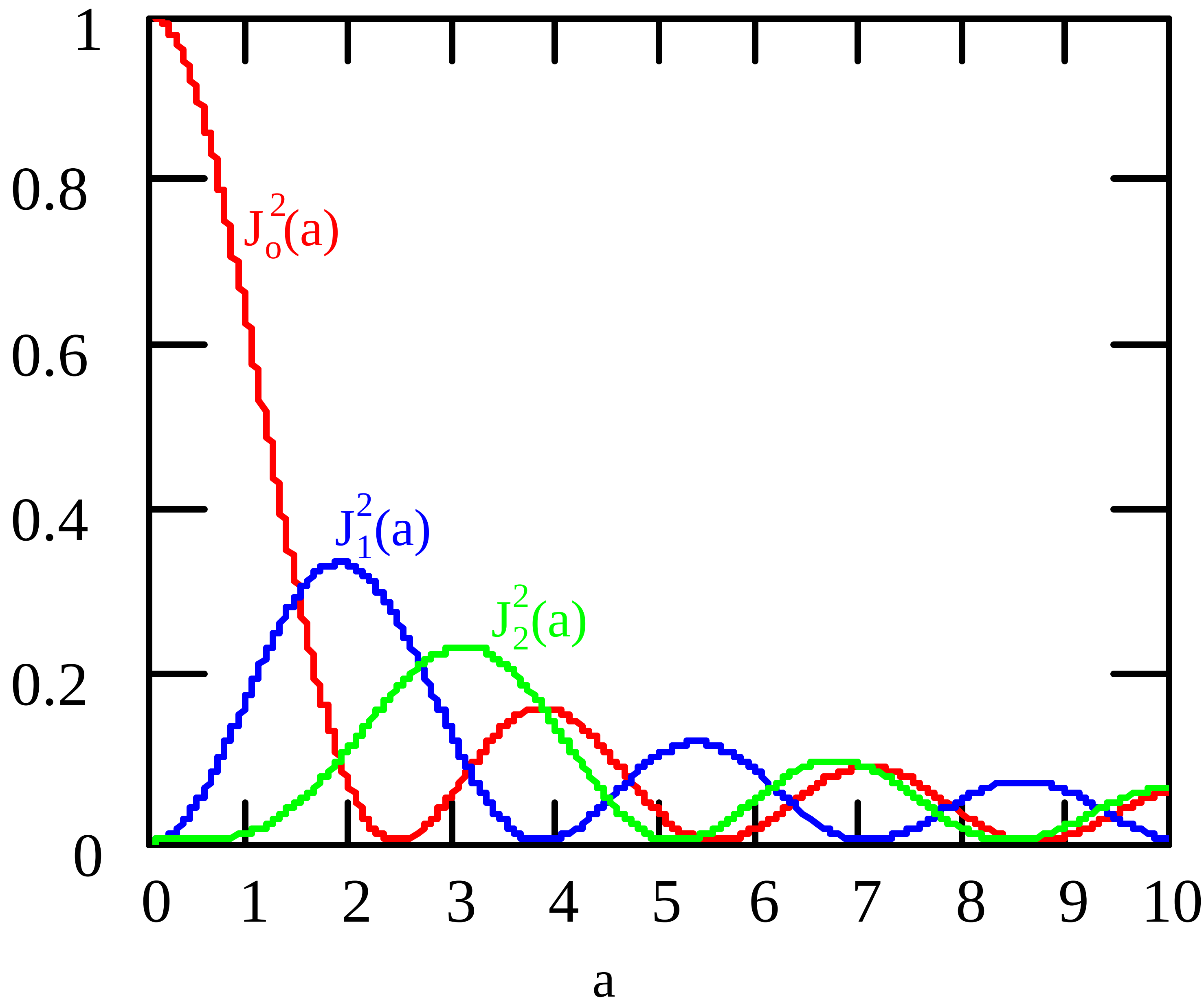
$$e^{-(E_r \pm \varepsilon + hm\omega_o)^2/4E_r k_B T}$$

Rate constants in presence of cw E-field

Schematically:



In polar electron transfer reactions, for
Reorganization Energy $E_r \cong h\omega_o$ (the quantum of applied laser field)

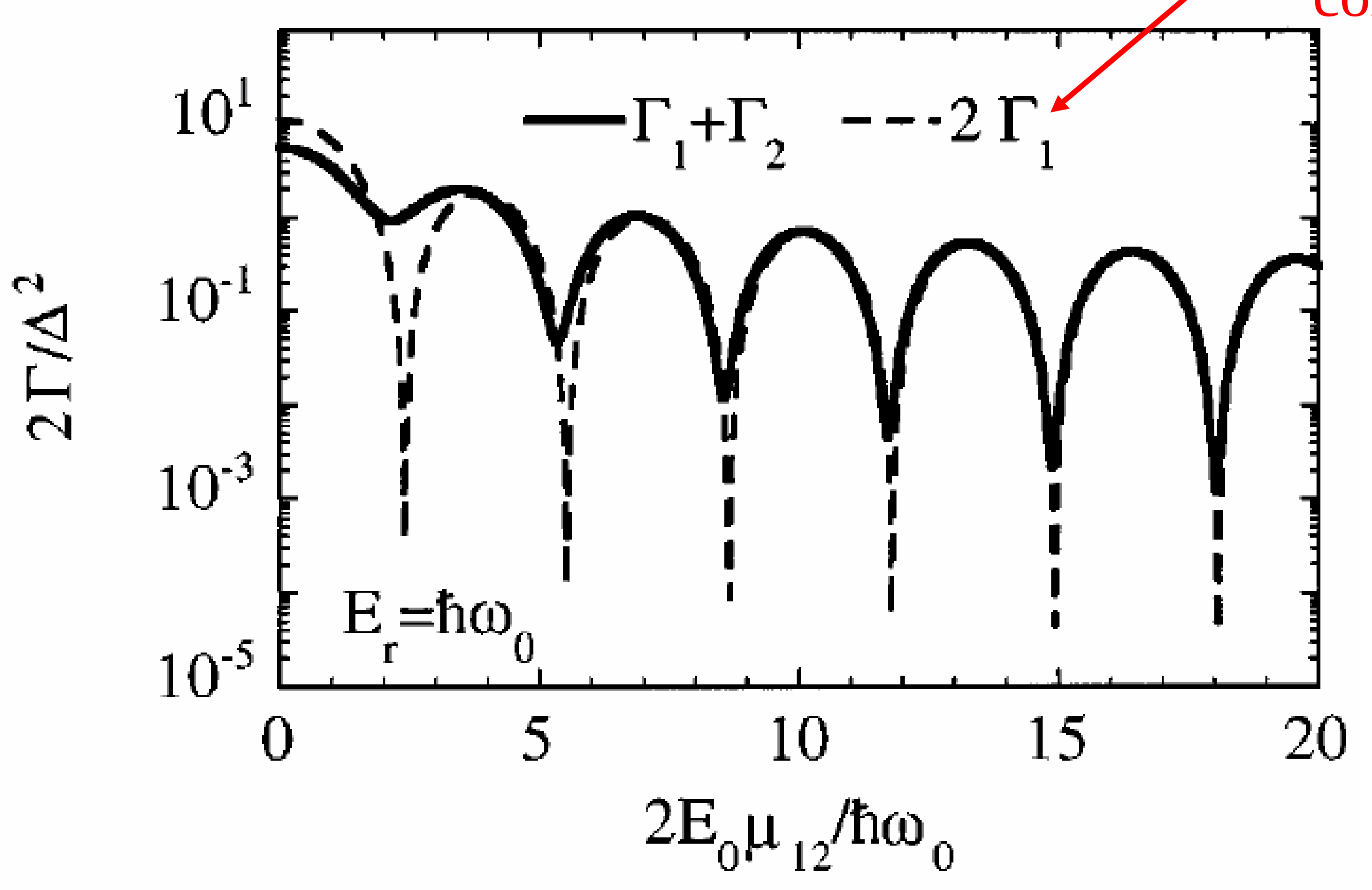


1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9
10
a
$J_o^2(a)$
$J_1^2(a)$
$J_2^2(a)$

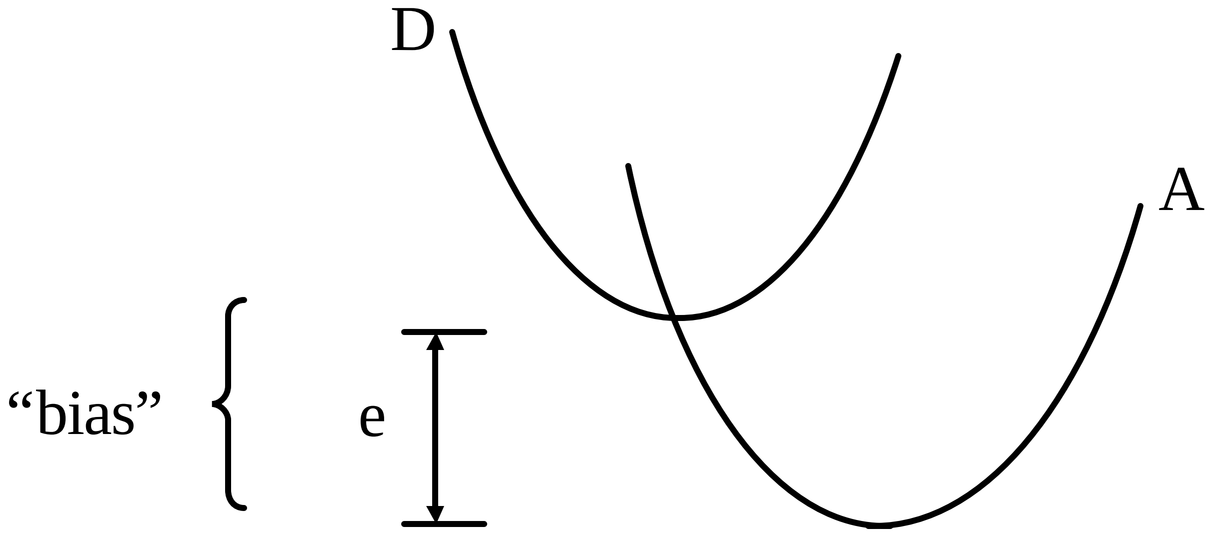
Dramatic perturbations of the “one-way” rate constants may be obtained by varying the laser field intensity:

[Activationless reaction, E_r=1eV]

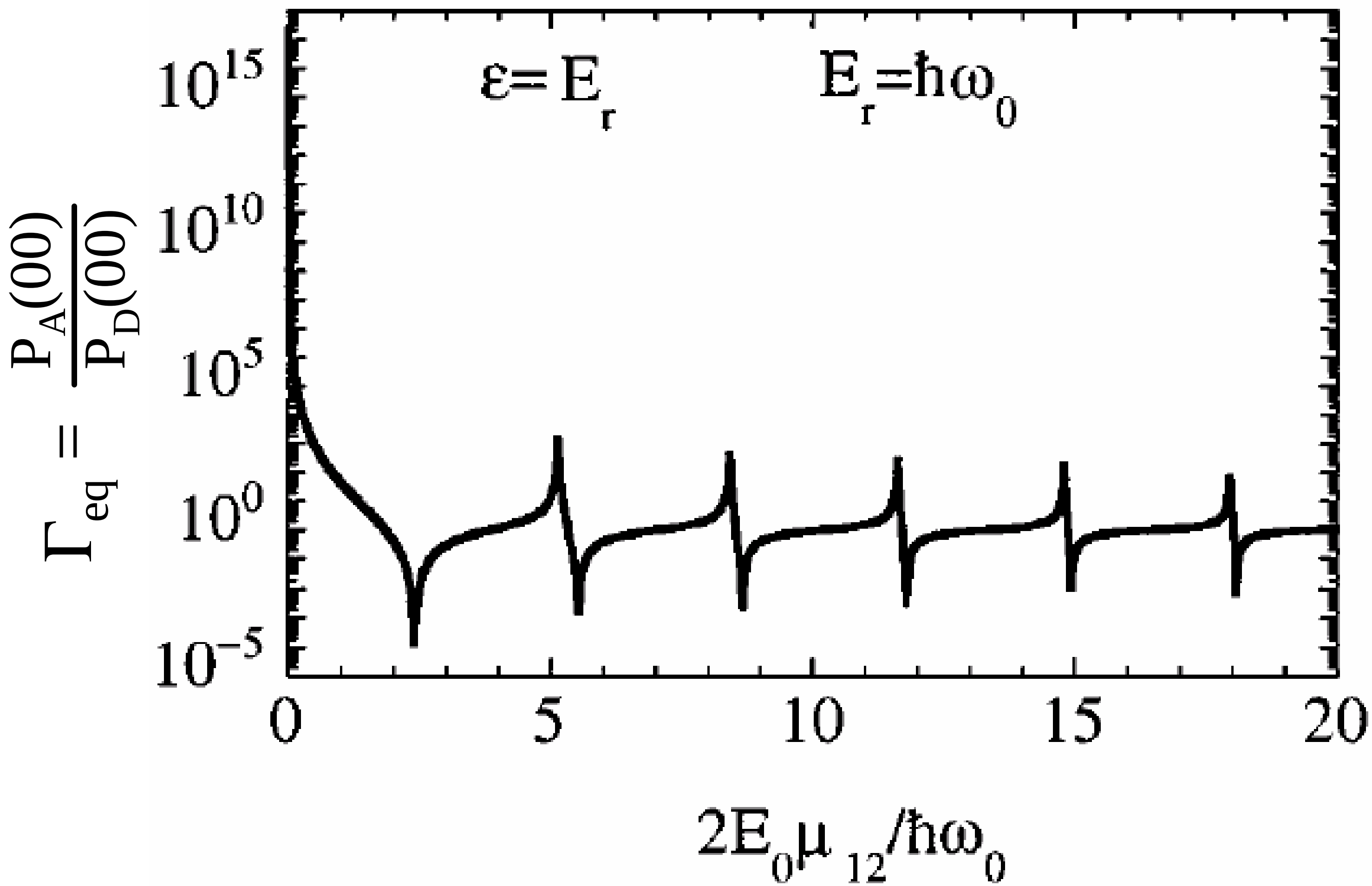
Forward rate constant



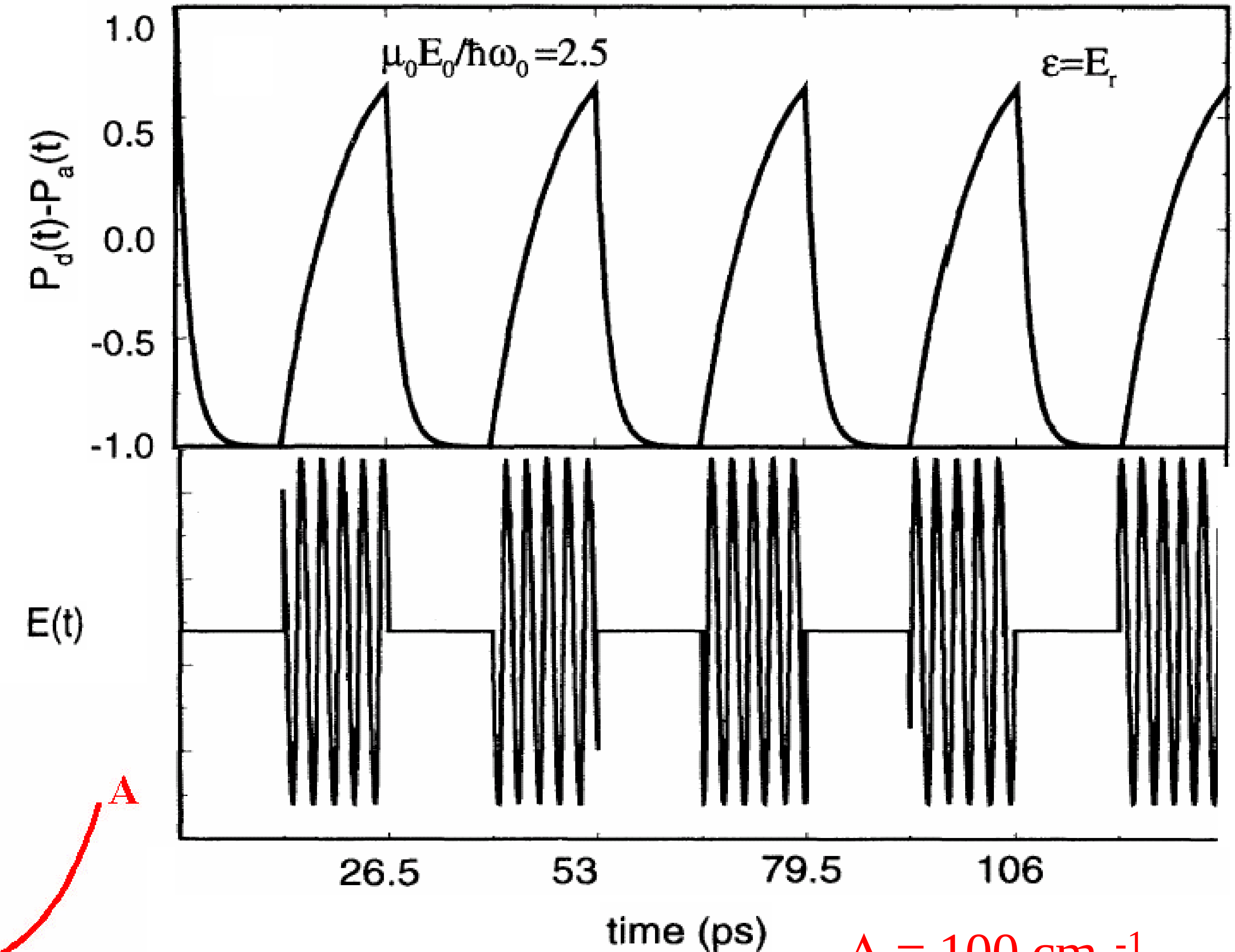
Dakhnovskii and RDC showed how this property can be used to control Equilibrium Constants with an applied cw field:



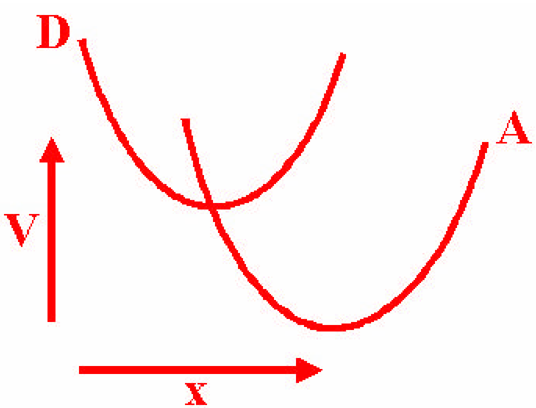
Results for activationless reaction:



Y. Dakhnovskii and RDC, J. Chem. Phys. 103, 2908 (1995)



Activationless ET



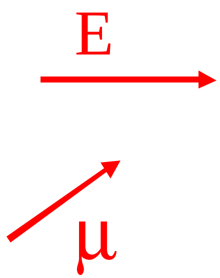
$\Delta = 100\ \mathrm{cm}^{-1}$

$E_r = \varepsilon = \hbar\omega_o = 1\mathrm{eV}$

Evans, RDC, Dakhnovskii & Kim,
PRL 75, 3649 (95)

REALITY CHECK on coherent control of mixed valence ET reactions in polar media

$\boxed{(1)}$ “$\vec{\mu}\cdot\vec{E}$”



→Orientational averaging will reduce magnitude of desired effects

[Lock ET system in place w/ thin polymer films]

$\boxed{(2)}$ Dielectric breakdown of medium?

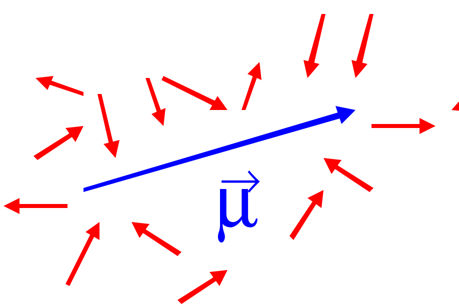
To achieve resonance effects for μ = 34D

$E_r = h\omega_o = 1eV$

$\rightarrow$Electric field $\approx 10^7$ V/cm

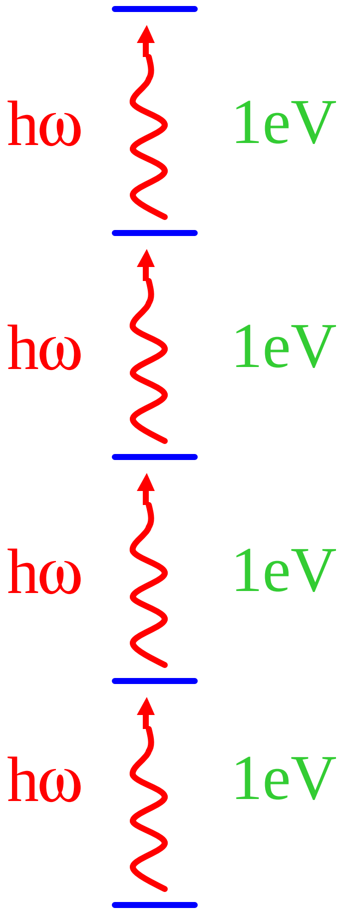
Giant dipole ET complex, solvent w/ reduced E_r, pulsed laser reduce likelihood of catastrophe]

$\boxed{(3)}$ Direct coupling of E(t) to polar solvent

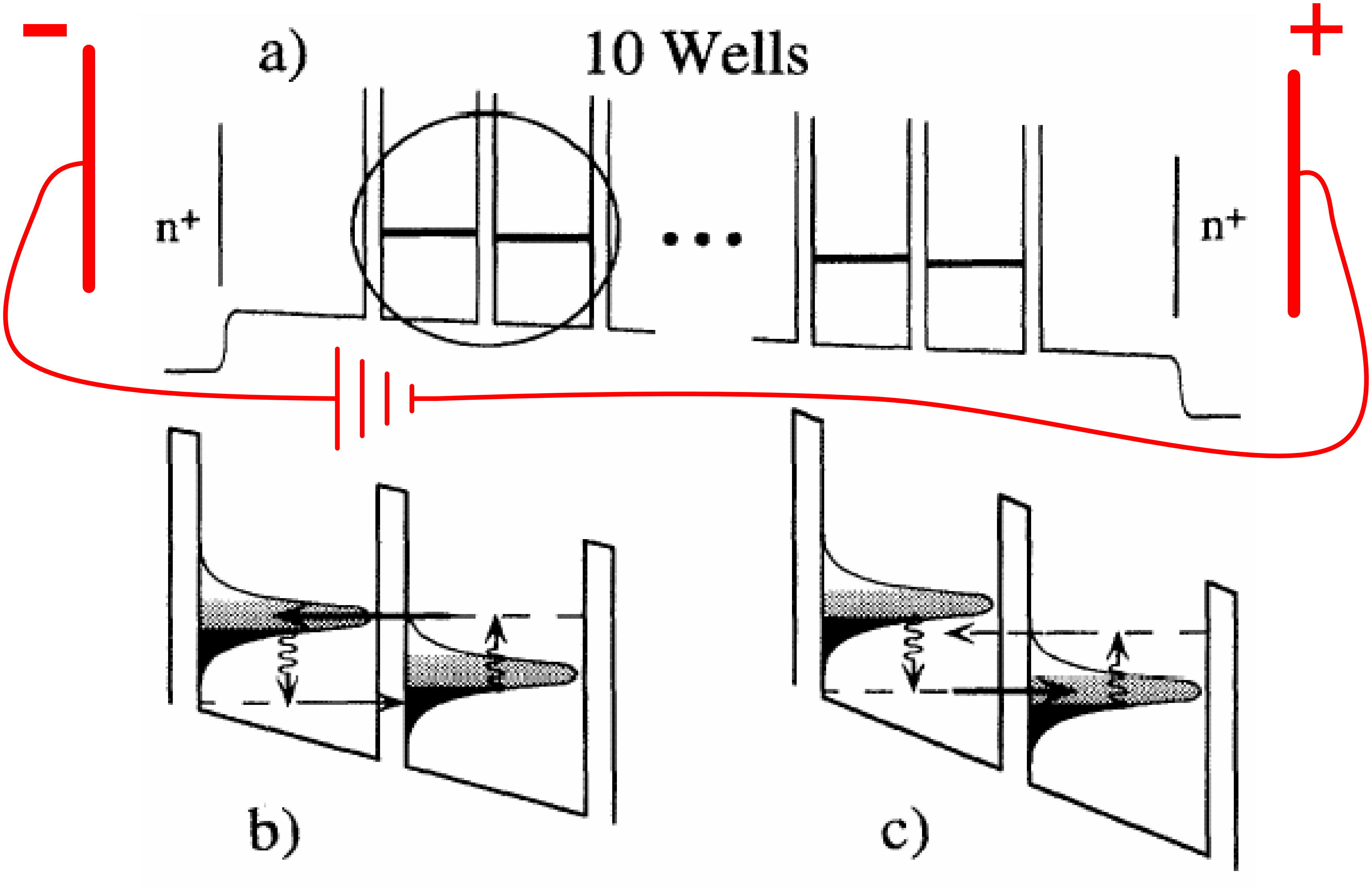


[Dipole moment of solvent molecules << Dipole moment of giant ET complex]

$\boxed{(4)}$ $h\omega_0 \cong 1eV$; intense fields $\Rightarrow$ (multiphoton) excitation to higher energy states in the ET molecule, which are not considered in the present 2-state model.

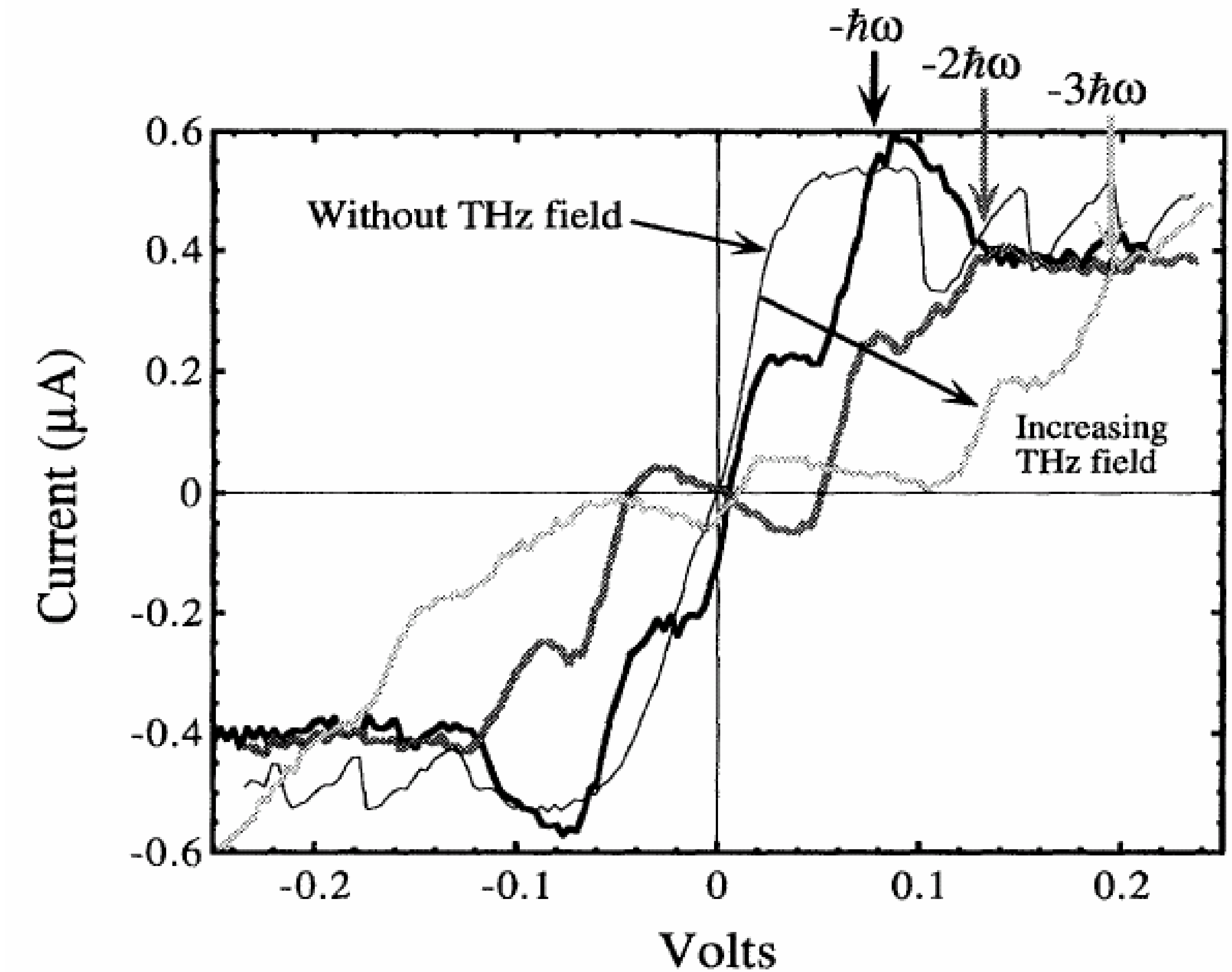


Absolute Negative Conductance in Semiconductor Superlattice



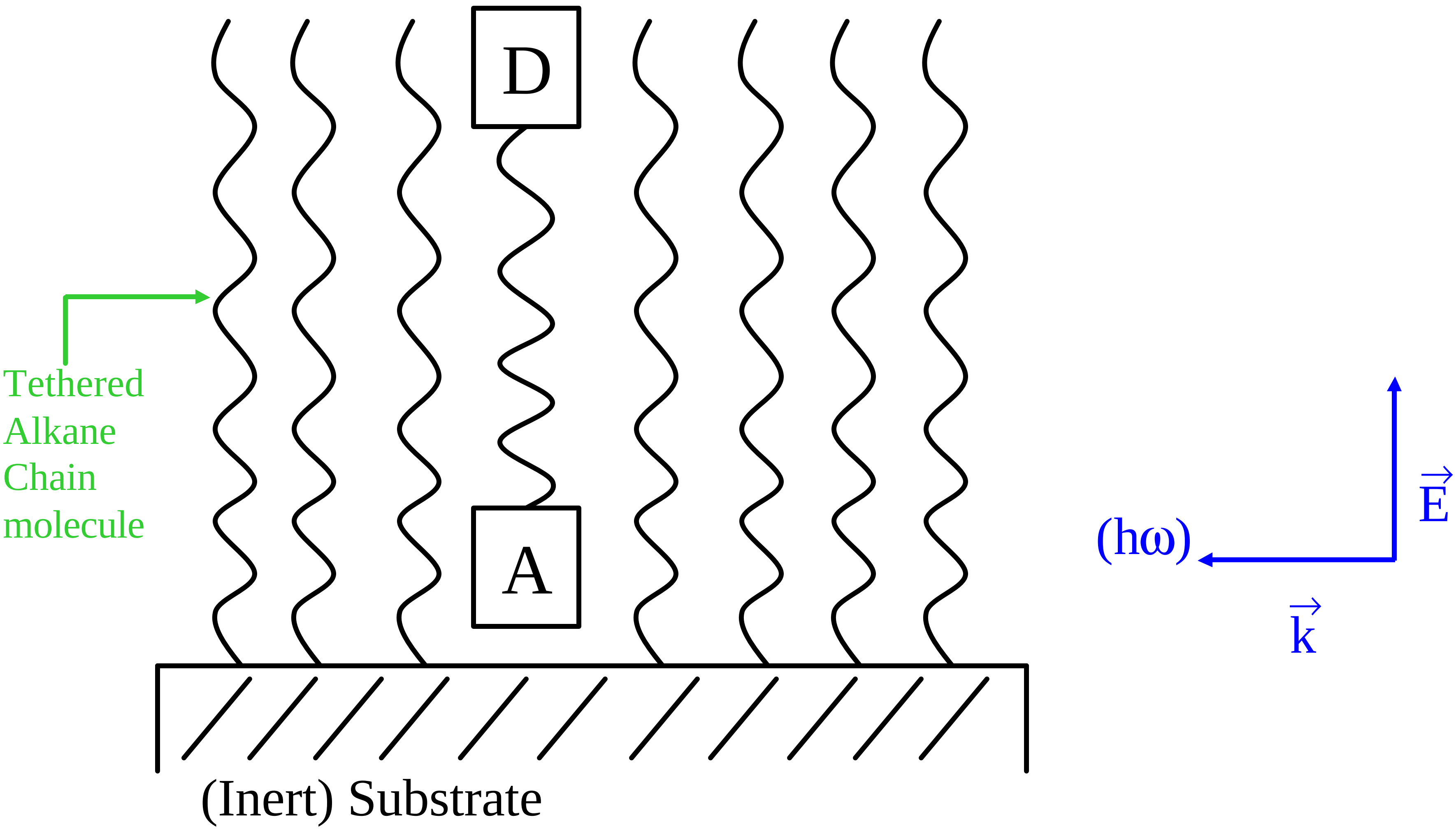
-Keay et al., Phys. Rev. Lett. 75, 4102 (1995)

Absolute Negative Conductance in Semiconductor Superlattice

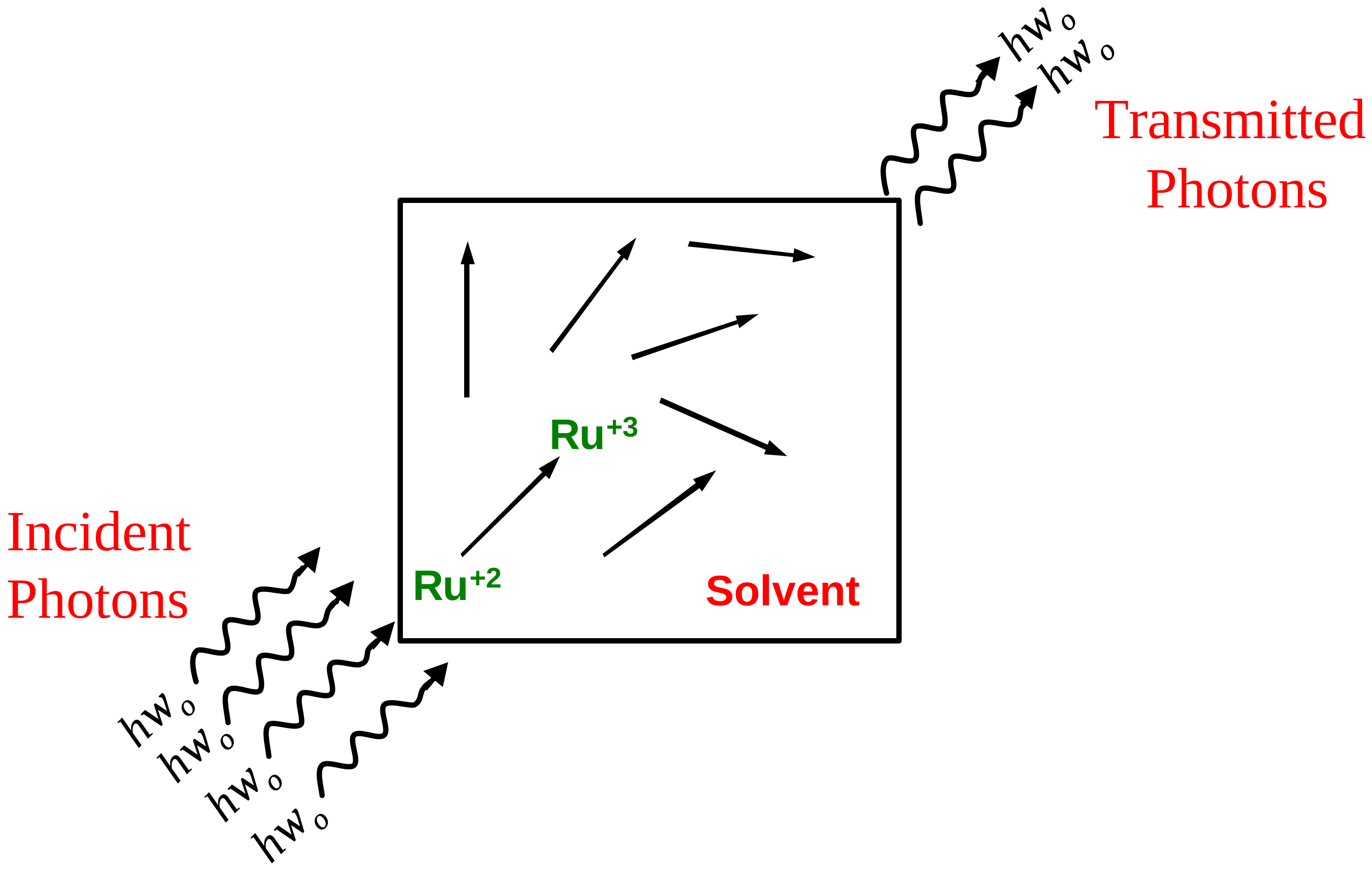


-Keay et al., Phys. Rev. Lett. 75, 4102 (1995)

Immobilized long-range Intramolecular Electron Transfer Complex:



Light Absorption by Mixed Valence ET Complexes in Polar Solvents:



Absorption cross section $K_{abs}(w_o) = \dfrac{\text{\# Absorbed Photons}}{\text{\# Incident Photons}}$

Absorption Cross Section Formula:

$$k_{abs} = \frac{1}{E_o^2} \frac{d\,\overline{E(a,w_o)}}{dt} \qquad (1)$$

$$\frac{d\,\overline{E(a,w_o)}}{dt} = n_1^{(eq)} \cdot \frac{\partial U_1}{\partial t} + n_2^{(eq)} \cdot \frac{\partial U_2}{\partial t} \qquad (2)$$

$$\frac{\partial U_{1,2}}{\partial t} = \frac{\hbar \Delta^2}{4} \left(\frac{p}{E_r k_B T} \right)^{1/2} \sum_{m=1}^{\infty} m\hbar w_o J_m^2(a) \quad \times \qquad (3)$$

$$\left[\exp\left(- \frac{\left(E_r \pm e - m\hbar w_o\right)^2}{4E_r k_B T} \right) - \exp\left(- \frac{\left(E_r \pm e + m\hbar w_o\right)^2}{4E_r k_B T} \right) \right]$$

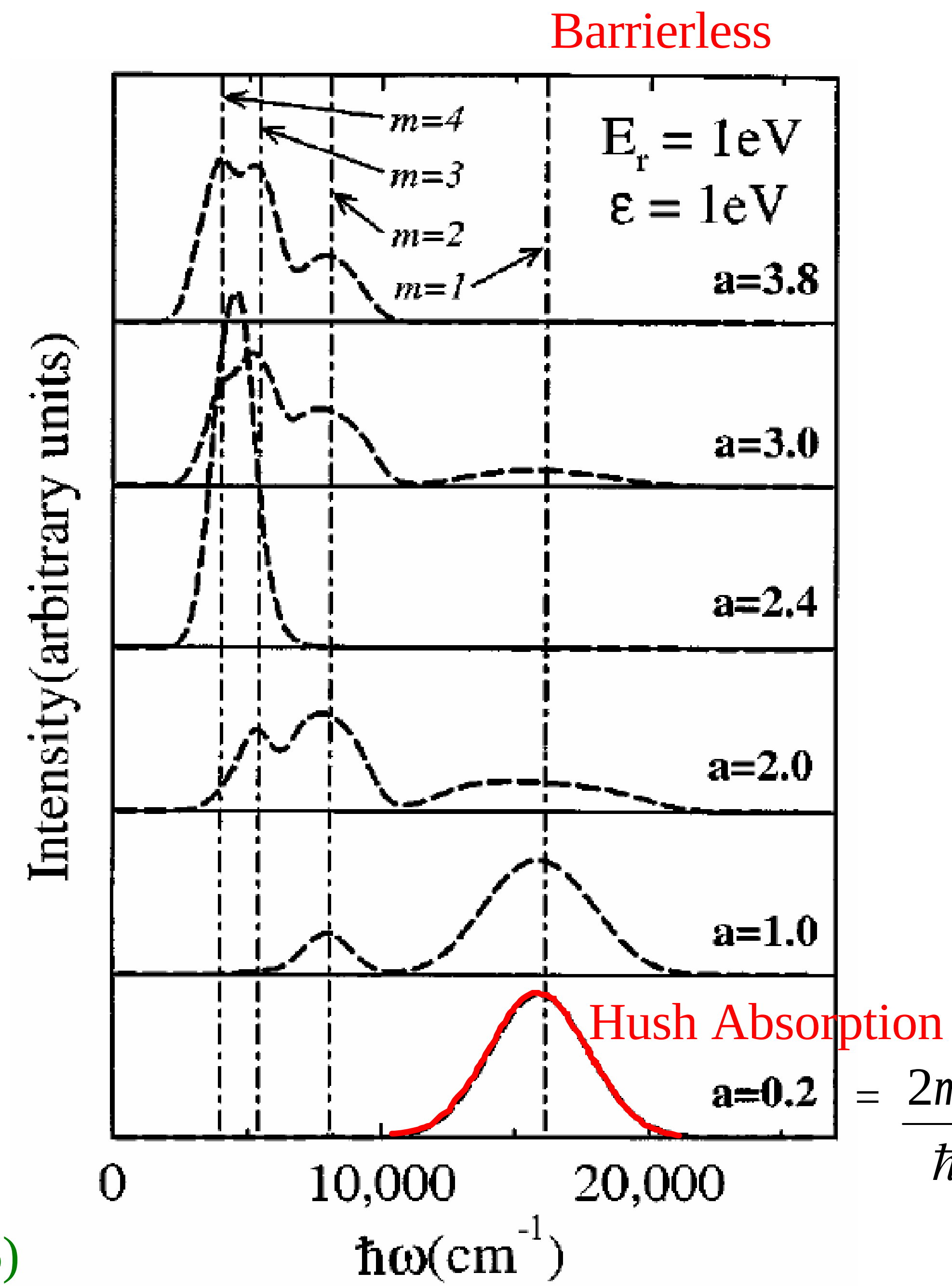
$$a = 2m_o E_o / \hbar w_o$$

$$\text{Hush Absorption Spectrum} \equiv s\,(w_L) = \frac{\#\,\text{Absorbed Photons}}{\#\,\text{Incident Photons}}$$

$$\propto w_L \Delta_{12}^2 \underbrace{\left[\text{FCF}\right]}_{\substack{\text{Marcus}\\ \text{Gaussian}}}$$

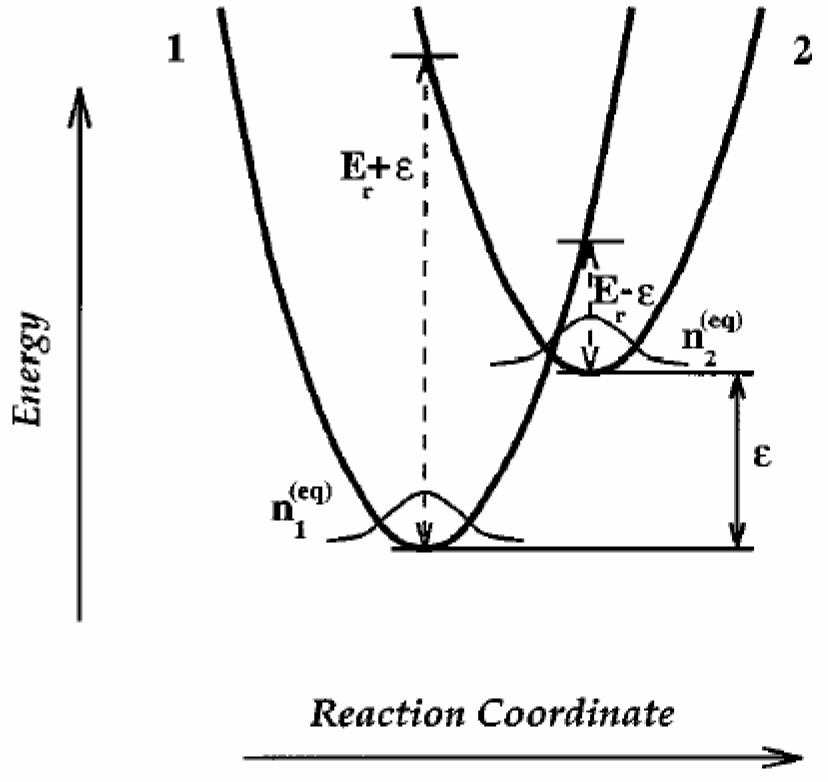
$$\text{w/ } \underline{\underline{\Delta_{12}}} = \text{effective "transition dipole moment"} = m \cdot \frac{?}{\hbar w_{\text{res}}} \quad << \quad m$$

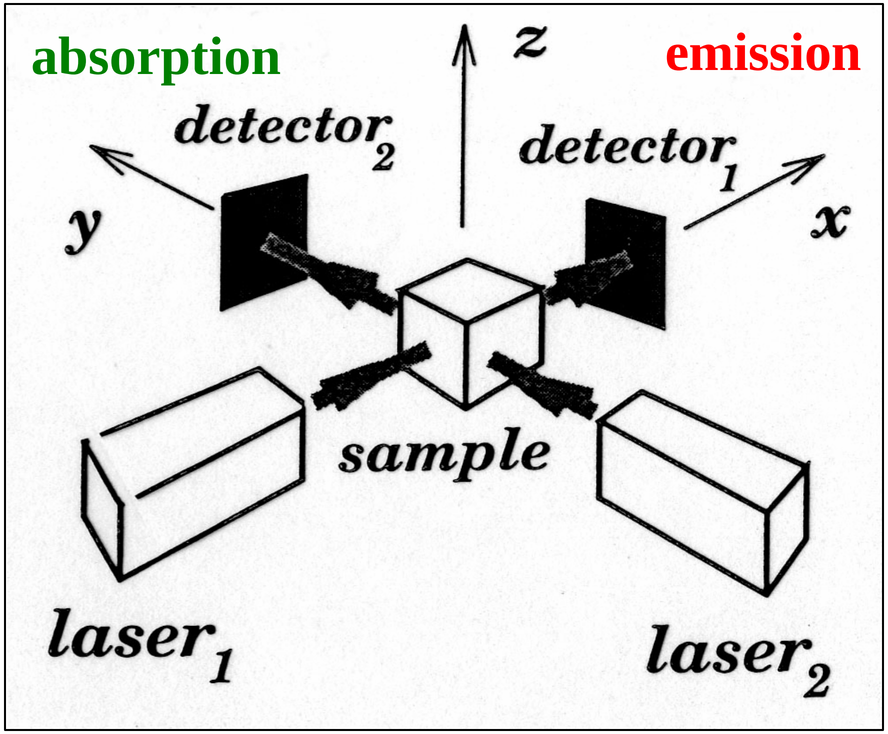
permanent
dipole moment
difference



$= \dfrac{2m_o E_o}{\hbar w_o}$

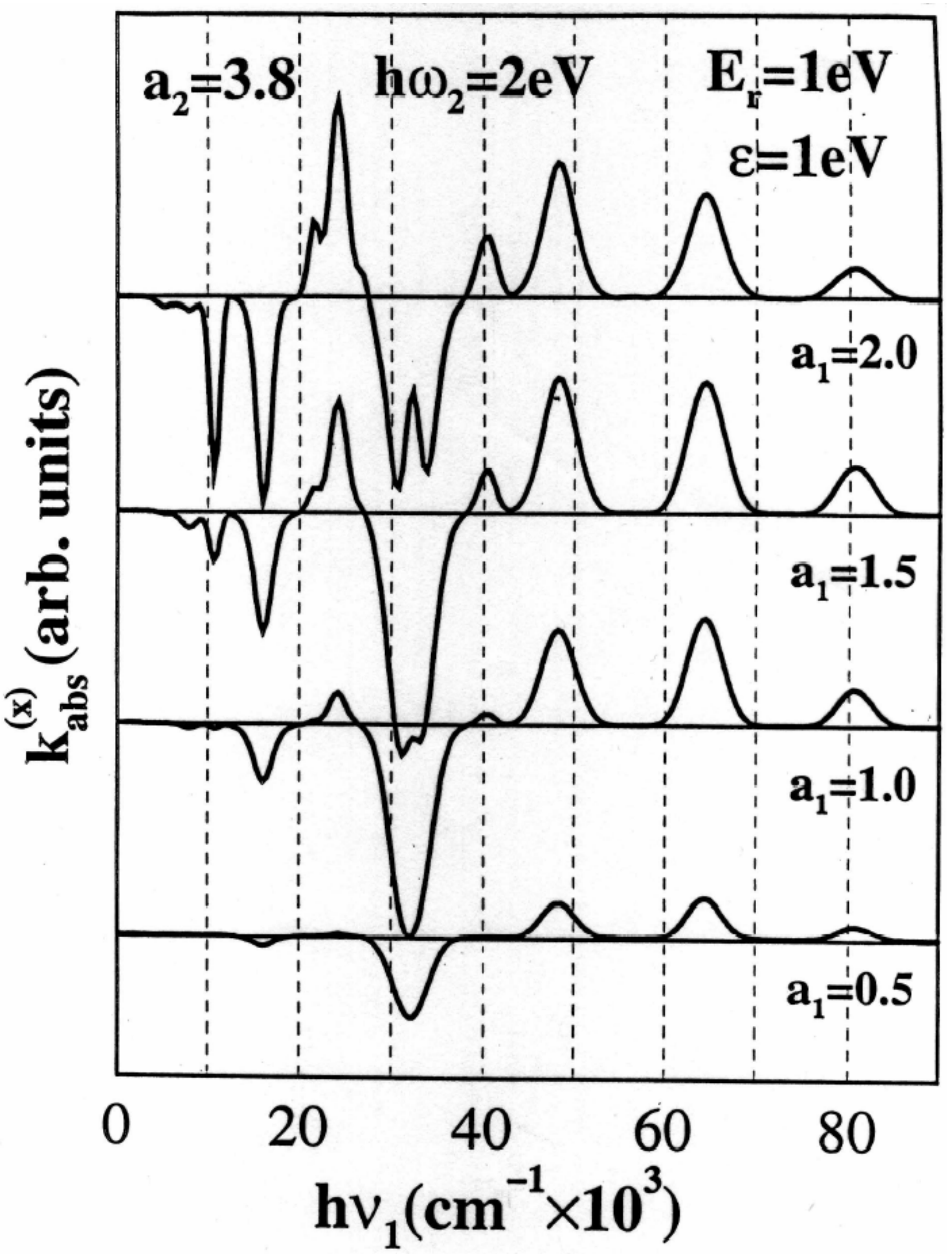
PRL 77, 2917 (1996)
J. Chem. Phys. 105, 9441 (1996)





Stimulated Emission using two incoherent lasers

J. Chem. Phys. 109, 691 (1998)



J. Chem. Phys. 109, 691 (1998)