Laser–Induced Control of Condensed Phase Electron Transfer

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[polar Solvent]
Tunneling in A 2-State System

Proton Transfer

Multi (Double) Quantum Well Structure

Electron Transport In Solids
For any of these systems:  \[ |\Psi(t)\rangle = c_D(t) |D\rangle + c_A(t) |A\rangle \]

where

\[
\begin{pmatrix}
H_{AA} & H_{AD} \\
H_{DA} & H_{DD}
\end{pmatrix}
\begin{pmatrix}
c_A \\
c_D
\end{pmatrix}
= \frac{i}{\hbar} \frac{d}{dt}
\begin{pmatrix}
c_A \\
c_D
\end{pmatrix}
\]

For a Symmetric Tunneling System:  \( H_{AA} = H_{DD} = 0; \ H_{AD} = H_{AD} = \Delta \ (< 0) \)
Given initial preparation in $|D\rangle$, for a symmetric system:

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

![Graph showing a cosine squared function with peaks at intervals of $\pi$ and $2\Delta$.](image)
Now, apply an electric field

Q: How does this modify the Hamiltonian??

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

Thus:

\[
\begin{pmatrix}
\Delta \\
\Delta
\end{pmatrix}
= \begin{pmatrix}
H_{AA} & \Delta \\
\Delta & H_{DD}
\end{pmatrix} - E \begin{pmatrix}
e_o R/2 & 0 \\
0 & -e_o R/2
\end{pmatrix}
\]
Analysis in the case of time-dependent \( E(t) = E_0 \cos \omega_o t \)

Consider first the symmetric case:

\[
i \frac{d}{dt} \begin{pmatrix} c_A \\ c_D \end{pmatrix} = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} - \mu E_0 \cos \omega_o t \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c_A \\ c_D \end{pmatrix}
\]

Permanent dipole moment difference

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: \( a = \frac{\mu E_0}{(h) \omega_o} \)

\( \text{N.B.: } \mu \int_0^t E_0 \cos \omega_o t' dt' = \frac{\mu E_0}{\omega_o} \sin \omega_o t \)

Thus, Interaction Picture S.E. reads:

\[
i \frac{d}{dt} \begin{pmatrix} c_A^I \\ c_D^I \end{pmatrix} = \begin{pmatrix} 0 & e^{-2i a \sin \omega_o t} \Delta \\ e^{2i a \sin \omega_o t} \Delta & 0 \end{pmatrix} \begin{pmatrix} c_A^I \\ c_D^I \end{pmatrix}
\]
Now note: \[ e^{i b \sin \omega t} = \sum_{m=-\infty}^{\infty} J_m(b) e^{i m \omega t} \]

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

\[ \approx \Delta \cdot J_0(2a) , \text{ for } \Delta/\omega_o << 1 \]

Thus, the shuttle frequency is renormalized to \[ \Delta |J_0(2a)| \]

NB: Trapping or localization occurs at certain \( E_o \) values!

[Grossman - Hänggi, Dakhnovskii – Metiu]
Add coupling to a condensed phase environment

\[
\hat{H} = \hat{T} + \left[ \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right] + \left[ \begin{array}{cc} V_D(x) & \Delta \\ \Delta & V_A(x) \end{array} \right] - \mu E_o \cos \omega_o t \left( \begin{array}{c} 1 \\ 0 \end{array} \right)
\]

Nuclear coordinate kinetic energy

Field couples only to 2-level system
Now:
\[
\begin{pmatrix}
T+V_D(x) & \Delta \\
\Delta & T+V_A(x)
\end{pmatrix}
- \mu E_0 \cos \omega_0 t \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\begin{pmatrix}
\phi_D(x,t) \\
\phi_A(x,t)
\end{pmatrix}
\]

\[= i \frac{d}{dt} \begin{pmatrix}
\phi_D(x,t) \\
\phi_A(x,t)
\end{pmatrix}\]
Construction of (Diabatic) Potential Energy functions for Polar ET Systems:

\[ V_A(x) \]

\[ V_D(x) \]
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

\[ |\Psi(t)\rangle = \begin{bmatrix} \phi_1(x,t) \\ \phi_2(x,t) \end{bmatrix} \]

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

$$\phi_1(x,0).$$

Then, $P_2(t) = \text{fraction of molecules in electronic state 2}$

$$= \langle \phi_2(x,t) | \phi_2(x,t) \rangle \cong k_{1\rightarrow 2}t$$

where $k_{1\rightarrow 2} = \text{(Golden Rule) rate constant}$
In classical Marcus (Levich-Doganadze) theory, $k_{1\rightarrow2}$ is determined by three molecular parameters: \( \Delta, E_r, \epsilon \)

\[
k_{1\rightarrow2} = \Delta^2 \left( \frac{\pi}{E_r k T} \right)^{1/2} e^{-(E_r - \epsilon)^2/4E_r k_B T}
\]

w/ \( E_r = \text{“Reorganization Energy”} \); \( \epsilon = \text{“Reaction Heat”} \)

For the “backwards” Reaction: \( k_{2\rightarrow1} = \Delta^2 \left( \frac{\pi}{E_r k T} \right)^{1/2} e^{-(E_r + \epsilon)^2/4E_r k_B T} \)
To obtain electronic state populations at arbitrary times, solve kinetic [“Master”] Eqns.:

\[
\frac{dP_1(t)}{dt} = -k_{1\rightarrow 2}P_1(t) + k_{2\rightarrow 1}P_2(t)
\]
\[
\frac{dP_2(t)}{dt} = k_{1\rightarrow 2}P_1(t) - k_{2\rightarrow 1}P_2(t)
\]

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

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

for Marcus formula rate constants

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

\[
k_{D \rightarrow A} = \Delta^2 \sum_{m=-\infty}^{\infty} J_m^2(a) \cdot \frac{\text{Re}}{\pi} \int_0^\infty dt \ e^{i m \omega_o t} \ \text{tr} \left\{ \hat{\rho}_\beta^D e^{-i \hat{h}_A t} e^{i \hat{h}_D t} \right\}
\]

\[
a = 2 \mu_{12} E_o / \hbar \omega_o
\]
\[
\kappa_{D\to A}^{A\to D} = \frac{\Delta^2}{4} \left( \frac{\pi}{E_r kT} \right)^{1/2} \sum_{m=-\infty}^{\infty} J_m^2 \left( 2\mu_1 E_o / \hbar \omega_0 \right) \cdot 
\]
\[
e^{-\sqrt{\frac{(E_r \pm \varepsilon + \hbar \omega_0)^2}{4E_r k_B T}}} 
\]

Rate constants in presence of cw E-field
Schematically:

In polar electron transfer reactions, for
Reorganization Energy $E_r \equiv \hbar \omega_o$ (the quantum of applied laser field)
Dramatic perturbations of the “one-way” rate constants may be obtained by varying the laser field intensity:

[Activationless reaction, $E_r=1$ eV]
Dakhnovskii and RDC showed how this property can be used to control Equilibrium Constants with an applied cw field:
Results for activationless reaction:

\[ \Gamma_{eq} = \frac{P_A(00)}{P_D(00)} \]

\[ \varepsilon = E_r \quad E_r = \hbar \omega_0 \]

Activationless ET

\[ E_r = \varepsilon = \hbar \omega_o = 1 \text{eV} \]

\[ \Delta = 100 \text{ cm}^{-1} \]

Evans, RDC, Dakhnovskii & Kim, PRL 75, 3649 (95)
REality Check on coherent control of mixed valence ET reactions in polar media

\[ \mu \cdot \vec{E} \]  

→ Orientational averaging will reduce magnitude of desired effects

[Lock ET system in place w/ thin polymer films]
(2) Dielectric breakdown of medium?

To achieve resonance effects for $\mu = 34D$

$E_r = h \omega_o = 1\text{eV}$

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

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

(3) Direct coupling of $E(t)$ to polar solvent

[Dipole moment of solvent molecules $\ll$ Dipole moment of giant ET complex]
\[ h\omega_0 \approx 1\text{eV} ; \text{intense fields } \Rightarrow \text{(multiphoton) excitation to higher energy states in the ET molecule, which are not considered in the present 2-state model.} \]
Absolute Negative Conductance in Semiconductor Superlattice

Absolute Negative Conductance in Semiconductor Superlattice

Immobilized long-range Intramolecular Electron Transfer Complex:

- Tethered Alkane Chain molecule
- (Inert) Substrate

\[ \text{(h} \omega \text{)} \]
Light Absorption by Mixed Valence ET Complexes in Polar Solvents:

Absorption cross section \( K_{\text{abs}}(\omega_0) = \frac{\# \text{ Absorbed Photons}}{\# \text{ Incident Photons}} \)
Absorption Cross Section Formula:

\[ k_{abs} = \frac{1}{E_o^2} \frac{d\,E(a, \omega_o)}{dt} \]  \tag{1} \]

\[ \frac{d\,E(a, \omega_o)}{dt} = n_1^{(eq)} \cdot \frac{\partial U_1}{\partial t} + n_2^{(eq)} \cdot \frac{\partial U_2}{\partial t} \]  \tag{2} \]

\[ \frac{\partial U_{1,2}}{\partial t} = \frac{\hbar \Delta^2}{4} \left( \frac{\pi}{E_r k_B T} \right)^{1/2} \sum_{m=1}^{\infty} m\hbar \omega_o J_m^2(a) \times \exp \left( - \frac{(E_r \pm \varepsilon - m\hbar \omega_o)^2}{4E_r k_B T} \right) - \exp \left( - \frac{(E_r \pm \varepsilon + m\hbar \omega_o)^2}{4E_r k_B T} \right) \]  \tag{3} \]

\[ a = 2\mu_o E_o / \hbar \omega_o \]
Hush Absorption Spectrum \( \equiv \sigma (\omega_L) = \frac{\# \text{Absorbed Photons}}{\# \text{Incident Photons}} \)

\[ \propto \omega_L \Delta_{12}^2 [\text{FCF}] \]

Marcus Gaussian

w/ \( \Delta_{12} = \text{effective "transition dipole moment"} = \mu \cdot \frac{?}{\hbar \omega_{\text{res}}} \ll \mu \)

permanent dipole moment difference
Barrierless

$E_r = 1\text{eV}$
$\varepsilon = 1\text{eV}$

$a = 3.8$

$a = 3.0$

$a = 2.4$

$a = 2.0$

$a = 1.0$

$Hush\ Absorption$

$a = 0.2$

$= \frac{2\mu_o E_o}{\hbar \omega_o}$

PRL 77, 2917 (1996)
Stimulated Emission using two incoherent lasers
