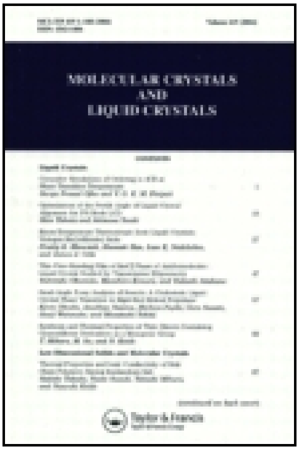

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Switch Phenomena in Molecular Three-Centre Electron Transfer Systems with Strong Electronic-Vibrational Coupling

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SWITCH PHENOMENA IN MOLECULAR THREE-CENTRE ELECTRON TRANSFER SYSTEMS WITH STRONG ELECTRONIC-VIBRATIONAL COUPLING

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Abstract Three-centre molecular and supramolecular electron transfer (ET) is important in device-like function of organized assemblies of bridge-group separated donor and acceptor units in solid-state or electrochemical systems. Other areas are solid-state phonon-kick charge capture, electrochemical ET via adsorbates or film impurities, large adsorbate STM, and long-range ET in redox metalloproteins. Optical three-level analogues are molecular Raman scattering and two-photon absorption.

Three-level ET behaviour rests on coupling to environmental nuclear motion. A frame is second order perturbation theory including full vibrational manifolds in all three states. We discuss such a formalism. Common superexchange is recovered for high intermediate state energies while vibrationally unrelaxed state population emerges for low energies. These limits are separated by finite resonances in characteristic "switch" patterns.

Intermediate state vibrational friction is briefly addressed and we note some biological and synthetic systems to which the formalism is appropriate.

INTRODUCTION

Molecular three-level electron transfer (ET) "triads" consisting of an electron donor (D), acceptor (A), and intermediate bridge group (B) are key structural units in molecular electronics. Notable examples are:

(A) Bridge group assisted intramolecular ET and photo-assisted ET in three-centre molecules. An impressive variety of systems is now available including mixed-valence binuclear transition metal complexes[1,2], aromatic hydrocarbon units separated by rigid σ-structures[3], and porphyrin/quinone structures simulating photosynthetic function[4]. The hemoquinone switch[5], and molecular phototransistor function belong to this class.

(B) Supramolecular assemblies of D-B-A molecules organized in Langmuir-Blodgett films and incorporated in solid-state[6] and electrochemical systems[7]. Diode-like function has been reported for this kind of systems[6,7].

(C) Heterogeneous D-B-A structures, represented by STM configurations for large adsorbate molecules including proteins and other macromolecules[8]. Asymmetric current-voltage characteristics is reported in one case[9].

Three-level ET is also encountered in broader contexts. The following are particularly interesting in relation to molecular electronics:

(D) Electrochemical ET through adsorbed atoms, or impurity atoms and vacancies in surface films[10,11]. Structure in current-voltage relations can be traced to voltage variation of ET-assisting levels in resonance or inelastic tunnel modes.

(E) Successive minority and majority-carrier capture by defect levels in semiconductors[12].

(F) ET in primary charge separation in bacterial photosynthesis, and in other multi-centre metalloprotein function where the protein conformation is possibly not fully relaxed between successive ET steps[13].

(G) Optical analogues of three-centre ET would be resonance Raman scattering and two-photon absorption strongly coupled to environmental nuclear motion[14].

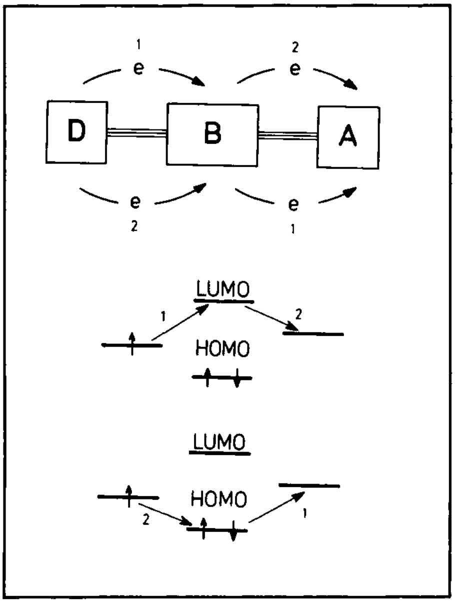
Bridge-group assisted long-range ET is frequently handled by superexchange concepts. These are adequate, also for covalent residues, but apply only to high B-energies. More sophisticated switch patterns arise if the B-orbital energies are low enough that external fields can bring the levels to accommodate the electron or hole during current flow. We discuss here a formalism which incorporates both limits, and the resonance-like transitions between them[15-17].

THREE-LEVEL ET IN MOLECULAR SYSTEMS

We consider the three-level system in fig.1. Fig.2 shows potential surface configurations representative of "chemical" ET, and STM or resonance Raman scattering[14-17]. We let the three potential surfaces be displaced harmonic oscillators

$$\begin{aligned} U_D(q) &= \tfrac{1}{2}\hbar\omega(q+q_o)^2;\; U_B(q) = \tfrac{1}{2}\hbar\omega q^2 + \Delta U_{BD}^{o} \\ U_A(q) &= \tfrac{1}{2}\hbar\omega(q-q_o)^2 + \Delta U_{AD}^{o} \end{aligned} \qquad (1)$$

where q_o is the displacement, ω the frequency, $2\pi\hbar$ Planck's constant while



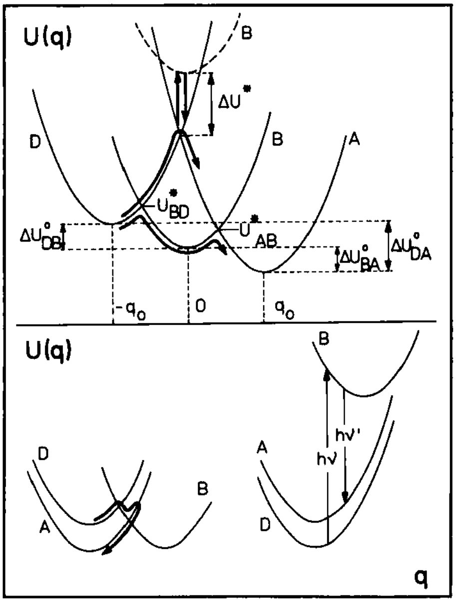


Fig.1. Schematic ET patterns in a molecular three-level ET or hole transfer system. Arrows and numbers indicate order of ET sequence.

Fig.2. Potential surfaces for three-level ET. Upper: "Chemical" ET. Dashed B-surface represents superexchange, fully drawn sequential ET. Lower: Adsorbate STM (left) and resonance Raman scattering. ν and ν' are the frequencies of incoming and scattered light, respectively.

Other forms can also be handled.

The transition probability per unit time, statistically averaged with respect to the nuclear motion is, by second order perturbation theory

$$W_{DA} = \frac{2\pi}{\hbar}(V_{BD})^2(V_{AB})^2 Z^{-1} \int_{-2\pi i/\alpha}^{2\pi i/\alpha} d\theta \sum_n \sum_\ell \exp(-\beta\ell\hbar\omega) \; x$$

$$\exp\{[\beta\hbar\omega(\ell-n) - \beta\Delta U^o_{AD}]\} \left| \sum_m \frac{S_{AB}S_{BD}}{\hbar\omega(\ell-n) + \Delta U^o_{BD} + i\gamma} \right|^2 \qquad (2)$$

$$Z = \sum_\ell \exp(-\beta\ell\hbar\omega) \; ; \; \beta = (k_BT)^{-1} \; ; \; \alpha = \tfrac{1}{2}\beta\hbar\omega \; ; \; \gamma \rightarrow 0+$$

In eq.(2) we have invoked the Condon approximation and recast the energy conserving Delta function $\delta[\hbar\omega(n-\ell) + \Delta U^o_{AD}]$ in integral form. ℓ, m, and n are vibrational quantum numbers in the donor, bridge and acceptor state, Z the initial state canonical vibrational statistical sum, V_{BD} and V_{AB} electron exchange factors coupling the states indicated by subscripts, while and S_{BD} and S_{AB} are the Franck Condon overlap factors. k_B is finally Boltzmann's constant and T the temperature.

Eq.(2) differs from common superexchange forms by the full vibrational summation in all three electronic states. This ensures workable current-voltage characteristics. Conversion of eq.(2) to useable rate constants rests on:

(1) introduction of specific, harmonic or quasiclassical nuclear wave functions.

(2) Recasting of the energy denominators in integral form, giving a triple integral, also known in the theory of Raman scattering.

(3). Lifting of the Delta-like energy divergence by "coarse graining", or by vibrational density matrix expansion. By the former procedure we obtain[15,17]

$$W_{AD} = \frac{\beta^3\pi}{\alpha\hbar}(V_{AB})^2(V_{BD})^2 \exp(-\alpha\Delta U^o_{AD}/\hbar\omega)\,\mathscr{F}$$

$$\mathscr{F} = \sum_{p=|n|}^{\infty} \frac{(2A)^{2p}}{(p-|n|!)(p+|n|!)} |\mathscr{F}_{2p}|^2 \qquad (3)$$

$$\mathscr{F}_{2p} = \alpha^{-1}i(-1)^{m+1}\int_o^{\pi} dt\, \exp(-2A\mathrm{ch}\alpha\, \sin^2{\textstyle\frac{1}{2}}t)(\sin{\textstyle\frac{1}{2}}t)^{2p}\cos(mt + A\mathrm{sh}\alpha \sin t)$$

where $n = |\Delta U^o_{AD}|/2\hbar\omega$ and $m = (\Delta U^o_{BD} - \Delta U^o_{AB})/2\hbar\omega$, regarded as integers. $A = \frac{1}{2}q_o^2/\mathrm{sh}\alpha$ represents the reorganization free energy of the D → B and B → A steps, i.e. $E_r^{BD} = E_r^{AB} = \frac{1}{2}\hbar\omega q_o^2 = A\alpha\hbar\omega$ $(A\alpha^2 >> 1)$.

The merit of eq.(3) is that it gives a finite, singly-integral W_{AD}-form valid at all energies including resonance between superexchange and sequential ET. It reduces, furthermore to the analytical forms in the off-resonance regions[15]

$$W_{AD} = (\pi/E_r^{AD}k_BT\hbar^2)^{1/2}(V_{BD}V_{AB})^2 \exp(-U^*_{AD}/k_BT)$$
$$U^*_{AD} = (E_r^{AD} + \Delta U^o_{AD})^2/4E_r^{AD}\ ;\ E_r^{AD} = E_r^{BD} \qquad (4)$$

This form corresponds to superexchange (or $m > A\alpha$), cf. fig.2. Sequential ET is represented by ($m < A\alpha$, $U^*_{BD} > U^*_{AB}$)

$$W_{AD} = (8\pi^{3/2}k_BT/\hbar Z)\,\gamma_{AD}\,\gamma_{AB}\exp(-U^*_{BD}/k_BT)$$

$$\begin{aligned}\gamma_{BD} &= (V_{BD})^2/\hbar v_{BD}(2\hbar\omega E_r^{BD})^{1/2}\ ;\ \gamma_{AB} = (V_{AB})^2/\hbar v_{AB}(2\hbar\omega E_r^{AB})^{1/2} \\ v_{BD} &= (2k_BT\omega/\hbar)^{1/2}\ ;\ v_{AB} = [2(U_{BD}-U^*_{AB})\omega/\hbar]^{1/2} \\ U^*_{BD} &= (E_r^{BD}+\ \Delta U^o_{BD})^2/4E_r^{BD}\ ;\ U^*_{AB} = \Delta U^o_{BD}+\ (E_r^{AB}+\ \Delta U^o_{AB})^2/4E_r^{AB}\end{aligned} \qquad (5)$$

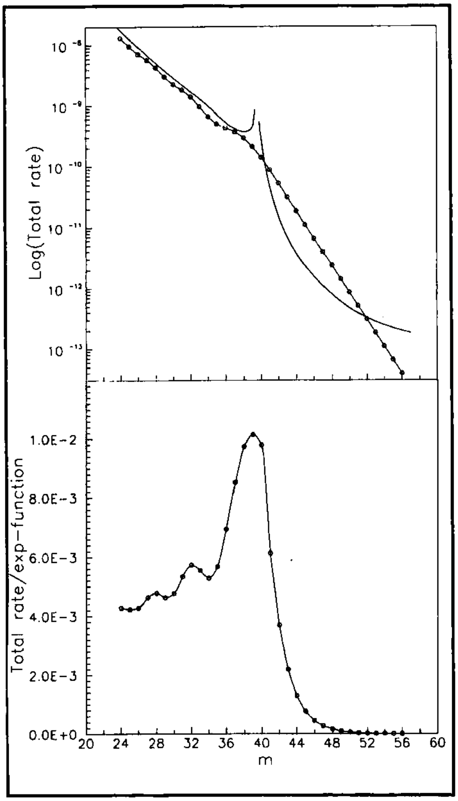
with a similar form when $U^*_{BD} < U^*_{AB}$. The sequential ET form clearly differs from two independent ET steps, by the two different (rather than a single) Landau-Zener velocities. Single-ET steps emerge when friction is added (Section 3), or by extension to multi-dimensional surfaces.

Eqs.(3)-(5) are the current-voltage relations for a three-centre process. Each analytical form is valid in broad energy ranges but diverges close to resonance, $\Delta U^* \rightarrow 0$ or $U^*_{BD} \rightarrow U^*_{AB}$ where the integral form, eq.(3) must be used. The equations also represent molecular "switch" function, appearing as changes in molecular behaviour when bias voltages shift the system between the limits.

Fig.3 and 4 show numerical calculations of eqs.(3)-(5) to illustrate the effects of the intermediate state energy and the D-B-A system behaviour in an external electric field. The potential surface shifts are represented by m and n. Fig.3 shows the variation of $U_B(q)$ or m calculated by eq.(3) and the asymptotic eqs. (4) and (5). The relations follow each other closely below resonance ($m \leq 40$). As $U_B(q)$ passes the D → A crossing a mild resonance and minor oscillations appear. Above resonance the relations also follow each other but calculations could not be extended far enough to reach the asymptotic limit, eq.(4) where W_{AD} is approximately independent of m. Fig.4 shows the variation of W_{AD} with ΔU^o_{AD} or n, at given m for sequential ET. n and m are related by

$$m = \Delta U^o_{BD}/\hbar\omega - m \qquad (6)$$

Variation of n at given m therefore implies that ΔU^o_{BD} and ΔU^o_{AB} both vary and and that the former variation is twice as fast as the latter. This behaviour is representative of D-B-A molecules oriented vertically between two enclosing electrodes. Resonance and switch effects appear as $\Delta U^*_{BD} \rightarrow \Delta U^*_{AB}$ (cf. eq.(5)) but the system remains in either the superexchange or sequential ET mode on simultaneous potential surface variation as in fig.4. Transitions only occur when the voltage induced shift of one potential surface dominates as in fig.3. Other configurations are discussed in ref.17.



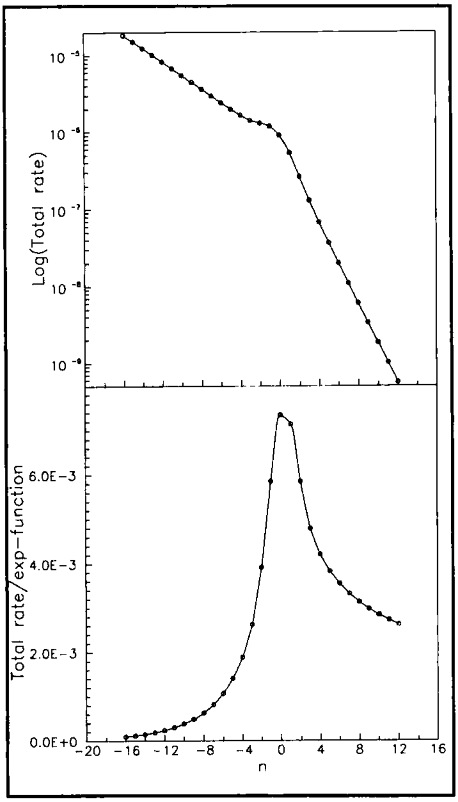


Fig.3. Variation in rate constant (top) and pre-exponental factor (bottom) with m. Resonance as $U_B(q)$ passes the D → A crossing (m ≈ Aα = 40). The thin curve in the top figure shows $W_{AD}(m)$ for the asymptotic eq.(4) which diverges at resonance. A = 200, α = 0.2, n = 5 (E_r^{AD} = 1.6 eV, ΔU^o_{AD} = - 0.1 eV).

Fig.4. Variation in rate constant (top) and pre-exponential factor (bottom) when both bridge group and acceptor energies vary in an external electric field. Variation of D/A energy gap twice as fast as for B/D energy gap. Sequential ET in the whole range but resonance as the B/D and A/B crossing energies coincide ($U^*_{BD} = U^*_{AB}$ or $\Delta U^*_{BD} = \Delta U^*_{AB}$ for n = ΔU^o_{AD}, cf. eq.(5)). A = 200, α = 0.2, m = 20 ($E_r^{BD} = E_r^{AB}$ = 0.4 eV). Resonance at n = ΔU^o_{AD} = 0.

A NOTE ON INTERMEDIATE STATE FRICTION

Eq.(4) is the sequential ET rate constant, involving a populated but vibrationally unrelaxed B-state and a single reactive B → A attempt. This pattern is notably modified when multiple attempts and environmental friction are added. These features are incorporated in the general rate constant

$$W_{AD} = Z^{-1} \int dq\, d\dot{q}\, \dot{q}\, \rho_{AD}(q,\dot{q}) \exp\{-[\tfrac{1}{2}\hbar\omega q^2 + \tfrac{1}{2}(\hbar/\omega)\dot{q}^2]/k_BT\} \qquad (7)$$

$\rho_{AD}(q,\dot{q})$ is the transition probability including multiple attempts and friction,

$$\rho_{AD} = P_{BD}P_{AB}\sum_{k=0}(1 - P_{BD})^k(1 - P_{AB})^k \tag{8}$$

$$P_{BD} \approx 4\pi\gamma_{BD}\ ;\ P_{AB} \approx 4\pi\gamma_{AB}$$

while P_{BD} and P_{AB} are individual passage probabilities. The attempt number, $n(U_B)$ can be derived when the frictional pattern is known. The specific time dependence $U_B = U_{BO}\exp(-\Gamma t)$ (counted from the B-state bottom), and $U^*_{BD} > U^*_{AB}$, gives

$$n(U_B) = (\omega/2\pi\Gamma)\ln(U_{BO}/U^*_{AB}) - ½ \tag{9}$$

Eqs.(7)-(9) provide a more complete rate constant which reduces to eq.(4) for a single attempt. We refer to more detailed discussion elsewhere[18] but note here, first that multiple attempts, i.e. weak damping reduce the pre-exponential factor to a single electronic factor. This reflects system approach to intermediate state vibrational relaxation. Secondly, strong friction keeps the attempt number low, leaving two electronic factors in this limit.

PERSPECTIVES AND CONCLUSION

The formalism above addresses aspects of long-range ET of interest in molecular electronics. "Switch" function is associated with field induced changes of U^*_{BD} and U^*_{AB} in sequential ET, and with transitions between superexchange and sequential ET. Particular perspectives relate to excited electronic states for which the latter is much more important than for ground state ET.

"Working" device-like, chemical, and biological systems to which the formalism is appropriate were listed above. A particular aspect is that of mutant excited state redox proteins, say hemoproteins hold a promise by prospective superexchange/sequential shift on mutation. Another one is that of electrochemically immobilized redox enzymes communicatively linked to the electrode by covalently bound electron transmitters. Molecular triad ET is thus a key feature of broad ranges of well characterized inorganic, organic, and biological systems. The formalism and its extensions offer a useful frame for their intriguing properties.

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