

Influence of Frequency Shifts on Electron Transfer Processes

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The quantum theory of electron transfer processes is extended to treat frequency changes between initial and final electronic states. In contrast to earlier extensions that include the effects of frequency changes, the final results emerge in a compact, physically transparent Marcus type form with two new added terms that depend on the frequency changes. The results exhibit an interesting situation where frequency changes can balance against the traditional reorganization energy.

I. Introduction

Electron-transfer plays an essential role in widespread phenomena ranging from biology (photosynthesis, respiration, enzyme action, etc.) to electrochemistry and to materials science (transport). The fundamental theoretical description of electron transfer by Marcus¹ has been re-derived in a quantum theory² and has since undergone many refinements and embellishments.³ Virtually all theoretical treatments of electron transfer are based upon the common model of a surrounding medium whose modes (polarization, “vibrations”, etc.) may suffer only geometric changes (i.e., shifts in equilibrium positions) in the transition between initial and final electronic states. This use of what is termed a linear coupling model is motivated, in part, by mathematical simplicity for depicting the basic phenomena. Indeed, recent extensions of the Marcus theory by Lin⁴ and by Voth⁵ and their respective co-workers to include mode frequency changes between the initial and final states have led to rather complicated expressions that render it difficult to extract simple physical understanding. Voth, in particular, provides extensive and compelling evidence for the relevance of frequency changes (also called quadratic coupling models) in describing electron transfer in several diverse systems. For example, it appears quite obvious that the frequencies of the polarization modes surrounding an ion and its neutral molecule should be quite different (see section V.C of ref 5a). Moreover, Lin and co-workers⁴ stress the need to account for the expectation that the modes in the initial and final electronic states are not parallel, as generally assumed in electron transfer theories. Rather, the final state modes must be linear combinations of those for the initial state.⁶

Voth and Lin use quite different theoretical methods, but both approaches reduce, as they should, in the limit of linear coupling to a standard Marcus version of electron transfer theory. Voth’s approach is based on deriving a free energy surface $F(X)$ for the reaction coordinate $X = \Delta E$, where ΔE is the energy difference between the initial and final molecular states in the electron-transfer process. The surfaces $F(X)$ for the initial and final states represent the “Marcus parabolas” that describe the influence of solvent fluctuations on the electron-transfer process. Lin, on the other hand, applies a truncated cumulant expansion approximation to the quantum mechanical generating function treatment of nonadiabatic processes that is based on the pioneering theory by Kubo and Toyozawa⁷ and that has subsequently been extended to radiationless processes in mo-

lecular systems.^{8–10} An earlier treatment of electron transfer by Weintraub and Bixon¹¹ also includes frequency changes within a classical multimode formulation but likewise produces rather complicated integral expressions for the rate. In this paper, we follow the generating function approach^{10,12} for treating the quadratic coupling model and introduce approximations that lead to compact, closed form, physically transparent expressions for the electron transfer rate with the following features: (a) In accord with the work of Lin and Voth, the expressions reduce in the high-temperature limit to those of the Marcus theory when the frequency changes between initial and final states vanish. The rate expressions are readily modified with the Hoffman–Ratner model¹³ to describe the freezing of solvent modes near and below the glass transition and its influence on the electron transfer process, although a more thorough description of the low-temperature behavior should probably include a treatment of the heterogeneity of the systems.¹⁴

The quantum theory is derived in the next section for systems in which the modes of the heat bath incur both frequency and geometry changes between the two states. The traditional high-frequency limit is introduced in section III to provide a generalized Marcus type rate expression, and the theory is combined with the Hofmann–Ratner model for the freezing out of modes near and below the glass transition temperature of the solvent.

II. Theory

We consider the nonadiabatic transition from a thermalized initial state s to a final state l . The “modes” in both states are assumed to be parallel but may suffer displacements in equilibrium geometries and frequencies. The thermally averaged golden rule transition rate for the electron transfer from s to l is given by the customary expression,³

$$W_{s \rightarrow l} = Z^{-1} (2\pi/\hbar) \int_{i,j} |T_{si,lj}|^2 \exp(-\beta E_{si}) \delta(E_{si} - E_{lj} - \Delta E) \quad (1)$$

where i labels the quantum state for the modes in state s , j is for the modes in state l , Z is the partition function for the modes in the initial state s , $\beta = 1/kT$, ΔE is the energy gap between the zero point levels in states s and l , and $T_{si,lj}$ is the matrix element of the transition operator.¹⁵ Adopting the Condon approximation for the transition amplitudes and introducing the Fourier representation of the delta function transforms eq 1 into

the generating function representation,^{10,12}

$$W_{s \rightarrow l} = (\hbar)^{-2} |T_{sl}|^2 \int_{-\infty}^{+\infty} dt f(t) \exp(i\Delta E t / \hbar) \quad (2)$$

where the parallel mode assumption implies that the generating function $f(t)$ is the product over all modes k of single mode generating functions $f_k(t)$

$$f(t) = \prod_{\text{modes } k} f_k(t) \quad (3)$$

and where $f_k(t)$ has been obtained analytically for harmonic oscillators that have different equilibrium positions and frequencies in the two electronic states.^{10,16} (The details are not reproduced here, but we note that ref 16 corrects some typos in eq A2 of ref 10 and also provides $f_k(t)$ in a more convenient form than that in ref 10.) When $f(t)$ decays rapidly, it suffices to employ a Gaussian approximation. For the linear coupling model in which the frequencies are identical in the two states, this Gaussian approximation produces the generalized Marcus type expression,¹⁰

$$W_{s \rightarrow l} = (2\pi/\hbar) |T_{sl}|^2 (4\pi D^2)^{-1/2} \exp\left[-\frac{(\Delta E + \lambda)^2}{2\hbar^2 D^2}\right] \quad (4)$$

where λ is the reorganization energy

$$\lambda = \frac{1}{2} \sum_k \hbar \omega_k \Delta_k^2 \quad (5)$$

with $\Delta_k^2 = (m_k \omega_k / \hbar)(Q_k^{(0s)} - Q_k^{(0l)})^2$ the square of dimensionless shift in oscillator positions between the two electronic states and the quantity D^2 given by

$$D^2 = \frac{1}{2} \sum_k (\omega_k \Delta_k)^2 \coth(\beta \hbar \omega_k / 2) \quad (6)$$

The Gaussian approximation becomes better in the high-temperature limit where $\beta \hbar \omega_k \ll 1$, whereupon eq 4 reverts to the standard Marcus form

$$W_{\text{Marcus}} = (2\pi/\hbar) |T_{sl}|^2 (4\pi \lambda k T)^{-1/2} \exp\left[-\frac{(\Delta E + \lambda)^2}{4\lambda k T}\right] \quad (7)$$

The contributions from high-frequency modes that violate the condition $\beta \hbar \omega_k \ll 1$ are readily treated by a convolution method,^{3,12} so eq 7 and the following only considers the low-frequency modes explicitly because the high-frequency “quantum” modes must be treated with their explicit Franck–Condon factors.^{3,11}

The same Gaussian approximation is now applied to the quadratic coupling model in which geometry and/or frequency changes exist between the two electronic states, but the modes are still assumed to be parallel. The conditions for the validity of this approximation should coincide with those used in obtaining the generalized Marcus expression in eq 4. After lengthy algebra, the final result emerges in a generalized Marcus form

$$W_{s \rightarrow l} = (2\pi/\hbar) |T_{sl}|^2 [4\pi(D_1^2 + P^2)]^{-1/2} \times \exp\left[-\frac{(\Delta E + \lambda_1 + \mu)^2}{2\hbar^2(D_1^2 + P^2)}\right] \quad (8)$$

where the new expressions for λ_1 and D_1 involve the frequency ratios $b_k = \omega_k^s / \omega_k^l$,

$$\lambda_1 = \frac{1}{2} \sum_k \hbar \omega_k^l \Delta_k^2 / b_k \quad (9)$$

$$D_1^2 = \frac{1}{2} \sum_k (\omega_k^l \Delta_k / b_k)^2 \coth(\beta \hbar \omega_k^s / 2) \quad (10)$$

and the new quantities μ and P^2 take similar forms as

$$\mu = \frac{1}{2} \sum_k \hbar \omega_k^l \frac{(1 - b_k^2)}{b_k} \coth(\beta \hbar \omega_k^s / 2) \quad (11)$$

$$P^2 = \frac{1}{2} \sum_k \left[\frac{(1 - b_k^2)}{b_k} \omega_k^l \coth(\beta \hbar \omega_k^s / 2) \right]^2 \quad (12)$$

One very important feature of the result in eq 8 is the fact that the new term μ may be of either sign depending of whether the frequencies in the initial state are cumulatively higher (making $\mu < 0$) or lower (making $\mu > 0$) and thereby subtracting or adding, respectively, a temperature-dependent contribution to the reorganization energy. Although the generating function approach does not involve computation of the “Marcus parabolas”, the close correspondence between eq 8 and the Marcus expression in eq 7 enables identifying the optical absorption maximum as $\Delta E + \lambda_1 + \mu$, etc.

III. Simplifying Limits and Discussion

The quantities λ_1 and D_1^2 are modified from the Marcus forms in eqs 5 and 6 by the frequency ratios b_k that may either decrease or increase them. Introducing the definition of b_k into the expressions for the new quantities μ and P^2 and defining the frequency shift ratio $\Gamma_k = \{(\omega_k^l)^2 - (\omega_k^s)^2\} / \omega_k^s^2$, we find

$$\mu = \frac{1}{2} \sum_k \hbar \omega_k^s \Gamma_k \coth(\beta \hbar \omega_k^s / 2) \quad (13)$$

$$P^2 = \frac{1}{2} \sum_k (\omega_k^s \Gamma_k)^2 [\coth(\beta \hbar \omega_k^s / 2)]^2 \quad (14)$$

which have the interesting high- and low-temperature limits

$$\begin{aligned} \mu(T \rightarrow \infty) &\equiv kT\mu_0 = kT \sum_k \{(\omega_k^l)^2 - (\omega_k^s)^2\} / \omega_k^s^2 \\ \mu(T \rightarrow 0) &= \frac{1}{2} \sum_k \hbar \{(\omega_k^l)^2 - (\omega_k^s)^2\} / \omega_k^s \end{aligned} \quad (15)$$

$$\begin{aligned} P^2(T \rightarrow \infty) &\equiv 2\rho(kT/\hbar)^2 = 2(kT/\hbar)^2 \sum_k \{(\omega_k^l)^2 - (\omega_k^s)^2\}^2 / \omega_k^s^4 \\ P^2(T \rightarrow 0) &= \frac{1}{2} \sum_k \{(\omega_k^l)^2 - (\omega_k^s)^2\}^2 / \omega_k^s^2 \end{aligned} \quad (16)$$

exhibiting more explicitly the fact that μ may be of either sign and that these two new quantities depended on the cumulative difference in squared frequencies and its square, respectively.

The theory is readily combined with the Hoffman–Ratner model for the freezing of motions near and below the glass transition. Essentially, their model emerges from the Marcus

rate expression of eq 4 by separating the contributions to D^2 from modes that become restricted near and below T_g and those modes that are unaffected by the glass transition

$$D^2 \rightarrow \frac{1}{2} \sum_k (\omega_k \Delta_k)^2 \coth(\beta \hbar \omega_k / 2) + \frac{1}{2} f(T) \sum_f (\omega_f \Delta_f)^2 \coth(\beta \hbar \omega_f / 2) \quad (17)$$

where, for simplicity, we retain the approximation of identical frequencies in both states. The sum over k in eq 17 contains those modes unaffected by the glass transition, whereas the sum over f contains the modes that become restricted near T_g . The switching function $f(T)$ is defined in eq 7 of ref 13. Because the restriction can be viewed microscopically as a reduction in the geometry shifts Δ_f , it would appear to be consistent to apply a similar separation to the reorganization energy

$$\lambda \rightarrow \frac{1}{2} \sum_k \hbar \omega_k \Delta_k^2 + \frac{1}{2} f(T) \sum_f \hbar \omega_f \Delta_f^2 \quad (18)$$

as a minor embellishment of their model. Similarly, the modes with frequency changes can be partitioned into those unaffected by the glass transition and those whose frequency shifts $\omega_f^1 - \omega_f^s$ are restricted near and below T_g .

The clearest connection with Marcus theory emerges by considering eq 8 in the high-temperature limit of $\beta \hbar \omega_k \ll 1$ for small frequency changes

$$W_{s \rightarrow l} \rightarrow (2\pi/\hbar) |T_{sl}|^2 [4\pi kT(\lambda + \rho kT)]^{-1/2} \times \exp \left[-\frac{(\Delta E + \lambda + \mu_0 kT)^2}{4kT(\lambda + \rho kT)} \right] \quad (19)$$

The difference between μ_0 and ρ implies that eq 19 cannot be

transformed exactly into the Marcus form of eq 7 with a redefined reorganization energy. The apparent activation energy $kT^2 d \ln(W_{s \rightarrow l})/dT$ emerges as a complicated function of kT due to the new terms in μ_0 and ρ , so this temperature dependence should be useful as an experimental probe for the relevance of frequency changes. As noted above, μ_0 may be of either sign, but the interesting case arises when μ_0 is negative because the initial state has (net) higher frequency modes that serve as a reservoir of energy to compensate against the usual Marcus reorganization energy λ .

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