

Virtual Transitions in Nonadiabatic Condensed-Phase Reactions

Julian S. Joseph*[†] and William Bialek[‡]

Graduate Group in Biophysics and Departments of Physics and Molecular and Cell Biology, University of California at Berkeley, Berkeley, California 94720, and NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

Received: August 6, 1992; In Final Form: December 15, 1992

We calculate the rate of a reaction proceeding through a virtual intermediate for arbitrary vibrational potentials in three electronic states, expressing it in a form amenable to saddle-point approximations. Treating the mode-specific case, in which a small number of vibrational modes are coupled to the electronic transitions, dissipation is included by vibrational coupling to a large collection of harmonic oscillators. A semiclassical saddle-point expansion at large energy denominator allows us to identify the criteria for the validity of the two-state approximation, in which the intermediate state is ignored, aside from generating an effective coupling between the initial and final states. We discuss the physical meaning of these criteria, which define a high-energy intermediate. In this case, virtual transfer may dominate over the two-step process. In the limit of a small energy denominator, we find that the virtual transfer rate is not necessarily negligible compared to the first step of a two-step transfer. In this case, the rate is found to depend on the damping of the vibrationally coupled modes over a certain range.

I. Introduction

Electron transfer in a condensed phase is often mediated by one or several virtual intermediate electronic states, in which coherence is maintained until arrival in the final state. In many cases of such virtual transfer (or "superexchange"),^{1–5} the energies of the intermediate electronic configurations are much higher than any energy scale associated with vibrational or polarization modes, so the vibrational dynamics in the intermediate states can be ignored. The intermediate states only serve to provide an effective electronic mixing matrix element between the initial and final states. There are problems, however, in which mediating electronic states are sufficiently close in energy to the initial and final states that vibrational coupling in the virtual transition may play a role in determining the reaction rate. Examples include certain intramolecular reactions^{6,7} and the primary charge separation^{8–19} and recombination reactions²⁰ in photosynthetic reaction centers. In such cases, the effect of the intermediate state(s) is more complex than generating an effective higher-order coupling between the initial and final states.^{6,7,21} This leads us to the general problem of calculating the rate from an initial state to a final state passing virtually through an intermediate state. The same physics may also be applicable to concerted proton transfer²² and energy transfer.

In section II.1 and Appendix A, we derive perturbatively in the electronic matrix elements the general expression for the nonadiabatic virtual rate. The behavior of a simplified three-state model suggests that the virtual rate can be perturbative even at small energy denominator¹⁹ and plausibly is for the primary photosynthetic electron transfer. Hu and Mukamel^{23,24} derived a different form of the general expression for the case of a macroscopic number of vibrational modes coupled to the electronic transitions and performed a short-time expansion to obtain useful approximations. We treat the "mode-specific" case, in which only a small number of vibrational modes are coupled to the electronic transitions, and express the virtual rate in a form amenable to saddle-point approximations that can capture some of the relevant dynamics at longer times. The treatment of mode-specific situations requires some form of damping to yield a finite

rate constant. We use the method of vibrational coupling to a large collection of harmonic oscillators^{25–28} to provide dissipation. Vol'kenshtein and co-workers,²⁹ Kharkats and co-workers,⁶ Lin,³⁰ Kharkats and Ulstrup,³¹ and Kuznetsov and Ulstrup³² considered examples in different regimes than that we will consider here and treated damping in different ways. For lightly damped modes, we find that the virtual rate at small energy denominator depends on the damping coefficient of the vibrationally coupled modes. The saddle-point approach described here could also be used to treat coherent recurrence, in which the dephasing rate is lower than the vibrational frequencies, by including contributions from further saddle-points.

Within models of three coupled electronic state surfaces, we seek systematic semiclassical approximations for the virtual rate. After motivating the approach in section III.1, we use a combination of saddle-point and short-time approximations for high-energy intermediates in section III.2. The leading term is found to be the rate of a two-state system consisting of the initial and final states, with an effective electronic matrix element that has a geometric interpretation in some cases. Physical interpretations can be assigned to the first quantum corrections beyond the leading term. In the case of low-energy intermediates (i.e., small energy denominators), we use the saddle-point approximation in section III.3 and find that many saddle-points contribute to the virtual rate, enhancing it considerably. Summarizing in section IV, we compare the virtual rate with the first rate of the two-step process to find that virtual transfer can dominate with a high-energy intermediate and need not be entirely negligible in the case of a low-energy intermediate.

II. Preliminary Theoretical Considerations

II.1. General Nonadiabatic Virtual Rate Expression. In this section we give a general expression for the virtual rate to go from the initial electronic state (state 1) to the final state (state 3) by means of a virtual transition through an intermediate state (state 2) at the lowest nonvanishing order of perturbation theory in the electronic mixing matrix elements.³³ In the case of electron transfer from the donor to acceptor through an intermediate site, state 1 is DIA, state 2 is D⁺I-A, and state 3 is D⁺IA⁻, where D, I, and A denote the donor, intermediate, and acceptor, respectively. Note, however, that the calculations presented here apply to any virtual electronic transition coupled to vibrational degrees of

* Graduate Group in Biophysics, University of California at Berkeley. Present address: Laboratory of Sensorimotor Research, National Eye Institute, NIH, Bethesda, MD 20892.

[†] Departments of Physics and Molecular and Cell Biology, University of California at Berkeley, and NEC Research Institute.

freedom. In the case of hole transfer, for example, the same formalism and approximations hold with the modification that state 2 is then DI^+A^- . Likewise, the analysis could apply to fluorescence or absorption.

Picture three electronic states and some other degrees of freedom denoted by y_α with conjugate momenta p_α . We can write the Hamiltonian for the system as

$$H = H_0 + H' \quad (1)$$

with

$$H_0 = \sum_{i=1}^3 |i\rangle \langle i| H_i(y_\alpha, p_\alpha) \quad (2)$$

and

$$H' = V_{12}|1\rangle \langle 2| + V_{23}|2\rangle \langle 3| + V_{13}|1\rangle \langle 3| + \text{hermitian conjugate} \quad (3)$$

For simplicity we have made the Condon approximation, so the electronic matrix elements V_{12} , V_{23} , and V_{13} are independent of all the coordinates and momenta. We assume the y_α are initially in thermal equilibrium in electronic state 1. The presence of these other degrees of freedom, and their coupling to the electronic transitions, is necessary for the existence of a well-defined reaction rate from state 1 to state 3, as without them the populations would merely oscillate.

The general expression for the perturbative rate k_{13} from $|1\rangle$ to $|3\rangle$, derived in Appendix A, is found to be $k_{13} = k_V + k_C + k_D$, where

$$k_V = \frac{1}{\hbar^4} \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds_1 \int_0^{\infty} ds_2 [\langle H_{12}(\tau_1) H_{23}(\tau_2) H_{32}(\tau_3) H_{21}(\tau_4) \rangle_1 - \langle H_{12}(\tau_1) H_{21}(\tau_4) \rangle_1 \langle H_{23}(\tau_2) H_{32}(\tau_3) \rangle_2] \quad (4)$$

$$k_C = -\frac{2}{\hbar^3} \text{Im} \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds \langle H_{12}(\tau - s) H_{23}(\tau) H_{31}(0) \rangle_1 \quad (5)$$

and

$$k_D = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau \langle H_{13}(\tau) H_{31}(0) \rangle_1 \quad (6)$$

The time-dependent operators are in the interaction picture with initial values $H_{ij}(0) = V_{ij}|i\rangle \langle j|$. The angle brackets with subscripts denote thermal averages over (y_α, p_α) in the indicated electronic states. In the absence of direct coupling V_{13} , the rate k_{13} reduces to the virtual rate k_V . If the intermediate state were not present, we would be left with a two-state problem, and k_{13} would reduce to the rate of direct transfer k_D .

II.2. Choosing a Class of Models. We now specify a class of three-state models within which we wish to calculate the virtual rate with the above expression. The simplest form we can take for the other degrees of freedom is that of a collection of harmonic oscillators. As discussed in refs 34 and 21, an effective harmonic description is valid for a wide variety of nonlinear systems if the coordinates coupled to the transitions exhibit *linear* response over the time scales relevant to the reaction dynamics. These time scales, which will be rigorously identified in the case of semiclassical dynamics in section III, are often too short for nonlinearities to develop. Simulations of ferrous-ferric transfer in solution³⁵⁻³⁷ indicate a striking degree of linear response. Furthermore, the result for harmonic degrees of freedom given at the end of this section is seen to depend on the potential surfaces only through two-time correlation functions. This suggests that a harmonic description is valid under more general circumstances, provided these correlation functions have well-defined spectral peaks.

We now specialize to the case of N harmonic modes. To simplify the discussion and to facilitate our understanding of the system, we assume there are no frequency shifts or mode rediagonalization in the transitions.

The model is specified by the Hamiltonian

$$H = H_0 + H' \quad (7)$$

$$H_0 = \sum_{r=1}^N \frac{P_r^2}{2} + \sum_{i=1}^3 |i\rangle \langle i| V_i(Q_1, \dots, Q_N) + H_{damping} \quad (8)$$

$$V_i(Q_1, \dots, Q_N) = \epsilon_i + \frac{1}{2} \sum_{r=1}^N \omega_r^2 (Q_r - \bar{q}_{ir})^2 \quad (9)$$

$$H_{damping} = \sum_{l=1}^N \frac{P_l^2}{2} + \frac{1}{2} \sum_{l=1}^N \omega_l^2 (X_l - \sum_{r=1}^N C_{lr} Q_r)^2 \quad (10)$$

$$H' = V_{12}|1\rangle \langle 2| + V_{23}|2\rangle \langle 3| + V_{13}|1\rangle \langle 3| + \text{hermitian conjugate} \quad (11)$$

This is the three-state analogue of a Hamiltonian that has been used in studies of the two-state problem.³⁸⁻⁴¹ The ϵ_i are the electronic-state energies when all the vibrational coordinates Q_r are at their equilibrium positions. There are N vibrational coordinates (Q_r) with frequencies ω_r , mass-weighted so that the kinetic energy is just $P_r^2/2$. In each of the three electronic states, these coordinates have different equilibrium positions \bar{q}_{ir} . To ensure a finite rate, we include damping through coupling to a bath of harmonic oscillators X_l .²⁶⁻²⁸ This has the effect of damping the vibrational correlation functions and destroying phase coherence. Appendix A of ref 41 argues that the Langevin equations for the Q_r are approximately decoupled, so we may as well make the assumption of separate baths for each coordinate; namely, $C_{lr} \neq 0$ for only one r . The correlation functions of the Q_r and P_r decay with time according to damping coefficients γ_r , determined by the C_{lr} and ω_l . We neglect pure dephasing in this treatment.

The thermal averages appearing in the rate expression can be computed with the help of a unitary transformation:^{40,42} $\mathcal{U} = \exp\{i/\hbar \sum_{r=1}^N \bar{P}_r \sum_{i=1}^3 |i\rangle \langle i| \bar{q}_{ir}\}$, where $\bar{P}_r = P_r + \sum_l C_{lr} P_l$. For example, the full four-point correlation function appearing in k_V becomes

$$\begin{aligned} \langle H_{12}(\tau - s_1) H_{23}(\tau) H_{32}(0) H_{21}(-s_2) \rangle_1 = & V_{12}^2 V_{23}^2 \exp\{i\epsilon_{12}(\tau - s_1 + s_2)/\hbar + i\epsilon_{23}\tau/\hbar\} \times \\ & \langle \exp\{i \sum_{r=1}^N q_{12,r} \bar{P}_r(\tau - s_1)/\hbar\} \exp\{i \sum_{r=1}^N q_{23,r} \bar{P}_r(\tau)/\hbar\} \times \\ & \exp\{i \sum_{r=1}^N q_{32,r} \bar{P}_r(0)/\hbar\} \exp\{i \sum_{r=1}^N q_{21,r} \bar{P}_r(-s_2)/\hbar\} \rangle \quad (12) \end{aligned}$$

where $\epsilon_{ij} = \epsilon_i - \epsilon_j$ and the time dependence of P_r is now given by

$$P_r(t) = \exp(i\bar{H}_0 t/\hbar) P_r(0) \exp(-i\bar{H}_0 t/\hbar) \quad (13)$$

with the purely vibrational Hamiltonian

$$\bar{H}_0 = \frac{1}{2} \sum_{r=1}^N (P_r^2 + Q_r^2) + H_{damping} \quad (14)$$

The thermal average on the right-hand side is also computed with respect to \bar{H}_0 and can be performed exactly by a second-order cumulant expansion in the q 's.

We therefore arrive at the rate $k_{13} = k_V + k_C + k_D$, with

$$k_V = (V_{12}V_{23}/\hbar^2)^2 \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds_1 \int_0^{\infty} ds_2 \times \exp\{f_A(\tau, s_1, s_2)/\hbar\} [\exp\{f_B(\tau, s_1, s_2)/\hbar\} - 1] \quad (15)$$

$$k_C = -2(V_{12}V_{23}V_{13}/\hbar^3) \text{Im} \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds \exp\{f_A(\tau, s, 0)/\hbar + f_B(\tau, s, 0)/\hbar\} \quad (16)$$

$$k_D = (V_{13}^2/\hbar^2) \int_{-\infty}^{\infty} d\tau \exp\{f_A(\tau, 0, 0)/\hbar + f_B(\tau, 0, 0)/\hbar\} \quad (17)$$

The functions f_A and f_B are given by

$$f_A(\tau, s_1, s_2) = i\epsilon_{13}\tau + i\epsilon_{12}(s_2 - s_1) + \sum_{r=1}^N q_{r,12}^2 [K_r(\tau - s_1 + s_2) - K_r(0)] + \sum_{r=1}^N q_{r,23}^2 [K_r(\tau) - K_r(0)] \quad (18)$$

$$f_B(\tau, s_1, s_2) = \sum_{r=1}^N q_{r,12} q_{r,23} [K_r(\tau - s_1) - K_r(-s_1) + K_r(\tau + s_2) - K_r(s_2)] \quad (19)$$

where $q_{r,ij} = \bar{q}_{ir} - \bar{q}_{jr}$ and

$$K_r(\tau) = \frac{1}{\hbar} \langle \tilde{P}_r(\tau) \tilde{P}_r(0) \rangle \quad (20)$$

is the two-time momentum correlation function.

The correlation function can be calculated by means of the fluctuation-dissipation theorem⁴³ and expressed⁴⁰ in terms of the frequency-dependent friction coefficient²⁷

$$\eta_r(\Omega) = -i\Omega \lim_{\delta \rightarrow 0^+} \sum_T \frac{(C_{ir}\omega)^2}{\omega_T^2 - (\Omega + i\delta)^2} \quad (21)$$

We work in the ohmic case where the friction coefficient η_r is independent of frequency for all $\Omega \ll \omega_c$ and assume the cutoff frequency ω_c is much higher than any other frequency in the problem. Assuming lightly damped modes ($\eta_r/2 \ll \omega_r$), we get

$$K_r(\tau) = \frac{\omega_r}{2} [e^{-i\omega_r\tau}(\bar{n}_r + 1) + e^{i\omega_r\tau}\bar{n}_r] e^{-\gamma_r|\tau|} \quad (22)$$

where $\bar{n}_r = (e^{\hbar\omega_r/k_B T} - 1)^{-1}$ is the thermal mean number of phonons in the r th mode, T is the temperature, and $\gamma_r = \eta_r/2$ is the damping coefficient of the r th mode. The presence of damping actually causes a shift in the oscillation frequency of the correlation function from the value ω_r appearing in the Hamiltonian. From here onward, ω_r will refer to the oscillation frequency. Because the damping oscillator bath has some finite correlation time $\sim \omega_c^{-1}$, we have $\eta_r(\Omega) \rightarrow 0$ as $\Omega \rightarrow \infty$. This means that the ohmic limit is only approximate and that the correlation function is actually an analytic function of the time, allowing contour distortion in the saddle-point approach that follows.

III. Semiclassical Saddle-Point Expansion

III.1. Application to the Two-State Problem. Semiclassical saddle-point methods ("steepest descent" or "stationary phase") have been used successfully in the past to analyze two-state electron transfer^{40,44,45} and the related problem of solid-state polaron motion.⁴⁶ The saddle-point method is a valid approximation whenever the transition is coupled to at least one mode with $S \equiv \lambda/\hbar\omega \gg 1$, even at zero temperature. Here the reorganization energy is $\lambda = \frac{1}{2}q_{12}^2\omega^2$, with q_{12} the displacement of a coordinate between the two vibrational potential surfaces. A brief review of the method will clarify the subsequent sections.

The two-state rate constant is expressed as an integral of the

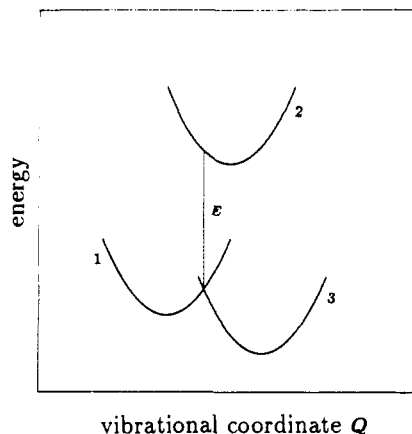


Figure 1. Three-state problem, showing the semiclassical energy denominator E .

form

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau \exp\{g(\tau)/\hbar\} \quad (23)$$

where V is the electronic matrix element and $g(\tau)$ is a function determined by the model parameters. Saddle-points are determined (usually numerically) by the equation $g'(\tau) = 0$, and it is these points about which g is expanded. When at least one mode has $S \gg 1$, the saddle-points are well-separated compared to their widths and the approximation is valid. This situation is referred to as the "semiclassical regime" (often called the "strong coupling case"); the more classical regime with $k_B T \gg \hbar\omega$ for all the modes will be referred to as the "high-temperature limit". The saddle-point method is capable of capturing non-Gaussian energy-gap dependence, which results when the saddle-points contributing to the integral are distant from the origin by an amount comparable to or greater than a vibrational period. This can happen if there are both "low-frequency" (L) modes with $S_L = \frac{1}{2}q_{L12}^2\omega_L/\hbar \gg 1$ and "high-frequency" (H) modes with $S_H = \frac{1}{2}q_{H12}^2\omega_H/\hbar \lesssim 1$ and $\hbar\omega_H > k_B T_{room}$. The shape of such non-Gaussian dependence has been described elsewhere.^{40,45} By contrast, the short-time approximation (expanding about the origin) yields a Gaussian energy-gap dependence.

Even when the phase coherence of the system is maintained for several vibrational periods, the saddle-point approach can still be used by including contributions from additional saddle-points. The coherence time,⁴⁷ the time for the phase of a wavepacket to be randomized, is given by⁴⁴

$$\tau_{COH} \sim \left[\sum_{r=1}^N \gamma_r \frac{q_{r,12}^2 \omega_r}{2\hbar} (2\bar{n}_r + 1) \right]^{-1} \quad (24)$$

The contribution from the n th saddle-point is smaller than that of the primary saddle ($n = 0$) by $\sim e^{-2\pi n/(\omega_r \tau_{COH})}$. The statement that coherent recurrence in the final state can be neglected is equivalent to the assumption $\omega_r \tau_{COH}/2\pi < 1$ for all modes. This is equivalent to neglecting all saddle-points except that closest to the origin, i.e., that most like the short-time approximation. These considerations motivate us to apply saddle-point methods to the three-state problem, rather than the short-time expansions used by many researchers.^{6,23,24,30}

III.2. Large Energy Denominator. *A. Asymptotic Expansion.* In the three-state problem, we are particularly interested in the extremes of large and small energy denominator. These cases are distinguished by whether the intermediate state is well-separated in energy from the initial and final states in some sense to be clarified below.

First consider the case of a high-energy intermediate state. The problem is depicted in Figure 1 for the case of one harmonic coordinate. We want an asymptotic expansion for the rate integral of the three-state system that has the two-state rate (with the

effective matrix element) as the leading term. Motivated by the success of the saddle-point method in approximating and elucidating the two-state problem, we seek an analogous approach for the three-state problem. We confine ourselves to situations where the activation energy is determined by the initial/final crossing; other situations have been studied by Kharkats and co-workers.⁶ Throughout the paper, we confine ourselves to a regime with $\omega_r \tau_{COH} / 2\pi \ll 1$ for all modes.

There are two features of the virtual rate integral k_V in eq 15 that could require deviations from the saddle-point approach used in the two-state problem. First, the integrand in k_V has two terms. The integral of each one separately is divergent. This can be seen by making a change of variables $s = 1/2(s_2 + s_1)$ and $a = s_2 - s_1$. We find that as $s \rightarrow \infty$ the integral over τ and a of each of the two terms approaches the finite value $k_{12}k_{23}$, where k_{12} and k_{23} are the two-state perturbative rates from states 1 to 2 and 2 to 3, respectively. (This can be seen from eqs 15, 18, 19, and 22). Performing the remaining s integral then only makes sense for the difference of the two terms and not for each of them separately. As shown in Appendix B, the case of large E can generally be dealt with by considering only the first term of the integrand. (This is not an issue for the cross-term k_C in eq 16.)

The second distinguishing feature of the three-state problem is that the limits on the s_1 and s_2 integrals only extend from 0 to ∞ . Recall that the critical points dominating an integral include not just the saddle-points but also the boundary of integration.⁴⁸ In the case of large E , we include the effects of the boundary by performing short-time expansions in s_1 and s_2 , while doing the saddle-point expansion in τ . The results of the calculation show that the typical values of s_1 and s_2 contributing to the integral are indeed short when the intermediate state is well-removed in energy from the initial and final states.

The procedure for generating the asymptotic expansion for k_V is as follows. Let $f \equiv f_A + f_B$ denote the argument of the exponential in the first term of eq 15. Setting $s_1 = s_2 = 0$, the saddle-points τ_* are determined from

$$f_r(\tau_*, 0, 0) \equiv \frac{\partial f}{\partial \tau}(\tau_*, 0, 0) = 0 \quad (25)$$

either numerically or, in some limits, analytically. In the large E case, damping is ignored in the computation of all derivatives. This is justified if the width of the saddle-points $\tau_{FC} \ll \tau_{COH}$. Examination of the integrand shows that this results in the same saddle-point equation as in the two-state initial/final problem. We expand f about $(\tau_*, 0, 0)$. Keeping the terms in s_1, s_2 , and $(\tau - \tau_*)^2$ up in the exponential, we expand the exponential of all other terms. This results in integrals of the form $\int_{-\infty}^{\infty} d\tau \tau^n e^{-\tau^2}$ and $\lim_{\delta \rightarrow 0^+} \int_0^{\infty} ds s^n e^{-is - \delta s}$, which can be done exactly. We assume that the τ contour can be distorted to pass through the saddle-point along the contour of steepest descent. We collect terms proportional to a given power of \hbar . (In doing this, we do not expand \bar{n}_r in powers of \hbar .) For the cross-term k_C in eq 16, we apply the analogous procedure with only one s variable. (This asymptotic expansion is similar in some ways to the loop expansion of quantum field theory⁴⁹ or quantum many-body physics.⁵⁰ The Feynman rules for a diagrammatic approach to this expansion have been given elsewhere.⁵¹)

B. Leading Term. The leading term is found to be identical with the rate of a two-state system consisting of only the initial and final states, with an effective matrix element $V_{12}V_{23}/E + V_{13}$:

$$k_{13}^{(0)} = (V_{12}V_{23}/E + V_{13})^2 / \hbar^2 (2\pi)^{1/2} \tau_{FC13} e^{f(\tau_*, 0, 0)/\hbar} \quad (26)$$

where the "Franck-Condon time" is

$$\tau_{FC13} \equiv (-\hbar / f_{rr}(\tau_*, 0, 0))^{1/2} \quad (27)$$

and the quantity playing the role of the semiclassical energy

denominator is

$$E \equiv -if_{s_2}(\tau_*, 0, 0) = if_{s_1}(\tau_*, 0, 0) \quad (28)$$

The exponential factor is precisely that of the direct transfer rate in a two-state system consisting of states $|1\rangle$ and $|3\rangle$. Because this has been obtained with a saddle-point expansion, it reproduces the non-Gaussian ϵ_{13} dependence already described in the two-state problem.^{40,45} This causes the full ϵ_{13} dependence of this expansion to differ from that of eq 4.12c of ref 24.

In the limit $\omega_r |\tau_*| \ll 1$ for all the modes, we retrieve the short-time approximation and, this becomes the well-known Marcus/Hopfield expression^{52,53} with the above effective matrix element. The physical meaning of the saddle-point time $|\tau_*|$ is the time the vibrational coordinates spend tunneling between electronic states. The limit $\omega_r |\tau_*| \ll 1$ then means that vibrational quantum effects are weak. This limit can occur if the reaction is activationless, i.e., if $\epsilon_{13} = \lambda_{13}$, where $\lambda_{13} \equiv \sum_{r=1}^N (1/2) q_{r,13}^2 \omega_r^2$ is the reorganization energy for the overall reaction. In this case, $\tau_* = 0$. This limit also occurs in the high-temperature limit, $\hbar \omega_r \ll k_B T$, for all the modes. If there are high-frequency modes coupled to the reaction that have $\hbar \omega > k_B T_{room} \sim 200 \text{ cm}^{-1}$, as there almost certainly are in the photosynthetic systems,^{54-56,45} we are never in the high-temperature limit and vibrational quantum effects qualitatively change the temperature and energy-gap dependences.⁵⁷⁻⁵⁹ In general, $\tau_* \neq 0$, and this leading term itself contains quantum effects.

As in the two-state problem, an important time scale is the width of the saddle-point, the Franck-Condon time τ_{FC13} . In the limit $\omega_r |\tau_*| \ll 1$ for each mode, this simplifies to

$$\tau_{FC13} = [\hbar / \sum_{r=1}^N q_{r,13}^2 \omega_r^3 (\bar{n}_r + 1/2)]^{1/2} \quad (29)$$

which in the high-temperature limit becomes $\tau_{FC13} = (\hbar / 2\lambda_{13} k_B T)^{1/2}$. The physical meaning of τ_{FC13} is the time for the energy of a vibrational wavepacket moving through the crossing point to change by one vibrational quantum due to the force exerted on it by the potential surfaces. On this time scale, vibrational forces cause two wavepackets, both initially at the crossing point, to lose coherent overlap with each other as they move on the initial- and final-state potential surfaces, respectively. For biological electron transfer, it is typically on the order of $\tau_{FC} \sim 10$ fs. In regimes of physical interest, it is this very short time scale τ_{FC} which governs the microscopic reaction dynamics, and so the response of the system to external forces needs to be linear only over this short time, supporting the validity of the harmonic approximation for the vibrational motions.^{21,34}

The semiclassical energy denominator is given by

$$E = \epsilon_{12} + \sum_{r=1}^N [q_{r,12} q_{r,13}^2 K_r^u(\tau_*) - 1/2 q_{r,12} q_{r,23} \omega_r^2] \quad (30)$$

Because we neglect damping in the computation of derivatives in this section, we introduce the undamped correlation function

$$K_r^u(\tau) = \frac{\omega_r}{2} [e^{-i\omega_r \tau} (\bar{n}_r + 1) + e^{i\omega_r \tau} \bar{n}_r] \quad (31)$$

In the case of only one mode, the energy denominator simplifies to

$$E = \epsilon_{12} - \epsilon_{13} \frac{q_{12}}{q_{13}} + \frac{1}{2} q_{12} q_{23} \omega^2 \quad (32)$$

which agrees with eq 9 of ref 31 in the case $q_{12} = q_{23}$. This is precisely the energy vertically from the initial/final crossing point to the intermediate state, as in Figure 1. Note that in the case of two or more modes the initial/final crossing is not a point but rather a curve, surface, or hypersurface of vibrational configurations. When the reaction is nearly activationless, so that $\omega_r |\tau_*| \ll 1$, the semiclassical energy denominator for N modes can be

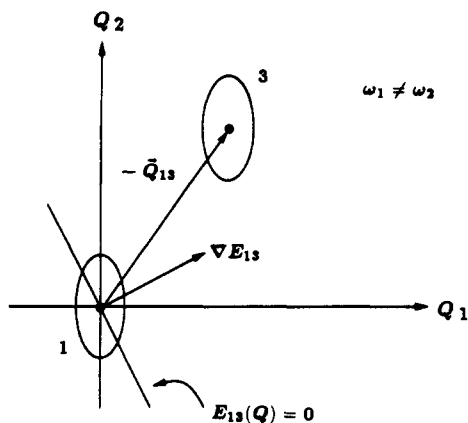


Figure 2. The semiclassical energy denominator is generally temperature-dependent for two or more vibrational modes. An explanation for this is that the energy gradient ∇E_{13} generally would not be the direction to go from the initial equilibrium through the minimum of the initial/final crossing.

written

$$E = \epsilon_{12} - \lambda_{12} + (\epsilon_{13} - \lambda_{13}) \frac{\sum_{r=1}^N q_{r,12} q_{r,13} \omega_r^3 (\bar{n} + 1/2)}{\sum_{r=1}^N q_{r,13}^2 \omega_r^3 (\bar{n} + 1/2)} \quad (33)$$

which agrees with the energy denominator of eq 5.3b of ref 24 if we make the correspondence

$$\int d^3r \bar{D}_j(\vec{r}) \cdot \bar{P}(\vec{r}) \rightarrow \sum_{r=1}^N \omega_r^2 q_{r,j} q_r \quad (34)$$

(Equation 30 is the generalization of this to situations with $\omega|\tau_*| \gtrsim 1$.) A geometric meaning for E may be extracted in the high-temperature limit, where E is just the energy vertically from the *minimum* of the initial/final crossing to the intermediate state (hyper)surface.

With more than one mode, E is slightly temperature dependent, barring the special cases of an activationless reaction, the high-temperature limit, and $\omega_1 = \omega_2$. Starting at the initial equilibrium, at low temperatures the system tends to follow the initial/final potential difference gradient (see Figure 2). This path generally does not pass through the minimum of the initial/final crossing. (Note that in cases without frequency shift, as we are considering, this minimum lies on the line connecting the initial and final equilibria.) At high temperatures the system may go against the gradient, and the easiest way of crossing to the final state without tunneling is by going to the initial/final crossing minimum. As the temperature is raised from low to high temperatures, the position at which the system most typically leaves the initial state shifts to the initial/final minimum, shifting the effective energy denominator E . Any corrections due to fluctuations about this minimum appear in the first corrections of the expansion, since they are of relative order $\sim (\hbar/E\tau_{FC})^2$.

C. Three-State Corrections. The higher terms of the expansion contain pieces that are also present in the two-state problem plus pieces that are unique to the three-state problem. Treating the system within the two-state approximation is then equivalent to neglecting these corrections, and we can gain physical insight into the meaning of the two-state approximation by investigating their significance. The physical meaning of these quantum corrections can be most easily extracted by examining the case of just one low-frequency mode. We find, through $\mathcal{O}(\hbar)$

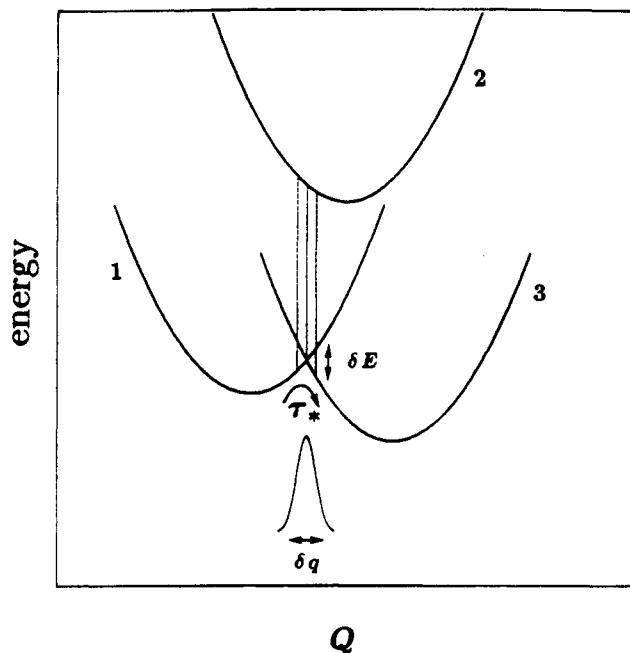


Figure 3. Deviation from two-state behavior. Wavepacket spreading during vibrational tunneling. The typical tunneling time is given by τ^* , the saddle-point location. During this time, a wavepacket at the crossing point spreads by an amount δq , blurring the energy denominator by δE .

corrections,

$$k_{13} \sim k_{13}^{(0)} \{1 + \text{"two state"} + \text{"spreading wavepacket"} + \text{"overlap loss"}\} \quad (35)$$

The leading term $k^{(0)}$ was given in eq 26 and described above.

The $\mathcal{O}(\hbar)$ two-state corrections appear in the semiclassical expansion of the two-state initial/final problem. The first two-state correction for one mode at $T = 0$ is $-(1/12)(\hbar\omega)/\lambda_{13}$. Thus even at $T = 0$, where any mode is quantum-mechanical in the sense that $\bar{n} \ll 1$, a mode may be semiclassical in the sense that its quantum is small compared to the "classical" energies of the problem, such as reorganization energies.

The other pieces of the $\mathcal{O}(\hbar)$ correction are entirely due to the three-state character of the problem. The first of these,

$$\text{"spreading wavepacket"} \equiv \hbar q_{12} q_{23} [K''(\tau_*) - K''(0)]/E^2 \quad (36)$$

is named for its interpretation in situations with $\omega|\tau_*| \ll 1$. In that limit, it is

$$\approx \frac{1}{2} \frac{\partial E_{12}}{\partial Q} \frac{\partial E_{23}}{\partial Q} (\hbar i\tau_*)/E^2 \quad (37)$$

where $E_{12}(Q) \equiv V_1(Q) - V_2(Q)$ and $E_{23}(Q) \equiv V_2(Q) - V_3(Q)$. The magnitude of the real time $i\tau_*$ is the time spent vibrationally tunneling from reactants to products. When the reaction is activationless or at high-temperatures, $\tau_* = 0$, because there is no need to tunnel. The quantity $\delta Q \equiv |\hbar i\tau_*|^{1/2}$ is then the amount of spreading of a wavepacket placed at the crossing point while the system tunnels from reactants to products. The spreading of a wavepacket is a purely quantum-mechanical phenomenon, with \hbar playing the role of a diffusion constant. Because of the gradients of the potential differences $\partial E_{12}/\partial Q$ and $\partial E_{23}/\partial Q$, this spread or blurring in position directly results in a blurring of the energy denominator δE , as shown in Figure 3. The two-state approximation assumes that spreading wavepacket $\ll 1$. This is equivalent to the statement that this blurring of the energy denominator is much smaller than the energy denominator itself. This correction could be viewed as being due to the coordinate dependence of the energy differences between the states and so reflects the "non-Condon" quality that the intermediate state surface induces on an effective matrix element coupling the initial

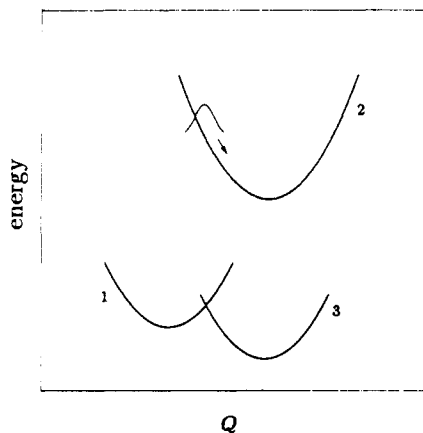


Figure 4. Deviation from two-state behavior. Dynamics in the virtual intermediate state. Vibrational forces move the wavepacket away from the crossing-point in a time typified by the Franck-Condon time, τ_{FC} .

and final states. When the reaction is activationless or in the high-temperature limit, $\tau_* = 0$ and this correction is negligible. The other three-state piece in the $\mathcal{O}(\hbar)$ correction is

$$\text{overlap loss} \equiv -2 \left(\frac{\hbar}{E\tau_{FC12}} \right)^2 \quad (38)$$

where $\tau_{FC12} \equiv [\hbar/\lambda_{12}\omega \coth(\hbar\omega/2k_B T)]^{1/2}$. If this correction is ≥ 1 , then during the time $\sim \hbar/E$ allowed in the virtual intermediate by the uncertainty principle, the vibronic force displaces a vibrational wavepacket from the crossing point enough to lose overlap with a wavepacket held fixed there. That is, the time that the system is allowed to spend in the virtual intermediate by the uncertainty principle is so long that vibrational dynamics in the intermediate state become significant (see Figure 4). The sign indicates that mixing is being cut short, reducing the rate. In terms of energies, this correction is $-4\lambda_{12}\hbar\omega(\bar{n} + 1/2)/E^2$. The energy in the numerator is the energy fluctuation due to the thermal and quantum coordinate fluctuations in the presence of the vibronic force $F_{12} \equiv \omega^2 q_{12}$. This correction also contains, for two or more modes, the effects of fluctuations along the initial/final crossing curve, since these are of order $\langle (F\delta q)^2 \rangle / E^2 \sim (\hbar/(E\tau_{FC}))^2$ relative to the leading term.

The $\mathcal{O}(\hbar^2)$ corrections are quite complicated in appearance. In activationless cases with nearly vanishing energy denominator, we have found numerically that the largest such correction is $2(\hbar/(E\tau_{FC12}))^4$, with the interpretation already discussed.

If only the leading term is considered, then in the presence of a matrix element V_{13} directly connecting the initial and final states it is possible for the direct coupling to precisely cancel the effective coupling $V_{12}/V_{23}/E$ from the virtual transition. If the rate were given exactly by the leading term, it would be proportional to $(V_{13} + V_{12}V_{23}/E)^2$ and there would be the possibility of making the rate vanish (as might be desirable for a recombination reaction) by appropriately adjusting the matrix elements and/or energy denominator. Quantum effects are responsible for corrections to the leading term that prevent complete destructive interference from occurring, placing a nonzero quantum minimum on the rate. At present, however, we know of no reaction that appears to approach this quantum minimum rate. Having said this, we treat only the case $V_{13} = 0$ for the remainder of the paper.

Here we give the detailed expressions for the virtual rate at large E , through the $\mathcal{O}(\hbar)$ corrections, organized by powers of E :

$$k_V \simeq \left(\frac{V_{12}^2 V_{23}^2}{E^2} \right) a_0 [1 + a_1/E + a_2/E^2] \quad (39)$$

with

$$a_0 = (1/\hbar^2)(2\pi)^{1/2} \tau_{FC13} e^{f(\tau_*, 0, 0)/\hbar} \quad (40)$$

$$a_1 = \frac{\hbar}{\left(\sum_{r=1}^N q_{r,13}^2 K_r^{u''}(\tau_*) \right)^2} \times \left[\left(\sum_{r=1}^N q_{r,13}^2 i K_r^{u'''}(\tau_*) \right) \left(\sum_{r=1}^N q_{r,12} q_{r,13} K_r^{u''}(\tau_*) \right) - \left(\sum_{r=1}^N q_{r,12} q_{r,13} i K_r^{u'''}(\tau_*) \right) \left(\sum_{r=1}^N q_{r,13}^2 K_r^{u''}(\tau_*) \right) \right] \quad (41)$$

and

$$a_2 = \frac{\hbar}{\sum_{r=1}^N q_{r,13}^2 K_r^{u''}(\tau_*)} \left[3 \left(\sum_{r=1}^N q_{r,12} q_{r,13} K_r^{u''}(\tau_*) \right)^2 - \left(\sum_{r=1}^N q_{r,13}^2 K_r^{u''}(\tau_*) \right) \left(\sum_{r=1}^N q_{r,12}^2 K_r^{u''}(\tau_*) \right) + 2 \sum_{r=1}^N q_{r,12} q_{r,23} (K_r^{u''}(\tau_*) + \omega_r^3(\bar{n}_r + 1/2)) \right] \quad (42)$$

Because τ_* is generally determined numerically from eq 25, these expressions cannot be simplified further. The function $K_r^u(\tau)$ is given by eq 31 as a simple combination of exponentials, and its derivatives will not be written here. The semiclassical energy denominator is most easily computed from eq 30. Two-state corrections have not been written here; they are small for the situations of interest.

III.3. Small Energy Denominator. The above expansion certainly breaks down when the semiclassical energy denominator $E \approx 0$. This may occur in the photosynthetic primary charge separation. Perturbation theory can be valid nonetheless, as indicated by the behavior of a simplified three-state model.¹⁹ The essential reason is that vibrational dynamics and dephasing processes limit the coherent mixing into and out of the intermediate state. The rates of these processes, τ_{FC}^{-1} and τ_{COH}^{-1} , can be much larger than the electronic mixing frequency (V/\hbar), thus rescuing perturbation theory. Furthermore, even in the extreme case $E = 0$ the system may still be semiclassical, in the sense that the electronic-vibrational coupling constants $S \gg 1$. At small E , we confine our calculations to nearly activationless reactions for the sake of simplicity; experiments indicate that the photosynthetic primary separation falls into this category.⁶⁰

We now estimate the virtual rate in situations with $E = 0$ and obtain corrections in powers of E , using a semiclassical saddle-point expansion. As discussed in Appendix B and below, we locate and evaluate the contributions from saddle-points of the first term in the integrand of eq 15. The second term plays the crucial role of canceling the first term very far from the origin, rendering the rate finite.

For small E , boundary effects are unimportant and the stationary points of the integrand are the dominant critical points. We look for the saddle-point in three (complex) dimensions. Here we work in cases where $E = 0$ and the reaction is activationless ($\epsilon_{13} = \lambda_{13}$). We assume $(\epsilon_{23} - \lambda_{23})^2 \tau_{FC23}^2 / \hbar^2 \gg 1$, where τ_{FC23} is defined as analogous to τ_{FC13} in eq 29. This means that k_{23} is far from activationless. We further assume $\tau_{COH} \gg \tau_{FC}$. In general the saddle-point structure is complicated. To simplify the situation, we suppose all the mode frequencies are equal (ω), as are the damping coefficients (γ). For light damping, we can ignore the damping in locating the saddle-points; this will be justified below. We then have a three-dimensional lattice of saddle-points spaced by $2\pi/\omega$. If the coherence time is much shorter than the vibrational period, all the saddle-points are exponentially attenuated relative to the one at the origin, except for those at $(\tau_* = 0, s_1 = n2\pi/\omega, s_2 = n2\pi/\omega)$, with $n \geq 0$. We will make this assumption, although longer coherence times can be handled by including additional saddle-points. Let $s = 1/2(s_2$

+ s_1) and $a = s_2 - s_1$, so the saddle-points are at ($\tau = 0$, $a = 0$, $s = n2\pi/\omega$). For $n \geq 1$, we can write the exponent function in eq 15 as

$$f = f_A + f_B \approx i\epsilon_{13}\tau + i\epsilon_{12}a + \sum_{r=1}^N q_{r,12}^2 [K_r^u(\tau + a) - K_r^u(0)] + \sum_{r=1}^N q_{r,23}^2 [K_r^u(\tau) - K_r^u(0)] + \sum_{r=1}^N q_{r,12}q_{r,23} [K_r^u(\tau + 1/2a - s) - K_r^u(1/2a - s) + K_r^u(\tau + 1/2a + s) - K_r^u(1/2a + s)] e^{-\gamma s} \quad (43)$$

where $K_r^u(\tau)$ is the undamped correlation function given in eq 31. The only approximation that has been made here is neglecting τ and a in the damping factors. This is justified because the range of τ and a contributing to the integral is on the order of τ_{FC} , which is small compared to the value of $s = n2\pi/\omega$ for $n \geq 1$. We will discuss the $n = 0$ saddle-point contribution shortly.

In most applications of the saddle-point method, the function would be expanded about the saddle-point to quadratic terms. If we neglect damping, however, the 3×3 Hessian matrix has a null eigenvector. We must include nonquadratic terms, but we must also include damping in the expansion to ensure that successive saddle-points give smaller contributions.⁶¹ For $\epsilon_{13} = \lambda_{13}$ and $E = 0$, with $\gamma \ll \omega$, the expansion gives

$$f \approx i\gamma\tau s \sum_{r=1}^N q_{r,12}q_{r,23}\omega^2 + i\tau(s - n2\pi/\omega)^2(1/2) \sum_{r=1}^N q_{r,12}q_{r,23}\omega^4 + \tau^2(1/2) \sum_{r=1}^N q_{r,13}^2 K_r^{u''}(0) + \tau a \sum_{r=1}^N q_{r,12}q_{r,13} K_r^{u''}(0) + a^2(1/2) \sum_{r=1}^N q_{r,12}^2 K_r^{u''}(0) \quad (44)$$

Other terms with damping can be neglected, because for $\gamma \ll \omega$ they have negligible effects on the rate, as shown below. We have included cubic terms that have s -dependence. All such cubic terms aside from that shown have vanishing coefficients at these saddle-points if damping is neglected. (Including damping in these coefficients only leads to negligible corrections in the rate.) The $\tau(s - n2\pi/\omega)^2$ term shown is the nonvanishing nonquadratic term of lowest order and must be included to obtain the contribution from the " n th" saddle-point at ($\tau = 0$, $a = 0$, $s = n2\pi/\omega$). Cubic terms without s -dependence lead to corrections that are small in the semiclassical limit.

We can now compute the n th saddle-point contribution. Assume the (τ, a) Hessian determinant does not vanish. We can extend the limits of the a -integral from $[-2s, +2s]$ to $[-\infty, +\infty]$; this is justified because the range of values of a contributing to the integral is of the order τ_{FC} , which is much smaller than s . After performing the Gaussian τ and a integrals, we have

$$k_V \approx V_{12}^2 V_{23}^2 \frac{2\pi}{\hbar^3 \Lambda^2} \int_0^\infty ds \sum_{n=1}^\infty \exp\left\{-\frac{u}{\omega^4} (2\gamma s + \omega^2(s - n2\pi/\omega)^2)^2\right\} \quad (45)$$

where

$$\Lambda^4 = \frac{1}{\hbar^2} \left[\left(\sum_{r=1}^N q_{r,12}^2 K_r^{u''}(0) \right) \left(\sum_{r=1}^N q_{r,13}^2 K_r^{u''}(0) \right) - \left(\sum_{r=1}^N q_{r,12}q_{r,13} K_r^{u''}(0) \right)^2 \right] \quad (46)$$

is the (τ, a) Hessian determinant⁶² and

$$u = \frac{\left(\sum_{r=1}^N q_{r,12}q_{r,23} K_r^{u'''}(0) \right)^2 \left(\sum_{r=1}^N q_{r,12}^2 K_r^{u''}(0) \right)}{2\hbar^3 \Lambda^4} \quad (47)$$

The saddle-points are well-separated compared to their widths, so may extend the integral over each saddle-point to the interval $[-\infty, \infty]$. In the exponential, we can rewrite $2\gamma s = 2\gamma n2\pi/\omega + 2\gamma(s - n2\pi/\omega)$ and neglect the latter term, since for $\gamma \ll \omega$ it does not vary appreciably from 0 over the width of the saddle. Multiplying out the square in the exponential, the cross-term quadratic in $(s - n2\pi/\omega)$ can also be neglected. Its variation from 0 is negligible for s in the width of the saddle and n contributing to the sum. The expression then factorizes into an integral and a sum. The integral is $\int_{-\infty}^\infty ds e^{-us^4} = 2u^{-1/4}(1/4)\Gamma(1/4) \approx 2u^{-1/4}$. The sum is $\sum_{n=1}^\infty \exp\{-n^2/2N_s^2\} \approx (\pi/2)^{1/2} N_s$, where

$$N_s = (\omega/2\pi\gamma)(\omega^4/8u)^{1/2} \quad (48)$$

is assumed $\gg 1$. This corresponds to the assumption $(\tau_{COH}/\tau_{FC})(2\bar{n} + 1) \gg 1$, which is consistent with our earlier assumption $\tau_{COH} \gg \tau_{FC}$. Corrections for nonzero E are computed by expanding the factor $e^{iEa/\hbar}$ inside the integral; corrections for non-zero activation energy can be computed similarly.

We must justify the neglect of all damping terms except that included in eq 44. The other damping terms change either the (τ, a) Hessian determinant or coefficients of cubic terms. The inclusion of such terms multiplies the exponent in eq 45 by $(1 + \mathcal{O}(1)\gamma s)$, which has a negligible effect on the saddle-point integral and on the sum over saddle-points. We can also clarify the validity of expanding about the points ($\tau = 0$, $a = 0$, $s = n2\pi/\omega$). This is valid if the combination of derivatives constituting Λ^4 and u undergo negligible changes $\Delta(\Lambda^4)$ and Δu upon displacement to the exact saddle-points. To lowest nonvanishing order in γ/ω , the deviations from the exact saddle-point locations are $\Delta\tau$, Δa , and Δs , each $\sim \mathcal{O}(1)\gamma/\omega^2$. We then have

$$\Delta(\Lambda^4)/\Lambda^4 \sim \mathcal{O}(1) \left| \frac{K_r^{u'''}(0)}{K_r^{u''}(0)} \right| \frac{\gamma}{\omega^2} \sim \mathcal{O}(1)(\gamma/\omega)(2\bar{n} + 1)^{-1} \ll 1 \quad (49)$$

and also

$$\Delta u/u \sim \mathcal{O}(1) \left| \frac{f_{\tau\tau s}}{f_{\tau s s}} \right| \frac{\gamma}{\omega^2} \sim \mathcal{O}(1)(\gamma/\omega)(2\bar{n} + 1) \quad (50)$$

To ensure the validity of expanding about these points, we must require $(\gamma/\omega)(2\bar{n} + 1) \ll 1$.

The computation of the $n = 0$ saddle-point contribution is complicated by the boundary of integration. For $n = 0$, we can neglect damping altogether in the expansion of eq 44, assuming $\tau_{FC} \ll \tau_{COH}$. Following the above procedure, we see that this saddle-point contribution is of the same order of magnitude as the others contributing to the sum, i.e., those with $n \lesssim N_s$. Since $N_s \gg 1$ under these assumptions, we are justified in neglecting the $n = 0$ saddle-point, because it is only one out of many contributing saddle-points.

We now summarize the expression for the virtual rate at small E , in the case of activationless reactions. We have assumed $(\epsilon_{23} - \lambda_{23})^2 \tau_{FC}^2 / \hbar^2 \gg 1$, $(\gamma/\omega)(2\bar{n} + 1) \ll 1$, and $\tau_{COH} \gg \tau_{FC}$. We have

$$k_V \approx \frac{V_{12}^2 V_{23}^2}{\hbar} b_0 [1 + b_2 E^2] \quad (51)$$

where

$$b_0 = N_s \frac{(2\pi)^{3/2}}{\hbar^3 \Lambda^2} u^{-1/4} \quad (52)$$

and

$$N_s = \frac{\omega}{2\pi\gamma} \left(\frac{\omega^4}{8u} \right)^{1/2} \quad (53)$$

if all the mode frequencies and damping coefficients are equal; in more complicated cases this gives the order of magnitude. Also,

$$\Lambda^4 = \frac{1}{\hbar^2} \left[\left(\sum_{r=1}^N q_{r,12}^2 \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right) \left(\sum_{r=1}^N q_{r,13}^2 \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right) - \left(\sum_{r=1}^N q_{r,12} q_{r,13} \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right)^2 \right] \quad (54)$$

and

$$u = \frac{\left(\sum_{r=1}^N q_{r,12} q_{r,23} \omega_r^4 \right)^2 \left(\sum_{r=1}^N q_{r,12}^2 \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right)}{8 \hbar^3 \Lambda^4} \quad (55)$$

Furthermore,

$$b_2 = - \left[1 + \frac{1}{\hbar^2 \Lambda^4} \left(\sum_{r=1}^N q_{r,12}^2 \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right) \left(\sum_{r=1}^N q_{r,13}^2 \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right) \right] / \left[-4 \hbar \sum_{r=1}^N q_{r,12}^2 \omega_r^3 \left(\bar{n}_r + \frac{1}{2} \right) \right] \quad (56)$$

The dependence of the rate on small E is roughly

$$k_V(E) \sim k_V(0) \left[1 - \mathcal{O}(1) \left(\frac{E \tau_{FC}}{\hbar} \right)^2 \right] \quad (57)$$

The energy scale \hbar/τ_{FC} controls the E -dependence near $E = 0$, as has been noted by Hu and Mukamel in the continuum case.^{23,24}

IV. Summary and Discussion

We have used saddle-point methods to investigate the problem of virtual transitions in vibrationally coupled three-state systems with a small number of vibronically coupled modes. We considered modes that are underdamped but have vibrational periods long compared to the coherence time.

At large energy denominator, the method reveals the corrections to two-state behavior. The two-state approximation can be checked for a given system by comparing the leading term of eq 39 with its higher terms. The physical interpretation of one of these corrections is the quantum-mechanical spreading of wavepackets about the initial/final crossing point. This leads to a spread of values for the energy denominator. Another correction is due to vibrational dynamics in the intermediate state. Because the virtual transition is energy nonconserving in this case, the uncertainty principle limits the time spent in the virtual intermediate to be no more than $\sim \hbar/E$. If this time becomes longer than the time scale on which vibrational dynamics occurs, τ_{FC} , we can no longer ignore the dynamics in the intermediate state.

For small values of the semiclassical energy denominator, the main results are contained in eqs 51–56. We found an inverse dependence of the virtual rate on the damping coefficient for light damping and an enhancement of the rate by the contributions of many saddle-points. This has the physical significance that as the coherence time increases, the virtual rate increases. This is essentially due to the nature of virtual transfer, in which coherence is maintained in the intermediate state. This distinguishes virtual transfer from direct transfer, where the rate is independent of damping in the regime we have considered.

In systems that are candidates for virtual transfer, we often want to know if the initial-state decay is dominated by the virtual rate k_V or by the first step of a two-step process, k_{12} . We assume the dephasing rates $\hbar/\tau_{COH} > V_{12}, V_{23}$, so the density of states has no structure on the energy scale of the matrix elements and both rates k_V and k_{12} are well-defined. We also assume $k_{23} \ll \gamma$, so that k_{23} is well-defined. With a high-energy intermediate, k_{12} is an uphill reaction and is exponentially attenuated. Meanwhile the virtual rate k_V is of a higher order in perturbation theory. If the initial/final activation energy is 0, the approximate criterion for the dominance of virtual transfer is

$$(V_{23}/E)^2 > \exp\{-\epsilon_{12}^*/k_B T\} \quad (58)$$

where ϵ_{12}^* is the energy from the initial equilibrium up to the initial/intermediate crossing. At sufficiently low temperatures, virtual transfer dominates in this regime. As the temperature approaches 0, the two-step process shuts off completely, while the virtual process continues to proceed.

In the case of a low-energy intermediate, the rate k_{12} can be nearly activationless as well, and it is natural to ask whether virtual transfer can be dominant in that case. Under the approximations of semiclassical dynamics and short coherence time and assuming the state 2 equilibration rate is greater than the second two-step rate, virtual transfer cannot dominate the transfer but can make a significant contribution. This can be shown by examining the orders of magnitude of k_V and k_{12} , while ignoring factors of order unity. In the case of two or more lightly damped modes with equal frequencies and damping coefficients, we estimate from eqs 51–55

$$k_V \sim \frac{\omega}{\gamma \hbar^4} V_{12}^2 V_{23}^2 \tau_{FC}^3 S^{-1/4} \left(\bar{n} + \frac{1}{2} \right)^{5/4} \quad (59)$$

while under the same assumptions

$$k_{12} \sim \frac{1}{\hbar^2} V_{12}^2 \tau_{FC} \quad (60)$$

If we require the rate k_{23} is slower than or on the order of the equilibration rate γ in the intermediate, we must have

$$\frac{1}{\gamma \hbar^2} V_{23}^2 \tau_{FC} \lesssim 1 \quad (61)$$

Other situations have been discussed by Kuznetsov and Ulstrup.³² Allowing $k_{23} > \gamma$ invalidates the virtual rate expression we are using in these estimates (see Appendix A). Nonetheless, we expect that if $k_{23} \lesssim \gamma$ the expressions we use here will be of the correct order of magnitude. We then obtain a limit for the relative contribution of virtual transfer:

$$\frac{k_V}{k_{12}} \lesssim \left(\frac{\hbar \omega (\bar{n} + 1/2)}{\lambda} \right)^{3/4} \quad (62)$$

Requiring that the Landau–Zener probabilities are small compared to unity does not yield a stronger relation. At room temperature and using $\lambda \approx 1200 \text{ cm}^{-1}$, the right-hand side of this relation can be estimated as $\approx (k_B T/\lambda)^{3/4} \approx 0.3$, which is not entirely negligible. Within these assumptions and approximations, therefore, it is possible for the virtual rate to make an appreciable contribution at small energy denominator along with two-step transfer.

Acknowledgment. We thank Professors R. Littlejohn and W. H. Miller for helpful conversations and the reviewers for their constructive comments on the manuscript. This work was funded in part by a University of California Regents Fellowship, a National Institutes of Health National Research Service Award (J.S.J.), and a National Science Foundation Presidential Young Investigator Award (W.B.), supplemented by funds from Cray Research Inc., Sun Microsystems, and the NEC Research Institute.

Appendix A: General Expression for the Virtual Rate in Perturbation Theory

In this Appendix, we derive the general expression for the virtual rate perturbatively in the electronic matrix elements in a system with three electronic states and vibrational degrees of freedom y_α . Suppose at time $t = 0$ the system is in state $|1\rangle$ and the vibrational coordinates are in thermal equilibrium. Note that if one calculates the decay rate of the state 1 population through terms of order $V_{12}^2 V_{23}^2$, one cannot identify such terms with the virtual rate, because the rate k_{12} contributes to the state 1 decay rate and it has perturbative corrections proportional to $V_{12}^2 V_{23}^2$. Thus we examine the state 3 population instead. The population of state $|3\rangle$ at a later time t is $P_3(t) = \sum_{i,j} P(i) \cdot |\langle 3|U(t,0)|i\rangle|^2$, where we have summed over all final states of the y_α and thermally averaged over initial states with the Boltzmann weight $P(i)$. $U(t,0) = T \exp\{-i/\hbar \int_0^t d\tau H'(\tau)\}$ is the time evolution operator in the interaction representation. We work in the Markovian limit,⁶³ assuming that the reaction time is much longer than the coherence time for each reaction. We further assume that all the rate constants are well-defined, requiring that γ , the rate of thermal equilibration in state 2, is much greater than k_{23} , the rate of the second step. (As shown in section IV, this does not rule out a dominant virtual process at large energy denominator and does not necessitate a negligible virtual contribution at small energy denominator. Situations in which relaxation in the intermediate is incomplete have been studied by Kuznetsov and Ulstrup.³² At times much shorter than reaction times but much longer than the coherence time, the population takes the form $P_3(t) \approx k_{13}t + 1/2 k_{12}k_{23}t^2$, the short-time solution of the master equations

$$dP_j/dt = \sum_i k_{ij}P_i - P_j \sum_i k_{ji} \quad (63)$$

Here k_{ij} is the rate constant to go from state $|i\rangle$ with vibrational coordinates starting in thermal equilibrium to state $|j\rangle$. The term $1/2 k_{12}k_{23}t^2$ is due to the two-step process in which state $|2\rangle$ appears as a *real* intermediate, in distinction from the term $k_{13}t$, which is due to a transition from state $|1\rangle$ to state $|3\rangle$ through state $|2\rangle$ as a *virtual* intermediate (the "superexchange" process), direct transfer from $|1\rangle$ to $|3\rangle$ due to V_{13} , and interference between the virtual and direct pathways. In order to calculate k_{13} , we must subtract from $P_{3,total}(t)$, the total population on state $|3\rangle$, a contribution that becomes $1/2 k_{12}k_{23}t^2 + (0)t$ as $t \rightarrow \infty$ ($t \gg \tau_{COH}$). The remaining population is just proportional to t at large times, and the coefficient of proportionality can be identified as the rate constant k_{13} . The total population on state $|3\rangle$ through order $(V_{12}^2 V_{23}^2, V_{13}V_{12}V_{23}, V_{13}^2)$ is $P_{3,total}(t) = P_{3,four-pt}(t) + P_{3C}(t) + P_{3D}(t)$, where

$$P_{3,four-pt}(t) = \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \times \\ \langle H_{12}(\tau_2)H_{23}(\tau_1)H_{32}(\tau_3)H_{21}(\tau_4) \rangle_1 \quad (64)$$

$$P_{3C}(t) = \frac{i}{\hbar^3} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \langle H_{12}(\tau_3)H_{23}(\tau_2)H_{31}(\tau_1) \rangle_1 + cc \quad (65)$$

$$P_{3D}(t) = \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle H_{13}(\tau_1)H_{31}(\tau_2) \rangle_1 \quad (66)$$

with $\langle \dots \rangle_1$ denoting thermal average in state 1. The operators $H_{ij} \equiv V_{ij}i$ (j depend on time in the interaction picture. We must subtract from this the two-step contribution, which at this order is

$$P_{3,two-step}(t) \equiv \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \times \\ \langle H_{12}(\tau_2)H_{21}(\tau_4) \rangle_1 \langle H_{23}(\tau_1)H_{32}(\tau_3) \rangle_2 \quad (67)$$

where the subscripts 1 and 2 on the thermal averages indicate

that the averages are taken in states 1 and 2, respectively. This is the same integral as in $P_{3,four-pt}(t)$ but with only the disconnected part instead of the full perturbation correlation function. See below for the demonstration that this is indeed the contribution to the final-state population due to the two-step process.

To get the rate k_{13} we now calculate the coefficient of t in the large- t limit of the expression $P_{3,one-step}(t) = P_{3V}(t) + P_{3C}(t) + P_{3D}(t)$, where $P_{3V}(t) = P_{3,four-pt}(t) - P_{3,two-step}(t)$. The simplest way to do this is to calculate

$$k_{13} = \lim_{t \rightarrow \infty} \frac{dP_{3,one-step}(t)}{dt} \quad (68)$$

It is useful to write $k_{13} = k_V + k_C + k_D$, where $k_V = \lim_{t \rightarrow \infty} dP_{3V}(t)/dt$, and similarly for k_C and k_D . Define the connected correlation function as

$$C_V(\tau_1, \tau_2, \tau_3, \tau_4) \equiv \langle H_{12}(\tau_1)H_{23}(\tau_2)H_{32}(\tau_3)H_{21}(\tau_4) \rangle_1 - \\ \langle H_{12}(\tau_1)H_{21}(\tau_4) \rangle_1 \langle H_{23}(\tau_2)H_{32}(\tau_3) \rangle_2 \quad (69)$$

so that

$$P_{3V}(t) = \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 C_V(\tau_2, \tau_1, \tau_3, \tau_4) \quad (70)$$

Thus

$$dP_{3V}(t)/dt = \frac{1}{\hbar^4} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 C_V(\tau_2, t, \tau_3, \tau_4) + \\ \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_4 C_V(\tau_2, \tau_1, t, \tau_4) \quad (71)$$

In each term we will change the integration variables so the arguments of the correlation function are $C_V(t_3 + s_1, t_3, -s_2, 0)$. This changes the regions of integration, and we must find what region is filled as $t \rightarrow \infty$. The first term covers the region defined by the inequalities

$$t_3 < t, \quad s_2 < 0, \quad 0 < s_2 + t_3, \quad -t < s_1 < 0 \quad (72)$$

The second term covers the region defined by

$$-t < s_2 < 0, \quad s_1 < 0, \quad s_2 + t_3 < 0, \quad -t < s_1 + s_2 + t_3 \quad (73)$$

As $t \rightarrow \infty$, the total region of integration becomes the quadrant $s_1 < 0, s_2 < 0$. We may change variables $s_1 \rightarrow -s_1, s_2 \rightarrow -s_2$, and $t_3 \rightarrow \tau$. This yields the virtual rate

$$k_V = \frac{1}{\hbar^4} \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds_1 \int_0^{\infty} ds_2 C_V(\tau - s_1, \tau, s_2, 0) \quad (74)$$

For some calculations it is convenient to make the change of variables $\tau \rightarrow \tau + s_2$ in the integral and then subtract s_2 from all four arguments of the correlation function (allowed by stationarity of the equilibrium ensemble). This gives

$$k_V = \frac{1}{\hbar^4} \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds_1 \int_0^{\infty} ds_2 C_V(\tau - s_1, \tau, 0, -s_2) \quad (75)$$

This is the virtual rate for a vibrationally-assisted transition at lowest order in the perturbation theory, regardless of the potentials seen by the vibrational coordinates.

The possibility that the above rate expression might be negative in some cases is not a great concern for the following reason. We are guaranteed that the final-state population is always positive, since it is the sum of squared amplitudes. At times greater than the coherence time but smaller than the reaction times we know this population varies with time as $P_3(t) \approx k_{13}t + 1/2 k_{12}k_{23}t^2$; this expression must be positive throughout this range of times. If $k_{13} < 0$, this expression is negative for times $t < |k_{13}|/(1/2 k_{12}k_{23}) \equiv t_{neg}$, and thus we can conclude that $t_{neg} < \tau_{COH}$. This means $|k_{13}| < 1/2 k_{12}k_{23}\tau_{COH}$. If k_{12} and k_{23} are well-defined rate constants,

then each of them must be $\ll 1/\tau_{COH}$. Thus $|k_{13}| \ll k_{12}$ and $|k_{13}| \ll k_{23}$, so the virtual process gives a negligible contribution to the final-state population compared to that of the two-step process. Therefore, if the virtual rate expression above ever does take on a negative value, its magnitude will be negligible and we may as well treat it as 0.

In the presence of a matrix element V_{13} coupling the initial and final states directly, we also need the "interference" (k_C) and "direct" (k_D) terms:

$$k_C = -\frac{2}{\hbar^3} \text{Im} \int_{-\infty}^{\infty} d\tau \int_0^{\infty} ds \langle H_{12}(\tau-s)H_{23}(\tau)H_{31}(0) \rangle_1 \quad (76)$$

$$k_D = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau \langle H_{13}(\tau)H_{31}(0) \rangle_1 \quad (77)$$

These can be obtained from $P_{3C}(t)$ and $P_{3D}(t)$, respectively, by the same technique we used to derive k_V from $P_{3V}(t)$. The general perturbative expression for the rate from state 1 to state 3, $k_{13} = k_V + k_C + k_D$, is then given by eqs 75, 76, and 77.

Finally, we show that the contribution to the final-state population due to the two-step process is

$$P_{3,two-step}(t) \equiv \frac{1}{\hbar^4} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \times \\ \langle H_{12}(\tau_2)H_{21}(\tau_4) \rangle_1 \langle H_{23}(\tau_1)H_{32}(\tau_3) \rangle_2 \quad (78)$$

We need to show that as $t \rightarrow \infty$ this becomes $1/2 k_{12} k_{23} t^2 + (0)t + \text{terms that remain bounded as } t \text{ grows large}$. Denote the Fourier transforms of $(1/\hbar^2) \langle H_{12}(\tau)H_{21}(0) \rangle_1$ and $(1/\hbar^2) \langle H_{23}(\tau)H_{32}(0) \rangle_2$ respectively by $\tilde{k}_{12}(\Omega)$ and $\tilde{k}_{23}(\Omega)$. From its above definition, we can now write

$$P_{3,two-step}(t) = t^2 \int_0^1 d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \times \\ \int \frac{dz_1}{2\pi} \frac{dz_2}{2\pi} \tilde{k}_{12}\left(\frac{z_1}{t}\right) \tilde{k}_{23}\left(\frac{z_2}{t}\right) e^{-iz_1(\tau_2-\tau_4)} e^{-iz_2(\tau_1-\tau_3)} \quad (79)$$

where we have introduced dimensionless frequencies z_1, z_2 choosing the time t as the scale. As $t \rightarrow \infty$, $\tilde{k}_{12}(z_1/t) \simeq \tilde{k}_{12}(0) + \tilde{k}'_{12}(0)(z_1/t)$. Note that $\tilde{k}_{12}(0) = k_{12}$ and $\tilde{k}_{23}(0) = k_{23}$, so in order to show that the t^2 piece is $1/2 k_{12} k_{23} t^2$, we just have to show that the dimensionless integral is equal to $1/2$. Do the z integrals first.

$$I \equiv \int_0^1 d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \int \frac{dz_1}{2\pi} \frac{dz_2}{2\pi} e^{-iz_1(\tau_2-\tau_4)} e^{-iz_2(\tau_1-\tau_3)} \\ = \int_0^1 d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \delta(\tau_2 - \tau_4) \delta(\tau_1 - \tau_3) \\ = \int_0^1 d\tau_1 \int_0^{\tau_1} d\tau_2 = 1/2 \quad (80)$$

The t piece is 0 since the corresponding dimensionless integrals can be shown to vanish. There is a contribution proportional to $\tilde{k}'_{12}(0)\tilde{k}_{23}(0)$ and a contribution proportional to $\tilde{k}_{12}(0)\tilde{k}'_{23}(0)$. The coefficient of $\tilde{k}'_{12}(0)\tilde{k}_{23}(0)$ is

$$J \equiv \int_0^1 d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \int \frac{dz_1}{2\pi} \frac{dz_2}{2\pi} \times \\ z_1 e^{-iz_1(\tau_2-\tau_4)} e^{-iz_2(\tau_1-\tau_3)} \quad (81)$$

Changing variables $z_1 \rightarrow -z_1, z_2 \rightarrow -z_2, \tau_1 \leftrightarrow \tau_3$, and $\tau_2 \leftrightarrow \tau_4$ gives $J = -J = 0$. The coefficient of $\tilde{k}_{12}(0)\tilde{k}'_{23}(0)$ can be shown to vanish in the same way.

Appendix B: The Importance of the Disconnected Part

Here we determine the criteria for the validity of neglecting the second term of the integrand of k_V in eq 15. The virtual rate was expressed in section II.2 as an integral of the difference of two terms. The integrand of the first term is a four-point correlation function of the interactions. The second term is the disconnected part of the correlation function. This corresponds

to the final-state population resulting from the two-step process. In the case of harmonic vibrational coordinates, this subtraction resulted in the two terms in eq 15. In estimating the virtual rate at large and small E in sections III.2 and III.3, we make saddle-point and short-time approximations on the integrand of only the first of the two terms of the integrand. Here we find the circumstances under which this is a valid procedure. It is important to emphasize at the outset that the second term is crucial if k_V is to be finite. We will clarify how this can be consistent with the neglect of the second term in saddle-point expansions.

Let $s = 1/2(s_2 + s_1)$, and $a = s_2 - s_1$. Notice that, if we fix s and imagine doing the τ and a integrals, the remaining integrand is the difference of two functions of s , call them $I_1(s)$ and $I_2(s)$, each of which approaches the same finite constant $k_{12}k_{23}$ at large s . This can be seen by examination of eqs 15, 18, 19, and 22. The first term has this value for $s \gg 1/\gamma$. The second term attains this value after the time τ_{FC} , because beyond that the a integral can be extended to $[-\infty, +\infty]$. Thus while the s integral of each of the two terms separately is infinite, the integral of the difference of the two terms is finite. The second term is crucial to arrive at a finite rate constant in any case. It is useful to define new functions $F_1(s) = I_1(s) - k_{12}k_{23}$ and $F_2(s) = I_2(s) - k_{12}k_{23}$. We then have $k_V = k_{V1} - k_{V2}$, where $k_{V1} = \int_0^{\infty} ds F_1(s)$ and $k_{V2} = \int_0^{\infty} ds F_2(s)$ are each finite.

In cases with $k_{V2} \ll k_{V1}$, we may neglect k_{V2} , but this does not correspond to neglecting the second term of eq 15. Rather it corresponds to neglecting the deviations of $I_2(s)$ from the constant $k_{12}k_{23}$. This constant is crucial for a finite rate, and indeed it is subtracted off from $I_1(s)$. We will find approximate criteria under which $k_{V2} \ll k_{V1}$.

Furthermore, the contributions to k_{V1} from $I_1(s)$ become negligible beyond a certain value of s . Let us refer to this value as s_{MAX} . The expansion of section III.2 reveals that $s_{MAX} \sim \hbar/E$ for large E . The expansion of section III.3 shows that $s_{MAX} \sim (\omega^4/8u)^{1/2}(1/\gamma)$ for small E , where u is given by eq 55. We intend to show that these expansions can be self-consistent. We know that $I_1(s) \simeq k_{12}k_{23}$ for $s \gg 1/\gamma$; this can be seen both from the general expression eq 15 and in the expansions at large and small E . The time $1/\gamma$ is long compared to s_{MAX} in both the large and small E cases. Therefore, $k_{12}k_{23}$ can be neglected in approximating k_{V1} by saddle-point and short-time methods, as long as $k_{12}k_{23}$ is much smaller than the values of $I_1(s)$ contributing to k_{V1} . We will determine when this is the case.

First we establish when we can neglect $k_{12}k_{23}$ in estimating k_{V1} by saddle-point and short-time approximations. Within the Gaussian energy-gap law,

$$k_{12}k_{23} \propto \exp\{-1/2(\epsilon_{12} - \lambda_{12})^2 \tau_{FC12}^2 / \hbar^2 - \\ 1/2(\epsilon_{23} - \lambda_{23})^2 \tau_{FC23}^2 / \hbar^2\} \quad (82)$$

where τ_{FC12} and τ_{FC23} are defined as analogous to τ_{FC13} in eq 29. (Deviations from energy-gap law behavior lead to corrections to the criteria derived here.) In this work, we only consider cases in which the activation energy for k_{13} is given by the initial/final crossing. For large E , $I_1(s)$ oscillates on a time scale \hbar/E at short times with some amplitude $I_{1MAX} \propto \exp\{-1/2(\epsilon_{13} - \lambda_{13})^2 \tau_{FC13}^2 / \hbar^2\}$. For small E , we confine ourselves to nearly activationless situations. The function $I_1(s)$ is approximated in this case in section III.3 as the integrand of eq 45. The contributions from successive saddle-points become negligible after a time $s_{MAX} \sim (\omega^4/8u)^{1/2}(1/\gamma)$. This occurs before the time $1/\gamma$, which is when the saddle-points approach the value $k_{12}k_{23}$. It will therefore be sufficient to require

$$(\epsilon_{12} - \lambda_{12})^2 \tau_{FC12}^2 / \hbar^2 + (\epsilon_{23} - \lambda_{23})^2 \tau_{FC23}^2 / \hbar^2 - \\ (\epsilon_{13} - \lambda_{13})^2 \tau_{FC13}^2 / \hbar^2 \gg 1 \quad (83)$$

This implies that $k_{12}k_{23}$ is much smaller than the values of $I_1(s)$ contributing to k_{V1} .

At high temperatures, this is tantamount to requiring that the activation energies of the reactions satisfy $E_{a12} + E_{a23} - E_{a13} \gg k_B T$. For large E this is easily satisfied, while for small E and small activation energy this is equivalent to assuming that k_{23} is far from activationless. Note that coherent recurrence alters the prefactor but does not affect this relative exponential attenuation. The requirement of eq 83 is therefore sufficient to ensure that the saddle-point and short-time methods of sections III.2 and III.3 are self-consistent means of approximating k_{v1} .

To find when k_{v2} is negligible compared to k_{v1} , we compute the exponentially small factor in k_{v2} . We write

$$I_2(s) = \left(\frac{V_{12}^2 V_{23}^2}{\hbar^4} \right) \int_{-\infty}^{\infty} d\tau e^{f_{23}(\tau)/\hbar} \int_{\tau-2s}^{\tau+2s} dv e^{f_{12}(v)/\hbar} \\ = \left(\frac{V_{12}^2 V_{23}^2}{\hbar^4} \right) \int_{-\infty}^{\infty} \frac{d\Omega}{2\pi} \frac{2 \sin(2\Omega s)}{\Omega} \int_{-\infty}^{\infty} d\tau e^{f_{23}(\tau)/\hbar} e^{i\Omega\tau} \times \\ \int_{-\infty}^{\infty} dv e^{f_{12}(v)/\hbar} e^{-i\Omega v} \quad (84)$$

where $v = \tau + a$ and

$$f_{ij}(\tau) = i\epsilon_{ij}\tau + \sum_{r=1}^N q_{ij,r}^2 [K_r(\tau) - K_r(0)] \quad (85)$$

To make further progress, we make the short-time approximations $f_{12}(v) \approx i(\epsilon_{12} - \lambda_{12})v - 1/2 v^2 / \tau_{FC12}^2$ and similarly for $f_{23}(\tau)$. This leads to

$$I_2(s) \approx \left(\frac{V_{12}^2 V_{23}^2}{\hbar^4} \right) (2\pi) \tau_{FC12} \tau_{FC23} \int_{-\infty}^{\infty} d\Omega \frac{2 \sin(2\Omega s)}{\Omega} \times \\ \exp \left\{ -\frac{1}{2} \tau_{FC23}^2 (\epsilon_{23} - \lambda_{23} + \hbar\Omega)^2 / \hbar^2 \right\} \times \\ \exp \left\{ -\frac{1}{2} \tau_{FC12}^2 (\epsilon_{12} - \lambda_{12} - \hbar\Omega)^2 / \hbar^2 \right\} \quad (86)$$

The exponentially small factor in $I(s)$ attains its maximum for $s \lesssim \hbar/\lambda$, where the function $\sin(2\Omega s)/\Omega$ is approximately constant over the range of Ω covered by the two Gaussians in the above expression. Let us assume that $I_2(s \lesssim \hbar/\lambda) \gg k_{12}k_{23}$. [If this is not the case, then $k_{v2} \propto \exp\{-1/2(\epsilon_{12} - \lambda_{12})^2 \tau_{FC12}^2 / \hbar^2 - 1/2(\epsilon_{23} - \lambda_{23})^2 \tau_{FC23}^2 / \hbar^2\}$, which by the above criterion is negligible compared to k_{v1} .] Treating the function $\sin(2\Omega s)/\Omega$ as a constant and performing the Gaussian integrals gives a proportionality of

$$k_{v2} \propto \exp\{-1/2(\epsilon_{13} - \lambda_{12} - \lambda_{23})^2 (\tau_{FC23}^{-2} + \tau_{FC12}^{-2})^{-1} / \hbar^2\} \quad (87)$$

The criterion for $k_{v2} \ll k_{v1}$ is then

$$(\epsilon_{13} - \lambda_{12} - \lambda_{23})^2 (\tau_{FC23}^{-2} + \tau_{FC12}^{-2})^{-1} / \hbar^2 - \\ (\epsilon_{13} - \lambda_{13})^2 \tau_{FC13}^2 / \hbar^2 \gg 1 \quad (88)$$

This holds for sufficiently small E_{a13} . In particular, for small E this is equivalent to k_{23} being activated. Note that the inequalities of eqs 83 and 88 really need only be weakly satisfied, because of the exponential dependence on their left-hand sides.

Under the criteria stated in this Appendix, self-consistent and valid approximations to the virtual rate can be obtained by performing an asymptotic expansion (saddle-point for small E or saddle-point/short time for large E) on only the first term of the integrand of eq 15. When these conditions are met, what essentially happens in the case of small E is that the function $I_1(s)$ consists of a series of peaks whose heights decreases appreciably over the time s_{MAX} . The heights of the peaks are much greater than $k_{12}k_{23}$ through that time. At the later time $1/\gamma$, the peaks decay to the constant value $k_{12}k_{23}$. Meanwhile, the function $I_2(s)$ is always exponentially smaller than those peaks of $I_1(s)$ that contribute appreciably to k_{v1} . Thus, it would be accurate to say that, although the disconnected correlation function in eq 15 is crucial to have a finite rate constant, there

are circumstances in which it can be neglected for the purpose of obtaining valid approximations for the rate.

References and Notes

- (1) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.
- (2) Mayo, S. L., Jr.; Ellis, W. R.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948.
- (3) Beratan, D.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1987**, *86*, 4488.
- (4) Onuchic, J. N.; Beratan, D. *J. Chem. Phys.* **1990**, *92*, 722.
- (5) Ratner, M. A. *J. Phys. Chem.* **1990**, *94*, 4877.
- (6) Kharkats, Y. I.; Madumarov, A. K.; Vorotyntsev, M. A. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1578.
- (7) Kuznetsov, A. M.; Ulstrup, J. *J. Chem. Phys.* **1981**, *75*, 2047.
- (8) Martin, J.-L.; Breton, J.; Hoff, A. J.; Migus, A.; Antonetti, A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 957.
- (9) Breton, J.; Martin, J.-L.; Migus, A.; Antonetti, A.; Orszag, A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 5121.
- (10) Breton, J.; Martin, J.-L.; Petrich, J.; Migus, A.; Antonetti, A. *FEBS Lett.* **1986**, *209*, 37.
- (11) Lockhart, D. J.; Goldstein, R. F.; Boxer, S. G. *J. Chem. Phys.* **1988**, *89*, 1408.
- (12) Bixon, M.; Jortner, J. *J. Phys. Chem.* **1988**, *92*, 7148.
- (13) Bixon, M.; Jortner, J.; Michel-Beyerle, M. E.; Ogrodnik, A. *Biochim. Biophys. Acta* **1989**, *977*, 273.
- (14) Friesner, R. A.; Won, Y. *Biochim. Biophys. Acta* **1989**, *977*, 99.
- (15) Holzapfel, W.; Finkle, U.; Kaiser, W.; Oesterheld, D.; Scheer, H.; Stiltz, H. U.; Zinth, W. *Chem. Phys. Lett.* **1989**, *160*, 1.
- (16) Holzapfel, W.; Finkle, U.; Kaiser, W.; Oesterheld, D.; Scheer, H.; Stiltz, H. U.; Zinth, W. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 5168.
- (17) Kirmaier, C.; Holten, D. *Biochemistry* **1991**, *30*, 609.
- (18) Bixon, M.; Jortner, J.; Michel-Beyerle, M. E. *Biochim. Biophys. Acta* **1991**, *1056*, 301.
- (19) Joseph, J. S.; Bruno, W.; Bialek, W. *J. Phys. Chem.* **1991**, *95*, 6242.
- (20) Franzen, S.; Goldstein, R. F.; Boxer, S. G. *J. Phys. Chem.* **1990**, *94*, 5135.
- (21) Bialek, W.; Bruno, W. J.; Joseph, J.; Onuchic, J. N. *Photosynth. Res.* **1989**, *22*, 15.
- (22) Kuznetsov, A. M. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1497.
- (23) Hu, Y.; Mukamel, S. *Chem. Phys. Lett.* **1989**, *160*, 410.
- (24) Hu, Y.; Mukamel, S. *J. Chem. Phys.* **1989**, *91*, 6973.
- (25) Holstein, T. *Philos. Mag.* **1978**, *37B*, 499.
- (26) Caldeira, A. O.; Leggett, A. J. *Phys. Rev. Lett.* **1981**, *27*, 211.
- (27) Caldeira, A. O.; Leggett, A. J. *Ann. Phys.* **1983**, *149*, 374.
- (28) Leggett, A. J.; Chakravarty, S.; Dorsey, A.; Fisher, M. P. A.; Garg, A.; Zwirger, W. *Rev. Mod. Phys.* **1987**, *59*, 1.
- (29) Vol'kenshtein, M. V.; Dogonadze, R. R.; Madumarov, A. K.; Kharkats, Y. I. *Dokl. Acad. Nauk SSSR Ser. Fiz. Khim.* **1971**, *199*, 124.
- (30) Lin, S. H. *J. Chem. Phys.* **1989**, *90*, 7103.
- (31) Kharkats, Y. I.; Ulstrup, J. *Chem. Phys. Lett.* **1991**, *182*, 81.
- (32) Kuznetsov, A. M.; Ulstrup, J. *Chem. Phys.* **1991**, *157*, 25.
- (33) For calculations treating one of the transitions adiabatically, see: Marcus, R. A.; Almeida, R. *J. Phys. Chem.* **1990**, *94*, 2973. Almeida, R.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 2978.
- (34) Bialek, W.; Onuchic, J. N. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 5908.
- (35) Kuharski, R. A.; Bader, J. S.; Chandler, D. *J. Chem. Phys.* **1988**, *89*, 3248.
- (36) Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501.
- (37) Bader, J. S.; Kuharski, R. A.; Chandler, D. *J. Chem. Phys.* **1990**, *93*, 230.
- (38) Newton, M. D.; Sutin, N. *Ann. Rev. Phys. Chem.* **1984**, *35*, 437.
- (39) Garg, A.; Onuchic, J. N.; Ambegaokar, V. *J. Chem. Phys.* **1985**, *83*, 4491.
- (40) Bialek, W.; Goldstein, R. F. *Phys. Scr.* **1986**, *34*, 273.
- (41) Onuchic, J. N.; Beratan, D. N.; Hopfield, J. J. *J. Phys. Chem.* **1986**, *90*, 3707.
- (42) Goldstein, R. F.; Bialek, W. *Phys. Rev. B* **1983**, *27*, 7431.
- (43) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Pergamon Press: Oxford, 1977.
- (44) Onuchic, J. N.; Wolynes, P. G. *J. Phys. Chem.* **1988**, *92*, 6495.
- (45) Onuchic, J. N.; Goldstein, R. F.; Bialek, W. In *Perspectives in Photosynthesis*; Jortner, J., Pullman, B., Eds.; D. Reidel: Dordrecht, Holland, 1990.
- (46) Holstein, T. *Ann. Phys.* **1959**, *8*, 343.
- (47) Since we do not include pure dephasing in our analysis, the coherence time given here is identical with the time for the damping to change the vibrational energy by one quantum.
- (48) Bleistein, N.; Handelsman, R. *Asymptotic Expansions of Integrals*; Dover: New York, 1975.
- (49) Ramond, P. *Field Theory: A Modern Primer*; Benjamin/Cummings: Reading, MA, 1981.
- (50) Negele, J. W.; Orland, H. *Quantum Many-Particle Systems*; Addison-Wesley: Redwood City, CA, 1988.
- (51) Joseph, J. S. Models of Photosynthetic Electron Transfer. Ph.D. Thesis, Graduate Group in Biophysics, University of California at Berkeley, 1991.
- (52) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
- (53) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.
- (54) Gunner, M. R.; Robertson, D. E.; Dutton, P. L. *J. Phys. Chem.* **1986**, *90*, 3783.

- (55) Warshel, A.; Chu, Z. T.; Parson, W. W. *Science* **1989**, *246*, 112.
(56) Chu, Z. T.; Warshel, A.; Parson, W. W. *Photosynth. Res.* **1989**, *22*, 39.
(57) Bialek, W.; Goldstein, R. F.; Kivelson, S. In *Structure, Dynamics and Function of Biomolecules*; Ehrenberg, A., Rigler, R., Graslund, A., Nilsson, L., Eds.; Springer-Verlag: Berlin, 1987.
(58) Onuchic, J. N. *J. Chem. Phys.* **1987**, *86*, 3925.
(59) Joseph, J. S.; Bialek, W. *Biophys. J.* **1992**, *63*, 397.
(60) Fleming, G. R.; Martin, J.-L.; Breton, J. *Nature* **1988**, *333*, 190.
(61) Neglecting damping entirely in the expansion might lead us to conclude that $\omega/2\pi\gamma$ saddle-points contribute to the rate, since we know for $s \gg 1/\gamma$

the saddle-points are canceled by the constant $k_{12}k_{23}$ provided by the second term of k_1 in eq 15. This oversight was made in refs 51 and 59; the small- E expressions there should be multiplied by the factor $(\pi\omega^4/16u)^{1/2}$. For the example considered in ref 59, this correction has the numerical value ≈ 0.7 at room temperature and ≈ 0.4 at $T = 10$ K.

(62) By the Schwarz inequality, we always have $\Lambda^+ \geq 0$, with equality occurring if and only if the N -component vectors \hat{q}_{12} and \hat{q}_{23} are linearly dependent. One particular example that falls into this category is that of only one mode coupled to the transitions. We therefore regard the case $N = 1$ to be somewhat pathological.

(63) See, e.g.: Mukamel, S. *Adv. Chem. Phys.* **1981**, *47* (1), 509.