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Nonperturbative Approach to Non-Condon Effects: Must a Nonadiabatic Transition Always Occur at the Potential Surface Crossing?**Robert F. Goldstein****Computer Center m/c 135 and Department of Chemistry, 1940 W. Taylor, University of Illinois at Chicago, Chicago, Illinois 60612-7352***Stefan Franzen†***Department of Chemistry, Stanford University, Stanford, California 94305***William Bialek***NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540**Received: February 4, 1993; In Final Form: July 23, 1993**

We present a generating function method for the computation of non-Condon effects in the context of nonadiabatic multiphonon transition theory. The method is nonperturbative in the electron–phonon coupling and nonperturbative in the dependence of the transition matrix element on nuclear coordinates, but it does assume the overall transition rate is small enough to be treated perturbatively. We do not assume the transition operator is given by the Born–Oppenheimer breakdown operator but rather consider more general forms of the transition matrix element $V(x)$, where x represents nuclear coordinates. In particular, for narrow forms of $V(x)$ such as a delta function, the optimum position (that position of $V(x)$ which produces the maximal transition rate) is temperature dependent and may not coincide with the transition state. This calls into question the classical notion that a transition occurs via a thermal fluctuation to the potential surface crossing. The classical significance of the transition state does appear valid, however, at low temperature and large electron–phonon coupling. Furthermore, when $V(x)$ is broad and the non-Condon effects are weak, the transition rate can be expressed in the Condon approximation with suitably scaled parameters. Since this scaling is temperature dependent, there may be an apparent change in the reorganization energy and in the enthalpy and entropy of activation. When many vibrational modes couple to the transition, there are circumstances under which a single promoting mode can dominate the vibrational effects. In the context of optical line shapes, this means there are circumstances under which a weakly coupled vibrational mode can cause the wings of a line to assume a strictly exponential, rather than Gaussian, shape.

Introduction

The Condon approximation, that the transition matrix element is independent of nuclear coordinates, has the virtue of considerable simplicity, but it is not always appropriate. We present a technique for nonadiabatic transition rate calculations that completely avoid the Condon approximation. In fact, it is nonperturbative in the functional form of the matrix element $V(x)$, although it does assume the overall transition is small enough to treat perturbatively.

Our technique is also nonperturbative in the electron–phonon coupling constant, which allows us to compute non-Condon effects for strongly coupled reactions, such as electron transfer. (Traditionally, non-Condon effects are ignored for electron-transfer processes. But Reimers and Hush¹ attribute a charge-transfer absorption band to the existence of promoting modes in an organic donor/acceptor system, and we will consider the role that non-Condon effects may play in photosynthetic electron transfer elsewhere.²)

Traditionally, vibrations are classified into two categories:³ (1) accepting modes, whose vibrational properties, such as

frequency or equilibrium position, differ between the electronic states, and (2) promoting modes, whose coordinates or momenta affect the electronic matrix elements. Since our emphasis is specifically on non-Condon effects, we will present results for the simplest case—a single harmonic mode with both promoting and accepting (equilibrium shift) character.

Many aspects of this problem have a long history in the context of impurities in solids and various molecular situations.^{4–6} For reviews with emphasis on the solid-state aspects, see Stoneham³ and Huang.⁷ Jortner and Mukamel⁸ discuss chemical issues, and DeVault⁹ reviews some applications to biological systems. There are other aspects of nonadiabatic transition theory, such as dissipation, resonance, and the adiabatic limit, that have been dealt with in the Condon approximation; the reader is referred to the literature, e.g., refs 10, 11, 12, and 13 and references therein.

There is also a clever reformulation of nonadiabatic barrier crossing in terms of path integrals by Wolynes¹⁴ and co-workers^{15,16} that has significant advantages for modeling complex systems. Because of the explicit use of path integrals, one can ask about which paths (in nuclear configuration space) or virtual processes make significant contributions to the overall transition and therefore which nuclear configurations favor the electronic transition, given a Condon approximation Hamiltonian.

But we will use our simpler non-Condon formulation to ask a

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different but related question using a different Hamiltonian. That is, how significantly is the rate affected by an electronic transition matrix element that is strongly peaked in a region of nuclear configuration space far from the crossing of reactants and products potential surfaces? (There are cases in which the optimum position of $V(x)$ is not at the potential surface crossing.) And further, what is an appropriate way to impose the Condon approximation on a system known to have promoting modes?

Considerations of non-Condon effects go back at least to Kovarskii¹⁷ and co-workers and later Scharf and Silbey,^{18,19,20} who showed that the Condon approximation can incur significant errors in the computation of transition rates. Kovarskii's computations were valid for weak coupling ($S \ll 1$) and were later extended to moderate coupling ($S \leq 1$) by Nitzan and Jortner.²¹

Still further progress was made by Freed and Lin,²² who used a Q-centroid approach to find the optimum vibrational coordinate at which to evaluate the transition matrix element. They found that this optimum coordinate was not always at the equilibrium position of the initial state, a conclusion we are able to support by the very different technique of allowing $V(x)$ to become a delta function.

Most studies incorporated non-Condon effects by using electronic wave functions that explicitly depend on nuclear coordinates. In contrast, Passler²³ obtained similar results by using crude adiabatic wave functions and putting the coordinate dependence into the transition operator. Later, Gutsche²⁴ and Huang²⁵ showed these approaches to be equivalent.

The above studies were generally concerned with computing the non-Condon transition rate between adiabatic states that is induced by the Born–Oppenheimer breakdown operator. (There are other transitions, however, such as Raman scattering, where non-Condon effects play a role, e.g., refs 26 and 27. We will comment later on the implications of non-Condon effects on optical line shapes.) They were often interested in comparing the results to experiments on internal conversion, where the electron–phonon coupling is weak.

In contrast, we will cast our discussion in terms of a more general model, namely, a generalized spin–boson system¹⁰ (a two-state “electronic” system coupled to a “nuclear” harmonic oscillator) which does not depend explicitly on the Born–Oppenheimer breakdown operator or on weak electron–phonon coupling. Thus, we make no assumptions about whether the electronic states are true Born–Oppenheimer states of the original molecular Hamiltonian and therefore no assumptions about the origin of the electronic matrix element, be it radiative, Born–Oppenheimer breakdown, overlap of nonorthogonal wave functions,²⁸ superexchange, etc.

In practice, one needs to consider a specific form of the electronic matrix element, $V(x)$, to compute a transition rate. We will provide formulas here for two functional forms of $V(x)$, namely, a Gaussian and a power series. Other functional forms, such as a Gaussian times a series of Hermite polynomials or an exponential times a power series, are straightforward to develop with the same techniques. Most functional forms of $V(x)$ are probably well approximated by some combination of these analytic forms. Elsewhere,² we consider a particular form of $V(x)$ derived from superexchange in photosynthetic electron transfer.

After we develop the methodology, we compute transition rates for the form $V(x) = \delta(x - x_0)$ for various values of x_0 . Although the transition rate for a general $V(x)$ cannot be expressed as a linear combination of rates due to delta functions, this nevertheless allows us to explore the importance of various regions of nuclear configuration.

We find that the crossing state is the most effective value of x_0 in the limit of low temperature and large electron–phonon coupling. In other parameter regimes, however, the optimum position of $V(x)$ is quite different from the potential surface crossing. This observation calls into question the semiclassical notion that a transition occurs via a thermal fluctuation to the

crossing, and it certainly challenges the notion that in making the Condon approximation one should choose the Condon matrix element, V_0 , to be the value of $V(x)$ at that crossing.

In fact, we show that when the coordinate dependence of $V(x)$ is mild one can make the Condon approximation provided one uses an effective matrix element and one renormalizes other parameters such as the reorganization energy. We call this approximation the “static” non-Condon approximation because the renormalized effective parameters are calculated as averages over the equilibrium distribution of reactants' coordinates and do not depend on the dynamics of vibrations.

The Model

The entire system consists of three coupled subsystems: (1) two electronic levels, which are operated on by Pauli spin matrices; (2) a discrete set of oscillators whose properties depend on the electronic state (i.e., the “vibrational” part of the Hamiltonian will depend on σ_z); and (3) a heat bath to provide thermal equilibration for the oscillators.²⁹ Although this heat bath assures the presence of vibrational relaxation, the electronic transition rate will be insensitive to the parameters (except for temperature) of this heat bath, for a wide range of values. The general restriction will be that of vibrational energy relaxation be fast compared to the electronic transition rate.

The Hamiltonian can now be written as

$$\mathcal{H} = \frac{1}{2}\epsilon\sigma_z + V(x)\sigma_+ + \sigma_-V^\dagger(x) + \mathcal{H}_{\text{vib}}(\sigma_z) + \text{HB} \quad (1)$$

where ϵ is the energy difference between the electronic states and $V(x)$ is the matrix element that connects the two states. HB denotes the heat bath terms. The electronic matrix element, $V(x)$, depends on the coordinates of all promoting modes, by definition.

For the moment, we make no assumption about the form of $V(x)$, or even that it is Hermitian. A non-Hermitian $V(x)$ might be useful for describing the effective coupling between reactants and products that occurs due to interaction with virtual states, particularly if the energies of those virtual states have imaginary components due to damping or other transitions.

When the electronic state is $|+\rangle$ (reactants), the vibrations obey the Hamiltonian $\mathcal{H}_{\text{vib}}(+)$, and similarly for $|-\rangle$. If the oscillators form a single simple harmonic mode whose equilibrium position depends on σ_z , then the annihilation operator for this mode is explicitly

$$c(\sigma_z) = \frac{1}{\sqrt{2\hbar}} \sum_j A_j \left[(x_j + \Delta_j \sigma_z) m_j \sqrt{\omega} + \frac{ip_j}{\sqrt{\omega}} \right] \quad (2)$$

Atomic positions and momenta are denoted x_j and p_j , where j denotes a specific Cartesian coordinate of a specific atom; the mass of that atom is denoted m_j . The equilibrium position in the $|\pm\rangle$ state is $\mp\Delta_j$. The relation between the $3n$ atomic coordinates x_j and the normal mode coordinate \tilde{q} is defined as $\tilde{q} = \sum_j A_j x_j m_j$.

Thus, the two adiabatic potential squares for reactants and products can be written

$$U_\pm(\tilde{q}) = \frac{1}{2}\omega^2(\tilde{q} \pm \eta\tilde{q}_{\text{zp}})^2 \pm \epsilon/2 \quad (3)$$

where $\tilde{q}_{\text{zp}} = \sqrt{\hbar/2\omega}$ is the rms zero-point motion of the coordinate \tilde{q} and $\eta = \sum_j A_j \Delta_j m_j / \tilde{q}_{\text{zp}}$ is the dimensionless displacement of reactants and products along the coordinate \tilde{q} . In the following, we will use the reduced coordinate $q = \tilde{q}/\tilde{q}_{\text{zp}}$. Thus, the reactants' minimum is $q = -\eta$, the products' minimum is $q = +\eta$, and the crossing is $q = -\epsilon/\eta\hbar\omega$.

Perturbation Theory

We will assume $V(q)$ is small and calculate the transition rate between eigenstates of σ_z perturbatively in $V(q)$. (Actually, the calculation treats the *shape* of $V(q)$ nonperturbatively but assumes the overall magnitude is small. That is, we do not treat just the

lowest orders of a Taylor expansion of $V(q)$.) We wish to treat electron-phonon coupling nonperturbatively, so we use a canonical transformation³⁰ to transform the general annihilation operator, $c(\sigma_z)$, into $a = c(\sigma_z \rightarrow +1)$, the annihilation operator of the reactants vibrations.

The Hamiltonian becomes

$$\mathcal{U}\mathcal{H}\mathcal{U}^\dagger = \frac{1}{2}\epsilon\sigma_z + V(q)F\sigma_+ + \sigma_-F^\dagger V^\dagger(q) + \hbar\omega(a^\dagger a + \frac{1}{2}) \quad (4)$$

The electronic transition term has acquired a factor $F = \mathcal{U}(\sigma_z \rightarrow +1)\mathcal{U}^\dagger(\sigma_z \rightarrow -1)$. Although $[V, F] \neq 0$, when the Hamiltonian is written as above, $V(q)$ is unaffected by the transformation.

In the usual way, lowest order perturbation theory expresses the transition rate, k , as the Fourier transform of a correlation function,

$$k = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{-i\epsilon\tau/\hbar} C(\tau) \quad (5)$$

where the correlation function is defined as

$$C(\tau) = \langle V(0) F(0) F^\dagger(\tau) V^\dagger(\tau) \rangle \quad (6)$$

The expectation value in the correlation function is to be evaluated in the thermal equilibrium state of the reactants' vibrational levels, because we assumed the electronic transition rate is much slower than vibrational relaxation.

Correlation Function Evaluation

In the single-mode, linear-coupling scheme we wish to treat here, F is given explicitly by³¹

$$F(t) = \exp\{(a^\dagger - a)\eta\} \quad (7)$$

The general form of $V(q)$ becomes more tractable if we use the Fourier transform:

$$V(q) = \int_{-\infty}^{\infty} dk V(k) \exp\{ikq\} \quad (8)$$

Since $a + a^\dagger = q + \eta$, the correlation function from eq 6 is now written

$$C(\tau) = \int_{-\infty}^{\infty} dk_0 \int_{-\infty}^{\infty} dk_\tau V(k_0) V^\dagger(-k_\tau) \times \langle e^{ik_0(a^\dagger(0)+a(0)-\eta)} e^{i\eta(a^\dagger(0)-a(0))} e^{-\eta(a^\dagger(\tau)-a(\tau))} e^{ik_\tau(a(\tau)+a^\dagger(\tau)-\eta)} \rangle \quad (9)$$

The product of exponentials in eq 9 can be combined into one exponential whose exponent is linear in a and a^\dagger , since the commutators such as $[a(0), a^\dagger(\tau)]$ are numbers, not functions of operators. In turn, the expectation value of this exponential reduces to an exponential of a quadratic function of η and κ because a and a^\dagger are Gaussian variables. The result can be factored into an accepting-mode correlation function, $C_a(\tau)$ (i.e., what $C(\tau)$ would be if $V(q)$ were constant), and the correction due to promoting modes, $C_p(\tau)$. If $S = \eta^2$ and $\bar{\nu} = 1/(\exp\{\hbar\omega/k_B T\} - 1)$, then $C(\tau) = C_a(\tau)C_p(\tau)$ where

$$C_a(\tau) = \exp\{-S(2\bar{\nu} + 1) + S(\bar{\nu} + 1)e^{i\omega\tau} + S\bar{\nu}e^{-i\omega\tau}\} \quad (10)$$

$$C_p(\tau) = \int_{-\infty}^{\infty} d\vec{k} V(k_0) V^\dagger(-k_\tau) \exp\{-\frac{1}{2}\vec{k} \cdot \mathbf{G}_p \cdot \vec{k} - i\vec{N}_p \cdot \vec{k}\} \quad (11)$$

We used κ_0 and κ_τ as integration variables and defined $\vec{\kappa} = (\kappa_0, \kappa_\tau)$. The definitions of \mathbf{G}_p and \vec{N}_p are

$$\mathbf{G}_p = \begin{bmatrix} 2\bar{\nu} + 1 & (\bar{\nu} + 1)e^{i\omega\tau} + \bar{\nu}e^{-i\omega\tau} \\ (\bar{\nu} + 1)e^{i\omega\tau} + \bar{\nu}e^{-i\omega\tau} & 2\bar{\nu} + 1 \end{bmatrix} \quad (12)$$

$$\vec{N}_p = \begin{bmatrix} ((\bar{\nu} + 1)e^{i\omega\tau} - \bar{\nu}e^{-i\omega\tau})\eta \\ ((\bar{\nu} + 1)e^{i\omega\tau} - \bar{\nu}e^{-i\omega\tau})\eta \end{bmatrix} \quad (13)$$

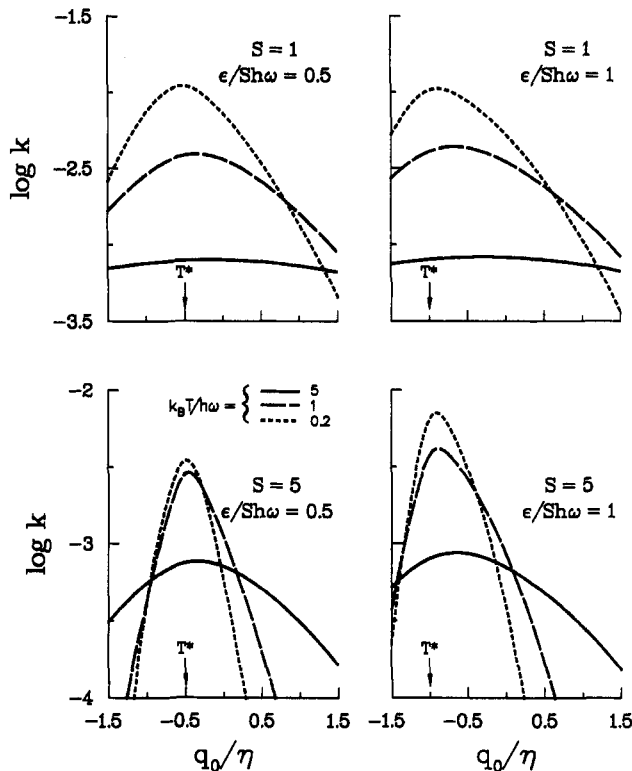


Figure 1. Log of reaction rate vs q_0 for $V(q) = \delta(q - q_0)$. The various values of S , $\epsilon/Sh\omega$, and $k_B T/\hbar\omega$ are as labeled. Note that the reactants' minimum position is always at $q/\eta = -1$ and that the products' minimum is always at $q/\eta = +1$. Furthermore, each graph has the location of the crossing state ($q = -\epsilon/\eta\hbar\omega$) marked as T^* .

Explicit Forms

In the case of a single mode with at most linear coupling, the forms in eqs 12–13 allow us to write explicit results for $C_p(\tau)$ for several simple forms of $V(q)$. Consider the Gaussian form,

$$V(q) = \frac{V_0}{\sqrt{2\pi\sigma^2}} \exp\left\{-\frac{(q - q_0)^2}{2\sigma^2}\right\} \quad (14)$$

where q_0 and σ are dimensionless parameters. This particular form allows us to evaluate the integral in eq 11 explicitly:

$$C_p(\tau) = \frac{V_0^2}{2\pi} \exp\left\{\frac{-(q_0 + \eta[(\bar{\nu} + 1)e^{i\omega\tau} - \bar{\nu}e^{-i\omega\tau}])^2}{2\bar{\nu} + 1 + \sigma^2 + (\bar{\nu} + 1)e^{i\omega\tau} + \bar{\nu}e^{-i\omega\tau}}\right\} \times [(2\bar{\nu} + 1 + \sigma^2)^2 - ((\bar{\nu} + 1)e^{i\omega\tau} + \bar{\nu}e^{-i\omega\tau})^2]^{-1/2} \quad (15)$$

When $\sigma^2 = 0$, $V(q)$ is a delta function. In such a case, Figure 1 shows the transition rate vs q_0 for several different values of S and $\epsilon\hbar\omega$ and $k_B T/\hbar\omega$. One might have expected the optimum value of q_0 to lie at the equilibrium value of the reactants, because that is where the reactants spend most of the time, or to lie at the transition state, because that is where the "transition" must classically occur. But Figure 2 shows that the optimum value of q_0 is usually temperature-dependent and is not generally either at the transition state or at the minimum of reactants or products.

We note in passing that this formalism can treat a $V(q)$ equal to a linear combination of Hermite polynomials times a Gaussian, because a Gaussian is the generating function for Hermite polynomials, and one can replace the Hermite polynomials with derivatives of the Gaussian in eq 14. Furthermore, the Hermite polynomials are complete, so essentially any functional form for $V(q)$ can be treated.

Yet another form of $V(q)$ that can be treated analytically is

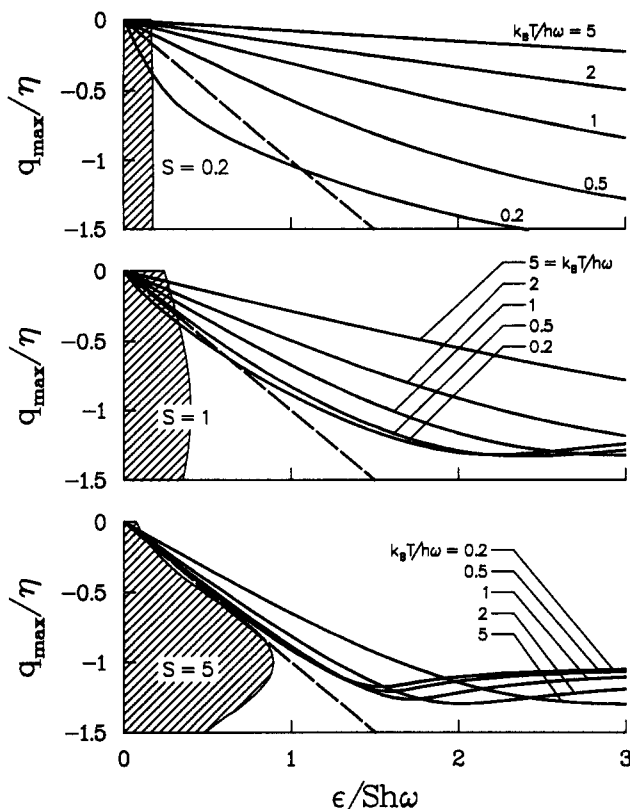


Figure 2. Optimum value of q_0 vs ϵ for various values of S (0.2, 1, 5) and various values of $k_B T / \hbar \omega$ (0.2, 0.5, 1, 2, 5). The axes are scaled so that the reactants' minimum is always at -1 and the products' minimum is always at $+1$. The dashed line shows the position of the crossing state, and the hatched area shows the probability density of the nuclear coordinate in the vibrational ground state of the reactants. If the optimum q_0 was always the crossing, the solid lines would all follow the dashed line. In most cases, however, the optimum value of q_0 is somewhat more negative (closer to the reactants' minimum).

the power series, with arbitrary coefficients A_j ,

$$V(q) = \sum_{j=0}^{\infty} A_j q^j \quad (16)$$

but instead of a Fourier transform, it is easier to write $V(q)$ as a series of derivatives:

$$V(q) = \sum_{j=0}^{\infty} A_j \left[\left(\frac{\partial}{\partial i\kappa} \right)^j e^{i\kappa(a+a^t-\eta)} \right]_{\kappa=0} \quad (17)$$

Then eq 11 reduces to

$$C_p(\tau) = \sum_j \sum_m A_j A_m \left[\left(\frac{\partial}{\partial i\kappa_0} \right)^j \left(\frac{\partial}{\partial i\kappa_\tau} \right)^m \times \exp\{-1/2\vec{\kappa} \cdot \mathbf{G}_p \cdot \vec{\kappa} - i\vec{N}_p \cdot \vec{\kappa}\} \right]_{\kappa=0} \quad (18)$$

Note the absence of poles in eq 18. If the Gaussian in eq 14 were approximated by any finite power series, the analytic structure of eq 15 would be changed by the absence of poles. This is most important for the use of the saddle-point approximation and shows why it was essential to treat the shape of $V(x)$ nonperturbatively.

Static Non-Condon Effects

When $V(q)$ is broad, one expects the non-Condon effects to be small; perhaps some parameters in the Condon approximation expressions should be replaced by appropriate thermal averages. Indeed, we derive this below, but the thermal averages affect not only the overall magnitude of $k(\epsilon)$ but the position (reorganization energy or Stokes' shift) and width of the energy gap law as well.

Since these effects depend on equilibrium averages, and not on the dynamics of nuclear motion, we term them "static" non-Condon effects. Thus, in this limit, the non-Condon rate constant can be written in terms of the Condon approximation value:

$$k_{\text{snc}}(\epsilon) = \frac{I_{\text{snc}}}{I_c} \frac{w_c}{w_{\text{snc}}} k_c \left((\epsilon - \hat{\epsilon}_c) \frac{w_{\text{snc}}}{w_c} - \hat{\epsilon}_{\text{snc}} + \hat{\epsilon}_c \right) \quad (19)$$

In this equation, $I = \int d\epsilon k(\epsilon)$ (if the transition were radiative, I would be the intensity of the corresponding spectral line); $\hat{\epsilon}$ is the energy gap that gives the maximum rate constant; and w is the width of $k(\epsilon)$, most easily obtained by $w = \int d\epsilon k(\epsilon) / k(\hat{\epsilon})$. The subscript c represent the Condon approximation value, and snc represents the static non-Condon value.

The shift of the maximum of the energy gap law can be easily obtained by considering an evaluation of k by the saddle-point method (whereby the log of the integrand in eq 5 is expanded about a saddle point, τ_s to second order in τ). From the form of eq 5, it is clear that $\partial k / \partial \epsilon = 0$ when the saddle point (τ_{sp}) is zero. Thus, the value of ϵ that maximizes the rate is exactly that value which produces $\tau_{\text{sp}} = 0$. In the Condon approximation this would be $\hat{\epsilon}_c = S\hbar\omega$, and in the present case

$$\hat{\epsilon}_{\text{snc}} = S\hbar\omega - iC_p'(0)/C_p(0) = \hat{\epsilon}_c - iC_p'(0)/C_p(0) \quad (20)$$

Since this value might be experimentally interpreted as the reorganization energy, then even a broad $V(q)$ acts to renormalize this value.

The integrated area $\int d\epsilon k(\epsilon)$ can be obtained directly from eq 5: $I_{\text{snc}} = 2\pi C_p(0)$. And $C_p(0) = V_0^2$ in the Condon approximation, so $I_c = 2\pi V_0^2$.

The peak value of the transition rate can be obtained by the saddle-point approximation when $\tau_{\text{sp}} = 0$, as mentioned above. The width of $k(\epsilon)$ then becomes

$$w_{\text{snc}} = \sqrt{2\pi [S\omega^2(2\bar{\nu} + 1) - C_p''(0)/C_p(0) + (C_p'(0)/C_p(0))^2]} \quad (21)$$

One can easily see from eq 21 that $w_c = \sqrt{2\pi S\omega^2(2\bar{\nu} + 1)}$.

Equations 20 and 21 provide the relations between $\hat{\epsilon}_{\text{snc}}$, w_{snc} , and C_p , but it remains to derive expressions for $C_p(0)$ and its first two derivatives in terms of thermal averages over $|V(q)|^2$. By substituting $\tau = 0$ into eq 11, and using the Fourier transform in eq 8, we obtain

$$C_p(0) = \sqrt{\frac{1}{2\pi(2\bar{\nu} + 1)}} \int dq |V(q)|^2 \times \exp\left\{ \frac{-(\eta + q)^2}{2(2\bar{\nu} + 1)} \right\} = \langle |V(q)|^2 \rangle_\tau \quad (22)$$

This is just $V^2(q)$ averaged over the thermal distribution of coordinates in the reactants' potential well.

The two derivatives can be derived in a similar fashion from eq 11 by ignoring the τ dependence of G_p but keeping the τ dependence of N_p . This is legitimate because the static non-Condon approximation is valid when $V(q)$ is slowly varying, and hence $V(\kappa)$ is small for large κ . The τ dependence in G_p is higher order in κ and therefore less important than that in N_p . After some tedious algebra, we find

$$C_p'(0) = \langle -i\eta\omega(\eta + q) |V(q)|^2 \rangle_\tau \quad (23)$$

$$C_p''(0) = \left\langle \left[-\eta^2\omega^2(\eta + q)^2 + \frac{\eta\omega^2(\eta + q)}{(2\bar{\nu} + 1)} + \eta^2\omega^2(2\bar{\nu} + 1) \right] |V(q)|^2 \right\rangle_\tau \quad (24)$$

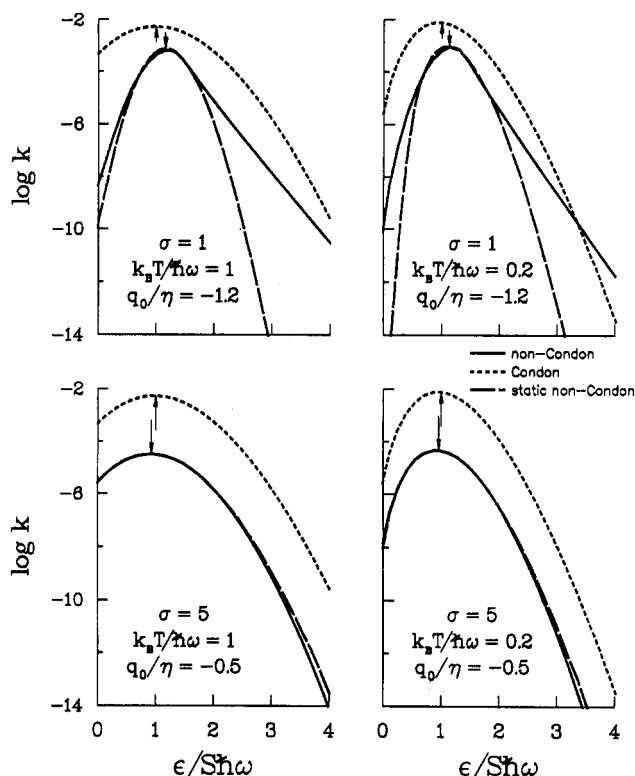


Figure 3. Transition rate vs ϵ for a Gaussian form of $V(q)$ (with σ and q_0 as marked, $S^* = 10$ throughout) and a comparison with the Condon approximation and with the Condon approximation scaled by the static non-Condon factors from eq 19. Clearly the accuracy of the static non-Condon effects is best at large σ , low temperature, and near $\epsilon = S^* \hbar \omega$. The peaks of the curves have been marked with arrows to show the shifts due to non-Condon effects. Note the reactants' (products') minimum lies at $q_0 = -\eta$ ($q_0 = +\eta$), and the crossing is defined by $q_0 = -\epsilon/\eta \hbar \omega$.

Figure 3 compares transition rates vs ϵ calculated by the Condon approximation, the static non-Condon scheme described above, and our general non-Condon method. We chose a Gaussian form for $V(q)$ and considered different values of q_0 , σ , and temperature. As expected, the wider form of $V(q)$ produced a better static non-Condon value. Note that the shapes of the non-Condon curves deviate significantly from those of the Condon curves at large ϵ , particularly when the width of $V(q)$, σ , is small. This is a generic effect of the pole in $C_p(\tau)$ and will be analyzed further in the Discussion section.

When the width of $V(q)$ is large enough, the Condon approximation must obtain. For the specific form of a Gaussian, one can derive validity conditions for the Condon approximation by expanding the various corrections in a power series in σ^{-1} . The result is that, for $I_{\text{snc}} \approx I_c$, $\sigma^2 \gg 2\bar{v} + 1 + (q_0 + \eta)^2$. For $\epsilon_{\text{snc}} \approx \epsilon_c$, the condition is $\sigma^2 \gg |2(2\bar{v} + 1)(1 + q_0/\eta)|$, and for $w_{\text{snc}} \approx w_c$, the validity condition is $\sigma^2 \gg 2(2\bar{v} + 1 + (q_0 + \eta)/(2\bar{v} + 1))$. Since $2\bar{v} + 1$ is the rms thermal motion of q in the reactants' potential well, and $\eta + q_0$ is the distance between the reactants' minimum and the Gaussian peak, these conditions mean that the Gaussian $V(q)$ should be wide compared to (1) the offset of the Gaussian from the reactants well and (2) thermal motion. In particular, the Condon approximation actually becomes better at low temperature.

Numerical Considerations

An explicit evaluation of the Fourier transform in eq 5 has two difficulties: (1) the integrand can oscillate wildly on different time scales, destroying precision, and (2) unless vibrational damping is included, the integral formally diverges. The saddle point (steepest descent or stationary phase) approximation has been used in multiphonon transition theory³²⁻³⁵ and succeeds in overcoming these problems.

One can deform the contour of integration of eq 5 off the real axis so that the largest contributions will come from neighborhoods where the phase of the integrand is stationary, namely, the saddle points. The integral is then made to converge by including only the contribution from the principal saddle point on the imaginary axis.

How can one justify discarding the contributions of the off-axis saddle points, particularly when they can sum to infinity? First, vibrational damping will attenuate the contributions from the off-axis saddle points. This is easiest to see for the case of a single vibrational mode in the Condon approximation. The principal saddle point, τ_s , can be found analytically, and the n th off-axis saddle point is then given by $\tau_n = \tau_s + 2\pi n/\omega$.

One includes frequency-independent damping by replacing $e^{\pm i\omega\tau}$ with $e^{\pm i\omega\tau - \gamma|\tau|}$ in the integrand in eq 5, where γ is the vibrational damping constant. Inclusion of a small γ will not materially affect the positions of the saddle points, but the integrand at τ_n will be attenuated by at least $\exp\{-2\pi n\gamma\epsilon/\hbar\omega^2\}$, even at low temperature. So for low-frequency ($\epsilon \gg \omega$) modes, the off-axis saddle points do not make large contributions.

High-frequency modes ($\omega \approx \epsilon$), on the other hand, do provide contributions from off-axis saddle points. Since the location of the principal saddle point varies slowly with ϵ , the effect of the off-axis saddle points can be seen by substituting τ_n into the factor $e^{-i\epsilon\tau}$ in the integrand in eq 5. Clearly when $n \neq 0$, one obtains an oscillating factor, $e^{-2\pi i n \epsilon/\hbar\omega}$. Thus, high-order off-axis saddle points contribute high-order Fourier components to the form of $k(\epsilon)$. In the undamped case, these components sum to form delta functions, physically due to resonances between reactant and product vibrational energy levels.

One can ignore this resonance effect by ignoring the contributions from off-axis saddle points, in effect "coarse graining" the form of $k(\epsilon)$. This is often reasonable for two reasons: (1) Each sharp resonance in $k(\epsilon)$ is widened by roughly $\sqrt{S k_B T \hbar \omega_{\text{low}}}$ due to other low-frequency modes. (2) If there are three or four or more high-frequency modes whose frequencies lie roughly 300 cm^{-1} apart, the resonances are likely to overlap. Thus, keeping only the principal saddle point is justified if one wants to compute the overall structure of $k(\epsilon)$ in terms of a small number of effective modes. So although the principal saddle-point method is strongly related to vibrational damping, its use in no way requires that the high-frequency vibrations be overdamped.

Once the decision to use the saddle-point approximation has been made, the next step is to locate the principal saddle point. In the Condon approximation, $\ln C(\tau)$ has no poles on the imaginary τ axis, and there exists a unique principal saddle point. But when one considers non-Condon effects with a Gaussian form of $V(q)$, there are two poles on the imaginary τ axis located at the roots of

$$2\bar{v} + 1 + \sigma^2 = [(\bar{v} + 1)e^{i\omega\tau} + \bar{v}e^{-i\omega\tau}] \quad (25)$$

These poles depend on ω and σ , but interestingly their sum does not: $i(\tau_1 + \tau_2) = \hbar/k_B T$. Fortunately, these poles are on opposite sides of the origin, and the residues are of opposite signs. Therefore, one can always deform the original contour of integration to pass through a saddle point on the imaginary τ axis without crossing a pole.

It may happen that $V(x)$ is expressible as a sum of a small number of terms, such as a constant plus a Gaussian. For the case of two terms,

$$V(x) = c_1 V_1(x) \pm c_2 V_2(x) \quad (26)$$

and the corresponding rate can be written

$$k = c_1^2 k_1 \pm 2c_1 c_2 k_{12} + c_2^2 k_2 \quad (27)$$

The rate constant must be positive, however, and this must be true for any value of the coefficients c_1 and c_2 . This requires that

$k_1 k_2 > k_{12}^2$, and therefore one can set an upper bound on the magnitude of the cross term before any calculation is done. If the sign of the cross term increases the transition rate, it can *at most* increase the rate by a factor of 2; if the sign of the cross term decreases the rate, it can decrease it to zero. But these extreme cases occur only when $c_1 k_1 = c_2 k_2$.

This is fortunate, because in many cases the cross term, k_{12} , may be much more difficult to compute than the values of k_1 and k_2 . When $c_1 k_1$ does not approximate $c_2 k_2$, the cross term may be numerically insignificant, and one can dispense with its calculation.

Discussion

When the dependence of the transition matrix element on the nuclear configuration is weak, static non-Condon effects are appropriate and easy to compute. When this dependence is strong, there are effects that demand a full nonperturbative calculation. One example occurs when $V(q)$ is a delta function. We will show that the optimum position of this delta function is not always the location of the potential surface crossing.

A second example is the dependence of k on ϵ for very large $|\epsilon|$ when $V(q)$ has the form $C(q) + G(q)$, where $G(q)$ is a narrow Gaussian and $C(q)$ is almost anything, including a constant. We will show that for large $|\epsilon|$, k acquires an exponential dependence on ϵ (in contrast to the Condon approximation result of an exponential dependence on ϵ^2) even if the coefficient of the Gaussian is small. In particular, this means the analogous radiative line shape would have exponential rather than Gaussian wings.

Optimum Configurations and Transition States. If the electronic matrix element is taken to be $V(q) = \delta(q - q_0)$, then by computing the transition rate as a function of q_0 for various values of $\epsilon/(S\hbar\omega)$, S , and $k_B T/\hbar\omega$, one can explore the importance of coupling in different regions of q . (See Figure 1.) That is, with this choice for $V(q)$, the transition from reactants to products can *only* take place at q_0 .

One might have expected the reaction rate to be a maximum when q_0 coincides with the potential surface crossing. After all, the semiclassical limit (high temperature) of the Condon approximation rate constant looks very much like $\exp\{-E^\ddagger/k_B T\}$, where E^\ddagger is the energy difference between reactants' minimum and the transition state. In fact, in the normal region (where $\epsilon < S\hbar\omega$), the rate is maximal when q_0 coincides with the transition state for $S \gg 1$ and $k_B T/\hbar\omega \ll 1$. But not for other conditions (see Figure 2). Also note the Arrhenius plots in Figure 4. Clearly, the position of a Gaussian $V(q)$ can dramatically affect the apparent activation energy.

One can rationalize this result by thinking of the transition as taking place between discrete vibrational levels of the reactants and products, rather than taking place by waiting for a thermal fluctuation to move the reactants up to the transition configuration. In such a case, one needs to compute the state-to-state vibrational overlap factors, weighted by $V(q)$. The fact that this weighting takes place can substantially alter which vibrational-state transitions significantly affect the overall electronic transition. (In the following discussion, q_0 represents the vibrational coordinate where the vibrational wave functions have the largest overlap. The value $q_0 = 0$ represents a position halfway between the reactants' and products' equilibrium positions, while $q_0 = -\eta$ represents the reactants' equilibrium and $q_0 = \eta$ represents the products' equilibrium.)

If the temperature is low (so only the reactants' vibrational ground state contributes) and the electron-phonon coupling, S , is large (so that only the tails of the vibrational wave functions overlap), then the place of best overlap between the reactants' ground state and the products' state of nearest energy is approximately the position of the transition state. If $\epsilon = 0$, then by symmetry $q_0 = 0$.

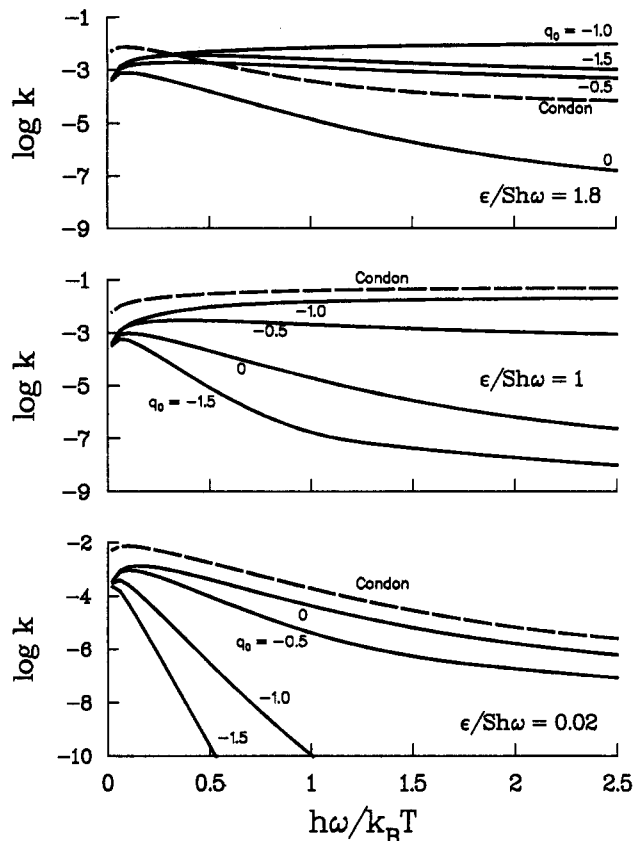


Figure 4. Arrhenius plots with $V(q) = \delta(q - q_0)$ for various values of $\epsilon/S\hbar\omega$ as marked. $S = 25$ for all curves. Each curve is marked with the value of q_0 . For comparison, the Condon approximation curves are shown for the same conditions.

As the energy gap, ϵ , becomes increasingly positive, the excited states of the products' surface come into play. Since these states have a larger variance, q_0 becomes increasingly negative, in parallel with the transition state. This is essentially the classical limit. But if the temperature is high, it is the excited vibrational states of the reactants that become significant. As the temperature rises, q_0 becomes more positive; this usually causes a deviation from the transition state.

In the inverted, or undercoupled, region, it is not the tails of the wave functions but rather the full wave functions that determine the best overlap. In this case, the best overlap is determined by where the reactants spend the most time. Indeed, in the strongly undercoupled regime, the best coupling takes place not too far from the reactants' minimum ($q_0 \approx -\eta$); this statement is mostly insensitive to temperature or to ϵ .

For weakly coupled systems ($S \ll 1$), the situation is complicated by the fact that the vibrational wave functions overlap a great deal at all values of ϵ and temperature. When q_0 is expressed as a fraction of the distance between reactants and products, it seems to be more sensitive to temperature and less sensitive to ϵ than in strongly coupled systems.

If one were to recast these arguments back into the classical picture, at least for strongly coupled systems, one might construct the following analysis: (1) In the normal, overcoupled, region and for low temperatures, the usual arguments for thermal fluctuations to the transition state still hold. As the temperature rises, q_0 moves in the positive direction (away from the reactants' minimum). This is because the system moves through the transition state faster, spending relatively less time in the transition state and more time further from the reactants' minimum. (2) In the overcoupled region, the system has to get at least to the transition state before a downward (in energy) electronic transition can take place. In the undercoupled region, however, a downward transition can almost always take place. Rather than thermal transitions to transition states, the reaction takes place from the

most probable configurations of the reactants. That is, the place of best coupling tends to lie near the reactants' minimum and is somewhat insensitive to ϵ .

Large $|\epsilon|$ Dependence. Assume that $V(q)$ is a Gaussian, and consider the dependence of the transition rate on ϵ when $|\epsilon|$ is very large. Then $C_p(\tau)$ from eq 15 has two poles on the imaginary τ axis. When $|\epsilon|$ is very large, the saddle point τ_{sp} will become essentially equal to one of the poles (which one depends on the sign of ϵ) and will be nearly independent of ϵ . Thus, the ϵ dependence of the rate becomes $\exp\{-i\tau_{pole}\epsilon\}$ where τ_{pole} is pure imaginary. (See the non-Condon curves for $\sigma = 1$ in Figure 3). Note that if $V(q)$ were a finite power series, there would be no poles, so the simplicity of this analysis depends on the nonperturbative nature of the calculation.

If the form of the matrix element were $V(q) = c_1 + c_2G(q)$ and if $c_1 \gg c_2$, then k would be well represented in the Condon approximation when ϵ is close to that for the maximum transition rate. But the Condon approximation rate falls off much faster than exponential at large ϵ , so the Gaussian part of $V(x)$ would dominate in this regime. Indeed, since the behavior of $k(\epsilon)$ is dominated by the location of a pole in $C_p(\tau)$, this analysis would obtain in the presence of multiple vibrational modes. Near the optimum for the transition rate, all the modes would contribute, but at larger or smaller ϵ , when the saddle point approaches the first pole of C_p , that mode which produced the pole would dominate. Due to the behavior of the poles at small σ , the dependence when ϵ is large and positive is $k \propto \exp\{-\sigma^2\epsilon\}$, but when ϵ is large and negative, $k \propto \exp\{\epsilon/k_B T\}$. In fact, when ϵ is large and negative, the exponential decay of k is never slower than this. If k represented a radiative line shape, the wings would be exponential with decay constants that depend simply on ϵ , σ , and temperature.

Conclusion

We have extended the calculations of multiphonon transitions, without use of the Condon approximation, into the strong coupling regime ($S \gg 1$). Furthermore, the method is nonperturbative in the dependence of the transition matrix element on vibrational coordinates. Thus, one can compute transition rates for systems with low-lying charge-transfer states, such as the chlorophyll dimers considered by Freed.³⁶ This is particularly useful if exchange or superexchange interactions produce a form of $V(x)$ that cannot be treated to lowest order without significant loss of accuracy.

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