

Temperature dependent activation energy for electron transfer between biological molecules

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This paper considers electron transfer between biological molecules in terms of a nonadiabatic multiphonon nonradiative decay process in a dense medium. This theoretical approach is analogous to an extended quantum mechanical theory of outer sphere electron transfer processes, incorporating the effects of both low-frequency medium phonon modes and the high-frequency molecular modes. An explicit, compact and useful expression for the electron transfer probability is derived, which is valid throughout the entire temperature range, exhibiting a continuous transition from temperature independent tunneling between nuclear potential surfaces at low temperatures to an activated rate expression at high temperatures. This result drastically differs at low temperatures from the common, semiclassical, Gaussian approximation for the transition probability. The experimental data of De Vault and Chance [Biophys. J. 6, 825 (1966)] on the temperature dependence of the rate of electron transfer from cytochrome to the chlorophyll reaction center in the photosynthetic bacterium Chromatium are properly accounted for in terms of the present theory.

I. PROLOGUE

An interesting example for electron transfer (ET) in a biological system^{1,2} involves the light-induced oxidation of cytochrome in the photosynthetic bacterium Chromatium.³⁻⁶ Optical excitation of the bacteria chlorophyll is followed by ET from the cytochrome to the chlorophyll reaction center.⁶ The detailed study of this system by De Vault, Parkes, and Chance⁶ resulted in the following information: (1) The half-life-time, τ , at 4.5 °K is $\tau = 2.3$ msec. (2) τ is practically constant in the temperature range 4.5–100 °K; the apparent activation energy in this temperature region is lower than 3.5×10^{-3} eV. (3) In the temperature range 100–300 °K, τ decreases from 2.3 msec to 2 μ sec. (4) The temperature dependence of τ in the range of 100–300 °K is consistent with an apparent activation energy of 0.14 ± 0.03 eV. This observation of a temperature dependent activation energy is an ET reaction of considerable interest for the elucidation of the nature of ET processes in biological systems and is also pertinent for a better understanding of ET between inorganic and organic ions in solution and in condensed phases.⁷⁻²⁵

Several mechanisms^{6, 26-30} have been advanced for ET processes in photosynthetic systems. The central role of the Franck-Condon principle in thermal ET processes^{7-9, 31} has been only recently realized²⁶⁻³⁰ for biological systems. Grigorov and Chernavskii²⁶ and Blumenfeld and Chernavskii²⁹ have pointed out that the ET probability is determined by the coupling with normal vibrations, being expressed in terms of the nuclear vibrational overlap factors. Hopfield³⁰ has developed a theory of electron transfer in biological systems which is analogous to the Forster-Dexter theory of electronic energy transfer^{32, 33} in condensed phases, and advanced a semiclassical rate equation to account for ET in Chromatium. Both of these multiphonon formalisms²⁶⁻³⁰ of ET are incomplete, as Chernavskii *et al.*^{28, 29} were able to provide only qualitative results, while Hopfield's semiclassical treatment³⁰ is inade-

quate (see Sec. III) to account for the ET rate as low temperatures.

In this paper we advance a theoretical description of ET in biological systems in terms of a nonadiabatic multiphonon process. This formalism rests on the physical arguments originally presented by Grigorov and Chernavskii,²⁶ Blumenfeld and Chernavskii,²⁹ and by Hopfield³⁰ in biological systems and is isomorphous with the theory of "outer sphere" ET reactions commonly encountered in solution chemistry and in electrochemistry.⁷⁻²⁵ There are three new qualitative features involved in the description of ET in a biological system such as Chromatium. Firstly, from the technical point of view one has to consider just the transition probability (i. e., a unimolecular rate constant) and complications due to diffusion of the electron donor D and the electron acceptor A are absent. Secondly, from the point of view of general methodology, the electron exchange matrix element involved in such ET process is expected (see Sec. V) to be sufficiently low so that interference effects¹⁵ are negligible and the ET process is definitely nonadiabatic, while it is still an open question^{7, 9} whether the nonadiabatic or the adiabatic formalism applies for ET in ionic solutions. Thirdly, and most interesting, in a biological system the role of configurational changes within (high-frequency) "quantum modes"^{15-20, 25} may be crucial in determining the transition probability, while for ET reactions in solutions a common state of affairs¹⁵ involves the dominating role of low-frequency exterior polar solvent modes. This paper is subdivided as follows: In Sec. II we advance a theoretical expression for ET probability incorporating the effects of both low-frequency phonon modes and of high-frequency molecular vibrational modes. Following the arguments of Soules and Duke,³³ it is shown that for the general situation the ET probability³⁰ cannot be recast in terms of the Forster-Dexter^{32, 33} mechanism. Considering next the special case of ET in Chromatium⁶ we argue on the basis of experimental evidence⁶ that in

this particular system the nuclear contribution to the ET probability is dominated by coupling with high-frequency molecular modes and a theoretical relation adequate for this situation is derived, which is valid throughout the entire temperature range. Under these circumstances the Forster-Dexter formalism^{32,33} for ET³⁰ is valid; however, as we shall demonstrate in Sec. III, the semiclassical approximation adopted by Hopfield³⁰ fails in the low temperature range. Model calculations for the temperature dependence of the ET probability when nuclear coupling with quantum modes plays a dominating role are presented in Sec. IV, while Sec. V provides an analysis of the experimental data in Chromatium.⁶ The central new result of the present work involves the derivation of an ET rate constant which is adequate throughout the entire temperature range, providing a proper semiquantitative description of the temperature dependence of the activation energy of an ET process.^{9,15,21} A special case of this result which discards the effects of coupling with the low-frequency medium modes will be applied to the ET process in Chromatium.

II. METHODOLOGY

The pioneering work of Marcus^{7,8} and the quantum mechanical theory of Levich^{9,10} disregarded "molecular type" configurational changes in the electron donor D and the electron acceptor A, focusing attention on the long-range coupling of the charge distribution with the low-frequency polar modes of the medium, i.e., the solvent, in determining the ET probability. The effect of configurational changes was treated by Marcus⁸ by a classical formalism, which is adequate for extremely high temperatures, while a complete quantum mechanical treatment of ET incorporating the effects of both low-frequency medium modes and high-frequency molecular modes was provided.^{15-17,25} These recent studies^{15,25} of nonadiabatic ET within the framework of multiphonon processes bear a close analogy to the formalism of electronic relaxation in large molecules³⁵ and in solids,^{35c} vibrational relaxation in condensed phases,³⁶ electronic energy transfer,^{33,34} and small polaron motion in solids.³⁸ This formalism will now be recast in a form suitable for the study of the temperature dependence of the ET rate constant.

Nonadiabatic ET can be conceptualized^{15,25} in terms of a (nonradiative) decay process between the vibronic levels $|a\nu\rangle \equiv \psi_a X_{a\nu}(\mathbf{Q})$ and $|b\nu\rangle \equiv \psi_b X_{b\nu}(\mathbf{Q})$, which are characterized by the electronic wavefunctions ψ_a and ψ_b and by the nuclear wavefunctions $X_{a\nu}(\mathbf{Q})$ and $X_{b\nu}(\mathbf{Q})$, respectively. $|a\nu\rangle$ and $|b\nu\rangle$ correspond to vibronic levels of DA and D⁺A⁻, respectively. The thermally averaged decay probability for the $\{|a\nu\rangle\} \rightarrow \{|b\nu\rangle\}$ process can be adequately expressed in terms of the Fermi golden rule (i.e., first order perturbation theory).^{9,15} For the case of displaced harmonic nuclear potential surfaces, characterized by the normal modes $\mathbf{Q} \equiv Q_1, Q_2, \dots, Q_i, \dots$, where the frequencies $\{\omega_i\}$ and reduced masses $\{\mu_i\}$ are identical in the initial and in the final states, the transition probability takes the well-known form^{33,34}

$$W = \hbar^{-1} |V_{ab}(R)|^2 \exp(-G) \times \int_{-\infty}^{\infty} dt \exp(-i\Delta E t) \exp[G_+(t) + G_-(t)], \quad (1a)$$

$$G_+(t) = \sum_i (\Delta_i^2/2)(\bar{\nu}_i + 1) \exp(i\hbar\omega_i t), \quad (1b)$$

$$G_-(t) = \sum_i (\Delta_i^2/2)\bar{\nu}_i \exp(-i\hbar\omega_i t), \quad (1c)$$

$$G = G_+(0) + G_-(0) = \sum_i (\Delta_i^2/2)(2\bar{\nu}_i + 1), \quad (1d)$$

$$\bar{\nu}_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}, \quad (1e)$$

$$\Delta_i = (\mu_i\omega_i/\hbar)^{1/2} \Delta Q_i^0, \quad (1f)$$

where $V_{ab}(R)$ is the electron exchange matrix element between D and A separated by the distance R ; ΔE corresponds to the energy gap between the minima of the initial and final nuclear potential surfaces (we shall specialize in isoenergetic and exoenergetic processes where $\Delta E \geq 0$); Δ_i represent the (dimensionless) nuclear displacement, ΔQ_i^0 , of the equilibrium configuration for the i th mode; while $\bar{\nu}_i$ denotes the mean thermal population of the i th mode. A brief comment concerning the physical features of Eq. (1a) is in order. The transition probability was recast as a product of an electronic term (which is practically independent of the nuclear coordinates) and a nuclear term, whereupon the electronic and the nuclear contributions to W are separable. The former involves a square of an intermolecular exchange integral while the latter is conveniently expressed in terms of a product of a Debye-Waller factor^{35c-e,36-38} $\exp(-G)$, multiplied by a Fourier transform of a characteristic generating function. The nuclear contribution to W is nothing but a compact expression for the thermally averaged nuclear Franck-Condon vibrational overlap integrals for the present problem. Note that the vibrational modes in Eq. (1) incorporate both high-frequency molecular vibrational modes of the donor and of the acceptor centers and low-frequency medium phonon modes of the entire system. The discrete high-frequency modes $\{Q_{c,j}\}$ will be characterized by the mean frequency $\langle\omega\rangle$ by reduced configurational displacements $\{\Delta_{c,j}\}$ and by an effective electron-phonon coupling strength³⁵ $S = \sum_j (\Delta_{c,j}^2/2)$. The low-frequency phonon modes of the exterior medium, $\{Q_{s,k}\}$, are specified in terms of a mean frequency $\langle\omega_s\rangle$, reduced displacements $\{\Delta_{s,k}\}$ and an effective coupling $S_s = \sum_k (\Delta_{s,k}^2/2)$. In a polar liquid^{6,9} $\hbar\langle\omega_s\rangle \sim 1-10$ cm⁻¹, in a "molecular" solid³⁹ $\hbar\langle\omega_s\rangle \approx 10-100$ cm⁻¹, while $\hbar\langle\omega\rangle$ can take values in the range^{15,25} 300-3000 cm⁻¹ depending on the nature of the molecular modes involved. This "Einstein-type" approximation for the medium and for the molecular modes seems to be adequate in view of our current ignorance of the relevant spectroscopic parameters in biological systems. It is important to note that the segregation of the vibrational modes of the entire system into two distinct categories does not rest solely on the different energy regions spanned by the high-frequency molecular modes and by the low-frequency medium modes. More interesting, the high-frequency modes correspond to intramolecular vibrations (vibrons) of the donor and of the acceptor centers,

so that each of the two centers is coupled to different molecular modes, while a given exterior polar phonon mode⁷ will couple simultaneously to both centers. Soules and Duke³³ have demonstrated that in the former case each electron coupling term Δ_{c_j} corresponds to a distinct contribution from a single (D or A) center whereupon S contains an incoherent superposition of contributions from the donor and from the acceptor centers. On the other hand, in the latter case the electron-phonon coupling terms Δ_{s_k} involve contributions from both centers so that S_s corresponds to a coherent sum of terms, contributions for D and A.

We now turn to some mathematical manipulations. Expansion of the exponential function in the integrand of Eq. (1a) results in an expression for W which can be recast in terms of a convolution of two line shape functions^{15, 25} denoted by F_s and F_c , which correspond to the contributions of the solvent modes and of the molecular modes, respectively,

$$W = 2\pi\hbar^{-1} |V_{ab}(R)|^2 \int d\epsilon F_s(\Delta E - \epsilon) F_c(\epsilon), \quad (2a)$$

$$F_s(\Delta E - \epsilon) = (\hbar\langle\omega_s\rangle)^{-1} \exp[-S_s(2\bar{v}_s + 1)] \times \sum_{m=0}^{\infty} \frac{[S_s(\bar{v}_s + 1)]^{m+\Delta E-\epsilon/\hbar\langle\omega_s\rangle} (S_s\bar{v})^m}{[m + (\Delta E - \epsilon)/\hbar\langle\omega_s\rangle]! m!}, \quad (2b)$$

$$F_c(\epsilon) = \exp[-S(2\bar{v} + 1)] \times \sum_{N=0}^{\infty} \sum_{M=0}^{\infty} \frac{[S(\bar{v} + 1)]^M [S\bar{v}]^M}{M! N!} \delta[\epsilon + (M - N)\hbar\langle\omega\rangle], \quad (2c)$$

$$\bar{v}_s = [\exp(\hbar\langle\omega_s\rangle/kT) - 1]^{-1}, \quad \bar{v} = [\exp(\hbar\langle\omega\rangle/kT) - 1]^{-1}, \quad (2d)$$

where "coarse graining" over the low-frequency modes has been performed⁴⁰ in Eq. (2c). We now invoke an old mathematical technique originally introduced for the study of optical line shape functions⁴¹ and of polaron motion⁴² in solids. Performing the energy integration in Eq. (3b) and utilizing the definition of the modified Bessel function,⁴³

$$I_n(z) = (z/2)^n \sum_{L=0}^{\infty} (z^2/4)^L / [L! (L+n)!] \\ = \pi^{-1} \int_0^\pi \exp(z \cos\theta) \cos(n\theta) d\theta = I_{|n|}(z).$$

We derive the compact result

$$W = (2\pi |V_{ab}(R)|^2 / \hbar^2 \langle\omega_s\rangle) \exp[-S_s(2\bar{v}_s + 1) - S(2\bar{v} + 1)] \\ \times \sum_{m=-\infty}^{\infty} [(\bar{v}_s + 1)/\bar{v}_s]^{p(m)/2} I_{|p(m)|} \{2S_s [\bar{v}_s(\bar{v}_s + 1)]^{1/2}\} \\ \times [(\bar{v} + 1)/\bar{v}]^m I_{|m|} \{2S [\bar{v}(\bar{v} + 1)]^{1/2}\}, \quad (3a)$$

where $p(m) = (\Delta E - m\hbar\langle\omega_c\rangle)/\hbar\langle\omega_s\rangle$ is taken as an integer⁴¹ closest to the value of $p(m)$.

It should be noted that Eq. (2a), which provides the starting point of the present analysis, is distinct from the Forster-Dexter³² result that provides the basis of Hopfield's original work [Eqs. (1) and (2), Ref. 30]. We have recast the ET probability in terms of a convolution of two generalized line shape functions which

correspond to the contributions of the low-frequency phonon modes and of the high-frequency intramolecular modes of the entire system. On the other hand, Hopfield's formalism³⁰ expresses the ET probability in terms of a convolution of an electron removal spectral distribution on D and an electron insertion spectral distribution on A. As demonstrated by Soules and Duke,³³ the Forster-Dexter result rests on the explicit assumption that the donor and the acceptor centers are coupled to different modes. When effective coupling with the external polar modes provides a substantial contribution to W (i.e., when $S_s \geq 1$), the Forster-Dexter formalism is inapplicable for the study of ET, as S_s involves a coherent superposition³³ of contributions from the D and the A centers. The Forster-Dexter formalism as outlined by Hopfield³⁰ is applicable to ET only when W is dominated by the contribution of high-frequency molecular modes (i.e., $S \gg S_s$), as S constitutes of an incoherent superposition of contributions from local molecular vibrational modes.

Equation (3) provides us with a new general result for the ET probability, which is valid throughout the entire temperature range. Several limiting situations are of interest:

(a) The extremely low temperature limit, $kT \ll \hbar\langle\omega_s\rangle \ll \hbar\langle\omega\rangle$. As $\bar{v} \rightarrow 0$ and $\bar{v}_s \rightarrow 0$ we can utilize the limiting form^{41, 42} of $I_n(z) \rightarrow (z/2)^n$ for small values of z , which results in

$$W = (2\pi |V_{ab}(R)|^2 / \hbar^2 \langle\omega_s\rangle) \times \exp(-S_s - S) \sum_{m=0}^{\infty} \frac{S_s^{p(m)} S^m}{[p(m)]! m!}, \quad (3b)$$

This low temperature result constitutes a sum where each term consists of a product of two Poissonian distributions. This physical situation corresponds to temperature independent (nuclear) tunneling between the zero point of the nuclear configuration of the initial state to the vibronic states of the final nuclear surface which are nearly degenerate with it.

(b) Thermal excitation of the medium phonon modes, while the molecular modes are still frozen, $\hbar\langle\omega_s\rangle \ll kT \ll \hbar\langle\omega\rangle$. When $\bar{v}_s \gg 1$, an asymptotic expansion^{41, 43} of the Bessel function for the solvent modes $I_{|p(m)|} \rightarrow (2\pi z)^{-1/2} \times \exp[z - p(m)^2/2z]$ for large values of z in Eq. (3) results in a Gaussian line shape function for the "classical" medium phonon modes, while the low temperature approximation still applies for the quantum modes, so that

$$W = (2\pi |V_{ab}(R)|^2 / \hbar) \exp[-S] [2\pi S_s \hbar\langle\omega_s\rangle kT]^{-1/2} \times \sum_{m=0}^{\infty} \exp\left(-\frac{(\Delta E - S_s \hbar\langle\omega_s\rangle - m\hbar\langle\omega\rangle)^2}{4S_s \hbar\langle\omega_s\rangle kT}\right) \frac{S^m}{m!}. \quad (3c)$$

The transition probability consists of a sum of products each involving a Gaussian and a Poissonian distribution.

(c) The intermediate temperature range $\hbar\langle\omega\rangle \geq kT \gg \hbar\langle\omega_s\rangle$. Now we have

$$W = (2\pi |V_{ab}(R)|^2/\hbar) \exp[-S] [2\pi S_s \hbar \langle \omega_s \rangle kT]^{-1/2} \times \sum_{m=-\infty}^{\infty} \exp\left(\frac{(\Delta E - S_s \hbar \langle \omega_s \rangle - m \hbar \langle \omega \rangle)^2}{4S_s \hbar \langle \omega_s \rangle kT}\right) \times [(\bar{\nu} + 1)/\bar{\nu}]^{m/2} I_{1,m}(S[(\bar{\nu} + 1)]^{1/2}) \quad (3d)$$

(d) The extreme high temperature limit $kT \gg \hbar \langle \omega \rangle \gg \hbar \langle \omega_s \rangle$. We can apply the Gaussian approximation [see (b)] both to $I_{1,p(m)}$ and to $I_{1,m}$ in Eq. (3a), resulting finally in a conventional activated rate equation

$$W = (2\pi |V_{ab}(R)|^2/\hbar) [2\pi(S_s \hbar \langle \omega_s \rangle + S \hbar \langle \omega \rangle) kT]^{-1/2} \times \exp\left(-\frac{(\Delta E - S_s \hbar \langle \omega_s \rangle - S \hbar \langle \omega \rangle)^2}{4(S_s \hbar \langle \omega_s \rangle + S \hbar \langle \omega \rangle) kT}\right) \quad (3e)$$

It is instructive to note that the classical rate equation (3e) was derived without invoking the concept of an "activated complex".

Concerning the temperature dependence of the activation energy $E_A = d \ln W/d(1/kT)$, we expect on the basis of the foregoing analysis that $E_A = 0$ in region A, rising to the value of $E_A \approx (\Delta E - S_s \hbar \langle \omega_s \rangle)^2/4S_s \hbar \langle \omega_s \rangle$ in region B, exhibiting a further increase in region C until it reaches the classical value

$$E_A = (\Delta E - S_s \hbar \langle \omega_s \rangle - S \hbar \langle \omega \rangle)^2/4(S_s \hbar \langle \omega_s \rangle + S \hbar \langle \omega \rangle)$$

in region D. Equations (3b)–(3e) constitute a generalization of the well-known results on the "transition" from a Poissonian distribution at low τ to the Gaussian distribution at high τ in the theory of optical line shapes^{34,41} and relaxation phenomena^{33,35c, e, 36c, d} to incorporate the role of high-frequency molecular vibrational modes.

Turning now to the experimental ET data in Chromatium,⁶ we recall that in the range 4.5–100 °K, the temperature dependence of $W = 1/\tau$ is small, within experimental uncertainty. In the latter temperature region thermal excitation of low-frequency "lattice" modes ($\hbar \langle \omega_s \rangle = 10\text{--}100 \text{ cm}^{-1}$) is expected to prevail. Obviously, behavior characteristic of range B will be exhibited only provided that $S_s \hbar \langle \omega_s \rangle$ is appreciable. On the basis of the experimental evidence,⁶ we assert that in this biological system the coupling of low-frequency phonon modes is negligible and the major contribution of vibrational overlap to W originates from high-frequency molecular-type quantum modes corresponding to the electron donor and the electron acceptor centers. We note in passing that in view of the dominating role of the molecular modes in the present case the Forster-Dexter formalism^{31,33} which was used by Hopfield³⁰ as a starting point of his analysis is adequate to handle ET in Chromatium. However, as we shall demonstrate in Sec. III, the semiclassical approximation for W utilized by Hopfield³⁰ is inadequate in the low temperature range. To derive a general result for the ET rate in a system where effective coupling between electric states and molecular-type vibrations dominates the nuclear contribution to the ET probability, we set $S_s = 0$ in Eq. (3a), which then results in the simple relation

$$W = A \exp[-S(2\bar{\nu} + 1)] \times I_p(2S[(\bar{\nu} + 1)]^{1/2}) [(\bar{\nu} + 1)/\bar{\nu}]^{p/2}, \quad (4)$$

where $A = 2\pi |V_{ab}(R)|^2/\hbar^2 \langle \omega_s \rangle$ and $p = \Delta E/\hbar \langle \omega \rangle$. Equation (4) exhibits a continuous transition from the Poissonian-type function^{41,33,34} $W \propto \exp(-S) S^p/p!$ in the low T range ($kT/\hbar \langle \omega \rangle \ll 1$) to an activated rate equation^{33,35c, e, 36c, d} $W \propto \exp[a(\Delta E - S \hbar \langle \omega \rangle)^2/4S \hbar \langle \omega \rangle kT]$ in the high T ($\gg \hbar \langle \omega \rangle/k$) region.

III. THE SEMICLASSICAL APPROXIMATION

A common approximation for a transition probability of a nonradiative process in the strong coupling ($S \gg 1$) situation involves a semiclassical Gaussian function for the corresponding line shape function.^{30,33,34,35c–36c,41} In the present context of ET when quantum modes dominate in W , Eq. (4) is replaced by

$$W_{sc} = \bar{A} [2\pi S(2\bar{\nu} + 1)]^{-1/2} \exp\left(-\frac{(\Delta E - S \hbar \langle \omega \rangle)^2}{2S(\hbar \langle \omega \rangle)^2(2\bar{\nu} + 1)}\right), \quad (5)$$

where $\bar{A} = 2\pi |V_{ab}(R)|^2/\hbar^2 \langle \omega \rangle$. We note in passing that for $\bar{\nu} \gg 1$, Eq. (5) reduces to the high temperature limit, Eq. (3e), for $S_s = 0$. Equation (5) was utilized by Hopfield³⁰ for the analysis of ET data in Chromatium throughout the entire temperature range. A symmetric derivation of Eq. (5) rests on a saddle point (asymptotic) approximation^{35c, d, 36c, 38, 44} to Eq. (1a) (which at $T = 0$ is expected to hold for $\Delta E/\hbar \langle \omega \rangle > \frac{1}{2}$), followed by a power series expansion of the saddle point solution.^{36c} The latter procedure is justified provided that^{15,36c}

$$\left| \frac{\Delta E}{S \hbar \langle \omega \rangle} - 1 \right| \ll (2\bar{\nu} + 1)^2, \quad (6)$$

which constitutes a general validity condition for the applicability of the Gaussian approximation. Thus, except for "pathological cases" (i. e., $\Delta E = S \hbar \langle \omega \rangle$), Eq. (5) will hold only for $\bar{\nu} \geq 1$, while in the low temperature limit the Gaussian approximation is inadequate. The failure of Eq. (5) at low T is immediately apparent when we examine the $T = 0$ limit for $p = 0$, where $W(T = 0) \propto \exp(-S)$ (which involves the proper Debye-Waller factor), while $W_{sc}(T = 0) \propto \exp(-S/2)/(2\pi S)^{1/2}$. For the sake of the skeptical reader we present in Fig. 1 a comparison between the exact solution, Eq. (4), and the Gaussian approximation, Eq. (5), for an isoenergetic ET process in the strong coupling situation. In the temperature range $kT/\hbar \langle \omega \rangle \geq 0.8$, Eq. (5) provides a faithful representation of W ; the accuracy of the Gaussian approximation is better than 10%. This is just what we expect on the basis of Eq. (6). However, in the low temperature range the semiclassical approximation fails seriously. For $kT/\hbar \langle \omega \rangle = 0$ (which cannot be shown in the conventional-type $\log W$ vs $1/T$ type plot of Fig. 1), $W_{sc}/W = 21$ for $S = 10$ while $W_{sc}/W = 2000$ for $S = 20$. Even in the temperature range $kT/\hbar \langle \omega \rangle = 0.2\text{--}0.5$, the deviations of W_{sc} from W are considerable for large values of S , as evident from Fig. 1. An attempt to utilize the semiclassical approximation for the fit of the temperature dependence of W throughout the entire temperature range³⁰ rests essentially on a fit of $W(T)/W(0)$ to Eq. (5). We have noted that W is properly given by Eq. (5) at higher T while it seriously overestimates the transition probability at low T . Thus, W_{sc} cannot be used for a mean-

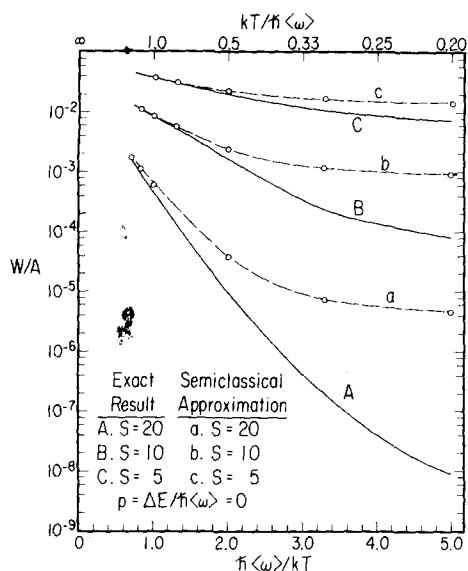


FIG. 1. A confrontation between the temperature dependence of the transition probability for ET as calculated from Eq. (4) (solid lines) and from the semiclassical Gaussian approximation, Eq. (5) (open circles and dashed lines). Data given for isoenergetic process in the strong coupling situation, $S=5-20$.

ingful fit of $W/W(T=0)$. We conclude that the semiclassical approximation is inadequate for the analysis of the ET data for strong coupling in the low and intermediate temperature range, a problem of primary interest for the understanding of ET in Chromatium.

IV. SOME RELATIONS AND CORRELATIONS

In Fig. 2 we present some numerical results of model calculations for W , Eq. (4), for an ET process characterized by strong coupling ($S=5-20$) with one type of mode (in the present case we shall subsequently consider the molecular modes) and which are specified by moderately low values of $p = \Delta E/\hbar\langle\omega\rangle$, as appropriate for nearly isoenergetic ET occurring in biological systems.⁶ In order to demonstrate the characteristic behavior of W throughout the entire temperature range, we prefer to plot $\log W$ vs $\log T$, a procedure adopted by De Vault and Chance,⁶ rather than to utilize the conventional $\log W$ vs T^{-1} plots. These data exhibit an "activationless" low temperature region at low T followed by a sharp (exponential-type) increase in W around $kT/\hbar\langle\omega\rangle \approx 0.1-0.2$. It is worthwhile to notice the following features: (1) The onset of the T dependent situation occurs far below the characteristic vibrational temperature $\hbar\langle\omega\rangle/k$. (2) The transition range from an activationless to an apparently activated process is rather narrow, occurring in the temperature range $kT/\hbar\langle\omega\rangle \approx 0.1-0.2$. (3) The temperature effect on W increases with increasing the coupling strength S at constant p . (4) At low p values and for a constant value of S ($\gg 1$) W at low T ($\ll \hbar\langle\omega\rangle/k$) increases as $S^p/p!$ with increasing p until it is expected to reach a maximum of the Poissonian distribution around $S=p$. This is the zero temperature analogue of free-energy

relationships for ET.^{7,9,25} (5) At high T the activation energy exhibits a parabolic dependence, $E_A = \hbar\langle\omega\rangle(p - S)^2/4S$, on p at constant S , which corresponds to the conventional Marcus-Levich^{7,9} free-energy relationship.

V. PARAMETERS

A recent analysis of the temperature dependence of the ET rate in Chromatium⁶ was provided by Hopfield³⁰ in terms of Eq. (5) which, on the basis of the analysis presented in Sec. III, is inadequate. We are now in a position to analyze the ET data in Chromatium⁶ in terms of the present theoretical results derived in Sec. II. Fitting Eq. (4) to the experimental data for the temperature dependence of W in Chromatium⁶ requires four parameters: A , ΔE , $\hbar\langle\omega\rangle$, and S . We start with the analysis of the relative rates [normalized to $W(T=0)$] making the following rough estimates of the latter three parameters: (1) The data at the highest temperatures (250–280 °K) studied by De Vault and Chance⁶ yield an upper experimental limit for the apparent activation energy $E_a = 0.17$ eV, whereupon we take this value to constitute the lower limit for the "classical" activation energy in the high T limit, so that $(\Delta E - S\hbar\langle\omega\rangle)^2/4S\hbar\langle\omega\rangle > 0.17$ eV. (2) The onset of the exponential increase of W with increasing T occurs somewhere in the range 60–100 °K, where $kT/\hbar\langle\omega\rangle \approx 0.1$, thus resulting in $\hbar\langle\omega\rangle \sim 0.05-0.1$ eV. (3) Utilizing the experimental ratio $\gamma \approx 10^3$ between the rate constants at 280 °K and at 4.5 °K, together with the high T and the low T limits of Eq. (4) and the "reasonable" values $\hbar\langle\omega\rangle \approx 0.05-0.10$ eV, $\hbar\langle\omega_s\rangle \approx 10^{-3}-10^{-2}$ eV, and $p=0-2$, we get $S \sim 15-22$. Guided by these crude but physically rea-

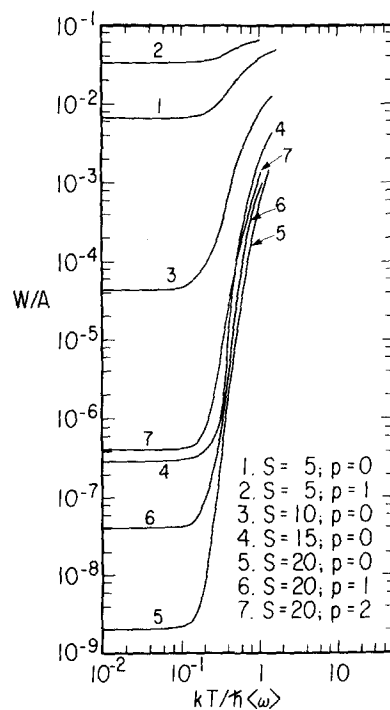


FIG. 2. Numerical results for the ET probability for isoenergetic and weakly exoenergetic processes in the strong coupling situation, $S=5-20$.

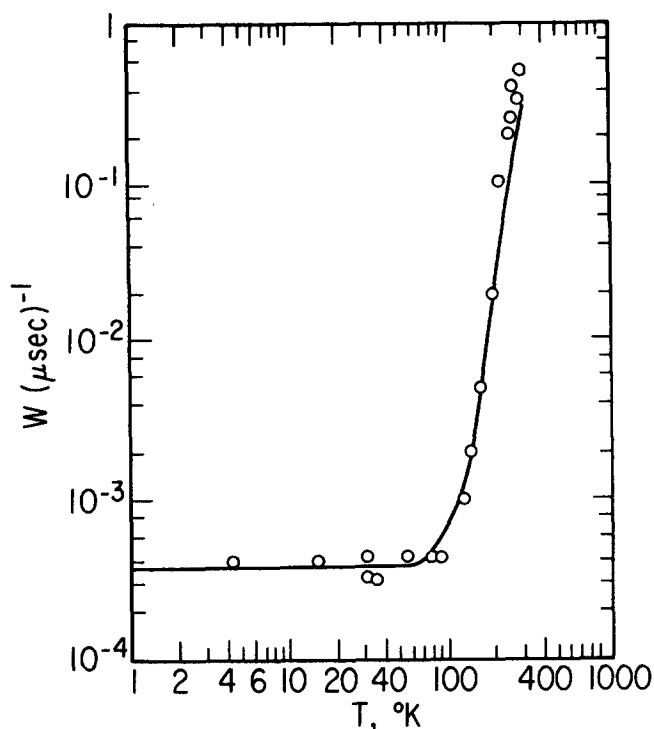


FIG. 3. The temperature dependence of the light-induced ET from cytochrome to chlorophyll in *Chromatium*. The circles represent the experimental data of De Vault, Parkes, and Chance [Ref. 6(a) and 6(b)]. The solid curve represents the prediction of Eq. (4) with the following parameters: $\Delta E = 0.1$ eV, $\hbar\langle\omega\rangle = 0.05$ eV, $S = 20$, and $A = 10^9$ sec $^{-1}$.

sonable estimates, a quantitative fit of the experimental data⁶ was attempted. A good fit of the experimental T dependence of W (Fig. 3) over three orders of magnitude of variation in W was obtained for $\hbar\langle\omega\rangle \approx 0.05$ eV (400 cm $^{-1}$), $S \approx 20$, and $\Delta E/\hbar\langle\omega\rangle \approx 2$ (i. e., $\Delta E \approx 0.1$ eV). It is, in particular, gratifying that the sharp onset for the transition from the activationless to an apparently activated regime is faithfully reproduced by the theory. The value $S \approx 20$ corresponds to the strong coupling situation, as expected. The value of $\hbar\langle\omega\rangle = 0.05$ eV is close to the frequency of the totally symmetric vibration of the coordination layer for transition metal complexes,¹⁵ which should mimic the gross features of the metal-ligand vibrational frequency in cytochrome and in chlorophyll. The values $\Delta E = 0.1$ eV together with $S = 20$ result in a high temperature activation energy $E_A(T \rightarrow \infty) = 0.2$ eV, which is consistent with the experimental lower limit $\tilde{E}_A = 0.17$ eV. It is also of some interest to evaluate the low temperature Franck-Condon factor $F = \exp(-S)(S^2/2) = 4 \times 10^{-7}$, which determines the activationless nuclear tunneling rate at low T . The present estimates of the nuclear configurational changes accompanying ET in *Chromatium*, $\Delta E/\hbar\langle\omega\rangle = 0.05$ eV and $S = 20$, should be confronted with Hopfield's results³⁰ ($\Delta E)_H/\hbar\langle\omega\rangle_H = 0$, $\hbar\langle\omega\rangle_H = 0.03$ eV, and $S_H = 33$. Clearly, the values of $\hbar\langle\omega\rangle$ and of S are quite similar. However, the low temperature Franck-Condon factor when calculated properly using Hopfield's parameters³⁰ is $F_H = \exp(-S_H) = 5 \times 10^{-15}$, as compared with our value of $F = 4 \times 10^{-7}$, reflecting the failure of the semiclassical approximation at low T .

Finally, we can provide an estimate of the electron exchange integral from the low T data where $W = (2\pi/\hbar^2\langle\omega_s\rangle)|V_{ab}(R)|^2F$. Utilizing the experimental value⁶ $W = 400$ sec $^{-1}$ at 4.5 °K, $F = 4 \times 10^{-7}$, and $\hbar\langle\omega_s\rangle = 10$ –100 cm $^{-1}$, we estimate $V_{ab}(R) = (1$ – $3) \times 10^{-5}$ eV (0.1–0.4 cm $^{-1}$). This two-center, one-electron exchange integral obtained herein is somewhat lower than the value $[V_{ab}(R)]_H = 4 \times 10^{-4}$ eV estimated by Hopfield.³⁰ The low value of $V_{ab}(R)$ provides a proper justification for the applicability of the nonadiabatic theoretical scheme for ET in this system.^{9,15} $V_{ab}(R)$ is lower (by about 1 order of magnitude) than the corresponding value of ~ 1 cm $^{-1}$ estimated¹⁵ for outer sphere ET in the Fe $^{2+}(\text{H}_2\text{O})_6$ –Fe $^{3+}(\text{H}_2\text{O})_6$ system in solution. Theoretical evaluations of (two-center) intermolecular exchange integrals are fraught with considerable difficulties as these are determined by the behavior of the “tails” of the molecular wavefunction.⁴⁵ As a reference we quote the work of Katz *et al.*⁴⁵ on electron mobility in organic crystals; they found that an intermolecular transfer integral of $V \sim 1$ cm $^{-1}$ corresponds to ET between large organic molecules separated by $R \approx 7$ –8 Å. When many-electron exchange effects are incorporated,⁴⁶ this electron transfer integral increases to the value of $V \sim 10$ cm $^{-1}$ at $R \approx 10$ Å and exhibits an exponential distance dependence^{46b} $d \ln V/dR \approx -1.3$ Å $^{-1}$. Provided that direct exchange contributions to $V_{ab}(R)$ dominate, and assuming that $d \ln V/dR \approx d \ln V_{ab}/dR$, we estimate $R \sim 12$ –13 Å for the distance scale of ET in *Chromatium*. This rough estimate of R somewhat exceeds the original estimate $R \approx 8$ –10 Å presented by Hopfield³⁰ and is comparable with the radius (~ 14 –17 Å) of the protein globule of the molecule of cytochrome C.²⁹ We would like to emphasize that the present estimate of the distance scale for ET, which rests on the assessment of direct exchange contributions, provides a lower limit for R . The small value of $V_{ab}(R)$ raises the distinct possibility that a superexchange type electronic coupling mechanism⁴⁷ (via virtual states, as distinct from thermal excitation to low-lying electronic states, mentioned in Sec. I) will contribute to the electronic matrix element in this system. Such a high-order contribution will result in $V_{ab} \approx V_{ab}^0 + \beta^2/\delta$, where V_{ab}^0 is the direct exchange contribution while β is an (off-diagonal) resonance integral between D (and A) and high-lying electronic states which are separated by the energy gap δ from the D and the A levels. For $\delta \approx 1$ eV a value of $\beta \approx 3 \times 10^{-2}$ eV is sufficient to provide a dominating superexchange contribution to the exchange integral. Thus, a small electronic mixing can go a far way, and long range electron transfer (over several molecular diameter) is possible in this system.

VI. EPILOGUE

The main merits of the theory for nonadiabatic multiphonon ET applied herein for a biological system lie in the demonstration of the intimate relation between outer sphere ET processes in physical chemistry and ET in a biological system, as well as in exploring the validity conditions for the applicability of the Forster-Dexter mechanism^{32,33} to describe ET processes.³⁰ We have also provided a new, compact, and general relation,

Eq. (3a), for the ET probability, which is valid throughout the entire temperature range. A special version of this result, Eq. (4), which discards coupling with medium modes was applied for ET in Chromatium. Concerning the approximations involved in the present treatment, these rest on the "Einstein-type" approximation for the intramolecular vibrational modes and, furthermore, we have neglected frequency changes and anharmonicity effects in the molecular type modes, all of which will affect the Franck-Condon nuclear overlap integrals. These sins of omission can be easily relaxed²⁵ (in principle) when detailed spectroscopic-type information concerning frequencies, configurational changes and anharmonicity constants for DA and for D^*A^- will become available. Such information is still only fragmentary even for the conventional case of ET between inorganic ions in solution.¹⁵ Regarding the Einstein-type approximation introduced for the low-frequency phonon lattice modes (whose contribution to ET in Chromatium was found to be negligible), it may be relaxed³³ by taking an average value for Δ_{sk}^2 in the appropriate contribution to $G \pm(t)$, Eqs. (1a) and (1c). More important, we have disregarded in the present treatment any possible (reversible) structural modifications in the biological system induced by temperature changes. For example, thermal expansion effects will result, in principle, in the temperature dependence of R , whereupon a new source for the T dependence of $V_{ab}(R)$ and of W creeps in. We have assumed that such effects are negligible.

We would like to emphasize that the present treatment focused attention on ET reactions; however, this formalism is applicable to any nonradiative multiphonon process. In particular, the present results may be quite useful in the fast developing field of the theory of vibrational relaxation³⁶ in a dense medium. Furthermore, the physical model advanced herein can be readily extended for a theoretical study of optical line shapes in charge transfer spectra (CTS) $DA \rightleftharpoons D^*A^-$ between organic or inorganic ions.⁴⁸ All that is required is to replace in Eq. (3) the electronic coupling V_{ab} by the electronic transition moment (at least within the framework of the Condon approximation) and to replace ΔE by $\Delta E - \hbar\nu$, where $\hbar\nu$ is the photon energy. With these substitutions, Eq. (3a) will constitute a general result for the optical line shape in CTS, which incorporates the effects of both low-frequency medium (solvent) modes and high-frequency molecular modes. The effects of the quantum modes, which were not previously considered,⁴⁹ may be crucial in providing a quantitative picture for the CTS by bridged mixed valence complexes, which were studied by Taube and colleagues.⁵⁰

The idea of a temperature dependent activation energy, originating from the transition from nuclear "tunneling" between BO potential surfaces at low temperatures to an activated rate process occurring near the intersection of the (multidimensional) potential surfaces at high temperatures, is explicit in early work on electronic³³⁻³⁵ and vibrational relaxation³⁶ in solid state and molecular physics. Regarding ET processes, Levich⁹ was the first to point out that thermal

excitation of low-frequency polar solvent modes will result in a temperature dependent activation energy (i. e., regions A and B of Sec. III). However, in view of the low "phonon" frequency⁵¹ in polar solvents, $\hbar\langle\omega_s\rangle = 1 - 10 \text{ cm}^{-1}$, the quantum effect predicted by Levich⁹ will be exhibited only at extremely low T (near liquid He temperatures). The effect of quantum modes on E_A , and on free-energy relationships,^{22,23,25} which is expected to be exhibited in an easily accessible temperature range, was only recently recognized. In many common cases of ET between ions in solution and in frozen glasses, the latter quantum effects are obscured by the dominating contribution of the low-frequency polar modes (i. e., $S\hbar\langle\omega\rangle < S_s\hbar\langle\omega_s\rangle$). Thus, for example, in the $Fe^{+2}(H_2O)_6 - Fe^{+3}(H_2O)_6$ system¹⁵ $S_s\hbar\langle\omega_s\rangle \approx 2 \text{ eV}$ while $S\hbar\langle\omega\rangle \approx 0.25 \text{ eV}$. The present discussion of ET in Chromatium provides the first example for a system where the coupling of nuclear quantum modes dominates the ET process.

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- $$F_s(\Delta E - \epsilon) = \exp[-S_s(2\bar{\nu}_s + 1)] \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{[S_s(\bar{\nu}_s + 1)]^m [S_s\bar{\nu}_s]^n}{m!n!} \times \delta[\Delta E - \epsilon + (m - n)\hbar\langle\omega_s\rangle].$$
- In view of the application of the Einstein approximation, neglecting the dispersion in the frequencies of the medium modes, we integrate this result over the energy range of the order of $\hbar\langle\omega_s\rangle$, which corresponds to the lowest characteristic energy involved in the problem. This is the essence of the "coarse-graining" procedure leading to Eq. (2b). Equation (2c) for the contribution of the quantum modes was not tampered with.
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