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Generalized Förster-Dexter theory of photoinduced intramolecular energy transfer

S. H. Lin and W. Z. Xiao
*Department of Chemistry and Center for the Study of Early Events in Photosynthesis,
Arizona State University, Tempe, Arizona 85287-1604*

W. Dietz
Department of Physics, Technical University of Munich, 8046 Garching, Germany

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In this paper, we generalize the Förster-Dexter theory to treat photoinduced electronic energy transfer for a system in dense media and for an isolated system (i.e., a system in the collision-free condition). Instead of expressing the rate of energy transfer in terms of spectral overlap, we obtain the expression of the energy-transfer rate constant by evaluating a Fourier integral using the saddle-point method. In this way, the energy-gap dependence and the effect of temperature and the isotope effect on the energy transfer can be easily studied. The effect of bridge groups connecting between donor and acceptor on the energy transfer is also studied.

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I. INTRODUCTION

The electronic energy-transfer process is important in such diverse areas as the excitation of the rare-earth laser [1], organic photochemistry [2] and photosynthesis [3–8]. For example, carotenoids provide photoprotection by rapidly quenching chlorophyll triplet states which are formed in antenna systems or photosynthetic reaction centers. This triplet-triplet energy transfer prevents chlorophyll-sensitized production of singlet oxygen, which is injurious to organisms [3]. In addition, carotenoids act as antennas by absorbing light in spectral regions where chlorophyll absorbs weakly and by delivering the resulting excitation to chlorophyll via a singlet-singlet energy-transfer process [4]. Finally, first excited singlet states of chlorophyll are quenched by nearby carotenoids [5]. This quenching has been ascribed to energy transfer [6], electron transfer [7], or to some other process leading to internal conversion, and may play a role in the regulation of photosynthesis [8].

Energy transfer can be roughly divided into intramolecular transfer and intermolecular transfer. Recently, more and more effort has been devoted to intramolecular energy transfer. There are two important aspects of intramolecular energy transfer. The first important aspect is that intramolecular transfer is independent of diffusion since it takes place between different components of a single molecule; the energy-transfer rate can be monitored directly. In this case, solvents may still affect the energy-transfer rate by an alteration of driving force and/or through the intervention of low-frequency solvent vibrational modes (i.e., reorganization energy). The second aspect of intramolecular energy transfer is that various parameters such as driving force, distance between donor and acceptor, and the orientation of donor with respect to acceptor, etc., which determine the energy-transfer rate, can be very well controlled by designing various kinds of model compounds [9]. Energy transfer may also be divided into singlet-singlet transfer and triplet-triplet transfer, etc., depending on the spins of initial and final states, and direct and indirect transfer depending on whether the intervening spacer is involved in transfer or not. Recently, intramolecular transfer under collision-free conditions has been observed by Speiser and co-workers [10]. They have studied the energy transfer of donor-acceptor (D-A) pairs such as benzene-biacetyl and naphthalene-anthracene in a supersonic jet expansion.

A direct-energy-transfer theory was worked out by Förster [11] for singlet-singlet transfer and by Dexter [12] for triplet-triplet transfer more than 40 years ago. It predicts the following:

(a) While for singlet-singlet energy transfer, both dipole-induced (Coulombic) interaction and exchange interaction are nonvanishing; for triplet-triplet energy transfer, only exchange interaction exists.

(b) The rate of dipole-induced transfer decreases as R^{-6} whereas the rate of exchange-induced transfer decreases as $\exp(-2R/L)$, where R is the donor-acceptor separation.

(c) The rate of dipole-induced transfer depends on the oscillator strengths of $D^* \rightarrow D$ and $A \rightarrow A^*$ radiative transitions, but the rate of exchange-induced transfer does not depend on either of the two oscillator strengths.

Notice that in the Förster-Dexter theory, the energy-transfer rate is expressed as a function of spectral overlap. The theory is inconvenient to use (1) when it is used to interpret the effects of driving force, temperature, and solvent on the energy-transfer rate since such information is buried in the spectral overlap, and (2) when the spectral overlap is too small to measure. Realizing the similarities between electron transfer and energy transfer, Sigman and Closs [13] have recently applied the electron-transfer theory to analyze the experimental data of energy-transfer rates. However, ignorance of the application conditions of the theories may lead to inappropriate conclusions. In other words, it is necessary to derive the energy-transfer theory in the framework of radiationless transition and discuss various factors which affect energy transfer.

Also notice that in the original derivation of the Förster-Dexter theory, continuum initial and final states were assumed. However, in molecular systems this assumption is not necessary and even inappropriate since the states in molecules are usually discrete or quasicontinuous. Therefore, a derivation of the Förster-Dexter theory based on discrete states or on a quasicontinuum is necessary, although the conclusions may remain the same.

Although the direct-energy-transfer theory is well understood, recent experiments clearly indicate that indirect energy transfer also plays a very important role in energy transfer. For the case in which the donor-acceptor separation is large, indirect transfer may be the dominant mechanism responsible for energy transfer. For example, Gust *et al.* [9] have studied the quenching of the porphyphrin triplet state by energy transfer to the attached carotenoid. Both donor and acceptor are attached to the benzene ring. Only the exchange interaction exists in this case since in triplet-triplet transfer the Coulombic interaction is spin forbidden. Although R (6.5 Å) is much larger than L (1.5 Å), and thus the direct energy transfer is small, the energy-transfer rate is still on the order of $10^7\ \mathrm{s}^{-1}$. They have also found that the compounds with D and A in the meta positions have the slowest energy-transfer rate (one order of magnitude slower) than those with D and A in the ortho or para positions. These are clear indications of the superexchange mechanism. Therefore, extension of the intramolecular energy-transfer theory to include the superexchange mechanism becomes necessary.

The purpose of this paper is as follows:

(1) To develop both direct- and indirect-energy-transfer rates in the framework of radiationless transition. The dependence of the energy transfer on driving force, distance, and solvent will be discussed. Special attention will be paid to the indirect energy transfer.

(2) To derive the generalized Förster-Dexter energy-transfer theory for systems which have discrete or quasicontinuous initial and final states.

II. GENERAL THEORY

In the Schrödinger picture, the time evolution of a system is described by

$$\hat{H}\psi(t)=i\hbar\frac{\partial\psi(t)}{\partial t}\ , \tag{2.1}$$

where $\hat{H}$ and $\psi(t)$ denote the Hamiltonian and wave function of the system and $\hat{H}=\hat{H}_0+V$. Depending on the choice of basis sets (determined by $\hat{H}_0$), V may represent the interaction for inducing intramolecular energy transfer (IET). In most cases, V is due to the electron-electron interaction. The transition rate for $i \rightarrow f$ is given by [14]

$$W_{fi}=\frac{2\pi}{\hbar}|\langle\phi_f|\hat{T}|\phi_i\rangle|^2\delta(E_f-E_i)\ , \tag{2.2}$$

where $\hat{T}$ denotes the transition operator.

$$\hat{T}=V+V\frac{1}{E_i-\hat{H}+i\varepsilon}V=V+\hat{T}^{(2)} \tag{2.3}$$

and

$$\hat{T}^{(2)}=V\frac{1}{E_i-\hat{H}+i\varepsilon}V\ . \tag{2.4}$$

It should be noted that for the case in which the system is embedded in a heat bath, ε describes the dephasing of the system. A main purpose of this paper is to examine the role of $\hat{T}^{(2)}$ in the photoinduced intramolecular energy transfer taking place between donor and acceptor groups. In particular, we are concerned with the effect of intermediate groups (i.e., bridge groups or spacers) connecting the donor and acceptor groups. In the conventional Förster-Dexter theory of energy transfer, $\hat{T}^{(2)}$ has been neglected. In the lowest approximation $\hat{T}^{(2)}$ is given by

$$\hat{T}^{(2)}=V\frac{1}{E_i-\hat{H}_0+i\varepsilon}V\ , \tag{2.5}$$

and we find

$$\hat{T}^{(2)}_{fi}=\sum_m\frac{V_{fm}V_{mi}}{E_i-E_m+i\varepsilon_{mi}}\ . \tag{2.6}$$

In applying Eq. (2.6) to photoinduced IET the intermediate virtual states $|m\rangle$ may represent the excited electronic states of the connecting group, i.e.,

$$D^*CA\rightarrow DC^*A\rightarrow DCA^*\ . \tag{2.7}$$

In molecular systems, the adiabatic approximation can be used as a basis set. If the vibrational relaxation is much faster than energy transfer, then vibrational equilibrium is established before energy transfer takes place; in this case the thermal average IET rate constant is expressed as

$$W_{fi}=\frac{2\pi}{\hbar}\sum_v\sum_{v''}P_{iv}|\langle\psi_{fv''}|\hat{T}|\psi_{iv}\rangle|^2\delta(E_{fv''}-E_{iv})\ , \tag{2.8}$$

where P_{iv} denotes the Boltzmann factor and (i,f) and (v,v'') represents the electronic and vibrational states, respectively.

Notice that

$$\langle\psi_{fv''}|\hat{T}|\psi_{iv}\rangle=V_{fv'',iv}+\langle\psi_{fv''}|\hat{T}^{(2)}|\psi_{iv}\rangle\ , \tag{2.9}$$

and that in the lowest approximation,

$$\langle\psi_{fv''}|\hat{T}^{(2)}|\psi_{iv}\rangle=\sum_{m,v'}\frac{V_{fv'',mv'}V_{mv',iv}}{E_{iv}-E_{mv'}+i\varepsilon_{mv',iv}}\ , \tag{2.10}$$

where, for example,

$$V_{fv'',mv'}=\langle\psi_{fv''}|V|\psi_{mv'}\rangle\ . \tag{2.11}$$

In the adiabatic approximation, ψ_{iv}, $\psi_{mv'}$, and $\psi_{fv''}$ can be written as products of electronic and vibrational wave functions, i.e.,

$$\psi_{iv}=\Phi_i\Theta_{iv},\quad \psi_{mv'}=\Phi_m\Theta_{mv'},\quad \psi_{fv''}=\Phi_f\Theta_{fv''}\ . \tag{2.12}$$

Substituting Eq. (2.12) into Eq. (2.9) yields

$$\langle \psi_{fv''}|\hat{T}|\psi_{iv}\rangle = \langle \Theta_{fv''}|V_{fi}|\Theta_{iv}\rangle + \sum_{m,v'} \frac{\langle \Theta_{fv''}|V_{fm}|\Theta_{mv'}\rangle\langle \Theta_{mv'}|V_{mi}|\Theta_{iv}\rangle}{E_{iv}-E_{mv'}+i\varepsilon_{mv',iv}} , \tag{2.13}$$

where, for example,

$$V_{fi} = \langle \Phi_f|V|\Phi_i\rangle . \tag{2.14}$$

Under collision-free conditions (i.e., for an isolated molecule), the IET rate constant depends on the excess vibrational energy (in general, rotational-vibrational energy). In the collision-free condition, there are two types of IET rate constants. One is the so-called single-level rate constant [15],

$$W_{iv} = \frac{2\pi}{\hbar} \sum_{v''} |\langle \psi_{fv''}|\hat{T}|\psi_{iv}\rangle|^2 \delta(E_{fv''}-E_{iv}) . \tag{2.15}$$

This case refers to the situation in which the intramolecular vibrational relaxation (IVR) is slow so that the IET takes place from the prepared single-vibronic level iv. On the other hand, if the IVR is much faster than the IET, then we have the so-called microcanonical rate constant [15],

$$W_{fi}(E) = \frac{2\pi}{\hbar} \sum_{v}\sum_{v''} P_{iv}(E)|\langle \psi_{fv''}|\hat{T}|\psi_{iv}\rangle|^2 \delta(E_{fv''}-E_{iv}) , \tag{2.16}$$

where $P_{iv}(E)$ denotes the microcanonical distribution,

$$P_{iv}(E) = \frac{\delta(E-E_{iv})}{\rho_i(E)} , \tag{2.17}$$

and $\rho_i(E)$ represents the density of the states of the system with vibrational excess energy E,

$$P_i(E) = \sum_{v} \delta(E-E_{iv}) . \tag{2.18}$$

These cases will be treated in the following sections.

Next, we consider the electronic matrix elememts involved in IET. For singlet-singlet transfer, we have [15]

$${}^1D^*C\,{}^1A \rightarrow {}^1DC\,{}^1A^* , \tag{2.19}$$

$$\Phi_i = \frac{1}{\sqrt{2}}(|X_D^+ X_{D^*}^- X_A^+ X_A^-| - |X_D^- X_{D^*}^+ X_A^+ X_A^-|) , \tag{2.20}$$

and

$$\Phi_f = \frac{1}{\sqrt{2}}(|X_D^+ X_D^- X_A^+ X_{A^*}^-| - |X_D^+ X_D^- X_A^- X_{A^*}^+|) , \tag{2.21}$$

where, for example, $|X_D^+ X_{D^*}^- X_A^+ X_A^-|$ denotes the Slater determinant with molecular orbitals X_D, X_{D^*}, and X_A. Here, for convenience, other molecular orbitals (MO's) not involved in energy transfer (from the excited state described by the MO X_{D^*} of D to the excited state described by the MO X_{A^*} of A) are not given. In this case, V is given by the electron-electron interaction

$$V = \sum_i \sum_j \frac{e^2}{\epsilon r_{ij}} , \tag{2.22}$$

where ϵ denotes the dielectric constant of the solvent. For the IET under collision-free conditions, $\epsilon = 1$.

Using Eqs. (2.20)–(2.22), we obtain

$$V_{fi} = 2\left\langle X_D X_{A^*} \left| \frac{e^2}{\epsilon r_{12}} \right| X_{D^*} X_A \right\rangle - \left\langle X_D X_{A^*} \left| \frac{e^2}{\epsilon r_{12}} \right| X_A X_{D^*} \right\rangle . \tag{2.23}$$

Here, the first term represents the Coulomb interaction, while the second term represents the exchange interaction. In the conventional Förster-Dexter theory, the exchange term is neglected and the multipole expansion is introduced in the Coulomb term assuming that D and A are well separated so that the electronic distributions of D and A do not overlap. In this case, V_{fi} takes the form

$$V_{fi} = \frac{1}{\epsilon R_{D\text{-}A}^3}\left[(\boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A) - \frac{3(\mathbf{R}_{D\text{-}A}\cdot\boldsymbol{\mu}_D)(\mathbf{R}_{D\text{-}A}\cdot\boldsymbol{\mu}_A)}{R_{D\text{-}A}^2} \right] , \tag{2.24}$$

where $\boldsymbol{\mu}_D$ and $\boldsymbol{\mu}_A$ denote the transition moments of D and A, respectively,

$$\boldsymbol{\mu}_D = \sqrt{2}\langle X_D|e\mathbf{r}|X_{D^*}\rangle \tag{2.25}$$

and

$$\boldsymbol{\mu}_A = \sqrt{2}\langle X_{A^*}|e\mathbf{r}|X_A\rangle . \tag{2.26}$$

Next, we consider the triplet-triplet transfer,

$${}^3D^*C\,{}^1A \rightarrow {}^1DC\,{}^3A^* . \tag{2.27}$$

To obtain V_{fi}, we consider only the spin state of $M_s = 1$, i.e.,

$${}^3\Phi_i(M_s=1) = |X_D^+ X_{D^*}^+ X_A^+ X_A^-| \tag{2.28}$$

and

$${}^3\Phi_f(M_s=1) = |X_D^+ X_D^- X_A^+ X_{A^*}^+| . \tag{2.29}$$

It follows that

$$V_{fi} = -\left\langle X_{D^*} X_A \left| \frac{e^2}{\epsilon r_{12}} \right| X_{A^*} X_D \right\rangle . \tag{2.30}$$

That is, only the exchange interaction is involved in the triple-triplet transfer of IET.

III. IET IN DENSE MEDIA

In the original Förster-Dexter theory, continuous initial and final states are assumed. However, for IET it is more convenient to treat initial and final vibronic manifolds as quasicontinua. For direct IET we have,

$$W_{fi} = \frac{2\pi}{\hbar} \sum_{v}\sum_{v''} P_{iv} |\langle \Theta_{fv''}|V_{fi}|\Theta_{iv}\rangle|^2 \delta(E_{fv''}-E_{iv}) . \tag{3.1}$$

In a previous paper [16], we have shown that by using the expressions for the absorption coefficient of A,

$$\alpha_A(\omega)=\frac{4\pi^2\omega}{3a\hbar c}\times\sum_{v}\sum_{v''}P_{iv}|\langle\Theta_{fv''}|\mu_A|\Theta_{iv}\rangle|^2\delta(\omega_{fv'',iv}-\omega)\ , \tag{3.2}$$

and for the normalized emission spectral distribution function of D,

$$I(\omega)_N=\frac{4\omega^2a'\tau_D}{3c^3}\times\sum_{v}\sum_{v''}P_{iv}|\langle\Theta_{fv''}|\mu_D|\Theta_{iv}\rangle|^2\delta(\omega-\omega_{iv,fv''})\ . \tag{3.3}$$

W_{fi} for the singlet-singlet transfer can be expressed in the spectral overlap [15,16],

$$W_{if}=\frac{3ac^4}{4\pi a'\epsilon^2R_{D\text{-}A}^6\tau_D}\int_{-\infty}^{\infty}\frac{d\omega}{\omega^4}\alpha_A(\omega)I(\omega)_N\ . \tag{3.4}$$

In Eqs. (3.2)–(3.4), a and a' are introduced to take care of the solvent effect on absorption spectra and emission spectra, respectively, while τ_D denotes the natural (or radiative) lifetime of D^*.

Similarly for the triplet-triplet transfer, we introduce the normalized distribution functions for absorption of A and emission of D defined by [15,16]

$$\sigma_A(\omega)=\sum_{v}\sum_{v''}P_{iv}|\langle\Theta_{fv''}|\Theta_{iv}\rangle|^2\delta(\omega_{fv'',iv}-\omega)=\frac{\alpha_A(\omega)/\omega}{\int_{-\infty}^{\infty}d\omega\frac{\alpha_A(\omega)}{\omega}} \tag{3.5}$$

$$\eta_D(\omega)=\sum_{v}\sum_{v''}P_{iv}|\langle\Theta_{fv''}|\Theta_{iv}\rangle|^2\delta(\omega-\omega_{iv,fv''})=\frac{I(\omega)_N/\omega^3}{\int_{-\infty}^{\infty}\frac{I(\omega)_N}{\omega^3}d\omega} \tag{3.6}$$

to obtain

$$W_{fi}=\frac{2\pi}{\hbar^2}|V_{fi}|^2\int_{-\infty}^{\infty}\sigma_A(\omega)\eta_D(\omega)d\omega\ . \tag{3.7}$$

Expressions such as Eqs. (3.5) and (3.6) hold only if the electronic transitions are dipole allowed.

As mentioned above, for the case in which the absorption spectra of A and emission spectra of D do not overlap significantly, the expression of the IET rate constant in terms of the spectral overlap is not convenient to use. Furthermore, the IET rate constant in this case is not expressed in terms of microscopic molecular properties.

Suppose that the energy difference between intermediate (or virtual) electronic E_m and E_i is much greater than vibrational energies. In this case, we can use the Placzek approximation to Eq. (2.10) and find

$$\langle\psi_{fv''}|\hat{T}|\psi_{iv}\rangle=\left\langle\Theta_{fv''}\left|V_{fi}+\sum_m\frac{V_{fm}V_{mi}}{E_i-E_m}\right|\Theta_{iv}\right\rangle=\langle\Theta_{fv''}|T_{fi}|\Theta_{iv}\rangle\ . \tag{3.8}$$

Using the Condon approximation, Eq. (3.8) becomes

$$\langle\psi_{fv''}|\hat{T}|\psi_{iv}\rangle=T_{fi}\langle\Theta_{fv''}|\Theta_{iv}\rangle\ , \tag{3.9}$$

where $\langle\Theta_{fv''}|\Theta_{iv}\rangle$ denotes the vibrational overlap integral.

It follows that

$$W_{fi}=\frac{2\pi}{\hbar}|T_{fi}|^2\sum_{v}\sum_{v''}P_{iv}|\langle\Theta_{fv''}|\Theta_{iv}\rangle|^2\delta(E_{fv''}-E_{iv})\ , \tag{3.10}$$

where $|\langle\Theta_{fv''}|\Theta_{iv}\rangle|^2$ denotes the Franck-Condon factor. Equation (3.10) indicates that the IET can be treated within the framework of radiationless transitions. The advantage of this type of treatment is that the IET rate constant is expressed in terms of microscopic molecular properties and can easily be used to study the temperature effect, energy-gap dependence, and isotope effect [17]. One should also notice the similarity between IET and photoinduced intramolecular electron transfer.

Using the integral representation for $\delta(E_{fv''}-E_{iv})$, Eq. (3.10) can be written as [17–19]

$$W_{fi}=\frac{1}{\hbar}|T_{fi}|^2\int_{-\infty}^{\infty}dt\,\exp(it\omega_{fi})\prod_j G_j(t)\ , \tag{3.11}$$

where

$$G_j(t)=\sum_{v_j}\sum_{v_j''}P_{iv_j}|\langle X_{fv_j''}|X_{iv_j}\rangle|^2\exp\left[\frac{it}{\hbar}(E_{v_j''}-E_{v_j})\right]\ , \tag{3.12}$$

where $|\langle X_{fv_j''}|X_{iv_j}\rangle|^2$ denotes the Franck-Condon factor for the jth vibrational mode. $G_j(t)$ has been evaluated for the cases of displaced harmonic oscillators, and displaced-distorted harmonic oscillators and of displaced anharmonic oscillators.

For displaced harmonic oscillators, $G_j(t)$ is given by

$$G_j(t)=\exp[-S_j\{(2\bar{n}_j+1)-(\bar{n}_j+1)e^{it\omega_j}-\bar{n}_je^{-it\omega_j}\}]\ , \tag{3.13}$$

where $\bar{n}_j=[\exp(\hbar\omega_j/kT)-1]^{-1}$ and S_j denotes the coupling constant (or Huang-Rhys factor) related to the vibrational coordinate displacement ΔQ_j by $S_j=(\omega_j/2\hbar)\Delta Q_j^2$.

Recently Sigman and Closs [13] have also used Eq. (3.10) to study IET. In their paper, they consider two vibrational modes in $\langle\Theta_{fv''}|\Theta_{iv}\rangle$, one high-frequency mode and one low-freqency mode. For the high-frequency mode, they evaluate the Franck-Condon factor $|\langle X_{fv_j''}|X_{iv_j}\rangle|^2$ exactly for $v_j=0$ and for the low-frequency mode ω_i they evaluate the Fourier integral in Eq. (3.11) by the short-time aproximation (i.e., the strong-coupling case $S_i\gg1$) and assume that $\hbar\omega_i/kT\ll1$ (i.e., the high T case).

Notice that substituting Eq. (3.13) into Eq. (3.11) yields

$$W_{fi}=\frac{1}{\hbar^2}|T_{fi}|^2\int_{-\infty}^{\infty}dt\,\exp\left[it\omega_{fi}-\sum_j S_j\{(2\bar{n}_j+1)-(\bar{n}_j+1)e^{it\omega_j}-\bar{n}_je^{-it\omega_j}\}\right]. \tag{3.14}$$

It is a good approximation to evaluate the Fourier integral in W_{fi} by the saddle-point method (or method of steepest descent) [15],

$$W_{fi}=\frac{1}{\hbar^2}|T_{fi}|^2\left[\frac{2\pi}{\sum_j S_j\omega_j^2\{(\bar{n}_j+1)e^{it^*\omega_j}+\bar{n}_je^{-it^*\omega_j}\}}\right]^{1/2}$$
$$\times\exp\left[it^*\omega_{fi}-\sum_j S_j(2\bar{n}_j+1)+\sum_j S_j\{(\bar{n}_j+1)e^{it^*\omega_j}+\bar{n}_je^{-it^*\omega_j}\}\right], \tag{3.15}$$

where t^* denotes the saddle-point value of the t to be determined by

$$\omega_{fi}=\sum_j S_j\omega_j[(\bar{n}_j+1)e^{it^*\omega_j}-\bar{n}_je^{it^*\omega_j}]. \tag{3.16}$$

Numerical demonstrations of Eq. (3.15) will be given in Sec. VI.

It should be noted that the summation over j in Eqs. (3.15) and 3.16) covers the vibrational modes in both A and D. Using Eqs. (3.15) and (3.16), we can determine how the electronic excitation energy is distributed after the IET takes place. For example, if there are only two modes involved in IET, one for A, say ω_k and one for D, say ω_l, and if $S_l=5$ and $S_k=0.1$, then we can expect that the vibrational excitation energy stays at D while A, although electronically excited after IET, is vibrationally unexcited if A is initially vibrationally unexcited.

It is often useful to consider a single-mode case. This is also equivalent to the multimode case of using average S_j and ω_j. In this case, W_{fi} is given by

$$W_{fi}=\frac{2}{\hbar^2\omega}|T_{fi}|^2e^{-S(2\bar{n}+1)}$$
$$\times\sum_{m=0}^{\infty}\frac{(S\bar{n})^m[S(\bar{n}+1)]^{m+(\omega_{if}/\omega)}}{m!\left[m+\frac{\omega_{if}}{\omega}\right]!} \tag{3.17}$$

which should be computed with the saddle-point approximation of W_{fi},

$$W_{fi}=\frac{1}{\hbar^2}|T_{fi}|^2\left[\frac{2\pi}{S\omega^2\{(\bar{n}+1)e^{it^*\omega}+\bar{n}e^{-it^*\omega}\}}\right]^{1/2}$$
$$\times\exp[it^*\omega_{fi}-S(2\bar{n}+1)$$
$$+S(\bar{n}+1)e^{it^*\omega}+S\bar{n}e^{-it^*\omega}], \tag{3.18}$$

where

$$e^{it^*\omega}=\frac{\omega_{if}2S_\omega}{(\bar{n}+1)}$$
$$+\frac{1}{2(\bar{n}+1)}\left[\left[\frac{\omega_{if}}{S\omega}\right]^2+4\bar{n}(1+\bar{n})\right]^{1/2}. \tag{3.19}$$

It should be noted that Eq. (3.17) can be put in the form of the modified Bessel function [20].

IV. IET IN ISOLATED MOLECULES

As mentioned in Sec. II, there are two types of IET rate constants for an isolated molecule (i.e., ion the collision-free condition). We first consider the single-vibronic-level case,

$$W_{iv}=\frac{2\pi}{\hbar}|T_{fi}|^2\sum_{v''}|\langle\Theta_{fv''}|\Theta_{iv}\rangle|^2\delta(E_{fv''}-E_{iv}), \tag{4.1}$$

which can be rewritten as

$$W_{iv}=\frac{1}{\hbar^2}|T_{fi}|^2\int_{-\infty}^{\infty}dte^{it\omega_{fi}}\prod_j G_{v_j}(t) \tag{4.2}$$

where

$$G_{v_j}(t)=\sum_{v_j''}|\langle X_{fv_j''}|X_{iv_j}\rangle|^2\exp\left[\frac{it}{\hbar}(E_{v_j''}-E_{v_j}\right]. \tag{4.3}$$

For the case of displaced oscillators, $G_{v_j}(t)$ has been evaluated as

$$G_{v_j}(t)=\exp[-S_j(1-e^{it\omega_j})]$$
$$\times\sum_{n_j=0}^{v_j}\frac{v_j!}{n_j![(v_j-n_j)!]^2}$$
$$\times[S_j(e^{(1/2)it\omega_j}-e^{-(1/2)it\omega_j})^2]^{v_j-n_j}. \tag{4.4}$$

In particular, if $v_j=0$, then

$$G_{0_j}(t)=-\exp[-S_j(1-e^{it\omega_j})] \tag{4.5}$$

and

$$W_{i0}=\frac{1}{\hbar^2}|T_{fi}|^2\int_{-\infty}^{\infty}dt\,\exp\left[it\omega_{fi}-\sum_j S_j(1-e^{it\omega_j})\right]. \tag{4.6}$$

Using the saddle-point method, Eq. (4.6) becomes

$$W_{i0}=\frac{1}{\hbar^2}|T_{fi}|^2\left[\frac{2\pi}{\sum_j S_j\omega_j^2e^{it^*\omega_j}}\right]^{1/2}$$
$$\times\exp\left[it^*\omega_{fi}-\sum_j S_j+\sum_j S_je^{it^*\omega_j}\right], \tag{4.7}$$

where

$$\omega_{if} = \sum_j S_j \omega_j e^{it^*\omega_j} \; . \tag{4.8}$$

It should be noted that W_{i0} also corresponds to the thermal average IET rate constant at $T=0$.

Substituting Eq. (4.4) into (Eq. 4.2) yields

$$W_{iv} = \frac{1}{\hbar^2} |T_{fi}|^2 \int_{-\infty}^{\infty} dt \exp\left[it\omega_{fi} - \sum_j S_j (1 - e^{it\omega_j}) \right] \times \prod_j \bar{G}_{v_j}(t) \; , \tag{4.9}$$

where

$$\bar{G}_{v_j}(t) = \sum_{n_j=0}^{v_j} \frac{v_j!}{n_j![(v_j-n_j)!]^2} \times [S_j(e^{(1/2)it\omega_j} - e^{-(1/2)it\omega_j})^2]^{v_j-n_j} \; . \tag{4.10}$$

If $\prod_j \bar{G}_{v_j}(t)$ does not vary significantly around t^*, then Eq. (4.9) can be evaluated as

$$\frac{W_{iv}}{W_{i0}} = \prod_j \bar{G}_{v_j}(t^*) \; , \tag{4.11}$$

where t^* is given by Eq. (4.8).

Next we consider the evaluation of $W_{fi}(E)$, the so-called microcanonical IET rate constant. Using the contour integral representation for the δ function,

$$\delta(E - E_{iv}) = \frac{1}{2\pi i} \int_c d\beta e^{\beta(E - E_{iv})} \tag{4.12}$$

we find

$$\rho_i(E) = \frac{1}{2\pi i} \int_c d\beta e^{\beta E} Q_i(\beta) \; , \tag{4.13}$$

where

$$Q_i = \sum_i e^{-\beta E_{iv}} \; , \tag{4.14}$$

which is the canonical partition function of the initial electronic state. Similarly, $W_{fi}(E)$ can be expressed as

$$W_{if}(E) = \frac{1}{\rho_i(E)} \frac{1}{2\pi i} \int_c d\beta e^{\beta E} Q_i(\beta) W_{fi}(\beta) \; , \tag{4.15}$$

where $W_{fi}(\beta)$ denotes the thermal average IET rate constant given by Eq. (2.8).

Equation (4.13) indicates the $\rho_i(E)$ is related to $Q_i(\beta)$ by the inverse Laplace transformation. Similarly, Eq. (4.15) shows that $W_{if}(E)$ is related to $Q_i(\beta) W_{fi}(\beta)$ by the inverse Laplace transformation. Applying the saddle-point method to Eq. (4.13) yields

$$\rho_i(E) = \frac{e^{\beta^* E} Q_i(\beta^*)}{\left[2\pi \left\{ \frac{\partial^2}{2\beta^{*2}} \ln Q_i(\beta^*) \right\} \right]^{1/2}} \; , \tag{4.16}$$

where β^* denotes the saddle-point value of β^* to be determined by

$$E = -\frac{\partial}{\partial \beta^*} \ln Q_i(\beta^*) \; . \tag{4.17}$$

Equation (4.17) indicates that β^* plays the role of "temperature" in the isolated system.

If $Q_i(\beta) W_{fi}(\beta)$ does not vary significantly around β^*, then Eq. (4.15) can be evaluated as

$$W_{if}(E) = W_{if}(\beta^*) \; . \tag{4.18}$$

Equation (4.18) indicates that for the case in which the IVR is much faster than IET, $W_{if}(E)$ can be approximated by $W_{if}(\beta^*)$ with β^* to be determined by E given by Eq. (4.17).

The single-vibronic-level IET rate constant W_{iv} can also be expressed in the spectral overlap form. For singlet-singlet direct transfer, Eq. (4.1) becomes

$$W_{iv} = \frac{2\pi}{\hbar} \frac{\eta_{A\text{-}D}^2}{R_{D\text{-}A}^6} \sum_{v''} |\langle \Theta_{fv''}^{(D)} | \mu_D | \Theta_{iv}^{(D)} \rangle|^2 \times |\langle \Theta_{fv''}^{(A)} | \mu_A | \Theta_{iv}^{(A)} \rangle|^2 \delta(E_{fv''} - E_{iv}) \; , \tag{4.19}$$

where $\eta_{A\text{-}D}$ describes the relative orientation between the A group and the D group.

Notice that the single-vibronic-level absorption coefficient for A is given by

$$\alpha_{iv}^{(A)} = \frac{4\pi^2\omega}{3\hbar c} \sum_{v''} |\langle \Theta_{fv''}^{(A)} | \mu_A | \Theta_{iv}^{(A)} \rangle|^2 \delta(\omega_{fv'',iv}^{(A)} - \omega) \; . \tag{4.20}$$

It follows that

$$\int_{-\infty}^{\infty} \frac{\alpha_{iv}^{(A)}(\omega)}{\omega} e^{it\omega} d\omega = \frac{4\pi^2}{3\hbar c} \sum_{v''} e^{it\omega_{fv'',iv}^{(A)}} |\langle \Theta_{fv''}^{(A)} | \mu_A | \Theta_{iv}^{(A)} \rangle|^2 \tag{4.21}$$

and that

$$W_{iv} = \frac{1}{\hbar^2} \frac{\eta_{A\text{-}D}^2}{R_{D\text{-}A}^6} \times \sum_{v''} \int_{-\infty}^{\infty} dt [e^{it\omega_{fv'',iv}^{(D)}} |\langle \Theta_{fv''}^{(D)} | \mu_D | \Theta_{iv}^{(D)} \rangle|^2] \times [e^{it\omega_{fv'',iv}^{(A)}} |\langle \Theta_{fv''}^{(A)} | \mu_A | \Theta_{iv}^{(A)} \rangle|^2] \; . \tag{4.22}$$

Here the integral representation of the δ function has been used.

Substituting Eq. (4.21) into Eq. (4.22) yields

$$W_{iv} = \frac{3c}{2\pi\hbar} \frac{\eta_{A\text{-}D}^2}{R_{D\text{-}A}^6} \times \int_{-\infty}^{\infty} d\omega \frac{\alpha_{iv}^{(A)}(\omega)}{\omega} \times \sum_{v''} |\langle \Theta_{fv''}^{(D)} | \mu_D | \Theta_{iv}^{(D)} \rangle|^2 \delta(\omega - \omega_{iv,fv''}^{(D)}) \; . \tag{4.23}$$

Using the normalized intensity distribution function of the single-vibronic-level emission of D,

$$I_{iv}^{(D)}(\omega)_N=\frac{4\omega^3}{3\hbar c^3 A_{iv}^{(D)}}\times\sum_{v''}|\langle\Theta_{fv''}^{(D)}|\mu_D|\Theta_{iv}^{(D)}\rangle|^2\delta(\omega-\omega_{iv,fv''}^{(D)}) \ . \quad (4.24)$$

Eq. (4.23) becomes

$$W_{iv}=\frac{9c^4}{8\pi\tau_{iv}^{(D)}}\frac{\eta_{A\text{-}D}^2}{R_{D\text{-}A}^6}\int_{-\infty}^{\infty}\frac{d\omega}{\omega^4}\alpha_{iv}^{(A)}(\omega)I_{iv}^{(D)}(\omega)_N \ , \quad (4.25)$$

where $\tau_{iv}^{(D)}$ denotes the single-vibronic-level (iv) radiative lifetime of D. The W_{iv} for triplet-triplet transfer can also be expressed in the spectral overlap in a similar manner.

V. EFFECT OF BRIDGE GROUPS ON IET

As can be seen from Secs. II and III, the effect of bridge groups on IET is described by $T_{fi}^{(2)}$, i.e.,

$$T_{fi}^{(2)}=\sum_m\frac{V_{fm}V_{mi}}{E_i-E_m} \ . \quad (5.1)$$

Properties such as Φ_m, E_m of intermediate (or virtual) states are usually determined by the bridge groups.

In most cases, no general expressions can be obtained for $T_{fi}^{(2)}$ except for the case in which all the bridge groups are equivalent, i.e., $DC_1C_2\cdots C_NA$. In this case, Φ_m can be expressed as

$$\Phi_m=\sum_n^N C_{mm}\phi_n \ , \quad (5.2)$$

where $\Phi_i\equiv D^*C_1C_2\cdots C_NA$, $\Phi_f\equiv DC_1C_2\cdots C_NA^*$ and, for example, $\phi_1\equiv DC_1^*C_2\cdots C_NA$.

The theory of molecular excitons can be applied to this case. We find

$$C_{mm}=\left[\frac{2}{N+1}\right]^{1/2}\sin\left[\frac{mn\pi}{N+1}\right] \quad (5.3)$$

and

$$E_m^{(e)}=\alpha+2\beta\cos\left[\frac{m\pi}{N+1}\right] \ , \quad (5.4)$$

where $m=1,2,\ldots,N$, $\alpha=H_{11}=H_{22}=\cdots=H_{NN}$, and $\beta=V_{nn+1}=V_{nn-1}$. It follows that

$$T_{fi}=V_{fi}+\frac{2\beta_i\beta_f}{N+1}\sum_{m=1}^N\frac{(-1)^m\sin^2\left[\dfrac{m\pi}{N+1}\right]}{(\alpha-E_i^{(e)})+2\beta\cos\left[\dfrac{m\pi}{N+1}\right]} \ , \quad (5.5)$$

where

$$\beta_i=\langle\phi_1|V|\Phi_i\rangle \ , \qquad \beta_f=\langle\Phi_f|V|\phi_N\rangle \ . \quad (5.6)$$

It has been shown that for the case of $(\alpha-E_i^{(e)})^2\gg\beta^2$, Eq. (5.5) reduces to

$$T_{fi}=V_{fi}+(-1)^N\frac{\beta_i\beta_f\beta^{N-1}}{(\alpha-E_i^{(e)})^N} \ . \quad (5.7)$$

VI. DISCUSSION

To demonstrate the application of the theoretical results given in the prevous sections, in this section we shall present some numerical results. First we shall show the dependence of W_{fi} on the electronic energy gap (or free-energy change). This is shown in Fig. 1. In Fig. 1(a), we show the single-mode case at 300 K; that is, $S=2.5$ and $\omega=100$ cm^{-1}. In Fig. 1(b), we show the multimode case. Here we choose six modes; $\omega_i=100$, 224, 750, 1200, 1400, 1520; $S_i=2.5$, 0.03, 0.02, 0.03, 0.02, 0.04; ω_i is in the unit of cm^{-1}. These six modes are commonly observed in chlorophylls.

In Fig. 2, we show the temperature effect on IET for the single-mode case. In this case, the temperature effect

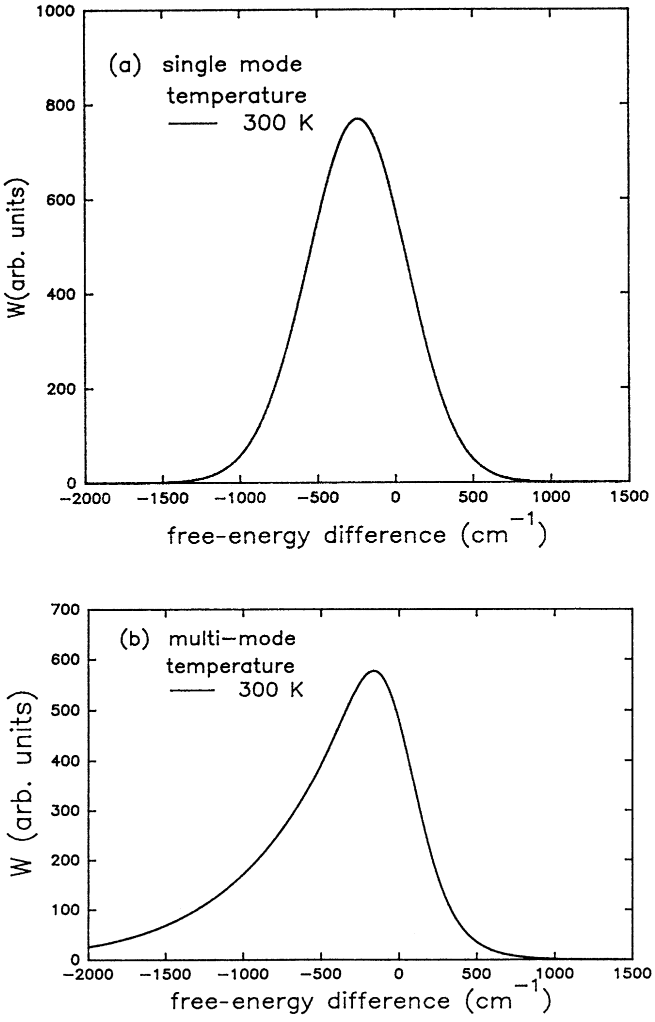

FIG. 1. Energy-gap dependence of W_{fi}. (a) Single-mode case. (b) Multimode case.

depends greatly on the electronic energy gap (or free-energy change). In Fig. 2(a), we show the case of $S=2.5$ and $\omega=100\ \mathrm{cm}^{-1}$, while in Fig. 2(b) we show the case of $S=30$ and $\omega=100\ \mathrm{cm}^{-1}$.

In Fig. 3, the temperature effect on IET for the multimode case is shown. In this case, the temperature effect is weak and does not change significantly with the electronic energy gap. Here the above-mentioned six modes are used. As can be seen from Fig. 3, for energy gaps below 1000 cm^{-1} the IET exhibits the inverse temperature dependence. Near 1000 cm^{-1}, the IET is independent of temperature. Above 1000 cm^{-1} the IET begins to show the normal temperature dependence.

Recently, Bigman, Karni, and Speiser[10] have reported some preliminary results of electronic energy transfer between benzene and biacetyl, and between naphthalene and anthracene in a supersonic jet expansion. Excitation of several vibronic levels of benzene (donor) in the presence of biacetyl (acceptor) shows quenching of benzene emission with simultaneous appearance of biacetyl fluorescence emission. Similar results for the pair of naphthalane (donor) and anthracene (acceptor) have been observed. Several single-vibronic-level energy-transfer rate constants for the benzene-biacetyl pair have been reported.

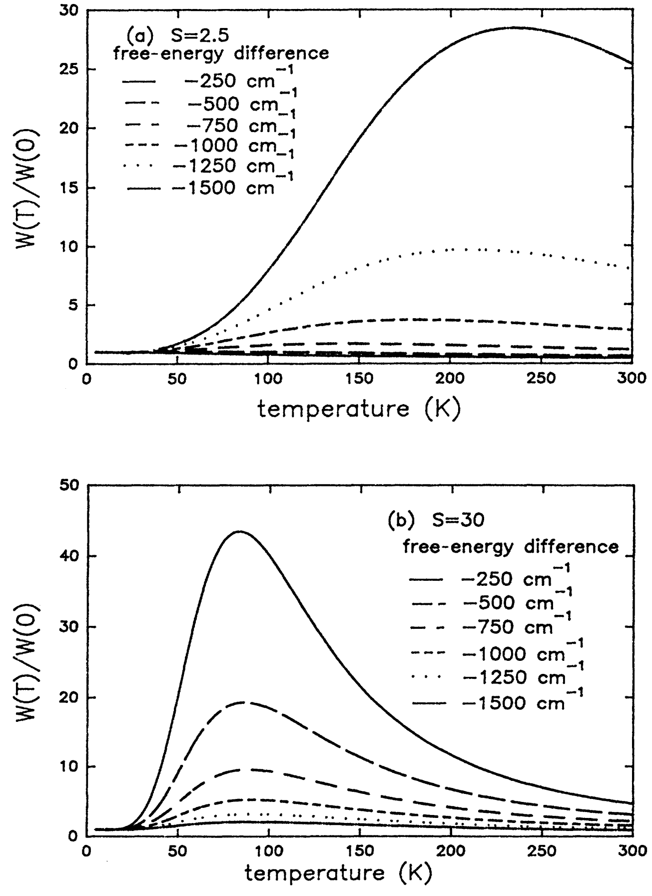

FIG. 2. Effect of temperature on W_{fi}: single-mode case. (a) $S=2.5$. (b) $S=30$.

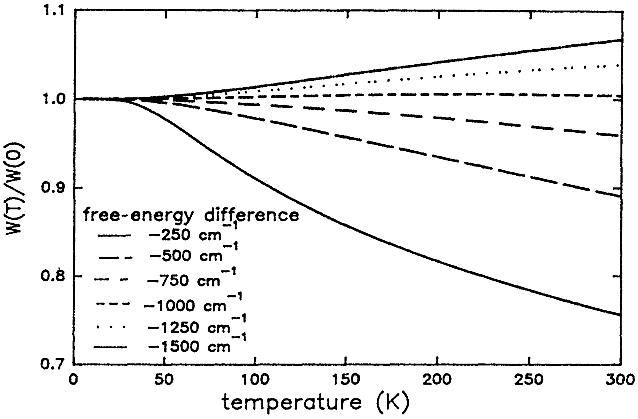

FIG. 3. Effect of temperature on W_{fi}: multimode case.

We can apply the theoretical results in Sec. IV to interpret the results by Bigman, Karni, and Speiser. If only one mode is vibronically excited in D, then Eq. (4.11) becomes

$$\frac{W_{iv}}{W_{i0}}=\bar{G}_{v_k}(t^*)\ . \tag{6.1}$$

Here, it is assmed that the kth mode of D is excited. Notice that if $v_k=1$, then

$$\frac{W_{i1}}{W_{i0}}=1+S_k(e^{1/2it^*\omega_k}-e^{1/2it^*\omega_k})^2\ , \tag{6.2}$$

and that if $v_k=2$, then

$$\frac{W_{i2}}{W_{i0}}=2+2S_k(e^{1/2it^*\omega_k}-e^{1/2it^*\omega_k})^2 + \tfrac{1}{2}S_k^2(e^{1/2it^*\omega_k}-e^{1/2it^*\omega_k})^4\ , \tag{6.3}$$

etc.

Similarly, if two modes are vibronically excited in D, then Eq. (4.11) becomes

$$\frac{W_{iv}}{W_{i0}}=\bar{G}_{v_k}(t^*)\bar{G}_{v_l}(t^*)\ . \tag{6.4}$$

For the benzene-biacetyl pair, Bigman, Karni, and Speiser have obtained

$$\frac{k_Q(6_1^2)}{k_Q(6_0^1)}=3.00\ . \tag{6.5}$$

Using Eqs. (6.2), (6.3), and (6.5) we obtain

$$S_k(e^{1/2it^*\omega_k}-e^{-1/2it^*\omega_k})^2=2.73 \tag{6.6}$$

for the ω_6 mode of benzene. In other words, we find

$$\frac{k_Q(6_0^1)}{k_Q(6_0^0)}=3.73 \tag{6.7}$$

and

$$\frac{k_Q(6_1^2)}{k_Q(6_0^0)}=14.2\ . \tag{6.8}$$

That is, using Eq. (6.6) we can predict other single-vibronic-level quenching rate constants associated with the ω_6 mode. Of course, it should be noted that the above anlaysis is based on the assumption that the ω_6 mode is a displaced oscillator. Other types of oscillators can be treated similarly.

Next we turn to the IET systems studied by Gust *et al.* In this case, both donor and acceptor are attached to a benzene ring. From Eq. (5.7), for $N=1$ we have

$$T_{fi}=V_{fi}-\frac{\beta_i\beta_f}{\alpha-E_i^{(e)}}\ , \tag{6.9}$$

where $\beta_i=\langle\phi_1|V|\Phi_i\rangle$ and $\beta_f=\langle\Phi_f|V|\phi_1\rangle$. Due to the fact that in the ortho, para, and meta substitutions, ϕ_1 will be somewhat different in these substitutions, β_i and β_t will be different for the ortho, para, and meta substituted DCA systems, and, hence, the IET rates will be different for these systems, but the differences are not large as shown by the experimental results.

An important feature of using the saddle-point method is that under collision-free conditions it will provide approximate information regarding the distribution of the initial electronic excitation energy in D and A after IET [21]. We can then study the IVR by using the transient absorption technique.

In conclusion, in this paper we have generalized the Förster-Dexter theory to treat IET. Instead of expressing the IET rate constant in terms of the spectral overlap, we have expressed it in terms of molecular parameters such as the electronic energy gap (or free-energy change), normal coordinate displaceent (or coupling constants), and normal frequency changes so that it can be used to study explicitly the effect of energy gap, temperature, and isotope on IET's. We have investigated the case of IET taking place in dense media and the case of IET taking place under collision-free conditions. Due to the fact that the saddle-point method has been employed to evaluate the Fourier integral involved in the Fermi-golden-rule expression of IET rate constants, the information on the energy distribution in the product after IET can be obtained and the multimode case can be treated. We have also studied the effect of bridged groups on IET.

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