

Intermolecular energy transfer: Retardation effects

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An extension of previous theoretical work on the unified theory of radiative and radiationless intermolecular energy transfer is presented. A generalized transfer rate accounting for molecular vibronic structure is derived, enabling the formal connection with the classical Förster formula to be fully established. The solution to an apparent paradox concerning the long-range R^{-2} dependence of the intermolecular energy transfer rate is demonstrated. It is shown that the inverse square behavior should be modified by inclusion of an exponential factor due to the presence of other acceptors. A corrected Förster decay rate including an R^{-4} contribution, in addition to the conventional R^{-6} term, is obtained and the means of characterizing distinctive features of the unified approach are discussed with reference to some model systems. Finally the relation between retardation and quantum uncertainty effects in molecular energy transfer are considered.

I. INTRODUCTION

The transfer of electronic excitation in condensed matter is a well-known phenomenon occurring in a wide variety of systems.¹⁻⁶ It is perhaps most familiar in connection with photosynthetic energy transfer between chlorophyll units, but it is also manifest in many nonbiological materials including mixed molecular crystals, solutions, glasses, etc. In recent years considerable attention has been paid to the study of collective problems in radiationless energy transfer, such as multistep transfer in an ensemble of randomly situated molecules.⁷⁻¹¹ Currently there is also a resurgence of interest in the detailed mechanism underlying the elementary act of intermolecular energy transfer, particularly with respect to the retardation effects which signal the interplay between radiative and radiationless transfer.¹²⁻¹⁸

The manifestation of retardation features in resonance energy transfer was first examined 25 years ago in pioneering studies by Avery¹⁹ and also Gomberoff and Power,²⁰ work which appears to have been sadly overlooked in the intervening years. One of the key features which emerged from these and later studies¹²⁻¹⁵ is that both short-range Förster transfer and long-range radiative transfer are no more than the asymptotic limits of a more general unified mechanism which applies over all distances R . The quantum electrodynamic²¹ formulation of this mechanism is cast in terms of virtual photon coupling.¹²⁻¹⁵ This treatment naturally accommodates retardation effects which modify the form of the inverse-power law governing the distance dependence of the transfer rate. The R^{-6} Förster limit corresponds to the case where the intermolecular coupling is essentially static in character: as distance increases, retardation effects begin to dominate and the virtual photon ultimately assumes the character of a real photon, producing R^{-2} dependence.

In this paper we extend previous theoretical work on retarded energy transfer in a number of ways. First, we present

a derivation of the generalized transfer rate incorporating molecular vibronic structure, thus enabling the formal connection with the classical Förster formula to be firmly established. Next, we demonstrate the solution to an apparent paradox concerning the long-range R^{-2} dependence of the intermolecular energy transfer rate, which in a system containing a large number of acceptor molecules would appear to lead to an anomalously large decay rate for a given donor molecule. Solving this problem, we show that an exponential factor due to the presence of other acceptors should be incorporated into the R^{-2} law. We obtain a modified Förster decay rate including an R^{-4} contribution in addition to the conventional R^{-6} term, and consider applications to some model systems. We then show that the distinctive features of the unified approach can be characterized over a critical retardation range of intermolecular distances, and we consider the hierarchy which exists between various critical distances in the theory of resonance energy transfer. We also discuss the interplay between retardation and quantum uncertainty effects. A number of related issues have been discussed in our previous paper²² on the range dependence of the transfer-induced fluorescence depolarization.

II. PAIR ENERGY TRANSFER RATE

According to the generalized Fermi rule, the rate of energy transfer associated with initial and final states, $|i\rangle$ and $|f\rangle$, is²³

$$W_{fi} = \frac{2\pi}{\hbar} |\langle f|T|i\rangle|^2 \delta(E_f - E_i), \quad (2.1)$$

where T is the transition operator given by

$$T = H_{\text{int}} + H_{\text{int}} \frac{1}{E_i - H + i\epsilon} H_{\text{int}}, \quad \epsilon \rightarrow +0. \quad (2.2)$$

Here H is the full Hamiltonian of the system,

$$H = H_0 + H_{\text{int}}, \quad (2.3)$$

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$|i\rangle$ and $|f\rangle$ being eigenstates of the zeroth-order (unperturbed) Hamiltonian H_0 with energies E_i and E_f .

This paper considers the resonant transfer of electronic excitation energy, in which the terms *donor* and *acceptor* indicate molecules between which energy is transferred. Our theory accommodates situations in which donor and acceptor are either the same or chemically different species. The initial state of the system consists of a donor in an excited electronic state $|\Psi_{D^*}\rangle$ and an acceptor in its ground state $|\Psi_A\rangle$, and the final state has the donor and acceptor in their ground and excited electronic states, $|\Psi_D\rangle$ and $|\Psi_{A^*}\rangle$, respectively. Separating the electronic and vibrational parts of the state vector, according to the Condon principle, we have

$$|i\rangle = |0\rangle |\Psi_{D^*}\Psi_A\rangle |\phi_{D^*}^{(n)}\rangle |\phi_A^{(m)}\rangle, \quad (2.4)$$

$$|f\rangle = |0\rangle |\Psi_D\Psi_{A^*}\rangle |\phi_D^{(l)}\rangle |\phi_{A^*}^{(p)}\rangle, \quad (2.5)$$

$$E_i = E_{D^*}^{(n)} + E_A^{(m)}, \quad (2.6)$$

$$E_f = E_D^{(l)} + E_{A^*}^{(p)}, \quad (2.7)$$

the states of all other molecules in the system being unspecified. Here $|0\rangle$ denotes the photon vacuum state vector, and $|\Psi_{D^*}\Psi_A\rangle$, $|\Psi_D\Psi_{A^*}\rangle$ are the electronic parts of the initial and final state vectors, respectively. The indices $l(m)$ and $n(p)$ indicate vibrational levels of the donor (acceptor) in its ground and excited electronic states, respectively, with $E_D^{(l)}$, $E_{D^*}^{(n)}$, $E_A^{(m)}$ and $E_{A^*}^{(p)}$ being the corresponding electronic plus vibrational energies of donor and acceptor with respect to the photon vacuum.

In the conventional approach to radiationless molecular energy transfer, the photon states are not included in the calculations and the transfer is considered to arise through a direct Coulomb interaction between molecules, $H_{\text{int}} = V_{\text{Coulomb}}$ (see, e.g., Refs. 1 and 6). Thus, the energy transfer can be represented as first-order perturbation process. Such an approach is justifiable when the donor-acceptor separation R , is much less than the reduced photon wavelength λ . At larger separation retardation effects come into play. To properly account for these we employ the formalism of molecular quantum electrodynamics.²¹ In the Power-Zienau-Woolley formulation, the energy transfer appears as a second-order process mediated by the propagation of transverse virtual photons. Although strictly speaking it is not possible within this framework to totally differentiate radiationless and radiative transfer, we will for convenience use these traditional terms to denote the short- and long-range limits. The unperturbed quantum electrodynamical Hamiltonian for the system can be represented as follows:

$$H_0 = H_{\text{rad}} + H_{\text{mol}}, \quad (2.8)$$

where H_{rad} is the radiation Hamiltonian and H_{mol} is the molecular Hamiltonian;

$$H_{\text{rad}} = \frac{1}{2} \int \{ \epsilon_0^{-1} \mathbf{d}^{12} + \epsilon_0 c^2 \mathbf{b}^2 \} d^3\mathbf{r}, \quad (2.9)$$

$$H_{\text{mol}} = \sum_{\xi} H_{\text{mol}}(\xi), \quad (2.10)$$

the sum being taken over all molecules ξ in the system. Similarly the interaction Hamiltonian can be expressed as

$$H_{\text{int}} = \sum_{\xi} H_{\text{int}}(\xi). \quad (2.11)$$

The above $\mathbf{d}^{\perp}(\mathbf{r})$ is the transverse electric displacement field operator, $\mathbf{b}(\mathbf{r})$ is the magnetic induction field operator, and $H_{\text{int}}(\xi)$ represents the interaction between molecule ξ and the radiation field. For our purposes it is sufficient to express $H_{\text{int}}(\xi)$ in the electric dipole approximation as

$$H_{\text{int}}(\xi) = -\epsilon_0^{-1} \boldsymbol{\mu}(\xi) \cdot \mathbf{d}^{\perp}(\mathbf{R}_{\xi}) \quad (2.12)$$

with $\boldsymbol{\mu}(\xi)$ being the electric dipole operator and \mathbf{R}_{ξ} the position vector of molecule ξ .

Both the radiation Hamiltonian and the electric displacement operator may be expanded in terms of normal modes as follows:

$$H_{\text{rad}} = \sum_{\mathbf{k}, \lambda} [a^{+(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) + \frac{1}{2}] \hbar c k, \quad (2.13)$$

$$\mathbf{d}^{\perp}(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} \left(\frac{\hbar c k \epsilon_0}{2V} \right)^{1/2} i \{ \mathbf{e}^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) a^{+(\lambda)}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} \}, \quad (2.14)$$

where in each expression a sum is taken over radiation modes characterized by wave vector \mathbf{k} and polarization vector $\mathbf{e}^{(\lambda)}(\mathbf{k})$; $a^{+(\lambda)}(\mathbf{k})$ and $a^{(\lambda)}(\mathbf{k})$ are the corresponding photon creation and annihilation operators and V is the quantization volume.

The transition operator T in Eq. (2.2) has the following series expansion:

$$T = T^{(1)} + T^{(2)} + \dots \quad (2.15)$$

with

$$T^{(1)} = H_{\text{int}}, \quad (2.16)$$

$$T^{(2)} = H_{\text{int}} \frac{1}{E_i - H_0 + i\delta} H_{\text{int}}, \quad (2.17)$$

etc. The principal term $T^{(1)}$ represents photoemission and photoabsorption by individual molecules, as shown by the time-ordered diagrams in Figs. 1(a) and 1(b). As illustrated in Figs. 1(c) and 1(d), the quantum electrodynamical representation of the resonance energy transfer arising from the second-order perturbation $T^{(2)}$ entails virtual photon coupling. Virtual photons, although potentially in resonance with the donor excitation energy, are not observed and theory requires a summation of their associated contributions over an infinite range of frequencies. As will be discussed in Sec. V, at small intermolecular separations, $R \ll \lambda$, this summation is essential over a wide region of photon energies, which is much larger than the energy transferred. In this case diagrams 1(c) and 1(d) are both important. On the other hand, at large separations, $R \gg \lambda$, only photons nearly in resonance with the donor excitation energy contribute substantially to energy transfer.

Using initial and final states (2.4) and (2.5) and performing a summation over the polarization of the intermediate photon states, we find the following expression for the matrix elements of the transition operator:

$$\langle f | T^{(2)} | i \rangle = T_{AD}^{(2)} \langle \phi_D^{(l)} | \phi_{D^*}^{(n)} \rangle \langle \phi_{A^*}^{(p)} | \phi_A^{(m)} \rangle, \quad (2.18)$$

where $T_{AD}^{(2)}$ is the electronic matrix element:

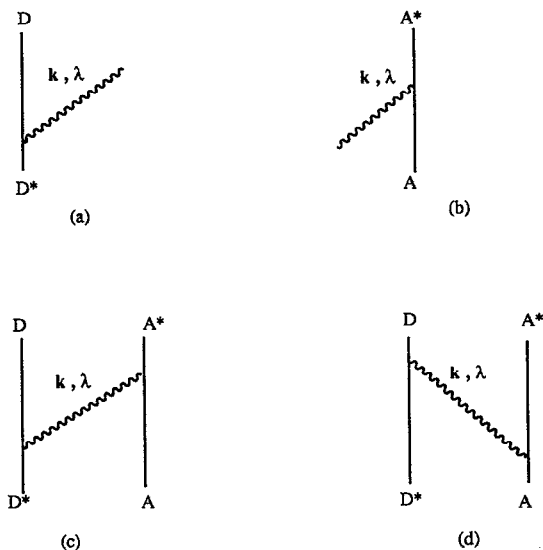


FIG. 1. Time-ordered diagrams for emission (a), absorption (b), and resonant energy transfer mediated by virtual photon exchange [(c) and (d)]. Diagram (d) represents an anomalous situation in which the virtual photon emission is associated with excitation of the acceptor and its absorption with deexcitation of the donor.

$$T_{AD}^{(2)} = - \sum_{\mathbf{k}} \frac{1}{2\epsilon_0 V} \mu_{A_i} \mu_{D_j} (\delta_{ij} - \hat{k}_i \hat{k}_j) k \times \left[\frac{e^{i\mathbf{k} \cdot \mathbf{R}}}{k - K - is} + \frac{e^{-i\mathbf{k} \cdot \mathbf{R}}}{k + K - is} \right]. \quad (2.19)$$

Here \mathbf{R} is the donor-acceptor separation vector, μ_{A_i} and μ_{D_j} are the components of the transition dipole moments of acceptor and donor, a summation over repeated tensor indicates is implied, and parameter K corresponds to the transfer energy:

$$\hbar c K = \hbar \omega = \Delta E_D = \Delta E_A \quad (2.20)$$

with

$$\Delta E_D = E_{D^*}^{(n)} - E_D^{(l)} \quad (2.21)$$

and

$$\Delta E_A = E_{A^*}^{(p)} - E_A^{(m)}. \quad (2.22)$$

Replacing the sum over \mathbf{k} by an integral and performing the angular integration one finds

$$T_{AD}^{(2)} = \mu_{A_i} \mu_{D_j} (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{1}{4\pi^2 \epsilon_0} G(K, R), \quad (2.23)$$

where

$$G(K, R) = \int_0^\infty \frac{\sin kR}{R} \left[\frac{1}{K - k + is} - \frac{1}{K + k - is} \right] dk \quad (2.24)$$

$$= \int_{-\infty + is}^{+\infty - is} \frac{\sin kR}{R} \frac{dk}{K - k} \quad (2.25)$$

$$= -\pi \frac{e^{iKR}}{R} \quad (2.26)$$

is the Green's function. It is to be pointed out that our ap-

proach based on the generalized Fermi rule (2.1) allows us to avoid analytical problems associated with the choice of the interaction contour of the Green's function, discussed previously.¹³ Indeed, the presence of the imaginary infinitesimal in the transition operator automatically gives the correct integration path in Eq. (2.25), shown as the contour C_4 in Fig. 2 of Ref. 13.

Substituting (2.26) into (2.23) we find the final expression for the electronic matrix element:²⁴

$$T_{AD}^{(2)} = \frac{K^3 \mu_A \mu_D e^{iKR}}{4\pi \epsilon_0} \left[\eta_3 \left(\frac{1}{K^3 R^3} - \frac{i}{K^2 R^2} \right) - \eta_1 \frac{1}{KR} \right], \quad (2.27)$$

where

$$\eta_j = \mathbf{e}_A \cdot \mathbf{e}_D - j(\mathbf{e}_A \cdot \mathbf{e}_R)(\mathbf{e}_D \cdot \mathbf{e}_R) \quad (j=1,3), \quad (2.28)$$

with \mathbf{e}_D , \mathbf{e}_A , \mathbf{e}_R being unit vectors oriented along the transition dipoles of the donor and acceptor molecules and their separation vector \mathbf{R} respectively. An expression for the retarded dipole-dipole resonance matrix element, equivalent to (2.27), was first obtained by Avery¹⁹ using an entirely different method based on the Breit interaction. More recently it was derived by Power and Thirunamachandran¹² in the Heisenberg representation of molecular quantum electrodynamics and by Andrews and Sherborne¹³ in the Schrödinger representation.

The excitation transfer rate as calculated from the generalized Fermi rule (2.1) is as follows:

$$W = \frac{2\pi}{\hbar} \sum_{n,l,m,p} |T_{AD}^{(2)}|^2 \rho_{D^*}^{(n)} \rho_A^{(m)} |\langle \phi_D^{(l)} | \phi_{D^*}^{(n)} \rangle|^2 |\langle \phi_{A^*}^{(p)} | \phi_A^{(m)} \rangle|^2 \times \delta(\Delta E_D - \Delta E_A). \quad (2.29)$$

Here the appropriate averaging over initial and summing over final states is carried out, $\rho_{D^*}^{(n)}$ and $\rho_A^{(m)}$ being the population distribution functions of the initial vibrational states of donor and acceptor. As in the conventional Förster theory, the excitation transfer rate can be expressed, using Eq. (2.27) for $|T_{AD}^{(2)}|^2$, in terms of an overlap integral between donor and acceptor spectra:

$$W = \frac{9}{8\pi \tau_D} \int F_D(\omega) \sigma_A(\omega) K^2 g(KR) d\omega \quad (2.30)$$

with

$$g(KR) = \eta_3^2 \frac{1}{K^6 R^6} + (\eta_3^2 - 2\eta_1 \eta_3) \frac{1}{K^4 R^4} + \eta_1^2 \frac{1}{K^2 R^2}, \quad (2.31)$$

$$F_D(\omega) = \frac{\omega^3 \tau_D \mu_D^2}{3\epsilon_0 \pi c^3} \sum_{n,l} \rho_{D^*}^{(n)} |\langle \phi_D^{(l)} | \phi_{D^*}^{(n)} \rangle|^2 \delta(\Delta E_D - \hbar\omega), \quad (2.32)$$

$$\sigma_A(\omega) = \frac{\pi \omega \mu_A^2}{3\epsilon_0 c} \sum_{m,p} \rho_A^{(m)} |\langle \phi_{A^*}^{(p)} | \phi_A^{(m)} \rangle|^2 \delta(\Delta E_A - \hbar\omega), \quad (2.33)$$

and $K = \omega/c$. Here, $F_D(\omega)$ is the donor radiation spectrum normalized to unity, $\sigma_A(\omega)$ is the acceptor absorption cross section and τ_D the radiative lifetime of the donor. Since the overlap region between the donor luminescence and acceptor absorption spectra $\Delta\omega$ is usually small compared to ω ,

the factor $K^2 g(KR)$ can be taken out of the integral (2.30) substituting K by its spectral average \bar{K} to obtain more simple approximate expression for the transfer rate.

For nonrigid systems where fast rotational motion of donor and acceptor takes place, the factor $g(KR)$ in Eq. (2.30) should be replaced by its orientational average

$$\bar{g}(KR) = \frac{2}{9} \left(\frac{3}{K^6 R^6} + \frac{1}{K^4 R^4} + \frac{1}{K^2 R^2} \right). \quad (2.34)$$

This function is related to the excitation transfer function $A(K, R)$ introduced in Ref. 14 by

$$\bar{g}(KR) = \left(\frac{4\pi\epsilon_0}{3K^3} \right)^2 A(K, R). \quad (2.35)$$

In general, the transfer rate (2.30) can be presented as a sum of three terms

$$W = W_F + W_I + W_{\text{rad}}, \quad (2.36)$$

where

$$W_F = \frac{9\eta_3^2 c^4}{8\pi\tau_D R^6} \int F_D(\omega) \sigma_A(\omega) \frac{d\omega}{\omega^4}, \quad (2.37)$$

$$W_I = \frac{9c^2}{8\pi\tau_D R^4} (\eta_3^2 - 2\eta_1\eta_3) \int F_D(\omega) \sigma_A(\omega) \frac{d\omega}{\omega^2}, \quad (2.38)$$

$$W_{\text{rad}} = \frac{9\eta_1^2}{8\pi\tau_D R^2} \int F_D(\omega) \sigma_A(\omega) d\omega. \quad (2.39)$$

The first term, $W_F \sim R^{-6}$, is identical to the standard Förster radiationless decay rate.^{1,25,26} As one should have expected, at small donor-acceptor separations, $KR \ll 1$, the transfer rate W reduces to W_F . In the opposite limit, $KR \gg 1$, we have $W \rightarrow W_{\text{rad}} \sim R^{-2}$, where W_{rad} can be identified as the usual result for two-stage (emission and reabsorption) radiative energy transfer.²⁷ The intermediate term $W_I \sim R^{-4}$ is important at critical retardation distances when $KR \sim 1$. For the range of intermolecular distances where this holds true, all three terms comprising the transfer rate W are equally significant. The separate terms in Eq. (2.36) differ not only in their distance dependence, but also their orientational factors. This leads to a sharp change in the transfer-induced fluorescence depolarization in the critical retardation region, as discussed in our previous paper.²²

III. INFLUENCE OF OTHER ABSORBERS

In deriving the results of the preceding section, the influence of other acceptor molecules on the pair transfer rate has not been considered. It this is not accounted for, it can lead to the erroneous prediction that the total rate of the transfer-induced donor decay, calculated as the sum of contributions from all surrounding acceptors, linearly increases with the system dimensions and can therefore grow to unrealistically large values. This paradox arises because the rate of transfer from a given donor to acceptor molecules at distances $R \gg \lambda$ behaves as R^{-2} , while for a uniform distribution the number of acceptors in any shell centered on the donor grows as R^2 . In this section a resolution of this problem is presented.

As mentioned earlier, the term W_{rad} , proportional to R^{-2} , is identical to the classical result for long-range excita-

tion transfer. This two-step process consists of the emission of a real photon by the donor and its subsequent absorption by an acceptor. Due to the presence of other potential acceptors, the transferred photon can however be absorbed before it reaches a given particular acceptor. Therefore the transfer rate should be multiplied by a factor $\exp(-\alpha R)$ representing the probability of the photon arriving at the acceptor site. Here $\alpha = \sigma_A N_A$ is the Beer's law absorbance, with N_A being the number of acceptors per unit volume.²⁸ Since the acceptor absorption cross-section σ_A is a function of the photon frequency, the exponential factor should multiply the integrand in Eq. (2.39) giving the following corrected radiative term:

$$W_{\text{rad}}^{\text{corr}}(R) = \frac{9\eta_1^2}{8\pi\tau_D R^2} \int F_D(\omega) \sigma_A(\omega) \times \exp[-\sigma_A(\omega) N_A R] d\omega. \quad (3.1)$$

In writing the above equation, an orientationally random distribution of absorbers between the donor and acceptor is assumed, enabling an isotropic cross-section σ_A to be employed. It is to be noted that the influence of such other acceptors becomes important only at distances of the order of the Beer length, $R \sim \alpha^{-1}$, far in excess of the average intermolecular separation²⁹ $a \sim N_A^{-1/3}$. At such or larger distances the terms $W_F(R_i)$ and $W_I(R_i)$ contribute negligibly to the total transfer rate, and thus no corrections are necessary. Consequently an appropriate rate equation is

$$W^{\text{corr}}(R) = W_F(R) + W_I(R) + W_{\text{rad}}^{\text{corr}}(R) \quad (3.2)$$

with $W_F(R_i)$ and $W_I(R_i)$ as defined by Eqs. (2.37) and (2.38) in the previous section. The total rate of energy transfer from a given donor to any acceptor is thus obtained by summing $W^{\text{corr}}(R)$ over all acceptors,

$$W^{\text{tot}} = \sum_i W^{\text{corr}}(R_i). \quad (3.3)$$

Since reabsorption is a macroscopic effect, the sum in the radiative contribution to Eq. (3.3) can be replaced by the integral

$$W_{\text{rad}}^{\text{tot}} = \sum_i W_{\text{rad}}^{\text{corr}}(R_i) \quad (3.4)$$

$$= \int d\Omega \int_0^{R(\Omega)} W_{\text{rad}}^{\text{corr}}(R') N_A R'^2 dR', \quad (3.5)$$

where the function $R(\Omega)$ is determined by the macroscopic shape of the sample. Substituting Eq. (3.1) for $W_{\text{rad}}^{\text{corr}}(R)$ into the above expression we obtain the following:

$$W_{\text{rad}}^{\text{tot}} = \tau_D^{-1} - W_{\text{esc}}, \quad (3.6)$$

where

$$W_{\text{esc}} = \frac{1}{4\pi\tau_D} \int d\Omega \int d\omega F_D(\omega) \exp[-\sigma_A(\omega) N_A R(\Omega)] \quad (3.7)$$

may be identified as the probability per unit time of photon emission and escape from the sample. For optically thick samples, where the characteristic system dimension L is much larger than the Beer length α^{-1} , the total radiative energy transfer rate $W_{\text{rad}}^{\text{tot}}$ approaches the rate of spontane-

ous photon emission by the donor molecule, τ_D^{-1} . In this case W_{esc} is much less than τ_D^{-1} . On the other hand, for almost transparent media, where $L \ll \alpha^{-1}$, we have the converse situation: $W_{\text{rad}}^{\text{tot}} \ll \tau_D^{-1}$ and $W_{\text{esc}} \rightarrow \tau_D^{-1}$.

In passing we note that the above formulas can be extended to the case of a nonuniform (but still spherical) distribution of acceptors around the donor. For this generalization all that is required is to substitute W_{esc} in Eq. (3.6) by

$$W_{\text{esc}} = \frac{1}{4\pi\tau_D} \int d\Omega \int d\omega F_D(\omega) \times \exp \left[- \int_0^{R(\Omega)} \sigma_A(\omega) N_A(R') dR' \right]. \quad (3.8)$$

Using Eqs. (3.2)–(3.6) we now obtain the following expression for the total donor–acceptor transfer rate:

$$W^{\text{tot}} = \sum_i W_{F_{\text{mod}}}(R_i) + \tau_D^{-1} - W_{\text{esc}}. \quad (3.9)$$

Here $W_{F_{\text{mod}}}(R_i)$ is a sum of the Förster and intermediate terms of the microscopic energy transfer rate

$$W_{F_{\text{mod}}}(R_i) = W_F(R_i) + W_I(R_i) \quad (3.10)$$

or, since the region of overlap between the donor and acceptor absorption spectra is generally sufficiently small to warrant replacing each factor $\omega = c\tilde{K}$ in Eq. (2.38) by its spectral average $c\tilde{K}$, taking the product outside the integral we have for the orientationally averaged rate the approximate result

$$\overline{W}_{F_{\text{mod}}}(R_i) = (1 + \frac{1}{3}\tilde{K}^2 R_i^2) \overline{W}_F(R_i). \quad (3.11)$$

The donor decay rate, representing a sum of the total donor–acceptor transfer rate (3.9), the emitted photon escape rate W_{esc} and the radiationless donor decay rate γ , is given by

$$W_D = \sum_i W_{F_{\text{mod}}}(R_i) + \tau_D^{-1} + \gamma. \quad (3.12)$$

Neglecting any back-transfer of energy from acceptors, the probability, P_D , for the donor to remain in its excited state obeys the standard kinetic equation

$$dP_D/dt = -W_D P_D \quad (3.13)$$

with the obvious exponential solution. Compared to the Förster theory the modified decay rate $W_{F_{\text{mod}}}$ has, in addition to $W_F(R_i) \sim R_i^{-6}$, the term $W_I(R_i) \sim R_i^{-4}$. This term becomes important at the critical retardation distance, $R \sim R_{\text{retard}} = \lambda$. In the next section the possible manifestation of such retardation effects in the critical region is discussed with reference to specific physical systems.

IV. APPLICATION TO MODEL SYSTEMS

The results obtained in the previous section can be applied to systems of various kinds of structure. The classical system consists of a donor surrounded by randomly distributed acceptors.^{1,25,26} Spatially averaging the exponential solution of Eq. (3.13) over the positional distribution of acceptors, and using the appropriate orientationally averaged form of the microscopic decay rates, one finds the following expression for the excited state donor population:

$$N_D(t) = N_D(0) \exp[-Q(t) - t/\tau], \quad (4.1)$$

where

$$Q(t) = N_A \int \{1 - \exp[-\overline{W}_{F_{\text{mod}}}(R)t]\} d^3R \quad (4.2)$$

and $\tau^{-1} = \tau_D^{-1} + \gamma$ is the natural rate of decay of the donor species. For the usual Förster transfer rates when $\overline{W}_{F_{\text{mod}}} \rightarrow \overline{W}_F \sim R^{-6}$, one obtains the well-known nonexponential decay law^{1,25,26} with $Q(t) \sim t^{-1/2}$. As shown above, $W_{F_{\text{mod}}}$ in general has an extra term, $W_I \sim R^{-4}$, more slowly decreasing with distance. Theoretically this will result in a change from a $t^{-1/2}$ to a $t^{-3/4}$ time dependence of $Q(t)$ at large times. In other words, the decay becomes more rapid than that given by Förster's $\exp(-t^{-1/2})$ law. However, since the contribution of W_I becomes important at critical retardation distances $R \sim R_{\text{retard}} = \lambda$, this modification of the decay law could be manifest only at extremely large times, $t \sim W_{F_{\text{mod}}}^{-1}(\lambda) > 10^7 \times \tau_D$. At such times, practically all donors will have decayed by spontaneous emission.

In order to observe the differences between our results and those of the normal Förster theory, one should optimally design a system in which a great number of acceptors is concentrated in the critical retardation region $R \sim R_{\text{retard}}$ or beyond. As an example, let us consider each donor surrounded by an acceptor shell. For simplicity we can assume that there is a constant concentration N_A of randomly oriented acceptors within this shell, between the inner and outer radii R_1 and R_2 , respectively, and zero concentration elsewhere. For such a system the total donor decay rate calculated according to Eqs. (3.11) and (3.12) is

$$W_D = Z \overline{W}_F(R_1) \{ [1 - (R_1/R_2)^3] + \tilde{K}^2 R_1^2 (1 - R_1/R_2) \} + \tau^{-1} \quad (4.3)$$

which for a thick shell, $R_2 \gg R_1$, becomes

$$W_D = Z \overline{W}_F(R_1) (1 + \tilde{K}^2 R_1^2) + \tau^{-1}. \quad (4.4)$$

Here, the factor $Z = 4\pi N_A R_1^3/3$ represents the number of acceptors placed in a volume equal to that of the inner sphere.³⁰ For $R_1 \sim \lambda$, this number can be quite large: for example, with a mean interacceptor separation within the shell $a \sim N_A^{-1/3} = 20 \text{ \AA}$ and $R_1 = 1000 \text{ \AA}$, one finds that $Z \sim 5 \times 10^5$. This is why, in spite of the fact that the microscopic decay rate at critical retardation distances is extremely small (of the order $10^{-7} \times \tau_D^{-1}$ or less), the total transfer-induced decay rate can be large enough to induce experimentally measurable changes in the donor decay rate. This may afford a means for the validation of our results.

In concluding this section we note that whereas we have focussed attention on the possibility of detecting energy transfer by monitoring changes in the rate of donor decay, it is also possible to register differences between standard theories and our approach through measurement of transfer-induced acceptor luminescence. However, in this case there is an additional constraint on the acceptor distribution, since it becomes necessary to minimize longer-range radiative contributions to the donor–acceptor energy transfer. For example, in the shell-like microsystems discussed above, the radius R_1 should lie within the critical retardation region,

$R_1 \sim \lambda$, and moreover $(R_2 - R_1)$ should be appreciably smaller than R_1 . It should be noted that in identifying the distinctive features of the unified theory of energy transfer, measurement of the polarization of acceptor fluorescence is more convenient than absolute fluorescence detection.²² The distinction is based on the completely different transfer-induced fluorescence depolarization in the limiting cases of Förster and radiative energy transfer. The transition between these limits, which characterizes the unified theory, can be identified at critical intermolecular transfer distances.

V. DISCUSSION

In this paper we have presented a theoretical investigation of single-step molecular energy transfer incorporating molecular vibrational structure. The unified theory of molecular energy transfer represents the pair transfer rate as a sum of three terms, each being proportional to R^{-6} , R^{-4} , and R^{-2} . In a sense, the R^{-4} and R^{-2} terms may be regarded as corrections to the Förster rate, and the R^{-6} and R^{-4} terms as corrections to the radiative rate. Over critical retardation distances where R is comparable to the reduced wavelength of the energy transferred, the unified theory produces results which differ both markedly and measurably from those predicted by either of the two traditional mechanisms. We have considered how the pair transfer function must be changed for an ensemble, and discussed applications to some model systems.

It is interesting to consider the status of critical distances in the generalized theory of donor-acceptor energy transfer. We have already made frequent reference to the critical retardation distance $R_{\text{retard}} = \lambda$ beyond which the Förster theory is no longer applicable. For energy transfer in the visible and near-infrared region R_{retard} has a value of the order of 10^3 \AA . In the standard theory of radiationless energy transfer another critical distance, R_F called the Förster radius is commonly quoted. This is defined as the distance where the orientationally averaged pair transfer rate \overline{W}_F is equal to the rate of spontaneous donor emission τ_D^{-1} . The Förster radius is related to R_{retard} by

$$R_F = \left(\frac{3}{4\pi} \frac{\langle \sigma_A \rangle}{\lambda^2} \right)^{1/6} R_{\text{retard}}, \quad (5.1)$$

where $\langle \sigma_A \rangle$ is the acceptor absorption cross-section averaged over the appropriate range of the donor emission spectrum. Since it is usually the case that the cross-section $\langle \sigma_A \rangle$ is less than 1 \AA^2 , R_F should be at least an order of magnitude smaller than R_{retard} . Finally there is one other critical distance associated with the range of applicability of the basic concept of an energy transfer rate. At very short distances, $R < R_{\text{coh}}$, coherence effects such as quantum oscillations in the donor-acceptor system come into play^{1,2} and the process of energy transfer can no longer be described in terms of time-independent transfer rates. The coherence distance, R_{coh} , is defined as the distance at which the excitation transfer matrix element expressed in \hbar units is equal to the inverse dephasing time. Typically R_{coh} is less than 20 \AA . Moreover, it should be borne in mind that the adoption of the electric dipole approximation for the description of intermolecular

coupling is valid when the molecular separation exceeds typical molecular dimensions.

As we have already mentioned, in the framework of molecular quantum electrodynamics the energy transfer is mediated by intermolecular propagation of virtual photons. The time $\delta t = R/c$ necessary for a photon to cover the distance R between the donor and acceptor is related to the photon energy uncertainty δE by $\delta E \delta t \gtrsim \hbar$, so that

$$\delta E \gtrsim \frac{\Delta E_D}{KR}, \quad (5.2)$$

where $\Delta E_D = \hbar c K$ is the donor excitation energy. Thus, for small donor-acceptor separations, $KR \ll 1$, the uncertainty in the virtual photon energy greatly exceeds the energy transferred. On the contrary at large separations, $KR \gg 1$, the virtual photon acquires real character so that effectively only those photons in resonance with the donor excitation energy participate in the energy transfer. The estimate (5.2) can also be obtained from the analysis of contribution of photon states to the electronic transfer matrix element $T_{AD}^{(2)}$.

It is instructive to consider the relationship between our results for the rate of donor-acceptor energy transfer and the standard R^{-2} result for the energy flux of a radiating donor, based on evaluation of the Poynting vector. In performing any such comparison, a number of caveats should be mentioned. First, we note that whilst the unified theory produces a long-range asymptote of the pair transfer rate which is identical to that obtained on the Poynting vector basis, the rate differs over distances $R \gg \lambda$ to a small but finite extent through inclusion of the additional R^{-6} and R^{-4} terms. Yet there is no reason to expect exact equality. When net energy flux is considered, the requirement for energy conservation necessitates R^{-2} behavior: however, in Poynting vector calculations measurement of the flux is not modelled, presupposing an ideal detector which is not dynamically coupled to the emitter. In calculating the rate of excitation transfer the dynamics of the detection process (i.e., the acceptor excitation) is explicitly incorporated. It is worth noting that for distances beyond the critical retardation region the difference resulting from inclusion of the R^{-4} and R^{-6} terms is in any case smaller than is physically determinable, as can be shown from elementary considerations of quantum uncertainty. It should also be pointed out that the incorporation into the excitation transfer rate equations of an exponential factor to allow for the effect of other absorbers is a feature which specifically relates to modelling of the transfer process, and removes the apparent paradox discussed in Sec. III. Thus, the total energy flux is not a conserved quantity, and the exponential factor is due to electromagnetic energy trapping within the system.

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- ²⁷In this paragraph it is implicitly assumed that the orientational factors η_1 and η_3 are nonzero, as is normally the case.
- ²⁸For simplicity it is here assumed that the absorbing species are all of one type. The theory can easily be extended to the case of multicomponent absorbers by replacing $\sigma_A N_A$ by $\sum \sigma_A N_A$.
- ²⁹For a typical absorption cross-section $\sigma_A \sim 1 \text{ \AA}^2$, the Beer length $\alpha^{-1} \sim a^3/\sigma_A$ should be at least 100 times larger than the average molecular separation a which normally cannot be less than 10 \AA .
- ³⁰Equation (4.4) also describes the situation in which the distribution of acceptors about a given donor is spherically symmetric only up to a certain distance $R^* \gg R$. This accommodates the possibility of microsystems which are not inherently spherical in their outer profiles.