

Multichromophoric Förster Resonance Energy Transfer

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The theory of Förster resonance energy transfer is generalized for multichromophoric (MC) and nonequilibrium situations. For the first time, it is clarified that the far-field linear spectroscopic information is insufficient for the determination of the reaction rate and that distance dependence of the rate can vary with the disorder and temperature. Application to a light harvesting complex LH2 reveals the important consequences of a MC structure.

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Recent advances in single molecule spectroscopy of multichromophoric (MC) systems such as the light harvesting complex LH2 [1–3] strongly suggest that the description of dynamical processes in these systems have to be reexamined. The most important of these dynamical processes is FRET (Förster resonance energy transfer) which has become the biological ruler for the 20–100 Å range distance determinations in molecules such as DNA [4] and proteins [5]. The original theory of FRET [6–8], developed more than 50 years ago, considered the transfer of electronic excitation energy from a single chromophoric donor (D) to a single chromophoric acceptor (A) (or to an ensemble of independent A 's). Application of this theory to large MC systems requires significant changes in the theory, some of which have appeared in recent years by Sumi *et al.* [9,10] and Scholes *et al.* [11,12]. These theories, however, are not general enough to provide reliable guidance of experiments in all possible situations. In this Letter, we present such a generalization, discuss important new characteristics of MC-FRET for the first time, and apply the theory to an important energy transfer process in LH2.

In MC systems, D (and/or A) consists of multiple chromophores, which are intimately coupled together to form excitonic states. Light harvesting complexes [1–3,13], proteins with multiple tryptophans nearby [8], dendrimers [14], conjugated polymers [15], and quantum dot arrays [16] have these characteristics. Therefore, understanding the dynamics of excitation energetics in MC systems is a crucial problem for quantitative description of photosynthetic light harvesting processes, for structural determination of a broader range of protein systems, and for better design of optoelectronic devices based on nanostructured materials. By nature or design, many MC systems have well-defined D and A sites, where inter- D - A chromophore distances are larger than intra- D and intra- A chromophore distances. Experimental data [13–16] demonstrate that the energy transfer processes in these systems exhibit rate behaviors which are suggestive of FRET or its multipolar generalizations [6–8]. However, applications of existing single chromophoric

theories to these MC systems can lead to significant errors due to the fact that the D - A distances are not large enough to justify point dipole or multipole approximation for the transitions in D and A , and that the transfer involves more than one pair of excitations or exciton states. Indeed, for the energy transfer from the B800 unit to the B850 unit in LH2 [13], experimental estimates of the rate are about 5–10 times larger than the prediction of single chromophoric FRET theory [13,17]. Mukai, Abe, and Sumi (MAS) [9,10] and Scholes and Fleming (SF) [11,12] independently attributed the discrepancy to contributions from dark exciton states of B850. Our theory includes the MAS-SF theory [9,12] as a limiting case, and we present simulation results that uncover an important microscopic feature of the B800 \rightarrow B850 energy transfer dynamics.

According to the single chromophoric FRET theory [6–8], the energy transfer rate from D to A , assuming immobile transition moments, is given by

$$k_F = \frac{J^2}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega E_D(\omega) I_A(\omega), \quad (1)$$

where J is the transition dipole-dipole coupling between D and A , depending on the inverse third power of the D - A distance, and

$$E_D(\omega) \equiv \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle e^{iH_D^g t/\hbar} e^{-iH_D^e t/\hbar} \rangle_{\rho_D^g}, \quad (2)$$

$$I_A(\omega) \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \langle e^{iH_A^e t/\hbar} e^{-iH_A^g t/\hbar} \rangle_{\rho_A^g}, \quad (3)$$

where H_D^g (H_A^g) is the ground state Hamiltonian of D (A) plus its environment, H_D^e (H_A^e) is the excited state Hamiltonian of D (A) plus its environment, and $\langle \cdots \rangle_{\rho_D^g}$ ($\langle \cdots \rangle_{\rho_A^g}$) denotes averaging over ρ_D^g (ρ_A^g)—the canonical density operator for H_D^g (H_A^g). The simple spectral overlap expression in Eq. (1), a central feature of the theory for spectroscopic rate determination, relies on the assumption that no given degree of freedom couples to both D and A . Appropriate formulation of this assumption is necessary for the following MC situation.

Let us consider MC systems where D and A consist of D_j ($j = 1, \dots, N_D$) and A_k ($k = 1, \dots, N_A$). We suppose the following forms of exciton Hamiltonians:

$$H_{D,0}^e = \sum_{j=1}^{N_D} \epsilon_{D_j} |D_j\rangle\langle D_j| + \sum_{j \neq j'} \Delta_{jj'}^D |D_j\rangle\langle D_{j'}|, \quad (4)$$

$$H_{A,0}^e = \sum_{k=1}^{N_A} \epsilon_{A_k} |A_k\rangle\langle A_k| + \sum_{k \neq k'} \Delta_{kk'}^A |A_k\rangle\langle A_{k'}|, \quad (5)$$

where ϵ_{D_j} (ϵ_{A_k}) is the energy of the excitation state $|D_j\rangle$ ($|A_k\rangle$), and $\Delta_{jj'}^D$ ($\Delta_{kk'}^A$) is the electronic coupling between $|D_j\rangle$ and $|D_{j'}\rangle$ ($|A_k\rangle$ and $|A_{k'}\rangle$). All other degrees of freedom except for the above electronic states will be termed as bath hereafter. If each $|D_j\rangle$ is coupled to a bath operator B_{D_j} , the total Hamiltonian for excited D , $H_D^e = H_{D,0}^e + \sum_{j=1}^{N_D} B_{D_j} |D_j\rangle\langle D_j| + H_D^g$. Likewise, the total Hamiltonian for excited A , $H_A^e = H_{A,0}^e + \sum_{k=1}^{N_A} B_{A_k} |A_k\rangle\langle A_k| + H_A^g$. The assumption that no given bath mode couples to both D and A can be imposed by the following conditions: $[H_D^g, H_A^g] = [H_D^g, B_{A_k}] = [H_A^g, B_{D_j}] = 0$. Otherwise, B_{D_j} , B_{A_k} , H_D^g , and H_A^g are arbitrary. For the present MC situation, $N_D \times N_A$ terms contribute to the coupling Hamiltonian, $H_c = \sum_{j=1}^{N_D} \sum_{k=1}^{N_A} J_{jk} (|D_j\rangle\langle A_k| + |A_k\rangle\langle D_j|)$, where J_{jk} is the transition dipole-dipole interaction between D_j and A_k . Even if each jk pair satisfies all the requirements for the use of Eq. (1), the incoherent sum of the analog of Eq. (1) for each pair is not in general valid because it neglects intra- D and intra- A quantum coherence.

We derive a MC generalization of Eq. (1), which also accounts for nonequilibrium effects, by adapting to the MC system described above a formalism that has recently been developed for a single chromophoric situation [18]. Initially (for $t < 0$), the total system is in the ground state canonical equilibrium represented by $\rho_D^g \rho_A^g$. If impulsive radiation that selectively excites D is applied at $t = 0$, the total density operator becomes $\rho(0) = |D_{\hat{\mathbf{e}}}\rangle\langle D_{\hat{\mathbf{e}}}| \rho_D^g \rho_A^g$, with $|D_{\hat{\mathbf{e}}}\rangle = \mathcal{N} \hat{\mathbf{e}} \cdot \sum_j \boldsymbol{\mu}_{D_j} |D_j\rangle$, where \mathcal{N} is a normalization constant, $\hat{\mathbf{e}}$ is the polarization vector of the radiation, and $\boldsymbol{\mu}_{D_j}$ is the transition dipole of $|D_j\rangle$. The probability for the acceptor molecule to be excited at time t is then given by $P_A(t) = \sum_{k=1}^{N_A} \text{Tr}\{\langle A_k| e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} |A_k\rangle\}$, where Tr denotes the trace over all the bath degrees of freedom and $H = H_D^e + H_A^e + H_c$.

Expanding $P_A(t)$ up to the second order of H_c , taking its time derivative, and employing the identity $[\sum_k |A_k\rangle\langle A_k|, H_D^g + H_A^g] = 0$, we obtain

$$k^{\text{MC}}(t) = \sum_{j'j''} \sum_{k'k''} \frac{2J_{j'k'} J_{j''k''}}{\hbar^2} \times \text{Re} \left[\int_0^t dt' \text{Tr}\{\langle A_{k'}| e^{-i(H_D^g + H_A^g)(t-t')/\hbar} |A_{k''}\rangle\langle D_{j'}| \times e^{-i(H_D^e + H_A^e)t'/\hbar} \rho(0) e^{i(H_D^e + H_A^e)t'/\hbar} |D_{j''}\rangle\} \right]. \quad (6)$$

We define a matrix $\mathbf{I}_A(\omega)$ with the following components:

$$I_A^{k'k''}(\omega) \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \times \text{Tr}_A \{ e^{iH_A^e t/\hbar} \langle A_{k'}| e^{-iH_A^e t/\hbar} |A_{k''}\rangle \rho_A^g \}, \quad (7)$$

where Tr_A denotes the trace over all the bath degrees of freedom for A . Inserting the inverse Fourier transform of Eq. (7) into Eq. (6), one can obtain the following compact expression for the MC and nonequilibrium FRET [19]:

$$k^{\text{MC}}(t) = \sum_{j'j''} \sum_{k'k''} \frac{J_{j'k'} J_{j''k''}}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega E_D^{j'j''}(t, \omega) I_A^{k'k''}(\omega), \quad (8)$$

with

$$E_D^{j'j''}(t, \omega) = 2\text{Re} \left[\int_0^t dt' e^{-i\omega t'} \text{Tr}_D \{ e^{-iH_D^e t'/\hbar} \langle D_{j'}| \times e^{-iH_D^e(t-t')/\hbar} |D_{\hat{\mathbf{e}}}\rangle\langle D_{\hat{\mathbf{e}}}| \rho_D^g e^{iH_D^e t'/\hbar} |D_{j''}\rangle \} \right], \quad (9)$$

where Tr_D denotes the trace over all the bath degrees of freedom for D . Within the cumulant approximation and in the absence of back reaction, $P_A(t) = 1 - P_D(t) \approx 1 - e^{-\int_0^t d\tau k^{\text{MC}}(\tau)}$.

Equation (8) is the major result of the present Letter, and includes other existing theories as limiting cases. For example, the single chromophoric nonequilibrium theory [18] is recovered when $N_D, N_A = 1$. The stationary MC-FRET expression is obtained from Eq. (8), taking the limit $t \rightarrow \infty$, and assuming the ergodicity, $\lim_{t \rightarrow \infty} e^{-iH_D^e(t-t')/\hbar} |D_{\hat{\mathbf{e}}}\rangle\langle D_{\hat{\mathbf{e}}}| \rho_D^g e^{iH_D^e(t-t')/\hbar} = \rho_D^e$, in Eq. (9). The resulting expression is

$$k_F^{\text{MC}} = \sum_{j'j''} \sum_{k'k''} \frac{J_{j'k'} J_{j''k''}}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega E_D^{j'j''}(\omega) I_A^{k'k''}(\omega), \quad (10)$$

where we have defined a matrix $\mathbf{E}_D(\omega)$ with components

$$E_D^{j'j''}(\omega) \equiv \int_{-\infty}^{\infty} dt e^{-i\omega t} \times \text{Tr}_D \{ e^{-iH_D^e t/\hbar} \langle D_{j'}| e^{iH_D^e t/\hbar} \rho_D^e |D_{j''}\rangle \}. \quad (11)$$

The rate expression derived by Sumi [10] is equivalent to Eq. (10). Additional approximations for some quantum coherence terms lead to the expression of MAS-SF [9,12]. New features become notable in the MC-FRET, according to Eq. (10), even at the stationary limit. We discuss the two most important issues [(i) and (ii) below].

(i) *Information on the far-field linear spectroscopic line shape is insufficient for the determination of the MC-FRET rate in general.* The reason is that the far-field emission and absorption spectra, even in the absence of ensemble disorder, are given by $E_D^{\hat{\mathbf{e}}}(t, \omega) = \sum_{j',j''} (\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{D_{j'}}) (\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{D_{j''}}) E_D^{j'j''}(t, \omega)$ and $I_A^{\hat{\mathbf{e}}}(t, \omega) = \sum_{k',k''} (\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{A_{k'}}) (\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{A_{k''}}) I_A^{k'k''}(t, \omega)$, where $\boldsymbol{\mu}_{D_j}$ and $\boldsymbol{\mu}_{A_k}$, respectively, are transition dipoles of $|D_j\rangle$ and $|A_k\rangle$. Except for dimeric D and

A, these weighted sums (three or less terms in each case) cannot convey the full information on $\mathbf{E}_D(\omega)$ and $\mathbf{I}_A(\omega)$ necessary for the calculation of Eq. (10). Nonlinear spectroscopic experiments [12] or theoretical data based on, e.g., semiempirical calculations [20] or time dependent density functional approaches [21], can in principle be used to obtain the missing information, but, in practice, they are not definitive. Whether a near-field probe method can be developed for general determination of the MC-FRET rate, through its capability to control other spectroscopic variables beyond polarization vectors, is an interesting issue to pursue.

(ii) *The distance dependence of MC-FRET can vary with disorder and temperature.* This temperature variation should be taken into account when temperature dependent structural changes of a MC system are studied by FRET. The reason becomes clear considering that each coefficient of $J_{j'k'}J_{j''k''}$ in Eq. (10) depends on the disorder and temperature in a different manner. Stated more physically, the disorder affects the spatial and energetic nature of exciton states, and temperature alters the relative populations of different exciton states and their mutual coherence. Therefore, effective “sizes” of respective excitons in D and A , which determine the distance dependence, vary with a specific realization of the disorder and temperature. For an illustration, we consider the following model of single chromophoric D and dimeric A . The zeroth order exciton Hamiltonians are $H_{D,0}^e = \epsilon_D |D\rangle\langle D|$ and $H_{A,0}^e = \epsilon_\alpha |A_\alpha\rangle\langle A_\alpha| + \epsilon_\beta |A_\beta\rangle\langle A_\beta| + \Delta(|A_\alpha\rangle\langle A_\beta| + |A_\beta\rangle\langle A_\alpha|)$. The total exciton Hamiltonians including baths are $H_D^e = H_{D,0}^e + B_D |D\rangle\langle D| + H_D^s$ and $H_A^e = H_{A,0}^e + B_\alpha |A_\alpha\rangle\langle A_\alpha| + B_\beta |A_\beta\rangle\langle A_\beta| + H_A^s$. All the bath modes are represented by harmonic oscillators such that $H_D^s + H_A^s = \sum_n \hbar \omega_n (b_n^\dagger b_n + 1/2)$. The coupling terms are $B_D = \sum_n \hbar g_{nD} (b_n + b_n^\dagger)$, $B_\alpha = \sum_n \hbar g_{n\alpha} (b_n + b_n^\dagger)$, and $B_\beta = \sum_n \hbar g_{n\beta} (b_n + b_n^\dagger)$. The spectral densities are given by $\sum_n \delta(\omega - \omega_n) g_{nD}^2 = 0.1(\omega + 0.5\omega^2/\omega_c)e^{-\omega/\omega_c}$ and $\sum_n \delta(\omega - \omega_n) g_{n\alpha}^2 = \sum_n \delta(\omega - \omega_n) g_{n\beta}^2 = 0.5(\omega + 0.5\omega^2/\omega_c)e^{-\omega/\omega_c}$. Each mode is coupled to a single excitation state only. The magnitudes of transition dipoles are denoted as μ_D , for D , and μ_A , for A_α and A_β . Figure 1(a) shows the orientations of these transition dipoles. In all the calculations, we set $\phi = \pi/4$, and use units where $\hbar = \omega_c = d = 1$. The refractive index is assumed to be unity, and the intra- A electronic interaction Δ is calculated assuming $\mu_A^2 = 1/2$. We consider two energetic situations, $\epsilon_D - 2 = \epsilon_\alpha = \epsilon_\beta$ (Case I), $\epsilon_D - 2 = \epsilon_\alpha + 1 = \epsilon_\beta - 1$ (Case II), and, for each case, two values of temperature, $k_B T = 0.1$ (LT) and $k_B T = 1$ (HT). The MC-FRET rate from D to A is calculated employing Eq. (10), where $E_D(\omega)$ is determined by numerical fast Fourier transform, and calculation of $\mathbf{I}_A(\omega)$ is made by a second order quantum master equation approach [22]. Figure 1(b) shows the values of $\kappa \equiv k_F^{\text{MC}} R^6 / (\mu_D^2 \mu_A^2)$ with the variation of R . The deviation from $1/R^6$ behavior in each case demonstrates breakdown

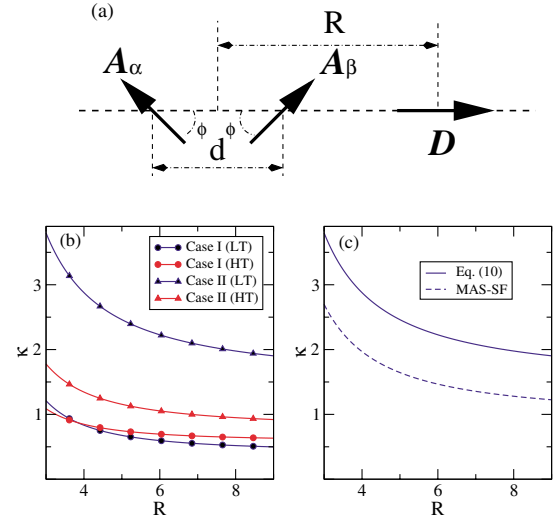


FIG. 1 (color online). (a) Transition dipoles of D , A_α , and A_β . All the vectors and coordinates are in the same plane. (b) Values of $\kappa = k_F^{\text{MC}} R^6 / (\mu_D^2 \mu_A^2)$ vs R , for Cases I and II, at $k_B T = 0.1$ (LT) and $k_B T = 1$ (HT). (c) Comparison of the expression of MAS-SF with Eq. (10), for Case II at $k_B T = 0.1$.

of dipole approximation as has been shown to be typical for many MC systems [11]. The main point of this calculation, however, is that the manner of deviation indeed depends on a specific realization of disorder and temperature as stated above.

While the original rate expression of Sumi [10] is equivalent to Eq. (10), ensuing applications by him and MAS [9,10] assumed that $\mathbf{E}_D(\omega)$ and $\mathbf{I}_A(\omega)$ are diagonal in the excitonic bases—the sets of eigenstates of $H_{D,0}^e$ and $H_{A,0}^e$. SF [12] made the same assumption. Since Eq. (10) is invariant with the choice of basis set, the excitonic bases of D and A can always be used for the rate expression. However, in general, $\mathbf{E}_D(\omega)$ and $\mathbf{I}_A(\omega)$ are nondiagonal even in the excitonic bases because H_D^e (H_A^e) does not commute with $H_{D,0}^e$ ($H_{A,0}^e$). Therefore, the expression of MAS-SF [9,12], which neglects coherence terms in the excitonic bases, is *valid only when the exciton-bath couplings are weak enough or diagonal in the excitonic bases*. We have compared the expression of MAS-SF with Eq. (10) for the model of Fig. 1(a) at $k_B T = 0.1$. We have found that the approximation of MAS-SF is accurate enough for Case I (not shown), but leads to substantial error for Case II, as shown in Fig. 1(c). This result demonstrates that consideration of all the coherence terms is important, especially when the disorder is comparable to the exciton-bath coupling.

We now apply the present theory to the calculation of the B800 \rightarrow B850 energy transfer rate within a single LH2. For the B850 unit, with 18 bacteriochlorophylls (BChls), we use an exciton-bath Hamiltonian [22]. Only one BChl is considered in the B800 unit [23]. Figure 2(a) shows the distributions of rates at $k_B T = 10 \text{ cm}^{-1}$, determined from an ensemble of 100 000

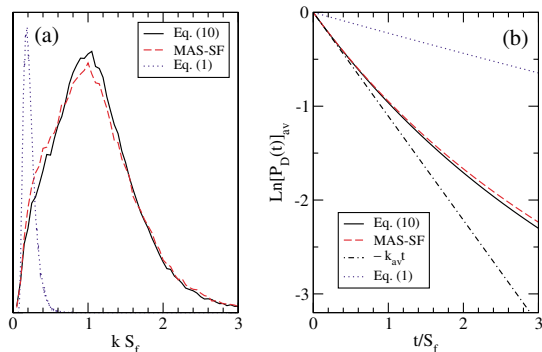


FIG. 2 (color online). (a) Distributions of FRET rates. The scale factor S_f , assuming unit refractive index, is $10^9/\mu_{\text{BChl}}^4$ in the units where $\hbar = c = 1$ and 1 \AA is the unit length. In applying Eq. (1), a unit orientational factor and the shortest BChl_{B800}-BChl_{B850} distance were used. The vertical scale of the distribution for Eq. (1) has been reduced by a factor of 7. (b) Logarithmic populations. $[P_D(t)]_{av} = \langle \exp(-kt) \rangle$ and $k_{av} = \langle k_F^{MC} \rangle$.

realizations of disorder [24]. The calculated MC-FRET rates are substantially larger than single chromophoric FRET rates, and the degree of enhancement is comparable to that observed experimentally [17]. The approximation of MAS-SF, which neglects coherence terms in the excitonic basis, turns out to be reasonably good for the present system, but still results in a small underestimation of Eq. (10). The distribution of the MC-FRET rates is very broad. The resulting ensemble averaged population decay of the excited D , assuming no back reaction [25], is *far from exponential*. This is contrary to the previous assumption of exponential decay [9,12], and indicates that care should be taken in the interpretation of multiexponential fittings of pump-probe data. A future study that includes nonequilibrium effects in Eq. (8) and employs more systematic modeling of the B800 unit can provide better quantitative explanation of relevant experimental results.

In summary, we have presented a MC-FRET theory applicable to a wide range of systems [1–3,8,13–16]. We have addressed two important issues unique for MC systems, (i) and (ii), which should be recognized in any spectroscopic attempt to determine the rate and to obtain distance information. Application to the B800 \rightarrow B850 energy transfer process has provided new evidence for very efficient and dispersive energy transfer dynamics caused by the MC effects. The present Letter reveals complexity hidden in a seemingly simple rate behavior, even without consideration of other prominent issues such as common mode effects, dynamic orientation factors, and local field corrections [7,8,11], but, on the other hand, suggests a new possibility that the FRET rate in MC systems can be controlled solely by the arrangement of chromophores.

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- [24] Based on a fit to an unpublished ensemble line shape for a mutant of *Rhodobacter sphaeroides* from the Völker group, we chose Gaussian energetic disorder with the following standard deviations: 250 cm^{-1} (BChl_{B850} excitation energy); 40 cm^{-1} (B850 ground state energy); 54 cm^{-1} (BChl_{B800} excitation energy).
- [25] Because of the large energy difference between the B800 and B850 bands compared to $k_B T = 10 \text{ cm}^{-1}$ and the spectral range of the bath, the contribution of back reaction is expected to be minor for the present system.