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LONG-RANGE RESONANCE ENERGY TRANSFER IN MOLECULAR SYSTEMS

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■ **Abstract** The current state of understanding of molecular resonance energy transfer (RET) and recent developments in the field are reviewed. The development of more general theoretical approaches has uncovered some new principles underlying RET processes. This review brings many of these important new concepts together into a generalization of Förster's original theory. The conclusions of studies investigating the various approximations in Förster theory are summarized. Areas of present and future activity are discussed. The review covers Förster theory for donor-acceptor pairs and electronic coupling for singlet-singlet, triplet-triplet, and superexchange-mediated energy transfer. This includes the transition density picture of Coulombic coupling as well as electronic coupling between molecular aggregates (excitons). Spectral overlaps and ensemble energy transfer rates in disordered aggregates, the role of dielectric properties of the medium, weak versus strong coupling, and new models for energy transfer in complex molecular assemblies are also described.

INTRODUCTION

Resonance energy transfer (RET), often known also as electronic energy transfer (EET), is a ubiquitous photophysical process whereby an electronically excited "donor" molecule transfers its excitation energy to an "acceptor" molecule by a nontrivial mechanism such that the excited state lifetime of the donor is diminished (1–6). In other words, the excitation energy is not transmitted by uncorrelated donor emission–acceptor absorption events.

The phenomenon of RET was originally revealed by careful fluorescence quenching experiments (7–17). In parallel to observations of RET in dye solutions, a number of studies were exposing the role of RET in various biological systems (18–23). For example, Emerson & Arnold (18) concluded that a large number of chlorophyll molecules were involved in the capture of light to initiate the first steps in photosynthesis. Other studies went on to explore carotenoid to chlorophyll RET in marine diatoms (19), and the question of whether the protein itself can absorb light and transfer this excitation to a bound chromophore (21).

An elegant theory relating experimental observables to the mechanism of RET was first put forward by Förster (10). The significance of Förster's formulation is evinced by the numerous, diverse areas of study that are impacted by his paper, examples of which include the measurement of distances between fluorescent tags in a protein by fluorescence resonance energy transfer (FRET) (24, 25), and the observation of the kinetics of conformational changes in RNA by time-resolved FRET (26). Similar kinds of experiments are employed to elucidate the structure and dynamics of polymer-polymer interfaces (27–32). RET is responsible for quenching of fluorescence in concentrated solution (33), and is used by photosynthetic organisms to harvest sunlight (34, 35), or tune the color of bioluminescence (36, 37). Inspired by nature, optimization of RET plays a fundamental role in the development of synthetic light-harvesting devices (38–46), as well as in color-conversion in electroluminescent polymer-based devices (47–50). Such studies have led to the synthesis of some remarkable supramolecular systems and molecular assemblies that have been the subject of studies revealing deeper insights into the mechanism of RET. The efficacy of RET-mediated energy migration along aromatic polymers can be used to harvest light, or naturally accelerate the photodegradation processes (52–58)—as put to use in the ingenious photodegradable plastics developed by Guillet (59).

Historically, RET was referred to as "transfer by inductive resonance." This descriptive term emphasizes that the electronic interaction promoting RET involves a coupling of transition moments of the donor and acceptor molecules via a Coulombic interaction, conceptually analogous to coupled oscillators. Early work also established that energy conservation in the weak coupling limit is ensured by overlap of the donor fluorescence spectrum with the acceptor absorption spectrum. Such a spectral overlap bundles a lot of complicated information into a simple form. The spectral overlap includes nuclear overlap factors, separated from the electronic coupling term by the Born-Oppenheimer approximation, in the form of Franck-Condon overlap factors. It also accounts for spectral line shapes—and thus the temperature dependence of the RET rate—as well as energy relaxation terms in the spirit of the Stokes' shift (10, 60). A typical schematic illustration of RET is shown in Figure 1, which demonstrates that a picture of coupled two-state systems is the minimal model. The genius of Förster theory for RET is that all this relevant information regarding electronic coupling and the entanglement of nuclear factors is obtained from simple experimental data.

There is an important synergism between experiment and theory in studies of RET phenomena as well as in the use of RET as a spectroscopic tool. In recent years the complexity of the systems being studied has escalated, and these systems have been investigated at a deeper level. This has necessitated the development of more general theoretical approaches and has uncovered some new principles underlying RET processes. This review brings many of these important new concepts together into a generalization of Förster's original theory. In addition, the conclusions of studies investigating the various approximations in Förster theory are summarized. The present review summarizes the current state of understanding of molecular

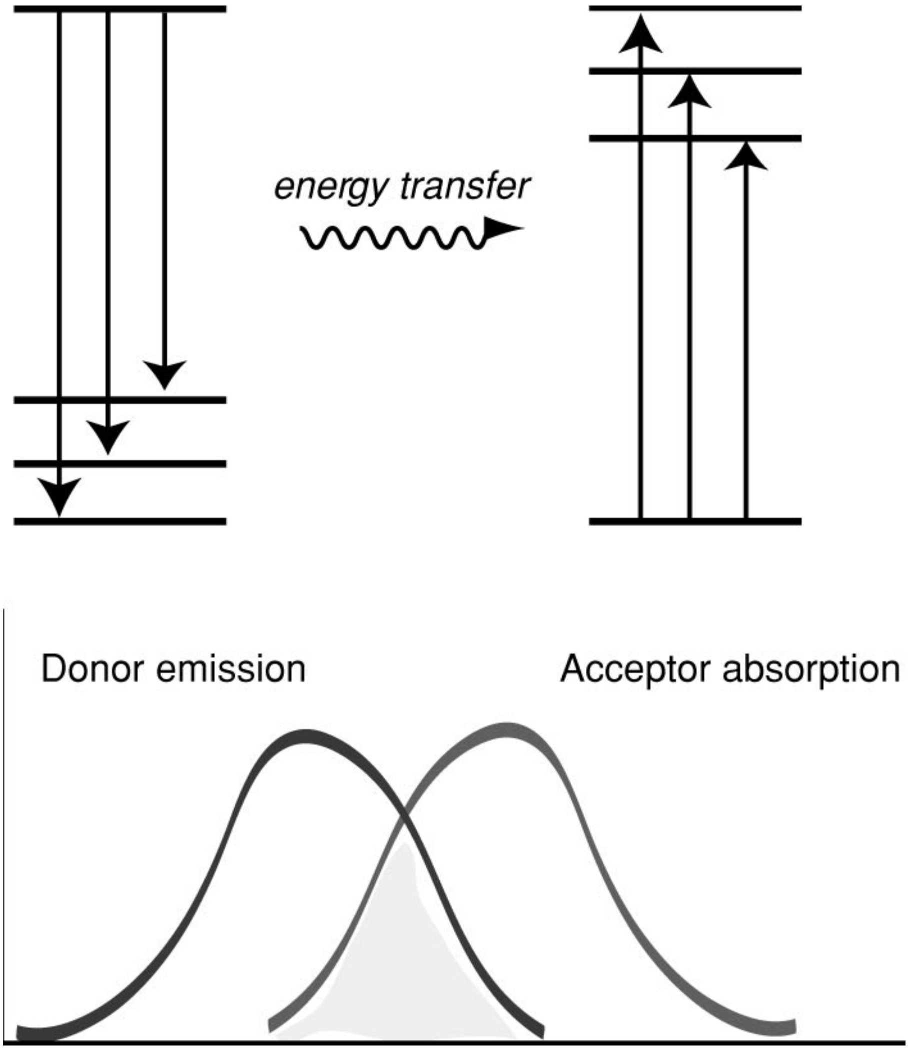

Figure 1 Model picture for energy transfer (*top*) showing fluorescence of the donor to multiple vibronic levels of the ground state, coupled to isoenergetic transitions of the acceptor. Energy conservation is thus determined by spectral overlap of donor emission and acceptor absorption (*bottom*).

RET, recent developments in the field are highlighted, and areas of present and future activity are discussed. The sheer volume of work on RET precludes the possibility of dwelling on specific studies, although some historical papers that assume greater relevance in the context of recent developments are mentioned. Some earlier reviews of RET can be found in References 1–4, 14, and 61.

WEAK VERSUS STRONG ELECTRONIC COUPLING

A recurring and important problem in RET theory is the discrimination between weak, intermediate, and strong electronic coupling (1, 62–81). Förster theory is formulated for the weak coupling limit (1, 10) because it is based on an equilibrium Fermi Golden Rule approach with a second-order perturbation theory treatment of the electronic coupling between donor and acceptor. The key assumptions are, first, that the bath equilibrates subsequent to electronic excitation of the donor on a timescale that is considerably faster than that of RET and, second, that the coupling to the bath, for example, as indicated by the absorption line shape, is much greater than the electronic coupling between donor and acceptor. This latter condition ensures that the RET is incoherent (Markovian) and irreversible. The complementary case is the strong coupling limit, in which the donor and acceptor electronic states mix strongly to produce new, delocalized states. In that situation, it makes no sense to discuss RET from donor to acceptor.

A particularly challenging problem has been to model RET dynamics in the intermediate coupling case. In this case, nonequilibrium relaxation of the bath on the timescale of RET and mixing of the donor and acceptor states can lead to coherent dynamics on short timescales. Recent theories for the intermediate coupling case (76–81) are particularly salient given the present capabilities of ultrafast spectroscopy. In the next few years, it will be interesting to model ultrafast spectroscopic data using such theoretical approaches in order to investigate the breakdown of the weak coupling approximation in various systems. Up to the present time it is worth noting that Fermi Golden Rule–type approaches often seem to provide a useful, and basically correct, physical picture for many complex donor-acceptor RET systems.

FÖRSTER THEORY FOR DONOR-ACCEPTOR PAIRS

The Förster theory for RET was derived according to the established theory for coupling of a state to a quasi continuum of secondary states. Such a model allows one to rationalize dynamic processes involving decay of a “stationary” state, as described by Robinson & Frosch for radiationless transitions (63). In this way, Förster was able to write a Fermi Golden Rule expression for the RET rate, wherein the matrix element of interaction between excited donor and ground-state acceptor is a purely electronic coupling *V*. Conditions of energy conservation and nuclear overlap factors, separated from the electronic coupling by the Franck-Condon principle, were shown to relate emission and absorption events of the donor and acceptor molecules,

$$k = \frac{2\pi}{\hbar} \int_0^\infty \mathrm{d}\varepsilon \sum_k \sum_l P(k)P(l) \left| u(\bar{\varepsilon}_\mathrm{d}^k, \bar{\varepsilon}_\mathrm{a}^l, \varepsilon) \right|^2, \qquad 1.$$

where $\overline{\varepsilon}_{\mathrm{d}}^{k}$ is the energy gap of the donor molecule, adjusted according to $P(k)$ for thermal population of mode k in the excited state, and similarly for $\overline{\varepsilon}_{\mathrm{a}}^{l}$ with respect to the acceptor ground state. Owing to the normalization adopted by Förster, the matrix element u is a dimensionless quantity. If the electronic coupling V is independent of energy then we can write

$$u = \sum_{k} \sum_{l} P(k)P(l) \left| u(\overline{\varepsilon}_{\mathrm{d}}^{k}, \overline{\varepsilon}_{\mathrm{a}}^{l}, \varepsilon) \right|^{2} = |V|^{2}\, J(\varepsilon), \qquad 2.$$

such that, in the absence of static disorder, the spectral overlap $J(\varepsilon)$, which ensures energy conservation, takes the simple form of an overlap between donor emission $f^{\mathrm{hom}}(\varepsilon)$ and acceptor absorption spectra $a^{\mathrm{hom}}(\varepsilon)$, which have each been normalized to unit area on an energy scale, $J(\varepsilon) = f^{\mathrm{hom}}(\varepsilon)a^{\mathrm{hom}}(\varepsilon)$. Thus Equation 1 is rewritten as

$$\begin{aligned} k &= \frac{2\pi}{\hbar} |V|^{2} \int_{0}^{\infty} \mathrm{d}\varepsilon\, J(\varepsilon) \\ &= \frac{1}{\hbar^{2} c} \left| \tilde{V} \right|^{2} \int_{0}^{\infty} \mathrm{d}\tilde{\nu}\, J(\tilde{\nu}), \end{aligned} \qquad 3.$$

where V is the electronic coupling between donor and acceptor, which for $\tilde{V}$ is expressed in units of cm^{-1}, and $\tilde{\nu} = \varepsilon/2\pi\hbar c$. Any dielectric screening of the electronic interaction owing to the surrounding medium is included in V, as discussed in a later section.

Förster went further and expressed the rate of EET from donor D to acceptor A as

$$k^{\text{Förster}} = \frac{1}{\tau_{\mathrm{D}}} \frac{9000(\ln 10)\kappa^{2}\phi_{\mathrm{D}} I}{128\pi^{5} N n^{4}} \frac{1}{R^{6}}, \qquad 4a.$$

or

$$k^{\text{Förster}} = \frac{\phi_{\mathrm{D}}}{\tau_{\mathrm{D}}} \left(\frac{R_{0}}{R} \right)^{6} = \frac{\phi_{\mathrm{D}}}{\tau_{\mathrm{D}}} \left(\frac{8.785 \times 10^{-25} I}{n^{4} R^{6}} \right), \qquad 4b.$$

where κ is the orientation factor associated with the dipole-dipole interaction between donor and acceptor (see below), R is their center-to-center separation in units of cm, and n is the refractive index of the intervening medium. N is Avogadro's number, ϕ_{D} is the fluorescence quantum yield, and τ_{D} is the lifetime of the donor (in the same units as $1/k^{\text{Förster}}$). The Förster spectral overlap I is obtained from the overlap—on a wavenumber (or wavelength λ) scale—of an experimentally measured absorption spectrum for A, where intensity is in molar absorbance, with an area-normalized emission spectrum of D. I has units of $M^{-1}\mathrm{cm}^{3}$.

$$I = \int_0^\infty \frac{a_A(\tilde{\nu}) f_D(\tilde{\nu})}{\tilde{\nu}^4} \mathrm{d}\tilde{\nu}$$
$$= \int_0^\infty a_A(\lambda) f_D(\lambda) \lambda^4 \, \mathrm{d}\lambda. \qquad 5.$$

In this usual representation of the Förster equation, the electronic and nuclear factors are entangled because the dipole-dipole electronic coupling is partitioned between $\kappa^2 \phi_D/(\tau_D R^6)$ and the Förster spectral overlap integral, which contains the acceptor dipole strength. In molecular aggregate systems, this is a problem, which means that Equation 3 is a better starting point for modifying Förster theory, as described in a later section.

The Förster equation, as it stands, is accurate provided that four conditions are satisfied: (*a*) A dipole-dipole (or convergent multipole-multipole) approximation for the electronic coupling can be employed appropriately for the donor-acceptor interaction. (*b*) Neither the donor fluorescence lifetime, emission line shape, acceptor absorption line shape, nor oscillator strength is perturbed because of interactions among donors or acceptors respectively. (*c*) Static disorder (inhomogeneous line broadening) is absent in the donor and acceptor line shapes. (*d*) The energy transfer dynamics are incoherent.

ELECTRONIC COUPLING

Singlet-Singlet Electronic Coupling

RET may be thought of as a virtual photon exchange between donor D and acceptor A that is promoted by electronic coupling $V = \langle \mathrm{DA}^* | H | \mathrm{D}^* \mathrm{A} \rangle$ and hindered by nuclear reorganization associated with the transitions $\mathrm{D}^* \rightarrow \mathrm{D}$ and $\mathrm{A} \rightarrow \mathrm{A}^*$. The electronic coupling may be partitioned into a Coulombic contribution V^{Coul}, operative at all separations when the RET is spin-allowed, and a short-range contribution V^{short} that is explicitly dependent on the degree of overlap between the donor and acceptor molecular orbitals. Thus, at all separations

$$V = V^{\mathrm{Coul}} + V^{\mathrm{Short}}. \qquad 6.$$

It is assumed in Förster theory that $V \approx V^{\mathrm{Coul}}$ and that the Coulombic coupling can be approximated as a dipole-dipole interaction between transition dipole moments of the donor and acceptor molecules,

$$V^{\mathrm{Coul}} \approx V^{\mathrm{dd}} = \frac{1}{4\pi\varepsilon_0} \frac{\kappa \mu_D \mu_A}{R^3}. \qquad 7.$$

The orientation factor is defined by

$$\kappa = \vec{\mu}_D \cdot \vec{\mu}_A - 3(\vec{\mu}_D \cdot \vec{R})(\vec{\mu}_A \cdot \vec{R})$$
$$= 2\cos\theta_D \cos\theta_A + \sin\theta_D \sin\theta_A \cos\varphi. \qquad 8.$$

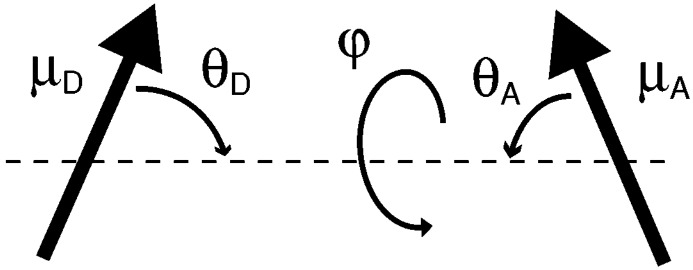

Figure 2 Definitions of the angles used for calculating the orientation factor between two dipoles, Equation 8.

The vectors and angles are defined in Figure 2 and the magnitude of the center-to-center separation of the molecules is *R*. The orientation-dependence of RET has been tested to show that no interaction is observed between perpendicularly oriented chromophores (82). The dipole-dipole approximation has proven to provide a useful and reliable estimation of the electronic coupling between pairs of molecules. The transition moment magnitude μ (in units of Debye) is related to the dipole strength of an absorption band, measured in media of refractive index *n*, according to (83)

$$\mu^2 = 9.186 \times 10^{-3} n \int [a(\tilde{\nu})/\tilde{\nu}]\, \mathrm{d}\tilde{\nu}. \qquad 9.$$

For some absorption bands the dipole strength may be dominated by borrowed intensity owing to strong vibronic coupling to a higher lying state. In that case, the orientation factor is calculated according to the orientation of the transition moment of the higher state from which the transition intensity is borrowed. Compelling evidence for vibronic coupling-mediated RET has been reported by Yip et al. (84). In general, the Coulombic interaction between state *i* of molecule *M* and state *k* of molecule *N*, where *i* is vibronically mixed with state *j* according to the vibronic coupling parameter υ, is written as (85)

$$V' = V_{ik}^{\mathrm{Coul}} + \upsilon V_{jk}^{\mathrm{Coul}}. \qquad 10.$$

A unified theory for the dipole-dipole, and higher multipole, interactions can be derived from quantum electrodynamics (QED) (86–88). Such an approach has the conceptual advantage of considering explicitly the fate of molecular electronic states as well as photons. Andrews (86, 87) has shown that the QED framework unifies the ideas of normal RET and the trivial process whereby a photon emitted from the donor propagates through the medium and is absorbed by an acceptor. The distance-dependences of these limits, as well as an intermediate regime, are connected in a single theory that converges to virtual photon exchange at close separations and real photon exchange at large separations. For randomly oriented chromophores, Equation 7 is modified according to the substitution

$$\frac{\kappa^2}{R^6} \rightarrow \frac{2(3 + k^2R^2 + k^4R^4)}{9R^6}, \qquad 11.$$

where $\mathbf{k}$ is the wavevector of the exchanged photon, $k = \omega/c$. In the "near zone" limit $kR \ll 1$, Equation 11 converges to the familiar $(2/3)R^{-6}$. In the "far zone" limit of the expression $kR \gg 1$, which corresponds to real photon exchange, the distance-dependence scales as $(2/9)k^4R^{-2}$. Such a mechanism would be operative at separations of $\sim$1 μm. The QED theory has proven to be useful for consideration of medium effects and fluorescence depolarization, and for exploring new mechanisms of RET (87, 89).

At sufficiently large separations between the donor D and acceptor A chromophores that the initial and final states for the RET are well described by the product wavefunctions $|D^*A\rangle$ and $|DA^*\rangle$, V^{short} is composed of contributions from penetration terms and a four-center, two-electron exchange integral (90). This latter term is the Dexter exchange integral (91)—a quantum mechanical correction to the Coulombic repulsion whose origin lies in the Pauli exclusion principle. It does not contribute significantly to V^{short} unless the donor and acceptor wavefunctions are very close to orthogonal (92, 93). However, in that case V^{Coul} should overwhelm the coupling, except in triplet-triplet energy transfer.

Whenever the donor and acceptor orbitals interpenetrate significantly, this simple picture of more or less isolated donor and acceptor breaks down. Effects deriving from the strong nonorthogonality between D and A wavefunctions need to be considered. To a first approximation this is often done variationally with the introduction of so-called charge transfer configurations (92). At close separations, interactions arising at this level of theory dominate V^{short} (93).

The significance of exchange and other short-range interactions, as well as higher multipole contributions to the Coulombic interaction, have been examined fairly extensively (94, 95). An interesting example is the report of Markovitsi et al. (96), in which the relative significance of short-range coupling interactions in columnar liquid crystals is directly measured. Our recent re-investigation of the origins and nature of the Coulombic interaction, however, lead inexorably to the conclusion that the electronic interaction that mediates RET at separations greater than 5 Å is invariably Coulombic. A compelling example is RET involving the dipole-forbidden $S_0 \rightarrow S_1$ transition in carotenoids reported by Fleming and coworkers (97). Interestingly, it seems that we thus return to the earlier conclusions of Kallmann & London (98), who first identified both the Coulombic and short-range exchange contributions to the electronic coupling. Moreover, it is evident for molecular systems that the dipole-dipole coupling cannot be improved by consideration of dipole-quadrupole, dipole-octupole, etc. terms in the multipole expansion. The shape of molecules becomes important as the dipole approximation breaks down. Owing to the importance of the Coulombic coupling that has now been established, a careful description of this interaction is timely.

Coulombic Coupling

The electronic transitions of molecules D and A can be thought of as quantum mechanical oscillators, which we can represent as transition densities connecting state K to L on molecule M, $P_{KL}^{M}(\mathbf{r}_1) = |K\rangle\,\langle L|$ (99, 100),

$$P_{KL}^{M}(\mathbf{r}_1) = N \int \Psi_K\left(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\right) \times \Psi_L^*\left(\mathbf{x}_1', \mathbf{x}_2', \ldots, \mathbf{x}_N'\right) \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N\, \mathrm{d}\mathbf{x}_2' \ldots \mathrm{d}\mathbf{x}_N'\, \mathrm{d}s_1, \qquad 12.$$

where N is a normalization constant, $\mathbf{x}_i$ are the spatial and spin coordinates of electron i, and s_1 is the spin of electron 1.

The Coulomb interaction between the D and A transition densities is the electronic coupling that promotes EET via virtual photon exchange,

$$V^{\text{Coul}} = \frac{e^2}{4\pi\varepsilon_0} \int \frac{P_{0m}^{D}(\mathbf{r}_1) P_{n0}^{A}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2. \qquad 13.$$

In optical spectroscopy the transition density of an allowed transition is characterized by its dipole moment,

$$\mu_{\alpha}^{LK} = \int (r_\alpha)_1 P_{KL}^{M}(\mathbf{r}_1)\, \mathrm{d}\mathbf{r}_1, \qquad 14.$$

where the index α denotes the x, y, and z components of the vector. It is this quantity μ_{α}^{LK} that determines the strength of electric dipole-allowed electronic transitions between states L and K according to the dipole approximation. This approximation is reasonable when the wavelength of light is much greater than molecular dimensions.

Similarly, if we assume that the donor and acceptor electronic transitions are electric dipole-allowed, and the condition $|\mathbf{r}_1 - \mathbf{r}_2| \gg$ the spatial extent of D and A is satisfied, then Equation 13 can be written in terms of transition multipoles (dipole, quadrupole, etc.) and a corresponding power series in $1/R$, where R is the center-to-center separation of the molecules. Förster was the first to propose a connection between electronic spectra and the electronic coupling based on these arguments, so this is the approximation normally used in conjunction with Förster theory. A multipolar expansion of the Coulombic interaction beyond the dipole-dipole level would seem to be useful for atomic systems, however, as pointed out by London (101) with respect to van der Waals forces:

> . . . it is clear that even the dipole terms of this power series must turn out to be quite inappropriate if one has to consider oscillators of some length extended over a large region of a chain molecule. Another molecule would interact chiefly with one end of such a long virtual oscillator, and this situation would be completely distorted if one were to represent the oscillator by a decomposition into point-form multipoles, all located in the center of the molecule. It would obviously be much more appropriate in this case to represent each oscillator by

> several distinct poles, “monopoles,” of different sign, suitably located in the molecule, thus directly taking account of the actual extension of the oscillator in question.

The conclusion is that the shape of molecules determines the essential shape of the transition densities, as illustrated in Figure 3. When the separation of the donor and acceptor molecules is comparable to their physical sizes, then the topology of the transition densities cannot be ignored (100). It is only when the two molecules are sufficiently far apart that all the points of interaction between the transition densities are similar that it is useful to calculate the interaction from multipole moments of the transition densities and one average donor-acceptor separation. A useful rule of thumb is to check whether the value of R is insensitive to the exact positions on the donor and acceptor molecules that are deemed to be the

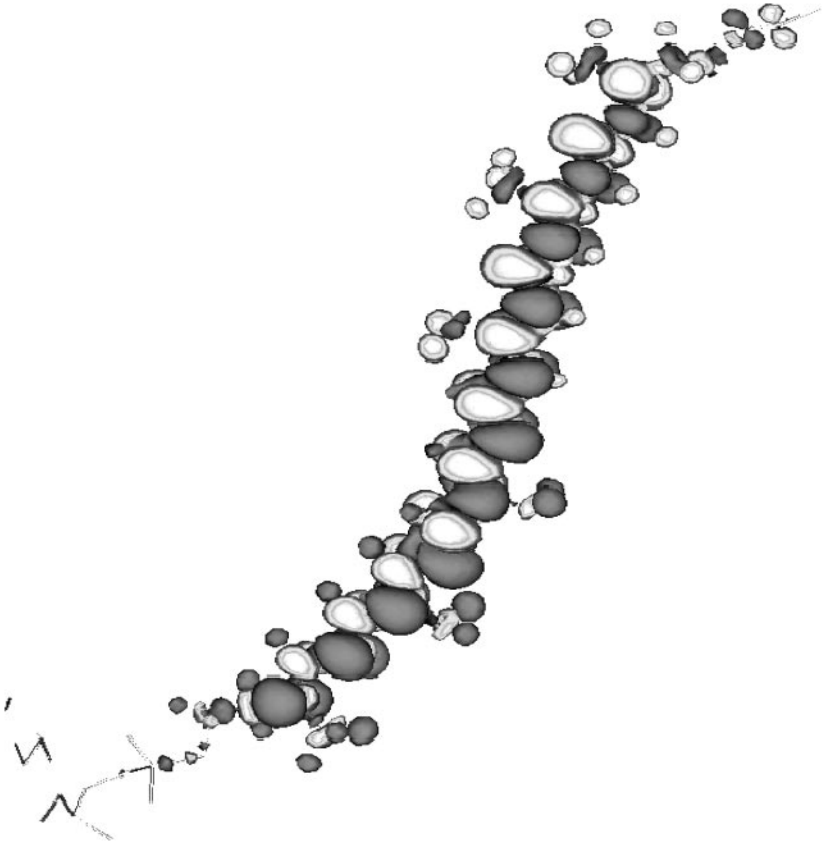

Figure 3 Plot of a transition density calculated for a rhodopin glucoside carotenoid from the peripheral light harvesting complex LH2 of *Rhodopseudomonas acidophila*. The molecule is about 25 Å long.

molecular centers. This will indicate whether a multipolar expansion of the interaction potential provides a useful route to evaluation of Equation 13. Otherwise a more sophisticated approach for evaluating Equation 13 is required. Czikklely et al. (102) formulated an extended dipole model to account for coupling in dye aggregates, which was based on an approximate treatment of the wavefunctions. Recently Krueger et al. (100) developed the transition density cube (TDC) method, which takes advantage of modern quantum chemical calculations of excited-state wavefunctions to obtain the transition densities of Equation 12.

We conclude that, when the donor and acceptor molecules are closely proximate relative to molecular dimensions, then the analogy between synergistic absorption and emission processes (coupled dipoles) and the V^{Coul} interaction breaks down. We now need to think about V^{Coul} in terms of "local interactions" between the donor and acceptor transition densities. When donor and acceptor molecules are large compared with their center-to-center separation, there is a distinct and important difference between averaging over wavefunctions, then coupling them (Equation 15) and averaging over the coupling between wavefunctions (Equation 16). In the former case we retrieve the dipole-dipole (or multipole-multipole) interaction,

$$V^{\text{dd}} = \frac{\kappa}{4\pi\varepsilon_0}\left|\sum_i q_i\vec{r}_i\right|\left|\sum_j q_j\vec{r}_j\right| \Big/ R^3, \qquad 15.$$

for discrete charges q_i at position r_i on donor molecule D and charges q_j at position r_j on acceptor A. $r_{ij} = r_i - r_j$, R is the center-to-center separation between D and A, and κ is the orientation factor between transition moments $\vec{\mu}_{\text{D}} = \sum_i q_i r_i$ and $\vec{\mu}_{\text{A}} = \sum_j q_j r_j$. In the latter case we have

$$V^{\text{Coul}} = \frac{1}{4\pi\varepsilon_0}\sum_{i,j} q_i q_j / r_{ij}. \qquad 16.$$

In the transition density cube (TDC) method (100), the coupling according to Equation 13 is calculated by discretizing the transition densities,

$$\tilde{P}^{M}_{KL}(x, y, z) = V_\delta \int_{z}^{z+\delta_z}\int_{y}^{y+\delta_y}\int_{x}^{x+\delta_x} P^{M}_{KL}(\mathbf{r}_1), \qquad 17.$$

where the δ_α denote the grid size of the transition density cube and $V_\delta = \delta_x\delta_y\delta_z$ is the element volume. The integration in Equation 13 is then converted to a summation, as in Equation 16. In the TDC method, the donor and acceptor transition densities are each represented in a 3D grid. Charge density in each cell of the donor q_i is coupled with the charge density in each cell of the acceptor q_j via Equation 16. Thus, the donor-acceptor interaction topology is accounted for at a fine level of detail.

In recent work, transition densities have been calculated from semiempirical wavefunctions, using for example INDO/S-CI methods (103–104; X.J. Jordanides, G.D. Scholes, W.A. Shapley, J.R. Reimers, G.R. Fleming, unpublished manuscript). This approach has the advantage that the parametrization intrinsic to semiempirical methods leads to better estimations of transition moment magnitudes, and hence transition densities that are better suited for reliable Coulombic coupling calculations, without needing to devise some kind of scaling strategy (100). The transition densities from INDO/S-CI are localized at molecular centers according to a distributed multipole expansion (X.J. Jordanides, G.D. Scholes, W.A. Shapley, J.R. Reimers, G.R. Fleming, unpublished manuscript),

$$P_{KL}^{M}(i|\mathbf{r}_1) \approx q_i \delta(\mathbf{r}_i - \mathbf{r}_1) + \vec{\mu}_i \cdot \nabla \delta(\mathbf{r}_i - \mathbf{r}_1), \qquad 18.$$

where q_i is the transition density monopole at atomic center i, and $\vec{\mu}_i$ is the corresponding transition dipole vector. The coupling is given by

$$V^{\mathrm{Coul}} \cong \frac{1}{4\pi\varepsilon_0} \sum_{i,j} \left(\frac{q_i q_j}{r_{ij}} + \frac{q_i [\vec{\mu}_j \cdot \hat{r}_{ij}]}{r_{ij}^2} - \frac{[\vec{\mu}_i \cdot \hat{r}_{ij}] q_j}{r_{ij}^2} + \frac{\vec{\mu}_i \cdot \vec{\mu}_j - 3[\vec{\mu}_j \cdot \hat{r}_{ij}][\vec{\mu}_i \cdot \hat{r}_{ij}]}{r_{ij}^3} \right). \qquad 19.$$

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Superexchange-Mediated Coupling

Electronic coupling between donor and acceptor can be mediated by intervening bonds or chromophores that act as virtual bridging states. This was suggested by Robinson and coworkers (106, 107), who sought to explain the rates of triplet-triplet energy transfer among guest molecules in aromatic crystals at liquid helium temperature. They suggested that the long-range energy migration between the guest molecules involved indirect electronic coupling through virtual states of the host. The D to A electronic coupling mediated through N identical intervening host molecules B has the form (106, 108–110)

$$V^{\mathrm{tb}} \approx V_{\mathrm{DB}} (V_{\mathrm{BB'}})^{N-1} V_{\mathrm{B'A}} / (-\Delta E)^N, \qquad 20.$$

where V_{DB} and $V_{\mathrm{B'A}}$ are the electronic couplings connecting the nearest bridge molecule to the donor and acceptor respectively, and $V_{\mathrm{BB'}}$ is the electronic coupling between adjacent bridge units. It is evident that the superexchange-mediated, or "through-bond," coupling V^{tb} depends critically on the energy difference between the donor absorption and the bridge absorption, ΔE. The energy gap dependence for singlet-singlet superexchange-mediated RET has been explored in recent work by Kilså et al. (111). The first observation of connecting sigma bonds promoting triplet-triplet RET in a supramolecular donor-bridge-acceptor system was reported by Closs and coworkers (112). More recent studies have examined evidence for the role of through-bond interactions in singlet-singlet RET (111, 113–118). Superexchange-mediated triplet-triplet RET is discussed below.

A general framework for describing superexchange coupling for energy transfer can be based on generating effective donor and acceptor wavefunctions that include mixing with bridge configurations (119). Thus, the Hamiltonian for each donor and acceptor (denoted M) is written as (120) $H = H_M + H_P + H'$ where the bridge (or "perturber") is labelled P, and H' is the interaction term that includes Coulombic interactions, spin-orbit terms, and charge transfer (CT) configurations (i.e., the possibility of significant overlap between the M and P wavefunctions). Hence, we write our molecule-perturber pair ground- and excited-state wavefunctions as (120)

$$\Phi^{00} = \phi_M^0 \phi_P^0, \tag{21.}$$

$$\Phi^{m0} = N\left(\phi_M^m \phi_P^0 + \lambda \phi_M^+ \phi_P^- + \mu \phi_M^- \phi_P^+ + \sum_p \eta_p \phi_M^0 \phi_P^p + \ldots\right), \tag{22.}$$

where Φ^{mp} denotes state m of the molecule and state p of the perturber, the λ, μ, and η are mixing coefficients described below, and N is the normalization constant that ensures $\langle \Phi^{m0} | \Phi^{m0} \rangle = 1$ ($N \approx 1$ for weak perturbations). The orbital overlap-mediated superexchange interactions are thus promoted by interactions that, in a perturbation representation, would look like $D^*PA \rightarrow D^-P^+A \rightarrow DP^*A \rightarrow DP^+A^- \rightarrow DPA^*$, etc.

It is usually thought that orbital overlap-dependent interactions are most significantly mediated through-bond. However, owing to their generally established significance, it is also possible that Coulombic interactions might be mediated through-bond. A mechanism by which Coulombic coupling can be effected by an intervening bridge system is analogous to the intensity enhancement of electronic transitions by a proximate "perturber" molecule described by Robinson (120). It can be shown that such perturbations would not significantly affect the energy of the $\Phi^{m0} \leftarrow \Phi^{00}$ transition. However, the electronic transition density can be significantly perturbed, which in turn perturbs the matrix element for energy transfer from D to A. This is signalled by a perturbation of the dipole transition moment for the $m0 \leftarrow 00$ transition of the MP pair,

$$\vec{\mu}_{m0;00} \approx \langle \Phi^{m0} | e\vec{r} | \Phi^{00} \rangle, \tag{23.}$$

which can be written as

$$\vec{\mu}_{m0;00} \approx \vec{\mu}_{m0}^{M} + \lambda \vec{\mu}_{+-;00} + \mu \vec{\mu}_{-+;00} + \sum_p \eta_p \vec{\mu}_{p0}^{P}, \tag{24.}$$

where monomer transition moments are indicated by superscripts M or P, the mixing coefficients λ and μ have been described in References 92 and 93, and the η_p are given by Robinson [terms X and XI of equation 8 of Reference 120]. Approximate expressions for these coefficients are

$$\lambda \approx -\beta_{ET}/A_{ET}, \tag{25.}$$

$$\mu \approx -\beta_{HT}/A_{HT}, \tag{26.}$$

$$\eta_p \approx -\frac{V_{0p;m0}}{A_{0p;m0}} + \sum_{n,q} \frac{V_{0p;nq} V_{nq;m0}}{A_{0p;m0} A_{nq;m0}}, \tag{27.}$$

where β_{ET} is the electron transfer matrix element between M and P, β_{HT} is the corresponding hole transfer matrix element, and A_{ET} and A_{HT} are the energy gaps between the charge-separated and locally excited configurations. The $V_{0p;m0}$, etc. are couplings between electronic excited states of the molecule and perturber, which usually dominated by the Coulombic interaction (i.e., $V_{0p;m0} \approx V^{\mathrm{Coul}}$).

Triplet-Triplet Electronic Coupling

Triplet-triplet (T-T) RET is overall a spin-allowed process; spin is conserved between the initial state $^3(^3\mathrm{D}^{*1}\mathrm{A})$ and the final state $^3(^1\mathrm{D}^3\mathrm{A}^*)$. It is known (91, 94) that T-T RET cannot be mediated by the Coulombic interaction because it is spin-forbidden. A Coulombic interaction can, in principle, promote T-T RET via spin-orbit coupling terms in the Hamiltonian. However, by considering a first-order perturbation treatment of singlet-triplet mixing (121), one can easily estimate that spin-orbit coupling–mediated Coulombic coupling would usually be $\sim 10^{-6} \times V^{\mathrm{Coul}}$, where V^{Coul} is the Coulombic interaction between the perturbing singlet states of donor and acceptor. Indeed, the insignificance of spin-orbit coupling–mediated T-T RET was demonstrated by Ermolaev (122), who investigated the quenching of benzophenone phosphorescence by naphthalene and its haloderivatives. The T-T RET probability was found to be independent of acceptor $S_0 \rightarrow T_1$ oscillator strength.

It is now well established that T-T RET is promoted by interactions that depend on the degree of orbital overlap between donor and acceptor (91, 92, 123, 124). The T-T coupling is given by the approximate expression

$$V^{\mathrm{T-T}} \approx (2\beta_{\mathrm{ET}}\beta_{\mathrm{HT}})\,/^3A - Z, \qquad 28.$$

where β_{ET} is the electron transfer matrix element between donor and acceptor, β_{HT} is the corresponding hole transfer matrix element, ^3A is the energy gap between the charge-separated ($\mathrm{D}^+\mathrm{A}^-$) and locally excited ($\mathrm{D}^*\mathrm{A}$) configurations, and Z is the two-electron exchange integral. Involvement of these charge-separated states in the mediation of orbital overlap-dependent interactions mediated through-bond has been suggested by studies of superradiant emission and polarizability of a series of rigidly linked naphthalene dimers (115).

Assuming HOMO → LUMO one-electron excitations for simplicity of notation, and writing the donor HOMO and LUMO as linear combinations of atomic orbitals in the usual way, $\psi_{\mathrm{HOMO}} = \Sigma_i\, c_i\phi_i$ and $\psi_{\mathrm{LUMO}} = \Sigma_j\, c_j\phi_j$ (similarly for the acceptor using subscripts r and s). β_{ET} and β_{HT} are given by the bond integrals

$$\beta_{\mathrm{ET}} = \sum_i \sum_r c_i c_r \left(h_{ir} - S_{ir} h_{ir}\right), \qquad 29a.$$

$$\beta_{\mathrm{HT}} = \sum_j \sum_s c_j c_s \left(h_{js} - S_{js} h_{js}\right). \qquad 29b.$$

Here the h_{pq} are screened one-electron integrals (125), $h_{pq} \approx \langle \phi_q\, |h|\, \phi_p \rangle + \sum_n 2(pq|t_n t_n) - (pt_n|qt_n)$, where $\{t_n\}$ are the set of doubly occupied core orbitals on the molecule, and S_{pq} are overlap integrals. The Dexter exchange integral is

$$Z = \sum_{i,j} \sum_{r,s} c_i c_j c_r c_s \,(ir|js). \tag{30.}$$

Each of the β_{ET} and β_{HT} are exponentially attenuated with distance; thus overall $V^{\text{T-T}}$ diminishes exponentially with donor-acceptor separation, and can often be modelled according to $V^{\text{T-T}} \approx A \exp(-2\alpha R)$, where R is the center-to-center separation of the overlapping orbitals. Typically α seems to be in the range 1.2 to 2.0 Å^{-1} for through-space coupling (126). However, this interaction is highly sensitive to molecular shape, size, and orientation, as evinced by the dependence on the atomic orbital coefficients and interactions. At separations of less than approximately 6 Å the first term in Equation 28 should dominate $V^{\text{T-T}}$, whereas at greater separations, or for heavy atoms, the exchange term should be most significant.

Through-bond coupling ameliorates the distance-dependence by reducing α (126). Usually the distance-dependence of experimentally measured through-bond triplet-triplet energy transfer rates is characterized according to $k = A' \exp(-\beta R)$. The attenuation factor β can take values from 1.33 Å^{-1}, for saturated hydrocarbon bridges (127), to 0.17 Å^{-1} for polyalkynes (128). Recently Harriman et al. (129) reported an attenuation factor of 0.11 Å^{-1} for polyacetylene/phenylene bridges. Andréasson et al. (130) demonstrated that through-bond T-T RET occurs with high efficiency through conjugated bridges, but not through saturated bridges. Polynorbornyl bridges seem to be a special case of saturated bridge optimized for through-bond coupling (110, 113, 114, 127). Klán & Wagner (131) showed that T-T RET is mediated through space when donor and acceptor are connected by flexible bridges.

Other Spin States

Usually RET is discussed only in terms of singlet-singlet or triplet-triplet energy transfer. However, RET between states of other spins is possible in some cases. Singlet-doublet RET can occur in the photosynthetic reaction center of purple bacteria when the special pair is oxidized (X.J. Jordanides, G.D. Scholes, W.A. Shapley, J.R. Reimers, G.R. Fleming, unpublished manuscript). This process occurs with a similar mechanism to singlet-singlet RET; however, it is more challenging to calculate the excited states of the dimeric doublet state acceptor. Various cases of spin-selection rules for RET are discussed by Naqvi (132). We note that, when spin-allowed, the Coulombic interaction can be written in terms of transition densities; then prefactors such as $(1/2)^{1/2}$ for singlet-doublet RET that are necessary in Naqvi's notation do not need to be added. These prefactors are accounted for already in the transition densities.

SPECTRAL OVERLAP AND ENSEMBLE AVERAGES

By definition, the line shapes $f^{\mathrm{hom}}(\varepsilon)$ and $a^{\mathrm{hom}}(\varepsilon)$ are identical for all donors and acceptors respectively. However, in many types of condensed phase media (e.g., glasses, crystals, proteins, surfaces), each of the donors and acceptors lies in a different local environment, which leads to a static offset of the excitation energy relative to the average that persists longer than the timescale for RET. In such a case, the measured donor emission and acceptor absorption spectra will not be representative of $f^{\text{hom}}(\varepsilon)$ and $a^{\text{hom}}(\varepsilon)$. When such "inhomogeneous" contributions to the line broadening become significant, Förster theory cannot be used in an unmodified form (133–138). What we observe is a distribution of rates that depends on the static disorder in the donor-emission and acceptor-absorption spectra.

If there is just a single donor-acceptor pair, then we must ensemble average the nuclear spectral overlap. For example, if the inhomogeneous line broadening present in the donor-emission spectrum $F(\varepsilon)$ and acceptor-absorption spectrum $A(\varepsilon)$ is described by a function $G(\varepsilon_m^0, \varepsilon_m)$, which provides a distribution (often taken to be Gaussian) of static offsets ε_m to the mean excitation energy ε_m^0, then $F(\varepsilon)$ and $A(\varepsilon)$ are given by Equations 31a and 31b. These donor-emission and acceptor-absorption spectra are both, individually, ensemble average quantities and so are not related in a simple way to the spectral overlap, Equation 31c, because $J(\varepsilon) \neq F(\varepsilon)A(\varepsilon)$.

$$F(\varepsilon) = \int f^{\text{hom}}(\varepsilon_d - \varepsilon)G\left(\varepsilon_d^0 - \varepsilon_d\right) \mathrm{d}\varepsilon_d, \qquad \text{31a.}$$

$$A(\varepsilon) = \int a^{\text{hom}}(\varepsilon_a - \varepsilon)G\left(\varepsilon_a^0 - \varepsilon_a\right) \mathrm{d}\varepsilon_a, \qquad \text{31b.}$$

$$J(\varepsilon) = \iint f^{\text{hom}}(\varepsilon_d - \varepsilon)G\left(\varepsilon_d^0 - \varepsilon_d\right)a^{\text{hom}}(\varepsilon_a - \varepsilon)G\left(\varepsilon_a^0 - \varepsilon_a\right) \mathrm{d}\varepsilon_d \, \mathrm{d}\varepsilon_a. \qquad \text{31c.}$$

Energy migration among a number of chromophores with inhomogeneously broadened spectra can be modelled using a Pauli master equation approach (137–145) as long as the excitation is localized as it hops from molecule to molecule. In such a model, the probability of finding the excitation on site i in the aggregate $P_i(t)$ is determined by solving the coupled differential equations,

$$\frac{\mathrm{d}P_i(t)}{\mathrm{d}t} = \sum_j \left[k_{ij}P_j(t) - \left(k_{ji} + \tau_i^{-1}\right)P_i(t)\right], \qquad \text{32.}$$

where the excited-state lifetime is τ_i and uphill RET rates can be calculated via detailed balance, $k_{ji} = k_{ij}\exp(-\Delta E_{ij}/kT)$, with ΔE_{ij} equal to the energy difference between donor- and acceptor-absorption maxima. Alternatively, k_{ij} and k_{ji} can be calculated independently according to the Förster equation. The site-site rates are calculated according to a spectral overlap involving homogeneous line shapes. A Monte Carlo sampling procedure is used to account for disorder, typically with $\sim$2000 iterations. At each iteration, the site energy offsets for each molecule in the aggregate δ_i are chosen randomly from a Gaussian distribution of standard deviation σ, $w(\delta_i) = \exp(-\delta_i^2/2\sigma^2)/(\sigma\sqrt{2\pi})$. A Gaussian distribution is in accord with the central limit theorem. It is useful to note that the standard deviation is related to the full width half maximum (FWHM) of the distribution by $\Delta = \sigma(8\ln 2)^{1/2}$. If the electronic coupling varies from aggregate to aggregate because, for example, the molecules are oriented differently, then this can also be included.

The Pauli master equation approach to calculating RET rates is particularly useful for simulating time-resolved anisotropy decay that results from RET within aggregates of molecules (143). In that case, the orientation of the aggregate in the laboratory frame is also randomly selected at each Monte Carlo iteration in order to account for the rotational averaging properly. The method has proven to be useful for disordered photosynthetic aggregates, but note the limitations of this model described by Scholes & Fleming (133). The implications and treatment of disorder in aggregated donor or acceptor assemblies are discussed in a later section. Disorder in the energies of the bridge states has been considered by Yeow & Ghiggino (146).

A further case of interest has been described by Yang & Fleming (147) and observed by Agarwal et al. (148). They noticed that site energies within each aggregate can be correlated, such that the mean site energy of each aggregate is offset from an overall average, as shown in Figure 4. The standard deviation of static offsets within each aggregate is σ, whereas the standard deviation of the distribution of mean offsets in an ensemble of aggregates is Σ. It is important to dissect the total width of the static disorder $\Delta = (\sigma^2 + \Sigma^2)^{1/2}$ into these contributions in order to calculate correctly the RET dynamics. Within each ensemble the site-site rates k_{ij} are determined only by σ.

DIELECTRIC PROPERTIES OF THE MEDIUM

In a dielectric medium, such as solvent, the Coulombic interactions between donor and acceptor are screened. If one assumes the dipole approximation for V, that donor and acceptor are well separated in a nondispersive, isotropic host medium, and that local field corrections are negligible, then the coupling is modulated by a factor $D = n^{-2}$, where $n = \varepsilon_r^{1/2}$is the refractive index of the medium at optical frequencies (149). Thus, V^{Coul} (screened) $= D \times V^{\mathrm{Coul}}$. This screening is the origin of the $1/n^4$ term in the Förster equation (10, 83), and it can have a substantial influence on the rate of RET. There has been some confusion about this screening parameter that has been nicely clarified by Knox & van Amerongen (83). An important point is that the $1/n^4$ factor in Förster's equation, Equation 4, arises from dielectric screening of the dipole-dipole coupling, and it has nothing to do with the relationship of the theory to spectra.

An unresolved question is how to treat screening effects when the donor and acceptor are closely proximate—that is, closer than a few molecular diameters. This is an especially salient point now that calculation of couplings from the interaction of transition densities is becoming more common. One of the most detailed investigations of medium effects in RET is that reported by Dow (149). Dow showed that the screening of the Coulombic interaction can be described according to

$$V^{\mathrm{Coul}}(\text{screened}) = \int \mathrm{d}^3\mathbf{r}\mathrm{d}^3\mathbf{r}_1\mathrm{d}^3\mathbf{r}_2 \frac{\mathrm{Re}\varepsilon_L^{-1}(\mathbf{r}, E)P_{0m}^D(\mathbf{r}_1)P_{n0}^A(\mathbf{r}_2)}{|\mathbf{r} + \mathbf{r}_1 - \mathbf{r}_2|}, \qquad 33.$$

where $\varepsilon_L^{-1}(\mathbf{r}, E)$ is the longitudinal dielectric function, and the transition densities of donor and acceptor are defined in Equation 12. Local field effects are

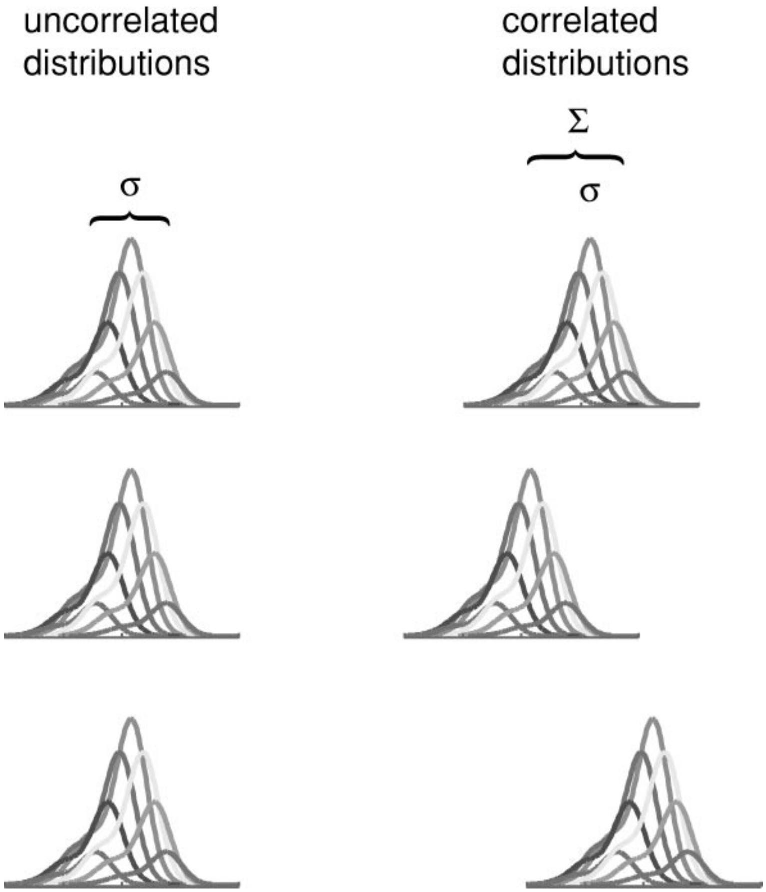

Figure 4 Illustration of inhomogeneously broadened absorption spectra of molecular aggregates where the disorder in molecule-site energies is uncorrelated to the aggregate (*left*) or correlated to the aggregate (*right*). In the second case, there is a second distribution of disorder of the mean excitation energy of the molecules in each aggregate.

neglected in this equation. At large donor-acceptor separations R, the Förster result is obtained by putting $\varepsilon_L^{-1}(\mathbf{r}, E) = \varepsilon^{-1}(E)\delta(\mathbf{r})$. However, a key effect that will become significant at close donor-acceptor separations is spatial dispersion arising from the **r**-dependence of $\varepsilon_L^{-1}(\mathbf{r}, E)$. Dow also postulated that virtual excitons might be important at these close separations. Craig & Thirunamachandran (150) considered virtual excitons in a microscopic theory based on the molecular QED framework for the influence of the medium on the rate of RET. In this case, the rate of RET may be either increased or decreased at close donor-acceptor separations.

Hsu et al. (151) reported a quantum mechanical model for the medium effects based on density function theory for the interaction of donor and acceptor transition densities with solvent. That theory can be employed for arbitrary charge distributions and separations. The first limiting case examined by Hsu et al. (151)—that of a well-separated donor-acceptor pair—recovers Equation 33. The relevant limiting case is their Equation 27 with $l = 1$, which yields a screening factor of $D = 1/\varepsilon(\omega) = 1/n^2$. That is because the multipole expansion in Reference 151 is taken of each transition density, as in our Equation 18, rather than in the coupling, so that the terms with $l > 1$ pertain to the charge-dipole, dipole-dipole, etc. terms in Equation 19, not to the usual multipole expansion about the intermolecular separation.

The second limiting case reported by Hsu et al. (151) considers two closely separated molecules. Then it makes sense to exclude the dielectric medium from a cavity that encloses both molecules. In that case, the medium can actually enhance the coupling between the molecules for certain orientations if the molecules are asymmetrically distributed in the cavity. This can happen owing to the formation of "mirror" transition dipoles in the dielectric medium. Such a phenomenon has not been observed, but is reminiscent of the energy transfer between a molecule and a metal surface (152–154). Tretiak et al. (155) have reported calculations of electronic couplings between chromophores of the peripheral light-harvesting antennae of various purple bacteria wherein the medium is accounted for via a self-consistent reaction field. In that work, a small number of the calculated couplings in the presence of the medium are increased relative to those same couplings in the absence of the dielectric medium.

Recently Juzeliunas & Andrews have reported a detailed many-body description of EET based on the QED formalism (156–158), explicitly based on the dipole approximation. By considering the energy transfer to be mediated by bath polaritons (medium-dressed photons), this theory accounts for the modification of the bare coupling tensor by both screening effects of the medium, as in the discussion above, but additionally includes local field effects. A widely applicable theory is derived, which, in the limit of large donor-acceptor separations (i.e., several molecular diameters), reduces to

$$D = \varepsilon_r^{-1}\,[(\varepsilon_r + 2)/3]^2\,. \qquad 34.$$

Note that this modification of the coupling is different from the usual refractive index-dependence owing to incorporation of local field effects in the theory. Local field effects (159) might increase the effective interactions in highly polarizable media by enhancing the effective transition moments of donor and acceptor.

ELECTRONIC COUPLING AND MOLECULAR EXCITONS

Recently it has emerged that aggregated donor or acceptor molecules behave quantitatively and qualitatively differently than predicted by the Förster equation (Equation 4). Förster-Dexter theory cannot be used in an unmodified form whenever there are interactions among donor or acceptor molecules that perturb the emission or absorption line shapes or dipole strengths. Returning to the concepts raised by Equations 15 and 16 regarding averaging over the Coulombic interaction between two transition densities versus averaging over the transition densities first, then interacting them according to the dipole-dipole approximation, another level of the dipole approximation is evident for molecular aggregates. Now, even if we apply the dipole approximation for pairwise interactions, a significant breakdown of the physical picture arises when the dipole approximation is extended to the donor/acceptor states of an aggregate (160). This is illustrated by some simple examples in Table 1. Information obtained from spectra always reflects the most severe dipole approximation because the wavelength of the probing light is much larger than molecular dimensions, and therefore cannot resolve the details of aggregated donor-acceptor interactions. In general, when donor and/or acceptor molecules act collectively because of the way they are assembled, Förster theory cannot apply, even though the dipole-dipole approximation may work well for calculating pairwise donor-acceptor couplings.

Valkunas and coworkers (161) considered such concepts in the calculation of RET rates between a monomer donor molecule and a large molecular J-aggregate acceptor. They found that, because the donor interacts most significantly with only a small part of the J-aggregate, electronic couplings are not proportional to the oscillator strength of the J-aggregate exciton states. Hence, excitation energy may be readily accepted into exciton states of the J-aggregate that have no oscillator strength in the optical absorption spectrum. Recently, Sumi (162, 163) and

TABLE 1 Simple examples of the electronic coupling[a] between a single donor molecule and an aggregate of acceptors, showing that the distributed dipole method often reveals a very different physical picture than that obtained by the dipole approximation[b] (Förster theory)

Distributed dipoles	Dipole approximation
$\rightarrow \quad [\leftarrow\rightarrow]$ $V = 3.2$	$\rightarrow \quad \odot$ $V = 0$
$\uparrow \quad [\uparrow\uparrow]$ $V = 2.5$	$\uparrow \quad \Big\uparrow$ $V = 1.8$
$\rightarrow \quad [\rightarrow\rightarrow\rightarrow\rightarrow]$ $V = 8.3$	$\rightarrow \quad \longrightarrow$ $V = 5$
$\rightarrow \quad [\rightarrow\rightarrow\leftarrow\leftarrow]$ $V = 5.6$	$\rightarrow \quad \odot$ $V = 0$

[a] The center-to-center spacing between the molecules in the aggregate is 5 Å, and the donor is positioned 20 Å from the center of the aggregate. Transition moments are set equal, and the couplings are in relative units.

[b] The details of the shape and structure of the aggregate, as seen by the donor, are averaged away by the dipole approximation, the aggregate as seen by light of wavelength much larger than the size of the aggregate.

Scholes & Fleming (133, 160, 164) arrived independently at the conclusion that RET in a molecular aggregate proceeds not via molecular units or their collective emission/absorption spectra, but via electronic states. Thus, if there are *m* molecules that together make up the donor and *n* molecules that comprise the acceptor, then the EET dynamics must be determined by $m \times n$ electronic couplings. Owing to the distinct way that each electronic excited state is composed of the molecular wavefunctions, these $m \times n$ couplings will generally differ from one another.

The challenge was to decide how to reformulate the problem in a general manner. Thus we introduced the idea of effective donor and acceptor states. The effective donor states $\{\delta\}$ are generated by interacting the donor molecules $\{\mathrm{d}\}$ in the absence of the acceptors to provide the set of donor molecular exciton states. The same is done for the effective acceptor states $\{\alpha\}$. We then calculate the set of effective electronic couplings between each pair of molecular exciton donor and acceptor states. This concept goes hand in hand with the treatment of multiple electronic states according to their associated multiple spectral overlaps. These ideas are described in the following section. Accounting correctly for the set of effective couplings $\{V_{\delta\alpha}\}$ and their associated spectral overlaps $\{J_{\delta\alpha}\}$ is crucial in order that the theory automatically reduces to the Förster theory limit when electronic couplings among the donors and among the acceptors are insignificant compared with the homogeneous line widths or inhomogeneous broadening.

The breakdown of the dipole approximation at the level of the molecular aggregate is well illustrated by numerical examples. For example, a long-standing problem was understanding the rate of RET between the accessory bacteriochlorophyll pigments and the special pair acceptor in isolated reaction centers from photosynthetic purple bacteria. On the one hand, the problem for Förster theory is that dipole-dipole electronic coupling from the accessory bacteriochlorophyll to the lower, dipole-allowed, exciton state of the special pair produces large results, but spectral overlap to this band is insufficient to account for the observed RET rate. On the other hand, spectral overlap is excellent between accessory bacteriochlorophyll emission and the upper, dipole-forbidden, exciton transition of the special pair, but dipole-dipole electronic coupling produces small results. It is revealed by the generalized Förster theory that in fact the electronic coupling is approximately equal for coupling to either exciton state (164). Satisfactory quantitative predictions of the RET were possible for large temperature ranges and for various species and mutants of the bacteria (164).

Under the assumption of the dipole approximation, the Coulombic coupling scales with the product of the dipole transition moment of the donor and that of the acceptor. We expect that such a relationship should break down when the donor and/or acceptor is a molecular assembly. A useful test is provided by the peripheral antenna system LH2 of photosynthetic purple bacteria. The donor molecule of the B800 ring is approximately monomer-like, and is located ∼18 Å away from the acceptor. The acceptor consists of the 18 bacteriochlorophylls of the B850 ring. We can therefore explore the B800–B850 coupling relative to the transition moment of each corresponding B850 electronic state for each of the 18 B850 acceptor states. Moreover, because each LH2 complex is slightly different spectroscopically, owing

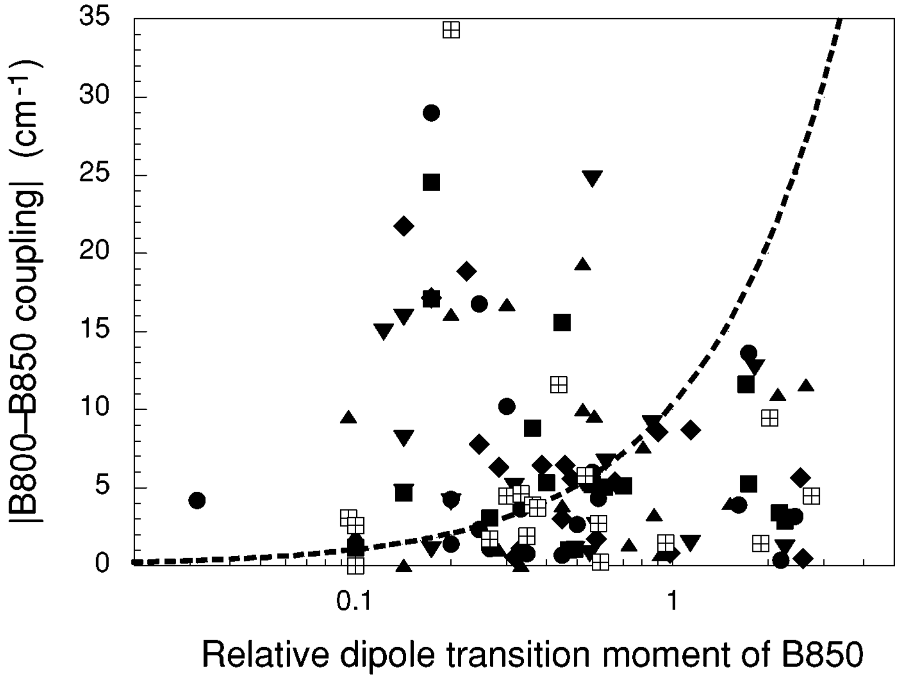

Figure 5 Comparison of the dipole transition moment of the B850 eigenstate to the electronic coupling calculated from B800 to that eigenstate of B850 in a number of statistically disordered LH2 complexes. The dashed line shows the correlation that would be expected if the dipole-dipole model provided any kind of guide to the magnitude of the coupling. Obviously there is no correlation.

to site inhomogeneity (133, 142), we can survey a number of LH2 complexes as well. The results are plotted in Figure 5. If the dipole-dipole approximation were to provide some guide as to the magnitude of the electronic couplings between the B800 donor and the B850 acceptor, then there would be some degree of correlation between the transition moment of each B850 acceptor state and the B800–B850 electronic coupling, according to the dashed line in Figure 5. We find that there is actually no correlation at all between these quantities, indicating for this system that the dipole-dipole approximation provides no useful information about the energy transfer rate or mechanism.

ENERGY TRANSFER IN MOLECULAR ASSEMBLIES

Recently, we have generalized Förster theory (160) in order to calculate rates of energy transfer in disordered molecular aggregates (133, 160, 164). We showed that for an aggregate consisting of *m* donor molecules and *n* acceptor molecules, we can divide the problem into $m \times n$ interactions between a set of effective donor states and a set of effective acceptor states. Each of these interactions provides a distinct energy transfer pathway. The ensemble average rate in disordered systems is calculated by Monte Carlo averaging of the basic rate expression. In the limit that the interactions between all pairs of molecules are very weak, such that the donor and acceptor absorption spectra are unperturbed from those of the monomers, then the energy transfer rate calculated by our theory reduces to a sum of Förster rates.

It is important to realize that the modifed Förster theory for molecular aggregates differs qualitatively from pairwise Förster theory. A quantitative discrepancy can often be obscured by "tweaking" of parameters in the theory, thus forcing Förster theory to fit the problem. It seems that it should be more important to understand the nature of the problem, which was our motivation for developing a flexible, modified Förster theory. In that case, one needs to consider carefully the constitution of donor and acceptor states and how they couple, the associated spectral overlaps, and the ensemble averaging of microscopic properties to give the observed ensemble rate. It thus turns out that considering separately the spectral overlap or the electronic coupling between two states is not very useful. These quantities are associated, so the key quantities that define the mechanism, and rate, of RET in molecular aggregates are the set of products $u_{\delta\alpha} = |V_{\delta\alpha}|^2 J_{\delta\alpha}$ (133, 160).

Under the assumption of weak coupling between donors and acceptors (but not among either donors or acceptors), a general expression for the rate of energy transfer from a donor aggregate to an acceptor aggregate is given by

$$k = \frac{2\pi}{\hbar}\left\langle \int_0^\infty \mathrm{d}\varepsilon \sum_{\delta,\alpha} P_\delta \,|V_{\delta\alpha}\,(\varepsilon_\mathrm{d},\varepsilon_\mathrm{a})|^2\, J_{\delta\alpha}(\varepsilon,\varepsilon_\mathrm{d},\varepsilon_\mathrm{a})\right\rangle_{\varepsilon_\mathrm{d},\varepsilon_\mathrm{a}}, \qquad 35.$$

where $V_{\delta\alpha}$ are the electronic couplings between the effective donor states δ and effective acceptor states α, and ε_d and ε_a represent static offsets from the mean of the individual donor and acceptor excitation energies. It is emphasized that both the couplings and the spectral overlaps depend upon disorder. Each electronic coupling factor is associated with a corresponding spectral overlap factor $J_{\delta\alpha}(\varepsilon,\ \varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$. It is assumed that each $V_{\delta\alpha}(\varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$ does not vary across the energy spectrum of its corresponding $J_{\delta\alpha}(\varepsilon,\ \varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$. P_δ is a normalized Boltzmann weighting factor for the contribution of δ to the thermalized donor state, $P_\delta = \exp\left[(\varepsilon_{\delta=1} - \varepsilon_\delta)/kT\right] / \sum_\delta \exp\left[(\varepsilon_{\delta=1} - \varepsilon_\delta)/kT\right]$. The angle brackets denote that an ensemble average is taken over many aggregate units so as to account for static disorder in the monomer site energies. The spectral overlap between bands δ and α is defined in terms of donor and acceptor densities of states,

$$J_{\delta\alpha}(\varepsilon,\varepsilon_\mathrm{d},\varepsilon_\mathrm{a}) = N_\alpha a_\alpha^{\mathrm{hom}}(\varepsilon,\varepsilon_\mathrm{d},\varepsilon_\mathrm{a}) N_\delta f_\delta^{\mathrm{hom}}(\varepsilon,\varepsilon_\mathrm{d},\varepsilon_\mathrm{a}). \qquad 36.$$

Note that each $J_{\delta\alpha}(\varepsilon,\ \varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$ is associated with a corresponding electronic coupling factor $V_{\delta\alpha}(\varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$ within the ensemble average. The dependence upon disorder is assumed to introduce a static offset of the origin, as is usually assumed (165). The $f_\delta^{\mathrm{hom}}(\varepsilon,\ \varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$ and $a_\alpha^{\mathrm{hom}}(\varepsilon,\ \varepsilon_\mathrm{d},\ \varepsilon_\mathrm{a})$ specify the donor and acceptor densities of states (DOS). These DOS represent the emission (absorption) line shape of the donor (acceptor), calculated without disorder (hence the superscript “hom”) and without dipole strength. N_δ and N_α are area normalization constants such that $1/N_\delta = \int_0^\infty \mathrm{d}\varepsilon\, f_\delta^{\mathrm{hom}}(\varepsilon)$ and $1/N_\alpha = \int_0^\infty \mathrm{d}\varepsilon a_\alpha^{\mathrm{hom}}(\varepsilon)$.

The foundation of this model is the formulation of the effective donor and effective acceptor states for the molecular assembly. In general, we can divide the system into a set of I donor molecules d_i, J acceptor molecules a_j, and, if present, K bridging molecules b_k. The bridging molecules may be involved in mediating superexchange interactions. The donors are those molecules selected by optical excitation; the acceptors are the remaining ground-state chromophores. For simplicity we assume that the overlaps between all these site wavefunctions are small so that $S_{mn} = \delta_{mn}$. The Schrödinger equation for the system is given by the secular equations

$$\sum_{n=1}^{N} (H_{mn} - E\delta_{mn})\lambda_n = 0, \quad m = 1, 2, \ldots N, \tag{37.}$$

where N indexes each of the I, J, and K. Here, and in the ensuing discussion, the dependence of energies and couplings on site energy disorder is assumed implicitly. If we collect and group the donor, acceptor, and bridge units, then separately diagonalize each of these blocks, we can write a partitioned matrix of secular equations in terms of the zeroth-order effective donor δ, acceptor α, and bridge states β,

$$\left[\begin{array}{cc|cc|cc} (H_{\delta\delta}-E)\lambda_\delta & 0 & H_{\delta\alpha}\lambda_\alpha & \cdots & \multicolumn{2}{c}{\text{donor-}} \\ 0 & \ddots & \vdots & \ddots & \multicolumn{2}{c}{\text{bridge}} \\ \hline H_{\alpha\delta}\lambda_\delta & \cdots & (H_{\alpha\alpha}-E)\lambda_\alpha & 0 & \multicolumn{2}{c}{\text{acceptor}} \\ \vdots & \ddots & 0 & \ddots & \multicolumn{2}{c}{\text{-bridge}} \\ \hline \multicolumn{2}{c|}{\text{donor-}} & \multicolumn{2}{c|}{\text{acceptor}} & (H_{\beta\beta}-E)\lambda_\beta & 0 \\ \multicolumn{2}{c|}{\text{bridge}} & \multicolumn{2}{c|}{\text{-bridge}} & 0 & \ddots \end{array}\right] = 0. \tag{38.}$$

The δ and α are the basis for the construction of our theory. When there is no bridge, we immediately obtain the effective couplings as $V_{\delta\alpha} = H_{\delta\alpha}$. When the influence of a bridge needs to be accounted for, the $V_{\delta\alpha}$ can be obtained either by iterative solution of the partitioned secular equations as described by Löwdin (166, 167), or by using the Green’s function and linear algebraic methods reported by Evenson & Karplus (168), or by using the configuration mixing method as employed by Harcourt et al. (92). According to the latter method, the effective coupling is obtained as a sum of mixing coefficient-weighted donor site–acceptor site couplings,

$$V_{\delta\alpha} = \sum_m \sum_n \lambda_{\delta,m}\lambda_{\alpha,n}(H_{nm} - E\delta_{nm}), \tag{39.}$$

where m include the donor sites and the bridge sites, n the acceptor sites and the bridge sites, and H_{nm} the couplings between these sites. The coefficients $\lambda_{\delta,m}$ are those obtained by solving the donor plus bridge eigenvalue problem; the $\lambda_{\alpha,n}$ are obtained by solving the acceptor plus bridge eigenvalue problem.

A model calculation of the transition from collective energy transfer to Förster RET was reported in Reference 169, where a single donor chromophore interacts with a small H-aggregate. This calculation shows how $|V|^2 J(\varepsilon) = \left\langle \sum_{\delta,\alpha} |V_{\delta\alpha}|^2 J_{\delta\alpha}(\varepsilon) \right\rangle$ reveals clearly that the RET is non-Förster–like at center-to-center donor-acceptor separations of 10 Å and 20 Å, but approaches the Förster picture at a separation of 100 Å (Figure 6). Applications of the theory to photosynthetic antenna systems have proven to be particularly illuminating (X.J. Jordanides, G.D. Scholes, W.A.

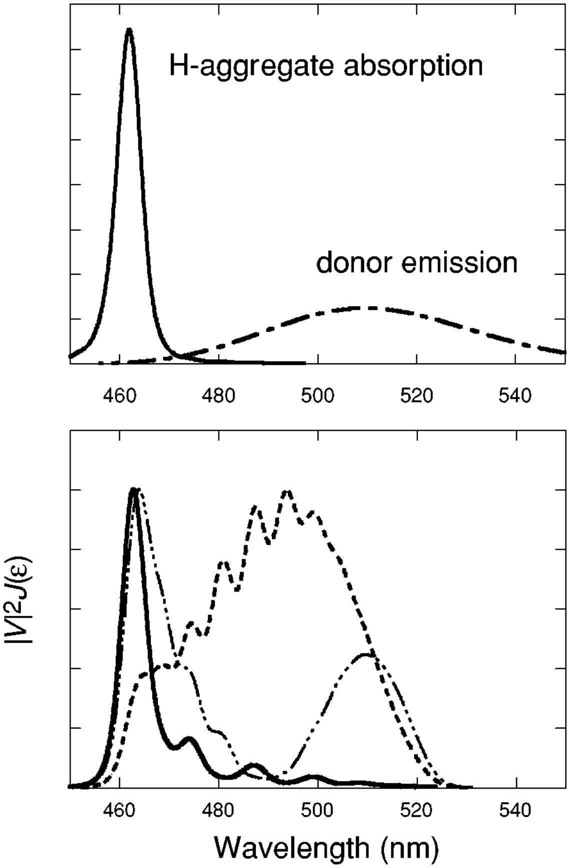

Figure 6 Model donor-emission spectrum (one molecule) and acceptor-absorption spectrum (a simple linear H-aggregate) (*top*). Note that the density of acceptor states spans the donor emission. The calculated $|V|^2 J(\varepsilon)$ is plotted (*bottom*) for donor-acceptor separations of 10 Å (*dashed curve*), 20 Å (*dash-dotted curve*), and 100 Å (*solid line*). It is evident that $|V|^2 J(\varepsilon)$ tends to the Förster spectral overlap only at large separations relative to the size of the aggregate.

Shapley, J.R. Reimers, G.R. Fleming, unpublished manuscript; 133, 164). That work is reviewed elsewhere (G.D. Scholes, G.R. Fleming, unpublished manuscript).

SINGLE-MOLECULE STUDIES OF RET

Recent advances in single-molecule fluorescence spectroscopy have led to the realization of single-molecule RET experiments (170a–170e, 176). In two-channel single-molecule RET experiments, the quenched donor emission and sensitized acceptor fluorescence are monitored simultaneously, enabling the mapping of donor-acceptor correlations (170b). An exciting application of single-molecule RET has been to study structural changes, such as folding, of single proteins. An advantage of such single-molecule studies over ensemble measurements is that individual folding processes, which would otherwise be obscured as subpopulations of an ensemble, can be studied and compared. Histograms of RET efficiencies can be plotted to compare distributions of donor-acceptor separations that are sampled during the donor lifetime (170b, 170d). An intriguing possibility for the future will be to combine single-molecule RET with the technique of single-molecule fluorescence polarization, developed by Goldman and coworkers (170f). In combination, it would then be possible to monitor the time-evolution of the orientation factor κ in addition to donor-acceptor separation.

RECENT DEVELOPMENTS

Albrecht Ferro & Jonas (171) have investigated the initial anisotropy of a coherently excited chromophore pair. They have shown that in pump-probe measurements, ground-state bleaching and excited-state absorption contributions must be considered in addition to stimulated emission in order to recover the uncoupled chromophore limit. This work helps to resolve discrepancies between initial anisotropies in molecular aggregates measured by fluorescence up-conversion and transient absorption.

Singlet-singlet energy transfer in a series of coupled chromophores has been studied by Speiser and coworkers (172). They systematically compared energy transfer in the bichromophores as a function of chain length, in stretched and unstretched polymer films. Lokan et al. (173) have reported an observation of remarkably efficient RET between dimethoxynaphthalene and a dione occurring through-bond over a distance of 12 Å. This work suggests that small chemical and structural changes can have a significant impact on RET rates and efficiencies. Adachi et al. (174) describe the use of RET to harvest both singlet and triplet excitations, thus increasing the efficiency of electroluminescent light emission. A recent review of FRET applications to protein-DNA complexes has been reported by Hillisch et al. (175). Kang et al. (177) show how RET can increase the overall quantum yield of a donor-acceptor pair by competing with nonradiative deactivation of a long-lived donor-excited state. Two recent reports (178, 179) demonstrate that RET rates can be influenced by photon confinement in an optical microcavity.

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