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Photophysics and Mechanisms of Intramolecular Electronic Energy Transfer in Bichromophoric Molecular Systems: Solution and Supersonic Jet Studies

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Contents

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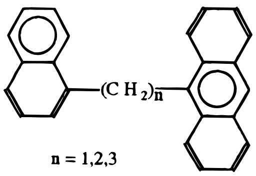
I. Introduction

Interaction between excited and ground states of two molecular chromophores has been the subject of considerable interest.[1] It is manifested in chemical reactions,[1] in complex formation,[2,3] and in photophysical processes such as electronic energy transfer (EET).[4] These processes play a key role in chemistry, biology, and physics. EET processes occur at distances ranging from 1 Å to more than 50 Å, and on time scales from femtoseconds to milliseconds. EET can be observed in the solid state, on surfaces, in solution, in the gas phase, and in isolated molecular systems in supersonic jet expansions. Until recent years most studies involved intermolecular EET (inter-EET) long-range processes between donor (D) and acceptor (A) chromophores. While these studies are well documented and summarized by numerous reviews,[5−9] some basic problems in molecular photophysics which involve short-range interactions manifested in intramolecular EET (intra-EET) and intramolecular electron transfer (intra-ELT) processes are still the subject of current investigations. Intra-EET can occur whenever two separated chromophores are incorporated in a single molecule. In such cases, control of the spatial relationship between donor and acceptor groups may exist without the randomness characteristic of intermolecular interactions. Furthermore, intra-EET can be observed in rigid or viscous media where encounters between separated molecules leading to short-range EET are not possible.

The first investigations of short-range intra-EET were reported by Weber[10−12] and by Schnepp and Levy.[13] Schnepp and Levy observed anthracene fluorescence irrespective of excitation wavelength in compounds **I** containing naphthalene and anthracene moieties joined by a varying number of CH_2 groups.

I



The quantum yield was independent of the number of methylene groups separating the two chromophores. Later, many other groups examined other bichromophoric systems.[14−24] In some cases, the donor and acceptor were attached to a rigid system so that their spatial relationship was known to a considerable degree (unfortunately, geometrical variations in such rigid systems were not feasible). The occurrence of intra-EET could be readily evaluated from knowledge of excitation and emission spectra of each moiety alone and comparison with the corresponding spectra of the separated chromophore molecules.

In all these cases, complete quenching of donor fluorescence was observed with concomitant emission *solely* from the acceptor. This was true even for donor chromophores with high fluorescence quantum yields. Residual donor emission together with the appearance of acceptor fluorescence implies that intra-EET rate is similar to that of donor decay by fluorescence or through other channels. This can be achieved in specially designed bichromophoric molecules which allow us to pursue *systematic* studies of the *mechanism* of intra-ET, as discussed in the present Review.

The first observation of dual fluorescence decay as a result of intra-EET processes, allowing mechanistic study of this phenomenon, was made with 1,8-(6′,7′-dioxododecamethylene)phenanthrene[25] (**II**, **Phenan-5,5**). Later, other bichromophoric molecular systems, such as compounds **III** and **IV** were studied in solution and in supersonic jets in order to elucidate the mechanisms of intra-EET and intra-ELT.[26−40]

EET has significant implications in biological systems,[41−43] energy transfer dye laser (ETDL) operation,[44−50] in the realization of molecular electronic devices,[51−53] in photodynamic therapy,[54] in light harvesting,[55,56] in photochemical synthesis,[57,58] in developing optical fiber sensors for pH determination in physiological systems,[59] in the determination of the conformation of macromolecules,[60−64] and in the elucidation of the photophysical behavior of large molecules.[65]

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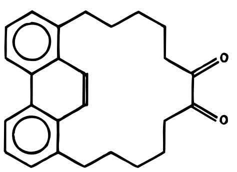
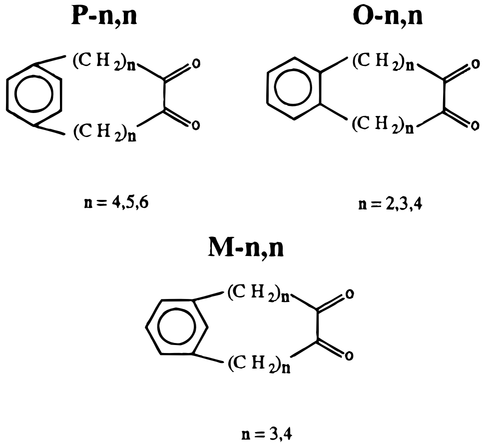
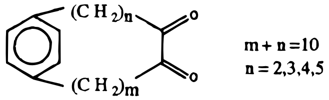


III



IV, P-n,m



The purpose of this Review is to discuss progress made in understanding the *photophysics* and the *mechanism* of intra-EET within the general framework of radiative and nonradiative processes in molecules. Therefore, while this Review is comprehensive in the coverage of the theory and experimental studies of intra-EET, mostly involving singlet—singlet EET, the photochemical aspects of these processes are discussed in relation with the mechanism of intra-EET and the implications for synthetic organic photochemistry are only briefly reviewed. The Review is organized as follows. Section II gives the theoretical background to EET, reflecting the progress made in understanding the mechanism of the process and focusing on intra-EET in specially designed bichromophoric molecular systems. Section III discusses mechanistic studies of long-range and short-range intra-EET in solution mainly involving singlet—singlet EET, complemented by recent extension of these investigations to isolated bichromophoric molecular systems in supersonic molecular beams, as addressed in section IV. Complementary photochemical aspects of intra-EET are surveyed in section V.

II. Theoretical Studies of Electronic Energy Transfer in Molecules

A. Radiationless Transitions and Electronic Energy-Transfer Processes

Inter-EET and intra-EET processes are special cases of nonradiative decay of excited molecular systems.[66] The basic model was first outlined by Robinson and Frosch[66] and later elaborated by Lin.[67] The concepts of radiationless transitions in isolated molecules were then formulated by Bixon and Jortner.[68] In their theory they described an inhomogeneous broadening of an excited molecular state as a result of coupling between an optically active mode, belonging to initially prepared discrete states that carry all the oscillator strength, and a manifold of quasi-continuum of different background states, which

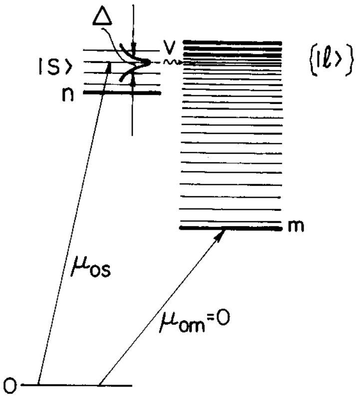


Figure 1. Schematic level diagram for describing nonradiative transitions in a large molecule, showing the levels involved coupled by the intramolecular interaction *V*.

can be, for example, highly lying vibrational states of the ground electronic or of some other lower excited electronic state. The discussion is done within the framework of the Born–Oppenheimer–Condon (BOC) approximation, where different vibronic states of the same spin are well characterized by different absorption or emission spectra. Thus, zero-order BOC states are a good approximation for describing the radiative properties of excited states.[68] Couplings between these states due to deviations from and breakdown of the BOC approximation[66–68] are responsible for all observed radiationless transitions phenomena. A radiationless transition occurs when a zero-order state decays faster through this coupling than by the competing radiative process. This means that the homogeneous width of this excitation is larger than that of the radiative one. It was shown that coupling of the optically active zero-order state (the doorway state $|s\rangle$) to a different *dense* manifold of optically inactive zero-order states $\{|l\rangle\}$, dilutes the doorway state by a finite number of molecular eigenstates, analogous to homogeneous broadening of this state.[68] This is depicted in Figure 1.

In the simplest case where one doorway state is coupled *isoenergetically*, by a constant coupling energy *V*, to a quasi-continuum manifold of equally spaced states characterized by a ρ density of states, the theory predicts a Lorentzian broadening of the doorway state having a width

$$\Delta = 2\pi V^{2}\rho \tag{1}$$

We distinguish between the "statistical limit" case in which the separation in energy, ϵ between states is smaller than the radiative width, δE, and the "intermediate level structure" where ϵ is larger than or comparable to δE.[68] In the statistical limit a real decay process of the doorway state can be observed. Although the quasi-continuum is not a real continuum, the recurrence time back to the doorway state is very large so that in actual experiments recurrences do not occur and an irreversible nonradiative decay is observed. The Lorentzian-shaped broadening corresponds to a single exponential decay, whose rate constant is given by the Fermi Golden Rule

$$k_{\mathrm{nr}} = 2\pi V^{2}\rho \tag{2}$$

The vibronic coupling between $|s\rangle$ and $\{|l\rangle\}$, in the BOC approximation, assuming normal or local mode vibrational separation is given by[67,68]

$$V = \hbar^{2}\sum_{i}\left\{\left\langle\prod_{k}\chi_{\mathrm{s}}^{k}\right|\left[\left\langle\phi_{\mathrm{s}}\left|\frac{\partial}{\partial Q_{i}}\right|\phi_{\mathrm{l}}\right\rangle_{q}\right]\frac{\partial}{\partial Q_{i}}\left|\prod_{j}\chi_{\mathrm{l}}^{j}\right\rangle_{Q}\right\} \tag{3}$$

where *q* and *Q* denote the electronic and nuclear coordinates respectively and ϕ and χ denote the electronic and vibrational wave functions. Vibrational modes are classified into promoting modes and accepting modes.[67b] In many cases some of the modes possess a dominant coupling compared to the rest, these *promoting modes* contribute a coupling matrix element which is rather independent of the promoting mode coordinate, in such a case eq 3 can be simplified to yield[67,69]

$$V = \hbar^{2}\sum_{k}\left\langle\phi_{\mathrm{s}}\left|\frac{\partial}{\partial Q_{kp}}\right|\phi_{\mathrm{l}}\right\rangle_{Q}\left\langle\chi_{\mathrm{s}}^{kp}\left|\frac{\partial}{\partial Q_{kp}}\right|\chi_{\mathrm{l}}^{kp}\right\rangle_{Q_{kp}}\left[\prod_{j}\langle\chi_{\mathrm{s}}^{j}|\chi_{\mathrm{l}}^{j}\rangle_{Q_{j}}\right] \tag{4}$$

where *j* extends over all nonpromoting modes and *k* sums over all promoting modes *p*. The nonpromoting term in eq 4 which reflects the *isoenergetic Franck–Condon overlap* between the coupled states is called *the Franck–Condon Factor* (FCF). The vibronic coupling matarix element *V* results from the breakdown of the BOC approximation.[67,68]

The harmonic promoting modes χ_{s} and χ_{l} differ by one quanta; however, the coupled states are separated by a large energy gap so that the lower zero-order states $\{|l\rangle\}$ include that gap as an excess energy, thus the FCF for the nonpromoting modes has to cover the energy gap. A nonvanishing value for the Franck–Condon integral is obtained only for modes that are different in the two coupled states, these are the so-called *accepting modes*. The energy dependence of the nonradiative rate scales approximately as the FCF of the these modes weighted by the density of states of the $\{|l\rangle\}$ manifold. The majority of the vibrational degrees of freedom, however, are similar in both interacting vibronic manifolds. These *nonactive modes* must obtain the same excitation quanta in the two states within the nonvanishing FC integral. Although the FCF of these modes is energy independent, they dominate ρ and thus the nonradiative decay rate. When this effect is taken into account we obtain

$$k_{\mathrm{nr}} = \frac{2\pi}{\hbar}V_{\mathrm{p}}^{\;2}\prod_{a}[F_{a}(\hbar\omega_{\mathrm{p}})] \tag{5}$$

where V_{p} denotes the promoting modes contribution to *V* and F_a is the FC weighted density of states (FCWD) integral associated with a particular accepting mode, for the coupling promoted by the mode *p*. The dependence of the nonradiative rate on the energy gap between the energy origins of the two coupled states[70] and the onset of intramolecular vibrational relaxation (IVR), which may alter the features associated with the single vibronic state nonradiative decay, for a given excess vibrational excitation in the s manifold, can also be formulated using this picture.[71]

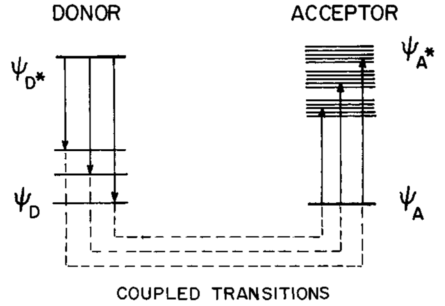


Figure 2. Coupled electronic transitions of donor and acceptor leading to electronic energy transfer under *isolated molecule* conditions.

It should be noted that the above discussion pertains mainly for *weak coupling*, which is applicable for describing EET processes; it is not an adequate description for *intermediate* or *strong coupling* cases.

Electronic energy-transfer processes involve nonradiative transfer of electronic excitation from an excited donor molecule D* to an acceptor molecule A. The transfer may be an intermolecular process which can be described in terms of a bimolecular quenching process

$$D^* + A \xrightarrow{k_q} D + A^* \qquad (6)$$

where the bimolecular quenching rate constant k_q is related to an *intermolecular* energy transfer rate constant k_{ET} by

$$k_{ET} = k_q[A] \qquad (7)$$

In most cases k_{ET} is attributed to two possible contributions. The long-range Coulombic contribution was formulated by Galanin[72] and by Förster[73−76] in terms of dipole−dipole interaction. This is particularly suitable for describing inter-EET in solution whenever conditions for favorable spectroscopic overlap between the emission of D* and the absorption of A are met (see section II.B).

The second contribution to EET can be realized whenever these conditions are not fulfilled. A short-range exchange interaction, as formulated by Dexter,[77] can then facilitate EET (see section II.C).

Intra-EET processes in bichromophoric molecules are usually described in terms of the process

$$D^*{-}B{-}A \xrightarrow{k_{ET}} D{-}B{-}A^* \qquad (8)$$

where the excitation energy is transferred from an excited donor D* chromophore moiety to a ground-state acceptor moiety A, resulting in quenching of D* fluorescence and sensitization of A. B denotes a molecular spacer bridge connecting the two chromophores. This bridge may play a role in promoting the transfer process (see section II.D).

In all EET processes discussed here, a resonance matching between the energy of the initial state of the system and that of its final state is required, this is depicted for the case of isolated molecules in Figure 2. In solution EET is slow compared to vibrational relaxation in D* and A*, so that the initial and final states are vibrationally relaxed, as shown in Figure 3 and the coupled EET transitions are determined by the Franck−Condon principle at the common overlap frequencies of D and A. It should be noted that Förster−Dexter theory preceded the development of nonradiative decay theory, the connection between the two was finally made by Lin.[78−80]

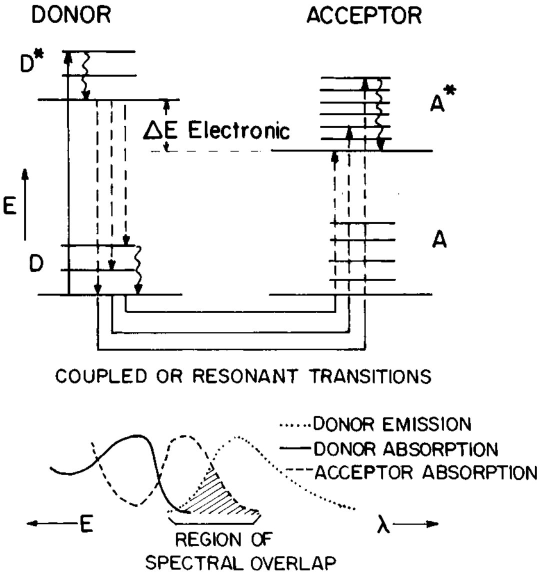


Figure 3. Coupled electronic transitions of donor and acceptor leading to electronic energy transfer in *thermalized* conditions in solution. Also shown is the corresponding region of spectral overlap, the degree of which determines the efficiency and the mechanism of transfer.

B. Coulombic Interaction−Förster Formulation

Förster[76] derived an expression to describe the rate of an EET process, in particular of the type shown in eq 5, within the framework of the weak coupling case. The EET rate is that of the transition from the initially prepared state of the D* + A system, described by its *two-electron antisymmetric* wave function[76−80]

$$\Psi_i = \frac{1}{\sqrt{2}}[\Psi_{D^*}(1)\Psi_A(2) - \Psi_{D^*}(2)\Psi_A(1)] \qquad (9)$$

to its final state D + A*, described by the wave function

$$\Psi_f = \frac{1}{\sqrt{2}}[\Psi_D(1)\Psi_{A^*}(2) - \Psi_D(2)\Psi_{A^*}(1)] \qquad (10)$$

where Ψ denotes the total wave function including the spin part which, within the BOC approximation, is given by

$$\Psi = \phi\chi \qquad (11)$$

The interaction matrix element describing the coupling between initial and final states of the bimolecular donor−acceptor system, leading to nonradiative EET, is given by

$$V_{ET} = \langle\Psi_i|V|\Psi_f\rangle = \langle\Psi_{D^*}(1)\Psi_A(2)|V|\Psi_D(1)\Psi_{A^*}(2)\rangle - \langle\Psi_{D^*}(1)\Psi_A(2)|V|\Psi_D(2)\Psi_{A^*}(1)\rangle \qquad (12)$$

where V is the perturbation part of the total Hamiltonian $\hat{H} = \hat{H}_o + V$ given by

$$V = e^2/\epsilon r_{12} \qquad (13)$$

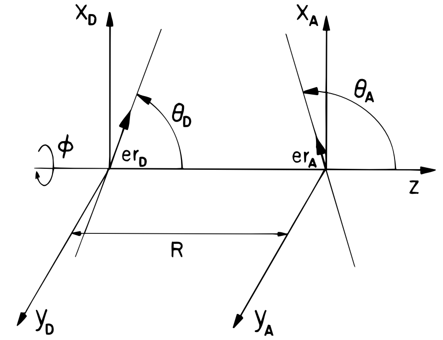


Figure 4. Geometrical configuration of dipole−dipole interaction between donor and acceptor molecules.

and r_{12} is the distance between the electrons and ϵ represents the dielectric constant of the medium. The first term in eq 12 is the Coulombic interaction and the second term is the exchange interaction. In most cases where the Coulombic interaction is significant we may neglect the exchange contribution. The Coulombic integral can then be approximated by expanding it in series and maintaining only the dipole−dipole term in the expansion thus obtaining

$$V_{\mathrm{ET}} = \frac{1}{\epsilon R^3}\left[\mathbf{M}_{\mathrm{D}}\cdot\mathbf{M}_{\mathrm{A}} - \frac{3}{R^2}(\mathbf{R}\cdot\mathbf{M}_{\mathrm{D}})(\mathbf{R}\cdot\mathbf{M}_{\mathrm{A}})\right]\prod_j\langle\chi_{\mathrm{i}}^j|\chi_{\mathrm{f}}^j\rangle \tag{14}$$

where R is the dipole−acceptor separation and $\mathbf{M}_{\mathrm{D}}$ and $\mathbf{M}_{\mathrm{A}}$ are the transition dipole moments of D → D* and A → A* transitions, respectively, given in terms of the molecular orbitals ϕ by

$$\mathbf{M}_{\mathrm{D}} = \sqrt{2}\langle\phi_{\mathrm{D}}|e\mathbf{r}_{\mathrm{D}}|\phi_{\mathrm{D}^*}\rangle \tag{15}$$

$$\mathbf{M}_{\mathrm{A}} = \sqrt{2}\langle\phi_{\mathrm{A}}|e\mathbf{r}_{\mathrm{A}}|\phi_{\mathrm{A}^*}\rangle \tag{16}$$

where $\mathbf{r}_{\mathrm{D}}$ and $\mathbf{r}_{\mathrm{A}}$ are the dipole moments vectors, as depicted in Figure 4. Equation 14 is valid only for point dipoles, *i.e.* when R is much larger than either $\mathbf{r}_{\mathrm{A}}$ or $\mathbf{r}_{\mathrm{D}}$.

By using the Fermi Golden Rule, the EET rate constant can be written as[78,79]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar^2}\sum_{\mathrm{i}}\sum_{\mathrm{f}}P_{\mathrm{i}}V_{\mathrm{ET}}^2\delta(E_{\mathrm{i}} - E_{\mathrm{f}}) \tag{17}$$

where P_{i} denotes the initial distribution and E_{i} and E_{f} are the energies of the initial and final states, respectively. Substituting eq 14 in eq 17 yields the rate constant for dipole−dipole EET processes[76,78,79]

$$k_{\mathrm{ET}}^{\mathrm{d-d}} = \frac{2\pi}{\hbar}\left[\frac{\mathbf{M}_{\mathrm{D}}\cdot\mathbf{M}_{\mathrm{A}}}{\epsilon R^3}\Gamma(\theta_{\mathrm{D}},\theta_{\mathrm{A}})\right]^2 \times \sum_{v'}\sum_{v''}\left\{\prod_j\left|\langle\chi_{\mathrm{i}_{v'j}}|\chi_{\mathrm{f}_{v''j}}\rangle\right|\right\}^2\delta(E_{\mathrm{i}_{v'}} - E_{\mathrm{f}_{v''}}) \tag{18}$$

where the v's are the vibrational quantum numbers and $\Gamma(\theta_{\mathrm{D}},\theta_{\mathrm{A}})$ is an orientational factor for the two dipoles (Figure 4)

$$\Gamma = [2\cos\theta_{\mathrm{D}}\cos\theta_{\mathrm{A}} - \sin\theta_{\mathrm{D}}\sin\theta_{\mathrm{A}}\cos(\varphi_{\mathrm{D}} - \varphi_{\mathrm{A}})] \tag{19}$$

and φ is the angle of rotation about the interdipole axis. In condensed isotropic media, such as in solutions, Γ should be averaged over all orientations and, in addition, the rate of vibrational relaxation is much faster than that of the EET process which requires also averaging the rate constant over all thermally available states as determined by the Boltzmann distribution, $P_{\mathrm{i}v'}$, thus

$$k_{\mathrm{ET}}^{\mathrm{d-d}} = \frac{2\pi}{\hbar}\left[\frac{\mathbf{M}_{\mathrm{D}}\cdot\mathbf{M}_{\mathrm{A}}}{\epsilon R^3}\Gamma(\theta_{\mathrm{D}},\theta_{\mathrm{A}})\right]^2 \times \sum_{v'}\sum_{v''}P_{\mathrm{i}v'}\left\{\prod_j\left|\langle\chi_{\mathrm{i}_{v'j}}|\chi_{\mathrm{f}_{v''j}}\rangle\right|\right\}^2\delta(E_{\mathrm{i}_{v'}} - E_{\mathrm{f}_{v''}}) \tag{20}$$

This expression is particularly useful for discussing the dependence of EET on the energy gap between D and E electronic states and on temperature and for discussion of isotope effects. Using the expressions for the absorption coefficient of A

$$\epsilon_{\mathrm{A}}(\omega) = \frac{4\pi^2\omega}{3a''\hbar c}\sum_{v'}\sum_{v''}P_{\mathrm{i}v}^{\mathrm{A}}\left|\langle\chi_{\mathrm{f}v''}^{\mathrm{A}}|\mathbf{M}_{\mathrm{A}}|\chi_{\mathrm{i}v'}^{\mathrm{A}}\rangle\right|^2\delta(\omega_{\mathrm{f}v'',\mathrm{i}v'}^{\mathrm{A}} - \omega) \tag{21}$$

and for the normalized spectral emission distribution of D,

$$\overline{F}_{\mathrm{D}}(\omega) = \frac{4\omega^3 a'\tau_{\mathrm{D}}}{3c^3}\sum_{v'}\sum_{v''}P_{\mathrm{i}v'}^{\mathrm{D}}\left|\langle\chi_{\mathrm{f}v''}^{\mathrm{D}}|\mathbf{M}_{\mathrm{D}}|\chi_{\mathrm{i}v'}^{\mathrm{D}}\rangle\right|^2\delta(\omega - \omega_{\mathrm{i}v',\mathrm{f}v''}^{\mathrm{D}}) \tag{22}$$

where a' and a'' are introduced to account for the dispersive properties of the medium, and using the integral representation of the δ function

$$\delta(\omega_{\mathrm{f}v'',\mathrm{i}v'}) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}t\,\exp(\mathrm{i}t\omega_{\mathrm{f}v'',\mathrm{i}v'}) \tag{23}$$

and carrying the integration over t, we finally obtain Förster expression for dipole−dipole-induced EET rate constant

$$k_{\mathrm{ET}}^{\mathrm{d-d}} = \frac{9000\ln 10\,\Gamma^2\Phi_{\mathrm{D}}}{128\pi^5 n^4 N_{\mathrm{A}}\tau_{\mathrm{D}}R^6}\int_0^{\infty}\frac{\overline{F}_{\mathrm{D}}(\bar{\nu})\epsilon_{\mathrm{A}}(\bar{\nu})\,\mathrm{d}\bar{\nu}}{\bar{\nu}^4} \tag{24}$$

where for random orientations $\Gamma^2 = {}^2/_3$. The matrix elements and the Franck−Condon factors in eq 18 are now expressed in terms of measurable spectroscopic quantities such as the refractive index of the medium, n, the fluorescence quantum yield of the donor, Φ_{D}, its fluorescence lifetime τ_{D}, the *normalized donor fluorescence spectrum*, $\overline{F}(\bar{\nu})$, the acceptor's absorption spectrum, expressed by its extinction coefficient, $\epsilon(\bar{\nu})$ units of liter mole^{-1} centimeter^{-1}, the average transition frequency $\bar{\nu}$ in centimeter^{-1}, and the Avogadro number N_{A}. Equation 24 can be written in terms of the Förster critical transfer radius R_0

$$k_{\mathrm{ET}}^{\mathrm{d-d}} = \frac{1}{\tau_{\mathrm{D}}}\left(\frac{R_0}{R}\right)^6 \tag{25}$$

where

$$R_0^{\ 6} = \frac{9000 \ln 10\, \Gamma^2 \Phi_D}{128\pi^5 n^4 N_A} \int_0^\infty \frac{\overline{F}_D(\overline{\nu})\epsilon_A(\overline{\nu})\, d\overline{\nu}}{\overline{\nu}^4} \quad (26)$$

Förster-type EET will be manifested for allowed transitions such as those encountered in singlet–singlet EET processes. For such transitions the critical transfer radii values range between 10 and 100 Å.[81] This range of values depends on the intensities of the relevant electronic transitions of D and A as well as on their spectral overlap, as expressed by the spectral overlap integral for dipole–dipole interaction

$$J_{dd} = \int_0^\infty \frac{\overline{F}_D(\overline{\nu})\epsilon_A(\overline{\nu})\, d\overline{\nu}}{\overline{\nu}^4} \quad (27)$$

Förster theory and its many extensions (see below) are ideally suited for quantitative interpretation and prediction of experimental observations of inter-EET in systems ranging from dye solutions and ETDL systems,[44–50,82–93] polymers,[60–64,94–96] molecules adsorbed on surfaces,[97–102] transfer between monolayers and monolayer assemblies,[103–105] in Langmuir–Blodget films,[106–110] in micellar solutions[111–113] to restricted geometries, fractals, and disordered systems.[114–123] For describing EET involving forbidden transitions one should consider exchange interaction contributions, as discussed in the next section.

C. Exchange Interaction—Dexter Formulation

Dexter considered the problem of sensitized luminescence in solids, in particular he studied sensitization via EET process of an impurity atom in a host crystal. The energy may be transferred either from the host or from another impurity atom even when the relevant electronic transitions are forbidden. Dexter's approach followed the general derivation discussed in the previous section. For forbidden transitions the Coulombic interaction is negligible and EET due to the exchange part in eq 12 is considered. For such a case the EET interaction matrix element is

$$V_{ET} = \left\langle \phi_{D^*}(1)\phi_A(2) \left| \frac{e^2}{r_{12}} \right| \phi_D(2)\phi_{A^*}(1) \right\rangle \prod_j \langle \chi_i^j | \chi_f^j \rangle \quad (28)$$

Substituting eq 28 in eq 17 yields the expression for the exchange interaction EET rate constant

$$k_{ET}^{ex} = \frac{2\pi}{\hbar} Z^2 \sum_{v'} \sum_{v''} P_v \left| \prod_j \langle \chi^i{}_{v'_j} | \chi^f{}_{v''_j} \rangle \right|^2 \delta(E_i - E_f) \quad (29)$$

where Z is the electronic exchange integral

$$Z = \left\langle \phi_{D^*}(1)\phi_A(2) \left| \frac{e^2}{r_{12}} \right| \phi_D(2)\phi_{A^*}(1) \right\rangle \quad (30)$$

Dexter has approximated Z by assuming hydrogen-like orbitals thus arriving at the final expression for the exchange interaction EET rate constant

$$k_{ET}^{ex} = \frac{2\pi}{\hbar} K J_{ex} \exp(-2R/L) \quad (31)$$

where L is an average van der Waals radius for the initial and final molecular orbitals of the donor–acceptor system, K is a parameter that, unlike in the case of Förster expression, eq 31 cannot be directly evaluated from measured spectroscopic data, and J_{ex} is the exchange interaction integral of spectral overlap between donor fluorescence and acceptor absorption spectra

$$J_{ex} = \int_0^\infty \overline{F_D}(\overline{\nu})\overline{\epsilon_A}(\overline{\nu})\, d\overline{\nu} \quad (32)$$

where $\overline{F_D}$ and $\overline{\epsilon_A}$ are the normalized donor fluorescence and acceptor absorption spectra, respectively

$$\int_0^\infty \overline{F_D}(\overline{\nu})\, d\overline{\nu} = 1 \qquad \int_0^\infty \overline{\epsilon_A}(\overline{\nu})\, d\overline{\nu} = 1 \quad (33)$$

We may thus summarize the basic features of Dexter–Förster theory as follows:

(a) For allowed singlet–singlet EET, both dipole–dipole-induced (Coulombic) interaction and exchange interaction are nonvanishing; for forbidden transitions such as triplet–triplet EET and for EET involving forbidden singlet–singlet transitions J_{DD} is negligible since $\epsilon_A(\overline{\nu}) \approx 0$, and only exchange interaction contributes to the observed EET process.

(b) The rate of dipole–dipole-induced EET decreases as R^{-6} whereas that of the exchange-induced process decreases as $\exp(-2R/L)$.

(c) The rate of dipole-induced EET depends on the oscillator strengths of D → D* and A → A* radiative transitions; however, the rate of exchange-induced transfer does not depend on either of the two oscillator strengths. Therefore, in contrast to J_{dd}, the magnitude of J_{ex} in eq 31 depends only on the spectral line shapes and not on their intensities. Thus, in addition to allowed transitions in D and A Dexter's theory can be applied to EET processes that are forbidden within the framework of the dipole–dipole mechanism. These include forbidden singlet–singlet EET, triplet–triplet EET, and triplet–triplet annihilation processes.

It should be noted that when applying Dexter's theory to EET involving *allowed* transitions, dipole–dipole interaction cannot be ignored since both interactions act in conjunction, not exclusively. This is especially important at small R values where modifications to the simple Dexter–Förster formulation become necessary.

D. Beyond Förster–Dexter Formulation

1. Significant Extensions of Förster–Dexter Theory for Long-Range Intermolecular EET

As formulated Förster's theory is especially suited to describe long-range ($R > 10$ Å) inter-EET processes in isotropic media. In fluid solutions and in the gas phase diffusion processes have to be considered.[4,5,124–126] Only when D and A are imbedded in frozen solutions or in polymer matrices diffusion free Förster kinetics can be observed. In such situations the normalized fluorescence signal $P(t)$ is no longer exponential. By assuming complete rotational averaging of Γ^2 an expression for $P(t)$ is obtained after averaging over a random distribution of R's[4,6,76,124,125,127,128]

$$P(t) = \exp(-t/\tau_D) \exp\{-{}^4/_3\pi^{4/3}[A]R_0{}^3(t/\tau_D)^{1/2}\} \quad (34)$$

Equation 34 is especially useful for analyzing inter-EET data following pulse excitation. Under steady-state conditions it is more useful to use the expression for the inter-EET quantum efficiency given by[76]

$$\Phi_{ET} = \sqrt{\pi}\Omega \exp(\Omega)^2(1 - \mathrm{erf}\ \Omega) \quad (35)$$

where

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-t^2)\ \mathrm{d}t \quad (36)$$

and $\Omega = [A]/[A_0]$, where

$$[A_0] = (\tau_D k_q)^{-1} = \frac{3}{4\pi R_0^3} \quad (37)$$

is the critical quenching acceptor concentration.

Similar averaging procedure for obtaining $P(t)$ in EET processes obeying Dexter's rate expression, eq 31 was performed by Inokuti and Hirayama.[129] They have rewritten eq 31 in the form

$$k_{ex} = \frac{1}{\tau_D} \exp\left[\beta\left(1 - \frac{R}{R_0}\right)\right] \quad (38)$$

where R_0 is defined, as in eq 25, as the distance between A and D for which the rate of EET via exchange interaction is equal to the fluorescence decay rate of D. The averaging then yields

$$P(t) = \exp\left[-\frac{t}{\tau_D} - \frac{\Omega g(z)}{\beta^3}\right] \quad (39)$$

where

$$g(z) = g[(\exp \beta)(t/\tau_D)] \approx (\ln z)^3 + 1.73(\ln z)^2 + 5.93\ln z + 5.44 \quad (40)$$

for $z > 10$.

The validity of eq 34 was demonstrated for many molecular systems, even for inter-EET on a picosecond time scale,[112,113,130-141] thus establishing the applicability of Förster's theory. However, even in such media, modifications, based on the general theory of radiationless transitions, are needed to discuss temperature dependence and isotope effects of the EET rate. Such an extension of the theory was performed by Lin[78,79] and was verified experimentally for the temperature dependence of inter-EET between aromatic donor molecules and dye acceptors.[142] The orientational dependence of inter-EET given in Förster theory by Γ should also be modified for treating other cases for which different averaging procedures should be invoked.[143-146] The requirements of Förster–Dexter theory for a nonvanishing spectral overlap integral are also well established. This implies resonant coupled transitions as shown schematically in Figure 3. It was predicted, however, that off-resonance, endothermic, Förster-type EET can still be observed by coupling a strong radiation field in the process. It was predicted that in such cases the intensity of the acceptor's fluorescence obeys the relation[147-150]

$$Y_A = \gamma I^{1/2} \quad (41)$$

where γ is a constant and I is the inducing laser intensity. This behavior was verified in the off-resonance laser-induced EET from an excited rhodamine 6G molecule to azulene acceptor.[150] Modified Förster–Dexter formulations are also needed for describing inter-EET in concentrated solutions, where exciton-type energy migration between donor molecules have to be considered,[151-154] in restricted geometries, such as for surface adsorbed D and A,[114-123] for describing inter-EET from highly excited D states[155] and in other specific EET situations,[6,156-162] some of which were recently reviewed by Bojarski and Sienicki.[9]

Other extensions and modifications of Förster–Dexter theory, significant for discussing exchange interaction and intra-EET processes, are described in more details in the next subsections.

2. Diffusion Effects and Collisional Inter-EET Processes: Intermolecular vs Intramolecular EET

As was stated in the previous section there are many examples of experimental studies that testify to the applicability of Förster theory for analyzing long-range inter-EET processes in solution[4-7,163-168] and in particular in rigid solutions.[142,169] There are, however, deviations observed in fluid solutions, such as in low viscosity solvents[163,168] or in the gas phase.[170-174] In these cases the movement of either the donor molecules or the acceptors, or both during the actual EET event, due to diffusion processes, has to be considered. The inclusion of diffusion will result in various modifications of the diffusion free Förster kinetics expressed by eqs 34 and 35.[126-128,175-184]

Birks[185] and Gösele *et al.*[126,178,179,186,187] suggested criteria to determine whether or not, and to what extent, diffusion plays a significant role at a particular experiment. These criteria are the result of analyzing inter-EET, involving diffusion, by discussing several possible kinetic models.

(a) The first model distinguishes between three different regimes according to the value of the mean molecular diffusion length r:[185]

Diffusion controlled Stern–Volmer kinetics, observed when $r > 3R_0$ where the donor fluorescence quantum yield is given by

$$1 - \Phi_{ET} = \frac{\Phi_D^0}{\Phi_D} = 1 + k_q\tau_D[A] \quad (42)$$

where Φ_D^0 is the donor fluorescence quantum yield in the absence of acceptor molecules. Under this circumstances eq 6 describes a genuine bimolecular quenching process involving molecular collisions *prior* to the actual EET process for which[4,5,65,165]

$$k_q = \frac{8RT}{3000\eta} \tag{43}$$

where η is the viscosity of the medium.

Förster kinetics, eqs 34 and 35, are obeyed whenever $r < R_0$.

Intermediate EET kinetics regime is observed for r at the range $3R_0 > r > R_0$. Here eq 35 is modified and the expression for Φ_{ET} depends explicitly on the total diffusion coefficient $D = D_D + D_A$.

(b) In the second, Gösele model,[126,178,179,186,187] the distinction between weak and pronounced diffusion effects is made by evaluating the parameter z_o, defined as

$$z_o = \frac{1}{2R_{DA}{}^2}\left(\frac{R_0{}^6}{\tau_D D}\right) \tag{44}$$

where R_{DA} is the distance of closest approach of D and A molecules.

Pure diffusion kinetics are observed for $z_o \ll 1$, in this case, which corresponds to the diffusion-controlled Stern–Volmer kinetics, eq 42, are obeyed.

Combined diffusion and long-range EET kinetics should be considered whenever $z_o \gg 1$. As in the previous case of *intermediate kinetics regime*, eqs 34 and 35 are modified to include D explicitly. Förster kinetics are obtained as a special case for the limit $D \rightarrow 0$.

(c) Gösele general model, deals with intermediate z_o values, capable of accounting for a large range of Förster radii combined with a wide range of diffusion coefficients.

Other specific cases of diffusion-dependent long-range dipole–dipole-induced EET[188] and of diffusion-dependent EET induced by short-range exchange interaction have been studied.[189,190]

In principle a clear discrimination between Förster- and Dexter-type EET processes can be made either through dynamic studies and the fit to either eq 34 or eq 39. Such a distinction, however, was made only in some limited cases in rigid media where indeed Förster[142,169] and Dexter[191–194] EET are manifested by an observed difference in the temporal decay profile of the donor fluorescence. In fact it was argued that a clear discrimination between the two EET mechanisms can only be made through dynamic studies of donor decay kinetics[191,195] and that steady-state measurements of the transfer efficiency are inadequate for this purpose.[94,196] When diffusion processes are involved the analysis becomes even more complicated. In the diffusion-controlled limit, obtained mostly for small R_0 values, *i.e.* for Dexter-type EET processes, the actual temporal decay profile is insensitive to specific donor–acceptor interaction, and the unique R dependence of the EET process cannot be measured.

Inter-EET in the gas phase may involve a combination of dipole–dipole and exchange interaction together with relative movement of D and A molecules. When exchange interaction predominates an actual collision may be needed to promote EET processes. Lin[78,79,179] and Lee and co-workers[174,198–200] worked out modifications to Förster and Dexter theories to account for these special effects.

The difficulties associated with assigning the correct mechanism to the observed EET process can be solved by studying the D* and A interactions *intramolecularly*. In this approach donor and acceptor moieties are combined chemically in a *single bichromophoric molecule* and the intra-EET process, eq 8 is followed. Both long-range Förster EET and short-range Dexter-type processes have been investigated in specially designed bichromophores. Short-range intra-EET is described in terms of Dexter exchange interaction picture, which should be modified, however, to account for variations due to incorporation of through-bond interaction, superexchange and the related, sometimes, competing process of photoinduced intramolecular ELT (see section D.3). The criteria invoked in choosing a bichromophoric molecule are discussed in section D.2.

3. Modifications of Dexter Theory for Short-Range Intra-EET: Orientational-Dependent Exchange Interaction, Super Exchange, and Through-Bond Interaction

Whenever the value of R_0 is smaller than molecular contact distances, electron exchange is considered to be the dominant interaction promoting EET. This was expressed by Dexter in terms of the exchange integral Z and a spectral overlap integral in eq 31. The latter was defined in terms of normalized D emission spectrum and normalized A absorption spectrum. This form of an overlap integral was supported by experimental observations made by Ermolaev[201] and questioned by others.[202] Even if there was no ambiguity as to the value of J_{ex}, the difficulties associated with the actual calculation of Z and the lack of direct connection between K and spectroscopic data make eq 31 rather useless for calculating the exchange contribution to the EET rate. It was, however, realized that a dependence of the transfer rate on the relative orientation of D and A must exist, particularly at small R values. Earlier experiments for measuring such an effect proved to be elusive in the case of triplet–triplet EET,[203] but recent study of singlet–singlet short-range intra-EET showed that indeed orientational dependence of exchange interaction can be of importance.[36–38] The exchange integral can be calculated using more realistic orbitals than the hydrogen atomic orbitals used by Dexter for deriving eq 31.[38,204] The orientation dependence of Z was calculated for the xylene-(D)–biacetyl(A) pair, showing that while for $R > 3$ Å Z falls exponentially with increasing R; for smaller R values Z depends on the relative orientation of the two molecules.[38]

Although in some experiments the temporal aspects of the decay kinetics due to short-range exchange interaction were studied,[191–194] the only way by which the detailed dependence of this type of EET on R and on other geometrical factors which determine D and A interactions can be studied, thus testing the validity of Dexter theory, is by examining intra-EET in bichromophoric molecules.

A bichromophoric molecule may be defined as a molecule built of two distinguishable molecular units connected by a molecular bridge. The properties of the bridge determine the flexibility of the whole bichromophoric structure. For a bichromophoric molecule the electronic absorption spectrum can be described by a simple superposition of the absorption spectra of the two chromophores. The bridge serves as a molecular spacer unit which does not influence the basic electronic structure of the two chromophores while preventing intrachromophore interaction in their ground state. However, electronic excitation of either chromophore may lead to intramolecular electronic interactions and to the observation of phenomena such as intramolecular complex formation,[1−3,205−209] intramolecular electron transfer[210−213] or intramolecular electronic energy transfer.[10−24] The main problem is to differentiate between all these processes which may act simultaneously and competitively. Thus, in addition to intra-EET processes described by eq 8 we should consider the processes

$$\mathrm{D^*{-}B{-}A} \rightarrow \mathrm{[D{-}B{-}A]^*} \quad \text{intramolecular exciplex formation} \tag{45}$$

and

$$\mathrm{D^*{-}B{-}A} \rightarrow \mathrm{D^+{-}B{-}A^-} \quad \text{photoinduced intra-ELT} \tag{46}$$

Sometimes an intra-EET process may precede ELT, and often bridge-relayed, *superexchange-mediated* intra-EET, intra-ELT and combinations of the two processes

$$\mathrm{D^*{-}B{-}A} \rightarrow \mathrm{D{-}B^*{-}A} \rightarrow \mathrm{D{-}B{-}A^*} \tag{47}$$

$$\mathrm{D^*{-}B{-}A} \rightarrow \mathrm{D^+{-}B^-{-}A} \rightarrow \mathrm{D^+{-}B{-}A^-} \tag{48}$$

$$\mathrm{D^*{-}B{-}A} \rightarrow \mathrm{D{-}B^*{-}A} \rightarrow \mathrm{D^+{-}B{-}A^-} \tag{49}$$

are observed.

There are many experiments, in particular photoinduced intra-ELT studies, that indicate such donor and acceptor interactions at D and A separations much larger than the sum of their van der Waals orbital radii. When selection rules exclude the possibility of dipole−dipole interaction, the proposed mechanism is a superexchange interaction operating beyond actual orbital overlap region, usually thought to be mediated by electronic coupling of the interchromophore bridge orbitals (processes 47−49). A review of the experimental work done on this aspect of intra-EET is given in section III.C.

Superexchange mechanism was first suggested to account for magnetic interactions in oxide crystals doped with transition metals,[214] it was then examined for ELT between metal ions.[215] A thorough theoretical analysis by McConnell showed that intra-ELT mediated through a σ-bonded bridge should decrease exponentially with the bridge length.[216] Orbital interactions promoting through-bond (TB) electronic coupling were first examined by Hoffman[217−218] and later discussed by Paddon-Row and coworkers.[213,219−220] Superexchange has been discussed in the context of EET by Monberg and Kopelman[221] and by Klafter and Jortner.[222] These studies were followed by a plethora of investigations of long-range photoinduced intra-ELT.[34,213,223−243] Significant and unambiguous experimental verifications of early theories were reported by Closs *et al.*[224] and later by Oevering *et al.*,[34] showing the particular distance dependence associated with the *cis−trans* linking-bridge chain configuration. For further discussion of these phenomena, the reader is referred to the review by Newton.[212]

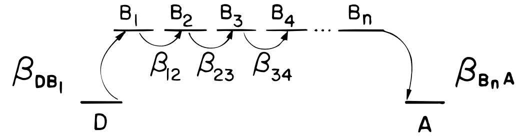


Figure 5. Schematic level diagram for describing through-bond interchromophore bridge-mediated interaction between energetically degenerate donor and acceptor moieties in a bichromophoric molecule.

The main experimental manifestations of TB superexchange interaction in EET and ELT are as follows:

(a) The R dependence of the efficiency of the process does not follow either Dexter or Förster predictions.

(b) Intra-EET and intra-ELT are still very efficient at $R > 10$ Å for dipole−dipole forbidden processes, especially in *rigidly linked* D−B−A molecules. However, it seems that in more *flexible* structures intra-EET is still controlled by short-range *through-space* Dexter-type interaction.

(c) The observed rates depend on the interchromophore bridge conformation for a relatively fixed mutual orientation of the interacting chromophores.

(d) For *trans* σ bonds bridge structure the transfer rate decreases exponentially with the number of bonds.

It should be noted that both exchange and superexchange, as well as other orbital overlap interactions are all manifested by an exponential R dependence and thus cannot be distinguished experimentally except for the interaction range. In this respect one cannot distinguish between superexchange and hops that occur in energy migration between identical molecules. The major approach for treating TB superexchange controlled short-range intra-EET is to generalize the theory by including TB, involving any number of bridge relay units in the interaction matrix element.[216,233−244] McConnell suggested that orbital sites intervening between D and A could facilitate ELT.[216] In his superexchange model, an electron is transferred between degenerate D and A orbitals, aided by the presence of empty (not necessarily degenerate) high-lying bridge orbitals (Figure 5). This model differs from a “hopping” model in that the electron does not actually occupy any of the bridge orbitals during the transfer process. McConnell’s expression for the coupling matrix element is given by

$$V_{\mathrm{DA}}^{(n)} = \left(\frac{\beta_{\mathrm{DB_1}}\beta_{\mathrm{B}_n\mathrm{A}}}{E_{\mathrm{AD}} - E_{\mathrm{B}_l}}\right)\left(\prod_{i=1}^{n-1}\frac{\beta_{i,i+1}}{E_{\mathrm{AD}} - \beta_{i+1}}\right) \tag{50}$$

where β_{ij} is the tunneling integral between orbitals i and j, E_{AD} is the degenerate D and A orbitals energy, E_{β_i} is the energy of the ith bridge orbital, and n is the number of B orbitals. It can be then shown that eq 50 leads to an exponential attenuation of the intra-ELT rate with an increase in the number of bridge

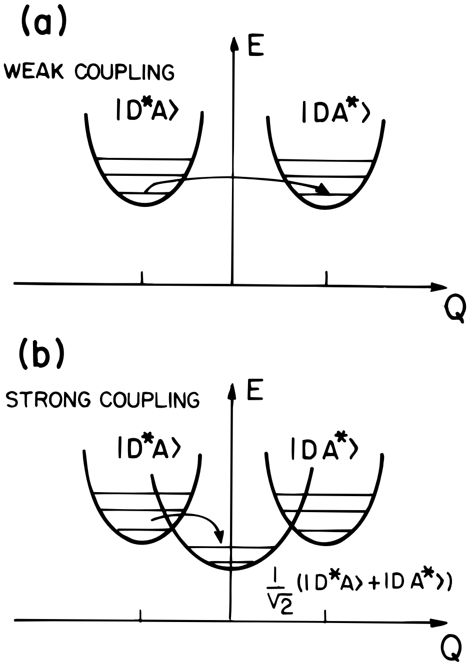


Figure 6. Potential energy surfaces showing weak (a) and strong coupling (b) cases of intra-EET. In the weak coupling the excitation can be localized on either chromophore while in the strong coupling limit a stationary state spread over the super bichromophoric molecule is being formed and no intra-EET process can be followed.

relay groups. The McConnell expression is useful for describing most superexchange situations involving electronic coupling of *degenerate D and A* well removed from bridge orbitals. It is, however, both time and vibrationally independent. In addition, McConnell's method is based on a tight bonding model and thus is very approximate. An extended model relaxes this restriction to a certain extent which makes it quite useful.[212,213] A time-dependent approach was formulated by Todd *et al.*,[235] while other theories, more relevant for describing intra-ELT involving superexchange have been worked out.[238,244] Theoretical treatments of bridge-mediated EET and ELT were presented by Reimers and Hush[226,245] for two[226] and three level[245] systems, for treatment of coherent transfer of energy between D and A centers via B states[226] or through a resonant bridge.[245] Resonant transfer in condensed matter was recently investigated using quantum electrodynamics (QED).[54,246,247] Unlike the case of inter-EET, in intra-EET electronic energy localization on either D or A chromophore can be assumed only for weak electronic coupling as compared to the vibronic bandwidth (Figure 6a). In the strong coupling limit the relative displacement of the potential energy surfaces of the D and A systems is expected to be large and the crossing between them is closer to the higher electronic state, as shown in Figure 6b. In such a case even if the system is initially prepared at $|D^*A\rangle$, it will rapidly dephase into the mixed stationary state of the type $1/\sqrt{2}(|D^*A\rangle + |DA^*\rangle)$ or $1/\sqrt{2}(|D^*A\rangle - |DA^*\rangle)$, where intramolecular vibrational modes may play a significant role. Also in this case resonance EET should be considered which can be formulated within the framework of QED theory.[246,247] A clear distinction between strong and weak coupling cases was offered by Kenkre and Knox for discussion of molecular pairs.[248]

In this Review we are concerned with weakly coupled chromophores which can also be coupled to the interchromophore bridge electronic states. This may lead to sequential transfer similar to cases of ELT studied by Mukamel *et al.*[249−251] In these cases we rewrite eq 17 in the more general form[67,238,244]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}\sum_{\mathrm{i}}\sum_{\mathrm{f}} P_{\mathrm{i}} |\langle \Psi_{\mathrm{i}} | \hat{T} | \Psi_{\mathrm{f}} \rangle|^2 \delta(E_{\mathrm{f}} - E_{\mathrm{i}}) \qquad (51)$$

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

$$\hat{T} = V + T^{(2)} = V + V\frac{1}{E_{\mathrm{i}} - \hat{H} + i\epsilon}V \qquad (52)$$

where ϵ describes the dephasing of the system. The effect of the interchromophore bridge is described by the matrix element

$$T^{(2)}_{\mathrm{fi}} = \sum_{\mathrm{m}} \frac{V_{\mathrm{fm}} V_{\mathrm{mi}}}{E_{\mathrm{i}} - E_{\mathrm{m}} + i\epsilon_{\mathrm{mi}}} \qquad (53)$$

where the summation is carried out over all virtual intermediate electronic bridge B_m states $|\mathrm{m}\rangle$, depicted schematically in Figure 5, and

$$V_{\mathrm{fm}} = \langle \Psi_{\mathrm{m}} | V | \Psi_{\mathrm{f}} \rangle \qquad V_{\mathrm{mi}} = \langle \Psi_{\mathrm{i}} | V | \Psi_{\mathrm{m}} \rangle \qquad (54)$$

In the conventional Förster−Dexter theory, where TB interaction is neglected, $T^{(2)} = 0$. Equation 52 is valid for isolated bichromophoric molecules, addressed in more detail in section II.D.5. Using eq 11 we obtain

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|T_{\mathrm{fi}}|^2 \sum_{v'}\sum_{v''} P_v |\langle \chi_{\mathrm{f}v''} | \chi_{\mathrm{i}v'} \rangle|^2 \delta(E_{\mathrm{f}v''} - E_{\mathrm{i}v'}) \qquad (55)$$

where T_{fi} denotes the electronic coupling matrix element

$$T_{\mathrm{fi}} = \langle \phi_{\mathrm{f}} | \hat{T} | \phi_{\mathrm{i}} \rangle \qquad (56)$$

The FC factors in eq 55 are similar to those important in photoinduced ELT showing the correspondence between short-range intra-EET and intra-ELT processes. Quantum mechanical theories of ELT may also be applied to the rate expression of eq 55.[252,253]

In solution, rapid vibrational relaxation takes place and the thermally averaged intra-EET rate constant, involving TB interaction, should be used. It is given by[238]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}\sum_{v'}\sum_{v''} P_{\mathrm{i}v'} \left| V_{\mathrm{f}v'',\mathrm{m}v} + \sum_{\mathrm{m}v} \frac{V_{\mathrm{f}v'',\mathrm{m}v} V_{\mathrm{m}v,\mathrm{i}v'}}{E_{\mathrm{i}v'} - E_{\mathrm{m}v} + i\epsilon_{\mathrm{m}v,\mathrm{i}v'}} \right|^2 \times \delta(E_{\mathrm{f}v''} - E_{\mathrm{i}v'}) \qquad (57)$$

where now the summation is carried out over all thermally averaged vibrational states. Without TB coupling eqs 20 and 24 or eq 31 is obtained as special cases of eq 57, suitable for describing *through-space* intra-EET rates via dipole−dipole or exchange interaction, respectively. By using eq 57 a similar expression to McConnell's eq 50 can be obtained as a special case.

We now turn to examine the role of vibronic effects in the TB superexchange-mediated intra-EET and intra-ELT processes. This is especially important for transfer processes studied in supersonic jet-cooled clusters and for the discussion of excitonic interactions involving vibronic transitions. The implications of such non-BOC corrections for calculating long-range ELT rates were discussed by Freed,[254] considering the suggestion made by Beratan and Hopfield[255] that when the BOC approximation is relaxed an enhancement of the intra-ELT rate is to be expected. This was supported by several experimental studies,[29,31,34,35,256] discussed in more detail in sections III.C and IV.

At the small D and A separations typical of short-range intra-EET in bichromophoric molecules, deviations due to breakdown of Förster point−dipole approximation should be considered. Thus even for allowed dipole transitions one should consider different ways of describing the Coulombic interaction. Chang[257] has studied a specific system in which she found deviations from Förster's expression for the distance dependence of the EET rate using a monopole model, for the case where the molecular size was substantial. The effects on the rate of EET of higher multipole interactions and small exchange contributions were examined in great detail by Scholes *et al.*[244] They have described second-order Coulombic interactions within the framework of molecular QED theory and added a correction due to first-order exchange mechanism. By using perturbation theory, the EET rate constant was calculated with the use of eqs 51 and 52. The matrix element in eq 52 was partitioned into exchange term involving only V and dipole−dipole term involving only $T^{(2)}$. The resulting rate expression is given by

$$k_{\mathrm{ET}}^{\mathrm{total}} = A^2R^{-6} + 2ABR^{-3}\exp(-\alpha R) + B^2\exp(-2\alpha R) \quad (58)$$

where $\alpha = L/2$ and A and B are constants given by

$$A = B\mathbf{M}_{\mathrm{D}}\cdot\mathbf{M}_{\mathrm{A}}\Gamma(\theta_{\mathrm{D}},\theta_{\mathrm{A}}) \quad (59)$$

and

$$B = \sqrt{\frac{2\pi}{\hbar}}\rho_{\mathrm{f}} \quad (60)$$

It was concluded that the use of multipole expansion in the interaction Hamiltonian is not always a good approximation for $R < 10$ Å. This was attributed to a combination of large molecular dimensions compared to R and wave function overlap effects. For larger interchromophore separations, the interaction can be described by the usual dipole−dipole coupling. The inclusion of small exchange effects at small to intermediate separations demonstrates the likelihood of a substantially larger EET rate than that predicted by either Förster theory or pure exchange Dexter-type interaction. This emphasizes the fact that in general both interactions act in conjunction. Scholes *et al.*[244c] have also investigated the electronic factors important in mediating EET at close range. They concluded that one-electron transfer processes via ionic, charge-transfer type, bridge configurations can make a major contribution to the observed EET rate, in addition to the exchange type two-electron steps normally considered. A theoretical calculation on the ethene dimer demonstrated that this "through configuration" interaction, rather than the Dexter exchange term, can dominate the orbital overlap dependent short-range interactions.[244d] However, the importance of these terms will most likely depend on the particular orbitals and on the particular relative orientation of the chromophores involved.

4. Theoretical Considerations in the Design of Bichromophoric Molecules

Bichromophoric molecules are ideal for investigating intra-EET processes. By using the powerful tools of synthetic organic and polymer chemistry, molecular systems can be engineered for a specific intra-EET study.

For the particular purpose of elucidating the mechanism of short-range, singlet−singlet, intra-EET in bichromophoric molecules, the following requirements should be met:

(a) The two coupled electronic transitions, D* → D and A → A*, should be forbidden and displaced in energy so as to ensure a negligible overlap integral, J_{dd}, resulting in $R_0 < 10$ Å. For such a D−A pair the prevailing intra-EET mechanism will be dominated by Dexter-type short-range exchange interaction.

(b) The interchromophore bridge should act as an inert spacer, minimizing any coupling between the ground electronic states of the two chromophores, allowing, however, for weak coupling between D* and A to promote short-range intra-EET. The bridge should be rigid enough to provide controlled geometrical relationship between the chromophores and to allow for only a limited number of molecular conformations. However, it seems that some flexibility is required whenever TB interaction needs to be minimized. Rigid bridge structures seem to be ideal for TB superexchange studies and for evaluating the mutual roles played by intramolecular EET and ELT processes.

(c) Both absorption and emission spectra should reveal two bands, attributed to D or A chromophores. The general features of the spectra should be similar to a superposition of the separate spectra of the chromophores.

An example for bichromophoric compounds that meet these specifications is the specially synthesized series of molecules, **II-Phenane-5,5**, **III-P-*n,n***, **O-*n,n***, **M-*n,n***, and **IV-P-*n,m***.[258,259] This series was designed with the expectation that variation of the number of methylene groups in each chain joining the two chromophores would result in variation of the distance separating them and allow evaluation of the dependence of intra-EET efficiency on interchromophore separation distance and relative chromophore orientation. Conformations of these molecules were determined by a combination of spectroscopic analysis (UV−vis, variable-temperature NMR), X-ray crystallography (where applicable), and molecular me-

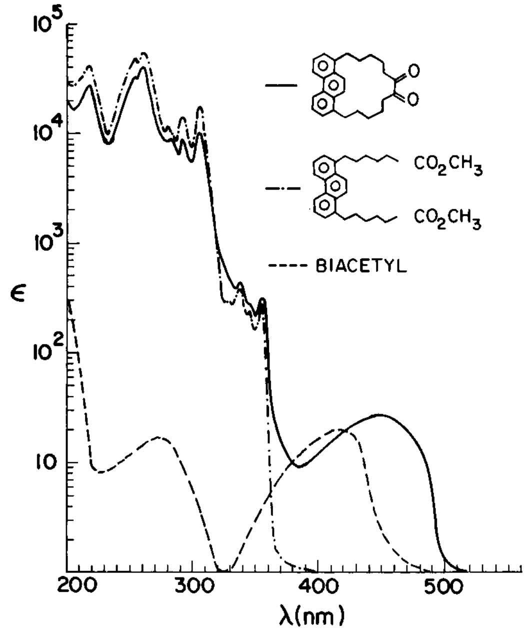


Figure 7. Absorption spectra of the **Phenane-5,5** bichromophoric molecule and its constituent chromophores.

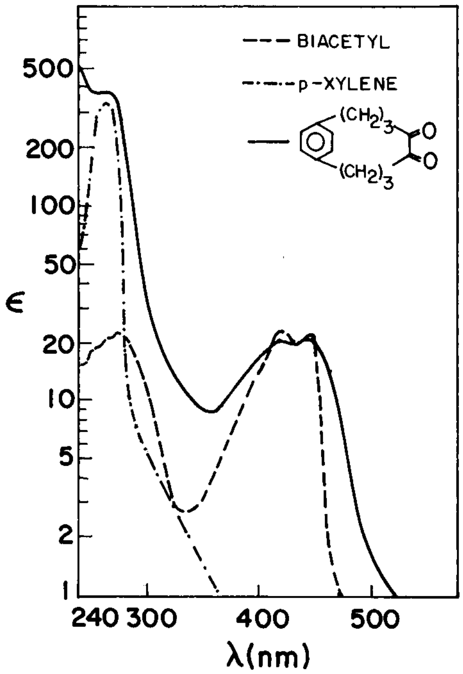


Figure 8. Absorption spectra of the **P-3,3** bichromophoric molecule and its constituent chromophores, typical of the spectra of *all* other molecules of series **III**, **IV**, **VIII**, **IX**, and **XVIII**.

chanics calculations. Most spectroscopic properties of these molecules are described by a superposition of those of their constituent chromophores, as shown in Figures 7 and 8.

Unique for these bichromophoric molecules is the fact that, depending on the molecular geometry, energy absorbed by the aromatic chromophore is transferred in part to the α-diketone and both chromophores emit their characteristic fluorescence spectra resulting in dual fluorescence characteristic of intra-EET process.[260,261]

Other specific requirements are needed for other types of studies or applications. For example, volatility of the bichromophoric molecules facilitates studies in supersonic jet expansions (section IV), while good spectral overlap and highly allowed transitions are needed for utilizing bichromophoric molecules as laser dyes in ETDL configurations.[44-46]

5. Intramolecular Electronic Energy Transfer in Isolated Molecules

Most of the reported intra-EET studies involve thermalized systems in solution. In recent years experimental studies of intra-EET in isolated molecular systems in supersonic jet conditions began to attract attention. These include bichromophoric molecular clusters, as well as a few examples of bichromophoric molecules.

Under these conditions two types of EET rate constants, above and below IVR threshold, suitable for describing isolated molecules in collision-free conditions, should be used. The generalized theory derived by Lin and co-workers provided such a rate expression which does not invoke the spectral overlap between D and A, a quantity which cannot be easily defined for these conditions.[80,262,263]

We first consider the case of intra-EET from a single-vibronic level of D*. The intra-EET rate constant depends on the excess vibrational excitation, when IVR is slow EET takes place from the originally prepared single vibronic state iv′. The situation can then be described by modifying eq 55 to read

$$k_{\mathrm{ET}}^{\mathrm{i}v'} = \frac{2\pi}{\hbar}|T_{\mathrm{fi}}|^2\sum_{v''}|\langle\chi_{\mathrm{f}v''}|\chi_{\mathrm{i}v'}\rangle|^2\delta(E_{\mathrm{f}v''} - E_{\mathrm{i}v'}) \quad (61)$$

It can be shown that for the case of displaced harmonic oscillators[80,262,263]

$$k_{\mathrm{ET}}^{\mathrm{i}v'} = \frac{1}{\hbar^2}|T_{\mathrm{fi}}|^2\int_{-\infty}^{\infty}\mathrm{d}t \times \exp\left[it\omega_{\mathrm{fi}} - \sum_j S_j(1 - \mathrm{e}^{it\omega_j})\right]\prod_j\overline{G_{v'_j}(t)} \quad (62)$$

where

$$\overline{G_{v'_j}(t)} = \sum_{n_j=0}^{v'_j}\frac{v'_j!}{n_j![(v'_j - n_j)!]^2}\times [S_j(\mathrm{e}^{(1/2)i\omega_jt} - \mathrm{e}^{-(1/2)i\omega_jt})^2]^{v'_j-n_j} \quad (63)$$

and S_j denotes the coupling constant related to the vibrational coordinate displacement ΔQ_j by

$$S_j = (\omega_j/2\hbar)\Delta Q_j \quad (64)$$

In particular, if $v_j = 0$, then by using the saddle-point method we find

$$k_{\mathrm{ET}}^{\mathrm{i}0} = \frac{1}{\hbar^2}|T_{\mathrm{fi}}|^2\left[\frac{2\pi}{\sum_j S_j\omega_j^2\mathrm{e}^{it^*\omega_j}}\right]^{1/2}\times \exp\left[it^*\omega_{\mathrm{fi}} - \sum_j S_j + \sum_j S_j\mathrm{e}^{it^*\omega_j}\right] \quad (65)$$

where t^*, representing the saddle-point value of t, is defined by

$$\omega_{\rm if} = \sum_j S_j \omega_j {\rm e}^{it^*\omega_j} \tag{66}$$

If $\Pi_j \overline{G_{v'_j}(t)}$ does not vary much around t^*, then

$$\frac{k_{\rm ET}^{{\rm i}v'}}{k_{\rm ET}^{\rm i0}} = \prod_j \overline{G_{v'_j}(t^*)} \tag{67}$$

Equation 67 is particularly useful for analyzing the excess vibrational excitation dependence of the single vibronic level intra-EET rate. Alternatively eq 61 can be used to derive the rate expression in terms of *single vibronic state* overlap integral. Following the procedure used to derive eq 24 we obtain

$$k^{\rm d-d}_{{\rm ET,i}v'} = \frac{9000 \ln 10\, \Gamma^2 \Phi_{\rm D}^{{\rm i}v'}}{128\pi^5 N_{\rm A} \tau_{\rm D}^{{\rm i}v'} R^6} \int_0^\infty \frac{\overline{F}_{\rm D}^{{\rm i}v'}(\bar{\nu})\epsilon_{\rm A}^{v}(\bar{\nu})\, {\rm d}\bar{\nu}}{\bar{\nu}^4} \tag{68}$$

where all the relevant photophysical parameters are associated with the single vibronic levels iv' in D and v in A. Equation 68 is useful as long as sufficient spectroscopic data is available. A similar expression for the exchange interaction promoted intra-EET, single vibronic rate constant can be obtained by modification of eqs 31 and 32.

Above the IVR threshold no single vibronic rate can be evaluated and the so-called microcanonical intra-EET rate constant should be used. This was discussed in great detail by Lin and co-workers.[80,262]

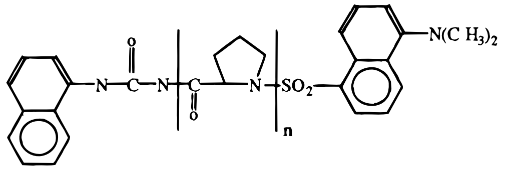
III. Intramolecular Electronic Energy Transfer in Bichromophoric Molecules in Solution

A. Long-Range Energy Transfer in Polymers

In small bichromophoric molecules, of the type **II**, **III**, and **IV** short-range exchange or medium-range TB superexchange interactions prevail and Dexter kinetics eq 32 holds. A situation characteristic of oligomers, polymers, and biopolymers is where two or more interacting D and A chromophores are attached to the polymeric backbone. If the sequence of D and A moieties along the polymer chain is regular and the distance R between them is larger than 15 Å, then excitation energy, initially located on D, will be transferred from the donor moiety to the acceptor chromophore by a Förster-type dipole–dipole interaction, at a rate governed by eq 25. Thus, structural information regarding the macromolecule can be gained as well as information regarding morphology.[60−64,94,143,264−274] Equation 25 can then serve as a *spectroscopic ruler*[270] for determining R from measurements of the intra-EET rate constants.

The first demonstration of such an application of long-range intra-EET was the study of the distance dependence of intra-EET in the oligomer system of poly-L-proline (**V**).[270] The oligomer served as the B spacer group for determining the separation between the donor chromophore, α-naphthyl attached to the carboxyl end of B, and the acceptor chromophore, a dansyl group, attached to the imino end. The observed intra-EET efficiency followed an R^{-6} dependence, in excellent agreement with the Förster model.

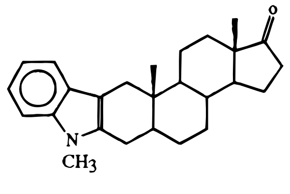
V



Another beautiful demonstration of the practical use of eq 25 for the structural analysis of macromolecules was given in a series of studies performed by Steinberg and co-workers.[271,272] They used solutions of oligopeptides of various chain lengths with N^5-(2-hydroxyethyl)-L-glutamine and D and A chromophores similar to those employed by Stryer and Haugland.[270] These chromophores were attached to the far ends of the peptides composed of four, five, six, seven, eight, and nine repeat units. Dual fluorescence due to the long-range intra-EET process (R_0 = 22 Å) was recorded, and the observed donor fluorescence lifetime was used to determine $k_{\rm ET}$. The results were then fitted to a model from which the distribution of end-to-end distances of the polymer chain was obtained. It should be noted, however, that in this study as well as in other similar investigations[143,264,267] a knowledge of the orientation factor Γ^2, which can be determined from study of polarized EET,[268] is needed before R could be evaluated with confidence. In other studies the various roles played by the chromophores and by the polymer spacer in the bichromophoric polymers were investigated.[273−279] Guillet, Liu, and co-workers examined both theoretically and experimentally the application of the spectroscopic ruler for studies of the dimensions of macromolecules[64,274] and their implication to light harvesting in polymers.[274c,d] Lakowicz and co-workers used the frequency-domain fluorometry technique to elucidate distribution of distances in D and A connected by a flexible methylene chain[275] and by proteins coils.[276−278] The effect played by a conjugated polymer spacer bridge on the intra-EET process was examined by Effenberger *et al.*[279−284] A time-resolved dynamics study of EET in dye-doped conjugated polymers was recently reported by Kurz and co-workers.[285]

In another study of long-range intra-EET Haugland and co-workers[286] examined the rigid bichromophoric molecule **VI** composed of N-methylindole as the donor moiety and a ketone as the acceptor, both fused to a steroid that served as the spacer group with R = 10.2 Å. By using nanosecond flash spectroscopy, the EET rate as a function of the spectral overlap integral, varied simply by altering the solvent, was deter-

VI

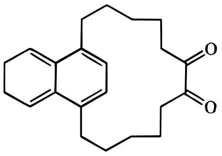


mined. Again good agreement with Förster theory, eqs 25−27, was found.

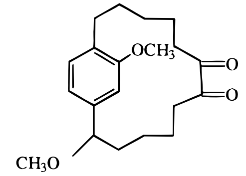
B. Short-Range Singlet–Singlet Energy Transfer

As already mentioned in the Introduction, many studies of short-range intra-EET have been reported.[10−40] However only very few of them utilized bichromophoric molecules that were prepared to allow for a mechanistic investigation of the process.[25−28,36−40]

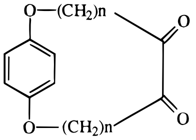
VII, 1,4-Naph-5,5



VIII, DiMeO-P-5,5



IX, HQ-n,n



An extensive and systematic study of through-space exchange-mediated short-range intra-EET, in specially designed bichromophoric molecules[258,259] was undertaken by Speiser *et al.*[25,27,28,36−38,287] Following the first demonstration of dual fluorescence resulting from an intra-EET process in **II-Phenane-5,5**,[25] the process was studied in a series of macrocyclic α-diketones (specifically para- and metacyclophanes) and their ortho analogs, benzocycloalkenediones, **III-P-*n,n***, **M-*n,n***, and **O-*n,n***, respectively, and other *symmetrical* aryl α-diketones (**VII-Naph-5,5**, **VIII-DiMeO-P-55**, and **IX HQ-*n,n***).[27,28,36−38,260,261] The results for the temperature-dependent intra-EET quantum yield were fitted to a model in which a distribution of several conformations of the bichromophoric molecules, some of which are in a favorable conformation for promoting intra-EET via Dexter-type exchange interaction mechanism, was assumed.[27,36,287] According to this model the intra-EET quantum yield Q, corrected for the specific temperature and spectral overlap dependence for these molecules, Q', depends exponentially on the average interchromophore separation $\overline{R}$

$$Q' = (Q/\tau_D\alpha)\exp(\beta^2/4\gamma) = \exp(-\beta\overline{R}) \qquad (69)$$

where α and β are defined in accordance with eq 32 through the relation

$$k_{\mathrm{ET}}^{\mathrm{ex}} = \alpha\exp(-\beta\overline{R}) \qquad (70)$$

and γ accounts for the flexibility of the interchromophore bridge manifested in the observed thermally activated intra-EET process.[27,36] For narrow conformational distributions it is given by[287]

$$\gamma^{-1} = (4\delta/\beta^2)\exp(-\Delta E/RT) \qquad (71)$$

where δ is the ratio between EET rate constants for the two conformers involved in the intra-EET process, separated by an energy gap ΔE.[27]

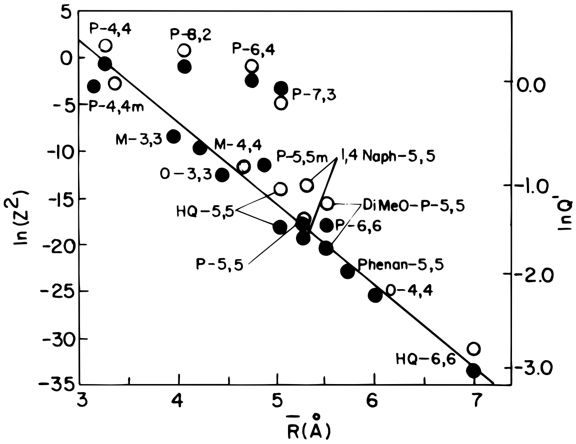


Figure 9. The fit of intra-EET experimental data Q' to a model based on Dexter through-space exchange interaction, eq 70, together with the calculated values of the exchange integral.

The experimental fit to this model is shown as the dark circles in Figure 9 together with a calculation of the corresponding exchange integral for these molecular systems (open circles).[38]

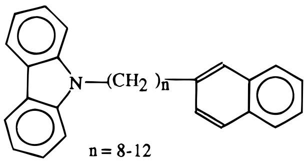
In a more recent study the investigation was extended to the asymmetrical bichromophoric structures **III-P-*n,m*** in which the orientation dependence of short-range exchange interaction was examined.[36] Using a calculation of the exchange integral for all these bichromophoric molecules it was concluded that although the relative orientation of the D and A chromophores play a role in the EET process, especially for the asymmetric molecules **P-*n,m***, most of the observed intra-EET yields could be accounted for by a Dexter-type mechanism eq 70, as manifested by the fit shown in Figure 9.[36,38] The possibility that this short-range interaction may also be propagated via the connecting methylene groups, *i.e.* by TB interaction, was not considered. However, the fit in Figure 9 suggests that such an interaction is unimportant for these molecules in view of the very short-range (R < 7 Å) exponential R dependence. This may be typical of bichromophoric molecules with *semiflexible* interchromophore bridge structures. Indeed in more rigid bichromophoric structures deviations from this simple dependence, which might be due to TB superexchange interactions, were reported.[26,29−35,288−290] These studies are discussed in more detail in the next section.

Most experimental studies of the mechanism of short-range intra-EET involve singlet−singlet processes, the very few examples of triplet−triplet EET exhibit similar features. These processes, however, are rather important in promoting intra-EET-induced photochemistry as discussed in section V.

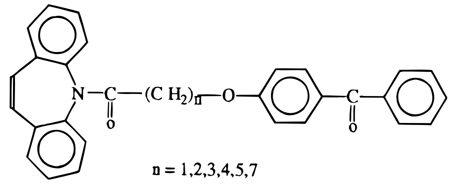
Triplet−triplet intra-EET is always promoted by either short-range exchange interaction or by medium- to long-range TB superexchange interaction mediated by the interchromophore bridge. Unlike the case of singlet−singlet transfer no quantitative correlation between the EET efficiency and the interchromophore separation could be made for the **O-*n,n***, **M-*n,n***, **P-*n,n***, and **P-*n,m*** series, although the efficiency was shown to be sensitive to molecular geometry.[28,37]

Yamamoto and co-workers have investigated triplet−triplet intra-EET in systems where the two chromophores were connected by a polymethylene chain of variable lengths.[291,292] The transfer yield at 77 K was measured as a function of the bridge length. The interchromophore distance dependence followed the Dexter model. Mapping of all possible molecular conformation for the systems **IX** and **X** by assuming a Boltzmann distribution yielded the distribution of interchromophore distances and an average value for *R*. At small *R* values the relative orientation of the chromophores plays a significant role as manifested in deviations from the fit to Dexter model.

X



XI



The effect of relative orientation was studied also by Engel *et al.* in the series of benzophenone donor attached through an ester spacer group to cyclic azoalkane acceptor.[293] Rentzepis and co-workers have measured the rate constant of intra-EET triplet−triplet process from anthrone (D) to naphthalene (A), for a rigid spiran system, to be 3×10^{10} s^{-1}.[294] The results were discussed in terms of Dexter theory. In another study highly efficient triplet−triplet intra-EET was found for a series of dyes attached to a 9-methylanthryl donor without, however, any mechanistic conclusions.[295]

Studies of dipole−dipole singlet−singlet intra-EET were reported by Valeur *et al.*[39,296,297] They used EET as a probe to gain experimental proof for calculated statistical distributions of conformations of the flexible polymethylene chains connecting donor and acceptor chromophores. The implications for realizing intramolecular ETDL systems were also discussed, including studies of the picosecond dynamics of the intra-EET process.[298−305] Related studies deal with intramolecular quenching processes,[306] with intramolecular exciplex formation,[206,207,209,307] with intramolecular photochemical reactions in bichromophoric molecular systems,[57,308] in studies of biological systems,[309] and of intra-EET in bichromophoric compounds of transition metals[310−317] and chelates.[318]

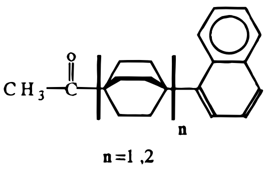
Of particular interest are the studies carried out by Hochstrasser and co-workers where femtosecond excitation was used to follow the rate of intra-EET in 9′,9-bifluorene and 2′,2-binaphthyl in a variety of solvents.[319,320]

C. Medium-Range Energy and Electron Transfer Involving Superexchange and Through-Bond Interaction

Experimental evidence for TB−superexchange interaction promoting bridge-mediated intramolecular transfer processes is especially available from studies of photoinduced intra-ELT. These studies have shown that the ELT rate is strongly dependent on the molecular structure, in particular on the interchromophore bridge conformation and configuration. A systematic study of these phenomena was undertaken by Verhoeven and co-workers.[34,239−243] They have examined intra-ELT in specially designed bichromophoric molecules, mostly having a rigid interchromophore bridge. The general conclusion that could be made is that the governing mechanism for this process is superexchange involving TB bridge interaction. In some cases the competition between through-bond and through-space interactions was examined, comparing rigid and flexible bichromophoric structures.[289]

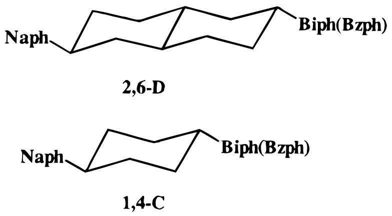
Studies of the analogous process of intra-EET in similar molecular structures showed that at least for rigidly linked bichromophoric molecules, TB interaction plays a significant role. Zimmermann *et al.*[26] examined the singlet−singlet intra-EET process between donor and acceptor linked together by the *rod-like* rigid interchromophore bridges consisting of bicyclo[2.2.2]octane moieties, **XII**. Partial energy transfer was observed even for the 7.5 Å interchromophore separation at a yield of 250 times larger than that for $R = 11.5$ Å. The observations did not fit either Förster or Dexter models. The conclusion was that EET was promoted by a short-range TB exchange interaction mediated through the five σ bonds.

XII



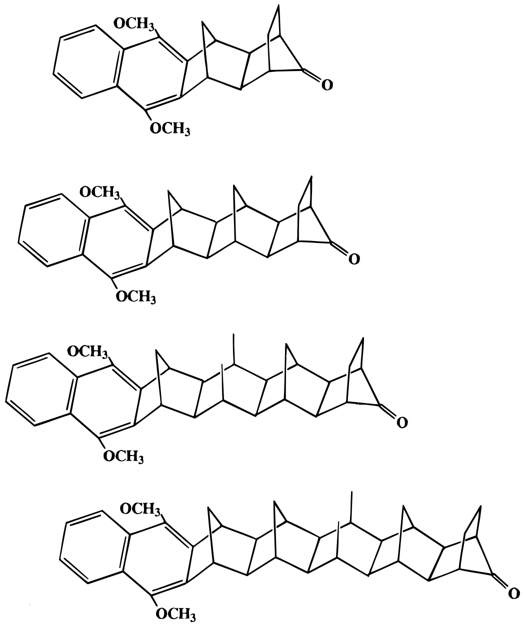
The first quantitative demonstration of the utilization of a σ-bond *spacer* in promoting efficient long-distance intra-EET was given by Closs *et al.*[32,33] They compared the rates of both triplet−triplet EET and ELT in the series of compounds **XIII**, consisting of a 4-biphenyl or 4-benzophenoyl donor chromophores, a 2-naphthyl acceptor, and cyclohexane (1,4-C) or decaline (2,6-D) spacers as the interchromophore bridge.

XIII



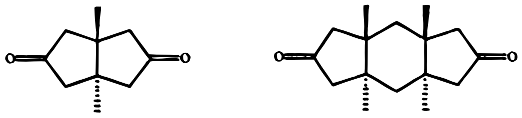
Following their intra-ELT work,[34] Verhoeven and co-workers examined singlet−singlet intra-EET processes in the series **XIV** of bichromophoric molecules containing *rigid* polynorbornyl interchromphore bridge spacers, separating the dimethoxynaphthalene donor from the carbonyl acceptor.[29−31] In the first series the two chromophores were connected via 4−10 σ bonds in an *all-trans* conformation. Intra-EET was observed even for $R = 11.5$ Å where direct orbital overlap is not possible. The measured transfer rate constant was much larger than that calculated from the Förster model and depended exponentially on the number of interchromophore σ bonds. Changing the conformation to *cis* or *gauche* resulted in much lower EET yield without, however, a marked change in R for the same number of σ bonds. It was concluded that intra-EET was mediated by a TB coupling which was hindered by adding a kink to the *all-trans* six-bond bridge, thus resulting in a much less efficient EET process. Comparison with intra-ELT results for bichromophoric molecular systems with similar bridge structures led to the conclusion that $k_{\mathrm{ET}} = k_{\mathrm{ELT}}^2$.[29]

XIV



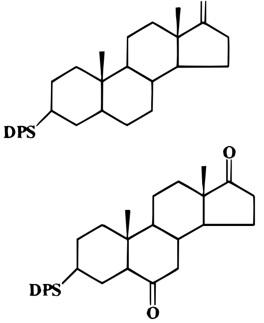
Schippers and Dekkers[321] studied singlet−singlet intra-EET between two ketone chromophores connected by the rigid structures **XV**. They observed that the rate for energy transfer through the four σ bonds was 1000 times higher than that through six bonds, thus concluding that TB superexchange mechanism is appropriate for explaining the observations.

XV



Morrison and co-workers[322] reported the observation of intra-EET by TB interaction in the rigid steroid system **XVI**. The donor chromophore was a dimethylphenylsiloxy (DPS) moiety and the acceptor was a carbonyl group, both attached to various positions of the steroid bridge. Again a superexchange mechanism was invoked to explain the observed EET for D and A moieties for which dipole−dipole interaction is not probable at interchromophore distances which exclude direct orbital overlap.

XVI



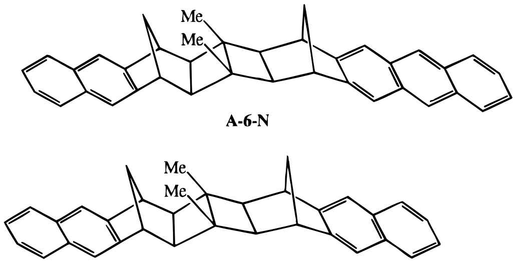
Sigman and Closs[323] have examined the free energy and structure dependence of triplet−triplet intra-EET in a series of model bichromophoric molecules. The 4-benzoylnaphthyl donor and a variety of acceptors were attached to the rigid 1,4-cyclohexanediyl spacer bridge. The results were interpreted in terms of TB superexchange mechanism directly employing intra-ELT theory. However, it was recently pointed out that such an approach may lead to inappropriate conclusions and that a modified theory, directly connected to radiationless transitions theory, as discussed in section II.D, should be employed.[80,238,262]

Gust *et al.*[324] have studied the quenching of the porphyrin triplet state by EET to the attached carotenoid system. Both donor and acceptor chromophores were attached to the benzene ring. Only exchange interaction exists in this case since triplet−triplet transfer is not allowed by dipole−dipole coupling. Although R (6.5 Å) is much larger than L (1.5 Å), thus making direct intra-EET less probable, the EET rate constant is rather high. Again this was taken as a clear manifestation of superexchange mechanism.

Recently[325] Eliott and co-workers have investigated the distance dependence of intra-EET in rigidly linked heterodinuclear Ru(II)/Fe(II) polypyridyl complexes on the interchromophore (metal−metal) distance and on the nature of the connecting bridge. They have concluded that *despite the fact that the bridges are quite different* the intra-EET rate was not influenced by this variation. Their conclusion was that the EET process which showed an exponential R dependence with $\beta = 0.87$ Å^{-1}, was not governed by either through-space or through-bond interaction and invoked a superexchange pathway that does not involve the intramolecular linkage and suggested the possibility of solvent mediated superexchange process. Similar behavior was observed for the bridged $\mathrm{Ru^{II}/Os^{II}}$ terpyridyl complexes[326] and in the isomeric porphyrin anthracene dyads.[327]

A systematic thorough investigation of short- to medium-range intra-EET in bichromophoric molecules was reported by Scholes, Ghiggino, and coworkers.[35,244,290] The main purpose of their study was to explore the role played by through-space and through-bond coupling in rigidly linked donor and acceptor moieties in the two bichromophoric molecules **XVII**. For intra-EET studies the bichromophoric molecule **A-6-N**, in which the naphthalene (**N**) donor and anthracene (**A**) acceptor chromophores were held in a known, well-defined orientation and separation (12.2 Å) by a rigid bisnorbornyl-bicyclo-[2.2.0]hexane bridge, six σ bonds in length, was used.[35] This configuration is of particular interest since EET between the naphthalene ^1L_b and ^1L_a states should not occur via a *direct* dipole–dipole coupling due to the orthogonality of the respective donor and acceptor transition dipole moments. Vibronic interactions, however, make EEyT via Coulombic interaction partially allowed although this cannot account for the measured high intra-EET rate which amounts to an EET quantum yield of 0.999, a value similar to that obtained for the *flexible* naphthalene–anthracene bichromophoric molecule **I** studied by Schnepp and Levy.[13] The results were explained in terms of a novel EET mechanism involving a combination of dipole–dipole interaction and exchange contributions (eq 58), relayed through the interchromophore bridge.[35] In addition, the related exciton interactions in the naphthalene pair bichromophoric molecule **N-6-N** were examined as well.[290a]

XVII

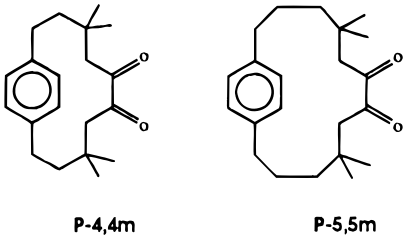


A-6-N

N-6-N

The apparent controversy[328,329] regarding the applicability of intra-ELT results for interpreting intra-EET studies seems to be settled. While TB–superexchange interaction plays a significant role in *rigidly* connected bichromophoric molecules, it is not the case for semi-*flexible* structures for which it was shown that through-space short-range exchange interaction is the dominant mechanism.[27,28,36–38,291,292] Recent studies with **P-4,4*m*** and **P-5,5*m***, **XVIII** molecules, in which **P-5,5** and **P-4,4 (III)** were modified by methyl substitution in the interchromophore bridge, confirm this conclusion.[330]

XVIII



P-4,4m

P-5,5m

IV. Supersonic Jet Studies of Intramolecular Energy and Electron Transfer in Bichromophoric Molecular Systems

A. Bichromophoric Molecular Clusters

Until recently most reported studies of intra-EET were performed in solutions where solvent effects cannot be ruled out and where complete vibrational relaxation of donor and acceptor excited electronic states precedes the EET event. Short-range inter-EET processes in the gas phase usually involve collisions[174,197] which may lead to the formation of a collision complex[331] for a period long enough for the process described by eq 8 to take place. There is evidence to support the validity of a modified Dexter formulation for the description of these gas-phase EET processes.[332,333] In general the prospects of investigating intra-EET in a bichromophoric molecule from a single excited donor vibronic state, under collisionless conditions in the low-pressure bulk gas phase, are not very high. Yet the unique conditions in a supersonic jet expansion offers a way of studying these processes in some detail. Although supersonic jet spectroscopy has been widely used for investigating molecular radiative and nonradiative processes, very few studies of EET under these conditions have been reported.

Intra-EET between D and A chromophores in a bichromophoric van der Waals molecular complex D–A, formed in a supersonic jet expansion, is a rather complicated process. Intra-EET in the jet involves interaction between specific vibronic states of the donor and acceptor molecules. However, intramolecular exciplex formation[334–339] and the limited chemical stability of the complex, which introduces dissociative channels, might interfere with observation of the intra-EET process, thus complicating the interpretation. On the other hand study of intra-EET in bichromophoric clusters is interesting as a source of information on the relative importance of these competing processes in the photophysics of such molecular systems. In an ideal case one should be able to study the dependence of the transfer efficiency on the particular vibronic excitation of the donor moiety in the bichromophoric cluster and to determine the transfer mechanism. One question that may be addressed is whether or not an EET process described by eq 8 can be observed, resulting as in solution in a dual fluorescence spectrum typical of a bichromophoric D–A cluster.

Intra-EET in a bichromophoric cluster was evidenced by Levy *et al.* in T-shape dimers of tetrazine following excitation of the $6a_0^2$ vibrational levels of the dimer.[340] The first reported study of intra-EET under supersonic jet conditions was that by Poeltl and McVey[341] on hydrogen-bonded dimers of benzoic acid. In particular the mixed dimer composed of bezoic-d_0 acid and benzoic-d_5 acid was studied. From the measurements of the dispersed fluorescence spectra they concluded that efficient EET process involving transfer from the deuterated moiety to the nondeuterated one took place. However due to limited spectral resolution no detailed quantitative interpretation was offered.

Tomioka and co-workers[342] did similar measurements on a mixed dimer of benzoic acid and *p*-toluic acid. They have concluded that intra-EET in the cluster from specific vibronic donor states competes efficiently with IVR within the donor manifold. The relative rates of energy transfer and of the IVR process were discussed in terms of the vibrational density of states of the bichromophoric complex.

Lahmani and co-workers[343] studied intra-EET in the bichromophoric system composed of perdeuterated and nondeuterated *p*-xylene (**pxd** and **px**, respectively) and *p*-difluorobenzene (**pdf**). Dispersed fluorescence resulting from excitation of the pdf was indicative of EET from the excited pdf moiety to the **px** (or **pxd**) chromophore. However, in all these cases, as in other previous intra-EET cluster studies, neither quantitative estimates of the transfer efficiency were done nor was there any indication which of the possible EET mechanisms contributed to the observed effects.

Recently two other systems of D–A clusters, the benzene (D)—biacetyl (A) pair and the naphthalene (D)—anthracene (A) pair were studied in a more quantitative fashion.[344–347] Investigations of inter-EET[348,349] and intra-EET[27,28,36,37] in solution, as well as gas-phase EET studies of the benzene–biacetyl pair[332,333] indicated that the basic EET mechanism operative in this case is the Dexter exchange interaction, whereas for the naphthalene–anthracene pair, solution studies[13,35] suggests that intra-EET proceeds via combination of exchange and dipole–dipole interactions. In a supersonic jet expansion we have to consider intra-EET from a specific excited vibronic state of D*. Thus, the overlap integral due to fluorescence of D* from vibrationally unrelaxed states overlapping with the corresponding, well-resolved, absorption spectrum of A (eq 68) should now be calculated. Such an overlap integral will exhibit sharp resonances, that depending on the excitation energy, may result in very low value of J_{dd}, amounting to low value of R_0, so that the dominating mechanism of intra-EET in the D–A complex will be the short-range Dexter-type exchange interaction, even though dipole–dipole interaction would have been the dominating EET mechanism for the two chromophores in solution.

This is the case for naphthalene and anthracene where some of the vibronic levels of naphthalene $^1B_{2u}$ state are in resonance with vibronic levels of anthracene $^1B_{2u}$, which, depending on the extent of spectral overlap, may be coupled either by exchange or by Coulombic interaction. The fluorescence excitation spectrum of naphthalene in the presence of anthracene is quenched simultaneously with the appearance of new spectral features and emission characteristic to only anthracene indicative of an intra-EET process.[344,345,347] The relative emission intensity from excited vibronic levels of the donor naphthalene moiety in the bichromophoric complex was measured as a function of added anthracene acceptor pressure. The emission intensity showed a pressure dependence which varied with the particular vibronic excitation of naphthalene. The results were interpreted by using a kinetic model which takes into account the dynamics of bichromophoric cluster formation,[350] the excitation of each chromophore, the decay dynamics of each chromophore and the additional nonradiative intra-EET channel open for the excited naphthalene. In addition, the existence of several isomers for the naphthalene–anthracene cluster, as confirmed by a recent calculation,[351] was invoked in order to rationalize the observations. Two extreme intra-EET regimes were considered. In the first, strongly interacting chromophores, manifested in highly efficient intra-EET process, are considered. In this case the donor fluorescence yield Y_D as function of the acceptor concentration C_A is given by

$$Y_D^0/Y_D = 1 + KC_A \tag{72}$$

where Y_D^0 is the donor fluorescence quantum yield in the absence of acceptor chromophores and K is the cluster association equilibrium constant which determines the amount of bichromophoric cluster in the jet.[350] It turns out that no information concerning the intra-EET dynamics can be obtained for cluster configurations for which the process is highly efficient; however, for cluster isomers in which donor and acceptor are weakly coupled the donor yield is given by[345,346]

$$Y_D^0/Y_D = 1 + \tau_f^{D^*A} k_{ET} KC_A \tag{73}$$

where $\tau_f^{D^*A}$ is the fluorescence lifetime of the donor moiety in the bichromophoric cluster. By using literature data on naphthalene and anthracene photophysical properties,[352–356] the quenching experiments yield the value of 0.3 μs^{-1} for the intra-EET rate constant for weakly interacting naphthalene and anthracene chromophores in a bichromophoric cluster.[345,347]

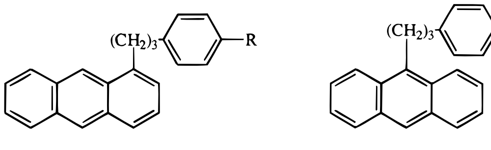
Similar results were obtained for the benzene–biacetyl cluster where intra-EET due to exchange interaction between specific vibronic levels of the benzene $^1B_{2u}$ state[357,358] and vibronic levels of the biacetyl ^1B_g state[359] was observed.[344,346] A dual fluorescence spectrum induced by excitation of the benzene chromophore in the cluster was indicative of the intra-EET process. Again apparent Stern–Volmer kinetics, eq 72, as a function of added biacetyl pressure were followed for four different vibronic excitations of the benzene moiety. In addition, the dependence of biacetyl fluorescence, as a result of intra-EET from these benzene excited levels, on biacetyl added pressure, was measured as well. The transfer rate constant depended on the particular vibrational excitation and not merely on the excess vibrational excitation testifying to the important role played by the different FCF of the coupled vibronic states in benzene and biacetyl. The vibronic state energy-dependent rate constant for the intra-EET process, for weakly interacting benzene and biacetyl, ranged between 6.3 and 24.4 μs^{-1}. The results could be fitted, in fair agreement, to the theoretical model, eq 67, of Lin and co-workers.[80,262]

While these studies demonstrate the possibility of following intra-EET in molecular clusters the interpretation is rather difficult due to the existence of many competing processes such as exciplex formation[334−339] and dissociation of the clusters.[350] In addition the low cluster concentration in the jet compared to that of unbound chromophores limits such studies to few favorable cases. Many of these complications and difficulties are eliminated when the dynamics of intra-EET from single vibronic states are studied in covalently bound donor and acceptor in bichromophoric molecules.

B. Isolated Bichromophoric Molecules

Only very few extensions of investigations of intra-EET in bichromophoric molecules in solution to supersonic jet expansions have been reported. Most studies on such systems concentrated mainly on intramolecular exciplex formation.[360−367] The importance of these studies to our discussion is in realizing that intramolecular exciplex formation may compete with intra-EET and, as demonstrated for the bichromophoric molecular system **IXX** exciplex formation, may also show specific dependence on the donor vibronic excitation.[364] The relative importance of these two processes in general is not known and no theoretical treatment addressing this issue has been attempted. On the other hand, the related process of intra-ELT in isolated, solvent-free, bichromophoric molecules has been investigated both theoretically and experimentally.[242,253,362,368−371]

IXX



1-An-DMA($R=N(CH_3)_2$)
1-An-DMA($R=N(C_2H_5)_2$)

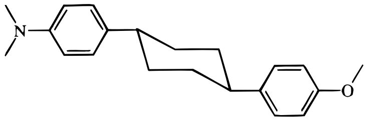
9-An-DMA($R=N(CH_3)_2$)
9-An-DMA($R=N(C_2H_5)_2$)

The first reported supersonic jet study of intra-EET was made by Ito and co-workers.[372] They have measured intra-EET between *o*-xylene and *m*-xylene connected by a chain of three methylene groups to *p*-xylene, in the bichromophoric compounds 1-*o*-tolyl-3-*p*-tolylpropane and 1-*m*-tolyl-3-*p*-tolylpropane, respectively. Both excitation and dispersed fluorescence spectra were recorded and compared with the corresponding spectra of the separated chromophores. The spectral data provided evidence for the occurrence of intra-EET from the *o*- and *m*-xylene donor chromophores to the *p*-xylene acceptor. The transfer rate was estimated to be 10^8−10^9 s^{-1}, depending on the density of states of bath modes belonging to the lower energy chromophore.

A more systematic investigation of intra-EET in isolated bichromophoric molecules was undertaken by Levy and co-workers.[40,373−375] Several bichromophoric molecules consisting of two aromatic moieties connected by an aliphatic spacer bridge were studied under jet-cooled conditions. The measurements included excitation and dispersed fluorescence spectra of all bichromophoric molecules, as well as the corresponding spectra of the individual chromophores. In addition the structures and the possible various conformations of the molecules were determined using a variety of structure determination techniques. Intra-EET was inferred from the spectra that revealed acceptor emission features upon excitation of a donor chromophore. The transfer efficiency depended on the particular vibronic excitation of the donor. The results were interpreted in terms of existing EET theories and the general theory of radiationless transitions in isolated molecules.

The first system which was studied was the bichromophoric system **XX** consisting of anisole donor (**AN**) chromophore and dimethylaniline acceptor (**DMA**) connected by a cyclohexane spacer bridge.[40] The results indicated that the intra-EET efficiency depended on the particular conformation of the bichromophoric molecule and was typical of an intra-EET process from a vibrationally unrelaxed system. The observation that EET for the *trans* isomers was slower than for the *cis* isomers was not consistent with either simple Förster picture, in which all isomers should have had the same intra-EET rate, or with Dexter formalism which predicts higher rates for the *trans* isomers.

XX



DMA-(cyclohexane)-AN

This study was next extended to a similar bichromophoric molecule keeping the same acceptor and spacer bridge and changing the donor moiety to naphthalene (**N**) instead of anisole.[373] The experimental procedure had to be changed because now the donor and acceptor emission spectra overlapped, thus preventing use of spectral changes as the signature of intra-EET. Instead the large difference between the corresponding fluorescence lifetimes provided the means of following the transfer process by monitoring the changes in lifetimes for of different vibronic levels due to intra-EET to **DMA**. The density of states increases very much at energies close to the zero-point level due to the presence of the **DMA** methyl groups, which in the case of the *cis* isomers leads to EET from naphthalene vibronic levels just above the zero-point level of **DMA**. Measurements of the intra-EET rate as a function of vibronic excitation showed that the onset of EEyT in these isomers occurs at a lower energy than that for the *trans* isomer, corresponding to a lower density of states.

A study of intra-EET in the indole (**IND**) donor connected by the cyclohexane bridge to **N** acceptor, bichromophoric system **XXI** (Figure 10), was made to determine the effect of the second acceptor excited state, S_2 in the $S_1 \rightarrow S_1$ transfer process between **IND** and **N** moieties.[374] In the energy region studied, the density of states of naphthalene S_1 state was much higher than that of the rather sparse density of its higher S_2 state. Upon excitation of **IND** strong emission of **N** and a rather weak emission of **IND** were observed, however, with the characteristic lifetime of **N**, thus indicating that intra-EET rate was much higher than the fluorescence decay of the **IND** donor moiety. The EET rate was fairly constant as a function of vibronic excitation up to the point where **IND** vibrational energy became isoenergetic with

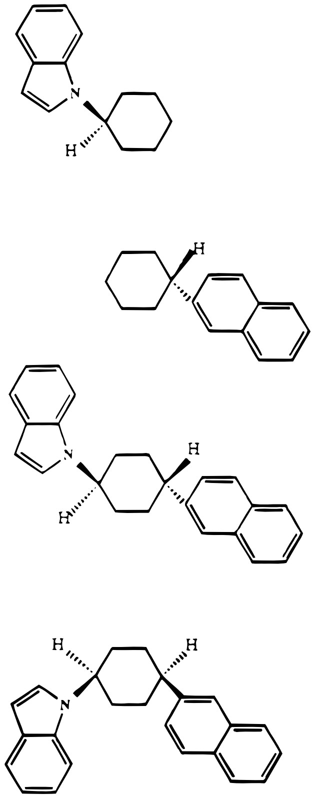


Figure 10. Bichromophoric molecules **XXI** used by Levy *et al.*[374]

naphthalene S_2 state. from this point, the rate first increased and then decreased as a function of excess vibrational excitation. Such a level structure is similar to that encountered in intersystem crossing mediated by a second excited triplet state,[375] thus a modified theory of mediated intersystem crossing was used for describing this intra-EET case.

Recently,[376] Levy and co-workers studied vibronic coupling and symmetry effects in intra-EET between two fluorene moieties in spirobifluorene. In this molecule the planes of the two fluorenes are perpendicular and so are their corresponding transition dipole moments between ground and first excited singlet states. In such a case the usual exciton coupling between the chromophores vanishes and there is an electronic degeneracy that can be removed by lowering the symmetry by substitution by either deuterium or by a methyl group. Thus, transitions due to localized states on either chromophore can be identified. In excited vibronic levels the coupling between the two chromophores is restored and intra-EET can be then measured as a function of vibrational excitation.

All these results show that intra-EET can be measured in isolated molecules and that it can be described in terms of the general theory of radiationless transitions. However, more experimental work and especially some novel theoretical models and molecular orbital calculations of electronic coupling matrix elements in EET are needed for better understanding of these phenomena.

V. Photochemical Implications of Intramolecular Electronic Energy Transfer

The present Review is mainly concerned with the photophysics underlining the mechanism of intra-EET processes in bichromophoric molecules. There are, however, some studies of the photochemical aspects of intra-EET.[1] The major contributions to the understanding of photochemistry involving intra-EET in bichromophoric molecules were made by Morrison and co-workers.[57,322,377−396] Morrison has pointed out that in the photochemistry of *trans*-4-hexen-2-one[377] one of the products the isomeric *cis*-4-hexen-2-one was produced as a result of an intra-EET process from the excited carbonyl chromophore to the nonconjugated double bond. This study was followed by photochemistry performed on two other bichromophoric molecules.[378] Morrison's conclusion was that "absorption of light at one site of the molecule results in a chemical reaction at a second, nonconjugated site". This pioneering work was followed over the years by a plethora of studies of other bichromophoric molecules were intramolecular sensitization, as a result of intra-EET was the photochemical route leading to the observed reactions.[378−396] The approach adopted in these earlier studies involved two different classes of molecules. The first class consisted of bifunctional acyclics which were flexible and relatively free of conformational constraints. In the second class of molecules well-defined cyclic substrates allowed a detailed study of the dependence of the observed triplet−triplet photophysical and photochemical energy transfer processes on the chromophore geometry.[379−385] These studies were later[386−396] extended to address problems of photochemical activation of distal functional groups in polyfunctional molecules, in particular the antenna-initiated photochemistry in trifunctional steroids should be noted. The photochemistry study was complemented by investigating the fluorescence spectroscopy of the bichromophoric molecule which revealed that the photochemical reaction was initiated by a singlet−singlet intra-EET process. In one case it was suggested that through-bond-mediated exchange interaction is involved.[322,395] Other molecules showed both singlet−singlet and triplet−triplet intra-EET where the polyfunctional steroid was suggested as a potential singlet−triplet switch, sometimes involving through-bond EET.[395]

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