

Review Paper

---

**NOVEL ASPECTS OF INTERMOLECULAR AND INTRAMOLECULAR ELECTRONIC ENERGY TRANSFER IN SOLUTION**

SHAMMAI SPEISER

*Department of Chemistry, Technion — Israel Institute of Technology, Haifa 32000 (Israel)*

(Received October 20, 1982; in revised form December 20, 1982)

**Summary**

Intermolecular and intramolecular singlet-singlet electronic energy transfer in solution is discussed. Special attention is given to novel developments such as temperature-dependent long-range dipole-dipole interactions, dual fluorescence resulting from short-range intramolecular transfer, structure determination by studies of energy transfer, the involvement of high-lying electronic states and dye laser operation using donor-acceptor pairs.

---

**1. Introduction**

Energy transfer (ET) processes play a major role in determining the dynamics of excited molecular systems. Our present understanding of these processes enables us to elucidate the mechanisms of photochemical reactions and the photophysical properties of complex molecular systems.

In the gas phase vibration-vibration, vibration-rotation and vibration-translation ET processes are of major importance. In addition, electronic to vibrational ET and electronic to electronic excitation ET are observed. ET in the gas phase is usually studied under collisionally dominated conditions. In contrast, in condensed media and especially in fluid and solid solutions intramolecular vibrational and rotational relaxation processes are extremely fast and therefore only electronic ET processes can be studied; in many cases long-range collisionless interactions promote these transfer processes.

In this review, in addition to covering the major aspects of the theory of ET in solution, we emphasize the following recent developments in this field: temperature-dependent ET, intensity-induced ET, involvement of high-lying electronic states in ET, determination of molecular structure and conformational change in macromolecules, dual fluorescence in small

molecules resulting from intramolecular ET and utilization of ET in dye laser operation. No attempt is made, however, to give a thorough literature survey of ET in photochemistry or to review its basic theory.

The fate of an electronically excited polyatomic molecule is determined by the various decay routes open to it. These include several photochemical processes such as unimolecular decomposition, isomerization or ionization. Photophysical processes such as radiative and non-radiative transitions involving electronic and vibrational relaxation often accompany photochemistry or may be the sole means for relaxation of the excited species. A non-decomposing excited molecule will decay back to its electronic ground state at a typical rate expressed in terms of its lifetime  $\tau$  which can generally be written as

$$\frac{1}{\tau(T)} = \frac{1}{\tau_{\text{rad}}(T)} + \frac{1}{\tau_{\text{nr}}(T)} \quad (1)$$

where  $\tau_{\text{rad}}(T)$  and  $\tau_{\text{nr}}(T)$  are the temperature-dependent radiative and non-radiative lifetimes respectively. The lifetimes  $\tau(T)$  can easily be measured down to picosecond time scales using laser excitation. Although the non-radiative decay times can sometimes be determined directly, in most cases they are obtained from measurements of the temperature-dependent quantum yield  $\phi(\tau)$  for the radiative process (fluorescence or phosphorescence) which is related to  $\tau_{\text{rad}}$  and  $\tau_{\text{nr}}$  by

$$\phi(T) = \frac{\tau(T)}{\tau_{\text{rad}}(T)} \quad (2)$$

Many molecules have fluorescence quantum yields of less than unity, which in many cases are independent of the molecular physical state, thus indicating a significant irreversible intramolecular relaxation. The various aspects of the radiationless transitions of molecules were the subject of a recent review by Freed [1].

In this review we are concerned with systems composed of at least two molecular species. Here, in addition to intramolecular radiative and non-radiative decay channels, excitation energy can be exchanged between molecules in an intermolecular electronic ET (inter-EET) process. In some molecular species intramolecular relaxation involves, in addition to vibrational and electronic transitions, a separate step of intramolecular electronic ET (intra-EET) between two molecular moieties incorporated in one molecule. ET processes can thus be described as a bimolecular quenching process



where excitation energy is transferred from an excited donor molecule  $D^*$  to a ground state acceptor molecule  $A$ , resulting in quenching of  $D^*$  and sensitization of  $A$ . For  $D^*$ , process (3) adds another non-radiative decay channel to its existing decay routes and thus its overall decay rate  $k(T)$  is given by the Stern-Volmer relation [2]

$$k(T) = \frac{1}{\tau(T)} + k_Q(T)[A] \quad (4)$$

where, as will be discussed below, the bimolecular quenching rate constant  $k_Q$  may depend on temperature.

### 1.1. Electronic energy transfer in solution

In all EET processes to be discussed a resonance condition between the initial state of the system  $D^* + A$  is required (Fig. 1). In solution EET is slow compared with vibrational relaxation in  $D^*$  so that the initial and final states are vibrationally relaxed and the ET transitions are determined by the Franck–Condon principle at the common overlap frequency of D and A (Fig. 1). Since lasers are now employed in photophysical studies [3], it should be noted that the donor–acceptor relation may be reversed under the influence of an intense radiation field [4]. In addition, transfer from highly excited electronic states is also possible [5]. These points are discussed below in more detail.

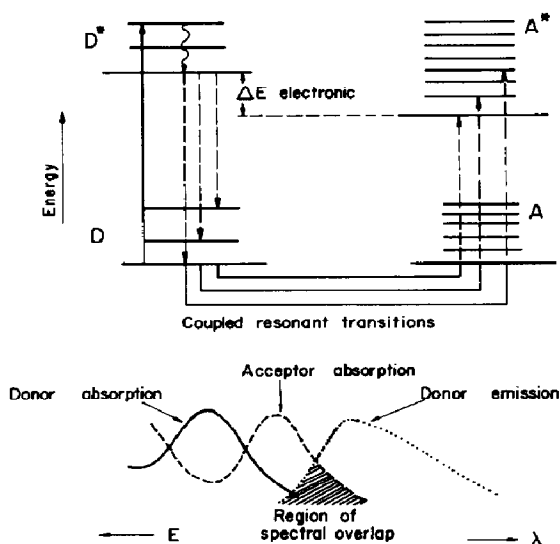


Fig. 1. Schematic energy level diagram for a typical donor–acceptor pair and associated absorption and emission spectra showing the region of spectral overlap.

ET processes are due to weak interactions between donor and acceptor molecules. The initial state of the system can be described by the wavefunction.

$$\psi_i = \frac{1}{2^{1/2}} (\psi_{D^*(1)}\psi_{A^{(2)}} - \psi_{D^*(2)}\psi_{A^{(1)}}) \quad (5)$$

and its final state by

$$\psi_f = \frac{1}{2^{1/2}} (\psi_{D^{(1)}}\psi_{A^*(2)} - \psi_{D^{(2)}}\psi_{A^*(1)}) \quad (6)$$

The interaction leading to ET can be described by an interaction hamiltonian  $H'$  and an interaction matrix element  $\beta$ :

$$\begin{aligned}\beta &= \int \psi_i H' \psi_f d\tau \\ &= \frac{1}{2} \int \psi_{D^*(1)} \psi_{A^{(2)}} H' \psi_{D^{(1)}} \psi_{A^*(2)} d\tau - \frac{1}{2} \int \psi_{D^*(1)} \psi_{A^{(2)}} H' \psi_{D^{(2)}} \psi_{A^*(1)} d\tau\end{aligned}\quad (7)$$

The first term in eqn. (7) is the coulombic interaction and the second term is the exchange interaction. When this expression is expanded in series, the first term in the coulombic contribution is the dipole-dipole interaction which is given by

$$\beta_{d-d} \approx \frac{M_D \cdot M_A}{r^3} \quad (8)$$

where  $M_D$  and  $M_A$  are the transition dipole moments of the  $D^* \rightarrow D$  and  $A \rightarrow A^*$  transitions respectively. The exchange interaction is a quantum mechanical effect arising from the symmetry properties of the wavefunctions with respect to exchange of spin and space coordinates of two electrons separated by a distance  $r_{12}$  in the D-A system. The space part of this interaction is given by

$$\beta_{ex} = \int \phi_{D^*(1)} \phi_{A^{(2)}} \frac{e^2}{r_{12}} \phi_{D^{(2)}} \phi_{A^*(1)} d\tau \quad (9)$$

where  $\phi_A$  and  $\phi_D$  are the contributions of the spatial wavefunction to the total wavefunctions  $\psi_A$  and  $\psi_D$  which include the spin functions. Integration over the spin coordinates yields the following spin selection rules (Wigner rules) for allowed ET by exchange interaction (these are the only selection rules for this type of interaction):

$$^1D^* + ^1A \rightarrow ^1D + ^1A^*$$

$$^3D^* + ^3A \rightarrow ^1D + ^5A^*$$

$$^3D^* + ^3A \rightarrow ^1D + ^3A^*$$

$$^3D^* + ^3A \rightarrow ^1D + ^1A^*$$

$$^3D^* + ^1A \rightarrow ^1D + ^3A^*$$

The transfer rate  $k_{ET}$  is given by the Golden Rule

$$k_{ET} = \frac{2\pi}{\hbar} \beta^2 \rho \quad (10)$$

where  $\rho$  is a measure of the density of the initial and final states which can interact, as determined by the Franck-Condon factors, and is related to the overlap integral  $J$ :

$$J = \int_0^\infty F_D(\bar{\nu}) \epsilon_A(\bar{\nu}) d\bar{\nu} \quad (11)$$

where  $F_D(\bar{\nu})$  and  $\epsilon_A(\bar{\nu})$  are the normalized emission spectrum of D and the extinction coefficient of A respectively, and

$$\int_0^{\infty} F_D(\bar{\nu}) d\bar{\nu} = \int_0^{\infty} \epsilon_A(\bar{\nu}) d\bar{\nu} = 1 \quad (12)$$

Substitution of eqns. (8) and (9) in eqn. (10) yields the Förster [6 - 8] relation for the long-range dipole-dipole ET rate  $k_{ET}^{d-d}$  and the Dexter relation [9] for the short-range exchange interaction ET rate  $k_{ET}^{ex}$ .  $k_{ET}^{d-d}$  is given by

$$k_{ET}^{d-d} = \tau_D^{-1} \left( \frac{R_0}{R} \right)^6 \quad (13)$$

where  $R_0$  is the critical transfer radius and

$$R_0^6 = \frac{9000(\ln 10)\chi^2\phi_D}{128\pi^5 n^4 N_0} \int_0^{\infty} F_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\nu^4} \quad (14)$$

Here  $\chi$  is an orientation factor for A and D dipoles ( $\chi^2 = 2/3$  for random distribution) and  $n$  is the refractive index of the medium. The exchange interaction ET rate is given by [9]

$$k_{ET}^{ex} = \frac{2}{\hbar} KJ \exp\left(-\frac{2R}{L}\right) \quad (15)$$

where  $R$  is the distance between the D and the A molecules,  $L$  is the average orbital radius involved in  $\psi_i$  and  $\psi_f$ , and  $K$  is a constant which is not related to any spectroscopic experimental parameter and thus, unlike  $R_0$ , has only a qualitative value. However, from a comparison of eqns. (13) and (15) we can conclude that unless  $R$  is less than 20 Å energy will be transferred mainly by the Förster mechanism.

In solution molecular diffusion may play a role in the ET process. In the limiting case where  $R_0 < 20$  Å exchange interaction is noticeable and the ET rate may become diffusion controlled [10]:

$$k_Q = \frac{8RT}{3000\eta} \quad (16)$$

where  $\eta$  is the viscosity of the medium. In other words the rate-determining step in the transfer process is the rate of molecular encounters; the transfer itself is fast and is governed by eqn. (15). In general the transfer kinetics in solution do not follow the simple Förster formula and various modifications have been suggested [10]. However, when D and A are embedded in a rigid medium, such as a polymer matrix, diffusion processes are excluded and the only transfer route possible is the long-range dipole-dipole interaction. In rigid media the normalized fluorescence signal  $P(t)$  is no longer exponential and the expression obtained for  $P(t)$  after averaging over a random distribution of  $R$ s is given by [8, 10]

$$P(t) = \exp\left(-\frac{t}{\tau_D}\right) \exp\left\{-\frac{4}{3} \pi^{3/2} [A] R_0^3 \left(\frac{t}{\tau_D}\right)^{1/2}\right\} \quad (17)$$

or

$$\delta(t) \equiv P(t) \exp\left(\frac{t}{\tau_D}\right) = \exp\left\{-\frac{4}{3}\pi^{3/2}[A]R_0^3\left(\frac{t}{\tau_D}\right)^{1/2}\right\} \quad (18)$$

Equation (18) shows that  $R_0$  can be obtained from a plot of  $\ln t$  versus  $t^{1/2}$ . A number of D-A pairs that follow Förster kinetics (eqns. (17) and (18)) have been studied [11 - 14]. Typical  $R_0$  values are summarized in Table 1 and a typical case of Förster kinetics is shown in Fig. 2 [12, 14]. A handbook of calculated  $R_0$  values for numerous D-A pairs is available [16].

Critical radii obtained from eqns. (17) and (18) can be related to  $k_{ET}^{d-d}$  by [10]

TABLE 1

Calculated and measured Förster ET radii

Donor	Acceptor	Calculated $R_0$ (Å)	Measured $R_0$ (Å)	Reference
Anthracene	Perylene	31	33	[15]
Perylene	Rubrene	38	41	[15]
9,10-dichloroanthracene	Perylene	40	45	[15]
Anthracene	Rubrene	23	28	[15]
Coronene	Rhodamine 6G	30	32	[14]
Coronene	Acridine yellow	38	38	[14]
Benzperylene	Acridine yellow	35	37	[14]

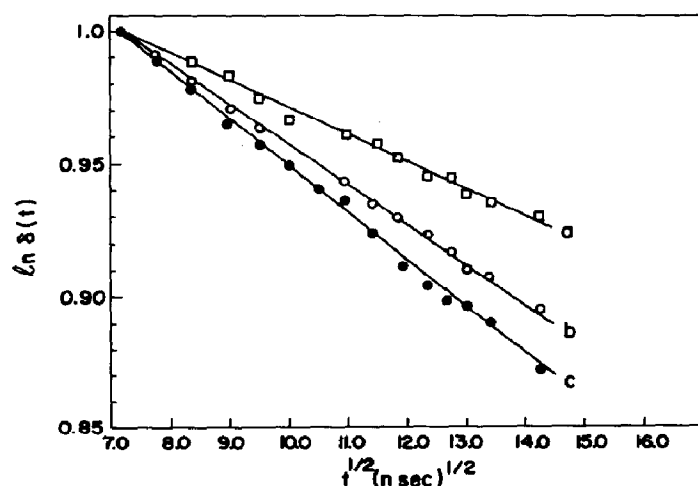


Fig. 2. Förster kinetics exhibited by coronene (donor) and rhodamine 6G (acceptor) [12, 14] in poly(methyl methacrylate) matrices at 295 K: curve a, coronene +  $0.72 \times 10^{-3}$  M rhodamine 6G; curve b, coronene +  $1.08 \times 10^{-3}$  M rhodamine 6G; curve c, coronene +  $1.26 \times 10^{-3}$  M rhodamine 6G.  $\delta(t)$  was determined for each temperature from similar non-exponential fluorescence decay measurements (eqns. (17) and (18)) and temperature-dependent lifetimes (Fig. 3).

$$k_{\text{ET}}^{\text{d-d}} = k_{\text{Q}}[A] = \frac{A}{\tau_{\text{D}}[A]_0} \quad (19)$$

where  $[A]_0$  is the critical acceptor concentration for which

$$[A]_0 = (\tau_{\text{D}}k_{\text{Q}})^{-1} = (4\pi R_0^3/3)^{-1} \quad (19a)$$

In less viscous media than polymer matrices it is possible that molecules will be displaced during the transfer process owing to thermal diffusion. This motion will distort the simple Förster picture and incorporation of the diffusion equation into the treatment will be required.

In what follows we shall focus on ET studies which exclude diffusion so that this point will not be discussed in more detail. The reader is referred to the original papers [17 - 21] in which treatments of energy transfer via dipole-dipole and exchange interaction to moving acceptors are given.

## 2. Recent examples and novel aspects of energy transfer studies

Most studies of EET have been concerned with the verification of Förster's and Dexter's relations [3, 10 - 14]. Here we shall concentrate on some novel effects in EET processes. In recent years modifications to the simple Förster picture to include the thermal activation involved in the transfer process have been investigated. These effects are studied in detail in Section 2.1. The use of intra-ET in studies of molecular conformation is discussed in Section 2.3. The approach to the experimental verification of Dexter's relation (eqn. (15)) is described in Section 2.2. ET from high-lying excited electronic states is discussed in Section 2.4. Finally, the use of EET in dye laser operation is analysed in Section 2.5.

### 2.1. Temperature-dependent Förster kinetics

Temperature-dependent Förster kinetics are discussed in ref. 14. As implied by eqns. (1) and (2), in general we expect to observe temperature-dependent lifetimes and fluorescence (or phosphorescence) quantum yields. Of particular interest are those molecules in which, owing to high symmetry, the lowest electronic transition is forbidden. Aromatic molecules serve as a good example [22]. In these circumstances studies of radiative and non-radiative vibronic coupling, temperature-dependent fluorescence decay, involvement of higher electronic states in the fluorescence decay and pump intensity effects may yield useful information about the various decay channels of the molecule. In particular the temperature dependence of the fluorescence quantum yield and of the fluorescence lifetime is important for the elucidation of the mechanism by which excitation energy in large molecules is dissipated. Both radiative and non-radiative decay channels may depend on temperature. Albrecht [23] has shown that a temperature dependence associated with the Boltzmann distribution of active low frequency vibrations is observed when Herzberg-Teller vibronic coupling

between two electronic states determines the transition intensity. This mechanism affects the radiative decay rate which will obey an Arrhenius-type temperature dependence [23]. In the absence of temperature-dependent non-radiative transitions the reciprocal fluorescence lifetime  $1/\tau(T)$  still follows an Arrhenius behaviour, but the fluorescence quantum yield  $\phi(T)$  does not. However, non-radiative processes such as intersystem crossing [24] and internal conversion are usually temperature dependent [22, 25]. Thus, eqns. (1) and (2) generally hold, showing that for a temperature-independent radiative decay  $\phi(T)$  is proportional to  $\tau(T)$ . Since the coupling mechanisms that are responsible for radiative decay are also involved in EET [10], it seems worthwhile to study temperature effects on the ET rate.

Good candidates for studies of temperature-dependent inter-ET are systems in which the photophysical properties of the acceptor are temperature independent while those of the donor show a strong dependence on temperature. In particular we should look for donor molecules whose radiative properties exhibit an increase in  $\phi$  as a function of temperature with a corresponding decrease in  $\tau(T)$ . Such behaviour is usually indicative of a larger radiative vibronic coupling at higher temperatures which increases the rate of a forbidden  $S_1 \rightarrow S_0$  transition due to thermal population of higher vibrational modes [23, 26]. In this case we expect an Arrhenius-type dependence for  $1/\tau$ . An analysis of an appropriate kinetic scheme yields [14]

$$\frac{1}{\tau^D(T)} = \frac{1}{\tau^D(0)} \left\{ 1 + \alpha^D \exp\left(-\frac{\Delta E}{RT}\right) \right\} \quad (20)$$

Coronene and 1,12-benzperylene meet these conditions [14], and indeed their fluorescence lifetimes exhibit the behaviour predicted by eqn. (20). Figure 3 shows the Arrhenius plots for the fluorescence lifetimes of coronene and 1,12-benzperylene. The activation energies and the kinetic parameters extracted from these plots are summarized in Table 2. Carter *et al.* [27] obtained a similar temperature dependence with the same value of  $\Delta E$  for 1,12-benzperylene. The activation energies obtained can be associated with the frequencies of low-lying vibrational levels in  $S_1$ . In coronene  $\Delta E = 415 \pm 80 \text{ cm}^{-1}$  corresponding to two  $e_{2g}$  modes at 370 and 570  $\text{cm}^{-1}$  [28] which allow the forbidden  ${}^1B_{2u} \rightarrow {}^1A_{1g}$  ( $S_1 \rightarrow S_0$ ) transition. In 1,12-benzperylene  $\Delta E = 710 \pm 50 \text{ cm}^{-1}$  which fits the antisymmetric  $\nu_2$  mode at 764  $\text{cm}^{-1}$  [29].

Lin [30] has derived an expression for a temperature-dependent EET rate  $k_{\text{ET}}(T)$ . The derivation involved calculation of the enhancement of the ET rate as a result of the thermal population of high vibrational states in  $D^*$  which will have a higher  $\phi$  and which will also increase the overlap with the coupled acceptor states. In its simplest form the result for  $k_{\text{ET}}(T)$  is [30]

$$k_{\text{ET}}(T) = k_{\text{ET}}(0) \left\{ 1 + \beta^D \exp\left(-\frac{\Delta E}{RT}\right) \right\} \quad (21)$$

Comparison of eqns. (20) and (21) shows that the same functional dependence on  $T$  is maintained since the same photophysical properties, *i.e.*



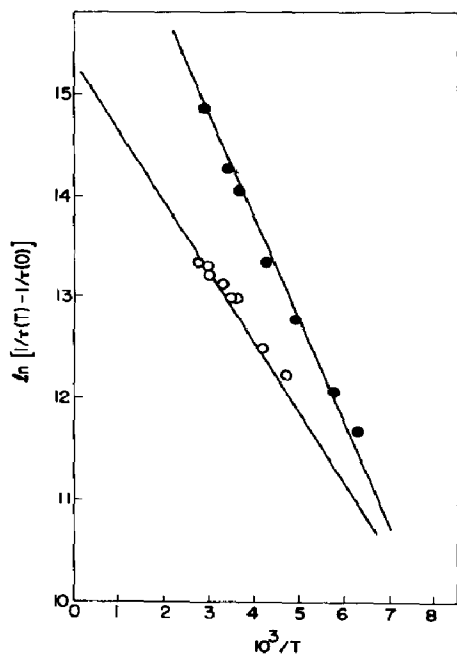


Fig. 3. Arrhenius plots for the fluorescence lifetimes of coronene (○) and 1,12-benzperylene (●).

TABLE 2

Temperature-dependent energy transfer parameters for some donor-acceptor pairs

	Coronene- rhodamine 6G	Coronene- acridine yellow	1,12-benz- perylene- acridine yellow
$\tau_D(0)$ (ns)	321	321	133
$R_0(0)$ (experimental) (Å)	32	38	37
$R_0$ (calculated) (Å)	30	38	35
$\alpha^D$	1	1	8
$\beta^D$	26	10	80
$k_Q(0) = k_{ET}(0)/[A]$ ( $l \text{ mol}^{-1} \text{ s}^{-1}$ )	$1.4 \times 10^{10}$	$2.4 \times 10^{10}$	$5.2 \times 10^{10}$
$\Delta E$ from eqn. (21) ( $\text{cm}^{-1}$ )	473	510	705
$\Delta E$ from eqn. (20) ( $\text{cm}^{-1}$ )	415	415	710

radiative coupling of the donor, are involved. The only difference lies in the fact that while  $\alpha^D$  involves donor properties  $\beta^D$  might in general also depend on the acceptor properties through the overlap integral  $J$ .

Temperature-dependent inter-EET has been demonstrated for coronene and 1,12-benzperylene with suitable dye acceptors incorporated in a poly-(methyl methacrylate) matrix [12, 14]. Typical Arrhenius plots of  $k_{ET}$  for these D-A pairs are shown in Fig. 4. The kinetic parameters obtained and

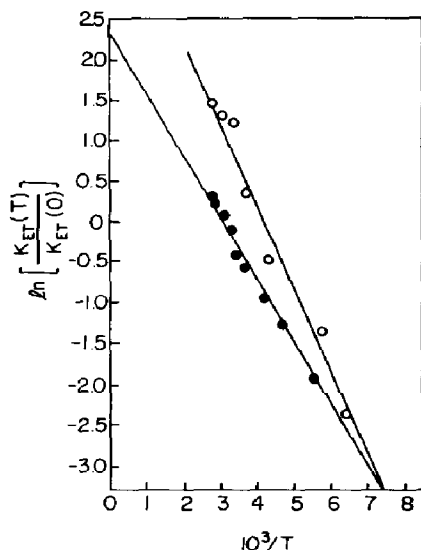


Fig. 4. Arrhenius plots of the temperature-dependent energy transfer rates for coronene-rhodamine 6G (●) and benzperylene-acridine yellow (○) [14]. Each rate constant is determined from the corresponding temperature-dependent  $R_0$  (Fig. 2 and eqns. (17) and (18)) using eqn. (19).

the calculated values for  $R_0$  are summarized in Table 2. It is evident that the  $\Delta E$  obtained from fluorescence decay data are in agreement with those obtained from ET data. Moreover, when the same D-A pairs are in fluid solution the ET is governed by diffusion-controlled kinetics (eqn. (16)) which results in a completely different  $\Delta E$  which is related to the temperature-dependent viscosity of the medium [12, 14]. Thus  $\Delta E$  is not associated with the acceptor employed nor is it a property of the polymer. It must be a molecular property of the donor, *i.e.* the same vibronic levels are involved in both photophysical processes. This statement is supported indirectly by the results obtained for pyrene in which  $\tau$  is a strong function of temperature owing to the occurrence of temperature-dependent *non-radiative* decay.  $\tau_r$  for this molecule is temperature independent [31] and it is not surprising that  $R_0$  is also independent of temperature [13]. This indicates that those molecules which exhibit the effects of radiative vibronic coupling in the features of their fluorescence decay also undergo temperature-dependent inter-EET.

## 2.2. Short-range intramolecular electronic energy transfer in small bichromophoric molecules

Short-range intramolecular EET in small bichromophoric molecules is discussed in ref. 32. So far we have discussed inter-EET processes in which D and A constitute different molecular systems. In solution ET proceeds by a combination of long-range dipole-dipole interaction and diffusion processes involving collisions and ET of the short-range exchange interaction type. A situation can be envisaged in which D and A molecules are forced

to stay in close proximity at distances in which the short-range transfer is the dominant route for the ET process. The easiest way to realize these situations is when D and A are two moieties of the same bichromophoric molecule.

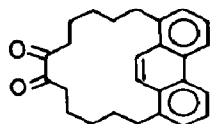
Interaction between the excited and the ground states of bichromophoric molecules has been a subject of considerable interest [33]. It is manifested in chemical reactions, complex formation [34, 35], biological systems [36], dye laser operation [37] (see below) and photophysical processes such as EET [38].

In these cases control of the spatial relation between donor and acceptor groups exists without the randomness characteristic of intermolecular interactions. Further, intra-EET can be observed in rigid or viscous media where encounters between separated molecules leading to short-range inter-EET are not possible.

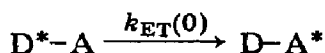
The first investigations of intra-ET were reported by Weber and co-workers [39] and Schnepf and Levy [40]. Schnepf and Levy [40] observed anthracene fluorescence irrespective of the exciting wavelength in compounds containing naphthalene and anthracene moieties joined by a variable number of  $-\text{CH}_2-$  groups. The quantum yield was independent of the number of methylene groups separating the two chromophores. Other workers [38] have examined similar systems involving isolated chromophores. In some cases the donor and acceptor were attached to a rigid system so that their spatial relation 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 a knowledge of the excitation and emission spectra of each moiety alone and comparison with spectra of the bichromophoric species.

In all these cases complete quenching of donor moiety fluorescence was observed with concomitant emission solely from the acceptor moiety. This was true even for donor chromophores with high fluorescence quantum yields. However, observed yields of emission from  $\text{A}^*$  were less than the theoretical maximum implying that  $\text{D}^*$  in the bichromophoric molecule decayed non-radiatively to the ground electronic state through channels unavailable to the separate D chromophore. Residual  $\text{D}^*$  emission might be anticipated in systems where non-radiative decay is not enhanced in the bichromophoric molecule and/or where the rate of intra-EET is similar to the fluorescence decay of  $\text{D}^*$ . Moreover, this residual emission is necessary to distinguish between a mere fast non-radiative decay of the composite D-A molecule and a genuine case of intra-EET.

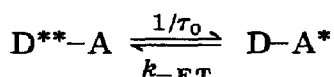
The ideal bichromophoric molecule for studies of intra-EET should have absorption and emission which can be described by a superposition of the corresponding spectra of its constituent moieties. This condition is met by 1,8-(6',7'-dioxododecamethylene)phenanthrene [32, 41]:



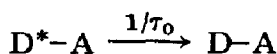
The important property of this molecule is the fact that the energy absorbed by the phenanthrene chromophore is transferred in part to the  $\alpha$ -diketone and *both chromophores* emit their characteristic fluorescence spectra. This dual fluorescence due to the intra-EET process in solution has been extensively studied as a function of the excitation frequency and the sample temperature [42]. It was demonstrated that energy is transferred efficiently to the  $\alpha$ -diketone moiety from a thermally activated state of the bichromophoric molecule [42]. The rate of this ET is comparable with the relaxation rate of the activated state. In contrast, the transfer process from the ground vibrational level of the first excited state of the phenanthrene moiety is rather slow (about  $10^7 \text{ s}^{-1}$ ). This study has shown that, in general, the dynamics of the intra-EET process can be described by the following kinetic scheme [32]:



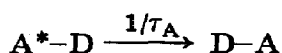
(intra-EET from the ground vibrational state of  $D^*$ )



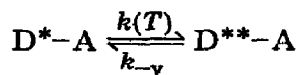
(intra-EET from an excited vibrational state  $D^{**}$  of  $D^*$ )



(fluorescence decay of the donor moiety)



(fluorescence decay of the acceptor moiety)



(thermal population of  $D^{**}$  states)

where  $D^{**}$  is an excited vibrational state of the donor excited electronic state  $D^*$ . ET may be enhanced by thermal population of excited vibrational states which are better coupled to A than the ground vibrational state is. This may involve symmetry correlations or genuine conformation changes of  $D^*$ . A temperature-dependent intra-EET rate (similar to eqn. (21)) is thus expected. In addition, intensity-dependent two-photon excited intra-EET from a highly excited state (not included in this kinetic scheme) is possible [32].

Another bichromophoric system in which dual fluorescence and intra-EET are observed was extensively studied by Zimmerman *et al.* [43]. Here the exchange interaction leading to a Dexter-type intra-EET rate (eqn. (15))

was established by changing the distance between the A and D moieties of the so-called "rod-like" molecule. It is expected that studies of this nature will clarify the relative importance of exchange interactions and dipole-dipole interactions in intra-EET.

### 2.3. Structural studies of macromolecules by long-range intramolecular electronic energy transfer

In small bichromophoric molecules short-range exchange interaction prevails and Dexter's eqn. (15) holds. A situation characteristic of polymers and biopolymers is where two or more interacting chromophores are attached to the polymeric "backbone". If the sequence of D and A molecules along the polymeric chain is regular and the distance  $R$  from D to A is larger than 15 Å then energy will be transferred from the donor moiety to the acceptor chromophore by dipole-dipole interaction at a rate governed by eqn. (13). Thus structural information regarding the macromolecule can be gained [44, 45]. Equation (13) provides a chemical ruler for determining  $R$  from measurements of  $k_{ET}^{d-d}$ .

A beautiful demonstration of the practical use of eqns. (13) and (14) for the structural analysis of macromolecules has been given in a series of studies performed by Steinberg and coworkers [46, 47]. They used solutions of oligopeptides of various chain lengths with  $N^5$ -(2-hydroxyethyl)-L-glutamine as the repeating unit and naphthalene and dansyl as the D and A moieties respectively. These chromophores were attached to the far ends of peptides composed of four, five, six, seven, eight and nine repeating units. Dual fluorescence due to long-range intra-ET ( $R_0 = 22$  Å) was observed and the observed fluorescence lifetime of the donor and the fluorescence quantum yield were utilized to determine  $k_{ET}^{d-d}$  which in turn yielded the desired distribution of end-to-end distances in the peptide chain.

In addition the results could be used to determine the effect of the relative orientation of the donor and the acceptor on the probability of ET. The brownian motion of the ends of the chain was investigated by varying the viscosity of the solvent.

### 2.4. Intermolecular electronic energy transfer from an upper singlet state of a polyatomic molecule

The Förster-Dexter EET processes discussed so far pertain to resonance transfer from the lowest electronically excited state of the donor which is usually long enough to allow kinetic investigation of the transfer process. The advent of picosecond laser pulse excitation has enabled EET from short-lived upper singlet states to be followed. Such an experiment has been performed with rhodamine 6G as the donor and 2,5-bis(5'-*tert*-butyl-2-benzoxazolyl)thiophene (BBOT) as the energy acceptor [5]. The  $S_2$  state of the rhodamine 6G molecule was excited by consecutive absorption of the first and second harmonics of a mode-locked  $Nd^{3+}$  glass laser. The ET was manifested by enhancement of the BBOT fluorescence. The intensity dependence of the EET yield was found to follow an extension of Förster-Dexter

predictions. In addition the results provided a value of  $3 \times 10^{-14}$  s for the lifetime of the  $S_2$  state of rhodamine 6G.

### 2.5. Dye lasers based on electronic energy transfer

Dye lasers based on EET are discussed in refs. 48 and 49. ET dye lasers (ETDLs) serve as an excellent example of the practical use of ET processes. In a typical ETDL system energy pumped into a donor-absorber is transferred either intermolecularly or intramolecularly to a lasing acceptor. The EET process can serve three purposes.

(1) The frequency range of dye laser operation can be increased (towards the IR) by using one pumping source (e.g. a nitrogen laser). A wide range of dyes may be excited even when the dyes do not directly absorb the laser frequency [19, 50 - 61].

(2) The dye laser performance can be improved by increasing its gain for a given pump power [55]. This can be achieved by a judicious choice of a D-A pair for which losses due to photoquenching [62] and other effects, which are not so pronounced in an ETDL configuration, are minimized. A complete computer simulation of such an ETDL has been performed [48]. For example, in the anthracene-perylene ETDL [54, 63], perylene is made to lase although perylene alone is a very poor lasing medium. Figure 5 shows the results for this ETDL system. The experimental points for the gain  $G$  obey the relation [48, 54]

$$G = \frac{\sigma_e \tau_A \alpha [D] [A]}{\beta [A] + \tau_A \alpha [D]} \quad (22)$$

for the dependence of  $G$  on  $[D]$  and  $[A]$ . Here  $\sigma_e$  is the stimulated emission cross section for the lasing acceptor dye and  $\alpha$  and  $\beta$  are quantities proportional to the pumping and ET rates.

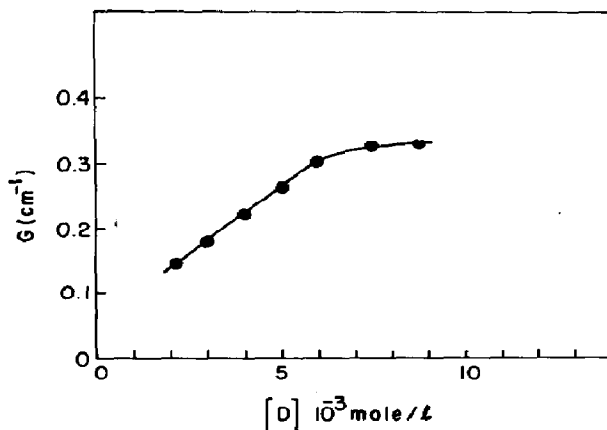


Fig. 5. Gain (at 474 nm) of the anthracene-perylene ETDL as a function of the anthracene concentration for a fixed ratio of anthracene to perylene concentrations ( $[D]/[A] = 1$ ). The nitrogen laser pump intensity was  $100 \text{ MW cm}^{-2}$ .

(3) Intra-EET in specially constructed bichromophoric dyes has been shown to improve the overall efficiency of flash-lamp-pumped dye lasers [41]. In this case the pump energy which is not efficiently absorbed by the acceptor dye molecule is very efficiently absorbed by the donor moiety and transferred to the acceptor dye moiety. This also serves to reduce the heat generated by competing non-radiative transitions.

Table 3 summarizes some useful ETDL systems, their tuning ranges and their optimum concentration ratios.

TABLE 3  
Systems of energy transfer dye lasers

<i>Donor absorber</i>	<i>Acceptor laser</i>	[D]/[A]	<i>Tuning range</i> (nm)	<i>Reference</i>
Coumarine	Acriflavine	50	470 - 500	[52]
Coumarine	Rhodamine B	35	600 - 650	[52]
2,5-diphenyloxazole	Perylene	1.3	450 - 490	[50]
2,5-diphenyloxazole	9,10-diphenylanthracene	120	400 - 440	[50]
<i>p</i> -bis( <i>o</i> -methylstyryl)-benzene	Perylene	70	450 - 490	[50]
Anthracene	Perylene	3	450 - 490	[50, 54]
Coumarine	Rhodamine 6G	1	560 - 620	[57]
Rhodamine 6G	Cresyl violet	1	630 - 690	[51]
Rhodamine 6G	3,3'-diethyloxadicarbo- cyanine	1	602 - 660	[64]
Rhodamine B	3,3'-diethyloxadicarbo- cyanine	1	615 - 676	[64]
Rhodamine B	Cresyl violet	1	612 - 695	[64]
Rhodamine B	DTDC <sup>a</sup>	1	682 - 758	[64]
Rhodamine 6G	Safaranin T	1	590 - 620	[65]

<sup>a</sup>DTDC, 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinylidene-1,3-pentadienyl)benzothiazolium iodide.

### 3. Concluding remarks

As is often the case, this review reflects the author's view of a developing field. Thermally enhanced ET rates are shown to play a role in inter-EET and intra-EET processes. For inter-EET processes a modification of Förster kinetics as a function of temperature is required which may involve vibronic interactions which are also manifested in other radiative and non-radiative photophysical processes. A complete ET theory incorporating these effects is still missing.

A Dexter-type exchange interaction can be examined in small bichromophoric molecular systems in which the rigid chemical link between the moieties is changed. Dual fluorescence is expected to be an inherent ingredient of an intra-EET process. ET due to long-range dipole-dipole interaction can be applied to the determination of the conformation of and conformational changes in macromolecules.

ET-based dye lasers are practical devices which make use of the ET process and serve as good model systems for further studies of inter-EET and intra-EET.

The use of high intensity lasers extends ET studies to cases in which high-lying electronic states are involved.

All these novel aspects of ET emphasize the major role that this process plays in biology, photochemistry and photophysics in solutions.

## References

- 1 K. F. Freed, *Acc. Chem. Res.*, **11** (1978) 74.
- 2 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966.
- 3 S. Kimel and S. Speiser, *Chem. Rev.*, **77** (1977) 472.
- 4 A. Ben-Reuven and J. Jortner, *Chem. Phys. Lett.*, **41** (1976) 401.  
I. Kaplan and J. Jortner, *Chem. Phys. Lett.*, **51** (1977) 1.
- 5 I. Kaplan and J. Jortner, *Chem. Phys.*, **32** (1978) 381.
- 6 Th. Förster, *Z. Naturforsch.*, **49** (1949) 321; *Z. Elektrochem.*, **53** (1949) 93.
- 7 Th. Förster, *Discuss. Faraday Soc.*, **27** (1959) 7.
- 8 Th. Förster, in O. Sinanoglu (ed.), *Modern Quantum Chemistry*, Vol. 3, Academic Press, New York, 1968, p. 93.
- 9 D. L. Dexter, *J. Chem. Phys.*, **21** (1953) 836.
- 10 N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra*, Dekker, New York, 1979, Chap. 5, and references cited therein.
- 11 R. G. Bennet, *J. Chem. Phys.*, **41** (1964) 3037.
- 12 R. Katraró, A. Ron and S. Speiser, *Chem. Phys. Lett.*, **52** (1977) 16.
- 13 N. Mataga, H. Obashi and T. Okada, *J. Phys. Chem.*, **73** (1969) 370.
- 14 R. Katraró, A. Ron and S. Speiser, *Chem. Phys.*, **42** (1979) 121.
- 15 W. Ware, *J. Chem. Phys.*, **66** (1962) 455.
- 16 I. B. Berlman, *Energy Transfer Parameters of Aromatic Compounds*, Academic Press, New York, 1973.
- 17 M. Yokota and O. Tanimoto, *J. Phys. Soc. Jpn.*, **22** (1967) 779.
- 18 A. Allinger and A. Blumen, *J. Chem. Phys.*, **72** (1980) 4608; **75** (1981) 2762.
- 19 U. K. A. Klein, R. Frey, M. Hauser and U. Gösele, *Chem. Phys. Lett.*, **41** (1976) 139.
- 20 Y. Elkana, J. Feitelson and E. Katchalski, *J. Chem. Phys.*, **48** (1968) 2399.
- 21 N. Nakashima, Y. Kume and N. Mataga, *J. Phys. Chem.*, **79** (1975) 1788.
- 22 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970.
- 23 A. C. Albrecht, *J. Chem. Phys.*, **33** (1960) 156.
- 24 S. Schoof, H. Gusten and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.*, **81** (1977) 305.
- 25 H. Lami, *Chem. Phys. Lett.*, **21** (1973) 140.
- 26 D. L. Dexter and W. E. Fowler, *J. Chem. Phys.*, **47** (1967) 1379.
- 27 J. G. Carter, L. G. Christophorou and C. E. Easterly, *J. Chem. Soc., Faraday Trans. II*, **69** (1973) 471.
- 28 K. Ohno, T. Kajiwara and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **45** (1972) 996.
- 29 J. B. Birks, C. E. Easterly and L. G. Christophorou, *J. Chem. Phys.*, **66** (1977) 4231.
- 30 S. H. Lin, *Mol. Phys.*, **21** (1971) 853.
- 31 J. L. Kroop, W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, **73** (1969) 1747.
- 32 D. Getz, A. Ron, M. B. Rubin and S. Speiser, *J. Phys. Chem.*, **84** (1980) 768.
- 33 F. C. De Schryver, N. Boens and J. Put, *Adv. Photochem.*, **10** (1977) 359.
- 34 H. D. Becker and K. Sandors, *Chem. Phys. Lett.*, **53** (1978) 228.  
H. D. Becker, K. Sandors, B. Karlsson and A. M. Pilotti, *Chem. Phys. Lett.*, **53** (1978) 232.
- H. D. Becker and K. Sandors, *Chem. Phys. Lett.*, **55** (1978) 458.



- 35 M. Yamamoto, K. Goshiki, T. Kanaya and Y. Nishijima, *Chem. Phys. Lett.*, **56** (1978) 333.  
I. H. Borbent, A. W. J. de Long, I. W. Verhoeven and Th. J. de Boer, *Chem. Phys. Lett.*, **57** (1978) 530.  
P. Sasman, J. W. Verhoeven and Th. J. de Boer, *Chem. Phys. Lett.*, **59** (1978) 381.
- 36 R. H. Conrad and L. Brand, *Biochemistry*, **7** (1968) 5777.  
T. Tamaki, *Bull. Chem. Soc. Jpn.*, **46** (1973) 2527.  
Y. J. Lee, W. A. Summers and J. G. Burr, *J. Am. Chem. Soc.*, **99** (1977) 7679.
- 37 F. P. Schäfer, Zs. Bor, W. Luttke and B. Liphardt, *Chem. Phys. Lett.*, **56** (1978) 454.  
B. Kopainsky, W. Kaiser and F. P. Schäfer, *Chem. Phys. Lett.*, **56** (1978) 458.
- 38 A. A. Lamola, P. A. Leermakers, G. W. Byers and G. S. Hammond, *J. Am. Chem. Soc.*, **87** (1965) 2322.  
A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43** (1965) 2129.  
D. Breen and R. A. Keller, *J. Am. Chem. Soc.*, **90** (1968) 1935.  
S. A. Latt, H. T. Cheung and E. R. Blout, *J. Am. Chem. Soc.*, **90** (1968) 6897.  
R. A. Keller and L. Y. Dolby, *J. Am. Chem. Soc.*, **91** (1969) 1273.  
N. Filipescu, J. R. De Member and F. L. Minn, *J. Am. Chem. Soc.*, **91** (1969) 4169.  
J. B. Bunting and N. Filipescu, *J. Chem. Soc. B*, (1970) 1750.  
J. A. Nairn, C. L. Braun, P. Caluwe and M. Szwarc, *Chem. Phys. Lett.*, **54** (1978) 469.
- 39 G. Weber, *Trans. Faraday Soc.*, **44** (1950) 185.  
G. Weber, *Nature (London)*, **180** (1957) 1409.  
G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **54** (1958) 640.
- 40 O. Schnepf and M. Levy, *J. Am. Chem. Soc.*, **84** (1962) 172.
- 41 S. Speiser, R. Katraró, S. Welner and M. B. Rubin, *Chem. Phys. Lett.*, **61** (1969) 199.
- 42 D. Getz, A. Ron and S. Speiser, *J. Mol. Struct.*, **61** (1980) 61.
- 43 H. E. Zimmerman, T. D. Goldman, T. K. Hirzel and S. P. Schmidt, *J. Org. Chem.*, **45** (1980) 3934.
- 44 A. Anders, *Opt. Commun.*, **26** (1978) 339.
- 45 P. K. Das, M. V. Encinas and J. C. Scaiano, *J. Photochem.*, **12** (1980) 357, and references cited therein.
- 46 E. Haas, M. Wilchek, E. Katchalski-Katzir and I. Z. Steinberg, *Proc. Natl. Acad. Sci. U.S.A.*, **72** (1975) 1807.
- 47 E. Haas, E. Katchalski-Katzir and I. Z. Steinberg, *Biopolymers*, **17** (1978) 11; *Biochemistry*, **17** (1978) 5064.
- 48 S. Speiser and R. Katraró, *Opt. Commun.*, **27** (1978) 287.
- 49 S. Speiser, *Appl. Phys.*, **19** (1979) 165.
- 50 I. B. Berlman, M. Rokni and C. R. Goldschmidt, *Chem. Phys. Lett.*, **22** (1973) 458.
- 51 A. Dienes and M. Madden, *J. Appl. Phys.*, **44** (1973) 4161, 5050.
- 52 S. A. Ahmed, J. S. Gergely and D. Infante, *J. Chem. Phys.*, **61** (1974) 1584.
- 53 G. A. Kenney-Wallace, J. H. Flint and S. C. Wallace, *Chem. Phys. Lett.*, **32** (1975) 71.
- 54 E. Weiss and S. Speiser, *Chem. Phys. Lett.*, **42** (1976) 220.
- 55 T. Urisu and K. Kajiyama, *J. Appl. Phys.*, **47** (1976) 3559, 3563.
- 56 K. Nagashima and T. Asakura, *Opt. Commun.*, **19** (1976) 7.
- 57 P. Burlamacchi and D. Cutler, *Opt. Commun.*, **22** (1977) 283.
- 58 Y. Kusumoto, H. Sato, K. Macno and S. Yahiro, *Chem. Phys. Lett.*, **53** (1978) 388.
- 59 K. B. Eisenthal, *Chem. Phys. Lett.*, **6** (1970) 155.
- 60 R. W. Anderson, R. M. Hochstrasser, H. Lutz and G. W. Scott, *J. Chem. Phys.*, **61** (1974) 2500.
- 61 R. M. Hochstrasser and A. C. Nelson, *Opt. Commun.*, **18** (1976) 361.
- 62 S. Speiser, R. van der Werf and J. Kommandeur, *Chem. Phys.*, **1** (1973) 297.  
S. Speiser, *Chem. Phys.*, **6** (1974) 479.  
S. Speiser and A. Bromberg, *Chem. Phys.*, **9** (1975) 191.
- 63 S. Speiser, *Opt. Commun.*, **29** (1979) 213.
- 64 F. B. Dunning and E. D. Stokes, *Opt. Commun.*, **6** (1972) 160.
- 65 P. J. Sebastian and K. Sathianandan, *Opt. Commun.*, **32** (1980) 422.