Time-resolved Studies of Intermolecular Electronic Energy Transfer Processes between Molecules in Solution

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A summary of the main energy transfer (ET) mechanisms between isolated pairs of molecules in solution is presented. Various ET models for many-molecules systems are discussed in their basic assumptions and their range of applicability. Time-resolved studies of ET in solution allow to determine the predominant ET mechanism and to test ET models.

KEY WORDS: Energy transfer, ET mechanism, molecule system.

1. INTRODUCTION

Energy transfer processes are widespread in nature. The intermolecular energy transfer (ET) from excited molecules to unexcited ones plays a major role e.g., in photosynthesis¹ and the visual process.²

Further, there is a great interest in the technical use of such ET processes because excitation energy can be transported with negligible losses over molecular distances (up to some 100 Å) within time intervals of less or much less than a nanosecond. In addition, energy can be transferred from one spectral region to another. Examples are the exciton migration in solids³ or the sensibilization of photophysical⁴ and photochemical processes.⁵

In the particular field of laser physics ET processes have been widely used to extend the lasing range, increase the output efficiency and

influence the spectral and temporal characteristics of the output pulses of energy transfer dye lasers^{6,7} or solid state laser materials.^{8,9}

Thus, the investigation of ET mechanisms is stimulated on the one hand by the aim to gain principal knowledge on these mechanisms and on the other hand to achieve successful technical utilization of some basic ET processes.

The early studies of ET, after the classical papers of Förster,¹⁰ Dexter¹¹ and Galanin,¹² were exclusively carried out with stationary methods, such as concentration quenching of luminescence and fluorescence depolarization.

It is, however, very difficult to distinguish between various ET mechanisms by use of these methods only. Time resolved ET studies have opened the possibility to determine the predominant energy transfer mechanism and with increasing accuracy of experimental data to refine ET transfer models.

The purpose of this paper is to give a summary of the main ET mechanisms occurring between interacting molecules in solution and to summarize briefly the substantial assumptions and limitations of the most important models. Further on we will shortly describe some time resolved studies of ET processes and compare their results with the theoretical predictions of relevant ET transfer models.

2. ENERGY TRANSFER MECHANISMS

Though nearly all ET theories are based on classical descriptions with parameters adapted to experiment, most of them can be derived from quantum mechanical considerations. An atomic system like a molecule in solution can be characterized by its Hamiltonian. If there is another independent molecule in the vicinity some kind of mutual interaction can take place, the strength of which depends on the distance and type of interaction energy. In the case of comparatively weak interaction between distant molecules the Hamiltonian of the system can be given by

$$\hat{H} = \hat{H}_{\text{Donor}} + \hat{H}_{\text{Acceptor}} + \hat{H}_{\text{int}} \quad (1)$$

Describing the initial state of the system of two molecules by the wavefunction

$$\psi_i = \frac{1}{\sqrt{2}} (\psi_{D^*}(1) \cdot \psi_A(2) - \psi_{D^*}(2) \psi_A(1)) \quad (2a)$$

and the final state by

$$\psi_f = \frac{1}{\sqrt{2}} (\psi_D(1) \cdot \psi_{A^*}(2) - \psi_D(2) \psi_{A^*}(1)) \quad (2b)$$

the following expression for the matrix element of the interaction Hamiltonian is obtained:

$$H_{if} = \langle \psi_i | \hat{H}_{\text{int}} | \psi_f \rangle = \langle \psi_{D^*}(1) \psi_A(2) | \hat{H}_{\text{int}} | \psi_D(1) \psi_{A^*}(2) \rangle - \langle \psi_{D^*}(1) \psi_A(2) | \hat{H}_{\text{int}} | \psi_D(2) \psi_{A^*}(1) \rangle \quad (3)$$

The first term is the coulombic interaction, whereas the second term represents exchange interaction and requires a spatial overlap of the electronic clouds of the acceptor and donor molecules and is therefore expected to be significant for small distances of the donor-acceptor pair. The coulombic interaction is of long-range, and the expansion of the interaction Hamiltonian in series yields contributions of dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, etc., interactions, the strength of which again depends on the mutual distance of donor and acceptor.

For a description of the energy transfer kinetics one could employ the density matrix approach¹³ for two coupled two-level systems (Figure 1), without using perturbation theory. However, when taking into account the broad spectral bands and the extremely short transverse relaxation times of polyatomic molecules in solution, time-dependent perturbation theory proves to be more fruitful. This

Figure 1 Simplified energy level scheme of donor and acceptor molecules. The ET process is given by: $D^* + A \xrightarrow{k_{\text{ET}}} D + A^*$ (no reverse process is assumed to take place).

approach starts from Fermi's Golden Rule for the transfer rate, implying that no reverse transfer is possible:

$$dK_{\text{ET}} = \frac{2\pi}{h} |H_{fi}|^2 \delta(\Delta E) \quad (4)$$

where $\Delta E = 0$ represents the condition of energy conservation, which is fulfilled by spectral-overlap of electronic and vibrational levels of donor and acceptor molecules (Figure 1).

Integration over all possible energy resonances and insertion of the particular matrix element yields the energy transfer rate for an isolated donor-acceptor pair. In the case of dipole-dipole interaction this specialization leads to:

$$K_{\text{ET}}^{dd}(R_{DA}) = \frac{1}{\tau_D} \left(\frac{R_0}{R_{DA}} \right)^6 \quad (5)^{10}$$

where R_0 is the so-called critical transfer radius (Förster radius) defined by

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

(χ —orientation factor,^{14,43} n —refractive index, η_D —isolated donor fluorescence quantum yield, N —Avogadro's number, F_D —normalized donor emission spectrum, ϵ_A —acceptor extinction coefficient).

In the case of exchange interaction the transfer rate becomes:

$$K_{\text{ET}}^{\text{ex}}(R_{DA}) = \frac{2}{\hbar} K^2 \exp\left(-\frac{2R_{DA}}{L}\right) \cdot \int_0^\infty F_D(\tilde{\nu}) \cdot \epsilon_A(\tilde{\nu}) d\tilde{\nu} \quad (7)^{11}$$

(K —constant, which is not related to any spectroscopic values, L —average orbital radius of wavefunctions).

As it is obvious from Eqs. (5) and (7) the transfer rate strongly depends on the intermolecular distance R_{DA} of the donor-acceptor pair.

It should be noted that several energy transfer mechanisms can act simultaneously in solution. The above-mentioned dipole-dipole and exchange transfer can be combined with a diffusion process of neighbouring molecules^{15,16} which determines the transfer rate. Also pure radiative energy transfer processes are possible.¹⁷ The predominant mechanism is determined mainly by the mean intermolecular distance

Figure 2 Energy transfer mechanisms and range of dominance: d —mean intermediate distance between donor and acceptor; a —molecular radius, R_T —collision radius, l_{Dif} —diffusion length; R_0 —critical energy transfer radius.

between donor and acceptor and some characteristic lengths (R_T , l_{Dif} , R_0) (Figure 2).

So far we have only dealt with an isolated donor–acceptor pair. However, quantities measured by fluorescence or absorption spectroscopic methods in disordered systems are mean numbers of excited donors and acceptors per volume, which can be obtained by averaging with respect to the spatial distribution of both donor and acceptor molecules.

Thus, in modelling energy transfer processes one has to make certain assumptions concerning the spatial distribution of donor and acceptor molecules independent on the predominant transfer mechanism. Several ET models are given below. In deriving these models a common rate equation method is used, implying that thermal equilibrium over the vibrational levels of the excited donor molecule is established, and further that coherent effects are neglected. The first condition can be violated, e.g., in intramolecular electronic ET,⁸ whereas the latter may not be fulfilled in the case of very strong interaction, leading to transfer times in the fs-time range.

3. MODELLING OF INTERMOLECULAR ET

In the following we would like to summarize some features of the most important models for intermolecular energy transfer.

3.1. Radiative energy transfer

In this case the ET consists of two independent intramolecular processes taking place successively in time: the emission of the photon of the primary excited donor and the absorption of it at the acceptor located in a certain distance. The absorption (= ET) probability is mainly determined by the optical density in the direction of observation. The self-absorption of fluorescence is an important case of radiative ET between identical molecules. It is very difficult to give a general description of self absorption because results strongly depend on the particular experimental geometry of observation.¹³ However, it can be stated that reabsorption strongly influences the measured decay time, which is generally prolonged. In the case of strong self-absorption the decay time measured from the ensemble of excited molecules depends not only on cavity dimension and geometry of excitation and detection, but also on wavelength of observation of the fluorescence light.

Under the assumption of weak self-absorption the measured decay time τ_m is independent of wavelength¹⁹ and the true molecular fluorescence decay time τ can be derived from it by:^{20,21}

$$\tau_m = \tau(1 - \eta_{fl} \cdot a)^{-1} \quad (8)$$

where

$$\eta_{fl} \cdot a \approx \int_0^\infty f(\lambda)[1 - 10^{-\varepsilon(\lambda)c \cdot x}] d\lambda \quad (9)$$

with $\tau_m(c \rightarrow 0) = \tau$. Here η_{fl} , $f(\lambda)$, $\varepsilon(\lambda)$ and c are the fluorescence quantum yield, the normalized fluorescence spectrum, the molecular extinction coefficient and the concentration of the emitting molecules, respectively. These formula can be used in a rough estimation for transverse observation of a point-like excited volume. The light penetrates a length x within the solution in the direction of observation (Figure 3). $\eta_{fl} \cdot a$ is the combined probability of emission followed by an absorption of light along the pathway of propagation x .

3.2. Diffusion controlled collisional energy transfer

In the diffusion model the excited donor molecule moves towards the unexcited acceptor and an encounter of both within a certain transfer (or encounter radius R_T) causes a de-excitation of the donor with a

Figure 3 Point-like excitation in a semi-infinite cuvette containing molecules with weak self-absorption of fluorescence.

certain probability. The diffusive motion is assumed to be incoherent and isotropic among homogeneous distributed molecules and the mutual donor acceptor interaction is restricted to the small encounter sphere ($R_T \approx 3 \dots 10 \text{ \AA}^{22,23}$). The diffusion length l_{Dif} which the donor travels during its excited state lifetime τ_D is determined by the solvent viscosity η

$$l_{\text{Dif}} = \sqrt{D_{\text{Dif}} \cdot \tau_D} \quad (10)$$

where D_{Dif} is the relative diffusion constant of both molecules in the solvent

$$D_{\text{Dif}} = D_D + D_A \propto \frac{1}{\eta} \quad (11)$$

For molecules in solution D is of the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1} \dots 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and ET by encounter is likely for $r_{DA} \leq l_{\text{Dif}}$.

The theory starts with the diffusion equation equation for the probability of a donor to be in the excited state at point r and time t^{15}

$$\frac{\partial}{\partial t} \rho_D(r, t) = D_{\text{Dif}} \Delta_L \rho_D(r, t) - \frac{1}{\tau_D} \rho_D(r, t). \quad (12)$$

Spatial averaging of the one-donor solution leads to the following

equation for the number of donors still excited after a delta function-like excitation pulse at $t = 0$.²²

$$D(t) = D(t=0)e^{-t/\tau_D} \cdot \exp \left\{ -4\pi D_{\text{Dif}} R_T N_A \cdot t - 8\pi^{1/2} R_T^2 N_A (D_{\text{Dif}} t)^{1/2} \right\} \quad (13)$$

On the other hand the increase of the excited acceptors is given by

$$\begin{aligned} A(t) = D(t=0) & \left\{ \frac{2\beta}{\sqrt{\gamma}} \left(1 + \frac{\beta}{\gamma} \right) \left[w \left(\frac{\beta}{\sqrt{\gamma}} \right) e^{-t/\tau_A} \right. \right. \\ & + w \left(\sqrt{\gamma t} - \frac{\beta}{\sqrt{\gamma}} \right) \cdot \exp \left\{ - \left(\frac{1}{\tau_D} + \alpha \right) t - 2\beta\sqrt{t} \right\} \Big] \\ & \left. + \frac{\alpha}{\gamma} \left(\exp \left\{ - \left(\frac{1}{\tau_D} + \alpha \right) t - 2\beta\sqrt{t} \right\} - \exp \{ -t/\tau_D \} \right) \right\} \quad (14) \end{aligned}$$

with the abbreviations:

$$\begin{aligned} \alpha &= 4\pi D_{\text{Dif}} R_T N_A \\ \beta &= 4\pi^{1/2} R_T^2 N_A D_{\text{Dif}}^{1/2} \\ \gamma &= \frac{1}{\tau_A} - \frac{1}{\tau_D} - \alpha \end{aligned} \quad (15)$$

and the so-called Karpov integral

$$w(z) = e^{-z^2} \int_0^z e^{x^2} dx \quad (16)$$

N_A and τ_A are the acceptor density in cm^{-3} and the acceptor lifetime in the excited state, respectively.

Equations (13) and (14) represent the temporal behavior of an ensemble of excited donors and acceptors, respectively. Thus Eqs. (13) and (14) also describe the donor and acceptor fluorescence after excitation by a very short light pulse. Besides the shortening of the exponential decay of an isolated donor

$$\exp \left(- \frac{1}{\tau_D} \cdot t \right) \Rightarrow \exp \left(- \left(\frac{1}{\tau_D} + k_T \right) t \right) \quad (17)$$

with

$$k_T = 4\pi D_{\text{Dif}} R_T N_A$$

a characteristic nonexponential term with $\sqrt{t}$ appears.

The diffusion theory can also be applied if there is no real motion of a molecule but only a migration of excitation energy, as it occurs, e.g., in molecular crystals by excitons. Then, of course, the parameter D_{Dif} has to be replaced by the exciton diffusion constant which strongly depends on the type of excitons and which can take values as large as $D_{\text{exc}} \approx (10^{-3} \dots 10^{+2} \text{ cm}^2 \text{ s}^{-1})$. Thus, diffusion length up to some microns can be obtained clearly demonstrating effective ET over large distances by excitons.¹³

A similar case exists for molecules in solution if the excitation energy is firstly spread among the highly concentrated donor ensemble ($N_D \gg N_A$) by repeated transfer steps ($D_i^* + D_j \rightarrow D_i + D_j^*$) until an encounter with an acceptor molecule occurs, $D_n^* + A \rightarrow D_n + A^*$. Thus, the donor excitation is quenched only in a final act (trap). The single step of such a cascade might be a real collision, a coulomb interaction, or an exchange interaction.

3.3. Exchange interaction

Starting from the matrix-element of exchange interaction (Eq. 3) Dexter¹¹ has derived the expression for the transfer rate of this kind of ET for an isolated donor acceptor pair (Eq. 7). This formula holds for distances $R > L$ where the overlapping electronic wavefunctions can be assumed to decline exponentially. A measurable quantity is again only the statistical average of the individual donor decays caused by this transfer rate.

This spatial averaging over an infinitely large number of acceptors which are randomly distributed in space leads to the following donor fluorescence decay function:

$$D(t) = D(t=0)e^{-t/\tau_D} \exp \left\{ -\frac{4\pi}{3} R_T^3 N_A \gamma^{-3} g(e^{\gamma \cdot t/\tau_D}) \right\} \quad (18)$$

Here R_T is the critical distance at which the exchange transfer occurs with the same probability as the spontaneous decay in an isolated donor, $\gamma = 2R_T/L$, and $g(z)$ is given by:

$$g(z) = -z \int_0^1 \exp(-z \cdot y) (\ln y)^3 dy \quad (19)^{24}$$

and results from the spatial averaging ($z = e^{\gamma \cdot t/\tau_D}$). For any $z > 0$ the

integration can be performed term-by-term leading to a Taylor series which can be expressed for sufficiently large z -values by:

$$g(z) = (\ln z)^3 + 1.732(\ln z)^2 + 5.934(\ln z) + 5.445 + O(e^{-z}(\ln z)^3 z^{-2}) \quad (20)^{24}$$

For other nonuniform spatial distributions of donors and acceptors the spatial averaging will yield mean donor decay functions differing from Eq. 18 by magnitude as well as time behavior.²⁵

3.4. Förster model of long-range energy transfer and related models

In this model the donor transfers its excitation energy to one acceptor of its surrounding via a dipole–dipole interaction (DDI). Further assumptions with respect to the spatial distributions of the molecules are:

i) The donor is surrounded by an homogeneous distribution of acceptor molecules which are fixed in space during the time of interaction.

ii) No mutual influence between donors exists.

iii) Each donor possesses its own acceptor environment.

These assumptions imply directly that the number of excited donors is much less than the number of unexcited acceptors ($N_D \ll N_A$), a condition obviously fulfilled in steady-state experiments but clearly not in the case of donor excitation by ultrashort light pulses. We will refer to this in Section 4, taking first the assumptions to be valid. Starting again from the rate equation for the deactivation of an excited donor

$$\frac{d}{dt} \rho_D^*(t) = -\frac{1}{\tau_D} \rho_D^*(t) - \sum_{i=1}^{N_A} K_{ET}^{dd}(R_{DA}) \rho_D^*(t) \quad (21)$$

where $\rho_D^*(t)$ is again the probability of finding the donor still excited and $k_{ET}^{dd}(R_{DA})$ is given by (5). The sum extends over all acceptors in the vicinity of the donor under consideration.

Averaging of the solution of Eq. (21) with respect to an homogeneous distribution of acceptors²⁶ leads to the well known $\sqrt{t}$ -law of Förster for the excitation decay of the donor ensemble:

$$D(t) = D(t=0) \exp \left\{ -\frac{t}{\tau_D} - 4\pi^{3/2} \cdot R_0^3 N_A (t/\tau_D)^{1/2} \right\} \quad (22)$$

N_A here denotes the acceptor density in cm^{-3} . The temporal behaviour of the excited acceptor ensemble can be expressed by means of Eq. (14) setting $\alpha = 0$ and

$$\beta = (2/3)\pi^{3/2}R_0^3N_A\tau_D^{-1/2} \quad 22$$

$$A(t) = D(t=0) \cdot \frac{\beta}{\sqrt{\gamma}} \left[w \left(\frac{\beta}{\sqrt{\gamma}} \right) e^{-t/\tau_A} + w \left(\sqrt{\gamma t} - \frac{\beta}{\sqrt{\gamma}} \right) \cdot \exp \left(-\frac{t}{\tau_D} + 2\beta\sqrt{t} \right) \right] \quad (23)$$

with γ and w from (15) and (16).

Figure 4 shows the time behaviour of the donor decay (Eq. 22) and the rise of acceptor excitation (Eq. 23) due to Förster model after δ -function-like excitation pulse of the donor ensemble. The optical transitions which form the overlapping integral of Eq. (6) can be of singlet or triplet type.²⁷

When DDI is weak because of a forbidden optical transition in the

Figure 4 Time resolved fluorescence decays indicating an ET from rhodamine 6 G (a) to oxacine 4 (b); streak camera measurement.³⁴

donor or acceptor higher terms of interaction (quadrupole) must be considered^{13,26} resulting in smaller R_0 values.

But large transfer distances are possible even for forbidden optical transitions of the donor if the quantum yield η_D is high (phosphorescence) and the acceptor optical transition is allowed (large ϵ_A).¹⁰

The critical ET radius R_0 can be related to a critical concentration where dipole–dipole ET becomes efficient.

$$N_{A0} = \frac{3}{2}(\pi^{3/2}R_0^3)^{-1} \quad \text{or} \quad C_{A0} = \frac{3000}{2}(\pi^{3/2}NR_0^3)^{-1} \quad (24)$$

(Here N_{A0} is in cm^{-3} and c_{A0} in mol l^{-1} ; N is Avogadro's number of molecules per mol).²⁷

There are some specific spatial configuration to which Förster-type ET can be applied under the restriction mentioned above. First there is the two-dimensional ET in monolayers,²⁸ where the donor decay becomes the form

$$D(t) = D(t=0) \exp \left\{ -\frac{t}{\tau_D} \Gamma\left(\frac{2}{3}\right) \cdot q \cdot \left(\frac{t}{\tau_D}\right)^{1/3} \right\} \quad (25)$$

Here q denotes the ratio $q = n_A/n_{A0}$ and n_A , n_{A0} are the two-dimensional concentration and critical concentration $n_{A0} \approx 1/\pi R_0^2$ in cm^{-2} and $\Gamma(2/3) \approx 1.354$.

Second in a quasi-one-dimensional system the donor decay function after spatial averaging has the form¹³

$$D(t) = D(t=0) \exp \left\{ -\frac{t}{\tau_D} - 2\Gamma\left(\frac{5}{6}\right) \cdot \left(\frac{3}{2}\chi^2\right)^{1/6} R_0 l_A \left(\frac{t}{\tau_D}\right)^{1/6} \right\} \quad (26)$$

and l_A is the linear density in cm^{-1} .

4. EXAMPLES OF TIME RESOLVED ET STUDIES

The simplest observable manifestation of ET is the quenching of fluorescence due to interaction between excited donors and unexcited acceptor, or conversely, the sensitization of fluorescence of a primarily unexcited acceptor.

Stationary measurements of concentration quenching of the fluore-

science²⁹ or the concentration depolarization³⁰ qualitatively indicate the existence of an ET process and permit to some degree the determination of characteristic transfer parameters.

Experimentally an exact distinction between the various ET mechanisms is only possible by means of time-resolved spectroscopic methods. Fortunately recent developments of lasers have delivered an almost ideal excitation source for time-resolved investigations of ET processes, which can produce monochromatic, short duration (nearly δ -like) pulse excitation. With excitation pulses of ps or even fs duration³¹ the time-lapse of the ET process can be investigated with very high time resolution.^{32,33}

This is necessary, because various mechanisms of ET differ mainly in the time domain shortly after excitation.

Until now, most of the time resolved investigations of ET of molecules in solution have been made by single-shot or synchroscan streak camera and single photon counting measurements of fluorescence (e.g. Refs. 34–36).

By means of excite-and-probe-beam spectroscopy using a ps- or fs-continuum the ET process can be observed in a broad spectral region, and even the excitation of non-fluorescent acceptors via ET-processes can be studied with high time resolution (e.g. Ref. 37).

4.1. Confirmation of Förster's $\sqrt{t}$ -law

There are a lot of experimental data which well agree with the theoretical predictions deduced from the common Förster model. In particular, in an intermediate acceptor concentration range of some $c_A = 10^{-2} \dots 10^{-3} \text{ mol l}^{-1}$ the validity of Förster's decay law (Eq. 17) is well proved^{33,34,38} in rigid solutions.

An example is given in Figure 4 which shows the fluorescence decay and rise of a donor and acceptor molecule according to Eqs. (22) and (23), respectively. The time resolved fluorescence was detected by a streak camera system.¹⁷

Another confirmation of a Förster model of the donor decay in a time interval ranging from 10 ps up to several nanoseconds was reported by Tredwell *et al.*³⁸ In the experiments the acceptor concentration range from 10^{-2} to $10^{-3} \text{ mol l}^{-1}$ in a rhodamine 6G (donor)-malachite green (acceptor) mixture in ethanol, Figure 5.

Figure 5 Fluorescence decay of rhodamine 6 G (10^{-4} mol/l) in ethanol with (A) 0 mol/l, (B) 10^{-3} mol/l, (C) $2.5 \cdot 10^{-3}$ mol/l, (D) $5 \cdot 10^{-3}$ mol/l malachite green in ethanol streak camera records.³⁸

For all concentrations a unique transfer radius of $R_0 = 52 \pm 1 \text{ \AA}$ was obtained from a plot of $\log I$ versus $t^{1/2}$ (Eq. 22).

4.2. Deviations from simple $\sqrt{t}$ -law

In low viscosity solvents, deviations from the Förster's decay law (Eq. 22) have been observed by additional motion of the molecules during the time interval of ET.

There are several attempts to take into account an additional diffusion of excitation energy³⁹⁻⁴¹ which are all based on an expansion of the ratio of diffusion length to the energy transfer radius l_{Dif}/R_0 .^{39,42,49}

Slight deviations from the dominating time behaviour according to Eq. (22) have been found experimentally for acceptor concentrations $c_A > 1 \cdot 10^{-3}$ in liquid solutions (e.g. in methanol $D_{\text{Dif}} = 2 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).^{43,44}

The experimental curves can be fitted well by modified equations for the donor decay, which take into account motion of the molecules (Eq. 13).

4.3. ET under the influence of inhomogeneous spatial distribution

Despite the various confirmations of the Förster model there have also been reported several experimental deviations from the Förster- $\sqrt{t}$ -law, which cannot be explained by additional diffusion^{5,35,37} in the low concentration range.

Even at such low concentrations of $10^{-4} \dots 10^{-5} \text{ mol l}^{-1}$ a very efficient ET was observed, suggesting an increase of the critical transfer radius R_0 in this concentration range which is in contradiction to its physical meaning (Table I).

The efficient donor-acceptor ET has also been demonstrated by the surprisingly fast rise of acceptor excitation in ps-excite-and-probe beam experiment (Figure 6). The rise time to the maximum of the acceptor excited state population amounts for different donor acceptor pairs: rhodamine 6 G (donor, cresyl violet, DOTCI, oxacine 725 (acceptors) $t_r = 20 \text{ ps}$, 40 ps and 50 ps , respectively, and shows no significant dependence on acceptor concentration or solvent viscosity.³⁷ Similar short transfer times have been observed for rhodamine 6 G to cresyl violet and malachite green.³⁶

These short rise times are also in discrepancy with theoretical

Table I Critical transfer radius R_0 calculated from the decay of the donor fluorescence in dependence on the acceptor concentration C_A .

Rh/CV in EtOH ³⁷ $C_D = 1 \cdot 10^{-3} \text{ mol/l}$			Rh/DOTC in EtOH ³⁷ $C_D = 1 \cdot 10^{-3} \text{ mol/l}$		DODC/MG in EtOH ³⁵ $C_D = 1 \cdot 10^{-4} \text{ mol/l}$		HPD Monomer/ Dimer in H ₂ O ⁵ $C_D = C_A \text{ mol/l}$	
C_A [mol/l]	R_0 [Å]	a/b *	C_A [mol/l]	R_0 [Å]	C_A [mol/l]	R_0 [Å]	C_A [mol/l]	R_0 [Å]
R_0 theor. Eq. (6)	56	—	R_0 theor. Eq. (6)	49	R_0 theor. Eq. (6)	59	R_0 theor. Eq. (6)	24
$4 \cdot 10^{-3}$	50	1			$5 \cdot 10^{-3}$	45	$4 \cdot 10^{-3}$	33
$2 \cdot 10^{-3}$	52	2			$2 \cdot 10^{-3}$	46		
$1 \cdot 10^{-3}$	61	9	$1 \cdot 10^{-3}$	45	$1 \cdot 10^{-3}$	48		
$5 \cdot 10^{-4}$	70	22	$5 \cdot 10^{-4}$	46	$5 \cdot 10^{-4}$	69	$4 \cdot 10^{-4}$	50
$3 \cdot 10^{-4}$	73	22	$1 \cdot 10^{-4}$	64	$2 \cdot 10^{-4}$	84		
					$1 \cdot 10^{-4}$	91		
$5 \cdot 10^{-5}$	94	57			$5 \cdot 10^{-5}$	120	$3 \cdot 10^{-5}$	75
					$1 \cdot 10^{-5}$	152		

* Correction of R_0 to $R_0 = 50 \text{ Å}$ assuming a raised concentration.

Figure 6(a) Spectral changes in optical density at various delay times after excitation. Curves obtained by a ps-excite-and-probe spectrometer with ps-continuum probe pulse; rhodamine 6 G donor, cresyl violet acceptor, in ethanol; $R_0 \approx 52 \pm 2 \text{ \AA}$.³⁷

Figure 6(b) Excitation density of donor and acceptor molecules versus delay time . . . rhodamine 6 G direct excitation by a 5 ps SHG ($\lambda = 532 \text{ nm}$)—laser pulse—cresyl violet excitation via ET from rhodamine 6 G $c_D = 1 \cdot 10^{-4} \text{ mol/l}$, $c_A = 5 \cdot 10^{-5} \text{ mol/l}$.³⁷

predictions of ≈ 400 ps (at $c_A = 10^{-2}$ mol l $^{-1}$) as derived from Förster's formula (Figure 4).³⁴

This contradiction can be removed by the assumption of a generalized Förster-model taking into account a possible inhomogeneous spatial distribution of acceptor molecules around the donor molecules. Charged dye molecules in solution are very likely interacting by weak static van-der Waals forces described by a Lenard-Jones potential, e.g., Figure 7, causing a mutual attraction of these molecules. In this way an inhomogeneous spatial distribution of acceptor molecules can be produced. Assuming a simple step-like sphero-symmetrical inhomogeneous distribution spatial averaging according to this inhomogeneity leads to an analytical expression with a modified time behaviour of the donor and acceptor ensemble.³⁷

$$D(t) = D(t=0)e^{-t/\tau_D} \exp \left\{ -\frac{4\pi^{3/2}}{3} R_0^3 b \left(\frac{t}{\tau_D} \right)^{1/2} \right. \\ \left. \cdot \left[1 + \frac{a-b}{b} Q(x_2(t)) - \frac{a}{b} Q(x_i(t)) \right] \right\} \quad (27)$$

$$Q(x_i(t)) = 1 - \phi(x_i(t)) + \frac{1 - e^{-x_i^2(t)}}{\sqrt{\pi} x_i(t)}$$

$$\phi(x_i(t)) = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-u^2} du$$

$$x_i(t) = \left(\frac{R_0}{R_i} \right)^3 \cdot \left(\frac{t}{\tau_D} \right)^{1/2}$$

For $a \rightarrow b$ and $R_1 \rightarrow 0$ this equation approaches normal Förster-like donor decay for a homogeneous acceptor distribution. The dependence on R_1 (the radius of forbidden volume) is not very significant, if it is small enough ($R_1 = 10$ Å).

By fitting an experimental curve with the numerical calculations of $A(t)$ one can derive the parameters of the model (Figure 8), e.g., $a/b = 25$, $R_1 = 10$ Å, $R_2 = 20$ Å for an ET of rhodamine 6 G to cresyl violet in ethanol with $R_0 = 50 \pm 2$ Å.³⁷

Thus from experimental data one may get not only information about the efficiency of ET(R_0) but also about the distribution of the molecules (a/b , R_1 , R_2).

Equation (27) can also be derived in a modified form for two-

Figure 7 Inhomogeneous spatial distribution of acceptors around one excited donor a , b increased and bulk density of acceptor molecules; R_1 , R_2 radii of sphere of raised acceptor concentration and forbidden volume.³⁷

Figure 8 Fitting of the numerical solution for the acceptor rise function in the case of an inhomogeneous distribution of acceptors to an experimental curve.³⁷

dimensional planar and also spherical geometry of the donor–acceptor assembly.²⁵ These models have been successfully applied in describing energy transfer processes in microstructured systems (micelles, bilayers) see, e.g., Refs. 45, 46 and 47, which present model systems of photosynthesis.

5. CONCLUSIONS

We have given a survey of the main ET mechanisms occurring between interacting molecules in solution, and have outlined their range of occurrence. Further we have summarized some of the most common models together with their substantial assumptions and limitations. It has been shown that these models, within their range of applicability, can be used to describe energy transfer processes in solution over a wide range of concentration ratios, solvents and molecular structures adequately.

We have not, for sake of shortness, gone into the problem of mutual donor–donor interaction as outlined in Refs. 48 and 49.

This problem is being treated in a forthcoming paper in detail, together with a detailed investigation of energy transfer processes in microstructured systems (Micelles, Vesicles, Bilayers).²⁵

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