

## **ELECTRONIC ENERGY TRANSFER: A COHERENT FORMALISM FOR PULSED AND STEADY STATE IRRADIATION**

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### **Summary**

Starting from the known equations describing the deactivation of electronic excitation energy of a donor in the presence of acceptors under either pulsed or steady state irradiation, and using a coherent mathematical formalism, a set of equations is derived which can easily be employed in luminescence quenching experiments. The strict connections and in some cases the equivalence between the various quantitative and theoretical approaches to the study of the transfer process are emphasized. Specific models of energy transfer, such as the Perrin-Ermolaev active sphere and the Stern-Volmer relation, may be expressed using the same formalism.

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### **1. Introduction**

A central problem in photochemistry and radiation chemistry is the study of the overall deactivation channels of any excited metastable state created by the absorption of UV or gamma photons in molecules, atoms, ions etc. in the gaseous, liquid and solid phases. An impressive number of original papers and reviews has been devoted to the theoretical and experimental aspects of this problem [1].

A significant channel of deactivation is the transfer of electronic excitation energy from excited to unexcited species. The quantitative aspects of this fundamental process have been thoroughly studied. However, as a consequence of the many different mathematical formalisms employed the connections among these theoretical approaches have often been overlooked, giving rise to various different interaction models. The purpose of this paper is not only to emphasize these connections, but also to present a set of equations describing with a coherent formalism electronic energy transfer under either pulsed or steady state irradiation.

The overall deactivation processes of an excited species have generally been described quantitatively by the so-called decay functions  $\bar{\rho}(t)$ ; of the

very many decay functions that have been developed [2 - 35], some that are relevant for the derivation of the energy transfer functions  $H(t)$  described in the following section are presented in the Appendix.

## 2. Pulsed excitation: energy transfer functions $H(t)$

When a donor-acceptor pair is flashed for a time which is much smaller than the lifetime of the excited donors (which are randomly distributed with respect to the acceptors) the relative decay functions  $\bar{\rho}(t)$  may be easily reduced to the following general equation which describes the energy transfer process:

$$\bar{\rho}(t) = \exp \left\{ -\frac{t}{\tau_0} - C_A H(t) \right\} \quad (1)$$

where  $C_A$  is the acceptor concentration in molecules per unit volume,  $1/\tau_0$  is the rate of any channel of decay of  $D^*$  and  $H(t)$  is a time dependent function, expressed in volume units, which describes any energy transfer process between  $D^*$  and  $A$ ; this equation obviously corresponds for pulsed irradiation to

$$\bar{\rho}(t) = \exp \left\{ -\sum_{m=1}^n k_m t - \sum_{m=1}^n C_A H(t)_m \right\} \quad (2)$$

unimolecular  
processes

bimolecular  
processes

where the first sum refers to any unimolecular radiative or non-radiative decay process of an excited donor  $D^*$  and the second sum refers to any bimolecular radiative or non-radiative decay process of an excited donor  $D^*$  in the presence of an acceptor and other unexcited donor species.

In general, the energy transfer function  $H(t)$  of eqn. (1) can be expressed as a time-dependent series containing power terms (which account for Coulombic multipolar interactions between an excited donor and acceptor) and logarithmic terms (which account for exchange interactions); *i.e.*

$$H(t) = \sum_{i=0}^n a_i t^{m_i} + \sum_{j=0}^n a_j (\ln At)^{m_j} \quad (3)$$

where  $a_i$ ,  $a_j$  and  $A$  are experimental parameters;  $m_i = \frac{7}{6}, \frac{6}{6}, \frac{5}{6}, \dots$  for dipole-dipole interactions;  $m_j = 1, 2, 3, \dots$ . Some of the possible terms of this series are lacking in the equations summarized in Table 1 depending on the approximations introduced when deducing the decay functions of the Appendix; *e.g.* in eqn. (A5), the error function  $\Phi(x)$  expanded as a series was

TABLE 1

Energy transfer functions  $H(t)$ (1) d-d interactions;  $D = 0$ 

$$H(t) = \frac{4\pi^{3/2}R_0^3}{3} \left(\frac{t}{\tau_0}\right)^{1/2}$$

(2) d-d interactions;  $D \neq 0$ 

$$H(t) = \frac{4\pi^{3/2}R_0^3}{3} \left(\frac{t}{\tau_0}\right)^{1/2} + \frac{16.8\pi^{3/2}R_0D\tau_0}{3} \left(\frac{t}{\tau_0}\right)^{7/6}$$

$$H(t) = 4\pi DRt$$

$$H(t) = 4\pi DRt + \frac{8\pi DR^2 t^{1/2}}{(\pi D)^{1/2}}$$

$$H(t) = 4\pi DRt + \frac{8\pi DR^2 t^{1/2}}{(\pi D)^{1/2}} + \frac{4\pi R_0^6 t}{12\tau_0 R^3} + \frac{8\pi R_0^6 t^{1/2}}{12\tau_0 R^2 (\pi D)^{1/2}}$$

(3) Exchange interactions;  $D = 0$ 

$$H(t) = \frac{\pi L^3}{6} \{(\ln At)^3 + 1.73(\ln At)^2 + 5.9(\ln At) + \dots\}$$

(4) Exchange interactions;  $D \neq 0$ 

$$H(t) = 4\pi DR_{\text{eff}}t + \frac{8\pi DR_{\text{eff}}^2 t^{1/2}}{(\pi D)^{1/2}}$$

truncated for terms with powers of  $t$  higher than  $t = \frac{1}{2}$ . In any case, the energy transfer function  $H(t)$  can be thought of as a "volume of interaction" that expands with time around an excited *randomly distributed* donor, containing different amounts of acceptor molecules. This "active volume" is of about  $10^{-19} \text{ cm}^3$  as an order of magnitude for a dipole-dipole (d-d) interaction at time  $t = \tau_0$ . At time  $t = t_0$  this expanding sphere reaches a critical value  $H(t_0) = V_0$  of radius  $R_0$ , when the first and the second term of the exponential of eqn. (1) become equal; this value  $H(t_0)$  of the energy transfer function consequently correlates with the Förster integral  $J_{D^*A}(\bar{\nu})$  ( $\text{cm}^6$ ) which corresponds to the overlapping between the excited donor emission and the acceptor absorption spectra in the case of d-d interaction and for  $D = 0$ , i.e.

$$H(t_0) = K \{J_{D^*A}(\bar{\nu})\}^{1/2} \text{ cm}^3 \quad (4)$$

where  $K$  is an experimental parameter.

The energy transfer functions  $H(t)$  which are valid under pulsed excitation are given more explicitly in the following sections.

## 2.1. Dipole-dipole interaction

### 2.1.1. Stationary donor-acceptor pair; diffusion coefficient $D = 0$

$$H(t) = \frac{4\pi^{3/2}R_0^3}{3} \left(\frac{t}{\tau_0}\right)^{1/2} \quad (5)$$

This function derives from the Förster [2] or Galanin [33] decay function  $\bar{\rho}(t)$  (see eqn. (A1)).

### 2.1.2. Non-stationary donor-acceptor pair; $D \neq 0$

$$H(t) \approx \frac{4\pi^{3/2}R_0^3}{3} \left(\frac{t}{\tau_0}\right)^{1/2} + \frac{16.8\pi^{3/2}R_0D\tau_0}{3} \left(\frac{t}{\tau_0}\right)^{7/6} \quad (6)$$

This function is derived, after some algebraic manipulation, from the decay function developed by Kurskii and Selivanenko [15] (eqn. (A2)) for donor-acceptor pairs in viscous solvents. Quite surprisingly the same function, apart from a small numerical difference, can be obtained from the Yokota and Tanimoto [16] decay function (eqn. (A4)); *i.e.*

$$H(t) \approx \frac{4\pi^{3/2}R_0^3}{3} \left(\frac{t}{\tau_0}\right)^{1/2} + \frac{7.2\pi^{3/2}R_0D\tau_0}{3} \left(\frac{t}{\tau_0}\right)^{7/6} \quad (7)$$

Both eqns. (6) and (7) contain one term in common with eqn. (5); this derives from the fact that in solution the energy transfer functions (eqns. (6) or (7)) consist of two terms, the first accounting for stationary and the second for diffusion-controlled interactions. Analogously, from the decay function developed by Kurskii and Selivanenko for low viscosity solutions (eqn. (A3)) the following  $H(t)$  function can be derived:

$$H(t) = 4\pi DRt + \frac{8\pi DR^2 t^{1/2}}{(\pi D)^{1/2}} + \frac{4\pi R_0^6 t}{12\tau_0 R^3} + \frac{8\pi R_0^6 t^{1/2}}{12\tau_0 R^2 (\pi D)^{1/2}} \quad (8)$$

It is worth observing that from the Smoluchowski reaction rate, which is valid for a simple diffusion-controlled collisional interaction, the following energy transfer function can be obtained [40]:

$$H(t) = 4\pi DRt + \frac{8\pi DR^2 t^{1/2}}{(\pi D)^{1/2}} \quad (9)$$

Consequently, in eqn. (8) the first two terms correspond to a simple diffusion-controlled collisional interaction, the third term to a stationary d-d and the fourth term to a diffusion-controlled d-d interaction.

Exactly the same equation can be obtained from the  $\bar{\rho}(t)$  function of Voltz *et al.* [17] reported in the Appendix as eqn. (A5).

It does not seem that either Yokota and Tanimoto or Voltz *et al.* were aware of these equivalences. Actually, the decay functions do not *explicitly* show the strict connections between them; however, once a coherent mathematical formalism is employed and the energy transfer process is described mathematically as in eqn. (1), similarities or equivalences become obvious. Nevertheless, both eqns. (6) and (8) are incorrectly attributed to Yokota and Tanimoto [16] and to Voltz *et al.* [17], respectively.

## 2.2. Exchange interaction

### 2.2.1. Stationary donor-acceptor pair; $D = 0$

$$H(t) = \frac{\pi L^3}{6} \{(\ln At)^3 + 1.73(\ln At)^2 + 5.9(\ln At) + \dots\} \quad (10)$$

This  $H(t)$  function derives from the Inokuti-Hirayama [4] decay function, and describes the exponential time-dependent interaction due to electronic overlapping between the donor and the acceptor molecules.

### 2.2.2. Non-stationary donor-acceptor pair; $D \neq 0$

$$H(t) = 4\pi DR_{\text{eff}}t + \frac{8\pi DR_{\text{eff}}^2 t^{1/2}}{(\pi D)^{1/2}} \quad (11)$$

This  $H(t)$  function, which is derived from the revised Pilling and Rice [14]  $\bar{\rho}(t)$  function (eqn. (A7)) correlates with the Smoluchowski collisional  $H(t)$  function of eqn. (9), the only difference being the  $R_{\text{eff}}$  value.

The order of magnitude at time  $t = \tau_0$  of the numerical parameters  $a_i$  and  $a_j$  in the series in eqn. (3) for some  $H(t)$  functions are given in the following equations:

Eqn. (5)

$$H(t) = 1.13 \times 10^{-19} \left(\frac{t}{\tau_0}\right)^{1/2} = 1.13 \times 10^{-19} \text{ cm}^3$$

Eqn. (6)

$$H(t) = 1.13 \times 10^{-19} \left(\frac{t}{\tau_0}\right)^{1/2} + 4.41 \times 10^{-19} \left(\frac{t}{\tau_0}\right)^{7/6} = 5.54 \times 10^{-19} \text{ cm}^3$$

Eqn. (7)

$$H(t) = 1.13 \times 10^{-19} \left(\frac{t}{\tau_0}\right)^{1/2} + 1.89 \times 10^{-19} \left(\frac{t}{\tau_0}\right)^{7/6} = 3.02 \times 10^{-19} \text{ cm}^3$$

Eqn. (8)

$$H(t) = 1.25 \times 10^{-19} \left( \frac{t}{\tau_0} \right)^{1/2} + 2.08 \times 10^{-19} \frac{t}{\tau_0} = 3.33 \times 10^{-19} \text{ cm}^3$$

The experimental parameters employed are  $R_0 = 24.8 \times 10^{-8}$  cm,  $R = 12.8 \times 10^{-8}$  cm,  $\tau_0 = 5.7 \times 10^{-9}$  s and  $D = 1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> [36, 37] for eqns. (5) - (8).

The ways in which the various terms of eqns. (5) - (11) affect the energy transfer functions  $H(t)$  are shown in Figs. 1 - 3. The parameters for eqns. (10) - (11) of Fig. 3 are  $R_{\text{eff}} = 10 \times 10^{-8}$  cm,  $L = 3.14 \times 10^{-8}$  cm,  $\tau_0 = 2.3 \times 10^{-4}$  s and  $R_0 = 12.9 \times 10^{-8}$  cm.

### 3. Steady state excitation

When the exciting light source is kept on continuously, the excited donor molecules are no longer distributed randomly and consequently under steady state conditions the physical meaning of a "sphere of interaction" expanding with time around an excited randomly distributed donor implied by the energy transfer function  $H(t)$  vanishes. Hence it is no longer possible to distinguish unimolecular from bimolecular decay processes, as in eqns. (1) and (2). For instance, the decay function of eqn. (A1) becomes [38]

$$\bar{\rho}(t) = \tau_0 [1 - \pi^{1/2} q \exp(q^2) \{1 - \text{erf}(q)\}] \quad (12)$$

### 4. Relative quantum yields

The importance of the relative quantum yields of  $\eta/\eta_0$  luminescence derives from their direct correlation with experimental results; although the decay functions  $\bar{\rho}(t)$  for pulsed and steady state irradiation are quite different the relative quantum yields are the same in both cases [38] even if only to a first approximation [39]. However, the lack of a coherent formalism in expressing the various models of interaction may also in this case be a source of confusion in their correct experimental use; hence, it seems useful to discuss briefly the various known relations.

#### 4.1. Stationary and diffusion-controlled processes

Under steady state as well as under pulsed irradiation the relative quantum yield is [40]

$$\frac{\eta}{\eta_0} = \frac{1}{1 - 4\pi D R C_A \tau_0} [1 - \pi^{1/2} q \exp(q^2) \{1 - \text{erf}(q)\}] \quad (13)$$

where  $R$  is the encounter distance of the donor-acceptor pair,  $C_A$  the acceptor concentration and  $D$  the mutual diffusion coefficient of the two species. When the diffusion coefficient  $D = 0$ , *i.e.* for stationary processes,

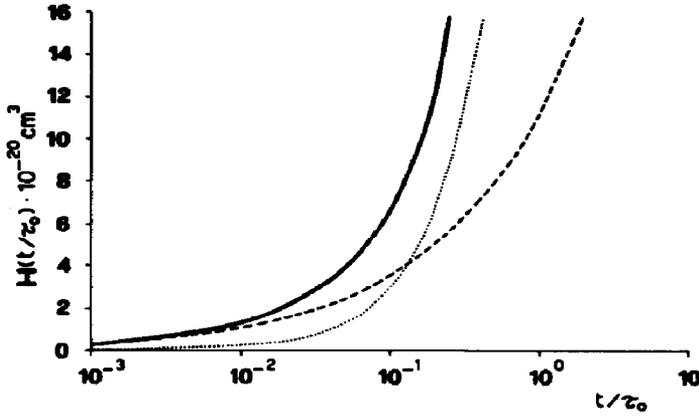


Fig. 1. Plots of various energy transfer functions against  $t/\tau_0$ : ---, eqn. (5); —, eqn. (6); ·····, 2nd term, eqn. (6).

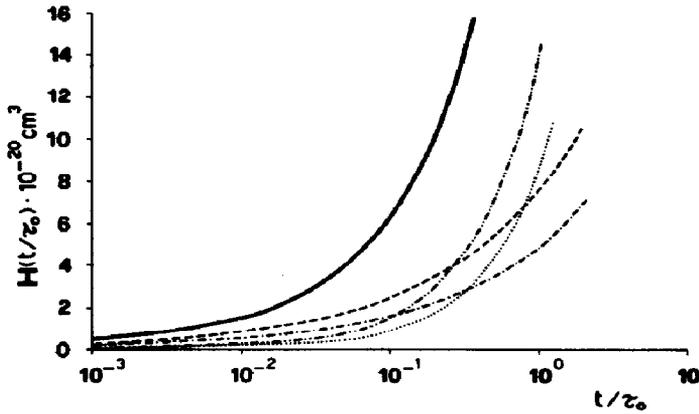


Fig. 2. Plots of various energy transfer functions against  $t/\tau_0$ : —, eqn. (8); ·····, first term, eqn. (8); ---, second term, eqn. (8); - · - · - ·, third term, eqn. (8); - - - -, fourth term, eqn. (8).

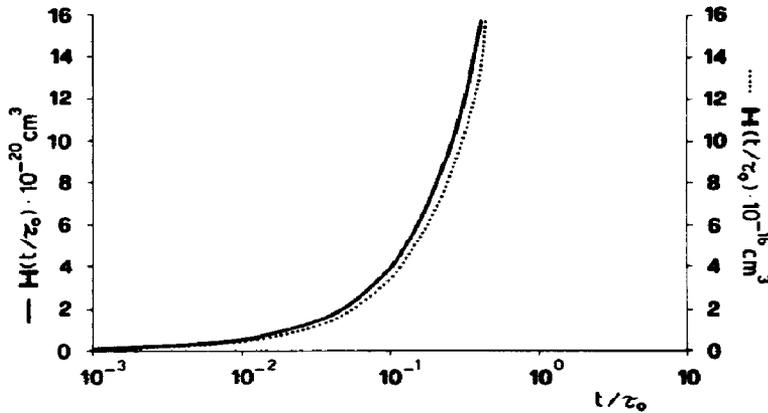


Fig. 3. Plots of various energy transfer functions against  $t/\tau_0$ : —, eqn. (11) (left ordinate); ·····, eqn. (10) (right ordinate).

eqn. (13) reduces to [2]

$$\eta/\eta_0 = 1 - \pi^{1/2} q \exp(q^2) \{1 - \operatorname{erf}(q)\} \quad (14)$$

The parameter  $q$  of eqn. (14) corresponds to  $(\frac{2}{3})\pi^{3/2}R_0^3C_A$ ; the same parameter, for the relative quantum yield of eqn. (13) is  $q = b/a^{1/2}$ , where  $a = 1/\tau_0 + 4\pi DR C_A$  and  $b = 4R^2C_A(\pi D)^{1/2}$ .

#### 4.2. Stern-Volmer model

This model corresponds to an energy transfer under steady state irradiation in solution; its relative quantum yield is generally expressed as [34]

$$\begin{aligned} \frac{\eta}{\eta_0} &= \frac{I_{SS}}{I_0} = \frac{1}{1 + K_{SV} C_A} \\ &= \frac{1}{1 + k_q \tau_0 C_A} \end{aligned} \quad (15)$$

where  $I_{SS}$  is the luminescence intensity under steady state irradiation in the presence of an acceptor and  $I_0$  the intensity in the absence of irradiation;  $K_{SV}$  is conventionally called the Stern-Volmer constant which is experimentally obtainable from the slope of the plot of the donor luminescence ratio  $I_{SS}/I_0$  versus the acceptor concentration  $C_A$ ;  $k_q$  is the quenching rate constant of luminescence.

This relation can be deduced using the same formalism described in the previous paragraphs; in fact, under steady state conditions in solution the luminescence intensity  $I_{SS}$  of an excited donor in the presence of an acceptor is given by

$$I_{SS} = \int_0^{\infty} I(t) dt \quad (16)$$

where  $I(t)$  is the luminescence intensity of the same donor after a light pulse at  $t = 0$ ; taking into account only the first term of eqn. (9),  $I(t)$  may be calculated [41] giving

$$I(t) = C_0 \exp(-at) \quad (17)$$

where  $C_0$  is a constant and  $a$  has been previously defined. Consequently, since  $I_0$  is the luminescence intensity of the donor in the absence of acceptors,

$$I_0 = C_0 \tau_0 \quad (18)$$

Hence,

$$\begin{aligned} \frac{I_{SS}}{I_0} &= \frac{\eta}{\eta_0} = \frac{\int_0^{\infty} C_0 \exp(-at) dt}{C_0 \tau_0} = \frac{1}{1 + 4\pi DR \tau_0 C_A} \\ &= \frac{1}{1 + K_{SV} C_A} \end{aligned} \quad (19)$$

where the various parameters have been previously defined. Equation (19) is formally equivalent to the Stern–Volmer relation (eqn. (15)) provided that  $K_{SV} = 4\pi DR\tau_0 = k_q\tau_0$ , where  $k_q$  is the usual Stern–Volmer quenching constant, expressed in  $M^{-1} s^{-1}$ . When  $I(t)$  accounts for both terms of eqn. (9), then eqn. (17) becomes [41]

$$I(t) = C_0 \exp(-at - 2bt^{1/2}) \quad (20)$$

and, for  $C_A \rightarrow 0$ , the Stern–Volmer constant  $K_{SV}$  defined in eqn. (19) becomes

$$K_{SV} = 4\pi DR\tau_0 + 4\pi R^2(D\tau_0)^{1/2}$$

where the first term corresponds to the previously reported  $K_{SV}$  of eqn. (19) and the second term gives the departure from the linear Stern–Volmer equation, as a result of the viscosity of the solution.

#### 4.3. Perrin–Ermolaev model

This model can also be deduced using the same formalism. In fact, the original Perrin model [35] corresponds to an energy transfer process whose rate constant is infinity for any distance between  $D^*$  and  $A$  less than  $R_0$ , and zero for any distance greater than  $R_0$ ; i.e. this model proposes an “active sphere of interaction”. Ermolaev [19] found, in particular, that such a model was convenient to explain triplet–triplet energy transfer experiments; it can be quantitatively expressed by the relation

$$\eta/\eta_0 = \exp(-C_A V_0) \quad (21)$$

where  $C_A$  is the concentration of the acceptor species (in molecules per unit volume) and  $V_0$  is the volume of the “active sphere of interaction”.

Referring to eqn. (1), at the critical time  $t = t_0$ ,  $H(t) = H(t_0)$  and both terms of the exponential become equal. Hence

$$\bar{\rho}(t_0) = \exp\{-2C_A H(t_0)\} \quad (22)$$

However [2],

$$\begin{aligned} \eta &= K \int_0^\infty \bar{\rho}(t) dt \\ &= K \int_0^\infty \exp\{-2C_A H(t_0)\} dt \end{aligned} \quad (23)$$

and

$$\eta_0 = K \int_0^\infty \exp\left(-\frac{t_0}{\tau_0}\right) dt \quad (24)$$

where  $K$  is a numerical constant. Consequently

$$\eta/\eta_0 = \exp\{-C_A H(t_0)\} = \exp(-C_A V_0) \quad (25)$$

which is identical to the Perrin–Ermolaev relation (eqn. (21)) and  $V_0 = (4\pi/3)R_0^3$  is the volume of the “active sphere”, *i.e.* the value of the energy transfer function when it reaches its “critical” value  $H(t_0)$  at time  $t = t_0$ .

The various relative quantum yields of luminescence described in this paragraph are summarized in Table 2.

TABLE 2

Relative quantum yields of luminescence

(1) Steady state and pulsed irradiation;  $D = 0$

$$\eta/\eta_0 = 1 - \pi^{1/2}q \exp(q^2) \{1 - \operatorname{erf}(q)\} \approx 1 - (4\pi/3)C_A R_0^3$$

(2) Steady state and pulsed irradiation;  $D \neq 0$

$$\frac{\eta}{\eta_0} = \frac{1}{1 + 4\pi R D C_A \tau_0} [1 - \pi^{1/2}q \exp(q^2) \{1 - \operatorname{erf}(q)\}]$$

(3) Steady state irradiation;  $D = 0$  (Perrin–Ermolaev model)

$$\frac{\eta}{\eta_0} = \frac{1}{1 + 4\pi R D C_A \tau_0} = \frac{1}{1 + K_{SV} C_A} = \frac{1}{1 + k_q \tau_0 C_A}$$

(4) Pulsed irradiation;  $D = 0$  (Perrin–Ermolaev model)

$$\eta/\eta_0 = \exp\{-C_A H(t_0)\} = \exp\{-C_A V_0\} \approx 1 - (4\pi/3)C_A R_0^3$$

## 5. Conclusions

From the previous paragraphs, the following conclusions may reasonably be drawn.

(1) The various decay functions that describe the deactivation processes which an electronically excited species undergoes after pulsed excitation can be easily reduced to the general eqn. (1). This reduction has the advantage of defining an energy transfer function  $H(t)$ , which more properly describes the energy transfer process, whether the nature of the interaction be coulombic or exchange. When the transfer processes are expressed in terms of these  $H(t)$  functions, the strict connections between the known equations obtained by theoretical approaches [2 - 35] become apparent, and in some cases their unexpected equivalence is also demonstrated. The influence of the various terms in the energy transfer functions  $H(t)$  is illustrated in Figs. 1 - 3; Table 1 summarizes the most useful transfer functions.

(2) The relative luminescence quantum yields  $\eta/\eta_0$  are derived for the various conditions of irradiation; also the well-known Stern–Volmer and Perrin–Ermolaev models can be derived and expressed employing the same formalism, as shown in Sections 4.2 and 4.3. Table 2 summarizes the

various equations. It is worth observing that the relative quantum yields discussed in Section 4.1 are based on the assumption that energy transfers occur from each excited donor to all but the nearest acceptors; as shown by Ore [42] the extension to include second nearest or higher order acceptors become significant only at acceptor concentrations higher than those usually found in luminescence quenching experiments [36, 37].

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## Appendix

The following decay functions  $\bar{\rho}(t)$  have been derived by various authors for different conditions, under pulsed excitation.

### A1. Dipole-dipole interaction

#### A1.1. $D = 0$ [2, 14, 33]

$$\bar{\rho}(t) = \exp \left\{ -\frac{t}{\tau_0} - 2q \left( \frac{t}{\tau_0} \right)^{1/2} \right\} \quad (\text{A1})$$

#### A1.2. $D \neq 0$

##### A1.2.1. Kurskii and Selivanenko [15]

$$\bar{\rho}(t) = \exp \left\{ -\frac{t}{\tau_0} - 2q \left( \frac{t}{\tau_0} \right)^{1/2} - \frac{8.4 \left( \frac{3}{2} D_1 + D_2 \right) \tau_0}{R_0^2} q \left( \frac{t}{\tau_0} \right)^{7/6} \right\} \quad (\text{A2})$$

##### A1.2.2. Kurskii and Selivanenko [15]

$$\bar{\rho}(t) = \exp(-At - Bt^{1/2}) \quad (\text{A3})$$

where

$$A = \frac{1}{\tau_0} + 4\pi D_{12} R_{12} \frac{N}{V} + \frac{4\pi R_0^6}{12\tau_0 R_{12}} \frac{N}{V}$$

and

$$B = 4\pi D_{12} \frac{N}{V} \frac{2R_{12}^2}{(\pi D_{12})^{1/2}} + \frac{4\pi R_0^6}{12\tau_0 R_{12}^2} \frac{N}{V} \frac{2}{(\pi D_{12})^{1/2}}$$

A1.2.3. Yokota and Tanimoto [16]

$$\bar{\rho}(t) = \exp \left\{ -\frac{t}{\tau_0} - \frac{4}{3} \pi^{3/2} C(\alpha t)^{1/2} \left( \frac{1 + 10.87x + 15.50x^2}{1 + 8.743x} \right)^{3/4} \right\} \quad (\text{A4})$$

where

$$x = D\alpha^{-1/3} t^{2/3} \quad \alpha = R_0^6/\tau_0$$

A1.2.4. Voltz et al. [17]

$$\bar{\rho}(t) = \exp \left[ -\frac{t}{\tau_0} - 4\pi DN' R C t \left( 1 + \frac{R_0}{12D\tau_0 R^4} \right) \left\{ 1 + \frac{R}{(\pi D)^{1/2}} \right\} \right] \quad (\text{A5})$$

## A2. Exchange interaction

A2.1.  $D = 0$

A2.1.1. Inokuti and Hirayama [4]

$$\bar{\rho}(t) = \exp \left[ -\frac{t}{\tau_0} - \frac{L^3}{8R^3 C_0} \{ (\ln At)^3 + 1.73(\ln At)^2 + 5.9(\ln At) + \dots \} \right] \quad (\text{A6})$$

A2.2.  $D \neq 0$

A2.2.1. Pilling and Rice [14]

$$\bar{\rho}(t) = \exp \left\{ -\frac{t}{\tau_0} - 4\pi R_{\text{eff}} D t - \frac{8\pi D R_{\text{eff}}^2 t^{1/2}}{(\pi D)^{1/2}} \right\} \quad (\text{A7})$$

Equations (A1) - (A7) contain the following parameters. In eqn. (A1),  $2q = (4/3)\pi^{3/2} R_0^3 C_A$ ,  $R$  is the distance between the excited donor and the acceptor,  $R_0$  is a critical distance at which unimolecular (in  $D^*$ ) and bimolecular processes (transfer to A) occur with the same probability,  $1/\tau_0$  is the rate of any channel of decay for  $D^*$  and  $C_A$  is the acceptor concentration; in Galanin's original paper [33],  $2q$  is expressed in terms of experimental spectroscopic data. In eqn. (A2),  $q = (\pi/2)^{1/2} (R_0/R)^3 N$ , where  $N$  is Avogadro's number and  $D_1$  and  $D_2$  are the diffusion coefficients of donor and acceptor. In eqn. (A3),  $D_{12} = D_1 + D_2$ ,  $R_{12}$  is the sum of the molecular radii of the donor and the acceptor, and  $V$  is the volume of the system. In eqn. (A5),  $N' = 6 \times 10^{20}$ . In eqn. (A6),

$$A = \frac{1}{\tau_0} \exp \frac{2R_0}{L}$$

where  $L$  is the Dexter parameter [3] corresponding to the average Bohr radius of either  $D^*$  and A. This parameter has been questioned by Dow [5] and other doubts were raised by Marshall *et al.* [6] on the possibility of employing this equation in the liquid phase:  $C_0 = 3/4\pi R_0^3$ . In eqn. (A7),  $R_{\text{eff}}$  is equal to  $R$  at normal viscosities ( $D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) and it is a rather complex function at other viscosities; the published equation contains some inconsistencies, probably due to misprints [14] revised in eqn. (A7).