Reversible Energy Transfer and Fluorescence Decay in Solid Solutions

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The article deals with the influence of reversible excitation energy transfer on the fluorescence decay in systems with random distribution of molecules. On the basis of a hopping model, we have obtained an expression for the Laplace transform of the decay function and an expression for the average decay time. The case of dipole-dipole interaction is discussed in detail.

1. Introduction

The possible processes of non-coherent non-radiative excitation energy transfer in a multicomponent luminescent solid solution are as follows: (i) energy migration among molecules of the same type (homotransfer), (ii) energy transfer from molecules of one component to molecules of another component (heterotransfer). To illustrate this, let us concentrate on a two-component solution. The component whose absorption and fluorescence spectra are in the region of the shorter wavelength is taken to be the donor. After exciting the donor molecules with a weak and short light impulse, the excitation energy may migrate among the donor molecules, may be transferred to the acceptor molecules, may migrate among acceptor molecules and may be transferred back to the donor molecules. These processes are accompanied by fluorescence and internal conversion. Usually, the energy transfer from acceptor to donor molecules is neglected. This is justified considering the Stokes shift of the fluorescence spectrum of the acceptor and the absorption spectrum of the donor. However, if excited electronic levels of donor and acceptor are close to each other, reversible transfer of energy should be taken into account. Such conditions exist in case of chlorophyll forms [1], ionic forms of dyes [2], heterogeneous broadening of energy levels [3], etc. The influence of reversible energy transfer on the fluorescence quantum yield has already been studied in [4, 5].

In this paper we deal with the influence of back transfer on the fluorescence decay. Our results are an extension of Ref. [6] for this case. In [6], using Bojarski and Domsta's model [7], we have investigated the influence of energy migration among donors on the donor fluorescence decay in a donor-acceptor system, neglecting back transfer. A number of papers have dealt with this problem, e.g. [8–15]. Burshtein [8] and Huber [11] distinguish two models for the energy migration in a donor-acceptor system. When there are many donors in the reach of an acceptor, the transfer of energy has a diffusive character. In the opposite case, excitation may in one jump change its acceptor surrounding. Such a model is called a hopping model. One may then assume absence of correlation between the donors. If dipole-dipole interaction is responsible for the energy transfer, the necessary condition for applying the diffusion model is the fulfilment of the inequality $R_{0DD} \ll R_{0DA}$. However, if $R_{0DD} \gtrsim R_{0DA}$, the hopping model is realized [8, 11]. R_{0DA} and R_{0DD} denote Förster's critical radii for donor-acceptor and donor-donor transfer, respectively [16, 17]. In this article we make use of the results of [6] obtained on the basis of the hopping model and assume that during the back transfer from acceptor to donor there is no correlation between acceptors. In case of dipole-dipole interaction, the application of our results is limited to systems in which the condition $R_{0AA} \gtrsim R_{0AD}$ is satisfied. In this sense, our results are approximate. It seems, however, that the above conditions are well fulfilled in real systems.

2. Theory

In [6] we have shown that in a donor-acceptor system the number $N^{(m)}(t)$ of excited donor molecules

after m acts of donor-donor energy transfer satisfies the relation

$$N^{(m)}(t) = \int_0^t A(t - t')\, N^{(m-1)}(t')\, dt' = A(t) * N^{(m-1)}(t),$$
$$(m = 1, 2, \ldots), \quad (1)$$

where $*$ denotes the convolution operation and $A(t)$ is a probability density of energy transfer from donor to donor, averaged over donor and acceptor positions. Expression (1) may be written in the form

$$N^{(m)}(t) = \phi^{(0)}(t) * K^{(m)}(t), \quad (2)$$

where $\phi^{(0)}(t) = N^{(0)}/N_0$ denotes the decay function of donor molecules originally excited by light, N_0 is the number of donor molecules excited at $t = 0$ by an impulse of light of Dirac δ type. The function $K^{(m)}(t)$ is determined as follows:

$$K^{(m)}(t) = A(t) * K^{(m-1)}(t), \quad (m = 1, 2, \ldots), \quad (3)$$
$$K^{(0)}(t) = N_0\, \delta(t). \quad (4)$$

Equation (2) shows that the fluorescence decay of molecules after m transfer acts differs from the decay of originally excited molecules by the form of the excitation function only. The excitation function of originally excited molecules is $K^{(0)}(t)$, whereas for molecules which obtained their energy after m transfers it is $K^{(m)}(t)$. A similar conclusion was drawn by Burshtein [18] and Hauser [19].

Expression (2) is the basis for further calculations. Let us assume that in the solution there are J components, whose molecules may transfer the excitation energy between themselves. Let us denote by $A_{ij}(t)$ ($i, j = 1, 2, \ldots, J$) the probability density of excitation energy transfer from the ith to the jth component, averaged over all configurations. $\phi_i^{(0)}(t)$ denotes the average fluorescence decay function of the originally excited molecules of the ith component. Let us assume, as in [6], that during the walk of excitation energy among randomly placed molecules their spatial configurations are not correlated. Let us determine functions $L_i^{(m)}(t)$:

$$L_i^{(m)}(t) = \sum_{z=1}^J A_{zi}(t) * L_z^{(m-1)}(t), \quad (m = 1, 2, \ldots), \quad (5)$$
$$L_i^{(0)}(t) = N_{0i}\, \delta(t), \quad (6)$$

where N_{0i} is the number of molecules of the ith component excited at $t = 0$. Analogically to (2) we can write

$$N_i^{(m)}(t) = \phi_i^{(0)}(t) * L_i^{(m)}(t), \quad (m = 0, 1, \ldots) \quad (7)$$

because $L_i^{(m)}(t)$ are excitation functions in this case. In order to continue the calculations it is convenient to carry out a Laplace transformation of (7). In Laplace space we have

$$\hat{N}_i^{(m)} = \hat{\phi}_i^{(0)}\, \hat{L}_i^{(m)}, \quad (8)$$

where

$$\hat{F}(s) = \int_0^\infty \exp(-st)\, F(t)\, dt. \quad (9)$$

On using (5), (8) and the identity $[\hat{\phi}_z^{(0)}]^{-1}\, \hat{\phi}_z^{(0)} = 1$ we get

$$\hat{N}_i^{(m)} = \hat{\phi}_i^{(0)}\, \hat{L}_i^{(m)} \quad (10)$$
$$= \hat{\phi}_i^{(0)} \sum_{z=1}^J \hat{A}_{zi}\, \hat{L}_z^{(m-1)},$$
$$= \hat{\phi}_i^{(0)} \sum_{z=1}^J [\hat{\phi}_z^{(0)}]^{-1}\, \hat{A}_{zi}\, (\hat{\phi}_z^{(0)}\, \hat{L}_z^{(m-1)})$$
$$= \hat{\phi}_i^{(0)} \sum_{z=1}^J [\hat{\phi}_z^{(0)}]^{-1}\, \hat{A}_{zi}\, \hat{N}_z^{(m-1)}, \quad (m = 1, 2, \ldots).$$

The transform $\hat{N}_i$ of the function $\sum \hat{N}_z^{(m)}$ describing the total number of excited molecules of the ith component is obtained from the expression

$$\hat{N}_i = \sum_{m=0}^\infty \hat{N}_i^{(m)}. \quad (11)$$

As a result, we get

$$\hat{N}_i = \hat{\phi}_i^{(0)} [1 - \hat{A}_{ii}]^{-1} \{ N_{0i} + \sum_{\substack{z=1 \\ z \neq i}}^J [\hat{\phi}_z^{(0)}]^{-1}\, \hat{A}_{zi}\, \hat{N}_z \}. \quad (12)$$

The above expression is a set of equations ($i = 1, 2, \ldots, J$) from which one may obtain the transformed function describing the number of excited molecules of any given component of the solution at the time t.

To illustrate this, let us consider now a two-component system. Solving the set of (12), we get

$$\hat{N}_1 = \hat{\phi}_1^{(0)} [(1 - \hat{A}_{11})(1 - \hat{B})]^{-1}$$
$$\cdot [N_{01} + \hat{A}_{21}(1 - \hat{A}_{22})^{-1} N_{02}], \quad (13)$$
$$\hat{N}_2 = \hat{\phi}_2^{(0)} [(1 - \hat{A}_{22})(1 - \hat{B})]^{-1}$$
$$\cdot [N_{02} + \hat{A}_{12}(1 - \hat{A}_{11})^{-1} N_{01}], \quad (14)$$

where

$$\hat{B} = \hat{A}_{12}\hat{A}_{21} [(1 - \hat{A}_{11})(1 - \hat{A}_{22})]^{-1}. \quad (15)$$

To compare this with the results obtained when reversible energy transfer is neglected, let us assume that only the first component is excited by light. Expres-

sions (13) and (14) then take the form

$$^1\hat{N}_1 = \hat{\phi}_1^{(0)} [(1 - \hat{A}_{11})(1 - \hat{B})]^{-1} N_{01}, \tag{16}$$

$$^1\hat{N}_2 = \hat{\phi}_2^{(0)} [(1 - \hat{A}_{22})(1 - \hat{B})]^{-1}$$
$$\cdot \hat{A}_{12} (1 - \hat{A}_{11})^{-1} N_{01}, \tag{17}$$

where the upper index in $^1\hat{N}_1$ and $^1\hat{N}_2$ denotes the excitation by light of the first component. Neglect of back transfer means $\hat{A}_{21} = 0$ and $\hat{B} = 0$. Expression (16) then takes the form

$$^1\hat{\phi}_1 = {}^1\hat{N}_1/N_{01} = \hat{\phi}_1^{(0)} (1 - \hat{A}_{11})^{-1}. \tag{18}$$

We obtained expression (18) in [6], and it was derived earlier in a different way by Vugmeister [10] in case of energy transfer in a system of spins.

3. Discussion and Results of Numerical Calculations for the Case of Dipole-Dipole Interactions

We now assume that dipole-dipole interactions are responsible for the energy transfer. In this case, generalizing the appropriate expressions from [6], we have

$$A_{ij}(t) = [\gamma_{ij}/(\tau_{0i} t)^{1/2}] \exp[-t/\tau_{0i} - 2\gamma_i(t/\tau_{0i})^{1/2}], \tag{19}$$

$$\phi_i^{(0)}(t) = \exp[-t/\tau_{0i} - 2\gamma_i(t/\tau_{0i})^{1/2}], \quad (i,j = 1,2,\dots,J), \tag{20}$$

where

$$\gamma_{ij} = (\pi^{1/2}/2)(c_j/c_{0ij}), \tag{21}$$

$$\gamma_i = \sum_{j=1}^{J} \gamma_{ij}, \tag{22}$$

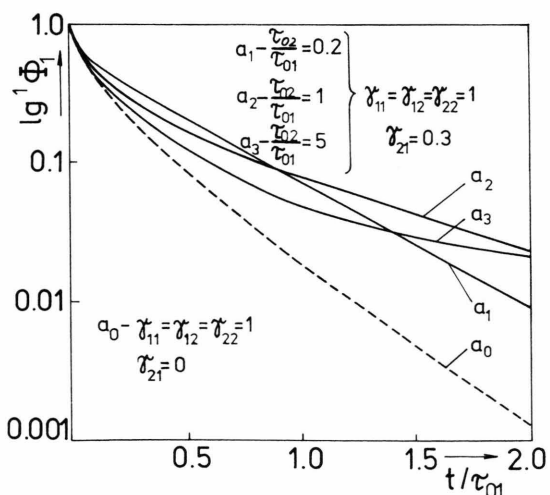
Fig. 1. Donor fluorescence decays $^1\phi_1$ for different values of τ_{02}/τ_{01}. Curves a_1, a_2, and a_3 account for back transfer and curve a_0 neglects back transfer.

τ_{0i} is the average fluorescence lifetime of the ith component in the absence of energy transfer, c_j is the concentration of the jth component and c_{0ij} is the critical concentration [17] in the process of energy transfer from the ith to the jth component. The Laplace transforms of (19) and (20) have the form

$$\hat{A}_{ij} = \alpha_{ij} f(x_i), \tag{23}$$

$$\hat{\phi}_i^{(0)} = (s + \tau_{0i}^{-1})^{-1} [1 - f(x_i)], \tag{24}$$

where

$$\alpha_{ij} = \gamma_{ij}/\gamma_i, \quad x_i = \gamma_i/(s\tau_{0i} + 1)^{1/2}, \tag{25}$$

$$f(x_i) = \pi^{1/2} x_i \exp(x_i^2)[1 - \mathrm{erf}(x_i)]. \tag{26}$$

For a two-component system, (16) and (17) in this case take the form

$$^1\hat{\phi}_1 = {}^1\hat{N}_1/N_{01} = [(s + \tau_{01}^{-1})(1 - \alpha_{11} f(x_1))(1 - \hat{B})]^{-1}$$
$$\cdot [1 - f(x_1)], \tag{27}$$

$$^1\hat{\phi}_2 = {}^1\hat{N}_2/N_{01}$$
$$= [(s + \tau_{02}^{-1})(1 - \alpha_{22} f(x_2))(1 - \hat{B})(1 - \alpha_{11} f(x_1))]^{-1}$$
$$\cdot [1 - f(x_2)] \alpha_{12} f(x_1), \tag{28}$$

where

$$\hat{B} = [(1 - \alpha_{11} f(x_1))(1 - \alpha_{22} f(x_2))]^{-1}$$
$$\cdot \alpha_{12} \alpha_{21} f(x_1) f(x_2). \tag{29}$$

Transform (27) was numerically inversed using the Stehfest procedure [20]. Figure 1 shows the calculated fluorescence decay curves $^1\phi_1$ for $\gamma_{11} = \gamma_{12} = \gamma_{22} = 1$ and for different values of τ_{02}/τ_{01}. The curves a_1, a_2, and a_3 were obtained when back transfer from component 2 to component 1 was taken into account and $\gamma_{21} = 0.3$, whereas the curve a_0 corresponds to neglect of back transfer ($\gamma_{21} = 0$). In Fig. 1 one can see that back transfer significantly increases the $^1\phi_1$ decay. For short times the curves a_0, a_1, a_2, and a_3 overlap because back transfer does not develope.

From the form of the transforms (27) and (28) we are able to calculate the quantum yield and fluorescence mean decay time. The quantum yield $^1\eta_i$ may be obtained from the relation

$$\tag{30}$$

$$^1\eta_i = k_{Fi} \int_0^\infty {}^1\phi_i(t)\, \mathrm{d}t = k_{Fi} {}^1\hat{\phi}_i(s=0), \quad (i=1,2),$$

which leads to

$$^1\eta_1 = \eta_{01} [(1 - \alpha_{11} f(\gamma_1))(1 - B)]^{-1} [1 - f(\gamma_1)], \tag{31}$$

$$^1\eta_2 = \eta_{02} [(1 - \alpha_{22} f(\gamma_2))(1 - B)(1 - \alpha_{11} f(\gamma_1))]^{-1}$$
$$\cdot [1 - f(\gamma_2)] \alpha_{12} f(\gamma_1), \tag{32}$$

where k_{Fi} and η_{0i} are rate constants for fluorescence and absolute quantum yield of the ith component, and $B = \hat{B}(s = 0)$. On the basis of (31) and (32) one can see that the relation $^1\eta_2/\eta_{02} = 1 - ^1\eta_1/\eta_{01}$ is fulfilled. The same formulae were obtained using a different method in [4]. An expression for the quantum yield is also given in [5]. However, in the limit of negligence of back transfer and energy migration ($B = 0$, $\alpha_{11} = 0$), the expression given in [5] does not become a generally accepted Förster's formula [16], contrary to expression (31). Furthermore, in [5] the energy migration between the acceptors is neglected.

For a given two-component system the critical concentrations c_{0ij} may be calculated from spectroscopic data. The quantum yields are functions of two variables: the concentration c_1 of the first component and the concentration c_2 of the second component. Thus, among the four reduced concentrations γ_{ij} only two are independent. As these two variables one may, for example, choose γ_{11} which depends on c_1 [see (21)], and γ_{22} which depends on c_2. By introducing $b = c_{022}/c_{012}$ and $c = c_{011}/c_{021}$ one may express all quantities occuring in (31) and (32) by the variables γ_{11} and γ_{22} and the parameters b and c. The relation between the quantum yield $^1\eta_1/\eta_{01}$ (31) and γ_{11} and γ_{22} is shown in Fig. 2 assuming $b = 1$ and $c = 0.3$, the approximate parameters of the rhodamine 6G-rhodamine B solution studied in [21]. For comparison, the concentration dependence $^1\eta_1/\eta_{01}$ ignoring the energy back transfer ($B = 0$) is shown in the same figure in the form of dashed curves. The energy back transfer increases the quantum yield value. For a fixed concentration of the first component (γ_{11} = const) the quantum yield decreases to zero with

increasing γ_{22}, while for a fixed concentration of the second component (γ_{22} = const) the yield increases to 1 with increasing γ_{11}. When γ_{11}/γ_{22} is fixed (equimolar solutions) the quantum yield moves to some value $(^1\eta_1/\eta_{01})_L$ (see (38)). This behaviour is the result of overlapping of two competitive processes: the escape of energy to the acceptor and the return of the energy from the acceptor to the donor. The limits may be calculated by moving γ_1 and γ_2 to infinity in (31) and (32). When $\gamma_1 \to \infty$ and $\gamma_2 \to \infty$, corresponding in this case to γ_{11} and/or $\gamma_{22} \to \infty$, we have the approximation

$$f(\gamma_i) = 1 - 1/(2\gamma_i^2) + 3/(2\gamma_i^2)^2 - 3\cdot 5/(2\gamma_i^2)^3 + \ldots, \quad (33)$$

leading to the formulae (α_{22} and $\alpha_{11} \neq 1$)

$$^1\eta_1/\eta_{01} \to \Gamma_2/(\Gamma_2 + \Gamma_1) \tag{34}$$

and

$$^1\eta_2/\eta_{02} \to \Gamma_1/(\Gamma_2 + \Gamma_1) \tag{35}$$

where

$$\Gamma_i = (1 - \alpha_{ii})\gamma_i^2 = \gamma_{ij}\gamma_i = \gamma_{ij}\gamma_{ii} + \gamma_{ij}^2, \ (j \neq i). \tag{36}$$

Taking into account that $\gamma_{12} = b\gamma_{22}$ and $\gamma_{21} = c\gamma_{11}$ we have

$$^1\eta_1/\eta_{01} \to (c^2\gamma_{11}^2 + c\gamma_{22}\gamma_{11})/$$
$$[c^2\gamma_{11}^2 + b^2\gamma_{22}^2 + (b + c)\gamma_{11}\gamma_{22}]. \tag{37}$$

From (37) for γ_{11} = const we obtain $^1\eta_1/\eta_{01} \to 0$ if $\gamma_{22} \to \infty$, and $^1\eta_1/\eta_{01} \to 1$ for fixed γ_{22} and $\gamma_{11} \to \infty$. For equimolar solutions ($\gamma_{11} = d\gamma_{22}$, d = const) we obtain

$$(^1\eta_1/\eta_{01})_L = (c^2 d^2 + cd)/[c^2 d^2 + b^2 + (b + c)d]. \tag{38}$$

The mean fluorescence decay time $^1\tau_i$ may be calculated from the relation

$$^1\tau_i = \int_0^\infty t\,^1\phi_i\,\mathrm{d}t / \int_0^\infty {}^1\phi_i\,\mathrm{d}t = -[(\mathrm{d}\,^1\hat{\phi}_i/\mathrm{d}s)/^1\hat{\phi}_i]_{s=0},$$
$$(i = 1, 2). \tag{39}$$

After some calculation we obtain

$$^1\tau_1 = \tau_1 + B(1 - B)^{-1}$$
$$\cdot [(m_{11} + 1)\tau_{11} + (m_{22} + 1)\tau_{22}], \tag{40}$$

where τ_1 is mean fluorescence decay time of the first component when back transfer is neglected ($B = 0$) and is calculated in [22]:

$$\tau_1 = [1 + \gamma_1^2 - (1.5 + \gamma_1^2)f(\gamma_1)]$$
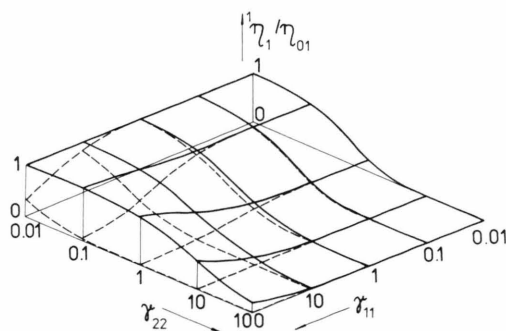$$\cdot [1 - f(\gamma_1)]^{-1}\tau_{01} + m_{11}\tau_{11}, \tag{41}$$

Fig. 2. Quantum yield of donor fluorescence $^1\eta_1/\eta_{01}$ versus reduced concentrations γ_{11} and γ_{22} for $b = 1$ and $c = 0.3$. Dashed curves represent $^1\eta_1/\eta_{01}$ when back transfer is neglected.
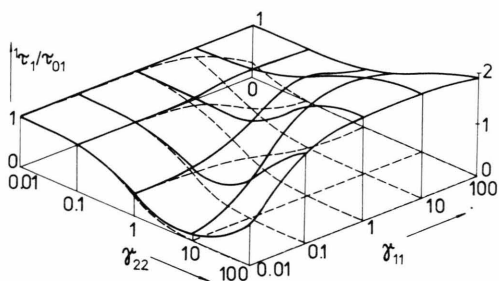
Fig. 3. Mean decay time of donor fluorescence $^1\tau_1/\tau_{01}$ versus reduced concentrations γ_{11} and γ_{22} for $b = 1$, $c = 0.3$, and $\tau_{02} = 2\tau_{01}$. Dashed curves represent $^1\tau_1/\tau_{01}$ when back transfer is neglected.
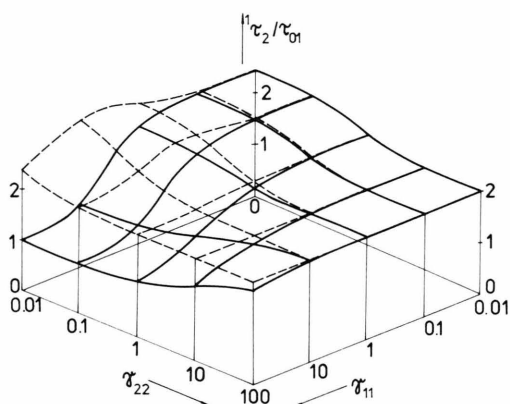

Fig. 4. Mean decay time of acceptor fluorescence $^1\tau_2/\tau_{01}$ versus reduced concentrations γ_{11} and γ_{22} for $b = 1$, $c = 0.3$, and $\tau_{02} = 2\tau_{01}$. Dashed curves represent $^1\tau_2/\tau_{01}$ when back transfer is neglected.

$$m_{ii} = \alpha_{ii} f(\gamma_i) [1 - \alpha_{ii} f(\gamma_i)]^{-1}, \tag{42}$$

$$\tau_{ii} = \tau_{0i} [0.5 f(\gamma_i) + \gamma_i^2 f(\gamma_i) - \gamma_i^2]/f(\gamma_i). \tag{43}$$

For sensitized fluorescence, the expression obtained for the mean decay time is

$$^1\tau_2 = \tau_2 + B(1-B)^{-1} [(m_{11}+1)\,\tau_{11} + (m_{22}+1)\,\tau_{22}]$$
$$+ (m_{11}+1)\,\tau_{11}, \tag{44}$$

where τ_2 is given by (41) when the index is changed from 1 to 2. All quantities occurring in (40) and (44) may again be represented by variables γ_{11} and γ_{22} and parameters b, c, τ_{01}, τ_{02}. The dependence of $^1\tau_1/\tau_{01}$ (40) and $^1\tau_2/\tau_{01}$ (44) on γ_{11} and γ_{22} is shown in Figs. 3 and 4. Similarly to the yields we have assumed that $b = 1$ and $c = 0.3$, and additionally $\tau_{02} = 2\tau_{01}$. The dashed curves represent the mean decay times without taking the back transfer into account. It may be seen

in Figs. 3 and 4 that back transfer increases $^1\tau_1/\tau_{01}$ and decreases $^1\tau_2/\tau_{01}$. The course of the curves is nonmonotonous, this pointing to the competition of the energy transfer to and from the acceptor. At a fixed concentration of the first component ($\gamma_{11} = $ const), $^1\tau_1/\tau_{01}$ and $^1\tau_2/\tau_{01}$ tend to values τ_{02}/τ_{01} (see also (45)), while for $\gamma_{22} = $ const. with an increase of γ_{11} they tend to 1. In the case of equimolar soltuions the average decay times tend to some fixed common limit $(^1\tau_1/\tau_{01})_L = (^1\tau_2/\tau_{01})_L$. For large values of γ_1 and γ_2, after using approximation (33) we find that (40) and (44) tend to a common limit:

$$^1\tau_1/\tau_{01} \to {}^1\tau_2/\tau_{01} \to (\Gamma_2 + \Gamma_1\,\tau_{02}/\tau_{01})(\Gamma_2 + \Gamma_1)^{-1}$$
$$= [c^2\,\gamma_{11}^2 + c\,\gamma_{11}\,\gamma_{22} + (b^2\,\gamma_{22}^2 + b\,\gamma_{11}\,\gamma_{22})\,\tau_{02}/\tau_{01}]$$
$$\cdot [c^2\,\gamma_{11}^2 + b^2\,\gamma_{22}^2 + (b+c)\,\gamma_{11}\,\gamma_{22}]^{-1}. \tag{45}$$

The appropriate limit values of the average decay times result from (45) for $\gamma_{11} = $ const., $\gamma_{22} \to \infty$, and for $\gamma_{22} = $ const., $\gamma_{11} \to \infty$, while for equimolar solutions ($\gamma_{11} = d\gamma_{22}$, $d = $ const) we obtain from (45)

$$(^1\tau_1/\tau_{01})_L = (^1\tau_2/\tau_{01})_L$$
$$= [c^2\,d^2 + c\,d + (b^2 + b\,d)\,\tau_{02}/\tau_{01}]$$
$$\cdot [c^2\,d^2 + b^2 + (b+c)\,d]^{-1}. \tag{46}$$

The limit expressions to which the quantum yields and the mean decay times converge are, of course, connected with the form of the decay functions $^1\phi_1$ and $^1\phi_2$ for large values of γ_1 and γ_2. Expressions (27) and (28) may be written in the following equivalent form:

$$^1\hat\phi_1 = [s + \tau_{01}^{-1} + (s + \tau_{01}^{-1})(1 - \alpha_{11})f_1(1 - f_1)^{-1}$$
$$\cdot (1 - f_2)(1 - \alpha_{22}f_2)^{-1}]^{-1}, \tag{47}$$

$$^1\hat\phi_2 = [s + \tau_{02}^{-1} + (s + \tau_{02}^{-1})(1 - \alpha_{11})^{-1}f_1^{-1}(1 - f_1)$$
$$\cdot (1 - f_2)^{-1}(1 - \alpha_{22}f_2)]^{-1}, \tag{48}$$

where

$$f_i = f(\gamma_i/(s\tau_{0i} + 1)^{1/2}), \quad (i = 1, 2). \tag{49}$$

Using the approximation (33), we get

$$f_i \simeq 1 - (s\tau_{0i} + 1)(2\gamma_i^2)^{-1}, \quad (i = 1, 2), \tag{50}$$

and (47) and (48) take the form (α_{22} and $\alpha_{11} \neq 1$)

$$^1\hat\phi_1 \to \Gamma_2(\Gamma_2 + \Gamma_1\,\tau_{02}/\tau_{01})^{-1} \tag{51}$$
$$\cdot [s + (\Gamma_2 + \Gamma_1)(\Gamma_2 + \Gamma_1\,\tau_{02}/\tau_{01})^{-1}\tau_{01}^{-1}]^{-1},$$

$$^1\hat\phi_2 \to \Gamma_1(\Gamma_2 + \Gamma_1\,\tau_{02}/\tau_{01})^{-1}\tau_{02}/\tau_{01} \tag{52}$$
$$\cdot [s + (\Gamma_2 + \Gamma_1)(\Gamma_2 + \Gamma_1\,\tau_{02}/\tau_{01})^{-1}\tau_{01}^{-1}]^{-1}.$$

From (51) and (52) it results that

$$^1\phi_1 \to \Gamma_2(\Gamma_2 + \Gamma_1 \tau_{02}/\tau_{01})^{-1} \tag{53}$$
$$\cdot \exp[-(\Gamma_2 + \Gamma_1)(\Gamma_2 + \Gamma_1 \tau_{02}/\tau_{01})^{-1} t/\tau_{01}],$$

$$^1\phi_2 \to \Gamma_1(\Gamma_2 + \Gamma_1 \tau_{02}/\tau_{01})^{-1} \tau_{02}/\tau_{01} \tag{54}$$
$$\cdot \exp[-(\Gamma_2 + \Gamma_1)(\Gamma_2 + \Gamma_1 \tau_{02}/\tau_{01})^{-1} t/\tau_{01}].$$

The Eqs. (53) and (54) show that for large γ_1 and γ_2 the fluorescence decays become exponential with a time constant described by (45).

The expressions derived by us are valid under the assumption that the heterotransfer has a hopping character [8, 11]. For dipole-dipole interactions, the criterion for the application of the hopping model may be in our case expressed by $R_{0ij} \lesssim R_{0ii}(i \neq j)$ for each $i, j = 1, 2, \ldots, J$, where R_{0ij}, R_{0ii} are critical radii. In this article we have assumed that spatial configurations of transfer partners are not correlated. Burshtein [18], using the ideas from [23], tried to improve [6] and [10] by an approximate consideration of correlations in the homotransfer processes. In our case this comes down to a substitution of all γ_{ii} quantities by $2^{-1/2}\gamma_{ii}$. Such a correction does not significantly change the results of our article. In case of back transfer there are certain correlations in heterotransfer processes, however their consideration is beyond the scope of this work.

Acknowledgement

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