

MOLECULAR SPECTROSCOPY

Concentration Dependence of the Sensitized Luminescence Quantum Yield upon Energy Transfer from High Excited States

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Abstract—A proper calculation of the quantum yield of sensitized luminescence of acceptors is carried out in the case of nonradiative energy transfer from high excited states of donor molecules. Processes of excitation migration and backward energy transfer from acceptors to lower-lying donor states are taken into account. The calculated concentration dependences are compared with available experimental results. An analogy with reversible electron transfer is noted.

INTRODUCTION

Nonradiative energy transfer from high excited states of molecules is of great interest for photochemistry, radiation chemistry, and photobiology. The existence of this process is established in [1–11].

In papers [3, 8–11], it is noted that, for the correct estimation of the irreversible energy transfer rate, the backward excitation transfer from an acceptor molecule (*A*) to lower-lying levels of a donor molecule (*D*) must be taken into account. The reverse transfer significantly lowers the efficiency of irreversible energy transfer to acceptors. To increase the efficiency of irreversible energy transfer, it is necessary to increase the acceptor concentration. The migration of excitations over acceptors, which increases in this case, results in a decrease in the probability of reverse energy transfer.

In papers [3–6, 8], the concentration dependence of the sensitized luminescence quantum yield of acceptors η_A was measured in the case of energy transfer from highly excited states of donors. A linear dependence was found in [4–6], and a nonlinear one was found in [3, 6, 8]. The authors of [8] showed that in the system chosen by them

$$\eta_A \sim n_A^2, \quad (1)$$

where n_A is the acceptor concentration. Such a dependence is caused by competition between processes of migration and forward and backward energy transfer. The probabilities of these processes increase with increasing n_A , because the average distance between molecules decreases. A quantitative description of the above concentration dependence is absent in [8].

Note that the nonlinear dependence of η_A on n_A was also found in [12].

The aim of this work is a proper consideration of energy migration and backward transfer in the calculation of the probability of irreversible energy transfer

from high excited states. The expressions obtained can be used for quantitative interpretation of experimental results [3–12].

Note that the forward and backward excitation transfer are similar to the photoinduced electron transfer in geminal recombination [13–18]. Indeed, after the pulse excitation of a molecule (an electron donor), the forward transfer of an electron to an acceptor takes place. Within the ion pair produced, a back electron transfer occurs, and the system returns to the ground state with a neutral donor and an acceptor. The rates of forward and backward electron transfer depend exponentially on the distance between molecules. If these processes occur in liquid solutions, it is necessary to take into account both the diffusion of particles described by the diffusion equation and the Coulomb interaction between ions.

Contrary to the electron transfer, the excitation transfer is frequently caused by the dipole–dipole interaction, when the transfer rate is proportional to the inverse sixth power of the distance between a donor and an acceptor. If the acceptor concentration is great, it is necessary to take into account the excitation migration over acceptors, which is not described by the diffusion equation (at least for small times [19, 20]). The finite lifetime of the excited state of the acceptor also influences the reversible energy transfer, because it shortens the time during which backward excitation transfer from the acceptor to the lower-lying donor level is possible.

DIAGRAM OF THE PROCESS AND BASIC NOTATIONS

Figure 1 presents the diagram of the electronic levels of molecules involved in the energy transfer from the high-lying states.

At the initial instant of time, level 2 of the donor molecule is excited. Excitation is either transferred with the rate $w_{32}(r_{DA})$, which depends on the distance r_{DA} between molecules, to the nearest acceptor A_1 (which undergoes transition to the excited state 3), or the donor molecule undergoes transition to the lower-lying state 1 with the rate $1/\tau_2$ (τ_2 is the lifetime of state 2 in the absence of acceptors).

From level 3, excitation is either transferred back to level 1 of the donor with the rate $w_{13}(r_{DA})$ or to another acceptor A_2 with the rate $w_{43}(r_{AA})$, or the molecule A_1 undergoes transition to the ground state with the rate $1/\tau_A$ (τ_A is the lifetime of the excited state of the acceptor in the absence of migration and quenching by the donor). Level 3 can be also occupied as a result of backward energy transfer from A_2 with the rate $w_{34}(r_{AA})$ ($w_{34} = w_{43}$).

According to the diagram presented in Fig. 1, we calculate the sensitization quantum yield η_A of acceptors using two methods: the Ore method [21] and the GAF method [19].

In numerical calculations, we will assume that the energy transfer occurs via dipole-dipole interaction, so that

$$w_{32} = \frac{1}{\tau_2} \left(\frac{R_{32}}{r_{DA}} \right)^6, \quad w_{13} = \frac{1}{\tau_A} \left(\frac{R_{13}}{r_{DA}} \right)^6, \quad (2)$$

$$w_{43} = w_{34} = \frac{1}{\tau_A} \left(\frac{R_{43}}{r_{AA}} \right)^6.$$

Here, R_{32} , R_{13} , and R_{43} are the critical transfer radii for the corresponding processes, and r_{DA} and r_{AA} are distances between corresponding molecules.

A generalization of the results obtained below to other mechanisms of the interparticle interaction presents no problems.

THE ORE METHOD

The main idea of the Ore method [21] is that the excitation is transferred from level 3 of an acceptor back to a donor (on level 1) only if the rate of this process $w_{13}(r_{DA})$ is greater than the rate $w_{43}(r_{AA})$ of energy transfer to the acceptor A_2 that is nearest to A_1 (Fig. 1)

$$w_{13}(r_{DA}) > w_{43}(r_{AA}). \quad (3)$$

This is possible if there are no other acceptors within the volume $V(r_{DA})$, which is part of a sphere of radius

$$r_{AA} = r_{DA} R_{43} / R_{13} \quad (4)$$

around the acceptor A_1 and which is beyond a sphere of radius r_{DA} around a donor D (the dashed area in Fig. 2).

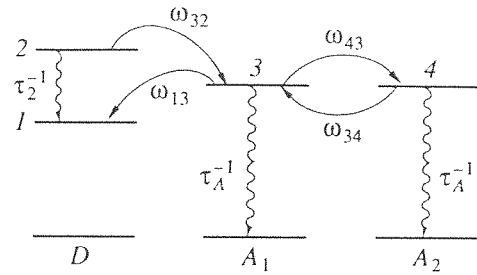


Fig. 1. Energy diagram of molecules participating in energy transfer.

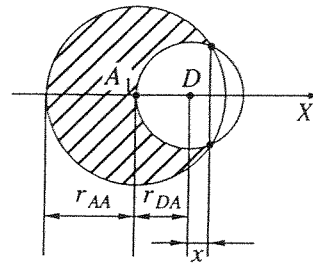


Fig. 2. Volume $V(r_{DA})$ (dashed area) around acceptor A_1 , where other acceptors are absent. X axis passes through A_1 and D. The origin coincides with the position of donor D. The parameters correspond to the case $r_{DA} < r_{AA} < 2r_{DA}$.

The volume of the dashed area can be easily calculated. It is equal to

$$V(r_{DA}) = 4\pi r_{AA}^3 / 3 - \pi [2r_{AA}^3 / 3 - r_{DA}(r_{AA}^2 - r_{DA}^2) - x(r_{AA}^2 - 2r_{DA}^2) + r_{DA}x^2], \quad r_{AA} \leq 2r_{DA}, \quad (5)$$

$$V(r_{DA}) = 4\pi(r_{AA}^3 - r_{DA}^3) / 3, \quad r_{AA} \geq 2r_{DA}, \quad (6)$$

$$x = r_{DA} [0.5(R_{43}/R_{13})^2 - 1]. \quad (7)$$

In formulas (5) and (6), radii r_{AA} and r_{DA} are related by equation (4).

The probability that no acceptors are present within the volume $V(r_{DA})$ is equal to $\exp[-n_A V(r_{DA})]$.

At the initial instant of time, level 2 is excited. The excitation relaxes on the donor with the probability

$$P_2 = \frac{1/\tau_2}{1/\tau_2 + w_{32}}. \quad (8)$$

The excitation will be on level 3 with the probability

$$P_{32} = \frac{w_{32}}{1/\tau_2 + w_{32}}. \quad (9)$$

Backward energy transfer to level 1 will occur with the probability

$$P_{13} = \frac{w_{13}}{1/\tau_A + w_{13}} \exp[-n_A V(r_{DA})]. \quad (10)$$

The exponential factor in formula (10) takes into account that the backward transfer is possible if, near molecule A_1 , there are only such molecules A_2 for which condition (3) is satisfied.

Because the total probability of all the processes is equal to unity, the excitation will be irreversibly transferred to acceptors with the probability

$$P_A(r_{DA}) = 1 - P_2 - P_{13}P_{32} \\ = \frac{\tau_2 w_{32}}{1 + \tau_2 w_{32}} \left[1 - \frac{\tau_A w_{13}}{1 + \tau_A w_{13}} \exp(-n_A V(r_{DA})) \right]. \quad (11)$$

The probability density of finding the acceptor A_1 nearest to the donor D at the distance r_{DA} is

$$4\pi r_{DA}^2 n_A \exp[-(4\pi/3)n_A r_{DA}^3]. \quad (12)$$

Therefore, the quantum yield η_A of acceptor sensitization is obtained by averaging the probability P_A with the distribution density (12)

$$\eta_A = \int_0^\infty 4\pi n_A r_{DA}^2 P_A(r_{DA}) \exp\left(-\frac{4\pi}{3}n_A r_{DA}^3\right) dr_{DA}. \quad (13)$$

(It has been noted repeatedly [15, 22], that the nearest neighbor approximation gives sufficiently exact results).

Let us change the variables of integration in (13):

$$y = 4\pi n_A r_{DA}^3 / 3. \quad (14)$$

Let us also introduce the dimensionless acceptor concentration c :

$$c = 4\pi R_{32}^3 n_A / 3. \quad (15)$$

Denote by z_{13} and z_{43} the following quantities:

$$z_{13} = (R_{13}/R_{32})^3, \quad z_{43} = (R_{43}/R_{32})^3. \quad (16)$$

Then expression (13) is transformed:

$$\eta_A = \int_0^\infty dy e^{-y} \frac{c^2}{y^2 + c^2} \left[1 - \frac{c^2 z_{13}^2}{y^2 + c^2 z_{13}^2} \exp(-\xi) \right], \quad (17)$$

$$\xi(y, z_{13}, z_{43}) = n_A V(r_{DA}). \quad (18)$$

Formula (17) allows one to calculate the concentration dependence of acceptor sensitization quantum yield at different ratios between the rates of migration (z_{43}) and forward and backward (z_{13}) energy transfer.

The results of such calculations for the dipole-dipole interaction of molecules (2) are discussed below.

THE GAF METHOD

Using the GAF method, the migration of excitations over donors can be taken into account more correctly.

Let at $t = 0$ the donor D (Fig. 1) be in the excited state 2. During the time τ_2 , relaxation of the excited

state will occur with the probability (8) and or energy transfer to level 3 of an acceptor will occur with the probability (9). After reaching level 3, the excitation participates in migration and in backward energy transfer.

The probability P_{13} of backward energy transfer can be written in the form

$$P_{13} = \frac{w_{13}}{1/\tau_{ex} + w_{13}}, \quad (19)$$

where τ_{ex} is the excited state lifetime of acceptor A_1 (Fig. 1). This lifetime is determined by relaxation processes in acceptor A_1 (occurring with the probability $1/\tau_A$) and by migration of excitation over acceptors. It is expressed in terms of luminescence decay kinetics $G_d(t)$ of the initially excited molecule (acceptor A_1) [23] (it is assumed that at the initial instant of time $G_d(0) = 1$)

$$\tau_{ex} = \frac{\int_0^\infty t \frac{d}{dt} G_d(t) dt}{\int_0^\infty \frac{d}{dt} G_d(t) dt} = \int_0^\infty G_d(t) dt \quad (20) \\ = \tilde{G}_d(p)|_{p=0} = \tilde{G}_d(0).$$

Here, $\tilde{G}_d(0)$ is the luminescence decay kinetics in the Laplace representation (the Laplace parameter $p = 0$). In the theory of nonradiative energy transfer of localized excitations, the function $G_d(t)$ presents a diagonal part of the Green function [19, 20], which describes the migration of excitations. Using a relation between τ_{ex} and $G_d(t)$, we can rewrite equation (19) in the form

$$P_{13} = \frac{w_{13} \tilde{G}_d(0)}{1 + w_{13} \tilde{G}_d(0)}. \quad (21)$$

The function $\tilde{G}_d(0)$ was calculated using the self-consistent diagrammatic GAF method [19]. In the two-particle approximation, we have [20]

$$\tilde{G}_d(0) = \frac{\tau_A}{(a + \sqrt{a^2 + 1})^2}, \quad (22) \\ a = \frac{\pi}{4\sqrt{2}} \frac{4\pi}{3} n_A R_{43}^3.$$

In the three-particle approximation, the function $\tilde{G}_d(0)$ is obtained from (22) by the substitution $a^2 \rightarrow 0.3882a^2$ [20]:

$$\tilde{G}_d(0) = \frac{\tau_A}{(a + \sqrt{0.3882a^2 + 1})^2}. \quad (23)$$

At the fixed distance r_{DA} between D and A_1 , the probability P_A of irreversible energy transfer to acceptors is [see formula (11)]

$$P_A(r_{DA}) = 1 - P_2 - P_{13}P_{32}. \quad (24)$$

The substitution of (8), (9), and (21) into (24) gives

$$P_A = \frac{\tau_2 w_{32}}{1 + \tau_2 w_{32} + w_{13} \bar{G}_d(0)}. \quad (25)$$

To obtain the quantum yield η_A , it is necessary to average P_A using the nearest neighbor distribution density (12). The change of integration variables and introduction of parameters (15) and (16) finally gives

$$\eta_A = \int_0^\infty dy \frac{c^2}{y^2 + c^2} e^{-y} \times \frac{y^2}{y^2 + z_{13}^2 c^2 / (a + \sqrt{0.3882a^2 + 1})^2}, \quad (26)$$

$$a = \frac{\pi}{4\sqrt{2}} z_{43} c. \quad (27)$$

From (26) it follows that, at very low concentrations of molecules ($c < 10^{-4}$), the quantum yield η_A depends linearly on n_A

$$\eta_A = \frac{\pi}{2} c \frac{R_{32}^3}{R_{32}^3 + R_{13}^3}. \quad (28)$$

At high concentrations ($c \gg 1, a \gg 1$), the quantum yield η_A becomes independent of concentration and reaches its maximum value

$$\eta_A = 1 - \int_0^\infty dy e^{-y} \frac{1.2308(z_{13}/z_{43})^2}{y^2 + 1.2308(z_{13}/z_{43})^2}. \quad (29)$$

RESULTS OF NUMERICAL CALCULATIONS AND DISCUSSION

Concentration dependences of the sensitization quantum yield η_A at different values of parameters z_{13} and z_{43} calculated from (17) (dashed lines) and (26) (solid lines) are presented in Figs. 3 and 4 (the points correspond to calculation in the two-particle GAF approximation).

At moderate concentrations, formulas (17) and (26) give coinciding results. At high concentrations, the deviation does not exceed 15%, the Ore method giving higher values of η_A .

The two-particle GAF approximation also gives higher values of η_A than the three-particle approximation, because the excitation diffusion coefficient is overestimated in this approximation [19].

At low concentrations, linear dependence (28) is observed. In the absence of migration ($z_{43} = 0$, Fig. 3),

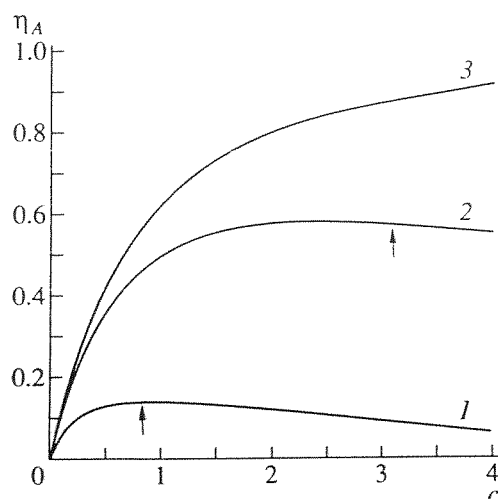


Fig. 3. The concentration dependence of the sensitization quantum yield in the absence of energy migration over acceptors ($z_{43} = 0$). Curves obtained by the Ore and GAF methods coincide in this case. The quantum yield decreases with an increase in the backward energy transfer rate: $z_{13} = 1$ (1), 0.1 (2), 0 (3).

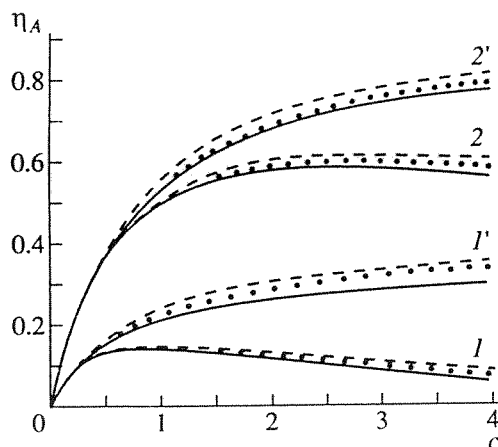


Fig. 4. The concentration dependence of the sensitization quantum yield in the presence of energy migration over acceptors ($z_{43} \neq 0$). The quantum yield increases with increasing energy migration: $z_{13} = 1, z_{43} = 0.1$ (1'), $z_{13} = 1, z_{43} = 1$ (1'), $z_{13} = 0.1, z_{43} = 0.1$ (2), $z_{13} = 0.1, z_{43} = 1$ (2'). The dashed lines correspond to the Ore method, points correspond to the two-particle approximation of the GAF method, solid curves correspond to the three-particle GAF approximation.

the quantum yield η_A initially increases, then (with further increasing concentration) reaches its maximum and begins to decrease. The position of the maximum (indicated by the arrow at the curves) depends on the rate z_{13} of the backward energy transfer. The quantum yield η_A decreases with increasing z_{13} , and the maximum shifts to lower concentrations.

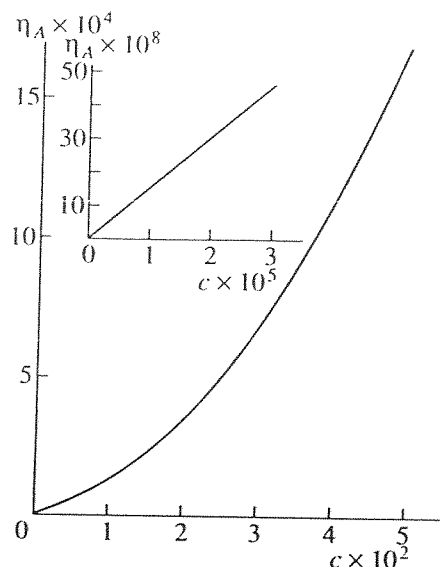


Fig. 5. The concentration dependence of the sensitization quantum yield at low concentrations and at $z_{13} = z_{43} = 100$. For $c < 5 \times 10^{-2}$, the dependence is nonlinear, and for $c < 10^{-4}$, the dependence is linear.

Consideration of excitation diffusion ($z_{43} \neq 0$, Fig. 4) leads to increase in η_A and a shift of the maxima of the curves to higher concentrations (a maxima are absent on curves 1' and 2').

Possibly, these results partially account for the experiments [12], where it was found that the energy transfer efficiency decreased with increasing acceptor concentration.

The experimental dependence $\eta_A \sim n_A^2$ obtained in [8] can be explained within the framework of the developed theory if one supposes that the maximum concentration used in [8] satisfies the condition

$$c = \frac{4\pi}{3} R_{32}^3 n_A \leq 0.05 \quad (30)$$

and $z_{13} \approx z_{43} \geq 100$ (Fig. 5). Because of the lack of necessary data for the estimate of parameters c , z_{13} , and z_{43} in [8], a more comprehensive comparison of the theory with the experiment is not possible.

CONCLUSION

Therefore, upon reversible energy transfer from high excited states, three types of the concentration dependence of the sensitized luminescence quantum yield can be observed. At low acceptor concentrations, the quantum yield initially rises linearly, and then this dependence becomes approximately quadratic. At high concentrations, the quantum yield, passing through a maximum, can begin to decrease, approaching a stationary value (29). The difference between the maximum and stationary values of the quantum yield depends on the relationship between the rates of excitation migration and backward energy transfer.

Due to the analogy noted in the Introduction, similar features should be observed in the case of reversible electron transfer.

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