

Kinetics of radiationless energy transfer from upper excited states

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Abstract

A model of the kinetics of radiationless energy transfer from upper excited states is presented, where both the possibility of back energy transfer from the excited acceptor to a lower lying level of the donor and the possibility of energy migration over acceptors is considered. The model leads to a complex variation of the energy transfer quantum yield with the acceptor concentration. This dependence results from the interplay of direct energy transfer, back energy transfer and energy migration. Back energy transfer reduces the efficiency of donor–acceptor overall transfer efficiency. On the other hand, energy migration over the acceptors decreases the efficiency of back energy transfer and results in an increase in the energy transfer quantum yield. The known experimental results of energy transfer from upper excited states are in qualitative agreement with the present treatment. © 1997 Elsevier Science B.V.

1. Introduction

The radiationless transfer of electronic energy from an excited donor (**D**) to a ground state acceptor (**A**) is a well known phenomenon [1,2]. In the past, it has clearly been demonstrated that energy transfer can occur from excited states other than the first excited singlet or triplet state [3,4]. Nevertheless, relatively few works have been published on this subject, despite its relevance in photochemistry, radiation chemistry and photobiology.

A distinctive feature of the process of energy transfer from upper excited states, is that back transfer is likely to occur, even when the donor and acceptor are alike molecules. Indeed, the acceptor molecule, after receiving the energy from the donor, can normally back transfer it to lower lying levels of the donor molecule, decreasing, in this way, the overall efficiency of transfer. For a high acceptor concentration excitation diffusion over acceptor molecules should also be considered, since it decreases the probability of back energy transfer. As a consequence of these two aspects, the efficiency of energy transfer has a complex dependence on the acceptor concentration.

Several authors [5–8] have experimentally confirmed that the back transfer of excitation from indirectly excited acceptor molecules to lower lying levels of the donor must be taken into account for a correct estimation of the efficiency of energy transfer from **D** to **A**. A linear dependence of the energy transfer quantum yield, η_{DA} , with acceptor concentration, was observed for low concentrations [3,5,9,10], while for higher concentrations a non-linear dependence was observed [5,9]. Ermolaev et al. [5], reported a quadratic dependence of η_{DA}

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with concentration in a limited acceptor concentration range, this being qualitatively explained by the competition between excitation migration over acceptors, direct and back energy transfer.

The aim of this Letter is to present a quantitative kinetic model that considers all the above described processes, in order to obtain the correct dependence of the energy transfer quantum yield on the acceptor concentration. Theoretical predictions are then compared with experimental data.

2. Results and discussion

A simplified scheme of the electronic levels of donor and acceptor molecules taking part in excitation transfer is shown in Fig. 1. Upon excitation, the upper electronic state **u** of the donor is populated. The excited donor can then relax to the lower excited state **l** with rate $1/\tau_u$ or transfer the energy to the nearest acceptor **A**₁ with rate w_d . The excited acceptor can decay to the ground state with rate $1/\tau_A$, transfer the energy to another acceptor **A**₂ with rate w_m , or back transfer the energy to the lower excited electronic state **l** of the donor with rate w_b . The first acceptor **A**₁ can also be re-excited by back energy transfer from the acceptor **A**₂ with rate w_b .

We assume that excitation energy transfer occurs by the dipole–dipole coupling interaction mechanism. The energy transfer rate is well known after the work of Förster [11] and Dexter [12] for thermally equilibrated vibronic levels of the excited electronic state. However, as the lifetime of the donor in the upper excited state is small ($\tau_u < 10^{-11}$ s) energy transfer may occur from a non-equilibrium vibrational distribution of that state. Nevertheless, Kaplan and Jortner [3] have shown that FD theory still holds for the case of slow vibrational relaxation on the timescale of the lifetime of the excited state. In the following, we will assume that energy transfer always occurs in one of the above limiting cases, with rate constants

$$w_d = \frac{1}{\tau_u} \left(\frac{R_d}{r_{DA}} \right)^6, \quad (1a)$$

$$w_b = \frac{1}{\tau_A} \left(\frac{R_b}{r_{DA}} \right)^6, \quad (1b)$$

$$w_m = \frac{1}{\tau_A} \left(\frac{R_m}{r_{AA}} \right)^6, \quad (1c)$$

where R_d , R_b and R_m are the critical radii of energy transfer for the direct transfer, back transfer and migration processes, respectively (see Fig. 1), and r_{DA} and r_{AA} are the D–A and A–A distances. We now consider the steady-state kinetics of the process.

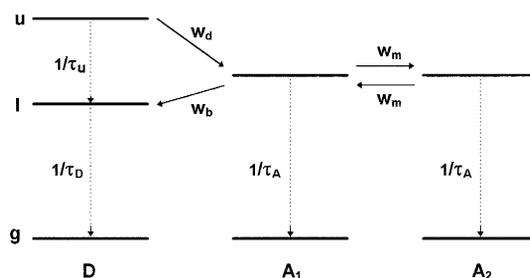


Fig. 1. Kinetic scheme for irreversible energy transfer from an upper excited state. The donor **D** is initially excited to state **u** and may either relax to a lower excited state **l** or transfer its excitation energy to a nearby acceptor **A**₁. This, in turn, may decay, transfer back to the donor **D**, or transfer to another acceptor **A**₂. Migration of excitation energy among acceptors may then occur.

The donor, after being excited into level **u**, relaxes to the lower excited state **I** with probability

$$P_1 = \frac{1/\tau_u}{1/\tau_u + w_d}, \quad (2)$$

or transfers the energy to the nearest acceptor with probability

$$P_d = 1 - P_1 = \frac{w_d}{1/\tau_u + w_d}. \quad (3)$$

Back energy transfer to level **I** can occur with probability

$$P_b = \frac{w_b}{1/\tau_{ex} + w_b}, \quad (4)$$

where τ_{ex} is the effective lifetime of the acceptor molecule **A**₁. This lifetime is determined by both the internal relaxation processes of the acceptor (rate $1/\tau_A$) and by excitation migration over the acceptors. It can be calculated once the Green function, $G(t)$, that describes the energy migration over the acceptors is known. Indeed,

$$\tau_{ex} = \frac{\int_0^t t (d/dt) G_d(t) dt}{\int_0^t (d/dt) G_d(t) dt} = \int_0^t G_d(t) dt = \tilde{G}_d(s)|_{s=0} = \tilde{G}_d(0), \quad (5)$$

$G_d(t)$ being the diagonal part of the Green function for the migration process, since we are only interested in the first excited acceptor molecule. Note that τ_{ex} is the Laplace transform of the Green function, $\tilde{G}_d(s)$, for $s = 0$. By substitution of Eq. (5) in (4), we obtain

$$P_b = \frac{w_d \tilde{G}_d(0)}{1 + w_b \tilde{G}_d(0)}. \quad (6)$$

The function $\tilde{G}_d(0)$ can be calculated by the Gochanour, Anderson and Fayer (GAF) self-consistent diagrammatic method [13]. The GAF method gives [14]

$$\tilde{G}_d(0) = \frac{\tau_A}{(a + \sqrt{\alpha a^2 + 1})^2}, \quad (7)$$

where $\alpha = 1$ in the two-body approximation and $\alpha = 0.3882$ in the three-body approximation, and

$$a = \frac{\pi}{4\sqrt{2}} \frac{4\pi}{3} n_A R_m^3, \quad (8)$$

n_A being the acceptor number density. Thus, the energy transfer quantum yield $\eta_{DA}(r_{DA})$, from the donor to the acceptor **A**₁, separated by a distance r_{DA} , is given by

$$\eta_{DA}(r_{DA}) = P_d(1 - P_b). \quad (9)$$

After substituting expressions (3), (4) and (7) into Eq. (9), we get

$$\eta_{DA}(r_{DA}) = \frac{\tau_u w_d}{1 + \tau_u w_d} \frac{1}{1 + w_b \tilde{G}_d(0)}. \quad (10)$$

This equation is derived for a fixed donor–acceptor separation, r_{DA} . In order to obtain the ensemble energy transfer quantum yield, $\eta_{\text{DA}}(r_{\text{DA}})$ must be averaged over the donor–acceptor distances, weighted by the appropriate donor–acceptor separation distribution function. Considering the nearest-neighbour distribution function ([15] and references therein)

$$g(r_{\text{DA}}) = 4\pi r_{\text{DA}}^2 n_{\text{A}} \exp\left(-\frac{4\pi}{3} r_{\text{DA}}^3 n_{\text{A}}\right), \quad (11)$$

we obtain for the energy transfer quantum yield:

$$\eta_{\text{DA}} = \int_0^\infty dy \frac{c^2}{y^2 + c^2} e^{-y} \frac{y^2}{y^2 + z_{\text{b}}^2 c^2 / \left[(\pi/4\sqrt{2}) c z_{\text{m}}^3 z_{\text{b}}^3 + \sqrt{\alpha \left((\pi/4\sqrt{2}) c z_{\text{m}}^3 z_{\text{b}}^3 \right)^2 + 1} \right]^2}, \quad (12)$$

where

$$y = \frac{4\pi}{3} r_{\text{DA}}^3 n_{\text{A}}, \quad (13)$$

$$c = \frac{4\pi}{3} R_{\text{d}}^3 n_{\text{A}}, \quad (14)$$

$$z_{\text{b}} = \frac{R_{\text{b}}}{R_{\text{d}}}, \quad (15)$$

$$z_{\text{m}} = \frac{R_{\text{m}}}{R_{\text{b}}}. \quad (16)$$

For low acceptor concentrations ($c \ll 10^{-4}$), Eq. (12) leads to a linear variation of η_{DA} with the reduced concentration c ,

$$\eta_{\text{DA}} = \frac{\pi}{2} c \frac{1}{1 + z_{\text{b}}^3}, \quad (17)$$

as experimentally observed in Refs. [3,9]. At high acceptor concentrations, the quantum yield departs from the linear dependence and, for $c \gg 1$, reaches a limiting value,

$$\eta_{\text{DA}} = 1 - \int_0^\infty dy e^{-y} \frac{1}{1 + \beta z_{\text{m}}^6 y^2}, \quad (18)$$

where

$$\beta = \frac{\pi^2 (\sqrt{\alpha} + 1)^2}{32}. \quad (19)$$

This kind of behaviour appears to correspond to the experimental results given in Refs. [3,9].

We now give some results for the quantum yield of intermediate acceptor concentrations, numerically calculated using the general formula, Eq. 12.

As can be seen from Fig. 2, the energy transfer quantum yield increases initially with the acceptor reduced concentration c , then reaches a maximum, and decreases afterwards (curves B and D).

It is seen that the quantum yield globally decreases and the maximum shifts to lower concentrations when the back energy transfer rate parameter z_{b} increases. On the other hand, the increase in the excitation migration over acceptors, as measured by z_{m} , leads to a quantum yield increase and shifts the curve maximum to higher concentrations (note that for curves A and C maxima are not visible in the concentration range displayed). These

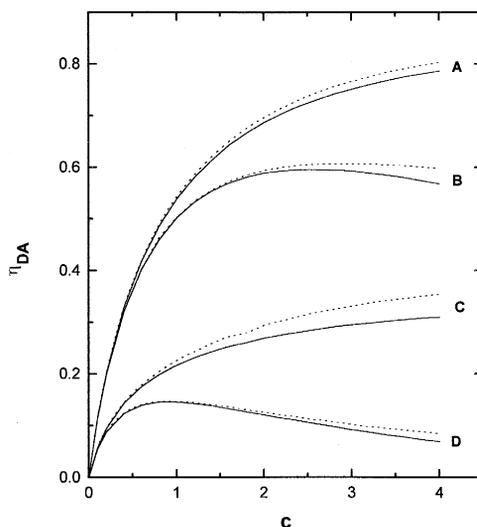


Fig. 2. Energy transfer quantum yield η_{DA} (Eq. 12) as a function of the acceptor reduced concentration c , for selected values of the reduced parameters z_b and z_m (Eqs. 15 and 16): $z_b = 0.5$, $z_m = 2$ (curves A), $z_b = 0.5$, $z_m = 1$ (curves B), $z_b = 1$, $z_m = 1$ (curves C), and $z_b = 1$, $z_m = 0.5$ (curves D). Dashed curves: 2-body GAF method; solid lines: 3-body GAF method. The limiting values of η_{DA} ($c \rightarrow \infty$) are (Eq. 18 in the 3-body approximation): 0.83 (case A), 0.35 (cases B and C), and 0.02 (case D).

results may explain experimental results where a decrease in energy transfer efficiency with acceptor concentration is observed.

The quadratic dependence of η_{DA} with c observed in Ref. [5], is also predicted in the framework of the developed theory, when the acceptor concentration is low, $c \leq 0.05$, but above the linear dependence range, as shown in Fig. 3.

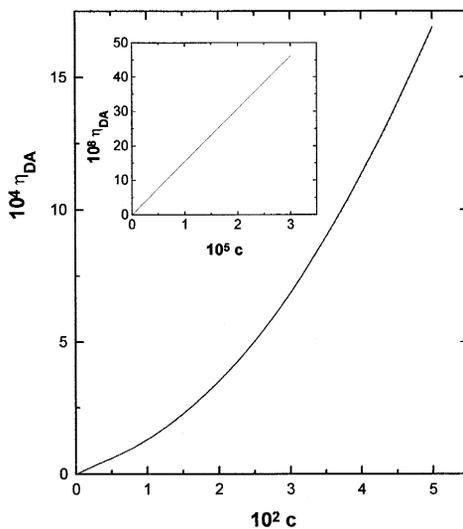


Fig. 3. Energy transfer quantum yield η_{DA} as a function of the acceptor reduced concentration c for $z_b = 5$ and $z_m = 1$, calculated by the 3-body approximation of the GAF method. A quadratic dependence is apparent. The insert shows that for low concentrations the dependence is linear.

3. Conclusions

A model of the kinetics of radiationless energy transfer from upper excited states was presented, where both the possibility of back energy transfer from the excited acceptor to a lower lying level of the donor and the possibility of energy migration over acceptors is considered. The model leads to a complex variation of the energy transfer quantum yield with the acceptor concentration, Eq. 12. This dependence results from the interplay of direct energy transfer, back energy transfer and energy migration. Back energy transfer reduces the efficiency of the donor–acceptor overall transfer efficiency. On the other hand, energy migration over the acceptors decreases the efficiency of back energy transfer and results in an increase in the energy transfer quantum yield. Three different kinds of concentration dependence of the energy transfer quantum yield (linear, quadratic and asymptotic) are predicted. The known experimental results of the energy transfer from upper excited states are well accounted for by the present formalism. A complete comparison between theory and experiment was, nevertheless, not possible because the data needed for the estimation of the parameters z_b , z_m and c are not available.

Acknowledgements

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