

variation in the value of α seems to indicate that the distribution is probably very close to a statistical one in these solvents. For example, when methyl cyclohexane, where the solute solubility is much less than in the solvents given in Table I, is used as a solvent over the same range of acceptor concentration deviations from Eq. (1) and a significant increase in energy transfer are readily observed. The latter observations are due to a preferential segregation of the solutes upon glass formation.

The second question is more difficult to answer. However, the essentially constant value of α found over a wide range of solvent molecular geometries would again argue that orientations are not too im-

portant. Also, since the proposed exchange mechanism requires essentially contact between donor-acceptor pairs the question of what distance we are discussing becomes quite clear. If the distance dependence was something like $1/R^n$ then the questions would become more serious. The uncertainties involved in interpreting the values of α because of the small values of R involved have been discussed above.

In conclusion, it is felt that the general conclusions stated in this paper are not affected by the use of glassy media except perhaps in an exact evaluation of the meaning of the transfer constant α . For the latter purpose, it is no doubt true that single crystals would be preferable.

Influence of Resonance Transfer on Luminescence Decay*

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The effects of dipole-dipole resonance transfer on the population and decay of excited donor molecules are discussed. The limitation of the previous treatments of this problem to flash excitation is demonstrated. The present treatment is applicable to systems which have achieved a steady state or have been flashed. Expressions are given for the donor quantum yields, the decay of excited donor molecules for flashed and steady-state systems, and the steady-state population of excited donor molecules.

INTRODUCTION

THE effects of resonance transfer, by dipole-dipole coupling between excited donor and unexcited acceptor molecules, on the luminescence decay of the former, has been considered theoretically by several investigators.¹⁻³ The expressions that have been obtained independently by these workers are identical. However, as will be shown in this paper, the expressions in Refs. 1-3 are correct only for the special case of flash excitation. The treatment and equations developed here, which include steady-state conditions, have more general applicability.

LUMINESCENCE DECAY OF A SYSTEM INITIALLY IN A STEADY STATE

The deactivation of an excited donor molecule can be effected by resonance interactions with acceptor

molecules as well as by processes that are independent of acceptor molecules. However, as a result of the resonance interactions, the probability of an excited donor losing its electronic energy is dependent upon the distribution of acceptors about it. Thus, excited donor molecules which would have the same probability of decay in the absence of acceptors now have different decay probabilities if they have different acceptor environments.

To emphasize this latter point, one can think of the physical system that consists of N_D unexcited donors and N_A unexcited acceptors as being composed of donor classes. For example, Class γ includes all donors that have the same acceptor surroundings and therefore have the same probability of decay when excited. By the configuration γ it is meant that all members of Class γ have an acceptor at positions R_1, R_2, \dots, R_{N_A} , where the positions of the acceptors refer to the donor being considered. In the present treatment, it is assumed that the numbers of excited donor and excited acceptor molecules are much smaller than the respective numbers of unexcited donors and acceptors. In addition, energy transfer and interactions between donors are neglected.

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¹ A. Y. Kurskii and A. S. Selivanenko, *Opt. Spectry (USSR)* **8**, 340 (1960) [*Opt. i Spektroskopiya* **8**, (1960)].

² M. D. Galanin, *Soviet Phys.—JETP* **1**, 317 (1955) [*Zh. Eksperim. i Teor. Fiz.* **28**, 485 (1955)].

³ Th. Förster, *Z. Naturforsch.* **4a**, 321 (1949).

The rate equation for excited donors belonging to Class γ is

$$dn_{\gamma}^*/dt = k_1(N_{\gamma} - n_{\gamma}^*) - (\tau)^{-1}n_{\gamma}^* - k_{\gamma}n_{\gamma}^*, \quad (1)$$

where n_{γ}^* is the number of excited donors at the time t belonging to Class γ ; k_1 is the collection of constants which includes the donor absorption coefficient (assumed to be the same for all donors) and the incident light intensity; N_{γ} is the total number of donors that belong to Class γ ; τ is the excited donor lifetime in the absence of acceptor molecules; R_i is the distance between Acceptor i and a donor of Class γ ; R_0 is the critical transfer distance for which the probability of nonresonance deactivation and resonance transfer is equal for a donor-acceptor pair; and k_{γ} is the resonance transfer rate constant for any excited donor belonging to Class γ . The resonance transfer rate constant can be written for the case of weak dipole-dipole coupling as^{4,5}

$$k_{\gamma} = \tau^{-1} \sum_{i=1}^{N_A} \left(\frac{R_0}{R_i} \right)^6. \quad (2)$$

It should be noted that the orientation factor that appears in the complete resonance transfer constant for dipole-dipole coupling has been averaged out in Eq. (2) assuming random orientations. It is generally felt that the use of an averaged orientation factor in the resonance transfer rate constant is legitimate only if the Brownian molecular rotation is much faster than resonance transfer. However, it is shown in Appendix A that the use of an averaged orientation factor in the transfer constant in these calculations does not depend on molecular rotation for its justification. One finds that the decay curves and therefore the quantum yields are not affected if the angular part of the transfer constant is not averaged out beforehand. The assumption that the number of excited donors is much smaller than the number of unexcited donors is equivalent to the requirement that $1/\tau \gg k_1$. The term $k_1 n_{\gamma}^*$ can be neglected therefore in Eq. (1). If the number of unexcited donors is not much greater than the number of excited donors at any time, then the present treatment can be modified suitably.

The steady-state concentration of excited donors belonging to Class γ is

$$n_{\gamma}^*(0) = k_1 N_{\gamma} / [\tau^{-1} + k_{\gamma}]. \quad (3)$$

After the incident radiation is turned off (at time $t=0$), the decay can be written as

$$n_{\gamma}^*(t) = n_{\gamma}^*(0) \exp[-t(\tau^{-1} + k_{\gamma})], \quad (4)$$

where $n_{\gamma}^*(0)$ is the steady-state concentration given in Eq. (3).

The number of unexcited donors N_{γ} is given by

$$N_{\gamma} = N_D P_{\gamma}\{d\gamma\}, \quad (5)$$

where $P_{\gamma}\{d\gamma\}$ is the probability of a given donor molecule having the acceptor environment γ . For a dilute system of donors and acceptors, it is assumed that the unexcited donors and unexcited acceptors are distributed randomly. Therefore, the probability can be written

$$P_{\gamma}\{d\gamma\} = \prod_{i=1}^{N_A} \frac{4\pi R_i^2 dR_i}{V}, \quad (6)$$

where R_i is the distance between Acceptor i and a donor of Class γ , and V is the volume of the container. When Eqs. (3) through (6) are combined, the number of excited donor molecules at a time t after the incident radiation is turned off is

$$n^*(t) = k_1 N_D \int_{N_A} \dots \int \frac{\exp[-t(\tau^{-1} + k_{\gamma})]}{(\tau^{-1} + k_{\gamma})} \prod_{i=1}^{N_A} \frac{4\pi R_i^2 dR_i}{V}. \quad (7)$$

If one now takes the time derivative of $n^*(t)$ and expresses k_{γ} as given in Eq. (2), one obtains the slope of the decay curve. This yields

$$\frac{dn^*(t)}{dt} = -k_1 N_D \times \exp\left(-\frac{t}{\tau}\right) \left\{ \int_0^{R_v} \exp\left[-\frac{t}{\tau} \left(\frac{R_0}{R}\right)^6\right] \frac{4\pi R^2 dR}{V} \right\}^{N_A}, \quad (8)$$

where R_v is the radius of the vessel. Förster³ has evaluated the integral appearing in Eq. (8) assuming that $(R_0/R_v)^6(t/\tau) \ll 1$. Since R_0 is much less than R_v , this assumption is good for all times of interest. Equation (8) then becomes

$$\frac{dn^*(t)}{dt} = -k_1 N_D \exp\left(-\frac{t}{\tau}\right) \left\{ 1 - \left[\pi \left(\frac{R_0}{R_v}\right)^6 \frac{t}{\tau} \right]^{N_A} \right\}. \quad (9)$$

Since it has been assumed that $(R_0/R_v)^6(t/\tau) \ll 1$, Eq. (9) can be expressed as

$$\frac{dn^*(t)}{dt} = -k_1 N_D \exp\left[-\frac{t}{\tau} - N_A \frac{R_0^3}{R_v^3} \left(\frac{t}{\tau}\right)^{\frac{1}{2}}\right]. \quad (10)$$

Integrating Eq. (10) with respect to time gives

$$n^*(t) = k_1 N_D \int_t^{\infty} \exp\left[-\frac{t'}{\tau} - N_A \frac{R_0^3}{R_v^3} \left(\frac{t'}{\tau}\right)^{\frac{1}{2}}\right] dt'. \quad (11)$$

If $S = t'/\tau$, $q = (N_A/2) R_0^3/R_v^3 \sqrt{\pi}$, and $x = S^{\frac{1}{2}} + q$, then Eq. (11) can be expressed as

$$n^*(t) = k_1 N_D \tau \int_{[(t/\tau)^{\frac{1}{2}} + q]}^{\infty} [\exp(q^2 - x^2)] 2(x - q) dx. \quad (12)$$

⁴ Th. Förster, *Ann. Physik* **2**, 55 (1948).

⁵ For a discussion of the various dipole-dipole coupling mechanisms see Th. Förster, "Excitation Transfer" in *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith, and J. L. Magee (John Wiley & Sons, Inc., New York, 1960), pp. 300-319.

After carrying out the integration in Eq. (12), one finds

$$n^*(t) = k_1 N_D \tau \left[\exp \left[-\frac{t}{\tau} - 2q \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \right] - \sqrt{\pi} q \exp(q^2) \left\{ 1 - \operatorname{erf} \left[q + \left(\frac{t}{\tau} \right)^{\frac{1}{2}} \right] \right\} \right], \quad (13)$$

where

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-y^2) dy.$$

The steady-state concentration is directly obtained from Eq. (13) by setting $t=0$. This gives

$$n^*(0) = k_1 N_D \tau \{ 1 - \sqrt{\pi} q \exp(q^2) [1 - \operatorname{erf}(q)] \}. \quad (14)$$

LUMINESCENCE DECAY OF A SYSTEM WHICH IS FLASHED

Consider now the damping of a system which was excited by a flash that had a duration much smaller than the lifetime of the excited state. Equation (4) retains the same form for this case, but $n_{\gamma}^*(0)$ is now the instantaneous population of excited donors in Class γ rather than the steady-state population. Hence

$$n_{\gamma}^*(0) = k_1' N_{\gamma}, \quad (15)$$

where k_1' is a collection of constants that include the donor absorption coefficient and the flash intensity. The treatment used for the steady-state calculation can be directly applied to the case of a flash. In place of Eq. (7), one has

$$n'^*(t) = k_1' N_D \iiint \dots \int \exp \left[-t \left(\frac{1}{\tau} + k_{\gamma} \right) \right] \prod_{i=1}^{N_A} \frac{4\pi R_i^2 dR_i}{V}. \quad (16)$$

Except for the constants k_1' and k_1 , Eq. (15) is the same as Eq. (8), which is the slope of the decay curve. This is not surprising since the time derivative of Eq. (7) removes that part of the steady-state expression $n_{\gamma}^*(0)$ which is dependent on the distribution of acceptor molecules. Thus, both dn^*/dt and $n'^*(t)$ are independent of the acceptor molecules at $t=0$. Carrying through the integration indicated in Eq. (16) one finds that

$$n'^*(t) = k_1' N_D \exp \left\{ -\frac{t}{\tau} - N_A \left[\pi \left(\frac{R_0}{R_{\sigma}} \right)^6 \frac{t}{\tau} \right]^{\frac{1}{3}} \right\}. \quad (17)$$

DISCUSSION OF THE DECAY CURVES

The expression for the luminescence decay obtained by the aforementioned investigators¹⁻³ is

$$n^*(t) = n_0 \exp \left\{ -\frac{t}{\tau} - N_A \left[\pi \left(\frac{R_0}{R_{\sigma}} \right)^6 \frac{t}{\tau} \right]^{\frac{1}{3}} \right\}, \quad (18)$$

where n_0 is the number of excited donor molecules at $t=0$, and the other symbols have been defined previously. This expression is identical with Eq. (17). Hence, the result of these investigators is applicable to a system which is flashed, but not to one which has reached a steady state. The limits of applicability of the calculations in Refs. 1-3 to a flashed system arise from the assumed distribution of excited donors. In their treatments, it is assumed that the excited donors are distributed randomly with respect to the acceptors. (In the present treatment, it is assumed that the unexcited donors and acceptors are distributed randomly.) However, the excited donors are not distributed randomly in the steady state. In the steady state the probability of finding an excited donor near an acceptor molecule is less than the probability of finding an excited donor molecule with an acceptor molecule farther away. Hence, the excited donor molecules are not distributed randomly in the steady state. However, in the flashed system, the distribution of the excited donors at $t=0$ is indeed a random one if the unexcited donors are distributed randomly. The exciting flash is of such short duration that there is not sufficient time from the start of the pulse to its conclusion for the excited donors to become nonrandomly distributed by $t=0$.

QUANTUM YIELDS

Although the decay curves for a system that was in a steady state differ from those of a system that was flashed, the quantum yields are the same for both cases, as shown in Appendix B. The relative donor quantum yield is

$$\eta/\eta_0 = 1 - \sqrt{\pi} q \exp(q^2) [1 - \operatorname{erf}(q)], \quad (19)$$

where η is the donor quantum yield in the presence of acceptors and η_0 is the donor quantum yield in the absence of acceptors. This result for the relative donor quantum yield is identical with the expressions obtained by Förster,³ Galanin,² and Kurskii and Selivanenko.¹ The predicted quantum yields are in excellent agreement with the experimental results.³

APPENDIX A

In this section, $n^*(t)$ will be calculated by use of the complete expression for the resonance transfer rate constant which includes the orientation term. The bulk of this paper employs an expression for k_{γ} in which the orientation term has already been averaged. This averaged orientation factor is included in R_0^6 and is equal to 2/3. The resonance transfer rate constant including angles can be written as

$$k_{\gamma} = \tau^{-1} (R_0/R)^6 \frac{2}{3} |\Phi|^2, \quad (A1)$$

where

$$|\Phi|^2 = |\sin\theta_D \sin\theta_A \cos\phi_A - 2 \cos\theta_D \cos\theta_A|^2, \quad (A2)$$

where θ_D , θ_A , and ϕ_A are the angles that the donor and acceptor dipoles, respectively, make with \mathbf{R} , the distance between the donor and acceptor.

The probability of a given donor molecule having the acceptor environment γ must now include the relative orientation of the donor and acceptors, which is

$$P_\gamma\{d\gamma\} = \prod_{i=1}^{N_A} \frac{\sin\theta_D d\theta_D}{2} \frac{R_i^2 \sin\theta_i dR_i d\theta_i d\phi_i}{V}. \quad (\text{A3})$$

Equation (8) can be written as

$$\begin{aligned} dn^*/dt = & -k_1 N_D \exp(-t/\tau) \\ & \times \left\{ \int_0^{R_0} \int_0^\pi \int_0^\pi \int_0^{2\pi} \exp\left[-\frac{t}{\tau} \left(\frac{R_0}{R_i}\right)^6 \frac{3}{2} |\Phi|^2\right] \right. \\ & \left. \times \frac{\sin\theta_D d\theta_D}{2} \frac{R_i^2 \sin\theta_i dR_i d\theta_i d\phi_i}{V} \right\}^{N_A}. \quad (\text{A4}) \end{aligned}$$

Let

$$\begin{aligned} I(t) = & \int_0^{R_0} \int_0^\pi \int_0^\pi \int_0^{2\pi} \exp\left[-\frac{t}{\tau} \left(\frac{R_0}{R_i}\right)^6 \frac{3}{2} |\Phi|^2\right] \\ & \times \frac{\sin\theta_D d\theta_D}{2} \frac{R_i^2 \sin\theta_i dR_i d\theta_i d\phi_i}{V}. \quad (\text{A5}) \end{aligned}$$

Integrating over R_i gives

$$\begin{aligned} I(t) = & \frac{1}{4\pi} \int_0^\pi \int_0^\pi \int_0^{2\pi} \frac{\sin\theta_D d\theta_D}{2} \sin\theta_i d\theta_i d\phi_i \\ & \times \left\{ 1 - \left[\pi \left(\frac{R_0}{R_v}\right)^6 \frac{3}{2} |\Phi|^2 \frac{t}{\tau} \right]^{\frac{1}{3}} \right\}. \quad (\text{A6}) \end{aligned}$$

[Equation (A6) was obtained assuming that $\frac{3}{2} |\Phi|^2 (R_0/R_v)^6 (t/\tau) \ll 1$.]

$$I(t) = 1 - \frac{1}{8\pi} \left\{ \pi \left(\frac{R_0}{R_v}\right)^6 \frac{3}{2} \frac{t}{\tau} \right\}^{\frac{1}{3}} \iiint |\Phi| \sin\theta_D d\theta_D \sin\theta_i d\theta_i d\phi_i. \quad (\text{A7})$$

The integral on the right side is the average value of $|\Phi|$, that is,

$$\begin{aligned} \langle |\Phi| \rangle_{Av} = & (\langle \Phi^2 \rangle)^{\frac{1}{2}} \\ = & \left(\frac{1}{8\pi} \int_0^\pi \int_0^\pi \int_0^{2\pi} |\Phi|^2 \sin\theta_D d\theta_D \sin\theta_i d\theta_i d\phi_i \right)^{\frac{1}{2}}. \quad (\text{A8}) \end{aligned}$$

This yields

$$\langle |\Phi| \rangle_{Av} = (2/3)^{\frac{1}{2}}. \quad (\text{A9})$$

Combining Eqs. (A5) and (A9) yields

$$I(t) = 1 - [\pi (R_0/R_v)^6 (t/\tau)]^{\frac{1}{3}}. \quad (\text{A10})$$

Equation (A4) can be written as

$$\frac{dn^*}{dt} = -k_1 N_D \exp\left(-\frac{t}{\tau}\right) \left\{ 1 - \left[\pi \left(\frac{R_0}{R_v}\right)^6 \frac{t}{\tau} \right]^{\frac{1}{3}} \right\}^{N_A}. \quad (\text{A11})$$

The result for dn^*/dt given in Eq. (A11) is identical with Eq. (9) where the orientation term in the transfer rate constant had already been averaged over angles. Similarly, the orientation term for the case of the flashed system does not alter the expression for $n^{*}(t)$ given in Eq. (17).

APPENDIX B

For the steady-state case, the donor quantum yield is

$$\eta = k_e n^*(0) / k_1 N_D. \quad (\text{B1})$$

Substituting $n^*(0)$ from Eq. (14) into Eq. (B1) gives

$$\eta = k_e \tau \{ 1 - \sqrt{\pi} q \exp(q^2) [1 - \text{erf}(q)] \}, \quad (\text{B2})$$

where k_e is the rate constant for donor emission. The donor quantum yield in the absence of acceptors is

$$\eta_0 = k_e k_1 N_D \tau / k_1 N_D = k_e \tau. \quad (\text{B3})$$

Combining Eqs. (B2) and (B3), one obtains

$$\eta / \eta_0 = 1 - \sqrt{\pi} q \exp(q^2) [1 - \text{erf}(q)]. \quad (\text{B4})$$

For the case of a system that is flashed, the donor quantum yield is

$$\eta = k_e \int_0^\infty n^{*}(t) dt / k_1' N_D. \quad (\text{B5})$$

Integrating Eq. (13) after substituting for $n^{*}(t)$ given in Eq. (17) allows

$$\eta = \frac{k_e k_1' N_D \tau \{ 1 - \sqrt{\pi} q \exp(q^2) [1 - \text{erf}(q)] \}}{k_1' N_D}. \quad (\text{B6})$$

In the absence of acceptors, the donor quantum yield for the case of a flash is

$$\eta_0 = k_e k_1' N_D \tau / k_1' N_D = k_e \tau. \quad (\text{B7})$$

One therefore obtains

$$\eta / \eta_0 = 1 - \sqrt{\pi} q \exp(q^2) [1 - \text{erf}(q)]. \quad (\text{B8})$$

The quantum yields are thus the same for the steady state and the flashed cases.