Depolarization of Photoluminescence of Isotropic Solutions Produced by Excitation Energy Migration*

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A theory of the excitation energy transfer between like molecules in isotropic solution based on a centre or shell model of a primarily excited luminescent molecule and on the extended Förster "excitation master equation" has been elaborated. Fluorescence and phosphorescence depolarization are shown to be governed by singlet-singlet energy migration and described by the same expression. The comparison of the theoretical curve with the experimental data obtained by Gondo et al. (1975) for benzo[f]quinoline in ethanol glass at 77 K results in the following critical distance R_0 for the excitation energy migration: 21.5 Å for fluorescence and phosphorescence, respectively.

1. Introduction

Intermolecular radiationless energy transfer (energy migration) is of considerable interest for both experimental and theoretical studies (see the reviews of Kawski [1] and Burshtein [2, 3]). In recent years, Jabłoński's model of a luminescent centre [4–6] was developed in order to describe the concentration depolarization (self-depolarization), the donor fluorescence quenching by foreign substances (acceptors), and the sensitized fluorescence. To this end, a multilayer shell model [7] and the Förster "master equation" [8], which describes the transfer of the excitation energy between donor (D) and acceptor (A) molecules in the singlet state (S), were employed. Reports on earlier attempts and further development of the theory referring to the multi-layer model can be found in [9–22].

In the present paper a concentration depolarization theory of photoluminescence of solutions is developed, based on the concept of the luminescence centre or the multilayer model, and taking into account the population of the luminescent singlet S_1 and triplet T_1 states via excited singlet state.

It is worth noting that the polarization spectra and the concentration depolarization curves are practically identical for fluorescence and delayed fluorescence thermally stimulated from the T_1-state* [24, 25]. Hence it was concluded that the triplet state T_1 exists as a certain inert state and the migration of the excitation energy does not occur for the luminescent molecule remaining in the triplet T_1 state. Furthermore, it has been found [26–28] that the concentration depolarization of the $T_1 \rightarrow S_0$-phosphorescence is governed by the singlet-singlet energy migration. It is therefore of special interest to develop the concentration depolarization theory including the T_1-state.

2. General Formalism

The theory of the luminescent centre (LC) or luminescent shell (LS) model interprets the transfer of the excitation energy between the initially excited luminescent molecule (LM) and the surrounding unexcited identical (or similar) molecules assuming the transfer to occur between the intracentre molecules only, and not between molecules belonging to different centres. Under these conditions, in what follows, we have considered a certain LC- or LS-center only, irrespective of the particular number k of luminescing centre molecules and their particular configuration.

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* The nomenclature is in accordance with the proposal of the commission on spectrochemical and other optical procedures for analysis [23].

In order to describe the excitation probabilities, $S_i(t)$, $T_i(t)$, of the molecule i of a centre in the S or T state at time t after the initial excitation, we can use the following extended system of Förster's master equations:

$$\frac{dS_i(t)}{dt} = -\left\{\Gamma_S S_i(t) - w_T T_i(t) \right.$$
$$\left. + \sum_{j=1}^{k} (\mu_{ij} S_i(t) - \mu_{ji} S_j(t)) \right\},$$
$$\frac{dT_i(t)}{dt} = -\Gamma_T T_i(t) + w_S S_i(t) . \tag{1}$$

$i, j = 1, 2, \ldots, k$, k is the number of the LM in the centre sphere ($\mu_{ij} = \mu_{ji} = 0$ for $i = j$), with the initial conditions $S_1(0) = 1$, $S_i(0) = 0$ for $i \neq 1$; $T_i(0) = 0$ for all i. μ_{ij}, μ_{ji} are the transfer rate constants between the i-th and j-th LM in the S state. The denotations used are given in the Jabłonski diagram (Figure 1).

Employing the approximations used in [29], the set of $2k$ (1) can be reduced to a system of six equations. For this purpose, the following designations are substituted

$$S(t) = \sum_{i=1}^{k} S_i(t) , \quad T(t) = \sum_{i=1}^{k} T_i(t) . \tag{2}$$

$S(t)$ and $T(t)$ are the probabilities that the centre excited at $t = 0$ at the molecule $i = 1$, at time t still remains excited at any one of the k-th centre molecules in the S or T state, respectively. By summing up (1) and using the designations (2), the following set of two equations can be obtained:

$$\frac{dS(t)}{dt} = -\Gamma_S S(t) + w_T T(t) ,$$
$$\frac{dT(t)}{dt} = -\Gamma_T T(t) + w_S S(t) \tag{3}$$

with the initial conditions $S(0) = 1$, $T(0) = 0$. The functions $S(t)$, $T(t)$ are independent of the energy transfer.

If one differentiates between the excitation of molecule $i = 1$ and of any other one of the k-centre molecules $i \neq 1$, one can find an analogical set of equations by introducing the designations

$$S_r(t) = \sum_{i=2}^{k} S_i(t) , \quad T_r(t) = \sum_{i=2}^{k} T_i(t) \tag{4}$$
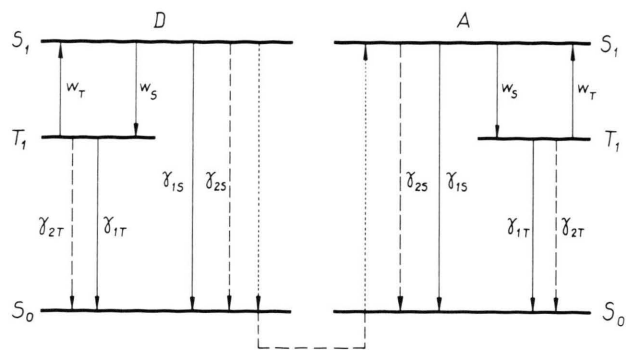

Fig. 1. Simplified Jabłoński diagram of donor (D) and acceptor (A) for transfer between like molecules. Notations: $\gamma_S = \gamma_{1S} + \gamma_{2S}$, $\gamma_T = \gamma_{1T} + \gamma_{2T}$, where γ_{1S} and γ_{1T} are the radiative deactivation rates of fluorescence and phosphorescence, γ_{2S} and γ_{2T} the radiationless deactivation rates of internal conversion $S_1 \rightsquigarrow S_0$ and $T_1 \rightsquigarrow S_0$, respectively. w_S and w_T are the radiationless deactivation and activation rates of intersystem crossing, repectively. The dotted line denotes the coupled-transfer transitions. Moreover, the following notations are used: $\Gamma_S = \gamma_S + w_S$, $\Gamma_T = \gamma_T + w_T$ and $\Gamma'_S = \Gamma_S + \mu_m + \mu_r$; μ_m and μ_r are the migration and remigration rate constants, respectively.

and performing the corresponding summation **

$$\frac{dS_1(t)}{dt} = -\Gamma_S S_1(t) - \sum_{j=2}^{k} \mu_{1j} S_1(t)$$
$$+ \sum_{j=2}^{k} \mu_{j1} S_j(t) + w_T T_1(t) ,$$
$$\frac{dS_r(t)}{dt} = -\Gamma_S S_r(t) + \sum_{j=2}^{k} \mu_{1j} S_1(t)$$
$$- \sum_{j=2}^{k} \mu_{j1} S_j(t) + w_T T_r(t) , \tag{5}$$

** Taking into account that

$$\sum_{j=1}^{k} (\mu_{1j} S_1 - \mu_{j1} S_j) = \sum_{j=2}^{k} (\mu_{1j} S_1 - \mu_{j1} S_j) \quad \text{as } \mu_{11} = 0 ,$$

and with regard to

$$\sum_{i=2}^{k} \sum_{j=1}^{k} (\mu_{ij} S_i - \mu_{ji} S_j)$$
$$= \sum_{i=1}^{k} \sum_{j=1}^{k} (\mu_{ij} S_i - \mu_{ji} S_j) - \sum_{j=1}^{k} (\mu_{1j} S_1 - \mu_{j1} S_j) ,$$

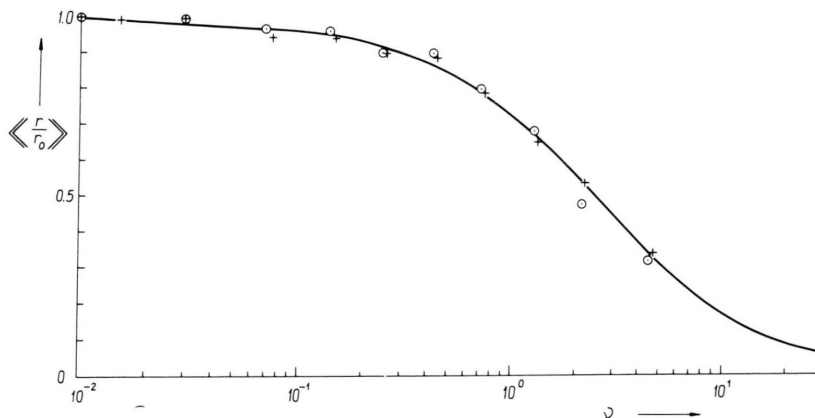where the first term on the right-hand side is equal to zero.

Fig. 2. A comparison of the theoretical curve $\langle\!\langle r/r_0 \rangle\!\rangle$ (25) with the experimental data of concentration depolarization of fluorescence ($\circ$) and phosphorescence (+) for benzo[f]quinoline in ethanol glass at 77 K.

and for the triplet state

$$\frac{dT_1(t)}{dt} = -\Gamma_T T_1(t) + w_S S_1(t) , \qquad (6a)$$

$$\frac{dT_r(t)}{dt} = -\Gamma_T T_r(t) + w_S S_r(t) . \qquad (6b)$$

Equations (5) contain no constants μ_{ij} for transfer between primarily unexcited molecules (i and $j \neq 1$). Approximating the different μ_{j1} by the mean value μ_r (the effective rate constant of remigration) and substituting $\mu_{j1} = \mu_r$ for $j = 2, 3, \ldots, k$, and $\mu_m = \sum_{j=2}^{k} \mu_{1j}$ (the migration rate constant) one obtains from (5)

$$\frac{dS_1(t)}{dt} = -(\Gamma_S + \mu_m) S_1(t) + \mu_r S_r(t) + w_T T_1(t) , \qquad (7a)$$

$$\frac{dS_r(t)}{dt} = -(\Gamma_S + \mu_r) S_r(t) + \mu_m S_1(t) + w_T T_r(t) . \qquad (7b)$$

Subtraction of (7b) from (7a) or (6b) from (6a) with the substitutions

$$\bar{S} = S_1 - S_r \quad \text{and} \quad \bar{T} = T_1 - T_r$$
$$S + \bar{S} = 2 S_1 \quad \text{and} \quad S - \bar{S} = 2 S_r \qquad (8)$$

leads to the equations

$$\frac{d\bar{S}(t)}{dt} = -\Gamma'_S \bar{S}(t) + w_T \bar{T}(t) + (\mu_r - \mu_m) S(t)$$

(where $\Gamma'_S = \Gamma_S + \mu_r + \mu_m$), $\qquad (9)$

$$\frac{d\bar{T}(t)}{dt} = -\Gamma_T \bar{T}(t) + w_S \bar{S}(t) .$$

The two pairs of (3) and (9) can be transformed by known routine methods to the four differential equations of the second order

$$\frac{d^2 S(t)}{dt^2} + b \frac{dS(t)}{dt} + c S(t) = 0 , \qquad (10a)$$

$$\frac{d^2 T(t)}{dt^2} + b \frac{dT(t)}{dt} + c T(t) = 0 , \qquad (10b)$$

$$\frac{d^2 \bar{S}(t)}{dt^2} + b' \frac{d\bar{S}(t)}{dt} + c' \bar{S}(t)$$
$$= (\mu_r - \mu_m) \left[\frac{dS(t)}{dt} + \Gamma_T S(t) \right] , \quad (10c)$$

$$\frac{d^2 \bar{T}(t)}{dt^2} + b' \frac{d\bar{T}(t)}{dt} + c' \bar{T}(t)$$
$$= (\mu_r - \mu_m) w_S S(t) \qquad (10d)$$

with the constants

$$b = \Gamma_S + \Gamma_T , \qquad b' = b + \mu_m + \mu_r ,$$
$$c = \Gamma_S \Gamma_T - w_S w_T , \quad c' = c + \Gamma_T (\mu_m + \mu_r) \qquad (11)$$

and the initial conditions

$$S(0) = 1 , \qquad T(0) = 0 ,$$
$$\frac{dS(0)}{dt} = -\Gamma_S , \quad \frac{dT(0)}{dt} = w_S ,$$
$$\bar{S}(0) = 1 , \qquad \bar{T}(0) = 0 ,$$
$$\frac{d\bar{S}(0)}{dt} = -\Gamma'_S + \mu_r - \mu_m , \quad \frac{d\bar{T}(0)}{dt} = w_S .$$
$$\qquad (12)$$

Corresponding to these relations, the solutions of the two homogeneous Eqs. (10 a, b) are

$$S(t) = A e^{-\lambda_1 t} + (1-A) e^{-\lambda_2 t}$$
$$T(t) = B (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{13}$$

with the notations

$$A = \frac{\lambda_2 - \Gamma_S}{\lambda_2 - \lambda_1}, \qquad B = \frac{w_S}{\lambda_2 - \lambda_1},$$
$$2\lambda_1 = b - (b^2 - 4c)^{1/2}, \quad 2\lambda_2 = b + (b^2 - 4c)^{1/2}. \tag{14}$$

The pair of inhomogeneous Eqs. (10 c, d) with the inhomogeneity terms formed by $S(t)$ and $dS(t)/dt$ has the following solutions

$$\bar{S}(t) = (\eta_r - \eta_m) S(t) + 2\eta_m S'(t),$$
$$\bar{T}(t) = (\eta_r - \eta_m) T(t) + 2\eta_m T'(t), \tag{15}$$

where

$$S'(t) = A' e^{-\lambda_1' t} + (1-A') e^{-\lambda_2' t},$$
$$T'(t) = B' (e^{-\lambda_1' t} - e^{-\lambda_2' t}) \tag{16}$$

are the solutions of the corresponding homogeneous pair with the assumed initial conditions. The dashed quantities are connected by relations identical to (14), taking the dashed values b', c', Γ_S'. The meaning of η_m, η_r is given by

$$\eta_m = \frac{\mu_m}{\mu_m + \mu_r}, \quad \eta_r = 1 - \eta_m = \frac{\mu_r}{\mu_m + \mu_r}. \tag{17}$$

With the relations (8), one obtains for the other quantities

$$S_1(t) = \tfrac{1}{2}[S(t) + \bar{S}(t)] = \eta_r S(t) + \eta_m S'(t),$$
$$T_1(t) = \tfrac{1}{2}[T(t) + \bar{T}(t)] = \eta_r T(t) + \eta_m T'(t). \tag{18}$$

3. Emission Anisotropy

If we assume, that the polarized photoluminescence emission is emitted by the initially excited molecule ($i = 1$) only (see [8, 30–33]), the momentary emission anisotropy $r(t)/r_0$ by radiation from the singlet or triplet state is given by

$$\left(\frac{r(t)}{r_0}\right)_S = \frac{S_1(t)}{S(t)} = \eta_r + \eta_m \frac{S'(t)}{S(t)} \quad \text{(fluorescence)},$$

$$\left(\frac{r(t)}{r_0}\right)_T = \frac{T_1(t)}{T(t)} = \eta_r + \eta_m \frac{T'(t)}{T(t)} \quad \text{(phosphorescence)}. \tag{19}$$

Time averaging according to the relation

$$\frac{\int_0^\infty \dfrac{r(t)}{r_0} S(t)\, dt}{\int_0^\infty S(t)\, dt} = \left\langle \frac{r(t)}{r_0} \right\rangle_S \tag{20}$$

$$= \int_0^\infty \frac{\eta_r S(t)\, dt + \int_0^\infty \eta_m S'(t)\, dt}{\int_0^\infty S(t)\, dt} \tag{20}$$

and the corresponding relation for the triplet emission results, using the values

$$\int_0^\infty S(t)\, dt = \frac{\Gamma_T}{c}, \quad \int_0^\infty S'(t)\, dt = \frac{\Gamma_T}{c'},$$
$$\int_0^\infty T(t)\, dt = \frac{W_S}{c}, \quad \int_0^\infty T'(t)\, dt = \frac{w_S}{c'},$$

for both emission anisotropies, in the identical relation

$$\left\langle \frac{r}{r_0} \right\rangle_S = \left\langle \frac{r}{r_0} \right\rangle_T = \eta_r + \eta_m \frac{c}{c'}. \tag{21}$$

This means that the fluorescence as well as the phosphorescence emission show the same polarization anisotropies, as observed experimentally by Gondo et al. [26, 27].

Substituting $\eta_r = 1 - \eta_m$ given by (17) into (21) and using the values c' according to (11) we can transform (21) into

$$\left\langle \frac{r}{r_0} \right\rangle_{S,T} = \frac{\dfrac{c}{\Gamma_T} + \mu_r}{\dfrac{c}{\Gamma_T} + \mu_r + \mu_m}, \tag{22}$$

where

$$\frac{c}{\Gamma_T} = \gamma_S + w_S \left(1 - \frac{w_T}{\Gamma_T}\right). \tag{23}$$

In the particular case of the simplified LC-model [5] with a sphere of radius R_1 having the mean number v of active LM, with $\mu_r = \mu$ and $\mu_m = (k-1)\mu$ assumed, we find for an LC with k molecules, according to (22), by the assumption of $c/\Gamma_T = \mu$:

$$\left\langle \frac{r}{r_0} \right\rangle_{S,T} = \frac{2}{k+1}. \tag{24}$$

The averaging (24) over all possible k values according to the Poisson distribution results in the

Jabłonski equation (see [5, 6, 34, 14, 15])

$$\left\langle\!\!\left\langle\frac{r}{r_0}\right\rangle\!\!\right\rangle_{S,T} = \sum_{k=1}^{\infty} e^{-v}\frac{v^{k-1}}{(k-1)!}\frac{2}{k+1}$$

$$= \frac{2(v-1+e^{-v})}{v^2}, \qquad (25)$$

where $v = Vn$ is the average number of the LM in the sphere $V = \frac{4}{3}\pi R_1^3$ (n is the concentration of LM in $1\,\text{cm}^3$).

4. Quantum Yields

With the denotations given in Fig. 1 and in its legend, the quantum yields are given by the relations

$$\Phi_{1S} = \gamma_{1S}\int_0^{\infty} S(t)\,dt = \gamma_{1S}\frac{\Gamma_T}{c} = \frac{\gamma_{1S}}{\Gamma_S - \dfrac{w_S\,w_T}{\Gamma_T}}$$

$$= \frac{\gamma_{1S}}{\gamma_{1S} + \gamma_{2S} + w_S\left(1 - \dfrac{w_T}{\gamma_{1T} + \gamma_{2T} + w_T}\right)}, \qquad (26)$$

$$\Phi_{1T} = \gamma_{1T}\int_0^{\infty} T(t)\,dt = \gamma_{1T}\frac{w_S}{c} = \frac{\gamma_{1T}\,w_S}{\Gamma_S\,\Gamma_T - w_S\,w_T}$$

$$= \frac{\gamma_{1T}\,w_S}{(\gamma_{1S} + \gamma_{2S} + w_S)(\gamma_{1T} + \gamma_{2T} + w_T) - w_S\,w_T}. \qquad (27)$$

5. Comparison of Theory and Experiment

Gondo et al. [26, 27] investigated the concentration depolarization of fluorescence and phosphorescence of some aromatic compounds in ethanol glass at 77 K. They confirmed the concentration depolarization of the both luminescence components to behave in the same way. That implies that the singlet-singlet migration causes the depolarization only. For the phosphorescence lifetime, no concentration dependence could be found up to concentrations as high as $10^{-1}\,\text{M}$. Thus, no process leading to phosphorescence quenching is involved in the observed concentration depolarization.

A comparison with experimental measurements of $\langle\!\langle r/r_0\rangle\!\rangle$ depending on the concentration was carried out for benzo[f]quinoline in ethanol glass at 77 K. These experimental data cover a widge range of concentrations and are in good agreement with the theoretical curve given by (25). The Jabłonski radius R_1 can be determined from the normalized curve (25). The theoretical half-value concentration v_H for which the condition

$$\frac{r}{r_0} = \frac{2(v_H - 1 + e^{-v_H})}{v_H^2} = \frac{1}{2}$$

is fulfilled, is

$$v_H = (4/3)\pi R_1^3 \cdot n_H = (4/3)\pi R_1^3 \cdot N' \cdot C_H = 2.55693,$$

where $N' = 6.02 \cdot 10^{20}$ is the number of molecules per millimole and C_H in mole l^{-1} is the half-value concentration determined from the experimental curve. Hence, we have

$$R_1 = \left(\frac{10.046}{C_H^{1/3}}\right)\text{Å}. \qquad (28)$$

The half-concentration C_H determined from the experimental curve [26, 27] for benzo[f]quinoline in ethanol glass at 77 K for fluorescence and phosphorescence amounts to $3.4 \cdot 10^{-2}\,\text{M}$ and hence from (28) the Jabłonski radius R_1 is 31 Å. The critical Förster distance $R_0 = R_1/(3)^{1/3}$ [35–37] is $R_0 = 21.5$ Å.

In the same way, by extrapolation of the experimental data [26] of concentration depolarization of perdeuterated naphthalene-d_8 and phenanthrene-d_{10}, the critical Förster distances $R_0 = 11.9$ Å ($C_H = 2 \cdot 10^{-1}\,\text{M}$) and 14.1 Å ($C_H = 1.2 \cdot 10^{-1}\,\text{M}$), respectively, were found.

6. Conclusions

In the present paper it has been shown theoretically that the singlet-singlet excitation energy migration between like molecules causes the concentration depolarization of phosphorescence. The concentration depolarization of phosphorescence coincides with that of fluorescence and is described by the same equation. Comparison of the theoretical curve with the experimental data permits the determination of the critical distances for the energy migration. The critical concentration (e.g. the critical distances) depend on the luminescent compound.

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