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

A. Kawski and J. Kamiński
Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

Z. Naturforsch. 42a, 813–818 (1987); received March 31, 1987

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, Jablonski'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 multilayer 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 $T_1$ $ightarrow$ $S_0$-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.

* This work was carried out under contract CPBP 01.06.

Reprint requests to Prof. Dr. Alfons Kawski, Uniwersytet Gdański, Instytut Fizyki Doświadczalnej, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

0932-0784 / 87 / 0800-0813 $ 01.30/0. - Please order a reprint rather than making your own copy.

* 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, \( S_j(t) \), \( T_j(t) \), 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:

\[
\frac{dS_i(t)}{dt} = -\left[ \Gamma_S S_i(t) - w_T T_i(t) + \sum_{j=1}^{k} (\mu_{ij} S_i(t) - \mu_{ji} S_j(t)) \right],
\]

\[
\frac{dT_i(t)}{dt} = -\Gamma_T T_i(t) + w_S S_i(t).
\]

(1)

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

\[
S(t) = \sum_{i=1}^{k} S_i(t), \quad T(t) = \sum_{i=1}^{k} T_i(t).
\]

(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:

\[
\frac{dS(t)}{dt} = -\Gamma_S S(t) + w_T T(t),
\]

\[
\frac{dT(t)}{dt} = -\Gamma_T T(t) + w_S S(t)
\]

(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

\[
S_r(t) = \sum_{i=2}^{k} S_i(t), \quad T_r(t) = \sum_{i=2}^{k} T_i(t)
\]

(4)

and performing the corresponding summation**

\[
\frac{dS_1(t)}{dt} = -\Gamma_S S_1(t) - \sum_{j=2}^{k} \mu_{ij} S_1(t) + \sum_{j=2}^{k} \mu_{ji} S_j(t) - \sum_{j=2}^{k} \mu_{ij} T_1(t) + w_T T_1(t),
\]

\[
\frac{dS_j(t)}{dt} = -\Gamma_S S_j(t) + \mu_{ij} S_1(t) + \sum_{j=2}^{k} \mu_{ji} S_j(t) - \mu_{ij} S_1(t) - \mu_{ij} T_j(t) + w_T T_j(t),
\]

(5)

** Taking into account that

\[
\sum_{j=1}^{k} (\mu_{ij} S_j - \mu_{ji} S_i) = \sum_{j=2}^{k} (\mu_{ij} S_1 - \mu_{ji} S_j) \quad \text{as} \quad \mu_{ii} = 0,
\]

and with regard to

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

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

Fig. 1. Simplified Jablonski diagram of donor (D) and acceptor (A) for transfer between like molecules. Notations: \( \gamma_S = \gamma_1S + 2\gamma_2S, \gamma_T = \gamma_1T + 2\gamma_2T \), where \( \gamma_S \) and \( \gamma_T \) are the radiative deactivation rates of fluorescence and phosphorescence, \( \gamma_2S \) and \( \gamma_2T \) the radiationless deactivation rates of internal conversion \( S \rightarrow S_0 \) and \( T \rightarrow S_0 \), respectively. \( w_S \) and \( w_T \) are the radiationless deactivation and activation rates of intersystem crossing, respectively. 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 \( \Gamma_S = \Gamma_S + \mu_m + \mu_i \), \( \mu_m \) and \( \mu_i \) are the migration and remigration rate constants, respectively.
and for the triplet state

\[
\begin{align*}
\frac{dT_1(t)}{dt} &= -\Gamma_T T_1(t) + w_S S_1(t), \quad (6a) \\
\frac{dT_r(t)}{dt} &= -\Gamma_T T_r(t) + w_S S_r(t). \quad (6b)
\end{align*}
\]

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

\[
\begin{align*}
\frac{dS_1(t)}{dt} &= -\left(\Gamma_S + \mu_m\right) S_1(t) \\
&\quad + \mu_t S_r(t) + w_T T_1(t), \quad (7a) \\
\frac{dS_r(t)}{dt} &= -\left(\Gamma_S + \mu_t\right) S_r(t) \\
&\quad + \mu_m S_1(t) + w_T T_r(t). \quad (7b)
\end{align*}
\]

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

\[
\begin{align*}
\tilde{S} &= S_1 - S_r \quad \text{and} \quad \tilde{T} = T_1 - T_r \\
S + \tilde{S} &= 2S_1 \quad \text{and} \quad S - \tilde{S} = 2S_r
\end{align*}
\]
leads to the equations

\[
\begin{align*}
\frac{d\tilde{S}(t)}{dt} &= -\Gamma_S \tilde{S}(t) + w_T \tilde{T}(t) + (\mu_t - \mu_m) S(t) \\
\frac{d\tilde{T}(t)}{dt} &= -\Gamma_T \tilde{T}(t) + w_S \tilde{S}(t).
\end{align*}
\]

(9)

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

\[
\begin{align*}
\frac{d^2S(t)}{dt^2} + b \frac{dS(t)}{dt} + c S(t) &= 0, \quad (10a) \\
\frac{d^2T(t)}{dt^2} + b' \frac{dT(t)}{dt} + c' T(t) &= 0, \quad (10b) \\
\frac{d^2S(t)}{dt^2} + b' \frac{d\tilde{T}(t)}{dt} + c' \tilde{T}(t) &= (\mu_t - \mu_m) \left[ \frac{dS(t)}{dt} + \Gamma_T S(t) \right], \quad (10c) \\
\frac{d^2\tilde{T}(t)}{dt^2} + b' \frac{d\tilde{T}(t)}{dt} + c' \tilde{T}(t) &= (\mu_t - \mu_m) w_S S(t). \quad (10d)
\end{align*}
\]

with the constants

\[
\begin{align*}
b &= \Gamma_S + \Gamma_T, \quad b' = b + \mu_m + \mu_t, \\
c &= \Gamma_S \Gamma_T - w_S w_T, \quad c' = c + \Gamma_T (\mu_m + \mu_t)
\end{align*}
\]
and the initial conditions

\[
\begin{align*}
S(0) &= 1, \quad T(0) = 0, \\
\frac{dS(0)}{dt} &= -\Gamma_S, \quad \frac{dT(0)}{dt} = w_S, \\
\frac{d\tilde{S}(0)}{dt} &= 1, \quad \frac{d\tilde{T}(0)}{dt} = 0.
\end{align*}
\]
Corresponding to these relations, the solutions of the two homogeneous Eqs. (10a,b) are

\[ S(t) = A e^{-\lambda_1 t} + (1 - A) e^{-\lambda_2 t} \]
\[ T(t) = B (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \]

with the notations

\[ A = \frac{\lambda_2 - \Gamma S}{\lambda_2 - \lambda_1}, \quad B = -\frac{wS}{\lambda_2 - \lambda_1}, \quad \lambda_2 = b + (b^2 - 4c)^{1/2}, \quad \lambda_1 = b - (b^2 - 4c)^{1/2}. \]

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

\[ \bar{S}(t) = (\eta_t - \eta_m) S(t) + 2 \eta_m S'(t), \]
\[ \bar{T}(t) = (\eta_t - \eta_m) T(t) + 2 \eta_m T'(t), \]

where

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

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 \( \eta_m', \gamma_m' \).

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

\[ S_1(t) = \frac{1}{2} \left[ S(t) + \bar{S}(t) \right] = \eta_t S(t) + \eta_m S'(t), \]
\[ T_1(t) = \frac{1}{2} \left[ T(t) + \bar{T}(t) \right] = \eta_t T(t) + \eta_m T'(t). \]

### 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

\[ \left< \frac{r(t)}{r_0} \right> \bigg|_S = \frac{S_1(t)}{S(t)} = \eta_t + \eta_m \frac{S'(t)}{S(t)} \] (fluorescence),
\[ \left< \frac{r(t)}{r_0} \right> \bigg|_T = \frac{T_1(t)}{T(t)} = \eta_t + \eta_m \frac{T'(t)}{T(t)} \] (phosphorescence).

Time averaging according to the relation

\[ \frac{\int_0^\infty \frac{r(t)}{r_0} S(t) \, dt}{\int_0^\infty S(t) \, dt} = \left< \frac{r(t)}{r_0} \right>_S \]
\[ \frac{\int_0^\infty \frac{r(t)}{r_0} S(t) \, dt}{\int_0^\infty S(t) \, dt} = \eta_t S(t) + \eta_m \int_0^\infty S'(t) \, dt \]
\[ \frac{\int_0^\infty \frac{r(t)}{r_0} T(t) \, dt}{\int_0^\infty T(t) \, dt} = \eta_t T(t) + \eta_m \int_0^\infty T'(t) \, dt \]

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

\[ \left< \frac{r}{r_0} \right>_S = \frac{\Gamma_{\Sigma}}{c} + \frac{\gamma_S}{c}, \quad \left< \frac{r}{r_0} \right>_T = \frac{\Gamma_T}{c'} \]
\[ \left< \frac{r}{r_0} \right>_S = \frac{\eta_t \Gamma_T}{c} + \frac{\gamma_T}{c'} \]
\[ \left< \frac{r}{r_0} \right>_T = \frac{\eta_t \Gamma_T}{c} + \frac{\gamma_T}{c'} \]

for both emission anisotropies, in the identical relation

\[ \left< \frac{r}{r_0} \right>_S = \left< \frac{r}{r_0} \right>_T = \eta_t + \eta_m \frac{c'}{c}. \]

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

\[ \left< \frac{r}{r_0} \right>_S \bigg|_{S,T} = \frac{c}{\Gamma_T} + \mu_t, \]
\[ \left< \frac{r}{r_0} \right>_T \bigg|_{S,T} = \frac{c}{\Gamma_T} + \mu_t + \mu_m \]

where

\[ \frac{c}{\Gamma_T} = \gamma_S + w_S \left( 1 - \frac{w_T}{\Gamma_T} \right). \]

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

\[ \left< \frac{r}{r_0} \right>_S \bigg|_{S,T} = \frac{2}{k + 1}. \]

The averaging (24) over all possible \( k \) values according to the Poisson distribution results in the
A. Kawski and J. Kamiński • Depolarization of Photoluminescence

The Jablonski equation (see [5, 6, 34, 14, 15])
\[
\left< \frac{r}{r_0} \right>_{S,T} = \sum_{k=1}^{\infty} e^{-v} \frac{v^{k-1}}{(k-1)!} \frac{2}{k+1}
\]
where \( v = Vn \) is the average number of the LM in the sphere \( V = \frac{4}{3} \pi R^3 \) (\( n \) is the concentration of LM in 1 cm\(^3\)).

4. Quantum Yields

With the denotations given in Fig. 1 and in its legend, the quantum yields are given by the relations
\[
\Phi_{1S} = \int_0^\infty \gamma_{1S} S(t) dt = \frac{\gamma_{1S}}{c} \frac{\Gamma_T}{\Gamma_S} w_S w_T = \frac{\gamma_{1S}}{\gamma_{1S} + \gamma_{2S} + w_S \left( 1 - \frac{w_T}{\gamma_{1T} + \gamma_{2T} + w_T} \right)},
\]
where \( \gamma_{1S} \) and \( \gamma_{2S} \) are the decay rates of singlet and triplet states, respectively, \( w_S \) and \( w_T \) are the transition probabilities, and \( \gamma_{1T} \) and \( \gamma_{2T} \) are the decay rates of triplet states.

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 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\(^{-1}\) M. Thus, no process leading to phosphorescence quenching is involved in the observed concentration depolarization.

A comparison with experimental measurements of \( <r/r_0> \) depending on the concentration was carried out for benzo[f]quinoline in ethanol glass at 77 K. These experimental data cover a wide range of concentrations and are in good agreement with the theoretical curve given by (25). The Jablonski radius \( R_1 \) can be determined from the normalized curve (25). The theoretical half-value concentration \( v_H \) for which the condition
\[
\frac{r}{r_0} = 2 \left( v_H - 1 + e^{-v_H} \right) = \frac{1}{2}
\]
is fulfilled, is
\[
v_H = \frac{(4/3) \pi R_1^3 \cdot n_H}{(4/3) \pi R_1^3 \cdot N' \cdot C_H} = 2.55693\ ,
\]
where \( N' = 6.02 \cdot 10^{20} \) is the number of molecules per millimole and \( C_H \) in mole-1 is the half-value concentration determined from the experimental curve. Hence, we have
\[
R_1 = \left( \frac{10.046}{C_H^{1/3}} \right) \text{Å}.
\]
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} M and hence from (28) the Jablonski 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 (\( C_H = 2 \cdot 10^{-1} \) M) and 14.1 Å (\( C_H = 1.2 \cdot 10^{-1} \) 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.

We wish to express our thanks to Professor A. Schmillen, for critically reading the manuscript.