

DEPOLARIZATION OF FLUORESCENCE OF ISOTROPIC SOLUTIONS PRODUCED BY EXCITATION TRANSFER BETWEEN LUMINESCENT MOLECULES

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The problem is considered of self-depolarization of fluorescence of rigid isotropic solutions in which depolarization is produced by excitation transfer between luminescent molecules. A new improved version is proposed of a theory put forward by the present writer many years ago. In this version some of the most drastic simplifications of the former theory are partially relaxed. An expression is derived for the emission anisotropy of fluorescence as a function of the concentration of the solution valid in cases in which certain conditions are fulfilled by the solution. It constitutes a particular case of a more general and more exact expression the application of which to practical calculations seems to be very difficult and so far not attempted.

Depolarization of photoluminescence produced by excitation transfer between luminescent molecules (LM) is a very complex phenomenon even in the simplest case of rigid isotropic solutions. A theoretical description of the dependence of the emission anisotropy (EA) of fluorescence on the concentration of a solution in which such depolarization occurs seems to be hardly possible without introducing some serious simplifications. Several simplifying assumptions were made in various so far published theories concerned. A critical review of these assumptions may be found in a paper by Knox [8]. Some of these assumptions were further discussed in [7]. The most serious simplifications were introduced in a theory put forward by the present writer many years ago [6]. Below a new improved version of this last theory is given in which some of the most drastic simplifications made in the former version are partially relaxed.

In what follows excitation of fluorescence of a rigid isotropic solution within its first absorption band by a parallel beam of plane polarized light is assumed throughout. LM primarily excited by absorption of the exciting light are called donors (*D*), and those primarily unexcited (excited by excitation transfer), acceptors (*A*).

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Let us now introduce the notion of a luminescent centre in a solution (as was already done in [6]). It is assumed to consist of a D together with a number $k-1$ ($k = 1, 2, 3 \dots$) of A present in the "active sphere" (sphere of action) of the D . A centre containing one D and $k-1$ A will be called a k -centre.

Our considerations are restricted to cases in which the intensity of the exciting light is not too high (no stimulated emission occurs and no centres containing more than one D practically appear), and, apart from this, the influence of the Boltzmann factor on the spatial distribution of LM can be neglected. In this case the k -distribution as created in the moment of excitation is given by

$$P(k) = e^{-v} \frac{v^{k-1}}{(k-1)!}, \quad (1)$$

where

$$v = \frac{4}{3}\pi R_a^3 N, \quad (2)$$

R_a being the radius of the active sphere and N the number density of A practically equal (under above conditions) to the number density of all LM in the solution. $P(k)$ fulfills of course the condition

$$\sum_{k=1}^{\infty} P(k) = 1. \quad (3)$$

It follows from Eq. (1) that the EA of fluorescence of the solution (by steady illumination with the exciting light) is

$$\langle r \rangle = \frac{e^{-v}}{\langle \eta \rangle} \sum_{k=1}^{\infty} \frac{v^{k-1}}{(k-1)!} \eta_k \langle r_k \rangle \quad (4)$$

where η_k is the quantum yield and $\langle r_k \rangle$ the mean value of EA of fluorescence emitted by k -centres. $\langle \eta \rangle$ denotes the quantum yield of fluorescence of the whole solution.

Eq. (4) is valid under assumption that LM situated on the outside of the active sphere, if ever excited by excitation transfer, emit fluorescence completely unpolarized. This assumption seems to be very plausible provided the radius R_a of the active sphere is chosen sufficiently large to practically exclude direct transfers from the D to such molecules.

If the transfer processes to the "outsiders" can be neglected

$$\langle \eta \rangle = e^{-v} \sum_{k=1}^{\infty} \frac{v^{k-1}}{(k-1)!} \eta_k, \quad (5)$$

otherwise it is somewhat larger.

No attempt is so far made to calculate theoretically the values of η_k . They may be perhaps treated as empirical parameters.

Let W_k be the probability that a photon emitted by a k -centre at a particular configuration and mutual orientation of LM in the centre is emitted by the D . The EA of fluorescence of such centre may be written as

$$r_k = W_k r_D + (1 - W_k) r_A^{(k)} \quad (6)$$

where r_D and $r_A^{(k)}$ are the respective values of EA of fluorescence of D 's and A 's.

$\langle r_k \rangle$ appearing in Eq. (4) are the mean values of r_k averaged over all configurations and mutual orientations of LM occurring in k -centres:

$$\langle r_k \rangle = \langle W_k \rangle r_D + \langle (1 - W_k) r_A^{(k)} \rangle \quad (7)$$

r_D being independent of configuration and of k (but not $r_A^{(k)}$!).

If $\langle r_k \rangle$ given by Eq. (7) are put into Eq. (4) one obtains the most accurate (although not absolutely accurate¹) general expression for $\langle r \rangle$ as a function of ν :

$$\langle r \rangle = \frac{e^{-\nu}}{\langle \eta \rangle} \sum_{k=1}^{\infty} \frac{\nu^{k-1}}{(k-1)!} \eta_k [\langle W_k \rangle r_D + \langle (1 - W_k) r_A^{(k)} \rangle]. \quad (8)$$

In practical calculations a limited number of terms of the sum need to be taken into account. This number depends on ν (on the concentration of the solution). If in all terms used $\langle W_k \rangle r_D \gg \langle (1 - W_k) r_A^{(k)} \rangle$ Eq. (8) becomes simpler:

$$\frac{\langle r \rangle}{r_D} = \frac{e^{-\nu}}{\langle \eta \rangle} \sum_{k=1}^{\infty} \frac{\nu^{k-1}}{(k-1)!} \eta_k \langle W_k \rangle \quad (9)$$

which may be valid for not too high values of ν .

The values of $\langle W_k \rangle$ depend *ceteris paribus* on the rate of excitation transfer μ and the radius of the active sphere.

Assumption that the transfer is due to dipole-dipole interaction of LM leads to

$$\mu = \frac{1}{\tau_0} \left(\frac{R_0}{R} \right)^6 F^2, \quad (10)$$

where $1/\tau_0$ is the transition probability per unit time of electronic transitions leading to the emission of the fluorescence band, R the mutual distance of A and D , and

$$F = \sin \alpha_1 \sin \alpha_2 \cos \varphi - 2 \cos \alpha_1 \cos \alpha_2, \quad (11)$$

α_1 and α_2 being angles made by the directions of dipoles of D and A respectively with that of R , and φ the angle between planes intersecting along R in which these dipoles lie. For a fixed distance and mutual orientation of a pair of LM

$$W_2 = \frac{1 + \mu\tau}{1 + 2\mu\tau} = \frac{1 + \mu\eta_0\tau_0}{1 + 2\mu\eta_0\tau_0}, \quad (12)$$

¹ It is not absolutely accurate because of the already introduced simplifications, *viz.* introducing of the active sphere and assumptions of η_k independent of the particular configuration and mutual orientations in a k -centre and unpolarized outsiders fluorescence.

where τ is the mean life of the excited state of LM resulting from the transitions with emission of fluorescence and radiationless transitions, and $\eta_0 = \tau/\tau_0$ the yield of fluorescence affected by radiationless transitions² (cf. Förster [5], Jabłoński [6] and [7], Knox [8]). The values of $\langle W_2 \rangle$ were calculated rather accurately by means of a computer, but so far for $\eta_0 = 1, 0.7, 0.5, 0.3$ and $R_a = cR_0$ with $c = 1, 2, 3$ only [7].

$\langle W_2 \rangle$ for other values of η_0 and c may be calculated in the same manner. Calculations of $\langle W_k \rangle$ for $k > 2$ may be also feasible but were not attempted so far. Until such calculations are performed approximate values of $\langle W_k \rangle$ for $k > 2$ as calculated in the manner given below may be used. The theory concerned is an improved version of the earlier theory [6] which will be summarized briefly. The most drastic simplification introduced there concerns the transfer rate: instead of a transfer rate depending on mutual distances and orientations of LM (as given e.g. by Eq. (10)) a transfer rate μ' ("effective transfer rate") is introduced the same for all pairs of LM present in various centres. μ' is treated as an empirical parameter whose value depends *ceteris paribus* on the radius R_a of the active sphere.

It was shown that under the above assumption

$$\langle W_k \rangle = \frac{1 + \mu' \eta_0 \tau_0}{1 + k \mu' \eta_0 \tau_0}. \quad (13)$$

If R_a is chosen so as to give $\mu' \eta_0 \tau_0 = 1$,

$$\langle W_k \rangle = \frac{2}{1+k} \quad (14)$$

results, and Eq. (9) with $\eta_k/\langle \eta \rangle = 1$ leads to

$$\frac{\langle r \rangle}{r_D} = 2 \frac{v-1+e^{-v}}{v^2} \quad (15)$$

(cf. [2] and [6]), which cannot claim because of simplifications made to describe accurately the dependence of $\langle r \rangle/r_D$ on concentration even in cases in which practically $\eta_k/\langle \eta \rangle = 1$.

The modification presently proposed is to use Eq. (13) for $k > 2$ with μ' determined from

$$\langle W_2 \rangle = \frac{1 + \mu' \eta_0 \tau_0}{1 + 2\mu' \eta_0 \tau_0}, \quad (16)$$

where the value of $\langle W_2 \rangle$ is that accurately calculated for a given form of μ and the value of R_a used in calculations.

The result is

$$\mu' \eta_0 \tau_0 = \frac{1 - \langle W_2 \rangle}{2\langle W_2 \rangle - 1} = M \quad (17)$$

² η_0 is not necessarily equal to η_2 appearing in Eqs (4) and (9).

and Eq. (9) becomes

$$\frac{\langle r \rangle}{r_D} = \frac{e^{-\nu}}{\langle \eta \rangle} \left(\eta_1 + \eta_2 \langle W_2 \rangle \nu + \sum_{k=3}^{\infty} \frac{\nu^{k-1}}{(k-1)!} \eta_k \frac{1+M}{1+kM} \right). \quad (18)$$

This equation contains no adjustable parameters and is expected to yield fairly accurate results for not too high concentrations, provided a sufficiently large radius of the active sphere is used in calculations. For the excitation transfer rate given by Eq. (10) the radius of the active sphere must be, as estimated, at least two times larger than R_0 .

In the case in which $\eta_k/\langle \eta \rangle = 1$ can be assumed for all significant terms in Eq. (18) R_0 can be determined in a simple way. To this end the theoretical curve representing $\langle r \rangle/r_D$ as a function of ν calculated for $R_a = cR_0$ has to be compared with the experimental curve representing $\langle r \rangle/r_D$ as a function of the number density $N \text{ cm}^{-3}$ of the solution. For the same value of $\langle r \rangle/r_D$ in both curves

$$\nu = \frac{4}{3}\pi c^3 R_0^3 N,$$

and thus

$$R_0 = \frac{1}{c} \sqrt[3]{\frac{3\nu}{4\pi N}}. \quad (19)$$

When comparison is made of the thus evaluated values of R_0 with those resulting from spectroscopic data one has to keep in mind that the transfer probability, as shown by Bauer [1] and by Dale and Bauer [4], depends in some cases on the frequency of the exciting light. This is due to the fact that, if LM are excited with frequencies higher than 0—0 frequency, the transfer probability is higher immediately after excitation, when the thermal equilibrium of the centre with the surrounding medium is not yet reached, than in the state of equilibrium. Thus only those values of R_0 have to be used for comparison which result from curves obtained by excitation with 0—0 frequency (*cf.* [4]).

Some computations based on Eq. (18) of the $\langle r \rangle/r_D$ curves were performed by means of a computer by Cherek [3] but so far for $c = 2$ and $\eta_0 = \eta_k/\langle \eta \rangle = 1$ only. In spite of the unrealistic assumption concerning the yields, the calculated curves compare well with the experimental curves of Kawski [9] for fluorescein and rhodamine 6 G in waterfree glycerol, as also do, let us say, the theoretical curves resulting from the Ore-theory as well as from the earlier version of the present theory (*cf.* Kawski [9]). R_0 's obtained by Cherek are somewhat larger than those of Kawski. No significance should be attributed to these differences because the results of Cherek must be considered as preliminary only. Let us also remark that the definition of R_0 used in this paper and used also by Cherek (*cf.* Eq. (10)) differs somewhat from that used by Kawski.

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