ANISOTROPY OF FLUORESCENCE OF MOLECULES EXCITED BY EXCITATION TRANSFER

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In memory of Professor H. Niewodniczański

Excitation transfer from donors (molecules initially excited by absorption of the primary light) to the acceptors (molecules initially unexcited) is one of the causes of concentration depolarization of photoluminescence of solutions. The case of an isotropic solution in which the only depolarizing factor present is the excitation transfer is considered. The emission anisotropy of fluorescence emitted by acceptors is calculated on the assumption that only pairs of luminescent molecules are involved in transfer processes, and the transfer probability per unit time is that resulting from dipole-dipole interaction (as given by F. Perrin and by Förster). The calculations performed (without introducing any simplifying assumptions) by means of a computer show that the emission anisotropy of acceptor fluorescence amounts to about 2.5 per cent of that of the donors. Obviously a much lower anisotropy would result for transfer processes in which more than two molecules are involved. Thus the assumption (made in the majority of theoretical considerations) that fluorescence emitted by acceptors is totally unpolarized constitutes a rather fair approximation. The size of the error introduced by some other simplifications is also discussed.

Introduction

Several simplifying assumptions are introduced in the known theories of depolarization of photoluminescence of isotropic solutions by excitation energy transfer among the luminescent molecules. Recently a new improved theory was published by Knox [7]. In this paper a critical review of the earlier theories (those of Förster [2], [8], Weber [11] and Jabłoński [4], [1]) is given, and the simplifying assumptions introduced there discussed. Let us quote two of the simplifications mentioned by Knox: *1.* assumption of the "loss of memory of the initial polarization by transferred excitation" (introduced in all theories except that of Weber), and *2.* replacement of the transfer probability per unit time by its mean value averaged over all angles on which this probability depends (*cf.* Eqs (1) and (8) below). These simplifications affect the results of the theories concerned. The unknown size of the error thus commited can be estimated by comparing the emission anisotropy calculated with and without introducing these simplifications. This is done in the present paper.

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Assumptions and results

The problem of excitation transfer between luminescent molecules in solutions was first treated by F. Perrin [10] and then by Förster [2]. The transfer probability per unit time between two like molecules, as given by latter author (for the case of linear virtual electronic oscillators, the only case considered here) may be written in the form

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

where R denotes the distance of the acceptor from the donor, τ_0 the natural mean lifetime of their excited state, and

$$F = \sin\alpha_1\sin\alpha_2\cos\varphi - 2\cos\alpha_1\cos\alpha_2,\tag{2}$$

α_1 and α_2 being angles made by the directions of the dipole transition moments of the donor and acceptor respectively with that of R, and φ the angle between planes in which these dipoles lie. R_0 is the distance at which $\mu = 1/\tau_0$ for $F^2 = 1$. R_0 thus defined differs slightly from that usually accepted (see *e.g.* Knox [7]). It follows from the meaning of F^2 that Eq. (1) can be applied only to such transfer processes in which two molecules are involved.

The fundamental emission anisotropy r_f of photoluminescence (which, let us recall, concerns the isotropic solutions excited by plane polarized primary light) is given for the case of linear absorption and emission virtual electronic oscillators by

$$r_f = 0.6\cos^2\beta - 0.2 = 0.4 - 0.6\,(1-\cos^2\beta) = 0.4 - 0.6\sin^2\beta,\tag{3}$$

where β denotes the angle between the absorption and the emission oscillator in the same molecule [5]. This is F. Perrin's expression [9] written in terms of emission anisotropy (EA). If the same transition moment is responsible for absorption and emission (fluorescence excited in the first absorption band), $\beta = 0$, and $r_f = r_p = 0.4$ (r_p principal EA).

Let the donors be excited in the first absorption band, and thus the fundamental EA of their fluorescence $r_f = r_p = 0.4$. We have to calculate the EA of fluorescence of the acceptors randomly oriented and distributed with respect to the donor. This will be done for transfer processes in which only pairs of molecules (donor + acceptor) are involved.

For a fixed position and mutual orientation of the two molecules the probability W_D that the emission will take place from a donor is

$$W_D = \frac{1+\mu\tau}{1+2\mu\tau},\tag{4}$$

where μ is that given by Eq. (1), and τ denotes the mean lifetime of the excited state the same for both (like!) molecules (*cf.* Förster [2], Jabłoński [4][1], Knox [7]).

The corresponding probability W_A for the acceptors is

$$W_A = 1 - W_D = \frac{\mu\tau}{1+2\mu\tau}.\tag{5}$$

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[1] The denominator of the second term on the right-hand side of both equations given in the footnote on p. 297, Vol. 14 of *Acta Phys. Polon.* should read $2(1+2\mu\tau)$ instead of $2(1+\mu\tau)$.

If the Perrin's relation

$$\tau = \tau_0 \eta \tag{6}$$

(η being the quantum yield of fluorescence and τ_0 the natural lifetime of excitation) is assumed to hold, equations (4) and (5) may be written as

$$W_D = \frac{1+\mu\eta\tau_0}{1+2\mu\eta\tau_0} \tag{4a}$$

and

$$W_A = \frac{\mu\eta\tau_0}{1+2\mu\eta\tau_0}. \tag{5a}$$

W_D and W_A are the relative values of the probabilities of emission from donors and acceptors respectively. Their sum does not depend on η and is always $W_D + W_A = 1$ (η being in our case the same for donors and acceptors).

In order to calculate the mean value r_A of EA of fluorescence emitted by acceptors an equation similar to Eq. (3) may be used in which, however, $\cos^2 \beta$ has to be replaced by the weighted mean value of $\cos^2 \theta$, θ being now the angle made by the donor oscillator with randomly oriented and localized acceptor oscillators. There results

$$r_A = 0.6 \frac{\langle \cos^2 \theta \cdot W_A \rangle}{\langle W_A \rangle} - 0.2. \tag{7}$$

From Eqs (5a) and (1), in which $R/R_0 = x$ is put for convenience, we have

$$W_A = \frac{F^2 \eta}{x^6 + 2F^2 \eta} \tag{8}$$

and

$$\cos^2 \theta \cdot W_A = \frac{\cos^2 \theta \, F^2 \eta}{x^6 + 2F^2 \eta}, \tag{9}$$

where $\cos \theta = \sin \alpha_1 \sin \alpha_2 \cos \varphi + \cos \alpha_1 \cos \alpha_2$ (for the meanings of α_1, α_2 and φ see Eq. (1)).

The average values of expressions (8) and (9) are calculated on the assumption that the donor is situated in the centre of a sphere ("active sphere") in which there is also one randomly oriented and localized acceptor present. The calculations are performed for sphers of radius cR_0, $c = 1, 2, 3$, with $\eta = 1, 0.7, 0.5$ and 0.3. The respective probability densities of α_1, α_2, φ and x are $(\sin \alpha_1)/2$, $(\sin \alpha_2)/2$, $1/\pi$ and $3x^2/c^3$.

With these densities

$$\left\langle \frac{F^2 \eta}{x^6 + 2F^2 \eta} \right\rangle = \frac{3}{4\pi c^3} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\varphi \int_0^c dx \, \frac{F^2 \eta x^2 \sin \alpha_1 \sin \alpha_2}{x^6 + 2F^2 \eta} \tag{10}$$

and

$$\left\langle \frac{\cos^2 \theta \, F^2 \eta}{x^6 + 2F^2 \eta} \right\rangle = \frac{3}{4\pi c^3} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\varphi \int_0^c dx \, \frac{\cos^2 \theta \, F^2 \eta x^2 \sin \alpha_1 \sin \alpha_2}{x^6 + 2F^2 \eta} \tag{11}$$

are calculated by means of a computer (Gier, at the Computing Centre of the Warsaw University)[2].

The values of r_A obtained are summarized in the Table I.

Average value $r_A \approx 0.01$. The values of r_A calculaced for various values of c and η given in the Table I appear to be equal within the limits of the accuracy of the calculations (this can be stated with certainty for the range of c and η actually used in calculations only!). As is seen r_A amounts to about 2.5 per cent of that of the donors ($r_D = 0.4$). A still lower value of r_A has to be expected for transfer processes in which more than one acceptor is involved. Although the calculations concern the ideal case of rigid solutions in which there are, apart from transfer processes, no other depolarizing factors, the results may be safely applied for estimates of r_A in more general cases. We may conclud that putting $r_A = 0$, as in the majority of theories concerned, constitutes a rather fair approximation.

TABLE I

The values of r_A

c \ η	1	0.7	0.5	0.3
1	0.0099	0.0072	0.0072	0.0080
2	0.0099	0.010	0.0097	0.0102
3	0.0089	0.0102	0.007	0.0101

The calculations become much simpler if F^2 in the denominators of integrals (19) and (11) is replaced by its mean value $\langle F^2 \rangle = 2/3$. Then,

$$\frac{\langle \cos^2 \theta \cdot W_A \rangle}{\langle W_A \rangle} \quad \text{becomes simply} \quad \frac{\langle \cos^2 \theta \cdot F^2 \rangle}{\langle F^2 \rangle} = 0.36 \tag{12}$$

(cf. Weber [11]). Hence, by virtue of Eq. (7)

$$r_A = 0.6 \cdot 0.36 = 0.016, \tag{13}$$

which is 60 per cent higher than the average value of r_A given in the Table I.

The problem in question has already been dealt with by Galanin and by Ketskeméty [6]. Their results correspond to rather higher values of EA of fluorescence of acceptors than that obtained in this paper on ground of Eqs (5) and (5a).

The EA of fluorescence emitted by a pair of molecules (donor+acceptor) is

$$r_{D+A} = r_D \langle W_D \rangle + r_A \langle W_A \rangle = r_D - (r_D - r_A) \langle W_A \rangle,. \tag{14}$$

or, for $r_D = 0.4$ and $r_A = 0.01$,

$$r_{D+A} = 0.4 - 0.39 \langle W_A \rangle. \tag{14a}$$

The computed values of $\langle W_A \rangle$ for various c and η are given in the Table II. By means of Table II the error arising from neglect the contribution of the acceptors to r_{D+A}, can

[2] The calculations were performed by Doc. Dr W. Woźnicki.

be easily estimated *viz.* by simply putting $r_{D+A} = r_D\langle W_D\rangle = r_D(1-\langle W_A\rangle)$. It amounts, *e.g.*, to 1.27 per cent for $c = 1$ and $\eta = 1$.

The last simplification to be considered here is the replacement of F^2 by its mean value $\overline{F^2} = 2/3$ in Eq. (8), from which $\langle W_A\rangle$ is calculated. Let the approximate values of $\langle W_A\rangle$ and $\langle W_D\rangle$ thus obtained be distinguished by a subscript s. For $\eta = 1$.

$$\langle W_A\rangle_s = \frac{3}{c^3}\int_0^c \frac{\langle F^2\rangle x^2}{x^6+2\langle F^2\rangle}\,dx = \frac{1}{c^3\sqrt{3}}\,\text{arc tg}\,\frac{2}{\sqrt{3}}\,c^3. \tag{15}$$

TABLE II

Values of $\langle W_A\rangle$

c \ η	1	0.7	0.5	0.3
1	0.339	0.314	0.291	0.256
2	0.0857	0,0730	0.0626	0.0494
3	0.0275	0.0231	0.0196	0.0153

The results (for $\eta = 1$) are given in the Table III in which the accurate values are also given for comparison.

$\langle W_A\rangle_s$ and $\langle W_D\rangle_s$ for $\eta \neq 1$ are not given in Table III (for accurate values see Table II).

TABLE III

Values of $\langle W_D\rangle$, $\langle W_A\rangle$, $\langle W_D\rangle_s$ and $\langle W_A\rangle_s$ for $\eta = 1$

c	$\langle W_A\rangle$	$\langle W_A\rangle_s$	Diff. (per cent)	$\langle W_D\rangle$	$\langle W_D\rangle_s$	Diff. (per cent)
1	0.339	0.419	23.6	0.661	0.581	12.1
2	0.0856	0.104	21.5	0.9144	0.896	2
3	0.00275	0.0327	18.8	0.9725	0.9673	0.5

It is hoped that this paper may be helpful in estimating the accuracy of various theories of self-depolarization in which the simplifications discussed are introduced. Only those of the theories of self-depolarization so far published are mentioned here to which our problem is most closely related (for other papers see the references in the papers cited[3]).

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