

EXPERIMENTAL VERIFICATION OF CONCENTRATIONAL DEPOLARIZATION THEORY INCORPORATING THE LAYER MODEL OF LUMINESCENCE CENTERS

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The emission anisotropy of plexiglas solutions of phloxin, rhodamin 6G and eosin has been measured. Results are compared with the theory of concentrational depolarization incorporating the layer model of luminescence centers (*Acta Phys. Polon.*, **22**, 211 (1962); **34**, 853 (1968)). In order to check this theory further, the absorption and emission spectra of the solutions under study were measured and on their basis the critical distances R_1 were calculated, which were then compared with the values of R_1 determined directly from the concentrational depolarization curves. There is satisfactory agreement between theory and experiment.

The model with layers of constant volume (I) and the model with layers of constant thickness (II) are discussed. It is shown that the values of emission anisotropy calculated in the cases (I) and (II) are practically identical, independently of the assumed layer thickness, as long as the total volumes of the centers are equal in the two cases.

Introduction

The phenomenon of concentrational depolarization of photoluminescence has been the subject of experimental and theoretical investigations for many years [1-13]. Of the several published theories, that given by Jabłoński [4] deserves attention because it accounts for the fluctuations of the concentration of luminescent molecules and reemigration of excitation energy. This theory, in its first approximation, employs a model with an active sphere, but does not assume any one law of interaction between the excited D^* and unexcited D luminescent molecule. A further generalization of this theory was achieved by applying the layer model of a luminescence center which consists of the initially excited luminescent molecule surrounded by concentric spheric layers of equal volume, within which unexcited molecules of the same kind may be found [8, 11, 14]. It should be emphasized that the layer model of a luminescence center (with equal-volume layers) differs from the shell model (introduced by Jabłoński [15]) consisting of the excited luminescent molecule surro-

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unded by monomolecular layers of solvent molecules, inside which molecules of the dissolved luminescent substance may reside. The layer model with equal-volume layers is also different than the layer model with equal-thickness layers recently introduced¹ [16, 17]. Assuming that the nonradiative transfer of energy from D^* to D takes place *via* quantum-mechanical resonance² and that the distribution of luminescent molecules in the solution is statistical, the following expression for emission anisotropy³ was obtained in the framework of the model with equal-volume layers [11]:

$$\frac{r}{r_0} = e^{-\nu z} \sum_{k_1, \dots, k_z} \frac{\nu^{k_1-1}}{(k_1-1)!} \prod_{l=2}^z \frac{\nu^{k_l}}{k_l!} \frac{\sum_{l=1}^z k_l + \sum_{l=1}^z \frac{k_l}{l^2} - 2}{\sum_{l=1}^z k_l \cdot \sum_{l=1}^z \frac{k_l}{l^2} - 1} \quad (2)$$

where $\nu = \nu n$ is the average number of molecules D in the volume of the layer ν ,

n is their number per cubic centimeter,

z is the number of layers, and

k_l is the number of luminescent molecules in the l -th layer, with $k_1 = 1, 2, 3, \dots$

and $k_l = 0, 1, 2, \dots$ for $l = 2, 3, \dots$

For $z = 1$ expression (2) becomes the expression stemming from Jabłoński's theory with the active sphere [4, 20],

$$\frac{r}{r_0} = 2e^{-\nu} \sum_{k=1}^{\infty} \frac{\nu^{k-1}}{(k-1)!} \cdot \frac{1}{k+1} = \frac{2(\nu-1+e^{-\nu})}{\nu^2} \quad (3)$$

There is only one constant, ν , in the expressions (2) and (3), and it stands for layer volume or active sphere volume, respectively. The values of the parameter ν are determined by comparing experimental results with the theoretical expression, whence it is chosen so that the agreement between theory and experiment is best. This way of testing the theory does not seem to be sufficient, however, because the parameter determined in this manner may not correspond to the assumptions made in the theory regarding its meaning. It is obvious that the compatibility of the same experimental results with expressions (2) and (3), which correspond to different simplifying assumptions accepted in the theory, may be achieved only by the use of different values of the parameter ν . Between the experimentally determined parameter $\nu = \frac{4}{3} \pi [R^{(1)}]^3$ and the critical distance R_1 characterizing the

¹ A detailed discussion regarding the applicability and physical grounds of the various luminescence center models is given in Ref. [18].

² In the case of dipole-dipole interaction the rate constant of this process is, after Förster [2],

$$\mu = \frac{1}{\tau} \left(\frac{R_1}{R} \right)^6 \quad (1)$$

where τ is the real mean lifetime of the excited molecule D^* in the absence of an energy acceptor ($n \rightarrow 0$), R_1 is the so-called critical distance (cf. Eq. (5)), and R is the distance between the molecules D^* and D .

³ Emission anisotropy r is associated with the degree of polarization P through the relation [19] $r = \frac{2P}{3-P}$.

The quantity r_0 denotes the emission anisotropy corresponding to the fundamental degree of polarization P_0 .

elementary event of interaction between molecules D^* and D there holds, in the case of the layer model of a center assuming $z = 3$ layers, the relation⁴ [21]

$$R^{(1)} = 1.276 R_1 \quad (4)$$

As the critical distance R_1 may be determined from two independent measurements, namely, from the absorption and emission spectra of the examined system, there is therefore a possibility of making another verification of theory.

The purpose of this work was to check experimentally the theory of concentrational depolarization of photoluminescence incorporating the layer model of a center in the form of expressions (2) and (4), and also to determine the critical distance from the above-mentioned independent measurements.

Experimental

With the purpose of making an experimental check of the theory of concentrational depolarization of photoluminescence incorporating the layer model in the form of Eq. (2), samples of solid solutions were prepared with various concentrations of phloxin ($C_{20}H_2Cl_4Br_4O_5Na_2$, molecular weight $M = 829.71$), rhodamin 6G ($C_{26}H_{27}O_3N_2Cl$, $M = 450.98$) and eosin ($C_{20}H_8O_5Br_4$, $M = 647.93$) in methyl polymethacrylate. The solid solutions were obtained by the process of thermal polymerization of solutions of methyl methacrylate monomer with an added ten per cent of ethyl alcohol. In the case of rhodamin 6G 5×10^{-3} mol/liter of HCl was added, and in the case of phloxin and eosin 5×10^{-3} mol/liter of NaOH in order to maintain a constant pH-value of the solutions during changes in their concentration. The ethyl alcohol was added to the methyl methacrylate to enhance the solubility of the examined substances.

The absorption spectra were measured on an MOM-201 spectrophotometer, and the emission spectra with the measuring arrangement described in [24], where there is also some additional information about the way solutions are prepared. The emission spectra were corrected for the spectral sensitivity of the photomultiplier and for the secondary luminescence according to the method presented in Ref. [25].

Emission anisotropies (degrees of polarization) were measured by the compensation photoelectric method [26, 27]. The luminescing objects were excited by the light of a DRSz-250 high pressure mercury lamp powered by d.c. current passed through an IF 550 (Zeiss) interference filter. The exciting light was polarized by means of a Glan prism in such a way that its electric vector would be vertical. The direction of observation made an angle of $\alpha = 35^\circ$ with the direction of propagation of the exciting beam, and was perpendicular to the sample surface. On the side of observations an OG 3 cutoff filter transmitting light of wavelengths $\lambda > 570$ nm was used. Angles of divergence for the exciting and observation

⁴ In the case of the model with the active sphere, instead of (4) the relation

$$R^{(1)} = 1.327 R_1 \quad (4')$$

is obtained (cf. also the comments on this matter in Refs [21, 22, 23]).

beams not greater than 0.1 rd were achieved by means of diaphragms. The modulation frequency was chosen to be 76 Hz in order that the a.c. mains current have the least effect possible. An EMI photomultiplier, type 9514 S, with a low dark current level was used for detecting the polarized light. The a.c. current in the photomultiplier circuit was measured with a "Unipan" selective nanovoltmeter, type 208.

The found degrees of polarization were calculated on the basis of the formula for the degree of polarization for a system of transparent plane-parallel plates [28, 29]. The calculations also accounted for the effect of secondary fluorescence according to the method presented in Ref. [30].

Results and discussion

The absorption and emission spectra of plexiglas solutions of phloxin, rhodamin 6G and eosin are presented in Fig. 1. They were measured in the ranges of concentration of 1.05×10^{-5} to 3.38×10^{-4} M/l for phloxin, 5.27×10^{-6} to 1.08×10^{-3} M/l for rhodamin 6G,

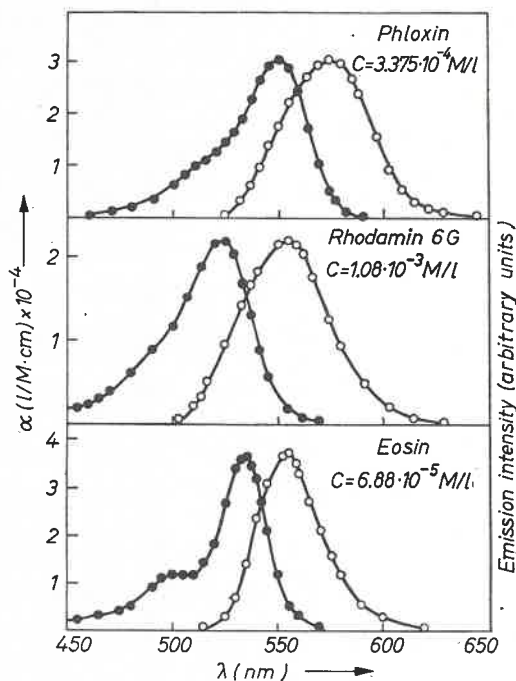


Fig. 1. Spectra of absorption α and emission F , in terms of number of quanta, of plexiglas solution of phloxin, rhodamin 6G and eosin

and 1.04×10^{-5} to 1.04×10^{-3} M/l in the case of eosin. The absorption spectra of rhodamin 6G did not undergo practically any change within the examined range of concentrations, whereas those of eosin and phloxin changed considerably with changes in solution concentration. In the case of eosin there was also a slight shift of the peaks of luminescence bands towards the longer waves when the concentration of eosin in the solution increases [31, 24].

Figure 2 presents the results concerning the emission anisotropy of the examined systems as a function of luminescent molecule concentration in solution and the theoretical curve, Eq. (2), for $z = 3$. The best conformity between experimental points for plexiglas solutions and the theoretical curve was achieved for the values of parameters arranged in Table I, where there are also given the values of R_1 calculated with relation (4) taken into account.

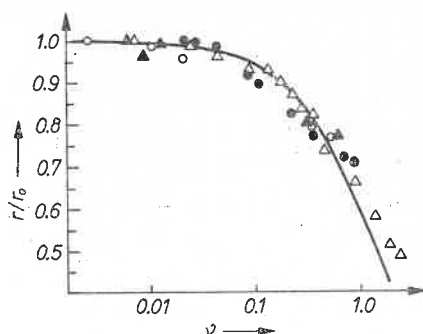


Fig. 2. Concentrational dependence of emission anisotropy of the photoluminescence of plexiglas solutions of phloxin (●), eosin (▲), rhodamin 6G (○) and glycerin-water solutions of rhodamin 6G (Δ). Continuous line is theoretical curve defined by Eq. (2) for $z = 3$

TABLE I

1	2	3	4	5	6	7	8	9	10	11	12
Plexiglas solutions	Model with active sphere			Layer model			I_v	$\langle \tilde{\nu} \rangle$	η_0	R_1 after (5)	P_0
	v	$R^{(1)}$	R'_1 after (4')	v	$R^{(1)}$	R'_1 after (4)					
	10^{-19}cm^3	Å	Å	10^{-19}cm^3	Å	Å					
phloxin	77.5	122.7	92.5	42.06	100.1	78.5	0.118	18.0	0.78	68.6	47.3
eosin	18.8	76.2	57.4	9.76	61.5	48.2	0.063	18.5	0.98	42.9	47.6
rhodamin 6G	15.4	71.5	53.9	8.07	57.7	45.3	0.065	18.9	1.00	42.7	43.8

It is seen in Fig. 2 that the divergence of the experimental points from the theoretical curve are rather pronounced, especially in the case of phloxin, but they do not differ by more than 10 per cent from the measured value. None the less, the deviation is quite high when it is considered that the triple standard error of the relative emission anisotropy $3\sigma_{r/r_0}$ did not exceed 2.5 per cent of the measured value.

These discrepancies may be explained by a systematical error associated above all with the calculation of the corrections conditioned by the effect of secondary fluorescence on r/r_0 . To apply the exact theory of this effect is extraordinarily difficult in practice [30]. In addition, the use of the method based on an approximation of the exact theory and leading to measurements of the degree of polarization (emission anisotropy) at three different sample thicknesses [32] has a very limited range of applicability. Namely, it should be used

only when the optical depths $\alpha_{\max}cd$ only slightly exceed the value of 0.1. In the case of the examined systems the thickness of the samples at a concentration of $c = 10^{-3}$ M/l that would fulfil this condition should be of the order of 0.1 mm, what is difficult to accomplish. Because of this, use was made of a simplified method [33], being a modification of the methods presented in Refs [30, 34]. The error arising thus may reach up to 5 per cent of the measured r/r_0 value, especially in the cases when $\alpha_{\max}cd \gg 0.1$ (when $\alpha_{\max}cd < 0.1$ the effect of secondary fluorescence on r/r_0 may be neglected [35]).

In the case of the results concerning phloxin and partially eosin, an additional source of systematic errors may stem from the found concentrational changes of absorption spectra. These changes, particularly pronounced in the case of phloxin, do not imply the occurrence of an association process of the dye molecules (there is a lack of isosbestic points), but rather their partial binding with the methyl methacrylate during the polymerization process. Recently, the existence of this type of interaction between anthracene compounds and methyl methacrylate has been reported [36]. In this case the concentration of dye molecules may be underestimated relative to the value assumed in the experiment.

In the light of the discussion concerning the possible systematic errors, above, the conformity of the presented experimental results with theory should be acknowledged as being satisfactory.

As mentioned in the *Introduction*, another criterion for checking the correctness of the theory is the comparison of the value of R'_1 determined from the concentrational depolarization curve (2) and relation (4) with the value of R_1 determined along independent lines from the absorption and emission spectra. In the latter case, R_1 can be calculated from the expression [2]:

$$R_1 = 5.856 \times 10^{-25} \frac{\eta_0 I \tilde{\nu}}{n^4 \langle \tilde{\nu} \rangle^4} \quad (5)$$

where

$$I_{\tilde{\nu}} = \int_0^{\infty} F(\tilde{\nu}) \alpha(\tilde{\nu}) d\tilde{\nu} \quad (6)$$

with η_0 the quantum yield, n the index of refraction of the medium, $\langle \tilde{\nu} \rangle$ the mean value of the wave number in the overlap region of the absorption and emission spectra, $\alpha(\tilde{\nu})$ the molar decimal coefficient of extinction, and $F(\tilde{\nu})$ the spectra distribution of fluorescence expressed in terms of numbers of quanta and normalized to unity ($\int_0^{\infty} F(\tilde{\nu}) d\tilde{\nu} = 1$). In Eq. (5)

R_1 is expressed in cm, $\tilde{\nu}$ in cm^{-1} and $I_{\tilde{\nu}}$ in l/M cm. The overlap integrals determined from Eq. (6), together with the values of $\langle \tilde{\nu} \rangle$ and η_0 , necessary for calculating R_1 by Eq. (5), are arranged in Table I. The absolute values of η_0 given in the table were determined relative to the corresponding values of η'_0 for these substances in ethyl alcohol. The energy yields η_E of eosin, rhodamin 6G and phloxin in ethyl alcohol were measured by Sen Gupta [37], who obtained for these dyes the respective values of 0.68, 0.73 and 0.27 with an exciting wavelength $\lambda = 365$ nm. Moreover, to calculate R_1 it was assumed that $n = 1.490$. When calculating $I_{\tilde{\nu}}$, account was not taken of the drop in quantum yields of the examined substances with increasing λ in the region of overlapping α and F spectra. These omissions

do not bear any greater effect on the calculated values of R_1 , however. If it is accepted that the quantities η_0 , I_r , n and $\langle \tilde{\nu} \rangle$, appearing in Eq. (5), are determined with accuracies not worse than 10, 10, 3 and 1 per cent, respectively, the relative error $\Delta R_1/R_1 = 6$ per cent is obtained. On the other hand, statistical analysis of R_1' determinations gives $\Delta R_1'/R_1' = 7$ per cent (standard error). It turns out that the values of R_1' (column 7) are higher than the values of R_1 (column 11) in all cases. We see that the best agreement is in the case of rhodamin 6G and eosin, whereas for phloxin the difference $R_1' - R_1$ is considerable and somewhat exceeds the limits of estimated errors. Figure 2 also presents the experimental values of emission anisotropy of glycerin-water solutions of rhodamin 6G, adopted from Ref. [38]. The agreement between experimental results and the theoretical curve, Eq. (2), for $z = 3$ is in this case much better than for the plexiglas solutions. This may be explained primarily by the independence of absorption spectra upon concentration and also by the possibility of using the cuvettes ensuring fulfilment of the condition $\alpha_{\max} cd < 0.1$ being used, hence, the elimination of the effect of secondary fluorescence on r/r_0 .

The obtained results were also compared with expression (3) (the model with the active sphere). The appropriate values of v , $R^{(1)}$ and R_1' are given in Table I. It is seen that in this case the values of R_1' considerably exceed those of R_1 . In the case of expression (7) (layer model with equal-thickness layers), the agreement with experimental results should be expected to be like that found for Eq. (2).

Let us notice that for the highest concentrations the experimental points pertinent to rhodamin 6G in glycerin deviate somewhat from the theoretical curve. As was shown in Ref. [38], this effect is associated with concentrational quenching by dimers. It should be stressed that the theory of concentrational depolarization of photoluminescence was additionally verified by independent determinations of R_1 from the spectra in but a few cases of glycerin solutions [7, 9, 39]. In the case of plexiglas solutions this kind of comparison has not been made, although in the case of eosin and rhodamin 6G in plexiglas both studies of spectra characteristics and polarization characteristics have been carried out [40, 41, 42].

Recently, Kawski and Kamiński [13] derived by a method like that applied in our earlier work [8, 11] for getting Eq. (2) the following expression for emission anisotropy in the framework of the model with layers of equal thickness⁵:

$$\frac{r}{r_0} = e^{-\sum_{l=1}^z A_l v_l} \sum_{k_1, \dots, k_z} \left[\frac{\eta_1^{k_1-1}}{(k_1-1)!} \prod_{l=2}^z \frac{(A_l v_l)^{k_l}}{k_l!} \frac{\sum_{l=1}^z \frac{k_l}{[1+(l-1)\delta]^6} + \sum_{l=1}^z k_l - 2}{\sum_{l=1}^z \frac{k_l}{[1+(l-1)\delta]^6} \sum_{l=1}^z k_l - 1} + 1 \right] \quad (7)$$

⁵ In Eq. (7) k_1 and k_l should take on values identical to those in the case of Eq. (2). However, the authors of Ref. [13] clearly state that the combination

$$k_1 = 1 \text{ and } k_l = 0 \text{ for } l = 2, 3, \dots, z \quad (7')$$

is excluded. This reservation is unnecessary and incorrect, because 1° The quotient with sums in Eq. (7) for the combination (7') of values of k does not give any indefinities but becomes reduced to unity, 2° At low concentrations of luminescent substance centers with only one molecule will be the most frequent and this situation cannot be excluded, for the theory would not be valid for the low-concentration range.

where

$$A_l = [1 + [l-1]\delta]^3 - [1 + (l-2)\delta]^3 \quad (8)$$

δ denoting the layer thickness. The quantities A_l designate the volumes of the individual layers, namely, $v_l = A_l v_1$ where $v_1 = \frac{4}{3}\pi R_1^3$ is the volume of the active sphere, v_1 is the average number of luminescent molecules in the volume v_1 and corresponds to the quantity ν in Eq. (2).

In deriving Eq. (7) the Förster-like dependence (1) was assumed, as in the case of Eq. (2). Equation (2) was derived within the framework of the model with layers of equal volume (I), whereas Eq. (7) within the model with layers of equal thickness (II).

In the case (I), the radii of the external spherical surfaces bounding the successive layers are

$$R_l = R_1 \sqrt[l]{l} \quad (9)$$

whereas in the case (II) they are

$$R_l = R_1 [1 + (l-1)\delta]. \quad (10)$$

Denoting by μ_l the value of μ for the molecule D in the l -th layer, and finding the volume of the active sphere in both case from the condition $\frac{1}{\tau} = \mu \equiv \mu_1$ after substituting Eqs (9)

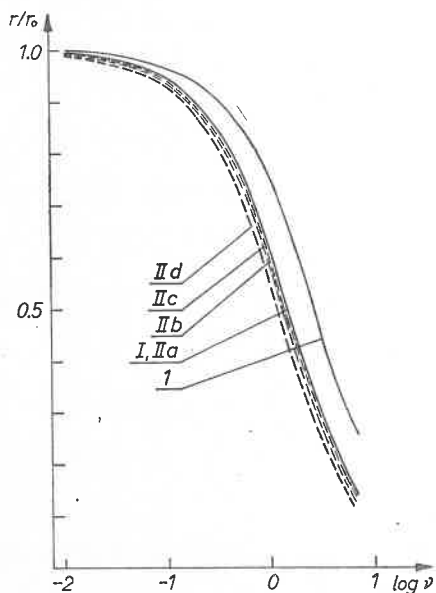


Fig. 3. Emission anisotropy of photoluminescence as a function of average number of luminescent molecules ν in the volume of the luminescence center layer. I — curve corresponding to model with active sphere ($z = 1$); $I, IIa, IIb, IIc, II d$ -curves corresponding to layer models of a luminescence center according to notation in Table II

and (10) into Eq. (1), the values of μ_l in the cases (I) and (II) are expressed by

$$\mu_l(\text{I}) = \frac{\mu_1}{l^2} \text{ and } \mu_l(\text{II}) = \frac{\mu_1}{[1+(l-1)\delta]^6}.$$

If in Eq. (2) ν is replaced by $\nu_l = A_l v_1$ and l^2 by $[1+(l-1)\delta]^6$, we get⁶ expression (7). It is obvious that Eq. (2) is much more simpler than Eq. (7). In Fig. 3 the ratio r/r_0 is presented as a function of ν , defined by Eqs (3), (2) and (7).

Table II compares the thicknesses of successive layers and the radii R_{\max} of the spherical surfaces bounding the outermost layers in the case of model (I) and in the case of the various

TABLE II

Layer model	Notation	Thickness of successive layers						R_{\max}
		in R_1 units						
		1	2	3	4	5	6	—
with layers of equal volume $z = 3$	I	1	0.260	0.182				1.442
with layers of equal thickness $z = 3; \delta = 0.22$	IIa	1	0.22	0.22				1.440
with layers of equal thickness $z = 4; \delta = 0.15$	IIb	1	0.15	0.15	0.15			1.45
with layers of equal thickness $z = 6; \delta = 0.1$	IIc	1	0.1	0.1	0.1	0.1	0.1	1.500
with layers of equal thickness $z = 6; \delta = 0.15$	II d	1	0.15	0.15	0.15	0.15	0.15	1.750

versions of model (II). The table shows in the cases (I), (IIa) and (IIb) R_{\max} is practically identical.

Figure 3 presents the r/r_0 curves for the cases arranged in Table II, and also the curve corresponding to the model with the active sphere ($z = 1$). It proves that curve (I) corresponding to the model with layers of equal volume for $z = 3$ exactly overlaps curve (IIa) and differs very slightly from curve (IIb), corresponding to the model with equal-thickness layers. It follows thence that the curve of r/r_0 as a function of ν does not in practice depend

⁶) In Eq. (7) the number one written by mistake beyond the fraction should be dropped.

on the assumed thickness of the layers surrounding the active sphere in the case of equal R_{\max} . The values of r/r_0 corresponding to the cases (IIc) and (II d) are a little smaller than in the cases (I), (IIa) and (IIb), what stems from the circumstance that a larger number of molecules D is accounted for. These molecules are highly probable acceptors of excitation energy which are located in the volume of spheres of greater radii R_{\max} .

Notwithstanding, this effect is small in this case. It should be clearly emphasized that both Eq. (2) and Eq. (7) may be usually applied in the range of low concentrations, at which concentrational quenching in the solution may be neglected.

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