

# ON PHOTOLUMINESCENCE QUANTUM YIELD OF PRIMARY LIGHT ABSORBERS AND THEIR NEAREST NEIGHBOURS IN SOLUTIONS

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Accepting the dipole-dipole mechanism of non-radiative transfer of electronic excitation energy between active molecules  $D$  in isotropic solution we obtained expressions for quantum yield of photoluminescence emitted by: 1. molecules  $D_0$  primarily excited by light absorption, 2. molecules  $D_1$  being the nearest neighbours of  $D_0$ , and 3. molecules  $D_2$  being the nearest neighbours of  $D_1$ . In the calculations selfquenching and excitation energy remigration were taken into account. In contradistinction to the similar problems regarded previously, [*Acta Phys. Pol.* A45, 85 (1974)] the present paper takes into consideration the presence of dimers  $D_{,,}$  in the luminescence centre. A discussion of the obtained results is given.

## 1. Introduction

To explain the influence of concentration on luminescence properties of condensed systems, such as the phenomenon of photoluminescence concentrational depolarization (PLCD), we apply the models of luminescence centre. In the recently developed [1] PLCD theory we introduced a model of luminescence centre called a model of most probable path (MPP) which, according to our assumption, consists of a molecule  $D_0$  primarily excited by light absorption and of molecules  $D_1, D_2 \dots D_n$  to which excitation energy can be transferred, in a non-radiative way, with the greatest probability ( $D_k$  is the nearest neighbour of molecule  $D_{k-1}$  or the second nearest one after  $D_{k-2}$ ). Molecules  $D_k$  may lose their excitation energy as a result of fluorescence emission (with relative probability  $P_F$ ), by internal conversion ( $P_q$ ) and/or by non-radiative transfer to a monomer  $D$  ( $P_{DD}$ ) or dimer  $D_{,,}$  ( $P_{DD,,}$ ). The transfer of excitation energy from  $D_{,,}$  to  $D$  is neglected because it is assumed that quantum yield of dimer photoluminescence (PL) amounts to zero. After many non-radiative transfers, the excitation energy can return to molecules  $D_0$ . Taking into account the energy remigration is of great importance in the PLCD theory, for it

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has been shown that only molecules  $D_0$  participate in fluorescence emission anisotropy (EA) when molecular dipoles are oriented at random [2-4].

For partial ordering of molecular dipoles, the EA of molecules  $D_1$  and  $D_2$  may also prove to be significant. Then it will be important to know the photoluminescence yields of molecule  $D_k$ . A comparison of the sum of the yield  $\eta_k$  of the molecules belonging to the luminescence centre with the yield  $\eta$ , computed under the assumption that an arbitrary number of molecules from the environment of  $D_0$  participates in PL emission, allows us to obtain some information as to the localization of excitation energy in the luminescence centre.

Recently, we have given [5] the formulae for the PL quantum yields  $\eta_0$ ,  $\eta_1$  and  $\eta_2$  of molecules  $D_0$ ,  $D_1$  and  $D_2$ , applying the MPP model. These formulae were obtained taking into consideration the excitation energy remigration as well as quenching by non-luminescent molecules. It was assumed in the calculations that all the molecules belonging to a centre were monomers. We assumed there that molecules  $D_{,,}$  did not appear in the luminescence centre though they were present in the solution. At the same time it was assumed that excitation energy could be transferred from molecules  $D_0$ ,  $D_1$  and  $D_2$  to any molecule  $D_{,,}$  in the solution.

In the present work we shall determine the role of PL quantum yields  $\eta_{(0)}$ ,  $\eta_1$  and  $\eta_2$  in the total yield  $\eta$  when we take into account the presence of dimers not only in the solution but also in the luminescence centre.

## 2. Quantum yields of photoluminescence

We shall assume, similarly as in Ref. [6], that in a luminescence centre the possible distributions of monomer  $D$  and dimer  $D_{,,}$  molecules can occur with the probabilities listed in Table I.

TABLE I

$N$	Distribution			Probability
	$D_0$	$D_1$	$D_2$	
1	$D$	$D$	$D$	$p_1 = \varphi^3$
2	$D_{,,}$	$D$	$D$	$p_2 = p_3 = p_4 = \varphi^2(1-\varphi)$
3	$D$	$D$	$D_{,,}$	
4	$D$	$D_{,,}$	$D$	
5	$D_{,,}$	$D_{,,}$	$D$	
6	$D_{,,}$	$D$	$D_{,,}$	$p_5 = p_6 = p_7 = \varphi(1-\varphi)^2$
7	$D$	$D_{,,}$	$D_{,,}$	
8	$D_{,,}$	$D_{,,}$	$D_{,,}$	$p_8 = (1-\varphi)^3$

$\varphi = \frac{c'}{c}$ ,  $(1-\varphi) = \frac{c''}{c}$  means the probability that an active molecule chosen at random will be a monomer (dimer);  $c'$ ,  $c''$  and  $c$  denote the concentrations of monomers and

dimers as well as the analytical concentration of active molecules in solution, respectively. For each of the distributions of molecules  $D$  and  $D_{ii}$ , listed in Table I, four<sup>1</sup> situational distributions are possible within the accepted MPP model. Two of them ( $a_1$  and  $b_2$ ) are presented in Fig. 1. In those distributions the fourth active molecule  $D_3$ , whose

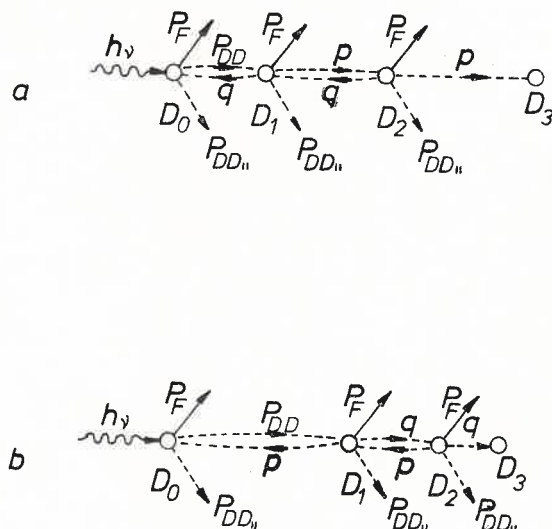


Fig. 1. Situational distributions of active molecules  $D_0, D_1, D_2, D_3$  and the schemes of possible processes (without internal conversion)

presence makes the screen  $D_2$  partially reflecting, is also regarded and its localization with respect to molecule  $D_2$  determines the probability of excitation energy transfer from molecule  $D_2$  to molecule  $D_1$ ; in cases  $a_1$  and  $b_2$  it amounts to [1]

$$q = \langle Q \rangle P_{DD} \quad \text{and} \quad p = (1 - \langle Q \rangle) P_{DD}, \quad (1)$$

respectively, at which [7]

$$\langle Q \rangle = \frac{\frac{16}{27} \langle P(\frac{27}{16} \gamma) \rangle}{\langle P(\gamma) \rangle}, \quad (2)$$

where

$$\langle P(\gamma) \rangle = \gamma \left[ \text{Ci}(\gamma) \sin \gamma - \text{Si}(\gamma) \cos \gamma + \frac{\pi}{2} \cos \gamma \right], \quad (3)$$

$$P_{DD} = \alpha f(\gamma), \quad (4)$$

<sup>1</sup> In Ref. [1] it has been proved that it is sufficient to consider only the distributions of  $a_1$  and  $b_2$ .

where

$$f(\gamma) = \pi^{1/2} \gamma \exp(\gamma^2) [1 - \operatorname{erf}(\gamma)], \quad (5)$$

$$\gamma = \gamma_D + \gamma_{D''} = \frac{\pi^{1/2}}{2} \left( \frac{c'}{c'_0} + \frac{c''}{c''_0} \right), \quad (6)$$

$$\alpha = \frac{\gamma_D}{\gamma}. \quad (7)$$

Function  $\langle Q \rangle$  means the probability that if molecule  $D_k$  is the nearest neighbour of molecule  $D_{k-1}$  then molecule  $D_{k-1}$  is likewise the nearest neighbour of  $D_k$ , when assuming the statistical distribution of active molecules in solution.  $\operatorname{Ci}(\gamma)$  and  $\operatorname{Si}(\gamma)$  denote the functions of integral cosine and sine,  $\operatorname{erf}(\gamma)$  — error integral and  $C'_0$  and  $C''_0$  — critical concentrations for non-radiative excitation energy transfer from  $D^*$  to  $D$  and from  $D^*$  to  $D''$ .

The mean value of PL relative quantum yield  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle$  of  $D_0$  type molecules can be put down as

$$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle = \varphi^3 \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3 + \varphi^2(1-\varphi) \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2 + \varphi(1-\varphi) \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_1, \quad (8)$$

where  $\eta_0$  is PL quantum yield of the solution for  $C \rightarrow 0$  and  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3$ ,  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  and  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_1$  denote PL quantum yields corresponding to distributions 1,3 as well as 4 and 7 from Table I computed as mean values from the PL quantum yields corresponding to the situational distributions of  $a_1$  and  $b_2$ . For yield  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3$  we obtained previously the expression [5]

$$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3 = \frac{1-f}{2} \left[ 2 + \frac{\langle Q \rangle P_{DD}^2}{M_1} + \frac{(1-\langle Q \rangle) P_{DD}^2}{M_2} \right], \quad (9)$$

where

$$M_1 = 1 - \langle Q \rangle (2 - \langle Q \rangle) P_{DD}^2 \quad (10)$$

$$M_2 = 1 - (1 - \langle Q \rangle)^2 P_{DD}^2. \quad (11)$$

A similar procedure applied to obtain Eq. (9) gives for PL quantum yields  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  and

$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_1$  of molecules  $D_0$  in the case of distribution 3 and distribution 4 and 7 from Table I the following expression, respectively<sup>2</sup>

$$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2 = \frac{1-f}{1-P_{DD}^2}, \quad (12)$$

$$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_1 = \frac{1-f}{1-P_{DD}}, \quad (13)$$

where  $f$  and  $P_{DD}$  denote as above.

The PL quantum yields of molecules  $D_1$  and molecules  $D_2$  can be put down as (comp. Table I)

$$\left\langle \frac{\eta_1}{\eta_0} \right\rangle = \varphi^3 \left\langle \frac{\eta_1}{\eta_0} \right\rangle_3 + \varphi^2(1-\varphi) \left\langle \frac{\eta_1}{\eta_0} \right\rangle_2, \quad (15)$$

$$\left\langle \frac{\eta_2}{\eta_0} \right\rangle = \varphi^3 \left\langle \frac{\eta_2}{\eta_0} \right\rangle_3, \quad (16)$$

where  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_3$  and  $\left\langle \frac{\eta_2}{\eta_0} \right\rangle_3$  are PL quantum yields corresponding to distribution 1 and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  to distribution 3. The calculations carried out within the MPP model give

$$\left\langle \frac{\eta_1}{\eta_0} \right\rangle_3 = \frac{1-f}{2} P_{DD} \left( \frac{1}{M_1} + \frac{1}{M_2} \right), \quad (17)$$

$$\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2 = P_{DD} \frac{1-f}{1-P_{DD}^2}, \quad (18)$$

$$\left\langle \frac{\eta_2}{\eta_0} \right\rangle_3 = \frac{1-f}{2} P_{DD}^2 \left( \frac{1-\langle Q \rangle}{M_1} + \frac{\langle Q \rangle}{M_2} \right). \quad (19)$$

In Fig. 2 the concentrational dependences  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle$ ,  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  and  $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$  are presented as

<sup>2</sup> In the case of distribution 4 and 7 molecules  $D_0$  cannot, within the MPP model, transfer the excitation energy to another monomer molecule in solution. These molecules can lose their energy only as a result of PL emission, internal conversion and its non-radiative transfer to dimers  $D''$ , respectively, with the probabilities

$$P_F = \eta_0[1-f(\gamma)], P_q = (1-\eta_0)[1-f(\gamma)], P_{DD''} = (1-\alpha)f(\gamma), \quad (14)$$

hence

$$\left\langle \eta_{(0)} \right\rangle_1 = \frac{P_F}{P_F + P_q + P_{DD''}} = \frac{\eta_{(0)}(1-f)}{1-P_{DD}}$$

determined by formulae (8), (15) and (16) for several values of  $K_\gamma$ , denoting the dimensionless constant in the process of dimer formation<sup>3</sup>. These dependences are shown by solid lines. In this figure the dependences (9), (17) and (19) are presented with dotted lines

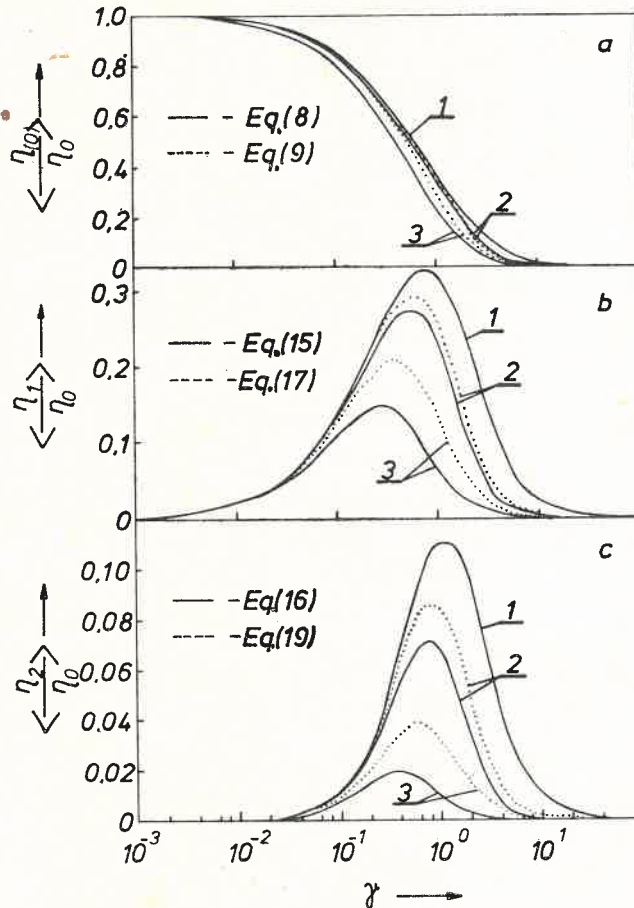


Fig. 2. PL quantum yields of molecules  $D_0$ ,  $D_1$  and  $D_2$  versus reduced concentration  $\gamma$ ; 1 -  $K_\gamma = 0$ ; 2 -  $K_\gamma = 0.1$ ; 3 -  $K_\gamma = 1.0$

<sup>3</sup> This magnitude is connected with dimerization constant

$$K = c''/c'^2$$

by the relation

$$K_\gamma = \gamma_{D_0} / \gamma_{D_0}^2 = 2Kc_0'^2 / \alpha^{1/2} c_0''$$

$K_\gamma$  comes into the formulae (8), (15) and (16) through the dependence

$$\varphi = \frac{\alpha}{(1-\alpha) \frac{c_0''}{c_0'} + \alpha}$$

where

$$\alpha = \frac{-1 + \sqrt{1 + 4K_\gamma \cdot \gamma}}{2K_\gamma \cdot \gamma}$$

which, in contra-distinction to the previous ones do not take into account the presence of dimers in the luminescence centre.

As seen from Fig. 2a the differences in values  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle$  for  $K_\gamma = 0$  and  $K_\gamma = 0.1$  are relatively slight, especially in the range of low and moderate concentrations; but very conspicuous for the values  $K_\gamma = 0$  and  $K_\gamma = 1.0$  in almost the entire range of concentrations (cf. solid curves 1 and 2 as well as 1 and 3). Also, taking into account the presence of dimers in the luminescence centre results in a remarkable decrease of PL quantum yield of molecules  $D_0$  only in the case of large  $K_\gamma$  (comp. solid and dotted curves).

In Fig. 2b the dependence (15) for several values of  $K_\gamma$  (solid curves) is presented. Yields  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  show maxima with decreasing values for the systems strongly inclined to association. In the range of high concentrations there is a noticeable difference in values  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  for  $K_\gamma = 0$  and  $K_\gamma > 0$  (cf. solid curves 1 as well as 2 and 3). In the range of concentrations  $\gamma < 0.1$  the influence of quenching on  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  is not significant. For the sake of comparison the curves determined by formula (17), not taking into account the presence of dimers in the luminescence centre (dotted curves), are also given. Large differences of values  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  appear only for  $K_\gamma = 1.0$  (curve 3). It should be emphasized that even at very large values of  $K_\gamma$ , the contribution of yield  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  to the luminescence observed is essential for moderate concentrations.

In Fig. 2c the concentrational dependence of yield  $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$  of  $D_2$  type molecules is presented as determined by expressions (16) and (19) corresponding to considering and neglecting the presence of dimers in a luminescence centre. As seen from the figure, the PL yield  $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$  really depends on the value of the dimerization constant  $K_\gamma$ . The contribution of yield  $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$  to the observed luminescence is not as big as yields  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle$  and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$ , especially for systems with a big values of  $K_\gamma$ . Expressions (8) and (15), describing quantum yields  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle$  and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$ , contain, respectively, 3 and 2 terms representing the contributions to the photoluminescence originating from molecules  $D_0$  and  $D_1$ . The mentioned terms appearing in Eq. (8) refer to the PL yield of molecules  $D_0$  belonging to the luminescence centre with 3, 2 and 1 active molecules and the terms appearing in Eq. (15) refer to the PL of molecules  $D_1$  belonging to the centre with 3 and 2 molecules. In Fig. 3, the concentrational changes of PL yield of molecules  $D_0$  (solid lines) and molecules  $D_1$  (dotted lines) are presented for a centre consisting of two active molecules  $D_0$  and  $D_1$ . There

we have an example of a group with two totally reflecting screens [1]. Absence of self-quenching ( $K_\gamma = 0$ ) means a complete limitation of excitation energy migration to the systems of molecules  $D_0$  and  $D_1$ . The asymptotic values for  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  as well as for  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  in this case amount to 1/2, (cf. curves 1 and 1') which is quite understandable and it results

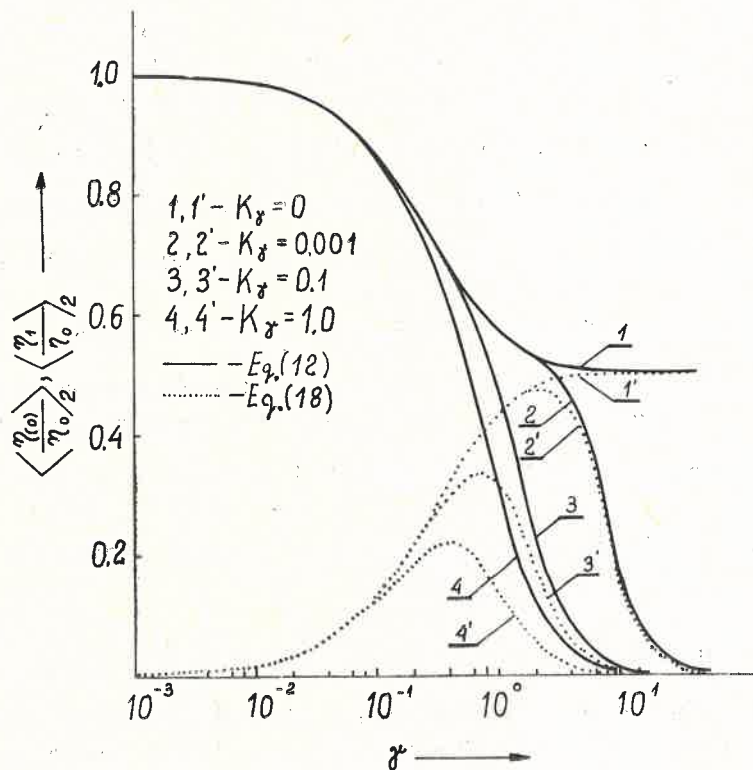


Fig. 3. Photoluminescence quantum yields  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  of molecules  $D_0$  and  $D_1$  in the case of a group with two active molecules.

directly<sup>4</sup> from formulae (12) and (18). Curves 2, 3 and 4 as well as 2', 3' and 4' present the concentrational changes of photoluminescence yields  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  for  $K_\gamma > 0$ .

In the range of concentration  $\gamma < 0.1$  the influence of self-quenching on values  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  can practically be neglected. For strongly dimerizing systems, essen-

<sup>4</sup> For  $K_\gamma = 0$ ,  $\alpha = 1$  and  $P_{DD} = f$  [cf. Eq. (6), (7), (4)]; for  $\gamma \rightarrow \infty$ ,  $P_{DD} = f(\gamma) \rightarrow 1$  [cf. Eq. (5)].



tial differences in values  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2$  and  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  appear already at  $\gamma = 1$ , but in the case of systems with a small value of  $K_\gamma$ , these differences appear in the range of larger concentrations. Let us add that the maxima of  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2$  are larger than those of  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_3$  corresponding to the same value  $K_\gamma$  (cf. curve 3' from Fig. 3 and the dotted curve from Fig. 2b). That is a result of the fact that in a group with three molecules the excitation energy can be transferred to molecules of type  $D_2$  while the probability of energy remigration to

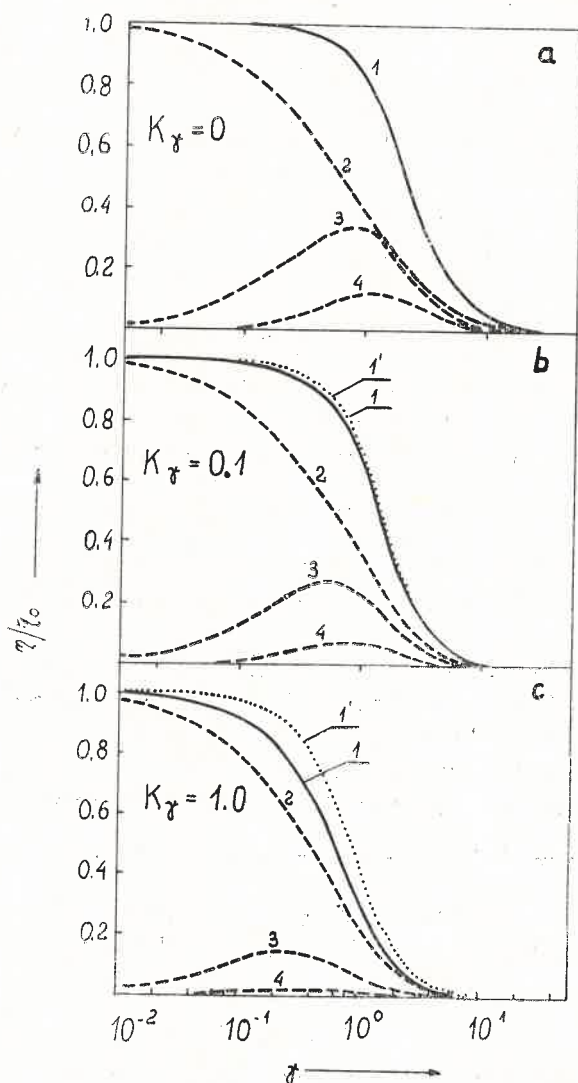


Fig. 4. Photoluminescence quantum yield  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_{\text{MPP}}$ ,  $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle$ ,  $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$  and  $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$  versus  $\gamma$

molecules  $D_1$  is smaller than unity. For similar reasons in the case of PL yield of molecules  $D_0$ , at the same  $K_\gamma$  and  $\gamma$  the inequality

$$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2 > \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3$$

is satisfied (cf. eg. curve 4 from Fig. 3 and the dotted curve 3 from Fig. 2a).

Within the model of the most probable path (MPP) we have assumed that merely molecules  $D_0$ ,  $D_1$  and  $D_2$  contribute to the emitted luminescence. In this approximation the PL quantum yield of a solution can be put down as:

$$\left\langle \frac{\eta}{\eta_0} \right\rangle_{\text{MPP}} = \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle + \left\langle \frac{\eta_1}{\eta_0} \right\rangle + \left\langle \frac{\eta_2}{\eta_0} \right\rangle. \quad (20)$$

Taking into account expressions from (8) to (13) and from (15) to (19) in (20) we obtain finally

$$\left\langle \frac{\eta}{\eta_0} \right\rangle_{\text{MPP}} = \varphi^3 \frac{1-f}{2} \left( 2 + \frac{P_{DD}(1+P_{DD})}{M_1} + \frac{P_{DD}(1+P_{DD})}{M_2} \right) + \varphi(1-\varphi^2) \frac{1-f}{1-P_{DD}}. \quad (21)$$

In Fig. 4 the concentrational dependence of quantum  $\left\langle \frac{\eta}{\eta_0} \right\rangle_{\text{MPP}}$  is presented for several values of  $K_\gamma$  (solid curves) and also for the photoluminescence quantum yield emitted by molecules  $D_0$ ,  $D_1$  and  $D_2$  (dashed curves).

It is seen from the figure that the luminescence emitted by molecules  $D_0$  contributes most remarkably to yield  $\left\langle \frac{\eta}{\eta_0} \right\rangle_{\text{MPP}}$ . Quantum yields  $\eta_1$  and  $\eta_2$  are considerably smaller than yield  $\eta_{(0)}$ . Only in the case when concentration quenching does not appear, the yields  $\eta_1$  and  $\eta_{(0)}$  are comparable merely in the range of high concentrations (cf. curves 2 and 3 in Fig. 4a).

Besides, there is evident a general regularity finding its expression in a much bigger drop of the yield at the fixed value of  $\gamma$  in strongly dimerizing systems. It is quite understandable because the dimers play a role of quenching centres trapping the excitation energy and transforming it into heat.

In Fig. 4 there are also presented the courses of concentrational changes of yield  $\left\langle \frac{\eta}{\eta_0} \right\rangle_{\text{MPP}}$  obtained formerly [5] for the case when dimers  $D_i$  do not appear in the luminescence centre (dotted lines). Obviously taking into account the presence of dimers in a luminescence centre is essential, especially for strongly dimerizing systems ( $K_\gamma = 1.0$ ).

### 3. Final remarks

The obtained expressions for PL quantum yields of molecules  $D_0$ ,  $D_1$  and  $D_2$  can be applied to determine the emission anisotropy  $r$  for systems with a partial ordering of molecular oscillators.

This problem was the subject of several works carried out by Kozlov and Sarshevskii [9-11]. These authors have shown that an investigation of EA concentrational dependence of partially orientated molecules can be applied to explain the concentrational quenching conditioned by non-radiative excitation energy transfer from the singlet level as well as from the triplet one. Emission anisotropy, according to Weber's addition law [12] can be written down as:

$$r = r_0 \frac{\eta_{(0)}}{\eta} + \sum_{i=1}^n r_i \frac{\eta_i}{\eta}, \quad (22)$$

where  $r_0$  and  $\eta_0$  denote<sup>5</sup> emission anisotropy and quantum yield of  $D_0$  type molecules, and  $r_i$  and  $\eta_i$  those of molecules  $D_i$ , respectively.

In the case of a statistical distribution of the directions of molecular oscillators the inequality

$$r_0 \gg r_1 \gg r_2, \quad (23)$$

is satisfied, where  $r_0, r_1 \dots$  - EA of the photoluminescence emitted by molecules  $D_0, D_1 \dots$ . Then it is sufficient to regard only the first component in sum (22).

Still in the case of luminescent systems containing groups of molecules with distinguished directions of transition moments inequality (23) may prove to be false. In this case in Eq. (22) for EA, it will be necessary to take into account the additional terms for which it is necessary to know the coefficients  $\eta_i$ . In the case of a statistical distribution of the directions of molecular oscillators when the emission anisotropy is determined practically only by yield  $\eta_0$ , it is indispensable to take into consideration the presence of dimers in the luminescence centre.

This mainly refers to luminescent systems strongly inclined to association (cf. solid and dotted curves in Fig. 2a). As it results from the course of concentrational changes of  $\eta_{(0)}/\eta_0$ , not taking into account the presence of dimers in the luminescence centre brings a certain increase of emission anisotropy.

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<sup>5</sup> The quantum yield of molecules  $D_0$  has been denoted by  $\eta_{(0)}$  instead of  $\eta_0$ , because the letter symbol has been used to denote the quantum yield of solution  $\eta$  for  $C \rightarrow 0$ .

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