

# CONCENTRATION DEPOLARIZATION BY EXCITATION TRANSFER. SELFQUENCHING CONSIDERATIONS

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A generalization of photoluminescence concentration depolarization worked out by FÖRSTER and ORE for the case of concentration quenching by nonluminescent dimers was made.

The obtained expression for emission anisotropy was compared with experimental results. It was found, that the generalized FÖRSTER-ORE theory can be applied to a wider range of concentration, first of all to the case of systems with a low value of dimerization constant.

## 1. Introduction

In the majority of the existing theories on photoluminescence concentration depolarization (PLCD) of isotropic solutions, photoluminescence concentration quenching (PLCQ) is either completely neglected or taken into account only approximately [1-15].<sup>1</sup>

The PLCD theories which do not take self-quenching into consideration describe the experimental results correctly only for not large concentration ranges of dye molecules. In the range of high concentrations photoluminescence depolarization is smaller than that predicted by these theories. The most noticeable lack of agreement with experiment of these theories is seen in the case of the systems in which repolarization takes place<sup>2</sup>. In the past attempts were made to generalize FÖRSTER-ORE's as well as JABLONSKI's theories for the case of self-quenching [4-8, 13, 14, 17]. SZALAY [6, 7] and KAWSKI [5] have succeeded in obtaining a better agreement of the FÖRSTER-ORE theory with experiment by replacing the reduced concentration  $\gamma$  appearing in the theory by an expression of type  $\sqrt{\eta(\gamma)} \cdot \gamma$ , where  $\eta(\gamma)$  denotes the photoluminescence (PL) quantum yield. A procedure of this kind is, however, not adequate to the quenching mechanisms accepted at present<sup>3</sup>, because it treats all the forms of quenching in a summary way.

<sup>1</sup> In [1-3] a review of the existing PLCD theories and a discussion as to the accepted simplifying assumptions is presented.

<sup>2</sup> This phenomenon observed for the first time by FEOFILOV and SVESHNIKOV [16] has been proved by SZALAY *et al.* [17] as well as by others [18-20]).

<sup>3</sup> These are [22-24]: (1) non-active absorption by non-luminescent dimers; (2) non-radiative energy transfer from excited monomers to dimers in one or many steps; (3) excitation energy degradation during its transfer between monomers.

Let us add that the non-active absorption of exciting light by dimers does not affect the observed PL polarization. The generalizations of the PLCD theory made by JABŁOŃSKI, presented in [8, 17], are of similar character. The FÖRSTER-ORE PLCD theory has recently been generalized by CRAVER and KNOX [11], who in their theory took into account the angular factor appearing in the expression for rate constant of non-radiative excitation energy transfer and also took into account the participation of the molecules  $D_1$  and  $D_2$  — the nearest neighbours of molecules  $D_0$ , primarily excited by light absorption in the process of excitation energy migration. A generalization of the FÖRSTER-ORE theory for the case of PL-quenching by dimers seems to be equally useful. The aim of the present work is to take into consideration the quenching conditioned by the non-radiative energy transfer from excited monomers  $D^*$  to dimers  $D_{II}$  both in a single and in several steps in the mentioned FÖRSTER-ORE theory.

## 2. The effect of self-quenching on emission anisotropy

Let us assume, similarly as in [13], that non-radiative energy transfer from excited monomers to non-excited ones causes merely depolarization, while energy transfer to dimers causes PL selfquenching. Moreover, assuming that PL self-quenching leading to a drop of quantum yield  $\eta/\eta_0$  causes parallel changes in the lifetime of molecules  $D$  in excited state, that is

$$\frac{\eta}{\eta_0} = \frac{\tau}{\tau_0}, \quad (1)$$

then, in conformity with PERRIN [25], changes in emission anisotropy can be described as:

$$\frac{r_0}{r} = 1 + \left( \frac{r_0}{r'} - 1 \right) \frac{\eta}{\eta_0}, \quad (2)$$

where  $r$ , introduced by Jabłoński in [26], connects the emission anisotropy (EA) with the polarization degree ( $P$ ) by the relation

$$r = \frac{2P}{3-P}, \quad (3)$$

in which  $r$  is the emission anisotropy dependent on dimer and monomer concentrations  $c''$  and  $c'$  respectively,  $r'$  denotes (EA) dependent only on  $c'$  and  $r_0$  the ground anisotropy. We assume that concentration changes in emission anisotropy  $r'/r_0$  are determined by the expression obtained by ORE [27]

$$\frac{r'}{r_0} = \int_0^{\infty} \frac{\xi^2 (\xi^2 + \gamma_D^2) \exp(-\xi) d\xi}{(\xi^2 + \gamma_D^2)^2 - \gamma_D^4 \exp\left(-\frac{11\xi}{16}\right)} \quad (4)$$

and the changes of quantum yield  $\eta/\eta_0$  are described by FÖRSTER's formula [28] taking into account a single-step mechanism of excitation transfer:

$$\frac{\eta}{\eta_0} = 1 - f(\gamma_{D_{II}}) = 1 - \sqrt{\pi} \gamma_{D_{II}} \exp(\gamma_{D_{II}}^2) [1 - \operatorname{erf}(\gamma_{D_{II}})]. \quad (5)$$

Here  $\xi$  is the mean number of luminescent molecules in the volume of a sphere of radius  $R$ ,  $\gamma_D$  and  $\gamma_{D_{II}}$  denote reduced concentrations of monomers and dimers, respectively, at which

$$\gamma_D = \frac{\sqrt{\pi}}{2} \frac{c'}{c'_0}; \quad \gamma_{D_{II}} = \frac{\sqrt{\pi}}{2} \frac{c''}{c''_0}; \quad (6)$$

where  $c'_0$  and  $c''_0$  are critical concentrations for non-radiative excitation transfer from  $D^*$  to  $D$  and from  $D^*$  to  $D_{II}$ , respectively.

In Fig. 1 the theoretical courses of  $r/r_0$  determined by formula (2) are presented, taking into account expressions (4) and (5) for  $r'/r_0$  and  $\eta/\eta_0$ , respectively. The computations were made for several values of the dimensionless constant  $\mathcal{K}_\gamma = \gamma_{D_{II}}/\gamma_D^2$ , which is connected with dimerization constant  $K = c''/c'^2$  by the equation

$$\mathcal{K}_\gamma = \frac{2Kc'_0{}^2}{\sqrt{\pi} c''_0}. \quad (7)$$

The values of the reduced concentrations  $\gamma_D$  and  $\gamma_{D_{II}}$  were calculated for each particular  $\mathcal{K}_\gamma$  from relation

$$\gamma_D = \alpha\gamma, \quad \gamma_{D_{II}} = (1-\alpha)\gamma, \quad (8)$$

where

$$\alpha = \frac{\sqrt{1+4\mathcal{K}_\gamma} - 1}{2\mathcal{K}_\gamma}, \quad (9)$$

$$\gamma = \gamma_D + \gamma_{D_{II}} \quad (10)$$

As seen from the figure, all curves for  $\mathcal{K}_\gamma > 0$  exhibit maxima, the position of which depends on the value of  $\mathcal{K}_\gamma$ . Similar results [13] were obtained from an analogous generalization of JABŁOŃSKI's PLCD theory. In [13] we compared JABŁOŃSKI's theory with the experimental results concerning the concentration changes of emission anisotropy of rhodamin 6 G in glycerin-water solutions and we found a good agreement of theory with experiment in the range of low and moderate concentrations and an approximate agreement in the range of high concentrations.

A comparison was made for the values of critical concentrations  $c'_0$  and  $c''_0$ , found on the basis of spectroscopic investigations ( $\kappa_{\text{theor}} = \frac{c'_0}{c''_0} = 1.29$ ) and for values

$c'_0$  and  $c''_0$  ( $\kappa_{\text{exp}} = \frac{c'_0}{c''_0} = 4.75$ ) obtained by comparing the appropriate experimental results with JABŁOŃSKI's theoretical expressions describing the concentration changes of  $r/r_0$  and  $\eta/\eta_0$ . The mentioned agreement of theory with experiment was obtained for  $\kappa_{\text{theor}}$ , but for  $\kappa_{\text{exp}}$  the deviations of the experimental points from the theoretical curve in the range of high concentrations were very big. In [13] we proved that the difference between the values  $\kappa_{\text{theor}}$  and  $\kappa_{\text{exp}}$  resulted from the fact that in

the theoretical expression for  $\eta/\eta_0$  given by JABŁOŃSKI the multi-step mechanism of non-radiative excitation energy transfer from monomers to dimers had been neglected.

Also Eq. (5) takes into account only the single-step mechanism of energy transfer from  $D^*$  to  $D_{II}$ . Recently we have worked out the PLCQ theory which takes into consideration the multi-step mechanism of energy transfer. For the quantum yield we obtained expression [23]

$$\frac{\eta}{\eta_0} = \frac{1-f(\gamma)}{1-\alpha f(\gamma)} \quad (11)$$

which in the case of  $\gamma_D \ll \gamma_{D_{II}}$  becomes Eq. (5). Substituting in Eq. (2) formulas (4) and (11) for  $r'/r_0$  and  $\eta/\eta_0$  and taking into account (8) we obtain:

$$\frac{r}{r_0} = 1 + \left\{ \int_0^\infty \frac{\xi^2 [\xi^2 + (\alpha\gamma)^2] \exp(-\xi) d\xi}{[\xi^2 + (\alpha\gamma)^2]^2 - (\alpha\gamma)^4 \exp\left(-\frac{11\xi}{16}\right)} \right\}^{-1} - 1 \cdot \frac{1-f(\gamma)}{1-\alpha f(\gamma)} \quad (12)$$

When dimers do not appear in solution ( $\alpha \rightarrow 1$ ), Eq. (12) becomes (4), but in the case when  $\gamma_{D_{II}} \gg \gamma_D$ ,

$$\alpha \rightarrow 0 \quad \text{and} \quad r/r_0 \rightarrow 1.$$

In Fig. 1 the curves determined by Eq. (12) for several values of  $\mathcal{K}_\gamma$ , are plotted with dashed lines. They also exhibit minima and, moreover, in the range of highest concentrations, the higher their courses are in relation to the corresponding solid curves, the lower is the value of  $\mathcal{K}_\gamma$ . In this figure the Förster-Ore curve corresponding to  $\mathcal{K}_\gamma = 0$  is also plotted and, in distinction from the other curves, it tends asymptotically to zero for  $\gamma \rightarrow \infty$ .

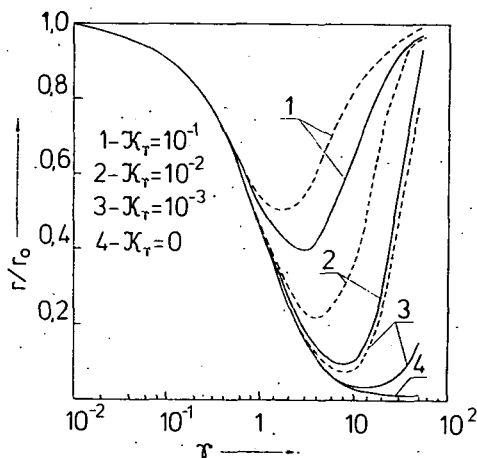


Fig. 1. Theoretical curves of concentration changes in emission anisotropy  
 ———— computed on the basis of (2), (4) and (5)  
 - - - - - computed on the basis of (12)

### 3. Comparison with experiment and final remarks

In Fig. 2 the experimental results referring to PL concentration depolarization of the systems listed in Table I are compared with formula (2), taking into account Eqs. (4) and (5), and with formula (12). The best agreement of experimental results with theory in the range of low and moderate concentrations was obtained for much higher values of  $\eta_0$  than in the Refs. quoted in column 8 of Table I, (comp. columns 3 and 9) and thus for other values of constants  $\mathcal{K}_\gamma$ ,  $c'_0$  and  $c''_0$ <sup>4</sup>. Table II contains the parameter values indispensable for the comparison of theory with experiment. Column 6 gives also the values  $\kappa_{\text{theor}} = (c'_0/c''_0)_{\text{theor}}$  found on the basis of spectroscopic investigations, and columns 15, 16, 17 the values  $\kappa_{\text{exp}}^*$  and  $\kappa_{\text{exp}}^{**}$  obtained by comparison of the experimental results with theoretical curves. Values of  $c'_0$  were found by comparing the experimental results  $r/r_0$  with Eq. (4) and  $c''_0$  values by comparing the experimental  $\eta/\eta_0$  with Eq. (5) and with Eq. (11), respectively; (the corresponding values are marked by  $c_0^{**}$  and  $c_0^{***}$ ).

The concentrations  $c_0^{***}$  listed in columns 12 and 13, respectively, were found for the values  $\alpha_0 = 1$  and  $\alpha_0 < 1$  assumed in formula (11), *i. e.* neglecting and taking into account the PL monomer quenching<sup>5</sup>. The comparison of values  $\kappa_{\text{theor}}$  with values  $\kappa_{\text{exp}}^*$  and  $\kappa_{\text{exp}}^{**}$  proves the best agreement of value  $\kappa_{\text{exp}}^{**}$  from columns 17 with  $\kappa_{\text{theor}}$ . This means that correct values of  $c''_{0\text{exp}}$  are obtained by comparing the experimental results of  $\eta/\eta_0$  not with Eq. (5) but with Eq. (11) for  $\alpha_0 < 1$ . Even for  $\alpha_0 = 1$  expr. (11) gives more correct values of  $c_0^{***}$  than expr. (5) (comp. values  $\kappa_{\text{theor}}$  and  $\kappa_{\text{exp}}^{**}$  from column 16).

Hence it can be concluded that in PL concentration quenching the basic role can be ascribed to the multi-step mechanism of non-radiative excitation energy transfer to dimers; also the mechanism of monomer quenching cannot be neglected. From Fig. 2 we see that in the range of highest concentrations the experimental points deviate from both the solid curves and the dashed ones in the case of all the systems investigated, differing by the value of dimerization constant. In the mentioned range of concentrations  $\gamma$  the solid curves determined by expressions (2), (4) and (5) lie distinctly below the experimental results (except the case of system III). A similar regularity could be found [13] in the case of the generalization of JABŁOŃSKI's PLCD theory, the point of which was the role of self-quenching conditioned by the presence of dimers in solution. Still a further generalization of the mentioned theory, in which both dimer and monomer quenching was taken into account, gave better agreement with experiment chiefly in the case of systems of low dimerization constant value. In the case of systems with high value of  $\mathcal{K}_\gamma$ , this agreement was slightly improved. It is to be expected that taking monomer self-quenching into account in the actually discussed FÖRSTER-ORE theory could bring an analogous improvement of the agreement between theory and experiment in the case of the results presented in Fig. 2.

The dashed curves determined by expr. (12) in which  $\eta/\eta_0$  was replaced by formula (11) lie distinctly above the experimental points in the range of highest

<sup>4</sup> Because  $\mathcal{K}_\gamma \sim \eta_0^{-1/2}$  and  $c_0 \sim \eta_0^{-1/2}$ ; comp. also footnote 1 in [20].

<sup>5</sup> Concrete values of  $\alpha_0$  to which the  $c_0^{***}$  listed in column 13 correspond have been taken from the Refs. quoted in Table I.

Table I

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
System	$\eta'$	$\eta_0$	$C_0'$	$C_0''$	$\times$ theor	K	Ref	$\eta_0$	$C_0'$	$C_0''$	$C_0'''$	$C_0''''$	$K_\gamma$	$\times_{exp}^*$	$\times_{exp}'''$	$\times_{exp}''''$
	P	—	$10^{-3}$ M/L		—	l/M		—	$10^{-3}$ M/L							
I. Na-FL/GW — Na-fluorescein in glycerin-water solutions	3.3	0.88	4.67	3.28	1.426	0.065	[19]	1.4	3.704	0.13	1.25	3.31	0.0004	28.49	2.963	1.410
II. Na-FL/GW — Na-fluorescein in glycerin-water solutions	0.43	0.6	6.06	4.25	1.427	0.54	[19]	0.83	5.15	0.071	2.33	4.80	0.005	72.577	2.211	1.262
III. Ac/GM — Acri- flavine in glycerin- methanol solutions	3.9	0.417	10.1	10.1	1	12	[20]	0.66	8.02	4.8	10.32	13.28	0.14	1.67	0.777	0.760
IV. R6G/GW — Rhodamin 6 G in glycerin-water solutions	5.3	0.6	3.47	2.68	1.29	11.1	[18]	0.82	2.965	0.886	1.99	2.94	0.06	2.63	1.49	1.180
V. R6G/GE — Rhodamin 6 G in glycerin-ethanol solutions	5.85	0.7	3.94	2.67	1.475	1	[29]	2.21	2.22	0.34	1.513	2.66	0.004	6.54	1.467	1.479
VI. RB/GW — Rhodamin B in glycerin-water solutions	7.4	0.7	2.83	2.22	1.276	0.23	[30]	1.52	1.93	0.06	0.47	2.10	0.0007	32.17	4.106	1.349

concentrations. In this case, taking into account the monomer quenching would even more increase the divergence between theory and experiment.

An approximate description of the experimental results can thus be obtained by applying expr. (5) in PERRIN's formula (2) and taking into account the energy transfer from  $D^*$  to  $D_{II}$  in one step<sup>6</sup>.

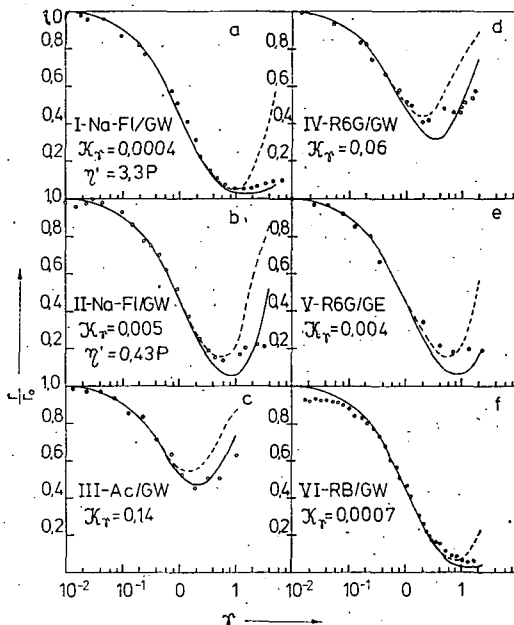


Fig. 2. Comparison of the generalized FÖRSTER-ORE theory with experimental results; ----- and ----- theoretical curves determined by equations (12) and (2), (4), (5) respectively; o are experimental points Fig. a and b: Na-fluorescein in glycerin-water solutions of 3,3 P and 0,45 P viscosities, respectively; Fig. c: acriflavine in glycerin-methanol solutions; Fig. d: rhodamin 6 G in glycerin-water solutions; Fig. e rhodamin 6 G in glycerin-ethanol solutions; Fig. f: rhodamin B in glycerin-water solutions.

This is so because the migration of excitation energy in a system of molecules  $D$  has already been taken into account in the expression for  $r'/r_0$  appearing in (2). We should state that the generalization of the FÖRSTER-ORE PLCD theory for the case of quencing by dimers allows to apply this theory to a wider range of concentrations, first of all to systems of low dimerization constant value. In strongly dimerizing systems and in ranges of high concentrations this theory does not fully describe the experimental results (there is only a qualitative agreement as to the repolarization effect). The reasons of the mentioned disagreement can be numerous; among others, the assumption (1) as to parallel lifetime and quantum yield changes

<sup>6</sup> Molecules  $D^*$  can be excited both by light absorption and as a result of excitation energy transfer.

is not generally valid, neither is the assumption of the independence of depolarization and self-quenching process. Let us add that the PLCD theory worked out by one of the authors [31] allows to describe correctly all the experimental results quoted in the present work in the whole range of concentrations [18–20, 29–31].

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#### КОНЦЕНТРАЦИОННАЯ ДЕПОЛЯРИЗАЦИЯ ПОСРЕДСТВОМ ПЕРЕНОСА ЭНЕРГИИ. УЧЕТ САМОТУШЕНИЯ

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Проведено обобщение теории концентрационной деполаризации фотоллюминесценции, разработанной Ферстером и Оре, на случай концентрационного тушения неллюминесцирующими димерами. Полученное выражение для анизотропии эмиссии сравнено с экспериментальными результатами. Установлено, что теория Ферстера–Оре может быть применена для более широкой области концентрации, особенно в случае систем с низким значением константы димеризации.