ON CONCENTRATIONAL DEPOLARIZATION OF PHOTOLUMINESCE IN SOLUTIONS AT DIFFERENT WAVELENGTHS OF EXCITING LIGHT

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Measurements of the concentrational dependence of photoluminescence emission anisotropy (EA) in glycerol—methanol solutions of acriflavine (system I) and glycerol—water solutions of rhodamin 6 G (system II), at excitation by v_{0-0} as well as $v > v_{0-0}$ frequencies, have been carried out.

At excitation by v_{0-0} frequencies in the range of high concentrations, repolarization effect and good agreement of experimental results with theory has been found.

However, at excitation by $v > v_{0-0}$ frequencies, the relative values of EA, $\left(\dfrac{r}{r_0}\right)_v$, appeared to be remarkably lower than the values of EA, $\left(\dfrac{r}{r_0}\right)_{v_{0-0}}$ at the excitation by v_{0-0} frequency, particularly in the range of high concentrations. In this case repolarization effect for system II was not observed.

Introduction

Concentrational depolarization of photoluminescence (CDPL) in isotropic solutions has been a subject of continous and intensive theoretical and experimental investigations [1—8]. Recently [9, 10] some investigations of CDPL in a wide range of concentration have been carried out. In the range of highest concentrations, a repolarization effect has been found in accordance with the prediction of the CDPL theory taking into account excitation energy remigration and concentrational quenching by dimers [6, 11].

This result was obtained at the excitation of luminescence by light of v_{0-0} frequency, corresponding to 0—0 transition, not disturbing the thermal equilibrium of active molecules in the medium.

At the excitation with $v > v_{0-0}$ frequency, however, there is a possible energy transfer before thermal relaxation in excited state occurs, if the interaction between D^* and D molecules is sufficiently strong [5, 12—18].

It can be expected that energy transfer of this kind will occur particularly in the range of high concentrations of active molecules in solutions.

In this work we present the results of investigations concerning the CDPL phenomenon in the range of high concentrations at v_{0-0} and $v > v_{0-0}$ frequencies of exciting light.

Experimental Part

The object of the investigations were glycerol—alcohol solutions of acriflavine ($C_{14}H_{14}N_3Cl$; m.w. $= 259,75$; system I) and glycerol—water solutions of rhodamine 6G ($C_{26}H_{27}O_3N_2Cl$; m.w. $= 450,98$; system II). In the case of system I the solvent was glycerol containing 5% (w/w) methanol and in the case of system II glycerol containing 10% (w/w) water with an addition of $3.4 \cdot 10^{-4}$ M/l HCl. All the dye-stuffs were purified in an ordinary way by recrystallization and the purity degree was checked spectroscopically. Glycerol ("Strem", Poland) and methanol (p.a. "Oświęcim", Poland) were applied without any further purification. For measuring the emission anisotropy EA, the quantum yield η/η_0 as well as fluorescence spectra, the methods and measuring apparatus described in [10] were applied.

In the case of EA measurements luminescence was excited by a high pressure mercury lamp DRSz-250, applying filters listed in Table I, which also gives those used in the observation.

Table I

Filters applied at the measurements of emission anisotropy

	Excitation	Observation
Acriflavine in glycerol—methanol solutions	SiF 436 Hg	OG-5 ($\lambda > 530$ nm)
	IF 475	OG-5
Rhodamine 6G in glycerol—water solutions	SiF 436 Hg	OG-3 ($\lambda > 570$ nm)
	IF 550	IF 575

For quantum yield measurements luminescence was excited by the light of an incandescent lamp. Instead of filters, monochromators were used for the excitation as well as for the observation.

In working out the results of the measurements, in the case of EA, corrections for secondary fluorescence and, in the case of η/η_0, for secondary fluorescence and anisotropy of the spatial distribution of fluorescence, were taken into account in the way described in [19—21].

The absorption spectra were measured with a VSU 2—P spectrophotometer.

Results and discussion

In Fig. 1 absorption and fluorescence spectra of the solutions are presented. In the case of acriflavine solutions the absorption and fluorescence spectra turned out to be practically independent of the concentration, contrary to the rhodamine 6G solutions which show remarkable changes in the absorption spectra.
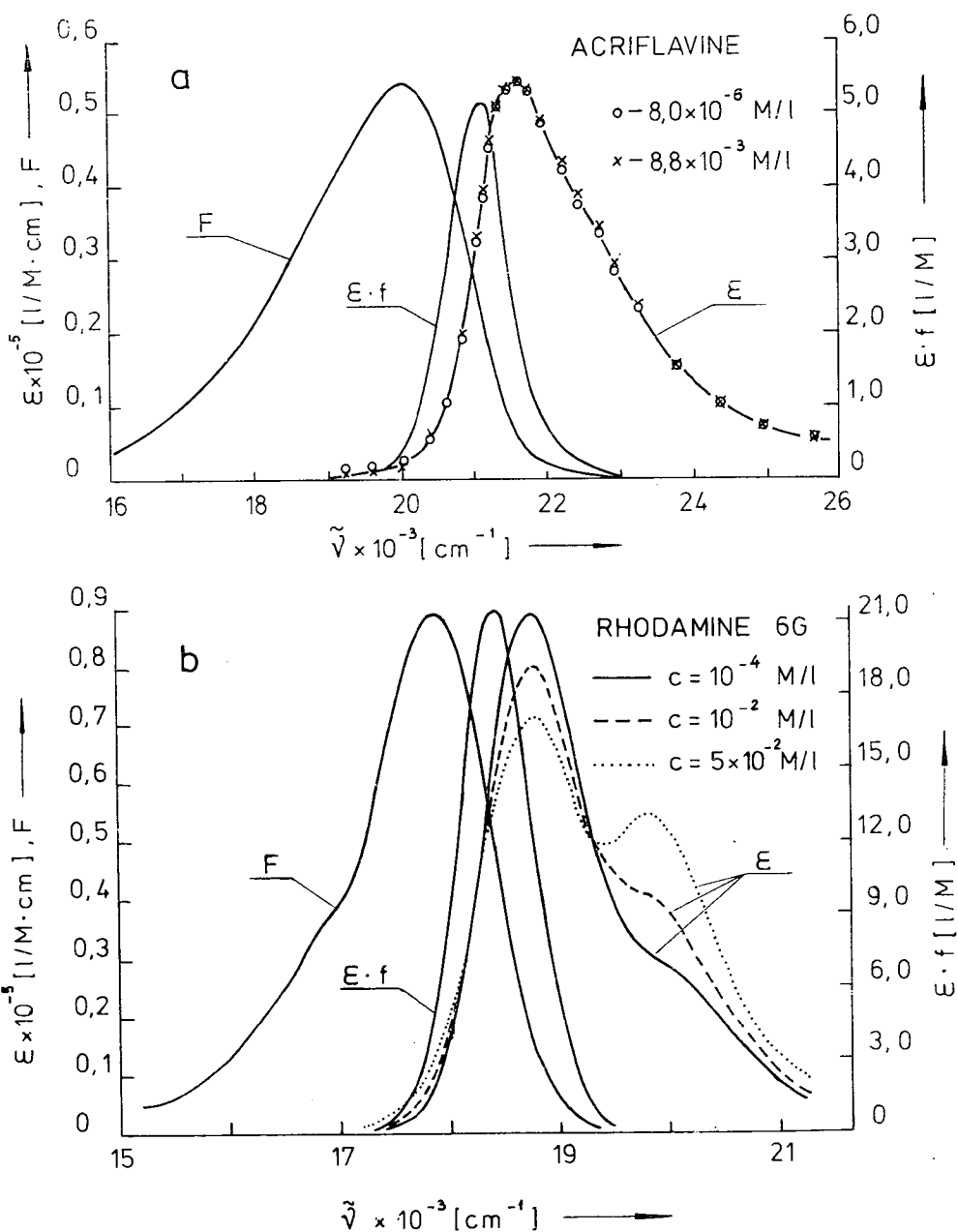
Fig. 1. Electron absorption spectra (ε), fluorescence quantum spectra (F) of glycerol—methanol solutions of acriflavine (a) and glycerol—water solutions of rhodamin 6G (b). Fluorescence spectra corrected for reabsorption and spectral sensitivity of the photomultiplier

In the case of rhodamin 6G solutions two isosbestic points at frequencies 18 200 cm^{-1} and 19 333 cm^{-1} are visible (Fig. 1b). On the base of our assumption, only two kinds of molecules, monomers and dimers appear in rhodamin 6G solutions in the concentration range investigated. Though the absorption spectra of acriflavine solutions do not exhibit practically any concentrational changes (comp. Fig. 1a) still the existence of monomers and dimers in them has been accepted. This assumption is necessary to explain the repolarization effect and the decrease of quantum yield observed in the range of high concentrations (comp. Fig. 2a). This assumption is justified because it has been pointed out before that proflavine as well as acriflavine form non-fluorescent dimers in solutions [22—24]. Let us add that the absence of concentrational dependence of absorption spectra, regarded by some authors [25, 26] as a criterion of the lack of any associates in solution, is not in general valid [27].

True enough the molecular exciton. theory [28, 29] predicts a split of the excited levels of interacting molecules in the dimer which leads to the appearing of
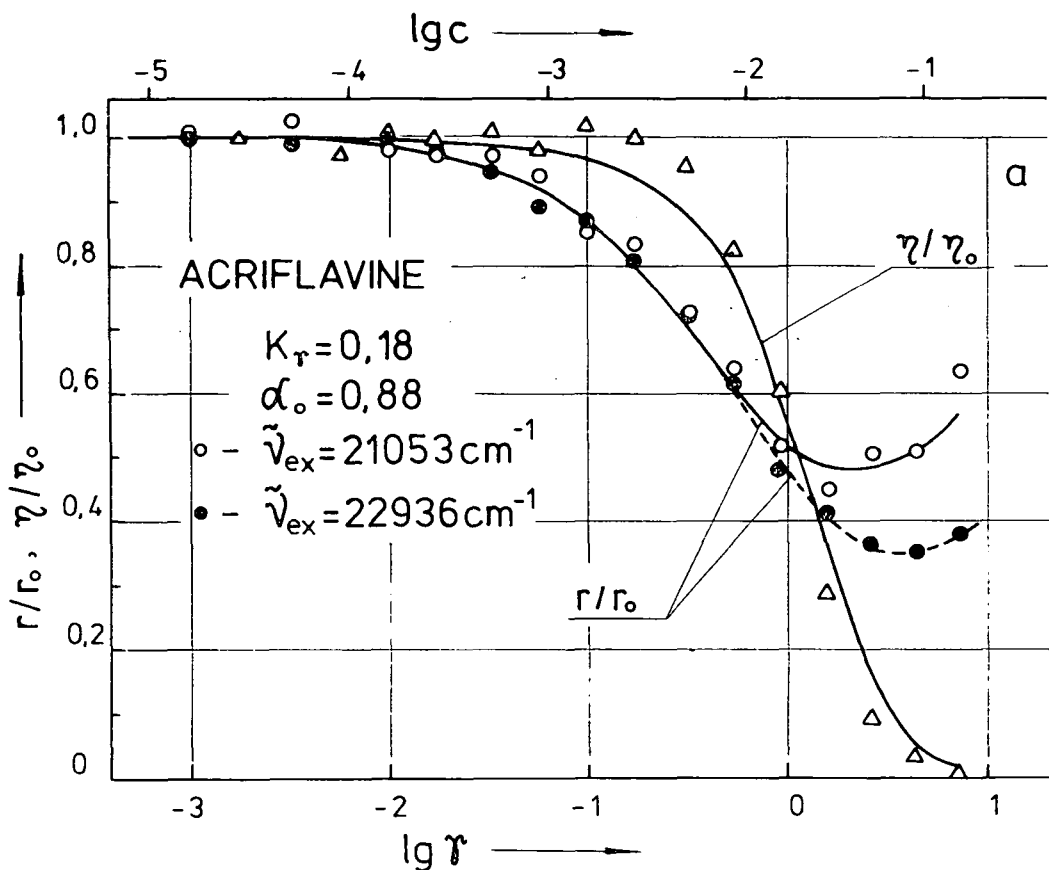

Fig. 2a

two bands in the absorption spectrum of the dimer. Still, depending on the distance and mutual position of monomer units in the dimer, the absorption spectra of the monomers ε' and dimers ε'' can practically overlap. In this case the absorption spectra of the solution do not change with concentration. In Fig. 2a, b the concentrational dependences of photoluminescence emission anisotropy at excitation frequencies $\nu \cong \nu_{0-0}$ (empty circles) and $\nu > \nu_{0-0}$ (full circles) are presented. At excitation frequencies $\nu \cong \nu_{0-0}$, when the thermal equilibrium between D^* molecules and the medium is not disturbed, the depolarization in both systems investigated is smaller than that at the excitation frequencies $\nu > \nu_{0-0}$. The difference $\left(\dfrac{r}{r_0}\right)_{\nu_{0-0}} - \left(\dfrac{r}{r_0}\right)_{\nu}$ of
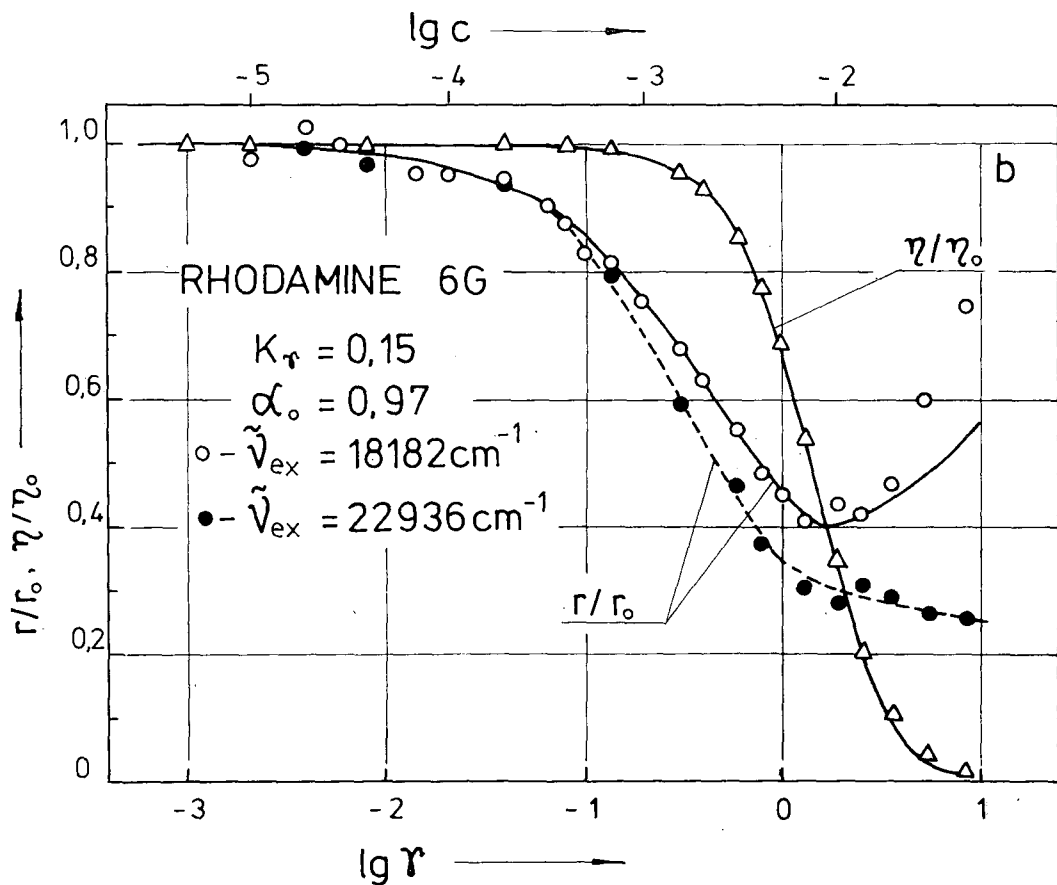

Fig. 2a, b. Concentration dependence of emission anisotropy $\dfrac{r}{r_0}$ and quantum yield η/η_0 of fluorescence of glycerol—methanol solutions of acriflavine (a) and glycerol—water solutions of rhodamin 6G (b). Solid lines: theoretical curves of $\dfrac{r}{r_0}$ and η/η_0, determined by Eqs. (1) and (2); $\bigcirc$, $\bullet$ and $\triangle$: experimental points

the EA values at the excitation frequencies v_{0-0} and v, increases with the dye concentration of the solution. At excitation frequencies v_{0-0} a repolarization effect connected with a strong concentrational quenching is visible.

This is proved by the course of the quantum yields curves as a function of dye molecule concentration (comp. Fig. 2a,b).

Concentrational dependences of emission anisotropy $\dfrac{r}{r_0}$ and quantum yield $\dfrac{\eta}{\eta_0}$ at the excitation frequency v_{0-0} can be described by formula (6) in [30], *i.e.*

$$\frac{r}{r_0} = (1 - \Phi)\left[1 + \frac{1}{2}\frac{\Phi^2}{1 - \frac{3}{4}\Phi^2}\right], \tag{1}$$

where

$$\frac{\eta}{\eta_0} = \frac{1-f}{1-\Phi}, \tag{2}$$

$$\Phi = \alpha_0 \alpha f, \tag{3}$$

$$\alpha = \frac{\gamma_D}{\gamma_D + \gamma_{D_{II}}}, \tag{4}$$

$$f = \sqrt{\pi}\,\gamma\,\exp(\gamma^2)[1 - \mathrm{erf}(\gamma)], \tag{5}$$

$$\gamma = \gamma_D + \gamma_{D_{II}} = \frac{\sqrt{\pi}}{2}\left(\frac{c'}{c_0'} + \frac{c''}{c_0''}\right). \tag{6}$$

Here c' and c'' denote monomer and dimer concentrations, c_0' and c_0''-critical concentrations for excitation energy transfer to monomers D and dimers D_{II}, α_0 is the probability of the non-occurence of excitation energy degradation during its transfer between monomers.

In Fig. 2a,b the solid lines $\dfrac{r}{r_0}$ and $\dfrac{\eta}{\eta_0}$ present the theoretical curves determined by expressions (1) and (2), plotted for the parameter values listed in Table II. Beside critical concentrations c_0' and c_0'', the corresponding critical distances R_0' and R_0'' are also given in the table [comp. Eq. (9)].

The values of the parameter $K_\gamma = \gamma_{D_{II}}/\gamma_D^2$ and the critical concentration c_0 can be found from the relations[1]

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[1] Relations (6) and (7) in this and in earlier papers [6, 9, 10, 24, 30] had a somewhat different form, namely instead of factor π they contained the factor $\pi\eta_0$. The presence of η_0 beside π was a result of excluding the factor $\eta_0^{1/2}$ from the expressions of type (8) for c_0' and c_0''. Then $\eta_0 = 1$ should have been put in expr. (8). In the papers quoted above, in spite of the explicit η_0 appearing in the expressions for γ and K_γ, $\eta_0 \neq 1$ was accepted by mistake in, expr. (8). As a result this led to the conclusion that $\gamma \sim \eta_0$ and $K_\gamma \sim \eta_0^{-1}$, whereas from relation (6), (7) and (8) it is clear that $\gamma \sim \eta_0^{1/2}$ and $K\gamma \sim \eta_0^{1/2}$. Let us add that all the conclusions and diagrams quoted in the above papers remain unchanged, only the formerly accepted value of η_0 should be replaced by η_0^2.

$$K_\gamma = \frac{2Kc_0'^2}{\sqrt{\pi}\,c_0''}, \tag{7}$$

$$c_0' = 5.18 \cdot 10^{-10} \frac{n^2 \overline{\tilde{v}'^2}}{(\bar{\varepsilon}'\eta_0)^{1/2}} \quad [\text{M/l}], \tag{8}$$

where $K = c''/c'^2$ is the dimerization constant, n the refractive index of the medium, $\tilde{v}'$ the mean value of the wave number in the overlapping region of absorption spetrum ε' of the monomer and the fluorescence spectrum F, $\bar{\varepsilon}'$ is the mean value of the molar decimal extinction coefficient in the overlapping region of ε' and F spectra, at which

$$\varepsilon' = \int_0^\infty \varepsilon'(v)F(v)dv \quad [\text{l/Mcm}], \quad \int F(v)dv = 1.$$

K_y and c_0'' can be determined directly on the basis of relations (7) and (8) in the case when the absorption spectra of the investigated systems exhibit sufficiently big concentrational changes. Then the absorption spectrum of dimers ε'' as well as the dimerization constant K can be found by means of the method worked out by FÖRSTER [31] and LEVSHIN [32].

Table II

Experimental data for glycerol—alcohol (GA) solutions of acriflavine and glycerol—water solutions (GW) of rhodamine 6G

System	1	2	3	4	5	6	7	8	9	10
	η	I	n	$\sqrt{\overline{r^2}}$ a)	$\bar{\varepsilon}'$	$\bar{\varepsilon}''$	$\tilde{v}_{0-0}$	$\tilde{v}'$	$\tilde{v}''$	η_0
	P	K	—	Å	10^4 1/Mcm		cm^{-1}	cm^{-1}	cm^{-1}	
Acriflavine in GA solutions	3,9	293.	1,460	1,45	0,556	0,556	20 934	21 200	21 200	0,417
Rhodamin 6G in GW solutions	1,7	293	1,456	1,02	1,68	0,332	18 360	18 389	17 953	0,435

System	11	12	13	14	15	16	17	18		19
	c_0'	c_0''	R_0'	R_0''	K	K_γ	α_0	r_0	b)	P_0
	10^{-3} M/l		Å		l/M	—	—	—		%
Acriflavine in GA solutions	10,1	10,1	33,6	33,6	12,0	0,18	0,88	0,3374 0,3044	c) e)	43,3 39,6
Rhodamine 6G in GW solutions	4,34	2,94	45,0	51,2	20,7	0,15	0,97	0,360 0,271	d) e)	45,8 35,8

a) mean displacement of luminescent molecule in Brownian diffusive movement during its mean lifetime in excited state.

b) r_0: emission anisotropy corresponding to the ground polarization degree P_0.

c) $\tilde{v}_{ex} = 21053$ cm^{-1}, d) $\tilde{v}_{ex} = 18182$ cm^{-1}, e) $\tilde{v}_{ex} = 22936$ cm^{-1}.

Still, in the case of GA solutions of acriflavine, a method of this kind could not be applied. Values K_y and α_0 for each of the systems investigated have been found by choosing from the family of theoretical curves r/r_0 and η/η_0 those which give the best agreement with experimental results.[2] The choice of K_y and α_0 is not arbitrary, because the fitting of experimental results to theoretical curves is possible only for a definite pair of parameter values K_y and α_0, as proved in [10, 33]. It can be seen from Fig. 2a,b that at excitation frequencies $\nu \cong \nu_{0-0}$ the agreement of experimental results with the CDPL theory is quite satisfactory, still, at excitation frequencies $\nu > \nu_{0-0}$ the experimental points remarkably deviate from the theoretical curves. It should be emphasized that in the case of the investigated systems the course of concentrational changes of the relative quantum yield does not depend on the frequency of exciting light ($\nu > \nu_{0-0}$). Investigations concerning CDPL of glycerol—methanol solutions of tripaflavine and rhodamine B with excitation by light of different frequencies ν have recently been carried out by BAUER and CHEREK [18]. These authors have stated a remarkable decrease of the value of $\left(\dfrac{r}{r_0}\right)_\nu$ at excitation frequency $\nu > \nu_{0-0}$ in comparison with values $\left(\dfrac{r}{r_0}\right)_{\nu_{0-0}}$ at the excitation frequency ν_{0-0}. They have observed a noticable effect $\left[\left(\dfrac{r}{r_0}\right)_{\nu_{0-0}} - \left(\dfrac{r}{r_0}\right)_\nu \sim 0.1\right]$ already in the range of moderate concentrations ($10^{-3} \div 5 \cdot 10^{-3}$ M). In the case of the systems investigated, only rhodamine 6G shows a comparable effect in this range of concentration (comp. Fig. 2b). The greatest effect could be expected in the case of highest concentrations when the value of rate constant k_{D^*D} for nonradiative excitation energy transfer from D^* to D, is comparable with the rate constant for vibrational relaxation[3]. Experiment has fully confirmed this point of view (comp. Fig. 2). BAUER and CHEREK have pointed out that the course of concentrational changes of EA at the excitation frequencies $\nu > \nu_{0-0}$ can be described in the range of low concentrations by the CDPL theory developed recently by JABŁOŃSKI [7]. The agreement of theory with experiment has been obtained there by accepting a bigger value for k_{D^*D}, which is equivalent to accepting a bigger value for the critical distance R_0 (smaller value of critical concentration c_0). However in the cases where repolarization effect appears, this kind of modifying the CDPL theory is not sufficient for a correct description of experimental results r/r_0 at excitation frequencies $\nu > \nu_{0-0}$, because this kind of modification merely leads to a shift of the experimental points along the y axis (comp. Fig. 2). On account of this explanation, the increasing effect of CDPL at excitation frequencies $\nu > \nu_{0-0}$, only by an increase of k_{D^*D} does not seem to be sufficient.

It could be supposed that an increase of the k_{D^*D} value would also influence the

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[2] To optimalize the choice of K_y and α_0 a special method described in Ref. [34] was applied.
[3] In the case when energy transfer is conditioned by dipole—dipole interaction, the rate constant for this process is [35]

$$k_{D^*D} = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6, \tag{9}$$

where τ_D is the mean lifetime of the donor molecule in excited state when $c \to 0$, R the distance between D^* and D molecules, R_0 critical distance.

effectiveness of nonradiative energy transfer from monomers D to dimers D_{II}. It turns out, however, that the courses of concentrational changes of η/η_0 at the excitation frequencies ν_{0-0} and $\nu > \nu_{0-0}$ are the same. Maybe the observed effect of the influence of the frequency of exciting light on the course of concentrational dependence of $\dfrac{r}{r_0}$ is connected with the decrease of the probability of the remigration of excitation energy to molecules D_0, primary absorbers of exciting light.

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<center>References</center>

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О КОНЦЕНТРАЦИОННОЙ ДЕПОЛЯРИЗАЦИИ ФОТОЛЮМИНЕСЦЕНЦИИ В РАСТВОРАХ ПРИ РАЗНЫХ ДЛИНАХ ВОЛНЫ ВОЗБУЖДАЮЩЕГО СВЕТА

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Произведены измерения концентрационной зависимости анизотропии эмиссии (АЭ) фотолюминесценции глицериново—спиртовых растворов акрифлавина (система 1), а также глицериново—водных растворов родамина 6Ж (система II) при возбуждении частотами v_{0-0} и частотами $v > v_{0-0}$. При возбуждении частотами v_{0-0} в области высоких концентраций обнаружен эффект реполяризации. Констатировано хорошее согласие экспериментальных результатов с теорией. При возбуждении же частотами $v > v_{0-0}$ относительные значения АЭ, $\left(\dfrac{r}{r_0}\right)_v$, оказались значительно низшими, чем значения АЭ, $\left(\dfrac{r}{r_0}\right)_{v_{0-0}}$, при возбуждении частотами v_{0-0}, особенно в области высоких концентраций. В этом случае эффект реполяризации для системы II не наблюдается.