ANTI-STOKES FLUORESCENCE IN RHODAMINE SOLUTIONS

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Measurements of the photoluminescence quantum yield of rhodamine B and rhodamine 6G in glycerol-water solutions versus dye stuff concentration at excitation in Stokes, as well as in anti-Stokes region were carried out. In the range of high concentrations a smaller drop of the relative quantum yield of fluorescence was stated in case of anti-Stokes excitation than in case of Stokes excitation. We are explaining the observed effect by a decrease in the absolute quantum yield in anti-Stokes region. It was proven that the hampering of the concentration quenching process in case of anti-Stokes excitation could not be explained by the presence of dimers in the solution.

Introductory remarks

According to the Vavilov law [1], the photoluminescence (PL) quantum yield of molecules is independent of the wavelength of the exciting light in the Stokes region of the absorption spectrum and it falls rapidly in the anti-Stokes region. This law has been confirmed experimentally for a number of dye solutions [2, 3].

Later on, BORISEVITCH at al. [4], as well as ERIKSON [5], did not find this kind of quantum-yield drop and they explained the earlier results of other authors* the presence of dimers and impurities in the investigated solutions. At the same time, the works of the physicists of the Hungarian School [7—9] proved quantum-yield drop in all the investigated cases. After all, despite the great number of works carried out, the problem of PL quantum-yield drop in the anti-Stokes region has not been decided.

In the present work, we are presenting the experimental results concerning the PL concentrational quenching conditioned by a non-radiative energy transfer from excited monomers to non-luminescent dimers at fluorescence excitation in the anti-Stokes region. Investigations of this type have not been carried out so far.** We shall prove below that PL resonance quenching at the anti-Stokes excitation is closely connected with the above-mentioned problem of quantum-yield drop.

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* Jabłoński [6] was the first to put forward the hypothesis that the quantum-yield drop could be explained by the non-active absorption of exciting light by dimers whose absorption coefficient in the anti-Stokes region usually surpasses remarkably the value of the absorption coefficient.

** A communication as to the preliminary results we presented formerly in ref. [10].

Experimental

The subjects of the investigations were glycerol-water solutions of rhodamine B, $C_{28}H_{31}ClN_2O_3$, M. W. 479,03 (system I) and glycerol-water solutions of rhodamine 6G, $C_{26}H_{27}O_3Na_2Cl$, M. W. 450,98 (system II).

Rhodamine B produced by GMBH & Co (Schuchardt), as well as rhodamine 6G produced by BDH, were purified additionally by a manifold crystalization from ethyl alcohol and evaporation under vacuum. Analitically pure glycerol produced by Polish "Strem" was applied without any additional purification.

The PL quantum yield as well as the fluorescence spectra were measured at a frontal excitation of the samples with the device described formerly [11]. In order to find the relative quantum yield η/η_0 the Förster method was applied [12], modified [13] for the case of systems in which the concentration changes of the absoprtion coefficient occur in the range of excitation and observation.

When working out the results of the η/η_0 measurements, we took into consideration some corrections for the secondary fluorescence and for the anisotropy of the spatial distribution of the emitted luminescence in the way described in refs. [14, 15]. When considering the PL excitation in the anti-Stokes region, we should pay a particular attention to the non-active absorption of the exciting light by dimers (*cp*. remarks in ref. [1]). Values η/η_0 corrected with regard to the non-active absorption were calculated on the basis of the relation:

$$\frac{\eta}{\eta_0} = \left(\frac{\eta}{\eta_0}\right)'\left[1 + \frac{1-x}{2x}\left(\frac{\varepsilon''}{\varepsilon'}\right)_{v_{ex}}\right], \tag{1}$$

where η/η_0 denotes the relative PL quantum yield not corrected for non-active absorbtion, x a part of the total number of active molecules in the form of monomers, ε'' and ε' absorption coefficients of dimers and monomers, respectively, v_{ex} frequency of exciting light. The correction factor represented by the expression in brackets may have a noticable value in the case of small x and large ratio $\left(\frac{\varepsilon''}{\varepsilon'}\right)_{v_{ex}}$. Small x-es are characteristic of the range of large concentrations and of systems with high value of dimerization constant $K = \dfrac{C''}{C'^2}$. (C' and C'' — concentrations of monomer sand dimers). The values of dimerization constant K (and thus also of x) were found on the basis of the method worked out by FÖRSTER [16] and LEVSHIN [17] applying the concentration dependence of the absorption spectra. In order to find the value of K, as well as the spectra of monomers $\varepsilon'(v)$ and dimers $\varepsilon'(v)$, a special program for computer was prepared [18]. A high value of ratio $\left(\frac{\varepsilon''}{\varepsilon'}\right)_{v_{ex}}$ may be at luminescence excitation in the anti-Stokes region where $\varepsilon''(v) > \varepsilon'(v)$. On account of the very low values of the absorption coefficient of the solution $\varepsilon(v) = x\varepsilon' + \dfrac{1-x}{2}\varepsilon''$ in region $v < v_{0-0}$ (v_{0-0} — frequency corresponding to transfer 0−0), measurements $\varepsilon(v)$ in this range of frequencies were carried out in appropriate thick cuvettes.

Conclusions and Discussion

In Fig. 1 the concentration changes of photoluminescence yield $(\eta/\eta_0)'$ of system RB/GW are presented for several frequencies of exciting light. It can be seen that, even when neglecting the correction for non-active absorption, the yield drop at the anti-Stokes excitation is smaller than at the excitation in the Stokes region (comp. curves $\times$ and $\triangledown$). In Fig. 2 the dependence of quantum yield η/η_0 (corrected for non-active bsorption) of the same system versus the reduced concentration γ can be seen.
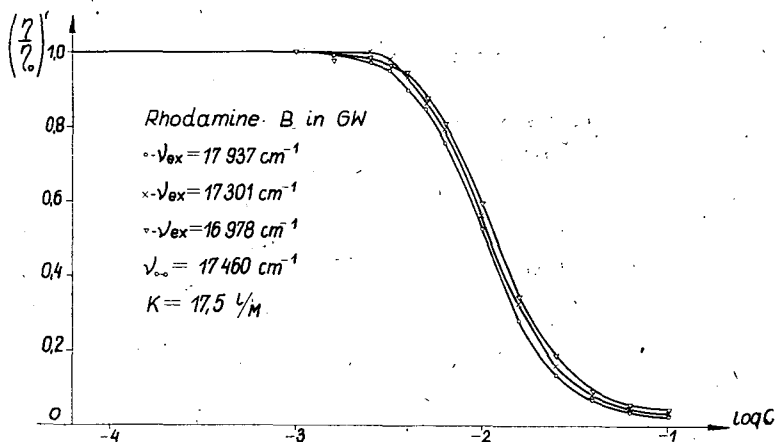

Fig. 1. Relative changes in the photoluminescence quantum yield (η/η_0) of rhodamine B in glicerolwater solutions versus concentration

Experimental points $\circ$, corresponding to PL excitation in the Stokes region are in good agreement with the theoretical curve 1 determined by formula [19]:

$$\frac{\eta}{\eta_0} = \frac{1-f(\gamma)}{1-\alpha\alpha_0 f(\gamma)} \tag{2}$$

where

$$f(\gamma) = \sqrt{\pi}\, \gamma \exp(\gamma^2)\left[1 - \frac{2}{\sqrt{\pi}} \int_0^\gamma \exp(-t^2)\,dt\right], \tag{3}$$

$$\gamma = \gamma_D + \gamma_{D\parallel} = \frac{\sqrt{\pi}}{2}\left(\frac{C'}{C_0'} + \frac{C''}{C_0''}\right), \quad \alpha = \frac{\gamma_0}{\gamma} \tag{4}$$

C_0' and C_0'' — critical concentration for excitation energy transfer to monomers D and dimers $D_{\parallel}$. α_0 — the probability that the excitation energy degradation does not occur at its transfer between monomers.
Critical concentrations were calculated on the basis of the relation:

$$C_0' = 5.18 \cdot 10^{-10} n^2 [I_v' \eta_0]^{-1/2}, \tag{5}$$

where

$$I_v' = \int_0^\infty F(v) \cdot \varepsilon'(v) \frac{dv}{v^4}, \tag{6}$$

n — is the refraction coefficient of the solution, $F(v)$ — the spectral distribution of fluorescence expressed in quantum number and normalized to unity, v — the wave number, $\varepsilon'(v)$ mole decimal extinction coefficient of monomers, η_0 — PL absolute yield of the solution at concentration $C = C' + 2C'' \rightarrow 0$. The numerical factor in (5) was obtained assuming $\overline{x^2} = \dfrac{2}{3}$ (cp. [20]), C_0' is expressed in M/l and I_v' in 1 cm³/M, when finding concentration C_0'', $\varepsilon'(v)$ in (6) should be replaced by $\varepsilon''(v)$.
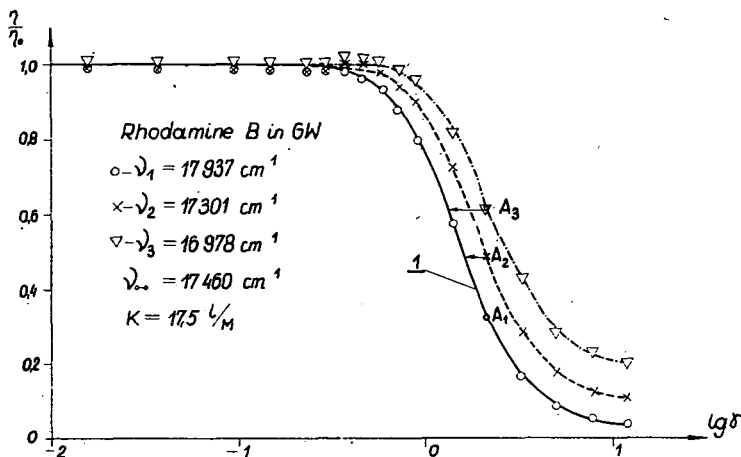

Fig 2. Relative changes in PL quantum yield of system RB/GW vs. reduced-concentration γ when taking into account the non-active absorption. 1 — theoretical curve determined by equation (2)

The values of critical concentrations as well as other parameters characterizing the investigated systems have been listed in Table *I*. The theoretical curve 1 has been plotted for a dimensionless dimerization constant $K_\gamma = \dfrac{\gamma_{D\parallel}}{\gamma_D^2} = \dfrac{2KC_0'^2}{\sqrt{\pi}\,C_0''} = 0.12$. At the excitation in the anti-Stokes region (by frequencies v_2 and v_3) values η/η_0 are remarkably higher as compared with values η/η_0 at the excitation by frequency v_1. In these cases the experimental points noticeably deviate from theoretical curve 1. In Fig. 2 the experimental values η/η_0 corresponding to the same fixed concentration γ and to different frequencies v_1, v_2 and v_3 of the exciting light have been denoted respectively by A_1, A_2 and A_3. In order to fit the experimental points to theoretical curve 1, we may accept much higher values of the critical concentration. And thus for point

* The reduced concentration γ, placed on the abscissa according to (4), depends on C_0' and C_0''. In order to estimate the changes in C_0', we have assumed $\gamma \approx \dfrac{\sqrt{\pi}}{2}\,\dfrac{C'}{C_0'}$, which in case of the investigated systems is a good approximation in the range of low and moderate concentrations.

A_2 concentration* C_0' should be higher than 29%, and for point A_3 than 63%. At that point, one can doubt whether the disagreement between the experimental points $\times$ and ∇ corresponding to the excitation by frequencies ν_2 and ν_3, is not caused by the long-wave shift of the fluorescence spectra occurring at the anti-Stokes excitation, because a shift of this kind causes a decrease in the overlap integral I_ν' and that evokes an increase in concentration C_0'. Thus neglecting the above mentioned effect means the acceptance of the reduced value C_0' and so that of the enlarged value γ, as well. The computations have proved, however, that the relative changes in the critical concentration $\dfrac{C_0'(\nu) - C_0'(\nu_{0-0})}{C_0'(\nu_{0-0})}$ amount only to 5.6% and 7.8% for $\nu = \nu_2$ and $\nu = \nu_3$, respectively, and they are very small as compared with changes C_0' necessary for the agreement of theory with values η/η_0 at the anti-Stokes excitation. In this situation we are to assume that the absolute yield η_0 is the quantity whose change at the anti-Stokes excitation can explain the experimental facts observed. Hence the conclusion that the absolute PL yield η_0 of system RB/GW drops at the anti-Stokes excitation.

Let us add that similar regularities as in case of system RB/GW we were also found [21] in case of rhodamine 6G in glycerin-water solutions — system R6G/GW, for which the concentrational changes η/η_0 are presented in Fig. 3. Theoretical curve 1 has been plotted for $K\gamma = 0.15$ & $\alpha_0 = 0.97$. It should be emphasized that, despite the fact that the absolute yield was not found experimentally, the conclusion as to the drop in yield η_0 is still valid. As mentioned at the beginning, some authors explain the observed yield-drop in the anti-Stokes region by non-active absorption of exciting light by dimers. Earlier we have proved on strongly dimerizing systems that the presence of dimers in a solution cannot explain the phenomenon in question. At the same time, a comparison of the courses of the concentration changes η/η_0 and (η/η_0) in Figs. 2 and 1 shows to what degree the neglect of the absorption of the exciting light by non-luminescent dimers can compensate the real stop of the yield drop at the anti-Stokes excitation.

Table I.

System	τ'	P	K (1/M)	Kᵥ* (—)	α₀ (—)	C₀' (10⁻³ M/l)	C₀'' (10⁻³ M/l)	ν₀₋₀	ν₁	ν₂	ν₃ (cm⁻¹)	$\left(\frac{\varepsilon''}{\varepsilon'}\right)_{\nu_1}$	$\left(\frac{\varepsilon''}{\varepsilon'}\right)_{\nu_2}$	$\left(\frac{\varepsilon''}{\varepsilon'}\right)_{\nu_3}$
Rhodamine in glycerol-water solution RB/GW	1.0	1.0	17.5	0.12	1.0	5.79	5.38	17 460	17 937	17 301	16 978	0.84	3.42	5.84
Rhodamine 6G in glycerol-water solution R6G/GW	1.7		20.7	0.15	0.97	4.34	2.94	18 360	18 802	19 342	17 331	2.50	1.00	18.60

Values K_γ, C_0 and C_0 corresponding to the absolute quantum yield equal to 0.120 and 0.435 for systems RB/GW and R6G/GW respectively.
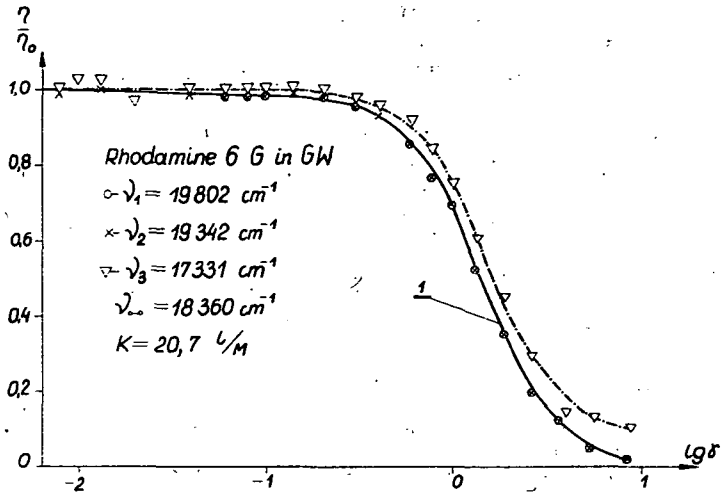
Fig 3. The same dependences as in Fig. 2 for system R6G/GW.

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АНТИСТОКСОВАЯ ФЛЮОРЕСЦЕНЦИЯ В РАСТВОРАХ РОДАМИНА

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Были проведены измерения квантового выхода фотолюминесценции родамина Б, а также родамина 6Ж в глицерино-водных растворах в зависимости от концентрации красителя при возбуждении в стоксовой и антистоксовой области.

В диапазоне высоких концентраций обнаружено меньшее падение относительного выхода флюоресценции при антистоксовом возбуждении чем в случае возбуждения в стоксовой области.

Наблюдаемый эффект объясняется уменьшением абсолютного квантового выхода в антистоксовой области. Доказано, что заторможение процесса концентрационного тушения в случае антистоксового возбуждения не может быть объяснено присутствием димеров в растворе.