Resonance Quenching of Anti-Stokes Luminescence from Rhodamine B in Water Solutions

C. Bojarski, A. Bujko, J. Dudkiewicz,
and R. Twardowski

Institute of Physics, Technical University, Gdańsk, Poland

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It was found that when exciting the photoluminescence of water solutions of rhodamin B in the anti-Stokes region the concentrational changes of quantum yield decrease with the decreasing frequency of the exciting light.

Measurements of the relative photoluminescence (PhL) quantum yield η/η_0 of rhodamine B in water solutions in a wide range of concentrations were carried out. Luminescence was excited by light with a frequency $\nu_{\mathrm{ex}} \approx \nu_{0-0}$ (ν_{0-0} frequency corresponding to $0-0$ transition) as well as in the anti-Stokes region ($\nu_{\mathrm{ex}} < \nu_{0-0}$).

To measure the quantum yield, the methods and devices described formerly[1] were applied. While working out the results a number of corrections for e. g. secondary fluorescence were taken into account in the manner described in Ref. [2]. Particular attention was paid to non-active exciting light absorption by non-luminescent dimers. The corrected values of the "true" quantum yield η/η_0 were obtained from the equation:

$$\frac{\eta}{\eta_0} = \left(\frac{\eta}{\eta_0}\right)' \left[1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)_{\nu_{\mathrm{ex}}} \mathcal{K} C x\right] \qquad (1)$$

where $(\eta/\eta_0)'$ = quantum yield not corrected for non-active absorption, $\varepsilon'', \varepsilon'$ = absorption coefficients of dimers and monomers respectively, $\mathcal{K}$ = dimerization constant, C = concentration of dyestuff molecules, x = fraction of dyestuff molecules in the form of monomers. The dimerization constant $\mathcal{K} = 1352$ l/M, was well as the dimer spectrum $\varepsilon''(\nu)$ and the monomer spectrum $\varepsilon'(\nu)$ were found on the basis of the contentrational dependence of the absorption spectra at temperature 293 K applying the Förster[3] and Levshin[4] methods. Hence the values $(\varepsilon''/\varepsilon')_{\nu_1} = 2.1$ and $(\varepsilon''/\varepsilon')_{\nu_2} = 6.8$ at the excitation frequencies $\nu_1 = 17301\ \mathrm{cm}^{-1}$ and $\nu_2 = 16978\ \mathrm{cm}^{-1}$ were obtained.

In Fig. 1 the concentrational dependence of the quantum yield at several frequencies of exciting light is presented. It can be seen that for the excitation values ν_{ex} in the anti-Stokes range, the yield concentrational changes η/η_0 are the smaller, the smaller th frequency of exciting light.

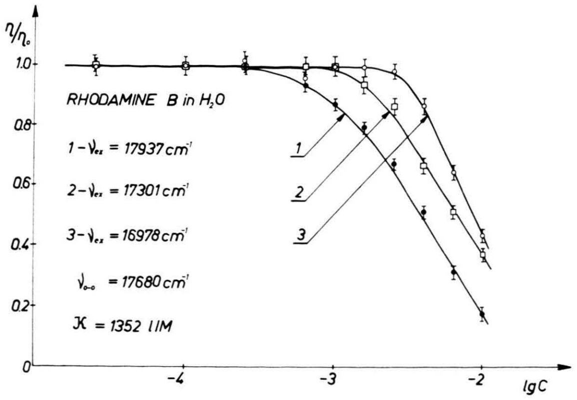

Fig. 1. Photoluminescence quantum yield of rhodamine B in water vs. log of dyestuff molecule concentration. ○, □, ● experimental points with errors.

Undoubtedly this effect, similar to the Weber effect[5–7] for the phenomenon of PhL concentrational depolarization, is connected with the decrease of the rate constants $k_{\mathrm{D}^* \to \mathrm{D}}$ and $k_{\mathrm{D}^* \to \mathrm{D}_{\|}}$ for non-radiative excitation energy transfer from primary absorbers of exciting light to non-excited active molecules in solution (monomers D and dimers $\mathrm{D}_{\|}$). Let us add that the effect observed cannot be explained by the increase in the critical concentration C_0 which results from the long wave shift of the fluorescence spectrum with anti-Stokes excitation, as the values C_0 at exciting light frequencies 17301 cm^{-1} and 16978 cm^{-1} are only slightly higher (5.2% and 5.3% respectively) than the value C_0 corresponding to Stokes's excitation.

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