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

(Z. Naturforsch. 30 a, 1091 [1975]; received May 6, 1975)

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

Measurements of the relative photoluminescence (PhL) quantum yield \( \frac{\eta}{\eta_0} \) of rhodamine B in water solutions in a wide range of concentrations were carried out. Luminescence was excited by light with a frequency \( v_{ex} \sim v_{0-0} \) (\( v_{0-0} \) frequency corresponding to 0–0 transition) as well as in the anti-Stokes region (\( v_{ex} < v_{0-0} \)).

To measure the quantum yield, the methods and devices described formerly 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 \( \frac{\eta}{\eta_0} \) were obtained from the equation:

\[
\frac{\eta}{\eta_0} = \left( \frac{\eta}{\eta_0} \right) ' \left[ 1 + \left( \frac{\varepsilon''}{\varepsilon'} \right) v_{ex} K C x \right]
\]

where \( \left( \frac{\eta}{\eta_0} \right) ' \) = quantum yield not corrected for non-active absorption, \( \varepsilon'' \), \( \varepsilon' \) = absorption coefficients of dimers and monomers respectively, \( K \) = dimerization constant, \( C \) = concentration of dyestuff molecules, \( x \) = fraction of dyestuff molecules in the form of monomers. The dimerization constant \( K = 1352 \text{ l/M} \), was well as the dimer spectrum \( \varepsilon''(r) \) and the monomer spectrum \( \varepsilon'(r) \) were found on the basis of the concentritional dependence of the absorption spectra at temperature 293 K applying the Förster 3 and Levshin 4 methods. Hence the values \( \left( \frac{\varepsilon''}{\varepsilon'} \right)_{v_1} = 2.1 \) and \( \left( \frac{\varepsilon''}{\varepsilon'} \right)_{v_2} = 6.8 \) at the excitation frequencies \( v_1 = 17301 \text{ cm}^{-1} \) and \( v_2 = 16978 \text{ cm}^{-1} \) were obtained.

In Fig. 1 the concentrical dependence of the quantum yield at several frequencies of exciting light is presented. It can be seen that for the excitation values \( v_{ex} \) in the anti-Stokes range, the yield concentrical changes \( \eta/\eta_0 \) are the smaller, the smaller the frequency of exciting light.

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

Undoubtedly this effect, similar to the Weber effect 5–7 for the phenomenon of PhL concentrical depolarization, is connected with the decrease of the rate constants \( k_{D^* \rightarrow D} \) and \( k_{D^* \rightarrow D||} \) for non-radiative excitation energy transfer from primary absorbers of exciting light to non-excited active molecules in solution (monomers D and dimers 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.

The authors express their gratitude to mgr eng. R. Bujko for his kind assistance.

This work was supported by the Polish Academy of Sciences under project PAN-3.2.07.

---

1 C. Bojarski and J. Dudkiewicz, Z. Naturforsch. 27 a, 1751 [1972].
3 Th. Förster and E. König, Z. Elektrochem. 61, 344 [1957].
4 V. L. Levshin and J. G. Baranova, Opt. Spektroskop. 6, 55 [1959].