Quenching of Photoluminescence of Solutions and Intermolecular Energy Transfer

C. BOJARSKI

Institute of Physics, Technical University, Gdańsk

and J. DOMSTA

Mathematical Institute of Polish Academy of Sciences, Gdańsk

(Z. Naturforsch. **25 a**, 1760 [1970]; received 8 May 1970)

The quenching of photoluminescence by foreign absorbing substances may be described by the following, well-known expression, obtained by FÖRSTER [1], as well as by other authors independently [2, 3]:

$$\frac{\eta}{\eta_0} = 1 - \sqrt{\pi}\,\gamma_A\, e^{\gamma_A^2}[1 - \mathrm{erf}\,(\gamma_A)]\,, \tag{1}$$

where

$$\gamma_A = \frac{\sqrt{\pi}}{2}\frac{C_A}{C_{OA}}\,, \tag{2}$$

η/η_0 denotes the relative yield of the donor's photoluminescence, C_A — the acceptor's concentration, and C_{OA} — the critical acceptor's concentration.

Expression (1) has been derived assuming a statistical distribution of the donor's (D) and acceptor's (A) molecules in the solution and an energy transfer from the excited molecule D* to A by the quantum mechanical resonance with FÖRSTER's [4] dependency of the rate constant for this process: $k_{DA} \sim R^{-6}$, where R is the distance between the interacting molecules D* and A.

In a more general theory of the influence of concentration on the photoluminescence of solutions, recently we have obtained the following expression for the relative quantum yield of the donor's photoluminescence:

$$\frac{\eta}{\eta_0} = \frac{1 - f(\gamma)}{1 - \alpha\, f(\gamma)} \tag{3}$$

where

$$f(\gamma) = \eta_T = \sqrt{\pi}\,\gamma\, e^{\gamma^2}[1 - \mathrm{erf}\,(\gamma)]\,, \tag{4}$$

$$\gamma = \gamma_D + \gamma_A = \frac{\sqrt{\pi}\,\eta_D}{2}\left(\frac{C_D}{C_{OD}} + \frac{C_A}{C_{OA}}\right) \tag{5}$$

and

$$\alpha = \gamma_D/(\gamma_D + \gamma_A)\,, \tag{6}$$

η_T is the quantum yield of the energy transfer from D* to A and D, and $\eta_D = \eta_0$ — the donor's absolute yield.

When

$$\gamma_D \ll \gamma_A \tag{7}$$

then the expression (3) turns into expression (1).

Figure 1 shows the dependence of η/η_0 on γ_A as determined by (3)–(6) for various values of $y = \gamma_D/\gamma_A$.

Expressions (1) and (3) have been obtained on the basis of similar assumptions. However, as opposed to the theories represented in [1–3], the nonradiative energy transfer from D* to D (not only to A) has been taken into account in obtaining (3).

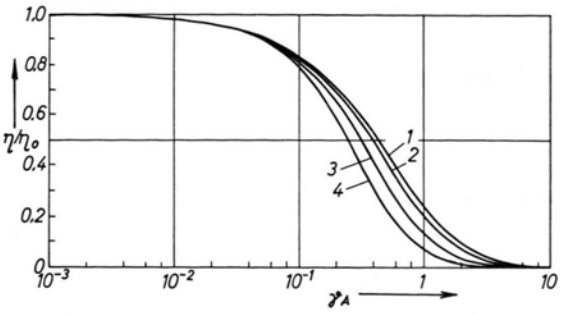

Fig. 1. The dependence of the relative quantum yield on γ_A; 1. $y=0$; 2. $y=\frac{1}{2}$; 3. $y=2$; 4. $y=5$.

It seems that the conditions for this transfer of excitation, consisting of several stages, may be satisfied in photosynthetic systems and also in chromoproteins [5, 6].

Also in the case of the quenching of photoluminescence by foreign absorbing substances the existence of this kind of energy transfer has been proved experimentally [7, 8].

Expression (3) may be applied for the description of luminescent systems, for which the condition (7) is not satisfied, and moreover especially for the description of the concentration quenching (self-quenching).

Assuming, that dimers (D_2) are responsible for the concentration quenching, then expression (3) may be applied for the description of the concentration dependence of yield if the quantity γ_A is substituted by the corresponding quantity γ_{D_2}. Generally $\gamma_D \gg \gamma_{D_2}$, though simultaneously with the increase of the concentration, γ_{D_2} increases too, but the inequality (7) is not satisfied, even for very great concentration.

The complete theory of the influence of the concentration on the photoluminescence of solutions, which includes the problem of depolarization is being prepared.

We should like to thank Professor I. ADAMCZEWSKI for his kind interest in this paper.

Reprints request to Doz. Dr. C. BOJARSKI, Institute of Physics, Technical University, ul. Majakowskiego 11/12, *Gdańsk*, Polen.

[1] TH. FÖRSTER, Z. Naturforsch. **4 a**, 321 [1949].
[2] M. D. GAŁANIN, Zh. Eksperim. Teor. Fiz. **28**, 485 [1955].
[3] A. M. SAMSON, Opt. i Spektrosk. **13**, 511 [1962].
[4] TH. FÖRSTER, Ann. Phys. Leipzig **2**, 55 [1948].
[5] TH. FÖRTSER, Radiation Research Supplement **2**, 326 [1960].
[6] L. N. M. DUYSENS, Progr. Biophys. Mol. Biol. **14**, 1 [1964].
[7] C. BOJARSKI, Acta Phys. Polon. **33**, 573 [1968].
[8] V. L. LEVSHIN and JU. I. GRINEVA, Acta Phys. Polon. **34**, 791 [1968].