# PHYSICS

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## Abstract

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PHYSICS

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# ON THE THEORY OF CONCENTRATION QUENCHING OF THE FLUORESCENCE OF SOLUTIONS

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Förster (2) pointed out that fluctuations in the distribution, in a solution, of the molecules of the fluorescing substance* must lead to the fact that concentration quenching of fluorescence for individual excited molecules will occur with different probabilities. A consequence of this, in turn, should be a nonexponential character of the fluorescence decay law of the quenched solution and the absence of proportionality between changes in the yield and changes in the fluorescence lifetime under concentration quenching—the yield should decrease with increasing concentration faster than the lifetime, which, as is known, agrees with experimental data.

In attempting to give a mathematical formulation of his hypothesis, Förster derived formulas for the decay law, the yield, and the fluorescence lifetime in quenched solutions for a fluctuational distribution of dissolved molecules. His reasoning, as we have shown (1), is not irreproachable. A rigorous solution of the problem is difficult; however, it is comparatively easy to calculate the quenching of fluorescence of an excited molecule by the nearest unexcited molecule, taking into account the fluctuational distribution of these molecules. The action of more distant quenching molecules will only reduce the fluctuation effects, i.e., diminish the distortions of the decay law and reduce the difference between changes in lifetime and changes in fluorescence yield, which are obtained if we restrict ourselves to taking into account quenching only by the first neighboring molecules. At the same time it should be noted that in the case of concentration quenching, for which it is usually assumed that the probability of quenching varies inversely as the sixth power of the distance between the excited and quenching molecules, the quenching will be determined mainly by the action of the first, nearest to the excited one, unexcited molecule of the given substance.

In order to obtain formulas for the decay law, the yield, and the fluorescence lifetime of quenched solutions when the action of the nearest unexcited molecules is taken into account, it is necessary to know the distribution law of the "nearest neighbor." A similar problem was first considered by P. Hertz (3). We reproduce his derivation as applied to our case.

Let $W(R)dR$ be the probability that the molecule nearest to some selected molecule of the same substance is located in the layer between $R$ and $R + dR$. Obviously, the desired probability, in turn, is equal to the product of two probabilities: the probability that some molecule is located in the layer from $R$ to $R + dR$, and the probability that in the volume from 0 to $R$ there is not a single molecule except the selected one, i.e.

$$W(R)\,dR = \left[1 - \int_0^R W(R)\,dR\right] 4\pi R^2 c\,dR \tag{1}$$

(where $c$ is the number of molecules per unit volume). Hence

$$W(R) = e^{-\frac{4}{3}\pi R^3 c} 4\pi R^2 c. \tag{2}$$

Knowing the distribution law for the nearest neighbor and assuming, in accordance with what was said above, that the probability of quenching by the first neighbor during the time from $t$ to $t + dt$ is equal to $\frac{p\,dt}{R^6}\rho(t)$ (where $p$ is a constant; $R$ is the distance from the excited molecule to the nearest neighbor and $t$ is the time from the moment of appearance of the excited molecule), we can write for the time variation of the probability $\rho(t)$ of retaining the excitation energy in the given molecule the equation

$$-\frac{d\rho(t)}{dt} = \left(\frac{1}{\tau_0} + \frac{p}{R^6}\right)\rho(t). \tag{3}$$

From (3) it is seen that $\rho(t)$ varies according to an exponential law.

Since we restrict ourselves to taking into account quenching only by the first nearest quencher molecule, the fluorescence decay for an entire group of excited molecules for which the distance to the nearest neighbors lies in the interval from $R$ to $R + dR$ will proceed according to the same law. The number of excited molecules belonging to this group will evidently be determined by the distribution law of first neighbors and is equal to $W(R)dR$. Hence, for the decay law of the entire ensemble of excited molecules $n(t)$, we have

$$n(t) = n_0 \int_0^\infty \exp\left\{-\left[\frac{1}{\tau_0} + \frac{p}{R^6}\right]t\right\} \exp\left[-\frac{4}{3}R^3 c\right] 4\pi R^2 c\,dR, \tag{4}$$

where $n_0$ is the number of excited molecules at the moment $t = 0$.

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* All of Förster' s reasoning, as well as that set forth below, applies to the case of viscous solutions, where the Brownian motion of the molecule during its stay in the excited state may be neglected.

Putting $R^3 = x$ and $\frac{4}{3}\pi c = a$, we obtain:

$$n(t) = a n_0 \int_0^\infty \exp\left[-\left(\frac{1}{\tau_0} + \frac{p}{x^2}\right) t\right] \exp[-ax]\, dx. \tag{5}$$

Knowing the fluorescence decay law, it is easy to write expressions for the relative yield and the fluorescence duration* in quenched solutions. We have:

$$\frac{B}{B_0} = \frac{a}{\tau_0} \int_0^\infty \int_0^\infty \exp\left[-\left(\frac{1}{\tau_0} + \frac{p}{x^2}\right) t\right] \exp[-ax]\, dx\, dt; \tag{6}$$

$$\tau = \frac{a}{\tau_0 B} \int_0^\infty \int_0^\infty t \exp\left[-\left(\frac{1}{\tau_0} + \frac{p}{x^2}\right) t\right] \exp[-ax]\, dx\, dt, \tag{7}$$

where $B, B_0$ are the yields; $\tau$ and $\tau_0$ are the fluorescence durations, respectively, in quenched and unquenched solutions.

It is not difficult to show that the double integrals appearing on the right-hand side of (9) and (10) are readily reduced to expressions containing tabulated integrals (5):

$$\begin{aligned} \frac{B}{B_0} &= a \int\limits_0^\infty e^{-ax}\, dx - ab^2 \int\limits_0^\infty \frac{e^{-ax}}{x^2 + b^2}\, dx \\ &= 1 - q\{\mathrm{ci}(q)\sin(p) - \mathrm{si}(q)\cos(q)\}^*, \end{aligned} \tag{8}$$

where

$$b = \sqrt{p\tau_0}, \qquad q = ab = \frac{4}{3}\pi c \sqrt{p\tau_0}; \tag{9}$$

$$\frac{\tau}{\tau_0} = \frac{1 - \frac{3}{2} q\{\mathrm{ci}(q)\sin(q) - \mathrm{si}(q)\cos(q)\} - \frac{q^2}{2}\{\mathrm{ci}(q)\cos(q) + \mathrm{si}(q)\sin(q)\}}{1 - q\{\mathrm{ci}(q)\sin(q) - \mathrm{si}(q)\cos(q)\}}. \tag{10}$$

Formulas (8) and (10) give the dependence of the yield and duration of fluorescence on a single variable $q$, which, according to (9), depends on the concentration of the dissolved substance and on two constants: the quenching probability $p$ and the fluorescence lifetime of the unquenched solution $\tau_0$.

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* The definition of the fluorescence duration for a nonexponential decay law is given in article (4).

Fig. 1

Figure 1: Fig. 1

Fig. 1

Figure 1 gives plots of the values of the functions $B/B_0$ and $\tau/\tau_0$ for various values of $q$. It is evident from the figure that, in agreement with experiment, the fluorescence lifetime changes, as the concentration of the fluorescing substance is increased, noticeably more slowly than the yield.

It is also of interest to note that in the region of very small concentrations of the fluorescing substance, i.e. for $q \ll 1$,

$$\frac{B}{B_0} = 1 - Q, \qquad \frac{\tau}{\tau_0} \approx 1 - \frac{1}{2}Q, \tag{11}$$

where $Q = q\{\mathrm{ci}(q)\sin(q) - \mathrm{si}(q)\cos(q)\}$.

Formulas (11) have the same form as the corresponding formulas of Förster—M. D. Galanin[6], and differ only in that $Q$ in these works represents another function of $c$, $\tau_0$, and $p$.

In conclusion it should be noted that in our treatment we not only did not take into account the action of more distant molecules, but also assumed a completely random distribution of all molecules. This cannot be valid for some sufficiently small distances between molecules, since they cannot approach one another closer than a certain critical distance. Moreover, the law of interaction of molecules at very small distances is probably substantially different from the interaction law assumed above.

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* $\mathrm{si}(p) = \int_p^\infty \frac{\sin t}{t}\,dt, \qquad \mathrm{ci}(p) = \int_p^\infty \frac{\cos t}{t}\,dt.$