intensities of two components of the hyperfine structure, one can find the numerical value of the quantum number J for split levels, and on the basis of this number determine the quantum numbers F_1, F_2, characterizing the total angular momentum of the whole atom. From the derived formulas it follows that if $I_B/I_A \approx 1$ (approximately equal intensity components), then the split level of the given lines will be characterized by a large value of the quantum number J; and, on the contrary, if $I_B/I_A > 1$ and attains a value in the interval (1.5 – 3.0) (component intensities strongly differing), then the split level will not have a large value for the size of the quantity J.

It follows from our data that if the terms are principal ones in the case of transitions corresponding to the lines 4206.37 and 4396.31 A, there is a split upper term; and on the contrary, in the case of lines 4393.87; 4468.48; 4504.80 A,there is a split lower term. It is possible, apparently, to consider that for the upper term of the line 4206.37 A and the lower term of the line 4504.80 A, the quantum numbers are $J = 1$, $F_1 = 1/2$ and $F_2 = 3/2$. It ought, nevertheless, to be noted that insofar as the majority of the split lines of plutonium have components of similar intensity, a large part of the terms are characterized by large values for the size of the numbers J.

Very simple deductions show,that for doublet structure of the levels, transitions between split levels in some cases can give three and four-component structure lines. Carefully scanning our spectrograms, we found only one line with four components (4521.04 A) and one with three (4535.95 A). Nevertheless, the structure of these lines ought to be investigated more thoroughly, since it is necessary to keep in mind that it is possible in each of these cases to have a superposition of two different lines, close in wavelength.

If one proceeds from the size of the spin of Pu^{239}, that has been determined, then, in correspondence with theory, the quadrupole moment of this nucleus equals zero.

Translated by D. J. Barth
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The Problem of the Effect of Concentration on the Luminescence of Solutions

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Improved experimental data are obtained on the effect of concentration on the luminescence of solutions of fluorescent dyes,in connection with their optical properties. It is shown that the theory of resonance excitation energy, correlating the transfer probability with the optical properties of molecular interactions, permits an approximate calculation of the depolarization constants which were previously introduced as empirical data, and also shows the relation between extinction and decrease of the duration of fluorescence.

I. INTRODUCTION

THE influence of the concentration of solutions on fluorescence is already noticeable at relatively small concentrations as concentration depolarization of fluorescence, concentration quenching and decrease of the duration of fluorescence, and is being explained as a resonance transfer of excitation energy between the molecules of the solutes. Vavilov[1-6] developed the general semi-phenomenological theory of these effects, in which

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[1] S. I. Vavilov, J. Exper. Theoret. Phys. USSR **13**, 13 (1943)

[2] S. I. Vavilov, *Structure of the World*, Moscow, 1950

[3] Th. Förster, Ann. Physik **2**, 55 (1948)

[4] Th. Forster, Z. Naturforsch, **4a**, 321 (1949)

[5] M. D. Galanin, J. Exper. Theoret. Phys. USSR **21**, 126 (1951)

[6] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953)

the transfer probability constants were introduced as empirical data. Further development of the theory of resonance transfer of excitation energy allows us to connect the transfer probability between the molecules with the electron transition probabilities in each of the molecules, and thus with their optical properties[3-6]. However, until now there has been made no quantitative comparison between the experimental data on concentration effects and theoretically calculated data. The significanceof this question arose lately from the use of the idea of resonance energy transfer; for instance, in the explanation of fluorescence by fast particles, and of the sensitized luminescence of crystal phosphors.

The experimental data on concentration effects available in the literature are insufficient for a comparison with the theory for their lack of exact spectral measurements. It is also desirable to work out more accurately the details of the method of measurement of the data on the duration of fluorescence.

This work is an attempt to obtain needed experimental data and to compare them with the theory.

2. THE THEORY ON THE INFLUENCE OF EXCITATION ENERGY TRANSFER ON THE LAW OF FLUORESCENCE DECAY

The calculation of the probability of excitation energy transfer between two molecules with known emission and absorption spectra was first developed in the publications of Forster[3,4], and in a more general way by Dexter[6]. The classical interpretation was given in references 5 and 7. If the transitions in both molecules are of the dipole type --- as is the case in the dye molecules discussed later --- then the transfer probability per unit time from molecule M_1 to molecule M_2, at a distance R from M_1 equals

$$W(R, \vartheta_1, \vartheta_2, \phi) = \frac{9}{8\pi}\left(\frac{\bar{\lambda}}{2\pi n}\right)^4 \frac{\bar{\alpha}}{\tau e}\frac{1}{R^6} \tag{1}$$

$$\times (2\cos\vartheta_1\cos\vartheta_2 - \sin\vartheta_1\sin\vartheta_2\cos\phi)^2,$$

in which $\bar{\alpha}$ = "average" absorption coefficient of the M_2 molecules (calculated for one molecule) in the region of the emission spectrum of M_1; $\bar{\lambda}$ = average wavelength of the region of overlap of these spectra*; n = index of refraction; τ_e = average natural lifetime of the excited molecule M_1; ϑ_1 and ϑ_2 = angles of the axes of the dipoles with the direction of $\mathbf{R}$; ϕ = azimuth angular difference of the dipoles. Applying Eq. (1) for the calculation of the energy transfer in the luminescence process, it is necessary to sum over all the molecules M_2 surrounding the excited molecule M_1, and to average the integrated average for the molecules M_1. There are possible different physical conditions. In the case of a sufficiently viscous solution, the average separation of the molecules in the mixture is small during the lifetime of the excited state, and the molecules may be considered immobile. In this case the sum of the transfer probabilities will not be constant over the lifetime of the excited state because the distance R between the various M_1 and M_2 will be different,and a strong dependence of the transfer probability on R will call for a larger summed transfer probability during the first part of the excited state than during the later parts of the excited state. Consequently,the decrease of the numbers of M_1--- and therefore the law of decay of the luminescence of M_1 --- will not be exponential[4].

For solutions with relatively low viscosity, with the average diffusion distance comparable or larger than the average distance between the interacting molecules, the assumption can be made that during the lifetime of the excited state of M_1, a continuous mixing with M_2 is taking place, and that the summed transfer probability will remain constant. Such a case was discussed in reference 5 to explain the extinction of fluorescence by absorbing matter.

Both cases must be limiting cases of the precise theory accounting for the influence of diffusion of molecules on the kinetics of the transfer. However, when a very viscous solvent is used in the experiments on the polarization of the luminescence, then the experimental conditions come very close

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[7] M. D. Galanin and I. M. Frank, J. Exper. Theoret. Phys. USSR 21, 114 (1951)

* A more accurate expression [3,6] must include $\int \frac{\alpha(\nu) F(\nu)}{\nu^4} d\nu$, in which $\alpha(\nu)$ = absorption coefficient of M_2; $F(\nu)$ = the normalized spectrum of M_1. As the region of overlap of the absorption spectrum $\alpha(\nu)$ and $F(\nu)$ is usually small, the $\int$ may be replaced by $\frac{\bar{\lambda}^4}{c^4}\int \alpha(\lambda) F(\lambda)\, d\lambda = \frac{\bar{\lambda}^4}{c^4}\bar{\alpha}$.

to the first case. Indeed the mean square free path length of the diffusional motion during the lifetime of the excited state ($\tau \sim 5 \times 10^{-9}$ sec) equals

$$\overline{\Delta x^2} = \frac{kT}{3\pi\eta}\,\frac{\tau}{r}, \tag{2}$$

in which η = viscosity, r = effective radius of the molecule. For viscosities of approximately 5 Poise (glycerine) $\sqrt{\overline{\Delta x^2}} \sim 1$ Å, which is considerably less than the average distance of transfer. Assuming the molecules to be immobile during the lifetime of the excited state, and further assuming a chaotic distribution in the solution, we can find the law of the decrease of the number $n(t)$ of the excited molecules M_1 with time:

$$n(t) = n_0 \exp\left\{-\frac{t}{\tau_0} - N\int\left(1 - e^{-W(R,\vartheta_1,\vartheta_2,\phi)t}\right)dv\right\}, \tag{3}$$

in which the $\int$ is taken over the entire volume. N = number of molecules M_2 in a unit volume, τ_0 = average duration of the excited state for $N = 0$, whereby τ_0 may be smaller than τ_e because of other processes of extinction of the second kind.

This expression can be obtained by the method indicated by Antonov-Romanovskii for a somewhat different case (bimolecular process)[8]. We carry out the deduction here since only the result is given in reference 8.

If $n(t)$ is the concentration of the excited molecules M_1^* at time and $n(r,t)$ is the concentration of the excited molecules at a distance r from the molecules M_2, $N(r, t)$ the concentration of molecules M_2 at a distance r from M_1^*, $W(r)$ = transfer probability from M_1^* to M_2 in unit time, at a distance r, N = concentration of M_2, $1/\tau$ the probability of emission from M_1, then

$$\frac{dn(t)}{dt} = -\left\{\frac{1}{\tau} + \int_0^\infty N(r,t)\,W(r)\,dv\right\}n(t). \tag{4}$$

If M_1 and M_2 are initially distributed statistically with respect to each other, then an expression can be written down for the decrease of the pairs of M_1 and M_2 which are separated by a distance r:

$$\frac{dn(r,t)}{dt} = -\left\{\frac{1}{\tau} + \int_0^\infty N(r,t)\,W(r)\,dv + W(r)\right\}n(r,t). \tag{5}$$

Taking into account that

$$n(t)\,N(r,t) = Nn(r,t), \tag{6}$$

we obtain Eq. (3) from Eq. (4) and Eq. (5). Introducing Eq. (1), the exponent can be written out*:

$$\begin{aligned}
&\int_0^\infty \left(1 - e^{-W(R,\vartheta_1,\vartheta_2\phi)t}\right)dv \qquad (7)\\
&= \iiint \sin\vartheta_1 \sin\vartheta_2\, d\vartheta_1\, d\vartheta_2\, d\phi \\
&\quad \times \int_0^\infty \left(1 - e^{-\Phi^2(\vartheta_1,\vartheta_2,\phi)t/R^8}\right) R^2\, dR \\
&= \iiint \frac{\sqrt{\Phi^2(\vartheta_1\vartheta_2\phi)\,t}}{3} \sin\vartheta_1 \sin\vartheta_2\, d\vartheta_1\, d\vartheta_2\, d\phi \int_0^\infty \\
&\quad \times \left(1 - e^{-1/x^2}\right)dx; \quad \int_0^\infty \left(1 - e^{-1/x^2}\right)dx \approx 1{,}8.
\end{aligned}$$

To integrate over the angles, one must take the absolute value of the angle-dependent factor $\Phi(\vartheta_1, \vartheta_2, \phi)$. In averaging over ϑ_2 one must, holding ϑ_1 fixed, direct the polar axis along the electrical field of the first dipole and to measure ϑ_2 from this direction, then to integrate over ϑ_1 taking into account the angular dependence of the absolute value of the electrical dipole field. Thus we obtain:

$$\begin{aligned}
&\iiint |\Phi(\vartheta_1, \vartheta_2, \phi)| \sin\vartheta_1 \sin\vartheta_2\, d\vartheta_1\, d\vartheta_2\, d\phi \qquad (8)\\
&= 2\int_0^{\pi/2} \sqrt{3\cos^2\vartheta_1 + 1}\,\sin\vartheta_1\, d\vartheta_1 \int_0^{\pi/2}\int_0^{2\pi} \cos\vartheta_2 \sin\vartheta_2 \\
&\quad \times d\vartheta_2\, d\phi \approx 4\pi \cdot 0{,}69.
\end{aligned}$$

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[8] V. V. Antonov-Romanovskii, Doklady Akad. Nauk SSSR 2, 93 (1936)

* At the integration over R the lower limit must equal the sum of the radii $2r_0$ of the interacting molecules. Taking zero for it does not introduce any considerable error because $(2r_0)^3 \ll a^3$ (see Sec. 3).

Substituting Eqs. (7) and (8) into Eq. (3) we obtain the law of extinction:

$$n(t) = n_0 \exp\left\{-\frac{t}{\tau_0} - 2q\sqrt{\frac{t}{\tau_0}}\right\}, \qquad (9)$$

$$q \approx 1{,}55 \left(\frac{\overline{\lambda}}{2\pi n}\right)^2 \sqrt{\frac{\tau_0}{\tau_e}\overline{\alpha} N}. \qquad (9')$$

An analogical law of extinction was obtained in a somewhat different way by Förster[4].

3. THE EFFECT OF EXCITATION ENERGY TRANSFER ON THE LUMINESCENCE OF SOLUTIONS

The dependence of the luminescence yield of the molecules M_1 on the concentration of M_2 can be obtained from Eq. (9). Introducing $t/\tau_0 = x$, we obtain:

$$B = B_0 \int_0^\infty e^{-x-2q\sqrt{x}}\,dx \qquad (10)$$

$$= B_0\left(1 - 2qe^{q^2}\int_q^\infty e^{-x^2}\,dx\right)$$

$$\approx B_0(1 - \sqrt{\pi}q + 2q^2 + \cdots).$$

The average lifetime τ of the excited molecules is determined by

$$\tau = \int_0^\infty tn(t)\,dt \Big/ \int_0^\infty n(t)\,dt = \tau_0 \qquad (11)$$

$$\times \left(\int_0^\infty xe^{-x-2q\sqrt{x}}\,dx \Big/ \int_0^\infty e^{-x-2q\sqrt{x}}\,dx\right)$$

$$= \tau_0 \left[\frac{\left(1 + q^2 - (3 + 2q^2)\,qe^{q^2}\int_q^\infty e^{-x^2}\,dx\right)}{\times\left(1 - 2qe^{q^2}\int_q^\infty e^{-x^2}\,dx\right)}\right]$$

$$\approx \tau_0\left(1 - \frac{\sqrt{\pi}}{2}q + \cdots\right).$$

These results apply to the case of M_1 and M_2 being different (extinction or sensibilized luminescence), as well as to the case when M_1 and M_2 are equal (concentration effects). In the latter case the reverse transfer from M_2 to M_1 is possible, but this transfer can be regarded as independent of the previous one, as the molecule returns very quickly to its normal excited state after the transfer.

In the case of equal molecules the extinction of molecules M_1 [by Eq. (10)] does not determine the decrease of the luminescence yield of the solution, as the larger part of the energy transfers does not lead to extinction,but causes only a depolarization of the luminescence.

For the determination of the relative number of transfers which do not lead to extinction, one must use the following: it is natural to assume that the decrease in luminescence yield in the anti-Stokes part of the spectrum is justified, not only at excitation by radiation from the outside, but also for excitation energy transfer, inasmuch as in both cases the same molecular energy states are participating*.Therefore, to determine the number of energy transfers with and without extinction, the average value of the yield must be found for the region of the overlap of the spectra:

$$\overline{\rho} = \int \rho(\lambda)\alpha(\lambda)F(\lambda)\,d\lambda \Big/ \int \alpha(\lambda)F(\lambda)\,d\lambda$$

in which $\rho(\lambda)$ = quantum yield of luminescence, depending on the wavelength of the exciting light**. The ratio of the numbers of transfers with extinction to the number of transfers without extinction is $(1 - \overline{\rho})/(\overline{\rho}$. Evidently the transfers without extinction do not reduce the lifetime of the excited state of the molecules. The reduction in lifetime, as well as the decrease in yield, is determined by the transfers with extinction. The depolarization of the luminescence depends on the relative number of molecules emitting before a transfer, and after one or several transfers. Assuming a complete depolarization of the emission after one transfer[2,9], we obtain tor the degree of depolarization:

$$P = \frac{\left(\sum \frac{2P_k}{3-P_k} I_k\right)}{\frac{\left(\sum \frac{2}{3-P_k} I_k\right) \approx P_0 I_0}{\left(\sum I_k\right)}}, \qquad (12)$$

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[9] M. D. Galanin, Trudy Fiz. Akad. Nauk SSSR 5, (1950)

* The shifting and broadening of the levels as a consequence of interaction for complex molecules is small compared to the width of the spectra.

** For the evaluation of the absolute value of ρ, it is necessary to consider only the "extinction of the first kind" since the "extinctions of the second kind", competing with the transfer, is calculated by the introduction of τ_0 instead of τ_e.

where P_k and I_k are the polarization and intensity after k transfers [taking $P_1 = P_2 \quad . \;. \;. \quad = 0$; $2/(3 - P_k) \approx 2/3$]. It appears that I_0 is proportional to the yield of emission of molecules which were not subject to an energy transfer, but $\Sigma\, I_k$ proportional to the yield of luminescence of all molecules.

On the basis of Eqs. (10), (11) and (12), we obtain the following expressions for the yield, duration and degree of polarization of the fluorescence as a function of the concentration, at small concentrations:

$$B/B_0 = 1 - \sqrt{\pi}\, q\,(1 - \bar{\rho}), \qquad (13)$$
$$\tau/\tau_0 = 1 - {}^1\!/_2 \sqrt{\pi}\, q\,(1 - \bar{\rho}),$$
$$P/P_0 = 1 - \sqrt{\pi}\, q,$$

in which q is determined by Eq. (9′). By a comparison of these expressions with the corresponding formulas in Vavilov's theory[1,2], it is possible to connect the empirical constants with factors determining the transfer probability. Vavilov's theory introduces the ratio of the transfer probability without extinction to the probability of emission τ_0/k_2, corresponding to the expression for the transfer with extinction τ_0/k_1. Vavilov's theory further postulates that there exists a "momentary" extinction within the sphere of action ω. The latter is required to explain the observation of the unproportional change of yield and τ. From Eq. (13) we obtain for the empirical constants

$$\frac{\tau_0}{k_2} = 2{,}74\left(\frac{\lambda}{2\pi n}\right)^2 \sqrt{\frac{\tau_0}{\tau_e}\,\bar{\alpha}}\,;\quad \frac{\tau_0}{k_1} \qquad (14)$$
$$= \omega = \frac{1}{2}\,\frac{\tau_0}{k_2}\,(1 - \bar{\rho}).$$

In accordance with Eq. (13), the change of the yield is not proportional to τ: at small concentrations the yield decreases twice as fast as τ. Thus the concentration extinction in itself does not represent a pure "extinction of the second kind"[2,4,9]. This result is obtained from the theory without the use of a "sphere of action of momentary extinction". From this standpoint the concept of the sphere of action gives an approximation to the decay law (9) (with the transfer probability changing during the duration of the excited state) for the momentary extinction, with the consequent exponential law of decay corresponding to the constant transfer probability. Figure 1 demonstrates the law of extinction (9) with $q = 0.5$, and the exponential law of decay with preceding instantaneous drop (the areas under the curves are equal), showing the degree of such an approximation. The radius of the sphere of action of Vavilov's theory can be compared (see also reference 4) with the characteristic distance $a = (3/4 \times q/N)^{1/3}$. At such a concentration, with the average distance between the molecules of the order of magnitude of a, the transfer probability becomes comparable to the emission probability.

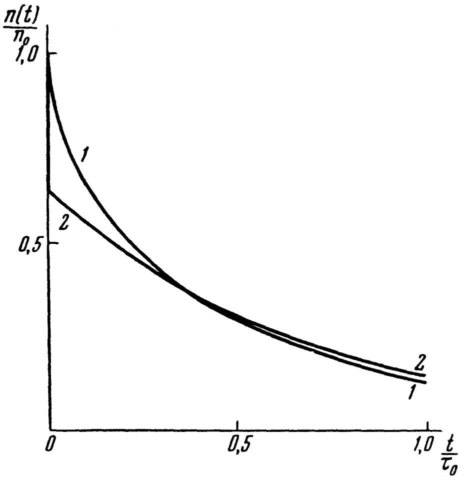

Fig. 1. Law of luminescence decay:
1. according to Eq. (9) with $q = 0.5$
2. exponential law with instantaneous extinction at the beginning.

4. METHOD OF MEASUREMENT

In empirical studies of the influence of the concentration of solutions on the luminescence, it is necessary to consider reabsorption and secondary emission[2,10]. Reabsorption can be avoided by the use of sufficiently thin layers. Vavilov[11] gives the method to account for the influence of secondary emission on the depolarization of the luminescence. In similar fashion, reabsorption can be avoided or accounted for by the measurement of the relative yield and the duration of the fluorescence. Up to now all measurements of the dependence of the duration of the fluorescence on the concentration have been made in thick layers. It was first mentioned in reference 9 that the duration of the fluorescence of a fluorescein solution is considerably increased by reabsorption and secondary emis-

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[10] S. I. Vavilov, M. D. Galanin and F. M. Pekerman, Izv. Akad. Nauk SSSR, Ser. Fiz. **13**, 18 (1949)

[11] S. I. Vavilov, Doklady Akad. Nauk SSSR **16**, 263 (1953)

sion. This effect was recently studied in detail by Bailey and Rolefson[12], and by Schmillen[13]. The following is a brief account of the method of measurement of this investigation.

a) POLARIZATION OF LUMINESCENCE

Polarization of luminescence was measured visually with the aid of Savard's plate and compensating glass wedge. The exciting light from a Hg-lamp with light filters for 436 mμ and 546 mμ was polarized with a polarizing prism. Thin layers were used to avoid secondary emission; they were obtained by squeezing a drop of the solution between two glass plates. From 5 to 10% of the exciting light was absorbed by these layers. For high concentrations it was difficult to obtain such layers, and corrections according to Vavilov's method[11] were applied.

b) RELATIVE YIELD

The relative yield was measured by the intensity of the long wavelength part of the fluorescence spectrum of thin layers. A monochromator UM-2 was used with a photomultiplier behind the exit slit. The absorption of the exciting light in the layer was measured simultaneously by means of a selenium cell. The thickness of the layers was such that 10 to 20% of the exciting light was absorbed.

c) ABSORPTION AND LUMINESCENCE SPECTRA

The absorption spectra in the visible part of the spectrum were measured with a recording spectrophotometer. The luminescence spectra were obtained with the monochromator UM-2 and a photomultiplier. The spectral sensitivity was established with an incandescent lamp of known color temperature. Thin layers of low concentration solutions were used to avoid distortion of the spectra by reabsorption. Within the region of concentrations used, the absorption and emission spectra do not change with concentration.

d) THE DEPENDENCE OF THE YIELD ON THE WAVELENGTH OF THE EXCITING LIGHT

The dependence of the yield on the wavelength of the exciting light in the long wavelength part was measured by excitation with light of different wavelength from the monochromator UM-2 (source: incandescent lamp).

The relative brightness of the solutions was measured with a photomultiplier through a filter transmitting the long wavelength part of the luminescence spectrum. Thick layers of considerable concentration were used to establish complete absorption of all wavelengths of the exciting light. The relative energy in the various spectral sections was measured with a thermopile.

e) FLUORESCENCE DURATION τ

The fluorescence duration τ was measured with a "phase-fluorometer"[14]. The time τ depends strongly on the thickness of the layer of the solution for reabsorption and secondary fluorescence. Table I shows the measured τ for solutions of fluorescein in glycerine at 10^{-4} g/ml and 10^{-3} g/ml under excitation with 436 mμ.

TABLE I

Dependence of τ of fluorescein solution on the thickness of the layer

Layer thickness mm	$\tau \times 10^9$ sec	
	$c = 10^{-4}$ g/ml	$c = 10^{-3}$ g/ml
8	5.5	6.1
1	5.0	5.9
0.2	4.0	5.2
0.04	—	4.2

The dependence of τ on concentration can be strongly distorted at measurements of thick layers as shown in Fig. 2 for Rhodamine 5G (compare references 12,13).

The dependence of τ on concentration was measured on thin layers similar to those used for the measurement of the relative yield. In measurements of the duration of luminescence by the phase method with sinusoidal modulation it is well to keep in mind that the result depends on the law of extinction and can be compared with an average τ as determined by Eq. (11) if this law is known. To arrive at τ from the phase shift it is useful in our

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[12] E. A. Bailey and G. K. Rolefson, J. Chem. Phys. 21, 1315 (1953)

[13] A. Schmillen, Z. Physik 135, 294 (1953)

[14] L. A. Tumerman, J. Exper. Theoret. Phys. USSR 11, 515 (1941); M. D. Galanin, Doklady Akad. Nauk SSSR 73, 925 (1950)

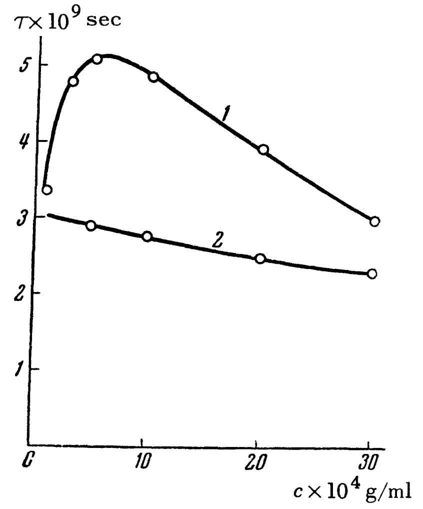

Fig. 2. Dependence of τ on concentration of Rhodamine 5G in glycerine:
1. thick layer
2. thin layer.

case to apply the formula established for the exponential decay and to apply a correction for the law of extinction (9) for small q. Exciting the luminescence with sinusoidally modulated light of frequency Ω, the phase shift x between excitation and luminescence with a decay law (9) can be found, with the phase determined in reference 9:

$$\int_0^\infty e^{-x-2q\sqrt{x}}\cos(\Omega\tau_0 x)\,dx. \qquad (15)$$

The solution gives:

$$\mathrm{tg}\,\psi = \Omega\tau_{\mathrm{fl}} = \Omega\tau_0[1-{}^1/_2\sqrt{\pi}\,qf(\Omega\tau_0)]. \qquad (16)$$

The correction to Eq. (11):

$$f(\Omega\tau_0)=\sqrt[4]{1+(\Omega\tau_0)^2}\,/\,\sqrt{1+{}^9/_4(\Omega\tau_0)^2}$$

is, in our case (with $1/\Omega = 6.8 \times 10^{-9}$ sec), between 0.8 and 0.9.

f) DETERMINATION OF "NATURAL" LIFETIME OF THE EXCITED MOLECULE IN THE ABSENCE OF ANY OTHER EXTINCTION PROCESSES

This lifetime was determined from the first absorption band under the supposition that the probabilities are equal for transitions from the ground state to the excited electronic state, and reverse. For such a case it is known that

$$\frac{1}{\tau_e} = \frac{8\pi c}{\bar{\lambda}_1^4}\int \alpha(\lambda)\,d\lambda, \qquad (17)$$

in which $\bar{\lambda}_1$ = average wavelength of the absorption band and $\alpha(\lambda)$ = absorption coefficient reduced for one molecule.

5. RESULTS OF MEASUREMENTS AND COMPARISON WITH THEORY

Measurements were made on three dyes in solution in glycerine: Fluorescein (alkaline solution); Rhodamine 5G and acridine orange. Figures 3, 4 and 5 show the dependence on concentration of the degree of polarization P, duration of fluorescence τ, and relative yield B. The general appearance of the curves corresponds qualitatively with Eqs. (10) and (11). For a quantitative comparison it is more appropriate to use the experimental data for low concentrations, since at higher concentrations complications occur that are unaccounted for by the theory. In Table II are listed the coefficients determined from the initial slope of the curves; these coefficients correspond to the empirical constants (14) of the phenomenological theory, and the values calculated from the transfer theory (13).

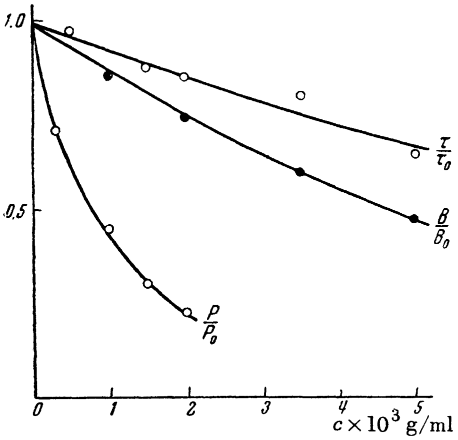

Fig. 3. Dependence of P, τ, and B on concentration of fluorescein solution.
(10^{-3} g/ml = 1.6×10^{18} molecules/cm^3)

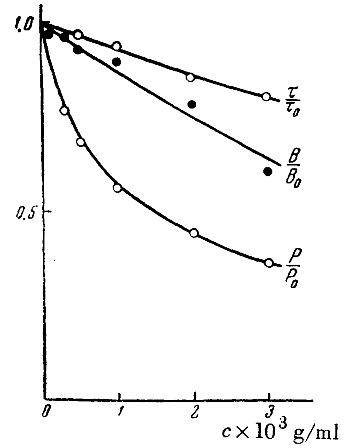

Fig. 4. Dependence of P, τ, and B on concentration of Rhodamine 5G solution. (10^{-3} g/ml = 1.3×10^{18} molecules/cm^3)

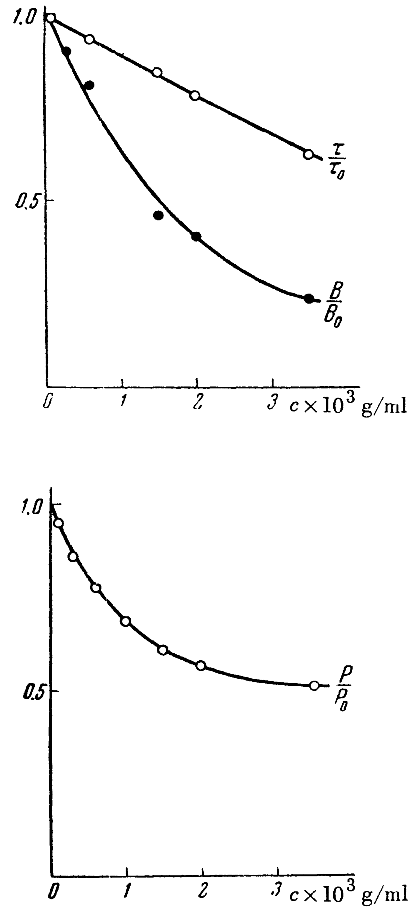

Fig. 5. Dependence of P, τ, and B on concentration of acridine orange solution. (10^{-3} g/ml ≈ 1.8×10^{18} molecules/cm^3)

Comparison of the experimental and theoretical data allows the following conclusions:

1. The probabilities (τ_0/k_2) calculated from the transfer theory agree satisfactorily with the τ_0/k_2 determined from the depolarization of the luminescence.

2. The ratio of the relative yield to τ (twice the slope of the yield as compared with τ, or in terms of the theory which includes the sphere of action, the equality $\tau_0/k_1 = \omega$) is noted approximately*. Deviations from this relation [see $k_1(\tau_0/k_1 + \omega)\tau_0$ in Table II] are within the experimental error.

3. The ratio between transfer probabilities with and without extinction, for fluorescein, agree to the order of magnitude with the decrease of the yield for the "anti-Stokes transfer". In the other two cases the transfer probability with extinction is considerably greater than would result from the dependence of the yield on the wavelength of the exciting light. This is apparently due to the quantum yield being close to unity for fluorescein in the Stokes region[15] while it is smaller than unity for the other two dyes, and it is possible that there exist extinctions of the first kind in addition to those of the second kind. Therefore, it is incorrect in these cases to normalize the yield to unity in the Stokes region, as it is being done for the calculation of $\bar{\rho}$ in the region of overlap of the spectra.

Thus the theory of excitation energy transfer satisfactorily agrees with the experimental data on fluorescent solutions of fluorescent solutions of dyes. Several observed discrepancies can be attributed to the inaccuracy of experimental data (possible error in the entity of the measurements which are necessary for a comparison with the theory should be estimated at not less than 20-30%), as well as to the fact that some complicating conditions have not been taken into account. It is, for instance, possible in some cases that a Coulomb repulsion has an effect on the statistical distribution of the molecules if they are ionized. As mentioned in reference 4, this influence is small at distances of transfer, all the more as the dielectric constant of the solvent

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* In the Table the values of (τ_0/k_1) (exp) were determined from the curve for τ, corrections introduced according to Eq. (16).

[15] M. D. Galanin and S. A. Chishikova, J. Exper. Theoret. Phys. USSR 26, 624 (1954)

TABLE II

Material	$\tau_e \times 10^8$ sec	$\tau_0 \times 10^8$ sec	$\bar{\lambda}$ mμ	$\bar{\alpha} \times 10^{-5} \left(\frac{\text{mol}}{\text{e}}\ \text{cm}\right)^{-1}$	$\frac{\tau_0}{k_2}$ (exp)	$\frac{\tau_0}{k_2}$ (theor)	$\frac{\tau_0}{k_1}$ (exp)	$\frac{\tau_0}{k_1}+\omega$ (exp)	$\frac{\frac{\tau_0}{k_1}+\omega}{\tau_0/k_2}$ (exp)	$1-\bar{\rho}$	$\frac{\frac{\tau_0}{k_1}+\omega}{\tau_0/k_1}$ (exp)	a Å
					$10^{20} \left(\frac{\text{molecules}}{\text{cm}^3}\right)^{-1}$							
Fluorescein	4.2	4.2	509	0.20	59	48	5.5	8.8	0.15	0.08	1.6	43
Rhodamine 5G	6.2	3.0	544	0.24	54	42	6.2	10	0.18	0.06	1.6	42
Acridine Orange	7.25	3.8	514	0.10	25	25	8.2	18	0.72	0.16	2.2	32

is very large ($\epsilon = 74$), but it may be significant for doubly charged ions. Also, density fluctuations need further precision for the energy transfer at concentrations when it is necessary to account for both, the first and subsequent transfers. As a consequence of the very strong dependence of the transfer probability on the distance after the first transfer, there is a relative increase of the number of excited molecules near unexcited molecules from which the excitation energy was obtained. Evidently this condition will have as a consequence a faster decay but a slower depolarization. The theory also does not account for the influence of the larger transfer probability of molecules whose dipole axes form a small angle; but it was assumed that already the first transfer leads to a complete depolarization.

Corrections to increase the mentioned accuracy apparently should not be large, but will have no influence on the qualitative explanation by the theory of resonance energy transfer, of the effects of concentration in the region of sufficiently small concentrations.

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