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Abstract

Full Text

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ON THE DEPOLARIZATION OF THE FLUORESCENCE OF SOLUTIONS DURING TRANSFER OF EXCITATION ENERGY BY RADIATION AND DURING NONRADIATIVE TRANSFER

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In the simplest description of the mechanism of migration of excitation energy between molecules of a dissolved substance, their interaction is considered as dipole interaction. Adopting this representation and assuming the probability of energy transfer to be proportional to the square of the cosine of the angle between the oscillator axes, S. I. Vavilov (^1) calculated the degree of polarization after a single act of transfer. M. D. Galanin (^2) drew attention to the circumstance that this latter assumption, admissible for transfer of energy in the wave zone (by means of radiation), is not applicable for distances smaller than the wavelength of light, where, according to classical electrodynamics, it is necessary to take into account the component of the electric vector along the direction of propagation of the field. This case is important in nonradiative transfer of excitation energy.

In work (^2), Galanin derived a formula for the degree of polarization of secondary radiation for both methods of transfer of excitation energy. As the basis of the calculations for energy transfer by radiation, Galanin took a simplified scheme in which it is assumed that the oscillator responsible for the secondary radiation is placed at the center of a uniformly fluorescing sphere. In this case the following formula was obtained*:

$$p_2' = \frac{7p_1p_2}{15 - 5(p_1 + p_2) + 4p_1p_2}. \quad (1)$$

Formula (1) is written by us for a mixture of two fluorescing substances; p_1 and p_2 denote the degrees of polarization of the first (donor) and second (acceptor—

* Formula (1) was obtained by V. I. Shirokov. It differs somewhat from the corresponding formula of M. D. Galanin in that a small inaccuracy was corrected.

Formula (1) can be obtained from the coefficients $P_{\parallel}'$ and $P_{\perp}'$, calculated in the work of Shirokov and the authors (^3), which determine the distribution along the axes OZ, OY, and OX of virtual oscillators oriented along the axis OZ:

$$P'_{\parallel} = \frac{1}{5}\frac{4P^0_{\parallel} + P^0_{\perp}}{P^0_{\parallel} + 2P^0_{\perp}}, \qquad P'_{\perp} = \frac{1}{10}\frac{P^0_{\parallel} + 9P^0_{\perp}}{P^0_{\parallel} + 2P^0_{\perp}}; \tag{2}$$

in (2)

$$P^0_{\parallel} = \frac{1+p}{3-p}, \qquad P^0_{\perp} = \frac{1-p}{3-p}, \tag{3}$$

where p is equal to p_1 for the donor and to p_2 for the energy acceptor.

The distribution of virtual oscillators along the axes for the donor is

$$n_{1z} = (P^0_{\parallel})_1, \qquad n_{1y} = n_{1x} = (P^0_{\perp})_1, \tag{4}$$

and for the acceptor

$$n'_{2z} \sim n_{1z}(P'_{\parallel})_2 + n_{1y}(P'_{\perp})_2 + n_{1x}(P'_{\perp})_2, \tag{5}$$

$$n'_{2x} \sim n_{1z}(P'_{\perp})_2 + n_{1y}(P'_{\parallel})_2 + n_{1x}(P'_{\perp})_2. \tag{6}$$

The required degree of polarization of the fluorescence of the acceptor is

$$p'_2 = \frac{n'_{2z} - n'_{2y}}{n'_{2z} + n'_{2y}}. \tag{7}$$

Substituting into (7), for n'_{2z} and $n'_{2y} = n'_{2x}$, their values from (5) and (6) and taking into account (2)–(4), we obtain (1).

···of the fluorescent substance upon excitation by polarized light from the light source, p'_2 is the degree of polarization of the acceptor fluorescence when it is excited by the donor fluorescence. For a solution containing one fluorescent substance, $p_1 = p_2$.

Underlying (1) is a very simplified scheme. Budo and co-workers considered the case in which the fluorescent solution is in a cylindrical cuvette, and observation and excitation are carried out from the same side. Such a scheme corresponds better to the experiment; however, the formula obtained by the authors is considerably more complicated than (1), and, since the experiments described below do not claim high accuracy of the quantitative data, we used (1). M. D. Galanin calculated the degree of polarization of the secondary radiation for the case of transfer of excitation energy over distances smaller than the wavelength of light. According to his formula, the degree of polarization of the secondary radiation in this case is $\sim 2.4\%$, whereas in the first case, according to (1), one may expect higher values of the degree of polarization. Thus, for example, for the excitation of rhodamine fluorescence, studied in the present work, by absorption of trypaflavine fluorescence ($p_1 = 0.36$ and $p_2 = 0.44$), one should expect $p_2' \approx 9.5\%$.

The aim of our work was to prove experimentally that the dependence of the degree of polarization of the secondary radiation on the method of energy transfer does in fact exist. The experiments were carried out for mixed solutions of trypaflavine and rhodamine B in glycerin ($C_t = C_r$). For excitation of the luminescence, the mercury line 436 mμ was used; it is strongly absorbed by trypaflavine and weakly by rhodamine. However, at sufficiently high concentrations of both dyes, the luminescence of rhodamine predominates. Earlier ([5]) it was shown that, in the concentration region below $1 \cdot 10^{-4}$ mole/liter, the fluorescence of rhodamine is excited mainly by absorption of trypaflavine fluorescence, whereas in the concentration region above $2 \cdot 10^{-4}$ mole/liter it is excited to a considerable degree by radiationless migration of energy.

We took three concentrations of the dyes: 2.5, 5, and $100 \cdot 10^{-5}$ mole/liter. The thicknesses of the cuvettes were inversely proportional to the concentrations*. For the experiments we used an apparatus with a monochromator, described in one of our papers ([6]). Excitation and observation were carried out from the same side.

Unfortunately, the fluorescence spectrum of trypaflavine falls off very slowly toward the long-wavelength side, whereas the fluorescence spectrum of rhodamine B falls off rather steeply. Therefore, although the spectral region chosen by us for observation (585 mμ) was the most favorable for rhodamine, nevertheless the trypaflavine solution also emitted in this region, and in determining the intensity of the rhodamine luminescence excited at the expense of trypaflavine, it was necessary each time to estimate the contribution made to the luminescence of the mixture by trypaflavine and rhodamine excited directly by the 436 mμ line. For this purpose we determined, in identical cuvettes, the intensity of luminescence in the 585 mμ region of trypaflavine, rhodamine, and their mixture, the absorption coefficients of trypaflavine and rhodamine for the 436 mμ line, and the absorption coefficient of rhodamine in the 585 mμ region**.

In addition, it proved necessary to take into account the depolarization of rhodamine luminescence caused by reabsorption of its own radiation. This depolarization depends on the fluorescence wavelength.

Table 1 gives the values of the degree of polarization for various portions of the fluorescence spectrum of rhodamine and trypaflavine at a dye concentration equal to $5 \cdot 10^{-5}$ mole/liter, in cuvettes of thickness 0.1 and 1.25 mm.

* For $1 \cdot 10^{-3}$ mole/liter the cuvette thicknesses were 0.05 and 0.1 mm.
** Of course, in estimating the fraction of the luminescence contributed to the luminescence of the mixture by trypaflavine (rhodamine), the competing absorption of the exciting light by rhodamine (trypaflavine) and the absorption

of trypaflavine luminescence in the region around 585 mμ by rhodamine were taken into account.

The first dye was excited by the mercury line 546 mμ*, the second by 436 mμ.

It is seen from the table that reabsorption by rhodamine of its own fluorescence lowers the values of fluorescence polarization in the region of 585 mμ by approximately 10 relative percent at a cuvette thickness of 1.25 mm.

	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ
d, mm	564	573	584	595	608	624	645	680
Rhodamine B	Rhodamine B	Rhodamine B	Rhodamine B	Rhodamine B	Rhodamine B	Rhodamine B	Rhodamine B	Rhodamine B
0.1	44.2	44.3	44.5	44.2	44.0	44.1	44.8	44.2
1.25	43.1	42.1	40.4	38.6	37.6	37.8	37.8	37.8

	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ	λ, mμ
	484	494	500	512	526	539	555	564	585
Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin	Tripaflavin
0.1	36.2	36.1	36.3	36.4	35.9	36.2	36.1	36.2	36.1
1.25	36.1	36.0	36.2	36.1	35.8	35.5	35.7	35.4	35.3

After the magnitudes of possible corrections had been calculated, we computed from the experimental data the values of the degree of polarization of the fluorescence of rhodamine excited through absorption of tripaflavin fluorescence for concentrations $2.5 \cdot 10^{-5}$ mol/l ($d = 2$ mm) and $5 \cdot 10^{-5}$ mol/l ($d = 1$ mm and $d = 2$ mm). To avoid the influence of random errors, the experiments were repeated many times. The obtained values of p_2' ranged from 4.5 to 7%. The mean value was 5.6–5.7%. Theory, as we indicated above, gives 9.5%.

If, for the concentration of the mixture components equal to $1 \cdot 10^{-3}$ mol/l ($d = 0.05$ and $d = 0.1$ mm), one determines by the method described above the polarization of the fluorescence of rhodamine excited by tripaflavin, negative values of the degree of polarization are obtained. This occurs because, at this concentration, the fluorescence of tripaflavin is quenched as a result of energy migration from the tripaflavin molecule to the rhodamine molecule. We attempted to take this quenching into account in the following way. We determined the fluorescence intensity of tripaflavin in the region of 506 mμ, where there is no emission of rhodamine, in the mixture and in the individual solutions for concentrations $5 \cdot 10^{-5}$ and $1 \cdot 10^{-3}$ mol/l at identical optical densities. Whereas the emission intensities of the individual solutions were approximately equal, in the mixture the emission of tripaflavin for the concentration $1 \cdot 10^{-3}$ mol/l was

1.5 times weaker. We took this quantity as the measure of quenching. After allowing for quenching, for the polarization of the fluorescence of rhodamine excited by tripaflavin we obtained values of the degree of polarization from 2.0 to 2.9%. The mean value was 2.5%.**

We believe that our results can serve as a qualitative confirmation of M. D. Galanin' s hypothesis.

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* Excitation of the fluorescence of a pure rhodamine solution by the 546 mμ line corresponds more closely to its excitation conditions in the mixed solution than excitation by the 436 mμ line. In the latter case the polarization of rhodamine fluorescence is equal to 4–5%.

** The polarization of the emission of rhodamine excited through absorption of tripaflavin fluorescence, at a concentration of $1 \cdot 10^{-3}$ mol/l, according to (1), is 6.7%, not 9.5%, as for $5 \cdot 10^{-5}$ mol/l. The reason for this is concentration depolarization of rhodamine fluorescence. At $1 \cdot 10^{-3}$ mol/l we obtain $p_2 = 32\%$ instead of 44% for $5 \cdot 10^{-5}$ mol/l.

Note: Figure translations are in progress. See original paper for figures.