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Abstract

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RELATION OF THE PROBABILITY OF RADIATIONLESS DEACTIVATION TO THE SPECTRAL CHARACTERISTICS OF COMPLEX ORGANIC COMPOUNDS

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In a number of works ($^{1-5}$), a relation was found between the values of the fluorescence quantum yield and the spectral characteristics of the objects studied. In the first works, the yield was compared with the position of the maximum of the corresponding fluorescence band. In the general case, the dependence of the absolute quantum yield $B_{\text{fl}}^{\text{qv}}$ on the position of the maximum of the fluorescence band $\nu_{\text{fl}}^{\max}$ is expressed by a curve consisting of two branches—A and B (^{2}). The latter was interpreted as the existence of at least two independent processes of radiationless deactivation. The process leading to a decrease in the yield with displacement of the fluorescence spectrum into the long-wavelength region (branch A) was identified with the process of direct radiationless conversion of excited molecules to the ground state (^{1,2,6}).

Although the relation between the values of $B_{\text{fl}}^{\text{qv}}$ and $\nu_{\text{fl}}^{\max}$ was observed for many compounds, there were nevertheless no grounds to suppose that comparison of $B_{\text{fl}}^{\text{qv}}$ with the position of the fluorescence band is the best one.

In a report at the XI Conference on Luminescence, the authors showed that in various cases the yield values may be related, in addition to the position of the fluorescence band, to the values of the corresponding Stokes shifts $\Delta\nu_{\text{st}}$, to the values of the electronic transition magnitude $\nu_{\text{el}} = (\nu_{\text{fl}}^{\max} + \nu_{\text{abs}}^{\max})/2$, and to the half-widths of the fluorescence spectra Δ_{fl} and absorption spectra Δ_{abs}.

From analysis of the results of comparing yields with spectral characteristics, conclusions could be drawn that were only qualitative in character. It is necessary to compare with the spectral characteristics not the values of the absolute fluorescence quantum yields, whose magnitude is the result of competition between radiative and various radiationless processes, but directly the values of the probabilities of the individual radiationless processes.

In the present work, a comparison was made of the values of the probabilities of radiationless deactivation with the spectral characteristics for a large number of

Fig. 1

Figure 1: Fig. 1

diverse substances in different solvents at 20°. The values of the probabilities of radiationless deactivation of excited molecules at the singlet level were calculated according to the formula

$$(q + r) = (1 - B_{\text{fl}}^{\text{qv}})/\tau,$$

where q is the probability of the process of direct radiationless conversion of excited molecules to the ground state; r is the probability of transition to a metastable level; τ is the mean lifetime of the excited state.*

The calculated values of the deactivation probabilities were compared with the magnitudes of the corresponding Stokes shifts. The result of the comparison for points corresponding to the yield values forming branch A of the dependence $B_{\phi l}$ on $\nu_{\phi l}^{\max}$ is shown in Fig. 1. Since the process leading to a decrease in the yield in branch A is identified with the process of direct conversion of excited molecules to the ground state, in what follows, to characterize the process under study of nonradiative deactivation we use only the notation q.

Fig. 1. Relation between the values of q and $\Delta\nu_{\text{st}}$ for solutions in various solvents: aminonaphthazirhodine (*a*) and dimethylaminonaphthazirhodine (*b*) (curve *I*); 4-dimethylamino-4′-nitrostilbene (*v*), 4-amino-4′-nitrostilbene (*g*), 4-dimethylaminobenzal-4-nitroanilide (*d*), 4-dimethylamino-4′-nitrodiphenyl (*e*), 4-amino-4′-nitrodiphenyl (*zh*), metanitrodiphenylamine (*z*) and 4-diphenylamino-*N*-methylphthalimide (*i*) (curve *II*); 4-amino-*N*-methylphthalimide (*k*) (curve *III*); 4-oxy-*N*-methylphthalimide (*l*) (curve *IV*). Mean values of ν_{el} in cm^{-1}: *I* –19 000; *II* –21 000; *III* –22 700; *IV* –25 000. The points encircled by a dotted line are transition points between branches *A* and *B*, at which the probability of transition to the metastable state can have an effect. The spectra were recalculated by the method described in (9).

Points corresponding to the values of the probability of nonradiative deactivation for different compounds fall near certain curves. Thus, curve *I* is formed by points corresponding to the values of the probability of nonradiative deactivation for aminonaphthazirhodine and dimethylaminonaphthazirhodine. Near

* In the general case, a direct proportionality is observed between the values of $B_{\text{fl}}^{\text{qv}}$ and τ. The absolute quantum yields were measured by the relative method according to the procedure described earlier (7), using an FEU-38 as the radiation detector. τ was determined on a phase fluorometer at the Institute of Molecular Biology of the Academy of Sciences of the USSR in the laboratory of L. A. Tumerman. We take this opportunity to express our deep gratitude to L. A. Tumerman for providing the possibility of measurements on the fluorometer, and to A. N. Surova, who directly carried out the measurements.

Fig. 2. Relation between the values of q and the quantities $\Delta\nu$st on a semilogarithmic scale. For symbols see the caption to Fig. 1

Figure 2: Fig. 2. Relation between the values of q and the quantities $\Delta\nu$st on a semilogarithmic scale. For symbols see the caption to Fig. 1

curve *II* lie the points for derivatives of stilbene, diphenyl, aniline, and phthalimide; all these chemically diverse compounds are characterized by close values of ν_{el}, $\Delta_{\phi l}$, and Δ_{abs}. For compounds whose points form curves *I*, *III*, and *IV*, different values of ν_{el}, $\Delta_{\phi l}$, and Δ_{abs} are characteristic. On going from one curve to another, the change in ν_{el} and $\Delta_{\phi l}$ occurs regularly: ν_{el} and $\Delta_{\phi l}$ increase from curve *I* to curve *IV*.

Thus, the assignment of individual compounds to definite curves is determined by the values of the spectral characteristics of the compounds under study, and not directly by features of their chemical structure.

The observed scatter of points on curve *II* (Fig. 1) may be attributed to somewhat different values of ν_{el}, $\Delta_{\phi l}$, and Δ_{abs}, both for different compounds and for the same compound in different solvents.

The dependences of q on $\Delta\nu_{\text{st}}$ on a semilogarithmic scale (see Fig. 2) are expressed by straight lines. For compounds with the closest values of ν_{el}, $\Delta_{\phi l}$, and Δ_{abs}, the corresponding straight lines coincide or lie very close to one another (straight line *II*). Consequently, at unchanged ν_{el}, $\Delta_{\phi l}$, and Δ_{abs}, the probability of nonradiative deactivation is exponentially related to the magnitude of the Stokes shift, i.e.,

$$q = q_{01} e^{k_1 \Delta\nu_{\text{st}}}. \tag{1}$$

Since each of the curves of the dependence of q on $\Delta\nu_{\text{st}}$ is characterized by a definite value of ν_{el}, it is possible to determine the character of the dependence

q on ν_{el}. Figure 3 presents the relation of q to ν_{el} at a constant value of $\Delta\nu_{\text{st}}$. Curve III was obtained as follows: for one value of $\Delta\nu_{\text{st}}$, points were taken that lie on different curves of the dependence of q on $\Delta\nu_{\text{st}}$ shown in Fig. 1; in all selected cases, for points lying on one curve of the dependence of q on ν_{el}, the quantities $\Delta\nu_{\text{st}}$, Δ_{fl} and Δ_{abs} change only slightly. Thus, each of the curves obtained by us in Fig. 3, relating the values of q to the quantities ν_{el}, is characterized by definite values of $\Delta\nu_{\text{st}}$, Δ_{fl} and Δ_{abs}. The character of the dependences obtained shows that in all cases studied the probability of radiationless deactivation, at one and the same value of $\Delta\nu_{\text{st}}$, decreases with increasing ν_{el}.

Fig. 2. Relation between the values of q and the quantities $\Delta\nu_{\text{st}}$ on a semilogarithmic scale. For symbols see the caption to Fig. 1

The relation of the values of q to ν_{el} was investigated by us in three different cases—for one compound in different solvents, for a series of related compounds in one solvent, and for a series of different compounds in different solvents. The character of the regularities obtained is the same for all the cases studied. Thus, the result obtained once again clearly emphasizes the connection between the values of the probability of radiationless deactivation and the spectral characteristics; the features of the chemical structure exert no direct influence.

The curves of the dependence of q on ν_{el} presented on a semilogarithmic scale are expressed by straight lines (Fig. 4), i.e., at unchanged $\Delta\nu_{\text{st}}$, Δ_{fl} and Δ_{abs}, the probability of the process of radiationless deactivation is related to the magnitude of the electronic transition by an exponential dependence

$$q = q_{02} e^{-k_2 \nu_{\text{el}}}. \tag{2}$$

The distance between the individual curves in Figs. 1 and 3 is determined not only by different values of ν_{el} (Fig. 1) or $\Delta\nu_{\text{st}}$ (Fig. 3), but also by different values of Δ_{fl} and Δ_{abs}. We do not have sufficient material to find a quantitative relation between the change in q and Δ_{fl} and Δ_{abs}, since we do not have series of substances in which only Δ_{fl} and Δ_{abs} would vary while ν_{el} and $\Delta\nu_{\text{st}}$ remained unchanged. However, on the basis of our data it may be said that an increase in Δ_{fl} and Δ_{abs} is accompanied by an increase in q.

It may be assumed that the process of radiationless deactivation, corresponding to the process of direct conversion of excited molecules to the ground state, proceeds by the excited molecules overcoming a certain energy barrier. In this case the value of the probability of radiationless deactivation can be expressed by the Arrhenius formula

$$q = q_0 e^{-E/kT}. \tag{3}$$

The change in the probability of deactivation at one and the same temperature is caused by a change in the magnitude of the barrier. Solving (1) and (3), or (2) and (3), one can establish the relation of the magnitude of the barrier to the spectral characteristics at constant temperature:

$$E = kT[\ln q_0 - \ln q_{01} - k_1 \Delta\nu_{\text{st}}] \quad \text{at constant } \nu_{\text{el}},\ \Delta_{\text{fl}} \text{ and } \Delta_{\text{abs}}; \tag{4}$$

$$E = kT[\ln q_0 - \ln q_{02} + k_2 \nu_{\text{el}}] \quad \text{at constant } \Delta\nu_{\text{st}},\ \Delta_{\text{fl}} \text{ and } \Delta_{\text{abs}}. \tag{5}$$

Thus, the magnitude of the energy barrier at a given value of the electronic-transition frequency decreases with increasing Stokes shift. At one and the same value of the Stokes shift, the barrier magnitude increases with increasing electronic-transition frequency.

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

Fig. 3. Relation between the values of q and ν_{el} for solutions of various compounds.
I—series of rhodamine dyes in ethyl alcohol (^{8}) (1—N, N'-bisethylenerhodamine, 2—rhodamine "B extra," 3—rhodamine 3B, 4—N, N'-dibenzylrhodamine);
II—4-amino-N-phenylphthalimide (1—glycerin, 2—ethyl alcohol, 3—cyclohexanone);
III: 1—4-dimethylaminobenzal-4′-nitroaniline in chloroform, 2—4-amino-N-methylphthalimide in water, 3—4-hydroxy-N-methylphthalimide in ethyl acetate.
Mean values of $\Delta\nu_{\mathrm{st}}$ in cm^{-1}: **I**—1000; **II**—4700; **III**—9700.

Fig. 4. Relation between the values of q and ν_{el} for solutions of a series of compounds on a semilogarithmic scale. For symbols see the caption to Fig. 3.

Expressions (4) and (5) do not make it possible to find the numerical value of E, since the experimental data obtained do not allow the constant q_0 to be determined. The expressions obtained make it possible to calculate only the change in the magnitude of the energy barrier with variation of one or another spectral characteristic:

$$\Delta E = kT \cdot k_1[-\Delta\nu_{\mathrm{st}\,2} + \Delta\nu_{\mathrm{st}\,1}] \quad \text{at constant } \nu_{\mathrm{el}},\ \Delta\phi_{\mathrm{fl}} \text{ and } \Delta_{\mathrm{abs}}; \tag{6}$$

$$\Delta E' = kT \cdot k_2[\nu_{\mathrm{el}\,2} - \nu_{\mathrm{el}\,1}] \quad \text{at constant } \Delta\nu_{\mathrm{st}},\ \Delta\phi_{\mathrm{fl}} \text{ and } \Delta_{\mathrm{abs}}. \tag{7}$$

Thus, an increase in the Stokes shift from $\Delta\nu_{\mathrm{st}\,1} = 6400$ cm^{-1} to $\Delta\nu_{\mathrm{st}\,2} = 9700$ cm^{-1} at $\nu_{\mathrm{el}} = 21\,000$ cm^{-1} (Fig. 1, curve **II**) decreases the barrier magnitude by $\Delta E = 580$ cm^{-1}. An increase in the electronic-transition frequency from $\nu_{\mathrm{el}\,1} = 19\,800$ cm^{-1} to $\nu_{\mathrm{el}\,2} = 26\,200$ cm^{-1} at $\Delta\nu_{\mathrm{st}} = 9700$ cm^{-1} (Fig. 3, curve **III**) leads to an increase in the barrier by $\Delta E = 540$ cm^{-1}.

The relation between the magnitude of the barrier and the spectral characteristics is determined by the fact that both the barrier magnitude and the spectral characteristics are functions of the same variables, changes in which characterize changes in the mutual arrangement of the potential surfaces.

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