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Abstract

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ON THE RELATION BETWEEN THE SPECTRA OF LUMINESCENCE AND ABSORPTION, THE YIELD, AND THE DURATION OF MOLECULAR LUMINESCENCE

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In 1956 B. I. Stepanov (1,2) proved the existence of a universal relation between the spectra of luminescence and absorption and found a relation expressing this connection:

$$\frac{W_\nu}{\chi_\nu} = \frac{8\pi n^* C^*(T)}{\nu^2 n C(T)} e^{h\nu_{\mathrm{el}}/kT} \nu^2 e^{-h\nu/kT} = \frac{n^* C^*(T)}{nC(T)} \nu e^{h\nu_{\mathrm{el}}/kT} u_\nu. \tag{1}$$

Here W_ν is the quantum power of luminescence of frequency ν (calculated per unit frequency interval); χ_ν is the absorption coefficient at the same frequency; u_ν is the quantum density of equilibrium radiation; n and n^* are, respectively, the total number of particles and the number of excited particles per unit volume; $C(T)$ and $C^*(T)$ are normalizing factors; v is the speed of light in the medium; ν_{el} is the frequency of the electronic transition; h and k are the Planck and Boltzmann constants. Some unknown coefficients entering into (1), as shown by B. S. Neporent (3), can be eliminated by normalizing the absorption and luminescence spectra to equality of areas.

Relation (1), called universal, holds when the following basic conditions are satisfied: before the act of emission an equilibrium distribution of excited molecules over the vibrational levels of the electronically excited state is established; in the object under study the absorbing and luminescing centers are of one kind; absorption of a light quantum is always accompanied by electronic excitation ("nonexciting" absorption is absent). Only when these conditions are fulfilled will the luminescence spectrum coincide in form with the spectrum of thermal emission of the substance.

For the purpose of experimental verification of the universal relation, M. N. Alentsev (4) represented (1) in logarithmic form, from which it follows that, if this relation is fulfilled, the function

$$F_\nu = \ln \frac{\chi_\nu}{W_\nu} + 2\ln\nu$$

must be linear, and the slope of the straight line F_ν must correspond to the temperature of the excited molecules. In subsequent works ($^{5-9}$) it was shown experimentally that, in the general case for condensed media, the universal relation is fulfilled, and that the temperatures of excited molecules found from the slopes of the straight lines F_ν correspond to the experimental temperatures.

Studying the function F_ν in a broader region of overlap of the luminescence and absorption spectra of solutions, the authors of works (^{7,10,11}) found that in the long-wavelength (anti-Stokes) region this function ceases to be linear. They quantitatively related the deviation of the function F_ν from linearity to the anti-Stokes decrease of the yield. In order to eliminate the violation of the linearity of the function F_ν in the anti-Stokes region, Ketskemety, Dombi, and Horvai

(7) introduced the luminescence yield into the universal relation. Later, in (12), it was shown that for solutions of thoroughly purified substances containing luminescing and absorbing centers of one kind, the function F_ν is linear over the entire region of spectral overlap, i.e., the universal relation in its original form (1) is fulfilled.

Alentsev (13) attempted to generalize the universal relation; however, he did not take into account that the factor n^* entering into (1)—the number of excited molecules—depends on the particular features of excitation, the properties of the object under study, the presence of quenchers, etc.

In the present work, on the basis of the universal relation, a general expression is obtained that connects the spectra of absorption and luminescence, the yield and the duration of luminescence; several consequences following from this expression are also formulated.

Let $\bar{f}$ and $\bar{d}$ be, respectively, the mean probabilities of radiative and nonradiative transitions. Then the number of transitions per unit time with emission of fluorescence will be $n^*\bar{f}$, and the total number of transitions during the same interval of time will be $n^*(\bar{f}+\bar{d})$. For a given frequency of the exciting light ν_{B},

$$n^*\bar{f} = \int_0^\infty W_{\nu,\nu_{\mathrm{B}}}\, d\nu. \tag{2}$$

Since the quantum yield of luminescence (14)

$$\gamma = \bar{f}/(\bar{f}+\bar{d}) \tag{3}$$

and the duration of luminescence

$$\tau = 1/(\bar{f}+\bar{d}), \tag{4}$$

then, dividing (2) by $n^*(\bar{f}+\bar{d})$, we find

$$n^* = \frac{\tau_{\nu_\text{B}}}{\gamma_{\nu_\text{B}}} \int_0^\infty W_{\nu,\nu_\text{B}}\, d\nu. \tag{5}$$

Substituting (5) into (1), we obtain the desired expression

$$\frac{W_{\nu,\nu_\text{B}}}{\chi_\nu} = \frac{C^*(T)\nu}{C(T)n}\, e^{h\nu_\text{el}/kT}\, u_\nu\, \frac{\tau_{\nu_\text{B}}}{\gamma_{\nu_\text{B}}} \int_0^\infty W_{\nu,\nu_\text{B}}\, d\nu. \tag{6}$$

All the factors entering relation (6), with the exception of $C^*(T)/C(T)$, are accessible to experimental determination. Difficulties arise in determining the absolute quantum power of luminescence at the frequency ν and the absolute integral power of luminescence. However, since these quantities stand on different sides of equality (6), it is sufficient to know their relative values, which are usually measured experimentally. Thus, the formula obtained can be used to determine the ratio of the normalizing factors $C^*(T)/C(T)$, which are functions of the statistical weights of the electronic-vibrational states.

Relation (6) can be simplified. Let us normalize the luminescence spectra so that, for all ν_B,

$$\int_0^\infty W_{\nu,\nu_\text{B}}\, d\nu = 1. \tag{7}$$

Then, since

$$W_{\nu,\nu_\text{B}} = \alpha_{\nu_\text{B}} W^0_{\nu,\nu_\text{B}}, \tag{8}$$

$$\int_0^\infty W_{\nu,\nu_\text{B}}\, d\nu = \alpha_{\nu_\text{B}}, \tag{9}$$

then (6) is transformed into the formula

$$\frac{W^0_{\nu,\nu_\text{B}}}{\varkappa_\nu} = \frac{C^*(T)}{C(T)}\,\frac{\nu}{n}\,\frac{\tau_{\nu_\text{B}}}{\gamma_{\nu_\text{B}}} u_\nu. \tag{10}$$

This relation is valid not only for condensed media, but also for rarefied vapors.* However, in the case of rarefied vapors the temperature of the excited molecules is, in general, not equal to the experimental temperature and depends on the energy of the exciting quantum (^{6,15,16}). The normalizing factor $C^*(T)$ will also be a function of ν_B.

For condensed media, during the lifetime of the molecules an equilibrium distribution of molecules over the vibrational levels of the excited electronic state, corresponding to the experimental temperature, is established for all frequencies ν_{B}. Owing to this, $C^*(T)$ will not depend on the frequency of the exciting light ν_{B}. Most often, for solutions the dependence of ν on n may be neglected. In this case relation (10) takes the form:

$$W^0_{\nu,\nu_{\mathrm{B}}}/\varkappa_\nu u_\nu = D\,\tau_{\nu_{\mathrm{B}}}/\gamma_{\nu_{\mathrm{B}}}, \tag{11}$$

where D is a constant independent of ν and ν_{B}. The product $\varkappa_\nu u_\nu$ corresponds to the power of thermal emission and, of course, does not depend on the frequency at which the luminescence is excited.

Some consequences follow from an analysis of relation (11). If the contour of the luminescence band $W^0_{\nu,\nu_{\mathrm{B}}}$ does not depend on ν_{B} and in form coincides with the spectrum of thermal emission $\varkappa_\nu u_\nu$, then the lifetime and quantum yield of luminescence must not depend on the frequency of the exciting light, or, with a change in ν_{B}, must change proportionally to one another. In other words, if the luminescence spectrum does not depend on ν_{B} and the universal relation (1) is fulfilled, then the condition

$$\tau_{\nu_{\mathrm{B}}}/\gamma_{\nu_{\mathrm{B}}} = \text{const.} \tag{12}$$

must be satisfied.

It is obvious that the universal relation will be fulfilled when foreign quenchers are introduced into a solution, provided they do not absorb in the region of overlap of the spectra of the main substance and do not change the contour of the luminescence spectrum, if in this case the yield and lifetime of luminescence change proportionally, i.e., in all cases of quenching of the second kind (according to the classification of S. I. Vavilov ([17])).

If, however, the contour of the luminescence spectrum, while remaining independent of ν_{B}, does not coincide in form with the spectrum of thermal emission, then it follows from (11) that different dependences of $\tau_{\nu_{\mathrm{B}}}$ and $\gamma_{\nu_{\mathrm{B}}}$ on the frequency of the exciting light must be observed. Such a case is known in the literature. Thus, despite the independence from ν_{B} of the contour of the luminescence spectrum of solutions of certain substances, violations of the universal relation were observed in the long-wavelength (anti-Stokes) region ([7,10,11]). Accordingly, for these samples in the anti-Stokes excitation region the quantum yield and lifetime changed nonproportionally (the decrease in the quantum yield of anti-Stokes luminescence was not accompanied by a change in the lifetime).

As already noted above, later in work ([12]) it was shown that, for solutions of thoroughly purified substances, the universal relation is fulfilled throughout the entire region of overlap of the absorption and luminescence spectra. Therefore condition (12) must be satisfied and, consequently,

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* It is assumed that, for rarefied vapors, formula (4) is fulfilled with a sufficient degree of accuracy.

if, upon transition to anti-Stokes excitation, the lifetime remains constant, then the quantum yield of luminescence of solutions also should not change.

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