SovietRxiv

Soviet-era science, translated into English

A. V. ARISTOV and B. Ya. SVESHNIKOV

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.66903

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

A. V. ARISTOV and B. Ya. SVESHNIKOV

ON THE DETERMINATION OF TRANSITION FREQUENCIES BETWEEN DIFFERENT STATES OF AN ACTIVATOR MOLECULE IN ORGANOLUMINOPHORES

(Presented by Academician A. N. Terenin, 12 VI 1961)

In the works of L. A. Kuznetsova and B. Ya. Sveshnikov (^1), and of G. A. Mokeeva and B. Ya. Sveshnikov (^2), it was shown that, with a considerable increase in the concentration of the activator in organoluminophores, not only the frequencies of nonradiative transitions to the normal state from the fluorescent and phosphorescent states may change, but also the frequency of the nonradiative transition from the fluorescent state to the phosphorescent one. In another paper by G. A. Mokeeva and B. Ya. Sveshnikov (^3) it was established that the frequency of the transition from the fluorescent state to the phosphorescent one may also change with increasing temperature. Finally, in the works of V. V. Zelinskii, V. P. Kolobkov, I. A. Zhmyreva, and V. A. Borgman (^4), evidence was presented in favor of the assertion that the frequency of the indicated transition changes when the fluorescence of solutions of organic substances is quenched by halogen-containing compounds.

In connection with the above-mentioned and certain other works, the problem of calculating the frequencies of nonradiative transitions in organoluminophores becomes highly topical. In describing the kinetics of the luminescence of organoluminophores, four frequencies of nonradiative transitions are usually introduced: r —the frequency of the transition from the fluorescent state to the phosphorescent one; ρ —the frequency of the reverse transition, occurring due to thermal fluctuations; q_1 and q_2 —the frequencies of transitions to the normal state, respectively, from the fluorescent* and phosphorescent states. The values of the listed frequencies can be calculated from experimental data under the sole assumption that the frequencies of spontaneous radiative transitions from the fluorescent (p) and phosphorescent (π) states do not depend on the presence of a quencher or on temperature. In a number of cases, in the calculations one may dispense with the assumption of the constancy of p or π. However, a significant change in at least one of these frequencies suggests a profound (chemical) change in the properties of the emitting center or the invalidity of those simple assumptions that were adopted by one of us (^5) in setting up the system of differential equations describing the luminescence kinetics of organoluminophores. These assumptions are as follows: 1) the phosphorescent level is unique, and from it, in accordance

SovietRxiv

with Jablonski' s scheme, two transitions to the normal state with emission are possible: one with a return to the fluorescent state and subsequent emission of the fluorescence type (α-phosphorescence), and the other corresponding to a direct transition to the normal state (β-phosphorescence); 2) the frequencies of all the listed six transitions do not depend on time; 3) the molecule enters the phosphorescent state from the fluorescent one, and this transition takes place throughout the entire time of residence

---

* With respect to fluorescence, the transition of the molecule to the phosphorescent state is also quenching, but q_1 denotes the frequency of the direct nonradiative transition from the fluorescent state to the normal one.

molecule in the fluorescent state* and 4) static quenching at the phosphorescent level is absent.

From the general solutions of the above-mentioned differential equations, the following formulas, relating the experimental quantities to the transition frequencies, can readily be obtained:

$$\tau_1 = (p + q_1 + r)^{-1}; \tag{1}$$

$$\tau_2 = [\pi + q_2 + \rho(1 - r\tau_1)]^{-1}; \tag{2}$$

$$\varphi = \frac{p\rho\tau_1\tau_2}{p(1 + \rho r\tau_1\tau_2) + r\pi\tau_2} + \frac{r\pi\tau_2}{p(1 + \rho r\tau_1\tau_2) + r\pi\tau_2}; \tag{3}$$

$$\varphi_\alpha = \rho r\tau_1\tau_2; \tag{4}$$

$$\frac{\Delta S_\alpha}{\Delta S_\beta} = \frac{p\rho\tau_1}{\pi}, \tag{5}$$

where τ_1 and τ_2 are, respectively, the mean lifetimes of the fluorescent and phosphorescent states of the molecule; φ is the relative yield of phosphorescence under stationary excitation, i.e., the ratio of the number of photons emitted during a certain time interval in α- and β-phosphorescence to the number of photons emitted during the same time interval in the total emission; φ_α is the ratio of the number of photons emitted in α-phosphorescence to the number of photons emitted in fluorescence under stationary excitation; ΔS_α and ΔS_β are the numbers of photons emitted in α- and β-phosphorescence during one and the same time interval, very short in comparison with τ_2, provided that excitation was produced by a pulse of light whose duration is also much less than τ_2,** and the time between the cessation of excitation and the observation is likewise much less than τ_2.

SovietRxiv

Thus, we have 5 equations for determining 6 unknown frequencies. The situation is considerably improved if, to these 5 equations, one adds 5 analogous equations for another quencher concentration or for another temperature at which α-phosphorescence also exists. Since, according to our assumptions, π and p do not depend on quenching or on temperature, we have 10 equations with 10 unknown frequencies. In addition, in this case an 11th equation can be written:

$$\frac{\Delta S_{\beta}^{(C_1)}}{\Delta S_{\beta}^{(C_2)}} = \frac{\pi_1 r_1 \tau_{11} k_1}{\pi_2 r_2 \tau_{12} k_2}, \tag{6}$$

where C_1 and C_2 are the quencher concentrations; τ_{11} and τ_{12} are the fluorescence lifetimes; π_1, π_2 and r_1, r_2 are the transition frequencies at the first and at the second quencher concentration; k_1 and k_2 are the absorption coefficients of the exciting line at the first and second concentration (or temperature). This formula can serve to test the constancy of π. If π is considered independent of the quencher concentration or temperature, then

$$\frac{\Delta S_{\beta}^{(C_1)}}{\Delta S_{\beta}^{(C_2)}} = \frac{r_1 \tau_{11} k_1}{r_2 \tau_{12} k_2}. \tag{7}$$

This formula immediately gives an answer to the question: does r change as a result of quenching?

* This refinement of Jablonski' s scheme and its experimental justification were made by one of us in 1947 (6). Lewis, Lipkin, and Magel (7) believed that the molecule passes into the phosphorescent state immediately after excitation, before its reorganization and transition to the fluorescent state.

** In this excitation, as indicated in article (5), very high intensities of the exciting light (saturation by light) should be avoided.

In the case where $\rho = 0$, i.e., only β-phosphorescence exists, the right-hand side of equations (4) and (5) becomes zero, and for two concentrations (temperatures), together with (6), we have only 7 equations for determining 8 unknown frequencies. Only if the measurements are performed for 3 concentrations (temperatures) will the number of equations correspond to the number of unknowns (i.e., 11). However, possible errors in determining the experimental quantities make such a procedure not very reliable. In many cases it is more expedient to assume that, in a phosphor containing no extraneous quencher and having a low activator concentration, at low temperatures there is no quenching either at the fluorescent or at the phosphorescent levels, i.e., $q_1 = q_2 = 0$. Then equations (1), (2), and (3) take the following form:

$$\tau_1 = (p + r)^{-1}; \tag{8}$$

SovietRxiv

$$\tau_2 = \pi; \tag{9}$$

$$\varphi = \frac{r}{p + r}. \tag{10}$$

Determining from these equations the values of p, π, and r, we can easily find from equations (1)–(6) for α-phosphorescence and (1), (2), (3), and (6) for β-phosphorescence the values of r_1, q_1, q_2, and ρ for a phosphor possessing some quenching, or for a higher temperature. In this case, for α-phosphorescence we have two equations, and in the case of β-phosphorescence one equation, for checking the assumptions adopted in the calculations.

In determining the values of the experimental quantities entering into (1)–(6), the greatest inaccuracies can usually occur in determining the relative yields of phosphorescence under steady-state and short excitation. Here, above all, good knowledge is required of the curves of the power distribution (in quanta) in the spectra of the total emission of α- and β-phosphorescence, especially in the long-wavelength part of the spectra. This is important in determining the areas of the spectra. Of great significance is also the determination of the ratio of the scales of the spectra for different emissions, i.e., comparison of the powers of emissions in narrow spectral intervals. In the case where there is confidence that some sufficiently intense part of the phosphorescence spectrum does not overlap at all with the fluorescence spectrum,* the ratio of the scales of the phosphorescence spectra and the total emission can be obtained directly in the course of measuring the spectrum of the total emission under steady-state excitation. In other cases a Becquerel phosphoroscope is used, the rotation speed of whose disks is chosen so that the time of one revolution of the disks is considerably less than the mean duration of phosphorescence.

The relative yield of phosphorescence under steady-state excitation is then determined by the formula

$$\varphi = \frac{S_{ph} k}{S_s + (k-1) S_{ph}}, \tag{11}$$

where S_{ph} and S_s are the light sums (in quanta) emitted over one and the same time interval, very small in comparison with τ_2, respectively in the form of phosphorescence and in the form of total emission, and $k = 360^\circ / n\alpha$, where α is the angular size of one aperture in the disk of the phosphoroscope and n is the number of apertures in the disk.

To determine the scales of two emissions under rapid excitation, i.e., $\Delta S_\alpha / \Delta S_\beta$ and $\Delta S_\beta^{C_2} / \Delta S_\beta^{C_1}$, we developed an apparatus consisting of a mercury lamp, a shutter of special design,** a monochromator, a photomulti-

* This can be checked with a Becquerel phosphoroscope.

SovietRxiv

** The shutter design was developed by B. A. Zaraiskaya under the supervision of A. V. Aristov.

amplifier and an ÉNO-1 oscillograph. The difference between this shutter and the purely mechanical shutter described in the work of V. A. Pilipovich and B. Ya. Sveshnikov [(8)] consisted in the fact that the interruption of the exciting light and the admission of the luminescence light to the photomultiplier were effected by means of electromagnetic shutters developed by N. A. Tolstoy et al. [(9)]. The time of light interruption by such a shutter does not exceed 0.001 sec. The duration of excitation is metered by means of a special control unit for the electromagnetic shutters, containing several multivibrators.

Received
1 VI 1961

REFERENCES

[1] L. A. Kuznetsova, B. Ya. Sveshnikov, *Izv. AN SSSR, ser. fiz.*, **20**, 433 (1956).
[2] G. A. Mokeeva, B. Ya. Sveshnikov, *Optika i spektroskopiya*, **9**, 601 (1960).
[3] G. A. Mokeeva, B. Ya. Sveshnikov, *Optika i spektroskopiya*, **10**, 86 (1961).
[4] V. V. Zelinskii, V. P. Kolobkov, *DAN*, **101**, 241 (1955); *Optika i spektroskopiya*, **1**, 560 (1956); V. V. Zelinskii, V. P. Kolobkov, I. A. Zhmyreva, V. A. Borman, *DAN*, **131**, 781 (1960).
[5] B. Ya. Sveshnikov, *ZhETF*, **18**, 878 (1948).
[6] B. Ya. Sveshnikov, *DAN*, **58**, 49 (1947).
[7] G. Lewis, D. Lipkin, Th. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).
[8] V. A. Pilipovich, B. Ya. Sveshnikov, *Optika i spektroskopiya*, **4**, 116 (1958).
[9] N. A. Tolstoy, A. M. Tkachuk, N. N. Tkachuk, E. S. Mansurova, M. Ya. Tsenter, *Optika i spektroskopiya*, **1**, 719 (1956).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.