QUANTUM YIELD OF FLUORESCENCE OF SOLUTIONS OF POLYATOMIC MOLECULES UNDER LONG-WAVELENGTH EXCITATION

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Abstract

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QUANTUM YIELD OF FLUORESCENCE OF SOLUTIONS OF POLYATOMIC MOLECULES UNDER LONG-WAVELENGTH EXCITATION

Numerous studies have been devoted to questions of anti-Stokes fluorescence of polyatomic molecules. Until recently it was generally accepted that, upon excitation in the anti-Stokes region, the fluorescence spectrum is deformed—the so-called "Stokes cutoff" of the spectrum—and the quantum yield of emission B decreases. In recent years a number of authors ([1,2]) have established that the deformations of spectra observed earlier were caused by the presence of impurities in luminophores; in the case of pure substances the contour of the fluorescence spectrum does not depend on the frequency of the exciting light throughout the entire absorption region, including the anti-Stokes region*.

With regard to the quantum yield, few special measurements with especially pure substances have been carried out. A number of works are known ([1,3,4]) that use the relation between absorption and emission spectra to elucidate the causes of the fall of B in the anti-Stokes region, and also the work ([5]), in which the constancy of B for the luminescence of one of the phthalimides in the gas phase was obtained. Finally, studies of the lifetime of the excited state ([6–8]) as a function of λ_{exc} showed the constancy of this quantity over the whole excitation spectrum.

Since the question of the efficiency of conversion of absorbed energy by luminescing molecules plays a very important role in the general theory of luminescence, we carried out a thorough study of the causes of the decrease of B in the anti-Stokes region. Special attention was devoted to purification of the substances, elimination of association, ionization, etc.; in other words, to all causes leading to the presence of several types of absorbing centers in solution. As a result, in many cases it proved possible to obtain independence of the fluorescence quantum yield of the investigated solutions from λ_{exc}.

The method of measuring the relative quantum yield differed little from the generally accepted one ([9]). A cuvette with the solution was placed at the center of an integrating sphere coated with Mg oxide. The exciting light from a mercury (SVDSh-500) or xenon (DKSSh-1000) lamp was isolated by means of a double

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

quartz monochromator and recorded by a barrier photoelement. The luminescence of the object under investigation was recorded by a vacuum photoelement STsV-4, protected from direct light by a screen, followed by an electronic amplifier. In front of the STsV-4 were placed a ground-glass window and a light filter that did not transmit the exciting light. Measurements of the quantum yield were carried out by comparing the glow of a standard whose quantum yield is constant over the entire spectral region investigated. As objects we took such luminophores for which the position and shape of the spectrum do not depend on λ_{exc} (^{2}). After simple mathematical transformations we obtain that

$$B_\nu^x = B_\nu^0 \frac{\bar{\nu}_0^{\text{em}} I_\nu^{x(\text{lum})}}{\bar{\nu}_x^{\text{em}} I_\nu^{0(\text{lum})}} \frac{I_{\nu(\text{fall})} - I^0_{\nu(\text{trans})}}{I_{\nu(\text{fall})} - I^x_{\nu(\text{trans})}}. \tag{1}$$

* By the anti-Stokes region we mean the region of frequencies lower than the frequency corresponding to the intersection of the absorption and fluorescence spectra.

The concentrations of the investigated and reference solutions were chosen so that $I^0_{\nu(\text{trans})}$ and $I^x_{\nu(\text{trans})}$ were equal. Then, for $B_\nu^0 = \text{const}$,

$$B_\nu^x = \text{const}\, \frac{I^x_{\nu(\text{lum})}}{I^0_{\nu(\text{lum})}}. \tag{2}$$

Solutions with concentrations from 10^{-4} to 10^{-6} g/cm^3 were prepared. On a spectrographic setup, the independence of the contour of the luminescence band of the investigated and reference solutions from concentration within the indicated limits, and then from λ_{exc}, was checked. The substances and solvents were selected so that: 1) the absorption spectra of the investigated and reference solutions overlapped, 2) the reference solution had a constant quantum yield, and 3) the exciting lines of the mercury lamp fell within the region of overlap of the spectra.

Fig. 1. Absorption spectra D, excitation I_g, luminescence I_λ, and quantum yield B of 3,6-tetramethyldiamino-*N*-methylphthalimide in benzene

Fig. 2. Spectra D, I_g, I_λ, and B of rhodamine 6g in ethanol

Analysis of possible errors in such a relative measurement of B shows that the total error in studying B as a function can hardly be reduced to less than 15-20%. In the anti-Stokes region of the spectrum, where absorption becomes small and the slope of the absorption curve is very large, the total error reaches 50% and more.

Figure 3. Spectra D, I_g, I_λ, and B of eosin in ethanol: a—the substance was subjected to special purification, b—the substance was not specially purified

Figure 2: Figure 3. Spectra D, I_g, I_λ, and B of eosin in ethanol: a—the substance was subjected to special purification, b—the substance was not specially purified

In this connection, in parallel with the generally accepted measurement method, the following simple procedure was used, making it possible to judge the constancy of B with higher accuracy. If B does not depend on λ_{exc}, then, as is not difficult to show, the luminescence intensity is proportional to the intensity of the exciting light, the quantum yield, and the optical density of the solution ($I_{\text{lum}} \sim aI_0BD$) for small values of D. Thus, coincidence of the optical-density spectrum and the excitation spectrum would unambiguously indicate the independence of B from λ_{exc}. In the case of a decrease of B in the anti-Stokes region, a pattern analogous to the "Stokes cut-off" observed in earlier works (7,10) for luminescence spectra should be observed in the excitation spectrum. For measurement, a self-recording spectrophotometer SF-10 was used, adapted for automatic recording of excitation spectra (11). The use of the same spectral apparatus for recording both spectra, recording them on one sheet "curve by curve," the use as the excitation source of an incandescent lamp with a diffuse spectrum, a significant reduction in the number of measured quantities, and, finally, automatic recording of the entire curve rather than measurements "point by point," make it possible in this variant to obtain an accuracy of 5-10%, which decreases only in the region of very small absorption and can be increased by increasing the concentration when studying the far "tails" of the spectra.

The results of measurements carried out with a solution of 3,6-tetramethyldiamino-N-methylphthalimide in benzene are presented in Fig. 1. When the excitation spectra were measured, the optical density of the solution under investigation was 0.08 (the cuvette length was everywhere $l = 1$ cm), and when the absorption spectra were measured $D = 0.83$. For this solution an KC-11 light filter was used, which retained the exciting light and transmitted part of the fluorescence. In the region 520-550 mμ the excitation and absorption spectra were recorded at a fivefold magnification relative to the main plot. The coincidence of the spectra under study indicates the constancy of the luminescence quantum yield. Under extreme long-wavelength excitation, $\lambda_{\text{exc}} = 546$ mμ, the value of the quantum yield obtained with the aid of an integrating sphere changes by 18%, which is within the limits of experimental error.

Fig. 3. Spectra D, I_g, I_λ, and B of eosin in ethanol: a—the substance was subjected to special purification, b—the substance was not specially purified

An analogous picture of the independence of the quantum yield of luminescence of the solution on λ_{exc} was obtained for 3,6-tetramethyldiamino-N-methylphthalimide in ethanol and rhodamine 6g in ethanol (Fig. 2). It should be noted that in alcoholic solutions of rhodamine 6g, at sufficiently high dye concentrations, changes are observed in the form of the absorption spectrum (a shift of the long-wavelength maximum toward longer wavelengths, broadening of the absorption band, and a decrease in the absorptivity of the solution ([12])). Apparently, the decrease in the quantum yield of luminescence of solutions of substances of this type that is usually observed is connected with the fact that, when measuring weak light fluxes, one has to work with high concentrations, at which the formation of nonluminescent associates is inevitable. We measured the excitation and absorption spectra for rhodamine 6g in water. In the region of the short-wavelength maximum of the absorption spectrum the quantum yield of luminescence decreased by 40%, but at a concentration of $6 \cdot 10^{-7}$ g/cm^3, which corresponds to $D = 0.085$, the long-wavelength decline of the quantum-yield curve did not appear.

In the case of eosin in ethanol we obtained the following picture: the excitation and absorption spectra of an eosin solution that had not been subjected to special purification do not give constancy of the quantum yield B; after repeated recrystallization, under long-wavelength excitation the quantum yield of luminescence remains constant over the entire long-wavelength region of the absorption spectrum (Fig. 3).

In a number of cases it was not possible to obtain complete constancy of B over the absorption spectrum. Thus, for 3-aminophthalimide a decrease in the quantum yield of luminescence is observed. However, as the substance is purified (recrystallization, paper chromatography), the boundary of the decrease shifts into the long-wavelength region of the spectrum. For solutions of fluorescein, rhodamines B and

For vitamin C and tripaflavin in ethanol, a complex dependence of the quantum yield on λ_{exc} is observed. It should be noted, however, that as the pH of the solutions changes, the excitation spectra change, and in fluorescein at pH 4.5 additional maxima appear on both sides of the principal one, which is explained by the formation in solution of nonfluorescing dimers (13). Nevertheless, taking into account the well-known facts concerning the dependence of the spectral properties of these compounds on the pH of the solvent, it is possible, by changing the acid–base properties of the solvent, to change also the spectrum of the quantum yield.

Summarizing all that has been said, one may regard the constancy of the fluorescence quantum yield of solutions over the entire absorption region of polyatomic molecules as experimentally established. A violation of such constancy always indicates the presence in the solution of absorbing centers of several types (associates, different ionic forms, impurities, etc.).

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