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Academician of the Academy of Sciences of the BSSR A. N. Sevchenko, L. G. Pikulik, M. Ya. Kostko

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Abstract

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ON THE DURATION OF FLUORESCENCE OF COMPLEX MOLECULES

The study of fluorescence duration, as S. I. Vavilov repeatedly noted, is an important method for investigating the excited states of luminescent molecules (^{1}). In this direction, the study of the duration of luminescence as a function of the frequency of the exciting light, including the anti-Stokes excitation region, is of undoubted interest. Reliable direct measurements of the fluorescence τ in the anti-Stokes region are in fact lacking. Meanwhile, the problem of anti-Stokes fluorescence is currently being discussed in the literature. Thus, in (^{2}) it is shown that, under strict conditions, constancy of the fluorescence spectrum of solutions can be observed under anti-Stokes excitation. In (^{3}), on the basis of an analysis of experimental data with the aid of a universal relation, a conclusion is drawn regarding the constancy of the quantum yield of vapors and solutions in the anti-Stokes excitation region. For one substance in vapors, direct measurements of the quantum yield are given.

In the present work we investigated the spectral dependence of the fluorescence duration of solutions on the frequency of the exciting light, including the anti-Stokes excitation region. Derivatives of phthalimide and other organic compounds were used as the objects of investigation. Water, alcohols, and dioxane were used as solvents. In choosing the objects of investigation, the degree of overlap of the absorption and fluorescence spectra, as well as the solubility of the substances, was taken into account.

The measurements were carried out on a phase fluorometer of the Institute of Physics of the Academy of Sciences of the BSSR, constructed essentially according to the type of the GOI fluorometer (^{4}). To increase the sensitivity of the instrument, a photomultiplier was selected with the lowest spectral density of noise at the operating frequency of 11.97 MHz. The range of lifetimes measurable on the instrument was $2 \cdot 10^{-10}$–10^{-7} sec. Measurement of τ for the same samples on our instrument and on the GOI fluorometer showed agreement of the absolute values of τ within ±10%. Excitation of the luminescence was carried out through the monochromator of an SF-4 spectrophotometer. A DKsSh-1000 lamp was used as the light source. An additional quartz lens was placed in front of the modulating cell, correcting the slightly divergent beam of light from the exit slit of the monochromator. Fluorescence was measured at a right angle to the exciting light in large square cuvettes. Scattering of the exciting light in

Figure 1

Figure 1: Figure 1

the cuvette with the luminescent solution can reduce the true fluorescence τ, especially in the region of weak luminescence. Special measures were taken to reduce scattered light that could reach the photomultiplier: careful shielding (black screens were introduced directly into the cuvette), and additional light filters on the photomultiplier.

The constancy of the fluorescence spectra at different wavelengths of excitation, including the anti-Stokes region, served as a criterion of the purity of the preparations. Measurements were carried out at different concentrations depending on the luminescence intensity. The absence of concentration quenching of fluorescence in phthalimides made it possible, when necessary, to set a concentration close to saturation. To reduce the influence of reabsorption, the luminescing volume was brought close to the side wall of the cuvette facing the photomultiplier.

The light filters placed on the photomultiplier, cutting off the scattered exciting light, in fact transmitted only the long-wavelength part of the fluorescence band. As shown in works (5, 6), in phthalimide solutions at room temperature a constancy of the luminescence duration over the fluorescence spectrum is observed. In Fig. 1, as an example, the asterisks mark the relative values of τ for the long-wavelength and short-wavelength parts of the emission band, isolated by the corresponding light filters. Therefore, the τ of the long-wavelength part of the fluorescence band, which was actually measured under anti-Stokes excitation, characterizes, for all the cases we studied, the τ of the entire fluorescence band.

Fig. 1. Fluorescence spectra (1), absorption spectra (2), and lifetimes of the excited state (3) for 3-amino-N-methylphthalimide in isobutanol. Asterisks are the relative values of τ for the long-wavelength and short-wavelength parts of the fluorescence band

Figures 1 and 2 present the fluorescence and absorption spectra and the relative course of the lifetime of the excited state for two of the compounds studied. As can be seen from the figures, constancy of the luminescence duration is observed over the entire Stokes region of the excitation spectrum. Similar results were obtained for all the other substances studied. Since in the case of quenching of the second kind the lifetime of the excited state is proportional to the quantum yield, which for phthalimides and dyes under ordinary conditions is fulfilled (1, 5), the results presented above thereby confirm Vavilov' s law on the constancy of the quantum yield in the Stokes excitation region.

Constancy of the fluorescence τ is also observed on passing into the anti-Stokes excitation region (as the beginning of the anti-Stokes region we take the frequency corresponding to the point of intersection of the fluorescence and absorp-

Figure 2

Figure 2: Figure 2

tion spectra). Table 1 gives the absolute values of the luminescence duration, as well as ν_{B1}—the excitation frequency corresponding to the point of intersection of the absorption and fluorescence spectra, and ν_{B2}—the excitation frequency for which it was still possible to measure the constancy of τ. The difference $\Delta\nu$ of the indicated frequencies characterizes the anti-Stokes region in which constancy of the luminescence duration was experimentally proved. Comparison of the data for τ in the anti-Stokes region for 3-amino-N-methylphthalimide in ethanol with the results of work (3) on estimating the yield in 3-aminophthalimide shows their agreement.

Fig. 2. Fluorescence spectra (1), absorption spectra (2), and lifetimes of the excited state (3) for acridine yellow in propanol (a) and 3-amino-N-methylphthalimide in ethanol (b)

The constancy of τ obtained by us confirms the conclusion of work (3) concerning the constancy of the quantum yield in the anti-Stokes excitation region.

Measurement of the fluorescence duration of the substances studied in the still longer-wavelength anti-Stokes excitation region showed a considerable decrease in τ. It should be kept in mind that in this region absorption falls sharply and the luminescence correspondingly weakens. This circumstance naturally makes it difficult to obtain reliable results. In this case the influence of scattered light also cannot be excluded. Therefore, the observed effect of a decrease in τ requires additional investigation.

Table 1

Substance	Solvent	$\tau \cdot 10^9$, sec	ν_{B1}, cm^{-1}	ν_{B2}, cm^{-1}	$\Delta\nu$, cm^{-1}
3-Amino-N-methylphthalimide	Water	12	22 300	20 700	1600
3-Amino-N-methylphthalimide	Ethanol	15	22 700	20 600	2100
3-Amino-N-methylphthalimide	Isobutanol	15.5	22 800	21 000	1800

Substance	Solvent	$\tau \cdot 10^9$, sec	ν_{B1}, cm^{-1}	ν_{B2}, cm^{-1}	$\Delta\nu$, cm^{-1}
3-Amino-N-methylphthalimide	Dioxane	13	23 900	22 700	1200
3-Aminophthalimide	Water	12	22 300	20 800	1500
Acridine yellow	Propanol	4	20 900	19 400	1500
Esculin	Ethanol	3.8	23 400	22 200	1200

Summing up, it may be said that the results we have obtained for the lifetime of the excited state evidently indicate the constancy of the quantum yield over a broad excitation region, including the anti-Stokes region.

It is known that constancy of the quantum yield when the frequency of the exciting light is decreased leads to an increase in the energy yield, which in the anti-Stokes excitation region may exceed unity. There are different points of view on this question in the literature ([1], [7]), and since it is of fundamental importance for the theory of luminescence, while reliable experimental data are lacking, the study of the duration of emission under excitation in the far anti-Stokes region seems important to us.

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