EXPERIMENTAL DETERMINATION OF EMISSION SPECTRA OF LUMINESCENT SOLUTIONS TAKING POLARIZATION INTO ACCOUNT

By

L. VIZE, L. GÁTI and F. PINTÉR

Institute of Experimental Physics, Attila József University, Szeged

It is shown that in determining the emission spectrum of Rhodamine 6G in glycerol solutions, a systematic error exceeding 10% may result from neglecting the dependence on wavelength of the degree of polarization of the emitted fluorescence.

1. The development of modern methods of measurement made it possible to determine the degree of polarization of absorption and emission spectra $\left(p(\lambda)\right.$ and $p(\lambda')$, respectively) in a wider wavelength range and more exactly than earlier. The measurements having shown that the degree of polarization of the emitted fluorescence substantially depends on the wavelength of observation λ', this circumstance has to be taken into account in determining the emission spectrum $f(\lambda')$. The aim of the present work was to determine the systematic error in the emission spectrum measured, resulting from neglecting the dependence of the degree of polarization from the wavelength of emission, at constant exciting wavelength.

Let us consider, according to [1], a cylindrical cuvette of radius R and length l, containing the luminescent solution, placed in a cartesian coordinate system $OX_1X_2X_3$, the illuminated end face of the cylinder being in the plane X_1X_2 and its axis in the direction of X_3. Then the quantum flow density of the fluorescence light excited in the optically inactive and isotropic fluorescent solution in the cuvette by a linearly polarized light beam travelling along X_3 with its electric vector parallel to X_1, the fluorescence oscillating (in the frequency interval $d\lambda'$) in the direction of X_1 or X_2, respectively, and observed in the centre of the illuminated end face is given by

$$B_{\lambda'1,2}\,d\lambda = \frac{\varrho}{n^2}\,\frac{3}{8\pi}\,\frac{1\pm p(\lambda,\lambda')}{3-p(\lambda,\lambda')}\,E_{\lambda 0}\eta_\lambda f(\lambda')k_\lambda\,\frac{1-e^{-(k_\lambda+k_{\lambda'})l}}{k_\lambda+k_{\lambda'}}\,d\lambda'. \qquad (1)$$

Here the factor ϱ/n^2 describes the reflexion loss and the widening of the solid angle of departure, $p(\lambda, \lambda')$ is the degree of polarization of the fluorescence, $E_{\lambda 0}$ the quantum flow density of the exciting light incident on the illuminated face of the cuvette (expressed in quantum number·sec^{-1} cm^{-2}), η_λ the absolute quantum yield of the solution, k_λ and $k_{\lambda'}$ the absorption coefficients for the wavelengths λ and λ' of

excitation and observation, and $f(\lambda')$ the true quantum distribution of the primary fluorescence.

If in the case of linearly polarized excitation only B_1 ($B_{\lambda'}$ oscillating in direction X_1) is observed, then on the base of Eq. (1), the true fluorescence spectrum is expressed by

$$f(\lambda') = \frac{B_1}{R(\lambda, \lambda')} \frac{3-p(\lambda, \lambda')}{1+p(\lambda, \lambda')};$$ (2)

where

$$R(\lambda, \lambda') = \frac{\varrho}{n^2} \frac{3}{8\pi} E_{\lambda 0} \eta_\lambda k_\lambda \frac{1-e^{-(k_\lambda+k_{\lambda'})l}}{k_\lambda+k_{\lambda'}}.$$ (3)

It can be seen from Eq. (2) that the degree of polarization $p(\lambda, \lambda')$ of the fluorescence may exert a considerable influence on the true fluorescence spectrum $f(\lambda')$. Concerning the systematic error caused by neglecting this influence, the following can be said:

a) In the case of aqueous fluorescein solutions, the degree of polarization is near to zero, (the highest value of p, depending on the wavelength, is 0.7% at 30 °C, [2]), and thus also the systematic error is nearly zero.

b) Examining only the region of the emission spectrum $f(\lambda')$ in which $p(\lambda, \lambda')$ is nearly constant, the systematic error will be nearly zero again.

c) However, using a highly viscous solvent (e.g. glycerol) and examining a region of the spectrum $f(\lambda')$ in which the degree of polarization $p(\lambda')$ of the emission spectrum undergoes changes, the effect of the change may become important.

2. Our measurements of $f(\lambda')$ and $p(\lambda')$ were performed with the polarization spectrofluorimeter described in [2]. In the observing detector no measurable dispersed exciting light (from 500 nm to 580 nm; $\lambda = 490$ nm, $\Delta\lambda = 4$ nm) could be found.

After calibrating measurements, an approximative emission spectrum was determined from Eq. (2), with electric vectors parallel to X_1 both for excitation and observation, considering the factor $(3-p)/(1+p)$ as constant. Instead of the factor $R(\lambda, \lambda')$ in Eq. (3) the factor

$$R^*(\lambda, \lambda') = \frac{1-e^{-(k_\lambda+k_{\lambda'})}}{k_\lambda+k_{\lambda'}}$$ (4)

could be used because, the exciting wavelengths being constant, ϱ/n^2, $E_{\lambda 0}$, η_λ and k_λ were constant, too. The correction for secondary luminescence could be neglected [3].

The absorption coefficients k_λ were measured with a spectrophotometer Optica Milano type CF 4.

The approximative emission spectrum

$$f_0(\lambda') = \frac{B_1}{R^*(\lambda, \lambda')}$$ (5)

calculated from the results of measurements is shown by open circles (○) in Fig. 1.

Then the degree of polarization of luminescence in the emission spectrum was measured. The dependence on λ' of the degree of polarization is shown in Fig. 2. With the values $p(\lambda')$ determined in this way, the factor $(3-p)/(1+p)$ in Eq. (2) was calculated, and by multiplying the corresponding values of the spectrum $f_0(\lambda')$
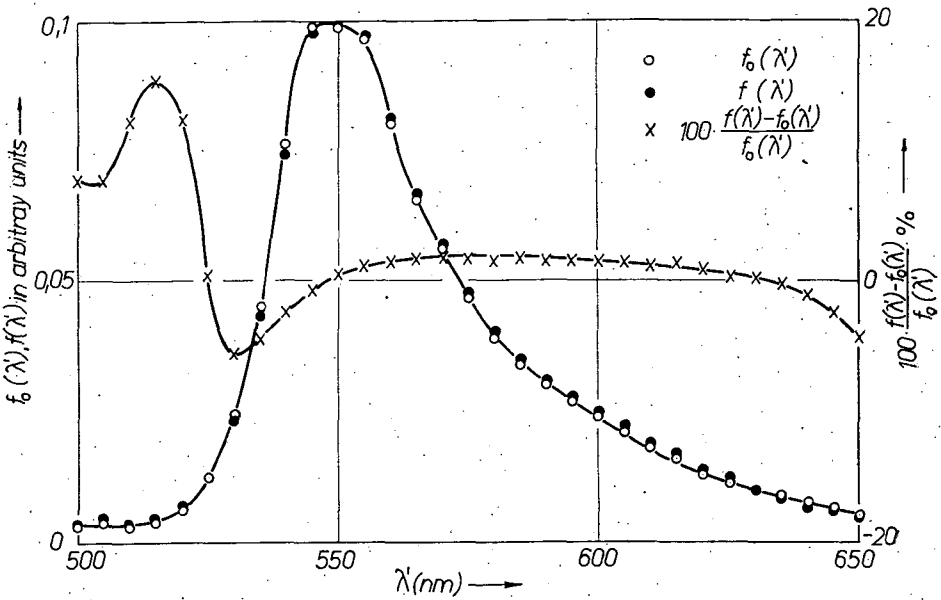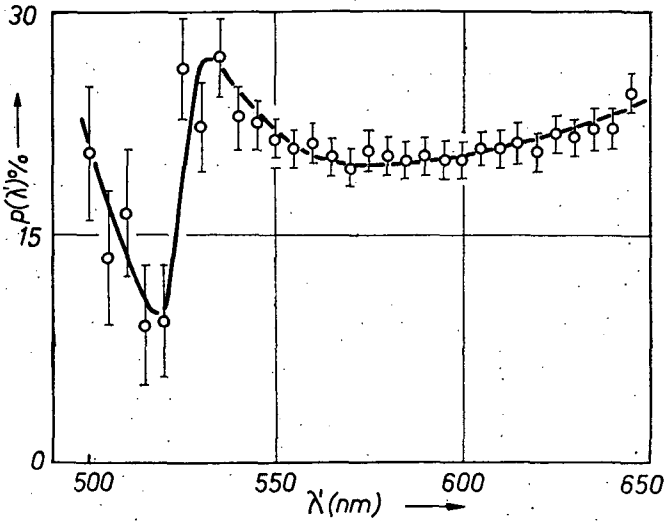
Fig. 1

Fig. 2

L. VIZE, L. GÁTI AND F. PINTÉR

wtih this factor, the emission spectram $f(\lambda')$, shown in Fig. 1 by full circles (●), was obtained.

By comparing the approximative spectrum $f_0(\lambda')$ and the spectrum $f(\lambda')$ corrected for changes in polarization, important differences were found in the wavelength range 500 nm to 550 nm. The relative deviation of $f_0(\lambda')$ from $f(\lambda')$ can be seen from Fig. 1, too. The random error of $f(\lambda')$ due to the random error of measurement of the degree of polarization is less than the systematic change caused by the factor $(3-p)/(1+p)$. While $\Delta f/f$ is $\approx 4\%$ between 500 nm and 550 nm, the systematic change in $f(\lambda')$ is about 12% in the same interval.

References

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ЭКСПЕРИМЕНТАЛЬНОЕ ОПРЕДЕЛЕНИЕ СПЕКТРА ЛЮМИНЕСЦЕНЦИИ ЛЮМИНЕСЦИРУЮЩИХ РАСТВОРОВ С УЧЁТОМ ПОЛЯРИЗАЦИОННЫХ СВОЙСТВ

Л. Визе, Л. Гати , Ф. Пинтер

Показано, что в случае красителя родамина 6Ж растворенной в глицерине без учёта степени поляризации люминесценции в зависимости от длины волны наблюдения, систематическая ошибка определения в спектре люминесценции составляет более чем 10%.