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Investigations on Emission and Absorption Characteristic of Organic Dyes of Xanthene Group**

Measurement of absorption and emission characteristics of xanthene dyes (Rhodamin B, R6 G, Fluorescein) and some their derivatives have been performed. The calculation of the singlet state life-time as well as of the gain are reported. Furthermore, the measurement of the characteristics of the mixtures of dyes was performed and broadening of spectrum was found. Dyes were excited by means of a 200 kW nitrogen laser and superradiant regime was achieved.

1. Introduction

Organic dyes have recently become an important active media for lasers, especially in the visible region of spectrum. Their attractiveness lies in the possibility of frequency tunning within a very broad range.

In the previous papers [1, 2, 3] the results of measurements of three most important dyes of the xanthene group — Fluorescein, Rhodamin B and Rhodamin 6G have been reported. The generation of stimulated radiation in impulse regime was achieved for all dyes by pumping with a nitrogen laser [6].

This paper reports the results of the measurement and calculation of some other important characteristics, as the life-time of the first singlet state, emission and absorption characteristics of dye mixtures and of derivatives of the basic dyes. The results are compared with those obtained for basic dyes and the capability for laser action is estimated.

2. Life-Time Measurement and Calculation

The calculation of the rate equation as well as the estimation of the ability of dyes to generate require the knowledge of the life-time of the first singlet state.

The life-time of organic dyes, being in the range of nanoseconds, may in general be measured by means of either fluorometer or picosecond impulse, as it was done in [4]. To perform such a measurement it is necessary to have one of these arrangements which not always are available. We have therefore made an attempt to calculate the life-time value from the absorption measurements, compare it with the measured one, and to estimate the error of calculation.

From molecular spectroscopy [5] it is known that the life-time of an excited state can be calculated from the following formula

$$\tau = \frac{3.5\cdot 10^8}{\bar{\nu}_m^2 \int \varepsilon(\nu) d\nu}, \tag{1}$$

where

$\bar{\nu}_m$ — is the central wavenumber of the absorption band,

$\int \varepsilon(\nu) d\nu$ — extinction coefficient, integrated over the whole absorption band.

For the symmetric absorption band this relation can be simplified as follows

$$\tau = \frac{3,5\cdot 10^8}{\bar{\nu}_m^2 \varepsilon_m \Delta\nu_{1/2}}, \tag{2}$$

where

ε_m is the maximum value of the extinction coefficient,

$\Delta\nu_{1/2}$ is the half-width of the absorption band.

The calculated values are expected to be slightly higher than the measured ones, the non-radiative transitions are not included in Eqs. (1) and (2).

The results calculated for Rhodamin B and Rhodamin 6G at different concentrations and solvents are presented in Table 1 and compared with the measured values of [4] in Fig. 1. The calculated values are not more than twice higher than the measured ones. It is worth noting that the calculated and measured values are reasonable consistent for higher concentrations.

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3. Special Characteristics of Dye Mixtures

Table 2

Dye 1	Dye 2	Mixing ratio	Relative intensity increase	Emission half width Å
RB (10^{-4})	R6G (10^{-4})	1 : 1	0.85	250
R6G (10^{-4})	Fluorescein (5×10^{-3})	1 : 1	0.5	820
RB (10^{-4})	Fluorescein (3×10^{-3})	1 : 1	–	250
R6G (10^{-4})	Fluorescein	1 : 1	0.8	700

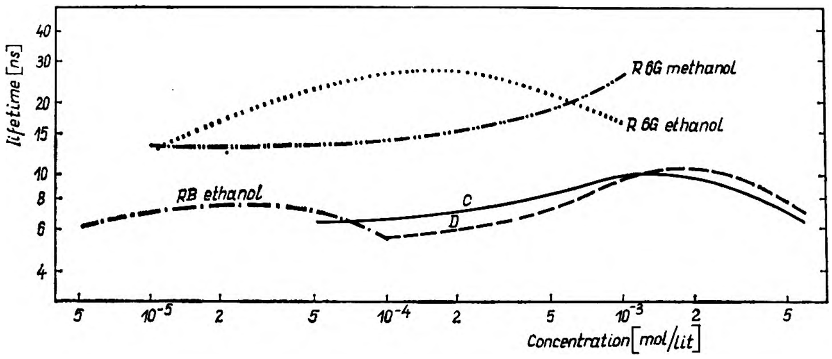

Fig. 1. Singlet state life-time of Rhodamin B and Rhodamin 6G versus concentration. Curves *C*, *D* according to [4] the remaining obtained by the author

Table 1

Dye	Solvent	Concentration [Mol/l]	$\varepsilon_{\max}$ 10^{-4}	Life-time τ [ns]
RB	etanol	10^{-5}	13.26	6.8
	distil. water	10^{-4}	7.65	6.8
	etanol	5×10^{-5}	7.25	7.2
	izoamyl-alcohol	5×10^{-5}	7.24	6.5
R6G	etanol	2×10^{-4}	2.32	10.7
	izoamyl-alcohol	2×10^{-4}	1.65	16.1
	distil. water	5×10^{-4}	1.12	21.5

For xanthene group the emission line width of dye solution in concentrations 10^{-5}–10^{-3} M is usually 200–400 Å. In paper [7] dye mixtures have been studied and in some cases an increased emission intensity was observed. The studied mixtures of the xanthene dyes are shown in Table 2. In all cases there is not only a slight decrease in the emission intensity but — what is more important — the broadening of the emission line have been stated. Best results were achieved for the mixture of Rhodamin 6G with Fluorescein, for which the typical emission line width is 800 Å (see Fig. 2).

4. Measurement of Emission Characteristics of Fluorescein Derivatives*)

The derivatives of fluorescein obtained in powder form were dissolved in redistilled water with (0.01–0.02 M) NaOH to the concentration 10^{-2} M. More diluted concentrations up to 10^{-5} M were obtained by means of buffer solutions with the pH ranging from 1.42 to 12.23. The buffer solutions were prepared according to the method given in paper [6]. The structure and molecular weight of the studied dyes are presented in Table 3.

For fluorescein derivatives the dependence of absorption and shift of absorption band on the pH factor is known from [8]. Our aim was to find out the pH effect on the emission spectrum. The measurement was performed by means of pulsed argon laser TRW Model 58 A, which emits at the

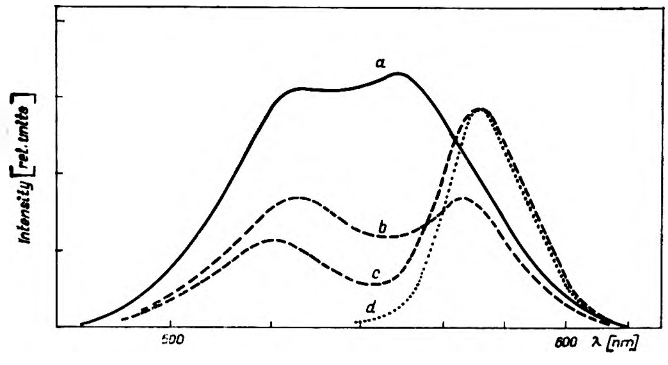

Fig. 2. Emission characteristics of dye mixtures according to Table 2. *a* — R6G+Fluorescein (1:1), *b* — R6G+Fluorescein (1:1) another concentration, *c* — RB+Fluorescein (1:1), *d* — RB+R6G (1:1),

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*) This part was done in cooperation with Dr J. Blabla, Institute of Electronics and Radiotechnics, Czechosl. Acad. Sci., Prague.

Table 3

Dye	Structure of molecule	Molecular weight
Fluorescein	$C_{20}HF_2O_5$	332.32
Tetrabrom-fluorescein (eosin)	$C_{20}H_6O_6Br_4Na_2$	647.88
Dibromfluorescein (eosin H8G (IG))	$C_{20}H_{10}O_5Br_2$	488.05
Dijodfluorescein (Erythrosin)	$C_{20}H_8O_5Na_2J_2$	627.86
Dichlortetrabrom-fluorescein (floxin)	$C_{20}H_6O_5Cl_2Br_4$	713.79
Dichlortetrajod-fluorescein (rose bengale)	$C_{20}H_6O_5Cl_2J_4$	904.77

wavelengths 0.476, 0.488, 0.496, 0.514 nm simultaneously with the corresponding relative intensities 13%, 100%, 6%, 21%. Duration of the pulse was 20μs, repetition rate 50 Hz. Fluorescence radiation was analyzed by means of spectrophotometer SPM-2, photomultiplier and pen recorder. The results are presented in Figs. 3 and 4.

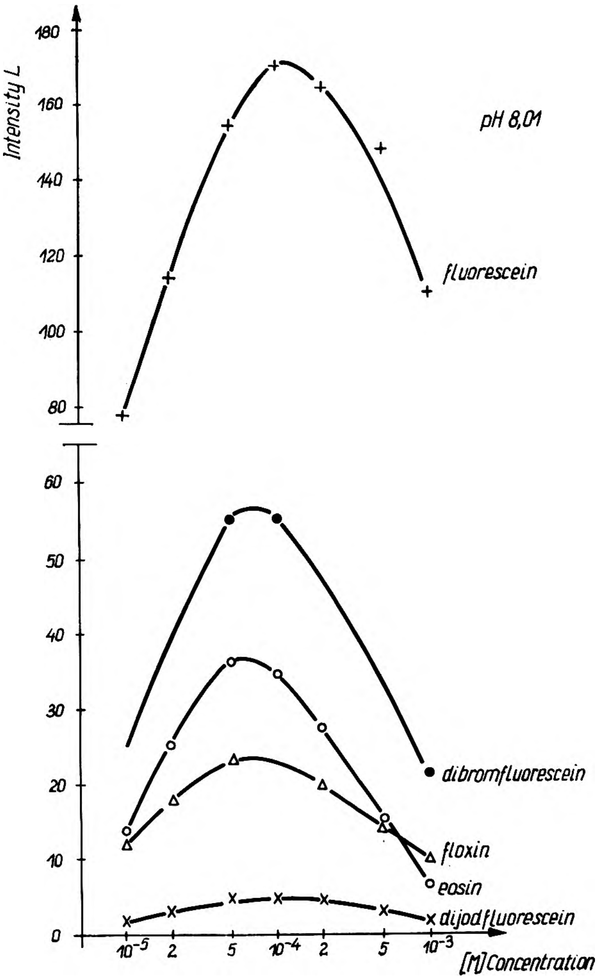

Fig. 3. Concentration dependence of emission intensity of Fluorescein derivatives for constant pH factor

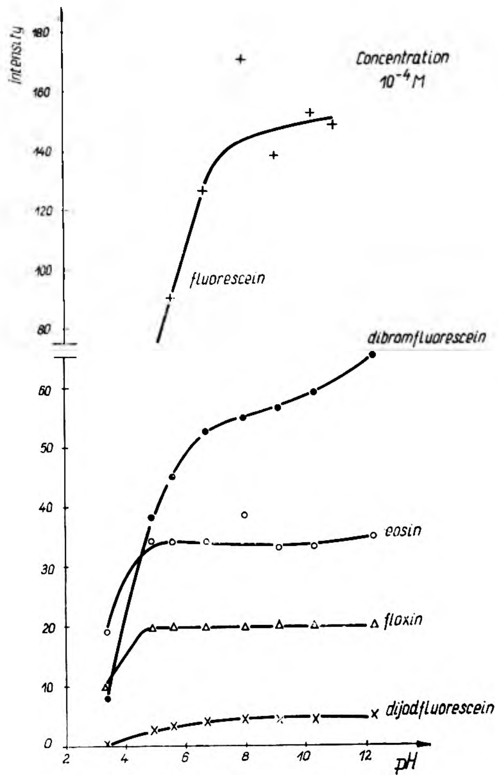

Fig. 4. Dependence of emission intensity of Fluorescein and its derivatives on pH factor for particular concentration (10^{-4}M)

Fig. 3 shows the dependence of concentration ranging within 10^{-5}–10^{-3} M on emission intensity for all derivatives with respect to some characteristics of the fluorescein. For all concentrations the pH factor was maintained constant (pH = 8.01). It is obvious that while the shift of the maximum of derivatives toward a lower concentration is negligible, the emission intensity in the best case dibromfluorescein is three times lower.

Fig. 4 presents the dependence of emission intensity on the pH ranging within 3.37–12. The measurement of solutions with a lower pH factor failed due to their coagulation. The obtained results are compared with those for fluorescein. In all cases the concentration was 10^{-4} M. For dibromfluorescein the emission intensity grows rapidly with the pH value increasing to pH = 7, while for other derivatives it grows only to pH = 5, thereupon being independent. In this experiment the shift of the maximum as well as the width of emission line have been also measured and the shift toward the longer wavelength was observed with the increasing molecular weight and the narrowing of emission line (cf. Table 4).

The obtained data are in agreement with the results given in [8] where a similar dependence was observed for absorption spectrum. On the other hand, the dependence of the shift of the maximum

Table 4

Dye	Mol. weight	Concentration	λ_{max} [nm]	Relative intensity	Linewidth [nm]	pH
Fluorescein	332.32	10^{-4}	521	170	34	8.01
Eosin (H8G)	488.05	5×10^{-5}	535	56	34	8.01
Eosin	647.88	5×10^{-5}	543	26	27	5.01
Erythrosin	627.86	10^{-4}	543	23	25	8.01
Floxin	713.79	5×10^{-5}	563	23	25	8.01

on pH factor has not been observed in our measurement.

5. Gain Calculation and Superradiant Generation

Previous data [1, 2, 3] as well as those under discussion enable us to calculate the gain of organic dye used as a laser medium. As it follows from the well known scheme of energetic levels, the dye gain is a function of the time-dependent inversion frequency, determined by the absorption and emission spectra and by other parameters of the solution (life-time, cross-section, concentration, length, solvent, temperature etc).

We shall follow a theory of dye gain, developed in [9]. According to this theory and under some simplifying assumptions for the frequency dependent gain of a unit length we can write:

$$G(\omega) = e(\omega)-a(\omega),$$

where

$e(\omega)$ — is total emission coefficient,

$a(\omega)$ — total absorption coefficient.

If we introduce the emission and the absorption cross-sections σ_s^a, σ_s^e (resp. σ_T^a, σ_T^e for triplet states) the expression for the gain can be rewritten in the form

$$G(\omega) = N_{s1}\sigma_{s1}^e(\omega)-N_{s0}\sigma_{s0}^a(\omega)-N_1\sigma_{s1}(\omega)-N_T\sigma_{T1}^a(\omega),$$

where N_i is the number of molecules in unit volume of i-th state.

Let the following relations for the cross-section coefficients be introduced

$$\sigma_{s1}^e(\omega) = \left[\frac{2\pi c}{\omega\cdot n(\omega)}\right]^2 f(\omega)$$

$$\frac{\sigma_{(\omega)}^a}{\sigma_{(\omega)}^e} = e\,\frac{\hbar(\omega-\omega_0)}{kT},$$

where $f(\omega)$ is the fluorescence function. Neglecting the influence of the triplet states, we obtain

$$G(\omega) = \left[\left(\frac{2\pi c}{\omega n}\right)^2 f(\omega)+\sigma_{s0}^a(\omega)\right]N_{s1}-\sigma_{s0}^a(\omega)N.$$

Our calculation based on this formulae was performed in [10]. The N_s/N ratio was chosen as a parameter. The values of absorption cross-section and calculated life-time for some xanthene dyes are given in Table 1. The values of quantum yield was assumed to be in accordance with that given in the literature e.g. for Rhodamin B $\Phi = 0.6$. The calculated results are shown in Fig. 5. It is obvious that the gain is positive for the very low values of the parameter N_s/N, that the emission maximum shifts to the shorter wavelength with the increasing inversion, and that there is sharp cut-off on the short wavelength side. The calculations of Rhodamin B as well as of R6G and Fluorescein were verified in a supperradiant regime. The dyes were excited by means of nitrogen laser with the following parameters: output power ~200 kW, wavelength 337 nm, impuls duration ~ 10 ns, repetition rate 20–50 Hz. Pumping radiation was focused by a spherical quartz lens into the dye cuvette and superradiation was achieved for all three dyes. The characteristics as well as generation of fluorescein derivatives are now under investigations.

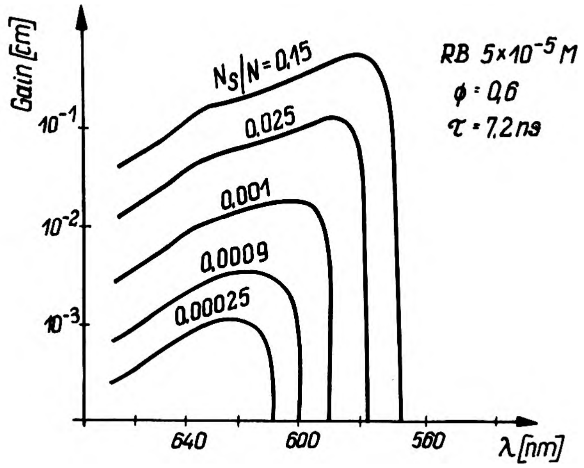

Fig. 5. Calculated gain characteristics of ethanolic solution of Rhodamin B

6. Conclusion

Some additional characteristics of xanthene dyes were calculated and compared with the results of experiment. Laser action was achieved for three dyes. The absorption and emission characteristics have been measured also for dye mixtures and for some of them very broad emission characteristics were found. The investigations included also the emission characteristics of fluorescein derivatives and their dependence on concentration and pH factor. It seems possible that the developed method of measurement of dye characteristics may be applied to dyes belonging to other groups.

Etude des caractéristiques d'émission et d'absorption des colorants xanthéniques

On a mesuré les caractéristiques d'émission et d'absorption des colorants xanthéniques (rodamine, B, RG, G, fluoréscéine) et de certains de leurs derivés. On a évalué la durée de vie moyenne des états de singulets ainsi que les amplifications. On a effectué la mesure des caractéristiques des mélanges de colorants et on a déterminé l'élargissement du spectre. Les colorants avaient été excités avec un laser de 200 kW refroidi à l'azote, utilisé en état de surradiation.

Исследование эмиссионных и поглотительных характеристик органических красителей ксантеновой группы

Произведены измерения эмиссионных и поглотительных характеристик ксантеновых красителей (родамин, B, R6G, флуоресцеин) и некоторых их производных. Приведены расчеты долговечности синглетных состояний, а также усиления. Измерены характеристики смесей красителей и определено расширение спектра. Красители возбуждались при помощи азотного лазера в 200 кВ, для которого достигнуто сверхрадиоактивное состояние.

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