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Laser Excited Emission Spectroscopy of Fluorescein and Rhodamin 6G

Absorption and emission spectra of R6G and fluorescein in different solvents and their dependence on concentration were measured. An impulse argon ion laser as a pumping source in blue and green range was used. The maximum luminescence intensity shift as well as pH-shift were found.

1. Introduction

The optical absorption and emission of complex molecules of organic dyes have been studied intensively in recent years because of their use as an active material for tunable lasers [1], [2]. The properties of many of them have been cataloguized [3]. Due to the fact that the absorption as well as emission depend strongly on the particular type of dye, its purity, type of solvent, concentration and the spectral profile of the pumping source it seems to be necessary to test the optical properties of a considered dye even if its use for a laser is generally known.

In this paper we report our measurements of the characteristics of the dyes of xanthene type, especially of fluorescein and Rhodamin 6G.

An energy level diagram (Fig. 1) first proposed by JABLONSKY [4] is useful for understanding the processes in dyes. The study of the processes involved in the absorption and emission of photons one starts with the molecule in the ground state S_0. After one-photon absorption, a molecule is excited to one of the vibrational states of S_1 from where it relaxes nonradiatively to the lowest states by transfering the corresponding vibrational energy to the solvent. This thermalization effect occurs with a relaxation time of the order of 10^{-12} s.

To the ground state S_0, a molecule can return by one of the following processes [2]:

1. By emitting a photon the excited states S_1 can be depopulated directly. This process is the so called fluorescence with the lifetime of few nanoseconds. The fluorescence spectrum lies partially in the tail of the absorption band on the side of longer wavelengths.

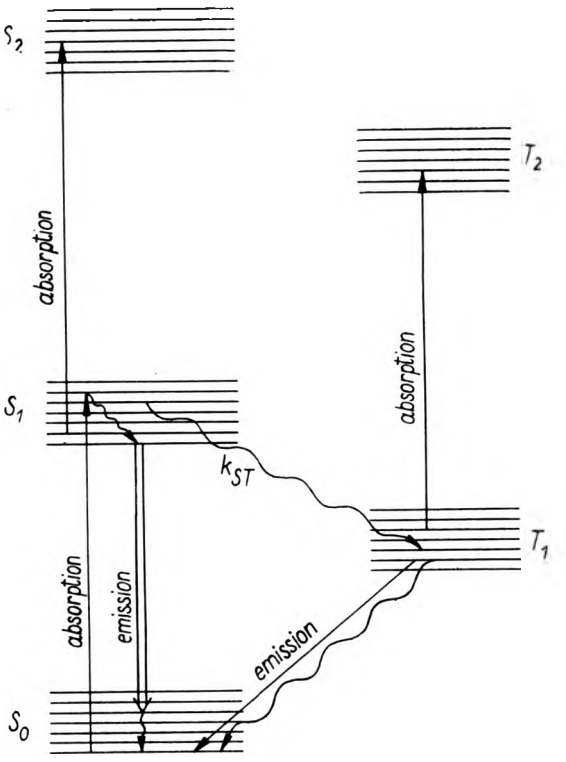

Fig. 1. Energy level diagram of an organic dye molecule after JABLONSKI [4]
S — singlet states, T — triplet states, ____ radiative transitions, ~~~ nonradiative transitions

2. By nonradiative transition $S_1 - S_0$ via the internal conversion. This process reduces the quantum efficiency of a fluorescence mechanism.

3. By nonradiative transition $S_1 - T_1$ between states of different multiplicity. This process populates

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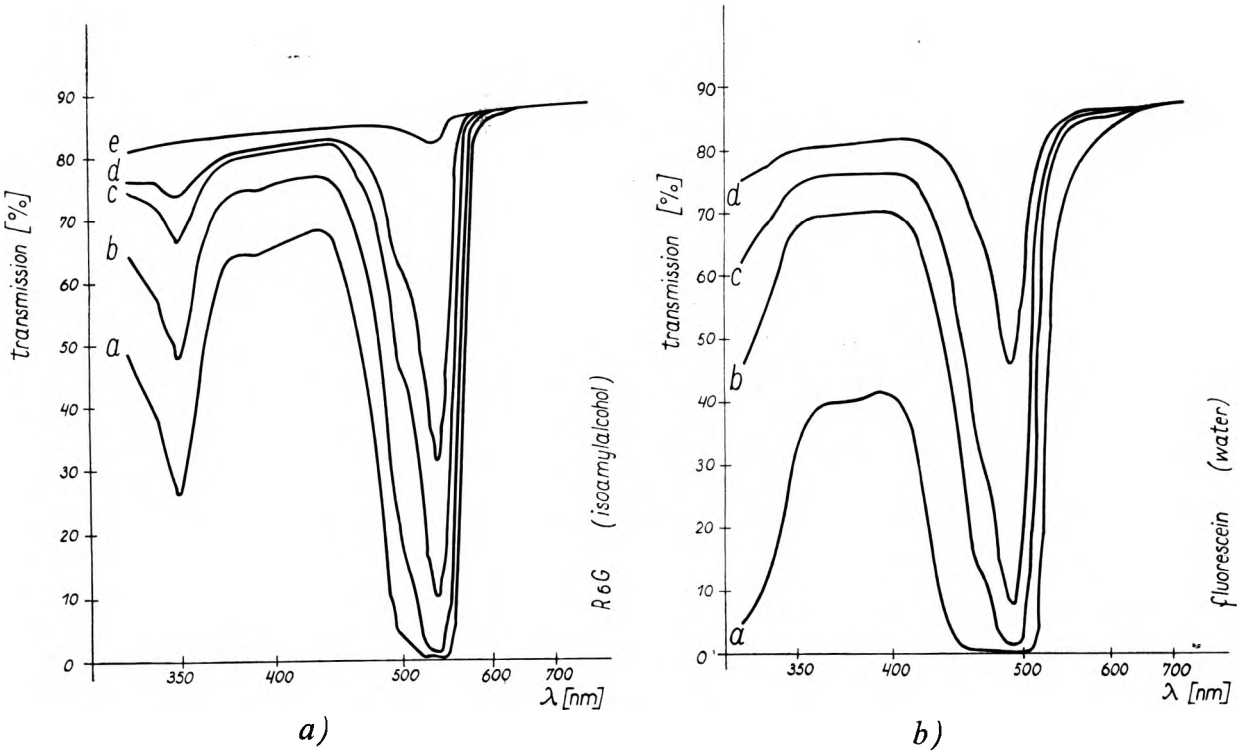

Fig. 2. Absorption of two types of xanthene dyes for different concentrations
a) R6G in isoamylalcohol: $a - 10^{-3}$ M, $b - 5 \cdot 10^{-4}$ M, $c - 2 \cdot 10^{-4}$ M, $d - 10^{-4}$ M, $e - 10^{-5}$ M, b) Fluorescein in distilled water: $a - 5 \cdot 10^{-4}$ M, $b - 10^{-4}$ M, $c - 5 \cdot 10^{-5}$ M, $d - 10^{-5}$ M, where M = mol/l

the metastable triplet state T_1, the lifetime of which varies in the range of 10^{-3} to 10^{-7} s depending on the contents of oxygen in the solution. A molecule being in the T_1 state returns to the state S_0 either by a phosphorescence or nonradiatively.

The higher excited states S_2 can be populated directly from the S_0 state or by a two-photon absorption the cross-section of which is much smaller than that of the one-photon process.

Transitions from the lowest triplet states T_1 to the triplet states T_2 (triplet-triplet absorption) can quench the fluorescence radiation in the singlet band if the frequences of both processes are the same.

From this brief review of the possible transitions we can conclude that especially the following parameters of a dye should be measured:

a) the singlet absorption, the bandwith and position of its maximum. This absorption process is frequently characterized by the extinction coefficient ε (1/molcm) or by the absorption cross-section $\sigma = 3.8 \cdot 10^{-21} \varepsilon$ [cm^2];

b) the lifetime of the S_1 states;

c) the fluorescence intensity, the bandwidth and the position of its maximum, the quantum efficiency of this process;

d) the dependence of the previous characteristics on physical and chemical properties of the dye (e.g. purity, photochemical effects, oxygen effects, temperature, pH-factor of solvent, concentration etc.);

e) the product $k_{ST}\,\tau_T$ where k_{ST} is the probability per unit that an excited singlet molecule will make a transition to the triplet state and τ_T is the triplet lifetime;

f) the triplet absorption cross-section.

2. Measurements and Results

We have measured some of the parameters above mentioned for fluorescein and Rhodamin 6G. The absorption spectra in the wavelength range of 300 nm to 800 nm were measured by means of Specord UV VIS Zeiss using a 3 mm thick cuvette. As an example, the spectra for Rhodamin 6G soluted in isoamylalcohol and fluorescein diluted in distilled water in concentrations from 10^{-5} to 10^{-3} M are shown in Fig. 2. In all measured cases there are two distinct absorption bands — one in the region of 350 nm, the other in the region of 540 nm. From the point of view of laser technique, this indicates that the dye can be optically pumped with a high efficiency either by nitrogen or argon ion lasers.

The luminiscence spectra were measured by means of the arrangement shown in Fig. 3. The argon laser was operated in fundamental transversal mode TEM_{00}

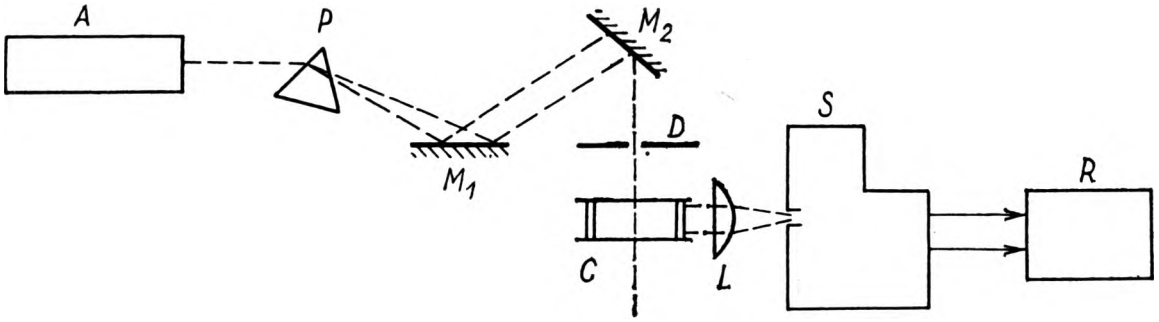

Fig. 3. Arrangement for the measurement of the emission spectra
A – argon pulse laser, *P* – prism, M_1, M_2 – totally reflecting mirrors, *D* – diaphragm, *C* – cuvette, *L* – cylindrical lens, *S* – SPM2 monochromator, *R* – plotter

in the pulse regime at repetition rate 50 c/s with the pulse length 50 μs. The laser beam was dispersed into five wavelengths 514.5, 496.5, 488.0,476,5 and 457.9 nm, each of which could be directed by the system of two mirrors (M_1, M_2) and the diaphragm *D* onto the 10 mm thick cuvette *C*. The relative intensity for different wavelengths was 1:0.1:0.4:0.15:0.02 respectively. The dyes were excited either by the green light ($\lambda = 514.6$ nm) or by blue lines ($\lambda = 496.5$, 488.0, 476.5 nm) simultaneously or by nondispersed beam. The fluorescent photons were collected by a cylindrical lens *L* on the slit of Zeiss SPM 2 monochromator *S* and recorded by a plotter *R*. A slightly modified arrangement was used for the cross-section measurements.

The conc ntration of the dyes was changed in the range of 10^{-2} to 10^{-5} M in several steps. Rhodamin 6G was dissolved in four solvents: ethylalcohol, methylalcohol, isoamylalcohol and distilled water. The fluorescein was dissolved in an alkaline doubly distilled water solution (2M NaOH/1M of fluorescein). Further chemical purification and deaerating of solution were not provided. The acidity of the water solution was changed in the range 7–12 pH.

Examples of emission spectra of both the measured dyes are in Fig. 4 and Fig. 5. In the first case the dependence of the fluorescence intensity on the wavelength for different concentrations of R6G as well as the frequency shift of maxima can be seen. In the second case the concentration profile of fluorescein in dependence on the pumping wavelength is displayed. The maxima of emissivity for the blue or the green pumping lines were found in different concentration regions. For the blue lines (a) the optimum concentration is 10^{-4} M while for the green line $\lambda = 514.5$ nm (b) the optimum is shifted to higher concentration ($5 \cdot 10^{-4}$M). In contrary, the maximum of the concentration profile is independent on the pumping wavelength in the case of Rhodamin 6G in the isoamylalcohol (see Fig. 6).

From Fig. 7 the influence of concentration in different solvents on the wavelength shift of the maximum

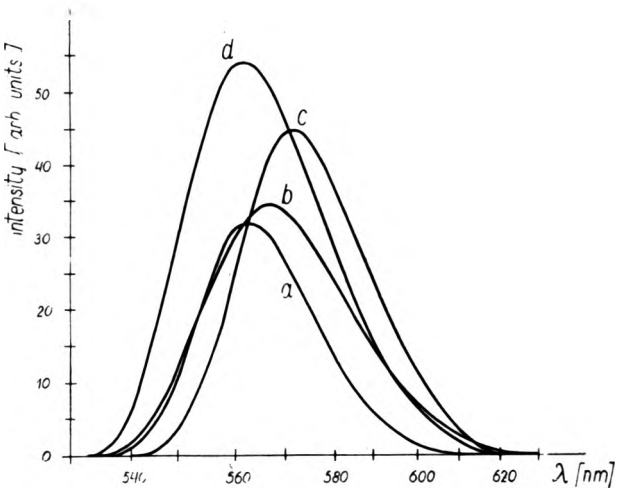

Fig. 4. Emission spectra for R6G in isoamylalcohol for different concentrations: *a* – 10^{-3} M, *b* – 10^{-4} M, *c* – $5 \cdot 10^{-4}$ M, *d* – $2 \cdot 10^{-4}$ M

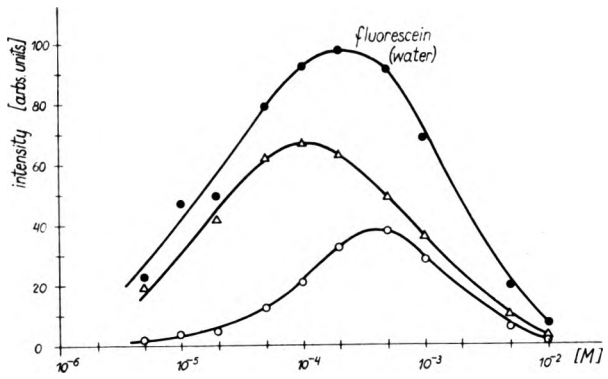

Fig. 5. Concentration profile of the fluorescein water solution pumped by different wavelengths of argon laser
△ – blue lines (496.5, 488.0 and 476.5 nm) pumping, ○ – green line (514.5 nm) pumping, ● – nondispersive beam pumping. The intensities are non normalized for different pumping intensities

fluorescence intensity may be seen. This dependence is linear in all measured solutions of Rhodamin 6G but its slope is altered by the solvent, especially in the case of isoamylalcohol. Similar results were found for fluorescein: the maximum of emissivity is shifted

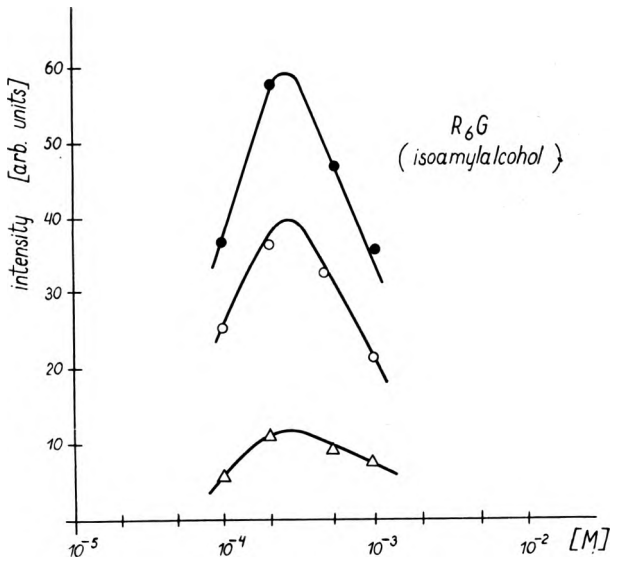

Fig. 6. Dependence of the luminiscence intensity on concentration for R6G in isoamylalcohol
● – nondispersive beam pumping, ○ – 514.5 nm pumping, △ – blue lines pumping

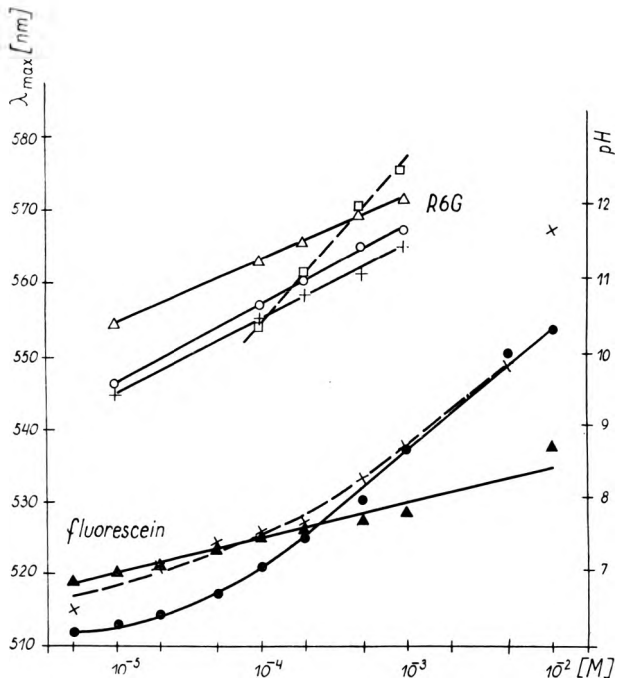

Fig. 7. Dependence of the maximum luminiscence intensity for R6G and fluorescein on concentration in different solvents. For Rhodamin 6G: + – methylalcohol, ○ – distilled water, △ – ethylalcohol, □ – isoamylalcohol. For fluorescein: ● – distilled water, ▲ – alcohols. The pH-scale is valid for the acidity of fluorescein in distilled water only [× – dashed curve]

with concentration towards longer wavelengths. It is also seen, that the acidity of the water solution changes with the concentration in the same manner.

The singlet absorption cross-section of dyes was measured by use of a comparative technique at various wavelengths of argon laser. The influence of both the solvent and the cuvette's windows was eliminated. The intensity of pumping radiation was measured after passing the beam firstly through the cuvette with the dye and secondly through the cuvette with the pure solvent only. In the last case the laser beam intensity was attenuated by means of calibrated filters to the value obtained in the previous measurement. The extinction coefficient ε was calculated from the measured results according to the formula

$$\varepsilon = \frac{1}{md} A,$$

where

m – is the concentration of dye (M = mol/l),
d – is the thickness of the dye [cm],
A = $\log_{10}(I_0/I)$ is the absorbance at the used wavelength.

The results for fluorescein show very good agreement with the curves published by PETERSON [5]. The results obtained for Rhodamin 6G differ from the measurements of authors [5], [6] nearly by the order of magnitude which can be explained by the presence of chemical impurities. The agreement as well as discrepancies for both measured dyes are presented in Fig. 8.

3. Conclusions

The dependence of the λ_{max}-shift on the concentration of the dye for different solvents was demonstrated for both R6G and fluorescein. This shift is especially

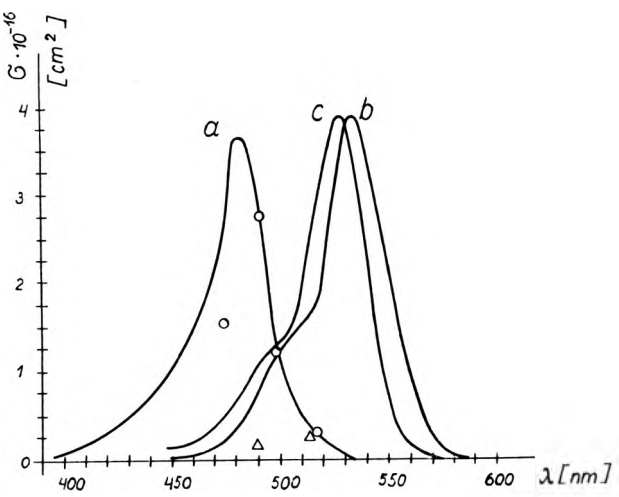

Fig. 8. Dependence of the absorption cross-section on the wavelength for fluorescein (curve *a* according to [5]) and for R6G, curve *b* according to [5], curve *c* according to [6]
○ – our measurement (fluorescein), △ – our measurement (R6G), concentration in all cases was 10^{-4} M

pronounced for R6G in isoamylalcohol. In this case, the slope of the linear part of the characteristic $k = 2.33 \cdot 10^4$ nm/M ($\Delta\lambda = 220$ Å for the concentration change of one order) is more than twice larger compared to ethylalcohol, methylalcohol or distilled water solvents ($k = 1 \cdot 10^4$ nm/M). For all these solvents the emission line intensities are comparable. In the case of fluorescein, the largest change of λ_{max} was observed with the distilled water solvent. In the linear part of the measured curve ($k = 1.72 \cdot 10^4$ nm/M) the shift $\Delta\lambda$ equals 170 Å for one order of the concentration change. All alcoholic solvents produce shifts almost three times smaller ($k = 0.67 \cdot 10^4$ nm/M).

Using these types of dyes for lasers, the concentration effect can be utilized in two different ways:

a) by a proper choice of the solvent it is possible to choose the rate of tuning of the laser by changing the concentration,

b) the solutions with small k-factors act as stabilizing media in the sense that both the wavelength and laser beam intensity are not strongly influenced by random changes of the concentration.

As shown in Fig. 7, the acidity of the solution may be an additional factor influencing the wavelength-shift.

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