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OPTICAL PROPERTIES OF RHODAMINE B
IN THE SOLUTIONS OF ETHANOL,
ACETIC ACID AND WATER

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OPTICAL PROPERTIES OF RHODAMINE B IN THE SOLUTIONS OF ETHANOL, ACETIC ACID AND WATER

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ABSTRACT

Absorption, fluorescence and fluorescence excitation spectra of rhodamine B at the concentration between 10^{-3} and 10^{-6} mol/l are examined in the solutions of ethanol, acetic acid and water. In the case of ethanolic solutions, influence of pH on the absorption spectra of rhodamine B is also examined. From the obtained experimental results, some explanations to clarify lasing mechanisms of rhodamine B dye laser are presented.

1. Introduction

Rhodamine B is widely used not only for dyestuffs but also for quantum counters (MELHUSH 1962). Recently with the development of dye laser research, rhodamine B in solutions have been found successful in lasing (McFARLAND 1967; SCHAEFER *et al.* 1967). Before the success of rhodamine B as a dye laser, its basic studies have clarified some of the optical and electronic properties in solid state (for example, NELSON 1954; CHO *et al.* 1963), and in solution (for example, WEBER, TEALE 1958), but satisfactory elucidation of dye laser mechanism in rhodamine B has not yet been obtained.

Rhodamine B has the structural formula as shown in Fig. 1, and rhodamine 3B is identical to rhodamine B except that COOH group is replaced by C_2H_5 and rhodamine 6G is different from rhodamine 3B only in that NH group is replaced by C_2H_5 . Therefore, there seems to be close resemblance, in chemical structure, of rhodamine B with rhodamine 3B and rhodamine 6G. Although optical absorption measurements in various solutions have been performed on rhodamine 3B and rhodamine 6G (LEVSHIN, BARANOVA 1959; BARANOVA 1962), the corresponding studies on rhodamine B have not been made so far.

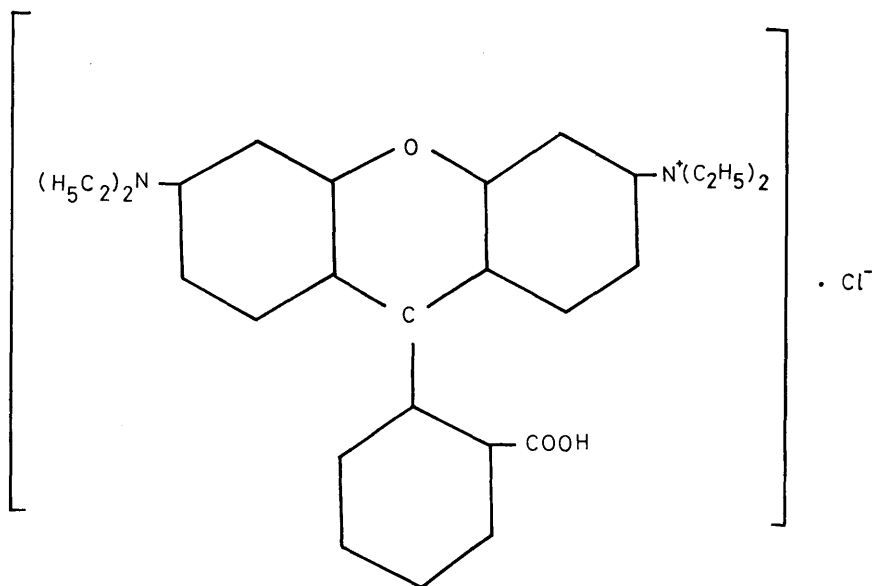


Fig. 1. Structural formula of rhodamine B.

In view of the above situations, we have examined experimentally fluorescence, absorption and fluorescence excitation spectra of rhodamine B in the solutions of ethanol, acetic acid and water. In addition to the experiments mentioned above, influence of pH on the absorption spectra of ethanolic solution has also been examined.

2. Experimentals

Absorption measurements at various concentrations and solutions are done using the apparatus as shown in Fig. 2. Sample cell is irradiated by monochromatic light obtained through monochromator-1 and only the transmitted light from the cell is selected by monochromator-2, which is capable of eliminating, on the detector, the efficient luminescent light from the dye. The detection of light was made by photomultipliers with S-4 or S-11 type photocathode.

Fluorescence excitation spectra are obtained by using the experimental apparatus as shown in Fig. 3. In Fig. 3, the thin sample cell of approximately 0.018 cm in width is irradiated by monochromatic light, obtained from tungsten-lamp monochromator system, and only the luminescence at 610 nm is selected by second monochromator, because there is scarcely self-absorption of the emitted light at this wavelength. Irradiating intensity from the first monochromator is measured by thermopiles.

A Hg lamp is used for the excitation to measure luminescence of rhodamine B. UV-DIB filter and two filters of VO-52 and KL-54 (Toshiba filters) are used to

Optical Properties of Rhodamine B in the Solutions

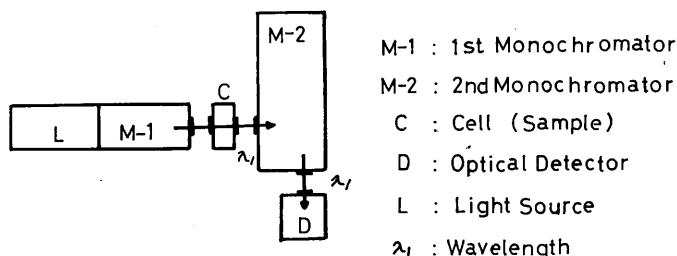


Fig. 2. Experimental apparatus for the measurement of absorption spectra.

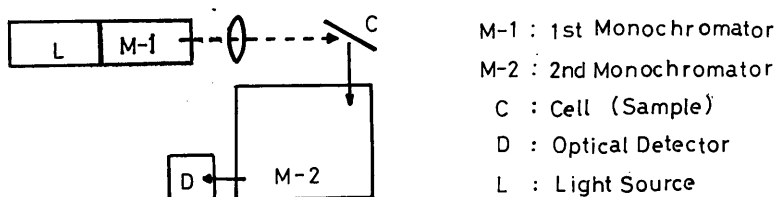


Fig. 3. Experimental apparatus for the measurement of fluorescence excitation spectra.

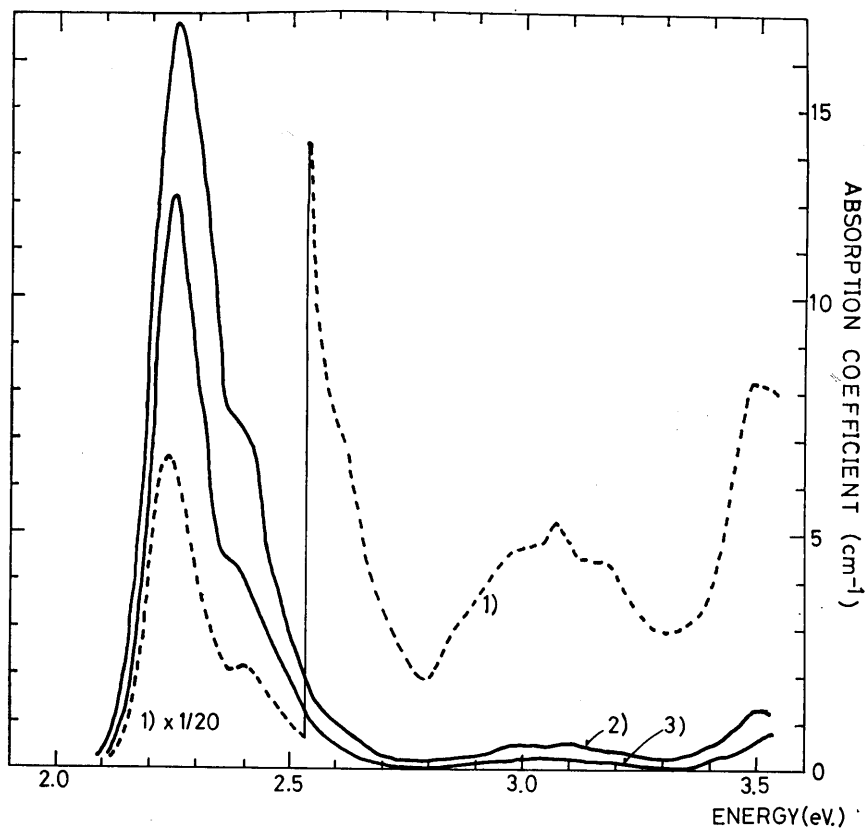
select 365 nm and 546 nm of Hg lamp respectively.

Rhodamine B used in our experiments is obtained from commercial use (reagent grade, Tokyo Kasei Industries) and no purification has been done in our laboratory.

3. Results and Discussions

Absorption coefficients in the photon energy region between 3.5 and 2.1 eV are measured at room temperature in the solutions of ethanol, acetic acid and water. Absorption spectra of rhodamine B in ethanolic solution are shown, as typical absorption results, in Fig. 4, in which three dominant absorption bands are found; main peaks between 2.2 and 2.5 eV, broad band at about 3.0 eV and the band of ultra-violet region at about and above 3.5 eV. Although the details of absorption bands are different for different concentrations, the existence of these three bands are clearly recognized in all the solutions examined and therefore these bands may be concluded to show the characteristics inherent to rhodamine B itself. In dilute solutions absorption coefficients beyond 2.5 eV become very small, although main absorption peaks still remain clearly to be seen. Therefore, we shall provisionally confine ourselves to a dominant one of three bands observed in the photon energy region between 2.1 and 2.5 eV and examine its detailed behaviours in the following way.

At first it may be pointed out that the mentioned dominant band in the range



1) 10^{-3} mol/l 2) 10^{-4} mol/l 3) $5 \cdot 10^{-5}$ mol/l

Fig. 4. Absorption spectra of rhodamine B in ethanol.

of photon energy from 2.1 to 2.5 eV has structure of two peaks or one peak and a shoulder. In spite of the rather complicated structure of absorption spectra of rhodamine B, its fluorescence spectra show only one red-yellowish fluorescence in all the solutions examined, either by the excitation of green light (546 nm) or by that of ultra-violet light (365 nm), (See Fig. 5).

Ethanolic Solution

Fig. 6 shows the molar absorption spectra of rhodamine B in ethanol in the photon energy range between 2.1 and 2.5 eV. In contrast to the results obtained for alcoholic solutions of rhodamine 6G and rhodamine 3B, which show slight changes in the absorption spectra at high and low concentrations (LEVSHIN, BARANOVA 1959), molar absorption coefficients of rhodamine B is found to increase with the decrease of concentration.

The above mentioned results in absorption spectra are due to the influence of polymers as will be described below. As the concentration decreases, much more

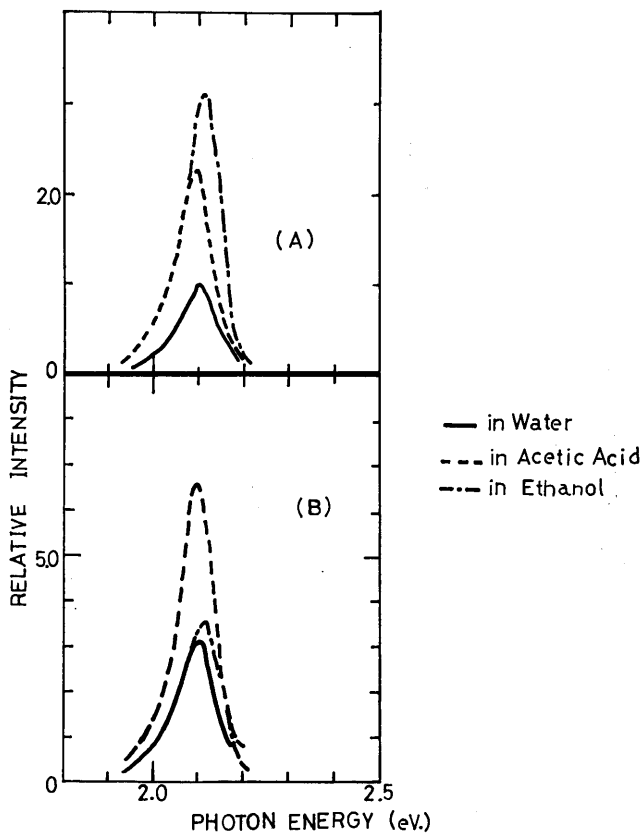


Fig. 5. Fluorescence spectra of rhodamine B in various solutions. 5(A) shows the fluorescence spectra excited by Hg lamp of 365 nm wavelength and 5(B), by that of 546 nm wavelength.

polymers are reasonably supposed to dissociate into dimers and monomers. If polymers are supposed to be non-absorbing or to show little absorption in the photon energy region mentioned above, the decrease of polymers in dilute solution leads to the increase of the fraction of monomers and/or dimers, and then to the resulting growth in the absorption coefficients due to the latters.

MAGNUSSON (1970) has separately measured monomeric and dimeric absorption spectra of water in carbon tetrachloride. However, only the total absorption spectra of rhodamine B have been measured in our experiment and then the absorption spectra of monomers and dimers are to be calculated by the aid of the method of analysis as shown later in the section of "Aqueous Solution." Unfortunately, the mentioned method of analysis cannot be applied to the case of ethanolic solution since fraction of polymers in our case and their absorption spectra are undetermined experimentally.

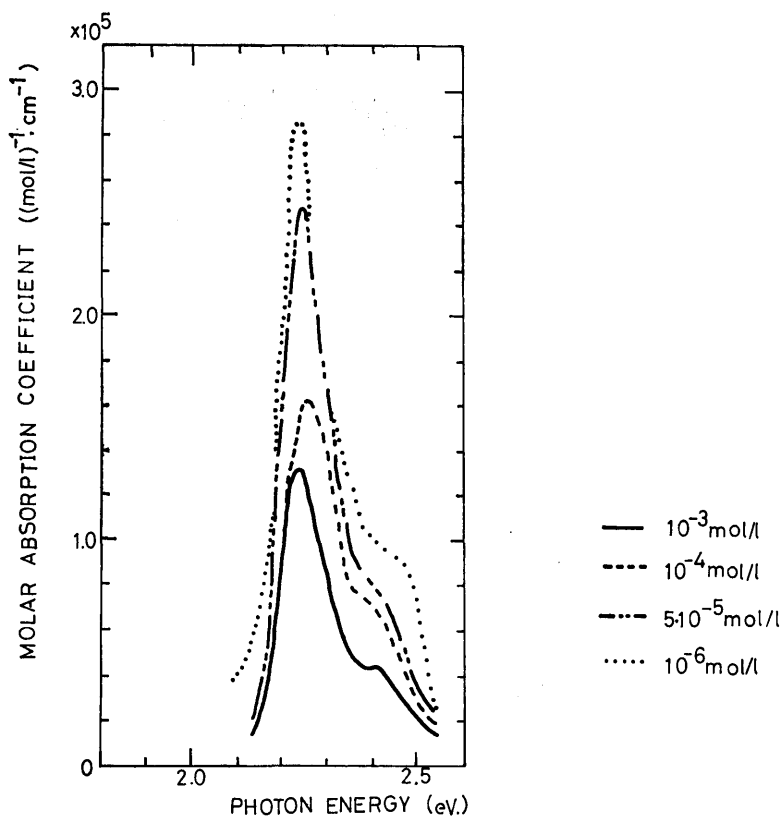


Fig. 6. Molar absorption spectra of rhodamine B in ethanol.

Influence of pH

Optical absorption and luminescence of organic compound of 4-methylumbelliferone are found to be very sensitive to HCl and NaOH and, moreover, lasing spectrum of 4-methylumbelliferone is observed to change drastically with acidification or alkalization (SHANK *et al.* 1970). Being suggested by the above mentioned result, we examined the influences of acid and alkali on the absorption spectra of rhodamine B in ethanolic solutions (Fig. 7). By the addition of 0.016 M NaOH in ethanolic solutions of $5 \cdot 10^{-5}$ mol/l rhodamine B, main absorption peak shifts slightly to larger photon energy side, whereas, by the addition of 0.13 M HCl, main absorption peak shifts slightly to smaller energy side. Large amount of HCl (67% ethanol and 33% HCl) decreases the absorption coefficient and broadens the band width to a considerable amount.

From the above mentioned results we are allowed to suppose that appreciable amount of rhodamine B molecules chemically react with HCl to form new other compounds which results in the decrease and broadening of the absorption spectrum. However, in the case of rhodamine B pH does not give rise to so influential effect upon optical absorption compared with that of 4-methylumbelliferone.

Optical Properties of Rhodamine B in the Solutions

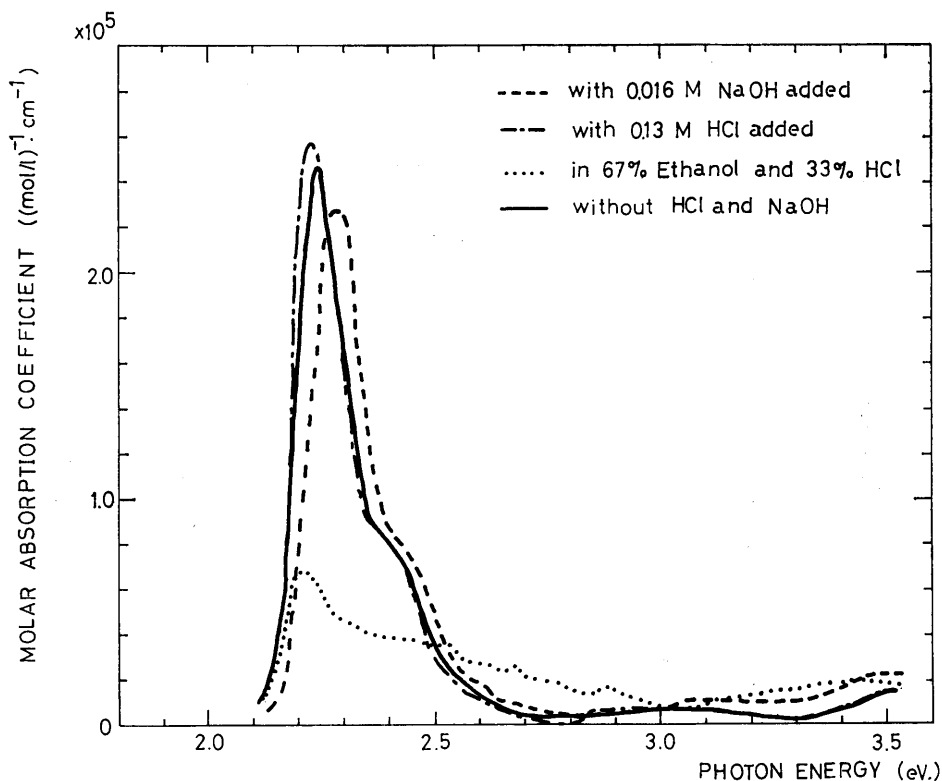


Fig. 7. Influence of HCl and NaOH on the absorption spectra of rhodamine B ($5 \cdot 10^{-5}$ mol/l) in ethanol.

Acetic Acidic Solution

In the solution of acetic acid, peak absorption coefficients of rhodamine B are observed to decrease with its increasing concentration in the range of 10^{-4} to 10^{-3} mol/l, while to decrease in the range of 10^{-6} to 10^{-4} mol/l. However, the shoulders of the absorption spectra show little change with concentrations as far as our measurements do concern, (See Fig. 8). It may reasonably be considered that monomeric molecules rather than polymeric ones are more effective for the absorption process as will be seen in the case of "Aqueous Solution."

The above mentioned characteristics may be understood as follows. In acetic acidic solution, the number of monomers of rhodamine B is supposed to be controlled by two processes; chemical equilibrium between monomers and polymers and chemical reaction of monomers with the solvent. As far as the chemical equilibrium does concern, it is well known that the relative number of monomers to polymers decreases with increasing concentration. Whereas, if a constant number of monomers is supposed to react with acetic acid, the corresponding decrease in the number of monomers leads to the decrease of molar absorption coefficients with decreasing concentration, as far as the transformation between monomers and polymers is

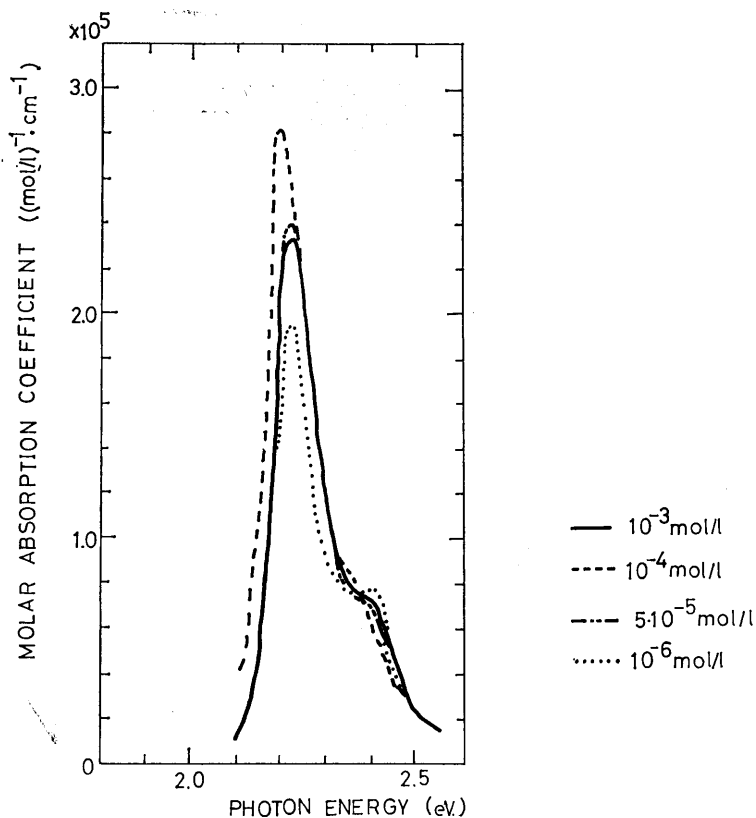


Fig. 8. Molar absorption spectra of rhodamine B in acetic acid.

disregarded. At higher concentrations ($>10^{-4}$ mol/l), the former process (monomer \rightleftharpoons polymer) may be expected to be predominant as compared with the latter (chemical reaction with acetic acid), and then the molar absorption coefficients decrease with increasing concentration. On the other hand, at lower concentrations ($<10^{-4}$ mol/l), the latter process seems to become more effective than the former and so the molar absorption coefficients increase with increasing concentration.*

Aqueous Solution

The absorption spectra of rhodamine B at different concentrations are shown

* The observed total molar absorption coefficient α is written as

$$\alpha = \alpha_m(L - Z/m - F(m)/m),$$

where α_m denotes molar absorption coefficient of monomers, Z , number of monomers which chemically reacts with acetic acid, $F(m)$, number of monomers which associate into polymers, L , number of molecules of rhodamine B per unit molecular weight and m shows concentration of rhodamine B in mol. At higher concentrations, $Z \ll F(m)$ and at lower concentrations, $Z \gg F(m)$.

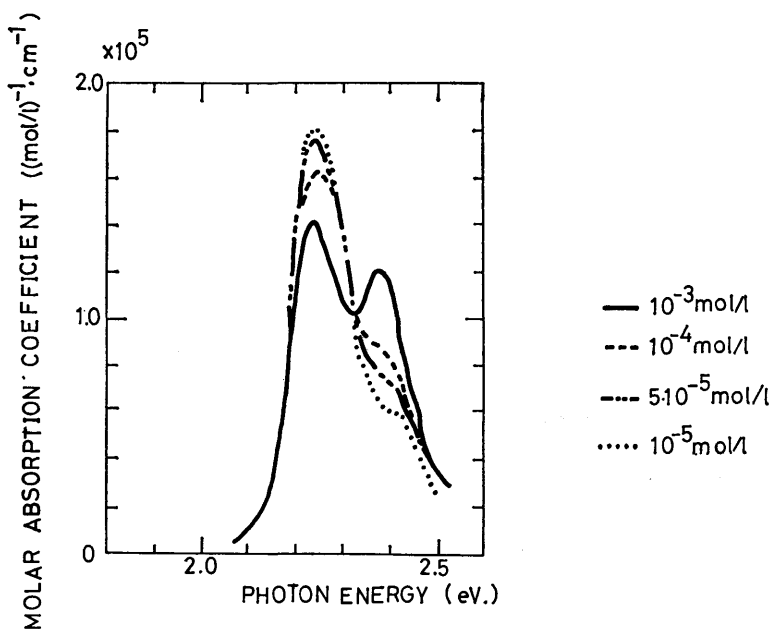


Fig. 9. Molar absorption spectra of rhodamine B in water.

in Fig. 9. The spectra at the concentration of 10^{-3} mol/l have two definite maxima at about 2.5 eV and 2.1 eV, and decrease of the concentration leads to a gradual decrease of smaller photon energy peak and to a corresponding growth of the larger photon energy peak. This concentration dependence of absorption spectra resembles to those obtained by LEVSHIN and BARANOVA (1959) on the aqueous solutions of rhodamine 6G and rhodamine 3B, in which concentration-dependence of absorption spectra is attributed to the dissociation and association between dimers and monomers.

In the following we shall calculate fraction of monomers at different concentrations in addition to the estimation of individual absorption spectra of monomer and dimer from the observed total absorption spectra, applying Baranova's method of analysis of rhodamine 6G and rhodamine 3B (LEVSHIN, BARANOVA 1959; BARANOVA 1962) to the present case. At first, we put for the relations of various absorption coefficients

$$\alpha(E) = \alpha_m(E) \cdot x + \alpha_d(E) \cdot (1-x), \quad (1)$$

where α , α_m and α_d are total molar absorption coefficient and those of monomers and dimers respectively at photon energy E , and x denotes fraction of monomers.

Next, from the law of mass action, we have

$$\frac{x^2}{1-x} = \frac{D}{C}, \quad (2)$$

assuming that chemical equilibrium of [monomer + monomer \rightleftharpoons dimer] exists between monomers and dimers. In (2) D is the equilibrium constant and C the concentration of rhodamine B.

It follows from (1) and (2),

$$\frac{(\alpha - \alpha_d)^2}{\alpha_m - \alpha} = \frac{D}{C} (\alpha_m - \alpha_d). \quad (3)$$

Since α_m is obtained experimentally at the limit of low concentrations, in which monomer fraction becomes almost unity as shown based on chemical evidence, there remain in (3) two unknown quantities α_d and D . Using (3) for two observed absorption spectra corresponding to two moderate concentrations for which the formation of higher polymers is negligible, α_d and D may be determined. From two equations (3) for two moderate concentrations C_1 and C_2 we obtain, eliminating D ,

$$\alpha_d = \frac{\alpha_1 - B\alpha_2}{1 - B}, \quad (4)$$

where

$$B = \sqrt{\frac{C_2(\alpha_m - \alpha_1)}{C_1(\alpha_m - \alpha_2)}},$$

α_1 and α_2 are the corresponding observed absorption coefficients. By the use of α_d obtained by (4) and (1) we can determine the fraction of monomer x for all the concentrations.

The calculated values of fraction of monomers are presented in Table 1 and estimated monomeric and dimeric absorption spectra are shown in Fig. 10, in which the lowest concentration of rhodamine B in our case, i.e., 10^{-5} mol/l is reasonably assumed to be completely monomeric. As shown in Table 1, concentration-dependence of the fraction of monomers of rhodamine B behaves in quite similar way

Table 1. Fraction of monomers (x) at different concentrations of rhodamine B, rhodamine 6G and rhodamine 3B in aqueous solutions.

Concentration (mol/l)	Rhodamine B*	Rhodamine 6G**	Rhodamine 3B**
$4 \cdot 16^{-6}$	—	(1.00)	(1.00)
$1 \cdot 10^{-5}$	(1.00)	0.95	—
$4 \cdot 10^{-5}$	—	0.87	0.95
$5 \cdot 10^{-5}$	0.85	—	—
$1 \cdot 10^{-4}$	0.73	0.72	0.90
$1 \cdot 10^{-3}$	0.35	0.35	0.58

* indicates our results and **, Baranova's results. (1.00) shows that all the molecules involved are assumed to be monomeric.

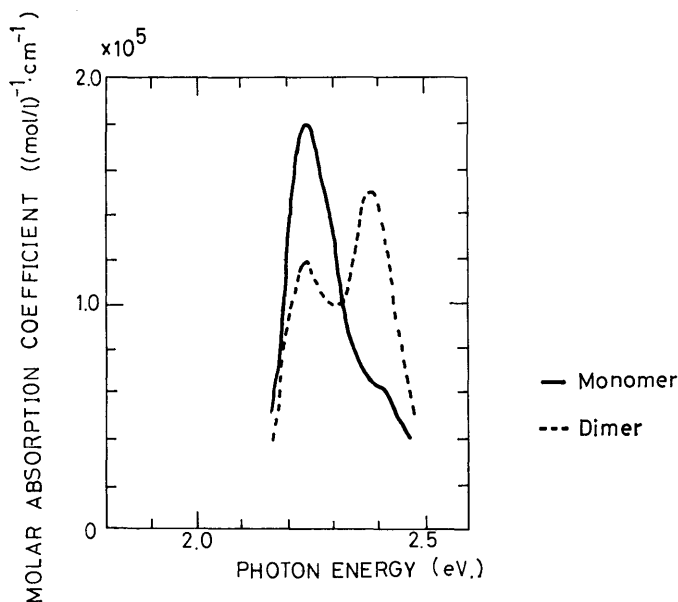


Fig. 10. Molar absorption spectra of monomers and dimers of rhodamine B in aqueous solutions.

to that of rhodamine 6G. On the other hand, spectral distribution of dimeric absorption of rhodamine B in Fig. 10, resembles to that of rhodamine 3B, in which a smaller one of two absorption peaks appears at the photon energy near the absorption maximum of monomer (BARANOVA 1962). Therefore, absorption characteristics of rhodamine B seem to be partly similar to rhodamine 6G and partly similar to rhodamine 3B, which characteristic behaviours are well understood, allowing for the structural formulas of those molecules as was already described in "Introduction" of this article.

In aqueous solutions, the fluorescent intensity is measured as a function of exciting photon energy. In the case when the light of photon energy E is incident on the front surface of the sample cell ($x=0$) with intensity $I(0, E)$, the light intensity $I(x, E)$ at depth x along incident beam of light may be written as

$$I(x, E) = I(0, E) \exp(-\alpha_t x), \quad (5)$$

in which α_t denotes total absorption coefficient of rhodamine B in aqueous solution

Fluorescence emission of rhodamine B in aqueous solution follows after optical absorption of exciting light. For fluorescence intensity $F(x, E', E)$ of photon energy E' , emitted at x , therefore, we have

$$F(x, E', E) = \eta \alpha I(x, E), \quad (6)$$

where α denotes absorption coefficient of some kind of molecule which contributes to fluorescence emission and η , its quantum efficiency.

From (5) and (6) we have, for total fluorescent intensity $F(E', E)$,

$$F(E', E) = \int_0^l F(x, E', E) dx = \eta \alpha l \bar{I}(E), \quad (7)$$

where

$$\bar{I}(E) = \frac{\int_0^l I(0, E) \exp(-\alpha_l x) dx}{\int_0^l dx}, \quad (8)$$

and l denotes length of the cell along incident light beam.

Hence

$$\frac{F(E', E)}{\bar{I}(E)} = \eta \alpha l. \quad (9)$$

In the case when $\alpha_l l \ll 1$, (9) can be written as

$$\frac{F(E', E)}{I(0, E)} = \eta \alpha l. \quad (10)$$

The left-hand sides of (9) and (10) are usually called the fluorescence excitation intensity.

Fig. 11 shows the fluorescence excitation spectra of both 10^{-3} and 10^{-4} mol/l

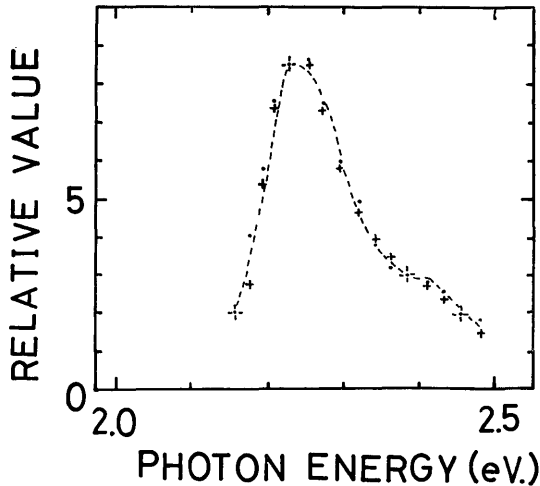


Fig. 11. Fluorescence excitation spectra and absorption spectrum of monomer in aqueous solutions of rhodamine B. $E' = 2.033$ eV, corresponding to $\lambda = 610$ nm.

Dots indicate fluorescence excitation intensity at 10^{-4} mol/l, crosses fluorescence excitation intensity at 10^{-3} mol/l and dashed line expresses normalized absorption coefficient of monomer.

concentration, in addition to monomeric absorption spectrum. In Fig. 11, fluorescence excitation spectrum of 10^{-3} mol/l is obtained by using (9) and that of 10^{-4} mol/l, by (10); because $\alpha_t l$ becomes larger than unity for some values of α_t at 10^{-3} mol/l, whereas $\alpha_t l \ll 1$ does hold always at 10^{-4} mol/l.

As shown in Fig. 11, fluorescence excitation spectra of both 10^{-3} and 10^{-4} mol/l rhodamine B are found to coincide well with suitably normalized monomeric absorption spectrum. The mentioned result shows that α of (9) and (10) becomes α_m (absorption coefficient of monomeric rhodamine B) and η (its quantum efficiency) is constant in the observed photon energy region. Then, $\alpha = \alpha_m$ leads to the conclusion that the fluorescence of rhodamine B at the above mentioned concentrations is originated mostly from light absorption and emission by monomers. On the other hand, dimers are seen to make little contribution to the fluorescence of rhodamine B in aqueous solution, though they do absorb actually some amount of exciting light. Unfortunately, absolute measurement of fluorescent intensity cannot be made in our experiments, only its relative values being observed. Therefore, absolute value of η is left unknown in our case.

From our result mentioned above, it may be concluded that almost all the lasing of rhodamine B in aqueous solutions is originated from the light absorption and emission associated with the transition between quantum states of monomers.**

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REFERENCES

- BARANOVA, E. G., (1962): Study of the Association of Rhodamine 3B and 6G in Aqueous Solutions, *Opt. Spectry.*, **13**, 387.; Study of the Association of Rhodamine 6G in Ethanol and Glycerol Solutions, *ibid.*, **13**, 452.
- CHO, B-Y., NELSON, R. C., and BROWN, L. C., (1963): Electron Spin Study of Some Organic Photoconductors, *J. Chem. Phys.*, **39**, 499.
- LEVSHIN, V. L., and BARANOVA, E. G., (1959): The Study of the Concentration Excitation of the Luminescence of Dyes in Various Solutions and Isolation of Various Types of Excitation, *Opt. Spectry.*, **6**, 31.
- MELHUISH, W. H., (1962): Calibration of Spectrometers for Measuring Corrected Emission Spectra, *J. Opt. Soc. Am.*, **52**, 1256.
- McFARLAND, B. B., (1967): Laser Second-Harmonic-Induced Stimulated Emission of Organic Dyes, *Appl. Phys. Lett.*, **10**, 208.
- MAGNUSSON, L. B., (1970): Infrared Absorbance by Water Dimer in Carbon Tetrachloride Solution, *J. Phys. Chem.*, **74**, 4221.

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Jun'ichiro MUTO

- NELSON, R. C., (1954): Organic Photoconductors. I. The Kinetics of Photoconductivity in Rhodamine B, *J. Chem. Phys.*, **22**, 885.
- SCHAEFER, E. P., SCHMIDT, W., and MARTH, K., (1967): New Dye Laser Covering the Visible Spectrum, *Phys. Lett.*, **24A**, 280.
- SHANK, C. V., DIENES, A., TROZZOLO, A. M., and MYER, J. A., (1970): Near uv to Yellow Tunable Laser Emission from an Organic Dye, *Appl. Phys. Lett.*, **16**, 405.
- WEBER, G., and TEALE, F. W. J., (1958): Fluorescence Excitation Spectrum of Organic Compounds in Solution Part I.-Systems with Quantum Yield Independent of Exciting Wavelength, *Trans. Farad. Soc.*, **53**, 640.