# Influence of Aggregation on the Fluorescence Decay of Organic Laser Dyes

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Singlet decay times in dependence on temperature, concentration, solvent and detergent were measured in solutions of organic laser dyes. In the temperature range from 300 K to 115 K the reciprocal decay time obeys an Arrhenius relationship, the parameters of which were determined. Additional measurements were carried out on Acridinorange because a biexponential fluorescence decay due to monomers ($\tau = 4.2$ ns) and aggregated molecules ($\tau = 14.7$ ns) was found.

## 1. Introduction

This work reports on measurements of the fluorescence decay of Rhodamine 6G, Rhodamine B, Acridinorange, Eosin blue, PPO and 7-diethylamino-4-methylcumarin. Especially the change of the fluorescence decay with formation of aggregates was investigated. Organic dye solutions consist of monomers and aggregated molecules. The equilibrium between them, given by the law of mass action, can be influenced in different ways [1]. There will result

- more aggregated molecules by lowering the temperature,
- more aggregated molecules by increasing the dye concentration,
- more aggregated molecules by using water as solvent and more monomers by using alcohol,
- more monomers by adding a detergent (Triton X 100),
- more monomers by increasing the temperature.

The last mentioned method could not be used in our case because of the thermal degradation of the dyes [2]. All the other methods were employed on six organic laser dyes. Three of these (Acridinorange, Rhodamine 6G, Rhodamine B) were investigated in more detail, because fluorescent dimers have been supposed by other authors [3, 4]. Since no spectroscopic analysis was done, superpositions of decay processes could only be identified if the decay times were sufficiently different.

## 2. Experimental

The dye samples, contained in a quarz cuvette, were excited by a pulsed coaxial nitrogen laser [5]. The pulse has a non-exponential decay characteristic of the intensity and a decay time less than 1,5 ns. Peak power was about 10 kW. Care had to be taken to suppress stimulated emission of the dyes by expanding the exciting pulse. A high speed 125 Ω photodiode (FD 125 from JTL, S 20 cathode) with a risetime of 0.2 ns monitored the time dependence of the fluorescence. A Tektronix R 7912 transient digitizer which operated as analog-to-digital converter recorded the $x$-signal. This information was stored and displayed on an $x$-$y$ monitor and registered by a camera. The risetime of the equipment was 0.8 ns. By using a Rhodamine 6G solution in methanol ($T = 300$ K, $c = 1 \cdot 10^{-5}$ m) the system was calibrated. The resulting decay time was $\tau = 4.7$ ns. Fluorescence and exciting pulse ($\lambda = 337$ nm) were separated by two Schott filters GG 18/2 and OG 22/1. For low temperature experiments the alcoholic solutions (a mixture of 10% methanol (uvasol) and 90% ethanol (uvasol)) were filled into a closed cuvette, then placed in an evacuated dewar [6] and continuously cooled by liquid nitrogen. The temperature was measured by a calibrated thermocouple inside the solution. The absorption measurements were made by a GCA-McPherson Dual Beam Spectrophotometer EU-707 at 300 K and 120 K. The thermocouple was mounted on the cell surface. The thickness of the layer was $d = 0.1$ mm. The dyes were bought either from Eastman-Kodak or Lambda Physics Göttingen.

## 3. Results and Discussion

### 3.1. Alcoholic Solutions

Figure 1a shows fluorescence versus time for Acridinorange ($5 \cdot 10^{-4}$ m) at three temperatures

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(300 K, 180 K, 115 K). Figure 1 b presents the same results using a semilogarithmic scale. For short times there is an apparent deviation from the exponential decay, which is due to the exciting pulse. For this reason we evaluated the decay curves usually for periods between 2 ns and 30 ns after the maximum only. For each of the six dyes we determined the fluorescence decay time at two concentrations and in the temperature range from 300 K to 115 K. The results are summarized in Table 1. Except Acridinorange, all the dyes show in the whole temperature range a single exponential course of the fluorescence decay.

The observed increase of the decay times with decreasing temperature can be described by the equation

$$1/\tau = K_{\mathrm{R}} + K_{\mathrm{NR}}\,, \tag{1}$$

$\tau$ = fluorescence decay time,
$K_{\mathrm{R}}$ = radiative rate constant,
$K_{\mathrm{NR}}$ = nonradiative rate constant.

The temperature dependence of the fluorescence decay time is given mainly by the temperature dependent probability of the radiationless transition:

$$K_{\mathrm{NR}} = K_{\mathrm{NR}}^{0} \exp[- E_{\mathrm{A}}/kT]\,. \tag{2}$$

Assuming this relation the fluorescence decay may be expressed by:

$$1/\tau = K_{\mathrm{R}} + K_{\mathrm{NR}}^{0} \exp[- E_{\mathrm{A}}/kT]\,. \tag{3}$$

In order to determine $K_{\mathrm{R}}$ we supposed a quantum efficiency of $\Phi = 1$ at $T = 115$ K for the monomers. $E_{\mathrm{A}}$ and $K_{\mathrm{NR}}$ were calculated from adjacent pairs of experimental data for $\tau$ and $T$ by simultaneously solving two sets of Equation (3). The results are given in Table 1.

Each dye (except Acridinorange) shows at $T = 115$ K a decay time which is independent of concentration thus confirming the above assumption that at low temperatures only one sort of molecules is fluorescent. The observed differences in the decay times at $T = 300$ K are induced by concentration quenching.

The temporal course of the fluorescence of Acridinorange at low temperatures is a superposition of two components. The resulting intensity may be expressed by the equation

$$J_{\mathrm{F}} = J_1 \exp[- \tau_1 t] + J_2 \exp[- \tau_2 t] \tag{4}$$

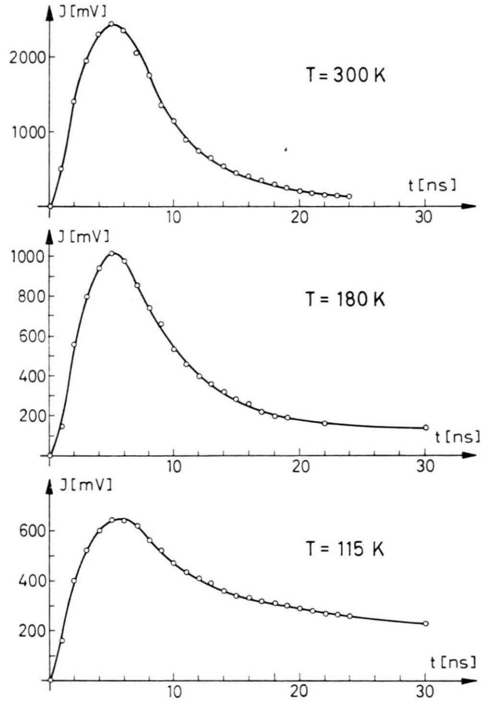

Fig. 1 a

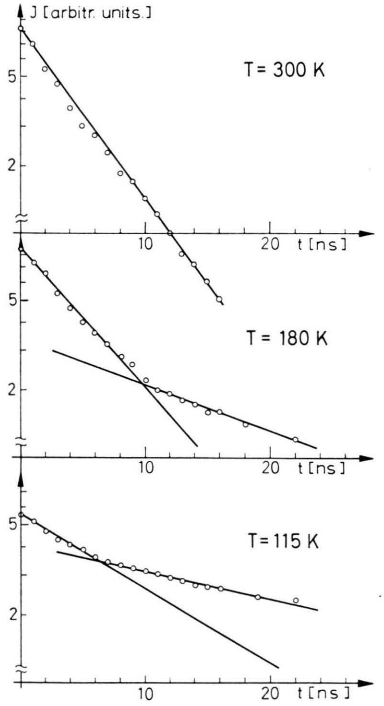

Fig. 1 b

Fig. 1. Measured decay curve of a $5 \cdot 10^{-4}$ m alcoholic solution of Acridinorange at $T = 300$ K, $T = 180$ K, and $T = 115$ K. (a) Linear plot (redrawed polaroid pictures), (b) semilogarithmic plot.

Table 1. Fluorescence decay times in dependence of temperature, (solvent mixture of 10% methanol + 90% ethanol) Arrhenius parameters $E_A$ and $K^0_{NR}$.

| Temperature [K] | | 300 | 275 | 255 | 235 | 215 | 195 | 175 | 155 | 135 | 115 | $E_A$ [cal] | $K^0_{NR}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PPO | $1 \cdot 10^{-3}$ m | 2.1 | 2.1 | 2.1 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | | |
| | $1 \cdot 10^{-4}$ m | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | — | — |
| Eosin blue | $1 \cdot 10^{-3}$ m | 3.6 | 3.6 | 3.7 | 3.8 | 3.8 | 3.9 | 4.0 | 4.0 | 4.1 | 4.1 | | |
| | $1 \cdot 10^{-4}$ m | 3.8 | 3.8 | 3.9 | 3.9 | 4.0 | 4.0 | 4.1 | 4.1 | 4.1 | 4.1 | 1261 | $1{,}5 \cdot 10^8$ |
| 7-diethyl | $1 \cdot 10^{-3}$ m | 3.6 | 3.9 | 4.2 | 4.4 | 4.5 | 4.7 | 4.8 | 4.9 | 4.9 | 4.9 | | |
| | $1 \cdot 10^{-4}$ m | 3.6 | 3.8 | 4.0 | 4.2 | 4.5 | 4.7 | 4.8 | 4.9 | 4.9 | 4.9 | 2440 | $43 \cdot 10^8$ |
| rhodamine 6G | $1 \cdot 10^{-3}$ m | 4.3 | 4.3 | 4.4 | 4.5 | 4.6 | 4.6 | 4.7 | 4.7 | 4.7 | 4.7 | | |
| | $1 \cdot 10^{-5}$ m | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | 4.7 | — | — |
| rhodamine B | $1 \cdot 10^{-3}$ m | 2.9 | 3.3 | 3.6 | 3.9 | 4.1 | 4.4 | 4.6 | 4.7 | 4.8 | 4.8 | | |
| | $1 \cdot 10^{-5}$ m | 3.2 | 3.6 | 4.0 | 4.3 | 4.4 | 4.6 | 4.7 | 4.7 | 4.8 | 4.8 | 2675 | $90 \cdot 10^8$ |
| acridinorange | $2 \cdot 10^{-3}$ m | 5.3 | 5.6 | 6.1 | 6.4 | 6.9 | 5–6 | 5–6 | 5–6 | 6–7 | 6–7 | | |
| | | | | | | | 10–12 | 12–14 | 14–16 | 16–18 | 18–20 | — | — |
| | $1 \cdot 10^{-3}$ m | 4.7 | 5.0 | 5.5 | 5.6 | 5.9 | 6.3 | 6.6 | 5–6 | 5–6 | 6–7 | | |
| | | | | | | | | | 9–10 | 10–15 | 15–20 | — | — |
| | $1 \cdot 10^{-4}$ m | 4.7 | 4.9 | 5.1 | 5.3 | 5.5 | 5.6 | 5.8 | 5.9 | 5.9 | 5.9 | 2256 | $19 \cdot 10^8$ |

where

$J_F$ = resulting fluorescence intensity,
$\tau_1$ = decay time of the short process,
$\tau_2$ = decay time of the longer process.

$\tau_1$ and $\tau_2$ may be determined without considering the first process at longer times. From the resulting value of $\tau_2$ we can calculate a value for $\tau_1$. By plotting the course of the two intensities in a semilogarithmic scale, we can correct both of them. The results are given in Table 1. The observed biexponential process of the fluorescence of Acridinorange confirms the spectroscopic measurements of Zanker [3]. He determined the distribution of the acridinfluorescence and absorption in the temperature range from 300 K to 100 K using as solvent a mixture of alcohol and ether at concentrations between $1 \cdot 10^{-5}$ m and $1 \cdot 10^{-2}$ m. At $T = 100$ K and $c = 1 \cdot 10^{-3}$ m he observed in the fluorescence spectrum three peaks namely at $\lambda = 5700$ Å (strong), $\lambda = 5400$ Å (strong), and $\lambda = 5050$ Å (weak). He explained these peaks by the fluorescence of monomers and aggregated molecules.

The two decay processes observed by us are different by the temperature dependence of the intensities. The intensity of the short process decreases with decreasing temperature, the longer process is distinguished by a slight increase (Figure 2). This corresponds to the behaviour of monomers (decreasing) and aggregated molecules (increasing) observed by Zanker [3]. Supposing that the decay processes are caused not only by monomers but also by aggregated molecules we made further experiments in aqueous solutions to verify these considerations.

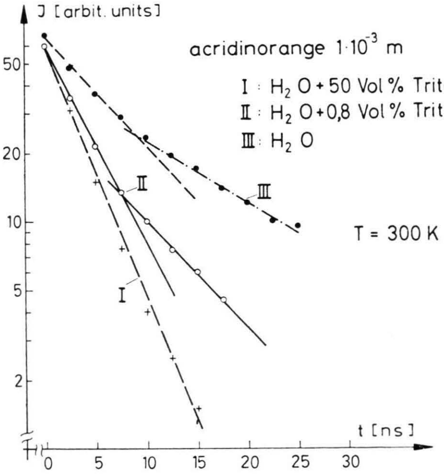

Fig. 2. Semilogarithmic plot of the measured decay curve of a $1 \cdot 10^{-3}$ m aqueous solution of Acridinorange with and without Triton X100 at $T = 300$ K.

### 3.2. *Aqueous Solutions*

Using a polare solvent like water it is possible to get a great number of aggregated molecules already at $T = 300$ K. Therefore we measured the decay process for Rhodamine 6G, Rhodamine B and Acridinorange solved in purified water and purified

Table 2. Fluorescence decay time in aqueous solution at $T = 300$ K; relative quantum efficiency $\Phi_T/\Phi_H$.

| Dye | Concentration [mol/l] | Solvent | Fluorescence decay time [ns] | $\Phi_T/\Phi_H$ |
|---|---|---|---|---|
| rhodamine B | $5 \cdot 10^{-4}$ | $H_2O$ | 3.0 | $1.5_3$ |
| | $5 \cdot 10^{-4}$ | $H_2O$ + 0.8 Vol % Triton | 4.6 | |
| | $1 \cdot 10^{-3}$ | $H_2O$ | 2.9 | $1.3_4$ |
| | $1 \cdot 10^{-3}$ | $H_2O$ + 0.8 Vol % Triton | 3.9 | |
| | $2 \cdot 10^{-3}$ | $H_2O$ | 2.8 | $1.1_8$ |
| | $2 \cdot 10^{-3}$ | $H_2O$ + 0,8 Vol % Triton | 3.3 | |
| | $2 \cdot 10^{-3}$ | $H_2O$ + 50 Vol % Triton | 3.7 | $1.3_2$ |
| rhodamine 6G | $5 \cdot 10^{-4}$ | $H_2O$ | 3.7 | $1.4_1$ |
| | $5 \cdot 10^{-4}$ | $H_2O$ + 0.8 Vol % Triton | 5.2 | |
| | $1 \cdot 10^{-3}$ | $H_2O$ | 3.6 | $1.2_5$ |
| | $1 \cdot 10^{-3}$ | $H_2O$ + 0.8 Vol % Triton | 4.5 | |
| | $2 \cdot 10^{-3}$ | $H_2O$ | 2.9 | $1.1_7$ |
| | $2 \cdot 10^{-3}$ | $H_2O$ + 0.8 Vol % Triton | 3.4 | |
| | $2 \cdot 10^{-3}$ | $H_2O$ + 50 Vol % Triton | 4.2 | $1.4_5$ |
| acridinorange | $5 \cdot 10^{-4}$ | $H_2O$ | 4–8/10–15 | |
| | $5 \cdot 10^{-4}$ | $H_2O$ + 0.8 Vol % Triton | 4.2 | |
| | $1 \cdot 10^{-3}$ | $H_2O$ | 4–8/10–15 | |
| | $1 \cdot 10^{-3}$ | $H_2O$ + 0.8 Vol % Triton | 4–7/10–14 | |
| | $1 \cdot 10^{-3}$ | $H_2O$ + 50 Vol % Triton | 3.7 | |
| | $2 \cdot 10^{-3}$ | $H_2O$ | 14.7 | |
| | $2 \cdot 10^{-3}$ | $H_2O$ + 0.8 Vol % Triton | 4–7/12–15 | |

water with Triton X 100 (as detergent) at different concentrations at $T = 300$ K. The results are summarized in Table 2.

When using 50 Vol% Triton care has to be taken that the fluorescence of Triton (decay time $\tau = 4.1$ ns) does not falsify the results. In the case of 0.2 Vol% Triton in the solution the fluorescence is too small to be detectable.

### a) Rhodamine B and Rhodamine 6G

The decay times of Rhodamine B increase with the concentration (concentration quenching) and decrease if a detergent is added, probably due to the reduced dimer concentration [7]. Rhodamine 6G shows a similar behaviour in agreement with the experiments of Alfano et al. [7]. Both dyes obey a single exponential decay-law.

A comparison of dye decay times resulting from experiments with and without Triton enable us to calculate the relative change of the quantum efficiency $\Phi$ when the detergent is added. The quantum efficiency $\Phi$ can be written as follows:

Aqueous solution:

$$\Phi_H = \tau_H/\tau_N \tag{5}$$

where

$\tau_H$ = decay time in water,

$\tau_N$ = natural decay time.

Aqueous solution with Triton:

$$\Phi_T = \tau_T/\tau_N \tag{6}$$

where

$\tau_T$ = decay time in water with Triton.

From Eqs. (5) and (6) one obtains

$$\Phi_T/\Phi_H = \tau_T/\tau_H\,. \tag{7}$$

The results are given in Table 2. With increasing concentration the influence of the detergent becomes smaller. For instance we get for Rhodamine B for $c = 5 \cdot 10^{-4}$ m, $\Phi_T/\Phi_H = 1.52$ and for $c = 2 \cdot 10^{-3}$ m, $\Phi_T/\Phi_H = 1.20$. These results can be explained by the constant number of Triton molecules and the increasing number of aggregated molecules. By enlarging the Triton concentration the decay time and consequently the relative quantum efficiency $\Phi_T/\Phi_H$ increases. The decay time of Rhodamine B ($2 \cdot 10^{-3}$ m) increases from $\tau = 2.8$ ns ($\Phi_T/\Phi_H = 1.0$ without Triton) to $\tau =$

3.3 ns ($\Phi_T/\Phi_H = 1.18$ with 8 Vol% Triton) and $\tau = 3.7$ ns ($\Phi_T/\Phi_H = 1.3$ with 50 Vol% Triton). Rhodamine 6G shows the same behaviour.

### b) Acridinorange

The above mentioned superposition of the fluorescences of monomers and aggregated molecules of Acridinorange in water could be shown by the following experiments:

1. A $5 \cdot 10^{-4}$ m solution without detergent shows two decay processes while the same solution with 0.8 Vol% Triton shows the short process ($\tau = 4.2$ ns) only (Table 2).
2. A $1 \cdot 10^{-3}$ m solution contains a higher percentage of aggregated molecules. Therefore a concentration of 0.8 Vol% detergent is too small to suppress the second process. When 50 Vol% Triton is used, the second process disappeares and only the short one ($\tau = 3.7$ ns) can be observed (Figure 2).
3. A $2 \cdot 10^{-3}$ m solution contains so many aggregated molecules that the short process of the monomers cannot be observed. The decay time of this solution is $\tau = 14.7$ ns. By adding Triton the number of monomers increases and consequently both processes can be detected (Figure 3).

As a result of this, it can be concluded that depending on the concentration ratio of monomers and dimers one of the two processes can be suppressed.

In order to evaluate the time constants we used semilogarithmic plotts and a range of values only.

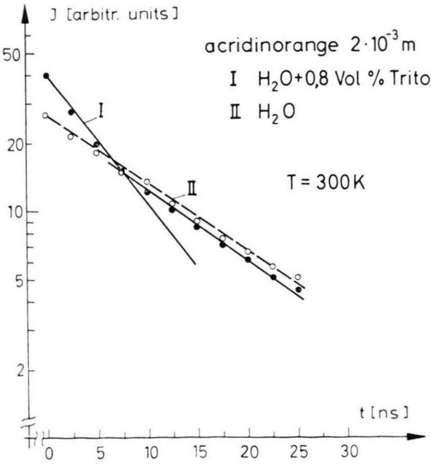

Fig. 3. Semilogarithmic plot of the measured decay curve of a $2 \cdot 10^{-3}$ m aqueous solution of Acridinorange with and without Triton X100 at $T = 300$ K.

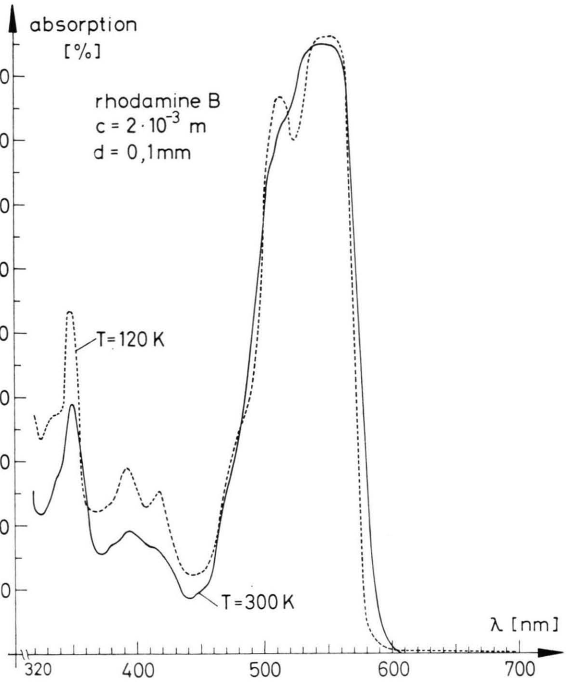

Fig. 4. Absorption spectrum of Rhodamine B, alcoholic solution; $c = 1 \cdot 10^{-3}$ m; $d = 0{,}1$ mm, $T = 300$ K and $T = 120$ K.

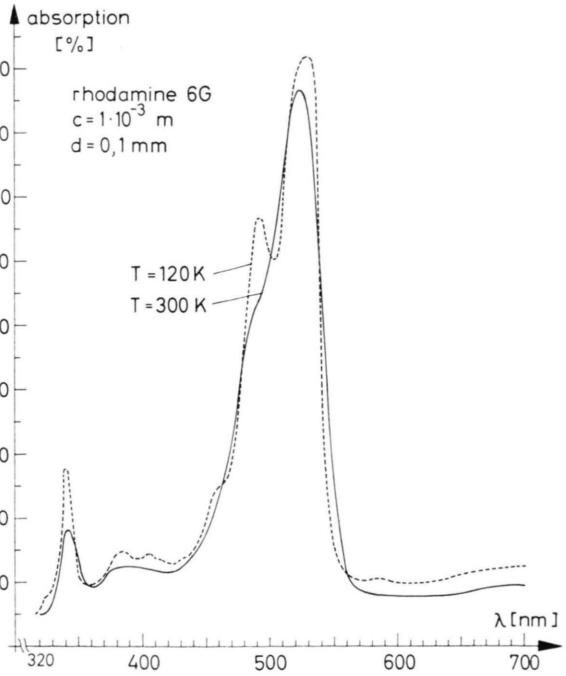

Fig. 5. Absorption spectrum of Rhodamine 6G, alcoholic solution; $c = 1 \cdot 10^{-3}$ m; $d = 0{,}1$ mm, $T = 300$ K and $T = 120$ K.

Better results can be obtained by a computer program [11] or by using aqueous solutions taking into account one process only. Consequently a $c = 5 \cdot 10^{-4}$ m aqueous solution with Triton represents the monomer decay ($\tau = 4.2$ ns) and a $2 \cdot 10^{-3}$ m solution without Triton the dimer decay ($\tau = 14.7$ ns).

### *3.3. Absorption Measurements*

The absorption spectra of Rhodamine 6G, Rhodamine B, and Acridinorange were determined at $T = 300$ K and $T = 120$ K at the concentrations $1 \cdot 10^{-3}$ m and $2 \cdot 10^{-3}$ m in order to check impurities in the dye solutions. The layer thickness was $d = 0.1$ mm. The solvent consisted of 10% methanol and 90% ethanol. Results are shown in Figures 4, 5, and 6.

The measured spectra of Rhodamine B (Fig. 4) indicated that there were neither an impurity nor precipitation during the cooling. At $T = 300$ K the spectrum is in good agreement with the results of Muto [8], who explained the peak at $\lambda = 5160$ Å by the formation of dimers. The slight shift of the maximum to longer wavelengths from $\lambda = 5500$ Å to $\lambda = 5550$ Å is in agreement with the results of Speas [9].

The maximum of Rhodamine 6G (Fig. 5) shifts with decreasing temperature from $\lambda = 5250$ Å to $\lambda = 5290$ Å as Lewshin observed before [10]. The peak at $\lambda = 4930$ Å is induced by dimers. Also with this dye neither an impurity nor precipitation was observed.

Acridinorange indicates neither impurity nor precipitation (Figure 6). The decrease of the absorption at $\lambda = 4930$ Å, the maximum at $\lambda = 4650$ Å, the weak peak at $\lambda = 4400$ Å and the shift of the maximum from $\lambda = 4780$ Å to $\lambda = 4930$ Å are in total agreement with the results of Zanker [3], who explained these variations by the formation of dimers and tetramers. In agreement with these, the three absorption peaks are the fluorescence peaks at $\lambda = 5700$ Å (tetramers), $\lambda = 5400$ Å (dimers), and $\lambda = 5050$ Å (monomers).

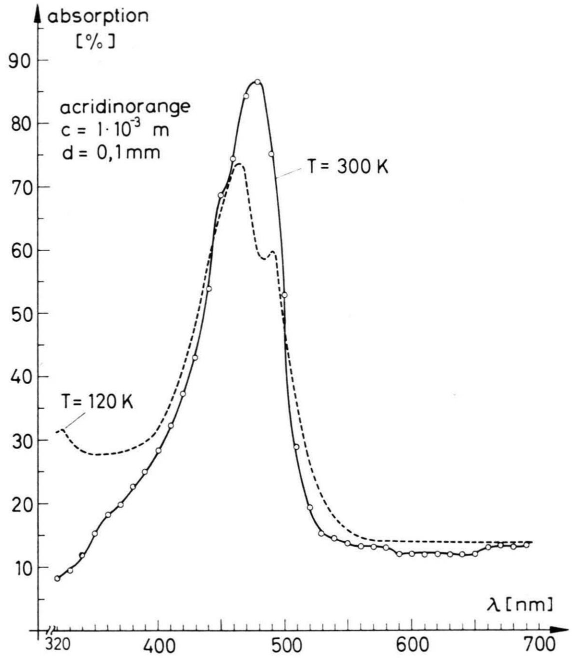

Fig. 6. Absorption spectrum of Acridinorange, alcoholic solution; $c = 1 \cdot 10^{-3}$ m; $d = 0{,}1$ mm, $T = 300$ K and $T = 120$ K.

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[1] Th. Förster, Fluoreszenz organischer Verbindungen, Vandenhoek & Ruprecht, Göttingen 1951.
[2] J. Weber, Physics Letters **57A**, 5 (1976).
[3] V. Zanker, Z. phys. Chemie **200**, 250 (1952).
[4] S. L. Chin, Physics Letters **48A**, 6 (1974).
[5] F. J. Theiss, Opt. Communic. **9**, 25 (1973).
[6] Ch. Heinsohn and J. Weber, Z. Naturforsch. **30a**, 606 (1975).
[7] R. Alfano, S. Shapiro, and W. Yu, Opt. Communic. **7**, 3 (1973).
[8] J. Muto, Keio Engineering Reports **25**, 6 (1972).
[9] W. E. Speas, Phys. Rev. **31**, 569 (1928).
[10] W. L. Lewschin, Z. Physik **72**, 382 (1931).
[11] H. R. Stadelmann, J. Luminescence **3**, 143 (1970).

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