

## TIME RESOLVED SPECTROSCOPY OF RHODAMINE DYE LASER\*

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**Abstract:** In this paper time resolved spectra of a flashlamp-pumped rhodamine 6G dye laser is investigated. Particular attention is given to the influence of triplet-state quencher, cyclooctatetraene, to the laser emission wavelength. Experimental results are favourably compared with the theory. The emission of the second laser line is observed at about 100 Å shorter wavelength than the first line whenever cyclooctatetraene present in ethanolic solution of rhodamine 6G.

### 1. Introduction

After the discovery of Sorokin and Lankard that organic dyes could be optically pumped to lase by lasers<sup>1)</sup> and by fast flashlamps<sup>2)</sup> keen interest has been developed for this new class of lasers. In some features their properties are superior to those of pulsed crystal and glass lasers. The most important quality is tunability. Namely the dye lasers are the first truly tunable lasers which operate throughout the visible spectrum. This quality combined with high-light power makes dye laser an almost ideal scientific tool in the fields of photobiology, photochemistry and photophysics.

However, until recently, it was possible to operate dye laser only in a pulsed regime what was a major drawback for some applications. A radical change has been achieved when Snavely et al.<sup>3)</sup> and Papalardo et al.<sup>4)</sup> used triplet state quenchers with the dyes (oxygen and cyclooctatetraene) and in this way they extended pulse length up to 1 ms for the flashlampexcited dye laser. Quite recently a continuous operation has been achieved for the first time<sup>5)</sup> in a dye laser pumped by continuous argon laser.

The basic theory and instrumentation of organic dye laser is the subject of several reviews<sup>6, 7, 8)</sup>. Therefore, here it will be given a minimum details

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of the theory of dye lasers related only directly to the experimental work presented in this paper.

The aim of this work is to study time resolved behaviour of the flashlamp — excited dye lasers in the presence of the triplet state quencher and to compare experimental results with existing theory<sup>7)</sup>.

## 2. Theory

A number of theoretical papers are devoted to dye laser operation but complete detailed theory has not yet been given, in spite of fact, that these lasers could be treated as an already well elaborated four level system. There are two major reasons for this failure. First emission from organic dyes occurs over a spectral band which may be as wide as 1500 Å and second the importance of molecular triplet states in the lasing process has not been yet properly assessed. This is mainly due to unavailability of triplet state data.

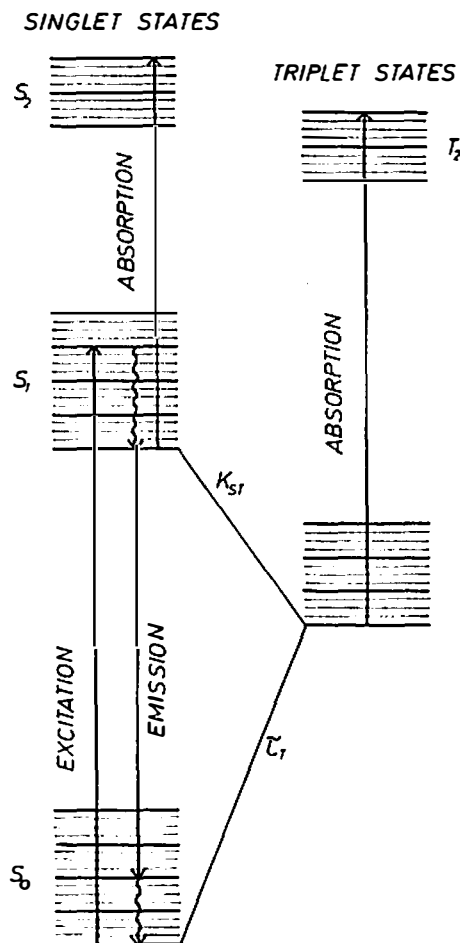


Fig. 1. Schematic energy-level diagram of a dye molecule showing the transitions important to dye laser action.

To simplify further discussion schematic diagram of an organic dye molecule and transitions important for dye laser operation is given in Fig. 1. During an optical pumping, dye molecules are excited into rotational-vibrational levels of  $S_1$  or higher electronic singlet states and quickly decay ( $10^{-10}$ — $10^{-11}$  s) to the lower level of  $S_1$ . From  $S_1$ , molecule relax either to the singlet ground state by fluorescence or to the triplet level system by intersystem

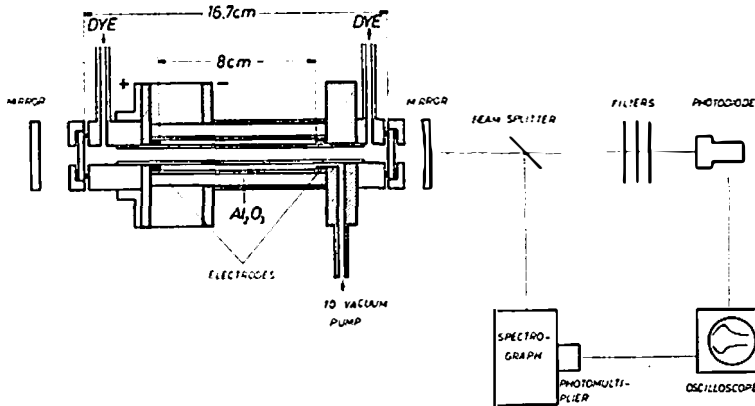


Fig. 2. Schematic diagram of dye laser and experimental arrangement used for spectra recording.

crossing at a rate governed by the intersystem crossing rate constant  $k_{ST}$ . Obviously intersystem crossing competes with fluorescence in the deactivation of  $S_1$  what is detrimental for the operation of the dye laser in several ways<sup>7)</sup>.

When the lowest triplet state is well below  $S_1$  it is usually metastable with a lifetime  $\tau_T > 10^{-4}$  s what is much longer than fluorescence lifetime  $\tau$  (typically  $5 \cdot 10^{-9}$  s). Relaxation from  $T_1$  occurs by phosphorescence or by non-radiative decay in the presence of quenching impurities.

Laser emission arises from transitions between the lower level  $S_1$  and high-lying vibrational levels of the ground state  $S_0$ . The gain of organic dye solution varies, with both frequency and time, during an optical pumping. To analyze this dependence it is necessary to consider a system of two sets of energy levels corresponding to the ground and first excited singlet state and lower level triplet states (Fig. 1) having populations per unit volume  $N_0$ ,  $N_1$  and  $N_T$  respectively. Triplet and excited state molecules are produced only in the active region (length  $L_1$ ) illuminated by the flash pump light. In this region the molecular conservation yields  $N_0 = N - N_1 - N_T$  where  $N$  is the total molecular concentration in the unexcited end regions of the dye cell of the total length  $L_2$ . For the laser with mirror reflectivities  $r_1$  and  $r_2$  Snavely<sup>7)</sup> gave wavelength dependent gain equation which includes stimulated emission and triplet state absorption

$$G(\lambda) = N_i \left[ \frac{\lambda^4 E(\lambda) \eta}{8 \pi \tau c} + \varepsilon_{SS}(\lambda) \right] - N_{\varepsilon_{SS}}(\lambda) \frac{L_2}{L_1} - N_T \left[ \varepsilon_{TT}(\lambda) - \varepsilon_{SS}(\lambda) \right] + \frac{1}{2L_1} \ln(r_1 r_2), \quad (1)$$

where  $c$  is velocity of light,  $\varepsilon_{SS}(\lambda)$  is molecular extinction coefficient and  $\varepsilon_{TT}(\lambda)$  the extinction coefficient for triplet state absorption.  $E(\lambda)$  is the spontaneous fluorescence lineshape function so that

$$\int_0^{\infty} E(\lambda) d\lambda = \phi,$$

where  $\phi$  is the fluorescence quantum yield.

From Equ. (1) it is possible to obtain the excited state population  $N_{ic}$  required for laser oscillation. Namely at the threshold of the laser oscillation  $G(\lambda) = 0$  and by setting Equ. (1) equal to zero and  $\frac{dG}{d\lambda} = 0$  one obtains

$$N_{ic} = K_1 N \left( \frac{L_2}{L_1} \right) + K_2 N_T + K_3, \quad (2)$$

where coefficients  $K_1$ ,  $K_2$  and  $K_3$  are defined by

$$K_1 = \frac{\varepsilon_{SS}(\lambda)}{A(\lambda)},$$

$$K_2 = \frac{\varepsilon_{TT}(\lambda) - \varepsilon_{SS}(\lambda)}{A(\lambda)},$$

$$K_3 = -\frac{\ln r_1 r_2}{2 L_1 A(\lambda)},$$

where  $A(\lambda) = \frac{\lambda^4 E(\lambda) \eta}{8 \pi \tau c} + \varepsilon_{SS}(\lambda)$ .

The Equ. (2) will be further used to compute critical inversion  $N_{ic}$  in function of wavelength, with  $N_T$  as a parameter, at the threshold of the laser operation for our experimental conditions. The result of this computation will be later compared with experiment.

### 3. Experimental setup and procedure

The laser system consisted of the flashlamp co-axial design<sup>9</sup> with discharge taking place in air through 2 mm thick annular region between inner and outer quartz cylinder, Fig. 2. The dye solution was contained in the inner cylinder while around outer quartz tube aluminium oxide was placed to

reflect part of the flashlamp radiation back into dye cuvette. The lamp assembly was mounted on the low inductance capacitor ( $10 \mu\text{F}$ ) which was

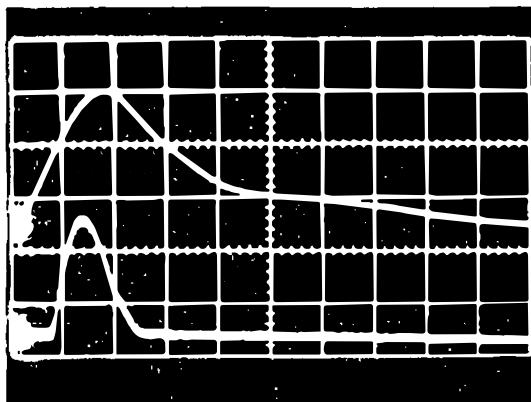


Fig. 3. Characteristic flashlamp pulse (upper trace) and laser emission from  $1 \cdot 10^{-4}$  M/l rhodamine 6G in ethanol. Time base  $1 \mu\text{s}/\text{cm}$ .

charged by high voltage power supply. The lamp was fired by reducing the pressure of air until breakdown occurred and capacitor discharged to produce a flash risetime of  $1.2 \mu\text{s}$ . Characteristic oscillogram of the flash lamp and laser pulse is given in Fig. 3.

The dye cell tube was 15 cm long, 6.5 mm i. d. with optical glass plane windows without antireflection coating. Hemispherical laser resonator consisted of one flat dielectric mirror coated for 99.8% and one curved mirror (radius 100 cm) with 99.0% reflectivity in the region 5800–6400 Å. These mirrors were spaced approximately 30 cm apart.

The laser experiments were carried out with air equilibrated ethanolic solution containing  $1 \cdot 10^{-4}$  M/l of rhodamine 6G with or without triplet state quencher-cyclooctatetraene (COT)  $7 \cdot 10^{-3}$  M/l.

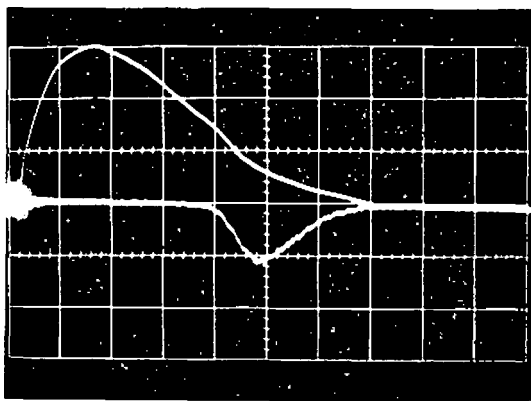


Fig. 4. Integrated laser output (upper trace) and time development laser intensity at 5905 Å. Time base  $0.4 \mu\text{s}/\text{cm}$ .

Spectral distribution of the laser emission was scanned in a shot-by-shot technique using Hilger Medium Quartz spectrograph equipped with photomultiplier attachment. Photodiode EGG SD100 was used to observe integrated laser output. For studies of development of emission frequency, spectrograph output was monitored with RCA 1P28 photomultiplier. The radiation from the flashtube was monitored after it has traversed a number of neutral density filters in order to work in the linear region of the response of the detector. Spectrograph-photomultiplier output was displayed together with flashlamp light or with spectrally integrated laser output on a double beam oscilloscope Tektronix 551. Characteristic oscillogram is given in Fig. 4. Integrated light output was used as a reproducibility check and in further analysis only oscillograms were taken, which did not differ one from another more than 5%. Similar oscillograms were taken at all lasing wavelengths and analyzed at various times after the beginning of the dye laser pulse.

#### 4. Results

Two examples of time and wavelength resolved spectra of rhodamine 6G dye laser are given in Fig. 5. a and b. All necessary measurements for this figure were performed under same experimental conditions (energy of the flashlamp, concentration of rhodamine 6G, laser mirrors etc). The only dif-

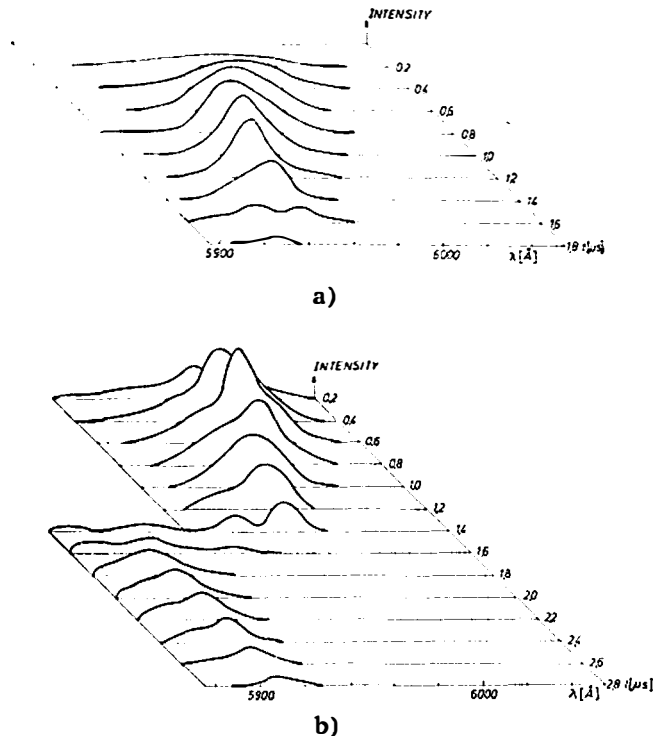


Fig. 5. Time and spectrally resolved laser pulse of rhodamine 6G laser a) without COT and b) with COT.

ference was the presence of triplet state quencher COT in one set of experiments, Fig. 5, b.

Wavelength dependence of the light output of dye laser Fig. 5. can be now used to determine triplet state population and critical inversion in the laser active medium. It is only necessary to evaluate critical inversion curves (Equ. 2) at various concentrations of  $N_T$  for our experimental conditions. All data for this calculus were taken from paper by Snavely<sup>7)</sup> ( $\epsilon_{SS}$ ,  $\epsilon_{TT}$ ,  $\phi$ ,  $A$ ,  $\tau$ ). Some results of our computation are given in Fig. 6. If one finds in Fig. 6 critical inversion curve with a minimum at the laser wavelength,  $N_{1c}$  can be read from the ordinate and  $N_T$  is the value of that particular curve. This procedure is much simplified if data of Fig. 6 are plotted in a different form (Fig. 7). If laser wavelength is known it is very simple now to determine  $N_T$  and  $N_{1c}$ .

Equ. 2 and results in Fig. 6 and 7 can apply correctly only to the laser working at the threshold of operation [ $G(\lambda) = 0$ ]. However if laser operates at low power output it can be assumed that gain is still very small [ $G(\lambda) \approx 0$ ] and curves in Fig. 7 could be further used, after the beginning of laser pulse to determine  $N_T$  and  $N_{1c}$ . This assumption should be satisfied for the laser operating near the threshold of operation as it was in this particular experiment.

### 5. Discussion and conclusion

By careful examination of Fig. 5, a and b one can draw following conclusions

- if COT is present in the dye solution lasing starts at longer wavelength,
- frequency shift of the laser output in the first microsecond is greater if there is no triplet state quencher in the active medium,
- lasing lasts longer with COT in the solution, and
- threshold for laser operation has been decreased for 20% when COT was introduced into the solution of rhodamine 6G. This has not been concluded on the basis of examination of Fig. 5 but experimentally determined.

Almost all these experimental facts could be explained, at least qualitatively on the basis of the theory of laser operation<sup>7)</sup>. First, if triplet state quencher is present in a dye solution, number of molecules in triplet state  $N_T$  decreases, wavelength of laser operation must increase (Fig. 7). From the same figure it is clear that the frequency shift is larger for higher concentration of molecules in triplet state and this is exactly the case when laser operates without COT. It should be noticed that all these consideration has

been limited to the first microsecond of the laser operation when flashlamp pulse increases linearly with time. At later times situation becomes more complicated when intensity of the flashlight decreases and triplet state concentration increases.

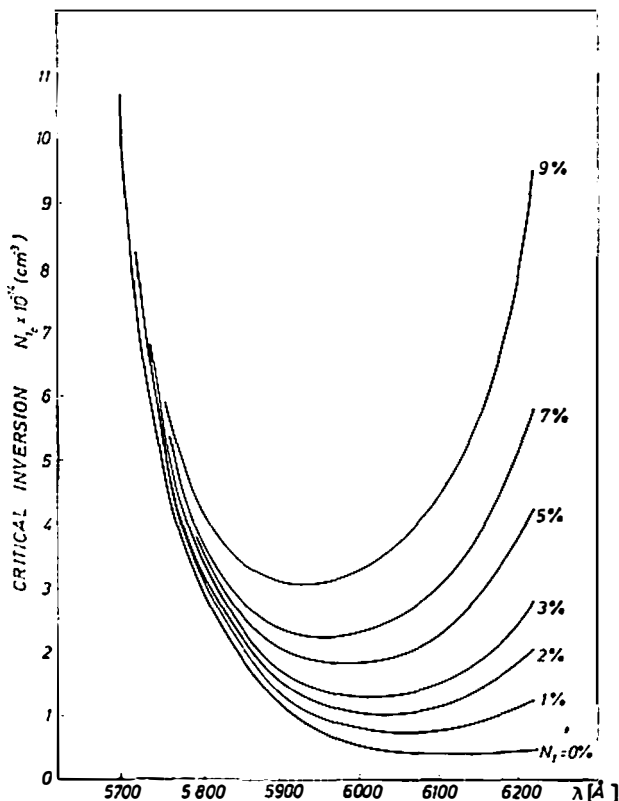


Fig. 6. Critical inversion  $N_c$  versus wavelength curves with triplet state concentration  $N_T$  as a parameter. The curves apply to a dye laser with  $L_1 = 8$  cm,  $L_2 = 16,7$  cm,  $r_1 = 99,8\%$ ,  $r_2 = 99,0\%$  using a  $1 \cdot 10^{-4}$  molar ethanol solution of rhodamine 6G.

Now it should be explained longer lasing time and lowering of threshold for laser operation when COT added into dye solution. It has been already mentioned that the accumulation of dye molecules in the metastable triplet state quenches lasing by absorption between triplet levels. However if this accumulation of dye molecules is reduced by adding a triplet state quenching additive COT into the laser solution lasing must start earlier and last longer.

Finally it is very interesting to notice the appearance of the second laser line at a wavelength about 100 Å shorter than that of the first line (Fig. 5, b). This effect was noticed first time by Röhr<sup>10)</sup> in rhodamine B dye laser but only at high pumping powers (1–2 kJ). He assumed that new line came from the transitions in the triplet system of the dye molecule. However our experiment was performed at pumping powers 10 to 15 times smaller but



the second line always appeared whenever COT was added. This clearly indicate that second line is not coming from the triplet state transition which are quite effectively quenched with COT. At the present no satisfactory explanation for this effect can be offered.

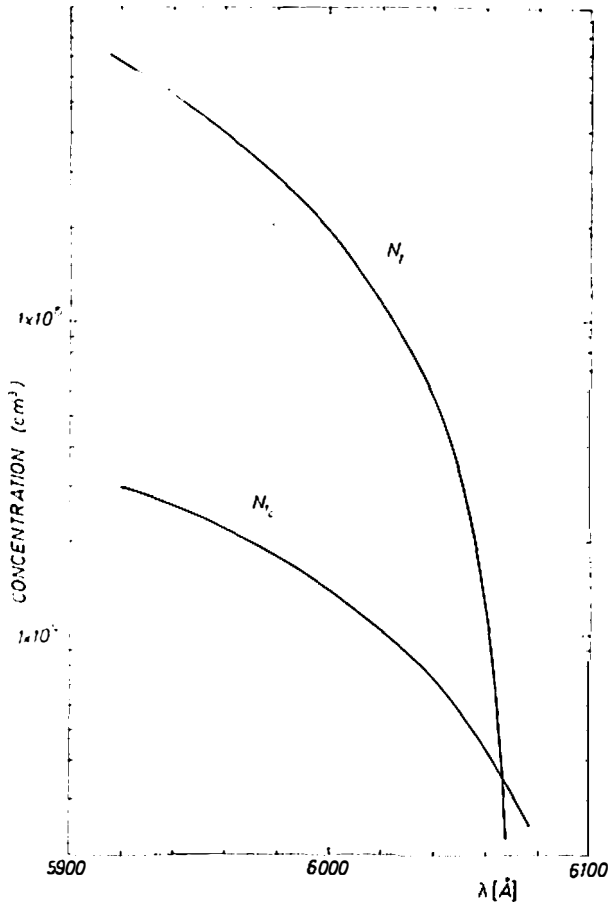


Fig. 7. Minimum values of critical inversion and triplet-state concentration corresponding to laser emission at a particular wavelength. The curves apply to a laser system with the parameters given in Fig. 6.

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## VREMENSKI RAZLOŽENI SPEKTRI TEČNOG RODAMINSKOG LASERA

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### S a d r Ź a j

U radu su ispitivani spektralno i vremenski razloženi spektri fleš lampom pobuđivanog tečnog lasera sa organskom bojom — rodaminom 6G. Posebna pažnja je posvećena uticaju ciklooktatetraena na talasnu dužinu i trajanje laserske emisije. Eksperimentalni rezultati se dobro slažu sa postojećom teorijom. U prisustvu ciklooktatetraena primećena je emisija druge laserske linije na oko 100 Å kraćoj talasnoj dužini u odnosu na prvu lasersku liniju.