Study of Lasing by Means of Energy Transfer in Organic Dye Mixtures Pumped by an N_2 Laser. 1. Apparatus (Lasers) and Rhodamine 6G–Cresyl Violet Dye Mixture System

By

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The nitrogen and dye laser system has been constructed and as an example of its application the laser characteristics of the rhodamine 6G–cresyl violet dye mixture system have been studied. It has been found that most of the pump power absorbed by rhodamine 6G is transferred to cresyl violet as a useful pump power. In addition, our laser system has been shown to be efficiently powerful for spectroscopic studies.

1. Introduction

The nitrogen laser has attained increased importance as a pump light source for dye lasers because of its convenient wavelength, short risetime, and high repetition rate. For this application the output power of the nitrogen laser should be as high as possible. In addition, the pumping nitrogen laser should also be of simple design and operation in order to maintain the advantage of the inherent simplicity of dye lasers. We have built the notorogen laser of the type developed by Basting et al.[1]

Dye lasers have made a great progress over a wide wavelength region from the ultra-violet (UV) to the infrared (IR). Hilderbrand[2] and Lin[3] reported near-IR dye laser emission from several polymethine dyes directly pumped by UV nitrogen laser radiation ($\lambda = 337.1$ nm). In general, however, it is difficult to obtain the efficient laser emission in longer wavelength regions (e.g., near-IR), from nitrogen-laser-pumped dye solutions, mainly because of very small absorption at 337.1 nm.

Recently, laser pumping of a dye through energy transfer process has been studied in some dye mixtures.[4-8] In those works, various dye mixtures were excited by 337.1-nm radiation from a nitrogen laser. The energy transfer process can provide a way of extending the wavelength regions in which lasing is achieved by using a mixture of dyes.

In this paper, we report the characteristics of our nitrogen laser and the results of an investigation of the energy transfer dye laser on a cresyl violet (CV)–rhodamine 6G (Rh–6G) dye mixture system pumped with the N_2 laser, as an example of the application.

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2. Experimental

2.1. Nitrogen Laser

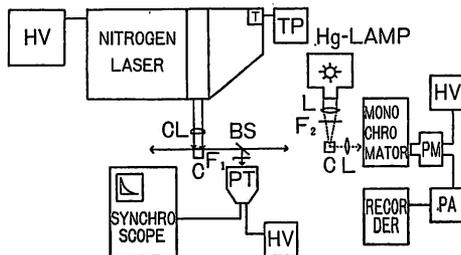An experimental arrangement for obtaining laser emission is shown in Fig. 1 together

Fig. 1. Experimental arrangement.

C: Dye and fluorescence cell; F_1 and F_2: ND- and glass-filters, respectively;
BS: beam splitter;   PM: photomultiplier tube;   PT: phototube;   PA: pream-
plifier; HV: high-voltage power supply;   T: trigger;   TP: trigger pulser.

with the fluorescence spectrophotometer constructed in our laboratory.   The nitrogen
laser used in the present work was constructed in our laboratory, which was almost identi-
cal to the system described by Basting et al.[1] and by Maeda and Miyazoe.[9]   The nitro-
gen laser consists of double parallel-plate transmission lines with a crossed field laser
tube, and a triggered air-spark-gap at the end.   The laser tube was made of acrylic resine.
One end of the laser tube was sealed by an aluminized plane mirror, the other by a quartz
glass window.   All seals were accomplished by rubber 0-rings.   The overall length of the
laser tube was 60 cm.   Rounded-off aluminum electrodes used were 50 cm long and 6 mm
wide with an electrode spacing of 15 mm.   The electrodes were supported by a spacer
system made of glass and acrylic resine.   The insulator for two parallel-plate transmission
lines was made of a polyester film of 250-μm thickness.   The conductors were made of
aluminum foil.   These were carefully pasted up by vacuum-pump oil to the polyester
film of high dielectric strength (dielectric constant $\varepsilon = 3.25$) on each side of the aluminum
foil.   Great care was taken so that no air bubbles or dust particles were included between
the aluminum foil and the polyester film.   Edges of the conductors were sealed using a
polyester film with epoxy resine to protect them from corona erosion.   Thus a breakdown
voltage up to al least 15 kV was obtained.   The capacitance of the transmission line
was 93 nF.   Nitrogen gas was let in at one end of the laser tube and pumped out at the
other end.

The nitrogen laser emission at 337.1 nm was detected by an Iwasaki SS–6100 synchro-
scope and a biplanar phototube (HTV R–617 U).   The emission spectrum of the nitro-
gen laser was recorded with a photoelectric recording system composed of a Nalumi
500 mm grating monochromator RM–21 equipped with a HTV R406 photomultiplier,
a DC preamplifier incorporating a Teledyne Philbrick operational amplifier model
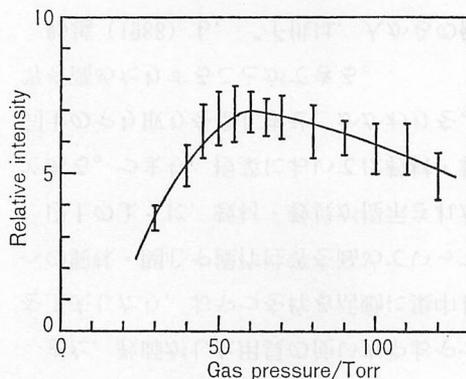1009, and a Hitachi recorder model 056, as also illustrated in Fig. 1.   The pulse width

Fig. 2. Nitrogen laser peak power as a function of nitrogen gas pressure. Impressed voltage: 12 kV.
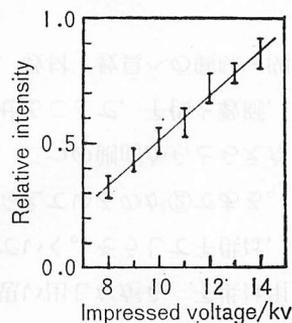
Fig. 3. Nitrogen laser peak power as a function of impressed voltage. Nitrogen gas pressure: 60 Torr.

was about 3 ns. The maximum output was obtained at a nitrogen pressure of *ca.* 60 Torr, as shown in Fig. 2. Figure 3 gives the output peak power as a function of the impressed voltage, showing the linear relationship. Since the laser output power could not be calibrated, we used the impressed voltage (V) instead of the calibrated output power (*e.g.*, kW unit) as the lasing threshold. Although the repetition frequency can be increased, the present experiment is carried out with the repetition frequency of *ca.* 1 Hz due to the stability of the trigger.

2.2. *Dye Laser*

The transversely pumped configuration used in this study is also shown in Fig. 1. The UV output beam from the pulsed nitrogen laser was focused by a cylindrical quartz lens CL (f = 10 cm) on the surface of the dye solution in a square quartz spectrofluorometer cell C (1 cm × 1 cm × 4.5 cm). The existence of a pulsed laser beam of the dye mixture was observed visually while the laser emission spectra were measured by the abovementioned photoelectric recording system.

2.3. *Fluorescence and Absorption Measurements*

The fluorescence spectra were also measured with the photoelectric recording system shown in Fig. 1. The fluorescence was analysed with the grating monochromator. The output of the photomultiplier was fed into the DC preamplifier and then to the recorder.

Excitation radiation was obtained from an Ushio 500-W super-high-pressure mercury arc lamp, type USH–500D. The excitation light beam was passed through a Toshiba glass filter UV–D1A.

The absorption spectra were measured with a Shimadzu MPS–50L multipurpose recording spectrophotometer. All the measurements were made at room temperature.

2.4. *Chemicals*

The structure of rhodamine 6G and the molecular formula of cresyl violet are shown

Rhodamine-6G (Rh-6G)
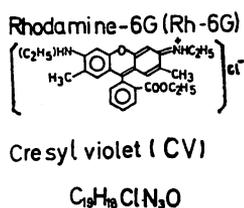
Cresyl violet (CV)

$C_{19}H_{18}ClN_3O$

Fig. 4. Molecular formula.

in Fig. 4.   Rhodamine 6G (the laser-dye grade; Eastman Kodak Co., U. S. A.) and cresyl violet (the guaranteed grade; E. Merck, Darmstadt, West Germany) were used without further purification. As for the solvent, methanol was used as obtained from Dojindo Lab. (the spectrograde).

3. Results and Discussion

3.1. Criteria for Selecting the Donor — Acceptor System

Two solutes, one a donor (Rh–6G) and the other an acceptor (CV) were dissolved in a solvent (methanol).   Here, it should be emphasized that this acceptor compound was employed because of its higher lasing threshold relative to the donor when pumped directly by the nitrogen laser. The donor was chosen according to two criteria: (1) a high molar extinction coefficient at the 337.1-nm excitation wavelength, and (2) good spectral overlap characteristics with the acceptor (i. e., good overlap of the donor fluorescence and the acceptor absorption spectrum).

3.2. Absorption and Fluorescence Spectra

The absorption and fluorescence spectra shown in Fig. 5 are for each of the two dyes, Rh–6G (Fig. 5a) and CV (Fig. 5b).   The absorption curves were obtained for a 10–mm absorption path length.   The fluorescence bands of Rh–6G and CV are centered at about 572 and 643 nm, respectively.   The molar extinction coefficients (ε) at the 337.1-nm excitation wavelength of Rh–6G and CV are 6×10^3 and 3×10^3 $cm^{-1}M^{-1}$, respectively. It has been known that the absorption cross sections at 337.1 nm are 2.4×10^{-17} cm^2 for Rh–6G and 4×10^{-18} cm^2 for CV.[5]   As can be seen in Fig. 5, these dyes have a good spectral overlap of the Rh–6G fluorescence and the CV absorption.   Therefore, it would be expected in a mixture of both dyes that most of the pump light is mainly absorbed by Rh–6G and a large portion of this excitation is transferred to CV in a distance small enough
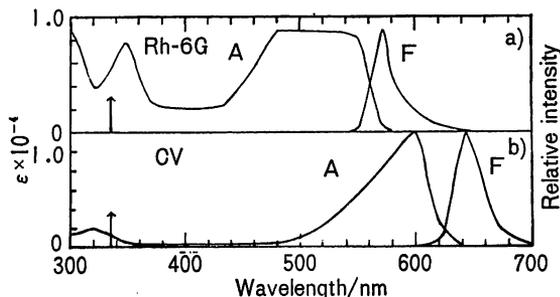

Fig. 5. Absorption (A) and fluorescence (F) spectra of rhodamine 6G (Rh–6G) and cresyl violet (CV). Absorption path length: 1 cm. Concn.: Rh–6G, 2.0×10^{-3} M; CV, 0.9×10^{-3} M; in methanol. The arrows on the abcissa refer to the 337.1-nm excitation wavelength.
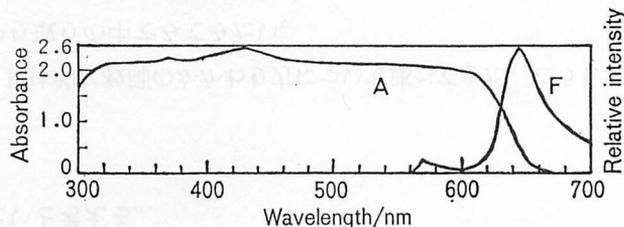
Fig. 6.   Absorption (A) and fluorescence (F) spectra of a dye mixture solution containing 2.0×10^{-3} M rhodamine 6G and 0.9×10^{-3} M cresyl violet in methanol. Absorption path length: 1 cm.

to give an efficiently effective pump power density.   Figure 6 shows the absorption and fluorescence spectra of a mixture of 2.0×10^{-3} M Rh–6G and 0.9×10^{-3} M CV.   The fluorescence bands centered around 642 and 570 nm are identified as originating from CV and Rh–6G, respectively.   As can be seen in Fig. 6, in the dye mixture the Rh–6G fluorescence is almost completely suppressed in favor of the longer-wavelength CV emission, indicating an efficient excitation transfer from Rh–6G to CV.   Therefore, it may be suggested that CV is pumped in both its UV and visible absorption bands and most of the fluorescence emission is due to excitation of the visible band through the energy transfer from Rh–6G.

3.3.   Laser Emission and Lasing Threshold

Figure 7 shows the measured laser emission spectrum for a solution containing 2.0×10^{-3} M Rh–6G and 0.9×10^{-3} M CV mentioned above.   The laser emission band in this dye mixture is centered at about 642 nm.   The lasing threshold was measured to be 6.4 kV.   For comparison, the laser spectrum for a 0.9×10^{-3} M CV-only solution was also measured and is shown in Fig. 8.   As can be seen in Fig. 8, the lasing wavelength in this CV-only solution is in good agreement with that in the dye mixture, while the lasing threshold in the former was measured to be 8.4 kV and is higher than that in the latter. All the results mentioned above support that the laser emission in the dye mixture originates from CV.   Therefore, it can be concluded that most of the excitation absorbed by Rh–6G is transferred to CV as a useful pump power, in other words pumping by excitation transfer is quite efficient.   Here, it should be referred to that similar experiments,
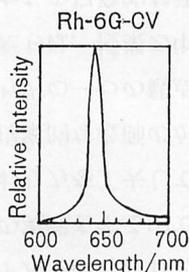
Fig. 7.   Lasing wavelengths of the same dye mixture solution as that in Fig. 6.
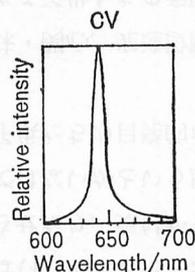
Fig. 8.   Lasing wavelengths of 0.9×10^{-3} M cresyl violet in methanol.