Lasing Efficiency and Photochemical Stability of IR Laser Dyes in the 710–1080-nm Spectral Region

PETER E. OETTINGER AND C. FORBES DEWEY, JR.

Abstract—The lasing efficiencies and photochemical stabilities of laser dyes useful in the 710-1080-nm spectral region have been investigated using a Q-switched ruby laser pumping source. The measured bleaching rates $P$ defined as the probability of irreversible decomposition of a dye molecule per absorbed photon, varied from $<1 \times 10^{-5}$ to $3 \times 10^{-4}$ for the different dye-solvent combinations investigated. Broadband lasing efficiencies (the ratios of dye laser output to ruby radiation input) ranged from 4 to 43 percent. Shifts of wavelength tuning range with variations in solvent, dye concentration, and dye laser cavity geometry are reported.

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INTRODUCTION

The lasing efficiency and photochemical stability of laser dyes useful in the near UV and visible portions of the spectrum (300-700 nm) have been characterized by numerous investigators [1]-[8]; the properties of laser dyes spanning the near IR region (700-1000 nm) are not as well defined [9]-[14]. Emission at these IR wavelengths is generally produced by long chain-like polymethine dyes, many of which are known to decompose readily in the presence of intense light. Major investigations of these polymethine dyes have been conducted by Miyazoe and Maeda [9], [11], and Maeda et al. [15], who found the general result that an increase in the length of the polymethine chain simultaneously shifted the lasing spectrum increasingly into the red and increased the propensity to photochemical degradation. Recently, an...
attempt has been made by Webb et al. [13] to reduce such photochemical instabilities by introducing ring-like structures into the center of the chain, thereby “strengthening” the molecule. The maximum wavelength at which dye lasers will operate is speculated to be near 1.5 μm [16], [17], where internal conversions  will become so large as to preclude the production of population inversions between the lasing levels.

Q-switched ruby lasers are the optical pumps most frequently used to excite dyes which lase in the near IR, although many of these dyes have more recently been excited with flash-lamps [13], [18] with favorable results. In both flashlamp-pumped and laser-pumped systems, the experiments which have been reported in the literature have utilized a variety of laser cavity geometries, dye solvents [19], and dye concentrations so that comparison between different investigations is difficult at best. Only fragmentary quantitative information exists on the photochemical stability of these dyes [11], [20].

This investigation was undertaken to provide a systematic comparison of the lasing efficiency and photochemical stability of 16 promising laser dyes which have been reported in the literature. Included in this list are the first organic laser dyes reported by Schaefer et al. [21] and Sorokin et al. [19] as well as four of the new polymethine structures announced by Webb et al. [13]. We have also investigated the shifts in laser output tuning range which can be achieved by utilizing different optical pumping arrangements and cavity geometries.

**Experimental Methods**

Our experiments deal exclusively with ruby laser pumped dye lasers. Three different optical pumping arrangements were utilized, as illustrated in Fig. 1(a)–(c). Fig. 1(a) is an angle-pumping system, employed in the majority of our experiments, in which the dye laser cavity axis is offset from the ruby pump beam propagation direction by 14°. Wavelength tuning of the 25-cm-long dye laser cavity was accomplished with a 75-percent reflecting gold-coated 600-l/mm diffraction grating blazed for 1.6 μm and operated in second order. A 5-pps 50-ns Q-switched multimode ruby laser averaging 1.4 MW during the pulse was the optical excitation source. The dye cell was a stoppered quartz spectrophotometer cell with an active thickness of dye (as measured along the dye laser optical axis) of 2.30 mm. The diameter of the ruby pump beam at the dye cell was 2 mm. The output mirror was 45-percent reflective across the spectral region of interest. To obtain broad-band lasing action, the grating was replaced with a fully reflecting (99 percent) plane mirror.

Two other pumping configurations were also employed, and are illustrated in Fig. 1(b) and (c). In the end-pumping configuration, a dichroic mirror directs the ruby laser beam along the axis of the dye laser. The closed cell used here was 15 mm long, six times longer than that for angle pumping. A side-pumped system with a 20-mm-long active dye region is shown in Fig. 1(c); this cell exhibited peak dye laser output at dye concentrations substantially larger (roughly a factor of 2 to 3) than the angle-pumped system. The e⁻¹ penetration depth of the ruby beam in the side-pumped cell was approximately 1 mm. For the arrangements of Fig. 1(b) and (c), the multimode Q-switched ruby laser produced a 30-ns 25-MW pulse with a 10-mm beam diameter.

Shown in Fig. 1(d) is the flashlamp-pumping geometry utilized by Webb et al. [13]. Their results for the wavelength of peak power broad-band lasing will be compared with ours. Note that their active dye length is 150 mm, or 65 times the length of the angle-pumped dye cell; comparable dye concentrations were utilized in the two systems.

The 16 dyes investigated are listed in Table I. Also included in Table I are four dyes which we did not study but for which substantial data are available in the literature. The numbering system follows that introduced in [22]; the numbers correspond (approximately) to the wavelength of peak laser power as reported by the original investigator. Inasmuch as many different dye solvents were tested in these early investigations, the numbers are only indicative of the spectral region covered.

Molar dye concentrations were established by adding a weighed amount of dye to a measured volume of solvent. All solvents were spectrophotometric grade, and several commercial sources of DMSO were used [14] with no measurable
Dye bleaching rates were calculated by comparing the ruby transmission through the dye cell as measured by a Hadron TRG Model 100 thermopile and Model 102 C energy meter and a Raytheon LA 31 vacuum silicon diode power meter, before and after exposure to 1500 laser pulses. Convective mixing assured uniform bleaching throughout the dye in the cell; this fact was substantiated by visual observations of the dye before and after bleaching.

Long-chain polyethylene dyes are quite sensitive to the UV emission from the flashlamp used to pump the ruby laser, and to the fluorescent lights of the laboratory; exposure to these sources generally bleaches the dyes within a few days. Consequently, a Schott RG 665 UV filter was used to prevent exposure of the dye to the short wavelengths, and the dyes were shielded as much as possible from laboratory illumination.

Dye laser broad-band (~200-Å) and narrow-band (7-Å) output energies and powers were measured with the same diagnostic instrumentation as was used to quantitate the ruby laser performance. Dye emission was spectrally resolved with a 1/4-m Jarrell Ash monochrometer.

**DISCUSSION**

The wavelength coverage, lasing efficiencies, bleaching probabilities, and quality factors of the sixteen dyes investigated are shown in Table II. Bleaching probabilities were obtained by first calculating the number of dye molecules bleached in a 2-mm-thick spectrophotometric cell when subjected to 50 mJ per pulse radiation at 5 pps for 5 min. Dye concentrations were adjusted for maximum lasing output; broad-band lasing was obtained from the dye cell throughout the bleaching tests.  

Let $N$ and $N'$ represent the number of intact dye molecules, respectively, before and after exposure to the ruby radiation. Their ratio may be related to the transmission of ruby laser light through the dye cell by

$$\frac{N'}{N} = \frac{\ln (I_0/I')}{\ln (I_0/I)} \tag{1}$$

where $I$ and $I'$ are the initial and final ruby intensities transmitted through the dye, and $I_0$ and $I'_0$ the corresponding incident intensities. Knowing the original dye concentration $N$ (1) can be used to calculate the number of molecules bleached

$$\Delta N = N - N'. \tag{2}$$

(Equation (2) does not specify that bleaching is irreversible and a bleached molecule no longer absorbs at the ruby wavelength; this assumption is consistent with our observations for all the dye-solvent combinations we have investigated.) A bleaching probability $P$, i.e., the number of dye molecules bleached per absorbed ruby photon, can be calculated from

$$P = \frac{h\nu\Delta N}{F} \tag{3}$$

where $h\nu$ is the energy per ruby photon and $F$ is the total ruby laser energy absorbed by the dye during the bleaching test.

The lasing efficiencies $E$ of the dyes, defined as the ratio of dye-output to absorbed ruby-input energies, were measured.

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**TABLE I**

<table>
<thead>
<tr>
<th>IR Laser Dyes Investigated</th>
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<tbody>
<tr>
<td>715 (a)</td>
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<td>950 (b)</td>
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<tr>
<td>972</td>
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<tr>
<td>990</td>
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<td>1020 (b)</td>
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\(a\) The numbers assigned to each dye signify (approximately) the center of the lasing band of each dye by the original reference in the literature. 
\(b\) Dyes not investigated extensively but included because of considerable data from other sources.
The polarization of the dye output was always the same as narrow-band efficiencies were measured. Peak output is proportional to the total number of dye laser photons for the angle-pumped dye cell, generally in a broad-band configuration with the dye radiation oscillating between a totally reflecting mirror and a 45-percent reflecting output coupler. The polarization of the dye output was always the same as that of the ruby input. For certain dyes, as shown in Table I, a gold-coated grating replaced the fully reflecting mirror, and narrow-band (7-Å) efficiencies were measured. Peak output powers up to 1 MW were observed, with peak broad-band efficiencies as large as 43 percent.

A "quality factor" \( Q \) for a dye is defined as

\[
Q = \frac{E}{P}
\]

(4)

\( Q \) is proportional to the total number of dye laser photons.
which may be extracted from a given volume of dye prior to the onset of deleterious bleaching; \( Q \) increases with increasing efficiency and decreasing bleaching rate.

The dyes were tested in the following solvents: methanol, ethanol, propanol, glycerol, ethylene glycol, acetone, dimethyl sulfoxide (DMSO), and water containing 5-percent Triton X-100. For almost all of these dyes, DMSO was found to be superior with respect to dissolving power, photochemical stability of the dye-solvent mixture, and lasing efficiency. Water containing 1-5-percent surfactant is a dye solvent excepting methanol (DMSO), and water containing 5-percent Triton X-100. Other solvents are also useful; for example, 1,1'-diethyl-2,2'-dicarbocyanine iodide (DDI, number 771) did not lase when dissolved in DMSO, but did lase in glycerol or ethylene glycol.

The lasing efficiencies \( E \) which we measured in the angle-pumped configuration are comparable to, and somewhat larger than, those obtained by previous investigators [9], [14], [15], [19]. In agreement with other published results [23], we find that the dye laser output is reduced by only 5-20 percent when the cavity is changed from one with a broad-band mirror to one with a higher dispersive element to achieve narrow-band operation. This is to be expected for a laser medium with homogeneous broadening operated far above threshold with a low reflectivity output coupler.

Fig. 2 illustrates that the 710-950-nm spectral region can be covered using five dyes exhibiting high efficiency. The solid lines indicate the peak grating-tuned efficiency of each dye, and a small reduction in output power should be anticipated near the ends of the tuning range of each dye [14]. An examination of Table II shows that other combinations of five dyes covering this spectral region are also possible; Fig. 3 graphically illustrates the overlap of spectral coverage of the dyes listed in Table II.

The wavelength tuning ranges listed in Table II were obtained using DMSO as a solvent and using the angle-pumping configuration of Fig. 1(a). Sorokin et al. [19] demonstrated that substantial shifts in output wavelength occur with changes in dye concentration and solvent; a comparison of the wavelength tuning ranges of Table II and those obtained by Miyazoe and Maeda [9] and Webb et al. [13] suggest that the dye laser cavity configuration and pumping geometry are also important variables affecting the dye tuning range.

Fig. 4 presents data we obtained with dyes 821, 940, and 980 using different solvents and pumping geometries. The angle-pumped cell exhibits laser output at shorter wavelengths than either the end-pumped or side-pumped systems. We attribute this to the fact that there is substantially more self-absorption by the dye with the longer dye cells used in the latter two configurations. It is a general result [9], [13], [19] for polymethine dyes that increasing dye concentration increases the lasing wavelength. Fig. 5 presents our
results and the results of Webb et al. [13] obtained in a flashlamp-pumped system. In general, the larger the product of dye concentration and cell length, the longer the lasing wavelength.

The tuning ranges given in Fig. 4 were obtained with dye concentrations corresponding to peak lasing efficiency. In order to achieve efficient lasing beyond 1000 nm, an end-pumped or side-pumped system is desirable. Most frequently DMSO also yields longer wavelengths than other solvents with a given dye, in accord with the results of Sorokin et al. [19].

If one adopts the premise that dye molecules which are irreversibly bleached by photochemical reactions do not participate in either the absorption process or the lasing process, then the effective concentration of dye should be decreased by bleaching and a shift of the peak spectral output to shorter wavelengths should occur as the dye is progressively bleached. This is in accord with our observations, as illustrated in Fig. 6. The magnitude of the spectral shift is in agreement with that which would be predicted from the measured value of $\Delta N$ and the wavelength-concentration curves of Fig. 5.

Several of the dyes we tested exhibited, in addition to a strong primary laser band, a weak secondary lasing peak at longer wavelength. Fig. 6 shows a monochrometer scan of the broad-band lasing output of dye 724 in the angle-pumping configuration. Such results have been noted before [14], [15]; an analogous result was also observed in the flashlamp-pumped geometry of Webb et al. [13], as noted in Fig. 5 (dye 910).

No systematic data regarding the bleaching rates of polymethine IR dyes have been reported previously. Miyazo and Maeda [11] irradiated dyes 715, 935, 809, and 820 with the output of an intense tungsten projector lamp and noted rapid bleaching in acetone, DMSO, and methanol. Their conclusion, as well as ours, was that the high-efficiency dye DTTC iodide (820) used by Sorokin et al. [19] and others [9], [14] is extremely sensitive to bleaching, both by UV and ruby laser light. The bleaching characteristics of this dye were such that no accurate measurements were possible in our experimental system. Dye 821 (DTTC bromide [21]) provided nearly equal efficiencies, covered the same wavelength region, lased efficiently in both DMSO and H$_2$O-surfactant solutions, and exhibited a bleaching probability of $4.6 \times 10^{-5}$ in H$_2$O surfactant.

Table III compares the bleaching rates of the polymethine IR dyes we have investigated under lasing conditions to the results obtained by others [1], [5], [6] who have measured, in nonlasing experiments, the degradation of laser dyes which are efficient in the visible and near UV. For the very best IR dyes, bleaching rates are comparable to those observed for shorter wavelength dyes, whereas some IR dyes bleach sufficiently rapidly (in ruby laser light) that their use is awkward at best.

Two of the new dyes manufactured by Eastman Kodak and reported by Webb et al. [13] (dyes 940 and 972) exhibited lower bleaching rates than any other IR dyes we have tested in the 840-920-nm spectral region. Dye 950 was not available to us during our experimental investigation, but according to the results of Webb et al. [13], the efficiency of this dye substantially exceeds that of 940 and 972, and should prove to be an excellent dye if the bleaching rate is as low as that of dyes 940 or 972.

**Conclusions**

Laser dyes spanning the near IR have been thought to be highly unstable and subject to rapid photochemical bleaching. This is indeed true for a number of dyes, but we have measured bleaching probabilities for some IR dyes which are comparable to values measured for dyes lasing in the visible.

The efficiency of ruby-pumped dyes can be very high. We have identified five dyes which span the 715-950-nm spectral region in a grating-tuned angle-pumping configuration, and for which the minimum efficiency is 13 percent.

Finally, we have investigated the effects of optical pumping...
arrangement, solvent, and dye concentration on the lasing wavelength of several dyes. We determined that, of the solvents tested, DMSO generally produces the longest lasing wavelengths. The lasing wavelength of a given dye-solvent combination increases as the product of cell length and dye concentration increases. Many of the dyes exhibit low bleaching rates and high efficiencies in H₂O-surfactant solutions, a result which is particularly important in cases where thermally induced refraction effects may otherwise limit dye laser performance.

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REFERENCES