

ible solvent. Finally, it should be pointed out that there are still some problems to be solved. Mainly, what is the exact nature of the second reaction B) resulting in the FR2 radicals? But the information necessary to answer this question is not yet available.

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REFERENCES

- [1] E. P. Ippen, C. V. Shank, and A. Dienes, "Rapid photobleaching of organic laser dyes in continuously operated devices," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-7, pp. 178-179, Apr. 1971.
- [2] A. D. Britt and W. B. Moniz, "The effect of pH on photobleaching of organic laser dyes," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-8, pp. 913-914, Dec. 1972.
- [3] J. Weber, "Study of the influence of triplet quencher on the photobleaching of rhodamine 6G," *Opt. Commun.*, vol. 7, pp. 420-422, Apr. 1973.
- [4] M. Yamashita and H. Kashiwagi, "Triplet-state esr of rhodamine 6G during laser irradiation," *J. Chem. Phys.*, vol. 59, pp. 2156-2157, Aug. 1973.
- [5] R. A. Berg and A. Ron, "Phosphorescence lifetimes of cationic dyes: Concentration and temperature effects," *J. Chem. Phys.*, vol. 59, pp. 3289-3296, Aug. 1973.
- [6] M. Yamashita and H. Kashiwagi, "Temperature effects on triplet lifetime of rhodamine 6G in ethanol and polymethylmethacrylate," *Japan. J. Appl. Phys.*, vol. 14, pp. 421-422, Mar. 1975.
- [7] —, "Optical saturation and quenching effects in the triplet state of rhodamine 6G," *J. Phys. Chem.*, vol. 78, pp. 2006-2009, Sept. 1974.
- [8] M. Yamashita, H. Ikeda, and H. Kashiwagi, "Laser pumped magnetophotoselection in triplet dyes," *J. Chem. Phys.*, vol. 63, pp. 1127-1132, Aug. 1975.
- [9] J. F. Gibson, M. C. R. Symons, and M. G. Townsend, "Unstable intermediates. Part II. Photolysis of hydrogen peroxide in solid alcohols: Some reactions of hydroxyl radicals," *J. Chem. Soc.*, pp. 269-276, 1959.
- [10] K. Shimokoshi, Y. Mori, and I. Tanaka, "An esr study of the aromatic-compounds-photosensitized decomposition of alcohol by the two-photon process," *Bull. Chem. Soc. Japan*, vol. 40, pp. 302-306, Feb. 1967.
- [11] S. Siegel and K. Eisenthal, "Triplet-triplet absorption in sensitized solvent decomposition: An esr study," *J. Chem. Phys.*, vol. 42, pp. 2494-2502, Apr. 1965.
- [12] K. Uchida, S. Kato, and M. Koizumi, "Photosensitized oxidation of leuco-uranine and the identification of the photobleached product of uranine in ethanol solution," *Bull. Chem. Soc. Japan*, vol. 35, pp. 16-22, Jan. 1962.

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 $\leq 1 \times 10^{-5}$ to 3×10^{-4} for the different dye-solvent combinations investigated. Broad-band 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 $1.5 \mu\text{m}$ [16], [17], where internal conversions $S_1 \rightarrow S_0$ 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 flashlamps [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 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 $1.6 \mu\text{m}$ 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

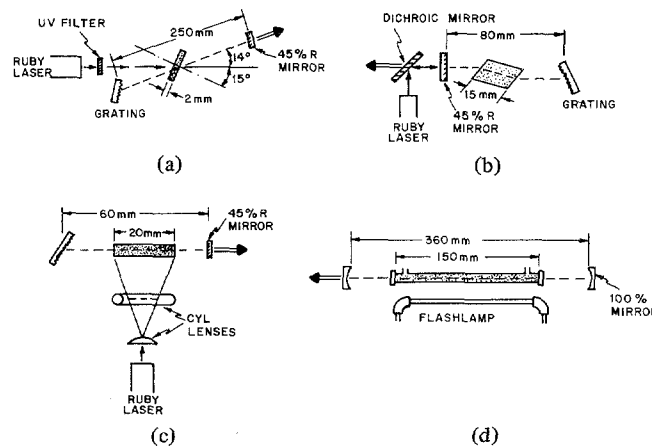


Fig. 1. Four dye laser optical pumping configurations. (a) Angle pumping. (b) End pumping. (c) Side pumping. (d) Flashlamp pumping.

TABLE I
 IR LASER DYES INVESTIGATED^a

715 ^b	- 3, 3'-diethyl-2, 2'-thiadiazocarbocyanine iodide (DTDC)
724	- 3, 3'-dimethyl-2, 2'-(5, 5'-dimethyl)-thiathiazolino-tricarbo-cyanine iodide
725	- 3, 3'-diethyl-2, 2'-oxatricarbocyanine iodide
735	- 3, 3'-dimethyl-2, 2'-oxatricarbocyanine iodide (DOTC)
757	- 3, 3'-diethyl-2, 2'-(6, 6'-dimethoxy)-thiadiazocarbocyanine iodide
771	- 1, 1'-diethyl-2, 2'-dicarbocyanine iodide (DDI)
800	- 1, 3, 3, 1', 3', 3'-hexamethyl-2, 2'-indotricarbocyanine iodide (HITC)
809	- 6-(3-ethyl-2-benzothiazolylidene)-2, 4-hexadienyli-dene thioindosinid (Merocyanine B)
820 ^b	- 3, 3'-diethyl-2, 2'-thiatricarbocyanine iodide (DTTC iodide)
821	- 3, 3'-diethyl-2, 2'-thiatricarbocyanine bromide (DTTC bromide)
830	- Kodak IR-123 tricarbocyanine salt
850	- 3, 3'-diethyl-2, 2'-(5, 6, 5', 6',-tetramethoxy)-thiatri-carbocyanine iodide
880	- 3, 3'-diethyl-2, 2'-(5, 5'-dimethoxy)-thiatricarbocyanine iodide
910	- Kodak IR-144 tricarbocyanine salt
931	- 1, 1'-diethyl-4, 4'-dicarbocyanine iodide
940	- Kodak IR-125 tricarbocyanine salt
950 ^b	- Kodak IR-140 tricarbocyanine salt
972	- Kodak IR-132 tricarbocyanine salt
980	- 3, 3'-diethyl-12-acetoxy-2, 2'-thiatetracarbo-cyanine perchlorate
1020 ^b	- 1, 1'-diethyl-4, 4'-quinotricarbocyanine iodide

^aThe numbers assigned to each dye signify (approximately) the center of the lasing band of each dye by the original reference in the literature.

^bDyes not investigated extensively but included because of considerable data from other sources.

differences in the results. After the solvent bottles were opened, no special precautions were employed (other than restoring the bottle cap after pouring the solvent) to inhibit trace moisture and oxygen from entering the DMSO. During and following dye solubilization, the laser solutions were exposed to the atmosphere for varying amounts of time. Convective mixing occurred in the solubilization process as well as in the stoppered dye laser cell during the bleaching tests. This suggests that the solutions contained substantial amounts of dissolved oxygen, but no attempts were made either to achieve oxygen saturation or to purge the solutions of dissolved oxygen. Bleaching tests with independently mixed solutions gave the same reproducibility in the bleaching probability P as replicate tests on a single solution (about ± 15 percent).

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 polymethine 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 ($\sim 200\text{-\AA}$) and narrow-band (7-\AA) 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 $\frac{1}{4}\text{-m}$ 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 ΔN 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.¹

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

$$\frac{N'}{N} = \frac{\ln(I'_0/I')}{\ln(I_0/I)} \quad (1)$$

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

$$\Delta N = N - N'. \quad (2)$$

(Equation (2) contains the premise 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

$$P = \frac{h\nu\Delta N}{F} \quad (3)$$

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 ratios of dye-output to absorbed ruby-input energies, were measured

¹The bleaching probabilities were measured under actual lasing conditions, and are therefore indicative of the degradation which occurs under conditions of practical use. However, lasing action decreases the mean lifetime of the dye molecules in the excited singlet state and in any triplet state formed by singlet-triplet transitions [19]. If bleaching proceeds from the excited singlet or triplet state, the values of P we have measured would be lower bounds to the values which would be measured in a nonlasing configuration.

TABLE II
IR DYE LASER CHARACTERISTICS

Dye	Molar Concentration $\times 10^4$	Wavelength Range (nm)	Lasing Efficiency E (%)	Bleaching Probability $P \times 10^3$	Broadband Quality Factor $Q \times 10^{-3}$	Comments
715 ^b	---	705-735	15 ^a	--	---	Also lases equally well in H ₂ O-surfactant and alcohols. Appears to be very stable against photochemical degradation.
724	4.1	710-765	43	30	1.4	Primary lasing 710-740 nm; secondary peak at 750 nm.
725	0.5	725-765	43,34 ^a	9	4.8	Primary lasing 725-745 nm; secondary peak at 760 nm. 3.9(10 ⁻⁴) M concentration extends range to 790 nm.
735	1.0	725-780	39,36 ^a	9	4.3	Primary lasing 725-755 nm; secondary peak at 770 nm. Peak shifted 2.5 nm during bleaching test. Unstable in light. With H ₂ O-5% triton as solvent E \sim 36%, P \sim 5(10 ⁻⁵), poor shelf life.
757	1.4	710-755	23	20	1.2	Primary lasing 710-725 nm; secondary peak at 745 nm.
771	1.0	740-770	4	5	0.8	Solvent was ethylene glycol; does not lase in DMSO. Good lasing in glycerol with P < 10 ⁻³ and similar spectrum.
800	3.7	790-840	30	8	3.8	Peak intensity shifted 5 nm during bleaching test. Good lasing in H ₂ O-5% triton with similar spectrum.
809	1.3	780-823	5	24	0.2	Primary lasing 780-810 nm; secondary peak at 820 nm. Peak shifted 4 nm during bleaching test.
820 ^b	---	816-855	26 ^a (est.)	--	---	Very unstable to ruby laser light.
821	0.9	810-830	18,12 ^a	14	1.3	Peak shifted 5 nm during bleaching test. With H ₂ O-5% triton as solvent and 1.8(10 ⁻⁴) M mixture, lased 800-845 nm with E \sim 18%, P \sim 4.6(10 ⁻⁵).
830	1.6	765-815	22 ^a	12	1.8	New Kodak "reinforced structure" dye. Rapid bleaching.
850	3.0	855-885	19	24	0.8	
880	1.7	820-875	24 ^a	11	2.2	Also lases efficiently when dissolved, at 150°F, in ethylene glycol [P = 5(10 ⁻⁵)].
910	2.2	835-890	21 ^a	6	3.5	New Kodak "reinforced structure" dye.
931	5.3	845-920	25	18	1.4	Good lasing in H ₂ O-5% triton, but poor shelf life.
940	2.3	840-920	14 ^a	≤ 1	14.0	New Kodak "reinforced structure" dye. Excellent resistance to bleaching.
950 ^b	---	\sim 850-930 (est)	> 35 (est)	--	---	New Kodak dye. Not available at time of these experiments. Should be comparable to 940 but with higher efficiency.
972	1.2	875-920	7 ^a	≤ 2	3.5	New Kodak "reinforced structure" dye. Heated to 150°F for good dissolution in DMSO.
980	0.8	920-950	20	17	1.2	Peak intensity shifted 6 nm during bleaching test. Poor shelf life.
1020 ^b	---	983-1081	--	--	---	Tested in end-pumped geometry only.

Note: Solvent is DMSO and angle-pumping configuration utilized unless specified otherwise.

^aNarrow band; measured in grating-tuned configuration.

^bDyes not investigated extensively but included because of considerable data from other sources.

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

$$Q = \frac{E}{P}. \quad (4)$$

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-100.² 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 exhibiting high heat capacity and low change of refractive index with temperature. It is therefore a useful solvent in minimizing Schlieren effects which have been found to degrade dye laser performance. The photochemical stability of water-surfactant solutions was generally poorer than for the DMSO, but frequently better than other solvents such as ethanol [20].³ 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 broadband 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

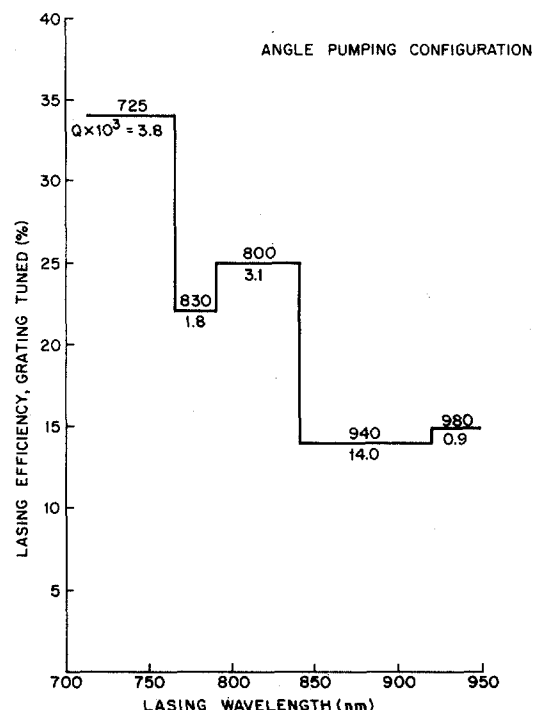


Fig. 2. Efficiency of laser dyes spanning the 710-950-nm spectral region. Efficiencies indicated are for a grating-tuned cavity angle pumped with a ruby laser.

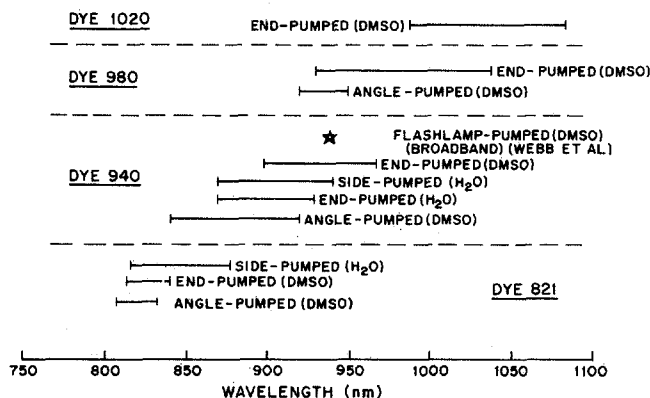


Fig. 3. Wavelength tuning ranges of 16 near-IR dyes in DMSO.

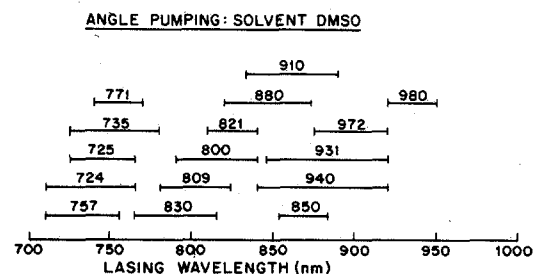


Fig. 4. Variation of wavelength tuning range with solvent and pumping configuration.

²Trademark of Rohm and Haas.

³Reference [20] indicates that H₂O-surfactant solutions of dye 735 exhibit excellent shelf life (at least several hundred hours) in the absence of photochemical bleaching. We find that the shelf life is 4-6 days at ambient temperature when shielded from ambient light. This discrepancy remains unresolved.

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

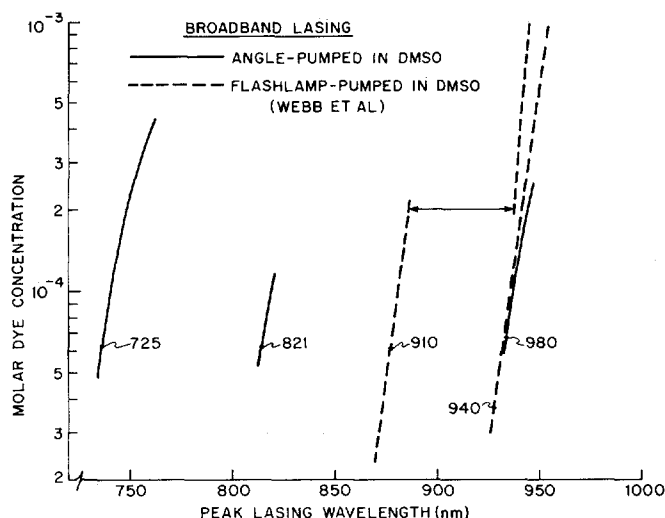


Fig. 5. Variation of peak lasing wavelength with dye concentration.

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 ΔN 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 monochromator 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. Miyazoe 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 ef-

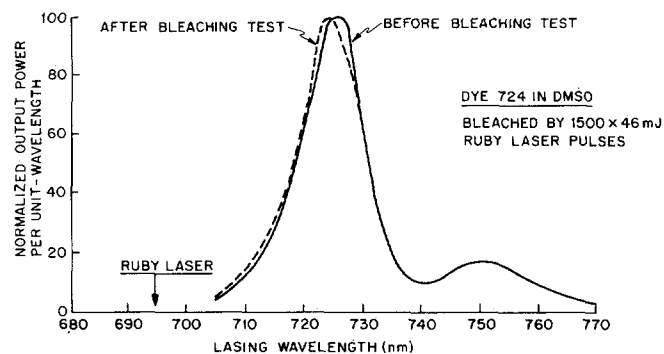


Fig. 6. Shift in spectral distribution of broad-band dye laser output with bleaching.

TABLE III
COMPARISON OF TYPICAL UV-VISIBLE AND IR LASER DYE BLEACHING RATES

	Dye	Solvent	Bleaching Rate $P (\times 10^5)$	Ref.
UV-Visible	Rhodamine 6G	ethanol	0.05; 0.1-1.1	1; 6
		H ₂ O + 5% X-100	0.8; 0.2-0.7; 0.7	1; 6; 5
	Na-Fluorescein	methanol	1.8	5
	Ct-Fluorescein	ethanol methanol	0.4; 1.1 9.5	1; 6 5
IR	940 (minimum P)	DMSO	≤ 1	This Study
	724 (maximum P)	DMSO	30	" "

ficiently in both DMSO and H₂O-surfactant solutions, and exhibited a bleaching probability of 4.6×10^{-5} in H₂O 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

- [1] E. P. Ippen, C. V. Shank, and A. Dienes, "Rapid photobleaching of organic laser dyes in continuously operated devices," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-7, pp. 178-179, Apr. 1971.
- [2] B. H. Winters, H. I. Mandelberg, and W. B. Mohr, *Appl. Phys. Lett.*, vol. 25, p. 723, 1974.
- [3] E. J. Schimitschek, J. A. Trias, M. Taylor, and J. E. Celto, "New improved laser dye for the blue-green spectral region," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-9, pp. 781-782, July 1973.
- [4] J. Weber, *Opt. Commun.*, vol. 7, p. 420, 1973.
- [5] D. Beer and J. Weber, *Opt. Commun.*, vol. 5, p. 307, 1972.
- [6] A. Britt and W. B. Moniz, "The effect of pH on photobleaching of organic laser dyes," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-8, pp. 913-914, Dec. 1972.
- [7] I. P. Kaminow, L. W. Stutz, E. A. Chandross, and C. A. Pryde, *Appl. Opt.*, vol. 7, p. 1563, 1972.
- [8] D. Kato and A. Sugimura, *Opt. Commun.*, vol. 10, p. 327, 1974.
- [9] Y. Miyazoe and M. Maeda, *Appl. Phys. Lett.*, vol. 12, p. 206, 1968.
- [10] L. D. Derkacheva, A. I. Krymova, A. F. Vompe, and I. I. Levkoev, *Opt. Spectrosc.* (USSR), vol. 25, p. 404, 1968.
- [11] Y. Miyazoe and M. Maeda, *Opto-Electron.*, vol. 2, p. 227, 1970.
- [12] A. Hirth, J. Faure, and D. Loughnot, *Opt. Commun.*, vol. 8, p. 318, 1973.
- [13] J. P. Webb, F. G. Webster, and B. E. Plourde, "Sixteen new IR laser dyes," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-11, pp. 114-119, Mar. 1975.
- [14] C. D. Decker and F. K. Tittel, *Opt. Commun.*, vol. 7, p. 155, 1973.
- [15] M. Maeda *et al.*, "Polymethine dyes used for laser emission," Bulletin 46, Japanese Research Institute for Photosensitizing Dyes Co., Ltd., 1973.
- [16] K. H. Drexhage, *Laser Focus*, p. 35, Mar. 1973.
- [17] F. P. Schaefer, *Laser Focus*, p. 33, Mar. 1974.
- [18] M. Maeda and Y. Miyazoe, *Jap. J. Appl. Phys.*, vol. 11, p. 692, 1972.
- [19] P. P. Sorokin, J. R. Lankard, E. C. Hammond, and V. L. Moruzzi, *IBM J. Res. Develop.*, vol. 11, p. 130, 1967.
- [20] C. E. Hackett and C. F. Dewey, Jr., "Improved temporal stability of polymethine laser dyes in aqueous solutions," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-9, pp. 1119-1120, Nov. 1973.
- [21] F. P. Schaefer, W. Schmidt, and J. Volze, *Appl. Phys. Lett.*, vol. 9, p. 306, 1966.
- [22] C. F. Dewey, Jr., "Excitation of gases using wavelength-tunable lasers," in *Modern Optical Methods in Gas Dynamic Research*, D. S. Dosanjh, Ed. New York: Plenum, 1971, pp. 221-270.
- [23] A. J. Gibson, *J. Sci. Instrum. (J. Phys. E)*, vol. 2, p. 802, 1969.