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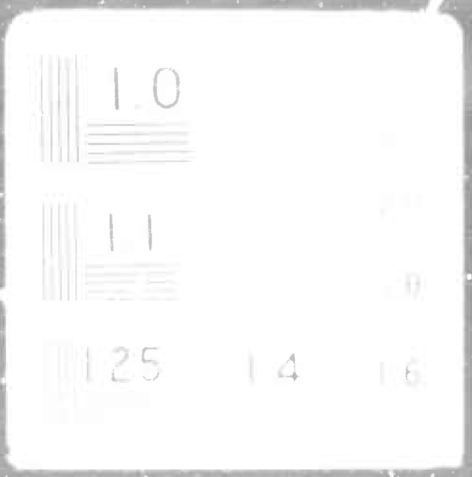

SPECTRAL PROPERTIES OF PASSIVELY Q-SPOILED LASERS

Final Technical Summary Report

Contract Nonr-5150(00)
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Project Code Number 015-710

A 32-Month Contract

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PROJECT SCIENTIST

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ABSTRACT

Description of experiments bearing on the problems of the spectral behavior of passive Q-switched lasers and of the physical behavior of passive Q-spoiling materials are given. The results of experiments of the temporal and frequency locking of two lasers, coupled by a bleachable dye are described. Further experiments pertinent to the problem of spectral cross-relaxation are described. The stimulated emission of several organic dyes in the visible spectrum and the demonstration of efficient spectral narrowing and tunability over a wide spectral range is described. The results of frequency doubling a dye laser are presented. Mode locking of the dye laser with picosecond pulses, tunable over a broad range, is reported. The results of experiments concerned with the thermal and photochemical responses of two polymethine dyes used for Q-spoiling the Nd laser are given.

Five articles published or to be published, all supported by this contract, are reproduced as appendices.

FOREWORD

This report was prepared by the Optical Physics Division of Korad Department, Electronics Division, Union Carbide Corporation, Santa Monica, California, under Contract Nonr-5150(00) entitled "Spectral Properties of Passively Q-spoiled Lasers". The study was conducted under the project leadership of B. H. Soffer with O. Cernichiari, H. Kimura, J. W. Linn, B. B. McFarland, and R. C. Pastor participating.

Section 1

INTRODUCTION

The object of this program was an experimental research study of passively Q-spoiled lasers and the physical behavior of passive Q-spoiling materials. In particular, the study has been directed toward gaining further insight into the mechanisms of spectral relaxation, diffusion, and spectral "hole burning" in laser and passive Q-spoiling materials. The distinction between these two classes of materials have been diminished because of recent demonstrations of stimulated emission from organic dye Q-spoiling materials as well as from other organic dye solutions. We have turned our attention in the latter half of this contract period to the interesting spectral, spatial and temporal problems associated with these dye lasers. We have also examined some photo and thermochemical responses of the dyes pertinent to the problems of stability.

Section 2

TECHNICAL DISCUSSION

A. Spectral Cross-Relaxation Studies

(1) Frequency Locking and Dye Spectral Hole Burning

Concurrent with the discovery of the passive Q-switch, we had observed that the output spectrum of a giant pulse ruby laser can be considerably narrowed, sometimes resulting in single frequency operation.[1/] Subsequently we have found that the usual wide spectral envelope of lines of the Nd^{3+} glass laser is efficiently condensed to a single narrow line when passively Q-spoiled with bleachable dye.[2,3/] We have similarly observed a narrow spectral output when the passive Q-spoiler was bleachable glass or semiconductor mirrors. Recently a single line output has been observed from a Nd^{3+} glass laser Q-spoiled with a rotating prism.[4/]

An early question that arose was whether this narrow spectral output of dye-switched lasers was due to the behavior of spectral diffusion or relaxation in the laser material, or whether it was due to narrow spectral hole-burning in the bleachable absorber. Theoretical analyses[5,6/] have indicated that if the

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[1/] B. H. Soffer, J. Appl. Phys., 35 2551 (1965)

[2/] B. B. McFarland, R. H. Hoskins and B. H. Soffer, Nature 207 1180 (1965)

[3/] B. H. Soffer and R. H. Hoskins, Nature 204, 276 (1964)

[4/] J. K. Wright, C. H. H. Carmichael and B. J. Brown, Phys. Letters 16, 264 (1965)

[5/] W. G. Wagner and G. Birnbaum, J. Appl. Phys., 32, 1185 (1961)

[6/] W. R. Sooy, Appl. Phys. Letters 7, 36 (1965) laser precursory state[1] lasts long enough, weaker modes are suppressed and eventually the stronger one (or ones) will dominate. This is a sufficient explanation for the spectral behavior of passively Q-spoiled lasers but it does not rule out the possibility of some mode selection by a degree of spectral hole-burning in bleachable absorbers used as Q-spoilers. The relaxation of at least the excited states of such dye molecules can be inferred to be much faster than the giant pulse times (10^{-8} sec), from the phenomena of Stokes shifted fluorescence so that one expects very fast spectral diffusion within any hole burned line; so fast, that it might not influence the spectral behavior of the laser. Indeed, experiments conducted (with phthalocyanine solutions), at the moment of the giant pulse with resolution times of the order of the duration of the giant pulse, seem to show a homogeneous saturation.[7,8] We report here experimental evidence in support of the existence of significant hole burning in these dyes.

The experiments utilized in the narrow spectral output of one passively Q-spoiled laser to bleach the passive cell of another laser. If the frequencies of the lasers locked together, and if other causes could be eliminated, then spectral hole-burning would be in evidence.

In the first set of experiments, two ruby lasers were set orthogonally with the output of one passively Q-spoiled laser directed upon the cell of the other (see Figure 1 and 2). The cell, with 4 polished windows and a path length of 17 mm, was near the dielectric mirror of maximum reflectivity. Equivalent results were obtained when solutions of an organic base salt of sulfonated metal-free phthalocyanine (see Figure 3) in methanol or solutions of sulfonated metal-free phthalocyanine

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[7] F. Gires and F. Combaud - J. de Physique <u>26</u>, 325 (1965)

[8] W. F. Kosonocky, S. E. Harrison and R. Stander, J. Chem. Phys. <u>43</u>, 831 (1965)

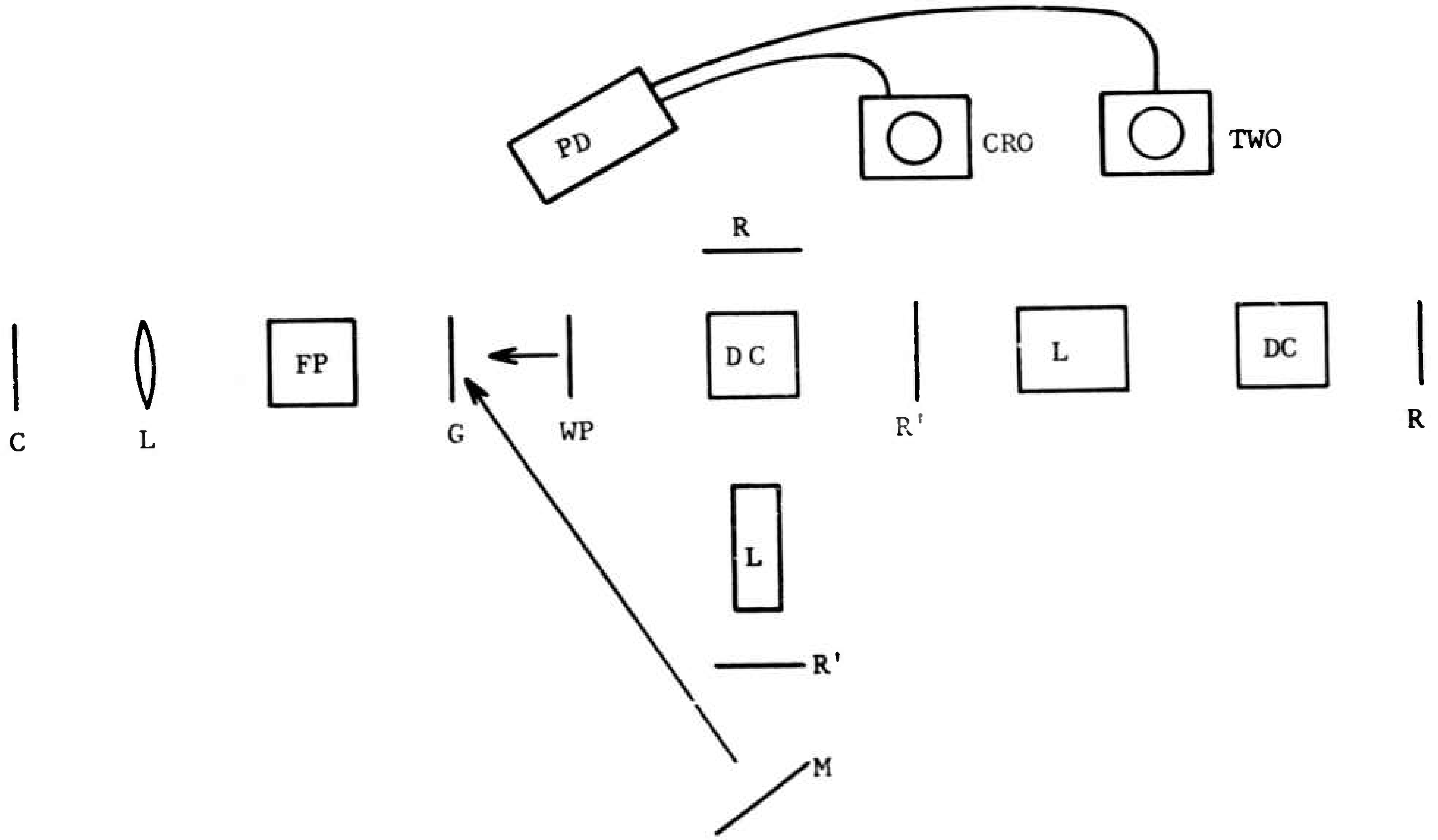

Figure 1

C	Camera
L	Lens
FP	Fabry Perot
G	Ground Glass
PD	Photodiode
SC	Scattering Cell
WP	Half Wave Plate if Required

R'	3mm Sapphire Resonant Reflector or 30% R Dielectric Reflector
L	Laser
DC	Dye Cell
R	100% Dielectric Reflector
M	Mirror
CRO	Cathode Ray Oscilloscope
TWO	Traveling Wave Oscilloscope

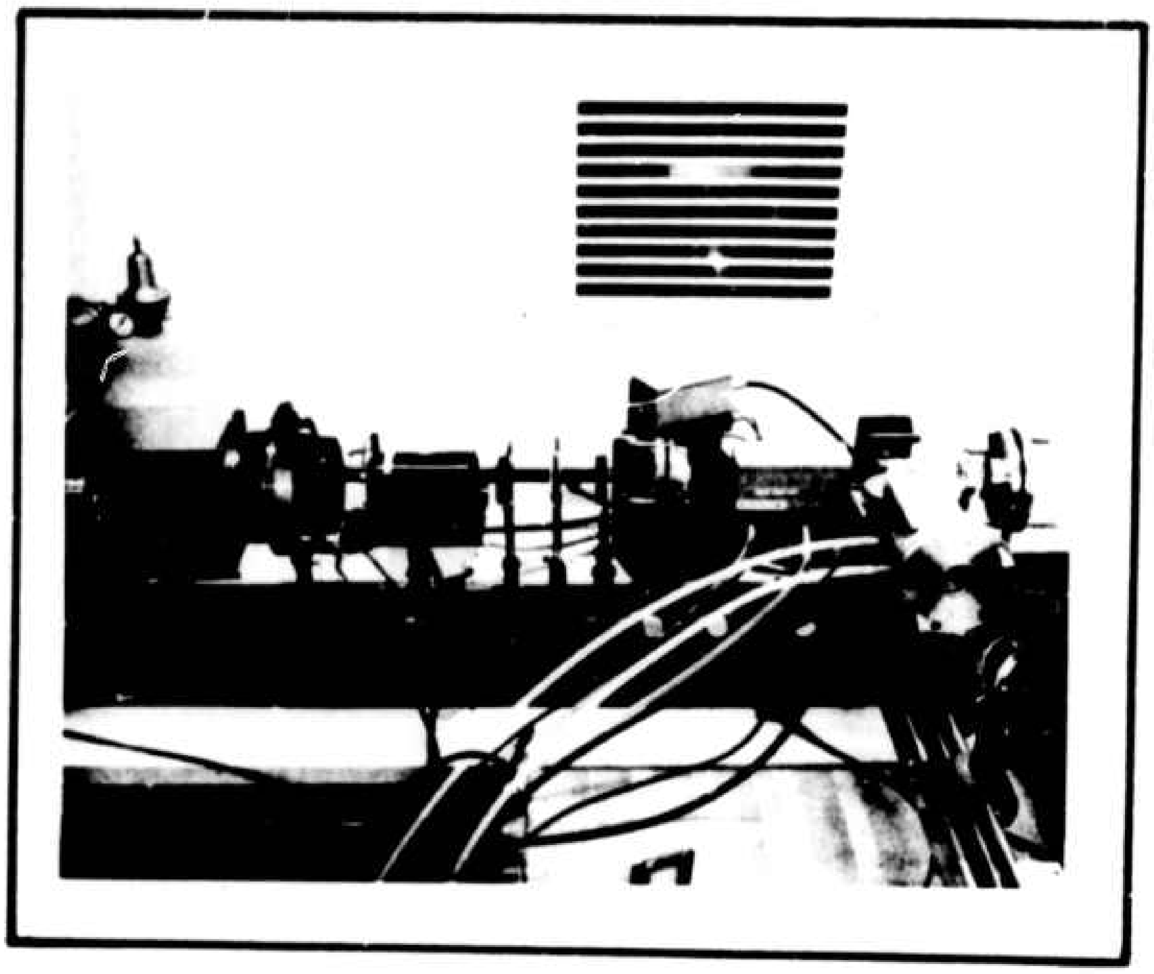

Figure 2

Experimental Arrangement for
Frequency and Temporal Locking Studies

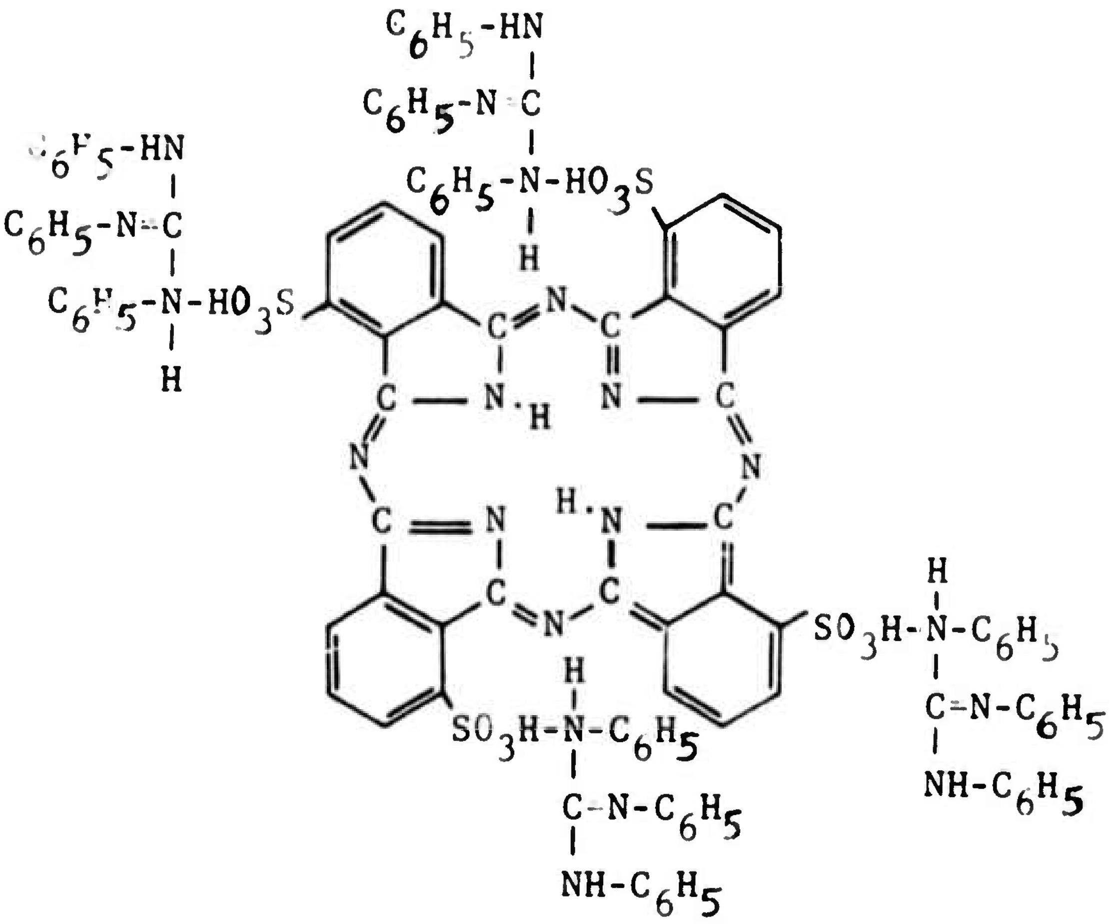

Figure 3

Schematic Diagram of Triphenyl Guanadine Salt of Tetra Sulfonated Metal-Free Phthalocyanine

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in methanol (solvated with a drop of water) were used. These dyes, with lifetimes of several nanoseconds and cross-sections $\sigma \sim 10^{-16}$ cm^2, are amongst the easiest to bleach and this solvent with its high threshold allows the possibility of obviating the spectral complications of the stimulated Raman and Brillouin effects.

Dielectric mirrors of ~ 30% reflection or sapphire resonant reflectors were employed as desired, at the output ends. Ruby rods, .05% Cr^{+3}, 10 cm x 1.4 cm were employed. Outputs, typically 1 x 10^8 watts, were monitored with a planar photodiode. The signals were displayed on a traveling wave oscilloscope. Both laser heads were water-cooled independently so that different operating temperatures (in the neighborhood of room temperature) could be achieved in order to effect spectral shifts.

To study the spectral behavior of the system, the Fabry-Perot interferograms using 4 cm and 1 cm spacers, were effectively bifurcated, each half showing only the spectrum of one of the two lasers. When the lasers were set with their polarizations coincident, for example, the plane of polarization of one of them was rotated by 90^o outside the cavity just before the Fabry-Perot with a half wave plate with principal axes at 45^o to the plane of polarization and the light was analyzed at the film plane of the Fabry-Perot apparatus. Care was taken to eliminate stray, scattered, depolarized and extraordinary laser light so that the representation was faithful.

When the input to each laser was adjusted so as to give a single comparable giant pulse, temporal synchronization did occur if the relative delay of inception of pumping was within definite limits (~ 400μ sec). With longer delays two characteristic and unsynchronized pulses were produced; one from each laser. When "synchronized", the synchronization was never exact but the pulse of the "slave" laser always followed by some 50 nanosec. (see Figure 4.)

With the lasers held at several degrees centigrade apart, and operated so as not to be synchronous, they always yielded disparate interferograms indicating operation at different frequencies as was to be expected. (See Figure 5A.) When the lasers were operated synchronously, the slave laser always locked to the frequency of the master and usually exhibited a set of extra lines not observed in the spectrum of the "slave" laser when fired alone. A typical example is shown in Figure 5B. The locked-in line is not always the most intense of the set.

A second experiment, a variation of the first, was performed wherein the lasers were set orthogonally, with crossed cavities (see Figure 6). A common passive Q-spoiling cell served for both lasers at the intersection of the cavities near the mirrors of maximum reflectivity. Exactly the same spectral and temporal results were obtained as described above. Either laser could be made to drive the other by varying pumping time and rates. As in the first experiment, the slave could be pumped to just below the point where it could lase alone and again it would slave with the same spectral and temporal properties already described. Again, as in the first experiment, the polarizations of these lasers could be set orthogonal (vertical and horizontal) and still each one could be made the master for the other. This has bearing on the question of scattering as discussed below, but it is noteworthy also for it shows that the dichroic dye molecules bleach isotropically even in the time of a giant pulse due to rapid collisions with the solvent.

In a third set of experiments, a non Q-spoiled "spiking" laser was the master laser outside the cavity of the slave in the

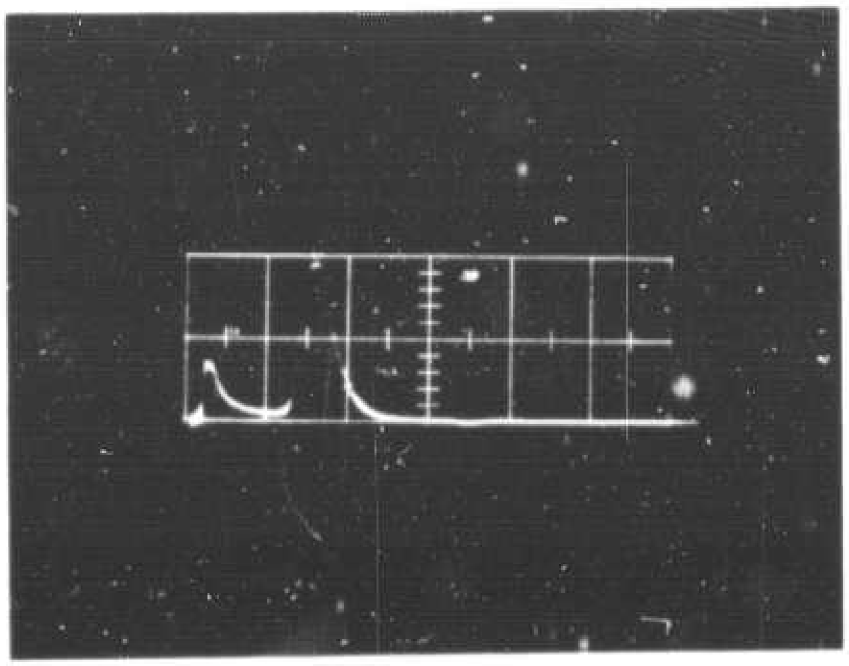

Figure 4

"Synchronized" pulses.
50 nanosec/div.

The pulses were made to appear with different amplitudes for identification.

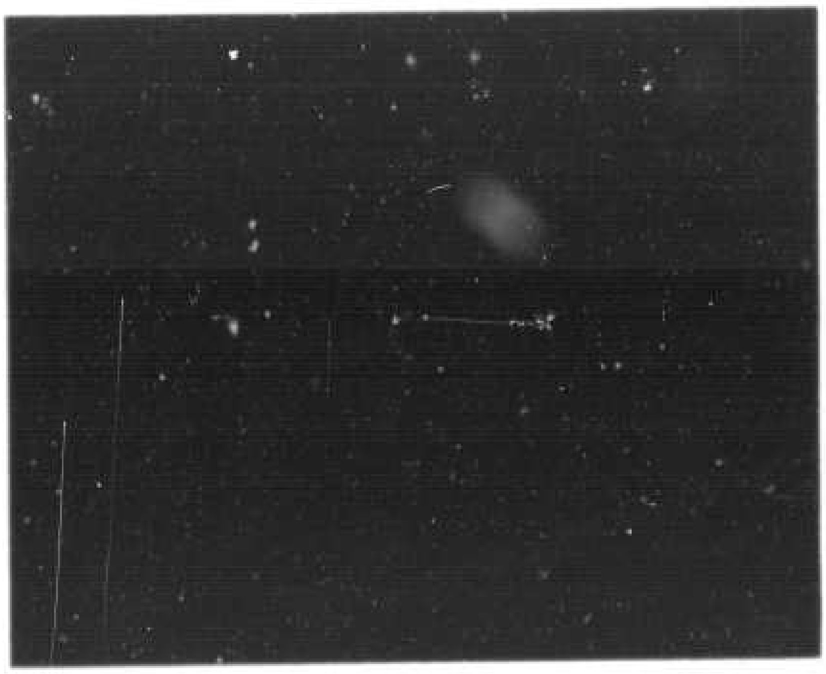

Figure 5A

Interferograms of unsynchronized giant pulses.

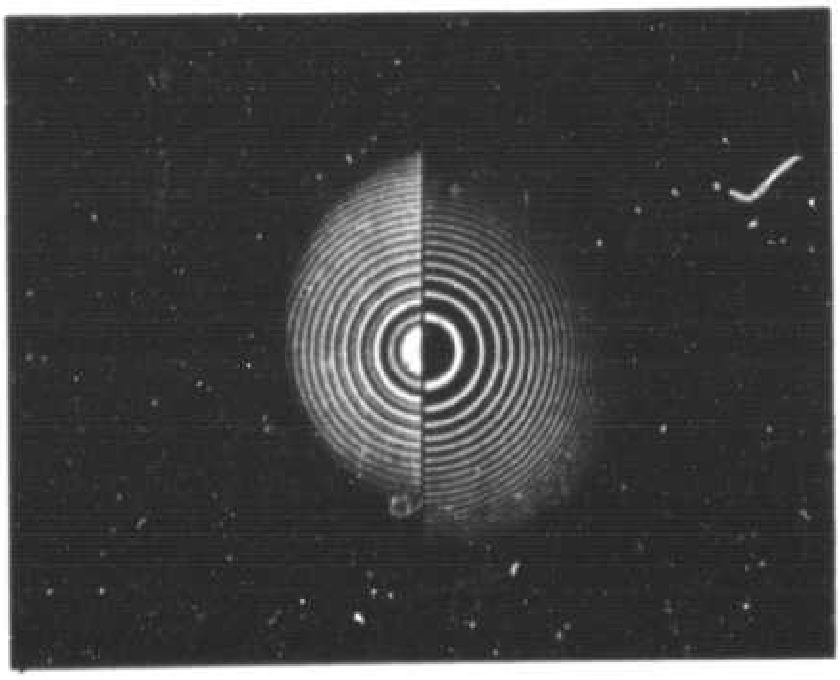

Figure 5B

Interferograms of "synchronized" giant pulses, showing one supernumerary line in the slave laser spectrum.

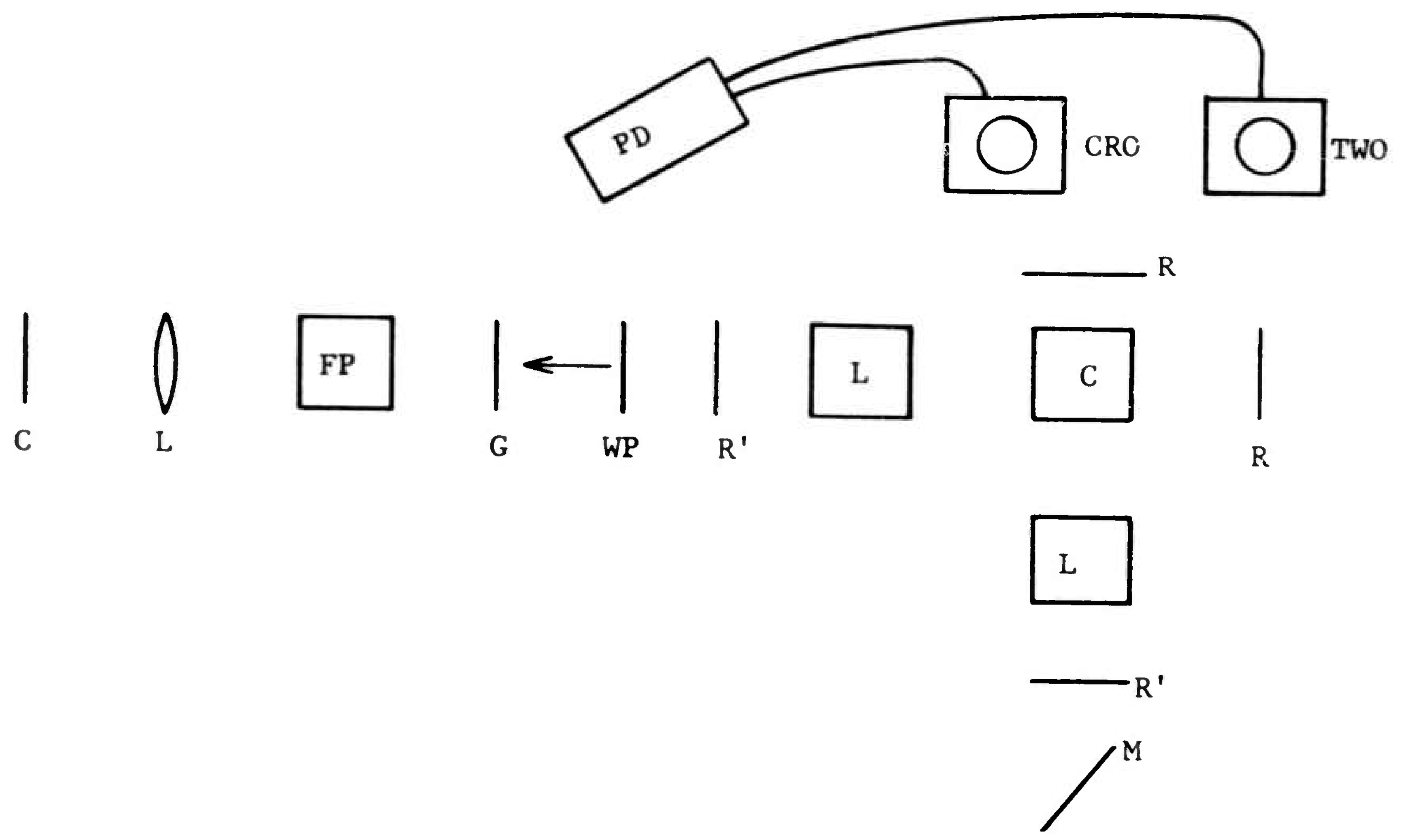

Figure 6

Scheme of Second Set of Experiments

configuration of the first experiments (see Figure 7). The spikes were typically of the order 10^5 watts peak power and 10^{-7} sec duration. The total envelope of the spikes was 2 x 10^4 sec. This was sufficient to trigger the giant pulse of the slave as could be determined by reducing the pumping of the slave to below where it would oscillate by itself. The giant pulse of the slave occurred 10^{-4} sec after initiation of the master. The ordinary laser was constrained to give a simple spectrum with a 1 cm^{-1} interorder spacing sapphire resonant reflector inserted in the cavity. The slave did exhibit frequency locking to that spectrum and also produced additional lines. Here again these results could be produced with the polarization of the lasers set orthogonal.

To check the possibility that these orthogonal cavities were coupled by scattering from the dye cell and thereby exhibiting common frequencies, an experiment was performed wherein light was deliberately scattered into the cavity of the giant pulse laser from the ordinary pulse laser. The beam was directed onto a cell containing a scattering solution of synthetic "cream', juxtaposed in series with the dye cell in the cavity of the giant pulse laser (see Figure 8). We separately measured the ratio of scattering cross-section of dye cell to scattering cell and the various depolarization ratios. Using a high "cream" concentration and adjusting the polarization of the lasers both vertical, we were able to scatter $> 10^2$ times more spectral power density into the giant pulse laser cavity than the dye cell did in the least scattering polarization configuration of the third set of experiments described above. No spectral locking nor any perturbation of the giant pulse spectrum was observed under these circumstances.

It is clear that scattered radiation was not responsible for frequency locking. We conclude from these experiments, that hole-burning in the dye, however rapid its spectral diffusion may be, is the cause of the frequency locking. The results of

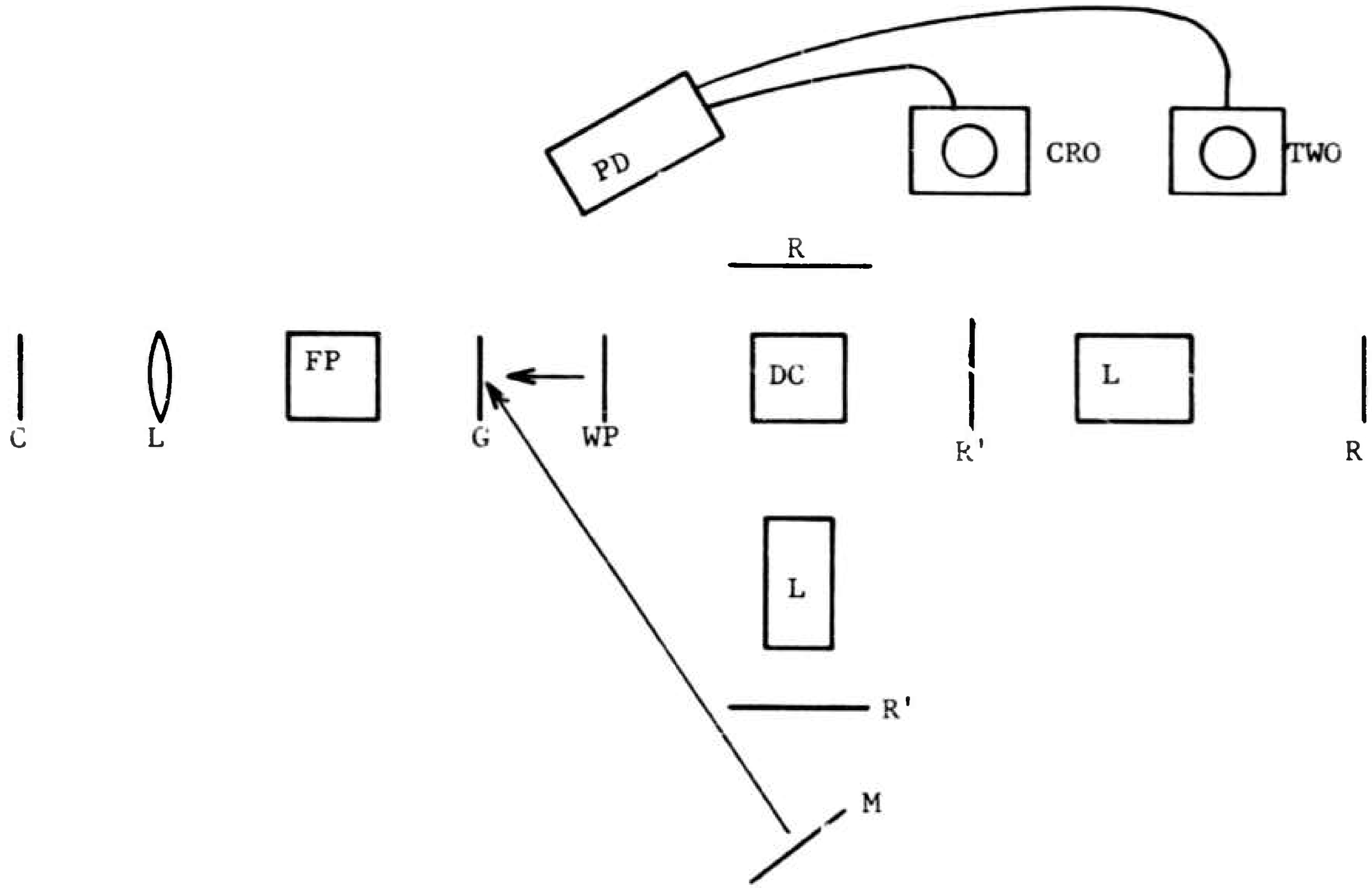

Figure 7

Scheme of Third Set of Experiments

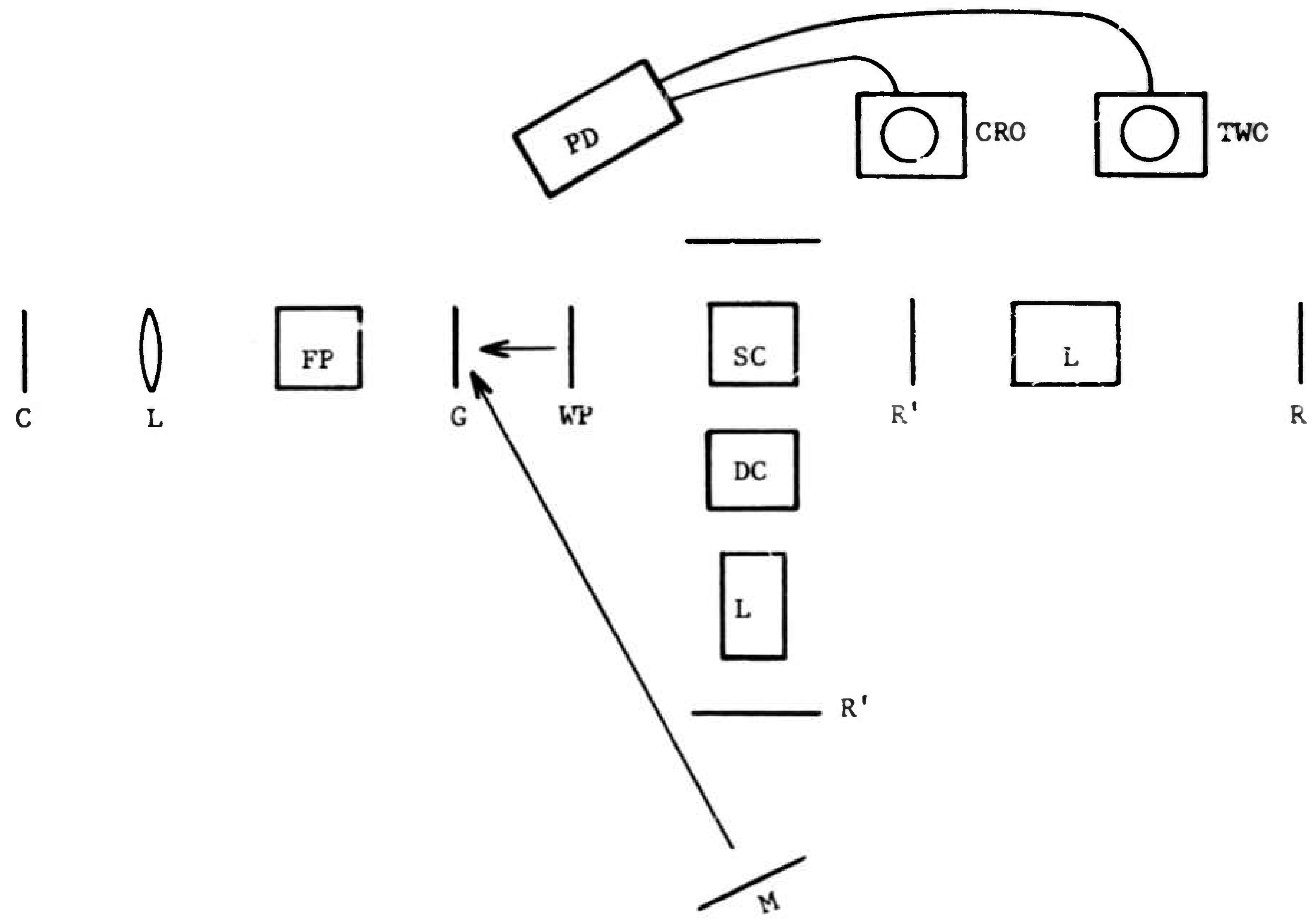

Figure 8

Scheme of Scattering Experiments

these experiments do not invalidate, but supplement the mode competition or "natural selection of modes" theory[6,9] of the spectral behavior of passively Q-spoiled lasers. The generation of still additional lines in the slave laser spectrum may possibly be explained by noting that the slave signal is somewhat deprived of its normally large number of loop transits building up out of nosie, which is believed required to suppress weaker modes.[6] However the existence of these lines may be evidence of frequency pulling by the master.

(2) Multi Spectral Line Bleaching

An experiment was performed to study the spectral cross-relaxation behavior of a polymethine dye used as a saturable absorber for Q-spoiling. The problem considered was the comparative efficacy of a single spectral laser line and several spectrally-separated lines of the same total power in bleaching the dye. If the dye solution has, for example, a very long spectral relaxation time, referred to a particular spectral separation (greater than the separation of the inhomogeneous components), then the several separated weak lines would not aid each other in the bleaching process and would not have the over-all bleaching effect of a single more powerful line operating in the more saturated region of the dye transmission characteristic. Thus, by varying the number of lines and their spectral separation, one might map the details of the spectral relaxation properties of the dye.

The dye studied was the Kodak Q-spoiling dye #9740 (EKD), which is undoubtedly* a polymethine dye in the carbocyanine dye

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[9] In support of this theory we found that the spectral linewidth of a ruby laser, mode selected with a 1 cm^{-1} resonant reflector, was a monotonic, increasing function of the angular velocity of the Q-spoiling prism. At the longest period (2.5 msec) the linewidth was 0.02 cm^{-1}. At a period of 0.64 msec the linewidth doubled.

* At this writing, Eastman Kodak will not reveal to us the chemical nature of the dye.

family, dissolved in chlorobenzene. An Nd^{+3} glass laser was employed in order to obtain large variations in both the number and separation of spectral components, as desired by the use of resonant reflectors. A schematic representation of the experimental apparatus used is given in Figure 9. The Nd^{+3} glass laser, Q-spoiled with EKD, was used as a source to bleach another cell of EKD. Two photodiodes sampled the signals both before and after the test cell to measure a bleaching or saturation characteristic curve (i.e., peak power transmission vs. peak power input). The signals from both diodes were displayed on a traveling wave oscilloscope trace, one signal being delayed some 50 nsec by a length of cable. Spurious reflections engendered by a non-matching T-connector were eliminated by terminating the cables with matching impedances at the photodiodes. The system was also operated with a cell of solvent alone, replacing the dye cell, as an aid to calibration and a check on solvent nonlinear behavior. The beam was finally directed to a 3.4 meter spectrograph where the laser spectrum was analyzed. The spectral plates were not photometrized -- all photometric data being recorded by the photodiodes.

A typical bleaching curve is shown in Figure 10. Single spectral component data points are distinguished from the multi-spectral component data points. In this set of data, the spectral separation of the components of the multi-lined channeled spectra was one wavenumber. No significant variation, outside of the experimental errors, can be noted even when as many as six spectral components were employed in a pulse. An analysis of the data shows that if any spectral "hole burning" occurred within the observable time resolution defined by the giant pulse experiment, then it was at least five times smaller an effect than the maximum effect expected for the case of very long spectral relaxation times -- the bound being set by the average deviation

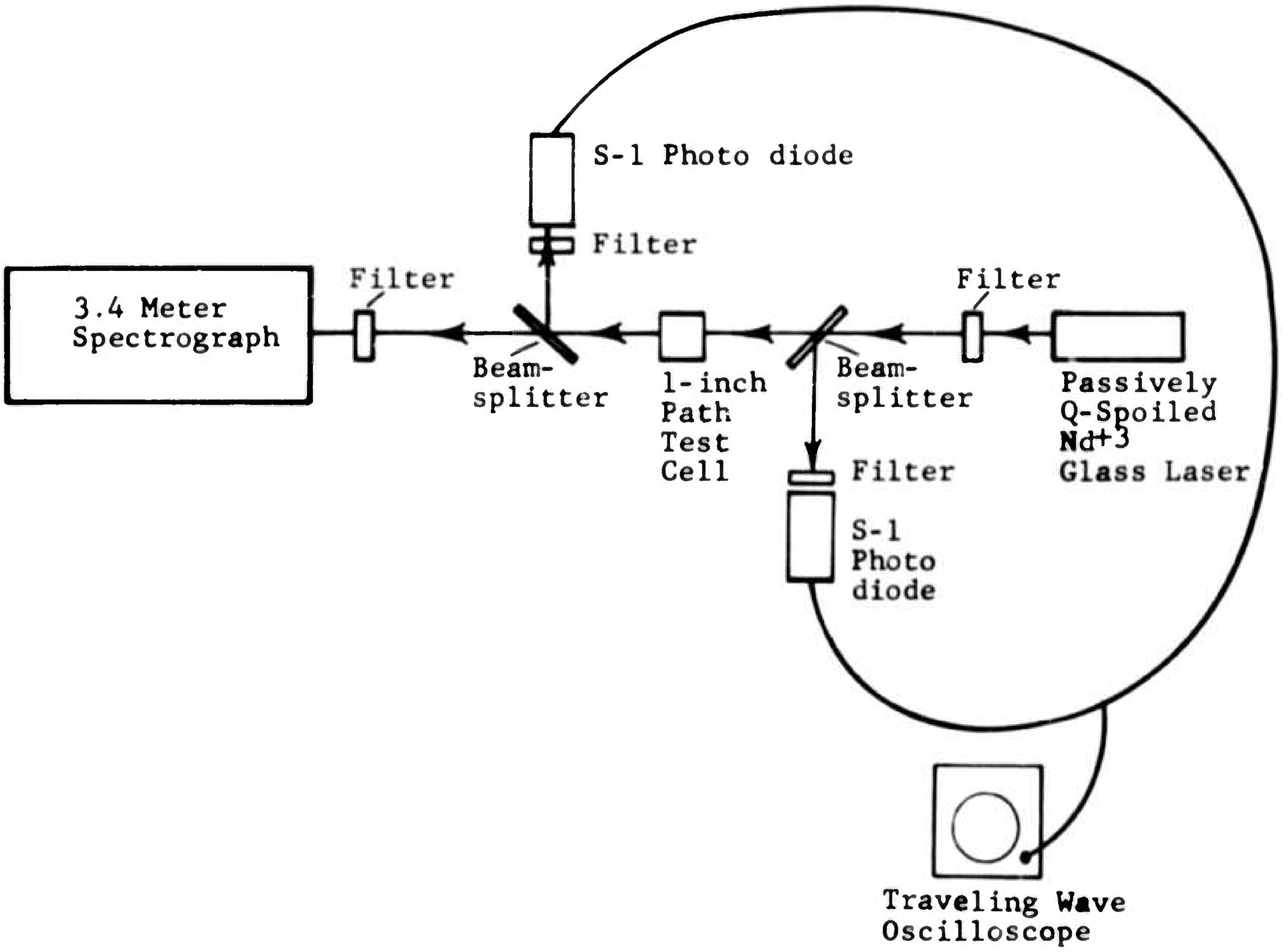


Figure 9

Schematic of Experimental Arrangement

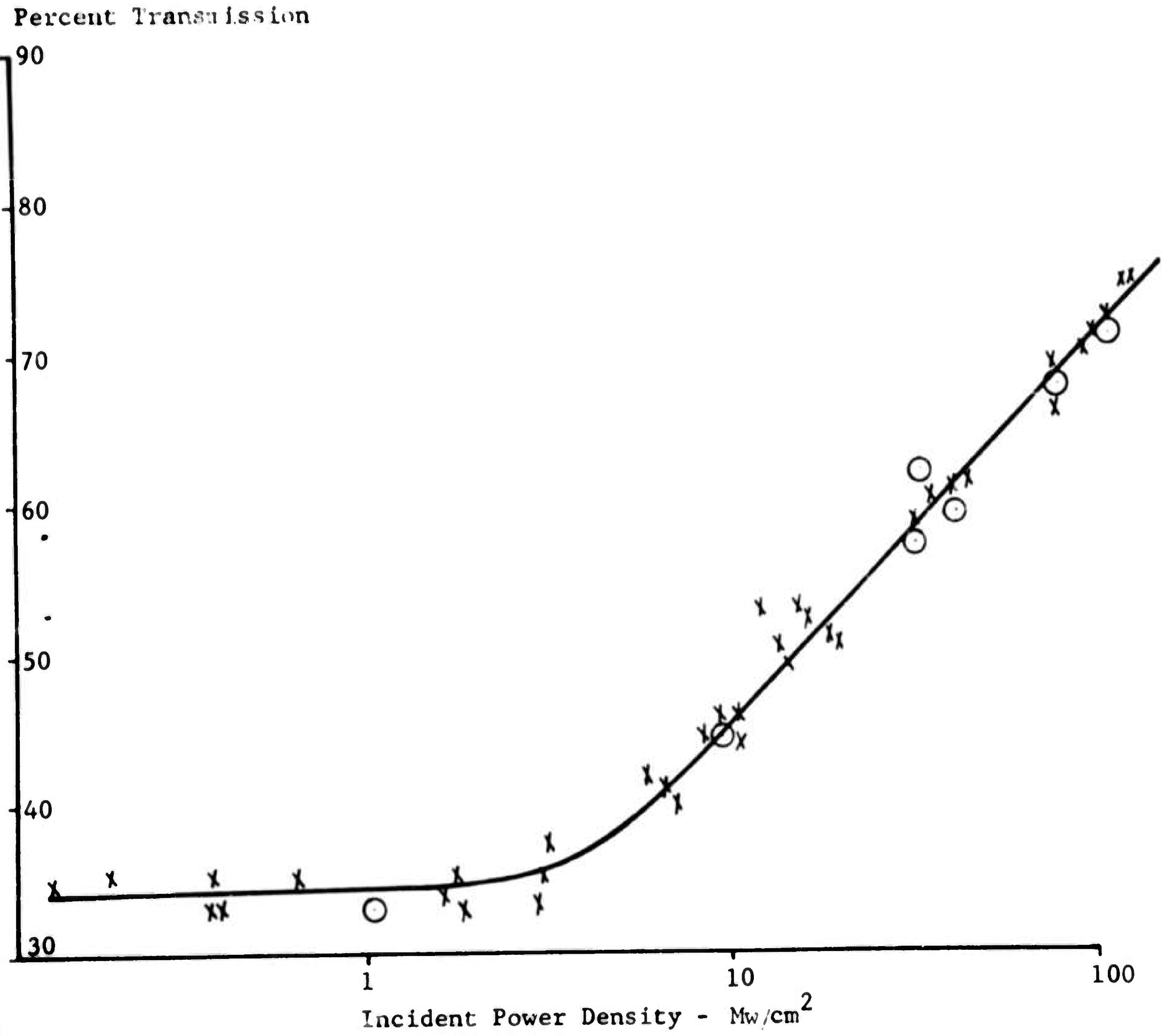


Figure 10

Saturation Behavior of Kodak Q-spoiling Dye #9740 (EKD)

X Single Spectral Component Pulse
○ Multi Spectral Component Pulse

of the errors in the measurements. Therefore, either the individual homogeneously broadened components of the dye absorption spectrum are wide, compared to about 6 cm^{-1}, or cross-relaxation times within this spectral range are too rapid to have consequences observable by this technique.

An incidental systematic effect observed in collecting this data is noteworthy. At any arbitrary positioning of the beam splitters (wedged to obviate interference effects) and the photodiodes, generally greater disparate skewed and structured laser power pulse shapes would be recorded, even with no dye or control cell interposed in the beam. This was carefully demonstrated not to be an instrumental problem by permuting the delay lines, the photodiodes, and other portions of the apparatus. Only by the judicious adjustment of the angular and spatial sample of the laser beam directed into each diode could the pulses be made congruent, the pulse shape depending on the particular choice made. We conclude from this, therefore, that each giant laser pulse is spatially and angularly quite variable in its temporal character and only the average over space and angle has the smooth "bell" shape character usually reported.

In the course of the spectral hole-burning studies described above, it was observed that the Nd^{+3} glass laser passively Q-spoiled with bleachable dyes exhibited a certain erratic spectral behavior from pulse to pulse. The laser would usually emit a single narrow line, and could easily be constrained to do so with resonant reflectors. But, even so constrained, the wavelength of the emission would vary from pulse to pulse. Occasionally, a burst of several lines would appear -- channeled at the inter-order spacing of the resonant reflector. Furthermore, this effect was observed to some degree with both the Korad[10/] and the Kodak Q-spoiling dyes.

[10/] B. H. Soffer and R. H. Hoskins, Nature, 204, 276 (1964). See also "Eastman Q-Switch Solution 9740", a circular released by Distillation Products Industries (October 1965).

B. Stimulated Emission in Organic Dyes

(1) Visible Stimulated Emission from Organic Dyes

Organic dyes have recently been shown to exhibit stimulated emission when excited with the high brightness of a ruby laser. These dyes have consequently emitted radiation in the near infrared. We have demonstrated efficient laser emission in the visible region using dyes such as the rhodamines and fluorescein. Dyes in the xanthene and related families have conspicuously high fluorescent quantum efficiencies -- the more commonly available ones having their absorption bands located in the ultraviolet and blue-green, precluding direct pumping with such lasers as the ruby or neodymium lasers at power levels of ~ 10 Mw/cm^2 (see Figure 11). Peak laser wavelengths are tabulated in Table I. Conversion efficiencies of more than 15% were obtained.

Table I

	Solvent	Laser Wavelength (mμ)	Source Wavelength (mμ)
Fluorescein (disodium salt)	water	535	347
Acriflavin hydrochloride	ethyl alcohol	510	347
Rhodamine-B	"	577	347,530
Rhodamine-G	"	585	347,530
Rhodamine-6G	"	565	347,530

The output beam angle of the dye laser can be narrower than that of the laser pump when the pumping is uniform as in the case of axial pumping. Over-all brightness gains have thus been realized. Thresholds, depolarization effects upon the pumping radiation, and other particular details are given in Appendix B, a reprint

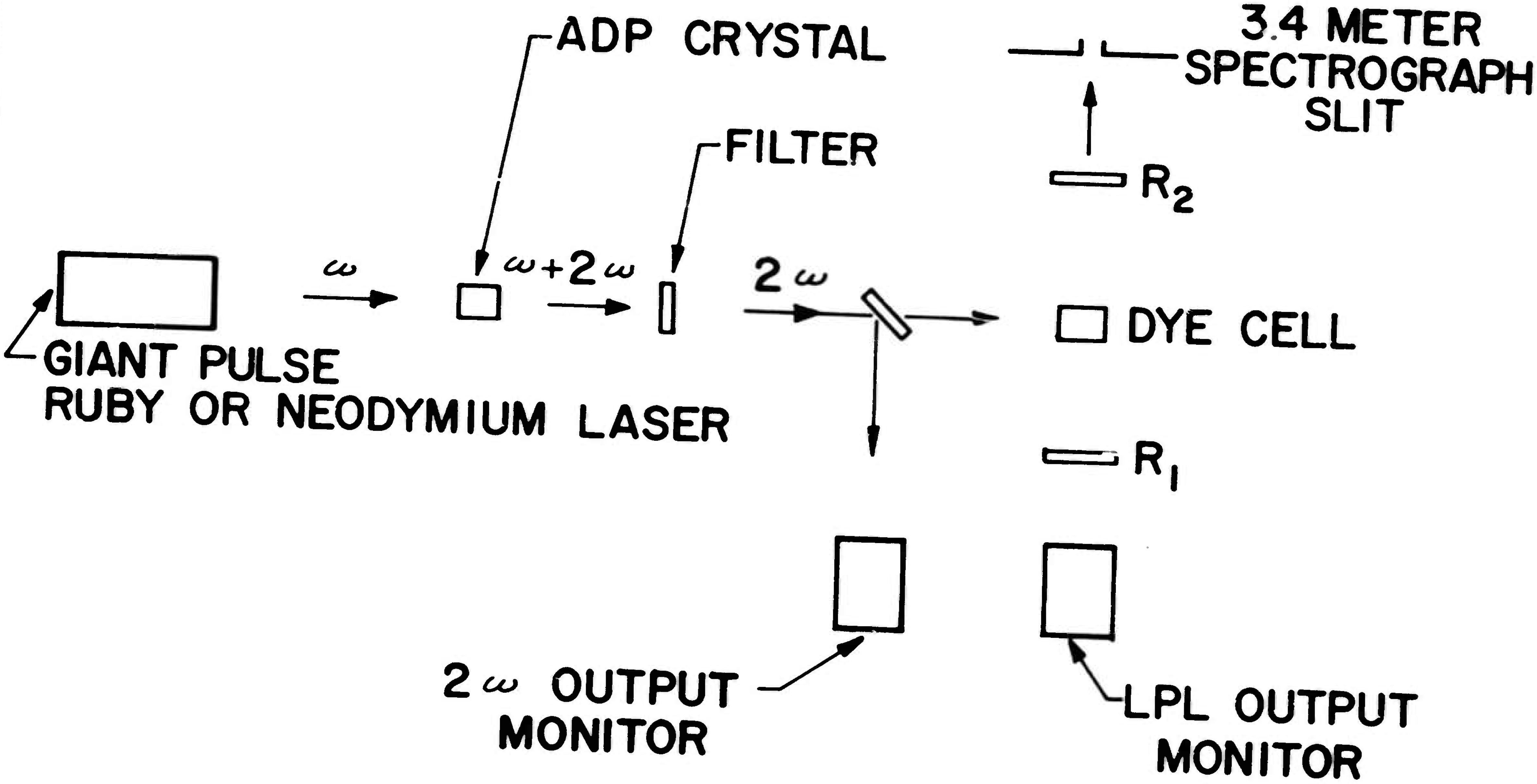

ADP CRYSTAL
FILTER
3.4 METER
SPECTROGRAPH
SLIT
R_2
ω
$\omega+2\omega$
2ω
DYE CELL
GIANT PULSE
RUBY OR NEODYMIUM LASER
R_1
2ω OUTPUT
MONITOR
LPL OUTPUT
MONITOR

FIG. 11

Figure 11

Schematic Diagram of Experimental Apparatus of a recent publication describing this work. It is noteworthy that the organic dye solution laser emits a spectrally variable and spectrally broad pulse up to some hundreds of wavenumbers wide, depending upon dye concentration, cavity length, and conditions of cavity gain (see Figure 12).

(2) Continuously-Tunable Narrow-Band Organic Dye Lasers

We have demonstrated efficient spectral narrowing and continuous tunability in organic dye lasers over bandwidths that are large compared to the ordinary lasing action by using diffraction gratings as cavity reflectors (see Figure 13). These effects have been demonstrated in the visible spectrum with rhodamine 6G and in the near infrared with a carbocyanine dye. With a particular rhodamine laser, for example, the spectral bandwidth was reduced from 60 Å to a single line of width 0.6 Å when a grating of 2160 ℓ/mm was employed. The efficiency of this spectral "condensation" was approximately 70% in the region of normal dye lasing action where peak output is obtained. The range of tunability at the half-power points was some 200 Å, a value greater than the bandwidth of normal lasing action (see Figure 14). Powers were in the range of 2×10^6 watts, but no attempt has yet been made to optimize or maximize this value.

Similar results were obtained with a solid sample of rhodamine 6G in polymethylmethacrylate pumped with the second harmonic of a Nd laser, the first demonstration of organic singlet-singlet lasing in the solid state. Furthermore, similar tunable lasing behavior was obtained in the near infrared region with 3,3' diethyl-thia-tricarbocyanine iodide in ethanol, pumping with a ruby laser. Additional details of the continuously tunable lasers are given in Appendix C, a preprint of a recent publication describing this work.

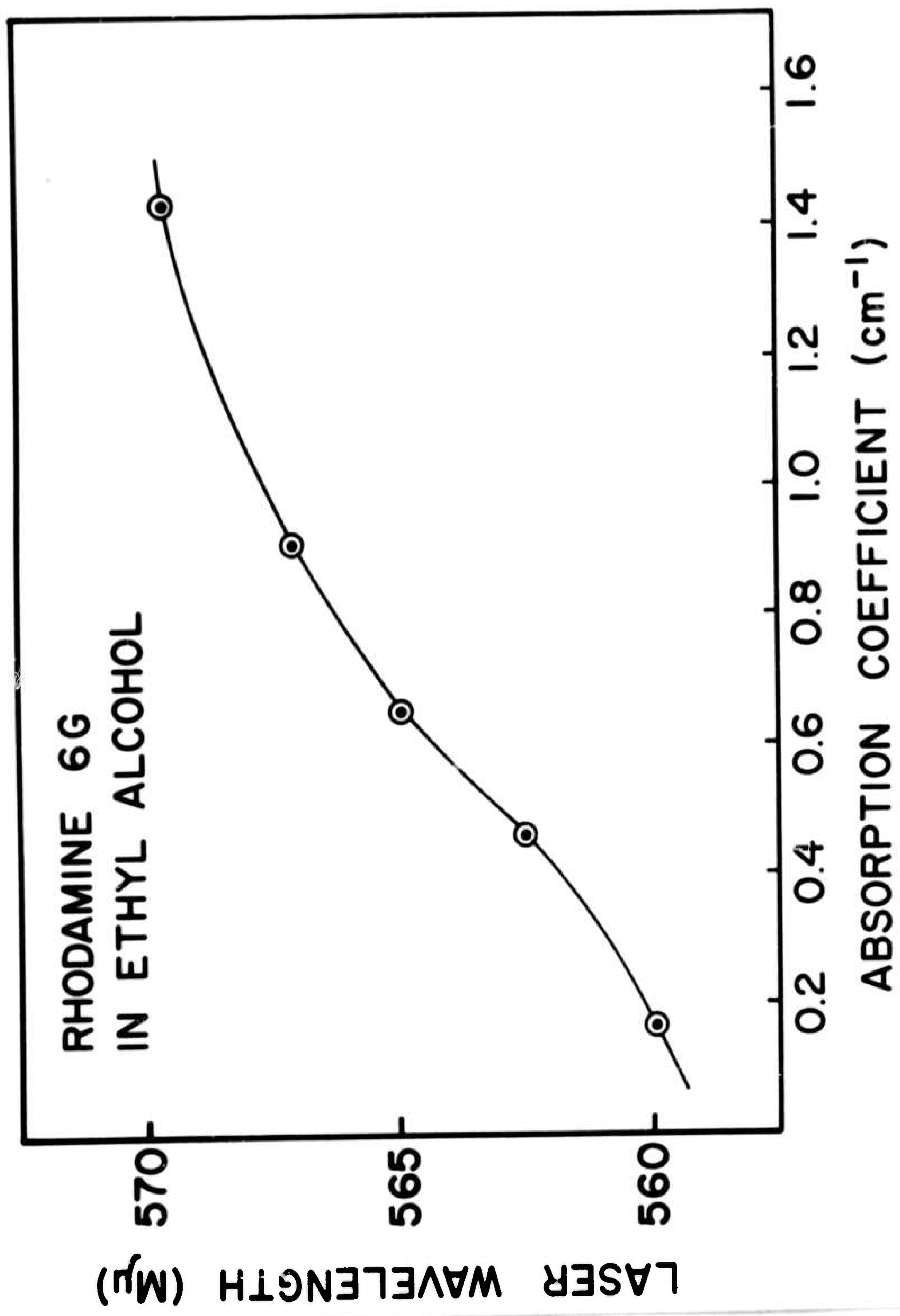

RHODAMINE 6G
IN ETHYL ALCOHOL
LASER WAVELENGTH (Mμ)
570
565
560
ABSORPTION COEFFICIENT (cm^{-1})
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

FIG. 12

Figure 12

LPL Emission Wavelength vs. Absorption Coefficient for Rhodamine 6G Dissolved in Ethyl Alcohol

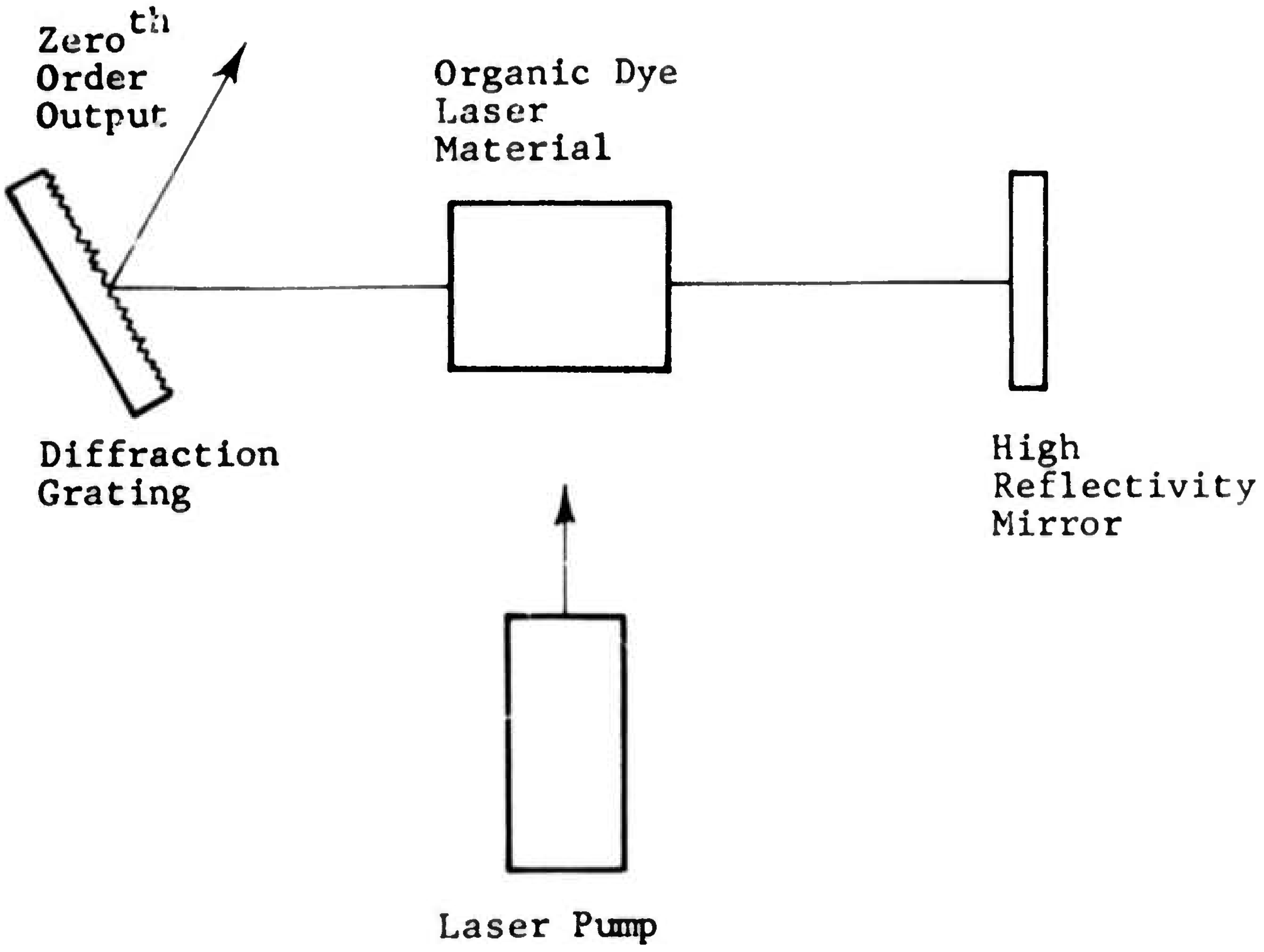


Figure 13

Schematic Diagram of Tunable Dye Laser

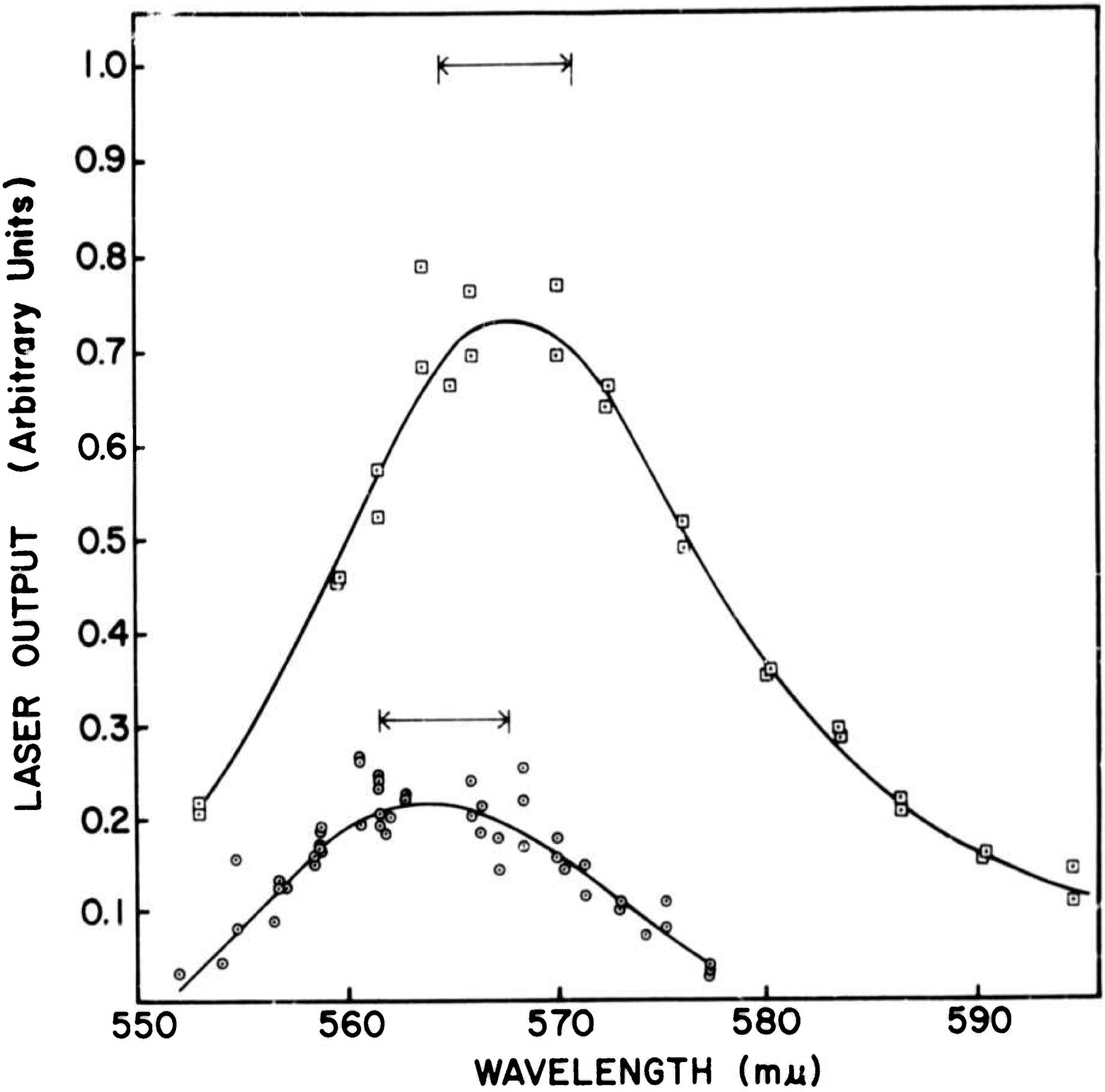


Figure 14

Relative efficiency of tunable rhodamine 6G laser vs. wavelength. Upper trace: ⊡ optical density, 1.3 (347 mμ), Grating in cavity, ↔ Dielectric reflectors. Arrows indicate spectral bandwidth for this case, Lower trace: ⊙ optical density 0.35 (347 mμ). Grating in cavity ↔ Dielectric reflectors.

The spectrally broad output of the various families of dyes thus far successfully employed as organic dye lasers has led observers to consider them as primarily inhomogeneously broadened systems. Broadening of the spectral emission with higher cavity gain conditions further supports this outlook. The high relative efficiency of narrow line emission we observe, however, points out the need for qualifying this view. The upper laser state is evidently homogeneously broadened.

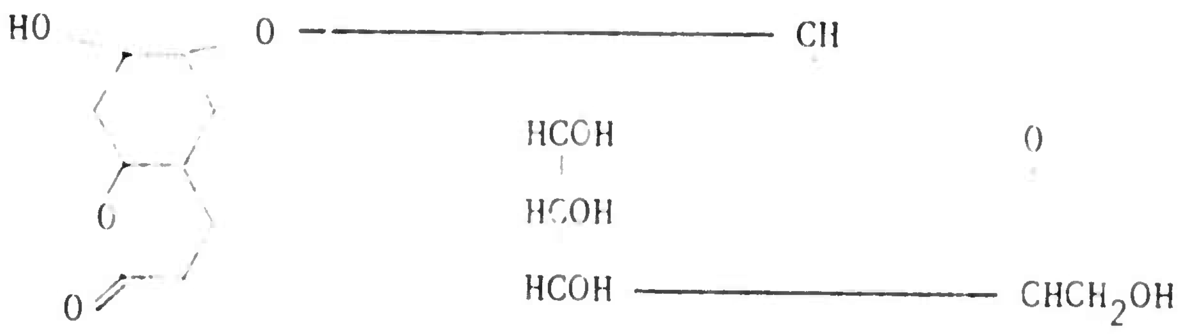
It is expected that many related dye families will behave in a similar fashion and that the entire wavelength domain, from 347 mμ (ruby second harmonic) to about 1μ, could be practicably spanned according to these techniques.

(3) Additional New Dye Laser Materials

Two new, blue-violet emitting successful organic dye laser materials were found in this period: Esculin and Acridone. Subsequently, almost simultaneously, other workers rediscovered these or related molecules as dye laser materials. The structural chemical formulas of these species are shown in Figure 15. The room temperature absorption and fluorescence spectra of these molecules in methanol solutions are displayed in Figure 16. Both species exhibit the typical mirror symmetry of absorption and fluorescence characterisitic of organic compounds, but it can be seen that the vibrational and other structural features evident in the spectrum of Acridone (upper trace) are mitigated in the diffuse and broad spectra of Esculin. It was thought that this may be caused by the sugar-like part of the Esculin molecule (cf. Figure 15) whose many possible steric forms may be responsible for an inhomogeneously broadened spectrum. Furthermore, this sugary part of the molecule imparts a small optical rotary power whose effects upon the generation of stimulated emission are of interest. Several relatives of Esculin without the sugar-like part, Coumarin, Esculatin and Umbeliferone were examined spec-

The structural formulas of

Esculin



and

Acridone.

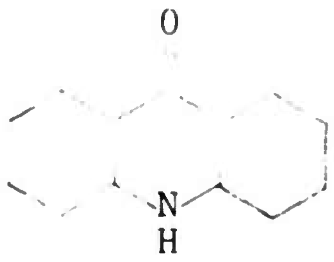
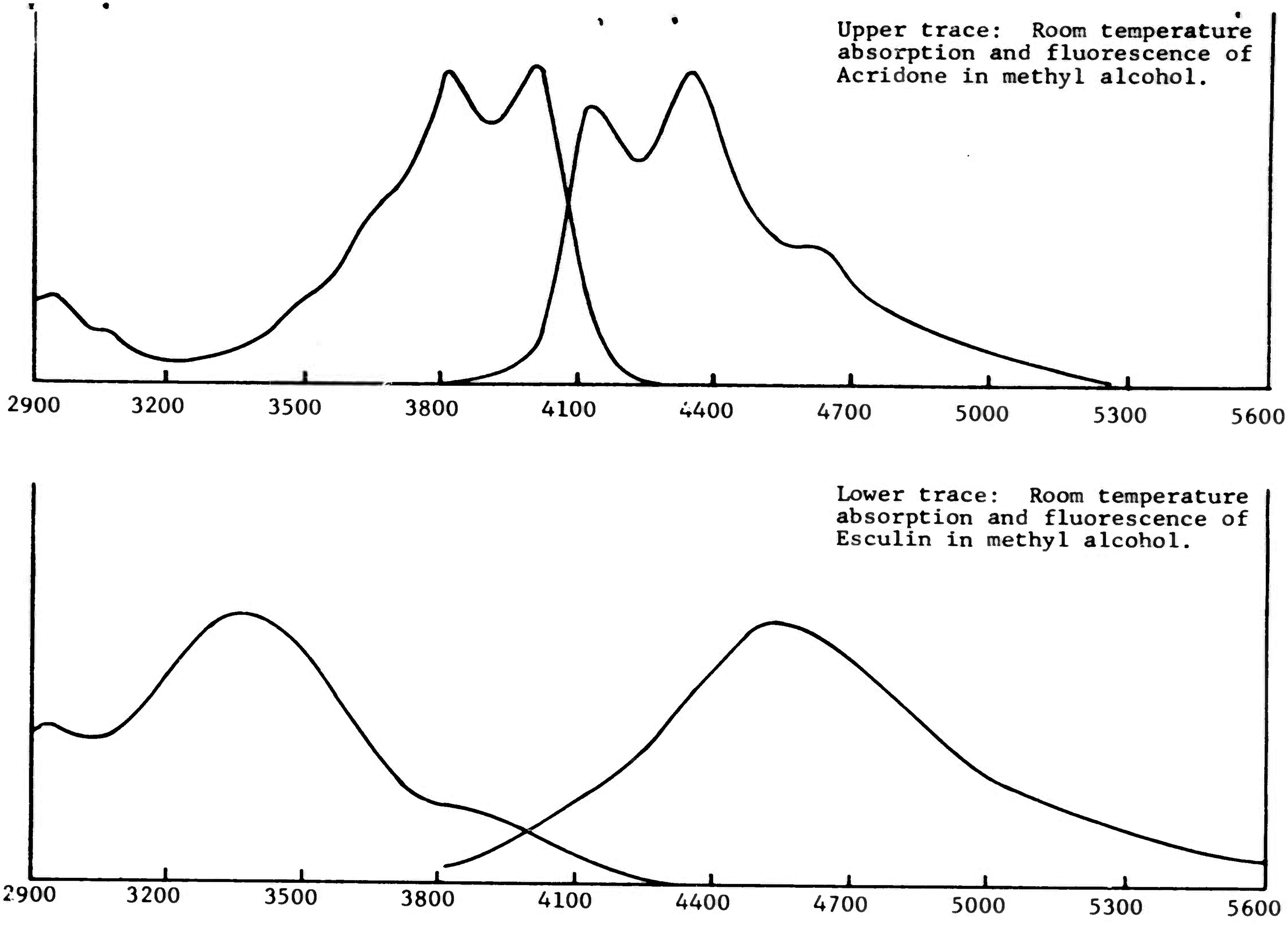


Figure 15

The Structural Formulas of Esculin and Acridone



Upper trace: Room temperature absorption and fluorescence of Acridone in methyl alcohol.

Lower trace: Room temperature absorption and fluorescence of Esculin in methyl alcohol.

Figure 16

troscopically. It was found that the spectra showed increasing complexity and broadening corresponding to the increasing number of OH groups in this series. The sugar-like part has little effect. Furthermore, no effects of the optical rotation upon lasing could be noted. The laser output when pumped with the second harmonic output of a giant pulse ruby laser (347 mμ), was found to be two times greater for the Acridone than for the Esculin solution (at optimum concentrations). The broad output of wavelengths for both dyes was centered in the neighborhood of 434 mμ. It should be noted (cf. Figure 16) that self-absorption in this region is more significant for Esculin (lower trace) than Acridone (upper trace). The Acridone laser at outputs of 1.5 megawatts had a power efficiency of 0.9% defined as output divided by ruby fundamental input. The ADP doubling crystal with an effective area of 0.6 cm^2 worked at 5% efficiency.

It is interesting to note that the added presence of 50 Mw/cm^2 ruby emission (694 mμ) in the pumping light tends to inhibit the lasing of Acridone but not of Esculin. The output was reduced to 0.5 Mw and the efficiency to 0.25% (including corrections for filter factors). As the ground state of Acridone does not absorb ruby light, one may ignore the possibility of thermal degradation of the optical quality of the Acridone laser and conclude that the effect is due to an excited state absorption from the upper lasing level.

(4) Frequency Doubling the Organic Dye Laser

Experiments were performed with an ADP frequency doubling crystal in the organic dye laser cavity. Pumping a solution of the dye 3,3' diethyl-thia-tricarbocyanine iodide was effected with ruby fundamental laser radiation. The broad 190 Å wide spectral emission of the fundamental near 0.8μ transforms into narrowed 20 Å spectral width to be consistent with a 4 x 10^{-3} radian beam angle. At a given orientation only a fraction of the available wavelengths in the fundamental are efficiently phase matched for frequency doubling. The wavelength of emission can be tuned by rotating the doubler crystal but the output power falls rapidly following the square of the fundamental power variation with wavelength. A diffraction grating was used, as described earlier, as a cavity reflector to efficiently condense the output into a single narrow 2 Å line using a 1200 ℓ/mm grating. To span the whole useful range with good efficiency the doubler crystal, as well as the grating must be rotated. The lasing efficiency of Acridone, using a fixed ruby fundamental power, was compared to that of the 3,3' diethyl-thia-tricarbocyanine iodide operating with the frequency doubler in the cavity. Acridone with η = 0.9% had twice the power efficiency. However, the reflectivity of the cavity mirrors was not optimized at both fundamental and harmonic frequencies to capitalize on possible regenerative effects of the doubled light.

A highly structured channeled spectrum was sometimes observed with this system (less the grating) but with poor reproducibility. These channelings have also been observed without the incorporation of a doubler crystal. As they have not been observed in a system operating with a specially constructed cell having Brewster windows on all surfaces, internal and external, we believe they must have occurred by accidental Fabry-Perot type resonance in the cavity.

(5) Mode Locking the Dye Laser

In our quarterly report (1 Oct - 31 Dec 1967) we reported preliminary observations which indicated a degree of mode locking in an organic dye laser which might be sufficient to yield picosecond pulses. A Rhodamine 6G dye laser was pumped with the second harmonic of a mode-locked Nd laser. The length of the organic dye laser was made equal to or a submultiple of the pump cavity length, and trains of pulses were observed with subnanosecond resolution in the output of the dye laser. The existence of these pulses, with proper temporal periodicity is a necessary condition for the dye laser to be mode locked to some degree. Similar observations done independently and simultaneously by another group were recently reported in the literature.[11/]

A mode-locked neodymium glass laser was constructed for use as a pumping source for the organic dye laser. A photo of the experimental apparatus and a schematic diagram may be seen in Figures 17 and 18. All intracavity reflective elements were set at the Brewster angle and mode locking was effected by the use of a bleachable absorber near the 100% reflector in a cell positioned to minimize the intensity of satellite spikes on the main pulse train. The pulse was structured in groups of 10 or 11 individual pulses separated by 1×10^{-10} sec, an interval determined by the internal round trip in the cavity output reflector. The surfaces of this glass reflector were wedged at 2' and one surface was coated with a 30% dielectric reflector creating a lower resonator. These groups of pulses themselves, were separated by 3×10^{-9} sec, 2L/C of the cavity with typically 10-15 sets between the half power points. Picosecond pulses were detected by the two photon excitation of fluorescence technique. A photo of this representation of the pulses is shown in Figure 19. A solution of Rhodamine 6G in ethyl alcohol was employed as the fluorescent medium. The second harmonic of this laser generated by an ADP crystal revealed the same pattern of pulses with the same temporal duration of $4 \pm 1 \times 10^{-12}$ sec. A solution of Esculin in ethyl alcohol was employed in this case as the two photon fluorescent medium. The spectral bandwidth of the output was 150 cm^{-1}.

[11/] W. H. Glenn, M. J. Brienza and A. J. DeMarice, Appl. Phys. Letters 12, 54 (1968)

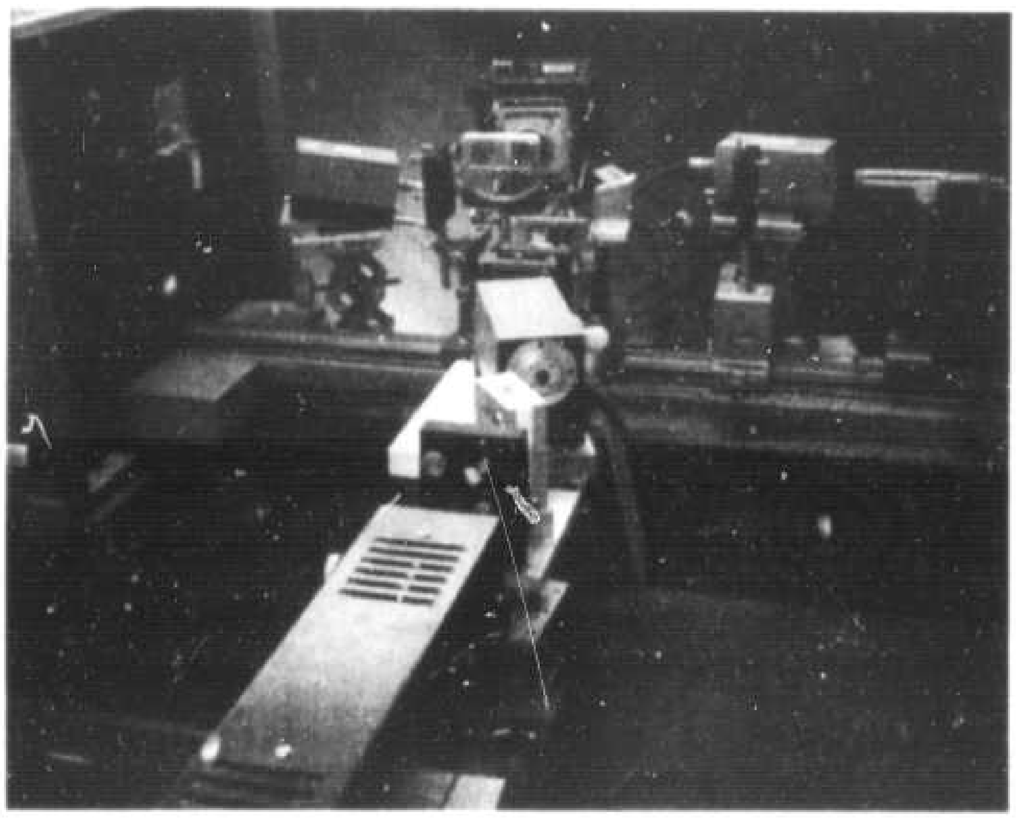


Figure 17

Photograph of Experimental Apparatus

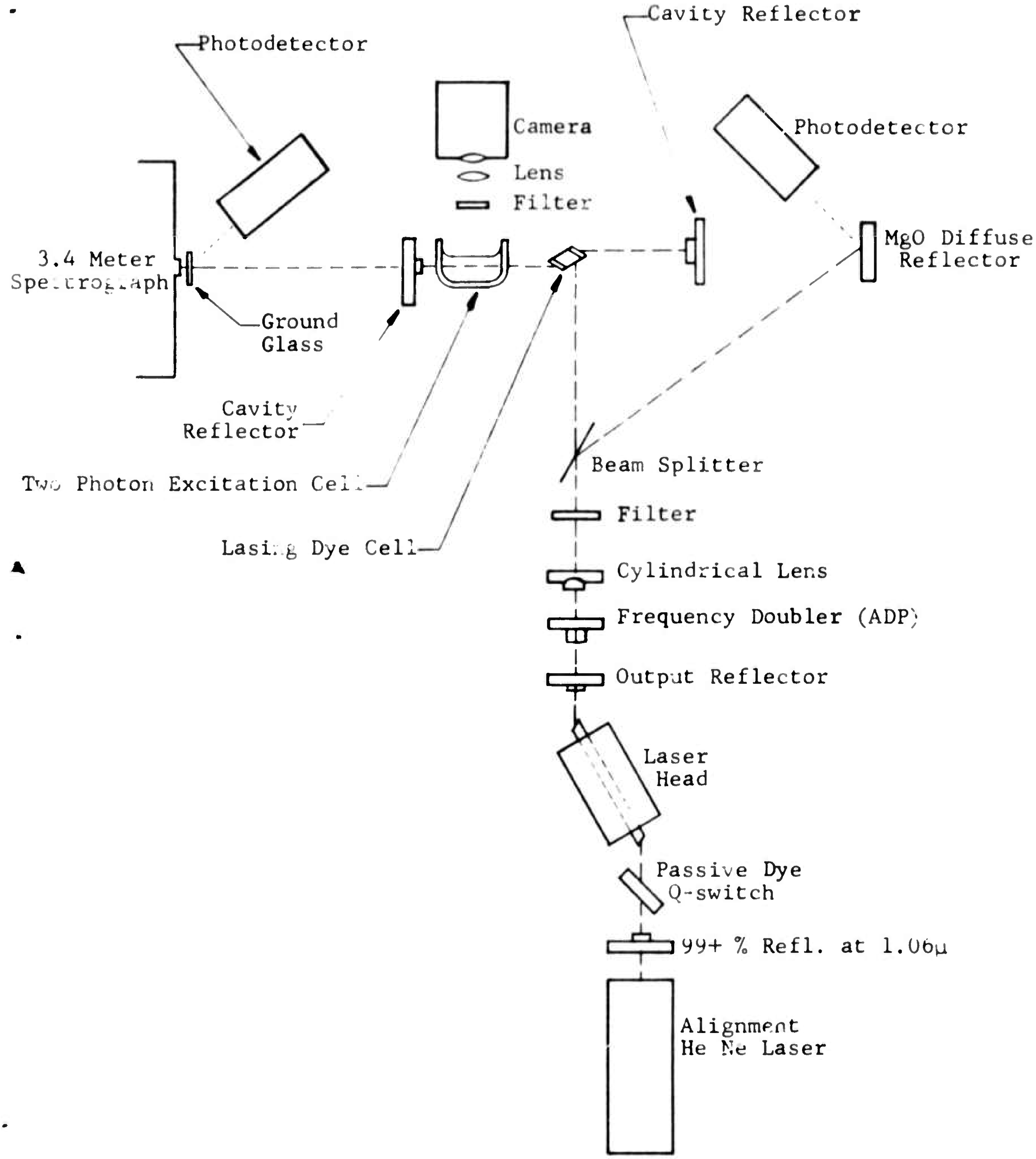


Figure 18

Schematic Diagram of Experimental Apparatus

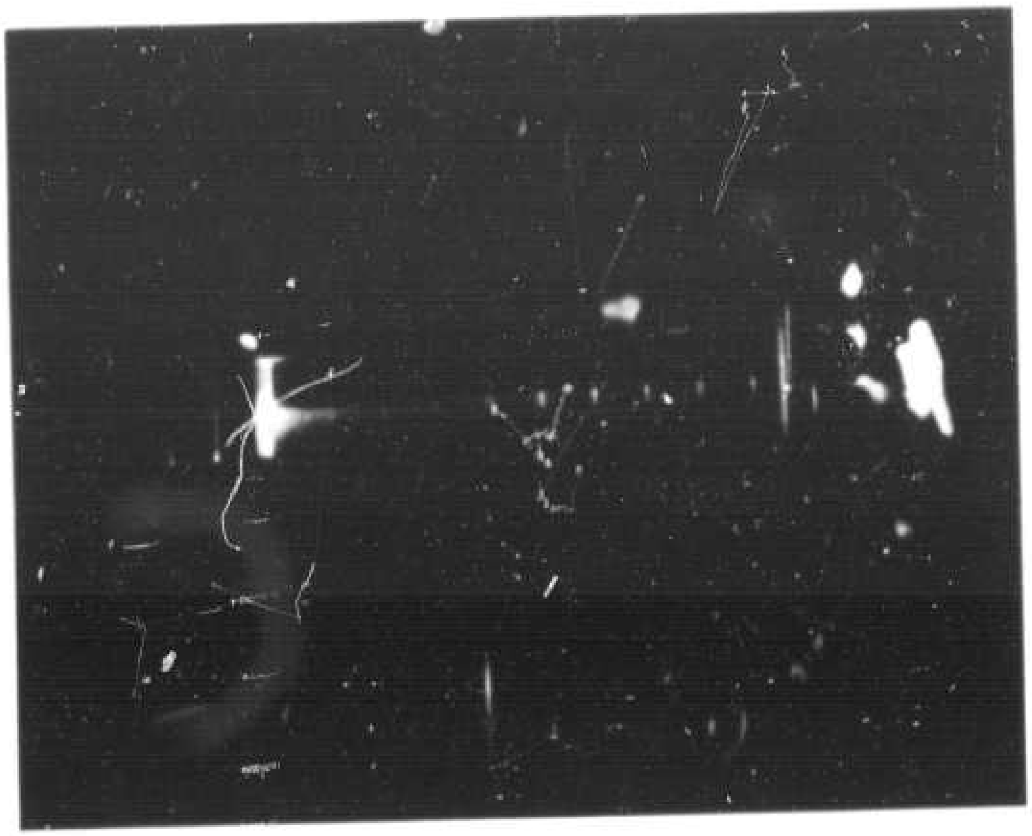


Figure 19

Two Photon Fluorescence Representation of Picosecond Pulses

These second harmonic pulses were used to transversely pump a Rhodamine 6G dye laser. An ethanolic solution of the dye with decadic absorption coefficient equal to 10 at 530 nm was contained in a cell constructed with internal and external window surfaces disposed at their respective Brewster angles. See Figures 17 and 18. The internal length of the cell was 1.15 cm. Laser action in unwanted directions was suppressed by degrading all optical surfaces excepting the windows. Wedged dielectric coated mirrors of ~ 99% reflectivity and of 60-90% output reflectivity were employed.

When the dye laser cavity optical length L_ℓ, was made equal to (or to a small submultiple of) the pump cavity optical length L_p and the Rhodamine laser dye cell put at the end of the cavity, trains of fully modulated pulses of periods equal to (or to small submultiples of) the pump pulse were observed with instrumental temporal halfwidth of 7×10^{-10} sec using a planar photodiode and traveling wave oscilloscope. With $L_p = L_\ell$ and the laser cell in intermediate harmonic positions L/n, $n = 3, 4$; two pulses separated by $2L/nc$ occurred for each pumping pulse with one predominantly intense, as may be expected if one considers that pulses traveling in opposite directions in the cavity, reach the dye cell together only once per pump pulse. With the cell centered and $L_\ell = mL_p/n$; $m/n = 2, 1, 2/3, 1/2$; $2n/m$ pulses are obtained for each pumping pulse, spaced at 3, 3/2, 1, and 3/4 nanoseconds respectively. These results are an extension of findings reported earlier. When the pulse interval approaches the pulse resolution time, the overlap of the instrumentally broadened pulses reduces the apparent modulation drastically. When two or more pulses per pump pulse occur, the first two are of approximately equal intensity and any remaining ones show rapidly diminishing intensity but with larger statistical variations in decay rates on successive pictures. The fluorescent lifetime of Rhodamine 6G has been recently redetermined as 5.5×10^{-9} sec for an approximately equal concentration solution. This time is greater than any of the periods described above, a condition which would diminish the effectiveness of this dye were it used as a passively bleachable absorber to engender mode locking with the cavity dimensions and configurations described above. However, this is a driven system with periodic gain modulation. The superradiant lifetime over the pumping intensity range employed was found to be greater than 1×10^{-9} and less than 3×10^{-9} sec by removing the cavity reflectors and observing the ability of the emitted radiation to follow stimulation of diminishing periodicity. The effective cavity lifetime including the driven dye laser cell was inferred from the multipulse decay rates to be between 1 and 2 nsec.

The picosecond pulse structure of the dye laser was observed using the alcoholic solution of Esculin. Multiple exposures were often required and so for convenience the two photon fluorescence cells were sometimes positioned in the cavity, a procedure empirically justified by the finding of no significant change in the observed pulse shapes. More dispersive, scattering, and generally non-linearly behaving solvents then ethanol might be expected to cause complications. Several of the cavity configurations mentioned above were tried all yielding similar picosecond pulse patterns. The additional expediency of increasing the f# of the camera lens with inexpensive positive portrait lenses allowed the use of less sensitive but higher gamma emulsions (Polaroid type 52, $\gamma \sim 3.5$ and type 146 L, $\gamma \sim 2.5$) to photograph the two photon excited fluorescence. This is an aid in densitometrically determining the contrast ratio (see below), as the fractional error in contrast ratio, for an error in optical density, is inversely proportional to gamma.

The structure of the picosecond pulses closely followed that observed for the pump except that the pulse width was $1.1 \pm 0.1 \times 10^{-11}$ sec. The contrast ratio was determined to be 2 ± 0.2, and the contrast ratio of the pump pulse was found to be 1.8 ± 0.2. Several approaches have been taken to attempt to realize more of the full mode locking potential of the ~ 150 cm^{-1} dye laser bandwidth which might yield pulses as short as 2×10^{-13} sec in duration. However, no significant changes in pulse widths were noted when the spatial width of the pumping pulse was narrowed from 12 to 1 mm by focusing with a cylindrical lens in order to bound the 10^{-11} sec pulse length, when fine variations were made in the position of the pulse in the dye cell and the position of the cell itself, or when operating the dye laser from 10 to as much as 20 times above threshold. Higher output mirror reflectivities produced only trivially shorter pulses within the estimated deviation.

One condition that might contribute to the pulse width is a frequency sweeping of the laser output, a circumstance reported for certain cyanine dye lasers. It should also be noted that because of the pulse structure of each laser burst in these experiments, each of the picosecond pulses displayed in the two photon fluorescence technique is actually an average over > 10^2 discrete pulses. Each pulse may be narrower than the average but broadened by aperiodicity within each 10^{-9} sec group of pulses or from one such 10^{-9} sec pulse to the next Furthermore, as has recently been discussed, two photon fluorescence pictures of picosecond pulses with contrast ratios of less than three, the maximum value which can be obtained as for example in the case of fully mode locked operation, are fraught with uncertainties about the actual nature of the pulses. Contrast ratios of two which are observed here might indicate a free running oscillation or random (initial condition) mode locked laser, but certainly not necessarily. It should further be noted that all experimental problems as for examples, scattering, and imperfect overlap of the beams, would tend to reduce the observed contrast ratio. Because of this uncertainty we can quote only the bounds of the average peak power between a maximum and a minimum were there no picosecond pulse content: for the pump $8 \times 10^6 <$ P watts $< 10^8$; for the dye laser $2 \times 10^6 <$ P watts $< 2 \times 10^7$ using an output reflectivity of 60%. A smaller number of picosecond pulses might be expected to yield higher powers. The full beam angle at half power density was measured as 2.0 mrad.

Efficiently confining the spectral output of the dye laser to 6 cm^{-1}, by replacing one of the cavity mirrors by a diffraction grating as described in an earlier publication, we have demonstrated a continuously tunable source of $1.1 \pm 0.1 \times 10^{-11}$ sec pulses over a half power tuning range of 600 cm^{-1}. Narrowing the spectral output much beyond this would, of course, broaden the pulse widths. The pulse pattern again resembled the pumping pulse structure and had a measured contrast ratio of $2 \pm .2$. The Rhodamine cell was centered in the cavity with $L_\ell = L_p$. Using a grating of 2,160 lines/mm of approximately constant first order reflectivity of 58% in the range of interest in the Littrow position and a 100% reflector, the average peak power output in the zeroth order at the peak of the tuning curve was greater than 50% of that obtained with the 60% dielectric reflector replacing the grating. The full beam angle at half power density was found to be 4.8 mrad.

It should be noted that pulse duration with narrow spectral output is identical to that obtained with no grating when the full 150 cm^{-1} bandwidth was generated. This indicates that no more than 6 cm^{-1} of the available bandwidth cooperated in mode locking to produce any one short pulse.

This technique, providing tunable short pulses, is expected to work well with many families of dyes, both in liquid and plastic hosts covering the entire range from the near ultraviolet to the near infrared. The flash lamp pumped self mode locked dye laser would also be ameanable to this technique.

Longitudinal pumping of the dye cell should, as has been demonstrated, reduce the dye laser beam divergence significantly. Single tunable picosecond pulses or pulses with other intervals should also be obtainable.

C. Reversible and Irreversible Bleaching of Dyes Used for Passive Q-spoiling.

In the course of these studies with lasers passively Q-spoiled with bleachable dyes, certain erratic behavior was often noticed from pulse to pulse. Bursts of several lines, wavelength shifts, and general deterioration of dye concentration is often observed with all of the polymethine family of Q-spoiling dyes. We have performed various theoretical and experimental studies, in part supported by this contract, which have bearing upon these Q-spoiling properties. A reaction scheme and model was developed to characterize the stability of these solutions of polymethine dyes with respect to other chemical species, temperature, and infrared, visible and ultraviolet radiation. The first feature is pertinent to contaminants occurring when the solutions are left open to air e.g., H_2O, CO_2 and O_2. The second feature bears on the problem of local heating during repetitive pulsing. The third feature is of interest from the standpoint of storage in ambient light and radiation leakage from the flash lamp. The observed equilibrium properties, as well as the kinetic and steady-state parameters favored a model based on a low-lying triplet state. The technical details of this study may be found in Appendix E, a preliminary version of a paper in preparation for publication. A practical consequence of this work was the achievement of a very stable Nd Q-switching solution such that more than 10^5 giant laser pulses of 3 Mw power were generated at a repetition rate of 10 sec^{-1} before double pulsing occurred in solutions of 3 cm^3 volume.

Section 3

SUMMARY

We have reported in this contract period, experimental evidence in support of the existence of significant spectral hole-burning in certain dyes used as passive bleachable Q-spoiling elements. The experiments were performed utilizing the narrow spectral output of one laser to bleach the passive cell of another laser. The frequency locking of the two lasers that ensued served to demonstrate the spectral hole-burning phenomenon. Another of the problems investigated was a study of the spectral cross-relaxation behavior of a polymethine dye. The problem considered was the comparative efficiency of a single spectral laser line and several spectrally separated lines of the same total power in bleaching the dye. If the dye solution has, for example, a very long spectral relaxation time, referred to a particular spectral separation (greater than the separation of the inhomogeneous components), then the several separated weak lines would not aid each other in the bleaching process and would not have the over-all bleaching effect of a single more powerful line operating in the more saturated region of the dye transmission characteristic. Thus, by varying the number of lines and their spectral separation, one might expect to map the details of the spectral relaxation properties of the dye.

The dye studied was the Kodak Q-spoiling dye, in conjunction with a Nd^{+3} glass laser. An analysis of the data showed that if any spectral hole-burning occurred within the observable time resolution defined by the giant pulse experiment, then it was at least five times smaller an effect than the maximum effect that could be expected for the case of very long spectral relaxation times. Therefore, either the individual homogeneously broadened components of the dye absorption are wide compared to about 6 cm^{-1}, or have consequences observable by this technique.

Both these categories of experiments, in and out of the laser cavity, all for hole-burning effects, have been repeated or independently performed in other laboratories. The results generally agree that hole-burning is observable in the cavity but not outside. This result holds for both the carbocyanine and phthalocyanine dye families. These results may be reconciled by assuming that the lines are homogeneously broadened with cross-relaxation times between homogeneous components short i.e., a few percent, compared to spontaneous decay times, but still finite. An alternate theory for the apparent hole-burning effect with crossed lasers operating on the dye in the cavity has been given in the literature in terms of a non-linear parametric process.

Organic dyes have recently been shown to exhibit stimulated emission when excited with the high brightness of a ruby laser. These dyes have consequently emitted in the near infrared. We have demonstrated laser-pumped laser emission in the visible region using dyes such as rhodamine and fluorescein. Pumping with the second harmonic of ruby or neodymium lasers at about 10 Mw/cm^2 gave conversion efficiencies of about 15%. Higher values have recently been reported with axial pumping by other workers who have also simultaneously reproduced the visible emission referred to above. It is noteworthy that the organic dye solution laser emits a spectrally variable and broad pulse, up to some hundreds of wavenumbers wide, depending upon dye concentration, cavity length and conditions of cavity gain.

We have demonstrated efficient spectral narrowing and continuous tunability in organic dye lasers over bandwidths large compared to the ordinary lasing action by use of diffraction gratings as cavity reflectors. These effects have been demonstrated in the visible and near infrared spectrum. With a particular rhodamine laser, for example, the spectral bandwidth of laser emission was reduced from 60 Å to a single line of width 0.6 Å with a "condensation" efficiency of 70% throughout the region of normal laser emission. The range of tunability at the half power (or half maximum efficiency) points was some 200 Å. The total available bandwidth was much greater.

Similar results were obtained here with a solid sample of Rhodamine 6G in plastic polymethylmethacrylate, the first demonstration of organic singlet-singlet lasing in the solid state.

The successful lasing of several new blue-violet dye laser materials of the coumarin family was first described in the reports of this contract. Frequency doubling of the dye laser to extend its useful range was successfuly carried out here and first reported in this contract period.

Mode locking of organic dye lasers has been reported recently by ourselves, and simultaneously by other groups using mode locked lasers as pumping sources. These studies reported the oscilloscopic observation, with subnanosecond resolution, of trains of pulses of considerable modulation, with periods of the round trip cavity times. The appearance of these possibly instrumentally broadened pulses with proper temporal periodicity is a necessary condition for the existence of some degree of mode locking. We reported here the direct observation of 1×10^{-11} sec pulses generated by a laser pumped dye laser. Furthermore, without degrading the pulsewidth, continuously tunable outputs of 6 cm^{-1} bandwidth have been demonstrated. This is direct evidence that no more than a small fraction of the available bandwidth cooperates in mode locking to produce individual short pulses.

Frequency Locking and Dye Spectral Hole Burning in Q-spoiled Lasers

B. H. Soffer and B. B. McFarland

APPENDIX A

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FREQUENCY LOCKING AND DYE SPECTRAL HOLE BURNING IN *Q*-SPOILED LASERS*

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(bleachable dyes; phthalocyanine; E)

(Received 7 March 1966)

Concurrent with the discovery of the passive *Q* switch, we had observed that the output spectrum of a giant pulse ruby laser can be considerably narrowed, sometimes resulting in single-frequency operation.[1] Subsequently we have found that the usual 50-Å envelope of lines of the Nd^{3+} glass laser is efficiently condensed to a single narrow line when passively *Q* spoiled with bleachable dye.[2,3] We have similarly observed a narrow spectral output when the passive *Q* spoiler was bleachable glass or semiconductor mirrors. Recently a single line output has been observed from an Nd^{3+} glass laser *Q* spoiled with a rotating prism.[4]

Theoretical analyses[5,6] have indicated that if the laser precursory state[7] lasts long enough, weaker modes are suppressed and eventually the stronger

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[*] This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense [Nonr 4130-(00)].

one (or ones) will dominate. This is a sufficient explanation for the spectral behavior of passively Q-spoiled lasers but it does not rule out the possibility of some mode selection by a degree of spectral hole burning in bleachable absorbers used as Q spoilers. The relaxation of at least the excited states of such dye molecules can be inferred to be much faster than the giant pulse times (10^{-8} sec), from the phenomena of Stokes shifted fluorescence so that one expects very fast spectral diffusion within any hole-burned line; so fast, that it should not influence the spectral behavior of the laser. Indeed, experiments conducted (with phthalocyanine solutions), at the moment of the giant pulse with resolution times of the order of the duration of the giant pulse, seem to show a homogeneous saturation.[7,8] The purpose of this Letter is to present experimental evidence in support of the existence of significant hole burning in these dyes.

The experiments utilized the narrow spectral output of one passively Q-spoiled laser to bleach the passive cell of another laser. If the frequencies of the lasers locked together, and if other causes could be eliminated, then spectral hole burning would be in evidence. In one set of experiments two lasers were set orthogonally with the output of one passively Q-spoiled laser directed upon the cell of the other. The cell, with 4 polished windows and a path length of 17 mm, was near the dielectric mirror of maximum reflectivity. Equivalent results were obtained when solutions of an organic base salt of sulfonated metal-free phthalocyanine in methanol or solutions of sulfonated metal-free phthalocyanine in methanol (solvated with a drop of water) were used. These dyes are among the easiest to bleach and this solvent allows the possibility of obviating the spectral complications of the stimulated Raman and Brillouin effects.

Dielectric mirrors of ~30% reflection or sapphire resonant reflectors were employed as desired at the output ends. Ruby rods, .05% Cr^{+3}, 10×1.4 cm, were employed. Outputs, typically 1×10^8 W, were monitored with a planar photodiode. The signals were displayed on a traveling wave oscilloscope and integrated signals on a conventional oscilloscope. Both laser heads were water cooled independently so that different operating temperatures (in the neighborhood of room temperature) could be achieved in order to effect spectral shifts.

To study the spectral behavior of the system, the Fabry-Perot interferograms using 4-cm and 1-cm spacers, were effectively bifurcated, each half showing only the spectrum of one of the two lasers. When the lasers were set with their polarizations coincident, for example, the plane of polarization of one of them was rotated by 90° outside the cavity just before the Fabry-Perot with a half-wave plate and the light was analyzed at the film plane of the Fabry-Perot apparatus. Care was taken to eliminate stray, scattered, depolarized, and extraordinary laser light so that the representation was faithful.

When the input to each laser was adjusted to give a single comparable giant pulse, temporal synchronization did occur if the relative delay of inception of pumping was within definite limits (~400 μsec). With longer delays two characteristic and unsynchronized pulses were produced—one from each laser. When "synchronized," the synchronization was never exact but the pulse of the "slave" laser always followed by some 50 nsec (Fig. 1).

With the lasers held at several degrees centigrade apart, and operated to not be synchronous, they always yielded disparate interferograms indicating operation at different frequencies as was to be expected (Fig. 2A). When the lasers were operated synchronously, the slave laser always locked to the frequency of the master and usually exhibited a set of extra lines not observed in the spectrum of the "slave" laser when fired alone. A typical example is shown in Fig. 2B. The locked in line is not always the most intense of the set.

A second experiment, a variation of the first, was performed wherein the lasers were set orthogonally, with crossed cavities. A common passive Q-spoiling cell served for both lasers at the intersection of the

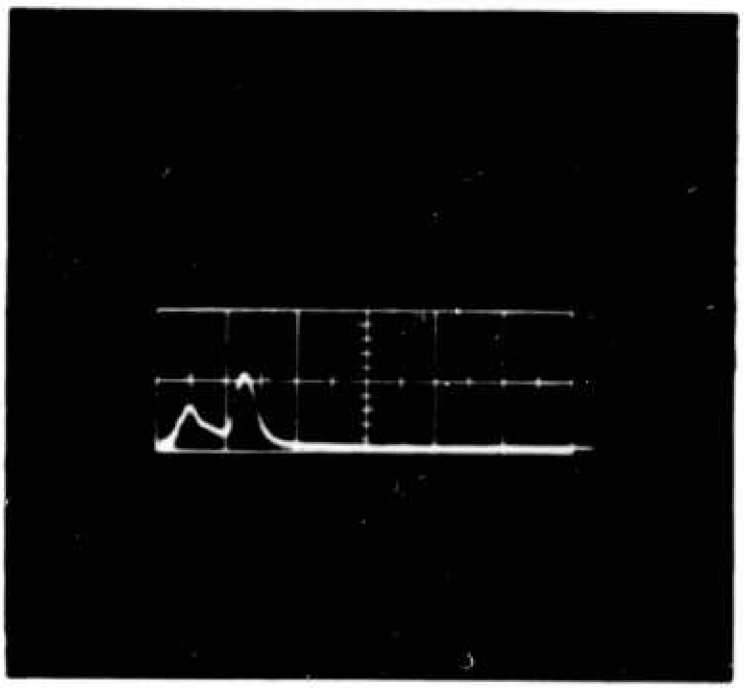

Fig. 1. "Synchronized" pulses. 50 nsec/div. The pulses were made to appear with different amplitudes for identification.

cavities near the mirrors of maximum reflectivity. Exactly the same spectral and temporal results were obtained as described above. Either laser could be made to drive the other by varying pumping time and rates. As in the first experiment, the slave could be pumped to just below the point where it could lase alone and again it would slave with the same spectral and temporal properties already described. Again, as in the first experiment, the polarizations of these lasers could be set orthogonal (vertical and horizontal) and still each one could be made the master for the other. This has bearing on the question of scattering as discussed below, but it is noteworthy also for it shows that the dichroic dye molecules bleach isotropically even in the time of a giant pulse due to rapid collisions with the solvent.

In a third set of experiments a non-*Q*-spoiled "spiking" laser was the master laser outside the cavity of the slave in the configuration of the first experiments. The spikes were typically of the order 10^5-W peak power and 10^{-7}-sec duration. The total envelope of the spikes was 2×10^{-4} sec. This was sufficient to trigger the giant pulse of the slave as could be determined by reducing the pumping of the slave to below where it would oscillate by itself. The giant pulse of the slave occurred 10^{-4} sec after initiation of the master. The ordinary laser was constrained to give a simple spectrum with a 1-cm^{-1} sapphire resonant reflector inserted in the cavity. The slave did exhibit frequency locking to that spectrum and also produced additional lines. Here again these results could be produced with the polarization of the lasers set orthogonal.

Fig. 2A. Interferograms of unsynchronized giant pulses.

Fig. 2B. Interferograms of "synchronized" giant pulses, showing one supernumerary line in the slave laser spectrum.

To check the possibility that these orthogonal cavities were coupled by scattering from the dye cell and thereby exhibiting common frequencies, an experiment was performed wherein light was deliberately scattered into the cavity of the giant pulse laser from the ordinary pulse laser. The beam was directed onto a cell containing a scattering solution of synthetic "cream," juxtaposed in series with the dye cell in the cavity of the giant pulse laser. We separately measured the ratio of scattering cross section of dye cell to scattering cell and the various depolarization ratios. Using a high "cream" concentration and adjusting the polarization of the lasers both vertical, we were able to scatter $>10^2$ times more spectral power density into the giant pulse laser cavity than the dye cell did in the least scattering polarization configuration of the third set of experiments described above. No spectral locking nor any perturbation of the giant pulse spectrum was observed under these circumstances.

It is clear that scattered radiation was not responsible for frequency locking. We conclude from these experiments, that hole burning in the dye, however rapid its spectral diffusion may be, is the cause of the frequency locking. The results of these experiments do not invalidate, but supplement the mode competition or "natural selection of modes" theory[8,9] of the spectral behavior of passively *Q*-spoiled lasers. The generation of still additional lines in the slave laser spectrum may possibly be explained by noting that the slave signal is somewhat deprived of its normally large number of loop transits building up out of noise, which is believed required to suppress weaker modes.[8] However the existence of these lines may be evidence of frequency pulling by the master. Further experiments are in progress to clarify these matters.

We thank Omar Cernichiari for synthesis of the dyes used in these experiments.

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[2] B. B. McFarland, R. H. Hoskins, and B. H. Soffer, *Nature* **207**, 1180 (1965).

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[9] In support of this theory we found that the spectral line width of a ruby laser, mode selected with a 1-cm^{-1} resonant reflector, was a monotonic, increasing function of the angular velocity of the Q-spoiling prism. At the longest period (2.5 msec) the line width was 0.02 cm^{-1}. At a period of 0.64 msec the line width doubled.

Laser Second Harmonic-Induced Stimulated Emission of Organic Dyes

B. B. McFarland

APPENDIX B

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LASER SECOND-HARMONIC-INDUCED STIMULATED EMISSION OF ORGANIC DYES*

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(Received 27 February 1967)

Solutions of several dyes of the fluorescein family have been made to exhibit stimulated emission in the visible when excited by ruby and neodymium second harmonics. Oscillation threshold and conversion efficiencies are given. Depolarization effects in the emission are described.

Recent investigations have pointed out the feasibility[1-3] and the practicality[4] of stimulated emission from laser-excited solutions of organic dyes (hereafter designated laser-pumped laser or LPL). All of the dyes reported to date have been excited with ruby lasers and emitted in the near infrared. This Letter describes the first observation of efficient LPL emission in the visible region of the spectrum obtained by laser second-harmonic excitation.

It is well known that dyes of the fluorescein family have nearly-unity fluorescent efficiencies, thus making them likely candidates for dye solution lasers. Their absorption bands are located in the ultraviolet and blue-green, precluding direct pumping with currently available high-power lasers such as ruby or neodymium. The author has found that effective pumping can be accomplished with the second harmonic of ruby or neodymium lasers generated in phase-matched ADP crystals. The experimental arrangement employed is shown schematically in Fig. 1. (Mirrors R_1 and R_2 had reflectivities nominally 99% and 50% respectively.) Using a Korad K1QP ruby or neodymium glass laser as the fundamental source, approximately 10 MW/cm² of unfocused 347-mμ or 530-mμ radiation was available at the dye cell.

Several dyes of the fluorescein family were in-

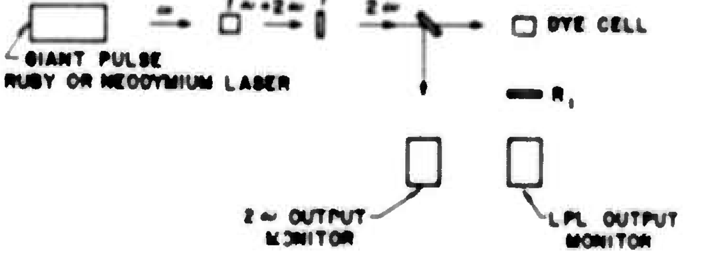

Fig. 1. Schematic diagram of experimental apparatus. $\vec{E}_{1\omega}$ is normal to the page.

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*This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense [Nonr 4130-(00)]

vestigated using one or both of the generated harmonics. Examples of the dyes exhibiting stimulated emission are listed in Table I. The wavelength of peak emission was determined with a 3.4-m Jarrell-Ash spectrograph. The right-hand column of the table indicates the wavelength of the exciting source. The values of λ given in the table are representative owing to the shift to longer λ characteristically accompanying an increase in dye concentration.[2,3] Figure 2, which is a plot of emission wavelength vs absorption coefficient for rhodamine-6G in ethyl alcohol, is typical of all the dyes listed in Table I. This wavelength shift is a consequence of the effects of self-absorption.[2] The spectral bandwidth of the laser emission of all the dyes listed in Table I were very broad; typically 50 to 100 Å.

Rhodamine-6G was selected for more detailed investigation since the location of its absorption band permits effective excitation with either ruby or neodymium laser second harmonic. More than 15% conversion of second-harmonic light to LPL emission, using either of the harmonics, was obtained from a 1.7-cm path length cell containing 2×10^{15} molecules/cm^3 of rhodamine-6G dissolved in ethyl alcohol. The absolute output, measured calorimetrically, was 0.012 J with a 5-nonosecond pulse width. Oscillation threshold in this configuration was achieved with 1.4 MW/cm^2 of 347-mμ radiation. This solution was then diluted to give the same absorption coefficient at 530 mμ (the absorption cross section (σ) at 347 mμ is 1/10 the σ at 530 mμ) and threshold was determined using neodymium second harmonic. The results indicate that the same power density (within 50%) is required of both sources to achieve oscillation.

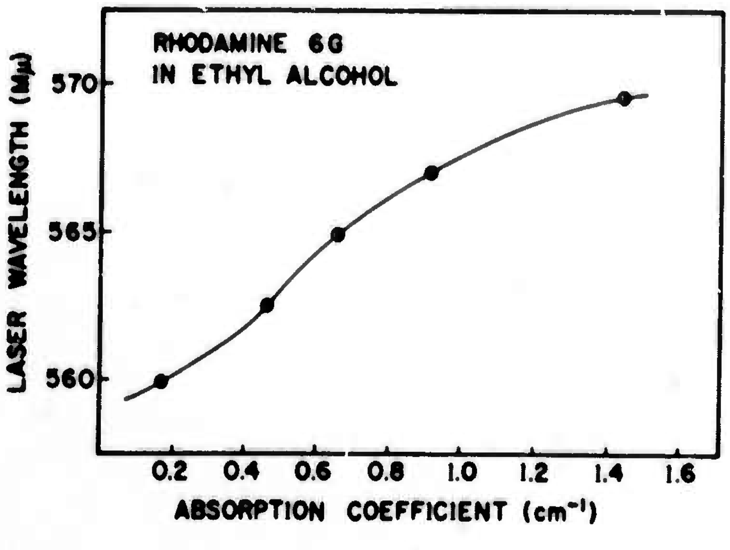

Fig. 2. LPL emission wavelength vs absorption coefficient for rhodamine-6G dissolved in ethyl alcohol.

Table I.

Dye	Solvent	Laser Wave-length (mμ)	Source Wave-length (mμ)
Fluorescein (disodium salt)	water	535	347
Acriflavin hydrochloride	ethyl alcohol	510	347
Rhodamine-B	"	577	347, 530
Rhodamine-G	"	585	347, 530
Rhodamine-6G	"	565	347, 530

One of the interesting aspects of exciting the same dye with two different monochromatic sources concerns the polarization of the LPL emission. The depolarization of molecular fluorescence and its absorption wavelength dependence has been studied extensively.[5] Many dyes, notably the rhodamines, exhibit a negative polarization when excited by uv and a positive polarization when excited by visible radiation.

When rhodamine-6G in ethyl alcohol was excited with ruby second harmonic at a power level approximately 4 times oscillation threshold, the LPL emission was predominantly polarized normal to the pump electric field. The measured polarization was $P = -0.9$. When this same dye was excited by 530-mμ radiation, sufficient depolarization occurs to cause the LPL emission to be polarized parallel to the exciting field (i.e., $P = +1$). This phenomenon, which has not been previously reported in stimulated emission, may well provide a useful method for the study of intramolecular cross-relaxation processes.

The author thanks Dr. R. H. Hoskins and B. H. Soffer for helpful suggestions and discussions.

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Continuously Tunable, Narrow-Band Organic Dye Lasers

B. H. Soffer and B. B. McFarland

APPENDIX C

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CONTINUOUSLY TUNABLE, NARROW-BAND ORGANIC DYE LASERS*

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(Received 3 April 1967)

Efficient spectral narrowing, and tunability over a wide spectral range, has been demonstrated in solid and liquid organic dye lasers using diffraction gratings as cavity reflectors.

The organic dye solution laser[1] has been observed to emit a spectrally broad pulse up to some hundreds of wave numbers wide, depending upon dye concentration, cavity length, and conditions of cavity gain. We report in this Letter efficient spectral narrowing and continuous tunability in dye lasers over bandwidths large compared to the ordinary lasing action, by use of diffraction gratings as cavity reflectors. We have demonstrated this effect with members of the xanthene and carbocyanine dye families. We further report the use of solid solutions of dyes in plastic as a practical dye laser material.

A typical experiment using alcoholic solutions of rhodamine 6G as the laser material will be described in detail. Ethanol solutions with decadic absorption coefficients 0.74 cm^{-1} and 0.20 cm^{-1} at 347 $m\mu$ were employed in a cubical glass cell, 1.75 cm ID, with four sides polished. Optical densities are preferred to concentration values as the associated molecules of rhodamine 6G in ethanol[2] have smaller optical cross sections. This furthermore makes it impractical to precisely prepare solutions of desired density by dilution from a standard solution of known concentration. Pumping was effected transverse to the cavity axis using the 10^{-8} sec, 10^{7} W/cm^2 second-harmonic output of a giant-pulse ruby laser. The 12-cm-long cavity consisted of a flat dielectric mirror of 95% reflectivity and a flat reflective diffraction grating with 2160 lines/mm blazed at 5000-Å first order with an approximately constant first-order reflectivity of 80 ± 3% for the wavelengths of interest, i.e., longer than 5520 Å. The approximate constant reflectivity is a consequence of there being no second order for these wavelengths. The grating was used in the Littrow arrangement and the output from the laser was obtained via the zeroth-order reflection or the small transmission of the dielectric reflector. Excepting the absolute power, all the measured characteristics of this laser were independent of this choice of outputs. Spectra were photographed with a 3.4-m spectrograph and the energetic and temporal behavior of the laser were recorded with photodiodes calibrated calorimetrically. Beam angle was measured by a self-calibrating photographic technique.[3]

The output of the laser was repeatedly measured using a set of dielectric mirrors of reflectivity approximating that of the grating. An output value for the reflectivity equaling that of the grating was found by interpolation. This value was normalized to one arbitrary unit when the high concentration of dye was employed (see Fig. 1). The absolute conversion efficiency was not optimized but was about 15%, yielding pulses in the 2 × 10^{6} W range, coupling via the zeroth-order reflection. Replacing the grating, we obtained the set of data shown in

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*This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense.

the upper trace of Fig. 1 showing relative efficiency vs wavelength of emission. The input pumping intensity was held approximately constant and the grating angle was varied to effect the tuning. Slight variations in input were normalized in the efficiency plot. Errors introduced here especially by the effects of multimoding upon the second-harmonic generation, contribute to the scatter of the data. Spectrograms taken simultaneously with this data, reveal the linewidth of the emission to have narrowed from 60 Å using the all-dielectric reflector cavity, to 0.6 Å when the grating was employed. The spectral condensation is seen to take place with ~70% efficiency in the region of the center of normal laser emission. The total available bandwidth is seen to be much greater than the bandwidth of the normal laser emission. In the lower trace of Fig. 1 we show the analogous results for a lesser dye concentration. Again the spectral condensation is seen to be efficient in the region of normal laser emission but here the normal laser emission itself is not as efficient as the case of higher concentration. Again the available bandwidth is greater than that of the normal laser of the same concentration. The tunable half-power bandwidth is approximately the same for both concentrations but shifted to longer wavelengths in the higher concentration case.

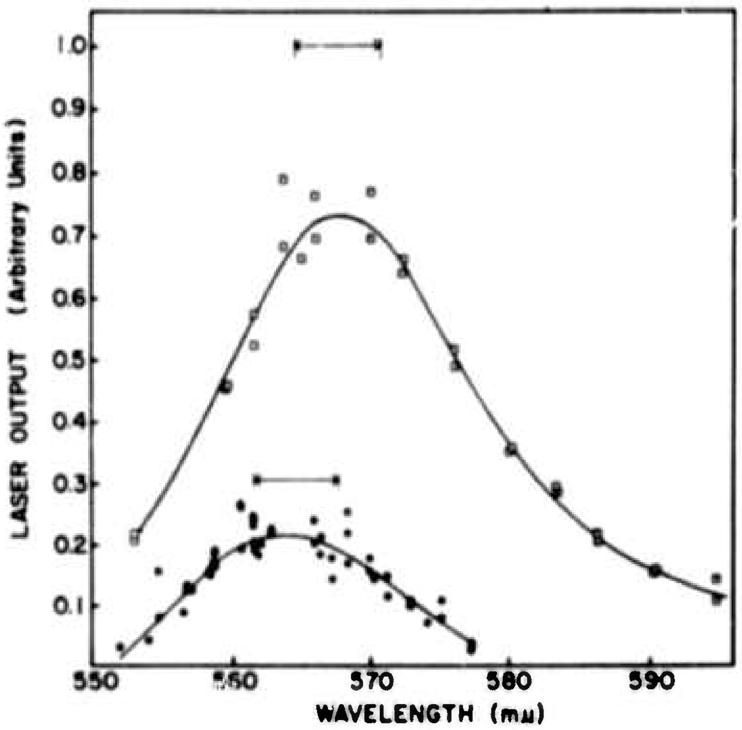

Fig. 1. Relative efficiency of tunable rhodamine 6G laser vs wavelength. Upper trace: ⊡ optical density, 1.3 (347 mμ). Grating in cavity. ↔ Dielectric reflectors. Arrows indicate spectral bandwidth for this case. Lower trace: ⊙ optical density 0.35 (347 mμ). Grating in cavity. ↔ Dielectric reflectors.

Beam angles in the plane of grating dispersion measuring ~5×10^{-3} rad were too large to account for the observed spectral narrowing by dispersion although we note that the temporal development of the integrated beam angle is presently unknown to us. The spectral content of the output was the same over the entire far-field distribution. It should be noted that a grating with 4 times lesser dispersion produced spectral outputs 8 times as broad.

Similar results were obtained with a solid sample of rhodamine 6G in polymethylmethacrylate, pumped with the second harmonic of a Nd laser. No room temperature phosphorescence could be detected in the rhodamine solid solution. A strong phosphorescence, typical of some dyes in solid solution, would of course be detrimental to laser action. The use of the solid matrix obviates the problems of convective schlieren, evaporation, and cells. Furthermore, similar results were obtained with 3, 3' diethyl-thia-tricarbocyanine iodide in ethanol in the near-infrared region pumping with *Q*-spoiled ruby laser. Alignment of the grating was effected using an image converter and autocollimator.

The broad spectral output of the various families of dyes thus far successfully employed as organic dye lasers[1] leads one to consider them as primarily inhomogeneously broadened systems. The high relative efficiency of narrow-line emission reported in this work, however, points out the need for qualifying this view.

It is expected that many related dye families will behave in a similar fashion and that the entire wavelength domain from 347 mμ (ruby second harmonic) to about 1 μ could be practicably spanned according to these techniques.

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Continuously Tunable Picosecond Pulse Organic Dye Laser

B. H. Soffer and J. W. Linn

APPENDIX D

To be published in Journal of Applied Physics,
December 1968

CONTINUOUSLY TUNABLE PICOSECOND PULSE ORGANIC DYE LASER*

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ABSTRACT

Picosecond pulse outputs, tunable over a broad spectral range, have been demonstrated in an organic dye laser. Evidence is presented that no more than a small fraction of the available bandwidth cooperates in mode locking to produce individual short pulses.

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*This research is part of Project Defender under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research and the Department of Defense.

CONTINUOUSLY TUNABLE PICOSECOND PULSE ORGANIC DYE LASER*

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Mode locking of organic dye lasers has been reported recently by several groups[1,2,3] using mode locked lasers as pumping sources. Most recently self mode locking of a flash lamp pumped dye laser has been described.[4] These studies reported the oscilloscopic observation, with subnanosecond resolution, of trains of pulses of considerable modulation, with periods of the round trip cavity times. The appearance of these possibly instrumentally broadened pulses with proper temporal periodicity is a necessary condition for the existence of some degree of mode locking. We report here the observation of 1×10^{-11} sec pulses generated by a laser pumped dye laser. Furthermore, without degrading the pulsewidth, continuously tunable outputs of 6 cm^{-1} bandwidth have been demonstrated.

A mode-locked neodymium glass laser was constructed for use as a pumping source for the organic dye laser.

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*This research is part of Project Defender under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research and the Department of Defense.

All intracavity reflective elements were set at the Brewster angle and mode locking was effected by the use of a bleachable absorber near the 100% reflector in a cell positioned[5] to minimize the intensity of satellite spikes on the main pulse train. The pulse was structured in groups of 10 or 11 individual pulses separated by 1×10^{-10} sec, an interval determined by the internal round trip time in the cavity output reflector. The surfaces of this glass reflector were wedged at 2' and one surface was coated with a 30% dielectric reflector creating a low Q resonator. These groups of pulses themselves, were separated by 3×10^{-9} sec, 2L/C of the cavity with typically 10-15 sets of pulses between the half power points. Picosecond pulses were detected by the two photon excitation of fluorescence technique.[6] A solution of Rhodamine 6G in ethyl alcohol was employed as the fluorescent medium. The second harmonic of this laser generated by an ADP crystal revealed the same pattern of pulses with the same temporal duration of $4 \pm 1 \times 10^{-12}$ sec. A solution of Esculin in ethyl alcohol was employed in this case as the two photon fluorescent medium. The spectral bandwidth of the second harmonic output was 150 cm^{-1}.

These second harmonic pulses were used to transversely pump a Rhodamine 6G dye cavity. An ethanolic solution of the dye with decadic absorption coefficient equal to 10 at 530 mμ was contained in a cell constructed with internal and external window surfaces disposed at their respective Brewster angles. The internal length of the cell was 1.15 cm. Laser action in unwanted directions was suppressed by degrading all optical surfaces excepting the windows. Wedged dielectric coated mirrors of ~ 99% reflectivity and of 60-90% output reflectivity were employed.

When the dye laser cavity optical length L_ℓ was made equal to (or to a small submultiple of) the pump cavity optical length L_p and the Rhodamine laser dye cell put at the end of the cavity, trains of fully modulated pulses of periods equal to (or to small submultiples of) the pump pulse were observed with instrumental temporal halfwidth of 7×10^{-10} sec using a planar photodiode and travelling wave oscilloscope. With $L_p = L_\ell$ and the laser cell in intermediate harmonic positions L/n, $n = 3, 4$; two pulses with one predominantly intense, for each pumping pulse with one predominantly intense, as may be expected if one considers that pulses travelling in opposite directions in the cavity, reach the dye cell together only once per pump pulse. With the cell centered and $L_{\ell} = mL_p/n$; $m/n = 2, 1, 2/3, 1/2$; $2n/m$ pulses are seen on the travelling wave oscilloscope for each pumping pulse, spaced at 3, 3/2, 1, and 3/4 nanoseconds respectively. These results are an extension of findings reported earlier.[2,3] When the pulse interval approaches the pulse resolution time, the overlap of the instrumentally broadened pulses reduces the apparent modulation drastically. When two or more pulses per pump pulse occur, the first two are of approximately equal intensity and any remaining ones show rapidly diminishing intensity but with large statistical variations in decay rates on successive pictures. The fluorescent lifetime of Rhodamine 6G has been recently redetermined as 5.5×10^{-9} sec for an approximately equal concentration solution.[7] This time is greater than any of the periods described above, a condition which would diminish the effectiveness of this dye were it used as a passively bleachable absorber to engender mode locking with the cavity dimensions and configurations described above. However, this is a driven system with periodic gain modulation. The superradiant lifetime over the pumping intensity range employed was found to be greater than 1 x 10^{-9} and less than 3 x 10^{-9} sec by removing the cavity reflector and observing the ability of the emitted radiation to follow stimulation of diminishing periodicity. The effective cavity lifetime including the driven dye laser cell was inferred from the multipulse decay rates to be between 1 and 2 nsec.

The picosecond pulse structure of the dye laser was observed using the alcoholic solution of Esculin. Multiple exposures were often required and so for convenience the two photon fluorescence cells were sometimes positioned in the cavity, a procedure empirically justified by the finding of no significant change in the observed pulse shapes. More dispersive, scattering, and generally non-linearly behaving solevents than ethanol might be expected to cause complications. Several of the cavity configuration mentioned above were tried all yielding similar picosecond pulse patterns. The additional expediency of increasing the f# of the camera lens with inexpensive positive portrait lenses allowed the use of less sensitive but higher gamma emulsions (Polaroid type 52, $\gamma \sim 3.5$ or type 146-L, $\gamma \sim 2.5$) to photograph the two photon excited fluorescence. This is an aid in densitometrically determining the contrast ratio (see below), as the fractional error in contrast ratio, for an error in optical density, is inversely proportional to gamma.

The structure of the picosecond pulses closely followed that observed for the pump except that the pulse width was 1.1 ± 0.1 x 10^{-11} sec. The contrast ratio was determined to be 2 ± 0.2, and the contrast ratio of the pump pulse was found to be 1.8 ± 0.2. Several approaches have been taken to attempt to realize more of the full mode locking potential of the ~ 150 cm^{-1} dye laser bandwidth which might yield pulses as short as ~ 2 x 10^{-13} sec in duration. However, no significant changes in pulse widths were noted when the spatial width of the pumping pulse was narrowed from 12 to 1 mm by focusing with a cylindrical lens in order to bound the 10^{-11} sec pulse length, when fine variations were made in the position of the pulse in the dye cell and the position of the cell itself, or when operating the dye laser from 10 to as much as 20 times above threshold. Higher output mirror reflectivities produced only trivially shorter pulses within the estimated deviation.

One condition that might contribute to the pulse width is a frequency sweeping of the laser output, a circumstance reported for certain cyanine dye lasers.[1,8] It should also be noted that because of the pulse structure of each laser burst in these experiments, each of the picosecond pulses displayed in the two photon fluorescence technique is actually an average over > 10^2 discreet pulses. Each pulse may be narrower than the average but broadened by aperiodicity within each 10^{-9} sec group of pulses or from one such 10^{-9} sec pulse to the next. Furthermore, as has recently been discussed[9,10] two photon fluorescence pictures of picosecond pulses with contrast ratios of less than three, the maximum value which can be obtained as for example in the case of fully mode locked operation, are fraught with uncertainties about the actual nature of the pulses. Contrast ratios of two which are observed here might indicate a free running oscillation[10] or random (initial condition) mode locked laser.[9] It should further be noted that all experimental problems as for examples, scattering, and imperfect overlap of the beams, would tend to reduce the observed contrast ratio. Because of this uncertainty we can quote only the bounds of the average peak power between a maximum and a minimum had there been no picosecond pulse content: for the pump

$8 \times 10^6 < P$ watts $< 10^8$; for the dye laser $2 \times 10^6 < P$ watts $< 2 \times 10^7$ using an output mirror reflectivity of 60%. A smaller number of picosecond pulses might be expected to yield higher powers. The full beam angle at half power density was measured as 2.0 mrad by a self-calibrating technique[11] which obviates the problem of film reciprocity.

Efficiently confining the spectral output of the dye laser to 6 cm^{-1}, by replacing one of the cavity mirrors by a diffraction grating as described in an earlier publication,[12] we have demonstrated a continuously tunable source of $1.1 \pm 0.1 \times 10^{-11}$ sec pulses over a half power tuning range of 600 cm^{-1}. Narrowing the spectral output much beyond this would, of course, broaden the pulse widths. The pulse pattern again resembled the pumping pulse structure and had a measured contrast ratio of 2 ± 0.2. The Rhodamine cell was centered in the cavity with $L_\ell = L_p$. Using a grating of 2,160 lines/mm of approximately constant first order reflectivity of 58% in the range of interest in the Littrow position and a 100% reflector, the energy output in the zeroth order at the peak of the tuning curve was greater than 50% of that obtained with the 60% dielectric reflector replacing the grating. The full beam angle at half power density was found to be 4.8 mrad.

It should be noted that pulse duration with narrow spectral output is identical to that obtained with no grating when the full 150 cm^{-1} bandwidth was generated. This indicates that no more than 6 cm^{-1} of the available bandwidth cooperated in mode locking to produce any one short pulse.

The technique described in this paper, providing tunable short pulses, is expected to work well with many families of dyes, both in liquid and plastic[12] hosts covering the entire range from the near ultraviolet to the near infrared. The flash lamp pumped self mode locked dye laser[4] would also be amenable to this technique. Single tunable picosecond pulses or pulses with other intervals should also be obtainable.

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Reversible and Irreversible Decay of Polymethine Dye Solutions

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APPENDIX E

To be published

REVERSIBLE AND IRREVERSIBLE DECAY OF POLYMETHINE DYE SOLUTIONS*

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ABSTRACT

A reaction scheme is presented to characterize the stability of solutions of polymethine dyes with respect to other chemical species, temperature, and radiation. The observed equilibrium properties as well as the kinetic and steady-state parameters favor a model based on a low-lying triplet state.

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APPENDIX E

I. INTRODUCTION

Three polymethine dyes used in passive Q-spoiling of lasers are: kryptocyanine,[1] KQS,[2] and EQS.[3] All three solutions bleach (decay) reversibly and irreversibly to varying degrees under repetitive Q-spoiling. These shortcomings prompted a study of the effects of chemical species in the environment, temperature, and radiation. In the homogeneous-phase decay of dilute solutions, the reaction scheme which plays the central theme has three stages. The dye in the iodide form and molecule in the ground singlet state is represented by RI.

Stage 1. a. $RI \rightleftharpoons (RI)^*$ b. $(RI)^* \rightarrow R^\cdot + I^\cdot$

Stage 2. a. $I^\cdot + RI \quad I_2 + R^\cdot$ b. $R^\cdot + RI \rightarrow R_2 + I^\cdot$

Stage 3. a. $I^\cdot + I^\cdot \rightarrow I_2$ b. $R^\cdot + R^\cdot \rightarrow R_2$

c. $I^\cdot + R^\cdot \rightarrow RI$.

The nature of the intermediate, (RI)*, will be taken up in Section III. Stages 2 and 3 are conventional in free radical reactions. The latter is a throttle to the former. These do not involve large activation energies, i.e., stage 1 provides the limiting rate. Stage 1.a. depicts reversible bleaching.[4] The rest is irreversible, an approximation valid for extremely dilute solutions.

II. MATERIALS AND APPARATUS

Kryptocyanine and EQS were obtained from Eastman Organic Chemicals. KQS was synthesized in the laboratory.[2] The solvents were methanol, quinoline, and chlorobenzene; spectrophotometric-grade reagents of J. T. Baker Chemical Co. The concentrations were 10^{-5} M (molar).

Optical density was measured in a 1-cm cell with a Beckman DK-1A, provided with a temperature-regulated cell holder. Control samples established the warm-up half-life for the cell assembly. A xenon-arc lamp, in conjunction with a 500-mm focal length grating monochromator, was used for irradiation in the visible and the near visible. More intensive irradiation at 1.06μ was carried out with a Nd-YAG laser (12 watts cw); for the near uv, a conventional high-pressure mercury-arc lamp was focussed into the cell. In KQS or EQS solutions, the 1μ-absorption was probed normal to the beam with a PbS-detector. Energy flux at the site of irradiation was measured with an Eppley thermopile.

III RESULTS AND DISCUSSION

A. Effects of Chemicals

Reversible bleaching by a change in pH is neither of interest nor pertinent to the working model. The irreversible bleaching considered is that caused by species in the environment at constant temperature in the dark. Stage 3.a. provides a basis for forced irreversible bleaching. At room temperature (27°C), the reverse direction has a half-life 10^{12} sec and the equilibrium constant for dissociation is 10^{-22} moles per liter.[5] As expected (stage 2), complete decomposition in the dark proceeds rapidly, limited by diffusion, when equivolumes of 10^{-5}M I_2 and KQS in methanol are mixed.[6] Thus, 10^8 RI per iodine atom is consumed in $<<$ 1 sec.

A vacuum manifold was employed to prepare KQS-quinoline in optical cells, to study the effect of oxygen. A known amount of dye as KQS-methanol was introduced into the cell. The solvent was removed by pumping. A known volume of quinoline, dried and refluxed in a column containing Mg turnings, was distilled into the cell. One cell was sealed under 0.42 mm and the other under 1.00 mm pressure of oxygen. All operations were carried out in the dark. Over a 300-hr interval, the decay of the fundamental (1μ-band) at room temperature was first order, 0.41% hr^{-1} for the 0.42 mm case and 0.44% hr^{-1} for the other, i.e., τ = 163 hr. The decay was not limited by the passage of oxygen across the gas-liquid interface. It is argued later (cf. III.B.) that (RI)* was the reactive species. A dark-reaction with oxygen is shown by all the solutions examined.

Stage 1 is dependent on the solvent. In the absence of oxygen, room-temperature stability of KQS solutions in the dark, in decreasing order, is methanol > chlorobenzene > quinoline >> α-chloronaphthalene. The stability ranges from no decomposition in methanol after a two-year storage to a half-life of two days in α-chloronaphthalene. In the presence of oxygen (air), under the same conditions, the respective half-lives are shorter, 3.7 hr in methanol, 120 hr in chlorobenzene, and 3-6 hr in quinoline.

The variable behavior in quinoline is caused by moisture which shows a catalytic influence. The following room-temperature response in the dark of KQS-quinoline (first-order decay) is typical: dry oxygen bubbled through, $\tau = 4$ hr; followed by dry nitrogen, after flushing out the previous gas, no decomposition in 15 hrs; wet nitrogen, $\tau = 30$ hr, presumably due to a small background of oxygen; wet oxygen, $\tau = 0.13$ hr. In kryptocyanine-water, the action of oxygen is striking. Material precipitates out. The deoxygenated solution is stable for indefinite periods.

B. Effect of Temperature

From Section I, the working model is,

$$\text{Model I:} \quad RI \underset{k_r}{\overset{k_f}{\rightleftarrows}} (RI)^* \xrightarrow{k_i} \cdots .$$

The k_i-path, as well as the reaction paths of the free radicals (stage 1), depend on the impurities (cf. III.A.), temperature, and radiation. In the study of thermal bleaching, spectrophotometric-grade materials were employed. Distillation of solvent and preparation of solutions were performed in vacuum (cf. III.A.). The optical cells were sealed. All operations were carried out in the dark, except for the probe at the fundamental.

Completely reversible bleaching means

$$k_i = 0 \tag{1}$$

and

$$y_{rev} = \frac{1}{1 + K}\left[1 + Ke^{-k_r(1 + K)t}\right]. \tag{2}$$

The concentration of KI is normalized; $y_{rev} = 1$ at $t = 0$, and

$$K = k_f/k_r \ . \tag{3}$$

The reversible-irreversible case where

$$k_f >> k_i \ , \tag{4}$$

is given by

$$y = \left[\frac{k_f - \frac{\beta}{\alpha}}{\alpha - \frac{\beta}{\alpha}}\right] e^{-\alpha t} + \left[\frac{\alpha - k_f}{\alpha - \frac{\beta}{\alpha}}\right] e^{-\frac{\beta}{\alpha} t} \ . \tag{5}$$

where

$$\alpha = k_f + k_r + k_i \tag{6}$$

and

$$\beta = k_f k_i \ . \tag{7}$$

The model explains thermal bleaching of KQS-quinoline in the measured range 40^{o}-180^{o}C, and EQS-chlorobenzene from 35^{o} to 124^{o}C. Unlike photo bleaching (cf. III.C.), only a general reduction in the absorption spectrum resulted from heating. The constants derived from curve analysis are plotted in Fig. 1. The dependence summarized in Table I was calculated by the method of least squares. The assumed inequality (4) is borne out. Due to the low value of k_i, stage 1.b. throttled stage 2, which otherwise, would have provided another decay path to RI.

The ratio of RI to solvent, 10^{-7}, is readily exceeded by that of impurities in reagent-grade materials. The rate constants were derived from total bleaching. A pertinent test of the model and reproducibility of the preparation is a prediction of the reversible fraction. If the solution is held at a temperature over a time interval $\Delta t >> (k_f^{-1}, k_r^{-1})$, the fraction decomposed equals $K\ k_i \Delta t$. Table 2 compares the reversible fraction of two solutions. Fig. 2 shows prediction vs. observation for the recovery of EQS-chlorobenzene after a 20-hr exposure.

Within the accuracy of the experiment, the enthalpy change for reversible bleaching and the energy barrier to irreversible bleaching is the same in the two solutions (cf. Table I). From equation (3), no activation is involved in k_r(EQS) which has τ_r (EQS) = 0.3 min. A small barrier, 600 cal $mole^{-1}$, exists in KQS-quinoline where, τ_r (KQS) = 3 min at 27^{o}C.

An interpretation of the nature of (RI)* is relevant. This intermediate does not appear to be a geometric isomer, there being only a general reduction in absorption. The frequency factor of k_f and k_r is very low. The energy barrier for recovery is marginal. (RI)* is most likely a low triplet, an "electronic isomer".[7] Since $k_f^{-1} << 163$ hr (cf. III.A.), a reaction between triplets would explain the dark-reaction with oxygen. And similarly with solvent stability where the sequence in

III.A. corresponds to decreasing solvent triplet-energy for the rarefied state. Since only RI was measured, any mechanism first order with respect to (RI)* would be in harmony with the results. However, in view of the reproducibility of the preparations and the low value of k_1, we believe that the path measured is intrinsic to the solute-solvent pair.

C. Effect of Radiation

Two main absorptions in the near visible characterize the solutions (cf. Fig. 3 below). In a given dye the position and absorption strength depend on the solvent.[8] The fundamental, one of the two main absorptions, has $\epsilon \approx 10^5$ liter mole^{-1} cm^{-1}. The two components of the fundamental are attributed to the cis and trans arrangements, the latter accounting for the lower-frequency absorption.[9] No observable bleaching resulted from low-intensity (10^{-2} watts) irradiation of KQS-quinoline at the fundamental.

More intensive irradiation of KQS-quinoline by a Nd-YAG laser (1.06μ) with energy inputs ≥ 50 joules into a 3 cm^3 solution, gave no response beyond a percent which is accounted for by thermal bleaching (cf. III.B.). Intersystem crossing from the first excited singlet, k_{2r}, is negligible compared to internal conversion, k_{21}, a feature pertinent to Q-spoiling. (Subscript 1 for the ground state, 2 for the first excited singlet and r for the first triplet.) Steady state between levels 1 and 2 is reached immediately, and since

$$k_{2r} << k_{21} , \qquad (8)$$

the steady-state distribution is

$$\bar{n}_2 k_{21} \approx \bar{n}_1 k_{12} . \qquad (9)$$

The duration of irradiation, τ_R, is much less than k_{r1}^{-1} (corresponds to k_r in III.B.). The fraction bleached, f, is

$$\bar{n}_2 k_{2r} \tau_R = f \bar{n}_1 . \tag{10}$$

The total number of photons absorbed, N, is given by

$$N = \bar{n}_1 k_{12} \tau_R V \tag{11}$$

where V is the volume of the solution. It follows from equations (9), (10) and (11) that

$$k_{2r} \approx \frac{f \bar{n}_1 V}{N} k_{21} . \tag{12}$$

From the results given above, $N \geq 3 \times 10^{20}$, $f < 0.1$, $V = 3$ cm^3 and $\bar{n}_1 = 10^{15}$ cm^{-3}; therefore, $k_{2r}/k_{21} < 10^{-6}$, in agreement with inequality (8). Disregarding the population of the triplet level, the saturation behavior of the fundamental absorption in kryptocyanine-CH_3OH, EQS-chlorobenzene and KQS-quinoline yields an interconversion rate of $k_{21} = 10^{11}$ sec^{-1}. Hence, in KQS-quinoline the intersystem-crossing mean lifetime is $k_{2r}^{-1} > 10^{-5}$ sec.

The other absorption, $\epsilon \approx 10^4$ liter mole^{-1} cm^{-1}, shows three components in KQS solutions, 0.52μ, 0.46μ and 0.38μ. Bleaching was effected in quinoline and chlorobenzene at 0.38μ with 8×10^{-4} watt incident and at 0.46μ with 6×10^{-3} watt incident, but not at 0.52μ with 8×10^{-3} watt incident. The decay with respect to the fundamental appeared to be zero order, relaxation to the ground state being dominant. Data on room-temperature irradiation of air-free solutions are collected in Table 3. The number of photons absorbed per molecule bleached is

$$\eta(\lambda) = \frac{I_o(\lambda) \zeta F \cdot \epsilon(1\mu) \cdot \ell}{6.0 \cdot 10^{20} V |A|} \tag{13}$$

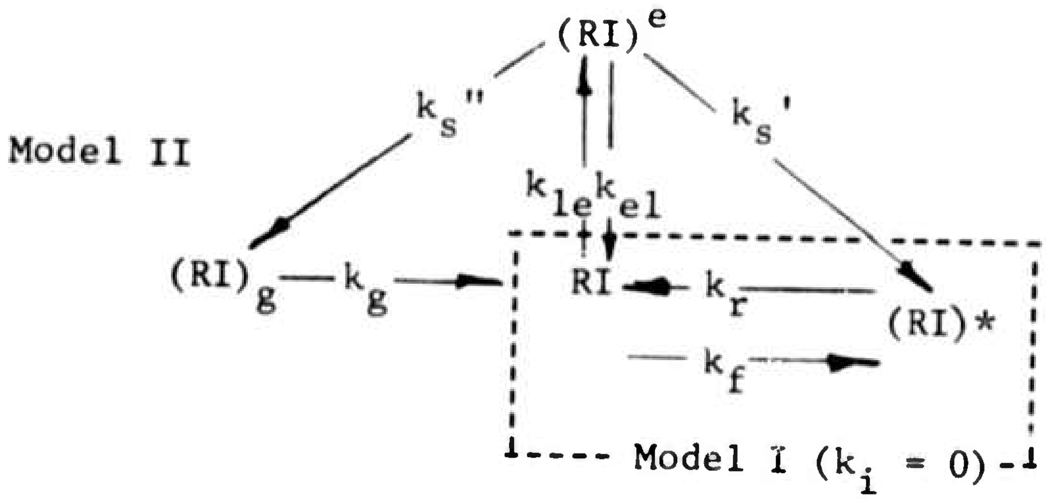
where I_o (λ) is the photon flux centered at λ, the irradiation wavelength. To calculate the fraction absorbed, F, a Lorentzian shape for the components in the absorption envelope and a triangular energy-distribution function from the monochromator were assumed. The geometric factor was $\zeta \approx 1$, the volume of the solution $V = 3.0$ cm^3 and the cell thickness $\ell = 1.0$ cm. The initial optical density, D_o, and the decline per unit time, A, during irradiation refer to the probe (fundamental) where $\epsilon(1\mu) = 1.2 \times 10^5$ liter mole^{-1} cm^{-1} in both solvents.

The absorption coefficient of the solvent, $\alpha(\lambda)$, shows that bleaching efficiency improves with solvent absorption. At 0.46μ, where the solvent is weakly absorbing, η seems independent of the solvent. If true, linear extrapolation to $\alpha = 0$ at 0.38μ would yield an intrinsic η. The existence of an intrinsic η is contradicted by KQS-methanol. No bleaching was effected at an irradiation dose (0.37μ) one order of magnitude larger. Absorption and photo-bleaching are clearly characteristic of the dye-solvent complex. In the calculation of F, $\alpha(\lambda)$ was not subtracted from the absorption coefficient of the solution. The last two columns in Table 3 are taken up below.

Under low-intensity irradiation, bleaching rate was established at $\tau_R < 10^2$ min. With $\tau_R = 2.6 \times 10^3$ min at 0.46μ, 6×10^{-3} watt incident, the total bleaching of KQS-quinoline was 25%. The irreversible fraction was > 90%. This was not unexpected when $k_i \tau_R \approx k$ for the fastest k_i-path. The solvent stability sequence (cf. III.A.) suggests solvent triplet species could participate in irreversible decay. (The triplet separation in rarefied quinoline is at 0.46μ.) Unfortunately, a more intense source was not available.

To study reversible bleaching due to electronic isomerism, it is necessary that a significant change be effected with $\tau_R << \tau_r$. The need for crossing accuracy of the probe and the irradiation beams was mitigated since the diffusion time between the two regions was shorter than τ_r. A high-pressure mercury lamp was used; 0.40 watt or a photon flux of 6.3×10^{17} sec^{-1} was absorbed. Fig. 3 shows the room-temperature absorption of KQS-quinoline after a constant-intensity irradiation at $\tau_R = 0$, 1 and 4 min. An isobestic point is evident here. The inserted figure, absorption of iodine in quinoline, can account for irreversible growth at 0.38μ (stage 3.a.). For $\tau_R = 1$ min a total bleaching of 50% was achieved, yet reversibility was > 90%.[10] From Fig. 3 $|\dot{A}| = 0.40$ min^{-1}. Since V = 3.0 cm^3, the bleaching rate was 1.0×10^{14} sec^{-1}. Hence, η (0.38μ) = 6.3×10^3 in agreement with the low-intensity case, 5.8×10^3 (cf. Table 3). The latter value is low because irreversible bleaching was larger. The present case, corrected for the time (15 sec) taken to record the peak of the fundamental, yields η (0.38μ) = 6.6×10^3. The total bleaching per joule absorbed at 0.38μ is the same for the low and high intensity cases, (1.6 ± 0.2) %j^{-1}. In spite of a scale-up factor of 10^3 in power absorbed, there is no evidence of saturation.

The results suggest additions to Model I pertinent to reversible photo-bleaching. In the scheme shown, RI and $(RI)_g$ are the trans and cis isomers, concentration n_1 and n_g, absorbing at 1.02μ and 0.90μ in KQS-quinoline, respectively. With broad-band uv, both species generate their respective (RI)*, concentration n_r, causing a general reduction at the fundamental. However,



only the limiting paths to, and away from, RI are pertinent. The imbalance in the two components of the fundamental reflects geometric conversion. Pertinent to reversible bleaching, note that

$$k_{1e} \gg k_f \tag{14}$$

and

$$\tau_R < k_r^{-1} < k_g^{-1}, \tag{15}$$

i.e., recovery from electronic is faster than geometric isomerism (cf. below). At the excited level, $(RI)_e$, concentration n_e, relaxation to the ground state is overwhelming and electronic conversion is faster than geometric (cf. below).

$$k_{e1} \gg k_{s'} > k_{s''} \tag{16}$$

From the inequalities and because n_e reaches steady state ($\bar{n}_e$) within $\Delta t \ll \tau_R$, the pertinent rates are

$$\left.\begin{aligned} &(a) \quad \dot{n}_1 = -(k_{s'} + k_{s''})\,\bar{n}_e \\ &(b) \quad \dot{n}_r = k_{s'}\,\bar{n}_e\,, \\ &(c) \quad \dot{n}_g = k_{s''}\,\bar{n}_e\,, \end{aligned}\right\} \tag{17}$$

and

$$\frac{\bar{n}_e}{n_1} = \frac{k_{1e}}{k_{e1}} \ll 1\,. \tag{18}$$

The rates add up to zero in reversible bleaching. Equations (17a) and (18) account for an apparent zero-order bleaching of the fundamental with a rate proportional to the photon flux. Recovery is a superposition of two processes: $k_{s'}\bar{n}_e\tau_R \exp(-k_r t)$ and $k_{s''}\bar{n}_e\tau_R \exp(-k_g t)$. The number of photons absorbed is $k_{1e}n_1\tau_R$. It follows from equations (17a) and (18) that

$$\eta = \frac{k_{e1}}{k_{s'} + k_{s''}} \tag{19}$$

and

$$\dot{n}_1 = -\frac{k_{1e}}{\eta}\, n_1 \;. \tag{20}$$

Thus, the fractional bleaching rate and η yields k_{1e}. A separate estimate for k_{1e} is given by ρB, the induced absorption rate. The Einstein B-coefficient was derived experimentally from the absorption curve (Lorentzian distribution). The energy distribution (triangular) was centered at the peak. Fair agreement is seen between the last two columns in Table 3. The constancy of the B-coefficient may be inferred from k_{1e}, there being a photon flux density one order of magnitude higher at 0.46μ than at 0.38μ (cf. footnote to Table 3).

Room temperature recovery from a more intensive photo bleaching, 30% at $\tau_R = 6$ sec but completely reversible, is shown in Fig. 4. Two processes are seen which lead to the assignment of $\tau_r = 2.6$ min for electronic, in good agreement with thermal bleaching, and $\tau_g = 460$ min for geometric isomerism. From the amplitudes, $k_{s'}/k_{s''} = 3.4$. It follows from equation (19) that, $k_{s''} = 3.4 \times 10^{-5}\, k_{e1}$. Since internal conversion between higher excited states is very fast, $k_{e1} \approx k_{21} \approx 10^{11}$ sec^{-1}.[11]

In summary, for KQS-quinoline bleached at 0.38μ, at room temperature, the pertinent rate parameters are $B = 8.2 \times 10^{19}$ cm^3 erg sec^{-2}; $k_{e1} \approx 10^{11}$ sec^{-1}; $k_{s'} \approx 1.2 \times 10^{7}$ sec^{-1}; $k_{s''} \approx 3.4 \times 10^{6}$ sec^{-1}; $k_{2r} < 10^{5}$ sec^{-1}; $k_r = 4.4 \times 10^{-3}$ sec^{-1}; and $k_g = 2.5 \times 10^{-5}$ sec^{-1}. From $k_{s'}$ and k_{2r}, the higher excited state is two orders of magnitude more favorable to intersystem crossing than the first excited singlet. Such is not usually the case because of efficient internal conversion.[12]

IV. CONCLUSIONS AND COMMENTS

The equilibrium, kinetic and steady-state behaviors of polymethine dye solutions were described by a three-stage chain reaction involving free radicals: initiation, propagation and termination. The dark-reaction with iodine evidenced chain propagation. With oxygen the reaction was much slower, the reactive species (dye) being the triplet. The latter, as an intermediate to thermal dissociation, is characterized by $\tau_i \approx 10^{10}$ min at room temperature in the dark. Other k_i-paths were examined under the same conditions. Thus, $\tau_i = 10^4$ min in the presence of oxygen alone. With oxygen and moisture, $\tau_i = 8$ min and the observed rate was probably limited by transfer through the interface. Water is believed to act as a catalyst under the conditions provided, because formation of the intermediate is characterized by $\tau_f = 50$ min. Also pertinent is the sequence of solvent stability which is in the order of the separation of their first triplet with the respective ground state.

At room temperature, intersystem (nonradiative) crossing from the first triplet to the ground state is $\tau_r = 3$ min by thermal bleaching and $\tau_r = 2.6$ min by photobleaching. The specific rate for the reverse process, k_f, obtained from these values may be taken as a gauge of the discrepancy, Δk_f, in the thermal method. It can be shown that,

$$|\Delta k_f| = \frac{K}{K+1} \cdot \frac{\Delta H}{RT} \cdot \frac{|\Delta T|}{T} \lambda \ , \qquad (21)$$

where λ is the specific rate (Newton's law) for the heating of the cell assembly. The pertinent data are: $T = 300^{\circ}K$, $K = 0.074$, $\Delta H = 6800$ cal mole^{-1}, $\lambda = 0.32$ min^{-1} and $|\Delta k_f| = 0.0027$ min^{-1}.

The discrepancy corresponds merely to a one percent deviation in temperature. Therefore, the two lifetimes are equal within experimental error.

A low-lying triplet contributes to the temperature dependence of the absorption coefficient, α, of the fundamental.[13] The equation of state from the model is

$$\frac{K+1}{K}\ \alpha = \frac{\Delta H}{RT} + \text{const.},^{14} \tag{22}$$

where K is temperature-dependent but not ΔH. In the case of pulsed excitation leading to a saturation of the fundamental, i.e., the passive Q-spoiling of lasers,[1,2] it is desirable that

$$E_s >> E_t \leq RT^* , \tag{23}$$

where E_s and E_t are the separations from the ground state of the first excited singlet and the lowest triplet, respectively, and T* is the steady-state temperature for a given pulse repetition rate. Population of the triplet by either intersystem crossing is apt to be inefficient. As longer chains are employed to push the fundamental past 1μ, ϵ falls rapidly. The absorption spectrum becomes flat due to various isomerizations and the solution becomes more reactive.[15] The latter is a consequence of a low-lying triplet. Because of these factors, the long-wavelength limit of Q-spoiling dye solutions operated at room temperature is ~ 1μ.

The net reaction in Model I is characterized by

$$k_I = \frac{K}{I+K}\, k_i \ . \tag{24}$$

A comparison of k_I, benzyl iodide (36°C)[5] vs. the polymethine chains gives 1:10:400, for benzyliodide-hexachlorobutadiene: KQS-quinoline: EQS-chlorobenzene.

Electronic and geometric conversions by photo excitation were more favorable at the higher states. Hence, crossing rates increased with excitation faster than internal conversion. The considerable electronic isomerism effected leaves no doubt that intersystem crossing was favored at the higher state. In geometric conversion, two cases of cis-trans isomerism are possible: occurrence at a high singlet or triplet. The latter implies a low frequency factor. Since $k_{s''} = 3.4 \times 10^6 \text{ sec}^{-1}$, crossing from the excited singlet is favored. Thus, the high singlet (0.38μ) was the source of branching for the two cases of isomerism, with electronic better than three times favored over geometric. However, in recovery (geometric case), $k_g = 2.5 \times 10^{-5}$ sec^{-1}, which may mean either a low frequency factor coupled with a low activation or a high frequency factor with a high activation.

Isomerization by photo excitation is influenced by the solvent. It appears necessary that the solvent absorb in the region matching the excitation of the higher states where significant branching occurs. Therefore, excited states of both solvent and solute species, or dye-solvent complex, are involved. This would provide a basis for the prevalence of irreversible bleaching in the weak-intensity case where $k_i\tau_R \approx 1$ and for the solvent-stability sequence. A modest coupling strength in the complex is in line with the observation that the balance of cis-trans isomers is dependent on the solvent and persists through moderate changes in temperature. Assuming a ratio of statistical weights close to unity for the geometric species $(RI)_g$ and RI, the observed distribution suggests an enthalpy difference of $\sim 10^2$ cal mole^{-1}, which also explains the insensitive variation of the distribution with temperature.

From these results, it is seen that uv leakage from laser excitation rather than the laser beam itself is more pertinent to the steady-state performance of the Q-spoiling solution. More than 10^5 laser pulses were generated at 10 sec^{-1} before the fractional loss in dye concentration amounted to 1/e.[16] Such a solution had a very low rate k_i-path, prepared according to the procedure described above. Breakdown occurred at the glass-solution interface, a black smudge ~ 1 mm diameter, probably caused by an inhomogeneous power density across the laser beam. Since a copious deposit formed before a significant decline in optical density, dye decomposition is secondary and the case is most likely solvent degradation through a chain reaction. This has been observed in both quinoline and chlorobenzene as solvents.

We are very grateful to M. A. Pearson for programming the calculations and rendering computer service. We thank E. G. Erickson for the loan of his Nd-YAG laser (KY-12).

Table 1

Summary of Constants for Thermal Bleaching
(Energy unit: cal.)

	KQS in Quinoline 40°-180°C	EQS in Chlorobenzene 35°-124°C
K	6830 exp (-6,800/RT)	4620 exp (-6,900/RT)
k_f, $\sec^{-1}$	55 exp (-7,400/RT)	210 exp (-6,800/RT)
k_i, $\sec^{-1}$	1.55×10^{12} exp (-32,900/RT)	2.08×10^{14} exp (-32,100/RT)

Table 2

Reversible Fraction of Total Thermal Bleaching

Soak temp., $^{\circ}C$	Recovery: KQS-Quinoline Δt, min	 Predicted %	 Obs. %	Recovery: EQS-Chlorobenzene Δt, min	 Predicted %	 Obs. %
80(a)	200	100	98	1000	96	94
130(b)	1000	83	84	300	0	--

(a) KQS-quinoline: $K = 0.43$ and $k_i = 4.6 \times 10^{-7}$ min^{-1}.
EQS-chlorobenzene: $K = 0.24$ and $k_i = 1.7 \times 10^{-4}$ min^{-1}.

(b) KQS-quinoline: $K = 1.37$ and $k_i = 1.3 \times 10^{-4}$ min^{-1}.
EQS-chlorobenzene: $K = 0.82$ and $k_i = 4.8 \times 10^{-2}$ min^{-1}.

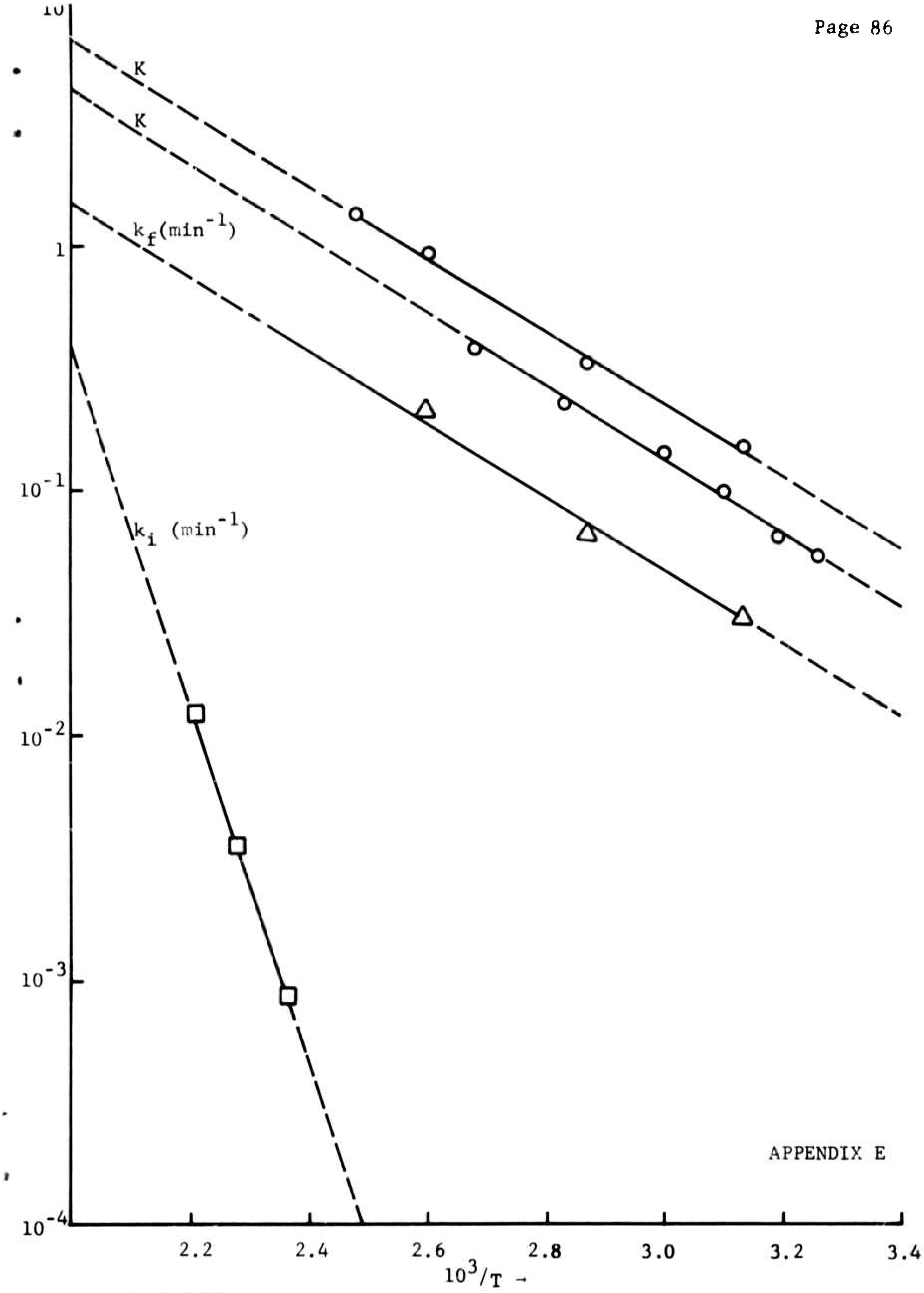
Table 3

Bleaching of KQS Solutions

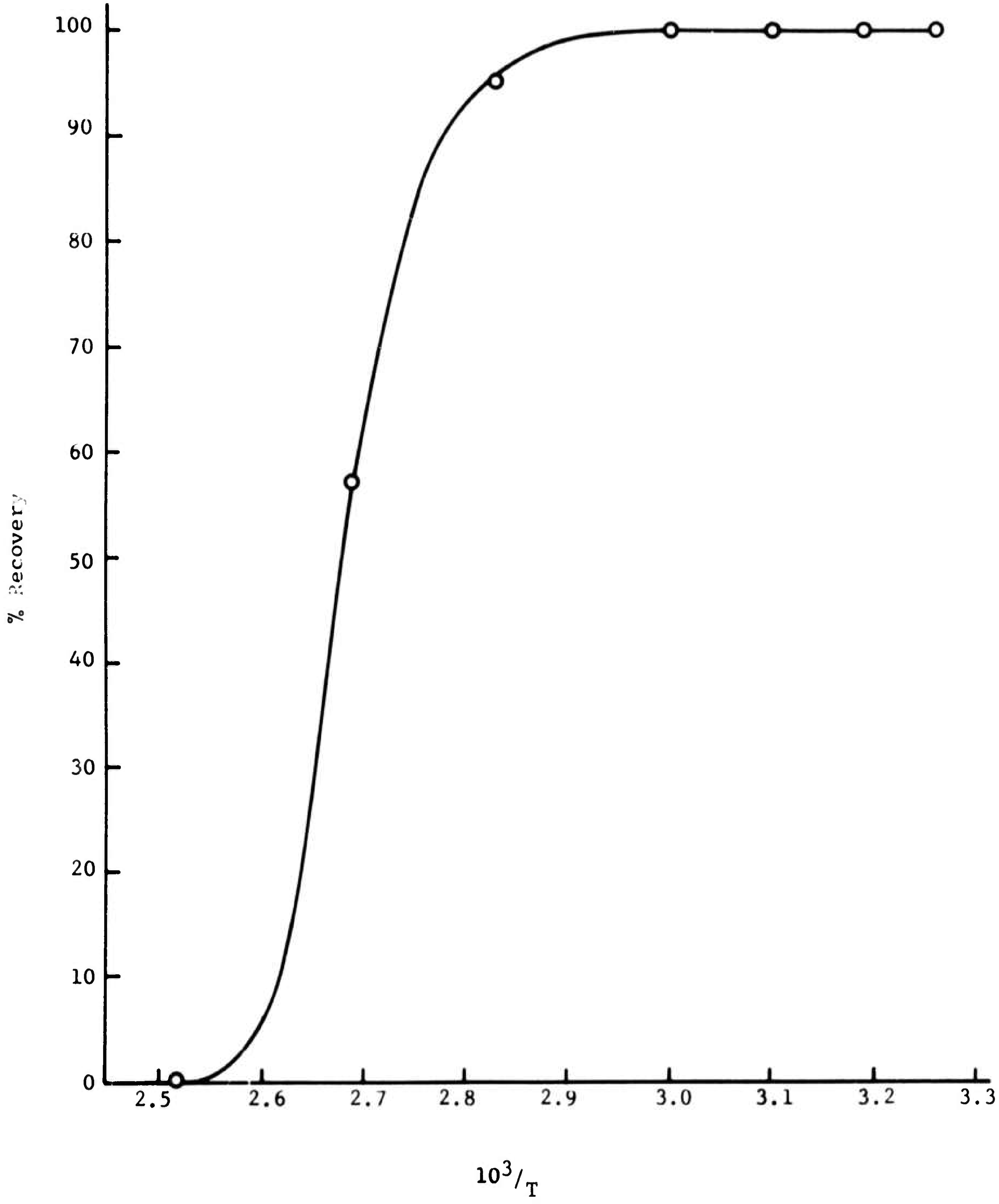
Solvent$^{(a)}$ $\alpha(\lambda)$, cm^{-1}	λ, μ	$-10^6 \cdot A$, sec^{-1}	D_o	$F^{(b)}$	$10^{-5} \cdot \eta(\lambda)$	k_{1e}, sec^{-1}	ρB, sec^{-1}
I : 0.06	0.464	3.13	1.353	0.38	1.1	0.26	0.34
0.43	0.380	7.42	1.362	0.42	0.058	0.032	0.039
II: 0.02	0.467	4.43	1.277	0.65	1.3	0.45	0.83
0.05	0.384	2.00	1.255	0.41	0.21	0.033	0.045

(a) I = quinoline, II = chlorobenzene and $I = I_o \exp(-\alpha \ell)$

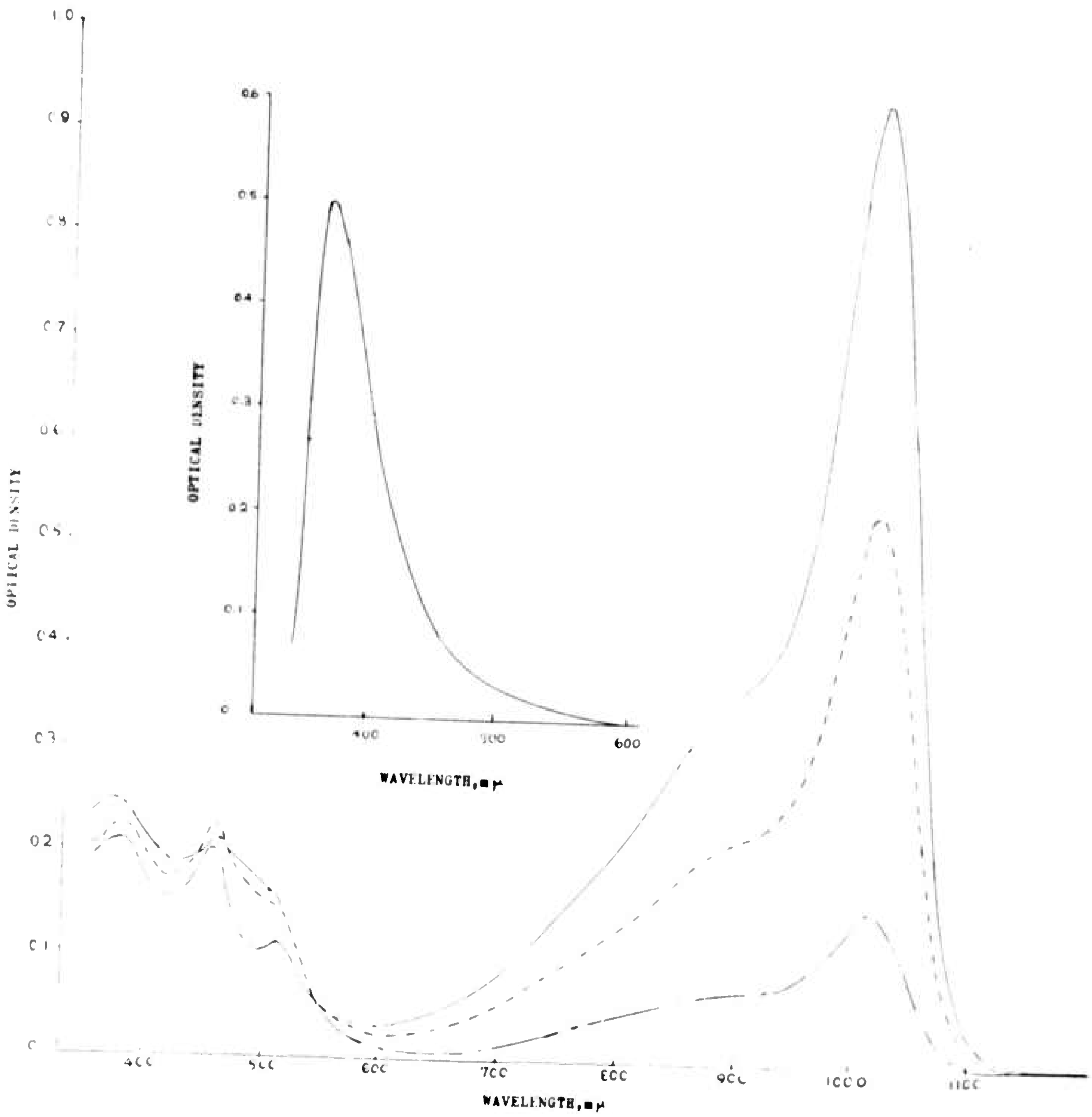
(b) Incident photon flux density: I_o (0.38μ) = 1.5 x 10^{15} sec^{-1} and I_o (0.46μ) = 1.4 x 10^{16} sec^{-1}.



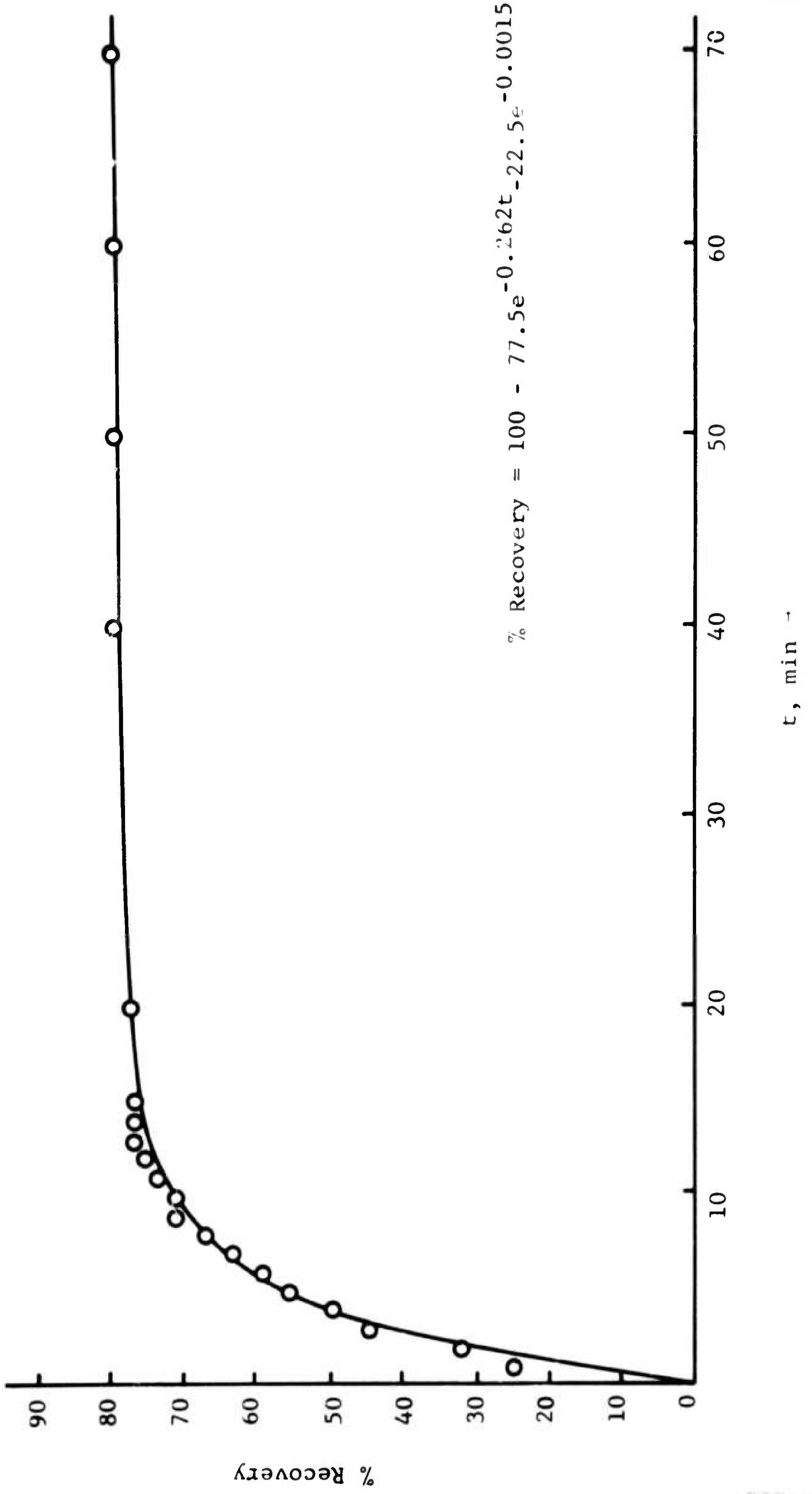
APPENDIX E


100
90
80
70
60
50
40
30
20
10
0
% Recovery
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
$10^3/T$

APPENDIX E


OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
500
600
700
800
900
1000
1100
WAVELENGTH, mμ
0.6
0.5
0.4
0.3
0.2
0.1
0
400
500
600
WAVELENGTH, mμ

APPENDIX E


% Recovery = 100 - 77.5e$^{-0.262t}$-22.5e$^{-0.0015t}$
% Recovery
0
10
20
30
40
50
60
70
80
90
t, min →
0
10
20
30
40
50
60
70

APPENDIX E

FIGURE CAPTIONS

Fig. 1 Equilibrium constant, K, and specific rates, k, vs. T^{-1}. KQS-quinoline (0, △ □) and EQS-chlorobenzene (●).

Fig. 2 Room-temperature recovery of EQS-chlorobenzene following 1200 min exposures at various temperatures. The curve is calculated from K and k_i. Circles stand for observations.

Fig. 3 Room-temperature absorption of KQS-quinoline.

—— $\tau_R = 0$ min

--- $\tau_R = 1$ min

—–$\tau_R = 4$ min

Insert spectrum is the absorption of I_2-quinoline.

Fig. 4 Room-temperature recovery of the fundamental absorption of KQS-quinoline photo bleached by irradiating at 0.38μ.

FOOTNOTES

[1] B. H. Soffer, J. Appl. Phys. 35, 2551 (1964); P. Kafalas, J. I. Masters, and E. M. Murray, op. cit., 2349 (1964).

[2] B. H. Soffer and R. H. Hoskins, Nature 204, 276 (1964). Like kryptocyanine, KQS is also a carbocyanine. The formula and preparation (literature) is given in the reference cited.

[3] "Eastman Q-switch Solution 9740," a circular released by Distillation Products Industries (Oct. 1965).

[4] Bleaching alludes to the fundamental absorption of species RI.

[5] M. Gazith and R. M. Noyes, J. Am. Chem. Soc. 77, 6091 (1955).

[6] The effect is obtained also with kryptocyanine or EQS. With aromatic solvents, the behavior is complicated, presumably by iodine-solvent complexing.

[7] A low-lying triplet, 7 kcal mole^{-1} in the present case, is not unexpected for a conjugated chain of 13-C atoms. The Chichibabin hydrocarbon, 18-C chain, has the triplet at 3 kcal mole^{-1} (cf. C. A. Hutchison, A. Kowalsky, R. C. Pastor, and G. W. Wheland, J. Chem. Phys. 20, 1485 (1952) and references cited).

8 Intramolecular resonance stabilizes the polar form, R^+I^-. The similar charge on the ends of the polymethine chain (R) favor the trans arrangements which account for the structure at the longer-wavelength region of the fundamental absorption. See L. G. S. Brooker, p. 573, in "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters and Related Fields," edited by T. S. Gore, B. S. Joshi, S. V. Sunthankar, and B. D. Tilak (Academic Press, 1962).

9 An interpretation based on dissociation of higher aggregates is not compatible with the results of thermal bleaching.

10 In the low-intensity case (0.38µ, cf. Table 3), the photon absorption rate, 7.4×10^{14} sec^{-1}, is three orders lower but the total bleaching is only one order lower. The present case shows photo-dissociation (net reaction of stage 1) can be avoided; otherwise, rapid irreversible bleaching occurs (stage 2).

11 The Einstein A-coefficient (spontaneous emission) at 0.38µ, for KQS-quinoline, is only 1.1×10^6 sec^{-1}, a negligible contribution to k_{el}.

12 F. Wilkinson, Quart. Revs. XX (No. 3), 403 (1966).

13 From the data, reversible thermal bleaching at 27°C is -0.26% deg^{-1} for KQS-quinoline and -0.11% deg^{-1} for EQS-chlorobenzene. Thermal expansion of the solvent (quinoline) adds -0.08% deg^{-1}.

14 From $\alpha = \sigma N$, the absorption cross-section, σ, is independent of T; thus, $d\ln \alpha/dT = d\ln N/dT$, where N is the density of absorbers.

15 See reference in footnote 8 and also, S. S. Malhotra and M. C. Whiting, J. Chem. Soc. 3812 (1960).

16 A Nd-YAG laser was used, 26j input and peak power ~ 3 Mw for the pulses. Volume of the solution was 3 cm^3.

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13. ABSTRACT

Description of experiments bearing on the problems of the spectral behavior of passive Q-switched lasers and of the physical behavior of passive Q-spoiling materials are given. The results of experiments of the temporal and frequency locking of two lasers, coupled in a bleachable dye are described. Further experiments pertinent to the problem of spectral cross-relaxation are described. The stimulated emission of several organic dyes in the visible spectrum and the demonstration of efficient spectral narrowing and tunability over a wide spectral range is described. The results of frequency doubling a dye laser are presented. Mode locking of the dye laser with picosecond pulses, tunable over a broad range, is reported. The results of experiments concerned with the thermal and photochemical responses of two polymethine dyes used for Q-spoiling the Nd laser are given.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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