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ANALYSIS OF DYE DEGRADATION EFFECTS ON OUTPUT ENERGY
OF THE PULSED ORGANIC DYE LASER

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
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Master of Science

by

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The Air Force Avionics Laboratory at Wright-Patterson AFB, Ohio has conducted and sponsored extensive research into the lasing properties of Krypton Red S. One of the important conclusions of this research was that a multiplier effect was causing a logarithmic decay in pulse energy that was associated with a linear rate of KRS degradation.

At this point it seemed advisable to try to explain the phenomena with a theoretical analysis. My thesis modeled the KRS laser and derived a method of predicting what effect several degradation mechanisms could have on its performance. My next step was to try to obtain the necessary information from the wealth of data recorded by the previous studies to test the model and then use it to explain the multiplier effect. Unfortunately, the specific data required to arrive at conclusive results was not available, through no lack of thoroughness on my predecessors' part. Most of the requirements for the analysis were not readily foreseeable, and are included in my recommendations for further research.

I would like to express my appreciation to Capt. David Hardin for his assistance in designing the computer programs, to Dr. Robert Schwerzel of the Battelle Laboratories in Columbus for his help in determining values for the model parameters, to my thesis typist Jill Rueger whose expertise and consideration were invaluable, and to my thesis advisor, Dr. Ernest Dorko, who blended the proper amounts of assistance and supervision into an enjoyable project.
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Notation

\( S_i \)  
ith singlet energy level

\( T_i \)  
ith triplet energy level

\( E_i \)  
ith energy level

\( N_i \)  
ith level population density

\( N_T \)  
T_1 triplet level population density

\( P_i \)  
ith energy level population density (normalized)

\( a_{ij} \)  
spontaneous radiation and radiationless transition rates combined

\( n \)  
cavity photon population

\( k_{S_1S_0} \)  
\( S_1 \rightarrow S_0 \) internal conversion rate

\( k_{S_1T_1} \)  
\( S_1 \rightarrow T_1 \) intersystem crossing rate

\( k_{T_1S_0} \)  
\( T_1 \rightarrow S_0 \) intersystem crossing rate

\( k_{QS} \)  
singlet quenching rate constant

\( k_{QT} \)  
triplet quenching rate constant

\( k_{QS(RP)} \)  
rate constant for singlet quenching by the reaction product

\( k_{QT(RP)} \)  
rate constant for triplet quenching by the reaction product

\( Q_S \)  
concentration of singlet quencher

\( Q_T \)  
concentration of triplet quencher

\( Q_{S(RP)} \)  
concentration of the reaction product = \( c_{RP} \)

\( \tau_F \)  
fluorescence lifetime

\( \tau_{F(R)} \)  
radiative fluorescence lifetime

\( \tau_{F(NR)} \)  
nonradiative fluorescence lifetime

\( \tau_P \)  
phosphorescence lifetime
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<td>$\tau_{P(R)}$</td>
<td>radiative phosphorescence lifetime</td>
</tr>
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<td>$\tau_{P(NR)}$</td>
<td>nonradiative phosphorescence lifetime</td>
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<td>$\tau_{C}$</td>
<td>cavity photon lifetime</td>
</tr>
<tr>
<td>$\tau_{H}$</td>
<td>photon cavity lifetime due to frontal mirror transmission only</td>
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<td>$\alpha$</td>
<td>absorption coefficient at the lasing wavelength</td>
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<td>$\eta$</td>
<td>quantum pump efficiency</td>
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<td>$\eta'$</td>
<td>modified quantum pump efficiency</td>
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<td>$\Pi$</td>
<td>pump absorption factor</td>
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<td>$\phi$</td>
<td>quantum efficiency of fluorescence</td>
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<td>$\lambda_{L}$</td>
<td>wavelength of a lasing photon</td>
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<td>$\nu_{L}$</td>
<td>frequency of lasing photon</td>
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<td>$\nu_{P}$</td>
<td>frequency of pump photon</td>
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<td>$\gamma$</td>
<td>laser gain coefficient</td>
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<td>$\varepsilon$</td>
<td>molar extinction coefficient</td>
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<td>$\varepsilon_{P}$</td>
<td>molar extinction coefficient at the pump wavelength</td>
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<td>$\varepsilon_{D}$</td>
<td>molar extinction coefficient at the lasing wavelength of the dye</td>
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<td>$\varepsilon_{RP}$</td>
<td>molar extinction coefficient of the reaction product at the lasing wavelength</td>
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<td>$\delta_{S}$</td>
<td>ratio of the $S_{0} \rightarrow S_{1}$ extinction coefficient to the $S_{1} \rightarrow S_{2}$ extinction coefficient at the lasing wavelength</td>
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<td>$\delta_{T}$</td>
<td>ratio of the $S_{0} \rightarrow S_{1}$ extinction coefficient to the $T_{1} \rightarrow T_{2}$ extinction coefficient at the lasing wavelength</td>
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<td>$\sigma_{A(D)}$</td>
<td>pump absorption cross section for the dye</td>
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<td>$\sigma_{A(RP)}$</td>
<td>pump absorption cross section for the reaction product</td>
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<td>$\rho$</td>
<td>number of pump photons absorbed per second by the medium</td>
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<tr>
<td>$\rho_{0}$</td>
<td>number of pump photons transmitted per second in the initial beam</td>
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Notation (continued)

\(N_{2,\text{TH}}\) threshold population for lasing
\(W_{P,\text{TH}}\) threshold pump power
\(P_{\text{laser}}\) power output of a laser
\(W(t)\) pumping function
\(W_{\text{max}}\) peak value of the Gaussian pumping pulse
\(T\) half-width at half-height of the pumping pulse
\(L\) length of the dye solution traversed by a photon during a single pass through the laser cavity
\(L\) distance between mirrors in the laser cavity
\(n_D\) index of refraction of the dye solution
\(R_1\) reflectivity of the frontal cavity mirror
\(R_2\) reflectivity of the rear cavity mirror
\(c_D\) concentration of the dye
\(c_{RP}\) concentration of the reaction product = \(Q_S(RP)\)
Abstract

The dominant excitation and relaxation mechanisms found in dye molecules are discussed and are then incorporated into a model for the xanthene dye laser. Rate equations for this model are presented which include terms that account for excited state singlet absorption and triplet absorption. The system of rate equations are solved using the "steady-state approximation to derive equations for the threshold pump and output power of the laser.

The output power and threshold pump power equations are modified to include variables that allow the following effects of dye degradation to be examined: dye concentration reduction, reaction product absorption of pump radiation, reaction product absorption of lasing radiation, and singlet quenching by the reaction products. Theoretical values based on available experimental data are derived for these variables. A computer program is used to integrate the output power of the laser over the duration of a flashlamp pulse to compute the pulse energy.

The computer program presented is designed to determine how the output energy of the laser decreases over the course of repeated pulsing as the specific degradation effects increase with the increase in the reaction product. The results obtained from the theoretical analysis are compared to experimental data that describe a logarithmic decay of output energy associated with a linear decay in the dye concentration (the multiplier effect). Of those mechanisms examined, the absorption of lasing radiation appears to be the most effective factor that could contribute to the multiplier effect; however, it cannot account for the magnitude of the multiplier effect without considering additional
mechanisms operating simultaneously. Further experimentation is recom-
mended to obtain specific data for conclusive identification of the
responsible mechanism.
I. Introduction

Background

Dye lasers are being closely examined by the Air Force for use on aircraft as sources for optical radar and other electro-optical systems. The laser must operate in the 630-670 nanometer (nm) region up to three hours without servicing. The xanthene dye Kiton Red S (KRS) is currently under investigation to determine if it is capable of meeting these standards.

The complex structure and size of laser dyes make them susceptible to photochemical dissociation into reaction products. The degradation and performance of KRS under both continuous wave (CW) and flashlamp pumping has been extensively investigated (Refs 15, 16, 20, 25). The photodissociation process has been shown to be a function of the wavelength of the irradiance. The precise mechanism appears to be extremely complex due to the formation of transient reaction products. The exact nature of the transient and final reaction products has not yet been determined (Ref 33). Two important conclusions have been reached concerning KRS: the number of dye molecules lost through degradation increases at a constant rate with the number of pulses, and an unidentified multiplier effect is operating that produces a large decrease in the pulse energy for a small increase in the amount of dye degradation (Ref 25).

Objective

The objective of this study is to perform a theoretical analysis of the KRS laser system to explain the multiplier effect. The interactions examined as possible causes are limited to absorption of the lasing
radiation by a reaction product, absorption of the pump radiation, and
singlet quenching by a reaction product.

Assumptions

The data on the degradation rate and the pulse energy decay presented
by Rabins et al. (Ref 25) are assumed to be correct. The most reliable
method of measuring the amount of degradation has been under contention
to some extent; the method used by Rabins based on the infrared (IR)
spectra of the dye solution appears to be the most accurate technique.

Approach and Presentation

The primary mechanisms involved with the structure and chemistry of
laser dyes are described in Section II. The energy levels of the dye
molecule and associated excitation and relaxation pathways are discussed:
these include fluorescence and phosphorescence, thermalization, internal
conversion, intersystem crossing, singlet and triplet quenching, and
triplet and excited state singlet absorption. The degradation effects
that the study is going to examine are then presented, and the section
concludes with a brief description of several important characteristics
of pulsed dye lasers.

In Section III, a model is proposed to represent the dye laser and
rate equations appropriate to this model are developed. Using the steady-
state approximation the rate equations are used to obtain equations
expressing the threshold pump power and the output power of the laser.

These equations are specifically applied to the KRS dye laser in
Section IV. The pulse energy is obtained by integrating the output power
over the duration of the flashlamp pulse by computer. Values for the
required parameters are selected and variables are then introduced to
provide a means of evaluating the reaction product effects. The section ends by presenting the results obtained from the computer analysis.

Several aspects of these results are briefly discussed in Section V. Conclusions and recommendations are given in Section VI.
II. Mechanics of the Dye Laser

The complex structure of organic laser dyes presents many facets to consider in understanding the lasing process. The numerous mechanisms involved and their interplay have hampered precise characterization of the dyes and have led to conflicting data in the literature. This section presents the structure and basic molecular mechanics of xanthene dyes to provide a background for the development of a workable model applicable to xanthene dye lasers.

Structure and Energy Levels of Dyes

Organic dyes are large, complex molecules that contain conjugated double bonds (Ref 31:7). These molecules can be approximated by a core and an electron cloud. The core consists of σ-bonding electrons that are well localized and do not participate in optical-wavelength transitions; the π-orbital electrons are delocalized over most of the molecule (Ref 40:31). This extended conjugated bond provides strong absorption in the visible region of the spectrum due to electronic transitions from the highest-filled bonding molecular orbital to the lowest antibonding molecular orbital (\(\pi^*\)) (Refs 9:184, 31:144). The family of xanthene dyes that includes KRS and the rhodamine compounds consist of the parent xanthene compound (Figure 1) with a 9-carbon substituent that provides the variations in characteristics of the individual dyes (Ref 9:182). The structures of KRS, Rhodamine B, and Rhodamine 6G are also shown in Figure 1 (Ref 13:3885). These compounds have the \(\pi\)-electron cloud extending over the nitrogen atoms (Ref 25:5). This \(\pi\)-electron cloud can be considered as a one-dimensional particle in a box to quantum-
mechanically determine approximate energy level eigenvalues for electron orbitals (Ref 31:18, 40:31). The energy level diagram of a typical dye molecule is shown in Figure 2. As the conjugated bonds become longer in the larger molecules, the separation between energy levels becomes smaller both in this free electron model and experimentally. Therefore the molecules with longer delocalized $\pi$ bonds will absorb at lower spectral energies (Ref 9:184, 40:31).

Due to the large size of the dye molecules and their structural complexity, many closely-spaced vibronic transitions, represented as the fine lines within the electronic levels, are possible with each electronic transition. In addition, every vibrational sublevel is further divided by rotational sublevels (not depicted) which are extremely broadened due to frequent collisions with solvent molecules.
The resultant density of these possible transitional levels provides broad quasi-continuous absorption and fluorescence bands; the latter band gives KRS a tunability from 589 nm to 642 nm (Ref 11:270).

The singlet multiplicity states shown on the left in Figure 2 represent the energy eigenstates that a molecule can attain when an electron transitions to a π* orbital and has maintained the spin orientation required in the ground state due to the Pauli exclusion principle. Once the electron has departed the ground state, it may change its spin orientation (spin-flip) and occupy one of the triplet energy levels depicted on the right in Figure 2. Each singlet level has a corresponding triplet level that is of slightly lower energy. The triplet levels are primarily populated by nonradiative relaxation from their corresponding singlet levels as depicted. This process is known as intersystem crossing. Direct singlet to triplet absorption
transitions do occur but at a rate several orders of magnitude slower than intersystem crossing and are therefore negligible. Intersystem crossing can be induced by internal perturbations as well as by external perturbations and the rate varies with the different dyes and as a function of the dye solvent and other parameters (Refs 9, 17, 19, 31:29).

Molecular deexcitation

Once a molecule reaches an excited state it has several paths through which it can return to ground state. These can generally be grouped into radiative and nonradiative transitions.

Radiative Transitions. The radiative transitions are fluorescence and phosphorescence, illustrated in Figure 3. A fluorescent transition is one that occurs between states of the same multiplicity; phosphorescent transitions occur between states of different multiplicity and therefore require a spin-flip (Ref 5:308). These terms are used to describe the \( S_1 \rightarrow S_0 \) and \( T_1 \rightarrow S_0 \) transitions respectively in

![Figure 3](image)

**Figure 3**
Fluorescence and Phosphorescence
the laser dyes. The former transition is usually the lasing transition (Refs 31:29, 37:4726). The rates of these transitions are expressed as the inverse of their lifetimes. The values found in the literature for the fluorescence lifetime $\tau_F$ and phosphorescence lifetime $\tau_P$ include nonradiative contributions to relaxation:

$$\frac{1}{\tau_F} = \frac{1}{\tau_F(R)} + \frac{1}{\tau_F(NR)} \quad (2.1)$$

$$\frac{1}{\tau_P} = \frac{1}{\tau_P(R)} + \frac{1}{\tau_P(NR)} \quad (2.2)$$

The subscripts (R) and (NR) refer to radiative and nonradiative lifetimes. The lifetimes $\tau_F$ and $\tau_P$ therefore give the overall lifetimes of the $S_1$ and $T_1$ states due to all relaxation processes (31:30). Fluorescence lifetimes are generally on the order of nanoseconds, while phosphorescence lifetimes usually vary from microseconds to seconds (Refs 31:30, 35:651). For a given compound, however, these values can change as the associated nonradiative relaxation rates are altered by external parameters.

**Nonradiative Transitions.** In addition to radiative relaxation, excited molecules can relax by several nonradiative processes: by thermal equilibration within the vibronic levels of an electronic state, by internal conversion back to the $S_0$ level, or by intersystem crossing. When an electronic level becomes significantly populated, thermalization establishes a dynamic equilibrium that results in a Boltzmann distribution among the continuum of vibrational and rotational states (Ref 35:650). These distributions are achieved in both the excited and ground state electronic levels and occur on a picosecond time scale (Ref 40:32).
Internal conversion takes place between electronic levels of the same multiplicity. Little is actually understood about the phenomena although rates for $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ internal conversion have been experimentally determined for various dyes. $S_2 \rightarrow S_1$ conversion is usually extremely fast, taking place in less than $10^{-11}$ sec. (Refs 29:962, 31:29). This is the dominant mechanism in depopulation of $S_2$ and higher-level states. Internal conversion between $S_1$ and $S_0$ competes with lasing. This rate has been found to range over several orders of magnitude (Ref 31:29). Figure 4 compares these relaxation processes and gives rates and lifetimes representative of xanthene dyes.

Several nonradiative processes are functions of the solvent and other solute molecules. These environmental effects include fluorescence quenching by charge transfer interactions and aggregation of dye molecules. Aggregation does not occur in organic solvents such as ethanol (Ref 31:159) and charge transfer interactions do not become a factor until the dye concentration exceeds $10^{-3}$ M (Ref 13:3892) so that neither will be applicable to this analysis.

Quantum Efficiency of Fluorescence. At this point it is worthwhile to define the quantum efficiency of fluorescence $\phi$. This is a measure of the probability that a dye molecule will emit a photon in fluorescence upon absorption of a photon. This can be expressed as the ratio of radiative and nonradiative transition lifetimes (Ref 31:30):

$$\phi = \frac{\tau_F}{\tau'_F} \quad \text{or} \quad \tau_F = \phi \tau'_F$$

(2.3)

Using the relaxation routes discussed, the formula for $\phi$ would be
Figure 4

Relaxation Mechanisms
\[ \phi = \frac{1}{\tau_F(R)} \]  

(2.4)

where

\[ k_{S_1T_1} = S_1 \rightarrow T_1 \]  

intersystem crossing rate

\[ k_{S_1S_0} = S_1 \rightarrow S_0 \]  

internal conversion rate

The quantity in the denominator is simply the inverse of the fluorescence lifetime \( \tau_F \) as previously defined.

**Competitive Absorption Processes**

Two additional absorption mechanisms have been observed in dye lasers that detract from the lasing efficiency. These are categorized as excited singlet state absorption (ESSA) and triplet absorption. ESSA occurs when \( S_1 \) molecules absorb the pump or lasing photons and transition to higher singlet states. They then relax back to the \( S_1 \) level primarily by internal conversion (Figure 5). The photons that were absorbed are lost to the lasing process, although the fast relaxation time of internal conversion maintains the population of the \( S_1 \) level basically undisturbed. ESSA has been shown to be a significant consideration in most dyes, to the point of quenching the lasing under certain conditions (Refs 29, 30, 42).

Triplet absorption is depicted in Figure 6. This is essentially the same as ESSA but with the absorptions taking place in the triplet manifold. This will only be a factor when lasing parameters allow the \( T_1 \) population to build up significantly, such as during long-pulse
pumping and CW operation. In these cases, triplet absorption has also demonstrated the capability to quench lasing (Refs 17, 19).

**Quenching**

The $T_1$ population can be controlled with triplet quenching. This mechanism promotes nonradiative relaxation of the $T_1$ level to ground state $S_0$, increasing the $T_1+S_0$ intersystem crossing rate and therefore decreasing $\tau_p$. Many triplet quenchers such as molecular oxygen ($O_2$) also quench the $S_1$ level. In many situations the triplet quenching by $O_2$ more than offsets its singlet quenching effects, but other compounds have been found that selectively quench the triplet manifold without the detrimental singlet state quenching. Cyclooctatetraene has been demonstrated to be an efficient triplet quencher for Rhodamine.
6G (Ref 31:59). The rate of quenching is usually expressed per unit concentration of the quenching agent by the constants $k_{QT}$ and $k_{QS}$ (M$^{-1}$sec$^{-1}$).

Degradation Effects

The dyes that lase in the long-wavelength range from about 550 nm into the infrared region are characterized by long conjugated chains that are particularly susceptible to photodecomposition from the pumping source. Most of the xanthene dyes have demonstrated definite photodecomposition which becomes a particularly serious problem under flashlamp excitation (Refs 8, 15, 16, 25, 33, 34). The precise nature of the reaction products of KRS have not yet been identified, and no specific mechanism has been shown to be the cause of the associated laser output deterioration (Ref 33). Two likely mechanisms responsible for the loss of output power as decomposition increases are absorption of the pump energy and absorption of fluorescence by the reaction products (Refs 12, 18). A third possibility suggested by the latest results of a study in progress (Ref 33) is that the photodegradation effectively increases intersystem crossing to the triplet manifold.

The absorption coefficient $\alpha$ gives the amount of absorption at a particular wavelength that will occur per centimeter traveled by the photon beam in a specific medium. If the reaction products were absorbing lasing photons the absorption coefficient of the dye at the lasing wavelength would progressively increase as the dye deteriorated. The lasing efficiency would in turn decrease as more lasing photons were lost through absorption while oscillating in the cavity.

If the pump photons were being absorbed by the reaction products the pump efficiency $\eta$ would decrease. The pump efficiency is defined
here as follows:

\[ \eta = \frac{\text{theoretical threshold pump power}}{\text{actual pump power required to reach threshold}} \]  

(2.5)

The threshold pump power is the power required from the pump to overcome cavity losses and initiate lasing. Pump efficiency considers losses due to pump absorption by impurities in the medium, in addition to losses due to broad-spectrum pumping in which some of the pump photons cannot be absorbed due to improper wavelengths and other losses that prevent the total energy expended by the pump from being absorbed by the dye. A decrease in \( \eta \) would cause a corresponding increase in the actual threshold pump power.

Pulsed Dye Lasers

A simplified schematic for the dye lasing mechanism is shown in Figure 7. The \( E_1 \) level population is commonly considered negligible due to thermalization in the ground state electronic level. The thermalization rate is approximately \( 10^{12} \text{sec}^{-1} \); the rapidity of this

![Four-Level Laser Schematic](image)

**Figure 7**

Four-Level Laser Schematic
relaxation is due to an ethanol-dye collisional cross-section on the order of $10^{-14} \text{ cm}^2$. The lasing transition places the molecule into a state that is unpopulated and the molecule then relaxes to the ground level immediately so that a population inversion is effectively established whenever any molecules are in the $S_1$ level. This is a distinct advantage over systems in which the lasing transition ends in a significantly populated level, and allows lasing to commence with very low threshold pump powers (Ref 41:155). This feature, combined with quantum fluorescence efficiencies greater than 0.7 for the xanthene dyes, gives flashlamp-pumped xanthene dye lasers efficiencies generally from 0.1 to 1 percent; a CW laser pumped by another argon-ion laser has produced light-to-light efficiencies as high as 30 percent (Ref 21:3786).

The population at level 2 can transition to any of the many vibrational-rotational levels within the $S_0$ state. The broad fluorescence spectrum provides the capability to selectively lase over a wide range of frequencies. One of the most common methods of tuning dye lasers consists of replacing one of the cavity mirrors with a diffraction grating that can be rotated to reflect only the desired wavelength back through the cavity and preclude the remaining wavelengths from oscillating. The singlet-state absorption and fluorescence spectra of Rhodamine 6G in ethanol are reproduced in Figure 8 (Ref 43:188). These spectra are fairly representative of organic dyes. Since the peak of the emission spectrum is at a longer wavelength than the peak of the absorption spectrum, dye lasers can be tuned to lase in a strong emission region away from strong competitive absorption. The separation between the peaks of the absorption and fluorescence spectra is known
Singlet-state absorption and fluorescence spectra of rhodamine 6G obtained from measurements with a $10^{-4}$ molar ethanol solution of the dye.

Figure 8

Absorption and Fluorescence Spectra

as the Stokes Shift. The overlap of the spectra determines the high-frequency limit of lasing. Some amount of self-absorption will usually be present at the lasing wavelength and will affect the values of $T_p$ and $\phi$ observed (Ref 13).
III. Rate Equation Analysis

The absorption, emission, and relaxation processes that were presented in the preceding section are illustrated in Figure 9 for the first two singlet and triplet levels of an organic dye. The diagram demonstrates the interdependence of the various molecular energy level populations during lasing. The derivation of rate equations for this system provides a standard method of analysis that considers in detail the transient and dynamical behavior of the energy level and cavity photon populations. The literature has examples of many rate equation analyses of dye lasers that are essentially the same in concept yet use different mathematical techniques to describe lasing (Refs 1-4, 17, 21, 27, 37, 38). The essential mathematics involved in the development of the rate equations presented in this section parallel the approach presented by Siegman (Ref 36:411-431). The equations necessarily incorporate more concepts than those considered in the basic model used in this reference. These additional factors were handled with methods consistent with the literature, if available, or in the manner judged most suitable by the author. The results are intended for application to xanthene dye laser systems and therefore assumptions applicable only to specific dyes such as KRS are withheld in this section; assumptions limited to xanthene dyes are used only when great simplification results.

Dye Laser Model

The mechanisms summarized in Figure 9 appear to have the most probable impact on dye laser performance; the relative importance of
Figure 9

Excitation and Relaxation Paths in Laser Dyes
each depends on the chemistry of the particular dye that is being examined. For the great majority of dyes the upper level internal conversion rates are extremely fast, on the order of $10^{12}$ sec$^{-1}$, so the $S_2$ and $T_2$ populations should remain minimal and interactions from these and higher levels will be considered negligible (Ref 29:963). The $T_2 \leftrightarrow S_1$ intersystem crossing rate would also be negligible in comparison to the $T_2 \leftrightarrow T_1$ internal conversion rate. The rate equations are developed around single mode operation of a laser that is homogeneously broadened (Ref 35:650). The cavity photon population ($n$) is assumed to be spatially uniform (Ref 40:37A). Schlieren effects are not addressed.

To initially focus on the most likely effects of reaction product formation a simplified four-level model that takes into account both excited singlet state absorption and triplet absorption is used (Figure 10). By making the assumption that the $S_2$, $T_2$, and upper-level $S_1$ and $S_0$ populations are immediately depleted by internal conversion and thermalization and are therefore negligible, these levels may be explicitly left out of the equations. It should be noted that although these populations are not addressed by the rate equations, terms that consider ESSA and triplet absorption of fluorescence photons can be introduced into the cavity photon population equation. By handling the absorption in this manner the absorbed photons are lost to the photon population yet the $E_2$ and $E_3$ populations remain unaffected. Several recent publications (Refs 1-4) include the $T_2$ and upper-level $S_1$ levels to allow a more detailed examination based on a six-level system (the $S_2$ level remains deleted). Appendix A presents an equation set based on this six-level model that also includes ESSA. These equations would enable a more
Figure 10

Rate Equation Model
refined analysis, particularly in conjunction with non-stationary computer solutions.

Rate Equations

The rate equation for the cavity photon population is

\[ \frac{dn}{dt} = \frac{N_2n}{\tau_F(R)} + \frac{N_2}{\tau_F(R)} - \frac{N_2n}{\delta T_F(R)} - \frac{N_n}{\delta T_F(R)} - \frac{n}{\tau_C} \]  

(3.1)

where

- \( N_2 \) = \( E_2 \) energy level population density
- \( N_T \) = \( E_3 \) energy level population density
- \( \tau_F(R) \) = radiative fluorescence lifetime
- \( \tau_C \) = cavity photon lifetime
- \( \delta_T \) = ratio of the \( S_0^+S_1 \) extinction coefficient to the \( T_1^+T_2 \) extinction coefficient at the lasing wavelength
- \( \delta_S \) = ratio of the \( S_0^+S_1 \) extinction coefficient to the \( S_1^+S_2 \) extinction coefficient at the lasing wavelength

The first two terms on the right in Eq (3.1) account for stimulated and spontaneous emissions from level 2; the spontaneous emission occurs at the same rate as stimulated emission when the photon population is set equal to 1 (Ref 36:416). The third and fourth terms account for ESSA and triplet absorption losses respectively. These terms were adapted from a triplet absorption expression in Keller's presentation (Ref 17:411). The ratios \( N_2n/\tau_F(R) \) and \( N_Tn/\tau_F(R) \) give absorption rates assuming the Einstein B coefficients for the \( S_1^+S_2 \) and \( T_1^+T_2 \) transitions are equal to the Einstein B coefficient for the \( S_0^+S_1 \) transition. The \( \delta \) factors in the denominators adjust the rates to account for the
actual differences in the B coefficients. The final term reflects losses associated with cavity parameters such as mirror transmission and ground state absorption by the laser medium at the lasing wavelength. The absorption coefficient of the dye solution at the lasing wavelength will increase with dye degradation if the reaction products absorb fluorescence photons; this increase will decrease $\tau_C$. The first two terms in Eq (3.1) can be combined:

$$\frac{dn}{dt} = -\frac{N_2}{T_F(R)}(n+1) - \frac{N_2n}{\delta T_F(R)} - \frac{N_n}{\delta_{T_F(R)} + \frac{n}{\tau_C}} \quad (3.2)$$

The rate equation for $N_2$ is

$$\frac{dN_2}{dt} = W(t)n - \frac{N_2}{T_F(R)}(n+1) - N_2(k_{S_1T_1} + k_{S_1S_0} + k_{QS}Q_S) \quad (3.3)$$

where

$W(t)$ = pumping function
$n$ = quantum pumping efficiency
$k_{S_1T_0}$ = $S_1 \rightarrow T_1$ intersystem crossing rate constant
$k_{S_1S_0}$ = $S_1 \rightarrow S_0$ internal conversion rate constant
$k_{QS}$ = singlet quenching rate constant
$Q_S$ = concentration of singlet quencher

The pumping function can be varied to describe the characteristics of the particular method of pumping. Linear and Gaussian models have commonly been used for flashlamp pumping (Refs 4, 17, 21, 29, 37).

The remaining rate equation is for $N_T$: 

22
\[
\frac{dN_T}{dt} = N_2(k_{S_1T_1} + k_{QS}Q_S) - \frac{N_T}{\tau_{P(R)}} - N_T(k_{T_1S_0} + k_{QT}Q_T)
\] (3.4)

where

- \(\tau_{P(R)}\) = radiative phosphorescence lifetime
- \(k_{T_1S_0}\) = \(T_1\rightarrow S_0\) intersystem crossing rate constant
- \(k_{QT}\) = triplet quenching rate constant
- \(Q_T\) = concentration of triplet quencher

Here it is assumed that singlet quenching increases intersystem crossing to the triplet manifold (Ref 31:58), augmenting the \(N_T\) population; the possibility also exists that it returns the molecules directly to the ground state (Ref 17:412). Pumping directly to the triplet manifold is neglected.

A rate equation for \(N_0\) is not required as this population's only interaction on lasing in the model has been represented by \(W(t)\). As long as the \(N_0\) molecules are replenished during actual lasing under pulsed excitation, a generalized \(W(t)\) function can successfully be used to describe the pulse of pump photons generated and \(N_2\) will follow the pumping rate in both the actual laser and the model. If the \(N_0\) molecules are significantly depleted during the lasing due to entrapment in the triplet manifold then the reduced pump photon absorption by \(N_0\) will not be reflected adequately by these equations and a closed-population system of rate equations that include \(N_0\) should be used (see Appendix A). This requirement is not anticipated for the xanthene dyes due to their high fluorescence efficiencies which indicate small triplet build-up rates. Triplet quenching and short flashlamp pulse duration also minimize triplet populations.
The complete set of rate equations is then

\[
\frac{dn}{dt} = \frac{N_2}{\tau_{F(R)}}(n+1) - \frac{N_2 n}{\delta_{S_{TF(R)}}} - \frac{N_n}{\tau_{F(R)}} - \frac{n}{\tau_C} \quad (3.2)
\]

\[
\frac{dN_2}{dt} = W(t)n - \frac{N_2}{\tau_{F(R)}}(n+1) - N_2(k_{S_{1T1}} + k_{S_{1S0}} + k_{QS_{S}}) \quad (3.3)
\]

\[
\frac{dN_T}{dt} = N_2(k_{S_{1T1}} + k_{QS_{S}}) - \frac{N_T}{\tau_{F(R)}} - N_T(k_{S_{1S0}} + k_{QT_{0}}) \quad (3.4)
\]

**Steady-State Solutions**

In most cases of interest a steady-state approximation to the rate equations simplifies their application and yields results comparable to the more demanding numerical methods of solution (Ref 17). This adiabatic approximation has been shown to favorably compare with numerical solutions of the rate equations for both CW operation and flashlamp pumping with pulses as short as one nanosecond (Ref 29.963). The flashlamp pulse duration was 500 nanoseconds in Rabins' experiment; the steady-state approximation should therefore yield useful results. The resulting equations are

\[
\frac{N_2}{\tau_{F(R)}}(n+1) = \frac{N_2 n}{\delta_{S_{TF(R)}}} + \frac{N_n}{\tau_{F(R)}} + \frac{n}{\tau_C} \quad (3.5)
\]

\[
W(t)n = \frac{N_2}{\tau_{F(R)}}(n+1) + N_2(k_{S_{1T1}} + k_{S_{1S0}} + k_{QS_{S}}) \quad (3.6)
\]

\[
N_2(k_{S_{1T1}} + k_{QS_{S}}) = \frac{N_T}{\tau_{F(R)}} + N_T(k_{S_{1S0}} + k_{QT_{0}}) \quad (3.7)
\]
Equations (3.6) and (3.7) can be simplified by grouping their respective radiationless rate constants into one rate constant:

\[ k_2 = k_{S_1 T_1} + k_{S_1 S_0} + k_{Q S S} \]  

(3.8)

\[ k_{ST} = k_{S_1 T_1} + k_{Q S S} \]  

(3.9)

\[ k_T = k_{T_1 S_0} + k_{Q T T} \]  

(3.10)

Equations (3.6) and (3.7) then become:

\[ W(t)\eta = \frac{N_2}{\tau_F(R)} - \left( \eta + 1 \right) + N_2 k_2 \]  

(3.11)

\[ N_2 k_{ST} = \frac{N_T}{\tau_P(R)} + N_T k_T \]  

(3.12)

Recalling Eqs (2.1) and (2.2), Eqs (3.11) and (3.12) can alternately be expressed as

\[ W(t)\eta = \frac{N_2\eta}{\tau_F(R)} + N_2 \left( \frac{1}{\tau_F} \right) \]  

(3.13)

\[ N_2 k_{ST} = N_T \left( \frac{1}{\tau_P} \right) \]  

(3.14)

Replacing \( \tau_F \) in Eq (3.13) by \( \phi \tau_F(R) \), we can write

\[ W(t)\eta = \frac{N_2}{\tau_F(R)} \left( \eta \frac{1}{\phi} \right) \]  

(3.15)
Solving Eq (3.5) for $n$, we get

$$n = \frac{N_2}{N_2 \left[ \frac{1}{\delta_S} - 1 \right] + \frac{N_T}{\delta_T} + \frac{\tau_F(R)}{\tau_C}}$$

(3.16)

The above-threshold condition occurs when the denominator approaches zero; this gives the above-threshold population for $N_2$ ($N_{2,TH}$):

$$N_{2,TH} = \left[ \frac{N_T}{\delta_T} + \frac{\tau_F(R)}{\tau_C} \right] \left[ \frac{\delta_S}{\delta_S - 1} \right]$$

(3.17)

$N_2$ saturates at this value so that above threshold $N_2 = N_{2,TH}$ (Ref 36: 424).

Solving Eq (3.12) for $N_T$ and substituting this value into Eq (3.17) we obtain

$$N_{2,TH} = \tau_F(R) \left[ \frac{\delta_S \delta_T (k_T^{TP(R)+1})}{\delta_S \delta_T (k_T^{TP(R)+1}) - \delta_T (k_T^{TP(R)+1}) - k_{ST} \delta S_{TP(R)}} \right]$$

(3.18)

Assuming $k_T^{TP(R)} >> 1$, Eq (3.18) can be simplified:

$$N_{2,TH} = \tau_F(R) \left[ \frac{\delta_S \delta_T k_T}{\delta_S \delta_T k_T - \delta_T k_T - k_{ST} \delta_S} \right]$$

(3.19)

Above threshold, $n >> 1$ so that Eq (3.15) can be approximated by

$$W(t)n = \frac{N_{2,TH}(n)}{\tau_F(R)} \text{ or } n = \frac{\tau_F(R)}{\tau_{N_{2,TH}}}$$

(3.20)

The output power of the laser ($P_{laser}$) can now be expressed as
\[ P_{\text{laser}} = \frac{nh\nu_L}{T_M} \]  

(3.21)

where

\[ h = \text{Planck's constant (} 6.626 \times 10^{-34} \text{ joule-sec)} \]

\[ \nu_L = \text{frequency of the lasing photon} \]

\[ T_M = \text{cavity photon lifetime due to mirror transmission only} \]

The threshold pumping rate \( W_{p, \text{TH}} \) is defined by the following equation:

\[ W_{p, \text{TH}} = \frac{N_{2, \text{TH}}}{t_F^n} \]  

(3.22)

This equation is based on one developed by Siegman (Ref 36:424) with the addition, for the present analysis, of \( \eta \) to account for possible loss in pump efficiency due to reaction product absorption. As \( N_{2, \text{TH}} \) is an implicit function of \( \alpha \) due to its dependence on \( \tau_c \), \( W_{p, \text{TH}} \) will increase with either pump or lasing absorption by the reaction products.
IV. Analysis of the Kiton Red S Laser

The rate equations presented in Section III now provide a means to examine KRS under flashlamp pumping and to attempt explanation of the multiplier effect observed by Rabins et al. (Ref 25). To the maximum extent possible this analysis will employ data directly from their experiments to reproduce their conditions and then try to obtain similar results analytically.

Calculation of Pulse Energy

Eq (3.21) expresses the power output of a laser as a function of the cavity photon population:

\[ P_{\text{laser}} = \frac{nhv}{\tau_M} \quad (3.21) \]

The assumption that \( k_T \tau_T^{(R)} \gg 1 \) is valid for \( \tau_T^{(R)} > 10^{-4} \) sec and \( k_{1_S^0} > 10^6 \) sec\(^{-1} \). Both of these conditions are very probable (Ref 32) although no specific data for \( k_{1_S^0} \) and \( \tau_T^{(R)} \) were discovered in the literature for KRS or the other xanthene dyes. Allowing this assumption, we can combine Eqs (3.19) and (3.20) to arrive at the following expression for \( P_{\text{laser}} \):

\[ P_{\text{laser}} = \frac{h\nu L W(t) \eta_T \tau_C}{\tau_M} \left[ \frac{\delta_S \delta_T \kappa_T - \delta_T \kappa_S - \kappa_ST \delta_S}{\delta_S \delta_T \kappa_T} \right] \quad (4.1) \]

The expressions for \( \tau_C \) and \( \tau_M \) are dependent upon the laser cavity geometry and are derived in Appendix B.
\[ \tau_C = \left( \frac{cL}{L + L(n_D - 1)} \right) \left[ \alpha + \frac{1}{2L} \ln \left( \frac{1}{R_1 R_2} \right) \right]^{-1} \]  

(4.2)

\[ \tau_M = \left[ \frac{e}{2\xi + 2L(n_D - 1)} \ln \left( \frac{1}{R_1} \right) \right]^{-1} \]  

(4.3)

where

- \( c \) = speed of light in vacuum
- \( L \) = length of dye medium traversed by a photon during a single pass through the laser cavity
- \( \xi \) = distance between mirrors in the laser cavity
- \( n_D \) = index of refraction of the dye solution
- \( \alpha \) = absorption coefficient of the dye solution at the lasing wavelength
- \( R_1 \) = reflectivity of the frontal cavity mirror
- \( R_2 \) = reflectivity of the rear cavity mirror

As the dye degrades, fewer dye molecules are available to absorb the pump photons and lase. The term \( \Pi \) is introduced to account for this reduction in dye concentration and its resultant decrease in output power. The derivation of values for \( \Pi \) is given in Appendix C. Substituting Eq (4.3) into (4.1) and including \( \Pi \) in the equation we arrive at

\[ P_{\text{laser}} = \frac{\Pi h c W(t) \eta C}{2\xi + 2L(n_D - 1)} \ln \left( \frac{1}{R_1} \right) \left[ \frac{\delta_S \delta_T k_T - \delta_T k_T - k_{ST} \delta_S}{\delta_S \delta_T k_T} \right] \]  

(4.4)

Eq (4.4) gives the output power of the laser in terms of \( W(t) \). The function used for \( W(t) \) in this analysis is the Gaussian distribution pulse approximation (Refs 17, 37, 38):
\[ W(t) = W_{\text{max}} \exp \left\{ - \left[ \left( \frac{t}{T_1} \right) \left( \ln 2 \right)^{1/2} \right]^2 \right\} \]  \tag{4.5}

\( T_1 \) is the half-width at half-height of the pumping pulse. This pulse peaks at the value \( W_{\text{max}} \) (photons/sec) at time \( t=0 \).

To calculate the energy in a shot the pulse was divided into 1 nanosecond units and the output power determined for each increment. The resultant power curve was integrated over the duration of the pulse by computer using a trapezoidal area approximation. The computer program used to calculate the pulse energy for different shots as the variables changed is listed in Appendix D.

**Experimental Data**

The experiment conducted by Rabins consisted of six photolysis trials. In the first three trials the amount of dye degradation that occurred during successive flashlamp pulses and the related pulse energy were determined. The dye solution in Trial 1 was purged with argon to remove the oxygen from the solution. Trials 2 and 3 had \( 1.0 \times 10^{-3} \text{ M} \) and \( 2.1 \times 10^{-3} \text{ M} \) of oxygen in solution respectively (Ref 25:45). These measurements were repeated in Trials 4 through 6 with the addition of a filter to eliminate high-energy regions of the pump spectrum. The dye solution in Trial 4 was purged with argon; Trials 5 and 6 had \( 2.1 \times 10^{-3} \text{ M} \) oxygen in solution. The degradation and output energy data used in the computer analysis were taken from the graphs in Appendix E which give the results of the first three trials (Ref 25:30–35). The dye concentration \( c_D \) was determined from the linear fitting on the graph rather than the plotted points to provide ideal data that simplified the interpretation of the theoretical results. For the same reason the data
was recorded to three decimal places. Table I lists the values used for these trials in the analysis.

**Parameter Values**

The values used for the independent parameters of the pulse energy are listed in Table II. A distinction is made here between parameters and variables: the parameters are considered constant throughout a trial, while the variables change with shot number. The dependent parameters $\tau_p$, $\tau_p$, and $\phi$ also remain constant through the trial since they are functions of the independent parameters. The values of $\tau_p$, $\tau_p$, and $\phi$ that were calculated from the independent parameter values in Table II are listed in Table III.

Tables II and III illustrate the difficulty encountered in trying to locate consistent values for the KRS parameters. Many of these parameters are difficult to evaluate in the laboratory and most of the data found in the literature was for Rhodamine 6G and Rhodamine B. Fortunately the analysis of pumping and lasing radiation absorption allows considerable latitude in the selection of these values as the independent parameters affect the absolute power output rather than the output difference between shots. This is apparent when we examine the expression for the output power given by Eq (4.4):

$$P_{\text{laser}} = \frac{\pi n L c \omega(t) \eta c}{2 z + 2 L(n_D - 1)} \ln \left( \frac{1}{R_1} \right) \left[ \frac{\delta_S \delta_T k_T - \delta_T k_T - k_{ST} \delta_S}{\delta_S \delta_T k_T} \right]$$  \quad (4.4)

The variables $n$, $\eta$, and $\tau_c$ are the only factors that reflect changes in pump and lasing absorption; the independent parameters $\delta_S$, $\delta_T$, $k_T$, and $k_{ST}$ will all remain unaffected. Singlet quenching by a reaction product
### Table I

**Experimental Data**

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<th>Laser Half-Life (# Shots)</th>
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<td>450</td>
</tr>
<tr>
<td></td>
<td>2.000</td>
<td>2.1x$10^{-3}$</td>
<td>215</td>
<td>450</td>
</tr>
</tbody>
</table>

$L = 28.0$ cm  
$L = 25.0$ cm  
$R_1 = 0.99$  
$R_2 = 0.22$  
$n_D = 1.36$ (99.8% ethanol @ 20°C)  
(Ref 25:16, 18)

* from Figures E-2, E-4, and E-6
Table II

Independent Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value Used</th>
<th>Values Reported</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_F(R) ) (sec)</td>
<td>3.1 \times 10^{-9}</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( \tau_F(R) ) (sec)</td>
<td>10^{-3}</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( k_{S_1 S_0} ) (sec(^{-1}))</td>
<td>10(^7)</td>
<td>10(^7)-10(^8)</td>
<td></td>
</tr>
<tr>
<td>( k_{S_1 T_1} ) (sec(^{-1}))</td>
<td>2.5 \times 10(^7)</td>
<td>1.8 \times 10(^7) (1)</td>
<td>19:229</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 \times 10(^7) (1)</td>
<td>31:58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5-6.7 \times 10(^7) (3)</td>
<td>37:4732</td>
</tr>
<tr>
<td>( k_{T_1 S_0} ) (sec(^{-1}))</td>
<td>10(^7)</td>
<td>10(^7)</td>
<td>32</td>
</tr>
<tr>
<td>( k_{Q_S} ) (M(^{-1})sec(^{-1}))</td>
<td>3 \times 10(^9)</td>
<td>3 \times 10(^{10}) (1)</td>
<td>31:58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 \times 10(^{10}) (4)</td>
<td>17:415</td>
</tr>
<tr>
<td>( k_{Q_T} ) (M(^{-1})sec(^{-1}))</td>
<td>10(^7)</td>
<td>10(^7)</td>
<td>33:2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3 \times 10(^9) (1)</td>
<td>31:58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5 \times 10(^9) (4)</td>
<td>17:415</td>
</tr>
<tr>
<td>( \delta_T )</td>
<td>10</td>
<td>10 (1)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3)</td>
<td>37:4728</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4)</td>
<td>17</td>
</tr>
<tr>
<td>( \delta_S )</td>
<td>10</td>
<td>--- (5)</td>
<td>---</td>
</tr>
</tbody>
</table>

(1) - Rhodamine 6G
(2) - Rhodamine B
(3) - Xanthene dyes in general
(4) - No specific dye referred to when given
(5) - Based on the following values for ESSA and triplet absorption cross sections for Rhodamine 6G:

\[ \sigma_T = 0.35 \times 10^{-16} \text{ cm}^2 \] (Ref 19:229)

\[ \sigma_{S_1 \rightarrow S_2} = 0.4-0.6 \times 10^{-16} \text{ cm}^2 \] (Ref 29:966)
will change $k_{ST}$, however, so that the values chosen for the associated relaxation rates will have some effect on the magnitude of change between successive shots when analyzing this mechanism. The value for $W_{\text{max}}$ was arbitrarily selected for each set of independent parameter values to equate the pulse energy of the first shot calculated by the computer program to the experimental value. A change in output energy due to varying a parameter could be absorbed by increasing or decreasing $W_{\text{max}}$ to compensate for the change.

Table III

Dependent Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calculated Value</th>
<th>Values Reported</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_T$ (sec)</td>
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<td>2.8x10^{-9}</td>
<td>9:85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.1x10^{-9}</td>
<td>13:3892</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5x10^{-9}</td>
<td>37:4728</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10^{-6}</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2x10^{-6}</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4x10^{-7}</td>
<td>(1)*</td>
</tr>
<tr>
<td>$T_T$ (sec)</td>
<td>1.0x10^{-7}</td>
<td>0.83±0.02</td>
<td>37:4728</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9</td>
<td>37:4728</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9</td>
<td>(3)</td>
</tr>
</tbody>
</table>

(1) Rhodamine 6G

(3) Xanthene dyes in general

* with 20% oxygen content in atmosphere above dye
The figure given for $k_{QT}$ from the Battelle Laboratories interim report (Ref 33) in Table II was much lower than would be expected from the previously reported figures also listed. This value may explain the reduction of output power Rabins noted in Trials 2 and 3 (see Table I). If $k_{QS}$ remains on the order of $10^9-10^{10}$ sec$^{-1}$ oxygen would prove to be more detrimental due to singlet quenching than beneficial due to triplet quenching. The values used in the analysis for $k_{QS}$ and $k_{QT}$ duplicated the initial output energies listed in Table I to within 10 mj while holding $W_{max}$ constant.

**Trial Variables**

The computer analysis was designed to work with three variables: the solution pump absorption factor $\Pi$, the quantum pump efficiency $\eta$, and the absorption coefficient $\alpha$ of the dye solution at the lasing wavelength ($\lambda_L$).

**Pump Absorption Factor $\Pi$.** The pump absorption factor was designed to compensate for the reduction in the dye concentration as lasing progressed. This variable is also dependent on the amount of the reaction product present if the reaction product absorbs the pump photons. Appendix C tabulates in Tables C-I and C-II the values for $\Pi$ in both cases and shows how these figures were calculated. Figure 11 presents the graph of the pulse energies computed using $\Pi$ as the only variable and compares this with the experimental values. This case represents the reduction in output due only to the reduced concentration of the dye. This factor is included in all of the following evaluations, using the appropriate values from Tables C-I and C-II.

**Pump Efficiency $\eta$.** This term is used to account for the reduced probability of a pump photon being absorbed by a dye molecule as
competitive absorption by the reaction products increases. This variable has been isolated from the remaining factors in the total pump efficiency \( \eta \) as defined in Eq (2.5) for the purposes of the analysis. Appendix C explains the derivation of \( \eta' \). This variable replaces \( \eta \) in the equation developed for the analysis.

Figure 12 is a graph of the concentration of dye versus shot number based on visible spectra (Ref 25:46). This appears contradictory to Figure E-3 which was determined from infrared (IR) spectra. Figure 12 indicates that absorption of pump photons at 552 nm by the dye solution increases initially with shot number. This could be due to the formation of a transient reaction product that absorbs at this wavelength but does not interfere with the absorption at the IR band used to determine the concentration curve in Figure E-3. Due to the uncertainty surrounding reaction product formation and identity several ratios of dye degradation to reaction product formation were formulated. The values for both \( \eta' \) and \( \Pi \) corresponding to these ratios that were used to examine pump absorption are provided in Table C-II. The analytical results based on these values are presented in Figure 13.

Absorption Coefficient \( \alpha \). The variable \( \alpha \) changes as the dye degradation alters the absorption capability of the dye solution. Figures 14 and 15 are the absorption spectra of the Trial 1 dye solution before lasing (shot 0) and after 3000 shots (Ref 26:95). A distinct reduction in absorption of the dye around 460 nm is obvious; this peak corresponds to \( S_0 - S_1 \) absorption. If the reaction products were increasing the absorption coefficient for the 625 nm to 635 nm \( \lambda_L \) region, a decrease in \( I/I_0 \) for shot 3000 should be indicated within this band. The maximum decrease in \( I/I_0 \) that could be consistent with Figures 14 and 15 was
Figure 11
Pulse Energies due to Dye Concentration Reduction

Trial 1

- ○ - dye concentration reduction
- X - experimentally observed pulse energies

Shot Number
Figure 12

Dye Concentration Versus Shot Number (Visible Spectra)
Figure 13

Pulse Energies due to Pump Absorption

Trial 1

$C_A(D) - C_A(RP)$

- pump absorption: 1 m dye + 1 m RP
- pump absorption: 1 m dye + 3 m RP
- experimentally observed pulse energies
Figure 14

Trial 1, Shot 0 Visible Absorption Spectrum
Figure 15

Trial 1, Shot 3000 Visible Absorption Spectrum
estimated to be 0.004. Any variation in the spectra within this amount is most likely due to noise or equipment inaccuracy, but could be the effect of narrow-band absorption differences. Appendix C gives the derivation of absorption coefficients that would result in this amount of an increase in the solution absorption at $\lambda_L$. These absorption coefficients were applied to Trial 1 data, and the pulse energies predicted by computer analysis are plotted in Figure 16. The additional plot of theoretical pulse energies in Figure 16 corresponds to a second set of absorption coefficients that were derived so as to provide reduction in output energy consistent with the reduction observed experimentally (these absorption coefficients are listed in Appendix C). To obtain an output energy of 9 millijoules at shot 3000 an absorption coefficient of 1.0 cm$^{-1}$ is required. This corresponds to an $I/I_0$ value of 0.90; a reduction in transmittance of this magnitude is not indicated by the spectrum in Figure 15. This result suggests that although the absorption of lasing radiation could contribute significantly to the multiplier effect, it would not be solely responsible for the reduction in output energy.

Figure 17 compares the pulse energies calculated for several different rates of lasing and pump radiation absorption that occur simultaneously.

**Singlet Quenching by Reaction Products**

The final mechanism examined by which the reaction product interferes with laser performance was singlet quenching. From their current studies of KRS degradation, Dr. Schwerzel et al. have proposed the formation of reactive triplets from the upper excited singlet states (Ref 33). In addition to promoting degradation, this triplet formation could
Figure 16
Pulse Energies due to Lasing Radiation Absorption

Trial 1
Lasing radiation absorption:
- O - $1/I_o$ at shot 3000 = 0.995
- □ - $1/I_o$ at shot 3000 = 0.90
- X - experimentally observed pulse energies
Simultaneous pump and lasing absorption:

$$\sigma_{A}(D) = \sigma_{A}(R)$$

and

$$1 \, m \, dyes + 3 \, m \, RP$$

lasing radiation absorption for

- $\bullet$ at shot 3000 = 0.10
- $\square$ at shot 3000 = 0.50
- $\circ$ at shot 3000 = 1.00
- $\times$ experimentally observed pulse energies

Figure 17

Pulse Energies due to Combined Effects
Figure 18

Pulse Energies due to Singlet Quenching by the Reaction Product

$\text{k}_{QS(RP)} = 5 \times 10^{10} \text{ sec}^{-1}$
affect the lasing directly by increasing triplet absorption, and would populate the triplet manifold at the expense of the singlet population. The potential of this possibility was assessed by adding an additional term to the rate constants $k_{ST}$ and $k_2$:

$$k_{ST} = k_{S_1 T_1} + k_{QS} Q_S + k_{QS(RP)} Q_{S(RP)}$$

$$k_2 = k_{S_1 T_1} + k_{S_1 S_0} + k_{QS} Q_S + k_{QS(RP)} Q_{S(RP)}$$

where

$k_{QS(RP)} =$ rate constant for singlet quenching by the reaction product ($M^{-1} \text{sec}^{-1}$)

$Q_{S(RP)} =$ concentration of reaction product

The quantity $Q_{S(RP)}$ is the same as $c_{RP}$ introduced previously and has been relabeled to maintain the nomenclature adopted for the rate equations.

The computer program used in the previous analyses was modified to incorporate Eqs (4.6) and (4.7) and to calculate the pulse energy as the reaction product concentration increased; this program is included in Appendix D. Several runs were made for different values of $k_{QS}$, $k_{QT}$, and $k_{QS(RP)}$ assuming that 1 molecule of dye produced one molecule of reaction product. The results are presented in Figure 18. One of the more revealing results is the linear decrease in pulse power obtained, which would tend to disqualify this mechanism as the primary cause of the logarithmic multiplier effect. Figure 19 is a comparison of the results from all of the mechanisms tested.

To provide a check on the accuracy of the computer program, $W_{\text{max}}$ was estimated from the efficiency of the flashlamp and its spectral output (Appendix F); the value calculated was $1.6 \times 10^{24}$ photons/sec.
Trial 1

- singlet quenching
- pump absorption 1 m dye + 3 m RP
- lasing radiation absorption; I/I₀ at shot 3000 = 0.995
- experimentally observed pulse energies

Figure 19
Comparison of Results
The value required to set the Trial 1, shot 1 pulse energy equal to 250 mj in all of the preceding computer analyses was $3.54 \times 10^{24}$ (photons/sec). This agreement should verify that no major flaws exist in the modeling.
V. Discussion

The computer program that was developed in this study has predicted output energy trends consistent with the known characteristics of the KRS laser and without apparent conflicts quantitatively. Its flexibility has been demonstrated by the ease with which the several variables could be accommodated and singlet quenching by the reaction products could be examined. As the parameters specific to KRS are more accurately determined, the model will be able to effectively predict the relative efficiencies of different operating regimes.

The results from the preceding section show that none of the phenomena that were modeled could account for the magnitude of the multiplier effect using the data available. The most effective mechanism was absorption at the lasing wavelength by the reaction products. Although the half-life for absorption was approximately 2650 shots compared to the demonstrated half-life of 550 shots and was based on the most favorable interpretation of the absorption spectra, the results demonstrate how minute increases in absorption by the dye solution can cause large reductions in the output energy. Both the absorption coefficient corrections and the pump efficiency corrections resulted in non-linear decreases in energy, although they were not logarithmic. In comparison with the experimental data, the theoretical curves for these two phenomena differed enough from the experimental to indicate that another mechanism is responsible, that multiple mechanisms are at work simultaneously, or that the theoretical variable values derived to consider the lasing and pump absorption are inaccurate.

One of the more valuable insights offered by this analysis is the importance of the wavelength of lasing. The parameters $\delta_s$ and $\delta_t$ are
both functions of $\lambda_L$ and may vary several orders of magnitude over the excited state singlet and triplet absorption ranges. If triplet absorption is significant at one wavelength, it could be reduced by lasing at a wavelength with a smaller extinction coefficient. The prime consideration in selecting a lasing wavelength would be the absorption band of the reaction product, if this band overlaps the lasing region of the dye.
VI. Conclusions and Recommendations

Conclusions

The analytical model developed to represent the KRS dye laser provides an accurate method of predicting pulse energy decay and relative laser performance as a function of dominant relaxation mechanisms and competitive absorption processes. The generality incorporated into the model enables various potential reaction product effects to be evaluated by simple modification of the power output equation and its associated parameters.

The lack of precise data has prevented this analysis from conclusively identifying the primary phenomena responsible for the multiplier effect.

1. The most effective mechanism of those examined is reaction product absorption at the lasing wavelength.
2. Reaction product absorption at the pump wavelength is a probable factor but is very unlikely to be the primary cause.
3. An increase in intersystem crossing to the triplet manifold due to the formation of reaction products would not produce the logarithmic decrease in energy observed.
4. Mechanisms other than pump and lasing radiation absorption by the reaction products are likely to be responsible for the effect.

Recommendations

The following recommendations are proposed for further study:

1. Repeat the measurement of dye degradation and the corresponding pulse energy decay using KRS in a tunable dye laser. Perform
the experiment at several lasing wavelengths within the 630–670 nm region to determine the effect that operation at different wavelengths has on the efficiency and half-life of the laser.

2. Measure the absorption coefficient of the dye solution at the specific lasing wavelength. Accuracy to a minimum of three decimal places is essential. One possible method would be to measure the attenuation of a laser beam tuned to $\lambda_L$ with a radiometer; this would require a highly stable laser beam to insure the required degree of accuracy. Maximizing the distance traveled by the beam through the dye solution will increase the ratio $I/I_0$ to provide greater accuracy in calculating the absorption coefficient.

3. Measure the threshold pump power required for each shot in a trial. This quantity will increase if the reaction product is absorbing the pump photons. Any increase in the absorption coefficient found due to lasing absorption by the reaction product must be accounted for first as this also affects the threshold pump power.

4. Run several trials using specific triplet quenching agents such as cyclooctatetraene. If the multiplier effect still occurs this will confirm that it is not attributable to triplet absorption or the loss of molecules to the triplet manifold.
Bibliography


26. Rabins, John M. Laboratory notes, Book 1, for above experimental study. Dept. of Physics, Air Force Institute of Technology, Wright-Patterson AFB, Ohio: in care of Dr. E. Dorko.


32. Schwerzel, Robert E. With Battelle, Columbus Laboratory (telephone conversation) September 1980.


41. Weichel, H. and L. Pedrotti. Staff Notes, Laser Physics I, Department of Physics, Air Force Institute of Technology, Wright-Patterson AFB, Ohio.

Appendix A

Seven-Level Laser Rate Equations

Baczynski et al. (Refs 1-4) have developed a six-level model for dye lasers that incorporates the T₂ level population. The six-level system takes into account triplet absorption but neglects excited state singlet absorption and the possibility of an S₂ population. The equation set

![Diagram of Seven-Level Laser Model with labels for E₁, E₂, E₃, E₄, E₅, E₆, E₇, a₁₂, a₁₅, a₁₆, a₁₇, a₂₃, a₃₄, a₄₇, a₆₇]
presented in this appendix is based on the seven-level model shown in Figure A-1. These rate equations include an original one that describes the \( S_2 \) (\( E_1 \) level) population, and terms appropriate to the \( S_2 \) interactions depicted in Figure A-1 have been added to the six-level rate equations.

The seven-level equations are

\[
\frac{dn}{dt} = -\frac{n}{\tau_C} + \frac{n}{\tau_F(R)}(p_3 - p_2) - \frac{n}{\delta_{T} F(R)}(p_5 - p_6) - \frac{n}{\delta_{S} F(R)}(p_3 - p_7) \quad (A.1)
\]

\[
\frac{dp_1}{dt} = a_{12}p_2 + a_{15}p_5 + a_{16}p_6 + a_{17}p_7 - (a_{41} + a_{71})p_1 \quad (A.2)
\]

\[
\frac{dp_2}{dt} = a_{23}p_3 + \frac{n}{\tau_F(R)}(p_3 - p_2) - a_{12}p_2 \quad (A.3)
\]

\[
\frac{dp_3}{dt} = a_{34}p_4 + a_{36}p_6 - (a_{53} + a_{23})p_3 - \frac{n}{\tau_F(R)}(p_3 - p_2) - \frac{n}{\delta_{S} F(R)}(p_3 - p_7) \quad (A.4)
\]

\[
\frac{dp_4}{dt} = a_{41}p_1 + a_{47}p_7 - a_{34}p_4 \quad (A.5)
\]

\[
\frac{dp_5}{dt} = a_{53}p_3 - a_{15}p_5 + a_{56}p_6 - \frac{n}{\delta_{T} F(R)}(p_5 - p_6) \quad (A.6)
\]

\[
\frac{dp_6}{dt} = a_{67}p_7 - (a_{56} + a_{16} + a_{36})p_6 + \frac{n}{\delta_{T} F(R)}(p_5 - p_6) \quad (A.7)
\]

\[
\frac{dp_7}{dt} = a_{71}p_1 - (a_{47} + a_{67} + a_{17})p_7 + \frac{n}{\delta_{S} F(R)}(p_3 - p_7) \quad (A.8)
\]
\[ p_1 + p_2 + p_3 + p_4 + p_5 + p_6 + p_7 = 1 \]  (A.9)

The normalized population density \( p \) gives the probability of finding a molecule in a particular level, and Eq (A.9) requires that it can exist only in one of the levels shown in the model. The \( a_{1j} \) coefficients are the spontaneous radiation and radiationless transition rates combined; \( a_{41} \) and \( a_{71} \) are pumping parameters. The remaining terms are consistent with the notation in the main body of the thesis. The numbering of the levels is consistent with the six-level presentation and differs from the numbering system used in the figures in Section III.
Appendix B

Derivation of $\tau_C$ and $\tau_M$

Figure B-1 represents the cavity of the dye laser. The gain in intensity of a beam of photons after a round trip through the cavity is

$$I(t + \Delta t) = R_1 R_2 e^{2(\gamma - \alpha)l} I(t) = I(t) + \Delta I(\Delta t) \quad (B.1)$$

where

- $I(t + \Delta t)$ = resultant intensity after a round trip
- $\Delta t$ = round-trip duration
- $R_1, R_2$ = cavity mirror reflectivities
- $\gamma$ = laser gain coefficient
- $\alpha$ = dye absorption coefficient
- $l$ = length of the medium traversed by the beam
- $I(t)$ = original intensity of beam
- $\Delta I(\Delta t)$ = change in intensity of the beam

![Figure B-1](image-url)

**Figure B-1**

Laser Cavity Diagram
Dividing Eq (B.1) by \( I(t) \) and taking the logarithm of each side we get

\[
\ln \left[ 1 + \frac{\Delta I(\Delta t)}{I(t)} \right] = 2L \left[ \gamma - \alpha - \frac{1}{2L} \ln \left( \frac{1}{R_1 R_2} \right) \right] \tag{B.2}
\]

For \( \Delta I(\Delta t) \ll I(t) \) we can approximate the term \( \ln \left( 1 + \frac{\Delta I}{I} \right) \) by \( \frac{\Delta I}{I} \) to obtain

\[
\Delta I = 2L \left[ \gamma - \alpha - \frac{1}{2L} \ln \left( \frac{1}{R_1 R_2} \right) \right] I \tag{B.3}
\]

The round-trip time \( \Delta t \) is

\[
\Delta t = \frac{2n_D L}{c} + \frac{2(\ell - L)}{c} \tag{B.4}
\]

where

- \( n_D \) = index of refraction of the dye solution
- \( c \) = speed of light in vacuum
- \( \ell \) = distance separating the cavity mirrors

Dividing \( \Delta I \) by \( \Delta t \) and approximating \( \frac{\Delta I}{\Delta t} \) by \( \frac{dI}{dt} \) we obtain the following differential equation:

\[
\frac{dI}{dt} = \frac{cL}{\ell + L(n_D - 1)} \left[ \gamma - \alpha - \frac{1}{2L} \ln \left( \frac{1}{R_1 R_2} \right) \right] I \tag{B.5}
\]

The number of photons \( n \) in the beam is directly proportional to the beam intensity, so that the photon rate equation is

\[
\frac{dn}{dt} = \frac{cL}{\ell + L(n_D - 1)} \left[ \gamma - \alpha - \frac{1}{2L} \ln \left( \frac{1}{R_1 R_2} \right) \right] n \tag{B.6}
\]
Without pumping, the gain coefficient $\gamma$ vanishes and the cavity photons are lost at the rate

$$\frac{dn}{dt} = \frac{cL}{\lambda + L(n_d - 1)} \left[-\alpha - \frac{1}{2L} \ln \left(\frac{1}{R_1 R_2}\right)\right] n \quad (B.7)$$

Integrating Eq (B.7) results in the equation

$$n(t) = n_0 \exp \left(-\frac{t}{\tau_c}\right) \quad (B.8)$$

where the cavity photon lifetime $\tau_c$ is

$$\tau_c = \left\{ \frac{cL}{\lambda + L(n_d - 1)} \left[\alpha + \frac{1}{2L} \ln \left(\frac{1}{R_1 R_2}\right)\right] \right\}^{-1} \quad (B.9)$$

This lifetime characterizes photon losses from the cavity population due to cavity parameters such as the mirror transmissions and absorption by the medium. This can be stated mathematically:

$$\frac{1}{\tau_c} = \frac{1}{\tau_a} + \frac{1}{\tau_{M1}} + \frac{1}{\tau_{M2}} \quad (B.10)$$

where

$\tau_a$ = cavity photon lifetime due to absorption losses

$\tau_{M1}$ = cavity photon lifetime due to mirror 1 transmission

$\tau_{M2}$ = cavity photon lifetime due to mirror 2 transmission

Eq (B.9) can be factored accordingly:

$$\frac{1}{\tau_c} = \frac{cL}{\lambda + L(n_d - 1)} \left[\alpha + \frac{1}{2L} \ln \left(\frac{1}{R_1}\right) + \frac{1}{2L} \ln \left(\frac{1}{R_2}\right)\right] \quad (B.11)$$
Selecting mirror 1 as the transmissive frontal mirror, $\tau_{M1}$ becomes $\tau_M$:

$$
\tau_M = \left\{ \frac{c}{L + L(n_D - 1)} \left[ \frac{1}{2} \ln \left( \frac{1}{X_1} \right) \right] \right\}^{-1}
$$

(B.12)

The inverse of $\tau_M$ gives the rate at which the cavity photons enter into the output beam of the laser. This development has followed the derivation presented by Weichel and Pedrotti (Ref 41:139-141).
Appendix C
Derivation of Values for $\Pi$, $\eta'$, and $\alpha$

Pump Absorption Factor $\Pi$

As the dye degrades, less molecules of dye are available to absorb the pump radiation and lase. To account for the dye reduction the Beer-Lambert Law is used:

$$\frac{I}{I_0} = e^{-\varepsilon c d} \tag{C.1}$$

where

- $I$ = intensity of a beam after passing through an absorbing medium
- $I_0$ = original intensity of the beam
- $\varepsilon$ = molar extinction coefficient of the medium at the wavelength of the beam
- $c$ = concentration of the absorbing medium
- $d$ = distance traveled through the medium by the beam

The number of photons transmitted per second in a beam of light is directly proportional to the intensity of the beam. Eq (C.1) can then be written:

$$\frac{(p_o - p)}{p_o} = \exp \left( - \varepsilon_p c d \right) \tag{C.2}$$

where

- $(p_o - p)$ = number of pump photons transmitted per second through the medium
- $p$ = number of pump photons absorbed per second by the medium
\( \rho_0 \) = number of pump photons transmitted per second in the incident beam

\( \varepsilon_p \) = molar extinction coefficient for pump absorption

The energy output of the laser should be proportional to \( \rho \); the output of successive shots can then be adjusted by the factor \( \Pi \) to account for the loss of dye molecules:

\[
\Pi = \frac{\rho}{\rho_1}
\]  
(C.3)

In this equation \( \rho_1 \) is the number of photons absorbed per second by shot 1, and \( \rho \) is determined for each subsequent shot according to the concentration of dye remaining by using Eq (C.4):

\[
\rho = \rho_0 \left[ 1 - \exp \left( -\varepsilon_p c_D d \right) \right]
\]  
(C.4)

In this case \( d \) is the diameter of the dye cavity illuminated by the flashlamp, and is 0.6 cm (Ref 25:16). The variable \( \Pi \) can now be expressed as

\[
\Pi = \frac{1 - \exp \left( -\varepsilon_p c_D d \right)}{1 - \exp \left( -\varepsilon_p c_{D1} d \right)}
\]  
(C.5)

The term \( c_{D1} \) is the concentration of the dye at shot number 1. A typical cross section for pump absorption is \( 10^{-16} \text{ cm}^2 \); this corresponds to \( \varepsilon_p = 2.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \) (Ref 31:33-34). Johnson (Ref 16:70) recorded an initial output of 352 mj at \( 10^{-4} \text{ M} \) dye and 510 mj to 547 mj at \( 5 \times 10^{-4} \text{ M} \) dye. Using 350 mj and 530 mj as representative values at these concentrations and considering the rate of the \( \rho \) values for these shots to be equal to the ratio of the output energies, \( \varepsilon_p \) was calculated to be
1.79 \times 10^4 \, m^{-1} cm^{-1}. The values for \( \pi \) that were used in the computer analysis of lasing without competitive absorption by the reaction product are listed in Table C-I.

**Pump Efficiencies \( \eta \) and \( \eta^* \)**

The number of molecules of reaction product (RP) produced from one dye molecule and the capacity of the reaction product to absorb the pump energy is unknown, although Figure 12 indicates that pump absorption may exist to some extent. To examine competitive absorption by the reaction product its absorption cross section \( \sigma_{A(RP)} \) was considered to be equal to the dye absorption cross section \( \sigma_{A(D)} \). Since one mole of dye producing two moles of reaction product with \( \sigma_{A(D)} = \sigma_{A(RP)} \) is equivalent to one mole of dye producing one mole of reaction product with \( \sigma_{A(RP)} = 2\sigma_{A(D)} \), this assumption will still be useful in analyzing the possibility of \( \sigma_{A(D)} \neq \sigma_{A(RP)} \).

The total pump efficiency \( \eta \) is a product of several factors; the flashlamp bandwidth, pump photon loss due to mechanisms such as reflection and scattering, and competitive absorption by impurities in the medium. All but the latter factor can be considered constants that can be absorbed into the term \( W_{\max} \), as this pump parameter is arbitrarily varied to equate the output energy computed to the experimentally-determined energy of the first shot of the trial being examined. This allows \( \eta \) to be modified to express only the probability that a pump photon will be absorbed by a dye molecule:

\[
\eta^* = \frac{c_D}{\eta + c_{RP}}
\]  

(C.6)
In addition to introducing \( \eta^- \), \( \Pi \) must reflect the increase in the number of absorbing molecules in the medium as the reaction product replaces the dye. Eq (C.4) can be modified as follows:

\[
\rho = \rho_0 \left( 1 - \exp\left[ - \epsilon_p (c_D + c_{RP})d \right] \right) \tag{C.7}
\]

The expression for \( \Pi \) then becomes

\[
\Pi = \frac{1 - \exp\left[ - \epsilon_p (c_D + c_{RP})d \right]}{1 - \exp\left[ - \epsilon_{F:D} c_d d \right]} \tag{C.8}
\]

The value of \( \Pi \) will be 1.0 for 1 m dye + 1 m RP; for the formation of multiple molecules of reaction product per dye molecule \( \Pi \) will be greater than 1.0. The values of \( \eta^- \) and \( \Pi \) used in Trial 1 for several ratios of reaction product formation are listed in Table C-II.

**Absorption Coefficient \( \alpha \)**

To determine the magnitude of the effect that reaction product absorption at the lasing wavelength could have on the output energy of the laser, molar extinction coefficients \( \alpha \) at \( \lambda_L \) for the undegraded dye and the reaction product were calculated assuming that one molecule of dye degraded to produce one molecule of absorbing reaction product. The extinction coefficients were determined using the Beer-Lambert Law in Eq (C.1):

\[
\frac{I}{I_0} = e^{-\epsilon c d} \tag{C.1}
\]

Eq (C.1) was modified to consider absorption by both the dye and the reaction product:
\[
\frac{I}{I_0} = \exp\left[-(c_D c_D + c_{RP} c_{RP})d\right]
\]  
(C.9)

where

- \(c_D\) = concentration of the dye
- \(c_{RP}\) = concentration of the reaction product

In this application, \(d\) equals 0.1 cm (Ref 25:22). The absorption coefficient for a specific amount of dye and reaction product can then be obtained directly from the concentrations and the respective extinction coefficients:

\[
\alpha = c_D c_D + c_{RP} c_{RP}
\]  
(C.10)

For shot 0, Trial 1, \(I/I_0\) was taken to be 0.999, resulting in \(c_D = 51.68\) \(M^{-1}cm^{-1}\). The \(I/I_0\) value used for shot 3000 was 0.995, resulting in \(c_{RP} = 1.077 \times 10^3\) \(M^{-1}cm^{-1}\). This is equivalent to a cross section for the reaction product of \(1.79 \times 10^{-18}\) \(cm^2\), which is two orders of magnitude smaller than the \(10^{-16}\) \(cm^2\) values for the ESSA and triplet absorption cross sections. The values for \(\alpha\) used in the computer analysis that correspond to the above amount of transmittance are listed in Table C-III. Table C-IV lists the absorption coefficients that produce pulse decay comparable to the observed experimental decay. Table C-V tabulates the values used for \(\Pi\), \(n\), and \(\alpha\) that produced the pulse energies plotted in Figure 17.
Table C-I

Dye Concentration Corrections

<table>
<thead>
<tr>
<th>Trial</th>
<th>Shot Number</th>
<th>$c_D$ (x10^{-4} M)</th>
<th>Π</th>
</tr>
</thead>
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</tr>
<tr>
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<tr>
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<td>0.9786</td>
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<tr>
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<td>1500</td>
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<td>0.9667</td>
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<td>1.675</td>
<td>0.9539</td>
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<td>1.610</td>
<td>0.9402</td>
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<td>3000</td>
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</tr>
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$\epsilon_p = 1.79 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$

d = 0.6 cm
### Table C-II

**Competitive Pump Absorption Corrections**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Shot Number</th>
<th>$c_D$ ($\times 10^{-4}$ M)</th>
<th>$c_{RP}$ ($\times 10^{-4}$ M)</th>
<th>$\Pi$</th>
<th>$\eta'$</th>
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<td></td>
<td></td>
</tr>
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</tr>
<tr>
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<td>500</td>
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<td>0.9664</td>
</tr>
<tr>
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</tr>
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<td>1 molecule dye + 2 molecules RP</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>1 molecule dye + 3 molecules RP</td>
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$\epsilon_p = 1.79 \times 10^4$ M$^{-1}$ cm$^{-1}$

$d = 0.6$ cm
Table C-III
Absorption Coefficients:
$I/I_0$ at shot 3000 = 0.995

<table>
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<tr>
<th>Trial</th>
<th>Shot Number</th>
<th>$c_D$ (x10^{-6} M)</th>
<th>$c_D^c_D$ (cm^{-1})</th>
<th>$c_{RP}$ (x10^{-6} M)</th>
<th>$c_{RP}^c_{RP}$ (cm^{-1})</th>
<th>$a$ (cm^{-1})</th>
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</tr>
<tr>
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$\varepsilon_D = 51.68 \text{ M}^{-1}\text{cm}^{-1}$

$\varepsilon_{RP} = 1.077 \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1}$

$d = 0.1 \text{ cm}$
### Table C-IV

**Absorption Coefficients:**

$I/I_0$ at shot 3000 = 0.90

<table>
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<tr>
<th>Trial</th>
<th>Shot Number</th>
<th>$c_D$ (x10^{-4}M)</th>
<th>$c_D^c_D$ (cm^{-1})</th>
<th>$c_RP$ (x10^{-4}M)</th>
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$c_D = 51.68$ M^{-1}cm^{-1}

$c_RP = 2.544 \times 10^{14}$ M^{-1}cm^{-1}

$d = 0.1$ cm
Table C-V
Variable Values for Plots in Figure 17

<table>
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<th>Shot Number</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$\Pi$</th>
<th>$\eta$</th>
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$\epsilon_D = 51.68 \text{ M}^{-1} \text{cm}^{-1}$

$\epsilon_{RP} = 0.236 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$

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<th>$\Pi$</th>
<th>$\eta$</th>
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$\epsilon_D = 1.262 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$

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<th>$\Pi$</th>
<th>$\eta$</th>
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</table>

$\epsilon_D = 51.68 \text{ M}^{-1} \text{cm}^{-1}$

$\epsilon_{RP} = 2.544 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$
Appendix D

Computer Programs for Computing Pulse Energies

Two computer programs are used in the analysis. Program 1 is used with the variables $II$, $\eta^-$, and $\alpha$. Program 2 considers $\eta^-$ and $\alpha$ constant and maintains $II$ as a variable. This program requires the concentration of the reaction product to be input for each shot and is designed to calculate output energy for various rates of singlet quenching by the reaction product. A provision for triplet quenching in addition to the singlet quenching has been included. For the analysis results given in Section IV triplet quenching by the reaction product was negated by setting the triplet quenching rate constant $k_{QT(RP)} = 0$.

Three constants ($C1$, $C2$, and $C3$) must be input as data. These are specific to the laser geometry and are the same for both programs:

\begin{equation}
C1 = h\nu_L \left[ \frac{c}{2L + 2L(n_D - 1)} \right] \ln \left( \frac{1}{R_1} \right) \tag{D.1}
\end{equation}

\begin{equation}
C2 = \frac{cL}{L + L(n_D - 1)} \tag{D.2}
\end{equation}

\begin{equation}
C3 = \frac{1}{2L} \ln \left( \frac{1}{R_1 R_2} \right) \tag{D.3}
\end{equation}

The parameters and variables correspond as follows:

- $N$ = number of intervals desired to divide the pulse into for the purpose of the trapezoidal approximation
- $W_{\text{MAX}} = W_{\text{max}}$
- $\tau_{\text{FR}} = \tau_{F(R)}$
- $\tau_{\text{PR}} = \tau_{P(R)}$
- $\delta_S = \delta_S$

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DELT = $\delta_T$

KS1SO = $k_{S_1S_0}$

KS1T1 = $k_{S_1T_1}$

KT1SO = $k_{T_1S_0}$

QS = $Q_S$

QT = $Q_T$

KQS = $k_{QS}$

KQT = $k_{QT}$

ABS = $\alpha$

PCTG = $\Pi$

ETA = $\eta$

KQSRP = $k_{QS(RP)}$

KQTRP = $k_{QT(RP)}$

RP = concentration of reaction product (M)

---

Data Input (Program 1)

CARD 1: N, C1, C2, C3, WMAX

Note: WMAX is selected to adjust the shot 1 energy to the desired value.

CARD 2: TAUFR, TAUFR, DELS, DELT, KS1SO, KS1T1, KT1SO

The first two cards above establish the parameter values used in the computer analysis. Sets of cards must be assembled for the specific shots of each trial as follows:

CARD A: TRIAL, NR

Use any convenient tag number to designate each trial;
use a negative number if a plot is not desired. NR is
the number of shot data cards submitted in the trial
(excluding the final dummy card).

CARD B: QS, QT, KQS, KQT
Input the parameter values applicable to the trial; this
card inputs data for singlet and triplet quenching such
as when oxygen is in solution.

CARD C #: SHOTNR, ABS, PCTG, ETA
One card will be submitted for each shot examined during
the trial. These cards input the variable values for each
shot. The card following the last shot card is a dummy
card with a negative ABS value (I use 9999,-1,9999,9999).

If additional trials are to be analyzed, begin each new set with
Cards A and B (applicable to the conditions in the new trial) and
be sure to end each set with the dummy data card. After the final
data card in the last trial (this will be the dummy card) the final
card in the data stack will be 0,0 (see the comment on line 28 of
the program readout).

The computer printout will be self-explanatory.
PROGRAM 1

PROGRAM LASER (INPUT, OUTPUT)
REAL LK2, K03, K0T, KS150, KS151, KT150, K2, KT, KST, MP150
INTEGER SHOTNR
DIMENSION T(15), P(15,20), MP150(171)
DIMENSION E(20), SHOT(20), MP150(20), A2(20), TAUC(20), QP(20)
READ*, C, C, C, C, C

C MAX IS SELECTED TO EQUATE THE SHOT ENERGY TO EXPERIMENTAL VALUES
C THESE PARAMETERS ARE CONSIDERED TO BE CONSTANTS
READ*, TAUF, TAUFR, DELS, DELT, KS150, KS151, KT150
PRINT*, "ABS, ETA, PCTG"
PRINT*, "NEGATIVE TRIAL NOS WILL NOT BE GRAPHED"
PRINT*, "WMAX = "
PRINT*, "KS150 = "
PRINT*, "KS151 = "
PRINT*, "KT150 = "
READ*, TRIAL, NR
IF (TRIAL.EQ.1.) GO TO 5
READ*, KS, KS, KQ, DT
C KOS AND KOT WILL DEPEND UPON THE SPECIFIC QUENCHING AGENT
K2 = KOS*OS+KS151+KS150
KST = KOS*OS+KS151
KT = KOT+KT150
TAUF = 1/(1/TAUFR+K2)
PHI = TAUF/TAUFR
ASSUMP = KT/TAUFR
PRINT*, "TRIAL NO = "
PRINT*, "ASSUMP"

C THE ABOVE PRINTOUT WILL CONFIRM THE VALIDITY OF THE ASSUMPTION, LINE 15
PRINT*, "SINGLET QUENCHING RATE CONSTANT (KOS) = "
PRINT*, "TRIPLET QUENCHING RATE CONSTANT (KOT) = "
PRINT*, "SINGLET QUENCHER CONCENTRATION (OS) = "
PRINT*, "TRIPLET QUENCHER CONCENTRATION (OT) = "
PRINT*, "K2 = "
PRINT*, "KST = "
PRINT*, "KT = "
PRINT*, "TAUFR = "
PRINT*, "PHI = "
C THE ABOVE VALUES INDICATE WHETHER THE PARAMETER VALUES ARE REASONABLE
PRINT*, "CASE = C
READ*, SHOTNR, ABS, PCTG, ETA
IF (ABS.LT.0.5) GO TO 10
C PLACE DUMMY DATA CARD WITH NEGATIVE ABS AT END OF THE TRIALS DATA CARDS
ICASE=TCASE+1
SHOOT(ICASE)=SHOTHR
AC(ICASE)=ABS
PCTG(ICASE)=PCT
OPETICASE)=EPA
TAUC(ICASE)=1/IC* (ABS+G3)
NMTH(ICASE)=1/ET/TAUC(ICASE)/CA
E(ICASE)=0.
OT=5E-7/(N=1)

C THE FOLLOWING LOOP COMPUTES THE ENERGY IN THE PULSE
DO 11=1,N
   T(I)=-2.5E-7+(I-1)*OT
   WP=MAX*EXP(-N2*(TI)**2)/(5E-7*2)
   NPHOT(I)=WP*TAUC(ICASE)*ETA*C4*PCT
   P(I)=C*I*NPHOT(I)
   F#1.
   IF (I.EQ.1.3R.I.EQ.N)F#3.5
   CONTINUE

10 PRINT*,"FOR SHOT NO ",SHOTHTR," ENERGY = ",E(I CASE)
PRINT*," THRESHOLD JUMP FONER (NMTH) = ",NMTH(ICASE)
PRINT*," PHOTON CAVITY LIFETIME (TAUC) = ",TAUC(ICASE)
PRINT*," GO TO 2
10 PRINT*,"=
PRINT*,"=
PRINT*,"=
C THIS LOOP PRINTS OUT THE VARIABLE VALUES USED IN THE TRIAL
DO 99 ICASE=1,NR
   PRINT*," SHOT ",SHOOT(ICASE)," ABS ",AC(ICASE)," PCTG ",PCTG( ICASE)," ETA ",OPETICASE)
99 CONTINUE
PRINT*,=
PRINT*,=
PRINT*,=

IF (TRIAL.LE.1) GO TO 4
C THE ABOVE STATEMENT ALLOWS BYPASSING THE PLOT SEQUENCE
CAIL DRAW(SHOT,E,NMTH,P,T,-2,1,NR,3,-1)
PRINT*,=
PRINT*,=
PRINT*,=
GO TO 4
STOP
END
PROGRAM 2

PROGRAM LASER (INPUT, OUTPUT)
REAL LN2,KST,KOT,KST50,KST11,KST115,CZ,KST,KPHOT,KOSRP,KOTRP
INTEGER SHOTNR
DIMENSION T(110),P(110),KPHOT(110)
DIMENSION E(110),SHOT(110),KPHOT(110),P(110),RPC(110)
READ*,N,CS,KT,WHAX
C WHAX IS SELECTED TO EQUATE THE SHOT 1 ENERGY TO EXPERIMENTAL VALUES
READ*,TAUF,TAUPR,DEL5,DEL,KS150,KST11,KST115,A5,ETA
C THE ABOVE PARAMETERS ARE CONSIDERED TO BE CONSTANTS
TARC=1/CG=(A35+C3))
PRINT*, "ASSUMPTION KT*TAUPR=1"
PRINT*, "NEGATIVE TRIAL NO NOT BE GRAPHED"
PRINT*, "WHAX = " WHAX
PRINT*, "ABS = " A35, ETA = " ETA
PRINT*, "DELS = " DEL5, DEL = " DEL
PRINT*, "KST50 = " KST115, " KST11 = " KST11
PRINT*, "KST50 = " KST115
PRINT*, ""
PRINT*, ""
PRINT*, ""
PRINT*, ""
PRINT*, "LNA=ALOG(2.)
(1) CASE=0
ICASE=0
45 READ*,SHOTNR,PCTG,RP
IF (SHOTNR.EQ.1.) GO TO 10
C PLACE DUMMY DATA CARD WITH NEGATIVE SHOTNR AT END OF THE TRIALS DATA CARDS
KST50*OS*KST11+KST110*KOSRP*RP
KST=KST50*OS*KST11+KST110*KOSRP*RP
KT=KOT*KT*KST50
C4=DEL5*DEL*KT*DEL5*KT-KST50*DEL*KT
TAUP=1/(1/TAUPR+KT)
TAUFR=1/(1/TAUPR+KT)
PM=TAUP/TAUPR
ICASE=ICASE+1
SHOT(ICASE)=SHOTNR
RPC(ICASE)=RP
PCTG(ICASE)=PCTG
PHI(ICASE)=1./ETA/PHI/TARC*C4
INCASE=0,
OT=3.5E-7/(I-1)
C THE FOLLOWING LOOP COMPUTES THE ENERGY IN THE PULSE
DO 17=1,N
T(I)=2.5E-7*(I-1)*OT
\( \text{N} = \text{MAX} \times \text{EXP}(-\text{L} \times (\text{I} \text{E}^2) \times (\text{E}^{-7})) \)

\( \text{N}_{\text{MAX}} = \text{N} \times \text{EXP}(-\text{L} \times (\text{I} \text{E}^2) \times (\text{E}^{-7})) \)

\( \text{P}(\text{I}) = \text{C} \times \text{N}_{\text{MAX}} \times \text{I} \)

\( \text{E}(\text{CASE}) = \text{E}(\text{CASE}) + \text{F}(\text{I}) \times \text{O} \)

\[ \text{IF} \ (\text{I}, \text{EQ}, 1, \text{OR}, \text{I}, \text{EQ}, \text{M}) \text{F} = 0.5 \]

\( \text{E}(\text{CASE}) = \text{E}(\text{CASE}) + \text{F}(\text{I}) \times \text{O} \)

\[ \text{PRINT}^* \]. \text{"FOR SHOT NO ", \text{"SHOTNO:"}, \text{"ENERGY = ", \text{"E(\text{CASE})"}, \text{"THRESHOLD PUMP POWER (\text{NPTH}) = ", \text{"NPTH(\text{CASE})"}, \text{"K2 = ", \text{"K2"}, \text{"KST = ", \text{"KST"}, \text{"KT = ", \text{"KT"}, \text{"TAUP = ", \text{"TAUP"}, \text{"ASSUMP"}}}, \text{"CONTINUE"}} \]

\[ \text{PRINT}^* \]. \text{"CONTINUE"} \]

\[ \text{PRINT}^* \]. \text{"\

THE ABOVE PRINTOUT WILL CONFIRM THE VALIDITY OF THE ASSUMPTION:
\]

\[ \text{PRINT}^* \]. \text{"FLUORESCENCE LIFETIME (TAUF) = ", \text{"TAUF"}, \text{"PHOSPHORESCENCE LIFETIME (TAUP) = ", \text{"TAUP"}, \text{"QUANTUM FLUORESCENCE (PHI) = ", \text{"PHI"}} \]

\[ \text{PRINT}^* \]. \text{"GO TO 2"} \]

\[ \text{PRINT}^* \]. \text{"GO TO 2"} \]

\[ \text{PRINT}^* \]. \text{"GO TO 2"} \]

\[ \text{PRINT}^* \]. \text{"GO TO 2"} \]

\[ \text{PRINT}^* \]. \text{"GO TO 2"} \]

\[ \text{END} \]

\[ \text{STOP} \]
Appendix E

Dye Degradation and Pulse Decay Data

The following graphs have been reproduced from Figures 13-18, Ref 25:30-35.

Figure E-1
Dye Concentration Versus Shot Number
for Trial 1
Figure E-2
Laser Energy Versus Shot Number
for Trial 1
Figure E-3
Dye Concentration Versus Shot Number for Trial 2
Figure E-4
Laser Energy Versus Shot Number
for Trial 2
Figure E-5

Dye Concentration Versus Shot Number

for Trial 3
Figure E-6

Laser Energy Versus Shot Number
for Trial 3
Appendix F

Estimation of $W_{\text{max}}$

The flashlamp in the dye laser used to obtain the degradation data produced a spectrum comparable to a 25,000-degree Kelvin (°K) blackbody. The voltage (V) across the capacitor bank immediately before the laser was pulsed was 18 kilovolts (Ref 25:16, 21). The capacitance (C) was 0.329 microfarads (Ref 26:12). The total energy expended by the capacitor ($E_T$) into the flashlamp was then

$$E_T = \frac{1}{2} CV^2 = \frac{1}{2}(0.329 \times 10^{-6} \text{f})(18 \times 10^3 \text{V}) = 53.3 \text{ joules} \quad (F.1)$$

The efficiency of the flashlamp is assumed to be 20% (Ref 26:13); this puts the energy output of one flashlamp pulse at 10.7 joules. Figure 14 shows the visible spectrum for the dye solution. The 460-600 nm peak corresponds to the $S_0+S_1$ fundamental transition absorption. The part of the total energy in the pulse that is within this band can be determined using blackbody radiation tables (Ref 24:229-230). By interpolating the figures given for 24,000°K and 26,000°K blackbodies, we find that 0.03 or 3% of the total energy of the pulse lies within this band. As indicated by the spectrum, not all of this energy will actually be absorbed by the dye solution, but additional energy from the pulse will be absorbed in overtone transitions. Considering the gain from the overtone bands to offset the losses in the fundamental band, the energy absorbed by the medium is $(10.7 \text{ j})(0.03) = 0.32 \text{ joules}$. For the Gaussian distribution pumping function, we can estimate $W_{\text{max}}$ by solving the integral equation.
\[
\int_{-T}^{T} W_{\text{max}} \exp \left[ - \ln 2 \left( \frac{t^2}{T^2} \right) \right] \, dt = 0.32 \text{ joules}
\]  

(F.2)

Eq (F.2) can alternately be expressed by Eq (F.3):

\[
W_{\text{max}} = \frac{0.32 \text{ joules}}{2 \int_{0}^{T} \exp \left[ - \ln 2 \left( \frac{t^2}{T^2} \right) \right] \, dt}
\]  

(F.3)

To determine this integral the following approximation is made:

\[
\int_{0}^{T} \exp \left[ - \ln 2 \left( \frac{t^2}{T^2} \right) \right] \, dt \approx \int_{0}^{\infty} \exp \left[ - \ln 2 \left( \frac{t^2}{T^2} \right) \right] \, dt
\]  

(F.4)

The average duration of the flashlamp pulse was 500 nanoseconds (Ref 25:16). Setting \( T = 250 \times 10^{-9} \) sec, we can now solve Eq (F.3) using definite integral tables (Ref 7:426) to get \( W_{\text{max}} = 6 \times 10^5 \) joules/sec.

Selecting 540 nm as the average pump photon wavelength, \( W_{\text{max}} \) can be expressed in photons/sec:

\[
W_{\text{max}} = (6 \times 10^5 \text{j/sec}) \frac{540 \times 10^{-7} \text{ cm}}{(3 \times 10^{10} \text{ cm/sec})(6.63 \times 10^{-34} \text{j/sec})} = 1.6 \times 10^{24} \text{ photons/sec}
\]  

(F.5)
Vita

Alan J. Briding

attended the United States Air Force Academy. He graduated on 6 June, 1973 with a Bachelor of Civil Engineering and received his commission in the USAF. He went through undergraduate pilot training at Reese AFB, Texas and received his wings in September 1974. He then served as a C-141 aircraft commander and flight instructor in the 14th Military Airlift Squadron, 63rd Military Airlift Wing at Norton AFB, California until entering the School of Engineering, Air Force Institute of Technology, in June 1979.
**Title:** Analysis of Dye Degradation Effects on Output Energy of the Pulsed Organic Dye Laser

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**ABSTRACT:**
The dominant excitation and relaxation mechanisms found in dye molecules are discussed and then incorporated into a model for the xanthene dye laser. Rate equations for this model are presented which include terms that account for excited state singlet absorption and triplet absorption. The system of rate equations are solved using the steady-rate approximation to derive equations for the threshold pump power and output power of the laser.

The output power and threshold pump power equations are modified to include variables that allow the following effects of dye degradation to be examined:
dye concentration reduction, reaction product absorption of pump radiation, reaction product absorption of lasing radiation, and singlet quenching by the reaction products. Theoretical values based on available experimental data are derived for these variables. A computer program is used to integrate the output power of the laser over the duration of a flashlamp pulse to compute the pulse energy. The energy decay curves computed using the theoretical data are presented and compared to the experimental pulse energy decay.