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

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Summary

Dyes that lase in the long wavelength range from about 550 nm into the IR region are characterized by long conjugated chains that are particularly susceptible to photodecomposition. A model was developed, based on a four-level laser system, to provide a means of assessing the relative importance of various factors which contribute to a decrease in laser output power. The model, based on a steady state analysis of the laser rate equations, was applied to the case of Kiton Red S laser beam energy degradation. Parameters were estimated on the basis of experimental or reported values for Kiton Red S or for other similar xanthene dyes. It was discovered that, while a decrease in dye concentration and absorption of pump radiation by the decomposition product can make small contributions to laser beam energy decay, the most critical effect is the absorption of laser photons by the decomposition product of the dye.

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1. Introduction

The dyes that lase in the long wavelength range from about 550 nm into the IR region are characterized by long conjugated chains that are particularly susceptible to photodecomposition. One class of such compounds is the xanthene dyes. The family of xanthene dyes includes the rhodamine dyes which consist of compounds with a C(9) substituent that provides the variations in characteristics of the individual dyes [1, 2]. The xanthene dyes have demonstrated definite photodecomposition which becomes a serious problem under flashlamp excitation [3 - 6]. One of the xanthene dyes which is undergoing extensive examination with regard to its decomposition is sulforhodamine B which is commonly known as Kiton Red S (KRS). The precise nature of the reaction products of KRS has not yet been identified, and no specific mechanism has been shown to be the cause of the associated

laser output deterioration [4, 7]. Two likely mechanisms responsible for the loss of output power as decomposition increases are absorption of the pump energy and absorption of the fluorescence by the reaction products [5, 8]. A third possibility, suggested by the latest results of a study in progress [4, 7], is that the photodegradation effectively increases intersystem crossing to the triplet manifold. The present analysis of the KRS laser system seeks to assess the relative importance of these mechanisms toward the decrease in beam energy due to photodecomposition of xanthene dyes.

If the reaction products absorb lasing photons, the absorption coefficient of the dye at the lasing wavelength would progressively increase as the dye deteriorated. The lasing efficiency would decrease as more lasing photons were lost through absorption while oscillating in the cavity.

If the pump photons are absorbed by the reaction products, the pump efficiency η would decrease. The pump efficiency is defined here as follows:

$$\eta = \frac{\text{theoretical threshold pump power}}{\text{actual pump power required to reach threshold}} \tag{1}$$

The threshold pump power is the power required from the pump to overcome cavity losses and to initiate lasing. Pump efficiency can now include losses due to pump absorption by dye degradation products. A decrease in η would cause a corresponding increase in the actual threshold pump power which, in turn, would result in a decrease in the laser beam energy.

2. Rate equation analysis

In order to perform the analysis to take into account the relative importance of these effects, the system was modeled as a four-level laser. Rate equations were developed and applied to the system. Results were compared with experimental results obtained previously with KRS [3].

2.1. General equations

The model shown in Fig. 1 was chosen to study dye laser performance; the relative importance of each process 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, of the order of 10^{12} s^{-1}, so the S_2 and T_2 populations should remain minimal and interactions from these and higher levels were considered negligible [9]. The $T_2 \rightarrow S_1$ intersystem crossing rate is also negligible in comparison with the $T_2 \rightarrow T_1$ internal conversion rate. The rate equations were developed for the single-mode operation of a laser that is homogeneously broadened [10]. The cavity photon population η was assumed to be spatially uniform [11]. Schlieren effects were not addressed.

A simplified four-level model that takes into account both excited singlet state absorption and triplet absorption was used. By making the assumption that the S_2, T_2 and upper-level S_1 and S_0 populations are im-
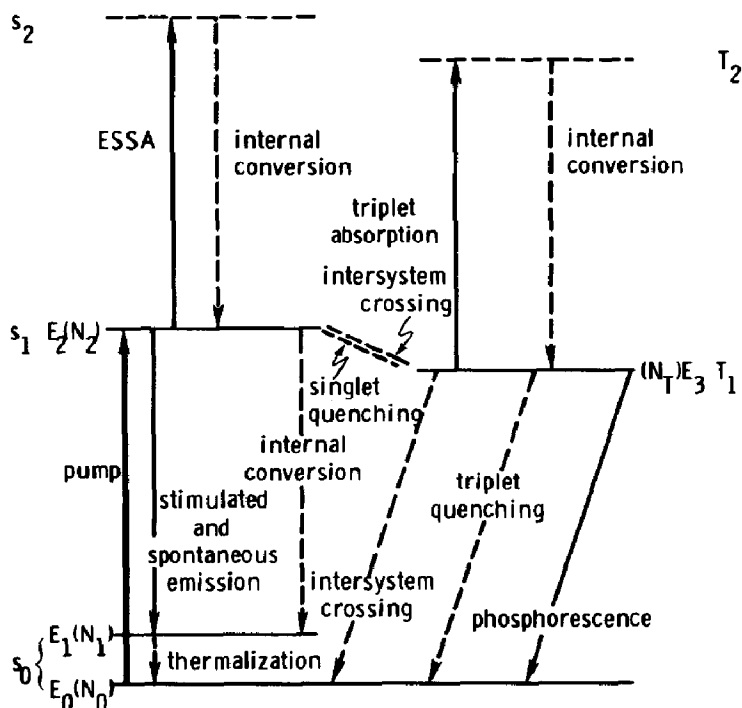
Fig. 1. Model of the lasing system used to derive the rate equations: E_i, ith energy level; N_i, population of the ith level.

mediately depleted by internal conversion and thermalization and are therefore negligible, then these levels may be explicitly left out of the equations. It should be noted that, although these populations are not addressed in the rate equations, terms that consider excited singlet state absorption (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 considered to be lost to the photon population, yet the E_2 and E_3 populations remain unaffected. Several recent publications [12 - 15] 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). These levels were not considered in the present analysis.

The derivation of the rate equations for the systems considered provides a method of analysis that considers in detail the transient and dynamic 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 [12 - 19]. The mathematical developments of the rate equations presented in this section parallel the approach presented by Siegman [20]. However, the equations developed in the present paper necessarily incorporate more concepts than those considered in the previous models. The results of the current paper are applied specifically to xanthene dye laser systems.

The complete set of rate equations is

$$\frac{dn}{dt} = \frac{N_2}{\tau_{F(R)}} (n + 1) - \frac{N_2 n}{\delta_S \tau_{F(R)}} - \frac{N_T n}{\delta_T \tau_{F(R)}} - \frac{n}{\tau_C} \qquad (2)$$

$$\frac{dN_2}{dt} = W(t)\eta - \frac{N_2}{\tau_{F(R)}} (n + 1) - N_2(k_{S_1 T_1} + k_{S_1 S_0} + k_{Q_S}[Q_S]) \qquad (3)$$

$$\frac{dN_T}{dt} = N_2(k_{S_1 T_1} + k_{Q_S}[Q_S]) - \frac{N_T}{\tau_{P(R)}} - N_T(k_{T_1 S_0} + k_{Q_T}[Q_T]) \qquad (4)$$

Equation (2) is the rate equation for the cavity photon population. The terms are defined as follows: N_2 is the E_2 energy level population density; N_T is the E_3 energy level population density; $\tau_{F(R)}$ is the radiative fluorescence lifetime; τ_C is the cavity photon lifetime; δ_T is the ratio of the $S_0 \rightarrow S_1$ extinction coefficient to the $T_1 \rightarrow T_2$ extinction coefficient at the lasing wavelength; δ_S is the ratio of the $S_0 \rightarrow S_1$ extinction coefficient to the $S_1 \rightarrow S_2$ extinction coefficient at the lasing wavelength.

The first term on the right-hand side of eqn. (2) accounts 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 unity [20]. The second and third terms account for ESSA and triplet absorption losses respectively. These terms were adapted from a triplet absorption expression in Keller's presentation [16]. The ratios $N_2 n/\tau_{F(R)}$ and $N_T n/\tau_{F(R)}$ give absorption rates assuming that the Einstein B coefficients for the $S_1 \rightarrow S_2$ and $T_1 \rightarrow T_2$ transitions are equal to the Einstein B coefficient for the $S_0 \rightarrow S_1$ transition. The δ 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. 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 τ_C.

Equation (3) is the rate equation for the change in the E_2 energy level population. The terms are defined as follows: $W(t)$ is the pumping function; η is the quantum pumping efficiency; $k_{S_1 T_1}$ is the $S_1 \rightarrow T_1$ intersystem crossing rate constant; $k_{S_1 S_0}$ is the $S_1 \rightarrow S_0$ internal conversion rate constant; k_{Q_S} is the singlet quenching rate constant; $[Q_S]$ is the concentration of singlet quencher.

The pumping function $W(t)$ can be varied to describe the characteristics of the particular method of pumping. Linear and gaussian models have commonly been used for flashlamp pumping [9, 15 - 17, 19].

Equation (4) is the rate equation for the change in the E_3 energy level population density. The terms are defined as follows: $\tau_{P(R)}$ is the radiative phosphorescence lifetime; $k_{T_1 S_0}$ is the $T_1 \rightarrow S_0$ intersystem crossing rate constant; k_{Q_T} is the triplet quenching rate constant; $[Q_T]$ is the concentration of triplet quencher. Here, it is assumed that singlet quenching increases intersystem crossing to the triplet manifold [21] and therefore augments the

N_T population; the possibility also exists that it returns the molecules directly to the ground state [16]. Pumping directly to the triplet manifold is neglected.

A rate equation for N_0, the E_0 population density, is not required. 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. If N_0 is significantly depleted during lasing, as a result of 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. This requirement is not anticipated for the xanthene dyes because of their high fluorescence efficiencies which indicate small triplet build-up rates. Triplet quenching and short flashlamp pulse duration also minimize triplet populations.

2.2. Steady state analysis

In most cases of interest, a steady state approximation to the rate equations simplifies their application and yields results comparable with those of the more demanding numerical methods of solution [16]. This adiabatic approximation has been shown to compare favorably with numerical solutions of the rate equations for both continuous-wave operation and for flashlamp pumping even with pulses as short as 1 ns [9]. In the present work the analysis dealt with flashlamp pulse durations of 500 ns; the steady state approximation should therefore yield meaningful results. By use of the groupings

$$k_2 = k_{S_1 T_1} + k_{S_1 S_0} + k_{Q_S}[Q_S] \tag{5}$$

$$k_{ST} = k_{S_1 T_1} + k_{Q_S}[Q_S] \tag{6}$$

$$k_T = k_{T_1 S_0} + k_{Q_T}[Q_T] \tag{7}$$

the steady state equations based on eqns. (2) - (4) were derived. They are

$$\frac{N_2}{\tau_{F(R)}}(n+1) = \frac{N_2 n}{\delta_S \tau_{F(R)}} + \frac{N_T n}{\delta_S \tau_{F(R)}} + \frac{n}{\tau_C} \tag{8}$$

$$W(t)\eta = \frac{N_2}{\tau_{F(R)}}(n+1) + N_2 k_2 \tag{9}$$

$$N_2 k_{ST} = \frac{N_T}{\tau_{P(R)}} + N_T k_T \tag{10}$$

Recalling that the fluorescence lifetime τ_F and the phosphorescence lifetime τ_P are often defined to include radiative and non-radiative contributions as

$$\frac{1}{\tau_F} = \frac{1}{\tau_{F(R)}} + \frac{1}{\tau_{F(NR)}} \tag{11}$$

and

$$\frac{1}{\tau_P} = \frac{1}{\tau_{P(R)}} + \frac{1}{\tau_{P(NR)}} \tag{12}$$

then eqns. (9) and (10) are written as

$$W(t)\eta = \frac{N_2 n}{\tau_{F(R)}} + N_2 \frac{1}{\tau_F} \tag{13}$$

$$N_2 k_{ST} = N_T \frac{1}{\tau_P} \tag{14}$$

Defining the quantum efficiency Φ of fluorescence as the ratio of radiative to non-radiative transition lifetimes [21] and considering the relaxation routes shown in Fig. 1, the formula for Φ is written as

$$\Phi = \frac{1/\tau_{F(R)}}{1/\tau_{F(R)} + k_{S_1 T_1} + k_{S_1 S_o}} \tag{15}$$

Replacing τ_F in eqn. (13) by $\tau_{F(R)}$ leads to

$$W(t)\eta = \frac{N_2}{\tau_{F(R)}} \left(n + \frac{1}{\Phi} \right) \tag{16}$$

Solving eqn. (8) for n,

$$n = N_2 \left\{ N_2 \left(\frac{1}{\delta_S} - 1 \right) + \frac{N_T}{\delta_T} + \frac{\tau_{F(R)}}{\tau_C} \right\}^{-1} \tag{17}$$

2.3. Above-threshold analysis

The above-threshold condition occurs when the term in braces in eqn. (17) approaches zero. This condition gives the above-threshold E_2 energy level population density $N_{2,Th}$:

$$N_{2,Th} = \left(\frac{N_T}{\delta_T} + \frac{\tau_{F(R)}}{\tau_C} \right) \frac{\delta_S}{\delta_S - 1} \tag{18}$$

N_2 saturates at this value, so that above the threshold $N_2 = N_{2,Th}$ [20].

If eqn. (10) is solved for N_T, this value can be substituted into eqn. (18). With the simplifying assumption that $k_T \tau_{P(R)} \gg 1$, eqn. (18) is written as

$$N_{2,Th} = \frac{\tau_{F(R)}}{\tau_C} \frac{\delta_S \delta_T k_T}{\delta_S \delta_T k_T - \delta_T k_T - k_{ST} \delta_S} \tag{19}$$

Above the threshold, $n \gg 1$ so that eqn. (16) can be approximated by

$$W(t)\eta \approx \frac{N_{2,Th}}{\tau_{F(R)}} n \tag{20}$$

and solving for n

$$n \approx W(t)\eta \frac{\tau_{F(R)}}{N_{2,Th}} \tag{21}$$

The output power P_{laser} of the laser can be expressed as the energy per unit time or

$$P_{\text{laser}} = \frac{nh\nu_{\text{L}}}{\tau_{\text{M}}} \qquad (22)$$

where h is Planck's constant, ν_{L} is the frequency of the lasing photon and τ_{M} is the cavity photon lifetime due to mirror transmission only.

Combining eqns. (19) and (21) and then substituting the result of this operation into eqn. (22) leads to

$$P_{\text{laser}} = \frac{h\nu_{\text{L}}W(t)\eta\tau_{\text{C}}}{\tau_{\text{M}}} \frac{\delta_{\text{S}}\delta_{\text{T}}k_{\text{T}} - \delta_{\text{T}}k_{\text{T}} - k_{\text{ST}}\delta_{\text{S}}}{\delta_{\text{S}}\delta_{\text{T}}k_{\text{T}}} \qquad (23)$$

The threshold pumping rate $W_{\text{p,Th}}$ is defined by the following equation

$$W_{\text{p,Th}} = \frac{N_{2,\text{Th}}}{\tau_{\text{F}}\eta} \qquad (24)$$

This equation is based on an equation developed by Siegman [20] with the addition of η to account for a possible loss in pump efficiency due to reaction product absorption.

3. Analysis of the Kiton Red S laser

3.1. Mathematical analysis

The rate equations presented in Section 2 will be used to provide a means to examine a characteristic xanthene dye (KRS) under flashlamp pumping in order to correlate the experimental data obtained previously [3, 22] and to assess the relative effects of the processes incorporated into the model on the output energy of the laser beam.

The expressions for τ_{C} and τ_{M} in eqn. (23) are dependent on the laser cavity geometry. For the laser of interest to us, the following expressions have been developed [23 - 25]:

$$\tau_{\text{C}} = \left[\frac{cL}{l + L(n_{\text{D}} - 1)} \left\{ \alpha + \frac{1}{2L} \ln\left(\frac{1}{R_1 R_2} \right) \right\} \right]^{-1} \qquad (25)$$

$$\tau_{\text{M}} = \left\{ \frac{c}{2l + 2L(n_{\text{D}} - 1)} \ln\left(\frac{1}{R_1} \right) \right\}^{-1} \qquad (26)$$

where c is the speed of light in vacuum, L is the length of dye medium traversed by a photon during a single pass through the laser cavity (this corresponds to the length of the cell containing the dye solution), l is the distance between the mirrors in the laser cavity, n_{D} is the index of refraction of the dye solution, α is the absorption coefficient of the dye solution at the lasing wavelength λ_{L} and R_1 and R_2 are the reflectivities of the cavity mirrors.

As the dye degrades, fewer dye molecules are available to absorb the pump photons and to lase. A term Π is introduced to account for this reduction in dye concentration and its resultant decrease in the output power of the laser. The evaluation of Π is given in Appendix A.

Finally, substituting eqn. (26) and Π into eqn. (23) leads to

$$P_{laser} = \frac{\Pi h\nu_L c W(t)\eta\tau_C}{2l + 2L(n_D - 1)} \ln\left(\frac{1}{R_1}\right) \frac{\delta_S\delta_T k_T - \delta_T k_T - k_{ST}\delta_S}{\delta_S\delta_T k_T} \tag{27}$$

Equation (27) gives the output power of the laser in terms of $W(t)$, the pumping function. The function used in this analysis is the gaussian distribution pulse approximation [16, 19, 26]:

$$W(t) = W_{max} \exp\left[-\left\{\frac{t}{T_1}(\ln 2)^{1/2}\right\}^2\right] \tag{28}$$

T_1 is the halfwidth at half-height of the pumping pulse. This pulse peaks at the value W_{max} (photons s^{-1}) at time $t = 0$.

To calculate the energy in a shot, the pulse was divided into 1 ns units and the output power P_{laser} was determined for each increment. The resultant power curve was integrated over the duration of the pulse using numerical integration techniques [23].

In eqn. (27) the variables Π, η and τ_C are the only factors that reflect changes in pump and lasing absorption; the independent parameters δ_S, δ_T, k_T and k_{ST} will all remain unaffected. Singlet quenching by a reaction product will change k_{ST}, however, so that values chosen for the associated relaxation rates will have some effect on the magnitude of the change between successive shots when analyzing this mechanism. The value for W_{max} in eqn. (28) was arbitrarily selected for each set of independent parameter values to equate the calculated pulse energy of the first shot to the experimental value. A change in calculated output energy due to varying a parameter was absorbed by increasing or decreasing W_{max} to compensate for the change.

3.2. Experimental data

The data which were used to determine the adequacy of the model are given in Table 1 [3, 22]. The values used for the independent parameters of the pulse energy are listed in Table 2. A distinction is made between parameters and variables: the parameters are considered to be constant throughout an experiment, while the variables change with shot number. The dependent parameters τ_F, τ_P and Φ also remain constant throughout the experiment since they are functions of the independent parameters. The values of τ_F, τ_P and Φ that were calculated from the independent parameter values in Table 2 are listed in Table 3.

The values reported in Tables 2 and 3 are either experimentally determined values for KRS or values considered to be reasonable on the basis of corresponding values for other xanthene dyes. The value given for k_{Q_T} [7] was much lower than would be expected from the previously reported values

TABLE 1

Experimental data[a]

Trial	Shot	Dye concentration C_D ($\times 10^{-4}$ M)	Shot 1 energy (mJ)	Laser half-life (shots)
1	1	1.935	250	550
	500	1.870		
	1000	1.805		
	1500	1.740		
	2000	1.675		
	2500	1.610		
	3000	1.545		

L = 28.0 cm; l = 25.0 cm; R_1 = 0.99; R_2 = 0.22; n_D = 1.36 (99.8% ethanol at 20 °C).
[a]From refs. 3 and 22.

TABLE 2

Independent parameter values

Parameter	Value used	Value reported	Reference
$\tau_{F(R)}$ (s)	3.1×10^{-9}	—	—
$\tau_{P(R)}$ (s)	10^{-3}	—	—
$k_{S_1 S_0}$ (s^{-1})	10^7	$10^7 - 10^8$	
$k_{S_1 T_1}$ (s^{-1})	2.5×10^7	1.8×10^7 [a]	[27]
		2×10^7 [b]	[21]
		$(1.5 - 6.7) \times 10^7$ [c]	[19]
$k_{T_1 S_0}$ (s^{-1})	10^7	10^7	[28]
k_{Q_S} (M^{-1} s^{-1})	3×10^9	3×10^{10} [a]	[21]
		2×10^{10} [d]	[16]
k_{Q_T} (M^{-1} s^{-1})	10^7	10^7	[7]
		3.3×10^9 [a]	[21]
		2.5×10^9 [d]	[16]
δ_T	10	$10^{a,c,d}$	[17]
			[19]
			[16]
δ_S	10^e	—	—

[a]Rhodamine 6G.
[b]Rhodamine B.
[c]Xanthene dyes in general.
[d]No specific dye referred to when given.
[e]Based on the following values for ESSA and triplet absorption cross sections for rhodamine 6G: $\sigma_T = 0.35 \times 10^{-16}$ cm^2 [23]; $\sigma_{S_1} \to S_2 = (0.4 - 0.6) \times 10^{-16}$ cm^2 [9].

also listed. It is an experimentally determined value for KRS and is felt to be accurate.

TABLE 3

Dependent parameter values

Parameter	Calculated value	Values reported	Reference
τ_F (s)	2.8×10^{-9}	2.8×10^{-9}	[1]
		3.1×10^{-9}	[2]
		5×10^{-9} [a]	[19]
τ_P (s)	1.0×10^{-7}	10^{-6} [a]	[29]
		2×10^{-6} [b]	[21]
		1.4×10^{-7} [b,c]	[21]
	0.90	0.99	[2]
		0.83 ± 0.02	[1]
		0.9 [a]	[19]

[a]Xanthene dyes in general.
[b]Rhodamine 6G.
[c]With 20% oxygen content in the atmosphere above the dye.

3.3. Calculations

The computer analysis was designed to work with the three variables Π, η' and α.

3.3.1. Pump absorption factor Π

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. Figure 2 presents the graph of the pulse energies computed using Π as the only variable and compares the result with the experimental values for trial 1 (Table 1). The calculation represents the reduction in laser output due only to the reduced concentration of the dye. This factor is included in all the following evaluations.

3.3.2. Pump efficiency η'

The pump efficiency η' is used to account for the reduced probability that a pump photon is 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 η, as defined in eqn. (1), for the purposes of the analysis. Appendix A explains the derivation of η'. η' replaces η in the equation developed for the analysis. Because of the uncertainty surrounding reaction product formation and identity, several ratios of dye degradation to reaction product formation were considered. The analytical results based on these values are presented in Fig. 3.

3.3.3. Absorption coefficient α

To determine the magnitude of the effect that reaction product absorption at the lasing wavelength could have on the output energy of the laser,
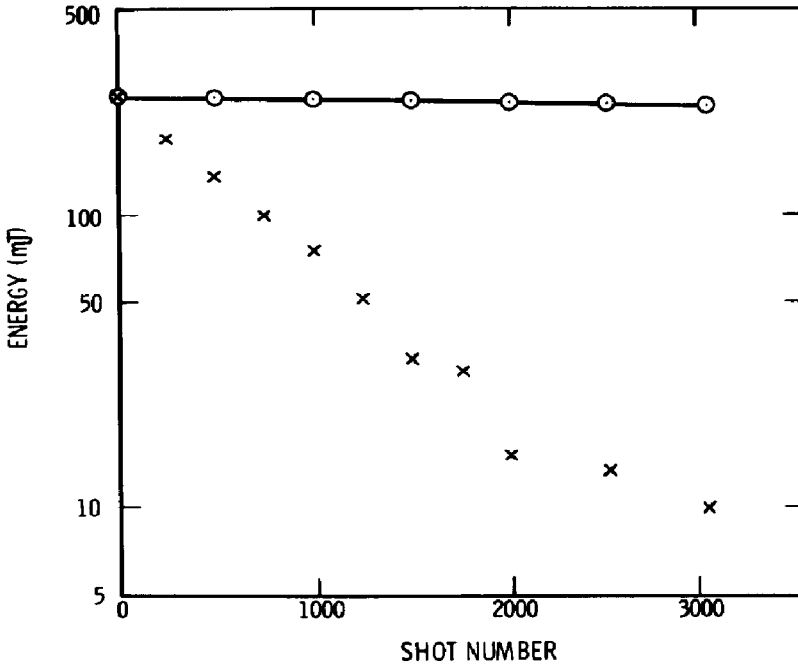
Fig. 2. Laser beam energies experimentally observed (×) and calculated assuming that the output depends only on the actual KRS concentration (⊙).
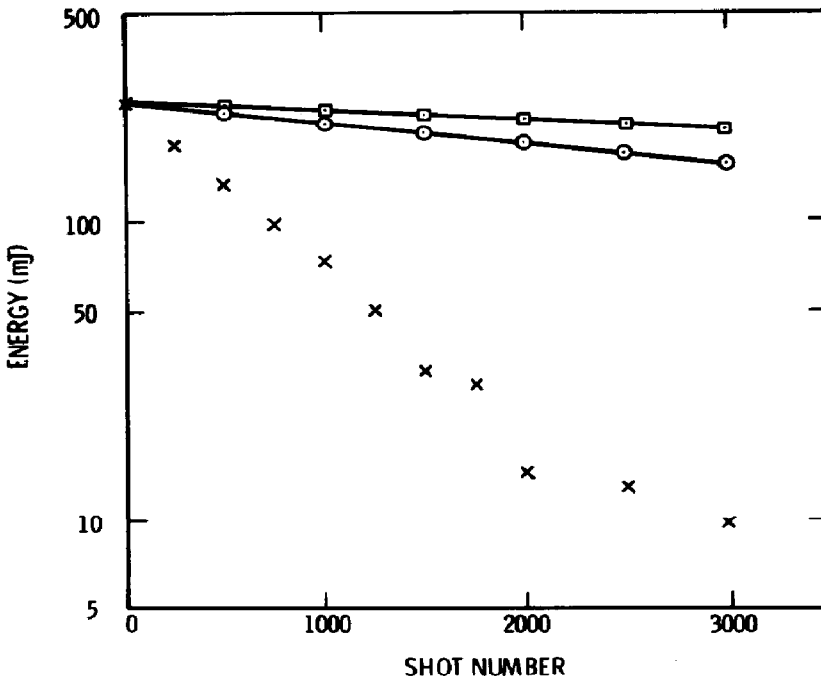

Fig. 3. Laser beam energies experimentally observed (×) and calculated assuming that the output depends only on the absorption of pump photons due to the reaction product and that $\sigma_{A(D)} = \sigma_{A(RP)}$ where $\sigma_{A(D)}$ and $\sigma_{A(RP)}$ are the absorption cross sections for the dye (D) and the reaction product (RP) respectively (□, D → RP; ⊙, D → 3RP).

molar extinction coefficients at λ_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. For KRS in ethanol, λ_L is 620 nm [30, 31]. Absorption measurements on samples of degraded dye indicate that there is an increase in absorption of the degraded dye in this spectral region. The major band at 460 nm becomes slightly broadened at its base and gradually a very weak peak appears at approximately 620 nm. This absorption has not been determined quantitatively, however.

The extinction coefficients were calculated using the Beer–Lambert law [32]. The absorption coefficient α for a specific concentration of dye (C_D) and reaction product (C_{RP}) can then be obtained directly from the concentrations and the respective molar extinction coefficients ϵ_D and ϵ_{RP}:

$$\alpha = \epsilon_D C_D + \epsilon_{RP} C_{RP} \tag{29}$$

and

$$\frac{I}{I_0} = \exp(-\alpha d) \tag{30}$$

Prior to lasing, I/I_0 at 620 nm was taken to be 0.999, and the concentration C_{RP} was taken to be zero. The calculation gave $\epsilon_D = 51.68$ M^{-1} cm^{-1}. Various values for I/I_0 were assumed for the case after the onset of lasing and values for α were calculated in this manner.

3.3.4. Final calculated results for Kiton Red S in ethanol

Table 4 gives a list of the values used for Π, η' and α that produced the pulse energies plotted in Fig. 4.

4. Discussion of results

The results of the application of the model to KRS show that a multiplier effect is operating, i.e. from Fig. 2 it is apparent that the laser pulse energy decay cannot be accounted for by a simple decrease in dye concentration due to dye decomposition. Figure 3 indicates that pump absorption by the reaction products accounts for a small, although not negligible, amount of the total decay. Finally, Fig. 4 indicates that the absorption of laser radiation by the reaction products, whether transient or long lived, plays a major role in the decay.

The absorptive materials can be stable reaction products or transient species. For example, triplet–triplet absorption has been shown to be a maximum in the region around 620 nm [33]. If the reaction product catalyzes KRS triplet formation, then triplet–triplet absorption of laser photons will add to the decrease in laser beam energy beyond the actual absorption due only to the reaction product. This absorption may be significant even if the triplet population increase is relatively small and transient.

TABLE 4

Variable values for plots in Fig. 4

Trial	Shot	α (cm^{-1})	Π	η'	
1	1	0.01000	1.0000	1.0000	
	500	0.02500	1.0186	0.9056	
	1000	0.04001	1.0349	0.8223	$\epsilon_D = 51.68\,M^{-1}\,cm^{-1}$
	1500	0.05501	1.0490	0.7484	$\epsilon_{RP} = 0.236 \times 10^4\,M^{-1}\,cm^{-1}$
	2000	0.07002	1.0612	0.6823	
	2500	0.08502	1.0719	0.6228	
	3000	0.10002	1.0812	0.5691	
1	1	0.01000	1.0000	1.0000	
	500	0.09169	1.0186	0.9056	
	1000	0.17339	1.0349	0.8223	$\epsilon_D = 51.68\,M^{-1}\,cm^{-1}$
	1500	0.25508	1.0490	0.7484	$\epsilon_{RP} = 1.262 \times 10^4\,M^{-1}\,cm^{-1}$
	2000	0.33678	1.0612	0.6823	
	2500	0.41847	1.0719	0.6228	
	3000	0.50016	1.0812	0.5691	
1	1	0.01000	1.0000	1.0000	
	500	0.17502	1.0186	0.9056	
	1000	0.34005	1.0349	0.8223	$\epsilon_D = 51.68\,M^{-1}\,cm^{-1}$
	1500	0.50507	1.0490	0.7484	$\epsilon_{RP} = 2.544 \times 10^4\,M^{-1}\,cm^{-1}$
	2000	0.67010	1.0612	0.6823	
	2500	0.83512	1.0719	0.6228	
	3000	1.00014	1.0812	0.5691	

Other mechanisms responsible for energy decay were examined by incorporation of the requisite terms into the basic model. For example, it has been proposed that reactive triplets are formed from upper excited singlet states [4, 7, 33]. In addition to promoting degradation, this triplet formation could affect the lasing by populating the triplet manifold at the expense of the singlet population. The potential of this possibility was assessed by adding an additional term $k_{Q_{S(RP)}}[Q_{S(RP)}]$ to the rate constants k_2 and k_{ST} of eqn. (5) and eqn. (6) respectively. The factor $k_{Q_{S(RP)}}$ is the rate constant for singlet quenching by the reaction product and the factor $[Q_{S(RP)}]$ is the concentration of the product. The effect of a decrease in the singlet population on pulse energy decay was calculated to be very small.

The final insight offered by this analysis is the importance of the wavelength of lasing. The parameters δ_S and δ_T are both functions of λ_L and may vary by 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 where there is a smaller extinction coefficient. This effect may account for the slight variations in lasing wavelength encountered with untuned dye lasers. The prime consideration in selecting a lasing wavelength is the absorption band of the reaction product, if this band overlaps the lasing region of the dye.
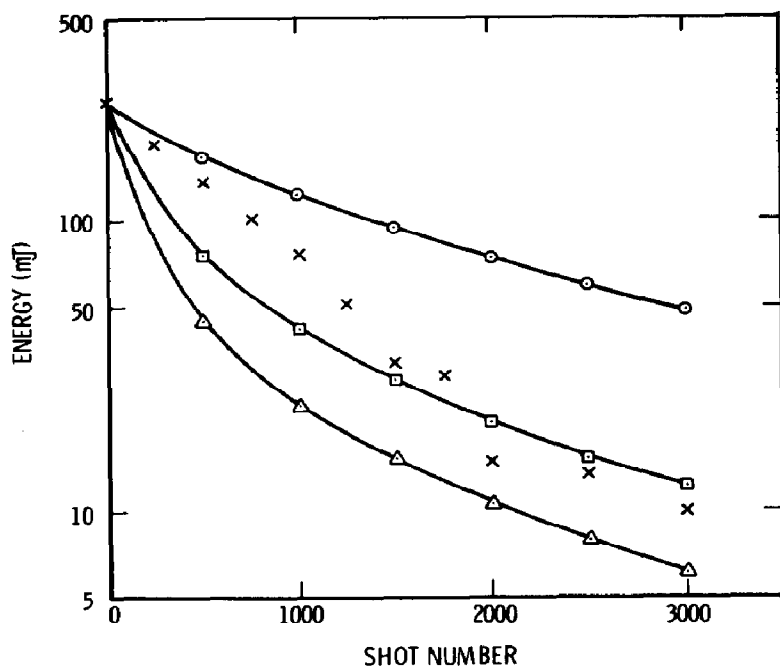
Fig. 4. Laser beam energies experimentally observed (X) and calculated taking into account the actual KRS dependence, the absorption of pump photons due to the reaction product ($\sigma_{A(D)} = \sigma_{A(RP)}$ and D → 3RP) and the absorption of photons at λ_L (⊙, α at shot 3000 equal to 0.10; ⊟, α at shot 3000 equal to 0.50; △, α at shot 3000 equal to 1.00).

It can be concluded that the analytical model developed to represent the KRS dye laser provides an accurate method of predicting laser pulse energy decay and relative laser performance as a function of dominant relaxation mechanisms and competitive absorption processes. Generality has been incorporated into the model which enables various potential reaction product effects to be evaluated by simple modifications of the power output equation and its associated parameters. The model has predicted output energy trends that are consistent with the known characteristics of the KRS laser. As the parameters specific to KRS and to other xanthene dyes are more accurately determined, the model will be able to predict the relative efficiencies of different operating regimes effectively.

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Appendix A

Derivation of expressions for Π and η'

As the dye degrades, less molecules of dye are available to absorb the pump radiation and to lase. To account for the decrease in absorption due to

dye reduction, the Beer–Lambert law [A1] was used. The number of photons transmitted per second in a beam of light is directly proportional to the intensity of the beam. The Beer–Lambert law can then be written as

$$\frac{\rho_0 - \rho}{\rho_0} = \exp(-\epsilon_p C_D d) \tag{A1}$$

where $\rho_0 - \rho$ is the number of pump photons transmitted per second through the medium, ρ is the number of pump photons absorbed per second by the medium, ρ_0 is the number of pump photons transmitted per second in the incident beam, ϵ_p is the molar extinction coefficient for pump absorption, C_D is the concentration of the decomposition product and d is the diameter of the dye cavity illuminated by the flashlamp. The energy output of the laser is proportional to ρ; therefore the output of successive shots can be adjusted by the factor Π to account for the loss of dye molecules if Π is defined as

$$\Pi = \frac{\rho}{\rho_1} \tag{A2}$$

In this equation, ρ_1 represents the number of photons absorbed per second during shot 1, and ρ is determined for each subsequent shot according to the concentration of dye remaining by the use of eqn. (A1). The variable Π can now be expressed as

$$\Pi = \frac{1 - \exp(-\epsilon_p C_D d)}{1 - \exp(-\epsilon_p C_{D1} d)} \tag{A3}$$

The term C_{D1} is the concentration of the dye during shot 1. Johnson [A2] recorded an initial output of 350 mJ at 10^{-4} M dye concentration and 530 mJ at 5×10^{-4} M dye concentration. Considering the ratio of the ρ values for these shots to be equal to the ratio of the output energies, ϵ_p was calculated to be 1.79×10^4 M^{-1} cm^{-1}.

The term Π must also reflect the increase in the number of absorbing molecules in the medium as the reaction product replaces the dye. The number of molecules of reaction product produced from one dye molecule and the molar extinction coefficient for pump absorption are not known. 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 molecule of dye producing two molecules of reaction product with $\sigma_{A(D)} = \sigma_{A(RP)}$ is equivalent to one molecule of dye producing one molecule of reaction product with $\sigma_{A(RP)} = 2\sigma_{A(D)}$, this assumption will still be useful in analyzing the situation when $\sigma_{A(D)} \neq \sigma_{A(RP)}$.

On incorporating the effects of the reaction product, eqn. (A3) becomes

$$\Pi = \frac{1 - \exp\{-\epsilon_p(C_D + C_{RP})d\}}{1 - \exp(-\epsilon_p C_{D1} d)} \tag{A4}$$

The total pump efficiency η is a product of several factors: the flashlamp bandwidth; the pump photon loss due to mechanisms such as reflec-

tion and scattering; the competitive absorption by material (*i.e.* dye, reaction product, absorbing impurities etc.) in the medium. All but the absorption due to the dye and the reaction product can be considered to be constants that can be absorbed into the term W_{max}. This allows η to be modified to express only the probability that a pump photon will be absorbed by a dye molecule:

$$\eta' = \frac{C_D}{C_D + C_{RP}} \tag{A5}$$

References for Appendix A

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