EFFECTS OF SECONDARY CHEMICAL REACTIONS UPON THE PERFORMANCE OF DYE LASERS

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Summary

The effect of absorption at the lasing wavelength due to the accumulation of reaction products from the photodegradation of a laser dye is analyzed theoretically. This analysis is used as a basis for the representation of data from dye degradation experiments in terms of absorption at the lasing wavelength. Studies of the effects of flashlamp pulse rate and time on the inferred absorption for a number of different dyes reveal the influence of secondary chemical reactions. The most significant effects are shown to be associated with spontaneous reactions where the reactants and products have markedly different molar absorptivities at the lasing wavelength.

1. Introduction

It is generally recognized that the degradation in performance associated with repetitious use of a dye laser is a consequence of photoinduced chemical reactions. Where the question has been addressed, it has been found that the predominant cause of degradation is the accumulation of products which absorb at the lasing wavelength [1 - 3]. It would not be unexpected for the complex organic molecules used as laser dyes to have equally complex products which undergo further reaction. This aspect of the degradation process which has largely been ignored is the focus of this paper.

Since the absorbing products are in direct competition with the population inversion, small amounts of product which would be difficult to detect by other means can have a significant effect on laser performance. To interpret this effect better, it is desirable to know the relationship between laser output and absorption at the lasing wavelength. A generally applicable approximation to this relationship results from the following analysis.

2. Theory

A general expression for the output of a flashlamp-pumped dye laser has recently been derived [4]. The analysis leading to this expression will be briefly summarized. The result will be extended to identify explicitly the effects on the slope efficiency and threshold of reaction products which absorb at the lasing wavelength.

The output of a flashlamp-pumped dye laser is approximately proportional to the difference between the rate of production of molecules in the upper lasing state and their rate of spontaneous deactivation integrated over the duration of the laser pulse. If the active radiant flux from the flashlamp is assumed to be proportional to the energy I supplied to the flashlamp, the rate of production of excited molecules can be written as fI where $f(t)$ is the rate of production per unit input energy determined by the shape of the flashlamp pulse as a function of time t, the laser geometry and the dye concentration. In the quasi-steady state approximation the rate of spontaneous deactivation of the excited state under lasing conditions is proportional to an approximately constant critical average population density divided by the fluorescence lifetime of that state. The critical population density is proportional, through parameters dependent on the laser geometry, to that population corresponding to the critical inversion as defined by Snavely and Peterson [5]. It is convenient to define x as the rate of spontaneous deactivation divided by I; thus $x = vn_{1c}/I$ where n_{1c} is the excited state population density corresponding to critical inversion and v is a constant determined by the laser geometry and the fluorescence lifetime. The output of the laser per flashlamp pulse can then be written as

$$\phi = \frac{uI}{\Sigma \tilde{l}_i} \int_{t_1}^{t_2} (f - x) \, \mathrm{d}t \tag{1}$$

where u is a constant inversely proportional to the product of the mean output wavelength and the cavity output lifetime, the interval from t_1 to t_2 is the time interval of the laser pulse and $\Sigma \tilde{l}_i$ is the sum of the mean values of the losses to which coherent photons in the laser cavity are subjected during the laser pulse.

The integral

$$F(x) = \int_{t_1}^{t_2} (f - x) \, \mathrm{d}t$$

in eqn. (1) is the gross production of coherent photons per unit flashlamp energy per flashlamp pulse. The dependence of this function on the flashlamp excitation energy is through the variable x. The beginning and end of the laser pulse are characterized by the vanishing of the integrand: $f(t_1) = f(t_2) = x$. The derivative $F' = -\tau(x)$ where $\tau = t_2 - t_1$ is the duration of the laser pulse corresponding to a particular value of x. When the values of x are

restricted to a range about a value x_m over which the change in τ is small compared with its magnitude, F can be approximated by

$$F \approx F_m - \tau_m(x - x_m) \tag{2}$$

When this result is substituted into eqn. (1) the output is given by

$$\phi \approx \frac{\kappa(I - t)}{\Sigma \tilde{l}_i} \tag{3}$$

where

$$\kappa = u(F_m + \tau_m x_m)$$

$$t = \frac{\tau_m v n_{1c}}{F_m + \tau_m x_m}$$

Since the emphasis here is on product absorption at the lasing wavelength, it is convenient to measure the losses in terms of the loss due to a uniformly dispersed absorber of unit single-pass absorbance. When the laser-configuration-dependent scaling parameter is absorbed into the constant u,

$$\Sigma \tilde{l}_i = \tilde{A}_0 + A_p$$

where A_0 is the equivalent single-pass absorbance associated with the laser in the absence of products and A_p is the sum of the losses due to the absorption of the products. Similarly, when the scaling factor is absorbed into v,

$$n_{1c} = A_d + \hat{A}_0 + A_p$$

where the absorbance A_d of the dye at the lasing wavelength measures the population of the lower lasing levels under the assumption that these levels can be approximated by the high energy thermal tail of the ground state population distribution. It should be noted that the product uv is independent of the choice of the loss scale. The loss terms $\tilde{A}_0$ and $\hat{A}_0$ are distinguished to allow for effects of transient processes such as triplet formation during the lasing process which, because of their inhomogeneity, may affect $\Sigma \tilde{l}_i$ and n_{1c} in somewhat different ways. The slope efficiency $k = \kappa/\Sigma \tilde{l}_i$ can now be expressed as

$$k \approx \frac{k_0}{1 + A_p/\tilde{A}_0} \tag{4}$$

where $k_0 = \kappa/\tilde{A}_0$ and

$$kt \approx k\delta + \alpha \tag{5}$$

where

$$\delta = \frac{\tau_m v(A_d + \hat{A}_0 - \tilde{A}_0)}{F_m + \tau_m x_m}$$

and $\alpha = uv\tau_m$ are parameters independent of the presence of absorbing products. Equation (3) can be rewritten to display explicitly the effect of the absorbing products as

$$\phi \approx \frac{k_0(I-\delta)}{1 + A_p/\tilde{A}_0} - \alpha \tag{6}$$

Where the transient effects are not large, $\tilde{A}_0 \approx \hat{A}_0$ is primarily a function of the index of refraction and the absorbance of the solvent, the optical components of the laser, the laser geometry and the lasing wavelength and is independent of the particular dye used. This implies that the sensitivity of the laser output to product absorbance is insensitive to which dye is used. The observation of this insensitivity was reported by Fletcher and Bliss [6] relative to the change in absorbance necessary to reduce the slope efficiency to one-half of its original value.

The dependence of the threshold t on product absorption is given by

$$t = t_0 + \frac{\alpha A_p}{\kappa} \tag{7}$$

where $t_0 = \delta + \alpha/k_0$. This equation together with eqn. (4) shows the opposing behavior of k and t first characterized by Fletcher [7].

If the product results from a straightforward global photolysis,

$$A_p = rT \tag{8}$$

where T is the sum of the flashlamp energies per unit volume of dye, $T = \Sigma I/V$ and r measures the overall photosensitivity of the reaction. More generally, the variation in A_p with T can be investigated using

$$\frac{A_p}{\kappa} = \frac{I-\delta}{\phi + \alpha} - \frac{1}{k_0} \tag{9}$$

which results from rearrangement of eqn. (6). The laser- and dye-dependent parameters α, δ and k_0 can be derived empirically from the dependence of ϕ on I at constant T.

It is evident from eqn. (9) that for each value of I there is a corresponding maximum value of the computed A_p/κ. These limits are a consequence of the linear truncation of the function F in eqn. (2). As the limit is approached for any value of I, that input energy ceases to be useful for characterizing product absorption. For this reason it is desirable to have output data taken over a range of flashlamp excitation energies at approximately the same value of T.

3. Experimental details

Most of the experimental conditions were the same as those previously described [8]; a Phase-R DL-10Y triaxial flashlamp was used for the test laser. In some experiments a Pyrex tube was used instead of the quartz tube separating the dye from the coolant to remove the UV portion of the flashlamp radiation (UV filtration). In addition, a Xenon Corporation N-851C water-cooled linear flashlamp pumped by their model 457 micropulser was

inserted in the return flow from the test laser to the storage and mixing vessel of the dye flow system. This provided a laser-like environment without mirrors capable of rapidly subjecting the dye solution to large quantities of radiation. This linear lamp was run at 10 J per shot at pulse rates varying from 1 to 25 Hz.

The flow system was closed to the atmosphere and was provided with a port for the introduction of arbitrary gases which were bubbled through the solution in the storage vessel. This provided for controlled atmospheres of a variety of cover gases which were equilibrated with the dye solution. This system is described in greater detail elsewhere [9].

4. Results

4.1. Results for some coumarin derivatives

For coumarin 102 dissolved in a 50:50 mixture of ethylene glycol: water, the output of the test laser proved to be a sensitive function of the rate at which energy was introduced into the solution by the micropulser lamp. Figure 1 shows results for a 1.5×10^{-4} M solution equilibrated with argon under UV-filtered conditions. As a consequence of the ambiguity in the interpretation of the initial slope efficiency, the reciprocal $A_p/\kappa + 1/k_0$ of the slope efficiency computed from eqns. (4), (6) and (9) is plotted in this figure. The parameters $\delta = 20.7$ J and $\alpha = 8.8$ mJ were estimated graphically from the output at 40 J and 50 J in the neighborhood of the minima at $T \approx$ 7 MJ dm^{-3} and $T \approx 16$ MJ dm^{-3}. When the initial pulse rate was about 25 Hz, the output increased to a relatively stable value. Change to a pulse rate of about 1 Hz resulted in rapid degradation of the output. This degradation was followed with 50 J shots of the test laser to $1/k$ values well in excess of the 40 J limit at 2.2×10^3. After an overnight rest, the output from the solution at about 25 Hz repeated the performance of the previous day at a lower overall output and approached an apparently quasi-steady degradation rate. The results for a 2×10^{-4} M solution under similar conditions are shown in Fig. 2.

These results imply that there is an extremely photosensitive component V in the products which absorbs at the lasing wavelength. The increase in this product in the absence of irradiation implies a photoproduced precursor X of lower molar absorptivity which reacts spontaneously to produce V. In global terms

$$D \xrightarrow{h\nu} X \tag{10}$$

$$X \longrightarrow V \tag{11}$$

The decrease in V associated with the high energy input rates implies that V photolyzes to a less absorbant product P:
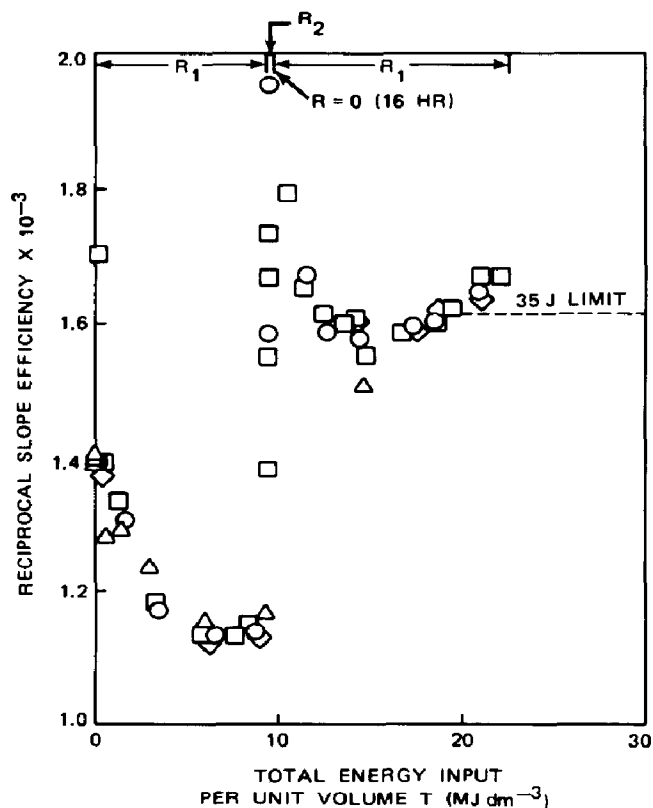
$$V \xrightarrow{h\nu} P \tag{12}$$

Fig. 1. Reciprocal slope efficiency as a function of total energy input for 1.5×10^{-4} M coumarin 102 in a 50:50 mixture of ethylene glycol:water equilibrated with argon under UV-filtered conditions. Each point was computed from an average of ten closely spaced test laser output determinations at the indicated input energy I ($\triangle$, 35 J; $\bigcirc$, 40 J; $\diamond$, 45 J; $\square$, 50 J). The micropulser input rates and the period over which they were applied are indicated at the top of the figure ($R_1 \approx 465$ J dm^{-3} s^{-1}; $R_2 \approx 19$ J dm^{-3} s^{-1}).

To account for the "yo-yo" effect of the repeated changes in pulse rate shown in Fig. 2, it is necessary that X also be photolyzable to a less absorbant product P′:

$$X \xrightarrow{h\nu} P' \tag{13}$$

The rate of reaction (11) was observed in an experiment similar to that shown in Fig. 1 where a large quasi-steady state concentration of X was generated at about 20 Hz followed by no irradiation except for the occasional 50 J single-shot measurements with the test laser required to follow the degradation in output. The end point was estimated from the near-equilibrium output obtained after 2 days without irradiation. The lifetime τ_{11} of X relative to reaction (11) was estimated from the slope of the linear regression on the single-shot measurements to be about 4 h.

Under the assumption that the change in average concentration of the various components resulting from the passage of an aliquot through the
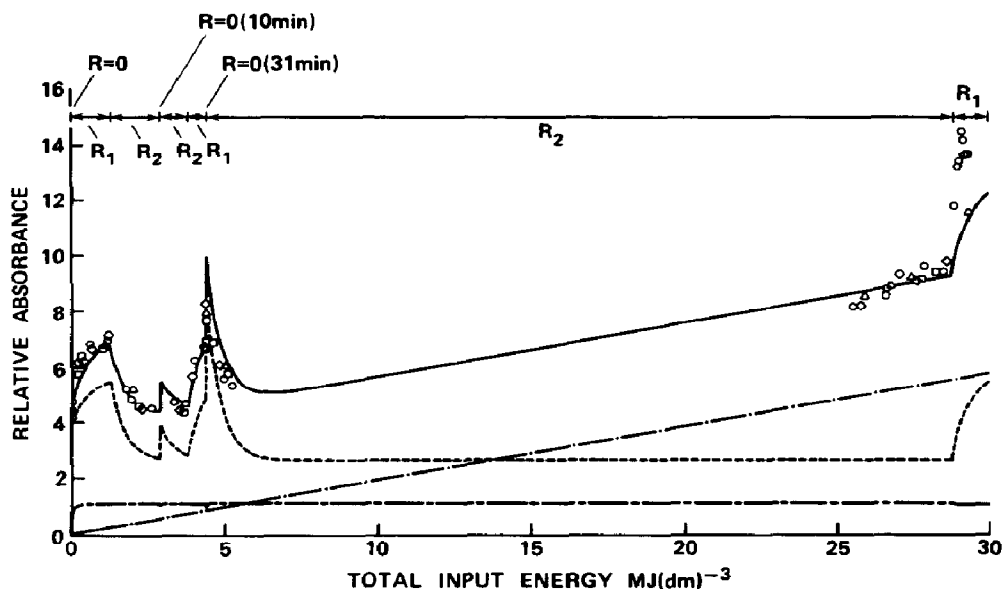
Fig. 2. Relative product absorbance as a function of total energy input for 2×10^{-4} M coumarin 102 in a 50:50 mixture of ethylene glycol:water equilibrated with argon under UV-filtered conditions. Each point was computed from the average of ten closely spaced test laser output determinations at the indicated input energy I ($\triangle$, 35 J; $\square$, 40 J; $\lozenge$, 45 J; $\bigcirc$, 50 J). The micropulser input rates are indicated at the top of the figure ($R_1 \approx 170$ J dm^{-3} s^{-1}; $R_2 \approx 370$ J dm^{-3} s^{-1}). Computed values based on an approximate fit to the data are plotted for the total absorbance (————) and for the individual absorbing products V (— — —), X (— · —) and P (— · —).

flow system is small, the pertinent measure of the rate $R = \mathrm{d}T/\mathrm{d}t$ of photolytic energy input is the rate of energy input divided by the volume of the system. If it is assumed that bleaching is negligible and P is P$'$, the kinetics associated with reactions (10) - (13) can be represented by

$$\frac{\mathrm{d}[X]}{\mathrm{d}T} = r_{10} - \frac{[X]}{R\tau_{11}} - r_{13}[X] \tag{14}$$

$$\frac{\mathrm{d}[V]}{\mathrm{d}T} = \frac{[X]}{R\tau_{11}} - r_{12}[V] \tag{15}$$

$$\frac{\mathrm{d}[P]}{\mathrm{d}T} = r_{13}[X] + r_{12}[V] \tag{16}$$

where the square brackets indicate concentration, r is the photosensitivity of the photolytic reactions and τ_{11} is the lifetime of X relative to reaction (11). The observed sensitivity to R when the results are viewed as a function of T is a consequence of the decrease in importance of the spontaneous reaction (11) relative to the photolytic reactions as R is increased.

The concentration of V corresponding to a single-pass absorbance of κ in the test laser was used as the unit of concentration, and the value of τ_{11}

estimated above and the values of δ and α estimated from Fig. 1 were employed to make a crude fit of the analytic solution of the kinetic equations (14) - (16) to the data plotted in Fig. 2. This fit shows the qualitative consistency between the observation and the global mechanism given above. While the fit is not precise or unique, it does exhibit the order-of-magnitude relationships required to obtain the observed "yo-yo" behavior (Table 1) and suggests that this behavior is dominated by the minor, yet highly absorbant, product species V.

TABLE 1

Parameters used for the computed curves in Fig. 2

Lasing parameters	
k_0	2.22×10^{-3}
δ (J)	20.8
α (mJ)	8.8
Reaction parameters[a]	
τ_{11} (h)	4
r_{10} (dm^3 J^{-1})	5.6×10^{-2}
r_{13} (dm^3 J^{-1})	2×10^{-5}
r_{12} (dm^3 J^{-1})	2×10^{-6}
Relative product absorptivities[b]	
ϵ_V	1
ϵ_X	4×10^{-2}
ϵ_P	3.4×10^{-4}

[a]$r_{10} \gg r_{13} \gg r_{12}$.
[b]$\epsilon_V \gg \epsilon_X \gg \epsilon_P$.

The greater sensitivity to the change in pulse rate for $T \approx 29$ MJ dm^{-3} relative to the initial sensitivity suggests the possibility that P (or P') is photolyzable back to X. This would result in a quasi-steady increase in [X] and [V] as well as [P] during the long duration segment at constant R. This would not affect the qualitative relationships shown in Table 1. However, it does suggest that the absorbance of P at the lasing wavelength may be negligible compared with those of the other products.

The results from a test of a 2×10^{-4} M solution of AC3F [10, 11] in ethanol equilibrated with argon are shown in Fig. 3. This test was conducted under UV-filtered conditions over a period of 7 days. In excess of 99% of the energy was introduced by the micropulser at about 23 Hz ($R \approx 385$ J dm^{-3} s^{-1}). The times during which micropulser energy was introduced are indicated by the T scale in the figure. The data were taken in closely spaced sets at 30, 35, 40 and 45 J using the test laser. The parameters $\delta \approx 18.4$ J and $\alpha \approx 13.3$ mJ were estimated from the intersection of the linear regression lines $\bar{\phi}(I)$ from data in the ranges 0.7 MJ dm$^{-3} < T < 6$ MJ dm^{-3} using all I values and 41 MJ dm$^{-3} < T < 46$ MJ dm^{-3} with $I > 30$ J. The initial slope efficiency $k_0 \approx 1.47 \times 10^{-3}$ was estimated from the mean values of $1/k$ computed from a data set taken before the micropulser was started.
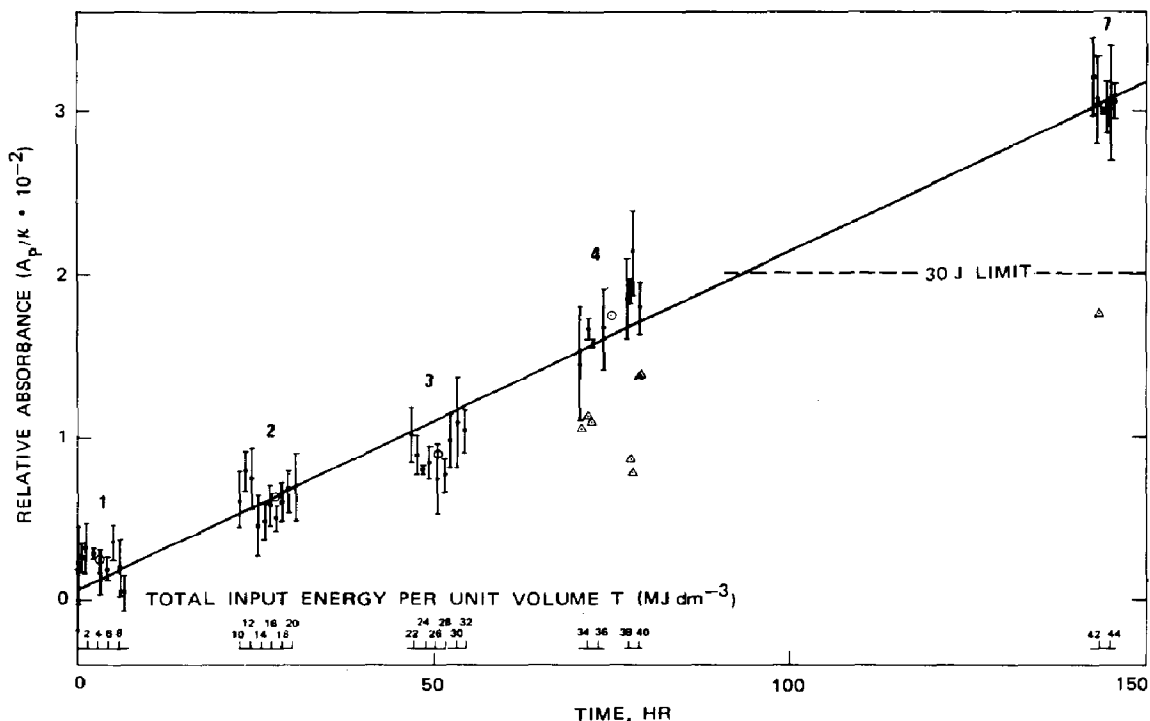
Fig. 3. Relative product absorbance as a function of time for 2×10^{-4} M AC3F in ethanol equilibrated with argon under UV-filtered conditions. The introduction of energy by the micropulser is indicated by the secondary energy input scale at the bottom of the figure ($R \approx 385$ J dm^{-3} s^{-1}). The points with error bars represent the centroid of the values computed from the average of ten test laser output determinations at each of the following values of input energy: 45, 40, 35 and 30 J (time, less than 60 h). Values computed from the 30 J data for time greater than 60 h are indicated by $\triangle$. The error bars indicate the standard deviation of the values computed from the various input energies used. The general correlation of these data with time is indicated by the linear regression line computed from the centroids $\odot$ of the data taken each day when the micropulser was on. The day number is indicated by the numeral associated with each of the data groups.

The most significant change in product absorbance at the lasing wavelength is that which occurred between days 4 and 7 when the micropulser was not running. This implies the spontaneous production of a product V from a precursor X of lower molar absorptivity (*i.e.* reaction (11)). The change in relative absorbance during the 70 h period from $t = 5$ h to $t = 75$ h is approximately the same as that during the period from $t = 75$ h to $t = 145$ h even though 51% of the excitation energy was introduced during days 2 and 3 of the first period. This suggests that the average concentration of X was not very different in the two periods. Hence the steady state X relative to reactions (10) and (13) is rapidly achieved and the lifetime of X relative to reaction (11) in this case is very much longer than the 4 h estimated for the previous example. There is evidence for the establishment of the steady state in the data for the first day. Comparison of the data set obtained prior to starting the micropulser with those obtained immediately after suggests that

this occurs with a total energy input of about 1 MJ dm^{-3}. That V is photo-lyzed to a somewhat lower molar absorptivity product P (reaction (12)) is suggested by the behavior of the data sets as a function of T during days 2 and 3. This would imply that the depletion in X during the long dark segment from day 4 to day 7 is at least in part masked by the presence of a large concentration of the highly absorbent product V.

While differing in detail, the examples illustrated in Figs. 2 and 3 exhibit the same gross mechanistic behavior. These examples are relatively unusual in our experience. A more common observation for coumarin derivatives under UV-filtered conditions is the rapid attainment of a quasi-steady increase in relative absorbance as a function of T with insignificant changes associated with changes in the rate of energy input or of overnight dark periods. Frequently the only indication of secondary reaction is that the extrapolation to k_0 based on the quasi-steady degradation rate is significant-ly smaller than that obtained just prior to the start of the degradation experiment. The preceding examples suggest that this is a consequence of the rapid establishment of a steady state X and that the quasi-steady degradation is a consequence of the accumulation of the secondary degradation products P and P$'$.

4.2. Results for some rhodamine derivatives

Data from a 1×10^{-4} M solution of rhodamine 116 perchlorate in ethanol (ambient atmosphere) are shown in Fig. 4. The degradation was accomplished using the test laser at a maximum value of $R = 8.9$ J dm^{-3} s^{-1} without UV filtration. The parameters $\delta \approx 9.3$ J and $\alpha \approx 9.5$ mJ were estimated from the intersection of the linear regression lines $\bar{\phi}(I)$ for $T < 25$ kJ dm^{-3} and 60 kJ dm^{-3} $< T <$ 86 kJ dm^{-3} (25 J excluded). The data were taken over 2 days with an overnight dark period of about 17 h. The slope efficiency $k_0 \approx 1.08 \times 10^{-3}$ in the absence of product was estimated from the intercept at $T = 0$ of the linear regression line $1/k$ *versus* T based on data from the first day. Based on the difference between the values A_p/κ computed from the linear regression lines corresponding to the 2 days, about 51% of the product absorbance was lost during the 17 h when there was no irradiation as a consequence of a spontaneous reaction like (11) introduced in Section 4.1. In this case, however, V has a lower molar absorptivity than that of X. As a consequence the absence of significant deviation from the quasi-steady increase in absorbance on both days suggests that the X is the significant product of the initial global photolysis reaction (10). The use of that concentration of X corresponding to a single-pass absorbance of κ in the test laser as unit concentration, along with the assumption of negligible bleaching, leads to $r_{10} \approx 1.3 \times 10^{-2}$ dm^3 J^{-1}. That the values derived from the slopes of the regression lines for the two days (1.26×10^{-2} dm^3 J^{-1} and 1.32×10^{-2} dm^3 J^{-1}) are not significantly different is consistent with reactions (10) and (11) being the only reactions of significance relative to the degradation of this dye. The assumption that V has negligible molar absorptivity at the lasing wavelength leads to a maximum value of r_{11} of about 24 h.
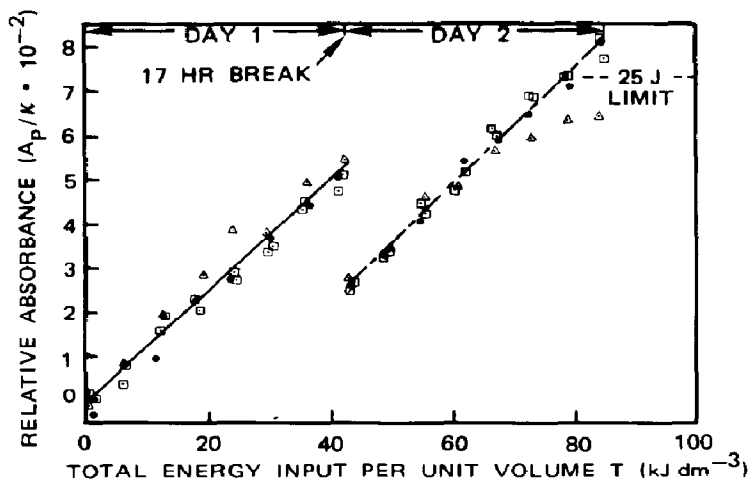
Fig. 4. Relative absorbance as a function of the total energy input for 1×10^{-4} M rhodamine 116 perchlorate in ethanol (ambient atmosphere). The points were computed from the average of five closely spaced test laser output determinations at the indicated input energy I ($\triangle$, 25 J; $\bullet$, 30 J; $\square$, 35 J; $\bigcirc$, 40 J). Linear regression lines were computed from the data for each of the 2 days (25 J excluded for $T > 70$ kJ dm^{-3}). Degradation was accomplished using the test laser at 40 J between each of the groups of points ($R \approx$ 8.9 J dm^{-3} s^{-1}).

This, together with the estimated value of r_{10}, would imply a change of about 10% in the slope of A_p/κ versus T over the first day of reaction which would not be appreciable relative to the apparent dispersion of the data.

Data from studies of a number of rhodamine dyes in ethanol (ambient atmosphere) without UV filtration show a consistent pattern of spontaneous reaction of an initial product to a secondary product of significantly different molar absorptivity at the lasing wavelength (Table 2). From eqn. (6) the difference in laser output associated with a change in product absorbance can be written as

$$\phi - \phi' = \frac{k_0(I - \delta)(A_p' - A_p)/\tilde{A}_0}{(1 + A_p/\tilde{A}_0)(1 + A_p'/\tilde{A}_0)} \tag{17}$$

Since the change in output is proportional to $I - \delta$, the effect of an overnight discontinuity is seen most significantly at the largest value of I used in the test laser. The change is positive if the product V has a lower molar absorptivity than that of the initial product X. The magnitude of the change is dependent on the details of the experiment as well as the kinetics. Since these details differ for the examples listed in Table 2, the magnitude of the percentage change provides a measure only of the significance of the sign of the observed change.

When some of these compounds were tested under UV-filtered conditions there was little or no evidence to suggest any effect of the spontaneous reaction (11). The most significant effect observed was for sulfarhodamine 101 where the effect was positive rather than negative as shown in Table 2 for the unfiltered conditions.

TABLE 2

Effect of overnight dark periods on the laser output from some rhodamine dyes

Dye (Eastman designation)	Molar concentration ($\times 10^4$)	Input energy (J)	Percentage change in output	Observed midpoint for broad band lasing (nm)
Rh 110	1	40	+23	572
Rh 116	1	40	+35	593
	2	40	+35	
Rh 19	1	35	+78	593
	2	35	+53	
Rh 6G	1	30	+90	597
	2	40	+50	
Rh B	1	35	+14	625
	2	40	+11	
SRh B	1	35	+56	626
	2	40	+42	
Rh 3B	1	40	+25	630
	2	40	+20	
Rh 101	1	30	—9	652
	2	35	—5	
SRh 101	1	35	—1	648
	2	35	—6	

5. Conclusions

Since the absorption of laser dye degradation products competes directly with the population inversion, the amount of absorption required to affect the output of the laser significantly is small. For lasers of the types used in these experiments, it has been estimated that about 1% absorption at the lasing wavelength is sufficient to reduce the laser output by 50% [6]. Thus laser performance is a sensitive measure of the presence of products which absorb at the lasing wavelength. As illustrated by the examples that have been discussed, eqn. (9) provides an approximate relative estimate of the total absorbance of the dye degradation products. When care is taken to exclude input energies near the threshold where the linear approximation to the function F is invalid, the demonstrated insensitivity of the apparent absorbance estimates to the flashlamp input energy tends to confirm that the observed effects on the laser output are dominated by product absorbance.

The estimated total product absorbance at the lasing wavelength does not discriminate among the various products present in the dye solution. By varying the experimental conditions, we have shown for a number of

examples that there are several products which absorb at the lasing wavelength. The discussion of these examples illustrated that the subsequent reactions of the early products can and do profoundly affect the degradation in performance of a repetitively pumped dye laser.

We have attempted to relate our observations to the mechanism of dye degradation in a gross global framework. This is unquestionably an over-simplification of the chemical complexity of laser dye systems. In the relatively simple case of coumarin 1, five photodegradation products have been identified for a laser environment using an unfiltered flashlamp with oxygen present [3]. Only one of these, the carboxylic acid resulting from successive photo-oxidation of the methyl group, absorbs strongly at the lasing wavelength and is responsible for the degradation in laser performance under these experimental conditions. When coumarin 1 is pumped using a nitrogen laser in the absence of oxygen, the output has been shown to degrade at a rate not much less than that observed when oxygen is present [12]. This suggests other, as yet unknown, reaction paths which are not significant in the presence of oxygen.

The most commonly encountered evidence for the contribution of secondary reaction products is an initial transient associated with the establishment of quasi-steady conditions. In this case the degradation in laser performance is dominated by the final product resulting from a sequence of reaction steps. Where one of those steps is a slow spontaneous reaction, the performance of the laser can be markedly affected by the pulse rate and the number of duty cycles. As an extreme example consider the data for AC3F [11] (Fig. 3). When the number of shots or the total output energy per unit volume before the output drops below some limiting value is taken as a measure of the utility of the dye, the utility would be approximately proportional to the average pulse rate of the laser. In contrast, let us consider the data for rhodamine 116 (Fig. 4). In this case the utility would tend to decrease as the average pulse rate was increased.

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Appendix A: nomenclature

$\widetilde{A}_0$	mean coherent photon loss in the absence of absorbing products expressed as an equivalent single-pass absorbance
A_p	single-pass absorbance of the absorbing products
F	gross production of coherent photons per unit flashlamp excitation energy per flashlamp pulse
h	Planck's constant
I	flashlamp excitation energy per pulse
k	slope efficiency
r	photosensitivity factor for chemical reaction
R	time derivative of T
t	apparent lasing threshold or time, depending on context
T	sum of the flashlamp excitation energies per unit volume of dye solution
α	composite parameter treated as an empirical constant
δ	composite parameter treated as an empirical constant
ϵ	molar absorptivity
κ	factor of proportionality relating the slope efficiency to the reciprocal of the sum of the coherent photon losses
ν	frequency of light
τ_{11}	exponential lifetime of reaction (11)
ϕ	laser output per flashlamp pulse