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Photobleaching of laser dye rhodamine 6G

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Abstract. The irreversible photobleaching of Rhodamine 6G occuring due to flash lamp pumping has been studied when the dye is subject to laser action. The absorption spectrum of the dye shows the gradual build up of the bleached molecules with the number of flash lamp pulses. The fall in the intensity of the laser output that occurs with the number of laser pulses was found to be correlated to the reduction in the absorption of the dye. A strong dependence of the rate of photobleaching on the size of the dye cell has also been found. This has been explained as being due to the dye molecules contained within the laser mode volume partaking in stimulated emissions, while the remainder of the excited dye in the dye cell is undergoing merely spontaneous fluorescence and other non radiative deexcitations.

1. Introduction

Organic dyes used in dye lasers suffer progressive deterioration due to irreversible bleaching (Schafer 1973, Snavely 1969) that occurs during the course of the irradiation of the dye molecules by pump radiation. It has been estimated (Ippen *et al* 1971) that the life time of a dye molecule like Rhodamine 6G is about 40 msecs** when subject to a CW pump beam of power 10^5 watt/cm^2 (roughly the threshold pump power for Rhodamine 6G) from an Argon ion laser at 5145 A The rate of bleaching however, depends in general on several parameters, like the nature of the solvent, its *p*H, temperature, presence or absence of triplet quenchers or promotors, the spectral and temporal nature of the pump and whether the UV radiation that may be present in the pump radiation is inhibited or not, the resonator geometry and pump coupling configuration in case of flash lamp pumped dye lasers, etc. The consequences of this photobleaching are : a reduction in the number of fluorescent monomers and a decrease in the fluorescent quantum efficiency, an increased absorption in the UV

This paper pertains to an investigation of photobleaching of the organic dye Rhomanine 6G used in a flash lamp pumped laser. Because of the complex

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** This computation is based on a quantum efficiency of about 5×10^{-7} molecules bleached/absorbed photon for Rhodamine 6G in ethanol solution measured by Ippen *et al* (1971).

dependence of the bleaching rate on many parameters listed above, the experiments reported in literature have not considered all the possible effects. For example, the results of subjecting a dye to narrow band (e.g., laser) or broad band irradiation (flash lamp) should be expected to be different as also when the dye is merely irradiated or while it is made to undergo laser action. This has indeed been found to be the case in our investigation.

In our experiments the differences between the two cases (1) wherein the dye is merely irradiated with a flash lamp and (2) where the dye is made to lase with the same pump, have been examined in detail.

2. Experimental details

A linear Xenon flash lamp (90 mm arc length) was used as pump, and it was coupled to the dye cell by means of an elliptic cavity. The dye cell (125 mm long) consisted of a fused silica or borosil tube of 8 mm i.d. and was provided with quartz windows.

A second laser head was used in addition to the one just described. The only differences were in the length of the Xenon flash lamp (50 mm arc) and the length (65 mm) and diameter of the dye cell Three different borosil tubes of diameter 8·2 mm, 6·5 mm and 5·5 mm were used The laser output power and duration were monitored by an EG and G Lite mike, calibrated Silicon photodiode. The signal from the photodiode was recorded on a Tektronix 7633 storage oscilloscope. The light from flash lamp was also monitored by a separate photodiode and recorded simultaneously to obtain the flash lamp rise time and its duration. A low inductance storage capacitor (40 μF, 5 kV) was directly discharged through the flash lamp without any external inductance, using a parallel trigger. (Prasad, Venkateshan and Yoganarasimha 1978).

Reagent grade Rhodamine 6G (BDH chemicals) was used as such without any further purification. Methanol (AR grade) was the solvent used in all the studies presented here. The dye solution of 1×10^{-4} molar concentration was introduced into the dye cell or extracted by means of a glass syringe.

The dye in the cell was removed after a predetermined number of shots and its absorption spectrum was obtained.

3. Results and discussion

The maximum input energy to the flash lamp was about 160 joules per pulse. When the quartz dye cell was used, it was observed that the laser action ceased after 5 or 6 shots in the longer cavity. This indicates that photobleaching had reduced the number of available fluorescent monomer dye molecules to such an extent that threshold could not be reached. The absorption spectrum of the

bleached dye is shown in Figure 1. It is to be noted here that the relative absorption of the bleached dye with respect to the unbleached dye has been recorded

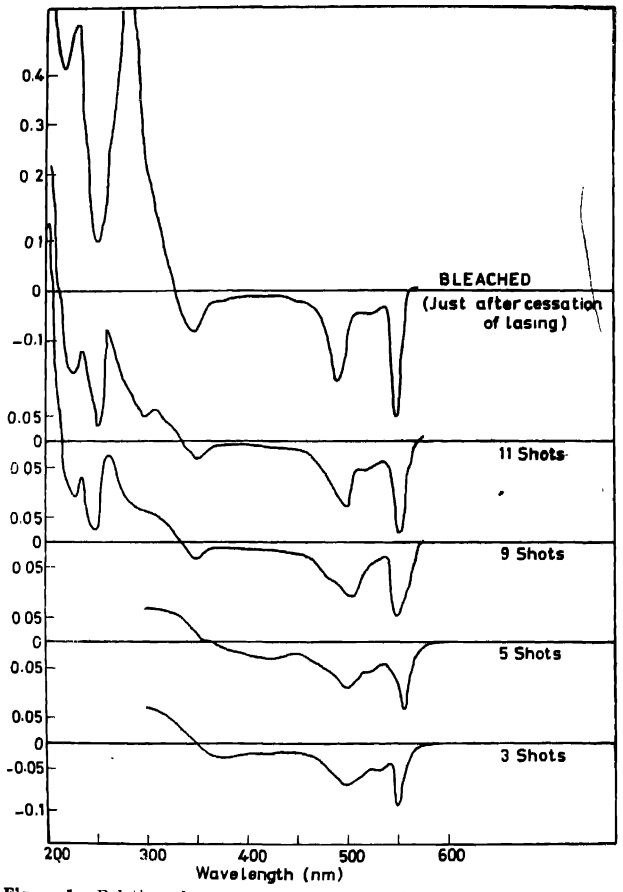

Figure 1. Relative absorption spectra of partially and fully bleached dye. Results are for the long cavity dye cell of diameter 7·8 mm.

by having the unbleached dye in the reference cell and the bleached dye in the sample cell of the dual beam spectrophotometer. Since it is well established (Loth and Meyer 1973) that the ultraviolet photons have a greater propensity to cause photochemical reactions, the fused silica tube was replaced by a borosil

glass tube (also 8 mm i.d.). It was found that the laser action could continue for more than 30 shots. However the laser output power undergoes a monotonic decrease after remaining nearly constant for the first 2 or 3 shots. The number of pulses during which lasing continues, depends on the diameter of dye cell, input pump energy, concentration of dye, etc.

Figure 1 also shows the absorption spectra of the dye subjected to 3, 5, 9 and 11 shots. It is seen from an examination of this figure that at 550 nm (the wave length of the peak absorption of Rhodamine 6G) the reduction in absorption is monotonically increasing with the number of shots the dye was subjected to. When the spectrum of this partially bleached dye was compared with that of dye merely subjected to the same number of flash lamp irradiations (without lasing), it was noticed that the absorption decrease was very much larger in the latter case This decrease in the relative absorption coefficient between the fresh dye and irradiated dye is a measure of the number of dye molecules bleached. For example, if we examine the case of dye subjected to 4 identical flash lamp pulses while lasing or while not lasing, the ratio of the relative absorption for the lased to merely irradiated dye is 0·44 (and it becomes 0·47 for 6 shots) After about 7 or 8 pulses of more irradiation, the dye does not lase if an attempt is made to lase it with the same pump power, and is then considered to be "fully bleached". From the measured absorption coefficients the number of molecules bleached has been found. The number of bleached molecules* is about $0{\cdot}62\times10^{16}$ when "fully bleached", (i.e., for the given maximum pump energy of 160 joules, this solution does not lase), and is $0{\cdot}22\times10^{16}$/ml and $0{\cdot}5\times10^{16}$ for dye subject to 4 shots while lasing and while not lasing respectively This implies a much larger bleaching rate in the absence of lasing action, which was also noticed in the experiments of Oettinger and Dewey (1976), who, however used laser excitation

Weber (1973) and Beer and Weber (1972) found that the addition of a triplet quencher like COT (C_8H_8) reduces the bleaching rate. This observation in conjunction with the fact that the life time of the first excited triplet state T_1 is much longer ($\approx 10^{-6}$ secs) than that of the excited singlet state S_1 and that the triplet state is more chemically reactive than the singlet state, implies that it is the dye in the triplet state that is primarily being photobleached (Britt and Moniz 1972, Marling *et al* 1970, Yamashita and Kashiwagi 1976).

The experiments described above wherein we have found that the propensity for the dye to be destroyed faster when the dye is merely excited and allowed to de-excite spontaneously, than when stimulated emissions are also taking place lends further support to the above hypothesis. In the experiments in which

* The number of dye molecules in the fresh (unbleached) dye solution is $6{\cdot}02\times10^{16}$/ml (corresponding to a concentration of 10^{-4} mole/liter),

laser action is also taking place, the deactivation of the S_1 state occurs primarily by : (a) spontaneous emission, (b) S_1–T_1 cross over, and (c) stimulated emission. The stimulated emissions that occur while the dye is lasing cause a larger number of S_1 molecules to return directly to the ground state G, than in the case when no lasing occurs In the latter situation a larger accumulation of molecules in the triplet state occurs thus giving a higher photobleaching rate.

For the long cavity laser Figure 2 shows the gradual decrease in the peak output power of the laser with the number of pulses As pointed out earlier, the dip in spectrum at 550 nm in Figure 1 is proportional to the reduction in number of active dye molecules which is growing with the number of pulses.

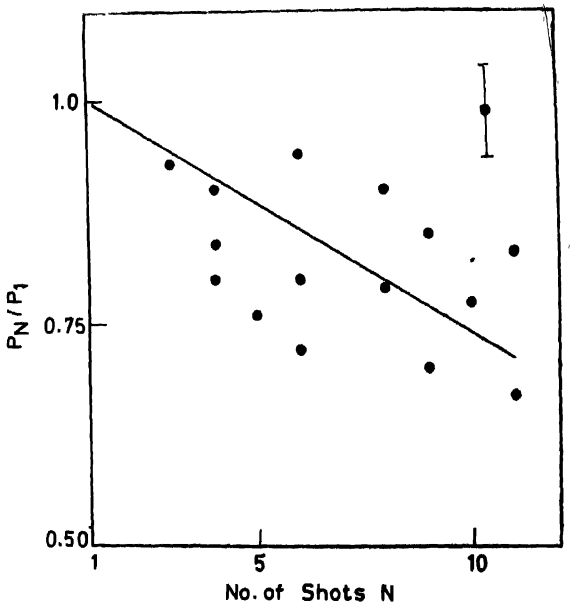

Figure 2. Reduction of normalized laser output (P_N/P_1) with number of shots N. P_1 is the laser peak power output.

So a cross correlation can now be made between the extent of this dip to the peak power output. This is shown in Figure 3, and indicates that the laser output power falls as more and more dye molecules are bleached out. The fairly wide scatter in the data points is to be expected, because, even in the most sophisticated flash lamp pumped lasers, shot to shot variations in intensity are in excess of 10%.

Furthermore in the experiments reported here, each experimental points represents a separate sequence of shots. In order to reduce the consequent errors a modular spectrophotometer has been constructed in our laboratory to directly scan the spectrum of the dye while it is within the dye cuvette in between successive laser shots. These experiments are now in progress and their results will be presented elsewhere.

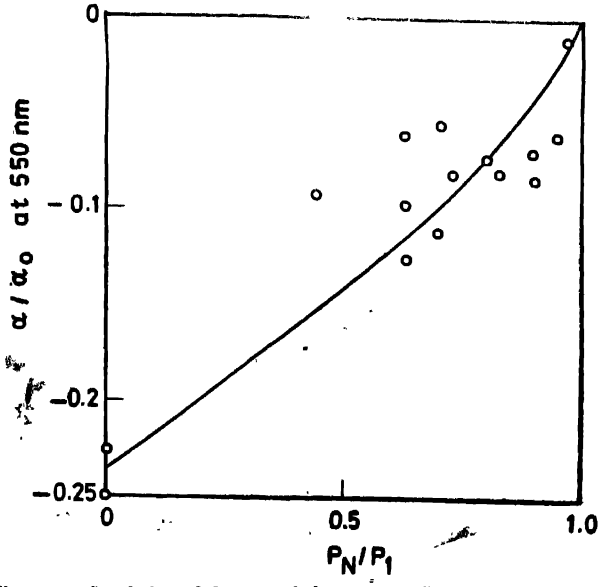

Figure 3. Correlation of the ratio of absorption coefficients of lased (α_N) to fresh dye solution (α_0) with (P_N/P_1). Absorption measured over 1 cm. path length.

The intensity of radiation within the dye cell will be nonuniform and depending on the TEM mode structure the intensity distribution has one or more maxima in the centre of the cell and decays to negligible values outside the mode volume. If the diameter of the dye cell is larger than the radial extent of the mode volume, then, since the dye contained in the region outside the mode volume should have a higher bleaching rate (because no stimulated emissions are occuring in this region) the overall life of the dye in a larger cell must be lower than that of a smaller dye cell. That this is indeed the case has been demonstrated (see Figure 4) by using dye cells of different diameters 5·5, 6·5 and 8·2 mm.

In these experiments the laser was made to oscillate in the TEM_{00} mode (Prasad *et al* 1979). The increase in diameter of dye cell also changes the radial distribution of pump power density in the dye. For a concentration of 10^{-4} moles/liter, the absorption coefficient of the dye is as high as 12 cm^{-1} at 550 nm

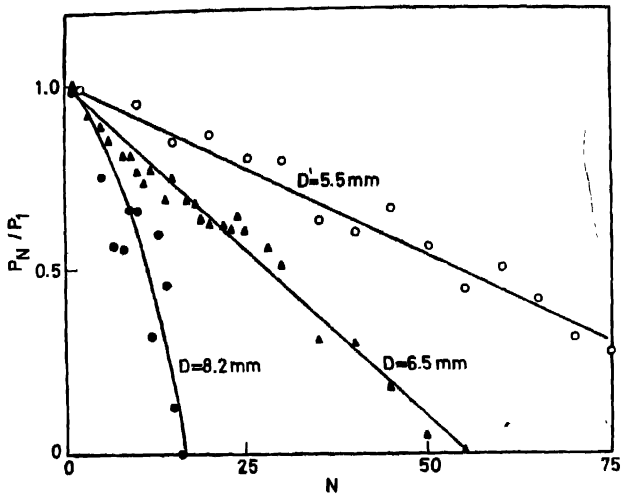

Figure 4. Effect of dye cell diameter on the bleaching rate, for the short cavity.

although it is smaller at other wavelengths. Thus an increase in diameter of the cell would cause a reduction in the pump power distribution at the center of the cell. Since the laser is operating in the TEM_{00} mode, such that the stimulated light intensity is a maximum at the center of the cell and the pump power distribution is such as to have larger populations of S_1 (and hence T_1) away from the center of the dye cell, the effect of increasing the diameter is to further enhance the rate of photobleaching A dramatic increase in the number of shots before the irreversible bleaching leads to cessation of laser action is seen as the mode volume fills a larger portion of the dye cell. A detailed analysis of this phenomenon (involving a solution of the transient rate equations of the laser) is necessary for quantitative descriptions of these effects. Such an analysis is under way and the results will be presented elsewhere.

Acknowledgment

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