The Effect of Triplet Quenchers
on Vapor-Phase Dye-Laser Performance

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Abstract. An XeF pumped vapor phase POPOP dye laser with a pulse duration of 300 ns was obtained when trans-stilbene was used as triplet quencher. An energy conversion efficiency of 7.5% with a peak power efficiency of 12% was measured.

The first organic dye shown to lase [1] in the vapor phase is 1,4-bis-(5-phenyloxazolyl-2)-benzene (POPOP). Although many other dyes have been shown to lase [2], the best dye in terms of lasing efficiency is still POPOP. A peak power efficiency of $\sim 7.5\%$ was demonstrated for pure POPOP vapor [3] transversely pumped by an N_2 laser (337 nm). The lasing performance was improved upon by adding a buffer gas [4]. The highest efficiency measure so far [5] is 22% (energy out/energy absorbed). However, the pulse duration in all these cases was limited to less than 20 ns because of the formation of triplet state POPOP molecules and photodecomposition. When an excited dye molecule goes to the triplet state, it is no longer available for lasing and, since it absorbs [6] at the laser wavelength (~ 390 nm), it becomes a loss factor in the laser cavity. Since the effective lifetime of the POPOP triplet state is on the order of 20 μs, the population of triplet molecules steadily increases during the pulse and terminates the lasing action.

The use of a buffer gas slows down this process. Both singlet triplet crossing time [7] and photodecomposition [8] have been shown to be temperature dependent. As the lasing process procedes with an absorption/emission cycle time of a few ns, the dye molecules are accumulating excess vibrational energy. Part of this comes from the fact that the dye molecule absorbs at a wavelength shorter than it lases. The major portion, however, is due to the absorption of laser photons by excited state molecules [4]. These doubly excited dye molecules return to the first excited

state by non-radiative processes leaving the energy in the vibrational manifold. This serves to "heat" up the molecule and greatly increase the singlet triplet crossing and photodecomposition rates. The buffer gas provides a means of removing this excess vibrational energy and controlling the dye molecule vibrational temperature. However, even at the high buffer gas pressure (35 atm of diethyl ether) and the low temperature (200 °C) used in the experiment reported in [5], the triplet accumulation terminated the pulse after 20 ns.

The results presented in this paper demonstrate the effectiveness of a triplet quencher [9] in increasing the pulse duration of a vapor phase dye laser. The compound trans-stilbene was added to the butane buffer gas to produce an XeF pumped POPOP dye vapor laser with a pulse duration of ~ 300 ns.

In general, the function of a triplet quencher is to return molecules trapped in the lowest triplet state back to the ground state. Organic molecules which serve this function have been used to dramatically increase the pulse duration and efficiency of solution phase dye lasers [9], and the mechanism for this process and the criteria for quencher selection have been decribed [9, 10]. Briefly, the quenching process involves an energy transfer from the triplet state of the dye molecule to the triplet state of the quencher. In order for this to occur, the triplet state energy of the quencher must be less than the triplet energy of the dye. Estimates for the triplet energy of POPOP range from 18,000 to 23,000 cm^{-1} ([11] and [12], respectively). It

is also important that the excited singlet-state energy of the quencher be well above that of the dye molecule and above that of the excitation photon. This is necessary so that the lasing state of the dye is not deactivated by the quencher and so the pump energy is not lost to exciting the quencher. These electronic energy level requirements were used to select potential triplet quencher candidates. The lowest triplet and first excited singlet energies of trans-stilbene are 17,400 and 29,800 cm^{-1}, respectively [13]. This, in combination with the vapor pressure properties, led to its choice as a triplet quencher. These same arguments (with the exception of the vapor pressure requirements) were used by Liphardt et al. [12] to select t-stilbene as an intramolecular triplet quencher for the dye dimethyl-POPOP. Their experiment demonstrated a very dramatic improvement in solution phase lasing efficiency with the attachment of the t-stilbene to the dye molecule. Vapor phase quenching of POPOP triplet states by cyclooctatetraene was measured [14] in triplet level absorption experiments. Unfortunately, this quencher's performance in enhancing the vapor phase lasing properties of POPOP was not tried in the experiments reported here.

The dye vapor was excited using an e-beam pumped XeF laser configured to provide a 450 ns pulse. The laser flux was focused into the dye laser tube using the lens configuration shown schematically in Fig. 1. The first lens started to focus the square profile (10 × 10 cm) of the laser output. The position of the second lens was then adjusted so as to focus the beam at the dye laser tube. The negative cylindrical lens transformed what would have been a square spot into a rectangular shaped profile oriented along the dye laser cavity axis. Apertures were used to carefully define the dimensions of the excitation zone (10 × 0.32 cm) and improve its spatial uniformity ($\pm 10\%$ in the vertical and 20%

along the dye laser cavity axis). The reflections off the oven window were directed to a photodiode which was used to monitor the time profile and shot to shot variation of the XeF laser. This was calibrated by using an energy meter (Scientec) mounted behing the slits (the dye laser tube removed).

The dye laser tube, laser cavity mirrors, and gas mixing line were contained inside an oven which was maintained at 285°C. The dye laser tube was constructed from a 1 cm ID, 2 mm wall quartz tube. The brewster windows were attached using quartz to quartz transfer tape (Vita Corporation). A graded seal and a pyrex to metal union were used to connect the tube to the gas line. The POPOP, trans-stilbene, and butane were premixed in a 0.5 l vessel also inside the oven. The POPOP density in the laser tube was determined from the transmission at 353 nm measured through the 1 cm transverse path. The trans-stilbene and butane pressures were measured using a high temperature pressure transducer (Bell and Howell type 4-317-0001).

The dye laser cavity was formed by a 1-meter radius of curvature mirror dielectrically coated for maximum reflectance at 390 nm and a flat output coupler coated for 80% reflectivity. The mirror separation was 40 cm. The dye laser output was measured using the energy meter. A beam splitter was used to direct a small portion of this beam to a photodiode to record the temporal profile. The XeF flux transmitted through the tube and the fluorescence emitted perpendicular to the laser axis were also measured using high-speed vacuum photodiodes.

Typical experimental results are shown in Fig. 2. The oscillogram on the left shows temporal profile of the XeF pump. The peak intensity represents a flux entering the dye laser tube of ~ 1 MW/cm^2. The trace in the upper right hand oscillogram corresponds to the

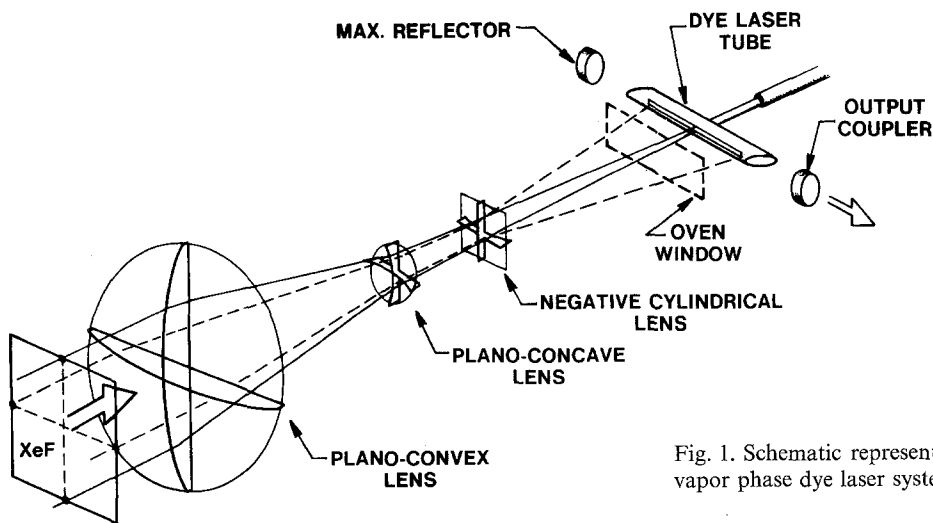Fig. 1. Schematic representation of the XeF pumped POPOP vapor phase dye laser system

XeF
Pump→

→| |←200 n sec
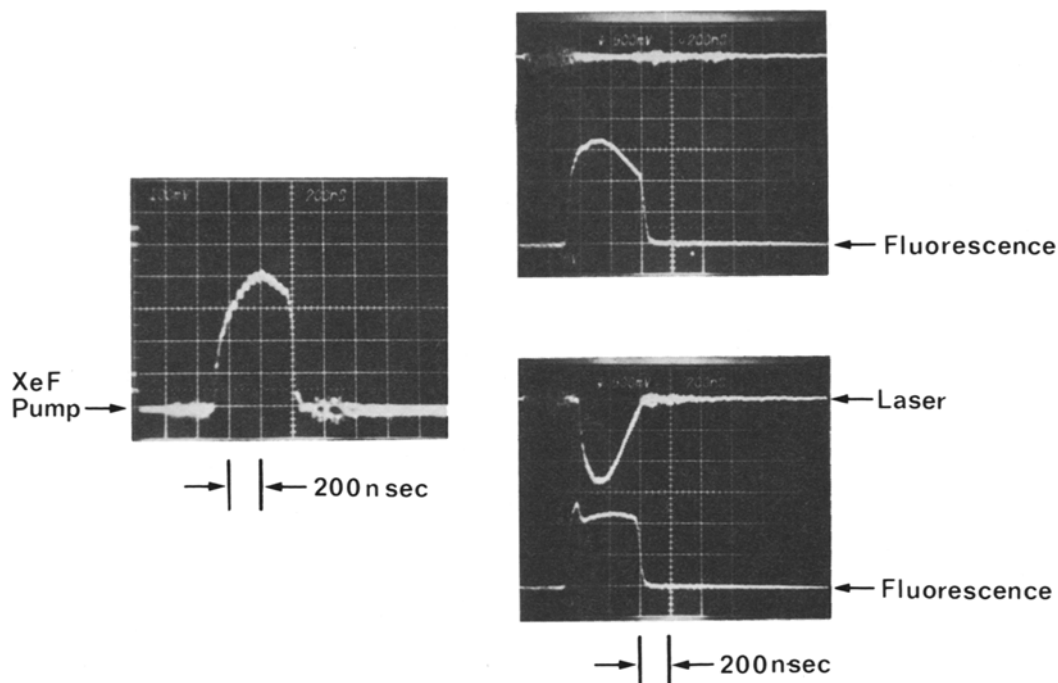
←Fluorescence

←Laser

←Fluorescence

→| |←200nsec

Fig. 2. Typical experimental data showing XeF, POPOP fluorescence, and POPOP laser output time profiles

POPOP sidelight fluorescence signal when there is no lasing. The lower right hand oscillogram shows the POPOP laser output and the suppressed sidelight emission. The laser mix composition used in this case was 0.25 Torr POPOP, 200 Torr trans-stilbene and 5000 Torr Butane. A plot of POPOP laser energy as a function of XeF energy absorbed by the dye is shown in Fig. 3. The XeF energy absorbed was evaluated by multiplying the calibrated input energy by one minus the XeF transmission through the tube measured just after the onset of lasing. The XeF input flux was reduced using neutral density filters.
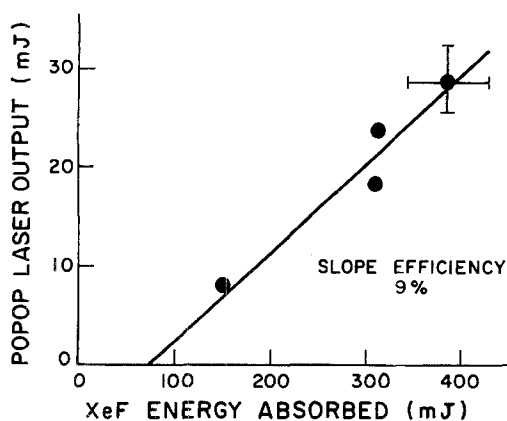
The energy efficiency evaluated for the high energy point in Fig. 3 is 7.5%. A least squares fit to the data shows a slope efficiency of 9%. The lasing efficiency measured in these experiments is comparable to those reported in [3, 4]. However, with the triplet quencher, it is possible to obtain much longer pulse durations. The data also indicates that the threshold pump flux for this system is about $170 \, kW/cm^2$.

The peak power efficiency measured was ~12%. This, however, decreases as the pulse continues. It can be seen in Fig. 2 that the POPOP laser pulse peaks early and decays relative to the XeF pump. What contributes to this decay is not clear at this time. Some indication can be obtained by looking at the fluorescence profile when there is no laser flux. Again, there is decay in the signal relative to the XeF pump. The rate constant for the quenching of the POPOP triplet state by trans-stilbene has been measured [6] and found to be $7 \times 10^{-11} \, cm^3 \, s^{-1}$. With this rate constant and the trans-stilbene pressure used, the characteristic time for quenching the triplets is 4.2 ns. Therefore, the observed relative decrease in fluorescence output is not due to triplet state build up but more likely due to photodecomposition. The loss of POPOP to this process during the 450 ns pump pulse is ~40%. This is consistent with the photodecomposition rate reported in [8].

Going to higher pressures of buffer gas will further improve the laser performance. As mentioned earlier, the dominant source of excess vibrational energy is

Fig. 3. POPOP dye laser output as a function of XeF energy absorbed

absorption of the laser flux by the excited singlet state. This limits the maximum flux density at which efficient lasing can occur. By going to buffer gas pressures in the range of 25 to 35 atmospheres (as was done in [5]), higher cavity fluxes are possible without increasing the dye vapor vibrational temperature. This will lower the excited state density thus reducing the rate of triplet formation and photodecomposition, and resulting in higher efficiencies and still longer pulse durations.

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