CHAPTER - 4
HIGHER ORDER ABSORPTIONS IN CRESYL VIOLET

4.1 Introduction

Cresyl violet is an oxazine dye belonging to the azine dye family, and absorbs strongly in the yellow-red regions of the spectrum. The structure of cresyl violet is shown in Fig.4.1a. Azine dyes are characterized by a heterocyclic ring with a nitrogen bridge as shown in Fig.4.1b, and they are classified (by the atom X) into Oxazine dyes \( X = O \), Thiazine dyes \( X = S \) and Diazine or Phenazine \( X = N \) dyes \[1\]. Oxazines are widely used as laser dyes, generally at longer wavelengths than those covered by the Rhodamines. Ethanol, methanol, ethylene glycol etc. are the recommended solvents. When pumped with the conventional \( \text{N}_2 \) laser or flashlamp, specified amounts of Rhodamine 6G or Rhodamine B may be added to these dyes for increasing the lasing efficiency by an energy transfer mechanism.

Oxazine molecules are planar and rigid like their xanthene relative, and they lase quite efficiently in the red and near infrared regions of the spectrum. They are competent substitutes for cyanines for generating tunable laser radiation in the infrared region. The position of the absorption maximum depends on the end groups of the chromophore in the same fashion as in xanthene dyes, and the fluorescence peak is shifted approximately by 30 nm for oxazine dyes in ethanol \[2\]. All oxazine dyes are photochemically much more stable than the Rhodamines. Owing to the smaller energy difference between \( S_1 \) and \( S_0 \), the influence of hydrogen vibrations at the end groups is more pronounced than in the xanthene dyes and it is comparatively difficult to suppress the processes of internal conversion. Usually triplet problems are not encountered in these dyes.

Laser action in an alcoholic solution of cresyl violet was reported for the first time by Marling et al \[3\] in 1970. With a tuned cavity, lasing was observed in the region 646 – 703 nm. Runge \[4\] demonstrated intracavity pumping of a cresyl violet solution with a He-Ne laser, where the dye acted as a mode locker for itself and the
Fig 4.1: (a) Structure of the Cresyl violet perchlorate molecule, (b) Structure of Azine dyes.
pump laser. The importance of dye purity was pointed out by Gacoin and Flamant [5] who reported a four-fold increase in the laser energy obtained from a specially purified cresyl violet solution. Continuous self mode-locking of the flashlamp pumped cresyl violet dye laser has been employed by Arthurs et al [6] to generate 3-5 ps laser pulses. Cresyl violet has a broad excited singlet state absorption spectrum, which has been investigated by Shah and Leheny [7].

The present chapter discusses the results obtained from the photoacoustic and antistokes fluorescence studies carried out in samples of cresyl violet perchlorate (CVP) dissolved in methanol and methanol:water (referred to as MW henceforth) solutions at various concentrations.

4.2 Absorption and Fluorescence properties

The recorded absorption spectrum of CVP (exciton) dissolved in methanol:water is shown in Fig.4.2. The peak absorption in the visible region is near 600 nm. We have recorded the fluorescence emission from various MW solution samples of CVP and the emission spectra corrected for the detector response are given in Figs.4.3a and 4.3b. The emission peak is found to be around 628 nm. The recorded absorption and emission spectra are in good agreement with those reported by Drexhage [2]. Due to the overlap of the absorption and emission bands in CVP, reabsorption of fluorescence occurs at higher concentrations leading to an apparent shift of the peak wavelength when observed at 90° geometry. The reabsorption effect is minimal for front surface fluorescence collection. (It may be remembered here that reabsorption of fluorescence was not observed in DCM samples). Above a certain threshold pump intensity stimulated emission starts, and the power plot obtained for fluorescence and stimulated emission is shown in Fig.4.3c. Whereas fluorescence increases almost linearly with pump energy (slope ≈ 0.8), stimulated emission is initially superlinear and saturates at higher pump energies.

4.3 Investigations by Photoacoustics: Results and Discussion

For preparing the samples, Cresyl violet perchlorate (purchased
Fig. 4.2: The Absorption spectrum obtained for a CVP + Methanol:water solution of $4.6 \times 10^{-4}$ moles/lt concentration. $\varepsilon(\lambda)$ is the absorbance. Absorption bands in the uv can be seen in the inset spectrum, which corresponds to a sample of $9.6 \times 10^{-6}$ moles/lt concentration.
Fig. 4.3a : Corrected Fluorescence emission spectra observed at 45° geometry from CVP + Methanol:water solutions. Emission peak is given in brackets. A - 1.4 \times 10^{-3} \text{ moles/lt} (635 \text{ nm}), D - 1.5 \times 10^{-4} \text{ moles/lt} (631 \text{ nm}), G - 9.6 \times 10^{-6} \text{ moles/lt} (628 \text{ nm})

Fig. 4.3b : Corrected Fluorescence emission spectra observed at 90° geometry from CVP + Methanol:water solutions. Emission peak is given in brackets. A - 1.4 \times 10^{-3} \text{ moles/lt} (640 \text{ nm}), D - 1.5 \times 10^{-4} \text{ moles/lt} (635 \text{ nm}), G - 9.6 \times 10^{-6} \text{ moles/lt} (627 \text{ nm})
Fig. 4.3c: Observed variation of Fluorescence from the samples F and G, and stimulated emission from C in CVP + Methanol:water solutions, with pump laser pulse energy.

Fig. 4.4: Modified experimental set up for PA measurements, where the laser beam diameter is initially reduced before focusing into the PA cell.
from Exciton) is dissolved in the solvents without further purification. The sample preparation method and the experimental arrangement used in the present studies are very much similar to those employed for the analysis of DCM samples, described in chapter 3. However we have used a modified configuration for the study of methanol solutions of CVP, where the laser beam is initially reduced in diameter approximately to 3.7 mm using two convex lenses. This beam is then focused by a 5 cm lens into the cell (Fig.4.4). This has been done to increase the laser intensity along the entire 5 cm beam path in the PA cell through the sample.

As seen from the absorption spectra the short wavelength tail of the first absorption band permits moderate absorption of the 532 nm pump radiation. Figs. 4.5a, 4.5b and 4.5c show the log laser pulse energy versus log PA amplitude plots obtained for the representative CVP samples dissolved in methanol. The concentration range of $4.8 \times 10^{-6}$ moles/lt to $4.6 \times 10^{-3}$ moles/lt is investigated. In Figs.4.6a and 4.6b, the same obtained for CVP + MW samples is given. The slopes of the log-log plots are calculated and plotted as a function of sample concentration in Figs.4.7a and 4.7b. When irradiated by 1064 nm radiation, for all concentrations and pump intensities the slopes are found to be very near to 1, in both solutions. The results for CVP + MW samples are shown in Fig.4.8a and 4.8b. The percentage error in the calculated slope values is estimated to be about ± 5%.

A general observation is that CVP samples give larger PA signals than the DCM samples for a given concentration and laser pulse energy. For example, when 13.5 mJ of energy at 532 nm is focused by a 5 cm lens into the PA cell containing a CVP + MW sample of $1.4 \times 10^{-3}$ moles/lt concentration, 1.66 mV of PA signal has been obtained without the preamplifier. On the other hand, a DCM + EGBA sample of the same concentration, under near identical conditions, gave only 500 µV of PA signal. Yet it is interesting to note that in general, a strong two-photon or ESA process is not indicated from the slopes in CVP samples. As compared to DCM, a relatively stronger nonradiative one-photon relaxation mechanism is found to be operative at 532 nm pump wavelength here. Hence the slopes do not increase significantly beyond 2. Moreover, the pump energy dependence of the slopes is not
Fig. 4.5: Log laser pulse energy versus log PA amplitude plots, obtained for CVP + Methanol solutions of (a) Low concentrations and (b) High concentrations, at 532 nm pumping.
Fig. 4.5c: Log laser pulse energy versus log PA amplitude plots, obtained for intermediate concentration solutions of CVP + Methanol, at 532 nm pumping.
Fig. 4.6: Log laser pulse energy versus log PA amplitude plots, obtained for CVP + Methanol:water solutions of (a) Low concentrations and (b) High concentrations at 532 nm pumping.
Fig. 4.7: Concentration dependence of the slope of the log-log plots for PA in CVP solutions at 532 nm pumping.
Fig. 4.8: (a) Log laser pulse energy versus log PA amplitude plots, obtained for CVP + Methanol:water solutions at 1064 nm pumping and (b) concentration dependence of the slopes.
very pronounced in this case, as it was for the DCM samples. Let us consider the energy level diagram of CVP shown in Fig.4.9, which is drawn from the previous absorption spectrum. The absorption is almost continuous in the uv and near uv regions, with prominent peaks situated approximately at 600 nm, 318 nm and 274 nm (16666 cm\(^{-1}\), 31447 cm\(^{-1}\) and 38486 cm\(^{-1}\) respectively). Since the 532 nm excitation is at the shorter wavelength region of the \(S_0 \rightarrow S_1\) absorption band of CVP, the molecules get excited to the higher vibrational levels of \(S_1\) (\(\approx 18800\) cm\(^{-1}\)) from which they thermalize to the lowest level of \(S_1\) (\(\approx 15900\) cm\(^{-1}\)) generating PA signals. It seems that this is the prominent mechanism of PA generation in MW solutions, as is evident from Fig.4.7b. Here most of the slopes lie between 1.2 and 1.3, indicating a predominant OPA mechanism. This is not surprising when we remember that the fluorescence quantum yield of CVP is as low as 0.5 in most solvents [8] leading to large \(S_1 \rightarrow S_0\) internal conversion rates. However, Excited state absorption (ESA) gains strength in the two lowest concentration samples at high pump energies, revealing higher slopes. It may be noted that the ESA process is stronger in methanol solutions, which is clear from the slopes nearing 2 (Fig.4.7a). This is, however, not because of any solvent effect: it results rather from the higher beam intensities available here due to the reduction of beam diameter before focusing. The slope increases towards higher concentrations in both solutions which is, in general, similar to the behaviour shown by the DCM samples.

Previous studies of ESA from the \(S_1\) level of CVP, carried out by means of saturable absorption and laser photolysis techniques have revealed that the ESA spectrum of the \(S_1\) state is a broad band that extends approximately from 2 eV (\(\approx 620\) nm) to 2.9 eV (\(\approx 428\) nm) [7]. These authors have estimated a quite significant ESA cross section of about \(1 \times 10^{-16}\) cm\(^2\) for 532 nm radiation in a methanol solution of CVP at a concentration of \(5 \times 10^{-4}\) moles/lt. The primary effect of ESA on laser performance is a reduction in fluorescence quantum efficiency whenever large pumping flux is required. The decrease in quantum efficiency is explained by the fact that this additional absorption merely recycles the molecules between the first and higher excited states.
At 1064 nm pumping, both solutions show the same behaviour: the slopes are constant around the value of one, indicating the occurrence of large overtone absorptions in the solvent and subsequent non-radiative relaxation.

4.4 Investigations by Fluorescence: Results and Discussion

The setup used for recording antistokes fluorescence from solution samples of CVP is the same as that described in chapter 3. Even though the OPA cross section at 1064 nm (8390 cm$^{-1}$) is negligible, energy-wise, the distribution of various levels is favourable for multiphoton absorption of the radiation. The corrected ASF emission spectra obtained for methanol and MW solutions of CVP are depicted in figures 4.10a and 4.10b respectively. The emission peak shift due to resorption is clearly seen at higher concentrations, and a net shift in the studied region amounts to about 20 nm. The dependence of concentration, as shown in Figs.4.11a and 4.11b. Log laser pulse energy versus log ASF plots and log laser pulse energy versus concentration curves are given in Figs.4.12 and 4.13 respectively. A distinct feature of the emission wavelength and the calculated slope of the curves is the observation that the slope becomes steeper than 5, in low concentration MW solutions (Fig.4.13b). Measurements have been taken at the peak emission wavelength and the calculated slope of the curves is estimated to be accurate within ±5%.

The range of slopes obtained from the present studies extend from 7.5 to 5, implying a maximum wavelength diffusion. Similar to that observed in DCH, these slopes also ASF intensity increases and slope decreases with concentration. Various reasons for this behaviour (stimulated emission, stimulated Raman scattering, enhanced ESA and $\chi^{(3)}$ absorption) have already been outlined in the previous chapter. In conclusion, the vibration or emitted fluorescence also can play a role in the case of CVP. However, there are a few differences too: whereas light quenching (radiation quenching) of ASF is observed in low concentrations of DCH, ASF considerably increases with pump energy in low concentrations of CVP. (In CVP+MW solution, light quenching of ASF is seen in one sample, but that is at the highest concentration studied (1.45 × 10$^{-3}$ moles/l)). The primary

Fig.4.9 : Energy level diagram for the CVP molecule.
At 1064 nm pumping, both solutions show the same behaviour: the slopes are constant around the value of one, indicating the occurrence of large overtone absorptions in the solvent and subsequent nonradiative relaxation.

4.4 Investigations by Fluorescence: Results and discussion

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The range of slopes obtained from the present studies extend from 2.5 to 5, implying large multiphoton absorptions. Similar to that observed in DCM samples, here also ASF intensity increases and slope decreases with concentration. Various reasons for this behaviour (stimulated emission, stimulated Raman scattering, enhanced ESA and \(S_0 \rightarrow S_1\) absorption) have already been outlined in the previous chapter. In addition to them reabsorption of emitted fluorescence also can play a role in the case of CVP. However, there are a few differences too: whereas light quenching (radiation quenching) of ASF is observed in low concentrations of DCM, ASF considerably increases with pump energy in low concentrations of CVP. (In CVP+MW solution, light quenching of ASF is seen in one sample, but that is at the highest concentration studied (1.45 \(\times\) 10\(^{-3}\) moles/l)). The primary
Fig. 4.10: Corrected antistokes fluorescence emission spectra observed in the right angle geometry from (a) CVP + Methanol solutions and (b) CVP + Methanol:water solutions at 1064 nm pumping.
Fig. 4.11: Increase of the antistokes fluorescence intensity with concentration for CVP solutions at 1064 nm pumping. Laser pulse energy is 100 mJ.
Fig. 4.12: Log laser pulse energy versus log ASF intensity plots obtained for CVP + Methanol solutions of (a) Low concentrations and (b) High concentrations, at 1064 nm pumping.
Fig. 4.12: Log laser pulse energy versus log ASF intensity plots obtained for CVP + Methanol:water solutions of (c) Low concentrations and (d) High concentrations, at 1064 nm pumping.
reasons for light quenching are stimulated emission and ESA and in the case of CVP it seems that the nonlinear multiphoton absorption process sections are large enough to supersede the quenching process (unlike in DCM). The high slopes seen in MW solutions support this assumption. Concentration quenching of ASF is seen only in methanol solutions (Fig.4.11a). This is due to the enhanced reabsorption, as well as the formation of closely spaced dimers. Dimer pairs [8] at high concentrations. In pure water solutions, strong quenching is expected at high concentrations, considering the presence of dimer and higher aggregates. However, it is interesting to note that in the present solutions quenching is not seen, and the ASF intensity steadily increases with concentration (Fig.4.11b). It appears that in methanol:water solution of CVP aggregates and closely spaced pairs form a negligible fraction. Further work is however required to confirm this assumption.

4.5 Conclusions

Multiphoton absorption at absorption phenomena in the laser dye Cresyl violet perchlorate have been investigated in the solvents methanol and methanol:water using photoacoustics and fluorescence techniques. The PA data reveal that large \( S_1 \rightarrow S_0 \) internal conversion barriers in the dye, which is in agreement with the low quantum yield values reported. Multiphoton absorptions at 1064 nm are found to be quite strong, especially in CVP+methanol:water solutions. Contrary to the normal expectation, aggregation effects appear to be less significant in CVP+methanol:water solutions.

Fig.4.13 : Concentration dependence of the slope of the log-log plots in (a) CVP + Methanol solutions and (b) CVP + Methanol:water solutions for ASF at 1064 nm pumping.
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Multiphoton and excited state absorption phenomena in the laser dye Cresyl violet perchlorate have been investigated in the solvents methanol and methanol:water using photoacoustics and fluorescence techniques. The PA data reveal that large $S_1 \rightarrow S_0$ internal conversion occurs in the dye, which is in agreement with the low quantum yield values reported. Multiphoton absorptions at 1064 nm are found to be quite strong, especially in CVP+methanol:water solutions. Contrary to the normal expectation, aggregation effects appear to be less significant in CVP+methanol:water solutions.
CHAPTER 4 - REFERENCES


SRS, SBS and a few other nonlinear optical phenomena result from the existence of a nonlinear polarization which is a cubic function of the electric field amplitudes present in the optical radiation. This is the lowest-order nonvanishing nonlinearity in media with inversion symmetry, in the absence of which homogeneous plane travelling waves propagate independently of each other. The nonlinearity of the...