Thermal lens spectra of aniline and certain organic dyes are described in this chapter. Two photon absorption spectrum of aniline are recorded using thermal lens technique with Optical Parametric Oscillator as the pump source. The C-H and N-H stretching overtones of aniline in liquid phase are investigated using this technique. A local mode model based on uncoupled, anharmonic X-H oscillators is used to analyze the observed spectra. The wavelength dependence of thermal lens signal of organic dyes such as rhodamine B and crystal violet are also recorded using this technique and details of which are given in this chapter.
5.1 Two photon absorption spectrum of aniline

5.1.1 Introduction

Albert Einstein in his famous discovery of the photoelectric effect reasoned that photons might ionize an atom only if they had energy greater than a particular threshold energy corresponding to the ionization energy of the atom. In 1931, Maria Göppert-Mayer [1] predicted theoretically that an atom or a molecule might absorb two or more photons simultaneously, thus allowing an atom or a molecule to be excited to states unreachable by single photon absorption. Since any observable effect of this phenomenon of multiphoton absorption could not be possible without a very intense beam of radiation, her prediction could not be investigated in detail until the invention of the first laser in 1960. Again it received relatively little consideration for practical applications because of the relatively small size of the effective cross-sections of the phenomenon for available materials. The interaction of intense monochromatic laser radiation with atoms and molecules opened a new field viz., nonlinear optical absorption spectroscopy. Two-photon absorption (TPA) is one of the important nonlinear optical phenomena which helps us in obtaining details about the excited states of molecules which are unobservable in one photon absorption (OPA) process. In this process a molecule absorbs two photons instantaneously and achieves an excited state that corresponds to the sum of the energy of the incident photons. There need not be an intermediate state for the atom to reach before arriving at the final excited state (as if it were moving up two stair steps by stepping one at a time). Thus through two-photon absorption one can populate high energy levels that are otherwise unreachable by single photon transitions from the ground state.

Kaiser and Garrett in 1961 [2] first observed TPA from Eu$^{2+}$ by monitoring fluorescence emission resulting from radiative relaxations by excited state
molecules. An important step in this regard made by Cagnac et al [3] in 1973 showed that TP excitations can be induced by relatively low power but narrow line lasers. Numerous investigations of TPA in various samples using fluorescence measurement method have been published [4-8]. Recently Brich (2001) published an excellent review on multiphoton excited fluorescence spectroscopy of bimolecular systems [9]. However, this method cannot be applied for molecules, which are nonfluorescent or those with low fluorescence quantum yield. Studies using the observation of direct optical absorption by molecules [10, 11] are also not a viable method since the magnitude of TPA cross-section is very small as compared to that in one photon absorption (OPA). Recent advances in synthesis and design of TPA materials and the advent of pulsed high power lasers have motivated a great deal of research into new technologies based on TPA induced processes [12-19]. Johnson and coworkers studied TP spectrum of substituted benzene using multiphoton ionization [20-25]. Recently Fisher and Tran reported the two photon induced fluorescence of dyes using cw TL technique with IR radiation from Ti: sapphire laser [26]. But there is serious drawback that all most all the solvents for the laser dyes have absorption in the near IR region.

Measurements using thermo-optic effect is an alternate method to identify multiphoton phenomena in nonlinear media where nonradiative de-excitation is monitored. Of the various thermo optic phenomena, optoacoustic spectroscopy and thermal lens spectroscopy are the two widely employed tools to detect very weak absorption processes [27-31]. TL effect is reported to be advantageous for investigating multiphoton absorption processes in liquids since (1) this method is very accurate in measuring weak absorption in solution (2) analysis can be done for light scattering liquids also. TL method to study TP absorption was first used by Twarowskki and Kliger to record the TL spectrum of benzene [32, 33]. Thermal lens effect has also been used to detect TPA in laser dyes by monitoring TL signal at a fixed pump beam.
wavelength [34, 37]. In certain cases, TP spectra were recorded using tunable dye lasers but each dye has only a narrow tuning range of about 5 to 20 nm in the visible part of the spectrum. [38-42].

Vibrational overtone spectrum of molecules involving X-H stretching vibrations (X=N, O, Cl etc) is now a well-established tool for information regarding molecular structure, dynamics and higher vibrational states in polyatomic molecules. Several investigations of the overtone spectra of the N-H stretching in aniline using fluorescence measurement method have been reported in the literature [43-46]. Ellis [47] performed some of the earlier work in liquid benzene by photographing the absorption spectrum. Later Martin and Kalanter [48], Hentry and Siderband [49], and Hayward and Hentry [50] have investigated the overtone spectra of substituted benzene by conventional spectroscopic technique. However this technique failed to investigate the overtone spectrum of the higher order harmonics. A higher vibronic transition has been reported in gaseous benzene by Bray and Berry [27] and in solids by Perry and Zewell [51]. Burberry and co workers using the technique of TL have identified overtones in liquid benzene and aromatic liquids [52, 53]. Rasheed et al [54] recorded fifth CH overtone of some organic molecules using thermal lens method. This chapter describes the use of TL effect to record the TP induced thermal lens spectra of aniline using tunable radiation from Optical Parametric Oscillator (OPO) as the excitation source. Optical parametric devices provide wide and continuous wavelength coverage, easy and rapid wavelength tunability, high-energy output and the advantage of being all solid-state. The sensitivity of TL technique is suitable to investigate TP induced overtone spectra of substituted benzene like aniline, toluene etc.
5.1.2 Materials
Among the benzene derivatives, the simplest amine, the aniline molecule has received particular attention because its spectroscopy is well known. Organic compounds with simple or conjugated unsaturated groups like aniline ($\text{C}_6\text{H}_5\text{NH}_2$) show characteristic bands in the UV spectrum. NH2 group is planar with the benzene ring [55]. Electronic transitions in aniline are often affected by the change in the intermolecular hydrogen bonding in suitable solvents or at low temperature. Hydrogen bonding enhances internal conversion. It has been noted that interaction between lone pair electron of nitrogen atom in NH2 group with ring $\pi$-electrons imparts $n\pi^*$ character to excited electronic states and nonradiative processes like intersystem crossing are influenced by such interaction.

5.1.3 Theory- Two photon absorption-Local mode model
The process of TPA is similar to ordinary single photon absorption but the selection rule is different [56]. To an electric–dipole approximation, two photon transitions are allowed between states of same parity whereas single photon transitions are allowed between states of different parity.

\[ \omega_1 \uparrow \quad \omega_2 \uparrow \]
\[ i \quad s \quad f \]

*Figure 5.1 TP excitation of a system from $i$ to $f$ via virtual intermediate state $s$.\*
Various theories based on perturbation theory as well as tensor theory have been made for the TPA studies [56-61]. The transition probability of two photon process was first derived by Goppert-Mayer [1] using second order perturbation theory. The two photon propagating in a nonlinear absorbing medium have the attenuation governed by the equation [61]

\[
\frac{dI_1}{dz} = -\omega_1 \gamma I_1 I_2 \\
\frac{dI_2}{dz} = -\omega_2 \gamma I_1 I
\]

(5.1) (5.2)

where two photon absorption coefficient \( \gamma \) and \( I_1 \) and \( I_2 \) are the beam intensities at \( \omega_1 \) and \( \omega_2 \) respectively.

The usefulness of the local mode (LM) model in describing the higher overtone hydrogen based vibrational stretching states of benzene and several other polyatomic molecules has been recognized by many workers [51-54, 62-65]. Progressions in the ground electronic state of overtones involving stretching motion of bonds containing hydrogen are seen to follow closely the one dimensional Birge-Sponer eqn for an anharmonic oscillator [66]. The transition energies for the prominent peaks in the overtone absorption spectra of molecules which contain X-H bonds are given as [51-53]

\[
\Delta E_{0 \rightarrow v} = \nu (A - B \nu) 
\]

(5.3)

where \( \Delta E_{0 \rightarrow v} \) is the observed energy difference between the ground state and \( \nu^{th} \) quantum level. \( A-B = X_1 \) is the mechanical frequency and \( B = X_2 \) is the anharmonicity of the X-H bond.
5.1.4 n-photon induced TL effect

Thermal lens is formed by the deposition of heat via a nonradiative decay process after laser energy has been absorbed by the sample and the focal length of the lens formed is given as [32,33]

\[
\frac{1}{f} = \frac{1}{f_0} \left( 1 + \frac{2n\tau}{t_c} \right)^{-2}
\]

(5.4)

\[
\frac{1}{f_0} = \frac{4lDN\sigma h n^2}{kJ\omega^{2n+2}}\left( \frac{dn}{dT} \right)\left( \frac{2}{\pi} \right)
\]

(5.5)

\[
t_c = \frac{\omega^2}{4D}
\]

(5.6)

\[
D = \frac{k}{\rho C_p}
\]

(5.7)

\[
H = \int_0^t p(t)dt
\]

(5.8)

where \( f \) is the time-dependent focal length of the thermal lens, \( f_0 \) is the focal length just after heating pulse, \( t_c \) is the characteristic time constant of decay, \( l \) is the sample length, \( D \) is the thermal diffusivity, \( N \) is the number of molecules, \( \sigma \) is the cross-section of absorption, \( \nu \) is the frequency of the heating laser, \( h \) is the Planck’s constant, \( n \) is the number of photons, \( H \) is the total output energy of the laser, \( k \) is the thermal conductivity, \( J \) is the Joule’s constant, \( \omega \) is the beam radius, \( \rho \) is the density, \( C_p \) is the specific heat and \( P(t) \) is the intensity of the heating laser. The probe beam interacting with the TL will be affected and the TL signal is usually measured as the relative change in the intensity at the probe beam center and is given as [34]
\[ \eta = \frac{I_{t=0} - I_{t=\infty}}{I_{t=0}} \]  

\[ = S_p = S_{(t=0)}(1 + 2t / t_c)^2 \]  

where

\[ S_{(t=0)} = \frac{5 \ln(10) AE_o \ dn}{\omega^2 \lambda \rho C_p \ dT} \]  

For n photon process [32,33]

\[ \eta = E^n \]  

where \( E \) is the energy of the incident photon. \( n \) is the number of photons involved in the absorption process. A plot of \( \log \eta \) vs \( \log E \) will give \( n \) as its slope.

5.1.5 Thermal lens Spectrum of Aniline

5.1.5.1 Experimental

Experimental setup used for the recording of thermal lens spectrum of organic compounds like aniline and dyes are described elsewhere [67]. The pump beam used for the present study is the radiation from an Optical Parametric Oscillator with tunable output in the range 450-650 nm. Freshly distilled aniline (Merck) in a quartz cuvette (1 mm) is kept one confocal length past the beam waist. The TL signal output is processed using a digital storage oscilloscope. The present work is done at a temperature of 26 °C. The thermal lens spectra are normalized to account for the spectral profile of the OPO output. The absorption spectrum of the sample is recorded using a UV-VIS-IR spectrophotometer.
5.1.5.2 Results and discussion

The present studies deals with the two photon absorption process in liquid aniline using pulsed TL technique. Absorption spectrum of aniline in the UV-VIS region recorded using a UV-VIS-IR spectrophotometer is given in figure 5.2. The spectrum does not have any peak in the visible region indicating absence of any resonant OPA. Two prominent peaks in the UV region at 220 nm and 290 nm correspond to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ related to $^1A_1 \rightarrow ^1B_2$ and $^1A_1 \rightarrow ^1B_1$ transitions respectively.

The TL spectrum of aniline is given in figure 5.3 which shows a sharp peak around 470 nm and prominent shoulder around 490 nm. In order to confirm the number of photons involved per absorption, log-log plot of TL signal strength to the pump laser power is made (figure 5.4).

![Figure 5.2. The absorption spectrum of aniline.](image)

Log-log plot of TL signal, $\eta$ vs $E$ gives a slope $n$ corresponding to the number of photons taking part in the multiphoton processes. At low pump power the
Thermal lens spectra

slope of log-log plot is around 1 while at higher laser power the slope is around 2. This means that at lower pump beam power, the phenomenon involved is OPA. However, spectrophotometric record shows absence of any such OPA processes. Hence only phenomenon responsible for OPA is overtone excitation.

Using data (Table 1) from a recent study of overtone absorption of aniline [68] it can be found that sixth and seventh overtones of ring CH stretching ($\Delta \nu = 7, 8$) lie at 531 and 475 nm while $\Delta \nu = 7$ and $\Delta \nu = 8$ bands due to NH oscillator lie at 488 and 438nm. These overtone absorptions overlap with the wavelength region of TL spectrum recorded in the present experiment. Thus at lower laser power, overtone excitations corresponding to CH and NH oscillators lead to the TL spectrum in the 460-500 nm region.

---

**Figure 5.3. Thermal lens spectrum of aniline**
At higher pump intensity, slope of log-log plot in figure 5.4 is around 2 indicating the existence of two photon absorption. The TL spectrum shows a sharp peak around 470 nm and prominent shoulder around 490 nm. As mentioned before, the absorption spectrum of aniline in the UV region (figure 5.2) shows two peaks at 200 - 250 nm and 250 - 350 nm regions matching to \( S_0 \rightarrow S_2 \) and \( S_0 \rightarrow S_1 \) transitions. TP absorptions corresponding to these transitions will be observed at 400-500 and 500-700 nm regions. Of these we get TL spectrum only in the 400-500 nm region equivalent to TPA corresponding to \( S_0 \rightarrow S_2 \) transitions. This means that transition \( S_0 \rightarrow S_2 \) corresponding to \( ^1A_1 \rightarrow ^1B_2 \) is TPA allowed while \( ^1A_1 \rightarrow ^1B_1 \) is not. This imply that \( ^1A_1 \) and \( ^1B_2 \) are of opposite symmetries and hence only OPA will be observed matching to \( ^1A_1 \rightarrow ^1B_2 \) transition. The fact that we get OP and TP absorptions corresponding to \( ^1A_1 \rightarrow ^1B_1 \) transition implies that \( ^1B_2 \) will

Figure 5.4 Log-log plot of thermal lens signal amplitude against laser power
also acquire certain symmetry characteristics of $^1A_1$ state through vibronic coupling [69-72]. Results obtained are presented in the figure 5.5.

Table 1. Local mode parameters and transition energies of the C-H and N-H oscillators in aniline [68]

<table>
<thead>
<tr>
<th>Local mode parameters</th>
<th>C-H overtone</th>
<th>N-H overtones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>$X_1$ = 3136.33</td>
<td>$X_1$ = 3549.56</td>
<td></td>
</tr>
<tr>
<td>$X_2$ = -55.83</td>
<td>$X_2$ = -77.16</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{0 \rightarrow 6}$ = 607.1</td>
<td>$\Delta E_{0 \rightarrow 6}$ = 553.9</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{0 \rightarrow 7}$ = 531.1</td>
<td>$\Delta E_{0 \rightarrow 7}$ = 487.7</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{0 \rightarrow 8}$ = 474.6</td>
<td>$\Delta E_{0 \rightarrow 8}$ = 437.8</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.5 Schematic energy level diagram showing relevant two photon and one photon absorptions (TPA, OPA) along with the overtone absorption in the case of Aniline. The level $S_2$ acquires the symmetry character of $S_0$ by vibronic coupling so that both OP and TP absorptions are possible.
5 Thermal lens spectra

5.2 Thermal lens spectrum of organic dyes using Optical Parametric Oscillator

5.2.1 Introduction

Eversince the discovery of photothermal lensing effect by Gordan et al [73] this technique of monitoring nonradiative relaxation in excited molecule has been refined by various researchers to suite for the study of various phenomena related to light-matter interactions [73-82]. Most important modification of the thermal lens technique is the dual beam method developed by Long et al [83] so that one can record the thermal lens spectrum of samples. Detection of thermal lens signal has been improved later on by incorporating optical fibre so as to introduce flexibility in the experimental configuration [84].

In this section we have studied the changes in the TL signal which results from the wavelength-dependent heating of the sample by absorption of the pump beam. A plot of these intensity changes therefore provides a characteristic signature of the absorption mechanism of the samples. Most of the studies reported earlier used tunable dye lasers as the pump beam. As mentioned before one of the drawbacks of dye lasers is the limited range of tunability. Recently Kawasaki et al recorded TL spectrum of NO₂ using OPO [85]. The present investigation describes the use of TL effect to record absorption spectrum of organic dyes in methanol using Optical Parametric Oscillator as the excitation source.

5.2.2 Materials and methods

Rhodamine B

Rhodamine B (RB) is a xanthene dye containing a carboxylic and quaternary ammonium group. RB is well known for their high fluorescence quantum
Thermal lens spectra

This dye has been used in different solvents as an active medium for tunable lasers. Therefore, the optical properties of RB in solution have attracted great attention. Molecular structure and environmental effects such as nature of solvent, pH, temperature etc control the photophysical properties of organic dyes in solution [86-105]. This compound exists in a number of neutral and ionic forms [85]. Figure 5.6 shows the structure of RB.

\[\text{Figure 5.6 Structure of rhodamine B}\]

The experimental setup is same as that used to record the TL spectrum of aniline. The absorption spectra of the sample having different concentration are recorded using a UV-VIS-IR spectrophotometer. Fluorescence spectra are recorded as described in chapter 2 section 2.5.3.

An accurately weighed amount of Rhodamine B is dissolved in methanol to give a concentration of 1.87 milli mol l\(^{-1}\). From this stock solution, sample solutions with different concentrations ranging from 2.68 micro mol l\(^{-1}\) to 460 micro mol l\(^{-1}\) are prepared. Investigations were carried out in crystal violet dye also.
5.2.3 Results and discussion

The absorption, TL and fluorescence spectra of Rhodamine B in methanol at a concentration of 2.68 micromol l\(^{-1}\) are given in figure 5.7. Absorption spectrum shows the peak absorption at 18315 cm\(^{-1}\) and a shoulder at 19380 cm\(^{-1}\) which reveals two prominent vibronic levels at 546 nm (18315 cm\(^{-1}\)) and 516 nm (19380 cm\(^{-1}\)) with intensity variation as determined by Franck Condon principle. As is clear from the figure, TL spectral peak and absorption peak do not coincide. The fact that these peaks do not coincide reveals the unequal magnitudes of radiative and nonradiative transition probabilities from the excited vibronic levels.

![Spectra of Rhodamine B](image)

Figure 5.7 Spectra of Rhodamine B for a concentration of 2.68 micro mol l\(^{-1}\) in methanol (a) absorption spectrum (b) thermal lens spectrum (c) fluorescence spectrum.
Thermal lens spectra

Excitation to 19380 cm\(^{-1}\) level is followed by nonradiative de-excitations to a large number of low-lying vibronic levels. One can conclude that probability of nonradiative de-excitations from 19380 cm\(^{-1}\) is more than that from 18315 cm\(^{-1}\) level so as to get the TL spectral peak at 19380 cm\(^{-1}\). This conclusion is also supported by the fact that fluorescence emission (and hence radiative relaxation cross-section) from this level is almost zero, as one would expect from the complementary nature of nonradiative and radiative relaxation processes. The fluorescence peak at longer wavelength accounts for the Stokes shift [90, 91]. Figure 5.8 shows the spectra of Rhodamine B in methanol at a concentration of 460 micro mol l\(^{-1}\). As is evidently observed from the figure, at higher concentration there is a relative enhancement in the TL signal as compared to that in the fluorescence spectrum.

![Figure 5.8](image)

*Figure 5.8 Spectra of Rhodamine B for a concentration of 460 micro mol l\(^{-1}\) in methanol (a) absorption spectrum (b) thermal lens spectrum (c) fluorescence spectrum.*
Red shift in the fluorescence spectral peak at higher concentration is also observed in the figure. With increasing dye concentration the possibility of transfer of energy between molecules by collisional mechanism makes the nonradiative part to become more prominent. Hence it is obvious that fluorescence quantum yield decreases as the concentration increases [35]. Increased nonradiative de-excitation processes are revealed by the relative enhancement in the TL spectrum. Enhancement in nonradiative processes with increase in concentration will also take place due to reabsorption of fluorescence emission, thereby causing the red shift in the fluorescence peak (figure 5.9). Concentration dependence of TL signal (figure 5.10) from rhodamine B at various pump wavelengths also revealed same intensity results.

![Figure 5.9 Concentration dependence of peak fluorescence wavelength of Rhodamine B.](image-url)
In solutions of low concentration, dyes dissolve practically completely into monomers. It should be mentioned that basic dyes like Rhodamine B may dissociate at high dilutions into cations and anions [85]. The absorption spectra are determined by the intrinsic absorption of the dye molecules and the dye – solvent interaction. At this concentration dye-dye interaction is negligible because of the large average distance between them. The absorption spectra (figure 5.8) contain contributions from the monomers and the aggregates, which makes the spectrum broader at higher concentration. For highly soluble dye like rhodamine B the solute - solute interaction becomes prominent at high concentrations since the mean distance between them becomes small [35].

Figure 5.10 Variation of TL signal amplitude with concentration for different pump wavelengths in nm (•) 520 (○) 540 (♦) 560 (♀) 570 (+) 574 and (▼)580.
On increasing the concentration of dye solution, the aggregate formation and reabsorption of fluorescence emission will result into the enhancement in absorption and nonradiative relaxations at higher wavelengths. This will enhance the TL signal.

5.3 Thermal lens spectrum of Crystal Violet (CV)

Crystal violet dye is derived from triphenylmethane are usually salts with OH or NH$_2$ in the pra positions with respect to the methane carbon. This dye is fairly reactive and can be easily converted to the free base on treatment with alkali or reduced to leuco form in a variety of ways. This dye is blue-violet in colour and broad absorption around 590 nm. The structure of the dye is shown in figure 5.11. This dye has many interesting features, which depends on its structure such as (1) the influence of concentration on the spectra and (2) the effect of interaction with a substrate and photochemistry. The absorption spectra of dilute aqueous solutions of CV ($10^{-7}$ M) consists of a single absorption maximum around 594 nm ($\alpha$ band).

![Figure 5.11 Structure of Crystal violet.](image)
Figure 5.12 Absorption (a) and thermal lens (b) spectra of crystal violet for a concentration of 65 micro mol l⁻¹.

Figure 5.12 shows the absorption and TL spectrum of crystal violet dye. In contrast to the TLS of rhodamine B dye, absorption and the TL spectra of CV have the same profile and their peak coincides. This indicates that unlike in the case of rhodamine B, there are no intermediate vibronic levels from which nonradiative de-excitation becomes prominent. CV has very low fluorescence quantum efficiency so that the nonradiative relaxation is the major channel by which molecules relax to the ground state.

5.4 Conclusion

We have demonstrated the efficiency and usefulness of pulsed TL technique to study the multiphoton process in nonfluorescent materials. TL spectrum of aniline has been recorded in the 460-500 nm region using radiation from an OPO as the excitation beam. The C-H and N-H stretching overtones of aniline are investigated using this technique. Results show that \(^1B_2\) acquires same
symmetry characteristics of $^1A_1$ through vibronic coupling. The nature of variation of TL signal amplitude with laser power clearly confirms the occurrence of two photon absorption in aniline. One of the important features of TL-based investigations is its effectiveness to study weak optical absorption arising due to weak phenomena like overtone absorption, singlet-triplet absorption, multiphoton absorption etc.

Our studies using optical parametric oscillator on organic dyes show that the simultaneous analysis of TL, absorption and fluorescence spectra will be helpful to understand relative magnitudes of nonradiative and radiative de-excitation probabilities from the excited states. TL signals from higher wavelength region (560-590 nm) get enhanced at higher concentration. This is due to increased nonradiative de-excitation probability on increasing the concentration.

References

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5 Thermal lens spectra