Chapter 2

Experimental Methods

This chapter presents a brief introduction to the experimental techniques which are employed in the present work.

2.1. Introduction

There are several characterization techniques available for measuring the third-order optical nonlinearities: these include degenerate four-wave mixing, nearly degenerate three-wave mixing, optical Kerr effect, ellipse rotation, interferometric methods, two-beam coupling, beam self-bending and third harmonic generation [7, 84]. The above methods are potentially sensitive techniques, but they are complex. Among the available techniques, z-scan technique offers simplicity as well as very high sensitivity in measuring the third-order optical nonlinearity and also allows computing the contributions of nonlinear absorption and nonlinear refraction towards the nonlinearity. Therefore, single beam z-scan technique was chosen for evaluating the third-order optical nonlinearity of the dyes and conducting polymers in the present research work.

2.2. Z-scan technique

2.2.1. Principle

Z-scan technique is based on the principle of spatial beam distortion. It was originally proposed by Sheik-Bahae et al. [84, 85] has been since then implemented and applied to the study of third-order optical nonlinearity [86, 87]. Using z-scan technique, the magnitude of nonlinear absorption and the sign and magnitude of nonlinear refraction can be determined simultaneously. When a high intensity laser beam propagates through a material, induced refractive index changes leads to self-focusing or defocusing of the laser beam. This enables to determine the third-order nonlinear optical properties of various materials in liquid, thin film or crystal forms.

In this technique, the sample under investigation is moved along the tightly focused Gaussian laser beam. The intensity of the laser beam changes as the sample is
moved. This is because the sample experiences different intensities, depending on the position of the sample relative to focus (z=0). The power transmitted through the sample is measured by translating the sample along the z-direction through the beam waist of a focused beam and hence the name z-scan. In our experiments a continuous wave He-Ne laser operating at 633 nm was used. The laser beam was focused using a 5 cm focal length lens. The beam waist is found to be 36.78 µm which can be calculated using the formula,\( \omega_0 = 1.22 \lambda f / d \), where \( \lambda \) is the wavelength of laser, \( f \) is the focal length of the lens and \( d \) is the diameter of laser beam. Another parameter known as Rayleigh length or Rayleigh range is defined as, the distance along the propagation direction of a laser beam from the waist to the place where the area of cross section is doubled. The Rayleigh length is estimated to be 6.71 mm which can be calculated using the formula, \( z = 2\pi\omega_0^2 / \lambda \).

The two important parameters required to determine the \( \chi^{(3)} \) is nonlinear refractive index \( n_2 \) and nonlinear absorptive coefficient \( \beta \). The nonlinear refractive index \( n_2 \) can be determined by performing closed aperture z-scan experiments and similarly the nonlinear absorptive coefficient \( \beta \), can be determined by performing open aperture z-scan experiments. A brief description on the open and closed aperture z-scan is given below.

### 2.2.2. Open aperture z-scan

When a Gaussian laser beam is incident on a nonlinear medium, it induces profound changes in the optical properties of the medium. Nonlinear absorption refers to the change in transmittance of the medium as a function of intensity or fluence. By performing the open aperture z-scan experiment, the nonlinear absorption coefficient \( \beta \) of the nonlinear medium can be computed. Figure 2.1 shows the schematic z-scan experimental set up used for the experiments.

In open aperture z-scan experiments, aperture (S = 1) is insensitive to nonlinear refraction. That is, there is no aperture in front of detector 2. The z-scan traces obtained with no aperture is expected to be symmetric with respect to the focus (z=0) where the transmittance is minimum.

In this experiment, the sample is made to traverse from one end of the farfield to the other end through the focus (z = 0). At the farfield, the intensity is low and
hence linear absorption occurs. In other words, the intensity is not sufficient to induce any nonlinear absorption in the farfield region. A graph of normalized transmittance along y-axis and the sample position along x-axis is plotted.

When the sample approach focus, the measured transmittance in detector either decreases or increases, forming a valley or peak at the focus. The process in which the measured transmittance forms a valley at the focus is known as reverse saturable absorption and is shown in figure 2.2 (a). The process in which the measured transmittance forms a peak at the focus is known as saturable absorption and is shown in figure 2.2 (b). The saturable absorption is also known as negative type of
absorption nonlinearity and reverse saturable absorption is known as positive type of absorption nonlinearity. Using the open aperture z-scan traces, the coefficient of nonlinear absorption is determined and it is related to the imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}$.

![Figure 2.2. Open aperture z-scan traces (a) saturable absorption and (b) reverse saturable absorption curves.](image)

### 2.2.3. Closed aperture z-scan

Closed aperture z-scan experiment is performed to measure the nonlinear index of refraction $n_2$. Nonlinear refraction is the phenomenon where the refractive index of medium varies at high intensity or fluence. In closed aperture z-scan experiment, an aperture is placed in front of detector 2. The experimental set up used for evaluating $n_2$ is shown in figure 2.3.

When a Gaussian laser beam is made to pass through the material medium, it acts like an intensity dependent lens. Along the beam path, the effective focal length of medium changes due to the change in input intensity. This results in the intensity distribution at the far field aperture. The amount of energy transmitting through the aperture depends on the sample location on the z-axis and on the sign of nonlinear refractive index $n_2$.

This can be explained by taking an example. Consider a material with negative refractive index $n_2$ and thickness less than Rayleigh length. When the sample is far from the focus that is at the farfield, the intensity of the beam is not strong enough to
cause any nonlinearity within the sample and the measured power on the detector remains approximately constant (figure 2.4 (a)). As the sample translates towards focus, the nonlinear absorption and refraction enhances and thus the sample acts like a variable lens. The sample will diverge the beam passing through it and a small amount of light will fall on the detector, resulting in increase in measured transmittance (figure 2.4 (b)).

Figure 2.3. (a) Schematic closed aperture z-scan setup and (b) closed aperture z-scan setup used in present work. D-Detector, S-Sample, L-Lens, A1 & A2-Aperture.

When the sample is at focus (figure 2.4 (c)), the lensing effect will be profound. However, the sample will not have any effect on the beam. As the sample moves away from the focus, the strength of the refraction decreases due to lower intensity.
This results in decrease in measured transmittance (figure 2.4 (d)). Finally, when the sample reaches farfield, the intensity is weak to initiate nonlinearity, so the measured power on the detector remains constant (figure 2.4 (e)). The prefocal transmittance maximum (peak) followed by post focal transmittance minimum (valley) behaviour is the characteristic of a material with a negative nonlinear refractive index. On the other hand, a valley followed by a peak is the characteristic of a positive nonlinear refractive index as shown in figure 2.5.

Figure 2.4. Depicting the graphical z-scan experiment, used to measure the optical nonlinearities.

The sign of the nonlinear refractive index $n_2$ is thus immediately clear from the shape of the graph. But the sign of nonlinear refractive index is not easily obtained in other techniques.
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Figure 2.5. Closed aperture z-scan transmittance curve depicting self-focusing and defocusing nature.

The above illustrated example is applicable only for ideal case, where the nonlinear absorption is neglected. But in most practical situations, the measured transmission will be more complex that is nonlinear refraction will occur in conjunction with nonlinear absorption [88, 89]. The sensitivity of nonlinear refraction is entirely due to the aperture, and removal of aperture completely eliminates the effect. Generally saturable absorption and reverse saturable absorption will modify the peak and valley characteristics. Saturable absorption enhances the peak and suppresses the valley, whereas reverse saturable absorption enhances the valley and suppresses the peak. This can be deduced by performing open aperture z-scan experiment. To extract pure nonlinear refraction traces, closed aperture data must be divided with the open aperture data. The data with open and closed aperture z-scan and the resultant data after division are shown in figure 2.6.
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Figure 2.6. (a) closed aperture z-scan trace, (b) open aperture z-scan trace and (c) closed/open aperture z-scan trace.

2.2.4. Theoretical analysis of open aperture z-scan traces

The nonlinear absorption is related to the imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}$ through the relation [84, 85],

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)},$$  \hspace{1cm} (2.1)

with the imaginary part related to the two-photon absorption coefficient $\beta$, through the relation [84, 85],

$$\chi_I^{(3)} = \frac{n_0^2 e_0 c \lambda \beta}{2\pi},$$  \hspace{1cm} (2.2)
where $n_0$ is the linear refractive index, $\varepsilon_0$ is the permittivity of vacuum, $c$ is the speed of light and $\lambda$ is the wavelength of laser used. The nonlinear index of refraction $n_2$ in esu is related to $\gamma$ in $m^2/W$ by [84, 85],

$$n_2(\text{esu}) = \left(\frac{cn_0}{40\pi}\right)\gamma (m^2/W).$$  (2.3)

The real part of $\chi^{(3)}$ is related to the nonlinear index of refraction $\gamma$ by [84, 85],

$$\chi_R^{(3)} = 2n_0^2 \varepsilon_0 c \gamma;$$  (2.4)

The intensity dependent nonlinear absorption can be expressed as [84, 85, 90],

$$\alpha(I) = \alpha + \beta I,$$  (2.5)

$$\frac{dI}{dz} = -\alpha(I)I,$$  (2.6)

where $\alpha$ is the linear absorption coefficient and $\alpha (I)$ includes linear and nonlinear absorption terms. The above equations (2.5) and (2.6) yield the irradiance distribution and phase shift of the beam at the exit surface of the sample as [84, 85],

$$I_e(z, r, t) = \frac{I(z, r, t) e^{-\alpha L}}{1 + q(z, r, t)}, \text{ and}$$  (2.7)

$$\Delta\phi(z, r, t) = \frac{k\gamma}{\beta} \ln [1 + q(z, r, t)],$$  (2.8)

where $q(z, r, t) = \beta I(z, r, t) \text{ L}_{\text{eff}}, z$ is the sample position, $\text{L}_{\text{eff}}$ is the effective length of the sample expressed as, $\text{L}_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, $L$ is the actual length of the sample. By combining the equation (2.7) and (2.8) the complex field at the exit surface of the sample can be determined [84, 85],

$$E_e = E(z, r, t) e^{-\alpha L/2} \left(1 + q\right)^{(ik/\beta - 1/2)},$$  (2.9)

$$E_e(r, z, t) = E(z, r, t) e^{-\alpha L/2} e^{i\Delta\phi(z, r, t)},$$  (2.10)
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Equation (2.9) reduces to (2.10) when two-photon absorption does not occur. In general, a zeroth-order Hankel transform of equation (2.10) gives the field distribution at the aperture which is used in equation (2.8) and (2.10) to yield the transmittance [84, 85],

\[
P_t(\Delta \phi_0(t)) = c e_0 n_r \pi \int_0^r |E_z(r,t)|^2 \, rdr,
\]

\[
T(z) = \frac{\int_{-\infty}^{\infty} P_t(\Delta \phi_0(t)) \, dt}{S \int_{-\infty}^{\infty} P(t) \, dt},
\]

where \( P_t(t) = \pi \omega^2_0 I_0(t) / 2 \), is the instantaneous input power and \( S = 1 - \exp(-2r^2 / \omega^2_0) \), is the aperture linear transmittance with \( \omega_0 \) denoting the beam radius at the aperture in the linear regime. Following the binomial series expansion in power of \( q \), equation (2.9) can be expressed as an infinite sum of Gaussian beams for \( |q| < 1 \) as [84, 85],

\[
E(z,r,t) = E(z,r,0,t) e^{-\omega_0^2 z^2 / 2} \sum_{n=0}^{\infty} q(z,r,t)^n \frac{\omega_{m0}}{m!} \prod_{n=0}^{\infty} \left[ i \frac{\omega_0 \gamma}{\beta} - 1 \right] \left( - \frac{r^2}{\omega_m^2} \right) \left( \frac{i k r^2}{2 R_m} + i \theta_m \right),
\]

where the Gaussian spatial profiles are implicit in \( q(z,r,t) \) and \( E(z,r,0,t) \). The complex field pattern at the aperture plane can be obtained and the result can be represented by [84, 85],

\[
E_a(r,t) = E(z,r,0,t) e^{-\omega_0^2 z^2 / 2} \sum_{m=0}^{\infty} \frac{i \Delta \phi_m(z,t)^m}{m!} \frac{\omega_{m0}}{\omega_m} \exp \left( - \frac{r^2}{\omega_m^2} - \frac{i k r^2}{2 R_m} + i \theta_m \right),
\]

where \( d \) is the propagation distance in free space from the sample to the aperture plane and \( g = 1 + \frac{d}{R(z)} \), and

\[
\omega_{m0}^2 = \frac{\omega^2(z)}{2m+1},
\]

\[
d_m = \frac{k \omega_{m0}^2}{2},
\]

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\[ \omega_m^2 = \omega_0^2 \left[ g^2 + \frac{d^2}{d_m^2} \right], \]

\[ R_m = d \left[ 1 - \frac{g}{g^2 + d^2 / d_m^2} \right]^{-1}, \]

\[ \theta_m = \tan^{-1} \left( \frac{d / d_m}{g} \right). \]

If we substitute the \((i\Delta \varphi_0(z, t))^{m/m!}\) terms in the sum by [84, 85],

\[ f_m = \frac{(i\Delta \varphi_0(z, t))^{m/m!}}{m!} \prod_{n=0}^{m} \left( 1 + i(2n-1)\frac{\beta}{2k\gamma} \right), \quad (2.15) \]

with \(f_0 = 1\). The coupling factor \(\beta/2k\gamma\) is the ratio of the imaginary to real parts of the third-order nonlinear susceptibility \(\chi^{(3)}\).

The z-scan transmittance variations can now be calculated. From equation (2.15), it is apparent that the absorptive and refractive contributions to the far field beam profile and hence the z-scan transmittances are coupled. Without the presence of aperture, the z-scan transmittance is insensitive to beam distortion and it is only a function of the nonlinear absorption. The total transmitted fluence for \(S = 1\), can be obtained by spatially integrating equation (2.7) without including the free space propagation process. By integrating equation (2.7) at \(z\) over \(r\), the transmitted power \(P(z, t)\) can be obtained as [84, 85],

\[ P(z, t) = P_i(t) e^{-\alpha t} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)}, \quad (2.16) \]

where \(q_0(z, t) = \beta I_0(t) L_{eff} / \left( 1 + z^2 / z_0^2 \right)\), and \(P_i(t)\) was defined in equation (2.12). For a temporally Gaussian pulse, equation (2.16) can be time integrated to give the normalized energy transmittance [84, 85],

\[ T(z, S=1) = \frac{1}{\sqrt{\pi q_0(z, 0)}} \int \ln[1 + q_0(z, 0)e^{-r^2}] d\tau, \quad (2.17) \]
For \(|q_0| < 1\), this transmittance can be expressed in terms of the peak irradiance as \([84, 85]\),

\[
T(z, S=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{\frac{1}{2}}} ,
\]

(2.18)

Thus from the open aperture (S = 1) z-scan experiment, the nonlinear absorption coefficient \(\beta\) can be deduced.

### 2.2.5. Theoretical analysis of closed aperture z-scan traces

For a cubic nonlinearity, the index of refraction \(n\) can be expressed in terms of nonlinear indexes \(n_2\) or \(\gamma\) through the relation \([84, 85]\),

\[
n = n_0 + \frac{n_2}{2} |E|^2 = n_0 + \gamma I ,
\]

(2.19)

where \(n_0\) is the linear refractive index, \(E\) is the peak electric field and \(I\) is the irradiance of laser beam within the sample.

For a TEM\(_{00}\) Gaussian beam of beam waist radius \(\omega_0\) travelling in +z direction, the electric field is expressed as \([84, 85]\),

\[
E(z, r, t) = E_0(t) \frac{\omega_0}{\omega(z)} \exp \left( -\frac{r^2}{\omega^2(z)} - \frac{ikr^2}{2R(z)} \right) e^{-i\phi(z,t)} ,
\]

(2.20)

where \(\omega^2(z) = \omega_0^2 \left( 1 + z^2/z_0^2 \right)\) is the beam radius, \(R(z) = z \left( 1 + z_0^2/z^2 \right)\) is the radius of curvature of the wave front at \(z\), \(z_0 = k\omega_0^2/2\), is the diffraction length of the beam and \(k = 2\pi/\lambda\) is the wave vector. \(E_0(t)\) represents the radiation electric field at the focus and it contains temporal envelope of the laser pulse. The term \(e^{-i\phi(z,t)}\) contains radially uniform phase variations. As the radial phase variations \(\Delta\phi\) (r) are concerned, the slowly varying envelope approximation (SVEA) is applied and all other phase changes that are uniform in ‘r’ are ignored.

If the sample length is small then the changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected and the
medium is regarded as “thin”. For linear diffraction, $L \ll z_0$, while for nonlinear refraction it is $L \ll z_0/\Delta \varphi (0)$. For all the $z$-scan experiments the second criteria is met as $\Delta \varphi$ is small. For the amplitude $\sqrt{I}$ and phase $\varphi$ of the electric field as a function of $z'$ are governed by the slowly varying envelope approximation with equations (2.6) and

$$\frac{d\Delta \phi}{dz} = \Delta n(I)k,$$  \hspace{1cm} (2.21)

where $z'$ is the propagation depth in the sample. In the case of cubic nonlinearity and negligible nonlinear absorption, equation (2.6) and (2.21) are solved to give the phase shift $\Delta \varphi$ at the exit surface of the sample. This follows the radial variation of the incident irradiance at the sample position $z$ and is given by [84, 85],

$$\Delta \varphi(z, r, t) = \Delta \phi_0(z, t) \exp \left( -\frac{2r'^2}{\omega^2(z)} \right),$$  \hspace{1cm} (2.22)

with

$$\Delta \phi_0(z, t) = \frac{\Delta \Phi_0(t)}{1 + z^2/z_0^2},$$  \hspace{1cm} (2.23)

$\Delta \Phi_0(t)$, the on-axis phase shift at the focus, is defined as [84, 85],

$$\Delta \Phi_0(t) = k\Delta n_0(t) L_{\text{eff}},$$  \hspace{1cm} (2.24)

Here $\Delta n_0 = \gamma I_0(t)$, with $I_0(t)$ being the on-axis irradiance at focus ($z=0$). The complex electric field exiting the sample $E_e$ contains the nonlinear phase distortion [84, 85],

$$E_e(r, z, t) = E(z, r, t) e^{-at^2} e^{i\Delta \phi(z, r, t)},$$  \hspace{1cm} (2.25)

By virtue of Huygen’s principle, the farfield pattern of the beam at the aperture plane through a zeroth-order Hankel transformation of $E_e$ can be obtained. By using the Gaussian decomposition method given by Weaire et al. [91], the complex electric field at the exit plane of the sample is decomposed into a summation of Gaussian beams through a Taylor series expansion of the nonlinear phase term $e^{i\Delta \phi(z, r, t)}$ in equation (2.25). That is,
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\[ e^{i\Delta \phi(z, r, t)} = \sum_{m=0}^{\infty} \frac{[i\Delta \phi_{0}(z, t)]^m}{m!} e^{-2mr^2/w^2(z)}, \quad (2.26) \]

Each Gaussian beam can now be simply propagated to the aperture plane where they will be resumed to reconstruct the beam. When including the initial beam curvature for the focused beam, the resultant electric field pattern at the aperture can be expressed as in equation (2.14). The expression (2.14) is a general case derived by Weaire et al., where a collimated beam (R = \infty) for which g = 1. The transmitted power through the aperture is obtained by spatially integrating \( E_a(\mathbf{r}, t) \) up to the aperture radius \( r_a \), giving equation (2.11). By including the pulse temporal variation, the normalized \( z \)-scan transmittance \( T(z) \) is expressed as equation (2.12).

For further analysis, a steady state result is considered that is an instantaneous nonlinearity and a temporal square pulse. This is equivalent to considering CW radiation. For a given \( \Delta \phi_0 \), the magnitude and shape of \( T(z) \) does not depend on the geometry or wavelength, as long as the far-field condition for the aperture plane, \( d >> z_0 \) is satisfied. The aperture size \( S \), is an important parameter since a large aperture reduces the variations in \( T(z) \). This reduction is more prominent in the peak transmittance which cannot exceed (1-S). For very large aperture or no aperture (\( S=1 \)), the effect vanishes and \( T(z) = 1 \) for all \( z \) and \( \Delta \phi_0 \). For small \( |\Delta \phi_0| \), the peak and valley occur at the same distance with respect to focus. For cubic nonlinearity, this distance is found to be \( \approx 0.86 \) \( z_0 \). With large phase distortions (\( |\Delta \phi_0| > 1 \)), equation (2.11), (2.12) and (2.13) shows that this symmetry no longer holds and the peak and valley move towards \( \pm z \) for the corresponding sign of nonlinearity (\( \pm \Delta \phi_0 \)). Such that their separation remains nearly constant and is given by,

\[ \Delta Z_{p-v} \approx 1.7z_0, \quad (2.27) \]

The measurable quantity \( \Delta T_{p-v} \) is defined as the difference between the normalized peak and valley transmittance \( T_p - T_v \). The variation of \( \Delta T_{p-v} \) is found to be linearly dependent on \( |\Delta \phi_0| \) (figure 2.7). For small phase distortion and small aperture (\( S \approx 0 \)),

\[ \Delta T_{p-v} \approx 0.406|\Delta \phi_0|, \quad (2.28 \text{ a}) \]
Numerical calculations show that this relation is accurate to within 0.5 percent for $|\Delta \Phi_0| \leq \pi$. For large apertures, the linear coefficient 0.406 decreases such that with $S = 0.5$, it becomes $\approx 0.34$, and at $S = 0.7$, it reduces to $\approx 0.29$. In our experiments the value of $S$ is 0.7. Based on numerical fitting, the following equation can be used to include such variations within ±2% accuracy,

$$
\Delta T_{p-v} \approx 0.406(1 - S)^{0.25} |\Delta \Phi_0| \quad \text{for} \quad |\Delta \Phi_0| \leq \pi
$$

(2.28 b)

Equations (2.28 a) and (2.28 b) is used to estimate the nonlinear index ($n_2$) with good accuracy after the z-scan experiment is performed. These expressions reveal the high sensitive nature of z-scan technique. The steady-state results to include transient effects induced by pulsed radiation by using the time-averaged index change $< \Delta n_0 (t) >$ through equation (2.24). With a nonlinearity having instantaneous response and decay times relative to the pulse width of laser, for a temporally Gaussian pulse [84, 85],

$$
< \Delta n_0 (t) > = \frac{\int_{-\infty}^{\infty} \Delta n_0 (t) I_0 (t) dt}{\int_{-\infty}^{\infty} I_0 (t) dt},
$$

(2.29)

The time-averaged $< \Delta \Phi_0 (t) >$ is related to $< \Delta n_0 (t) >$ through equation (2.24). All these equations obtained are based on a cubic nonlinearity. A similar analysis can be performed for higher order nonlinearities. Following the above steps, a similar result for third-order nonlinearity is obtained by [84, 85],

Figure 2.7. Graph illustrating the meaning of $\Delta T_{p-v}$. 

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The time-averaged $< \Delta \Phi_0 (t) >$ is related to $< \Delta n_0 (t) >$ through equation (2.24). All these equations obtained are based on a cubic nonlinearity. A similar analysis can be performed for higher order nonlinearities. Following the above steps, a similar result for third-order nonlinearity is obtained by [84, 85],
\[ \Delta T_{p-v} \approx 0.21(1 - S)^{0.25} |\Delta \Phi_0| \]  

(2.30)

In conclusion, single beam z-scan is a simple and sensitive technique. Using z-scan technique, the magnitude and sign of the nonlinear absorption and nonlinear refraction can be determined simultaneously.

### 2.2.6. Advantages and disadvantages of z-scan technique

**Advantages:**

1. It is simple and very sensitive technique to measure the nonlinear refraction and absorption coefficients.
2. It has no difficult alignment other than beam aligning on the aperture.
3. It can be used to determined sign and magnitude of \( n_2 \).
4. Data analysis is quick and simple.
5. It can determine both real and imaginary parts of \( \chi^{(3)} \).
6. Z-scan can also be modified to study nonlinearities of higher order contributions.

**Disadvantages:**

1. It requires a high quality Gaussian TEM\(_{00}\) beam for absolute measurements.
2. The analysis must be different if the beam is non-Gaussian.
3. Sample distortions, tilting of sample during translation, can cause the beam to walk off the far field aperture.
4. The introduction of second beam of different frequency requires careful alignment of the two beams.

### 2.3. Optical power limiting measurements

The development of lasers marked remarkable changes in the science and technology and led to a wide variety of applications in research, industry, medical and military
fields. The recent development of powerful and wide wavelength range laser sources necessitates the protection of sensors, optical components and human eyes against the high intensity. The primary aim of the protective device is to block the hazardous intensity reaching the sensor without the device being opaque. The device should possess good linear transmission at low intensity light so that some parts of the ambient visible light transmits through the material [92].

Optical limiter is the one which display decrease in transmittance as a function of fluence or intensity. An ideal optical limiter exhibits a linear transmission below a limiting threshold value and above that it clamps the output to a constant value protecting the sensors. The working of an ideal optical power limiter is shown in figure 2.8.

![Figure 2.8. Schematic diagram of ideal optical limiter.](image)

The criteria required for a material to act as a possible optical limiter is [93],

- Low limiting threshold,
- High optical damage threshold and good stability,
- Fast response time,
- High linear transmittance,
• Broad band spectral response,

• Optical clarity and robustness.

After a certain threshold value known as limiting threshold, the transmitted power decreases and deviates from linear regime. The limiting threshold can be defined as the incident power at which the sample transmittance falls to 50% of the linear transmittance. Further increase in the input power, the transmitted power attains a steady value and clamping of input power takes place. This process is known as optical clamping. With the further increase in the input power, the transmitted power saturates to a constant value and the optical damage value can be determined.

The first experimental optical power limiter was demonstrated by Leite et al. [90], based on the laser induced thermal lens effect using 488 nm CW Ar+ laser beam with an aperture in front of the detector. The change in the power through the aperture was only 3% of the total input power, this idea and setup is still the basis of most optical limiting experiments. Optical limiting can be achieved by means of various nonlinear mechanisms viz., self-focusing, self-defocusing, induced scattering, induced refraction, induced aberration, excited state absorption, two-photon absorption, photo refraction and free carrier absorption in the nonlinear medium [93, 94]. The optical limiting devices are divided in to two categories (i) energy spreading and (ii) energy absorbing type.

2.3.1. Energy spreading optical limiter

In this type an aperture or pinhole is placed in front of the detector. The limiting effect is based on the changes in spatial energy distribution of the transmitted beam. With the increase in input intensity or fluence, the laser beam spreads and decreases the amount of light entering the aperture.

Figure 2.9 illustrates the various energy spreading optical limiting devices. In all cases, the limiting behaviour depends on the input laser intensity, nonlinear medium, pinhole or aperture and the geometry of the optical system. The size of the aperture is chosen such that for a low input intensity, the transmitted beam after passing through the medium just passes through the aperture without blocking. Figure
2.9 (a) and (b) represents self-focusing and defocusing type. In both cases, at high
input energy levels, the detected energy is significantly reduced due to the energy
spreading in the aperture. Figure 2.9 (c) shows the optical limiter based on laser
induced and intensity dependent scattering. Here the medium is a system of linearly
absorbing particles, randomly distributed in a transparent host material. For an input
beam with low intensity, the temperature and refractive index changes are neglected.
At higher input intensity, the absorption induced temperature changes is no longer
negligible and each particle becomes an individual center. Due to this local heating,
the medium becomes highly inhomogeneous and major amount of energy will spread
out in to a wider range and the amount of light passed through the aperture will be
limited [95-97].

Figure 2.9. Illustrating the energy spreading type of optical limiters.

Figure 2.9 (d) also uses a similar concept, where the medium is a mixed system
composed of two components, one is liquid and other is solid and they have same
static refractive index but are in different phases. Figure 2.9 (e) is based on induced
aberration. The induced refractive index change is a function of the local intensity
distribution of the laser beam inside the medium. An irregular spatial distribution of
light intensity may lead to random refractive index change at higher intensity levels, which causes aberration. By placing a small pinhole in the focal plane of a lens, the amount of energy passing through the pinhole will decrease as the induced aberration increases [7, 98].

When compared with various optical effects related to refractive index changes, the thermo-optic induced refractive index change is of important. The main causes for thermally induced refractive index change are;

- The presence of small amount of impurities giving rise to a non-zero residual linear absorption in transparent and non-resonantly absorptive medium. At high intensity, the linear absorption will be strong and leads to changes in the thermally induced refractive index.

- For resonant and linearly absorbing medium, thermally induced refractive index change will be weak for a CW laser beam.

### 2.3.2. Energy absorbing optical limiter

Optical limiting is also achieved by employing the nonlinear absorption mechanism without using an aperture or pinhole in the experiment; here optical limiting relies on the transmittance of the nonlinear medium. The major nonlinear absorption mechanism that leads to optical limiting is reverse saturable absorption [99-103]. The optical limiting based on this mechanism is referred as energy absorbing type of optical limiters. Figure 2.10 shows the schematic representation of energy absorbing type of optical limiter. In organic materials, the optical limiting arises due to the nonlinear process two-photon absorption and excited state absorption. In semiconductors, metals and metal nanoparticles, the optical limiting is due to two-photon absorption and free carrier absorption process [92].

![Figure 2.10. Schematic optical limiting device based on nonlinear absorption.](image)
Third-order optical nonlinearity and optical power limiting of Organic materials under CW laser illumination

Figure 2.1. (a) Schematic optical power limiting set up and (b) optical power limiting set up used in present work. D-Detector, S-Sample, L-Lens, NDF-Neutral Density Filter, A1-Aperture.

In the current investigation, the experimental setup used to evaluate the optical power limiting of organic materials is energy absorbing type. The schematic experimental set up used for the optical power limiting measurement is shown in figure 2.11 (b).

2.4. Spectroscopic techniques used for material characterizations

The spectroscopic techniques used for the evaluating the optical materials are,

- Ultraviolet-Visible (UV-VIS) spectroscopy,
- Fourier Transform Infrared (FTIR) spectroscopy and
- Linear refractive index measurements
2.4.1. Ultraviolet-Visible (UV-VIS) spectroscopy

The UV-VIS spectroscopy is one of the oldest instrumental techniques used for the analysis of analytes in a sample. Figure 2.12 shows the UV-VIS spectroscopic instrument used. To obtain a UV-VIS spectrum, the sample is irradiated with the electromagnetic radiation varied over a range of wavelength. The amount of the radiation absorbed at each wavelength is measured and plotted against the wavelength to obtain the spectrum. Thus, a typical UV spectrum is a plot of the intensity of absorption versus wavelength or frequency. The UV spectra are characterised by two major parameters, namely, the position of the maximum of the absorption band called $\lambda_{\text{max}}$ and the intensity of the bands. The $\lambda_{\text{max}}$ refers to the wavelength at which absorption is maximum and is a measure of the difference in the electronic energy levels involved in the transition. The intensity on the other hand is indicative of the probability of the transition i.e., whether the transition is allowed or not. It also depicts the concentration of the absorbing material [104, 105].

![Figure 2.12. UV-VIS spectrophotometer used in present work.](image)

2.4.2. Fourier transform infrared (FTIR) spectroscopy

Infrared spectroscopic technique is used for organic and inorganic materials for structure elucidation and compound identification [105]. The bond between two atoms in a molecule is not rigid. It has elasticity and as a consequence the atoms in the
molecule do not remain fixed in their positions. They are in a constant state of motion around their mean position. The molecule is said to be undergoing vibrational motion. The quantum mechanical treatment of the molecular vibrational motion shows that it is quantised. As the transitions between these quantised energy levels takes place by the electromagnetic radiation in the infrared range gives rise to an IR spectrum. Since the excitation among the quantised vibrational energy levels of the molecules are involved, the IR spectroscopy is also known as vibrational spectroscopy.

Among the available types of IR spectroscopy, FTIR spectroscopy is widely used to elucidate the structure of a molecule. The usual range covered while conducting the analysis is from 500 to 4000 cm\(^{-1}\). For structure determination of organic molecules, the infrared spectrum can be broadly divided into two regions. The region spanning from 3600 to 1200 cm\(^{-1}\) is called the functional group region and the region that includes all frequencies below 1200 cm\(^{-1}\) is called the fingerprint region. The two regions are important in the determination of the identity of the molecule. The FTIR instrument used to elucidate the structure of polymer is shown in figure 2.13.

![Figure 2.13. FTIR spectroscopic instrument used in present work.](image)

In order to study FTIR spectroscopy of polymers and copolymers, pellets were prepared by mixing the synthesised compounds with pure potassium bromide (KBr) in the ration 1:100. The prepared polymer pellets were 1 mm thickness. The pellet maker and the prepared pellets are shown in figure 2.14.
Third-order optical nonlinearity and optical power limiting of Organic materials under CW laser illumination

Chapter 2

2.4.3. Linear refractive index measurements

The refractive index of liquids or solids can be measured with refractometers. The first laboratory refractometers were developed by Ernst Abbe in 19th century. The Abbe’s refractometer is the most widely used refractometer. Abbe’s refractometer was used to measure the linear refractive index of dyes and polymers. The Abbe’s refractometer used to determine the refractive index of samples is shown in figure 2.15.

Figure 2.14. Pellet maker and prepared polymer pellets in present work.

Figure 2.15. Abbe’s refractometer used in present work.
2.5. Specifications of instruments

i) Laser

Mode: Continuous wave
Wavelength: 633 nm
Output power (maximum): 35 mW
Divergence: 0.66 mrad
Beam Diameter: 1.22 mm
Transverse intensity distribution: Gaussian

ii) Power / Energy meter

Model and make: PM320E Dual channel energy and power meter Thor Labs
Spectral range: 400 – 1100 nm
Power range: 1 mW – 100 W

iii) Detectors

Model and make: S121C Thor Labs
Detector type: Silicon Photodiode
Spectral range: 400 – 1100 nm
Active area: 9.7 mm × 9.7 mm
Optical power range: 500 nW – 500 mW
Dark current: 1.805 nA

iv) Z-scan system

Model and Make: HZSS12 Holmarc
Scan rate: 62,000 microns
Sample holder make: Quartz
Scan step size: 500 microns
Sample holder (cuvette): \( L(1 \text{ cm}) \times B(1 \text{ mm}) \times H(4 \text{ cm}) \) (inner diameter)

v) UV-VIS spectrophotometer

Model and Make: UV-1800 Shimadzu
Optical system: Double beam optics
Light source: less than 0.02% NaI at 220 nm, \( \text{NaNO}_2 \) at 340 nm, less than 1% KCl at 198 nm
Detector: Temperature controlled DLATGS detector
Wavelength range: 190 nm – 1100 nm
Sample holder make: Quartz
Sample holder (cuvette): \( L(1 \text{ cm}) \times B(1 \text{ cm}) \times H(4 \text{ cm}) \) (inner diameter)
Sample compartment: \( W450 \text{ mm} \times D490 \text{ mm} \times H270 \text{ mm} \)
Resolution: 1 nm

vi) FTIR spectrophotometer

Model and Make: 8400S Shimadzu
Interferometer: Michelson type with 30° incident angle,
Optical system: Single beam optics
Beam splitter: Germanium-coated KBr plate
Light source: High brightness ceramic
Detector: Temperature controlled DLATGS detector
Wavenumber range: 7800 cm\(^{-1}\) – 350 cm\(^{-1}\)
Sample compartment: \( W200 \text{ mm} \times D230 \text{ mm} \times H170 \text{ mm} \)
Resolution: 16 cm\(^{-1}\)

vii) Abbe refractometer

Make: The National Scientific Instruments
Light source and sample type: Sodium lamp (\( \lambda = 589.3 \text{ nm} \)), liquid