CHAPTER 2

NEW, ORGANIC DYE-PVA NANOCOMPOSITES: FABRICATION SCHEME AND CHARACTERIZATION TOOLS

A brief discussion of the experimental methodology adopted for the investigation is presented in this chapter. This includes a brief description of the fabrication process of the organic dye-PVA nanocomposite films and, the tools and the techniques employed for the optical, morphological and structural analysis of the nanocomposite film samples. The Z-scan technique and its theory, based on which the nonlinear absorption and nonlinear refraction measurements were performed, are also discussed here. It also includes an account of the Degenerate Four Wave Mixing (DFWM) technique employed for the generation of phase conjugate wave in the nanocomposite film.
2.1 Introduction

During the past two decades, high performance functional materials are in demand owing to the scientific, technological and industrial applications that can be realized with them. Numerous efforts to synthesize novel and interesting structures including structurally modified organic materials, composites and organic compounds, with large nonlinear optical properties suitable for optical and other photonic device applications have been reported [Marder et al., 1991; Prasad and Williams, 1991]. Materials such as semiconductors, polymers, liquid crystals, metallic nanoclusters and organic compounds have been successfully incorporated in solid hosts for the purpose, because, for most of the device applications including that in optical limiting, solid-state materials are required. The fabrication of organic-polymer composites has received significant interest for the reason that these engineered materials can display superior property combinations suitable for technological applications. This chapter describes the experimental methodology adopted for the fabrication and characterization of the organic dye-polymer nanocomposite films used for the present study. A detailed investigation of the microstructure and morphology is essential for understanding the different physical and structural properties of the material, to custom-tailor their properties for specific applications. For the present work, this has been accomplished by employing complimentary techniques like X-ray diffraction analysis, vibrational and electronic spectroscopy, scanning electron microscopy, atomic force microscopy, etc.

2.2 Fabrication of Organic Dye-Polymer nanocomposite films:

The guest-host method

In a guest-host system [Lessard et al., 1993], the active compound is incorporated into the host polymer as a dissolved guest [Prrimagi et al., 2005]. The guest is physically mixed with the host and only noncovalent interactions are active between the two components, and the guest is hence only embedded in the host. Guest molecules generally contribute with their chemical activity and need the structural support of polymers to become a part of a hybrid functional material. Such guest-host systems are flexible and cost effective as they only require mixing of the constituents to produce a desired compound. Compared to
conventional guest-host systems, organic dye-polymer composite systems allow the possibility of increasing the dye content by reducing the probability of dye aggregation by means of possible weak bonding interactions between the dye molecules and polymer [Primagi et al., 2007]. By combining higher doping levels of active moieties with optimized molecular design, hybrid functional materials can be synthesized for nonlinear optical applications.

Various methods are employed for the synthesis of multifunctional nanocomposites. One approach to prepare nanocomposites has been the incorporation of well-defined organic components into a singular (polymer) material. By the combination of functionalized fillers with a polymeric support, composite materials with outstanding properties and applications can be prepared [Lu et al., 2007; Guo et al., 2010]. One of the greatest challenges in fabricating high quality polymer nanocomposites is the lack of the synergy between the polymer matrices and the nanofillers. In principle, the polymers could serve as a template for nanoparticle fabrication [Guo et al., 2010; K. J. Lee et al., 2009]. According to recent reports, micro and nano pore morphologies exist in polymer templates [Vargeese et al., 2008; Ulbricht, 2006]. The incorporation of very small wt %s (<0.5 %) of the fillers in the polymer templates, allows the target material to grow according to the patterns of the template [Zhao et al., 2008]. Such a matrix-mediated synthesis that uses organic additives and templates can control / modify the growth of nanostructures [Vargeese et al., 2008]. Solvent casting (guest-host method) is one of the easiest and less time-consuming methods for the synthesis of polymer nanocomposites [Lagashetty and Venkataraman, 2005; Lessard et al., 1993]. The advantages of this technology include uniform thickness distribution, maximum optical purity and homogeneity in the dispersion of fillers. For the present work, a simple processing technique based on the solution-cast method was used to fabricate the nanocomposite films, in which very small wt% (< 0.2 wt%) of the organic chromophores are incorporated in the host polymer PVA (guest-host system), which serves as a template for the nanostructured growth of the dye molecules [Zidan, 2003; Bhajantri et al., 2006; Guo et al., 2010; Mahendra et al., 2011; Abdelaziz and Ghannam, 2010; Ravindrachary et al., 2011; Strawhecker and Manias, 2001; Johnsy et al., 2009]. However, the fabrication method was improved by allowing film formation in a dark, enclosed environment at room temperature, to avoid
interaction with ambient light during the film formation [Frobel et al., 2011; Sreekumar et al., 2011, 2009; George et al., 2008].

A known amount (5 wt%) of PVA (molecular weight=125000 g/mol; sdfine+Chem Limited, Mumbai, India) was dissolved into the desired quantity of distilled water at 90 °C, with magnetic stirring, until the polymer was completely dissolved (~2 hours). The clear solution was then cooled to room temperature with continuous stirring. Different concentrations (<10⁻³ M) of the organic dye were then dissolved into the solution with continuous stirring (~1 hour), and the resulting mixture was ultrasonically agitated for 30+45 minutes to get a perfectly homogeneous solution. The mixture containing different concentrations of the organic dye molecules was then casted onto perfectly leveled glass micro+slides. Good quality transparent films of uniform surface finish and, thickness in the range 30+35 μm were thus obtained within five to six days, after slow evaporation in dry air. Figure 2.1 shows the photographs of the organic dye+PVA nanocomposite films deposited onto 7.5×2.5 cm² microslides (glass). These composite films (figure 2.1 (a)+(c)) posses ease of handling as they can be simply peeled off intact from the micro+glass slides on which they are deposited.

![Figure 2.1](image_url)

**Figure 2.1:** Photographs of (a) IC+PVA (b) PR+PVA and (c) Li+PVA nanocomposite films deposited onto glass substrates (7.5×2.5 cm² microslides).

Guest+host method offers a number of advantages like usage of a variety of chromophores, ease of processing into thin films, easy fabrication onto a very large area of substrate of any dimension, considerably high mechanical strength, unlimited selection of the desired NLO active guest+host components, possibility of wide range of operating frequencies and low dielectric constant.
2.3 Characterization Tools

The properties of the composite films depend not only on the constituent materials but also on their structure, morphology, interfacial characteristics, interactions between the guest and host etc. Implementation of the functional materials in technological applications requires fundamental understanding of the underlying physical processes as well as structure-property relationships. A detailed investigation as regards the structure, microstructure, optical and nonlinear optical properties are therefore essential. A brief account of the tools and techniques used for determining the structure, morphology, linear and nonlinear optical properties of the nanocomposite films are presented in the following sections.

2.3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique widely applied for the characterization of crystalline materials. The method has been traditionally used for phase identification, quantitative analysis and determination of structure imperfections. In recent years, applications have been extended to new areas, such as the determination of crystal structures and the extraction of three dimensional micro-structural properties. In this method, X-rays of a known wavelength are passed through a sample in order to identify the crystal structure. The phenomenon of the x-ray diffraction by crystals results from a scattering process in which x-rays are scattered by the electrons of the atoms without change in wavelength. A diffracted beam is produced by such scattering only when certain geometrical conditions are satisfied, which may be expressed in either of two forms, the Bragg law or the Laue equations. The resulting diffraction pattern of a crystal, which is a unique pattern, comprising both the positions and intensities of the diffraction effects, is a fundamental physical property of the substance. The analysis of the diffraction pattern helps in the identification of crystalline compounds. Phase identification is accomplished by comparing the peaks and relative intensities from the unknown sample with peaks and relative intensities from a very large set of standard data provided by the International Center for Diffraction Data.

The instrument used for the present study is a Bruker AXS+ D8 Advance X-ray diffractometer using Ni-filtered CuKα radiation of wavelength 1.54 Å with
a graphite monochromator. The scan was taken in the 2θ range 10°-70° with a scanning step size of 0.14°.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is one of the most common and powerful techniques used by organic chemists for the structural identification and detection of functional groups in pure compounds and mixtures. Absorption of light in the ultraviolet (UV) and visible regions of the electromagnetic spectrum occurs when electrons are excited from lower energy molecular orbitals to higher ones. Organic molecules also absorb in electromagnetic energy in the infrared (IR) region of the electromagnetic spectrum. IR radiation does not have sufficient energy to cause excitation of electrons; however, it causes atoms and groups of atoms to vibrate faster about the covalent bonds which connect them [Kalsi, 1996]. These vibrations are quantized and as they occur, the compound absorbs infrared energy in particular regions of the spectrum, characteristic of the functional groups present in them. The position of IR absorption band is specified in wavenumber units. In an IR spectrophotometer, IR radiation of successively increasing wavelength is passed through the sample and the transmittance is measured. The readily examined region for organic compounds is 4000-650 cm⁻¹, as it covers the absorptions due to the fundamental vibrations of almost all functional groups of organic compounds. The functional groups in organic molecules have absorptions which are characteristic not only in position but also in intensity. Therefore, a successful interpretation of the IR spectrum is largely dependent on an appreciation of the intensities of the observed bands.

For the present work, infrared spectra were obtained using an FTIR spectrometer (PerkinElmer) with ATR device, in the Transmittance Mode. The samples were scanned in the wavenumber range from 4000 to 400 cm⁻¹ during 40 scans, with a resolution of 4 cm⁻¹.

2.3.3 Atomic Force Microscopy (AFM)

AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. High-resolution visualization of a sample's morphology, which is a key feature of AFM, defines most of its applications and is commonly used for atomic and nanoscale measurement of
various properties, including surface topography, friction, adhesion, and viscoelasticity [Bhushan-2005, Bhushan-2007]. AFM provides a number of advantages over conventional microscopy techniques. AFMs probe the sample and make measurements in three dimensions, x, y, and z (normal to the sample surface), thus enabling the presentation of three-dimensional images of a sample surface.

The AFM consists of a micro scale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces. A laser beam is projected on the upper surface of the cantilever close to the tip. Typically, the deflection of the cantilever is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. The flexural angle $\theta_c^x$ and twist of the cantilever $\theta_c^z$ are obtained by calibrating the vertical and lateral voltage outputs of the photodiode, respectively. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometers.

The atomic force microscope used in the present work is Digital Instruments Nanoscope E, having Si$_3$N$_4$, 100 μ cantilever with 0.58 N/m force constant. The AFM data are subsequently used to calculate the average roughness and root-mean-square (RMS) roughness which is a measure of the standard deviation of heights within the given area.

2.3.4 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution image of a sample surface. In a typical SEM,
Electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB$_6$) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). It uses a focused beam of high-energy electrons, rather than light to generate a variety of signals at the surface of solid specimens. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. As the accelerated electrons penetrate the surface, a number of interactions occur that can result in the emission of secondary electrons or photons from (or through) the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors to generate an image on screen; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen and an image is formed in which the same way as a TV. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Due to the manner in which the images are created, SEM images have a 3-D appearance and are useful for grudging the surface morphology of the sample. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm).

The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require that sample should be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation make the SEM one of the most popularly used instruments in current research areas.
In the present study, the scanning electron microscope used for recording the morphology of the composite films is JEOL JSM 5600.

### 2.3.5 Optical microscopy

A polarized light microscope is used to observe and photograph specimens. Normal light from the microscope lamp vibrates in all directions perpendicular to the axis of propagation of light. To obtain polarized light, the microscope consists of a polarizer, positioned in the light path somewhere before the specimen and an analyzer (a second polarizer), placed in the optical pathway between the objective rear aperture and the observation tubes or camera part. When the plane polarized light interact with the specimen, two individual wave components are produced and are polarized in mutually perpendicular planes. The light components become out of phase, after the excitation of the specimen. But the polarized light components recombine constructively or destructively, when they pass through the analyzer. A polarized light microscope can be used in both reflected and transmitted light. Reflected light is useful for the study of opaque materials such as mineral oxides and sulphide, metals and silicon wafers.

In the present work, Leica DFC 280 optical microscope is used for obtaining the morphology of the samples.

### 2.3.6 Optical Absorption Spectroscopy

The optical absorption spectroscopy, which includes UV, visible, near IR and IR, is an important tool for the structural determination of organic compounds. Spectroscopic analysis is based on the absorption of electromagnetic radiation of a specified energy by matter. When light passes through a sample, spectrophotometer makes a comparison of the intensities of the incident and transmitted beams at each wavelength. If the material absorbs at a particular wavelength, the intensity of the transmitted beam will be less than the incident intensity; and the absorbance at particular wavelength is given by,

$$ A = \log \frac{I_0}{I} $$

where 'I₀' is the intensity incident on the sample and 'I' is the transmitted intensity, which is a function of the depth of material. The increase in energy
imparted to the electron promotes it to a higher excited state energy. Linear absorption (a one photon process) is independent of incident intensity but depends on the number or density of available absorbing sites.

The process of absorption of radiation is governed by two basic laws: Beer's law and Lambert's law. According to Beer's law, the amount of radiation absorbed is proportional to the number of molecules absorbing the radiation. Hence the absorbance of a sample is proportional to the concentration of the sample. Lambert's law states that the fraction of incident radiation absorbed by a transparent medium is independent of the intensity of the incident radiation and each successive layer of the medium absorbs an equal fraction of the incident radiation. According to this law, the intensity of the transmitted light passing through a homogeneous medium decreases geometrically as the thickness of the layer increases arithmetically. According to Beer-Lambert's law, which is obtained by combining the two previous laws, the absorption ($A$) is expressed as,

$$A = \varepsilon CL$$ (2.2)

Where $\varepsilon$ is the molar extinction coefficient, 'C' is the concentration and 'L' is the path length of light through the sample.

The absorbance and transmittance are related as,

$$A = \log \left( \frac{I_0}{I} \right) = \log \left( \frac{1}{T} \right)$$ (2.3)

Since the intensity of light falls exponentially with the distance propagated through the sample according to $I = I_0 \exp(-\alpha x)$, the relationship between $A$ and the absorption coefficient $\alpha$ is given by,

$$\alpha = \frac{1}{L \log e} \frac{A}{N}$$ (2.4)

The linear absorption cross section $\sigma$ is defined as the ratio of the absorption coefficient to the number density $N$,

$$\sigma = \frac{\alpha}{N}$$ (2.5)

The UV-Vis analysis for the present work has been done using a Shimadzu UV-2450 spectrophotometer in the wavelength range 200-900 nm.

### 2.3.7 Photoluminescence Emission Spectroscopy
Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials [Prasad-2004, Gunzler-2001]. PL analysis can give various informations about the properties of the materials such as band gap, material quality, recombination mechanisms, and impurity levels. Photoluminescence is a process in which a chemical compound absorbs electromagnetic radiation (photons), thus promoted to a higher electronic energy state, and then radiates photons back out, on returning to a lower energy state. Technically, it is "luminescence arising from photoexcitation". The period between absorption and emission depends on the life time of the excited state (typically a few nanoseconds).

An organic dye molecule in the lowest vibrational sublevel (level ‘a’) of the ground state $S_0$ can absorb a photon, producing transitions to one of the upper vibrational levels of $S_1$ denoted by level B. The molecule then undergoes a radiationless decay (B→b) to the lowest vibrational sub level (level ‘b’) of $S_1$. The radiationless transition involves a rearrangement of the total energy within a system without photon emission. In most instances, the energy is absorbed in increased kinetic energy or motion of the atoms in the system and appears as heat. After some finite time, given by the excited state lifetime of $S_1$ (typically a few nanoseconds), the molecule may decay spontaneously to the lower energy level $S_0$, conserving energy in the process with the release of a photon. This is known as spontaneous emission or fluorescence with the photon energy equal to the energy difference, $E_b - E_A$ between the states in which the transition occurs. The wavelength is given by

$$\lambda_{sh} = \frac{hc}{E_b - E_A} \quad (2.6)$$

where $h= 4.136 \times 10^{-15} \text{eV}$ and $c=3\times10^8 \text{m/s}$. Another radiationless transition, A→a, returns the excited molecule to its ground state. Notice that the wavelength of light emitted by the dye when it fluoresces is longer (lower energy) than that of the absorbed light, $\lambda_{ab} < \lambda_{sh}$. The energy of the emitted light (photoluminescence) is detected which relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state.

A Perkin Elmer LS-55 Fluorimeter was used to carry out the fluorescence emission studies in the present work.
### 2.3.8 The Z-scan technique

Various techniques, such as Degenerate four wave mixing, Third harmonic generation, Electro absorption technique, Time resolved optical Kerr effect and Transient absorption technique, Z-scan method, Nonlinear imaging technique with a phase object (NIT-PO), etc. have been employed for the measurement of optical nonlinearities. The analysis of nonlinear optical characteristics of different materials using nonlinear interferometry, the Degenerate Four-Wave Mixing (DFWM), and non degenerate three-wave mixing is sufficiently precise and versatile. However, the study of nonlinear optical characteristics with these methods requires rather complex instrumentation, and the interpretation of the results is rather complicated because of the simultaneous presence of two or more nonlinear mechanisms. In most cases, these techniques are insufficiently sensitive for separating the contributions of several nonlinear mechanisms [Ganeev-2005]

For the present investigation, measurements of the nonlinear optical properties of the dye-polymer films were carried out, employing the standard Z-scan technique. Developed by Sheik Bahae et al. in the year 1989 at the Center for Research in Electro-Optics and Lasers (CREOL), Florida, the Z-scan technique has now emerged as a premier, most popular and widely used technique for the measurement of optical nonlinearities [Sheik-Bahae et al., 1990]. This technique has been used for the measurement of nonlinear optical properties of various materials in femtosecond to millisecond timescale.

The Z-scan technique is a simple, sensitive single beam technique that makes use of the effect of beam distortions induced due to the nonlinear interactions between the incident beam and the nonlinear medium, in the spatial and temporal profiles of the input beam, to obtain a qualitative as well as quantitative measure of the optical nonlinearities. The technique known for its sensitivity comparable to that of interferometric methods [Chapple-1997], allows the simultaneous determination of the sign and the magnitude of absorptive as well as refractive nonlinearity associated with a material medium and, hence, can differentiate between the contributions of real and imaginary parts of the third-order nonlinear susceptibility, $\chi^{(3)}$ which is not possible by optical Kerr gate or degenerate four-wave mixing technique.
In this technique, the material medium is scanned along the propagation direction of a tightly focused Gaussian beam from one side of the focal plane to the other (the z-direction) and the far field intensity is measured as a function of the sample position. There are two versions of this method, viz. the closed aperture (CA) and the open aperture (OA) Z-scans. In the CA Z-scan technique, the transmitted light is measured through an aperture placed in the far field with respect to the focal region; whereas, in the OA Z-scan technique, a lens which would collect the entire transmitted light replaces the aperture. In the CA Z-scan the transmitted light is sensitive to nonlinear refraction as well as nonlinear absorption; hence, can provide accurate information regarding the nonlinear refraction occurring in the sample, in addition to furnishing the effect on nonlinear absorption. However, in the OA Z-scan, the transmitted light is sensitive only to nonlinear absorption and contains accurate information regarding absorptive nonlinearity such as saturable absorption (negative nonlinear absorption), reverse saturable absorption (positive nonlinear absorption) or a flip of one to the other. Since the Z-scan technique was discovered, some alternative or improved Z-scan techniques were also developed, mainly concerning the input beam profiles such as the eclipsing beam [Xia et al., 1994], the two colour Z-scan [Sheik Bahae et al., 1990], the time resolved Z-scan [Wang et al., 1994], and the reflection Z-scan [Petrov, 1996]. All such modified Z-scan techniques should belong to the technical and/or functional improvements such as the melioration of sensitivity and signal to noise ratio.

The Z-scan technique has several advantages. As a single-beam technique, it has no difficult alignment. It can be used to determine both sign and magnitude of nonlinear refraction and nonlinear absorption. The data analysis is quick and simple, making it a good method for screening new nonlinear
materials. Z-scan technique is also highly sensitive, capable of resolving a phase distortion of \( \sim \lambda/300 \) in samples of high optical quality. Z-scan measurements are very sensitive to the homogeneity of the sample and hence, impose stringent conditions on the quality of the films deposited for NLO studies.

Figure 2.3: Photograph of the Z-scan experimental arrangement.

### 2.3.8.1 The closed aperture Z-scan: theoretical aspects

In a Z-scan technique, nonlinearities of any order can be considered. However, for the simple case of cubic nonlinearity where the index of refraction \( n' \) is expressed in terms of nonlinear index \( n_2(\text{esu}) \) or \( \gamma \) (m\(^2\)/W) as,

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

(2.7)

where \( n_0 \) is the linear index of refraction, \( E \) is the peak electric field (cgs) and \( I \) denotes the irradiance (MKS) within the sample. Here \( n_2 \) and \( \gamma \) are related through the conversion formula

\[
n_2(\text{esu}) = \left( \frac{Cn_2}{40\pi} \right) \gamma \left( \frac{m^2}{W} \right).
\]  

(2.8)

where \( C \) (m/s) is the speed of light in vacuum. Assuming a TEM\(_{00}\) Gaussian laser beam with waist radius \( \omega_0 \) travelling in the +z direction, the electric field \( E \) can be written as,

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

(2.9)
Where $\omega^2(z) = \omega_0^2 \left(1 + \left(\frac{z}{z_0}\right)^2\right)$ is the beam radius, $R(z) = Z \left(1 + \left(\frac{z_0}{z}\right)^2\right)$ is the radius of curvature of the wave front at $z$, $z_0 = \frac{k\omega_0^2}{2}$ is the diffraction length of the beam, here $k = \frac{2\pi}{\lambda}$ is the wave vector, and $\lambda$ is the laser wavelength, all in the free space. $E_0(t)$ denotes the radiation electric field at the focus. The $e^{-i\varphi(x)}$ term contains all the radially uniform phase variations. If the sample length is small enough such that changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected, the medium is regarded as thin ($L \ll z_0$); in which case the self-refraction process is referred to as ‘external self action’. For calculating the radial phase variations, the Slowly Varying Envelope Approximation (SVEA) can be applied and all other phase changes that are uniform in ‘r’ are neglected. Now, the amplitude $\sqrt{\mathcal{I}}$ and phase $\varphi$ of the electric field as a function of propagation depth $Z'$ in the sample are now governed by the SEVA by a pair of equations as,

$$\frac{d\Delta \varphi}{dz'} = \Delta \alpha(t).k,$$  
$$\frac{d\mathcal{I}}{dz'} = -\alpha(t).\mathcal{I},$$  

$\alpha(t)$ includes linear and nonlinear absorption terms. In the case of cubic nonlinearity, and negligible nonlinear absorption equation (4) and (5) can be solved to yield the phase shift $\Delta \varphi$ at the exit surface of the sample as,

$$\Delta \varphi(z,r,t) = \Delta \varphi_0(z,t)\exp\left(\frac{-2\alpha}{\omega_0^2}\right),$$  

where

$$\Delta \varphi_0(z,t) = \frac{\Delta \varphi_0(z,t)}{1 + \left(\frac{z}{z_0}\right)^2},$$  

Here $\Delta \varphi_0(t) = k\Delta n_0(t)L'_{\text{eff}}$ is the on-axis phase shift at the focus. $L'_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, with $L$ the sample length and $\alpha$ the linear absorption coefficient. Here $\Delta n_0(t) = \gamma I_0(t)$ with $I_0(t)$ being the on-axis irradiance at the focus.

Now, the complex electric field $E'$ exiting the sample contains nonlinear phase distortions, and can be written as

$$E'(r,z,t) = E(r,z,t)e^{\frac{-\alpha t}{z}}e^{i\Delta \varphi(z,r,t)}.$$  

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Using the Gaussian decomposition (GD) method [D. Weaire et al.;1979], the complex electric field at the exit plane of the sample can be 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 (8) as,

\[
e^{i\Delta \phi(z,r,t)} = \sum_{m=0}^{\infty} \frac{[i\Delta \phi_0(z,r)]^m}{m!} \frac{\omega_m}{\omega} e^{-\frac{z^2}{2\omega_m^2}}
\]  

(2.15)

Each Gaussian beam can now propagate to the aperture plane, where they will be resumed to reconstruct it. The resultant electric field pattern at the aperture can now be derived as,

\[
E''(r,t) = E(z,r = 0,t) e^{\frac{-a_l}{z}} \sum_{m=0}^{\infty} \frac{[i\Delta \phi_0(z,r)]^m}{m!} \frac{\omega_m}{\omega} \exp\left(-\frac{r^2}{\omega_m^2} - \frac{ikr^2}{2R_m} + i\theta_m\right)
\]  

(2.16)

Here,

\[
\omega_m^2 = \frac{\omega_0^2(z)}{2m+1}
\]

\[
d_m = \frac{k\omega_m}{2}
\]

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

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

and

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

Here \( d \) is the propagation distance in free space from the sample to the aperture plane and \( g = 1 + \frac{d}{R(z)} \). The transmitted power through the aperture is obtained by spatially integrating \( E'' \) up to the aperture radius \( r_a \), giving

\[
P_T(\Delta \phi_0(t)) = C \varepsilon_0 \pi \int_0^{r_a} |E''(r,t)|^2 r dr
\]  

(2.17)

Where \( \varepsilon_0 \) is the permittivity of vacuum. The laser temporal pulse shape can be taken into account by performing separate time integration. Then the normalized Z-scan transmittance \( T(z) \) can be calculated as,

\[
T(z) = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_0(\tau) |E_0(z,\tau)|^2 \phi(\tau) d\tau \phi(\tau) d\tau}{S}
\]  

(2.18)

Where \( P_0(\tau) = \frac{\pi\varepsilon_0^{\frac{5}{2}} S \omega_0^2}{\chi^2} \) is the instantaneous input power within the sample and \( S = 1 - \exp\left(-\frac{z^2}{\omega_0^2}\right) \) is the aperture linear transmittance, with \( \omega_0 \) denoting
Putting \( r = 0 \) in equation (2.16) will give the on axis electric field at the aperture plane. Also, for small nonlinear phase change (\(|\Delta \varphi_c| \ll 1\)) only two terms in the sum of equation (2.16) need to be retained. Following such simplifications, the normalized Z-scan transmittance can be written as,

\[
T(z, \Delta \varphi) = \frac{|E_0(z, r = 0, \Delta \varphi)|^2}{|E_0(z, r = 0, \Delta \varphi = 0)|^2}
\]

\[
= \frac{[\left(1 + \frac{r^2}{\Delta z^2}\right)_0 - \Delta \varphi_c] \left(1 + \frac{r^2}{\Delta z^2}\right)_0 + \Delta \varphi_c}{\left(1 + \frac{r^2}{\Delta z^2}\right)_0 - \Delta \varphi_c}
\]

(2.19)

Equation (2.19) can be further simplified, assuming the far field condition (\(d << Z_0\)), giving the geometry-independent normalized transmittance as,

\[
T(z, \Delta \varphi) = 1 - \frac{4 \Delta \varphi_c x}{(x^2 - 3)(x^2 + 1)}
\]

(2.20)

where, \( x = \frac{z}{Z_0} \). For very small values of \(|\Delta \varphi_c|\), the peak and valley occurs at same distance with respect to the focal plane, and for a cubic nonlinearity, this distance is equal to 0.86z0 approximately. But for larger phase variations, this symmetry no longer exists and the peak and valley move towards \( \pm z \) depending on the sign of the nonlinearity (\( \pm \Delta \varphi_c \)), such that their separation remains nearly constant, and is given by \( \Delta z_{p-v} = 1.7z_c \). Theoretical fit to the experimental data with equation (2.20) is used to check the validity of the experiment and provides the value of \( \Delta \varphi_c \).

Even though the Z-scan technique, introduced by Sheik-bahae et al [1990], is simple and sensitive, there are certain limitations for this method. A simple division of closed aperture Z-scan data with open aperture Z-scan data is conveniently employed to eliminate the effect of nonlinear absorption from nonlinear refraction. However, the results obtained by the division method have certain error, which can reach even up to 50% for a highly absorbing medium. When both nonlinear refraction and nonlinear absorption takes place simultaneously, the equation (2.20) has to be modified so as to include the effect of nonlinear absorption, and in that case, normalized transmittance of the sample can be obtained as [Yin et al., 2000],

\[
T(z) = 1 - \frac{4x^2 \Delta \varphi_c}{(x^2 - 3)(x^2 + 1)} - \frac{4(x^2 - 3) \Delta \varphi_c^2}{(x^2 - 3)(x^2 + 1)}
\]

(2.21)
where $\Delta \varphi = k_n L_{s\text{ff}}$ and $\Delta \varphi' = \beta l L_{s\text{ff}}$ are the parameters which determine the phase shift near the focal point as a result of nonlinear refraction and nonlinear absorption of the medium. Equation (2.21) can provide better fit to the Z-scan data, with high accuracy for a highly absorbing medium.

2.3.8.2 The open aperture Z-scan: Theoretical aspects

The Z-scan traces with a fully open aperture ($s=1$) is insensitive to nonlinear refraction. Such Z-scan traces with no aperture are expected to be symmetric with respect to the focus ($z=0$), where they have a minimum transmittance (multiphoton absorption) or maximum transmittance (Saturation absorption). The coefficients of nonlinear absorption can be easily calculated from such transmittance curves. Several different mechanisms, such as, two photon absorption (TPA), excited state absorption (ESA), multi photon absorption etc can be used for explaining the positive nonlinear absorption. The theoretical model, based on TPA, developed by Sheik Bahae et.al can be applied to ESA also, as it is a sequential TPA process, where two photons are successively absorbed. However, the theoretical model provides the effective nonlinear absorption coefficient $\beta_{\text{eff}}$ for ESA.

Reverse saturable absorption (RSA)

In an open aperture Z-scan experiment, the intensity dependent nonlinear absorption coefficient $\alpha(I)$ can be written as

$$\alpha(I) = \alpha + \beta I$$  \hspace{1cm} (2.22)

Here $\beta$ is the nonlinear absorption coefficient known as TPA coefficient. This will yield the irradiance distribution and phase shift of the beam at the exit surface of the sample as,

$$I'(z,r,t) = \frac{I(z,r,t)e^{-\Delta \varphi}}{1-q(z,r,t)}$$  \hspace{1cm} (2.23)

and

$$\Delta \varphi(z,r,t) = \frac{k\nu}{\beta} \ln (1 + q(z,r,t))$$  \hspace{1cm} (2.24),

where $q(z,r,t) = \beta I(z,r,t)L_{s\text{ff}}$. Combining equations (2.23) and (2.24) will give complex electric field at the exit surface of the sample as,

$$E' = E(z,r,t)e^{-\frac{2l}{\alpha}}(1 + q)^{\left(\frac{k\nu}{\beta} - \frac{1}{2}\right)}$$  \hspace{1cm} (2.25)
Above equation reduces to equation (2.14) in the absence of nonlinear absorption. A zeroth-order Hankel transform of the above equation will give the field at aperture plane. But for \(|q| < 1\), following binomial series expansion in powers of \(q\), above equation can be expressed as an infinite sum of Gaussian beams as,

\[
E' = E(z, r, t) e^{-\frac{\beta}{2} \sum_{m=0}^{\infty} \frac{q(z,r,t)^m}{m!}} \left[ \prod_{n=0}^{\infty} \left( \frac{\omega_m}{\omega_0} - \frac{1}{z} - n + 1 \right) \right] \tag{2.26}
\]

The complex field pattern at the aperture plane be obtained as before

\[
E_a(r, t) = E(z, r = 0, t) e^{-\frac{\beta}{2} \sum_{m=0}^{\infty} F_m \cdot \frac{\omega_m}{\omega_0} e^{\frac{i}{2} \pi r^2} \frac{\omega_m}{2 \eta m}} \tag{2.27}
\]

where \(F_m = \frac{(i\omega_0 \varphi(z,r,t))^m}{m!} \prod_{n=0}^{m} \left( 1 + i(2n - 1) \frac{\beta}{2\eta} \right) \tag{2.28}\)

with \(F_0 = 1\). When the aperture is removed (\(s = 1\)) the Z-scan transmittance is insensitive to beam distortions and is only a function of the nonlinear absorption. The total transmitted fluence in this case can be obtained by spatially integrating equation (2.23) at \(z\) over \(r\)

\[
P(z, t) = P_c(t) e^{-\alpha t} \ln \left( 1 + q_0(z) \right) \tag{2.29}
\]

where \(q_0(z, t) = \frac{\beta l_0 z}{1 + \frac{\beta l_0 z}{1 + z_0}}\). For temporal Gaussian pulse equation (20) can be time integrated to give normalized energy transmittance

\[
T(z, s = 1) = \frac{1}{\sqrt{\pi} q_0(z_0)} \int_{-\infty}^{\infty} \ln \left( 1 + q_0(z, 0) e^{-\tau^2} \right) d\tau \tag{2.30}
\]

For \(|q_c < 1|\), this transmittance can be expressed in terms of peak irradiance in a summation form as,

\[
T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[q_0(z/0)]^m}{(m+1)^{\frac{1}{2}}} \tag{2.31}
\]

Thus the nonlinear absorption coefficient \(\beta\) can be determined from the open aperture Z-scan.

When multiphoton absorption other than 2PA is present the nonlinear absorption coefficient \(\alpha(t)\) in equation (2.22) will contain additional terms. For a simple three photon absorption process, the nonlinear absorption coefficient \(\alpha(t)\), can be represented as,

\[
\alpha(t) = \alpha_c - \beta t + y t^2 \tag{2.32}
\]
where, \( \tilde{\sigma} \) and \( \gamma \) are the 2PA and 3PA coefficients respectively. Propagation of the laser beam through the nonlinear medium, which exhibits three photon absorption, is governed by,

\[
\frac{\partial I}{\partial z} = -\gamma I^2
\]  

(2.33)

Equation (2.33) provide the intensity distribution at the exit surface of the medium as,

\[
I(z) = \frac{\tilde{\sigma} z}{[1 + 2\gamma z \tilde{\sigma}]^2}
\]  

(2.34)

And the transmittance of the sample is given by,

\[
I(z) = \frac{I}{[1 + 2\gamma z \tilde{\sigma}]^2}
\]  

(2.35)

Equations (2.30) and (2.35), which provide the values of \( \beta \) and \( \gamma \) respectively, are used for the theoretical fitting to the experimental data, when TPA and 3PA are present.

**Saturable absorption (SA)**

Saturable absorption (SA) occurs when a sample is excited at its resonant wavelength. In a saturable absorber, nonlinear absorption coefficient is considered as negative, owing to the decreased absorption in the sample with an increase in input intensity. Saturable absorption occurs as a result of depletion of the ground state population at a particular value of the input intensity known as the saturation intensity \( I_s \). In such situations, direct application of equation (2.30), which was derived for a TPA process, may not be useful for the analysis of the experimental data. Therefore it seems reasonable to investigate the possibility of using other absorption saturation models. A simple kinetic model, which is a two-level model, is often used, when the saturation is considered in terms of depletion of the ground state concentrations; and is governed by the equation,

\[
\frac{dN}{dz} = \frac{\tilde{\sigma} l}{\chi} (N_s - N) - \frac{N}{\tau} = 0
\]  

(2.36)

where \( N \) is the concentration of the excited state molecules, \( N_s \) is the undepleted ground-state concentration, \( \sigma \) is the absorption cross section, \( h\nu \) is photon energy, and \( \tau \) is the life time of the excited state population. In this model, it was assumed that the absorption coefficient \( \alpha \) is proportional to the ground state
absorption population (i.e. $\alpha = \sigma (N_g - N)$), and the equation, which describes saturation is given by,

$$\alpha = \alpha_0 \frac{1}{1 + \frac{\tau \sigma I}{h \nu}} = \alpha_0 \left(1 + \frac{I}{I_{sat}}\right)^{-1}$$

(2.37),

where, $I_{sat} = \frac{h \nu}{\sigma \tau}$ is the saturation intensity and $\alpha_0 = \sigma N_g$. The phenomenon described by equation (2.37) is often referred to as homogeneous saturation. Presence of bimolecular recombination of excited species will modify the equation, but it is rather inconsistent with the intensity – independent single exponential decays of DFWM curves.

For a two level system with an inhomogenously broadened states and hole burning, which lead to a decreased absorption, the saturation can be described by [Malcuit et al., 1984],

$$\alpha = \alpha_0 \frac{1}{\left[1 + \frac{I}{I_{sat}}\right]^{\frac{1}{2}}}$$

(2.38)

In certain situations the experimental curves were not fitted properly with the equations (2.37) and (2.38), where an adhoc formula proposed by Samoc et.al [1998] can be used for the theoretical fitting, which provides better fitting to the experimental data and is given by,

$$\alpha = \alpha_0 \frac{1}{\left(1 + \frac{I}{I_{sat}}\right)^{0.5}}$$

(2.39)

2.3.9 Degenerate Four-Wave Mixing (DFWM)

The phase conjugate wave can be generated in a number of ways and the most often used method is degenerate four-wave mixing (DFWM). It involves the
interaction of three coherent input waves of same frequency in a nonlinear medium to generate a fourth output wave that is phase conjugate to one of the input waves [Sharma+1994]. The presence of a third-order optical nonlinear susceptibility $\chi^{(3)}$ leads to the creation of various components of material polarization, giving rise to new optical fields. If the phase-matching condition is fulfilled (i.e. the phase relation between the waves emitted by different parts of the nonlinear medium leads to constructive build up of the resulting wave), new beams of light are created. If the fields are of identical frequencies, the process is called Degenerate Four Wave Mixing and the output beam will have the same frequency.

Figure 2.4 shows the (backward) DFWM geometry. In this geometry, the forward pump wave ‘$f$’ and the backward pump ‘$b$’ propagate opposite to each other. They interact with a third wave called the probe beam ‘$p$’ at an angle (usually less than 45°) to ‘$f$’. In general, the beams have the same polarization state and the path lengths of all the waves reaching the sample should be matched with in the coherence length of the laser. The three inputs stimulate a third-order nonlinear polarization $P^{(3)}$, which radiates an output wave ‘$c$’ that is the phase conjugate of the probe wave ‘$p$’. The conjugate wave ‘$c$’ propagates exactly opposite to ‘$p$’ and retraces its wavefronts. In terms of the grating picture, the spatial interference pattern of ‘$f$’ and ‘$p$’ waves gives rise to a medium.
excitation grating that is phase matched to scatter the ‘b’ wave counterpropagating to ‘p’. The resulting grating wave vector amplitude is $k = 2\pi/\Lambda$. The fringe period ($\Lambda$) is given by the formula $\Lambda = \lambda/2\sin(\theta/2)$, where $\lambda$ is the laser wavelength and $\theta \pm$ are the angle between the forward+pump and probe beam with respect to the normal to the nonlinear medium; it results in a complex volume hologram due to a spatial distribution of the refractive index (Kerr-like media), or of the absorption (saturable absorbers), or of the gain when the conjugator is the laser medium itself. Similarly the ‘b’ and ‘p’ waves form another grating that scatters the ‘f’ wave back along the direction of ‘p’. These gratings in general would be a combination of amplitude and phase gratings. The phase-conjugate reflectivity ($R_{pc}$) is defined as the ratio of the amplitude of the PC wave to the probe beam amplitude. There are other diffraction processes taking place in the DFWM geometry, but they do not lead to the conjugate of the probe wave.