Part I

Z-scan Technique
Chapter 1

Characterization of Nonlinear Optical Materials

"Truth is ever to be found in the simplicity, and not in the multiplicity and confusion of things." - Isaac Newton

ABSTRACT

A concise introduction to nonlinear optics and various nonlinear optical interactions are given in this chapter. A short survey of emerging nonlinear optical materials and some of the characterization techniques are also discussed here. This chapter briefly describes various nonlinear optical phenomena which can be used to probe the secrets of light-matter interaction. Description of z-scan is given as a separate section at the end. Only a brief and commonly used theoretical formalism of z-scan technique is provided in this section. Appropriate modifications and more details of data interpretations are given in succeeding chapters.

1.1 Nonlinear Optical Properties and Materials

Nonlinear optics is a broad field of research and technology that includes subject matter in the fields of physics, chemistry, biology and engineering. The diversity of nonlinear optics stems, in part, from the need for all-optical and electro-optical devices for applications in telecommunications, optical storage, and all-optical computing. In addition, many nonlinear optical effects have proved to be versatile probes of fundamental issues such as the electronic structure of compound semiconductors, phase transitions in liquid crystal films etc. Nonlinear optical materials use nonlinear dependence of the refractive index on
the applied electric field to produce other frequencies. Basic concepts of nonlinear optics and some of the important nonlinear optical materials are discussed below.

1.1.1 Introduction to Nonlinear Optics

The invention of the laser ushered in a new field of studies in optical phenomena in the early 1960s – 'nonlinear optics'. Because laser light can be sufficiently intense, it can actually change the index of refraction of a material through which it passes. Thus, the behavior of a transparent medium can depend on how intense the light is - a 'nonlinearity' that has led to such interesting phenomena as self-focussing of light and optical harmonic generation, resulting into the creation of new colors of light from a single color. Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system in the presence of light. Nonlinear optical phenomena are nonlinear in the sense that they occur when the response of a material system to an applied optical field is a nonlinear function of the strength of the optical field. For example, second harmonic generation occurs as a result of the part of the atomic response that depends quadratically on the strength of the applied optical field[1]. In order to describe more precisely what is meant by an optical nonlinearity, let us consider how the dipole moment per unit volume, or polarization \( \mathbf{P}(t) \), of a material system depends on the strength \( \mathbf{E}(t) \) of the applied optical field. In the case of conventional (i.e., linear) optics, the induced polarization depends linearly on the electric field strength in a manner that can often be described by the relationship

\[
\mathbf{P}(t) = \chi^{(1)} \mathbf{E}(t)
\]  

where the constant of proportionality \( \chi^{(1)} \) is known as the linear optical susceptibility. In nonlinear optics, the nonlinear optical response can often be described by generalizing Equation 1.1 by expressing the polarization \( \mathbf{P}(t) \) as a power series in the field strength \( \mathbf{E}(t) \) as

\[
\mathbf{P}(t) = \chi^{(1)} \mathbf{E}(t) + \chi^{(2)} \mathbf{E}^2(t) + \chi^{(3)} \mathbf{E}^3(t) + \ldots
\]

\[
= \mathbf{P}^{(1)}(t) + \mathbf{P}^{(2)}(t) + \mathbf{P}^{(3)}(t) + \ldots
\]  

The quantities \( \chi^{(2)} \), \( \chi^{(3)} \) etc are known as the second and third - order nonlinear optical susceptibilities, respectively. Here \( \chi^{(1)} \) is a second rank tensor, \( \chi^{(2)} \), third rank tensor etc. It is also assumed that the polarization at time \( t \) depends
only on the instantaneous value of electric field strength, or that the medium is lossless and dispersionless. But in general, the nonlinear susceptibilities depend on the frequencies of the applied electric field, and the equations for polarization need to be modified. We call \( \tilde{P}^{(2)}(t) = \chi^{(2)} \tilde{E}^2(t) \) as the second order nonlinear polarization and \( \tilde{P}^{(3)}(t) = \chi^{(3)} \tilde{E}^3(t) \) as the third order nonlinear polarization. The physical processes that occur as a result of \( \tilde{P}^{(2)} \) are distinct from those that occur as a result of \( \tilde{P}^{(3)} \). Second order nonlinear optical interactions can occur only in noncentrosymmetric crystals, that is, in crystals that do not have inversion symmetry. Since liquids, gases, amorphous solids (such as glass), and even many crystals do display inversion symmetry, \( \chi^{(2)} \) vanishes for such media, and consequently they cannot exhibit second order nonlinear optical phenomena. On the other hand, third order nonlinear optical interactions (i.e., those described by \( \chi^{(3)} \)) can occur both for centrosymmetric and noncentrosymmetric media. An Important point to be noted is that in order to make the series in Equation 1.2 convergent, the ratio of \((n + 1)^{th}\) to \((n)^{th}\) coefficient should be very much less than unity.

The most common procedure for describing nonlinear optical phenomena is by expressing the polarization \( \tilde{P} \) in terms of the applied field strength \( \tilde{E} \). The reason why polarization plays a key role in the description of nonlinear optical phenomena is that a time-varying polarization can act as the source of new components of the electromagnetic field. For example, the wave equation in nonlinear optical media often has the form

\[
\nabla^2 \tilde{E} - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 \tilde{P}}{\partial t^2}
\]

where \( n \) is the refractive index and \( c \) is the speed of light in vacuum. We can interpret this expression as an inhomogeneous wave equation in which the polarization \( \tilde{P} \) drives the electric field \( \tilde{E} \). This equation expresses the fact that, whenever \( \frac{\partial^2 \tilde{P}}{\partial t^2} \) is nonzero, charges are being accelerated and generate electromagnetic radiation.

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1It is interesting and useful to have an idea about the order of magnitude of NLO effects. Assume the nonlinearity is electronic in origin. Under conditions of non resonant excitation, \( \chi^{(2)} \) will be of the order of \( \frac{\chi^{(1)}}{E_{at}} \). For condensed matter, \( \chi^{(1)} \) is of the order of unity, and therefore, \( \chi^{(2)} \) will be of the order of \( \frac{1}{E_{at}} \). Since \( E_{at} \), the atomic electric field strength is given by \( E_{at} = \frac{\varepsilon_0}{a_0} = 2 \times 10^7 \text{esu} \) (-\( \varepsilon \) is the charge of electron and \( a_0 \) the Bohr radius), \( \chi^{(2)} \sim 5 \times 10^{-8} \text{esu} \) and \( \chi^{(3)} \sim 3 \times 10^{-15} \text{esu} \).
1.1.2 Descriptions of Nonlinear Optical Interactions

Nonlinear optical interactions of laser fields with matter provide powerful spectroscopic tools for the understanding of microscopic interactions and dynamic processes. A topic of keen interest in this field is the generation of higher harmonics of the laser frequency, using the nonlinear response of atoms or plasma in intense optical fields. The high fluence available from lasers enable such various nonlinear phenomena to take place, some of which are described below.

Consequences of Second Order Polarization

1. Optical Second Harmonic Generation (OSHG): OSHG is a nonlinear process which leads to frequency doubling when an intense laser beam travels through a nonlinear optical medium\(^2\).

The second harmonic generation is illustrated schematically in Figure 1.1 Here a laser beam whose electric field strength is expressed as

\[ E'(t) = E e^{-i\omega t} + c.c \]  (1.4)

is incident on a crystal for which \( \chi^{(2)} \) is non-zero. The nonlinear polarization that is created in such a crystal is given as

\[ \hat{P}^{(2)}(t) = 2\chi^{(2)}EE^* + (\chi^{(2)}E^2e^{-2i\omega t} + c.c). \]  (1.5)

We see that the polarization consists of a contribution at non-zero frequency (the first term) and a contribution at frequency \( 2\omega \) (the second term). This latter contribution can lead to the generation of radiation

\(^2\)The characteristic length for significant second harmonic generation under phase matched condition is \( L \sim \lambda E_a / E \) where \( E \) is the incident optical field and \( \lambda \) is its wavelength. For \( \lambda = 1\mu m \) we see that \( L = 1 \text{ cm} \) for power density of \( 1\text{MW/cm}^2 \) (\( 3 \times 10^8 \text{V/m}^{-1} \) incident field.)
at second-harmonic frequency. As an example, the Nd:YAG laser that operates at 1064 nm, produces radiation at wavelength 532 nm by SHG. Historically, nonlinear optics originated with the experimental observation of SHG by P. A. Franken, who in 1961 noticed that a weak optical signal at 347.1 nm could be generated in a quartz crystal when the material was illuminated with a high-power ruby laser at 694.2 nm [2]. Franken concluded that this new light source was due to the coherent mixing of two optical electric fields in the quartz so as to produce a "second harmonic" response in the bulk region of the material.

2. Sum and Difference Frequency Generation (SFG and DFG): SFG and DFG refer to the generation of light with a frequency that is the sum or difference of two input frequencies in a nonlinear medium. (SHG is a special case of this). This technique is being used extensively to produce tunable laser pulses in the mid infrared region. This region of the spectrum is very important for the sensing of a great variety of (transient) molecular species. Femtosecond IR pulses can be used to interact selectively with the bonds in a molecule. The mid-IR region is ideally suited to determine the presence of specific molecules in a sample. Therefore, a great deal of effort has been invested over the last decade to produce femtosecond pulses tunable in the near- and mid-IR region. The vast majority of techniques now in use are based on parametric difference-frequency generation processes. When an optical field with two distinct frequency components are incident on a nonlinear medium, which is represented as,

\[ \tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c \]  

(1.6)

the second-order contribution to the nonlinear polarization can be written as[1]

\[ \tilde{P}^{(2)}(t) = \chi^{(2)} \tilde{E}^2(t) \]

\[ = \chi^{(2)} [E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1 + \omega_2) t} + 2E_1 E_2^* e^{-i(\omega_1 - \omega_2) t} + c.c] + 2\chi^{(2)} [E_1^* E_1 + E_2 E_2^*]. \]  

(1.7)

The complex amplitude of the various frequency components are hence
given by

\[ P(2\omega_1) = \chi^{(2)} E_1^2 \ldots (SHG) \] (1.8a)
\[ P(2\omega_2) = \chi^{(2)} E_2^2 \ldots (SHG) \] (1.8b)
\[ P(\omega_1 + \omega_2) = 2\chi^{(2)} E_1 E_2 \ldots (SFG) \] (1.8c)
\[ P(\omega_1 - \omega_2) = 2\chi^{(2)} E_1^* E_2^* \ldots (DFG) \] (1.8d)
\[ P(0) = 2\chi^{(2)} (E_1 E_1^* + E_2 E_2^*) \ldots (OR) \] (1.8e)

where OR is ‘optical rectification’ and other acronyms are as mentioned before.

3. Optical Parametric Oscillation (OPO): Optical Parametric Oscillation is the generation of a signal and idler waves using a parametric amplifier in a resonator. In the process of DFG, the presence of radiation at frequency \( \omega_2 \) or \( \omega_3 \) can stimulate the emission of additional photons at these frequencies. If the nonlinear crystal used in this process is placed inside an optical resonator, (as shown in Figure 1.2) the \( \omega_2 \) and/or \( \omega_3 \) fields can build up to large values. Such a device is known as optical parametric oscillator. This device is tunable because any frequency \( \omega_2 \) (less than \( \omega_1 \)) can satisfy the condition \( \omega_2 + \omega_3 = \omega_1 \) for some frequency \( \omega_3 \). In practice, one controls the output frequency by adjusting the phase-matching condition. The applied field frequency \( \omega_1 \) is often called the pump frequency, the desired output frequency is called the signal frequency, and the other unwanted frequency is the idler frequency.

4. Optical Parametric Amplification (OPA): OPA the amplification of a signal input in the presence of a higher-frequency pump wave, at the same time generating an idler wave. This can be considered as DFG. A modern optical parametric amplifier is an extension of microwave parametric amplifier in optics employing the same principle. It essentially consists of two modes, as mentioned before, the signal and the idler (\( \omega_s \) and \( \omega_1 \) respectively) coupled through a nonlinearity in a crystal (for example) having a \( \chi^{(2)} \) coefficient by a strong pump mode at higher frequency.

\(^3\)How large should be an incident optical field to allow atoms and molecules to reveal their nonlinear properties? In most cases the incident field should not be negligible in comparison with the internal field \( E_a \) which binds together the electrons. \( E_a \sim 3 \times 10^{10} \text{V} \text{m}^{-1} \) and to obtain such fields an incident intensity of \( 10^{14} \text{Wcm}^2 \) is required. But in practice this much intensity will not be necessary for materials to show their NLO behavior. It is because under specific conditions, the induced dipoles oscillate coherently with definite phase relationship. This will result in the radiated fields to add constructively. This constructive interference is termed as 'phase matching'.
\( \omega_1 = \omega_2 + \omega_3 \)

\[ \chi^{(2)} \]

\( \omega_2 \) (signal)

\( \omega_3 \) (idler)

Figure 1.2: The optical parametric oscillator. The cavity end mirrors have high reflectivity at frequencies \( \omega_2 \) and/or \( \omega_3 \).

\[ \omega_p = \omega_s + \omega_i. \]  
(1.9)

The pump is usually assumed to be in a larger amplitude coherent state and hence to produce a classically modulated interaction between the signal and the idler modes. If the signal and the idler frequencies are equal, the amplifier is said to operate in a degenerate mode. The optical parametric amplification can be treated as a three-wave mixed amplifying process. When the pump and the signal are injected into the nonlinear medium, they induce polarization with frequency \( \omega_i = \omega_p - \omega_s \) through the second order optical susceptibility. At the same time, the idler signal coupled with the the pump, induces the polarization with frequency \( \omega_s = \omega_p - \omega_i \). This generates intensity enhanced signal beam [5]. Because the pump is much stronger than the signal and the idler, if the phase matching condition is well satisfied, this nonlinear frequency mixing will act continuously along the space. This results in the optical parametric amplification.

The condition for energy conservation is given by Equation 1.9 and the condition for momentum conservation is

\[ k_p = k_s + k_i. \]  
(1.10)

If the three wave vectors are all in the same direction, this becomes,

\[ n_p \omega_p = n_s \omega_s + n_i \omega_i. \]  
(1.11)

The spatial variation of the optical fields in the nonlinear medium is given by the equations,
where $\omega_1/c = k_1/n_i$ and $\omega_3 = \omega_1 + \omega_2$. In OPA, $\omega_3 = \omega(pump)$ and $\omega_1 = \omega(signal)$ and $\omega_2 = \omega(idler)$.

Figure 1.3: Wave vector diagram for SPDC

5. **Spontaneous Parametric Down Conversion (SPDC):** SPDC is an important process in quantum optics. A nonlinear crystal splits incoming photons into pairs of photons of lower energy whose combined energy and momentum is equal to the energy and momentum of the original photon. “Parametric” refers to the fact that the state of the crystal is left unchanged in the process, which is why energy and momentum are conserved (this is related to phase matching in nonlinear optics). The process is spontaneous in the same sense as spontaneous emission, it is initiated by random vacuum fluctuations. Consequently, the photon pairs are created at random times. However, if one of the pair (the “signal”) is detected at any time then we know its partner (the “idler”) is present. This then allows for the creation of optical fields containing a single photon. As of now, this is the predominant mechanism for experimentalists to create single photons (also known as Fock states).
Consequences of Third Order Polarization

Some of the important consequences of third order polarization are given below.

1. **Third Harmonic Generation (THG):** THG is the generation of light with a tripled frequency or one-third the wavelength of the incident radiation. Consider the third order contribution to nonlinear polarization,

   \[ \tilde{P}^{(3)}(t) = \chi^{(3)} \tilde{E}^3(t) \]  \hspace{1cm} (1.13)

For electric field of the form

   \[ \tilde{E}(t) = \varepsilon \cos(\omega t) \]  \hspace{1cm} (1.14)

\( \tilde{P}^{(3)}(t) \) will contain a term with frequency \( 3\omega \) which is due to third harmonic generation. This is illustrated in Figure 1.4. When we consider the third order polarization, there is one component in it at the frequency of the incident field; this term leads to a nonlinear contribution to the refractive index experienced by a wave at frequency \( \omega \). The refractive index in the presence of this type of nonlinearity depends on the intensity of the laser light and leads to what is known as 'intensity dependent refractive index', (IDRI).

2. **Intensity Dependent Refractive Index (IDRI):** IDRI is defined as the change of the index of refraction in a material, due to the presence of intense optical waves. Third order polarization causes a modification in refractive index in such cases and is defined as

   \[ n = n_0 + n_2 I \]  \hspace{1cm} (1.15)
where \( n_0 \) is the linear refractive index and

\[
 n_2 = \frac{12\pi^2}{n_0^2 c} \chi^{(3)}
\]  

(1.16)

is an optical constant that characterizes the strength of the nonlinearity. \( I = \frac{n_0 c E^2}{8\pi} \) being the time-averaged intensity of the incident wave. Because the intensity has units \( W/cm^2 \), the unit used for \( n_2 \) is \( cm^2/W \). There are a variety of mechanisms that can cause the change in the index of refraction, and it has numerous applications. Self-focusing (defocusing) and optical bistability are two important consequences of the IDRI.

3. **Self Focussing**: One consequence of intensity dependent refractive index is self-focusing. This can happen when a light beam of non-uniform transverse intensity distribution, propagates through a material for which \( n_2 \) is positive. Under these conditions, the material effectively acts as a positive lens and causes the rays to converge towards each other, resulting in self-focusing. This is of great practical importance because, the intensity at the focal spot of the self-focussed beam is usually sufficiently large to lead to optical damage of the material. If the intensity of a light beam varies across its diameter, as in the case of Gaussian beams, then the refractive index of the material through which the beam propagates varies accordingly. Let us consider the case of a Gaussian beam. In the center of the beam the intensity is higher than at the edges. If \( n_2 > 0 \), the optical path length is larger at the center than at the edges, as in a converging lens. The beam is then focused as it propagates through the medium. If \( n_2 < 0 \), then the beam path is larger at the edge, and the beam will defocus [4]. In the case of self-focusing, if the nonlinear medium is of small path length, the focusing will occur outside the medium, and hence it cannot damage the material. But if the nonlinear medium is long enough, the focusing occurs inside the material and damage may occur for input intensities that are sufficiently high. Another interesting phenomenon that can take place inside a long nonlinear medium is the self-trapping of light. This takes place when the tendency of the beam to self-focus is compensated by its tendency to spread due to diffraction. Then, the beam has a constant diameter over a relatively large distance inside the material.

4. **Optical bistability**: Optical bistability means that for an input laser intensity, there are two possibilities of the output signal, exactly as with magnetic hysteresis[6]. In this case, the transmittance of an optical device,
may change from a low value to a high value for a sufficiently high intensity and remains at this value until the intensity is reduced by appropriate amount. Such a device can be realized with a Fabry-Perot interferometer containing a nonlinear medium (nonlinear Fabri-Perot interferometer). As in common bistable systems, here also, two output intensities are possible at a given input intensity. The device can be used as an optical memory element or as a switch in optical communication and in optical computing. If the input intensity is a given value \( I_b \) (with \( I_l < I_b < I_h \)), where \( I_l \) and \( I_h \) are the lower and upper limits, there are two possible output intensities. This situation corresponds to storing binary information. If a pulse of light is sent through the device, the system can make a transition to the higher state. If the input light is blocked momentarily, the system makes a transition to the lower state.

5. **Optical Kerr Effect**: Consider an isotropic liquid comprising asymmetric molecules placed in an electric field. Its molecules tend to align themselves parallel to the direction of the field. Because the molecules are not symmetrical, this alignment causes the liquid to become anisotropic and birefringent. That is, a light wave which enters the liquid, splits into two waves traveling at different velocities. Due to this the material offers different refractive indices for different polarized light. This electric field induced birefringence in isotropic liquid is called the Kerr effect. If a constant field is applied, the liquid behaves as a birefringent crystal with indices \( n_o \) and \( n_e \). The optic axis is parallel to the direction of the field. The birefringence is proportional to the square of the applied voltage. In other words, the change in refractive index is proportional to the square of the electric intensity of the external field.

6. **Kerr-Lens Mode locking (KLM)**: It has been known for a long time that intense laser beams are subject to self-focussing when they propagate through optical media that have a nonlinear index of refraction. This Kerr self-focussing effect leads to slight changes in the spatial intensity profile of the resonator mode in laser oscillators. As a consequence, by introducing an intra cavity aperture, a power-dependent loss can be created. When carefully optimized, this passive amplitude-modulation mechanism favors a high intra-cavity power, i.e., mode-locked operation over free-running laser oscillation. Owing to the quasi-instantaneous response of nonresonant Kerr nonlinearities, the amplitude modulation induced by self-focussing is able to simulate ultra-fast saturable-absorber
action and support pulse formation down to the femtosecond regime in solid-state lasers that have long gain-relaxation times. The technique has been termed self mode-locking or Kerr lens mode locking (KLM) [7].

7. Self-phase Modulation (SPM): SPM is another important nonlinear optical effect resulting out of light-matter interaction. An ultrashort pulse of light, when traveling in a medium, will induce a varying refractive index of the medium due to the optical Kerr Effect. This variation in refractive index will produce a phase shift in the pulse, leading to a change of the frequency spectrum of the pulse. Self-phase modulation is an important effect in optical systems that use short, intense pulses of light, such as lasers and optical fibre communication.

For an ultrashort pulse with a Gaussian shape and constant phase, the intensity at time $t$ is given by,

$$I(t) = I_0 \exp\left(-\frac{t^2}{\tau^2}\right)$$  \hspace{1cm} (1.17)

where $I_0$ is the peak intensity, and $\tau$ is half the pulse duration. If the pulse is traveling in a medium, the optical Kerr effect produces a refractive index change with intensity as given earlier (Equation 1.15). As the pulse propagates, the intensity at any one point in the medium rises and then falls as the pulse goes past. This will produce a time-varying refractive index:

$$\frac{dn(I)}{dt} = n_2 \frac{dI}{dt} = n_2 I_0 \frac{-2t}{\tau^2} \exp\left(-\frac{t^2}{\tau^2}\right)$$  \hspace{1cm} (1.18)

This variation in refractive index produces a shift in the instantaneous phase of the pulse:

$$\phi(t) = \omega_0(t) - \frac{2\pi}{\lambda_0} n(I) L$$  \hspace{1cm} (1.19)

where $\omega_0$ and $\lambda_0$ are the carrier frequency and (vacuum) wavelength of the pulse, and $L$ is the distance through which the pulse has propagated. The phase shift results in a frequency shift of the pulse. The instantaneous frequency $\omega(t)$ is given by:

$$\omega(t) = \frac{d\phi(t)}{dt} = \omega_0 - \frac{2\pi L}{\lambda_0} \frac{dn(I)}{dt}$$  \hspace{1cm} (1.20)
and from the equation for $dn/dt$ above, we get

$$\omega(t) = \omega_0 + \frac{4\pi L n_2 I_0}{\lambda_0 \tau^2} t \exp\left(-\frac{t^2}{\tau^2}\right)$$  \hspace{1cm} (1.21)

Plot of $\omega(t)$ against $t$, shows the frequency shift of each part of the pulse. The leading edge shifts to lower frequencies ('redder' wavelengths), trailing edge to higher frequencies ('bluer') and the very peak of the pulse is not shifted. For the center portion of the pulse (between $t = \tau/2$), there is an approximately linear frequency shift (chirp) given by:

$$\omega(t) = \omega_0 + \alpha t$$  \hspace{1cm} (1.22)

where $\alpha$ is:

$$\alpha = \left. \frac{d\omega}{dt} \right|_0 = \frac{4\pi L n_2 I_0}{\lambda_0 \tau^2}$$  \hspace{1cm} (1.23)

It is clear that the extra frequencies generated through SPM broaden the frequency spectrum of the pulse symmetrically. In the time domain, the pulse is not changed, however in any real medium the effects of dispersion will simultaneously act on the pulse. In regions of normal dispersion, the 'redder' portions of the pulse have a higher velocity than the 'bluer' portions, and thus the front of the pulse moves faster than the back, broadening the pulse in time. In regions of anomalous dispersion, the opposite is true, and the pulse is compressed temporally and becomes shorter. This effect can be exploited to produce ultrashort pulse compression.

8. Cross-phase Modulation (XPM): XPM is a nonlinear effect where the intensity of one beam influences the phase change of another beam. Cross-phase modulation is the change of the optical phase of a light beam caused by the interaction with another beam in a nonlinear medium, specifically a Kerr medium. This can be described by a change of the refractive index,

$$\Delta n(\lambda_2) = 2n_2 I(\lambda_1)$$  \hspace{1cm} (1.24)

with the nonlinear coefficient $n_2$. Compared to the corresponding equation for SPM, there is an additional factor of 2. This factor 2 is valid for beams with the same polarization (for cross-polarized beams, it must be replaced by $2/3$). XPM can be relevant under different circumstances. For example, it leads to an interaction of laser pulses in a medium, which
allows to measure the intensity of one pulse by monitoring a phase change of the other one (without absorbing any photons of the first beam). This is the basis of a scheme for quantum non-demolition (QND) measurements. The effect can also be used to synchronize two laser cavities using the same gain medium, in which the pulses overlap and experience XPM. In optical fiber communications, XPM in fibers can lead to problems with channel crosstalk. Sometimes it is said that cross-phase modulation can be used for channel translation (wavelength conversion), but in this context one typically refers to a kind of XPM which is not based on the Kerr effect, but rather on changes of the refractive index via the carrier density in a semiconductor optical amplifier.

9. Nonlinear Light Scattering:

(a) Stimulated Brillouin Scattering- Brillouin Scattering occurs when light in a medium (such as water or a crystal) interacts with density variations and changes its path. The density variations may be due to acoustic modes, such as phonons, or temperature gradients. As described in classical physics, when the medium is compressed, the index of refraction changes and the light path bends.

From a quantum point of view, Brillouin Scattering is considered to consist of interaction of light photons with acoustic or vibrational quanta (phonons). The scattered light has a wavelength that is changed slightly by a variable quantity known as the Brillouin shift; it is sometimes referred to as a ‘red shift’ since it may increase the wavelength of light in a spectrum. For intense beams (e.g. laser light) traveling in a medium, the variations in the electric field of the beam itself may produce acoustic vibrations in the medium via electrostriction. The beam may undergo Brillouin inelastic scattering from these vibrations (acoustic waves), usually in opposite direction to the incoming beam, a phenomenon known as Stimulated Brillouin Scattering (SBS). For liquids and gases, typical frequency shifts are of the order of 110 GHz (wavelength shifts of 110 pm for visible light).

Stimulated Brillouin Scattering is one effect by which optical phase conjugation can take place[5]. In this process a very small part of photon energy transfers to the phonon, consequently a tiny frequency shift of the light wave is induced. When an intense laser beam or pulse propagates in the medium, the coherent acoustic wave will be
Figure 1.5: Raman scattering showing Stokes and Anti-Stokes lines

enhanced by the electrostriction and the scattered light wave is amplified coherently. As a result, the scattering process becomes SBS. This was predicted and calculated by Leon Brillouin in 1922, and was later observed experimentally in liquids. The wave number of frequency shift is only about $0.1 \text{ cm}^{-1}$.

(b) Stimulated Raman Scattering (SRS)- When a strong pump with frequency $\omega_p$ injects into some medium, such as hydrogen gas, liquid $CS_2$, or solid silica, a scattering radiation $\omega_{\text{Raman}}$ with considerable frequency red-shift is generated. The Raman scattering is the inelastic scattering of light waves by the vibration energy levels in the medium. In this process a part of photon energy, which equals the vibration level energy $\hbar \omega_{\text{vibration}}$, is transferred to the optic phonon. In this case a light wave with a shift of about 100 to 1000 $\text{cm}^{-1}$ is produced and is called stimulated Raman scattering. Figure 1.5 shows the spontaneous Raman scattering spectrum. In Figure 1.5a, $\nu = 1$ is the real vibrational level and the left vertical line in 1.5 b is the red-shifted Stokes line $\omega_s = \omega_{s1}$ corresponding to $\nu = 1$ level scattering. The anti-Stokes process in Figure 1.5(a) is really a four-wave mixing, and the right vertical line in 1.5(b) is the blue-shifted anti-Stokes line $\omega_{as}$ for which no real level exists. Qualitatively, the first Stokes (stimulated) and anti-Stokes (FWM) are

$$\omega_{\text{Stokes}} = \omega_{\text{pump}} - \omega_{\text{vibration}} \quad (1.25)$$

$$\omega_{\text{anti-Stokes}} = 2\omega_{\text{pump}} - \omega_{\text{Stokes}} = \omega_{\text{pump}} + \omega_{\text{vibration}} \quad (1.26)$$
If the injected laser beam or pulse are very intense, the scattered light wave will be amplified with significant gain \(G_{\text{Raman}}\) and enhanced coherently. As a result, the scattered process becomes stimulated raman scattering (SRS). At the same time, FWM reveals comparatively efficient and a series of spectrum lines corresponding to \(\omega_{s2}, \omega_{as2}, \omega_{s3}, \ldots\) are obtained. These are all generated by FWM, and the wave-vector diagrams are shown in Figure 1.6.

10. **Optical Phase Conjugation:** It is possible, using nonlinear optical processes, to exactly reverse the propagation direction and phase variation of a beam of light. The reversed beam is called a conjugate beam, and thus the technique is known as optical phase conjugation (also called time reversal, wavefront reversal and retroreflection).

The most common way of producing optical phase conjugation is to use a four-wave mixing technique, though it is also possible to use processes such as SBS. A device producing the phase conjugation effect is known as a phase conjugate mirror (PCM).

For the four-wave mixing technique, we can describe four beams \((j = 1,2,3,4)\) with electric fields as given in Equation 1.27.

\[
\tilde{E}_j(x,t) = \frac{1}{2} E_j(x)e^{i\omega_j t - k_j \cdot x} + \text{c.c}
\]  

(1.27)

where \(E_j\) are the electric field amplitudes. \(\tilde{E}_1\) and \(\tilde{E}_2\) are known as the
two pump waves, with $\tilde{E}_3$ the signal wave, and $\tilde{E}_4$ the generated conjugate wave. If the pump waves and the signal wave are superimposed in a medium with a non-zero $\chi^{(3)}$, this produces a nonlinear polarization field,

$$P_{NL} = \chi^{(3)}(\tilde{E}_3 + \tilde{E}_2 + \tilde{E}_3)^3$$

resulting in generation of waves with frequencies given by $\omega = \omega_1 \omega_2 \omega_3$ in addition to third harmonic generation waves with $\omega = 3\omega_1, 3\omega_2, 3\omega_3$.

As above, the phase-matching condition determines which of these waves is the dominant. By choosing conditions such that $\omega = \omega_1 + \omega_2 - \omega_3$ and $k = k_1 + k_2 - k_3$, this gives a polarization field,

$$P_{\omega} = \frac{1}{2} \chi^{(3)} \epsilon_0 \epsilon_2 \epsilon_3^* e^{i(\omega t - k \cdot x)} + c.c.$$  \hspace{1cm} (1.29)

This is the generating field for the phase conjugate beam, $\tilde{E}_4$. Its direction is given by $k_4 = k_1 + k_2 - k_3$, and so if the two pump beams are counter-propagating ($k_1 = -k_2$), then the conjugate and signal beams propagate in opposite directions ($k_4 = -k_3$). This results in the retro reflection. Further, it can be shown for a medium with refractive index $n$ and a beam interaction length $l$, the electric field amplitude of the conjugate beam is approximated by

$$\tilde{E}_4 = \frac{i\omega l}{2nc} \chi^{(3)} \epsilon_1 \epsilon_2 \epsilon_3^*$$  \hspace{1cm} (1.30)

(where $c$ is the speed of light). If the pump beams $E_1$ and $E_2$ are plane (counter-propagating) waves, then $\tilde{E}_4(x) \propto \tilde{E}_3^*(x)$ i.e., the generated beam amplitude is the complex conjugate of the signal beam amplitude. Since the imaginary part of the amplitude contains the phase of the beam, this results in the reversal of phase.

Note that the constant of proportionality between the signal and conjugate beams can be greater than 1. This is effectively a mirror with a reflection coefficient greater than 100%, producing an amplified reflection. The power for this comes from the two pump beams, which are depleted by the process. The frequency of the conjugate wave can be different from that of the signal wave. If the pump waves are of frequency $\omega_1 = \omega_2 = \omega$, and the signal wave is higher in frequency such that $\omega_3 = \omega + \Delta\omega$, then the conjugate wave is of frequency $\omega_4 = \omega - \Delta\omega$. This is known as frequency flipping.
11. **Two-photon Absorption (TPA):** The process of two-photon absorption is similar to ordinary single photon absorption. In this process an electron absorbs two photons at approximately the same time (or within less than a nanosecond) 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). Instead, the atom is excited to a "virtual state" which need not correspond to any electronic or vibrational energy eigenstate.

Selection rules for these transitions logically follow from the selection rules for one photon transitions. With one photon absorption, an electron may undergo transition only if the change in angular momentum (change in \( L \)) is +1 or -1. Since photons have angular momentum of +1 or -1, an electronic state absorbing two photons simultaneously may change angular momentum by +2, 0. Two \( L = +1 \) photons cause a change of +2; a photon of \( L = +1 \) and \( L = -1 \) cause a change of 0.

Through two-photon absorption we can populate high energy levels that are otherwise unreachable by single photon transitions from the ground state. Once electrons have absorbed two photons and are at a high energy level, it takes no more than the absorption of another photon to release the electron and ionize the atom. If there is an intense, monochromatic photon source (such as a high energy laser) used to excite these atoms through two-photon absorption, it is assured that there are ample photons to continue the excitation process and ionize the electron before it radiates back to a lower energy level.

### 1.1.3 Nonlinear Optical Materials

Nonlinear optical materials are materials in which the intensity of light input, including its frequency, is not related to the intensity of light output by a simple proportionality constant. Because of this nonlinear behavior, an intense light beam propagating through a nonlinear optical material will produce new effects that cannot be seen with weak light beams.

The properties of materials that make them suitable for nonlinear optical applications are not that handled by the traditional material scientist[8]. Familiar properties like elasticity, hardness, etc. of a material may play an indirect role in terms of establishing the life time of a suitable optical material. However, the essence of a good nonlinear optical material lies in the magnitude of
the so-called "nonlinear optical response function" or "nonlinear dielectric susceptibility," which provides a measure of how the material reacts to modify an incoming light beam. The latter quality can be partitioned somewhat arbitrarily into a resonant and nonresonant optical response. Resonant optical response can involve either light absorption or amplification due to coupling to the dipole oscillators making up the material. A nonresonant optical response involves essentially non-modification to the amplitude of the impinging light signal but, rather, induces an intensity dependent phase change. Hence the refractive index of the material gets modified. In reality both absorption/amplification and refraction changes occur simultaneously but one or the other can be enhanced depending on the requirement.

There is little doubt that nonlinear optics, whether realized in an all-optical or a hybrid electro-optical mode, will have an increasingly important impact on modern technology. The search for suitable materials to satisfy future technology needs is an ongoing challenge.

1. Inorganic nonlinear Optical Materials

In the early days of nonlinear optics, studies mainly concentrated on inorganic materials such as quartz; KDP; and semiconductors such as cadmium sulfide, selenium, and tellurium. These materials were first studied because they were found to give population inversion necessary for laser research. Later, inorganic materials such as KTP and BBO became prominent due to high efficiency and widespread use for harmonic generation or other device applications.

2. Organic nonlinear Optical Materials

Organic compounds with delocalized conjugated \( \pi \)-electrons have gained much attention because of their large non-linear optical properties and quick response. Polydiacetylene and one-dimensional metal complexes exhibit excellent non-linear optical properties. Some examples are porphyrins and phthalocyanines. This will be discussed in detail in subsequent chapters.

3. Semiconductors

Semiconductor nanoparticle suspensions are used as NLO media and these are usually prepared by laser ablation technique. The local field enhancement of nanoparticles in colloidal suspensions and considerable nonlinear optical susceptibilities of chalcogenide structures make these semiconductor nanoparticles interesting materials. Aqueous colloidal suspensions of
As2S3 and CdS nanoparticles are examples. The semiconductor chalco­genide structures show promise for applications in information processing systems due to such properties as high nonlinearities, high transparency in the infrared range, and easy processing. Among other potential applications of amorphous chalcogenides are wave conjugation, optical image processing, optical switching, integral optical devices, and holographic optical elements. Chalcogenide films such as As2S3, As20S80, 2As2S3/As2Se3, and 3As2S3/As2Se3 can be prepared by the evaporation of chalcogenide glass components (for example, As2S3, As20S80, As2Se3) onto the surfaces of BK7 glass substrates.

1.2 Measurement Techniques for NLO Properties

Some of the commonly used measurement techniques for nonlinear optical properties are discussed below.

1.2.1 Degenerate Four Wave Mixing (DFWM)

Frequency mixing represents one of the most general but nonetheless important phenomena in nonlinear optics. In this process, two or more waves interact in a nonlinear medium to produce an output at various sum or difference frequencies. Four-wave mixing can take place in any material. It refers to the interaction of four waves via the third order nonlinear polarization. When all waves have the same frequency, the process is called degenerate, although their wave vectors are different. This process results from the nonlinear index of refraction. Degenerate four-wave mixing (DFWM) can yield phase conjugation and is useful, for example, for correcting aberrations by using a phase conjugate mirror (PCM).

As a technique, DFWM is one of those most heavily employed in characterizing third order nonlinear materials. In all the configurations for DFWM, the working principle is that two beams interfere to form some type of grating (e.g. intensity grating) and a third beam scatters off this grating, generating the fourth beam named the conjugate or signal beam. The most frequently used DFWM configuration is the phase-conjugate geometry as given in Figure 1.7. Two common DFWM experimental geometries are given in this Figure. Three beams with wavevectors \( k_1, k_2, \) and \( k_3 \) interact in a sample to generate a fourth beam with wavevector \( k_4 \). The interacting beams and the sample are drawn in the x-y plane in the first line, and the coordinates of the beam wavevectors
are plotted in the second line. For clarity, the x and y axes are not in scale. (a) Beams 1 and 2, and beams 4 (signal) and 3, are counterpropagating. (b) All input beams travel towards the positive x direction. The beams are distinguished by a slightly different z direction.

1.2.2 Nearly Degenerate Four-Wave Mixing

Nearly degenerate four-wave mixing (NDFWM) can be demonstrated by simultaneously injecting two waves of slightly different frequencies in the same direction. A new frequency wave at an expected frequency for NDFWM is observed with the same order of output as that of the injected light. The output power ratio of the three beams is strongly dependent on the sign of the frequency detuning. Theoretical analysis can be done by considering the carrier rate equation coupled with nonlinear Maxwell's equations. The procedure will ultimately yield the value of $n_2$.

1.2.3 Ellipse Rotation

These types of measurements depend on an estimate of the beam profile, for a focused beam. The experimental set up can be calibrated by measuring the ellipse rotation for CS$_2$ whose $\alpha + 2\beta$ values can be obtained from other techniques. Strong enough focussing of the beam into the sample will ensure that the
entire ellipse rotation takes place within the sample volume[9]. The laser source in the given example is a ruby laser, giving 20 ns pulses. The Rochon prism P1 determines the plane of polarization prior to introduction into the Fresnel Rhomb R1 which produces an elliptically polarized input. R2 is oriented parallel to R1 so as to produce a linearly polarized output in the absence of ellipse rotation. This is followed by Wollaston prism P2, which directs the maximum “transmitted” signal into D3 and the minimum “nulled” signal into D2, when there is no ellipse rotation. With suitable light intensity, the polarization ellipse will rotate and this will be revealed as a relative increase in the “nulled” signal. By performing some detailed calculations one can obtain the value of nonlinear index of refraction n2.

1.2.4 Beam Distortion Measurements

This is a pump probe technique which allows one to investigate non-degenerate components of the nonlinearity[10]. Figure 1.9 shows the principle of the method. A pump beam is used to introduce a ‘phase object’ in the sample. In the simplest case the object may be just the circular spot created by suitably focussing the pump beam. A probe beam crosses the sample and acquires the phase distortion via XPM. Free propagation of this beam converts this phase distortion into amplitude variations in the far field. Since the pump beam is chopped at some frequency, relatively small amplitude modulation can be readily detected using a lock-in amplifier. Modulation of the local intensity of the probe beam will appear when either a phase distortion (due to the real part of $\chi^{(3)}$) or an amplitude distortion (due to the imaginary part of $\chi^{(3)}$) occurs. However, the presence of a phase distortion can be detected only in the far field while the amplitude distortion is detectable at the sample plane itself. Therefore, choosing the position of the imaging lens to image either the sample plane or the far field region onto the detector aperture, one can distinguish between the imaginary and real parts of the nonlinearity.
1.2.5 Photothermal and Photoacoustic Techniques

These techniques are not widely used for the determination of nonlinear optical parameters. However some of them are very interesting [11, 12].

1. Photothermal method

Optical nonlinearity originating in photothermal effects causes SPM in the medium, and this can be characterized by use of heat-conduction analysis [11]. The refractive-index distributions that are due to the photothermal optical nonlinearity will be determined by two different methods. One method is analytical solution of Kirchhoffs diffraction integral including the higher-order nonlinear phase distribution. Another method is by analytical solution of a heat-conducting equation. The method yields the values of nonlinear refractive index.

2. Photoacoustic method

One of the method to study nonlinear optical response of a material is the coherent photoacoustic technique for measuring excited-state absorption. The experimental set up is as shown in Figure 1.10. It involves a picosecond pulse sequence with four pulses. The first pulse populates the excited state. Then, a pair of time coincident pulses cross in the sample, making an optical interference pattern and generating an acoustic diffraction grating. The amplitude of the acoustic grating is proportional to the excited-state absorption cross section. The amplitude is measured by the Bragg diffraction of the fourth pulse from the acoustic grating. This method can be readily applied to liquids, glasses or crystals. The results
of ESA measurements from this experiments, are used in addressing the mechanism for acoustic diffraction of a probe beam nearly resonant with a strong and narrow ground-state transition, e.g., pentacene in p-terphenyl. It has been demonstrated by researchers that there is a density wave induced spectral shift contribution to the acoustic grating which results in greatly increased diffraction efficiency near resonance. For more details and description of the experimental set up, one can refer [12].

1.2.6 Z-scan

Z-scan is a technique based on the principles of spatial beam distortion, but offers simplicity as well as very high sensitivity. For many practical cases, nonlinear refraction and its sign can be obtained from a simple linear relationship between the observed transmittance changes and the induced phase distortion without the need for performing detailed calculations. This technique has been employed in investigating the NLO properties of various materials reported in this thesis. Therefore a detailed description is presented below as a separate section.

1.3 Z-scan: Experimental Technique and Theory

This is a very commonly used experimental configuration to measure the nonlinear absorption and nonlinear refraction of thin sample medium. This was proposed as a technique with complete theory by Sheik Bahea et al in 1990 [13, 14]. They used an extension to the Gaussian decomposition method suggested by Weaire et al [15].

1.3.1 Experimental Technique

A single Gaussian laser beam in a tight focus geometry is used in this method. And the the transmittance of the nonlinear medium through a finite aperture in the far field as a function of the sample position $z$, is measured with respect to the focal plane. (see diagram of experimental set up in chapter 2). This is called the z-scan trace.

To understand how this z-scan trace is related to the nonlinear refraction of the sample, consider the following cases. Assume that the material has a negative nonlinear refractive index and a thickness smaller than the diffraction
Figure 1.10: Experimental set up for photoacoustic determination of excited state absorption
length of the focused beam. This can be regarded as a thin lens of variable focal length. Starting the scan from a distance far away from the focus (negative z), the beam irradiance is low and negligible nonlinear refraction occurs; hence, the transmittance remains relatively constant. As the sample is brought closer to focus, the beam irradiance increases, leading to self-lensing in the sample. A negative self-lensing prior to focus will tend to collimate the beam, causing a beam narrowing at the aperture which results in an increase in the measured transmittance. As the scan in z continues and the sample passes the focal plane to the right (positive z), the same self-defocussing increases the beam divergence, leading to beam broadening at the aperture, and thus a decrease in transmittance. Therefore the trace will cross the 'zero' point in this process. This is analogous to placing a thin lens at or near the focus, resulting in a minimal change of the far-field pattern of the beam.

Therefore, a negative nonlinear refraction results in peak-valley structure. Positive nonlinear refraction, following the same analogy, gives rise to an opposite valley-peak configuration. It is an extremely useful feature of the z-scan method that the sign of the nonlinear index is immediately obvious from the data, and the magnitude can also be easily estimated using a simple analysis for a thin medium. By suitable modification of the experimental set up, theoretical formalism and detection schemes, it is possible to extract details of nonlinear absorption, nonlinear refraction, excited state absorption etc. from the z-scan signal. Some of these methods are illustrated in the next two chapters, where it is suitably described with the experimental results from metal phthalocyanines. In the next section, the theory to find nonlinear absorption coefficient ($\beta$) and nonlinear refraction coefficient ($\gamma$) has been briefly explained.

1.3.2 Theory

The nonlinear optical coefficients $\beta$ and $\gamma$ are extracted from the z-scan data, as follows. In the case of cubic nonlinearity the index of refraction is given by

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

(1.31)

where $n_0$ is the linear refractive index, $I$ is the intensity of the incident light, expressed in $W/m^2$, $E$ is the peak electric field (cgs) and $\gamma$ is the nonlinear refractive index in SI units, expressed in $m^2/W$ and $n_2$ is the same in CGS esu units. In Equation 1.31 assuming a Gaussian $TEM_{00}$ beam we can write the normalized transmittance when no aperture is kept before the detector, (OA or
linear transmittance, \( S=1 \) as

\[
T(z, S = 1) = \frac{1}{\sqrt{\pi}q_0(z, 0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z, 0)e^{t^2}]dt
\]  

where \( q_0(z, t) = \beta_0(t)L_{\text{eff}} \) and \( L_{\text{eff}} = \frac{(1-e^{-\alpha L})}{\alpha} \) is the effective sample path length, \( L \) the sample length and \( \alpha \) is the linear absorption. Thus once an open aperture z-scan is performed, the nonlinear absorption coefficient \( \beta \) can be determined. \( \gamma \) can then be deduced from the z-scan signal, if one keeps an aperture in front of the detector, which is often referred to as closed aperture (CA) z-scan for which \( S \neq 1 \). This is done as follows. For a sample with small nonlinear absorption, the equation for CA transmittance is expressed conveniently as

\[
T(z) = 1 - \frac{4z}{(1 + x^2)(9 + x^2)}
\]

where \( \Delta \phi_0 \) is the on axis nonlinear phase shift at focus, \( x \) is the dimensionless sample position \( \frac{z}{z_0} \). The nonlinear phase shift is given by \( \Delta \phi_0 = k\gamma I_0 L_{\text{eff}} \) where \( k = \frac{2\pi}{\lambda} \). This equation is used to calculate the value of \( \gamma \), \( \Delta \phi \) being obtained from the CA z-scan fit.

### 1.3.3 Advantages & Disadvantages of Z-scan over other Techniques

Z-scan is a technique that is particularly useful when the nonlinear refraction is accompanied by nonlinear absorption[17]. One advantage of the technique is that the z-scan signals are linearly related to the nonlinear phase shift, and therefore z-scan results do not suffer from the ambiguity of those methods that measure the modulus of \( \chi^{(3)} \). However, the use of z-scan for thin films of polymers is quite difficult because of the need to use relatively high light intensities and large refractive-index changes to obtain a measurable signal on a short propagation path, which often leads to the appearance of permanent refractive-index changes that distort the measurement results. Z-scan is, however, a convenient technique for solution measurements. However, there are certain aspects one needs to take into account while setting up and acquiring the transmittance data from the z-scan experiment. Usually, it is difficult to get any information about the time scale of the refractive-index changes that are being detected. Thus one may be misled by phenomena that occur on a longer time scale than the laser pulses but provide cumulative effects from pulse to pulse. For this careful modification of the experiment and detection schemes should be made.
A few of such techniques are mentioned in the next section.

### 1.3.4 Possible Variants of the Z-scan Experiment

Depending on the nonlinear mechanisms that we want to study and also the type of laser (repetition rate, pulse width etc.) used for excitation, one should modify the detection schemes and also the theory used to interpret the data. There can be slow and fast components to nonlinearity, cumulative effects etc, which needs careful attention while data handling. Several modification to the previously mentioned experimental set up are used by various researchers. A few of them are,

1. Single beam time resolved z-scan

   In the conventional technique, as explained previously, the measurements are usually carried out with fast 'subnanosecond' response Kerr-like media, in a spectral region where the sample is transparent. The laser frequency will usually be far from any resonance of the medium, the nonlinear susceptibility is fairly small, and its measurement demands a high intensity light, only achieved with Q-switched or modelocked lasers. In the resonance region, the nonlinear susceptibility is large and thus, even a low power CW laser would be suitable for its measurement. Moreover, if the optical nonlinearity arises due to the population of a long-lived electronic state or if it has a thermal origin, the medium will present a slow 'millisecond' response. In this situation, the sensitivity of the z-scan technique can be substantially improved by eliminating any parasitic linear effect by means of a time resolved signal detection.

   The experimental setup is shown in Figure 1.11. The light source is CW. In order to keep the same optical alignment an electro-optical modulator (EOM) is used to change the light intensity. The use of this device is important if the same region of the sample has to be probed at different intensities. A spatial filter (SF) assures a good transverse mode quality. After passing through the spatial filter the beam is focused (lens L1) on the chopper blade that mechanically modulates the radiation, such that the on-off transition time is minimized. Lens L2 recollimates the beam while L3 produces the focus at \( z = 0 \). The rest of the diagram is as in the ordinary z-scan set up. For a slow response medium, the use of the chopper and the microcomputer allows the monitoring of the transmittance temporal evolution, which can be used to eliminate linear effects. For more details see reference [7].
Immediately after the chopper opens at $t=0$, there was not enough time for any long-lived excited state to be populated; neither had the sample absorbed enough energy to increase its temperature. Therefore, the transmittance is purely linear at $t=0$. As the time evolves, the sample heats and/or excited states become populated and nonlinear effects start to manifest themselves. For times much longer than the characteristic relaxation time, the steady state is reached and the final transmittance presents both linear and nonlinear contributions.

2. Reflection $z$-scan

This technique is suitable for opaque or highly absorbing samples. The incident Gaussian beam propagates along the $z$ axis, with its waist located at $z=0$ (see Figure 1.12). The distance between the beam waist and the sample surface is $z$ and the aperture plane is placed at the distance $d$ from the beam waist. The terms used in this diagram are common. The application of this method is to measure nonlinear parameters and the surface expansion of highly absorptive materials - even opaque samples. Here also calculation of the far-field pattern of the beam at the aperture plane is by applying the “Gaussian decomposition method.” [19]

There are numerous other techniques like eclipsed $z$-scan, dual beam $z$-scan etc [20].
1.4 Conclusions

There are several experimental techniques for studying the nonlinear optical properties of materials. However, z-scan is one of the simplest methods that has been employed by several researchers. In this thesis, the nonlinear optical behavior of certain phthalocyanines are studied using both closed aperture and open aperture z-scan. These are dealt with in detail in the next chapters.
References