Chapter 1
Introduction

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Chapter 1

INTRODUCTION

This chapter presents a brief description on the essentials of the studies carried out on different organic compounds. It is followed by some glimpses of elementary theoretical formalisms in nonlinear optics that leads to certain fundamental relations which govern the interaction of optical field with a nonlinear medium. At the end sections, some remarks about the second order nonlinearity and third order nonlinear polarization mechanisms have also been discussed.

1.1 MOTIVATION

Nonlinear optics refers to the branch of optics that deals with intense light-matter interaction and resultanty evolved wide array of optical phenomena. The enormous progress in the theoretical and experimental studies of nonlinear optical effects has contributed to the development of various scientific and technological gadgets and they play an indispensible role in the day-to-day affairs of modern man. Innumerable applications can be pointed out in this context. Some areas of science and technology blessed with nonlinear optics are wavelength conversion [1-3], nonlinear microscopy [4, 5], optical data storage [6, 7], short and ultra short laser systems [8-10], optical communication systems [11-13], etc. The most interesting aspect of this field is that both wave-like and photon-like nature of light can be splendidly used for interpreting and analysing various optical phenomena. At times, wavy nature of light is sufficient to explain certain concepts and at other times, it is convenient to interpret in terms of quantum nature of light.

Various nonlinear optical devices have been proven to be technically feasible, at least in laboratory conditions. But, many are still in its grooming stage, because of the lack of availability of appropriate nonlinear materials with stipulated material specifications to use in actual ground conditions [14]. Hence a significant part of frontier research in nonlinear optics focus on synthesis and characterization of materials with large and fast nonlinear response with additional features like wide transparency range, easy processability, high damage threshold and long lasting material stability. Further, a deeper understanding of the relation between nonlinear polarization mechanism and the structure is essential for the design and development of novel nonlinear optical materials. In this context, synthesis and
characterization of new materials and developing novel strategies for improving nonlinear responses are very much essential.

Currently, much research efforts have been directed towards developing new organic molecular and polymeric materials in different forms. In recent past, the superiority of organic materials over other classes of materials has been realized by the scientific community. Their versatility and the flexibility for improvising material properties by appropriate molecular engineering have enabled us to synthesize numerous materials for various nonlinear applications. In addition, organic materials also exhibit large nonlinear figures of merit, high laser damage threshold, and ultrafast response time. The work reported in this thesis is a humble effort to identify various novel organic compounds as potential nonlinear optical materials and understand the associated microscopic mechanisms leading to such effects. At certain cases, efforts have also been taken to apply strategies to enhance the optical nonlinearity via polymerization and by embedding photoresponsive chromophoric units in the molecular back bone [15].

1.2 PRESENT WORK

This thesis is a detailed investigation of third-order nonlinear optical properties of some newly synthesized coumarin, indole and azopolyester based molecular systems by employing Z-scan, Optical limiting and Degenerate Four Wave Mixing (DFWM) techniques. For certain molecular systems, we have also tried to explore their second-order nonlinear optical responses via Second Harmonic Generation technique. The major experimental set-ups- Z-scan and DFWM were employed to extract and compare the third-order nonlinear susceptibility values of the compounds. We have also explored the ultra short pulse response of certain selected samples by using Z-scan set up with a Ti: Sapphire laser, beaming 100fs pulses at 800nm. This could enable us to compare the performance of materials under different time-scales and intensities, meanwhile facilitating to understand the contribution of pure electronic nonlinearity in compounds.

In this work, the materials for NLO characterization were prepared in different forms such as solution and doping in polymer matrix and by forming composite with graphene oxide. Both linear and nonlinear optical characterizations were done. Besides characterization, one of our key objectives is to understand the relationship that exists between the molecular structure and their third order nonlinear response. Our study reveals that third order nonlinear parameters are largely influenced by the nature of substituents, the
extent of \( \pi \)-electron conjugation, donor-acceptor functionalities, spatial orientation, planarity, steric effect etc. For certain classes of compounds computational chemistry calculations have been done using Gaussian 09W simulation package to explore the structure-property relationship [16].

1. 3 ESSENTIALS OF NONLINEAR OPTICS

When the electric field associated with an optical beam is high, as it is with an intense laser beam propagating through a nonmagnetic material medium, the material properties are drastically affected by the incident field. The electrical susceptibility coefficient \( \chi \) of the medium would be the most predominantly affected material parameter. The resulting macroscopic electric polarization \( \tilde{P} \) then tends to be a complicated function of the externally applied electric field strength \( \tilde{E} \). In such a typical case, the electric polarization \( \tilde{P} \) can be expanded in a Taylor series in terms of the external electric field strength [17].

\[
\tilde{P}(\tilde{E}) = \tilde{P}(0) + \left( \frac{\partial \tilde{P}}{\partial \tilde{E}} \right)_{\tilde{E}=0} \tilde{E} + \frac{1}{2!} \left( \frac{\partial^2 \tilde{P}}{\partial \tilde{E}^2} \right)_{\tilde{E}=0} \tilde{E} \cdot \tilde{E} + \frac{1}{3!} \left( \frac{\partial^3 \tilde{P}}{\partial \tilde{E}^3} \right)_{\tilde{E}=0} \tilde{E} \cdot \tilde{E} \cdot \tilde{E} + \ldots \quad (1.1)
\]

By applying Einstein’s summation convention of adding over common indices of tensors, above expression may be reframed in component form as follows

\[
\tilde{P}_i(\tilde{E}) = \tilde{P}_i(0) + \left( \frac{\partial \tilde{P}_i}{\partial \tilde{E}_j} \right)_{\tilde{E}=0} \tilde{E}_j \tilde{E}_j + \frac{1}{2!} \left( \frac{\partial^2 \tilde{P}_i}{\partial \tilde{E}_j \partial \tilde{E}_k} \right)_{\tilde{E}=0} \tilde{E}_j \tilde{E}_k \tilde{E}_k + \frac{1}{3!} \left( \frac{\partial^3 \tilde{P}_i}{\partial \tilde{E}_j \partial \tilde{E}_k \partial \tilde{E}_l} \right)_{\tilde{E}=0} \tilde{E}_j \tilde{E}_k \tilde{E}_l \tilde{E}_l + \ldots \quad (1.2)
\]

where, the bracketed coefficients are respectively, the linear \( (\chi^{(1)}) \), second order \( (\chi^{(2)}) \) and third order \( (\chi^{(3)}) \) susceptibility tensors. Those coefficients can be expressed in SI system in the following way.

\[
\chi^{(1)}_{ij} = \frac{1}{\varepsilon_0} \left( \frac{\partial \tilde{P}_i}{\partial \tilde{E}_j} \right)_{\tilde{E}=0} \quad \text{Linear or first-order susceptibility} \quad (1.3)
\]

\[
\chi^{(2)}_{ijk} = \frac{1}{2\varepsilon_0} \left( \frac{\partial \tilde{P}_i}{\partial \tilde{E}_j \partial \tilde{E}_k} \right)_{\tilde{E}=0} \quad \text{Second-order susceptibility} \quad (1.4)
\]

\[
\chi^{(3)}_{ijkl} = \frac{1}{6\varepsilon_0} \left( \frac{\partial \tilde{P}_i}{\partial \tilde{E}_j \partial \tilde{E}_k \partial \tilde{E}_l} \right)_{\tilde{E}=0} \quad \text{Third-order susceptibility} \quad (1.5)
\]
It is also worth mentioning that, in general, $\chi^{(1)}$ is a second rank tensor with nine components, $\chi^{(2)}_{ij}$ is a third rank tensor with 27 components and $\chi^{(3)}_{ijkl}$, a fourth rank tensor consisting of 81 components. With the substitutions shown in equations (3), (4) and (5), the resulting macroscopic polarization in a material is expressible in a compact form as follows.

$$\tilde{P}_i(\tilde{E}) = \tilde{P}_i(0) + \varepsilon_0(\chi^{(1)}_{ij} \tilde{E}_j + \chi^{(2)}_{ijk} \tilde{E}_j \cdot \tilde{E}_k + \chi^{(3)}_{ijkl} \tilde{E}_j \cdot \tilde{E}_k \cdot \tilde{E}_l + \ldots)$$  \hspace{1cm} (1.6)$$

The nonlinear optical responses of a medium are fully described by its nonlinear susceptibility tensors $\chi^{(n)}$, with $n>1$. In the present work, most of the materials used do not have appreciable intrinsic macroscopic dipole moment under no field condition. This means that the first term in the above equation vanishes and we obtain,

$$\tilde{P}_i(\tilde{E}) = \varepsilon_0(\chi^{(1)}_{ij} \tilde{E}_j + \chi^{(2)}_{ijk} \tilde{E}_j \cdot \tilde{E}_k + \chi^{(3)}_{ijkl} \tilde{E}_j \cdot \tilde{E}_k \cdot \tilde{E}_l + \ldots)$$ \hspace{1cm} (1.7)$$

In an analogous fashion, the microscopic (molecular/atomic) polarization $\tilde{p}$ is also expressible as

$$\tilde{p}_i(\tilde{E}) = \varepsilon_0(\alpha_{ij} \tilde{E}_j + \beta_{ijk} \tilde{E}_j \cdot \tilde{E}_k + \gamma_{ijkl} \tilde{E}_j \cdot \tilde{E}_k \cdot \tilde{E}_l + \ldots)$$ \hspace{1cm} (1.8)$$

where $\alpha_{ij}$ is the linear polarizability (first-order molecular susceptibility), $\beta_{ijk}$ is the first hyperpolarizability (second-order molecular susceptibility), and $\gamma_{ijkl}$ is the second hyperpolarizability (third-order molecular susceptibility) of the entity under consideration. The susceptibilities $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ and the polarizabilities $\alpha$, $\beta$, $\gamma$ are generally complex quantities with an amplitude $|\chi^{(n)}|$ and a phase $\phi^{(n)}$, which gives the phase lag of the nonlinear polarization relative to the driving electric field. In fact, the optical field generates a nonlinear response of the material polarization $P(E)$, which in turn affects the optical field itself through the equation [18].

$$n(\tilde{E}) = \sqrt{1 + \chi^{(n)}(\tilde{E})}$$ \hspace{1cm} (1.9)$$

where, $n(E)$ is the effective refractive index of the material in the presence of an electric field $E$. For most of the molecular systems, interactions of the molecule with an input optical beam largely depend on the intensity of the field. Under exposure to an intense field, the displacement of the associated electron cloud responds nonlinearly to the field and the oscillation of the induced dipole becomes anharmonic. In this regime, the strong interaction
between the molecule and the field results in the generation of new fields or modification of the properties of the original fields which results in different nonlinear optical phenomena. It is also worth mentioning that even-order nonlinear susceptibilities exist only in noncentrosymmetric media. It is because all of the susceptibility tensors are invariant under spatial inversion and the polarization vector and applied field are polar vectors which do not change sign under spatial inversion. Since even powered terms are absent in most of the isotropic materials lacking inversion symmetry, one can write polarization \( P = P^{(L)} + P^{(NL)} \), where \( P^{(L)} \) is the linear part and \( P^{(NL)} \) is the nonlinear part that essentially arises from third order nonlinearity. Further, the series expansion of \( P \) can be truncated to include the nonlinear term of lowest order, which is, the cubic nonlinear polarization term.

In general, the linear and third-order susceptibility coefficient consists of real and imaginary parts and they are respectively proportional to the refractive index and absorption coefficient of the material. The combination of both real and imaginary parts can be expressed using a single complex variable [19].

\[
\tilde{\chi}^{(n)} = \chi_r^{(n)} + i\chi_i^{(n)}
\]  

(1.10)

Further, nonlinearity can be treated either in the time domain or in frequency domain. Meanwhile for monochromatic laser beams, treatment in the frequency domain is sufficient.

1.4 MICROSCOPIC AND MACROSCOPIC PARAMETERS - CONCEPT OF MICROSCOPIC POLARIZABILITY AND MACROSCOPIC SUSCEPTIBILITY

Theoretical approaches in nonlinear optics have been bifurcated into macroscopic and microscopic treatments. Microscopic treatments largely depend on quantum mechanical and statistical formalisms. On the other hand, the macroscopic approach, to compute the nonlinear response of an infinite network of molecular/atomic system, depends on structural properties of the system such as energy bands and elementary excitations.

Organic materials are usually composed of microscopic entities, namely molecules, which interact with each other to form large systems. The intramolecular interaction energy is generally much larger than the intermolecular interaction. This is because intermolecular interactions are usually of van der Waal’s type, whereas intramolecular interactions are of covalently bonded type. Therefore organic molecules can be viewed as collections of
weakly interacting molecular units, each interacting independently with the external electromagnetic field. For organic materials, the macroscopic susceptibility can hence be suitably related to the microscopic molecular polarizability parameters.

In case multiple number of laser frequencies are involved in the interaction in a nonlinear organic medium, the time dependent electric field $\vec{E}(r,t)$ can be written as a superposition of monochromatic electric fields and is given by

$$E(r,t) = \frac{1}{2} \sum_n \left[ \tilde{E}^{\omega_n}(r) e^{-i\omega_n t} + c.c \right]$$

(1.11)

where c.c denotes the complex conjugate of the first term and describes the wave travelling in the negative direction and $\omega_n$ represents the angular frequencies contained in the laser field. Similarly, for the time dependent macroscopic $\mathbf{P}(r,t)$ and microscopic $\mathbf{p}(r,t)$ polarizations, the same convention can be applied resulting in

$$\mathbf{P}(r,t) = \frac{1}{2} \sum_n \left[ \tilde{P}^{\omega_n}(r) e^{-i\omega_n t} + c.c \right]$$

(1.12)

and,

$$\mathbf{p}(r,t) = \frac{1}{2} \sum_n \left[ \tilde{p}^{\omega_n}(r) e^{-i\omega_n t} + c.c \right]$$

(1.13)

These two parameters are interrelated through the relation

$$\mathbf{P}(r,t) = N \left< \mathbf{p}(r,t) \right>$$

(1.14)

where $N$ is the number density of microscopic dipoles per unit volume and $\left< \right>$ represents an orientational averaging over all the microscopic dipoles. Further, in the relation between the macroscopic susceptibilities $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ and the microscopic properties $\alpha$, $\beta$, $\gamma$, the local field corrections have to be considered as the molecule itself experiences the external field $E$ altered by the polarization of the surrounding material. For convenience, instead of using $\vec{E}$, the local electric field representation, $\vec{E}_{\text{loc}}$ can be used. In the most widely used Lorentz approximation, the molecule is assumed to be at the centre of a spherical cavity in a homogeneous media and the local field follows according to the relation [20]

$$\vec{E}_{\text{loc}} = \vec{E} + \frac{1}{3e_0} \vec{p} = \left( I + \frac{\chi^{(1)}}{3} \right) \vec{E} = L(\omega) \vec{E}$$

(1.15)
where \( L(\omega) \) is the Lorentz local field factor given by

\[
L(\omega) = \left( \frac{n_o^2 + \frac{2}{3}}{\omega} \right)
\]

Hence, for the monochromatic optical field of a laser, the relation between macroscopic and microscopic polarizations can be related as

\[
\chi^{(1)} = NL(\omega)\alpha
\]

\[
\chi^{(2)} = NL'(\omega)\beta
\]

\[
\chi^{(3)} = NL'(\omega)\gamma
\]

If the intermolecular arrangement is more complicated, then polarizabilities and hyperpolarizabilities have to be integrated over the parameter space with the probability function. But the experiments in this thesis have been performed mainly in liquid solutions or polymer films where isotropic-distribution assumption is sufficient, similar to the assumption in an ideal gas. For large concentrations of molecules in solution or in a polymer matrix, the dimerization or aggregation may start and violate this basic assumption. A concentration versus nonlinearity plot will help us to evaluate the assumption of ‘independent entities’. In view of this, a concentration dependence of \( \chi^{(3)} \) has been appended at appropriate places in the thesis. A linear increase of \( \frac{\chi^{(2)}}{\chi^{(3)}} \) with concentration indicates that the response of the molecules are like independent entities.

1.5 CONCEPT OF REFRACTIVE INDEX AND ABSORPTION – MAXWELLIAN PERCEPTIONS

For a non-magnetic, non-conducting and homogeneous dispersive dielectric medium the Maxwell’s equations are given by [21]

\[
\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}
\]

\[
\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}
\]

\[
\nabla \cdot \mathbf{D} = \rho_{\text{encl}}
\]

\[
\nabla \cdot \mathbf{H} = 0
\]

By applying the curl operation to the second Maxwell’s equation and setting the electric displacement vector relation for the nonlinear organic material as
\[ D = \varepsilon_0 E + P_{lin} + P_{nl} \]  

the resulting nonlinear wave equation for electric field follows as

\[ \nabla \times \nabla \times E + \mu_0 \frac{\partial^2}{\partial t^2}(\varepsilon_0 E + P_{lin}) = -\mu_0 \frac{\partial^2 P_{nl}}{\partial t^2} \]  

(1.25)

By inserting the curl operator identity \( \nabla \times \nabla \times E = \nabla(\nabla \cdot E) - \nabla^2 E \), Eqn. (1.25) can be rewritten in a different form given by

\[ \nabla^2 E - \mu_0 \varepsilon_0 \left(1 + \chi^{(1)}\right) \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P_{nl}}{\partial t^2} \]  

(1.26)

Since the right hand side of the equation acts as a source term for nonlinear interaction, the left hand side alone can be considered for a general solution for all points other than the source. Including the complex form (phasors) of \( E \) and \( P \) in the relation (1.26), we obtain,

\[ \nabla^2 \tilde{E}^\omega(r) + \mu_0 \varepsilon_0 \omega^2 \left(1 + \chi^{(1)}\right) \tilde{E}^\omega(r) = -\mu_0 \omega^2 \tilde{P}^\omega_{nl}(r) \]  

(1.27)

Considering the left hand side alone for regions other than the source, we obtain it in the standard form of the Helmholtz equation as

\[ \nabla^2 \tilde{E}^\omega(r) + \left[k_{\omega,\omega}^2 \right] \tilde{E}^\omega(r) = 0 \]  

(1.28)

where \( k_{\omega,\omega} = \omega \left[\mu_0 \varepsilon_0 \left(1 + \chi^{(1)}\right)\right] \). The solutions of Helmholtz equation are waves with the factor \( e^{i k_{\omega,\omega} r} \) and the wave vector \( k_{\omega,\omega} \). As per definition, the wavevector is the ratio of the frequency and speed of the wave in the material media given by the relation \( k_{\omega,\omega} = \omega n_{\omega}/c \), the refractive index of the media at the frequency \( \omega \) is given by the relation (1.9). At the vicinity of resonance frequency, the linear susceptibility \( \chi^{(1)}(\omega) \) is a complex quantity and hence the linear refractive index \( \tilde{n}(\omega) \) also, in principle, becomes a complex quantity and expressible in the form [22]

\[ \tilde{n}(\omega) = n(\omega) + i \kappa(\omega) \]  

(1.29)

where, \( n(\omega) \) is the normal refractive index and \( \kappa(\omega) \) is the extinction coefficient which is directly related to the absorption coefficient of the medium. The real and imaginary part become physically meaningful if the above equation is introduced in to the relation

\[ \tilde{E}^\omega(r) = E^{\omega k_{\omega,\omega}, \omega}(r) e^{i k_{\omega,\omega} r} e^{-\kappa(\omega) k_{\omega,\omega} r} \]  

(1.30)
It implies that the real part affects the phase component and the imaginary part deals with the absorption losses of the wave in the medium. If the electric field and polarization are plane waves propagating in the z-direction with an electric field amplitude $E_0^\omega$ constant in the x-y plane perpendicular to the propagation direction, then the relation assumes the form

$$\tilde{E}^\omega(z) = E_0^\omega(z) e^{i(\omega)k_0 z} e^{-\kappa(\omega)k_0 z}$$

(1.31)

Since absorption loses are usually described with the Beer law. On comparing the above relation with Beer law and taking into account the intensity-electric field relation $I=(\varepsilon n_0 \mu E^2)/2$, we can relate the absorption coefficient per unit length as

$$\alpha(\omega) = 2k_\omega \kappa(\omega) = \frac{4\pi}{\lambda} \kappa(\omega)$$

(1.32)

1.6 CONCEPT OF NONLINEAR REFRACTIVE INDEX AND NONLINEAR ABSORPTION

One of the key aspect of the third-order susceptibility $\chi^{(3)}$ is its connection to the nonlinear refractive index $n_2(\omega)$ and two-photon absorption coefficient $\alpha_2(\omega)$. Under irradiance with high intense laser beam, the effective refractive index $n(\omega)$ is no more a material constant. A correction term arises with the linear index $n_0(\omega)$ which is proportional to the input intensity of the laser beam. From equation (1.24) we obtain

$$D = \varepsilon_0 \left[ E + \chi^{(1)} E + \chi^{(3)} E.E.E \right]$$

(1.33)

Since refractive index and dielectric constant are related through the relation $n = \sqrt{\varepsilon_r}$, modification of the relation (1.33) leads to an intensity dependent refractive index of the form

$$n(\omega, I) = n_0(\omega) + n_2(\omega) E^2 \frac{2n_0(\omega)}{\varepsilon_0 c}$$

(1.34)

Replacing $E^2$ with optical intensity $I^\omega$, the effective refractive index can be expressed as

$$n(\omega, I) = n_0(\omega) + n_2(\omega) I^\omega$$

(1.35)

where, $n_2(\omega) = \chi^{(3)}(\omega) / \varepsilon_0 c$. On similar lines, the effective absorption coefficient can be expanded in terms of the optical intensity through the relation

$$\alpha(\omega, I) = \alpha_0(\omega) + \alpha_2(\omega) I^\omega$$

(1.36)
where $\alpha_2(\omega)$ represents the nonlinear absorption coefficient, which again is frequency dependent. If the nonlinear polarization modifies the medium, then the Helmholtz equation given in equation (1.28) must be adjusted by including the third order contribution as follows:

$$\nabla^2 \vec{E}''(r) + \mu_0 \varepsilon_0 \omega^2 \left( 1 + \chi^{(1)} + \frac{3}{4} \chi^{(2)} \left| \vec{E}''(r) \right|^2 \right) \vec{E}''(r) = 0$$  \hspace{1cm} (1.37)

Now, the equation (1.9) will take a new form for the effective (apparent) refractive index of the medium

$$\tilde{n}(\omega) = \sqrt{1 + \chi^{(1)}(\omega) + \frac{3}{4} \chi^{(2)}(\omega) \left| E''(r) \right|^2}$$ \hspace{1cm} (1.38)

where the squared electric field strength can be replaced with equivalent expression for intensity

$$\tilde{n}(\omega) = \sqrt{1 + \chi^{(1)}(\omega) + \frac{3}{2\varepsilon_0 c n_0(\omega)} \chi^{(2)}(\omega) I''(\omega)}$$ \hspace{1cm} (1.39)

In an analogous way, as given in equation (1.29), by neglecting the higher order effects, the effective refractive index of the material is expressible as the sum of linear and nonlinear contributions given by

$$\tilde{n}(\omega) = [n_0(\omega) + i\kappa_0(\omega)] + [n_2(\omega) + i\kappa_2(\omega)] I''(\omega)$$ \hspace{1cm} (1.40)

On squaring equation (1.39) and (1.40) and equating the real and imaginary parts separately, we get the following results.

$$n_0^2(\omega) + \kappa_0^2(\omega) = 1 + Re \left\{ \chi^{(1)}(\omega) \right\}$$ \hspace{1cm} (1.41)

$$2n_0(\omega)\kappa_0(\omega) = Im \left\{ \chi^{(1)}(\omega) \right\}$$ \hspace{1cm} (1.42)

$$n_0(\omega)n_2(\omega) + \kappa_0(\omega)\kappa_2(\omega) = \frac{3}{4\varepsilon_0 c n_0(\omega)} Re \left\{ \chi^{(2)}(\omega) \right\}$$ \hspace{1cm} (1.43)

$$n_0(\omega)\kappa_2(\omega) + \kappa_0(\omega)n_2(\omega) = \frac{3}{4\varepsilon_0 c n_0(\omega)} Im \left\{ \chi^{(2)}(\omega) \right\}$$ \hspace{1cm} (1.44)
The equation (1.43) and (1.44) depict the nonlinear refractive index \( n_2(\omega) \) and the two-photon absorption coefficient \( \alpha_2(\omega) \). If the linear loss \( \kappa_0(\omega) \) is assumed to be zero, then nonlinear refractive index and two-photon absorption coefficient can be deduced as follows [23].

\[
\begin{align*}
    n_2(\omega) &= \frac{3}{4\varepsilon_0 c n_0^2(\omega)} \text{Re} \left\{ \chi^{(3)}(\omega) \right\} \\
    \alpha_2(\omega) &= \frac{3\pi}{\varepsilon_0 c \lambda n_0^2(\omega)} \text{Im} \left\{ \chi^{(3)}(\omega) \right\}
\end{align*}
\]

(1.45) 
(1.46)

In general, \( \chi^{(3)} \) is non-zero in any material and is responsible for various interesting nonlinear optical phenomena. But phase matching condition and lack of transparency (resonant absorption) of the medium restricts them from producing large scale macroscopic effects. Hence all materials in general, do not exhibit observable macroscopic third order effects. It is also worth mentioning that in the third order regime, the consequence of anisotropy on the nonlinear effects are of little importance from practical point of view and hence, the tensorial nature of \( \chi^{(3)} \) shall not be taken into account hereafter in the thesis; instead, third order nonlinear optical susceptibility coefficient will be considered as a scalar parameter.

1.7 SOME REMARKS ON SECOND ORDER NONLINEAR OPTICAL EFFECTS

The nonlinear optical response characterized by the parameter \( \chi^{(2)} \) render numerous optical phenomena and useful applications. The second-order nonlinearity is responsible for second-harmonic generation (SHG or frequency doubling), sum and difference frequency generation, and parametric amplification and oscillation. As referred to earlier, \( \chi^{(2)} \), in general, is a third-rank tensor comprising twenty seven components, expressed in tensorial form as \( \chi^{(2)}_{\mu\nu\lambda} \) [23]. Second-order nonlinear processes are possible only in such materials that lack inversion symmetry since \( \chi^{(2)} \) is zero in centrosymmetric crystals.

Some of the important second order phenomena are briefly described below.

1.7.1 Second Harmonic Generation (SHG)

After the invention of laser in 1960, SHG is the first ever reported second order nonlinear optical process. It is also the simplest second order nonlinear optical process in which photons with the same frequency interacting with a nonlinear material are
effectively "combined" to generate new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons. The resulting polarization can be expressed as

\[ P(2\omega) = \varepsilon_0 \chi^{(2)}_{ijk} E_i E_j \] (1.47)

The SHG phenomena is used in laser industry to make green (532 nm) lasers from a IR source (1064 nm) [24, 25]. In biological and medical science, the effect of second harmonic generation is used for high-resolution optical microscopy [26].

1.7.2. Sum and difference frequency generation

In this type of second order nonlinear process, two photons having different frequencies \(\omega_1\) and \(\omega_2\) combine nonlinearly to generate a third photon of frequency \(\omega_3\) [27]. For sum frequency generation, \(\omega_3 = \omega_1 + \omega_2\) and the resulting polarization is given by the equation

\[ P(\omega_1 + \omega_2) = \varepsilon_0 \chi^{(2)}_{ijk} E_i E_j \] (1.48)

And, for difference frequency generation \(\omega_3 = \omega_1 - \omega_2\) and the polarization expression is given by

\[ P(\omega_1 - \omega_2) = \varepsilon_0 \chi^{(2)}_{ijk} E_i E_j \] (1.49)

The processes of sum and difference frequency generation are very useful not only in generating specific frequencies at which standard laser sources are not available but also in generating new tunable frequencies at new wavelengths especially in dye lasers [28, 29].

1.7.3 Optical parametric amplification (OPA) and oscillation (OPO)

Optical parametric amplification can be used to generate squeezed states of optical beams, while, optical parametric oscillation is widely used in tunable solid state lasers (e.g., Ti:sapphire lasers) to generate new frequencies [30]. In OPA, transfer of power takes place from a strong pump beam at \(\omega_3\) to two less intense waves at lower frequencies \(\omega_1\) and \(\omega_2\), such that, \(\omega_3 = \omega_1 + \omega_2\). It is fundamentally similar to the case of second-harmonic generation treated in Section 1.7.1. The only difference is in the direction of power flow. In SHG, power is fed from the low frequency optical field at \(\omega\) to the field at \(2\omega\). In OPA, the power flow is
from the high frequency strong field ($\omega_3$) to the low frequency fields at $\omega_1$ and $\omega_2$. If $\omega_1$ and 
$\omega_2$ are the same, then the phenomena is exactly the reverse of SHG. OPA processes are 
essentially the outcome of second order nonlinear optical mixing of three beams. The 
fundamental condition to be satisfied by the three wave vectors, $k_1$, $k_2$ and $k_3$ of the beams 
involved in optical mixing is

$$\vec{k}_3 = \vec{k}_1 + \vec{k}_2 \quad (1.50)$$

If the pump frequency $\omega_3 = \omega_1 + \omega_2$ is fixed, then two frequencies $\omega_1$ and $\omega_2$ are free to 
spread over a wide range of values depending on the orientation and temperature of the 
crystal. Then the process is usually known as optical parametric oscillation (OSO) [31]. The 
necessary condition to be satisfied by such a process is given by

$$\omega_3 = m\omega_1 + n\omega_2 \quad (1.51)$$

where, $m$ and $n$ are indices whose values can be varied over a range. The frequencies $\omega_1$, $\omega_2$ 
and $\omega_3$ are respectively known as signal, idler and pump frequencies. Practical significance of 
such phenomena relies on the ability of the material to generate two distinct frequencies 
namely, signal and idler frequencies, which can be tuned over a large spectral range. 
Parametric oscillation was first observed by Giordmaine and Miller in 1965 [32]. The output 
was tuned by changing the temperature of the Lithium Niobate crystal (LiNbO3). The output 
was tuned by changing the temperature in a range of 11°C which produced a wavelength 
range of 9680Å to 11540Å.

### 1.8 Gaussian Profiled Optical Beam

In previous sections, we have treated nonlinear optical interactions in the 
approximation that all the interacting waves are taken to be infinite plane waves. However, in reality, 
the laser beam is usually focused in to a nonlinear optical medium in order to 
increase its intensity and thereby to increase the efficiency of the nonlinear optical processes 
as it is done in many of the material characterization processes presented in this thesis. Laser 
beams are available with different beam profiles like top-hat (flat-top), Gaussian [33], super 
Gaussian etc. In this work, we have used temporally and spatially Gaussian profiled optical 
beam and hence its beam parameters and characteristics need to be worth mentioning.
1.8.1. Characteristics of a Focussed Gaussian beam

If we examine the electromagnetic character of a TEM\(_{00}\) laser beam, we would find that its wavefronts are essentially spherical surfaces with long radii of curvature that increase as the beam advances along the propagation axis [34, 35]. The combined wavefront and irradiance variation of a TEM\(_{00}\) laser beam passing through a converging lens appears like the one shown in Figure 1.1.

![Figure 1.1](image)

**Figure 1.1** a) Intensity profile of a focussed Gaussian beam (Longitudinal view), b) Intensity profile as a function of distance from beam axis (Transverse view). Intense regions are represented with dark shades.

The solid red lines shown, above and below the propagation axis, represent the locus of points for which the beam’s electric field irradiance in a transverse direction is equal to 1/e\(^2\) of its value at the beam axis. These lines are used to define a continuously changing beam width \(w(z)\), with the minimum at the focal plane designated with \(w_0(z)\). Those thin sky-blue arcs drawn transverse to z-axis indicate the wavefronts with radius \(R(z)\) of the beam. Spatial and temporal dependence of the electric field component of such a propagating wave may be expressed as [36]

\[
E(z,r,t) = E_0 \left( \frac{w_0}{w(z)} \right) e^{-\frac{r^2}{w(z)^2}} e^{-i\frac{kr^2}{2R(z)}} e^{-\phi(z)}
\]  

(1.52)

where, \(r^2=x^2+y^2\), \(w(z)\) and \(w_0\) are related for a wavelength \(\lambda\) through the relation

\[
w(z)^2 = w_0^2 \left[ 1 + \left( \frac{\lambda z}{\pi w_0^2} \right)^2 \right]
\]  

(1.53)
In equation (1.52), $E_0$ is the amplitude at the origin and $k$ is the propagation constant. The first exponential term describes the magnitude of electric field in any transverse plane at a fixed $z$ and how it falls off as a Gaussian function with peak intensity $E_0$ on the $z$-axis (See Figure 1.1 b)). The second exponential term indicates the geometry of the wavefront for the laser beam as a spherical surface of radius $R(z)$. Finally, the end term explains how the phase information is dependent on $z$.

A collimated laser beam is a Gaussian beam with a long waist. The collimated beam length is usually defined as the distance between two symmetrical, transverse planes on either side of the beam waist, the two planes being those in which the spot size $w(z)$ has been increased by a factor of $\sqrt{2}$ over the spot $w_0$ at the waist. The distance from the beam waist to the plane at which the beam width has increased to $\sqrt{2}w_0$ is known as Rayleigh range and is denoted as $z_R$.

![Figure 1.2](image)

**Figure 1.2** The longitudinal beam profile of a collimated Gaussian beam, it explains the geometrical significance of Rayleigh range $z_R$.

At Rayleigh distance from the beam waist, the beam area gets doubled and hence the beam intensity gets halved. The Rayleigh range can be estimated from the relation (1.55) by setting $w(z) = \sqrt{2}w_0$ and solving for $z = z_R$ [36]. Thus,

$$w(z) = \sqrt{2}w_0 = w_0 \left[ 1 + \left( \frac{\lambda z_R}{\pi w_0^2} \right)^2 \right]^{1/2}$$

(1.54)

From which, it yields that

$$z_R = \frac{\pi w_0^2}{\lambda}$$

(1.55)

Thus, the collimated region extends over two Rayleigh ranges on either side of the beam waist. The more rapidly the beam diverges as it leaves the waist, the smaller the Rayleigh
range, or the distance over which the beam remains collimated with a nearly constant diameter and planar wavefront.

1.8. 2. Intensity of a temporally and spatially Gaussian profiled laser beam

The intensity (energy/area/time) of an electromagnetic wave is generally a well understood quantity. But, the laser beams are not of pure plane waves; they possess different spatial and temporal beam geometries. Since the electric field profile of a Gaussian wave is not uniform throughout the beam cross-section, the parameterization of laser intensity requires different practical definitions that depend on the temporal and spatial characteristics of the optical beam [37].

In case of a simple radial “top-hat” beam having uniform spatial and temporal profile, the intensity \( I_0 \) for a given time duration \( \tau \) and beam radius \( w_0 \) is expressible in the form

\[
I_0 = \frac{E_{\text{Beam}}}{\pi w_0^2 \tau} \tag{1.56}
\]

where \( E_{\text{Beam}} \) is the beam energy. A different expression for \( I_0 \) is obtained if the temporal and spatial profile of the pulse is different. In case of a top-hat temporally Gaussian pulse, the time dependent part of the intensity may be written as \( I(t) = \exp \left[ -2(\frac{t - \alpha t^2}{\tau^2}) \right] \) where \( \tau \) is the time at which the intensity falls to \( 1/e^2 \) of its maximum value. An appropriate integration will yield the expression for \( I_0 \) as

\[
I_0 = \frac{\sqrt{2} E_{\text{Beam}}}{\pi^{3/2} w_0^2 \tau} \tag{1.57}
\]

Finally, if the beam possesses both transverse (in the beam cross-section plane) and temporal Gaussian profile, with the spatial dependence of electric field expression given by \( E(r) = E_0 \exp \left( -2r^2/w_0^2 \right) \), then, the intensity expression will take the form [38]

\[
I_0 = \frac{4 \sqrt{\ln 2} E_{\text{Beam}}}{\pi^{3/2} w_0^2 \tau} \quad (W/m^2) \tag{1.58}
\]

The entire experiments reported in this thesis employ temporally and spatially Gaussians profiled Nd:YAG and Ti:Sapphire laser beams and hence equation (1.58) will be used in subsequent intensity calculations.
1.9. MANIFESTATION OF NONLINEAR REFRACtion AND ABSORPTION IN MATERIALS PROBED WITH GAUSSIAN BEAMS.

In previous sections, we have seen that a Gaussian profiled beam has its lowest diameter at the beam waist. If a nonlinear sample is placed at the beam waist plane, it will be exposed to the maximum beam irradiance and hence yield its optimum nonlinear response.

1.9.1. Gaussian beam and nonlinear refraction

We have seen that when a highly intense optical beam passes through a nonlinear medium, the effective refractive index of the medium gets changed. The intensity dependent nonlinear refractive index induced in a medium may in turn affect the propagation characteristics of the beam within the medium. In other words, the temporal and spatial characteristics of the output beam from a nonlinear medium would depend upon the intensity of the input beam. Hence, the effective refractive index of the medium to the incident frequency $\omega$ is expressible in the form

$$n_{\text{eff}}(\omega, I) = n_0(\omega) + n_2(I)I$$

where, $n_0(\omega)$ denotes the linear refractive index of the medium at frequency $\omega$, $n_2(I)$ represents the induced nonlinear refractive index at laser intensity $I$ [19]. In SI system, the unit of $n_2$ is $m^2/W$. It is also obvious that nonlinear refractive index emerges as a result of intensity of the beam and this part is quite obscure at low intensity regime and hence in linear optics this part is not taken care of. Nonlinear refractive index of materials are observable either in the self-focussing form ($n_2 > 0$) or in the self-defocusing form ($n_2 < 0$). Equation (1.45) relates the nonlinear refractive index of a material with the real part of the third order susceptibility coefficient.

![Figure 1.3 a) Self focussing of Gaussian beam due to $n(I) > n_0$, b) Self defocusing of Gaussian beam due to $n(I) < n_0$.](image)

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Figure 1.3 illustrates the self-focussing and defocusing of Gaussian beam in nonlinear materials. A Gaussian beam has the highest intensity at the beam axis and hence the medium will be most affected along the axial path and least affected along the paraxial path where the intensity is one half of that at the axial path. This may in turn, lead to the formation of either a concave/convex shaped wavefront depending on the type of nonlinear material, and subsequently leads to focusing or defocusing of the propagating beam.

Nonlinear refractive index also induces a phase change ($\Delta\phi$) in the incident optical wave front, which is a function of both intensity of the beam and path length as given by the relation

$$\Delta\phi(I, L_m) = \frac{2\pi}{\lambda} n_2 I L_m$$  \hspace{1cm} (1.60)

where $\lambda$ is the wavelength of the laser and $L_m$ is the thickness of the nonlinear material up to which beam has passed through the material. This spatially induced phase shift can either contribute in speeding up or retarding the phase front and lead to many interesting propagation effects.

On similar lines, the temporally dependent intensity distribution $I(t)$ can lead to self-phase modulation (SPM) which implies an instantaneous time dependent frequency change given by

$$\delta\omega(t) = -\frac{\partial}{\partial t} (\Delta\phi) = -\frac{2\pi}{\lambda} n_2 \text{material} L_m \frac{\partial I(t)}{\partial t}$$  \hspace{1cm} (1.61)

Here, the frequency change is proportional to the time derivative of intensity of the temporally Gaussian pulse. When the leading edge of the pulse (positive slope) passes through the medium it becomes red-shifted whereas the trailing edge (negative slope) gets blue shifted while propagating through the medium. The cumulative effect of these two phenomena is the apparent pulse broadening. For ultra short pulses with large intensities (like that of mode locked Ti: Saphire laser), this may lead to the generation of broadband continuum white light [39, 40].

1.9.2 Gaussian beam and nonlinear absorption

When the intensity of optical flux propagating through a material is substantially intense, it leads to the depopulation of the ground state of the constituent atoms/molecules of
the material. This, in turn may affect the absorption characteristics of the material and the absorption coefficient of the material would no longer be an intensity independent parameter. In 1929, Maria Goppert Mayer, in her seminal paper proposed that an atom or a molecular system can simultaneously absorb two or more photons thereby an electron can transit to a state unreachable by a single photon absorption [41, 42]. Due to the unavailability of high intense beam of optical radiations at that time, any observable effect of this proposed phenomenon could not be identified until the construction of the first laser in 1960 [43].

**A) Gaussian beam and Two-Photon Absorption (TPA)**

While absorbing multiple photons simultaneously, an atom can proceed to an intermediate state corresponding to a characteristic virtual state. These virtual states are not real eigen states because they correspond to no specific quantum numbers and no population of electron transition takes place to these virtual states. The life time of these virtual states is transient relative to the nearby quantum mechanically allowed (eigen) states [44]. In fact, the closer the virtual state is to an actual eigen state, the longer the lifetime of the virtual state. In case of two-photon absorption (TPA), the absorption of the first photon by any quantum state of an atom/molecule will introduce some perturbation to the wave function of the lower excited state. If the absorption of the second photon takes place before the perturbation ceases to exists, a transition to a higher excited state is achieved (Figure 1.4a)). Since the life time of such perturbation takes place in ultrafast time scale, the incident photon flux density must hence be large enough to give a reasonably high probability that the two photons can be absorbed before the perturbation vanishes. The nonlinear absorption in this case is proportional to the square of the beam intensity. The spatial rate of decay of optical intensity in such a TPA is given by

\[
\frac{\partial I}{\partial z} = -\alpha I - \beta_{\text{TPA}} I^2
\]  

(1.62)

where \(\alpha\) is the linear absorption coefficient attributable to the inherent absorption level at the optical frequency or due to the presence of impurities and \(\beta_{\text{TPA}}\) is the two-photon absorption coefficient which is a macroscopic parameter characterizing the material and is related to the imaginary part of \(\chi^{(3)}\) in the following way [20, 45].

\[
\beta_{\text{TPA}} = \frac{3\pi}{\varepsilon_0 c n_0^2 \lambda} \text{Im}\{\chi^{(3)}(\omega)\}
\]  

(1.63)
TPA is a specific case of a more general multiphoton absorption process, which implies the simultaneous absorption of n photons from a single beam or multiple beams. From a general perspective, an n+1 photon absorption from a single beam is expressible in the form

\[
\frac{\partial I}{\partial z} = -(\alpha + \zeta^{(n+1)}(\omega)I^n)I
\]  

(1.64)

where \(\zeta^{(n+1)}(\omega)\) is the (n+1) photon absorption coefficient with units \(m^{(2n-1)}/W^n\). The case where n=1 implies TPA with \(\zeta^{(1)}(\omega)\) equals \(\beta_{\text{TPA}}(\omega)\) so on [20].

If there is no resonant sequential one-photon plus excited state absorption, all molecules may be assumed to be in the ground state, in the low energy regime of the beam. In such a case, negligible value can be assumed for \(\alpha\), and for simultaneous two-photon absorption process above relation can be modified as

\[
\frac{\partial I(z)}{\partial z} = -\beta_{\text{TPA}}(\omega)I(z)^2
\]  

(1.65)

For an incident intensity \(I_0\), at the boundary, the intensity at a propagation distance z from the boundary can be expressed as:

\[
I(z) = \frac{I_0}{I + \beta_{\text{TPA}}(\omega)I_0z}
\]  

(1.66)

It proves how the two-photon absorption leads to amplitude attenuation of a suitable optical beam in a nonlinear way. The same process plays the key role in phenomena like passive optical limiting in many materials when used for various laser pulse shaping and pulse compression applications.

Here, the macroscopic parameter \(\beta_{\text{TPA}}\) is related to the individual molecular two-photon absorption cross-section \(\sigma_{\text{TPA}}(\omega)\) through the relation [46]

\[
\sigma_{\text{TPA}}(\omega) = \frac{\hbar \omega \beta_{\text{TPA}}}{N_d}
\]  

(1.67)

where \(N_d\) is the number density of the molecules (cm\(^{-3}\)) in the system and \(\omega\) is the incident radiation frequency.
In a typical light transmission measurement, transmittance can be appropriately defined as the ratio of the transmitted and incident intensities. For a pulsed laser beam with a spatial and temporal Gaussian profile, the transmittance $T$ in the presence of two-photon absorption is given by

$$T = \frac{(1-R)^2 e^{-\alpha L}}{\sqrt{\pi q_0}} \int_{-\infty}^{+\infty} \ln[1 + q_0 e^{-\tau^2}] d\tau$$

where $R$ is the Fresnel reflection coefficient at the interface of the material with air and $L$ the thickness of the material through which the transmission occurs. The parameter $q_0$ is given by

$$q_0 = \beta_{TPA} (1-R) I_0 L_{eff}$$

where $I_0$ is the peak on-axis intensity incident on the material and $L_{eff}$ is the effective length of the medium which takes into account the linear absorption of the medium and is given by

$$L_{eff} = \frac{1-e^{-\alpha L}}{\alpha}$$

For weakly absorbing materials, the effective absorption length tends to be the same as the geometrical length of the sample [47].

**B) Gaussian beam and Three-Photon Absorption (3PA)**

In a single beam 3PA case, the transition of the atomic/molecular system from the ground state to a higher excited state takes place by the simultaneous absorption of three photons from the incident beam. Schematic representation of 3PA is shown in Figure 1.4 b) [48, 49]. If the medium contains some impurities to introduce linear absorption $\alpha$, the propagation equation for the medium having significant three-photon absorption can be expressed as
\[ \frac{\partial I}{\partial z} = -\alpha I - \gamma I^3 \]

where \( \gamma \) is the three-photon absorption coefficient and is related to the imaginary part of the fifth order nonlinear susceptibility coefficient given by the relation [20]

\[ \gamma = \frac{5\pi}{\varepsilon_0 n^2 c^2 \lambda} \text{Im}[\chi^{(5)}(\omega)] \]  

(1.72)

When a temporally and spatially Gaussian profiled beam passes through such a fifth order material, the transmittance of the system is given by [50]

\[ T(z) = \left(1 - R\right)^2 e^{-\alpha L} \frac{\int_{-\infty}^{+\infty} \ln\left[1 + p_0^2 e^{-2\tau^2} + p_0 e^{-\tau^2}\right] d\tau}{\sqrt{\pi} p_0} \]

(1.73)

where,

\[ p_0 = \sqrt{2\gamma (1 - R)^2 I_0^2 L_{\text{eff}}} \]

(1.74)

where \( I_0 \) is the peak on-axis intensity incident on the material and \( L_{\text{eff}} \) is the effective length in the medium given as,

\[ L_{\text{eff}} = \frac{1 - e^{-2\alpha L}}{2\alpha} \]

(1.75)

Of course, with negligible linear absorption, \( L_{\text{eff}} \) can again assume the real geometrical length \( L \) of the sample.

**C) Saturable Absorption (SA)**

Nonlinear absorption can occur due to a variety of processes when a medium is exposed to intense optical irradiance. Suppose the number of photons incident simultaneously on a sample is just equal to the number of molecules in the lower energy state and the entire absorbing species is excited to the higher level making the lower energy level momentarily empty. If one more photon of the same energy is incident after this, there will be no more absorption and the photon simply “passes” through the medium which is termed as optically induced transparency. Thus the material which was opaque to a smaller number of photons has now become transparent when a large number of photons are beamed into it. This is known as saturable absorption. At sufficiently high beam intensity, the molecules in the ground state of a SA material gets excited into an upper energy state at such a rate that there
is insufficient time for them to decay back to the ground state before the ground state becomes depleted and resultantly absorption saturates [51, 52].

Consider a two-level system with ground state energy $E_{\text{grd}}$ and excited state $E_{\text{exc}}$. Let the number of atoms/molecules per unit volume of the sample in the respective system be $N_{\text{grd}}$ and $N_{\text{exc}}$ and the medium is irradiated with a beam of intensity $I$. If we assume a simple two level kinetic model, and under the steady state condition

$$\frac{dN_{\text{exc}}}{dt} = \frac{\sigma I}{h\nu} (N_{\text{grd}} - N_{\text{exc}}) - \frac{N_{\text{exc}}}{\tau} = 0$$

(1.76)

where $N_{\text{grd}}$ is the undepleted ground state concentration, $\sigma$ is the absorption cross-section, $h\nu$ is the photon energy, and $\tau$ is the lifetime of the excited state. Linear absorption coefficient $\alpha$ can be related to the ground state population $N_{\text{grd}}$ through the relation, $\alpha=\sigma(N_{\text{grd}}-N_{\text{exc}})$. If the ground state linear absorption is taken as $\alpha_0=\sigma N_{\text{grd}}$, the intensity dependent linear absorption coefficient $\alpha(I)$ can be represented as

$$\alpha(I) = \alpha_0 \frac{I}{I_s + \left(\frac{I}{I_s}\right)}$$

(1.77)

where $I_s=h\nu/\sigma\tau$ is called the saturation intensity, at which the absorption coefficient $\alpha(I)$ reaches half the value of the ground state linear absorption coefficient.

Saturable absorbers are being used for various photonic applications like Q-switching, mode-locking and pulse compression [53]. Further, an optical limiter combined with a saturable absorber can be used for improved pulse compression. In such a configuration, the leading edge of an optical pulse is preferentially attenuated by a saturable absorber and the trailing edge of the pulse is preferentially attenuated by the optical limiter. The net result is a more temporally compressed and symmetrically shaped pulse.

D) Reverse Saturable Absorption (RSA)

In case of polyatomic systems with multiple energy levels, when molecule is excited to a higher energy state by a suitable laser beam, it may get further excited to higher lying states. Resultantly, upper levels may get momentarily depleted, leading to further absorption and a corresponding reduction in transmittance. This effect is known as reverse saturable absorption (RSA) [54-56]. RSA is a sequential one-photon absorption process and the phenomena can be schematically represented as shown in Figure 1.5.
Consider a three level case with $N_1$ atoms in the ground state 1, $N_2$ atoms in next higher state 2 and $N_3$ atoms in the state 3. On laser irradiation, some of the molecules in the ground state are excited to the state 2. For an appropriately chosen laser frequency and material, the excited molecules may make another transition from the state 2 to a higher excited state 3 through another, one-photon absorption. The possibility of this process depends on the number of molecules $N_2$ at the first excited state 2, incident beam intensity $I$ and the excited state absorption cross section $\sigma_{23}$. On the other hand $N_2$ is related to $N_1$ and $I$ by the relation,

$$N_2 \propto \sigma_{12} N_1 I$$

(1.78)

where $\sigma_{12}$ is the absorption cross section of the transition from the ground state to the state-2. It is obvious from the above relation that, the number of molecules in state-2 ($N_2$) continuously grows with the incident intensity $I$ and the one-photon absorption from the state 2 to state 3 become more intense, provided that the absorption cross section $\sigma_{23}$ of this transition is considerably larger than $\sigma_{12}$. Under the steady-state condition, the intensity change of the laser beam in the nonlinear medium along its propagation direction can be expressed as,

$$\frac{dI}{dz} = -\sigma_{12}(N_1 - N_2)I - \sigma_{23} N_2 I$$

(1.79)

If $N_1 \gg N_2$, where $N_1$ is the number density of the absorbing molecules, the above relation may be rewritten as

$$\frac{dI}{dz} = -\sigma_{12} N_1 I - \sigma_{23}(b \sigma_{12} N_1 I) I$$

(1.80)

where $b$ is a proportionality constant. By replacing, $\sigma_{12} N_1$ with $\alpha_0$ and $b \sigma_{12} \sigma_{23} N_1$ with $\beta'$, the above relation can be modified as
\[
\frac{dI}{dz} = -\alpha_0 I - \beta I^2
\]  \hspace{1cm} (1.81)

Above relation is similar to the equation for two-photon absorption. Therefore, a similar formalism can be used to solve it and extract the values of relevant parameters. Hence, the values of excited and ground state absorption cross-sections can be estimated. In case \(\sigma_{12} > \sigma_{23}\), \(\beta\) decreases (+vely signed \(\beta\) will decrease and -vely signed \(\beta\) will increase) with increasing intensity and the resulting absorption is called saturable absorption. In contrast, if the opposite condition exists, such that, \(\sigma_{12} < \sigma_{23}\) the populated first excited state has a pathway to depopulate by transitng to any higher lying states. Here, absorption will increase with increasing intensity and the process is called reverse saturable absorption. It is worthwhile to note that these excited state absorptions are pulse-width dependent since their temporal responses are governed by the life-time of the populated excited states.

1.10. CERTAIN MATERIAL PROPERTIES LEADING TO THIRD-ORDER NONLINEAR POLARIZATION

In addition to the effect of intense optical field, there are certain material properties that can also lead to nonlinear optical effects in materials. The relative contribution of these material mechanisms may be significantly different in different cases. Identification of the predominance of a particular mechanism in a specific phenomenon is a matter of intense research. A brief account of such material properties are presented below.

1.10.1. Electronic polarization

The spread of electron cloud (still, bound electrons) around an atom/molecule determines the microscopic value of polarizability, which includes all orders of polarizability. The more the distortion of the cloud under the action of a given optical field, the higher will be the order of nonlinear response induced. If the atom or molecule is highly polarizable, then it can exhibit a significant electronic nonlinearity. The third order nonlinear susceptibility, for example, is related to the second hyperpolarizability represented as \(\gamma_h\), is a microscopic parameter directly linked to the electron cloud distortion. For a typical non-absorbing type of material, its value is approximately \(~10^{-36}\) esu and, for large organic molecules it may reach as high as \(~10^{-33}\) esu. Such electronic processes are usually very fast and occur in the time scale of \(~10^{-15}\) sec [19, 57].
1.10.2. Molecular orientation

This phenomenon usually happens in anisotropic materials. The molecules of a given anisotropic material may get aligned nonuniformly under the action of an external field. Liquid Carbon disulphide, for example, is optically nonlinear due to molecular orientation under the action of a suitable optical field. When a strong electric field is applied to such a system, the induced dipole moment of the molecules experiences a torque, attempting to align along the most polarizable axis with the applied field. Another incident optical field, polarized along the direction of the strong field, will experience an increase in the local index of refraction. The optical waves then experience a modified value for effective refractive index. When the applied field is strong enough, the system responds to the time averaged field squared and the effect is known as optical Kerr effect [20, 57].

1.10.3. Thermo-Optic effect

The propagation of laser beam through a material is thermodynamically an exothermic process. Material can undergo either expansion or contraction depending on the nature and phase. Gases usually undergo expansion on heating, which may reduce the overall refractive index, whereas, in condensed matter, refractive index can either increase or decrease with change in temperature, depending upon the internal structure of the material. The refractive index variation with temperature is generally known as thermo-optic effect [58]. The role of thermo-optic effect in inducing thermal nonlinearity and the consequent self focusing/defocusing will be discussed in detail in Chapter 4.

1.10.4. Electron delocalization

Certain polymers known as conjugated polymers can possess an extremely large nonlinear optical response. A polymer is said to be conjugated if it contains alternate single and double (or single and triple) bonds. A polymer molecule is said to be saturated if it contains only single bonds. According to convention, a single line between two carbon atoms represents single bonds and double lines represent double bonds (see Figure 1.6). A single bond always has the structure of a $\sigma$ bond; in contrast, a double bond consists of a $\sigma$ bond and a $\pi$ bond that is made up of the overlap of two p orbitals, one from each atom that is connected by the bond. Moreover, p orbitals can extend both to the left and to the right of each carbon atom, and thus there is considerable vagueness as to which bond we should call single bond and which should we call double bond. The actual form of the polymer chain
thus, would be a superposition of the two configurations as shown in Figure 1.6 c). Hence the less tightly bound electrons in the \( \pi \)-bonds are readily influenced by the incident optical field and show increased nonlinear response than molecules that contains less number of alternate single and double bonds (or, mere single bonds).

![Figure 1.6 a) Common representation of an ordinary chain like polymer b) Two representations of the same polymer chain with the locations of the single and double bonds interchanged c) Representation of the charge distribution of a conjugated chainlike polymer as the superposition of both states.

![Figure 1.6 d) Typical \( \pi \), \( \sigma \) and K-electron distribution in a linear polymeric molecule (Acetylene). The diagram shown above represents the molecular potential well of the electrons in the \( \pi \), \( \sigma \) and K-shells.]

The optical response of \( \sigma \) bonds is very different from that of \( \pi \) bonds because \( \sigma \) electrons (electrons contained in \( \sigma \) bond) are more rigidly bound in space whereas \( \pi \)-electrons tend to be more loosely bound. Hence \( \pi \)-electrons are delocalized, and they are susceptible to applied optical field fluctuations [59-61]. They thus tend to produce larger linear and nonlinear optical responses. The \( \pi \)-electrons tend to be delocalized in the sense that a given electron can be found anywhere along the polymer chain. Thus, one can conceptualize the \( \pi \)-electrons of a conjugated chain-like polymer as a one-dimensional square well potential (Figure 1.6 d)) whose length is equal to the linear dimension of the polymer chain. Quantum computations show that the linear polarizability (\( \alpha_{\text{linear}} \)) and second hyperpolarizability (\( \gamma_h \)) of such molecules can be expressed in terms of the average molecular length \( L \) as [62]

\[
\alpha_{\text{linear}} = \frac{8L^3}{3a_0^2\pi^2N}
\]

\[
\gamma_h = \frac{256L^5}{45a_0^3e^2\pi^2N^3}
\]
where, \( N \) is the number of electrons per unit length of the molecule and \( a_0 \) is the Bohr’s radius. The above relations show that nonlinear polarization increases much more rapidly than the linear polarization with increase in conjugation length.

### 1.10.5 Electrostriction

Electrostriction is the tendency of certain materials to get denser in the presence of strong optical field [62]. Electrostriction mechanism in materials, often play a crucial role in inducing third-order nonlinear optical response. The density change in the material due to electrostriction also leads to change in refractive index. A focussed, intense laser beam usually provides a gradient electric field within the material, and this may cause density variations. For a typical glassy material with \( n_0 \sim 1.5 \), the electrostriction contribution to the nonlinear index coefficient is of the order of \( \sim 10^{-19} \text{ m}^2/\text{V}^2 \). For the case of optical fibers, it has been found that electrostriction can make an approximately 20% contribution to the third-order susceptibility [63]. Often, its response time is of the order of few nanoseconds in glassy materials.
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