Chapter 1

Introduction

This Chapter presents the introduction to nonlinear optics, various process and mechanisms due to $\chi^{(3)}$, objectives and organization of the thesis.

1.1. Introduction to nonlinear optics

Nonlinear optics is the study of phenomena in which modification of the optical properties of a material system takes place due to intense light. Laser is a high intensity source that is strong enough to induce nonlinear optical mechanism, even in weak nonlinear materials. The induced dipole moment per unit volume known as electric polarization plays an important role in the nonlinear optical phenomena. During the process, inherent charges in the material interact with the electromagnetic field of the incident light causing its phase, frequency, amplitude or polarization to be altered [1]. The discovery of second-harmonic generation by Franken et al. [2] in 1961, led the beginning of the field of nonlinear optics. When the ruby laser light with wavelength at 6493 Å, was made to traverse through the quartz crystal, they observed that the emergent light was in ultraviolet region. The transmitted light frequency was double, $2\omega$ (wavelength $\lambda/2$) than that of the incident light.

Nonlinear optical materials are of great importance in photonic devices [1, 3, 4]. Nonlinear optics has evolved and linked to different branches and rapid technological advances in fiber optics and optical communications [5]. The conduct of nonlinear optics, range from the fundamental studies of the light-matter interaction to the advancement of component and devices for variety of applications in science, military and medical fields. In the last two decades, the technological growth led to an ever-increasing demand for new photonic devices. Nonlinear optics is considered to be a field that provide variety of photonic devices. Currently there is a great demand in photonics for nonlinear optical materials whose optical properties are very sensitive to an applied electric field. Thus making it suitable for applications in nonlinear spectroscopy, correcting optical distortions, optical switching, optical logic gates,
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optical data processing, Q-switching, mode-locking, optical limiting, optical communications, waveguide switches, modulators, photodynamic therapy, etc., [5-7].

1.2. **Basics of nonlinear optics**

Matter consists of a collection of positively charged atoms or molecules, surrounded by negatively charged electrons. When a monochromatic light with frequency ω and electric field E interacts with matter, separation of charges is induced as shown in figure 1.1. This separation of charge results in a collection of induced dipole moments μ. Therefore, the induced electric polarization P is defined as the net average dipole moment per unit volume and is given by,

\[
P = e_0 \chi E,
\]

where \(e_0\) is the permittivity of free space and \(\chi\) is the optical susceptibility. Any permanent dipoles within the medium are ignored, as they will not oscillate at the optical frequencies and hence will not radiate electromagnetic waves [8].

![Diagram of the response of a dielectric medium](image)

**Figure 1.1.** Illustration of the response of a dielectric medium (a) without and (b) with, the application of optical field.

When an intense monochromatic laser beam (of the order of \(10^7\) to \(10^{10}\) V/cm), interacts with matter, the response of the medium to the induced polarization is no longer linear. At such high optical fields, the relationship between the polarization P and electric field E is no longer linear and the nonlinear effect begins to take place. The field strengths of atomic and inter atomic field are perturbed, therefore the optical parameters tends to change. Thus the nonlinear polarization is given by [1, 7, 9],
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\[ P = \varepsilon_0 \left[ \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \chi^{(4)} E^4 + \ldots \right] \]  \hspace{1cm} (1.2)

where \( \chi^{(1)} \) is the linear optical susceptibility,

\( \chi^{(2)} \) is the second-order nonlinear optical susceptibility,

\( \chi^{(3)} \) is the third-order nonlinear optical susceptibility,

\( \chi^{(4)} \) is the fourth-order nonlinear optical susceptibility, and so on…

Consider an optical field incident upon a medium which is represented by [9],

\[ E = E_0 \cos \omega t, \]  \hspace{1cm} (1.3)

Substituting equation (1.3) into equation (1.2),

\[ P = \varepsilon_0 E_0 \left[ \chi^{(1)} \cos \omega t + \chi^{(2)} E_0 \cos^2 \omega t + \chi^{(3)} E_0^2 \cos^3 \omega t + \chi^{(4)} E_0^3 \cos \omega t + \ldots \right] \]  \hspace{1cm} (1.4)

By using trigonometric relations, the equation becomes [9],

\[ P = \frac{1}{2} \varepsilon_0 \chi^{(2)} E_0^2 + \varepsilon_0 \left( \chi^{(1)} + \frac{3}{4} \chi^{(3)} E_0^2 \right) E_0 \cos \omega t + \frac{1}{2} \varepsilon_0 \chi^{(2)} E_0^2 \cos 2\omega t + \frac{1}{4} \varepsilon_0 \chi^{(3)} E_0^3 \cos 3\omega t + \ldots \]  \hspace{1cm} (1.5)

The equation (1.5) clearly shows the presence of new frequency components due to nonlinear polarization. In the equation, the first term is a constant term which gives rise to a dc field through the medium. The second term is the external polarization, called as first or fundamental harmonic of polarization. The third term oscillates at a frequency of 2\( \omega \) and called as second harmonic of polarization. The fourth term oscillates at a frequency of 3\( \omega \) and called as third harmonic of polarization and so on. The contributions from the second and third order terms to the nonlinear polarization are predicated from different symmetry properties of the medium. A contribution from \( \chi^{(2)} \) can occur only from non-centro symmetric media, whereas \( \chi^{(3)} \) contributions can occur from any medium regardless of symmetry [1].
1.3. Maxwell’s equation in nonlinear optical media

The electromagnetic wave interaction with a medium free of surface and volume charge density follows Maxwell’s equations. The equations are given by [1];

\[
\begin{align*}
\nabla \cdot \vec{D} &= 0, \\
\nabla \cdot \vec{B} &= 0, \\
\n\nabla \times \vec{E} &= -\frac{\partial \vec{B}}{\partial t}, \\
\n\nabla \times \vec{H} &= \varepsilon_0 \frac{\partial \vec{E}}{\partial t},
\end{align*}
\]

where \( \vec{E}, \vec{D}, \vec{B} \) and \( \vec{H} \) are the electric field, electric displacement, magnetic induction and magnetic field respectively. The above equations are derived from the basic laws Gauss's law, Gauss's law for magnetism, Faraday's law of induction, and Ampère's law with Maxwell's correction.

The electric field, electric displacement, magnetic induction and magnetic field terms from the Maxwell’s equations, are related with each other. The terms \( \vec{B} \) and \( \vec{H} \) are related by the equation, \( \vec{B} = \mu_0 \vec{H} \), where \( \mu_0 \) is the magnetic permeability. Whereas \( \vec{E} \) and \( \vec{D} \) are related by the equation, \( \vec{D} = \varepsilon_0 \vec{E} + \vec{P} \), where \( \vec{P} \) is the polarization [1].

To derive the optical wave equation, consider the Maxwell’s equation \( \nabla \times \vec{E} \), by interchanging the order of space and time derivatives on the right-hand side of the resulting equation, to replace \( \nabla \times \vec{B} \) by \( \mu_0 \left( \frac{\partial \vec{D}}{\partial t} \right) \) to arrive at the equation [1],

\[
\nabla \times \nabla \times \vec{E} + \mu_0 \frac{\partial^2 \vec{D}}{\partial t^2} \vec{D} = 0,
\]

By using \( \vec{D} = \varepsilon_0 \vec{E} + \vec{P} \), to eliminate \( \vec{D} \) from above equation, we obtain the expression [1],

\[
\nabla \times \nabla \times \vec{E} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \vec{P}}{\partial t^2},
\]

where \( c \) is the speed of light.
In the equation (1.7), $\mu_0 = 1/e_0c^2$. The above equation is the general wave equation in nonlinear optics. By using an identity from vector calculus, the first term on the left-hand side of equation (1.8) can be written as [1],

$$\nabla \times \nabla \times \vec{E} = \nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E},$$  \hspace{1cm} (1.9)

In linear optics of isotropic source free medium, the first term on the right-hand side of equation (1.9) vanishes because, in the Maxwell equation $\nabla . \vec{D} = 0$, implies that $\nabla . \vec{E} = 0$. But in nonlinear optics, this term does not vanish even for isotropic medium, due to the relation between $\vec{D}$ and $\vec{E}$. In nonlinear optics, if $\vec{E}$ is of the form of a transverse, infinite plane wave, the term $\nabla . \vec{E}$ vanishes. For slowly varying amplitude approximation, the first term is negligibly small and the wave equation can be written in the form [1],

$$\nabla^2 \vec{E} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} = \frac{1}{\varepsilon_0c^2} \frac{\partial^2 \vec{P}}{\partial t^2},$$  \hspace{1cm} (1.10)

The above equation can also be written as [1],

$$\nabla^2 \vec{E} - \frac{1}{\varepsilon_0c^2} \frac{\partial^2}{\partial t^2} \vec{D} = 0,$$  \hspace{1cm} (1.11)

The polarization $\vec{P}$ can be split in to its linear and nonlinear parts as [1],

$$\vec{P} = \vec{P}^L + \vec{P}^{NL},$$  \hspace{1cm} (1.12)

where $\vec{P}^L$ is the part that depends linearly on the electric field strength $\vec{E}$. Similarly, the displacement field $\vec{D}$ can be expressed in to its linear and nonlinear parts as [1],

$$\vec{D} = \vec{D}^L + \vec{P}^{NL},$$  \hspace{1cm} (1.13)

The wave equation expressed in equation (1.10) can also be written with respect to above equation as [1],
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\[ \nabla^2 \tilde{E} - \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \tilde{D}^L}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \tilde{P}^{NL}}{\partial t^2}. \]  

(1.14)

1.4. Nonlinear optical process generated due to \( \chi^{(3)} \)

The nonlinear optical process generated in a nonlinear medium due to the third-order optical nonlinearity \( \chi^{(3)} \) are described briefly.

1.4.1. Intensity dependent refractive index \( \chi^{(3)} \) \( \omega; \omega, \omega, - \omega \)

The optical materials refractive index depends on the intensity of the light used to measure it. The intensity dependent refractive index can be expressed as [1],

\[ n = n_0 + \bar{n}_2 \langle \tilde{E}^2 \rangle, \]  

(1.15)

where \( n_0 \) is the linear field refractive index and \( \bar{n}_2 \) is the second-order index of refraction. \( \bar{n}_2 \) represents the rate at which the refractive index increases with increasing optical intensity [1]. The angular brackets for the quantity \( \tilde{E}^2 \) represent the time average. Consider, if the optical field is given by [1],

\[ \tilde{E}(t) = E(\omega)e^{-i\omega t} + c.c. \]  

(1.16)

For \( \langle \tilde{E}(t)^2 \rangle = 2E(\omega)E(\omega)^* = 2|E(\omega)|^2, \)  

(1.17)

Then the above equation (1.15) becomes [1],

\[ n = n_0 + 2\bar{n}_2 |E(\omega)|^2, \]  

(1.18)

The change in refractive index expressed in equation (1.15) and (1.18) is called as the optical Kerr effect, in which the refractive index of a material changes by an amount that is proportional to the square of the strength of an applied static electric field.

The interaction of a beam of light with a nonlinear optical medium can also be described in terms of the nonlinear polarization. The part of the nonlinear polarization that influences the propagation of a beam of frequency \( \omega \) is given by [1],
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\[ P^{NL}(\omega) = 3\varepsilon_0 \chi^{(3)}(\omega = \omega + \omega - \omega) |E(\omega)|^2 E(\omega), \quad (1.19) \]

By considering that the light is linearly polarized and are suppressing the tensor indices of \( \chi^{(3)} \), the total polarization of the material system is then given by [1],

\[ P^{TOT}(\omega) = \varepsilon_0 \chi^{(3)}(\omega) + 3\varepsilon_0 \chi^{(3)} |E(\omega)|^2 E(\omega) = \varepsilon_0 \chi_{\text{eff}} E(\omega), \quad (1.20) \]

where the effective susceptibility is given by,

\[ \chi_{\text{eff}} = \chi^{(1)} + 3 \chi^{(3)} |E(\omega)|^2, \quad (1.21) \]

The nonlinear third-order optical susceptibility \( \chi^{(3)} \) is related to the nonlinear refractive index \( n_2 \), by the relation [1],

\[ n^2 = 1 + \chi_{\text{eff}}, \quad (1.22) \]

By substituting equation (1.18) and (1.21) on the left-hand and right-hand side in the equation (1.22), we get [1],

\[ \left[ n_0 + 2n_2 |E(\omega)|^2 \right] = 1 + \chi^{(1)} + 3 \chi^{(3)} |E(\omega)|^2, \quad (1.23) \]

By expanding the equation (1.23) with terms of order \( |E(\omega)|^2 \) we get,

\[ n_0^2 + 4n_0 n_2 |E(\omega)|^2 = \left( 1 + \chi^{(1)} \right) + \left[ 3 \chi^{(3)} |E(\omega)|^2 \right], \quad (1.24) \]

The above equation shows that the linear and nonlinear refractive indices are related to the linear and nonlinear susceptibilities by [1],

\[ n_0 = \left( 1 + \chi^{(1)} \right)^{1/2}, \quad (1.25) \]

and

\[ \bar{n}_2 = \frac{3 \chi^{(3)}}{4n_0}, \quad (1.26) \]
1.4.2. Third-harmonic generation $\chi^{(3)}(3\omega; \omega, \omega, \omega)$

In this process, three photons of frequency $\omega$ are incident on the medium. The resulting photon frequency is three times the frequency of that of the input beam and is shown in figure 1.2. This phenomenon is known as third harmonic generation. The third order polarization can be represented as [1],

$$P^{(3)} = e_0 \chi^{(3)} E^3,$$

(1.27)

This process can occur in both centro-symmetric and non-centro-symmetric materials.

![Figure 1.2. Schematic representation of third-harmonic generation. (a) geometry of the interaction, (b) energy-level description.](image)

1.4.3. Electric field induced second harmonic generation $\chi^{(3)}(-2\omega; 0, \omega, \omega)$

The development of organic materials with large nonlinear coefficients has gained a lot of interest. The key requirement for molecular nonlinear parameter is $\beta$, the first hyperpolarizability and the main motive is to screen new organic materials for large $\beta$ values, without the use of costly and difficult program of growing single organic crystals [1, 7]. A convenient way for screening new materials is to place them in solution. But, a solution is centro symmetric and hence will not produce $\chi^{(2)}$. The breaking of symmetry can be conducted by applying an external electric field to the solution and this produces an electric field induced second harmonic (EFISH).

EFISH is a third-order nonlinear process and all materials will create an EFISH signal through their second order molecular hyperpolarizability [7]. In this, the fundamental harmonic is polarized along the applied dc field direction and thus, the
generated second harmonic will also be polarized along this direction. The lowest nonlinear response in isotropic systems is the third-order and the nonlinear polarization at \(2\omega\) is given as \([7, 10]\),

\[
P_{2\omega} = \varepsilon_0 \Gamma E_0 (A_\omega)^2,
\]

\[
\Gamma = 3\chi^{(3)}_{zzzz}(-2\omega, 0, \omega, \omega)
\]

is the EFISH third-order macroscopic susceptibility.

1.4.4. **Degenerate four wave mixing** \(\chi^{(3)}(\omega_4; \omega_1, \omega_2, \omega_3)\)

Four wave mixing is the interaction of four waves in a nonlinear material through the third-order polarization. The process of generation of new frequencies takes place, when all the four waves have different frequencies. If all the four waves have same frequency, it is termed as the degenerate case [7].

Degenerate four wave mixing have two geometries, (a) backward geometry and (b) forward geometry. In backward geometry shown in figure 1.3 (a), the two counter propagating strong pump beams are known as the forward pump beam \(E_f\) and backward pump beam \(E_b\), a third wave is incident at an angle \(\theta\) to the direction of forward pump and is known as probe beam \(E_p\). A fourth beam known as the conjugate beam \(E_c\) is generated and it propagates in counter direction to the probe beam. A third-order polarization oscillating at the frequency \(\omega\) is generated during the interaction. This process is phase matched as \(k_f = -k_b\) and \(k_p = -k_c\). In forward geometry shown in figure 1.3 (b) all the four waves travel in the forward direction.

![Figure 1.3. Schematic of degenerate four wave mixing (a) backward geometry and (b) forward geometry.](image-url)
1.4.5. Two photon absorption $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$

When an incident radiation field passes through a medium, transition from the ground state to a higher lying state takes place by the simultaneous absorption of two photons. This process is known as two photon absorption (TPA).

![Figure 1.4. Schematic diagram of (a) self and (b) pump – probe two photon absorption process.](image)

Figure 1.4 shows the two possible cases of two photon absorption. In figure 1.4 (a), two photons from the same incident field oscillating at frequency $\omega$ are absorbed to make the transition. Whereas in figure 1.4 (b), two fields pump and probe beam are incident on a medium and one photon from each field with frequency $\omega_1$ and $\omega_2$ is absorbed for the transition respectively. In both the figures 1.4 (a) and (b), the virtual state is not a real state (i.e., it does not involve a real stationary state) and the system absorbs two photons simultaneously. This process is sensitive to the instantaneous optical intensity.

1.4.6. Stimulated Raman scattering $\chi^{(3)}(\omega_S; \omega_L, -\omega_L, \omega_S)$

Raman scattering is a two-photon process [7, 4]. The schematic of Raman scattering process is shown in figure 1.5. In this process, an incident photon is destroyed and a new photon with different frequency is created. It implies that this scattering is inelastic and the material medium is in a different energy state. If the scattered photon is having lower energy or frequency, then it is assumed to be Stokes shifted as shown in figure 1.6 (a). The shift in Stokes photon frequency is related to a characteristic frequency of the medium. The Stokes frequency $\omega_S$ is given by [1, 7],

$$\omega_S = \omega_L - \omega_L,$$  \hspace{1cm} (1.29)
where $\omega_L$ is the incident laser frequency and $\omega_V$ is the materials excitation frequency. Thus the occurrence of Raman (Stokes) scattering is due to the excitation from the ground state to an excited state of a medium through a two-photon inelastic scattering.

Figure 1.5. Schematic representation of spontaneous Raman scattering.

However, if the material is in an excited state due to thermal excitation, as shown in figure 1.6 (b), then the scattered photon will be having higher energy or frequency and it is said to be anti-Stokes photon. Since $h\omega >> k_B T$, spontaneous Raman scattering is dominated by Stokes emission.

In stimulated Raman scattering, both Stokes and laser photons are incident on a medium as shown in figure 1.6 (b). The result is the stimulation of an additional Stokes photon current with the incident Stokes photons. Thus the Stokes field experiences gain and similar to spontaneous Raman scattering, stimulated Raman scattering leaves the medium in an excited state.

Figure 1.6. Schematic energy level diagrams for (a) Stokes Raman scattering and (b) Anti-Stokes Raman scattering.

The stimulated Raman scattering is related to third-order optical nonlinearity. The rate of generation of Stokes photon in the limit of large number of photons is related to the polarization through the energy theorem [7, 4],

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\begin{equation}
\frac{\hbar\omega_s}{dt} \frac{dm_s}{dm_s} \propto \text{Re}[i\omega_s E_s P_s^k] \propto m_s \omega_s \propto |E_s|^2 |E_s|^2,
\end{equation}

The above equation implies that the Stokes polarization is third-order in the field that is, \( P_S \propto |E_s|^2 \). Thus the third-order Raman susceptibility can be defined as [7],

\begin{equation}
P_i^{(3)}(\omega_s) = 6\varepsilon_0 \sum_{jkl} \chi^{(3)}_{ijkl}(-\omega_s,\omega_L,\omega_L,\omega_s) E_j(\omega_L) E_k^*(\omega_L) E_l(\omega_s),
\end{equation}

1.4.7. **Stimulated Brillouin scattering \( \chi^{(3)}(\omega_S; \omega_1, - \omega_1, \omega_S) \)**

In a medium, the scattering of light disturbances from acoustic waves or photons is known as Brillouin scattering. The light scattered in Brillouin scattering is considered as acoustic wave front’s Doppler shifted reflection or the photon scattering from an acoustic phonon and is represented in figure 1.7. In the figure, an incident wave interacts with incoming and outgoing acoustic waves. For the conservation of momentum and energy, the wave vector and frequency of scattered wave \((\omega', k')\) must be related to the incident wave \((\omega, k)\) using the equation [1, 7],

\begin{equation}
k' = k \pm K, \quad \omega' = \omega \pm \Omega,
\end{equation}

where \( \pm K \) and \( \Omega \) are the wave vector and frequency of the acoustic wave. In laser scattering due to acoustic disturbances, both the incident laser and Brillouin scattered waves superimpose to form a travelling beat wave with frequency \( \Omega \) and wave vector \( K \). For intense lasers, beat wave drives the acoustic wave coherently through electrostrictive and thermal forces. As the acoustic wave enhances, they scatter the incident laser radiation and this leads to a stronger beat wave. This mutual reinforcement produces an amplified Brillouin wave and this process is known as stimulated Brillouin scattering.
1.5. Physical mechanisms for third-order nonlinearity $\chi^{(3)}$ in optical materials

In nonlinear optics, there are several physical mechanisms that contribute to the third-order nonlinear optical susceptibility $\chi^{(3)}$. Some of the mechanisms contributing to the nonlinearity in the optical medium are described briefly.

1.5.1. Electronic polarization

In this mechanism, there is a distortion of the electron cloud near an atom or molecule by the incident optical field. For a centro symmetric material, the lowest order nonlinearity that occurs is the third-order term. If the atomic unit is symmetric, then there is no preferred direction of axes [8]. The nonlinear susceptibility can be related to the second hyperpolarizability. If the optical frequency is near to a single photon or two-photon resonance, then the contribution from the second hyperpolarizability dominates. When $\omega$ is smaller, the two-photon resonance term will give rise to positive nonlinear index of refraction ($n_2$). This is because; the excited state linear polarizability is larger than that of the ground state. On the other hand, a negative nonlinear index of refraction ($n_2$) is generated due to single photon resonance. This is because; molecular polarizability decrease due to the partial depletion of ground state. For nonresonant electronic processes in dielectrics, the value of second hyperpolarizability is $\gamma \sim 10^{-36}$ esu $\sim 10^{-61}$ C-m$^4$/V$^3$, whereas organic materials have $\gamma \sim (100’s \ to \ 1000’s) \times 10^{-36}$ esu [7]. The materials experiencing electronic polarization...
are found to have the value of $\chi^{(3)}$ to be $\sim 10^{-14}$ esu $\sim 10^{-22}$ m$^2$/V$^2$ and $n_2 \sim 10^{-13}$ esu $\sim 10^{-21}$ m$^2$/V$^2$ respectively [7]. Nonresonant electronic processes are very fast, with the time responses $\sim 10^{-15}$ s [7].

1.5.2. Raman induced Kerr effect

This effect is related to stimulated Raman scattering, in this a strong beam induces a refractive index change for a weak probe beam. The strong laser beam at frequency $\omega_1$ and a weak probe beam of frequency $\omega_2$ are incident on a Raman active medium. The weak beam is referred to as the Stokes beam with $\omega_2 < \omega_1$ [7].

Figure 1.8. A schematic representation of Raman scattering.

Figure 1.8 shows the Raman scattering process with a response time of $10^{-12}$ s [7]. The real part of the third order Raman susceptibility have a value of $\chi_R^{(3)} \sim 10^{-20}$ m$^2$/V$^2$ [7].

1.5.3. Molecular orientational effects

Anisotropic molecules exhibit an isotropic behaviour in a bulk material, when their orientations are randomly distributed. When a strong optical field is applied, the induced dipole moments will experience a torque and attempts to re orient with the applied field, by working against the thermal fluctuations. The incident optical wave gets polarized in the strong field direction and it experience an increase in the local refractive index, as more highly polarizable molecules are present and they are absent when the strong field is absent. This is depicted schematically in figure 1.9.
The nonlinearities that are associated with small anisotropic systems are $\chi^{(3)} \sim 10^{-13}$ to $10^{-12}$ esu [7]. The nonlinear refractive index $n_2 \sim 10^{-12}$ to $10^{-11}$ esu and with the response time is $\sim 10^{-12}$ s [7].

![Diagram showing weak and strong field effects on anisotropic molecules]

**Figure 1.9. Strong electric field induced anisotropic molecular reorientation.**

### 1.5.4. Electrostriction

An electrostriction phenomenon depends on the inhomogeneous field. This will occur when interference patterns with bright and dark fringes are formed due to the superposition of coherent waves or along the transverse direction of a Gaussian beam. This type of inhomogeneous field induces a force on the molecular system and is known as electrostrictive force.

The electrostrictive force is directly related to the square modulus of the electric field. Even a system of isotropic molecules will be electrostrictive in nature. The contribution of electrostriction to the nonlinear refractive index coefficient $n_2$ is $\sim 10^{-9}$ m$^2$/V$^2$ [7]. Its response time is $\sim 10^{-9}$ s i.e., about three orders of magnitude lower compared to response of the molecular reorientation [7].

### 1.5.5. Population redistribution

This process occurs when the frequency of incident beam is near a resonant energy transition of an atom or molecule. For a finite period of time, the electrons occupy real excited states. The optical polarization can be determined by the total number of atoms in the ground electronic state (for low light intensity) and the population redistribution induces a change in the index of refraction. This effect occurs in atomic vapours, gases, and organic liquid solutions, semiconductors and transparent dielectric
solids doped with metal ions or colour centres. The value of $\chi^{(3)} \sim -1.6 \times 10^{-16}$ m$^2$/V$^2$ and $n_2 \sim -1.2 \times 10^{-16}$ m$^2$/V$^2$ with the response time of the order of $\sim 10^{-9}$ s [7].

1.5.6. Thermal contributions

Thermal processes lead to large nonlinear optical effects [2]. The origin of thermal nonlinear effects takes place when the incident laser power is absorbed as it passes through an optical material. The temperature of the illuminated portion of the material increases consequently, and this leads to change in materials refractive index. For gases, the refractive index consistently decreases with increasing temperature. For condensed matters, with change in temperature, the refractive index can either increase or decrease. The time scale for changes in the temperature of a material can be long of the order of seconds. Consequently thermal effects lead to strong time-dependent nonlinear optical phenomena [1]. The thermal effects can be expressed by considering that the refractive index $\tilde{n}$ varies with temperature as [7],

$$\Delta n = \frac{dn}{dT} \Delta T, \quad (1.33)$$

where $dn/dT$ is called the thermo-optic coefficient. In the liquids and solids it is due to a density change (i.e., expansion) with temperature and the refractive index is proportional to density. Due to the expansion, density decreases and this contributes to $dn/dT$ and hence the negative sign. In semiconductors, the absorption band edges will red shift with temperature and this produces a positive thermo-optic coefficient. The linear absorption coefficient $\alpha$ can be the materials intrinsic absorption or the absorption due to the presence of impurities. In the steady state condition, materials that are having some absorption exhibits thermal nonlinear index of refraction. In the steady state, time constant $\tau$ signifies the thermal diffusion time. Times that are short when compared to the diffusion time, represents laser pulse width. Thus thermal contribution results in the change of index even before a steady state is reached. This is because, change of index is directly related to the deposited energy in the system and it increases with time. The values of $|dn/dT|$ ranges from $10^{-6}$ to $10^{-3}$ K$^{-1}$ [7]. The value of $\chi^{(3)} \sim 10^{-6}$ esu and $n_2 > 10^{-5}$ esu with the response time of the order of $\sim 10^{-3}$ s [7].
1.5.7. Photorefractive effect

In this mechanism, the refractive index change does not dependent on the intensity of laser beam. Due to the spatial variation of intensity, the change in refractive index is nonlocal. The effect was first observed in electro-optic crystals in the year 1966 and it was described as “optical damage”.

When two coherent waves of intensities, I₁ and I₂ overlap, interference fringes are produced and results in photorefractive effect. The photorefractive medium is demonstrated as a wide band gap semiconductor that is transparent at the incident radiation frequency. The energies of donor and acceptor impurities in the semiconductor lie within the region of forbidden gap. It is assumed that N₀ >> Nₐ; where N₀ and Nₐ are the number densities of donor and acceptors respectively. A small number of donors are ionized thermally and in the dark, the number of these ionized donors equals Nₐ. Acceptors will not contribute directly to the photorefractive effect and they maintain charge neutrality.

The neutral donors are photo-ionized by the incident light and create free carriers. Charge transports ensue due to diffusion. With the application of external field, there will be a drift current. As the free carriers diffuse through the crystal, they can be trapped by ionized donors. In the steady state condition, this occurs in the dark regions of the intensity distribution and thus establishes a space charge density pattern. The formation of space charge density leads to the growth of an internal space charge field and results in index grating by linear electro-optic (Pockels) effect. Thus, non-centro symmetric medium behave as photorefractive.

1.5.8. Excited state (saturable and reverse saturable) absorption

If the incident intensity is greater than saturation intensity, the excited state gets populated significantly. In polyatomic molecules and semiconductors, a high density of states is present near the state that is involved in the excitation. The excited electrons can rapidly transit to one among these states before it reaches the ground state. Similarly there are a number of excited states that couples radiatively with these intermediate states. The excited states energy differences are in near-resonance region with the incident photon energy. Therefore, before the electrons transits to the ground
state, they may experience absorption and get excited to a higher-lying state and this type of process is called as excited state absorption (ESA). This type of process occurs when the input intensity is strong enough to deplete the ground state.

If the absorption cross-section of excited state is lesser than the absorption cross-section of ground state i.e., if $\sigma_e << \sigma_g$, then it results in enhanced transmission of the system and this type of process is called as saturable absorption (SA). On the other hand, when $\sigma_e >> \sigma_g$, then the system will be less transmissive and this type of process is called as reverse saturable absorption (RSA). Figure 1.10 shows the energy level diagram of saturable and reverse saturable absorption [7].

In semiconductors, when an electron absorbs a photon having energy greater than the band gap energy, then the electron gets excited to conduction band. In this band, the electron becomes a free carrier and contributes to the flow of current with the application of field. The excited electron thermalizes rapidly and relaxes to the lower level of the conduction band. Thereafter, the electron will recombine with an excited hole in the upper level of valence band after completing a characteristic recombination time. However, when the intensity is sufficiently high, the excited electron in the conduction band may absorb another photon. This type of process is called as free carrier absorption (FCA) and it is similar to reverse saturable absorption [7].
A five level model of a polyatomic molecule with five distinct electronic states is shown in figure 1.11 [11]. Within each electronic state, there exist various vibrational–rotational states. When an electron gets shifted from one electronic state to another electronic state, the electrons will transfer to one of these vibrational–rotational states. However, with a small amount of energy transfer, electrons thermalize rapidly due to the collisions and will settle to the lower-lying vibrational–rotational level. From here, either the electrons absorb another photon or they may relax to any of the lower-energy states. The ground electronic state is called as singlet state and they have a pair of electrons with anti-parallel spins. The selection rules does not allow any radiative energy transition that produces a pair of electrons with parallel spins [7]. The absorption from the ground state results in a transition only to another singlet electronic state.

Figure 1.11. Schematic diagram of five level energy level diagram.

It is possible to produce a spin flip by internal process such as strong spin–orbit coupling. Under such conditions, the first excited electronic state may make a radiation less transition to a lower-lying triplet state. This type of radiative transition is allowed by selection rules only to another triplet state. Hence the singlet–singlet and triplet–triplet radiative transitions involves in molecular systems.

The process of absorption in a five-level system is explained briefly. When the electron absorbs the incident photon it gets promoted to the first excited singlet state. From this state following process will be possible,
• The electron can relax to the ground state by a radiative or non-radiative transition.

• The electron can undergo a spin-flip transition to a triplet state and this process is called intersystem crossing.

• The electron may absorb another photon and gets excited to a higher-lying singlet state; from there it later relaxes back to the first excited singlet state.

For an electron residing in the lowest triplet state, there are two possibilities that it may experience. First possibility is that it may relax by another spin-flip transition to the ground state and this is due to phosphorescence. Another possibility is that the molecule will absorb another photon, thereby promoting the electron to a higher-lying triplet state and then the electron relaxes back to the lowest triplet state. The relaxation rates from higher-lying singlet states and triplet states are very large [7, 12, 13], so that the population densities of these states $S_n$ and $T_n$ in figure 1.11, are very small and thus they are ignored. The stimulated emission process from the excited states is ignored, as the absorption excites the electrons to vibronic levels and there relaxation to the bottom vibronic level is very fast [7].

**1.5.9. Electron delocalization**

Delocalized electrons are found in conjugated systems and occur due to $\pi$ bond. Conjugated molecules contain alternating single and double (or single and triple) bonds. A single bond always has the structure of a $\sigma$ bond and a double bond consists of a $\sigma$ bond and a $\pi$ bond. A $\pi$ bond is made up of the overlap of two $p$-orbitals, one from each atom that is connected by the bond. The optical response of $\sigma$ bonds is very different from that of $\pi$ bonds because $\sigma$ electrons (that is, electrons contained in an $\sigma$ bond) tend to be localized in space. In contrast, $\pi$ electrons tend to be delocalized. Because $\pi$ electrons are delocalized, they tend to be less tightly bound and can respond more freely to an applied optical field. They thus tend to produce larger linear and third-order nonlinear optical responses [1].
1.6. Summary of literature review

In recent decades, an extensive search for materials exhibiting nonlinear optical properties is carried out. These effects are of great importance for applications in electronic and photonic devices. Light induced refractive index changes that employ third-order nonlinear optical properties of materials are of particular interest. For optical device applications, the nonlinear materials must have a high nonlinearity, low absorption, fast response time, large dynamic range and broadband spectral response [14]. The nonlinear optical materials can alter the features of light propagating through them purely by optical means, providing scope for the possibility to control light by light and hence be used in a wide range of applications such as all-optical signal processing, optical switching, optical image processing, optical limiting, laser beam shaping, opto-electronic devices, three dimensional optical memory devices, optical modulation, telecommunications, photodynamic therapy, etc., [6, 14, 16-18].

The realization of nonlinear optical effects requires novel materials. The minimum criteria required for a material to behave the third-order nonlinear optical property are to have a large third-order nonlinear coefficient, good transparency, low optical losses, fast response time, commercial availability and low cost [19, 20]. To fulfil the requirements, materials exhibiting nonlinear optical properties are being explored. The nonlinear optical materials can be classified in to inorganic and organic materials. Both organic and inorganic materials have their own advantages and disadvantages. The materials in its various forms have been investigated for nonlinear optical properties by using pulsed and continuous wave lasers. Wide variety of photonic materials have been investigated which includes, semiconductor thin films, inorganic and organic crystals, liquid crystals, polymers, doped glasses, dyes, phthalocyanines, porphyrins, quantum dots and nanomaterials of both semiconductors and insulators. Here some of the nonlinear materials reported in the literatures are presented.

Yan et al. [21] investigated the dependence of optical limiting properties of quinolone based azo derivatives using Q-switched Nd:YAG laser at 532 nm wavelength. They concluded that the nonlinear absorption and limiting properties improve with increase of intermolecular interaction. The large π-electron
delocalization in molecules resulted with lower energy gap between HOMO and LUMO, further facilitating intermolecular charge transfers in the excited state and thus enhancing the limiting property.

Saadon et al. [22] synthesized new organotellurium compounds containing azomethine and azo groups, [2-(2-hydroxynaphthylazo)phenyl] [2-(2-methoxybenzylideneamino)-5-methylphenyl] tellurium dibromide and [2-(2-hydroxynaphthylazo)-5-nitrophenyl] [2-(2-methoxy benzylideneamino)-5-methyl phenyl] tellurium dibromide and doped in polyvinylprodidone matrix. They studied the nonlinear optical properties of these compounds and doped polymer using z-scan technique and by using Q-switched Nd:YAG laser at 532 nm wavelength. The values of nonlinear refractive index and nonlinear absorption coefficient are found to be $10^{-7}$ cm$^2$/W and $10^2$ cm/kW respectively.

Rodrigues et al. [23] synthesized new fluorescent oxazolone derivatives with high two-photon absorption cross-section. They appended electron donor and acceptor groups to the methylene end of 4-(methylidene)-2-phenyl-1,3-oxazol-5(4H)-one to produce an highly conjugated $\pi$-system with push-pull geometry and they determined the linear and nonlinear optical properties of the oxazolones. They used a Ti:Sapphire laser at wavelength 710 - 990 nm as an excitation source. They found that compounds with a high charge transfer from the substituent group to the oxazolone ring have relatively high two-photon absorption cross-sections.

Al-Ahmad et al. [24] determined the third-order nonlinear optical properties of bromocresol purple by means of thermal self-diffraction using CW diode laser beam with the wavelength of 473 nm. They determined the magnitude of the nonlinear refractive index $n_2$ based on the diffraction ring patterns obtained as a result of thermal self-diffraction induced by self-phase modulation. Their results indicate that the films have large nonlinear refractive index $n_2$ for near resonance absorbance under 473 nm excitation. This is due to the excitation energy at 473 nm is nearer to the band gap energy of the films. Hence the linear absorption and the nonlinear optical properties of the films are large at 473 nm wavelength. The nonlinear refractive index $n_2$ and the thermo-optic coefficient $dn/dT$ are found to be the order of $10^{-5}$ cm$^2$/W and $10^{-7}$ K$^{-1}$ respectively.
Ara et al. [25] presented the preparation and characterization of SnO$_2$ semiconductor quantum dots. The measurements for SnO$_2$ quantum dots were measured by employing a CW He–Ne laser at 632.8 nm. The nonlinear refractive index $n_2$ and nonlinear absorption coefficient $\beta$ were measured using z-scan technique. The nonlinear refraction indices of the quantum dots were found to be of the order of $10^{-7}$ cm$^2$/W and the nonlinear absorption coefficients were obtained of the order $10^{-3}$ cm/W.

Organic crystals have very large nonlinear susceptibilities but their use is impeded by the inability to produce large crystals [26]. Raj et al. [27] studied the L-Asparaginium picrate crystal with metallic dopant cobalt (Co$_{2^+}$) and claimed that it is a good nonlinear optical material having large second harmonic generation efficiency. They studied the nonlinear optical behaviour of Co$_{2^+}$ doped L-Asparaginium picrate crystals using Kurtz–Perry technique.

Caroline et al. [28] synthesized and grown the bulk single crystals of pure L-alanine and cobalt doped crystals by slow-cooling method. The second harmonic generation signals were observed using Nd: YAG laser with fundamental wavelength of 1064 nm in pure and metal doped crystals. They measured the laser damage threshold for pure and metal doped L-alanine crystals and also tested using a Q-switched Nd: YAG laser showed enhanced value for metal (Co$_{2^+}$) doped LA crystal compared to pure LA crystal and this is due to the metallic substitutions thus proving their useful candidature for nonlinear optical applications.

Dhanuskodi et al. [29] synthesised and studied the lithium-p-nitrophenolate trihydrate single crystals. They conducted the powder second harmonic generation and third order nonlinear response using a modified Kurtz–Perry and z-scan technique with a He–Ne laser at 632.8 nm and with power of 35 mW. The nonlinear optical parameters intensity dependent refractive index $n_2$, nonlinear absorption coefficient $\beta$ and third order susceptibility $\chi^{(3)}$ were estimated to be $10^{-12}$ cm$^2$/W, $10^{-4}$ cm/W and $10^{-8}$ esu respectively.

Ramamurthy et al. [26] studied the optical limiting and nonlinear refractive index behaviour of transparent organic crystal bis (2-aminopyridinium)-succinate -
succinic acid using continuous wave He-Ne laser. The crystal exhibited defocusing nonlinearity and the observed behaviour is attributed to the thermal nonlinearity. They reported the value of nonlinear refractive index, the threshold value for saturation to be $-10^{-8}$ cm$^2$/W and 11.2 mW respectively.

Kumar et al. [30] investigated the third-order optical nonlinearities or organometallic crystal of MnHg(SCN)$_4$ using z-scan technique. The crystal exhibited self-defocusing property and the calculated nonlinear refractive index, absorption coefficient and third order susceptibility were found to be of the order of $10^{-11}$ cm$^2$/W, $10^{-6}$ cm/W and $10^{-9}$ esu respectively. They declared that the observed nonlinearity in crystals is due to the presence of SCN ligand and the investigated crystal is a potential material for third harmonic generation applications.

Arivazhagan and Rajesh [31] grown an organic nonlinear optical material 4,4′-dimethoxybenzoin single crystal by vertical Bridgman technique using single wall ampoule. The nonlinearity of the crystal by Kurtz and Perry powder technique and the SHG efficiency was found to be 2 times greater than KDP.

Li et al. [32] grown the Na$_3$La$_2$(BO$_3$)$_3$ crystal by the top-seeded solution growth method using Na$_2$O–B$_2$O$_3$–NaF as flux. They computed the nonlinear optical coefficients by the Maker fringe technique. For second-harmonic generation of 1064 nm, the effective NLO coefficient ($\beta_{\text{eff}}$) of type I phase-matching reaches the maximum value (1.44 pm/V) at the phase-matching angles $\theta=77.0^0$, $\phi=212.1^0$, which is larger than that of LiB$_3$O$_5$(LBO). First-principle calculations suggest that Na$_3$La$_2$(BO$_3$)$_3$ possesses two types of NLO-active atom groups, BO$_3$ group with $\pi$-orbital system and La-centered polyhedron with large polar displacement, of which the latter could be considered as a new type of NLO active atom group.

Dhanraj et al. [33] conducted studies on the third-order nonlinear optical parameters on nicotinium trifluoroacetate single crystals using z-scan technique. The crystals exhibited self-defocusing and saturable absorption behaviour. The nonlinear refractive index, absorption coefficient and third order susceptibility were found to be of the order of $-10^{-8}$ cm$^2$/W, $-10^{-4}$ cm/W and $10^{-6}$ esu respectively.
Patil et al. [34] grown a new nonlinear optical organic crystal 2,4,5-trimethoxy-4′-bromochalcone by a slow evaporation solution growth technique at an ambient temperature. They measured the second harmonic generation efficiency of the crystal by the classical powder technique using Nd:YAG laser and was found to be 1.8 times more efficient than reference material, urea. Also, they measured the third order nonlinear parameters by z-scan technique. They obtained the nonlinear absorption coefficient and nonlinear refraction coefficient to be 1.20 GW/cm and $-10^{-6}$ GW/cm$^2$ respectively.

Dhanaraj et al. [35] synthesised a novel organic crystal 2-Aminopyridinium trichloroacetate from aqueous solution employing the technique of controlled evaporation. The crystal displayed negative nonlinear optical parameters and they were derived by the z-scan technique. They used a CW He–Ne laser of wavelength 632.8 nm as the source. The obtained values of $n_2$, $\beta$ and $\chi^{(3)}$ of 2-Aminopyridinium trichloroacetate crystal are $-10^{-8}$ cm$^2$/W, $-10^{-4}$ cm/W and $10^{-6}$ esu respectively.

Organic molecules with multiple conjugated bonds, broadly classified as dyes are good optical absorbers and many of them found to exhibit optical nonlinearities. Choubey et al. [36] measured the laser induced nonlinear absorption coefficient of Brilliant Green solution by single beam open aperture z-scan technique using a continuous wave He–Ne laser at the wavelength of 632.8 nm. They found that the material exhibits multi-photon absorption type optical nonlinearity and claimed that significant optical nonlinearity is an indicative that Brilliant Green dye is prominent material for low power nonlinear applications. The nonlinear absorption coefficient $\beta$ and $\chi^{(3)}$ were found to be of the order of $10^{-3}$ cm/W and $10^{-7}$ esu.

Koushki et al. [37] carried out the close aperture z-scan experiment using Fresnel–Kirchhoff diffraction theory and a special shape of closed z-scan curves was determined based on the properties of the diffraction ring pattern. A 35 mW powered He–Ne laser ($\lambda=632.8$ nm wavelength) was used for the experiment. They computed the nonlinear refractive index of acid blue 9 dye using the above method for the very first time. They evaluated the numerical relation to calculate the nonlinear refraction index and it is found to be $10^{-6}$ cm$^2$/W.
Third-order optical nonlinearity and optical power limiting of Organic materials under CW laser illumination

Diallo et al. [38] reported the intensity-dependent refractive index $n_2$ and the nonlinear susceptibility $\chi^{(3)}$ of Hibiscus Sabdariffa dye in the nanosecond regime at 532 nm wavelength. The variation of $n_2$, $\beta$, real and imaginary parts of $\chi^{(3)}$ was been carried out by z-scan and optical limiting techniques. They used a Q-switched Nd:YAG laser operating at 532 nm as an excitation source. The third-order nonlinearity of the Hibiscus Sabdariffa dye was found to be dominated by nonlinear refraction, which leads to strong optical limiting of laser beam. The values of $n_2$, $\beta$, real and imaginary parts of $\chi^{(3)}$ were found to be of the order $-10^{-4}$ esu, $-10^{-4}$ esu, $-10^{-6}$ esu and $-10^{-8}$ esu respectively.

Vinitha and Ramalingam [39] measured the third-order nonlinear optical properties of dyes from the Triarylmethane family in 1-Butanol and in dye-doped polymer films by using z-scan technique. A CW diode-pumped Nd:YAG laser at 532 nm wavelength was used as source of excitation. The dyes exhibited a large negative optical nonlinearity resulting due to the thermal effect. The relative contributions from the nonlinear absorption and nonlinear refraction are dependent on the chemical structure and linear absorption of the dyes. The nonlinear refractive coefficient $n_2$, nonlinear absorption coefficient $\beta$ and susceptibility $\chi^{(3)}$ of dyes are of the order $10^{-8}$ cm$^2$/W, $10^{-4}$ cm/W and $10^{-6}$ esu respectively in both liquid and solid media. The results show that these dyes have potential applications in nonlinear optics.

Milanchian et al. [40] studied the nonlinear optical properties of the two oxazine dyes, oxazine 720 and oxazine 750, in aqueous solution and in polyacrylamide hydrogel matrix using z-scan technique and CW He–Ne laser at 632.8 nm. They were characterized with negative nonlinearity of the order of $10^{-8}$ cm$^2$/W and reverse saturable absorption of the order of $10^{-4}$ cm/W. The observed nonlinear results were reported to be due to the thermo-optic effect. They declared that these effects are due to the thermo-optical induced refractive index gradient and a concentration gradient induced by a temperature gradient present in a medium.

Sreekumar et al. [41] investigated the nonlinear refraction and optical limiting of amido black 10 B dye films prepared in polyvinyl alcohol by guest–host method using z-scan technique. Refractive nonlinearity of the solid medium was investigated using single beam z-scan technique under CW laser illumination at 632.8 nm
wavelength. The samples exhibited a negative (defocusing) nonlinearity and the nonlinearity is attributed to thermally induced variation in the medium. The nonlinear refractive index was of the order $10^{-7}$ cm$^2$/W and the limiting threshold value for saturation was 2 mW.

Ghaleh et al. [17] investigated the nonlinear response and optical limiting behaviour of fast green FCF dye (Acid blue 3) using continuous wave He-Ne laser. They measured the second order refractive index and nonlinear absorption coefficient by using z-scan technique. The optical limiting behaviour was investigated by transmission measurement through the sample. They reported the value of nonlinear refractive index, nonlinear absorption coefficient and the limiting threshold value for saturation as $10^{-8}$ cm$^2$/W, $10^{-5}$ cm/W and 7mW respectively.

Geethakrishnan et al. [42] investigated the third-order nonlinearity of triphenylmethane dye (Acid blue 7) using z-scan technique with a continuous wave He-Ne laser at 633 nm. The samples exhibited self-defocusing and saturable type of absorption behaviour. The $\chi^{(3)}$, $n_2$ and $\beta$ was of the order of $10^{-6}$ esu, $-10^{-7}$ cm$^2$/W and $-10^{-3}$ cm/W respectively.

Zidan et al. [18] investigated the optical limiting properties of acid blue 29 dye in various solvents irradiated using a 35 mW continuous wave He-Ne laser. The optical limiting behaviour was investigated by using transmission measurement through samples with different concentrations. They found that the strength of the optical limiting was influenced by the solvent and the threshold value for saturation was found to be 3 mW. Nonlinear refraction is the dominant mechanism for the optical limiting behaviour of acid blue 29 dye.

Mamedbeili et al. [43] investigated the laser induced third-order nonlinear optical responses of Brilliant Green solution (belongs to triphenylmethane organic dye group) by utilizing single beam z-scan technique using a continuous wave He–Ne laser at the wavelength of 632.8 nm. They observed that the material exhibits self-defocusing and saturation absorption type optical nonlinearity behaviour. They carried out the measurements to evaluate the real and imaginary parts of the third-order nonlinear optical susceptibility at various intensity and concentrations. The increase in
incident laser intensity or concentration leads to the linear increase in the nonlinear refractive index. The obtained value of the third order nonlinearity of Brilliant Green solutions is found to be $10^{-3}$ esu.

Sendhil et al. [44] studied the optical nonlinearity and optical limiting behaviour of zinc tetra phenyl porphyrin in polymer membrane. Porphyrins are $\pi$-conjugated materials with delocalized electrons and are considered to be good third-order nonlinear optical materials [40-43]. The measurements were conducted using z-scan technique with continuous wave laser operating at 632.8 nm. The incorporation of zinc tetra phenyl porphyrin in polymer membrane inhibits photo-degradation effects rendering the porphyrin in the solid membrane form for nonlinear optical applications. The nonlinear refractive index to be $-10^{-7}$ cm$^2$/W and the optical limiting threshold value was as low as 1.42 mW.

Notaras et al. [45] prepared $A_2B_2$-type push–pull porphyrins with a strong intramolecular dipole moment via Heck and Suzuki coupling reactions as novel materials for use in nonlinear optics. The porphyrins displayed both saturable and reverse saturable absorption properties for a Q-switched Nd:YAG laser at 532 nm. They described that the material’s nonlinear optical response is characterized by reverse saturable absorption occurring at lower intensity levels whereas the onset of saturable absorption prevails at higher levels.

Lu et al. [46] designed and synthesized (R)-meso-5,10,15,20-tetra-(2,6-dimethyl-5-heptenyl) porphyrin [(R)-H$_2$T(C$_9$H$_{17}$)$_4$P(1)] and (R)-meso-5,10,15,20-tetra-(2,6-dimethyl-5-heptenyl) porphyrinato zinc complex [(R)-ZnT(C$_9$H$_{17}$)$_4$P(2)]. They studied the third-order nonlinear optical properties using z-scan technique. The nonlinear absorption coefficient $\beta$ was found to be $10^{-11}$ m/W.

Zhu et al. [47] designed a new ferrocene-porphyrin derivative 5,15-bisferroacenyl-porphyrinato zinc. They investigated the nonlinear optical properties of ferrocene-porphyrin derivative using z-scan technique and a mode-locked Nd:YAG laser at 532 nm wavelength. The material exhibited saturation absorption in the absence of bipyridine and reverse saturation absorption in the presence of bipyridine. The $\beta$ and $n_2$ were found to be $10^{-11}$ m/W and $10^{-11}$ esu respectively.
Sukumaran and Ramalingam [48] studied the spectral characteristics and the nonlinear optical properties of the dye malachite green in polymethylmethacrylate. They studied thermally induced nonlinearity of malachite green dye in n-butyl Acetate using CW He–Ne laser at 632.8 nm as source of excitation, in solution and solid film forms and they compared the property of dye in solid matrix with that in liquid medium. They characterized the optical response by measuring the intensity dependent refractive index $n_2$ of the medium, using z-scan technique. They described that the origin of optical nonlinearity in this dye is attributed to laser-heating induced nonlinear effect. The dye exhibited negative (defocusing) nonlinearity and the results show that the dye can be a promising material for optical limiting applications.

Mathews et al. [15, 48] investigated the third-order nonlinear optical susceptibility of 2,3,9,10,16,17,23,24-octa-kis-(heptyloxy)-phthalocyanine and tetra tert-butyl phthalocyanine compounds. The experiments were performed using z-scan technique under continuous wave laser at 633 nm wavelength. The phthalocyanines demonstrated negative nonlinear refraction and saturable absorption type of behaviour and the observed nonlinearity was primarily thermal in nature. The obtained value of $\chi^{(3)}$, $n_2$, $\beta$ and the limiting threshold value for saturation for 2,3,9,10,16,17,23,24-octa-kis-(heptyloxy)-phthalocyanine and tetra tert-butyl phthalocyanine found to be $10^{-4}$ esu, $-10^{-6}$ cm$^2$/W, $-10^{-3}$ cm/W, 1.8 mW and $10^{-4}$ esu, $-10^{-6}$ cm$^2$/W, $-0.49$ cm/W and 7 mW respectively.

Kumar et al. [50] studied the optical nonlinearity and optical limiting behaviour of 2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanines using 633 nm continuous wave laser. The reported value of nonlinear refractive index, nonlinear absorption coefficient, the limiting threshold value for saturation found to be $-10^{-7}$ cm$^2$/W, $-10^{-3}$ cm/W, 7 mW respectively and the observed nonlinearity was attributed to thermal in nature.

Sanusi et al. [51] studied the nonlinear optical properties for 2(3),9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)phthalocyaninato indium(III) chloride (InPc) when covalently linked to CdSe/ZnS or CdSe quantum dots. They obtained experimental nonlinear optical parameters from z-scan measurements. The contributions from two-photon absorption are due to the InPc and free-carrier
absorption by quantum dots are identified as the main factors responsible for the enhanced optical limiting. The effective nonlinear absorption coefficient for InPc-CdSe/ZnS was found to be 700.0 cm/GW. The FCA cross-sections for InPc-CdSe/ZnS and InPc-CdSe composites were found to be $10^{-19}$ cm$^2$ and $10^{-20}$ cm$^2$ respectively. They claimed that a limiting threshold of 92 mJ/cm$^2$ was observed for InPc-CdSe/ZnS nanocomposite and hence it is suitable for use as optical limiting material.

Liu et al. [52] investigated the third-order nonlinear optical properties of µ-oxo-bridged phthalocyanine heterodimer using z-scan technique. They used an Nd:YAG laser at 355 nm wavelength as the source. They calculated the nonlinear refraction coefficient $n_2$ and imaginary part of third-order nonlinear susceptibility and are found to be $10^{-32}$ esu and $10^{-11}$ esu respectively.

Li et al. [53] studied the third-order optical nonlinearity of an azobenzene substituted zinc phthalocyanine in chloroform by picosecond z-scan technique at 532 nm respectively. They found that the azo-ZnPc shows a large positive nonlinear refraction and positive nonlinear absorption, exhibiting the defocusing effect and reverse saturable absorption respectively. The molecular second hyperpolarizability of the azo-ZnPc dyad was measured to be $10^{-30}$ esu. They concluded that the results suggest that the azo-ZnPc dyad have potential applications in the field of nonlinear optics.

Sathiymoorthy et al. [54] studied the thermally induced optical nonlinearity of chloro aluminium phthalocyanine (ClAlPc) in ethanol in the regime of low laser powers using a CW He–Ne laser as the source of excitation. They characterized the optical response by measuring the intensity dependent refractive index $n_2$ of the medium using the z-scan technique. They found the value of $n_2$ to be $10^{-12}$ m$^2$/W. The predominant mechanism of nonlinearity is the thermally induced refractive index variation. They investigated self-diffraction of the laser beam arising due to self-phase modulation by experimental and theoretical route.

Semiconductor nanoparticles have been extensively investigated due to their promising applications for various opto-electronic devices [55, 56]. Dehghani et al.
[57] studied the optical nonlinearity of Zinc sulfide nanoparticles by a simple chemical method and using poly vinylpyrrolidone as capping agent. The sample was characterized by z-scan technique and CW He–Ne laser at 632.8 nm. They obtained the sign of the nonlinear refractive index to be negative that indicates that the material exhibits self-defocusing optical nonlinearity. They reported the value of nonlinear refractive index, nonlinear absorption coefficient as \(-10^{-8}\) cm\(^2\)/W and \(10^{-3}\) cm/W respectively.

Yu et al. [58] investigated the optical nonlinearity and optical limiting behaviour of In\(_2\)O\(_3\) nanoparticles. They reported the measurements on effective intensity dependent nonlinear coefficient \(n_2\) with surface modification for the first time. The results show that coated In\(_2\)O\(_3\) nanoparticles has a large effective nonlinearity and a strong thermal induced lensing effect. The reported values of nonlinear refractive index and the limiting threshold value for saturation was found to be \(-10^{-7}\) cm\(^2\)/W and 780 W/cm\(^2\) respectively.

Naderi et al. [59] studied and synthesized the birnessite type manganese oxide (\(\gamma\)-MnO\(_2\)) nano-particles by Gelation routes method. At first they calculated the linear absorption for these nano-particles by optical limiting setup. They measured the nonlinear optical properties of (\(\gamma\)-MnO\(_2\)) nano-particles using close and open-aperture z-scan by using continuous-wave He–Ne laser with a wavelength of 632.8 nm at different incident powers. The nonlinear refractive index \(n_2\) and nonlinear absorption coefficient \(\beta\) of (\(\gamma\)-MnO\(_2\)) nano-particles were measured to be \(10^{-7}\) cm\(^2\)/W and \(10^{-2}\) cm/W respectively.

Another class of organic materials are liquid crystals that are known to possess good nonlinear optical responses. Zhang et al. [60] investigated the nonlinear optical properties of a series of azo benzene liquid-crystalline materials, which have different side-chain lengths in their molecular structure from one to another using z-scan method under picosecond pulse laser at 532 nm, 1064 nm and CW 488 nm excitation. They discussed the mechanism accounting for the process of nonlinear refraction under different laser excitations. They found that the polymer films possess very high nonlinear refraction at three different laser excitations and were of the order of \(10^{-10}\) cm\(^2\)/W, \(10^{-12}\) cm\(^2\)/W and \(10^{-6}\) cm\(^2\)/W respectively. The results indicate that the
nonlinear refractive index increases as the length of side-chain increases under pulse excitation at 1064 nm wavelength.

Ono and Kawatsuki [61] studied the optical intensity limiting of a He-Ne laser beam with guest-host liquid crystals. The optical clamping was found to be of 1.5 mW. The optical limiting effect originates from the spatial self-phase modulation owing to the photo thermal effect in the crystals.

1.7. Proposed research investigations

Literature review indicates that wide variety of materials have been explored to study their nonlinear optical properties. Among them, organic materials are attractive because of their inherent synthetic flexibility, efficient molecular nonlinearity over a broad frequency range, low dielectric constant, low cost, high optical damage threshold, ultrafast response with better process ability, ease of fabrication and possible integration in to devices [62]. These factors of organic materials allow one to fine tune the chemical structure and properties for a given nonlinear optical process. They consist of chemically bonded molecular units interacting in the bulk media through weak Vander Waals interactions. From empirical observations, it is observed that the nonlinear absorption coefficient $\beta$ can be enhanced by either increasing the electronic asymmetry by increasing the donating and accepting groups or increasing the conjugation length between the donors and acceptors [63-77]. Among the organic materials, dyes and polymers are emerging as promising candidates for nonlinear optics.

Dyes are the compound which consists of chromophores in the aromatic structure. The optical property of the dyes can be enhanced by the substitution of donors and acceptors in the structure. The nonlinear optical property of these materials is governed by the nonlinear optical characteristics of the constituent individual molecular chromophores. The chromophores containing donors and acceptor groups linked through an intervening $\pi$-backbone reveals larger nonlinear optical response.

It is also clear from the literature review that, the nonlinear optical properties of polymers have not been explored greatly. Polymers with $\pi$-electrons in the back
bone are termed as conducting polymers. Conducting polymers have conjugated backbone which enables π-electron delocalization. The nonlinear optical properties depend on the density of π-electrons. The nonlinear optical properties increase with increase in conjugation [78]. Polymers have low dielectric constant and hence respond faster to the applied field and also they have a high damage threshold.

Literature review indicates that most of the work is carried out on pulsed lasers and little work is carried on continuous wave regime. Many researchers have carried out studies on the optical nonlinearity and optical limiting properties of various classes of dyes and polymers to understand the nonlinear process and its applications to photonic and opto-electronic devices [41, 79-83]. The potential of these numerous dyes, conducting polymers and their derivatives remains yet to be explored under continuous wave regime.

In the present work, organic dyes and conducting polymers were chosen for the nonlinear optical studies under continuous wave regime. The synthesis of conducting polymers and copolymers of aniline were carried out. To investigate the third-order nonlinear optical susceptibility of dyes and polymers, single beam z-scan technique was employed using a continuous wave He-Ne laser operating at 633 nm wavelength as the source of excitation. Third-order nonlinear optical susceptibility, optical limiting and clamping properties, self-induced diffraction rings pattern and laser induced spot size variations for dyes and polymers were explored for possible nonlinear device applications.

1.8. Objectives of thesis

The main goals of research work reported in this thesis are,

1. Evaluation of third-order nonlinear optical properties of dyes and conducting polymers.
2. Establishing the influence of molecular structure on the nonlinear optical properties and relationship between them.
3. Nonlinear investigation of dyes and polymers as a possible candidate for optical power limiting devices.
1.9. **Organization of thesis**

The thesis is organized in to the following six chapters;

- Chapter 1 contains a detailed introduction to the basics of nonlinear optics, different process and mechanisms involved. A brief literature survey of the experimental studies on various classes of materials is presented. Followed by proposed research investigation and objectives of the thesis.

- Chapter 2 gives the brief experimental and theoretical description of experimental methods. It contains a detailed description of single beam z-scan and optical limiting techniques which are employed to determine the third-order nonlinear optical properties and optical limiting and clamping values. This is followed by a concise description of different spectroscopic characterization techniques and specification of instruments.

- Chapter 3 begins with the brief introduction and classification of anthraquinone dyes. In the experimental section, materials molecular structure and sample preparation for nonlinear optical studies are discussed. It also contains the brief results and discussions on the UV-VIS absorption spectroscopy, linear refractive index measurements, third-order optical nonlinearity, optical limiting and clamping properties, self-diffraction rings and laser spot size variation of the anthraquinone dyes.

- Chapter 4 starts with the overview of conducting polymers. The synthesis of polymers, materials molecular structure, sample preparation for nonlinear optical studies, UV-VIS absorption spectroscopy, FTIR spectroscopy, linear refractive index measurements, the third-order optical nonlinearity, optical limiting and clamping properties, self-diffraction rings and laser spot size variation of conducting polymers are presented.

- Chapter 5 begins with the introduction to copolymers. The synthesis, molecular structure of copolymers, sample preparation for nonlinear optical studies, UV-VIS absorption spectroscopy, FTIR spectroscopy, linear refractive index measurements, third-order optical nonlinearity, optical limiting and
clamping properties, self-diffraction rings and laser spot size variation of copolymers of aniline experiments are reported briefly.

- Chapter 6 presents the conclusions of the present work and ends with the directions towards the future scope of work.