Z-scan and Degenerate Four Wave Mixing Studies in Certain Photonic Materials

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CERTIFICATE

Certified that the work presented in the thesis entitled "***Z-scan and degenerate four wave mixing studies in certain photonic materials***" is based on the original work done by Mr. Unnikrishnan K P, under my guidance and supervision at the International School of Photonics, Cochin University of Science & Technology, Cochin - 682 022, India and it has never been included in any other thesis submitted previously for award of any degree.

Cochin - 682 022
March 10, 2003

Prof. C. P. Girijavallabhan

DECLARATION

Certified that the work presented in this thesis entitled "***Z-scan and degenerate four wave mixing studies in certain photonic materials***" is based on the original work done by me under the guidance and supervision of Dr. C P Girijavallabhan, Professor, International School of Photonics, Cochin University of Science & Technology, Cochin - 682 022, India and it has not been included in any other thesis submitted previously for award of any degree.

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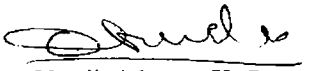

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Preface

Observation of second harmonic generation (SHG) by P A Franken in 1961 marked the birth of nonlinear optics as a new discipline of laser matter interaction. Nonlinear optics is the study of phenomena that result from light induced modifications in the optical properties of the materials. This branch of science explores the coherent coupling of two or more electromagnetic fields in a nonlinear medium to generate new frequencies that are sum or difference of coupling frequencies. Franken attributed the new result to coherent mixing of two optical fields at 694 nm to produce an optical field at 347 nm.

Since then nonlinear optics has been an important area of science and technology. Interest in the study of nonlinear laser matter interactions arises because of two main reasons: (1) it is an effective method of understanding the nonlinear optical (NLO) properties of materials as well as spatial and temporal evolution of the nonlinearity and (2) a number of technological application have been realized and many others have been proposed using NLO effects. In this context investigation of NLO properties of certain important photonic materials was chosen as the topic of research outlined in the proposed thesis. Third order NLO effects are particularly interesting partly because third order effects have greater technological relevance and partly because third order effects are present, in varying degree of strength, in all materials irrespective of symmetry of materials. Organic materials, nanomaterials and photonic band gap materials are among the NLO materials of recent interest. Phthalocyanines (Pcs) and naphthalocyanines (Ncs) are typical organic NLO materials. They form one class of materials investigated here. The other type of material studied in this work is silver nanosol, aqueous solution of silver nanoparticles, which may be considered as a representative of nanomaterials. Origin and dynamics of linear as well as nonlinear optical properties of nanoparticles are completely different from those of organic compounds like Pcs and thus two distinct class of materials have been

investigated. Degenerate four wave mixing and Z-scan were chosen as the experimental techniques for the present investigation. The proposed thesis contains seven chapters. The content of each chapter is described briefly.

Chapter 1: In this chapter, the basic concepts and salient features of nonlinear optics are described. Some of the important nonlinear optical effects like optical limiting, optical phase conjugation (OPC) and second harmonic generation (SHG) are mentioned and a few applications of these phenomena in technology are explained. A brief survey of important NLO materials such as organic materials, nanoparticles, nanotubes, quantum wires, quantum dots, photonic band gap (PBG) materials is also given. Emphasis is given to organic materials like Pcs and metal nanoparticles, which are the materials of present investigation. The motivation for the present work as well as concise description important results obtained during this work is given at the end.

Chapter 2: This chapter contains the relevant theory and experimental details of the degenerate four wave mixing (DFWM) and Z-scan techniques. Back scattering geometry of DFWM was used for the experiments. Variants of Z-scan techniques and other possible configurations of DFWM are mentioned. Specifications of excitation sources and other instruments used for making the measurements are also given.

Chapter 3: This chapter contains the results obtained from open aperture Z-scan experiments carried out in solutions of metal substituted phthalocyanines and naphthalocyanines at a fixed wavelength (532nm). Nonlinear absorption coefficient was measured and optical limiting property of these samples was analyzed. All these samples were found to exhibit reverse saturable absorption (RSA) at this wavelength. Samples selected include metal mono phthalocyanines (LaPc, MoOPc) metal subsituted naphthalocyanines (ZnNc, MgNc) , metal substituted bis – phthalocyanines [$Eu(Pc)_2$, $Sm(Pc)_2$, $Nd(Pc)_2$] and a bis- naphthalocyanine $Eu(Nc)_2$. It may be noted that the samples selected cover different structural variants of phthalocyanines.

Besides, metal ions are also different. Among (mono) MPcs, LaPc was found to be better nonlinear absorber. Among bis-Pcs, $Eu(Pc)_2$ was found to be better nonlinear absorbing material. Pcs in solution form can exhibit negative nonlinear refraction due to thermal lensing effect. Closed aperture measurements were taken in solutions of Pcs and exhibited thermal nonlinearity as expected.

Chapter 4: Studies on wavelength dependence of nonlinear absorption in bis-Pcs are too few. In this chapter, a comparative study of wavelength dependence of nonlinear absorption in three bis - Pcs viz. $Eu(Pc)_2$, $Sm(Pc)_2$ and $Nd(Pc)_2$ in the blue side of their Q-band is given. Objective of the work was to find out the upper wavelength limit for reverse saturable absorption. Such studies help to know whether these samples exhibit optical limiting property over a wide spectral range. Besides, saturation intensity I_s, nonlinear absorption coefficient β and imaginary part of third order susceptibility $Im[\chi^{(3)}]$ were measured and resonant enhancement of $Im[\chi^{(3)}]$ was also investigated. It was observed that magnitude of resonant enhancement is different in these samples. $Nd(Pc)_2$ exhibited resonant enhancement of two orders of magnitude but in other two samples, resonant enhancement was not as intense as in the case of $Nd(Pc)_2$. While $Eu(Pc)_2$ and $Nd(Pc)_2$ exhibited reverse saturable absorption at 604nm, $Sm(Pc)_2$ exhibited a clear saturable absorption at this wavelength. Since all these samples have similar structures, small but experimentally observable differences between these samples might be arising from slightly varying influence of these metal ions.

Chapter 5: This chapter contains the results of degenerate four wave mixing studies carried out in solutions of metal substituted phthalocyanines and naphthalocyanines. Polarizations of interacting beams were so chosen that formation of thermal grating is prevented so that the response we get is entirely electronic. Third order susceptibility $\chi^{(3)}$, figure of merit of third order nonlinearity $F = \chi^{(3)}/\alpha$ and isotropically averaged second hyperpolarizability $\langle\gamma\rangle$ were measured. Samples selected include metal mono

phthalocyanines (LaPc, MoOPc, FePc), metal subsituted naphthalocyanines (ZnNc, MgNc, VoONc), metal substituted bis – phthalocyanines [$Eu(Pc)_2$, $Sm(Pc)_2$] and a bis- naphthalocyanine $Eu(Nc)_2$. It may be noted that the samples selected covers different structural variants of Pcs with different levels of π electron conjugation. Moreover metal substituents in these samples also vary. Level of π electron conjugation, nature of metal substituent and dimensionality of the molecules significantly influence the $\langle\gamma\rangle$ values. The measurements were carried out with view to exploring the combined influence of these factors on $\langle\gamma\rangle$. The results obtained were explained by taking in to account the level of π electron conjugation, nature of metal substituent and dimensionality of the samples.

Chapter 6: The results of nonlinear absorption studies in silver nanosol using open aperture Z-scan technique at selected wavelengths near plasmon band are included in this chapter. Nanosol exhibited surface plasmon resonance (SPR) peak around 416nm. An interesting result of this investigation is that this material could act as a reverse saturable absorber and a saturable absorber at the same wavelength, depending entirely on the incident intensity. The results were explained in terms of plausible effects of SPR bleach and photochemical change induced absorption. Besides, closed aperture Z-scan experiments were also performed at 532nm, but result was negative. Divided Z-scan curve did not reveal any sign of positive or negative refraction. Possible reasons for this negative result are also mentioned.

Chapter 7: This chapter contains a brief description of future prospects along with summary and conclusions.

Most of the results included in this thesis have been published / communicated for publication, details of which are given below.

Publications (in journals)

1. Third order nonlinear optical studies in europium naphthalocyanine using degenerate four wave mixing and Z-scan **K P Unnikrishnan**, Jayan Thomas, V P N Nampoori, C P G Vallabhan, Opt. Commun. **204** (2002) p. 385 – 390
2. Degenerate four wave- mixing in some metal phthalocyanines and naphthalocyanines by **K P Unnikrishnan**, Jayan Thomas, V P N Nampoori, C P G Vallabhan, Chem. Phys. **279** (2002) p. 209-213
3. Wavelength dependence of nonlinear absorption in a bis-phthalocyanines studied using Z-scan technique. **K P Unnikrishnan**, Jayan Thomas, V P N Nampoori and C P G Vallabhan, App. Phys. B. **75** (2002) p. 871-874
4. Nonlinear absorption in certain metal phthalocyanines at resonant and near resonant wavelengths. **K P Unnikrishnan**, Jayan Thomas, V P N Nampoori, C P G Vallabhan, Opt. Commun. **217** (2003) p. 269 - 274
5. Nonlinear absorption and optical limiting in solutions of some rare earth substituted phthalocyanines. **K P Unnikrishnan**, Jayan Thomas, Binoy Paul, Achamma Kurian, Pramod Gopinath, V P N Nampoori and C P G Vallabhan, J. of Non. Opt. Phys. & Mater. **10**. No. 1(2001) p. 113-121
6. Second hyperpolarizability of certain phthalocyanines and naphthalocyanines. **K P Unnikrishnan**, Jayan Thomas, V P N Nampoori and C P G Vallabhan, Submitted to Synthetic Metals
7. Nonlinear optical absorption silver nanosol: **K P Unnikrishnan,** V P N Nampoori, V Ramakrishnan and M Umadevi and C P G Vallabhan. Communicated to J. Physics. D. App. Phys.

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1. Nonlinear absorption and optical limiting in solutions of a bis-phthalocyanine. **K P Unnikrishnan**, B Paul, A Kurian, P Gopinath, V P N Nampoori and C P G Vallabhan, Proceedings of the National Laser Symposium – 2000 (NLS- 2000). A Malik, K N Srivastava and S Pal (Eds). Allied Publishers Ltd. New Delhi. p. 167

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4. Nonlinear absorption in a bis-phthalocyanine: $Sm(Pc)_2$. **K P Unnikrishnan**, Jayan Thomas, V P N Nampoori and C P G Vallabhan, Proceedings of International Conference in on Fibre Optics and Photonics (in CD form). PHOTONICS - 2002 held at TIFR, Mumbai, India

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Unnikrishnan K P

Contents

1

Introduction
Nonlinear optics and nonlinear optical materials

Abstract

The fundamentals of nonlinear optics are introduced in this chapter. Physical origin of optical nonlinearity and the concept of phase matching are explained. A few important applications of nonlinear optical effects are also described briefly. An over view of important nonlinear optical (NLO) materials is given. A few of the materials investigated in this thesis viz., phthalocyanines, naphthalocyanines and nanoparticles, are described in detail.

1. Introduction

Observation of the second harmonic generation (SHG) by P A Franken in 1961 marked the birth of nonlinear optics as a new discipline in the area of laser-matter interaction. Franken observed that light of 347.1 nm could be generated when a quartz crystal was irradiated with light of 694.2 nm, obtained from a ruby laser. He attributed this novel result to the coherent mixing of two optical fields at 694.1 nm in the crystal to produce 347.1 nm [1]. Nonlinear optics is essentially concerned with the study of phenomena that result from field induced modifications in the optical properties of the materials. This branch of science explores the coherent coupling of two or more electromagnetic fields in a nonlinear medium. During these coupling processes, new frequencies can be generated that are the sum or the difference of the coupling frequencies. Though the discovery of SHG marked the birth of nonlinear optics as a new branch of experimental investigation, SHG was not the first nonlinear optical (NLO) effect to be observed. Optical pumping is a nonlinear optical phenomenon, which was known prior to the invention of laser [2]. A brief description of NLO interactions and NLO materials is given in the following sections.

2. Nonlinear polarization

Light is transverse electromagnetic (EM) wave. EM field is a vector field. Therefore, in principle, when interaction of light with matter is formulated, the effect of both the electric field ($\vec{E}$) and magnetic field ($\vec{B}$) as well as their directional nature must be considered. Besides, spatial and temporal variation of $\vec{E}$ & $\vec{B}$ is also to be taken into account [2]. However, light-matter interaction in nonmagnetic materials is described in terms of $\vec{E}$ only. In non-magnetic materials, $\vec{B}$ is neglected [3]. Magnitude of $\vec{B}$ is less than that of $\vec{E}$. In fact, $\vec{B}$ is related to $\vec{E}$ through the velocity of light, c by the relation

$$\vec{B} = \vec{E}/c \qquad (1.1)$$

Based on the concept of harmonic oscillator, the basic physics of the light-matter interaction can be summarized briefly as follows. $\vec{E}$ of light can interact with charged particles in the matter, mainly electrons, and hence distort the equilibrium charge distribution, which results in the separation of unlike charges to produce an electric polarization. The polarization thus generated is related to externally applied electric field through a characteristic property of the medium, called optical susceptibility [χ] [2]. It determines the magnitude as well as the direction of induced electric polarization for a given field strength, at a particular wavelength. The magnitude of optical susceptibility depends on various factors such as molecular and atomic structure of the materials, wavelength of excitation and intensity of light [2]. It has been found that when excitation intensity is increased, induced polarization becomes a nonlinear function of applied electric field strength [2,4-6]. The consequence of the nonlinear relationship between $\vec{E}$ and $\vec{P}$ is that, at very high values of intensity, a number of new and interesting phenomena begin to manifest macroscopically.

In this context, it is highly desirable to examine the strength $\vec{E}$ associated with light obtained from various sources used for optical excitation and compare the same with interatomic field. $\vec{E}$ associated with conventional light sources such as Xenon lamp and Mercury lamp, which were mainly used to excite samples in the pre-laser era, is very low in comparison with interatomic electric field. Because of its low electric field strength, light from conventional sources cannot appreciably perturb the molecular charge distribution. For instance, atomic field is of the order of 10^8 or 10^9 Vcm^{-1} [2, 6, 7], whereas electric field strength associated with conventional sources is $10^2 - 10^5$ Vcm^{-1}. Under the action of such a low electric field, electrons bound to the nucleus are displaced only by about 10^{-18} m, which is very small in comparison with interatomic distance, of the order of 10^{-10} m [4]. Therefore, it can be said that this small displacement is within the elastic limit and hence, there is no unharmonicity in the oscillations of induced polarization. Hence, measurements using conventional

light sources gave a polarization $\vec{P}$, which is linearly dependent on electric field strength. $\vec{P}$, in this case can be written as [6]

$$\vec{P} = \varepsilon_0 \chi^{(1)} \vec{E} \qquad (1.2)$$

where ε_0 is the susceptibility of vacuum. This domain of interaction of electric field with matter is referred to as linear optics. Linear effects, also called first order effects, include linear optical properties such as linear refractive index, linear absorption, and birefringence.

With invention of lasers, which has high degree of spectral purity, coherence and directionality, it has become possible to irradiate atoms and molecules with an $\vec{E}$ that is comparable to interatomic field. This is because of the fact that lasers can be focussed to a very small spot size, of the order of its wavelength, giving very large intensity and consequently extremely high electric field strength, at the focal region. This results in a considerable distortion of the equilibrium charge distribution, which gives rise to a large displacement of electrons with respect to their equilibrium position. Consequently, vibration of the electrons becomes highly unharmonic. It is also interesting to note that, when laser beam is tightly focussed photon density at the focal region approaches atomic density. In such cases, the potential which electrons experience cannot be approximated to a parabolic one. Consequence of this unharmonicity is that unlike in eq.(1.2), induced polarization becomes a function of higher powers of electric field too, i.e. nonlinear dependence on electric field strength. In such cases the polarization is expressed as a power series in the applied field as [8]

$$\vec{P}_{NL} = \varepsilon_0 \left(\chi^{(i)} E + 2D_2 \chi^{(2)} E_1 E_2 + 4D_3 \chi^{(3)} E_1 E_2 E_3 + \cdots\cdots \right) \qquad (1.3)$$

Here, $\chi^{(2)}$ and $\chi^{(3)}$ correspond to second order and third order susceptibilities respectively. D_1, D_2 etc. are related to degeneracy [8]. In the nonlinear optical regime, a number of interesting phenomena that are conspicuous by their absence in linear regime, emerge. One significant difference between linear and nonlinear optical interactions is that unlike in the linear case, in nonlinear optical processes two light beams can interact and exchange energy through induced nonlinear polarization of the medium [2]. In the case of very intense laser beams, even air itself can act as nonlinear medium. It is well known that femtosecond laser pulses get self-focussed in air [9]. One of the best examples of nonlinear process is the generation of super continuum (white light), which occurs when some materials are irradiated with terra watts of power. Many of these nonlinear optical effects have important scientific and technological relevance. Therefore, study of nonlinear effects is very important. It helps us to understand the mechanism of nonlinearity as well as its spatial and temporal evolution. Besides, detailed knowledge of NLO processes and their dynamics is also essential for the implementation of these techniques in appropriate areas of technology such as optical switching [10], optical communication [11], passive optical power limiting [12-14], data storage [15] and design of logic gates [16,17].

The wavelength at which nonlinear parameters are measured is also important. If the wavelength of excitation is close to one, two or three-photon resonance, resonant enhancement of nonlinearity will occur. At and near resonant frequencies, refractive index becomes a complex quantity. If wavelength of the light interacting with matter is at or near resonance, the power series expansion as in eq.(1.3) is not relevant. In the case of resonant excitation [2] (one photon, two-photon or three-photon), the nonlinear susceptibility term corresponding to resonant absorption can have enormously large magnitude. Generally, resonant nonlinearity has large magnitude but slow response, whereas non-resonant nonlinearity has very fast response but low in magnitude. Usually, observed nonlinear susceptibility is due to the response of

weakly bound outer most electrons of atoms or molecules. If $\bar{E}_a$ is the average electric field experienced by such electrons due to nucleus and neighboring electrons, we can consider the expansion in eq.(1.3) in terms of a dimensionless quantity, $\bar{E}/\bar{E}_a$. If the wavelength of excitation is far away from resonance, order of magnitude of nonlinear susceptibility terms can then be written as $\langle\chi^{(2)}\rangle \approx \langle\chi^{(1)}\rangle/E_a$ and $\langle\chi^{(3)}\rangle \approx \langle\chi^{(1)}\rangle/E_a^2$ and so on [2]. However, if the wavelength of excitation is very close to any of resonant frequency, magnitude of nonlinearity can be much higher. If the expansion of nonlinear polarization as power series in electric field is valid, the corresponding nonlinearity is called weak nonlinearity. On the other hand, if the frequency of excitation is very close to resonance, power series expansion as in eq. (1.3) is not correct. Such nonlinearity is called strong nonlinearity [2].

3. Some important nonlinear effects

All the nonlinear optical effects can be broadly classified into two categories; one is concerned with frequency conversion and the other one is concerned with optical modulation [18]. Examples of frequency conversion processes are sum and difference frequency generations. Processes concerned with optical modulation include Kerr effect, self phase modulation etc. In optical modulation processes, light modulates some property of the medium like refractive index. Generation of new frequencies in frequency conversion processes is due to the oscillations of induced nonlinear polarization at appropriate frequency. Obviously, frequency conversion processes are instantaneous and take place in a time scale as short as the inverse of the frequencies involved ($\approx \nu^{-1}$). However, common practice is to broadly classify the NLO effects on the basis of the susceptibility term involved like second order, third order etc.

All the nonlinear optical interactions consist of two successive processes; (1) intense light beam induces a nonlinear response (i.e. nonlinear polarization) in the medium and (2) the medium reacts on the light, which induced the nonlinear polarization, and modifies the light in a nonlinear way [2,8]. The first process is governed by the

constitutive equations, which are general relations between external field and induced polarization, written in terms of optical susceptibility $\chi^{(n)}$. The second process is governed by Maxwell's equations, which describe the generation of new frequencies in presence of nonlinear polarization. It is to be noted that the nonlinear polarization acts as a source term in Maxwell's equations [2,8].

All the nonlinear interactions should satisfy certain conditions called "phase matching condition" for macroscopic manifestation of NLO effects [2]. Physically, this corresponds to the necessary condition for the constructive interference of new waves generated in the interaction length. Mathematically, phase matching condition can be written as

$$\vec{k}_f - \vec{k}_i = \Delta\vec{k} = 0 \qquad (1.4)$$

i.e. change in wave vector must be zero. If this condition is not satisfied, we will not be able to observe any nonlinear effects macroscopically, even if the medium is nonlinear. Phase matching condition depends on a number of factors such as polarization of the light, symmetry of the sample etc.

As indicated earlier, propagation of EM waves in a nonlinear medium is governed by Maxwell's equation [2]

$$\nabla^2\vec{E} = \sigma\mu\frac{\partial\vec{E}}{\partial t} + \mu\varepsilon\frac{\partial^2\vec{E}}{\partial t^2} + \mu\frac{\partial^2}{\partial t^2}\vec{P}_{NL}(r,t) \qquad (1.5)$$

Here σ, μ and ε are conductivity, magnetic permeability and susceptibility of the medium respectively. It is interesting to point out here that while Maxwell's equation explains how new frequencies are generated in a nonlinear medium in presence of nonlinear polarization, it does not tell how a nonlinear polarization is generated. The later part is described solely by constitutive equations.

3.1 Second order effects

Second order effects which are related to $\chi^{(2)}$, correspond to all three wave mixing phenomena such as second harmonic generation (SHG) $\chi^{(2)}(2\omega;\ \omega,\ \omega)$, optical rectification $\chi^{(2)}(0;\ \omega,\ -\omega)$, parametric mixing $\chi^{(2)}(\omega_1 \pm \omega_2;\ \omega_1,\ \pm\ \omega_2)$, Pockel's effect $\chi^2(\omega;\omega,\ 0)$ [8]. Constitutive equation for typical second order process, under dipole approximation, is given by [5]

$$P_i^{(2\omega)} = \sum_{j,k=x,y,z} d_{ijk}^{2\omega} E_j^{(\omega)} E_k^{(\omega)} \qquad (1.6)$$

Summation over repeated index is assumed. Centro symmetric materials posses inversion symmetry i.e. $V(\mathbf{r}) = V(-\mathbf{r})$. Eq. (1.6) can satisfy this requirement only if $d_{ijk}^{(2\omega)}$ vanishes completely. Hence, second order effects appear only in non-centro symmetric materials. The most popular second order effect is SHG. Efficiency of SHG is proportional to phase mismatch $\Delta\mathbf{k}$ as given by the relation [5]

$$\eta_{SHG} \propto \frac{\sin^2(\Delta kl/2)}{(\Delta kl/2)^2} \qquad (1.7)$$

It is obvious that as $\Delta\mathbf{k}$ deviate from zero, the conversion efficiency steadily decreases.

3.2 Third order effects

Third order effects involve all four wave-mixing phenomena. Some of the important third order effects are third harmonic generation (THG) $\chi^{(3)}(3\omega;\ \omega,\ \omega,\ \omega)$, non degenerate four wave mixing $\chi^{(3)}(\ \omega_1 + \omega_2 \pm \omega_3;\ \omega_1,\ \omega_2,\ \pm\ \omega_3)$, Raman scattering $\chi^{(3)}$ $(\omega \pm \Omega;\ \omega,\ -\omega,\ \omega \pm \Omega)$, instantaneous AC Kerr effect (degenerate four wave mixing) $\mathrm{Re}\chi^{(3)}(\ \omega;\ \omega,\ \omega,\ -\omega)$, Brillouin scattering $\chi^{(3)}$ $(\omega \pm \Omega;\ \omega,\ -\omega,\ \omega \pm \Omega)$, DC Kerr effect

Re $\chi^{(3)}(\omega; \omega, 0, 0)$, two photon absorption $Im[\chi^{(3)}(\omega; \omega, -\omega, \omega)]$ and electric field induced second harmonic generation $\chi^{(3)}(2\omega; \omega, \omega, 0)$ [8].

Unlike $\chi^{(2)}$, $\chi^{(3)}$ is present in all the materials [2], irrespective of their symmetry. Therefore, third order nonlinearity is the lowest order universally occurring nonlinearity. Real part of third order nonlinearity is responsible for optical switching applications while imaginary part is responsible for optical limiting or nonlinear absorption. Therefore, third order nonlinear optical effects are very important in the context of technological applications. The general constitutive equation for the third order process can be written, neglecting nonlocal terms, as

$$\vec{P}_i^{(3)}(r,t) = \sum_{a,d,c} \chi_{ijkl}^{(3)}(\omega_a + \omega_b + \omega_c, \omega_a, \omega_b, \omega_c) E_j(\omega_a, \vec{r}) E_k(\omega_b, \vec{r}) E_l(\omega_c, \vec{r}) \tag{1.8}$$

3.3. Cascaded nonlinearity

Cascaded nonlinearity refers to a situation where a few lower order effects occur in a sample successively to produce an effective higher order nonlinear process. There are many occasions where first order and second order effects or first order and third order nonlinear effects occur successively. For example, in degenerate four-wave mixing experiments (DFWM) if two-photon absorption (TPA) is present, the optical phase conjugate (OPC) signal is related to pump beam intensity through its fifth power, instead of normal cubic dependence [19,20]. Photorefractive effect is also an example for cascaded nonlinear effect. In this case, initially linear absorption (first order phenomenon) takes places in the sample, which is followed by the occurrence of quadratic electro-optic effect, which is a second order phenomenon [21,22]. Therefore, it need to be ensured that in the experiments involving NLO effects, no unintended cascaded nonlinear effects does interfere with measurements.

3.4 Susceptibility tensor and hyperpolarizability

In isotropic materials, orientation of induced polarization $\vec{P}$ or electric induction vector $\vec{D}$, given by eq. (1.9), [23]

$$\vec{D} = \varepsilon\vec{E} = \varepsilon_0\vec{E} + \vec{P} \tag{1.9}$$

is along the direction of external electric field. But in anisotropic materials, electric induction vector is not oriented along the direction of inducing field alone, but it can have components in other directions as well. Magnitude of different components is usually different. Since refractive index (and hence velocity of light) is related to polarization, non-parallelism between the cause (excitation) and the response (polarization) gives rise to optical anisotropy. Therefore, susceptibility is generally a tensor. Optical double refraction is the most familiar example of optical anisotropy. In the case of solids, the origin of non-parallelism between the response and excitation can be found in the crystalline nature of matter. In this type of materials, the vectorial nature of light is very important [23].

The n^{th} order susceptibility $\chi^{(n)}_{i_1\ldots i_n}$ is a tensor of rank (n+1) with $3^{(n+1)}$ components. However, when symmetry conditions are applied, the number of independent components may be reduced. In certain experiments, it is possible to select different components by properly choosing the polarizations of interacting beams. The susceptibility tensors satisfy symmetry relationship, as shown below [2]:

$$\left.\begin{aligned}
&[\chi^{(2)}_{ijk}(\omega_1+\omega_2,\omega_1,\omega_2)]^* = \chi^{(2)}_{ijk}(-\omega_1-\omega_2,-\omega_1,-\omega_2)\\
&[\chi^{(3)}_{ijkl}(\omega_1+\omega_2+\omega_3,\omega_1,\omega_2,\omega_3)]^* = \chi^{(2)}_{ijk}(-\omega_1-\omega_2-\omega_3,-\omega_1,-\omega_2,-\omega_3)\\
&\chi^{(2)}_{ijk}(\omega_1+\omega_2,\omega_1,\omega_2) = \chi^{(2)}_{ikj}(\omega_1+\omega_2,\omega_2,\omega_1)\\
&\chi^{(3)}_{ijkl}(\omega_1+\omega_2+\omega_3,\omega_1,\omega_2,\omega_3) = \chi^{(3)}_{ikjl}(\omega_1+\omega_2+\omega_3,\omega_2,\omega_1,\omega_3)
\end{aligned}\right\} \tag{1.10}$$

For isotropic non dissipative media, there are only three independent components as is evident from following equations [2].

$$\left.\begin{aligned}
&\chi_{xxxx} = \chi_{yyyy} = \chi_{zzzz} \\
&\chi_{yyzz} = \chi_{zzyy} = \chi_{zzxx} = \chi_{xxzz} = \chi_{xxyy} = \chi_{yyxx} \\
&\chi_{yzyz} = \chi_{zyzy} = \chi_{zxzx} = \chi_{xzxz} = \chi_{xyxy} = \chi_{yxyx} \\
&\chi_{yzzy} = \chi_{zyyz} = \chi_{zxxz} = \chi_{xzzx} = \chi_{xyyz} = \chi_{yxxy} \\
&\chi_{xxxx} = \chi_{xxyy} + \chi_{xyxy} + \chi_{xyyx}
\end{aligned}\right\} \qquad (1.11)$$

Nonlinear susceptibility $\chi^{(n)}$ is a macroscopic quantity, which corresponds to the response of bulk material. Corresponding microscopic quantity is the atomic polarizability $\alpha^{(n)}$. In very dilute media, where dipole-dipole interaction can be neglected, $\chi^{(n)}$ is related to $\alpha^{(n)}$ by the equation [2]

$$\chi^{(n)} = N\alpha^{(n)} \qquad (1.12)$$

where, N is the number of molecules per unit volume. In presence of induced dipole-dipole interaction

$\chi^{(n)} = L^4 N\alpha^{(n)}$ where L, the local field correction factor, is given by $L = \frac{(n^2+2)}{3}$

(n is the refractive index)

4. Applications

As indicated earlier, there are a number of applications for NLO effects in various fields of technology and basic research [10-17]. Hence, study of NLO effects is highly relevant and desirable. Apart from the magnitude of nonlinearity, other parameters relevant to the applications of NLO effects are its (1) sign, (2) response time and (3) nature (real or imaginary) of the nonlinearity at the wavelength of excitation. In this section, a few important NLO effects are described briefly.

4.1 Frequency mixing

High power lasers in different spectral regions can be obtained by sum and difference frequency generations. For example, lasers in the infrared region can be obtained by difference frequency generation, whereas laser beams in the visible and UV regions can be obtained from sum frequency generations. Frequency doubled YAG laser is the most popular source of green light. Frequency tripled YAG laser is used for fusion applications. Optical parametric oscillators, which work on the principle of parametric wave mixing, are now used to get continuously tunable laser output from 400 nm to 2000 nm [24].

4.2 Optical short pulse generation and measurement

Optical pulses having pulse width less than nanosecond can be obtained only by using nonlinear techniques. Picosecond pulses can be obtained by mode locking technique [5]. Among different mode locking techniques, passive mode locking using nonlinear saturable absorbers is preferred due to intrinsic speed limit of active mode locking techniques using acousto-optic & electro-optic modulators [6]. Organic films, dye jets, bulk semiconductor quantum wells etc are some of the nonlinear media used for this purpose [25]. Pulse width of less than one picosecond is usually measured by autocorrelation technique which utilizes SHG [5]. Frequency resolved optical grating (FROG) is a nonlinear optical technique used for measuring the time dependant intensity and phase of a femtosecond pulses [26]. Thus, generation and characterization of ultra short pulses is possible only with appropriate nonlinear processes.

4.3 Nonlinear optical effects in optical communications

The sign of the refractive nonlinearity determines whether self-focussing or self-defocusing will occur in a medium when intense light propagates through it [2]. In communication, Stimulated Brillioun Scattering, Stimulated Raman Scattering etc. are detrimental effects, as they can cause optical loss and also frequency shift during

propagation of laser beams through fibers. Fiber amplifiers are used to compensate the attenuation. Stimulated Brillioun Scattering is particularly important in single mode fibers. Self phase modulation is also an important nonlinear phenomenon in optical fiber communications as it can effect pulse broadening. Today's fiber communication employs optical/ eletrical/optical converters at the transmitter and receiver ends. The bandwidth of optical signal is very much higher than that of electronics and therefore, the optical/ eletrical/optical conversion processes act like a bottleneck in the exploitation of full bandwidth of optics. This bottleneck can be removed if all optical devices are fabricated using NLO effects [27,28].

4.4 Optical switching

Organic materials with large and fast nonlinearity are promising candidates for optical switching [10]. The response time of the nonlinearity depends on the mechanism of evolution of nonlinearity. Therefore, it determines the operating speed of the devices. Refractive nonlinearity is responsible switching [29].

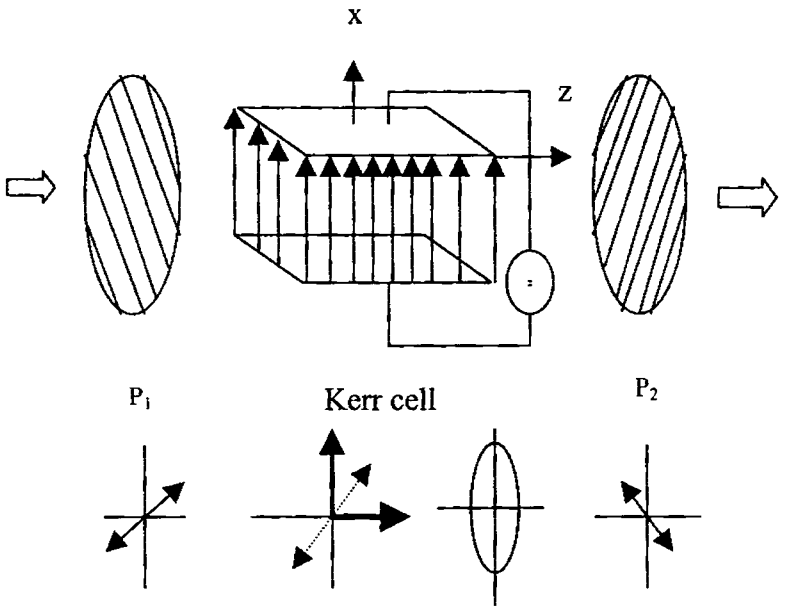

Fig. 1. Working of an optical switch

Schematic diagram of optical switching is shown in fig. 1. Ultimate goal is the design and fabrication of switches, wires, transistors and gates made of single field responsive molecule connected by photonic wires [30]. The difference between an electronic wire and a photonic wire is that the latter supports excited energy transfers rather than electron/hole transfer process [31]. Absorption of a photon as input by a chromophore at one end, causes emission of a photon at other end as out put. Optical switching by third order effects (e.g. optical Kerr effect) has advantages over linear electro-optic effect. The former has instantaneous response (response time around a picosecond) while the latter's response time can be higher [4]. This is because of the fact that electro-optic effects involve charge separation and hence the speed of switching is determined by the mobility of carries [26]. All optical switching requires a phase shift of more than π to be induced by light intensity through refractive index modulation [29].

4.5 Optical limiting

Passive optical power limiters are used to protect sensors, including human eyes, from intense laser light [12-14]. An ideal optical limiter [fig.2] will have a linear transmission upto a threshold input fluence I_{th} value, which can vary for different materials.

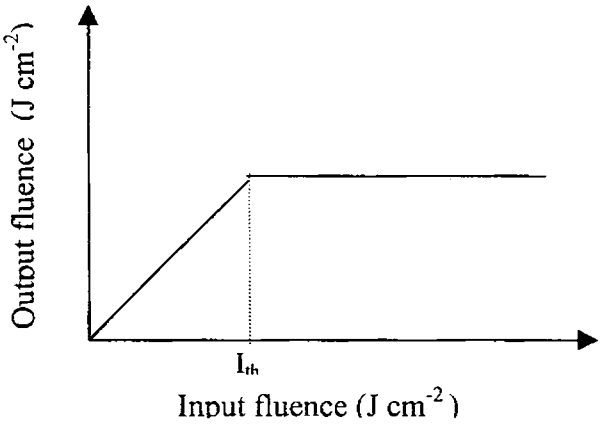

Fig. 2. Ideal optical limiting curve