CHAPTER - I

Nonlinear Optics: Materials and Importance

1.1 Introduction

Nonlinear optical materials play a pivotal role in the future evolution of nonlinear optics and its impact in technology and industrial applications are excellent. This chapter provides a general review on the field of nonlinear optics (NLO) and nonlinear optical materials. Nonlinear Optics (NLO) took its birth in 1875, with the commencement of the observations on a quadratic electric field induced change in the refractive index of CS$_2$ by Kerr, known as Kerr effect [1]. This was followed by the observation of a similar but linear electric field effect in quartz known as the Pockels effect [1]. However, in the field of optics, nonlinear effects became a subject of interest only after the invention of the laser. After the invention of laser, many classical experiments in NLO such as experiments on Second Harmonic Generation (SHG) by Franken $et$ al, [2] in 1961, Sum Frequency Generation (SFG) by Bass $et$ al [3] in 1962 and optical rectification by Bass $et$ al [4] in 1962 were performed. Since then, NLO had become a rapidly growing field in Physics. Nonlinearities are found everywhere in optical applications and at present, nonlinear optical properties of many optical materials with significant relevance to technological and optical applications have been found [5]. Vibrational spectroscopic techniques combined with quantum chemical computations have recently been used as an effective tool for the investigation of the structural features responsible for the nonlinear optical properties.

In the present scenario, where a lot of emphasis is devoted to the growth and structural elucidation of nonlinear optical materials, this thesis presents a detailed investigation of the nonlinear optical properties of certain materials using the vibrational spectroscopic techniques aided by theoretical methods. Charge transfer
interactions within the molecules is a requirement for the molecule to be nonlinearly active which are investigated through techniques of Fourier Transform Infrared (FT-IR) and Fourier Transform Raman aided by Density Functional Theory (DFT) computations. The aim of the present work is to optimize geometry, elucidate structure-property relationship, analyze second-order nonlinear behavior and evaluate structural and electronic effects of the chosen materials. The investigation initially starts with the possibility of obtaining the structural information on the chosen materials. Furthermore, the investigations encompass the confirmation of nonlinear optical activity of the chosen materials by hyperpolarizability calculations and Second Harmonic Generation (SHG) measurements.

1.2 Research Motivation

Currently, research on organic nonlinear optical (NLO) materials is strongly aggravated due to the demand of higher data rates in prospect optical communication technologies. Organic conjugated molecules are special candidates with nonlinear optical properties because of their high second and third order responses [6]. The \( \pi \)-conjugated systems having a donor and an acceptor show large NLO responses which enhance the study of these materials. Allied with the delocalized \( \pi \)-electrons, they exhibit large and ultra-fast NLO responses and as such the structural and electronic effects on the nonlinear optical materials provide a wide scope for additional expansion of the cited ambition.

1.2.1 Motivation to Opt Organic Materials with Nonlinear Optical Applications

In current research, nonlinear optics has emerged as the most attractive field of study due to its applications in areas such as optical modulation, optical switching, frequency shifting and optical data storage for the development of technologies in telecommunications and information processing and as such, nonlinear optical
processes are of vast scientific potential [7-15]. Materials exhibiting nonlinear optical properties form the basis of nonlinear optics and so the development of materials with significant nonlinear optical properties plays an important role in the present scenario. Design of materials possessing second order NLO effects relies on the relationship between molecular structure and property. For the design of the SHG materials the factors that have to be taken into account are: (i) the material should be polarizable (ii) there should be asymmetric charge distribution (iii) it should contain a π-conjugated electron pathway [16]. Moreover the electronic effects such as Hybridization, Backdonation, Induction and Hyperconjugation influences the structure, reactivity and properties of molecule. Based on these characteristics, it has been decided to opt nonlinear optical materials with NLO applications for the research purpose.

1.2.2 Motivation for the Chosen Experimental and Theoretical Study

Both the experimental and theoretical techniques are necessary for the accurate measurement of the properties of NLO materials. Furthermore, for the systematic analysis of the properties of these NLO materials, designing of optimization strategies are also important and this can be enhanced by understanding the relationship between electronic and geometric structure. In this regard, quantum chemical computations which are particularly useful for the determination of molecular properties and interpretation of experimental data those are inaccessible experimentally has to be carried out. Keeping these in mind, efforts were made to grow five nonlinear optically active crystals by slow evaporation technique and were characterized using FT-IR, FT-Raman and UV-visible spectral techniques and interpreted by quantum chemical computations using Gaussian 09 program package.
1.3 Nonlinear Optics (NLO)

Nonlinear Optics is a branch of optics that deals with the behavior of light in nonlinear media. It deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic fields altered in phase, frequency, amplitude or other physical properties [17]. The field of nonlinear optics finds a large intersection with theoretical and experimental physics, chemistry and engineering and has applications in all physical and life sciences. Nonlinear optical processes include processes such as harmonic generation, sum and difference frequency generation, intensity dependence of the complex refractive index, light-by-light scattering and stimulated light scattering. These processes lead to the applications of optical switching, optical power limiting, image manipulation, and image processing [10]. For the design and operation of a wide range of potential devices involving light, understanding the concepts of nonlinear optics are essential.

1.3.1 Concepts of Nonlinear Optics

Before the advent of lasers, transparent optical materials were assumed to be transparent and were unaffected by light traveling through them. The high power of laser beams made it possible for the first time to observe, that, the presence of light can affect the optical properties of the medium [18].

According to classical theory of Raman Effect, when a molecule is put in a static electric field, the positively charged nuclei is attracted by the negative pole of the field and the negatively charged electrons are attracted towards the positive pole of the field. This separation of charge centers causes an induced dipole moment to be setup in the molecule and the molecule is said to be polarized. The induced dipole moment per unit volume is called polarization \( P \) and for a linear, isotropic material polarization is linearly related to the strength of the field \( E \) as
\[ \vec{P} = \chi \vec{E} \]  

(1.1)

where \( \chi \) is the linear susceptibility of a collection of molecules which is related to the dielectric constant and refractive index of the material.

When a large electric field is incident upon an anisotropic material, the polarization may be expanded in a Taylor series to obtain

\[
\vec{P} = \chi' \vec{E} + \chi^2 \vec{E}^2 + \chi^3 \vec{E}^3 + \ldots \ldots \ldots (1.2)
\]

\[
P_i = \chi_0 E_i + \chi_2 E_j E_k + \chi_3 E_i E_j E_k E_l \ldots \ldots (1.3)
\]

where \( \chi^2 \) is the second order nonlinear susceptibility and \( \chi^3 \) is the third order nonlinear susceptibility [19].

The present work emphasizes more only on the second order nonlinear effects. For example, considering a second-order nonlinear optical process, the interaction of the optical electric field at frequency \( \omega \) and amplitude \( E_\omega \) can be written as

\[
E_\omega(t) = E_\omega \cos(\omega t) = \frac{1}{2} E_\omega (e^{i\omega t} + e^{-i\omega t}) \]  

(1.4)

where \( E_0 \) is a static electric field in the medium with a nonzero \( \chi^2 \). The second order polarization field in this medium is

\[
\vec{P}^{(2)}(t) = \chi^2 \vec{E}^2(t) = \chi^2 [E_\omega \cos(\omega t) + E_0]^2
\]

\[
= \chi^2 \left[ \frac{1}{2} E_\omega e^{i\omega t} + \frac{1}{2} E_\omega e^{-i\omega t} + E_0 \right]^2
\]

\[
= \chi^2 \left[ \frac{1}{4} E_\omega^2 (e^{i2\omega t} + e^{-i2\omega t}) + E_0 E_\omega (e^{i\omega t} + e^{-i\omega t}) + \frac{1}{2} E_\omega^2 + E_0^2 \right]
\]

\[
= \chi^2 \left[ \frac{1}{2} E_\omega^2 \cos(2\omega t) + 2E_0 E_\omega \cos(\omega t) + \frac{1}{2} E_\omega^2 + E_0^2 \right] \]  

(1.5)

The resulting polarization field contains components oscillating at various frequencies. In equation (1.5), the first term oscillates at \( 2\omega \) and depends only on the presence of the optical electric field and not the static field. This effect is known as
Second Harmonic Generation (SHG) or frequency-doubling. The second term oscillates at $\omega$ and causes variation in the refractive index of the medium and this effect is called the linear electro-optic effect. The third term is known as optical rectification and is a conversion of the oscillating electric field to a static electric field. These phenomena are due to the mixing of electric fields of various frequencies in a nonlinear medium [20].

For a material to generate second-order nonlinear optical effect, it should possess, a noncentrosymmetric structure along the direction of the electric field. Consider a material with inversion center such that it is symmetric in all directions. If an electric field with time-dependent magnitude

$$E(t) = E_0 \cos \omega t$$ (1.6)

is incident upon such a medium, the magnitude of the resultant second-order polarization field will be

$$P_2(t) = \chi^2 E^2(t)$$ (1.7)

Due to inversion symmetry,

$$-P_2(t) = \chi^3 E^3(t)$$ (1.8)

$$-P_2(t) = \chi^3 E_2(t)$$ (1.9)

Equations (1.8) and (1.9) are true only when the polarization field is zero [20]. It indicates $\chi^2$ is zero for centrosymmetric media and only a material having noncentrosymmetric structure will generate a nonlinear optical response.

### 1.4 Importance of Nonlinear Optical Materials

Nonlinear optical materials have applications in areas such as optical modulation, optical switching, frequency shifting and optical data storage for the development of technologies in telecommunications and information processing and
as such they have received much attention in recent years [10,21]. In the last decade, extensive research has proved that, organic crystals often possess a higher degree of optical nonlinearity than their inorganic counterparts [22,23]. Hence nowadays, organic nonlinear optical materials have been investigated extensively [24,25]. More over organic materials have the advantage of high nonlinearity, structural diversity or flexibility and rapid response in electro-optic effect. Another advantage of organic materials is that their properties can be optimized by modifying the molecular structure using molecular engineering and chemical synthesis [26].

From equations (1.8) and (1.9) it is clear that, for a material to have strong second-order NLO properties, it must crystallize in a noncentrosymmetric structure to have a nonzero $\chi^{2}$. Another requirement is that the material should have a large molecular hyperpolarizability ($\beta$). The second-order molecular nonlinearity can be enhanced by large delocalized $\pi$-electron systems with strong donor and acceptor groups [27-29]. Since the existence of large molecular hyperpolarizability is the basis of strong Second Harmonic Generation (SHG), organic molecules with long conjugation systems that usually exhibit large $\beta$ values are certainly candidate molecules for NLO materials [30]. The large value of the first hyperpolarizability, $\beta$, is associated with the intramolecular charge transfer resulting from an electron cloud movement through a $\pi$ conjugated framework from electron donor to electron acceptor groups. With an increase in conjugation length between the donor and the acceptor, the magnitudes of molecular polarizability and hyperpolarizability coefficients are found to increase superlinearly. Large molecular hyperpolarizabilities require highly polarizable electrons (to be able to respond to an electric field) and asymmetry on the molecular level. Large polarizability is achieved through
conjugation, where $\pi$-electron bonds between unsaturated atoms in organic compounds are delocalized and easily moved by electric fields [30].

Under the perturbation of an external electric field, the conjugated $\pi$-electron system provides a pathway for the entire length of conjugation. Fictionalization of both ends of the $\pi$ conjugated system with appropriate electron donor and acceptor groups can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical non-linearity [17].

1.5 Review of Literature

The design of efficient organic materials for applications in nonlinear optical effect is based on asymmetric polarization, induced by electron donor and electron acceptor groups on either side of the molecule at appropriate positions in the molecular systems. Due to their commercial importance in the fields of optical communication, signal processing, sensing and instrumentation, nonlinear optical materials capable of producing second harmonic generation, have been studied [31,32]. In order to understand the microscopic origin of nonlinear behavior of organic NLO materials, considerable theoretical and experimental investigations have also been made [33,34]. These efforts have brought its fruits in applied aspects of nonlinear optics. To obtain information on the behavior of normal modes, the effect of various types of intermolecular forces and the nature of hydrogen bonding on these nonlinear optical materials, IR and Raman spectroscopy has been used. Information about electronic transitions can be achieved by the analysis of UV-visible spectrum [35]. Since atoms or molecules absorb UV-visible radiation at different wavelength, spectroscopy is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.
For the computation of molecular structure, vibrational wavenumbers and energies of molecules, *ab initio* community has accepted Density functional theory (DFT) study as a popular post-HF (Hartree Fock) approach [36] because of its efficiency and accuracy with respect to the evaluation of a number of molecular properties. DFT calculations are also useful for gaining insight into the nonlinear optical properties of conjugated molecules. In a series of recently performed overlay calculations, a force field for some conjugated molecules has been constructed [37-41] and full normal coordinate analysis has been performed by means of the MOLVIB program written by T. Sundius [42,43]. This includes transformation of the DFT force field to natural internal coordinates and scaling of the quadratic force field according to Pulay’s method [44,45] by a set of scale factors refined in a least-square procedure which helps to achieve better agreement between the calculated and observed frequencies. Based on these informations, in the present work, the density functional three-parameter hybrid model (DFT/B3LYP) at the 6-31G(d), cc-pvdz and cc-pvqz basis set levels have been adopted to calculate the properties of the grown molecules and the normal modes are derived by employing MOLVIB program.

Cinnamic acid, a derivative of phenylalanine is extensively studied because of its very specific structure. In the cinnamic acid molecule, the carboxylic group is separated from the aromatic ring by a double bond. It causes conjugation between the \(-\text{C}=\text{C}–\) bond and the \(\pi\)-electron system. In order to study the existence of the hydrogen bonds in dimer, the polarized IR spectra of cinnamic acid has been studied by H.T. Flakus and M. Jabiojska [46]. Tiane-Jye Hsieh *et al* [47] had studied the molecular structure of cinnamic acid using the B3LYP/6-31G(d). The effect of alkali metals (Li, Na, K, Rb and Cs) on the electronic structure of cinnamic acid has been studied by means of FT-IR, FT-Raman, Nuclear Magnetic Resonance (NMR) and quantum
mechanical calculations [48]. From the analysis made by Bena Jothy et al [49] on ethyl-3-(3,4-dihydroxyphenyl)-2-propenoate, the charge transfer interactions through the $\pi$-conjugated bridge has been understood. The influence of electronic effect on the C-H stretching vibrations can also be identified.

Phthalate based crystals possess high piezoelectric coefficients with acousto-optical interaction [50,51]. They are often used as diffracting crystals because they are relatively inexpensive, easily cleaved, and sufficiently bendable for a compact spectrograph. The growth, optical, thermal and mechanical properties of ammonium acid phthalate crystal has been reported by A. Arun Kumar et al [52]. The enhancement of the second harmonic generation efficiency of Sodium hydrogen phthalate single crystals when dopped with zinc has been studied by Neeti Goel et al [53]. S. Sudhahar et al have studied the effect of Sm$^+$ rare earth ion on the structural, thermal, mechanical and optical properties of Potassium Hydrogen Phthalate single crystals [54]. The intramolecular charge transfer, vibrational spectroscopic and the Z-scan studies of nonlinear optical material Sodium acid phthalate hemihydrate has been studied by D. Sajan et al [55]. The interaction between lone pair oxygen and the $\sigma^*$ orbital of O-H confirms the existence of intermolecular O-H…O hydrogen bonding which is revealed by the Natural Bond Orbital (NBO) analysis. The higher degree of conjugation between the substituent groups has also been identified.

Among many organic compounds, chalcone derivatives have excellent nonlinear optical properties. They show preference to crystallize as noncentrosymmetric structures. Due to this fact they have been the objective of several experimental and theoretical studies. Synthesis, growth, optical (UV–vis–NIR absorption) and thermal (TGA/DTA) characterization of 3-Br-4’-methoxychalcone have been carried out by P.S. Patil et al [56]. V. Shettigar et al [57] have reported the
growth and characterization of an efficient π-conjugated potential push–pull NLO chromophore, 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one. Jose P. Abraham et al [58] have carried out an investigation on the intramolecular charge transfer of this molecule by using IR and Raman spectroscopy and Density Functional Theory (DFT) computations. The electronic effects such as induction and backdonation on the methyl hydrogen atoms have been identified from the vibrational analysis. FT-IR, FT-Raman and UV-visible spectral and the thermal analysis of 1-(4-Aminophenyl)-3-(3,4-dimethoxyphenyl)-prop-2-en-1-one have been carried out by Lynnette Joseph et al [59]. The intramolecular charge transfer, delocalization and the conjugation effects are discussed and the thermal behavior has been characterized by DSC and TGA/DTA method.

Picric acid forms stable picrates with various organic molecules through π-bonding or hydrogen bonding. S.R. Thilagavathi et al [60] have grown Glycinium Picrate Mono Glycine crystal and measured its Second Harmonic Generation (SHG) efficiency. Although this crystal crystallizes in the centrosymmetric space group, it exhibit SHG efficiency. The theoretical and vibrational spectra of 8-hydroxyquinolinium picrate have been studied by A. Basoğlu et al [61]. A nonlinear optical crystal from the aminoacid family, L-Threoninium picrate has been grown by S. Natarajan et al [62] and its structural, spectroscopic and nonlinear optical studies have been carried out. The presence of N-H…..O hydrogen bonding has also been observed. Vibrational spectral studies and nonlinear optical properties of L-leucine L-leucinium picrate with the help of Density Functional Theory (DFT) has been carried out by Sameh Guidara et al [63]. The existence of intermolecular hydrogen bonding on this system has also been discussed.
\[ \pi \text{-bridged donor-acceptor-donor systems are candidates for their nonlinear} \]

optical properties. K.J. Akerman and O.Q. Munro \cite{64} have carried out the X-ray crystallographic and density functional theory study of (3Z)-4-(5-ethyl-sulfonyl-2-hydroxy-anilino) pent-3-en-2-one and (3Z)-4-(5-tert-butyl-2-hydroxy-anilino) pent-3-en-2-one. They have elucidated the presence of inter and intramolecular hydrogen bonding on these compounds. A. Collas and F. Blockhuys \cite{65} have grown (E)-1-(2,4,6-Trimethoxyphenyl)pent-1-en-3-one compound and carried out X-ray diffraction studies. 4-(5-Bromo-2-hydroxyphenyl) but-3-ene-2-one crystals have been grown by A. Zonouzi et al \cite{66}. From the analysis it has been established that the molecular structure and theoretical calculations support the hypothesis, that, the conjugation in a molecule is the determining factor for the position of the enol H atom. Stefan Ellinger et al \cite{67} have prepared a family of multi-heterocycle donor–acceptor–donor telechelic conjugated oligomers designed for two-photon absorption and emission in the near-infrared (near-IR) and investigated the relationship between their spectral, structural, and electrochemical properties.