CHAPTER- 2

EXPERIMENTAL TECHNIQUES FOR CHARACTERIZATION

2.1 INTRODUCTION

Several techniques are used for the characterization of the grown crystals to study its properties. The characterization of crystal consists of evaluation of its structure and the study of their different properties. X-ray topography can be used to detect the structure of the crystal. The optical properties include the study of optical absorption of the crystal and SHG conversion efficiency. The vibrational energy transitions of the molecules are identified by Infrared (IR) and Raman Spectroscopy. The experimental method of characterization employed in the present work includes X-ray diffractometry, Fourier Transform Infrared spectroscopy, Fourier Transform Raman spectroscopy, UV-vis spectroscopy and SHG test to check the non-linear response of the crystal. The instruments, its principle and the salient features are discussed in this chapter.

2.2 SYNTHESIS TECHNIQUE

Growth of crystals from solution is the only method for the crystallization of substances which undergo decomposition before melting. Growth of crystal from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically

important crystals. The crystals obtained during the development of this work were grown by slow evaporation technique at room temperature. L- Leucinium Squarate Monohydrate was synthesized by dissolving L-Leucine and Squaric acid in the ratio 1:1 in double distilled water. Crystal seeds with perfect shape and free from macro defects were formed by spontaneous nucleation in a supersaturated solution at room temperature. The same steps was adopted to synthesize the other crystals with different concentration: Zinc Salicylate Dihydrate, Triphenylphosphine oxide-4-nitrophenol, Potassium 3,5-dinitrobenzoate and Zinc Benzoate .

2.3 STRUCTURAL STUDIES

2.3.1 Powder X-ray Diffractometer (PXRD)

The identity test of a crystal starts with the X-ray diffraction studies. X-ray diffraction provides an efficient and practical method for structural characterization of the crystals (Wilson, 1970, Klung and Alexander, 1973). Out of the various possible X-ray diffraction methods, the powder method is of special importance. This is because the powder method is the only technique which is readily applicable to all crystalline material. This method is the widely used diffraction method to determine the structure of crystalline solids. The sample is used in the form of fine powder containing large number of tiny crystallites with random orientation. X-ray powder diffraction is a rapid analytical technique primarily used for phase identification of a crystalline

material and can provide information on unit cell dimensions. The analyzed material is finally ground, homogenized, and the average bulk composition is determined.

2.3.1.1 Principle

Max von Laue, in 1952, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube; filtered to produce monochromatic radiation, collimated to concentrate, and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law $(2d\sin\theta = n\lambda)$ (Fig.2.1).
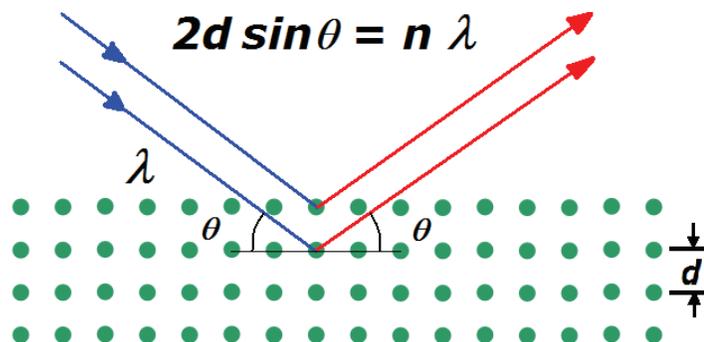

Fig. 2.1: Pictorial representation of Bragg's law

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings, allows identification of mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

2.3.1.2 Instrumentation

X-ray diffractometer consists of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying the voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_{α} and K_{β}. $K\alpha$ consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength

and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromaters, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single crystal diffraction, with CuKα radiation= 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle 'θ' while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of '2θ'. The instrument used to maintain the angle and rotate the sample is termed as goniometer. For typical powder patterns, data is collected at '2θ' from ~5° to 70° angles that are present in the X-ray scan.

2.3.2 Single Crystal X-ray Diffractometer (SXRD)

The most common experimental method of obtaining a detailed structure of a molecule that allows resolution of individual atoms is single crystal X-ray diffraction (SXRD) studies. It is performed by analyzing the

pattern of X-rays diffracted by an ordered array of many identical molecules (single crystal). When a monochromatic X-ray beam is passed through a single crystal, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation to produce a unique image pattern. Multiple images are recorded, with an area X-ray detector, as the crystal is rotated in the X-ray beam. Computationally intensive analysis of a set images results in a solution for the 3D structure of the molecule. SXRD is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond lengths, bond angles and details of site ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure. In the present investigations, the SXRD analysis of grown crystals was carried out using using Bruker AXS Kappa Apex2 CCD diffractometer with graphite monochromated Mo Kα (λ= 0.7107 Å). The detector is a scintillation counter. A single crystal is mounted on a thin glass fiber fixed on the goniometer head. The unit cell dimensions and orientation matrix are determined using 25 reflections and then the intensity data of a given set of reflections are collected automatically by the computer. The structure was solved by direct method and refined by the full matrix least squares technique using the SHELXL program (Sheldrick, 2007).

2.4 VIBRATIONAL SPECTROSCOPY

During the recent years vibrational spectroscopy has become an important tool in research, both for structural and functional studies. It is used to study a wide range of sample types and can be carried out from a simple identification test to an in-depth, full spectrum, qualitative and quantitative analyses. Vibrational spectroscopy includes the most important techniques infrared and Raman spectroscopy is based on the transition between quantized vibrational energy states of molecules. Though, fundamentally different in experimental design and physical background, provide complementary information on molecular vibrations that are extensively employed for the elucidation of molecular structure.

2.4.1 Infrared spectroscopy

IR spectroscopy is an important and popular tool for structural elucidation and compound identification. Simply, IR spectroscopy deals with the infrared part of the electromagnetic spectrum; it measures the absorption of different IR frequencies by a sample positioned in the path of an IR beam. It has emerged in recent years as the analytical method of choice in an enormous variety of applications. Two basic aspects make IR spectroscopy potentially attractive to the researchers. First, the technique is truly molecular level in nature. One is able to probe directly the structure of the molecule or system under study and information is obtained about functional groups, bonding forms, conformations and environmental influences that affect the molecular

frequencies. Second, IR spectroscopy needs relatively small quantity of the sample to be studied. Substances can be studied in the solid or liquid or gaseous state. Even water samples are being studied successfully (Aruldas 2004). The infrared region of the electromagnetic spectrum includes 3 regions; the near-, mid- and far-infrared regions based on their proximity to visible light. Conventional IR spectroscopy typically applies mid-infrared light (4000-400 cm^{-1}) and is useful in studying fundamental vibrations and structural composition (Bellamy, 1975).

2.4.1.1 Theory of infrared spectroscopy

The infrared spectroscopy is one of the most fundamental and useful spectroscopic techniques for organic and inorganic chemists. Infrared radiation is the part of electromagnetic spectrum between the visible and microwave regions. Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration, either stretching or bending. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The IR radiation is not energetic enough to cause electronic transitions, but the absorption of such radiation can cause vibrational and rotational transitions. As a molecule vibrates, a regular fluctuation in the dipole moment occurs establishing a field that can interact with the electric field of the IR radiation. If the frequency of the radiation exactly matches a natural vibrational frequency of a molecule then a net transfer of energy occurs

and there is a resultant change in the amplitude of the molecular vibration (Skoog and Leary, 1992), which is reflected as a change in the radiation power monitored at the detector. This means that the IR spectrum of a molecule is characteristic of that compound and may be used for identification (Skoog and Leary 1992, Aruldhas 2004). Upon irradiation of a sample by a broad-band source of IR energy, the absorption of light having appropriate frequencies results in transitions between molecular, vibrational and rotational energy levels. A vibrational transition might be approximated by the consideration of atoms bonded together within a molecule, as a harmonic oscillator. Based on Hooke's law, the vibrational frequency between two atoms might be approximated as:

$$\upsilon_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad\qquad (2.1)$$

where the reduced mass is given by μ which for a diatomic system is:

$$\mu = \frac{m_1 m_2}{m^1 + m_2} \qquad\qquad (2.2)$$

Molecular vibrations are analogous to the mechanical model of two atoms attached to a spring where μ is found from the atomic masses and the value of k is that of the force constant for the spring (i.e. the bond). The molecular mechanics model is too simplistic for particles of atomic dimensions. It is necessary to take quantum effects into account (Skoog and

Leary 1992). The simplest example for vibrational spectroscopy is that of the diatomic molecule.

It is known that vibrational energy levels are quantized, and can be described in terms of the number of quanta of excitation for each normal mode. Each normal mode acts like a harmonic oscillator with the energy content given by (Bernath 1995) as:

$$E_n = (v + \frac{1}{2})h\upsilon_o \qquad (2.3)$$

where v is the number of quanta of excitation involved and υ_o is the classical frequency of the particular oscillator. Transitions are caused by radiation that exactly matches that of the energy difference (ΔE) between the vibrational quantum states.

$$\Delta E = h\upsilon_o \qquad (2.4)$$

Therefore when an absorption band at a frequency υ is seen in vibrational spectroscopy, this implies that the molecule has a normal mode of frequency υ (Aruldhas 2004). The anharmonicity produces deviations from the harmonic case. At higher quantum numbers, ΔE becomes smaller and the selection rules are not rigorously followed. As a result of anharmonicity, transitions of $\Delta\upsilon = \pm 2, \pm 3,...$ are observed which are not possible with the harmonic oscillator model (Brame and Grasselli 1976). The vibrational energy expression for the anhormonic oscillator is given by,

$$G(v) = \upsilon_e(v + \frac{1}{2}) - \upsilon_e x_e(v + \frac{1}{2})^2 \qquad (2.5)$$

where υ_e is the oscillation frequency and x_e is the anharmonicity constant (Bernath 1995). A more general form of the energy-level expression is given by the Dunham potential (Bernath 1995) which uses a Taylor series expansion to give an infinite number of anharmonicity corrections as:

$$G(v)=\upsilon_e(v+\tfrac{1}{2})-\upsilon_e x_e(v+\tfrac{1}{2})^2+\upsilon_e y_e(v+\tfrac{1}{2})^3+\upsilon_e z_e(v+\tfrac{1}{2})^4 + \ldots \tag{2.6}$$

The anharmonicity constants decrease rapidly in magnitude as:

$$|\upsilon_e x_e| \gg |\upsilon_e y_e| \gg |\upsilon_e z_e| \tag{2.7}$$

The various types of possible IR transitions have specific names associated with them. The main transition of interest is the fundamental which is a $v =1 \leftarrow 0$ transition, while any transition originating from other than $v'\neq0$ is called a hot band. Overtone transitions are those where, $v'= 2,3,4,5\ldots$ (Aruldhas 2004, Banwell and Mccash 1995).

For a fundamental vibrational mode to be able to absorb IR energy, a change in the molecular dipole must take place during the molecular vibration. Typically, atoms in a molecule that possess different electro-negativities and that are chemically bonded will undergo a change in the net dipole moment during normal molecular motion. As a result, antisymmetric vibrational modes and vibrations due to polar groups are more likely to exhibit prominent IR absorption bands (Brame and Grasselli 1976).

2.4.1.2 Selection rule

In IR spectroscopy, the necessary condition for the absorption of a quantum of radiation 'hν' by the molecule should be equal to the energy difference between the two states represented by the wave functions 'ψ_i' and 'ψ_j'. The transition between these states under the influence of electromagnetic radiation depends on the interaction of the electric field of the radiation with the electric dipole moment of the molecule (Hendra, 1997). According to quantum mechanical theory of a molecular system, the probability of transition from a state 'i' to the state 'j' is proportional to the square of the transition moment.

$$\mu_{ij} = \int \psi_i {}^* \mu \psi_j \, d\tau \tag{2.8}$$

where, 'μ' is the dipole moment of the molecule.

The dipole moment of a molecule is a function of the normal coordinates 'Q_k' of the vibrational mode and can be expanded in a Taylor series as:

$$\mu = \mu_0 + \left(\frac{\partial \mu}{\partial Q_k} \right)_0 Q_k + \ldots \tag{2.9}$$

On neglecting higher terms,

$$\mu_{ij} = \mu_0 \int \psi_i^* \psi_j \, d\tau + \left(\frac{\partial \mu}{\partial Q_k} \right)_0 \int \psi_i^* Q_k \psi_j \, d\tau \tag{2.10}$$

The first term vanishes (orthogonality condition) and the conditions for the second term to be non-zero are:

(i) $\left(\dfrac{\partial \mu}{\partial Q_k}\right)_0$ must be finite at least for one component of the dipole moment.

That is, for a mode of vibration to be infrared active; the vibrational motion of that mode must give rise to change in dipole moment.

(ii)The integral $\int \psi_i^* Q_k \psi_j \, d\tau$ must be finite, which is possible only if the vibrational quantum number change $\Delta v = \pm 1$ under harmonic approximation and for anharmonic oscillator, $\Delta v = \pm 1, \pm 2, \pm 3 \ldots$ (Colthup *et al.*, 1990). In addition, the symmetry of the molecule also restricts the activity of vibrations. Homo-nuclear diatomic has no dipole moment and also they have no change in dipole moment during vibration. Hence vibrational spectra are observable only in the case of hetero-nuclear diatomic.

2.4.1.3 Anharmonicity

Anharmonicity in the oscillations of real molecules gives rise to weak bands in the spectra due to combinations and overtones. Combination bands result from the sum or difference of two different fundamentals, while overtone results from multiples of a single fundamental. There are two main sources of anharmonicity. They are mechanical anharmonicity due to deviations from the harmonic potential and electrical anharmonicity due to higher order terms in the dipole moment or polarizability. If overtones or combinations along with its fundamentals are observed in the spectra, it indicates the presence of mechanical anharmonicity. If electrical

anharmonicity is present, the overtones and combinations appear even if the fundamental is absent.

2.4.1.4 Mutual Exclusion Principle

Infrared absorption and Raman scattering are two different physical processes. The studies in one field frequently supplement or confirm the information derived from the other. This information is summarized as mutual exclusion principle. The IR and Raman activities of different modes of vibration of a molecule depend on its symmetry properties. An analysis of the IR and Raman spectra of a large number of molecules lead to an important general rule known as the rule of mutual exclusion principle (Long, 1977; Banwell & McCash, 1995). It states that, "for a molecule having a centre of symmetry the Raman active vibrations are IR inactive and vice versa". However, if the molecule does not have a centre of symmetry then some vibration may be Raman as well as IR active. The application of this rule can provide very useful structural information. Although IR and Raman measurements complement each other, to obtain the complete vibrational picture of a molecule, both the techniques are needed. This exhibits their togetherness in elucidating the structural information of complex molecules.

2.4.1.5 Factors affecting the vibrational modes

Since molecules are harmonic oscillators, any disturbance will lead to deviation from its equilibrium state which leads to vibrations of molecules in

such a way that, the motion can be considered to be a superposition of a number of simple harmonic vibrations, called normal modes of vibration. Some of the factors that affect the normal modes of vibrations are given below.

2.4.1.5.1 Group Frequencies

Group frequencies are vibrations that are associated with certain structural units and appear in fairly constant region in the spectrum (Rao, 1975; Nalwa & Miyata, 1997). They are described in terms of the motions that the nuclei in a structural group in the molecule undergoing vibration. The approximate constancy of the position of group frequencies forms the basis for the structural analysis of the compounds.

The relative constancy of spectral positions of group frequencies depends on the following factors.

1. Mass of atoms of the molecule

2. Force constant of the bonds between the atoms

3. Symmetry of bonds between atoms and

4. Interaction of vibrations

When these factors remain reasonably constant for related vibrations in a series of compounds, a characteristic group frequency will be found. Factors affecting group vibrations are:

(1) Internal factors involving changes in

a. atomic mass

b. vibrational coupling

c. resonance field effects

d. hydrogen bonding

e. bond angle strain etc.

(2) External forces involving physical state (gas, liquid, solid, solution, solvent and concentration) and temperature.

Often one factor is isolated from the rest, so that its influence upon one particular group frequency can be studied (Zyss and Chemla, 1987).

2.4.1.5.2 Solid state effects

The vibrations of an individual molecule in the gas phase are subjected only to the symmetry restrictions based on its own intrinsic point symmetry whereas, in crystals they are subjected to the symmetry restrictions arising out of its crystalline environment. Three features which distinguish the condensed phase spectra from the gaseous phase spectra are

1) Changes in the vibrational wavenumbers with occasional changes in intensities.

2) Appearance of entirely new bands in the low wavenumber region (<800 cm^{-1}), mainly a solid state characteristic phenomenon.

3) Splitting of single bands into multiplets.

Two levels of approximations have frequently been used for analyzing the

bands observed in molecules.

i. Site symmetry approximation:

If the symmetry of the site is lower than the molecular symmetry and the point group for the site is a subgroup of the molecular point group, then it leads to the removal of degeneracy, shifting of fundamental frequencies and the activation of inactive modes. This effect ignores the dynamical interactions between molecules and the surroundings are treated as static. This site symmetry approximation fails if the unit cell contains more than one formula unit.

ii. Correlation field approximation:

This mainly arises due to interaction between identical vibrations of molecules in unit cell. Interactions between molecules of different unit cells also contribute to this effect. This effect leads to the splitting of both non degenerate and degenerate modes. One fundamental vibration may split into a maximum of 'm' bands, where 'm' is the number of ions in the primitive unit cell (Sherwood, 1972). However, all these 'm' bands may not be IR or Raman active, some may even degenerate. In ionic compounds, the site group splitting is greater than the correlation field splitting whereas, in covalent compounds both the splitting are found to be of the same order. Correlation field effect is also known as dynamical field effect. Coupling between internal modes and that between internal and external modes may also lead to the splitting of

degenerate fundamentals. A splitting of the order 1-5 cm^{-1} is normally expected due to these couplings (Sherwood, 1972).

2.4.1.5.3 Overtones and Combinations

While deriving the selection rules for Raman and IR spectra, the normal vibrational modes are assumed to be harmonic in which case, only fundamental modes would be expected. When anharmonicities in potential energy and polarizability or electric dipole moment are taken into account, overtones and combination bands are also permitted. In Raman spectra, such bands are very weak and less in number when compared with the IR spectra. The anharmonic terms in potential energy leads to the mechanical anharmonicity. Due to this an overtone may occur if the fundamental is active and combinations which involve at least one active fundamental are allowed. Anharmonic terms in polarizability or electric dipole moment contribute to electrical anharmonicity. In this case, the overtones and combinations can be active even if the fundamental vibration is not active (Smith, 1999; Kalsi 2001; Dollish *et al.*, 1997). The electrical anharmonicity may be present even if the mechanical anharmonicity is absent. The opposite is less frequent.

2.4.1.6 Factors Affecting Group Frequencies

2.4.1.6.1 Symmetry

The vast majority of organic molecules have little or no symmetry. Nevertheless, some knowledge of symmetry can be of considerable help in

understanding the factors that affect intensities of group frequencies. Occasionally, a group frequency is not observed in the spectrum. This is usually a consequence of symmetry. If a molecule possesses a center of symmetry, all vibrations that are symmetric with respect to that center are inactive in the spectrum because they do not produce a change in the dipole.

2.4.1.6.2 Mechanical coupling of vibrations

Two completely free identical diatomic molecules will, of course, vibrate with identical frequencies. When the two diatomic groups are part of a molecule, however, they can no longer vibrate independently of each other because the vibration of one group causes displacements of the other atoms in the molecule. These displacements moment are transmitted through the molecule and interact with the vibration of the second group. The resulting vibrations appear as in-phase and out-of-phase combinations of the two diatomic vibrations. When the groups are widely separated in the molecule, the coupling is very small and the two frequencies may not be resolved.

2.4.1.6.3 Fermi resonance

Two or more molecule of polyatomic molecule belonging to different vibrations or combination of vibration may have nearly same energy, i.e. they may be accidentally degenerate. In such cases, the anharmonic terms which ordinarily might produce little effect may split the nearly degenerate levels quite considerably. The extent of splitting will depend on how close the unperturbed levels are to one another and on the magnitude of the anharmonic

terms. If the wave function of the two nearly degenerate levels have different symmetries. If the unperturbed levels are not very close, resonance may increase the intensity of the weaker band considerably but with little change in the frequency. Fermi was the first to recognize such perturbation in the case of a fundamental and the first overtone of CO2 molecule.

2.4.1.7 Hydrogen Bonding

Hydrogen bonding (X-H $\cdots$ Y) occurs between the hydrogen atom of a donor X-H group such as OH or NH and an acceptor atom Y which is usually O or N. The main effects are broadening of bands in the IR spectra and shifts of group frequencies. X-H stretching frequencies are lowered by hydrogen bonding, and X-H bending frequencies are raised. Hydrogen bonding also affects the frequencies of the acceptor group, but the shifts are less than those of the X-H group. Inert solvents can reduce the extent of hydrogen bonding and even eliminate the effect in very dilute solutions.

2.4.1.7.1 Intermolecular Hydrogen Bonding

Hydrogen bonding is a donor-acceptor interaction involving hydrogen atom (Prasad and Williams 1991). To form a hydrogen bond D-H$\cdots$A, the electronegativity of 'D' relative to 'H' should be greater enough to withdraw electrons, leaving the protons unshielded. To interact with 'D-H', the acceptor 'A' should have lone pair electrons or polarizable 'π' electrons. The intermolecular hydrogen bonding produces geometrical perturbations and causes changes in the vibrational characteristics. The hydrogen bond causes

the shifting of D-H stretching wavenumbers to lower values (red- shift). This is followed by band broadening and increase in intensity, depending upon the strength of hydrogen bonding. Opposite behavior is observed for C-H⋯O interactions for which the C-H stretching wavenumber increases followed by the decrease of C-H bond distance. This is known as blue shifting of hydrogen bond (Prasad and Williams 1991).The general trend of hydrogen bonding interaction is to shift the D-H deformation band to higher frequency. Some new bands corresponding to H⋯A stretching and bending may appear in the low wavenumber range. Small shift in vibrational frequencies for modes involving hydrogen bond acceptor atom can also be observed. Since the D-H stretching modes are pure and relatively free from vibrations of molecules, the vibrational spectroscopy provides a powerful technique to understand the nature and strength of hydrogen bonding.

2.4.1.7.2 Intramolecular Hydrogen Bonding

Intramolecular hydrogen bonding is formed between donor and acceptor atoms in the same molecule, when the molecular configuration brings them within the hydrogen bond geometry (Jeffrey 1997, Herzberg 2008). Intramolecular hydrogen bonds are formed in all three phases, but in crystalline state, their strength competes with that of intermolecular hydrogen bonds. The carbohydrates are rich in intramolecular hydrogen bonding due to the presence of hydroxyl groups attached to the adjacent carbon atoms. The vibrational spectral consequences of such interactions can he noticed in the

spectra, such as the appearance of H···A stretching band and the shifting of D-H stretching band position.

2.4.1.8 Electronic Effects

Effects arising from the change in the distribution of electrons in a molecule produced by a substituent atom or group can often be detected in the vibrational spectrum. There are several mechanisms such as inductive and resonance effects, which can be used to explain observed shifts and intensity changes in a qualitative way. These effects involve changes in electron distribution in a molecule and cause changes in the force constants that are, in tum, responsible for changes in group frequencies. Inductive and resonance effects have been used successfully to explain the shifts observed in C=O stretching frequencies produced by various substituent groups in compounds such as acid chlorides and amides. High C=O stretching frequencies are usually attributed to inductive effects and low frequencies arise when delocalized structures are possible.

2.4.1.8.1 Conjugation

The conjugation effect operates on systems with conjugate n-bonds, alternate 'σ' and 'π' bonds, in which the electron displacement is relayed through the n-electron system. The vibrational spectral influence of conjugation differs for various systems. For an aliphatic conjugation of carbon-carbon double bonds, the splitting of C=C stretching band is resulted (Bellamy 1975). The conjugation of the carbonyl group causes appreciable

shift in C=O stretching band position and hence most of the aryl ketones produce C=O absorption band in the lower wavenumber range, 1680-1690 cm^{-1}. For unsaturated aldehydes containing double bond in the α or β-positions show a fall in the carbonyl frequency due to conjugation. Aromatic ring in conjugation with the aldehyde groups also show marked effect on band position and C=O absorption occurs in the range 1710 - 1695 cm^{-1} (Smith 1999, Lin-Vien *et al.* 1991).

2.4.1.8.2 Intramolecular Charge Transfer

The compounds having the electron donor and electron acceptor at the end positions of the π - conjugated system is related to the existence of large intramolecular charge transfer responsible for second order NLO activity (Effenberger *et al.* 1995). The ICT causes the electron releasing effect in the acceptor moiety, affecting the spectral modes. In C=C stretching mode of acceptor subunit occurs at lower wavenumber compared to the corresponding mode of the donor subunit (Ruiz Delgado *et al.* 2003). For the conjugated path, ICT induces large variation in the dipole moment as well as in the molecular polarizability simultaneously during vibration. This produces the IR and Raman activity for the same mode and hence comparable intensities of IR and Raman bands arise from the vibrations of conjugated system (Ruiz Delgado *et at.* 2003). The electron donating effect of donor unit also causes wavenumber shifting for the vibrations of the donor group.

2.4.1.9 Fourier Transform Infrared spectroscopy

Fourier Transform Infrared (FT-IR) spectroscopy is a simple mathematical technique to resolve a composite wave into its frequency components. Since the early 1950s, IR spectroscopy has been a routine analytical tool for chemists. In the past, spectra were recorded using the so-known dispersive technique, i.e., with grating-type or prism instruments. In the last decade, FT-IR spectrometers have become increasingly available for routine laboratory work (Horlick & Yuen, 1978).

2.4.1.10 Principle of the FT-IR spectrometer

First signal referred to as an interferogram is generated by the interferometer. The interferogram obtained is a record of the signal by the infrared detector as a function of the difference in the path for the two beams of the interferometer. The spectrum is obtained by carrying out the Fourier transform of the interferogram. In this, the intensity, which is a function of path difference, x, is subjected to transformation as a whole to give the spectrum S, which depends only on frequency v. Hence,

$$S(v) = \int_{-\infty}^{+\infty} I(x)\, e^{+i2\pi v x} dx = F^{-1}[I(x)] \qquad (2.11)$$

In which

$$I(x) = \int_{-\infty}^{+\infty} S(v)\, e^{-i2\pi v x} dv = F[S(v)] \qquad (2.12)$$

Where the 1st integral is called the inverse Fourier transform and the 2nd integral is called the Fourier transform. Thus, the integral given by Eqn. (2.2) converts the interferogram $I(x)$, which is a function of path difference x to spectrum $S(v)$, which in turn is a function of frequency v. This calculation is carried out on a dedicated computer (Hoffman & Knozinger, 1987).

2.4.1.11 Fourier Transform Infrared spectrometer

A mathematical operation known as a Fourier transform can separate the individual absorption frequencies from the interferogram, producing a spectrum virtually identical to that obtained with a dispersive spectrometer. This type of instrument is known as Fourier transform infrared spectrometer (Perkins, 1968a). The diagram of FT-IR spectrometer is shown in Fig. 2.2.

The majority of commercially available FT-IR instruments are based upon the Michelson interferometer. The FT-IR uses a Michelson interferometer to process the energy sent to the sample. In the interferometer, the source energy passes through a beam splitter, a mirror placed at a 45º angle to the incoming radiation, which allows the incoming radiation to pass through but seperates it into two perpendicular beams, one undeflected, the other oriented at a 90º in Fig. 2.2, goes to a stationary or fixed mirror and is returned to the beam splitter.

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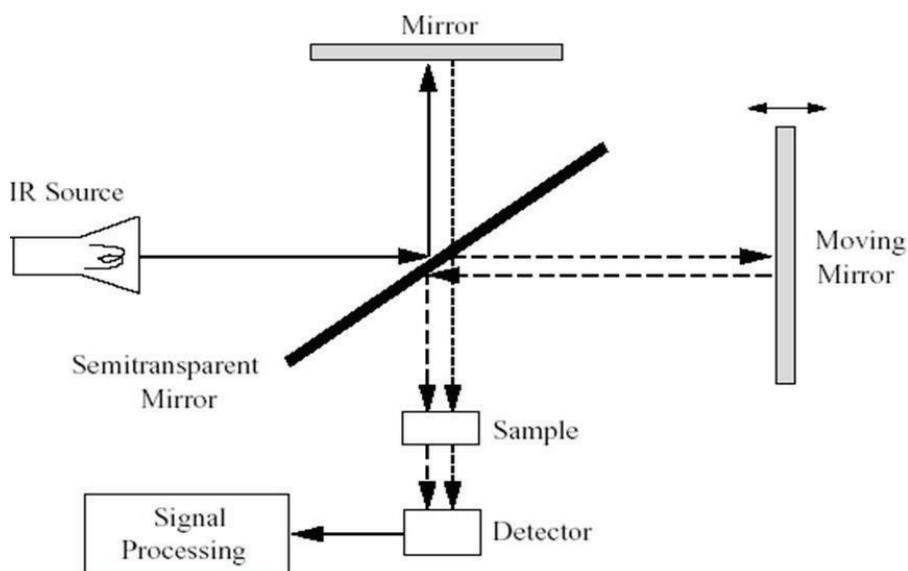
Fig. 2.2: Schematic diagram of FT-IR spectrometer

The undeflected beam goes to a moving mirror and is also returned to

the beam splitter. The motion of the mirror causes the path length that the

second beam transverses to vary. When the two beams meet at the beam

splitter, they recombine, but the path length differences of the two beams

cause both constructive and destructive interferences. The combined beam

containing these interference patterns is called the interferogram. This

interferogram contains all of the radiative energy coming from the source and

has a wide range of wavelengths. The interferogram generated by combining the two beams is oriented toward the sample by the beam splitter. As it passes through the sample, the sample simultaneously absorbs all of the frequencies that are normally found in its infrared spectrum. The modified interferogram signal that reaches the detector contains information about the amount of energy that was absorbed at every frequency. The computer compares the modified interferogram to a reference laser beam to have a standard of comparison. The final interferogram contains all of the information in one time-signal, a signal that cannot be read by a human. A mathematical process called a Fourier transform must be implemented by computer to extract the individual frequencies that were absorbed and to reconstruct and plot what we recognize as a typical infrared spectrum.

2.4.2   Raman spectroscopy

Raman spectroscopy is scattering technique; it is based on Raman Effect. The Raman Effect was first predicted by Smekal in 1923 but was first observed by Raman in 1928 (Gardiner & Graves, 1989). Professor Sir C.V. Raman and his student, Krishnan published their research work in 'Nature' journal, heralding the experimental finding of "a new type of secondary radiation" (Raman & Krishnan, 1928). In 1930, Professor Sir C. V. Raman was awarded the Nobel Prize for this discovery and the technique that would bear his name was born.

2.4.2.1 Theory of Raman Effect

Basically, the Raman Effect can be described as the inelastic scattering of light by matter. When a photon of visible light, too low in energy to excite an electronic interaction, interacts with a molecule it can be scattered in one of three ways. It can be elastically scattered and thus retain its incident energy or it can be in elastically scattered by either giving energy up to, or by removing energy from, the molecule photons undergoing inelastic loss of energy give rise to Stokes scattering whilst photons undergoing inelastic gain of energy give rise to anti-Stokes scattering. The energy gained by the molecule in Stokes scattering appears as vibrational energy and where a molecule has excess vibrational energy above the ground state, it is this energy which is lost to the anti- Stokes scattered photons (Long, 1977).

2.4.2.1.1 Classical Theory

The approach to a description of the Raman Effect regards the scattering molecule as a collection of atoms undergoing simple harmonic vibrations and takes no account of quantization of the vibrational energy. When a molecule is placed in an electric field, its electrons are displaced relative to its nuclei, thus developing an electric dipole moment. For small fields, the induced dipole moment μ_i is proportional to the field strength E.

$$\mu_i = \alpha E \qquad (2.13)$$

The proportionality constant α is the polarizability of the molecule, which is the ease with which the electron cloud of the molecule can be distorted. A fluctuating electric field will produce a fluctuating dipole moment of the same frequency. Electromagnetic radiation generates such an electric field which can be expressed as

$$E = E_0 \cos 2\pi\nu_0 t \qquad (2.14)$$

E_0 is the equilibrium field strength and ν_0 is the angular frequency of the radiation. Thus electromagnetic radiation will induce a fluctuating dipole of frequency ν_0 in the molecule. This induced dipole will emit or scatter radiation of frequency ν_0. This is Rayleigh scattering. Consider the particular case of a diatomic molecule which vibrates with a frequency of ν_v. If it performs simple harmonic vibrations, then a coordinate q_v along the axis of vibration at time t, is given by

$$q_v = q_0 \cos 2\pi\nu_v t \qquad (2.15)$$

If the polarizability changes during the vibration, its value for small vibrational amplitude will be given by

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 q_v \qquad (2.16)$$

Substitution of Eqn. (2.15) in Eqn. (2.16) yields;

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 q_0 \cos 2\pi\nu_v t \qquad (2.17)$$

If incident radiation of frequency ν_0 interact with the molecule then from Eqn. (2.13) and Eqn. (2.14)

$$\mu_i = \alpha E = \alpha E_0 \cos 2\pi \nu_0 t \tag{2.18}$$

Substitution of Eqn. (2.17) in Eqn. (2.18) yields;

$$\mu_i = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 E_0 q_0 \cos 2\pi \nu_v t \cos 2\pi \nu_0 t \tag{2.19}$$

This can be written as

$$\mu_i = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 \frac{E_0 q_0}{2} [\cos 2\pi(\nu_0 + \nu_v)t + \cos 2\pi(\nu_0 - \nu_v)t]$$

$$\tag{2.20}$$

The first term in Eqn. (2.20) describes the Rayleigh scattering and the remaining terms describe the Stokes and anti-Stokes Raman scatter. Eqn. (2.20) indicates that light will be scattered with frequencies.

$$\nu_0 = \text{Rayleigh scatter}$$

$$\nu_0 \pm \nu_v = \text{Raman scatter}$$

In addition Eqn. (2.20) shows that for Raman scattering to occur.

$$\left(\frac{\partial \alpha}{\partial q_v}\right)_0 \neq 0$$

That is, the polarizability of the molecule must change during a vibration if that vibration is to be Raman active (Steudal 1995).

2.4.2.1.2 Quantum Theory

In explaining Raman scattering using quantum hypothesis, incident radiation of frequency 'υ_o' is considered as a stream of particles undergoing collision with sample molecules. Perfect elastic collision will not exchange any energy between the photons and the molecules, but, inelastic collision will exchange energy between the two. Molecules that participate in the collision process either give up or lose energy equal to the energy difference 'ΔE' between any two of its allowed states. If the molecule gains energy, the scattered photons will have energy h (v_o - v_v) (Stokes lines). On the other hand, if the molecule loses energy, the scattered photons will have energy h (v_o + v_v) (anti-Stokes line). The energy level diagram of the entire transitions is shown in Fig 2.3.
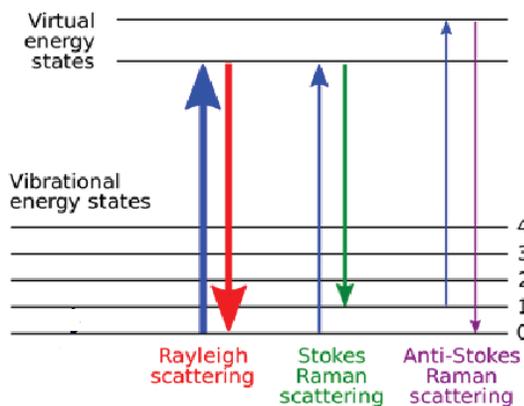

Fig. 2.3: Schematic representation of energy level diagram of Raman scattering

At room temperatures, most molecular vibrations are in the ground, v=0 state and thus the anti-Stokes transitions are less likely to occur than the Stokes transitions resulting in the Stokes Raman scattering being more intense. This greater relative intensity becomes increasingly greater as the energy of the vibrations increases and the higher vibrational energy levels become less populated at any given temperature. For this reason it is usually the Stokes Raman scattering which routinely studied and implied in Raman spectroscopy.

Incident radiation makes an upward transition to a virtual state of the system that corresponds to a combined state of the molecules and radiations (Ferraro *et al.* 2003). Most of the molecules of the system return to the original state from the virtual state resulting in Rayleigh scattering. However, a very small fraction returns to states of higher and lower energies giving rise to Stokes and anti-Stokes lines respectively. The intensity of a spectral line depends on a number of factors, the most important being the initial population of the state from which the transition originates. The Stokes line originating from v=O and the anti-Stokes from v= 1 give the same Raman shift. Based on Boltzmann distribution for the population in states, the intensity ratio of Stokes to anti-Stokes is given by

$$\frac{I_{Stokes}}{I_{anti-Stokes}} = \frac{{v_o - v_v}^4}{{v_o + v_v}^4} e^{hv_m/KT} \qquad (2.21)$$

where, 'h' is the Planck's constant; K, the Boltzmann's constant and T, the absolute temperature. It is evident that Stokes lines are more intense than that

of the anti-Stokes lines primarily due to the Boltzmann distribution between the lowest vibrational states.

2.4.2.1.3 Depolarization Ratio

The Raman scattered light is the result of the interaction of the electric field of the incident light with the scattering species. Further, the lasers used for the excitation are polarized, i.e., the electric field of the radiation vibrates in a specific direction. It is expected that the scattered light would also be similarly polarized. However, in actual practice some of the scattered light is found to be depolarized to varied extents. This depends on the symmetry of the molecular vibration causing the scattering and is a result of the nature of the polarizability changes during the vibration. The polarizability of the scattered light is measured by passing it through a Nicol prism or a Polaroid film called analyzer. The intensity of the light passing through the analyzer is measured as the analyser is rotated. The intensity would be maximum when the analyzer is parallel to the plane of maximum polarization and would decrease as the analyzer is rotated. It will be minimumnwhen the analyzer is perpendicular to the plane of maximum polarization. For the convenience of expression, the nature of the scattered light is expressed in terms of degree of depolarization. The degree of depolarization p is defined as, $p = I_I/I_{II}$ where I_I and I_{II} are the minimum and the maximum intensity measured by the analyzer. It helps in the assignment of signals in Raman spectrum. In general, a symmetric vibration

gives a polarized Raman line whereas the non- symmetric vibration gives depolarized signals. According to scattering theory, when the minimum degree of depolarization for a non-symmetric vibration is 6/7, it is termed as depolarized; whereas the degree of depolarization for the symmetric vibrations which is always less than 6/7 is called polarized.

2.4.2.2 Fourier Transform Raman Spectrometer

FT-Raman spectrometers are designed to eradicate the fluorescence problem encountered in conventional Raman spectrometer (Parker et al., 1988). The conventional Raman spectrometer measures intensity vs. frequency. But, FT-Raman is a time-domain spectroscopy, which measures the intensity of light of many frequencies simultaneously. This spectrum is then converted to conventional spectrum by applying Fourier transform. The block diagram of a FT-Raman spectrometer is shown in Fig. 2.4.
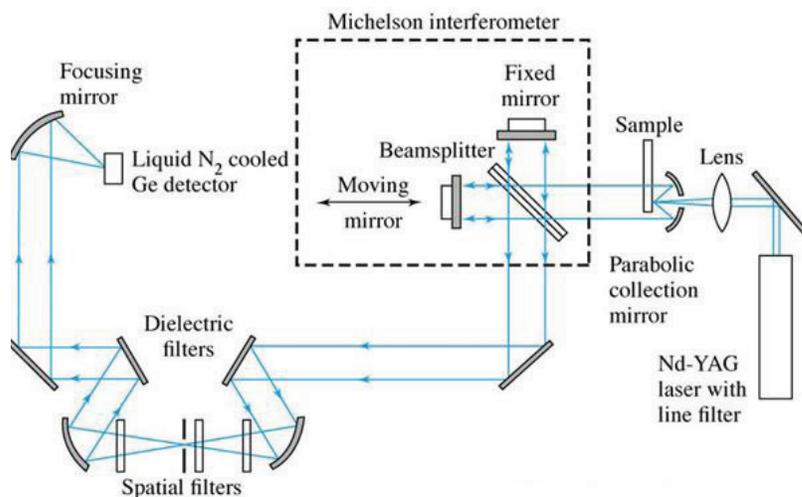

Fig. 2.4: Schematic diagram of FT-Raman spectrometer

The interferometer is the same type as is used in infrared instruments. The transducer is a liquid nitrogen-cooled germanium photoconductor. Because the intensity of the Rayleigh line is several orders of magnitude greater than that of the Raman line, holographic interference filters called notch filters or a monochromator are usually used in the instrument to limit the radiation reaching the transducer to wavelengths longer than that of the source. The laser are commonly used as radiation sources in FT-Raman spectrometer, mostly a 1064 nm Nd:YAG laser. The FT-Raman spectrometer has an interferometer to produce an interferogram, which encodes the unique frequencies of the Raman scattering into a single signal. The interferometer employs a beam splitter optimized for near infrared (NIR) radiation, which divides the incoming Raman signal and scatter into two optical beams, one transmitted and one reflected. The reflected beam travels to and reflects off a flat fixed mirror. The transmitted beam also travels to and reflects off a flat moving mirror, which has a constant frequency and fixed motion. The two beams recombine at the beam splitter. Depending on their path difference, the two beams constructively and destructively interfere with each other. Constant frequency and fixed motion of the moving mirror modulates the interference pattern. The resulting interferogram has the unique property that every data point has information about every frequency of the Raman scatter collected from the sample. The signal can be measured very quickly, making signal averaging fast and accurate. Detector reflects the interferogram signals and

feed it to the computer. It is the time domain spectrum and records the detector response changes vs. time within the mirror scan. If the sample happens to absorb the signal at this frequency, the amplitude of the sinusoidal wave is reduced by an amount proportional to the amount of sample in the beam. The interferogram contains the information over the entire Raman region to which detector is responsive. The required Raman shift is obtained after calibrating the original data with respect to the known wavenumber relationship. The plot represents the wavenumber and the relative scattering intensity in photon count.

2.4.3 Ultraviolet -visible spectroscopy

In the case of ultraviolet and visible (UV-vis/ electronic) spectroscopy, the transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels. As a molecule absorbs energy, an electron is promoted from an occupied orbital to an unoccupied orbital of greater potential energy. Generally, the most probable transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). UV-vis region of the spectrum is conventionally divided into three sub-domains termed as near UV (185-400 nm) and visible (400-700 nm). Most commercial spectrophotometers cover the spectral range of 200-900 nm (Rouessac & Rouessac 2007).
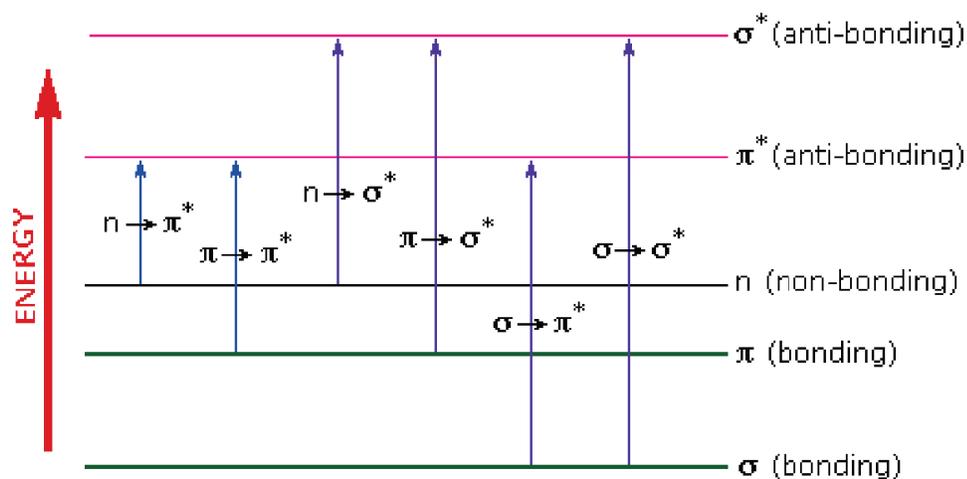
Fig. 2.5: Relative energies of electronic transition in UV-vis region

According to molecular orbital theory, the excitation of a molecule by the absorption of radiation in the UV-vis regions involves promotion of its electrons from a bonding, or non-bonding (n) orbital to an anti-bonding orbital. There are σ and π bonding orbitals associated with σ* and π* anti-bonding orbitals, respectively. Non-bonding *(n or p)* orbitals are not associated with anti-bonding orbitals because non-bonding or lone pair of electrons present in them does not form bonds. Following electronic transitions are involved in the UV-vis region (Fig. 2.5): (i) $\sigma \rightarrow \sigma$* (ii) n $\rightarrow \sigma$* (iii) $\pi \rightarrow \pi$* (iv) n $\rightarrow \pi$*

2.4.3.1 Theory of electronic spectroscopy

A UV-vis spectrophotometer records a UV or visible spectrum as a plot of wavelengths of absorbed radiations versus the intensity of absorption in terms of absorbance *A* or molar absorptivity as defined by the Lambert-Beer

law. According to Lambert's law, the fraction of incident monochromatic radiation absorbed by a homogeneous medium is independent of the intensity of the incident radiation while Beer's law states that the absorption of a monochromatic radiation by a homogeneous medium is proportional to the number of absorbing molecules. From these laws, the remaining variables give the following equation which expresses the Beer-Lambert law.

$$A = -logT = log\frac{I_0}{I}$$

Where, I_0 is the intensity of radiation, I is the intensity of radiation transmitted through the sample (Mantele & Deniz, 2017).

2.4.3.2 Ultraviolet-visible spectrophotometer

The typical ultraviolet-visible spectrophotometer consists of a light source, a monochromator, and a detector as shown in Fig. 2.6. The light source is usually a deuterium lamp, which emits electromagnetic radiation in the ultraviolet region of the spectrum. A second light source, a tungsten lamp, is used for wavelengths in the visible region of the spectrum. The monochromator is a diffraction grating; its role is to spread the beam of light into its component wavelengths. A system of slits focuses the desired wavelength on the sample cell. The light that passes through the sample cell reaches the detector, which records the intensity of the transmitted light I. The detector is generally a photomultiplier tube, although in modern instruments photodiodes are also used.
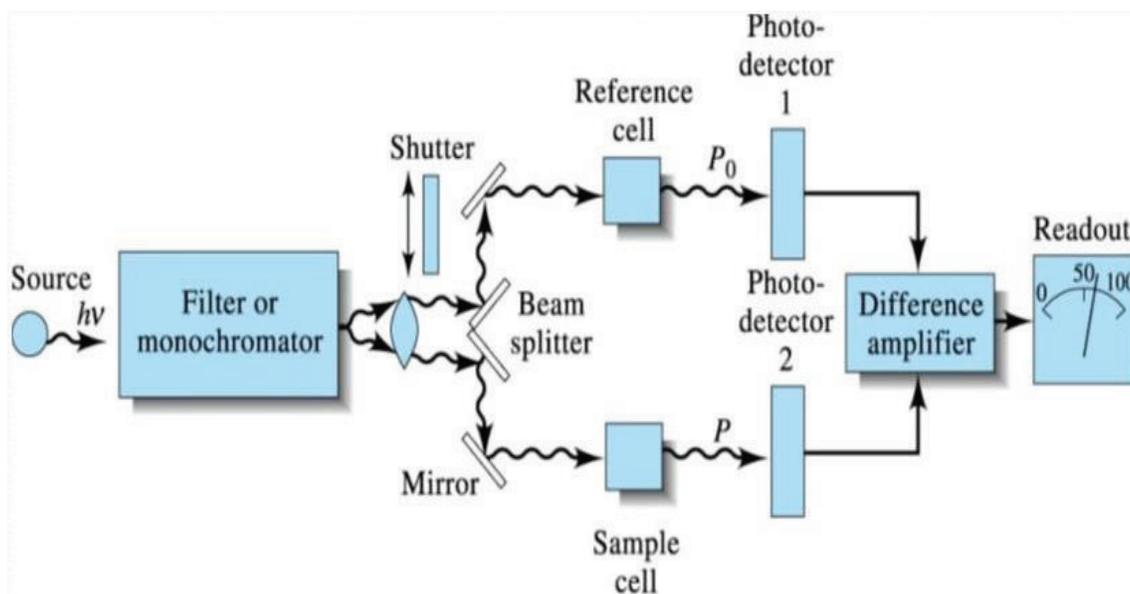
Fig. 2.6: Schematic diagram of a double-beam UV-vis spectrophotometer

In a typical double-beam instrument, the light emanating from the light source is split into two beams, the sample beam and the reference beam. When there is no sample cell in the reference beam, the detected light is taken to be equal to the intensity of light entering the sample I_0.

2.4.4 Kurtz and Perry powder SHG method

Growth of large single crystal is a slow and difficult process. Hence, it is highly desirable to have some technique of screening crystal structures to determine whether they are non-centrosymmetric or not and it is also equally important to know whether they are better than those currently known for second harmonic generation (SHG) activity. Such a preliminary test should enable us to carry out the activity without requiring oriented samples. Kurtz and Perry proposed a powder SHG method for comprehensive analysis of the second order optical non-linearity. The non-linear optical property of the

crystals grown in this work was tested by passing the output of Nd:YAG Quanta ray laser through the crystalline powder sample. The schematic of the experimental setup used for SHG studies is shown in Figure 2.7.
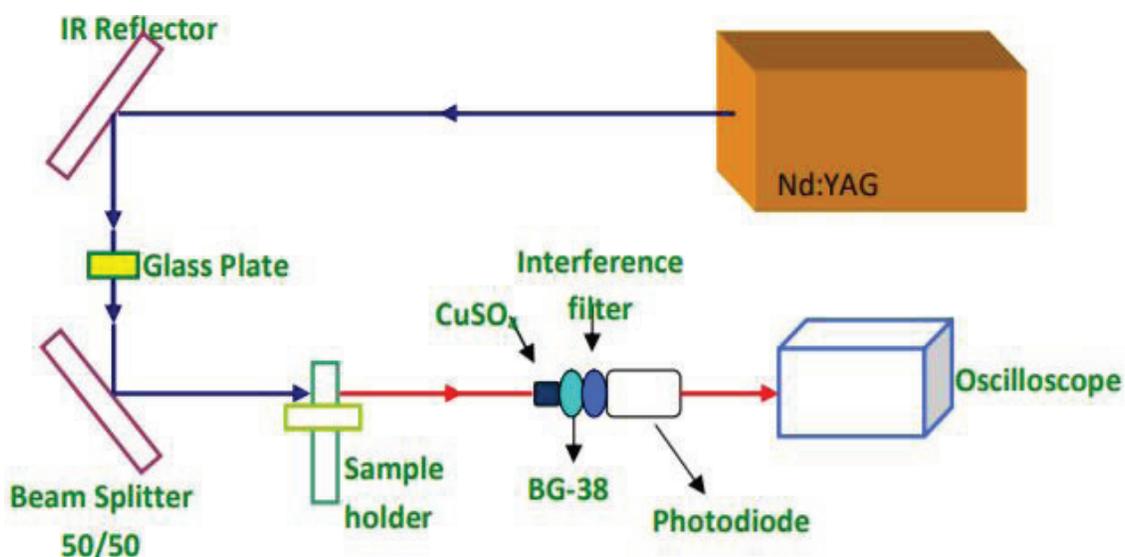

Fig. 2.7: Schematic experimental setup for SHG efficiency measurement

A Q-switched, mode locked Nd:YAG laser was used to generate about 6 mJ/pulse at the 1064 nm fundamental radiation. This laser can be operated in two modes. In the single shot mode, the laser emits a single 10 ns pulse. In the multi shot mode, the laser produces a continuous train of 10 ns pulses at a repetition rate of 10 Hz. A single shot mode of 8 ns laser pulse with a spot radius of 1mm was used. The experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 6 mJ. The input laser beam was passed through an IR reflector and then directed on to the microcrystalline powdered sample packed in a capillary tube of diameter 0.154

mm. The photodiode detector and oscilloscope assembly measure the light emitted by the sample. The SHG efficiency of the crystals was evaluated by Kurtz and Perry powder test method using the microcrystalline powder of urea/KDP as the reference material.