CHAPTER III

VARIOUS CHARACTERIZATION TOOLS APPLIED TO CHARACTERIZE THE SINGLE CRYSTALS

ABSTRACT

The studies on vibrational spectroscopy give a dynamical picture of the molecule. This has resulted in a large volume of data on the vibrations of molecules. The characterization tools employed such as IR, Raman, NLO and Optical transmission studies were dealt briefly.
3.1 INTRODUCTION

Vibrational spectroscopy gives valuable insight into the structural characteristics of molecules. It yields essential information about molecular structure, inter and intra molecular forces, crystalline environments, vibrational interactions, distortion of molecules, hydrogen bonding, isomerism and molecular rotations etc. [39-42]. It can be employed directly as molecular fingerprints to characterize and identify a molecule. The total energy of a molecule can be separated into three additive components associated with the motion of electrons in the molecule ($E_{el}$), the vibrations of the constituent atoms ($E_{vib}$), and the rotations of the molecule as a whole ($E_{rot}$).

$$E_{total} = E_{el} + E_{vib} + E_{rot}$$

...(3.1)

Vibrational spectroscopy is concerned with vibrational transitions due to absorption and emission of electromagnetic radiations. These transitions appear in the $10^2$ to $10^4$ cm$^{-1}$ region and originate from the vibrations of nuclei constituting the molecule. Vibrational transitions can be observed from infrared (IR) and Raman spectra. Infrared spectroscopy has contributed more to this field than Raman spectroscopy due to rapid developments in infrared instrumentation. With the introduction of laser as a source, Raman spectroscopy is also increasingly employed in this endeavour. The combination of powerful new computation tools and rapid growth of instrumental facilities are leading to new era in vibrational spectroscopy. The use of vibrational spectroscopy as a means of probing the structure of simple and even complex molecules has been of inestimable value in the field of
structural study of organic, inorganic, organometallic compounds, biological molecules, polymers and minerals. [43-47].

3.2 INFRARED SPECTROSCOPY

Infrared absorption spectrum arises from the absorption of infrared radiation by the molecule. The molecule undergoes a transition from a lower vibrational energy state to higher one. IR technique when coupled with intensity measurements may be used for qualitative and quantitative analysis. Currently, this technique has become more popular as compared to other physical techniques (X-ray diffraction, electron spin resonance, etc.) in the elucidation of the structure of unknown compounds.

INFRARED ACTIVITY

The following arguments lead to a general selection rule for infrared spectroscopy:

A normal mode will be active in the infrared spectrum if the permanent dipole moment of the molecule changes during a vibrational cycle. The induced dipole moment is often called the transition dipole moment. Strong infrared bands arise from normal modes that have large transition moments. Conversely, weak transitions have low values of the transition moment. If each mode has a unique frequency and a unique set of atomic displacements, then we would need to tabulate data on every molecule in order to match spectrum and structure for an unknown sample. Many molecular fragments have vibrations that occur within a relatively narrow range of frequencies. This leads to the concept of a group frequency, even
though many atoms in a molecule will move during a normal mode of vibration, most of the motion may be thought of as localized within a certain molecular fragment that will vibrate with a characteristic frequency.

**SELECTION RULE FOR IR**

According to quantum mechanics, the selection rule for the infrared spectrum is determined by the integral

\[ [\mu] v' v'' = \int \Psi_{v''}^* (Q_a) \mu \Psi_{v'} (Q_a) \, dQ_a \quad \ldots(3.2) \]

Here \( \mu \) is the dipole moment in the electronic ground state. \( \Psi \) is the vibrational eigen function, \( v' \) and \( v'' \) are the vibrational quantum numbers of the states before and after transition respectively and \( Q_a \) is the normal coordinate whose activity is to be determined. The dipole moment can be resolved into three components in the \( x, y \) and \( z \) directions as

\[ [\mu_x] v' v'' = \int \Psi_{v'} (Q_a) \mu_x \Psi_{v''} (Q_a) \, dQ_a \]

\[ [\mu_y] v' v'' = \int \Psi_{v'} (Q_a) \mu_y \Psi_{v''} (Q_a) \, dQ_a \]

\[ [\mu_z] v' v'' = \int \Psi_{v'} (Q_a) \mu_z \Psi_{v''} (Q_a) \, dQ_a \quad \ldots(3.3) \]

For the vibrations to be infrared active, at least one of the components of the derivative of the dipole moment with respect to the normal coordinate, taken at the equilibrium position should be non-zero. If all the integrals are zero, the vibration is infrared inactive [46].
3.3 RAMAN SPECTROSCOPY

Raman spectroscopy is an important method for investigating molecular vibrations. Raman spectroscopy either alone or in conjunction with infrared spectroscopy is used for identification and spectroscopic characterization of ionic and molecular species. The selection rules and relative intensities of Infrared and Raman bands are so dissimilar that Infrared and Raman spectroscopies are often viewed as complementary. Not all normal modes of vibration can be investigated by infrared spectroscopy. In many instances, vibrational modes that are not observed by infrared absorption can be studied by Raman spectroscopy. Raman scattering is a result of inelastic collisions between photons and molecules. Suppose that a photon of a given energy and wavelength collides with a sample. When energy is transferred from a molecule to the photon, light of higher energy (lower wavelength) will be scattered by the sample (anti-Stokes scattering). When energy is transferred from the photon to the molecule, light of lower energy (higher wavelength) will be scattered by the sample (Stokes scattering).

The amount of energy exchanged between molecule and photon changes the vibrational and rotational states of the molecule. For large
molecules, most of the Raman scattered light is due to changes in vibrational energy. Hence, in stokes scattering, the molecule undergoes a vibrational transition from a low vibrational state to a higher vibrational state. The opposite is true for anti stokes scattering.

![Stokes and Anti-Stokes Scattering](image)

At room temperature, most large molecules are in the \( v = 0 \) state; they do not have sufficient thermal energy to overcome the energetic barrier to the \( v = 1 \) state. For this reason, stokes scattering is more favorable than anti-stokes scattering. Also, anti stokes scattering from \( v > 1 \) states is very unlikely.

**SELECTION RULE FOR RAMAN SPECTRA**

Different molecules will react to the oscillating electric field differently: some molecules may resist charge redistribution because of strong interactions between nuclei and electrons, other molecules will not resist redistribution as much. The ability of a molecule to be distorted by an electric field is referred to as its Polarizability (\( \alpha \)). All molecules will experience an induced dipole moment oscillating at the frequency of the incoming radiation. This oscillating dipole will emit radiation at that
frequency. Phenomenologically, this amounts to Rayleigh scattering (the frequency of the outgoing beam is the same as the frequency of the incoming beam). However, in a vibrating molecule, it is possible that interactions between electrons and nuclei will change periodically. In this case, it will oscillate with a frequency that matches the vibrational frequency of the normal mode. The induced dipole moment now oscillates at a slightly different frequency, the electric field component contributes a frequency $v_{in}$ and the oscillating polarizability contributes a frequency $v'$ (the characteristic vibrational frequency of the normal mode). There are two possibilities for the frequency of the oscillating dipole, $v_{in} + v'$ and $v_{in} - v'$. Hence, light will be emitted by the molecule at three frequencies, $v_{in}$, $v_{in} + v'$, and $v_{in} - v'$. The first corresponds to Rayleigh scattering and the latter two correspond to Raman scattering. From the discussion above, the following selection rule results: A vibrational mode will be active in the Raman spectrum if it induces a change in the polarizability of the molecule. In vibrational Raman spectroscopy, transitions with $\Delta v = \pm 1$ are allowed.

The magnitude of induced dipole moment $P$ depends on the strength of the electric field $E$ of the incident radiation and the polarizability of the molecule. If the magnitude of the electric field is not too high then to a first approximation, the electric dipole transition moment $[P]$ associated with an induce transition from an initial state to the final state is given by the linear relationship.
\[ [P] \alpha E \]

\[ [P] = \alpha_{ij} E_j \]

The polarizability describes the ease with which molecular orbitals are deformed by the presence of external electric field. The polarizability of the molecule \( \alpha \) is a tensor of rank two and it consists of six components \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz} \) and \( \alpha_{xz} \). For the polarizability component \( \alpha_{ij} \) subscript \( i \) refers to the direction of induced dipole moment by the oscillating electric field component in the \( j \) direction.

If the molecule is placed in an electric field the nuclei are attracted by the negative pole of the field and the electrons are attracted the positive way. An applied electric field can induce an electric dipole moment in the molecule such an induced dipole moment oscillates with the frequency of incident radiation and acts as a second source for electromagnetic radiation.

The nine polarizability components may be written in an ordered array as follows

\[
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\]

This constitutes a representation of the tensor \( \alpha \). For a real symmetric polarizability tensor \( \alpha_{ij} = \alpha_{ji} \) i.e., \( \alpha_{xy} = \alpha_{yx}, \alpha_{xz} = \alpha_{zx}, \alpha_{yz} = \alpha_{zy} \), the tensor has only six distinct real components.
3.4 SPECTRA OF SOLIDS

The spectrum of a material exhibits the following characteristics when the material undergoes gaseous or liquid state to solid state

❖ Small shifts in the position of bands.

❖ Splitting of some of the bands into multiples.

❖ Appearance of entirely new bands in the low frequency region.

The vibrational spectra of solids do not exhibit fine structure due to molecular rotation, since free rotation is absent in most crystalline solids. The spectral changes observed for the solid in general may arise from

❖ the presence of an electrostatic field around the molecule in the crystal.

❖ the lowering of the symmetry of an isolated molecule due to the environment in the crystal.

❖ the coupling between vibrations of different molecules in the unit cell.

Electrostatic interaction between molecules is important in ionic crystals while hydrogen bonding and Vander Waals forces may be dominant in organic and molecular crystals. The intermolecular interactions in crystal can act only as small perturbations on the internal force field causing the observed shifts in the frequencies and also the band splitting. A study of spectra of molecular crystals provides an understanding of the weak intermolecular forces. Information on the barriers hindering free rotation of the groups in the solid states could also be obtained.
INTERMOLECULAR FORCES IN SOLIDS

In the solid state the interaction of the molecule with the environment causes changes in the spectrum. Intermolecular forces determine the molecular packing in crystals. Magnitude of the intermolecular interaction can usually be related to the magnitude of the gas to crystal shift of the bands and the magnitude of the splitting of the bands. Infrared and Raman besides other spectroscopic techniques have been used to probe intermolecular forces in solids.

3.5 INSTRUMENTATION FOR NLO

The Kurtz and Perry powder SHG method [48] is used to measure the NLO efficiency of the materials and thus it is a valuable tool for initial screening of NLO materials. The experimental setup is shown in Fig. 3.1. The crystal was ground into powder and it was packed densely between 2 transparent glass slides. An Nd: YAG (DCR 11) laser was used as a light source. A fundamental laser beam of 1064 nm wavelength, 8ns pulse in depth with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter and it is 5.7 mJ/pulse. The transmitted fundamental wave was passed over a monochromator (Czerny turney monochromator), which separates 532 nm (SHG signal) from 1064 nm and absorbed by a CuSO₄ solution. F1 that removes the 1064 nm light. F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4nm and central wavelength 532 nm. The green light was detected by a photo multiplier tube (Hamamatsu RC 109, a visible PMT) and displayed on a
storage oscilloscope (TDS 3052 B 500 MHz phosphor digital oscilloscope). KDP crystal was powdered to the identical size and was used as reference materials in the SHG measurement.

![Schematic setup of SHG](image)

**Fig. 3.1 Schematic setup of SHG**

All of these applications rely on the manifestation of the molecular hyperpolarizability of the materials. The variety of applications has led to the invention new non-linear optical materials [49].

### 3.6 UV-VISIBLE SPECTRAL ANALYSIS

To perform multi various tasks, there are hundred of spectrometers available in the UV-Visible range from simple, inexpensive to complex and costly. Commercial instruments (UV-Visible range) designed to perform complicated tasks, which cannot be done with simpler ones has been discussed in the cited references [50,51].
A schematic diagram of a simple typical spectrometer is shown in the Fig. 3.2. The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as $I$. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. In recording the solid UV spectrum for the sample, the instrument used for taking liquid samples can also be used simply by changing the sample holder. Here the powder sample is powdered well and then a drop of liquid paraffin is added and made into a paste. This paste is smeared on a Whatman filter paper and the spectra are recorded. A blank filter paper which is cut to the same size as the sample paper is kept on the reference side. Otherwise it is left as such and the baseline correction is done with AIR as reference.
If the sample compound does not absorb light of a given wavelength, \( I = I_0 \). However, if the sample compound absorbs light then \( I \) is less than \( I_0 \), and this difference may be plotted on a graph versus wavelength, as shown on the right. Absorption may be presented as transmittance (\( T = I/I_0 \)) or absorbance (\( A = \log I_0/I \)). If no absorption has occurred, \( T = 1.0 \) and \( A = 0 \). Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as \( \lambda_{\text{max}} \).