CHAPTER-II

Experimental and Theoretical Methods

2.1 Vibrational Spectroscopy

Vibrational spectroscopy is a technique used to analyze the structure of molecules by examining the interaction between electromagnetic radiation and nuclear vibrations in molecules. It serves as a front line tool for the study of atomic and molecular structure and is used in the analysis of a wide range of samples. A vibrating molecule interacts with electromagnetic radiation of suitable frequency and when the frequency matches with one of the normal modes of vibration, the molecule may either absorb or emit the radiation. Using vibrational spectroscopic methods it is possible to measure exactly which wavelengths of light are absorbed by a molecule. The two types of vibrational spectroscopic methods are infrared (IR) spectroscopy and Raman spectroscopy. Both IR and Raman produce a spectrum which reflects the vibrational modes of the sample, and is therefore, characteristic of its molecular structure. Thus vibrational spectroscopy is a valuable tool for the elucidation of molecular structure and hence can be utilized as molecular “finger prints” to characterize and identify the molecule. It also provides important information about the intramolecular forces acting between the atoms in a molecule, and the nature of the chemical bond [68]. The studies on vibrational spectroscopy have resulted in a large volume of data on the vibrations of polyatomic molecules.

2.1.1 Vibrations of Polyatomic Molecules

A molecule of \( n \) atoms has \( 3n \) degrees of freedom corresponding to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, out of the \( 3n \) degrees of freedom, three degrees correspond to rotation and another three to translation. Hence a nonlinear molecule of \( n \) atoms has \( 3n-6 \) degrees of freedom.
These 3n-6 vibrations are called fundamental vibrations or vibrational degrees of freedom. A normal vibration is a molecular vibration in which all the atoms move in phase and with the same frequency. In a linear molecule, only two degrees of freedom are required to describe rotation. Hence a linear molecule has 3n-5 degrees of freedom [69]. The fundamental vibrations are of two types namely external and internal vibrations. The external vibrations include rotational and translational vibrations whereas the internal vibrations include stretching and bending or deformation. In addition to the fundamentals there are also secondary vibrations called overtones and the additional vibrations arise from the interactions between fundamentals and overtones.

2.1.2 Vibrational Assignment and the Concept of Group Frequency

The normal vibrations of a molecule are associated with the appropriate Raman and Infrared frequencies. The applications of infrared and Raman spectroscopy rely largely on the correct assignment of the spectra. The assignment of the infrared and Raman spectra is made on the basis of the group frequency concept. The presence of certain groups such as C-H, N-H, C=O, C=N etc., in various molecules may be linked with the constant occurrence of absorption bands in the infrared spectra whose positions are only slightly altered on going from one compound to another [70].

In a molecule, the atomic group vibrates independent of other groups and has its own frequency. These frequencies are called characteristic group frequencies. They appear in fairly constant regions in the spectrum. The approximate constancy of the position of group frequencies form the basis for the structural analysis of compounds. Chemical groups have characteristic frequencies and are affected by the molecular environment of the group only to a slight extent [70]. This is the main hypothesis of
group frequency and can be used as an aid for the interpretation of the vibrational spectra.

2.1.3 Factors Affecting Vibrational Frequencies

There are a number of factors that shift the vibrational frequencies from their expected values to a different value. Each molecular group is influenced by the structure of the molecule or different electronic environments [71]. In a molecule, vibrational frequencies are shifted from their normal values due to the electronic and steric effects of other groups present in it. Some of the important factors, which affect the vibrational frequencies of bonds, are discussed below.

2.1.3.1 Fermi Resonance

Interactions taking place between fundamental vibration and overtones or combination tones are known as Fermi resonance. The Fermi resonance effect usually leads to two bands appearing close together out of which only one is expected. When an overtone or a combination band has the same frequency as, or a similar frequency to, a fundamental, two bands appear, split either side of the expected value and are of about equal intensity [72]. This is due to the perturbation of two nearly identical energy levels with one another. The condition for Fermi resonance to occur is that the overtone and the fundamental must belong to the same symmetry species [73].

2.1.3.2 Hydrogen Bonding

Hydrogen bonding is defined as the attraction that occurs between a highly electronegative atom carrying a non-bonded electron pair (such as fluorine, oxygen or nitrogen) (donor) and a hydrogen atom, itself bonded to a small highly electronegative atom (acceptor). Formation of the hydrogen bond lowers the stretching frequencies of both the groups involved in it. Also it changes the shape and intensity of the absorption bands. The stronger the hydrogen bond, the lower is the O-H stretching
frequency. Thus the value of O-H stretching frequency is a test for hydrogen bonding as well as a measure of the strength of hydrogen bonds [74]. Hydrogen bonds can occur within one single molecule, between two like molecules, or between two unlike molecules. Hydrogen bonds are of two types, intermolecular and intramolecular.

Intramolecular hydrogen bonds are those which occur within one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. For this to happen, both a hydrogen donor and an acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. Intermolecular hydrogen bonds occur between separate molecules in a substance [75]. They can occur between any numbers of like or unlike molecules as long as hydrogen donors and acceptors are present in positions in which they can interact.

2.1.3.3 Coupled Interactions

The energy of a vibration and thus the wavelength of its absorption peak may be influenced by other vibrations in the molecule. Some important factors [76] which influence the extend of coupling are:

i. When vibrations are of the same symmetry species.

ii. When the vibrations have a common atom, strong coupling between stretching vibrations occur.

iii. When a common bond is present between the vibrating groups, interactions between the bending vibrations occur.

iv. Coupling between a stretching and a bending vibration can occur if stretching bond forms one side of the angle that varies in the bending vibrations.
v. When the coupled groups have approximately equal individual energies the interaction is greatest.

vi. If groups are separated by two or more bonds, little or no interaction occurs.

### 2.1.3.4 Electronic Effects

In the case of carbonyl compounds of the formula RCOX, the nature of the substituent group X influence the frequency of C=O stretching by inductive effects. This is due to the different electro negativities of the carbonyl carbon and of the substituents like X. It involves the electrons in the sigma bonds. Electron withdrawing groups such as chloro and nitro suppress the polar contribution with an effective increase in the double bond character. Thus it leads to an increase in the force constant of the C=O bond. In other words, the inductive effect reduces the length of the C=O bond and thus increases its force constant and consequently the frequency of absorption. Various electronic effects such as Hybridization, Backdonation, Induction, and Hyperconjugation influence the C-H stretching intensities. The decrease in C-H stretching intensity occurs due to different hybridization from sp$^3$ to sp$^2$ and the carbon atom acquires stronger electro negativity which makes the hydrogen atom more positive. In the backdonation effect the electronic charge is backdonated from the lone pair (s) of electronegative atom such as oxygen or nitrogen atom, of the molecule to the $\sigma^*$ orbital of a C-H bond and it results in the increase of IR band intensities. When an electronegative atom is present in the molecule induction occurs. This effect results in the decrease of C-H stretching intensity and hence the vibrational wavenumber is increased. Backdonation and induction is caused by the presence of oxygen or nitrogen atom adjacent to CH$_3$ group. This effect can enhance the IR band intensities and reduce the C-H stretching wavenumbers.
Hyperconjugation decreases the C-H stretching intensity because of the interaction of the orbital of a methyl group with the π orbital of an aromatic ring system [77].

2.2 Experimental Techniques

2.2.1 Infrared Spectroscopy

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. Infrared radiation is the part of electromagnetic spectrum, between the visible and microwave regions. When the infrared radiation falls on the molecules of a chemical substance, the molecule undergoes a transition from a lower vibrational energy state to a higher one. The selection rules determine whether the absorption of radiation by the molecules can take place or not. After absorption of IR radiations, the molecules of the chemical substance vibrate and gives rise to absorption bands called IR absorption spectrum [78]. Many bands corresponding to the characteristics functional groups and bonds in the chemical substance will be present in the spectrum. Thus by using infrared spectroscopy it is possible to identify a chemical substance and it also gives useful information about the structure of molecule quickly.

The IR region is generally divided into three regions:

Near IR (12,500- 4000 cm\(^{-1}\))
Middle IR (4000-400 cm\(^{-1}\))
Far IR (400-50 cm\(^{-1}\)).

The far-infrared region which lies adjacent to the microwave region has low energy and may be used for rotational spectroscopy. The mid-infrared region is used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy region near IR region can excite overtone or harmonic vibrations [79].
2.2.1.1 Infrared Activity

A molecule has a center of positive charge and a center of negative charge. If these two centers are separated by a distance \( l \), the dipole moment \( \mu \) is defined as:

\[
\mu = e l
\]  
(2.1)

Where ‘\( e \)’ represents the amount of electrical charge at the charge center of the molecule.

The fundamental requirement for infrared activity is that there must be a net change in dipole moment during the vibration for the molecule or the functional group. \( i.e. \) the electronic charge distribution from one side of the bond to the other must occur [78].

Mathematically, the requirement of infrared activity is expressed that the derivative of dipole moment with respective to the vibration at the equilibrium position is not zero.

\[ i.e. \quad \left( \frac{\partial \mu}{\partial q} \right)_{q=0} \neq 0 \]  
(2.2)

where, \( \partial \mu \)=change in dipole moment and \( \partial q \)=change in the magnitude of normal vibration.

Also for infrared absorption, the energy of the infrared light must be equal to a vibration energy level difference in the molecule.

\[ i.e. \quad \Delta E = h \nu \]  
(2.3)

where,

\( \Delta E \)= vibration energy level difference in a molecule

\( \nu \)= wave number in cm

\( h \)=Planck’s constant
2.2.1.2 Infrared Instrumentation

The instrument that is used to determine the absorption spectrum for a compound is known as the infrared spectrometer. It determines the positions and relative sizes of all the absorptions or peaks in the infrared region and plots them. This plot of absorption intensity versus wavenumber is referred to as the infrared spectrum of the compound. Two types of infrared spectrometers are available and they are Dispersive and Fourier Transform (FT) instruments. Both of them can provide spectra of compounds in the common range of 4000-400 cm\(^{-1}\). But FT-IR spectrometers have advantage over the dispersive one as they provide the infrared spectrum much more rapidly than the dispersive instruments [80].

2.2.1.2.1 Fourier- Transform Infrared Spectrometer

Fourier-transform Infrared (FT-IR) Spectroscopy is the most widely used vibrational spectroscopic technique. In FT-IR spectroscopy the Fourier transform method is used to obtain an infrared spectrum in a whole range of wavenumbers simultaneously. It is based on the idea of the interference of radiation between two beams to yield an interferogram. A plot of light interference intensity as a function of optical path difference is called an interferogram. The interferogram is a complex signal and its wave-like pattern contains all the frequencies. A mathematical operation known as Fourier transform can separate the individual absorption frequencies from the interferogram and produces a spectrum. This type of instrument is known as a Fourier Transform infrared spectrometer. The Fourier transform is based on the fact that any mathematical function can be expressed as a sum of sinusoidal waves. The sum of sinusoidal waves includes all the information of wave intensity as a function of wavelength. The Fourier Transform (FT) transfers information of a function in the time (t) domain to its corresponding frequency (\(\omega\)) domain [81].
In an FT-IR instrument, using the Fourier transform operation, the intensity versus optical path difference is converted to the intensity versus wavenumber. The optical path difference can be considered to be in the time domain because it is obtained by multiplying time with the speed of a moving mirror. The wavenumber can be considered in the frequency domain because it is equal to frequency divided by the light speed.

The advantage of an FT-IR instrument is that it acquires the interferogram in less than a second [80]. Hence it is possible to collect dozens of interferograms of the sample and accumulate them in the memory of a computer. An FT-IR instrument has greater speed and greater sensitivity than a dispersive instrument. The schematic diagram of an FT-IR spectrometer is shown in Fig. 2.1.
The basic components of an FT-IR spectrometer are:

2.2.1.2.1.1 Michelson Interferometer

The heart of the optical hardware in a FT spectrometer is the interferometer. The most common interferometer used in infrared spectrometers is a Michelson interferometer and its schematic illustration is given in Fig. 2.2.

![Optical diagram of a Michelson Interferometer](image)

**Fig. 2.2 Optical diagram of a Michelson Interferometer**

It consists of two mutually perpendicular plane mirrors, a fixed mirror and a movable mirror. The beamsplitter, which is a semi-reflecting mirror, bisects the planes of these two mirrors. If a collimated beam of monochromatic radiation of wavelength ($\lambda$) emitted by a source is passed into an ideal beam splitter, it transmits half of the infrared (IR) beam and reflects the other half. The transmitted and reflected beam strike the fixed mirror and the moving mirror, respectively. The two beams are reflected from these mirrors and returns to the beamsplitter. At the beamsplitter, they recombine and interfere. The moving mirror changes the optical path lengths in order to generate light interference between the two split beams. If the moving mirror is located at the same distance from the beam splitter as the fixed mirror, the optical paths of the two split beams are the same. Hence path difference is zero. An optical
path difference ($\delta$) will be introduced by translating the moving mirror away from the beam-splitter [72]. The two split beams will show constructive and destructive interference periodically, with continuous change of $\delta$ value. There will be completely constructive interference when $\delta = n\lambda$, but completely destructive interference when $\delta = n + \frac{1}{2}\lambda$.

2.2.1.2 Sources and Detectors

For the mid-infrared region, FTIR spectrometers use a Globar or Nernst source. The Nernst source is composed of mainly oxides of rare-earth elements and the Globar is composed of silicon carbide. If the far-infrared region is to be examined, then a high-pressure mercury lamp has to be used. Tungsten–halogen lamps are used as sources for the near infrared region [80].

The infrared detector is a device used to measure the energy of infrared light from the sample being examined. It functions as a transducer to convert infrared light signals to electric signals. There are two commonly used detectors employed for the mid-infrared region. One is a pyroelectric device incorporating deuterium tryglycine sulfate (DTGS) in a temperature-resistant alkali halide window and another is the mercury cadmium telluride (MCT). In the far-infrared region, germanium or indium–antimony detectors are used that operates at liquid helium temperatures. For the near-infrared region, the detectors used are generally lead sulfide photoconductors [80].

2.2.1.2.3 Beam Splitter

Beam-splitters should be made of a material which is semi-transparent to infrared light. The function of the beam-splitters is to reflect one half portion of infrared light to the moving mirror while transmitting the rest infrared to a fixed mirror. The most common beam-splitter is a sandwich structure, with a thin layer of
germanium (Ge) between two pieces of potassium bromide (KBr). It works well in the wavenumber range 4000-400 cm\(^{-1}\). Ge is able to split infrared light and KBr is a good substrate material because it is transparent to infrared light, yet has good mechanical strength. It functions as a protective coating for the Ge. The drawback of KBr is that it tends to absorb water vapor from the atmosphere and fog is readily formed. Thus, all FT-IR instruments require low humidity or are sealed from atmosphere. The low humidity environment around the beam-splitter can be obtained by purging with dry air or nitrogen. More conveniently, the instrument is sealed such that the infrared beam passes through a window to reach the sample [80].

2.2.1.2.1.4 Computer

The computer performs a number of functions such as setting the scan speeds and scanning limits, and starting and stopping scanning. When the spectrum is scanned, it reads the spectra into the computer memory from the instrument. By using the computer one can add and subtract spectra or can expand areas of the spectrum of interest. The computer is also used to scan the spectra continuously and average or add the result in the computer memory. The computer is also used to plot the spectra [80].

2.2.1.2.2 Fourier Transform Infrared Spectra

An infrared spectrum converted from an interferogram by Fourier transform is called a single beam spectrum. A single beam spectrum includes both spectra from the sample and background. The background spectrum contains only the information from the instrument and atmosphere, not from the sample being examined. The instrument contributions to background spectrum are from the detector, beam-splitter, mirror and the IR source. The atmospheric contributions are mainly from water vapor and carbon dioxide. To eliminate the background influence, the ratio of the single
beam spectrum of a sample with the background spectrum should be made. This process results in a transmittance spectrum [78]. Transmittance (T) is defined as the ratio of intensities.

$$T = \frac{I}{I_0}$$  \hspace{1cm} (2.5)

Where I is the intensity measured in a single beam spectrum of sample and I₀ is the intensity measured in the background spectrum. The spectrum can also be presented as absorbance (A) versus wavenumber. From the transmittance, the absorbance can be calculated as [78],

$$A = -\log T = \log \frac{I_0}{I}$$  \hspace{1cm} (2.6)

Hence an FT-IR spectrum can be expressed either as a transmittance spectrum or as an absorbance spectrum.

### 2.2.1.2.3 Sample Preparation

For recording an IR spectrum, the sample can be in any state i.e, gas, liquid, solid or a solution of any of these. For the preparation of solid samples, commonly the KBr pellet and mull methods are used. In the KBr pellet method the powder sample is mixed with powdered KBr and the mixture is pressed under high pressure. Under pressure, the KBr melts and seals the compound into a matrix. The resultant KBr pellet is then mounted on holder and is placed in sample beam of IR spectrophotometer. In the Mull technique, a mull of the substance is prepared by grinding it into a fine powder and dispersing it in the mulling agent usually nujol. The mull is placed between two sodium chloride plates and these plates are subjected to IR beam. The mull method is simple and inexpensive. But the mulling agent contains long and straight chains of hydrocarbons, which absorb strongly around 3000 and 1400 cm⁻¹. Hence it may complicate the sample spectrum [82].
The liquid sample is prepared by making a capillary thin film of the liquid. The capillary thin film is made by placing a drop of liquid on a KBr plate and sandwiching it with another KBr plate. This method is not suitable for volatile liquids. For volatile liquid and toxic liquid samples, liquid cells can be used. The cell is made of an infrared-transparent material like KBr and since KBr is hygroscopic in nature, for holding samples containing water, ZeSe or AgCl can be used. They are infrared transparent but not water soluble. Cells for gas samples are structurally similar to cells for liquid but the dimension is much larger [78].

2.2.2 Raman Spectroscopy

Raman spectroscopy is an important method for investigating molecular vibrations. When electromagnetic radiation strikes on a molecule, photons will be scattered by the molecules both elastically and inelastically. In elastic scattering, called Rayleigh scattering the scattered photon has the same frequency as that of the radiation. But the inelastically scattered photons have frequencies lower and higher than the incident frequency. This phenomenon is referred to as Raman scattering [83]. The elastic and inelastic scattering can be understood in terms of energy transfer between photons and molecules. The scattered photons have frequency shifts characteristic of the vibrational or rotational energies of the molecule. These weak lines of modified frequencies are referred to as the Raman spectrum [84].

2.2.2.1 Quantum Theory of Raman Scattering

According to quantum theory, the scattering is due to the collision between the light photon and the molecule. When a photon of the incident light beam collides with the molecule, the molecule will be excited to the virtual state whose height is equal to the energy of the incident radiation. In this state the molecule remains for a very short mean life time. Hence according to Heisenberg uncertainty
principle, the uncertainty in energy is large. The virtual state then radiates light in all
directions except along the direction of the incident light. When returning to the
ground electronic state, a quantum of vibrational energy may remain with the
scattering species. In this case the frequency of the scattered radiation decreases and
thus gives rise to Stokes line. If a molecule is in an excited vibrational state and is
raised to the virtual state by interacting with the incident radiation it may return to the
ground electronic and vibrational state on scattering a photon. Then the energy of the
scattered photon is equal to the sum of the energy of the incident photon and the
energy difference between excited and ground vibrational levels. In this case the
frequency of the scattered radiation is greater than that of the incident radiation and
gives rise to anti-stokes lines. When a molecule in the ground state interacts with a
photon and goes to the virtual state, it may leave the unstable electronic state and then
it returns to the ground vibrational level in the ground electronic state. In this case the
scattered photon has the same frequency as the incident radiation which results to
Rayleigh scattering [85]. The quantized energy differences correspond to the
difference in the vibrational energy levels of the molecule. Thus the incident radiation
perturbs the system and induces transitions between energy levels. A schematic
energy level diagram showing Rayleigh and Raman lines are shown in Fig. 2.3.
2.2.2.2 Fourier Transform Raman (FT-Raman) Spectrometer

The spectrometer which provides maximum Raman collection efficiency is known as Fourier Transform Raman (FT-Raman) spectrometer. An FT instrument records the spectrum in a shorter time. The advantage of FT-Raman spectroscopy is the accuracy of the wavenumber values in a spectrum. A Fourier Transform Raman (FT-Raman) spectrometer consists of a laser, one or more filters, an interferometer and a highly sensitive detector. The FT-Raman spectrometer uses a NIR laser for sample excitation, usually Nd$^{3+}$:YAG which emit at 1064 nm [86]. The laser radiation is filtered and is focused to the sample. Light is reflected and scattered off the sample which is in a direction that is the reverse of illumination and is filtered using the filters to remove the Rayleigh scattered light. Only the Raman scattered light is allowed to pass. In the Fourier transformation step, the noise associated with the intense Rayleigh scattering is distributed over the entire spectrum and degrades the desired Raman spectrum. Then the latter passes through the interferometer. The interferogram is collected and detected by the detector. The germanium photoresistor operating at the liquid nitrogen temperature or indium doped gallium arsenide photodetector
operating at room temperature is employed. The detector signal is digitized and Fourier transformed by an FT program to produce the spectrum. The spectrum is recorded as intensity of scattering versus frequency shift using software. A Fourier transform Raman spectrometer is shown in Fig. 2.4.

Fig. 2.4 Schematic Diagram of a Fourier Transform Raman Spectrometer

2.2.2.3 Sample Preparation

One of the advantages of Raman spectroscopy is that it can be used for a wide variety of sizes and forms of the sample. Samples in gas, liquid and solid states can be examined easily and should be dust free [85].

For recording the Raman spectra of gases, cells having larger path length are required. The gas is filled in a glass or silica tube of 1 to 2 cm diameter. To record the Raman spectrum of a liquid, about 0.3 ml of the liquid is required. The sample could be taken in glass capillaries as glass is transparent in Raman. The spectra can be measured directly from the reaction vessel and since water is a poor Raman scatterer, it can be used as a solvent for recording the Raman spectra [85].
The Raman spectra of solids as polycrystalline material or as single crystals can be recorded. The Raman spectrum of a polycrystalline sample can be recorded by taking the finely powdered sample in a capillary tube. The crystal can be mounted in a goniometer on a glass or silica fibre. The spectrum is measured for different orientations of the crystal [85]. In the case of single crystals, when polarized light is used as incident radiation, the Raman spectrum varies depending on the direction of the crystal axis. Raman spectra can also be recorded for different temperatures and pressures.

### 2.2.2.4 Raman Activity

When a molecule is placed in an electric field, the positively charged nuclei are attracted towards the negative pole of the field and its electrons are attracted towards the positive pole of the field and hence an induced dipole is generated. Polarizability ($\alpha$) is a measure of the capability of inducing a dipole moment ($\mu$) by an electric field and is given by:

$$\mu = \alpha E$$  \hspace{1cm} (2.7)

Where ‘$E$’ is the strength of electric field.

If this polarizability in the molecule is changed during the normal vibration, then the vibration is Raman active [87]. Mathematically, Raman activity requires that the first derivative of polarizability with respect to vibration at the equilibrium position is not zero.

$$i.e. \left( \frac{\partial \alpha}{\partial q} \right)_{q=0} \neq 0$$  \hspace{1cm} (2.8)

is said to be Raman active.

Where $\partial \alpha =$ Change in molecular polarizability $\alpha$

$\partial q =$ Change in the magnitude of normal vibration
2.2.3 Ultraviolet-visible (UV-vis) Spectroscopy

UV-visible spectroscopic studies deals with the changes in electronic energy levels within the molecule arising due to the transfer of electrons from $\pi$ or non-bonding orbitals. It provides the knowledge about $\pi$-electron systems, aromatic compounds etc. UV-vis spectroscopy is used to measure the multiple bond or aromatic conjugation within molecules. It is based on the selective absorption of electromagnetic radiation in the 200-800 nm wavelength range. On passing electromagnetic radiation in the ultraviolet and visible regions through a compound with multiple bonds, a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the compound. Thus the electrons are promoted from the ground state orbital to higher energy, excited state orbitals or anti-bonding type orbitals. Since the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule, it is called as electronic spectroscopy [88].

Generally, there are two bonding type molecular orbitals, MO ($\sigma$ and $\pi$), one non-bonding (n) type lone pair MO and two anti-bonding type MO ($\sigma^*$ and $\pi^*$). For most molecules, the lowest-energy occupied molecular orbitals are $\sigma$ orbitals, which correspond to $\sigma$ bonds. The $\pi$ orbitals lie at relatively higher energy levels than $\sigma$ orbitals and the non-bonding orbital that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals ($\pi^*$ and $\sigma^*$) are orbitals of highest energy. A transition in which a bonding s electron is excited to an antibonding $\sigma$ orbital is referred to as $\sigma$ to $\sigma^*$ transition. $\pi$ to $\pi^*$ represents the transition of one electron of a lone pair (non-bonding electron pair) to an antibonding $\pi$ orbital [89]. Thus by the absorption of ultraviolet and visible light there occurs the electronic transitions such as $\sigma$ to $\sigma^*$, n to $\sigma^*$, n to $\pi^*$ and $\pi$ to $\pi^*$. 
Organic molecules with conjugated double bonds, carbonyl groups, carboxyl groups, and nitro groups are the best absorbers in the UV-vis range. Each functional group has a wavelength associated with an absorption maximum that can be used for qualitative identification in an unknown sample.

2.2.3.1 Principles of Absorption Spectroscopy: Beer’s and Lambert’s Law

If the number of molecules that absorb light of a given wavelength is greater, then the extent of light absorption and the peak intensity in the absorption spectrum will be higher. If the number of molecules that absorb radiation is less, the total absorption of energy and intensity of peak is lowered. This makes the basis of Beer-Lambert Law and it states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path [82].

When radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

\[ \log \frac{I_o}{I} = \varepsilon c l \]  \hspace{1cm} (2.9)

Where \( I_o \) = Intensity of the incident light
\( I \) = Intensity of the transmitted light
\( c \) = concentration of the solute in \( \text{mol l}^{-1} \)
\( l \) = path length of the sample in cm
\( \varepsilon \) = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation.

The ratio \( I / I_o \) is known as transmittance \( T \) and the logarithm of the inverse ratio \( I_o / I \) is known as the absorbance \( A \) [82].

\[ \text{i.e.} \quad \log \frac{I_o}{I} = A = \varepsilon c l \]  \hspace{1cm} (2.10)

Hence the Beer-Lambert law can be written as,
The UV-Vis spectra are usually measured in very dilute solutions and the most important criterion in the choice of solvent is that the solvent must be transparent within the wavelength range being examined. Highly pure, non-polar solvents such as saturated hydrocarbons do not interact with solute molecules either in the ground or excited state and the absorption spectrum of a compound in these solvents is similar to the one in a pure gaseous state. However, polar solvents such as water, alcohols etc. may stabilize or destabilize the molecular orbitals of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent. In the case of $\pi \rightarrow \pi^*$ transitions, the excited states are more polar than the ground state and the dipole-dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of $\pi \rightarrow \pi^*$ transition. In case of $n \rightarrow \pi^*$ transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states [82]. Therefore, in polar solvents the energies of electronic transitions are increased.

2.2.3.2 UV-visible Spectrophotometer

Spectrophotometer is a device used to measure the transmittance or absorbance as a function of the wavelength of light. The schematic diagram of an UV-visible spectrometer is shown in Fig. 2.5. The basic parts of a spectrophotometer are radiation source, filter, sample and reference cells, monochromator and one or more detectors.
2.2.3.2.1 Radiation Source

The radiation sources used often are Deuterium arc lamp, Hydrogen lamp, Xenon discharge lamp, Mercury arc lamp, Tungsten lamp, Mercury vapour lamp and Carbonone lamp. While selecting the radiation source, it is important that the power of the source does not change abruptly over its wavelength range. Also they should have a stable, high intensity output that covers a wide range of wavelengths [90].

![Schematic Diagram of UV-visible Spectrophotometer](image)

**Fig. 2.5 Schematic Diagram of UV-visible Spectrophotometer**

2.2.3.2.2 Filter

It is used to provide a narrow band of radiation. It may be glass filters, organic dye filters, interference filters or Fabry perot etalons [90].

2.2.3.2.3 Monochromator

The monochromator contains an entrance slit, a dispersion device, a collimating lens such as a prism or grating, a focusing lens and an exit slit. The entrance slit allows the polychromatic radiation from the source to enter in to the monochromator. The beam is collimated and strikes the dispersing device at an angle and splits into component wavelengths. Through the exit slit, radiation of a particular
wavelength leaves the monochromator. This can be done by moving the dispersing device or the exit slit. Further this light is split into two beams before it reaches the sample [90].

2.2.3.2.4 Sample and Reference Cells

One of the two divided beams is passed through the sample solution and the other is passed through the reference solution. The sample and reference solution are contained in cells. The cells should be transparent to the wavelength region which is to be recorded. Usually the cells made up of silica or quartz is used. Glass cannot be used for the cells as it absorbs light in the UV region [90].

2.2.3.2.5 Detectors

The detector converts the electromagnetic radiation into alternating current. A good detector should have high spectral sensitivity, good wavelength response, fast response time and high signal to noise ratio. The commonly used detectors are Photodiodes, Charged Coupled Device (CCD) and Photomultiplier tubes [91]. The sample and reference beam are measured using two detectors, which are photodiodes. One of the detectors receives beam from sample cell and the second detector receives beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the detectors. Since this current is of low intensity it is amplified using an amplifier. A computer connected to it stores all the data generated and produces the spectrum of the desired compound [92].

The UV-visible spectrum is a plot of absorbance (A) versus wavelength (\(\lambda\)). The wavelength at which the sample absorbs the maximum amount of light is known as \(\lambda_{\text{max}}\) [92].
2.2.4 Second Harmonic Generation (SHG)

Second Harmonic Generation (SHG) is a nonlinear optical process, in which photons with the same frequency interacting with a nonlinear material are effectively combined to generate new photons with twice the energy, and therefore twice the frequency of the initial photons. SHG was demonstrated after the invention of laser. With the application of an electric field of frequency $\omega$ the dipoles are oscillated and it radiates electric field of $2\omega$ as well as $\omega$. SHG is only allowed in mediums without inversion symmetry. It is a special case of sum frequency generation. In centrosymmetric materials, SHG cannot be demonstrated, because of the inversion symmetries in polarization and electric field [93]. The schematic representation of Second harmonic generation is described in Fig. 2.6.

![Fig. 2.6 Schematic Diagram of Second Harmonic Generation](image)

Here a single pump wave having fundamental frequency $\omega$ is incident on a nonlinear medium and produces a wave at second harmonic frequency.

2.2.5 Thermal Analysis (TA)

Thermal analysis is a group of techniques in which a physical property of a substance is measured as a function of temperature [78]. The most commonly used thermal analysis techniques are the Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).
Thermogravimetry (TG) is mainly used to examine the decomposition of materials by examining mass change with temperature. Here, the sample is analyzed under a designed temperature profile. The temperature profile may take several forms such as a constant heating rate, a modulated heating rate or an isothermal profile. The measurements are displayed as thermal analysis curves. TA results can be significantly affected by experimental parameters such as sample dimension, mass, heating (or cooling) rates and atmosphere surrounding the sample. Hence in order to ensure reliable TA data, the sample dimension and mass should be small. For most TA techniques, powdered samples with mass less than 10 mg are preferred. In such a sample heat transfer between the sample and atmosphere will be faster. Hence during analysis the thermal equilibrium is more likely to be achieved between sample and atmosphere. During TA analysis, in order to approach thermal equilibrium, a slow heating rate is often favorable. If the heating rate is fast, a thermal lag between the heating source and sample occurs. Also it will generate a temperature gradient surrounding the sample and hence there exist errors in the measurement of the sample temperature [78].

The atmosphere surrounding the sample provides transfer of heat and supplies or removes gaseous reactants or products. Thus, its chemical nature and flow affect the TA data. In most TA methods, an inert atmosphere is needed to prevent the sample from oxidation reactions. Maintaining a certain flow rate is important for TA involving a gaseous product; for example, examination of thermal decomposition and the flow will provide a stable partial pressure of products [78].

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flow associated with transitions in materials due to the function of time and temperature. The technique provides qualitative and quantitative information about
physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity using minimal amounts of sample [78].

Differential Thermal Analysis (DTA) is a thermoanalytic technique, similar to DSC. DTA may be defined as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference [94]. This differential temperature is then plotted against time, or against temperature (DTA curve, or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation.

2.3 Theoretical Methods

2.3.1 Quantum Chemical Computation

The electronic wavefunction of a polyatomic molecule depends on several factors like the bond distances, the bond angles and dihedral angles of rotation about single bonds. A full theoretical treatment of a polyatomic molecule involves calculation of electronic wavefunction for a range of each of these parameters. The equilibrium bond distances and angles are those values that minimize the electronic energy including nuclear repulsion. The quantum chemical investigations are helpful to rationalize the experimental results and rank the existing molecular structures according to their linear and nonlinear susceptibilities. Thus it is possible to design and synthesize novel promising compounds. This investigation helps to understand
the structure-property relationships in terms of acceptor strength, substitution pattern and conjugation length [95].

2.3.1.1 Ab initio Method

The term *ab initio* is Latin for “from the beginning” and indicates that this calculation is based on fundamental principles. *Ab initio* computations are the computations that are derived directly from theoretical principles with no inclusion of experimental data. This is an approximate quantum chemical calculation. The most common type of *ab initio* calculation is called a Hartree-Fock (HF) calculation. In HF calculation, the primary approximation is the central field approximation. Here the Coulombic electron-electron repulsion is taken into account by integrating the repulsive term. It gives the average effect of the repulsion. This is a variational calculation, which implies that the approximate energies calculated are all equal to or greater than the exact energy. Though the accuracy of the calculation depends on the size of the basis set used, due to the central field approximation, the energies from HF calculations are always equal or greater than the exact energy and tend to a limiting value called Hartree-Fock limit [96].

The second approximation in HF calculations is due to the fact that the wavefunction must be described by some mathematical function, which is known exactly for only a few one-electron systems. The combinations of either Slater Type Orbitals (STO), exp(-ar) or Gaussian Type Orbitals (GTO), exp(-ar²) are the mostly used basis functions. The wavefunction is formed from the linear combinations of basis functions. Because of this approximation, most HF calculations give a computed energy greater than the Hartree-Fock limit. The exact set of basis functions used is either STO-3G or 6-311++g**. In general, *ab-initio* calculations give very good
qualitative results. As the molecules become smaller, it will give increasingly accurate quantitative results also [96].

2.5.1.2 Density Functional Theory (DFT) Method

Density Functional Theory (DFT) is a computational quantum mechanical modeling method. It has become very popular in recent years. This theory has been developed more recently than other ab initio methods and is used to determine the electronic structure of molecules. The energy of a molecule can be determined from the electron density instead of a wavefunction which forms the basis of DFT. A practical application of this theory was developed by Kohn and Sham and formulated a method which is similar in structure to the Hartree-Fock method. In this formulation, the electron density is expressed as a linear combination of the basis functions to HF orbitals. A determinant is then formed from these functions and is called Kohn-Sham orbitals which describe the behavior of electrons in a molecule. The electron density from this determinant of orbitals is used to compute the energy. A density functional is then used to obtain the energy for the electron density [96]. The DFT calculation leads to an approximate effective or model Hamiltonian and to an approximate expression for the total electron density. DFT methods are very accurate and of little computational cost. The ground state molecular energy, wavefunction, and all other molecular electronic properties for the molecules with a non-degenerate ground state can be determined by the ground state electron probability density $\rho_0(x,y,z)$, which is a function of only three variables. The ground state electronic energy $E_0$ is a function of $\rho_0$. ie. $E_0=E_0[\rho_0]$. Thus DFT attempts to calculate $E_0$ and other ground-state molecular properties from the ground state electron density $\rho_0$ [97].
2.3.2 Gaussian Basis Sets

A basis set is a set of functions used to describe the shape of the orbitals in an atom. When \textit{ab initio} or DFT calculations are done, a basis set must be specified. Basis sets for use in practical Hartree-Fock, DFT calculations make use of Gaussian type function. Gaussian functions are closely related to exponential functions, which are of the form of exact solutions to the one electron Hydrogen atom. The simplest possible atomic orbital representation is termed as the minimal basis set. Minimal basis sets are used for very large molecules, qualitative results, and in certain cases quantitative results. The most popular minimal basis set is the STO-3G set [98,99].

2.3.2.1 STO-3G Minimal Basis Set

It comprises only those functions required to accommodate all the electrons of the atom, while still maintaining its overall spherical symmetry. Each of the basis functions in the STO-3G representation is expanded in terms of three Gaussian functions, where the values of the Gaussian exponents and the linear coefficients have been determined by least squares as best fits to Slater-type functions [99].

2.3.2.2 3-21G, 6-31G and 6-311G Split Valence Basis Sets

The split-valence basis set represents core atomic orbitals by one set of functions and valence atomic orbitals by two sets of functions. Hydrogen is provided by two s-type functions, and main group elements are provided by two sets of valence s and p-type functions. The simplest split-valence basis sets are 3-21G and 6-31G. Each core atomic orbital in the 3-21G basis set is expanded in terms of three Gaussians, while basis functions representing inner and outer components of valence atomic orbitals are expanded in terms of two and one Gaussians respectively. 6-31G basis sets are similarly constructed, with core orbitals represented in terms of six Gaussians and valence orbitals split into three and one Gaussian components.
Additional valence shell splitting should lead to even greater flexibility. 6-311G basis sets split the valence functions into three parts instead of two, these being written in terms of three, one and one Gaussians respectively [98].

2.3.2.3 6-31G*, 6-31G**, 6-311G* and 6-311G** Polarization Basis Sets

The 6-31G* and 6-311G* are the simplest polarization basis sets which are constructed from 6-31G and 6-311G, respectively, by adding a set of d-type polarization functions written in terms of a single Gaussian for each heavy atom. For 6-31G*, a set of six second-order Gaussians is added and in the case of 6-311G* a set of five pure d-type Gaussians is added. Gaussian exponents for polarization functions have been chosen to give the lowest energies for representative molecules. Polarization of the s orbitals on hydrogen atoms is necessary for an accurate description of the bonding in many systems. The 6-31G** basis set is identical to 6-31G*, except that it provides p-type polarization functions for hydrogen. Similarly, 6-311G** is identical to 6-311G* except for its description of hydrogen [99].

2.3.2.4 cc-pvdz, cc-pvtz and cc-pvqz Basis Sets

Most of the basis sets commonly used with correlated models, namely density functional models, MP2 models and configuration interaction models, are based on Hartree-Fock calculations. Normally, Gaussian exponents and linear expansion coefficients are first determined to minimize the Hartree-Fock energy of the ground-state atom, and are then uniformly scaled to reflect the “tighter” nature of atoms in molecules. The basis sets, cc-pvdz (correlation consistent polarized valence double zeta), cc-pvtz (correlation consistent polarized valence triple zeta) and cc-pvqz (correlation consistent polarized valence quadruple zeta), are instead formulated to yield the lowest possible CISD ground-state atom energies and better suited than basis sets as 6-31G* to capture most of the correlation energy [99].
cc-pvdz basis sets for first-row atoms are made up of nine s-type Gaussians, four sets of p-type Gaussians and one set of d-type Gaussians, contracted to three s, two p and one d functions. The corresponding cc-pvtz basis sets comprise of ten s-type, five p-type, two d-type and one f-type Gaussians, contracted to four s, three p, two d and one f functions, and cc-pvqz basis sets comprise of twelve s-type, six p-type and three d-type, two f-type and one g-type Gaussians, contracted to five s, four p, three d, two f and one g functions. “Pure” d, f and g functions are employed [99].

2.3.3 Optimization of Geometry

Many systematic mathematical procedures exist to find local minimum of a function of several variables. By using these mathematical procedures it is possible to find the local minimum of the electronic energy in the neighbourhood of the initially assumed geometry. The process of finding such a minimum is called geometry optimization or energy minimization. To find the global minimum for molecule with several conformations, the local minimum search procedure has to be repeated for each possible conformation [99].

The first step for the geometry optimization is to start with a guess for the equilibrium structure. The guessed structure is based on typical values for bond lengths, bond angles and dihedral angles, guessed based on the experience with similar compounds. After guessing the geometry, the minimum nearest initially assumed geometry is searched [99] and then a z-matrix is constructed by using the molecular geometry guesses specified in internal coordinates such as bond distance, bond angles and dihedral angles.

2.3.4 Normal Coordinate Analysis (NCA)

Normal Coordinate Analysis (NCA) is nowadays commonly used as an aid in the interpretation of the vibrational spectra of large molecules. NCA is very much
used and is necessary for the complete assignment of the vibrational frequencies of polyatomic molecules and for quantitative description of the vibration. The results of NCA are helpful in the study of vibration-rotation and electronic-vibrational interactions [100].

NCA begins with formulation of Hessian matrix, which holds the second partial derivatives of the potential V with respect to displacement of the atoms in Cartesian coordinates. This process of forming an appropriate potential model and calculating the second derivatives of the potential with respect to the Cartesian coordinates yields the force constant matrix, which is often sparse. Normal coordinates are obtained from the solution of the Eigen value problem,

\[ | G F - E \lambda | = 0 \]  

(2.12)

where G is the matrix representation for kinetic energy, F is the matrix representation for the potential energy and E is the unit matrix. The Eigen value (\( \lambda \)) and eigenvectors of this matrix characterizes the vibrational frequencies and displacement patterns of each atom. Also, the extreme sensitivity of the Hessian matrix to even small changes in structure in a state of mechanical equilibrium, results in imaginary vibrational frequencies and the mixing of modes. NCA requires the diagonalization of very large spare matrices which demands excessive computational effort [100].

Normal coordinate treatments are particularly useful in the quantitative study of infrared and Raman band intensities. NCA is a mathematical procedure that gives the normal coordinates, frequencies and force constants. In order to get meaningful results, knowledge about the vibrational force field is necessary. As the number of atoms increases, the number of force constants also grows quadratically. Hence many approximations have to be employed in the calculation of harmonic force fields even for moderately large molecules. A number of programs have been developed for the
calculation of force field [101-104]. About 1970, Gwinn [105] developed a program for normal coordinate analysis using mass-weighted Cartesian coordinates. It eliminates the redundancy problems arising when internal valence coordinates are used, as in Wilson’s GF-method [106]. MOLVIB is a program developed by Sundius [107], based on the same fundamental idea and is used for the calculation of classical molecular force fields. In this, all the calculations are done in mass-weighted Cartesian coordinates, which eliminates most problems with redundant coordinates. The force field is refined by a modified least squares method, as described by Sundius [108]. This program can also be used for the scaling of vibrational force fields by treating the scale factors as ordinary force constants.

Normally the force constants are not defined in terms of Cartesian coordinates, but are rather expressed in internal coordinates or their linear combinations [43]. Internal coordinates are more natural, from the chemical point of view, because they can be directly related to molecular bond lengths and bond angles. In matrix form, the relationship between the internal coordinates $S_i$ and the Cartesian displacement coordinates $x_i$ can be expressed as

$$S = Bx$$  \hspace{1cm} (2.13)

Where $B$ is a rectangular matrix and with the help of $B$-matrix and the eigen vector matrix $U$, $L$-matrix can be calculated as:

$$L = BM^{-1}U$$  \hspace{1cm} (2.14)

With the $L$-matrix, normal modes can be conveniently characterized and it gives the transformation from normal to internal coordinates. Also the normal modes can be characterized by means of the potential energy distribution (PED) that can be calculated from the $L$-matrix and $F$-matrix in internal coordinates according to the formula
\[ P_{ij} = (L_{ij})^2 F_{ij} / \lambda_i \]  

(2.15)

The PED gives the fractional contribution of the diagonal matrix elements of F to the normal modes. It can be used for the complete symmetry classification of the normal vibrations of the molecule [100].

2.3.5 Natural Bond Orbital (NBO) Analysis

Natural Bond Orbital (NBO) analysis provides an efficient method for studying intra and intermolecular bonding and charge transfer or conjugative interaction in molecular systems. NBO method was developed by Weinhold and co-workers which is becoming a powerful and popular method for the study of bonding concepts [109]. NBO analysis can also be employed to identify and substantiate the possible intra and intermolecular interactions that would form the hydrogen bonded network [110]. Existence of intermolecular O-H...O hydrogen bonds which are due to the interaction between the lone pair (LP) of oxygen with the antibonding orbital (\(\sigma^*\)) has been confirmed by the results of NBO analysis. NBO analysis is carried out by examining all possible interactions between ‘filled’ (donor) Lewis-type NBOs and ‘empty’ (acceptor) non-Lewis NBOs, and estimating their energetic importance by second order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as delocalization corrections to the zeroth-order natural Lewis structure [109]. For each donor NBO and acceptor NBO, the stabilization energy \(E(2)\) associated with delocalization can be estimated from the second-order perturbation approach as:

\[
E(2) = -n_{\sigma} \frac{\langle \sigma | F | \sigma \rangle^2}{\epsilon_{\sigma}^2 - \epsilon_{\sigma}^*} = -n_{\sigma} \frac{F_{ij}^2}{\Delta E}
\]  

(2.16)
Where $\langle \sigma \left| F \right| \sigma \rangle^2$ or $F_{ij}^2$ is the Fock matrix element between i and j NBO orbitals, $\varepsilon_\sigma$ and $\varepsilon_{\sigma^*}$ are the energies of $\sigma$ and $\sigma^*$ NBO’s and $n_\sigma$ is the population of the donor $\sigma$ orbital.

If the value of $E(2)$ is large, interaction between the electron donors and electron acceptors is intensive. Thus the donating tendency from electron donors to electron acceptors and the extent of conjugation of the whole system will be more [111].

2.3.6 Frontier Molecular Orbital (FMO) Analysis

For describing chemical reactivity, Kenichi Fukui developed a powerful practical model [112, 113] called the Frontier Molecular Orbital (FMO) theory. The important aspect of the frontier electron theory is the focus on the Highest Occupied and Lowest Unoccupied Molecular Orbitals (HOMO and LUMO). Both the HOMO and LUMO are the main orbital that take part in chemical stability.

The frontier-orbital approach is based on the assumption that bonds are formed by a flow of electrons from the HOMO of one reactant or participating bond to the LUMO of another reactant or bond. According to the frontier orbital theory, the chemistry of $\pi$-conjugated systems is largely determined by the HOMO and LUMO $\pi$ orbitals in the reactant molecules. Molecular orbitals, HOMO and LUMO and their properties such as energy are the very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most relative position in $\pi$-electron systems and also explains several types of reaction in conjugated system. The higher the energy of a HOMO, the easier the electrons can be removed from it. The lower the energy of a LUMO, the easier the electrons can be transferred to it [114].
2.3.7 Hyperpolarizability

Hyperpolarizability is the nonlinear optical property of a molecule and is defined as the second-order electric susceptibility per unit volume. It describes how easily the electrons can be pushed or pulled around the molecule. For various molecule-molecule interactions, hyperpolarizability is a useful measure.

In the presence of an applied electric field, the energy of a system is a function of electric field. First hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components by the Kleinman symmetry [115]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous,

\[
E = E_0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l + \cdots \tag{2.17}
\]

where, \(E_0\) is the energy of the unperturbed molecules, \(F_i\) is the field at the origin, \(\mu_i\), \(\alpha_{ij}\), \(\beta_{ijk}\) and \(\gamma_{ijkl}\) are the components of dipole moment, polarizability, the first hyperpolarizabilities, and second hyperpolarizabilities respectively. The mean polarizability \(\alpha_0\) and the anisotropy of the polarizability \(\Delta \alpha\) using the x, y, z components are defined as:

\[
\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2.18}
\]

\[
\Delta \alpha = 2^{-\frac{1}{2}} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \alpha_{xx}^2 \right]^{\frac{1}{2}} \tag{2.19}
\]

The mean first hyperpolarizability \(\beta_{\ell k}\), can be determined by using the relation,

\[
\beta_{\ell k} = \left( \beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{\frac{1}{2}} \tag{2.20}
\]

Where \(\beta_x\), \(\beta_y\) and \(\beta_z\) are the components of first hyperpolarizability and is given as:
The theoretical determination of hyperpolarizability can be used for understanding the relationship between the molecular structure and nonlinear optical properties. Using vibrational spectroscopy, many organic molecules containing conjugated π-electrons can be characterized by large values of molecular first hyperpolarizabilities. These quantities are expected to be helpful for investigating the stability of chemical bonds and characteristics of intermolecular interactions too [116].

By combining these experimental and theoretical methods, the spectroscopic investigations aided by DFT computations have been carried out on certain NLO materials to elucidate the structure-property relationship, NLO properties, electronic effects, hydrogen bonding etc. and are described in the following chapters.