CHAPTER – I
VIBRATIONAL SPECTROSCOPY THEORY AND TECHNIQUES

Introduction

Spectroscopy deals with interaction of matter with electromagnetic energy and spectroscopists harvest wealth of information, about the matter, from these interaction. Molecular spectroscopy aims to understand the interaction of molecular energy with electromagnetic radiation. A molecule possesses various forms of energy due to its different kinds of motion and intermolecular interactions. For instance, it possesses translational energy, Rotational energy, vibrational energy, etc., and these energies are quantized and interactions between them are very weak. Electromagnetic radiations can be allowed to interact with the molecular energy levels and investigation of these interactions can provide various information regarding their rotation, charge localization, molecular structure, symmetry, vibration, etc. It is an established fact that the interaction of electromagnetic energy with the vibrational energy levels of a molecule provide amazing information on the molecular dynamics [1] and vibrational spectroscopy emerged with theories and techniques to deal with such interactions.

The frontiers of vibrational spectroscopy are very wide, as the technique is applicable to solids, crystals, powder; liquids, solutions, melt, gases, films and absorbed species. Its important application are: Molecular structural determinations, calculation of intra molecular & inter molecular forces, computation of degree of association in condensed phases, elucidation of molecular symmetries, identification and characterization of new molecules, deducing thermo dynamical properties of molecular systems, etc. [2]. Vibration spectroscopy has also contributed significantly to the
growth of other areas such as polymer chemistry, catalysis, fast reaction dynamics, charge-transfer complexes, etc [3].

Vibrational spectroscopy involves different methods, the most important of which are infrared and Raman spectroscopy. Molecular vibrations, which modulate the molecular dipole moment, are visible in the infrared spectrum, while those vibrations, which modulate the polarizability, appear in the Raman spectrum. These two techniques yield complementary and/or confirmatory information regarding molecular vibrations. Thus both these methods should necessarily be used for a complete vibrational analysis of a molecule [4]. The present thesis is entirely devoted to the proper use of infrared and Raman spectroscopy in the vibrational analysis of some important polyatomic and substituted benzene molecules. Thus important topics relevant to this dissertation, including theoretical background, instrumentation and sample handling for infrared and Raman spectroscopy, group theoretical approach in vibrational analysis, various force fields and theory of normal coordinate analysis are presented here.

**Infrared spectroscopy**

**Molecular vibrations**

A molecule is not a rigid assembly of atoms; it can be viewed as a system of balls and springs of varying strengths, corresponding to the atoms and chemical bonds of the molecule. There are two kinds of fundamental vibrations for molecules: stretching, in which the distance between two atoms decreases or increases, but the atoms remain in the same bond axis, and bending (or deformation), in which the position of the atom changes relative to the original bond axis. Each of the vibrational motions of a molecule occurs with a certain frequency, which is characteristic of the molecule and of the particular bond. The energy involved in a particular vibration is
characterized by the amplitude of the vibration, so that the higher the vibrational energy, the larger the amplitude of the motion [5].

According to the results of quantum mechanics, only certain vibrational energies are allowed to the molecule, and thus only certain amplitudes are allowed. Associated with each of the vibrational motions of the molecule, there is a series of energy levels (or vibrational energy states). The molecule may be made to go from lower energy level to a higher energy level by absorption of a quantum of electromagnetic radiation, such that

\[ E_{\text{final}} - E_{\text{initial}} = n\hbar \nu \rightarrow 1.1 \]

In undergoing such a transition, the molecule gains vibrational energy, and this is manifested in an increase in the amplitude of the vibration. The frequency of light required to cause a transition for a particular vibration is equal to the frequency of that vibration, so that we may measure the vibrational frequencies by measuring the frequencies of light, which are absorbed by the molecule. Since most vibrational motions in molecules occur at frequencies of about $10^{14}\text{sec}^{-1}$, then light of wavelength $\lambda = \frac{c}{\nu} = 3 \times 10^{10} \text{cm/sec}/10^{14}\text{sec}^{-1} = 3 \times 10^{-4} \text{cm} = 3 \text{microns}$ will be required to cause transitions [6]. As it happens, light of this wavelength lies in the infrared region of the spectrum, IR spectroscopy deals with such transitions between vibrational energy levels in molecules and is therefore constitute a part of vibrational spectroscopy.

**Vibrational Degrees of Freedom**

A molecule has as many degrees of freedom as the total degrees of freedom of its individual atoms. Each atom has 3 degrees of freedom in the Cartesian coordinates (x, y, z), necessary to describe its position with respect to a fixed point in the molecule.
A molecule of n atoms therefore has 3n degrees of freedom. Of the 3n degrees of freedom, for non-linear molecules, 3 degrees of freedom describe translation and 3 describe rotation and the remaining 3n–6 degrees of freedom describe vibrational degrees of freedom. Linear molecules have only 3n–5 vibrational degrees of freedom, since only 2 degrees of freedom are required to describe rotation. In the case of polymers the number of vibrational degrees of freedom becomes 3n–4, as rotation is constrained to only one axis [7]. Of the 3n–6 vibrational modes, (n–1) modes are bond stretching vibrations and the other 2n–5 [(2n–4) for a linear molecule] modes are angle-bending vibrations [8]. The number of vibrational degrees of freedom gives the number of fundamental vibrational frequencies of the molecule, or in other words, the number of normal modes of vibrations.

**Normal modes of vibration**

A molecule may consist of many numbers of atoms and the atomic nuclei may be regarded as mass points in the potential field due to the bonding. When the atoms of a molecule are slightly displaced from their equilibrium position and released, they perform vibrations of complicated nature. In the absence of other normal modes, each normal mode is nothing but the simple harmonic motion of every nucleus about its equilibrium position and all these oscillations are in phase.

**Infrared vibration spectra**

During the vibrational motion of a molecule the charge distribution undergoes a periodic change, and therefore in general the dipole moment changes periodically. For a particular vibrational mode, in order to directly absorb infrared electromagnetic radiation, the vibrational motion associated with that mode must produce a change in the dipole moment of the molecule. Normal vibrations that are connected with a change
of dipole moment and therefore, appear in the infrared spectrum are called infrared active modes, while vibrations for which the change of charge distribution is such that no change of dipole moment arises and which, therefore, do not appear in the infrared spectrum are called infrared inactive modes [4].

Let \( \mu_x, \mu_y \) and \( \mu_z \) are the three components of the dipole moment \( \mu \) of the molecule in the direction of the axes, of a Cartesian coordinate system fixed in the molecule, in a displaced position of the nuclei. If \( \mu_x^0, \mu_y^0 \) and \( \mu_z^0 \) are the components of the dipole moment \( \mu^0 \) in the equilibrium position, then, for sufficiently small displacements, we can expand \( \mu_x \) as

\[
\mu_x = \mu_x^0 + \sum_k \left[ \left( \frac{\partial \mu_x}{\partial x_k} \right)_0 x_k + \left( \frac{\partial \mu_x}{\partial y_k} \right)_0 y_k + \left( \frac{\partial \mu_x}{\partial z_k} \right)_0 z_k \right] + \cdots \quad \rightarrow 1.2
\]

Where the \( x_k, y_k \) and \( z_k \) are the displacements coordinates of nucleus k. Similar relations hold for \( \mu_y \) and \( \mu_z \). If we use normal coordinates \( q_1, q_2, q_3 \ldots q_k \) we have

\[
\mu_x = \mu_x^0 + \left( \frac{\partial \mu_x}{\partial q_k} \right)_0 q_k + \frac{1}{2} \left( \frac{\partial^2 \mu_x}{\partial q_k^2} \right)_0 q_k^2 + \cdots \quad \rightarrow 1.3
\]

With \( q_k = q_k^0 \cos (2\pi v_k t + \varphi_k) \) \quad \rightarrow 1.4

And similarly we can express \( \mu_y \) and \( \mu_z \).

Thus generally we can write the molecular dipole moment

\[
\mu = \mu^0 + \left( \frac{\partial \mu}{\partial q_k} \right)_0 q_k + \frac{1}{2} \left( \frac{\partial^2 \mu}{\partial q_k^2} \right)_0 q_k^2 + \cdots \quad \rightarrow 1.5
\]
According to equation (1.4) and (1.5), the dipole moment $\mu$ of the molecule will change with the frequency $\nu_k$ of a normal vibration $k$ if and only if at least one of the derivatives \( \left( \frac{\partial \mu_x}{\partial q_k} \right)_0, \left( \frac{\partial \mu_y}{\partial q_k} \right)_0, \left( \frac{\partial \mu_z}{\partial q_k} \right)_0 \) is different from zero. The intensity of this infrared fundamental band is proportional to the square of the vector representing the change of the dipole moment for the corresponding modes of vibration near the equilibrium position; that is,

\[
I \propto \left( \frac{\partial \mu_x}{\partial q_k} \right)_0^2 + \left( \frac{\partial \mu_y}{\partial q_k} \right)_0^2 + \left( \frac{\partial \mu_z}{\partial q_k} \right)_0^2 \quad \Rightarrow 1.6
\]

The above discussion is based on the assumption that the vibration of the molecule is simple harmonic. If the anharmonicity is taken into account, the vibrational motion contain also the frequencies $2\nu_k, 3\nu_k, \ldots$, and furthermore $\nu_k + \nu_i, \nu_k - \nu_i, 2\nu_k + \nu_i, \ldots$. Therefore, in the infrared spectrum in addition to the fundamentals, overtones and combination vibrations may also occur, if they are connected with a change of dipole moment. However, they will be much weaker than the fundamentals, since the anharmonicities in general are slight, except for very large amplitudes of the nuclei [1].

**Infrared selection rule**

Selection rule for the infrared activity can be obtained by expressing equation (1.5) using the transition moment integral, as

\[
\left[ \mu_{ij} \right] = \mu_e \int \psi_i \psi_j d\tau + \sum_k \left[ \left( \frac{\partial \mu}{\partial q_k} \right)_0 \int \psi_i q_k \psi_j d\tau \right] \quad \Rightarrow 1.7
\]
Neglecting the higher order terms. As $\mu_o$ is a constant and also due to the orthogonal of the wave functions the first integral is zero except for $i = j$. Since we are considering a transition from state $i$ to $j$, the first term vanishes. Consequently, the permanent dipole moment of the molecule has no effect on the vibrational transitions.

The second term gives the transition probability for the infrared absorption. In this term, there is a factor $\left( \frac{\partial \mu}{\partial q_k} \right)_o$, which gives a change in dipole moment $\mu$ around the equilibrium position during a vibration. For at least one of the components $q_k$ of $\mu$, the dipole moment must be non-zero. Accordingly, $\frac{\partial \mu}{\partial q_o} \neq 0$, then a normal mode $q_k$ will be active in the infrared absorption spectrum [3].

**RAMAN SPECTROSCOPY**

**Raman Effect**

When electromagnetic radiation of energy content $h\nu$ irradiates a molecule the energy may be transmitted, absorbed or scattered. The scattering mechanisms can be classified on the basis of the difference between the energies of the incident and scattered photons. If the energy of the incident photon is equal to that of the scattered one, the process is called Rayleigh scattering. If the energy of the incident photon is different to that of the scattered one, the process is called Raman scattering. When the substance is illuminated by monochromatic light, the spectra of the scattered light consists of a strong line (the exciting line) of the same frequency as the incident light together with weaker lines on either side shifted from the strong line by frequencies ranging from a few cm$^{-1}$ to about 3500 cm$^{-1}$. The lines of frequency less than that of exciting line are called Stokes lines, the others anti-Stokes lines. [9].
Classical Theory

The classical theory of Raman effect, while not wholly adequate, is worth consideration since it leads to an understanding of the concept – the polarizability of a molecule. For a molecular vibration to be Raman active there must be a change in the polarizability of the molecule. A hypothetical atom with a spherically symmetrical electron cloud has no permanent dipole moment. When such an atom is irradiated by an electromagnetic radiation the electric field of the radiation displaces the electron and positively charged nucleus in opposite directions. This separation is called polarization and the atom now has an induced dipole moment. If \( E \) represents the electric field of the radiation and \( \mu' \) represents the induced dipole moment oriented parallel to the direction of \( E \), which can be described by its components

\[
\begin{align*}
\mu'_x &= \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\
\mu'_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \quad \Rightarrow 1.8 \\
\mu'_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z
\end{align*}
\]

All \( \alpha_{ij} \) are components of a tensor \( \alpha \), which projects one vector, the electric fields vector \( E \) to produce another vector \( \mu' \), the induced dipole moment. This can be written in matrix notation as

\[
\begin{bmatrix}
\mu'_x \\
\mu'_y \\
\mu'_z
\end{bmatrix} =
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix} \quad \Rightarrow 1.9
\]

or as

\[
\mu' = \alpha E \quad \Rightarrow 1.10
\]
Since the electric field associated with the incident radiation of frequency $\nu_o$ alternates the induced dipole moment also alternates at the same frequency $\nu_o$. Thus the molecule emits electromagnetic radiation of the frequency $\nu_o$. Rayleigh scattering is due to this process [4].

A molecule is not static; it continuously vibrates (also rotate) when radiations fall on it. This vibratory motion of the molecule is capable of modulating the polarizability of the molecule. Consequently, the induced dipole moment and therefore also the amplitude of the emitted field is modulated by the frequency of the vibration. The modulation of the polarizability of a molecule, vibrating with the frequency $\nu_k$ is

$$\alpha_k = \alpha_0 + \left( \frac{\partial \alpha}{\partial q_k} \right)_0 q_k^0 \cdot \cos 2\pi \nu_k t + \cdots \quad \Rightarrow 1.11$$

Here $q_k^0$ represent the normal coordinates. As a consequence of irradiation, molecular polarizability get modulated with the frequency of electric field $\nu_o$ of incident light and gives the induced dipole moment as

$$\mu_k' = \alpha_0 E_o \cos 2\pi \nu_o t + \left( \frac{\partial \alpha}{\partial q_k} \right)_0 q_k^0 E_o \cdot \cos 2\pi \nu_o t \cdot \cos 2\pi \nu_k t \quad \Rightarrow 1.12$$

This is equivalent to

$$\mu_k' = \alpha_0 E_o \cos 2\pi \nu_o t + \left( \frac{\partial \alpha}{\partial q_k} \right)_0 q_k^0 E_o \left[ \cos 2\pi (\nu_o - \nu_k) t + \cos 2\pi (\nu_o + \nu_k) t \right] \quad \Rightarrow 1.13$$

According to this equation, the induced dipole moment acquires three components $\nu_o$, $(\nu_o - \nu_k)$ and $(\nu_o + \nu_k)$. When light is emitted by these induced dipoles, the emitted light also posses the above frequencies. The first term in equation (1.12) describes Rayleigh
scattering, the second term concerns Stokes, and the third anti-Stokes Raman scattering [2]. The intensity of the emitted radiation is proportional to the square of the absolute value of the second derivative of the induced dipole moment:

\[ S \propto \langle |\vec{\mu}'|^2 \rangle \quad \rightarrow \quad 1.14 \]

Just as in case the infrared spectrum, if the anharmonicity is taken into account, in addition to the fundamentals, overtone and combination vibrations may also appear as Raman shifts if they are connected with a change of polarizability. When the anharmonicity is small, the intensity of Raman lines corresponding to overtone and combination vibrations will be very small compared to those corresponding to fundamentals.

**Quantum Theory**

The description of Raman Effect will be complete if we use quantum theory [9]. Suppose a molecule is initially in state \(|i\rangle\) with the energy \(E_i\) and after interaction with monochromatic radiation of angular frequency \(\nu_0\) goes to state \(|f\rangle\) with energy \(E_f\).

From the conservation of energy

\[ E_i + h \nu_0 = E_f + h (\nu_0 \pm \nu_f) \quad \rightarrow \quad 1.15 \]

Where \(h\nu_f = E_f - E_i\)

And \(h (\nu_0 \pm \nu_f) = h \nu_s\), the energy of the scattered photon.

If \(E_f > E_i\), \(\nu_s = \nu_o - \nu_f\) (stokes) \(\rightarrow \quad 1.16\)

If \(E_f < E_i\) \(\nu_s = \nu_o + \nu_f\) (anti-stokes) \(\rightarrow \quad 1.17\)
The stoke lines are more intense than the anti-stokes lines, a consequence of the different populations of molecule in the ground and first excited vibrational state, as described by the Boltzmann distribution. Application of the Boltzmann distribution law shows that the ratio of the intensities for the Stokes and the corresponding anti-Stokes Raman lines is given by

\[
\frac{I_{AS}}{I_S} = \left( \frac{\nu_o + \nu_{fi}}{\nu_o - \nu_{fi}} \right)^4 \exp\left( -\frac{\hbar \nu_{fi}}{kT} \right) \quad \Rightarrow 1.18
\]

Where \(\nu_{fi}\) is the magnitude of the Raman shift and \(\nu_o\) is the frequency of the incident beam. Thus the intensity of anti-stokes lines decreases greatly at higher vibrational frequencies [3].

**Raman selection rules**

The induced transition moment associated with a transition from the initial state to the final state \(j\) and \(I\) are given by

\[
\mu'_{ij} = \int \psi_i \mu' \psi_j d\tau \quad \Rightarrow 1.19
\]

\[
\mu'_{ij} = \int \psi_i \alpha_{ij} \psi_j d\tau \quad \Rightarrow 1.20
\]

Where \(\mu'_{ij}\) is the induced dipole moment, \(\psi_i\) and \(\psi_j\) are the wave functions of the lower and final excited vibrational states respectively [10]. Using equations (1.11) and (1.20) we obtain

\[
\mu'_{ij} = E\alpha_0 \int \psi_i \psi_j d\tau + E \sum_k \left( \frac{\partial \alpha}{\partial q_k} \right) \int \psi_i q_k \psi_j d\tau \quad \Rightarrow 1.21
\]
Where \( q_k \) is given by the equation (1.4). The first term of the above equation (1.21) disappears for all values, except for \( \psi_i = \psi_j \) due to mutual orthogonal of the wave functions. This first term accounts for Rayleigh scattering. The components of \( \alpha_o \) are nonzero for all molecules and hence it follows that the Rayleigh scattering is never forbidden. The second term shows that the transition probability depends on the transition moment integrals involving the components of the molecular polarizability matrix element \( \alpha_{ij} \) which transform with the normal coordinate \( q_k \).

**Mutual exclusion principle**

To understand the presence and absence of lines in IR and Raman spectra, the understanding of the Mutual exclusion principle is necessary. It gives the relation between the symmetry of the molecular structure and their infrared and Raman activity. The rule is: For molecules with a centre of symmetry, transitions that are allowed in the infrared are forbidden in the Raman spectrum; conversely, transitions that are allowed in the Raman spectrum are forbidden in the infrared. This rule implies that if there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infrared active. It should be realized that the above rule does not imply that all transitions that are forbidden in the Raman scattering active in the infrared.

The rule can also be explained as follows: in the infrared, only transitions between states of opposite symmetry with respect to the centre of symmetry \( i \) are allowed \(( g \leftrightarrow u)\) whereas in the Raman spectrum, only transitions between states of same symmetry with respect to \( i \) can takes place \(( g \leftrightarrow g, u \leftrightarrow u)\). This rule arises mainly due to the fact that all the components of magnetic dipole moment \( \mu \), change sign for a reflection at the centre of symmetry, but the components of polarizability \( \alpha \), which behave as the product of two components of induced dipole moment \( \mu' \) remain
unchanged [1]. From the mutual exclusion rule, we can conclude that the observance of Raman and infrared spectra showing no common lines implies that the molecule has centre of symmetry. But, it has to be done cautiously because some times a vibration may be Raman active but too weak to be observed. However, if some vibrations are observed to give coincident infrared and Raman bands it is certain that the molecule has no centre of symmetry.

Vibrational spectroscopy of polymers

Structural study of polymers based on vibrational spectroscopic technique does not attract many due to the inherent difficulties present in the polymers. Thus the unique technique, precautions, extra-care required in the study of polymers needs special mention.

I. Infrared spectroscopy

For the study of polymers, among the available spectroscopic techniques infrared spectroscopy is proved to be the best technique because the majority of functional groups present in the polymers give rise to bands in the infrared region [11]. The success of infrared spectroscopic method for the polymer analysis also lies in its easy sampling techniques and the fast and sensitive spectrophotometers. As in polyatomic molecules, characteristic group frequencies present in the infrared spectra of polymers makes the vibrational analysis effective. The advantage of characteristic group frequencies is that they generally appear in the same region for polymers as for other molecules [12]. When chemical groups of the same structure and energy are present in a polymer, their vibrational motions often produce coupling or resonance. This may lead to new modes, as a characteristic of the length of the polymer chain and it is confirmed from the spectra of ordered polymers [13].
Polymers usually contain a large number of additives, fillers, pigments, lubricants, and mold release agents, etc and many of these substances may result in interference in the infrared spectrum [12]. Thus many of the polymers require prior removal of impurities or special sample preparative techniques. It is also possible that the infrared sample preparation techniques sometimes destroy or modify the characteristics of interest.

It is well known that there are many preparative methods are available for the same polymer and different manufacturers uses different methods. This may lead to the same polymer having similar but different characteristics, which may appear in the spectrum [14]. Recording infrared spectra of a polymer can also pose some problems like background noise. The main source of this noise in polymers is the partial non-absorbing scattering of the infrared radiation from in-homogeneities in the polymer sample. FTIR spectrometer eliminates this by spectral subtraction technique [13]. Bands introduced by artifacts, solvents and other impurities can also removed by this technique.

II. Raman spectroscopy

Till the advent of FT Raman spectrometers, Raman method was rarely used in the polymer vibrational study. The basic reason for this practical limitation is due to the occurrence of fluorescence but the FT technique combined with Nd: YAG laser as source removed this problem to a greater extent. Raman spectrometers are capable of covering lower wave numbers, up to 100 cm$^{-1}$ or lower, than those of infrared and so can reveal information relating to polymer structures which are not easily available using other techniques [14]. As already mentioned infrared and Raman methods are often provide complementary information. These differences in the vibrational patterns
of infrared and Raman can be used to a grater advantage in the determination of structure of molecules. Often in the Raman spectra of polymers, the skeletal vibrations give characteristic bands which are usually very weak and not of much use for characterization in the infrared.

Since water is a highly polar molecule, it is a strong infrared absorber, but it can be studied using Raman spectroscopy. Thus water-soluble polymers such as surfactants can be successfully carried out with Raman technique. Filled polymers can be easily studied by using Raman spectroscopy because fillers such as silica, clay and glass are weak Raman scatters and do not interfere with the Raman spectrum of the polymer matrix [13]. In contrast to infrared the Raman does not require elaborate sample preparatory techniques. Care should be taken that the polymer sample should not get heated by the laser radiation as it may lead to poor Raman spectra, phase change, decomposition, etc. Heating can be avoided by rotating the sample while the spectrum is recorded [14].

**Instrumentation – Infrared Spectroscopy**

Infrared spectrometers generally falls under two categories namely: dispersive and interferometer instruments. Conventional spectrometers are *dispersive instruments* using prism or grating as dispersive elements. In order to overcome shortcomings of these devices spectrometers based on interferometer technique were developed. This type of instruments records the interferogram of the signal and later with the help of Fourier transformation methods, it is converted into conventional spectrum and these instruments are called FTIR spectrometers.
A. Conventional IR spectrometers

It essentially consists of a source which generates light of desired wave numbers, a monochromater (either a salt prism or a grating with finely spaced etched lines) separates the source radiation into its constituent wavelengths and a slit selects the collection of wavelengths that shine through the sample at any given time. In double beam operation, a beam splitter separates the incident beam in two; half goes through the sample, and half to a reference. The sample absorbs light according to its chemical properties. A detector collects the radiation that comes out of the sample, and in double-beam operation, compares its energy with that of the reference. The detector generates an electrical signal proportional to the collected radiation and sends to an analog recorder. A link between the monochromater and the recorder allows us to record energy as a function of frequency or wavelength, depending on how the recorder is calibrated [15].

Although very accurate instruments can be designed on these principles, there are several important limitations. First, the monochromater/slit limits the amount of signal that can be obtained at a particular resolution. To improve resolution, the slit must be narrow but it decreases intensity. Second, there is no easy way to run multiple scans to build up signal-to-noise ratios. Finally, the instrument must be repetitively calibrated, because the analog connection between the monochromater position and the recording device is subject to misalignment and wear [2].
B. Fourier Transform IR spectrometer

A Fourier transform infrared spectrometer consists of a source, an interferometer (an addition which makes the instrument unique) and a detector.

Sources

Most of the FT instruments use a heated ceramic source. The composition of the ceramic and the method of heating vary from instrument to instrument but the idea is always the same a ceramic is heated to suitable temperature to obtain IR radiations of required range. Modern FTIR instruments use a conducting ceramic or a wire heater coated with ceramic as source. The advantage with the heated ceramics is that at high temperature they emit IR radiation of all wavelengths with reasonable intensity. Care should be taken to maintain the temperature of the heater at constant value and this is achieved by monitoring the source output, and using part of the output signal as feedback to control the electrical power [16].

In recent years, tunable dye lasers are emerging as very precise sources with resolution of $10^{-6}$ cm$^{-1}$. The wave number range of tunable dye lasers is however restricted and hence their applicability is limited. The use of carbon dioxide laser and Semiconductor lasers in the infrared spectroscopic analysis has also been reported [3].

Interferometers

The interferometer is the heart of any FTIR instrument. It is this part which analyses the infrared radiation and hence enables us to generate a spectrum. The classical Michelson Interferometer involves a beam splitter – which sends the light in two directions at right angles. One beam goes to a stationary mirror then returns back to the beam splitter. The other goes to a moving mirror. The motion of the mirror produces path difference with respect to the stationary mirror. When the two beams
meet again at the beam splitter, they recombine, but the difference in path lengths creates constructive and destructive interference producing an interferogram.

The recombined beam passes through the sample. The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector now reports variation in energy versus time for all wavelengths simultaneously. A laser beam (usually a He-Ne Laser having a wavelength near 632.8 nm) is superimposed to provide a reference for the instrument operation i.e for the measurement of path difference. Thus the output of the detector is an interferogram.

A mathematical function called a Fourier transform allows us to convert this intensity-vs.-time spectrum into an intensity-vs.-frequency spectrum [17]. The Fourier theorem states that any complex wave can be viewed as a superposition of series of sine and cosine waves. The Fourier Transform uses the above concept to convert an interferogram into constituent vibrations. The Fourier transformations connects two physical descriptions using the integral

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{-i\omega t} d\omega \quad \rightarrow 1.22$$

This relates an f(t) - a function of time with F(\omega) - a function of frequency. We can also express the relation as,

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \quad \rightarrow 1.23$$

The F (\omega) function gives the frequencies at which the signal is non-zero and the f(t) function gives the corresponding time of the signal. Both of these functions are suitable descriptions of a waveform or physical system. If one is known the other function can
be obtained from it [18]. An interferogram, as mentioned earlier, is a function of time and hence it can be transformed into a function of frequency using the above equation. The intensity detected by the detector of a FTIR instrument can be mathematically expressed as

\[ I(x) = \int_{0}^{\infty} S(\nu)[1 + \cos 2\pi\nu]d\nu \]

\[ \rightarrow 1.24 \]

The above equation can also written as

\[ S(\nu) = 2 \int_{0}^{\infty} I(x)[1 + \cos 2\pi\nu]dx \]

\[ \rightarrow 1.25 \]

Where \( x \) is the path difference. Thus using \( I(x) \) and \( S(\nu) \) as the Fourier transform pair, a Fourier transformation can be performed using the above equation on the interferogram and a spectrum as a plot of percentage transmission against the wave numbers can be obtained [3]. Since, all modern FT instruments are computer-interfaced, a small computer program will do the transformation in a matter of seconds (or less) and the output of the detector is digitized. The Discrete Fourier-Transform (DFT) is an algorithm for doing the transform with discrete data, which was used previously. The DFT is an order \( N^2 \) calculation, meaning that the number of multiplications is equal to the square of the number of data points. This algorithm has been supplanted by Fast Fourier-Transform (FFT) algorithms, which reduce redundancies and take much less computer time. The order of this calculation is \( N\log(N) \) [18].

**Detectors**

Various detectors are encountered in FTIRs and the majority of which are photo resistors i.e. they have a very high resistance in the dark and this falls as light falls on them. The most sensitive are the Ge and InGaAs semi-conductor devices and others are Golay cell, thermocouple, and pyroelectric detectors. Some of detectors give adequate
performance (an acceptable useful S:N ratio) at room temperature but others must be
cooled. Cooling detectors invariably reduces the amount of noise they develop, but
unfortunately cooling shifts the absorption edge towards shorter wavelength. In an
FTIR, one normally finds a TGS or similar detector for ordinary use. If better results
are required, one then resorts to the use of a cryogenically cooled mercury cadmium
telluride semi-conductor detector [16]. Thus, these are invariably used in infrared
microscopy and very often in diffuse reflection experiments.

**There are several advantages in the modern FTIR instruments**

All of the source energy gets to the sample, improving the inherent signal-to-noise
ratio. This is usually called as *energy advantage*.

- Resolution is limited by the design of the interferometer. The longer the path of
  the moving mirror, the higher the resolution. Even the least expensive FT
  instrument provides better resolution than all the best CW instruments were
  capable of.

- During spectral acquisition all the frequencies were recorded simultaneously
during the whole period of the detection and it is called multiplexing. This
  method gives rise to *multiplex advantage* or *Fellgett advantage* [19].

- The radiation from the source reaching the detector in an interferometer is not
  limited by the entrance and exit slits as in a dispersive spectrometer thus the
  brightness of the detected signal increases enormously which is called as
  *Jacquinot’s advantage* or *throughput advantage* [20].

- The digitization and computer interface allows multiple scans to be collected,
  also dramatically improving the signal-to-noise ratio.
Most of the computer programs today allow further mathematical refinement of the data: you can subtract a reference spectrum, correct the baseline, edit spurious peaks or otherwise correct for sample limitations.

**Instrumentation - Raman Spectroscopy**

The problem facing the development of Raman spectroscopic instrumentation is the inherent weakness of the inelastic scattering. Therefore to produce a detectable Raman signal a high-powered light source is required. In addition, Raman requires a spectrometer with a very high degree of discrimination against the Rayleigh elastic scattered light. Finally, since very few Raman photons are generated, the detection system must be very sensitive to detect the Raman signal over the dark noise background [2]. The above facts delayed the use of Raman technique in research and industrial laboratories.

It was not until early sixties that the Modern renaissance took place with the development of commercial continuous wave visible lasers. In recent years, microelectronics revolution has further improved the technique with the developments of stepper motor drives, photon counting devices, digital data acquisition techniques and computer data processing and provided the Chemists and physicists a technique which is more useful and versatile than infrared spectroscopy [14]. Some of the advantages of Raman over infrared technique are: Raman spectroscopy is a scattering process, so samples of any size or shape can be examined; Very small amounts of materials can be examined; glass and closed containers can be used for sampling; fiber optics can be used for remote sampling; aqueous solution can be analyzed. Recent development in Fourier transform instrumentation now made these advantages available to researchers.
Sources

Before the inventions of lasers, radiation emitted by the mercury arc, especially at 435.8 and 404.7 nm, has been used for exciting Raman spectra [4]. Today, most types of lasers, like continuous wave (CW) and pulsed, gas, solid state, semiconductor lasers, etc., with emission lines from the UV to the near-IR region, are used as radiation sources for the excitation of Raman spectra. Especially argon ion lasers with lines at 488 and 515 nm are presently employed. Near-IR Raman spectra are excited mainly with a neodymium doped yttrium-aluminum garnet laser (Nd:YAG), emitting at 1064 nm [2]. The main advantage of a laser light source for Raman spectroscopy are: (i) directionality which makes focusing simple, (ii) coherency which enhances the usable power, (iii) intensity which yields a high power density and (v) monochromatic which eliminates multiple Raman lines.

Conventional Raman Spectrometers

Raman spectroscopy until recently relayed on conventional single-channel spectrometers. They are designed to generate Raman signal and differentiate it from the unwanted stronger Raleigh-scattered light from the weaker Raman signal and count the Raman photons. These conventional Raman spectrometers are the simplest and are readily available for routine work when interfering fluorescence is not a major problem. It is essentially consists of a powerful laser irradiating in the visible region, an illuminating chamber for the sample, a high performance light dispersion system to resolve the more intense, elastically scattered light from the weak, in-elastically scattered Raman signal, a light detection and amplification system capable of detecting weak light levels and a recorder [4].
**Fourier Transform Raman Spectrometer**

FT-Raman spectrometers are designed to eliminate the fluorescence problem encountered in conventional Raman spectroscopy [21]. The FT-Raman instrument has the following components: (1) A near IR Laser excitation source, generally an Nd:YAG laser working at 1.06 μm. (2) An interferometer equipped with an appropriate beam splitter, made of glass, and a detector for the near IR region. The detector is usually InGaAs or Ge semiconductor detector. (3) A sample chamber with scattering optics that match the input port of the Fourier transform instrument. (4) An optical filter rejection of the Raleigh–scattered light.

Utilizing an excitation frequency well below the threshold for any fluorescence process eliminates fluorescence. To focus and align the invisible Nd:YAG laser beam a visible He:Ne laser beam is co-aligned with the Nd:YAG beam. Another method of optical alignment can be realized by using fiber optics [16]. With fiber-optic components, optical alignment is virtually eliminated which allows rapid switching from one sample to another.

One of the advantages of FT instrument is that it can collect all the scattered radiation over the entire range of frequencies simultaneously during the whole period of the detection and it is called multiplexing. This becomes a disadvantage, as the intense Rayleigh line is the primary source of noise. Multiplexing redistributes the noise associated with Rayleigh line across the entire spectrum by the FT-process and this is called as *multiplex disadvantage* [22]. Interferometer can be combined with Rayleigh line filters (notch filters) in order prevent the consequences of the multiplex disadvantage. The Rayleigh line filters minimizes the amount of Rayleigh scattered light entering the interferometer [23] and is essential for FT-Raman spectroscopy.
Dual Instruments

Due to the rapid developments in the instrumentation techniques, nowadays both infrared and Raman spectrometers are incorporated into a single instrument assembly and available commercially as a single package. The main advantages of such instruments are: switching over from one technique to other is simple; they are compact, and comparatively cheaper. Bruker's FTIR spectrometers IFS 66/S fitted with FRA 106/S, Thermo Nicolet’s Nexus/Magna FTIR & FTR systems, ABB Bomen MB157 series these are some of the commercially available dual instrument packages. Figure-1.5 shows the schematic diagram of Bruker’s FTIR spectrometers IFS 66/S fitted with Raman module FRA 106/S, which was used in the present work.

Sample handling

I. Infrared spectroscopy

One of the advantages of infrared spectroscopy is that it can be applied to nearly all types of substances. The infrared spectra of samples can be measured in gas, liquid or solids. The spectra obtained may, however, to some extent, depend on the physical state of the system. A wide range of sampling technique is available for mounting the sample in the infrared instruments. The technique depends on whether the sample is a gas, a liquid, a solid or a polymer.

Solids

Solids are usually examined as a mull, a pressed disc, or as a deposited glassy film. Mulls are prepared by thoroughly grinding 2-5 mg of a solid in a smooth agate mortar. Grinding is continued after the addition of one or two drops of the mulling oil. Care must be taken in grinding to achieve particles of size less than 2 μm so that excessive scattering of radiation can be avoided. The mull is examined as thin film
between flat salt plates. Nujol, high boiling point petroleum oil, is commonly used as a mulling agent. The mull technique has the advantage of non-reactivity with samples, reproducibility of results and rapidity of preparation. But the Nujol shows strong absorption near 2915 cm\(^{-1}\) and medium bands around 1462 and 1376 cm\(^{-1}\) so it can not be used if bands in the C-H stretching or CH\(_3\) deformation region are to be observed [24]. Preparing a second mull using perfluoro-kerosene, halocarbon oil or hexachloro-butadiene as the mulling agent can circumvent this. The disadvantages with this technique are: if the sample concentration is too low, the spectrum will be that of the mull, but if too much sample is used the mull will not transmit the radiation. Also excess mull lead to poor transmission of radiation but little quantity of mull leads to very weak spectrum [4].

The pressed disc technique depends upon the fact that dries, powdered potassium bromide or other alkali halides, can be pressed in an evacuated die under high pressure to form transparent discs. The sample is thoroughly mixed with about 100 mg of dry powdered potassium bromide. The mixture is pressed with special dies under a pressure of about 10,000 – 15,000 pounds per square inch into a transparent disk. Since the making of good pellet requires expertise and its use is often avoided. Such KBr technique can be less formidable through the Mini-press that affords a simple procedure and greatly simplified the task of making discs [24]. The main advantage of pressed disc technique is that the concentration of the sample and thickness of the disk can be controlled easily. It is also possible to store the disc for future reference. The limitations of the technique are: sample grinding with KBr may lead to polymorphism and the high pressure applied can bring physical and chemical changes in the sample.
Liquids

In most instances the spectra of liquids are measured in either a demountable type cell or in fixed thickness or sealed cells. The spectra of pure samples can be measured as very thin films squeezed between two alkali halide windows of a demountable cell. This technique can produce a film of thickness 0.01 mm or less. This method is most useful for qualitative work only because sample thickness cannot be controlled. Liquid cells consists of two alkali halide windows, usually NaCl or KBr, separated by a spacer of suitable thickness made of Teflon or lead which limits the volume of the cell. Capillary dropper or hypodermic syringe is used to fill or emptying such cells [4].

Solutions are handled in cells of 0.1 – 1 mm thickness. Usually solutions of 1 to 10 % can be used in commercially available cavity cells of path length 0.01 to 0.1 m. commonly used solvents for infrared spectra are CCl₄, CHCl₃, CS₂, CH₂Cl₂, C₆H₆ and n-heptane. The solvents selected must not chemically react with the solute and it should not exhibit intense absorption with the frequency range of interest. For obtaining spectrum in a wide frequency range several solvents must be used [24].

Polymers

The technique used in the study of organic and inorganic polyatomic molecular samples can, in many cases, is simply applied to polymers. For recording infrared spectra, liquids may be studied in thin cells having transparent IR windows. Liquids may also be studied as thin films stretched by surface tension between transparent plates. Using suitable solvents solids can be dissolved and examined. Polymeric samples in powder form may be examined by preparing discs and mulls [14]. Brittle solid polymers can be ground to powder form, of suitable particle size, and then used as
discs or mulls. Thermoplastic polymers or elastomers can be studied by cooling them below its glass transition temperature before grinding. If the polymer is in the form of thin film it can be examined directly [13]. Thermoplastic polymers can be made to thin films using hot press.

II. Raman spectroscopy

Raman spectrometer but the important thing to be taken care of while preparing sample is that they should be dust free can study gases, liquids and solids. Glass is almost transparent in the Raman frequency region and thus samples in different phases can be measured in glass or silica containers or capillaries [4].

Liquids

Liquids may be examined neat or in solution and normally liquids of about 0.3 ml enclosed in glass or silica containers or capillaries may be required for obtaining good spectrum. Even though water cannot be used as solvent in IR studies, in the Raman studies water is one of a good solvent. Thus spectra of aqueous solutions can be easily studied and also spectra of water-soluble biological material can be easily recorded [2].

Solids

Solid as poly crystalline material or as a single crystal can be studied with the help of Raman technique. Solvents or alkyl halides or mull are not required for recording the spectra. Solids in the form of fine powder enclosed in a glass or silica fiber can be used. When the measurement is made as a single crystal, depending on the orientation of the crystal axis and polarization of the incident radiation the spectra may
vary. Raman spectra can also be recorded for adsorbed species. Samples can also be studied using the Raman technique at various pressures and temperatures [4].

**Polymers**

Polymers do not require elaborate sample preparation techniques for Raman study. Polymers samples often produce fluorescence due to contaminants on their surface. Wiping the sample with a solvent like acetone or alcohol can reduce the fluorescence [14]. Even very small amount of polymeric samples can be studied. Polymeric sample containing Glass fibers can be examined without prior treatment [2]. A simple technique to determine the inorganic fillers incorporated in polymers is simply burn the sample and examines the residue in spectrometer [13].

**Application of group theory to vibrational spectroscopy**

Symmetry is a visual concept as reflected by the geometrical shapes of molecules such as ammonia, benzene, etc. The link between molecular symmetry and quantum mechanics is provided by the group theory. In vibrational spectroscopy, group theory can be effectively used for: (1) determining the symmetry types of normal mode vibrations of the molecule, (2) predicting the infrared and Raman activity of a normal mode of vibration of a particular symmetry types and (3) simplification of method of obtaining the relation between force constants and vibrational frequencies [10]. The group theory was used, first time by Wigner (1930), for the study of molecular vibrations [25].

The molecular symmetry is systematized quantitatively by introducing the concept of ‘symmetry operation’. A symmetry operation transforms the molecular framework into an equivalent configuration or identical configuration. A symmetry
element is a geometrical entity such as point, an axis or a plane about which one or more symmetry operations are carried out. Five kinds of fundamental symmetry operations are utilized in specifying molecular symmetry. (i) Proper axis of symmetry ($C_n$) it is rotation once or several times by an angle $\theta = (2\pi/n)$ about the axis, (ii) Plane of symmetry (σ) one or more reflections in the plane, (iii) Improper axis of symmetry ($S_n$) rotation about an axis followed by reflection in a plane perpendicular to the rotation axis, (iv) centre of symmetry (I) inversion of all atoms through the centre of symmetry, (v) identity element (E) rotation of the molecule through $0^\circ$ or $360^\circ$ which leaves the molecule unchanged [8].

All the symmetry operations present in a molecule form a group and such groups are called point groups. In a point group all the elements of symmetry present in the molecule intersect at a common point and this point remains fixed under all the symmetry operations of the molecule Although theoretically large numbers of such groups are possible most molecules falls under dozen point groups. Some of the common molecular point groups are $C_s$, $C_n$, $C_{nv}$, $C_{nh}$, $C_{sv}$, $D_n$, $D_{nh}$, $D_{vd}$, $S_n$, $T$, $T_d$, $O$, $O_h$, $I_h$, $D_{vd}$, etc. Molecules can be fixed to point groups using the following steps [26].

I. For a linear molecule:

No centre of symmetry : $C_{sv}$ Group

Centre of symmetry present : $D_{vd}$ Group

II. For a molecule of Octahedral shape:

No i present : O Group

i present : $C_{sv}$ Group

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III. For a molecule of Tetrahedral shape:

No $\sigma_d$ present : T group

$6\sigma_d$ present : $T_d$ group

If the molecule does not belong to any of the above categories, look for the $C_n$ axis of highest order present.

IV. If $n = 1$ and

No other elements present : $C_1$ group

$i$ present : $C_1$ group

$\sigma$ present : $C_s$ group

V. $C_n$ with $n > 1$ exists and there are no $C'_2$ axis perpendicular to $C_n$ and if

No other elements present : $C_n$ group

$\sigma_h$ exists : $C_{nh}$ group

no $\sigma'_v$ exists but no $\sigma_h$ : $C_{nv}$ group

VI. $C_n$ with $n > 1$ exists and there are $C'_2$ axis perpendicular to $C_n$ and if

No $\sigma$ exists : $D_n$ group

$\sigma_h$ exists : $D_{nh}$ group

no $\sigma'_d$ exists but no $\sigma_h$ : $D_{nd}$ group

VII. $C_n$ with $n > 1$ exists and there exists a $S_{2n}$ coincident with $C_n$ and no other element of symmetry (sometimes $i$ may present) exists

: $S_{2n}$ group
Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinates x, y & z of an atom into a set of new coordinates x', y' & z'. The two sets of coordinates can be related with the help set of equations or a matrix. The matrix is referred as the transformation matrix and a specific transformation matrix can represent each symmetry operation. Such matrices for the various symmetry operations of a point group form a representation. Representations can be divided into two types: Reducible representation and irreducible representation.

Let A, B, C and S is the matrices in the representation T of a group. Let S be the similarity transformation matrix in this group. By similarity transformation the matrices A, B, C and S are changed to A', B', C' and S' as

\[ S^{-1}AS = A' \quad ; \quad S^{-1}BS = B' \quad ; \quad S^{-1}CS = C' \quad ; \quad S^{-1}DS = D' \]

If the resulting matrices can be blocked into smaller matrices, then the representation T is called a reducible representation. If it is not possible to find a similarity transformation matrix, which will reduce the matrices of representation T, then the presentation is said to be irreducible [8]. Every point group consists of a certain number of irreducible representations. The characters of matrices in the different irreducible representations of a point group can be listed in a table known as character table. Character table plays a vital role in solving problems such as molecular vibrations. The character table for a point group can be constructed with the knowledge of properties of irreducible representations.

The construction of character table requires practice, expertise and knowledge of theorems in group theory such as orthogonal theorems, theorems of representation theory, etc. Without elaborating the procedure, the character table for two point groups
[10] C\textsubscript{s} and C\textsubscript{2v}, (the molecules chosen for the present thesis falls under these groups) are given below:

In the tables A and B represents representation which is symmetric and anti-symmetric with respect to the main axis of rotation, \( \uparrow, \downarrow \) –represents symmetric and anti-symmetric with respect to a plane of symmetry, and 1,2 (as subscripts) represents symmetric and anti-symmetric with respect to a rotation axis (C\textsubscript{n}). The last two columns of each character table list the infrared and Raman activity of the particular species. Polarizability components are listed for Raman activity and translational and rotational components are listed for infrared activity.

Based on the character table the selection rules for infrared and Raman activity can be obtained with the help of group theory and quantum mechanics.

**Character Table for C\textsubscript{s} point Group**

<table>
<thead>
<tr>
<th>C\textsubscript{s}</th>
<th>E</th>
<th>( \sigma\textsubscript{2v} )</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Infrared</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Raman</td>
</tr>
<tr>
<td>A'</td>
<td>1</td>
<td>1</td>
<td>( T_z, T_y, R_z )</td>
</tr>
<tr>
<td>A''</td>
<td>1</td>
<td>-1</td>
<td>( T_z, R_x, R_y )</td>
</tr>
</tbody>
</table>
Character Table for $C_{2v}$ point Group

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
<th>Activity</th>
<th>Infrared</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$T_z$</td>
<td>$T_z$</td>
<td>$\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$</td>
<td>$R_z$</td>
<td>$\alpha_{yz}$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$T_x$, $R_y$</td>
<td>$T_x$, $R_y$</td>
<td>$\alpha_{xz}$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$T_y$, $R_z$</td>
<td>$T_y$, $R_z$</td>
<td>$\alpha_{yz}$</td>
</tr>
</tbody>
</table>

Infrared-Active Vibrations

The point group of a molecule will have a definite number of symmetry operations. These operations are of two types: Proper Rotations – a rotation through an angle $\pm \varphi$ about some axis of symmetry and Improper Rotations – rotation followed by a reflection in a plane perpendicular to the axis of rotation. A quantity called character is necessary for the determination of the selection rules and number of fundamentals of each vibration type. For a given vibration type there is a separate character for each class of symmetry operations. These characters can be found from the character table.
Vibrations active in infrared spectra are determined by character $\chi_M$ of the dipole moment given by

$$\chi_M = \pm 1 + 2 \cos \varphi \quad \rightarrow \text{1.26}$$

The + sign is for proper rotations and – sign for improper rotations. The character $\chi_M$ for a given class is always a linear combination of the characters of the vibration types for that class. This linear combination is done by means of the reduction formulae

$$N_i = \frac{1}{g} \sum n_M \chi_M \chi_i \quad \rightarrow \text{1.27}$$

Where $g$ is the number of elements in a point group, $\chi_M$ the number of elements in each class, $\chi_i$ is the character of the vibration type, $N_i$ the number of times the character $\chi_i$ of the vibration appear in $\chi_M$. The value of $N_i$ if equal to zero than that vibration type is infrared inactive otherwise active [10].

**Raman Active Vibrations**

Vibrations active in Raman spectra are determined by character $\chi_\alpha$ of the polarizability $\alpha$ given by

$$\chi_\alpha = (2 \pm 2 \cos \varphi) + (2 \cos 2\varphi) \quad \rightarrow \text{1.28}$$

The character $\chi_\alpha$ must likewise be some linear combination of the $\chi_i$ using the reduction formulae 1.27. Here also if the $N_i$ if equal to zero than that vibration type is Raman inactive otherwise active [8].
Number of fundamentals in each symmetry type

The number of vibrations of each type depends upon the geometry of the molecule. To find the number of fundamentals of each type a quantity \( \xi(R) \) for every symmetry operations required. \( \xi(R) \) is given by:

\[
\xi(R) = \begin{cases} 
(U_R - 2)(1 + 2\cos \varphi) & \text{for proper rotation} \\
U_R (-1 + 2\cos \varphi) & \text{for improper rotation}
\end{cases}
\]

where \( U_R \) is the number of nuclei unchanged by the symmetry operation. Knowing \( \xi(R) \), the number of frequencies of each type is determined by using the relation [10]:

\[
n_i = \frac{1}{g} \sum n \xi(R) \chi_i
\]

Normal coordinate analysis

The problem of finding the normal modes of vibrations of a polyatomic molecule can be solved by the method of classical mechanics. For carrying out the normal coordinate analysis first the vibrational frequencies observed in the infrared and Raman spectra must be assigned to individual normal modes of vibration. The next step is the calculation of the relative amplitudes of the normal (or symmetry) coordinates in any normal mode. The main technique behind this is framing the vibrational secular equations and solving these equations. The theoretical background of the normal coordinate analysis is briefed below:

The technique of normal coordinate analysis is highly helpful and essential for complete assignment of the vibrational frequencies of the spectra of a polyatomic molecule and it also leads to a quantitative description of the vibrations. Intermolecular
force constants, which hold the structure, can be obtained and used for the understanding of the molecular vibrational frequencies of other molecules. The force constants supply alternative ways of probing bonding and structural characteristics and they can be correlated with inter-atomic repulsions and bond nature. It is also useful in the quantitative study of vibrational band intensities and to study interaction between vibration and rotation levels.

**Framing the secular equations**

Consider a molecule undergoing vibrational motion and let there be many number of normal modes of vibration. The centre of gravity of the molecules in its equilibrium configuration may be chosen as the origin of the coordinate system so as to express the displacement in each normal vibration in terms of Cartesian coordinates. The total kinetic energy is given by the formula,

\[ 2T = \sum_{i=1}^{n} m_i \left( \dot{X}_i^2 + \dot{Y}_i^2 + \dot{Z}_i^2 \right) \]  \[ \rightarrow 1.31 \]

This equation can be simplified by using a new set of Cartesian coordinates called the reduced displacement coordinates

\[ q_1 = \sqrt{m_1} X_1 \quad , \quad q_2 = \sqrt{m_2} X_2 \quad , \quad q_3 = \sqrt{m_3} X_3 \quad , \quad q_4 = \sqrt{m_4} X_4 \quad , \quad \ldots \]  \[ \rightarrow 1.32 \]

now the equation 1.31 can be written as

\[ 2T = \sum_{i=1}^{3n} a_{ij} \dot{q}_i \dot{q}_j \]  \[ \rightarrow 1.33 \]

If the vibrations are simple harmonic then the potential energy, in reduced coordinates, can be written as
The \( b_{ij} \) values are constants and the \( a_{ij} \) values are functions of the atomic masses. \( q_i \) and \( q_j \) are the \( i^{th} \) and \( j^{th} \) coordinates.

The classical equation of motion for the \( i^{th} \) mass by using the Newton’s equation in the Lagrange form is:

\[
\frac{\partial}{\partial t} \left( \frac{\partial T}{\partial \dot{q}_i} \right) + \frac{\partial V}{\partial q_i} = 0 \tag{1.35}
\]

Using equations 1.33 and 1.34 in 1.35 we get

\[
\sum_j (a_{ij} \ddot{q}_j + b_{ij} q_j) = 0 \tag{1.36}
\]

The general solutions of the above equation is given by

\[
q_i = A_j \sin(\lambda^{1/2}t + \phi) \tag{1.37}
\]

Which is an equation characteristic of wave motion with \( \lambda = 4\pi^2\nu^2 \) where \( \nu \) is the frequency, and \( A \) & \( \phi \) are amplitude and phase constant respectively. From equations 1.36 and 1.37, we can write

\[
\sum_{j=1}^{3n} (b_{ij} - a_{ij}\lambda) A_j = 0 \tag{1.38}
\]

Where \( j = 1, 2, 3, \ldots, 3n \). For non-trivial solution the determinant of the coefficients must be equal to zero i.e.
The equation 1.39 is called as the secular determinant. It has 3n roots, \( \lambda_i \) for which the above equation is satisfied. Each of these \( \lambda \) values expresses the harmonic vibration of a mass particle with frequency \( \nu \). These \( \nu \) values are the normal frequencies of the vibrations. The values of \( \lambda \) can be substituted back in equation 1.38 and \( A_j \) can be calculated which will describe the vibration [27].

**Evaluation of the secular determinant**

The evaluation of the secular determinant is simplified by the transformation to a new set of coordinates \( Q_i \), such that the cross product terms in 1.33 and 1.34 disappears. The old and new coordinates can be related by an orthogonal transformation

\[
 q_k = \sum_{i=1}^{3n} B_{ki} Q_i \rightarrow 1.40
\]

The coordinates \( Q_i \) are called the normal coordinates for the molecular system. Based on the equation 1.29 the kinetic and potential energies can be written as

\[
 2T = \sum_i \dot{Q}_i^2 \rightarrow 1.41
\]

\[
 2V = \sum_i \lambda_i Q_i^2 \rightarrow 1.42
\]

Employing equations 1.40 and 1.41 in 1.35, we get,

\[
 \ddot{Q}_i + \lambda_i Q_i = 0 \rightarrow 1.43
\]
The solution of this expression is given by, similar to equation 1.26,

\[ Q_i = B_i \sin(\frac{1}{2} \lambda_i t + \varphi) \rightarrow 1.44 \]

The vibrational problem is much easier to describe by means of matrix algebra. Thus the expression for kinetic and potential energies in matrix notation is

\[ 2T = \dot{Q}^T \dot{Q} \rightarrow 1.45 \]

And \[ 2V = Q^T \Lambda Q \rightarrow 1.46 \]

Where \( \Lambda \) is the diagonal matrix with element \( \lambda_i \) and \( Q^T \) represents the transpose of the column matrix \( Q \) of the normal coordinates. The simplified form of the secular equation can now be written as

\[ \left| \Lambda - E \lambda \right| = 0 \rightarrow 1.47 \]

This equation will have \( 3n - 6 \) roots \( \lambda_i \) and each value of \( \lambda \) corresponds to a normal vibrational frequency of the molecule. All the atoms vibrate with the same frequency and phase in each normal mode \( Q_i \) [3].

**Solution of secular equation in internal coordinates**

If internal coordinates are used as the initial coordinates the solution of the secular determinant 1.47 is greatly simplified. The internal coordinates are defined as the increments in bond lengths and bond angles. The principle advantage of internal coordinates is the representation of the potential energy or force constant matrix in terms of bond stiffness and resistance to bond angle deformations, which make these
coordinates physically comprehensible. The size of the secular equation in internal coordinates is smaller and hence easier to solve.

The kinetic energy in terms of internal coordinates is given by the expression

\[ 2T = \sum_{i,j} G_{ij}^{-1} \dot{r}_i \dot{r}_j \rightarrow 1.48 \]

Where \( G_{ij}^{-1} \) is the inverse kinetic energy element for each pair of is coordinates \( r_i \) and \( r_j \).

Similarly, the potential energy in internal coordinates is

\[ 2V = \sum_{i,j} f_{ij} r_i r_j \rightarrow 1.49 \]

Where \( f_{ij} \) are the harmonic force constants.

In matrix notation, the equation 1.48 and 1.49 can be suitably expressed by the equations,

\[ 2T = \dot{\mathbf{R}}^T \mathbf{G}^{-1} \dot{\mathbf{R}} \rightarrow 1.50 \]

And

\[ 2V = \mathbf{R}^T \mathbf{F} \mathbf{R} \rightarrow 1.51 \]

Where \( \mathbf{G}^{-1} \) is the inverse kinetic energy matrix and \( \mathbf{F} \) is the potential energy matrix comprises of the intermolecular force constants. Using equations 1.50 and 1.51 in the Newton’s equation in Lagrange form given by equation 1.35 and simplifying we get the secular determinant as

\[ \left| \mathbf{G} \mathbf{F} - E \mathbf{\lambda} \right| = 0 \rightarrow 1.52 \]
Where $E$ is the unit matrix. The expression 1.52 expresses the secular equation by involving the product term $GF$. Wilson first described this method of expressing the secular equation and so it is often referred as Wilson’s FG matrix method [9].

In order to frame a secular equation 1.52 for a polyatomic molecule it is necessary to select suitable set of internal coordinates and then set up the $F$ and $G$ matrix. At least $3n - 6$ internal coordinates are necessary to describe the vibration of an $n$-atom molecule. Sometimes it necessary to include more than $3n - 6$ internal coordinates and this will result in redundancies. These redundancies (interdependence of internal coordinates) can be removed later by a suitable coordinate transformation. While choosing the internal coordinates the rules given by Decius [28] will be much helpful.

**Solution of secular equation in symmetry coordinates**

After setting up the $F$ and $G$ matrix, the secular determinant 1.52 can be solved for Eigen values and Eigen vectors. But the size of the determinant is very high for most of the polyatomic molecules. It is therefore be advantageous to reduce the order of the determinant by taking advantage of the molecular symmetry. The simplification can be effected by the use of symmetry coordinates [29] and they are simple linear combinations of internal coordinates. For introducing symmetry coordinates the first step is to classify the normal vibrations according to the irreducible representation of the point group to which the molecule belongs. The symmetry coordinates are next selected so as to transform according to the appropriate irreducible representations of the molecular point group. These coordinates block diagnosis the secular determinant. Hence the problem of solving the determinant of the order $3n - 6$ is reduced to the problem of solving several independent determinants of smaller order [27].
By using an orthogonal coordinate transformation internal coordinates $R$ can be transformed to symmetry coordinates $S$ and such an operation is written as,

$$S = UR \quad \rightarrow 1.53$$

Where $U$ is an orthogonal matrix. The $G$ and $F$ matrices in internal coordinates can be block-diagonalised using the $U$-matrix as below

$$UGU^T = G_s \quad \rightarrow 1.54$$
$$UFU^T = F_s \quad \rightarrow 1.55$$

The above equations give the $G$ and $F$ matrices in symmetry coordinates. Now the secular determinant in terms of symmetry coordinates is

$$|G_s F_s - E\lambda| = 0 \quad \rightarrow 1.56$$

This expression has the same roots as the secular equation 1.52 in terms of internal coordinates and thus the Eigen values and Eigen vectors of both 1.56 and 1.52 are the same.

When the Eigen values $\lambda$ are determined, the Eigen vectors $L$ for each of the Eigen values can be evaluated from

$$|G_s F_s - E\lambda| L = 0 \quad \rightarrow 1.57$$

The $L$ matrix consisting of the Eigen vectors which are normalized. It provides the transformation from internal coordinates to the normal coordinates [3].
Potential energy distribution

In the normal coordinate analysis, potential energy distribution (PED) plays an important role in obtaining a detailed understanding about the nature of the normal modes. Morino and Kuchitsu [30] have shown that the potential energy distribution rather than the normalized amplitudes is a more satisfactory quantity to use in band assignments.

The normal coordinates ($R_i$) are related to the normal coordinates ($Q_k$) as follows

$$ R_i = \sum_{k=1}^{3n-6} L_{ik} Q_k \quad \Rightarrow 1.58 $$

Where $L_{ik}$ is the component of the L-matrix. Substitution of equation 1.58 to the potential energy expression 1.44 yields the potential energy of the molecule, for a vibration of frequency $\nu_k$, associated with a normal coordinate $Q_k$,

$$ 2V = Q_k^2 \sum_{i,j} f_{ij} L_{jk} L_{jk} \quad \Rightarrow 1.59 $$

Such terms are large only when $i = j$, since the diagonal force constants $f_{ij}$ are much greater than the off-diagonal constants $f_{ij}$. Consequently to get the PED, only the terms $f_{ii} L_{ik}^2$ need to be calculated. The normalization condition $L^T f L = \Lambda$, gives the relation of the form,

$$ \sum_{i,j} f_{ij} L_{ik} L_{jk} = \lambda_k \quad \Rightarrow 1.60 $$

Neglecting the cross terms yields

$$ \sum_i f_{ii} L_{ik}^2 = \lambda_k \quad \Rightarrow 1.61 $$
We can therefore get a normalized potential energy distribution (PED), whose terms are

\[ PED = V_{ik} = \frac{f_{ik}^2 L_{ik}^2}{\lambda_k} \rightarrow 1.62 \]

It is the contribution of the \( i^{th} \) symmetry coordinates to the potential energy of the vibration whose frequency is \( \nu_k \) [31]. The contribution of the potential energy from the individual diagonal elements gives rise to a conceptual link between the empirical analysis of the vibration spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computation of the normal modes.

**Force field approximations**

The primary aim of vibrational analysis is to theoretically calculate the vibrational frequencies of a molecule from the force constants. But the vibrational frequencies are easily observable from IR and Raman spectra. With some difficulty it is possible to compute the force constants from the observed frequencies. To achieve this, the observed vibrational frequencies should be first correctly assigned to the symmetry species of a molecular point group. Force constants can also be calculated from molecular data like Coriolis coupling constants, centrifugal distortion constants and mean amplitude of vibration.

For many molecules it is not possible to evaluate all the force constants from the experimental data and it becomes necessary to reduce the force constants. This is accomplished by making assumptions about the nature of the potential energy function. Some of the important restrictive force fields are:
Computer programs for solving the secular equations

The advent of computers gas certainly aided the normal coordinate analysis of molecules since computers can compensate some of the inherent difficulties and problems in the method. The multiplication of matrices and the solving of secular equations become highly simplified and completed in least time. With the developments of high-level computer languages, a large number of programs are developed for the normal coordinate treatment. Schachtschneider (1965) [30], Shimanouchi (1968) [31], Fuhrer et al (1976) [32], are some of the notable program developers for normal coordinate analysis. Many such programs are also available commercially for instance, Vibratz by Eric Dowty (1998) [33]. Some programs, under public domain, are also available in Internet like Prometheus by Martin Jursch (1997) [34].

After introducing necessary modifications in the program developed by Fuhrer et al, was used for the normal coordinate analysis in the present thesis. The necessary information that is needed for the calculation is an initial vibrational force field and the structural parameters of the molecules. These parameters may be both the bond lengths and bond angles or the Cartesian coordinates of the atoms with respect to an arbitrarily chosen origin. Force constants from structurally similar molecules can be transferred as initial values and if necessary some additional force constants can be added. The program is designed to consist of modules so that the output from one calculation serves as a part of the input to the next. The vibrational frequencies of normal modes and potential energy distribution are obtained as output. With the help of the program the initial set of force constants can be refined to give an excellent fit between the calculated and observed frequencies. Least squares procedure is used to refine the force field calculations.
Experimental details

All the compounds are used in this thesis for investigation are purchased from Sigma-Aldrich chemicals, USA with spectroscopic grade and it is used as such without any further purification. The FTIR spectra of the compounds have been recorded in Perkin-Elmer 180 Spectrometer in the range of 4000–100 cm$^{-1}$. The spectral resolution is ± 2 cm$^{-1}$. The FT-Raman spectra of the compounds are also recorded in the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.064 μm line widths with 200 mW powers. The spectra are recorded with scanning speed of 30 cm$^{-1}$ min$^{-1}$ of spectral width 2 cm$^{-1}$. The frequencies of all sharp bands are accurate to ± 1 cm$^{-1}$.

Computational details

The quantum calculations were performed with Gaussian 03W program [35] using Hartree-Fock (HF), DFT and Hybrid fundamentals, supplements with different basis sets. Initial geometry of the molecules were generated from standard geometrical parameters were minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the standard basis sets. The geometries were then reoptimised at B3LYP level using basis sets. The optimized structural parameters were then used for the vibrational frequency calculations to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of the molecules were used for predicting IR intensities and Raman depolarization ratios. Vibrational frequencies are scaled by 0.9067 in HF calculations and the range of wave numbers above 1700 cm$^{-1}$ by 0.958 and for the range below 1700 cm$^{-1}$ scaled by 0.983 in B3LYP [36]. The results of the GAUSSVIEW program [37] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy introduced by using a least-square optimization of the computed to the experimental data. The assignments of
certain modes have been made by calculating PEDs. The PEDs are computed quantum chemically from calculated vibrational frequencies using VEDA program [38]. Gauss view program has been used to get visual animation and for the verification of the normal modes.

**GAUSSIAN**

Gaussian [39-40] is a computational software program initially released in 1970 by John Pople and research group at Carnegie-Mellon University. It has been continuously updated since then. The recent version is Gaussian 09. The name originates from the word Gaussian function or orbital, a choice made to improve the computing capacity of then existing software which used a function or orbital called Slatter type. Gaussian functions are widely used in statistics where they describe the normal distributions. In this Quantum computation, it represents the wave function of the ground state of a harmonic oscillator. The linear combinations of such Gaussian functions for a molecular orbital is called as Gaussian orbital. The Gaussian software program is used by Physicists, Chemists, Chemical engineers, Biochemists and others for research in established and emerging areas of molecular physics or chemistry. Starting from the basic laws of quantum mechanics, Gaussian predicts the energies, molecular structures, vibrational frequencies and other molecular properties derived from these basic quantities. It can be used to study molecules and reactions under a wide range of conditions, including both stable and short lived intermediate compounds.

Computational techniques consist of three areas: Ab-initio methods, semi-empirical methods, and molecular mechanics. Molecular mechanics utilizes classical physics to solve large systems of molecules and is considered the least accurate due to
the fact that no electron behavior is factored in. Semi-empirical methods are more accurate because of utilization of quantum physics to account for some of the electron behavior, but its scope is still limited since it relies on extensive approximations and empirical parameters. Ab-initio methods are based purely on quantum physics and use no approximations from classical physics to describe the electronic structure of the molecule very accurately. The drawback of using ab-initio methods is that the computations are extremely taxing and so is limited to much smaller systems such as individual molecules. However, ab-initio methods give a lot of information on the electronic structure without having to actually synthesize the molecule experimentally. The fundamental idea behind ab-initio calculations is to solve Schrödinger’s equation with a set of mathematical functions called a “basis set”.

**Basic theory**

In many body electronic structure calculations, the nuclei of the molecules or clusters are treated as fixed, in abeyance with the Born- Oppenheimer approximation, and that generate a static potential V in which electrons are

$$\hat{H}\Psi = [\hat{T} + \hat{V} + \hat{U}] \psi = \left[ \sum_{i} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i>j} \sum_{i>j} U(\vec{r}_i, \vec{r}_j) \right] \psi = E\Psi$$

Moving a stationary electronic state is described by a wave function $\psi(r_1, r_2 \ldots r_n)$, satisfying the many electron time independent Schrödinger Equation [36]

$$V(i)$$

Where H is the Hamiltonian, E is the total energy, T is the kinetic energy, V is the potential energy from the external field due to positively charged nuclei and U is
the electron-electron interaction energy. The operators T and U are called Universal operators as they are the same for any N-electron system, while V is system dependent.

In theory, solving the Schrödinger equation yields wave functions $\psi$ that describe the system fully. Unfortunately the Schrödinger equation cannot be solved analytically for many body systems, so approximations are to be made. Typical solution algorithms therefore is to fix the atomic positions and then solve the Schrödinger equation for a specific value of the atomic coordinates $r$, This is repeated many times to obtain the energy of the system as a function of the atomic coordinates.

The complicated many particle equations are not separable into simpler single particle equations because of the interaction term U. However the single-particle approximation simplifies calculations notably, as it does not account for electron-electron interaction. This method is known as Hartree-Fock method.

**Hartree – Fock (HF) Method**

The origin of the Hartree–Fock method dates back to 1927, soon after the derivation of the Schrödinger equation. D.R.Hartree introduced a procedure to calculate the approximate wave functions and energies for atoms and ions. Hartree was guided by some earlier, semi-empirical methods of the early 1920s (by E. Fues, R. B. Lindsay, and himself) based on the old quantum theory of Bohr. In the Bohr model of the atom, the energy of a state with principal quantum number $n$ is given in atomic units as $E = -1/n^2$. It was observed from atomic spectra that the energy levels of many-electron atoms are well described by applying a modified version of Bohr's formula. By introducing the quantum defect $d$ as an empirical parameter, the energy levels of a
generic atom was well approximated by the formula \( E = -1/ (n + d)^2 \). The existence of a non-zero quantum defect was attributed to electron-electron repulsion, which clearly does not exist in the isolated hydrogen atom. This repulsion resulted in partial screening of the bare nuclear charge. These early researchers later introduced other potentials containing additional empirical parameters with the hope of better reproducing the experimental data. Hartree sought to do away with empirical parameters and solve the many-body time-independent Schrödinger equation from fundamental physical principles, i.e., \textit{ab-initio}. His first proposed method of solution became known as the **Hartree method**.

This method is an approximate method for the determination of the ground-state wave function and ground-state energy of a quantum many-body system. This method assumes that the exact, \( N \)-body wave function of the system can be approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case of bosons) \( N \) spin-orbitals. By invoking the variational principle, one can derive a set of \( N \)-coupled equations for the \( N \) spin orbitals. Solution of these equations yields the Hartree–Fock wave function and energy of the system, which are approximations of the exact ones.

The **Slater type of orbitals (STO)** is of the general form

\[
STO = \frac{\xi^3}{\pi^{0.5}} e^{-\xi}
\]

where \( \xi \) is orbital exponent which reflects the spatial extent of the orbital. The HF method is also called, especially in the older literature, the **self-consistent field method** (SCF) as the solutions to the resulting non-linear equations behave as if each particle is
subjected to the mean field created by all other particles. The equations are almost universally solved by means of an iterative, fixed-point type algorithm.

It is important to remember that STO leads to very tedious calculations. Thus S.F. Boys developed an alternative type of orbital called Gaussian type orbital (GTO) for calculations, which are of the form

$$GTO = \frac{2\chi}{\pi^{0.75}} e^{-x^2 r^2}$$

The difference between STO and GTO lies in the spatial coordinate $r$. The GTO has square of $r$ so that the product of one Gaussian gives another Gaussian. Ultimately it is found that more the combination of Gaussians, more the accuracy of the equations.

This solution scheme is not the only one possible and is not an essential feature of the HF method. For molecules, Hartree–Fock is the central starting point for most ab-initio quantum chemistry methods. The above discussion is only for the Restricted Hartree–Fock method, where the atom or molecule is a closed-shell system with all orbitals (atomic or molecular) are doubly occupied. Open-shell systems, where some of the electrons are not paired, can be dealt with by either restricted open-shell Hartree–Fock (ROHF) or Unrestricted Hartree–Fock (UHF) method.

**Other Methods**

Additional modifications have been implemented with the previous Hartree–Fock approximations to account for electron correlation. There are three methods, among several, that account for electron correlation: Configuration-Interaction, Moller-Plesset perturbation, and Density Functional Theory.
Configuration interaction (CI) method

In Hartree–Fock, it is assumed that a wave function can be written as a product of one–electron wavefunctions. In Configuration interaction (CI) method (2), some multi–electron wave functions are added back into the basic Hartree–Fock method to account for their coordinated motion. This is done systematically by constructing multi–electron wave functions as a sum of the Hartree–Fock wavefunctions for different electronic states. A slight improvement of this method is CISD where one or two electron is assumed to be in excited states. S and D stand for single and double.

Couple cluster (CC) methods are conceptually similar but differ mathematically in the construction of multi electron wave functions. Unlike in CI, CC uses an exponential ansatz to guarantee size extensivity of the solution. The calculations may also include single, double and triple excitations, leading to CCSD and CCSDT methods.

Moller–Plesset Perturbation Theory (MPPT)

The alternative to multi–electron wavefunctions is to choose an approximation for the correlation energy. In this theory, an additional term is added to the total energy and is treated as a perturbation. The perturbed wave function and perturbed energy are expressed as a power series to the $n^{th}$ order (MPn) such as MP2, MP4 etc, although it is not always convergent with increasing the power n.

Density Functional Theory (DFT)

The previous methods are fundamentally based on the wavefunction approach. They scale poorly the complexicity of the molecule with a number of of basis functions the atomic s, p, d etc., orbitals are used to describe the molecular orbitals. Instead of
solving for the wavefunction in order to calculate the energy of the molecule, density functional theory calculates the energy directly from the ground state electron density \( n(\vec{r}) \)

Here DFT provides an appealing alternative, being much more versatile as it provides a way to systematically map the many-body problem, with \( \hat{U} \), onto a single-body problem without \( \hat{U} \). In DFT the key variable is the particle density \( n(\vec{r}) \) which for a normalized \( \Psi \) is given by

\[
n(\vec{r}) = N \int d^3 r_2 \int d^3 r_3 \cdots \int d^3 r_N \psi^* (\vec{r}, \vec{r}_2, \ldots, \vec{r}_N) \psi (\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)
\]

This relation can be reversed, i.e. for a given ground-state density \( n_0(\vec{r}) \) it is possible, in principle, to calculate the corresponding ground-state wavefunction \( \psi_0 (\vec{r}_1, \ldots, \vec{r}_N) \).

In other words, \( \psi_0 \) is a unique functional of \( n_0 \).

\[
\psi_0 = \psi_{n_0}
\]

and consequently the ground-state expectation value of an observable \( \hat{O} \) is also a functional of \( n_0 \)

\[
O[n_0] = \langle \psi \left[ n_0 \right] | \hat{O} | \psi \left[ n_0 \right] \rangle
\]

In particular, the ground-state energy is a functional of \( n_0 \)

\[
E_0 = E \left[ n_0 \right] = \langle \psi \left[ n_0 \right] | \hat{\mathcal{H}} + \hat{V} + \hat{U} | \psi \left[ n_0 \right] \rangle
\]
Where the contribution of the external potential \( \langle \psi [n_0] | \hat{V} | \psi [n_0] \rangle \) can be written explicitly in terms of the ground-state density \( n_0 \)

\[
V[n_0] = \int V(\vec{r}) \, n_0(\vec{r}) \, d^3r
\]

More generally, the contribution of the external potential \( \langle \psi | \hat{V} | \psi \rangle \) can be written explicitly in terms of the density \( n \),

\[
V[n] = \int V(\vec{r}) \, n(\vec{r}) \, d^3r
\]

The functionals \( T [n] \) and \( U [n] \) are called universal functionals, while \( V [n] \) is called a non-universal functional, as it depends on the system under study. Having specified a system, i.e., having specified \( \hat{\mathcal{H}} \), one then has to minimize the functional

\[
E[n] = T[n] + U[n] + \int V(\vec{r}) \, n(\vec{r}) \, d^3r
\]

With respect to \( n(\vec{r}) \), assuming one has got reliable expressions for \( T[n] \) and \( U[n] \). A successful minimization of the energy functional will yield the ground-state density and thus all other ground-state observables.

The variational problems of minimizing the energy functional \( E[n] \) can be solved by applying the Lagrangian method of undetermined multipliers. First, one considers an energy functional that doesn't explicitly have an electron-electron interaction energy term,

\[
E_s[n] = \langle \psi_s[n] | \hat{T} + \hat{V} | \psi_s[n] \rangle
\]
Where \( \hat{T}_s \) denotes the non-interacting kinetic energy and \( \hat{V}_s \) is an external effective potential in which the particles are moving. Obviously, \( n_s(\vec{r}) \overset{\text{def}}{=} n(\vec{r}) \) if \( \hat{V}_s \) is chosen to be

\[
\hat{V}_s = \hat{V} + \hat{U} + (\hat{T} - \hat{T}_s)
\]

Thus, one can solve the so-called Kohn-Sham equations of this auxiliary non-interacting system,

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})
\]

Which yields the orbital’s \( \phi_i \) that reproduce the density \( n(\vec{r}) \) of the original many-body system.

\[
\overset{\text{def}}{=} n_s(\vec{r}) = \sum_i^n |\phi_i(\vec{r})|^2
\]

The effective single-particle potential can be written in more detail as

\[
V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d^3r' + V_{XC} [n_s(\vec{r})]
\]

Where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term \( V_{XC} \) is called the exchange-correlation potential. Here, \( V_{XC} \) includes all the many-particle interactions. Since the Hartree term and \( V_{XC} \) depend on \( n(\vec{r}) \), which depends on the \( \phi_i \), which in turn depend on \( V_s \), the
problem of solving the Kohn-Sham equation has to be done in a self-consistent way. Usually one starts with an initial guess for \( n(\vec{r}) \), then calculates the corresponding \( V_\sigma \) and solves the Kohn-Sham equations for the \( \phi_\sigma \). From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached. A non-iterative approximate formulation called Harris functional DFT is an alternative approach to this.

**Approximations (Exchange-Correlation Functionals)**

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

\[
E_{XC}^{LDA}[n] = \int \epsilon_{XC}(n) \, n(\vec{r}) \, d^3r
\]

The local spin-density approximation (LSDA) is a straightforward generalization of the LDA to include electron spin:

\[
E_{XC}^{LSDA}[n_\uparrow, n_\downarrow] = \int \epsilon_{XC}(n_\uparrow, n_\downarrow) \, n(\vec{r}) \, d^3r
\]

Highly accurate formulae for the exchange-correlation energy density \( \epsilon_{XC}(n_\uparrow, n_\downarrow) \) have been constructed from quantum Monte Carlo simulations of a free electron model.
Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate:

$$E_{\text{XC}}^{\text{GGA}}[n_\uparrow,n_\downarrow] = \int \epsilon_{\text{XC}}(n_\uparrow,n_\downarrow,\nabla n_\uparrow,\nabla n_\downarrow) n(\mathbf{r}) d^3r$$

Using the latter (GGA) very good results for molecular geometries and ground-state energies have been achieved. Potentially more accurate than the GGA functionals are the meta-GGA functionals. These functionals include a further term in the expansion, depending on the density, the gradient of the density and the Laplacian (second derivative) of the density. Difficulties in expressing the exchange part of the energy can be relieved by including a component of the exact exchange energy calculated from Hartree-Fock theory. Functionals of this type are known as hybrid functionals.

**Hybrid Methods**

Indeed, it is common to use calculations that are a hybrid of the two methods the popular B3LYP scheme is one such hybrid functional method. The mixture of exact HF exchange and approximate DFT exchange is commonly employed to increase performance. Several different mixing ratios have been advocated. Becke Half-and-Half LYP uses a 1:1 ratio of HF and DFT exchange energies. ie

$$E_{\text{XE}} = \frac{1}{2} E_X(\text{HF}) + \frac{1}{2} E_X(\text{Becke88}) + E_C(\text{LYP})$$

The most commonly employed hybrid method is the Becke 3-parameter scheme (B3). The scheme is represented as

$$E_{\text{XE}} = 0.2 E_X(\text{HF}) + 0.8 E_X(\text{LSDA}) + 0.72 E_X(\text{Becke88}) + 0.81 E_C(\text{LYP}) + 0.19 E_C(\text{LYP})$$

Becke derived the parameters by fitting to a set of thermo chemical data, the G1 molecule set. When B3 is paired with a correlation function other than LYP, the LYP
coefficients are retained. Becke also developed a one parameter fit (B). Another option is to use modern valence bond methods. The MPW1PW91 method was developed by Barone and Adamo. It employs a modified PW91 exchange functional with original PW91 correlation functional and employs a HF and DFT exchange ratio of 0.25: 0.75.

**Basis Sets**

A *basis set* [41] is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of similar functions with the weights or coefficients to be determined.

One characteristic of a molecule that explains a great deal about the properties is their molecular orbitals. The following diagram must be considered in order to calculate the molecular orbitals.
One of the three major decisions is which of the basis set to use. There are two general categories of basis sets:

**Minimal basis sets**

A basis set that describes only the most basic aspects of the orbitals.

**Extended basis sets**

A basis set with a much more detailed description.

Basis sets were first developed by J.C. Slater. Slater fit linear least-squares to data that could be easily calculated. The general expression for a basis function is given as: $\text{Basis Function} = N \times e^{(-\alpha \times r)}$

Where:

- $N =$ normalization constant
- $\alpha =$ orbital exponent
- $r =$ radius in angstroms

All basis set equations in the form STO-NG (where N represents the number of GTOs combined to approximate the STO) are considered to be "minimal" basis sets. The "extended" basis sets, then, are the ones that consider the higher orbitals of the molecule and account for size and shape of molecular charge distributions.

There are several types of extended basis sets:

- Double-Zeta, Triple-Zeta, Quadruple-Zeta
- Split-Valence
- Polarized Sets
- Diffuse Sets
Double-Zeta, Triple-Zeta, Quadruple-Zeta

Previously with the minimal basis sets, all orbitals are approximated to be of the same shape. However, this is not true. The **double-zeta basis set** is important because it allows treating each orbital separately when Hartree-Fock calculation is conducted. This gives us a more accurate representation of each orbital. In order to do this, each atomic orbital is expressed as the sum of two Slater-type orbitals (STOs). The two equations are the same except for the value of $\zeta$ (zeta). The zeta value accounts for how diffuse (large) the orbital is. The two STOs are then added in some proportion. The constant ‘d’ determines how much each STO will count towards the final orbital. Thus, the size of the atomic orbital can range anywhere between the value of either of the two STOs. For example, let's look at the following example of a 2s orbital:

$$\phi_{2s}(r) = \phi_{2s}^{STO}(r, \zeta_1) + d\phi_{2s}^{STO}(r, \zeta_2)$$

In this case, each STO represents a different sized orbital because the zetas are different. The ‘d’ accounts for the percentage of the second STO to add in. The linear combination then gives the atomic orbital. Since each of the two equations is the same, the symmetry remains constant.

The triple and quadruple-zeta basis sets work the same way, except the use of three and four Slater equations instead of two. The typical trade-off applies here as well, better accuracy for more time or work.

Split-Valence Basis sets

Often it takes too much effort to calculate a double-zeta for every orbital. Instead, it can be simplified by calculating a double-zeta only for the valence orbital. Since the inner-shell electrons aren't as vital to the calculation, they are described with
a single Slater Orbital. This method is called a **split-valence basis set**. A few examples of common split-valence basis sets are 3-21G, 4-31G, and 6-31G.

An example is given below. It will be of help to understand the subject. Here, a 3-21G basis set is used to calculate for the carbon atom. This means 3 summing Gaussians for the inner shell orbital, two Gaussians for the first STO of the valence orbital and 1 Gaussian for the second STO. Here is the output file from the Gaussian Basis Set Order Form for carbon given a 3-21G basis set.

The simplest split valence set provided by SPARTAN is the 3-21G.

This description means that the core orbitals are represented by three Gaussians, whereas the inner and outer valence orbitals consist of two and one Gaussians, respectively.

SPARTAN offers two other split valence bases: the 6-31G and the 6-311G. Both have six Gaussian cores. The 6-31G is triply split basis, with an inner orbital represented by three Gaussians and outer orbitals represented as single Gaussians. The 6-311G is triply split basis, with an inner orbital represented by three Gaussians, and
middle and outer orbitals represented as single Gaussians. The triple split improves the description of the outer valence region.

<table>
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<tr>
<th>CARBON</th>
<th>$(5s,3p) \rightarrow [3s,2p]$</th>
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</thead>
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<td></td>
<td>2 25.9109000 0.358794000</td>
</tr>
<tr>
<td></td>
<td>3 5.3335000 0.700713000</td>
</tr>
<tr>
<td>L 2</td>
<td>1 3.66499000 -0.395697000 0.23540000</td>
</tr>
<tr>
<td></td>
<td>2 0.7705545000 1.21584000 0.850519000</td>
</tr>
<tr>
<td>L 1</td>
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</table>

There is another common method of displaying data. Notice the numbers are labeled so it is easy to match this data with the corresponding data in the output file.

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<th>$\alpha_{2s}$</th>
<th>$\alpha_{2p}$</th>
<th>$d_{1s}$</th>
<th>$d_{2s}$</th>
<th>$d_{2p}$</th>
<th>$\alpha_{2s} = \alpha_{2p}$</th>
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</tbody>
</table>

Once a basis set output file is retrieved, these numbers can be used to calculate equations. For a carbon, three equations will be needed: 1s orbital, 2s orbital, and 2p orbital.

This equation combines the 3 GTO orbitals that define the 1s orbital.

$$
\phi_{1s}(r) = \sum_{i=1}^{3} d_{1s} \phi_{1s}^{GF} (r, \alpha_{1s}) \\
= 0.6176 \phi_{1s}^{GF} (r, 172.256) + 0.3587 \phi_{1s}^{GF} (r, 25.910) + 0.7007 \phi_{1s}^{GF} (r, 5.533)
$$
This equation combines the 2 GTO orbitals that make up the first STO of the double-zeta, plus the 1 GTO that represents the second STO for the 2s orbital.

\[
\phi_{2s}(r) = \sum_{i=1}^{3} d_{2s, i} \phi_{2s}^{GF}(r, \alpha_{2s, i}) + d'_{2s} \phi_{2s}^{GF}(r, \alpha'_{2s})
\]

\[
= -0.395 \phi_{2s}^{GF}(r, 3.664) + 1.215 \phi_{2s}^{GF}(r, 0.771)
+ 1.000 \phi_{2s}^{GF}(r, 0.195)
\]

This equation combines the 2 GTO orbitals that make up the first STO of the double-zeta, plus 1 GTO that represents the second STO for the 2p orbital.

\[
\phi_{2p}(r) = \sum_{i=1}^{3} d_{2p, i} \phi_{2p}^{GF}(r, \alpha_{2p, i}) + d'_{2p} \phi_{2p}^{GF}(r, \alpha'_{2p})
\]

\[
= -0.395 \phi_{2p}^{GF}(r, 3.664) + 1.215 \phi_{2p}^{GF}(r, 0.771)
+ 1.000 \phi_{2p}^{GF}(r, 0.195)
\]

Now, using these three equations, the LCAO can be calculated for the carbon atom.

**Polarized Sets**

In the previous basis sets atomic orbitals are treated as existing only as 's', 'p', 'd', 'f' etc. Although those basis sets are good approximations, a better approximation is to acknowledge and account for the fact that sometimes orbitals share qualities of ‘s’ and ‘p’ orbitals or ‘p’ and ‘d’, etc. and not necessarily have characteristics of only one or the other. As atoms are brought close together, their charge distribution causes a polarization effect (the positive charge is drawn to one side while the negative charge is drawn to the other) which distorts the shape of the atomic orbitals. In this case, ‘s’
orbitals begin to have a little of the 'p' flavor and 'p' orbitals begin to have a little of the 'd' flavor. One asterisk (*) at the end of a basis set denotes that polarization has been taken into account in the 'p' orbitals. Notice in the graphics below the difference between the representation of the 'p' orbital for the 6-31G and the 6-31G* basis sets. The polarized basis set represents the orbital as more than just 'p', by adding a little 'd'.

Original 'p' orbital                      Modified 'p' orbital

\[
\text{Original 'p' orbital} = 6-31G \\
\text{Modified 'p' orbital} = 6-31G^* \\
\]

Two asterisks (**) means that polarization has taken into account the 's' orbitals in addition to the 'p' orbitals. Below is another illustration of the difference of the two methods.

Original 'S' orbital                      Modified's’ orbital

\[
\text{Original 'S' orbital} = 6-31G \\
\text{Modified's’ orbital} = 6-31G^{**} \\
\]

Diffuse Sets

In chemistry the valence electrons are the main concern which interacts with other molecules. However, many of the basis sets that are talked about previously
concentrate on the main energy located in the inner shell electrons. This is the main area under the wave function curve. In the graphic below, this area is that to the left of the red dotted line. Normally the tail (the area to the right of the dotted line), is not really a factor in calculations.

However, when an atom is in an anion or in an excited state, the loosely bond electrons, which are responsible for the energy in the tail of the wave function, become much more important. To compensate for this area, computational scientists use diffuse functions. These basis sets utilize very small exponents to clarify the properties of the tail. Diffuse basis sets are represented by the '+-' signs. One '+' means the 'p' orbitals are accounted, while '+' signals mean both 'p' and 's' orbitals, (much like the asterisks in the polarization basis sets).

The tradeoff/relationship between basis sets and accuracy is represented in the diagram below. The ultimate goal is to calculate an answer to the Schrödinger’s Equation (right bottom corner). However, we are still a long way from being able to complete this calculation. Right now we are in the top left corner of the chart. In that first box, we are treating each electron independently of the others. As moved across to the right, we can find calculations that account for the interactions of electrons. As
moved down the column, more complex and more accurate basis set calculations can be found.

There are other trade-offs for using each type of basis set. The more complex basis sets are more accurate but, they use up a great deal of computing time. Thus, it is important to choose the correct basis set that can be run fastest without compromising desired level of accuracy.