CHAPTER I
INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

ABSTRACT

The density functional theory (DFT) was explained using quantum theory of vibration of the molecular systems. Computational details were elaborated. Moreover, the capability of Gaussian 03W software was also mentioned. Selection rules for Raman and IR transitions, Fourier transformation basics were outlined. The working of Fourier transform infrared (FT-IR) and Fourier transform Raman (FT-Raman) spectrometers, types of sources, detectors and sampling techniques were elaborated. The basic principle of normal coordinate analysis (NCA) was explained using classical analysis of the vibrations of the molecular systems. The computational studies such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and natural bonding orbital (NBO), hyperpolarizability were also discussed. In addition an introduction to single crystal X-ray diffraction (XRD) study and its applications were also discussed.
CHAPTER - I
INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

1.1. INTRODUCTION

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter. The most important consequence of such interaction is that, energy is absorbed or emitted by the matter in discrete amounts called quanta. The various branches of spectroscopy generally involve measurements of two important experimental parameters namely: the energy of the radiation absorbed or emitted by the system and intensity of the spectral lines.

Molecular spectroscopy is concerned with the interaction of electromagnetic radiation with molecular systems. Modern spectroscopic methods covering the entire electromagnetic spectrum have become powerful tools in the investigations of the physical properties of molecules viz., molecular structure, nature of chemical bonds, hydrogen bonding, isomerism etc.

Vibrational spectroscopy is one of the most valuable technologies for elucidating the molecular structure and characteristics of organic, inorganic, coordination compounds and polymers. Vibrational spectroscopy has contributed significantly to the growth of other areas such as catalysis, fast reaction dynamics, charge transfer complexes etc. Vibrational spectroscopy is mainly concerned with vibrational transitions due to absorption and emission of electromagnetic radiations. Vibrational transitions can be observed as infrared (IR) and Raman spectra. They also provides important information about the intra-molecular forces acting between the atoms in a molecule, the inter-molecular forces in condensed phase and the nature of the chemical bond.
1.2. INFRARED

SPECTROSCOPY

IR spectroscopy is widely used for the identification of organic compounds because of the fact that their spectra are generally complex and provide numerous maxima and minima that can be used for comparison purposes. IR spectroscopy is generally concerned with the absorption of radiation incident upon a sample.

The absorption of IR radiation depends on increasing the energy of vibration or rotation associated with a covalent bond in a molecule, provided such an increase causes a change in the dipole moment of the molecule. Hence, for IR absorption the necessary condition is that, there should be a change in the magnitude or direction of the dipole moment of the molecule. Only under these conditions the alternating field of the IR radiation can interact with the molecule and cause changes in its motion.

IR technique when coupled with intensity measurements may be used for qualitative and quantitative analysis. Currently, this technique has become more popular when compared to other physical techniques (X-ray diffraction, electron spin resonance, etc.,) in the elucidation of the structure of unknown compounds.

1.2.1. Infrared Activity

For a normal mode of vibration to be IR active, there must be a change in the dipole moment of the molecule during the course of vibration. During the vibrational motion of a molecule, a regular fluctuation in the dipole moment occurs, and a field is established which can interact with the electrical field associated with radiation. For the absorption of IR radiation, a molecule must undergo a net change in its dipole moment as a result of its vibrational or rotational motions.
1.2.2 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 IR 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 IR spectrum are called IR active modes, while vibrations for charge distribution has no change of dipole moment and, therefore, do not appear in the IR spectrum are called IR inactive modes (Pavia et al., 2003).

Let $\mu_x$, $\mu_y$ and $\mu_z$ are the three components of the dipole moment 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 $\mu^0_x$, $\mu^0_y$ and $\mu^0_z$ are the components of the dipole moment in the equilibrium position, then, for sufficiently small displacements, we can expand $\mu_x$ as

$$\mu_x = \mu^0_x + \sum_k \left[ \left( \frac{\partial \mu_x}{\partial x_k} \right)_0 x_k + \left( \frac{\partial \mu_x}{\partial y_k} \right)_0 y_k + \left( \frac{\partial \mu_x}{\partial z_k} \right)_0 z_k \right] + \ldots$$

(1.1)

Where the $x_k$, $y_k$ and $z_k$ are the displacements coordinates of nucleus k, similar relations hold for $y$ and $z$. If we use normal coordinates $q_1,q_2,q_3,\ldots,q_k$ we have

$$\mu_x = \mu^0_x + \left( \frac{\partial \mu_x}{\partial q_k} \right)_0 q_k + \frac{1}{2} \left( \frac{\partial^2 \mu_x}{\partial q_k^2} \right)_0 q_k^2 + \ldots$$

(1.2)
with

$$q_k = q_k^0 \cos (2\pi v_k t + \phi_k) \quad ...$$ \hspace{1cm} (1.3)

And similarly we can express \( y \) and \( z \).

Thus generally we can write the molecular dipole moment

$$\mu = \mu^0 + \left( \frac{\partial \mu}{\partial q_k} \right)_0 q_k + \frac{1}{2} \left( \frac{\partial^2 \mu}{\partial q_k^2} \right)_0 q_k^2 + ... \hspace{1cm} (1.4)$$

According to equation (1.3) and (1.4) the dipole moment of the molecule will change with the frequency \( v_k \) of 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 IR 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,

$$I \propto \left( \frac{\partial \mu_x}{\partial q_k} \right)_0^2, \left( \frac{\partial \mu_y}{\partial q_k} \right)_0^2, \left( \frac{\partial \mu_z}{\partial q_k} \right)_0^2 \hspace{1cm} (1.5)$$

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 \( 2v_k, 3v_k \), and furthermore \( v_k + v_i, v_k - v_i, 2v_k + v_i \) therefore, in the IR spectrum in addition to the fundamentals, over tones 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 that anharmonicities in general are slight, except for very large amplitudes of the nuclei (Herzberg, 1985).
1.2.2 FTIR Spectroscopy Theory

The Fourier theorem states that any complex wave can be viewed as a superposition of series of sine and cosine waves. The FT uses the above concept to convert an interferogram into constituent vibrations. The Fourier transformations connects two physical descriptions using the integral.

\[ f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{-i\omega t} d\omega \]  \hspace{1cm} (1.6)

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

\[ F(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \]  \hspace{1cm} (1.7)

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 (Brian, 2000). 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

\[ I(x) = \int_{0}^{\infty} S(\nu) [1 + \cos 2\pi \nu t] dv \]  \hspace{1cm} (1.8)

The above equation can also written as

\[ S(\nu) = 2 \int_{0}^{\infty} I(x) [1 + \cos 2\pi \nu x] dx \]  \hspace{1cm} (1.9)

Where, \( x \) is the path difference. Thus using \( I(x) \) ans \( S(\nu) \) as the FT pair, a Fourier transformation can be performed using the above equation on the interferogram and a spectrum as a plot of percentage tranmission against the
wavenumbers can be obtained (Schrader, 1995). 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 is an algorithm for doing the transform with discrete data, which is used previously. The discrete Fourier-Transform is an order $N^2$ calculation, meaning that the number of multiplications are equal to the square of the number of data points. This algorithm has been supplanted by Fast Fourier-Transform algorithms, which reduce redundancies and take much less computer time. The order of this calculation is $N \log(N)$.

1.2.3. Selection Rule for IR

The selection rule for IR activity is determined by the integral,

$$
\int \psi^* (Q_a) \mu \psi (Q_a) dQ_a
$$

(1.10)

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

$$
[ x ]_{V'V''} = \int \psi (Q_a) [ x ] \psi (Q_a) dQ_a
$$

(1.11)

$$
[ y ]_{V'V''} = \int \psi (Q_a) [ y ] \psi (Q_a) dQ_a
$$

(1.12)

$$
[ z ]_{V'V''} = \int \psi (Q_a) [ z ] \psi (Q_a) dQ_a
$$

(1.13)

For the vibrations to be IR active, at least one of the components of the derivative of the dipole moment with respect to the normal coordinate, taken at the equilibrium position should be non-zero. If all the integrals are zero, the vibration is IR inactive.
1.2.4 Background for FT-IR

FT-IR spectroscopy is an interference technique through which recent advances in digital computer technology has demonstrated in superiority to dispersive IR techniques. Fourier transform spectroscopy uses the Michelson interferometer as the multiplex optical device (Griffiths and Haseth, 1986). The block diagram of FT-IR spectrometer is shown in Fig. 1.1.

1.2.4.1 Source

The most commonly used radiation source is globar operating on the basis of the block body radiation. It consists of a SiC (silicon carbide) dimensions 2 cm in length and 0.5 cm in diameter heated to about 1450 K. Globar is generally used in the spectral range up to 100 cm. The Globar is operated in vacuum only. Nernst glower (sintered mixtures of the oxides of Zr, Tm, Ce, Y, and Er) is also used as source in some spectrometers depending upon the spectral range. For more sophisticated applications, gas plasma must be used as radiation source. Besides thermic Microwave generators like klystrons or Magnetrons are also used for wide frequency range.

Fig. 1.1. Block diagram of FT-IR spectrometer
1.2.4.2 Interferometer

The interferometer is the heart of the FT-IR instrument. The interferometer is the bit that analyses the IR or near IR and hence enable us to generate the spectrum. The classic Michelson interferometer is shown in Fig. 1.2, contains a source, detector, stationary and moving mirrors and a beam splitter. The beam splitter is the crystal of potassium bromide coated with germanium (Mille et al., 1985), splits the incident light equally reflecting half to the stationary mirror while transmitting the other half to the moving mirror.

The white light from the source located at the focus of lens L1 is separated into two parts by the beam splitter. The reflected part is focused into the detector D. After reflection from the stationary mirror M1 and after a second split by the beam splitter. The transmitted part of the light is also focused on to the detector after it is reflected from the moving mirror M2 is movable, which produce the path difference between the two beams thereby developing interference pattern at the detector. Their intensity I(x) depends on the position x of the mirror M2. I(x) is termed interferogram function.

Fig. 1.2. Optical paths in Michelson Interferometer
If the incident beam is monochromatic of the form \( E(x, t) = E_0 \cos (kx - \omega t) \), the field \( E_0 \) at the detector is

\[
E_0 = \frac{1}{2} \left[ E_0 \cos (\omega_0 t - k_0 x) + E_0 \cos \left[ k_0 (x + 2\Delta x) - \omega_0 t \right] \right]
\] (1.14)

Where \( 2\Delta x \) is the optical path difference between the two beams. The intensity at the detector is given by the following expression

\[
I(x) = c_0 E_0^2 < E^2 > = \frac{c_0 E_0^2}{4} \left[ 1 + \cos (4\pi \nu x) \right]
\] (1.15)

In terms of the spectral intensity \( I(\nu) = c_0 E_0^2 \delta(\nu - \nu_0)/2 \), the above equation can be written as

\[
I(x) = \frac{1}{2} \int\limits_0^\infty I(\nu) \left[ 1 + \cos (4\pi \nu x) \right] d\nu
\] (1.16)

Generalizing this equation to an arbitrary intensity spectrum \( I(\nu) \) yields the basic relationship for Fourier spectroscopy.

\[
\Gamma(x) = I(x) - \frac{1}{2} \int\limits_0^\infty I(\nu) d\nu = \frac{1}{2} \int\limits_0^\infty I(\nu) \cos (4\pi \nu x) d\nu
\] (1.17)

The interferogram function \( I(x) \) or \( \Gamma(x) \) contains the whole information about the spectrum \( I(\nu) \). In fact, \( \Gamma(x) \) is the Fourier transform of \( I(\nu) \) performed with a cosine function. The observed intensity \( I(x) \) oscillates around an average intensity \( \bar{I} I(\nu) d\nu/2 = I_0/2 \) which is exactly half of the original total intensity of the beam.

For \( x=0 \) it reaches its maximum value of \( I_0 \) as immediately seen from equation (1.17). This position corresponds to zero optical path differences. It is
called the white light position. For \( x \to \infty \), the coherence of the radiation is lost, and therefore the intensity at the detector becomes \( I_0/2 \).

A Fourier transformation (FT) of \( I'(x) \) yields for \( x = y/2 \),

\[
\int I'(y/2) \cos(2\pi v'y) dy = \frac{1}{2} \int I(v) dv \int \cos(2\pi vy) \cos(2\pi v'y) dy = I(v')/2 \quad (1.18)
\]

Since the integration over \( y \) gives \( \delta(v - v') \), this equation shows that the spectral components of the light are obtained directly from the interferogram by FT, without any spectral dispersion (Kuzmnay, 1998). This Fourier spectroscopy has many basic advantages when compare to dispersive spectroscopy.

The ‘energy advantage’ originates from the fact that during the whole period of measurement, nearly the total beam intensity is captured by the detector. This means the detection operates on a high signal level, which improves the signal-to-noise ratio, particularly for weak radiation sources.

The ‘Fellgett’ or the ‘multiplex advantage’ originate from the simultaneous measurement of full spectrum. To obtain spectra from radiation of very low intensity such as astronomical sources, all the frequencies are recorded simultaneously during spectroscopy as in dispersive spectroscopy, they are said to be ‘multiplexed’. In dispersive spectroscopy \( N \) parts of the widths \( \Delta v \) of the spectrum will be measured successively so that for each part only the time \( T' = T/N \) is available. The signal-to-noise ratio would be smaller by \( \frac{1}{\sqrt{4N}} \).

Interferometer also has greater ‘throughput’ than dispersive IR methods. ‘Throughput’, a measure of the optical efficiency of the system, is defined as the
product of the area and solid angle of the beam passing from the source to the detector. Since there is no slit in FT-IR spectrometer, the cross section of the beam of radiation in an interferometer can be much larger than that of a dispersive spectrometer, which leads to considerable improvements in signal-to-noise ratio. But in much chemical and analytical application the sample size limits the energy advantage. The optimum resolution is obtained by using the theoretical relationship

\[ r = F \sqrt{\frac{2}{R_0}} \]

where \( r \) is the radius of the entrance pinhole and \( R_0 \) is the resolution. This yields for the brightness of the interferometer.

\[ E = \left( \frac{r^2 \pi A^2}{F^2} \right) = \left( \frac{2 \pi A^2}{R_0} \right) = \left( \frac{2 \pi A^2}{\nu \delta \nu} \right) \]

(1.19)

Where \( A \) is the beam diameter in the spectrometer, for dispersive spectrometer the brightness is given by

\[ E = \frac{(AR_0H\delta \lambda)}{F} \]

(1.20)

Where \( H \) and \( F \) are the height of the slit and the focal length of the grating spectrometer, respectively. By comparing these two equation 1.15 and 1.16, it is found that for Fourier spectrometer the enhancement of the brightness is of the order of 500 times greater than the grating and prism spectrometer known as the ‘Jacqui not advantage’.

The dispersive spectrometer suffer from greater wavenumber errors, of a less predictable form owing to their general mechanical and thermal instability and can also be affected by non-uniform illumination across the monochromator entrance slit (Crookell et al., 1990). The FT spectrometer typically uses the He-Ne lasers as a reference beam to monitor the displacement of the moving optical
element, so providing an active internal absolute wavelength calibration (Cones and Cones, 1966). This feature of Fourier transform spectrometers is known as the ‘Cannes advantage’.

1.2.4.3 Detector

There are two detector commonly used depending upon the energy reaching the detector. The function of a normal detector for routine work is based on pyro electric effect. Crystals such as deuterium tri glycine sulphate in temperature resistant alkali halide window, with a permanent electric dipole moment respond to a sudden change in the dipolar order with the generation of compensating surface charges. The voltage accompanying the compensation charges can be used to detect the IR to the heat pulse.

The commonly used system is the Golay detector, which works under a pneumatic principle. A thin film absorbs the incident IR light. The generated heat increases the pressure in the gas chamber, which drives a mirror. The mirror is a part of an optical system that images a grating onto itself. Any small motion of the mirror leads to change in the overlap between grating and the image and thus gives a signal to the detector.

1.2.5 Sampling Methods in IR Spectroscopy

A wide range of sampling technique is available for mounting the sample. The technique depends on whether the sample is a gas, liquid, solid or polymer. Sampling techniques play an important role in recording IR spectrum. A choice of sampling technique is available for all states of matter depending on the applications.
Solids are usually examined as a mull, a pressed disc or as deposited glassy films. Mulls are prepared by grinding the solid and then suspending with 1-2 drops of mulling agent followed by grinding until the suspended particles are less than 2 cm. The mull is then examined as a thin film between flat salt plates. This technique has the advantage of speed but suffers many disadvantages. If the sample concentration is too low, the spectrum is due to mulling agent. On the other hand, if too much sample is used the mull will not transmit radiation. The commonly used mulling agents are nujol, hexa chloro butadiene and a drop of 3s oil (halogenated hydrocarbon) depending upon the spectral region.

1.2.5.1 Alkali Halide Disc

The solid is mixed with suitable dry alkali halide (100-200 mg) ground in a mortar or ball mill and subjected to a pressure of about 10 ton/sq. inch in an evacuated dye. This sinters the mixture and produces a clear transparent disc of diameter 10-15 mm. The advantage of this method over mull technique is that it eliminates the problem of bands, which appear due to mulling agent. The most commonly used alkali halide is KBr, which is transparent in the commonly scanning region. The commonly used other alkali halides are NaCl, CsI and CsBr.

1.2.5.2 Solutions

The sample can be dissolved in a solvent and the spectrum of this solution can be recorded. The solution (usually 5%) is placed in a solution cell, which has length of usually 0.1-1.0 mm. The solvent chosen must satisfy certain criteria; (i) It has to dissolve the compound (ii) It should be non-polar as possible, to minimize solute solvent interactions (iii) It should not react with the sample (iv) It should not
absorb IR radiation (v) It should be volatile and not viscous and (vi) It should be pure and dry CS₂, CCl₄, CHCl₃ and C₂H₂Cl₄ are some of the solvents commonly used.

1.2.5.3 Reflectance Method

The Reflectance technique is used for samples with low transmission, which cannot be analyzed by the normal transmittance method (Urban, 1996). This method depends on the total internal reflectance of light. The refractive index of the prism used for this purpose should be greater than refractive index of the sample and the angle of incidence of IR radiation is greater than the critical angle.

1.2.6 Limitations of Infrared Spectroscopy

The materials such as KBr, NaCl, LiF and the like do not yield characteristic IR absorption spectra. Hence, it is fortunate that they are useful as prisms, window materials and other optical components (Kendall, 1966). Molecules such as H₂, O₂, N₂ etc. will not yield any useful IR spectra because no change in dipole moment occurs during their lone stretching vibrations. The detectability limits of the usual IR quantitative procedure are not very great except for analytical methods relaying on absorption arising from vibration involving very high polar bonds between atoms. The inability to transfer quantitative analytical methods from one instrument to another, inspite of its make and model it has limitation. Optical isomers yield identical absorption spectra and therefore IR studies cannot distinguish between them.

1.3. RAMAN SPECTROSCOPY

A simple method for obtaining vibrational and rotational frequencies of molecule is through observation of Raman Effect. According to Raman, if any
substance, gas, liquid or solid is exposed to radiation of definite frequency, then the light scattered at right angles contains frequency different from the incident radiation, and is characteristic of the substance under examination. The scattered light was observed to have a slightly different frequency from that of incident light and there is a change in atomic oscillation within the molecule. If $v_i$ and $v_s$ are the frequencies of incident and that of scattered light respectively, then the difference $v = v_i - v_s$ is known as Raman frequency. The spectrum of the scattered light is made of lines of the incident light together with series of lines on either side of them. This series of lines in the scattered light is known as Raman Spectra. The Raman lines on the lower frequency side of the incident radiation are called stokes lines i.e., where $v_i > v_s$ and those on the higher frequency side are termed as anti-stokes lines i.e., $v_s > v_i$.

1.3.1. Raman Activity

For a molecular vibration to be Raman active, there must be a change in the polarizability of the molecule during this vibration. This change can be considered as being a change in the shape of the electron cloud surrounding the molecule (polarization ellipsoid). In a molecule without any symmetry elements, all the normal vibrations are accompanied by polarizability changes and the corresponding frequencies appear in the Raman spectrum. But in a symmetric molecule, some of these vibrations may not produce any change in polarizability and the corresponding normal frequencies are not observed. Such vibrations are Raman inactive. Raman spectrum gives information about molecular symmetry, which can then be used to determine the molecular configuration. There are various chemical problems, which have been successfully solved with the help of Raman spectra.
1.3.2. Selection rule for Raman spectra

The selection rule for the Raman spectrum is determined by the integral,

\[ [\mu']_{v'v''} = \int \psi_{v'}^* (Q_a) \mu' \psi_{v''} (Q_a) \, dQ_a \]  

(1.21)

The polarisability of the molecule \( \alpha \) consists of six components \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{xz} \) and \( \alpha_{yz} \). For the vibration to be Raman active, at least one of these integrals should be non-zero. If all the integrals are zero, the vibration is said to be Raman inactive.

1.3.3 Fourier Transform Raman Spectroscopy

1.3.3.1 Introduction to Raman Spectroscopy

As stated in the previous section, vibrational transitions can be observed in either IR or Raman spectroscopy. Although Raman is complementary to FT-IR, it is based on different principle. Where IR absorption is based on the changes in the dipole moment, Raman spectroscopy involves in elastically scattered light and is based on changes in the polarizability of the molecules. Fig.1.3 illustrates the differences between the two methods.

Fig. 1.3. Comparison of IR (absorption) and Raman (scattering) spectroscopy
1.3.3.2 The Principles of Raman Spectroscopy

Raman spectroscopy differs from the rotational and vibrational spectroscopy considered above in that it is concerned with the scattering of radiation by the sample, rather than an absorption process. It is named after the Indian physicist who first observed it in 1928, Sir. C. V. Raman. Both the rotational and the vibrational Raman spectroscopy is possible. The energy of the exciting radiation will determine which type of transition occurs - rotational transitions are lower in energy than vibrational transitions. In addition to this, rotational transitions are around 3 orders of magnitude slower than vibrational transitions. Therefore, collisions with other molecules may occur in the time in which the transition is occurring. A collision is likely to change the rotational state of the molecule and so the definition of the spectrum obtained will be destroyed. Rotational spectroscopy is therefore carried out on gases at low pressure to ensure that the time between collisions is greater than the time for a transition.

In Raman spectroscopy, a sample is irradiated by an intense source (usually a laser) in the UV-Vis or IR region and the scattered light is generally observed in a direction perpendicular to the incident beam. The scattered light consists of two types:

The elastic Rayleigh scattering is strong and has the same frequency as the incident beam ($\nu_0$). The inelastic Raman scattering is weak, approximately 10^5 times weaker than the incident beam and has frequencies of ($\nu_0 \pm \nu_m$) where $\nu_m$ is a vibrational frequency of a given molecule. In Raman spectroscopy, the $\nu_m$ is measured as a shift from the incident frequency ($\nu_0$) (Ferraro and Nakamoto,
1994). Stokes lines are those represented by the \((\nu_0 - \nu_m)\) shift, while the Anti-stokes lines are those represented by the \((\nu_0 + \nu_m)\) shift, the process of Raman scattering can be explained using electromagnetic theory.

The electric field strength \((\vec{E})\) of the laser beam fluctuates with time \((t)\):

\[
\vec{E} = \vec{E}_0 \cos 2\pi \nu_0 t
\]  
(1.22)

Where, \(\vec{E}_0\) the vibrational amplitude and \(\nu_0\) is the incident beam frequency. The simplest case is that of a diatomic molecule irradiated by this laser where an electric dipole moment \((P)\) is induced with the proportionality constant \((P)\) and is given by

\[
P = \alpha \vec{E} = \alpha \vec{E}_0 \cos 2\pi \nu_0 t
\]  
(1.23)

\(\alpha\) is known as the polarizability. If a given molecule vibrates with a frequency of \(\nu_m\) then the nuclear displacement \(q\) is given by the following equation:

\[
q = q_0 \cos 2\pi \nu_m t
\]  
(1.24)

Where, \(q_0\) is the vibrational amplitude. If the vibration has a small amplitude, then \(\alpha\): is a linear function of \(q\).

Therefore:

\[
\alpha = \alpha_0 + \left( \frac{\delta \alpha}{\delta q} \right)
\]  
(1.25)

The polarizability at the equilibrium point is given as \(\alpha_0\) where, \(\left( \frac{\delta \alpha}{\delta q} \right)\) is the rate of change of \(\alpha\) with respect to the change in \(q\), which is evaluated at the equilibrium position.
Combining all the above equations, the following relationships are obtained:

\[ P = \alpha \tilde{E}_0 \cos 2\pi v_0 t \]  
(1.26)

\[ P = \alpha_0 \tilde{E}_0 \cos 2\pi v_0 t + \left( \frac{\delta \alpha}{\delta q} \right) q \tilde{E}_0 \cos 2\pi v_0 t \]  
(1.27)

\[ P = \alpha_0 \tilde{E}_0 \cos 2\pi v_0 t + \left( \frac{\delta \alpha}{\delta q} \right) q_0 \cos 2\pi v_m t \tilde{E}_0 \cos 2\pi v_0 t \]  
(1.28)

\[ P = \alpha_0 \tilde{E}_0 \cos 2\pi v_0 t + \left( \frac{\delta \alpha}{\delta q} \right) q_0 \tilde{E}_0 \left( \cos (2\pi v_0 + v_m) t + \cos (2\pi v_0 - v_m) t \right) \]  
(1.29)

Therefore according to classical theory, the first term represents an oscillating dipole that radiates light of frequency \( v_0 \) (Rayleigh scattering), while the second term corresponds to Anti-stokes Raman scattering \( (v_0 + v_m) \) and the third term corresponds to stokes Raman scattering \( (v_0 - v_m) \).

If \( \left( \frac{\delta \alpha}{\delta q} \right) = 0 \), then the vibration is not Raman active, i.e. the rate of change of polarizability with respect to the vibration must be non-zero for the vibration to be Raman active (Cones and Cones, 1966).

1.3.4 Background for Raman Spectroscopy

FT-Raman spectrophotometer is designed to eliminate the fluorescence problem encountered in conventional Raman spectroscopy (Parker et al., 1988). The FT-Raman instrument has the following components: i) A Near Infrared (NIR) laser excitation source, generally an Nd:YAG (Neodymium-doped yttrium aluminum garnet) laser working at 1.06 cm, ii) an interferometer equipped with an appropriate beam splitter, made of glass and a detector for the NIR region. The detector is usually In Ga, As or Germanium semiconductor detector, iii) a sample
chamber with scattering optical that match the input port of the Fourier Transform instrument, iv) an optical filter rejection of the Rayleigh-scattering light. Block diagram of such an instrument is shown in Fig. 1.4.

Fluorescence is eliminated by utilizing an excitation frequency well below the threshold for any fluorescence process. To focus and align the invisible Nd:YAG laser beam visible Helium: Neon laser beam is co-aligned with the Nd:YAG beam. Another method of optical alignment can be realized by using fiber optics (Hendra, 2001), with fiber optic components, optical alignment is virtually eliminated which allows rapid switching from one sample to another. One of the advantage of Fourier Transform 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 Fourier Transform process and this is called as multiplexing disadvantage (Cutleer, 1990). Interferometer can be combined with Rayleigh line filters (notch filters) in order to prevent the consequences of the multiplex disadvantage. The Rayleigh line filter minimizes the amount of Rayleigh scattered light entering the interferometer (Hirschfeld and Chase, 1986) and is essential for FT-Raman spectroscopy.
1.3.5 Dual Instruments

Due to the rapid development in the instrumentation techniques, now-a-days both IR and Raman spectrophotometer are incorporated into a single instrument assembly and available commercially as a single package. The main advantages of such instruments are: i) Switching over from one technique to other is simple; ii) They are compact and iii) Comparatively cheaper. Bruker’s FT-IR spectrophotometer IFS 66/S filter with FRA 106/S. Thermo Nicolet’s Nexus/Magna FT-IR and FT-Raman systems, ABB Bomen MB157 series these are some of the commercially available dual instrument package.

1.3.6 Sampling Methods in Raman Spectroscopy

Gases, liquids and solids can be studied by Raman spectrometer. But the important thing to be taken care while preparing sample is that, they should be dust free. 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 (Colthup et al., 1964).
1.3.6.1 Solids

Solids 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 under various pressures and temperatures (Colthup et al., 1964).

1.3.6.2 Liquids

Liquids may be examined neatly in solution and normally liquids of about 0.3 ml enclosed in glass or silica containers of 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 (Schrader, 1995).

1.3.7 Uses of Raman Spectroscopy

Raman spectroscopy is useful for analyzing molecules without a permanent dipole moment, which would not show up on an IR spectrum. A useful 'exclusion rule' states that for molecules with an inversion center, no modes can be both in IR and Raman as active. It can be used to determine bond lengths in non-polar molecules. It is useful for determining the identity of organic and inorganic species in solution, as the Raman transitions for these species are more characteristic than for IR, where the transitions are much more affected by the other species present in the solution.
1.4 VIBRATIONAL ASSIGNMENTS AND GROUP FREQUENCY

The normal vibrations of a molecule are associated with appropriate Raman and IR frequencies and this process is referred to as vibrational assignment. The applications of IR and Raman spectroscopy rest largely on the correct assignment of the spectra. The assignment of the IR and Raman spectra is generally made on the basis of the group frequency concept. By comparison of the spectra of a large number of compounds, it has been observed that the presence of certain groups, for example C–H, O–H, N–H, C=O, C=N etc., in various molecules may be correlated with a constant occurrence of absorption bands in the IR spectra whose positions are only slightly altered on going from one compound to another. The atomic group vibrates independently from the other groups in the molecules and has its own frequency. These frequencies are called characteristics group frequencies (Sathyanarayana, 2004). The vibration of the functional group is assumed to occur independently from the rest of the molecule. A number of characteristic group absorptions have been established. The group frequency concept is extremely useful as an aid to the interpretation of vibrational spectra.

1.5. ULTRAVIOLET–VISIBLE SPECTROSCOPY

Ultraviolet-Visible (UV) spectroscopy or Ultraviolet-Visible spectrophotometry (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the UV-Vis spectral region. This means it uses light in the visible and adjacent (near-UV and NIR) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that
fluorescence deals with transitions from the excited state to the ground state, while absorption measure transitions from the ground state to the excited state (Skoog, 2007).

The principles of UV Centre on the fact that molecules have the ability to absorb UV or visible light. The absorption corresponds to the excitation of outer electrons in the molecules concerned. When a molecule absorbs energy an electron is promoted from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). It must be noted that occupied molecular orbitals (MOs) with the lowest energy are the σ orbitals, and then at a slightly higher energy are the π-orbitals and non-bonding orbitals (those with unshared pairs of electrons) at still a higher energy. The highest energy orbitals belong to π* and σ*, i.e. the unoccupied or as otherwise known as, the antibonding orbitals (Pavia 2003). The electronic energy levels and transitions are shown in Fig. 1.5.

![Diagram of electronic energy levels and transitions](image)

Fig. 1.5. Electronic energy levels and transitions
The schematic diagram of a double-beam UV-Vis spectrophotometer is shown in Fig. 1.6.

![Schematic diagram of a double-beam UV-Vis spectrophotometer](image)

**Fig. 1.6. Schematic diagram of a double-beam UV-Visible spectrophotometer**

### 1.5.1. Instrumental Components

#### 1.5.1.1. Sources of Visible Radiation

The tungsten filament lamp is commonly employed as a source of visible light. This type of lamp is used in the wavelength range of 350 - 2500 nm. The energy emitted by a tungsten filament lamp is proportional to the fourth power of the operating voltage. This means that for the energy output to be stable, the voltage to the lamp must be very stable indeed. Electronic voltage regulators or constant-voltage transformers are used to ensure this stability.

#### 1.5.1.2. Wavelength Selector (Monochromator)

All monochromators contain the following component parts:

- An entrance slit
- A collimating lens
- A dispersing device (usually a prism or a grating)
- A focusing lens
- An exit slit
Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.

1.5.1.3. Cuvettes

The containers for the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required for spectroscopy in the UV region. These cells are also transparent in the visible region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 and 2000 nm.

1.5.1.4. Detectors

The photomultiplier tube is a commonly used detector in UV-Vis spectroscopy. It consists of a photoemissive cathode (a cathode which emits electrons when struck by photons of radiation), several dynodes (which emit several electrons for each electron striking them) and an anode. A photon of radiation entering the tube strikes the cathode, causing the emission of several electrons. These electrons are accelerated towards the first dynode (which is 90V more positive than the cathode). The electrons strike the first dynode, causing the emission of several electrons for each incident electron. These electrons are then accelerated towards the second dynode, to produce more electrons which are accelerated towards dynode three and so on. Eventually, the electrons are collected
at the anode. By this time, each original photon has produced $10^6 - 10^7$ electrons. The resulting current is amplified and measured. Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers; they are limited to measuring low power radiation.

The **linear photodiode array** is an example of a multichannel photon detector. These detectors are capable of measuring all elements of a beam of dispersed radiation simultaneously. A linear photodiode array comprises many small silicon photodiodes formed on a single silicon chip. There can be between 64 to 4096 sensor elements on a chip, the most common being 1024 photodiodes. For each diode, there is also a storage capacitor and a switch. The individual diode-capacitor circuits can be sequentially scanned. In use, the photodiode array is positioned at the focal plane of the monochromator (after the dispersing element) such that the spectrum falls on the diode array. They are useful for recording UV-Vis absorption spectra of samples that are rapidly passing through a sample flow cell, such as in High pressure liquid chromatography detector.

**Charge-Coupled Devices** are similar to diode array detectors, but instead of diodes, they consist of an array of photo capacitors. UV-Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions highly conjugated organic compounds, and biological macromolecules.

### 1.6 NORMAL COORDINATE ANALYSIS

Detailed description of vibrational modes can be studied by means of NCA. NCA is a procedure for calculating the vibrational frequencies which relates the observed frequencies of preferably the harmonic IR and Raman frequencies to the
force constants, equilibrium geometry and the atomic masses of the oscillating system. NCA has proven useful in assigning vibrational spectra but its predictive ability depends on having reliable intra-molecular force constants. The problem of the normal vibrations of a polyatomic molecule is satisfactorily dealt with, in particular, for small molecules by the method of classical mechanics. The frequency of a molecular vibration is determined by its kinetic and potential energies. The molecular vibrations are assumed to be simple harmonic. Analysis of molecular vibrations from classical mechanics will give valuable information for the study of molecular vibrations by quantum mechanics because of the relationship between classical and quantum mechanics.

1.6.1 Structure of Molecule

Usually the structure of the molecule is available from X-ray studies or electron diffraction studies. In case the structure is not available it is assumed and the molecular parameters from the related systems are transferred.

1.6.2 Classification of normal modes

By applying group theory, the point group symmetry of the molecule and normal modes of vibrations are classified according to the irreducible representations. Further these vibrations are distributed to various symmetry species to which they belong. Applying IR and Raman selection rules, the number of genuine vibrations under each species is determined.

1.6.3 Internal Coordinates and Symmetry Coordinates

Internal coordinates are the changes in bond lengths and bond angles. The symmetry coordinates are constructed from the internal coordinates and they
should be normalized and orthogonalised. If \( R \) is a column matrix consisting of the internal coordinates and \( r \) is the column matrix of the Cartesian coordinates, then

\[
R = Br
\]  

(1.30)

where \( B \) is the transformation matrix of the order \((3n-6)*3N\), \( N \) being the number of atoms in the molecule. If \( U \) is the orthogonal transformation matrix and \( S \) is a column matrix of the symmetric coordinates, then \( S = UR \).

**1.6.4 Removal of Redundant Coordinates**

The number of internal coordinates must be equal to or greater than \( 3n-6 \) \((3n-5) \) degrees of vibrational freedom of molecule containing \( N \) atoms. If more than \( 3n-6 \) \((3n-5) \) coordinates are selected as the internal coordinates, it implies that these coordinates are independent of each other. In complex molecules it is very difficult to recognize a redundancy in advance. If a sufficient number of internal coordinates is used, the number of redundancies can be found by subtracting \( 3n-6 \) (the number of internal degrees of freedom) from the number of internal coordinates. However, essential internal coordinates may have been inadvertently omitted. If a molecule has any symmetry, these considerations can be applied separately to each species. The number of independent coordinates in each species can be obtained by reducing the representation formed by the Cartesian coordinates and subtracting the translations and rotations appropriately. The number of internal symmetry coordinates is similarly obtained for each species, and any excess represents redundancy. One of the common form of redundancies are also likely to appear in ring and these may involve the bond stretching coordinates as well as the bond angles. In the software developed for solving the vibrational secular equation,
the redundant coordinates dropout as zero roots of the secular equation when the symmetrized kinetic energy matrix is diagonalized.

1.6.5 Potential Energy Matrix

The potential energy ‘V’ of a molecule is the harmonic approximation and is given by the expression,

\[ 2V = \sum_{ij} f_{ij} r_{ij} \]  

(1.31)

where \( f_{ij} \) are the force constants. This equation can be written in the matrix form as,

\[ 2V = R' FR \]  

(1.32)

which becomes interms of symmetric coordinates as,

\[ 2V = S' FS \]  

(1.33)

where,

\[ F = U' FU \]  

(1.34)

R', S' and U' are the transposes of R, S and U - matrices respectively.

1.6.6 Kinetic Energy Matrix

The kinetic energy can be expressed in the form

\[ 2T = S' G^{-1} S \]  

(1.35)

where \( S' \) is the derivative \( \left\{ \frac{\partial s_i}{\partial r} \right\} \) of the \( j^{th} \) internal coordinate \( G^{-1} \) is the inverse kinetic energy matrix obtained from B - matrix

\[ G = BM^{-1} B' \]  

(1.36)

where \( M^{-1} \) is an inverse diagonal matrix of masses of the atoms of the molecule.

1.6.7 Secular Equations

After evaluation the elements of potential and kinetic energy matrices, the secular equation

\[ |FG - E\lambda| = 0 \]  

(1.37)
is to be solved for evaluating the potential energy constants. In the above equation 
E is the unit matrix and \( \lambda \) is a diagonal matrix and it is related to the frequencies as 
\[
\lambda_k = 4\pi C^2 v_k^2
\] 
(1.38)

1.6.8 Force Constant Refinement Process

It is very difficult to solve the unsymmetrical FG - matrix in the secular 
equation. Cyvin's W – matrix method is followed to overcome this difficulty.

The G matrix is factorised into a non singular matrix such that

\[
G = PP'
\] 
(1.39)

where \( P \) is an upper triangular matrix

\( P' \) is a lower triangular matrix

A trial F - matrix is set up by transferring the force constants from the 
molecules of similar environment and by diagonalising the W - Matrix. \( W = P' FP \) 
and the values are obtained.

The process of successive approximation is continued till all the calculated 
frequencies are in good agreement with the observed values. This method 
introduces several non-vanishing off-diagonal elements in the \( F \) matrix, which are 
useful in calculating interaction force constants.

1.6.9 Computation of L Matrix

L-Matrix is obtained from the force field by factorising the symmetrised G 
- matrix into a product of triangular matrices T and T' 

\[
G = PP'F
\]
\[ G = LL' \]  \hspace{1cm} (1.40)

\[ L = PO \]

where \( O \) is an orthogonal matrix.

The secular equation \( |FG - E\lambda| = 0 \) can be written in the form

\[ LFL = \Lambda \]

\[ P'O'FPO = \Lambda \]  \hspace{1cm} (1.41)

\[ O'(P'FP)O = \Lambda \]

\[ O'WO = \Lambda \]

Here \( \Lambda \) is a diagonal matrix containing eigen values of \( \lambda \) and \( P'FP \) is already defined. The \( O \) - matrix is obtained by diagonalising the \( W \) - matrix so as to give the elements of matrix.

**1.6.10 Potential Energy Distribution**

In order to get the complete and accurate picture of the normal modes of vibrations, the potential energy distribution (PED) has to be calculated in the present investigation using the relation,

\[ \text{PED} = \frac{F_{ii}L^2_{ia}}{\lambda_a} \]  \hspace{1cm} (1.42)

where \( F_{ii} \) is the potential energy constant

\[ L_{ia} \] is the \( L \) matrix element and

\[ \lambda_a \] is equal to \( 4\pi^2c^2v_a^2 \)
1.6.11 SCALING OF *AB INITIO* FORCE FIELDS BY MOLVIB

Quantum mechanical methods yield harmonic force constants. On the other hand, the observed frequencies are anharmonic, but are possible to calculate the harmonic frequencies of small molecules from the observed vibrational spectra.

NCA is now-a-days commonly employed as an aid in the interpretation of the vibrational spectra of large molecules. In order to get meaningful results, knowledge of vibrational force field is necessary. Since the number of force constants grow quadratically with the number of atoms, one has to employ many approximations in the calculation of harmonic force field even for moderately large molecules. To overcome this difficulty, one can determine a force field for a set of related molecules using the overlay method introduced by Snyder and Schachtschneider in the 1960's (Schachtschneider, 1963). Gwinn developed a program for NCA using massweighted Cartesian coordinates (Gwin, 1977) which eliminates the redundancy problems arising when internal valance coordinates are used as in Wilson's GF-method. Molvib (Sundius, 1980; Sundius 1990) a Fortran program is based on the above idea developed for the calculation of harmonic force fields and vibrational modes of molecules with upto 30 atoms. All the calculations are performed interms of mass weighted Cartesian coordinates, instead of internal coordinates as in the conventional GF-method. This makes it possible to overcome problems with redundant coordinates. The force field is refined by a modified least squares fit of observed normal frequencies.

Molvib can be used for the scaling of vibrational force fields by treating the scale factors as ordinary force constants. They can thus be calculated from a least
squares fit of the calculated and observed frequencies (Sundius, 2002). To perform the scale factor calculations, the program needs the atomic coordinates, and the Cartesian force constants from an ab initio calculation. An auxiliary program (Rdarch) is used to extract these data from the archive part of the out file of ab initio calculations. In addition, this program can also extract the dipole derivatives and the polarization derivatives, which are needed for intensity calculations. Molvib will convert the gaussian force constants, which are expressed in atomic units into the units used by the program. Since the optimal values of the scale factors usually are less than 1, it is good to start with an initial calculation, where all the scale factors have been set to 1, and check that Molvib can reproduce the frequencies calculated by the ab initio program.

In Molvib, three methods are available for the scale factor calculations. In two of these methods, the non diagonal terms in the potential energy will depend non-linearly on the scale factors as,

$$2V = \sum_k S_{ifijq}q + \sum_i \sum_{j \neq 1} \sqrt{S_i S_j} f_{ijq} q_i q_j$$  \hspace{1cm} (1.43)

The factor $\sqrt{S_i S_j}$ that occurs in front of the non-diagonal force constant has to be repeated. The frequency fit usually converges in four or five iterations, and often just a few repetitions are necessary. The initial values for the scale factors are set to 1. It is also possible to use individual scale factors for the non-diagonal force constants. In this case, scale factors should be associated both with diagonal and non-diagonal terms. Similar ideas have been proposed by Blom and Altona (Parr et al., 1989). However, too many different scale factors should not be used in this
case, but instead group similar factors together, so that the total number of scale factors must be very minimum. The scale factors are calculated from a least square fit of the observed vibrations in a similar way as the force constants.

1.7. GAUSSVIEW

Gaussview is an affordable, full-featured graphical user interface for Gaussian 03W. With the help of Gaussview, one can prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. The first step in reducing a Gaussian input file is to build the desired molecule. The bond lengths, bond angles and dihedral angles for the molecule will be used by Gaussview to write a molecular structure for the calculation.

Gaussview incorporates an excellent Molecule Builder. One can use it to rapidly sketch in molecules and examine them in three dimensions. Molecules can be built by atom, ring, group, amino acid and nucleoside. Gaussview is not integrated with the computational module of Gaussian, but rather is a front-end/back-end processor to aid in the use of Gaussian. Gaussview can graphically display a variety of Gaussian calculation results, including the following:

- Molecular orbitals
- Atomic charges
- Surfaces from the electron density (ED), electrostatic potential and other properties. Surfaces may be displayed in solid, translucent and wire mesh modes.
- Surfaces can be colored by a separate property.
- Animation of the normal modes corresponding to vibrational frequencies.
Animation of the steps in geometry optimizations, potential energy surface scans and molecular dynamics trajectories from BOMD and ADMP calculations.

1.8 *AB INITIO METHODS*

*Ab initio* MO methods are useful to predict harmonic force constants and frequencies of normal modes. The *ab initio* methods first optimize the molecular geometry and then evaluate the second derivative at the equilibrium positions usually using analytical derivatives. Such methods provide reliable values for harmonic vibrational for fairly large sized molecules. Additionally, such calculations can be used to predict barriers to internal rotation as well as relative stabilities of different conformers. The information obtained from structural parameters, conformational stabilities, force constants, vibrational frequencies as well as IR and Raman band intensities gives significant contributions to the field of vibrational spectroscopy.

Harmonic force constants in Cartesian coordinates can be directly derived from *ab initio* calculations. These force constants can be transformed to force constants in internal or symmetry coordinates. *Ab initio* calculations followed by NCA are very helpful in making reliable vibrational assignments. Band intensities from *ab initio* studies are another important output. Such band intensity data can also be very useful in making vibrational assignments. Two principally different quantum mechanical methods addressing the vibrational problems are namely Hartree-Fock (HF) and Density Functional Theory (DFT) method.
DFT calculation has emerged in the past few years as a successful alternative to traditional HF method. The DFT method, particularly hybrid functional methods (Castella-Ventura, 2000; Shin, 1998; Giese, 2002; Parr, 1989) have evolved a powerful quantum chemical tool for the determination of the electronic structure of molecules. In the framework of DFT approach, different exchange and correlation functionals are routinely used. Among these, the Becke-3-Lee-Yang-Parr (B3LYP) combination (Becke, 1993; Lee et al., 1988) is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and standard various basis sets, provide an excellent compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational frequencies calculated by applying DFT methods are normally overestimated than experimental values by 2-5% on an average. This overestimation is due to the neglect of electron correlation, anharmonicities, and incomplete basis sets.

This overestimation can be narrowed down by empirical scaling factors ranging from 0.8 to 1.0. The scaling factors depend both on method and basis sets and they are partially compensated for the systemic errors in the calculation of frequencies. Selective scaling, multiple scaling are some scaling methods advocated to minimize the overestimation of the frequency differences. Ab initio calculation could be performed using GAUSSIAN 03W software package (Frisch et al., 2009).

If the quantum-mechanical force field is not corrected, especially in the case of large deviations from the experimental results, this omission can
complicate the theoretical analysis of the vibrational spectrum of a molecule and lead to errors in the assignment of the experimental frequencies. Therefore, determining empirical corrections to quantum mechanical force fields is important. It is shown that (Panchenko et al., 1995; Panchenko, 1997; Panchenko, 1996) of all the method for empirically correcting quantum-mechanical force fields, the one with the best physical basis is the modern version of the Pulay method.

1.8.1 COMPUTATIONAL DETAILS

Development of the performance of computers and the theory has made computational simulations as important tools today; increasingly accurate results can be obtained in a reasonable time for even large and complicated molecular systems. Modeling molecular properties is an important aspect of the quantum mechanical based electronic structure theory calculations (Jensen, 1999; Cramer, 2004; Levine, 2004). The electronic structure methods broadly fall into two methods: semi-empirical methods, \textit{ab initio} and DFT methods. Semi-empirical methods use parameters derived from experimental data to simplify the computation. They solve an approximate form of the Schrödinger equation that depends on having appropriate parameters available for the type of chemical system under investigation.

\textit{Ab initio} methods use no experimental parameters in their computations and are based solely on the laws of quantum mechanics and use only physical constants like speed of light \((c)\), masses \((m)\), charges of the electrons and nuclei \((e)\) and Plank’s constant \((h)\). They compute solutions to the Schrodinger equation using a series of rigorous mathematical approximations. Ab initio computations
provide high quality and quantitative predictions for a broad range of system and are not limited to a class of molecules. The simplest type of \textit{ab initio} electronic structure calculation in the HF scheme, in which the Columbic electron-electron repulsion is not specifically taken into account; only its average effect is included in the calculation.

DFT is a quantum mechanical method used in physics and chemistry to investigate the electronic structure theory, in particular HF theory and its descendants, are based on the complicated many electron wave functions. The main objective of DFT is to replace the many-body electronic wavefunction with the electronic density as the basic quantity (Foreman et al., 1993), whereas the many-body wavefunction is dependent on 3N variables, three spatial variables for each of the N electrons, the electronic density is only a function of three variables and is a simpler quantity to deal with body conceptually and practically (Jensen, 1999; Cramer, 2004; Ira et al., 2004; Foreman et al., 1993; Hehre, 1986; Hohenberg et al., 1964; Kohn, 1965).

The most common implementation of DFT is through the Kohn-Sham (Kohn et al., 1965) method. Within the framework of Kohn-Sham DFT, the intractable many-body problem of interacting electrons in a static external potential which is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential which is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Columb interactions between the electronic, e.g. the exchange and correlation
interactions. Since the electronic density is not known explicitly, many functions have been defined to calculate electronic density of the system.

They are broadly classified into Local Density Approximations (LDA) methods (eg.: SVWN which takes into account a local spin density exchange by Slater, combined with the correlations function of Vosko, Wilk and Nusair); Generalized Gradient Approximation (GGA) methods (e.g. BLYP Slater exchange along with corrections involving the gradient of the density combined with the correction function of Lee-Yang and Parr); PW91 (with the non-local correlation provided by Perdew/Wang 91 correction functional); PW86 (the Perdew 86 correction functional) etc; Hybrid methods (e.g. B3LYP: Becke’s three parameter hybrid functional combined with Lee-Yang-Parr correlation functional); BP86 (Becke’s 1988 exchange functional combined with the gradient-corrected correction function of Perdew); B3P86 (Becke’s three parameter hybrid method with the non-local correlation provided by Perdew/Wang 91 expression) etc (Jensen, 1999; Cramer, 2004; Ira et al., 2004; Foreman et al., 1993; Hehre, 1986; Hohenberg et al., 1964; Kohn, 1965).

The acronyms like GGA, VWN (Vosko, Wilk and Nusair) etc are generic names in practice. The most popular method to calculate electronic density is the hybrid method and B3LYP is one of the most popular hybrid methods. In B3LYP method, three parameter have been used to give satisfied theoretical results compared to the experimental results in many cases. In all of these approaches, in addition to the choice of method, it is necessary to choose a basis set.
1.8.2 Basis Sets

A basis set is used to form a mathematical representation of the MOs. To exactly represent the MOs, the basis functions should form a complete set. This requires an infinite number of basis functions, while in practice, a finite number are used (Levine, 1991). MOs are expressed as the linear combinations of a predefined set of one-electron functions known as basis functions. An individual molecular orbital (MO) is defined as:

$$\phi_i = \sum_{\mu=1}^{N_i} c_{i\mu} \chi_\mu$$ (1.44)

Where $c_{i\mu}$ are known as MO expansion coefficients. The basis functions, $X_i, \ldots, X_N$, are usually chosen to be normalized. Gaussian and most other ab initio programs use Gaussian-type functions for their basis sets. These Cartesian Gaussian functions have the general form:

$$g(\alpha, \tilde{r}) = cx^n y^m Z^l e^{-ar^2}$$ (1.45)

Where $\tilde{r}$ is composed of $x$, $y$, and $\alpha$ is a constant determining the size (radial extent) of the function. The constant of normalization ($c$) is determined by:

$$\int_{all \ space} g^2 = 1$$ (1.46)

The normalization constant therefore depends on $\alpha$, $l$, $m$, and $n$. Linear combinations of the primitive Gaussians as seen above are used to form the actual basis functions called the contracted Gaussians which have the form:

$$X_\mu = \sum_p d_{\mu p} g_p$$ (1.47)

Where $d_{\mu p}$ are fixed constants within a given basis set. These functions are also normalized. Therefore the MOs for a basis set can be described as:
It is essential to understand basis sets because they are the foundation of modern \textit{ab initio} techniques (Foreman and Frisch, 1993). The size and quality of the basis set used in an \textit{ab initio} calculation largely determines the quality of the final result. Many basis sets have been optimized and tested over the years. A minimal basis set has one Slater-Type Orbital (STO) per atomic orbital. Each STO is then approximated as a linear combination of \( N \) Gaussian functions, where the coefficients are chosen to give the best least-squares fit to the STO. Most commonly, \( N=3 \), which gives the basis set STO-3G. Therefore the minimal basis set of Slater-Type Orbitals (STOs) for a compound containing only first-row elements and hydrogen is denoted by (2s lp/ls) (Evine, 1991).

A basis set can be improved by increasing the number of basis functions per atom. Polarized basis sets allow for the addition of orbitals with angular momentum beyond what is required for the ground state description of each atom; this allows for flexibility in different bonding situations. The polarized basis set 6-31G* is a basis set that adds d polarization functions on each non-hydrogen atom. The 6-31G** basis set adds p functions to the hydrogens as well. The 6-31+G** basis set adds diffuse functions (+) to the non-hydrogen atoms, which are important for systems with lone pairs, anions, and some excited states, as well as the polarization functions. The 6-311G** basis set is commonly used for electron correlation calculations on molecules containing first-row atoms. The 6-311G** basis set, which is single zeta for the core and triple zeta for the valence atomic orbitals, contains five d-type Gaussian polarization functions on each non-

\[
\varphi_i = \sum_{\mu} C_{\mu i} X_\mu = \sum_{\mu} C_{\mu i} \left( \sum_{\nu} d_{\mu \nu} g_\nu \right)
\] (1.48)
hydrogen atom and three p-type polarization functions on each hydrogen atom (Cizek, 1960). Even larger basis sets are available which add multiple polarization functions per atom the triple zeta basis set (Foreman and Frisch, 1993) or additional functions for the valence shell.

1.8.3 Density Functional Theory

DFT has become one of the most frequently used tools in quantum chemistry for the description of atoms, molecules, and chemical reaction systems. An impressive number of applications of DFT have proven its usefulness and reliability (Pople et al., 1987). The DFT approach is based upon a strategy of modeling electron correlation via general functional of the ED.

Computational methods based on DFT are attractive because they tend to be less resource intensive than conventional ab initio calculations and Quadratic Configuration Integral Spin Density (QCISD) while also taking into account the effects of electron correlation. DFT was established by W. Kohn and L. Sham (1965), who showed that the ED could be used as a fundamental quantity to develop a rigorous many-body theory. DFT is different from HF since it replaces the exchange-correlation energy by a one-electron integral involving the local electron spin densities or by an integral involving these spin densities and their gradients. When these functionals are used in conjunction with the Kohn-Sham (KS) procedure (Kohn and Sham, 1965) and an expansion of the KS orbitals in terms of a basis set, then the techniques become analogous to conventional HF theories with the addition of electron correlation (Johnson et al., 1993).
Formal DFT methods are based on the LDA given by the following equation, where $\rho(r)$ is the ED:

$$E_{xc}^{LDA}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})) d\vec{r}$$

(1.49)

where $\varepsilon_{xc}(n)$ is the accurately known exchange-correlation energy per particle of a uniform electron gas of density $n$. The LDA is exact for a homogeneous system and arbitrarily accurate for a system with varying density. Therefore LDA is the most basic approximation for $E_{xc}$ since it requires only the energy ($\varepsilon_{xc}$) of the uniform electron gas and is found to yield only fair agreement with experimental molecular properties. The local spin-density approximation (LSDA) is an improvement on LDA since it uses different orbitals and different densities for electrons with different spin (Levine, 1991). A better functional would exhibit effects of the inhomogeneity of the ED, since atoms and molecules do have inhomogeneous Electron densities (EDs), but this effect is ignored in the LDA model. The addition of gradient corrections to the LDA model allows for better modeling of the ED (Parr, et al., 1989) A gradient-corrected DFT method calculates not only the magnitude of the density, but also considers how rapidly the density is changing about a point in space. The more common hybrid DFT methods incorporate some HF exchange with the ED calculation (University of Minnesota, 1997) which includes gradient corrections.

The functionals that are used in DFT are separated into exchange and correlation parts. The exchange part can be either Slater (S), which corresponds to a free-electron gas, or Becke (B), which includes a gradient correction. The correlation part can either be ignored or treated with the VWN (Vosko et al., 1980)
parameterization for exact uniform gas results or treated with the gradient corrected functional of Lee, Yang, and Parr (LYP) (Lee et al., 1988). A common gradient corrected DFT method uses the Becke Yang Parr (BLYP) functionals which combines a local exchange functional with the gradient correction from Becke and uses the LYP correlation functional. The Becke’s three parameter hybrid functionals B3LYP method differs from the BLYP method because it utilizes a functional that is a hybrid of exact (HF) exchange with local and gradient-corrected exchange and correlation terms (Stephens, 1994). DFT methods are appealing for many types of molecules because they can provide results that are as accurate as conventional methods, but DFT is much less resource intensive than such methods as Moller-Plesset, Coupled Cluster, and QCISD (Foreman and Frisch, 1993). Current evidence (Parr and Yang, 1989; Scott and Random, 1996) suggests that vibrational frequencies calculated using DFT is close to those found by experiment.

All electronic structure calculations can be performed using Gaussian 03W suite of programs (Gaussian 03W, 2004). The software Gaussian 03W is capable of predicting many properties of molecules and reactions. They are:

- molecular energies and structures;
- energies and structures of transition states;
- bond and reaction energies;
- molecular orbitals;
- multipole moments;
- atomic charges and electrostatic potential;
- vibrational frequencies and
- IR and Raman spectra.

The Gaussian 03W program accepts molecular specifications in several different formats, like Cartesian coordinates, Z-matrix format (internal coordinates) and mixed internal and Cartesian coordinates. All molecular specifications require the charge and spin multiplicity.

1.8.4 Geometry optimization

The majority of molecules studied in this thesis have unknown or unconfirmed structures. A geometry optimization can be used to locate minima on a Potential energy surface scan (PES) and can predict the equilibrium structure of the molecule in question. A point on a PES where the forces are zero is called a stationary point and these are the points generally located during an optimization. Whether these points are local or global minima, or even transition states, is another matter (Fig. 1.7)

![Potential energy curve](image)

Fig. 1.7. Potential energy curve
An input geometry is provided for geometry optimization and the calculation proceeds to move across the PES. At each point the energy and the gradient are calculated and the distance and direction of the next step are determined. The force constants are usually estimated at each point and these constants specify the curvature of the surface at that point; this provides additional information useful to determining the next step. Convergence criteria about the forces at a given point and the displacement of the next step determine where a stationary point has been found (Foreman and Frisch, 1993). To determine whether the geometry optimization has found a minimum or a transition state, it is necessary to perform frequency calculations. Transition state is a point that links two minima on the PES (Fig. 1.7) and is characterized by one imaginary frequency. The eigenvector from the Hessian force constant matrix determines the nature of the imaginary frequency and indicates a possible reaction coordinate. A minimum structure will have no imaginary frequencies. Distinguishing local minima from global minima relies on chemical intuition and a thorough search of alternative structures.

1.8.5 Frequency Calculations

Frequency calculations yield some of the most important information discussed in this thesis. IR and Raman spectra of molecules can be predicted for any optimized molecular structure. The position and relative intensity of vibrational bands can be gathered from the output of a frequency calculation. This information is independent of experiment and can therefore be used as a tool to confirm peak positions in experimental spectra or to predict peak position and intensities when experimental data is not available. Calculated frequencies are
based on the harmonic model, while real vibrational frequencies are anharmonic. This partially explain discrepancies between calculated and exprimental frequencies.

1.8.6 Calculation of Harmonic Vibrational frequencies

The total energy of a molecule comprising N atoms near its equilibrium structure may be written as

$$E = T + V = \frac{1}{2} \sum_{i=1}^{3N} q_i^2 + V_{eq} + \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{eq} q_i q_j$$  \hspace{1cm} (1.50)

Here the mass-weighed Cartesian displacements, $q_i$, are defined in terms of the locations $X_i$ of the nuclei relative to their equilibrium positions $X_{i, eq}$ and their masses $M_i$,

$$q_i = M_i^{1/2} (X_i - X_{i, eq})$$  \hspace{1cm} (1.51)

$V_{eq}$ is the potential energy at the equilibrium nuclear configuration and the expansion (1.50) of a power series is truncated at second order (Schrader, 1995). For each such a system, the classical mechanics equation of motion takes the form

$$q_i = \sum_{j=1}^{3N} f_{ij} q_j \quad j = 1, 2, 3...3N$$  \hspace{1cm} (1.52)

The $f_{ij}$ term quadratic force constants are the second derivatives of the potential energy with respect to mass-weighed Cartesian displacement, evaluated at the equilibrium nuclear configuration, that is

$$f_{ij} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{eq}$$  \hspace{1cm} (1.53)
The \( f_{ij} \) may be evaluated by numerical second differentiation,

\[
\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\Delta (\Delta V)^{\epsilon}}{\Delta q_i \Delta V_{q_j}}
\]  \hspace{1cm} (1.54)

By numerical first differential of analytical first derivatives,

\[
\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\Delta (\partial V / \partial q_i)}{\Delta q_i}
\]  \hspace{1cm} (1.55)

or by direct analytical second differentiation, Eq (1.55). The choice of procedure depends on the quantum mechanical model employed, that is, single-determinant or post-Hartree-Fock, and practical matters such as the size of the system.

Equation (1.52) may be solved by standard methods (Arnett and Larsen, 1969) to yield a set of 3N normal-mode vibrational frequencies. Six of these (Five for linear molecules) will be zero as they corresponding to translational and rotational (rather than vibrational) degrees of freedom.

1.9 MOLECULAR ORBITAL

The MO theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. Because electrons are the fundamental constituents of matter involved in bonding, their involvement in bonding has been studied constantly by chemists. Electrons are shared among individual atoms in a molecule to form covalent chemical bonds. Generally, up to three bonds can be formed between atoms in a molecule. Single, or sigma covalent bonds result from the interaction between the nuclei of two discrete atoms;
multiple bonds then can result due to the additional formation of \( \pi \)-bonds between overlapping orbitals of like symmetries. Electrons in \( \sigma \) bonds are located between the nuclei, while electrons in \( \pi \)-bonds are delocalized in regions above and below the nuclei. The spatial and energetic properties of electrons within atoms are fixed by quantum mechanics to form orbitals that contain these electrons. While atomic orbitals contain electrons within a single atom, MOs, which surround a number of atoms in a molecule, contain valence electrons between atoms. The MO theory, which was proposed in the early twentieth century, revolutionized the study of bonding by approximating the positions of bonded electrons, the MOs as Linear Combinations of Atomic Orbitals (LCAO). These approximations are made by applying the DFT and HF models to the Schrödinger equation.

The MO theory applies the wave like behavior of electrons as predicted by quantum mechanics, in that electrons no longer deterministically are given defined coordinates, but rather are given probable locations according to the mathematical wavefunction defining all the possible positions of the electrons. These wavefunction or electron eigen states, quantitatively describe the atomic orbital basis in which an electron temporarily can reside. The MOs result from the mixing of these atomic orbitals. In this theory, each molecule has a set of MOs, in which it is assumed that the MO wave function \( \psi_j \) can be written as a simple weighted sum of the \( n \) constituent atomic orbitals \( \chi_i \), according to the following equation:

\[
\psi_j = \sum_{i=1}^{n} c_{ij} \chi_i.
\]  

(1.56)
1.10 NON LINEAR OPTICAL PROPERTY

Analysis of organic compounds having conjugated π-electron systems and large hyperpolarizability using IR and Raman spectroscopy has evolved as a subject of research. The potential application of the title molecule in the field of non-linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement by analyzing the vibrational modes using IR and Raman spectroscopy.

The first hyperpolarizability ($\beta_0$) of this novel molecular system and related properties ($\beta$, $\alpha_0$, $\mu$ and $\Delta\alpha$) of some polyatomic molecules are being calculated based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry, (1962). It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrices is a tetrahedral. The components of $\beta$ are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma$$  \hspace{1cm} (1.57)

Where $E^0$ is the energy of the unperturbed molecules, $F_\alpha$ is the field at the origin $\mu_\alpha$, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizability, respectively. The total static dipole moment $\mu$, the mean
polarizability $\alpha_0$, the anisotropy of the polarizability $\Delta \alpha$ and the mean first hyperpolarizability $\beta_0$, using the x, y, z components they are defined as:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\Delta \alpha = 2^{-1/2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right]^{1/2}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_x = \beta_{xxx} + \beta_{xxy} + \beta_{xxz}$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yyz}$$

$$\beta_z = \beta_{zzz} + \beta_{xzz} + \beta_{yzz}$$

1.11 NATURAL BOND ORBITAL

The Natural bond orbital (NBO) is a calculated bonding orbital with maximum ED. The Natural bond orbitals (NBOs) are one of the sequences of natural localized orbital sets that include "natural atomic orbitals" (NAO), natural hybrid orbitals" (NHO), "natural bonding orbitals" (NBOs) and "natural (semi-)localized molecular orbitals" (NLMO). These natural localized sets are intermediate between basis atomic orbitals and MOS:

Atomic orbital$\rightarrow$ NAO$\rightarrow$ NHO$\rightarrow$ NBO$\rightarrow$ NLMO$\rightarrow$ Molecular orbital

Natural (localized) orbitals are used in computational chemistry to calculate the distribution of ED in atoms and in bonds between atoms. They have the "maximum occupancy character" in localized 1-center and 2-center regions of the molecule. The NBOs include the highest possible percentage of the ED, ideally
close to 2.000, providing the most accurate possible “natural Lewis structure” of ψ. A high percentage of ED (denoted % - ρL), often found to be >99% for common organic molecules, correspond with an accurate natural Lewis structure.

Each bonding NBO σAB (the donor) can be written in terms of two directed valence hybrids (NHOs) hA, hB on atoms A and B, with corresponding polarization coefficients cA, cB:

\[ \sigma_{AB} = c_A h_A + c_B h_B \]  \hspace{1cm} (1.65)

The bonds vary smoothly from covalent (cA = cB) to ionic (cA>>cB) limit.

Each valence bonding NBO σ must be paired with a corresponding valence anti-bonding NBO σ* (the acceptor) to complete the span of the valence space:

\[ \sigma_{AB}^* = c_A h_A - c_B h_B \]  \hspace{1cm} (1.66)

The bonding NBOs are of the "Lewis orbital"-type (occupation numbers near 2); antibonding NBOs are of the "non-Lewis orbital"-type (occupation numbers near 0). In an idealized Lewis structure, full Lewis orbital’s (two electrons) are complemented by formally empty non-Lewis orbitals. Weak occupancies of the valence anti-bonds signal irreducible departures from an idealized localized Lewis structure, which means true "delocalization effects”.

With a computer program that can calculate NBOs, the optimal Lewis structures can be found. An optimal Lewis structure can be defined as that one with the maximum amount of electronic charge in Lewis orbital’s (Lewis charge). A low amount of electronic charge in Lewis orbitals indicates strong effects of electron delocalization.
1.12 ELECTROSTATIC POTENTIAL MAPS

An electrostatic potential map, also known as electrostatic potential energy maps or molecular electrical potential (MEP) surfaces, illustrates the charge distributions of molecules three dimensionally. These maps allow us to visualize variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another.

Electrostatic potential maps are very useful three-dimensional diagrams of molecules. They enable us to visualize the charge distributions of molecules and charge related properties of molecules. They also allow us to visualize the size and shape of molecules. In organic chemistry, electrostatic potential maps are invaluable in predicting the behavior of the complex molecules.

1.13 HOMO-LUMO

The highest occupied molecular orbital (HOMO) is the molecular orbital of highest energy that is occupied by electrons. The lowest unoccupied molecular orbital (LUMO) is the molecular orbital of lowest energy that is not occupied by electrons. The HOMO and LUMO are important in determining such properties as molecular reactivity and the ability of a molecule to absorb light. A number of approaches can be used to determine the sites of reactivity in a molecule. The choice of approach will depend on the size, type of the molecule and the type of reaction. Atomic Partial charges are useful in reactions that are charge controlled (e.g. Protonations/deprotonations). Electrostatic Potentials can be used where polar reagents are involved. The largest lobes of the Homo and Lumo work best for reactivity prediction when these orbital are well-separated in energy from the other MO. With larger molecules the energy difference between the Homo and Lumo,
and the other MO becomes smaller. The MO close in energy to the Homo or Lumo help to determine the reactivity, and various reactivity indices (electrophilic, nucleophilic, or radical susceptibilities, depending on the molecule) can be calculated.

Besides the traditional reactivity descriptors, such as HOMO & LUMO, there are certain other chemical reactivity descriptors such as electronegativity ($\chi$), global hardness ($\eta$), global softness ($s$) and global electrophilicity ($\omega$) which are defined by Koopman’s theorem (Hauptvogel et al., 2007 and Silverstein et al., 1981) as follows.

Electronegativity ($\chi$) is a measure of the power of an atom or a group of an atom to attract electrons and can be calculated from HOMO-LUMO as

$$\chi = \frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (1.67)$$

Global hardness ($\eta$) is a measure of the resistance of an atom to charge transfer and it can calculated as

$$\eta = \frac{1}{2}(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (1.68)$$

The global softness ($S$) describes the capacity of an atom or a group of atoms to receive electrons and is equal to reciprocal of global hardness.

$$S = \frac{1}{\eta} = -2(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (1.69)$$

The global electrophilicity index ($\omega$) can be calculated from the electronegativity and chemical hardness using the relation

$$\omega = \frac{\chi^2}{2\eta} \quad (1.70)$$
1.14 MULLIKEN POPULATION ANALYSIS

Mulliken populations can be used to characterize the electronic charge distribution in a molecule and the bonding, anti-bonding, or non-bonding nature of the MOs for particular pair of atoms (Mulliken, 1955). To develop the idea of these populations, consider a real, normalized MO composed from two normalized atomic orbitals.

\[ \Psi_i = C_{ij}\phi_j + C_{ik}\phi_k \]  \hspace{1cm} (1.71)

The charge distribution is described as a probability density by the square of this wave function.

\[ \Psi^2 = C_{ij}^2\phi_j^2 + C_{ik}^2\phi_k^2 + 2C_{ij}C_{ik}\phi_i\phi_j \]  \hspace{1cm} (1.72)

Integrating over all the electronic coordinates and using the fact that the MO and atomic orbitals are normalized:

\[ 1 = C_{ij}^2 + C_{ik}^2 + 2C_{ij}C_{ik}S_{jk} \]  \hspace{1cm} (1.73)

Where, \( S_{jk} \) is the overlap integral involving the two atomic orbitals.

Mulliken's interpretation of this result is that one electron in MO \( \Psi_t \) contributes \( c_{ij}^2 \) to the electronic charge in atomic orbital \( \phi_j \), \( C_{ik}^2 \) to the electronic charge in atomic orbital \( \phi_k \), and \( 2C_{ij}C_{ik}S_{jk} \) to the electronic charge in the overlap region between the two atomic orbitals. Here therefore called \( c_{ij}^2 \) and \( c_{ik}^2 \), the atomic orbital populations, and \( 2C_{ij}C_{ik}S_{jk} \) the overlap population. The overlap population is \( >0 \) for a bonding MO, \( <0 \) for an anti-bonding MO, and \( 0 \) for a non-bonding MO.

1.15 THERMODYNAMIC PARAMETERS

At rigid molecules approximation there can be determined a number of thermodynamic parameters: formation enthalpy \( H \), specific heat capacity at
constant volume $C_v$, entropy $S$ by neglecting the anharmonicity of fluctuations and some other effects (McQuarrie and Simon, 1999).

The formation enthalpy $H$ is defined as follows

$$H \approx H_{elec} + H_{vib}^0 + \Delta_{vib} (T) + H_{rot} (T) + H_{trans} (T) + RT$$  (1.74)

Where $H_{elec}$-electronic part of enthalpy, $H_{vib}$-Vibrational part of enthalpy, $H_{vib}^0$-enthalpy of ground state point, $H_{rot}$ rotational part of enthalpy, $H_{trans}$-transational part of enthalpy, $R$-universal gas constant, $T$-temperature. The formation energy $E$ has been calculated similarly.

Rotary and transational components of enthalpy are presented as follows:

$$H_{rot} = \frac{3}{2} NKT$$  (1.75)

Where, $N$-the total number of atoms, $K$-Boltzmann constant.

$$H_{trans} = \frac{5}{2} NKT$$  (1.76)

Fluctuations enthalpies are a function of $(3N-6)$ vibrational frequencies of the molecules.

The enthalpy of the ground state point:

$$H_{vib}^0 = \frac{1}{2} \sum_{i=1}^{3N-6} h v_i$$  (1.77)

Where, $h$-Plank’s constant, $v_i$-$i^{th}$ fluctuations frequency.

Vibrational contribution to the enthalpy (depends on $T$):

$$H_{vib}^0 = \frac{1}{2} \sum_{i=1}^{3N-6} \frac{h v_i}{\exp{(\frac{h v_i}{RT})} - 1}$$  (1.78)

Entropy is defined as follows:

$$S = S_{trans} + S_{rot} + S_{vib} + S_{elec} - nR[\ln(nN_0)-1]$$  (1.79)

Where $N_0$-the Avagadro constant, $n$-number of moles of molecules

The transational entropy components $S_{trans}$ is:
\[ S_{\text{trans}} = nR \left\{ \frac{2}{3} + \ln \left[ \left( \frac{2MKT}{h^2} \right)^{\frac{3}{2}} \left( \frac{nRT}{p} \right)^{\frac{1}{2}} \right] \right\} \]  

(1.80)

Rotary \( S_{\text{rot}} \) and fluctuating \( S_{\text{vib}} \) components of the entropy are calculated similarly to the components of the enthalpy.

Heat capacity at constant volume with account of previous approximations is determined by the following formula:

\[ C_v = C_{v(\text{trans})} + C_{v(\text{rot})} + C_{v(\text{vib})} \]  

(1.81)

1.16 SINGLE CRYSTAL X-RAY DIFFRACTION

1.16.1 Introduction

Single crystal X-ray analysis is an ultimate non-destructive analytical technique that provides a wealth of information about the crystalline lattice, unit cell dimensions, and atomic positions inside the unit cell from a very small amount of material. By analyzing a sample with a volume of 0.1 mm\(^3\) one can establish the crystal composition, identify all molecular or ionic species present, their symmetry, conformations, and mutual arrangement in the lattice. More importantly, oxidation states, interatomic distances and angles as well as torsion angles are established with high precision. Visual representation of the X-ray single crystal analysis result is found in the form of molecular drawing everywhere - from popular scientific journals (Putnis, 1992).

1.16.2 Crystals

It is always a pleasure to look at crystals - they signify a transition from chaos to perfection. There are several requirements for a crystal to be suitable for an X-ray diffraction (XRD) experiment. Ideally, it should measure up to 0.5 mm along each side and have as few internal imperfections as possible. The crystal does not have to be beautiful or have well formed facets and edges as long as it
looks wholesome, with no cracks, striations and bubbles. We use an optical microscope equipped with a polarizer to select crystals.

The crystals are selected under paratone oil. There are several reasons for that: the oil protects the crystals from air and moisture, which is important when crystals are air- and moisture-sensitive; when crystals are cut they don't fly off the slide but remain in the field of view; when the crystals are put on the diffractometer in the stream of cold nitrogen, the oil solidifies and keeps the crystal protected and firmly attached to the mount. And after the experiment if you decide to do additional analyses on the crystal the oil will thaw and the crystal becomes available - that's impossible to do with glue. The crystal is mounted onto a nylon loop and transferred to an instrument.

1.16.3 Instruments

The single crystal XRD diffractometer has two types, such as a) Bucky and b) Gromit and are shown in Figs. 1.8(a) and (b). The "Bucky" is optimized for analyzing crystals of organic compounds and "Gromit" analyzing the in-organic crystals.

There are three basic components in a diffractometer - a radiation source, sample holder, and detector supported by a large platform.

- The X-ray source is a cathode ray tube that produces radiation with a characteristic wavelength of its target material. Here we have a Cu-radiation X-ray source with the wavelength of 1.54Å. The size of the X-ray beam is 0.5 mm (0.02 inches).
The sample is mounted on a goniometer head and is centered in the X-ray beam by means of a video camera.

A state-of-the-art two-dimensional charge coupled device (CCD) detector (not unlike two-dimensional chips in your digital cameras) is optimized for detection of X-ray photons - it converts X-rays into an electrical signal recorded by a computer.

The other instrument, named Gromit, is ideal for analyzing organometallic and inorganic materials. It also contains a goniometer that supports a CCD detector, crystal, and a radiation source. The tube radiation source is unique, and this is only the second instrument of this type in the USA. The source produces a very brilliant beam of Mo radiation with the wavelength of 0.71073Å, which is harder than the Cu radiation and if the radiation of choice for materials with high absorption, such as inorganic and organometallic compounds.
Fig. 1.8 (a) and (b). Single crystal XRD instruments
1.16.4 Applications

Single-crystal X-ray diffraction is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice. Bond-lengths and angles are directly related to the atomic positions. The crystal structure of a mineral is a characteristic property that is the basis for understanding many of the properties of each mineral. Specific applications of single-crystal diffraction include:

- New mineral identification, crystal solution and refinement
- Determination of unit cell, bond-lengths, bond-angles and site-ordering
- Characterization of cation-anion coordination
- Variations in crystal lattice with chemistry
- With specialized chambers, structures of high pressure and/or temperature phases can be determined
- Determination of crystal-chemical vs. environmental control on mineral chemistry
- Powder patterns can also be derived from single-crystals by use of specialized cameras (Gandolfi).

1.16.5 SHELXL - Structure Refinement

SHELXL is a program for the refinement of crystal structures from diffraction data, and is primarily intended for single crystal X-ray data of small
moiety structures, though it can also be used for refinement of macromolecules against data to about 2.5Å or better. It uses a conventional structure factor summation, so it is much slower (but a little more accurate) than standard FFT-based macromolecular programs. SHELXL is intended to be easy to install and use. It is very general, and is valid for all space groups and types of structure. Polar axis restraints and special position constraints are generated automatically. The program can handle twinning, complex disorder, absolute structure determination, crystallographic information file (CIF) and programe database (PDB) output, and provides a large variety of restraints and constraints for the control of difficult refinements. An interface program SHELXPRO enables macromolecular refinement results to be displayed in the form of Postscript plots, and generates map and other files for communication with widely used macromolecular programs. An auxiliary program CIFTAB is useful for tabulating the refinement results via the CIF output file for small molecules.

Once the initial crystal structure is solved, various steps can be done to attain the best possible fit between the observed and calculated crystal structure. The final structure solution will be presented with ‘R factor’ value, which gives the percent variation between the calculated and observed structures. The single-crystal structure refinement page provides further information on the processes and steps involved in refining a crystal structure.