1.1 INTRODUCTION

In the modern era of scientific research, spectroscopy finds a wide range of application in all branches of science. The various spectroscopic methods are based on the measurement of the electromagnetic radiation absorbed or emitted by matter and they are classified according to the region of electromagnetic radiation involved as X-rays, ultraviolet, visible, infrared, microwave and radio frequency regions. The nature of the information required decides the selection of the particular spectroscopic technique.

Spectroscopy has become an indispensable tool to the present day physicists and chemists owing to the availability of very sophisticated instruments. The various spectroscopic methods are the most powerful and useful techniques employed for the understanding of molecular structure, nature of bonding between the atoms, conformation analysis, symmetry of molecular groups or ions in crystal and so forth. Building on the development of quantum mechanics and employing sophisticated methods of handling electromagnetic radiation and processing data, the area of spectroscopy has reached an important status today [1, 2].

The various types of energy associated with different motions of the molecule are independent of one another. A molecule can have many levels of these different energies. The frequency of radiation absorbed or emitted depends on the energy difference ($\Delta E$) between the two levels involved in the transition and this energy difference is different for rotational, vibrational, and electronic energies. Consequently, the corresponding spectra occur in different regions of the electromagnetic spectrum. Transition between the electronic energy levels gives the
spectrum in the visible or ultraviolet region and is referred to as electronic spectra. Vibrational spectra are due to the transitions between the vibrational levels within the same electronic level which fall in the infrared region. Transitions between the rotational levels within the same vibrational level give rotational spectra. The quantum of infrared energy required is much less than that in the UV-Visible region [3].

Photons on colliding with molecules undergo inelastic scattering and they have frequencies lower (stokes lines) and higher (anti stokes lines) than the incident frequency, which is known as Raman scattering. The infrared and Raman spectroscopic methods yield complementary types of information [4].

Spectroscopy is the study of the interaction of matter with electromagnetic energy. From these interaction, Spectroscopist observe lot of information about the matter. Molecular spectroscopy aims to understand the interaction of molecular energy with electromagnetic radiation. Due to the different kinds of motion and intermolecular interactions, a molecule possesses various forms of energy. For instance, it possesses Translational energy, Rotational energy, Vibrational energy etc., and these energies are quantized and interactions between them are very weak. Electromagnetic radiations can be allowed to interact with the molecular energy levels and investigations of these interactions can provide various information regarding their rotation, charge localization, molecular structure, symmetry, vibration etc. It is an established fact that the interaction of electro magnetic energy with the vibrational energy levels of a molecule provide information on the molecular dynamics [5] and
vibrational spectroscopy emerged with theories and techniques to deal with such interactions.

The vibrational spectroscopy technique is applicable to solids, crystals, powder, liquids, solutions, melt gases, films and absorbed species. The important applications are: molecular structural determinations, calculation of intramolecular and intermolecular forces, computation of degrees of association in condensed phases, elucidation of molecular symmetries, identification and characterization of new molecules, deducing thermo dynamical properties of molecular systems etc., [6]. Vibrational spectroscopy has also contributed significantly to the growth of other areas such as polymer chemistry, catalysis, fast reaction dynamics, charge transfer complexes etc. [1].

Vibrational spectroscopy involves different methods, the most important of which are Infrared and Raman spectroscopy. Infrared spectroscopy is the study of the interaction of matter with infrared light. The fundamental measurement obtained in infrared spectroscopy is an Infrared spectrum, which is a plot of measured infrared intensity verses wave length (or wave number) of light. Infrared spectroscopy is sensitive to the presence of chemical functional groups in a sample. Molecular vibrations, which modulate the molecular dipolemoment are visible in the infrared spectrum, while those vibrations, which modulate the polarizability, appear in the Raman spectrum. These two techniques yield complementary and / or confirmatory information regarding molecular vibrations. Hence, both these methods should necessarily be used for complete vibrational analysis of a molecule [7].
1.1.1 The nature of molecular vibrations

When a molecule absorbs infrared radiations, its chemical bonds vibrate. The bonds can stretch, contract and bend. This is why infrared spectroscopy is a type of vibrational spectroscopy. The vibrational motion excited by infrared absorbance is complex. Fortunately, the complex vibrational motion of a molecule can be broken down into a number of constituent vibrations called normal modes. All mechanical systems have normal modes, and will vibrate at some frequency given the right conditions. Each of the vibrational motions of a molecule occurs with a certain frequency, which is characteristic of the molecule and of the particular bond. The energy involved in a particular vibration is characterised by the amplitude of the vibration so that the higher the vibrational energy, the larger the amplitude of the motion [8].

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

\[ E_{\text{final}} - E_{\text{initial}} = h\nu \]

In such a transition, the molecule gains vibrational energy, and this is manifested in an increase in the amplitude of the vibration. The frequency of light that cause a transition of a particular vibration is equal to the frequency of that vibration, so that we may measure the vibrational frequencies by measuring the frequencies of light, which are absorbed by the molecules. Since most vibrational motions in
molecules occur at frequencies about $10^{14}$ Sec$^{-1}$, then light of wavelength=3microns will be required to cause transitions [9]. Hence, light of this wavelength lies in the infrared region of the spectrum and IR spectroscopy thus deals with such transitions between vibrational energy levels in molecules and therefore constitutes a part of vibrational spectroscopy.

A molecule has as many degrees of freedom as that of the total degrees of freedom of its individual atoms. Each atom has three degrees of freedom in the cartesian coordinates (x, y, z), necessary to describe its position with respect to a fixed point in the molecule. A molecule of N atoms has 3N degrees of freedom. Of the 3N degrees of freedom for non-linear molecules, 3 degrees of freedom describe translation and 3 describe rotation and the remaining 3N–6 degrees of freedom describe vibrational degrees of freedom. Linear molecules have 3N–5 degrees of freedom, since only 2 degrees of freedom are required to describe rotation. In the case of polymers, the number of degrees of freedom becomes 3N–4 as rotation is constrained to only one axis [10]. Of the 3N–6 vibrational modes, (N–1) modes are bond stretching vibrations and the other (2N–5) modes are angle-bending vibrations [11]. The number of vibrational degrees of freedom gives the number of fundamental vibrational frequencies of the molecule - the number of normal modes of vibrations [5].

A molecule may consist of many numbers of atoms and the atomic nuclei may be regarded as mass point in the potential field due to the bonding. When the atoms of a molecule are slightly displaced from their equilibrium positions and released, they perform vibrations of complicated nature. In the absence of other normal modes, each
normal mode is nothing but the simple harmonic motion of every nucleus about its equilibrium position and all these oscillations are in phase. During the vibrational motion of a molecule the charge distribution undergoes a periodic change, and hence the dipole moment changes periodically. Normal vibrations connected with the change of dipole moment that appear in the infrared spectrum are called infrared active modes.

1.2 INFRARED SPECTROSCOPY

The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to microwave region, at wave numbers between 14000 and 20 cm$^{-1}$. The near-infrared region meets the visible region at about 12,500 cm$^{-1}$ and extends at about 4000 cm$^{-1}$ and there are many absorption bands resulting from harmonic overtone of fundamental and combination bands, often associated with hydrogen atom. The mid-infrared region is the most useful region, which covers frequencies from 4000-200 cm$^{-1}$ and the fingerprint region, 300-650 cm$^{-1}$, in the group frequency region and the principal absorption bands are due to vibrational units consisting of only two atoms of a molecule. The major factors in the spectrum of fingerprint region are single band stretching frequencies and bending vibrations of polyatomic system. The far infrared region 667-10 cm$^{-1}$ contains the bending vibrations of carbon, nitrogen, oxygen and fluorine with heavier atoms and additional bending motions in cyclic or unsaturated systems.

Infrared spectroscopy is an important field of chemical analysis. Anyone interested in identifying the components of measuring the concentrations of molecules in a sample should become familiar with this technique. The first task in the infrared
analysis of any sample is obtaining the spectrum itself. This involves preparing the sample, placing it in an infrared spectrometer, and measuring the response of the sample to infrared light. All of the aspects of a spectrum, the position, height, width and pattern of bands carry important information about a sample.

Infrared spectroscopy has many advantages as a chemical analysis technique. It is a universal technique. Solids, liquids, gases, semi-solids, powders and polymers are all routinely analysed. Infrared spectroscopy is relatively fast and easy technique. It is also a sensitive technique.

The absorption of infrared radiation by a molecule takes place when there is a transition between the various vibrational and rotational states. In order to absorb infrared radiation, a molecule must undergo a net change in the dipole moment as a consequence of its vibrational or rotational motion. Coupling with electromagnetic radiation occurs when the vibrating molecules produce an oscillating dipole moment that can interact with the electric field of the radiation. The transitions in vibrational energy levels result in radiation, governed by the selection rule $\Delta v = \pm 1$. Vibrations fall into basic categories of stretching and bending. A stretching vibration involves a change in the interatomic distance along the axis of the bond between two atoms. Bending vibrations are characterized by a change in the angle between two bonds and are of four types - scissoring, rocking, wagging and twisting. Complex polyatomic molecules contain several types of atoms as well as bonds and they give rise to infrared spectra that are difficult to analyse. A polyatomic molecule containing N atoms has $(3N-6)$ degrees of freedom involving interatomic motion and hence represents the number of possible vibrations within a molecule.
1.2.1 The origin of peak intensities and peak widths

Peak intensities are useful in infrared spectral interpretation because one can distinguish between the spectra of different functional groups based on peak intensity. The different vibrations of the different functional groups in the molecule give rise to bands of different intensity. This is because the change in reduced mass with respect to the change in band length from equilibrium position is different for each of these vibrations. An additional factor that determines the peak heights in infrared spectra is the concentration of molecules in the sample.

The equation that relates concentration to absorbance is Beer’s law, which has the following form:

\[ A = \epsilon l c \]

Where:
- \( A \) – absorbance
- \( \epsilon \) – Absorptive
- \( l \) – Path length
- \( c \) – Concentration.

The absorbance is measured as peak height, peak height ratio, or peak area ratio in the infrared spectrum. The path length is typically on the order of microns for solids and liquids, and centimeters to meters for gases in infrared spectroscopy. Concentrations can be measured in moles / liter, %, pressure, or any of a number of other units depending on the type of sample analyzed.

The absorptivity is an absolute measure of infrared absorbance intensity for a specific molecule at a specific wave number. The absorptivity does change from molecule to molecule and from wave number to wave number for a given molecule. However, for a given molecule and wave number, the absorptivity is a fundamental
physical property of the molecule, as invariant as its boiling point or molecular weight [12].

In addition to peak positions and peak intensities, peak widths also provide useful information about a sample. Different functional groups give rise to bands with different peak widths, and this property can be used to distinguish between them. Some functional groups give infrared bands so wide that the widths of the bands by themselves give away the presence of that functional group in a sample.

In solid and liquid samples, interactions between nearest neighbor molecules are relatively strong. This is because of the high densities and close packing of molecules found in these phases. Samples with strong intermolecular interactions have more chemical environments than samples with weak intermolecular interactions because electronic effects are greater for strong interactions. Thus, a non–polar molecule has fewer chemical environments than a polar molecule. The more chemical environment a sample has, the more slightly different wave number of light it will absorb. Therefore, broad infrared bands are observed for samples with many chemical environments, and narrow infrared bands are observed for samples with few chemical environments [13].

1.2.2 Instrumentation

The basic components of an infrared spectrophotometer are the same, though slightly differing techniques are followed for different regions of IR, viz., far-IR, mid-IR and near-IR. Radiation from the source is split into two beams, half passing into the sample cell compartment and the other half into the reference area. The
reference beam then passes through an attenuator and on to a chopper. The chopper consists of a motor driven disk, which alternately reflects the reference or transmits the sample beam into the monochromator. After dispersion by the monochromator, a prism or grating, the alternating beam falls on a detector and is converted to an electric signal. The signal is amplified and passed to the synchronous rectifier that is mechanically or electrically coupled to the chopper. If the two beams are identical in power, the signal from the rectifier is an unfluctuating direct current. But if the two beams differ in power, a fluctuating current is produced, the phase of which is determined by which beam is more intense. The current from the rectifier is filtered and further amplified to drive a synchronous motor in one direction or the other depending upon the phase of the input current. It is mechanically linked to both the attenuator and pen drive of the recorder and causes both to move until the null is achieved. A second synchronous motor drives the chart and varies the wavelengths simultaneously [14].

The common infrared radiation source is an electrically heated black body radiator, which is either a globar filament or Nernst glower. Nernst glowers are constructed from a fused mixture of oxides of zirconium, yttrium and thorium molded in the form of rods and can be heated to as high as 1500°C and this is very effective in infrared region. The globar is a silicon carbide rod and is also electrically heated to 1300-1500°C and this is very effective in the far-infrared region. An ordinary tungsten filament lamp is the convenient source for the near infrared region. In the very far-infrared region, black body type sources are ineffective and they are replaced by high pressure mercury arcs, tunable carbon dioxide laser sources etc. The monochromator splits the polychromatic radiation into its component wavelengths, which can be
accomplished by means of interference filters, prisms or gratings. Generally, gratings are used in conjunction with filters. After the selection of wavelength by the monochromator, the reference beam is attenuated to match that passing through the sample. The attenuator takes the form of a fine toothed comb which moves when a difference in power is detected.

Thermocouples and bolometer are the commonly used thermal detectors. Pyroelectric detectors are better choices in Fourier transform spectrophotometer. Pyroelectric materials include triglycine sulphate (TGS), deuterated triglycine sulphate (DTGS), Lithium tantalite (LiTaO$_3$), Lithium neonate (LiNbO$_3$), barium titanate (BaTiO$_3$) and some polymers and they possess temperature sensitive dipole moments. Golay detector is a sensitive xenon gas thermometer, which is used in the far-infrared regions. Sample handling is an important part of spectral recording. The spectrum of gas samples can be obtained by permitting the sample to expand into an evacuated cell. The infrared spectra of solutions are obtained with the proper choice of the solvent and the cell that are transparent in the infrared region. The spectrum of pure liquid is taken by squeezing a drop of the neat liquid between two rock- salt plates and mounted in the beam path. The spectra of solid samples are derived either by mull or pellet technique. Mull technique involves grinding 2-5 mg of the finely powdered sample with one or two drops of a heavy hydrocarbon oil (Nujol), and is then examined as a film between flat salt plates, the finely ground sample is mixed with dried potassium bromide powder (KBr) and the mixture is then pressed into a pellet and the pellet is then examined.
1.2.3 FTIR spectroscopy and instrumentation

Fourier transform spectroscopy was first developed by astronomers in the early 1950s to study the infrared spectra of distant stars. The Fourier technique could isolate the very weak signals from environmental noise and since then it has been developed into a powerful experimental technique [15, 16]. The conventional spectroscopy is the frequency domain spectroscopy, in which the radiant power is recorded as a function of frequency. The Fourier transform spectroscopy is domain spectroscopy, so that the radiant power changes with time. The Michelson interferometer is used for the modulation of the high frequency signal. The basic components of a Fourier transform interferometer are the moving mirror, a fixed mirror and a beam splitter. Fig 1.1 shows the optical design of a double beam Fourier Transform Infrared spectrometer. Radiation from the infrared source is collimated by a mirror and the resultant beam is divided at the beam splitter; half the beam passes to the fixed mirror and half is reflected to the moving mirrors, which are at right angles to each other. After reflection, the two beams interfere constructively or destructively depending on the path difference. When the movable mirror is moved with a constant velocity the intensity of the emerging radiation is modulated in a regular sinusoidal manner. The modulated frequencies after passing through the sample compartment are focused on to the detector. The detector signal is sampled at precise intervals during mirror scan. The resulting signal from the detector is known as interferogram and the spectrum is reconstructed using Fourier Transformation. The transformation is carried out by a computer and the spectrum is plotted in a paper.
Components of infrared spectrometer

The basic components of an IR spectrometer are
a. Radiation source
b. Monochromators
c. Sample cell and sample substance
d. Detectors

a. Radiation source

The infrared instruments require a source of radiant energy which provides a means for isolating narrow frequency bands. The various popular sources of IR radiations are:

i. Incandescent lamp

Such lamps are used as sources in the near - infrared instruments. They fail to work in far-infrared regions.

ii. Nernst Glower

It consists of a hollow rod which is about 2 mm in diameter and 30 mm in length. The glower is composed of rare earth oxides such as zirconia, yttria and
thoria. It is non-conducting at room temperature and must be heated by external means to bring it to a conducting state. It starts working in a temperature range of 1000°C to 1800°C.

iii. Globar source

It is a rod of sintered silicon carbide which is about 50 mm in length and 4 mm in diameter. When it is heated to a temperature between 1300°C and 1700°C it strongly emits radiation in the IR region. It emits maximum radiation at 5200 cm⁻¹. The disadvantage is its less intensity.

iv) Mercury Arc

It is generally used in far-infrared region. Beckman devised the quartz mercury lamp for the same region in unique manner.

b. Monochromators

The radiation source emits radiations of various frequencies. As the sample in IR spectroscopy absorbs only at certain frequencies, it therefore becomes necessary to select desired frequencies from the radiation source and reject the radiations of other frequencies. This selection has been achieved by means of monochromators which are mainly of two types.

1. Prism Monochromator
2. Grating monochromator

c. Sample cell and sample substance

In IR absorption spectrometer, the sample is either solid, liquid or gas, (i.e.) the three phases of the sample have to be handled. But the treatment for different
phases of the substances is different. The important point to remember here is that the material containing the sample is made transparent to IR radiation.

1. Sampling of Solids

Four techniques are generally employed for preparing solid samples. They are:

i. Solids run in solution

In this method the solid is first dissolved in suitable solvent, so that the solution of the sample is formed. Then it is used to record the spectrum. But it is not applicable to all solids, because the solvents are in limited number.

ii. Solid films

If a solid is amorphous in nature the sample is deposited on the surface of KBr or NaCl cell by evaporation of solution of the solid. This technique is useful for rapid qualitative analysis but becomes useless for carrying out quantitative analysis.

iii. Mull technique

In this method the finely ground solid sample is mixed with Nujol to make a thick paste, which is then made to spread between IR transmitting windows. This is then mounted in the path of infrared beam and the spectrum is run. This method is good for qualitative analysis but not for quantitative analysis.

iv. Pressed pellet technique:

In this technique a small amount of finely ground solid sample is intimately mixed about 100 times its weight of powdered Potassium Bromide. The finely
ground mixture is then pressed under very high pressure to form a small pellet. The resulting pellet is transparent to IR radiation and is run as such.

2. Sampling of liquids

Samples that are liquids at room temperature are usually put frequently with no preparation, into rectangular cells made of NaCl, KBr or ThBr and their IR spectra are obtained directly. The sample thickness should be selected that the transmittance lies between 15 and 70%. For most of liquids this will represent a thin layer of 0.01 mm to 0.05 mm in thickness.

3. Sampling of Gases

The gas sample is put into a special cell generally about 10 cm long, which is then kept across the path of the infrared beam. The end walls of the cell are generally made up of Sodium Chloride. For measuring very dilute gases long path cells are to be employed. Since the sampling area of most spectrometers are restricted in length, mirrors are used to bring out multiple reflections to make the effective path length as long as 40cm.

d. Detectors

Detectors are classified into two groups. They are:

1. Thermal detectors

It utilizes the heating effect of radiation. The thermal detectors must possess a short response time and the absorbed heat must be lost rapidly.

   Example: Bolometers, Thermocouples, Thermistors, Golay cell.
2. Photo detectors

Utilizing the quantum photoelectric effect (the freezing of bound electrons by the absorption of single quanta of energy)

Example: Dielectric cells, doped Ge and Si cells etc.,

Photo conductivity cells have high sensitivity and good speed of response to infrared detection, but it suffers from many practical disadvantages. When operated at room temperature, it has a very restricted range, usually to the near infrared. The range can be broadened by drastic cooling.

1.2.4 Applications of FTIR spectroscopy

The applications of FTIR spectroscopy are tremendous due to increased signal to noise ratio and the minimum measurement time. The application can be discussed in different types like quantitative and biological. The quantitative applications of FTIR spectroscopy is related to functional group identification and structural elucidation. This method is highly advantageous since it supplies information about whole molecule. The quantitative applications of frequency, intensity and width of the band of the vibrational mode are used to determine band strengths, distance of molecule, thermo dynamic functions, reaction mechanisms, salvation number, phase transition, intermolecular interactions etc. Both quantitative and qualitative applications are employed in the quality control analysis of pharmaceutical products, petroleum products, food materials etc. Regarding the biological applications, Infrared Spectroscopy is a potential tool in a large number of biological systems such as conformational analysis of polypeptides, proteins, biopolymers etc. The advancement of FTIR spectroscopy in the study of biological fluids as blood, serum, synovial
fluid, amniotic fluid etc. are very significant. The FTIR spectrometers are better than dispersive infrared spectrometers in terms of scanning, signal to noise ratio, sensitivity, resolution and data processing [17].

1.3 RAMAN SPECTROSCOPY

Raman Spectroscopy arises due to the scattering of light by atoms or molecules. When a substance is irradiated by a monochromatic light, most of the photons are scattered elastically (Rayleigh scattering) but a few of them undergo inelastic scattering. Those in elastically scattered photons have frequencies lower (Stokes lines) and higher (Anti-stokes lines) than the incident frequency, which have been observed by Sir C.V. Raman in 1928 and is known as Raman scattering. The scattered photons have frequency shifts in the region 4000-10 cm\(^{-1}\), characteristic of the vibrational or rotational energies of the molecule or in other words the difference in wavelength between the incident and scattered radiation corresponds the wavelength in the mid-infrared region. Thus the Raman scattering spectrum and infrared absorption spectrum often resemble one another quite closely and are complementary. It is to be noted that the magnitude of the Raman shifts are independent of the wavelength of excitation [18, 19].

The Raman Effect arises when a beam of intense monochromatic radiation passes through the sample that contains molecules that undergo a change in molecular polarizability as they vibrate. For a vibrational mode to be active in the Raman Effect, the polarizability of the molecule must change during the vibration. According to classical electromagnetic theory, the dipole moment \( \mu \) of a molecular bond when it is subjected to the electric field E is related to the polarizability \( \alpha \), by \( \mu = \alpha E \). The
electric field $E$ varies as a function of time as $E=E_0 \cos 2\pi vt$. It is required that the polarizability of a bond varies as a function of atomic distance for the bond to be Raman active.

According to quantum theory, the photons of frequency $\nu_o$ do not exchange energy with the molecule during elastic scattering. However, the molecule gains or loses energy equal to the energy difference $\Delta E$ between any two of its allowed states. If the molecule gains energy, the scattered photons will have energy $h\nu_o-h\nu_m$ where $\nu_m=\Delta E/h$ (Stoke’s line). If the molecule loses energy, the scattered photons will have energy $h\nu_o+h\nu_m$ (anti-Stokes line). The brightness of the difference modified lines can be described to the differences in the Einstein co-efficient of probability of the transitions by the radiation. According to Boltzmann’s distribution, the number of molecules in the excited state is always less than the number in the ground state. The intensity of anti-Stokes lines is much less than Stoke’s lines.

In addition to intensity and frequency information, Raman measurements provide an additional parameter, depolarization ratio which is useful sometimes in determining the structure of the molecules. The scattered light is found to be plane polarized to different extent even if the exciting radiation is completely unpolarized. If a completely plane polarized light is passed through an analyzer, the light will be completely extinguished when the axis of the analyzer is perpendicular to the plane of polarization, whereas it is allowed fully without decrease in intensity when its axis is parallel. The situation is different when the incident light is plane polarized. The scattered light is not completely extinguished even if the axis is perpendicular to the plane of polarization. The degree of polarization is measured by the depolarization
ratio $\rho = I_\perp / I_{\parallel}$ where $I_\perp$ is the minimum and $I_{\parallel}$ is the maximum intensity passed by the analyser. Thus $\rho = 0$ for completely polarized light and $\rho = 1$ for completely unpolarized light and it varies between 0 and 1 for intermediate degrees of polarization. Theoretical considerations show that if $\rho > 6/7$, the line would be polarized to different extends depending on the value of $\rho$. In other words the fundamentals of totally symmetric vibrations give polarized or partially polarized Raman lines ($\rho < 6/7$) while asymmetric vibrations give depolarized Raman lines ($\rho > 6/7$). A measurement of degree of polarization of Raman line is helpful in the assignment of Raman lines to their appropriate molecular vibrations and in the determination of molecular structure. This important parameter in Raman spectroscopy has no counterpart in infrared [20].

Infrared and Raman scattering represent two drastically different physical processes. Certain molecular vibrations interact only with infrared radiation whereas certain others show Raman Effect. If a molecule has a centre of symmetry, the symmetric vibration cannot produce a change in dipole moment. They are infrared inactive but Raman active because they produce a change in polarizability. The anti symmetric vibrations with respect to the centre of symmetry are infrared active, but they are Raman inactive. Thus infrared and Raman measurements complement each other and the complete picture of vibrational problem can be obtained by using both techniques. But all the vibrations are active both in infrared and Raman in those molecules which do not possess centre of symmetry.
1.3.1 Instrumentation

Instrumentation for modern Raman spectroscopy consists of components; a laser source, a sample illuminating system and a suitable spectrometer. The sources used in modern spectrometry are always lasers, as high intensity beam is necessary to produce Raman scattering of sufficient intensity that are to be measured with a reasonable signal to noise ratio. As the intensity of Raman scattering varies as the forth power of the frequency, Argon and Krypton lasers are used which emits wavelengths at 488nm and 647.1nm. As they produce fluorescence in some samples, now near infrared sources as diode laser (782 nm) and Nd-YAG (1064 nm) are more useful. These sources have two major advantages. They can be operated at much high power without causing photo decomposition of the sample. Fluorescence is much less intense or existent with these lasers. The Nd-YAG line at 1064 nm is particularly effective and it is used as the source in FT-Raman spectrophotometer and it completely eliminates background fluorescence.

Sample handling for Raman spectroscopic measurements is extremely simple. Glass can be used for windows, lenses and other optical components instead of the more fragile and atmospherically less stable crystalline Halides as an infrared spectroscopy. As laser source is easily focused on a small sample area and the emitted radiation is efficiently focused, a very small amount of sample can be investigated and the sample can be almost in any state; liquid, solution, transparent solid, translucent solid, powder, pellet or gas. A common sample holder for non-absorbing liquid samples is an ordinary glass container. Other widely used solvents are carbon disulfide, carbon tetrachloride, chloroform and acetonitrile. Liquid samples containing colloidal or suspended particles scatter sufficient amounts of laser
beam and make the observations difficult. Such samples must be treated to remove the solids before a Raman spectrum is obtained. Raman scattering due to water is quite weak and hence aqueous solutions may be easily examined by Raman spectroscopy. This advantage is particularly important for biological and inorganic systems and in studies dealing with water pollution.

Raman spectra of solid samples are often acquired by grinding the sample to a fine powder and filling the cavity with the sample. For gas samples, a multipass gas cell is used which is a cylindrical glass tube fitted with mirrors at both ends and filled with the sample gas. The excitation laser beam is passed through a small window in one of the mirrors and subsequently passed through the gaseous sample numerous times. The resulting Raman scattering is focused on the entrance slit of the spectrometer by a large lens. Another advantage of Raman spectrometry is that the visible or near-infrared radiation can be transmitted for a considerable distance through optical fibers [21].

The early Raman studies were carried out with prism spectrographs and the spectra were recorded on photographic films or plates and the intensities were determined by measuring the blackness of the lines. Later versions employed double grating systems to minimize spurious radiation reaching photomultipliers which acted as detectors. With the advent of Fourier transform spectroscopy, now most of the Raman spectrometers are coupled with the technique and are Fourier Transform Raman spectrometers as shown in Fig 1.2. They use Michelson interferometer for wave length analysis and are of the same type as used in infrared instruments. The radiation source is Nd-YAG laser with output power ranging upto 3 watts which
supplies continuous wave laser wavelength of 1064 nm. The transducer is liquid nitrogen cooled germanium photo conductor. The cryogenic temperature is required to lower the noise level and to increase the signal to noise ratio. As the intensity of Rayleigh line is of several orders of magnitude greater than that of Raman line, holographic interference filters called notch filters or monochromators are usually used to limit the radiation of longer wavelength than that of the source reaching the detector. With this arrangement only stokes portion of the spectrum is used.

Fig. 1.2 Schematic diagram of FT-Raman spectrometer
Fig. 1.3 Optical path in Michelson Interferometer

Fig. 1.4 Schematic diagram of Nd: YAG laser
1.4 APPLICATION OF GROUP THEORY TO VIBRATIONAL SPECTROSCOPY

Symmetry is a visual concept as reflected by the geometrical shapes of molecules such as ammonia, benzene, etc. The link between molecular symmetry and quantum mechanics is provided by the group theory. In vibrational spectroscopy, group theory can be effectively used for: (1) determining the symmetry types of normal mode vibrations of the molecule, (2) predicting the infrared and Raman activity of a normal mode of vibration of a particular symmetry types and (3) simplification of method of obtaining the relation between force constants and vibrational frequencies [22]. The group theory was used, first time by Wigner (1930), for the study of molecular vibrations [23].

The molecular symmetry is systematized quantitatively by introducing the concept of ‘symmetry operation’. A symmetry operation transforms the molecular framework into an equivalent configuration or identical configuration. A symmetry element is a geometrical entity such as point, an axis or a plane about which one or more symmetry operations are carried out. Five kinds of fundamental symmetry operations are utilized in specifying molecular symmetry. (i) Proper axis of symmetry ($C_n$) - it is rotation once or several times by an angle $\theta = (2\pi/n)$ about the axis, (ii) Plane of symmetry ($\sigma$) - one or more reflections in the plane, (iii) Improper axis of symmetry ($S_n$) rotation about an axis followed by reflection in a plane perpendicular to the rotation axis, (iv) centre of symmetry ($I$) - inversion of all atoms through the centre of symmetry, (v) identity element ($E$) - rotation of the molecule through 0° or 360° which leaves the molecule unchanged [11].
All the symmetry operations present in a molecule form a group and such groups are called point groups. In a point group, all the elements of symmetry present in the molecule interest at a common point and this point remains fixed under all the symmetry operations of the molecule. Although theoretically large numbers of such groups are possible, most molecules falls under dozen point groups. Some of the common molecular point groups are $C_s$, $C_n$, $C_{nv}$, $C_h$, $C_{s\infty}$, $D_n$, $D_{nh}$, $D_{nd}$, $S_n$, $T$, $T_d$, $O$, $O_h$, $I_n$, $D_{\infty h}$, etc. Molecules can be fixed to point groups using the following steps.

1. For a linear molecule
   - No centre of symmetry : $C_{\infty v}$ group
   - Centre of symmetry present : $D_{\infty h}$ group

2. For a molecule of Octahedral shape
   - No $i$ present : $O$ group
   - $i$ present : $C_{s\infty}$ group

3. For a molecule of Tetrahedral shape
   - No $\sigma_d$ present : $T$ group
   - $6\sigma_d$ present : $T_d$ group

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

4. If $n = 1$ and
   - No other elements present : $C_1$ group
   - $i$ present : $C_1$ group
   - $\sigma$ present : $C_s$ group
5. $C_n$ with $n > 1$ exists and there are no $C'_2$ axis perpendicular to $C_n$ and if
   No other elements present : $C_n$ group
   $\sigma_h$ exists : $C_{nh}$ group
   $n\sigma'_v$ exists but no $\sigma$ : $C_{nv}$ group

6. $C_n$ with $n > 1$ exists and there are $C'_2$ axis perpendicular to $C_n$ and if
   No $\sigma$ exists : $D_n$ group
   $\sigma_h$ exists : $D_{nh}$ group
   $n\sigma'_d$ exists but no $\sigma_h$ : $D_{nd}$ group

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

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

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

\[ S'AS = A'; \quad S'BS = B'; \quad S'CS = C'; \quad S'DS = D' \]
If the resulting matrices can be blocked into smaller matrices, then the representation \( T \) is called a reducible representation. If it is not possible to find a similarity transformation matrix, which will reduce the matrices of representation \( T \), then the representation is said to be irreducible \([11]\). Every point group consists of a certain number of irreducible representations. The characters of matrices in the different irreducible representations of a point group can be listed in a table known as character table. Character table plays a vital role in solving problems such as molecular vibrations. The character table for a point group can be constructed with the knowledge of properties of irreducible representations.

The construction of character table requires practice, expertise and knowledge of theorems in group theory such as orthogonal theorems, theorems of representation theory, etc. Without elaborating the procedure, the character table for two point groups \([20]\) \( C_\text{s} \) and \( C_{2\nu} \) are given below:

In the tables, \( A \) and \( B \) represent representations which are symmetric and anti-Symmetric with respect to the main axis of rotation, \( ' \), \( " \)-represents symmetric and anti-symmetric with respect to a plane of symmetry, and \( 1 \), \( 2 \) (as subscripts) represent symmetric and anti-symmetric with respect to a rotation axis \( (C_n) \). The last two columns of each character table list the infrared and Raman activity of the particular species. Polarizability components are listed for Raman activity and translational and rotational components are listed for infrared activity.

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

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

Vibrations active in infrared spectra are determined by character $\chi_M$ of the dipole moment given by
\[ \chi_M = \pm 1 + 2 \cos \varphi \] \hspace{1cm} \text{........... 1.1}

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

\[ N_i = \frac{1}{g} \sum n_M \chi_M \chi_i \] \hspace{1cm} \text{........... 1.2}

Where \( g \) is the number of elements in a point group, \( \chi_M \) the number of elements in each class, \( \chi_i \) is the character of the vibration type, \( N_i \) the number of times the character \( \chi_i \) of the vibration appear in \( \chi_M \). The value of \( N_i \) if equal to zero than that vibration type is infrared inactive otherwise active [22].

1.4.2 Raman active vibrations

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

\[ \chi_\alpha = (2 \pm 2 \cos \varphi) + (2 \cos 2\varphi) \] \hspace{1cm} \text{........... 1.3}

The character \( \chi_\alpha \) must likewise be some linear combination of the \( \chi_i \) using the reduction formulae 1.2. Here also if the \( N_i \) is equal to zero then that vibration type is Raman inactive otherwise active [11].

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

\[ \xi(R) = \begin{cases} (U_R - 2)(1 + 2 \cos \varphi) & \text{for proper rotation} \\ U_R (-1 + 2 \cos \varphi) & \text{for improper rotation} \end{cases} \] \hspace{1cm} \text{........... 1.4}
Where \( U_R \) is the number of nuclei unchanged by the symmetry operation. Knowing \( \xi(R) \) the number of frequencies of each type is determined by using the relation [10].

\[
n_i = \frac{1}{8} \sum n \xi(R) \chi_i
\]

\[\text{......... 1.5}\]

1.5 NORMAL COORDINATE ANALYSIS

For carrying out the normal coordinate analysis first the vibrational frequencies observed in the infrared and Raman spectra must be assigned to individual normal modes of vibration. The next step is the calculation of the relative amplitudes of the normal (or symmetry) coordinates in any normal mode. The main technique behind this is framing the vibrational secular equations and solving these equations.

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

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

\[ 2T = \sum_{i=1}^{n} m_i (\dot{X}^2_i + \dot{Y}^2_i + \dot{Z}^2_i) \] ........ 1.6

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

\[ q_1 = \sqrt{m_1} X_1, \ q_2 = \sqrt{m_2} X_2, \ q_3 = \sqrt{m_3} X_3, \ q_4 = \sqrt{m_4} X_4 \ldots \] ........ 1.7

now the equation 1.6 can be written as

\[ 2T = \sum_{i=1}^{3n} a_{ij} \dot{q}_i \dot{q}_j \] ........ 1.8

If the vibrations are simple harmonic then the potential energy, in reduced coordinates, can be written as

\[ 2V = \sum_{i,j} b_{ij} q_i q_j \] ........... 1.9

The \( b_{ij} \) values are constants and the \( a_{ij} \) values are functions of the atomic masses. \( q_i \) and \( q_j \) are the \( i^{th} \) and \( j^{th} \) coordinates.

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

\[ \frac{\partial}{\partial t} \left( \frac{\partial T}{\partial \dot{q}_i} \right) + \frac{\partial V}{\partial q_i} = 0 \] ........... 1.10

Using equations 1.8 and 1.9 in 1.10 we get

..
\[ \sum_j (a_{ij} q_j + b_{ij} q_j) = 0 \] ............ 1.11

The general solutions of the above equation is given by
\[ q_i = A_j \sin (\lambda^{1/2} t + \varphi) \] ............ 1.12

which is an equation characteristic of wave motion with \( \lambda = 4\pi^2 \nu^2 \) where \( \nu \) is the frequency. \( A \) and \( \varphi \) are amplitude and phase constant respectively. From equations 1.11 and 1.12, we can write

\[ \sum_{i=1}^{3n} (b_{ij} - a_{ij} \lambda) A_j = 0 \] ............ 1.13

Where \( j = 1, 2, 3, \ldots, 3n \). For non-trivial solution the determinant of the coefficients must be equal to zero i.e.,

\[ |b_{ij} - a_{ij} \lambda| = 0 \] ............ 1.14

The equation 1.14 is called as the secular determinant. It has \( 3n \) roots, \( \lambda i \) for which the above equation is satisfied. Each of these \( \lambda \) values expresses the harmonic vibration of a mass particle with frequency \( \nu \). These \( \nu \) values are the normal frequencies of the vibrations. The values of \( \lambda \) can be substituted back in equation 1.13 and \( A_j \) can be calculated which will describe the vibration [24].

**1.5.1 Evaluation of the secular determinant**

The evaluation of the secular determinant is simplified by the transformation to a new set of coordinates \( Q_i \), such that the cross product terms in 1.33 and 1.34 disappears. The old and new set of coordinates can be related by the orthogonal transformation.
\[ q_k = \sum_{i=1}^{3n} B_{ki} Q_i \] ...

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

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

\[ 2V = \sum_i \lambda_i Q_i^2 \] ...

Employing equations 1.15 and 1.16 in 1.10, we get,

\[ \dot{Q}_i + \lambda_i Q_i = 0 \] ...

The solution of this expression is given by, similar to equation 1.1,

\[ Q_i = B_i \sin\left(\lambda_i^{\frac{1}{2}}t + \varphi\right) \] ...

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

\[ 2T = \dot{Q}^T \dot{Q} \] ...

and \[ 2V = Q^T \Lambda Q \] ...

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

\[ |\Lambda - E\lambda| = 0 \] ...

The equation will have \( 3n-6 \) roots \( \lambda_i \) and each value of \( \lambda \) corresponds to a normal vibrational frequency of the molecule. All the atoms vibrates with the same frequency and phase in each normal mode \( Q_i \) [1].
1.5.2 Solution of secular equation in internal coordinates

If internal coordinates are used as the initial coordinates the solution of the secular determinant 1.22 is greatly simplified. The internal coordinates are defined as the increments in bond lengths and bond angles. The principal advantage of internal coordinates is the representation of the potential energy or force constant matrix in terms of bond stiffness and resistance to bond angle deformations, which make these coordinates physically comprehensible. The size of the secular equation in internal coordinates is smaller and hence easier to solve.

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

\[ 2T = \sum_{i,j} G^{-1}_{ij} \dot{r}_i \dot{r}_j \] ........... 1.23

Where \( G^{-1}_{ij} \) are the inverse kinetic energy elements for each pair of coordinates \( r_i \) and \( r_j \). Similarly, the potential energy in internal coordinates is

\[ 2V = \sum_{i,j} f_{ij} r_i r_j \] ........... 1.24

where \( f_{ij} \) are the harmonic force constants. In matrix notation, the equation 1.23 and 1.24 can be suitably expressed by the equations,

\[ 2T = \hat{\mathbf{R}}^T G^{-1} \hat{\mathbf{R}} \] ........... 1.25

and \[ 2V = \mathbf{R}^T \mathbf{F} \mathbf{R} \] ........... 1.26

where \( G^{-1} \) is the inverse kinetic energy matrix and \( \mathbf{F} \) is the potential energy matrix comprises of the intermolecular force constants. Using equations 1.25 and 1.26 in the Newton’s equation in Lagrange form given by equation 1.27 and simplifying we get the secular determinant as
where E is the unit matrix. The expression 1.27 expresses the secular equation by involving the product term GF. Wilson first described this method of expressing the secular equation and so it is often referred as Wilson’s FG matrix method [25].

In order to frame a secular equation 1.27 for a polyatomic molecule it is necessary to select suitable set of internal coordinates and then set up the F and G matrix. At least 3n-6 internal coordinates are necessary to describe the vibration of an n-atom molecule. Sometimes it necessary to include more than 3n-6 internal coordinates and this will result in redundancies. These redundancies (interdependence of internal coordinates) can be removed later by a suitable coordinate transformation. While choosing the internal coordinates the rules given by Decius [26] will be much helpful.

**1.5.3 Solution of secular equation in symmetry coordinates**

After setting up the F and G matrix, the secular determinant 1.27 can be solved for Eigen values and Eigen vectors. But the size of the determinant is very high for most of the polyatomic molecules. It is therefore be advantageous to reduce the order of the determinant by taking advantage of the molecular symmetry. The simplification can be effected by the use of symmetry coordinates [27] and they are simple linear combinations of internal coordinates. For introducing symmetry coordinates the first step is to classify the normal vibrations according to the irreducible representation of the point group to which the molecule belongs. The symmetry coordinates are next selected so as to transform according to the appropriate irreducible representations of the molecular point group. These coordinates block diagnosis the secular determinant.
Hence the problem of solving the determinant of the order 3n-6 is reduced to the problem of solving several independent determinants of smaller order [24].

By using an orthogonal coordinate transformation internal coordinates $R$ can be transformed to symmetry coordinates $S$ and such an operation is written as,

$$S = UR$$

........ 1.28

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

$$UGU^T = G_s$$

........ 1.29

$$UFU^T = F_s$$

........ 1.30

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

$$|G_s F_s - E\lambda| = 0$$

........ 1.31

This expression has the same roots as the secular equation 1.27 in terms of internal coordinates and thus the Eigen values and Eigen vectors of both 1.31 and 1.32 are the same.

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

$$|G_s F_s - E\lambda| L = 0$$

........ 1.32

The $L$ matrix consisting of the Eigen vectors which are normalized. It provides the transformation from internal coordinates to the normal coordinates [1].
1.5.4 Potential energy distribution

In the normal coordinate analysis, potential energy distribution (PED) plays an important role in obtaining a detailed understanding about the nature of the normal modes. Morino and Kuchitsu [28] have shown that the potential energy distribution rather than the normalized amplitudes is a more satisfactory quantity to use in band assignments.

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

\[
R_i = \sum_{k=1}^{3n-6} L_{ik} Q_k \tag{1.33}
\]

where \( L_{ik} \) is the component of the L-matrix. Substitution of equation 1.33 to the potential energy expression 1.19 yields the potential energy of the molecule, for a vibration of frequency \( \nu_k \), associated with a normal coordinate \( Q_k \),

\[
2V = Q_k^2 \sum_{i,j} f_{ij} L_{ik} L_{jk} \tag{1.34}
\]

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

\[
\sum_{i,j} f_{ij} L_{ik} L_{jk} = \lambda_k \tag{1.35}
\]

neglecting the cross terms yields

\[
\sum_i f_{ii} L_{ik}^2 = \lambda_k \tag{1.36}
\]
The normalized potential energy distribution (PED) becomes

\[
PED = V_{ik} = \frac{f_{ij} L_{ik}^2}{\lambda_k} \quad \ldots \ldots 1.37
\]

It is the contribution of the \( i^{th} \) symmetry coordinates to the potential energy of the vibration whose frequency is \( \nu_k \) [29]. The contribution of the potential energy from the individual diagonal elements gives rise to, an analysis of the vibration spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computation of the normal modes.

**1.6 FORCE FIELD APPROXIMATIONS**

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

For many molecules it is not possible to evaluate all the force constants from the experimental data and it becomes necessary to reduce the force constants. This is accomplished by making assumptions about the nature of the potential energy function. Some of the important restrictive force fields are:
1.6.1 The general quadratic potential function

In this potential function, for a non-linear molecule the potential energy is expressed in a quadratic form,

\[ 2V = \sum_{i,j=1}^{3n-6} F_{ij} R_i R_j \] ........ 1.38

The main drawback with this force field is that, except for molecules of high symmetry, the number of force constants necessary to describe the potential energy of a molecule is always greater than the number of fundamental frequencies [30].

1.6.2 The central force field

This force field function accounts only for the forces in molecules among the atoms along the lines joining them. It fails to account for angle forces, bending vibrations and out-of-plane vibrations [30].

1.6.3 The valence force field

This force field consider only the forces associated with valence bonds. In this approximation forces between the non-bonded atoms are not considered. Here the number of force constants that have to obtain is usually less than the number of observed frequencies [29].

1.6.4 The simple general valence force field

It is an extension of valence force field and it takes into account the interaction force constants. This method employs stretching and bending force constants and also the interaction force constants between them [1]. The number of interaction force constants becomes increasingly larger as the molecule is larger. Some of the difficulty
can be overcome by neglecting interaction terms of frequencies of the same symmetry, which are widely separated from one another. This method also neglects the force between the non-bonded atoms. This is one of the effective potential functions employed for normal coordinate calculations. The simple general valence force field (SGVFF) has been to be very effective in normal coordinate analysis of hydrocarbons, peptides, amides and pyrimidine bases [31].

1.6.5 The Urey-Bradley force field

Basically it is a GVFF superimposed with some repulsive force constants between non-bonded atoms. The repulsive force term was introduced by Urey and Bradley [32] and Shimanouchi [33]. Pure UBFF is unsatisfactory for polyatomic molecules except tetrahedral (Td) molecules and it has been found necessary to introduce additional valence type interactions [34].

1.6.6 Computer programs for solving the secular equations

The advent of computers has certainly aided the normal coordinate analysis of molecules since computers can compensate some of the inherent difficulties and problems in the method. The multiplication of matrices and the solving of secular equations become highly simplified and completed in least time. With the developments of high-level languages, a large number of programs are developed for the normal coordinate treatment. Schachtschneider (1965) [35], Shimanouchi (1968) [36] Fuhrer et al (1976) [37], are some of the notable program developers for normal coordinate analysis. Many such programs are also available commercially for instance, Vibratz by Eric Dowty (1998) [38]. Some programs, under public domain, are also available in Internet like Prometheus by Martin Jursch (1997) [39].
After introducing necessary modifications in the program developed by Fuhrer et al. [37], was used for the normal coordinate analysis in the present thesis. The necessary information that is needed for the calculation is an initial vibrational force field and the structural parameters of the molecules. These parameters may be both the bond lengths and bond angles or the Cartesian coordinates of the atoms with respect to an arbitrarily chosen origin. Force constants from structurally similar molecules can be transferred as initial values and if necessary, some additional force constants can be added. The program is designed to consist of modules so that the output from one calculation serves as a part of the input to the next. The vibrational frequencies of normal modes and potential energy distribution are obtained as output. With the help of the program the initial set of force constants can be defined to give an excellent fit between the calculated and observed frequencies. Least squares procedure is used to define the force field calculations.

1.7 THEORY OF AB INITIO AND DFT METHODS

Predicting and understanding the properties and behavior of real material systems is of great importance both from technological and academic points of view. The theoretical problems associated with these systems are quite complex. Computational chemistry uses the results of theoretical chemistry, incorporated into efficient computer programs, to calculate the structure and properties of molecules and solids. While the results normally complement the information obtained by chemical experiments, it can, in some cases predict hitherto unobserved chemical phenomena. It is widely used currently in the design of new drugs and materials. In the pharmaceutical industry, computational chemists are often asked to predict the
structural features that lead to an efficient drug by considering the nature of receptor site. Then, organic chemists synthesize the proposed molecule, which are in turn tested by biochemists for efficiency. The process is often iterative, with experimental results feeding back into the calculations, which in turn generate new proposals for efficient molecules and so on. The computed time for such studies increases with the size of the system being studied. The system can be a single molecule, a group of molecules or a solid. The methods are based on theories which range from highly accurate, but suitable for small systems, to very approximate, but suitable for large systems. The accurate methods are called \textit{ab initio} methods, as they are based entirely on theory from first principles. The less accurate methods, like MM1-4 methods are called empirical or semi-empirical, because some experimental results, often from atoms or related molecules are used with the theory.

The great computational speed of molecular mechanics allows for its use in procedures such as molecular dynamics, conformational energy searching, and docking that require large number of energy evaluation. The computational study of chromatographic separations has become increasingly important in recent years. It supplies useful information about the mechanism of chromatographic separations and the design of stationary phases. The chromatographic separations of chiral benzimidazole type sulphoxides were analysed utilizing computation tools by Hatice Ozdemir Can [40]. Macrolide antibiotics have been known to play an important role in therapeutics, particularly with the emergence of new pathogens. Molecular mechanics has been used for the conformational analysis of dissymmetric macrolide antibiotics by Salah Belaidi \textit{et al} [41]. The molecular mechanics simulation method is well suited for investigating many-particle systems microscopically, and so it fills the
gap between the theoretical and the experimental. The geometrical structure of the sea
anemone and sea pansies neuropeptide Pol-RFamide II Glu\textsuperscript{1}-Trp\textsuperscript{2}-Leu\textsuperscript{3}-Lys\textsuperscript{4}-Gly\textsuperscript{5}-
Arg\textsuperscript{6}-Phe\textsuperscript{7}-NH\textsubscript{2} was studied using molecular mechanics [42].

Semi-empirical methods represent a “middle road” between the mostly
qualitative results available from molecular mechanics and the computationally time-
consuming quantitative results available from \textit{ab initio} methods. Semi-empirical
methods are a good choice for those users who are less interested in very accurate
numerical results and are more interested in developing the ability to use computing
to understand structure, properties and activities of molecules. When used judiciously,
semi-empirical methods like AM1, PM3, MNDO can give great insight into structure
and reactivity of even moderately large molecules. The heats of formation for 19
molecules have been calculated with PM3 and AM1 methods by P. Scano and C.
Thomson [43]. The values obtained have been compared with experimental heats of
formation. The results obtained suggest that the parametrization should be done
including larger molecules. The atomic structure optimization and calculation of the
electronic structure of the Si\textsubscript{20}, Si\textsubscript{20}-NaSi\textsubscript{20} and KSi clusters using AM1 and PM3
methods has been reported by N.A. Borschch, et al [44] The methods have also been
used to calculate ligand-protein binding enthalpies for use in the rational design of
new drugs [45].

\textit{Ab initio} computer programs such as ATMOL, GAUSSIAN, IBMOL,
POLYAYTOM, Cache are being used to speed up calculations of molecular orbitals.
The commercial package GAUSSIAN is considered by most to be the “industry
standard”, although other packages like Spartan, HyperChem are challenging
Gaussian for computational performance, and use by the research community. Gaussian is the benchmark by which all other \textit{ab initio} codes are measured. The primary advantage of \textit{ab initio} methods is the accuracy with which calculations are performed. To the degree that a researcher needs to know a property that most accurately matches experimental data or that most approximates a theoretical prediction, the \textit{ab initio} method is chosen. Fundamentally, it is the most accurate and precise of currently available methods in molecular modeling. \textit{Ab initio} methods are used by researchers to study the properties of molecules which are of great importance in pharmaceutical industry, materials science and in drug designing.

Gaussian 98W program was used by Mansoureh Zahedi Tabrizi \textit{et al} \cite{46} to study the compound napthazarin, a natural product with antitumour and antiviral property, while 5-amino-2-chlorobenzoic acid, a component of vitamin B-complex has been studied by N. Sundaraganesan \textit{et al} \cite{47} using Gaussian 03W program package. An important industrial chemical hexamethylenetetramine \cite{48} was analysed using Gaussian 98 package, and another chemical used in rubber industry to accelerate the vulcanization process, 2-mercaptobenzothiazole has been analysed using Gaussian 03W program \cite{49}. Gaussian 03W has also been used to analyse the structure of some pharmaceutical compounds like flucytosine \cite{50} and p-anisaldehyde \cite{51}.

1.7.1 \textbf{Ab-Initio Calculations}

\textit{Ab-initio} (Latin- “from first principles”) involves mathematical modeling, based on Schrodinger’s equation. Using several constants such as speed of light, Planck’s constant and the masses of the electrons and nuclei, one can use \textit{ab initio} methods to calculate a wide variety of properties like the energy of the molecule, its vibrational frequencies, its thermodynamic properties and the values of its molecular
orbitals, to name a few [52]. The primary advantage of *ab-initio* methods is the accuracy with which calculations are performed. To the degree that a physicist needs to know a property that most accurately matches experimental data, or that most approximates a theoretical prediction, the ab-initio method is chosen. Ab-initio is regarded as the most accurate and precise of all of the currently available methods in molecular modeling. These methods are currently applied largely to small molecular systems [53]. Most computational chemists hold the upper limit for use of *ab initio* methods to be around 50 atoms. For the biologist this limitation rules out the study of proteins and molecules of biological importance, which are typically thousands of atoms in size.

### 1.7.2 Hartree-Fock theory

Virtually all ab-initio calculations start out at the Hartree-Fock level, named after those physicists who developed the system. The “HF” method is also sometimes known as the “self-consistent field” (SCF) theory, which better describes what happens. The “Restricted Hartree-Fock” (RHF) is used for closed-shell systems and the “Unrestricted Hartree-Fock” (UHF) is used for open-shell species [54]. For many purposes, such as geometry optimization of neutral molecules, the HF method is the method of choice. The method is mathematically quite complicated, but relatively simple in concept. The procedure involves the following steps:

(i) A set of approximate orbitals (a basis set) is chosen for all the electrons in the system.

(ii) One electron in the system is chosen as the starting electron.

(iii) The potential (the energy of the system) in which the electron moves is calculated by “freezing” the distribution of all the other electrons and treating
their averaged distribution as a single (“centro symmetric”) source of potential.

(iv) The Schrödinger equation for the selected electron is calculated, resulting in a new, more accurate orbital for that electron.

(v) The procedure is repeated for all the other electrons in the system.

(vi) A cycle is deemed to be completed once each electron of the system has been evaluated. The process is begun again with the first electron evaluated, and using the newly calculated orbitals as the starting point.

(vii) The iteration process is continued until a pass through the calculations does not change the values for the orbitals.

(viii) Finally, the calculations are considered ‘completed’, since the orbital are now considered being “self-consistent”.

By calculating the energy of an electron as measured against all of the other electrons combined into one big electron, we have an “uncorrelated system”. This lack of electron correlation introduces a fair degree of inaccuracy to the calculations. The electron correlation effects become important while studying charged species, highly strained molecules, transition states and calculations of spectral frequencies. This limitation of the HF method is being addressed with the development of newer, “post-SCF” methods that attempt to take into account electron correlation. Moller-Plesset (MP) perturbation theory, Configuration Interaction (CI) theory, Coupled Cluster (CC) theory are some these methods. Also, density functional (DFT) methods take into account electron correlation, even though in a less systematic and less well defined way than \textit{ab initio} methods.
1.7.3 Density Functional Theory

The DFT [55] was set forth in the work of Hohenberg and Kohn [56]. Zeigler reported that the use of DFT in the ab initio calculation of molecular properties [57] has recently increased dramatically. This can be attributed to the development of new and more accurate density functional and the increasing efficiency and availability of DFT codes and superior ratio of accuracy to effort exhibited by DFT computations relative to other ab initio methodologies [58]. Chacon Villalba et al. reported quantum chemistry vibrational study using density functional theory (DFT) [59]. A number of Density functional methods like B3LYP, B3P86, B3PW91, BH and H, BH and HLYP are available. The density functional method used in this study is B3LYP.

B3LYP

The B3LYP represents the hybrid Becke 3 Lee – Yang – Parr correlational function. This functional is a hybrid of exact (HF) exchange with local and gradient corrected exchange and correlation terms, as first suggested by Becke. The exchange-correlation functionals proposed and tested by Becke [60] was

\[ E_{xc} = (1-a_0) E_x^{LSPA} + a_0 E_x^{HF} + \Delta E_x^{B88} + E_c^{LSDA} a_c \Delta E_c^{PW91} \]

Here \( \Delta E_x^{B88} \) is Becke’s gradient correction to the exchange functional and \( \Delta E_c^{PW91} \) is Perdew – Wang gradient correction [61] to the correlation functional. He suggested coefficients \( a_0 = 0.2, a_x = 0.72, a_c = 0.81 \) based on fitting to heats of formation of small molecules. The functional containing only one parameter, fits the exact Hartree – Fock exchange energies of a wide variety of atomic systems with remarkable accuracy, surpassing the performance of previous functionals containing two parameters or more.
1.7.4 Basis set choices

Slater-type orbitals (STOs) were used in ab initio calculations in the early stages. But, the evaluation of the resulting one- and two- centered integrals presented a major computational problem. To solve this, researchers replaced the STO by a mathematically more tractable combination of Gaussian-type orbitals (GTOs). Initially, the STOs were replaced with a linear combination of Gaussian functions. Ultimately, it was shown that viable results usually could be obtained with three Gaussian terms. These STO-3G orbitals were used in many early ab initio studies and are still used for rapid survey calculations before spending time on higher levels of calculations. As a rule of thumb, the computational time varies approximately as the fourth power of the number of basis functions. STO-3G is referred to as a minimum basis set, because it uses only the number of orbitals required to accommodate the number of electrons for the atom in question. As with semi-empirical molecular orbitals, there are scale factors to be introduced in determining useful orbitals. In some studies minimizing the energy of each atom carried this out, but a more usual approach is to refine the scale factors using the energies and geometries of small molecules.

Minimal basis sets suffer because of their inability to adjust to charge and lone pairs that may be part of the structure. Compare water to the hydronium ion, the same set of orbital are used for the neutral and charged species. Reasonably, the orbital of the positively charged ions should be contracted when compared to their neutral counterparts. In other words, STO-3G orbitals are too “hard” to be non-polarizable. One approach to a solution is to increase the number of primitive Gaussians used to
describe the orbital and in essence split the orbital into an inner “hard” core and an outer “soft” or more polarizable shell. The inner-shell orbitals are represented by a single orbital made up of a set number of Gaussians, while the valence-shell orbitals are split into two parts each, resulting in what is known as a split-basis set. The separation between the inner and outer function can be justified by parameter choice. Typical split-valence basis sets are the 3-21G and 6-31G sets [62]. The first number gives the number of primitive Gaussians in the inner-core orbitals. The split-valence orbitals are given with the number of Gaussians for the inner portion (two or three in these cases) and the number of Gaussians for the outer portion (one in each case). In contrast, even the inner-shell orbitals may also be split, in which case the basis set is described as a double zeta set.

Two additional basis-set corrections should be done. Both split and double zeta sets lead to orbitals centered about the nucleus. Molecules with small or highly strained rings as well as those, which are very polar, require orbital that allow a non-uniform distribution of charge. This can be effected by adding additional d functions or a combination of ‘d’ and ‘p’ functions. This combination of two functions produces two new orbitals. One way of designating these polarized basis sets is by listing the functions added, i.e., 6-31G(d, p), which adds ‘d’ functions to the non-hydrogen atoms and ‘p’ functions to the hydrogen atoms. This notation is also given as 6-311G **. The combination of triple Zeta function 6-311G(d,p) is used in the present investigation for calculating the vibrational assignment of the compounds chosen.
1.8 THE SCALED QUANTUM MECHANICAL (SQM) FORCE FIELD

For molecules of chemical interest, force fields or vibrational spectra are computed either by ab initio, Hartree-Fock or DFT method and then combined with experimental information. The calculated harmonic frequencies are usually higher than the corresponding experimental quantities, due to a combination of electron correlation effects and basis set deficiencies. In the SQM approach the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules.

In the SQM procedure, the molecule geometry is expressed in terms of a full set of non redundant natural internal coordinates [63, 64]. Natural internal coordinates use individual bond displacement as stretching coordinates and linear combinations of bond angles and torsions as deformational coordinates. Suitable linear combinations of bends and torsions are selected using group theoretical arguments based on local pseudosymmetry. On the basis of chemical institution, the natural internal coordinates are stored into groups sharing a common scaling factor, and factors for each group are determined by a least-square fitting procedure to experimental vibrational frequencies. Force constants, originally calculated in Cartesian coordinates, are transformed into an internal coordinate representation, and scaling is applied to the elements of the internal coordinate force constant matrix according to

\[ F_{ij} \text{ (scaled)} = (s_is_j)^{1/2} F_{ij} \]

where \(s_i\) and \(s_j\) are scaling factors for natural internal coordinates \(i\) and \(j\), respectively.

The accuracy obtained by selective scaling in this way is naturally greater than if just a single overall scaling factor were used. Additionally, scaling the force
constant matrix also affects the resultant modes, and hence the calculated intensities, leads to better agreement with experimental intensities.

1.8.1 Computational methods

The quantum chemical calculations (geometry optimizations, force field and vibrational frequency calculations in harmonic approximation) were done with the Gaussian03 program package. Follow-up normal coordinate calculations were performed inorder to scale the force fields and obtain the vibrational energy distributions (PEDs or TEDs) among internal or symmetry coordinates. These calculations were done with the MolVib program (version V7.0) written by Sandius [65]. For this, the QM force field matrix and the dipole and polarizability derivatives (expressed in Cartesian coordinates) were transferred from the archive part of the Gaussian output to MolVib and transformed to the appropriate set of internal coordinates. Scaling of the force field was done according to the selective scaling method using the recommended values of transferable scale factors first, with subsequent least-squares fitting of the frequencies through refinement of the scale factors.
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