CHAPTER - 1

BASICS OF

VIBRATIONAL SPECTROSCOPY
1.1 Introduction

The use of a beam of light to probe the structure of molecules represents a continuing challenge to scientists as the information required become more penetrating and sophisticated. Infrared rays were discovered in 1800 by William Herschel [1]. The rays also obey the laws of reflection and refraction and subsequently it was determined that this radiation could be absorbed by matter and that absorption occurred in the form of several bands localized in discrete frequency intervals. The frequency range is from 1 to 10,000 cm\(^{-1}\).

At ordinary temperatures organic molecules and polymers are in a constant state of vibration each bond having its characteristic stretching and bending frequency and being capable of absorbing light of that frequency. The stretching absorptions of a bond appear at higher frequencies in the infrared spectrum than the bending absorptions of the same bond. The vibrational frequency of a bond is expected to increase when the bond strength increases, and also when the reduced mass of the system decreases.

Infrared spectroscopy is one of the most powerful analytical techniques which offers the possibility
of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis. This method can solve many problems in organic chemistry and coordination chemistry. This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region.

The limitations imposed by early IR spectrometers, which had restricted range and low sensitivity and by poor sample preparation meant that organic compounds often gave diffuse and variable spectra. But after several decades of technical advance and much pioneering work on simple organic and well characterized synthetic minerals of known composition, it became clear that IR spectroscopy could provide a wealth of information from investigations of organic and mineral compound, much of the information unique to the IR technique.

1.2 IR Spectrophotometer

The radiation emitted is split into two beams. One beam passes through the sample, which absorbs radiation at wave number corresponding to its characteristic molecular vibrational frequencies, while the other serves a reference. The attenuator in the reference beam is servo controlled. The two beams
are combined by a rotating mirror to form a single beam consisting of alternate pulses of radiation from the sample and reference beam. The combined beam then passes into the monochromator where it is dispersed by the grating into spectral components. The radiation then passes through one set of optical filters and is focussed onto a thermocouple detector. The recorder chart is driven in synchronism with the instrument monochromator so that the pen, moving across the chart, records the simple transmittance as a function of wave number.

1.2.1 Sample cells and sampling substances:

As infrared spectroscopy is used for the characterisation of solid, liquid or gas samples, it is evident that samples of different phases are handled. But these salts are treated differently. However, the only common point to the sampling of different phases is that the material containing the sample must be transparent to infrared radiation. This condition restricts our selection to only certain salts like NaCl or KBr. However, a final choice of salt will depend on the wavelength range to be studied [2].

1.2.2 Sampling of solids:

Solids run in solution:

The solution of solid is prepared in a suitable solvent and then the solution is run in
one of the cells for liquid. But this method cannot be used for all solids because suitable solvents are limited in number and there is no single solvent which is transparent throughout the IR region.

1.2.3 Solid films:

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

1.2.4 Mull technique:

In this technique the finely ground solid sample is mixed with Nujol (mineral oil) to make a thick paste which is then made to spread between IR transmitting windows. This is then mounted in a path of IR beam and the spectrum is run. Although Nujol is transparent throughout IR region, yet it has the disadvantage that it has the absorption maxima at 2915, 1462, 1376 and 719 cm$^{-1}$.

When IR spectrum of a solid sample is taken in Nujol mull, absorption bands of the sample that happen to coincide with the absorption bands of the Nujol Mull will be hidden, but others will be clearly seen in the IR spectrum. The solid sample in the Nujol is used in combination with hexachlorobutadiene which
absorbs in the regions 1630-1510, 1200-1140 and 1010-760 cm$^{-1}$. As the absorption bands in Nujol mull and hexachlorobutadiene appear in different regions, their use in combination permits the recording of IR spectrum.

1.2.5 Pressed pellet technique:

In this technique a small amount of finely ground solid sample is intimately mixed with about 100 times its weight of powdered potassium bromide. The finely ground mixture is pressed under very high pressure in a press to form a small pellet (about 1.2 mm thick and 1 cm in diameter). The resulting pellet is transparent to IR radiation and is run as such. The advantage of this method over Nujol mull method is that the use of KBr eliminates the problem of bands which appear in the IR spectrum due to the mulling agent.

1.2.6 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 so selected that the transmittance lies between 15 and 70 percent. For most liquids this will represent a thin layer of 0.01-0.05 mm in thickness.
If a cell possesses good quality windows, flat and parallel, its thickness $t$ in cm can be calculated from the following equation:

$$2t = \frac{N}{W_1 - W_2}.$$

where $N$ is the number of fringes between wave numbers $W_1$ and $W_2$.

1.2.7 Sampling of gases:

The gas sample is put into a special cell generally but about 10 cm long which is then kept across the path of IR beam. The end walls of the cell are made up of NaCl. For measuring very dilute gases, long path cells are employed. Since the sampling area of most spectrometers is restricted in length, mirrors are used to bring about multiple reflections to make effective path length as long as 40 cm (3).

1.2.8 Preparation of polymer samples for IR examination:

The first consideration in sampling polymers will be whether the physical state of the sample, as well as its chemical nature is of interest. The most direct way of obtaining IR spectrum of a polymer is to measure the transmission spectrum of a thin film.
A very simple and often successful method is to spread a thin layer of the liquid latex over a glass plate and to put the plate under an infrared lamp to drive off the water. If the samples turn to a layer of powder, rather than a continuous film it is worth trying again in an oven at a higher temperature, as this may cause the resin to melt and flow into a film as the water evaporates. Once dry, the film can usually be removed from the glass plate by easing it from the edges with a razor blade, using a few drops of water as lubricant. Then the sample is mounted over a hole in a card mount of a size suitable for the spectrometer.

1.3 Raman Scattering:

Light is scattered by a material in several different ways, and the scattering processes are usually named after the scientists who made major contributions to the field. Raman scattering is an inelastic process in which light exchanges energy with the sample and consequently appears at a different frequency. Sir C.V. Raman [4] first observed the effect, which is very weak compared to Rayleigh scattering.

To observe the Raman effect, monochromatic light has to pass through a substance which is transparent or at least not wholly opaque, and emerging again from its
opaque, and emerging again from its interior after being scattered by its molecules. The monochromatic light used is examined after scattering and found that the spectrum of scattered light is not identical with the spectrum of the light first used, but contains new line in addition to the original light. The substance used plays an essential part in the phenomenon, for the number and position in the spectrum of the new rays observed depend on the substance used and are characteristic of it.

In the 1960s the advent of the laser had an enormous impact on Raman spectroscopy. The laser as a light source was quickly adopted by spectroscopists because of the radiation's high power, coherency and monochromaticity. It also eliminates the problem of sample decomposition. Among the continuous wave lasers Argon and Krypton lasers can be tuned with various discrete wavelengths between 324 and 799 nm [5].

Some laser sources suitable for Raman experiments emit a train of short lived high power pulses. One advantage of pulsed lasers is that they can be frequency doubled by passing the beam through certain inorganic crystals. In experiments using pulsed lasers the Raman photons arrive at the photon multiplier tube in pulses and the resulting signal is normally analysed
using a box car integrator. Pulsed lasers in general, used in conjunction with multiplex detectors, are being used increasingly to obtain Raman spectra within a short time span.

The monochromatic radiation provided by a laser is focussed on to or into the sample and some of the resulting scattered light is gathered by collecting optics and directed to a dispersing system. The latter which is usually a double monochromator, spatially separates the scattered light on the basis of frequency. At the exit part of the monochromator the Raman spectrum forms an image consisting of series of very fine lines. These are directed and recorded, either sequentially by a single photomultiplier used with a scanning monochromator, or simultaneously by a multichannel detector which is the modern electric equivalent of a photographic plate.

1.4 Theory on molecular vibrations:

Spectroscopic methods provide a powerful tool for the investigation of molecular structure. The problem of obtaining the spectrum of even complicated molecules has been simplified by the sophisticated experimental techniques employed in the Raman and infrared spectroscopy. Detailed information on the molecular dynamics can be derived employing the recently
developed mathematical techniques like group theory and matrix algebra, once the fundamental vibrational frequencies and the structural parameters are known.

The disposition of the vibrating nuclei, the force field which restores the molecule to its equilibrium configuration and the atomic mass involved determine the vibrational frequencies of a molecule.

For a vibration to be infrared active it should cause a variation in the electric dipole moment of the molecule. The selection rule for this, obtained from the transformation property of electric moment is:

$$\sum_{R} (\pm 1 + \cos \phi_{R}) \chi_{l}(R) = 0 \text{ inactive}$$

Where $\chi_{l}(R)$ is the character of the irreducible representation $\Gamma_{l}$ to which the normal coordinate belongs.

The summation extends over all the operations that constitute the group. Raman activeness is due to the change in polarizability.

The selection rule is:

$$\sum_{R} 2 \cos \phi_{R} \chi_{l}(R) = 0 \text{ inactive}$$

The plus and minus sign indicates whether the operation is a rotation or rotation reflection in both the cases.
The change in the energy of the electrons binding the nuclei together give the force field. The force constant which may be defined as the resistive force per unit displacement (bending or stretching) gives a measure of the strength of the chemical bond between the atoms. A molecule and its isotopic analogues have almost the same set of force constants, since isotopic substitution does not alter the nature of the chemical bond. Thus it is possible to deduce the fundamental wave numbers of the isotopic substitutes when the force field of a molecule is known. This method is very useful especially when the spectrum of isotopic substitute can be easily obtained. Conversely, the force constants can be evaluated with greater precision once the spectrum of a molecule and its isotopic substitutes are known accurately.

Since the concept of group frequencies is an universally accepted fact, the force constants which are characteristic of certain group vibrations can be transferred from molecule to molecule. Hence it is possible to subject the nature of force fields in large molecules from those of smaller molecules. The force constants mainly depend on the bond order and on mass factors. The vibration of force constants with bond order for bonds between a given pair of
atoms indicate that the force constants may be used to elucidate the bond character in the same way as the bond lengths have employed. Badger [6] has given empirical relations between the stretching force constants and bond lengths. Gordy [7] has related the stretching force constants to the product of electronegativities of the bonded atoms and bond length. Thus a knowledge of force constants enables us to calculate the interatomic distances. A detailed knowledge of force field helps to know the normal coordinates associated with each vibrational frequency which is essential for the absolute intensity studies. Infrared and Raman intensities have been used along with force constants successfully to obtain the bond dipole moments, polarizabilities and their derivatives [8].

The atoms constituting the molecule will be vibrating at all temperatures as the molecule is not a rigid structure. The mean square amplitudes of vibration provide an additional set of parameters required to describe the non-rigid model of the molecule. These quantities may be determined from electron diffraction experiments and also from spectroscopic data.

The spectra obtained using infrared and Raman techniques have been analysed on the basis of molecular
symmetry and group theory. The normal vibrations can be divided into two principal groups:

1.4.1 Stretching vibration:

In this type of vibrations, the atoms move essentially along the bond axis, so that the bond length increases or decreases periodically. As this type of vibrations corresponds to one dimensional motion, it means that there will be \( n-1 \) stretching vibrations for non-cyclic systems.

1.4.2. Bending vibrations:

In this type, there occurs a change in bond angles between bonds with a common atom or these occurs when the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another.

1.4.3 Types of stretching and deformation vibrations:

In a polyatomic molecule, the same bond can perform stretching and bending simultaneously. Stretching vibrations are of two types:

i) symmetric vibrations,

ii) asymmetric vibrations

Deformation vibrations are more as compared to stretching vibrations. They are of two types:

i) in-plane deformation vibrations,

ii) out-of-plane deformation vibrations.
1.5 Vibrational assignments:

Most molecules contain characteristic groups such as CH$_3$, NO$_2$ etc and these usually produce a characteristic group frequency, which can be used for identification and assignment. These group frequencies must be used with care, since mixing of the group vibrations can occur and cause significant and unexpected changes in the group frequency.

The assignment of infrared and Raman spectra of small molecules is a relatively simple process. However, the complexity of the spectrum increases rapidly with each added atom and unequivocal assignments are still sought for some molecules with as few as four or five atoms. The correct assignments of all the normal modes of vibration of a polyatomic molecule is still problematic.

The tools which may be brought to bear in vibrational assignments, include empirical correlations and the group frequency concept, infrared and Raman selection rules, rotational structure and the shapes of infrared and Raman bands, frequency shifts in isotopic molecules, the polarization characteristic of Raman bands, infrared dichroism, infrared and Raman intensities, theoretical calculation of vibrational frequencies and band assignments. However, for
polyatomic molecules generally one has to rely on Raman and infrared vibrational frequencies. Experimental approach alone may not be sufficient for the understanding of the complicated spectra of complex molecules. There are three stages in the utilization of new spectral data. The observed frequencies are first classified according to the normal modes of vibration belonging to each irreducible representation of the point group of the molecule. Following this the assignment of frequencies may be made by correlation with related molecules. These correlations may be carried out usually both on the basis of vibrational frequencies and band intensities are usually empirical in nature [9].

1.5.1 Structure of the molecule:

The structure of the molecule should be known. Usually this data is available from X-ray structure determination. If the structure is not available, the structure is assumed and bond lengths and bond angles are transferred from related molecules whose structures are known. This introduces some uncertainty, when the structures of the molecule is unknown. From the structural data the point group of the free isolated molecule can be fixed.
1.5.2 Vibrational modes:

For the molecular modes chosen, the number of vibrations, stretching \((n_R)\) bending \((n_\phi)\) torsion \((n_T)\) and out-of-plane bending \((n_{\Pi})\) are determined from the number of atoms in the molecule \((a)\) number of bonds \((b)\), number of atoms taking part in only one bond formation \((a_1)\) and the number of atoms forming more than two bonds (multiplicity: \(m > 2\)).

The number of stretching vibrations are given by \(b\) and the number of bending vibrations by \(4b-3a+a_1\), while the number of torsional modes are equal to \(b-a_1\). The number of out-of-plane bending co-ordinates \((n_{\Pi})\) is obtained by replacing \((m-2)\) in plane bending modes \(n_\phi\) by \(n_{\Pi}\) s.

1.5.3 Classification of normal modes:

The normal modes are classified according to the irreducible representations of the point group to which the molecule belongs. This may be done by using the relation:

\[
N_i = \frac{1}{h} \sum_R n_{\gamma}(R) \chi(i)
\]

where \(h\) is the order of the group, \(n\) is the number of symmetry elements in a symmetry class \(\gamma(R)\) is the character of the reducible representation and \(\chi(i)\) is the character of the irreducible representation.
\( \chi(R) \) can be determined from the relation
\[ \chi(R) = (U_R - 2)(1+2 \cos \phi) \]
for proper rotation and
\[ \chi(R) = U_R(-1+2 \cos \phi) \]
for improper rotation where \( U_R \) represents the number of atoms unmoved and \( \phi \) is the angle of rotation for the operation \( R \).

Infrared and Raman activity can be determined using the formulae earlier discussed. The infrared and Raman spectra are first assigned by group frequencies from IR and Raman structural correlation charts and assignments in structurally related molecules.

1.5.4 Interpretation of spectra-rules:

The following are the rules relating to the interpretation of spectra:

1) Unsaturated bonds like \(-\text{C}=\text{C}-\), \(-\text{C}≡\text{C}-\), etc., tend to give rise to very strong Raman bands and to weak infrared bands between 1600 and 2300 cm\(^{-1}\).

2) Bonds containing one or more heavy atoms will give rise to extremely strong Raman scattering and sometimes to strong IR absorption.

3) The stretching frequencies of the polar-NH and \(-\text{OH}\) bonds give rise to very strong IR absorption but weaker Raman scattering.

4) The \(-\text{OH}\) and \(-\text{NH}\) bending bands are generally weak in the Raman spectrum, but strong in the IR spectrum.
5) The methyl and methylene bending frequencies are strong in IR spectrum but weak in Raman spectrum.

6) -C-C-C- stretching bonds are strong in Raman but weak in IR spectrum.

7) The -SH and -S-S- stretching frequencies are strong in Raman spectrum but weak in IR spectrum.

8) The C-H- stretching frequencies are strong in Raman spectrum but weak to moderate in IR spectrum.

9) Carbonyl and carboxyl frequencies are strong both in IR and Raman spectrum.

10) Ring compounds have a very strong Raman band associated with the symmetric expansion and contraction of the rings.

11) Aromatic compounds tend to have strong IR absorption and Raman scattering.

12) Ring deformation vibrations are weak in Raman spectrum but strong in IR spectrum.

13) Polynuclear aromatic compounds will tend to have a complex IR and Raman spectra composed of strong sharp bands.

14) In hydrogen-bonded compounds the -OH and -NH stretching and bending may produce shifts in amides or carbonyl stretching frequencies.
### TABLE - 1: POSITIONS OF VARIOUS BOND VIBRATIONS

<table>
<thead>
<tr>
<th>Bond</th>
<th>Mode</th>
<th>Relative Strength</th>
<th>Wave Number ( \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>Stretch</td>
<td>S</td>
<td>2700 - 3300</td>
</tr>
<tr>
<td>C-H</td>
<td>Stretch (2)</td>
<td>M</td>
<td>5600 - 6300</td>
</tr>
<tr>
<td>C-H</td>
<td>Stretch (3)</td>
<td>W</td>
<td>8300 - 9000</td>
</tr>
<tr>
<td>C-H</td>
<td>Stretch (C)</td>
<td>M</td>
<td>4200 - 5000</td>
</tr>
<tr>
<td>C-H</td>
<td>Bend inplane</td>
<td>M-S</td>
<td>1300 - 1500</td>
</tr>
<tr>
<td>C-H</td>
<td>Bend out of plane</td>
<td>W</td>
<td>800 - 830</td>
</tr>
<tr>
<td>C-H</td>
<td>Rocking</td>
<td>W</td>
<td>600 - 900</td>
</tr>
<tr>
<td>C-C</td>
<td>Stretch</td>
<td>M-W</td>
<td>800 - 1200</td>
</tr>
<tr>
<td>C-C</td>
<td>Stretch</td>
<td>M</td>
<td>900 - 1300</td>
</tr>
<tr>
<td>C-C</td>
<td>Stretch</td>
<td>M</td>
<td>1600 - 1700</td>
</tr>
<tr>
<td>C≡C</td>
<td>Stretch</td>
<td>S</td>
<td>1600 - 1900</td>
</tr>
<tr>
<td>C≡C</td>
<td>Stretch (2)</td>
<td>M</td>
<td>3300 - 3600</td>
</tr>
<tr>
<td>C≡C</td>
<td>Stretch (3)</td>
<td>W</td>
<td>5000 - 5300</td>
</tr>
<tr>
<td>C-N</td>
<td>Stretch</td>
<td>M-S</td>
<td>1600 - 1700</td>
</tr>
<tr>
<td>C≡N</td>
<td>Stretch</td>
<td>M-W</td>
<td>2100 - 2400</td>
</tr>
<tr>
<td>C≡N</td>
<td>Stretch</td>
<td>M</td>
<td>2100 - 2400</td>
</tr>
<tr>
<td>C-F</td>
<td>Stretch</td>
<td>S</td>
<td>1000 - 1400</td>
</tr>
<tr>
<td>C-Cl</td>
<td>Stretch</td>
<td>S</td>
<td>600 - 800</td>
</tr>
<tr>
<td>C-Br</td>
<td>Stretch</td>
<td>S</td>
<td>500 - 600</td>
</tr>
<tr>
<td>C-I</td>
<td>Stretch</td>
<td>S</td>
<td>500</td>
</tr>
<tr>
<td>O-H</td>
<td>Stretch</td>
<td>S</td>
<td>3000 - 3700</td>
</tr>
<tr>
<td>Bond/Mode</td>
<td>Description</td>
<td>Symbol</td>
<td>Frequency Range</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>--------</td>
<td>-----------------</td>
</tr>
<tr>
<td>O-H</td>
<td>Stretch (2)</td>
<td>S</td>
<td>6700 - 7100</td>
</tr>
<tr>
<td>O-H</td>
<td>Bending</td>
<td>MW</td>
<td>1200 - 1500</td>
</tr>
<tr>
<td>N-H</td>
<td>Stretch</td>
<td>M</td>
<td>3000 - 3700</td>
</tr>
<tr>
<td>N-H</td>
<td>Stretch (2)</td>
<td>S</td>
<td>6300 - 7100</td>
</tr>
<tr>
<td>N-H</td>
<td>Stretch (3)</td>
<td>W</td>
<td>9000 - 10000</td>
</tr>
<tr>
<td>N-H</td>
<td>Stretches (c)</td>
<td>M</td>
<td>4800 - 5300</td>
</tr>
<tr>
<td>N-H</td>
<td>Bending</td>
<td>M</td>
<td>1500 - 1700</td>
</tr>
<tr>
<td>N-H</td>
<td>Rocking</td>
<td>SM</td>
<td>700 - 900</td>
</tr>
</tbody>
</table>

---

S = Strong
M = Medium
W = Weak

2 - Second harmonic
3 - Third harmonic
C - Combination frequency.
1.6 Mathematical formulation of the molecular potential constants:

1.6.1 Molecular force field:

When the force field or the potential field is not generally known then the object of force constants calculation is to determine this field. A non-linear molecule having N atoms will have \((3N-6)\) vibrational frequencies, \((3N-5)\) for a linear molecule \((3N-4)\) for a polymer and \(n\) internal displacement co-ordinates. For such a molecule to describe a general quadratic force field \(n(n+1)/2\) potential energy constants are required. The number of potential constants is larger than the number of normal vibrations and hence all the force constants of a particular molecule cannot be determined from the observed frequencies alone. In such cases, the solution is then obtained either by introducing additional equations from isotopic cases which may be having the same force constants or by borrowing the force constants from molecules which posses similar bonds. Another solution is to make specific assumptions about the nature of the force in the molecules such that the number of force constants to be determined is not large. Several approximations proposed by different workers are given below:
1.6.2 Central force field:

Dennison [10] assumed that the force acting on a given atom in a molecule is the resultant of the attraction and repulsion by all other atoms i.e. only central force acts between the atoms in a molecule. The attraction and repulsion depends only on the distance from other atoms and along the lines connecting them with the atom under consideration. This is equivalent to assuming that potential energy is purely a quadratic function of the changes of the distances between the nuclei. But this force field is rarely used due to its limitations and the omission of bending motions. Further, there are no quadratic term in this potential function, which would resist this motion so that zero frequency would be predicted.

1.6.3 Simple valence force field:

This approximation developed by Bjerrum [11] involves a restoring force in the line of every valence bond if the distance between the two bonded atoms is changed and a restoring force opposing a change of the angle between two valence bonds connecting one atom with two others. But this force field excludes the forces between non-bonded atoms. The number of force constants are less than the number of frequencies. Further, calculated frequencies differ from observed
frequencies by more than 10%. Hence this force field fails to account for the vibrational frequencies of many molecules. This force field is inadequate to explain the out-of-plane bending in planar molecules.

1.6.4 Orbital valence force field:

This force field is a modified form of valence force field devised by Heath and Linnett [12]. The orbital valence force field involves angular distortion in the molecule. Two considerations have been introduced here:

i) Van der Waal's repulsive force between non-bonded atoms.

ii) Condition for stability of molecules.

Under the circumstances, this force field therefore postulates a three component potential function which considers the bending vibrations strictly in accordance with the modern theory of directed valency.

1.6.5 Urey Bradley force field:

Stretching and bending force constants as well as repulsive constants between non-bonded atoms are the main features of Urey - Bradley force field [13]. This force field is inadequate for complicated systems due to the exclusion of interaction between non-neighbouring stretching vibrations and the bending vibrations in this force field. This force field
suits well when the non-bonded nuclei are closer than the sum of their covalent radii, and worst suited for hybrids. Further, UBFF force constants are transferrable as shown by Mizushima and Shimanouchi [14]; Overend and Scherer [15, 16].

1.6.6 Modified Urey Bradley force field:

Shimanouchi [17] from his study of ethane and ethylene found the inadequacy in explaining the rocking motion by simple UBFF and introduced 'Flexible bond model' which includes additional bending force constants due to bond flexibility besides the usual UBFF terms. Still the MUBFF is not able to explain the interaction between non-neighbouring stretching vibrations as in UBFF.

1.6.7 Hybrid bond force field:

The UBFF was unable to produce true quadratic force constants particularly in the case of Ammonia [18-20]. This is because of the fact that the UBFF does not account properly for the interaction between valence bond stretching and the angle bending displacement in the potential function of Ammonia. To account for this a Hybrid bond model is proposed in which the bond energy function depends on the hybridisation of the bond forming orbitals and the central force terms between non-bonded atoms.
1.6.8 General quadratic valence force field:

This force field is a better representation of the intermolecular forces and has been widely used in normal co-ordinate analysis. Besides the stretching and bending force constants, the various possible interaction between stretching and stretching, bending and bending, bending and stretching vibrations of not only neighbouring atoms but also between non-neighbouring atoms are also included.

1.7 F-G Matrix method:

In the present investigation GQVFP has been used throughout. Wilson's F-G matrix method [21] has been employed in the calculation of force constants. By applying the group theory, the number of genuine vibrations for each species is obtained. Corresponding to the number of vibrations under each symmetry type, symmetry co-ordinates which are linear combinations of internal co-ordinates comprising changes in bond distance and inter-bond angles are constructed. The symmetry co-ordinates are normalised, orthogonal and transfers in accordance with the character of the symmetry type to which they belong.

If \( R \) denotes the column matrix consisting of internal co-ordinates and \( S \) the column matrix of symmetry co-ordinates, then

\[
S = UR
\]
where $U$ is an orthogonal transformation matrix. The potential energy $(V)$ of a molecule in the harmonic approximation is given by the expression

$$2 \, V = \sum_{ij} f_{ij} r_i r_j.$$ 

This expression is written in the matrix form

$$2 \, V = R' f R.$$

In terms of symmetry co-ordinates this becomes

$$2 \, V = S' F S.$$

where $F = U f U'$. $R'$, $S'$ and $U'$ are transposes of $R$, $S$ and $U$ matrices.

The kinetic energy $(T)$ when expressed in matrix notation takes the form

$$2 \, T = \bar{S} G^{-1} \bar{S}.$$

Wilson [21] has shown that the elements of $G$ matrix for non-degenerate vibrations are obtained from the relation

$$G_{jl} = \sum_p \mu_p q_p (S_{jt} S_{kt})$$

where $l$ and $j$ refer to the symmetry co-ordinates, $p$ to a set of equivalent atoms, a typical one of the set being $t$, $\mu_p$ is the reciprocal mass of the typical atom $t$ and $q_p$ is the number of equivalent atoms in the $p^{th}$ set, the summation being extended over all the set of equivalent atoms in the molecule. For degenerate vibrations the relation is given as:

$$G_{jl} = \frac{1}{d} \sum_p \mu_p q_p \sum_a S_{ja}, t. S_{pa}, t.$$
where \( d \) is the degree of degeneracy. The \( S \) Vectors in the above expressions are obtained from the relation
\[
S_{jt} = \sum_k U_{jk} S_{kt}
\]
where \( U_{jk} \) is the coefficient of \( k^{th} \) internal co-ordinates \( r_k \) in the symmetry co-ordinate \( S_j \) and the summation is taken over all internal co-ordinates. The expressions for the \( S_{kt} \) vectors have been given by Wilson et al. [22]. Ferigle and Meister [23] have given the modified method for the determination of \( G \) matrix for linear molecules.

After having obtained the \( F \) and \( G \) matrices, the secular equation of the form,
\[
|FG - E \lambda| = 0
\]
is to be solved for evaluating force constants. In the above equation, \( E \) is the unit matrix and the roots of the secular equations are related to the wave number of the fundamentals (\( \text{cm}^{-1} \)) as.
\[
\lambda_i = 4 \pi^2 c^2 \gamma_i^2
\]
The force constants have been judiciously chosen employing the data in molecules containing similar bond environments. The successive approximation is carried out to solve the secular equation and the process is continued until the calculated frequencies agree fairly well with the observed ones.
In the present investigation the observed spectra have been analysed adopting General Quadratic Valence Force Field for both in-plane and out-of-plane vibrations. The bond lengths and bond-angles are taken from Sutton's table [24]. The normal co-ordinate analysis has been carried out using the programme given by Schachtschneider [25].

The Potential Energy Distribution has been calculated using the relation

\[ P.E = F_{ii} \frac{L^2_{ik}}{\lambda_k} \]

The Potential Energy Distribution calculated confirms the validity of the assignments. In the normal co-ordinate analysis potential energy distribution plays an important role for the characterisation of the relative contributions from each internal co-ordinate to the potential energy associated with a particular normal co-ordinate of the molecule. The contribution to the PE from the individual diagonal element gives rise to a conceptual link between the empirical analysis of vibrational spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computation of normal modes. In case of group frequency vibrations the total vibrational potential energy of the normal mode is localised in a few bonds or bond type and it is
also transferable and independent of the larger part of the surrounding structure of the molecule.

The observed spectra are capable of furnishing answers to a great variety of questions arising in Physics and Chemistry and of yielding an inexhaustible wealth of information regarding the structure of molecules and their behaviour at all possible conditions. They establish conclusively the identity of two samples that have identical spectra. It contains many absorptions associated with the interacting vibrating systems in the molecule. Since it is uniquely characteristic of each molecule, this gives rise to a uniquely characteristic set of absorption bands in the spectrum.

By examining a large number of compounds known to contain a functional group one can establish which infrared absorptions are associated with that functional group. The far infrared spectra is sensitive to the physical state of a substance and the conformation of its molecules. This is advantageous where polymers with the same chemical structure but different conformation must be analysed. It also reflects the structure of a molecule, especially the masses of the constituent atoms and the intramolecular forces acting between them, as well as the intermolecular forces operating in the crystalline state. It establishes clearly the distinction between the amorphous and crystalline states.