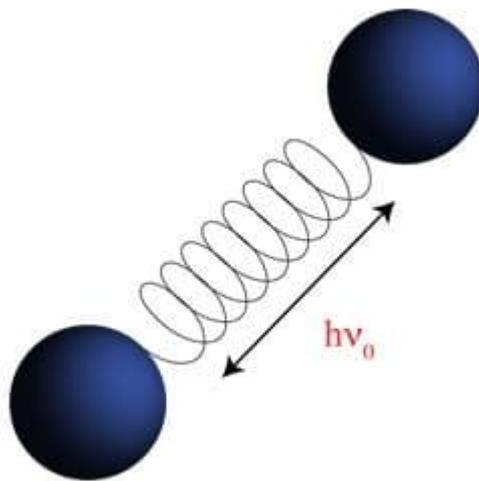# CHAPTER - 1

INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

CHAPTER – 1

1.1 INTRODUCTION

Spectroscopy is techniques that widely use the interaction of energy with a sample to carry out structural analysis. It deals with interaction of matter with electromagnetic energy and spectroscopists harvest huge amount of information, about their matter, from these interaction. The intention of molecular spectroscopy is to understand the interaction of molecular energy with electromagnetic radiation. A molecule possesses different kinds of energy owing to its various kinds of motion and intermolecular interactions. The total energy of molecule can be separated into the additive components linked with the translational energy is the energy of motion through space (E_{trans}), the motion of electrons in the molecule (E_{el}), the vibrations of the constituents atoms (E_{vib}) and the rotations of the molecule as a whole (E_{rot}). The quantization and interactions between them are quite weak.

$$E_{total} = E_{trans} + E_{el} + E_{vib} + E_{rot} \qquad (1.1)$$

Electromagnetic radiations can be permitted to interact with the molecular energy levels with an exploration of these interactions can supply assorted information regarding their rotation, charge localization, molecular structure, symmetry vibration, etc... It is a well known fact that the interactions of electromagnetic energy along with the vibrational energy levels of a molecule provide remarkable information on the molecular dynamics (Herzberg, 1945) and vibrational spectroscopy emerge with theories and techniques to deal with the interactions.

There are so many diverse categories of spectroscopy as these are the forms of energy sources. Here are few examples such as (1) Astronomical spectroscopy (2) Atomic absorption spectroscopy (3) Attenuated total reflectance spectroscopy (4) Electron paramagnetic spectroscopy (5) Electron spectroscopy (6) Fourier Transform spectroscopy (7) Gamma-ray spectroscopy (8) Infrared spectroscopy (9) Laser spectroscopy (10) Mass spectrometry (11) Multiplex or Frequency-Modulated spectroscopy (12) Raman spectroscopy (13) X-ray diffraction spectroscopy. Among these different methods, the most important of which are Infra-red and Raman spectroscopy.

1.2 VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy is one of the most expensive technologies for elucidating the elements or compounds in physics, chemistry and many other fields. The study of vibrational spectroscopy has resulted in a bundle of data on the vibrations of polyatomic molecules. Vibrational spectroscopy produces a dynamic picture of molecules. The introduction of Fourier transform Infrared (FT-IR) spectrometers and lasers which is a basic source for recording vibrational spectroscopy, Raman spectra has become well-organized tool for the explication of molecular structure (Colthup *et al.,* 1964; Dyke *et al.,* 1981).

Vibrational spectroscopy is chiefly concerned with vibrational transition owing to absorption and emission of electromagnetic radiations. These transitions come out in the range from $10^2 cm^{-1}$ to 10^4 cm^{-1} region and originate from the vibrations of nuclei constituting the molecule. The vibrational energies of the molecule can be best studied by infrared and Raman spectroscopies. The Infrared and Raman spectroscopic methods often proceed complementary types of information. For an entire vibrational analysis, both methods should essentially be used (Woodward., 1972; Guillory., 1977; Turrell., 1972).

Vibrational spectroscopy has contributed extensively to the growth of several areas as polymer chemistry, catalysis, fast reaction dynamics and charge-transfer complexes (Satyanarayana, 2004). The use of spectroscopy as a means of restrained structure of simple and even complex molecules has been of immeasurable values in the field of structural study of organic, inorganic and organometalic compounds, biological molecules, polymers and minerals (Colthup *et al.,* 1964; Dyke *et al.,* 1981; Nair., 1971; Dodd., 1962; Ross., 1972; Nakamoto., 1977; Degen., 1995; Krishnan., 1998).

The frontiers of vibrational spectroscopy are widely used tools, as the technique is applicable to solids, crystals, powder, liquids, solutions, gases, films and absorbed species. It is important applications are provides information about the molecular structural determinations, calculation of intra molecular forces acting between the atoms in a molecule, the inter molecular forces or the degree of association in condensed phase, the nature and strength of the chemical bond and in the determination of molecular symmetries, identification and characterization of new molecules, deducing

thermodynamical properties of molecular systems, etc., (Bernhard., 1995). Vibrational spectroscopy has also contributed significantly to the growth of other areas such as polymer chemistry, catalysis, fast reaction dynamics, charge-transfer complexes, etc (Nair, 1971).

Molecular vibrational information can be obtained from the absorption or the emission of infrared radiation and also from the inelastic scattering of light. The study of molecular structure by spectrometry depends chiefly on the existence of the vibrating motion of atoms within the molecule. These motions in turn depend on the nature and orientation of the constituents atoms. Radiant energy, specifically infrared, incident upon the matter, is affected by the presence of such motions. A study of this behavior of infrared radiation indirectly gives valuable information on molecular structure.

1.3 INFRARED SPECTROSCOPY

This is a family of spectroscopic techniques in which the sample is irradiated by all relevant wavelengths simultaneously for a less period of time. The absorption spectrum is obtained by applying a mathematical analysis to the resulting energy method. Infrared spectroscopy gives information on molecular vibrations or more precisely on transitions between vibrational and rotational energy levels in molecules. Absorption of radiation in the infrared region results the excitation of bond deformations either stretching mode or bending mode. Various stretching and bending vibrations occur at certain compute frequencies. When infrared light of that frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased.

Infrared spectroscopy is broadly used for the identification of organic compounds because of the fact that their spectra are generally complex and provide numerous maxima and minima that can be used for comparison purposes. Infrared spectroscopy is commonly concerned with the absorption of radiation incident upon a sample. IR technique when coupled with intensity measurements may be used for both qualitative and quantitative analysis. Currently, this technique has become more popular as compared to other physical techniques such as X-ray diffraction, electron spin resonance, etc… in the elucidation of the structure of unknown compounds.

1.3.1 Infrared Activity

Normal modes of vibrations to be infrared active, there must be a change in the dipole moment of the molecule during the course of vibration. An ordinary fluctuation in the dipole moment takes place and the field is conventional which can interact with the electrical field linked with radiation with the vibrational motion of the molecule. For the absorption of infrared radiation and change in the amplitude of the molecular vibration, a molecule must undergo a net change in its dipole moment as the result of its vibrational or rotational motions.

1.4 RAMAN SPECTROSCOPY

The infrared absorption spectrum of a substance is sometimes called as molecular fingerprint. Although frequently used to identify materials, infrared spectroscopy also used to quantify the number of absorbing molecules. Raman scattering of light by molecules may be used to give information on a sample's chemical composition and molecular structure.

When a beam of light is scattered through a crystal clear substance, a little quantity of the radiation energy is dispersed, thereby scattering persists even if all dust particles are thoroughly disqualified from the substances. If monochromatic radiation of a very narrow frequency band, is used the scattered energy will consist almost entirely radiation of the incident frequency (the so-called Rayleigh scattering) but, in addition, certain discrete frequencies above and below that of the incident beam will be scattered, which is referred to as Raman scattering (Mohan., 2003; Banwell., 2004; Rao., 1963).

### 1.4.1 Quantum Theory of Raman Effect

A simple method for obtaining vibrational frequency and rotational frequency of molecule is through observation of Raman effect. Quantum mechanics delivers a qualitative description about of Raman effect. A simplified energy level diagram is shown in Figure 1.1. The photon interaction of the incident light beam with the molecule in its ground electronic and vibrational state ($v=0$) may temporarily move up the molecule to a time dependent quasi-excited electronic state whose height is above the initial energy level. Virtual states are those in which the molecule has a very short mean lifetime and

hence also the uncertainty in energy is large according to the Heisenberg uncertainty principle.

The molecule at the ground electronic state (v=0) is excited to the virtual electronic state, and then radiates light in all the directions except along the direction of the incident light in case of stokes line. On looking back to the ground state, quantum vibrational energy may stay behind with the scattering species and there will be a reduction in the occurrence of the scattered radiation.

Anti-Stokes lines arise when the molecule is already in an excited vibrational state (say v=1) and is raised to quasi-excited state and reverse to ground electronic state (v =0) on scattering of photon. Scattered photon is the total sum of the energy of incident photon and the energy between the vibrational levels v=1 and v=0.

In another illustration, a molecule in the ground state on interacting with a photon and attaining the virtual state may depart the unstable electronic state and return to the ground state. In this case, scattered photon has the same energy as incident radiation and the result is Rayleigh scattering.
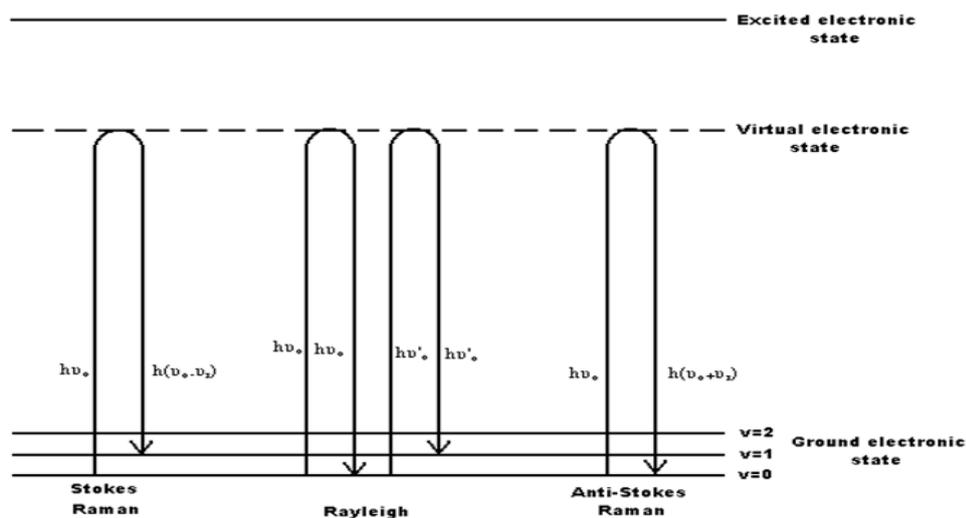
Figure 1.1 Energy levels involved in Raman and Rayleigh scattering

1.4.2 Raman Activity

For a molecular vibration to be Raman active and there must be a change in the polarizability of the molecule during this vibration. These alterations could be considered as being a change in the shape of the electron clouds surrounding the molecule. In a molecule without any symmetry elements, all the general vibrations help out by polarizability alterations and the equivalent frequencies appear in the Raman spectrum. But in symmetric molecules, some of these vibrations may not form any change in polarizability and the corresponding normal frequencies are not observed. Such vibrations are Raman inactive (Colthup., 1964; Woodward., 1972; Ross., 1972; Beaven., 1962; Albert cotton., 1990; Bellamy., 1980; Jones., 1956).

Raman spectrum gives information about molecular symmetry, which can be used to analyze the molecular configuration (Brame., 1976; Wilson., 1955). There are several chemical problems, which have been successfully solved with the aid of Raman spectrum (Drago., 1977; King., 1964).

1.5 VIBRATIONS OF POLYATOMIC MOLECULES

In a polyatomic molecule, each atom having three degrees of freedom in three directions, which are perpendicular to one another. Accordingly, a polyatomic molecule needs three times as many degrees of freedom as the number of its atoms. Thus, a molecule of n atoms has 3N degrees of freedom. For a non-linear molecule, three of the degrees of freedom elucidate the rotation and three others describe about translation; the remaining 3N−6 degrees are vibrational degrees of freedom or fundamental vibrational frequencies. In a linear molecule, only two degrees of freedom are needed to describe rotation of molecule. Thus, a linear molecule has 3N−5 vibrational degrees of freedom (Sharma, 1995).

The number of degrees of freedom possessed by molecule is the number of co-ordinates required to entirely specify the positions of the nuclei. The number of normal modes is equal to the number of vibrational degrees of freedom possessed by molecule. In any one normal mode of vibration, every atom performs a simple harmonic motion with the same characteristic frequency.

The theoretical fundamental vibrations or absorption frequencies given by (3N–6)/(3N–5) will seldom be observed because overtones and combination tones elevates the number of bands, while some other phenomena minimize the number of bands.

The number of observation bands in the spectra may be less than the number of normal modes, due to several reasons:

- The symmetry of the molecule is such no change in dipole moment results from a particular vibration.
- The energies of two vibrations are to be identical.
- The intensity may be low as to be detected by ordinary means.
- The characteristic of vibration alters as a result of the coupling with another vibration.

These couplings are influenced by several factors.

- Strong coupling between two stretching vibrations occur only when there is a common atom of the two vibrations.
- Interaction between two bending vibrations needs a common bond between the vibrating groups.
- Coupling between stretching vibration and bending vibration is possible if the stretching bond forms one side of angle that differs in the bending vibrations of molecule.
- If the individual groups have identical energy and its interaction will be large.
- Little or no interaction is possible between groups which are separated by one or more bonds.
- Coupling vibration that happens between vibrations of same symmetry species.

The theoretical numbers of bands are reduced by following reasons:

- Some of fundamental frequencies are fall beyond the range of the instruments.
- Some fundamental vibrational bands are too weak to be observed.
- Fundamental vibrations, which are very close and may overlap.

- Occurrence of a degenerate band from several absorptions of the same frequency in symmetrical molecules.
- Certain vibrational bands don't appear in the infrared spectral region due to lack of required change in dipole property of the molecules.

1.6 FORCE CONSTANTS OF MOLECULES

The vibrational frequencies when supplemented by structural data are significant in estimating the nature of the forces holding the atoms of the molecule and in the evaluation of several molecular constants. The fundamental vibrational frequencies of a molecule obtained from infrared and Raman spectra can be utilized to solve the secular equations to get potential energy or force constants.

The force constant may be defined as the restoring force per unit displacement, stretching or bending is a measure of the strength of the chemical bonding between the atoms. The force constants are useful to understand the normal coordinates associated with each vibrational frequency. A molecule and its isotopic analogues have almost the same set of force constant, as isotopic substitution does not change 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 especially useful when the spectrum of the isotopic substitute cannot be easily obtained. Conversely, when the spectra of a molecule and its isotopic substitutes are known accurately, the force constants can be assessed with greater precision. Generally, the number of force constants to be analyzed is greater than the number of equations and hence it is not possible to obtain unique solutions of such equations. One way to get over this difficulty is by choosing the initial set of force constants from molecules containing similar bonds and environments. A trail F matrix is set up and interacts with them to give a weighted least square fit to all the observed frequencies. Another solution is to make specific assumptions about the forces in the molecules and thereby reducing the number of force constants to be determined. Several such force fields have been assumed, each one having its own merits and limitations.

Knowledge of force constants help to visualize, certain bonding properties such as electron delocalization and inter atomic interactions. The force constants also yield

information regarding valence state of atoms in the molecule. This also helps us to know the normal coordinates associated with each vibrational frequency essential for the absolute intensity studies. Raman and Infrared intensities have been utilized along with the force constants effectively to attain the bond polarizabilities, dipole moments and their derivatives (Golike, 1956).

1.7 SELECTION RULES FOR IR AND RAMAN SPECTRA

The rules that limit the number of transition between energy levels of molecule are called selection rules. All the transitions may not be active in both IR spectrum and Raman spectrum. Some may be active in IR spectrum while inactive in Raman or vice versa. Some of the transitions may be immobile in both IR spectrum and Raman spectrum. In a molecule having a center of symmetry, Raman active transitions are IR inactive and IR active vibrational modes are inactive in Raman.

1.7.1 Selection Rule for IR spectra

According to quantum mechanics, the selection rule for the infrared spectrum is determined by the integral formula

$$[\mu]_{v'v''} = \int \psi_{v'} * (Q_a)\mu\psi_{v''}(Q_a)dQ_a \qquad (1.2)$$

Where μ is dipole moment in the electronic ground state. ψ is the eigen value function of the vibration, v' and v'' are the quantum numbers of vibratons of the states before and after transitions, respectively and Q_a is a general coordinate whose activity is to be evaluated. The dipole moment can be resolved into three components by x, y and z directions, as

$$[\mu_x]_{v'v''} = \int \psi_{v'}(Q_a)\mu_x\psi_{v''}(Q_a)dQ_a$$
$$[\mu_y]_{v'v''} = \int \psi_{v'}(Q_a)\mu_y\psi_{v''}(Q_a)dQ_a$$
$$[\mu_z]_{v'v''} = \int \psi_{v'}(Q_a)\mu_z\psi_{v''}(Q_a)dQ_a$$

For the active infrared vibrations, atleast one of the components of the derivative of the dipole moment irrespective to the normal mode coordinate taken at the equilibrium

position, should be non-zero. If all the integrals are zero, the vibration is inactive in infrared spectrum (Nakamoto, 1977).

1.7.2 Selection Rule for Raman Spectra

The selection rule for the Raman spectrum is evaluated by the integral.

$$[\alpha]_{v'v''} = \int \psi_{v'}^{*} (Q_a) \, \alpha \psi_{v''} (Q_a) \, dQ_a \qquad (1.3)$$

The polarizability of the molecule α consists of six components such as α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{yz} and α_{xz}. For the vibration to be active in Raman spectrum, at least one of these integrals may be non-zero. If all the integrals are zero, the vibration is said to be inactive in Raman spectrum.

1.8 TYPES OF FORCE FIELDS

1.8.1 Central Force Field (CFF)

The force acting on the given atom in a molecule is the result of the both attraction and repulsion by all other atoms (i.e.) only central force acts between the atoms in a molecule. Both attraction and repulsion depend only on the distance from other atoms and act along the lines connecting them with the atom under consideration. This is equivalent to consider the potential energy to be solely quadratic function of the change in distance between the nuclei. But this force field is used rarely by case of its limitations and fails to report for the bending vibrations in linear molecules. It is also fails to account for angle forces, bending and out-of-plane vibrations. This type of force field is appropriate only if the atoms were held together by ionic forces. Further, the frequencies predicted by this force field often differ from the observed vibrations.

1.8.2 Simple Valence Force Field (SVFF)

Simple valence force field developed by restoring force in the line of each and every valence bond, if the distance between the two bonded atoms is altered and restoring force opposing the change of the angle between two valence bonds, linking one atom with two other atoms. In this force field, the potential function includes concept involving

changes in interatomic distances and also alters in angles between two valence bonds. But simple valence force field excludes the forces between non-bonded atoms.

The potential energy function under this method is expressed as

$$V = \frac{1}{2}\sum_i f_{r_i}(r_i)^2 + \frac{1}{2}\sum_i f_{\alpha_i}(\alpha_i)^2 \qquad (1.4)$$

Where r is bond lengths, α is bond angles, f_r is stretchingforce constants and f_α is bending force constants.

Shimanouchi *et al.,* (1966) applied this model successfully to number of molecules containing hydrogen atoms and a single heavy atom such that H_2O, NH_3 and CH_4. However, this method is not readily suitable for molecules having more than one heavy atom. This force field is higher to the central force field and chemically more meaningful, yet often fails to reproduce the observed frequencies.

1.8.3 General Valence Force Field (GVFF)

The simple valence force field potential functions may be modified in order to get correct description of the vibrational frequencies by introducing some judiciously chosen interaction constants.

In this model the potential energy function which includes all interaction terms in addition to the valence forces are given in expression (1.4). It is expressed in its general form as,

$$V = \frac{1}{2}\sum f_{r_i}(r_i)^2 + \frac{1}{2}\sum f_{\alpha_i}(\alpha_i)^2 + \frac{1}{2}\sum f_{r_i r_j}(r_i r_j) + \sum_{i \neq j} f_{\alpha_i \alpha_j}(\alpha_i \alpha_j) + \sum f_{r\alpha}(r\alpha) \qquad (1.5)$$

Where r is the change in bond lengths and α is the bond angle. In the equation (1.5), the force constants f_r is the principal stretching, f_α is the bending force constant and f_{rr} is the stretch-stretch interactions, $f_{\alpha\alpha}$ is the bend-bend interactions and $f_{r\alpha}$ refers to the stretch-bend interactions. This is a very expedient force field from a practical point of view. Since the force constants can be directly transferred from one molecule to other molecule.

1.8.4 Urey-Bradley Force Field (UBFF)

The Urey and Bradley force field (1931) is a grouping of central force field and valence force field. The UBFF adds interaction terms between non-bonded atoms to the simple valence force field.

Urey and Bradley force field includes the bond stretching force constants K, angle bending force constants H, torsional force constants Y and repulsive force constants F. The potential energy functions under this model written as (Shimanouchi., 1970).

$$V = \frac{1}{2} \Sigma K_{ij}(r_{ij})^2 + \frac{1}{2} \Sigma H_{ijk}(\alpha_{ijk})^2 + \frac{1}{2} \Sigma Y(t_{ijk}) + \frac{1}{2} \Sigma F_{ij}(R_{ij})^2 \qquad (1.6)$$

Where r, α, t and R are the changes in bond lengths, bond angles, angle of internal rotation and distance between non-bonded atom pairs, respectively. The general validness of this type of field has been demonstrated by Shimanouchi (1970). In this model, the VFF is supplemented by force between non-bonded nuclei. The merits of these force fields are:

a) It requires only a few parameters to describe the potential energy completely.
b) Force constants similar bonds can be transferred from related molecules.
c) Determination of force constants of complex molecules is also possible.

It has its own limitations. Sometimes, the force constants may not give a good estimation of frequencies for certain types of vibrations, such as vibrations involved in hydrogen atoms. In such cases modifications have been suggested (Labonville., 1972; Shimanouchi., 1957, 1961; Scherer and Overand., 1960,1961,1964; Scherer *et al.,* 1962; Periseau *et al.,* 1963). The resulting force field is also known as modified urey-bradley force field (MUBFF).

1.8.5 Orbital Valence Force Field (OVFF)

This force field is a modified form of valence force field devised by Health and Linnett (1948). Orbital valence force field eliminates the difficulty of introducing separate angle bending constants for out-of-plane bending vibrations and makes use of the same

constants as those used for in-plane bending vibrations and strictly in accordance with modern theory of direct valence (Pauling, 1970).

In this field, orbital valence force field is assumed that the bond forming orbitals of an atom X are at definite angles to each other. The most stable bond is formed when one of these orbitals overlaps the bond forming orbitals of another atom Y to the maximum extent possible. If Y is displaced perpendicular to the bond, a force will be set up tending to restore it to the most stable position. The possible energy function is expressed as,

$$V = \frac{1}{2} K \Sigma (r_i)^2 + K'_\alpha \Sigma (\beta_i)^2 + A \sum_{jk} (R_{jk})^2 - B \sum_{jk} (R_{jk}) + B' \Sigma (r_i) \qquad (1.7)$$

Where r is the change in bond lengths, R is the distance between non-bonded atom pairs and β_i is the angular displacement. The symbol K, K'_α, B and A stands for the stretching, bending and non-bonding repulsion force constants respectively.

This model was shown by Health and Linnett (1948) to be a very satisfactory one for tetrahedral XY_4 and planar XY_3 types of molecules and ions. While later, it has been shown by Kim *et al.,* (1968) to be a best model to the usual one using inter bond angles for a series of octahedral hexahalides.

Considerable attention has been focused in recent years on the application of this model to different types of systems (Pauling., 1970; Kim *et al.*, 1968; Sharma., 1975; Krebs and Muller., 1967; Mohan *et al.,* 1972; Sanyal *et al.*, 1969). A tailored form of MOVFF also known as modified orbital valence force field has been successfully functional to octahedral systems (Labonville., 1972; Overand, 1960; Mills, 1963).

1.8.6 Hybrid Orbital Force Field (HOFF)

Mills (1963) proposed this model by incorporating the idea of changes in the hybridization orbitals because it attributes the molecular deformation to changes in bond angles. Therefore, it accounts for the stretch-bend interactions. The relation between stretch-bend interactions and stretching force constants under this model is given by Mills (1963).

$$F_{ij} = -\frac{\delta R_i}{\delta \lambda_i}\left[\frac{\delta \lambda_i}{\delta \alpha_i}\right]F_{ii} \qquad (1.8)$$

Hence R_i, α_j refers to the internal stretching and bending coordinates, respectively, and λ_i is the hybridization parameter associated with R_i.

The HOFF has been applied successfully by several workers (Aldous., 1963; Duncan., 1964; Fletcher., 1963) to a variety of compounds. It is evident that the simplified force fields are essential when one has to evaluate the force constants from frequency data alone. The approximation involved in framing the models is arbitrary and empirical, through the degree to which they are diverse. Several groups of molecules or ions are found to respect different force fields, depending on how perfectly the assumptions made correspond to the actual state of affairs.

1.9 VIBRATIONAL ASSIGNMENT AND GROUP FREQUENCIES

The observed spectrum of any molecule consists of a large number of bands and a band is said to be assigned. The normal vibrations of a molecule are associated with appropriate infrared frequencies and Raman frequencies and this phenomenon is called as vibrational assignments of any molecule. The applications of infrared spectroscopy and Raman spectroscopy are rest largely on the correct assignment of the spectra. The assignment of the infrared spectrum and Raman spectrum is usually made on the basis of the group frequency concept.

By comparison of the spectra of large number of compounds, it has been found that the presence of certain groups, for example C–H, O–H, N–H, C=O, C=N etc... in different molecules may be correlated with a constant incidence of absorption bands in the infrared spectra whose positions are only slightly altered on going from one compound to another. The atomic group vibrates independently of the other groups of molecules and has its own frequency. These frequencies are called characteristics group frequencies (Satyanarayana., 2004) of selected compounds. The vibration of the group frequency is assumed to happen independently of the rest of the molecule. A number of characteristic group absorptions have been established in well.

The group frequency concept is most useful as an aid to the interpretation of vibrational spectra. The force constant of the bond changes with its electronic structure, the resulting characteristic small shifts in the vibrational frequency enable to gather more information about the respective bond. A number of characteristic group absorptions have been well established. The general technique of assigning group frequencies begins with the vibrational assignments of small molecules and proceeds to the assignments of larger molecules. If certain vibrations retain fairly constant spectral positions, they can be considered as best group frequencies.

Frequency shifts, commonly conclude from mechanical or electronic effects. Mechanical effects arise from alterations in mass or from pairing of vibrations. They do not affect the force constant of any bond. Electronic effects affect the vibrations by altering the force constants using inductive, conjugative and other effects. Chemical bonds plays a key role in transmission of electronic effects. At some instance, steric effects may take place, resulting in either the hindrance to electronic effects or to dipolar effects transmitted through space by field effect.

1.9.1 Factors Influencing Vibrational Frequencies

Many factors influence the precise frequency of a molecular vibration, and it is usually impossible to isolate one effect from another. Each molecular group is influenced by the structure of the molecule or different electronic environments (Colthup., 1964; Sathyanarayana., 2004). Some of the essential factors that are responsible for shifting the vibrational frequencies of certain groups from their normal values are discussed below:

(a) Coupled Interactions

When a bond oscillation shares a common atom they almost never behave as individual oscillators unless the individual oscillation frequencies are quite different. Mechanical coupling interaction between the oscillators is responsible for this behavior. For example CO_2, consists of two C=O bonds (O=C=O) with a common carbon atom. Thus, CO_2 has two fundamental stretching vibrations. Labeling of vibrations as symmetric or asymmetric is done with reference to an axis known as axis of symmetry.

(b) Hydrogen Bonding

Hydrogen bonding takes place in any system containing a proton donor group (X–H) and a proton acceptor group (Y), if the s-orbital of the proton can effectively overlap the p or π orbital of the acceptor group. In Hydrogen bonding, atoms of X and Y are electronegative with Y possessing lone pair of electrons. In organic molecules, the common proton donor groups are carbonyl, hydroxyl amine or amide groups and common proton acceptor atoms are oxygen, nitrogen and the halogens. The strength of the hydrogen bond is at its maximum, if the proton donor groups and the axis of the lone pair orbital are co linear.

The force constant of both the group X and Y is altered as a result of hydrogen bonding (Kim *et al.,* 1962). Hence frequencies of both stretching vibrations as well as bending vibrations are changed because of hydrogen bonding. The X–H stretching bands moves to lower frequencies usually with higher intensity and bands widening. The H–X bending vibration usually shifts to higher frequencies or shorter wavelength whenever bonding occurred. Thus hydrogen bonding changes the position and shape of an infrared band.

Intermolecular hydrogen bonding involves association of two or more molecules of the same or different compounds, and it may result in dimmer molecules as in carboxylic acids. Intramolecular hydrogen bonds are formed when proton donor and acceptor are found in a single molecule under specific conditions that allows the required overlapping of orbital e.g., formation of 5 or 6 member ring. The extent of both intermolecular and intramolecular hydrogen bonding depends upon the temperature. In general, intermolecular hydrogen bonds give rise to broad bands, while intramolecular hydrogen bonds give sharp and well defined bands.

(c) Fermi Resonance

When interactions occur between functional vibrations and overtone or combination tones vibrations, such interactions are known as Fermi resonance. This phenomenon may occur when two vibrational transitions are having nearly the same energy and both belong to the same symmetry. In such a case, instead of strong band due

to the fundamental band and a weak intensity band due to the overtone, two nearly equal intense bands may be observed. The two energy levels involved repel one another so that both the levels are trouble. Evidence of Fermi resonance may be obtained by taking the spectra in various solvents and form the spectra of isotopically substituted molecules such as $NC_{18}O$, $N_{13}CO$ etc.

(d) Electronic Effect

Apart from external factors such as hydrogen bonding and molecular association, various internal factors may affect the electronic structure of the carbonyl group. The nature of the substituted group X in carbonyl compounds of the formula RCOX may influence the frequency of C=O stretching by inductive and mesomeric effects. Inductive effect arises due to the different electronegativities of the carbonyl carbon and of the substituted in compounds of the type RCOX. It involves the electrons in the sigma bonds. The mesomeric effect involves the electrons in the π and non-bonding orbitals and it operates in general opposite to that of the inductive effect.

1.10 GROUP THEORY AND MOLECULAR VIBRATIONS

The application of the principles of group theory together with the consideration of the symmetry properties of molecules simplifies the vibrational analysis. It aids in finding out qualitatively the infrared and Raman spectral activity of the fundamentals as well as the overtone and combination bands. Knowledge of the point group symmetry of a molecule is useful to determine the optical activity of molecule. Different symmetries of a molecule have qualitatively different spectra (Herzberg., 1945; Straghaun and Walker., 1976; Joshi., 1963).

1.10.1 Normal Modes of Vibrations

Normal modes (or fundamental modes) of vibrational molecule are internal atomic motions in which all the atoms move in phase with the same frequency but with different amplitudes. The amplitude and direction of every atom may be depicted by a displacement vector. Several displacement of the atoms in a given normal mode of vibration may be represented by a linear combination of atomic displacements known as normal coordinates which are functions of both angles and distances (Brittain., 1970). The most significant

property of these vibrations is the non-degenerate normal modes of vibration. The normal coordinates and the vibrational wave functions are either symmetric or antisymmetric owing to the symmetry operations of the point group symmetry of the molecule in its position.

For degenerating the general mode of vibration, the symmetry operation will transform a set of vibrations that possess degeneracy into a linear combination of symbiotic degenerate general coordinates. A normal mode in a molecule is equivalent to a simple harmonic motion of certain mass and force constant, and can be vibrate independently without exciting any other mode for small amplitude motion. The number of molecular vibrations of a chemical compounds that depends upon the number of atoms about molecular composition. The molecular vibration allowed in the IR or Raman spectra depends upon its molecular symmetry operation.

1.10.2 Symmetry Elements and Symmetry Operations

The Symmetry is a visual concept as reflected by the geometrical shapes of molecules such as benzene, methane etc. In spectroscopy, the symmetry possessed by a molecule may be utilized with the merits to simplify the calculation of energy levels of the system and to determine which transitions are allowed or forbidden. The molecular symmetry is systematized by introducing the concept of 'symmetry operation'. It is an action which moves the nuclear frameworks into a position equivalent to the original one and related to the symmetry operation is the 'symmetry element'. The symmetry element is a geometrical entity such as a line, a point, an axis or a plane with respect to one or more symmetry operations may be carried out. This is a process in which the molecule is moved from one configuration to another such that the resulting configuration is indistinguishable.

Symmetry elements and symmetry operations are closely related that one cannot go without the other. During the course of symmetry operation, there is no translational motion in a molecule. All molecular symmetries can be treated in terms of the symmetry elements explained in literature (Albert cotton., 1990; Raman., 1990) A symmetry operation of the molecule will transform a member of a degenerate set of vibrations into a linear combination of the members of the degenerate set.

1.10.3 Point Groups

All axes and planes are symmetry by a molecule and that must intersect at least one general point that the symmetry operation performed on molecule must leave at least one point unaffected. A possible combination of symmetry operations that leaves at least one point unchanged is called point group. This combination satisfies the number of group atoms. Mathematical group theory delivers that only a limited number of such combinations or point groups exist. In a point group, the symmetry of space about a point is uniquely described by a collection of symmetry elements about that point and also point groups that is used to describe the symmetry of isolated molecules.

1.11 MUTUAL EXCLUSION RULE

In a molecule with a center of symmetry it is seen that vibrations that are Raman active are infrared inactive and vice-versa, and this is called the principle of mutual exclusion. To understand the presence and absence of lines in IR spectrum and Raman spectrum, the understanding of the mutual exclusion principle is necessary. The mutual exclusion principle gives the relation between the symmetry of the molecular structure and their infrared and Raman activities. The prime rule is, for molecules with centre of symmetry, transitions that are allowed in the Raman spectrum are forbidden in infrared and conversely, transitions that are allowed in the infrared spectrum are forbidden in Raman. This rule implies that if there is no centre of symmetry then some (but not necessarily all) vibrations may be both infrared and Raman active. It should be realized that the above rule does not involve that all transition that are forbidden in the Raman scattering active in the infrared.

The rule is in Raman effect, only transitions between states of same symmetry with respect to the centre of symmetry can takes place (g↔g, u↔u), however in the infrared, only transition between the states of opposite symmetry with respect to the centre of symmetry are allowed (g↔u). This rule is clear that all the components of magnetic dipole moment μ, change sign for a reflection at the centre of symmetry, but the components of polarizability α, which behave as the product of two components of induced dipole moment μ', remain unchanged (Herzberg., 1945). From the mutual exclusion rule, we can conclude that the observance of infrared and Raman showing no common lines implies

that the molecule has centre of symmetry. But, it has to be done carefully because some time a vibration may be of Raman active but too weak to be observed. However, if some vibrations are observed to give infrared bands and Raman bands it is certain that the molecule has no centre of symmetry. Thus, for a fundamental vibrational transition, only the vibrational modes (g) which are symmetric with respect to the centre of symmetry can be Raman active and those are asymmetric (u) with respect to centre of symmetry can be infrared active if they also grasp the selection rule requirements.