1.1 INTRODUCTION

Spectroscopy is the interaction of electromagnetic radiation with matter. Electromagnetic radiations are produced by the oscillation of electric charge and magnetic field residing on the atom. Spectroscopy is one of the important experimental techniques for determining the electronic structure of atoms and molecules. A molecule possesses various forms of energy due to its different kinds of motion and intermolecular motions. The molecule possesses translational energy by virtue of the motion of the molecule as a whole. It possesses rotational energy due to the bodily rotation of the molecule about an axis passing through the centre of gravity of the molecule. The molecule possesses vibrational energy due to periodic displacement of its atoms about their equilibrium positions. It also possesses electronic energy since the electrons associated with each atom and bonds are in constant motion. As a first approximation, the total energy of a molecule can be expressed as the sum of the constituent energies, that is

\[ E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + \ldots \]  \hspace{1cm} \ldots (1.1)

The various types of energy associated with different motions of the molecule are independent of one another. Among the various types of spectroscopy, vibrational spectroscopy gives valuable insight into the structural features of molecules.

1.2 VIBRATIONAL SPECTROSCOPY

The study on vibrational spectroscopy has resulted in a large volume of data on the vibrations of polyatomic molecules. Vibrational spectroscopy gives a dynamical picture of the molecule. With the introduction of Fourier transform infrared spectrometers and laser as source for recording Raman spectrum, vibrational spectroscopy has become an effective tool for the elucidation of molecular structure. It also provides important information about the intramolecular forces acting between
the atoms in a molecule, the intramolecular forces in condensed phase and the nature of the chemical bond. Vibrational spectroscopy has contributed significantly to the growth of different areas as polymer chemistry, catalysis, fast reaction dynamics, charge-transfer complexes etc. [1-4].

1.3 INFRARED SPECTROSCOPY

In infrared spectroscopy, infrared light passes through a sample and certain frequencies of the light are absorbed by the chemical bonds of the substance, leading to molecular vibrations. The frequencies and intensities of absorbed infrared light depend on the specific bond strengths and atoms of that molecule, and the absorption pattern (spectrum) is unique for each material. Infrared spectroscopy is a very powerful tool for both qualitative and quantitative analysis. The most powerful function of infrared spectroscopy is in establishing the identity of a sample by comparison using same medium.

The infrared region of the electromagnetic spectrum is divided into three regions: the near infrared region between 12,500 and 4000 cm\(^{-1}\), the medium infrared region from 4000-400 cm\(^{-1}\) and the far infrared region extending from 400 to about 50 cm\(^{-1}\). If the radiation is in the medium infrared region, both the vibrational and rotational energies of the molecule will change. Thus, the infrared absorption spectra of molecules result from transitions between vibrational and rotational energy levels [5, 6].

1.3.1 Infrared activity

The power of infrared spectroscopy arises from the observation that different functional groups have different characteristic absorption frequencies. The technique is very useful as a means of identifying which functional groups are present in a molecule. If infrared light is passed through an unknown sample, some bonds absorb
infrared light more strongly than others, and some bonds do not absorb at all. In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule. Such vibrations are said to be infrared active.

1.4 RAMAN SPECTROSCOPY

When a beam of light is passed through a transparent substance, a small amount of the radiation energy is scattered, the scattering persisting even if all dust particles are rigorously excluded from the substance. If the monochromatic radiation of a very narrow frequency band is used, the scattered energy will consist almost entire radiation of the incident frequency (the so-called Raleigh scattering) but, in addition, certain discrete frequencies above and below that of the incident frequency will be scattered, which is referred to as Raman scattering [7].

The Raman Effect occurs when the electromagnetic radiation impinges on a molecule and interacts with the electron density and the bonds of the molecule. For the spontaneous Raman Effect, which is a form of scattering, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes, it emits a photon and it returns to a different vibrational state. The difference in energy between the original state and the new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman Effect, which is a light scattering phenomenon, should not be confused with absorption where the molecule is excited to a discrete energy level.

If the final vibrational state of the molecule is more energetic than the initial state, the scattered photon will be shifted to a lower frequency for the total energy of the system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final vibrational state is less energetic than the initial state, then the inelastically scattered photon will be shifted to a higher frequency, and this is designated as an
anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during the interaction.

1.4.1 Quantum theory of Raman effect

The occurrence of Raman scattering may be most easily understood in terms of the quantum radiation. This treats radiation of frequency ν as consisting of a stream of particles (called photons) having energy hv, where h is Planck’s constant. Photons can be imagined to undergo collisions with molecules and, if the collision is perfectly elastic, they will be deflected unchanged. A detector placed to collect energy at right angles to an incident beam will thus receive photons of energy hv, i.e., radiation of frequency ν.

However, it may happen that energy is exchanged between photon and molecule during the collision: such collisions are called ‘inelastic’. The molecule can gain or lose amounts of energy only in accordance with the quanta laws, i.e., its energy change, ΔE joules, must be the difference in energy between two of its allowed states. If the molecule gains energy ΔE, the photon will be scattered with energy hv-ΔE and the equivalent radiation will have a frequency ν-ΔE/h. Conversely, if the molecule loses energy ΔE, the scattered frequency will be ν + ΔE/h.

Radiation scattered with a frequency lower than that of the incident beam is referred to as ‘Stokes’ radiation, while that at higher frequency is called ‘anti-Stokes’ radiation. Since the former is accompanied by an increase in molecular energy while the latter involves in a decrease. Stokes radiation is generally more intense than anti-Stokes radiation [3, 5, 8-11].
1.4.2 Raman Activity

A molecular vibration to be Raman active there must be a change in polarizability of the molecule during the vibration. In a molecule without any symmetry elements, all the normal vibrations are accompanied by polarizability changes and the corresponding frequencies appear in the Raman spectrum. But in a symmetric molecule, some of the vibrations may not produce polarizability changes and hence corresponding normal frequencies are not observed. Such vibrations are Raman inactive [2, 5, 8].

1.5 SELECTION RULES FOR INFRARED AND RAMAN SPECTRA

From quantum mechanics, the selection rule for the infrared spectrum is determined by the integral

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

… (1.2)
Where \( \mu \) is the dipole moment in the electronic ground state, \( \Psi \) is the vibrational eigen function. \( \nu' \) and \( \nu'' \) are the vibrational quantum numbers of the states before and after transition respectively, and \( Q_a \) is the normal coordinate whose activity is to be determined. The dipole moment can be resolved into three components in the \( x \), \( y \) and \( z \) directions, as

\[
[\mu_x]_{\nu'\nu''} = \int \psi_{\nu'}^* (Q_a) \mu_x \psi_{\nu''}^* (Q_a) dQ_a \quad \ldots (1.3)
\]

\[
[\mu_y]_{\nu'\nu''} = \int \psi_{\nu'}^* (Q_a) \mu_y \psi_{\nu''}^* (Q_a) dQ_a \quad \ldots (1.4)
\]

\[
[\mu_z]_{\nu'\nu''} = \int \psi_{\nu'}^* (Q_a) \mu_z \psi_{\nu''}^* (Q_a) dQ_a \quad \ldots (1.5)
\]

If one of these integrals is not zero, the normal vibration associated with \( Q_a \) is infrared active. If all the integrals are zero, the vibration is infrared-inactive.

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

\[
[\alpha]_{\nu'\nu''} = \int \psi_{\nu'}^* (Q_a) \alpha \psi_{\nu''}^* (Q_a) dQ_a \quad \ldots (1.6)
\]

The polarizability of the molecule \( \alpha \) consists of six components \( \alpha_{xx} \), \( \alpha_{yy} \), \( \alpha_{zz} \), \( \alpha_{xy} \), \( \alpha_{yz} \) and \( \alpha_{xz} \). If one of these integrals is not zero, the normal vibration associated with \( Q_a \) is Raman active. If all the integrals are zero, the vibration is Raman-inactive [9].

### 1.6 MOLECULAR FORCE CONSTANTS AND ITS SIGNIFICANCE

The force constant is defined as the restoring force per unit displacement of a bond. Force constants serve as a basis for probing chemical bonding and structural characteristics. The intramolecular force constants are related to the electronic structure and are correlated with bond nature, electron delocalization and interatomic repulsions. Force constants serve as a basis to calculate new fundamental frequencies of other molecules and also to calculate the frequencies which may be inactive in the infrared and Raman spectra. From the empirical relations of Badger, it is possible to
calculate the inter-atomic distances by force constants [12]. The other important molecular constants can be evaluated from force constants.

The changes in the energy of the electrons binding the nuclei together give the Force field. Force field helps to know the normal coordinates associated with each vibrational frequency essential for the absolute intensity studies. Infrared and Raman intensities have been used along with force constants in order to obtain the dipole moments, polarizabilities and their derivatives [13].

1.7 VIBRATIONS OF POLYATOMIC MOLECULES

A polyatomic molecule containing N atoms can be described by a set of Cartesian coordinates, three for each atom. The molecule is then said to have 3N degrees of freedom. Certain combinations of these individual degrees of freedom of each atom correspond to the translational motion of the molecule as a whole without any change in the interatomic molecules. For a non-linear molecule, three of the degrees of freedom describe rotation and three describe translations, the remaining 3N-6 degrees are vibrational degrees of freedom or fundamental vibrations. In a linear molecule, only two degrees of freedom are required to describe rotation. Thus, a linear molecule has 3N-5 vibrational degrees of freedom [14].

1.8 GROUP THEORY AND MOLECULAR VIBRATIONS

The application of group theoretical concept is useful in the classification of the normal vibrations and the examination of infrared and Raman activity. A very important property of the normal vibrations is that they transform according to the irreducible representations of the point group of the molecule. Because of their relationship with the normal coordinates, the vibrational wave functions also behave in the same way. Therefore, the normal coordinates and the vibrational wave functions are classified according to their symmetry properties [1, 15-17].
1.8.1 Molecular symmetry and point groups

Symmetry is a visual concept as reflected by geometrical shapes of molecules such as benzene, methane, etc. Symmetry defines the mutual relationship of parts of something in respect of magnitude and position. Its importance in many theoretical problems in chemistry and physics arises from the reflection, exchange or inversion of equivalent features of the system. The consideration of the role of symmetry in chemistry is basically a consideration of its role in quantum mechanics.

In spectroscopy, the symmetry possessed by a molecule may be used with advantage to simplify the calculation of energy levels of the system and to determine which transitions are allowed or forbidden. The link between molecular symmetry and quantum mechanics is provided by point group. The symmetry of a rigid system is easily defined in geometric terms. The molecular symmetry is systematized quantitatively by introducing the concept of ‘symmetry operation’. It is an action which moves the nuclear framework into a position equivalent to the original one. Related to the symmetry operation is the ‘symmetry element’. The symmetry element is a geometrical entity such as a point, an axis or a plane passing through the body about which action takes place.

The application of symmetry operation on a molecule should leave it physically indistinguishable from the original one and its centre of gravity must also remain fixed in space under all the symmetry operations. All the axes and planes of symmetry of the molecule must intersect at least one common point. Thus, the symmetry operations leave at least one point unaffected. Such groups are called point groups. In a point group, the symmetry of space about a point is uniquely described by a collection of symmetry elements at that point. Point groups are used to describe the symmetry of isolated molecules [1].
1.9 VIBRATIONAL ASSIGNMENT AND GROUP FREQUENCIES

The normal vibrations of a molecule are associated with appropriate Raman and infrared frequencies and this process is referred to as vibrational assignment. The applications of infrared and Raman spectroscopy rest largely on the correct assignment of the spectra. The assignment of the infrared and Raman spectra is generally made on the basis of the group frequency concept. By comparison of the spectra of large number of compounds, it has been observed that the presence of certain groups, for example, C-H, N-H, C=O, C=N, etc., in various molecules may be correlated with a constant occurrence 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 in the molecule and has its own frequency. These frequencies are called characteristic group of frequencies. The vibration of the group is assumed to occur independently of the rest of the molecule. The force constant of a bond changes with its electronic structure, consequently small shifts in the vibrational frequency enable to gather more information about the respective bond. A number of characteristic group absorptions have been established. The group frequency concept is extremely useful as an aid to the interpretation of the vibrational spectra. The general technique of assigning new group frequencies begins with the vibrational assignments of small molecules and proceeds to the assignments of larger molecules [1].

1.10 FACTORS INFLUENCING VIBRATIONAL FREQUENCIES

Many factors influence the precise frequency of a molecular vibrations 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
[5, 10]. Some of the important factors which are responsible for shifting the vibrational frequencies of certain groups from their normal value are discussed below:

(a) Coupled interactions

The energy of a vibration and thus the wavelength of its absorption peak may be influenced by other vibrations in the molecule [14]. The extent of coupling is influenced by the following important factors.

- Strong coupling between stretching vibrations occurs only when the two vibrations have a common atom.
- Interaction between bending vibrations occurs only when a common bond is present between the vibrating groups.
- Coupling occurs between a stretching and a bending vibration if stretching bond forms one side of the angle that varies in the bending vibrations.
- Interaction is greatest when the coupled groups have individual energies that are approximately equal.
- If groups are separated by two or more bonds, little or no interaction occurs.
- Coupling occurs when vibrations are of the same symmetry species.

(b) Hydrogen bonding

Hydrogen bonding gives rise to downward frequency shifts. Stronger the hydrogen bonding greater the absorption shift towards lower wavenumber from the normal value. It is possible to distinguish two types of hydrogen bonds by the infrared technique. Intermolecular hydrogen bonds give rise to broad bands, whereas bands arising from intramolecular hydrogen bonds are sharp and well defined. Intermolecular hydrogen bonds are concentration dependent. On dilution, the intensities of such bands decrease and finally disappear. Intramolecular hydrogen bonds are independent of concentration. Frequency difference between free and associated
molecules is smaller in case of intramolecular hydrogen bonding than that in inter-
molecular association [18].

c) Fermi resonance

Fermi resonance may occur when two vibrational transitions, a fundamental
and an overtone have nearly the same energy and both belong to the same symmetry.
Therefore, instead of observing a strong band due to the fundamental and a weak
intensity band due to the overtone band, two nearly equally intense bands may be
observed.

d) Electronic effects

Changes in the absorption frequencies for a particular group take place when
the substituents in the neighbourhood of that particular group are charged. The
frequency shifts are due to the electronic effects which include Inductive effect,
mesomeric effects, field effects etc. Under the influence of these effects, the force
constant or the bond strength changes and its absorption frequency shift from the
normal value.

The introduction of alkyl group causes +I effect which results in the
lengthening or the weakening of the bond and hence the force constant is lowered and
the wavenumber of absorption decreases. The introduction of an electronegative atom
or group causes –I effect which results in the bond order to increase. Thus, the force
constant increases and hence the wavenumber of absorption rises. In most of the
cases, mesomeric effect works along with inductive effect and cannot be ignored. It is
important to note that only inductive effect is considered, when the compound is
meta-substituted.

In para substitution, both inductive and mesomeric effects become important
and the domination of one over the other will decide the wavenumber of absorption.
In ortho substitution, inductive effects, mesomeric effect along with steric effects are considered. In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is called field effect.

1.11 ULTRAVIOLET SPECTROSCOPY

Electronic spectroscopy provides vital information about molecular structure such as nature of chemical bonds, functional groups and extent of conjugation in organic compounds. Electronic spectra arise due to the absorption of energy by the molecule in the ultraviolet region and make transitions between the electronic energy levels. These transitions are quantized and depend on the electronic structure of the molecule. The energy differences between electronic energy levels in most molecules vary from 125 to 650 kJ/mol. When a molecule absorbs energy an electron is promoted from an occupied orbital to an unoccupied orbital of greater potential energy. Generally, the most probable transitions is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [19, 20].

1.11.1 Principles of UV absorption spectroscopy

When electromagnetic radiations of ultraviolet and visible wavelengths are passed through the compound with multiple bonds, a portion of radiation is normally absorbed. Amount of absorption depends on the wavelength of radiation and the structure of the compound. The amount of light absorbed by the sample is explained by the following empirical expression, known as the Beer-Lambert Law.

\[ A = \log \left( \frac{I_0}{I} \right) = \varepsilon cl \] … (1.6)

Where A is the absorbance, \( I_0 \) is the intensity of light incident upon the sample cell, I is the intensity of light leaving the sample cell, \( c \) is the molar concentration of
solute, $l$ is the length of the sample cell and $\varepsilon$ the molar absorptivity. The term $\log (I_0/I)$ is known as absorbance. The molar absorptivity $\varepsilon$ (molar extinction coefficient) is a property of the molecule undergoing an electronic transition.

The size of the absorbing system and the probability of electronic transition will control the absorptivity, which ranges from 0 to $10^6$. The Beer-Lambert Law is strictly obeyed when a single species gives rise to the observed absorption.

**1.11.2 Types of electronic transitions**

The ultraviolet absorption bands are associated with the chemical bonds containing the organic molecules. Ultraviolet absorption occurs due to the transitions of valence electrons in the molecule. That is, the excitation of an electron from the occupied orbital (bonding orbital) to an unoccupied orbital (anti-bonding orbital). The lowest energy occupied molecular orbitals are the $\sigma$ orbitals, which correspond to $\sigma$ bonds. The $\pi$ orbitals have quite higher energy levels and hold unshared pairs. The nonbonding ($n$) orbitals have very higher energy levels. The unoccupied (anti-bonding) orbital of $\pi^*$ and $\sigma^*$ are the orbitals of highest energy. The electronic energy levels and transitions are shown in Fig 1.2. The promotion of an electron from a $\pi$-bonding orbital to an anti-bonding ($\pi^*$) orbital is designated as $\pi \rightarrow \pi^*$.

As shown in Fig 1.2 it is clear that $n \rightarrow \pi^*$ transition requires less energy compared to $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ transition. For many applications the transition of lowest energy is the most essential. Saturated organic compounds such as alkanes provide $\sigma \rightarrow \sigma^*$ transitions with $\lambda_{\text{max}}$ around 190 nm. The saturated compounds with one heteroatom with unshared pair of electrons such as saturated halides, alcohols, ketones and amines may undergo $n \rightarrow \sigma^*$ transition. The compounds with unsaturated centers such as alkenes, aromatics, carbonyl compounds give $\pi \rightarrow \pi^*$ transition. Unsaturated molecules that contain atoms such as oxygen or nitrogen may also...
undergo $n\rightarrow\pi^*$ transition. Most $n\rightarrow\pi^*$ transitions are forbidden and hence are of low intensity [21, 11].

Fig.1.2 Electronic energy levels and transitions

1.11.3 Factors affecting the position of $\lambda_{\text{max}}$

The position of $\lambda_{\text{max}}$ depends on number of factors, including conjugation of chromophores, auxochromes and solvent.

A covalently unsaturated group such as C=C, C=O and NO$_2$ responsible for electronic absorption are known as chromophores. Auxochromes are saturated groups with nonbonding electrons. Furthermore, auxochromes alter the wavelength and intensity of absorption while attached to chromophores. The bathochromic shift (a shift to longer wavelength) occurs due to the conjugation of chromophores, auxochromes and hyperconjugative effects. In auxochromes, the resonance interaction of lone pair with the double bond increases the length of the conjugated system. The exact position and intensity of the absorption band of the conjugated system can be correlated with the extent of conjugation in the system. The hyperconjugative interaction takes place due to the overlap of C-H bonding orbitals with the $\pi$ system.
The choice of solvent can shift the peaks to longer or shorter wavelengths. This will depend on the nature of the interaction of the particular solvent with the environment of the chromopore. Additionally, solvent effect influences the fine structure of the absorption spectrum. A nonpolar solvent does not affect the fine structure of the spectrum since it does not make hydrogen bond with chromophore, whereas polar solvents definitely influence the fine structure of the spectrum due to the hydrogen bonding of solvents with chromophore, consequently solute-solvent complex [10, 22, 23].
REFERENCES


