Spectroscopy

Introduction

Molecular spectroscopy is the study of the absorption or emission of the electromagnetic radiation by molecules. The experimental data that such studies provided are the frequencies, or wavelengths, of the radiation and the amount of radiation emitted or absorbed by the sample.

One can often understand the nature of the molecular changes that are responsible for the emission or absorption of the radiation. In such cases, the experimental spectroscopic data can be used to determine quantitative values for various molecular properties. In this way, as will be seen, remarkably detailed and exact measurements of the **size, shape, flexibility, and electronic arrangement of a molecule** can be obtained. It will become apparent that spectroscopy offers one of the most powerful tools for a great variety of molecular -structure studies.

Spectrum: It is an array of waves which spreading according to increasing or decreasing properties of wave such as wavelength (λ), frequency (ν) etc.

Atomic Spectrum: It involves transition of electron from one electronic orbit to another electronic orbit. It is sharp line.

Molecular Spectrum: It involves transition of electron from one M.O. to another M.O. It is band spectra due to rotational, vibrational and translational motion.

Spectroscopy: It is the study of the interaction of energy (electromagnetic radiation) with matter or, Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules, atom or ions of a sample move from one energy level to another energy level.
Molecular spectroscopy can yield information about shape of molecules. It can give information about bond length, bond angle, and dissociation energy of a molecule etc.

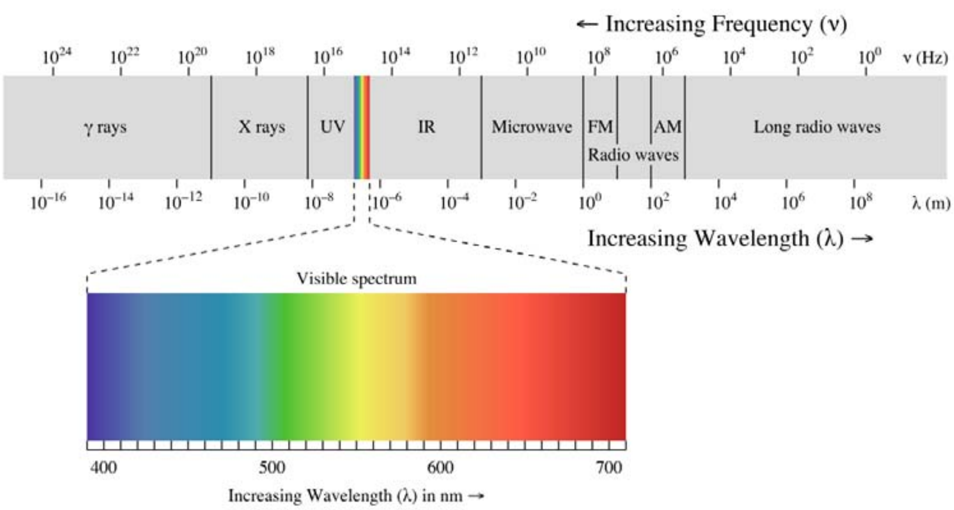

Figure 1: The electromagnetic Spectrum

Different types of molecular spectra

i) **Pure rotational (Microwave) spectra:** If the energy absorbed by the molecules is so low that it can cause transition only from one rotational level to another within the same vibrational level, the result obtained is called the rotational spectrum. These spectra are, therefore, observed in the far infra-red region or in the microwave region whose energies are extremely small ($\bar{\upsilon}$) 1-100 cm^{-1})

ii) **Vibrational rotational spectra:** If the exciting energy is sufficiently large so that it can cause a transition from one vibrational level to another within the same electronic level then as the energies required for the transitions between the rotational levels are still smaller, both types of transition viz., vibrational and rotational will take place. The result is therefore, a vibration- rotation spectrum. Since such energies are available in the near infra-red region, these spectra are observed in the region ($\bar{\upsilon}$=500-4000 cm^{-1}) and are called **infra-red spectra.**

iii) **Electronic Band spectra:** If the exciting energy is higher such that it can result in a transition from one electronic level to another, then this will also be accompanied by vibrational level change and each of these further accompanied by rotational level changes. For each vibrational a set of closely spaced lines is observed due to rotational level changes. Such a group of closely spaced rotational lines is called a **band.** Thus, for a given electronic transition, a set of bands is observed. This set of bands is called a **band group or a band system.** Each electronic transition gives a band system. The complete set of band system obtained due to different electronic transitions gives the electronic band spectrum of the gaseous molecule. As such high excitation energies are obtained from the visible and ultraviolet regions, these spectra are observed in the **visible region** (12500-25000 cm^{-1}) and ultraviolet region (25000-70000 cm^{-1}).

iv) **Raman Spectra:** This is also a type of vibrational -rotational spectrum but is based on the scattering of radiation and not on the absorption of radiation by the sample. It is based scattering of radiation and not on the absorption of radiation by the sample. It is based upon the principle that when a sample is hit by the monochromatatic radiation of the visible region and scattering is observed at right angle to the direction of the incident beam, the scattered radiation has frequency equal that to of the incident beam (called **Rayleigh scattering**) as well as frequencies different (higher as well as lower) from that of the incident beam (called ***Raman Scattering***). The difference in the frequencies of the incident beam and that of the scattered beam (called Raman frequencies) are similar to those observed for the vibrational and rotational transitions. However, by suitably adjusting the frequency of the incident radiation, Raman spectra are observed in the visible region (12500-25000 cm^{-1}).

v) **Nuclear Magnetic Resonance (NMR) Spectra:** This type of spectrum arises from the transitions between the nuclear spin energy levels of the molecule when an external magnetic field is applied on it. The energies involved in these transitions are very high which lie in the radio frequency region (5-100MHz). The method is based upon applying such frequencies on the sample so that it resonates with the applied frequency.

vi) **Electron Spin Resonance (ESR) Spectra:** This type of spectrum arises from the transitions between the electron spin energy levels of the molecule when an external magnetic field is applied on it. These involve frequencies corresponding to microwave region (2000-9600 MHz). Frequencies of this range are applied on the sample to bring the sample in resonance condition.

Characterization of Electromagnetic Radiation

Molecular spectroscopy may be defined as the study of interaction of electromagnetic waves and matter. Spectroscopy can tell us of the structure of matter which determined its physical properties, reactivity and biological activity, mechanism etc.

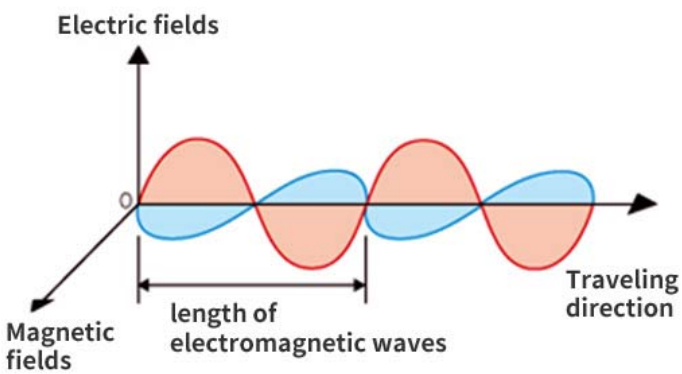

Fig 2: Picture of Electric and magnetic field components of plane polarized electromagnetic radiation.

Electromagnetic radiation is of different types e.g., visible light, radio waves, infrared, x-ray and gamma rays. According to the wave model these radiations may be described as oscillating electric and magnetic fields. Radiation travelling in the z-direction consists of electric field and magnetic field mutually perpendicular to each other and to the z direction. The picture shown above represents the plane polarized radiation. Electromagnetic radiation propagates with same speed in vacuum and this is equal to the velocity of light in vacuum. Since, electromagnetic radiation is considered as harmonic wave, so its property follows the Sine equation i.e., y= ASinθ, which is plotted in figure3. Here A is the amplitude of the wave and θ is the angle which vary from 0 to 2π.

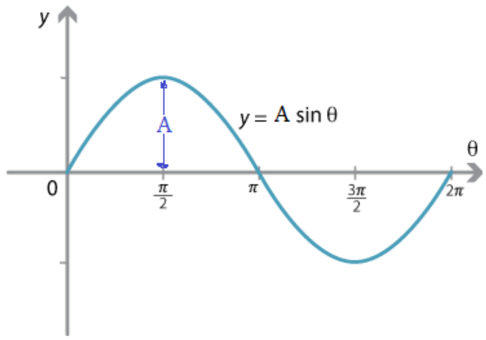

Figure3: The curve of y= ASinθ

Different terms used in the study of electromagnetic waves are discussed as under:

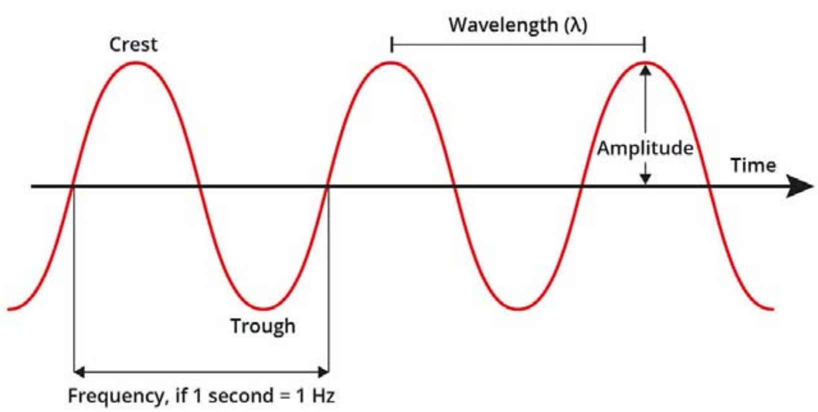

Fig 4: A single electromagnetic wave

i) **Frequency (ν):** It is the number of successive crests (or troughs) which pass a stationary point in one second. The unit is hertz; $1Hz = 1S^{-1}$

ii) **Wavelength(λ):** It is the distance between successive crests (or troughs). λ is expressed in centimeters (cm) meter (m), or nanometers (nm)
$1nm = 10^{-9}m$

iii) **Wave number ($\bar{\upsilon}$):** It is the reciprocal to wavelength. Its unit is cm^{-1}.
$\bar{\upsilon} = 1/\lambda$

Relation between Frequency, wavelength and wave number

Frequency and wavelength of an electromagnetic radiation are related by the equation

$$\nu\lambda = c$$

or

$$\nu = c/\lambda$$

where c is the velocity of light. It may be noted that wavelength and frequency are inversely proportional. That is, higher the wavelength lower is the frequency; lower the wavelength higher is the frequency.