

CHAPTER: 1. PRINCIPLES OF SPECTROSCOPY

INTRODUCTION: Spectroscopy is the branch of science which deals with the study of interaction between the electromagnetic waves and matter. It is one of the most powerful tools used for the study of atomic and molecular structures as well as in the analysis or determination of the structure of organic compounds. The classical techniques which were successful with macro quantities of organic compounds failed when the organic compounds under investigation were available in micro or semi micro amounts. Several types of spectroscopy have been applied to the study of such organic compounds.

These spectroscopic techniques possess numerous merits over the classical techniques which are as follows:

1. They take much less time.
2. They require very small amounts of the compound being studied.
3. They are generally very fast and economical in the long run.
4. They are generally non-destructive. i.e. the compounds being studied remain unchanged during spectroscopic examination and can be reused for other tests, if required.
5. They are highly reliable in establishing the identity of two compounds.
6. They give information which is recorded in the form of a permanent chart generally in an automatic or semi-automatic manner.

Electromagnetic Radiation: Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocity. It does not require any supporting medium for its transmission. It passes readily through vacuum. Electromagnetic radiations consist of electric and magnetic waves oscillating at right angles to each other and at right angles to the direction of propagation of radiation. Fig:1. represents a single electromagnetic wave (radiation) moving along X-axis.

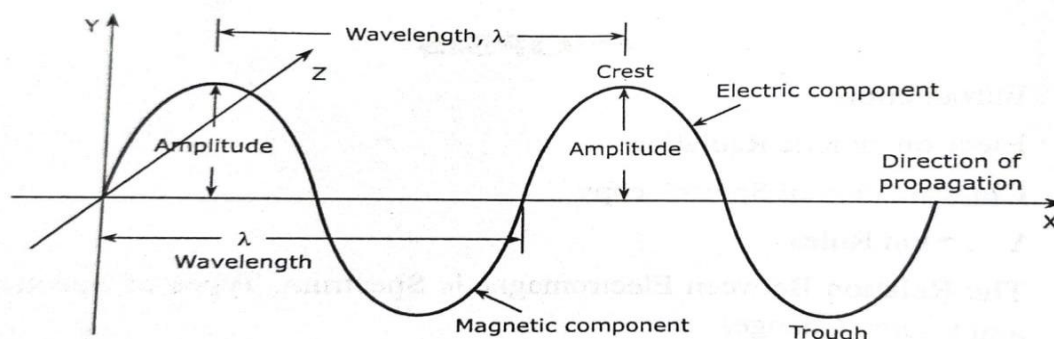


Fig1. Single Electromagnetic wave

Electromagnetic waves travel away from the source with the velocity of light 'C' in vacuum. The most common example of electromagnetic radiation is light. An electromagnetic radiation has dual nature having the characteristics of both, wave and particle. Electron radiation is released as photons, which are bundles of light energy that travel at the constant speed of light ($2.99 \times 10^8 \text{ ms}^{-1}$) as quantised harmonic waves.

Some important characteristics of electromagnetic radiations are as follows:

1. These radiations are produced by the oscillations of electric charge and magnetic field residing on this atom. The electric and magnetic components are mutually perpendicular to each other and are coplanar.
2. These are characterized by their wavelength or frequencies or wave numbers.
3. The energy carried by an electromagnetic radiation is directly proportional to its frequency. The emission or absorption of radiation is quantized and each quantum of radiation is called a photon.

4. All types of radiations travel with the same velocity and no medium is required for their propagation. They can travel through vacuum.
5. When visible light (a group of electromagnetic radiations) is passed through a prism, it is split up into seven colours which correspond to definite wavelengths. This phenomenon is called as dispersion. Thus, a group of electromagnetic radiations can be split up into various components for analysis.

The energy changes within a molecule during absorption and emission of electromagnetic radiation are quantized. The energy changes in a molecule are specified using the terms of frequency, wavelength and wavenumber which are explained below:

1. Amplitude: It is the distance from the maximum vertical displacement of the wave to the middle of the wave (Fig.1). This measures the magnitude of oscillation of a particular wave. Larger amplitude means higher energy and lower amplitude means lower energy. Amplitude tells us the intensity or brightness of a wave (light) in comparison with other waves.

2. Wavelength: It is the distance of one full cycle of the oscillation. It is denoted by Lambda λ . longer wavelength waves such as radio waves carry low energy and shorter wavelength waves such as X-rays carry higher energy which can be harmful for our health.

The relationship between the speed of light 'C', the frequency 'v' and wavelength ' λ ' is given as:

$$C = \lambda v$$

Shorter wavelength means greater frequency and greater frequency means higher energy, Wavelength tells us the type of wave (light) [Fig.1). **Wavelength is expressed in cms or nm or A° units. (1 A° = 10⁻⁸ cm & 1 nm = 10⁻⁹ cm)**

3. Frequency: It is the number of cycles per second. It is denoted as (nu) 'v'. **It is expressed in S⁻¹ or in Hertz (Hz), where 1Hz = 1 cycle/ sec.**

Frequency \propto 1/ wavelength	$v = C / \lambda$
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Where, C= velocity of electromagnetic radiation.

4. Period: It is the time a wave takes to travel one wavelength. It is denoted by 'T' & is measured in seconds (s).

5. Velocity: The velocity of a wave is denoted by 'v' and is expressed as:

$$V = \lambda .v$$

For electromagnetic wave, the **velocity in vacuum is 2.99 x 10⁸ m/s.**

6. Wave number: It is the number of waves per centimetre in vacuum. It is denoted nu bar, $\bar{\nu}$. **It is the reciprocal of wavelength and is measured in cm⁻¹.** It is frequently used in infra-red technique. If the wavelength of a light is known wavenumber can be calculated.

$$\bar{\nu} = 1 / \lambda$$

7. Energy: Energy of a wave of the particular radiation can be expressed in 'eV' Or Joule / mole.

And can be calculated by the relation:

$$E = h.v = h . C / \lambda$$

Where, **h** = Planck's constant = 6.626 X 10⁻²⁷ egr sec.

v = Frequency of radiation in cycles sec⁻¹

C = Velocity of electromagnetic radiation

λ = Wavelength in centimeters.

When the frequency is high, energy is higher and wavelength is smaller. When the wavelength is large, energy is lower. These energy were called as **Photons or Quanta**, they travel in the direction of propagation of the radiation with the velocity equals to that of light.

Problem no.1. Calculate the energy associated with a radiation having wavelength 4000 \AA .

Solution:

$$\lambda = 4000 \text{ \AA} = 4000 \times 10^{-8} \text{ cm}$$

$$E = h \cdot C / \lambda$$

$$= \frac{(6.628 \times 10^{-27}) \times (2.998 \times 10^{10})}{(4000 \times 10^{-8})}$$

$$\text{Ans. } E = 4.968 \times 10^{-12} \text{ ergs}$$

ELECTROMAGNETICE SPECTRUM: A spectrum is defined as the characteristic wavelength of electromagnetic radiation that is emitted or absorbed by an object or a substance, atom or molecule. The Electromagnetic Spectrum is an uninterrupted existence of all electromagnetic waves arranged according to frequency and wavelength. It is the entire range of wavelengths or frequencies over which the electromagnetic radiation extends from gamma rays to the longest radio-waves, including visible light. Fig.2: gives the entire Electromagnetic Spectrum. **The narrow range of visible light is shown enlarged in middle.** The visible region is very small part of entire spectrum ranges from **400 nm (Violet) to 800 nm (Red)**. Wavelength slightly shorter falls in ultraviolet region & slightly longer falls in infrared region.

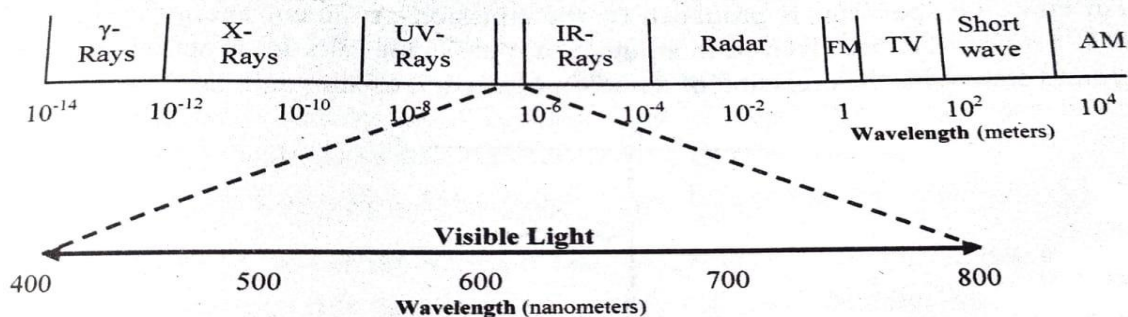


Fig:2: Electromagnetic Spectrum with highlighted Visible light

PRINCIPLE OF SPECTROSCOPY: Spectroscopy is the analysis of the electromagnetic radiation scattered, absorbed or emitted by the molecules. According to quantum mechanics, the energy levels of all the systems are quantized and are designated by the appropriate quantum numbers. The spectrum arises as follows:

Consider two molecular energy levels E_1 and E_2 as shown below in Fig.3. If a photon of frequency ν falls on a molecule in the ground state and its energy $h\nu$ is exactly equal to the **energy difference $\Delta E = E_2 - E_1$ between the two molecular energy levels**, then the molecule undergoes a transition from the lower energy level to the higher energy level with the **absorption of a photon of energy $h\nu$** . The spectrum thus obtained is **Absorption Spectrum**. If the molecule falls from the excited state to the ground state with the emission of a photon of energy $h\nu$, the spectrum obtained is called the **Emission Spectrum**.

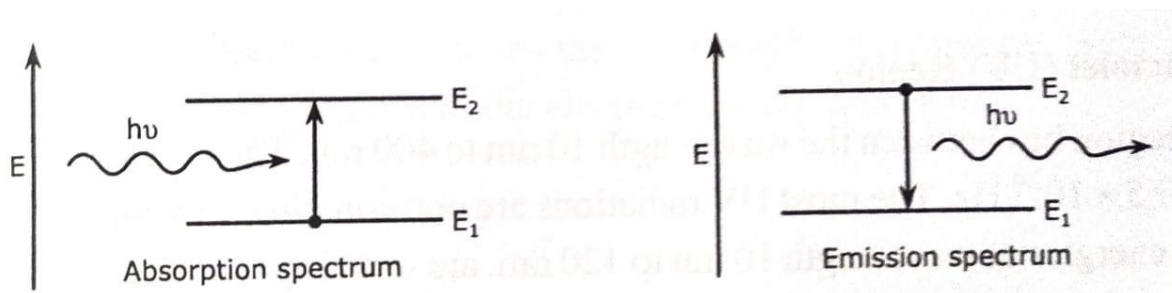


Fig: 3- Types of Spectrum

Table:1 summarizes the wavelengths, frequencies, wave numbers and energies of the different regions of the electromagnetic spectrum.

Regions	Frequency(ν) (Hz) (decreasing)	Wavelength(λ)(nm) (increasing)	Energy(E)(Jmol ⁻¹) (decreasing)	Wave number ($\bar{\nu}$) (cm ⁻¹)(decreasing)
Gamma ray(γ)	3×10^{25} - 3×10^{18}	0.01-1	10^{11} - 10^9	10^{10} - 10^8
X- ray	3×10^{18} - 3×10^{16}	1-10	10^9 - 10^7	10^8 - 10^6
UV rays	3×10^{16} - 7.5×10^{14}	10-400	10^7 - 10^5	10^6 - 10^5
Visible ray	7.5×10^{14} - 4.3×10^{14}	400-750	10^5 - 10^4	10^5 - 10^4
IR region	4.3×10^{14} - 3×10^{12}	$750 - 10^5$	10^4 - 10^3	10^4 - 10^2
Microwave region	3×10^{12} - 3×10^{10}	10^5 - 10^8	10^3 - 10	10^2 - 1
Radio frequency	3×10^{10} - 3×10^6	$> 10^8$	10 - 10^{-3}	1 - 10^{-3}

Table:2- Uses of Electromagnetic Waves

Electromagnetic Waves	Uses
Gamma Rays	Doctors use them for checking the organs inside our body. They are also used to kill the bacteria in marshmallows and to sterilise medical equipment. The biggest gamma-ray generator is the universe.
X- Rays	They are used to image bone structure by the dentists and doctors. They are used to screen the luggage by the airport security.
UV Rays	These rays are emitted by the Sun and they tan and burn the skin. Bees can see into these as the flowers stand out more clearly at this frequency
Visible Rays	Human eyes can see this light. Fireflies, light bulbs, and stars emit this light.
IR Rays	Night vision goggles pick up this light emitted by our skin and objects with heat. Therefore, used in heat sensors. It is also used for laser metal cutting. In space, this light helps in mapping the dust between the stars.
Microwave Rays	They are used for cooking in microwave ovens. They are also used in radar. Astronomers use them to learn about the structure of nearby galaxies.
Radio Waves	These are used in radios, televisions, etc. These waves are also emitted by stars and gases in space.

Classification of Spectroscopy: Chemicals can be analysed qualitatively and quantitatively by a number of different analytical methods. One big area of analysis is by using Spectroscopy. It studies the interaction between electromagnetic radiation and matter. These interactions may give rise to the **electronic excitations, molecular vibrations or nuclear spin orientations**. Spectroscopy finds wide range of applications in daily life. It is used in analytical chemistry Phyto-chemistry (plant chemistry), biology, health care and medicine.

The classification can be done on three bases:

(A) Based on the Atomic or Molecular Level of Study: When the light (electromagnetic radiation) is allowed to pass through the substance, the changes observed are at atomic level or molecular level. Thus, the spectroscopy can be of two types as follows:

(1) Atomic Spectroscopy: In this case the energy changes take place at atomic levels. This was the first application of spectroscopy. Atoms of different elements have distinct spectra. Thus, atomic spectroscopy can quantify and identify a sample's composition. The main types of atomic spectroscopy include Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectroscopy (AES) or Flame Emission Photometry, and Atomic Fluorescence Spectroscopy (AFS).

(i) AAS: In AAS, the atoms absorb ultraviolet or visible light to get excited to a higher energy level. AAS quantifies the amount of absorption of ground state atoms in the gaseous state. AAS is commonly used in the detection of metals.

(ii) AES (Flame Emission Photometry): In AES, the atoms are excited by the heat of a flame to emit the light. AES is used to determine the quantity of an element in a sample by measuring the intensity of light emitted. Instead of heat of a flame, if heat from plasma is used for emission, then it is plasma emission and if an arc is used, it is arc emission spectroscopy (photometry). AES is used to detect multiple elements simultaneously.

(iii) AFS: In AFS, it is a beam of light that excites the atoms in the analytes causing them to emit the light. The fluorescence from a sample is then analysed using a fluorometer, AFS is commonly used to analyse the organic compounds.

(2) Molecular Spectroscopy: In this case the energy changes take place at molecular levels. The characters like molecular absorption, emission and vibration are studied. These include colorimetry, ultraviolet (UV) and Visible Spectroscopy, Infrared (I/R) Spectroscopy, Fourier-Transform infrared (FTIR) Spectroscopy, Fluorimetry or Fluorescence Spectroscopy.

(i) Colorimetry: It is used to determine the concentration of coloured compounds in solution. Colorimeter is a device used to test the concentration of a solution by measuring its absorbance at a specific wavelength of light. The principle used is based on Beer-Lambert's law which states that the amount of light absorbed by a coloured solution is directly proportional to the concentration of the solution and the length of a light path passing through the solution.

(ii) Ultraviolet and Visible Spectroscopy: These analyse the compounds using the electromagnetic radiation spectrum from 10 nm to 750 nm. In this region valence electrons get excited and move from one energy level to another in the molecule. This electronic change in the molecule causes changes in the electric dipole which interacts with the electric field of the electromagnetic radiation. The interaction gives rise to the spectrum in the UV-Visible region. In this Atom must be in gaseous state. This Spectroscopy can be used to measure the concentration of samples using the principles of Beer-Lambert Law. Spectroscopy can also be used to identify the presence of free electrons and double bond within a molecule. UV spectroscopy is a valuable technique for the identification of organic compounds. It gives information about the presence or absence of multiple bonded systems, conjugated systems, aromatic systems and heteroaromatic systems. It is used in the determination of certain functional groups in organic compounds. It can be used to find the concentration of protein and DNA in a solution.

(iii) Infrared Spectroscopy: IR spectrum can be split into near IR, mid IR and, far IR. Near IR has the greatest energy and can penetrate a sample much deeper than mid or far IR. IR spectroscopy is **less sensitive than UV and Visible Spectroscopy** as the energies involved in the vibration of atoms are small. IR spectroscopy works on the principle that molecules vibrate with the bonds stretching and bending, when they absorb infrared radiations. During vibration, the molecules undergo change in the dipole moment. When the frequency of IR matches with the vibrational frequency of the bonds, absorption takes place and the spectrum can be recorded. These vibrational spectra **can be used to determine the functional groups present in an organic compound**. IR spectroscopy is used to show **what types of bonds are present in a sample** by measuring different types of inter-atomic bond vibrations at different frequencies. It relies on the fact that molecules absorb specific frequencies which depends on their chemical structure.

(iv) **FTIR:** The FTIR was first developed by astronomers to study the infrared spectra of stars. The conventional IR instruments have slow response. High speed IR instruments are necessary. In **Fourier Transform Infrared instruments**, the Infrared spectras are rapidly and accurately recorded. FTIR spectroscopy makes use of all the frequencies from an IR source simultaneously. As all the wavelengths of IR spectrum are measured simultaneously, the method is faster than conventional IR spectroscopy. Even the traces of the sample can be analysed by this method. FTIR provides complete spectral range without using movable parts like slits, grating, chopper, etc., which are used in conventional IR spectroscopy.

(v) **Fluorimetry or Fluorescence Spectroscopy:** If a beam of light is incident on some substances, they emit radiations. Such a phenomenon is **known as 'fluorescence'**. This phenomenon is **instantaneous**. It starts after the absorption of light and stops when the incident light is cut off. The substances showing fluorescence are called **'fluorescent'** substances. As only a few substances exhibit fluorescence, it is a valuable tool for analytical chemistry. **Fluorimetry is 100 times more accurate than the absorbance methods.** Using Fluorimetry, it is possible to determine two components, emitting same fluorescence colour simultaneously, provided their respective wavelengths are sufficiently far. The only **limitation in fluorimetry is that fluorescent intensity depends on pH. A careful buffer solution is required to be used.**

B) Based on the Property of Absorption or Emission: In this classification, the principle of absorption or emission of electromagnetic radiation is considered. Thus, there are two types of spectroscopy as follows:

- 1) **Absorption Spectroscopy:** In this type, there is absorption of light by the sample takes place and the extent of absorption and the wavelength of the absorbed light are considered. **The wavelength of light absorbed tells us the nature of the compound, and the intensity of absorbed light tells us the concentration.** The main types of absorption spectroscopy include Colorimetry, UV-Spectroscopy, IR-Spectroscopy, NMR Spectroscopy, Atomic Absorption Spectroscopy (AAS).

NMR Spectroscopy: Nuclear Magnetic Resonance (NMR) spectroscopy uses **Resonance spectroscopy and nuclear spin** states for spectroscopic analysis. All nuclei have a nuclear spin which depends on its intramolecular environment and the external applied field. When nuclei of a particular element are in different chemical environments within same molecule, there will be carried magnetic field strengths experienced due to shielding and de-shielding of electrons causing different resonance frequencies. Spin-spin coupling takes into account that the spin states of one nucleus affects the magnetic field which is experienced by neighbouring nuclei. Spin-spin coupling causes absorption peaks of each group of nuclei to be split into a number of components. The NMR spectrum of a compound shows the resonance signals which are emitted by the atomic nuclei present in a sample and these can be used to identify the structure of a compound. **NMR spectroscopy mainly used for analysis of organic compounds. It can provide extensive information about the structure, dynamics and chemical environment of atoms. Different functional groups can be distinguished by using NMR spectroscopy.**

- 2) **Emission Spectroscopy:** In this type, **the emitted light is measured.** When a beam of light is incident on the sample, some of it is absorbed. This absorption of light leads to transition of electrons from ground state to excited state. These excited electrons return back to ground state by release of electromagnetic radiation of specific wavelength. The intensity of the emitted light gives the concentration, and the wavelength tells us the nature of the compound. The main types of emission spectroscopy are fluorimetry or fluorescence spectroscopy, atomic emission spectroscopy (AES) or Flame photometry.

(C) Based on the Level of Study like Electronic or Magnetic Levels: Here the study is done based on electronic or magnetic properties of the compound. There are two types of spectroscopy as follows:

1) Electronic Spectroscopy: When a compound is analysed without using a magnetic field, it is called electronic spectroscopy. This type of spectroscopy includes colorimetry, UV-Visible spectroscopy, IR spectroscopy, Fluorimetry or Fluorescence spectroscopy, etc.

2) Magnetic Spectroscopy: In this case the compound is studied under the presence of external magnetic field. This includes Nuclear Magnetic Resonance (NMR) spectroscopy and Electron Spin Resonance (ESR) Spectroscopy.

ESR Spectroscopy: Electron Spin Resonance (ESR) spectroscopy is similar to NMR spectroscopy which is **used for studying materials with unpaired electrons**. In this case the electron spins are excited and not the spins of atomic nuclei like in case of NMR spectroscopy. ESR is concerned with the magnetically induced splitting of electronic spin states, while NMR describes the splitting of nuclear spin states.

Selection Rules: Suppose we have an electron within the given atom and that electron gains a certain quantity of energy in form of a photon of light that has just the right frequency, then the electron jumps from a lower energy state to a higher energy state. Conversely, the opposite can also take place. If the electron transition takes place from a higher energy to a lower energy, it will release a photon of light that has a certain given frequency. In quantum mechanics, certain electron transitions are more likely to take place than others. Those transitions having high probability of taking place are known as **“allowed transitions”**. The transitions which are very improbable and less likely to take place are known as **“forbidden transitions”**. In quantum mechanics, a set of rules exist, **known as “Selection Rules”**, that basically explains which transitions are allowed transitions. The basic 'Selection Rules' for electronic transitions are as follows:

- A) **Rule No. 1: $\Delta s = 0$** , this rule says that spin angular momentum of an electron does not change during the absorption or emission of light. In other words, the change in the spin quantum number during a transition is zero
- B) **Rule No. 2: $\Delta l = \pm 1$** , this rule says that the change in the orbital quantum number during a transition is either + 1 or - 1. When $\Delta l = +1$, it means that an electron jumps from a lower to a higher energy state. When $\Delta l = -1$, it means that an electron jumps from a higher energy state to a lower energy state. Thus, this rule tells us that an electron cannot jump between two orbitals that differ by more than one orbital quantum number and the change in l cannot be equal to zero, i.e., $\Delta l \neq 0$. Also, two or more electrons cannot get excited simultaneously. That is why + 1 and not ± 2 or ± 3 .
- C) **Rule No. 3: $\Delta m = 0, \pm 1$** : This rule says that the change in the magnetic quantum number is either zero, or +1, or - 1.

On the basis of selection rules, transitions can be categorized as:

- (1) **Allowed transitions:** They are spectral transitions which obey selection rules. They are stronger and more intense. They yield spectral lines with greater intensity than the forbidden ones.
- (2) **Forbidden Transitions:** They are spectral transitions which do not obey the selection rules. They are weak and less intense. They yield spectral lines which have less intensity than the forbidden ones.

APPLICATIONS OF MOLECULAR SPECTROSCOPY:

- i) It is used in structural investigation. Electronic energy levels, bond lengths, bond angles and strength of bonds can be determined with the help of molecular spectroscopy.
- ii) It can be used to monitor changing concentrations of reactants or products in kinetic studies.
- iii) It helps to understand the colour in the world around us.
- iv) Emission spectroscopy is used for the study of energetically excited reaction products.