Sem II_Unit IV

Applications of Spectroscopic Techniques_

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Syllabus:

- *Principles of Spectroscopy and selection rule

- *Electronic spectroscopy-Basic principle, Lambert Beer's law, Woodward Fischer Rule for conjugated dienes, fluorescence, phosphorescence, Jablonski diagram and its application

- * Nuclear Magnetic resonance- basic principles, chemical shift, spectral interpretation of some simple compounds and Magnetic resonance imaging

Scope of Syllabus

- **Unit-4 APPLICATIONS OF SPECTROSCOPIC TECHNIQUES**
- Marks: 11 Hours: 08
- Principles of Spectroscopy
- **Parameters of electromagnetic radiation-Definition only, Interaction of EMR with matter (Definition or Principle only), Spectrometer (brief description), Spectrum (only statement), Types of Spectra (Definition only -Continuous Spectra, Absorption Spectra, Emission Spectra, formation of absorption bands)**
- Selection Rules **(related to UV spectroscopy)**
- Electronic Spectroscopy- Basic Principles **(definition of electronic spectroscopy, electronic transition and its type(π–π*, n–π*, σ–σ* and n–σ*), concept of Chromophore and Auxochrome)**
- Lambert- Beer’s law **(Only statement and final mathematical expression, numericals) Page 2 of 4**

Continued…..

- Woodward Fischer Rule for Conjugated Dienes **(Statements and rules for calculating absorption maximum, Numericals on Woodward Fischer rule for alicyclic dienes like butadiene, hexatriene, homo-annular, hetero-annular, and other substituents like ring residue)**
- Application of UV and visible spectroscopy
- fluorescence, phosphorescence **(in brief) Jablonski diagram (Energy level, Absorption, Fluorescence, Phosphorescence, Internal conversion, Vibrational relaxation, Intersystem crossing) and its application**
- Nuclear Magnetic Resonance- Basic Principles,
- chemical shift **(Delta scale (δ) and Tau scale (t),**
- NMR Spectra **(in brief -Number of signal (peak), equivalent and non-equivalent proton, position of signal (peak)- shielding, deshielding, factors affecting chemical shift-types of proton, Inductive effect, Anisotropic effect, Hydrogen bonding); intensity of signal (peak); splitting of signal (peak)-(not to be considered)**
- spectral interpretation of some simple compounds **(ethane, ethyl bromide, ethanol, acetaldehyde, 1,2-dibromo ethane, cyclo propane, cyclo butane, benzene, aniline, toluene, phenol, bromo benzene, amino-phenol and benzaldehyde)**
- **Application of NMR (structure elucidation not to be considered)**
- magnetic resonance imaging **(brief introduction)**

Introduction

- Electromagnetic radiations are **radiations** having **two mutually perpendicular waves** oscillating in in planes **perpendicular** to the direction of propagation

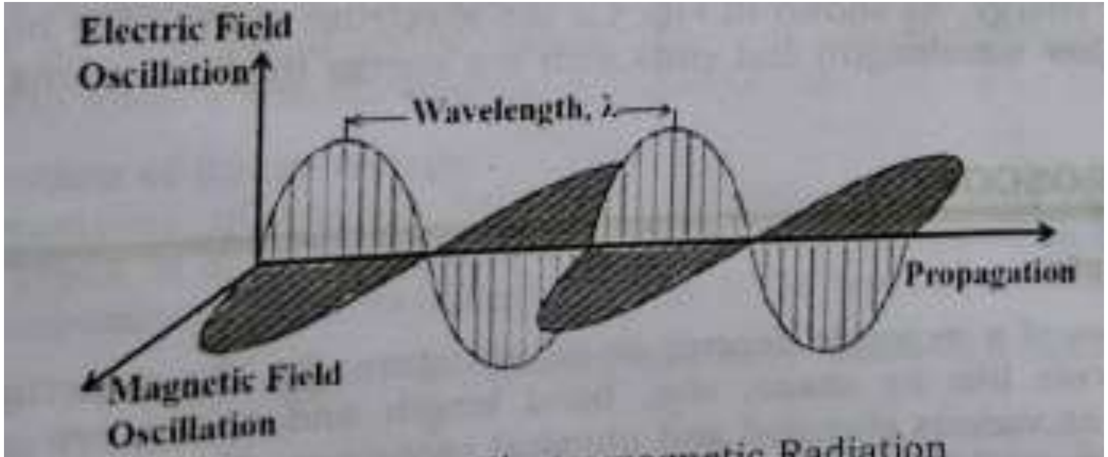


Figure 4.1: Electromagnetic Radiation

Parameters of electromagnetic radiation

- include frequency, wavelength and Speed
- Frequency is cycles per second (Hertz),
- wavelength is distance traveled to complete 1 cycle and
- period is time to complete 1 cycle.
- The higher the frequency, the shorter the wavelength
- The electromagnetic radiations travel with the speed of light i.e. 3×10^8 m/s.
- These radiations have dual nature that is particle as well as wave nature, as per the de-Broglie hypothesis. It is made up of photon energy of each Photon is given by

$$E = h\nu$$

- (where h is Planck's constant = 6.626×10^{-34}JS).
  - The velocity, wavelength and frequency of radiations are related to each other by $C = \nu \lambda$

Electromagnetic radiations are characterized by the following parameters-

SN	Parameters	Symbol	Dimension	Units
1	Wavelength is the distance between two successive points on wave which are in same phase.	λ	Length	m, cm, nm, Å
2	Frequency is the number of waves passing through a point in unit time.	υ	time^{-1}	s^{-1}, Hz
3	Wavenumber is the number of waves per unit distance.	$\bar{\upsilon}$	length^{-1}	m^{-1}, cm^{-1}
4	Velocity is the distance travelled per unit time.	c	length•time^{-1}	m s^{-1}

The interrelation between these parameters is as follows-

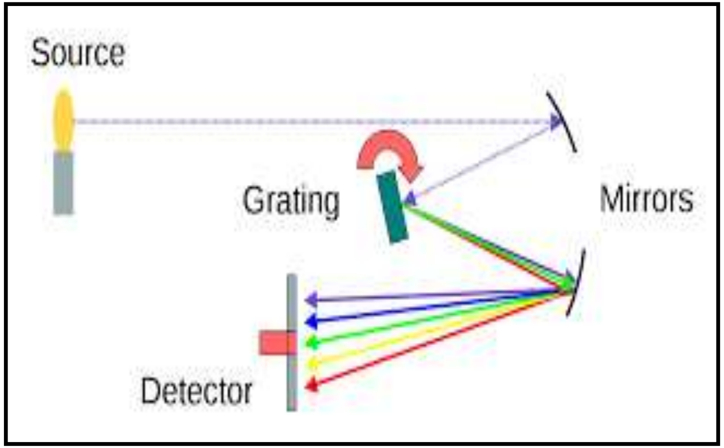
$\upsilon = \frac{c}{\lambda}$ or $c = \upsilon\lambda$ $\quad \bar{\nu} = \frac{1}{\lambda} \quad E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}$

Interaction of EMR with matter_Principle of Spectroscopy

- *Spectroscopy is a study of the **interaction** between the **matter** and **electromagnetic radiations** as a function of **wavelength** or **frequency** of radiation.*
- The radiation when absorbed by matter causes various excitations in atoms and molecules of the matter. These excitations provide structural information about the atoms and molecules of matter.
- It uses **absorption** and **emission** of the **light** and/ or the other **radiations** by matter on which it is **incident**.
- The **study** of the **spectrum** as a **function** of **wavelength** or **energy** of **electromagnetic** radiation allows us to understand the **behavior** of the **molecule**.

- **Spectrometers**

It splits the incoming light wave into its component colors. Using this, they can determine what material created the light.



Spectrum:

When electromagnetic radiation is passed through a prism or grating it is split up and forms a collection of lines representing different wavelengths. This is called **spectrum**.

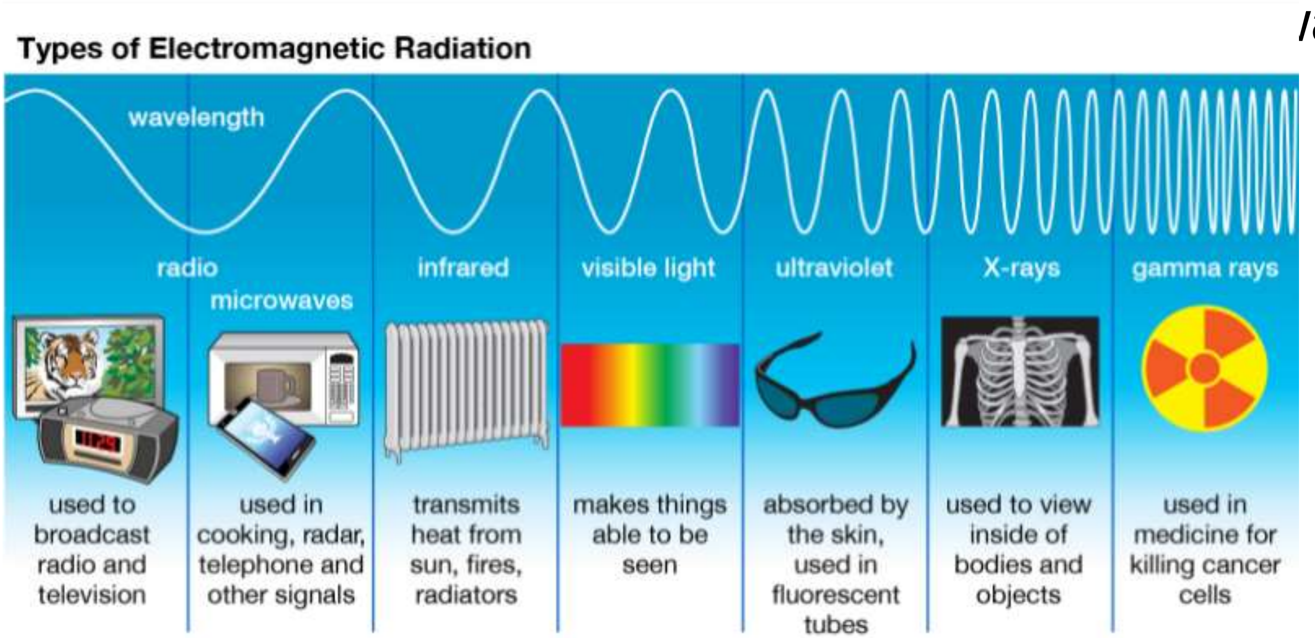
Electromagnetic spectrum is the **arrangement** of different types of electromagnetic radiations in **increasing order** of their **wavelength** or **decreasing** order of their **energy**.

Types of electromagnetic waves that make up the electromagnetic spectrum are radio waves, microwaves, infrared light, visible light, ultraviolet light, X-rays and & gamma rays

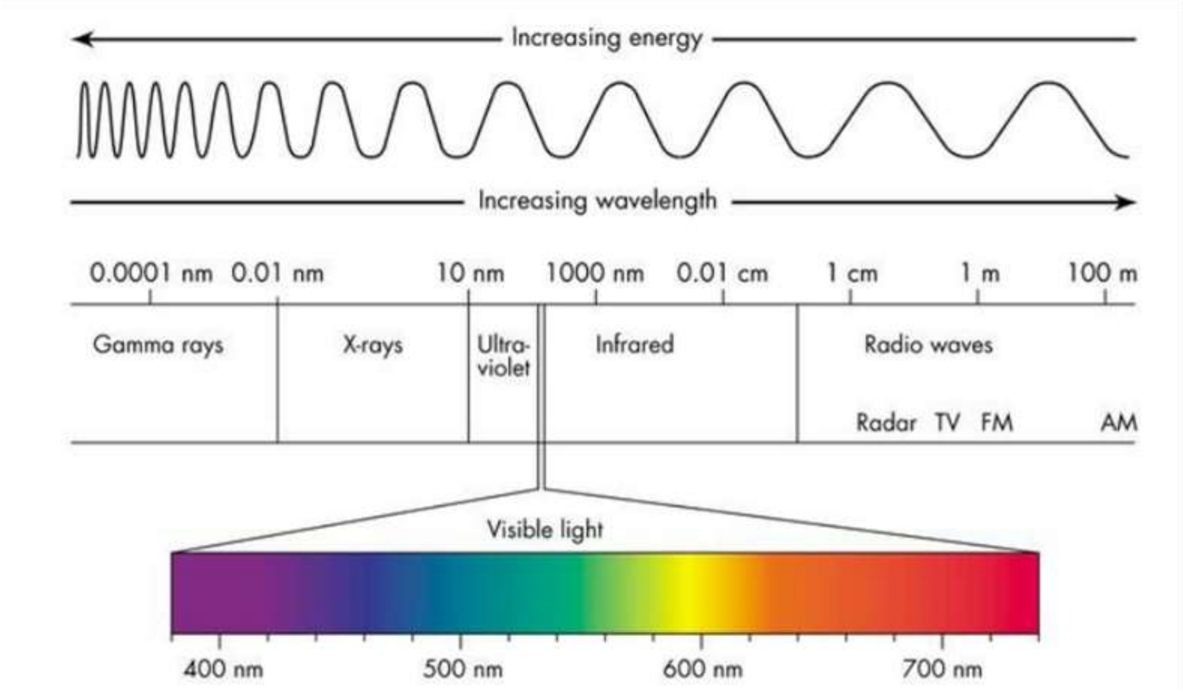
Visible light makes up just a small part of the full electromagnetic spectrum.

Electromagnetic waves with shorter wavelengths and higher frequencies include ultraviolet light, X-rays, and gamma rays.

Electromagnetic waves with longer wavelengths and lower frequencies include [text covered by image] /aves.



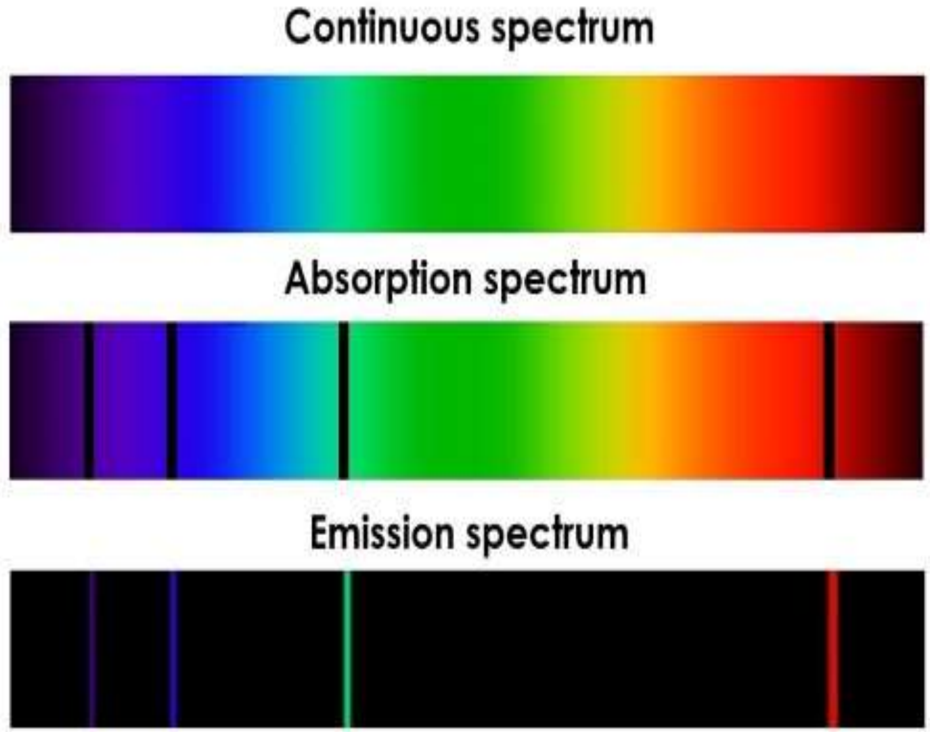
The Electromagnetic Spectrum



The **spectra** can be divided into two **types** viz., emission and absorption **spectra**.

- An **absorption spectrum** occurs when light passes through a cold, dilute gas and atoms in the gas absorb at characteristic frequencies; since the re-emitted light is unlikely to be emitted in the same direction as the **absorbed** photon, this gives rise to dark lines (absence of light) in the **spectrum**.
- Absorption spectrum: a spectrum of electromagnetic radiation transmitted through a substance, showing dark lines or bands due to absorption at specific wavelengths.
- The **emission spectrum** of a chemical element or chemical compound is the **spectrum** of frequencies of electromagnetic radiation **emitted** due to an atom or molecule making a transition from a high energy state to a lower energy state.

- A **continuous spectrum** a **spectrum** having no apparent breaks or gaps throughout its wavelength range. This contains many different colors, or wavelengths, with no gaps. Perfectly white light shined through a prism causes dispersion of the light, and we see a rainbow. This is a **continuous spectrum**
  Most **continuous spectra** are from hot, dense objects like stars, planets, or moons. The **continuous spectrum** from these kinds of objects is also called a thermal **spectrum**, because hot, dense objects will emit electromagnetic radiation at all wavelengths or colors.

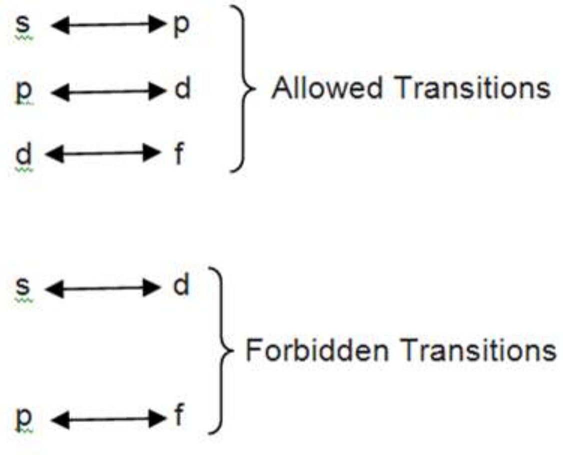


- **Selection Rules:**
- If a photon of light of the right frequency is absorbed by an electron, the electron jumps to a higher energy state (E2). And if the electron releases a photon light, it will jump to a lower energy state (E1). These are called Electronic Transitions.
- **Allowed Transitions:** The transition that have a high probability of occurring are called allowed transition
- **Forbidden Transition:** The transition that are less likely to take place are called forbidden transitions
- **Selection Rules:** A set of rules that tell us the about allowed transitions.

Rule I :

- Electron can jump from any energy level (Principle Quantum No.) to any energy level.
- $\Delta n = \pm 1, \pm 2, \pm 3, \pm 4$…………………

- **Rule II : Laporte’s Selection Rule:**
- Electron cannot jump between two orbital that differ by more than one orbital
- $\Delta l = \pm 1$ allowed transition
- $\Delta l \neq \pm 1$ Not allowed (forbidden) transition
- This rule is related to Azimuthal Quantum No. (l) i.e. s, p, d, f



- **Rule III: Spin selection Rule:**
- Spin multiplicity of electron should not change (Spin of electron should not changed after transition)
- This rule is related to **spin quantum no. (s)**
- **Spin angular momentum (s)**
- $\Delta S = 0$ allowed transition
- Spin multiplicity of electron should not change (Spin of electron should not changed)
- $\Delta S \neq 0$ Not allowed (forbidden) transition

Rule IV: Total angular momentum change Rule:

$\Delta J = 0, \pm 1$ allowed transition

$\Delta J \neq 0, \pm 1$ forbidden transition

Total angular momentum = Orbital angular momentum + Spin angular momentum

J = (L+S)……….(L-S)