Engineering Chemistry

First Year Engineering

(Sem- II)

Topic- 1 Principles of Spectroscopy

- **Introduction**
- **Recently, Spectroscopic methods used in analysis / structure determination of organic compounds.**
- **Merits of Spectroscopic methods-**
- **1) Take less time .**
- **2) Require small amount of compound.**
- **3) Very fast and economical methods.**
- **4) Non destructive methods.**
- **5) Highly reliable to identify two compounds.**
- **6) Output information recorded in form of automatic permanent chart.**

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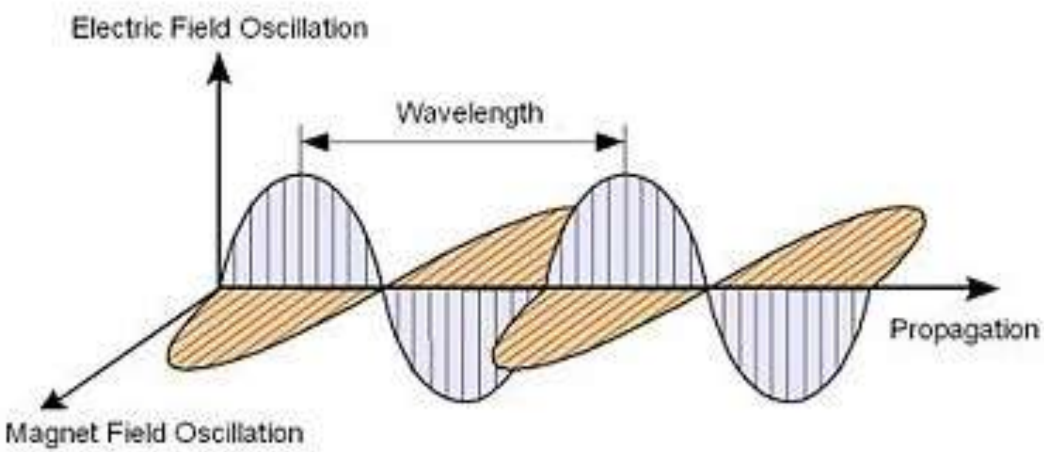
- **Electromagnetic Radiation**
- **Def. " Electromagnetic radiation is a simple harmonic wave with the properties of sine wave".**
- **Electromagnetic radiations travels in a straight line unless it is refracted or reflected.**



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- **Characteristics of Electromagnetic Radiation**
- 1) Produced by oscillations of electrical field and magnetic field residing on this atom. electric and magnetic components are mutually perpendicular to each other and coplanar.
- 2) It is Characterized by their wavelength/frequency/wave number.
- 3) Energy carried by electromagnetic radiation is directly proportional to its frequency.
- 4) All types of radiations travels with same velocity and no medium is required for their propagation.
- 5) When visible light (group of electromagnetic radiations) passed through prism, it is split into seven colours which correspond to definite wavelength.

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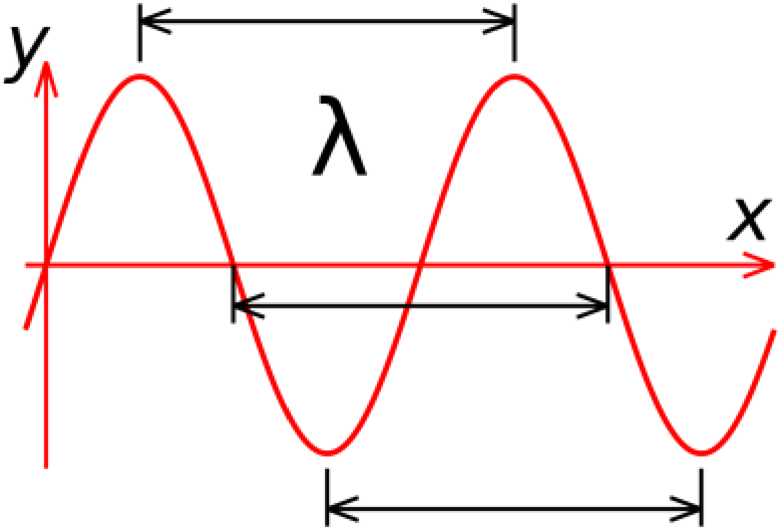
- **a) Wavelength;**
- It is a distance between the two crests or troughs in a particular wave.
- It is denoted by Lambda (λ) .
- It can be expressed in Angstrom units (A^0) or in millimicrons ($m\mu$).
- $1\ A^0 = 10^{-8}$ cm; $1\ m\mu = 10^{-7}$ cm



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- **a) Wavelength;**
- 1) The wave range of visible light is from 3800 A^0 (violet end) to 7600 A^0 (red end).
- 2) Different colours of light have different wavelengths.
- 3) Human eye is sensitive and fails to detect Ultraviolet range
  (λ < 3800 A^0) and Infrared range λ < 7600 A^0)
- 4) It is measure of the radiant power of radiation.

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- ## b) Frequency;
- " It is the number of waves which can pass through a point in one second".
- It is expressed in υ(nu) in cycles per second or in Hertz (Hz).
- Where, 1 Hz = 1 cycle sec^{-1}.
- Frequency $\alpha \frac{1}{Wavelength}$
- Frequency $\upsilon = \frac{c}{\lambda}$
- Where; c = velocity of electromagnetic radiation.

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- ## c) Wave Number;
- " The number of waves that exists over a specific distance is called wave number".
- It is expressed in $\bar{v}$.
- It is reciprocal of wavelength and expressed in per cm.
- It is frequently used in infra-red techniques.
- If wavelength of light radiation is known, the corresponding wave number can be calculated.
- $\bar{v} = \frac{1}{\lambda}$

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- ## d) Energy;
- “ Energy of wave of the particular radiation can also be calculated by the relation;
- $E = h\upsilon = h.\frac{c}{\lambda}$
- Where;
- h = Planks constant = 6.626 x 10^{-27} org sec.
- υ = Frequency of radiation in cycles sec^{-1} .
- c = Velocity of electromagnetic radiation.
- λ = Wavelength in centimeters.
- Note: When the frequency is high, energy is higher and wavelength is smaller. When the wavelength is large, energy is lower.

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- **Numericals on Electromagnetic Radiations;**

1)

ON ELECTROMAGNETIC RADIATON

1. Calculate the energy associated with a radiation having wavelength 4000 A°. Give answer in kcal mole^{-1} and also in Kilo Jules mole^{-1}.

Solution :

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

$$E = h \cdot \frac{c}{\lambda}$$

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

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

$$= \frac{4.968 \times 10^{-12} \times 6.023 \times 10^{23}}{4.18 \times 10^{10}}$$

$$= 71.6\ \text{kcals mole}^{-1}$$

Also 1 kcal = 4.184 kJ

$$\therefore\ E = 71.6 \times 4.184 = 299.5\ \text{kJ mole}^{-1}$$

$$\boxed{\begin{aligned} \text{Ans. : } E &= 71.6\ \text{kcals mole}^{-1} \\ E &= 299.5\ \text{kJ mole}^{-1} \end{aligned}}$$

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- **Numericals on Electromagnetic Radiations;**

2)

2. The energy for a quantum of light is 4.97×10^{-19} J. What is the wavelength and frequency of this light?

Solution :

$$E = 4.97 \times 10^{-19}\ J$$

$$E = h \cdot \frac{c}{\lambda}$$

$$\therefore \lambda = h \cdot \frac{c}{E}$$

$$= \frac{(6.62 \times 10^{-34}) \times (3 \times 10^{8})}{(4.97 \times 10^{-19})}$$

$$= 3.99 \times 10^{-7}\ m$$

$$\nu = \frac{c}{\lambda}$$

$$\nu = \frac{3 \times 10^{8}}{3.99 \times 10^{-7}} = 7.52 \times 10^{14}\ Hz$$

Ans. : $\lambda = 3.99 \times 10^{-7}$ m
$\nu = 7.52 \times 10^{14}$ Hz

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- **Numericals on Electromagnetic Radiations;**

3)

3. Calculate the energy of green light of wavelength 535×10^{-9} m.

Solution :

$$\lambda = 535 \times 10^{-9} \text{ m}$$

$$E = h \cdot \frac{c}{\lambda}$$

$$= \frac{(6.625 \times 10^{-34}) \times (3 \times 10^{8})}{(535 \times 10^{-9})}$$

$$= 3.71 \times 10^{-19} \text{ J}$$

$$\boxed{\text{Ans. : } E = 3.71 \times 10^{-19} \text{ J}}$$

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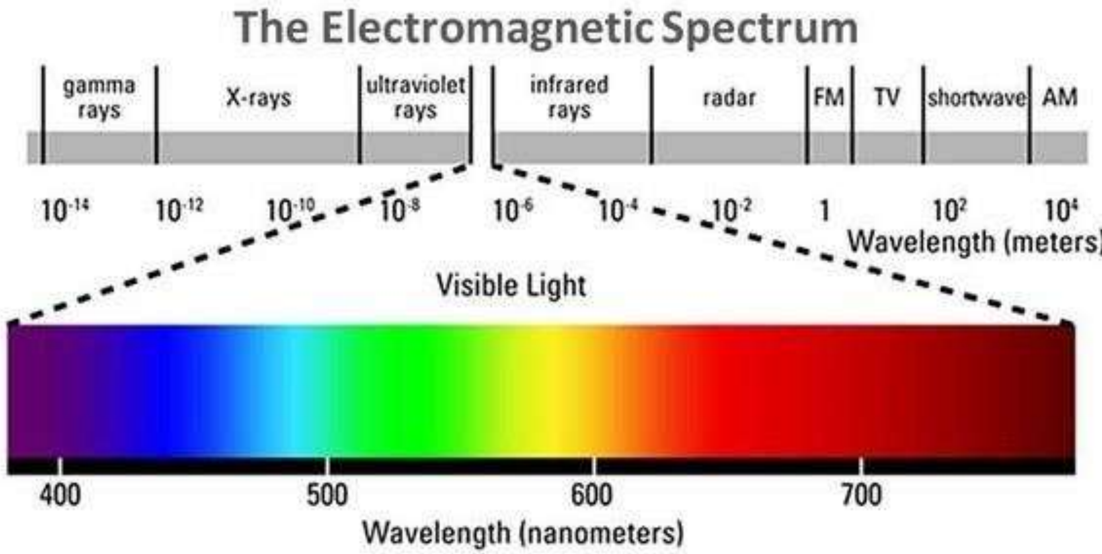
- **Electromagnetic Spectrum;**
- Several electromagnetic radiations extending from cosmic rays to radio waves are a part of electromagnetic spectrum.
- It consist of different radiations according to their wavelengths and frequencies.
- The visible region, very small part of entire electromagnetic spectrum i.e. range from 400 nm (violet) to 800 nm (red).



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- **Types of Spectroscopy;**
- **1) Absorption Spectroscopy:**
- **Absorption spectroscopy is a spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum.**
- **This method is used to measure concentration of ions like sodium and calcium in blood.**
- **E.g. U.V. absorption spectroscopy and IR spectroscopy.**

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- **Types of Spectroscopy;**
- **2) Emission Spectroscopy:**
- **Emission spectroscopy is uses the range of electromagnetic spectra in which substance radiated.**
- **Emission spectroscopy is a spectroscopic technique which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state.**

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- **Types of Spectroscopy;**
- **3) Scattering Spectroscopy:**
- **Raman scattering spectroscopy, like infrared absorption spectroscopy, is a technique used to observe the vibrational states (also rotational in some cases) of a molecule.**
- **It makes it possible to characterize the molecular composition of a sample by identifying the chemical groups that constitute it.**

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- **Selection Rules;**
- The probability of transition between two given energy levels is determined by selection rules.
- The selection rules of the electronic transition are as follows,
- 1) Spin selection rule:
- There should not be any change in spin orientation during these transition. The S-S, T-T transition allowed but S-T, T-S transition not allowed.
- 2) Symmetry rule:
- The product of two electric diploe vector and the group theoretical representation of the two states are symmetric.

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- **Selection Rules;**
- **3) Angular Momentum rule:**
- **The change in angular momentum must be within one unit. (0 or ± 1).**

- **On the basis of selection rule, transitions can be categorized as:**
- **a) Allowed Transition: It is spectral transition who obeys selection rule, stronger and more intense. They have yield spectral lines with greater intensity than forbidden.**
- **b) Forbidden Transition: It is special transition who do not obeys selection rule, week and less intense. They have yield spectral lines with less intensity than allowed.**

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- **Application of Molecular Spectroscopy;**
- 1) It is used in structural investigation, electronic energy levels, bond lengths, bond angles, and strength of bond can be determined.
- 2) Used to monitor changing concentration of reactants or products in kinetic studies.
- 3) It helps to understand colour in the world around us.
- 4) Emission spectroscopy is used to energetically excited reaction products.

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- **Types of Molecular Energies;**
- Molecular energy regarded as the sum of rotational, vibrational and electronic energies.

  $E_{int} = E_{elec} + E_{vib} + E_{rot}$

1) Rotational Energy:

It is associated with rotational motion of the molecule as a whole.

$$E_{rot} = \frac{1}{2} I\omega^2$$

- Where I = Momentum of Inertia and ω = angular velocity of rotating molecule.

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2) Vibrational Energy:

It is associated with vibration of constituent atom in the molecule.

$$E_{vib} = h\upsilon_0 \left[\upsilon + \frac{1}{2}\right]; \text{ for } \upsilon = 0, 1, 2, 3 \ldots\ldots$$

- Where υ_0 = zero pint vibrational frequency and υ = Vibrational quantum number.

3) Electronic Energy:

- It is associated with the motion of electrons while considering the nuclei of atoms in a molecule as fixed points.

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- Types of Molecular Spectroscopy;
- The types of molecular spectroscopy with their nature of transition, energy range frequency, and wavelength range is shown in following table;

Type	Nature of Transition	Energy Range	Frequency Range	Wavelength Range
γ-ray	Nuclear	10-12 GJ/mol	30 EHz-300EHz	1000 pm to 10 pm
X-ray	Inner electronic	10-100 MJ/mol	30PHz-30EHz	10 pm to 10 nm
UV	Outer electronic	300-1000 KJ/mol	800THz-30PHz	10 nm to 380 nm
Visible	Outer electronic	100-300 KJ/mol	400THz-800THz	380 nm to 750 nm
Infrared	Vibration, Rotation	10^3-10^5 J/mol	300GHz-400THz	750 nm to 1mm
Microwave	Rotation	10^1-10^3 J/mol	300MHz-300GHz	1 mm to 100 mm
Radiofrequency	Nuclear spin	10^{-3}-10^1 J/mol	1-1000MHz	10 m to 1 cm

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- **Types of Molecular Spectroscopy;**
- **1) The Microwave Spectroscopy:**
- **A polar molecule e.g. HCl has permanent dipole moment.**
- **On rotating the molecule about its center of gravity, the positive and negative charges change places periodically.**
- **As result, interaction between fluctuating dipole and radiation energy may emitted or absorbed.**
- ***Rotation of polar molecule gives rise to spectrum in a microwave region.***

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- **Types of Molecular Spectroscopy;**
- **2) The Infrared (IR) Spectroscopy:**
- **Absorption of IR radiation leads to vibrational transition of the molecule.**
- ***The absorption bands in this region corresponds to fundamental vibrational frequencies of molecules.***

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- **Types of Molecular Spectroscopy;**
- **3) The Visible and Ultra-Violet (UV) Spectroscopy:**
- **In this region valance electrons get excited and move from one energy level to another.**
- **These changes causes change in electric dipole which interacts with the electric field of the electromagnetic radiation.**
- ***The interaction gives rise to the spectrum in the UV- Visible region.***

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- **Types of Molecular Spectroscopy;**
- **4) Nuclear Magnetic Resonance (NMR) Spectroscopy:**
- **Is concerned with the study of interaction of energy with spin-active nuclei.**
- **Spin-active nuclei have permanent magnetic moments and quantitized nuclear spin states.**
- ***NMR spectroscopy measures the energy necessary to bring about transitions between these energy levels by subjecting the nuclei to a powerful magnetic field and simultaneously irradiating it with radio frequency range.***
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