Spectroscopy

By

Dr. Pangkita Deka

Introduction

- The beautiful phenomenon of “RAINBOW” was the first dispersed spectrum.
- 1665 - Newton took the first & most important step towards the development of spectroscopy.

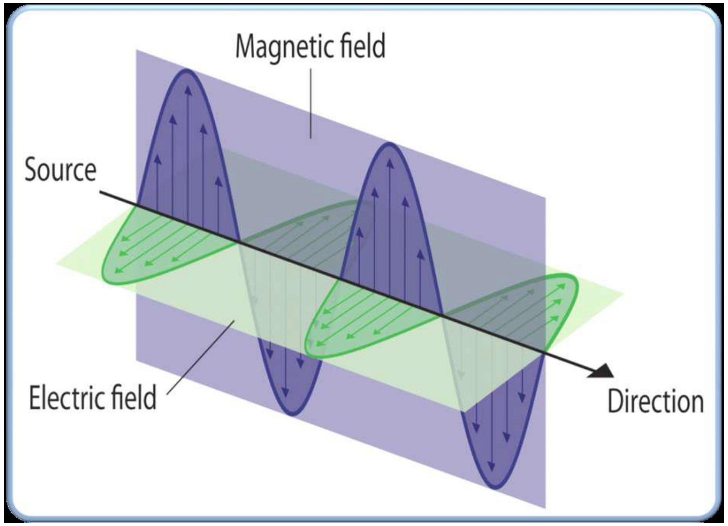
Introduction

- **Some important definitions:**
  - **Spectroscopy:** Study of interaction of matter and electromagnetic radiation.
  - Spectrometry: an analytical technique in which emission (of particle/radiation) is dispersed according to some property of the emission and the amount of dispersion is measured. eg. mass spectrometry.
  - Spectrophotometry: a quantifiable study of electromagnetic spectra.
  - Spectrography: another name for spectroscopy.

Electromagnetic Radiation

- Electromagnetic radiation consist of discrete packages of energy which are called as photons.

- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.



Electromagnetic Radiation

- **Frequency (ν):**

  It is defined as the number of times electrical field radiation oscillates in one second.

  The unit for frequency is Hertz (Hz).

  1 Hz = 1 cycle per second

- **Wavelength (λ):**

  It is the distance between two nearest parts of the wave in the same phase i.e. distance between two nearest crest or troughs.

Electromagnetic Radiation

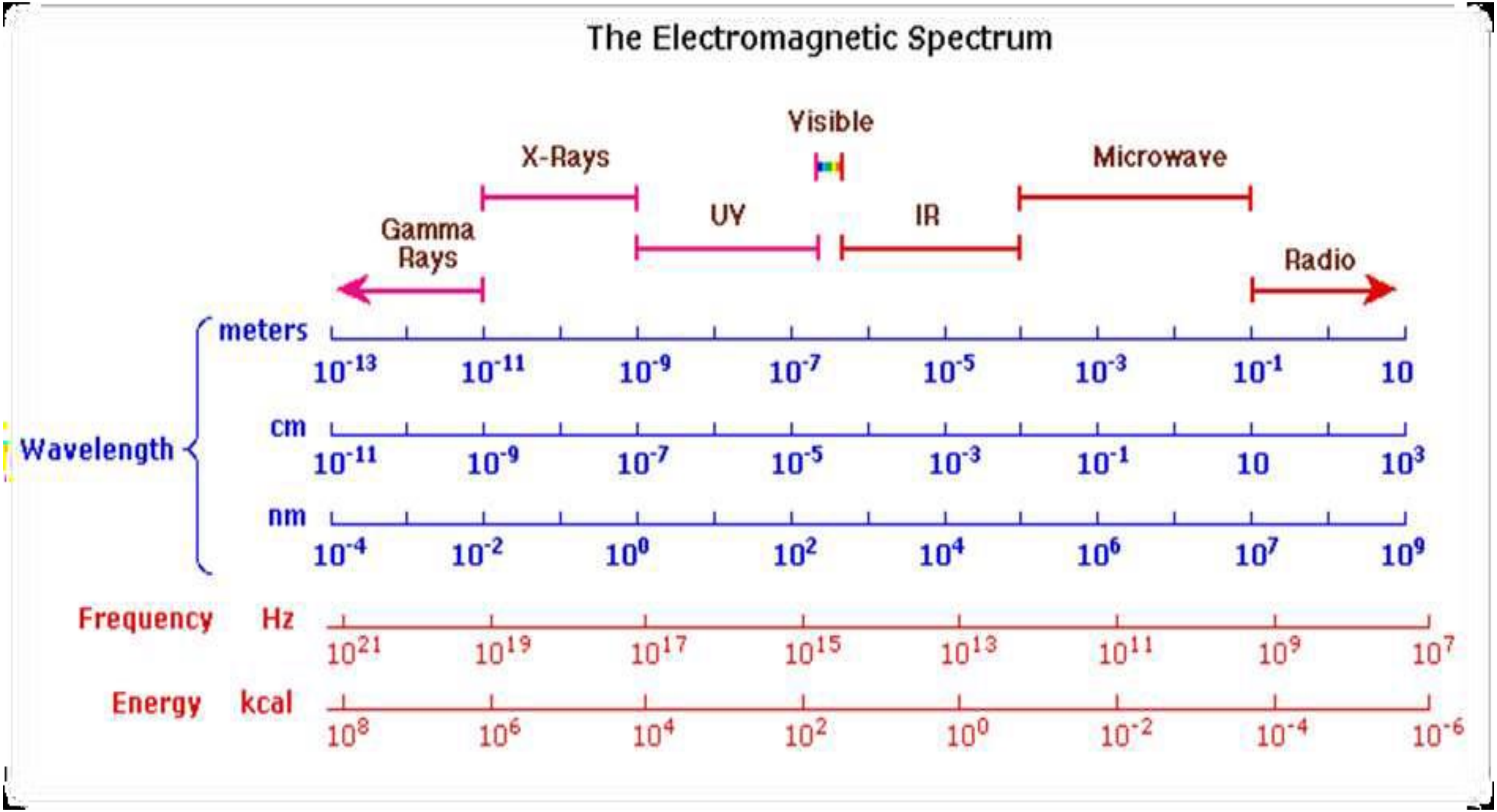
- The relationship between wavelength & frequency can be written as:

$$c = \nu \lambda$$

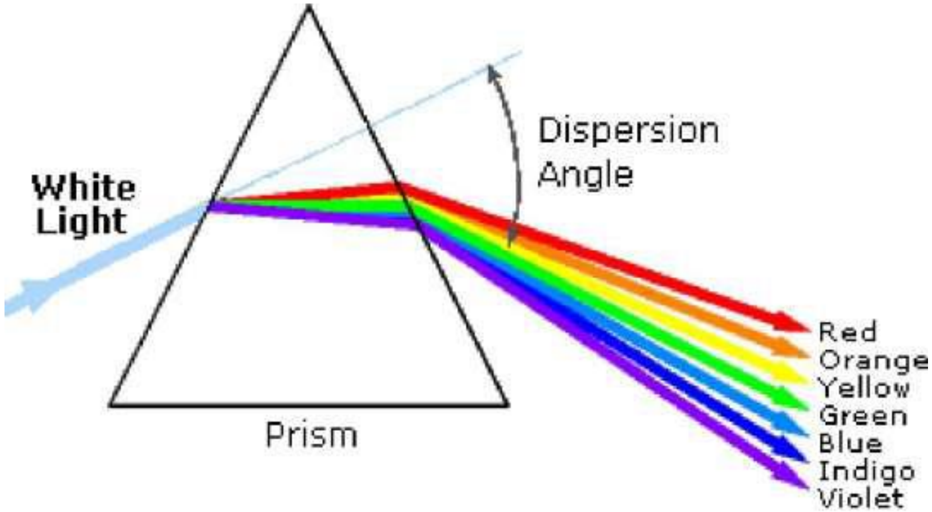
- As photon is subjected to energy, so

$$E = h \nu = h c / \lambda$$

Electromagnetic Radiation



Electromagnetic Radiation



Violet	400 - 420 nm	Yellow	570 - 585 nm
Indigo	420 - 440 nm	Orange	585 - 620 nm
Blue	440 - 490 nm	Red	620 - 780 nm
Green	490 - 570 nm		

Principles of Spectroscopy

- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.

- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).

- Spectrometer is an instrument design to measure the spectrum of a compound.

Principles of Spectroscopy

1. Absorption Spectroscopy:

An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.

- e.g. UV (185 - 400 nm) / Visible (400 - 800 nm) Spectroscopy, IR Spectroscopy (0.76 - 15 μm)

Principles of Spectroscopy

2. Emission Spectroscopy:

An analytical technique in which emission (of a particle or radiation) is dispersed according to some property of the emission & the amount of dispersion is measured.

- e.g. Mass Spectroscopy

Interaction of EMR with matter

1. Electronic Energy Levels:

- At room temperature the molecules are in the lowest energy levels E_0.

- When the molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as E_1, E_2, ...E_n, etc is called as electronic transition and the difference is as:

ΔE = h ν = $E_n - E_0$ where (n = 1, 2, 3, ... etc.)

ΔE = 35 to 71 kcal/mole

Interaction of EMR with matter

2. Vibrational Energy Levels:

- These are less energy level than electronic energy levels.

- The spacing between energy levels are relatively small i.e. 0.01 to 10 kcal/mole.

- e.g. when IR radiation is absorbed, molecules are excited from one vibrational level to another or it vibrates with higher amplitude.

Interaction of EMR with matter

3. Rotational Energy Levels:

- These energy levels are quantized & discrete.

- The spacing between energy levels are even smaller than vibrational energy levels.

$\Delta E_{rotational} < \Delta E_{vibrational} < \Delta E_{electronic}$

Lambert's Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

- Let I be the intensity of incident radiation.

x be the thickness of the solution.

Then

Lambert's Law

$$-\frac{dI}{dx}\,\alpha I$$

So, $-\frac{dI}{dx} = KI$

Integrate equation between limit

$I = I_o$ at $x = 0$ and

$I = I$ at $x=l$,

We get,

$$\ln\frac{I}{I_o} = -Kl$$

Lambert's Law

$$2.303 \log \frac{I}{I_0} = -Kl$$

$$\log \frac{I}{I_0} = -\frac{K}{2.303} l$$

Where, $\log \frac{I_0}{I} = A$ Absorbance

$$\frac{K}{2.303} = E$$ Absorption coefficient

$A = E.l$ Lambert's Law

Beer's Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light as well as concentration of the solution.

- Let I be the intensity of incident radiation.

x be the thickness of the solution.

C be the concentration of the solution.

Then

Beer's Law

$$-\frac{dI}{dx} \alpha C.I$$

So, $$-\frac{dI}{dx} = K'C.I$$

Integrate equation between limit

I = Io at x = 0 and

I = I at x=l,

We get,

$$\ln\frac{I}{I_0} = -K'C.l$$

Beer's Law

$$2.303 \log \frac{I_0}{I} = K.C.l$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} C.l$$

Where, $\log \frac{I_0}{I} = A$ Absorbance

$\frac{K}{2.303} = E$ Molar extinction coefficient

$A = E.C.l$ Beer's Law

Beer's Law

$$A = E.C.l$$

From the equation it is seen that the absorbance which is also called as optical density (OD) of a solution in a container of fixed path length is directly proportional to the concentration of a solution.