SPECTROSCOPY

Scientists around the world are interested in knowing the structure of molecules but they are of infinitesimally small dimensions that it is not possible to see them.

The knowledge about molecular structure is derived indirectly from the technique known as Spectroscopy, which deals with the transition that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules.

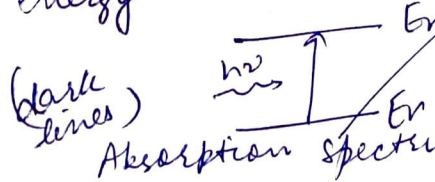
Spectro means radiation & scopy means measurements. Thus, Spectroscopy means measurement of radiations. It is defined as the branch of science which is associated with the interaction of radiations of different wavelengths with matter.

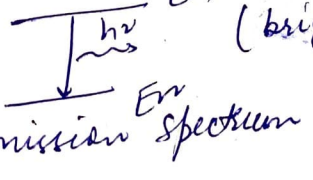
Quantum mechanics tells us that the energy levels of all systems are quantized & are designated by appropriate quantum numbers. These energy levels are obtained by the solutions of the time-independent Schrödinger equation.

Consider two molecular energy levels E_n & E_m. If a photon of frequency ν falls on a molecule in ground state & its energy $h\nu$ is exactly equal to the energy difference ΔE ($E_m - E_n$) between the two molecular energy levels, then the molecule undergoes a transition from the lower to the higher energy level with the absorption of a photon of energy $h\nu$.

Easier to interpret

$E_m - E_n = h\nu$ (Bohr's frequency formula)





The spectrum thus obtained is called the 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.

The molecular spectra are governed by the so-called selection rules which specify the changes in the quantum numbers accompanying a particular transition. The selection rules are the backbone of spectroscopy & are obtained from the quantum theory of interaction of radiation with matter. The selection rules, however, are not always obeyed strictly. This is because certain approximations which have been used in the derivation of the selection rules are not valid strictly. The spectral transitions which obey a given selection rule are called allowed transitions whereas those which violate a selection rule are called forbidden transitions.

In general, the allowed transitions are more intense (stronger) than the forbidden transitions, which are weak. The selection rule for spectral transitions are derived from time-dependent perturbation theory.

Any atomic or molecular system possesses energy only in certain special amounts, which are called energy levels of the system.

If a spectral line is to be observed, there must be a substantial population of the systems in the initial energy level.

Electromagnetic Radiation :

An electromagnetic radiation is the radiant energy emitted from any source in the form of heat or light or sound.

Characteristics are!

- Electromagnetic radiation possess particle as well as wave nature. Thus, they have a dual nature. A light beam consists of a stream of particles (photons) moving in the form of waves. This is called wave-particle duality.

$$\lambda = \frac{h}{p}$$ (de Broglie equation)

p = momentum of particle (photon here) (particle nature)

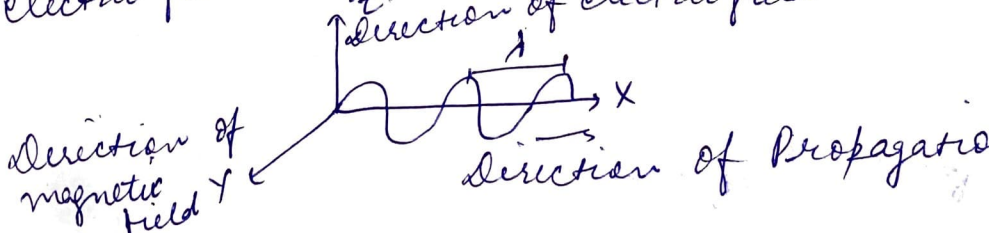
λ = wavelength of radiation (wave nature)

h = Planck's constant $= 6.6 \times 10^{-34}$ Js.

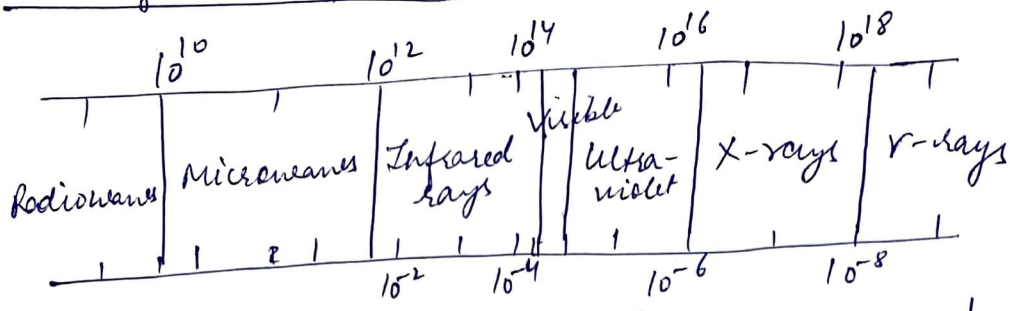
- Electromagnetic radiation travel with the velocity of visible light.

- The elemagnetic waves have electric & magnetic fields associated with them at right angles to one another.

Thus, if the radiation is moving along X-axis, the magnetic field is oriented along Y-axis & the electric field is oriented along the Z axis.



Visible light, X-rays, microwaves, radiowaves etc. are all electromagnetic radiations. Collectively, they make up the electromagnetic spectrum:



Electromagnetic radiation travel away from the source with velocity of light in vacuum. Different terms used in the study of electromagnetic waves are:

1. Frequency (ν): It is the number of successive crests (or troughs) which pass a stationary point in one second. Unit is Hz or s^{-1}.
(Hertz)

2. Wavelength (λ): It is the distance between successive crests or troughs. Unit is cm / m / nm.

3. Wave number ($\bar{\nu}$): It is the reciprocal of wavelength & hence unit is cm^{-1}.

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

c = velocity of light $= 3 \times 10^8 \, m \, s^{-1}$.

$$\boxed{\nu = \frac{c}{\lambda}}, \quad \boxed{\nu = c\bar{\nu}}$$

Electromagnetic radiation behaves as consisting of discrete wavelike particles called quanta or photons. Photons possess the characteristics of wave & travel with velocity of light in the direction of the beam. The amount of energy corresponding to 1 photon is:

$$E = h\nu = \frac{hc}{\lambda}$$