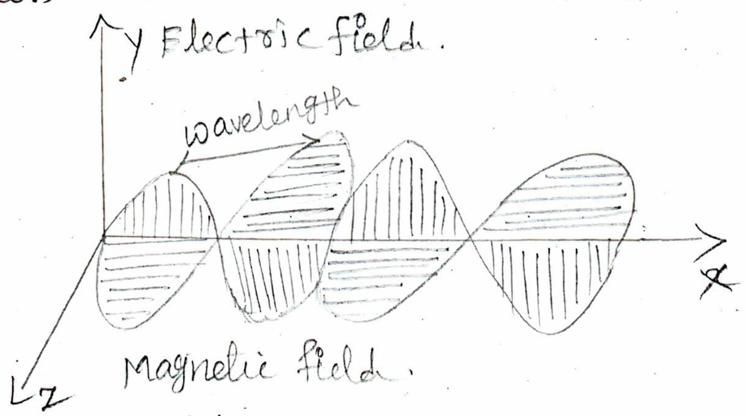
UNIT–I Electromagnetic Radiation

EM waves

It is defined as a form of energy that is produced by the movement of electrically charged particles travelling through a matter (or) vacuum by oscillating Electric and magnetic disturbance. Electric and magnetic fields come at 90° to each other and the combined waves move ⊥lar to both electric and magnetic oscillating field occuring the distrubance.

Electromagnetic radiation were first investigated by James, Maxwell in 1864. EMR consist of electromagnetic waves which are synchronized oscillations of electric and magnetic fields that propagate at the speed of light in vacuum. Electromagnetic radiation and it's interaction with matter



depends on it's frequency. Lower frequencies have longer wavelength. Higher frequencies have shorter wavelength. It comes in many different types. Although difference between them are qualitative and quantitative. It is composed of particles called photons and each photon has an energy E.

They travel with the velocity of light (c) and can be treated in terms of frequency (v) of the oscillating electric and magnetic fields. The frequency, wavelength (λ) and velocity of these radiations are connected by the relation

$$c = \nu\lambda$$

and the energy associated with the wave is given by,

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

Where h is the Planck's constant and is equal to 6.626×10^{-34} Js.

Electromagnetic Spectrum: The names of the different regions along with the order of the range of frequencies and wavelengths. The regions from radio frequency to gamma rays together is called the electromagnetic spectrum. The different regions are primarily based on the experimental techniques used in the generation, dispersion or detection of the radiation. In fact, the name 'visible region' is based on the detection system. It occupies only a very small region of electromagnetic spectrum. It includes Radio waves, microwaves, Infrared waves, visible, ultraviolet, x-rays and gamma rays.

The commonly used units for wavelength are metre, centimetre, micrometre, nanometre and Angstrom. They are related as,

$$1\,Å = 10^{-1}\,nm = 10^{-4}\,\mu m = 10^{-8}\,cm = 10^{-10}\,m.$$

In molecular spectroscopy, very often instead of frequency (v) and wavenumber ($\bar{\nu}$) is used.

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

Radio waves :

It is a type of electromagnetic radiation with wavelengths. radio is used primarily for Communications including voice data and entertainment media.

Microwaves :

Microwaves fall in the range of electromagnetic Spectrum between radio and IR. microwaves are used for high bandwidth Communications radar and as a heat source for microwave ovens and industrial applications.

Infrared :

IR is in the range of em Spectrum between microwaves and visible light. IR light is invisible to human eyes, but we can feel it as heat if the intensity is sufficient.

Visible :

visible light is found in the middle of the electromagnetic Spectrum between IR and UV. It has frequencies of about 400THZ–800THZ.

Ultraviolet :

UV is in the range of EM Spectrum between visible light and x-rays. UV is a light Component of Sunlight. It has numerous medical and Industrial applications. but, It can damage living tissue.

X-Rays :

x-rays is in the range of EM Spectrum between UV and gamma rays. x-rays are produced accelerating electrons.

Gamma Rays :

γ-rays are in the range of Spectrum above Soft X-rays. It causes damage to living tissue. which makes it useful for killing cancer cells.

Interaction of Electromagnetic Radiation with Matter

Absorption of Radiation :

When Electromagnetic radiation passes through matter, a variety of phenomena may occur. Some of these are as follows,

(i) If the photons of radiation possess the appropriate energies, they may be absorbed by the matter and result in electronic transitions, vibrational changes or rotational changes or combination of these. After absorption, atoms and molecules become excited. They give out energy quickly either by losing energy in the form of heat or by re-emitting electromagnetic radiation.

(ii) It is not necessary that the radiation passing through the matter may be absorbed completely. The portion of electromagnetic radiation which passes into matter, instead of being absorbed, may undergo scattering or reflection or may be re-emitted at the same wavelength or a different wavelength.

(iii) When electromagnetic radiation is neither absorbed nor scattered, it may undergo changes in orientation or polarisation.

(iv) In some cases, the molecules after absorbing radiation become excited but they do not lose energy very quickly but with some delay. In such cases the energy is re-emitted as radiation, usually of longer wavelength than was originally absorbed. This phenomenon is termed as Fluorescence. If in some cases, there is a detectable time delay in re-emission, the phenomenon is termed as Phosphorescence.

Molecular Spectroscopy

It is the Study of absorption of light by molecules. In the gas phase at low temperature, molecules exhibit absorption in narrow lines which are very characteristic of the molecules as well as the temperature and pressure of it's environment.

Different types of Molecular energies :

In molecular spectroscopy a molecule may possess Internal energy which can be Subdivided into three Classes.

1. Rotational energy
2. Vibrational energy
3. Electronic energy.

$$E_{Internal} = E_{electronic} + E_{vibrational} + E_{rotational}$$

$$E_{electronic} > E_{vibrational} > E_{rotational}$$

The laws of Quantum energy which are applicable to atomic Spectra and also applicable to molecular Spectra. Thus on the basis of Quantum theory the three components of molecular energy can have only discreate and Quantised Values.

Translational Energy :-

It is associated with the uniform motion of a molecule as a whole. This motion is generally described with respect to the Centre of mass of the Molecules.

Classical energy due to translational

motion is given by

$$E_t = \frac{1}{2} m v^2$$

E_t → Translational energy of molecular mass m.

v → moving with velocity with respect to centre of mass.

Due to translational motion the molecule is free to move in three perpendicular directions x, y, z. It has three degrees of freedom. But translational energy of a molecule of a gas by the classical theorem of the equipartition of energy along any axis is $\frac{1}{2}kT$ (or) $\frac{1}{2}RT$ per mole. Therefore translational energy of the molecule of a gas along three mutually perpendicular axes will be $\frac{3}{2}kT$ (or) $\frac{3}{2}RT$ per mole. In solids the translational freedom is restricted. According to Quantum mechanics equation of translational motion of an isolated molecule of mass M in a Rectangular box of dimension a×b×c. the value of translational energy is given by.

$$E_t = \frac{h^2}{8M}\left[\left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{b}\right)^2 + \left(\frac{n_z}{c}\right)^2\right]$$

The concept of translational energy is not of much use in molecular spectroscopy.

Rotational Energy:

This type of energy is associated with the overall rotation of molecule with atoms considered as fixed point masses.

According to classical theory the value of rotational energy is given by

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

I - Moment of Inertia

ω - Angular velocity of rotating molecule.

However Quantum mechanical formula for the rotational energy of a simple linear molecule is given by,

$$E_{rotational} = J(J+1)\frac{h^2}{8\pi^2 I}$$

J - zero (or) positive integer called rotational quantum number.

Each rotational level has (2J+1) fold degeneracy. The above equation does not apply in the liquid phase where molecular collision are frequent. It is important that only the polar molecules can rotate in an Electromagnetic field. Monoatomic molecule possesses only one rotational degree of freedom. But a non-linear triatomic (or) polyatomic molecule may rotate the three perpendicular axis passing through the centre of gravity. It is said to have 3-degrees of freedom. A linear molecule cannot rotate the axis passing through the nuclei of the bonded atoms. It means that one of it's rotational degrees of freedom is restricted. Hence, a linear molecule possesses only two rotational degree of freedom.

Vibrational Energy :

This type of energy associated with the oscillation of atoms which are considered as point masses about equilibrium positions. This type of energy can be treated on a quantum mechanical basis.

The vibrational energy of a molecule may be given by,

$$E_{vibrational} = h\nu\left(v + \frac{1}{2}\right)$$

ν → vibrational frequency

v → zero (or) +ve integer called vibrational quantum number.

The above equation does not fulfil the convention that the energy shall be zero for the ground state.

The ground state corresponds to $v = 0$ with an energy $\frac{h\nu}{2}$. This is known as zero point energy.

The vibrational degree of freedom for,

Non linear molecule = $3n - 6$

linear molecule = $3n - 5$

When a molecule absorbs energy, increase in vibration motion of the molecule is usually accompanied by increased rotational of same molecule. This combination provides the basis of IR absorption spectroscopy.

Electronic Energy !

It is associated with the motion of electrons while considering the nuclei of atoms as fixed Points. increase in the electronic energy of a molecule occurs due to an ↑ in the kinetic energy required to move electron from the ground State to excited State varies with the type of molecular bond in which the electron exist.

Further the vibrational and rotational energies of the molecules are added to the electronic energies.

There is no general formula for electronic energies interms of simple Quantum number except for hydrogen like atom.

Spectrum

Spectrum is the range of different Colours which is produced when light Passes through a glass prism or through a drop of water. A rainbow Shows the Colours in the Spectrum.

when white light falls on a prism, Place in a Spectrometer. The waves of different wavelengths are deviated to different directions by the prism.

If the slit illuminated with light from Sodium vapour lamp. Two images of the Slit are Obtained in the yellow region of the Spectrum These images are the emission line of sodium having wavelengths 5896 Å and 5890 Å This is known as Spectrum of Sodium.

Spectrum has two types,

1. Emission Spectrum
2. Absorption Spectrum.

1) Emission Spectra:

When the light emitted directly from a source is examined with a spectrometer. the emission spectrum is obtained. This type of spectra may be produced either by temperature radiation method or luminescence method. Every source has it's own characteristic emission spectrum.

The emission spectrum is of three types

1. Continuous Spectrum
2. Line Spectrum
3. Band Spectrum.

Continuous Spectrum:

Source of light emits continuous spectra when the matter in bulk is heated. emission type continuous spectra are observed solids such as heated lamp filaments, the mouth of a hot furnace, molten glass, hot iron. The distribution of energy in such a spectrum only upon temperature of source. The continuous spectrum of an element gives us information about the interaction between matter and energy. Since we know that in a solid the atoms are more densely packed exert a considerable force upon one another. Therefore they are not in position to emit characteristic wavelength spectra.

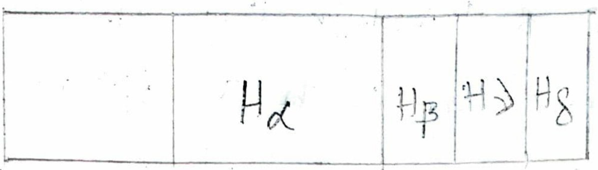
Important characteristic:

The spectrum contains a wide range of continuous wavelength lines which are not separable. In the continuous spectrum of a solid, the intensity is not uniformly distributed over the entire observed spectrum. The intensity is maximum at a particular wavelength and decrease on both sides of the point of maximum intensity. The point of maximum intensity shifts towards the violet end of the spectrum as the temperature of the solid is increased.

In general continuous spectrum is independent of the material of the source of light. so long as the material is in the position of emitting continuous spectra.

Line spectra:

Line spectra are sharp lines of definite wavelengths. It is the characteristic wavelength of the emitting substance. It is used to identify the gas. Atoms in the gaseous state, (i.e) free excited atoms emit line spectrum. The substance in atomic state such as sodium in sodium vapour lamp. Mercury in mercury vapour lamp and gases in discharge tube gives line spectra. line spectra are produced when the emitting element is in the atomic state and therefore they are also called atomic spectra. The spectral lines are regularly spaced and the wavelength of the lines emitted are the characteristic of the element under consideration.



When these lines are observed under a high resolving power instrument, The different lines are regularly spaced but they differ in their intensities. Line Spectrum can be observed against a dark or a faint continuous background.

Band Spectrum :

This type of Spectrum arises when the emitter in the molecular State is excited. It consists of a number of bright bands with a sharp edge at one end but fading out at the other end.

Band Spectra are obtained from molecules. It is the characteristic of the molecules. Calcium or Barium salts in a bunsen flame and gases like carbon-di-oxide, ammonia and nitrogen in molecular State in the discharge tube give band Spectra. When the bands are examined with high resolving power spectrometer, each band is found to be made of a large number of fine lines, very close to each other at the Sharp edge but spaced out at the other end. Using band Spectra the molecular Structure of the Substance can be studied.

2) Absorption Spectra:

When the light emitted from a source is made to pass through an absorbing material and then examined with a spectrometer. the obtained spectrum is called absorption spectrum. It is the characteristic of the absorbing substance.

Absorption spectra is also three types.

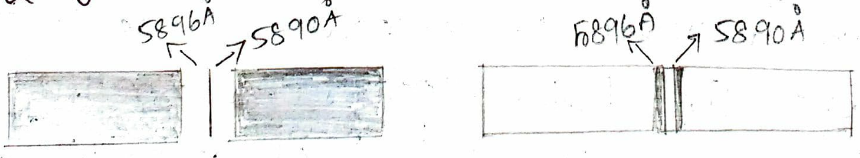
1. Continuous absorption spectrum
2. line absorption spectrum
3. Band absorption spectrum.

1. Continuous absorption spectrum:

This type of spectrum arises when the absorbing material absorbs a continuous range of wavelength. Red glass absorbs all colours except red; hence a continuous absorption spectrum will be obtained.

2. Line absorption spectrum:

Sharp dark lines will be observed when the absorbing substance is a favour or a gas. The spectrum obtained from



Sun gives fraunhofer absorption lines corresponding to vapours of different elements which are supposed to be present on the surface of the sun.

3. Band absorption spectrum:

If white light is allowed to pass through iodine vapour or dilute solution of blood or chlorophyll or certain solutions of organic and inorganic compounds, dark bands on continuous bright background are obtained. The band absorption spectra are used for making dyes. Aqueous solution of $KMnO_4$ gives five absorption bands in the green region.

Fraunhofer lines:

When an atomic or molecular system is excited into higher energy state by absorption of energy. It returns back to lower energy state in a time less than 10^{-5} second and the system is found to glow brightly by emitting radiation of longer wavelength.

When ultra violet light is incident on certain substances, they emit visible light. fluorescence

It may be noted that the fluorescing substance exists as long as the incident ultraviolet light remain exposed to incident ultraviolet light and re-emission of light stops as soon as incident light is cut off.

The fraunhofer lines are typical spectral absorption lines. Absorption lines are dark lines, narrow regions of decreased intensity, that are the result of photons being absorbed as light passes from the source to the detector. In the sun, fraunhofer lines are a result of a gas in the photosphere, the outer region of the sun. The photosphere gas has lower temperatures than gas in the inner regions, and absorbs a little of the light emitted from those regions. The depths of the absorption lines provide information about temperature, and wavelengths shifts of the lines tell us the motion of the gas.