CHAPTER 18
THE ATOMIC SPECTRA

The sunlight of the atomic spectra deals with the measurement of the wave length and intensities of the electromagnetic radiation emitted or absorbed by atom.

EMISSION SPECTRA:

When an atom is excited, its electron is lifted from its ground state to one of the higher states (higher orbits). The energy supplied is called absorption energy, when electron come back to its ground state, its emits spectral line, this is called emission spectrum it consist of a series of line.

ABSORPTION SPECTRA:

When electron absorbs energy it jumps from lower to higher orbit. The energy absorb is equal to the difference between the energies of the two orbit since energy can be expressed in term of frequency ($E=h\upsilon=\frac{hc}{\lambda}$) therefore we can Say that the electron absorbed the certain frequency during exaction of an atom. The set of all frequencies that are absorbed by the atom of an element is called "absorption spectrum" the spectrum consist the dark lines against the bright back ground.

POSTULATES OF BOHR'S ATOMIC THEORY:

1. An electron moves only in those circular orbits for which its orbital angular momentum is an integral multiple of $\frac{h}{2\pi}$.

i.e $L = mvr = \frac{nh}{2\pi}$

Where m = mass of an electron

V = velocity of electron, r_n = radius of the nth orbit, n = 1, 2, 3…., h = plank's constant=$6.63\times 10^{-34} J.S.$

2. The total energy of an electron remains constant as long as it remains in the same orbit i.e it does not radiate energy while revolving around the nucleus.

3. When an electron jumps from a higher orbit having energy E_i to a lower orbit having energy E_f then energy is released in the form of a photon of energy hν.

$$h\upsilon = \frac{hc}{\lambda} = E_i - E_f$$

Where υ = frequency of photon, λ = wave length of photon, C = speed of light

HYDROGEN ATOM:

A hydrogen atom consists of a photon in the nucleus and an electron revolves the nucleus. The mass of a proton is about 1836 times the mass of an electron.

RADII OF VARIOUS ORBITS OF HYDROGEN ATOM:

Consider an electron of charge e^- revolving in a orbit of hydrogen atom around a nucleus of charge Ze^+ with constant speedv.

If F be the Coulomb force between the electron and the proton is equal to centripetal force applied on electron,

$$F_e = F_c$$

$$\frac{K\,Ze^2}{r^2} = \frac{mv^2}{r}$$

$$\frac{1}{r} = \frac{m}{K\,e^2}(v^2) \text{ ------------(i)} \qquad \text{For hydrogen Z=1.}$$

Applying postulate of Bohr's atomic model,

Angular momentum of electron = $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr}$$

Squaring both the sides,

$$v^2 = \frac{n^2h^2}{4\pi^2 m^2 r^2}$$

Substitute the value of v^2 in eq^n(i),

$$\frac{1}{r} = \frac{m}{K\,e^2}\left(\frac{n^2h^2}{4\pi^2 m^2 r^2}\right)$$

$$r_n = \frac{n^2h^2}{4\pi^2 Kme^2} \text{ -----------(ii)}$$

This expression is called expression for radius of n^{th} orbit of hydrogen atom. Where, h = plank's constant=$6.63\times 10^{-34} J.S.$, $\pi = 3.14$, $K=9\times 10^9 N.m^2/c^2$, $m=9.1\times 10^{-31} kg$, $e=1.6\times 10^{-19} C$.

By putting these values in equation(ii) , we have

$$r_n = (0.53\times 10^{-10} n^2)meter$$

This shown that radii are proportional to the square of the integer number (n = 1, 2, 3, …) called the principal quantum number.

ENERGIES OF VARIOUS ORBITS OF HYDROGEN ATOM:

An electron revolving around the nucleus possesses both kinetic as well as potential energies. Total energy of electron in n^{th} orbit is equal to the sum of kinetic and potential energy of electron,

T.E.=K.E.+P.E.

$$E_n = T + V \text{ --------- } (i)$$

FOR K.E.

If F be the Coulomb force between the electron and the proton is equal to centripetal force applied on electron,

$$F_e = F_c$$

$$\frac{K\,Ze^2}{r^2} = \frac{mv^2}{r}$$

$$mv^2 = \frac{Ke^2}{r_n} \qquad \text{for hydrogen } Z=1.$$

Dividing by 2 on both the sides,

$$\frac{1}{2}mv^2 = \frac{Ke^2}{2r_n}$$

$$T = \frac{Ke^2}{2r_n}$$

FOR P.E.

The potential energy of proton-electron system is the total work done by the electron against electrostatic field by the nucleus from r = r to r = ∞.

$$P.E. = V = \int_r^\infty \vec{F}.\,\vec{\Delta r} = -\frac{Ke^2}{r_n}$$

By substituting the values of T and V in equation(i),

$$E_n = \frac{Ke^2}{2r_n} + \left(-\frac{Ke^2}{r_n}\right)$$

$$E_n = -\frac{Ke^2}{2r_n} \text{ ----------------(ii)}$$

This expression is called expression for total energy of electron in n[th] orbit of hydrogen atom. Where, K=9 × $10^9 N.m^2/c^2$, e=1.6× $10^{-19} C$ and $r_n = (0.53 \times 10^{-10} n^2) mete.$
By putting these values in equation(ii) , we have

$$E_n = -\frac{13.6}{n^2}\,eV$$

Let, $E_o = 13.6eV$

$$E_n = -\frac{E_o}{n^2}$$

Negative sign shows that the electron is bound with the nucleus. When the energy of the electron becomes positive it will leave the atom and the electron is free.

WAVE NUMBER OF WAVE LENGTH OF RADIATION EMITTED:

When an electron jumps from a higher orbit to lower energy orbit it radiates energy in the form of a photon which is given by.

$$h\upsilon = E_i - E_f$$

$$\frac{hc}{\lambda} = E_i - E_f$$

Here, $E_i = binding\ energy\ of\ electron\ in\ n_i\ th\ orbit = -\frac{E_o}{{n_i}^2}$

$E_f = binding\ energy\ of\ electron\ in\ n_f\ th\ orbit = -\frac{E_o}{{n_f}^2}$

$$\frac{hc}{\lambda} = -\frac{E_o}{{n_i}^2} - (-\frac{E_o}{{n_f}^2}!)$$

$$\frac{1}{\lambda} = \frac{E_o}{hc}\left[\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2}\right]$$

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H\left[\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2}\right]$$

Where R_H = Rydberg constant = 1.097 × 10^7 m^{-1}.

THE SPECTRUM OF HYDROGEN ATOM:

The spectrum of hydrogen atom is simplest one. It consist of five series, their empirical formula are given below:

1- Lyman series for ultra violet region

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H\left[\frac{1}{(1)^2} - \frac{1}{{n_i}^2}\right]$$

Where, $n_i = 2,3,4, ---$

2- Balmer series for visible region.

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H\left[\frac{1}{(2)^2} - \frac{1}{{n_i}^2}\right]$$

Where, $n_i = 3,4,5, ---$

3- Paschen series for infrared region.

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H\left[\frac{1}{(3)^2} - \frac{1}{{n_i}^2}\right]$$

Where, $n_i = 4,5,6, ---$

4- Brackett series for infrared region.

$$\bar{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = R_H \left[\frac{1}{(4)^2} - \frac{1}{{n_i}^2}\right]$$

Where, $n_i = 5,6,7, - - -$

5- P'fund series for infrared region.

$$\bar{\boldsymbol{v}} = \frac{\mathbf{1}}{\boldsymbol{\lambda}} = R_H \left[\frac{1}{(5)^2} - \frac{1}{{n_i}^2}\right]$$

Where, $n_i = 6,7, - - -$

λ = wave length of the radiations emitted and $\bar{\boldsymbol{v}}$ = wave number

EXCITATION AND IONIZATION POTENTIAL:

A hydrogen atom consists of an electron and therefore the only allowed orbit n = 1 which is called ground state where as states with n = 2, 3, 4, … are called excited states. If energy is supplied to an atom so that it attain an excited state then the energy supplied is called excitation energy and the corresponding potential is called excitation potential (energy = Ve). Excitation energy is the difference between the energies of the states (i.e energy of higher state – energy of lower state). The excitation potential is defined as the accelerating potential which moves the electron of the atom form the ground state to the higher state.

There are many ways by which the electron of an atom an be excited to different states. If the atomic gas is heated the electron may be excited by thermal motion collision. If the gas is an electric discharge a free electron which has been accelerated by the electric field may hit the atom of the gas when illuminated may absorb energy form a photon and are excited.

If an electron lying in the ground state of the atom is given sufficient energy so that it is raised to the orbit for which n = ∞ it will discharge itself from the atom. The atom with become positively charged. It is said to be ionized. The energy supplied is called ionization energy and the corresponding potential is called ionization potential. The ionization potential is defined as the accelerating potential which moves the electron completely form an atom. For hydrogen atom the energy needed to ionize it is 13.6 ev and the corresponding potential is 13.6 volts.

X-RAYS SPECTRA:

X-rays wave discovered by Withelm K. Roentgen and thus also known as roentgen rays. These rays are of shorter wave length. The range is usually considered to be 0.1 to 1 nm. X-rays are produced if heavier atoms are bombarded by high energy electron.

PRODUCTION OF X-RAYS:

X-Rays can be produced by an apparatus shown in the figure. Electrons are produced by heating a filament F. these emitted electrons are accelerated towards the metal target T by applying a high potential V of the order of several thousand volts. When the electrons hot the target T X-Rays are produced the study of the X-Rays spectrum shows that there are two X-Rays spectra..

1. Continuous spectrum of frequencies or X-rays brems strahlung.
2. Characteristics spectrum or a line spectrum, of a limited number of fairly definite frequencies.

X-RAR CONTINUOUS SPECTRA OR X-RAY BREMSSTRAHLUNG:

When electrons hit the metal target a continuous spectrum of frequencies of X-rays is emitted. The frequencies of the X-rays depend upon the accelerating voltage and are very nearly independent of the material of the target.

Graph between wave length and intensity of X-rays are shown in the figure. The minimum wave length decreases i.e frequency increases with the increase of accelerating voltage and is very nearly independent of the material of the target.

The continuous spectrum or brems strahlung spectrum is a result of the fact that when electrons pass close to the atomic nuclei they are deflected and allowed down due to which they lose their energy. The energy lost be decelerating electrons appears in the form of photons in the x-rays range. This is an effect similar to inverse photo electric effect.
The process is represented as atom + e(fast) → atom + e- (slow) + hν

Characteristics X-Ray spectra (Inner shell transition):
In the heavy atom the electron are assumed to be arranged in concentric shells at increasing distance form the nucleus. These shell are labeled as K, L, M, N etc. the electron of the inner shells are tightly bound as compared to the electrons of outer shells. Large amount of energy is required to their displacement form their normal energy levels consequently. Photons of large energy are emitted when the atom returns to their normal states. Thus the transition of inner shell electrons in heavy atoms gives rise to the emission of high energy X-ray photons or characteristics X-rays. For that purpose the target material of high atomic number.

When highly energetic incident electron knock an electron form the K shell these occurs a vacancy in that shell. This vacancy is filled by the arrival of an electron form outside the K shell emitting the excess energy as X-ray photon. An X-ray photon due to transition from L shell to the vacancy in the K shell is called a k∝ characteristics x-ray. The transitions from M and N shells to the K shell are called k_β and K_γ x-ray. This transition from the shells L, M, N and so on to the K shell give rise to a series of lines $K_\propto$, K_β, K_γ and so called K_β series. When incident electrons dislodge electrons form the L shell the vacancy is filled by electrons form the remaining M, N, O shells etc. these transition give rise the L series i.e $L_\propto$, L_β, L_γ and so on as shown in the figure.

USES OF X-RAYS:

1. X-rays are used in checking fractures of bones conditions of teeth and jaws computerized tomography scan (CT scan) etc.
2. High energy X-rays are used to destroy cancer cells.
3. It is used to detect arms explosives precious metals at security posts.
4. Diffraction of X-rays is used to study the structure of crystals.

LASER:
Laser stands for light amplification by stimulated emission of radiation. The laser is an device form producing and monochromatic light beams. Different types of lasers solid state gas semi conductor liquid are used for producing light at high frequencies form the for infrared t the ultraviolet regions.
The principle of laser can be explained by understanding the following terms.
1. Stimulated absorption
2. Spontaneous emission
3. Stimulated emission

1. STIMULATED ABSORPTION:
Consider a photon of energy $h\nu = E_2 - E_1$,
Where E_1 = energy of ground state
E_2 = Energy of the higher state

Incident on an electron in the ground state. The electron absorbs the photon and jumps to higher state. This phenomenon is known as stimulated absorption. The atom becomes excited i.e atom + photon → atom

2. SPONTANEOUS EMISSION:
The atom remains in an excited state only for a limited time called the life time of the state usually of the order of 10^{-8}sec, within this time the electron falls back to ground state emitting a photon. This phenomenon is known as spontaneous emission i.e atom → atom + photon.
Since different electrons in to ground state at different times the emitted photons are not in phase.

3. STIMULATED EMISSION:

When a photon of energy $h\nu = E_2 - E_1$ is accident on an atom in an excited state E_2 the photon induces the atom is fall back to the ground state by emitting a photon of same energy. The incident and emitted photons are in same phase. This phenomenon is called stimulated emission.
i.e atom + photon → atom + 2 photons

THE LASER PRINCIPLE:

Principle of laser can be explained by considering an atom with three energy levels is E_1, E_2 and E_3. E_1 is the ground state E_3 is the short lived state of the order of 10^{-8} sec and E_2 is an intermediate meta stable state having life time of the order of 10^{-3}sec i.e life time of meta stable state E_2 about 10^{-3} times the life time of E_3. Further the transition from E_3 to E_1 is not allowed while transition from E_3 to E_2 is allowed.

When a beam of photon of energy $h\nu = E_3 - E_1$ is incident on the atoms in ground state. The atoms are excited t state E_3. Due to spontaneous emission the electrons jumps to spontaneous emission the electrons jumps to state E_2 emitting photons of energy E_3-E_2.

Since the life time of state E_2 is large spontaneous emission will take place very slow. As a result of which large number of atoms will accumulate in state E_2. Thus the population of atoms in state E2 becomes much greater than in state E_1. This process is called population inversion.

This method of transferring atoms form the ground state to the meta stable state is called optical pumping. After population inversion is obtained if a photon of energy $h\nu = E_2 - E_1$ is incident to the atom it can stimulate an electron to jump from energy state E_2 to E_1. This jump creates a photon identical to and in phase with the incident photon. These two photons stimulate two more atoms. Now there are four photons. As this process continues the number of photons increases and the intensity of light is amplified. This is achieved by confining the emitted radiations in an assembly. The ends of which are fitted with mirrors. One mirror is totally reflecting while the other is made partially reflecting for the laser beam to pass through it.

RUBY LASER:

Ruby is a crystal of aluminum oxide (Al2O3) in which some of the aluminum ions are replaced by chromium ions (C_r^{++}). The chromium gives the ruby its characteristics red colour. Ruby crystals are given the shape of a cylinder both the ends of the cylinder are made perfectly parallel to each other. One end is heavily silvered while the other end is partially silvered. A high intensity helical xenon flash lamp is used to excite the chromium atoms form state E_3 is very small (i.e of the order of 10^{-8} sec) therefore most of the atoms reaches state E_2. (i.e meta stable whose life time is of the order of 10^{-3}sec). thus population inversion is achieved.

A few chromium atoms make transitions spontaneously form state E_2 to E_1 emitting photons of wavelength $\lambda = 694.3$ nm. These photons stimulate further transitions. The emitted photons travel exactly in the direction of the axis is reflected several times and they are capable of stimulating emission repeatedly. Thus an intense coherent monochromatic beam o red light is obtained which leave through the partially transparent end of the rod.

APPICATION OF LASER:

There are number of application of laser technology. Some applications are given below.
1. It is used in holography i.e in taking three dimensional images of objects.
2. It is used for welding detached retina.
3. It is used to perform precision surveying and length measurement.
4. It is a used as a potential energy source for inducing nuclear fusion reaction.
5. It is used for telephone communication along optical fibers
6. It is used for precision cutting of metals and other materials.