

Spectroscopy Module No 2

Radiant energy is the energy transmitted from one body to another in the form of radiation.

The term radiation includes electromagnetic vibration ranging from the electric waves of low frequency through ultraviolet rays, visible spectrum and passes to the Infrared rays to the high frequency (short wavelength) X-rays and γ -rays.

According to Maxwell (1864) an alternating current of high frequency radiates in the form of waves which travel in a space with the same speed as that of light. and these are known as electromagnetic waves or electromagnetic radiation.

speed of the light [$c = 2.997 \times 10^8$ metres/sec].

Each type of electromagnetic radiation has both the properties of wave as well as particle.

Region of electromagnetic spectrum:-

Spectrum:-

When a narrow beam of light is allowed to pass through a prism or grating, it is dispersed into seven colours from Red to violet and the set of colours or band produced is called spectrum.

Radiation: Radiation is the energy travelling through space as a series of waves or stream of particles in order of their increasing frequencies and decreasing wavelength. It is called electromagnetic spectrum. In the order of increasing wavelength i.e.

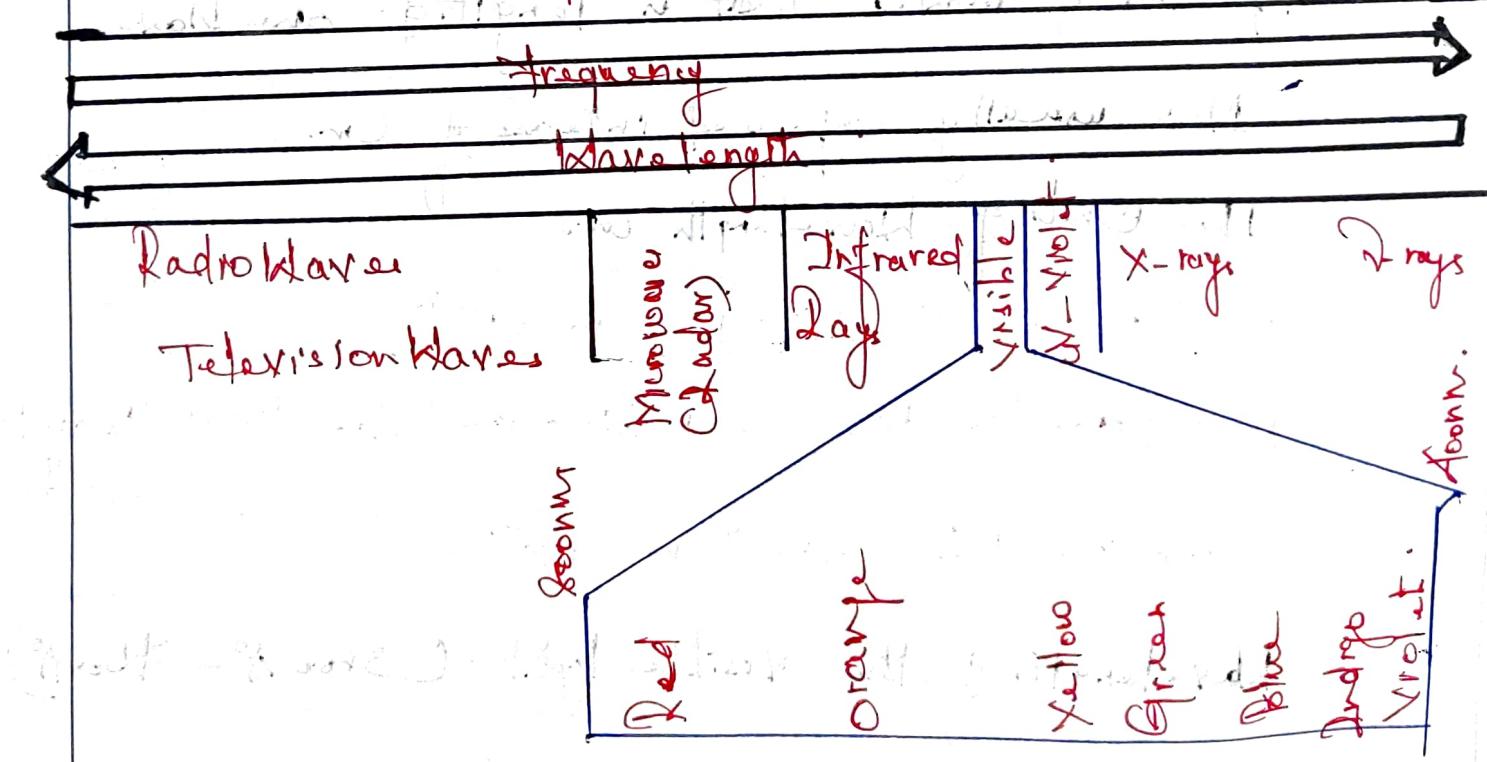
Radiowaves < Microwaves < Infrared < Visible <
Ultraviolet < X-rays < γ -rays < Cosmics.

Spectroscopy is the study of interaction of electromagnetic radiation with matter. When different types of electromagnetic radiation interact with the matter they also give rise to different types of spectroscopy.

For example absorption of electromagnetic radiation by the matter with resonance frequency region gives rise to Nuclear magnetic resonance (NMR) or electron spin resonance spectroscopy.

In microwave region separation between rotational level of molecule gives rise to rotational spectroscopy.

Molecular vibration absorption of radiation by an organic compound called vibrational spectroscopy.



electromagnetic transitions are caused from atoms and molecules
and so it is called as electromagnetic spectroscopy.

Properties of the electromagnetic radiation

The properties of the electromagnetic radiation are demonstrated by various parameters such as:

1. Velocity
2. Frequency
3. Wavelength & Amplitude

Wavelength (λ)

It is the distance between two successive peaks of waves that is length of one wave.

It is usually expressed in terms of cm.

The units of wavelength are

- 1) Angstrom \AA^0 ($1\text{\AA}^0 = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$)
- 2) Nanometre (nm) or millimicron (\mu m) $1\text{nm} = 1\text{\mu m} = 10^{-7} \text{ cm}$
 $= 10^{-9} \text{ m.}$
- 3) Micron (μm) $= 10^{-4} \text{ cm} = 10^{-6} \text{ m}$

Wavelength of the visible light $\in [3800 \text{\AA} - 760 \text{\AA}]$

Frequency (ν): The number of waves which is represented by the Number of Waves per second is called a frequency of an Electromagnetic radiation.

$$\text{Frequency } (\nu) = \frac{\text{Speed of light} \cdot (c) \text{ in cm/sec}}{\text{Wavelength in cm.}}$$

The unit of frequency is cycles per second (Hz). One cycle per second sometimes called Hertz.
1 Hertz = 10^6 cycles per second.

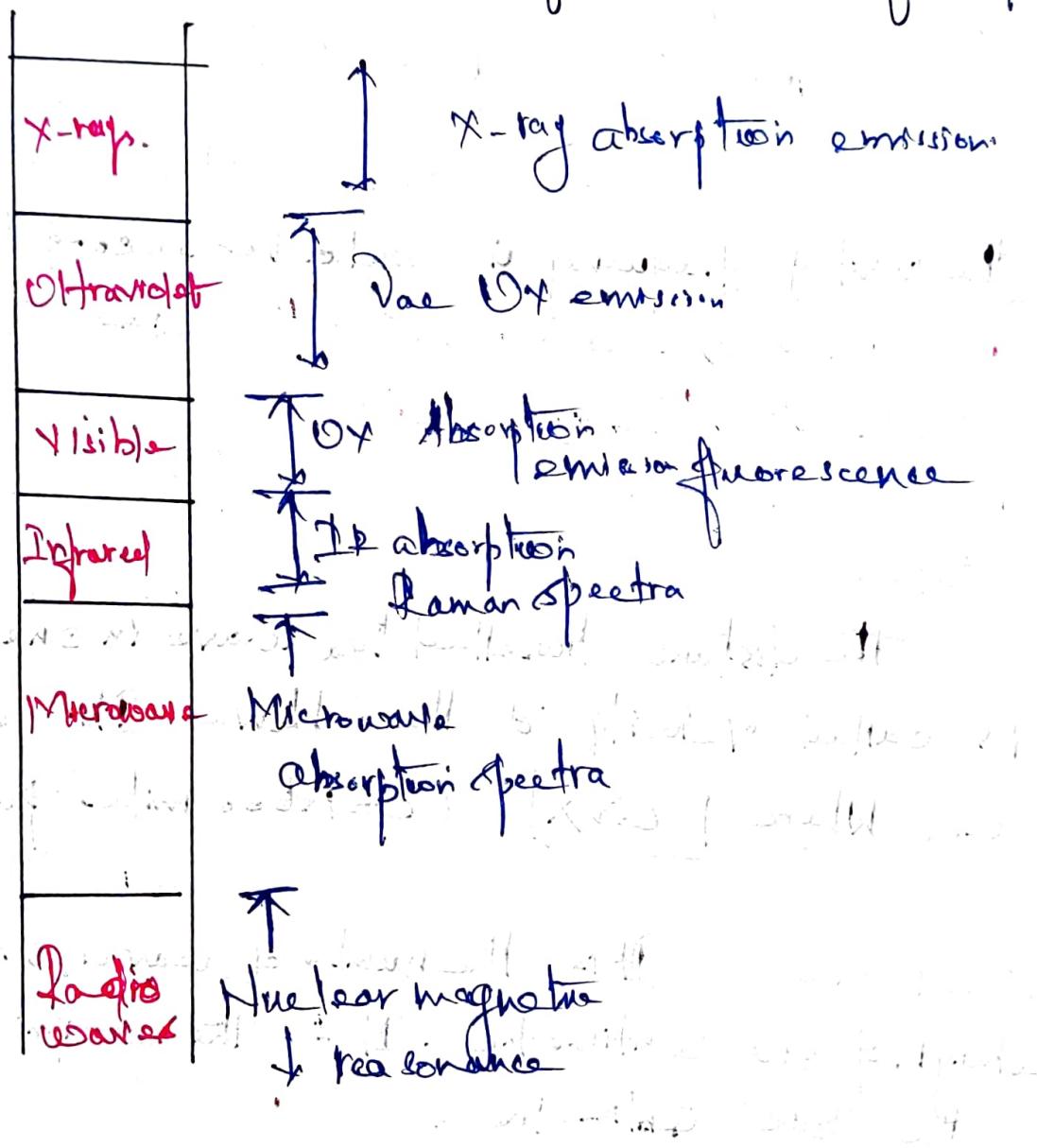
Velocity:

The distance travelled by a wave in one second is called Velocity of the wave. It is denoted by c. Where $c = \nu \lambda$ ($c = 18600 \text{ miles per sec}$)

Wave Number ($\bar{\nu}$): It is the number of waves spread in a length of one centimetre. It is the reciprocal of the one centimetre.

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

Spectroscopy is the most powerful tool available for the study of atomic and molecular structure and is used in the analysis of wide range of samples.



Types of Interaction

Atomic Interaction

Interaction of the electromagnetic radiation with atom in their lowest energy state called the Ground State.

Molecular Interaction

Interaction of the electromagnetic radiation with the molecule. This results in transition between Rotational and Vibrational energy levels in addition to electronic transition.

Selection Rules

The molecular spectra are usually governed by the Selection Rules which specifies the changes in the Quantum Numbers accompanying a particular transition. If the molecule obeys the transition then it is called allowed transition.

If it is not obeyed then it is called forbidden transition.

Principles of electronic Spectroscopy.
The electronic spectra of ultraviolet and visible of compounds are associated with the measurement of energy gets absorbed.

Due to the energy gets absorbed the electron gets promoted from lower energy level to the higher energy level.

In general the electronic transition occurs in the range from 180 nm to 780 nm. the region extending from 200 to 380 nm called Hear or Quartz ultraviolet region.

The region is from 10 to 200 nm is known as Far Infrared Region.

The major difference between the ultraviolet and visible method is that the ion, atom or molecule absorbed in the ultraviolet region absorb more energy for excitation. In the visible region.

How to represent the energy levels.

The energy levels represented by the electron jump from E_1 to E_2 level.

The system will absorb the energy level of Quanta mentioned by $\Delta E = E_2 - E_1$

The energy difference between the two energy levels is denoted by

$$\boxed{\Delta E = h\nu} \quad \text{Bohr Condition}$$

If the system undergoes the state changes from E_1 to E_2 represented as an emission represented by

$$\boxed{\Delta E = E_2 - E_1}$$

How the excitation of electron occurs.

When the molecule absorbs the UV light, its electron gets promoted from the Ground State to its excited state.

This highly probable transition due to absorption of quantized energy levels involves the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest Unoccupied molecular orbital (LUMO).

Principles of Ultraviolet (Electronic) Spectra

The total energy of the molecule is due to the presence of electron charge distribution.

- ① electron-electron Interaction
- ② Hucleus-Hucleus Interaction
- ③ Electron-Nucleus Interaction

It is also distributed to the presence of vibrational, rotational and translational modes of electron.

Electronic Spectra

Intensities, based on absorption of light by the Beer-Lambert law governing the amount of radiation transmitted through sample can be arranged to give

$$\log_{10} \left(\frac{I_0}{I} \right) = ECl$$

Where I_0 is the Incident

I is the transmitting Intensity

C is the molar Concentration of absorbing species

l is the path length

E is the molar extinction coefficient.

Given in the units of $M^{-1} \text{cm}^{-1}$.

E_{max} is the Convenient guide to the absorption intensity

Electrode spectra can be described in terms of the
 ϵ and E_{max}

ϵ is the molar absorptivity is the measure of the observed colouring the metal complex.

Molar absorptivity (ϵ) for an electron transition is governed by the probability of the electron transition will occur.

Selection Rules for electrode Spectroscopy.

The Spin multiplicity Rule.

* this rule states that transitions between states of the same spin multiplicity are allowed and transition between different spin multiplicity are different.

$$\Delta S = 0$$



allowed

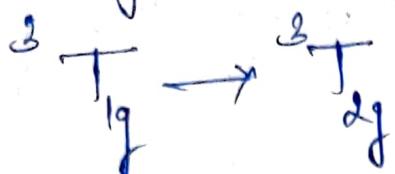
$$\Delta S \neq 0$$



forbidden

that is spin allowed Transition

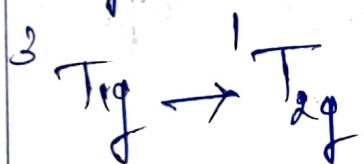
Singlet \rightarrow Singlet



spin forbidden Transition

As $\neq 0$

Singlet \rightarrow Triplet



Second type of Selection Rule is

Laporte allowed (parity) orbital selection rule

(or) symmetry selection rule

In a centrosymmetric molecule (or) in a transition between same parity are forbidden

and the only allowed transitions are those accompanied by a change of parity.

Forbidden transitions are without change in the angular momentum (Δl) nature of orbital are forbidden

Reporte allowed

$$\Delta l = \pm 1$$



Reporte forbidden

$$\Delta l = 0, \pm 2$$



The principle is based on the Born-Oppenheimer approximation.

According to the Born-Oppenheimer approximation, the motion of the nucleus is slower than the motion of the electron due to its heavy mass.

According to the total energy is represented by

$$T E = E_{\text{elect}} + E_{\text{vib}} + E_{\text{translational}}$$

The energies due to electronic motion and nuclear motion are separated by

$$H = H_e + H_n$$

H_e = kinetic energy of electron & P.E of $e^- - \text{Nucleon}$

H_n = Potential energy of electron + P.E of Nucleon - Neutron Interaction

Electronic Spectroscopy for H atom

It is well known that atom consists of central positively charged nucleus and surrounded by negatively charged electrons in sufficient number to balance the nuclear charge.

Hydrogen is the smallest and simplest atom, has a nuclear charge of +1 units (where as the electronic charge 1.60×10^{-19} coulomb) and one electron.

To solve these Schrödinger wave equation need to predict the probability of an electron by using the Greek expression ψ , and ψ^2 is the probability finding the total No. of electrons.

Shape of the Quantum Numbers

shape of the orbital

Quantum Number Allowed Values Function

Principal n .

1, 2, 3

Govern the energy
and size

$(n-1), (n-2) \dots$ shape of the orbital

Orbital, l .

$l, l+1, l+2 \dots$ direction of the orbital

Magnetic, m_l values +, 0, - and electron behaviour

Spin, s . $\pm \frac{1}{2}$ cause rotation in magnetic field

Govern the direction

angular momentum of the e.

mode in which the particle moves in the field

1. Orbital (or azimuthal) Quantum Number l also has Integral

values only but these must be less than n .

thus for $n=3$, l can be 2, 1 or 0

Governs the shape of the orbital and angular momentum of the electron as it revolves about the nucleus on its orbit

2. Magnetic Quantum Number m depends upon the integral value of l .

thus for $l=2$, m can be +2, +1, 0, -1, -2

In general $(2l+1)$ values.

m determines the shape of the direction of the orbital.

Spin Quantum Number $\pm \frac{1}{2}$ measures the spin angular momentum which the electron possess whether in the atom or in the free space.

Spectrum Hydrogen atom:

In general energy of the orbital varies from atom to atom Due to two reasons) attraction between electron and nucleus 2) Repulsion between electrons in the same atom.

We consider the first. the case of hydrogen atom in some detail. Due to the absence of the interelectrons effects all the orbitals are in the same energy level. In the hydrogen

as, $2p$ orbitals are in degenerate with the $1s, 2s, 2p$ orbitals

$$\boxed{\therefore \Psi_{1s} = f\left(\frac{r}{a_0}\right) \exp\left(-\frac{r}{na_0}\right)}$$

Where r : Interatomic distance

a_0 = Interatomic space

Ψ : Wave function

n_s = orbital no in the principal quantum number

s is the spin quantum number.

Schrodinger equation shows that the energy is

$$E_0 = \frac{mc^2}{8\pi^2 \epsilon_0 h^2}$$

$$E_n = -\frac{mc^2}{8\pi^2 \epsilon_0 h^2 n^2} = -\frac{R}{n^2} \text{ cm}^{-1} \quad (n=1,2,3)$$

ϵ_0 is the vacuum permittivity.

R is the Rydberg constant: since p and d orbitals have the same energies corresponds to the hydrogen only.

The lowest value of E_n is plainly $E_n = -R \text{ cm}^{-1}$ where $n=1$ is the most stable ground state.

If $E=0$ $n=\infty$ represents the removal of the electron.

A. To solve these use the selection rule

$\Delta n = \text{anything}$ $\Delta l = \pm 1$ only.

$1s \rightarrow np$ ($n>1$) electrons in the ground state undergo transition

while the dp electron can have transition either into

5 state or d state

$dp \rightarrow hs$ (or) hd .

since s and d orbitals are in the degenerate level
then the transition tree is

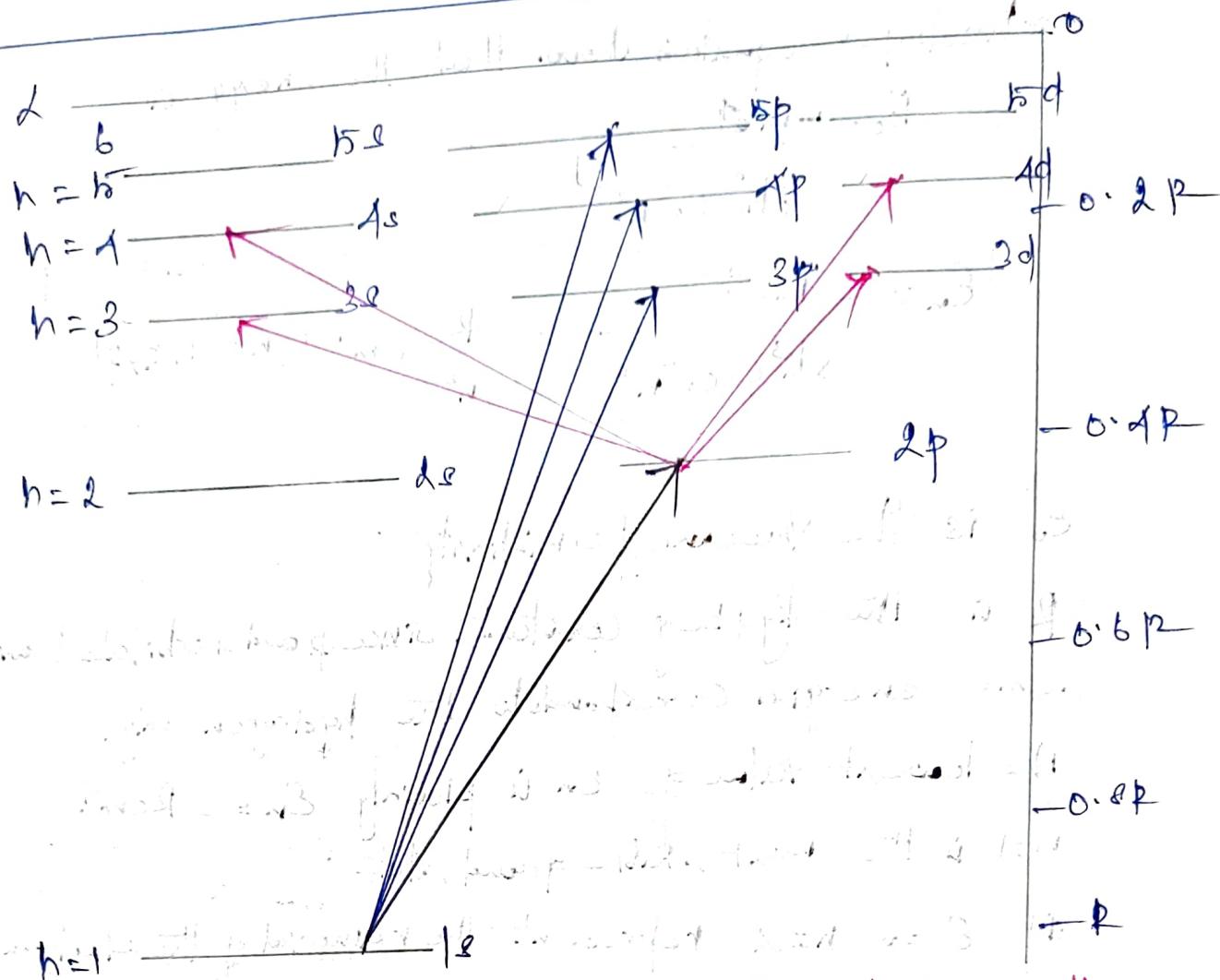


Figure shows the same lower transition between them for the single electron of the hydrogen atom.

In general other electrons in the lower state n'' can undergo transition into the higher state n' , with the absorption of the energy.

$$\Delta E = E_{n'} - E_{n''} \quad \text{in } \text{cm}^{-1}$$

therefore

$$\lambda_{\text{spect}} = \frac{-R}{n'^2} - \left(\frac{-R}{n''^2} \right) = R \left(\frac{1}{n'^2} - \frac{1}{n''^2} \right) \text{cm}^{-1}$$

An identical spectral line in emission if the electron falls from state n' to state n'' . In both cases Δn must change by unity.

Let us consider a few other transitions, restricting ourselves to absorption for multiplicity.

$$\bar{V}_{\text{Lyman}} = R \left[\frac{1}{1} - \frac{1}{n'^2} \right] \quad R = \frac{R}{h^2} \text{ cm}^{-1}$$

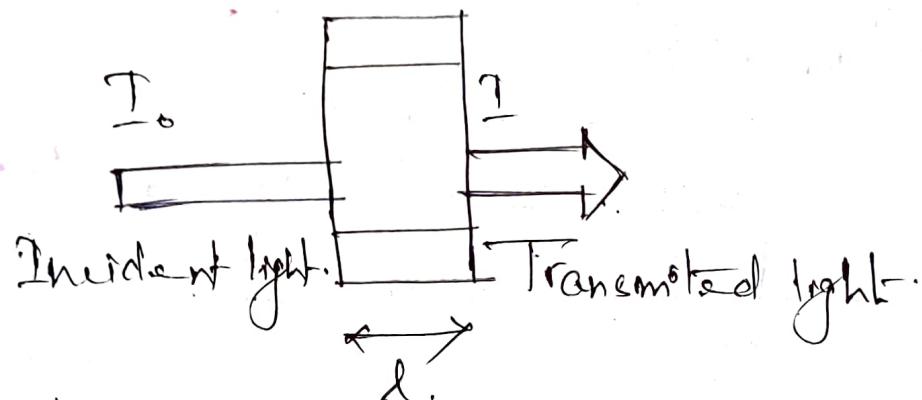
$$= \frac{3R}{1}, \frac{8R}{9}, \frac{15R}{16}, \frac{24R}{25} \text{ cm}^{-1} (\text{for } n' = 2, 3, 4, 5)$$

The Rydberg constant value = $R = 109677.581 \text{ cm}^{-1}$

\bar{V}'' clearly show that one electron from the shell due to the Ionization

Beer-Lambert law state that-

The linear relationship between the concentration and the absorbance of the solution. Which enables that Concentration determined by measuring its absorbance.



Absorbance is directly proportional to the concentration of the solution

$$\log\left(\frac{I_0}{I}\right) = \epsilon cl$$

ϵ = Molar absorption Coefficient $\left[\text{L Mol}^{-1} \text{cm}^{-1}\right]$