X-rays - ik is

Spectroscopy (V)

M.. [illegible]

F.S—:

What is spectroscopy?

It is a branch of science which deals with the Interaction of electromagnetic radiation with matter.

What is EMR?

It is a form of energy which travels through space with enormous velocity. This is characterised by wavelength, wavenos. & frequency.

It requires no medium. It can travel through vaccum also unlike other radiations.

The phenomenon associated with absorption and emission of radiation energy can not be explained by making use of wave model of radiation. Therefore it is necessary to view electromagnetic radiation as discrete particles of energy called photons.

Hence, when the EMR passes through matter a variety of phenomenon may occur.

1. If the photons of radiation possess the appropriate energies, they may be absorbed by the matter and result in electronic transitions, rotational & vibrational changes.

2. After absorbing the photons, the atoms & molecules become excited. They give out the energy either in the form of heat or re-emitting the electromagnetic radiat

3. It is not necessary that the radiation passing through the matter may be absorbed completely.

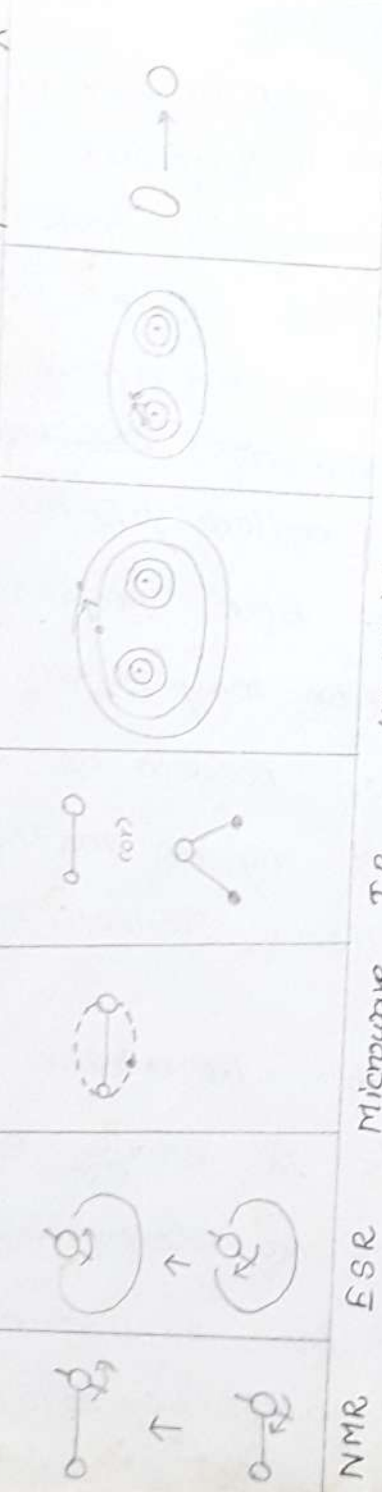
4. Thus - The portion of EMR that passess into being absorbed, may undergo scattering or re-emitted at the same or different wavelength.

The Important EMR are $\gamma$-rays, X-rays, U.V, visible, I.R, Microwaves, radiowaves etc.

The arrangement of various types of EMR in the order of increasing or decreasing frequencies is known as Electromagnetic spectrum.

## The Regions of EMRS

om | 100cm | 1cm | 100μm | 1μm | 10nm | 100pm | λ



| NMR | ESR | Microwave | IR | UV-Visible | X-ray | $\gamma$-ray. |
|---|---|---|---|---|---|---|
| Change of spin | Change of orientation (Molecular rotation) | change of configⁿ. (Molecular vibration) | Change of $e^-$ distribution: Electronic transition outer shell | Electronic transition (Inner shell) | Change of nuclear configⁿ. Nuclear |  |

Increasing order of λ :-

$\gamma$ rays < X-rays < U.V < visible < I.R < microwaves < Radio waves.

Increasing order of Energy :-

Radio waves < microwaves < I.R < visible < U.V < X-rays < $\gamma$-rays.

X-rays - K & L shell e⁻s

F.U.V - Middle shell e⁻s

Near U.V & Visible } - valency e⁻s

Near & Mid I.R - Molecular vibrations

Far I.R - Molecular rotation & low lying vibrations

Microwave - Molecular rotations.

Different types of molecular energies:.

A molecule possess internal energy which can be divided into three classes.

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

Acc. to Born-Oppenheimer approximation, the total energy of a molecule is given by

$$E_{tot} = E_{tr} + E_{rot} + E_{vib} + E_{el} \rightarrow (1).$$

Translational energy:.

This energy is associated with uniform motion of the molecule as a whole. This arises when the centre of gravity changes as a result of motion. This energy is not quantised and is negligibly small. Hence, it can be neglected.

Rotational energy:.

This energy is associated with the rotation of the molecule $\perp^r$ to the internuclear axis. Here, the centre of gravity is not changed.

Vibrational energy:.

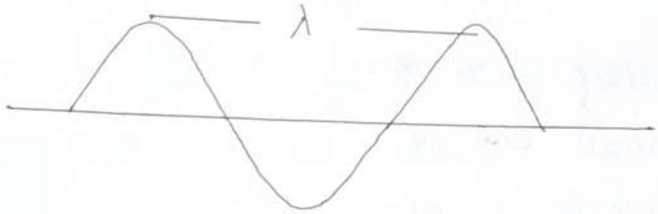
This arises due to the to & fro motion of the ~~nuclei~~ molecule. such as stretching,

3) Wave number :($\bar{\nu}$)

bending of covalent bonds which undergo transition between vibrational energy levels. Since vibration is accompanied by rotational transition, this is also termed as vibrational - rotational spectra.

Electronic energy :-

This energy is associated with the transition of $e^-$ from ground state level to excited state by the absorption of photon of suitable frequency.




Electromagnetic radiation.

Electromagnetic radiations are emitted in the form of packets called quanta (or) photons. Each photon carries the energy $h\nu$ where $h$ is Planck's const. This energy is directly proportional to the frequency of radiation.

1) Wave length ($\lambda$) :-

It is the distance between two adjascent crests or troughs in a particular wave. The symbol is $\lambda$ and the usual unit is cm. $\lambda$ is inversely $\propto$ to its energy.

2) Frequency :- ($\nu$)

The no. of waves which can pass through a point in one second is called frequency.

$$\text{Freq.} \propto \frac{1}{\lambda}$$

$1\ MHz = 10^6$ cy. per sec.

Unit :- cycles per second (or) Hz. It is a direct measure of energy. Freq $\propto$ Energy.

3) Wave number :($\bar{\nu}$)

It is the no. of waves spread in a length of one cm. It is a direct measure of the energy of radiation.

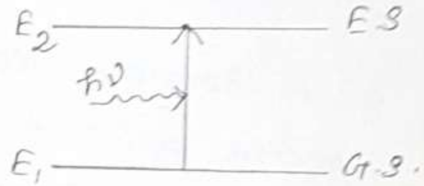
$$\bar{\nu} = \frac{1}{\lambda}.$$

Interaction of EMR with matter:.

It involves two processes.

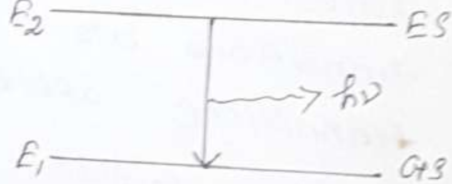
1. Absorption of EMR.
2. Emission of EMR.

1) Absorption of EMR:-




Consider an atom or a molecule having two energy levels $E_1$ & $E_2$. When a beam of EMR is allowed to fall on a molecule, the molecule absorbs a photon of energy $h\nu$, equivalent to the energy difference and under-goes a transition from lower energy to higher energy level. This results in rot, vib, & electronic transitions in a molecule. The spectrum thus obtained is called as absorption spectrum.

2) Emission of EMR:.




If a molecule falls from excited state to ground state with the emission of a photon of energy $h\nu$, then, that is called emission of EMR and the spectrum obtained will be called as emission spectrum.

It is not necessary that the EMR radiation should always be absorbed completely. A portion of it hits the matter and undergoes scattering or reflection or reemitted at the same $\lambda$.

In some cases molecules after absorbing radiation become excited but loses energy and return to the G.S within $10^{-6}$ sec in the form of light called fluorescence. It stops, once ~~the~~ when the Irradiating light is removed.

But when the excited molecule reemits the radiation very slowly or after some time it is called ~~ff~~ delayed fluorescence or phosphorescence. It continues even after the irradiating light is removed.

Molecular Spectra:

Atomic spectra arises from transition of $e^-$ between the atomic energy levels, whereas molecular spectra arise from three types of transitions namely, rotational, vibrational and electronic transitions.

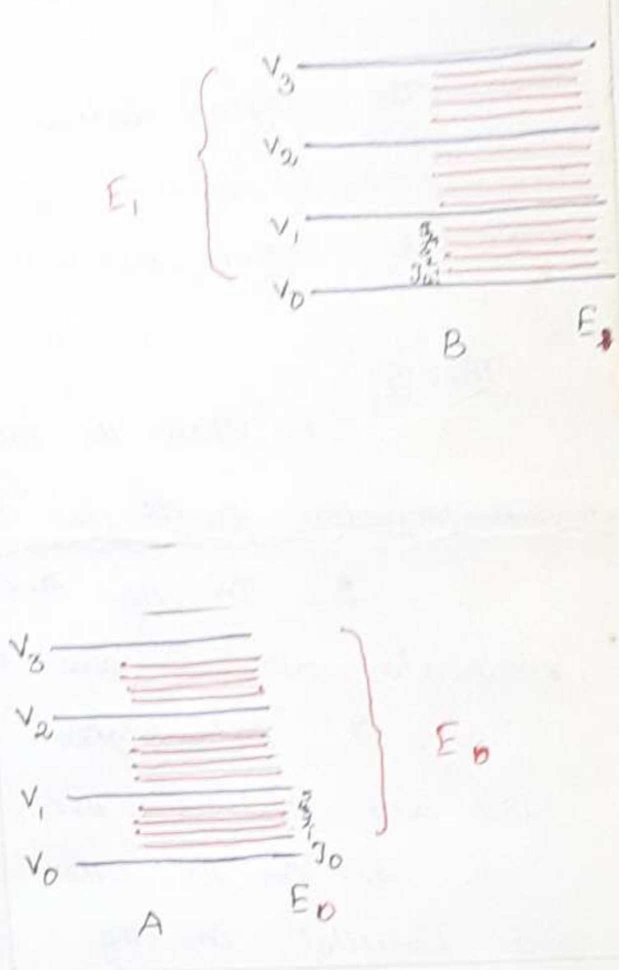
The molecular spectra are governed by selection rules which specify the changes in quantum no/. accompanying particular transitions. The transitions which obey the given selection rule are called allowed transitions where as those which violate the selection rule are called forbidden transitions. In general allowed transitions are more intense than the forbidden transitions which are weak.

Energy levels:

There are various electronic energy levels in a molecule similar to those in atoms. In each electronic state, the molecule has a no/. of vibrational sub levels. Each vibrational level is characterised by a vibrational quantum no/. v. Further, each vibrational level has a set of rotational sub-levels. The rot. energy depends on the rotational quantum no/. J.

In the following fig. the various energy levels are present in which A & B are two electronic levels, each having a series of vibrational sub levels, $v = 0, 1, 2, 3 \ldots$ and every vibrational level has a no. of rotational levels for which $J = 0, 1, 2 \ldots$ The spacing of rotational level is responsible for fine structure of molecular spectra.

Energy Level Diagram.



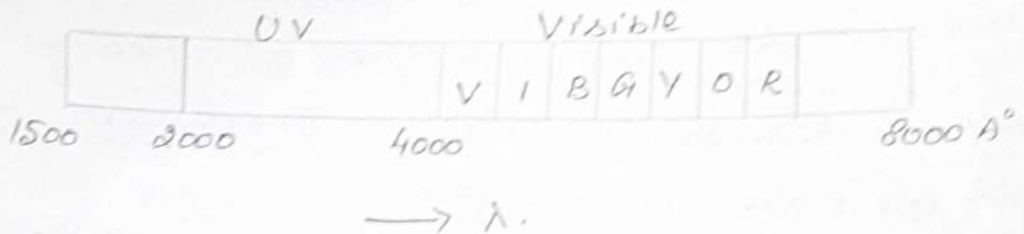

Transitions between different electronic levels give rise to spectra in the visible or U.V region which are called electronic spectra. The transitions between vibrational levels within the same electronic state are responsible for spectra in near I.R. This is called vibrational - rotational spectra. Spectra observed in far I.R & microwave region are arising from transitions between the rotational level belonging to the same vibra-tional level. These are called pure rotational spectra or microwave spectra.

UV - Visible Spectroscopy :-

The alternate title for this spectroscopy is Electronic spectroscopy as it involves the excitation of e's from the ground state to the excited state. It is very useful to measure the no. of conjugated double bonds and also aromatic conjugation within the molecules.

* Normally, the absorption a UV results in simple

The wavelength of range of UV radiation starts at the violet end of visible light (about 4000 A°) and ends 2000 A°. The U.V region is subdivided into two spectral regions.




1) The region below 2000 A° is called as far (or) vaccuum UV region.

2) The region between 2000 - 4000 A° is called as near UV region.

Theory :-

1. When the molecule absorbs U.V light, its e's get promoted from the G.S to higher energy state.

2. In the G.S, the spins of the e's in each molecular orbital are essentially paired.

3. In higher energy state, if the spins of the e's are paired, then it is called excited singlet state.

4. On the other hand, if the spins of the e's are parallel in the excited state, it is called excited triplet state.

5. The triplet state is always lower in energy than the corresponding excited singlet state. ∴ triplet state is more stable when compared to the excited singlet state.

6. In the excited triplet state the e's are far apart in space, and thus e⁻-e⁻ repulsion is minimised.

7. Normally, the absorption of UV results in singlet ground state to singlet excited state.

8. The transition from singlet ground state to triplet excited state will not take place.

Types of Electronic transitions :- In UV we have 4 types of electronic transitions. They are

$\sigma - \sigma^*$ , $n - \sigma^*$ , $\pi - \pi^*$ & $n - \pi^*$.

The energy required for various transition obey the following order.

$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$