SPECTROSCOPY

Types of spectroscopy

The study of spectroscopy can be carried out under the following headings

(i) Atomic spectroscopy

(ii) Molecular spectroscopy

(i) Atomic spectroscopy

- It deals with the interaction of the electromagnetic radiation with atoms.
- During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

(ii) Molecular spectroscopy

- It deals with the interaction of electromagnetic radiation with molecules.
- This results in transition between rotational, vibrational and electronic energy levels.

Table 4.1. Difference between molecular spectra and atomic spectra

S.No	Atomic spectra	Molecular spectra
1.	It occurs from the interaction of atom + electromagnetic radiation.	It occurs from the interaction of molecules + electromagnetic radiation.
2.	An atomic spectra is a line spectra.	Molecular spectra is a complicated spectra.
3.	It is due to electronic transition in an element.	It is due to vibrational, rotational and electronic transition in a molecule.

SPETCRUM

How does a spectrum arise?

1. Absorption spectrum

- Consider a molecule having only two energy levels E1 and E2 as shown in the fig. 4.1.

(a) Absorption spectrum **(b) Emission spectrum**

Fig 4.1 spectra

- When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state, the molecule the absorption photon energy hv and undergoes a transition from the lower energy level to the higher energy level.
- The measurement of this decrease in the intensity of radiation is the basics of Absorption spectroscopy.
- The spectrum thus obtained is called the absorption spectrum. (fig 4.1. a)

2. Emission spectrum

- If the molecule comes down from the excited state to the ground state with the emission of photons of energy hv, the spectrum obtained is called emission spectrum, (fig. 4.1.b)

ABSORPTION OF RADIATION

When electromagnetic radiation is passed through a matter, the following changes occur.

- As the photons of electromagnetic radiations are absorbed by the matter, electronic transition, vibrational transition or rotational transition may occur. After absorption, molecules get excited from the ground state to excited state. Then they liberate energy quickly in the form of heat or re-emit electromagnetic radiation.
- But in some cases, the portion of electromagnetic radiation, which passes into the matter, instead of being absorbed may be scattered or reflected or re-emitted.
- When the electromagnetic radiation is absorbed or scattered, it may undergo changes in polarization or orientation.

- In some cases the molecules absorb radiation and gets excited. Then the excited molecules undergo the following process.

(a) Fluorescence

- If the exited state molecules re-emits the almost instantaneously (within 10^{-8} seconds), it is called fluorescence.

(b) Phosphorescence

- If the excited molecules re-emits the radiation after some time (slowly), it is called phosphorescence

FACTORS AFFECTING ABSORBANCE

The fraction of photons being absorbed by matter depends on,

- **The nature of the absorbing molecules.**
- **The concentration of the molecule :** If the concentrations of the molecules are more, the absorbed photons will be more.
- **The length of the path of the radiation through the matter :** If the length of the path is long, the larger number of molecules are exposed and hence greater the photons will be absorbed.

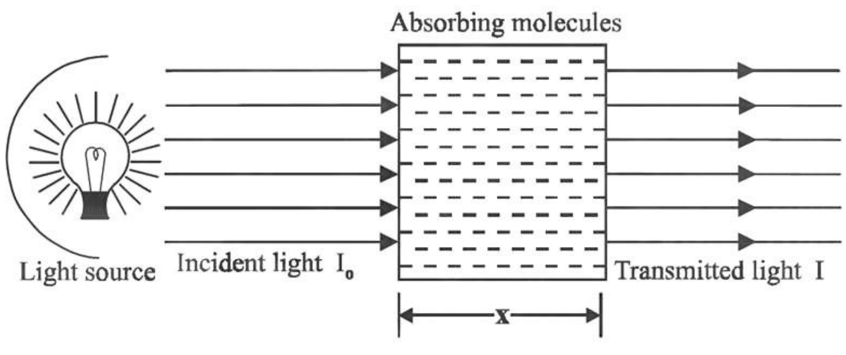

Fig.4.2 Absorbance of photons by the matter

ELECTROMAGNETIC RADIATION

- Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity.
- As the name implies, an electromagnetic radiation has an electric component.
- Fig 4.3 represents electromagnetic radiation (wave) moving along the x-axis.

- The electric field varies in the direction of y-axis and magnetic field varies in the direction of z-axis.

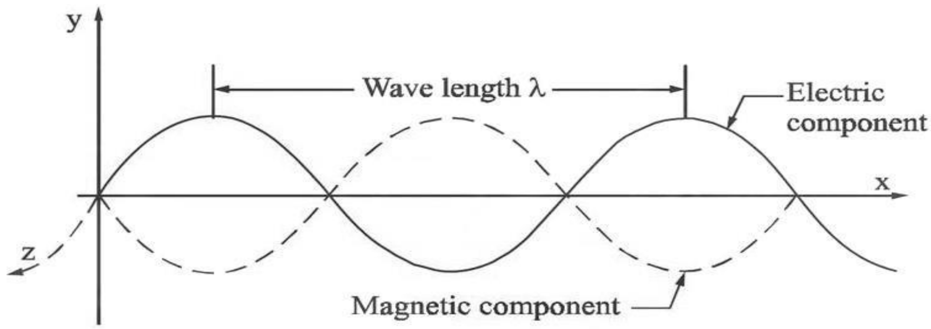

Fig 4.3 Electromagnetic radiation

Characteristics of electromagnetic radiation

- Electromagnetic radiation, consists of waves of energy, is characterized by the following parameters.

1. Wavelength (λ)

- It is the distance between two successive peaks (or) crests on an electromagnetic wave.

2. Frequency (v)

- It is the number of wave lengths passing through a point per second.

3. Wave number ($\bar{v}$)

- It is number of waves per centimeter.

4. Velocity (C)

- It is the product of wavelength and frequency. **i.e.,** λ v = C

Relationship between λ , $\bar{v}$, v and C

- Relationship between wavelength, frequency, wave number and velocity is given as

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

MOLECULAR (OR) ABSORPTION SPECTRA

The molecular spectra arises from the following three types of transitions, viz.,

1. Rotational transition 2. Vibrational transition.3. Electronic transition.

These transitions are accompanied by the absorbance of electromagnetic radiation.

Born- Oppenhiemer approximation

According to born-oppenheimer approximation, the total energy of a molecule is given by

$$E_{int} = E_{tra} + E_{rot} + E_{vib} + E_{ele} \quad .... (1)$$

Where, E_{tra}, E_{rot}, E_{vib}, E_{ele} are translational energy, rotational enegy, vibrational energy and electronic energies respectively. Its order of energy is

$$E_{int} >> E_{tra} >> E_{rot} >> E_{vib} >> E_{ele}$$

Since E_{tra} is negligibly small equation (1) becomes

$$E_{int} = E_{rot} + E_{vib} + E_{ele}$$

ENERGY LEVEL DIAGRAM

- The energy level diagram, showing different transition in molecules, are shown in the fig 4.4
- From the energy level diagram it is clear that each electronic energy level contains several vibrational energy levels. These are denoted by V_0, V_1, V_2, V_3, V_4, etc,
- Each vibrational energy level contains several rotational energy levels. These are denoted by r_0, r_1, r_2, r_3, r_4, etc,

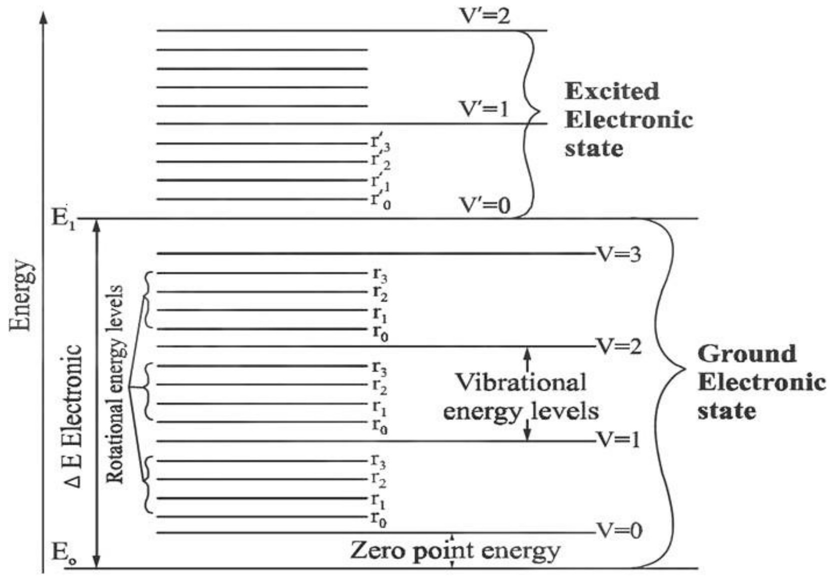

Fig. 4.4 Energy level diagrams

- Thus a molecule of a compound has a large number of energy levels. Small amount of energy is required for transition between some of these while large amount of energy is required for other levels.
- The various types of spectra, the regions in which these spectra lie and energy changes that take place in the molecules due to absorption of radiation are listed below.

Rotational (microwave) spectra (or) rotational transition

- Rotational energy arises when the molecule rotates about an axis perpendicular to the inter nuclear axis.
- Rotational spectra results from transition between the rotation energy levels of a molecule, due to the absorption of radiation in the microwave region (far- infrared region).
- Microwave spectra occur in the spectral range of 1-100 cm $^{-1}$.

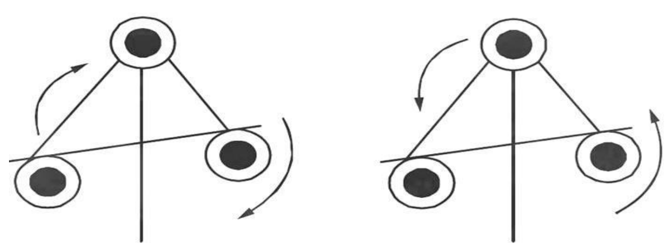

Fig. 4.5 Rotational energy

Examples

(i) Rotational spectra are shown by the molecules Like HCl, CO, H_2O, NO, ect., when possess a **permanent dipole moment.**

(ii) Homonuclear diatomic molecules such as H_2, Cl_2, ect., and linear polyatomic molecules like CO_2, **do not possess a dipole moment.**

Vibrational (infrared) spectra (or) vibrational transition

- Vibrational energy arises due to the to-and-fro motion of the molecule i.e. stretching, contracting and bending of covalent bonds in a molecule.
- Vibrational spectra and vibratioanal -rotational spectra results from transitions between the vibrational energy levels of a molecule, due to the absorption of radiation in the infrared region.
- IR spectra occur in the spectral range of 500-4000cm^{-1}. Since vibrational transition is accompanied by rotational transition, vibrational spectra are also termed as **Vibrational rotational spectra.**

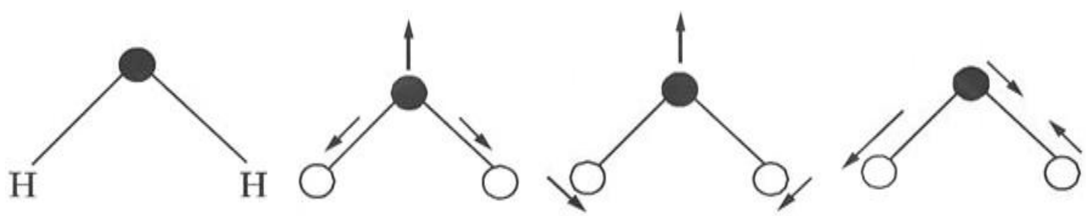

Fig 4.6 Vibrational energy

Examples:

- Vibrational spectra are shown by the molecules like CO_2, H_2O etc., when vibrational motion is accompanied by a change in the dipole moment of the molecule.

Electronic spectra (or) electronic transition

- Electronic energy arises due to the motion of electrons while considering the nuclei of atoms of a molecule as fixed points.
- Electronic spectra results from the transition of electron from the ground state energy level to an excited state energy level of a molecule, due to the absorption of radiations in the visible and ultraviolet regions.

- Electronic spectra occur in the visible region of 12,500- 25,000 cm-1, those in the UV region of 25,000-70,000cm-1. Since electronic transitions in molecules are accompanied by vibrational and rotational transitional, the electronic spectra of molecules are highly complex.

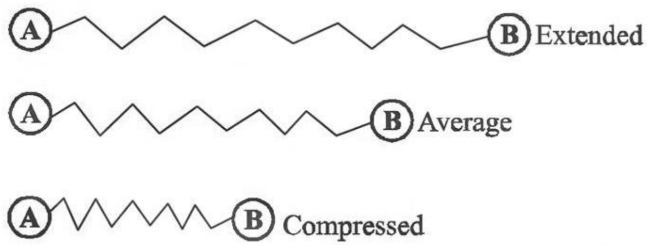

Fig. 4.7 Electronic energy

ELECTROMAGNETIC SPECTRUM

- The entire range over which electromagnetic radiation exists is known as electromagnetic spectrum. The electromagnetic spectrum covers larger range of wavelength.
- Fig.4.8 shows a diagrammatic representation of the electromagnetic spectrum. A logarithmic scale is used in this representation. The divisions between the different spectral regions indicate the origin of radiation. The limits indicated in fig. 4.8 are arbitrary.

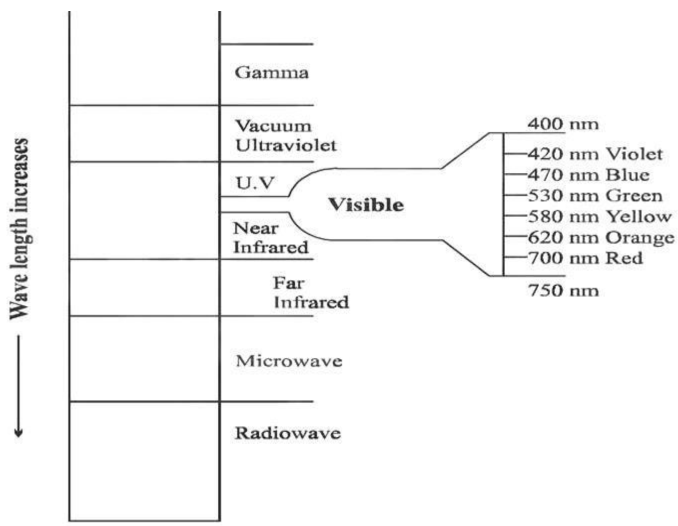

Fig. 4.8 Electromagnetic Spectrum

Characteristic of electromagnetic spectrum

- The major characteristics of various spectral regions are described as follows:

Spectral region and sources	Wave length range	Energy change involved	characteristics
Gamma rays	100 to 1 pm	10^9 to 10^{11} J/ mole (nuclear level)	Shortest wave length emitted by atomic nuclei.
X – rays	10 nm to 100 nm	10^7 to 10^9 J / mole (K and L electrons)	--
Ultraviolet	100 to 400 nm	10^7 to 10^6 J/ mole (middle and valance shell electrons)	--
Visible	400 to 750nm	10^6 to 10^5 J / mole (valency electrons)	Within the visible region, a person with normal colour vision is able to sense the colour.
Infrared	0.75 to 1000 µm	10^3 to 10^5 J / mole (molecular vibration and rotation)	This region corresponds to change in the vibration of the molecules.
Microwave	0.1 to 50 cm	10^1 to 10^3 J/ mole (molecular rotation spin orientation)	It corresponds to change in the rotation of molecule.
Radio wave	1 to 30 m	Less than 10^1 J/ mole	It corresponds to change the spin of the electron.