

ELECTROMAGNETIC RADIATION:-

Radiations may be considered as energy that is propagated by means of electric and magnetic fields, that oscillate in a direction perpendicular to the direction of travel of energy.

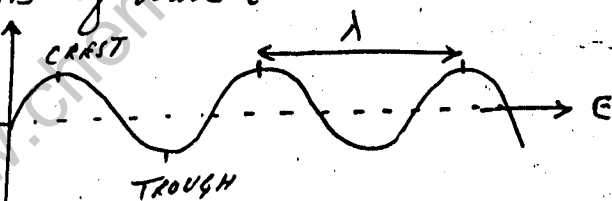
Waves similar to electromagnetic waves are produced when a stone is thrown in a pond of water. The stone makes the water molecules vibrate up and down and transmit its energy as wave on the surface of water. These waves travel to the bank of the pond.

Electromagnetic radiations are named so because they have an electrical and magnetic component. These are produced by periodic motion of charged particles. The vibratory motion of electrons produces electromagnetic radiations with exact oscillating electric and magnetic fields.

Radiant energy travels with velocity of light in vacuum i.e.  $3 \times 10^8$  m/sec.

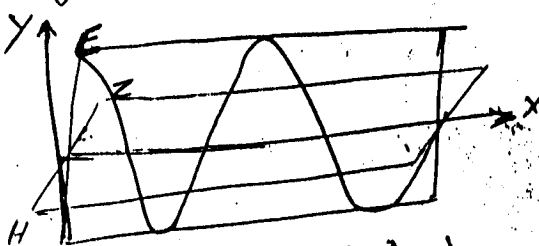
The waves are characterized by following terms.

**WAVE LENGTH:** " $\lambda$ " It is defined as distance between two successive crests or troughs of wave train. It is expressed in metres or Angstroms, or nanometers.



FREQUENCY " $\nu$ "

The number of crests or trough which pass a given point per second is called frequency. Its unit is  $\text{sec}^{-1}$  or Hertz (Hz).

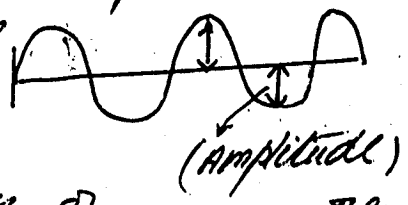


The frequency is related to wavelength and speed by following relationship

$$c = \nu \times \lambda$$

The speed of all electromagnetic radiations is same in vacuum which is  $3 \times 10^8$  m/sec

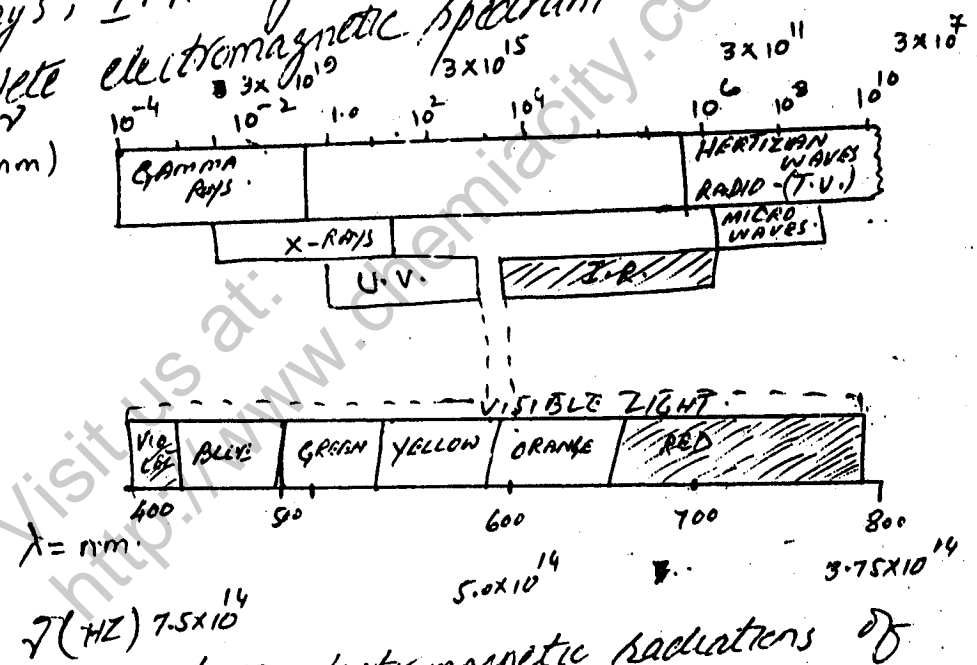
**AMPLITUDE**:- The maximum distance from horizontal mid-line to either crest or trough is called Amplitude. In case of a vibrating string amplitude determines loudness of the tone while frequency determines the pitch.



In electromagnetic radiations the amplitude of the charges in electric and magnetic fields determines the intensity of electromagnetic radiations.

**WHAT IS ELECTROMAGNETIC SPECTRUM:-**

The orderly arrangement of electromagnetic radiations, according to their wavelength or frequency is called electromagnetic spectrum. Electromagnetic radiations include waves of different wavelengths. These different wavelengths are named divided into different regions such as visible light, X-ray, gamma rays, U.V. rays, I. R. rays. Visible light is a very small part of complete electromagnetic spectrum.



White light is composed of electromagnetic radiations of wavelength ranging from 400 nm to 700 nm. Each wave has a characteristic colour.

When a beam of white light is passed through a prism, different wavelengths are refracted through different angles. Thus white light splits into seven different colours. When received on screen these colours form continuous

series of colour bands from red to violet. This series of bands that forms a continuous rainbow of colours is called a continuous spectrum.

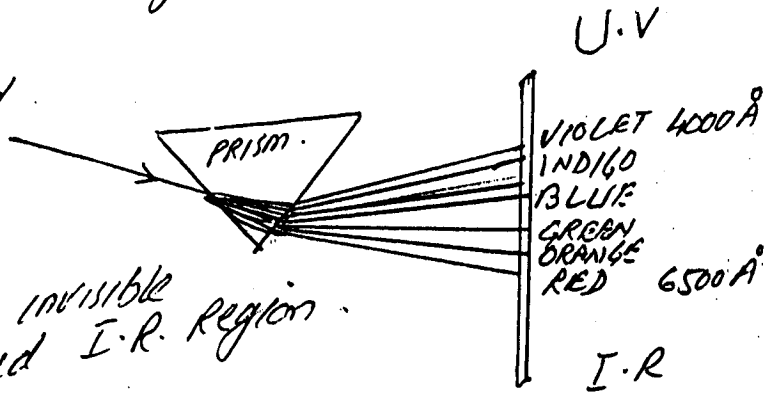
CONTINUOUS SPECTRUM) A continuous spectrum is one in which all wavelength components of visible portion of electromagnetic spectrum are present

ULTRAVIOLET REGION

The invisible region beyond the violet is called U.V. region.

INFRARED REGION

region below red is called I.R. region.



**WRITE A NOTE ON ATOMIC SPECTRUM.**

There are two types of atomic spectra viz Absorption spectrum and emission spectrum. Let us discuss these one by one

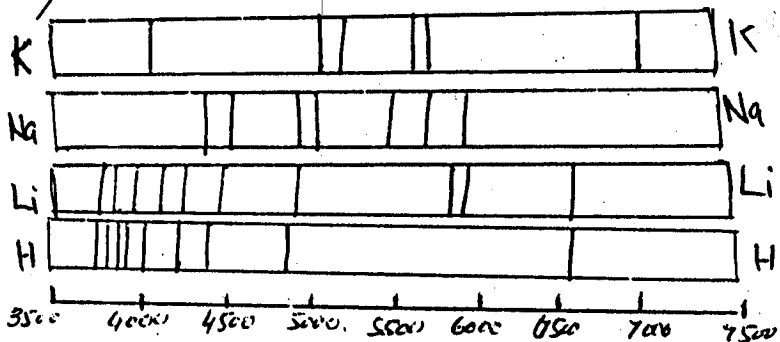
ATOMIC EMISSION SPECTRUM

When an element in vapour phase or gas phase is heated in a flame, or a discharge tube atoms are excited and it emit light radiations of characteristic wave length and colour. The colour depends upon the element being investigated. For example

- (i) Sodium and sodium containing compounds give off bright yellow colour. While potassium containing compounds give off violet colour.

When emitted light is passed through a spectroscope and spectrum is found on photographic plate it is found to consist of bright lines separated by dark bands. Such a spectrum in which each bright line represents the wavelength emitted by element is called Emission Line spectrum of element

The emission spectra of some elements is shown over here



INTERACTION OF ELECTROMAGNETIC RADIATIONS AND MOLECULES  
 If a beam of electromagnetic radiations is passed through a molecule, it will absorb some radiations and get excited from  $E_0$  energy level to  $E_1$  energy level. The molecule will absorb only those radiations whose energy is equal to the energy difference between two energy levels of molecule. The frequency of radiations absorbed is " $\Delta E = h\nu$ ". Where  $\Delta E$  is energy difference between two energy levels of molecule.

SPECTROSCOPY: The measurement of frequencies & wavelengths absorbed by a molecule as a result of interaction of electromagnetic radiations with molecule is called spectroscopy.

SPECTRUM: The results of interactions of radiations with molecule are recorded as plot of either transmittance "T" or Absorbance (A) versus frequencies or wavelength or wave number. This plot is called spectrum.

TRANSMITTANCE "T": The ratio of intensity of transmitted radiations to the intensity of incident radiations is called TRANSMITTANCE.

$$T = \frac{I}{I_0}$$

( $I_0$  = Intensity of Incident radiations  
 $I$  = Intensity of transmitted radiations)

ABSORBANCE "A"

$$A = \log \frac{I_0}{I}$$

OR

$$A = \log \frac{1}{T}$$

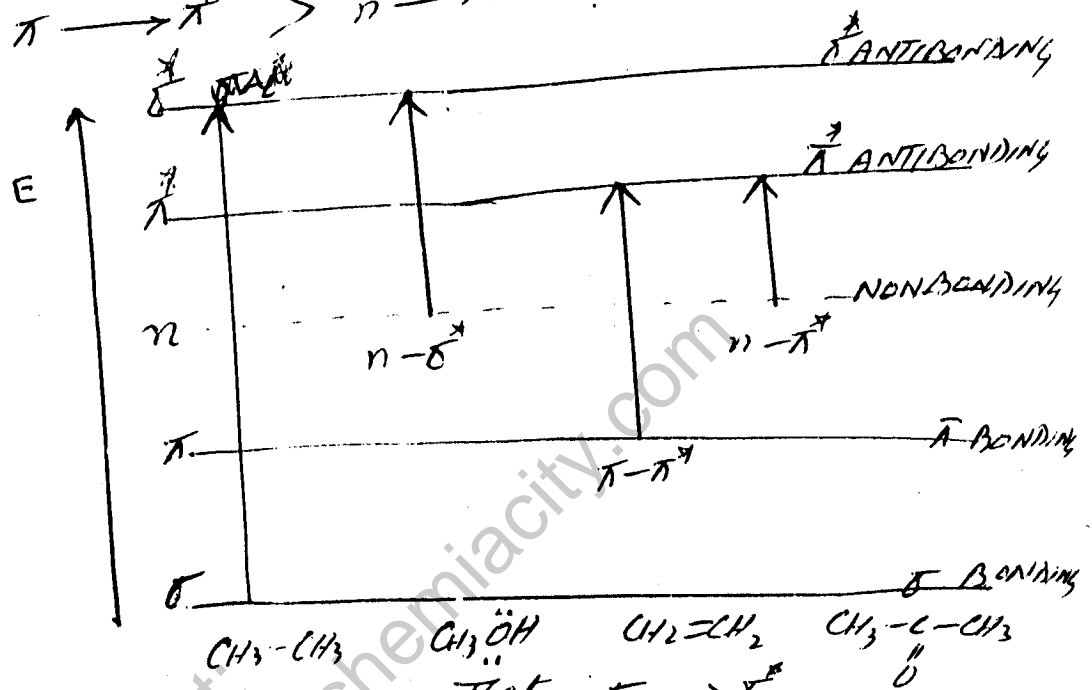
The frequency of radiation absorbed a sample is used for qualitative analysis (each molecule absorbs at different frequency) and extent of Absorbance is used for quantitative analysis. Different types of molecules transitions require different amounts of energy. Thus each type of transition requires different range of frequencies and wavelength. For example electronic transitions require high energy and for these transitions, U.V. visible radiations absorbed. The transition from lower vib. energy level to higher vib energy level requires lesser energy hence these transitions require I.R. radiations.

# ULTRAVIOLET/VISIBLE SPECTROSCOPY - 250 -

UV/VISIBLE spectroscopy deals with absorption of radiations in the range of (200-400nm) and 400-800nm. These radiations have high energy and these radiations cause electronic transition from "HOMO" to "LUMO".

"HOMO": Highest occupied MO and "LUMO": lowest unoccupied MO.

The wavelength absorbed depends upon the energy difference between "HOMO" to "LUMO". There are four types of electronic transitions from  $\sigma \rightarrow \sigma^*$  >  $n \rightarrow \sigma^*$  >  $\pi \rightarrow \pi^*$  >  $n \rightarrow \pi^*$ .

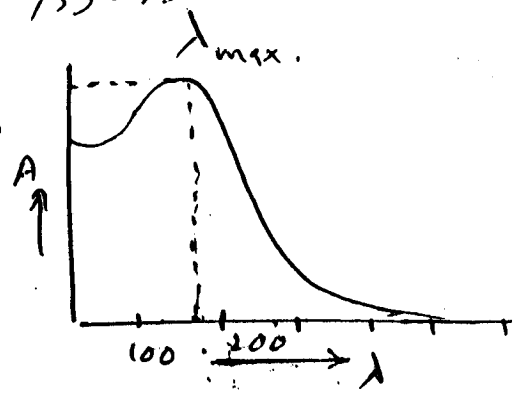


It is clear from above diagram that  $\sigma \rightarrow \sigma^*$  requires max. energy and  $n \rightarrow \pi^*$  requires minimum energy. Thus compounds having only sigma bonds will absorb at shortest wavelength (vacuum U.V. below 200nm) while compounds having lone pairs and  $\pi$  bonds absorb at longer wavelength, UV/visible.

An isolated double or triple bond absorbs in U.V. vacuum region but a conjugated system of unsaturated bonds absorbs in UV region.

Example: - Ethene having only one d.b. absorbs at 171 nm (U.V. vacuum) while 1,3-Butadiene absorbs at 217 nm (U.V. region).

The wavelength at which abs. is max. is called  $\lambda_{max}$ . The  $n \rightarrow \pi^*$  transitions requires lesser energy so  $\lambda_{max}$  for



Commonly compounds is 275-295 nm.

There are two main characteristics of Absorption band.

(1) POSITION OF BAND (2) INTENSITY OF BAND  
 POSITION OF BAND indicates the wavelength at which a comp. absorbs. It indicates quality of compound. The position of band depends upon the difference of energy between HOMO and LUMO.

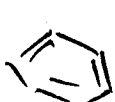
INTENSITY OF BAND The intensity of band depends upon probability of transitions. The probability depends upon relative symmetries of orbitals at ground state and excited state. The intensity of absorption is expressed in terms of molar absorptivity  $\epsilon''$ .

The molar absorptivity  $A = \epsilon'' c l$   
 to each other by  $A = \epsilon'' c l$ .  $\epsilon''$  = path length in cm  
 $c$  = concentration in mole/l.

The " $\epsilon = 10000$ " for  $\pi \rightarrow \pi^*$  transitions while  $\epsilon < 100$  for  $n \rightarrow \pi^*$  transitions. Thus carbonyl group of aldehydes and ketones are identified by a high intensity and short wavelength transition and an absorption band of low intensity and longer wavelength due to  $n \rightarrow \pi^*$  transitions.

CHROMOPHORE The structural feature of molecule which is responsible for absorption in visible region is called Chromophore. Some important chromophores are given below.

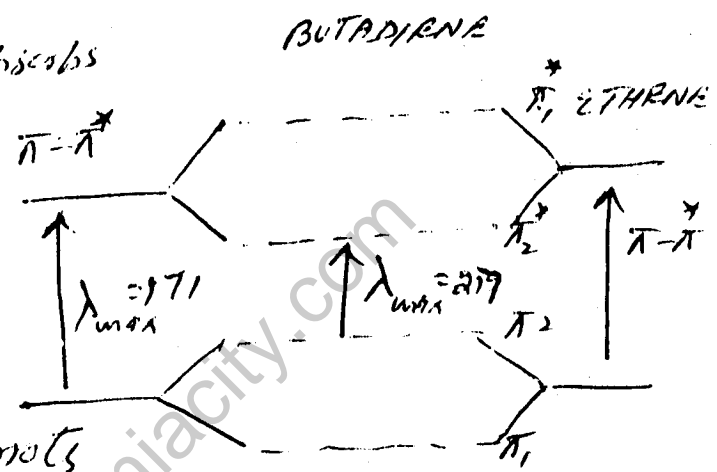
AUXOCHROMES The functional groups which shift the  $\lambda_{max}$  of chromophore to longer wavelength are called Auxochromes. These are not chromophores themselves but when attached to chromophore shift  $\lambda_{max}$  to longer wavelength. Most of auxochromes have non bonding electron pairs. Some examples are  $-OH$ ,  $-NH_2$ ,  $-OCH_3$  etc.

CHROMOPHORE	$\lambda_{max}$	TRANSITION
$C=C$	171	$\pi \rightarrow \pi^*$
$C \equiv C$	173	$\pi \rightarrow \pi^*$
$C=O$	(i) 190 (ii) 280	$n \rightarrow \pi^*$
$C \equiv N$	167	$\pi \rightarrow \pi^*$
$\bar{N} \equiv \bar{N}$	338	$n \rightarrow \pi^*$
	254	$\pi \rightarrow \pi^*$

For example  $-C=CH_2$ , when attached to ethylenic db. shifts  $\lambda_{max}$  from 171 to 190 nm in  $CH_2=CH-C=CH_2$ .  
 RED SHIFT or BATHOCHROMIC SHIFT: The shift of  $\lambda_{max}$  to longer wavelength is called Red Shift or bathochromic shift.  
 A shift to shorter wavelength is called Blue Shift.

CONJUGATED SYSTEMS The chromophore which is in conjugation with another chromophore shifts  $\lambda_{max}$  to longer wavelength. For example ethene has  $\lambda_{max}$  171 nm while 1,3-butadiene ~~with~~ absorbs at  $\lambda_{max}$  217 nm. It is due to the fact that four p-orbitals of conjugated system form four molecular orbitals two  $\pi$  and two  $\pi^*$  m.o.

Similarly 1,3,5-Hexatriene absorbs still at longer wavelength ( $\lambda_{max} = 258$ )  
 Compounds having twenty double bonds in conjugation are yellow coloured. The red colour of tomato and carrots is due to conjugated systems.



Similarly methyl vinyl ketone absorbs at 215 nm.  
SOME IMPORTANT POINTS  
 (1) Carbonyl group and carbon to carbon double bonds in conjugation with chromophore shifts  $\lambda_{max}$  to longer wavelength. The greater the number of multiple bonds the more compound or longer is wavelength.  
 (2) Nonconjugated alkene show intense absorption band below 200 nm (vacuum UV). It is not in range of U.V. spectrophotometer.

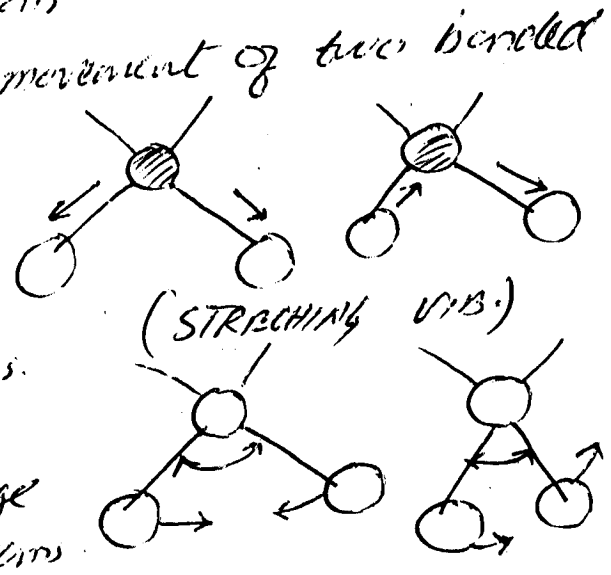
- (3) Nonconjugated carbonyl comp. have weak Abs. band. in 280-300 nm due to  $n \rightarrow \pi^*$  transitions.  $\lambda_{max} = 270$  For Acetone
- (4) Polyenes with 8 or more db. absorb in visible region of spectrum.
- (5) Conjugated alkenes absorb at longer wavelength than alkenes.

INFRARED SPECTROSCOPY

At ordinary temp. organic molecules are constantly vibrating with a definite frequency. This frequency of vibration depends upon the strength of bond and mass of bonded atoms.

There are two types of vibrations:

(i) STRETCHING VIBRATIONS / The movement of two bonded atoms along the bond axis.  
 The interatomic distance increases or decreases in these vibrations.



(ii) BENDING VIBRATIONS / These vibrations cause a change in angle between bonded atoms.

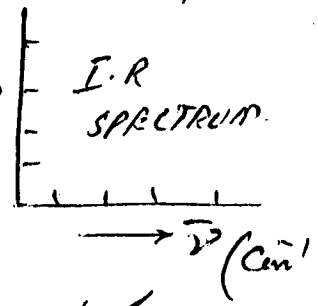
ENERGY REQUIREMENT / A stretching vibration requires more energy than a bending vibration. For example C-H stretching absorption occurs at  $3000 \text{ cm}^{-1}$  while C-H bending vib. occurs at  $1400 \text{ cm}^{-1}$ . Similarly stretching vib. of  $\text{C}=\text{O}$  will require more energy than a single bond. For example consider  $\text{C}\equiv\text{C}$  (at  $2200 \text{ cm}^{-1}$ )  $\text{C}=\text{C}$  (at  $1600 \text{ cm}^{-1}$ ) and  $\text{C}-\text{C}$  (at  $900 \text{ cm}^{-1}$ ) (SEE P-45 GILMAN-KASSO) and P-633 BY YOUNG

I.R. ACTIVE VIBRATIONS / For a vibration to be I.R. the dipole moment at one extreme of vibration must be different than at other extreme of vibration. The vibrations which do not cause a change in dipole moment will not interact with I.R. radiations. Such vib. are I.R. inactive. When a molecule absorbs I.R. radiations the intensity of vibration is increased but the frequency of vibration remains the same.



INFRARED SPECTRUM

A plot of absorbance (A) or transmittance (T) of I.R. radiations versus wave length or wave number is called I.R. spectrum. The I.R. spectrum may be divided into two parts



FUNCTIONAL GROUP REGION The area from 5000 cm<sup>-1</sup> to 1330 cm<sup>-1</sup> is called functional group region.

The bands in this region are useful in determining the types of functional groups present in the molecule. Each functional group absorbs at a specific position which depend upon the nature of a single bond, d.b. or t.b present in functional group and nature of bonded atoms.

Consider some important functional groups.

$\text{-C-H}$	ALKANES	2950 - 2850
$\text{=C-H}$	ALKENES	3100 - 3000
$\text{≡C-H}$	ALKYNE	3300 - 3300
$\text{-C=C-}$	(AROMATIC RINGS)	1600 - 1450
$\text{-C=C-}$	ALKENE	1680 - 1620
$\text{-C≡C-}$	ALKYNES	2200 - 2100
$\text{C(=O)-H}$	ALDEHYDES	2880 - 2700
$\text{-O-H}$	ALCOHOLS	3650 - 3600
"	Hydrogen bonded (Aldehyde)	3600 - 3200
$\text{>C=O}$	KETONES	1750 - 1700
$\text{C(=O)-OH}$	CARBOXYLIC ACID (BROAD PEAK)	2500 - 3500
$\text{>N-H}$	AMINES	3500 - 3300

SEE ABSORPTION BANDS FROM TEXT BOOK.  
(2) SEE I.R. spectrum from text books.

FINGER PRINT REGION This region extends from  $1300 - 667 \text{ cm}^{-1}$ . It provides set of absorption bands which is characteristic of each compound. Each compound has different <sup>pos. in</sup> fingerprint region. Most of absorption bands in this region are due to bending vibrations. Some stretching vibrations like C-C, C-N, C-O also occur in this region.

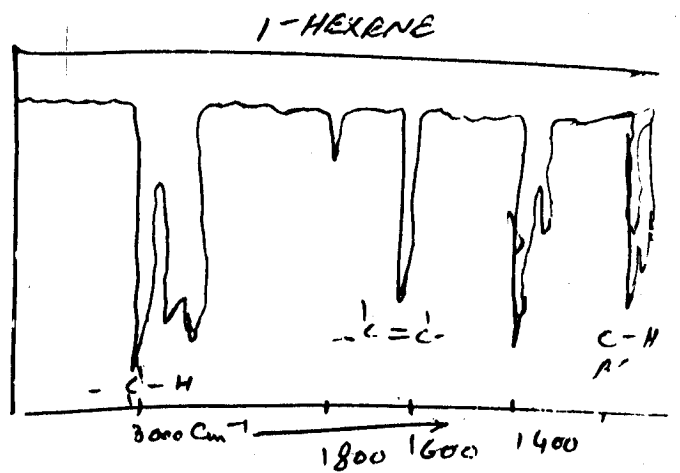
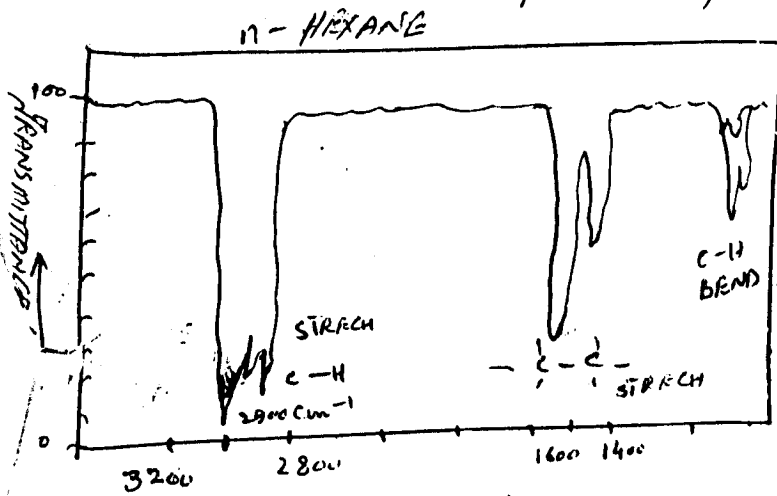
The absence of a particular absorption band in functional group region indicates the absence of that functional group.

INTERPRETATION OF SPECTRA (HYDROCARBONS)  
Inorganic compounds exhibit a peak near  $3000 \text{ cm}^{-1}$  due to C-H stretching vibrations. In n-Hexane C-H vib. occurs at  $3000 \text{ cm}^{-1}$ . While that of 1-Hexene occurs at  $3090 \text{ cm}^{-1}$ . In Hexene there is an additional peak at  $1640 \text{ cm}^{-1}$ . Such a peak is also shown by benzene with a characteristic pattern of peaks at  $700 - 900 \text{ cm}^{-1}$  region (due to C-H bending vibrations).

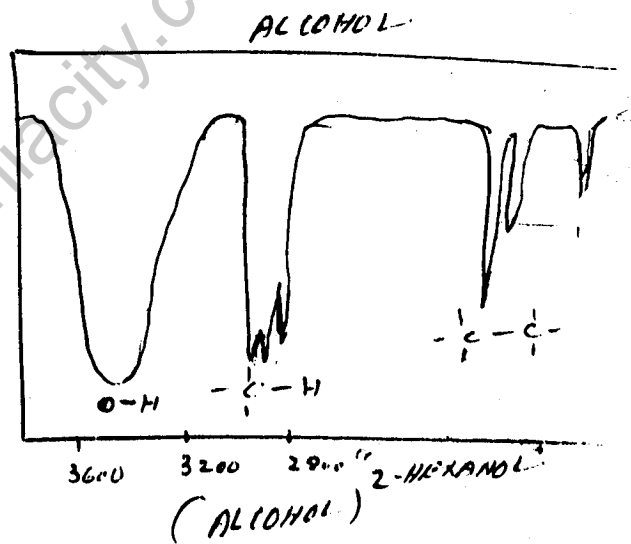
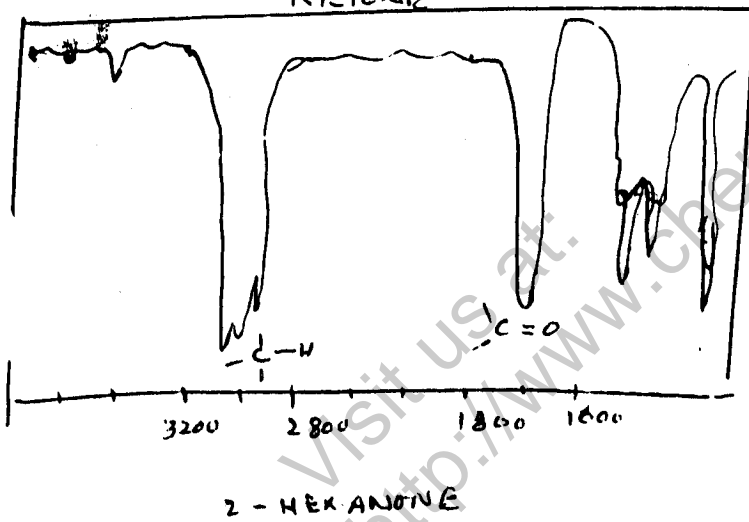
ALCOHOLS Alcohols exhibit a broad peak at  $3400 \text{ cm}^{-1}$  due to hydrogen bonded -OH group. On dilution hydrogen bonding is decreased and an additional peak at  $3600 \text{ cm}^{-1}$ .

ALDEHYDES & KETONES Carbonyl compounds exhibit a v. strong band at  $1750 - 1700 \text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  stretching vibrations. The exact position depends upon the substituents (-H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> etc.). In Aldehydes there is an additional peak at  $2700 \text{ cm}^{-1}$  due to  $\text{C}-\text{H}$  stretching vib. This peak is absent in ketones. It can be used to distinguish between Aldehydes & Ketones. A v. broad peak between  $2500 - 3600$  due to O-H stretching vibration of hydrogen bonded -OH in Carboxylic acids.

The I.R. Spectroscopy can be used to follow the progress of reaction. For example peak at  $1715\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of ketone disappears and a peak at  $3400\text{ cm}^{-1}$  when ketone is converted into sec. Alcohol. Some important spectra are shown for comparison.



NOTE :- 1-HEXENE CAN BE DISTINGUISHED FROM n-HEXANE BY PRESENCE OF PEAK AT  $1640\text{ cm}^{-1}$  DUE TO  $\text{C}=\text{C}$  STRETCHING VIB. "KETONE"



How will you distinguish between following pairs by I.R. Spectroscopy?

- 1) 1-BUTYNE & 2-BUTYNE
- 2) 2-HEXANOL & 2-HEXANONE
- 3) ACETONE & ACETALDEHYDE
- 4) BENZENE & CYCLOHEXANE
- 5) 2-HEXENE & 2-HEXYNE

HINT

$\equiv\text{C}-\text{H}$  STRETCH  
 $\text{O}-\text{H}$  IN ALCOHOL,  $\text{C}=\text{O}$  KETO  
 $\overset{\text{O}}{\parallel}\text{C}-\text{H}$  ALDEHYDE  
 $\text{C}=\text{C}$  STRETCH  
 $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  STRETCH