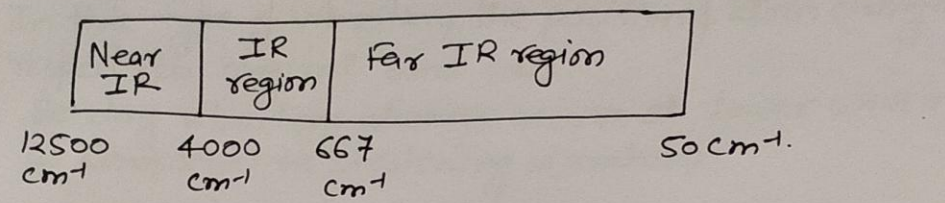
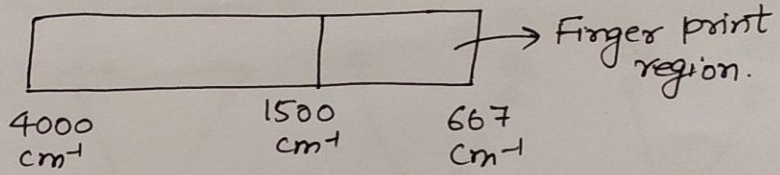
Infra Red Spectroscopy

Organic compounds also absorb electromagnetic energy in the IR region of the spectrum. IR radiation does not have sufficient energy to cause the excitation of electron. It causes atoms and group to atom of organic molecule to vibrate. The IR vibrations are also quantized.



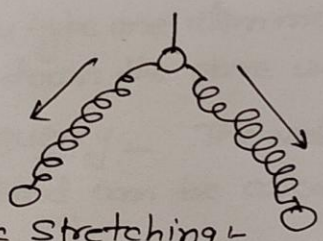


* The bonds between the atoms in a molecule are assumed as spring. When the IR light is passed through the sample the molecule will absorb IR light of suitable frequency and the atoms in the molecule start vibrating.

Types of Fundamental vibrations :-

[1] Stretching Vibrations :-

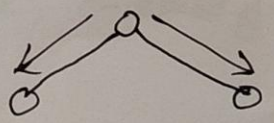
In this type of vibrations the distance between the two atom increases or decreases but atom remain on same bond axis.



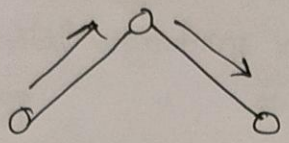
Stretching.

(a) Symmetric Stretching :-

In this type, the movement of atoms with respect to a particular atom in a molecule is in the opposite direction.



(b) Asymmetric stretching :- In these vibrations one atom approaches the central atom while other atom departs from central atom.

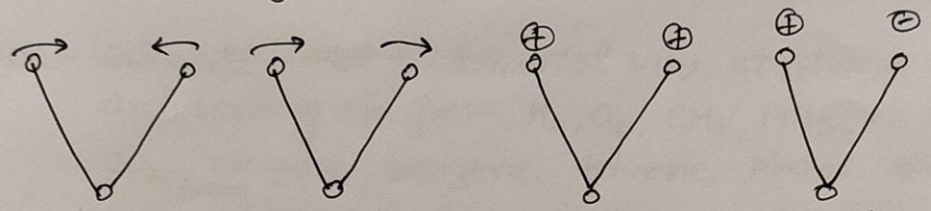


[2] Bending Vibrations :-

In this type of vibrations the positioning atom changes with respect to original bond axis.

* Bending vibrations always occurs at lower wavenumber as compaired to stretching vibrations.

types of bending vibrations :-



Scissoring :- In this type, two atom approach each other.

Rocking :-

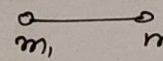
~~Wagging~~ :- In this type the movement of atom take place in the ~~sma~~ same direction.

Wagging :- Two atom move up and below the plane with respect to central atom.

Twisting :- In this type one atom move up the plane while the other move down the plane w.r.t to central atom.

Vibrational frequency :- The value of stretching vibrational frequency of a bond can be calculated by Hooke's law

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$



μ = reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$

K = force constant, c - speed of light.

Total Fundamental Vibrations :-

(a) For linear molecule - like N_2, O_2, CO_2, $CH \equiv CH$ etc.

Total Fundamental vibrations = $3N-5$; N- No of atoms in a molecule.
Stretching " = $N-1$
Bending " = $2N-4$

(b) For Non-Linear molecule :- e.g CH_4, benzene etc.

Total fundamental vibrations = $3N-6$
Stretching " = $N-1$
Bending " = $2N-5$

Ques:- Calculate total fundamental vibs, stretching vibs and bending vibs for :- H_2, O_2, CH_4, NH_3, H_2O CO_2, $CH \equiv CH$, benzene, toluene, phenol. etc.

Ans:- $\rightarrow O_2 \rightarrow N = 2$ $O = O$ linear
total vibs = $3N-5 = 3\times2-5 = 1$
Str " = $N-1 = 2-1 = 1$
bend " = $2N-4 = 2\times2-4 = 0$

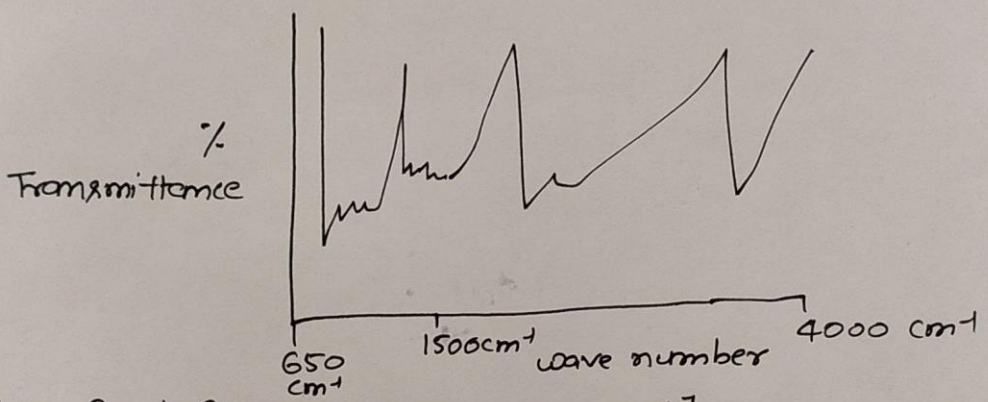
$\Rightarrow$ CO_2, $N = 3$, $O = C = O$ linear
Total vibs = $3N-5 = 3\times3-5 = 4$
Str. " = $N-1 = 3-1 = 2$
Bend " = $2N-4 = 2\times3-4 = 2$

$\Rightarrow$ toluene $\rightarrow C_6H_5CH_3$ $-N = 15$ non linear
Total vibrations = $3N-6 = 3\times15-6 = 39$
Str. " = $N-1 = 15-1 = 14$
Bend " = $2N-5 = 2\times15-5 = 25$

⇒

Compound type	Stretching frequency Range (cm^{-1})
C–C	750 -1100
C=C	1600 -1680
C≡C	2100 -2200
C=O	1690 - 1760
O-H	3610 - 3640
N-H	3300 - 3500

IR spectra :-



Finger Print Region :- [650 - 1500 cm^{-1}]

The region from 4000 - 1500 cm^{-1} is useful for the identification of functional group. This region normally shows absorption due to stretching of functional groups.

The region from 650 -1500 cm^{-1} is usually very complex since both stretching and bending modes give rise to absorption and we get a very complex spectra. We can not predict which signal correspond to which group.

The region from 650 - 1500 cm^{-1} is usually called finger print region because the pattern of absorption in this region are unique to any particular compound, just as a person finger print are unique.