

## 1.2 Infra-red spectroscopy:-

i) Molecular vibration, Hooke's law:-

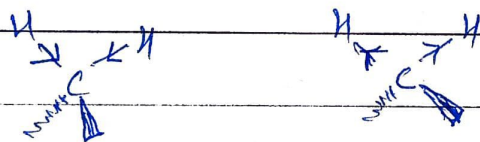
Infrared radiation are passed through organic compounds. vibrational and rotational energies of the molecule get increased. A nonlinear molecule can undergo two kinds of fundamental vibrations.

1) Stretching vibrations:-

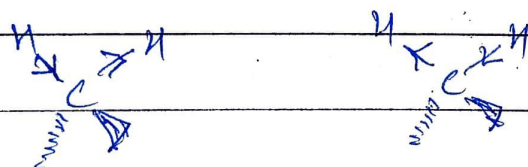
In this type of vibrations the distance between two atoms increase or decrease but atom remain in the same bond axis.

Stretching vibration are of two types

i) Symmetric stretching:-



ii) Asymmetric stretching:-



2)

2) Bending vibrations:-

In this type of vibrations, the positions of the atoms change with respect to the original bond axis. Bending vibrations, also called as deformations, are of two types.

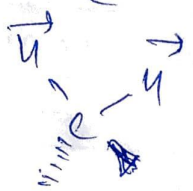
1) In plane bending vibrations

These are of two types.

i) Scissoring :- Two atoms approach each other (change in angle)



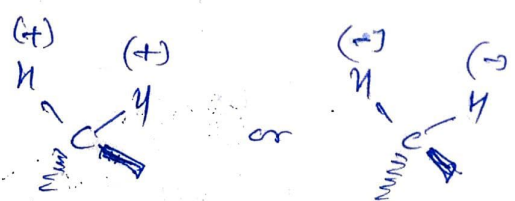
ii) Rocking :- Two atoms move in the same direction. (no change in angle)



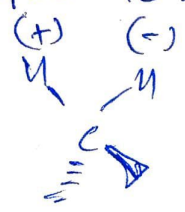
2) Out of plane bending vibrations

There are of two types.

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



ii) Twisting :- One of the atoms move up the plane while the other move down the plane with respect to the central atom.



(+) & (-) indicate movement of bonds perpendicular to the plane of page.

Bonding vibrations are more as compared to stretching vibrations & require lesser energy.

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\* HOOK'S LAW'S -

The value of stretching vibrational frequency of a bond can be calculated by the application of HOOK'S LAW which is expressed as

$$\bar{\nu} \text{ (wave number)} = \frac{1}{2\pi c} \sqrt{\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass}$$

$m_1, m_2$  are masses of two atoms

$k$  - force constant (dyn/cm)

$c$  - velocity of light ( $2.998 \times 10^{10}$  cm/sec)

## Fingerprint region:-

~~It is not~~

The region between 1500-667 cm<sup>-1</sup> is called fingerprint region because every compound has unique absorption pattern in this region. The fingerprint region contains many absorption bands caused by bending vibrations as well as absorption bands caused by C-C, C-O, & C-N stretching vibrations.

## Functional group region

The region bet<sup>n</sup> 4000-1500 cm<sup>-1</sup> is called functional group region.

### Examination of the functional group regions

- A) 3600-3200 cm<sup>-1</sup> :- This region shows -OH, NH<sub>2</sub> & -NH group in the comp. The ≡C-H stretching also shows a medium band near-3300 cm<sup>-1</sup>.
- B) 3200-3000 cm<sup>-1</sup> :- Absorption due to =C-H stretch & A<sub>2</sub>-H stretching.
- C) 3000-2500 - The absorption due to C-H stretching of CH<sub>2</sub> & CH<sub>3</sub> groups occurs this region.  
3000-2500 cm<sup>-1</sup> - shows -O-H stretch of carboxylic acid. Two weak bands at 2720 cm<sup>-1</sup> & 2820 cm<sup>-1</sup> are most characteristic of C-H stretching in aldehyde.



d)  $2300-2100 \text{ cm}^{-1}$  :

In this region alkynes, cyanides, cyanates & isocyanates give absorption.

The  $\text{C}\equiv\text{C}$ - stretching bet<sup>n</sup>.  $2140-2100 \text{ cm}^{-1}$

$\text{C}\equiv\text{N}$  stretching.  $2260-2200 \text{ cm}^{-1}$

Isocyanate  $-\text{N}\equiv\text{C}$  stretch.  $2280-2250 \text{ cm}^{-1}$

e)  $1900-1700 \text{ cm}^{-1}$  :- strong band due to  $\text{C}=\text{O}$  stretching in aldehyde, ketone, carboxylic acid, amide, ester & lactone occurs in this region

Anhydride -  $1850-1740 \text{ cm}^{-1}$ .

Amide -  $1700 \text{ cm}^{-1}$ .

f)  $1700-1600 \text{ cm}^{-1}$  :- Monosubstituted olefins absorb near  $1640 \text{ cm}^{-1}$ , Disubstituted & trisubstituted olefins absorb near  ~~$1670 \text{ cm}^{-1}$~~   $1740-1670 \text{ cm}^{-1}$ .

g)  $1650-1515 \text{ cm}^{-1}$  :- primary and secondary amides & a few lactam display band in the region  $1650-1515 \text{ cm}^{-1}$ .



### iii) Interpretation of IR spectra of simple organic compounds.

(1)	C-H stretching of methyl group - (alkane)	2850 - 2970
(2)	C-H stretching of alkene	<del>2962 &amp; 2872</del> <sup>3010 - 3095</sup> <del>3030</del> $\text{cm}^{-1}$
(3)	C-H stretching of alkyne	<del>3300</del> $\text{cm}^{-1}$ <span style="float: right;">1610 - 1680 <math>\text{cm}^{-1}</math></span>
(4)	C=C stretching of alkene.	1600 - 1400 $\text{cm}^{-1}$ .
(5)	C≡C stretching of alkyne	2100 - <del>2260</del> $\text{cm}^{-1}$ .
(6)	C=O stretching of	C≡N - 2110 - 2260 $\text{cm}^{-1}$
	a) primary alcohol	~ 1050 $\text{cm}^{-1}$
	b) secondary alcohol	~ 1100 $\text{cm}^{-1}$
	c) tertiary alcohol	~ 1150 $\text{cm}^{-1}$
	d) ester.	~ 1200 $\text{cm}^{-1}$
	e) acid.	~ 1200 $\text{cm}^{-1}$
(7)	C-H stretch of aldehyde.	<del>29</del> 2720 & 2850 $\text{cm}^{-1}$
(8)	O-H stretch of alcohol, phenol	3300 - 3600 $\text{cm}^{-1}$ .
	acid.	2500 - 3000 $\text{cm}^{-1}$ .
(9)	C≡N stretching.	(2250) $\text{cm}^{-1}$
(10)	C=O stretch.	
	Benzaldehyde, Acetaldehyde	1750 $\text{cm}^{-1}$ & 1720 $\text{cm}^{-1}$
	ester - methyl benzoate	1735 - 1750 $\text{cm}^{-1}$ .
	Benzoic Acid.	1700 - 1720 $\text{cm}^{-1}$
	Ketone Acetone,	1715 - 1700 $\text{cm}^{-1}$ .
	Acetophenone	
	N-H	3300 - 3500 $\text{cm}^{-1}$

① C-H stretching Aromatic comp  
 alkane - 2960, 2870 cm<sup>-1</sup> C-H str - 14 3030  
 alkene - 3030 cm<sup>-1</sup>  
 alkyne - 3300 - 2900 cm<sup>-1</sup>

② C-O - stretch phenol C-O str  
 primary-alcohol - 1050 cm<sup>-1</sup> 1200 cm<sup>-1</sup>  
 secondary-alcohol - 1100 cm<sup>-1</sup>  
 tertiary alcohol - 1150 cm<sup>-1</sup>

③ -OH stretch - 3300 - 3600 cm<sup>-1</sup> acid - 3000 - 2500 cm<sup>-1</sup>

④ C=C str - 1500, 1600,

⑤ C=O stretch of ketone - 1715 cm<sup>-1</sup> - CC(=O)CC

C1=CC=CC=C1 - C-Cl - 1700 cm<sup>-1</sup>

Acetyl Aldehyde CC(=O)C=O 1740 - 1720

C-H str 2720, 2828 cm<sup>-1</sup>

Benzene 1700 cm<sup>-1</sup>

C-H - 2720, 1828 cm<sup>-1</sup>

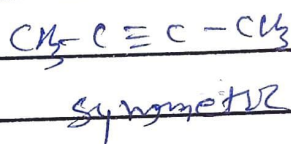
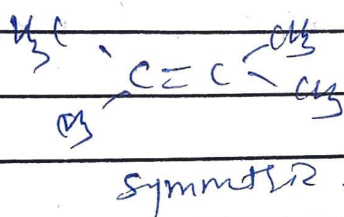
C=C 1602, 1493, 1455 cm<sup>-1</sup>

Benzocacetone - CC(=O)C1=CC=CC=C1 broad  
 -OH - 2500 cm<sup>-1</sup>  
 C=O - 1711 cm<sup>-1</sup>

C=C str of alkene 1635 cm<sup>-1</sup>  
 C≡N - 2250 cm<sup>-1</sup>

# condition for absorption.

only those bands that have a dipole moment that changes as a function of time are capable of absorbing infrared radiation. Symmetric bonds, such as those of  $H_2$  or  $Cl_2$ , do not absorb infrared radiation. Symmetric A. bond must present an electrical dipole that is changing at the same frequency as the incoming radiation for energy to be transferred.



$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$C \equiv C$	$C = C$	$C - C$
2150	1650	1200 $cm^{-1}$

← Increasing  $k$

$C-H$	$C-C$	$C-O$	$C-Cl$	$C-Br$	$C-I$
3000	1200	1100	750	600	500 $cm^{-1}$

↑ Increasing  $\mu$ .

C-H stretching  
-300

C-H bending  
1340  $cm^{-1}$



$$c = c = \bar{v} = 4.12 \sqrt{\frac{k}{\mu}}$$

$$k = 410 \times 10^5 \text{ dynes/cm}$$

$$\mu = \frac{12 \times 12}{12 + 12} = 6$$

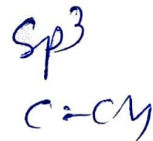
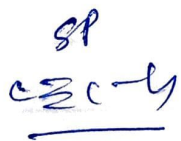
$$4.12 \sqrt{\frac{410 \times 10^5}{6}} = 1682 \text{ cm}^{-1} \text{ calcd.}$$

$$\bar{v} = 1650 \text{ cm}^{-1} \text{ (expt)}$$

$$\epsilon_{\mu} =$$

$$= 4.12 \sqrt{\frac{5 \times 10^5}{0.923}} = 3032 \text{ cm}^{-1} \text{ calcd.}$$

$$\bar{v} = 3000 \text{ cm}^{-1} \text{ expt.}$$



3300 cm<sup>-1</sup>

3100 cm<sup>-1</sup>

2900 cm<sup>-1</sup>



① Ethane  $\text{C}_2\text{H}_6$

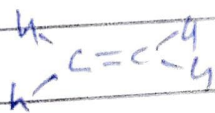


Ethane show following IR. bands

① -C-C stretching weak band shows at  $1100-1300 \text{ cm}^{-1}$ .

② C-H stretching of  $\text{CH}_3$  group appears at  $2850-2970 \text{ cm}^{-1}$ .

② Ethene  $\text{C}_2\text{H}_4$



① =C-H stretching absorption band appears at  $3030 \text{ cm}^{-1}$

② C=C stretching absorption band appears at  $1610-1680 \text{ cm}^{-1}$ .

③ Ethyne  $\text{C}_2\text{H}_2$

$\text{C}\equiv\text{C}$  stretch -  $2210 \text{ cm}^{-1}$

$\text{C}\equiv\text{C}-\text{H}$  stretch -  $3300 \text{ cm}^{-1}$ .

④ Benzene



$\text{A}\text{E}-\text{H}$  stretching -  $3030 \text{ cm}^{-1}$ .

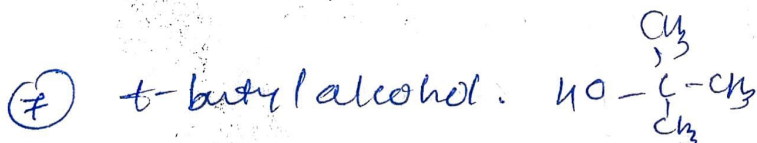
$\text{C}=\text{C}$  stretch -  $1450, 1500, 1600 \text{ cm}^{-1}$ .



- ① C-H stretch 2850 & 2970  $\text{cm}^{-1}$
- ② C-C stretch 1100-1300  $\text{cm}^{-1}$
- ③ C-O stretch 1100  $\text{cm}^{-1}$
- ④ O-H stretch 3200-3600  $\text{cm}^{-1}$ .



- ① C-H stretch 2850 & 2970  $\text{cm}^{-1}$ .
- ② C-C stretch 1100-1300  $\text{cm}^{-1}$ .
- ③ C-O stretch 1050  $\text{cm}^{-1}$
- ④ O-H stretch 3200-3600  $\text{cm}^{-1}$ .



- ① C-H stretch - 2850-2970  $\text{cm}^{-1}$
- ② C-O stretch 1150  $\text{cm}^{-1}$
- ③ O-H stretch 3200-3600  $\text{cm}^{-1}$ .




- ① Aromatic C-H stretch - 3030  $\text{cm}^{-1}$ .
- ② C=C stretch 1445, 1500, 1600  $\text{cm}^{-1}$
- ③ C-O stretch 1200  $\text{cm}^{-1}$ .
- ④ O-H stretch 3200-3600  $\text{cm}^{-1}$ .



9 Acetone  $\text{CH}_3\text{-CO-CH}_3$  :-

①  $\text{C}=\text{O}$  stretch  $1715 \text{ cm}^{-1}$ .

②  $\text{C-H}$  stretch -  $2850$  &  $2970 \text{ cm}^{-1}$ .

10 Acetophenone 

①  $\text{C-H}$  stretch -  $2850$  &  $2970 \text{ cm}^{-1}$

②  $\text{C}=\text{O}$  stretch -  $1700 \text{ cm}^{-1}$ .

③ <sup>Aromatic</sup>  $\text{C}=\text{C}$  stre  $1600, 1500, 1600 \text{ cm}^{-1}$ .

④  $\text{A}_2\text{-H}$  stretch  $3030 \text{ cm}^{-1}$

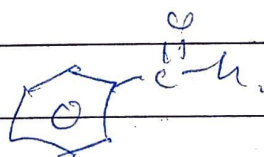
⑤  $\text{C-H}$  bend  $690$  &  $710 \text{ cm}^{-1}$ .

11 Acetaldehyde  $\text{CH}_3\text{-C(=O)-H}$

①  $\text{C-H}$  stretch -  $2850$  &  $2970 \text{ cm}^{-1}$

②  $\text{C}=\text{O}$  stretch  $1720 \text{ cm}^{-1}$ .

③  $\text{C-H}$  stretch -  $2720$  &  $2820 \text{ cm}^{-1}$ .

12 Benzaldehyde 

①  $\text{C}=\text{C}$  stre  $1600, 1500$  &  $1600 \text{ cm}^{-1}$

②  $\text{A}_2\text{-H}$  stretch  $3030 \text{ cm}^{-1}$

③  $\text{C}=\text{O}$  stretch  $1700 \text{ cm}^{-1}$

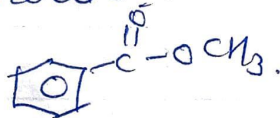
④  $\text{C-H}$  stretch aldehyde  $2720$  &  $2820 \text{ cm}^{-1}$

13) Benzoic acid



- 1) C=C stretch 1400, 1500 & 1600 cm<sup>-1</sup>
- 2) A<sub>2</sub>-H stretch - 3030 cm<sup>-1</sup>
- 3) C=O stretch - 1700 cm<sup>-1</sup>
- 4) C-O stretch 1200 cm<sup>-1</sup>
- 5) O-H stretch 3000-2500 cm<sup>-1</sup>

14) Methyl benzoate:-



- 1) Asymmetric C=C - 1400, 1500, 1600 cm<sup>-1</sup>
- 2) A<sub>2</sub>-H stretch 3030 cm<sup>-1</sup>
- 3) C=O stretch 1710 cm<sup>-1</sup>
- 4) C-O stretch 1200 cm<sup>-1</sup>
- 5) C-H stretch 2800 & 2970 cm<sup>-1</sup>

15) Phenyl cyanide



- 1) Asym C=C - 1600, 1500, 1400 cm<sup>-1</sup>
- 2) A<sub>2</sub>-H - 3030 cm<sup>-1</sup>
- 3) C≡N stretch 2200 cm<sup>-1</sup>