

## ER Measurement of the IR spectra using KBr pellet method

Aim:- Identifying organic compounds by comparing the spectrum of unknown compounds with the reference spectrum

Learning to identify different functional groups of unknown substances

Theory:- Spectroscopy is the study of electromagnetic radiation (as a function of wavelength & frequency of radiation) that is absorbed by organic/inorganic molecule.

i) Other name for IR spectroscopy is vibrational spectroscopy.

\* Total number of vibrations in non linear molecules

$$= 3N - 6 \quad N \rightarrow \text{Total number of atoms present}$$

\* Total number of vibrations in a linear molecule

$$= 3N - 5 \quad N \rightarrow \text{Total number of atoms present}$$

## TR spectroscopy applications

- Structural elucidations
- Determination of purity
- Study of chemical reaction
- Tautomerism
- Geometrical isomerism
- Presence of moisture / water in a sample

When the frequency of IR radiation is equal to the natural frequency of vibration, the molecule absorbs IR radiation.

Frequency of vibration can be calculated by Hooke's law

→ wavenumber

→ frequency

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{or} \quad v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \bar{v}_c = \frac{v}{c}$$

→ Vibrational quantum number

$$u = m_1, m_2 \rightarrow \text{reduced mass}$$

$$m_1 + m_2$$

$$\text{Energy of molecule} = \text{Rotational energy} + \text{Vibrational energy} + \text{Electronic energy}$$

Only if dipole moment of molecule is changing it is considered to be active

$$E_v = \left( \frac{v' + 1}{2} \right) h\nu$$

Not all rotational bands display bands in IR spectrum.  
Only polar bands do (IR active).

Stretching vibrations  $\rightarrow$  symmetric stretching  
 $\rightarrow$  asymmetric stretching

Bending vibrations  $\rightarrow$  In plane  $\rightarrow$  Scissoring  
 $\rightarrow$  rocking  
Out of plane  $\rightarrow$  twisting  
 $\rightarrow$  wagging

$$\text{wavelength} = \frac{1}{\text{wavenumber}}$$

### KBr pellet method

- It works on property that alkali halides become plastic when subjected to pressure and form sheet that is transparent in infrared region.

### Features of IR spectra

- Absorption spectrum is presented as percentage transmittance ( $\% T$ ) vs wavenumber ( $\bar{\nu}$ )
- Two regions of spectra:
- Fundamental group region (FGR),  $4000\text{cm}^{-1}$  to  $1500\text{cm}^{-1}$
- Finger print region (FPR),  $1500\text{cm}^{-1}$  to  $400\text{cm}^{-1}$

Nature of spectral bands (intensity and shape)  
Strong, medium, weak, Broad, narrow

## Interpretation of spectra

- Doublet and amides  $\rightarrow 3200\text{cm}^{-1}$  to  $3100\text{cm}^{-1}$
- Before assigning amide check for carbonyl "concern"
- Peak at  $3600\text{cm}^{-1}$   $\rightarrow$  hydroxyl peak
- Line at  $3000\text{cm}^{-1}$  is useful as  $> 3000\text{cm}^{-1}$  alkenes  
 $< 3000\text{cm}^{-1}$  alkane
- peak at  $2200\text{cm}^{-1}$  to  $2050\text{cm}^{-1}$  presence of triple bond  $\rightarrow \text{C}\equiv\text{N}$  or  $\text{C}\equiv\text{C}$
- carbonyl  $\text{C}\equiv\text{O}$   $\rightarrow 1650 - 1830\text{cm}^{-1}$
- Terminal have a characterisee C-H stretch around  $2800\text{cm}^{-1}$  like  $\text{Ph}-\text{C}\equiv\text{C}-\text{H}$

Materials Required: Mortar & Pestle, KBr Press Disc, Press load, Forceps, Spatula, Anhydrous KBr, Anhydrous sample

Procedure: Clean the apparatus properly using ethanol. Ethanol is used as it does not last. Since we do not want any impurities (as it gives unwanted peaks in spectrum) we use ethanol for cleaning.

Add a spatula of anhydrous KBr in a mortar and grind it using pestle into powder ( $10''$ ) both mortar and pestle of 121.8

Till it gets converted to powder form.

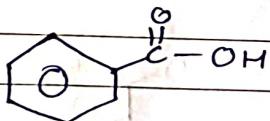
Make a thin transparent pellet using this fine powder.

Perform a background run using the IR spectrophotometer without any sample in it. We do this to eliminate IR peaks of active species in the air. (Background correction)

Put the pellet in holder and place it in spectrophotometer. Now generate the IR spectrum of the loaded sample.

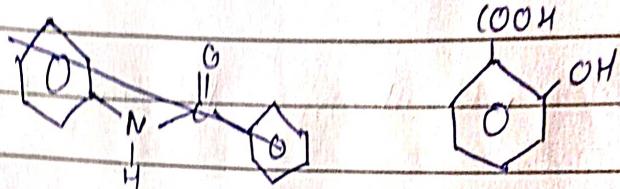
Sample 1

Benzene acid



Functional group	Type of peak	Value of peak
C-H	Weak	3057 cm <sup>-1</sup>
C=O	Strong	1720 cm <sup>-1</sup>
C=C	Medium	1598 cm <sup>-1</sup>
C-O	Medium	1186 cm <sup>-1</sup>
C-H	Medium	730 cm <sup>-1</sup>

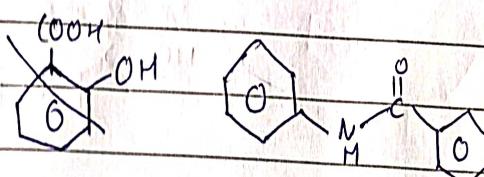
Samp. 1 2

Salicylic acid  
Benzanilide

Functional group	Type of Peak	Value of Peak
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1) OH- stretch	Broad	3736 cm <sup>-1</sup>
2) C-H (Aromatic)	Weak	3243 cm <sup>-1</sup>
3) C=C (Aromatic)	Strong, sharp	1613 cm <sup>-1</sup>
4) C=O	Strong, sharp	1659 cm <sup>-1</sup>
5) C-O (Asymmetric)	Strong	1484 cm <sup>-1</sup>
6) C-O (Symmetric)	Strong	1446 cm <sup>-1</sup>
7) $\pi(C-H)$ (out of plane)	Sharp, strong	759 cm <sup>-1</sup>

Samp. 1 3

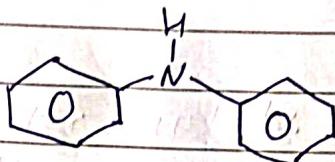
Benzanilide  
Salicylic acid

Functional group	Type of peak	Value of peak
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1) N-H Stretch	Medium	3350 cm <sup>-1</sup>
2) Aromatic (C-H)	Medium	3054 cm <sup>-1</sup>
3) Aromatic (C=C)	Strong	1597 cm <sup>-1</sup>
4) aromatic (C=O)	Strong	1659 cm <sup>-1</sup>
5) C-N stretch, Symmetric	Strong	1080 cm <sup>-1</sup>
6) C-N stretch, Asymmetric	Strong	1030 cm <sup>-1</sup>
7) $\pi(C-H)$ out of plane	Strong	759 cm <sup>-1</sup>

Sample 4

Diphenylamine



Functional group

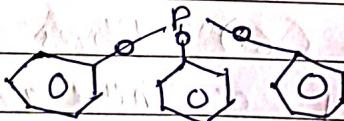
Type of peak

Value of peak

1) N-N (Asymmetric)	medium, sharp	$3408 \text{ cm}^{-1}$
2) N-H symmetric	strong, sharp	$3385 \text{ cm}^{-1}$
3) (=C-H)	broad, medium	$3041 \text{ cm}^{-1}$
4) C=C	strong, short	$1597 \text{ cm}^{-1}$
5) C-N	medium, sharp	$1320 \text{ cm}^{-1}$
6) $\pi(\text{C-H})$ out of plane	sharp, strong	$750 \text{ cm}^{-1}$

Sample 5

Triphenylphosphite



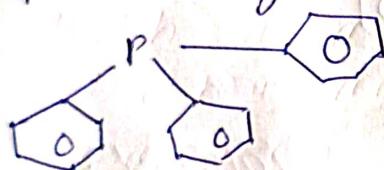
Functional group

Type of peak

Value of peak

1) C=C - H	medium	$3050 \text{ cm}^{-1}$
2) C=C (Asymmetric)	sharp	$1591 \text{ cm}^{-1}$
3) C=C (Symmetric)	sharp	$1484 \text{ cm}^{-1}$
4) O-P	long, sharp	<del><math>1312 \text{ cm}^{-1}</math></del>
5) $\pi(\text{C-H})$ out of plane bending	strong, sharp	$748 \text{ cm}^{-1}$
6) C-O	sharp, strong	$1484 \text{ cm}^{-1}$

Sample analysis (6) Rhos Triphenylphosphine  
 $\therefore$  There are 5 types of functional groups to be studied in this molecule



### Functional group

- 1)  $C=C-H$
- 2)  $C=C$  asymmetric
- 3)  $C-P$
- 4)  $C=C$  asymmetric
- 5)  $\pi(C-H)$  out-of-plane

### Type of peaks

medium

sharp

long

sharp

sharp, strong

### Value of peaks

$3066\text{ cm}^{-1}$

$1582\text{ cm}^{-1}$

$1436\text{ cm}^{-1}$

$1475\text{ cm}^{-1}$

$741\text{ cm}^{-1}$

## Precautions

- 1) Powder sample and KBr must be crushed to reduce the particle size. Otherwise, large particles scatter the infrared beam and cause a sloping baseline of spectrum.
- 2) Do not crush the KBr to too finely powder as reduced particle size or fine powder gains moisture from the environment due to its hygroscopic nature and forms the bands in certain IR region.
- 3) If the pellet breaks on removal from the die, this indicates the disk is too thin, caused by too little powder or too much pressure for too long.
- 4) If the disc is not transparent, this can be due to
  - uneven distribution of powder in die
  - too much sample
  - too much KBr
  - poorly dispersed sample
  - water in disk
  - pressed at low pressure or for a short time

## Conclusion:-

We compared IR spectrum of 5 samples with reference data through the peaks which were there in IR spectrum we got the major groups

- Samples were
- 1) Benzoic acid
  - 2) Benz anilide
  - 3) Salicylic acid
  - 4) Diphenyl amine
  - 5) Triphenyl phosphine
  - 6) Triphenyl phosphite

If we conclude some common ranges of functional groups as :- approximately

CH (stretch) aromatic	$\approx 3050 \text{ cm}^{-1}$
C=O (estretch) aromatic	$\approx 1600 \text{ cm}^{-1}$
C=C aromatic	$\approx 1600 \text{ cm}^{-1}$
C-O stretch asymmetric	$\approx 1500 \text{ cm}^{-1}$
C-O stretch symmetric	$\approx 1400 \text{ cm}^{-1}$
$\pi(\text{C}-\text{H})$ out of plane	$\approx 750 \text{ cm}^{-1}$
N-H stretch	$\approx 3300 \text{ cm}^{-1}$
O-H stretch	$\approx 3700 \text{ cm}^{-1}$
=C-H stretch	$\approx 3060 \text{ cm}^{-1}$
C-P stretch	$\approx 1400 \text{ cm}^{-1}$
P-O stretch	$\approx 1300 \text{ cm}^{-1}$
C-N stretch	$\approx 1320 \text{ cm}^{-1}$