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BS-chem 6-sem (Regular)

INFRARED SPECTROSCOPY

and PROBLEMS

(i)

RANGE OF WAVELENGTH, FREQUENCY & ENERGY OF IR

Spectrum:-

The wavelength range = 2.5 to 16 μm

The frequency range = 4000 to 625 cm^{-1}

The energy range = 48 to 7.5 KJ/mol

Units of IR Spectrum:- An IR spectrum is a plot of per cent transmittance (100T) as ordinate against wavelength (μm) or frequency (cm^{-1})

(ii)

RELATION OF WAVELENGTH & FREQUENCY WITH WAVE NUMBER:-

Wavelength, λ in (cm) = 1

Frequency, v = $\frac{\text{velocity of light } (\text{cm/s})}{\text{wave number } (\text{cm}^{-1})}$

Convert 200 cm^{-1} to Hertz:-

$$v = c \times v, 3.0 \times 10^8 \times 200$$

$$= 6.0 \times 10^3 \text{ Hz}$$

ii- 2500 cm^{-1} to micrometer:-

$$\lambda = \frac{1}{\nu} = \frac{1}{2500 \text{ cm}^{-1}} = 4.0 \times 10^{-4} \text{ cm} = 4.0 \text{ nm}$$

iii- $7.5 \mu\text{m}$ to wavenumber:-

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{7.5 \mu\text{m}} = \frac{1}{7.5 \times 10^{-4} \text{ m}} = 1333 \text{ cm}^{-1}$$

→ (iii) for

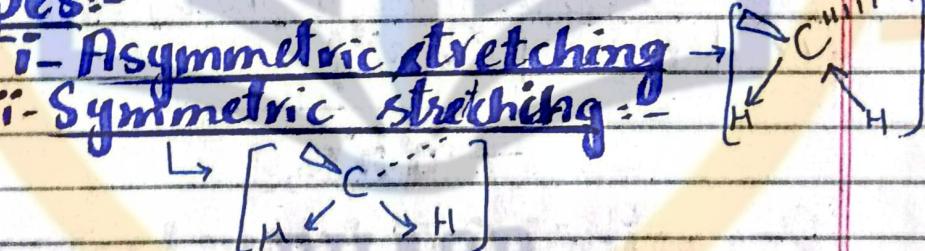
MODES OF FUNDAMENTAL

VIBRATION:-

Modes of vibration are as:-

i- **Stretching vibration:** The movement along bond axis in such a way that inner atomic distance increases or decreases. → No change in dipole moment.

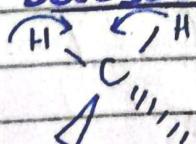
Types:-



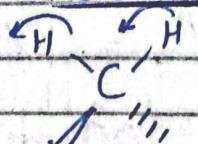
ii- **Bending Vibration:-** Due to change in bond angles with bonds.

Types:-

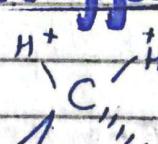
• Scissoring



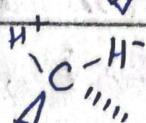
-Rocking



• Wagging



• Twisting:



Modes Of Vibration:-

• In Water:- \rightarrow non linear molecule.
 $3N - 6$

$$= (3 \times 3) - 6, 9 - 6 = 3.$$

Possible modes of vibration in water is **3**.

• In CO_2 : linear molecule

$$3N - 5, = (3 \times 3) - 5 \\ 9 - 5 = 4$$

Possible modes of vibration in CO_2 is **4**.

CONDITION FOR ABSORPTION

OF TR BY MOLECULE:-

A molecule must involve a net charge or dipole moment during its vibration motion in order to absorb IR region.

MOLECULE DON'T ABSORB IN IR:-



H_2, O_2 & N_2 do not absorb in IR region.

VIBRATION OF CO_2 :-

The symmetric stretching vibration of CO_2 , does not

cause change in dipole moment Therefore IR inactive. The asymmetric stretching vibration causes change in dipole moment by it is **IR active**.

→ **viii; p**

ABSORPTION BAND CO. EXHIBIT IN IR SPECTRUM.

The linear triatomic molecule of CO_2 has four fundamental vibration out of which symmetric stretching vibration is IR inactive by 2 scissoring vibration are degenerate. It only exhibited 2 absorption band.

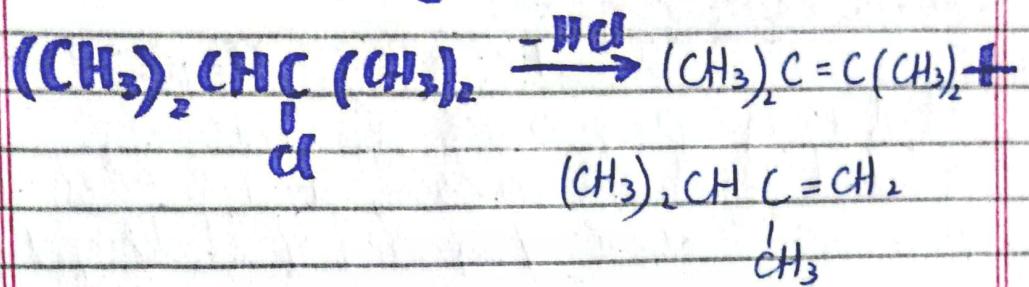
→ **Px p**

ETHENE DON'T SHOW $\text{C}=\text{C}$ STRETCHING BAND, WHEREAS PROPENE

DOES:- Ethene is symmetrical molecule and $\text{C}=\text{C}$ stretching vibration does not involve any change in dipole moment. The change in dipole moment occurs when propene, unsymmetrical molecule is excited. A change in dipole moment during vibration is must for IR absorption.

→ **x p**
E 2 dehydrohalogenation of 2,3-dimethyl-2-chlorobutane lead 2 possible

Products - How they distinguish by IR spectroscopy :-



The symmetrical tetramethylethylene molecule does not show $\text{C}=\text{C}$ stretching vibration absorption, whereas 2,3 dimethyl-1-butene which is unsymmetrical molecule shows $\text{C}=\text{C}$ stretching absorption band at 1640 cm^{-1} . Also shows out of plane bending vibration of $=\text{CH}_2$ at 890 cm^{-1} .

$\sim \text{Q(Xi)}_{80} \sim$

WAVELENGTH & WAVE NO.

of $\text{C}=\text{O}$ group:-

According to Hooke's law:-

$$\bar{v} = \frac{1}{2\pi c} \times \left[\frac{\mu}{m_A - m_B / (m_A + m_B)} \right]^{1/2}$$

$$= \frac{1}{2 \times 3.143 \times 3.0 \times 10^10} \times \left[\frac{10 \times 10^5}{(19.92 \times 10^{-24}) \times 26.56 \times 10^{-24}} \right]^{1/2}$$

$$(19.92 + 26.56) \times 10^{-24}$$

$$\boxed{\text{Wave No.} = 1573 \text{ cm}^{-1} = \bar{v}}$$

$$\text{Wavelength } (\lambda) = \frac{1}{\bar{v}} = \frac{1}{1573 \text{ cm}^{-1}}$$

$$\boxed{\lambda = 6.357 \text{ micrometer}}$$

$\sim \text{Q(Xii)}_{80} \sim$

Why stretching frequency of

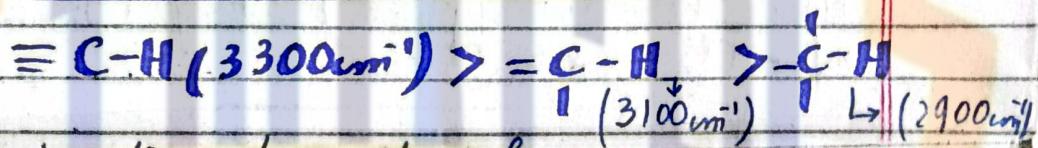
O-D bond is 2600cm^{-1} whereas O-H bond is 3600cm^{-1} - Both have same force constant :-

According to Hook's law, stretching frequencies are inversely related to atomic masses, an increase in mass decreases frequency of stretching absorption.

→ Ques(xiii) part

STRETCHING FREQUENCY OF

CH bond decreases in order:-



The strength of C-H bonds depends on the hybridization of carbon atoms by decreases in order $\text{sp} > \text{sp}^2 > \text{sp}^3$ - Thus stretching frequency decreases in order:-



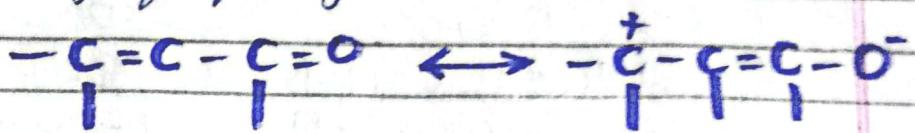
→ Ques(xiv) part

CONJUGATION OF $\text{C}=\text{O}$ with $\text{C}=\text{O}$

Lowers its stretching frequency :-

Conjugation of carbonyl compound ($\text{C}=\text{O}$) with $\text{C}=\text{C}$ increases its single bond character thus decreases its force

constant which results in its lower stretching frequency:-



→ (xv) po

COMPONENTS OF SPECTRO-

PHOTOMETER:-

Three basic components:-

- radiation
- source
- monochromator
- detector.

→ (xvi) po

SOLVENT USED IN IR spectrum:-

The solvent most commonly used in IR are:- $CHCl_3$, CCl_4 & CS_2

Water & ethanol don't used:-

because they dissolve the NaI used for plates, causing fogging on their surfaces. They also absorb strongly in several IR regions.

→ (xvii) po

IMPORTANT REGIONS IN IR spectrum & explain significance:-

The stretching absorption occurs in region



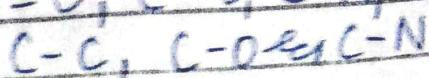
$3700 - 2500 \text{ cm}^{-1}$



$2300 - 2100 \text{ cm}^{-1}$



$1900 - 1600 \text{ cm}^{-1}$

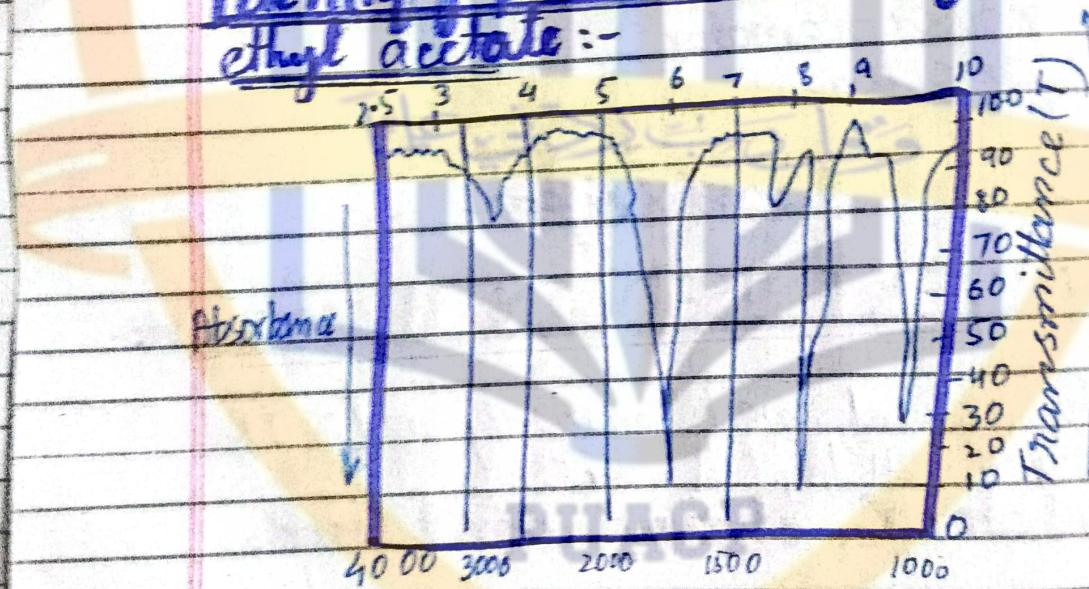


$1300 - 600 \text{ cm}^{-1}$

Region from $4000 - 1600 \text{ cm}^{-1}$ Known as functional group region from $1600 - 600 \text{ cm}^{-1}$ Known as finger print region bcz due to variety & complexity of bending vibration

not (XVIII) nor

Identify peaks A-E of ethyl acetate :-



Peak	Waveno. (cm^{-1})	
A	(2900 cm^{-1})	C-H stretching
B	(1740 cm^{-1})	C=O "
C	(1375 cm^{-1})	CO-CH ₃ "
D	(1230 cm^{-1})	Ac-O "
E	(1050 cm^{-1})	CH ₂ O "

Wavelength

DIFFERENCE

Near infrared

The region of electro-magnetic spectrum from 0.8 to 2.5 μm called **near infrared**.

Far infrared

The region of electro-magnetic spectrum from 16 to $10^3 \mu\text{m}$ called **far infrared**.

IR active vibration

A vibration that causes a change in dipole moment result in absorption of IR radiation called **IR-active vibration**.

IR-inactive vibration

The vibration that does not cause change in dipole moment will not absorb the IR radiation called **IR-inactive vibration**.

Fundamental vibration:

Transition from zero to 1st excited level called **fundamental vibration**. ($v_0 \rightarrow v_1$)

Overtones:

Transition from 0 to second excited level or 0 to 3rd excited level called **overtones**.
 $v_0 - v_2, v_0 - v_3$

Combination band

Two fundamental frequencies same interact to give combination of different bands arises when absorption by molecules

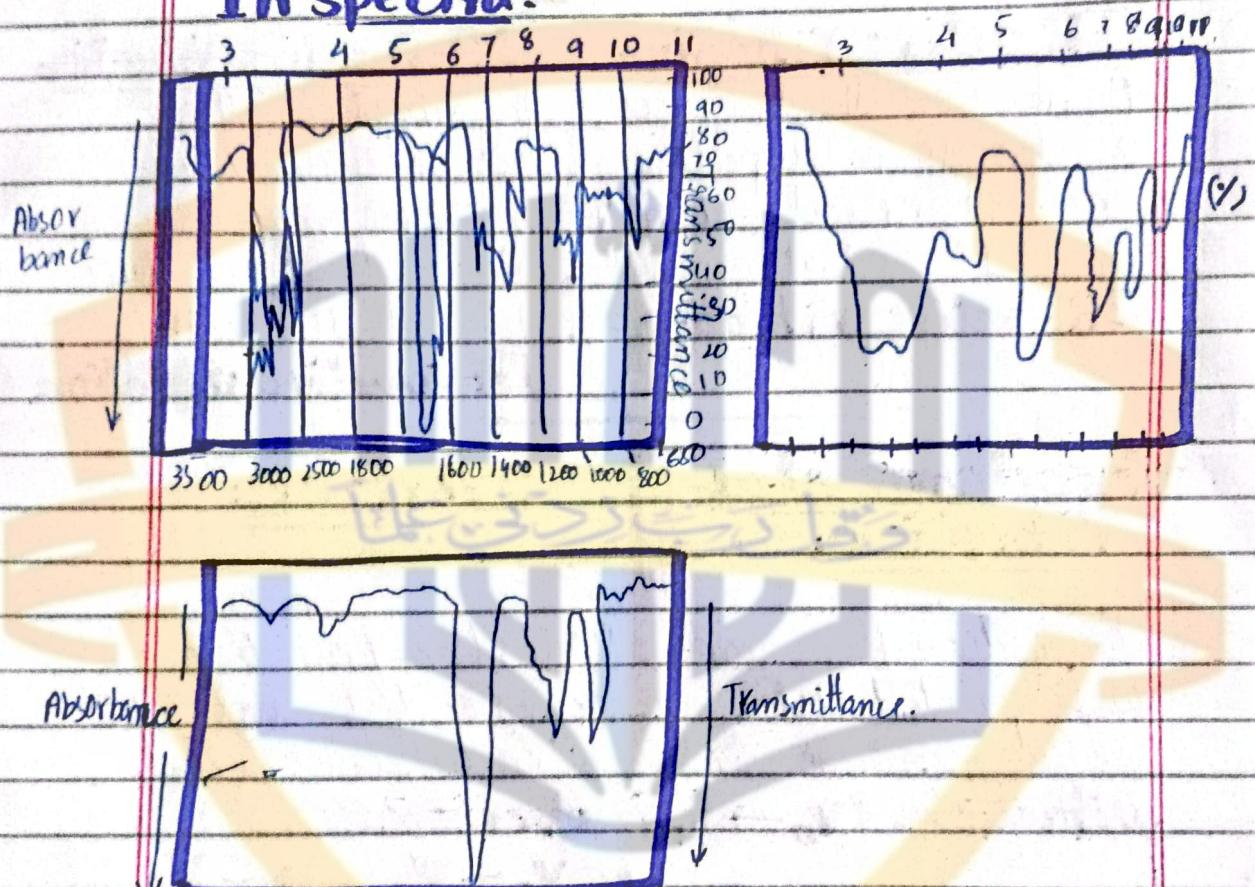
Difference band

Arises when molecule already existing in excited vibrational state absorb enough additional radiant energy to be excited

results in excited 2 fundamental vibration ($\nu_1 + \nu_2$) to another vibration level of different vibration mode ($\nu_2 - \nu_1$)

~~($\nu_1 + \nu_2$)~~

Match compound $\text{CH}_3\text{COOCH}_3$, $\text{CH}_3\text{CH}_2\text{CHO}$ & $\text{CH}_3\text{CH}_2\text{COOH}$ with IR spectra:-



A very strong band b/w 1750 & 1700cm^{-1} for C=O stretching present in all spectra. A double bond b/w 2850 - 2700cm^{-1} in spectrum (a) is characteristics of an aldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$). A very broad band from 3500 to 2500cm^{-1} in spectrum (b) is characteristics of carboxylic acid ($\text{CH}_3\text{CH}_2\text{COOH}$). The spectrum (c) with no characteristics

feature is left for ketone (CH_3COCH_3)

~Q(Xxi)~

Liquid film IR-spectrum of acetylacetone shows absorption band - Assign group vibrations of these bands:-

Acetylacetone exists as a keto-enol equilibrium mixture. In the enolic form which is about 85% an intramolecular hydrogen bond involving O-H \leftrightarrow C=O groups, is formed. It shows a broad O-H stretching band at $3400-2500\text{cm}^{-1}$ & a broad C=C stretching absorption band at rather lower frequency (1600cm^{-1}). The keto form shows normal C=O stretching absorption at 1710cm^{-1}

~Q(Xxii)~

Match n-hexane, cyclohexane, 1-hexene & 1-hexyne with IR spectra:-

1-Hexyne, a terminal alkyne, shows a strong C-H stretching band at 3300cm^{-1} & sharp medium C≡C stretching band at 2120cm^{-1} in spectrum

(a) - A sharp band at 3090 cm^{-1} (C-H str) and a band at 1640 cm^{-1} (C=C) in spectrum (c) shows that this spectrum belongs to 1-hexene.

Out of remaining two spectra, The spectrum

(b) belongs to n-hexane bcz it shows two C-H bending band in $1470-1370\text{ cm}^{-1}$ region, whereas cyclohexane has only one C-H bending band in this region spectrum (d).

QUESTION

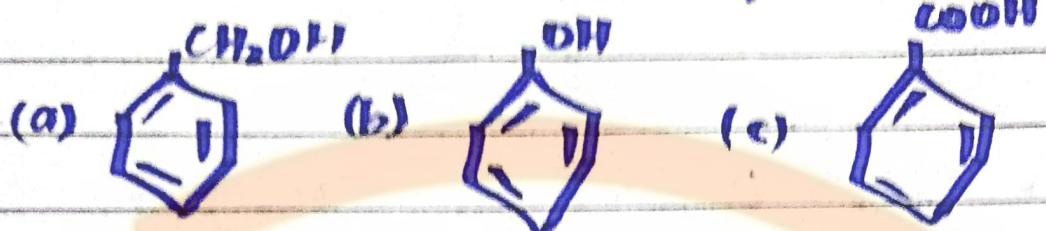
STRUCTURE OF HYDROCARBON

THAT SHOW STRONG ABSORPTION

OPTION:-

The degree of unsaturation suggests that Hydrocarbon C_6H_{12} is either hexene or cyclohexane. The absence of absorptions at 1650 cm^{-1} (C=C stretching) above 3000 cm^{-1} ($=\text{C-H stretching}$) and at 1375 cm^{-1} (methyl C-H bending) rule out hexene. The absorptions at 2920 cm^{-1} , 2840 cm^{-1} & at 1450 cm^{-1} are due to methylene C-H stretching & bending vibrations. The given hydrocarbon is cyclohexane.

Ques (xxiv) :-
The compound is more consistent with IR spectrum:-



(a) Benzyl alcohol - The IR spectrum shows absorption bands for O-H stretching ($3500 - 3100 \text{ cm}^{-1}$) & methylene C-H bending (1460 cm^{-1}) as it lacks the C=O absorption.

DISTINGUISH COMPOUND

ON BASE OF IR spectroscopy :-

n-Hexane

Has two C-H bending absorption in $1470 - 1370 \text{ cm}^{-1}$ region.

cyclohexane

Has only one C-H bending absorption in this region

- 1-Butyne

It shows C=C stretching band at 2120 cm^{-1} .
also give an $\equiv \text{C}-\text{H}$ at $\sim 3315\text{ cm}^{-1}$

2-Butyne

Being symmetrical does not absorb in this region.

CH_3CHO

It shows a doublet blur $2850 - 2700\text{ cm}^{-1}$

CH_3COCH_3

It does not show such doublet but absorb only at $1750 - 1700\text{ cm}^{-1}$

PhCONH_2

It shows two absorption bands in $1700 - 1500\text{ cm}^{-1}$ region characteristics of amides.

PhCH_2NH_2

It shows only one band in this region due to N-H bending vibration.

CH_3NH_2

In dilute soln shows 2 absorption bands, one near 3500 cm^{-1} & other near 3400 cm^{-1}

$(\text{CH}_3)_2\text{NH}_-$

If shows just one band near 3300 cm^{-1}

$(\text{CH}_3)_3\text{N}^-$

It does not absorb in this region

2-Hexanol

It shows broad band in $3400 - 3200\text{ cm}^{-1}$ region

2-hexanone

It shows an intense band

PUNJAB GROUP OF COLLEGES

Name: Roll No:

Class: Section:

Subject: Date:

Student's Signature: Teacher's Signature:

but no absorption in
 $1750 - 1700 \text{ cm}^{-1}$ region

in $1750 - 1700 \text{ cm}^{-1}$

region but no
absorption in $3400 - 3200 \text{ cm}^{-1}$ region.

Cyclo hexanol

It shows C-H stretching
absorption below 300 cm^{-1}

Phenol

It shows C-H
stretching absor-
ption above 3000 cm^{-1}
It would also exhibit
typical aromatic C-H
out of plane bending
absorptions in $900 - 700 \text{ cm}^{-1}$
region.

Note:-

Cyclohexanol & phenol both
exhibit O-H stretching absorption
at $3400 - 3200 \text{ cm}^{-1}$, phenol
being on lower side.

JAZAKALLAH