14th January 2025

ICH 435
APPLIED SPECTROSCOPY

TOPIC: INTRODUCTION

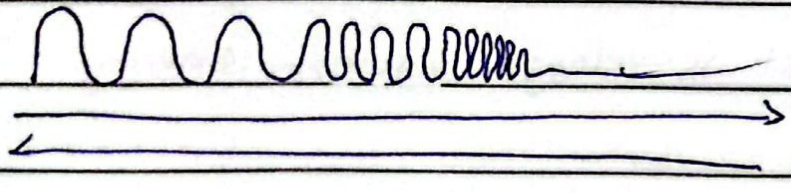
Spectroscopy has to do with light interaction. Techniques that are based on the principle of spectroscopy are numerous.

1 - UV Spectroscopy
2.- IR Spectroscopy
3.- NMR Spectroscopy
4.- Mass spectrometry

Spectroscopy involves the techniques which deals with the study of effect of interaction of electro-magnetics. This provide the basis for sensitive method of detection and quantification of organic matters

EMR (Electromagnetic Radiation)

Radio wave Micro wave visible UV IR X-ray γ-ray



→ Wavelength reduces
← Wavelength increases

Radiation is a form of energy that has both magnetic and chemical properties, hence the name ELECTROMAGNETIC PROPERTIES

EM Properties contains of different (rght, frequency and energy. Energy in EMR is called PHOTON energy and exists in quantum (fixed energy)

Wavelength (λ): Wavelength is defined as the distance between successive peak of electro-magnetic wave.  It is measured in NANOMETER.

Frequency (ν): Frequency is defined as number of successive peaks passing a given point per sec.

$$\nu = \frac{c}{\lambda}$$

ν = frequency λ = wavelength.
c = constant (speed of light)

NB: The higher the ν (frequency) the lesser the ENERGY

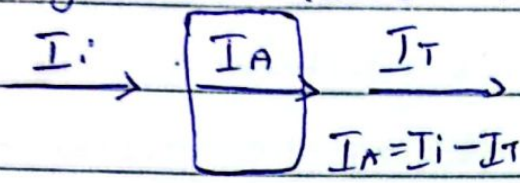
$E = h\nu$ $E = \frac{hc}{\lambda}$ where $\nu = c/\lambda$

RANGE OF ELECTROMAGNETIC SPECTRUM

1) Radio wave: highest wavelength, lowest energy
2) Microwave
3) Infrared
4) Visible region
5) Ultraviolent
6) X-ray
7) γ-ray: Shortest and most Powerful

EFFECT OF LIGHT ON SUBSTANCES

1. Absorption : When light intends with matter adsorption can take place, when there is adsorption of light the intensity of transmitted light is lesser than that of incident light.



Where I_i = Intensity of incident light
I_A = Intensity of Adsorbed light
I_T = Intensity of Transmitted light

NB: When light in UV visible region is adsorped, electronic exitation takes place.

(a) Atomic adsorption
(b) Molecular adsorption

2. Emmission : Emmission takes place where excited atoms returns to its ground state.
Excitation induces emission of light, when the excited compounds returned back to the ground state.

(a) Atomic Emission
(b) Molecular emission

TYPES OF EMISSION

1. Fluorescence : When light is emitted from excited compound in electronic singlet state, it is called FLUORESCENCE.

2. Phosphorescence:- When there is emission from excited electronic tripplet state, it is called phosphorescence.

3. Vibration: When light in the IR region interacts with some compounds, different forms of vibration occurs and it is the basis of IR Spectroscopy.

4. Optical Rotation: When light interacts with some substances, there is an observable change of the face of the incident light.
This is the basis for technologies as

TYPES OF SPECTROSCOPY

(A) Classification Based on Nature of light Radiation that is absorbed or emitted

- UV Visible spectroscopy
- Infrared Spectroscopy
- NMR Spectroscopy (Nuclear Magnetic Resonance)
- Mass Spectrometry
- X-ray spectroscopy
-

(B) Classification Based On Effect Of Light

- Electronic Spectroscopy techniques involvement movement of electron from ground state to excited

- Vibrational spectroscopy
- Rotational spectroscopy (associated with techniques)

(C) Classification Based on Light Adsorption Or Emission.

- Absorption spectroscopy
- Emission Spectroscopy

UV cannot be used when there is no = bond

UV - Visible Spectroscopy

UV visible region of EMR lies within 100nm to 800nm. The spectroscopy techniques carried out within this region is known as Electronic Spectroscopy. There are different electronic translation that is possible when light is incident on a compound.

1. $\sigma \rightarrow \sigma^*$ Translation: This is the translation of electron to bonding sigma orbital to anti-bonding sigma orbital. Any organic Compound with sigma

bond can undergo this type of translation.

2. $n \rightarrow \sigma^*$; Movement of lone pair of electrons to lone pair of light is radiated.

$C - C = \ddot{O}H$

Compounds with Nitrogen, Oxygen

This is translation from lone pair electrons (non-bonding orbital) to anti-bonding sigma orbital. This type of translation is possible in compound with hetero atom with lone pairs e.g Alkylhalides, ROH alcohol, and Amines RNH_2

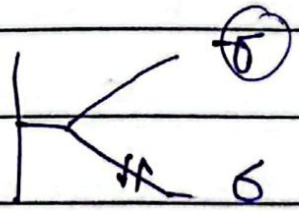
3. $n \rightarrow \pi^*$: possible with

$C - C = C^{-O}$

Compounds with double, triple bond and lone pair.

In Summary :-

1. $\sigma \rightarrow \sigma^*$ Translation
2. $n \rightarrow \sigma^*$ Translation
3. $n \rightarrow \pi^*$ Translation
4. $\pi \rightarrow \pi^*$ Translation



Date : 21/Jan/2025

UV spectroscopy obeys Beer-Lambert's law

Beer And Lambert's Law

* BEER'S LAW : states that the absorption of light is directly proportional to the number of absorbing molecules (Concentration).

$A \propto C$ → (Concentration) K → [Constant]

(Absorbance of light)

* LAMBERT'S LAW : states that the absorption of light through a sample is directly proportional to the thickness of the absorbing medium

$A \propto L$ → (Thickness / path length of the radiation through the sample).

(Absorbance of light)

BEER- LAMBERT'S LAW

This is the combination of Beer's law and lambert law that is the absorbance of light through a sample is directly proportional to the concentration and the path length of the absorbing medium.

ε → (Molar absorptivity)

c → (Molar Concentration)

⇉ [$A = \varepsilon lc$]: it is used when concentration is in mole/dm^3

[A = A% lc] → it is used when concentration is in percentage.

A = (extinction coefficient when L is 1cm)

A = (specific absorptivity)

EXERCISE

EQ Calculate the concentration of an unknown sample if the absorbance is 1.5 at a wavelength of 265 nm, the path-length is 1cm and molar absorptivity is 12.35 $dm^3/mol/cm$ ($dm^3 mol^{-1} cm^{-1}$)

Solution

To calculate the concentration of the unknown sample, we use the Beer-Lambert Law:

$$A = \varepsilon . c . l$$

Where A is the absorbance (1.5)

ε is the molar absorptivity (12.25 $dm^3/mol/cm$).

c is the concentration (unknown, in mol/dm^3)

l is the path length (1 cm).

Rearranging for c: $c = \frac{A}{\varepsilon . l}$

Substitute the values: $c = \frac{1.5}{12.25 \times 1}$

$c = \frac{1.5}{12.25} \approx 0.1224$ mol / dm^3

Final Answer: The concentration of the unknown sample is approximately 0.122 mol/dm³.

2. A drug was analyze with UV spectroscopy. If the specific absorptivity is 5.57 at a wavelength of 291nm and the absorbance of light at that wavelength is 0.557. Calculate the concentration?

Solution

To calculate the concentration, we use the Beer-Lambert law: $A = a \cdot c \cdot l$

Where A is the absorbance (0.557)

a is the specific absorptivity ($5.57 dm^3/g/cm$),

c is the concentration (in g/dm^3),

l is the path length (assume 1cm, unless stated otherwise).

Rearranging for c: $c = \frac{A}{a \cdot l}$

Substitute the values: $c = \frac{0.557}{5.57 \times 1}$

$c = \frac{0.557}{5.57} = 0.1 g/dm^3$

∴ The concentration of the drug is $0.1 g/dm^3$

→ UV light can be used for quantitative determ...

Exercise 3: Hydrocortison Sodium-Phosphate at wavelength of 248 nm. If the absorbance is 0.6 and the specific absorptivity is 353. Calculate the Concentration?

Solution

To calculate the concentration of Hydrocortison Sodium phosphate using the Beer-Lambert law

$$A = a \cdot c \cdot l$$

Where A is the absorbance (0.66),
a is the specific absorptivity (353 $dm^3/g/cm$),
c is the concentration (in g/dm^3)
l is the path length (assume 1 cm, unless stated otherwise)

Rearranging for C: $c = \frac{A}{a \cdot l}$

Substitute the given values: $c = \frac{0.66}{353 \times 1}$.

$$c = \frac{0.66}{353} \approx 0.00187\ g/dm^3.$$

∴ The concentration of Hydrocortisone Sodium Phosphate is approximately $0.00187\ g/dm^3$.

PRINCIPLE OF UV SPECTROSCOPY

→ UV spectroscopy is based on the to absorb UV light at a particular wavelength. According to Beer-Lambert's law, the intensity of the light has a relationship with the concentration of the sample.

This is applied for quantitative and qualitative determination of UV sensitive compound.

UV sensitive compound must have **Chromaphores**

UV SPECTROSCOPY INSTRUMENTATION

1. UV Light Source: [E.g Deuterium Lamp, Quartz halogen light and Tungsten lamb]
2. A Monochromator [It functions to ensure that only UV-light passes through the sample.].
3. Optics [Its function is to split the light]
4. Sample-Bottle [It is the small bottle used to experiment the bottle].
5. Detection: [It detects the intensity]
6. Recorded [involves your data and UV spectrum)

IMPORTANT TERMS

1) CHROMOPHORE : This is a group or a site of the The chemical structure of an organic compound capable of absorbing in the UV-visible region.

Any substance without a chromophore is not UV spectrum sensitive.

Examples of Chromophore

① C=C ② C≡C ③ Aromatic ring ④ C=N

⑤ C=O

* AUXOCHROME : Is any substitute that alters the wavelength or intensity of a chromophore.

Eg OH, -SH, N-O, -O.

* BATHOCHROMIC SHIFT : This is the condition in which there is a shift in the wavelength of absorption from a LOWER wavelength to HIGHER wavelength. The other name is RED SHIFT.

* HYPSOCHROMIC SHIFT : This is the shift in the wavelength of absorption from higher to lower wavelength. [It is also called BLUE-SHIFT].

* HYPERCHROMIC SHIFT: This is a shift in the intensity of absorption from a lower intensity to a higher intensity

*HYPOCHROMIC SHIFT: This is a shift in the intensity of absorption from a higher to the lower intensity of absorption.

APPLICATION OF UV SPECTROSCOPY DETERMINATION

① Detection of Sample or Qualitative? This is because different sample have their own maximum wavelength.

② For Quantitative Determination by applying the Beer-Lambert's law. You can use it to calculate the concentration.

③ To differentiate between isomers. Eg the wavelength maximum will be different for the wavelength maximum for trans isomer will be different from Cis isomer Conjugated Conjugated compound will have a different

When UV light hit a substance : Higher region = fingerprint region
Electron translation

wavelength mass from an unconjugated isomers.

4) For Monitoring reaction kinetics.

Date : 28th January 2025

INFRARED SPECTROSCOPY (IR)

The interaction of infrared region of light with matter leading to molecular vibration or rotation. The infrared region of EMR is having the longer wavelength and a lower frequency than UV visible region.

3 Different Ranges Of IR

1. Far Infra Red - Wavelength 50 - 1000 μm
   Wavenumber 200 - 10 cm^{-1}
2. Middle Infra Red : lies within wavelength 2.5 - 50 μm and within wavenumber 4000 - 200 cm^{-1}
3. Near Infra Red : lies within 0.8 - 2.5 μm and within wavenumber 12500 - 4000 cm^{-1}

NB : 1 and 2 are significant,

IR spectroscopy makes use of IR within the range of 400 cm^{-1} to 4000 cm^{-1} (for Middle infra-red and Near Infrared).

AD Higher to lower $4000cm^{-1}$ $400cm^{-1}$

(IR)

PRINCIPLES OF INFRA RED SPECTROSCOPY

* Electromagnetic Radiation (EMR) between the range of $4000cm^{-1} - 400cm^{-1}$ is passed through the sample
* Absorption of IR causes bond vibration or bond rotation.
* The wavelength of absorption in IR region is characteristics of compounds i.e no two different compounds can have the same absorption. Thus IR spectroscopy is a technique that is useful in detecting the structure and functional group of a compound.

TYPES OF MOLECULAR VIBRATION

Molecules have different electronic energy level that determines the various forms of electron transition that is possible. As explained, UV spectroscopy deals with excitation of electron from ground state to excited state when an appropriate amount of energy in UV region is absorbed.

Similarly, molecules possesses vibrational energy levels and transitional energy levels. When an appropriate energy in IR region is absorbed by a compound there is change from ground state vibrational

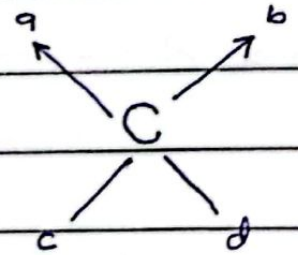
C(=O)–OH → Carboxylic acid

energy level and rotational energy level to a higher level.

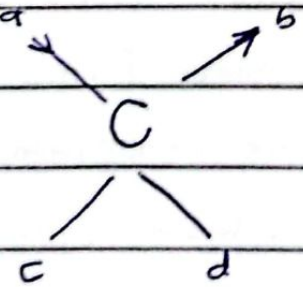
The following are the major types of fundamental vibrations that are of applications in IR spectroscopy.

1. Streching Vibration: Energy required to stretch the bonds between each atom in a molecule lies within a region of $4000cm^{-1} - 1300cm^{-1}$. There are two types of molecular streching vibration.

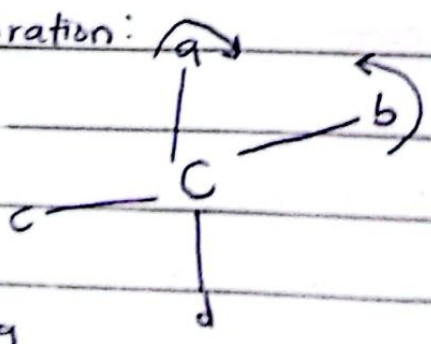
(a) Symmetrical Vibration: Uniform expansion & Compress



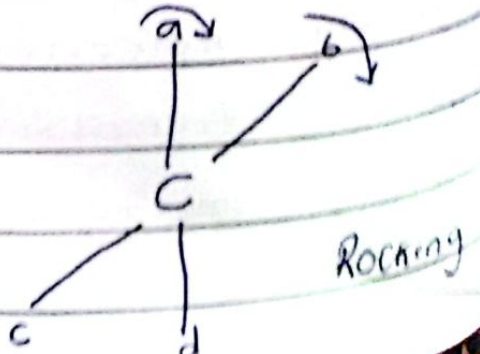
(b) Assymetrical Vibration: Non uniform expansion & compression of bond



2. Bending Vibration: There are four (4) types of bending vibration:

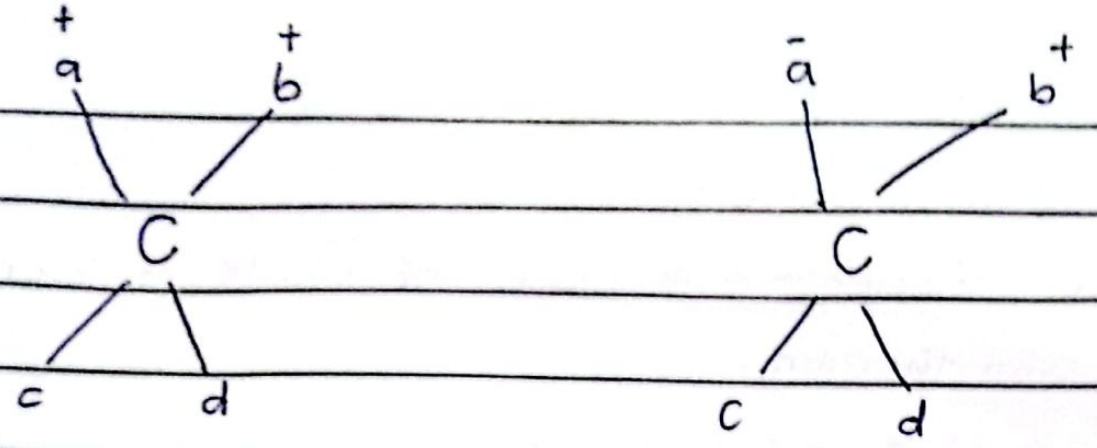


Scissoring



Rocking

Nb: IR can be used for either Organic or Inorganics



Wagging (gang inside and outside) Twisting (in and out)

Vibration Types	Types of Molecule	Group Frequency (cm^{-1})
C-H stretch	Alkene, Alkane e.t.c	3010 - 3095
O-H stretch	R-OH, Phenol	3200 - 3600
O-H stretch	Carboxylic Acid	2500 - 3000

THE INSTRUMENTATION OF IR SPECTROSCOPY

IR spectroscopy instrument is called SPECTROPHOTOMETER It is designed to measure the enery absorbed by the bonds in molecule at different wavelength or wave number to produce a CHART called INFRARED SPECTRUM. The instrument is similar with that of UV spec., the difference is the replacement of UV light source with IR light source.

COMPONENTS OF IR SPECTROSCOPY

1. IR Radiation Source :

   (a) Nearnst Glower - a mixture of oxide of zicro -nium and thorium.

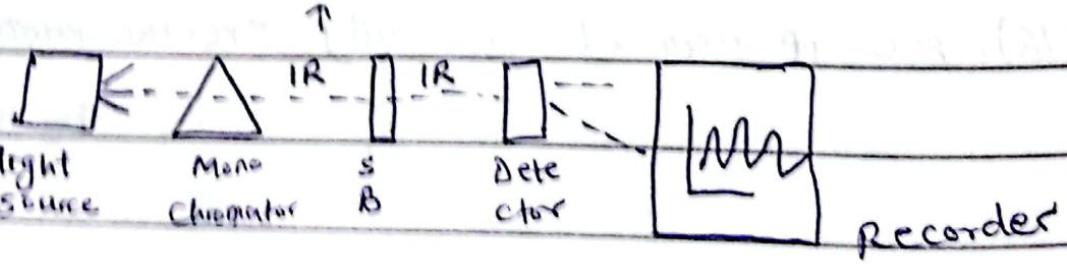
   (b) Globber Unit - silicon Rod.

2. Monochromator (Mono - one, chromator - Colour) - Glass prism or grating that absorbs all other spectrum of light but only allow the passage of IR radiation.

3. Sample bottle

4. Detector

5. Recorder

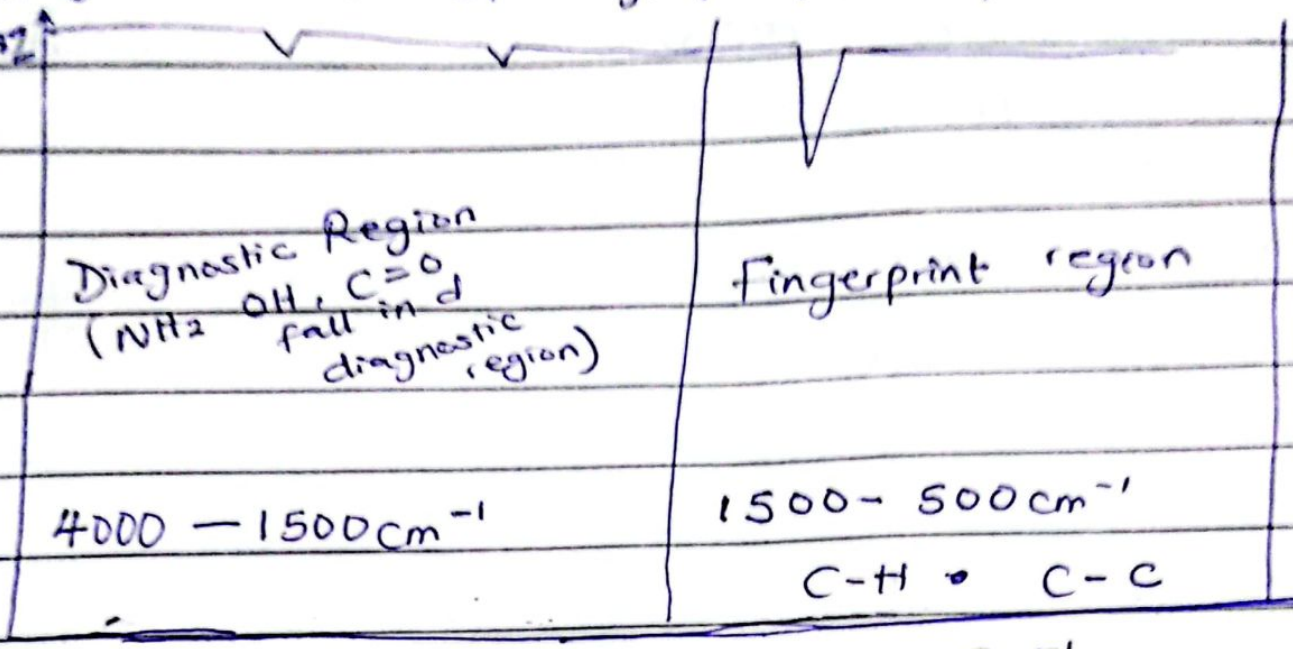


APPLICATION OF IR SPECTROSCOPY

1. It is useful for identifying functional groups
2. To differentiate between two different samples
3. De ection of impurities (some impurities are IR sensit

4th February 2025 IR SPECTROSCOPY CONTD

1. Regions in IR spectograph / IR spectrum



a) Diagnostic region

b) Fingerprint - region

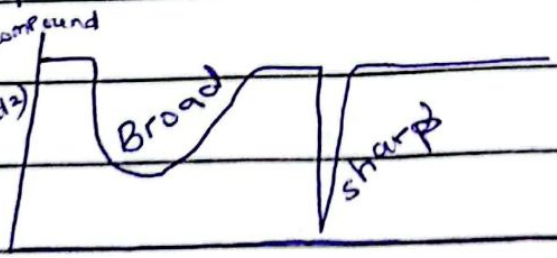
INTERPRETING IR SPECTRUM

1. Peak value:

2. Nature of the peak:

(a) Broad — Polar compound — H-bond (OH, NH2)

(b) Sharp — Non-Polar Cmpd

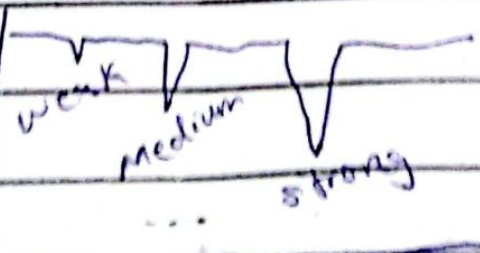


3. Intensity of the weak

a) Weak peak

b) Medium Peak

c) Strong Peak

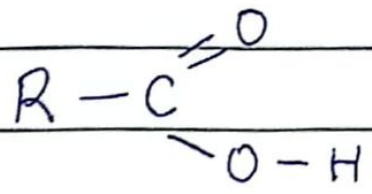


NB Concentration determines the intensity

Fingerprint region 1500-500

C-C	1000 – 1200 cm^{-1}
C=C	1600 – 1660 cm^{-1}
C≡C	2200 cm^{-1}
C-N	1000 – 1200 cm^{-1}
C=N	1650 cm^{-1}
C≡N	2200 cm^{-1}
C-O	1000 – 1300 cm^{-1}
C=O	1700 cm^{-1}
S-C≡N	2150 cm^{-1}
N=C=O	2250 cm^{-1}
C=C=C	1950 cm^{-1}

RCOOH & ROH



OH - Broad OH stretch

2500 – 3100 cm^{-1}

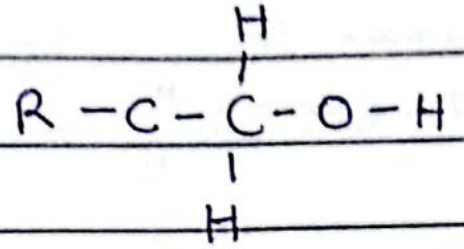
C-O – 1200 cm^{-1}

C=O – 1700 cm^{-1}

The absence of C= indicates the presence of Alcohol

$RC(=O)-O-R$ (ester)

ROH



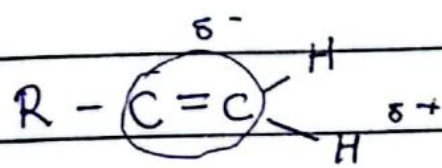
Absorption for OH $-3000-3300\ cm^{-1}$

$C-O$ $1000-1150 cm^{-1}$

$C=O$ No absorption cause alcohol doesn't have that

Alkene ($R-C=C-R$)

- Terminal Alkene $R-C=CH_2$
- Internal Alkene $R-C=C-R$



$C=C$ $1600-1660 cm^{-1}$

$=CH_2$ Terminal alkene (-H stretch at $3000-3100\ cm^{-1}$

NB it is terminal because the double bond is on the first carbon

$R-C=C-R$

$C=C$ at $1600-1660\ cm^{-1}$

$C-H$ 1200

(3)

The more the bond, the stronger the — H

ALKYNE (C≡C)

- Terminal Alkyne $R-C\equiv C-H$

- Internal Alkyne $R-C\equiv C-R$

IR spectra for $RC\equiv C-H$

C≡C	2100 – 2200 cm^{-1}
≡C–H	3100 – 3300 cm^{-1}
C–H	1200 cm^{-1}

CARBONYL IR (IR for Carbonyl)

Alkanal $R-C(=O)-H$

Alkanone $R-C(=O)-R$

Alkanal (Aldehyde)

$R-C(=O)-H$

C=O	1700 cm^{-1}
C–H Terminal	2700 cm^{-1}

Alkanone

$R-C(=O)-R$

C=O 1700 cm^{-1}

no C–H terminal.

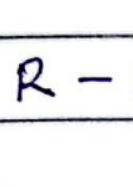
NB NH2 broad splits. EQ Formula Bond / Peak / nature

NORMAL ALKANE

C-C 1000 - 1200 cm^{-1}

C-H 1200

ESTER AND ETHER

Ester	Ether
	R - O - R
C - O - CH_3	C - O - C
C=O 1700 cm^{-1}	C-O 1200 cm^{-1}
C-O 1200 cm^{-1}	NO C=O

AMINE AND AMIDE

Amine

1° Amine (Primary Amine)	$R-NH_2$	NH - Broad Splitted 3100 - 3500 cm^{-1}	(N-H & C-N)
2° Amine (secondary Amine)	R_2NH		
3° Amine (Tertiary Amine)	R_3NH		

2° Amine : Broad

Not as broad as OH

Not splitted 3100 - 3500 cm^{-1}

3° Amine : Broad is absent

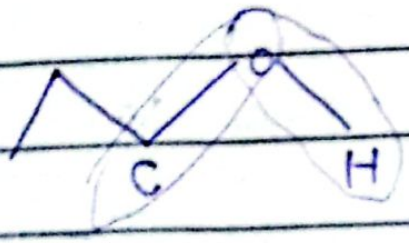
Just C–N

AMIDE

3° Amine : Broad is absent
Not Splitted
C-N 1000 - 1200 cm^{-1}

NB: All the 3 have C-N bond and only Primary amine will be splitted.

Experimenting IR spectrum for Ethanol.
The oil is characterized by strong bond



1) The only spectrum is O and O-H
Nature is broad
C-O 1200 cm^{-1}
O-H 2500 - 3100 cm^{-1}
∴ The compound is ethanol

Butan-2-ol is Broad, Not Splitted also
O-H
C-O

18-03-2025 NMR SPECTROSCOPY
(Nuclear Magnetic Resonance)

It is a scientific technique use to give detailed information about structural frame work of organic com

It is based on the magnetic property resulting from the interferance of an atom.

Radiowave is a region of EMR that is next to IR. The wavelength is longer than IR region and have being experimentally found to contain frequencies of light which is equavalent to quantum energy required to cause excitation of nuclei spin. Not all atoms are NMR active, it must have odd mass number.

^{1}H, ^{13}C, ^{31}P, ^{19}F are all NMR active

Classes Of NMR

1. Proton NMR : it can be use to predict hydrogen environments in different structures. You can also predict the structure of an organic compound.
2. ^{13}C : NMR can be used to get Carbon environment in organic compounds

Forms Of NMR

- 2D NMR : Give 2-D arrangement of atoms
- 3D : will give

Nuclei with even mass number are NMR inactive.

Determination Of Spin State Of Nucle

A spining positive charge particle have ele
-cal & Magnetic components.

To Know the magnetic spin use

$$M = 2(I) + 1$$ where:

M = Magnetic moment which determines the number
spin state of the nucleus

I = Spin Quantum number.

* For atoms with odd mass number $I = 1/2, 3/2$

When $I = 1/2$

$\therefore M = 2(1/2) + 1 = 2$

$\therefore$ We have 2 equivalent spin state, When $I = 3/2$

$\therefore M = 2(3/2) + 1 = 4$

$\therefore$ We have 3 equivalent spin state

* For atoms with even mass number

$I = 0, 1, 2, 3, 4$

$M = 2(0) + 1$

$M = 1$ (then is NMR inactive)

When $I = 1$

$M = 2(1) + 1$

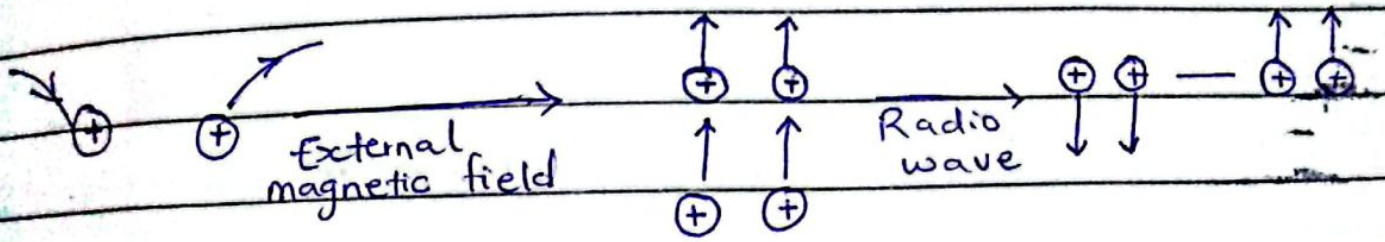
$M = 3$ (is still NMR inactive because it is odd number)

^{12}C, ^{16}O, ^{32}P are NMR inactive

Principle Of NMR Spectroscopy

1) A spinning Nuclei generates magnetic moment

2) Application of external magnetic field which cause all nuclei to be in alignment.

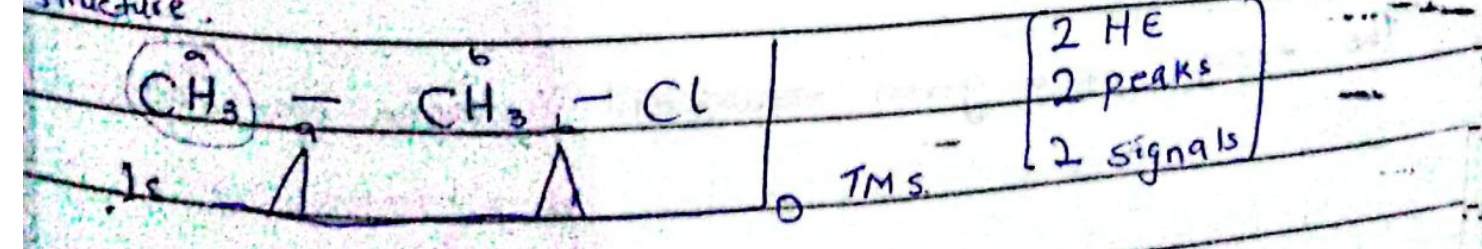


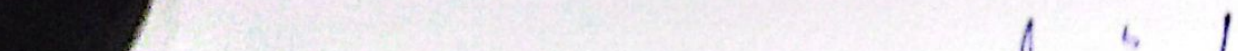
The energy emitted is measured as NMR.

NB:- Proton NMR is use to get proton environment / carbon NMR for carbon environment.

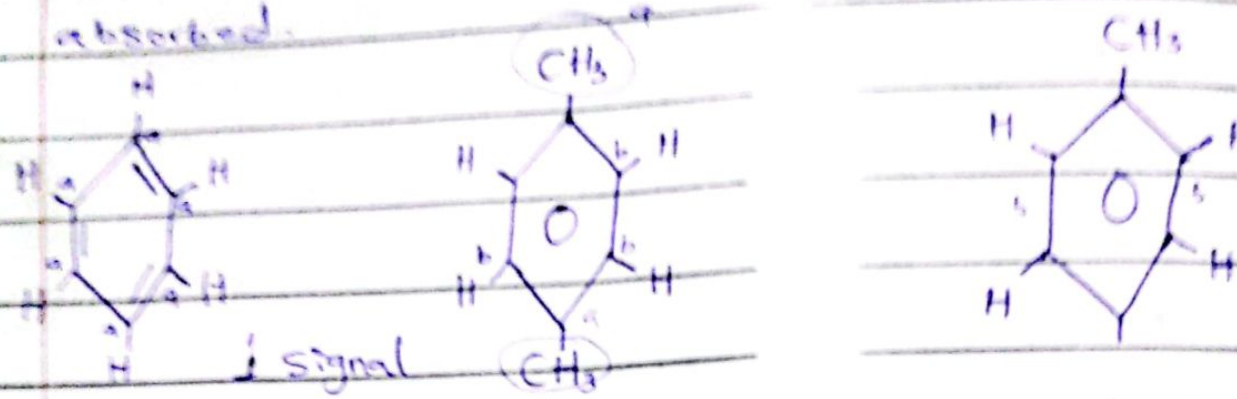
NMR Spectroscopy Parameter

1) Number Of Signals : Number of signals indicates number of equivalent proton environment present in a structure.





Chemical shift is the expression of energy that is absorbed.



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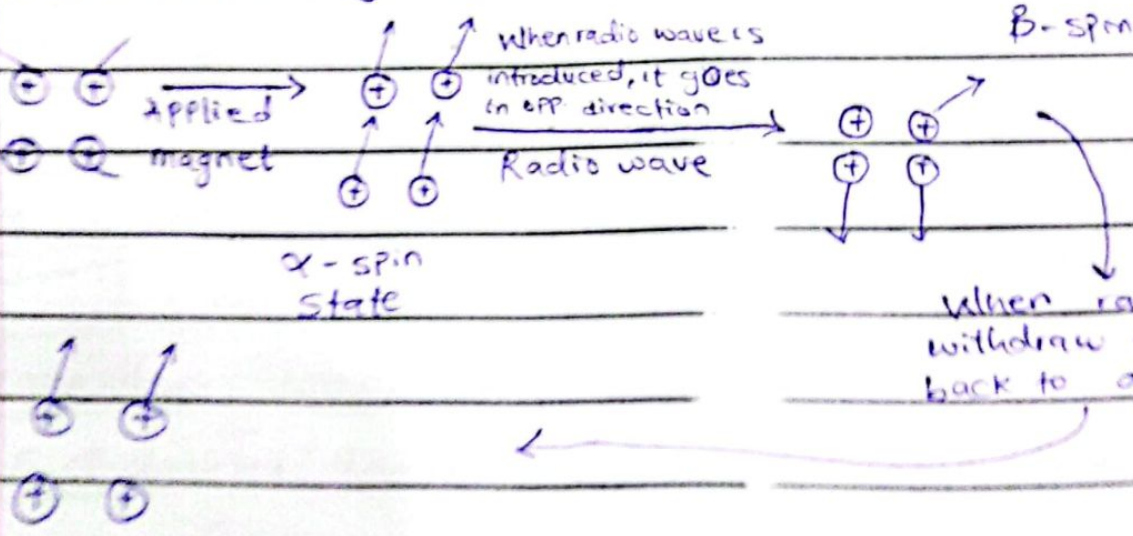
2) Chemical Shift : Chemical shift is a measure of the energy gap Between alpha Spin state and Beta spin state of a given nucleus.



The energy of a given signal hydrogen environment. The value of chemical shift from 1 chemical environment to another chemical envi

and hence can be used to characterised any given chemical environment.

There are 2 types of parameters that are used to express the value of chemical shift.

(a) δ - (sigma) : This is expressed in part per million (ppm) and it is the value of chemical shift of a particular chemical environment with reference to TMS

$$\delta = \frac{\text{Frequency of (RN) for H sample} - \text{Frequency (RN) TMS}}{\text{Frequency (RN) TMS}}$$

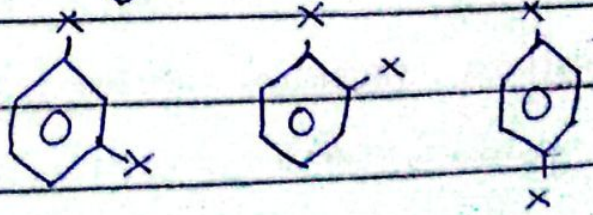
Range of δ = 1 to 15 ppm, where TMS (the reference sample) is the arbit y at 0ppm

CH_3 Aliphatic methyl group | 0.5 - 1.5 ppm |

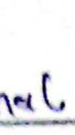
CH_3 that is attached to either O or N $O-CH_3$ is | 2.5 - 4.0 ppm | e.g CH_3OH, CH_3NH_2 $N-CH_3$ $-CH_3$ attached to benzene.

is | 2.0 - 3.0 ppm |

for monosubstitute e.g benzene  is 7.0 - 8.0 ppm
e.g C_6H_5Cl

for disubstitute benzene like  is

6.5 - 7.5 ppm e.g
1,2 dichlorobenzene

* For unsubstitutional benzene  is 6 - 8 ppm

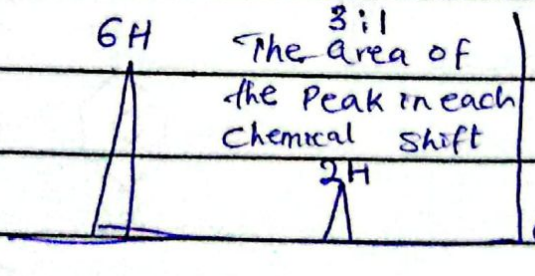
* For heteroaramatic ring (e.g foran and pyridine) is 6.0 - 9.0 ppm

* For COOH is 10 - 12 ppm

⟹ The higher the value of chemical shift, the greater the energy gap required to cause alpha-Beta spin state. Hydrogen in equivalent chemical environment will have the same chemical shift.

③ Peak Area Value : Peak area is the integration of the area under the peak of any given Hydrogen environment and is a measure of the ratio of the relative Hydrogen atoms present in each chemical environment.

NB: Every chemical environment is affected by the neighbour

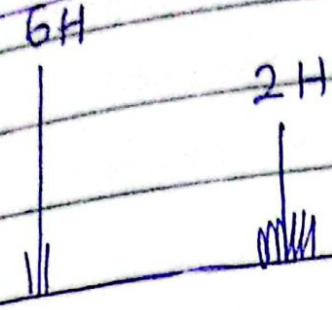


④ Splitting Pattern (Spin - Spin) :- The splitting pattern tells us how many Hydrogen is in the neighbourhood

Look for more Hydrogen in the neighborhood

$CH_3-CH_2-CH_3$ → has 7 splitting cuz of the neighbours

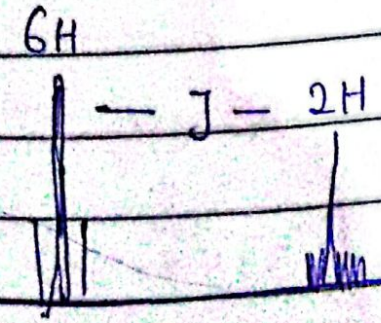
1+2=3 → have just 3 splitting patter.



Another Example 2+1+3=6 1+2=3 1+2=3

$CH_3-O-CH_2-CH_2-CH_3$

⑤ Coupling Constant (J value): It is measured in Hertz. This is the distance between the multiplet, and it is a measure of the effectiveness of coupling expressed in cycle per sec or hertz. There are some complex compounds that doesn't follow first order rule of predicting the splitting pattern, for such complex compound there J-value is used to predict or determine ther splitting pattern.



⑥ Double Bond Equivalent: This gives an idea of the number of double bonds present in a samele.

$$DBE\ (\Omega) = C + 1 - \frac{(H - N)}{2}$$

Where $\curvearrowright$ = Double bond equivalent

C = No. of carbon present

H = No of Hydrogenation

N = No. of Hydrogen

* For double bond, $\curvearrowright = 1$
* For tripple bond, $\curvearrowright = 2, 3$
* For benzene ring, $\curvearrowright = 4$

QUESTION: A Compound has a tripple signal at 1.2ppm Qualet signal at 3.6ppm & siglet signal at 4.8ppm which of the following compound will likely suit this detail.

(a) $CH_3 - O - CH_2 - CH_3$ (b) $CH_3 - CH_2 - CH_2 - OH$

(c) $CH_3CH_2 - OH$

Solution

T (1.2ppm) 3 signals

Q (3.6ppm) & 8 splitting = (3+4+1=8)

S (4.8ppm)

Checking it

(a) $CH_3 - O - CH_2 - CH_3$

T - CH_3 $C_{(4+1=5)}$ 0.5-1.5 S(CH_3) 0.5 - 1.5

Q - CH_2 $C_{(3+2=5)}$

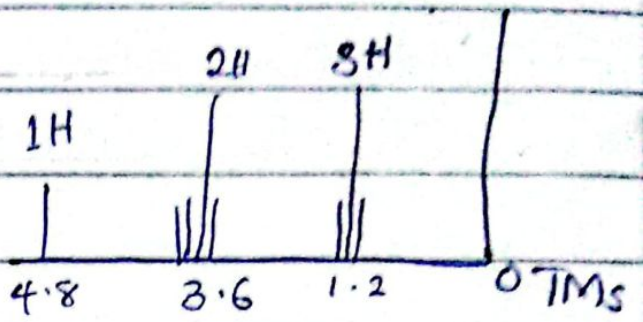
(b) $CH_3-CH_2-CH_2-OH$ ✗

(c) $\overset{a}{CH_3}-\overset{b}{CH_2}-OH$ (c)

T = 1+2 = 3 (0.5 - 1.5 ppm)

Q = 3+1 = 4 (3.6 ppm)

S = (4.8 ppm)



(2) Predict from the structure below which is most suitable for the H-NMR data given S (2.1 ppm), S (11.5 ppm).

(a) HCOOH (b) CH_3OH (c) CH_3COOH (d) CH_3OCH_3

Solution

(a) $HCOOH$ — 2.0, 11.5

(b) CH_3OCH_3 — 3.6, 4.6

(c) CH_3COOH — S (2.1 ppm), S (11.5 ppm)

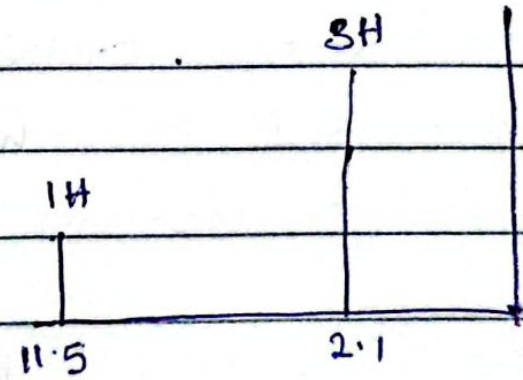
(d) CH_3-O-CH_3 — Equivalent

(a) NBS CH_3 aromatic

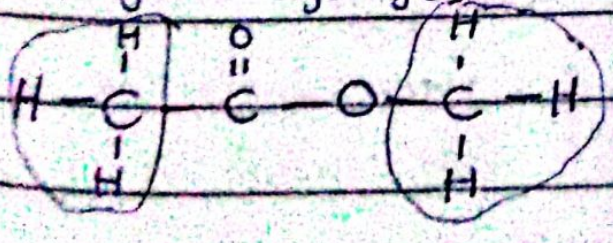
CH_2 OH

COOH methyl group

NB2: Draw the peak using the highest hydrogen.

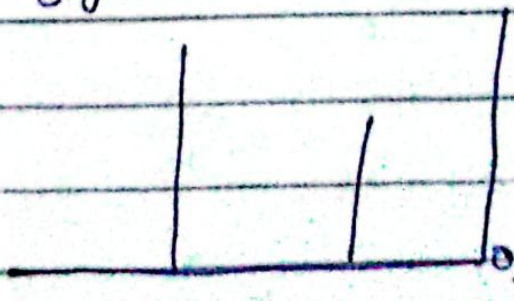


(3)



The one directly close to the oxygen is lower, while the one close to H is higher.

2 signals



Factors Affecting NMR Spectra

1) Inductive Effect:

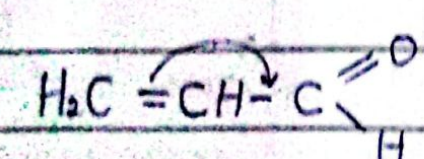
CH_3CH_3 CH_3CH_2Cl, CH_3CHCl_2, CH_4

A B

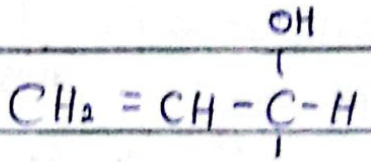
The presence of electron withdrawing group substituent near the nuclei in consideration will affect the chemical shift of that nuclei.

2) The Presence Of Resonance Or Conjugation:

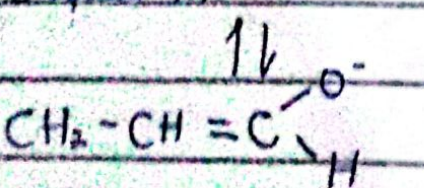
Resonance is when a particular structure can give different arrangement in canonical form. The presence of resonance will cause a higher chemical shift than expected for instance, cyclohexane, H will have lower chemical shift than benzene hydrogen because of the presence of resonance.



Compound A



Compound B



No resonance

The Presence of resonance increases Chemical shift

Aromatic is higher

followed by

Normal Conjugation

then least

Normal benzene

NB: The more inductive a substituent is the higher the Chemical shift.

3) Anisotropic Effect: Is a phenomenon whereby electron cloud of some compounds generate local magnetic field that affect the nucleus before an external magnetic field is applied. For instance, in benzene, the empty P-orbitals overlap when occupied f- orbital to form electron cloud. Anisotropic effect exerts internal magnetic field that is present in an electron cloud. therefore for any external magnetic field to be able to cause a spining from α to β state on any given nucleus, it must be able to overcome the magnetic field generated by the nucleus and the one generated by the bi electron cloud. In the presence of anisotropic effect, chemical shift is hogher than a compound without anisotropic effect.

4) The nature of Substituent: Different substituent have different effect on the nucleus of Hydrogen atta-ched to them. This is determined by wheather they are electron withdrawing group or electron donating group, there position on the periodic table or there electr-onegativity value. and

Most electronegative atom

CH_4 $CH_3(H)$, CH_3Cl, CH_3I, CH_3Br

2ppm 4.5ppm 3.10ppm 2.5ppm 2.2ppm

The NMR signal of 2 chloro substituent hydrogen give 3.1ppm and 3.8ppm chemical shift respectively. If the compounds are 3.8ppm CH_3Cl and CH_2Cl_2 which of them would have higher chemical shift Ans CH_2Cl_2

Uniqueness Of NMR

1. Non - destructive
2. It provides more information about the molecular frame work of organic compound, hence can be conviniently use to predict the structure of substance more than IR spec.
3. Provide more detailed information about the atoms present in the molecule.

MASS SPECTROMETRY

Mass spectrometry is an analytical technique use to determine the mass and structures of organic compound base on the principles of fragmentation of molecule.

Stages Of Mass Spectrometry

1. Ionization / Fragmentation Of Sample : The molecule is ioni involves the various method use to generate ions

from a sample in their gaseous state. There are different processes available for ionization.

NB: These processes does not only produce ion but produce different fragments of the sample.

(a) Electron impact ionization Technique (EI)

bombarded with fast e⁻ moving electron

Eg sample —(vapourice)→ Sample —(a) 70 volt→ Sample$^+$ + $M^+ + M^+ + M^+$ (a)

(b) Chemical Impact Ionization (CI): In the case, the sample is not ionized directly but rather a reagent present in the instrument is first ionized (usually CH_4 or NH_3) by bombarding with fast moving electron.

$NH_3 \xrightarrow[70 \text{ volt}]{e^-} NH_3^+$ Let the sample be M

M (ionized) + $NH_3^+ \longrightarrow M^+ \xrightarrow{\text{fragmentation}} M^+ + M^+ + M^+$

⇒ CI is only suitable for non-polar samples.

(c) Fast Atom Bombardment Ionization (FAB):

- Sample is mixed with prop-2,2,3-mol or 2-nitrobenzyl alcohol.
- The mixture is then bombarded with fast moving ^4He He causing Ionization and fragmentation of sample.

$M + Xe \xrightarrow[6-9 \text{ volts}]{} M^+$ + different fragment ion

⇒ This is suitable for polar sample and biomolecules.

(d) Matric Assisted Lazer Distruption Ionization (MALD)

* Sample is mixed with benzene or any heteroaromatic solvent
* The mixture is then irradiated with lazer radiation to generate different ions and fragments
⇒ This is suitable for polar samples & biomolecule

(e) Electron Spray Ionization (EST)

* Sample dissolved in water, alcohol or in the presence of modifiers (traces of acid or acetic acid)
* The mixture is then sprayed with fast moving e^-

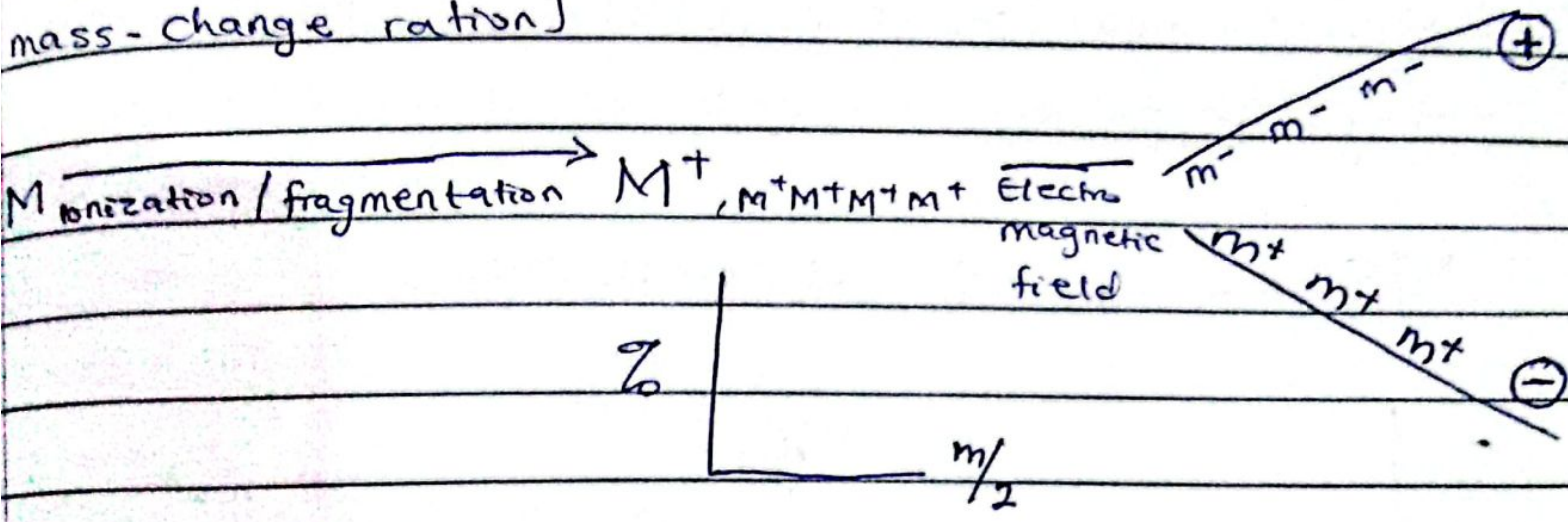
$$M \xrightarrow{\text{dissolution}} M \xrightarrow[\text{solution}]{\text{fast } e^-} M^+ + \text{diff. fragments of sample}$$

The solvent is the Vapouri -sed to obtain gaseous fragments

(2) Seperation Of Ions

The fragments and ions are passed through an

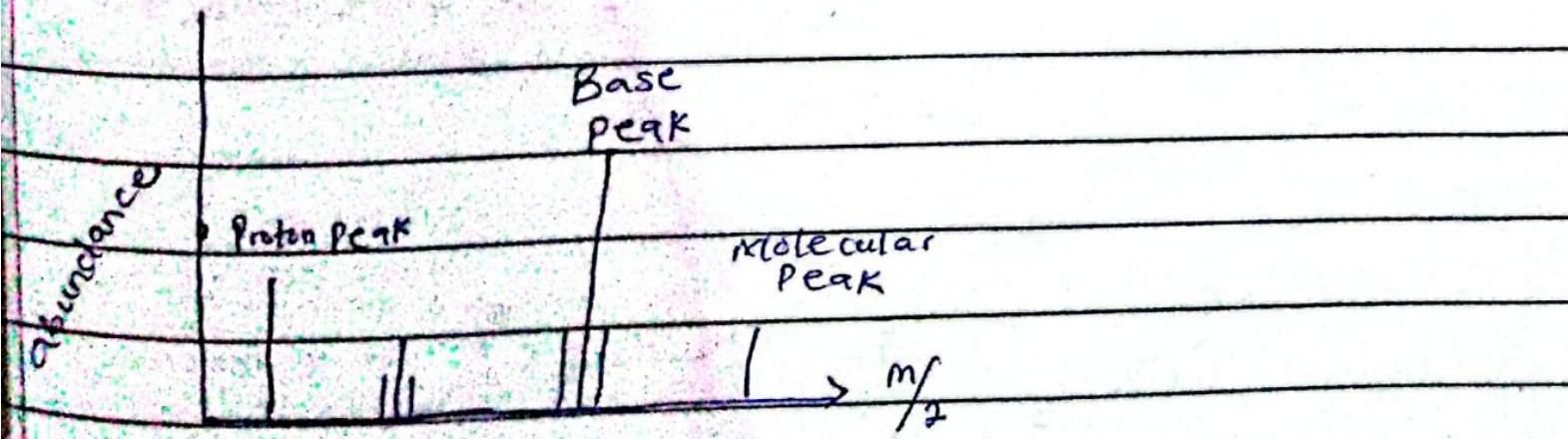
electromagnetic field to seperate the various ions/ fragments through deflection based on their m/z ratio/ mass-change ration)



(3) Detection Of Fragments:

Each fragments are detected by the detector since their signal will vary based on the m/z value and changed nature.

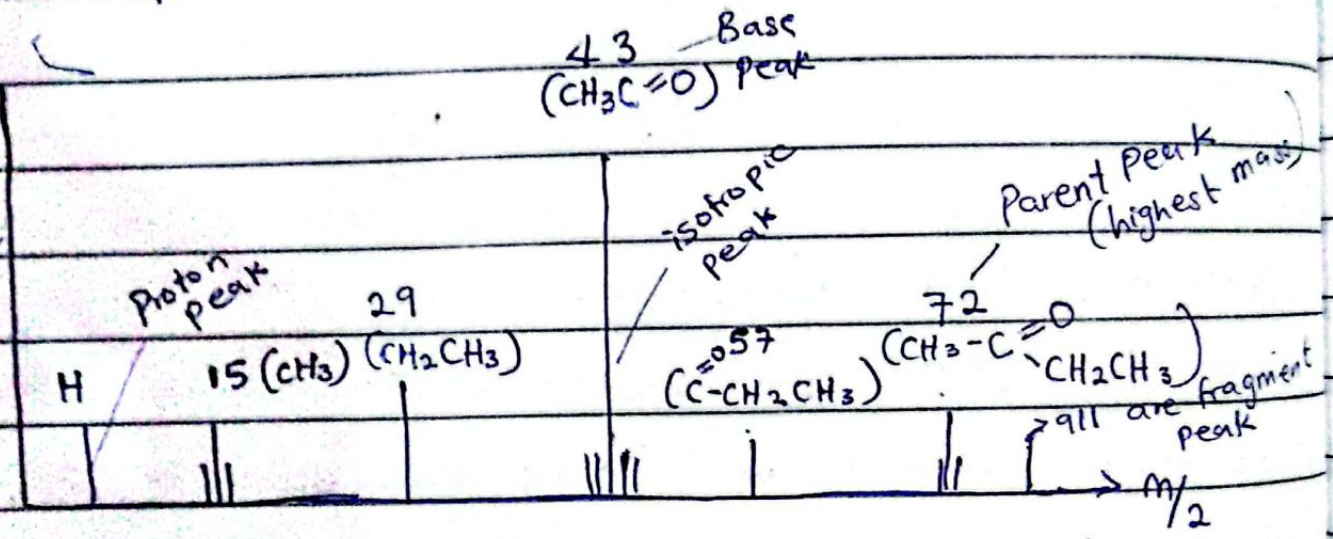
(4) Recording: The signal generated is recorded on the computer as % abundance vs m/z curve.



Component Of MS Spectrum

a) Base peak
b) Molecular peak (Parent peak)
c) Fragment peak
d) Isotopic peak
e) Proton Peak
f) Functional group peak.

MS spectrum for $CH_3COCH_2CH_3$



There will be ionization across the bond on different weight

$CH_3 \rightarrow 12+3 = 15$

CH_3 (15) + $C{=}O$ CH_2CH_3 (57)

$CH_3-C{=}O$ CH_2CH_3 → $CH_3C{=}O^+$ (43) + CH_2CH_3 (29)

This is the base peak it is the most stable cabocation

$CH_2-C{=}O$ CH_2CH_3 → $CH_3-C{=}O$ CH_2CH_3 + C (72)

Parent peak (Peak for of molecule)

$CH_2CH_3 + H^+$

(a) Base Peak: This is the most interested peak which indicate the fragment with the highest relative/percentage abundance. That also indicates the most stable ion among all the fragments associated with the molecules.

(b) Fragment Peak: The fragment peak represent all the peaks that are associated with signals from each fragments.

(c) Isotopic Peak: Each fragment is expected to have a signal but it has being experimentaly found that there are other low peaks around each of the fragment signals, this is due to the presence of isotopes. (Peak due to isotopes is the isotopic Peak) the one that have one is isotop.

(d) Proton Peak: This is the peak due to the presence of Hydrogen ion generated during the process of ionization. The one that is more than one is the proton peak.

(e) Molecular Peak: This is the peak that correspond with the molecular mass of the main molecule when it is ionized by the removal of an electron.

$$CH_3COCH_2CH_3 \longrightarrow CH_3C^{+}{=}O - CH_2CH_3 + e^-$$

The one with the largest m/z ratio is the parent / molecular peak.

⑥ Functional Group Peak: This is due to the signal from a specific functional group.

Advantages Of Mass Spectrometry

1. Is more detailed than other spectrometry methods Spectroscopy techniques.
2. More accurate
3. More versatile
4. Can be use for crude sample with 50 different compounds.

Limitations Of Mass Spectrometry

Any sample being fragmented / ionized is destroyed and cannot be used again for another analysis.

NITROGEN RULE

- Molecules containing H, C, O, S, N & halogens will have even number molecular weight.
- Molecules containing odd numbered Nitrogen isotope will have odd numbered molecular weight
- If the molecules contains even number Nitrogen atoms

the molecular weight will be even

Common Fragmentation Patterns

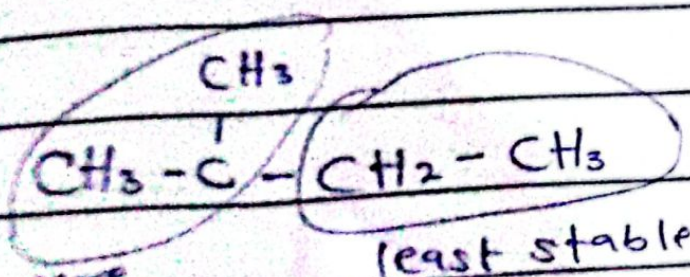
a) Alkane fragment pattern

If is linear

$CH_3 - CH_2 - CH_2 - CH_3$

→ $CH_3^+ + CH_2CH_2CH_3$
most stable heterolytic cleavage

→ $CH_3\dot{C}H + CH_2CH_3$
Not stable homolytic cleavage



more stable

least stable.