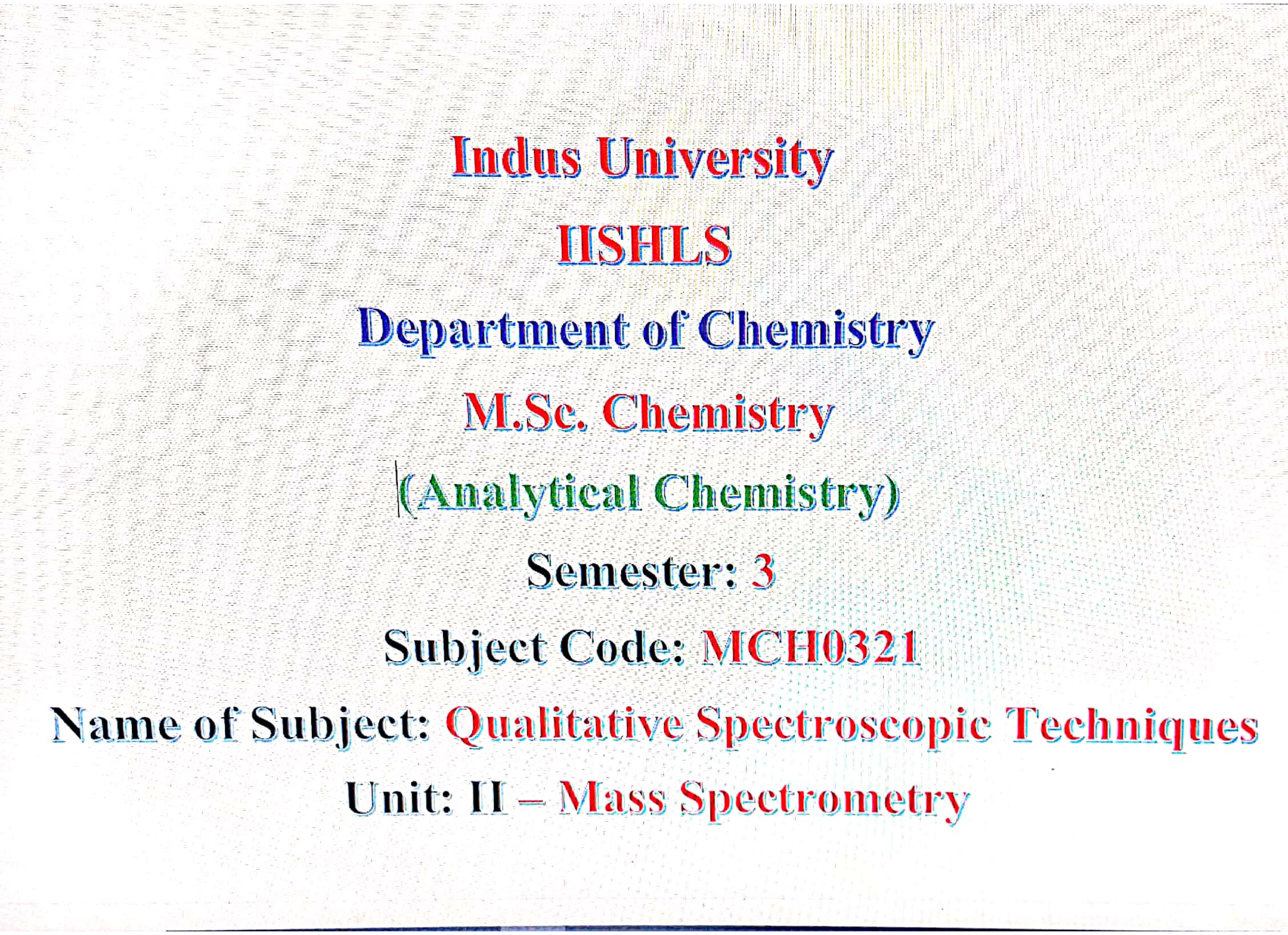


Indus University

IISHLS

Department of Chemistry

M.Sc. Chemistry

(Analytical Chemistry)

Semester: 3
Subject Code: MCH0321
Name of Subject: Qualitative Spectroscopic Techniques
Unit: II – Mass Spectrometry

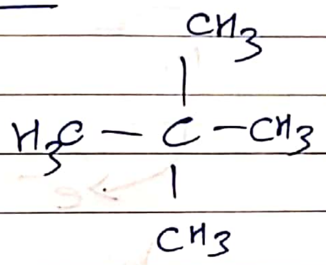
Mass Spectrometry

⊛ Basics & Principles :-

→ Mass spectroscopy (MS) is used to determine molecular mass of the compounds.

→ It is most accurate method among all the spectroscopic techniques.

→ **e.g** Neopentane: $[C_5H_{12}] = (12\times5)+(1\times12)$



$= 72$

↗

Molecular mass.

→ Signal will appears in the form of mass to charge ratio (m/e or m/z).

→ Generally, charge will be +1 in most of the cases, rarely it will be +2.

i.e. $\frac{72}{+1} = 72$ → Molecular weight

✯ Principle :-

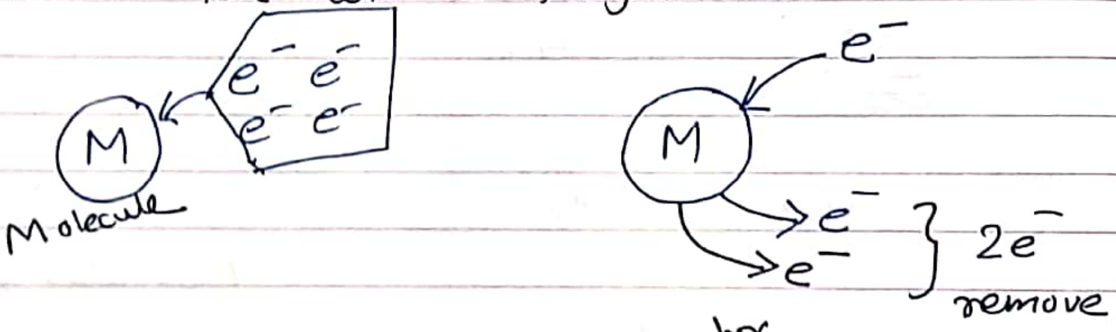
"

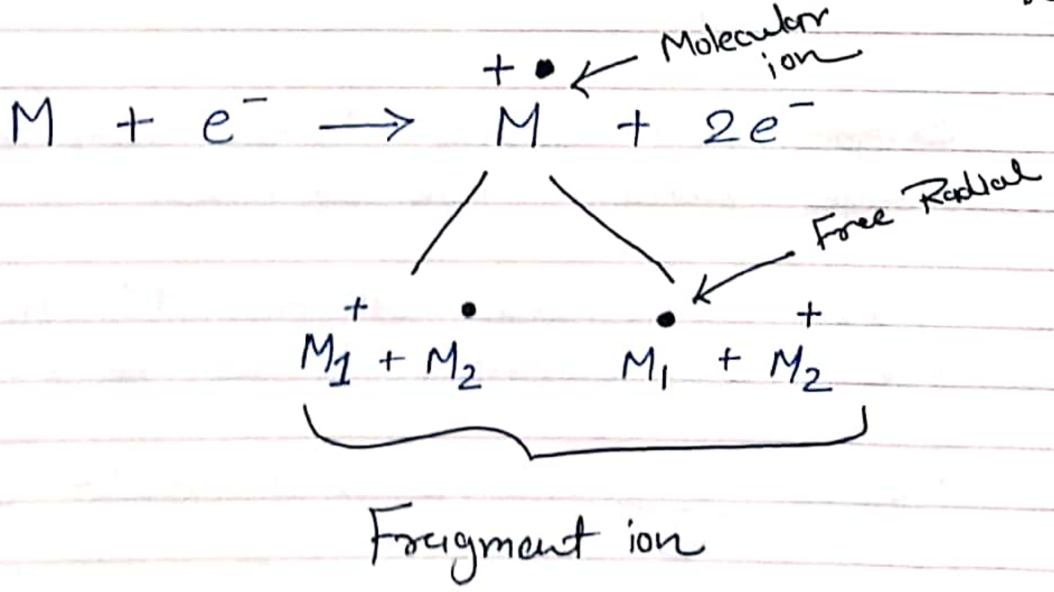
- A beam of electrons will be bombarded in the analyte compound & it will leads to removal of 1 electron from analyte.

- Due to removal of electron, molecule will be positively charged and known as the molecular ion.

- Molecular ion will be fragmented."

e.g.

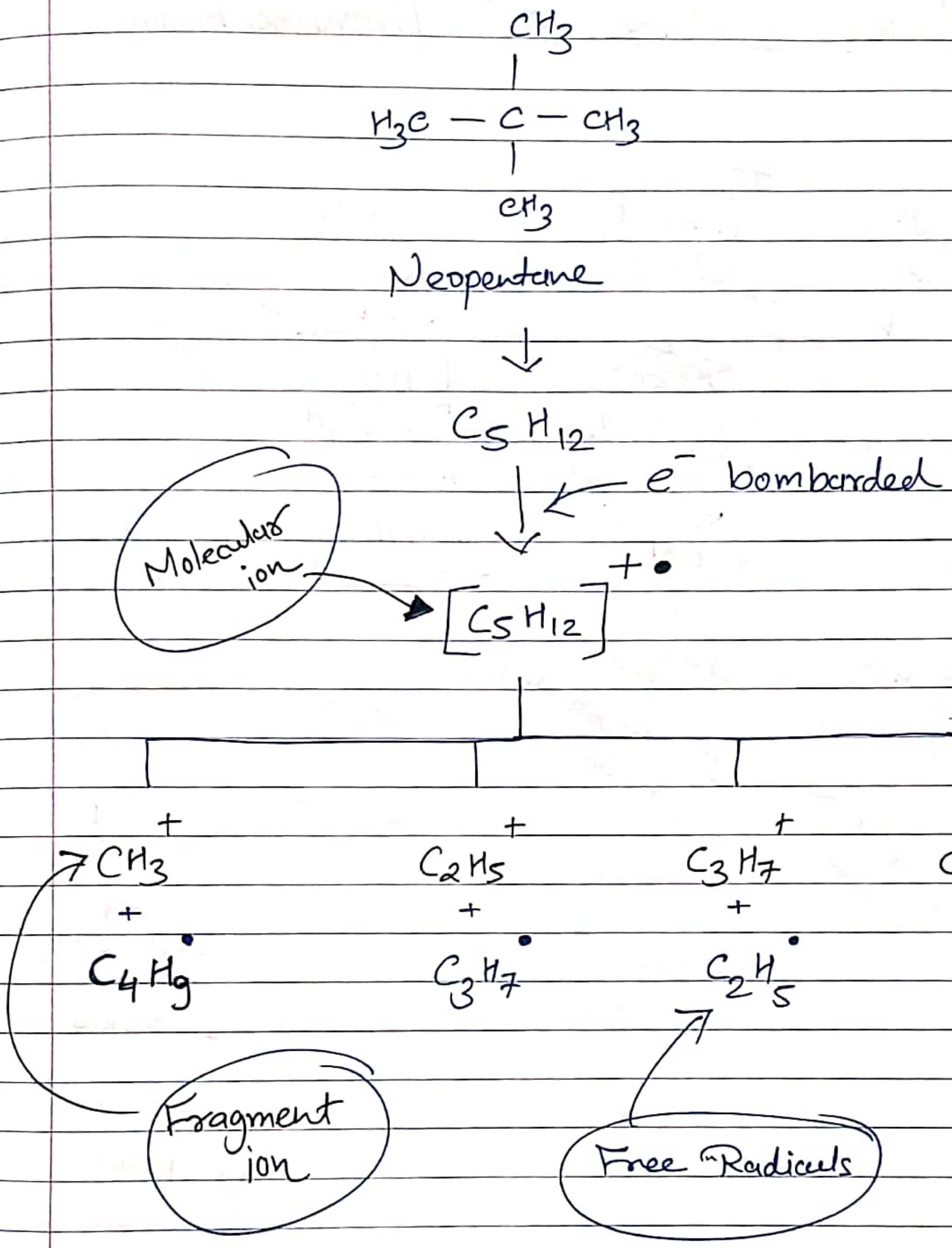




$$M + e^- \longrightarrow M^{+\bullet} + 2e^-$$

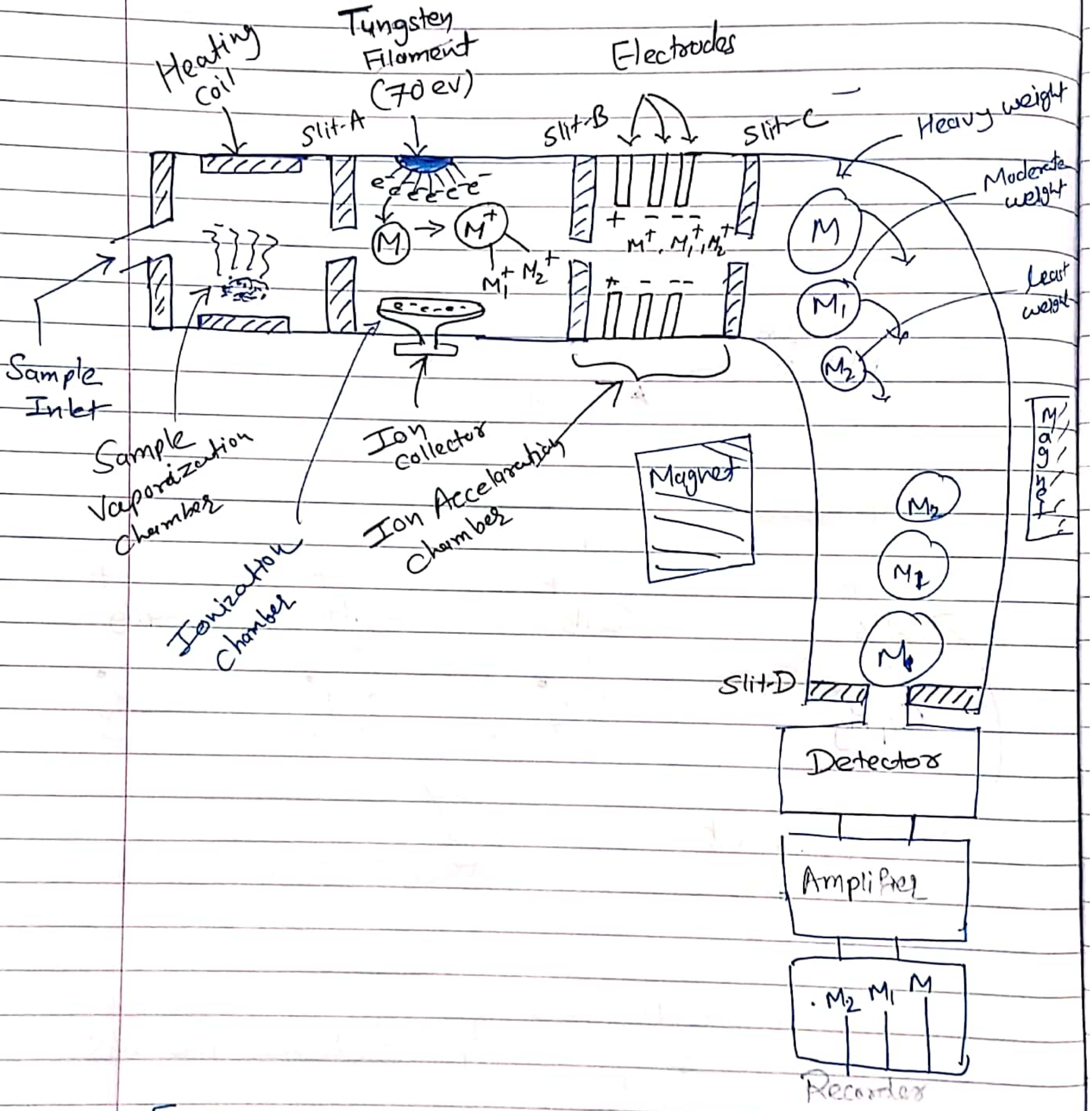
$$\underbrace{\overset{+}{M_1} + \overset{\bullet}{M_2} \qquad \overset{\bullet}{M_1} + \overset{+}{M_2}}_{\text{Fragment ion}}$$

Only $M^{+}_{\bullet}$, M_1^{+}, M_2^{+} → Detected in MS.



Molecular ion & Fragment ion } detected in MS.

* Brief Outline of Instrumentation.



[Instrumentation of Mass spectrometry]

→ * Sample Inlet

- Sample may be in liquid, gas or solid form.

- First of all sample is introduced through sample inlet.

→ * Sample vaporization Chamber :

- In this chamber, sample is vaporized through high temprature. i.e. by Heating coil.

- Then ~~so~~ vaporized sample passed through slit. A into the ionization chamber.

→ * Ionization chamber

- Minimum potential required to convert M to M^+, approximate 8 to 15 eV.

- Here tungsten filament is used as electron source. (70 eV)

- A beam of electrons will be bombarded in the sample & it will leads to removal of one electron from the sample.

- Therefore, Sample will be ionized in different ions i.e. molecular ion, fragments ion and free radicals.

Page No.:
Date:

- Extra bombared electrons will be collected by ion. collector in this chamber.

- Further this M^+, M_1^+ & M_2^+ and radicals are passed through the slit-B and ~~entre~~ enter in the next chamber i.e. Ion acceleration chamber.

→ * <u>Ion Acceleration chamber</u>

- In this chamber, One positive electrode, One negative electrode and one highly negative electrode has been arranged.

- These electrode produce the positive potential, negative potential and more negative potential respectively.

- The electrode potential of this chamber is approximately 8 to 10 KV.

- Due to this negative potential, all the ~~posive~~ positive ion will be attracted by these negative potential. and it will be reppelled by these positive electrode

- So, all the positive ions will gain certain velocity after this ion acceleration chamber. and other all the free radicals remain in this chamber.

⊛ Mass Analyser

- So, Kinetic energy of these positive ions will be.

$$\frac{1}{2} mv^2 = eV \quad \dots \quad \dots \quad \dots ①$$

m = mass of the ion
v = velocity of ion
e = charge on the ion
V = potential difference

- In next step M^+, M_1^+ & M_2^+ will enter into the magnetic field.

- If the applied magnetic field is H, it will feel the reflection force due to magnetic field and it is denoted by,

$$HeV = \frac{mv^2}{r} \quad \dots \quad \dots \quad \dots ②$$

H = Applied magnetic field
r = Radius of the path

- Squaring both the sides in eqn ②;

$$\therefore H^2e^2 \cdot V^2 = \frac{m^2V^4}{r^2} \quad \dots \quad \dots \quad \dots ③$$

$$H^2e^2 = \frac{m^2v^2}{r^2} \quad \dots \quad \dots \quad \dots ④$$

- Rearrange Eq^n ①;

$$mV^2 = 2eV \quad \ldots \quad \ldots \quad \ldots ⑤$$

- Put the value of mV^2 from Eq^n ⑤ to ④;

$$H^2 e^2 = \frac{m \cdot 2eV}{r^2}$$

$$H^2 e = \frac{2mV}{r^2}$$

$$\therefore \boxed{\frac{m}{e} = \frac{H^2 r^2}{2V}} \quad \ldots \quad \ldots \quad \ldots ⑥$$

- Those ions having high molecular weight will reach first to the detector.

- For example, Here molecular weight of M^+ is high, molecular weight of M_1^+ is moderate and M_2^+ having the least molecular weight.

- So, that M^+ will reach first ~~and~~ then M_1^+ and at last M_2^+ will reach to the detector.

- So, in mass analyzer, the molecule ion will separated on the basis of their mass.

- There are different type of Mass Analyzer.

  ① Magnetic field deflection

  ② Double focusing

  ③ Quadrupole

  ④ Time of flight

  ⑤ FT-ICR (Fourier Transform ion cyclotoon Resonance.)

* Detector :-

- So from mass analyzer, it will go to the detector. In detector diodes are used.

* Amplifier :-

- Then it will go to the amplifier. In MS, Direct electric amplifier is used.

* Recorder :- It will record the signals.

☆ Ionization Techniques :-

- Mass spectrum significantly depended upon the ionization method.

- Variation ~~of~~ in the spectrum is introduced in terms of → Number of Peaks
  → Intensity of Peaks. (Specially molecular ions)

- Ionization Techniques can be categorized into two parts.

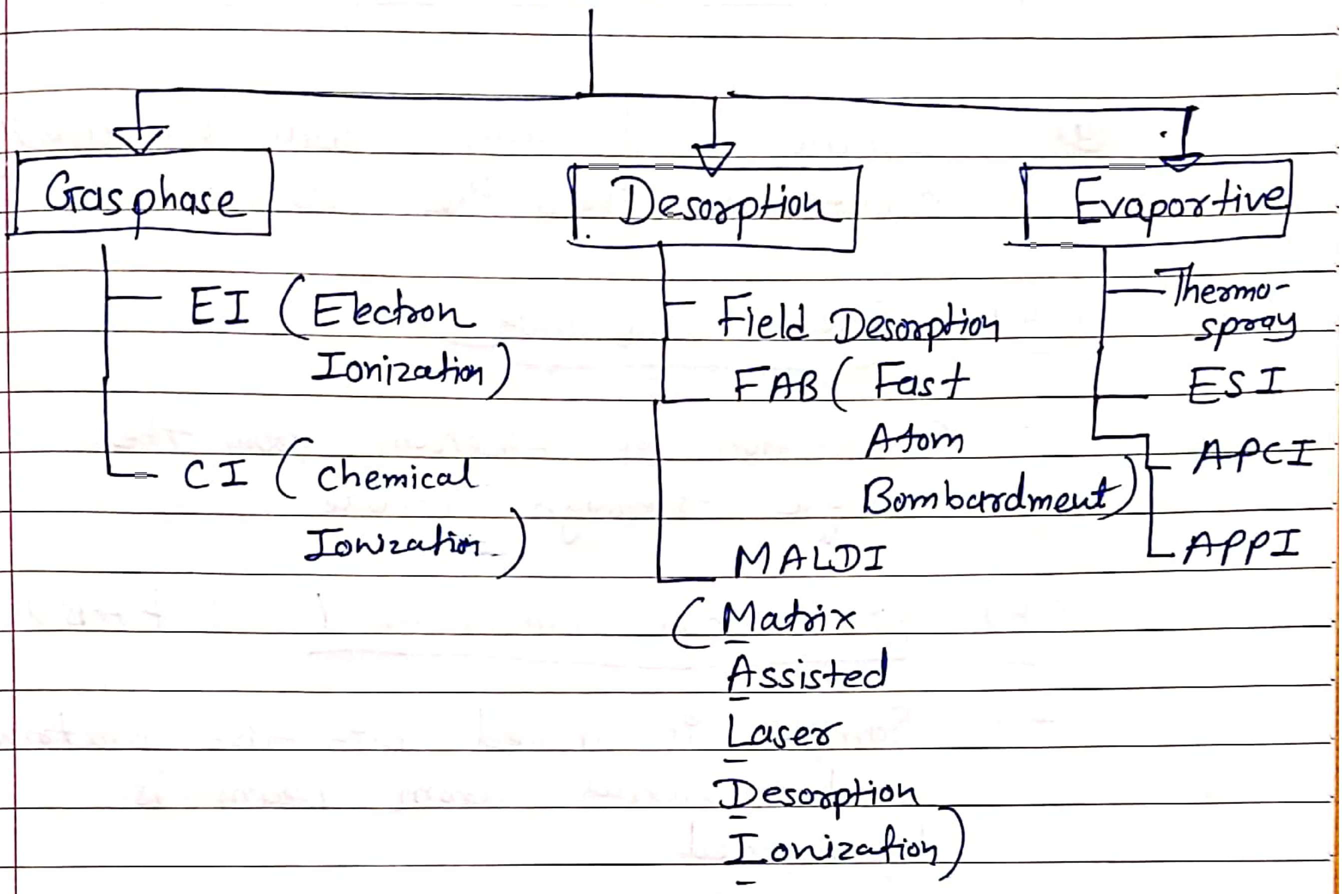
Hard Ionization Techniques

- High energy ⇒ ↑ fragmentation

Soft Ionization Technique

- Low energy ⇓ ↓ fragmentation

Different methods for Ionization



Gas-phase method

- Oldest & most popular method
- Sample is vaporized before ionized.

(a) Electron Ionization (EI)

- Direct ionization through electron beam

(b) Chemical Ionization (CI)

- Carrier gas will be ionized, then secondary ions will be produced & ions will be transfered through the analytes.

-•- Desorption Ionization Method

(◎) - Liquid / solid samples will be directly converted into the gaseous ions.

(a) Field Desorption

- Desorption of electrons from the analyte through anode

(b) Fast Atom Bombardment (FAB)

- Sample is mixed with the matrix and neutral atom beam is bombarded.

(c) Matrix Assisted Laser Desorption Ionization (MALDI)

- Mixed with the polar matrix & Laser light is used for ionization.

-•- Evaporative Ionization Method

- Solvent molecules are stripped by evaporation.
- These techniques are specially used in chromatography.

(a) Thermo - Spray Ionization (TSI)

- It is mainly used in aqvous liquid chromatography

(b) Electro Spray Ionization (ESI)

- It is mainly used in HPLC.

(c) Atmospheric Pressure Chemical Ionization (APCI)

- It is advanced version of chemical ionization. technique

(d) Atmospheric Pressure photo Ionization (APPI)

- Photons will be used for ionization of the molecule.

(*) Types of Ions & Peaks in MS

1) Molecular Ion | Parent Ion

→ When a molecule is bombarded with electron in high vacuum in Mass-Spectrometer, it is converted into positive ions by loss of an electron. These ions are called Moleculers or Parent ions.

→ $$\underset{\text{Molecule}}{M} + e^- \longrightarrow \underset{\text{Molecular ion | Parent ion.}}{\overset{\bullet +}{M}} + 2e^-$$

→ The order of energy required to remove electron is as follows -

σ electrons > Non-conjugated π > Conjugated π > Non-bonding or lone pair of electron

2) Fragmentation Ion | Daughter Ions

→ Many of these moleculer ions ($\overset{\bullet +}{M}$) disintegrate at 10^{-10} to 10^{-13} seconds to give a positively charged fragments and a radical in the simplest case.

- If some molecular ions remain intact long enough (about 10^{-6} seconds) to reach the detector.

• Characteristics of Molecular ion :-

- Molecular peak is observed if molecular ions will remains intact long enough (10^{-6} sec.) to reach the detector.

- This peak will give the molecular weight of the compound. The molecular ion peak is usually the peak of the "highest mass number."

- The molecular ion $M^{\bullet +}$ has mass, corresponding to the molecular weight of the compound from which it is generated.

- Thus the mass of a molecular ion $M^{\bullet +}$ is an important parameter in the identification of the compound.

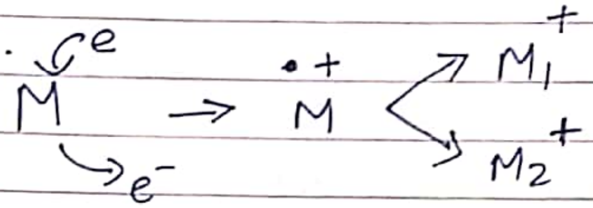
• Significance of Molecular ion :-

- Molecular ion peak gives the molecular weight of the compound.

- i.e. m/z of molecular ion = molecular weight of the ~~compoud~~ compound

2) Fragment ion / Daughter ion

- When the energy is given to Moleculer ion during electron impact, further cleavage takes place and ions of lower mass number Known as Fragment ions are produced.



- This fragmentation take place by two mechanism.

① By unstability of this M^+ ion to stable itself, it will be convert in form of M_1^+ & M_2^+.

② There will be applied potential for ionization of this M (molecule), due to that applied potential, this M^+ further fragment in the form of M_1^+ & M_2^+

3) Rearrangment ions:-

- These ions are the fragments whose origine cannot be described by simple cleavage of bonds in the parent ion.

but are result of intermolecular atomic rearrangement during fragmentation.

- These ions are probably due to recombination of fragment ions & known as rearrangement peaks.

4) Multi charged ions :-

- Some times ions may also exist with two or three charges instead of usual single charge in the mass spectrum. These are known as doubly, or triply charged ions. They are created as follows:

$$\overset{+\cdot}{M} + e^{-} \longrightarrow \overset{++}{M} + 3e^{-}$$

- But under normal operating conditions, most of the ions produced are single charged. The doubly or triply charged ions are recorded at a half or one third of the m/z value of the single charged ions.

- Formation of these multiple charged ions is more common in hetero aromatic compounds.

- They are also common in inorganic mass spectrum. Gases such as CO, N_2, CO_2 have measurable peaks corresponding to CO^{2+}, N^{+2}, O^{+2}.

5) Metastable Ions :-

- Fragment of a parent ion will give rise to a new ion (daughter) plus either a neutral molecule or a radical.

$$M_1^+ \longrightarrow M_2^+ + \text{Non charged particle}$$

- An intermediate situation is possible ; M_1^+ may decompose to M_2^+ while being accelerated.

- The resultant daughter ion M_2^+ will not be recorded at either M_1 or M_2, but a position $M^\bullet$ as a rather broad, poorly focused peak. Such an ion is called a Metastable ion.

- Some fragmentation may occur during their flight down the ion tube field free region instead of the ionization chamber.

- They reach to the detector at masses lower than the actual mass & gives broader peak.

- They have lower kinetic energy than normal ions and metastable peaks are smaller than the M_1 & M_2. They are useful in helping to establish fragments routes.

6) Quasi Molecular Ion :-

- It is also known as protonated molecular ion.

- An ion formed by the removal of one hydrogen atom from molecular ion is known as Quasi Molecular Ion.

$$M + H^+ \rightarrow [MH]^+$$

$$M^+ \longrightarrow [M - H]^+ + H$$

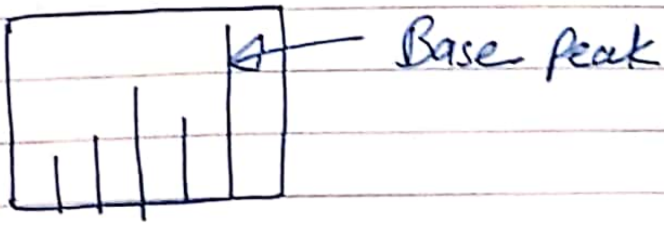
(Minus)

* Types of Peak :

① Base Peak

- The most intense / tallest peak in the mass spectrum.

- It is due to the greatest relative abundance.



Page No.:
Date:

② Isotope Peaks :-

- Due to presence of heavier isotope elements.

- Gives very less intense peak.

- e.g.

$^{1}_{1}H \rightarrow 99.985\ \%$	$^{12}_{6}C \rightarrow 98.89\ \%$
$^{2}_{1}H \rightarrow 0.015\ \%$	$^{13}_{6}C \rightarrow 1.11\ \%$

☆ Fragmentation process:-

→ Bombardment of molecules by an electron beam with energy between 10-15 eV usually results in the ionization of molecules by removal of one electron (Molecular ion formation).

→ When the energy of electron beam is increased between 50-70 eV, these molecular ions acquire a high excitation resulting in their break down into various fragments. This process is called "Fragmentation process."

* General rules for fragmentation :-

① The relative height of the molecular ion peak is greatest for the straight chain compound & decrease as the degree of branching increases.

② The relative height of the molecular ion peak usually decreases with increasing molecular weight in a homologous series.*

*Homologous series :- In the field of organic chemistry, a homologous series is a sequence of compounds with the same functional group & similar chemical properties in which the members of these series can be branched or unbranched.

e.g. Alkanes - C_nH_{2n+2}
Alkenes - C_nH_{2n}
Alcohol - $C_nH_{(2n+1)}OH$

③ Cleavage is favoured at alkyl substituted carbon atom; the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbon atom over a secondary, which in turn is more stable than a primary.

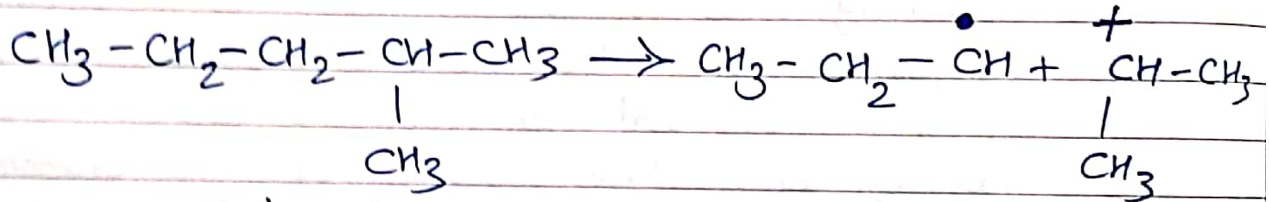
$$\boxed{\overset{+}{C}H_3 < R\overset{+}{C}H_2 < R_2\overset{+}{C}H < R_3\overset{+}{C}}$$

- ## STEVENSONS RULE :-

→ When an ion fragments, the positive charge will remain on the fragment of lowest ionization potential.

→ Generally the largest substituent at a branch is eliminated most readily as a radical, presumably because a long chain radical can achive some stability by delocalization of the lone pair electron.

→ **Ex**:- Cleavage of 1-methyl pentane.



$$CH_3-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3 \longrightarrow CH_3-CH_2-\overset{\bullet}{C}H + \overset{+}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}-CH_3$$

1- methyl pentane

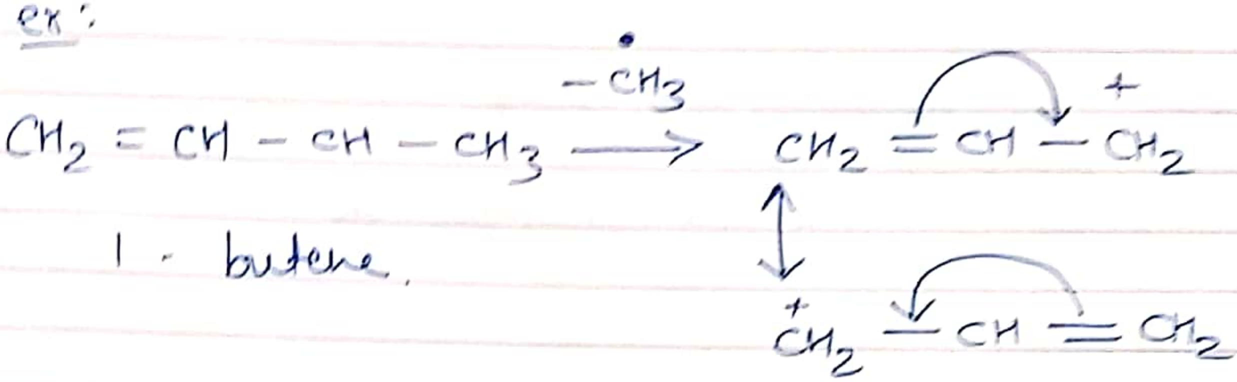
Largest fragment

→ In this fragmentation, positive charge remains on the more high substituted fragments, i.e. the one with lower ionization potential.

④ Double bonds, cyclic structure & specially aromatic or hetero aromatic rings stabilize the molecular ion & thus increase the probability of its appearance.

⑤ Double bonds favour allylic cleavage & give the resonance stabilized allylic carbonium.

ex:

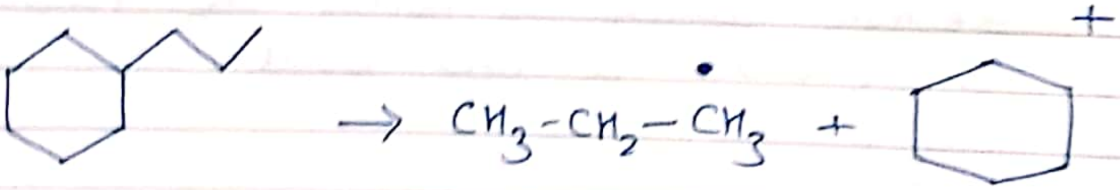


$CH_2=CH-CH-CH_3 \xrightarrow{-\dot{C}H_3} CH_2=CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2-CH=CH_2$

1- butene.

⑥ Saturated rings tend to lose alkyl side chains at α carbon atom. The positive charge tends to stay with the ring fragment.

ex: n- propyl cyclohexene



⑦ Cleavage is often associated with elimination of small, stable, neutral molecules such as CO, olefins, H_2O, NH_3, H_2S, HCN, ketones or alcohols, often with rearrangement.

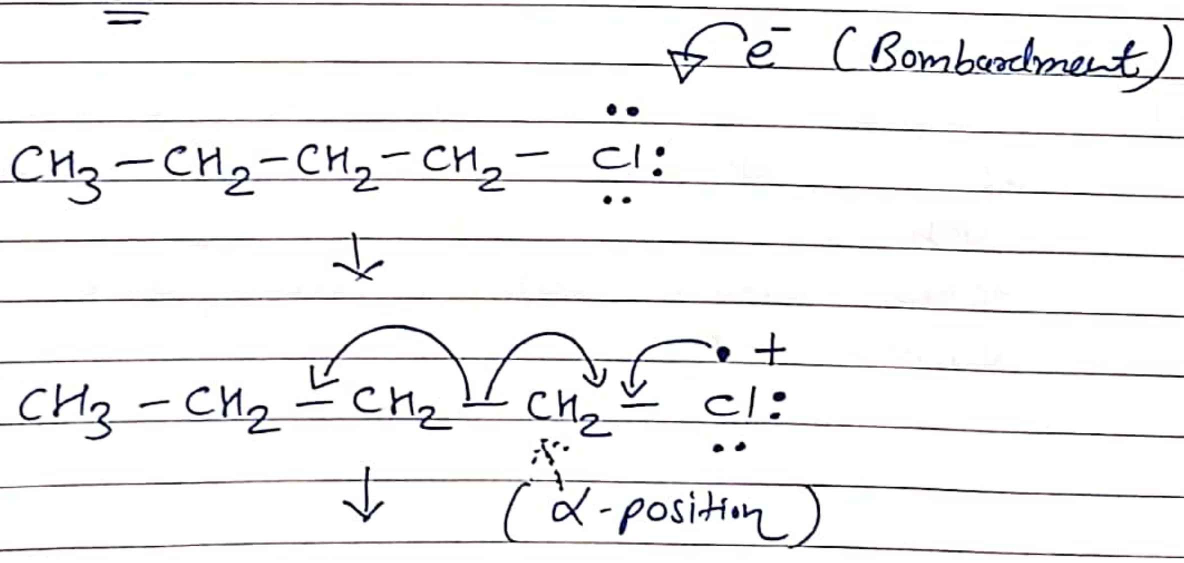
- Factor influencing fragmentation process:-
  - Bombardment Energies
  - Functional group
  - Thermal decomposition.

☆ Fragmentation Pattern in MS

General modes or of Fragmentation :-

⇒ ■ **Homolytic Cleavage** [α- cleavage]

- It is initiated by the radical site.
- Odd electron ions have an unpaired electron which is having the tendency to create a new bond
- e.g.



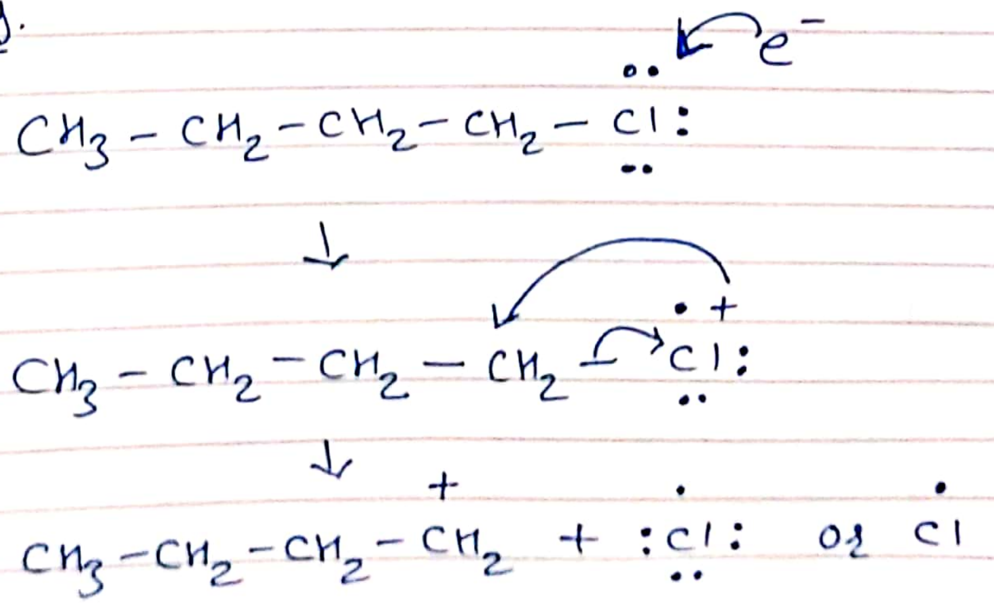
$$\downarrow$$

$$CH_3-CH_2-\dot{C}H + CH_2=\overset{+}{\underset{\cdot\cdot}{Cl}}: \text{ or } CH_2=\overset{+}{Cl}$$

Free Radical   Positive ion
↑
Detected in MS.

⇒ ■ Heterolytic cleavage :-

- Cleavage of C−X bond take place which is more difficult than C−C bond.
- Here X = Heteroatoms like N, O, S, Cl etc.
- Positive charge is carried by carbon atom. instead of Heteroatom.
- e.g.



$$CH_3-CH_2-CH_2-CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \quad \leftarrow e^-$$

$$\downarrow$$

$$CH_3-CH_2-CH_2-CH_2-\overset{\cdot +}{\underset{\cdot\cdot}{Cl}}:$$

$$\downarrow$$

$$CH_3-CH_2-CH_2-\overset{+}{C}H_2 + :\overset{\cdot}{\underset{\cdot\cdot}{Cl}}: \text{ or } \dot{Cl}$$

Positive ion   free Radical.

⊛ McLafferty Rearrangement :

→ It involves cleavage of α, β bond followed by transfer of a gamma(γ) hydrogen atom.

→ Fragmentation due to the rearrangement of Molecular ion or Parent ion:

- Here cleavage of bonds in molecular ion is due to the intermolecular atomic rearrangement.

- This leads to fragmentation whose origin cannot be described by simple cleavage of bonds.

- When fragments are accompanied by bond formation as well as bond for breaking, a rearrangement process is said to have occurred.

- Such rearrangement involves the transfer of hydrogen from one part of the molecular ion to another via, preferably, a six-membered cyclic transition state.

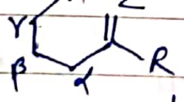
- This process is favoured energetically because as many bonds are formed as are broken.

- Compounds containing hydrogen atom at position gamma to carbonyl group have been found to a relative intense peak. This is probably due to rearrangement & fragmentation is accompanied by the loss of neutral molecule. This rearrangement is known as McLafferty rearrangement.

- The rearrangement results in the formation of charged enols & a neutral olefins.

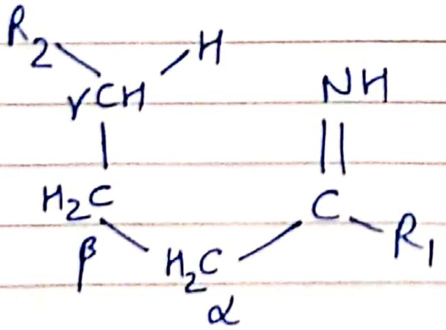
- To undergo McLafferty rearrangement, a molecule must passes
  - An appropriately located heteroatom (ex:- O, N)
  - A double bond (=)
  - An abstractable Hydrogen atom which is at γ (gamma) to C–O system.

e.g.

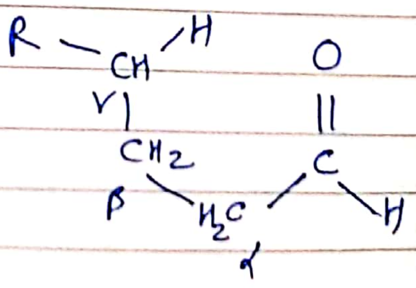


$(Z = C, N, O)$

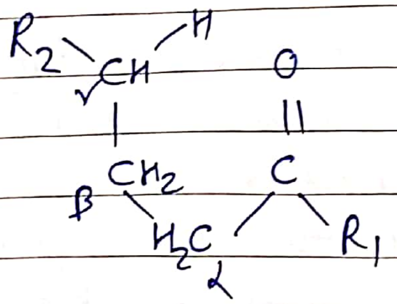
- McLafferty rearrangement can take place in following types of molecule



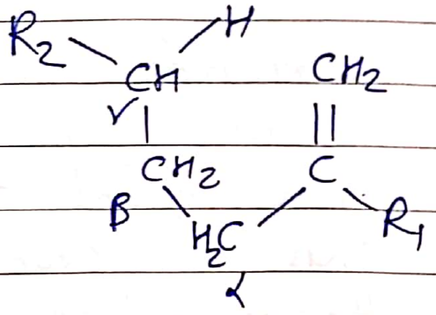
[Amines]



[Aldehyde]

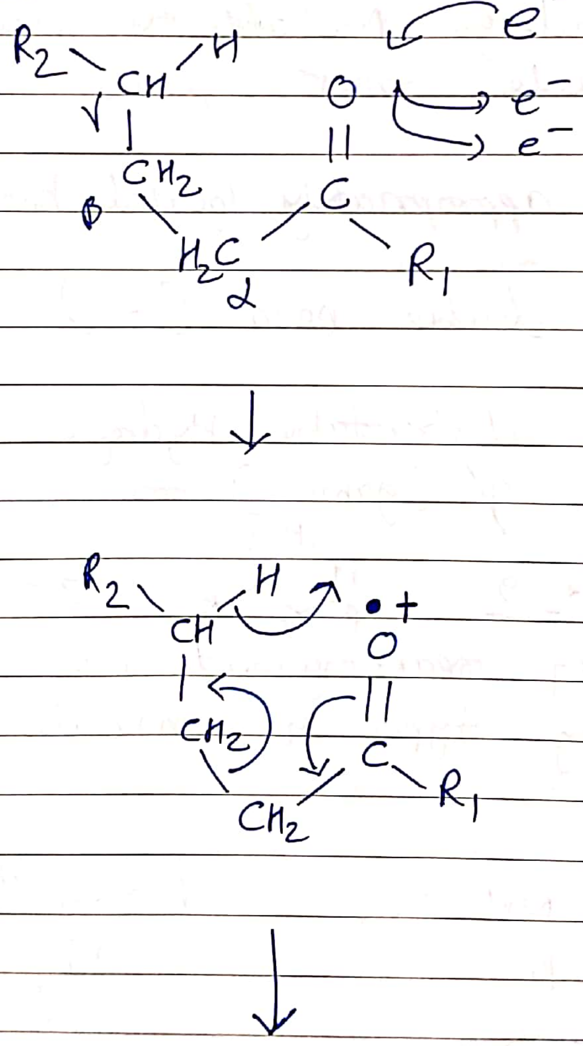


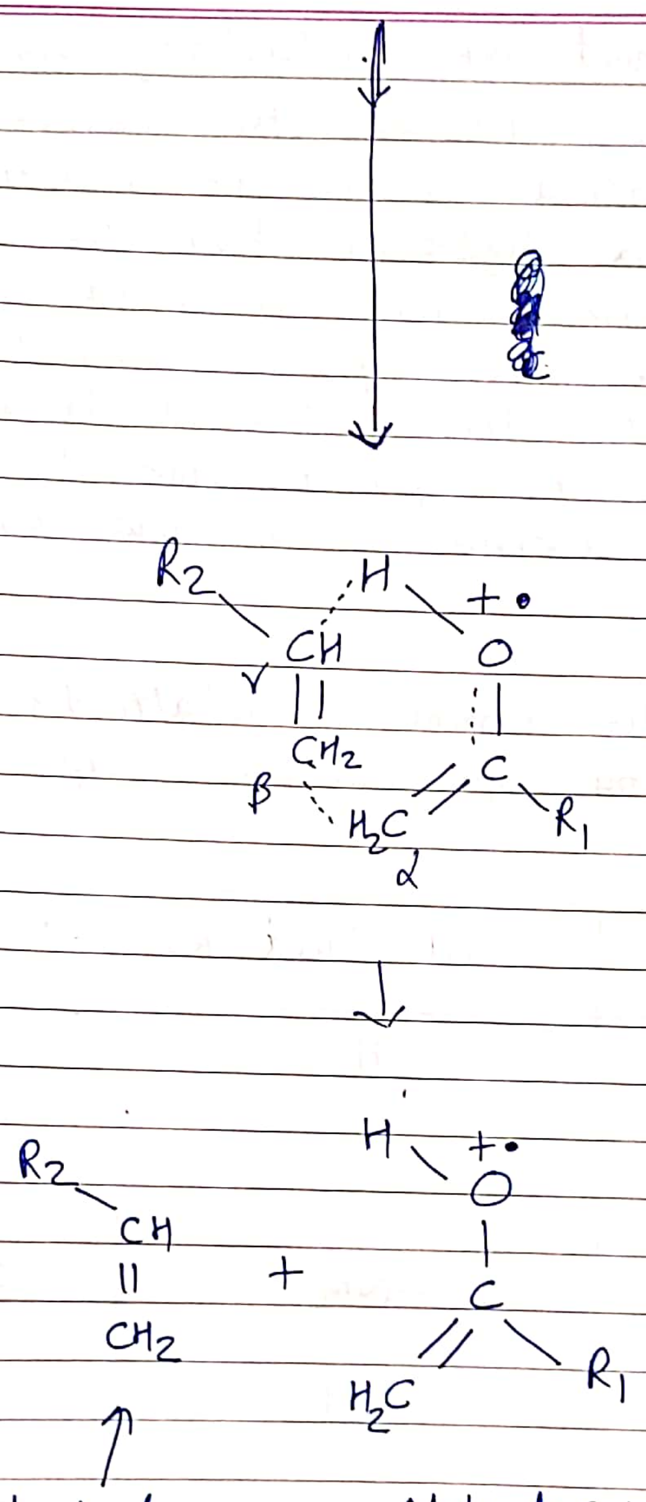
[Ketone]



[Unsaturated Compound]

e.g. **Ketone** (McLafferty Rearrangement)





Transition state

π bond formed bet^n β & γ.

σ bond broken bet^n α & β position

Neutral molecule

Molecular ion
(Enol radical cation)

If $R_1 \Rightarrow CH_3$, then the peak will be observed at m/z = 58.

⇒ " Statement of McLafferty Rearrangement

→ In the McLafferty rearrangement reaction, radical centre in molecular ion abstracts one hydrogen from the gamma(γ) position during which π bond is formed between the beta (β) & gamma(γ) position and the σ bond between the alpha (α) & beta(β) position is broken & produce alkene & a new radical cation."

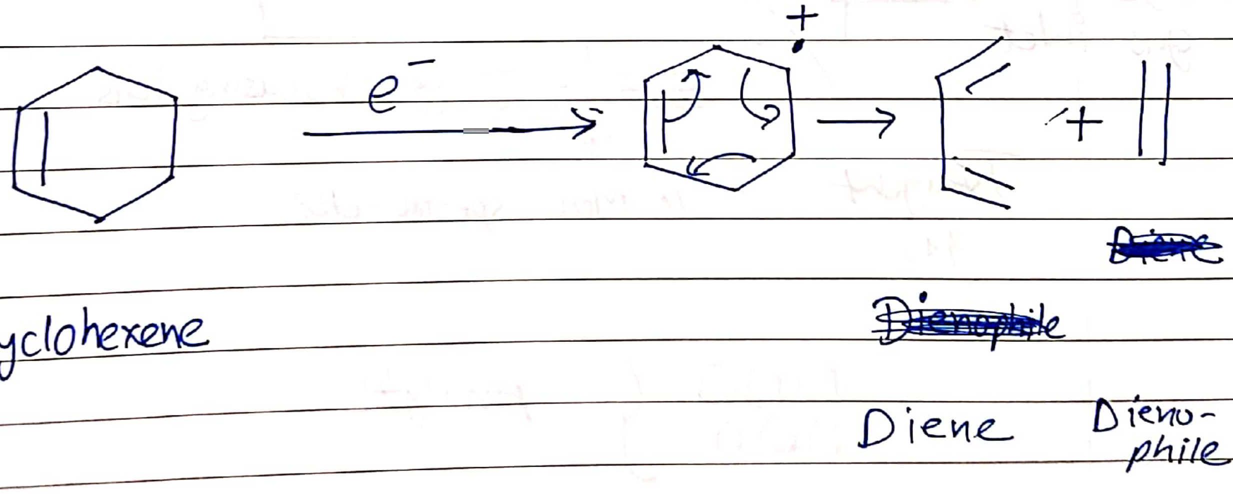
⇒ Table for the common McLafferty peak in the spectra of carbonyl group.

Compound Type	Substituent (R)	McL Peak
Aldehyde	$-H$	44
Methyl ketone	$-CH_3$	58
Amide	$-NH_2$	59
Acid	$-OH$	60
Ethyl ketone	$-CH_2CH_3$	72
Methyl ester	$-OCH_3$	74

* Retro Diels – Alder Reaction :-

→ Unsaturated six membered rings can undergo a Retro Diels-Alder fragmentation to produce the radical cation of a diene and a neutral alkene – the hypothetical precursors to the cyclohexene derivative.

→ If it had been prepared in the forward direction via [4π + 2π] diene + dienophile cycloaddition known to every organic chemist as the Diels - Alder reaction.



→

⊛ Nitrogen Rule

- Nitrogen rule is useful for identification of molecular ion because many signals /peaks can be ruled out on the basis of structural requirements.

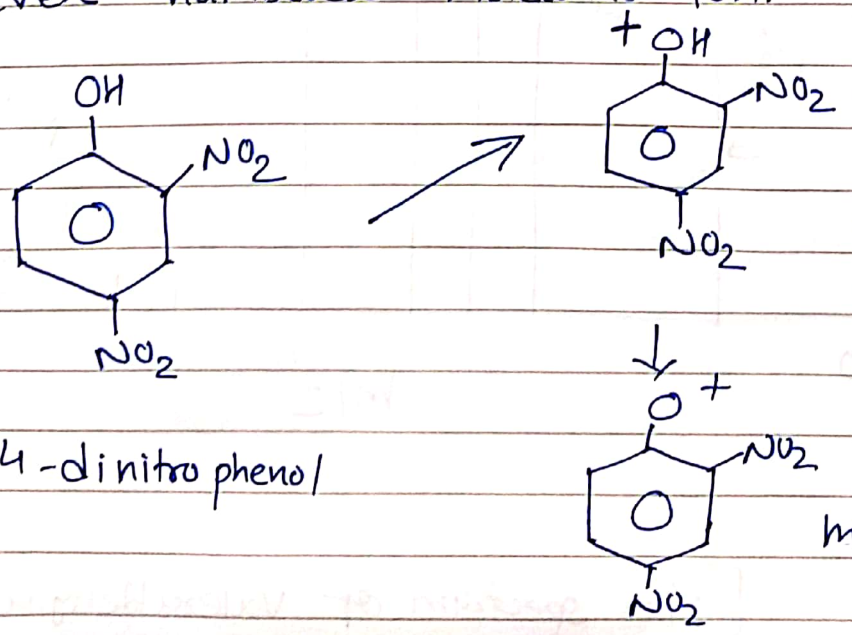
- Nitrogen rule states that –

→ ① "A molecule of even number of molecular mass should not contain any Nitrogen atom."

OR

"It must contain even number of Nitrogen atom"

- Fragmentation at a single bond gives an odd numbered fragment ion from an even numbered molecular ion.



2,4-dinitro phenol

molecular ion
m/z=184

Fragment ion
m/z = 183.

→ ② "An odd number of molecular mass requires odd number of nitrogen atom."

- Odd number of molecular ion will give the even number of fragment ion.

$CH_3-CH_2-NH_2 \rightarrow CH_3-CH_2-\overset{\cdot +}{N}H_2$ Molecular ion (m/z = 45)

$\downarrow$

$\dot{C}H_3 + CH_2=\overset{+}{N}H_2$ Fragment ion (m/z = 30)

→ This Nitrogen Rule is applicable for all compounds having C, H, N, S, O & halogens.

→ The fragment ion must contain all Nitrogen atoms present in the molecular ion, then only rule is applicable.

* Fragmentation Patterns and Fragmentation characteristic relation to Parent structure and Functional groups.

[1] Saturated Hydrocarbons.

(A) Straight chain compounds.

- Following are the features of mass spectra of Alkanes.

- The relative height of the parent peak decreases as the molecular mass increases in the homologous series.

- The molecular ion peak (although weak) is normally present.

- The spectra generally consists of clusters of peaks separated by 14 mass units corresponding to differences of CH_2 groups.

- The largest peak in each clusters represents C_nH_{2n+1} fragment. This is accompanied by C_nH_{2n} & C_nH_{2n+1} fragment corresponding to the loss of one and two H atoms respectively.

[**Base Peak**:- Most stable cation will give base peak]

Example :- Butane

e (Bombardment)

$CH_3-CH_2-CH_2-CH_3$ (Molecular weight = 58)

Butane

$\bar{e}$

e

$\downarrow$

$CH_3-CH_2-CH_2-CH_3^{\bullet +}$ Molecular ion ($m/z = 58$)

$\downarrow$

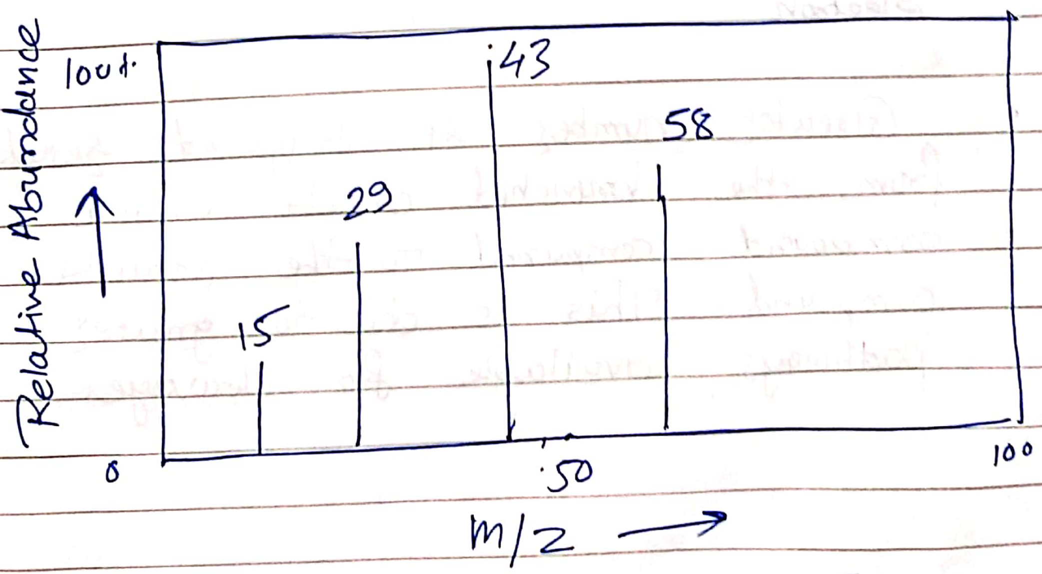
$CH_3-CH_2-\overset{+}{CH_2} + \overset{\bullet}{CH_3}$ $m/z = 43$ (Base peak)

$\downarrow$

$CH_3-\overset{+}{CH_2} + CH_3-\overset{\bullet}{CH_2}$ $m/z = 29$

$\downarrow$

$\overset{+}{CH_3} + \overset{\bullet}{CH_2}-CH_2-CH_3$ $m/z = 15$



[Mass Spectra of Butane]

- As the carbon skeleton becomes more highly branched, the intensity of the molecular ion peak decreases.

[B] Branched Chain Hydrocarbon

- Greater the branching in alkanes, less is the appearance of the molecular ion and if it appears, intensity will be low.

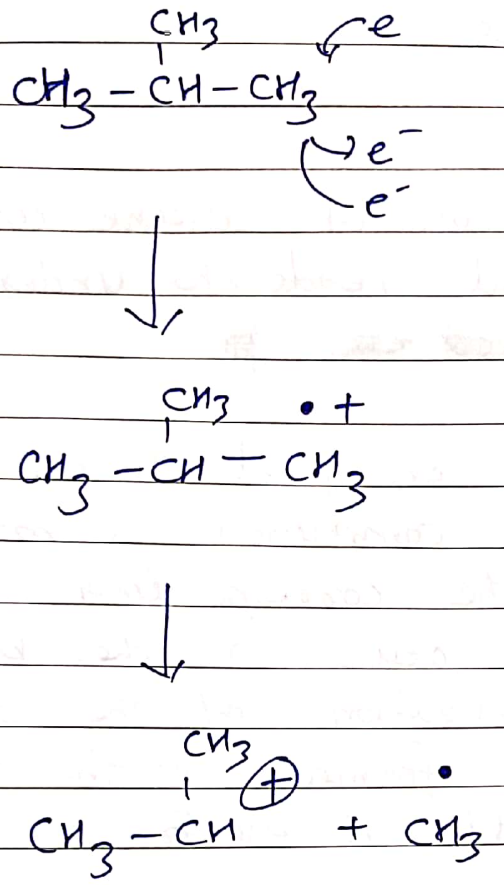
- Bond cleavage take place preferably at the site of branching. Due to such cleavage, more stable secondary or tertiary carbonium ions results.

- Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by the delocalization of lone pair of electron.

- Greater number of fragments results from the branched ~~chain~~ chain compound compared to the straight compound. This is due to greater pathways available for cleavage.

e.g.

Isobutane

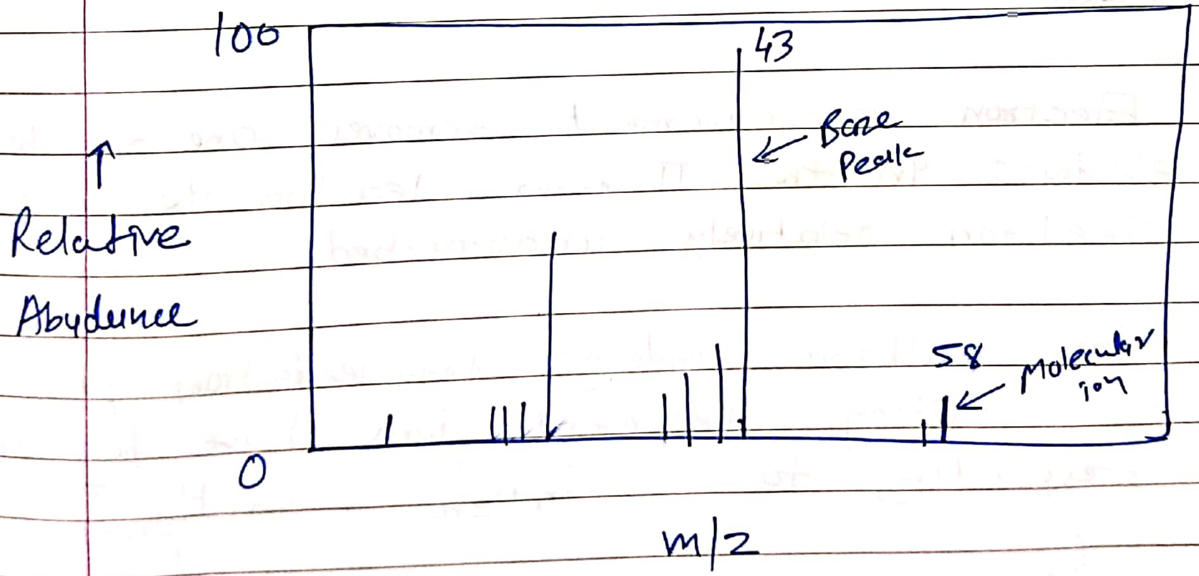


$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_3 \xrightarrow{e^-} CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_3^{\bullet +} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}H^{\oplus} + \overset{\bullet}{C}H_3$$

M.W. = 58

M/z = 58
(Molecular ion)

m/z = 43
(Base peak)



[Mass spectra of isobutane]

- Here as the branch increases, the intensity of molecular ion will decrease.

[2] Alkenes

→ The molecular ion of alkene containing one double bond tends to undergo allylic cleavage ~~ie~~. ~~at the β~~

→ The molecular ion peak in the spectra of unsaturated compounds is more intense than the corresponding saturated analogues. The reason is the better resonance stabilization of the charge on the cation formed by the removal of one of the π-electrons.

→ The relative abundance of the molecular ion peak decrease with increase in molecular mass.

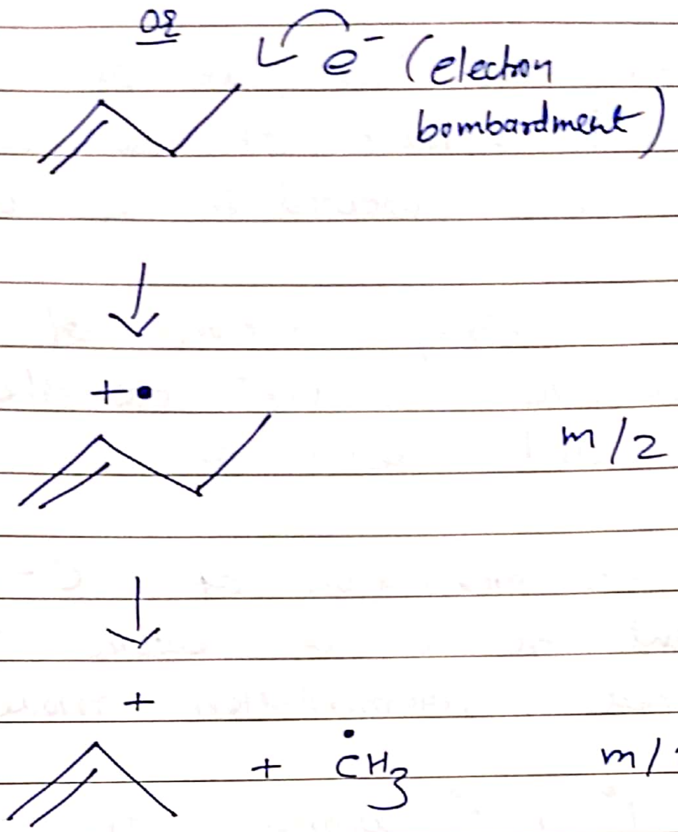
→ Electron bombardment removes one of the electrons in the π bond, leaving the carbon skeleton relatively undisturbed.

→ When alkene undergo fragmentation process, the resulting fragment ions have formulas corresponding to $C_nH_{2n}^+$ & $C_nH_{2n-1}^+$.

→ It is sometimes difficult to locate double bonds in alkenes since they migrate readily.

Eg. 1- butene

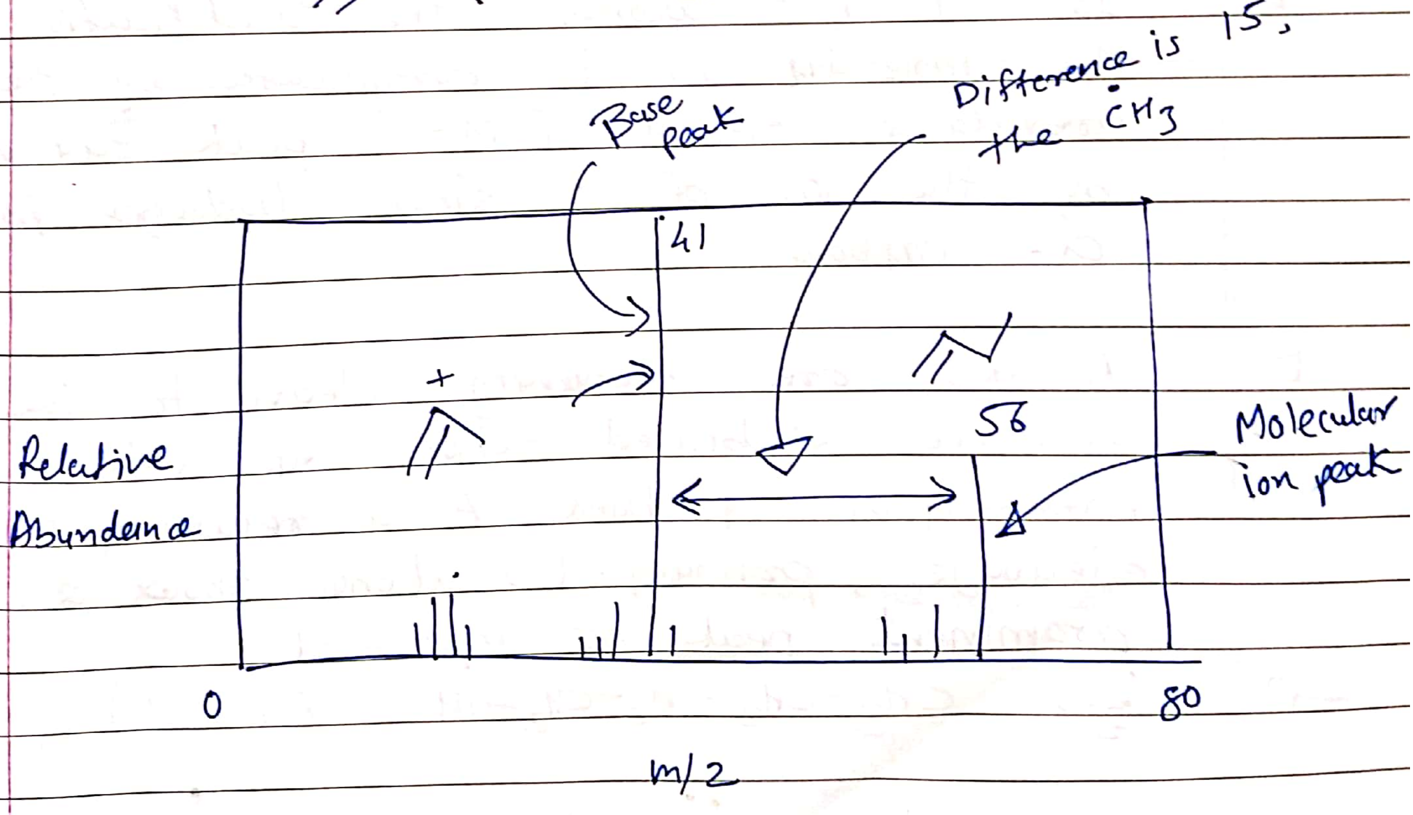
$CH_2=CH-CH_2-CH_3$ molecular weight = 56



m/z = 56

m/z = 56

m/z = 41



[Mass-spectra of 1-butene]

[3] Alcohols :-

→ The molecular ion peak of 1°, & 2° alcohol is usually of low abundance. It is not detected in 3° alcohol.

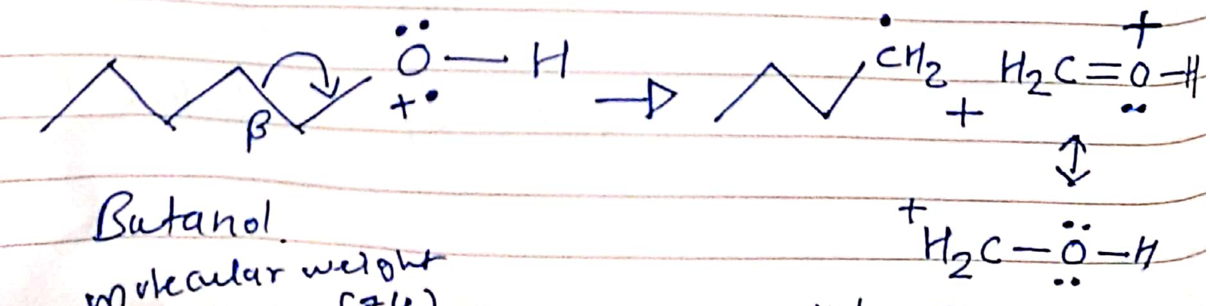
→ Common fragementations of alcohols are α - cleavage adjacent to the hydroxyl group and dehydration.

→ The fragmentation of C−C bond adjacent to Oxygen atom is the prefferred fragmentation mode. i.e. α-cleavage.

→ In 1° & 2° alcohols, the identification of the molecular ion is complicated by the prevalance of a [M−1] peak caused by the loss of a single hydrogen from α- carbon.

→ Alcohols are frequently cleave to give resonance stabilized cations due to the breaking of β bond. As a result of this cleavage, primary (1°) alcohol shows a prominent peak at m/z = 31.

→ e.g. $CH_3-CH_2-CH_2-CH_2-OH$ (Butanol)



Butanol.
molecular weight (74)

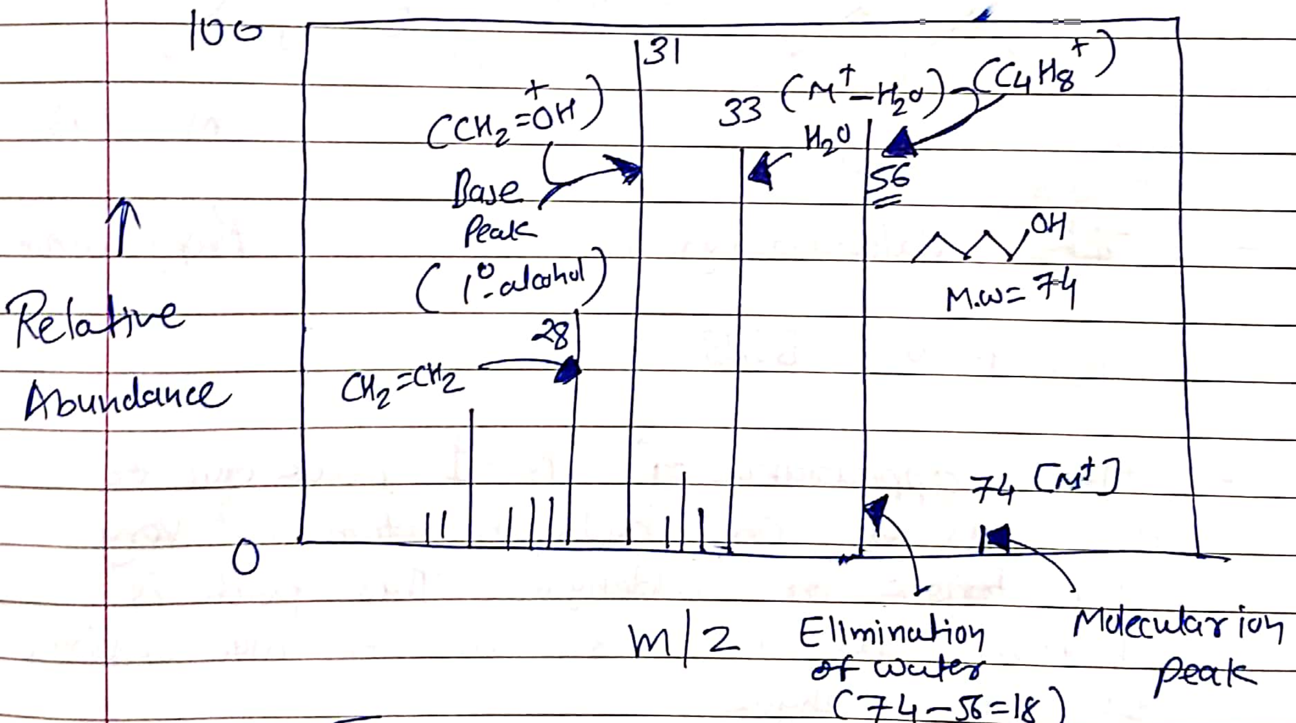
m/z = 31

- ~~The presence of a~~

- Alcohol also frequently undergoes the rearrangement resulting in a [M−18] peak from the loss of water. This peak is most easily visible in primary alcohols. but can be found in 2° & 3° alcohols. as well.

- Primary alcohol also can lose both water & an alkene

$$CH_3-CH_2-CH_2-CH_2-OH \rightarrow H_2O + CH_2=CH_2 + \overset{+}{CH_3-CH_2}$$



[Mass spectra of Butanol]

[4] Aldehydes

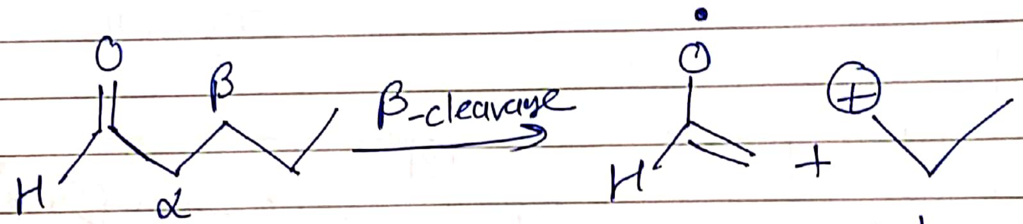
- The molecular ion peak of aliphatic aldehydes is weak.

- Aromatic aldehydes shows moderate intense peak.

- Characteristic feature of Aromatic aldehyde is loss of α hydrogen.

$$R-CH=O \xrightarrow{\alpha\text{-cleavage}} R-C\equiv O^{+} + H^{+}$$

- For aliphatic aldehyde is β cleavage



m/z = 43

$C_5H_{10}O$

- ~~The~~ [Valeraldehyde] Propyl cation

M.W. = 86.13.

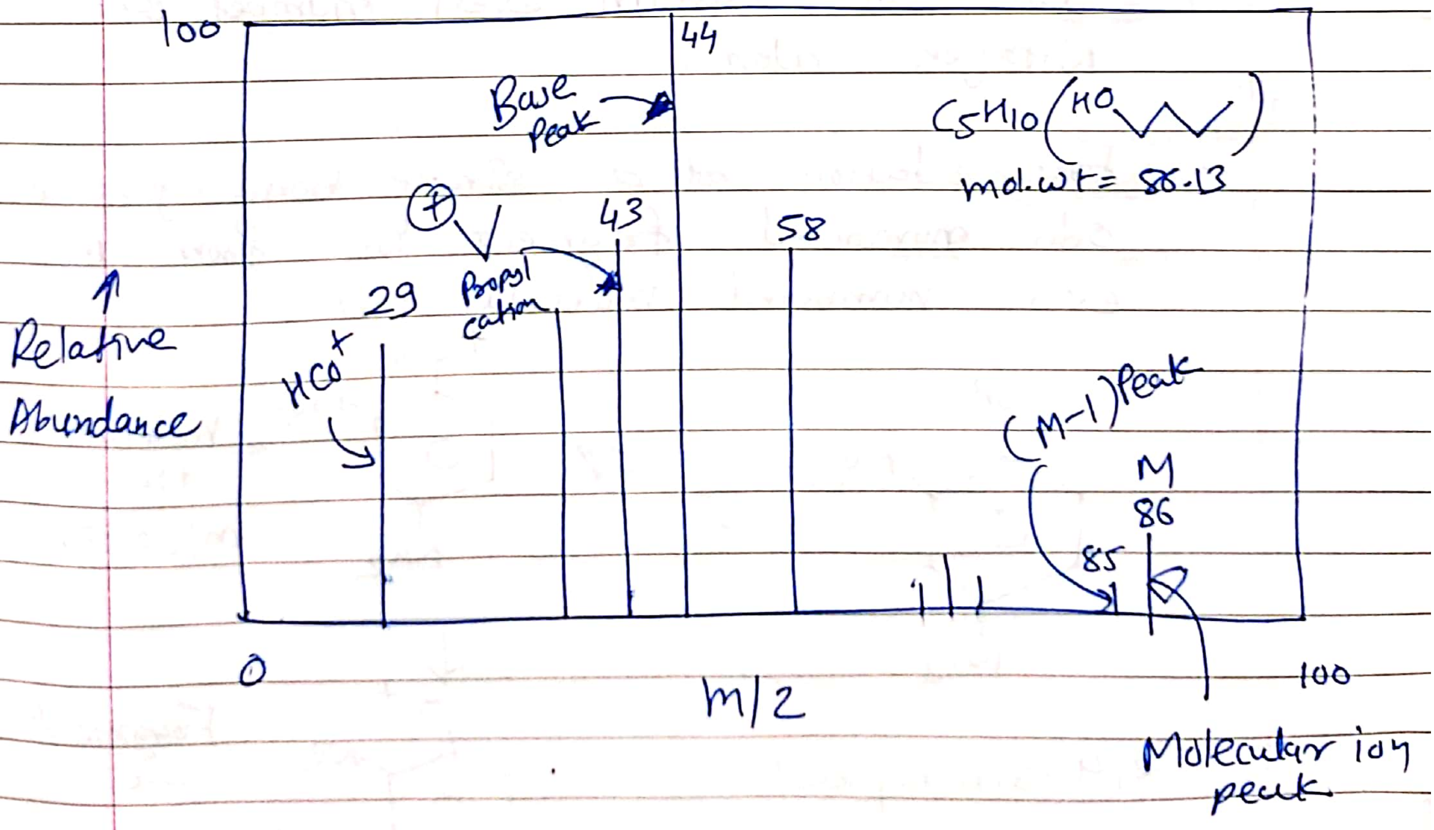
- The appearance of M-1 peak due to the loss of one hydrogen atom is very characteristic of aldehydes. This peak is observed at m/z = 85 in the mass spectrum of valeraldehyde.

- The peak due to the formation of HCO^+ can be observed at m/z = 29.

- The second important mode of fragmentation for aldehyde is known as β cleavage.

- In the case of valeraldehyde, β-cleavage creates a propyl cation. (m/z = 43.)

- The third ~~major~~ major fragmentation pathway for aldehyde is the McLafferty rearrangement. The fragment ion formed in this rearrangement has m/z = 44. and is the base peak in the spectrum of valeraldehyde.



[Mass spectrum of valeraldehyde]

* Chemical Ionization Mass Spectroscopy : (CIMS)

→ Chemical ionization is a gaseous phase ionization method; it is very important soft ionization technique.

→ Fragmentation is very less and gives intense peak of molecular ion. (i.e. more no. of M^+)

→ Some molecules like alcohol, ether, amines, esters, amino acids are highly ~~fragmentated~~ fragmented in electron ionization, so molecular ion peak will not be detected. To get proper molecular ion peak, we are using chemical ionization.

→ Steps of chemical ionization

(1) A carrier gas / reagent gas is introduced into the ionization source at slightly higher pressure (~ 1 torr). The carrier gas are: Methane, Ammonia, Isobutane etc.

(2) Carrier gas will be ionized due to electron impact from the ionization source

$$CH_4 + e^- \rightarrow \boxed{CH_4^{+\bullet}} + 2e^-$$

Primary ions.

$$CH_4^{+\bullet} \rightarrow \boxed{CH_3^{+}} + H^{\bullet}$$

(3) Primary ions ($CH_4^{+\bullet}$, CH_3^+) will react with excess CH_4 & it will produce different type of secondary ions. (i.e. CH_5^+, $C_2H_5^+$, $C_3H_5^+$)

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

$$C_2H_5^+ + CH_4 \rightarrow C_3H_5^+ + 2H_2$$

(4) Secondary ion will react with analyte molecule and form ions by three ways.

(A) Proton transfer

$M + CH_5^+ \rightarrow [M-H]^+ + CH_4$

$M + C_2H_5^+ \rightarrow [M-H]^+ + C_2H_4$

(B) Hydride Transfer

$M + C_2H_5^+ \rightarrow [M-1]^+ + C_2H_6$

(C) Electrophilic Addition

$M + CH_3^+ \rightarrow [M-CH_3]^+$

* Rule of thirteen in Mass Spectroscopy.

- High-resolution mass spectrometry provides molecular mass information from which the user can determine the exact molecular formula directly.
- When such molar mass information is not available, however, it is often useful to be able to generate all the possible molecular formulas. for a given mass.
- A useful method for generating possible molecular formulas for a given molecular mass is the Rule of Thirteen.
- As a first step in the Rule of thirteen, we generate a Base formula, which contains only carbon & Hydrogen.
- The base formula is found by dividing the molecular mass (M) by 13 (the mass of one carbon + one hydrogen.). This calculation provides a numerator 'n' & remainder 'r'.

$$\boxed{\frac{M}{13} = n + \frac{r}{13}}$$

- The base formula becomes.

$$\boxed{C_n H_{n+r}}$$

⇒ The Index of hydrogen deficiency :- (U).

- The index of hydrogen deficiency (unsaturation index) U that corresponds to the preceding formula is calculated easily by applying the following relationship.

$$\boxed{U = \frac{(\eta - \xi + 2)}{2}}$$

- Carbon / Hydrogen Equivalents for some common elements.

Add element	Substract Equivalent	Add ΔU
C	H_{12}	7
H_{12}	C	-7
O	CH_4	1
O_2	C_2H_8	2
O_3	C_3H_{12}	3
N	CH_2	½
N_2	C_2H_4	1
S	C_2H_8	2
^{35}Cl	C_2H_{11}	3
^{79}Br	C_6H_7	-3
F	CH_7	2
Si	C_2H_4	1
P	C_2H_7	0

* Application of Rule 13.

→ A simple application of "The Rule of 13" could result from the observation of molecular ion at mass 78. in mass spectrum.

$$\begin{array}{r|l} & 6 \leftarrow n \\ 13 & 78 \leftarrow M \\ & 78 \\ \hline & 00 \leftarrow r. \end{array}$$

→ The base formula is then $C_n H_{n+r}$ i.e. $C_6 H_6$.

→ The degree of unsaturation from $u = \frac{(n-r+2)}{2}$

$$= \frac{6-0+2}{2}$$

$$= 4.$$

→ So, the formula C_6H_6 with four degree of unsaturation. would represents benzene.

* Substitution of Carbon-Hydrogen Equivalents.

→ Chemical formulas containing elements other than carbon & Hydrogen can be obtained by subtracting the carbon hydrogen mass equivalent of the element of interest from the base formula before adding the selected element.

→ For example: CH_4 (mass-16) could be replaced by oxygen (O), while CH_2 (mass-14) could be replaced by nitrogen (N).

→ Example:

* Given Molecular mass = 142. Now we have to find out possible chemical formula with help of Rule No 13.

→
$$\begin{array}{r|l} & 10 \leftarrow n \\ \hline 13 & 142 \leftarrow M \\ & 13 \\ \hline & 12 \leftarrow r \end{array}$$

→ So, the base formula will be $C_n H_{n+r}$

∴ $C_{10}H_{22}$.

→ Substitution of other elements for carbon hydrogen using information from the C-H equivalent table.

→
$$\begin{array}{r} C_{10}H_{22} \\ -\; C_1H_4 + O \\ \hline C_9H_{18}O \end{array}$$
— Possible formula ①

→
$$\begin{array}{r} C_{10}H_{22} \\ -\; C_2H_{11} + Cl \\ \hline C_8H_{11}Cl \end{array}$$
— Possible formula ②

→
$$\begin{array}{r} C_{10}H_{22} \\ -\; C_2H_4 + N_2 \\ \hline C_8H_{18}N_2 \end{array}$$
— Possible formula ③