

## Mass Spectrometry.

- Mass spectroscopy is the most accurate method for determining the molecular mass of the compound and its elemental composition.
- In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionised and broken up into many fragments, some of which are positive. Each kind of ion has a particular ratio of mass to charge i.e.  $m/e \propto m/z$  value. For most ions, the charge is one and thus  $m/e$  ratio is simply the molecular mass of the ion.
- Mass spectra is used in two general ways
  - (i) To prove the identity of two compounds.
  - (ii) To establish the structure of a new compound.
- The mass spectrum of a compound helps to establish the structure of a new compound in several different ways.
  - (i) It can give the exact molecular mass.
  - (ii) It can give a molecular formula or it can reveal the presence of certain structural units in a molecule.

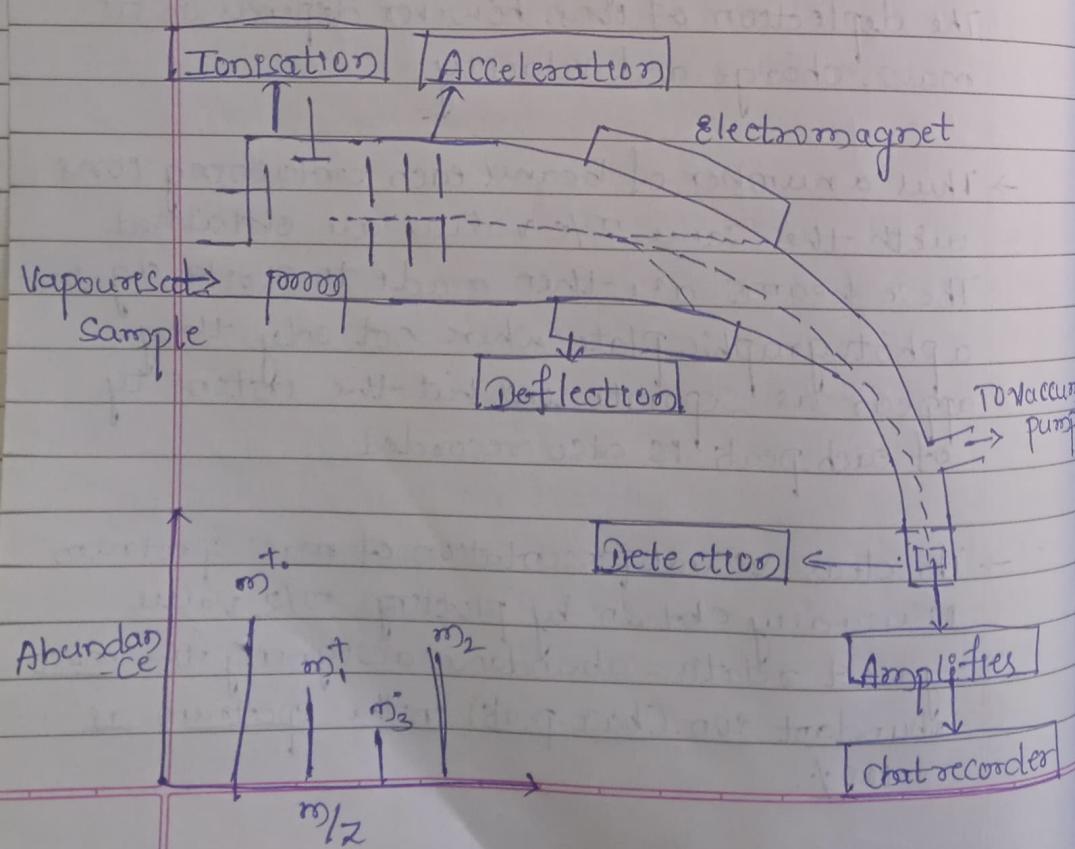
## Principle.

- Mass spectroscopy deals with the examination of the characteristic fragments (ions) arising from the breakdown of organic molecules.

- A mass spectrum is the plot of relative abundance of ions against their mass / charge ratio.
- The basic aspect of organic mass spectrometry consist of bombarding the vapour of an organic compound with a beam of energetic electrons accelerated from a filament to an energy of 70 eV to form positively charged ions (molecular ions).
- The additional energy of the electrons is dissipated in breaking the bonds in the molecular ion, which undergoes fragmentation to yield several neutral or positively charged species.
- This fragmentation may result in the formation of an even electron ion and radical. The various fragments thus formed, can be accelerated and deflected by magnetic or electric field. The depletion of ions, however depends on its mass, charge and velocity.
- Thus a number of beams each containing ions with the same m/e values are obtained. These beams are then made to strike against a photographic plate where not only they appear as separate lines but the intensity of each peak is also recorded.
- The clear visual presentation of mass spectrum is usually obtain by plotting m/z value against relative abundance assigning the most abundant ion (base peak) in the spectrum as 100%.

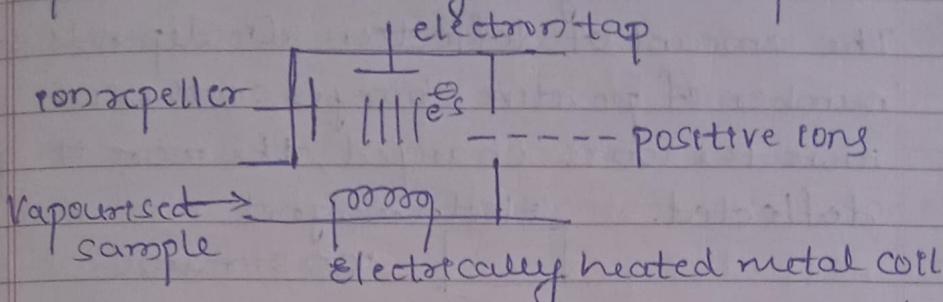
- Though organic mass spectrometry is routine used along with I.R., NMR and UV for structure determination its basic theory is different from others.
- In mass spectrometry no characteristic selective absorption of radiation is involved as in the case of the other three methods. Secondly in the mass spectrometry, the compound undergoes irreversible chemical changes unlike in the others, where the changes are reversible physical change.
- The mass spectral reactions are much more drastic than usual chemical reactions.
- IR, UV & NMR - Non destructive methods  
mass spectra - Destructive method.

### Instrumentation.



### → Ionisation :

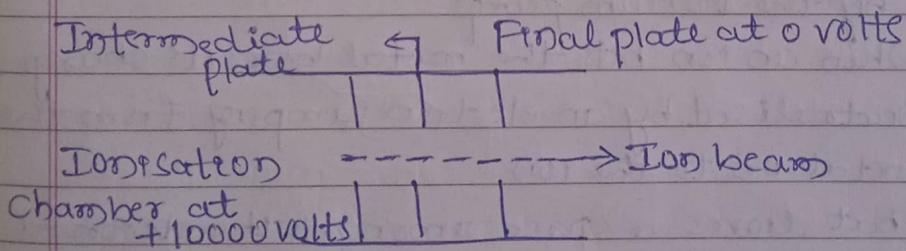
The atom is ionised by knocking one or more electrons off to give a positive ion. (mass spectrometers always work with positive ions).



The particles in the sample are bombarded with a stream of electrons to knock one or more electrons out of the sample to make positive ions. Most of the positive ions formed will carry a charge of +1. These positive ions are persuaded out into the rest of the machine by ion repellor which is another metal plate carrying a slight positive charge.

### → Acceleration :

The ions are accelerated so that they all have the same kinetic energy.



The positive ions are repelled away from the positive ionisation chamber and pass through three slits with voltage in the decreasing order.

The middle slit carries some intermediate voltage & the final at 0 volts.

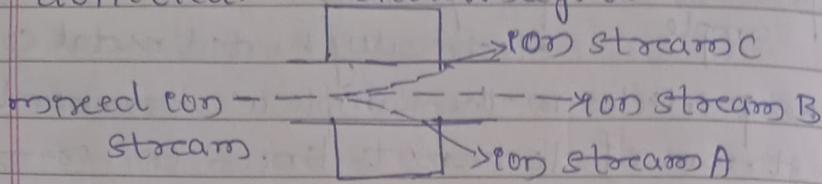
All the ions are accelerated into a finely focused beam.

## → Deflection:

The ions are then deflected by a magnetic field according to their masses, the lighter they are the more they are deflected.

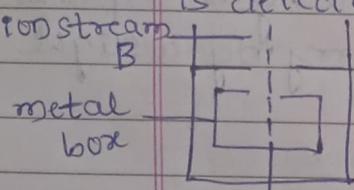
The amount of deflection also depends on the number of positive charges on the ion. The more the ion is charged, the more it gets deflected.

Electromagnet



## → Detection:

The beam of ions passing through the machine is detected electrically.



only ion stream B makes it right through the machine to the ion detector. The other ions collide with the walls where they will pickup electrons and be neutralised.

They get removed from the mass spectrometer by the vacuum pump.

→ When an ion hits the metal box, its charge is neutralised by an electron jumping from the metal on to the ion.

→ That leaves a space amongst the electrons in the metal and the electrons in the wire shuffle along to fill it.

→ A flow of electrons in the wire is detected as an electric current which can be amplified and recorded. The more ions arriving, the greater is the current.

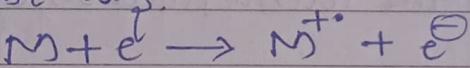
## Fragmentation Process.

- Bombardment of molecules by an electron beam with energy between 10-15 eV usually results in the ionisation 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 breakdown into various fragments. This process is called Fragmentation process.

### Types of Ions.

#### ① Molecular ion or Parent ion

When a molecule is bombarded with electrons in high vacuum in mass spectrometer, it is converted into positive ions by loss of an electron. These ions are called as Molecular ions or Parent ion.



where  $M$  — molecule

$M^+$  — molecular ion or parent ion.

The order of energy required to remove electron is as follows—

$\sigma$  electrons  $>$  non-conjugated  $\pi$   $>$  conjugated  $\pi$   $>$  non-bonding or lone pair of electrons.

- Many of these molecular ions ( $M^+$ ) dissociate rapidly at  $10^{-10}$  to  $10^{-13}$  seconds to give a positively charged fragment and a radical in the simplest case. If some molecular ions remain intact long enough to reach the detector,

→ Most molecules show a peak for the molecular ion, the stability of which is usually in the order -

Aromatic > conjugated acyclic polyenes >  
Alicyclics > n-hydrocarbons > ketones > ethers  
> Branched chain hydrocarbons > alcohols

### Characteristics of molecular ion

→ Molecular peak is observed if molecular ion remains intact long enough to reach the detector. This peak gives the molecular weight of the compound. The molecular ion peaks is usually the peaks of the highest mass numbers.

→ The molecular ion  $n^+$  has mass corresponding to the molecular weight of the compound from which it is generated. Thus the mass of a molecular ion  $n^+$  is an important parameter in the identification of the compound.

### Significance of molecular ion

Molecular ion peaks gives the molecular weight of the compound.

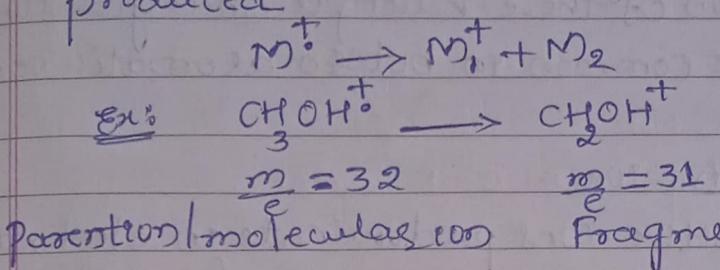
i.e.  $\frac{m}{z}$  of molecular ion = molecular weight of compound

Ex:  $C_2H_5^+$  ( $m/e = 29$ ) gives molecular weight of ethane

$(C_6H_6)^+$  ( $m/e = 78$ ) gives molecular weight of Benzene

## ② Fragment Ions

When the energy is given to molecules during electron impact, further cleavage takes place and ions of lower mass number known as fragment ions are produced.



## ③ Rearrangement ions

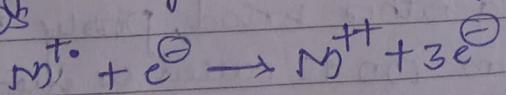
Rearrangement ions are the fragments whose origin cannot be described by simple cleavage of bonds in the parent ion, but are result of intramolecular atomic rearrangement during fragmentation.

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

Ex: Prominent peak in spectrum of diethyl ether occurs at  $m/e 31$ . This is due to the ions  $\text{CH}_3^+$  which is formed by rearrangement of  $\text{C}_2\text{H}_5\text{O}^+$  ions.

## ④ Multi charged ions

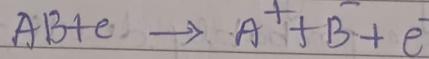
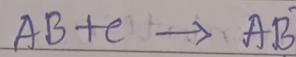
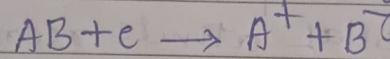
Sometimes ions may also exist with two or three charges instead of usual single charge in mass spectrum. These are known as doubly or triply charged ions. They are created as follows



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

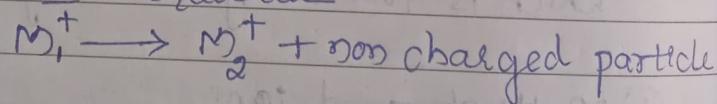
### ⑤ Negative ion

The positive ions predominate in electronic impact ionization because of greater stability. The negative ions are not very useful in structural determinations. The formation of negative ions is very rare but these can be produced in three ways.



### ⑥ Metastable ion

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



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 at a position  $M^*$  as a rather broad, poorly focused peak such as ion is called as metastable ion.

## General rules for Fragmentation.

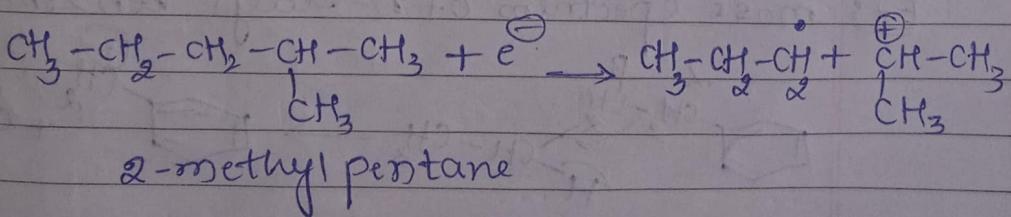
- ① The relative height of the molecular ion peaks is greatest for the straight chain compound and decreases as the degree of branching increases.
  - ② The relative height of the molecular ion peaks usually decreases with increasing molecular weight in a homologous series.
  - ③ Cleavage is favoured at alkyl substituted carbon atoms, the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbon atom over a secondary than primary.
- $$CH_3^+ < RCH_2^+ < R_2CH^+ < R_3C^+$$

### Stevenson's Rule:

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

Generally the largest substituent at a branch is eliminated most readily as a radical because long chain radicals can achieve some stability by delocalisation of the lone electron.

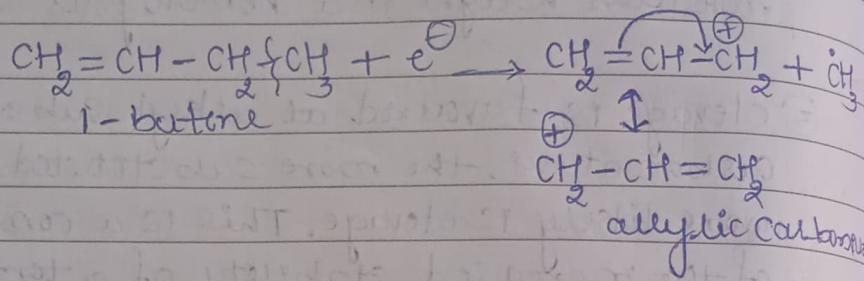
Ex: cleavage of 2-methylpentane



④ Double bonds, cyclic structures and especially aromatic or hetero aromatic rings stabilize the molecular ion and thus increase the probability of its appearance.

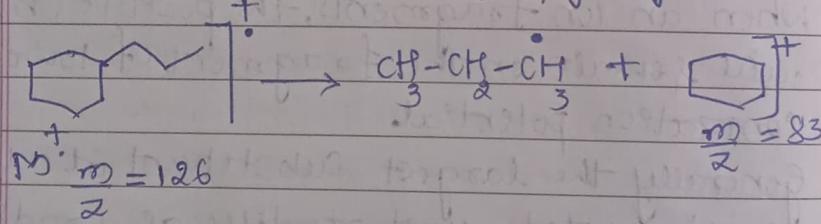
⑤ double bonds favour allylic cleavage and give the resonance stabilised allylic carbonium.

Ex: Mass spectrum of 1-butene



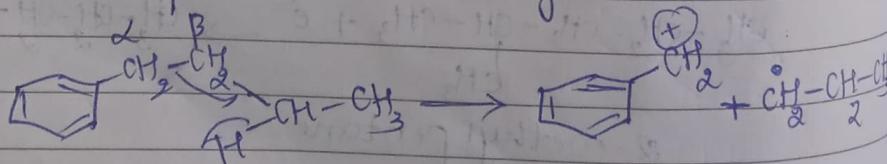
⑥ Saturated rings tend to lose alkyl side chains at the  $\alpha$ -carbon atom. This positive charge tends to stay with the ring fragment.

Ex: Mass spectrum of *n*-propyl cyclohexane



⑦ In alkyl substituted aromatic compounds cleavage is very probable at the bond  $\beta$  to the ring, giving the resonance stabilised benzyl ion or more likely tropylion ion.

Ex: mass spectrum of *n*-butyl benzene



⑧ cleavage is often associated with elimination of small stable, neutral molecules such as carbon monoxide, olefins, water, ammonia, hydrogen sulphide, hydrogen cyanide, mercaptans, ketone or alcohols, often with rearrangement.

### Factors influencing fragmentation Process.

- Bombardment energies.
- Functional Groups.
- Thermal decomposition.

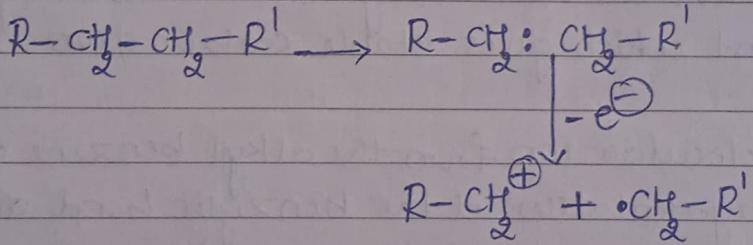
### General modes of fragmentation.

Fragmentation of the molecular ion takes place in following modes

- Simple cleavage.

#### ① Homolytic cleavage:

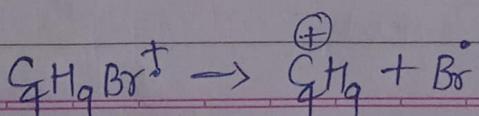
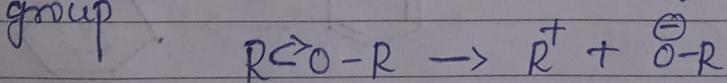
Here fragmentation is due to electron redistribution between bonds.



#### ② Heterolytic cleavage:

Fragmentation by movement of two electrons.

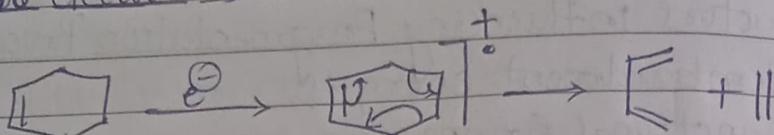
In this type of cleavage both the electrons of the bond are taken over by one of the atoms; the fragments are an even electron cation and radical with the positive charge residing on the alkyl group.



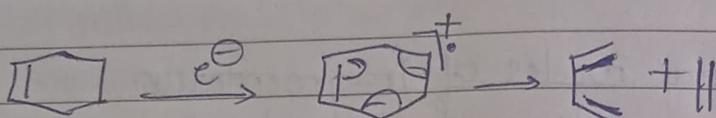
### ③ Retro Diels-Alder reaction:

Elimination by multiple σ bond rupture  
Cyclohexene is broken down to diene and  
dienophile. It can be explained by one or  
two electron mechanism.

→ Two electron mechanism.



→ One electron mechanism:

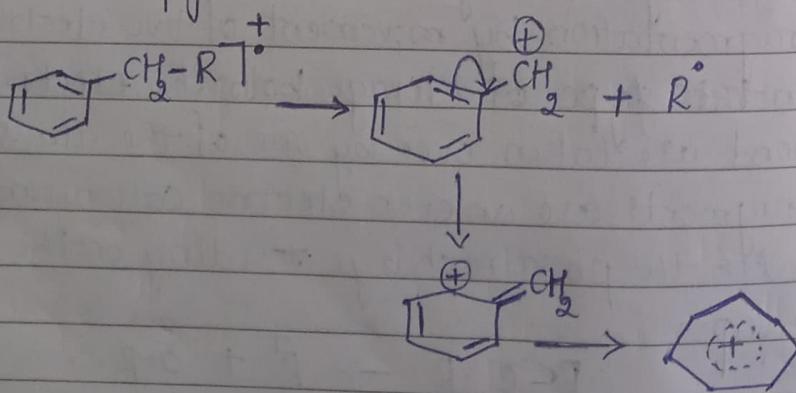


→ Rearrangement reactions accompanied by transfer of atoms.

#### ① Scrambling.

Fragmentation giving rise to stable carbocation  
In certain cases fragmentation takes place at  
bond which gives stable carbocation.

Ex: Molecular ion from the alkyl benzene undergoes fragmentation at the benzylic bond and final product is seven membered cyclic ion known as Tropylidium ion.



Tropylidium ion.

## ② McLafferty Rearrangement.

Fragmentation due to rearrangement of molecules or parent ion.

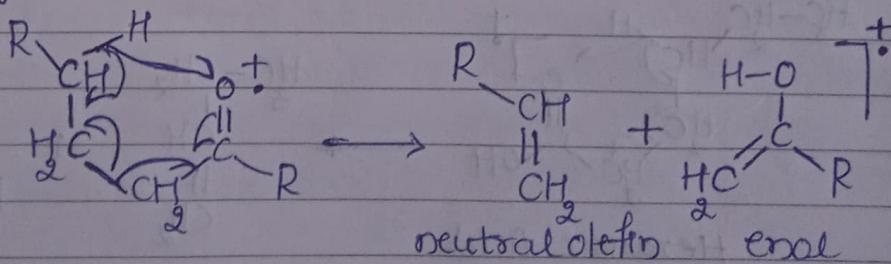
→ Here cleavage of bonds in molecular ion is due to the intramolecular atomic rearrangement.

This leads to fragmentation whose origin cannot be described by simple cleavage of bonds. When fragments 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 molecule 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 and 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 and a neutral olefins.



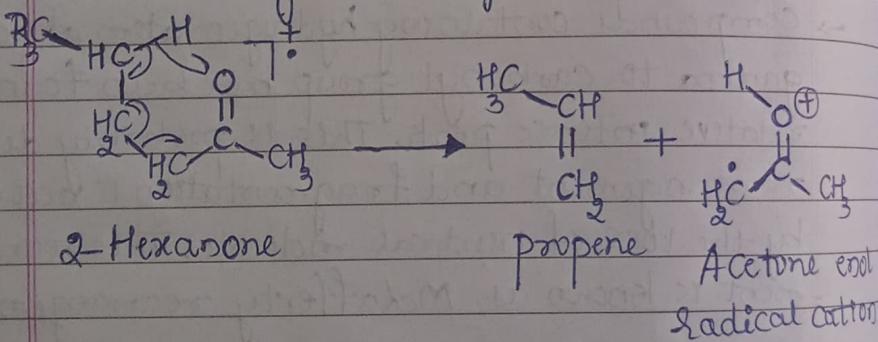
To undergo McLafferty rearrangement, a molecule must possess:

- An appropriately located hetero atom (Conjugate)
- A double bond
- An abstractable hydrogen atom which is  $\gamma$  (gamma) to  $C=O$  system.

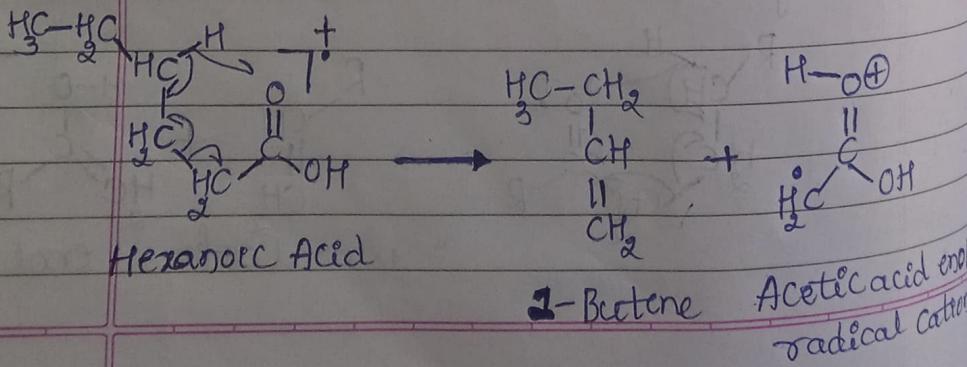
Table for the common McLafferty peaks in the spectra of carbonyl group.

Compound	Type	Substituent	McL peaks
Aldehyde		-H	44
Methyl Ketone		-CH <sub>3</sub>	58
Amide		-NH <sub>2</sub>	59
Acid		-OH	60
Ethyl Ketone		-CH <sub>2</sub> CH <sub>3</sub>	72
Methyl ester		-OCH <sub>3</sub>	74

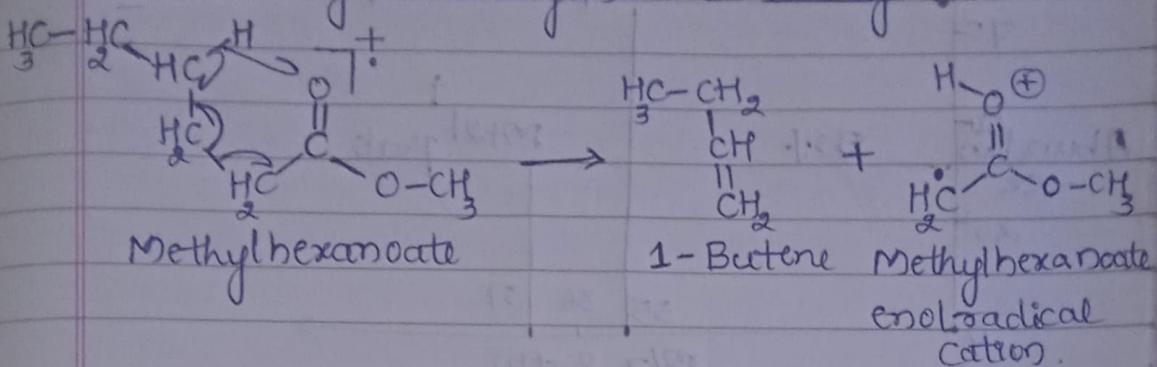
→ McLafferty Rearrangement of 2-Hexanone



→ McLafferty Rearrangement of Hexanoic acid.



→ McLafferty rearrangement of Methyl hexanoate.



Isotopic Abundance

Elements having same atomic masses are called as isotopes.

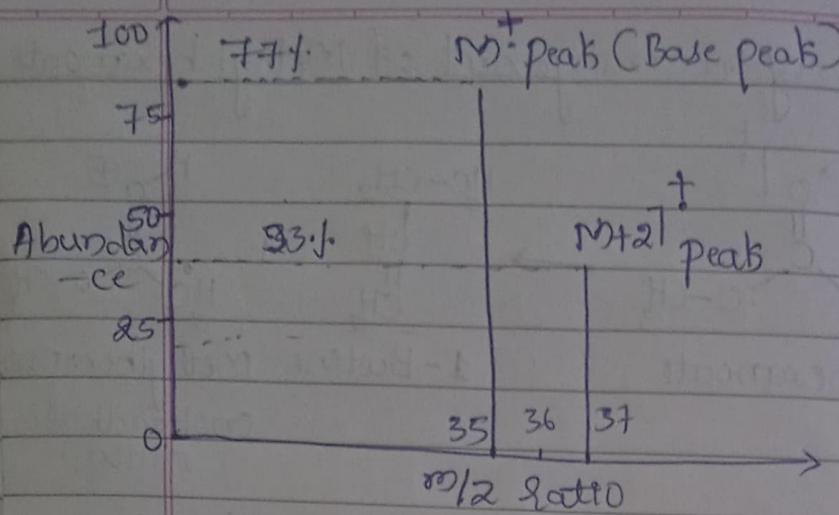
Ex: Cl<sup>35</sup>, Cl<sup>37</sup>

B<sub>79</sub>, B<sub>81</sub>

C<sup>12</sup>, C<sup>13</sup> etc

The relative abundance of an isotope is the percentage of atoms with a specific atomic mass found in a naturally occurring sample of an element.

→ The average atomic mass of an element is a weighted average calculated by multiplying the relative abundances of the element's isotopes by their atomic masses & then summing the products. The relative abundance of each isotope can be determined using mass spectrometry.



Cl with atomic weight 35 shows  $M^+$  peak with abundance 77.1. Cl with atomic weight 37 shows  $(M+2)^+$  peak with 23.1%.

p.e out of 100 Cl  $\begin{cases} 35 \\ 37 \end{cases}$