➢ Introduction

Mass spectrometry is a powerful analytical technique used to quantify known materials, to identify unknown compounds within a sample, and to elucidate the structure and chemical properties of different molecules. The complete process involves the conversion of the sample into gaseous ions, with or without fragmentation, which are then characterized by their mass to charge ratios (m/z) and relative abundances.

This technique basically studies the effect of ionizing energy on molecules. It depends upon chemical reactions in the gas phase in which sample molecules are consumed during the formation of ionic and neutral species.

➢ Principle

"The basic principle of mass spectrometry (MS) is to generate ions from either inorganic or organic compounds by any suitable method, to separate these ions by their mass-to-charge ratio (m/z) and to detect them qualitatively and quantitatively by their respective m/z and abundance.

➢ Basic terminology used in mass spectrometry(MS)

(1) **Molecular ion peak:** In the mass spectrum, the heaviest ion (the one with the greatest m/z value) is likely to be the molecular ion. It is represented by $M^{+\cdot}$

It is sometimes also known as **Parent ion peak.**

(2) **Fragment ion peak** The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion is called **Fragment ion** and the other is an uncharged free radical.

$$M\cdot^{+} \rightarrow X^{+} + Y\cdot$$

(3) Base peak: In mass spectrum more intense peak is known as Base peak. Its intensity taken 100%. Other all peak intensity determined respect to base peak.

(4) Metastable ion peak: A mass spectrum sometimes molecule uion further fragment in accelerating region to produce ion is called Metasatble ion.

- **Characteristic of metastable ion peak**
  - ✓ It is non-integral mass
  - ✓ Weak intense peak
  - ✓ Used for mechanism of fragmentation.

Short Questions	
1. Who invented mass spectrometers?	J.J Thompson
2. In mass spectrometer, the sample that has to be analysed is bombarded with which of the following?	electron
3. Which symbol molecular ion peak represent?	$M^{+\cdot}$
4.Higest intense peak in mass spectrum is called	Base peak
1. Metastable ion peak value	Half integer

➢ Instrumentation of Mass Spectrometer

The essential components of a mass spectrometer are:

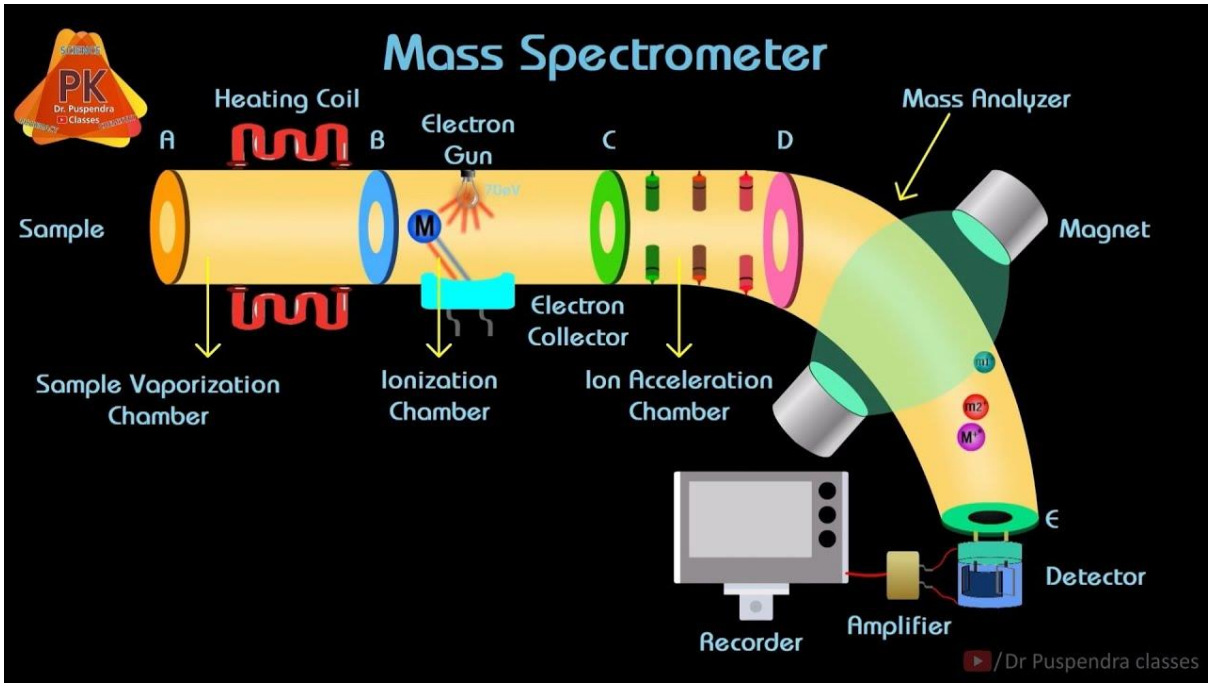
• Inlet device

• Ionisation chamber or Ion Source

• Analyser

• Detector

• Processing and output devices



The inlet device loads the sample into the ionisation chamber where the analyte is ionised by a suitable method and the molecular ion and/or the fragment ions obtained by fragmentation of the molecular ion are directed towards the analyser. In the analyser these ions obtained by the fragmentation of the molecular ion are sorted out on the basis of their m z value by using one of the many available techniques and are sent to the detector. The processing unit records the magnitude of these electrical signals as a function of m z and gives an output in the form of a mass spectrum.

2. **Inlet Devices**

The purpose of the inlet device is to load the sample into the ionisation chamber. The device used depends on the nature of the sample. The solid samples are placed on the tip of a rod called direct insertion probe which is inserted into the evacuated chamber having a vacuum-tight seal. This is then heated to evaporate or sublime the sample to get the molecules in the gas phase. The gases and heat volatile liquids, on the other hand are generally introduced through specially designed devices with controlled flow**.**

3. **Ionisation Chamber or Ion Source**

Different method of ionization technique given below:

(I) Electron ionisation (EI): This is the oldest and probably the best-characterized of all the ionisation methods. In this method, a high energy beam of electrons passes through the sample in the gas-phase. These electrons generally have energy of 10-150 eV. The electrons on colliding with the neutral analyte molecule knock off an electron from it and generate a positively charged ion. This process produces either a molecular ion or one of its fragments. This method is good for volatile compounds but the molecular ion peak is either weak or absent.

(II) Chemical ionisation (CI): The chemical ionisation method uses ion/molecule reactions to produce ions from the analyte. For this purpose a reagent gas such as methane, isobutene or ammonia is passed into the ionisation chamber where it gets ionised by electron ionisation. For example, methane gas gives mainly $^{+}CH_4$ and $^{+}CH_3$ ions as follows

(III) Fast atom bombardment (FAB): In this method the analyte is dissolved in a liquid Mass Spectrometry matrix like glycerol and a small amount of this is placed on a target. The target is then bombarded with a beam of fast atoms (e.g., xenon or argon atoms at several keV).These desorb positive and negative analyte ions from the sample.

4. **Mass Analyser**

→ The analyse deflects the ionic beam into different fragment depending on their mass/charge i.e. (m/z) value.

→ In analyser tube the ions are subjected to a uniform magnetic field which is generated by an electromagnet and is perpendicular to the direction of the beam.

→ In the magnetic field the ions, an electric field as well as magnetic field is applied hence the instrument is known as **double focusing** mass analyser.

Short questions	
1. **Mass spectrometer separates ions on the basis of which of the following?**	Mass to charge(m/z) ratio
2. **In mass spectrometer, the ions are sorted out in which of the following ways?**	By accelerating them through electric and magnetic field
3. Which of the following ions pass through the slit and reach the collecting plate?	Positive ions of specific mass
4. Write any one name of ionization technique	Electron ionization
5. Write the name detector used in mass spectrometer	photoelectric

5. Detector or Ion Collector

In the mass spectrometers the ions after passing through the analyser are generally detected by a suitable electron multiplier. The electron multipliers are capable of providing quick response times and high current gains. The electrical signal so obtained can be processed, stored or suitably displayed.

➢ General fragmentation mode mass spectra

Intensity of peak in MS depend on stability of fragment ion and radicals formed.

Different kind of cleavage possible in organic molecule described below.

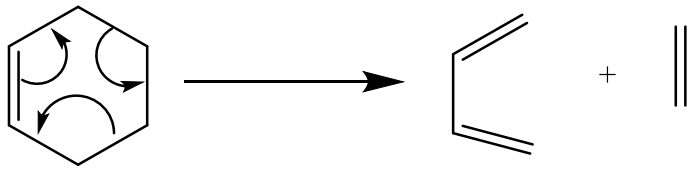
The fragmentation of a bond can proceed through two pathways,either homolytic or heterolytic cleavage

1. Simple cleavage

a) Homolytic cleavage : The fragmentation produced by a hemolytic cleavage results from the movement of single electrons.

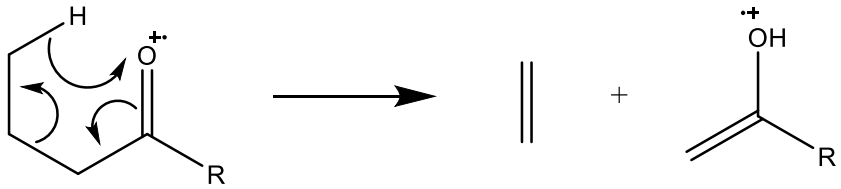
b) Heterocyclic cleavage : In the heterolytic cleavage, a pair of electrons move towards the charged site as illustrated by the double headed arrow producing a cation and a radical.

2 **Retro Diel's alder Reaction** : The retro-Diels–Alder reaction (rDA) is the microscopic reverse of the Diels–Alder reaction—the formation of a diene and dienophile from a cyclohexene. It can be accomplished spontaneously with heat, or with acid or base mediation



cyclohexene butadiene ethylene

3. **Mc-Lafferty Rearrangement :** In this Rearrangement involve ϒ-H migrate to carbonyl oxygen by cleavage of β-bond break via six memberd transition state to elimination neutral alkene molecule from carbonyl compound like aldehyde ,ketone etc.



Carbonyl compound ethylene enol form

This type of rearrangement also take place in acid, aldehyde, ester, amide, nitriles.

➢ Mass spectra of alkanes

For a saturated hydrocarbons and those organic structure containing large saturated hydrocarbons (straight chain and branched) the method of fragmentation are quite predictable.

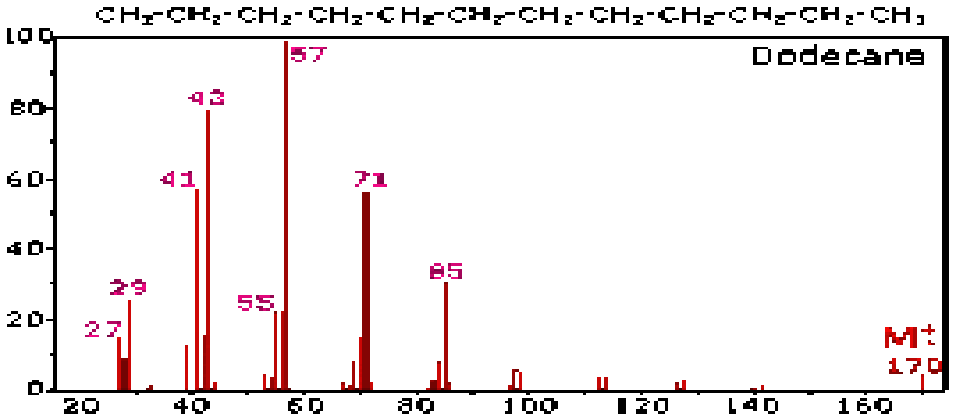
Fragmentation depend upon stability of carbocation produced.

Some important feature of the mass spectra

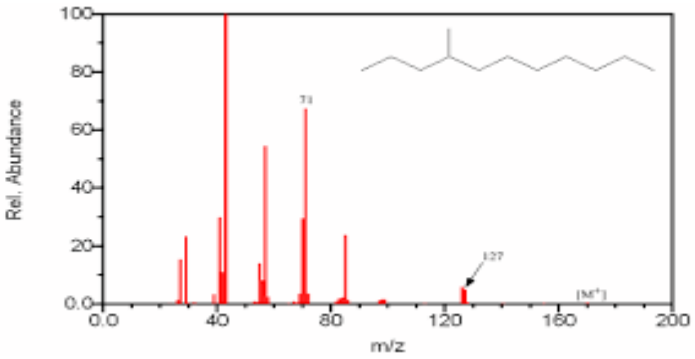
- The relative height of the molecular ion peak decreases the molecular mass increases in homologous series.
- The molecular ion peak of a straight-chain saturated hydrocarbon is always present though of a low intensity for long- chain compounds.

- Cleavage is favoured at alkyl substituted carbon, the more substituted, the more likely is the cleavage. This is because a tertiary carbocation(3^0) is more stable than secondary(2^0), which turn is more stable than primary carbocation(1^0)

Mass spectra of n-dodecane



Mass spectra of branched dodecane



➢ Application of Mass Spectrometry

Mass spectrometry finds extensive applications in diverse areas like chemical analysis biochemistry, clinical chemistry, environmental pollution monitoring, food adulteration, doping in sports, and archaeology, etc.

The most common applications of the mass spectrometry are:

→ Determination of molar mass of the analyte or sample
→ Determination of molecular formula of the analyte or sample
→ Determination of the structure of the analyte or sample
→ Identification of the analyte (alone or in a mixture)

Short Questions	
11.Which types of cleavage free radicals produced	Homolytic
12.Minimum number of carbon require in Mc-Lafferty rearrangement	Four carbon
13. What information can be obtained from mass spectra	Exact molecular mass

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Unit-3 Chapter-6: Mass Spectrometry