and hence the relative intensities of the peaks decreases from mass number 15 to 12, because the species are formed at the expense of the parent species.

3. At high voltage 50 eV, these fragmentation patterns and relative intensities become constant.

In fragmentation process, the highest mass detected is usually of the ionized molecule. This peak is cal parent peak and the mass as parent mass PM.

## 5. McLafferty Rearrangement

In some cases, fragments are observed, which are not a part of the original molecule. These are known rearrangement ions, which are formed from the molecular ion via rearrangement of atoms or gro Hydrogen transfer rearrangements are very common. A well known example of H–transfer observed in m spectrometry is McLafferty rearrangement first reported by Fred McLafferty in 1952.

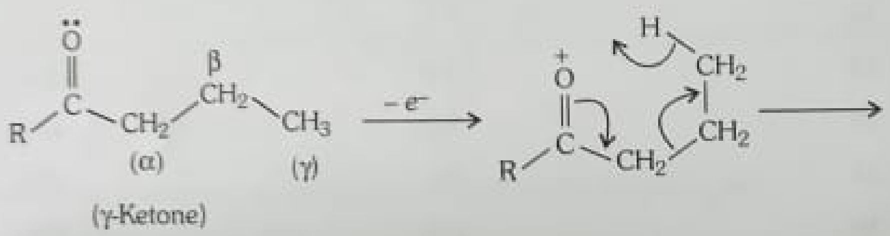
This is an example of fragmentation of a carbonyl compound containing radical cation via β-cleavage to g enol radical cation and alkene.

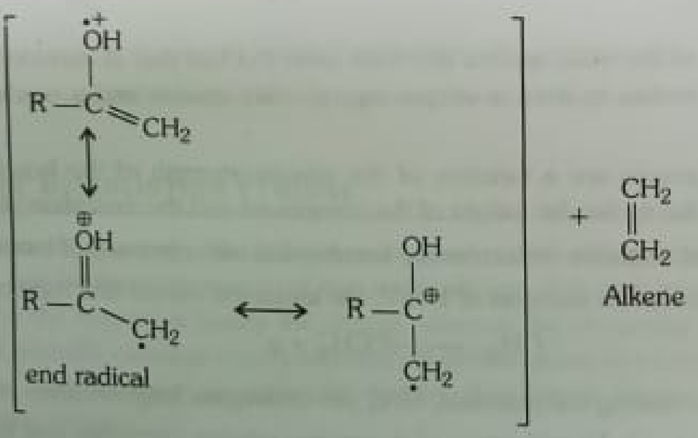
Normally McLafferty rearrangement is a two step process :

(i) 1, 4 H-atom migration to the carbonyl O-atom

(ii) Followed by bond cleavage in the intermediate.

In such rearrangement β-cleavage with concomitant specific transfer of a γ-hydrogen atom in a six membe transition state in monounsaturated systems take place irrespective of whether the rearrangemen formulated by a radical or an ionic mechanism and irrespective of the position of the charge. For exam



In organic compounds, there is generally a small peak appearing one mass unit higher than the pare peak (the $M + 1$ peak) due to small abundance of $^{13}C$ & $^{2}H$ in these compounds.

If organic molecules contains a $\pi$-electron system, the stability of the molecular ion is more tha molecular ion having a $\pi$ bond. In general, the relative height of the parent peak decreases in th following order among organic compounds.

Aromatic compounds > conjugated alkenes > alicyclics > sulphides > unbranched hydrocarbons ketones > amines > esters > ethers > carboxylic acids > branched hydrocarbons > alcohols.

With the help of parent peak of molecular ion, the exact molecular weight of sample can be calculated.

2. **Base Peak** : If in mass spectrometry an electron beam of energy of 70 eV is used, the molecular io produced by loss of a single electron further undergoes splitting to form many fragments. In such sta the parent peak in the mass spectrum is called the base peak and the heights of all other peaks a measured with respect to it.

3. **Multiply Charged Ions:** In mass spectrometer, the ions generally carry a single positive charg However, sometimes double or even triply charged ions have been observed in the mass spectrum The formation of multiple charged ions have been reported in heteroatomic molecules. The doubly triply charged ions are recorded at a half or $\frac{1}{3}$ of the $m/e$ value of the singly charged ion.

4. **Metastable Ions** : When the life time of a molecular ion is so small that it undergoes decompositi during its movement from the source to the collector units of a spectrometer, the resulting ions betwe the source and the magnetic analyser are called **metastable ions.** Metastable ions appear in t spectrum as broad peaks at non-integral mass numbers. Such peaks although weaker in intensity yet a useful in studying the mechanism of fragmentation.

The relationship between the apparent mass/charge ratio of the metastable ion and its parent peal given mathematically

$$m_1^+ \longrightarrow m_2^+ + m_0$$

The metastable ion is observed at a mass $m^*$ which is related to $m_1$ and $m_2$ as :

$$m^* = \frac{m_2^2}{m_1^2}$$

where, $m_1$ and $m_2$ are the mass of the parent ion and metastable ion, respectively.

$m^*$ is the apparent mass of metastable ion, while $m_0$ is mass of neutral fragment.

## 4. Fragmentation or Dissociation Process

The molecular ion produced in the mass spectrometer is mostly associated with considerable amoun energy. This energy causes one or more cleavages of the molecule ion and such process is termec fragmentation process. One of the fragments retains the charge, whereas the remaining fragments may stable molecules or radicals. Generally cleavage occurs at branched carbon atom. In a homologues series extent of cleavage increases with increase of molecular weight. Sometimes fragmentation proces accompanied by rearrangement process.

directly to the inlet of a mass spectrometer. The flow from the column is passed through a needle through that is 10 – 15μm at its tip.

2. **The Mass Analyzer**: Once the particle ionized, the ion are sorted and separated according to **mass-to-charge** $(m/e)$ ratio. There are a number of mass analyzers in use. The mass analyzer often works in concert with the ion detection system.

3. **Ion Detection System** : The separated ions are then measured and sent to a data system where the $m/z$ ratios are stored together along with their relative abundance. A **mass spectrum** is in a simple way the $m/e$ ratios of the ions present in a sample plotted on horizontal axis against their intensities at vertical axis. Each peak in a mass spectrum shows a component of unique $m/e$ in the sample, and heights of the peaks indicate the relative abundance of the various components in the sample, whereas the position of the peak gives the mass number of the particles.

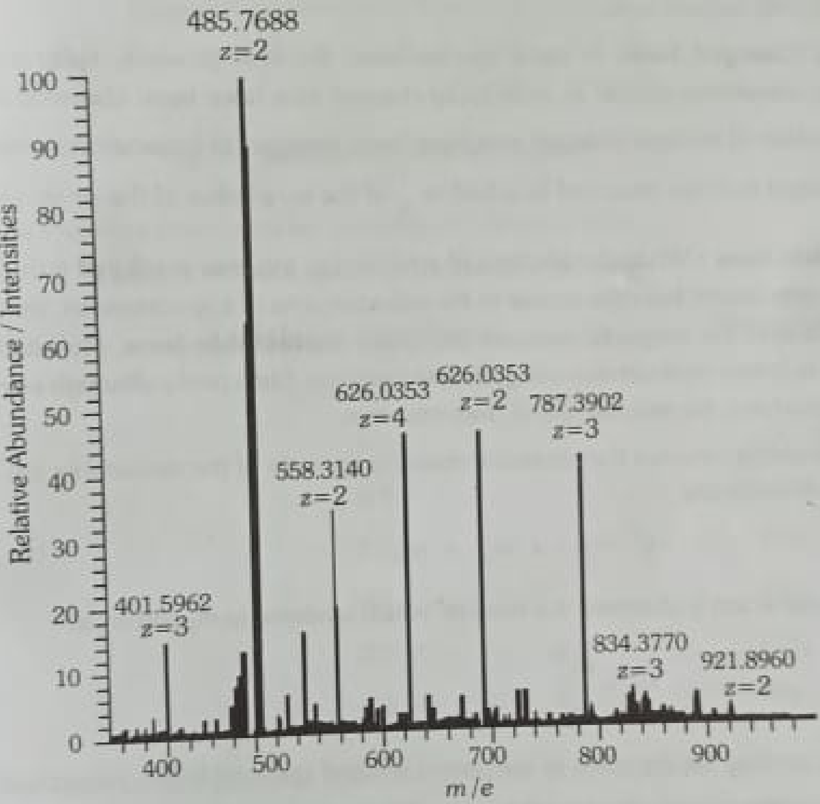



**Fig. 1: Example of a mass spectrum**

**In reporting data, the most intense peak (the base peak) in any mass spectrum i arbitrarily assigned a value of 100 and other peaks and reported as percentage of this.**

## 3. Types of Ions Produced in a Mass Spectrometer

1. **Molecular Ion or Parent Peak** : When a sample is bombarded with electrons of energies of 9 to 1 eV, the molecular ion is produced by loss of a single electron which gives rise to a very simple ma spectrum with all ions appearing in one peak called parent peak.

For example, mass spectrum of methane is obtained as shown in fig. below

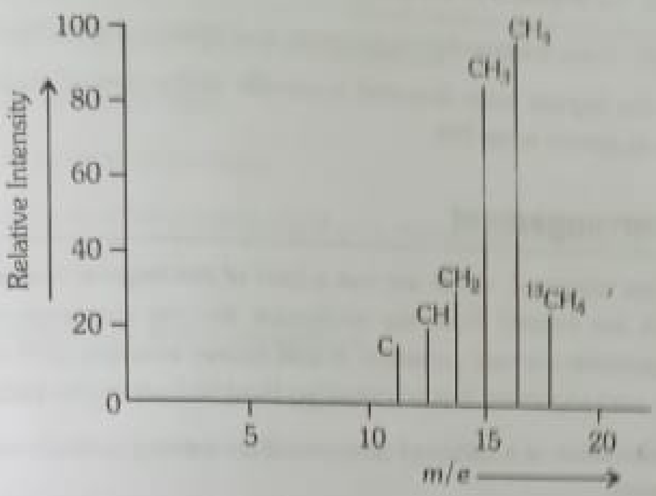



**Fig. 2: Mass spectrum of methane**

The mass spectral lines of methane have been recorded as in following table.

**Table 1 : Mass spectral lines of methane**

| m/e mass/charge ratio | Relative abundance | Fragments |
|---|---|---|
| 1 | 3.1 | H |
| 12 | 1.0 | C |
| 13 | 3.9 | CH |
| 14 | 9.2 | $CH_2$ |
| 15 | 85 | $CH_3$ |
| 16 | 100 | $CH_4$ |
| 17 | 1.1 | $^{13}CH_4$ |

The interpretation of the mass spectra depends upon the fact that at considerable amount of energy each molecular species ionizes to from a unique reproducible species and a predictable pattern. This is called fragment pattern.

The produced fragments are a function of the relative strength of the bonds within the molecules, the constituent atoms, the molecular weight of the compound and the ionization potential.

Suppose vapourized methane molecules are bombarded with electrons of increasingly higher energies:

1. At comparatively low energies of 10 eV, the ionization occurs and molecular ions are formed ($CH_4^+$)

$$CH_4 \longrightarrow CH_4^+ + e^-$$

2. On further increasing the potential, $CH_4^+$ ion undergoes fragmentation producing fragments of mass number 15, 14, 13, 12 with peaks of decreasing relative intensities and loss of 1, 2, 3, 4 H atoms. As more energy is needed for each successive breakage of bond, the probability of rupture is decreased

magnet is $Hev$, and the balancing force of the particle is $\frac{mv^2}{r}$. When the particles start moving uniformly around the circular path, the two forces become equal, *i.e.*,

$$\frac{mv^2}{r} = Hev \quad ...(3)$$

or
$$\frac{1}{r} = \frac{Hev}{mv^2}$$

or
$$r = \frac{mv}{He} \quad ...(4)$$

where $r$ is the radius of the circular path.

On putting value of $v$ according to equation (2) in equation (4)

$$r = \frac{m}{eH} \cdot \sqrt{\frac{2eV}{m}}$$

or
$$r^2 = \frac{m^2}{e^2H^2} \cdot \frac{2eV}{m} \quad ...(5)$$

or
$$r = \sqrt{\frac{2Vm}{H^2e}}$$

From equation (5)

$$\frac{m}{e} = \frac{H^2r^2}{2V} \quad ...(6)$$

From equation (6), it follows that the radius of the circular path of particles depends on the accelerating voltag $V$, magnetic field $H$ and the ratio $\frac{m}{e}$. Since, $e$, $V$ & $H$ are constant, the radius of the ionised molecule depend on $m$ its mass and this is the basis of separation of particles according to their masses.

## 2. Mass Spectrometer

Typically, mass spectrometer can be used to identify unknown compounds via

→ molecular weight determination

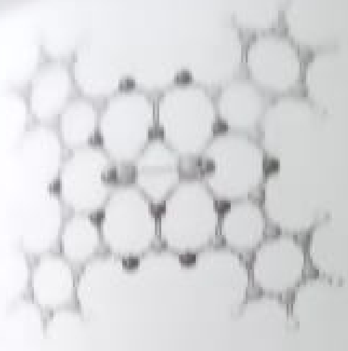
→ to quantify known compounds and

→ to determine structure and chemical properties of molecules.

Every mass spectrometer consists of at least following three components :

1. Ionization source
2. Mass analyzer
3. Ion detection system

1. **The Ionization Source:** Molecules are converted to gas-phase ions so that they can be moved abo by external electric and magnetic fields. In laboratory, nanoelectrospray ionization method is use Nanoelectrospray ionization can directly couple the outlet of a small-scale chromatography colun



# UNIT-VII

# Introduction to Mass Spectrometry

## 1. Introduction

Mass spectrometry is an analytical tool useful for measuring the mass to charge ratio ($m/z$) of one or more molecules present in a sample. These measurements are often used to calculate the exact molecular weight of the sample components. In mass spectrometry, the compound is bombarded with a beam of electrons which produced an ionic molecule or inoic fragments of the molecule, which are then separated according to their masses. The spectrum so produced is known as mass spectrum; it gives information regarding various masses produced and their relative ratio.

### 1.1 Principle of Mass Spectrometry

The mass spectrometer is an instrument, which help in separating the individual species due to difference in their masses.

Suppose a molecule A, which is bombared with a beam of electrons, ionises as follows:

$$A + e^- \longrightarrow A^+ + 2e^-$$

where $A^+$ is an ionised molecule and $e^-$ is electron.

The ions are them accelerated in an electric field at voltage $V$. In this condition the energy given to each particle is $eV$ and this will be equal to kinetic energy $\frac{1}{2}mv^2$. Hence,

$$eV = \frac{1}{2}mv^2 \quad \text{...(1)}$$

$$v^2 = \frac{2eV}{m}$$

$$v = \sqrt{\frac{2\,eV}{m}} \quad \text{...(2)}$$

where $v$ is the velocity of particle of mass $m$

$V$ is accelerating voltage and $e$ is charge on electron.

After the charged particles have been accelerated by an applied voltage, these are entered in a magnetic field $H$. Magnetic field attracts the particles and particles move in a circle around it. This attractive force due to