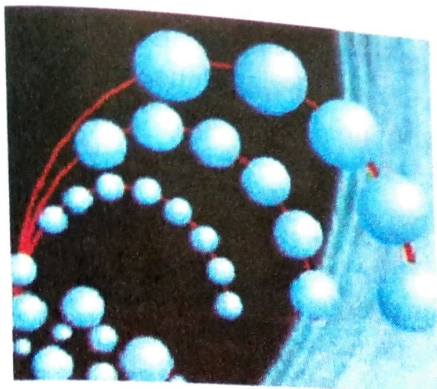
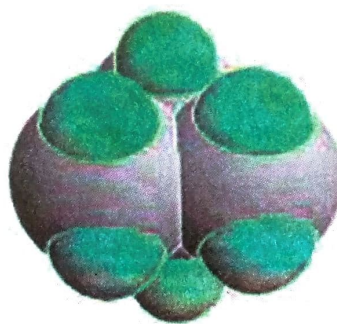


- 7.1 Basic principles
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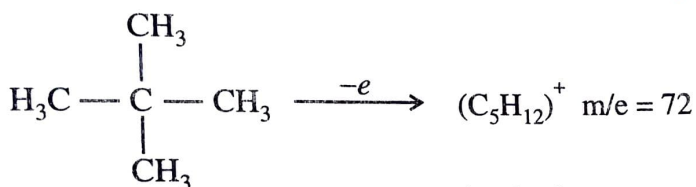
Mass spectrometry is the most accurate method for determining the molecular mass of the compound and its elemental composition. In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionised and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge, *i.e.*  $m/e$  ratio (value). For most ions, the charge is one and thus,  $m/e$  ratio is simply the molecular mass of the ion. Thus, for Neopentane



Mass Spectrometry



Neopentane



	Molecular ion			
	Fragmentation			
	$\text{C}_4\text{H}_9^+$	$\text{C}_3\text{H}_5^+$	$\text{C}_2\text{H}_5^+$	$\text{C}_2\text{H}_3^+$
	57	41	29	27
<i>Relative intensity</i>	100	41.5	38.5	15.7

The molecular ion (here  $\text{C}_5\text{H}_{12}^+$ ) is called parent ion and is usually designated as  $\text{M}^+$ . It is a positively charged molecule with an unpaired electron.

The set of ions (fragment ions or daughter ions) are analysed in such a way that a signal is obtained for each value of  $m/e$  that is represented. The intensity of each signal represents the relative abundance of the ion producing the signal. The largest peak in the structure is called the base peak and its intensity is taken as 100. The intensities of other peaks are represented relative to the base peak.

**Note.** The molecular ion (parent ion) peak may not be confused with the base peak. The base peak has 100% abundance. Mass spectrum of a compound is a plot which represents the intensities of the signals at various  $m/e$  values. It is highly characteristic of a compound. No two compounds can have exactly similar mass spectra. A single mass spectrum is equivalent to dozens of physical properties of that compound for revealing the structure. Mass spectra is used in two general ways:

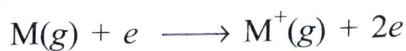
- To prove the identity of two compounds.
- To establish the structure of a new compound.

The mass spectrum of a compound helps to establish the structure of a new compound in several different ways:

- (a) It can give the exact molecular mass.  
 (b) It can give a molecular formula or it can reveal the presence of certain structural units in a molecule.

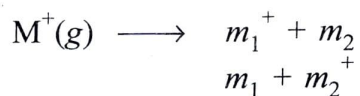
## 7.2 Theory

A parent ion results when one electron is removed from the parent molecule of the substance

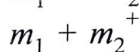


The  $m/e$  value of the parent ion is equal to the molecular mass of the compound. In a few cases, the parent ion peak may be the base peak and can be easily recognised. In most of the cases, parent ion peak is not the base peak and is often of very small abundance. Many elements occur naturally as isotopes, out of these the lightest one greatly predominates. The mass spectrometer is designed to perform three basic functions. These are:

- To vapourise compounds of varying volatility.
- To produce ions from the neutral compounds in the vapour phase.
- To separate ions according to their mass over charge ratio and to record them. The plot of  $m/e$  values taken along abscissa and their relative intensities along the ordinate is called the mass spectrum.



or



Neutral particles, produced in the process of fragmentation (whether neutral molecules or radicals) cannot be detected in the mass spectrometer.

The mass spectrum of Neopentane is shown as follows:

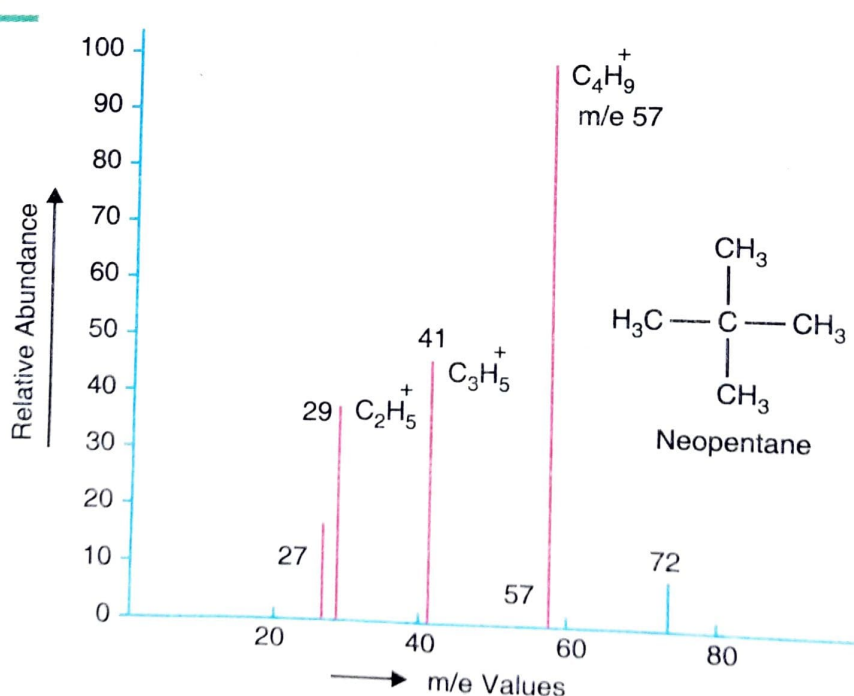


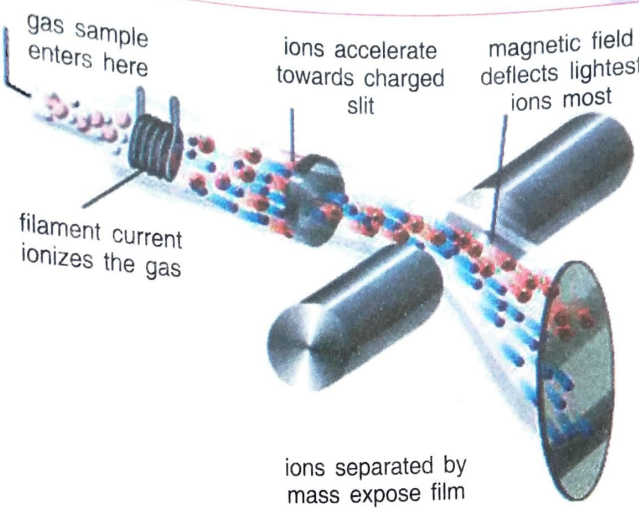
Fig. 7.1. Mass spectrum of Neopentane.

## 7.3 Instrumentation

The instrument needed to produce the mass spectrum of a compound consists of the following parts:

- Ion source.** The first and an important step in obtaining the mass spectrum is to ionise the sample under examination. The minimum energy required to ionise an atom or a molecule is called **ionisation potential**. The common technique used for the production of ion in mass

Mass spectrometer is by the bombardment of electrons. The bombarding electrons are produced from an electrically heated tungsten filament. A few mgm of the substance is introduced as a vapour in the source at an operating pressure of  $10^{-6}$  mm. The vapour is allowed to pass through slit A into the ion chamber. Here, it is bombarded by a stream of electrons produced from a tungsten filament. The bombarding electrons have energy of about 70 eV. Due to bombardment, the molecules generally lose one electron to form a parent ion radical\*.



Instrumentation

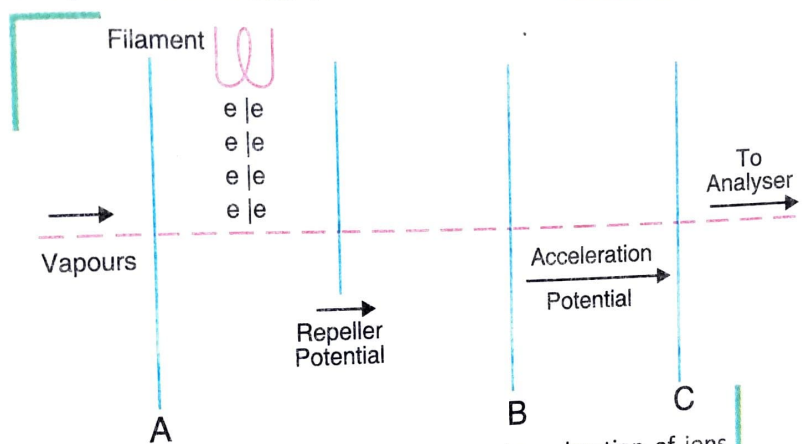
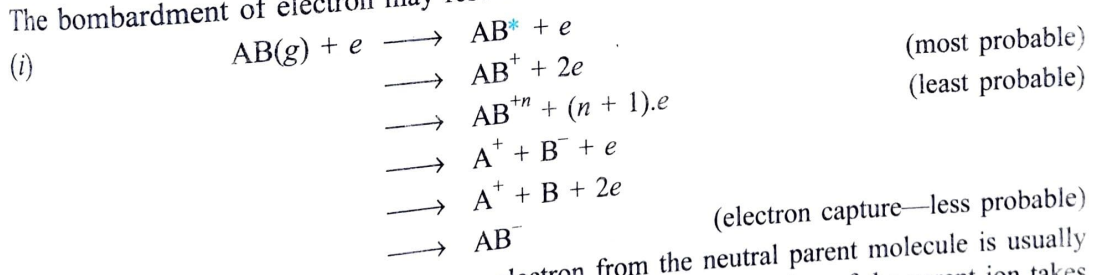


Fig. 7.2. Ionisation of sample and acceleration of ions.

The bombardment of electron may result in the following types of ions:



The energy required for removing one electron from the neutral parent molecule is usually 10 eV. With this much energy, no ions are formed, i.e., no fragmentation of the parent ion takes place. But if the energy of the bombarding electron is around 70 eV, then additional energy is consumed in fragmenting the parent ion. This results in the formation of fragment ions or the daughter ions. The positive ion (fragment) whether even electron or odd electron species is detected in the mass spectrometer whereas the neutral molecules or the radicals are left undetected.

(b) **Mass analyser.** The positively charged ion (parent or fragment ions) produced in the ion chamber are accelerated by applying an acceleration potential. These ions then enter the mass analyser. Here the fragment ions are differentiated on the basis of their  $m/e$  ratio. The positive ions are directed through a slit B. Repeller potential is applied between A and B. The ions are accelerated

\* Ion radical is formed by the removal of one electron since all organic molecules are even electron species without exception.

by applying an acceleration potential, of the order of 8 kV through the slit C. Acceleration potential is applied between the plates B and C, (see Fig. 7.2). The positive ions travel through whole of the analyser portion of the mass spectrometer with high velocity and are separated according to their  $m/e$  ratio.

Dempster's mass spectrometer is used for the purpose. The positive ions travel in a circular path through  $180^\circ$  under a magnetic field  $H$ . Suppose an ion having a charge  $e$  is accelerated through a voltage  $V$ . Then the kinetic energy of the ions is expressed as:

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

where

$v$  = velocity of the ions after acceleration

$V$  = potential applied

It may be noted that a massive ion will travel, slowly in a circular path compared to the lighter fragment.

In a magnetic field  $H$ , any ion will experience force  $Hev$ . It produces an acceleration of  $v^2/r$  in a circular path of radius  $r$ .

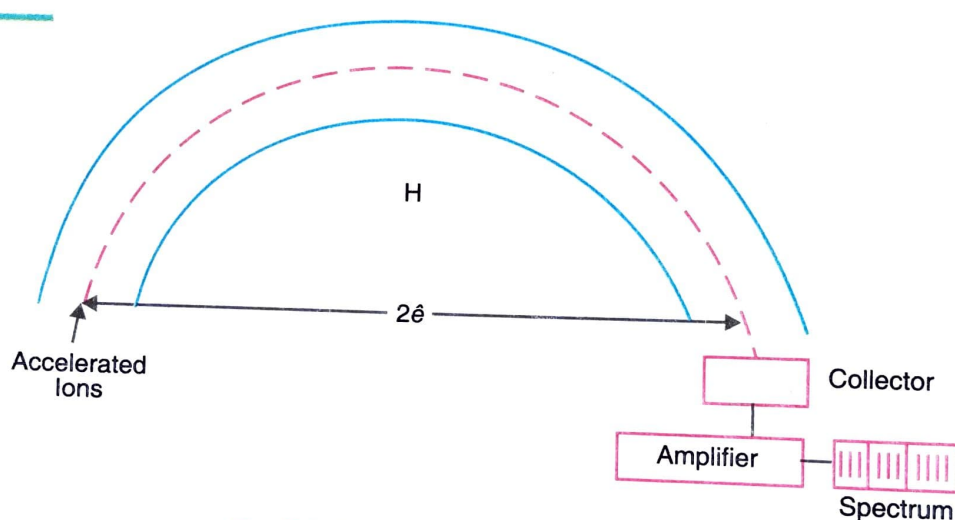


Fig. 7.3. Dempster's mass spectrometer.

Hence, from Newton's second law of motion

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

Squaring both sides

$$H_2 e^2 v^2 = \frac{m^2 v^4}{r^2}$$

$$H^2 e^2 = \frac{m^2 v^2}{r^2} \quad \dots(3)$$

But  $\frac{1}{2}mv^2 = eV$  (from 1)

$\therefore mv^2 = 2eV$

Putting the value of  $mv^2$  in (3)

$$H^2 e^2 = \frac{m \cdot 2eV}{r^2} \quad \text{or} \quad H^2 e = \frac{2mV}{r^2}$$

or

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

From this equation, it is clear that at a given magnetic field strength and accelerating voltage, the ions of  $m/e$  value will follow a circular path of radius  $r$ . The ions of various  $m/e$  values reach the collector, amplified and recorded. The mass spectrum can be obtained either by

- (i) Changing  $H$  at constant  $V$  or
- (ii) Changing  $V$  at constant  $H$

When magnetic field is varied, the method is called magnetic scanning. It is called electric voltage scanning when potential is varied at constant field strength  $H$ .

### Limitation and Modification

The limitation in the above instrument is that the resolving power is limited by initial spread of translational energy of ion leaving the source. The problem is overcome by passing the ions through electric field prior to the magnetic field. The electric field effects will cause focussing of the ions by placing a slit between the electrostatic and magnetic analysers. The ions of closely defined kinetic energies can be thus, selected prior to mass analysis. Instruments incorporating such a system are called **Double focussing mass spectrometers**. These instruments are capable of attaining much higher resolving power than single focussing instruments. It is possible to distinguish between the ions which have the same integral mass but differ in exact masses. This may be possible for isotopes of elements which do not have integral masses.

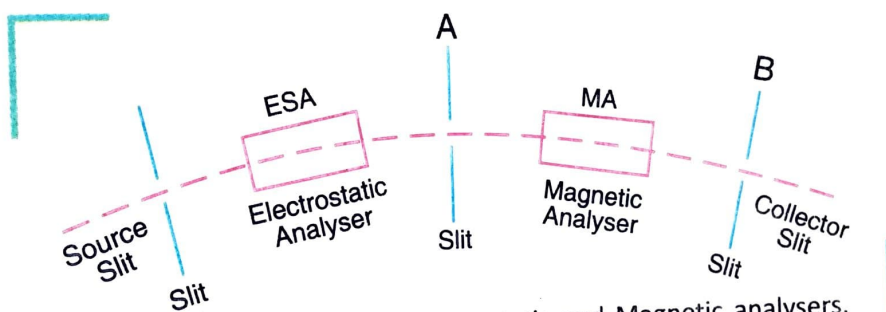


Fig. 7.4. Passage through Electrostatic and Magnetic analysers.

### Ion detector

The ions which are separated by the analyser, are detected and measured electrically or photographically. The ions pass through the collecting slit one after the other and fall on the detector. The spectrum is scanned by going up the scale. The ion currents are amplified using a direct current amplifier. The spectrum is recorded by using a fast scanning oscillograph. In this type of recording, three to five records of the same peak are made with galvanometers having different sensitivities.

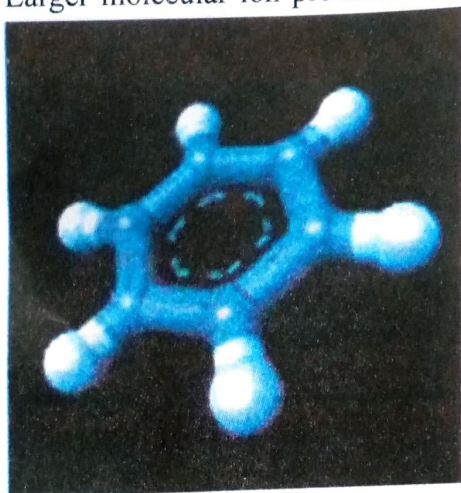
## 7.4 Mass Spectrum

It is a record of the masses and the relative abundances of the molecular ion and the positively charged fragments formed from it by the electron bombardment. The  $m/e$  ratios are taken along the abscissa while the relative abundances are taken along the ordinate. Base peak is the highest peak or the most intense peak in the spectrum. Relative abundance of an ion means the percentage of the total ion current.

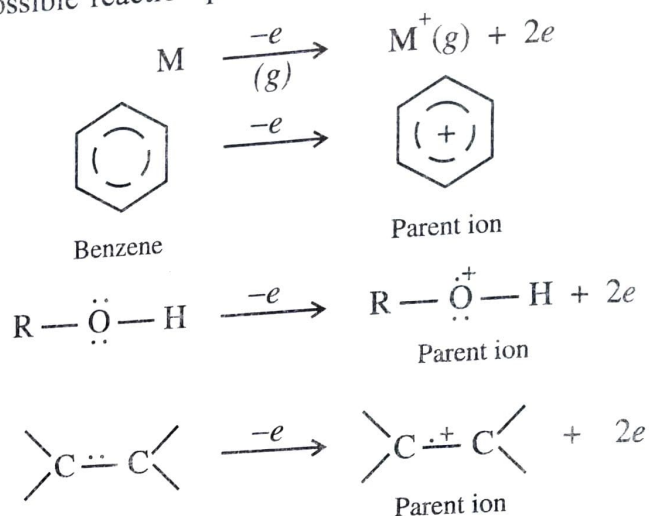
### The molecular ion or parent ion

The electron bombardment with energy 10-15 eV usually removes one electron from the molecule of the organic compound in the vapour phase. It results in the formation of molecular ion. The highest occupied orbital of aromatic system and non-bonding electron orbitals on oxygen and nitrogen atoms readily lose one electron. An electron from double bond (two  $\pi$ -electrons) or triple bond (four  $\pi$ -electrons) is usually lost. In alkanes, the ionisation of C—C sigma bonds is easier than that of C—H bonds.

The mass of the parent ion gives the molecular mass of the sample. In the mass spectrum, it is important to locate the molecular ion at the high mass region of the spectrum. The stability of the parent (molecular) ion decides its relative abundance. The peak intensity of the molecular ion differ from one compound to another. In some cases, parent ion peak is not formed which means that the rate of decomposition of parent ion is too high for its detection. It is important to note that the rate of decomposition of the molecular ion increases with the molecular size in the homologous series. Larger molecular ion provides more possible reaction path ways for detection.



Benzene



**Exercise.** Predict the relative abundance of the parent ion in case of (i) propane and (ii) *n*-pentane.

**Ans.** The relative abundance of the propane molecular ion is more.

The abundance of the molecular ion peak can be increased with respect to the abundance of fragment ions by running the spectrum at low ionisation potential, *i.e.*, by bombarding low energy electrons.

**Some important features of the parent ion peak are as follows:**

(a) The molecular ion peak in aromatic compounds is relatively much intense due to the presence of  $\pi$ -electron system.

(b) Conjugated olefines show more intense molecular ion peak as compared to the corresponding non-conjugated olefines with the same number of unsaturation. Conjugated olefines are more stable than the corresponding non-conjugated olefines.

(c) Unsaturated compounds give more intense peak as compared to the saturated or the cyclic molecule.

(d) The relative abundance of the saturated hydrocarbon is more than the corresponding branched chain compound with the same number of carbon atoms. For example, the molecular ion peak for *n*-pentane is more intense than that of neopentane.

(e) The substituent groups like —OH, —OR, —NH<sub>2</sub> etc. which lower the ionisation potential increase the relative abundance in case of aromatic compounds. Also the groups like —NO<sub>2</sub>, —CN etc. which increase the ionisation potential, decrease the relative abundance of the aromatic compounds.

(f) Absence of molecular ion peak in the mass spectrum means that the compound under examination is highly branched or tertiary alcohols. Primary and secondary alcohols give very small molecular ion peaks.

(g) In case of chloro or bromo compounds, isotope peaks are also formed alongwith the molecular ion peak. In case of bromo compounds, M<sup>+</sup> and (M<sup>+</sup> + 2) peaks are formed in the intensity ratio 1 : 1. In case of chloro compounds, M<sup>+</sup> and (M<sup>+</sup> + 2) peaks are formed in the intensity ratio 1 : 3.

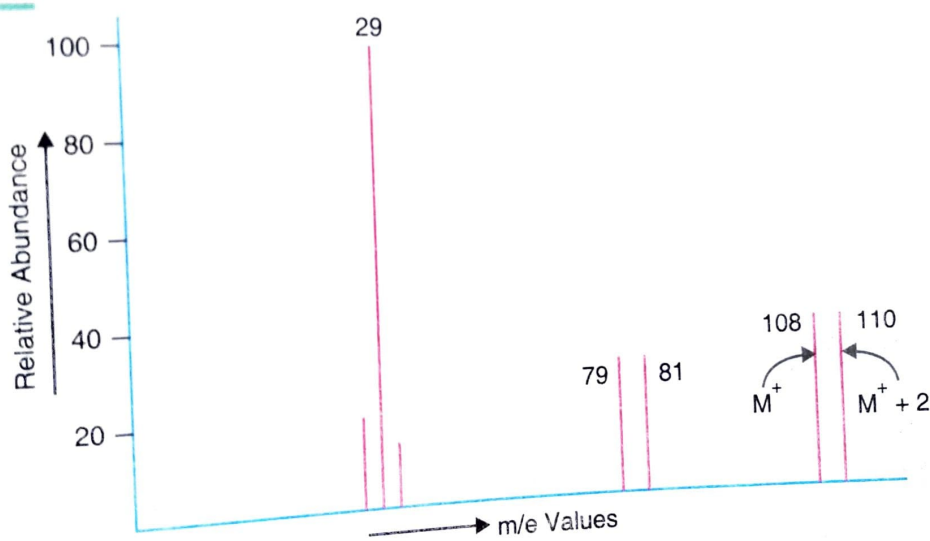
**Important.** Nitrogen containing compounds with an odd number of nitrogen atoms in the molecule must have an odd molecular mass. An even number of nitrogen atoms or absence of nitrogen atoms in the compound show that the molecular mass of the compound must be even.

## 5 Determination of Molecular Formula

The mass spectrum is a plot representing the  $m/e$  values of the various ions (parent as well as fragment ions) against their corresponding relative abundances. The peak on the extreme right (particle of highest mass) corresponds to the molecular mass of the original molecule. In case of straight chain hydrocarbons, the abundance of the parent ion peak is fair and it also shows a small ( $M^+ + 1$ ) peak which is of 9.9% abundance compared to the parent peak. Consider that a straight chain alkane because fragment peaks are formed 14 units apart. In case of straight chain hydrocarbon, a peak due to  $C_3H_7^+$  is most abundant *i.e.*, a **base peak**. Thus, a molecular formula of the compound can be obtained. In case an organic compound gives fragment as well as parent peaks in pairs which are two units apart, then

- if the pair of peaks are in the intensity ratio of 1 : 3, then it must be a chloro compound.
- If the pair of peaks appear in the intensity ratio of 1 : 1, then it must be a bromo compound.

Let us determine the molecular formula of the compound from the following mass spectrum.



**Fig. 7.5.** Mass spectrum of Ethyl bromide.

As the pair of peaks are of equal intensity, it is a bromo compound. The isotopes of bromine are  $^{79}\text{Br}$  and  $^{81}\text{Br}$ . The pair on the extreme right corresponds to  $M^+$  and  $(M^+ + 2)$  peaks. The spectrum corresponds to the molecular formula  $C_2H_5\text{Br}$ .

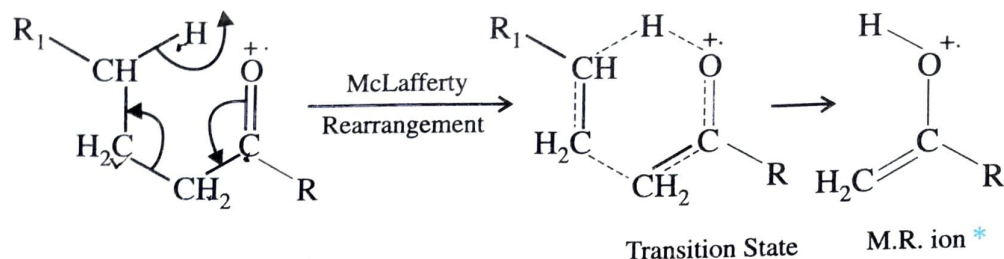
In some cases, a McLafferty rearrangement ion peak gives an important clue in the determination of molecular formula of the compound. For example, all straight chain aldehydes containing a  $\gamma$ -hydrogen atom form a base peak at  $m/e$  44 (McLafferty rearrangement ion peak). Also in aldehydes a fairly abundant  $M^+$  peak (parent peak) follows a less abundant  $(M^+ - 1)$  peak. Let us consider a simple mass spectrum having  $m/e$  values at 72, 71, 44 (100%), 43, 29 etc.

Here a signal at  $m/e$  44 (100%) is due to McLafferty rearrangement ion. This shows that it is a straight chain aldehyde as  $M^+$  peak at 72 also accompanies  $M^+ - 1$  peak at 71 and hence the formula of the compound is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ .

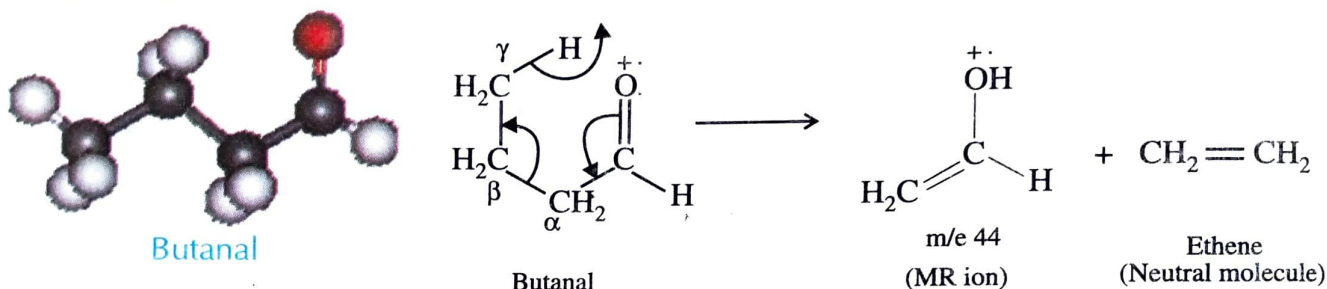


## 7.6 McLafferty Rearrangement

It involves the migration of  $\gamma$ -hydrogen atom followed by the cleavage of a  $\beta$ -bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds through a sterically hindered six membered transition state. Consider a general compound (ketone).



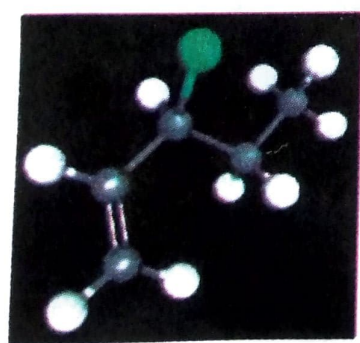
Butanal contains a  $\gamma$ -hydrogen atom. The McLafferty rearrangement ion formed in this case is shown below:



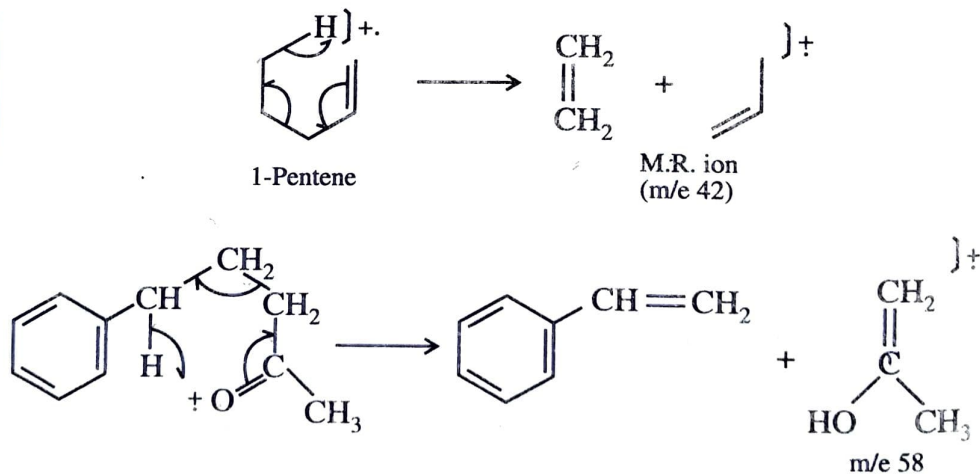
Similarly, a large number of organic compounds, viz. ketones, amines, alcohols, esters, acids which contain a  $\gamma$ -hydrogen atom forms a McLafferty rearrangement ion.

Thus, the molecular formula of the unknown compound can be determined from the various fragment ions and also the parent ion of the mass spectrum.

More examples of McLafferty rearrangement are:

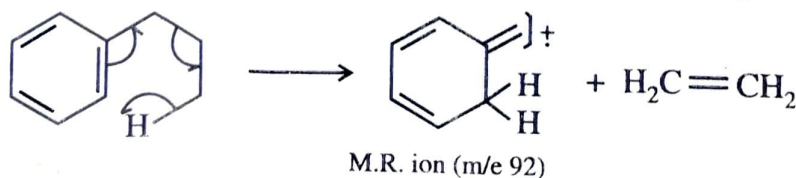


1-Pentene



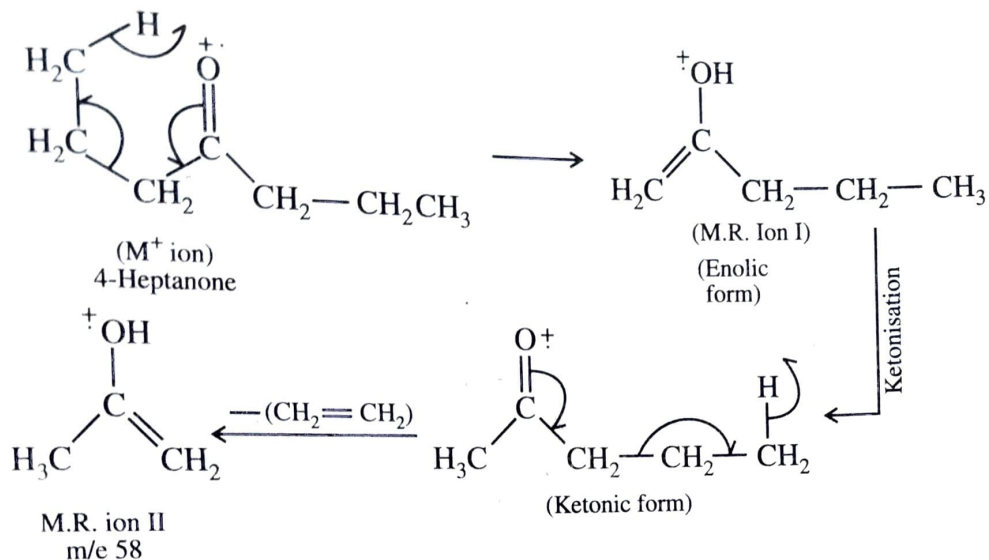
**Note.** The structural requirement for this rearrangement is a side chain containing at least three carbon atoms, the last bearing a hydrogen atom and a double bond which may be a carbonyl group, an olefinic double bond or an aromatic system.

*n*-propyl benzene shows a McLafferty rearrangement ion peak in large abundance at  $m/e$  92.



A double McLafferty rearrangement is also reported in certain ketones. The second hydrogen atom originates exclusively from the  $\gamma$ -position. A secondary hydrogen is preferred to a primary hydrogen atom in this process. The mechanism involves,

- (i) Ketonisation of the intermediate enol ion by the hydrogen transfer.
- (ii) Hydrogen transfer to enolic oxygen. Consider the McLafferty rearrangement in 4-Heptanone.



### 7.7 Metastable Ions or Peaks

Metastable peaks can be easily determined in a mass spectrum. Some important characteristics of these peaks are:

- (i) They do not necessarily occur at the integral  $m/e$  values
- (ii) These are much broader than the normal peaks and
- (iii) These are of relatively low abundance.

**Formation of metastable ions.** Consider that  $M_1^+$  is the parent ion and  $m_1^+$  is the daughter ion. If the reaction  $M_1^+ \rightarrow m_1^+$  takes place in the source, then the daughter ion,  $m_1^+$  may travel the whole analyser region and is recorded as  $m_1^+$  ion. On the other hand, if the transition  $M_1^+$  to  $m_1^+$  occurs after the source exist and before arrival at the collector, then  $m_1^+$  is called a metastable ion. We know that in double focussing mass spectrophotometer, there are two field free regions. These are called drift regions. The ions pass through these regions after acceleration. The first field free region refers to the portion of the ion path immediately before the electrostatic analyser. The second field free region lies between electrostatic analyser and magnetic analyser.

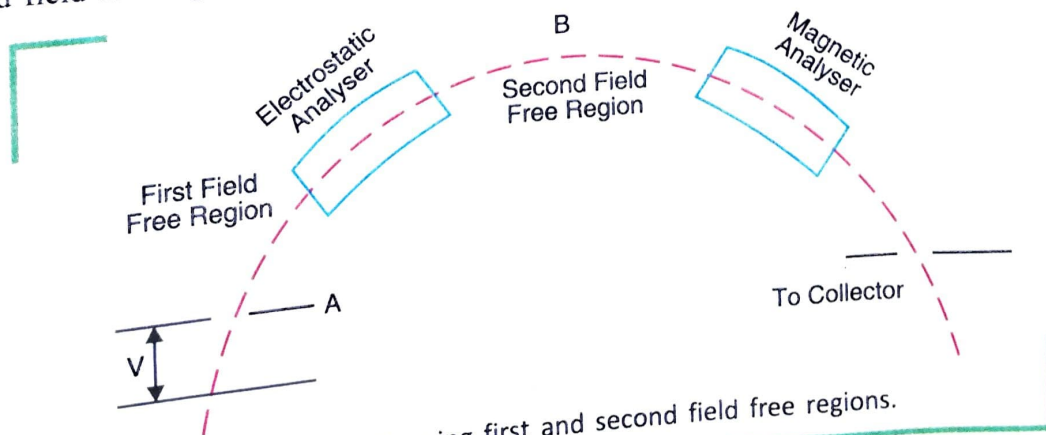


Fig. 7.6. Showing first and second field free regions.

An ion with charge  $e$  after being accelerated through a potential,  $V$  volts will possess kinetic energy equal to  $eV$ . Thus, all ions arriving at  $A$  will have translational energy equal to  $eV$  and thus, energy of the ion will be independent of its mass.

Now suppose the reaction,  $M_1^+ \rightarrow m_1^+$  occurs in the second field free region, then the daughter ion ( $m_1^+$ ) will have kinetic energy equal to  $\frac{m_2}{m_1} eV$ . Also the neutral particle ( $M_1 - m_1$ ) will have kinetic energy equal to  $\frac{M_1 - m_1}{M_1} eV$ . It may be noted that the neutral particle is not detected by the mass spectrometer.

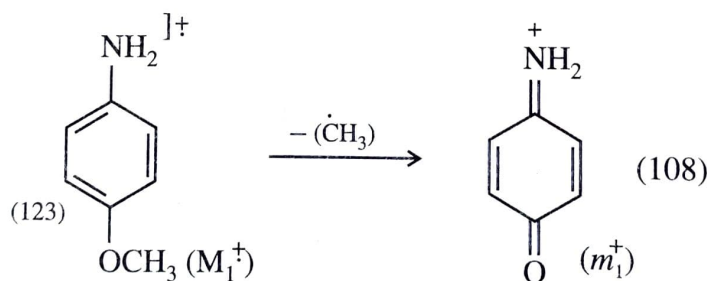
Thus,  $m_1^+$  ion formed in the second field free region will have less kinetic energy than it would have possessed if it were formed in the source. Clearly, the peak for the daughter ion ( $m_1^+$ ) will not appear at the normal position for  $m_1^+$  on the mass scale. Instead, the signal (peak) appears at  $m_1^2/M_1$ . Hence, we conclude that the position of the metastable peak ( $m^*$ ) due to the reaction  $M_1^+ \rightarrow m_1^+$  occurring in the second field free region is such that

$$m^* = m_1^2/M_1$$

**Important notes.** 1. It is important to remember that for a reaction  $M_1^+ \rightarrow m_1^+$ ,  $m^*$  (metastable peak) has a distance below  $m_1$  on the mass scale. The distance is approximately similar to the distance that  $m_1$  lies below  $M_1$ .

2. The relative abundance of the metastable peak ( $m^*$ ) is often of the order of  $10^{-2}$  or less compared to the abundance of parent or the daughter ions in 70 eV spectrum.

Consider the formation of metastable peaks in the spectrum of p-aminoanisole. The parent (molecular) ion appears at  $m/e$  123. Suppose the fragmentation of parent ion into daughter ion, (due to the loss of methyl radical, *i.e.*, loss of 15 mass units) takes place in between the electrostatic and the magnetic analysers, *i.e.*, in second field free region. The position of the metastable peak can be calculated as follows:

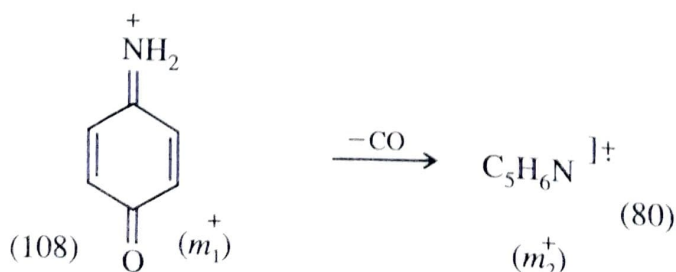


The position of the metastable peak

$$m^* = \frac{m_1}{M_1} = \frac{108 \times 108}{123} = 94.8$$

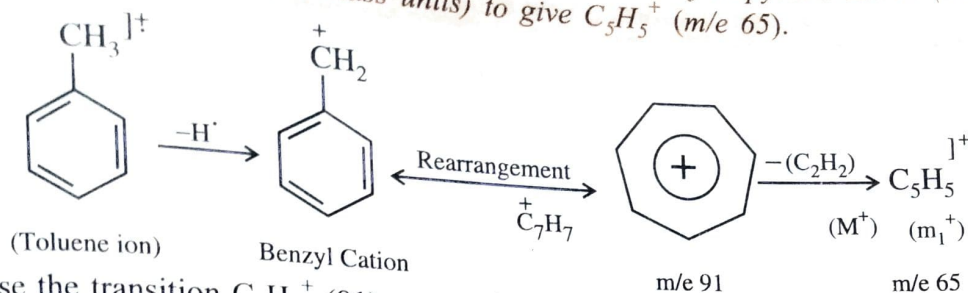
We see that the position of metastable peak (94.8) below  $m_1^+$  ion (108) is approximately the same as  $m_1$  ion is below  $M_1^+$  (123) on the mass scale which is linear.

The position of the metastable peak due to the following fragmentation in the second field free region can also be determined.



The position of metastable peak  $m^* = \frac{80 \times 80}{108} = 59.2$ .

**EXAMPLE 2.** Consider the mass spectrum of toluene. Two strong peaks at  $m/e$  91 and at  $m/e$  65 are formed. The peak at  $m/e$  91 is due to the formation of tropylium cation (stable) which loses a molecule of acetylene (26 mass units) to give  $C_5H_5^+$  ( $m/e$  65).



Suppose the transition  $C_7H_7^+$  (91) to  $C_5H_5^+$  (65) occurs in the second field free region, then a metastable peak is formed. The position of the broad metastable peak is determined as:

$$m^* = \frac{m_1^2}{M_1} = \frac{65 \times 65}{91} = 46.4.$$

A metastable peak in case of toluene appears at 46.4 in the mass spectrum.

**Importance of metastable peaks.** The metastable peaks in the mass spectrum greatly contribute in structure elucidation. From the positions of the parent ion and the daughter ion, the position of the metastable ion is calculated as above and confirmed in the spectrum under examination. In the spectrum of toluene, the formation of less intense metastable peak at 46.4 lends weight to the structure of toluene. It is due to the fragmentation of  $C_7H_7^+$  ion to  $C_5H_5^+$  ion in the second field free region. Similarly, the presence of metastable peaks at the expected positions of the suspected compounds lends weight to its structure.

**Why metastable peaks are broadened.** The most likely reason for the broadening of the metastable peak is the possibility that some of the excitation energy leading to bond capture may be converted into additional kinetic energy.

## 7.8 The Nitrogen Rule

Many signals (peaks) can be ruled out as possible molecular ions simply on the grounds of reasonable structural requirements. The nitrogen rule is often helpful in this regard. It states that **a molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms. An odd numbered molecular mass requires an odd number of nitrogen atoms.** This rule holds for all compounds containing carbon, hydrogen, oxygen, nitrogen, sulphur and halogens.

An important corollary of this rule states that the fragmentation at a single bond gives an odd numbered ion fragment from an even numbered molecular ion. Similarly, an even numbered ion fragment results from an odd numbered molecular ion. For this corollary to hold, the fragment ion must contain all the nitrogen atoms of the molecular ion. To explain the nitrogen rule, let us consider nitro-benzene ( $C_6H_5NO_2$ ). The signal for molecular ion appears at  $m/e$  123; i.e., at odd numbered molecular mass since the compound contains only one (odd number) nitrogen atom. Two important ion fragments which are formed in the mass spectrum of this compound are (i)  $NO_2^+$  at  $m/e$  46 and (ii)  $NO^+$  at  $m/e$  30. Both these fragment ions appear at even mass number.

Consider a compound containing two (even number) nitrogen atoms, say 2, 4-dinitrophenol. Its molecular ion ( $M^+$ ) signal appears at  $m/e$  184. The fragment ions appear at (i)  $M^+ - H$  i.e., at  $m/e$  183 and (ii)  $(M^+ - H - CO)$  i.e., at  $m/e$  155. Thus, we see that the fragment ions containing both the nitrogen atoms appear at odd mass number. This proves the validity of the nitrogen rule.

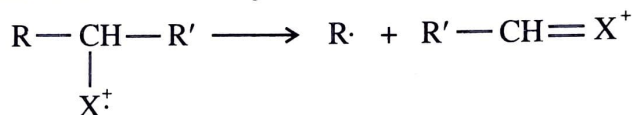
## 7.9 General Fragmentation Modes

The relative abundance of the fragment ion formed depends upon (i) the stability of the ion and (ii) also the stability of the radical lost. The stability of the ion can be judged by stabilisation of the charge which depends upon (a) Resonance (b) Inductive effect, (c) Polarisability and so on. The radical site is reactive and can form a new bond. The formation of a new bond is a powerful driving force for ion decompositions. The energy released during bond formation is available for the cleavage of some other bonds in the ion. Some important fragmentation modes are described below:

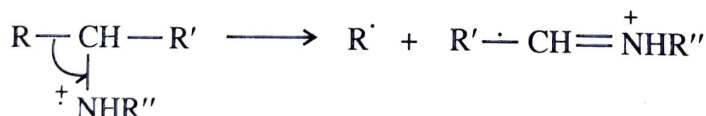
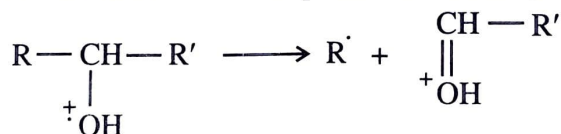
**1. Simple cleavage.** This process involves homolytic or heterolytic cleavage of a single covalent bond. The homolytic cleavage is initiated by a radical site.

**(i) Homolytic cleavage.** Odd electron ions have an unpaired electron which is capable of new bond formation. When a bond is formed, energy is released. The energy released by bond formation can help offset the energy required for the cleavage of some other bond in the ion. Homolytic cleavage reactions are very common and can be classed in the following types:

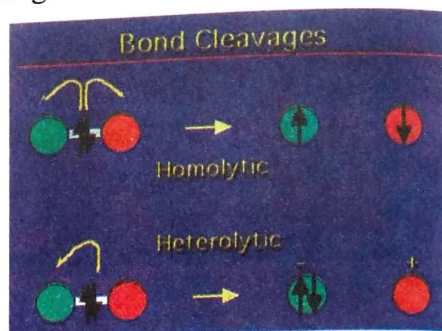
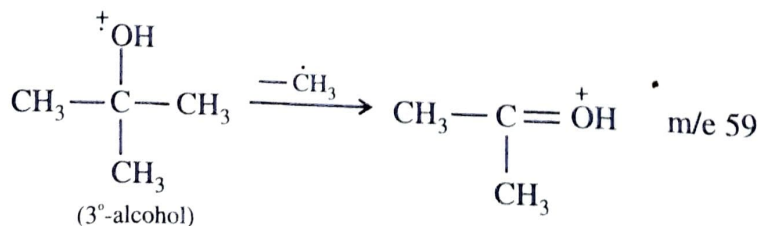
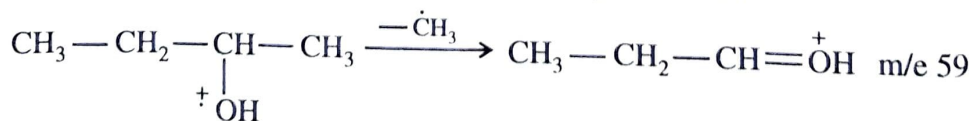
**(a) Mode I.** This fragmentation mode operates in compounds in which a hetero atom is singly bonded to a carbon atom. Parent ion is formed by the removal of one electron from the hetero atom. A new bond is formed with the adjacent atom through the donation of the unpaired electron and the transfer of an electron from the adjacent bond.



More abundant peaks are formed by the cleavage of carbon-carbon bond which is in the  $\alpha$ -position to the hetero atom in the mass spectra of alcohols, amines, ethers etc.

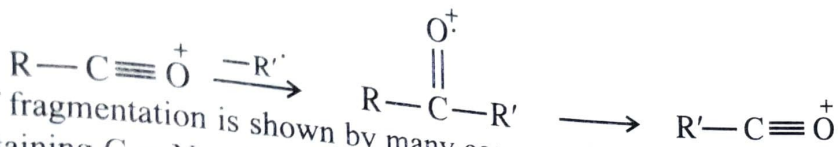


The mass spectra of three isomeric butyl alcohols are different. Secondary and tertiary butanols undergo this type of simple cleavage. *n*-Butanol undergoes elimination to give a peak at *m/e* 56. Consider the cleavage in 2-Butanol (2°) and 2-Methyl-2-butanol.



Homolytic and Heterolytic

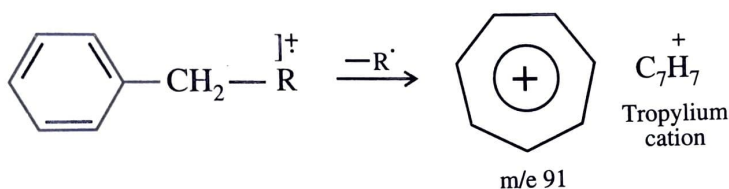
(b) **Mode II.** When a hetero atom is attached to a carbon atom by a double bond,  $\alpha$ -cleavage is the preferred fragmentation mode.



This type of fragmentation is shown by many compounds such as ketones, esters, amides etc. Compounds containing  $\text{C}\equiv\text{N}$  or  $\text{C}=\text{S}$  groups do not show this type of fragmentation. In ketones, significant peaks are observed due to the cleavage of carbon-carbon bond which is alpha ( $\alpha$ ) to the carbonyl group. Unsymmetrical ketones show two types of peaks since either alkyl group can be lost. The elimination of a bigger alkyl radical is preferred. In the same way, the fragmentation mode in aldehydes, esters and amides leads to the cleavage of  $\text{C}-\text{H}$ ,  $\text{C}-\text{O}$  and  $\text{C}-\text{N}$  bond respectively.

The presence of amino and hydroxyl groups which are electron donating in nature reduce the relative abundance of acylium ( $\text{R}-\text{C}\equiv\overset{+}{\text{O}}$ ) ion. The presence of electron withdrawing substituents such as nitro and cyano increase the relative abundance of the ion.

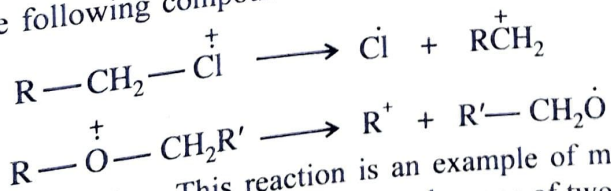
(c) **Mode III.** Benzylic cleavage is an energetically preferred fragmentation mode. It involves the cleavage of a carbon-carbon bond which is beta ( $\beta$ ) to the aromatic ring.



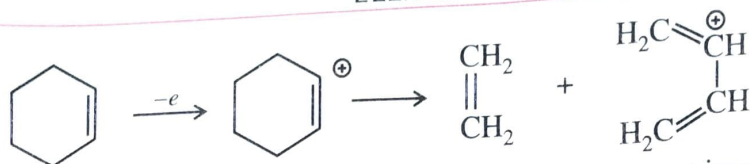
Considerable stabilisation of the tropylium cation is provided by the aromatic-system. Thus, the mass spectrum of ethyl benzene has a very intense ( $\text{M}^+-\text{CH}_2$ ) ion at m/e 91.

(ii) **Heterolytic cleavage.** It may be noted the cleavage of  $\text{C}-\text{X}$  ( $\text{X} = \text{O}, \text{N}, \text{S}, \text{Cl}$ ) bond is more difficult than that of a  $\text{C}-\text{C}$  bond. In such a cleavage, the positive charge is carried by the carbon atom and not by the hetero atom. It can be shown in the fragmentation of alkyl halide. In the spectra of monohalogenated compounds, hydrocarbon ions are formed in more abundance. As the size of the halogen atom increases, the  $\text{C}-\text{X}$  bond becomes weak. Accordingly  $\text{C}-\text{X}$  bond in alkyl bromides and iodides are easily broken while alkyl chlorides are less susceptible to fragmentation. In *n*-butyl bromide and *n*-butyl iodide, simple cleavage leads to the loss of halogen atom. It forms a more abundant even electron ion at m/e 57. In *n*-butyl chloride, cleavage of  $\text{C}-\text{Cl}$  is difficult. Thus, elimination of  $\text{HCl}$  by a rearrangement process gives rise to a peak at m/e 56.

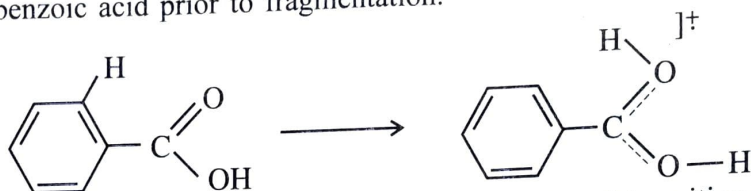
In ethers, the cleavage of  $\text{C}-\text{O}$  bond leads to the formation of an alkyl ion rather than an alkoxy ion. In di-*n*-propyl ether, propyl ion appears as a base peak at m/e 43. If the stability of the positive charge at carbon atom is increased by alkyl substitution, then this fragmentation mode is preferred. Consider the following compounds and their fragmentation modes.



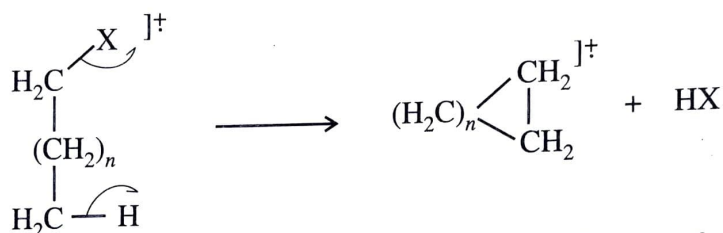
**2. Retro-Diel's-Alder reaction.** This reaction is an example of multicentred fragmentation which is characteristic of cyclic olefines. It involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed. This process is not accompanied by any hydrogen transfer rearrangement. The charge can be carried by any one of the fragments. The more highly substituted or more conjugated fragment which has a lower ionisation potential carries a charge. In simple system, the charge is carried by a diene.



**3. Hydrogen transfer rearrangements.** The simplest rearrangement involves the transfer of a hydrogen atom from one part of the molecule to another. These processes are very common in mass spectrometry. These involve intramolecular hydrogen transfer rearrangements in aliphatic hydrocarbons and aromatic compounds. Rearrangements involving the migration of groups heavier than hydrogen are called skeletal rearrangement processes. Consider hydrogen transfer from the ortho position in benzoic acid prior to fragmentation.

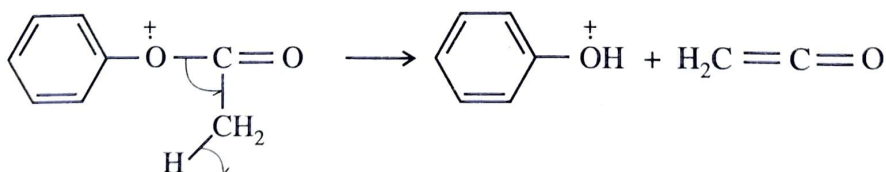
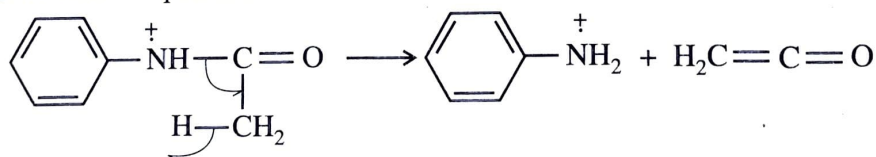


In hydrogen transfer rearrangements, generally a six membered transition state is formed but other transition states are also common.

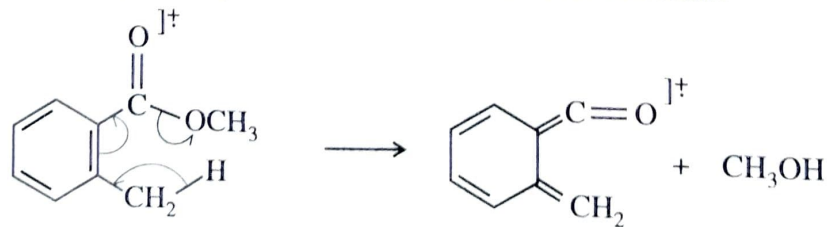


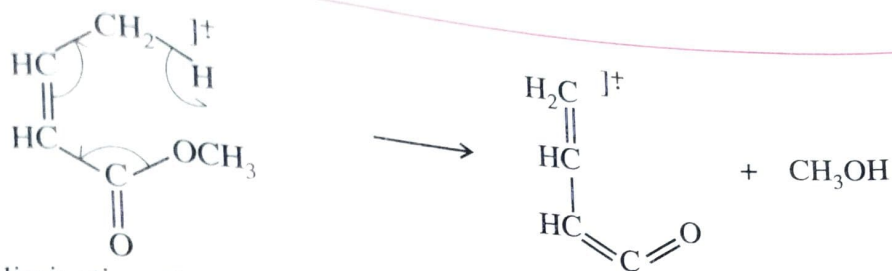
Elimination reactions operate not only from the molecular ion but also from the fragment ion. The positive charge generally remains on the carbon containing fragment. Alcohols usually eliminate a molecule of water from the molecular ion. *n*-Butyl and *n*-Pentyl chlorides undergo hydrogen chloride elimination by the abstraction of  $\alpha$ -hydrogen atom by 1, 3 mechanism.

The elimination of ketene ( $\text{CH}_2 = \text{C} = \text{O}$ ) is a characteristic fragmentation mode of *n*-alkyl amides and O-acetates of phenols.



In ortho, substituted aromatic compounds or in cis olefines, the substituent and a hydrogen atom can come in close proximity so as to eliminate a neutral molecule.





Such an elimination distinguishes (i) between cis and trans isomers and (ii) ortho substituted compound from meta and para substituted isomers.

4. **McLafferty rearrangement ion.** This rearrangement involves the cleavage of a  $\beta$ -bond followed by a  $\gamma$ -hydrogen transfer. The mechanism involves a six membered transition state (For details, see page 277).

10 **Important Features of the Mass Spectra of Hydrocarbons**

(a) **Alkanes (saturated hydrocarbons).** Some important features of the mass spectra of alkanes are as follows:

- (i) The relative height of the parent peak decreases as the molecular mass increases in the homologous series.
- (ii) Groups of peaks in the mass spectrum are observed 14 mass units apart. The most abundant peaks correspond to  $C_n H_{2n+1}^+$  ion.
- (iii) The most intense peaks are due to  $C_3$  and  $C_4$  ions at  $m/e$  43 and  $m/e$  57 respectively.
- (iv) There is no preferred charge stabilisation site to favour any specific cleavage.
- (v) The peaks corresponding to  $C_n H_{2n+1}^+$  ions are also accompanied by  $C_n H_{2n}^+$  and  $C_n H_{2n-1}^+$  ions in much less abundance.

The mass spectrum of dodecane ( $C_{12}H_{26}$ ) is shown below:

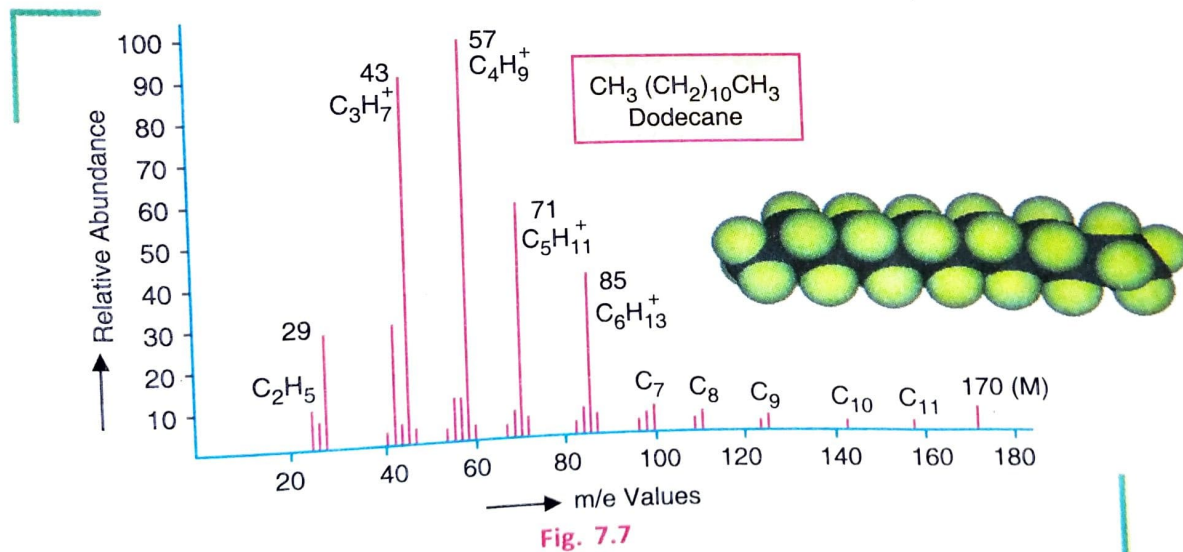


Fig. 7.7

It is very important to note that relative abundance of the ion (fragment ion) formed depends upon the (i) stability of the ion formed and also (ii) the stability of the radical which is lost.

**Note.** The stability of the carbocation has the order allylic > tertiary > secondary > primary > methyl. The stability of the free radical lost depends upon:

- (i) The length of the straight chain since it allows greater dispersal of the odd electron. Greater the dispersal of odd electron, greater is the stability of the free radical. *n*-butyl free radical is more stable than *n*-propyl free radical. Greater the stability, easier the formation.



by the energetics of fragmentation and elimination processes also follow this rule. Thus for example, the fragmentations normally occur to give most stable possible cations and *tert*-butyl chloride in its mass spectrum gives a large peak at  $m/z = 57$  due to the formation of *tert*-butyl cation. The charge easily ends up on *tert*-cation than on the electronegative chlorine (Scheme 6.2). The  $M^{+\cdot}$  from cyclohexene undergoes a retro Diels-Alder reaction (Scheme 6.2, see also Scheme 6.7 and Fig. 6.17) to give  $C_4H_6^{+\cdot} + C_2H_4$  in preference to  $C_4H_6 + C_2H_4^{+\cdot}$  since the ionisation energy of 1,3-butadiene is 9 eV and that of ethylene is 10 eV. It must however, be admitted that predicting fragmentation is not always that straightforward. Due to high energy which is available plenty of bond cleavage may occur. Rearrangements are also common, particularly when a stable ion can be reached *e.g.*, toluene gives tropylium ion (*e.g.*, see Figs. 6.18 and 6.19).

#### 6.4 DETECTION OF THE ISOTOPES OF THE ELEMENTS AND THE RECOGNITION OF MOLECULAR ION PEAK — USE OF HEAVIER ISOTOPE PEAKS

Mass spectra often contain peaks of significant intensity that are attributed to the presence of isotopes. Two of these are called the  $M + 1$  and  $M + 2$  peaks, where  $M$  is the mass of the parent ion ( $M^{+\cdot}$ ) and 1 and 2 represent mass increases due to the heavier isotopes of 1 or 2 mass units. Thus, the  $M^{+\cdot}$  peak is not the peak of highest  $m/z$  value. The molecular ion peak, therefore, must be of largest mass in the spectrum, apart from the natural isotope peaks due to the presence of  $^{13}C$ , etc. Most elements occur naturally as several isotopes and generally the lightest of these predominates while the heavier ones occur to lesser extent. In Table 6.2 the percentages are derived by setting the mass of the lowest weight isotope to 100 per cent and computing the percentages of the other isotopes relative to it.

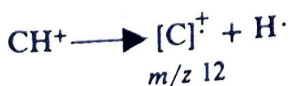
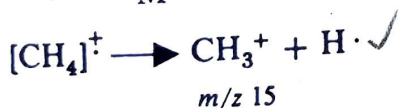
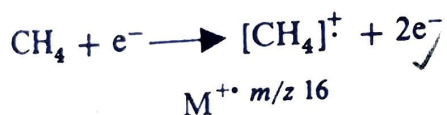
Table 6.2 : Isotopic composition of some common elements

Element	$M^{+\cdot}$	$M + 1$	$M + 2$
hydrogen	$^1H$	100.0%	
carbon	$^{12}C$	98.9%	$^{13}C$ 1.1%
nitrogen	$^{14}N$	99.6%	$^{15}N$ 0.4%
oxygen	$^{16}O$	99.8%	
sulfur	$^{32}S$	95.0%	$^{33}S$ 0.8%
chlorine	$^{35}Cl$	75.5%	$^{37}Cl$ 24.5%
bromine	$^{79}Br$	50.5%	$^{81}Br$ 49.5%
iodine	$^{127}I$	100.0%	

The mass spectrum of methane (Fig. 6.2) is shown in both bar graph as well as tabular form which explains some of these points. The most intense peak (the base peak) represents the molecular ion ( $m/z$  16).

An unusual feature found in the mass spectra of typical organic compounds, is found, in the spectrum of methane as well (Scheme 6.3). This feature is the presence of a small (1.1 per cent) monoisotopic peak  $m/z = 17$ ; it is designated ( $M + 1$ ) or ( $M^{++} + 1$ ). How is it possible to have a molecular ion present that has an extra mass unit? The answer lies in the fact that carbon is not isotopically pure. About 1.1 per cent of natural carbon is the  $^{13}\text{C}$  isotope (Table 6.2), giving rise to the additional peak. The  $[M + 1]$  fragment results from molecular ion that contains a  $^{13}\text{C}$  instead of  $^{12}\text{C}$ . Thus in the mass spectrum of methane the  $m/z = 17$  peak has 1.1% of the intensity of the  $m/z = 16$  peak.

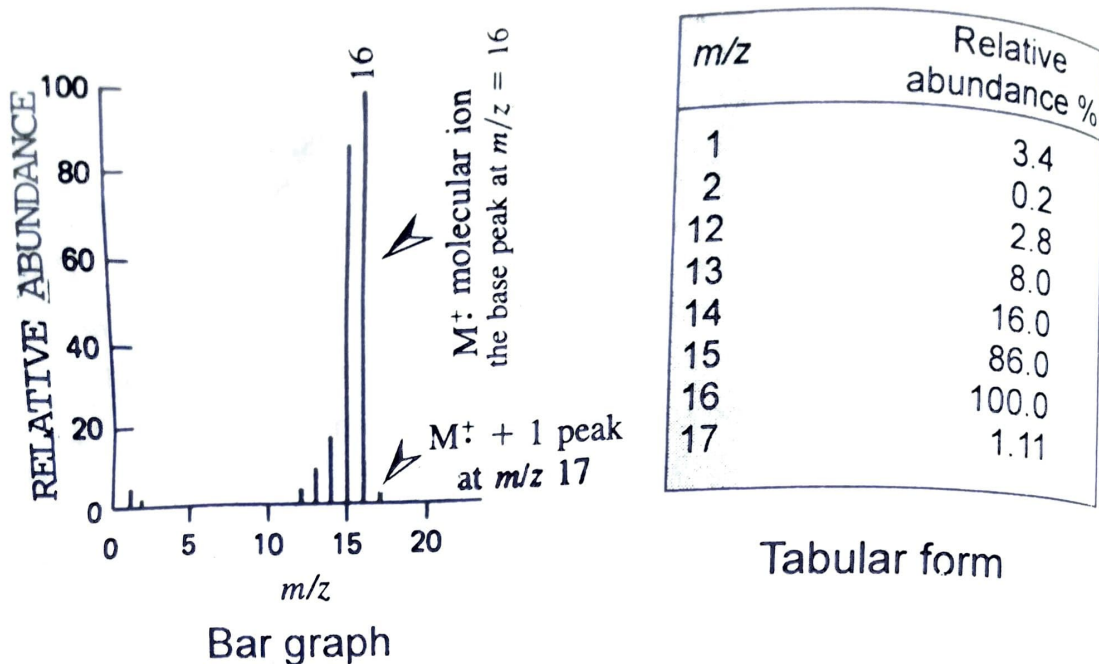
Hydrogen, too, has a naturally occurring higher isotope; deuterium, with about 0.015 per cent abundance. This proportion is so small that deuterium is normally ignored when mass spectral patterns are considered. The probability of finding two  $^{13}\text{C}$  atoms in a typical molecule is so low that  $M + 2$  peaks due to the carbon isotope are often not important. Thus for most compounds the  $M + 2$  peak is small, however, for compounds containing chlorine bromine or sulphur the  $M + 2$  isotopic peak is substantial. Whereas fluorine and iodine are isotopically pure, chlorine



- The most intense (the base peak) is the molecular ion  $M^{++} \ m/z = 16$ .
- The peaks at  $m/z = 15, 14, 13$  and  $12$  arise by the successive losses of hydrogen atoms.
- The small peak at  $m/z = 17$  is the ( $M^{++} + 1$ ) peak which is shown by methane molecules which contain  $^{13}\text{C}$ .
- The first C-H bond is cleaved readily to give the peak at  $m/z = 15$  which is 86% of the abundance of the molecular ion.
- The breaking of additional C-H bonds is more difficult and relative abundances of the species as shown by the height of the peaks is a good indication of their relative formation.
- Often an ion may eject an ionized hydrogen molecule to give a weak peak at  $m/z = 2$ .

**Fragmentation of  
Methane in the Mass  
Spectrometer**

Scheme 6.3



### The mass spectrum of methane

Fig. 6.2

and bromine are not, therefore, *e.g.*, compounds containing one bromine atom display in their mass spectra pairs of peak of roughly equal intensity separated by two mass units. This is due to almost equal abundance of the two isotopes, *i.e.*, 1:1 mixture of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  (Table 6.2). As a consequence, the mass spectrum of, *e.g.*, methyl bromide (Fig. 6.3, compared with that of methane) shows two very intense peaks at  $m/z$  94 and 96 which are the  $M^{++}$  and  $M + 2$  peaks (in fact one should say that the mass spectrum shows two molecular ions).

By the same token, the spectra of monochloroalkanes show two molecular ions, two mass units apart for  $\text{R}^{35}\text{Cl}$  and  $\text{R}^{37}\text{Cl}$ , but in this case in a 3:1 ratio; because of the different isotopic composition of this element (Fig. 6.3a).

The characteristic doublets observed in the mass spectra of compounds containing chlorine and bromine are an excellent way of diagnosing the presence of these elements. Similarly, the contribution (4.4 per cent) of the  $^{34}\text{S}$  isotope to the  $M + 2$  peak, is of help in the identification of sulphur containing compounds.

Iodine is recognised by the presence of the iodonium ion  $\text{I}^+$ , at  $m/z$  127 in the spectrum. This clue is combined with a characteristic 127 (unit) gap in the spectrum corresponding to loss of the iodine radical.

In summary, a compound with no sulfur, chlorine or bromine has a small  $M + 1$  peak and an even smaller  $M + 2$  peak. If a compound contains sulfur, the  $M + 2$  peak is larger than the  $M + 1$  peak — about 4 per cent of the  $M^{++}$  peak. If chlorine is present, the  $M + 2$  peak is about a third as large as the  $M^{++}$  peak. If bromine is present, the  $M^{++}$  and  $M + 2$  ions have about

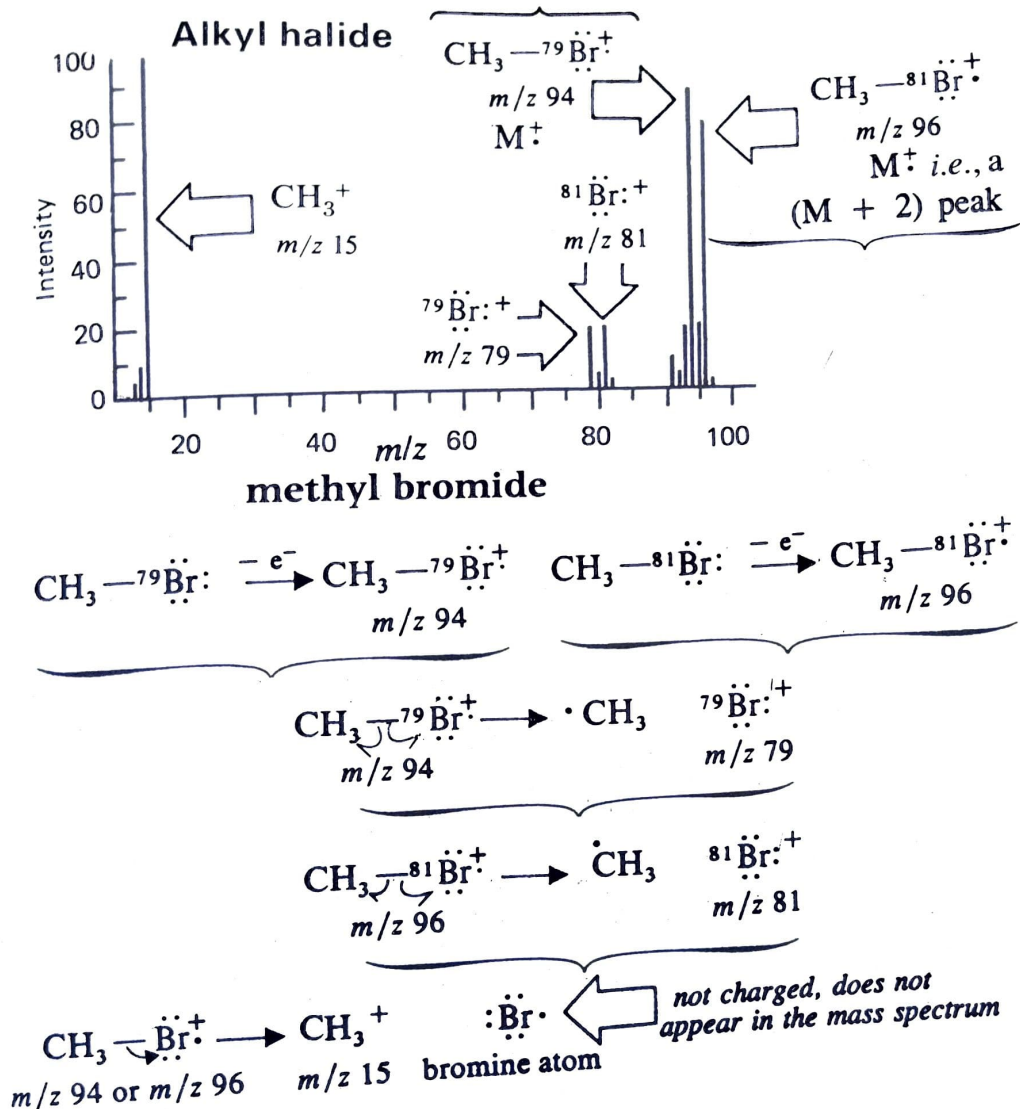
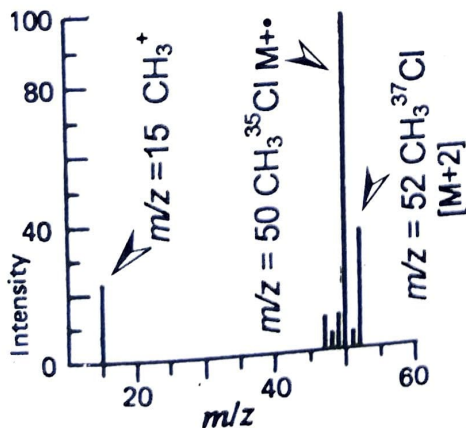


Fig. 6.3



1. Most distinctive  $M+2$  peaks appear when bromine or chlorine is present in a molecule.
2. With the presence of bromine half of the molecules contain  $^{79}\text{Br}$  and half  $^{81}\text{Br}$ . A pair of peaks with almost same intensity appear separated by two mass units.
3. With chlorine  $^{35}\text{Cl}/^{37}\text{Cl} = 3/1$ , the  $M+2$  peak is about a third as large as the  $M^+$  peak.

Mass spectrum of methyl chloride

Fig. 6.3a