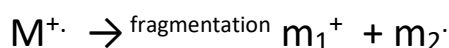


MASS SPECTROMETRY

Mass Spectrometry deals with the examination of characteristics fragments and arising from the breakdown of organic molecules. The mass spectrum is the plot of relative intensity of the ions against their mass to charge ratio. In the case of M.S., molecule are bombarded with a energetic electrons and the molecules are ionised and broken into the many fragment ions, some of species are positive ions, and each kinds of ions has a particular mass to charge ratio. Generally, the charge of each ion is one, so the mass to charge is simply the mass of the single ions.



Neutral molecule High energy electron Molecular ion or radical cation



Molecular ion

fragmented ions

Terminology Used in Mass Spectrometry

Base Peak : The most intense peak in the MS assigned 100% intensity.

Molecular Ions:The ion obtained by the loss of one electron from the molecule.

Mass to charge ratio: It is a dimensionless ratio of mass number (M) of the given particles to the number (Z) of the electrostatic units (e) carried out by the particles.

Radical Cations : Positive charge species with the an odd number of electrons.

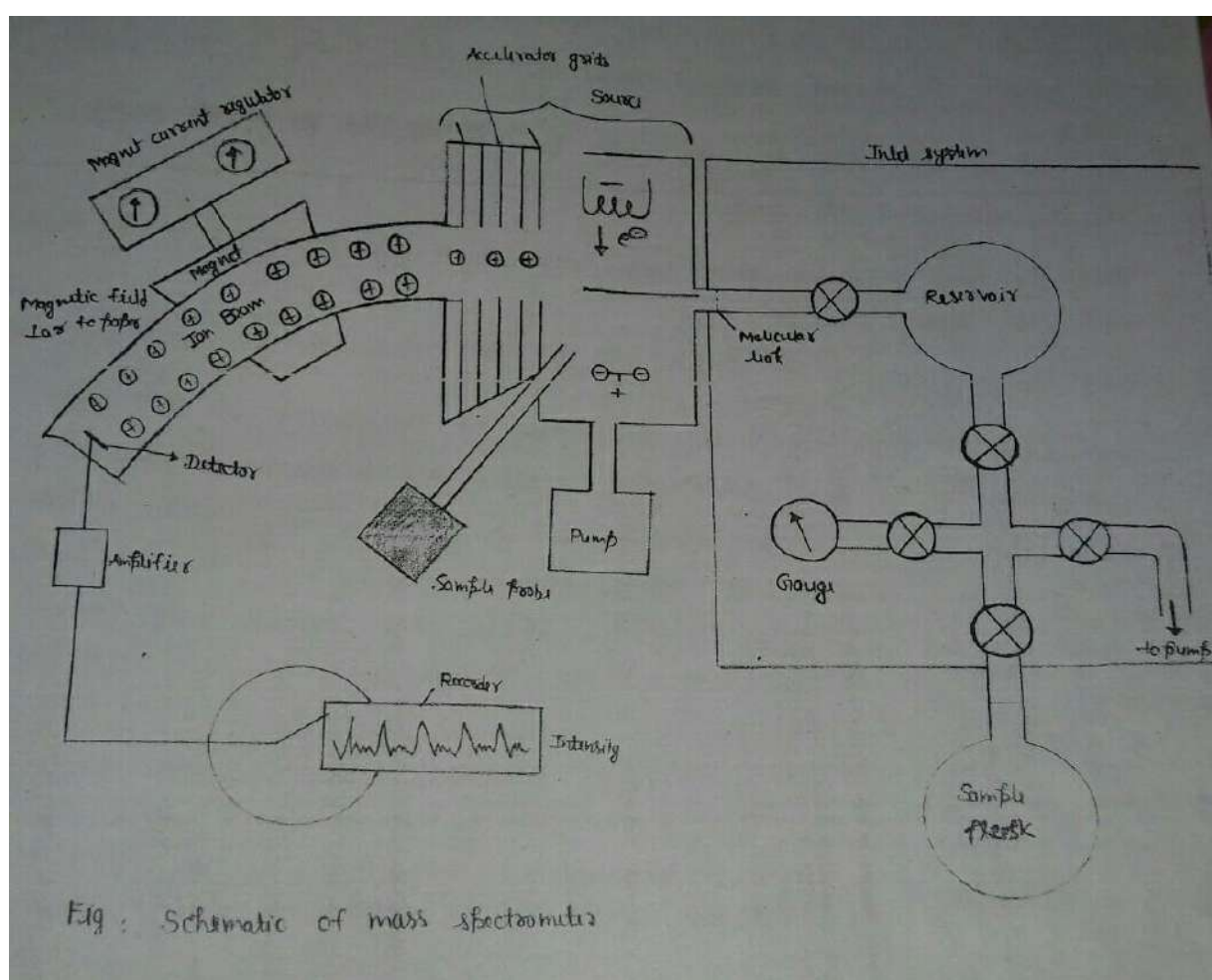
Fragmented Ions: Lighter cation formed by the decomposition of the molecular ion. In other wards, the ion produced from the molecular ion by the cleavage of the bonds are called as fragmented ion. Fragmentation of molecular ion may occur by the cleavage of bonds in two ways: (i) Heterolytic cleavage i.e. full arrow and (ii) Homolytic cleavage i.e. half arrow, "Fish hook".

Instrumentation- The Mass Spectrometer

A mass spectrometer is an instrument which:

- (i) Generates a beam of positively charged ions from the sample under investigation.
- (ii) Separates these ions according to their mass-to-charge ratios.
- (iii) Records the relative abundance of each ion.

Under figure shows the essential components of a mass spectrometer and their function.



The inlet system: The inlet system includes devices for introducing the sample, determining the amount of sample introduced, metering the sample into the ionization chamber and a vacuum pump with appropriate control valves and stopcocks to maintain the pressure in the range of 10^{-3} to 10^{-1} torr.

Requirement for the inlet system: Three major requirement for the inlet system are the following:

- The sample must be in the vapour phase prior to ionization.
- The sample should not undergo thermal decomposition during the vaporization process.
- The pressure inside the mass spectrometer be kept as low as possible during the introduction of the sample.

Thus, the type of inlet system used will depend upon the nature of the sample and its thermal stability.

Process for introducing the sample into a mass spectrometer

Introduction of the gases is simply a matter of transferring the gas from a container (usually a pyrex bulb equipped with a ground glass joint and vacuum stopcock) to the reservoir. Highly volatile liquids can be handled using a cold inlet system in the same manner as gases. Usually the liquid is first frozen and the air is pumped out of the container, then the sample is re-melted and introduced into the spectrometer. Liquid may also be introduced by injection with a syringe through a silicon rubber as is done in gas chromatography.

Heated inlet system are used for less volatile organic solids that have sufficient vapour pressure at about 100-150°C. Less volatiles solid may also be admitted to the ion source using the direct insertion probe. It consist of a glass sample holder fitted into a retractable metal rods . This probe unit is inserted directly into the ion source via a vacuum lock. The probe tip is then extended until it is only a short distance away from the electron beam. Heating the ion source and the probe tip between 50°C and 200°C is sufficient to volatilize the most organic solids.

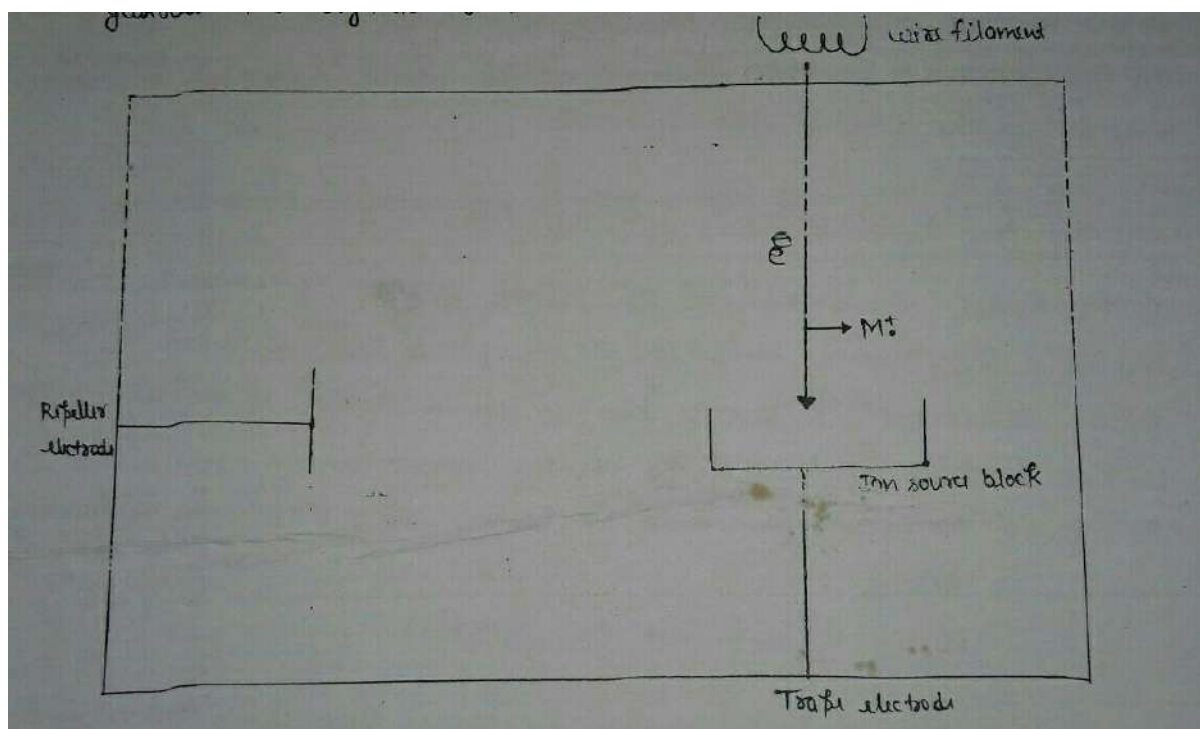
ELECTRON IONIZATION METHOD

It is an ionization method in which the energetic electrons are interact with the gas phase atoms or molecule to produce the ion and this technique is used in mass spectrometry particularly for gaseous and organic volatile molecules.



(where M is the analyte molecule being ionized, e^{-} is the electron and M^{+} is the resulting ions)

In electron ionization source, electrons are produced through the emission of the heating is wire filament that has electric current coming through it.



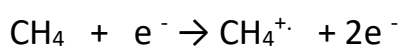
The electrons are accelerated to 70 eV in the region between the wire filament and the entrance to the ion source block. The accelerated electrons are then concentrated into a beam by extracted to the trape electrode. The sample under investigation which contains the neutral molecules is introduced to the ion source in a perpendicular direction to the electron beam. The close passage of high energetic electrons, referred to as hard ionization source, causes the large fluctuations in the electric field around the neutral molecule and induced ionization and fragmentations. The radical cation product are then directed towards the mass analyzer by a repeller electrode.

The ionization frequency and production of fragments ions depends strongly on the analytes and the energy of the electrons. At the low energy around 20eV, the interaction between the electron and the analytes molecules do not transfer enough energy to causes ionizations. At around the 70 eV, the electrons matches the length of typical bonds in the organic molecules (about

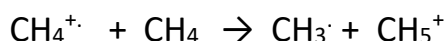
0.14nm) and energy transfer to organic analyte molecules is maximized, leading to the strongest possible ionization and fragmentation. So under these condition, about 1 to 1000 analytes molecule in the same ion source are ionized. At higher energies (above 70 eV) the de Broglie wavelength of the electron becomes smaller than the bond length in typical analytes; the molecules then becomes "transparent" to the electron and ionization efficiency decreases.

CHEMICAL IONIZATION (C I) METHOD

In this method, the reagent such as methane, isobutene or ammonia is introduced into the high pressure source (0.1 to 1 torr) and these are ionized by the electron bombardment. The primary ions are produced undergo by molecular collision to form a stable population of the secondary reagent ions. For example; the methane is ionized by electron impact (EI) forming the primary molecular ion, in the usual way as per the equation :

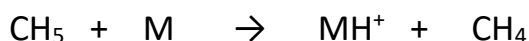


Due to high pressure in the chemical ion source, there is a probability of the molecular ion colliding with another methane molecules.



This is an acid base reaction. $\text{CH}_4^{+\cdot}$ is as a molecular ion and acting as the proton donor as an acid and CH_4 is acting as proton acceptor, a base.

The introduction of the small amount of the sample in the vapour phase, into the chemical ion source results in the reaction between the reagent ion (CH_5^+) and the sample molecules leading to the formation of the analyte (M) and these ions are separated magnetically and electrostatically in the normal way usually by means of protonation reaction as per the equation.



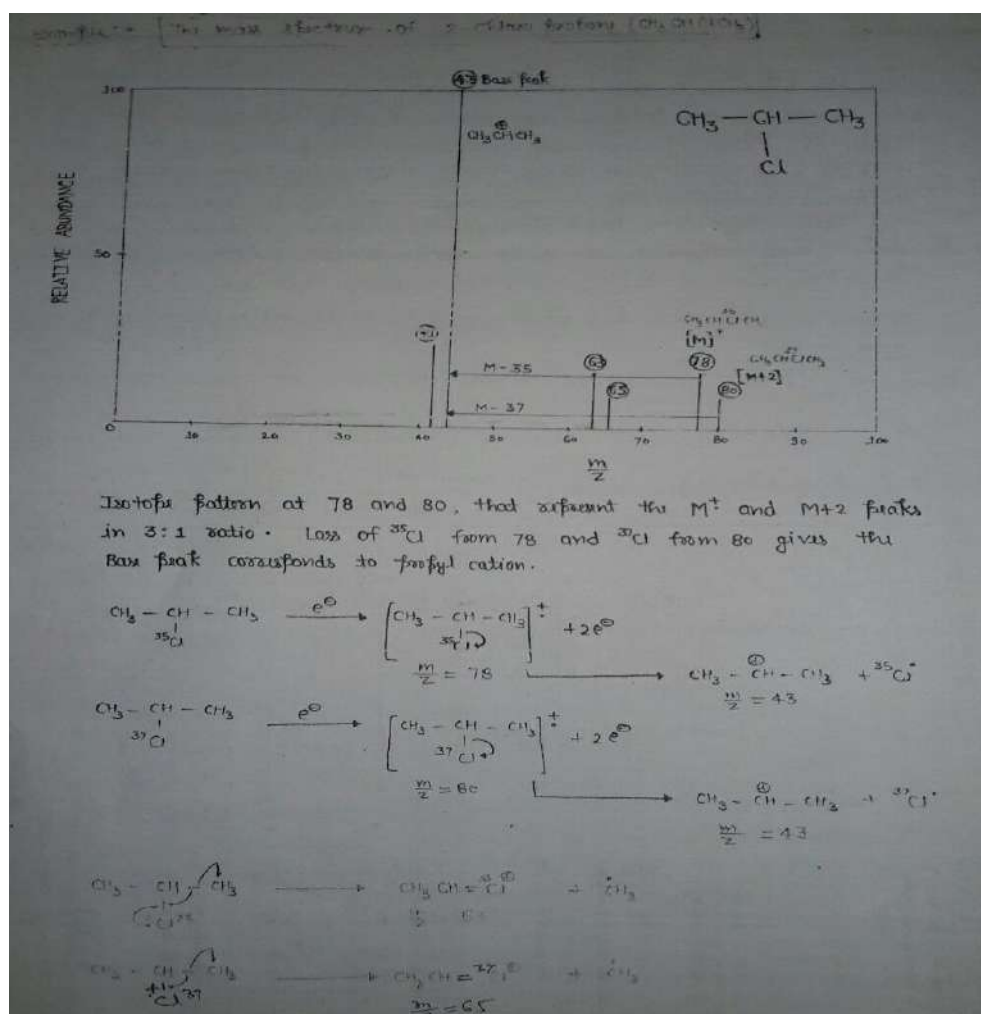
reagent ion sample molecule protonated ion methane

The ion (MH^+) having an m/z value one a.m.u. greater than that of the molecular ion, is known as quasi-molecular ion.

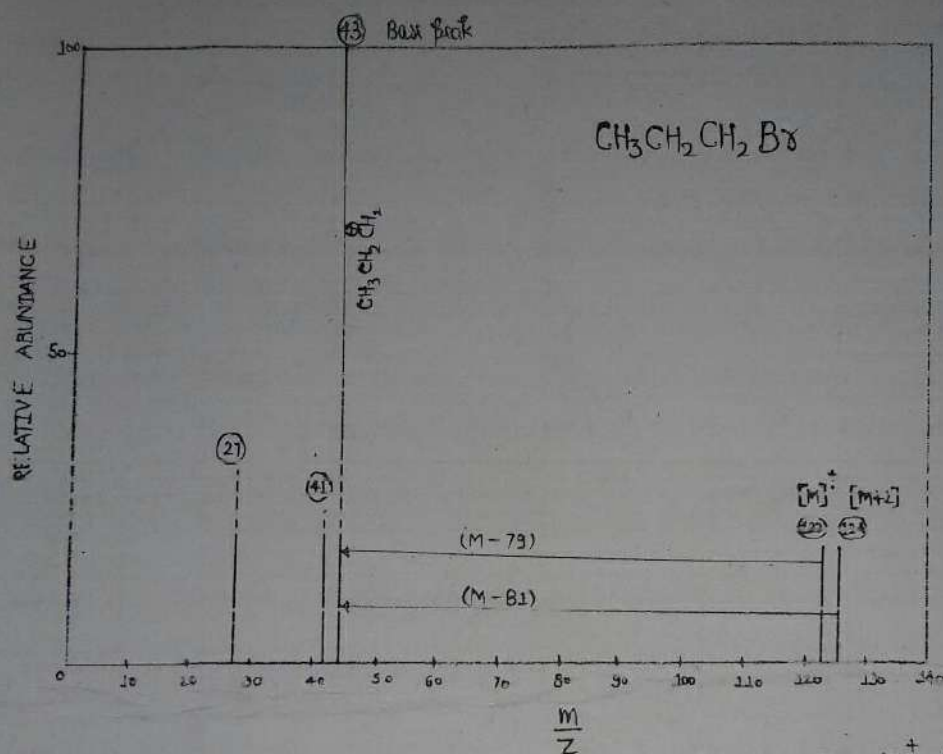
Isotope Patterns:

- Mass spectrometer are capable of separating and detecting individual ions even those that only differ by a single atomic mass unit.
- Mass spectra 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 ions (M^{+}) and 1 and 2 represents mass increases due to the heavier isotopes of 1 or 2 mass unit. Thus the M^{+} Peak is not the peak of highest m/z value.
- This is most apparent when atoms such as Bromine or Chlorine are present (^{79}Br and ^{81}Br intensity 1:1 ; ^{35}Cl and ^{37}Cl intensity 3:1)
- M+1 peaks are seen due to the presence of ^{13}C in the sample

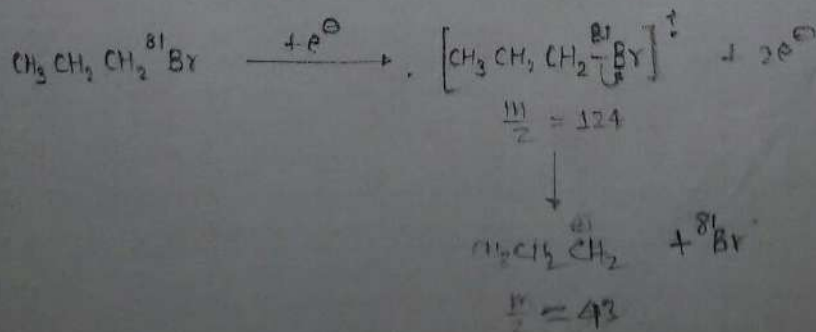
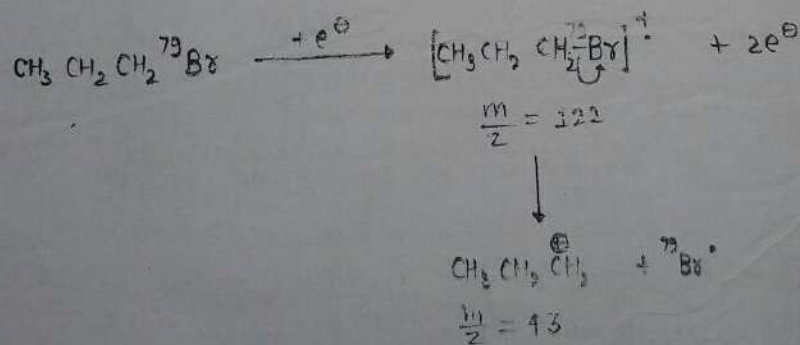
Following two mass spectra shows the examples of characteristic isotope pattern:



Example: The mass spectrum of 1-Bromopropane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$)



Isotope pattern at 122 and 124, that represent the M^+ and $M+2$ peaks in 1:1 ratio. Loss of ^{79}Br from 122 and ^{81}Br from 124 gives the Base peak corresponds to propyl cation.



Metastable Ions:

In this case, $m_1^+ \rightarrow m_2^+ + R \cdot$ -----(1)

Accelerated Detected Neutral

$$m^* = (m_2)^2/m_1 \text{ ----- (2)}$$

where m^* is known as metastable ion

When a mass m_1 is accelerated and then begins to decompose. The neutral fragment $R \cdot$ Will be continued with some of the kinetic energy, the mass m_2 which is charged is accelerated and deflected. The process ends up in a peak with properties of m_1 and m_2 but occurring at a new mass m^* which is given by the equation (2) where $m_1 > m_2$. For Example, The utility of metastable ion , a meta stable peak at $m/z = 92.1$ is observed in the spectrum of Acetophenone ($m/z = 120$) corresponding to the fragmentation and the predicted mass, $m^* = (105)^2/120 = 91.88$

Nitrogen Rule: Nitrogen rule states that, the compounds containing an even number of nitrogen atoms (zero in an even number) will give a molecular ion with an even mass number. For example, the following compounds give their molecular ions at even mass numbers:

CH_4 ($m/z=16$);

CH_3OH ($m/z=32$);

$CClF_3$ ($m/z=104$);

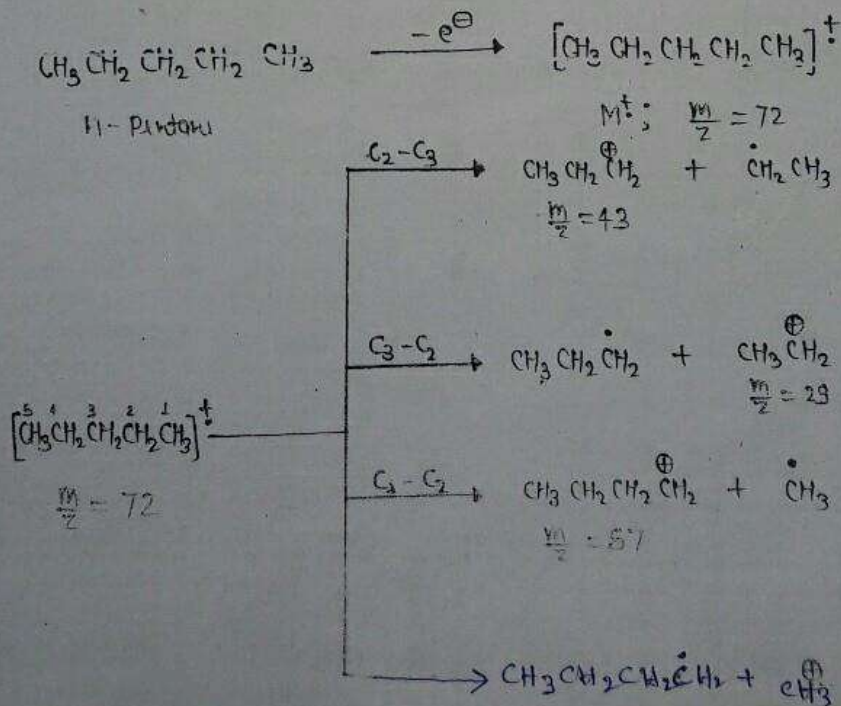
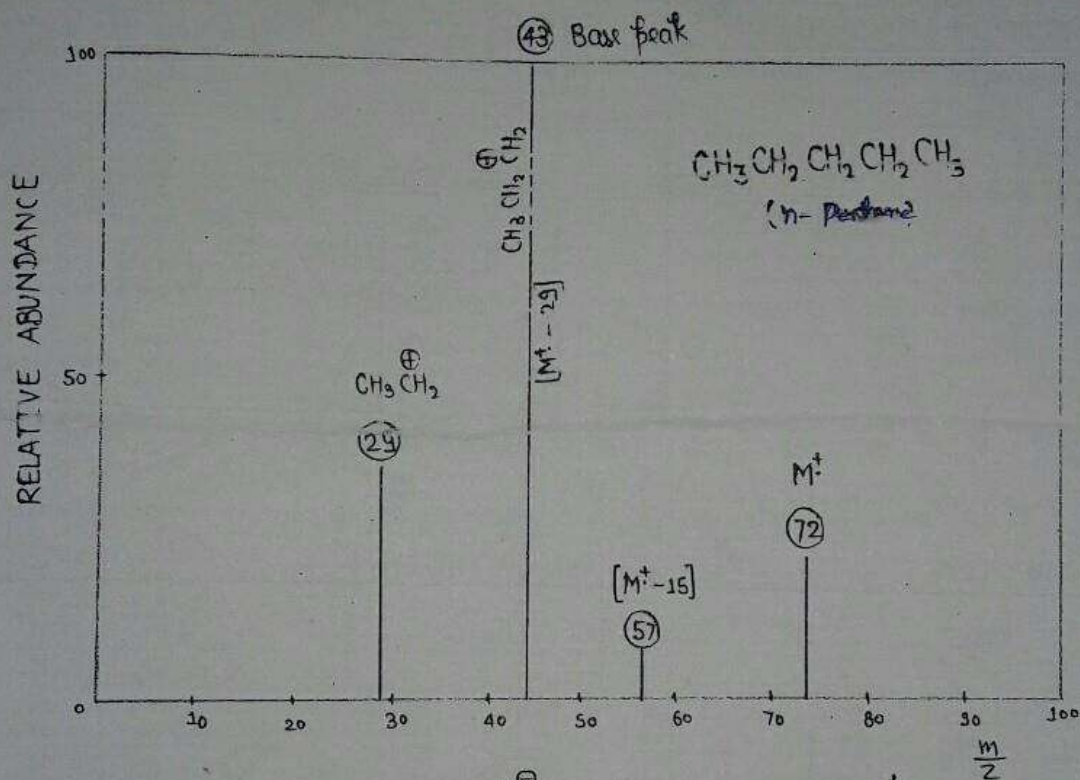
C_6H_5OH ($m/z=94$);

H_2NNH_2 ($m/z=32$);

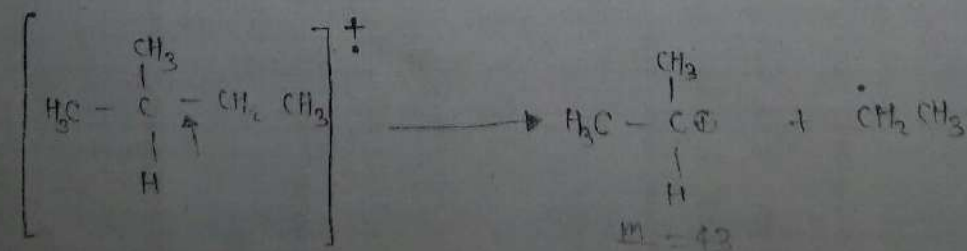
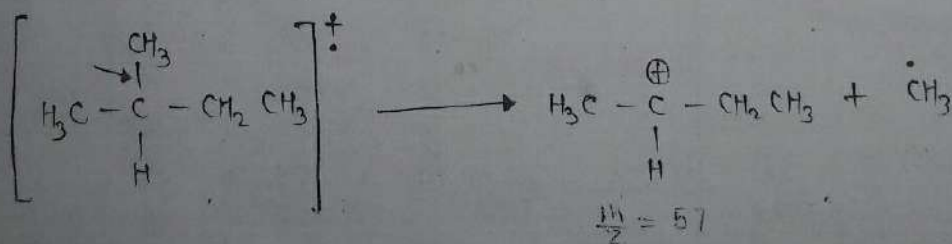
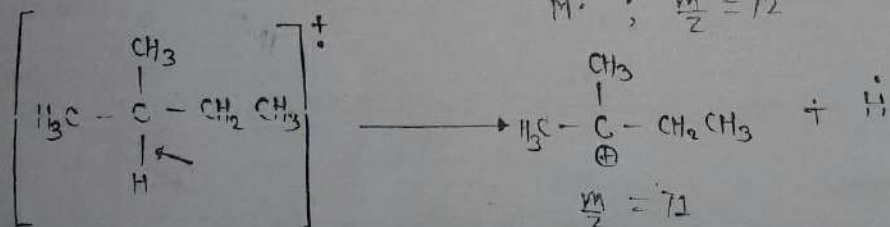
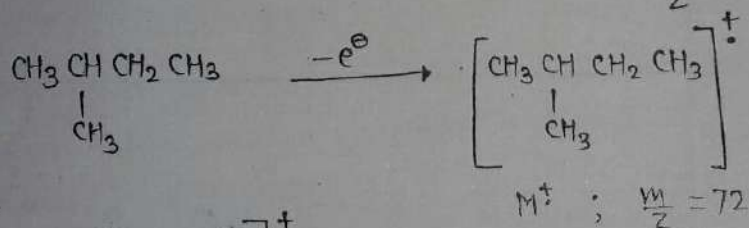
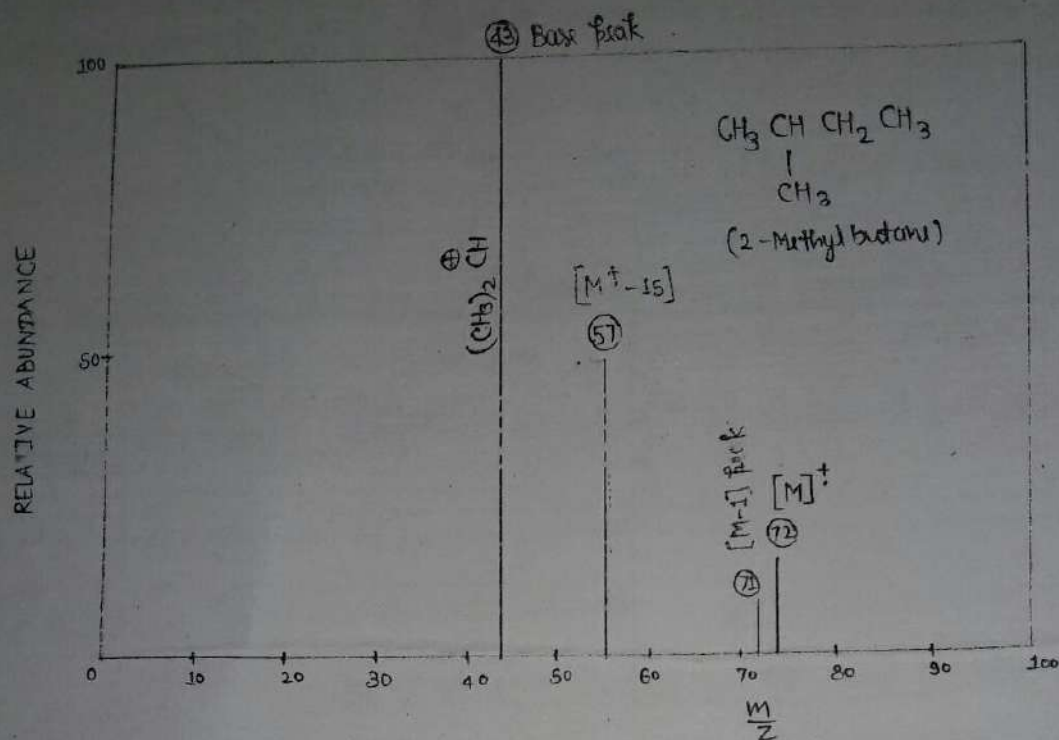
$C_6H_5N_2$ ($m/z=94$). And an odd number of nitrogen atoms causes the molecular ion to be at odd number e.g. NH_3 ($m/z=17$) and $C_2H_5NH_2$ ($m/z=45$).

In other wards, the nitrogen rule may be stated as: an odd electron ion will be at an even mass number if it contains an even number of nitrogen atoms. In the same way, an even electron ion with an even number of nitrogen atoms will appear at an odd mass number.

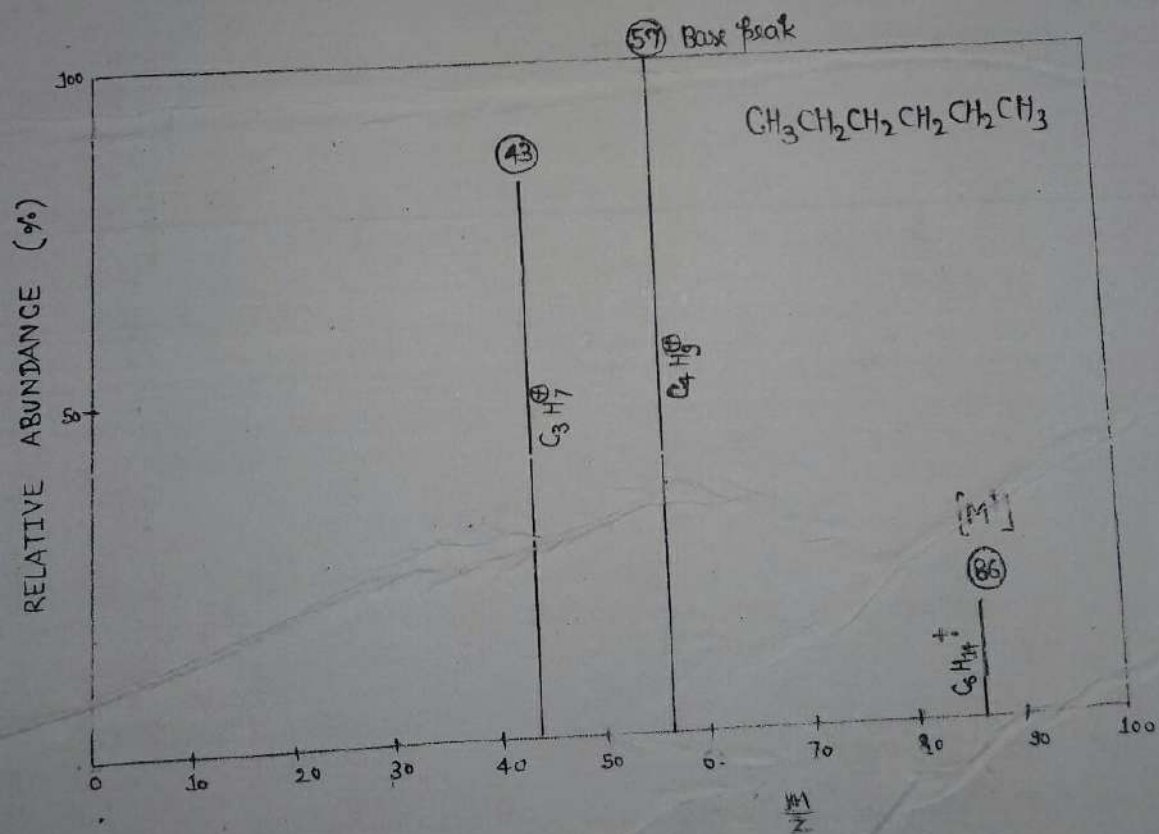
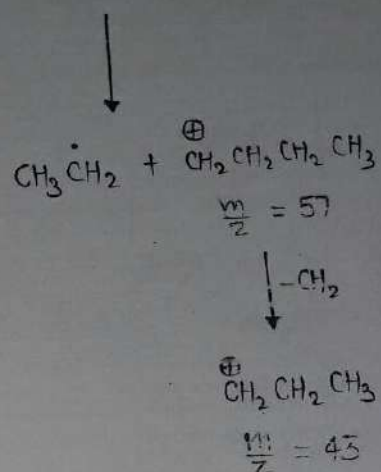
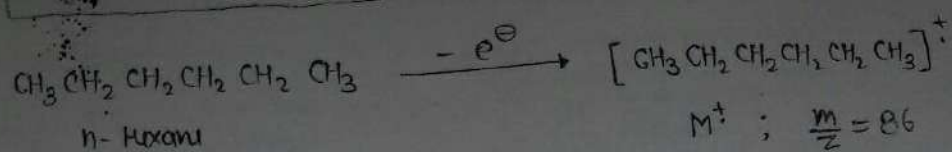
Fragmentation of n-pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)



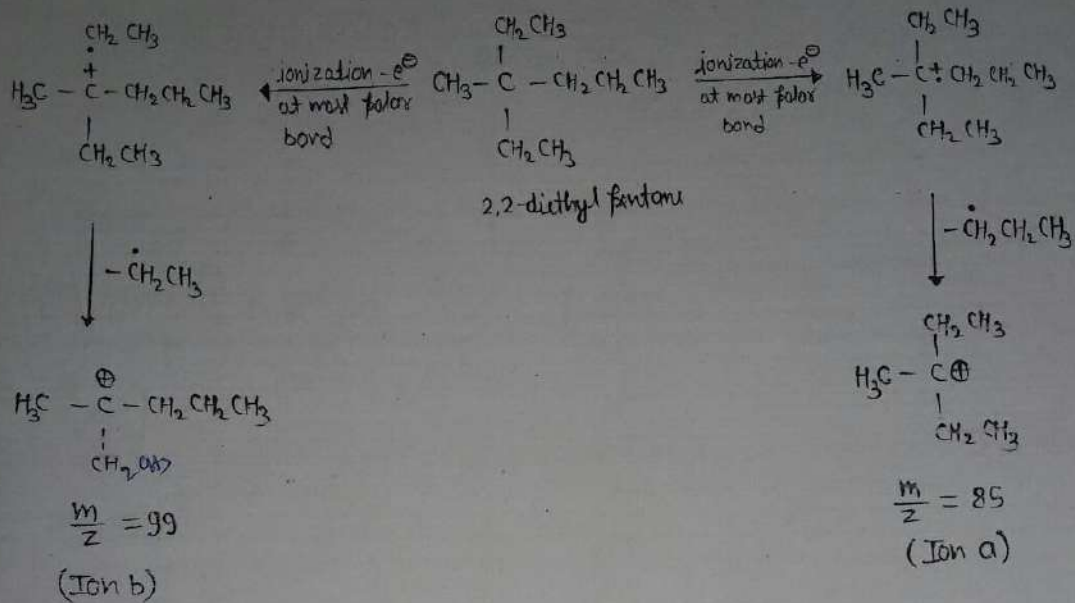
Eg → [Fragmentation of 2-methyl butane ($\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$)]



Fragmentation pattern of n-Hexane



eg: Fragmentation pattern of 2,2-diethyl pentane



Question The mass spectrum of two different cycloalkane both shows the molecular ion peak at $\frac{m}{z} = 98$. One spectrum shows the base peak at $\frac{m}{z} = 69$ and other shows the base peak at $\frac{m}{z} = 83$. Identify the cycloalkane.

Answer $[M]^+_1 = 98$, Base peak, $\frac{m}{z} = 69$

$[M]^+_2 = 98$, Base peak, $\frac{m}{z} = 83$

For first cycloalkane :-

$98 - 69 = 29$; It means loss of ethyl group (CH_2CH_3)

General formula of cycloalkane = $C_n H_{2n}$

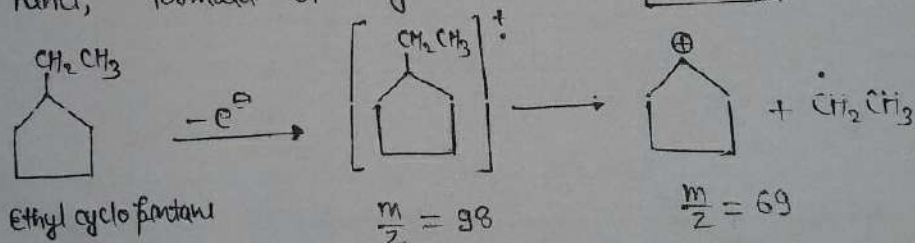
Hence, $\frac{m}{z} = 98$

$$12n + 2n = 98$$

$$14n = 98$$

$$n = 7$$

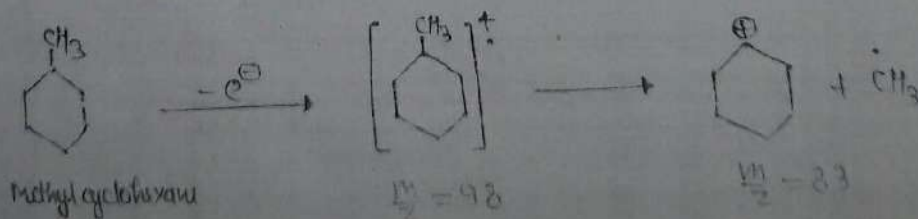
Hence, formula of cycloalkane ; C_7H_{14}



Hence, first cycloalkane was, Ethyl cyclopentane.

For second cycloalkane :-

$98 - 83 = 15$; It means loss of methyl group ($-CH_3$)



Mass spectrum of 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)

