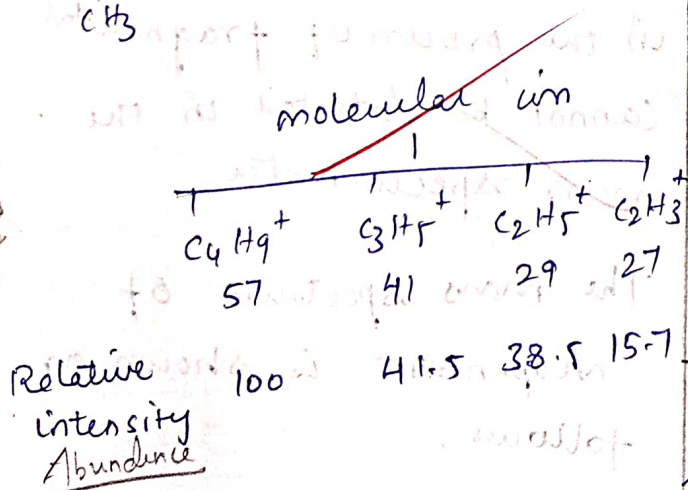
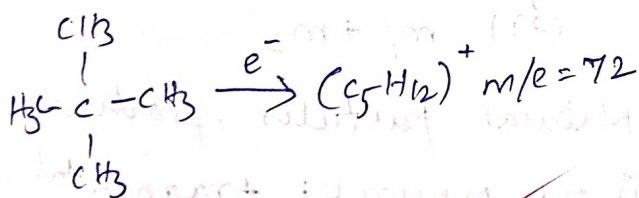


Mass Spectroscopy

Basic principle:

Mass spectrometry is the most accurate method for determining the molar 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. For most ions, the charge is one and their m/e ratio is simply the molecular mass of the ions.



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

The set of 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 represent 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 intensity of other peak represented relative to the base peak) i.e.

Note - The molecular 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 represent the intensities of the signals at various m/e value. It is highly characteristic of a compound.

No two compound can have exactly similar mass spectra. A single mass spectrum is correlated to

dozen of physical properties of that compound for revealing the structure. (Mass spectrometry is used in two general ways

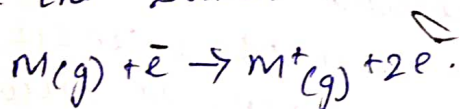
- To prove the identity of two compounds
- To establish the structure of a new compound.

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

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

Theory:

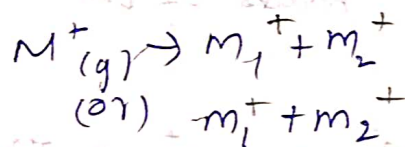
A parent ion results when one electron is removed from the parent molecule of the substance



The m/e value of the parent ion is equal to the molecular mass of the compound. In a first order ionization, the parent ion peak is not the base peak and is often

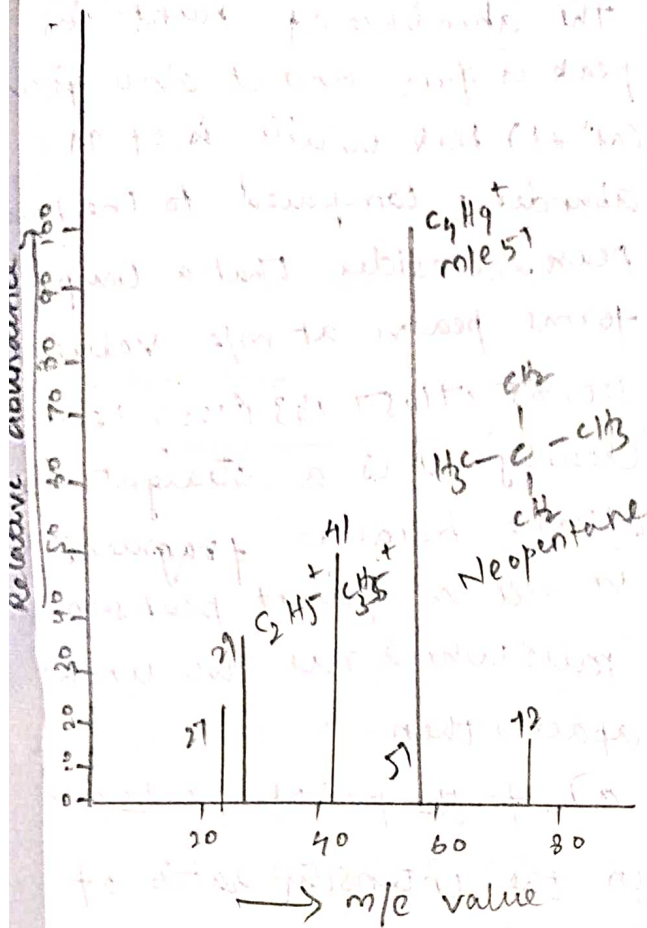
of very small abundance. Many elements occur naturally as isotopes and of these the lightest one greatly predominates. The mass spectrometer is designed to perform three basic functions. These are:

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



Natural particles, produced in the process of fragmentation cannot be detected in the mass spectrometer.

The mass spectrum of neopentane is shown as follows:



Mass spectrum:

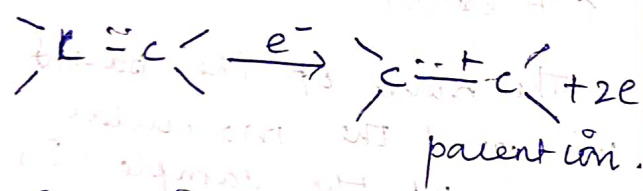
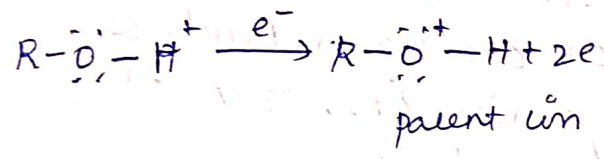
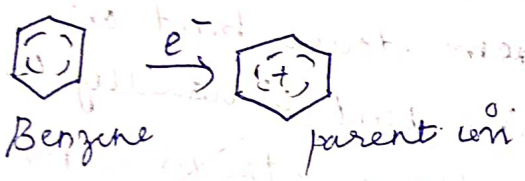
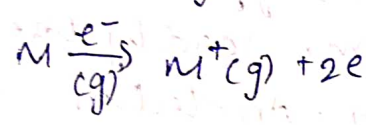
It is a record of the masses and the relative abundance of the molecular ion and the positively charged fragments formed from it by the electron bombardment. The m/e ratios are taken along the abscissa while the relative abundance are taken along the ordinate. Base peak is the highest peak or the most intense peak in the spectrum. Relative abundance of an ion means the percentage of the 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 orbital on oxygen and nitrogen atoms readily lose one electron. An electron from double bond or triple bond 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 higher mass region of the spectrum. The stability of the parent (molecular) ion decides its relative abundance. The peak intensity of the molecular ion differs from one compound to another. In some cases, parent ion peak is not

c 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 a decomposition of the molecular ion increase with the molecular size in the homologous series + larger molecular ion provides more possible reaction path way for detection.



Determination of molecular formula

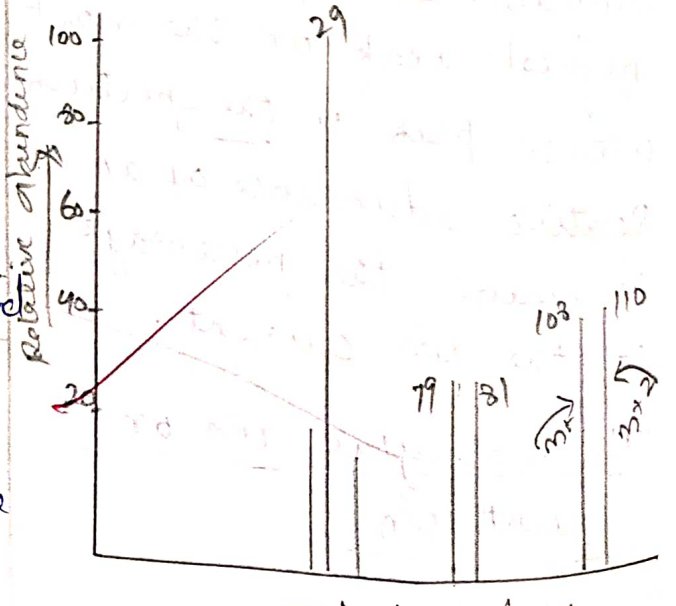
The mass spectrum is a plot representing the m/e value of the various ion against their corresponding relative abundance. The peaks on the extreme right correspond to the molecular mass of the original molecule. In case of straight chain hydrocarbon, the

the abundance of parent ion peak is fair and it also gives (M+1) peak which is of 99% abundance compared to the parent peak. Consider that a compound forms peaks at m/e values: 100, 85, 71, 57, 43 (100%) etc. Clearly, it is a straight chain alkane because fragment or well as parent peak pairs which are two units apart, then

a) If the pair of peaks are in the intensity ratio of 1:3 then it must be a chloro compound.

b) 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.



As the pair of peaks are of equal intensity on the extreme right corresponds to M^+ and $(M^+ + 2)$ peaks. The spectrum corresponds to the molecular formula (C_2H_5Br) ✓

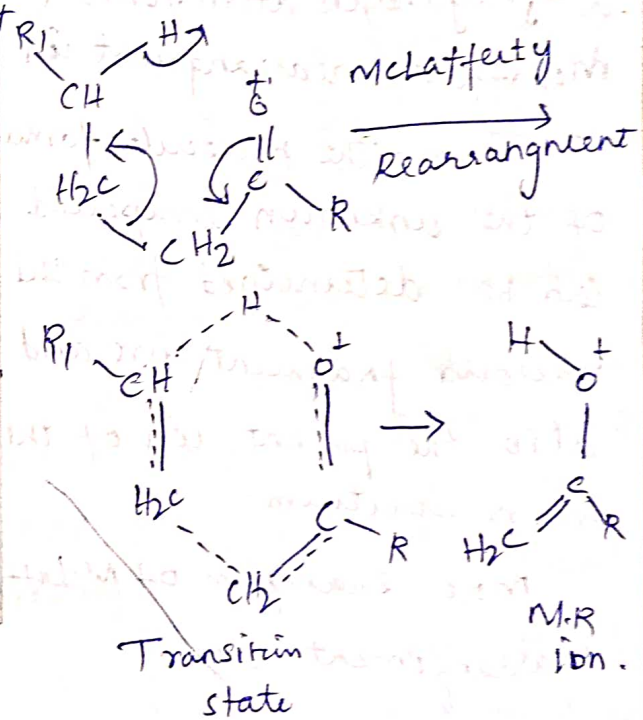
In some cases, a McLafferty rearrangement ion peak gives an important clue in the determination of molecular formula of the compound.

For example, all straight chain aldehydes containing a γ -hydrogen atom form a base peak at m/e 44. Also in aldehyde a fairly abundant M^+ peak (parent peak) follows a less abundant $(M^+ - 1)$ peak. Let us consider a simple mass spectrum having m/e value at 72, 71, 44 (100%), 43, 29 etc.

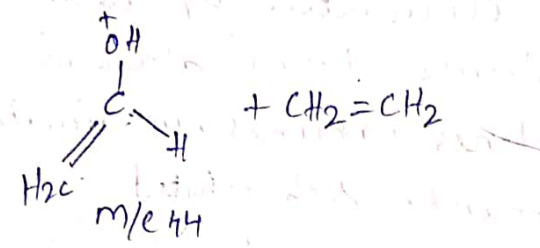
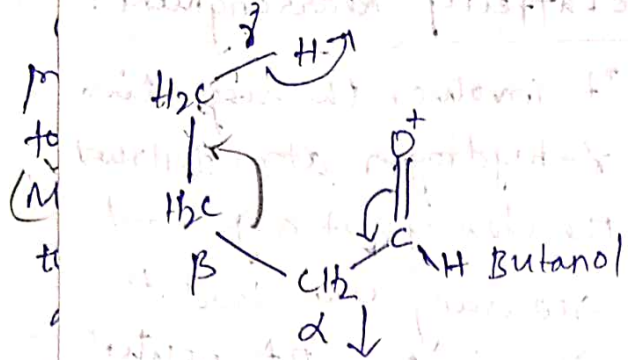
Here a signal at m/e 44 (100%) is due to McLafferty rearrangement ion. This shows that it is a straight chain aldehyde as M^+ peak at 72 also accompanies $M^+ - 1$ peak at 71 and hence the formula of the compound is $(CH_3CH_2CH_2CHO)$ ✓

McLafferty Rearrangement:

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



Butanol contains a γ -hydrogen atom. The McLafferty rearrangement ion formed in this case is shown below

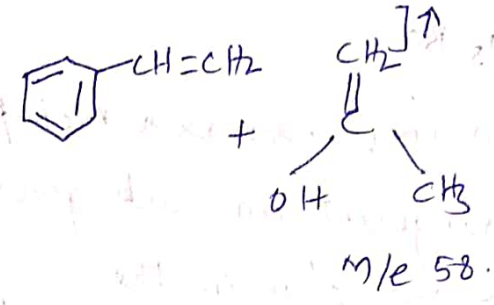
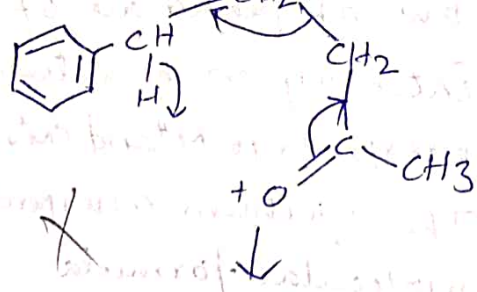
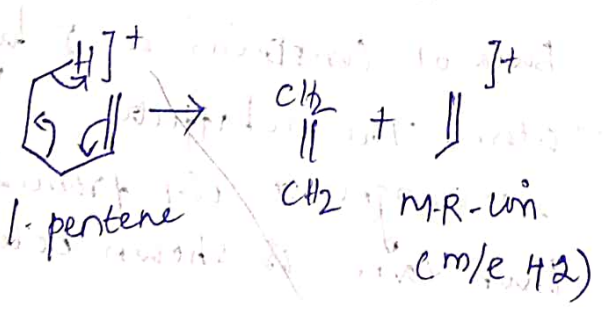


(M.R. ion)

Similarly a large number of organic compounds, viz, ketones, amines, alcohols, esters, acids, which contain a γ -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.

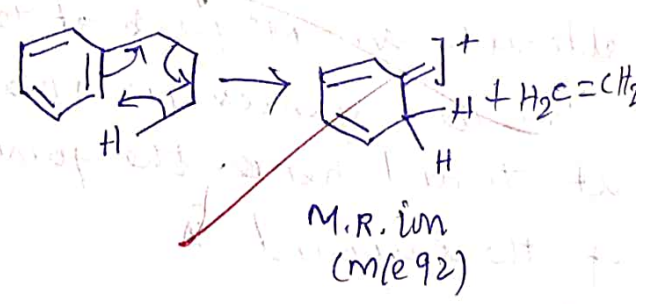
more examples of McLafferty rearrangement are



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 ben benzene shows a McLafferty rearrangement ion peak in 92



Metastable ions or peaks

Metastable peaks can be easily determined in a mass spectrum some of these peaks are.

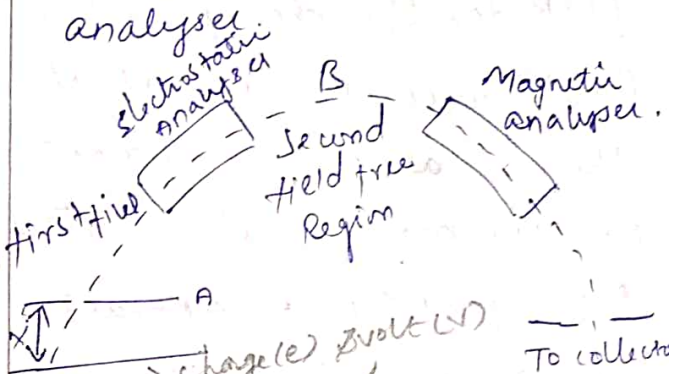
- i) They do not necessarily occur at the integral m/e value.
- ii) They are much broader than the normal peaks and
- iii) They are of relatively low abundance.

Formation of metastable ions

Consider that M_1^+ is the parent ion. If the reaction $M_1^+ \rightarrow m_1^+$ takes place in the source, then the daughter whole analysed region and is recorded as m_1^+ ion. On the other hand if occurs after the source exists and before arrival at the collector. then m_1^+ is ^{metastable ion} we know that is double focussing mass spectrometer, these are two are called drift regions.

The ion pass through these region after acceleration region refers to the position

of the ion path immediately before the electrostatic analyser. Second field free region lies between electrostatic analyser and magnetic analyser.



(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 their 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 particles is not detected by the mass spectrometer.

Then, m_2^+ ion formed in the secondary field free region will have less kinetic energy than it would have produced 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_2 . Hence we conclude that the position of the metastable peak (m^*) due to the reaction of $M_1^+ \rightarrow m_1^+$ occurring in the secondary field free region is such that

$$m^* = m_1^2 / M_2$$

The Nitrogen Rule:

Many signals (peak) can be ruled out or possible molecular ion simply on the ground of ~~para~~ reasonable structural requirements. The nitrogen rule is often helpful in 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 number 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 nitrobenzene ($C_6H_5NO_2$). The signal for molecular ion appear at m/e 123; i.e. at odd numbered molecular mass since the compound contains only one 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 31. Both these fragment ions

appear at odd mass number.
 This proves the validity of
 the nitrogen rule.

Retro-Diels-Alder reaction:

(This reaction is an example of multivalent fragmentation which is characteristic of cyclic olefins).
 (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.)

