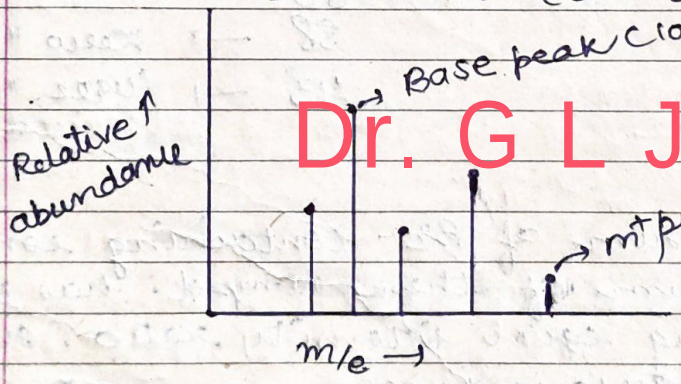
-:° Mass Spectroscopy °:-

1. This technique is useful for the determination of exact molecular mass & elemental analysis & some information about the structure of given compd.

⇒ **Basic principle:-**
The molecules are bombarded by a beam of energetic electrons, due to this molecules undergo fragmentation. & produces fragments in which some of them are positively charged only positively charge species can be detected by the mass spectrometer. These positively charged species are captured on a -vely charged plate and a mass spectrum is observed

Theory:-
Mass spectrum is plotted between relative abundance (intensity) of various +ve ion & their m/e values. (e = charge on species)



$M^{\oplus}$ peak:- A peak which is appeared at highest m/e value is called M^+ peak or parentionpeak or molecular ion peak.
M^+ peaks tells the molecular mass of the compd.

Base peak:-
Such a peak has a highest intensity in the mass spectrum is called base peak. It represent the most stable fragment of the compd. This peak may appear as $M^{\oplus}$ peak.

Intensity of each peak in mass spectrum depends on relative no. of ions. it means intensity indirectly depends on stability of the fragments.
Intensity of m^+ peak can be increased by decreasing the energy of bombarding electrons

Determination of elements :-

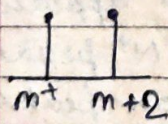
→ Nitrogen Rule :-
when m^+ peak is observed at even m/e value it indicates comp. may have even or zero N atom. odd m/e value of m^+ peak indicates the compd must have odd no. of N-atom.

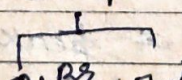
∴ compds :-
CH_3NH_2
CH_3NONH_2
$NH_2 \infty NH_2$
CH_3COCH_3
N_3H

∴ value of m/e of m^+ peak
81 → 1 N atom
59 → " " "
60 → two " "
58 → zero " "
43 → three " "

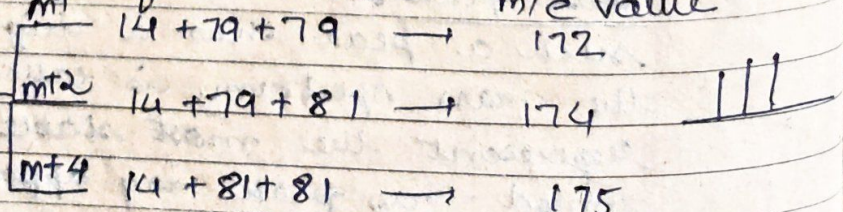
→ Mass spectrum of Br - containing compds :-
Mass spectrum of these compd. has M^+ & m+2 peaks having equal intensity ratio. since Br element has two isotopes.

^{79}Br : ^{81}Br
50 : 50
(natural abundance)





eg. In the mass spectrum of methylene bromide [CH_2Br_2] peaks were observed at 172, 174 & 176 due to isotopes of bromine.

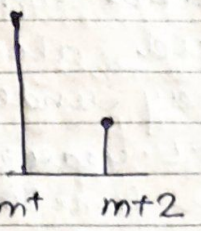


CH_2Br_2

m/e value

→ Mass spectrum of Cl containing compounds :-
M+ & M+2 peaks are observed having intensity ratio 3:1

^{35}Cl : ^{37}Cl
75% : 25%
3 : 1

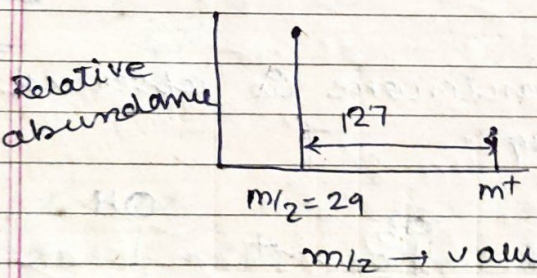


for CH_2Cl_2 M+ : M+2 : M+4
9 : 3 : 1

CH_2Cl_2 — m+ : 14+35+35 → 114
m+2 : 14+35+37 → 116
m+4 : 14+37+37 → 118

m+ m+2 m+4.
9 : 3 : 1

→ Mass spectrum of Iodine containing compds :-
mass spectrum of I containing compds.
These compds shows m+ 127 peak it means there will be a longer gap



→ Mass spectrum of S-containing compounds :-
These compds shows m+2 peak which has 4.4% intensity ratio w.r.to. m+ peak.

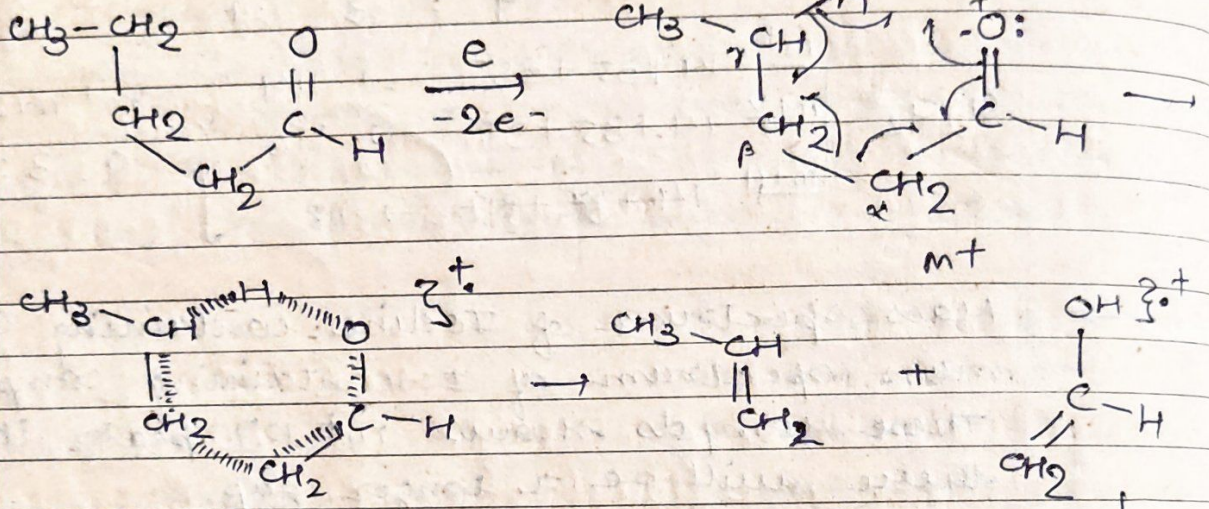
→ calculation of no of C-atoms :-
These can be calculated as.
Intensity of m+1 peak w.r.to. m+ peak.
= N × 1.1
N = no. of carbon atoms

A. cal the intensity of M+1 peak in fullerenes (C_{60}) = 60 × 1.1 = 66%.

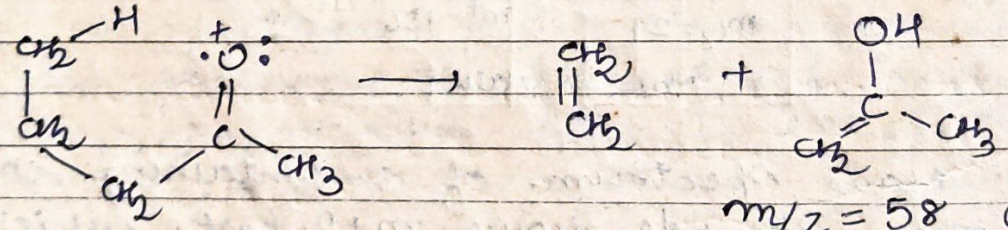
B. Suppose intensity of m+1 peak is 16.5% w.r to m+ peak, then no of C = $\frac{16.5}{1.1}$ = 15

→ Mc Lafferty Rearrangement :-
compounds like alkenes, carbonyl compd, esters, amides, nitriles, isonitriles, carboxylic acid, alcohol etc which have γ-hydrogen may undergo Mc. Lafferty rearrangement. In M·L rearr. γ-hydrogen is transffered on on functional grp. & β-bond undergo breakage Generally M·L ion gives base peak in mass spectrum.

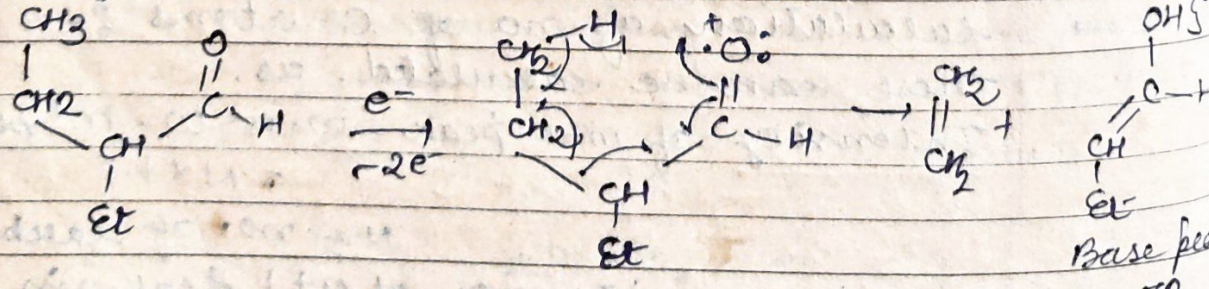
eg ①



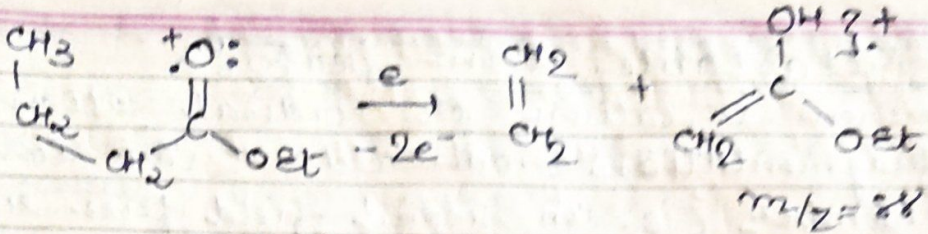
eg 2. Base peak for 2-pantenone is observed at m/z=58 due to M·L rearrag.



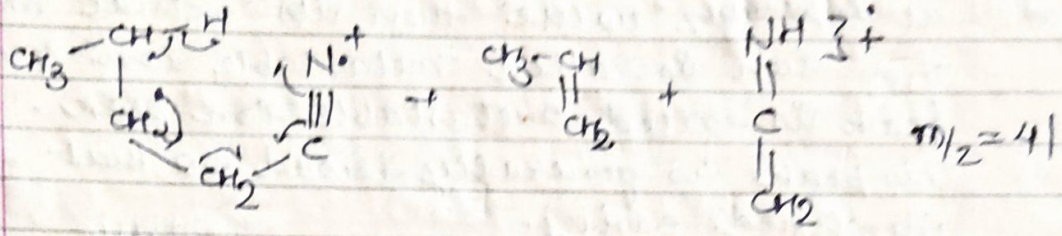
eg (3) Ethyl butanol.



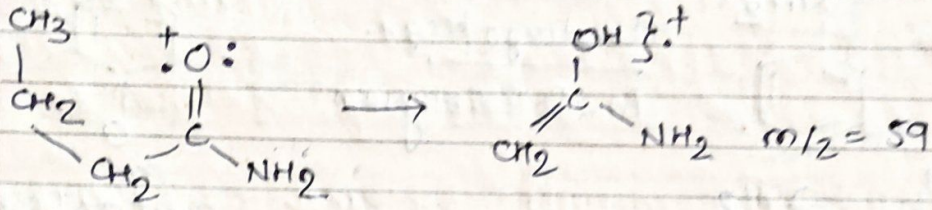
eg. 4.



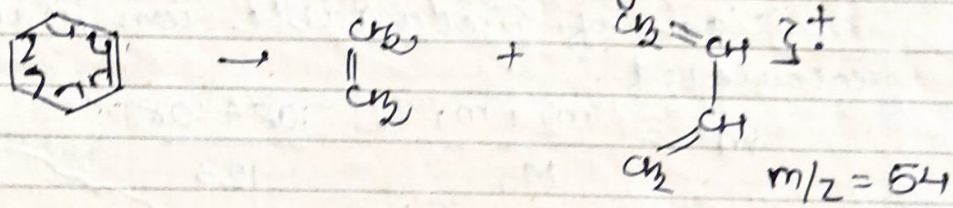
eg. 5 Pentane nitrile



eg. 6. Butanamide :-

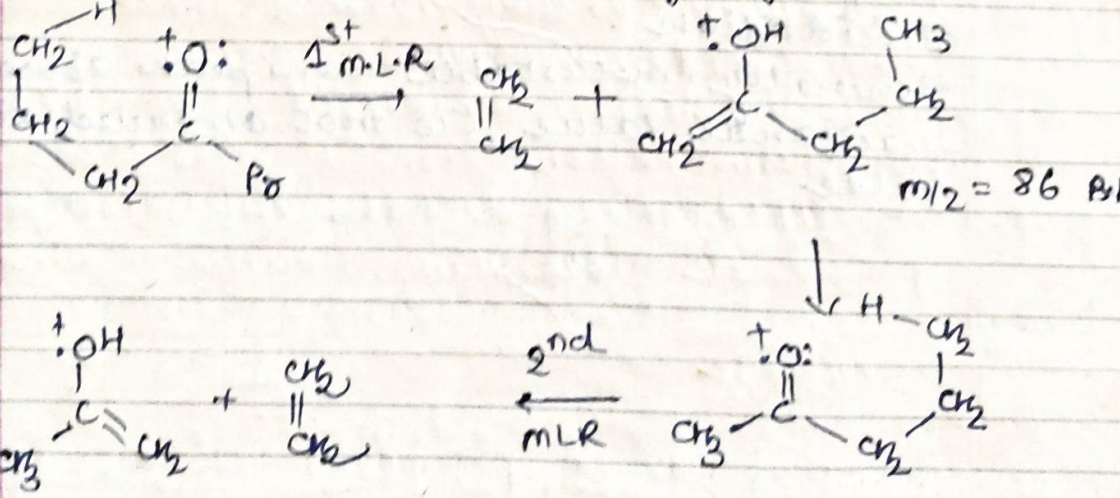


→ Retro diels Alder Rearrangement :-



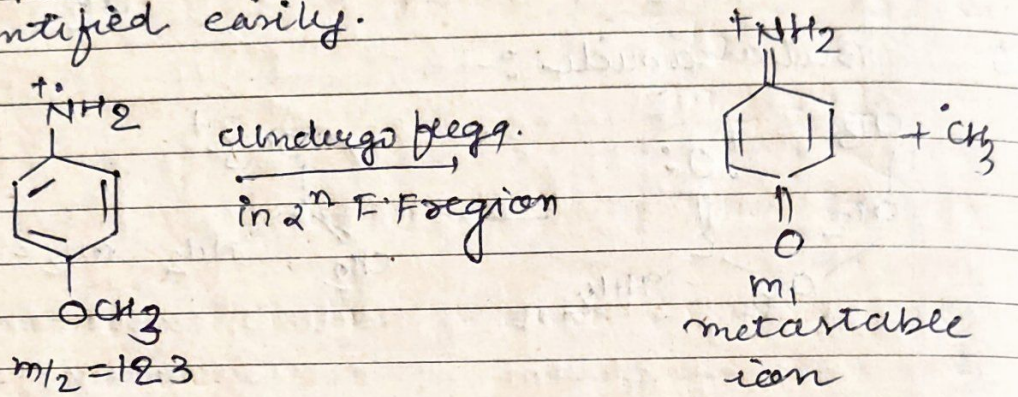
→ Double m.L. Rearrangement :-

It is also shown by carbonyl compds in which two sides have γ hydrogens.



→ **Metastable ion peak :-**

When a cation or radical cation undergo fragmentation from out of the ionization chamber (ie. in second field free region) the newly formed cation or radical cation appear at less m/z value than its actual m/z value. This ion is called metastable ion & corresponding peak is called metastable ion peak. This peak is generally broad so that it can be identified easily.



Position of metastable ion peak can be calculated.

$$m^+ = \frac{m_1 + m_1}{M_1} = \frac{108 + 108}{123}$$

$$m^+ = 94.8$$

Significance of metastable ion peak :-

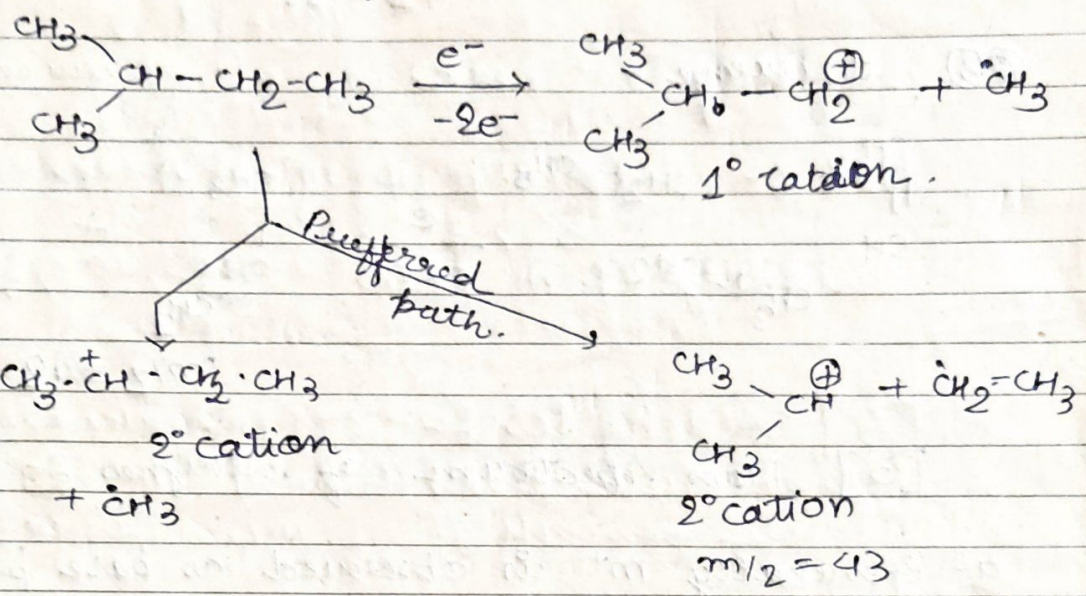
It provide extra evidence in the structure elucidation.

generally metastable ion peak appeared at fractional value (ie not observed at integral value.

Ephansiyan:

[1] mass spectrum of Alkanes :-

① Fragmentation follow such a way due to which most stable fragments (cation & radical) are generated.



② Intensity of m^+ peak is more for un-branched alkanes compared to branched alkanes.

③ Generally m^+ peak is absent in highly branched alkane.

④ Straight chain alkanes give peak at m^+-15, $m^+-(15+14)$, $m^+-(15+28)$ etc.

eg. peak for n-hexane.

$m^+ = 86$, $m^+-15 = 71$, $m^+-29 = 57$, $m^+-43 = 43$.

[2] Mass Spectrum of Alkenes :-

a- See the possibility of m.L- Rearrangement (m/z = 42)

b- After this see the possibility of formation of allyl cation or radical cation.

eg- ① $CH_2=CH-CH_2-CH_3 \longrightarrow CH_2=CH-CH_2^+ + \cdot CH_3$

m/z = 41