

Figure: Components of a Mass Spectrometer

Experiment No: 8

1) Aim: → To analyze the mass spectrum of a given compound using mass spectroscopy

2) Instrumentation: → There are three major components

Ioniser: → For producing gaseous ions of materials used

Analyzer: → For resolving the ions into their characterization mass components according to their mass/charge ratio

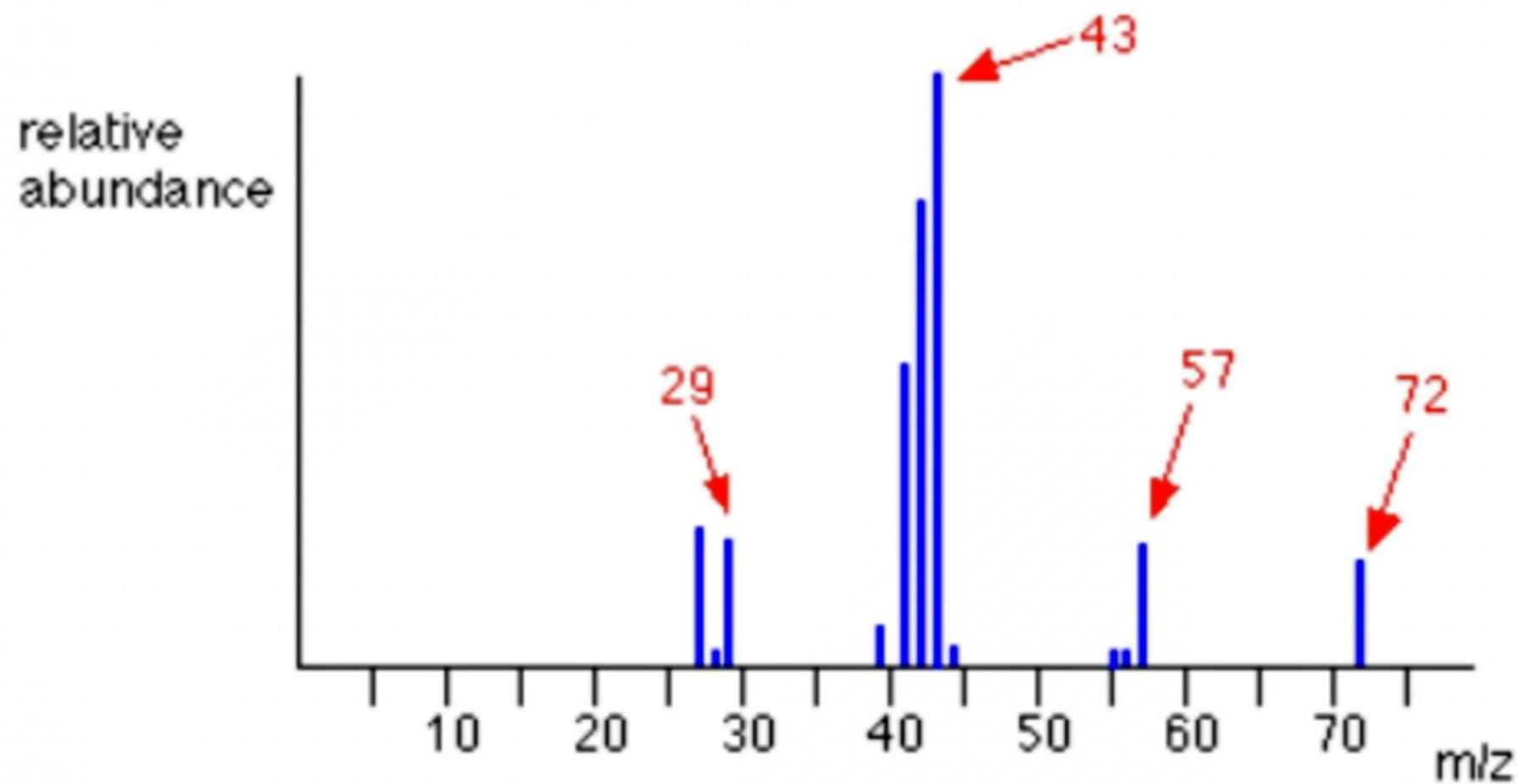
Detector: → For detecting the ions and recording the relative abundance of each of the resolved ionic species

With the components mentioned above, the mass spectrometer should always perform the following

1) Produce ions from the sample in the ionization source.

2) Separate these ions according to their m/z ratio

simplified mass spectrum of pentane - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



in analyzer

Eventually fragment the selected ions & analyze the fragments in a second analyzer.

Detect the ions emerging from last analyzer & measure their abundance

Process the signals from detector & control using feedback

3) Theory

Mass Spectrometry is fast becoming an indispensable field for analyzing biomolecules.

Until the 1970's the only analytical techniques which provided similar info were electrophoresis, chromatographic or ultracentrifugation method.

The results were not absolute as they were based on characteristics other than the molecular weight. Thus the only possibility of knowing the exact molecular weight of a macromolecular remained its calculation based on its chemical structure.

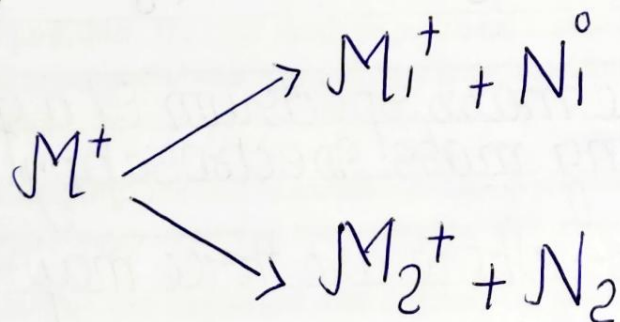
The development of desorption ionization methods based on the emission of pre-existing ions such as plasma-desorption desorption (PD), fast atom bombardment (FAB) or laser desorption (LD), allowed the application of spectrometry for analyzing complex biomolecules.

4.) Principle

A mass spectrometer generates multiple ions from the sample under investigation. It then separates them according to their specific mass to charge ratio (m/z) & then records the relative abundance of each ion type.

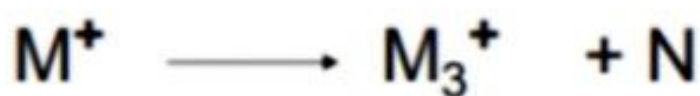
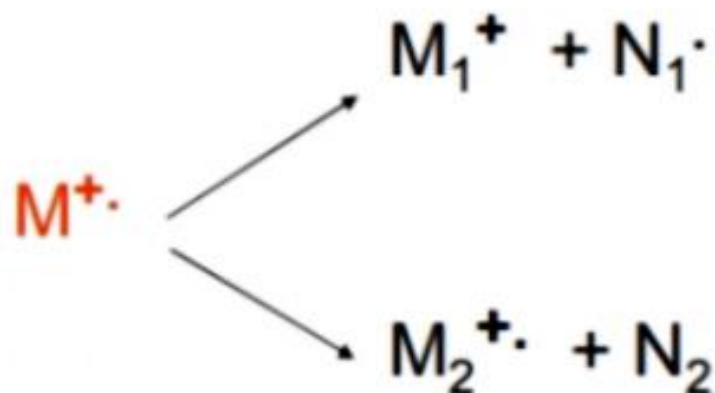
- 1) The first step in the mass spectrometric analysis of compound is the production of gas phase ions of the compound, usually by electron ionization.
- 2) This molecular ion undergoes fragmentation. Each primary product ion derived from the molecular ion, in turn undergoes fragmentation and so on.
- 3) A mass spectrum of the molecule is thus produced. It displays the same results

Fragmentation.



- ★ $M^+ \rightarrow$ Radical ion (odd e^-)
- ★ $N^0 \rightarrow$ Neutral radical (odd e^-)
- ★ $N \rightarrow$ Neutral (odd e^-)

Fragmentation:



- $M^{\bullet+}$ Radical ion (odd e)
 N^{\bullet} Neutral radical (odd e)
 N Neutral (even e)

M^+ (even e) would not break up into a radical ion....

in the form of a plot of ion abundance versus m/z / charge ratio

- 4) Ions provide info concerning the nature & the structure of their precursor molecule. In the spectrum of a pure compound, the molecular ion, if present, appears at the highest value of m/z followed by ions containing heavier isotopes & gives the molecular mass of the compound.

5) Parent/Molecular Peak M^+

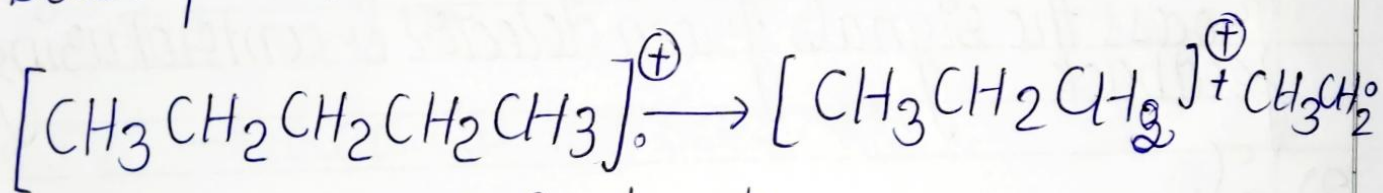
A molecular ion that has not lost/gained atoms. The normal mass of which is calculated with the mass no of predominant isotopes of atoms.

- 1) Base Peak: It is the peak from the most abundant ions which is often the most stable ion.
- 2) Fragment Peaks: Fragment peaks other than molecular ions peak is given by the symbol α then its isotopes would be α^+ , α^2

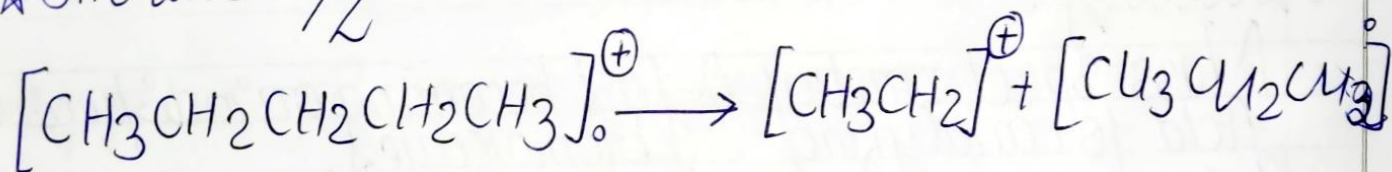
Observation 2-Methyl Pentane

Molecular ion peak = $M/Z = 72$

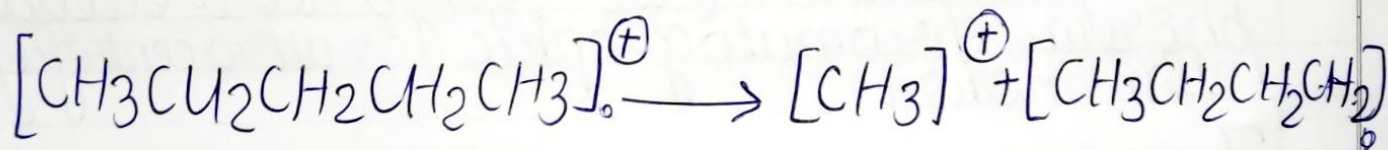
The tallest and the most abundant fragment has the value of $M/Z = 43$. Thus forms the base peak.



★ The line $M/Z = 29$ is due to



★ The line $M/Z = 57$ is due to



How many carbon atoms are there in this ion? There can't be 5 because $5 \times 12 = 60$. What about 4? $4 \times 12 = 48$. That leaves 9 to make up a total of 57. How about C_4H_9^+ then?

C_4H_9^+ would be $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]^+$, and this would be produced by the following fragmentation:



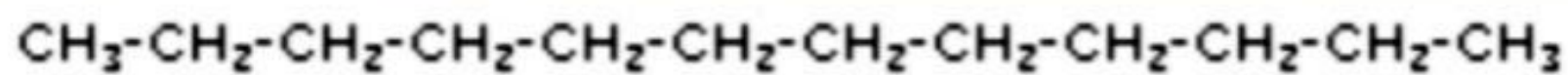
The methyl radical produced will simply get lost in the machine.

The line at $m/z = 43$ can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:

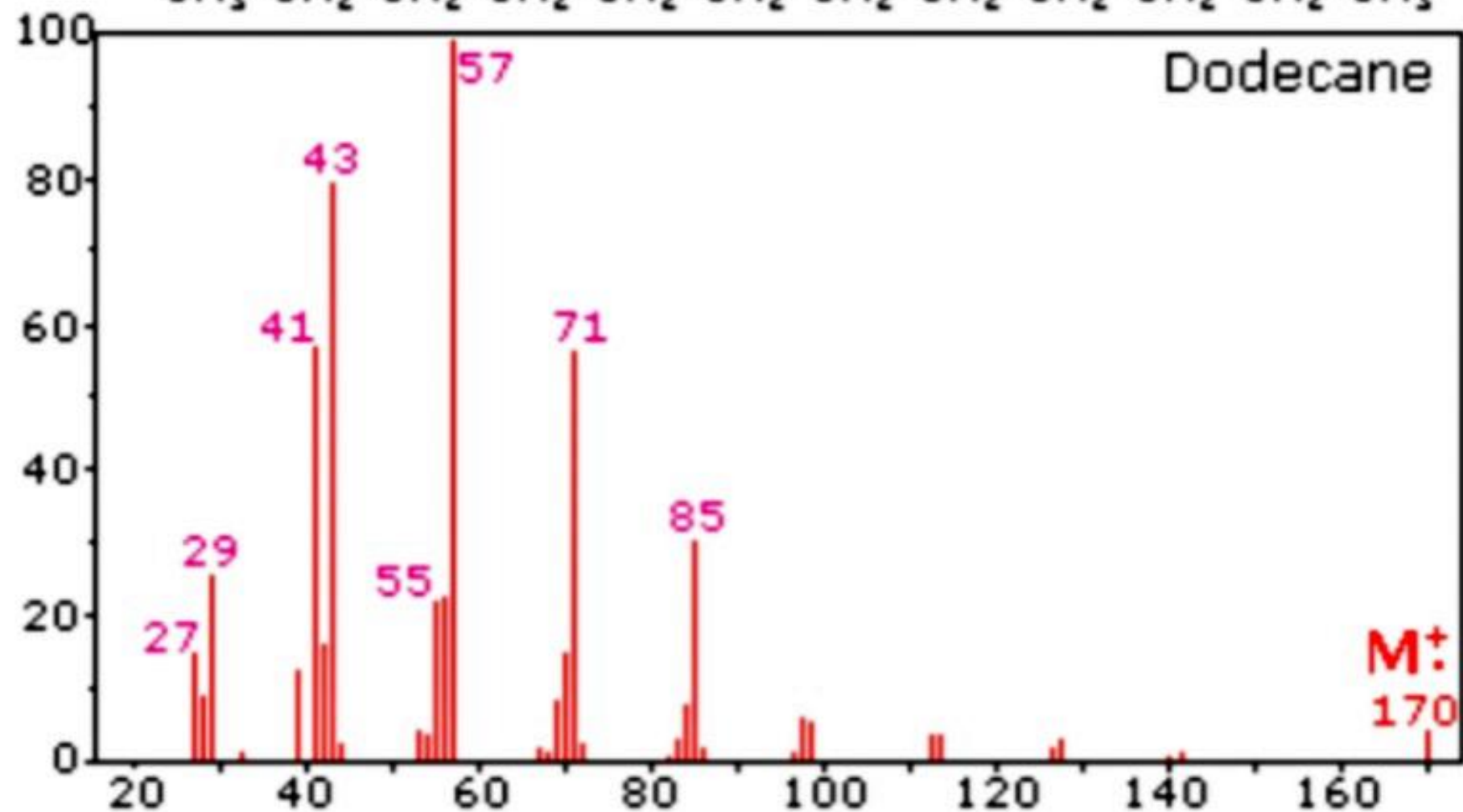


The line at $m/z = 29$ is typical of an ethyl ion, $[\text{CH}_3\text{CH}_2]^+$:





Dodecane



Example: Dodecane ($C_{12}H_{26}$)

- It illustrates the behaviour of an unbranched alkane.
- Since, there is no heteroatom in the molecule, there are no bonding valence shell electrons.
- Consequently the radical cation character of the molecular ion ($m/z = 170$) is delocalized over all the covalent bond.
- Fragmentation of C-C bonds occurs because they are usually weaker C-H bonds & this produces a mix. of alkyl radicals & alkyl carbocations.
- The positive charge commonly resides on the smaller frag, so we have a homologous series of hexyl ($m/z = 85$), pentyl ($m/z = 70$), butyl ($m/z = 57$), propyl ($m/z = 43$), ethyl ($m/z = 29$) & methyl ($m/z = 15$) cations.
- These are accompanied by a set of corresponding alkyl carbocations ($m/z = 55, 41, 27$) formed by a loss of $2H$.

- All of the significant fragment ions in the spectrum are even electron ions. In most alkane spectra, the propyl & butyl ions are the most abundant.

Finish.