MASS SPECTROMETRY

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Before you start it would be helpful to…

- **know that atoms are made up of protons, neutrons and electrons**
- **know that like charges repel**

MASS SPECTROMETRY

The first mass spectrometer was built in 1918 by Francis W Aston, a student of J J Thomson, the man who discovered the electron. Aston used the instrument to show that there were different forms of the same element. We now call these isotopes.

Francis Aston

In a mass spectrometer, particles are turned into positive ions, accelerated and then deflected by an electric or magnetic field. The resulting path of ions depends on their 'mass to charge' ratio (m/z).

Particles with a large m/z value are deflected least

those with a low m/z value are deflected most.

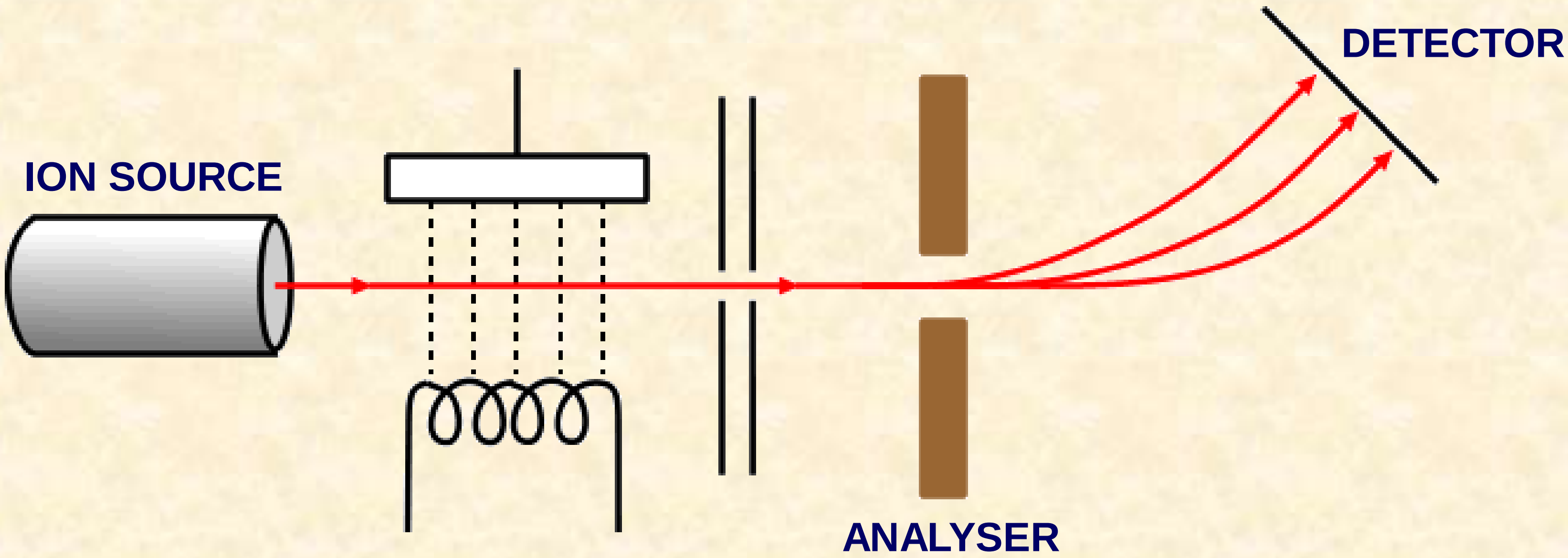
The results produce a mass spectrum which portrays the different ions in order of their m/z value.

USES

Mass spectrometry was initially used to show the identity of isotopes.

It is now used to calculate molecular masses and characterise new compounds

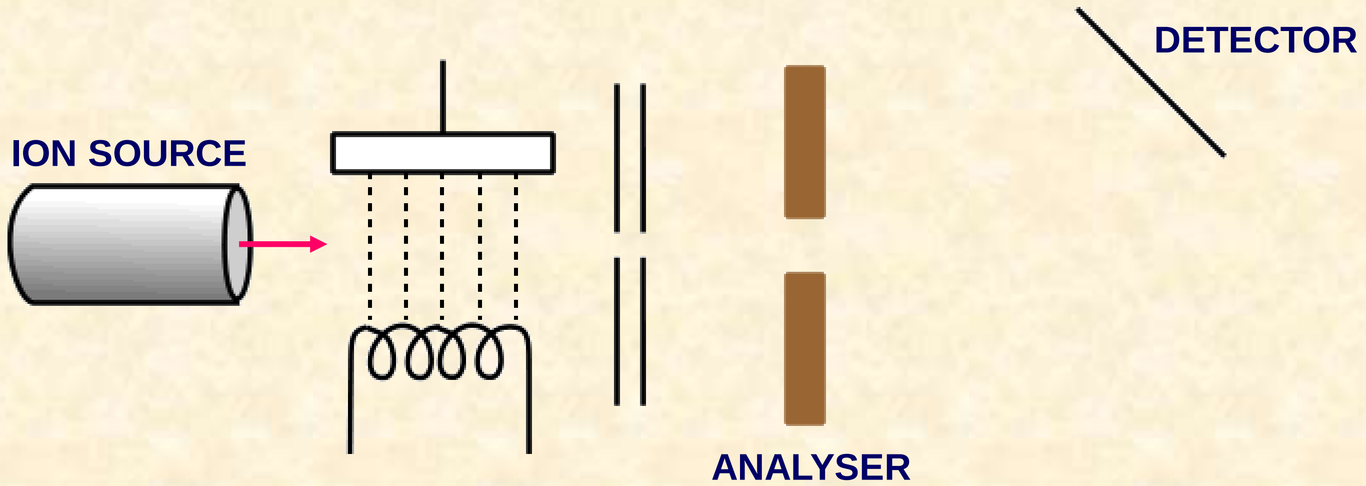
A MASS SPECTROMETER



A mass spectrometer consists of ... an **ion source**, an **analyser** and a **detector**.

PARTICLES MUST BE IONISED SO THEY CAN BE ACCELERATED AND DEFLECTED

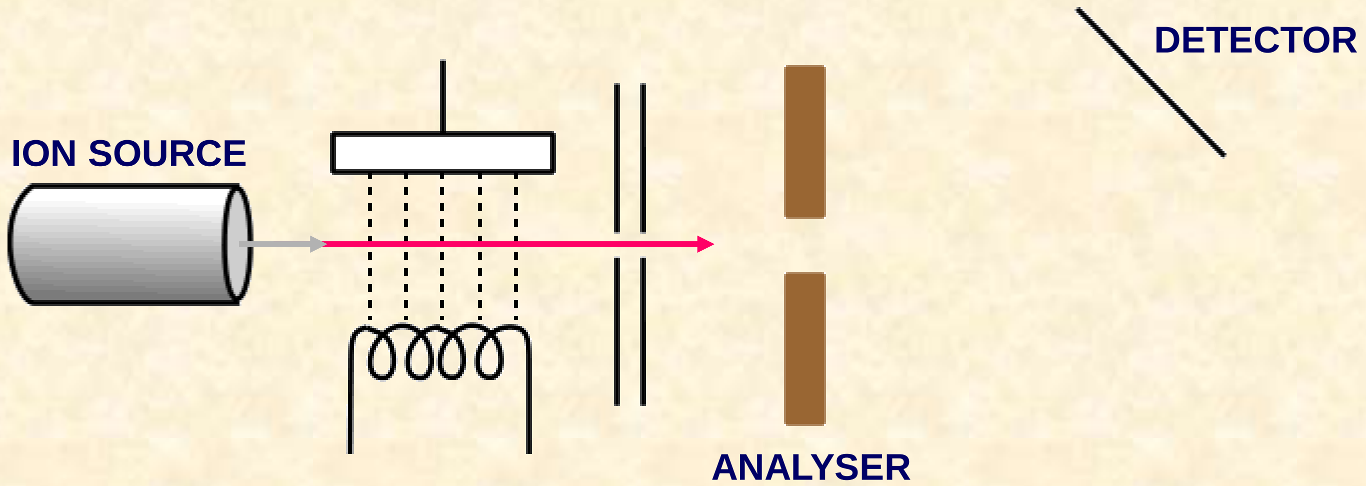
HOW DOES IT WORK?



IONISATION

- gaseous atoms are bombarded by electrons from an electron gun and are IONISED
- sufficient energy is given to form ions of 1+ charge

HOW DOES IT WORK?



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ACCELERATION

- ions are charged so can be ACCELERATED by an electric field

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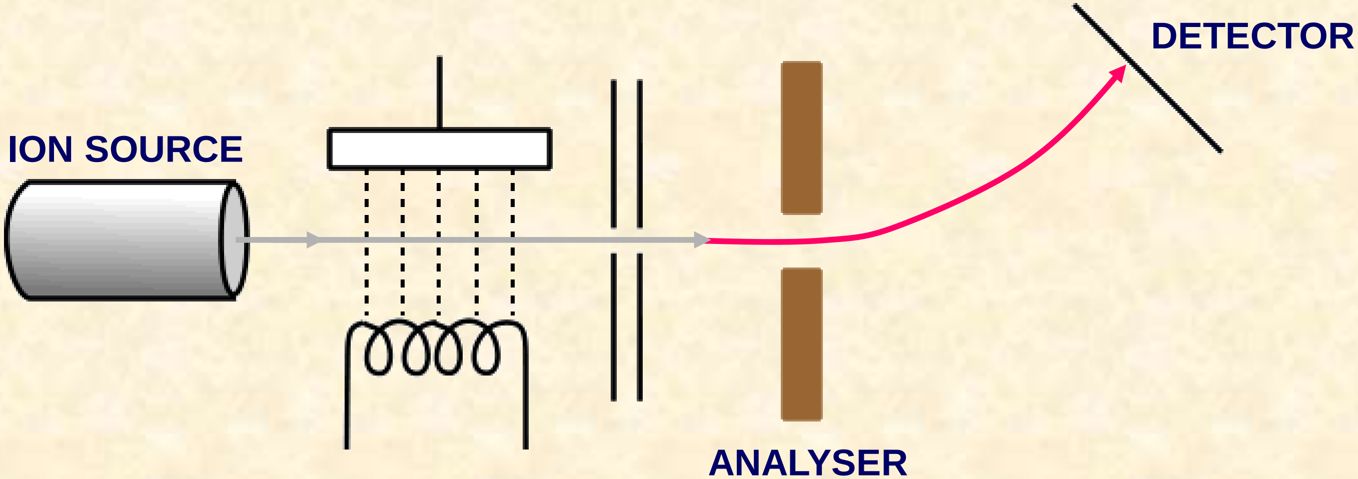

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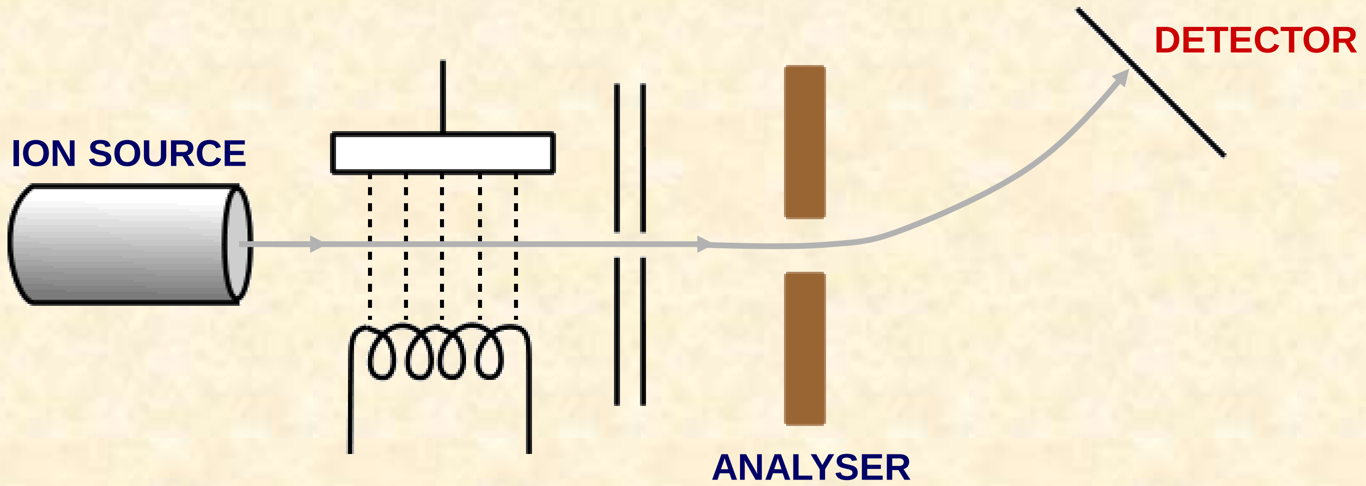
ACCELERATION

- ions are charged so can be ACCELERATED by an electric field

DEFLECTION

- **charged particles will be DEFLECTED by a magnetic or electric field**

HOW DOES IT WORK?



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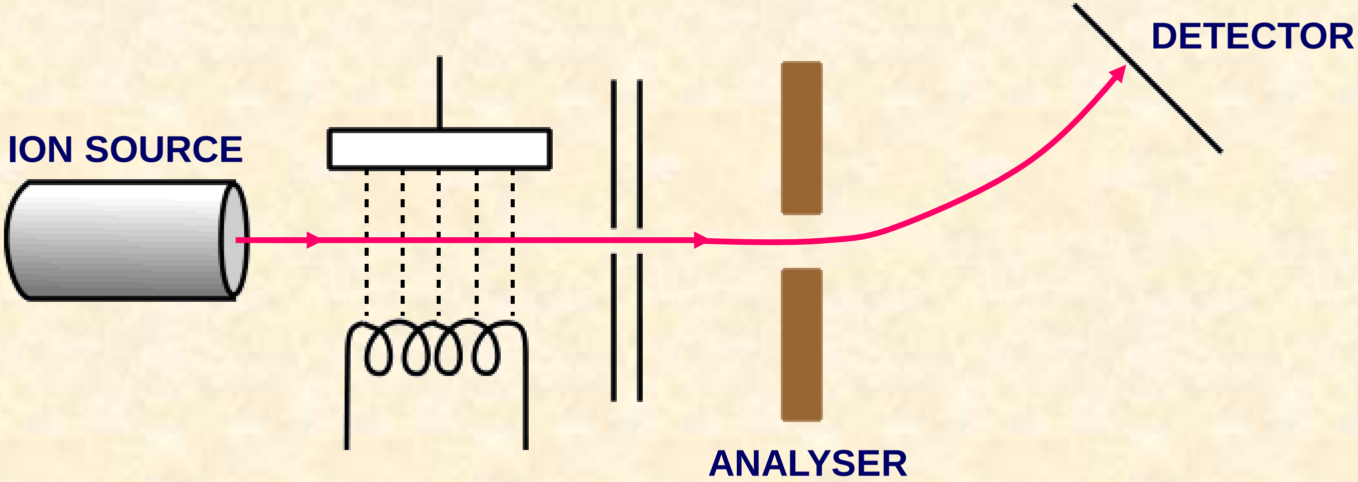
DETECTION

- by electric or photographic methods

HOW DOES IT WORK?



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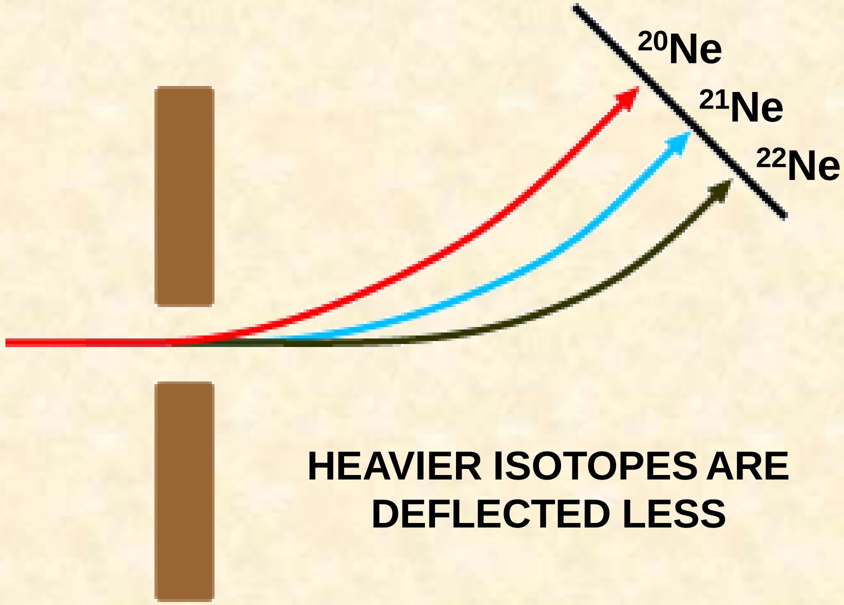
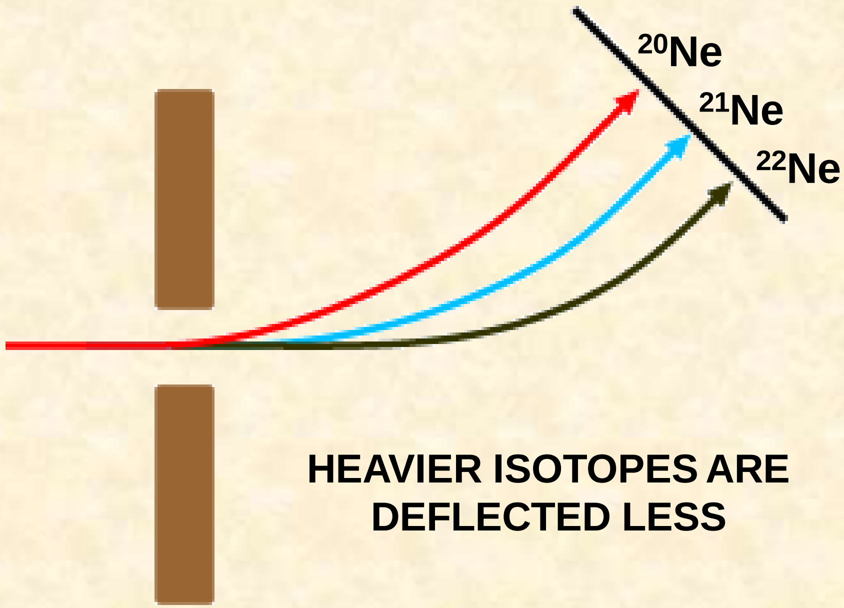
HOW DOES IT WORK? - Deflection

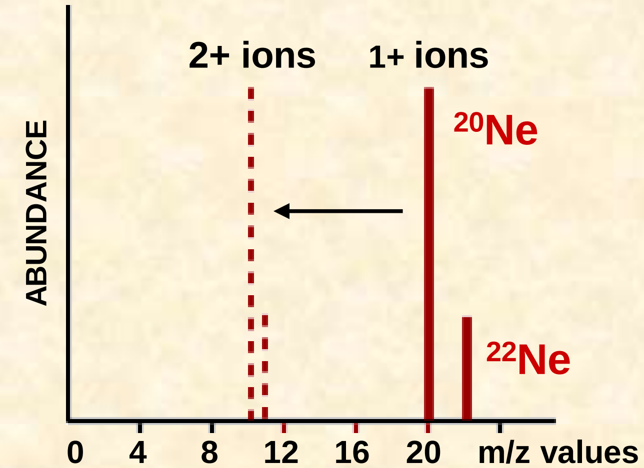


HEAVIER ISOTOPES ARE
DEFLECTED LESS

- the radius of the path depends on the value of the mass/charge ratio (m/z)
- ions of heavier isotopes have larger m/z values so follow a larger radius curve
- as most ions are 1+charged, the amount of separation depends on their mass

HOW DOES IT WORK? - Deflection



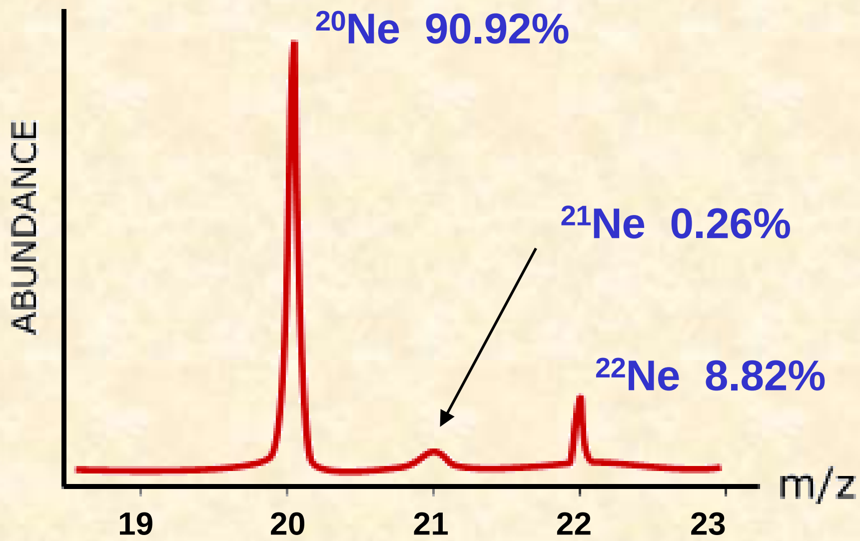


Doubling the charge, halves the m/z value
Abundance stays the same

- the radius of the path depends on the value of the mass/charge ratio (m/z)
- ions of heavier isotopes have larger m/z values so follow a larger radius curve
- as most ions are 1+charged, the amount of separation depends on their mass
- if an ion acquires a 2+ charge it will be deflected more; its m/z value is halved

WHAT IS A MASS SPECTRUM?

MASS SPECTRUM OF NEON

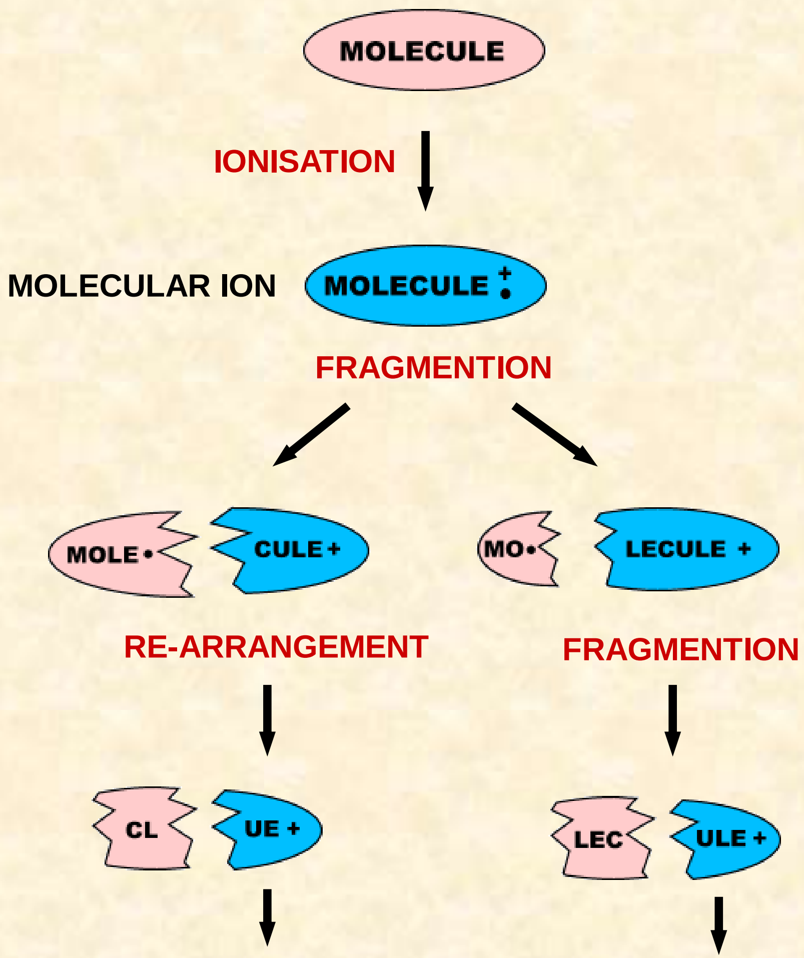


In early research with a mass spectrograph, Aston (Nobel Prize, 1922) demonstrated that naturally occurring neon consisted of three isotopes ... ^{20}Ne, ^{21}Ne and ^{22}Ne.

- positions of the peaks gives atomic mass
- peak intensity gives the relative abundance
- highest abundance is scaled to 100% and other values are adjusted accordingly

OTHER USES OF MASS SPECTROMETRY

- MOLECULAR MASS DETERMINATION -



Nowadays, mass spectrometry is used to identify unknown or new compounds.

When a molecule is ionised it forms a **MOLECULAR ION** which can also undergo **FRAGMENTATION** or **RE-ARRANGEMENT** to produce particles of smaller mass.

Only particles with a positive charge will be deflected and detected.

The resulting spectrum has many peaks.

The **final peak (M^+)** shows the **molecular ion** (highest m/z value) and indicates the **molecular mass**. The rest of the spectrum provides information about the structure.

TYPES OF PEAKS IN MS

- Molecular ion peak
- Fragment ions peak
- Rearrangement ions peak
- Metastable ion peaks
- Multicharged ions
- Base peak
- Negative ion peak

Molecular ion Peak:-

When a sample is bombarded with electrons of 9 to 15 eV energy, the molecular ion is produced, by loss of single electron.

$$M \xrightarrow{e^-} M^+ + 2\,e^-$$

Fragment ions Peak:-

when an energy is given further more upto 70 eV, fragment ions produced, it have lower mass number.

Rearrangement ion Peak:-

Recombination of fragment ion is known as Rearrangement Peaks.

Metastable ion Peak:-

The ions resulting from the decomposition between the source region and magnetic analyser are called as Meta stable ions.These appear as broad peaks called Metastable ion Peaks.

Multicharged ions:-

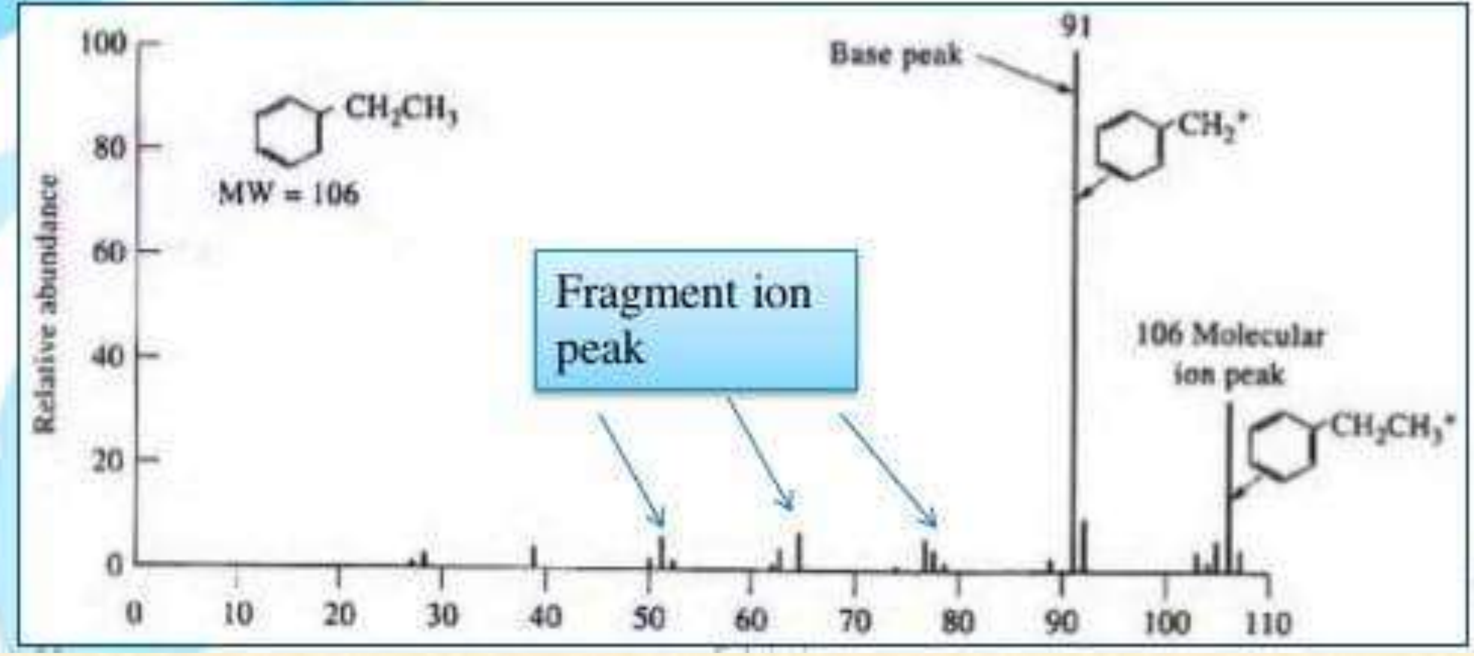
Ions may exist with 2 or 3 charges instead of usual single charge.The peaks due to these charged ions are known as Multicharged ion peaks.

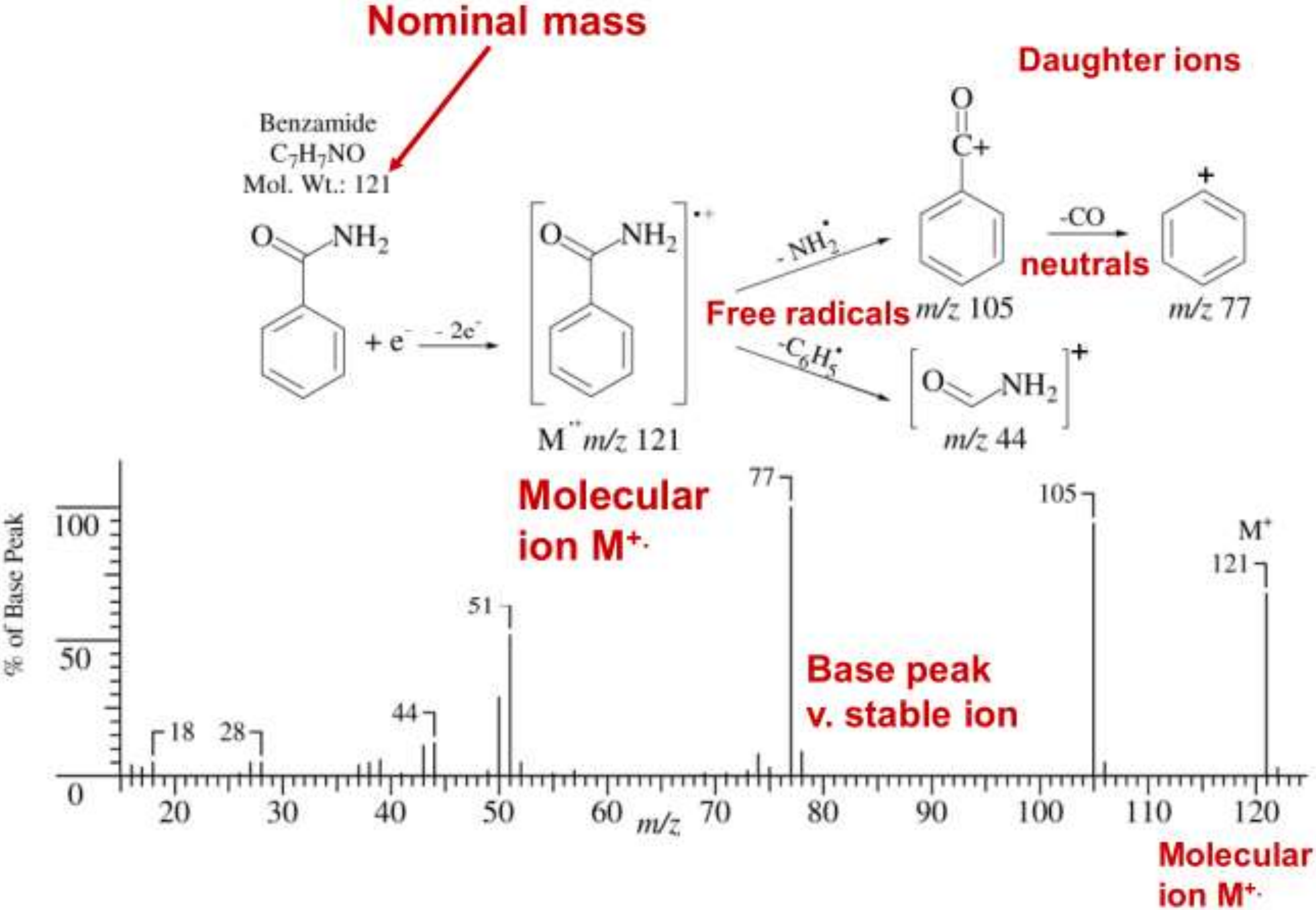
Base Peak:-

The largest peak in the mass spectrum corresponding to the most abundant ion or most intense peak in the spectrum is called as Base Peak.

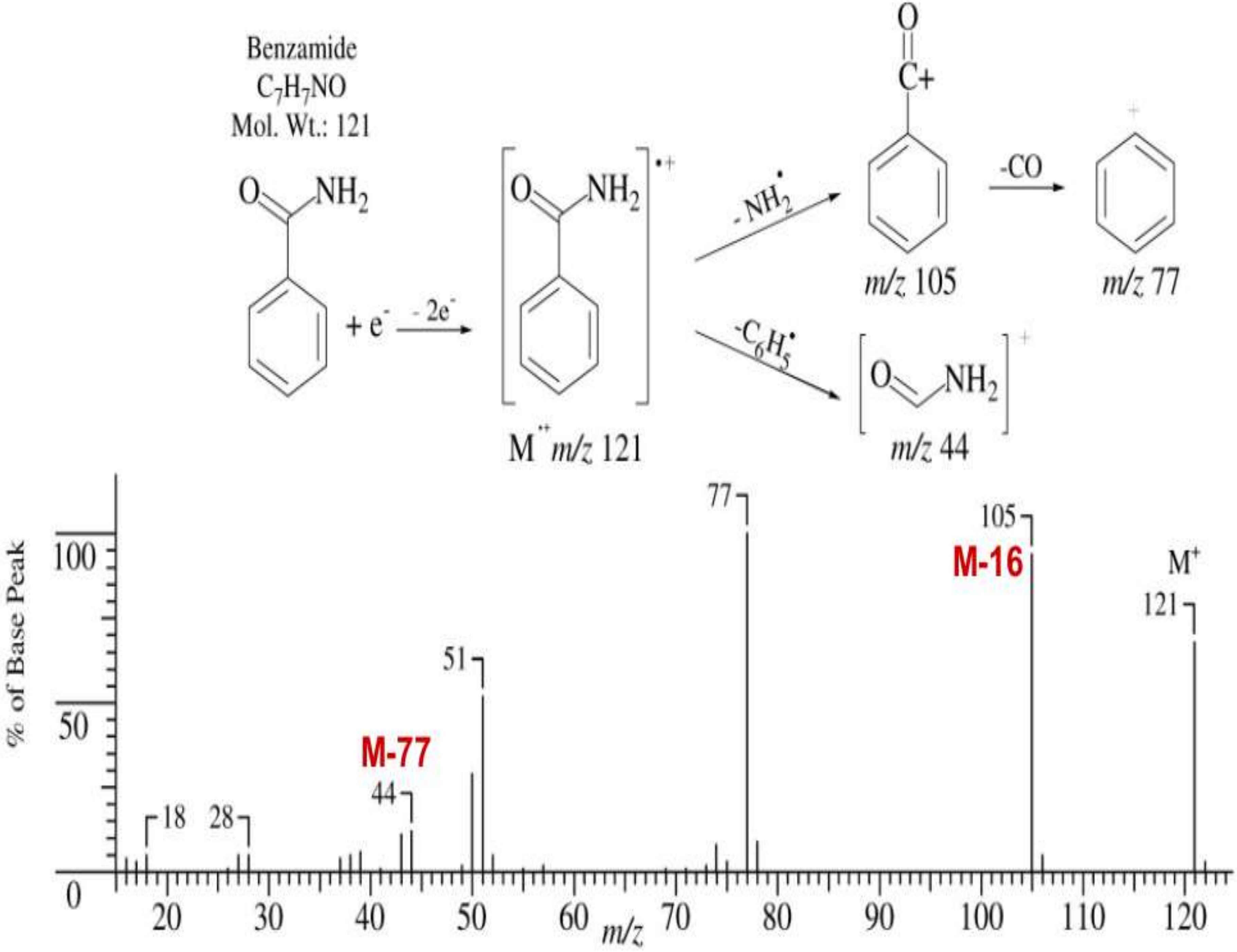
Negative ion Peak:-

Negative ions are formed from electron bombardment of sample. These results due to the capture of electron by a molecule during collision of molecules





Mass Spectrum presented as a bar graph.



Benzamide
C_7H_7NO
Mol. Wt.: 121
O
NH_2
+ e^-
$- 2e^-$
$M^{\cdot+}$ m/z 121
$- NH_2^{\cdot}$
C+
m/z 105
-CO
m/z 77
$-C_6H_5^{\cdot}$
m/z 44
% of Base Peak
100
50
0
m/z
20
30
40
50
60
70
80
90
100
110
120
18
28
44
51
77
105
121
M^+
M-77
M-16

Parent/Molecular Peak $M^{+\cdot}$:

An molecular ion that has not lost/gained atoms.
The nominal mass of which is calculated with the mass numbers of the predominant isotopes of atoms.

Base peak:

Base peak is the peak from the most abundant ion, which is often the most stable ion.

Fragment peaks other than the molecular ion peak is given the symbol A, then it's isotopic peaks would be A+1, A+2, ,,,

Fragmentation:

$$M^{+\cdot} \longrightarrow M_1^{+} + N_1^{\cdot}$$

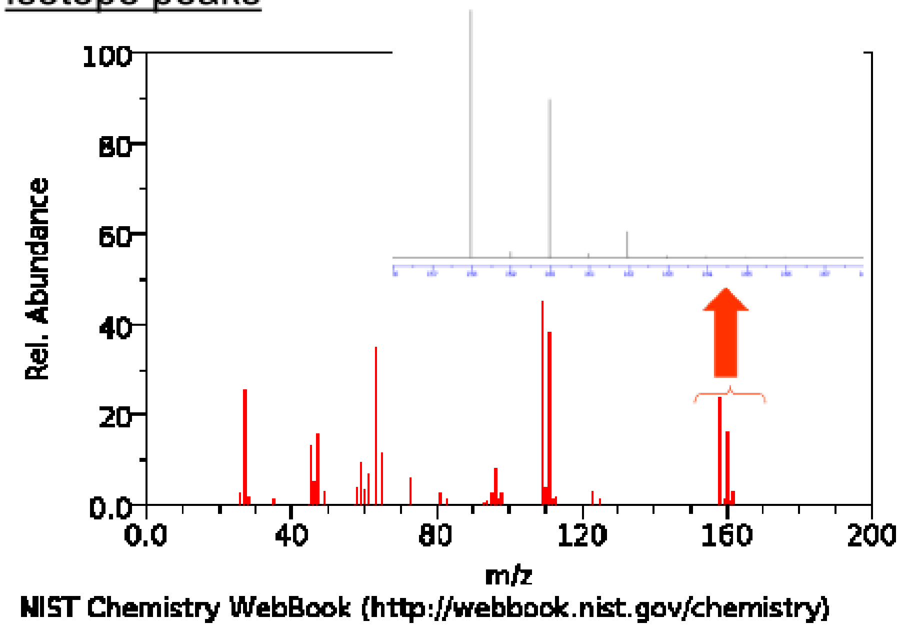
$$M^{+\cdot} \longrightarrow M_2^{+\cdot} + N_2$$

$$M^{+} \longrightarrow M_3^{+} + N$$

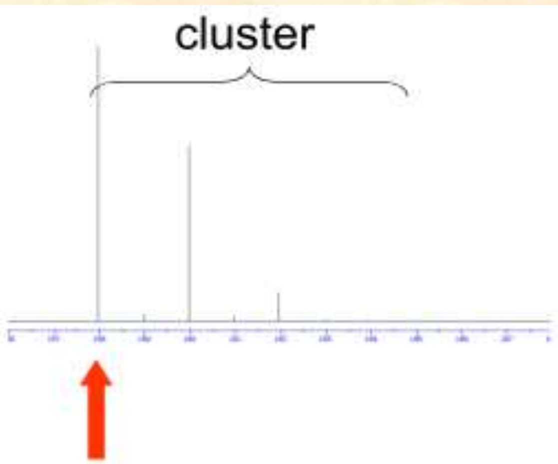
$M^{+\cdot}$	Radical ion (odd e)
$N^{\cdot}$	Neutral radical (odd e)
N	Neutral (even e)

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

Isotope peaks



$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$

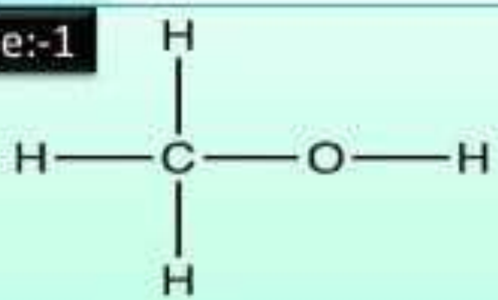


A peak made up of the principal isotopes of atoms making up the ion.

Nitrogen rule:-

The nitrogen rule states, that a molecule that has no or even number of nitrogen atoms has an even nominal mass, whereas a molecule that has an odd number of nitrogen atoms has an odd nominal mass.

Example:-1



molecular formula = CH_4O

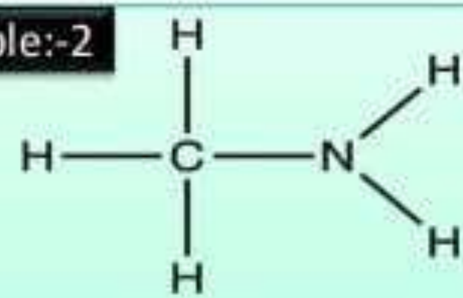
nominal mass = (1x12) + (4x1) + (1x16)

= 32

N atoms = 0

nominal mass = 32 (even #)

Example:-2



molecular formula = CH_5N

nominal mass = (1x12) + (5x1) + (1x14)

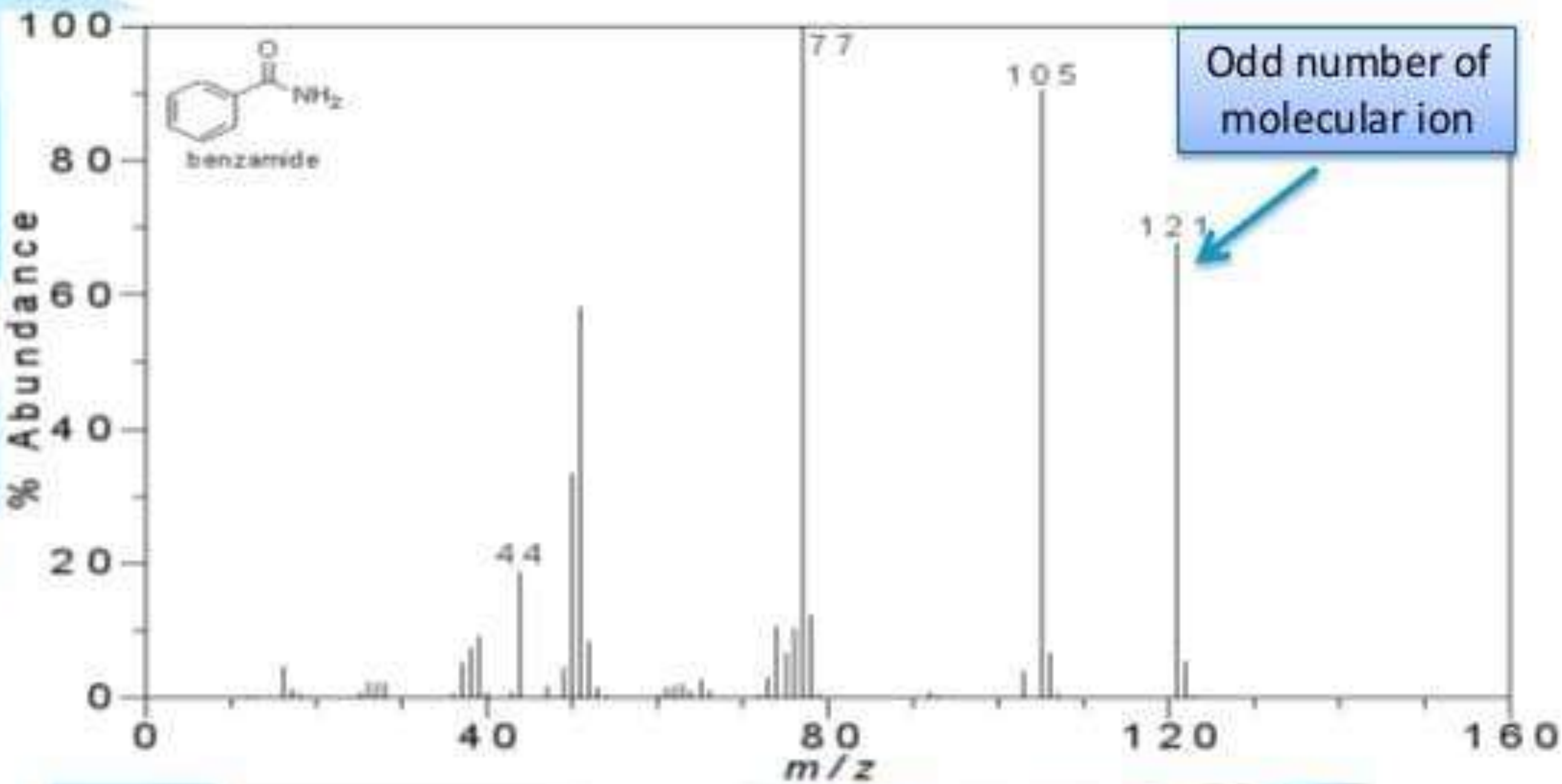
= 31

N atoms = 1 (odd #)

nominal mass = 31 (odd #)

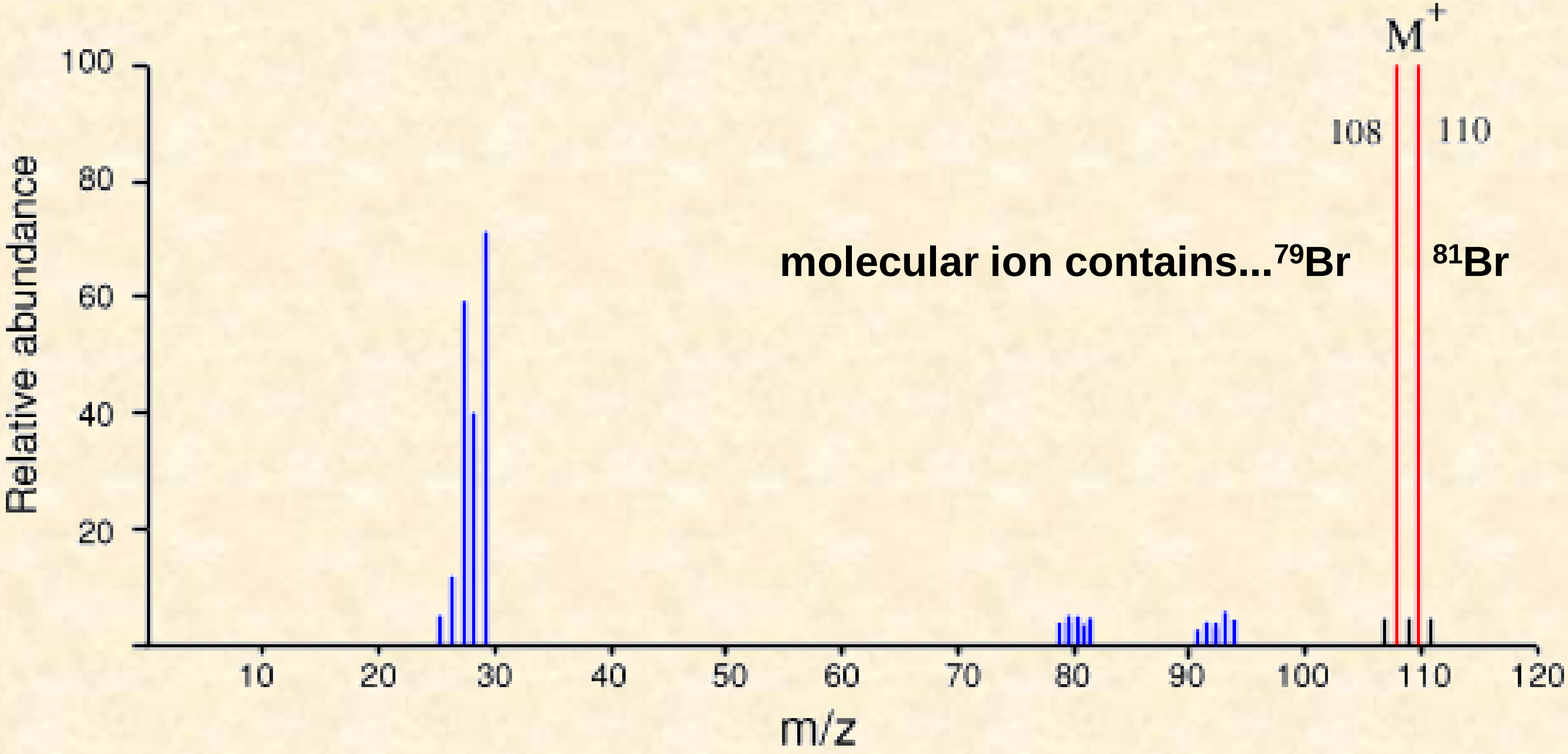
Contd….

The molecular ion appears at m/z 121, indicating an odd number of nitrogen atoms in the structure.

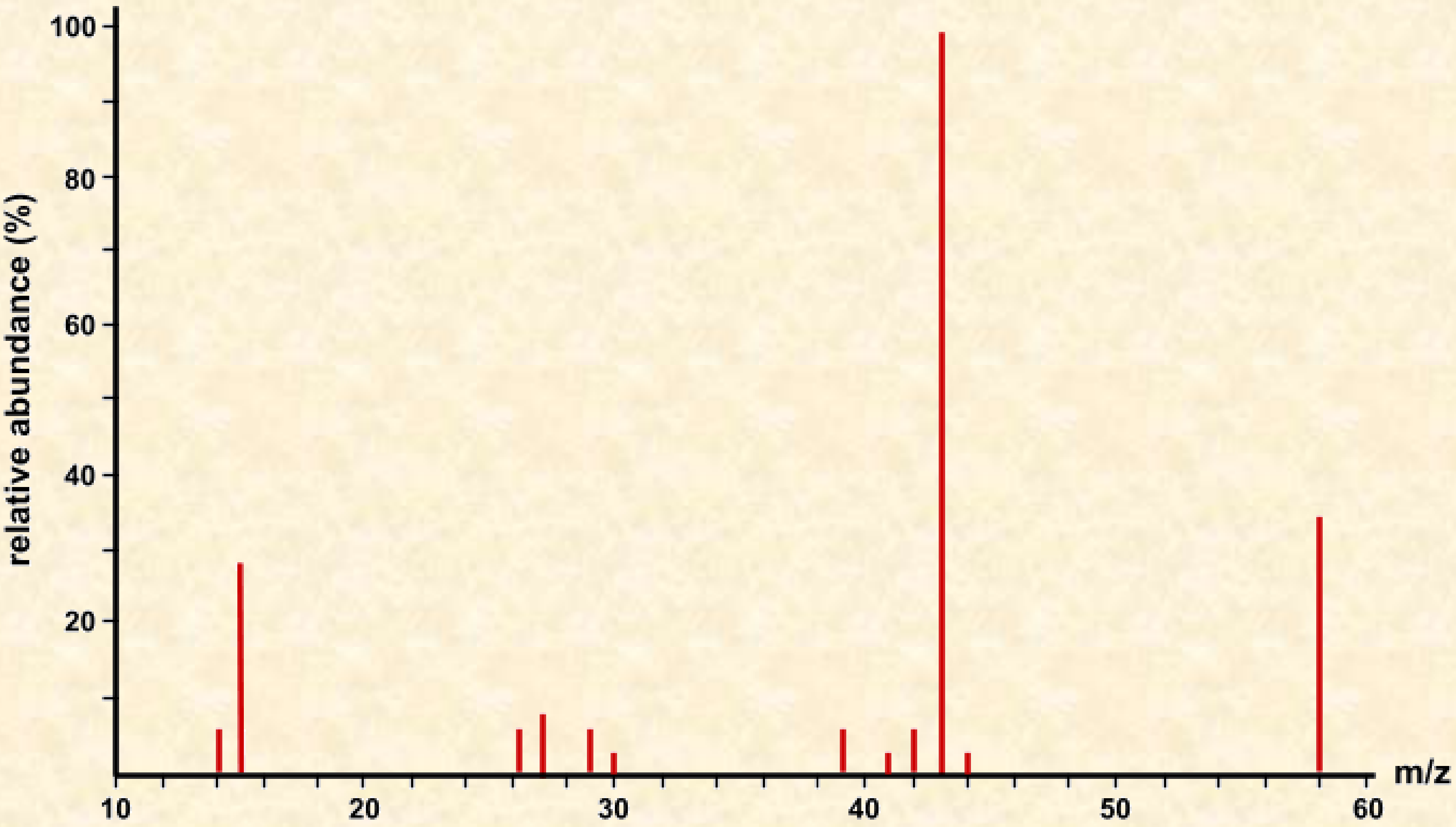


MASS SPECTRUM OF C_2H_5Br

The final peak in a mass spectrum is due to the molecular ion. In this case there are two because Br has two main isotopes. As each is of equal abundance, the peaks are the same size.



IDENTIFY THE PEAKS



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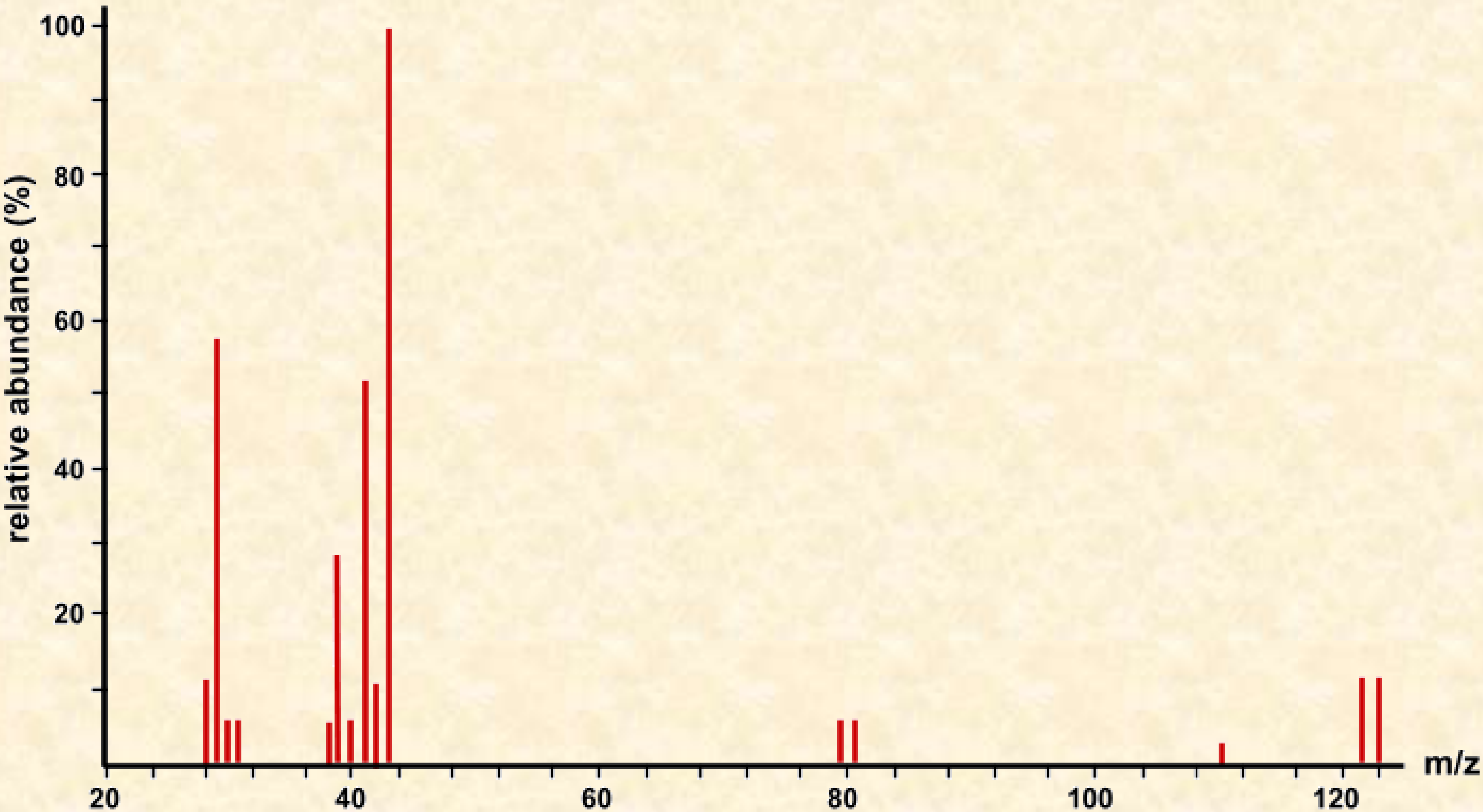

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