Cambridge (CIE) A Level Chemistry

Your notes

Mass Spectrometry

Contents

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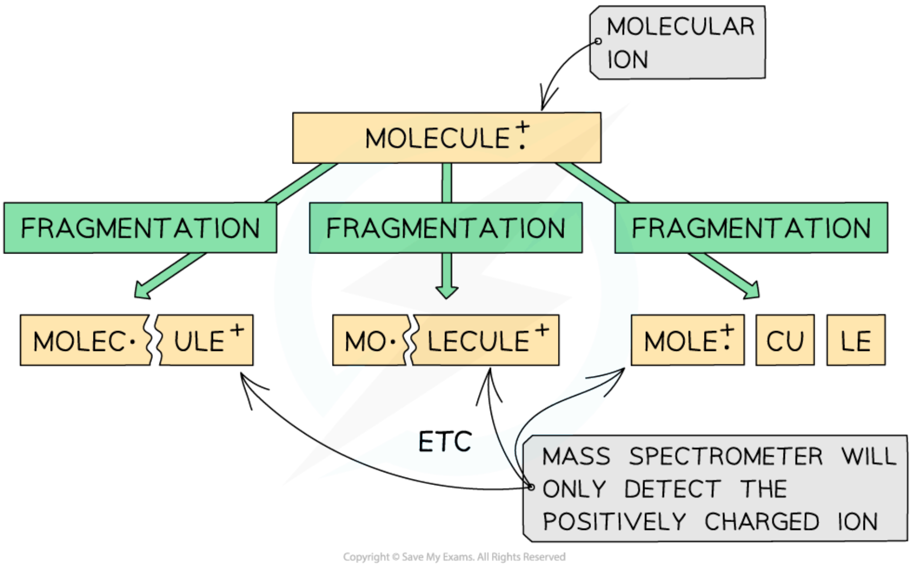
Interpreting Mass Spectra

- **Mass spectroscopy** is an analytical technique used to identify unknown compounds
- The molecules in the small sample are **bombarded** with high energy electrons which can cause the molecule to lose an electron
- This results in the formation of a positively charged **molecular ion** with one unpaired electron
  - One of the electrons in the pair has been **removed** by the beam of electrons

$$\text{MOLECULE} \xrightarrow{\text{Electron bombardment}} \text{MOLECULE}^{+}\bullet + e^{-}$$

- **MOLECULE^{+}•** represents the molecular ion
- The molecular ion can further **fragment** to form new ions, molecules, and radicals

Fragmentation of a molecule in mass spectroscopy



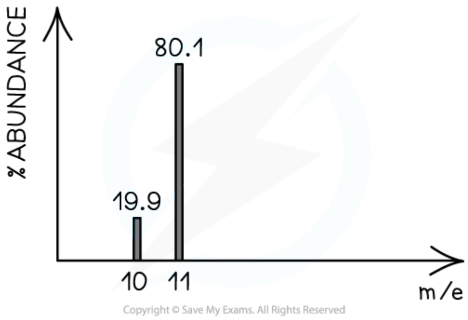
The same molecule can produce several different fragments in mass spectroscopy

- These **fragmentation** ions are **accelerated** by an electric field
- Based on their mass (***m***) to charge (**e**) ratio, the fragments of ions are then separated by deflecting them into the **detector**
  - For example, an ion with mass 16 and charge 2+ will have a *m/e* value of 8
- The smaller and more positively charged fragment ions will be **detected** first as they will get **deflected** the most and are more attracted to the **negative pole** of the magnet
- Each fragment corresponds to a specific **peak** with a particular *m/e* value in the mass spectrum
- The **base peak** is the peak corresponding to the most **abundant** ion

Isotopes

- Isotopes are different atoms of the **same element** that contain the same number of **protons** and **electrons** but a different number of **neutrons**.
  - These are atoms of the same **elements** but with different mass number
  - For example, Cl-35 and Cl-37 are isotopes as they are both atoms of the same element (chlorine, Cl) but have a different mass number (35 and 37 respectively)
- Mass spectroscopy can be used to find the **relative abundance** of the isotopes experimentally
- The **relative abundance** of an isotope is the proportion of one particular isotope in a mixture of isotopes found in nature
  - For example, the relative abundance of Cl-35 and Cl-37 is 75% and 25% respectively
  - This means that in nature, 75% of the chlorine atoms is the Cl-35 isotope and 25% is the Cl-37 isotope
- The **heights** of the peaks in mass spectroscopy show the proportion of each isotope present

Example mass spectrum of boron



The peak heights show the relative abundance of the boron isotopes: boron-10 has a relative abundance of 19.9% and boron-11 has a relative abundance of 80.1%

Worked Example

In a sample of iron, the ions $^{54}Fe^{2+}$ and $^{56}Fe^{3+}$ are detected.

Calculate the *m/e* value ratio and determine which ion is deflected more inside the spectrometer.

Answer:

- *m/e* ($^{54}Fe^{2+}$) = $\frac{54}{2} = 27$
- *m/e* ($^{56}Fe^{3+}$) = $\frac{56}{3} = 18.7$
  $= 19$

Examiner Tips and Tricks

A small *m/e* value corresponds to fragments that are either **small** or have a **high positive charge** or a combination of **both**

Calculating Relative Atomic Mass

- **Isotopes** are different atoms of the **same element** that contain the same number of **protons** and electrons but a different number of **neutrons**.
  - These are atoms of the same **elements** but with different mass numbers
- Because of this, the mass of an element is given as **relative atomic mass (A_r)** by using the average mass of the isotopes
- The relative atomic mass of an element can be calculated by using the **relative abundance** values
  - The relative abundance of an isotope is either given or can be read off the mass spectrum
- $A_r = \frac{(\text{relative abundance}_{\text{isotope 1}}\ \text{mass}_{\text{isotope 1}}) + (\text{relative abundance}_{\text{isotope 2}}\ \text{mass}_{\text{isotope 2}})\ \text{etc.}}{100}$

Worked Example

Calculate the relative atomic mass, A_r, of oxygen to 2 d.p.

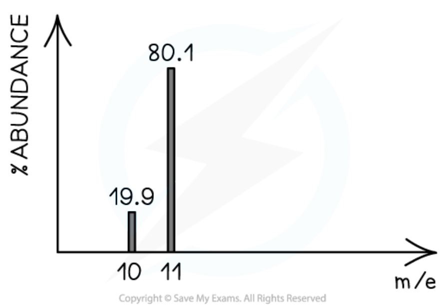
Isotope	Percentage abundance
^{16}O	99.76
^{17}O	0.04
^{18}O	0.20

Answer:

- $A_r = \frac{(99.76 \times 16) + (0.04 \times 17) + (0.20 \times 18)}{100}$
- A_r = 16.0044
- A_r = **16.00** (to 2 d.p)

Worked Example

Calculate the relative atomic mass of boron using its mass spectrum, to 2 d.p.



Answer:

- $A_r = \frac{(19.9 \times 10) + (80.1 \times 11)}{100}$
- $A_r = 10.801$
- $A_r =$ **10.80** (to 2 d.p)

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Mass Spectrometry: Deducing Molecular Formula

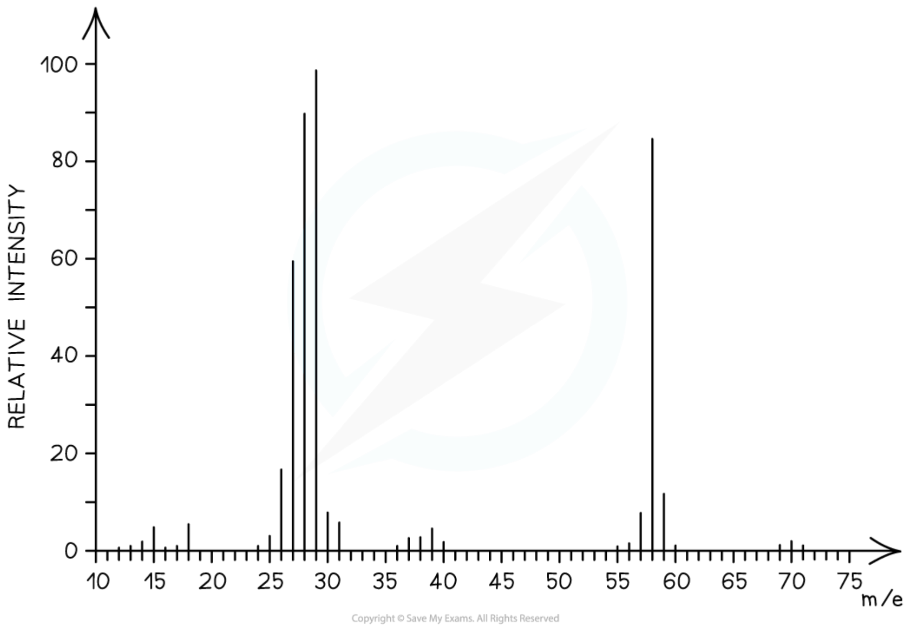
- Each **peak** in the mass spectrum corresponds to a certain **fragment** with a particular ***m/e*** value
- The peak with the highest ***m/e*** value is the molecular ion (**M⁺**) peak which gives information about the **molecular mass** of the compound
- The molecular ion is the entire molecule that has lost one electron when bombarded with a beam of electrons

$$\text{MOLECULE} \xrightarrow{\text{Electron bombardment}} \text{MOLECULE}^{+\bullet} + e^-$$

- The **[M+1]** peak is a smaller peak which is due to the natural abundance of the isotope carbon-13
- The height of the [M+1] peak for a particular ion depends on how many carbon atoms are present in that molecule; the more carbon atoms, the larger the [M+1] peak is
  - For example, the height of the [M+1] peak for an hexane (containing six carbon atoms) ion will be greater than the height of the [M+1] peak of an ethane (containing two carbon atoms) ion

Worked Example

Determine whether the following mass spectrum corresponds to propanal or butanal.



Answer:

- The mass spectrum corresponds to propanal as the molecular ion peak is at *m/e* = 58
- Propanal arises from the $CH_3CH_2CHO^+$ ion which has a molecular mass of 58
- Butanal arises from the $CH_3CH_2CH_2CHO^+$ ion which has a molecular mass of 72

Identifying Molecules using Fragmentation

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- The molecular ion peak can be used to identify the **molecular mass** of a compound
- However, different compounds may have the same molecular mass
- To further determine the structure of the unknown compound, **fragmentation** is used
- Fragments may appear due to the formation of **characteristic fragments** or the **loss of small molecules**
  - For example, a peak at 29 is due to the characteristic fragment $C_2H_5^+$
  - Loss of small molecules gives rise to peaks at 18 (H_2O), 28 (CO), and 44 (CO_2)

Alkanes

- Simple alkanes are fragmented in mass spectroscopy by breaking the C-C bonds
- ***M/e*** values of some of the common alkane fragments are given in the table below

m/e values of fragments table

Fragment	m/e
CH_3^+	15
$C_2H_5^+$	29
$C_3H_7^+$	43
$C_4H_9^+$	57
$C_5H_{11}^+$	71
$C_6H_{13}^+$	85

Mass spectrum showing fragmentation of alkanes

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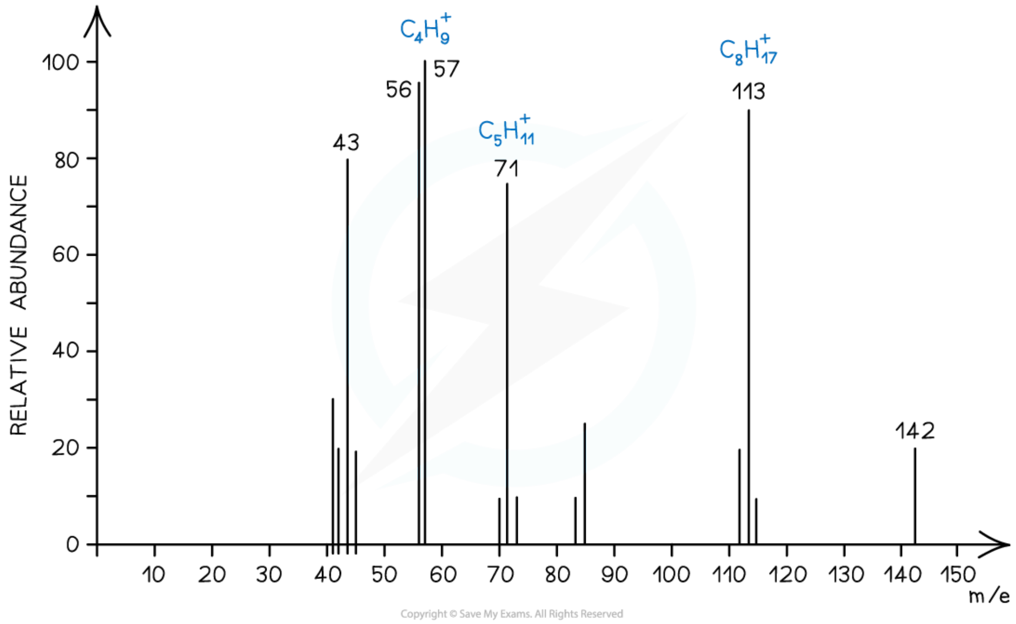
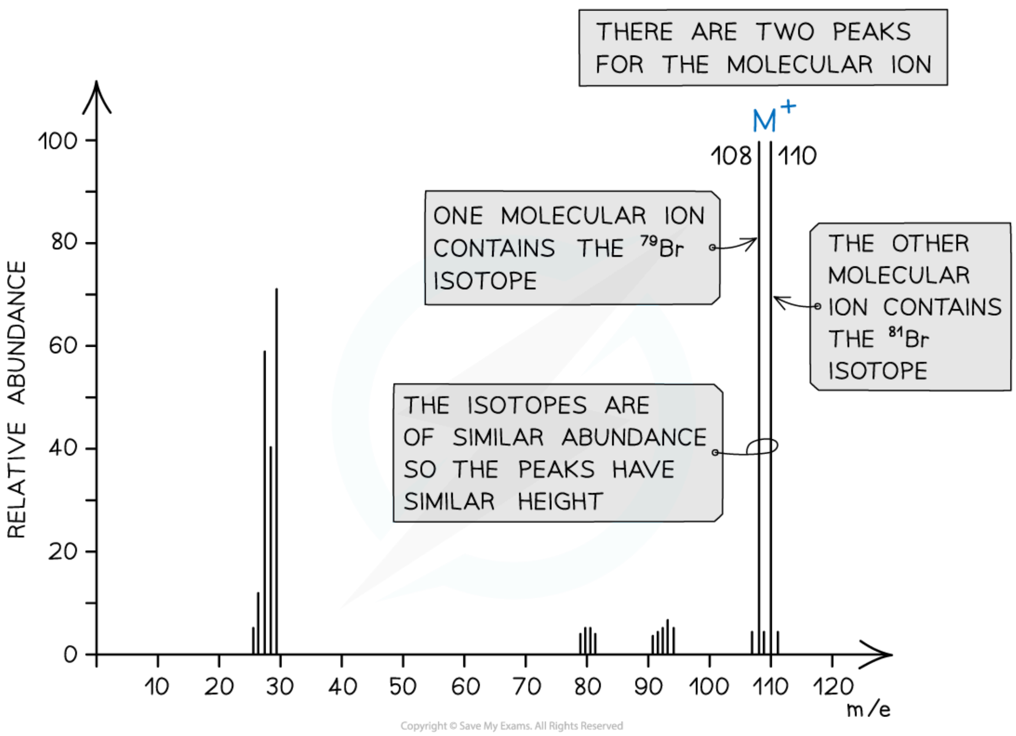


Straight chain alkanes show characteristic peaks

Halogenoalkanes

- Halogenoalkanes often have multiple peaks around the molecular ion peak
- This is caused by the fact that there are different isotopes of the halogens

Mass spectrum for a bromine containing species

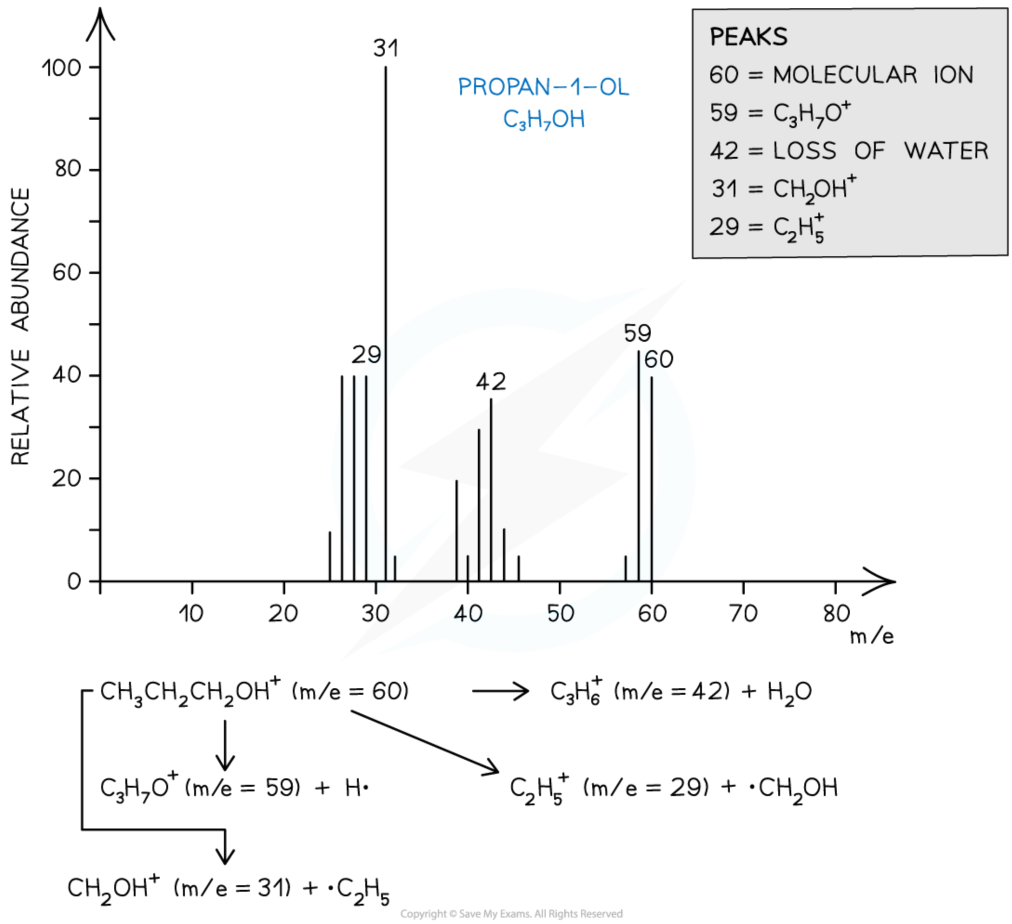


Mass spectra show different halogen isotopes in the molecular ion

Alcohols

- Alcohols often tend to lose a **water molecule** giving rise to a peak at **18 below the molecular ion**
- Another common peak is found at *m/e* value 31 which corresponds to the CH_2OH^+ fragment
- For example, the mass spectrum of propan-1-ol shows that the compound has fragmented in four different ways:
  - Loss of $H^•$ to form a $C_3H_7O^+$ fragment with *m/e* = 59
  - Loss of a water molecule to form a $C_3H_6^+$ fragment with *m/e* = 42
  - Loss of a $•C_2H_5$ to form a CH_2OH^+ fragment with *m/e* = 31
  - And the loss of $•CH_2OH$ to form a $C_2H_5^+$ fragment with *m/e* = 29

Mass spectrum of propan-1-ol



Mass spectrum showing the fragmentation patterns in propan-1-ol (alcohol)

Worked Example

Which of the following statements about the mass spectrum of CH_3Br is correct?

1. There is one peak for the molecular ion with an m/e value of 44
2. There is one peak for the molecular ion with an m/e value of 95

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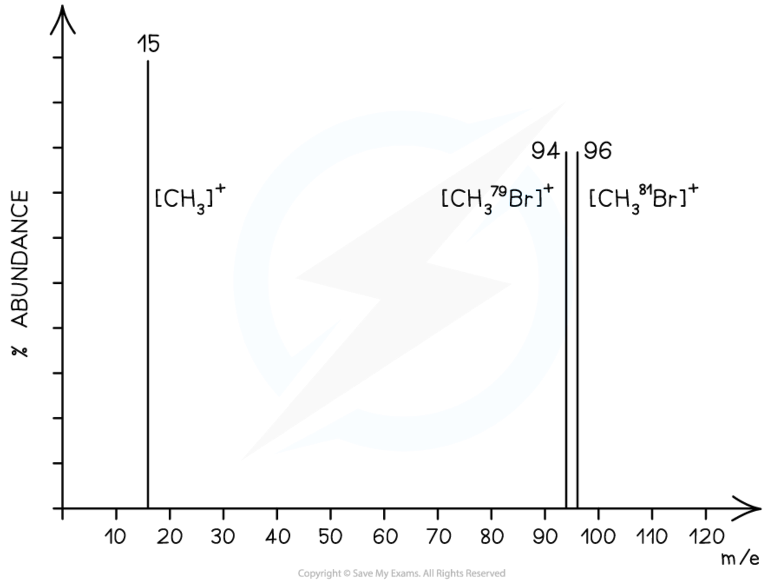
3. The last two peaks have abundances in the ratio 3:1 and occur at m/e values of 94 and 96
4. The last two peaks are of equal size and occur at m/e values of 94 and 96

Answer:

- The correct answer is **D** as bromomethane (CH_3Br) will fragment into 3 peaks
    - $CH_3{}^{81}Br \rightarrow [CH_3{}^{81}Br]^+ + e^-$ at m/e 96
    - $CH_3{}^{79}Br \rightarrow [CH_3{}^{79}Br]^+ + e^-$ at m/e 94
    - $CH_3Br \rightarrow [CH_3]^+ + {}^\bullet Br$ at m/e 15
- The last two peaks (which correspond to the molecular ion peak) therefore are equal in size and occur at *m/e* values of 94 and 96



Worked Example

Which alcohol is not likely to have a fragment ion at *m/e* at 43 in its mass spectrum?

1. $(CH_3)_2CHCH_2OH$
2. $CH_3CH(OH)CH_2CH_2CH_3$
3. $CH_3CH_2CH_2CH_2OH$
4. $CH_3CH_2CH(OH)CH_3$

Answer:

- The correct answer is **D** because a line at *m/e* = 43 corresponds to an ion with a mass of 43 for example:
    - $[CH_3CH_2CH_2]^+$
    - $[(CH_3)_2CH]^+$
- 2-butanol is not likely to have a fragment at *m/e* = 43 as it does not have either of these fragments in its structure

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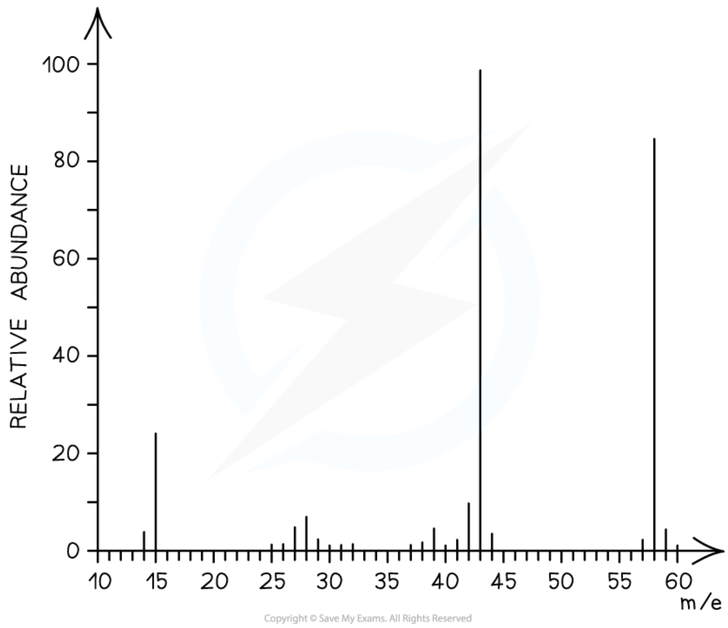
Determine Number of Carbon Atoms Using M+1 Peak

- The **[M+1]** peak is caused by the presence of the carbon-13 (^{13}C) isotope in the molecule
- Carbon-13 makes up approximately 1.1% of all carbon atoms
- Therefore, the [M+1] peak is much smaller than the M peak as the isotope is less common
  - The ratio of ^{13}C to ^{12}C is approximately 1:99
- Thus, the greater the number of carbon atoms present in a molecule the greater the height of the [M+1] peak
- The number of carbon atoms, **n**, in a compound can be deduced using the [M+1] peak and the following formula:
  - $n = \frac{100 \times \text{abundance of } [M+1]}{1.1 \times \text{abundace of } M^{+} \text{ ion}}$

Worked Example

Determine the number of carbon atoms of compound **X** with the following mass spectrum:



Answer:

- The M⁺ ion peak is at *m/e* 58 with a relative abundance of around 85
- The [M+1] peak is at *m/e* 59 with a relative abundance of 3
- Therefore, the number of carbon atoms (n) is:

- $n = \frac{100 \times 3}{1.1 \times 85} = 3.21$
- There are therefore 3 carbon atoms present in compound **X**

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Detecting Bromine & Chlorine Atoms Using M+2 Peak

- The presence of bromine or chlorine atoms in a compound gives rise to a **[M+2]** and possibly **[M+4]** peak

Chlorine

- Chlorine exists as two isotopes, ^{35}Cl and ^{37}Cl
- A compound containing **one** chlorine atom will therefore have two molecular ion peaks due to the two different isotopes it can contain
  - ^{35}Cl = **M^+** peak
  - ^{37}Cl = **[M+2]** peak
  - The ratio of the peak heights is 3:1 (as the relative abundance of ^{35}Cl is 3× greater than that of ^{37}Cl)
- A compound containing **two** chlorine atoms will have three molecular ion peaks due to the different combinations of chlorine isotopes they can contain
  - $^{35}Cl + {}^{35}Cl$ = **M^+** peak
  - $^{35}Cl + {}^{37}Cl$ = **[M+2]** peak
  - $^{37}Cl + {}^{37}Cl$ = **[M+4]** peak
  - The ratio of the peak heights is **9:6:1**

Mass spectra of chlorine containing compounds

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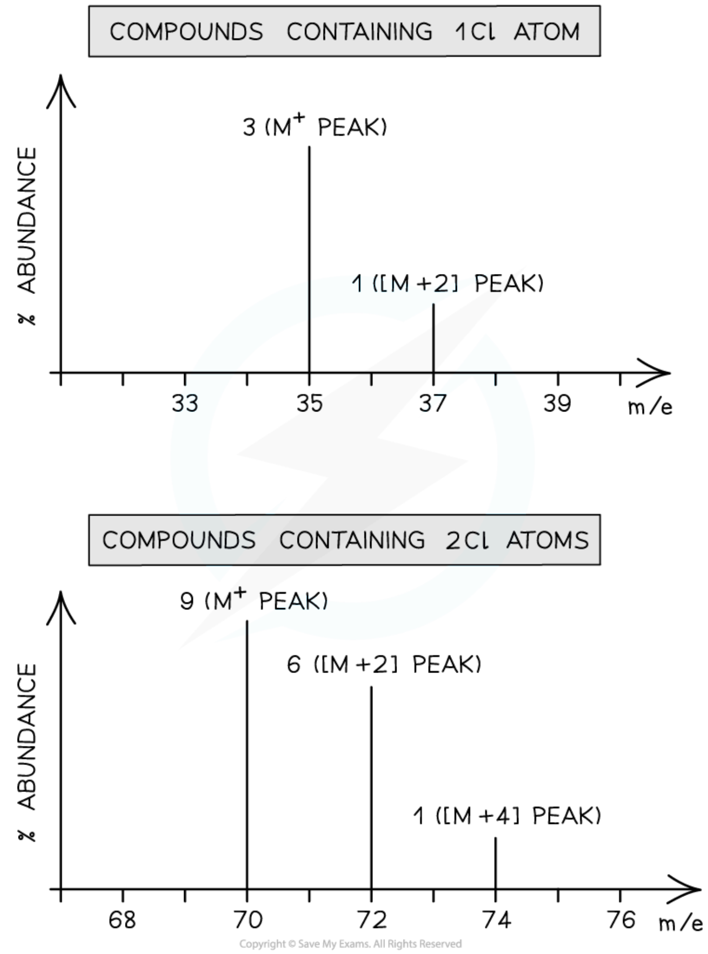
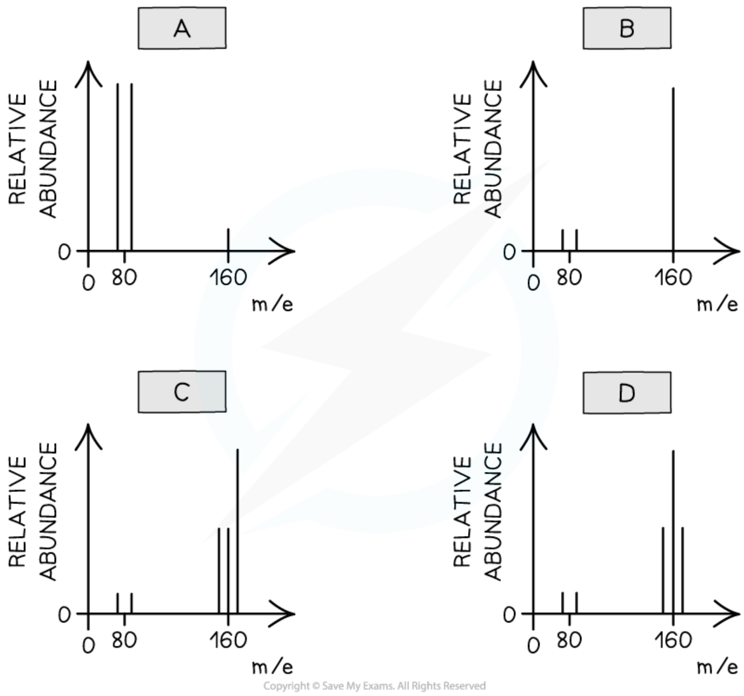


Mass spectrum of compounds containing one chlorine atom (1) and two chlorine atoms (2)

Bromine

- Bromine too exists as two isotopes, ^{79}Br and ^{81}Br
- A compound containing **one** bromine atom will have two molecular ion peaks
  - ^{79}Br = **M^+** peak
  - ^{81}Br = **[M+2]** peak
  - The ratio of the peak heights is 1:1 (they are of **similar** heights as their relative abundance is the same!)
- A compound containing **two** bromine atoms will have three molecular ion peaks
  - $^{79}Br + ^{79}Br$= **M^+** peak
  - $^{79}Br + ^{81}Br$ = **[M+2]** peak
  - $^{81}Br + ^{81}Br$= **[M+4]** peak
  - The ratio of the peak heights is **1:2:1**

Mass spectra of bromine containing compounds

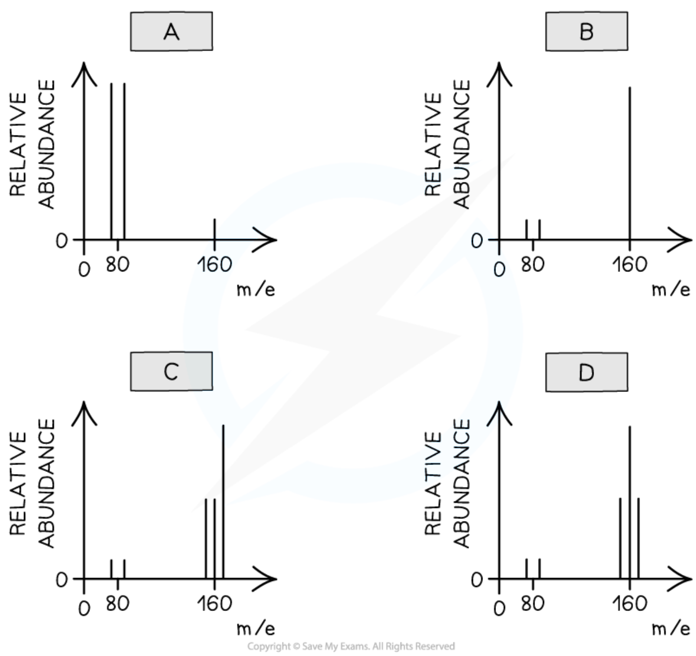


Mass spectra of four bromine-containing compounds (A–D), illustrating characteristic patterns due to the presence of two isotopes: 79 Br 79 Br and 81 Br 81 Br. Each spectrum shows distinctive peak groupings depending on the number of bromine atoms in the molecule.

Worked Example

Two stable isotope of bromine have relative masses of 79 and 81

Which is the correct pattern of peaks in the mass spectrum of molecular bromine?



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Answer:

- The correct answer is **D**
- Bromine is a diatomic molecule there will be 5 peaks on the mass spectrum of bromine
- Bromine consists of molecules, not individual atoms
- When bromine is passed through the mass spectrometer, an electron is given off to give the **molecular ion, Br_2^+**
- Some of these will fragment to make Br + Br^+
  - $Br_2^+ \rightarrow Br + Br^+$
- The Br atom passes through the machine, and the Br^+ ions will give lines at 79 and 81
- There will also be a line for the unfragmented Br_2^+ ion
- This will give 3 molecular ion peaks
  - Br_2^+ ion containing the isotopes 79 + 79 = 158
  - Br_2^+ containing the isotopes 79 + 81 = 160
  - Br_2^+ containing the isotopes 81 + 81 = 162

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