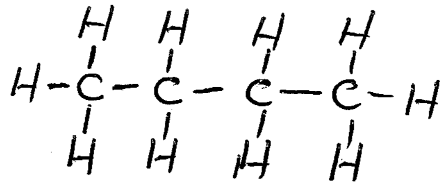
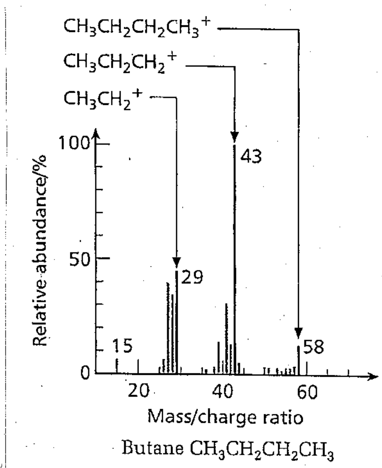
Mass Spectrometry (A2)

Fragmentation

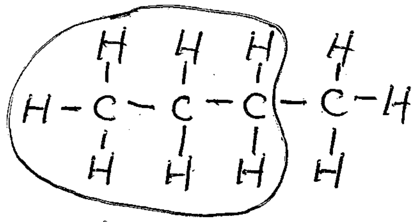
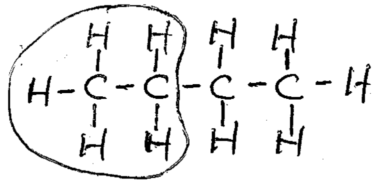
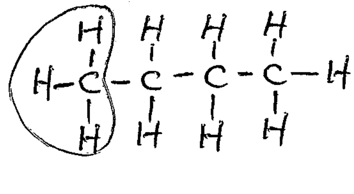
1. Molecules can split up in the mass spectrometer and produces fragments. However fragments do not recombine.

Example: butane





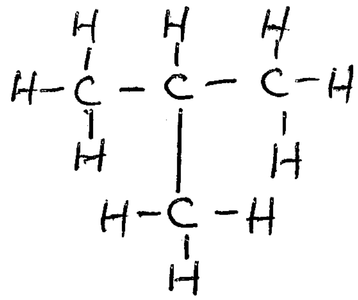
mass spectrum of butane

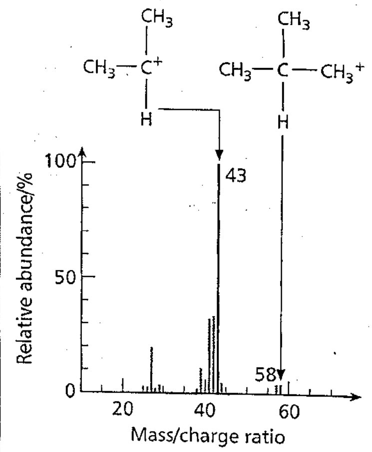
$\frac{m}{e}$	ions	
58	$CH_3CH_2CH_2CH_3^+$	molecular ion
43	$CH_3CH_2CH_2^+$	
29	$CH_3CH_2^+$	
15	CH_3^+	

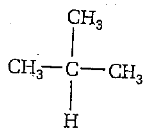
2. Usually a few ions remain intact to give a peak at the relative molecular mas of the compound. This is called the molecular or parent ion.

The molecular ion is the peak of the highest mass, not the tallest peak.

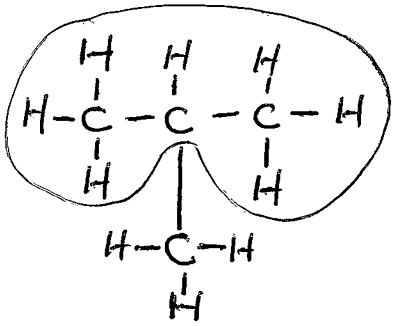
Example : methylpropane





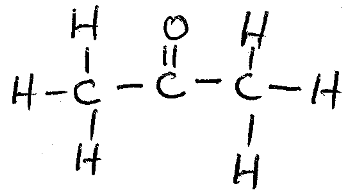
Methylpropane 

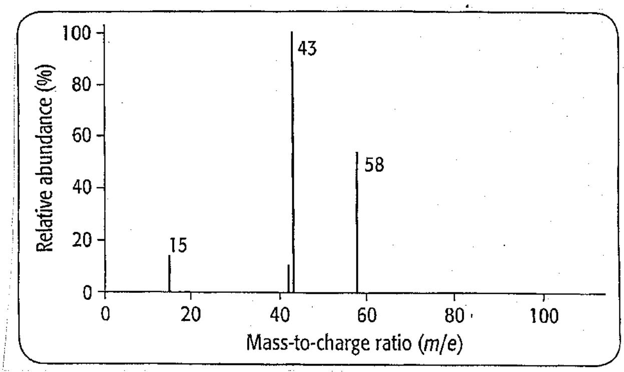
Mass spectrum of methylpropane

m/e	ion	
58	$CH_3CH(CH_3)CH_3^+$	molecular ion (highest mass)
43		← gives tallest peak

3. From the fragments, information regarding the formula or structure of a complicated compound can be obtained.

Example: propanone

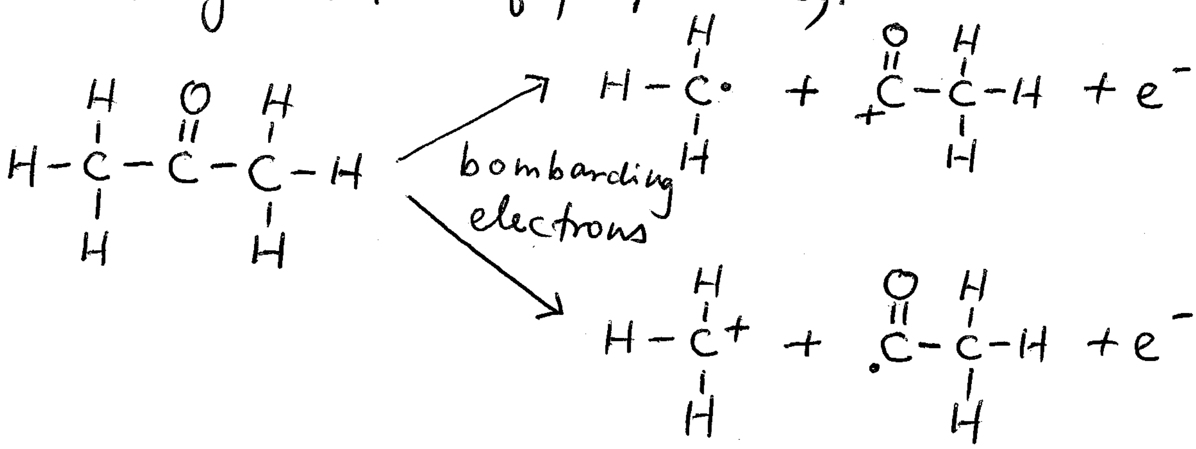




The mass spectrum of propanone

m/e	ion	
58	$CH_3COCH_3^+$	molecular ion
43	CH_3CO^+	
15	CH_3^+	

The fragmentation of propanone,



Question 1

An organic acid has the following composition by mass, C: 40%, H: 6.7%, O: 53.3%. Its mass spectrum shows major peaks (including the molecular ion) at the following m/e values: 15, 43, 45 and 60.

a. Calculate the empirical formula of the acid and use the mass spectrum to suggest its molecular formula and its structural formula.

b. By suggesting their molecular formulae, identify the various species responsible for the peaks in the mass spectrum.

Workings

a.

	C	H	O
mass (g)	40	6.7	53.3
Ar	12	1	16
n(mol)	3.33	6.7	3.33
ratio	1	2	1

Empirical formula : CH_2O

Mr of $(CH_2O)_n$ is 60

$n(12+2+16) = 60$

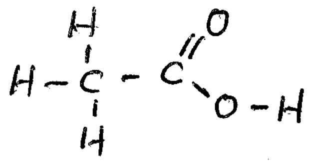
$30n = 60$

$n = 2$

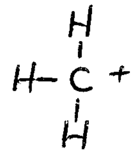
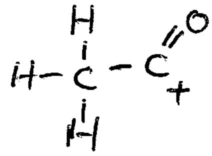
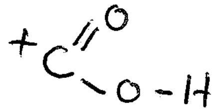
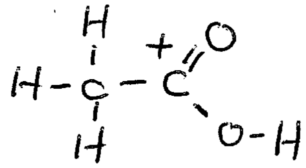
Molecular formula $C_2H_4O_2$

Structural formula : CH_3COOH

b.



displayed formula

m/e	molecular fragment/ion	
15		(CH_3^+)
43		(CH_3CO^+)
45		$(COOH^+)$
60		(CH_3COOH^+) molecular ion

Question 2

a. Identify the fragments that would cause peaks in the mass spectrum of $HOCH_2COCH_3$ with the following m/e values:

i) $m/e = 15$

ii) $m/e = 17$

iii) $m/e = 31$

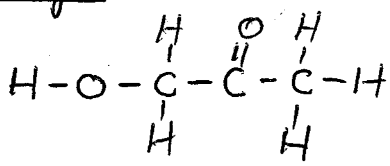
iv) $m/e = 43$

v) $m/e = 57$

vi) $m/e = 59$

b. At what value for m/e would you find the molecular ion peak?

Workings



a. i) $m/e = 15$ CH_3^+

ii) $m/e = 17$ OH^+

iii) $m/e = 31$ CH_2OH^+

iv) $m/e = 43$ CH_3CO^+

v) $m/e = 57$ $CH_3COCH_2^+$

vi) $m/e = 59$ $HOCH_2CO^+$

b. molecular ion will form peak at $m/e = 74$.

High-resolution mass spectra

High-resolution mass spectrometers can distinguish between ions that appear to have the same mass on a low-resolution mass spectrum.

The accurate relative isotopic masses of the most common atoms found in organic molecules are as follow:

Isotope	Relative isotopic mass
^{1}H	1.0078246
^{12}C	12.0000000 (by definition)
^{14}N	14.0030738
^{16}O	15.9949141

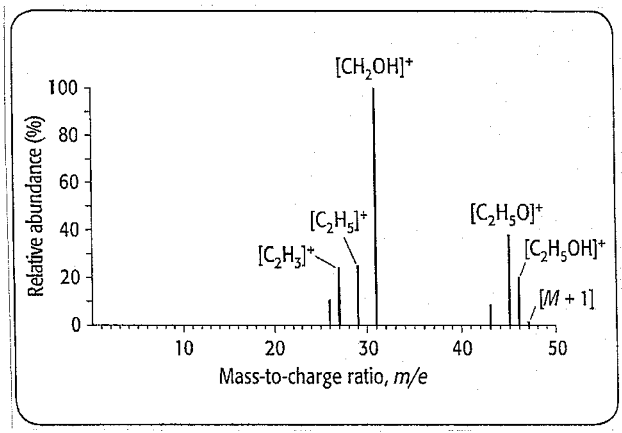
These accurate isotopic masses allow us to measure the mass of the molecular ion so accurately that it can only correspond to one possible molecular formula.

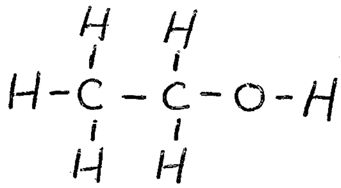
Eg.

Fragment ion	m/e Low-resolution mass spec	m/e high-resolution mass s.
$C_2H_7N^+$	45	45.057846
CH_3NO^+	45	45.021462

[M+1] peak

There will always be a very small peak just beyond the molecular peak at a mass of [M+1].
This is caused by molecules in which one of the cabon atoms is the ^{13}C isotope.
This is shown in the mass spectrum of ethanol as follow:





$M_r = 46$

m/e	Species	
27	$C_2H_3^+$	$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH + e^- \longrightarrow C_2H_3^+ + H_3O\cdot + 2e^-$
29	$C_2H_5^+$	$C_2H_5OH + e^- \longrightarrow C_2H_5^+ + \cdot OH + 2e^-$
31	CH_2OH^+	$CH_3CH_2OH + e^- \longrightarrow CH_3\cdot + CH_2OH^+ + 2e^-$
45	$C_2H_5O^+$	$C_2H_5OH + e^- \longrightarrow C_2H_5O^+ + \cdot H + 2e^-$
46 [M]	$C_2H_5OH^+$	$C_2H_5OH + e^- \longrightarrow C_2H_5OH^+ + 2e^-$
47 [M+1]	$^{13}C^{12}CH_5OH^+$	$^{13}C^{12}CH_5OH + e^- \rightarrow {}^{13}C^{12}CH_5OH^+ + 2e^-$

In any organic compound there will be 1.10% cabon 13.

Based on this, the number of carbon atoms (n) in a molecule can work out as:

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } [M+1]^+ \text{ ion}}{\text{abundance of } M^+ \text{ ion}}$$

Example:

An unknown compound has a molecular ion peak, M^+, with a relative abundance of 54.5% and has an $[M+1]^+$ peak with a relative abundance of 3.6%. How many carbon atoms does the unknown compound contain?

Substituting the values of relative abundance into the equation:

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } [M+1]^+ \text{ ion}}{\text{abundance of } M^+ \text{ ion}}$$

$$n = \frac{100}{1.1} \times \frac{3.6}{54.5}$$

$$= 6.0$$

Each molecule has 6 carbon atoms.

Example

A hydrocarbon has a molecular ion peak at a mass-to-charge ratio of 84 (relative abundance of 62.0%) and an [M+1] peak with a relative abundance of 4.1%.

a. How many carbon atoms are in the hydrocarbon?

b. What is its molecular formula?

c. The hydrocarbon does not decolourise bromine water. Name the hydrocarbon.

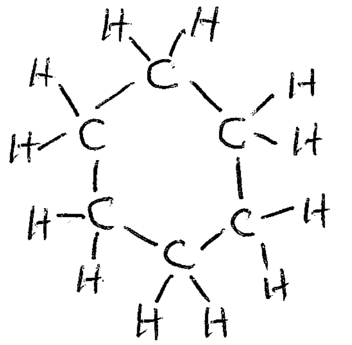
Answers

a. $$n = \frac{100}{1.1} \times \frac{4.1}{62.0}$$

$$= 6$$

b. relative mass of hydrogens $= 84 - 6(12) = 12$

$\therefore C_6H_{12}$

c. 

cyclohexane.

[M+2] and [M+4] peaks

If the sample compound contains chlorine or bromine atoms, peaks are formed beyond the molecular ion peak because of isotopes of chlorine and bromine.

Chlorine has two isotopes, ^{35}Cl and ^{37}Cl.

Bromine too has two isotopes, ^{79}Br and ^{81}Br.

The approximate percentage of each isotope in naturally occuring samples are as follow:

Isotopes	Approximate %
^{35}Cl	75
^{37}Cl	25
^{79}Br	50
^{81}Br	50

<u>One Cl or Br atom per molecule</u>.

Imagine a sample of chloromethane, CH_3Cl.

75% of molecules are $CH_3{}^{35}Cl$ and 25% are $CH_3{}^{37}Cl$.

The molecular ion will be $CH_3{}^{35}Cl^+$, and two units beyond that on the mass spectrum will be the peak for $CH_3{}^{37}Cl^+$.

The peak for $CH_3{}^{37}Cl^+$ will be <u>one-third</u> the height of the molecular ion. This is the [M+2] peak.

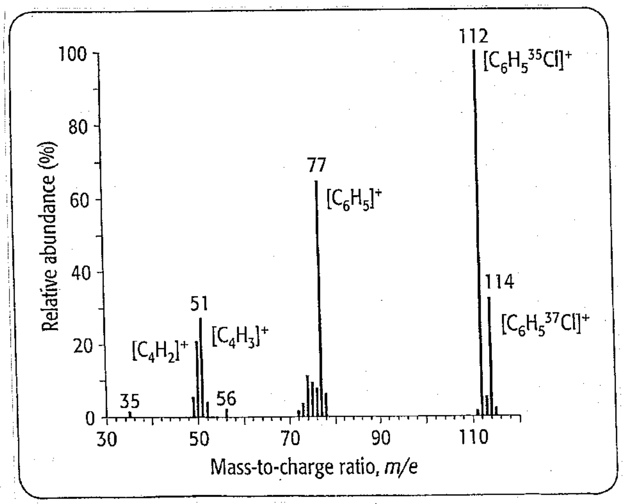
In the mass spectrum of bromomethane, CH_3Br, there are two molecular ion peaks of approximately the <u>same height</u>

- one for $CH_3{}^{79}Br^+$ (M peak)
- one for $CH_3{}^{81}Br^+$ (the [M+2] peak)

When interpreting mass spectra, relative heights of $[M+2]^+$ peak and M^+ peak provide important informations:

- If the [M+2] peak is one-third the height of the M peak, this suggests the presence of one chlorine atom per molecule.
- If the [M+2] peak is the same as the height of the M peak, this suggests the presence of one bromine atom per molecule.

<u>Example</u>: mass spectrum of chlorobenzene



The mass spectrum of chlorobenzene, showing the [M+2] peak.
(Notice that there are also tiny [M+1] and [M+3] peaks corresponding to ^{13}C in the molecules)

Two Cl or Br atoms per molecule

The situation is a little more complex with two chlorine atoms in a molecule as there are three possibilities.

Consider dichloromethane, CH_2Cl_2, the peaks are:

molecular ion	peak	Abundance		ratio
$^{35}Cl-CH_2-^{35}Cl^+$	the M peak	9		
$^{35}Cl-CH_2-^{37}Cl^+$	the [M+2] peak	3	6	9:6:1
$^{37}Cl-CH_2-^{35}Cl^+$	the [M+2] peak	3		
$^{37}Cl-CH_2-^{37}Cl^+$	the [M+4] peak	1		

For compound containing two Br atoms:

molecular ion	peak	Abundance		ratio
$^{79}Br-R-^{79}Br^+$	the M peak	1		
$^{79}Br-R-^{81}Br^+$	the [M+2] peak	1	2	1:2:1
$^{81}Br-R-^{79}Br^+$	the [M+2] peak	1		
$^{81}Br-R-^{81}Br^+$	the [M+4] peak	1		

Example

a. List the ions responsible for the M, [M+2] and [M+4] peaks in a mass spectrum of dibromomethane.

b. What would be the mass-to-charge ratio and relative abundances of the major peaks with the highest charge-to-mass ratios in the mass spectrum of chloroethane

c. How many peaks would you see beyond the molecular ion peak in 1,1-dibromoethane? What would be their mass to charge ratios and abundances relative to the molecular ion? (Ignore peaks due to ^{13}C)

Answers.

a.

peak	M	M+2	M+4
ion	$CH_2{}^{79}Br{}^{79}Br^+$	$CH_2{}^{79}Br{}^{81}Br^+$	$CH_2{}^{81}Br{}^{81}Br$

b.

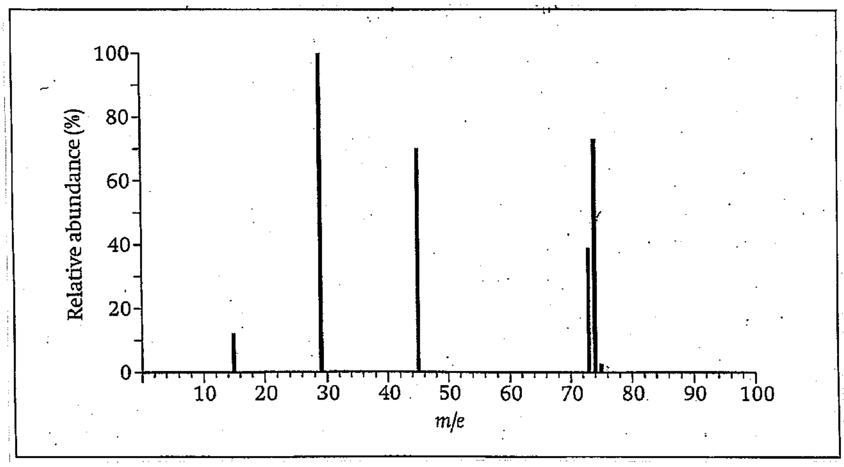
	M	M+2
m/e	64	66
ion	$C_2H_5{}^{35}Cl^+$	$C_2H_5{}^{37}Cl^+$
relative abundance	3 :	1

c. 2 peaks ($[M+2]^+$ and $[M+4]^+$) beyond the M^+ ion

	M	M+2	M+4
m/e	186	188	190
ion	$C_2H_4{}^{79}Br_2^+$	$C_2H_4{}^{79}Br{}^{81}Br^+$	$C_2H_4{}^{81}Br_2^+$
relative abundance	1	2	1

Question

The mass spectrum of an aliphatic carboxylic acid is as follow:



a. Identify the molecular-ion peak.

b. Find the number of carbon atoms in the molecule using the M and [M+1] peaks.

c. List the fragmants that can be identified on the spectrum and show how they may have been produced.

d. Suggest a structural formula for this acid.

Workings

a. molecular-ion peak, M^+ at $m/e = 74$

b.

peak	height/mm
M^+	31
$[M+1]^+$	1

$$n = \frac{\text{height } [M+1]^+ \text{ peak}}{\text{heigh } M^+ \text{ peak}} \times \frac{100}{1.1}$$

$$= 2.9$$

no carbon atoms in the molecule = 3

c.

	m/e	ion	
	15	CH_3^+	$CH_3CH_2COOH^+ \rightarrow CH_3^+ + CH_2COOH\cdot$
	29	$CH_3CH_2^+$	$CH_3CH_2COOH^+ \rightarrow CH_3CH_2^+ + COOH\cdot$
	45	$COOH^+$	$CH_3CH_2COOH^+ \rightarrow COOH^+ + CH_3CH_2\cdot$
	73	$CH_3CH_2COO^+$	$CH_3CH_2COOH^+ \rightarrow CH_3CH_2COO^+ + H\cdot$
M^+	74	$CH_3CH_2COOH^+$	$CH_3CH_2COOH \rightarrow CH_3CH_2COOH^+ + e^-$
$[M+1]^+$	75	$^{13}CH_3CH_2COOH^+$	$^{13}CH_3CH_2COOH \rightarrow {}^{13}CH_3CH_2COOH^+ + e^-$

d.