

Solving structures with mass, IR and NMR spectra

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Mass spectrometry gives the relative molecular mass from the molecular ion and the structure from fragments, infrared spectroscopy identifies functional groups from bond absorptions, and proton and carbon-13 NMR show how many hydrogen and carbon environments exist and how they are joined. Together the three methods determine an unknown structure.

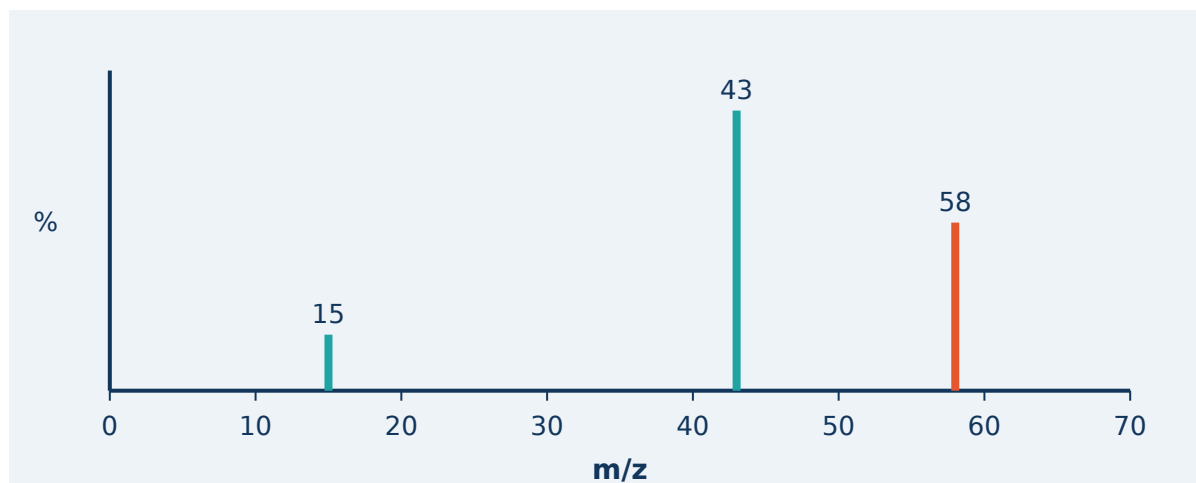
Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB S3.2

What does a mass spectrum tell you?

Definition

In **mass spectrometry** a sample is ionised and the ions are sorted by their mass-to-charge ratio, m/z . The peak with the largest m/z is usually the **molecular ion**, M^+ , formed when the molecule loses one electron without breaking.

The m/z of the molecular ion equals the relative molecular mass, M_r . Smaller peaks come from fragments. For propanone the molecular ion is at 58 and the tallest peak, the base peak, is at 43 from CH_3CO^+ . Fragment peaks reveal how the molecule is built, because the bonds next to a $\text{C}=\text{O}$ or a branch break most easily.



Mass spectrum of propanone: M^+ at m/z 58 (red) and the base peak at 43 from CH_3CO^+ .

Carbon-13 makes a small peak one unit above M^+ . About 1.1 % of carbon atoms are ^{13}C , so each carbon adds about 1.1 % to the $M+1$ peak. Chlorine and bromine give distinctive pairs: chlorine shows M and $M+2$ in a 3 : 1 ratio and bromine in a 1 : 1 ratio.

m/z	Typical fragment
15	CH ₃ ⁺
29	C ₂ H ₅ ⁺ or CHO ⁺
43	C ₃ H ₇ ⁺ or CH ₃ CO ⁺
57	C ₄ H ₉ ⁺ or C ₂ H ₅ CO ⁺

Worked example 1

An ester shows M⁺ at m/z 88 with height 20.0 mm and an M+1 peak of height 0.9 mm. Find the number of carbon atoms.

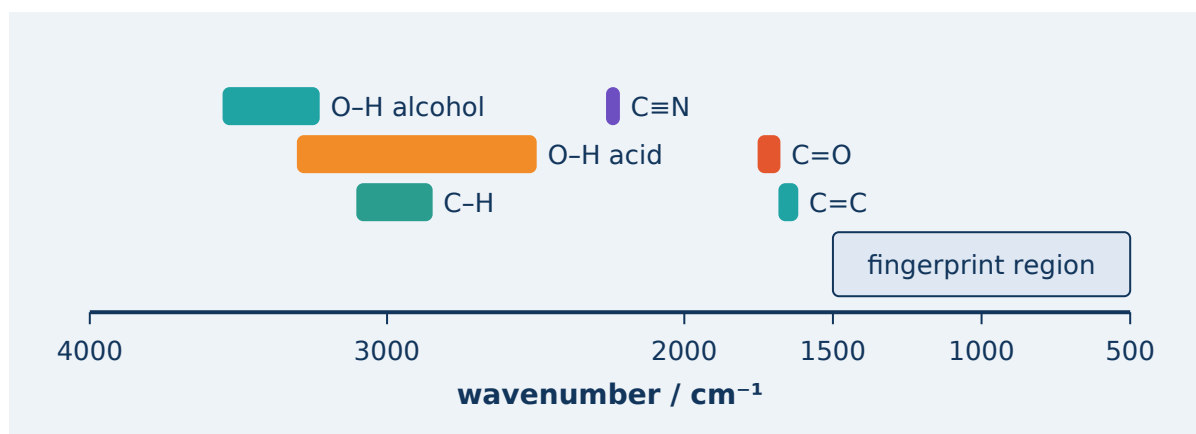
Ratio = $0.9 \div 20.0 = 4.5\%$. Number of C = $4.5 \div 1.1 = 4.1$, so there are **4 carbon atoms**.
 With Mr = 88: $88 - 48 \text{ (C}_4\text{)} - 32 \text{ (O}_2\text{)} = 8$, so the formula is C₄H₈O₂.

How does infrared spectroscopy identify bonds?

Definition

Infrared (IR) spectroscopy measures the wavenumbers, in cm⁻¹, at which bonds absorb radiation and vibrate more strongly. A bond absorbs at a characteristic wavenumber, so an absorption shows which functional groups are present.

Wavenumber is 1 divided by wavelength in centimetres. Stronger and lighter bonds absorb at higher wavenumbers, which is why O-H and C=O lie far apart. Compare your spectrum with the chart, and use the region below 1500 cm⁻¹ only to match a compound with a reference.



Typical infrared absorption ranges. The fingerprint region is unique to each compound.

Common mistake

Do not assign the fingerprint region bond by bond. It is a complex pattern that only matches a known sample, whereas groups such as C=O and O-H are read above 1500 cm⁻¹.

What does proton NMR show?

Hydrogen nuclei in different chemical environments absorb at different chemical shifts, δ , measured in ppm from tetramethylsilane, TMS ($\delta = 0$). Four pieces of information appear: the **number of signals** (the number of environments), the **chemical shift** (the surroundings), the **integration** (the ratio of hydrogens) and the **splitting**.

Environment	Approximate δ / ppm
$\text{CH}_3\text{-C}$ or $\text{-CH}_2\text{-C}$	0.9-1.5
$\text{CH}_3\text{-C=O}$	2.0-2.5
-O-CH_2 and -O-CH_3	3.3-4.3
Aromatic H	6.5-8.0
Aldehyde -CHO	9.4-10.0

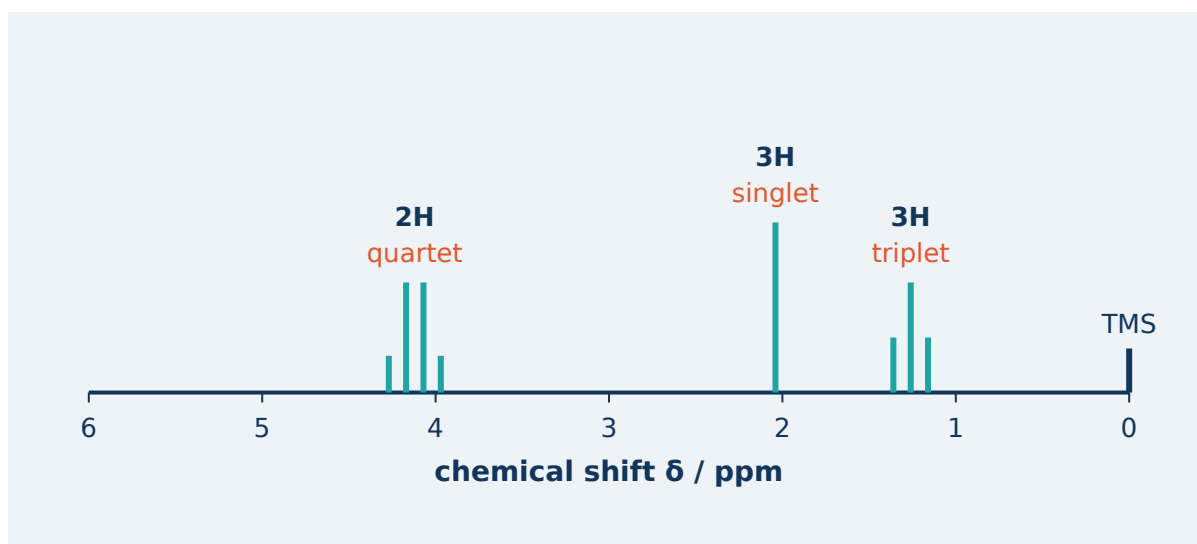
A hydrogen with n equivalent neighbours on adjacent carbons splits its signal into $n + 1$ lines.

1	0 neighbours: singlet
1 1	1 neighbour: doublet
1 2 1	2 neighbours: triplet
1 3 3 1	3 neighbours: quartet

The $n + 1$ rule: a signal is split into $n + 1$ lines when the hydrogens have n neighbouring hydrogens.

Worked example 2

Ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, has three environments. The CH_3 of ethyl (δ 1.26) has two neighbours, so a triplet of 3H. The CH_2 (δ 4.12) is next to oxygen, which pulls electron density away, and has three neighbours, so a quartet of 2H. The CH_3CO group (δ 2.04) has none, so a **singlet of 3H**.



Proton NMR of ethyl ethanoate: three signals, integration 2 : 3 : 3, and splitting by the $n + 1$ rule.

What does carbon-13 NMR add?

Each carbon in a different environment gives one signal, normally a single line. Ethyl ethanoate shows four signals, at about 14, 21, 60 and 171 ppm. Carbons in C=O absorb at 160–220 ppm, those bonded to oxygen at 50–90 ppm, alkene and aromatic carbons at 110–150 ppm, and simple alkyl carbons below 55 ppm.

How do you solve a structure from several spectra?

Take M^+ for the formula, use IR to identify groups, count ^{13}C signals for symmetry, then use proton NMR to join the pieces. Check each fragment of your structure against the data.

Lina's tip

Write the signal list in a table first: shift, integration, splitting. Then draw the fragment for each row, and join the fragments so that every neighbour count works.

Key points to remember

- Molecular ion M^+ has m/z equal to M_r ; each carbon adds about 1.1 % to the $M+1$ peak.
- IR: C=O at 1680–1750 cm^{-1} , O–H alcohol at 3230–3550 cm^{-1} , acid O–H very broad at 2500–3300 cm^{-1} .
- Proton NMR gives number of signals, shift, integration and $n + 1$ splitting; TMS is at $\delta = 0$.
- ^{13}C NMR shows one signal per carbon environment; C=O appears at 160–220 ppm.

Solving structures with mass, IR and NMR spectra: frequently

asked questions

What does the molecular ion peak show?

The molecular ion peak shows the relative molecular mass of the compound, because M^+ is the molecule with one electron removed. It is normally the peak with the highest m/z , apart from a small $M+1$ peak.

Why is TMS used as a standard in NMR?

TMS gives one sharp signal because its twelve hydrogens are equivalent, and this appears at the right-hand end of the scale at $\delta = 0$. It is chemically inert and volatile, so it is easy to remove.

How do you recognise a carboxylic acid in IR?

A carboxylic acid shows a very broad O-H absorption from about 2500 to 3300 cm^{-1} together with a strong C=O absorption near 1710 cm^{-1} . An ester shows C=O but no broad O-H.

What does the $n + 1$ rule predict?

A signal for hydrogens with n equivalent neighbours on adjacent carbons splits into $n + 1$ lines. Two neighbours give a triplet and three neighbours give a quartet.

How many signals does ^{13}C NMR show?

It shows one signal for each different carbon environment. Symmetrical molecules give fewer signals than the number of carbon atoms.