9701 CHEMISTRY · TOPICS 22 & 36 · AS + A LEVEL

Analytical Techniques

01 · MASS SPECTROMETRY — READING IT

x-axis m/z, y-axis relative abundance. The peak at the **highest m/z is the molecular ion M^+**, and its value is the M_r.

Peaks below it are **fragments**, formed when M^+ breaks apart. The **base peak** is simply the tallest, from the most stable fragment.

02 · COMMON FRAGMENTS

m/z	Fragment
15	CH_3^+
17	OH^+
29	$C_2H_5^+$ or CHO^+
43	$C_3H_7^+$ or CH_3CO^+
45	$COOH^+$

Work out the **difference** between M^+ and a fragment — a loss of 15 means a methyl group, 17 an –OH, 29 an ethyl or CHO.

03 · THE M+1 AND M+2 PEAKS

M+1 comes from the 1.1 % of carbon that is ^{13}C. Its relative height divided by 1.1 gives the **number of carbon atoms**.

M+2 reveals a halogen: **chlorine** gives M and M+2 in a 3 : 1 ratio, **bromine** in a 1 : 1 ratio, because of their two abundant isotopes.

04 · INFRARED SPECTROSCOPY

Bonds absorb IR at frequencies that make them **vibrate** — stretching and bending. Each bond has a characteristic wavenumber, so the spectrum shows which groups are present.

The x-axis runs right to left in cm^{-1} and the peaks point downwards as transmittance falls. Below 1500 cm^{-1} is the **fingerprint region** — unique to a compound, matched against a database rather than interpreted peak by peak.

05 · IR ABSORPTIONS TO RECOGNISE

Bond	cm^{-1}	Shape
O–H acid	2500–3300	very broad
O–H alcohol	3200–3600	broad
N–H amine	3300–3500	sharp, often double
C–H	2850–3100	sharp
C≡N	2200–2250	sharp
C=O	1680–1750	strong, sharp
C=C	1620–1680	weak

A very broad O–H **with** a strong C=O means a carboxylic acid; a C=O with no O–H means an aldehyde, ketone or ester.

06 · WORKED EXAMPLE — IR PLUS MS

$M^+ = 60$. IR shows a very broad absorption at 3000 cm^{-1} and a strong peak at 1710 cm^{-1}. Fragments at 45 and 15.

Broad O–H + C=O → carboxylic acid
Loss of 15 from 60 → a CH_3 group
45 = $COOH^+$
→ **ethanoic acid**, CH_3COOH

07 · NMR — THE PRINCIPLE A2

Nuclei with an odd mass number, ^1H and ^{13}C, behave as tiny magnets. In a strong field they absorb radio waves as they flip alignment; the frequency depends on the electron environment around them.

TMS is the reference at δ = 0 — inert, volatile, non-toxic, and its twelve equivalent protons give one sharp peak. Samples dissolve in $CDCl_3$, which has no ^1H to interfere.

08 · READING A ^1H SPECTRUM A2

Number of peaks = number of different proton environments.

Chemical shift δ = the type of environment; electronegative neighbours shift protons downfield.

Integration = the ratio of protons in each environment.

Splitting = how many protons are on the neighbouring carbon.

09 · THE N+1 RULE A2

Neighbours	Peak
0	singlet
1	doublet
2	triplet
3	quartet

A **quartet next to a triplet** in a 2 : 3 ratio is the signature of an ethyl group, CH_3CH_2–.

10 · CHEMICAL SHIFTS TO KNOW A2

Proton	δ / ppm
R–CH_3	0.9
CH next to C=O	2.0–2.9
CH next to O	3.3–4.3
aromatic H	6.5–8.0
CHO	9.3–10.5
COOH	10–12

Values come from the data booklet — learn the pattern, not the numbers.

11 · O–H AND N–H PROTONS A2

These appear as broad singlets at variable shift and do not split their neighbours. Shaking the sample with **D_2O** exchanges them for deuterium and the peak **disappears** — the standard way to confirm an –OH or –NH.

12 · WORKED EXAMPLE — NMR A2

$C_3H_6O_2$ gives three peaks: δ 1.2 triplet (3H), δ 2.4 quartet (2H), δ 11.5 broad singlet (1H) that vanishes with D_2O.

Triplet + quartet in 3 : 2 → an ethyl group
Broad singlet at 11.5, D_2O exchangeable → COOH
CH_3CH_2 + COOH = $C_3H_6O_2$ ✓
→ **propanoic acid**, CH_3CH_2COOH

13 · ^{13}C NMR A2

Each peak is one carbon environment, with no splitting and no useful integration. It is the quickest way to count how many distinct carbons a molecule has, and to tell symmetrical isomers apart: propanone gives two peaks, propanal three.

MARKS LOST HERE

— Reading the base peak as the molecular ion.

— Trying to interpret individual peaks in the fingerprint region.

— Applying the n+1 rule to protons on the **same** carbon rather than the neighbouring one.

— Forgetting that an –OH peak is broad, unsplit and removed by D_2O.