Analytical techniques

Reading infrared spectra to identify functional groups, and using mass spectra for relative atomic mass, molecular mass, fragmentation, the number of carbon atoms and the presence of bromine or chlorine.

22.1 Infrared spectroscopy

Bonds absorb **infrared radiation** at characteristic wavenumbers, which makes their vibrations stronger. The spectrum plots **% transmittance** (peaks point downwards) against **wavenumber** (cm^{-1}). The absorptions to know (the Data section gives the values):

Bond	Wavenumber / cm^{-1}	Appearance
O–H (alcohol)	3200–3600	strong, broad
O–H (carboxylic acid)	2500–3300	very broad
N–H (amine, amide)	3300–3500	medium
C–H	2850–3100	strong
C≡N	2200–2280	medium
C=O	1680–1750	strong, sharp
C=C	1620–1680	weak to medium
C–O	1000–1300	strong

Use the **fingerprint region** below about 1500 cm^{-1} to compare with a known sample. A very broad band from 2500 to 3300 cm^{-1} together with C=O shows a carboxylic acid; C=O with no O–H and no N–H is an aldehyde, ketone or ester (ester also has C–O). Water in the sample would add an O–H absorption, so samples must be dry.

Read the axes before assigning a bond

On a transmittance spectrum, downward troughs indicate absorption; an absorbance spectrum uses the opposite visual convention. Wavenumber is reciprocal wavelength, measured in cm^{-1}, not a frequency in hertz. Locate a feature using its range, shape and intensity. A small feature near one tabulated value is weaker evidence than a clear broad acid OH band together with a strong carbonyl absorption.

Worked example: a sample has a strong C=O band and very broad OH absorption extending roughly 2500–3300 cm^{-1}. This combination supports a carboxylic acid. An alcohol has a differently shaped OH

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region and need not have C=O. An ester can show C=O and C–O but lacks the acid OH band. Interpret the combination rather than naming every compound with one carbonyl peak.

Functional groups versus exact identity

Different aldehydes and ketones can have similar carbonyl absorptions. IR often identifies functional groups more readily than the exact carbon skeleton. Matching the fingerprint region with a known reference can provide further evidence because its complex pattern depends on the whole molecule. A broad OH feature from contamination can obscure conclusions, so sample purity matters.

Worked comparison: propanal and propanone both have a carbonyl absorption and molecular formula C_3H_6O. The main C=O peak alone does not distinguish them reliably. A positive Tollens' test supports propanal; a negative result plus suitable iodoform evidence supports propanone. Use a technique for what it measures rather than expecting one spectrum to answer every structural question.

> **TRY IT**
>
> Can absence of a broad OH band distinguish every alcohol from every other class without further evidence?

Answer: No. It argues against a substantial OH-containing component in a suitable clean spectrum, but concentration, overlap and sample conditions matter. Combine it with other absorptions and chemical evidence before assigning a complete structure.

22.2 Mass spectrometry

In a mass spectrometer the sample is ionised and the ions are separated by their **mass/charge ratio,** m/e (the charge is usually +1, so m/e is the mass). You do not need to know how the machine works.

Relative atomic mass from isotopic abundances

$$A_r = \frac{\sum(\text{isotopic mass} \times \text{abundance})}{\sum \text{abundances}}$$

> **TRY IT**
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> A sample of chlorine has ^{35}Cl 75% and ^{37}Cl 25%. Find A_r.

$A_r = (35 \times 75 + 37 \times 25)/100 = 35.5.$

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The molecular ion and fragmentation

- The **molecular ion,** M^+, is the intact ionised molecule. Its m/e gives the relative molecular mass when its charge is +1. It need not be the tallest peak and may be weak or absent; isotope peaks can lie above it. Identify its cluster rather than blindly choosing the highest recorded mass.
- **Fragmentation** breaks the molecular ion into smaller pieces. Peaks at known values identify the fragments: 15 is CH_3^+, 29 is $C_2H_5^+$ (or CHO^+), 43 is $C_3H_7^+$ (or CH_3CO^+), 45 is $COOH^+$ (or $C_2H_5O^+$). Differences between peaks show the groups lost.

The M + 1 peak and the number of carbon atoms

About 1.1% of carbon atoms are ^{13}C, so there is a small peak one unit above M^+. The number of carbon atoms n is:

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

> **TRY IT**
>
> A compound has M^+ with height 40.0 and $[M+1]^+$ with height 1.76. How many carbon atoms?

$n = (100 \times 1.76)/(1.1 \times 40.0) = 4.0$, so 4 carbon atoms.

The M + 2 peak: chlorine and bromine

- **Chlorine** has isotopes ^{35}Cl and ^{37}Cl in the ratio **3 : 1**, so one Cl atom gives M^+ and $[M+2]^+$ in a **3 : 1** ratio.
- **Bromine** has ^{79}Br and ^{81}Br in a ratio of about **1 : 1**, so one Br atom gives M^+ and $[M+2]^+$ of **equal height**.

Compounds with two halogen atoms give M, $M+2$ and $M+4$ peaks in characteristic ratios (for two bromine atoms 1 : 2 : 1).

Ion mass, charge and peak height

The horizontal axis is mass-to-charge ratio, often written m/z. For a singly charged ion, a peak at 58 corresponds to ion mass 58 on the relative scale. A doubly charged ion of mass 58 would appear near 29. Ordinary syllabus organic fragmentation questions usually specify or imply singly charged ions, but the definition of the axis still matters.

The tallest peak is the **base peak**, assigned relative intensity 100. It indicates the most abundant detected ion under those measurement conditions, not necessarily the heaviest ion or the most abundant original

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molecule. Only charged fragments are detected; neutral fragments lost during fragmentation do not themselves give the corresponding ion peak unless separately ionised.

Worked example: a molecular ion at 72 and a major fragment at 57 differ by 15, consistent with loss of a methyl radical. A fragment at 43 may be an acylium ion or a hydrocarbon ion depending on composition. A nominal mass alone rarely identifies a unique fragment without other structural evidence.

> **TRY IT**
>
> A spectrum has a base peak at 43 and a molecular-ion cluster starting at 86. What relative molecular mass is indicated for a singly charged parent?

Answer: 86. The base peak at 43 is the most intense detected ion, not automatically the molecular ion.

Carbon count from the isotope ratio

The $M + 1$ calculation compares its abundance with **M**, not necessarily with the base peak. If M has intensity 50.0 and $M + 1$ has intensity 2.75, their ratio is 5.50%; dividing by approximately 1.1% per carbon gives five carbons. Using 2.75/100 would incorrectly use the arbitrary base-peak normalisation as the molecular-ion abundance.

Worked formula deduction: a compound has molecular mass 88, five carbons from its $M + 1$ ratio, and contains only C, H and O. Five carbons contribute 60, leaving 28 mass units. One oxygen leaves 12 hydrogens, giving $C_5H_{12}O$. Check chemical plausibility and other evidence; if the arithmetic gives an impossible hydrogen count, reconsider the isotope assumption or allowed elements.

The simple 1.1%-per-carbon approximation assumes the relevant cluster is identified and other isotope contributions do not dominate. Use supplied isotope abundances when provided. Treat a result close to an integer with the precision of the data in mind rather than inventing a fractional carbon atom.

> **TRY IT**
>
> M has intensity 80.0 and $M + 1$ intensity 5.28. Estimate carbon count.

Answer: $(5.28/80.0) \times 100 = 6.60\%$, so approximately $6.60/1.10 = \mathbf{6}$ carbons.

Halogen clusters and combined interpretation

For one chlorine, the parent isotope pair is separated by two mass units with about 3 : 1 intensity. For one bromine, the pair is about 1 : 1. A compound with two chlorine atoms has approximate 9 : 6 : 1 proportions across M, M+2 and M+4 because the isotope combinations follow the product of two 3 : 1 distributions. Do not interpret this three-peak pattern as three separate compounds automatically.

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Worked identification: a parent cluster at 108/110 with equal heights supports a one-bromine molecule with lighter parent mass 108. If the compound contains only C, H and Br, subtract 79 to leave 29, consistent with C_2H_5. The formula C_2H_5Br fits. A fragment near 29 then supports loss of bromine, though independent evidence should still be considered.

> **TRY IT**
>
> A compound gives parent peaks two units apart in roughly 3 : 1 proportions, and IR indicates C=O without OH. What has been established, and what remains unknown?

Answer: The evidence supports one chlorine atom and a carbonyl-containing structure without a substantial OH feature. It does not uniquely identify the carbon skeleton or decide aldehyde, ketone or another carbonyl class without further information.

Chapter check: identify axes, distinguish base peak from molecular ion, use the M-relative isotope ratio and combine independent constraints. More powerful structural deductions follow in **A Level analytical techniques**.

References and further reading

Scope follows section 22 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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