Mass spectra and infrared spectra

Using the molecular ion and fragmentation patterns in mass spectra, infrared absorptions of functional groups, and combined analysis of unknowns.

Mass spectrometry of organic compounds

A mass spectrum plots abundance against m/z.

- The **molecular ion**, M^+, is the molecule with one electron removed. Its m/z is the **relative molecular mass**. It is usually the peak at highest m/z (ignoring small isotope peaks).
- Other peaks come from **fragmentation**: the molecular ion breaks into a positive fragment ion and a neutral fragment (or radical). Only the **positive** fragment is detected.

NOTE

Common fragments: m/z 15 (CH_3^+), 29 ($C_2H_5^+$ or CHO^+), 43 ($C_3H_7^+$ or CH_3CO^+), 45 ($C_2H_5O^+$ or $COOH^+$). A loss of 17 suggests an $-OH$ or NH_3; a loss of 18 is water.

Using a spectrum

1. Identify the molecular ion and find M_r.
2. Subtract the other peaks from the molecular ion to find the neutral fragments lost.
3. Link the fragments to the functional group and structure.

A peak at 43 that is the base peak suggests a propyl group or an ethanoyl group, CH_3CO^+ (a methyl ketone).

TRY IT

A compound has M^+ at m/z = 58 and a strong peak at 43. It contains C, H and O only. Suggest a structure.

$M_r = 58$ fits propanone, CH_3COCH_3 (C_3H_6O). The peak at 43 is CH_3CO^+ ($58 - 15$, loss of CH_3). Propanal also has $M_r = 58$, but its fragments would include 29 (CHO^+ or $C_2H_5^+$), so the 43 peak points to propanone.

Note Academy

Peaks at $M + 1$

A small peak one unit above M^+ comes from molecules with a ^{13}C atom. Its height relative to M^+ (about 1.1% per carbon) can give the number of carbon atoms.

Compounds containing chlorine or bromine show a pair of peaks: for one chlorine M and $M + 2$ in the ratio 3 : 1, and for one bromine in the ratio 1 : 1.

Infrared spectroscopy

Covalent bonds **vibrate** (stretch and bend) at characteristic frequencies. A molecule absorbs infrared radiation when the frequency matches a vibration that changes the dipole of the molecule. The spectrum plots **transmittance** against **wavenumber** (cm^{-1}), so absorptions appear as downward troughs.

Bond	Wavenumber / cm^{-1}	Found in
C–H	2850–3100	Alkanes, alkenes, aldehydes (the aldehyde C–H around 2700–2900)
C=C	1620–1680	Alkenes
C=O	1680–1750	Aldehydes, ketones, carboxylic acids, esters, amides
O–H (alcohol)	3200–3600 (broad)	Alcohols
O–H (carboxylic acid)	2500–3300 (very broad)	Carboxylic acids
N–H	3300–3500	Amines
C–X	500–800 (C–Cl 600–800)	Halogenoalkanes

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Look first for the strong, sharp $C=O$ peak near 1700 cm^{-1}, then the broad O–H absorption at 3200–3600 (alcohols) or the very broad one over 2500–3300 (acids). The region below about 1500 cm^{-1} is the fingerprint region, which is unique to each compound.

TRY IT

A compound has M_r = 60 and an infrared spectrum with a broad absorption centred near 3300 cm^{-1} and none near 1700 cm^{-1}. Which functional group is present?

The broad absorption at 3200–3600 cm^{-1} is the $O-H$ of an alcohol; with no C=O, it is not an acid, aldehyde or ketone. The compound is propan-1-ol or propan-2-ol ($M_r = 60$).

Combining the techniques

To find a structure:

1. Use **percentage composition** or combustion data to find the empirical formula.
2. Use the molecular ion in the **mass spectrum** to find the molecular formula.
3. Use **infrared** to identify the functional groups.
4. Use fragments and (later) **NMR** to place them in the structure.
5. Use **chemical tests** (bromine water, 2,4-DNPH, Benedict's, sodium carbonate) to confirm the group.

Core Practical 8 analyses unknown organic and inorganic compounds using test-tube tests together with spectra.

Note Academy