

Analytical techniques

A-Level Chemistry 9701 · Topic 22 revision notes

Everything from the 2 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Infrared spectroscopy.

2. Mass spectrometry.

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1 Infrared spectroscopy

Syllabus 22.1

Covalent bonds are always **vibrating** (stretching and bending). A bond absorbs infrared radiation whose frequency matches its natural vibration frequency, provided the vibration **changes the dipole** of the molecule. Positions are quoted as **wavenumber** in cm^{-1} , and each bond absorbs in a characteristic range listed in the Data Booklet, for example **O-H in alcohols $3200\text{--}3600\text{ cm}^{-1}$ (broad)**, **O-H in carboxylic acids $2500\text{--}3000\text{ cm}^{-1}$ (very broad)** and **C=O $1670\text{--}1740\text{ cm}^{-1}$** . A spectrum plots transmittance against wavenumber, so every absorption is a **dip**. The **fingerprint region** below 1500 cm^{-1} is unique to each compound and is matched against a database. The same absorption by C=O and O-H bonds in CO_2 and H_2O is what makes them **greenhouse gases**.

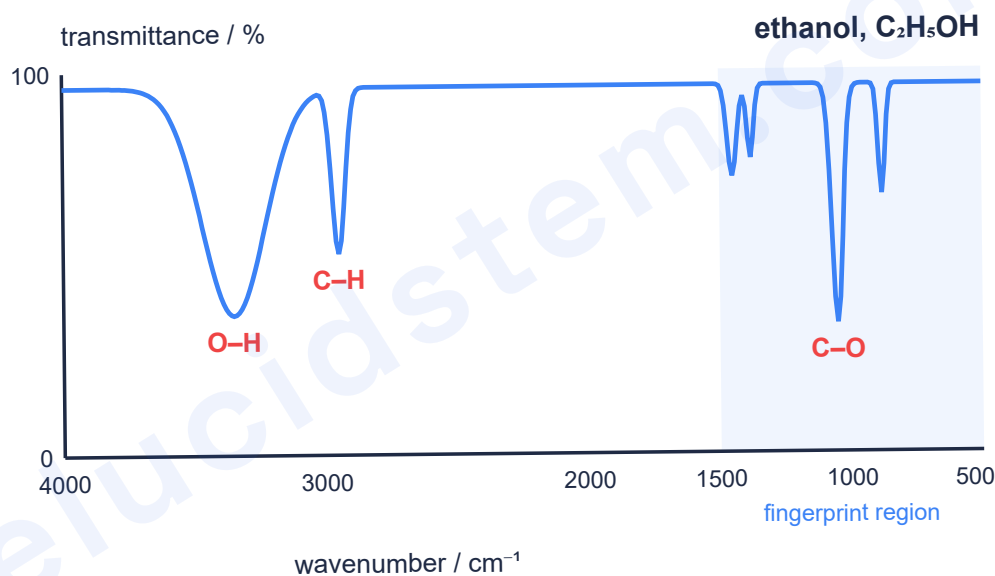


Fig. 1: simplified infrared spectrum of ethanol, with the broad alcohol O-H, the C-H and the C-O absorptions

Alcohol O-H, acid O-H, C=O, C-O.

- ✓ **Alcohol O-H:** 3200–3600 cm^{-1} , broad.
- ✓ **Acid O-H:** 2500–3000 cm^{-1} , very broad.
- ✓ **C=O:** 1670–1740 cm^{-1} , strong and sharp.
- ✓ **Fingerprint:** below 1500 cm^{-1} , match to a database.

Watch out!

Spectra are drawn with wavenumber **decreasing** from left to right, and absorptions point **down**. Do not call every peak near 3000 an O-H; C-H at 2850–2950 is in almost every compound. The acid O-H is **very broad and lower** (2500–3000) than the alcohol O-H (3200–3600). An ester has C=O and C-O but **no** O-H. You cannot identify a compound from the fingerprint region by eye: it needs a database match.

2 Mass spectrometry

Syllabus 22.2

In the spectrometer a molecule loses an electron to form the **molecular ion**, M^+ . The M^+ peak, at the highest m/z apart from its isotope peaks, gives the M_r . Some molecular ions break into a **fragment ion** and a neutral radical; only the ion is detected, so peaks such as **15** (CH_3^+), **29** (C_2H_5^+ or CHO^+) and **43** (C_3H_7^+ or CH_3CO^+) reveal pieces of the structure. About 1.1% of carbon is ^{13}C , so a small **$M+1$ peak** appears and the number of carbon atoms is $n = 100 \times (M+1 \text{ height}) / (1.1 \times M \text{ height})$. An **$M+2$ peak** one third the height of M shows one **Cl** atom ($^{35}\text{Cl} : ^{37}\text{Cl} = 3 : 1$); M and $M+2$ of **equal height** show one **Br** atom ($^{79}\text{Br} : ^{81}\text{Br} = 1 : 1$).

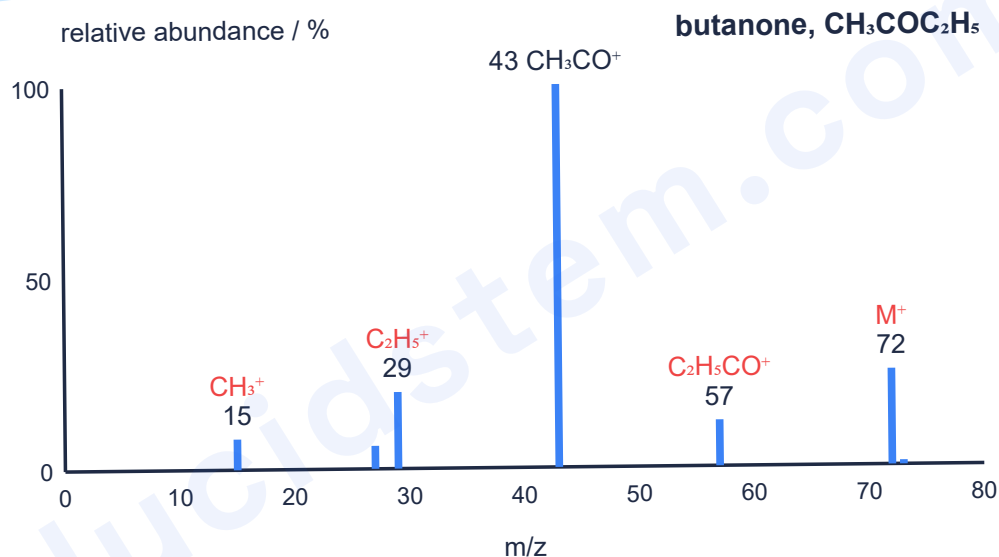


Fig. 1: simplified mass spectrum of butanone, with the molecular ion at m/z 72 and the main fragment ions

M, fragments, M+1, M+2.

- ✓ **M⁺:** last major peak, gives M_r.
- ✓ **Fragments:** 15 CH₃⁺, 29 C₂H₅⁺, 43 C₃H₇⁺ or CH₃CO⁺.
- ✓ **M+1:** $n = 100 \times (M+1) / (1.1 \times M)$.
- ✓ **M+2:** 3 : 1 is Cl, 1 : 1 is Br.

Watch out!

The M⁺ peak is the **last significant peak** before its own small isotope peaks, not the tallest (the tallest is the base peak). In the M+1 formula use **peak heights**, not m/z values, and put the M+1 height on top. Only **ions** are detected, never the radical lost. A 3 : 1 pair two units apart means **chlorine**; 1 : 1 means **bromine**, so do not swap them.

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