CAIE Chemistry A-level

22: Analytical Techniques

Notes

Infra-red Spectroscopy

When infra-red radiation is directed at a compound, **specific frequencies are absorbed** by bonds in the molecule. The percentage transmittance of infra-red at each frequency is recorded by a detector and then plotted on a graph.

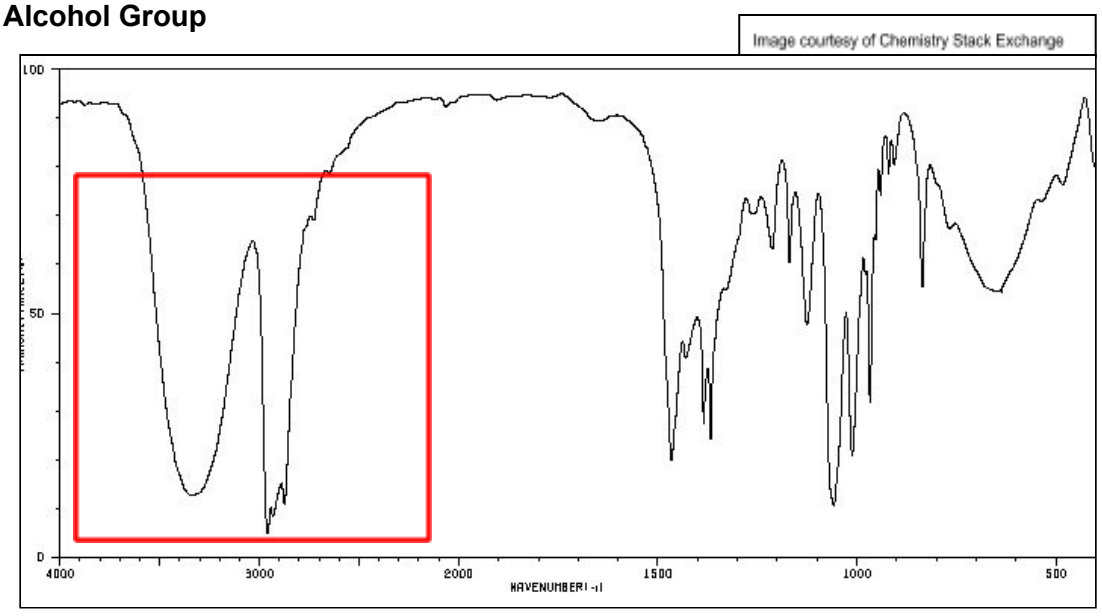
Energy that is absorbed by the compound causes bonds to **vibrate**, meaning the bond **stretches or bends**. The amount of vibration depends on the **length of the bond** and the mass of the atoms.

The peaks on an infra-red spectrum can be used to identify the functional groups present in a molecule as **each bond absorbs a specific frequency of IR radiation**. A peak can be compared with known values in the data book to identify the bond.

The **fingerprint region** on an infra-red spectrum is the region (typically between 1500cm^{-1} and 500cm^{-1}) that contains a complicated series of absorptions. Every compound has a **unique** fingerprint region.

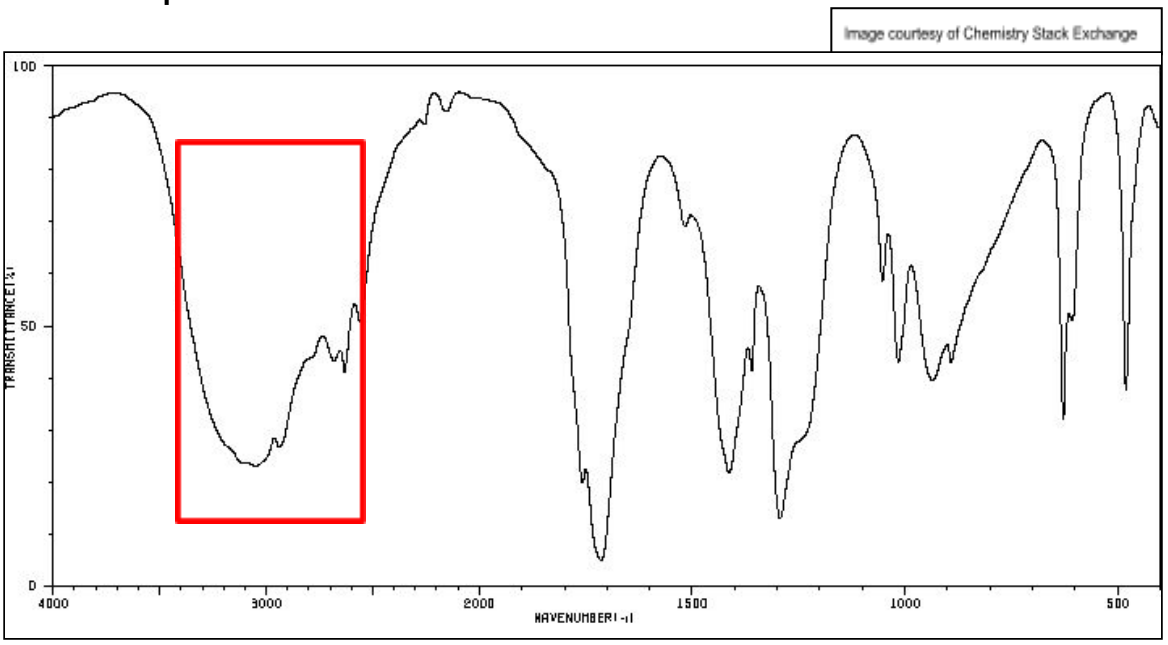
A **spectrum** is produced from the measurements which has **characteristic curves** for the different functional groups:

-OH Alcohol Group



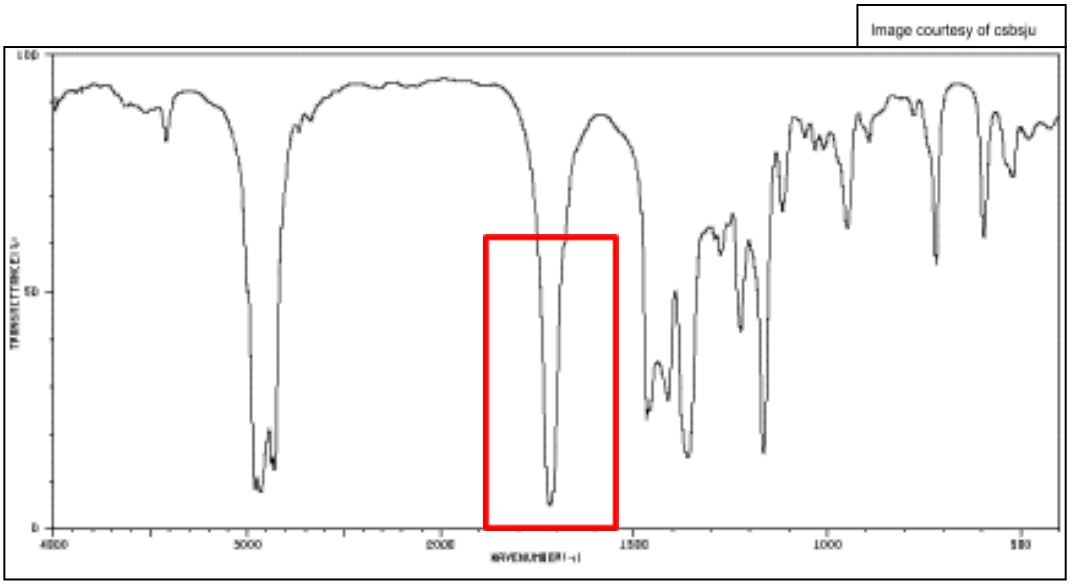
The characteristic peak is in the range 3230-3550 cm^{-1}

-OH Acid Group



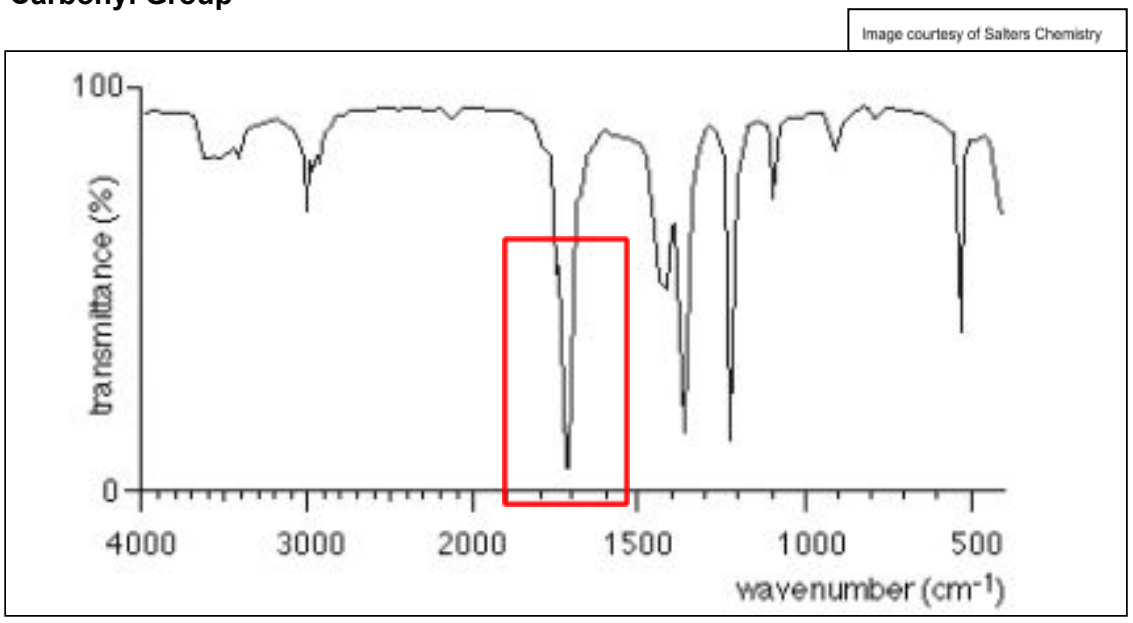
The characteristic peak is in the range 2500-3300 cm^{-1}

C=C Unsaturated Group



The characteristic peak is in the range 1620-1680 cm^{-1}

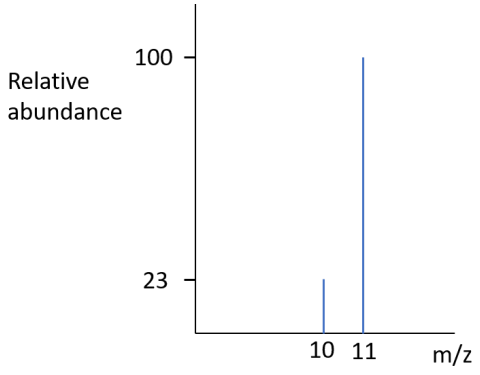
C=O Carbonyl Group



The characteristic peak is in the range 1680-1750 cm^{-1}

Mass Spectrometry

During mass spectrometry, a **vaporised** sample (atoms or molecules) is turned into positive ions. The ions are then accelerated, deflected by a magnetic field and then detected. A graph is produced with the **mass to charge ratio (m/z)** on the x axis and **relative abundance** on the y axis:



This graph can be used to calculate the isotopic abundance of ^{10}B:

23 ÷ (100 + 23) = 0.187

To calculate the relative atomic mass of an atom of boron:

(10 x 23) + (11 x 100) = 1330

1330 ÷ (23 + 100) = 10.8

Molecular Mass

The molecular ion peak (M^+) is the peak with the **greatest mass to charge ratio**. The molecular mass of a compound is equal to the m/z value of this peak.

M^{+1} peak

The M^{+1} peak is a tiny peak which is 1 unit to the right of the molecular ion peak. This is **caused by the presence of the ^{13}C isotope** (the relative abundance of ^{13}C is 1.11%). ^{13}C has one more neutron than ^{12}C meaning that the relative formula mass is increased by 1.

The relative heights of the M^+ and M^{+1} peaks can be used to predict the number of carbon atoms (n) in a molecule:

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

M^{+2} peak

Compounds which contain **chlorine** or **bromine** also have a M^{+2} peak on their mass spectrum.

Chlorine

Chlorine in these compounds can be one of **two isotopes**: ^{35}Cl or ^{37}Cl. Compounds containing the ^{37}Cl isotope will have a relative formula mass that is 2 units larger than compounds containing the ^{35}Cl isotope which causes the M^{+2} peak. The peak heights of the M^+ and M^{+2} ions are in the **ratio 3:1** because the chlorine atom is 3 times more likely to be ^{35}Cl than ^{37}Cl.

Bromine

Bromine has **two isotopes**: ^{79}Br and ^{81}Br. The heights of the M^+ and M^{+2} peaks will be in the **ratio 1:1** because the ratio of the two isotopes is 1:1.

For a compound with 4 bromine atoms, there will be **5 molecular peaks** because there are 5 combinations ways that you can have 4 bromine atoms (as there are two isotopes):

79 + 79 + 79 + 79
79 + 79 +79 + 81
79 + 79 +81 + 81
79 + 81 +81 + 81
81 + 81 +81 + 81

Fragmentation

Fragment ions are formed when an **unstable molecular ion breaks** up into a positive ion and an uncharged **free radical** (a species which contains an unpaired electron):

$$M^+ \rightarrow X^+ + Y\bullet$$

Only charged particles are detected so the free radical (Y●) will not produce a line on the spectrum. Each line on the mass spectrum represents a different fragment ion.

The combination of fragment ions in a mass spectrum can be used to identify a molecule.Below is a table showing some common fragment ions:

m/z value	Fragment ion
15	CH_3^+
17	OH^+
29	$C_2H_5^+$
43	$C_3H_7^+$
57	$C_4H_9^+$