

## 22 Analytical techniques

This chapter deals with the analytical techniques of infrared spectroscopy and mass spectrometry for AS Level. Other analytical techniques covered in the A Level syllabus are dealt with in [Chapter 37](#).

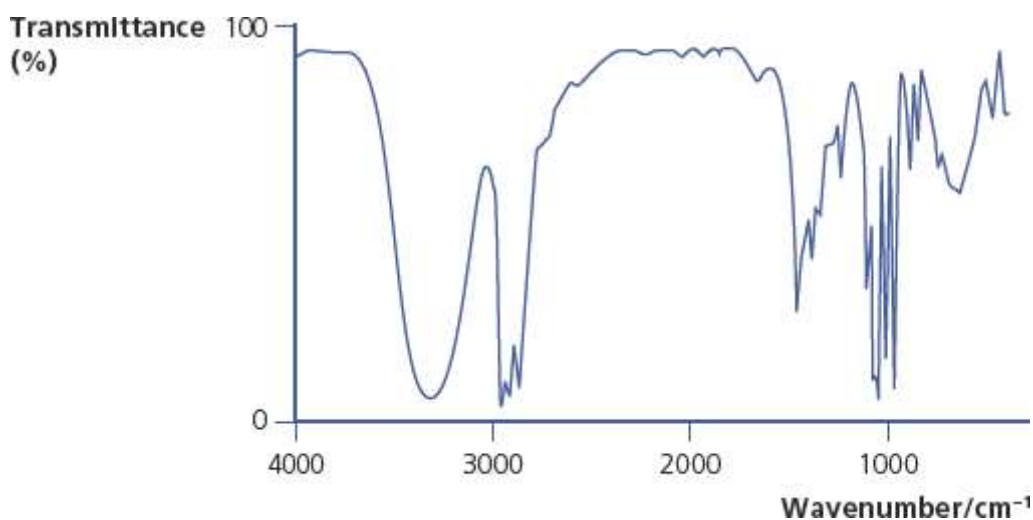
### Infrared spectroscopy

- Infrared spectroscopy is useful for detecting bonds and/or functional groups in organic molecules.
- If you direct a range of infrared frequencies one at a time through a sample of an organic compound, some frequencies are **absorbed** by the compound and some pass through.
- A detector on the other side of the compound shows that some frequencies pass through the compound with almost no loss, but other frequencies are strongly absorbed.
- If a particular frequency is absorbed as it passes through the compound being investigated, it means that energy is being transferred to the compound.

#### KEY TERM

**Absorptions** in infrared spectra are measured at particular wavenumbers. These are  $1 \text{ cm}$  divided by the wavelength of the energy.

- Energies in the infrared region of the spectrum correspond to the energies involved in bond vibrations. These can be bond-stretching or bond-bending vibrations. A typical infrared spectrum is shown in [Figure 22.1](#).



**Figure 22.1** The infrared spectrum of propan-1-ol

You need to practise using key absorptions to identify the functional groups present in molecules and deducing the structure of the molecule from its molecular formula. A list of the bonds you need to be able to recognise is given in [Table 22.1](#).

**Table 22.1**

Bond	Functional groups containing the bond	Absorption range in wavenumbers/cm <sup>-1</sup>
C—O	Hydroxy, ester	1040–1300
C=C	Aromatic compound, alkene	1500–1680
C=O	Amide	1640–1690
	Carbonyl, carboxyl	1670–1740
	Ester	1710–1750
C≡N	Nitrile	2200–2250
C—H	Alkane	2850–2950
N—H	Amine, amide	3300–3500
O—H	Carboxyl	2500–3000
	Hydroxy	3200–3600

## NOW TEST YOURSELF

- 1 If the infrared spectrum of the compound  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$  was recorded, indicate which bonds would show absorptions in the infrared range, and at what wavenumber range you would expect to find them.

## Mass spectra of elements

- The atomic mass of an element can be measured using a **mass spectrometer**. You do not need to know how the instrument works, only that it produces positive ions of atoms, or fragments of molecules, and separates them according to their masses. Molecular fragmentation is covered later (see page 125).
- On injecting a sample of an element into a mass spectrometer, atoms of the element become positively charged and then separated according to their masses.
- Most elements are made up of atoms with the same number of protons but different numbers of neutrons. This means that they have different masses.
- The data can be used to calculate the average atomic mass of the sample.

Figure 22.2 shows the mass spectrum of a sample of the element magnesium. The average atomic mass of the sample of magnesium is made up of the contribution each isotope makes:

$$\begin{aligned}A_r &= (24 \times 0.79) + (25 \times 0.10) + (26 \times 0.11) \\ &= 24.32\end{aligned}$$

Remember that samples may not always contain just one isotope, or even the same mix of isotopes.

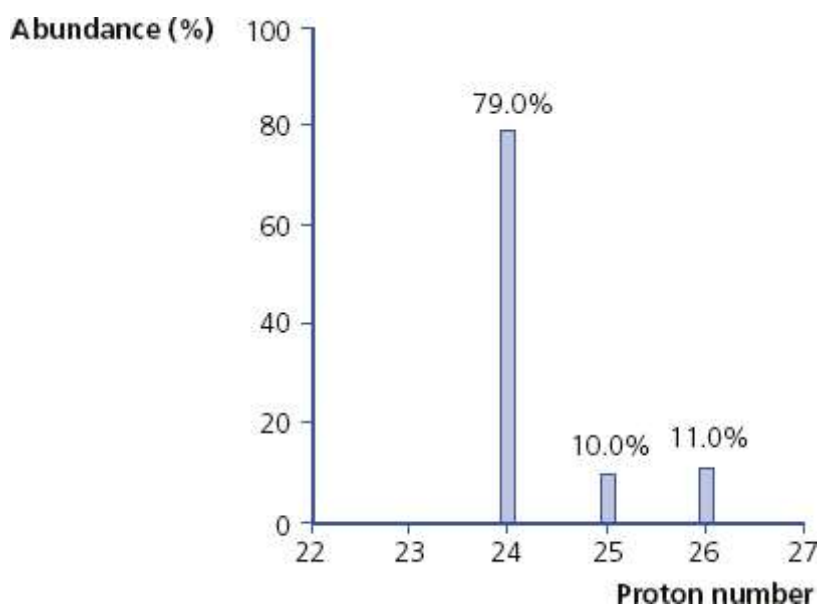


Figure 22.2 Mass spectrum of magnesium

## Mass spectra of organic compounds

You saw above how mass spectrometry can be used to determine accurate atomic masses. It can also give useful information about organic molecules. Mass spectrometry can give three different types of information:

- Measurement of the relative heights of peaks corresponding to the ion corresponding to the molecular mass ( $M$ ) and the ion one higher than the molecular mass ( $M+1$ ) allows us to determine the number of carbon atoms in a molecule. Similar examination of the  $M$  and  $M+2$  peaks can identify the presence of chlorine or bromine.
- Measurement of the accurate mass of the molecular ion (the  $M$  peak) enables us to determine the molecular formula.
- Identification of fragment ions produced in a mass spectrometer may allow the piecing together of the structure of the parent molecule.

### Using the $M+1$ peak

Naturally occurring carbon consists almost entirely of  $^{12}\text{C}$  and  $^{13}\text{C}$  in the ratio 98.9%  $^{12}\text{C}$  to 1.1%  $^{13}\text{C}$ . You can use this information, together with the

abundance of the M and M+1 peaks, to calculate the number of carbon atoms,  $n$ , in a molecule:

$$n = \frac{100 \times A_{M+1}}{1.1 \times A_M}$$

where  $n$  is the number of carbon atoms and  $A_M$  and  $A_{M+1}$  are the abundances of the M and M+1 peaks.

## NOW TEST YOURSELF

- 2 In the mass spectrum of an organic compound the M : M+1 peak height ratio was 8.0 : 0.43. Calculate the number of carbon atoms in the molecule.

## Using the M and M+2 peaks

The halogens chlorine and bromine occur naturally as mixtures of two predominant isotopes. This is shown in [Table 22.2](#).

**Table 22.2**

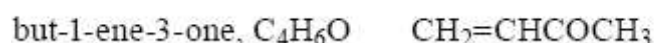
Element	Isotope	Relative abundance	Approximate ratio
Chlorine	$^{35}\text{Cl}$	75.8%	3 : 1
	$^{37}\text{Cl}$	22.4%	
Bromine	$^{79}\text{Br}$	50.5%	1 : 1
	$^{81}\text{Br}$	49.5%	

You can see that if the ratio of the abundance (height) of the M and M+2 peaks is 3 : 1 it indicates the presence of a chlorine atom in the molecule. If the ratio is 1 : 1 then it indicates the presence of a bromine atom. If more than one atom of the halogen is present, there would also be an M+4 peak and you would be able to determine which halogen atoms are present from the ratios.

## Using accurate molecular masses

With high-resolution mass spectrometers you can measure the mass to charge ( $m/e$ ) ratios to five significant figures (at least 1 part in 100 000). This means that it is not only possible to measure the  $M_r$  of a compound accurately, but also to determine its molecular formula.

The two compounds below have the same  $M_r$  to the nearest whole number:



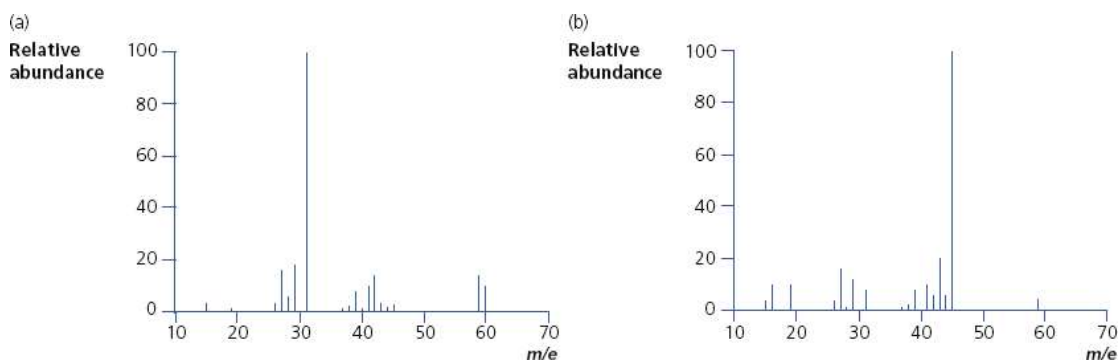
Using *accurate* relative atomic masses for hydrogen, carbon and oxygen ( $H = 1.0078$ ,  $C = 12.000$ ,  $O = 15.995$ ) you can determine the *accurate* relative molecular masses of the two compounds.

$$C_5H_{10} = (5 \times 12.000) + (10 \times 1.0078) = 70.078$$

$$C_4H_6O = (4 \times 12.000) + (6 \times 1.0078) + 15.995 = 70.0418$$

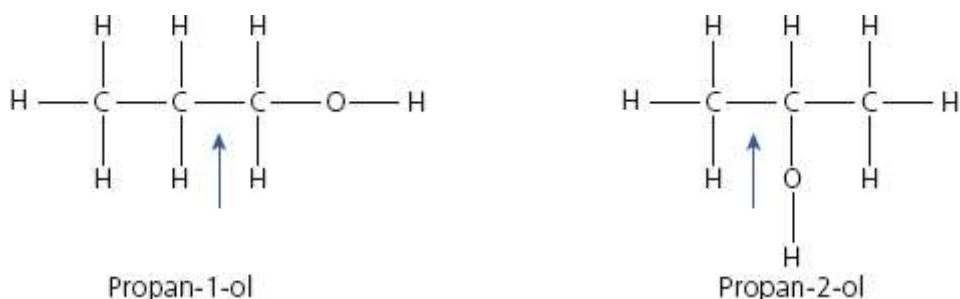
## Using fragmentation patterns

- The electron beam that produces positive ions in the mass spectrometer can also break bonds, producing fragments of the parent molecule.
- Some of these fragments will have a positive charge and produce further peaks in the mass spectrum. The fragmentation pattern can help to distinguish between structural isomers because they form different fragments.
- The two mass spectra shown in [Figure 22.3](#) were obtained from propan-1-ol and propan-2-ol.



**Figure 22.3** Mass spectra of (a) propan-1-ol, (b) propan-2-ol

These mass spectra have very different fragmentations. In propan-1-ol the highest peak is at  $m/e$  31, whereas in propan-2-ol the largest peak is at  $m/e$  45. What are the fragments that cause these two peaks, and how are they formed from the parent molecules? Figure 22.4 shows the two isomers.



**Figure 22.4**

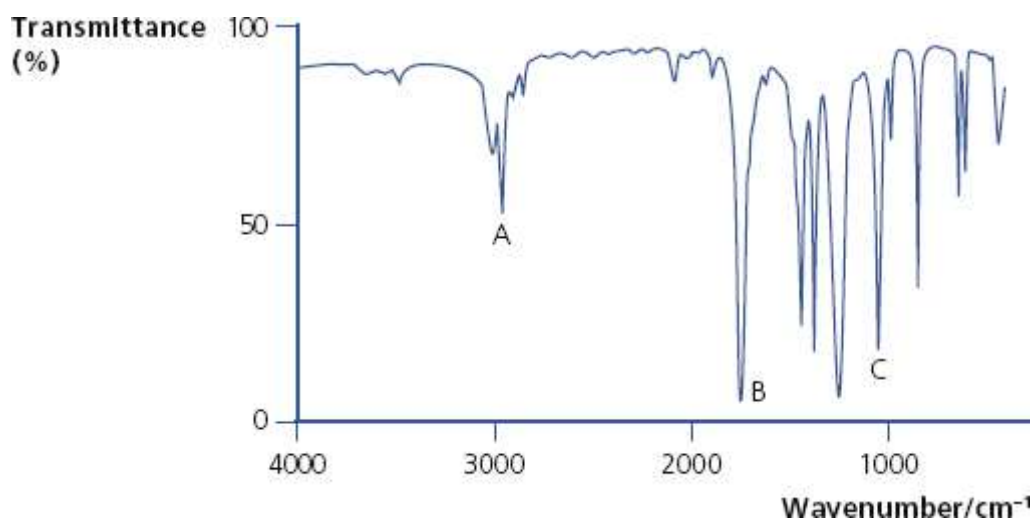
Look at the spectrum of propan-1-ol. A break in the middle of the molecule (where the arrow is) produces either  $\text{CH}_3\text{CH}_2^+$  and  $\bullet\text{CH}_2\text{OH}$ , or  $^+\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CH}_2\bullet$ . The uncharged species do not appear in the mass spectrum; the charged species have peaks at  $m/e$  values of 29 and 31.

In propan-2-ol, fragmentation between the first two carbon atoms produces either  $\text{CH}_3^+$  ( $m/e = 15$ ) or  $^+\text{CH}(\text{OH})\text{CH}_3$  ( $m/e = 45$ ) as the charged species.

The fragments in each case can be found in the relevant spectrum in Figure 22.4. You do not need to be able to explain *why* particular fragments form, just to be able to identify *what* their formulae might be.

## REVISION ACTIVITY

- a What part of a molecule is responsible for the absorption of infrared energy?
- b Why can two different molecules have similar infrared spectra?
- c The infrared spectrum of a compound R is shown here:



- i What functional groups are likely to be responsible for the peaks labelled A, B and C?
  - ii Compound R contains three carbon atoms and has a formula mass of 74. Write a molecular formula for R.
  - iii Give the structural formula for R.
- d Suggest the identity of the major fragments and their  $m/e$  values in the mass spectrum of propanone.

## END OF CHAPTER CHECK

By now you should be able to:

- analyse the infrared spectrum of a simple molecule and identify functional groups present
- analyse mass spectra in terms of  $m/e$  values and isotopic abundances; calculate the relative atomic mass of an element given these data
- deduce the molecular mass of an organic molecule from the molecular ion peak in a mass spectrum and deduce the number of carbon atoms present in the molecule using the  $M : M+1$  peak ratio
- suggest the identity of molecules formed by simple fragmentation in a mass spectrum



- deduce the presence of Br or Cl atoms in a compound using the M : M+2 peak ratio