

Spectroscopy gives us ways of investigating the structure of substances by looking at their spectra

MASS SPECTROMETRY

Description

Particles are bombarded with electrons, which knock other electrons out of the particles making positive ions. The ions are accelerated in an electric field forming an ion beam. The particles in this beam can be sorted according to their masses using an electric field.

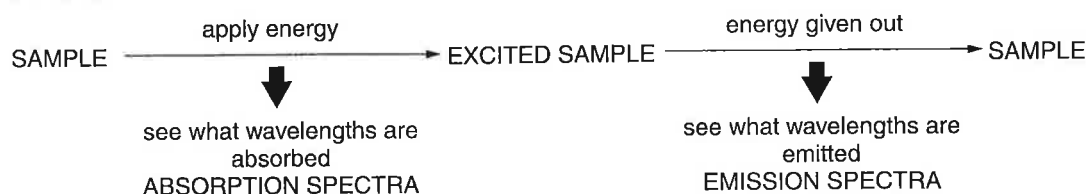
Uses

- to measure relative atomic masses
- to find the relative abundance of isotopes in a sample of an element
- to examine the fragments that a molecule might break into so that the identity of the molecule can be found

ULTRAVIOLET, VISIBLE, INFRARED, AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Description

Energy, in the form of electromagnetic radiation, is applied to the sample. Either the energy taken in by the sample or the energy it gives out is studied.



The energy of different parts of the electromagnetic spectrum is related to the frequency of that part of the spectrum by the equation

$$E = h\nu, \text{ where } E \text{ is the energy, } h \text{ is a constant, and } \nu \text{ is the frequency.}$$

The frequency is related to the wavelength of the radiation by

$$\nu = c/\lambda, \text{ where } c \text{ is the speed of light and } \lambda \text{ is the wavelength.}$$

So in summary, the shorter the wavelength, the higher the frequency and the higher the energy.

Different parts of the molecule interact with different wavelengths of radiation. The table below shows how different wavelengths of radiation cause different changes in the particles.

Frequency/MHz	3	3×10 ²		3×10 ⁴		3×10 ⁶		3×10 ⁸		3×10 ¹⁰		
Wavelength/m	10 ²	10	1	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸	10 ⁻⁹
Name of radiation	radio waves			microwaves			infra-red	visible	ultra-violet		X-rays	
What happens in the particles	nuclei rotate or spin			molecules rotate			molecules vibrate	electrons in atoms and molecules change orbitals				

USES

Ultraviolet and visible

- to work out electronic structures of atoms and molecules
- indicators in acid/base chemistry
- quantitative analysis in both inorganic and organic chemistry

Infrared

- detecting the presence of functional groups in organic compounds

Nuclear magnetic resonance

- detecting the number and position of atoms with odd mass numbers in molecules (usually ¹H, but also ¹³C, ¹⁵N, ¹⁹F, and ³¹P)

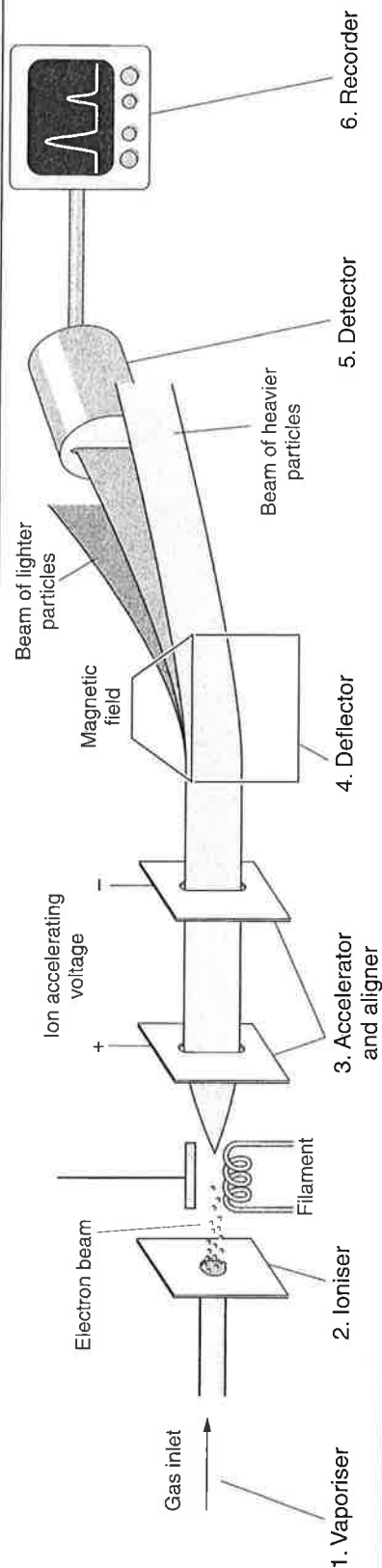
Mass spectra

THE EXPERIMENTAL SET-UP

A gaseous sample is hit by an electron beam which knocks electrons off the particles making them into positive ions:

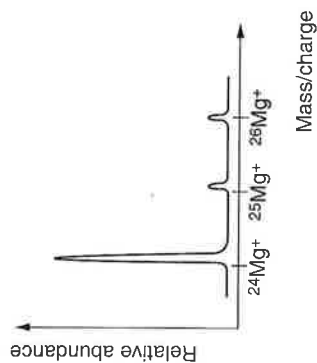


These ions are accelerated in an electric field and aligned into an ion beam. The beam is passed through either an electrostatic field or a magnetic field or both where it is deflected. The deflected particles are then detected and recorded.

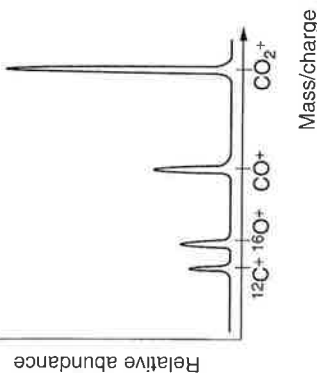


THE SPECTRUM

Magnesium spectrum



Carbon dioxide spectrum

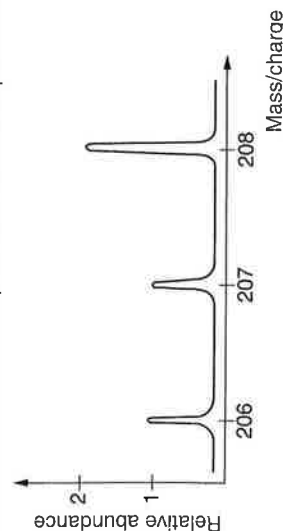


The spectrum for elements shows a different peak for each isotope. The height of the peak indicates the amount of each isotope.

The spectrum for compounds will show peaks representing the whole compound particle (this will have the largest mass) and fragments of it which broke up when they were ionised in the electron beam.

CALCULATIONS FROM MASS SPECTRA

The mass spectrum below is produced from a sample of lead



From it we can see that:

- there are three peaks: this tells us that there are three different isotopes present in the sample.
- the peak at 208 is twice as high as the other two peaks at 206 and 207. This tells us that there is twice as much of the isotope of mass number 208 as there is of the other two: so the relative amounts of the three isotopes are: 25% each of 206 and 207 and 50% of 208
- the relative atomic mass of this element is:

$$(206 \times \frac{25}{100}) + (207 \times \frac{25}{100}) + (208 \times \frac{50}{100}) = 207.25$$

EXPLAINING THE SPECTRUM

The mass spectrometer depends on the fact that a charged particle travelling in an electric field will be deflected and the amount of deflection depends on:

- the mass of the particle
- the speed of the particle
- the strength of the field
- the charge on the particle

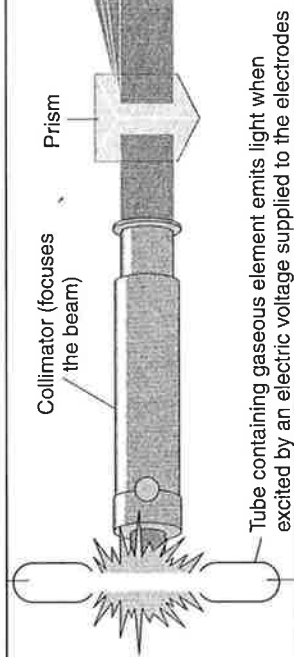
In a mass spectrometer the field strength is steadily changed so that particles of increasing mass arrive one after the other at the detector.

Ultraviolet and visible spectra

The experimental set-up

Emission spectra. A gaseous sample is excited with electrical or thermal energy. Ultraviolet or visible radiation is given out; this is focused into a beam and then split by a prism or diffraction grating; the radiation is then viewed through the telescope or detected photographically.

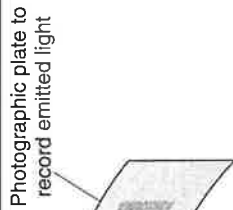
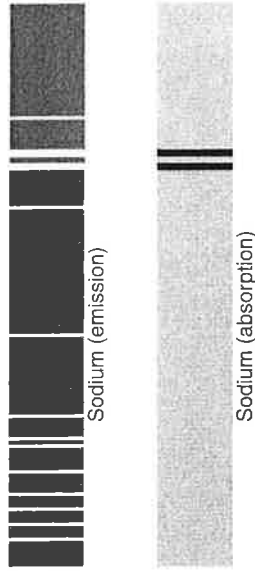
Absorption spectra. White light from a lamp is directed through a gaseous sample of the substance.



The spectrum

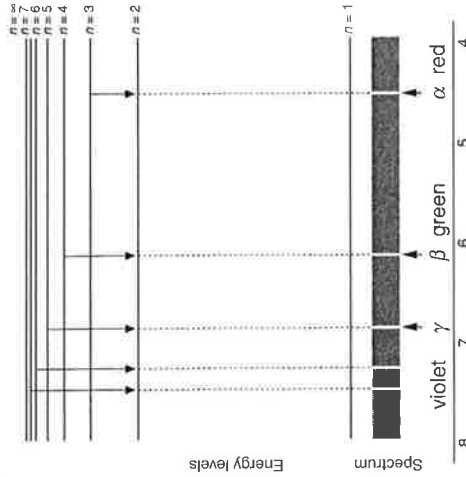
The spectrum produced differs from the normal spectrum of white light in two ways:

- it is made up of separate lines (it is discontinuous).
- the lines are in a converging pattern, getting closer as the frequency or energy of the lines increases.



The hydrogen spectrum

In the visible part of the hydrogen spectrum four lines can be seen. Each of these lines represents electrons falling back to the second energy level from one of the levels above. The visible part of the hydrogen spectrum is called the Balmer series.



Flame tests

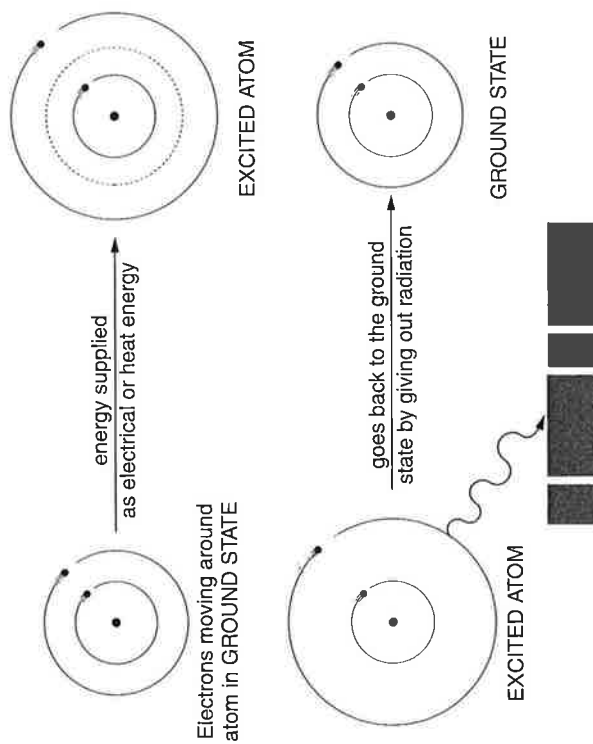
The emission spectrum of each element is unique to that element and can be used to identify the element. Flame tests, in which a sample of the element or its compound is heated on a wire in a bunsen flame can be used to identify some elements, especially in the s block.

Group 1 element	Flame colour	Group 2 element	Flame colour
sodium	orange	calcium	brick red
potassium	pale purple (lilac)	strontium	crimson
		barium	apple green

Explaining the emission spectra

Electrons in an atom are each in a particular energy level. When a sample is excited, electrons in the atom take in the extra energy by either moving faster or moving out, away from the nucleus. So they move to a higher energy level. Sometime later, the energy is given out as radiation as the electrons slow down or move back in.

Lines are seen in the spectrum because the energy of electrons is *quantised*. This means that only certain energy levels are allowed in the atom and the electrons can only move between these levels. So each line in an emission spectrum is the result of electrons moving from one quantised energy level to a lower one. The difference in energy between the two levels is related to the frequency of the radiation by Planck's constant: $\Delta E = h\nu$



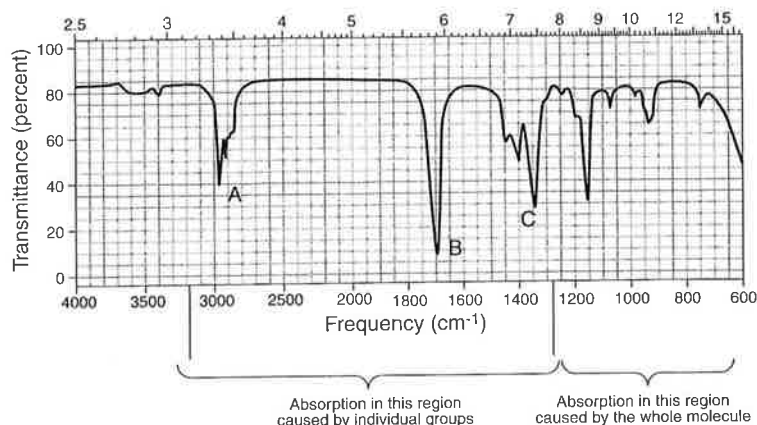
this radiation is one of the lines in the spectrum

Infrared spectra

Explaining the spectrum

In this kind of spectrometry, infrared radiation is absorbed causing the atoms at each end of a bond to vibrate relative to each other. Like a stretched spring between two masses, the energy absorbed by a bond depends on the masses of the atoms and the bond strength. So, as in visible and UV spectra, the vibrational energies are quantised, each kind of bond absorbing its own band of radiation. Only those molecules with charge separation along their bonds absorb in the *infrared* region and only if this results in a change of dipole moment.

The wavelengths of the energy absorbed, often expressed in **wavenumbers**, appear as dips in the spectrum. Some of these dips indicate the presence of particular functional groups and others are characteristic of the whole molecule.



The greenhouse effect

The amount of carbon dioxide (and other gases) is increasing in the atmosphere as the result of burning fossil fuels and other human activities. It is suggested that the increasing amounts of these gases are absorbing more infrared radiation — heat — and so causing the atmosphere to heat up producing the effect known as global warming or the greenhouse effect.

Infrared spectrum of butanone

A: energy absorbed by C – H bonds stretching

B: energy absorbed by C = O bonds stretching

C: energy absorbed by $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$ bonds bending

Nuclear magnetic resonance spectra

Explaining the spectrum

Nuclei with an odd number of protons or neutrons have a magnetic moment as though they were spinning in a magnetic field. Normally, there is an equal number of atoms in a sample with each direction of spin and so they cancel each other out. When a strong magnetic field is applied, half the spins align with the field and half against it. This splits the nuclei in terms of energy. Nuclear magnetic resonance, NMR, happens when the nuclei aligned with the field absorb energy and change the direction of their spin. The amount of energy absorbed while they do this depends on the nucleus and its molecular environment and on the magnetic field strength. So NMR can reveal the presence of hydrogen atoms (and other nuclei) in different functional groups. For example, in propanol, there are CH₃—, —CH₂—, and —OH groups and the hydrogens in each of these groups will come into resonance at different frequencies. The frequencies are always measured relative to those for the protons in tetramethylsilane, TMS.

