

# Introduction to Spectroscopy

## What is spectroscopy?

One of the frustrations of being a chemist is the fact that no matter how hard you stare at your test tube or round-bottomed flask you can't actually see the individual molecules you have made! Even though your product looks the right colour and seems to give sensible results when you carry out chemical tests, can you be really sure of its precise structure?

Fortunately, help is at hand. Although you might not be able to 'see' molecules, they do respond when light energy hits them, and if you can observe that response, then maybe you can get some information about that molecule. This is where **spectroscopy** comes in.

Spectroscopy is the study of the way **light** (electromagnetic radiation) and matter interact. There are a number of different types of spectroscopic techniques and the basic principle shared by all is to shine a beam of a particular electromagnetic radiation onto a sample and observe how it responds to such a stimulus; allowing scientists to obtain information about the structure and properties of matter.

## What is light?

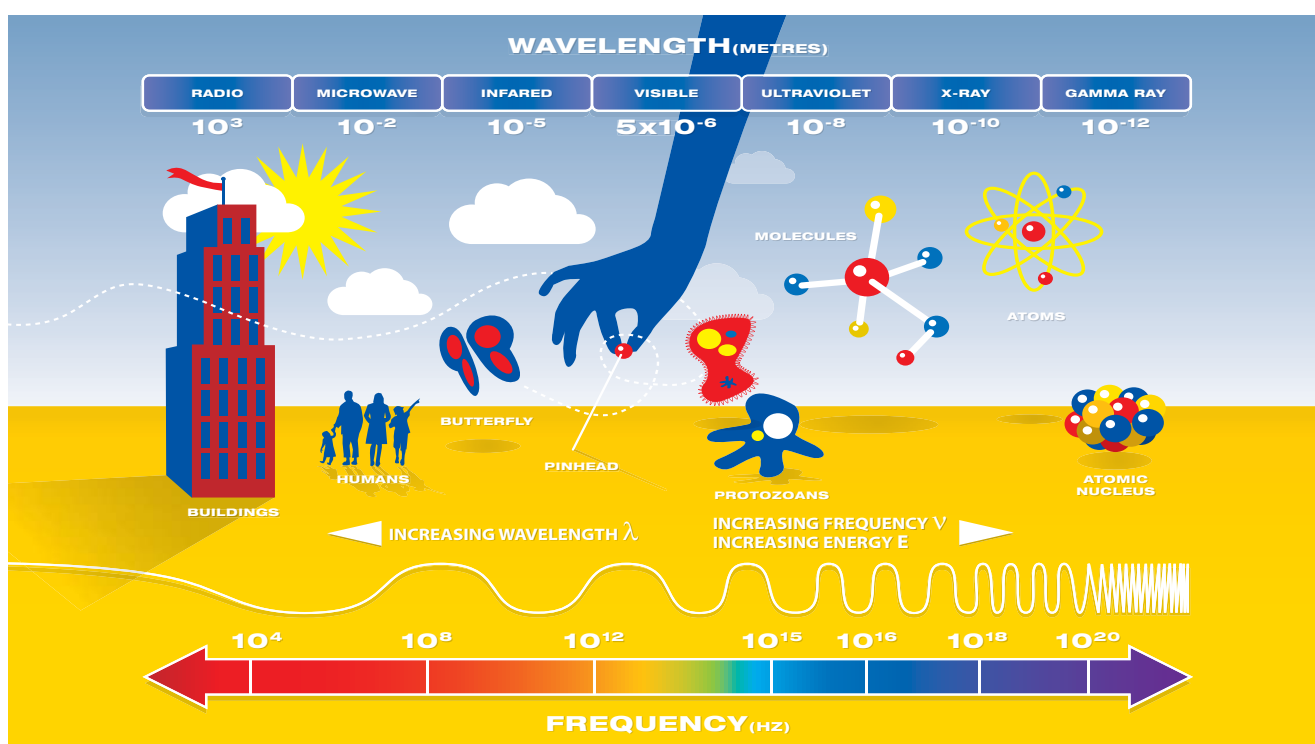
Light carries **energy** in the form of tiny particles known as photons. Each photon has a discrete amount of energy, called a quantum. **Light** has wave properties with **characteristic wavelengths** and **frequency** (see the diagram below).

The **energy** of the photons is related to the **frequency ( $\nu$ )** and **wavelength ( $\lambda$ )** of the light through the two **equations**:

$$E = h\nu \text{ and } \nu = c/\lambda$$

(where  $h$  is Planck's constant and  $c$  is the speed of light). Therefore, high energy radiation (light) will have high frequencies and short wavelengths.

The range of wavelengths and frequencies in light is known as the **electromagnetic spectrum**. This spectrum is divided into various regions extending from very short wavelength, high energy radiation (including gamma rays and X-rays) to very long wavelength, low energy radiation (including microwaves and broadcast radio waves). The visible region (white light) only makes up a small part of the electromagnetic spectrum considered to be 380-770 nm. [Note that a nanometre is  $10^{-9}$  metres].



When matter absorbs electromagnetic radiation the change which occurs depends on the type of radiation, and therefore the amount of energy, being absorbed. Absorption of energy causes an electron or molecule to go from an initial energy state (ground state) to a high energy state (excited state) which could take the form of the increased **rotation, vibration** or **electronic excitation**. By studying this change in energy state scientists are able to learn more about the physical and chemical properties of the molecules.

- **Radio waves** can cause nuclei in some atoms to change magnetic orientation and this forms the basis of a technique called **nuclear magnetic resonance (NMR)** spectroscopy.
- Molecular rotations are excited by **microwaves**.
- Electrons are promoted to higher orbitals by **ultraviolet** or **visible** light.
- Vibrations of bonds are excited by **infrared** radiation.

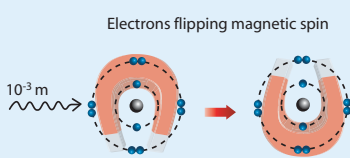
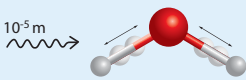
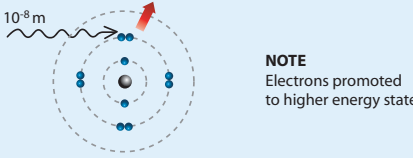
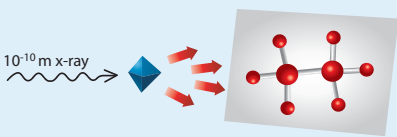
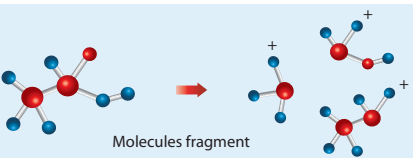
The energy states are said to be quantised because a photon of precise energy and frequency (or wavelength) must be absorbed to excite an electron or molecule from the ground state to a particular excited state.

Since molecules have a unique set of energy states that depend on their structure, **IR, UV-visible** and **NMR** spectroscopy will provide valuable information about the structure of the molecule.

To 'see' a molecule we need to use light having a wavelength smaller than the molecule itself (approximately  $10^{-10}$  m). Such radiation is found in the X-ray region of the electromagnetic spectrum and is used in the field of **X-ray crystallography**. This technique yields very detailed three-dimensional pictures of molecular structures – the only drawback being that it requires high quality crystals of the compound being studied. Although other spectroscopic techniques do not yield a three-dimensional picture of a molecule they do provide information about its characteristic features and are therefore used routinely in structural analysis.

**Mass spectrometry** is another useful technique used by chemists to help them determine the structure of molecules. Although sometimes referred to as mass spectroscopy it is, by definition, not a spectroscopic technique as it does not make use of electromagnetic radiation. Instead the molecules are ionised using high energy electrons and these molecular ions subsequently undergo fragmentation. The resulting mass spectrum contains the mass of the molecule and its fragments which allows chemists to piece together its structure.

In all spectroscopic techniques only very small quantities (milligrams or less) of sample are required, however, in mass spectrometry the sample is destroyed in the fragmentation process whereas the sample can be recovered after using IR, UV-visible and NMR spectroscopy.

TECHNIQUE	RADIATION		WHAT CAN IT SEE?
Nuclear Magnetic Resonance (NMR) spectroscopy	Radio waves ( $10^{-3}$ m)		How neighbouring atoms of certain nuclei (e.g. $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ , $^{31}\text{P}$ ) in a molecule are connected together, as well as how many atoms of these type are present in different locations in the molecule.
Infra-red spectroscopy	Infra-red ( $10^{-5}$ m)		The functional groups which are present in a molecule.
UV-visible spectroscopy	Ultra-violet ( $10^{-8}$ m)		Conjugated systems (i.e. alternating single and double bonds) in organic molecules as well as the metal-ligand interactions in transition metal complexes.
X-ray crystallography	X-rays ( $10^{-10}$ m)		How all the atoms in a molecule are connected in a three-dimensional arrangement.
Mass spectrometry	Non-spectroscopic technique		The mass to charge ratio of the molecular ion (i.e. the molecular weight) and the fragmentation pattern which may be related to the structure of the molecular ion.