Chem Factsheet

www.curriculum-press.co.uk Number 81

UV and Visible Spectroscopy

To succeed in this topic you need to:
- **Be familiar with the other spectroscopic techniques (outlined in Factsheets 54, 55 and 61);**
- **Be able to name and recognise organic molecules.**

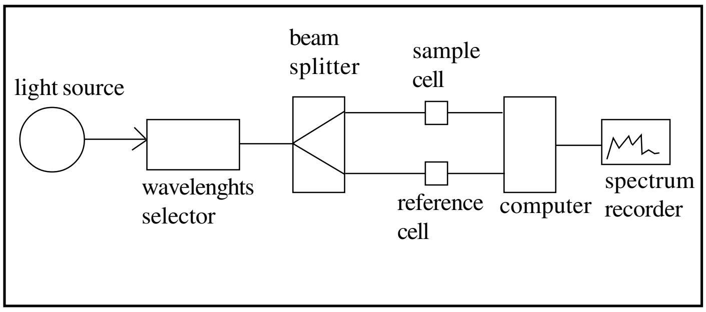
After working through this Factsheet you will:
- **Have a basic understanding of how a UV-Visible spectrometer works;**
- **Know how UV-Visible spectra can assist analytical chemists;**
- **Be able to recognise UV-Visible spectra;**
- **Be able to assign peaks on a UV-Visible spectrum if given the necessary data;**
- **Recognise conjugated systems within molecules;**
- **Be aware of the effect of conjugation on UV-Visible spectra.**

Ultraviolet-visible spectroscopy is a useful tool for the analytical chemist when presented with an unknown organic compound. As with IR spectra, there is little for the A2 level candidate to fear as at this level only a basic understanding and interpretation of spectra is required.

All organic molecules absorb radiation in the IR region of the electromagnetic spectrum (Factsheet 54). Because different bonds absorb different wavelengths of IR, the spectra are used to characterise molecules.

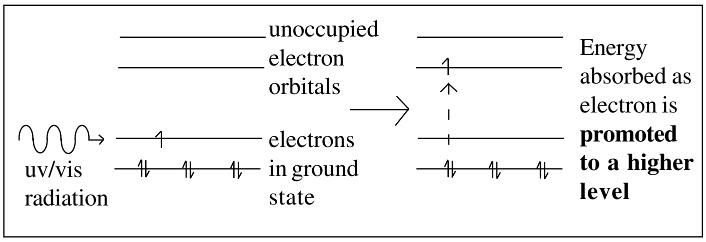
The operation and workings of a UV-Visible spectrometer are similar to those of the IR spectrometer. The key difference, of course, is that it is UV and visible light that is passed through the sample and not IR radiation.

Fig 1. UV spectrometer



The useful UV region is from around 200 to 400 nm wavelength, and the visible light region is from around 400 to 750 nm wavelength.

This high energy radiation has the ability to cause electronic transitions in certain bonds.



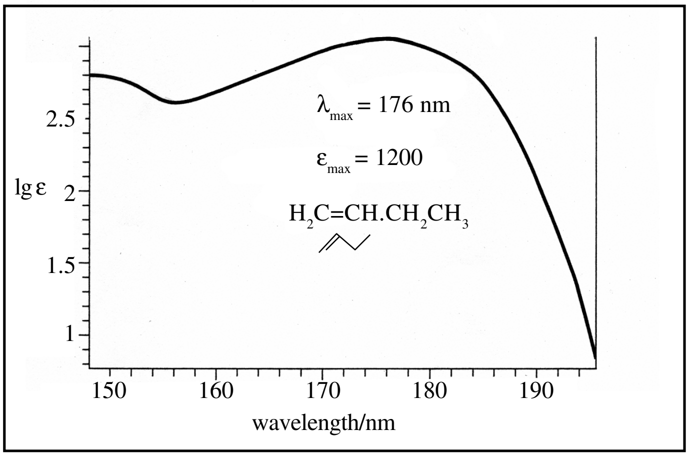
Electrons in different environments absorb UV-Visible radiation of different wavelengths, so a characteristic absorption spectrum can be generated. The absorbing groups are called **chromophores**.

Typical absorptions for simple isolated functional groups:

Chromophore	Absorption wavelength λ_{max} (nm)
Nitrile	160
Alkyne	170
Alkene	175
Alcohol	180
Ether	180
Ketone	180 280
Aldehyde	190 290
Amine	190
Acid	205
Ester	205
Amide	210
Thiol	210
Nitro	271
Azo	340

The generated absorption spectra have the following appearance:

Fig 2. Butene



The spectrum is shown as the strength of absorption, as lg ε, on the y-axis against the wavelength, λ, in nm. The spectra tend to show broad peaks, with chemists looking for the maxima of these peaks to identify the wavelength at maximum absorption, λ_{max}, and the corresponding value of lg ε, from which ε is calculated.

For the above example, the spectrum indicates the presence of a C=C group due to the absorption peak being present at 176 nm. Other spectroscopic techniques such as mass spectrometry would help to identify the alkene as but-1-ene.

As each compound has its own unique UV-Visible absorption spectrum, like a fingerprint, analytical chemists can compare the spectrum of an unknown compound with many others on a vast database and hence identify the unknown chemical.

It should be pointed out that due to the nature of the UV-Visible spectra, the broad quite featureless peaks which can often engulf one another if more than one chromophore is present, are not as useful as IR or NMR in terms of identifying molecular structure. UV-Visible spectroscopy is most useful for identifying π-electron systems. Because the π electrons are less strongly held in their ground state orbitals than σ electrons, π electrons absorb light intensely – producing clear, characteristic absorption peaks.

The most common use of UV-Visible spectroscopy is in the detection of multiple carbon-carbon bonds and detecting whether or not they are part of a **conjugated system**.

A conjugated system of double bonds is where a carbon chain has double bonds **alternating** with single bonds.

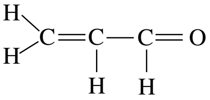
Examples of conjugated alkenes:

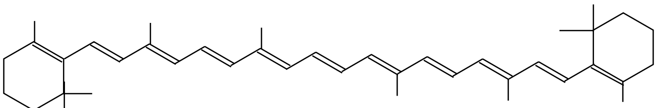
Buta-1,3-diene	CH_2=CH-CH=CH_2
Hexa-1,3,5-triene	CH_2=CH-CH=CH-CH=CH_2

Contrast these structures with the following **isolated** systems (where there is <u>**not**</u> conjugation).

Pent-1-ene	CH_2=CH-CH_2-CH_2-CH_3
Hexa-1,4-diene	CH_2=CH-CH_2-CH=CH-CH_3

Conjugation does not just occur in simple alkenes, there is conjugation in the following molecules also:


$$H_2C{=}\underset{H}{C}{-}\underset{H}{C}{=}O$$



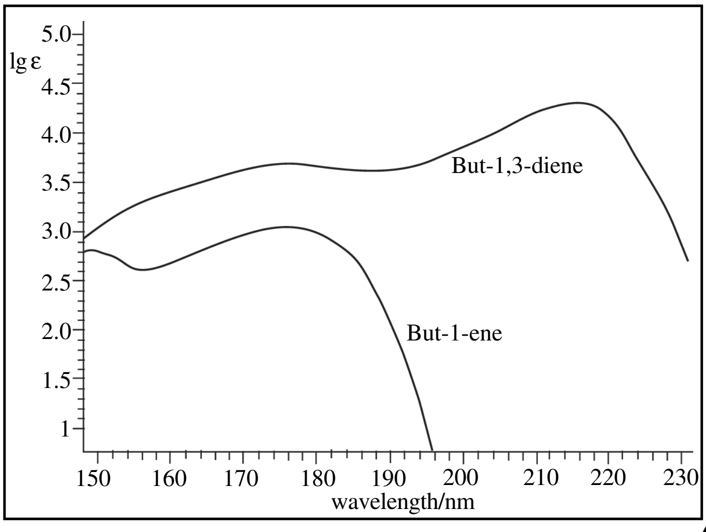
β- carotene (from carrots)

Conjugation has a marked effect on the UV-Visible spectrum of a compound. If conjugation is present in a molecule, the absorption peaks are:

- Shifted to a longer wavelength
- Significantly larger, more intense peaks

The following trace contrasts the absorption spectra of but-1-ene, with an isolated C=C, and buta-1,3-diene, a conjugated system Fig 3..

Fig 3. Absorption spectra



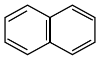
Consequently UV-Visible spectroscopy can be used to help assign where double bonds may be occurring in a carbon chain.

Key points for success at A-level:
- Be able to recognise UV-Visible spectra.
- Use supplied data to assign peaks.
- Be able to recognise conjugated and isolated systems.
- Be aware of the effect of conjugation on a spectrum.

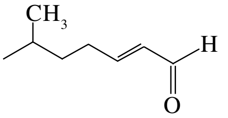
Practice Questions

1. Do the following molecules contain conjugated systems?

   (a) CH_2=CHCH=CHCH=$CHCH_3$

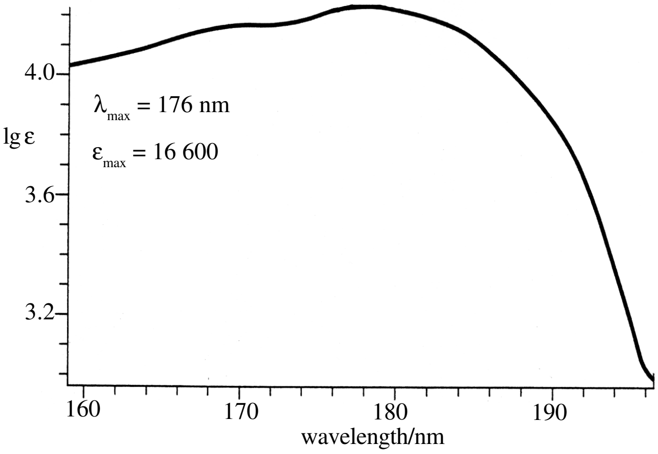
   (b) 

   (c) octa-1,4-diene

   (d) 

2. Using IR and mass spectrometry chemists identified an unknown compound as a pentadiene, C_5H_8, but were unable to assign the positions of the double bonds within the molecule.

   What structural information can be gained from the UV-Visible spectrum of the compound shown below?



Hint: Use the data table showing typical absorptions for isolated functional groups.

Answers.

1. (a) yes
   (b) yes
   (c) no
   (d) yes
2. Penta-1,4-diene contains just one type of functional group, the C=C double bond. The expected position for the absorption peak for a C=C double bond is at λ = 175 nm. In the illustrated spectrum, the absorption peak appears close to this value. A conclusion can then be made that the pentadiene does <u>**not**</u> contain a conjugated system, then the double bonds are isolated.
   The compound is likely therefore be pent-1,4-diene.
   CH_2=CH-CH_2-CH=CH_2

Acknowledgements: This Factsheet was researched and written by Kieron Heath. ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***