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4. Ultraviolet/visible spectroscopy

Visible light absorption is known to all of us, because this is what causes objects to be coloured. For example, a blue dye appears blue because the light at the red end of the spectrum is absorbed, leaving the blue light to be transmitted (*Fig. 1*).

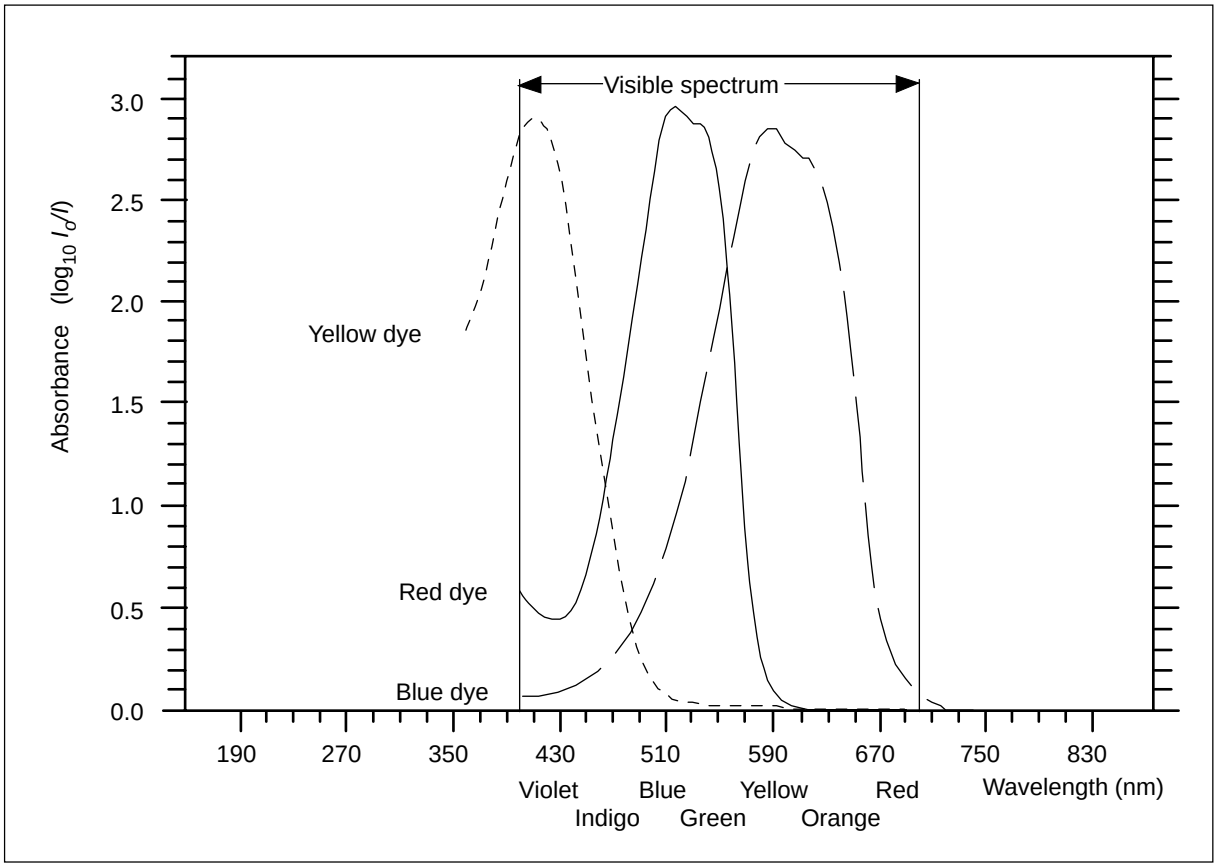

Figure 1 Absorption of light by dyes

The theory

Visible light lies in the wavelength range 4.0 – 7.0 x 10^{-7} m (*Fig. 2*). To keep the numbers more manageable it is usually quoted in nanometres (10^{-9} m) so that the range becomes 400–700 nm. When light is absorbed by a material, valence (outer) electrons are promoted from their normal (ground) states to higher energy (excited) states.

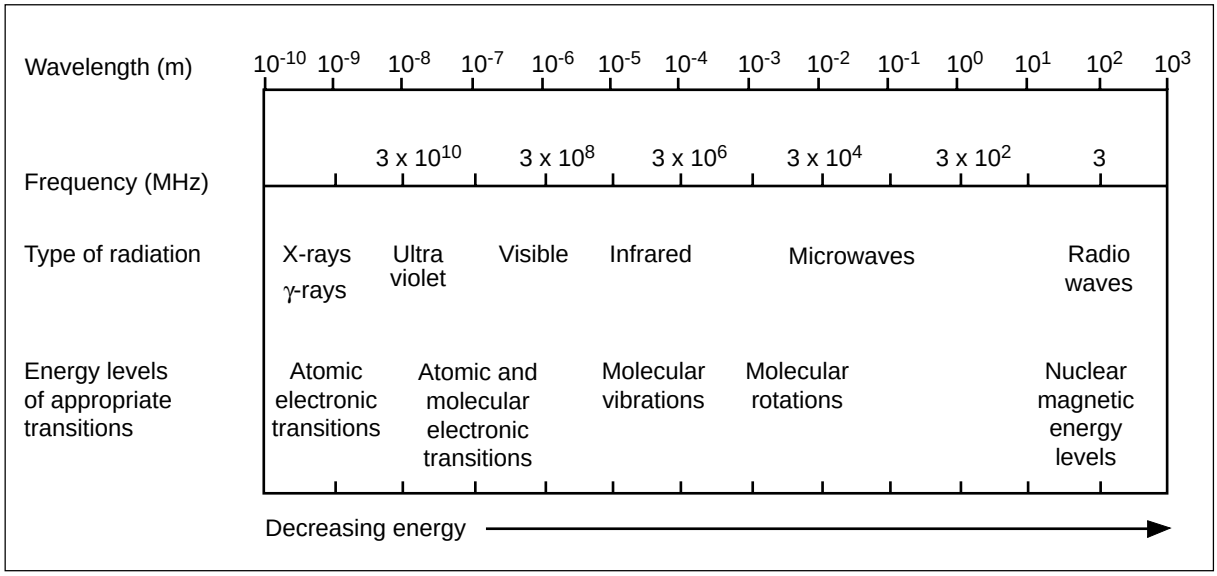

Figure 2 Regions of the electromagnetic spectrum

The energy of visible light depends on its frequency, and is approximately equivalent to 170 kJ mol^{-1} (mole of photons) for red light and 300 kJ mol^{-1} for blue light. The promotion of electrons to different energy levels is not restricted to electromagnetic radiation in the visible part of the spectrum; it can also occur in the ultraviolet region. To encompass the majority of electron transitions the spectrum between 190 and 900 nm is usually considered (Table 1).

Table 1 Frequency, wavelength and energy of radiation in the part of the spectrum used for ultraviolet/visible spectroscopy

Frequency (ν) (Hz)	Wavelength (λ) (m)	(nm)	Energy (kJ mol^{-1})	
3.33×10^{14}	9.0×10^{-7}	900	137.5	(infrared)
4.29×10^{14}	7.0×10^{-7}	700	171.2	(red light)
7.50×10^{14}	4.0×10^{-7}	400	299.3	(blue light)
1.58×10^{15}	1.9×10^{-7}	190	630.5	(ultraviolet)

Frequency, wavelength and energy are interrelated:

$$c = \nu\lambda$$

where c = velocity of light (3.00×10^8 ms^{-1})
ν = frequency in Hz
λ = wavelength in m

and

$E = h\nu$ or $E = h\nu L$ for one mole of photons

where E = energy of one mole of radiation
h = Planck's constant (6.63×10^{-34} Js)
L = Avogadro constant (6.02×10^{23} mol^{-1})

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The origin of the absorptions

Valence electrons can generally be found in one of three types of electron orbital:

1 single, or σ, bonding orbitals;

2 double or triple bonds (π bonding orbitals); and

3 non-bonding orbitals (lone pair electrons).

Sigma bonding orbitals tend to be lower in energy than π bonding orbitals, which in turn are lower in energy than non-bonding orbitals. When electromagnetic radiation of the correct frequency is absorbed, a transition occurs from one of these orbitals to an empty orbital, usually an antibonding orbital, σ^* or π^* (*Fig. 3*).

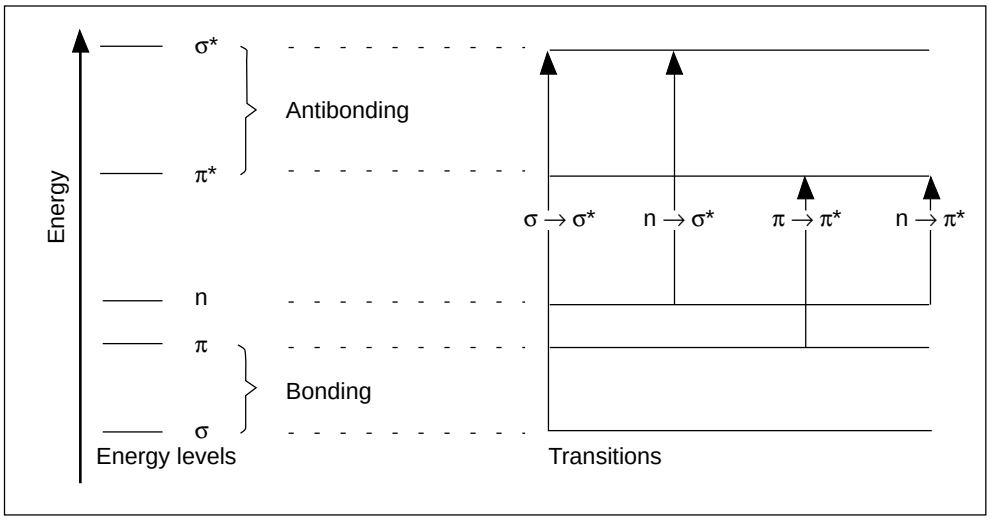

Figure 3 Electron transitions in ultraviolet/visible spectroscopy

The exact energy differences between the orbitals depends on the atoms present and the nature of the bonding system.

Most of the transitions from bonding orbitals are of too high a frequency (too short a wavelength) to measure easily, so most of the absorptions observed involve only $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions. A common exception to this is the d→d transition of d-block element complexes, but in most cases a knowledge of the precise origin of transitions is not required.

The spectrometer

Because only small numbers of absorbing molecules are required, it is convenient to have the sample in solution (ideally the solvent should not absorb in the ultraviolet/visible range however, this is rarely the case). In conventional spectrometers electromagnetic radiation is passed through the sample which is held in a small square-section cell (usually 1 cm wide internally). Radiation across the whole of the ultraviolet/visible range is scanned over a period of approximately 30 s, and radiation of the same frequency and intensity is simultaneously passed through a reference cell containing only the solvent. Photocells then detect the radiation transmitted and the spectrometer records the absorption by comparing the difference between the intensity of the radiation passing through the sample and the reference cells (*Fig. 4*). In the latest spectrometers radiation across the whole range is monitored simultaneously, see page 111.

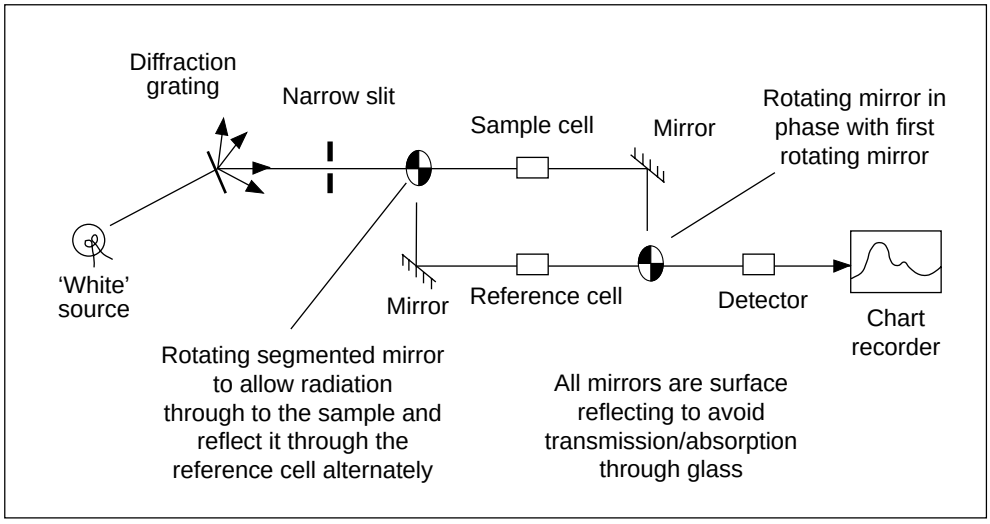

Figure 4 Diagram showing how the ultraviolet/visible spectrometer works

No single lamp provides radiation across the whole of the range required, so two are used. A hydrogen or deuterium discharge lamp covers the ultraviolet range, and a tungsten filament (usually a tungsten/halogen lamp) covers the visible range. The radiation is separated according to its frequency/wavelength by a diffraction grating followed by a narrow slit. The slit ensures that the radiation is of a very narrow waveband – *ie* it is monochromatic.

The cells in the spectrometer must be made of pure silica for ultraviolet spectra because soda glass absorbs below 365 nm, and pyrex glass below 320 nm.

Detection of the radiation passing through the sample or reference cell can be achieved by either a photomultiplier or a photodiode, that converts photons of radiation into tiny electrical currents; or a semiconducting cell (that emits electrons when radiation is incident on it) followed by an electron multiplier similar to those used in mass spectrometers (see page 8). The spectrum is produced by comparing the currents generated by the sample and the reference beams.

Modern instruments are self-calibrating, though the accuracy of the calibration can be checked if necessary. Wavelength checks are made by passing the sample beam through glass samples (containing holmium oxide) that have precise absorption peaks, and the absorption is calibrated by passing the sample beam through either a series of filters, each with a specific and known absorption, or a series of standard solutions.

Absorption laws

Beer's law tells us that absorption is proportional to the number of absorbing molecules – *ie* to the concentration of absorbing molecules (this is only true for dilute solutions) – and Lambert's law tells us that the fraction of radiation absorbed is independent of the intensity of the radiation. Combining these two laws, we can derive the Beer-Lambert Law:

$$\log_{10} \frac{I_o}{I} = \varepsilon l c$$

where I_o = the intensity of the incident radiation
I = the intensity of the transmitted radiation

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ε = a constant for each absorbing material, known as the molar absorption coefficient (called the molar extinction coefficient in older texts) and having the units mol^{-1} dm^3 cm^{-1}, but by convention the units are not quoted
l = the path length of the absorbing solution in cm
c = the concentration of the absorbing species in mol dm^{-3}

The value of $\log_{10} (I_o/I)$ is known as the absorbance of the solution (in older texts it is referred to as the optical density), and can be read directly from the spectrum, often as 'absorbance units'. A useful constant is the molar absorption coefficient, ε, because it is independent of concentration and path length, whereas absorption depends upon both. The other useful piece of information is the wavelength at which maximum absorption occurs. This is given the symbol λ_{max} (*Fig. 5*). These two pieces of information alone are frequently sufficient to identify a substance, although identification is not the most common use of this technique. Conversely, if the values of ε and λ_{max} are known, the concentration of its solution can be calculated – this is the more common application. The values of both ε and λ_{max} are strongly influenced by the nature of the solvent, and for organic compounds, by the degree of substitution and conjugation.

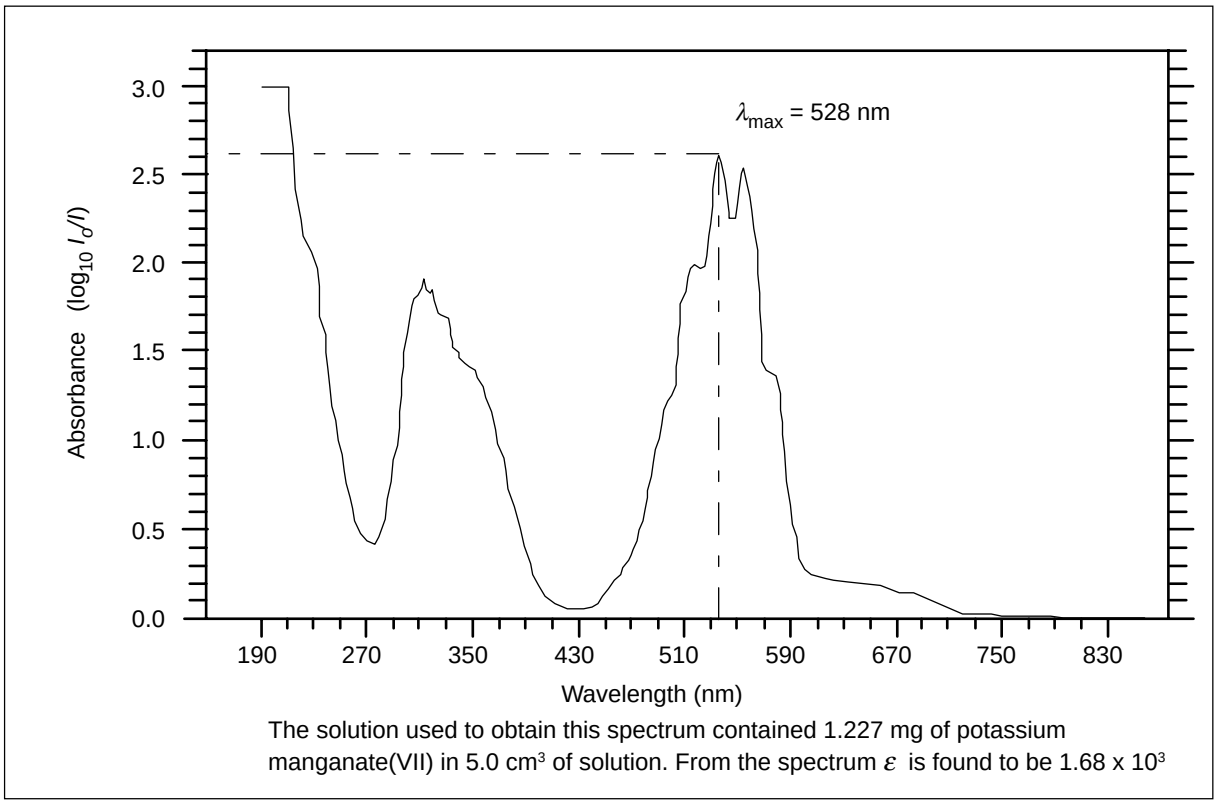

Figure 5 Ultraviolet/visible spectrum of potassium manganate (VII), $KMnO_4$, showing λ_{max}

Absorption curves

The energies of the orbitals involved in electronic transitions have fixed values, and as energy is quantised, it would be expected that absorption peaks in ultraviolet/visible spectroscopy should be sharp peaks. However this is rarely, if ever, actually

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observed. Instead, broad absorption peaks are seen. This is because a number of vibrational energy levels are available at each electronic energy level, and transitions can occur to and from the different vibrational levels (*Fig. 6*). This results in peak broadening. The situation is further complicated by the fact that different rotational energy levels are also available to absorbing materials (Table 2). Only in a few cases, often in the vapour phase or in non-polar solvents, can fine structure be observed – *eg* the vibrational fine structure of the 260 nm band of benzene (*Fig. 7*).

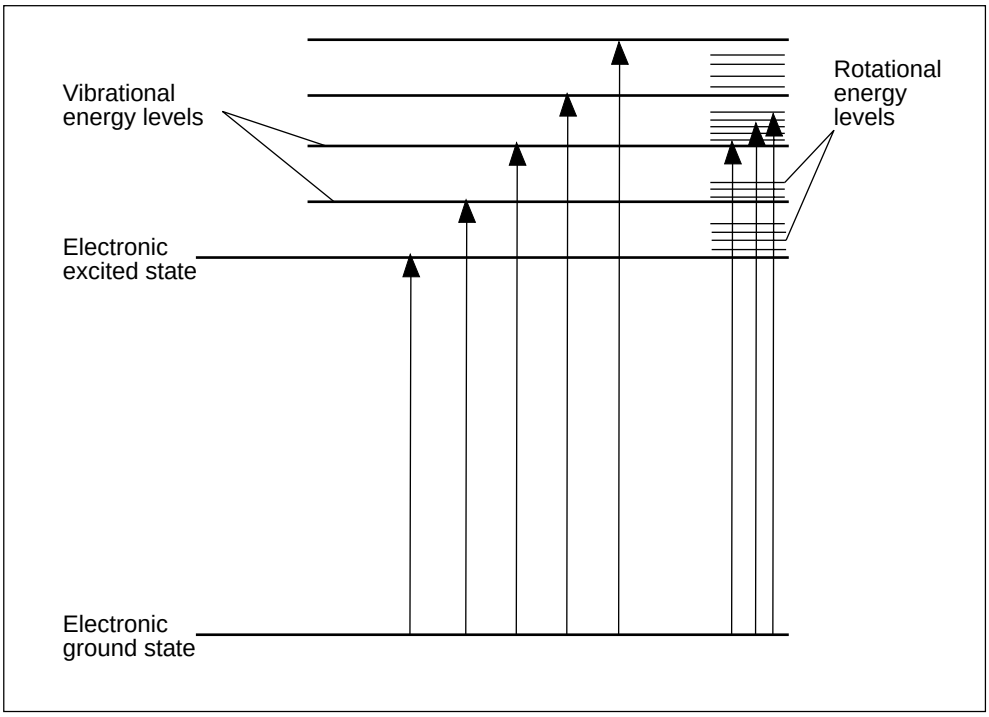

Figure 6 Electronic and vibrational levels

Table 2 Energy level differences

between electronic levels	≈100	kJ mol^{-1}
between vibrational levels	≈ 1	kJ mol^{-1}
between rotational levels	≈ 0.01	kJ mol^{-1}

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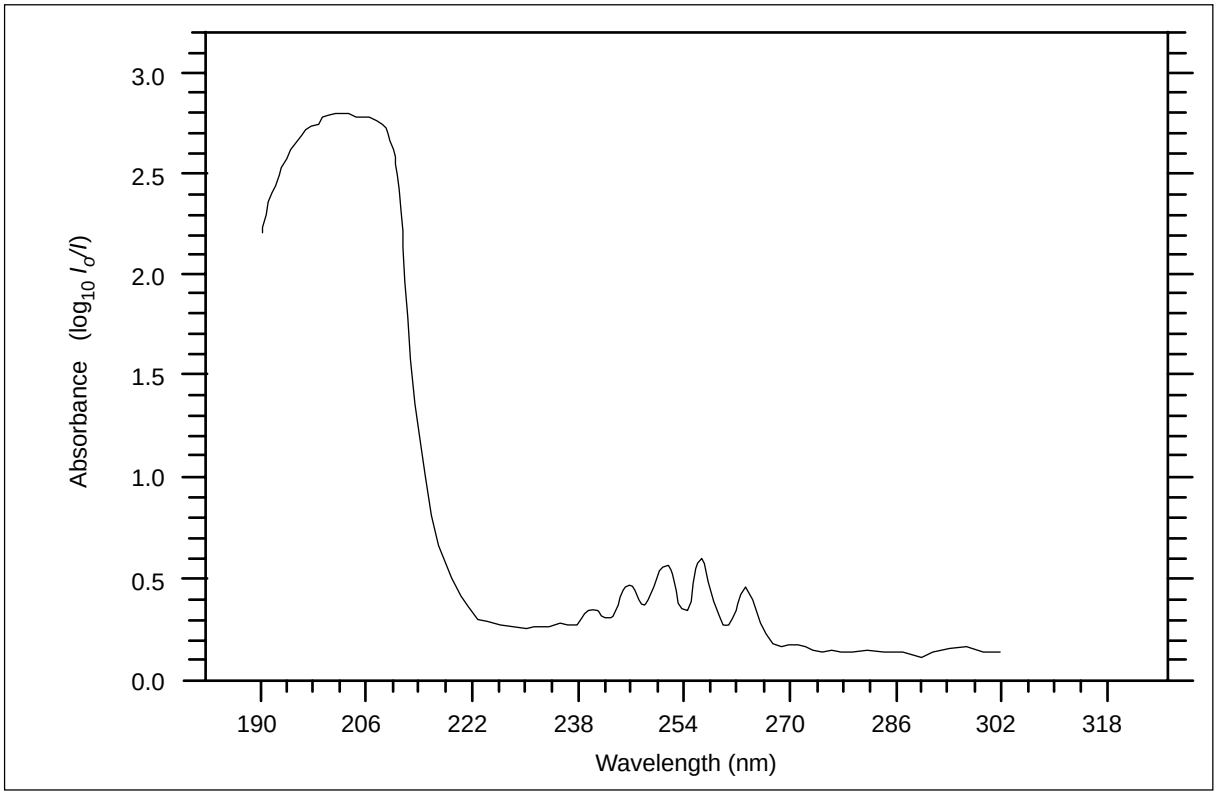

Figure 7 Ultraviolet/visible spectrum of benzene showing vibrational fine structure

Copper complexes

Uncomplexed copper(II) ions appear white or colourless because the transition between the highest occupied orbital and the lowest unoccupied orbital is at too short a wavelength to see. In hydrated copper (II) ions the energy levels of the 3d orbitals are split (*Fig. 8*), and when visible light is absorbed a transition is possible. For the hydrated copper (II) ion the absorption occurs at the red end of the spectrum (*Fig. 9*) hence the complex appears blue. The amount of splitting of the energy levels depends on the ligand, so if ammonia replaces water and ΔE increases, the colour of the complex becomes blue/violet *ie* absorption occurs at the middle of the visible spectrum *(Fig. 10)*. Note that ε is larger (both spectra contain the same concentration of copper ions).

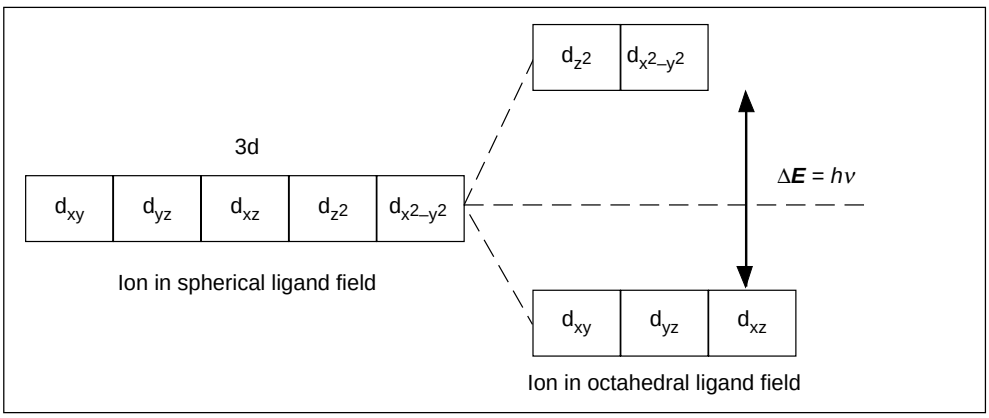

Figure 8 Splitting of d orbital energy levels in $Cu(H_2O)_6^{2+}$

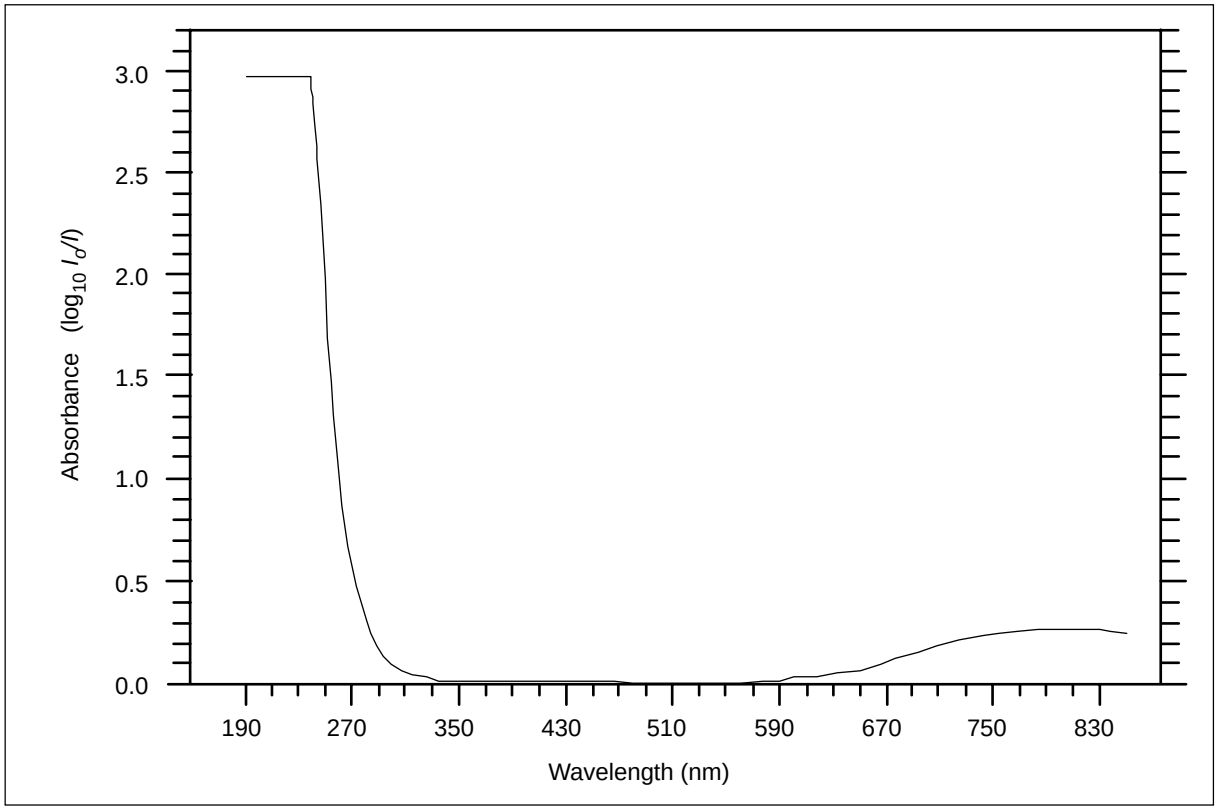

Figure 9 Ultraviolet/visible spectrum of $Cu(H_2O)_6^{2+}$

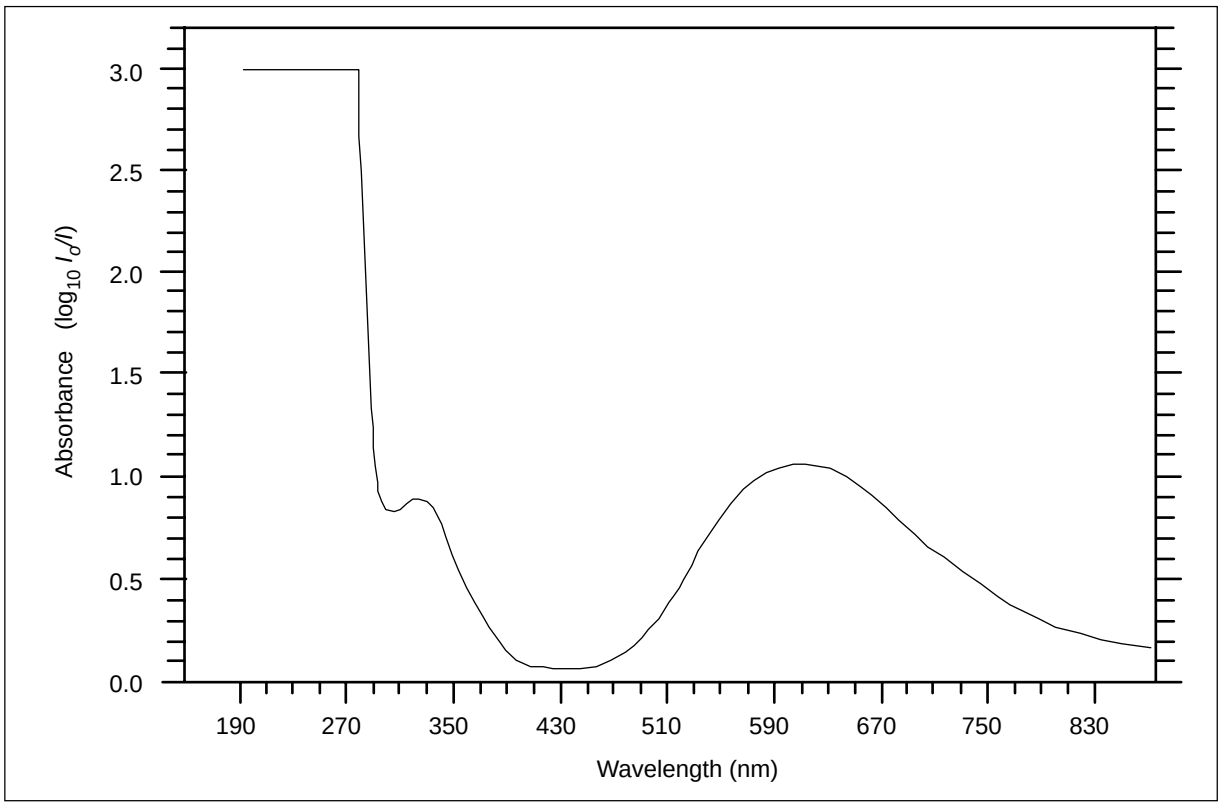

Figure 10 Ultraviolet/visible spectrum of $Cu(NH_3)_4(H_2O)_2^{2+}$

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Changing the ligands around a transition metal ion can increase the stability of the complex formed because the difference between the energy levels of the d orbitals increases (*Fig. 11*). (Stability in this context is taken to be the extent to which the complex will form from, or dissociate into, its constituents at equilibrium.)

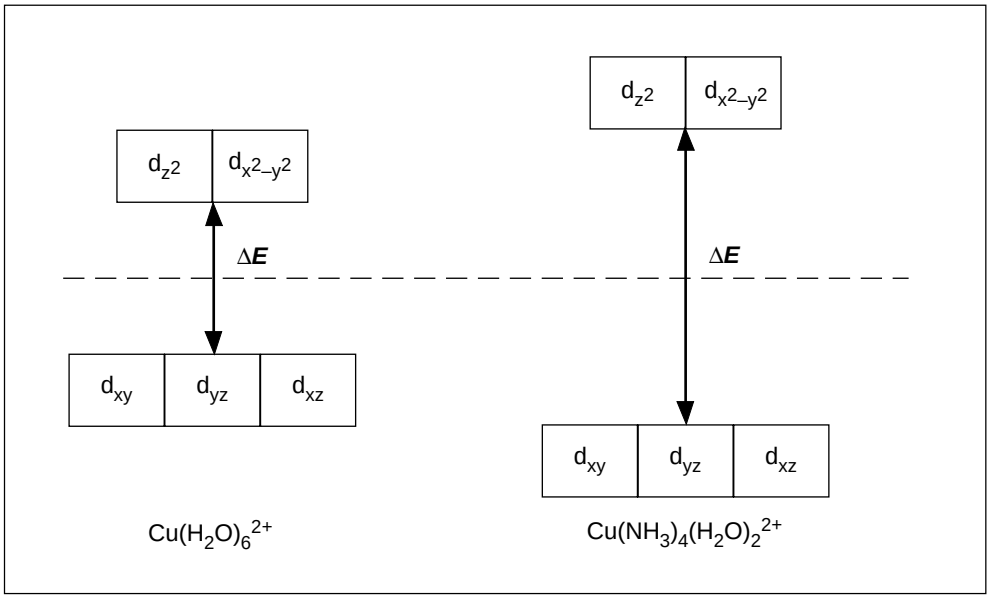

Figure 11 Increased splitting of d orbital energy levels

Some ligands giving increasing separation of energy levels (and therefore increasing stability to the ions) are:

I^-	smallest separation of energy levels
Br^-	
Cl^-	
OH^-	
F^-	
H_2O	
NH_3	
$NH_2CH_2CH_2NH_2$	
CN^-	largest separation of energy levels

This list forms part of the spectrochemical series and the order can vary depending on the metal ion in the complex.

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Stability of complex ions

It is possible to measure the relative stabilities of complexes through equilibrium constants called stability constants. If the successive replacement of water molecules by ammonia molecules in the $Cu(H_2O)_6^{2+}$ ion is used as an example, the first substitution can be described by the equation

$$Cu(H_2O)_6^{2+} + NH_3 \rightleftharpoons Cu(H_2O)_5NH_3^{2+} + H_2O$$

The equilibrium constant for this is

$$K_1 = \frac{[Cu(H_2O)_5NH_3^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]}$$

Similarly for the substitution of the second water molecule:

$$Cu(H_2O)_5NH_3^{2+} + NH_3 \rightleftharpoons Cu(H_2O)_4(NH_3)_2^{2+} + H_2O$$

there is an equilibrium constant

$$K_2 = \frac{[Cu(H_2O)_4(NH_3)_2^{2+}]}{[Cu(H_2O)_5NH_3^{2+}][NH_3]}$$

Likewise replacement of the third and fourth water molecules give rise to the constants K_3 and K_4:

$$Cu(H_2O)_4(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(H_2O)_3(NH_3)_3^{2+} + H_2O$$

$$K_3 = \frac{[Cu(H_2O)_3(NH_3)_3^{2+}]}{[Cu(H_2O)_4(NH_3)_2^{2+}][NH_3]}$$

$$Cu(H_2O)_3(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cu(H_2O)_2(NH_3)_4^{2+} + H_2O$$

$$K_4 = \frac{[Cu(H_2O)_2(NH_3)_4^{2+}]}{[Cu(H_2O)_3(NH_3)_3^{2+})][NH_3]}$$

It is also possible to quote a constant for the replacement of four water molecules together.

$$K = \frac{[Cu(H_2O)_2(NH_3)_4^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]^4}$$

This is in fact the product of the four step-wise constants *ie*

$$K = K_1 \times K_2 \times K_3 \times K_4$$

The values of the constants quoted are:

$K_1 = 1.78 \times 10^4$ $K_2 = 4.07 \times 10^3$ $K_3 = 9.55 \times 10^2$
$K_4 = 1.74 \times 10^2$ $K = 1.20 \times 10^{13}$

Complexes with large stability constants are more stable than those with small constants. For example, using chloride ions to replace the water ligands surrounding copper ions gives a less stable complex. This is demonstrated simply by adding aqueous ammonia to a solution containing the $CuCl_4^{2-}$ ion – the solution turns from yellow to deep blue. The reduced stability is also evident in the smaller stability constants:

$K_1 = 631$ $K_2 = 398$ $K_3 = 3.09$ $K_4 = 5.37$ $K = 4.17 \times 10^5$

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Chromophores

Many organic molecules absorb ultraviolet/visible radiation and this is usually because of the presence of a particular functional group. The groups that actually absorb the radiation are called chromophores.

Mathematical treatments of the energy levels of orbital systems suggest that some electronic transitions are statistically probable (said to be 'allowed', and these absorptions are strong, and tend to have ε values in excess of 10 000). Other transitions have a probability of zero – they are not expected to occur at all – and are said to be 'forbidden' but they frequently do occur, to give weak bands with ε values that rarely exceed 1 000. Some particularly useful forbidden transitions are: d→d absorptions of transition metals; the $n \rightarrow \pi^*$ absorption of carbonyl groups at *ca* 280 nm; and the $\pi \rightarrow \pi^*$ absorption of aromatic compounds at *ca* 230–330 nm, depending on the substituents on the benzene ring.

Factors af fecting absorption

The solvent

The excited states of most $\pi \rightarrow \pi^*$ transitions are more polar than their ground states because a greater charge separation is observed in the excited state. If a polar solvent is used the dipole–dipole interaction reduces the energy of the excited state more than the ground state, hence the absorption in a polar solvent such as ethanol will be at a longer wavelength (lower energy, hence lower frequency) than in a non-polar solvent such as hexane (*Figs. 12a* and *12b*).

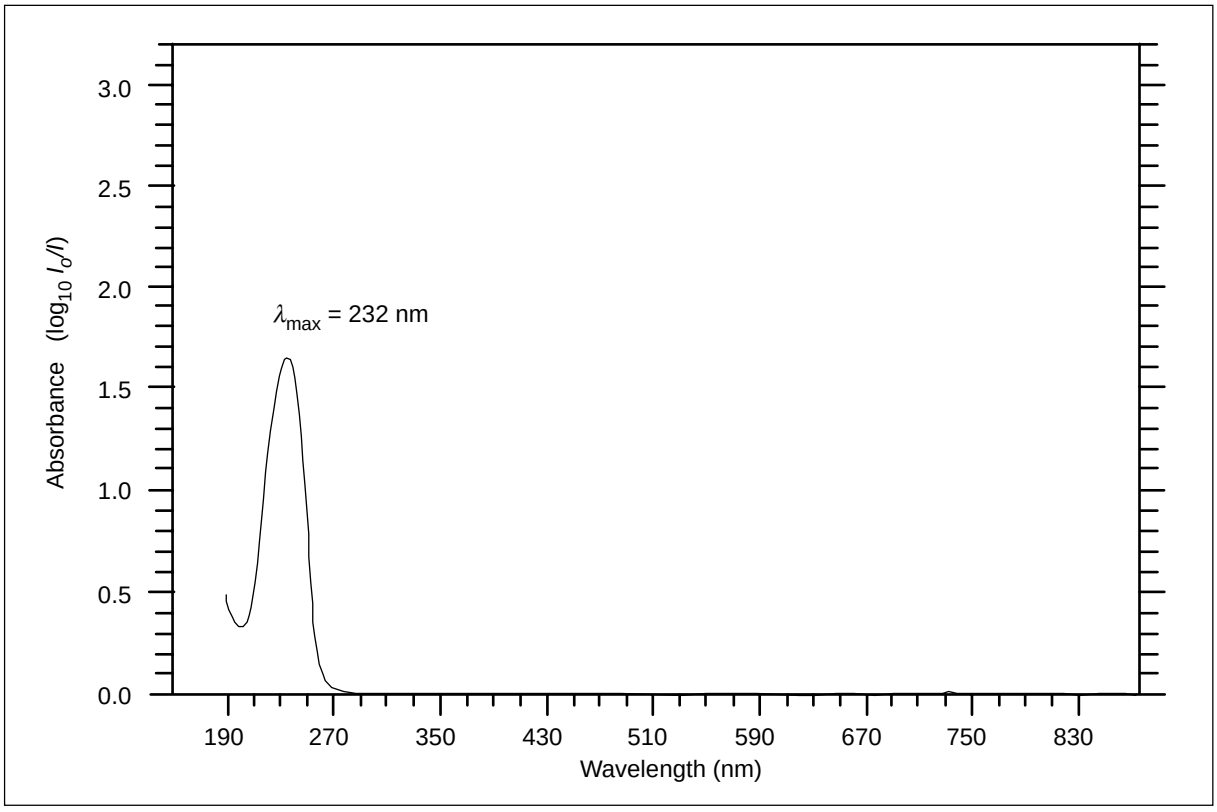

Figure 12a Ultraviolet/visible spectrum of 4-methyl-3-penten-2-one (mesityl oxide) in hexane

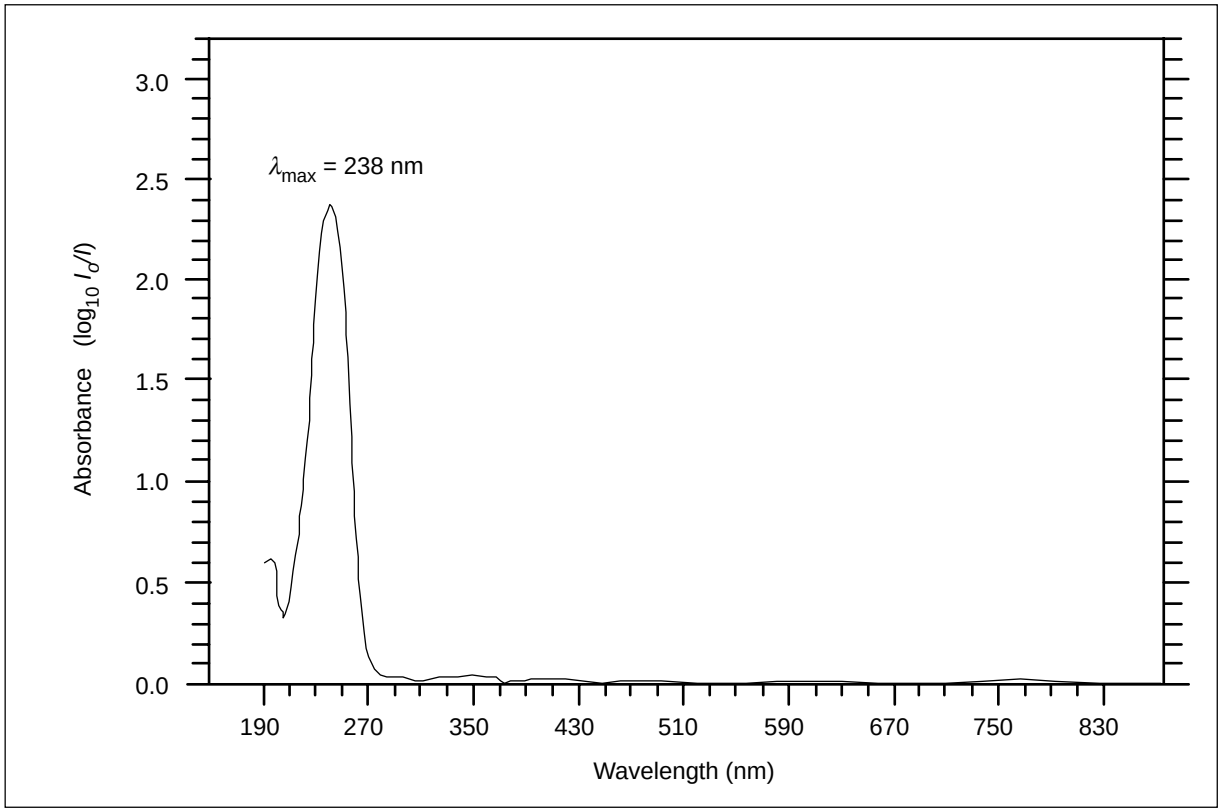

Figure 12b Ultraviolet/visible spectrum of 4-methyl-3-penten-2-one (mesityl oxide) in ethanol

The reverse is also observed if the excited state reduces the degree of hydrogen bonding. Here the transitions are $n \rightarrow \pi^*$ and the shift of wavelength is due to the lesser extent that the solvent can hydrogen bond to the excited state. Carbonyl groups in particular hydrogen bond to their solvent. For example changing from hexane to water as the solvent for propanone, the absorption maximum moves from 280 to 257 nm (*Figs. 13a, 13b* and Table 3).

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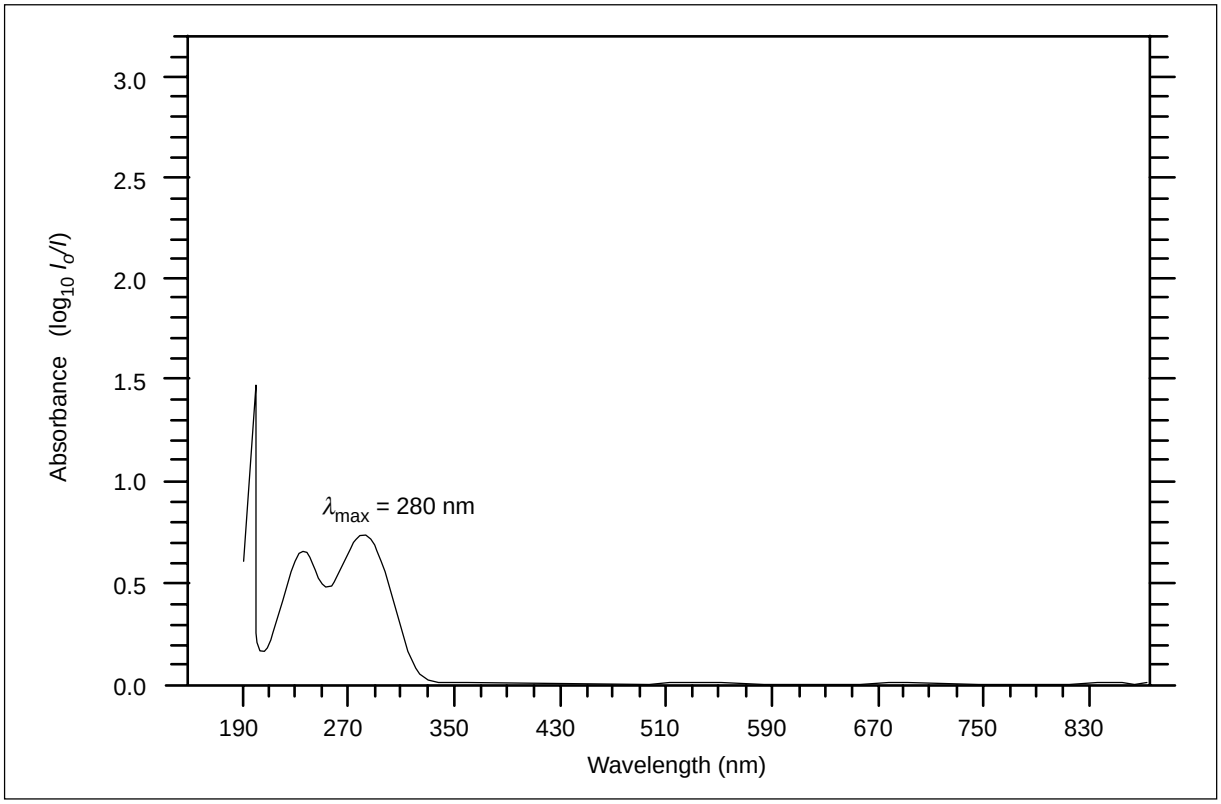

Figure 13a Ultraviolet/visible spectrum of propanone in hexane

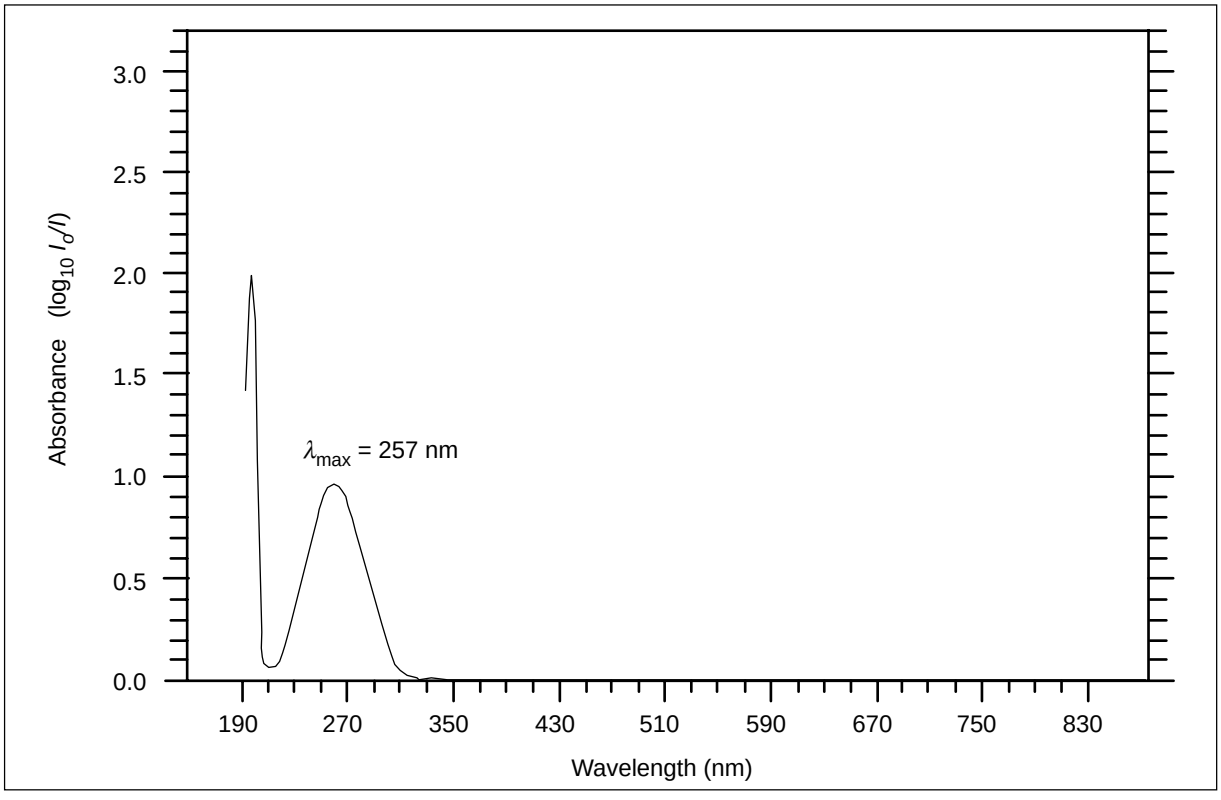

Figure 13b Ultraviolet/visible spectrum of propanone in water

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Table 3 The effect of the solvent on the absorption maximum of propanone

Solvent	λ_{max}/nm	ε at λ_{max}
Hexane	280	14.8
Trichloromethane	277	17.0
Ethanol	271	15.2
Water	257	17.4

Care must be taken when choosing a solvent, because many solvents absorb in the ultraviolet region. The minimum wavelengths at which some solvents are useful are given in Table 4.

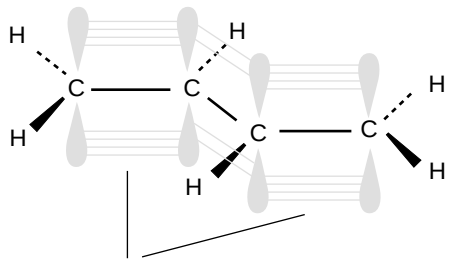
Table 4 Minimum wavelength at which different solvents are useful

Solvent	Minimum wavelength (nm)
Ethanonitrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Ethoxyethane	215
Dichloromethane	220
Trichloromethane	237
Tetrachloromethane	257

Degree of conjugation

Ethene, containing only one double bond, has an absorption maximum at 185 nm (ε = 10 000). If the carbon chain length is increased this peak shifts to a slightly longer wavelength because the σ bonded electrons of the alkyl group interact with the π bond electrons in the double bond (*ie* the energy of the excited state is reduced).

The shift in wavelength is small compared with the effect of increasing the number of double bonds, especially if the electrons in the π systems (the double bonds) can interact with each other. The simplest example is buta-1,3-diene, CH_2=CH–CH=CH_2 (*Fig. 14*). Buta-1,3-diene has an absorption maximum at 220 nm, with an absorption coefficient of 20 000 – *ie* both the wavelength and the intensity of the absorption have increased. This difference arises because instead of the double bonds absorbing in isolation of each other the π system extends over the length of the carbon chain – *ie* the system is conjugated (or delocalised) – and lowers the energy of the excited state.



Overlap of these two pairs of orbitals results in the structure CH_2---CH---CH---CH_2

Figure 14 Conjugation in buta-1,3-diene

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The longer the conjugated carbon chain in the absorbing system, the greater the intensity of the absorption. This is shown by the spectra of the polyenes CH_3-$(CH{=}CH)_n$-CH_3, where n=3,4 and 5 (*Fig. 15*).

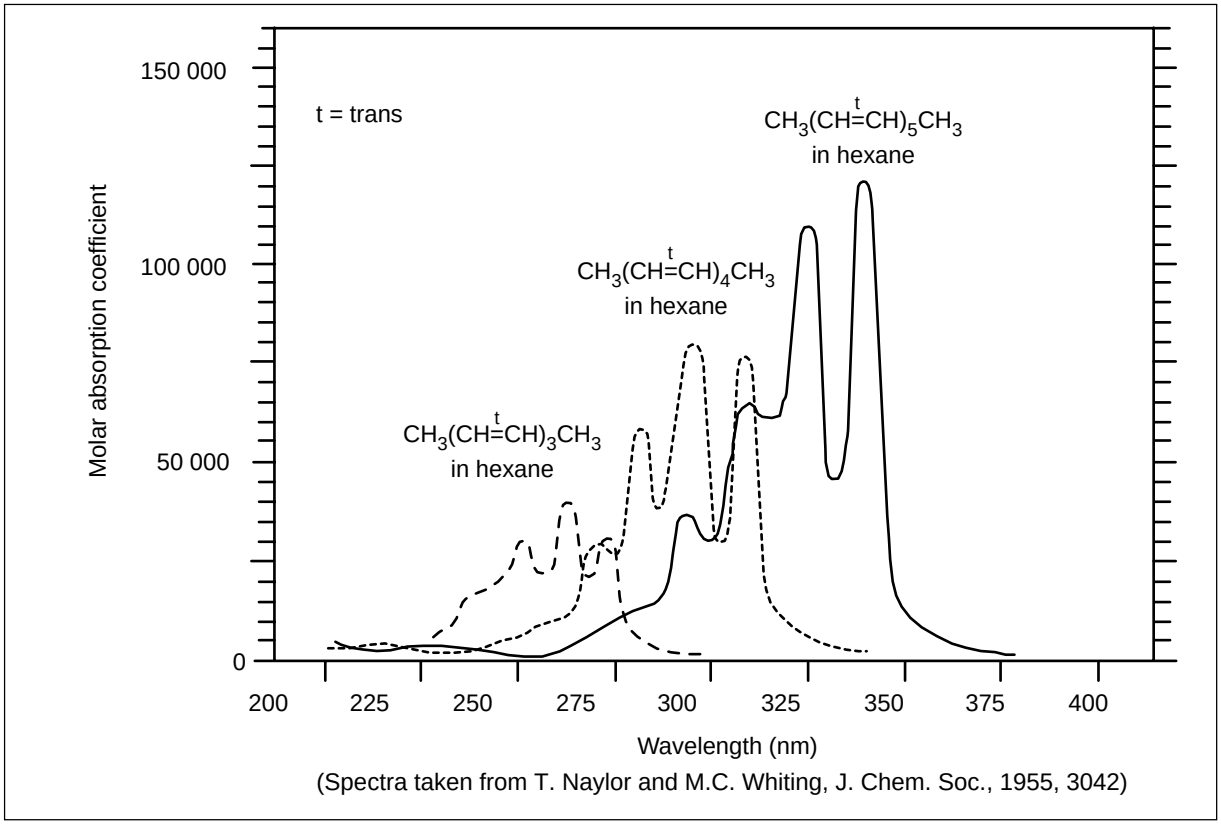

Figure 15 Ultraviolet/visible spectra of the polyenes $CH_3(CH{=}CH)_nCH_3$, where n=3,4 and 5

β-carotene, a vitamin found in carrots, and used in food colouring, has eleven conjugated double bonds (*Fig. 16*) and its absorption maximum has shifted out of the ultraviolet and into the blue region of the visible spectrum, hence it appears bright orange (*Fig. 17*).

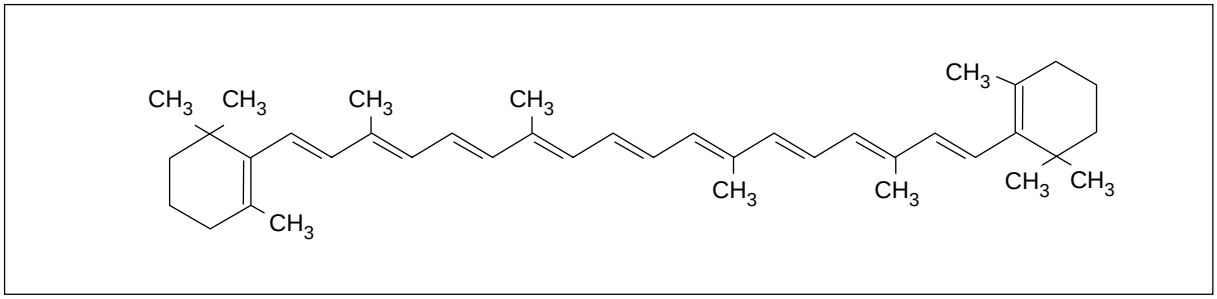

Figure 16 β-carotene

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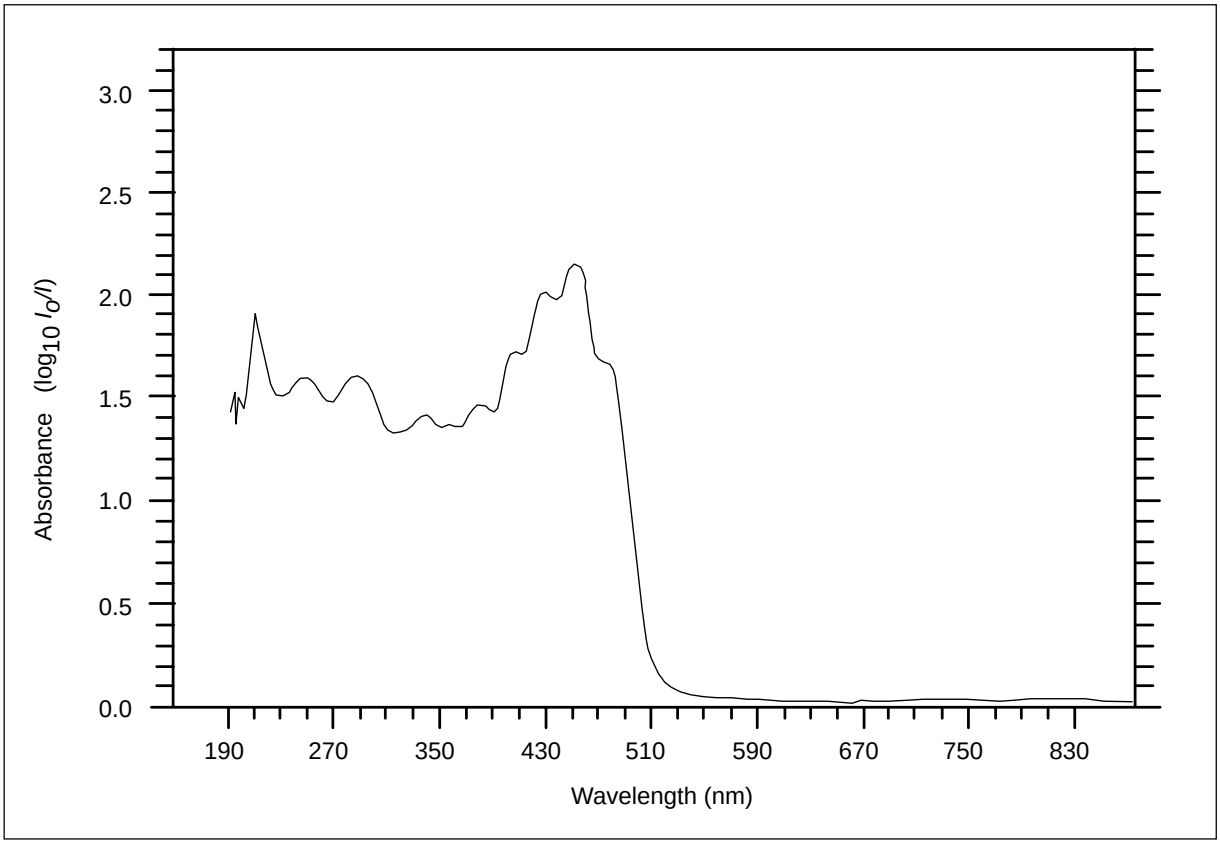

Figure 17 Ultraviolet/visible spectrum of β-carotene

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Conjugation does not have to be restricted to atoms of the same type. For example, the unsaturated carbonyl compound 3-butene-2-one, CH_2=CH–CO–CH_3 (methyl vinyl ketone), has an absorption maximum at 212 nm with $\varepsilon = 7.125 \times 10^5$ (*Fig. 18*). Neither the C=C double bond nor the carbonyl on their own have intense maxima above 200 nm.

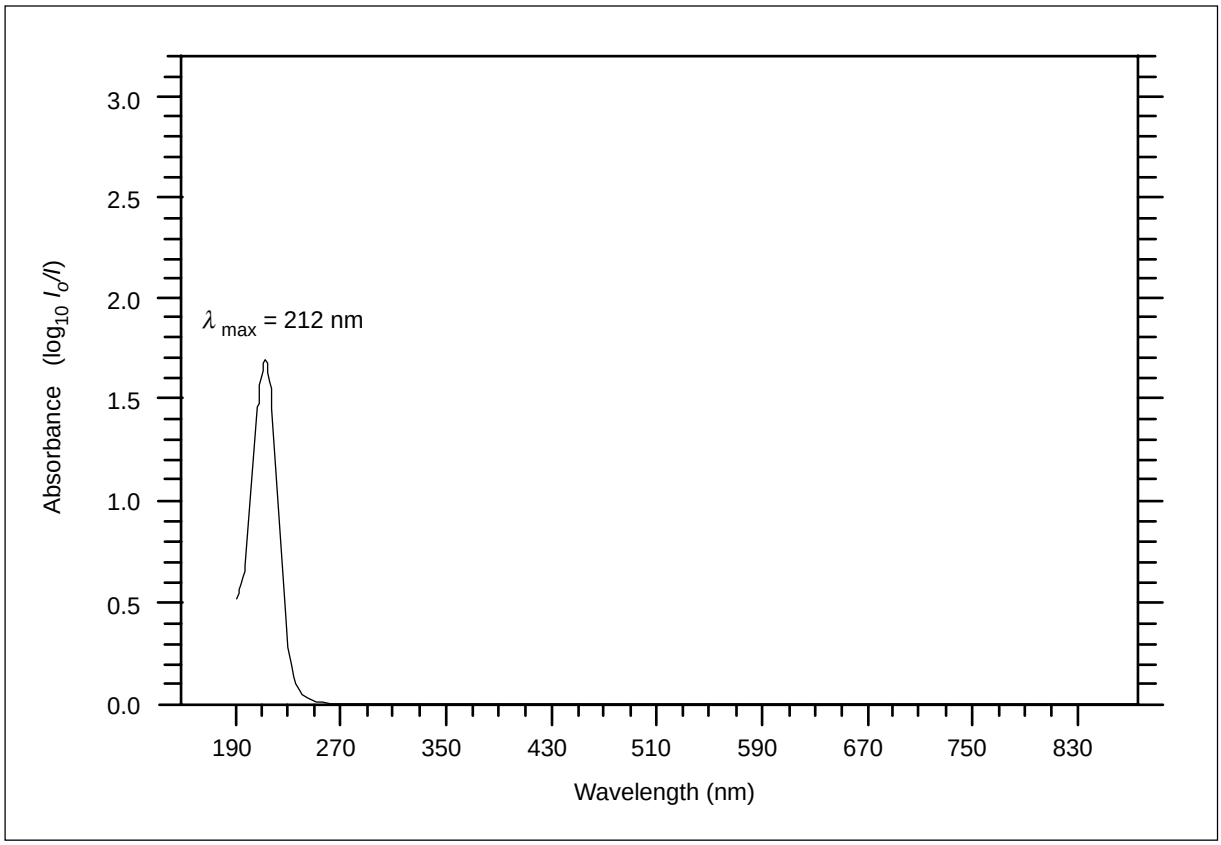

Figure 18 Ultraviolet/visible spectrum of CH_2=CH-CO-CH_3

Acid-base indicators

Absorption is advantageous in the acid-base indicators. A small change in the chemical structure of the indicator molecule can cause a change in the chromophore and it will absorb in different parts of the visible spectrum. The spectra of phenolphthalein and litmus (*Figs. 19a, 19b, 20a* and *20b*) illustrate this point.

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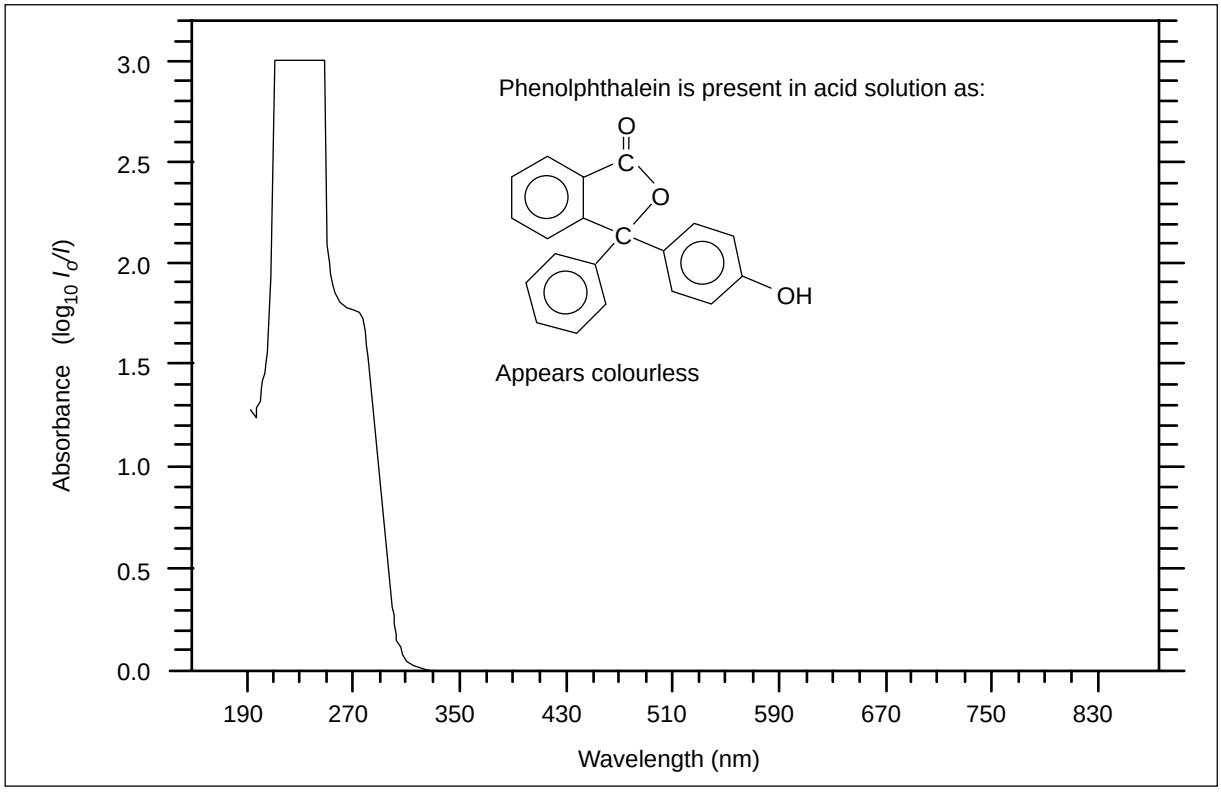

Figure 19a Ultraviolet/visible spectrum of phenolphthalein (pH = 1)

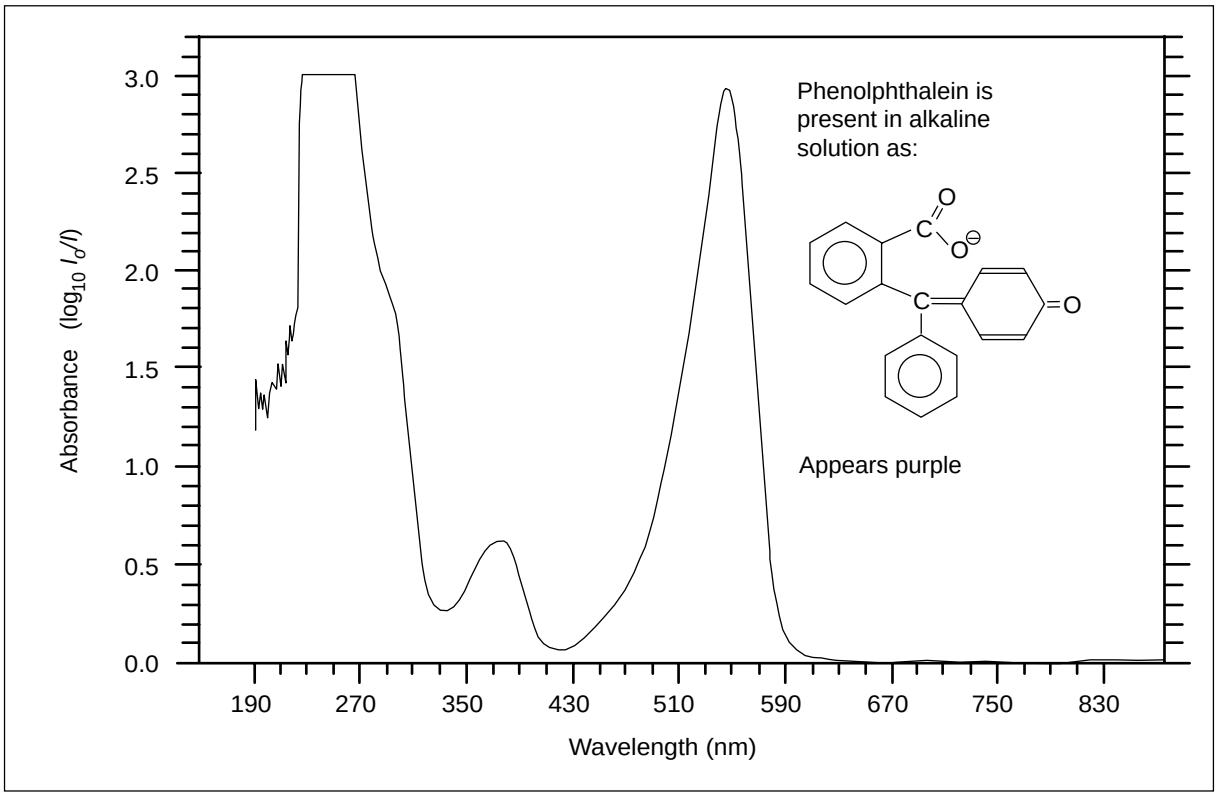

Figure 19b Ultraviolet/visible spectrum of phenolphthalein (pH = 13)

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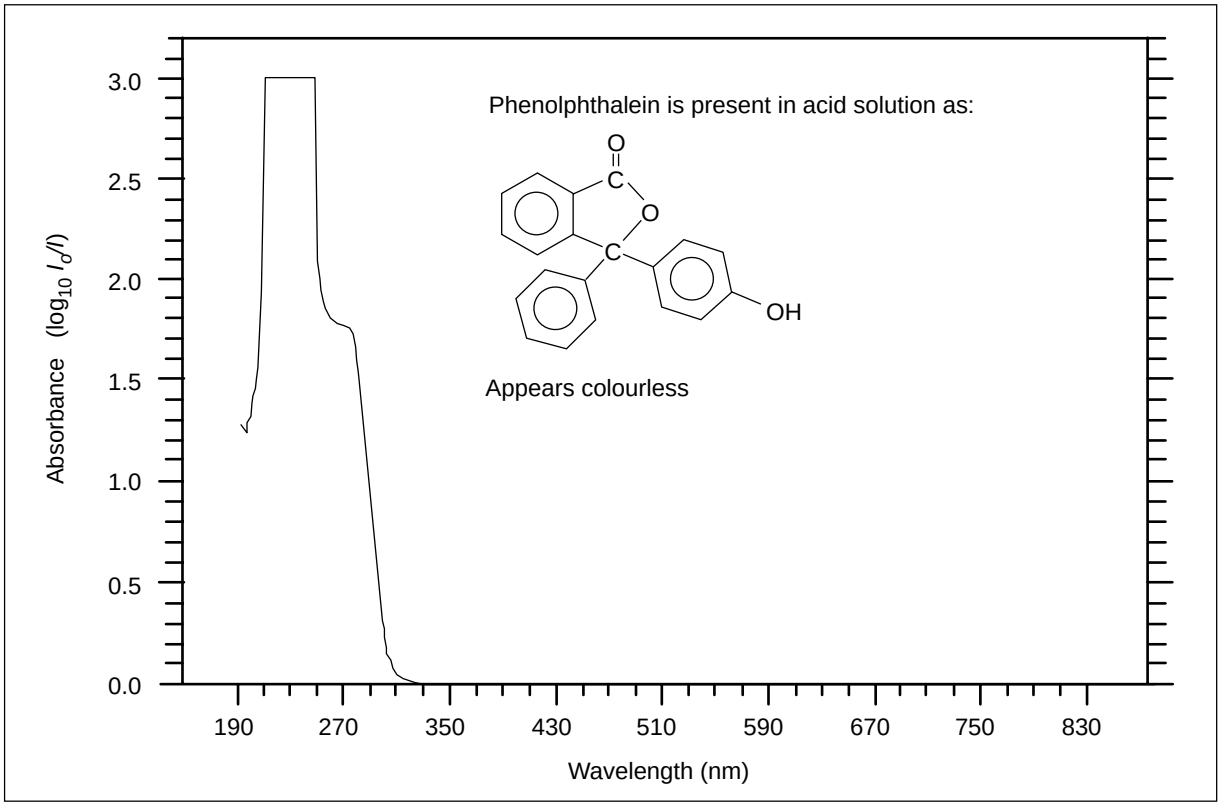

Figure 20a Ultraviolet/visible spectrum of litmus (pH = 1)

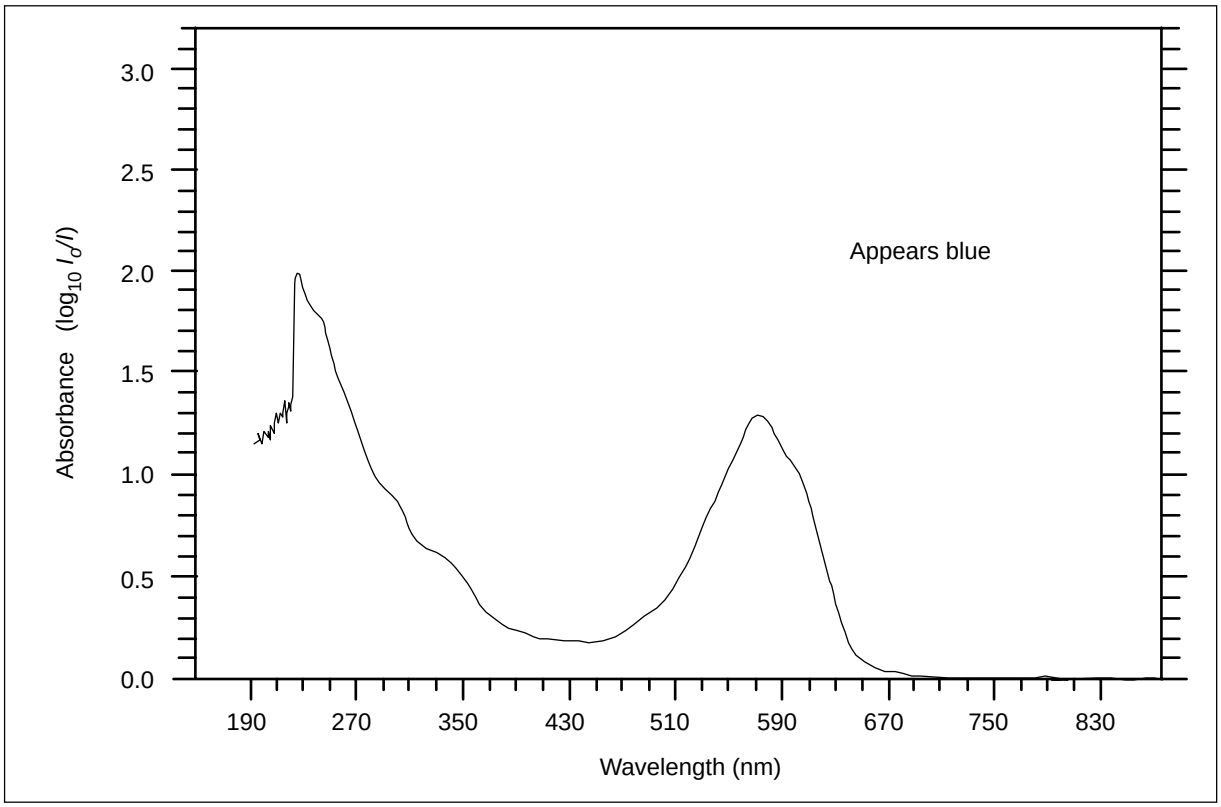

Figure 20b Ultraviolet/visible spectrum of litmus (pH = 13)

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Recent trends

Single beam, as well as double beam instruments are now on the market. These have the advantage that they are capable of measuring a spectrum very quickly. The principles of the single beam instrument are the same as for the double beam, but data on the reference are taken first, followed by the sample. The complete spectrum can be obtained very quickly. The diode array detector can be used to achieve this (see page 155). A computer can then interpret the two sets of data and plot the spectrum on a chart. This type of system can be in joint application with another technique *eg* the outflow from a chromatography column is passed through a small volume cell (often less than 10^{-2} cm^3) so that its ultraviolet/visible spectrum can be obtained as it flows through.

This has several advantages:

1 the different solutes do not have to be separated and collected in individual tubes so that their spectra may be obtained subsequently;

2 each spectrum can be determined in a fraction of a second; and

3 the spectra are stored by a computer so the spectrum of each solute can be compared with a library of known compounds.

One application is in the dope testing of race horses (page 150).

An alternative method of monitoring for particular substances is to pass the outflow from a chromatography column through a cell in a variable wavelength spectrometer. If the radiation is set at a wavelength known to be absorbed by the substance its presence will be shown by an absorption peak on the chart output of the spectrometer. An example of this is given in the section on caffeine/theobromine analysis (page 138).

Applications of ultraviolet/visible spectroscopy

In research, ultraviolet/visible spectroscopy is used more extensively in assaying than in identification. The trace metal content of an alloy, such as manganese in steel, can be determined by firstly reacting the sample to get the metal into solution as an ion. The ion is then complexed or made to react so that it is in a form that can be measured – *eg* manganese as the manganate(VII) ion. When the spectrum is recorded, the most useful piece of information is the absorbance because if the absorption coefficient of the chromophore is known the concentration of the solution can be calculated, and hence the mass of the metal in the sample.

The same principle can be applied to drug metabolites. Samples are taken from various sites around the body and their solutions are analysed to determine the amount of drug reaching those parts of the body. A useful feature of this type of analysis is the ability to calculate very small concentrations (of the order 0.0001 mol dm^{-3}) with extreme accuracy. It is important that the absorbance of the solution remains below two for quantitative measurements because of limitations of the instrument and solute-solute interactions that can cause deviations from the Beer-Lambert law.

The absorption of ultraviolet light is a feature of optical whiteners put into washing powders. The whitener absorbs radiation in the near ultraviolet and re-emits it in the visible range (*Fig. 21*).

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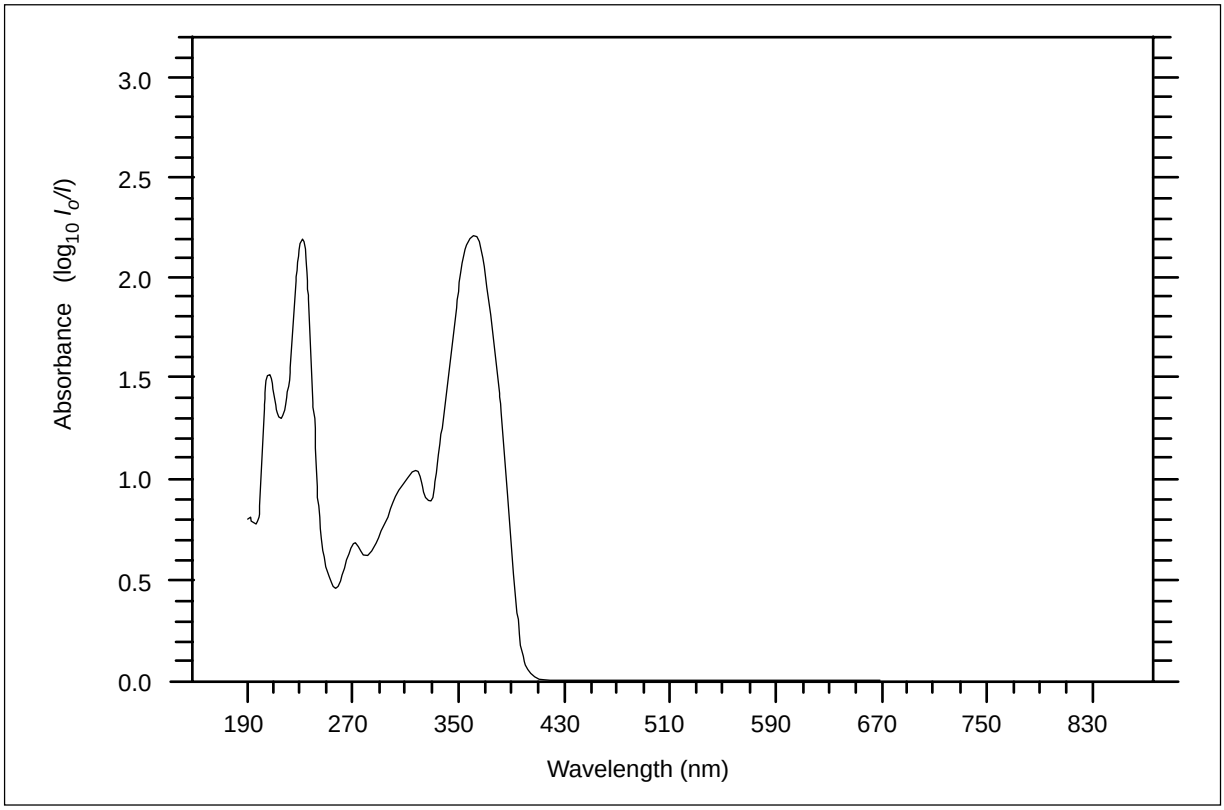

Figure 21 Ultraviolet/visible spectrum of an optical whitener used in a washing powder

Optical whiteners are also added to many toothpastes and detergent powders. They are often evident in discos that have ultraviolet lighting. White shirts and blouses frequently appear purple/blue, and people with false teeth should not smile!

Other applications include adding ultraviolet absorbing inks to water marks on paper so that they show up under an ultraviolet lamp; postcoding of household valuables with ultraviolet sensitive ink; and using invisible (but ultraviolet fluorescent) inks for signatures in building society savings books.

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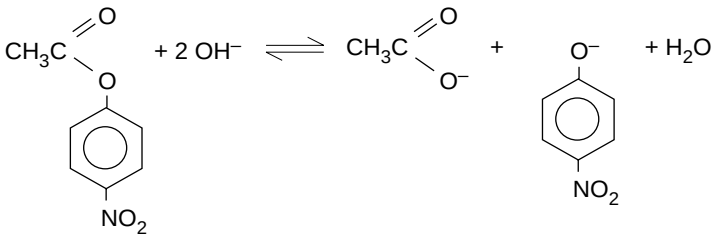
Exercise

Ultraviolet/visible spectroscopy can also be used to study reaction rates. If a reagent or a product of the reaction absorbs radiation at a particular frequency the spectrometer can be set to measure the absorption at that frequency as a function of time.

The rate of hydrolysis of an ester (4-nitrophenylethanoate)

4-Nitrophenylethanoate hydrolyses in alkaline solution to give 4-nitrophenoxide ions and ethanoate ions:



In the experiment the concentration of hydroxide ions is kept constant by a buffer solution and the progress of the reaction is followed by the absorption of light of wavelength 400 nm. The solution turns yellow as the 4-nitrophenoxide ion is liberated.

25.0×10^{-6} dm^3 (25.0 µl) of a solution of 0.01 mol dm^{-3} 4-nitrophenylethanoate in methanol is injected into 2.50 cm^3 of a buffer solution in a 1 cm cell. The buffer, at pH 10.9, consists of 0.01 mol dm^{-3} sodium carbonate neutralised with 1.0 mol dm^{-3} hydrochloric acid to the required pH. The reaction is followed by monitoring the appearance of the 4-nitrophenoxide chromophore at 400 nm with time. The absorption curve at 400 nm is shown in *Fig. 22*.

From the absorption curve determine:

1 the order of the reaction with respect to 4-nitrophenylethanoate;

2 the rate constant, k ; and

3 the absorption coefficient of the 4-nitrophenoxide ion.

Answers

Absorbance, on the y-axis, is directly proportional to the concentration of the 4-nitrophenoxide ion since

$$\text{Absorbance} = \log_{10}\frac{I_o}{I} = \varepsilon l c$$

The concentration of the 4-nitrophenoxide ion at time t, $[\text{4-nitrophenoxide}]_t$, is therefore given by

$$[\text{4-nitrophenoxide}]_t \ \alpha \ \text{absorbance}$$

From the equation for the reaction it is clear that for each mole of 4-nitrophenoxide ion formed one mole of the ester is hydrolysed. Thus, the concentration of the remaining ester is equal to its initial concentration less the concentration of 4-nitrophenoxide ion at that time, *ie*

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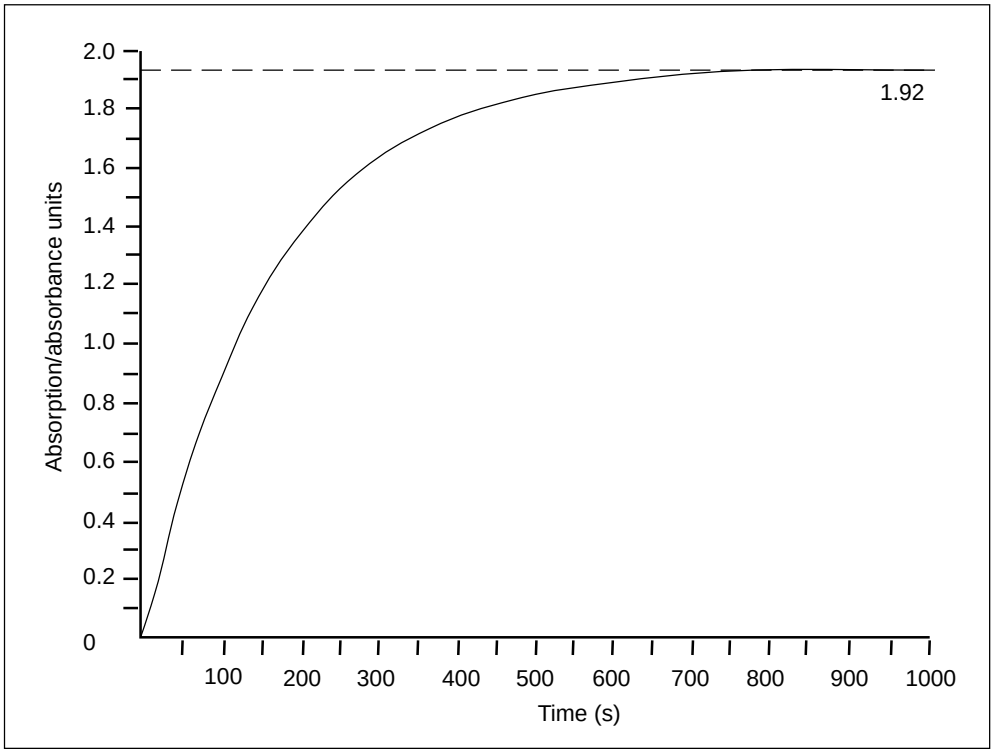

Figure 22 Absorption at 400 nm in a hydrolysis experiment

$$[\text{ester}]_t = [\text{ester}]_o - [\text{4-nitrophenoxide}]_t$$

where $[\text{ester}]_t$ = concentration of ester at time t
$[\text{ester}]_o$ = original concentration of ester
$[\text{4-nitrophenoxide}]_t$ = concentration of 4-nitrophenoxide ion at time t

The concentration of the ester is therefore given by

$$[\text{ester}]_t \propto \text{absorbance}_\infty - \text{absorbance}_t$$

From *Fig. 22* the absorption at $t = \infty$ is 1.92, so

$$[\text{ester}]_t \propto 1.92 - \text{absorbance}_t$$

Once the concentration of the ester at different times has been calculated, graphs can be plotted as follows to determine the order of the reaction with respect to the ester:

zero order:	[ester] versus time will be a straight line
first order:	ln [ester] versus time will be a straight line
second order:	1/[ester] versus time will be a straight line

From *Fig. 22,* the following data can be deduced:

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Time (s)	Absorbance units [4-nitrophenoxide]	$[ester]_t$	$\ln [ester]_t$	$1/[ester]_t$
0	0.00	1.92	0.65	0.52
100	0.89	1.03	0.03	0.97
200	1.37	0.55	–0.60	1.82
300	1.63	0.29	–1.24	3.45
400	1.76	0.16	–1.83	6.25
500	1.84	0.08	–2.53	12.50
600	1.88	0.04	–3.22	25.00

The only graph that produces a straight line is ln [ester] versus time, so the reaction must be first order with respect to the ester.

The gradient of this plot is equal to $-k$ where k is the rate constant.
From the graph,

$$\text{Gradient} = -k = \frac{-3.22 - 0.03}{500} = \frac{-3.19}{500} = -0.0064 \text{ s}^{-1}$$

Thus $\underline{k = 0.0064 \text{ s}^{-1}}$

From this it is possible to calculate the half-life of the reaction quite simply:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.0064} = 108.3 \text{ s}$$

The absorption coefficient of the 4-nitrophenoxide ion can be calculated as follows:

From the Beer–Lambert law

$$\text{absorbance} = \log_{10} \frac{I_o}{I} = \varepsilon l c$$

The absorbance can be measured directly from *Fig. 22*, and the path length of the cell is 1 cm (*ie* $l = 1$). The 0.01 mol dm^{-3} ester solution was diluted from 0.025 cm^3 to 2.525 cm^3 (0.025 cm^3 +2.5 cm^3), *ie* by a factor of 101. Its final concentration was therefore

$$\frac{0.01}{101} = 0.000099 \text{ mol dm}^{-3}$$

Substituting these values,

$$1.92 = \varepsilon \times 1 \times 0.000099$$

$$\varepsilon = \frac{1.92}{0.000099} = 19\,392 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$$

By convention the units are not usually quoted, and absorption coefficients are commonly given to fewer significant figures.
Thus, $\underline{\varepsilon = 19\,400}$.