

## Option A – Modern Analytical Chemistry (Additional Higher Level)

## A8 Visible and Ultraviolet (UV-Vis) Spectroscopy

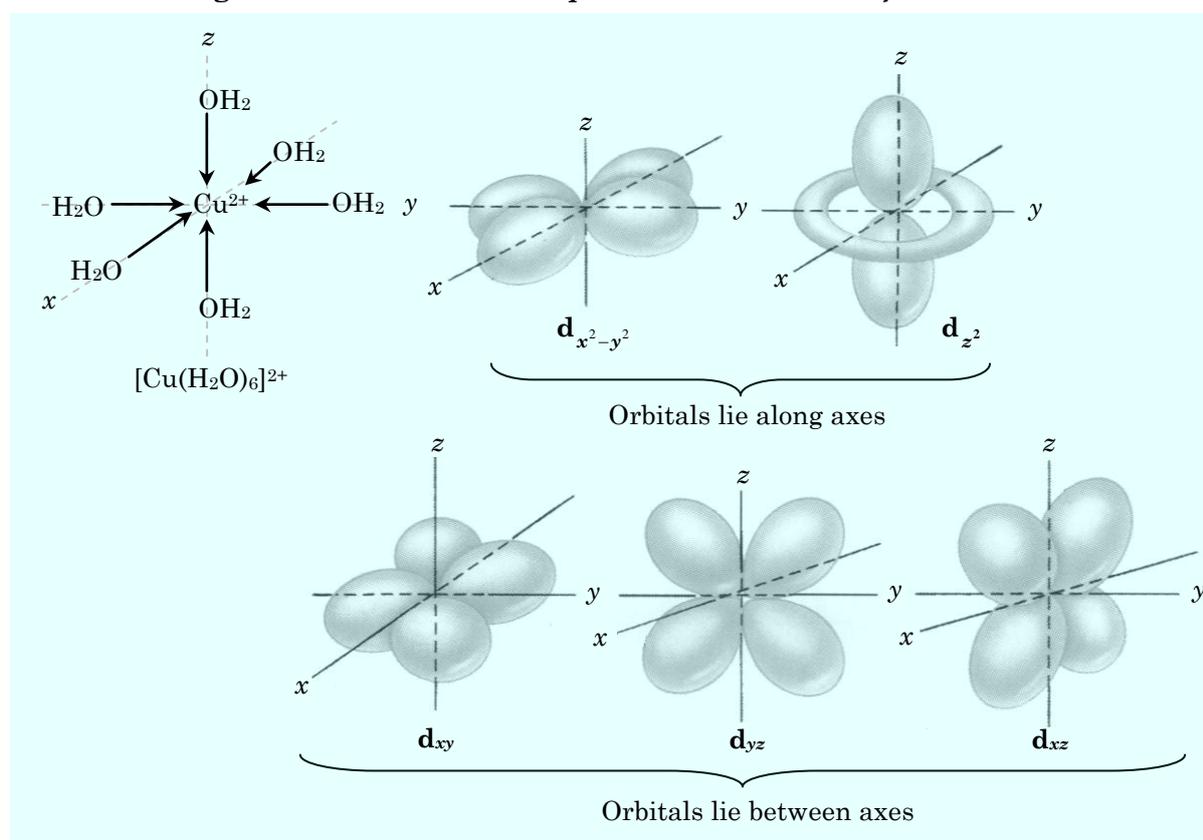
Ultraviolet-visible (UV-Vis) spectroscopy is similar in principle to IR spectroscopy but this time shorter wavelength, and therefore higher energy, visible and UV light is directed at the sample. Whereas IR radiation causes molecules to vibrate, UV and visible radiation cause electronic transitions in atoms and molecules.

## Colour in Transition Metal Complexes

We have looked in some detail at the origin of colour in transition metal complexes in Section 13.2. What follows here is a summary of that section plus some more detail on the factors that determine the colour of the complex. If you do not fully remember the electronic structure of the first row of the transition metals, the nature of ligands and the structure of complex ions, you should review Section 13.2 before continuing.

In an isolated transition metal atom or ion (for example in the gas phase) the five d atomic orbitals are degenerate, that is, they have the same energy. However, in a complex ion the d orbitals split into two sets, with one set slightly higher in energy than the other. Let's use the hexaaquacopper(II) ion,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , as an example. This complex, like others with a coordination number of 6 (six ligands around the central atom or ion), is octahedral in shape. The six ligands form dative covalent bonds to the transition metal along the  $x$ ,  $y$  and  $z$  axes in three-dimensional space.

**Figure A20 Octahedral Complex and Orientation of d Orbitals**

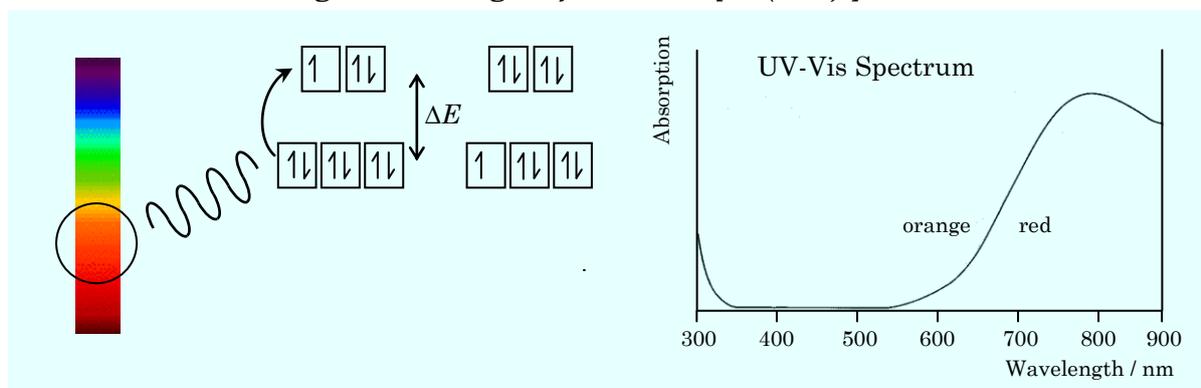


Two of the five d orbitals point along the axes while the other three lie between the axes. This means that electrons in the  $d_{x^2-y^2}$  and the  $d_{z^2}$  orbitals feel more repulsion from the ligands and are therefore slightly higher in energy than electrons in the other three d orbitals. The energy gap,  $\Delta E$ , between the two sets of d orbitals in the octahedral complex corresponds to the frequencies of visible light in the electromagnetic spectrum.

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The copper(II) ion in the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complex has an electron configuration  $[\text{Ar}]3d^9$ . The energy gap between the two sets of d orbitals in this complex corresponds to the wavelength of red-orange light. Red-orange light is selectively absorbed when an electron is promoted from the lower energy set of d orbitals to the higher energy set of d orbitals. This means that we see the complimentary colour (the colours not absorbed, see Figure 13.4 in Topic 13), so the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion appears pale blue in colour.

**Figure A21 Origin of Colour in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  Ion**



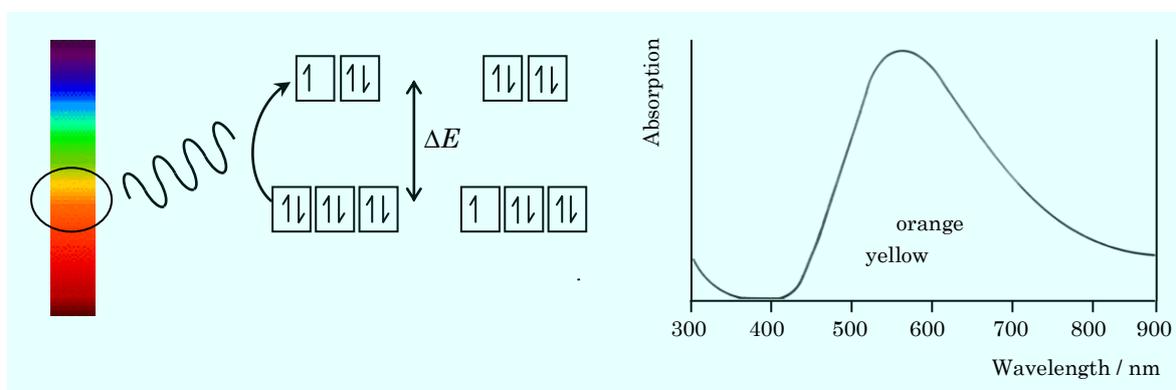
Whereas we see sharp lines in the line emission spectra of excited atoms (such as the line emission spectrum of hydrogen shown in Figure 2.3), the absorption spectra of transition metal complexes is typically broad in nature. This is because some of the extra energy of the excited electrons in the transition metal ion or atom goes into increasing the vibrational energy of the complex. The dative covalent bonds between the ligands and the central metal vibrate backwards and forwards, varying the splitting between the d orbitals. This means a range of wavelengths of light is absorbed in exciting electrons between the d orbitals.

The precise colour of a transition metal complex depends on a number of factors:

### 1. Ligand

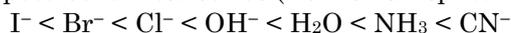
For the same transition metal, complexes having different ligands typically display different colours. Ligands have different electron densities and repel electrons in d orbitals to different extents. This changes the splitting between the two sets of d orbitals and, therefore, the energy gap,  $\Delta E$ . For example, changing the ligands in the copper(II) complex from water to ammonia increases the energy gap. The wavelength of light absorbed in promoting an electron between d orbitals in the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  complex is therefore shorter than in the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion. Yellow light is predominantly absorbed and the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  complex appears blue-violet in colour.

**Figure A22 Colour in  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  Ion**



This colour change can be seen when ammonia solution is added dropwise to a pale blue aqueous solution of copper(II) ions. The first few drops of ammonia solution forms a pale blue precipitate of copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$ . When excess ammonia is added, this precipitate redissolves to form the attractive blue-violet colour of the tetramminecopper(II) complex ion.

The higher the electron density of the ligand, the greater is the splitting between the d orbitals. The order of splitting by the ligands is known as the **spectrochemical series**. Part of the spectrochemical series (from small splitting to large splitting of the d energy level) is:



## 2. Identity of the metal

Metal ions with the same electronic configuration (that is, metals that are isoelectronic) also show different colours in complexes with the same ligand. For example,  $Fe^{3+}$  and  $Mn^{2+}$  both have the electron configuration  $[Ar]3d^5$ . The hexaaquairon(III) ion,  $[Fe(H_2O)_6]^{3+}$ , is yellow-brown in colour, whereas the hexaaquamanganese(II) ion,  $[Mn(H_2O)_6]^{2+}$ , is pale pink. The difference is because manganese and iron have different nuclear charges (atoms of iron have one more proton in the nucleus) and this affects the energy of the d orbitals.

## 3. Oxidation state of the metal

If we compare the colours of  $Fe^{2+}$  and  $Fe^{3+}$  complexes, the nuclear charge is the same but the electron configuration is different:  $Fe^{2+}$  is  $[Ar]3d^6$  and  $Fe^{3+}$  is  $[Ar]3d^5$ . Again, the colours of the complexes are different, for example,  $[Fe(H_2O)_6]^{3+}$  is yellow-brown and  $[Fe(H_2O)_6]^{2+}$  is pale green.

## 4. Geometry of the complex

Complexes have different shapes depending on the number of ligands surrounding the central metal atom or ion. For example, many complexes with a coordination number of 4 are tetrahedral in shape (see Section 13.2). In a tetrahedral complex, electrons in the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  are closer to the ligands and are higher in energy than electrons in the other two d orbitals; the splitting is reversed compared to that seen in an octahedral complex. If a few drops of concentrated hydrochloric acid are added to a solution of pale-blue  $[Cu(H_2O)_6]^{2+}$  ions, the colour changes to emerald green as the tetrahedral  $[CuCl_4]^{2-}$  ion forms.

## Colour in Organic Molecules

We have seen that colour in transition metal complexes arises from electron transitions between non-degenerate d orbitals in the metal atom or ion. At least one of the d orbitals in the higher energy set of d orbitals must have space into which an electron can be promoted. Either this higher energy d orbital already has one electron, in which case the excited electron pairs up in the same orbital (as in Figures A21 and A22), or the d orbital may be unoccupied in the ground state. This is a key point, and one that was made when we first talked about atomic orbitals in Topic 12. An orbital is a space into which two electrons can fit. The orbital may not be occupied but it still exists! We can promote electrons from occupied orbitals into higher energy unoccupied orbitals. Energy in the form of heat or electromagnetic radiation is absorbed in this process. The energy gap between different electron energy levels in an atom is normally much larger than the splitting in the d sub-level in transition metal complexes.

We can apply the same principle to molecules. We saw in Section 14.2 that overlap of atomic orbitals in two atoms can give rise to a bonding molecular orbital with increased electron density between the two bonded atoms. In a  $\sigma$  (sigma) bond, the electron density in the molecular orbital is directly between the bonded nuclei; in a  $\pi$  (pi) bond, the electron density is above and below the plane containing the bonded nuclei. Each bonding molecular orbital in a molecule contains a pair of bonding electrons. Molecular orbital theory accurately predicts the shape and energy of  $\sigma$  and  $\pi$  bonds. Without going into the details of molecular orbital theory (see following Study Hint), it predicts that the overlap of *two* atomic orbitals must form *two* molecular orbitals. One molecular orbital is a bonding molecular orbital in which the wave properties of the atomic orbitals overlap constructively, and the other is anti-bonding molecular orbital in which the wave properties overlap destructively. The bonding molecular orbital is of lower energy than either of two overlapping atomic orbitals so the electrons in a bonding molecular orbital are energetically more stable than in the separate atoms. In the antibonding molecular orbital there is decreased electron density between the two atoms. The antibonding molecular orbital is of higher energy than either of the two individual atomic orbitals; it is energetically less stable than the separated atoms.

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### Study Hint:

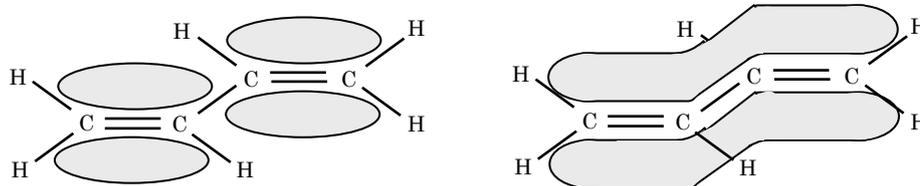
Molecular orbital theory provides an alternative explanation of bonding. It is a complex mathematical model based on the wave theory of electrons and is very useful for explaining certain unusual molecular properties. Some advocates of molecular orbital theory insist that there is no need for valence bond theory and the concept of hybridisation (Section 14.2) to explain the bonding in molecules and their shapes. You do not need any detailed knowledge of molecular orbital theory for the exam. If you wish to know more, Clugston & Fleming's excellent text *Advanced Chemistry* has a clear overview, and the basics of molecular orbital theory applied to UV-Vis spectroscopy is explained nicely on the following page on Jim Clark's useful website: <http://www.chemguide.co.uk/analysis/uvvisible/bonding.html>

Let's take the simplest example of a molecule, the hydrogen molecule. The "head on" overlap of the 1s atomic orbital in two hydrogen atoms forms a bonding  $\sigma$  molecular orbital and an antibonding  $\sigma^*$  molecular orbital (Figure A23). The two electrons normally occupy the lowest energy bonding molecular orbital. The result is a single covalent bond between the two atoms.

We can also apply molecular orbital theory to molecules containing double bonds. In a double bond we have a  $\sigma$  bonding and  $\sigma^*$  antibonding molecular orbital, and a  $\pi$  bonding and  $\pi^*$  antibonding molecular orbital. The molecular orbital diagram, of course, looks a little more complicated. But the important thing is that the energy gap between the  $\pi$  and  $\pi^*$  molecular orbitals is smaller than between the  $\sigma$  and  $\sigma^*$  molecular orbitals. Less energy is needed to promote an electron from an occupied  $\pi$  molecular orbital to an unoccupied  $\pi^*$  molecular orbital.

For ethene,  $\text{CH}_2=\text{CH}_2$ , the simplest organic molecule containing a  $\text{C}=\text{C}$  double bond, the energy gap between the  $\pi$  and  $\pi^*$  molecular orbitals is  $750 \text{ kJ mol}^{-1}$ . To promote an electron between these two molecular orbitals, electromagnetic radiation of a wavelength equal to  $162 \text{ nm}$  is absorbed. This is in the UV region of the spectrum. No visible light is absorbed and therefore ethene is colourless.

What happens if there are two  $\text{C}=\text{C}$  bonds in the molecule? Let's look at buta-1,3-diene,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ . The double bonds are separated by a single bond. Molecular orbital theory suggests that the  $\pi$  electron density is not localised in two positions in the molecule but is instead delocalised, or spread, over the whole molecule.



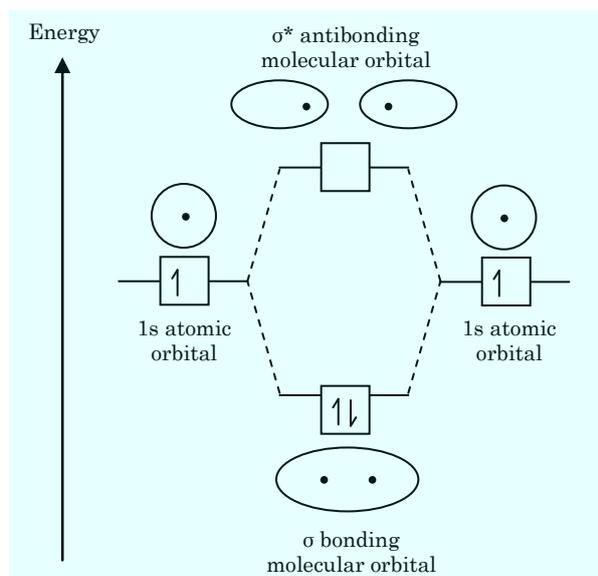
In buta-1,3-diene the  $\pi$  electron density is not localised over the two  $\text{C}=\text{C}$  double bonds but delocalised over the whole molecule

When  $\pi$  electrons are delocalised in this way, two very important things happen:

- The energy of the  $\pi$  molecular orbital decreases; the molecule is more stable.
- The energy gap between the  $\pi$  bonding molecular orbitals and the  $\pi^*$  molecular orbitals decreases.

According to molecular orbital theory, when the *four* p atomic orbitals from the four C atoms in buta-1,3-diene overlap, *four* molecular orbitals form: two bonding  $\pi$  bonding molecular orbitals and two  $\pi^*$  antibonding molecular orbitals. The energy gap between the highest occupied  $\pi$

**Figure A23 Molecular Orbital Diagram for a Hydrogen Molecule**



molecular orbital and the lowest unoccupied  $\pi^*$  antibonding molecular orbital in buta-1,3-diene is  $550 \text{ kJ mol}^{-1}$ . This still corresponds to UV radiation but of a shorter wavelength than that absorbed by a molecule of ethene. What happens if we extend the delocalised system? In hexa-1,3,5-triene,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ , the energy gap is  $450 \text{ kJ mol}^{-1}$ . This corresponds to radiation of a wavelength of 265 nm, still in the UV region but even closer to the visible region.

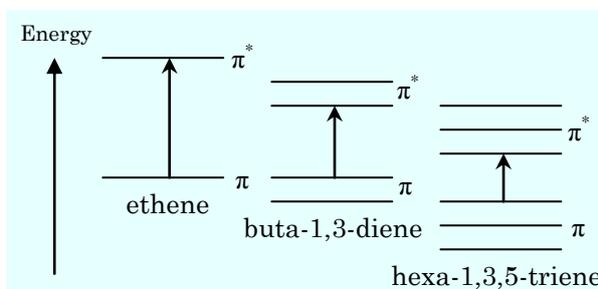
This interaction between near-neighbour  $\pi$  bonds is called **conjugation**. Conjugation occurs when there is a continuous system of **alternating single and double bonds** in the molecule. As a result of the overlap between the molecular orbitals, the electrons in the  $\pi$  bonds are delocalised and the molecule is more stable. Most importantly for us in this context, it means that it takes less energy to promote an electron into a higher unoccupied energy level.

The conjugated atoms do not necessarily have to be C atoms. N or O atoms, for example, can be involved in conjugation as long as the p orbital is in the same plane as the other p orbitals so that they can overlap. A non-bonding pair of electrons in a p orbital can also be used to extend the conjugation in a molecule.

We saw the same type of delocalisation occurring in benzene in Section 14.3. In the Kekulé structure of benzene there are alternating single and double carbon-carbon bonds. Benzene absorbs a maximum amount of UV radiation ( $\lambda_{\text{max}}$ ) at 250 nm. In line with our findings above, naphthalene, with two benzene rings fused together, and therefore a longer conjugated system, has a  $\lambda_{\text{max}}$  at a longer wavelength (lower energy) of 280 nm.

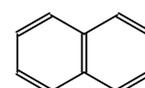
Let's take our chain building further so that we have a very long conjugated system. The molecule  $\beta$ -carotene has 11 double bonds and a very long conjugated structure. The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is much smaller than we have seen so far. The molecule absorbs visible light when electrons are promoted, mostly violet and blue, and therefore appears orange in colour.  $\beta$ -Carotene is responsible for the orange colour of carrots and other fruits and vegetables.

**Figure A24 Schematic Showing Energy of  $\pi$  Molecular Orbitals in Organic Molecules (not to scale)**



benzene

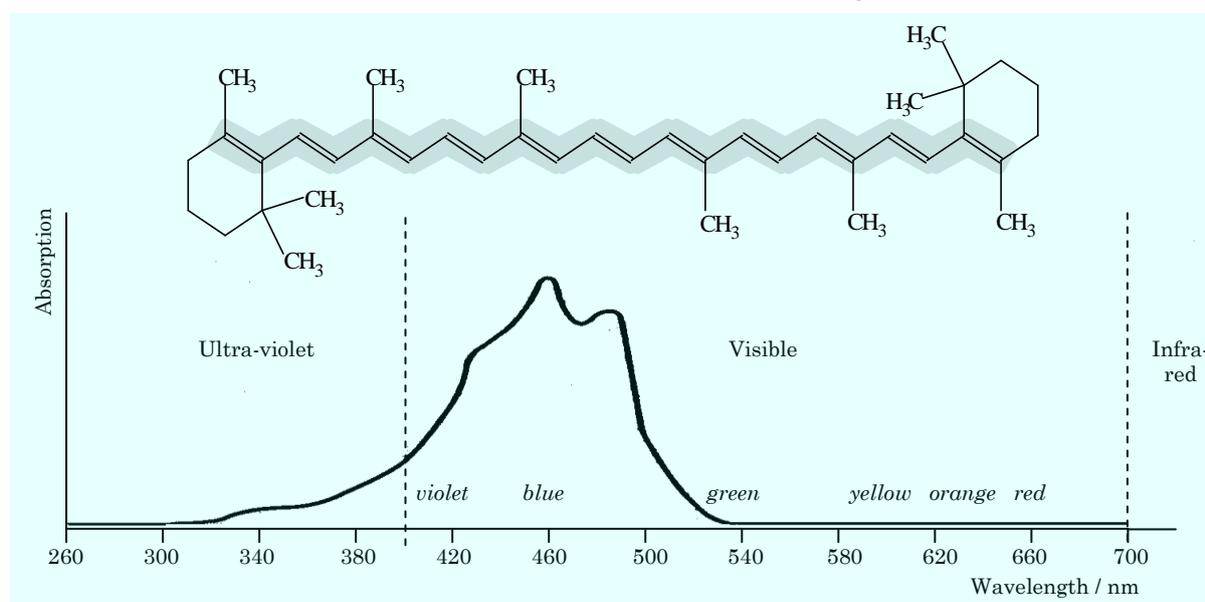
$\lambda_{\text{max}} = 250 \text{ nm}$



naphthalene

$\lambda_{\text{max}} = 280 \text{ nm}$

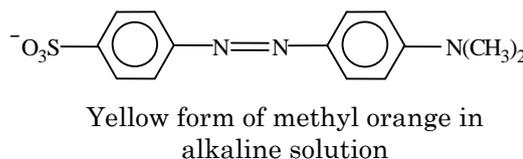
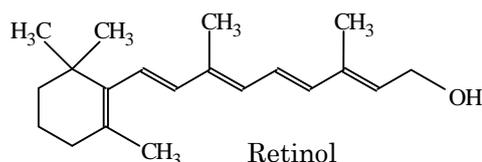
**Figure A25 Structure and UV-Vis Spectrum of  $\beta$ -Carotene**



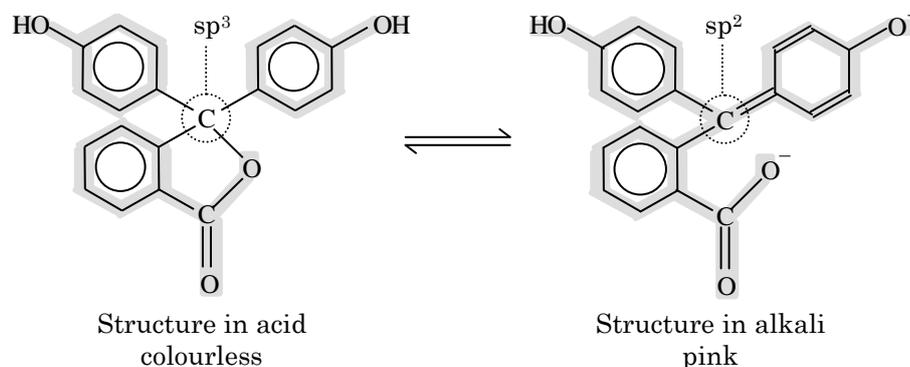
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Most coloured organic molecules contain an extensive conjugated system like  $\beta$ -carotene. Conjugation can exist through C=C double bonds and other groups that contain multiple bonds, like C $\equiv$ C, benzene rings, N=N, C=O and NO<sub>2</sub>. These structural elements are called **chromophores**, from the Greek words *chroma* meaning “colour” and *phoros* meaning “bearing”. The presence of certain other groups in organic molecules can make the colour more intense because they have non-bonding pairs of electrons that can take part in the delocalised system. These groups are called **auxiochromes**. Examples of auxiochromes are –OH, –NH<sub>2</sub> and –Hal.

Other examples of important coloured organic molecules are chlorophyll, hemoglobin (see Figure 13.3), retinol (vitamin A) and the important family of azo dyes. The conjugation in azo dyes runs through the azo –N=N– chromophore. The acid-base indicator methyl orange is an azo compound.



A good illustration of the need for an extensive conjugated system is the structure of another acid-base indicator, phenolphthalein, in acidic and basic solution:



In acidic solution, conjugation is limited to isolated parts of the molecule which are separated from each other by an sp<sup>3</sup> hybridised C atom. This sp<sup>3</sup> C atom interrupts the single bond – double bond alternating system. This form of the molecule absorbs radiation in the UV region of the spectrum and appears colourless. In alkaline solution, on the other hand, this central C atom is sp<sup>2</sup> hybridised and part of a more extensive connected conjugated system. As a result, this structure absorbs yellow-green light and appears intense pink (magenta) in colour.

### Study Hint:

We can extend the idea of delocalisation and its effect on electronic transitions to the case of metals. Here the atomic orbitals of a vast number of metal atoms overlap to form an equally vast number of bonding and antibonding molecular orbitals (the name persists although metals are not molecular). In fact, there are so many orbitals that they form continuous bands of orbitals. In metals the filled and unfilled bands overlap. As a result, the electrons can easily be promoted between orbitals and move through the whole structure.

The phenomenon of selective absorption of visible light by organic molecules finds application in dyes and in acid-base indicators. Molecules that strongly absorb ultraviolet radiation are useful in sunscreens (sun-blocks and suntan lotions). One of the most common ingredients in sunscreens is 4-aminophenylmethanoic acid (para-aminobenzoic acid, PABA), which absorbs a wide spectrum of UV radiation, but especially more harmful higher energy UVB radiation that can cause sunburn and skin cancer. Sunscreens also contain inorganic compounds like zinc oxide and titanium dioxide which absorb and scatter UV light.



## UV-Vis Spectroscopy Experiments

Beer-Lambert law, which we saw in the context of atomic absorption spectroscopy in Section A6, can also be applied to molecules that absorb in the visible region of the spectrum. Beer-Lambert law says that for a given molecule and frequency of radiation, the absorbance,  $A$ , of electromagnetic radiation is directly proportional to the concentration,  $c$ , of absorbing species:

$$\text{Absorbance, } A = \epsilon cl$$

where  $\epsilon$  is the molar absorptivity and  $l$  is the path length of light through the sample. As both  $\epsilon$  and  $l$  are measurable constants, the Beer-Lambert relationship enables us to determine the concentration of a UV-Vis active species in solution by measuring how much light the solution absorbs.

It is important to select a wavelength of light that is absorbed by the substance under test. This can be achieved in one of the following ways:

- Running a full UV-Vis spectrum for the substance and determining the wavelength of light at maximum absorbance,  $\lambda_{\text{max}}$ .
- Looking up the  $\lambda_{\text{max}}$  value in literature tables.
- In simple colorimeter experiments, choosing a filter which is the complimentary colour of the colour of the substance in solution. The wavelength of light that is transmitted by the colorimeter is then the same as that absorbed by the substance.

A series of standard solutions with known concentrations of the substance under test are made and their absorbance measured. A calibration curve is then drawn (see Figure A17). The absorbance of the unknown solution is then measured and the concentration interpolated from the calibration plot.

## A9 Nuclear Magnetic Resonance (NMR) Spectroscopy

We saw in Section A5 that the nucleus of a  $^1\text{H}$  atom behaves like a tiny bar magnet. The nucleus of a proton can be aligned with an external magnetic field or against it. The nucleus can be made to flip from one orientation to the other by absorbing radio frequency radiation. Different protons in a molecule absorb radiation of slightly different frequencies when they flip (the resonance frequency) because they are in different electronic environments. The presence of nearby electrons, which also have the property of spin, influences the precise magnetic field that each proton experiences.

We learned in Section A5 that the following information can be obtained from a low-resolution proton NMR spectrum of a molecule:

1. The number of signals in the proton NMR spectrum tells us the number of different electronic environments in which protons exist in the molecule.
2. The area under each signal tells us the number of protons in each identical electronic environment. We call these chemically equivalent protons.

This information tells us about the different component parts of the molecule but not necessarily how these component parts are put together. Much more information about the structure of the molecule under test comes from looking in detail at the *high*-resolution spectrum.

### Chemical Shift

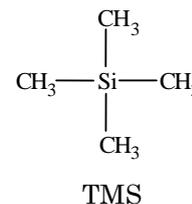
The resonance frequency of different protons in a molecule depends on the electronic environment around the proton. Nearby electrons create a local magnetic field that opposes the external magnetic field. If a proton is near to an electronegative atom in a molecule, the proton feels a smaller local magnetic field because electron density is withdrawn from it. The proton flips more easily and will resonate at a lower frequency. Look back at the low-resolution proton NMR spectrum of ethanol in Figure A12. The signal for the proton bonded directly to the O atom in the alcohol functional group is furthest to the left in the spectrum (we say that this signal is furthest *downfield*). Next furthest downfield is the signal for the two chemically identical protons in the next closest position to the O atom.

We know protons in a molecule can resonate at different frequencies due to difference in the local electronic environment in the molecule. But how do we compare the resonance frequency of protons in one molecule to those in another molecule? For example, does the O–H proton in ethanol flip more easily than the O–H proton in butanoic acid? Chemists use an internal

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standard to compare resonance frequencies from one sample to the next, and from one spectrometer to the next. The substance chosen for the internal standard is **tetramethylsilane**,  $\text{Si}(\text{CH}_3)_4$ , or **TMS** for short. TMS is used for the following reasons:

- All 12 protons in TMS are chemically equivalent because they are in the same molecular environment. This means they give a single intense peak in the NMR spectrum.
- Silicon is one of the few atoms that bonds covalently to C which is less electronegative than C; Si is electron-releasing compared to C. This increases the electron density on the  $-\text{CH}_3$  groups. The protons feel a stronger local magnetic field due to electrons and therefore have a higher resonance frequency. In practice, this means that the peak for the protons in TMS appear at the extreme right-hand side of the NMR spectrum, further *upfield* than other signals.
- TMS is non-toxic and unreactive, so it does not interfere with the sample under test.
- TMS is volatile (it has a low boiling point) so can easily be removed from the sample after testing.

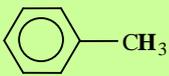
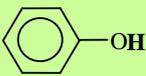
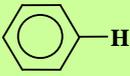


A little TMS is added to each sample before it is analysed in the NMR spectrometer. The peak in the NMR spectrum due to the protons in TMS is given an arbitrary value of 0 ppm. The difference in resonance frequency of the protons in the test sample compared to that for TMS is called the **chemical shift** (symbol  $\delta$ ). The chemical shift values for protons in different molecular environments are listed in reference tables.

If you take another look at the proton NMR spectra shown previously in Section A5, you will see that each spectrum has a small peak at 0 ppm. This is the signal due to the protons in the TMS added in each test.

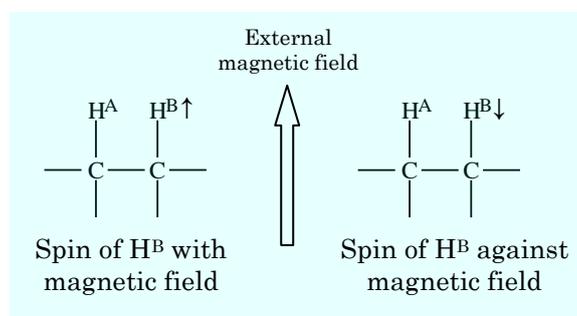
In the exam, you do not need to predict or explain the chemical shift for protons in the organic molecule under study. The chemical shifts for protons in a variety of different local molecular environments are given in the data booklet and repeated below in Table A5. All you need to do is to match the chemical shift of those shown in the NMR spectrum with those from the table.

**Table A5  $^1\text{H}$  Chemical Shift Values**

Type of Proton	Chemical Shift / ppm	Type of Proton	Chemical Shift / ppm
$\text{R}-\text{CH}_3$	0.9–1.0	$\text{R}-\text{O}-\text{CH}_3$	3.3–3.7
$\text{R}-\text{CH}_2-\text{R}$	1.3–1.4	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{R}$	3.8–4.1
$\text{R}_3\text{CH}$	1.4–1.6	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{H}$	9.0–13.0
$\text{CH}_3-\text{C}(=\text{O})-\text{OR}$	2.0–2.5	$\text{R}-\text{O}-\text{H}$	4.0–12.0
$\text{CH}_3-\text{C}(=\text{O})-\text{R}$	2.2–2.7	$\text{R}-\text{CH}=\text{CH}_2$	4.5–6.0
	2.5–3.5		4.0–12.0
$\text{R}-\text{C}\equiv\text{C}-\text{H}$	1.8–3.1		6.9–9.0
$\text{R}-\text{CH}_2-\text{Hal}$	3.5–4.4	$\text{R}-\text{C}(=\text{O})-\text{H}$	9.4–10.0

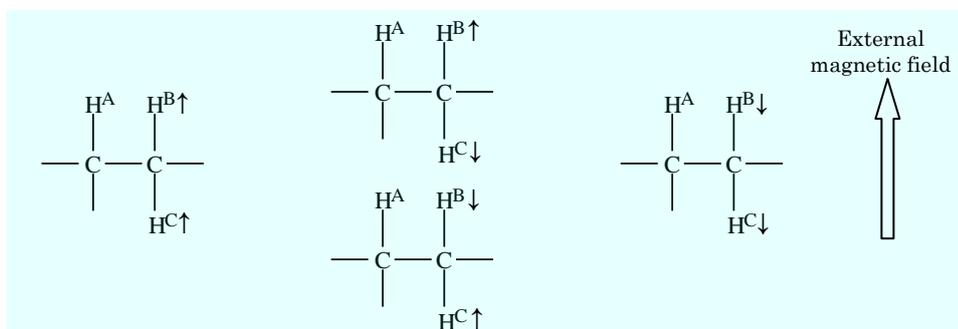
## Spin-Spin Splitting

In high-resolution proton NMR spectra many of the signals are split into a set of narrower peaks. This is because the precise resonance frequency of chemically equivalent protons is affected not only by the presence of nearby electrons but also by the magnetic field of neighbouring non-equivalent protons. Consider the following portion of an organic molecule:



The magnetic field felt by proton  $H^A$  depends on the spin state of the neighbouring proton  $H^B$ . If the spin of neighbouring proton  $H^B$  is aligned with the external magnetic field, proton  $H^A$  feels a slightly stronger magnetic field and resonates at a slightly higher radio frequency. If the spin of proton  $H^B$  is aligned against the magnetic field, this decreases the local magnetic field around  $H^A$ . Because there are approximately equal numbers of  $H^B$  in each spin state, there are two “types” of proton  $H^A$  which resonate at slightly different frequencies. This means that the signal in the NMR spectrum due to proton  $H^A$  is split into two peaks. We call this set of two peaks a **doublet**.

What happens if proton  $H^A$  has two neighbouring protons? There are three possible energy states for  $H^A$  depending on the spin states of the neighbouring protons (including two permutations of the same state):



The coupling of spin states means that the signal for proton  $H^A$  is split into three peaks called a **triplet**. The three peaks have the intensity ratio 1:2:1.

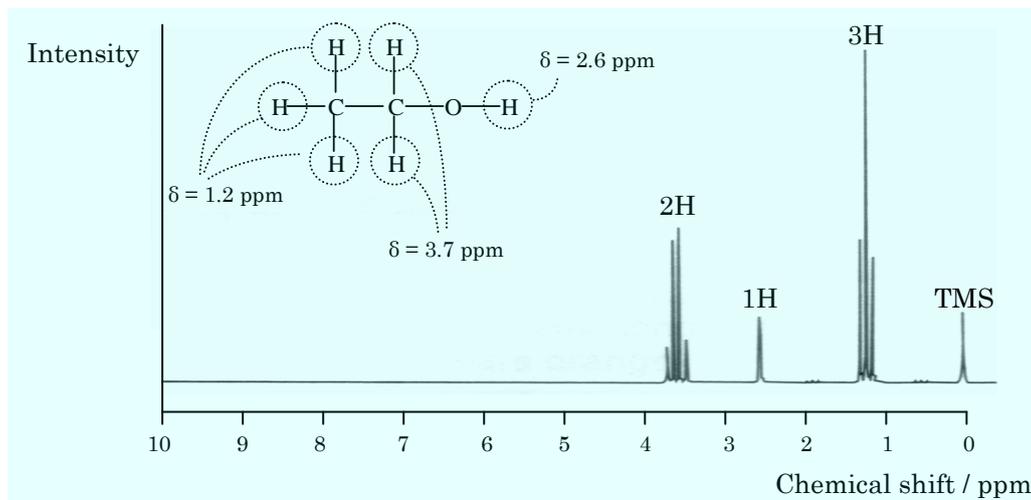
We saw the low-resolution proton NMR spectrum of ethanol in Figure A12. Now look at the high-resolution spectrum in Figure A26 on the next page.

The signal for the  $-\text{CH}_3$  protons at  $\delta = 1.2$  ppm is split into a triplet by spin-spin coupling with the  $-\text{CH}_2-$  protons on the neighbouring C atom in the molecule. Now look at the signal for the  $-\text{CH}_2-$  protons at  $\delta = 3.7$  ppm. It is split into four separate peaks called a **quartet** by the magnetic fields of the neighbouring  $-\text{CH}_3$  protons, with signal intensity 1:3:3:1. The possible alignments of three protons are shown on the right. You will also see that the two sets of peaks at 1.2 ppm and 3.7 ppm are not exactly symmetrical but lean towards each other. This leaning is typical of signals that are coupled together.

Alignment of protons	Signal intensity
↑↑↑	1
↑↑↓ or ↑↓↑ or ↓↑↑	3
↑↓↓ or ↓↑↓ or ↓↓↑	3
↓↓↓	1

## Option A – Additional Higher Level

**Figure A26 High-Resolution Proton NMR of Ethanol**

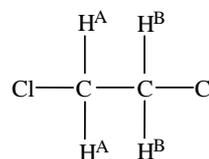


The more observant of you will notice that the O–H proton signal has a different chemical shift in Figures A12 and A26. This is because the ethanol is dissolved in different solvents when the two spectra were run. This is one of the problems with identifying the O–H proton in a NMR spectrum. There is a wide range of possible chemical shift values depending on the solvent, the purity of the sample and the presence of water. The O–H proton signal is not split in the high-resolution spectrum in Figure A26 because rapid exchange of the proton between ethanol molecules averages out the different possible energy levels due to spin-spin coupling.

The splitting of a proton NMR signal due to spin-spin coupling can be summarised by the  $n+1$  rule:

**The NMR signal for chemically equivalent protons is split into  $n$  peaks by  $n+1$  non-equivalent adjacent protons**

Notice the italics in the definition. A signal for a proton or a set of protons in a molecule is not split by chemically equivalent protons. Take the molecule 1,2-dichloroethane on the right as an example. The signal for protons  $H^A$  is not split by the magnetic fields of protons  $H^B$ , and vice-versa, because the two pairs of protons are chemically identical. Only one peak, a singlet, is seen in the proton NMR spectrum of this molecule. Replace one of the chlorine atoms with a bromine atom to form the molecule 1-bromo-2-chloroethane,  $\text{ClCH}_2\text{CH}_2\text{Br}$ , and the two pairs of protons are no longer chemically equivalent. Two sets of peaks are seen in the proton NMR spectrum, and each signal is split into a triplet by the two protons on the neighbouring C atom. The technique of proton NMR and splitting patterns is covered in the following excellent video: <http://www.youtube.com/watch?v=uNM801B9Y84>



### Interpreting a High-Resolution NMR Spectra

The following basic steps will help you interpret a high-resolution proton NMR spectrum:

1. Identify the number of different electronic environments for protons in the molecule from the number of groups of signals in the spectrum.
2. Identify the number of chemical equivalent protons under each signal from the integration trace (the integration trace may not be given to you; instead the number of protons under each signal may be written next to each signal on the spectrum).
3. At this point, use any other information given to you, like the molecular formula or any functional groups present, to sketch possible structures for the molecule.
4. Match the chemical shifts in the NMR spectrum with the ranges for different protons in the table in the data booklet (Table A5).
5. Check and confirm your proposed molecular structure with the splitting patterns seen in the NMR spectrum.