ANDERSON SERANGOON JUNIOR COLLEGE
H3 CHEMISTRY
ULTRAVIOLET/VISIBLE SPECTROSCOPY

Unsaturation

CONTENT

LEARNING OUTCOMES

Students should be able to:

a) explain that ultraviolet/visible absorption in organic molecules requires electronic transitions ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions; forbidden and allowed transitions) between energy levels in chromophores which contain a double or triple bond, a delocalised system, or a lone pair of electrons [detailed knowledge of instrumentation is not required]

b) predict whether a given organic molecule will absorb in the ultraviolet/visible region by identifying the chromophore

c) explain qualitatively how increasing conjugation in an organic molecule decreases the gap between energy levels and hence shifts the absorption towards longer wavelength

d) use the Beer–Lambert law, absorbance = $\lg(I_0/I) = \varepsilon cl$, where ε is taken merely as a constant characteristic of the substance concerned, to calculate the concentration of a given species (either organic or inorganic) in solution

e) apply ultraviolet/visible spectroscopy to quantitative analysis of a given species (either organic or inorganic) in solution

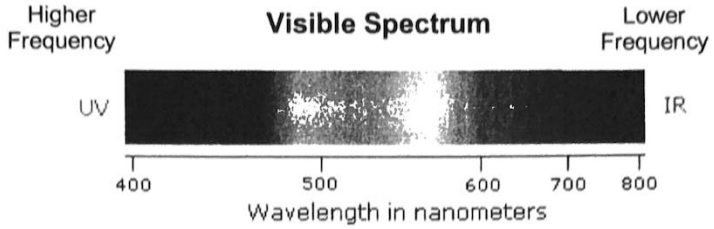
BIG QUESTIONS

1. Have you ever wondered why some organic substances are coloured? (E.g. why are carrots orange in colour?)
2. How do we "see" colours using our eyes?
3. Is there a way to measure the concentration of substances without using chemical methods such as titration?

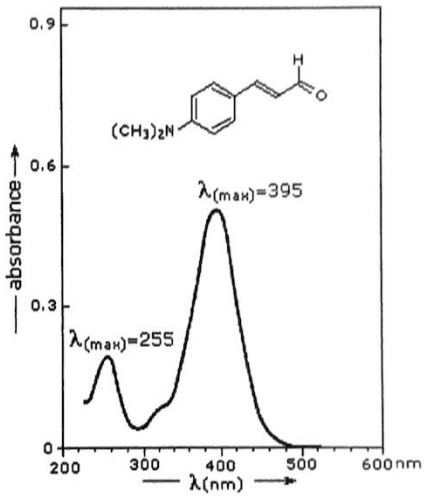
1. INTRODUCTION

Ultraviolet/visible spectroscopy is the study of the absorption of ultraviolet and visible radiation by molecules.

The **visible (VIS)** region of the electromagnetic (EM) spectrum extends approximately from **400 to 800 nm** (150 – 300 kJ mol^{-1}). The **ultraviolet (UV)** region extends from 10 to 400 nm, but the narrow range from **200 to 400 nm** (300 – 600 kJ mol^{-1}) is of greatest interest to organic chemists.



A UV–VIS spectrum is recorded by irradiating a solution of the compound with UV–VIS radiation of continuously changing wavelength. When the wavelength corresponds to the energy required to excite an electron, radiation is absorbed. The absorbance is plotted against wavelength to give the spectrum, e.g.



The energy of photons in the UV/VIS region of the spectrum is the same order of magnitude as the gaps between adjacent **electronic energy levels** of some molecules and ions.

2. ULTRAVIOLET/VISIBLE ABSORPTION IN ORGANIC MOLECULE

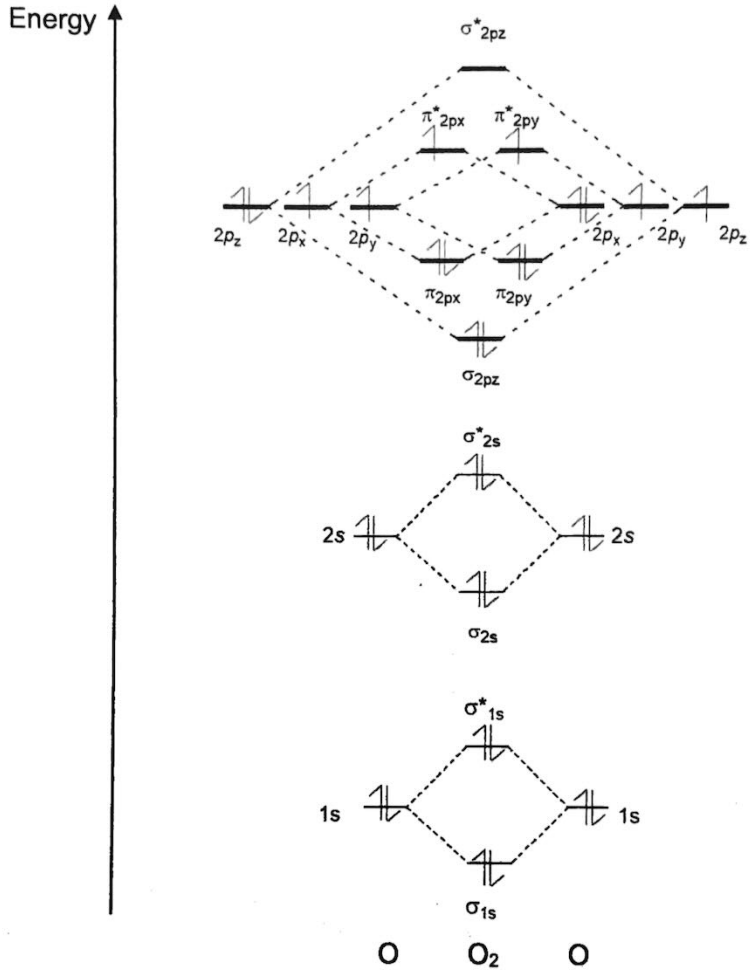
2.1 Chromophore

A chromophore is the part of a molecule that absorbs UV/VIS region of the EM radiation. This can occur as the energy difference between two different molecular orbitals falls within UV/VIS range of the EM spectrum.

2.2 (Simplified) Molecular Orbital Theory

When 2 atomic orbitals (AO) of 2 atoms overlap, 2 molecular orbitals (M.O.) are formed: a bonding M.O. of lower energy level (σ or π) and an anti–bonding M.O. of higher energy level (σ^* or π^*). [Whether σ or π depends on whether it is a head–on or side–way overlap.]

Molecular Orbital Diagram of O_2

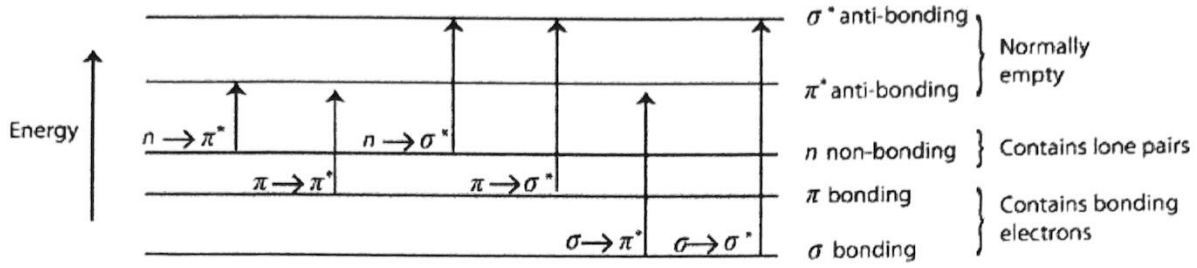


When each has 1 electron in their AO, the two electrons will occupy the MO of lower energy. The highest energy MO with any electrons is known as **H**ighest **O**ccupied **M**olecular **O**rbital (**HOMO**) while the next higher energy MO which is empty is known as **L**owest **U**noccupied **M**olecular **O**rbital (**LUMO**).

There can also be no overlapping of AO and in such cases, the AO will remain at the same energy level and is known as non–bonding MO (*n*).

2.3 Electronic Transition in Organic Molecules

The following diagram shows the relative energies of various types of MOs that could exist in an organic molecule.



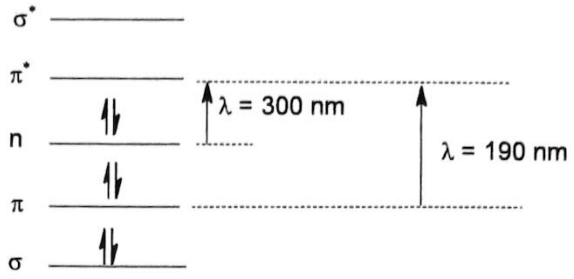
When a photon is absorbed by a molecule, an electron gains the photon's energy and is promoted to a higher energy orbital. The electrons normally reside in the bonding orbitals (σ or π), or in the non–bonding orbitals (*n*) if they are lone pairs on atoms such as nitrogen or oxygen. The higher energy orbital to which they are promoted is almost invariably an anti–bonding orbital (σ* or π*).

The diagram above also shows the possible electronic transitions that can occur between three different types of MOs.

The following table describes some electronic transitions that occur between MOs:

σ → σ*	An electron in a bonding σ orbital is excited to the corresponding anti–bonding orbital. The energy required is large. For example, methane (which has only C–H bonds, and can only undergo σ → σ* transitions) shows an absorbance maximum at 125 nm. Hence, absorption maxima due to σ → σ* transitions are **not seen** in typical UV/VIS spectra (200 – 800 nm).
n* → σ	**Saturated compounds containing atoms with lone pairs** (non–bonding electrons) are capable of *n* → σ* transitions. These transitions usually need less energy than σ → σ* transitions. They can be initiated by light whose wavelength is in the range 150 – 250 nm. The number of organic functional groups with *n* → σ* peaks in the UV region is small.
n* → π **and** **π → π***	**Most** absorption spectroscopy of organic compounds is based on transitions of *n* or π electrons to the π* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 – 800 nm). These transitions need an **unsaturated group** in the molecule to provide the π electrons.

Of all the possible electronic transitions, **only $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions normally produce absorption in the uv/visible region**. Therefore, organic molecules should have chromophores that contain π electrons or have atoms with lone pairs of electrons to give characteristic UV/VIS spectra.
In methanal, $CH_2=O$, two electronic transition absorbing in the uv/visible region is shown below.



The common chromophores and their electronic transitions in organic molecules are represented in the table below.

Chromophore	Example	Electronic transition	λ / nm
C=C	ethene	$\pi \rightarrow \pi^*$	171
C≡C	1-hexyne	$\pi \rightarrow \pi^*$	180
C=O	ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180
N=O	nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200
C–X (X=Br, I)	bromomethane iodomethane	$n \rightarrow \sigma^*$	205 255

2.4 Factors Affecting The Energy Gap Of Electronic Transition

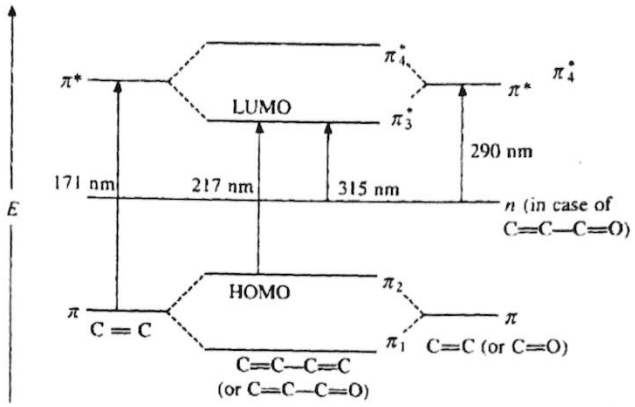
(a) Conjugation

Chromophores with a conjugated π system that consists of a series of alternating single and double bonds shows absorbance at longer wavelengths.

lower energy

In a conjugated diene, the π MOs of the separate alkene groups combine to give two new bonding MOs designated π_1 and π_2, and two anti–bonding MOs designated π_3^* and π_4^*. The energetically most favorable $\pi \rightarrow \pi^*$ excitation occurs from the highest energy bonding π MO (HOMO) to the lowest energy π* MO (LUMO).

The following diagram shows the $\pi_2 \rightarrow \pi_3^*$ transition, the promotion of an electron from HOMO to LUMO in 1,3–butadiene. The energy required is lower for 1,3–butadiene as compared to $\pi \rightarrow \pi^*$ transition in ethene resulting in longer wavelength for the absorption in 1,3–butadiene.



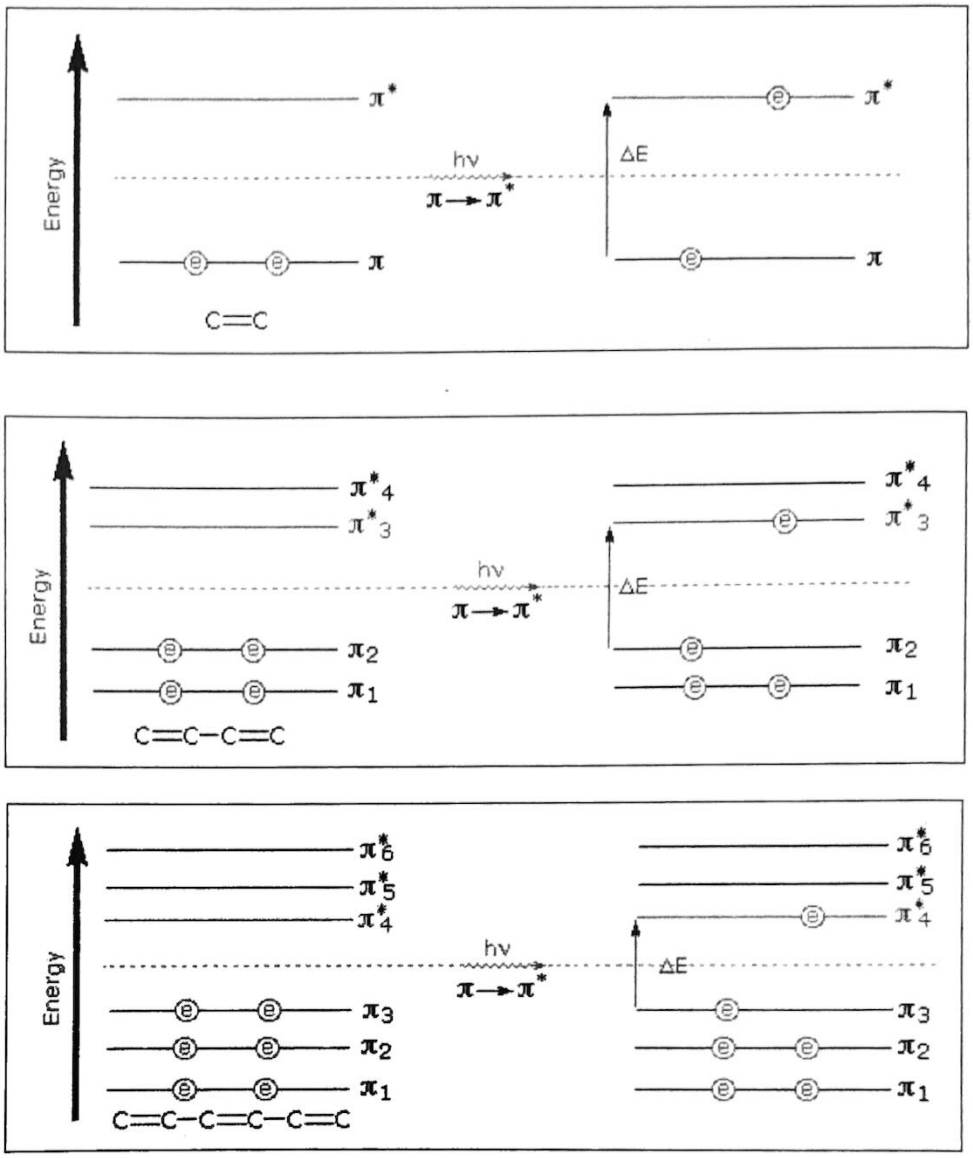
HOMO & LUMO

Reason

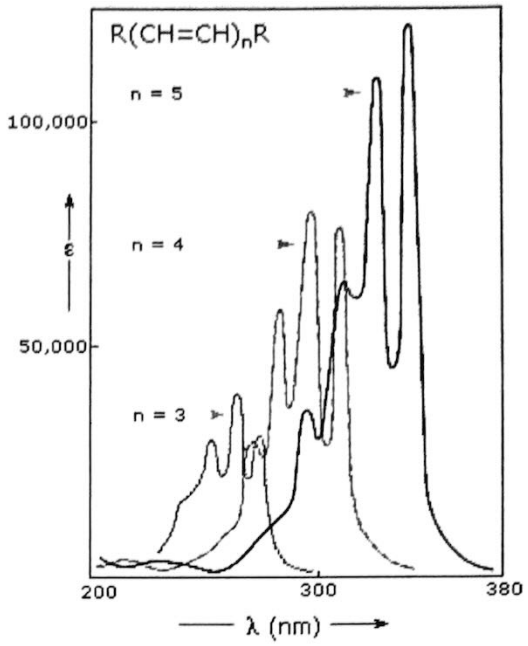
① Conjugation of π bonds reduces the energy gap between the π and the π* MOs. This shifts the absorption towards ③ longer wavelength (bathochromic shift).

Hence the more conjugated a system is, the lower the energy gap between π and the π* MOs. As a result, the ② lower the amount of energy that is required to excite an electron, and absorption would thus be seen at longer wavelengths.

The following diagrams illustrate the excitation for an isolated double bond (only two pi–orbitals) and for a conjugated diene and triene. It can be seen that increased conjugation brings the HOMO and LUMO orbitals closer together. The energy (ΔE) required to excite an electron is therefore less, and the wavelength that provides this energy is increased correspondingly. It may even lie in the visible region of the EM spectrum if the conjugated system is long enough.



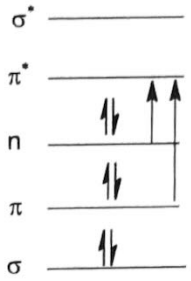
From the polyene spectra shown below, it is clear that each additional double bond in the conjugated pi–electron system shifts the absorption maximum about 30 nm in the same direction. Also, the molar absorptivity (ε) roughly doubles with each new conjugated double bond.



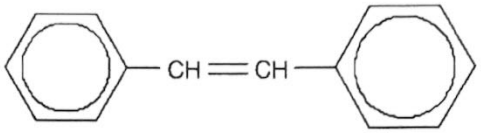
	* energy gap / kJ mol^{-1}	λ□/ nm
R–CH=CH–R	690	190
R–CH=CH–CH=CH–R	520	230
R–CH=CH–CH=CH–CH=CH–R	235	275

(b) Atom with lone pair of electron

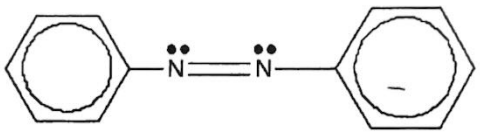
The incorporation of **an atom with a lone pair of electrons** into the molecule can cause a major **shift** of absorbance to **longer wavelengths**, since the $n \rightarrow \pi^*$ energy gap is smaller than the $\pi \rightarrow \pi^*$ energy gap. However, because the $n \rightarrow \pi^*$ transitions are symmetry forbidden, the absorptions are weak (low in absorbance compared to other transitions).



For example,

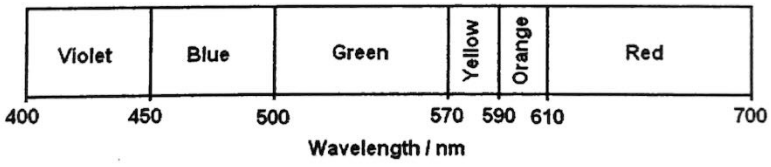


Absorption at 296 nm, appears colourless as absorption is out of the VIS region.

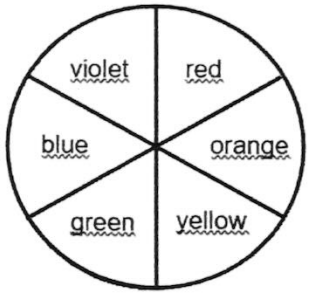


Absorption at 400 nm, i.e. blue–violet, appears orange in colour. Colour observed is complementary to the colour absorbed.

The complementary colours are illustrated with the following colour wheel.



Visible region of the spectrum



Colour wheel

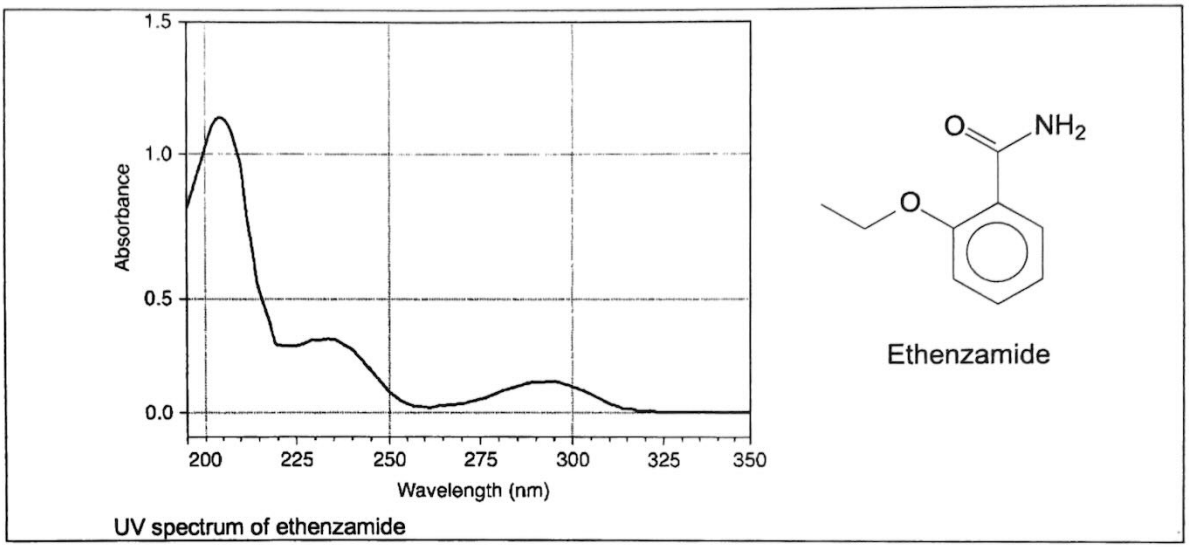
Opposite colours in the wheel are **complementary** colours

2.5 UV/VIS Spectrum

Although the energy of absorption is discrete, we will never obtain an absorption spectrum that corresponds to only a few specific lines of EM radiation being absorbed. Instead, a complex spectrum would be obtained. This is because other than the pure electronic transition, there is also the superposition of rotational and vibrational transitions onto the electron transition, and these give rise to a combination of overlapping spectra lines.

Therefore, the actual electronic transition spectrum appears as a continuous absorption band rather than discrete lines. Sometimes the solvent that is being used to dissolve the compound would affect the absorption spectrum obtained.

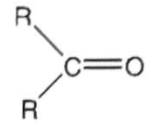
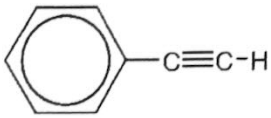
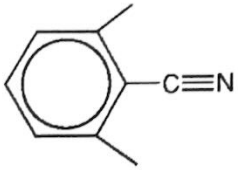
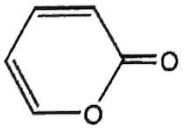
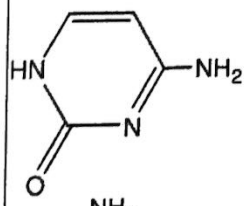
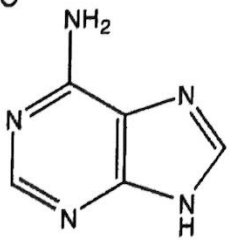
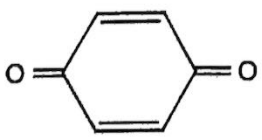
A typical UV spectrum corresponding to ethenzamide is shown below. There are three absorption peaks due to three different electronic transitions ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ or $n \rightarrow \sigma^*$). But it is not possible to allocate a specific transition to each wavelength due to the broadness of the absorption peaks. Thus, it **not** possible to use the position of the absorption peaks to determine the identity of a compound.



UV spectrum of ethenzamide

In addition, it can be seen from Table 1 on page 12 that many different chromophores absorb at nearly about the same wavelength. **The UV/VIS absorption is therefore not very useful for identifying compounds.**

Summary of the wavelengths at which some chromophores absorb radiation

	Absorption wavelengths
	190 nm (>10,000), 300 nm (30)
R–CH=CH-CH=CH R	230 nm (15,000)
R–CH=CH-CH=O	230 nm (12,000)
 (benzene)	184 nm (60,000), 203 nm (7400), 254 nm (204)
	234 nm (25,100), 246 nm (22,400)
	280 (1800), 290 (2000)
	300 nm (5000)
 (cytosine)	267 nm (6130)
 (adenine)	260 nm (13,500)
 (quinone)	242 nm (24,000), 281 nm (400), 434 nm (20)

values in brackets after the wavelengths are the molar extinction coefficients (see text)

3 QUANTITATIVE ANALYSIS

3.1 Beer-Lambert Law

The main use of UV/VIS spectroscopy is to analyse **quantitatively** how much of a particular compound is present in a solution using Beer–Lambert Law (Beer's Law).

$A = \log_{10}(I_o/I) = \varepsilon lc$ ✱ memorise	A = absorbance I_o = intensity of incident radiation I = intensity of emerging radiation ε = the *molar extinction coefficient, or molar absorptivity* c = concentration of compound (in mol dm^{-3}) l = path length of the absorbing solution (in cm)

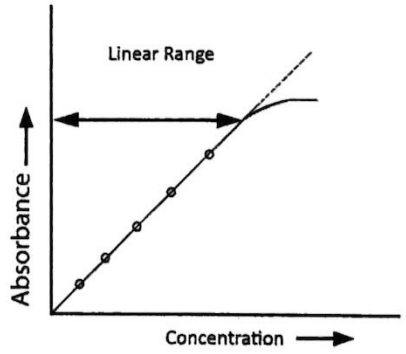
(The cells usually used in UV-VIS spectrophotometer are usually 1 cm^2 in cross section, so l = 1.0 cm)

The **molar extinction coefficient** (its units are $dm^3\ mol^{-1}\ cm^{-1}$, but by convention the units are never expressed) is how much light of **a particular wavelength** is absorbed by a 1.0 cm sample cell of a 1.0 mol dm^{-3} solution of a particular chemical.

Hence, this linear relationship between the concentration and the absorbance of the solution, enables the concentration of a solution to be calculated by measuring its absorbance.

3.2 Procedure involved in determining the concentration of an unknown

1. Run the UV/VIS spectrum of the compound in question, and of other compounds that may be present in the mixture by making a scan through the various wavelengths.
2. Choose a wavelength where there is a large absorption of the compound in question but only a small absorption of the other compounds present.
3. Prepare a series of standard solutions of the compound in question, to cover the range of concentrations expected.
4. Using a UV/VIS spectrophotometer, use these solutions to prepare a calibration curve of *absorbance* against *concentration*.
5. Place the sample of unknown concentration in the spectrophotometer, and measure the absorbance.
6. Read the concentration of the compound in question from the calibration curve.



If the molar extinction coefficient, ε, is known, the concentration can be calculated directly from the absorbance using the Beer's law equation.

3.3 Limitation of Beer-Lambert Law

The law only applies to dilute solutions typically ***below concentrations of 0.01 mol dm^{-3}***.

At higher concentrations, the individual particles of the analyte no longer behave independently of each other. The resulting interaction between particles of analyte may change the analyte's absorptivity.

The analyte's absorptivity depends on the sample's refractive index. The refractive index varies with the analyte's concentration, so the values of A and ε may change. For sufficiently low concentrations of analyte, the refractive index is essentially constant and the calibration curve is linear.

At higher concentrations, the absorbance vs concentration plot begins to show deviations from linear behaviour.