

What is spectroscopy?

- The study of the interaction of **matter** and **electromagnetic radiation**

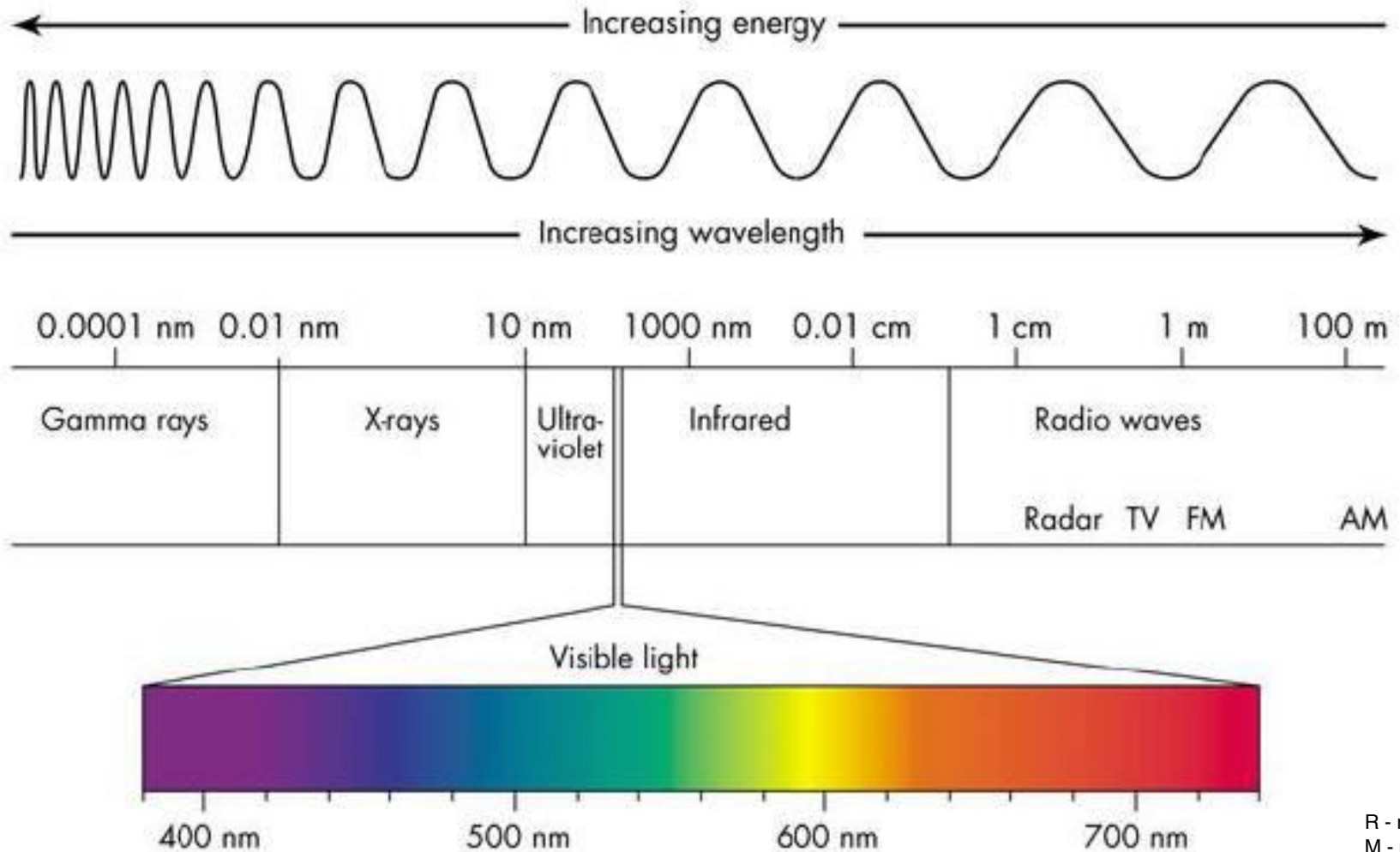
What is electromagnetic radiation (EMR)?

- EMR is radiant energy that displays the properties of both particles and waves
- There are different types of electromagnetic waves that make up the **electromagnetic spectrum (EMS)**

An example of electromagnetic radiation

- Visible light

The electromagnetic spectrum



R - radio waves
M - micro waves
I - infrared waves
V - visible light
U - utrlaviolet
X - x rays
G - gamma rays

Gamma rays

*are emitted from the nuclei of some radioactive elements and because of their **high energy** can severely damage biological organisms.*

X-rays

are less harmful than gamma except in high doses.

UV light

is responsible for sunburn. Repeated exposure leading to skin cancer by damaging DNA molecules in skin cells.

Visible light

electromagnetic radiation that we see.

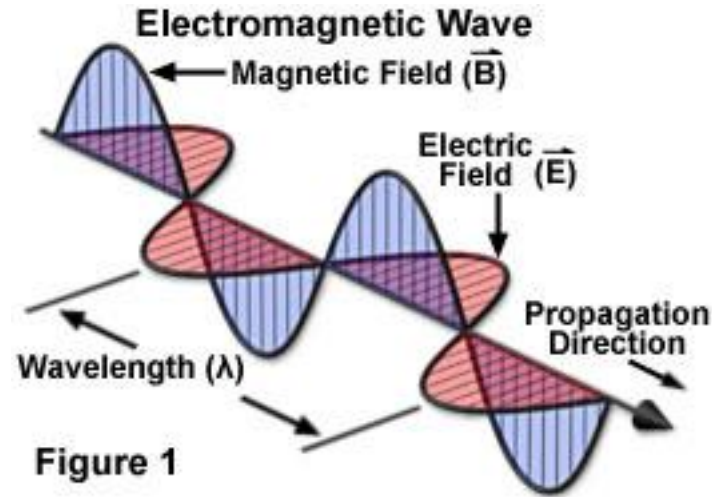
Infrared radiation

We feel IR as heat

Radio waves

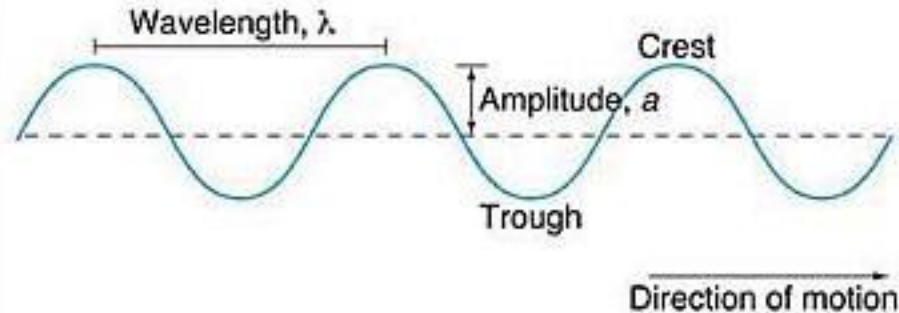
*have the **lowest energy** (frequency) Radio, TV. Radio waves are also used in NMR and in magnetic resonance imaging MRI*

The nature and properties of electromagnetic radiation



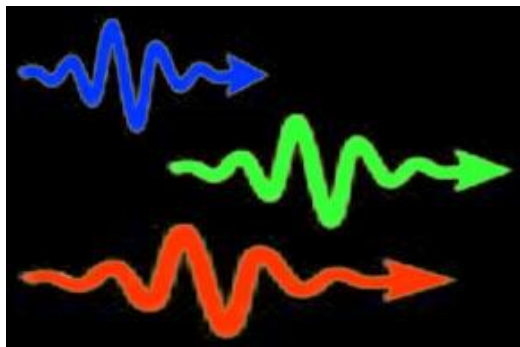
- Electromagnetic radiation has 2 components: an electric field and a magnetic field which are in planes at right angles to each other.
- A given point in space experiences a periodic disturbance in **electric** and **magnetic** fields as the wave passes by.
- A KEY Difference between electromagnetic waves and other types of waves, (e.g. sound, water and seismic waves which exist only by virtue of the medium in which they move), EM waves can travel through a vacuum.

The nature and properties of electromagnetic radiation



- **Frequency, ν** = the number of crests of the wave that pass a point per second. The SI unit of frequency, ν , is the *reciprocal second*, s^{-1} , which is also called the **hertz, Hz**.
- **Wavelength, λ** = distance between two adjacent crests or troughs of the wave. The SI unit of wavelength, λ , is *metres*, **m**, though multiples such as **nm** (10^{-9} m) are frequently used.
- **Velocity**, in a vacuum all electromagnetic waves travel with the same velocity: **$c = 2.998 \times 10^8 \text{ ms}^{-1}$** .
- These are related by the following equation: **$c = \lambda \nu$**

The nature and properties of electromagnetic radiation



Light is **quantised** and can also be treated as a 'particle'. A particle of electromagnetic radiation is called a **photon**.

The *energy*, **E** , of a photon is given by **$E = h\nu$**
(h is Planck's constant, $h = 6.626 \times 10^{-34} \text{ J s}$)

$$E = h\nu \quad \text{-----(1)}$$

$$c = \lambda\nu \quad \text{----- (2)}$$

so

$$E = \frac{hc}{\lambda}$$

Energy of the photon (wave) is **directly** proportional to **FREQUENCY**

Energy of the photon (wave) is **inversely** proportional to **WAVELENGTH**

The SI unit of energy is the **joule, J** (although **kJ mol^{-1}** is often quoted).

Wavenumbers: $E = hc (1/\lambda) = \underline{hc} \bar{\nu}$ The SI unit of $\bar{\nu}$ is m^{-1} .

Unfortunately cm^{-1} is much more common. $\bar{\nu}/\text{m}^{-1} = 100 \times \bar{\nu}/\text{cm}^{-1}$

Example

Given that a UV photon of light that damages DNA has a wavelength of 234 nm calculate the frequency of the photon in Hertz and its energy in kJ mol⁻¹ and in electron volts, eV.

$$c = \lambda \nu$$

$$\nu = c/\lambda = 3 \times 10^8 / 234 \times 10^{-9} = 1.3 \times 10^{15} \text{ Hz}$$

$$E = hc/\lambda$$

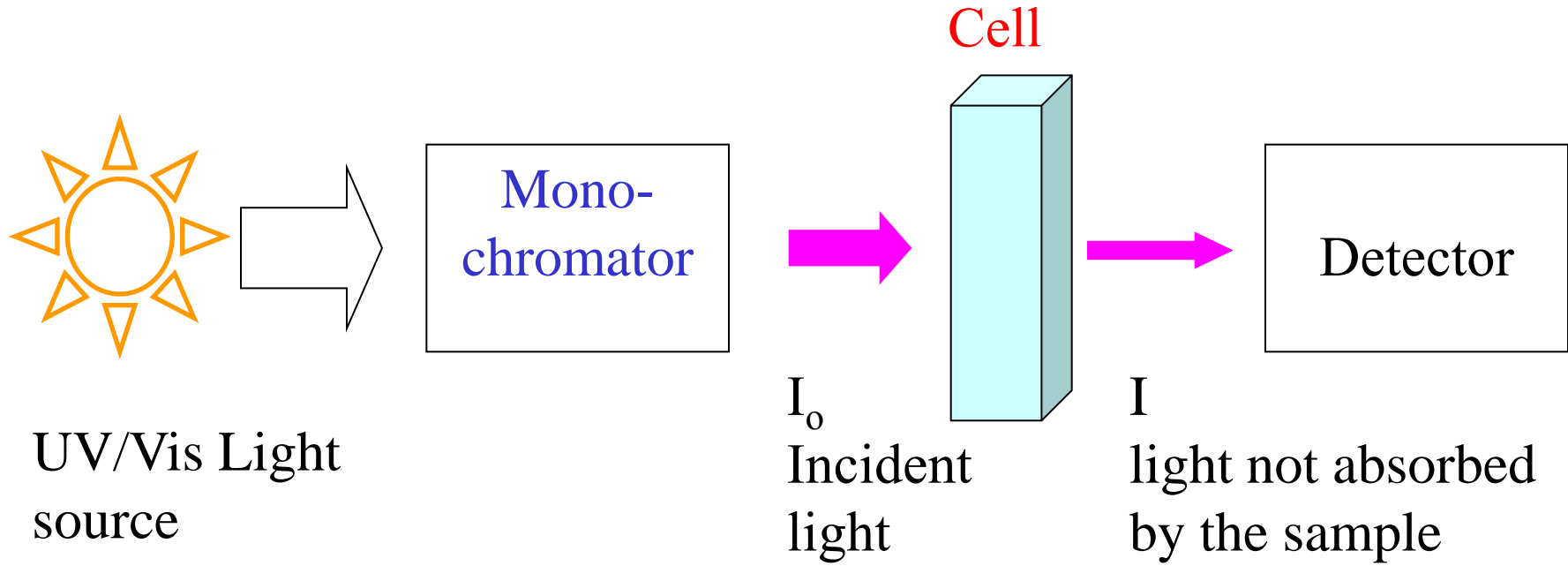
$$E = 8.49 \times 10^{-19} \text{ J}$$

$$= 1.28 \times 10^{-45} \text{ kJ mol}^{-1} \text{ (dividing by avagadro number } 6.626 \times 10^{23} \text{ and } 10^3)$$

$$= (8.49 \times 10^{-19}) / (1.6 \times 10^{-19}) \text{ eV}$$

$$= 5.31 \text{ eV}$$

UV/Visible spectroscopy



The **monochromator** selects a single wavelength from the wide range provided by the light source.

The **cell** (cuvette) can be glass or plastic for visible light but must be quartz for UV light (glass and plastic absorb UV).

What factors control the amount of absorbance?

There are three factors which govern the amount of absorbance exhibited by a sample.

1. The thicker the sample, the more absorption takes place.
2. More absorption is seen for more concentrated samples (more molecules present to absorb the light).
3. Some molecules are better than others at absorbing a particular wavelength; it is an inherent property of the molecule.

Amount of absorbance = Thickness of the sample x Concentration of the sample x Inherent property of the molecule

Quantitative Absorption

The Beer-Lambert law - at a single wavelength

Absorbance, A , of a sample depends on:

1. **concentration, c** , of the absorbing species. mol L^{-1}

(Thickness) 1. **length of light path, l** , through the cell. cm

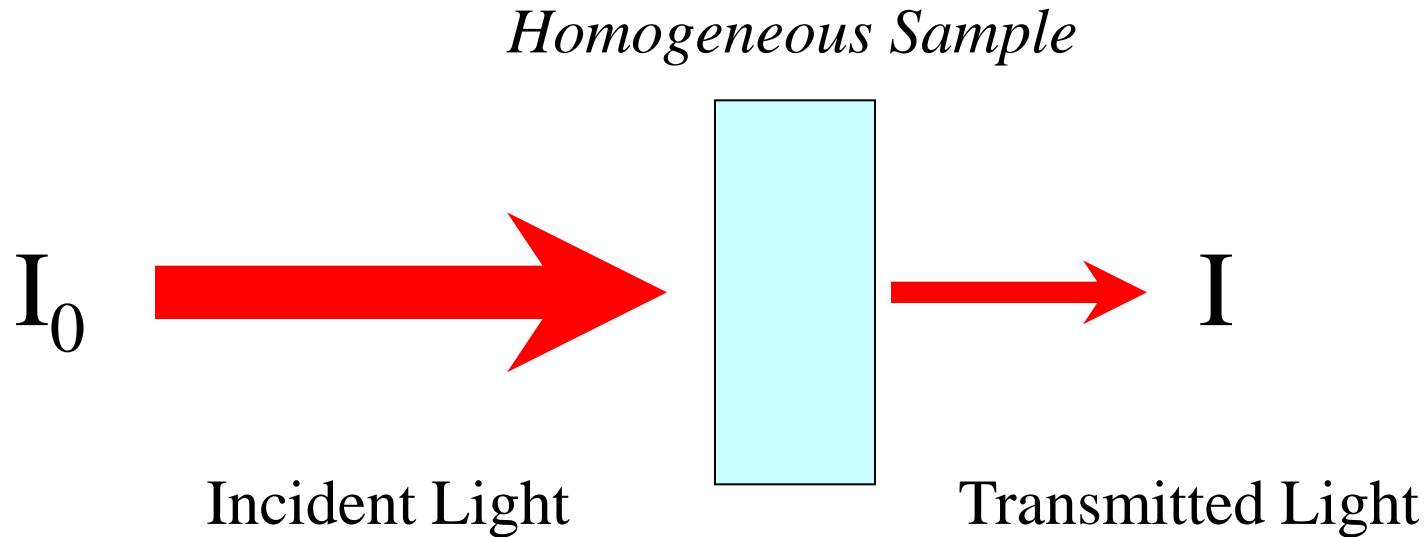
1. **molar absorption coefficient, ϵ** . $\text{L mol}^{-1} \text{cm}^{-1}$

$$\mathbf{A} = \mathbf{\epsilon c l} \quad \text{strictly better to write } \mathbf{A}_{\lambda} = \mathbf{\epsilon_{\lambda} c l}$$

Molar absorption coefficient, ϵ : some molecules are better than others at absorbing a particular wavelength; it is an inherent property of the molecule. ϵ is also known as the molar absorptivity and the extinction coefficient in older textbooks.

Quantitative Absorption

The Beer-Lambert law - measurement



$$I = I_0 10^{-\epsilon lc}$$

$$A = \epsilon lc = \log_{10}(I_0 / I)$$

The Beer-Lambert Law needs BOTH definitions of A

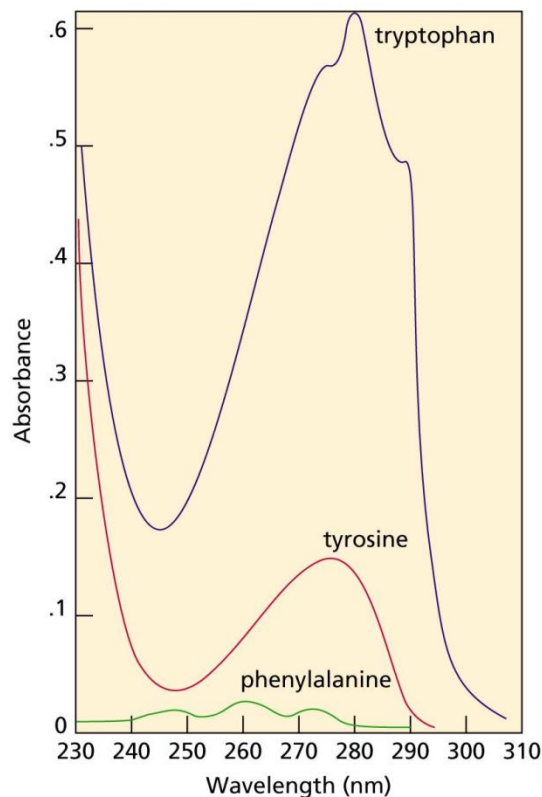
Transmission, T

Absorption data can also be reported as transmission

$$T = I/I_0 \quad \text{so} \quad A = -\log_{10}(T)$$

EXAMPLE

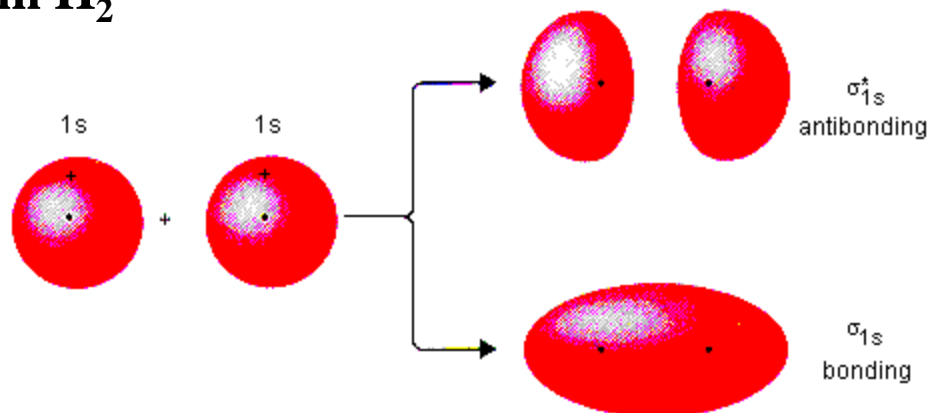
Radiation of wavelength, 280 nm passed through 1.0 mm of a solution that contained an aqueous solution of the amino acid tryptophan at a concentration of 0.50 mmol L⁻¹. The light intensity is reduced to 54% of its initial value. Calculate the absorbance and the molar absorption coefficient of tryptophan at 280 nm. What would be the transmittance through a cell of thickness 2.0 mm?



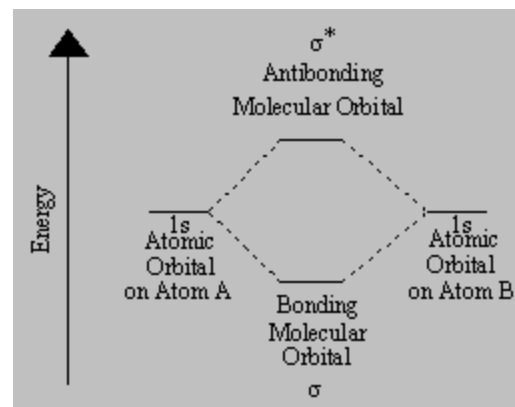
Absorbance = 0.268
Transmittance T = 0.54
Molar absorption coeff $\epsilon = 5.36 \times 10^5$

Energy levels: Molecular Orbital Theory - revision

Sigma orbitals in H_2



N.B. In an *antibonding MO* there are no electrons between the nuclei to counteract the internuclear repulsion therefore it is of higher energy than the AOs.



Molecular Orbital Theory - six basic rules:

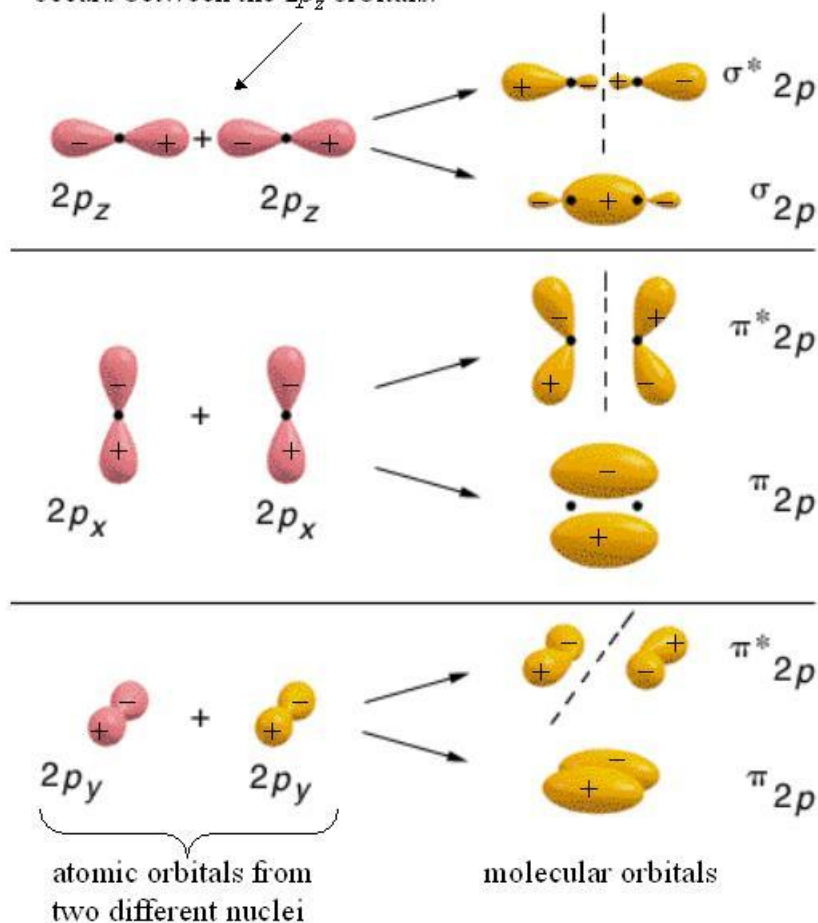
Basic premise: when atoms get close enough to bond, their *atomic orbitals* reshape themselves and become a set of *molecular orbitals* that no longer belong to any one atom but are orbitals for the *entire molecule*.

1. The **number of molecular orbitals** = the **number of atomic orbitals** combining.
2. If two atomic orbitals combine then, of the two MO's created, one is a **bonding** orbital (**lower energy**) and one is an **antibonding** orbital (**higher energy**).
3. Electrons enter the **lowest** orbital available.
4. The **maximum** number of electrons in an orbital is **2** (*Pauli Exclusion Principle*).
5. Electrons **spread out over orbitals of equal energy** before pairing up (*Hund's Rule*).
6. Orbitals on an atom that can't combine with any on the other become **non-bonding orbitals**.

molecular orbitals = atomic orbitals
2 AO combine => 2 MO created : bonding and antibonding
electrons enter in lowest orbital
max no. of electron : 2 (pauli exclusion principle)
electrons spread out over equal energy (hund's rule)
atom cant combine with other become non bonding orbitals

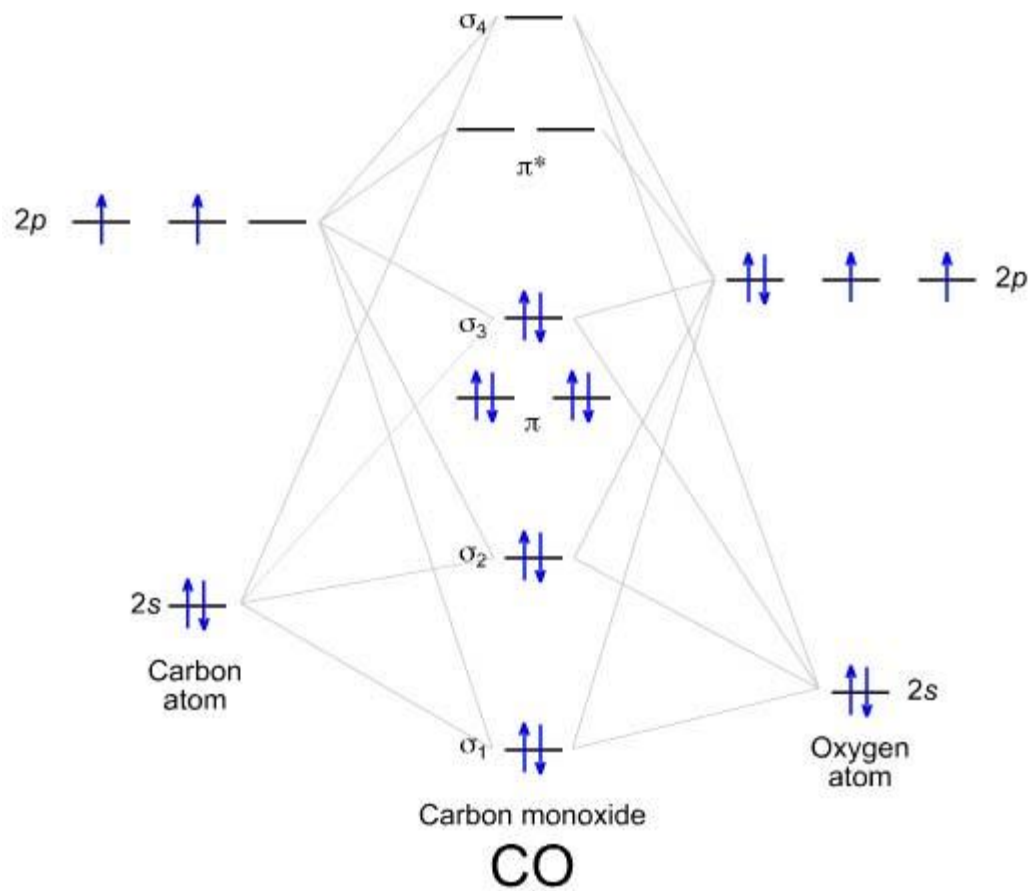
Molecular orbitals from 2p atomic orbitals

2p atomic orbitals give rise to both σ and π type molecular orbitals. The strongest overlap occurs between the $2p_z$ orbitals.

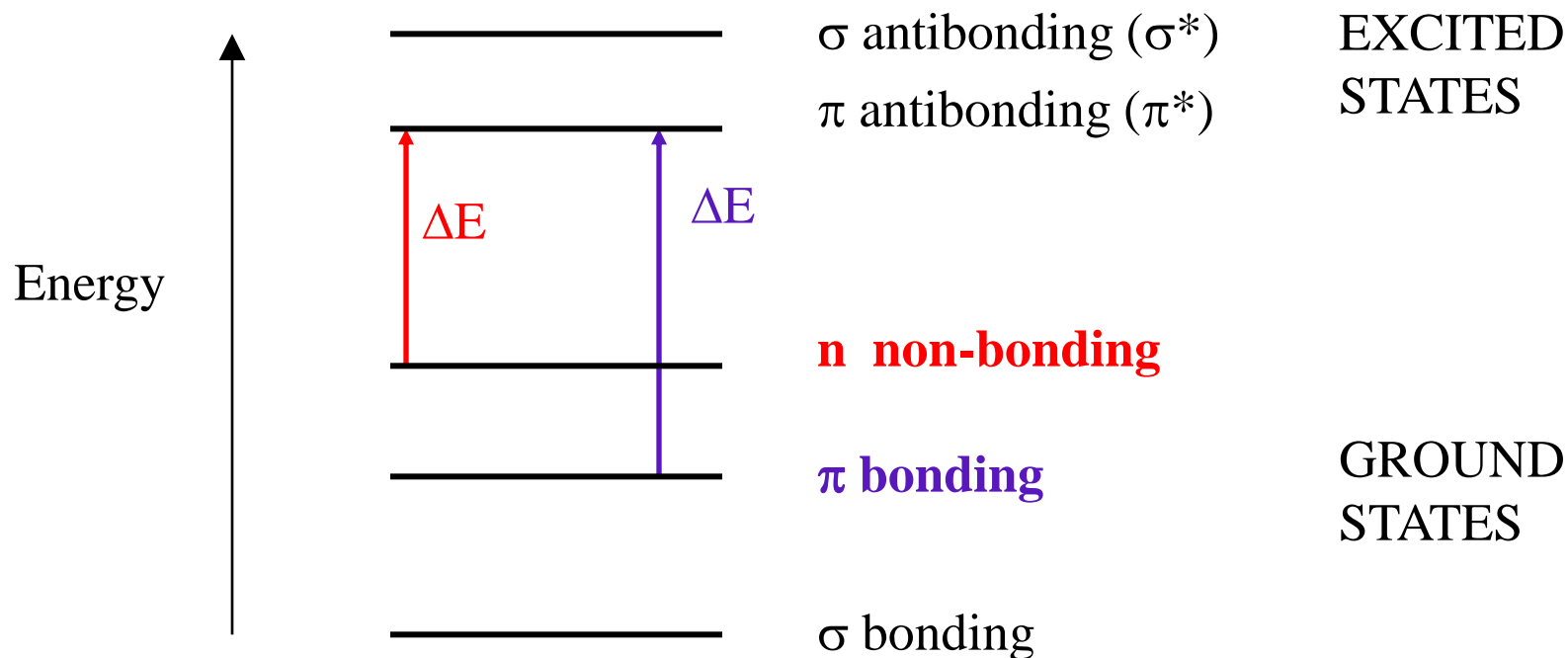


- A sigma (σ) bond is formed by s-s overlap and 2p-2p (head to head)
- A bond formed by 2p orbitals overlapping side-side is called a pi (π) bond
- Non-bonded electrons:
- **non-bonding molecular orbital**

Molecular Orbital diagram for CO



Relevance to UV/Vis Spectroscopy



- Visible light **400nm** (violet) to **750nm** (red), UV 200-400 nm.
- The energy of the UV/Vis is usually insufficient to promote electrons from sigma bonds but is in the region covered by **π** electrons and non-bonding, **n**, electrons.
- We see two types of transition **n to π*** and **π to π***

Transitions

Normal configuration of a molecule = **GROUND STATE**

(all electrons are in the available orbitals with the lowest energy)

HOMO: Highest occupied molecular orbital

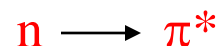
LUMO: lowest unoccupied molecular orbital

- A change between energy levels is called a *transition*.
- The lowest energy transition moves an electron between the HOMO and LUMO orbitals. Generally the excited state will also be *vibrationally* excited.
- Excited states only last for *very short periods of time* (1 to 10 nanoseconds), because the higher energy state is energetically unstable.
- The extra energy is lost through *relaxation processes* such as emission of light or heat.

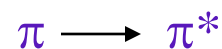
UV/Vis Transitions - summary

- UV/Vis wavelengths have sufficient energy for 2 types of transitions:

n to pi star



pi to pi star



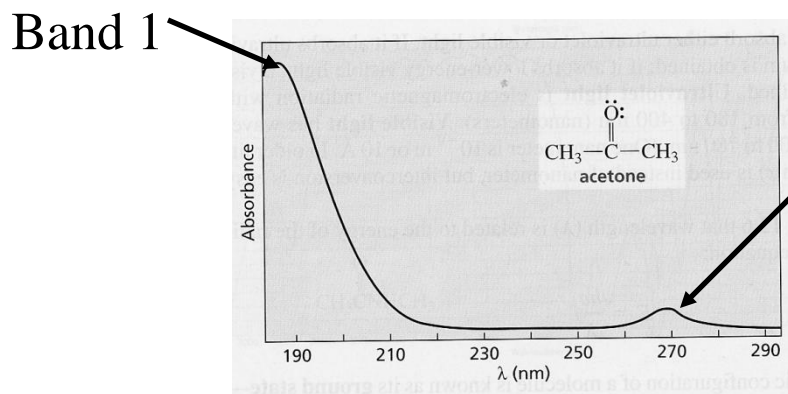
- Therefore only compounds with π electrons or non-bonding electrons usually produce UV/Vis spectra.

n to π^* is less energy than **π to π^***

$$E = \frac{h c}{\lambda}$$

therefore the lower the energy the longer the λ

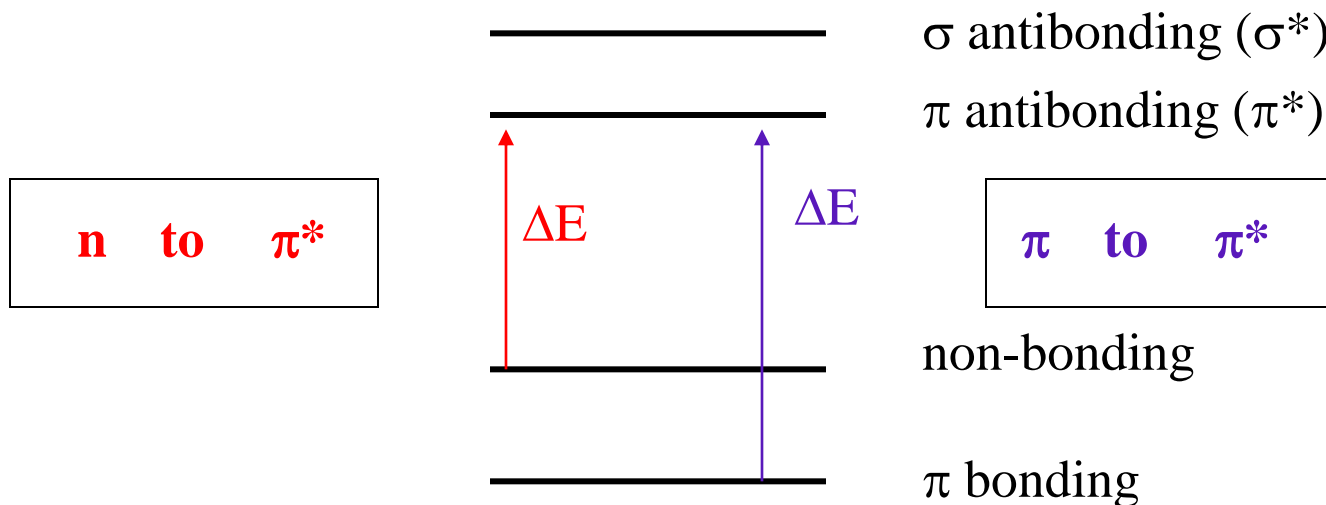
UV/Vis Spectrum - Acetone (carbonyl chromophore)



λ_{max} = the wavelength corresponding to the maximum of the absorption band

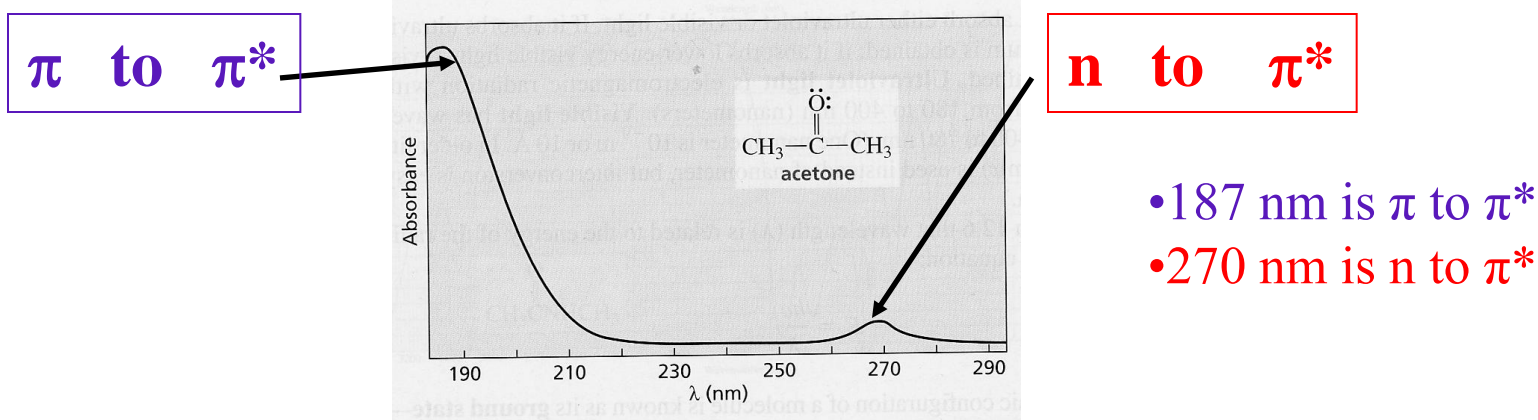
λ_{max} for acetone = 187 nm and 270 nm

Acetone has π and **nonbonded** electrons. Therefore there are 2 possible transitions



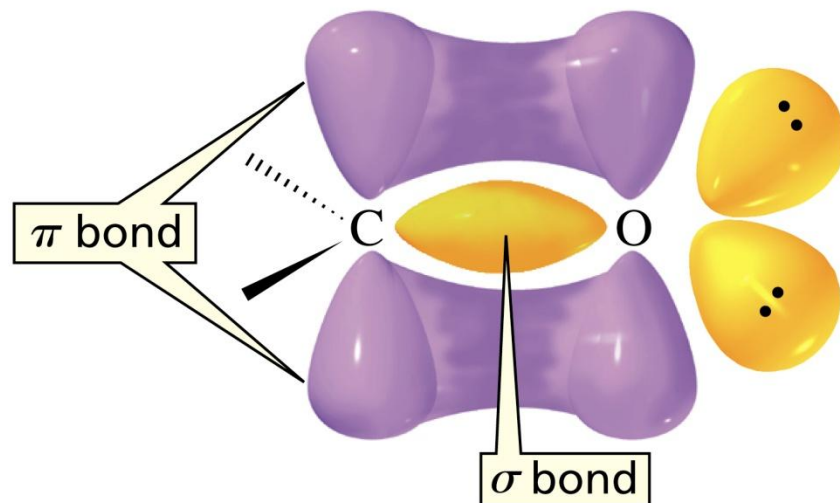
Which band is which? - The lower the energy the longer the λ

UV/Vis Spectrum - Acetone



Why are the two λ_{max} absorption peaks different heights?

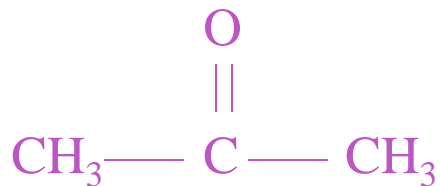
One important distinguishing characteristic of n to π^* transitions results from the fact that the **lone-pair (n) electrons** are concentrated in a different region of space from the π electrons. This makes the n to π^* transition less probable than the π to π^* .



Transition intensities

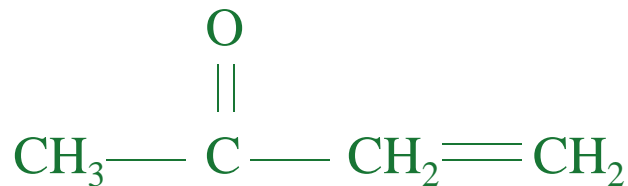
1. Although n to π^* transitions often occur at lower energy (longer wavelength) than π to π^* they are *less probable*.
2. A given photon of n to π^* light must encounter many more molecules before it is absorbed than a π to π^* photon.
As it's wavelength is longer than pi to pi photon.
3. This difference shows up experimentally in an absorption spectrum as an intensity difference; π to π^* absorptions are generally much more intense (strong absorption) than n to π^* absorptions (weak).
4. The difference in intensity is 2-3 orders of magnitude (i.e. 100-1000 times).

Effect of conjugation on wavelength



acetone

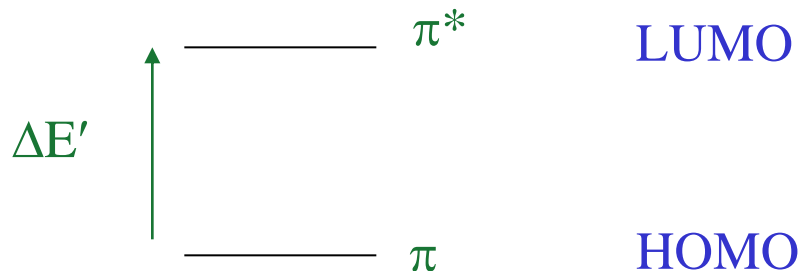
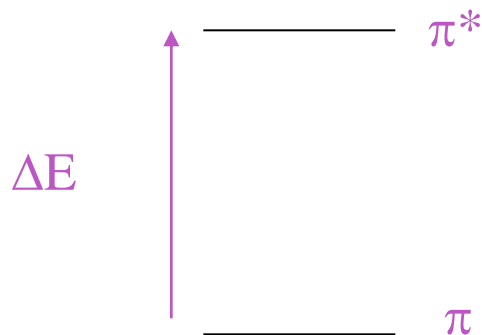
$$\lambda_{\text{max}} = 187 \text{ nm and } 270 \text{ nm}$$



Methyl vinyl ketone

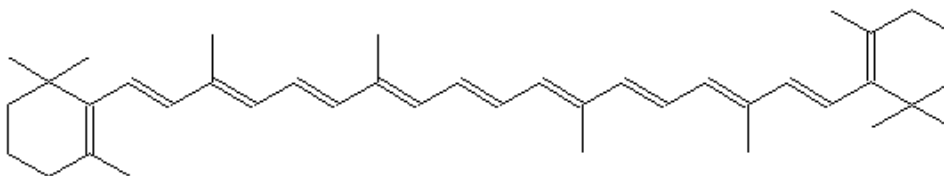
$$\lambda_{\text{max}} = 219 \text{ nm and } 324 \text{ nm}$$

- The π system of **methyl vinyl ketone** is more extended than that of **acetone**.
- Because of the more extensive π -system of **conjugated** double bonds in methyl vinyl ketone both the **n to π^*** and **π to π^*** transitions of methyl vinyl ketone occur at a longer wavelength.

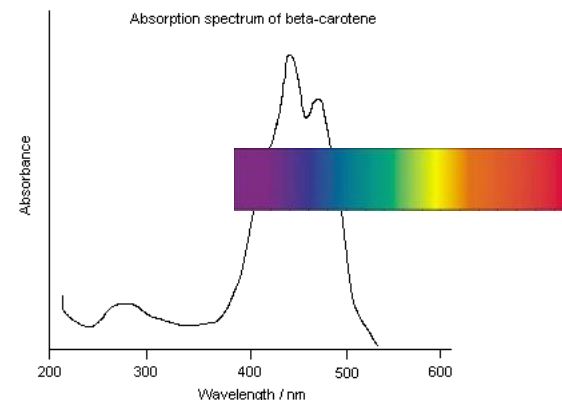


Effects of conjugation

1. Conjugation decreases the energy gap between HOMO and LUMO.
2. Hence less energy is required for electronic transitions.
3. Therefore transitions occur at longer wavelengths.
4. If a compound has enough double bonds it will absorb visible light and the compound will be coloured, e.g. **β -carotene** which is orange and is found in carrots and tomatoes has $\lambda_{\text{max}} = 455\text{nm}$

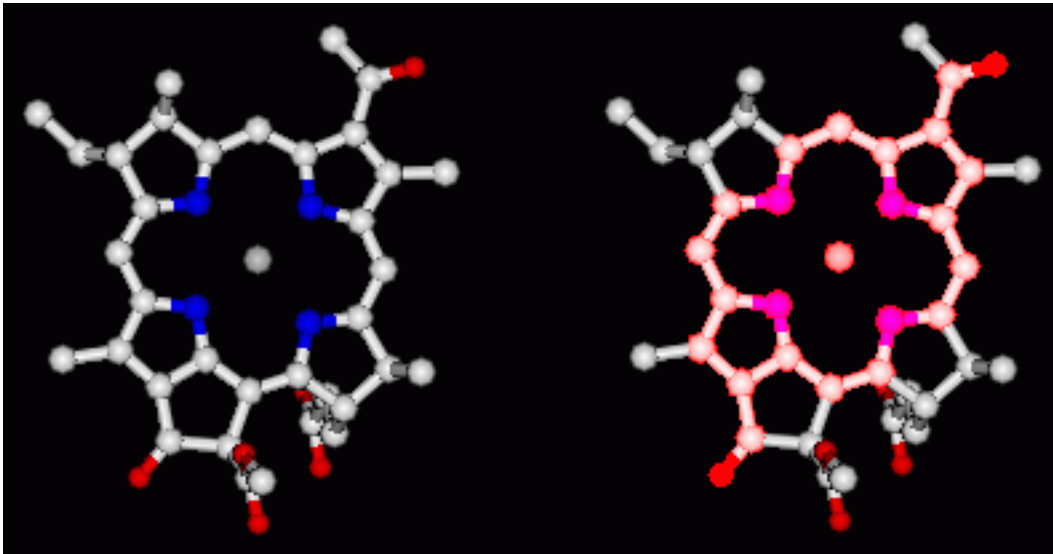


β -carotene absorbs most strongly between 400-500 nm (**green/blue** part of the spectrum) So appears orange, because the red/yellow colours are reflected back.

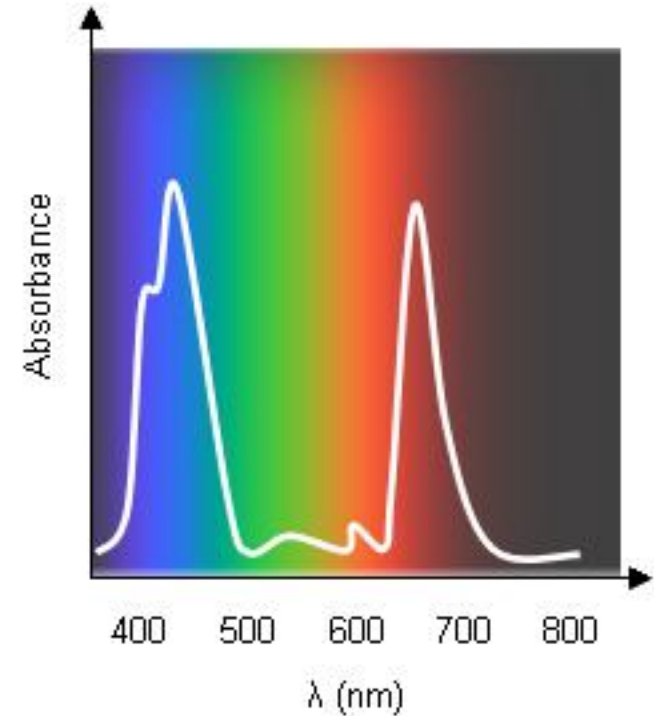


Chromophores and Auxochromes

A molecule or part of a molecule that can be excited by absorption is called a **chromophore**.



Chlorophyll *a* chromophore.



It absorbs **blue** and **red** light and therefore appears **green** from reflected light.