UV-Visible Spectroscopy

"Master Organic Chemistry"
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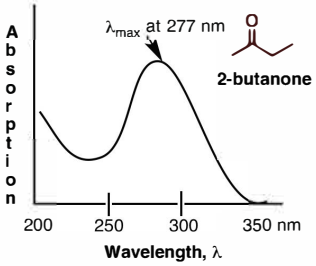
Note - this sheet is not meant to be comprehensive. Your course may provide additional material, or may not cover some of the material shown here. Your course instructor is the final authority.

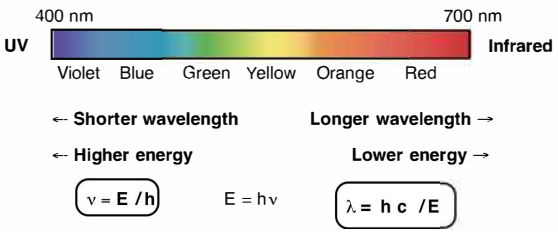
Key points:

- UV-Vis spectroscopy measures a molecule's absorption of light at different wavelengths λ
- The wavelength of maximum absorbance (λ_{max}) is largely determined by the # of consecutive **conjugated** pi bonds (π bonds)
- Generally: the greater the number of conjugated pi bonds, the higher the λ_{max} ("lambda max")
- The lambda max (λ_{max}) tells us the energy ΔE required to promote an electron from the highest-energy occupied molecular orbital (HOMO) of the pi system to the lowest-energy unoccupied molecular orbital (LUMO).
- As the number of consecutive pi bonds increases, this HOMO-LUMO energy gap (ΔE) **decreases**. Many important pigments (e.g. heme, chlorophyll, carotene) have multiple conjugated pi bonds and absorb in the visible region. We see the "complementary" color (e.g. chlorophyll absorbs in yellow, but we see it as green).
- C=O bonds also absorb UV light (typically around 300 nm)

Example of a UV-Vis spectrum



The Electromagnetic Spectrum



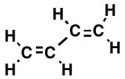
Examples

Ethene ("**ethylene**")

1 pi bond

λ_{max} **180 nm (UV)**

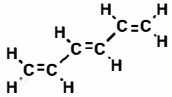
Butadiene ("**1,3 butadiene**")



2 conjugated pi bonds

λ_{max} **217 nm (UV)**

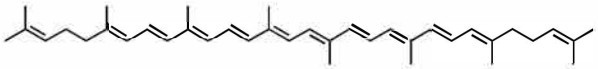
Hexatriene ("**1,3,5 hexatriene**")



3 conjugated pi bonds

λ_{max} **258 nm (UV)**

An extreme example:
Lycopene - the red pigment of tomatoes



14 conjugated pi bonds

λ_{max} **450 nm (blue)**

Other great examples
- carotene (carrot pigment)
- chlorophyll (leaves)
- heme (blood)

As # of conjugated pi bonds increases, λ_{max} increases, representing a smaller HOMO-LUMO energy gap (ΔE)

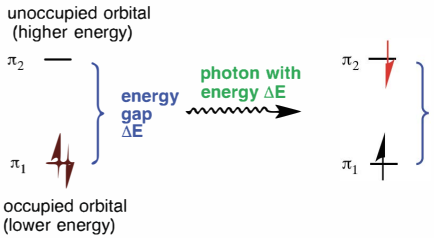
Absorption of C=O Bonds

- Molecules with C=O bonds will also absorb UV light, however the observed transition is slightly different.
- For a non-conjugated aldehyde or ketone like 2-butanone, the π to π^* transition occurs beyond the detection limit (< 190 nm)
- However a different type of transition, n to π^* ,where n is the non bonding electron pair, is observed with C=O bonds.
- **Typical absorbance is around 300 nm** (e.g. 277 nm for 2-butanone)

What do pi (π) bonds have to do with absorption of light ?

- Molecules with pi bonds will have filled pi orbitals (lower energy) and empty pi orbitals (higher energy) separated by an energy gap ΔE
- If the molecule is exposed to a photon of energy E equal to the energy gap ΔE, it can **absorb** the photon and **promote** an electron from the **lower energy level** to the **higher energy level**

Promoting an electron with a photon of energy ΔE



Electron has been promoted from lower-energy orbital (HOMO) to higher energy orbital (LUMO)

- Since $E = h\nu$ we can relate this energy E to frequency ν. $\nu = E / h$
- Since frequency is related to wavelength by $c = \nu\lambda$ we can relate it to wavelength) $\lambda = h c / E$

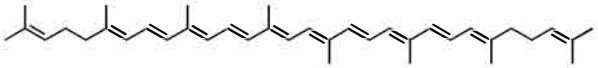
Bottom Line

As # of conjugated pi bonds *increases* → decrease ΔE → increase λ_{max} to longer wavelengths

As # of conjugated pi bonds *decreases* → increase ΔE → decrease λ_{max} to shorter wavelengths

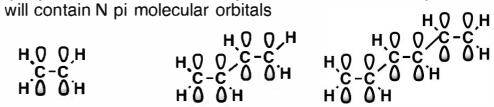
Large energy gap ---> high ν, short λ
(e.g. ethene, absorbs in UV at 180 nm)

Smaller energy gap ---> lower ν, longer λ
(e.g. lycopene, absorbs in visible at 450 nm)



Pi Systems - Conjugated Pi Bonds

The larger the number of **adjacent** p orbitals, the larger the "pi system" that can form. A system of N consecutive p orbitals will contain N pi molecular orbitals



Ethene (two p orbitals) — Two π orbitals in the π system

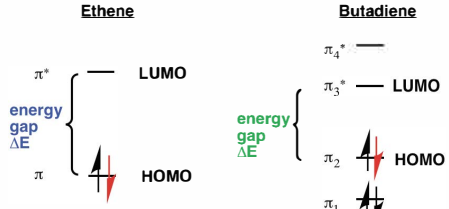
Butadiene (four p orbitals) — Four π orbitals in the π system

Hexatriene (six p orbitals) — Six π orbitals in the π system

The larger the pi system, the smaller the ΔE gap will be between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

This translates into a longer wavelength for λ max (i.e. towards the visible)

Compare ethene (180 nm) vs butadiene (217 nm). Butadiene has a smaller HOMO-LUMO energy gap, which means a less energetic (i.e. longer-wavelength) photon is required to promote an electron:



ΔE (ethene) > ΔE (butadiene)

This translates into

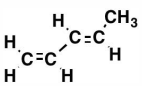
λmax (ethene) < λmax (butadiene)
180 nm 217 nm

the λmax gradually increases as the size of the pi system increases

What's meant by "Conjugation" ?

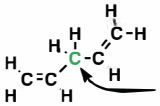
It's important that the pi bonds are adjacent (conjugated). For example, both molecules below have two pi bonds, but **A** will absorb at a longer wavelength than **B** because of conjugation.

A



Double bonds are conjugated (adjacent)

B



Double bonds NOT conjugated

The sp^3 hybridized carbon attached to 4 atoms has no p orbitals available for overlap with the pi system

*Note: atoms w/ lone pairs **can** contribute to the pi system*

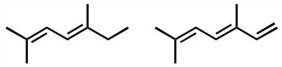
Typical Questions

1. What will absorb at longer wavelength?

A **B**

A - double bonds are conjugated in **A**, but not in **B**

2. What will absorb at longer wavelength?



A **B**

B - has more conjugated double bonds (3, vs. 2 for **A**)

Omissions, Mistakes, Suggestions?
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