Ultraviolet-Visible Spectroscopy

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Introduction to UV-Vis Spectroscopy

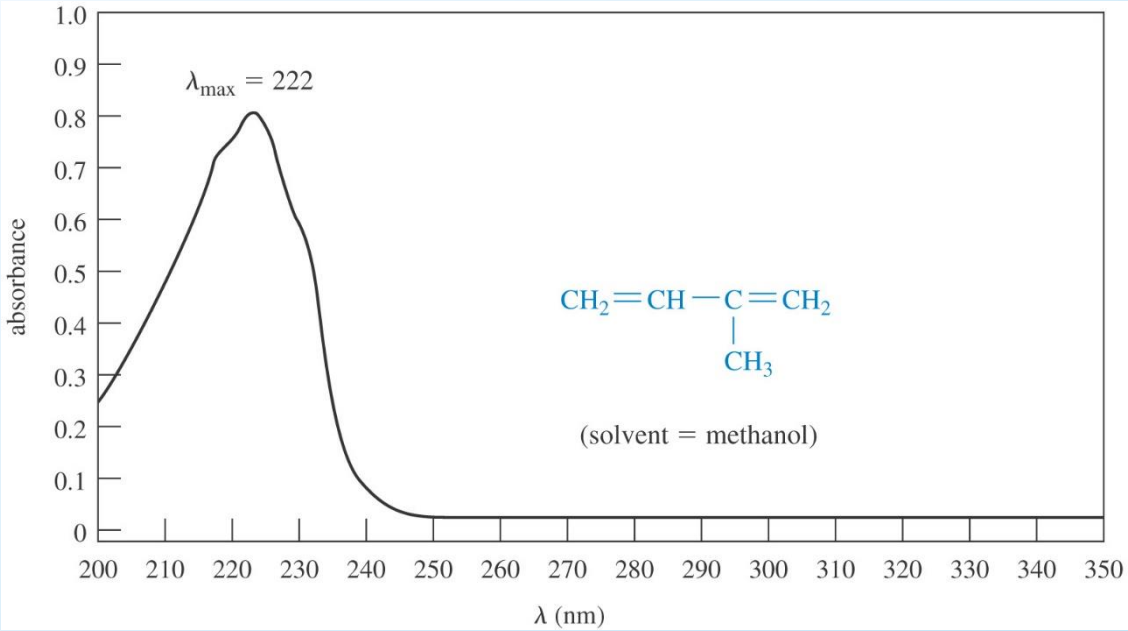
Ultra-violet – Visible (UV-Vis) spectroscopy measures the energy required for an electron to transition from one energy level to another. The degree of conjugation can determine the absorption spectrum obtained in this spectroscopy,.

- In both UV (200-400 nm) and Visible regions (400-800 nm), photons excite electrons from a bonding orbitals to antibonding orbital i.e. electron transitions are occurring.
- One instrument can be used to study both UV and visible spectroscopy.
- The common units are wavelength in nm.
- Wavelength is inversely proportional to frequency and energy.

UV-Visible Spectrum – A First Look

UV-Vis spectrum is graph of signals that look like small hills and have peaks.

- The x-axis is wavelength nm and y-axis is absorbance.
- There are usually very few peaks in UV-Vis spectrum, and each will have a specific electron transition associated with it. As a chemist one can determine which peak is the most significant in their area of study.

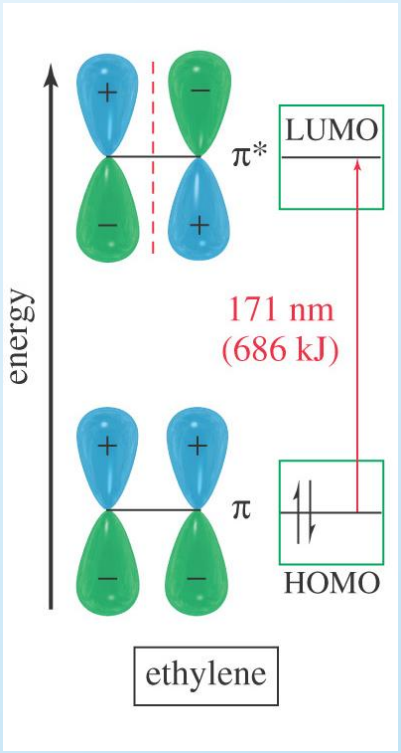


Theory - Ultraviolet-Visible Spectroscopy

Molecular theory explains that atomic orbitals combine to give molecular orbitals (MO). These MOs are bonding (low energy), where similar wavefunctions overlap with minimum number of nodes, and antibonding (high energy) as number of nodes increase.

When energy is absorbed by molecules, electrons from the highest occupied MO (HOMO) jumps to the lowest unoccupied MO (LUMO).

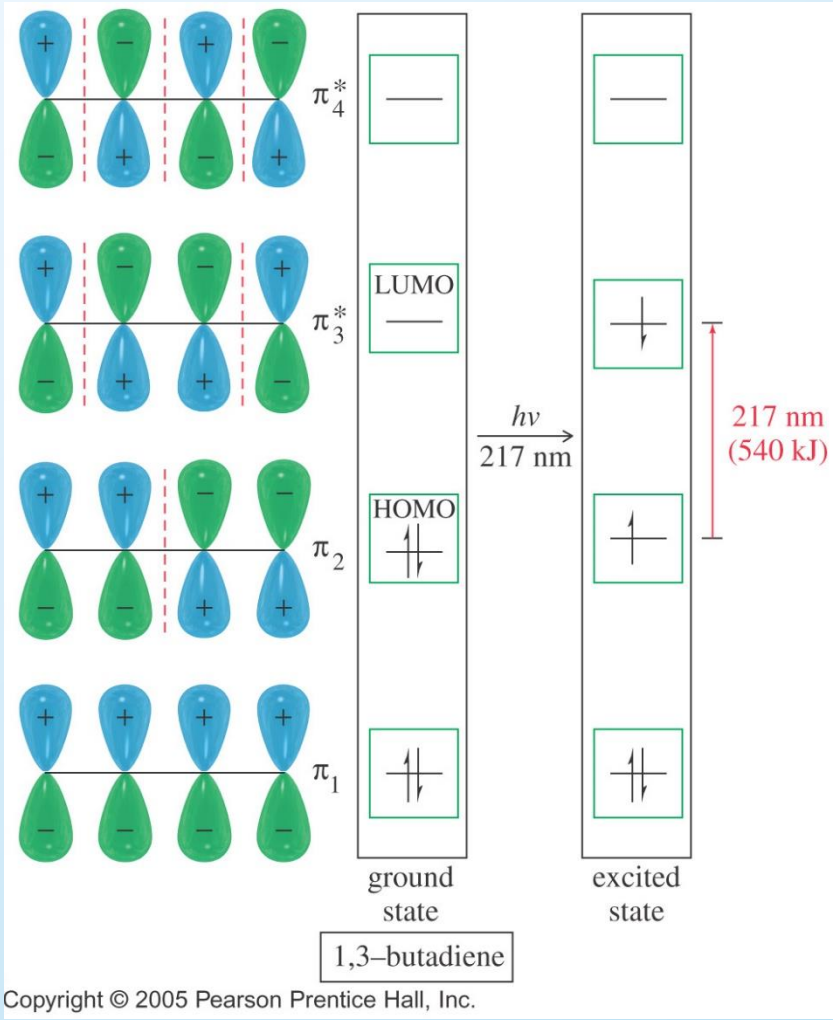
Hybridized sigma bond's bonding MOs are too low in energy and antibonding are too high in energy for electron transitions.



Theory – HOMO – LUMO Transition

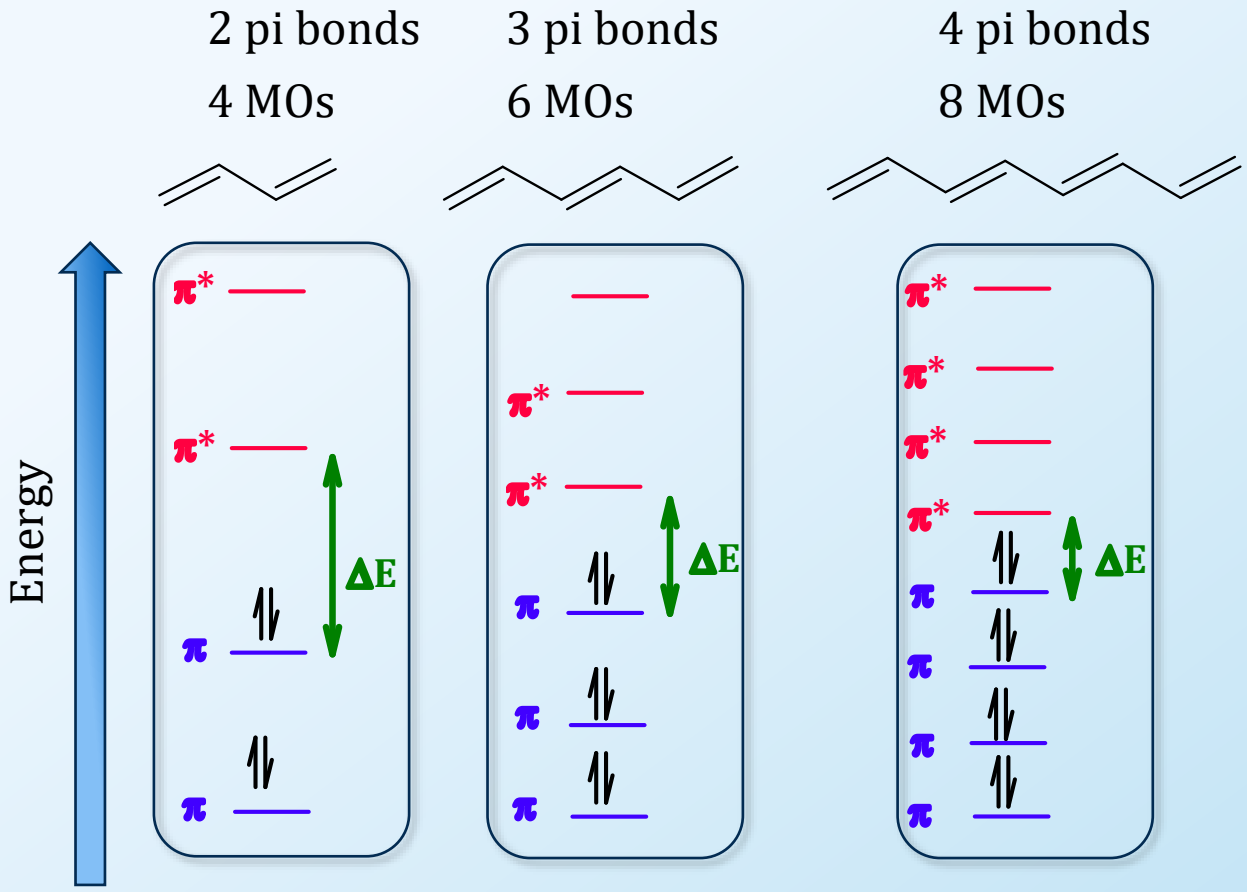
- As the number of pi bonds increase, the number of MOs increase. See the figure on the right for butadiene.
- The distance between HOMO and LUMO decreases making it easier for electrons to transition from HOMO to LUMO. Butadiene electron transition occurs at 540 kJ, compare that to ethene transition energy at 686 kJ (from previous slide).
- In terms of UV-Vis spectroscopy, transition of conjugated systems occurs at a higher wavelength (lower energy).

$\pi \rightarrow \pi^*$ for butadiene



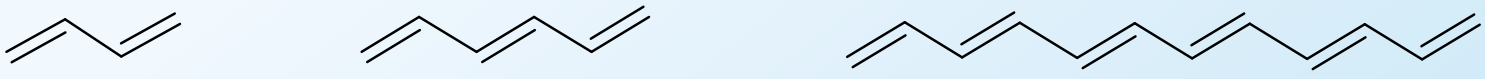
Theory – HOMO – LUMO Conjugation

Here is a diagram of how HOMOs and LUMOs look as conjugation increases.



Theory – Conjugation and Wavelength

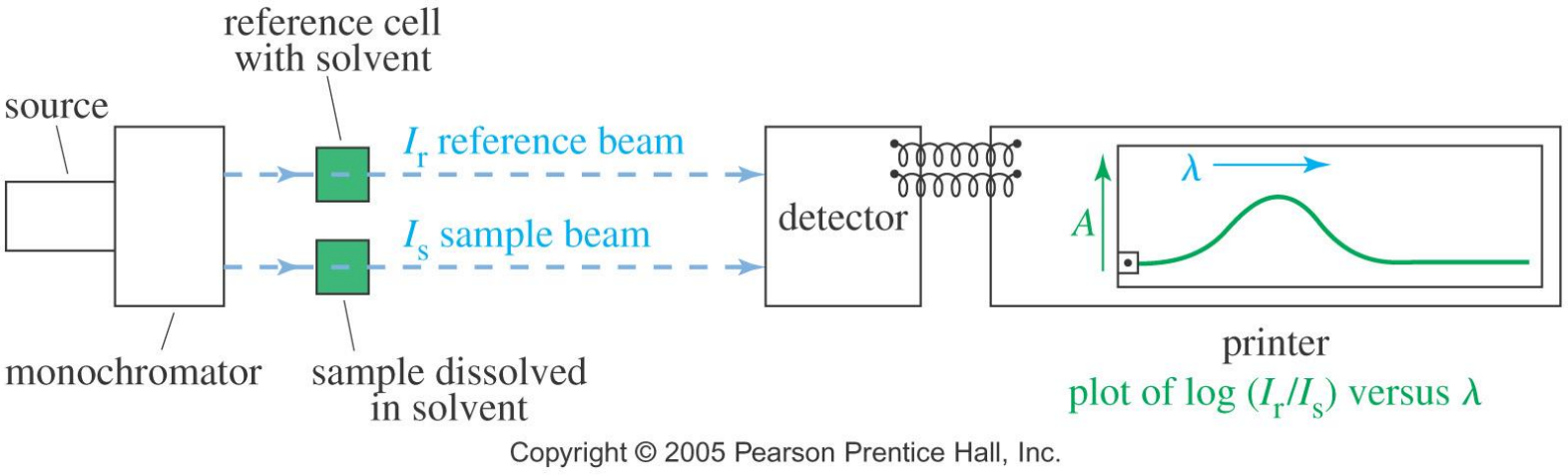
As conjugation increases MOs are closer in energy, thus less energy is needed by the electron to jump from HOMO to LUMO. Again, in terms of UV-Vis as conjugation increases the molecule absorbs more in the higher wavelength region (low energy).



λ_{max} = 217 nm λ_{max} = 268 nm λ_{max} = 364 nm

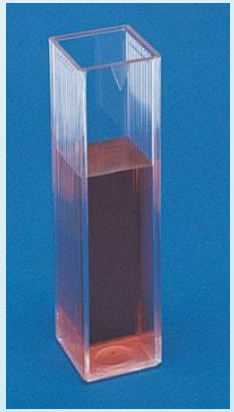
Increasing conjugation
Increasing λ_{max}

Instrumentation - UV-Vis Spectrophotometer



- The spectrometer measures the intensity of a reference beam through solvent only ($\boldsymbol{I}$) and the intensity of a beam through a solution of the sample ($\boldsymbol{I_0}$).
- Absorbance is the log of the ratio both the beams.

Sample Preparation



Solvent: Sample is dissolved in an appropriate solvent. The solvent should not absorb in the UV-Vis range. The common organic solvents CH_2Cl_2 and MeOH can be obtained in spectral grade which don't interfere in the UV-Vis region.

Sample Holder: A cuvette, shown on the right, is used as the sample holder. This cuvette should also be UV-Vis inactive.

Samples should be made in the right concentrations: if they are dilute then all their absorptions may not be visible. On the contrary if they are made in high concentration, then their λ_{max} may be not be in scale of the y-axis.

To study the area under the graph, extinction coefficient (ε), Beers Law ($A = \varepsilon cl$) has to be used and thus sample should be made in a specific concentration.

Sample can be recovered after analysis.

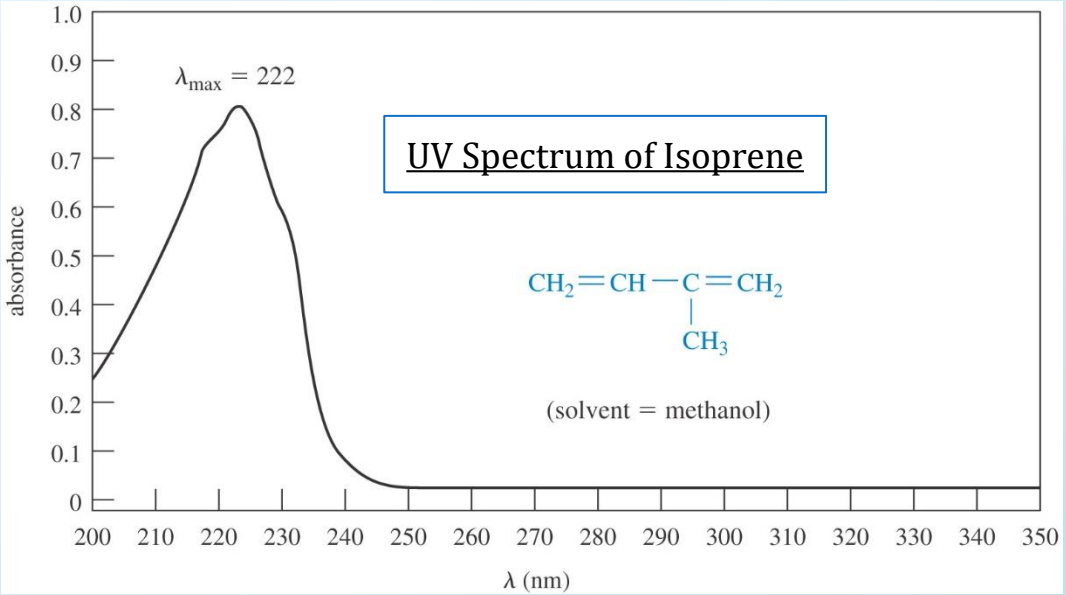
Analyzing The UV-Vis Spectrum

The spectrum usually shows broad peaks. The number of peaks cannot be predicted in most cases.

The quick data needed from the graph is generally the λ_{max} .

The area under the graph (extinction coefficient, ε) gives a great deal of information about the electron transitions occurring in that region. To calculate this a more quantitative experiment is conducted and Beer's law is used to calculate the value of ε.

Beer's Law: $A = \varepsilon cl$: where
A is absorbance (*obtained from the graph*);
ε is the molar absorptivity (*extinction coefficient*);
c is the sample concentration in moles per liter, and
l is the length of the light path in centimeters (*usually 1 cm as per cuvette size*).

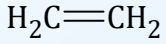


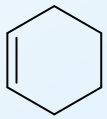
Examples of UV-Vis Absorptions

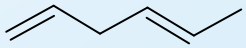
Here are some examples of absorptions of alkenes and conjugated systems.

You will note that in some cases there is no direct correlation of absorption as in the 1,3-cyclohexadiene and 3-methylenecyclohexene, this is because there are other rules that also govern absorption.

Isolated double bonds

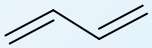


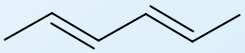


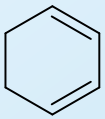


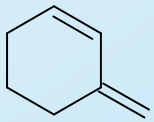
	ethylene	cyclohexene	1,4-hexadiene
λ_{max}	171 nm	182 nm	180 nm

Conjugated dienes



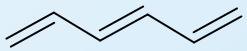


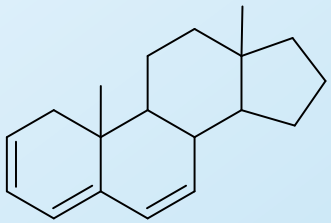




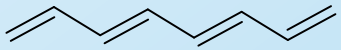
	1,3-butadiene	2,4-hexadiene	1,3-cyclohexadiene	3-methylenecyclohexene
λ_{max}	217 nm	227 nm	256 nm	232 nm

Conjugated trienes





Conjugated triene

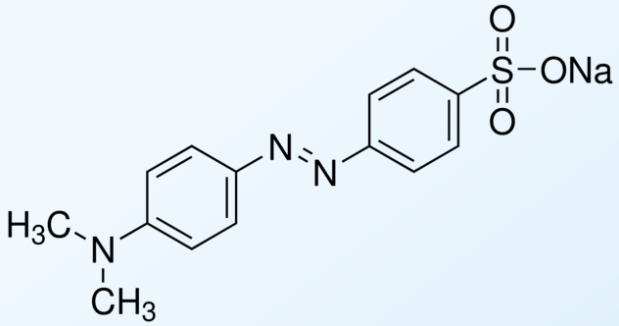


	1,3,5-hexatriene	a steroid	1,3,5,7-octatetraene
λ_{max}	258 nm	304 nm	290 nm

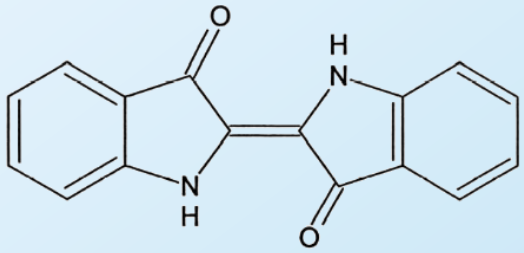
Visible Region Absorption of Dyes

Dyes absorb in the visible region because of conjugation.

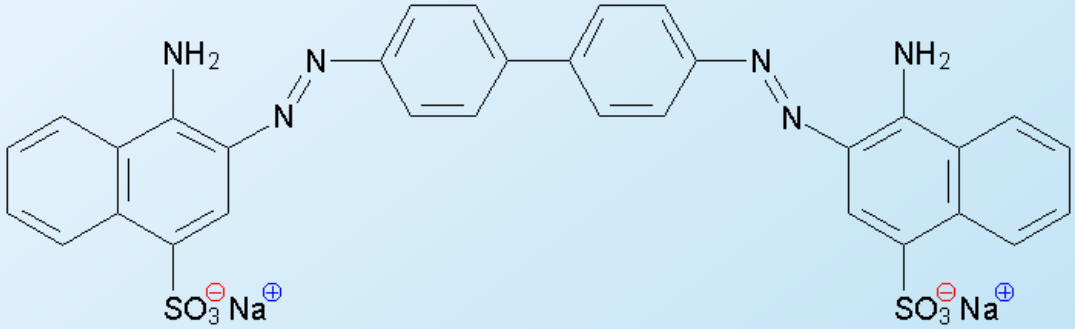
Methyl orange (λ_{max} =440 nm)



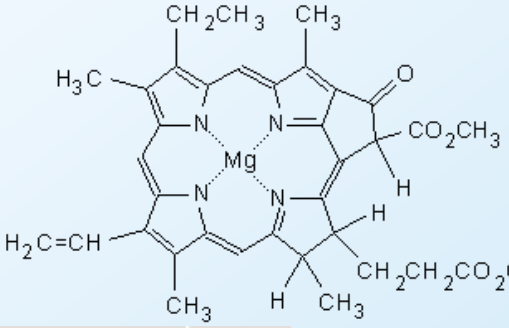
Indigo (λ_{max} =600 nm)



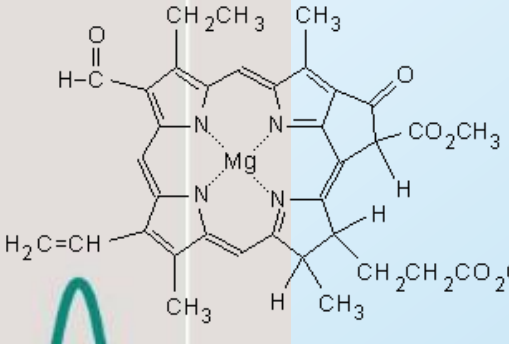
Congo Red (λ_{max} =500 nm)



Chlorophyll a and b UV-Vis



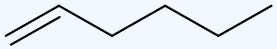
Chlorophyll a



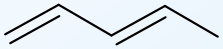
Chlorophyll b

Worked Example: For each set of compounds given below, arrange them in order of increasing wavelength.

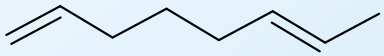
a



1



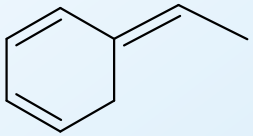
2



3

2 > 3 > 1

b



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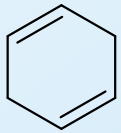

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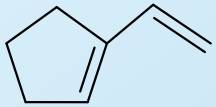

3

1 > 3 > 2

Key Concepts

- Recognize conjugation
- Predict which molecule will absorb in the red or violet region of UV-Vis.