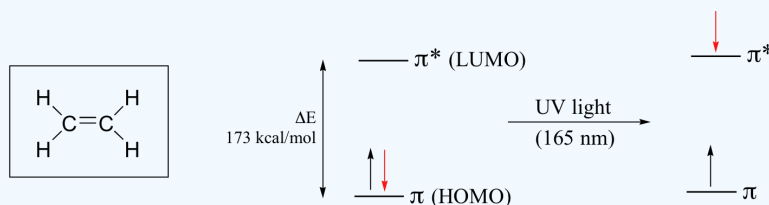


16.10: INTERPRETING ULTRAVIOLET SPECTRA - THE EFFECT OF CONJUGATION

UV SPECTROSCOPY AND π ELECTRON TRANSITIONS BETWEEN THE HOMO AND LUMO

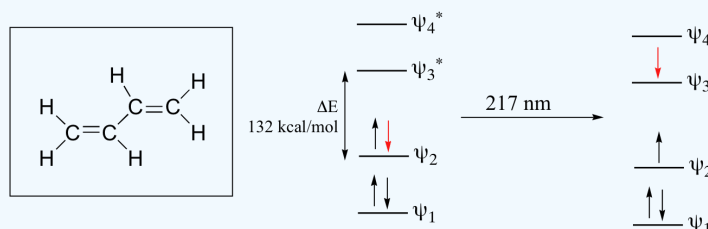
The ultraviolet absorption maximum of a conjugated molecule is dependent upon the extent of conjugation. As the conjugation increases, the Molecular Orbital energy decreases so that the π electron transitions occur in the UV and visible regions of the electromagnetic spectrum. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a $\pi - \pi^*$ transition. Because π^* energy gaps are narrower than $\sigma - \sigma^*$ gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



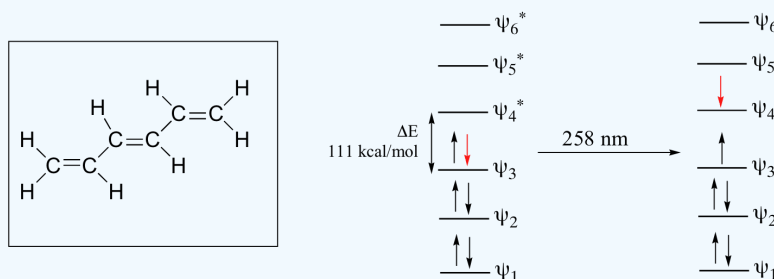
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated π systems. In these groups, the energy gap for $\pi - \pi^*$ transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer.

Let's revisit the MO picture for 1,3-butadiene, the simplest conjugated system. Recall that we can draw a diagram showing the four π MO's that result from combining the four $2p_z$ atomic orbitals. The lower two orbitals are bonding, while the upper two are anti-bonding.

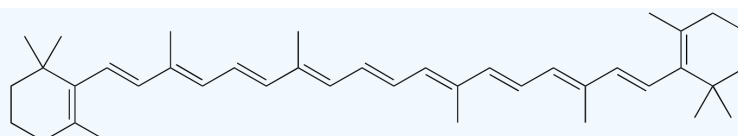


Comparing this MO picture to that of ethene, our isolated π -bond example, we see that the HOMO-LUMO energy gap is indeed smaller for the conjugated system. 1,3-butadiene absorbs UV light with a wavelength of 217 nm.

As conjugated π systems become larger, the energy gap for a $\pi - \pi^*$ transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the $\pi - \pi^*$ transition in 1,3,5-hexatriene, for example, occurs at 258 nm, corresponding to a ΔE of 111 kcal/mol.

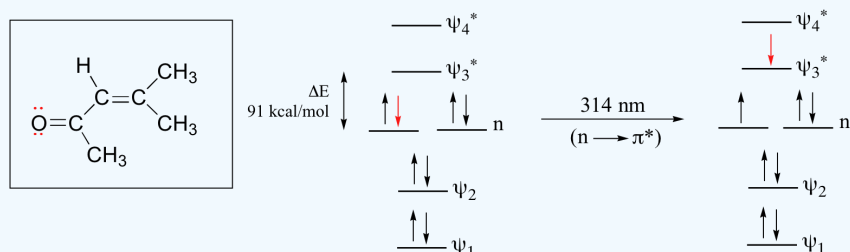


In molecules with extended π systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather than the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



β -carotene

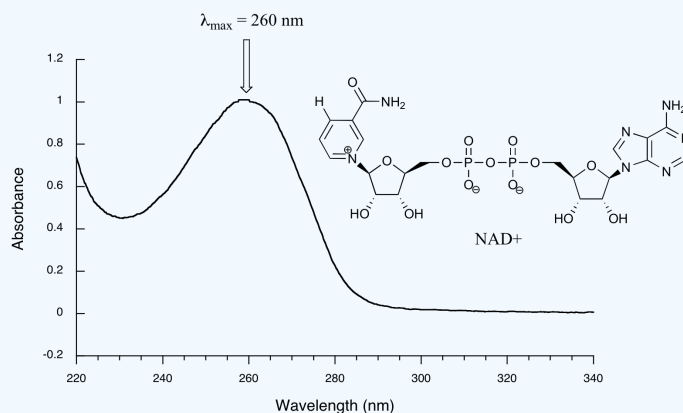
The conjugated pi system in 4-methyl-3-penten-2-one gives rise to a strong UV absorbance at 236 nm due to a $\pi - \pi^*$ transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π^* antibonding MO:



This is referred to as an **$n - \pi^*$ transition**. The nonbonding (n) MO's are higher in energy than the highest bonding p orbitals, so the energy gap for an $n - \pi^*$ transition is smaller than that of a $\pi - \pi^*$ transition – and thus the $n - \pi^*$ peak is at a longer wavelength. In general, $n - \pi^*$ transitions are weaker (less light absorbed) than those due to $\pi - \pi^*$ transitions.

LOOKING AT UV-VIS SPECTRA

We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is the same as for IR spectroscopy: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred. Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+ (we'll learn what it does in [section 16.4](#)) This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.



You'll notice that this UV spectrum is much simpler than the IR spectra we saw earlier: this one has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm) rather than in cm^{-1} as is the convention in IR spectroscopy.

Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum.. The first is λ_{max} , which is the wavelength at maximal light absorbance. As you can see, NAD^+ has $\lambda_{\text{max}} = 260 \text{ nm}$. We also want to record how much light is absorbed at λ_{max} . Here we use a unitless number called **absorbance**, abbreviated 'A'. This contains the same information as the 'percent transmittance' number used in IR spectroscopy, just expressed in slightly different terms. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength *before* it passes through the sample (I_0), divides this value by the intensity of the same wavelength *after* it passes through the sample (I), then takes the \log_{10} of that number:

$$A = \log I_0/I$$

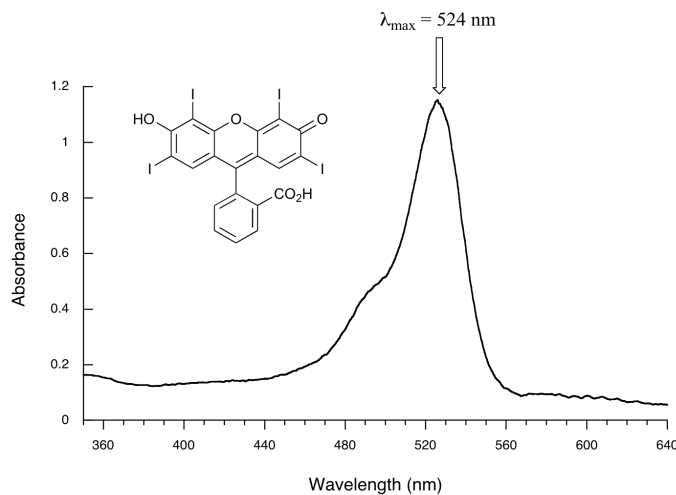
You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

Exercise

14. Express $A = 1.0$ in terms of percent transmittance (%T, the unit usually used in IR spectroscopy (and sometimes in UV-vis as well)).

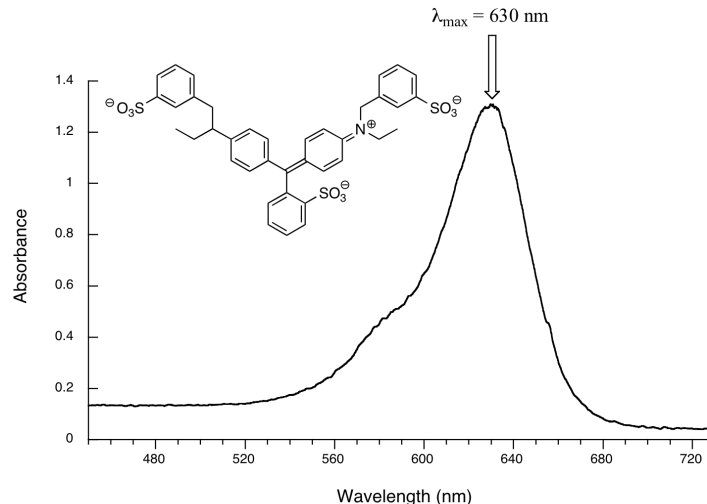
[Solution](#)

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes.

Now, take a look at the spectrum of another food coloring, Blue #1:



Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

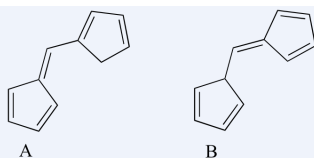
Exercise

15. How large is the $\pi - \pi^*$ transition in 4-methyl-3-penten-2-one?

[Solution](#)

Exercise

16. Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.



Solution

Exercise

17. Which of the following would show UV absorptions in the 200-300 nm range?

Answer

17. B would be the only one to show in that range.

CONTRIBUTORS AND ATTRIBUTIONS

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

16.10: Interpreting Ultraviolet Spectra - The Effect of Conjugation is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.