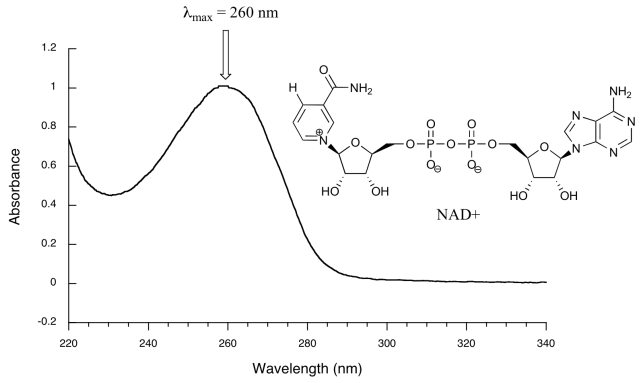
3.6: Interpreting Ultraviolet Spectra

Objective

- be able to interpret UV-Vis spectra.
- understand the effect of conjugation.

The wavelength necessary to make the transition from π -π* in a conjugated molecule depends on the energy gap between the HOMO and LUMO. This energy gap depends on the conjugated system of the molecule being studied. If you recall from Section 3.3, the energy gap for π -π* transitions is smaller for conjugated systems than for isolated double bonds, and thus the wavelength absorbed is longer. Therefore, by measuring the UV spectrum of a molecule, structural information can be derived about the nature of the conjugated pi electron system present.

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: 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^+. This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.

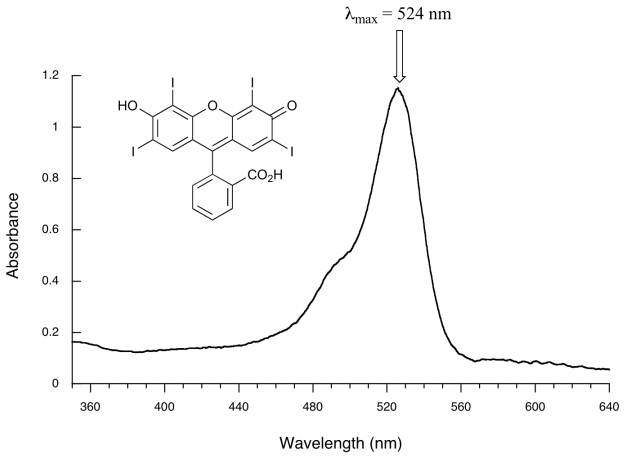


You'll notice that this UV spectrum has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm). 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 lambda max (λ_{max}), which is the wavelength at maximal light absorbance. As you can see, NAD^+ has λ_{max} = 260 nm. We also want to record how much light is absorbed at λ_{max}. Here we use a unitless number called absorbance, abbreviated 'A'. 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:

$$A = \log I_0/I$$

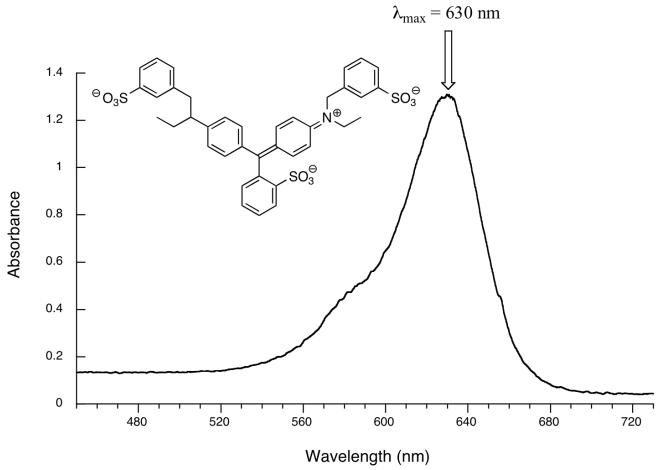
You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

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.

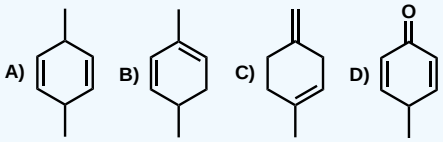
Now, take a look at the spectrum of another food coloring, Blue #1:



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

Exercise 3.6.1

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

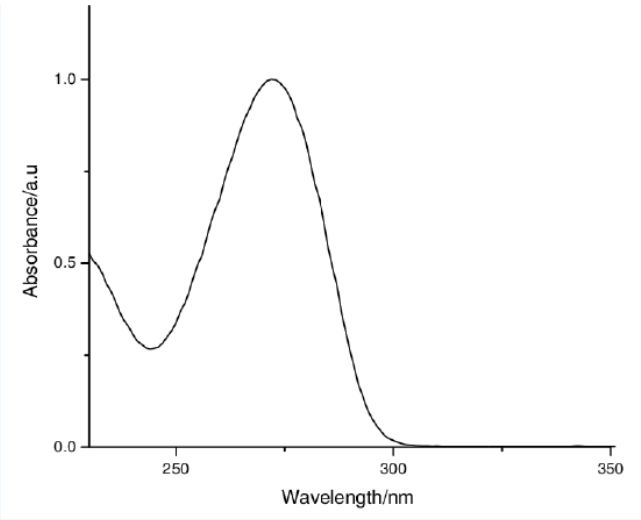


Answer

You are looking for conjugated systems, which leads to B and D.

Exercise 3.6.2

What is the lambda max for caffeine?



UV-vis spectra of caffeine in water

Belay, Abebe & Beketie, Kassahun & Redi, Mesfin & Asfaw, Araya. (2008). Measurement of Caffeine in Coffee Beans with UV/Vis Spectrometer. Food Chemistry. 108. 310-315. 10.1016/j.foodchem.2007.10.024.

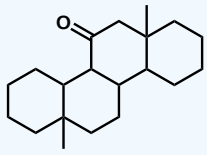
Answer

λ_{max} of 275 nm.

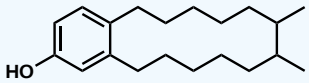
Exercise 3.6.3

A colleague has isolated a compound that has the formula $C_{20}H_{32}O$ and a λ_{max} of 275 nm. Your colleague subjected the product to hydrogenation (Pd/C and H_2), which resulted in no change in the λ_{max}. They then tried to reduce the molecule with sodium borohydride, which led to no change in λ_{max}. They have proposed four different structures, but cannot figure out what structure they have isolated. Which do you think is most likely?

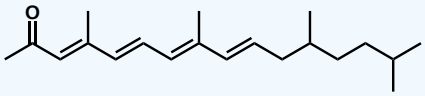
A)



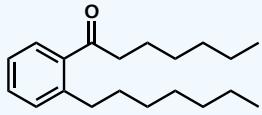
B)



C)

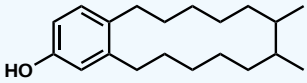


D)



Answer

With a λ_{max}, there needs to be a conjugated pi system. A is lacking a conjugated pi system, so it can't be molecule A. Ketones can be reduced to alcohols when treated with sodium borohydride, which means the λ_{max} would change for both C and D. Therefore it can't be C or D. In additon, C would react under the hydrogenation conditions, so again its λ_{max} would

change. It can definitely not be C. Which leaves us B. It has a conjugated pi system and would not react in either set of conditions, so its λ_{max} would stay the same. The isolated compound is B - 

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