

# SUNSCREENS: CONJUGATION AND UV PROTECTION

Organic molecules with alternating single and double bonds that are parallel and overlap within the same plane are known as *conjugated* molecules. Conjugated systems are very stable because electron orbitals are spread between several atoms through overlapping pi ( $\pi$ ) bonds. The  $\pi$  electrons are delocalized and are spread evenly over all of the atoms in the system. Figure 1 shows non-conjugated and conjugated molecules, and the delocalized electrons that act as one molecular orbital within a conjugated molecule. Note that double bonds between any two atoms contribute to conjugation, and electron delocalization extends through the entire alternating bond system within a single plane.

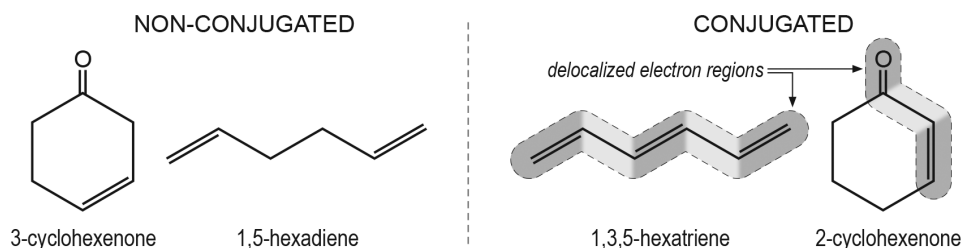


Figure 1. Conjugated areas of organic molecules contain delocalized pi ( $\pi$ ) electrons

Ultraviolet-visible (UV-Vis) spectroscopy provides information about the extended pi bonding in organic molecules. The wavelength(s) of light absorbed by an organic compound depends on the extent of conjugation. Electrons in sigma ( $\sigma$ ) bonds are not as easily excited by electromagnetic radiation as electrons in  $\pi$  bonds or in nonbonding electrons (lone pairs). When  $\pi$  bonds form, electrons move to the lower energy  $\pi$  bonding orbitals while the antibonding orbitals remain empty. Ground state electrons either from lone pairs or from a  $\pi$  bonding orbital can absorb energy and move to an empty antibonding orbital when excited. Electrons in the highest occupied molecular orbital (HOMO) are promoted to the lowest unoccupied molecule orbital (LUMO) when UV photons are absorbed. In general, more conjugated double bonds lessen the gap between the HOMO and LUMO. As shown in Figure 2, a shorter energy gap between HOMO and LUMO allows electrons in conjugated molecules to absorb lower energy, longer wavelengths closer to visible light.

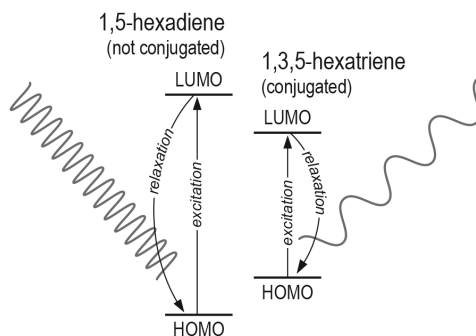


Figure 2. Conjugation reduces the energy gap

As a general rule, each set of double-single-double bonds in a conjugated system increases absorbance wavelengths by a value of 30 nm. The greater the degree of conjugation in a molecule, the longer the peak absorption wavelength. For example, the two conjugated organic molecules in Figure 1 are colorless because they absorb shorter wavelengths in the UV region of the electromagnetic spectrum.

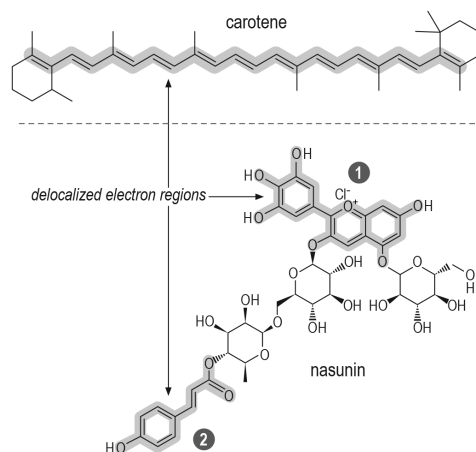


Figure 3. Highly conjugated organic molecules transmit color

The orange carotene and purple nasunin plant pigment molecules shown in Figure 3 are colored because their higher degree of conjugation allows them to absorb longer wavelengths in the visible region. Notice delocalization extends beyond  $\pi$  bonds and can include lone pairs on oxygen (or nitrogen) atoms within the system. Nasunin has two regions of conjugation because they are in different planes. As you can see in Figure 3, region 1 of the nasunin molecule has more conjugated areas than carotene, so it absorbs longer wavelengths than carotene. Yellow is absorbed and purple is transmitted in nasunin while blue is absorbed and orange is transmitted in carotene.

UVA wavelengths (320–400 nm) cause premature skin aging while more energetic UVB wavelengths (280–320 nm) cause DNA damage, sunburn, and skin cancer. Melanin, the highly conjugated pigment molecule that produces skin color, absorbs some but not all of the UV radiation you encounter during long periods of sun exposure. Sunscreens can help absorb excess UV radiation. Two common types of sunscreens are:

- Physical sunscreens: Active ingredients are inorganic compounds which reflect UVA and UVB wavelengths, with a small amount of UV absorption.
- Chemical sunscreens: Active ingredients take advantage of conjugated systems in organic molecules which absorb UVA and UVB wavelengths.

There are two main ways in which a chemical sunscreen active ingredient may work. In one mechanism, electrons in a conjugated molecule absorb UV radiation and are excited into the antibonding  $\pi$  orbitals. Molecules that absorb UV radiation can redistribute that energy from electronic excitation to internal energies of vibration or rotation which we feel as heat. Other active ingredients may use the absorbed energy to react chemically and break down into simpler components. By choosing conjugated organic molecules with different absorption ranges, sunscreen manufacturers can protect their customers from the effects of both UVA and UVB radiation. In this investigation, you will analyze the spectra of light absorbed by different types of sunscreens and explain the results in terms of molecule conjugation.

## Objectives

- Relate the chemical structure of active ingredients in sunscreen with UV absorbance.

## Materials and Equipment

- Windows or Mac Computer
- UV-Vis Spectrometer
- Cuvettes with caps, UV-compatible (4)
- Analytical balance (readability: 0.0001 g)
- Volumetric flask, 50-mL
- Funnel to fit volumetric flask
- Plastic beaker, 50-mL
- Beaker, 100-mL
- Test tubes, 10 cm x 1.2 cm or 10-mL capacity (3)
- Test tube rack or beaker to hold test tubes
- Stirring rod
- Filtration apparatus and filter paper
- Graduated pipette and bulb, 1-mL
- Graduated pipette and bulb, 5-mL
- Disposable pipet
- 91% Isopropyl alcohol, ~250 mL
- Sunblock samples: same brand and similar active ingredient(s), different SPF (2)
- Sunblock sample: different active ingredient(s)
- Labeling pen
- Lint-free lens wipes

## Safety

Follow these important safety precautions in addition to your regular classroom procedures:

- Wear safety goggles at all times.
- Work in a fume hood or in a well-ventilated area. No open flames are permitted during this investigation.
- Follow your instructor's disposal directions.

## Procedure

1. Connect the UV-Vis Spectrometer to your computer. Turn on the Spectrometer.
2. Select two sunscreen samples of the same brand with the same active ingredients, and different SPF values. In Table 1, report the brand, concentration of active ingredient(s), and SPF values stated on the product packaging.
3. Tare the plastic beaker on the analytical balance. Measure about 0.0600 g of the higher SPF value sunscreen into the beaker. Record the actual mass in Table 1.
4. Remove the beaker from the balance and add a few milliliters of 91% isopropyl alcohol (IPA) to the sample.
5. Use the stirring rod to smear the sample along the bottom of the beaker to assist in forming a mixture with the IPA. Some ingredients may be insoluble, however it is important to break down surface area as much as possible before moving on to the next step.
6. Set the funnel in the volumetric flask. Quantitatively transfer the mixture to the flask, rinsing the stirring rod, beaker, and funnel with small amounts of IPA.
7. Remove the funnel and fill the flask with IPA until the bottom of the meniscus reaches the calibration line.
8. Seal the flask and invert several times to mix.

9. Filter the mixture according to your instructor's directions. A sample filtration apparatus is shown in Figure 4. Pour the solution into a Buchner funnel that contains a quantitative disc filter. The tube leading out of the second filter flask is connected to a hand-operated vacuum pump or water aspirator.

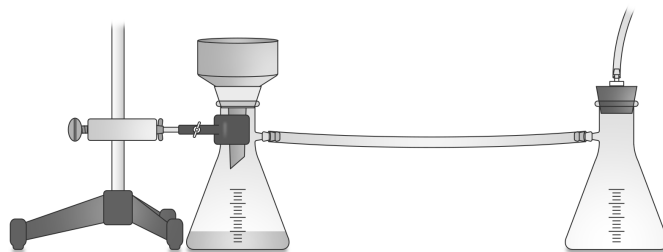


Figure 4. Sample filtration setup

10. Label a test tube with the sunscreen sample information.
11. Use the 1-mL graduated pipette to transfer 0.65 mL of the filtrate to the test tube.
12. Use the 5-mL graduated pipette to transfer 4.35 mL of IPA to the test tube.
13. Gently strike the side of the test tube with your finger to mix the contents without splashing. Transfer the solution to a cuvette.
14. Fill a second cuvette with IPA. This is your calibration blank.

**NOTE:** Fill cuvettes  $\frac{3}{4}$  full. Do not overfill. Handle by the sides that are not clear. If bubbles are present, gently tap the cuvette to dislodge the bubbles.

15. Calibrate the spectrometer with the blank 📱📱.

**NOTE:** Wipe the clear sides of the cuvette with a lint-free lens wipe. Insert the cuvette with the clear sides in line with the light and spectrum icons on the device.

16. Start recording data 📱. If any absorbance peaks are significantly higher than 1, dilute the sample by 10% increments until the highest absorbance is at or near 1. Make note of the final dilution percentage and dilute all samples in this investigation by the same percentage.
17. UVA wavelengths range from 280-315 nm and UVB wavelengths range from 315-400 nm; therefore the range of interest is from 280-400 nm. Use the Coordinates tool 📱 to identify no more than 3 major absorbance peaks in the region of interest. Record results in Table 1, then stop recording data.
18. Wash and dry the plastic beaker and stirring rod. Rinse the 1-mL pipette, filter flask, funnel, Buchner funnel, and volumetric flask thoroughly with IPA.
19. Repeat steps 3 through 13 to prepare the second sunscreen sample in a second test tube.
20. Start recording data. In Table 1, record absorbance values for the same peak wavelengths identified in the first sample, then stop recording data.
21. Repeat step 18 and select a third sunscreen sample having different active ingredients. Record brand, identity and concentration of active ingredient(s), and SPF value in Table 1.
22. Prepare the third sample and record data as before, adding results to Table 1.

## Data Collection

Table 1. Sunscreen product summary

Sunscreen brand	Active ingredient(s)	SPF value	Mass (g)	Mass concentration (g/mL)	Absorbance peak(s) $\lambda$ (nm) and value(s)	Absorbance to concentration ratio ( $\text{mL}^{-1}/\text{g}$ )

## Questions and Analysis

1. Calculate the mass concentration for each sample (in g/mL) and enter the results in Table 1. Next, divide each peak absorbance for each sunscreen product by the mass concentration to calculate the absorbance to concentration ratio. Show work for the first sample below.
2. Based on the absorbance-to-concentration ratio, does a higher SPF value translate to a predictable difference in UVB absorbance, from a consumer perspective? Support your answer with data.

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