ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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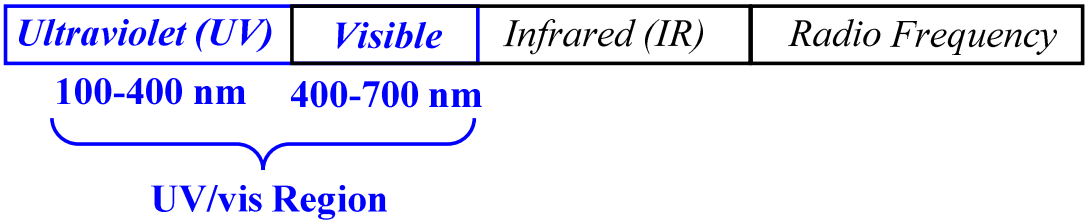
Lesson VII.1. Interaction of Ultraviolet and Visible Light with Molecules

Electromagnetic spectrum

Different energies of light elicit different changes in molecules that absorb them. In this course, we will consider UV, visible, IR and radio frequency radiation:

higher energy

lower wavelength



First, we will focus on how UV and visible light, collectively abbreviated UV–visible (UV/vis) light, interact with organic molecules. The UV/vis part of the spectrum we will consider spans a wavelength range from ~100–700 nm.

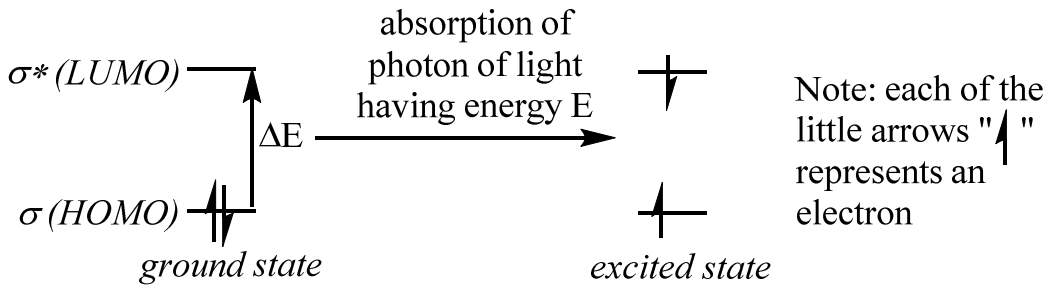
Notes

Lesson VII.1. Interaction of Ultraviolet and Visible Light with Molecules

HOMO-LUMO gap and electronic transitions

When a molecule absorbs UV/vis radiation of an appropriate energy, it causes one of the electrons to undergo an **electronic transition** from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

An electron in a σ-bond gets promoted to a **σ-antibonding (σ*) orbital**:

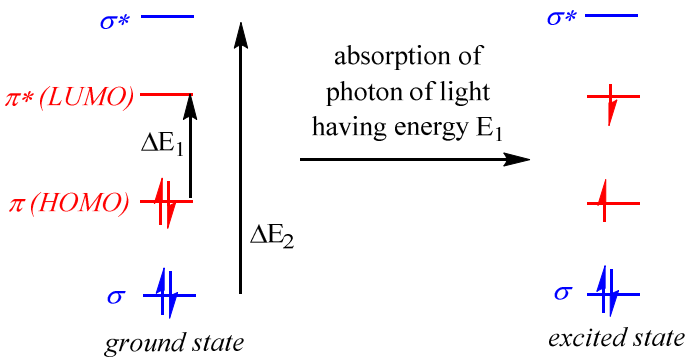


Notes

Lesson VII.1. Interaction of Ultraviolet and Visible Light with Molecules

"Sigma to sigma star and pi to pi star transitions"

An electron in a π-bond gets promoted to a **π-antibonding (π*) orbital**:



Compared to the σ→ σ* transition, the π→ π* is:

A

Furthermore, the longer the π conjugated system, the lower the energy of the photon needed to promote the π→π* transition.

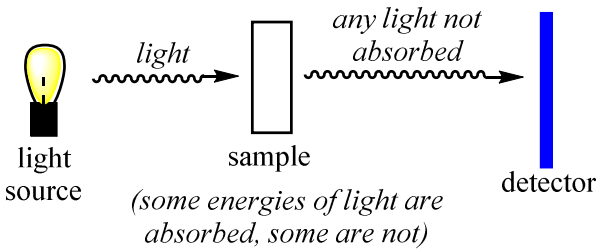
B

Notes

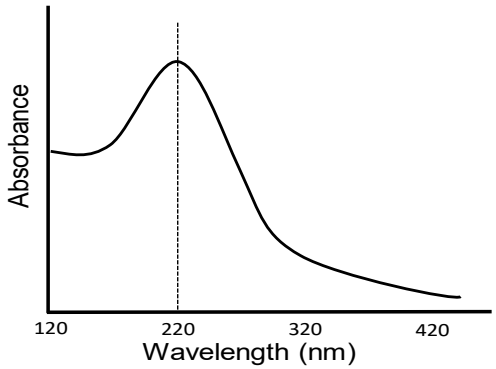
Lesson VII.2. UV-vis Spectroscopy

UV/vis spectrometer

A UV-vis spectrometer is set up as follows:



The spectrum is a plot of absorbance versus wavelength:



Notes

Lesson VII.2. UV-vis Spectroscopy

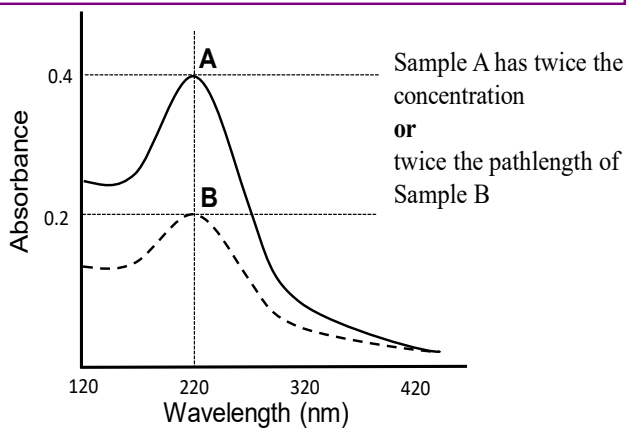
Beer-Lambert Law and the molar extinction coefficient

The amount of light absorbed per mole of a sample is called the **molar absorptivity** or **molar extinction coefficient**.

The **Beer-Lambert Law** provides an equation relating the absorbance (A), pathlength (b), concentration (c) and extinction coefficient (ε):

A

For a constant pathlength, then, it is easy to monitor concentration, and thus to follow the reaction rate. If a species we are following gives spectrum **A** (absorbing at 220 nm) at the start of a reaction, and spectrum **B** after 1 h, we know that half of the compound is consumed in that one hour, because the absorption is halved.



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