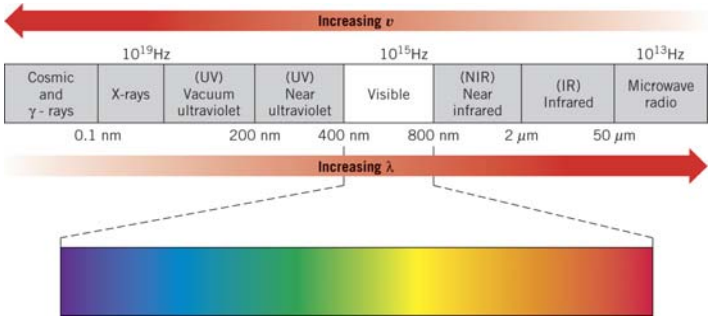
Ultra-Violet Spectroscopy

A UV-Vis spectrum is typically measured from 200-800 nm, spanning the near UV and visible regions

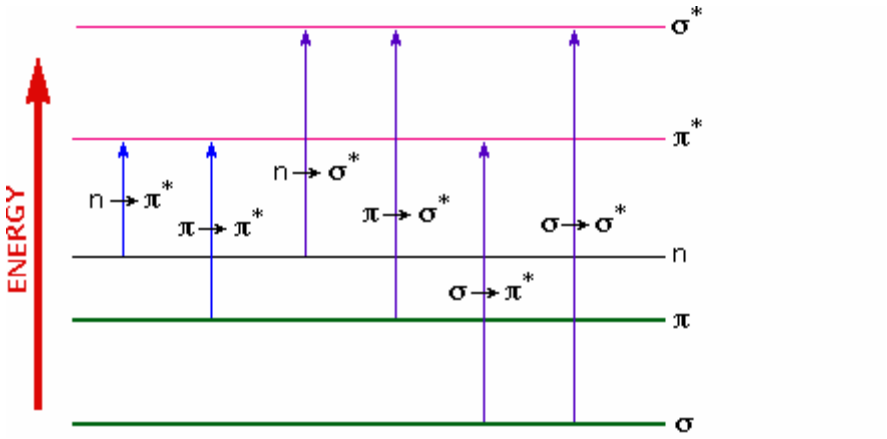


The wavelength of maximum absorption (λmax) is reported in units of nanometers (nm)

Formulas:

Molar Absorptivity
Absorbance is directly proportional to the path length, *b*, and the concentration, *c*, of the absorbing species. *Beer's Law* states that:

- A is the observed absorbance,
- C is the molar concentration of the sample and
- l is length of the sample cell in centimeters
- **ε** is a constant of proportionality, called the *absorbtivity*

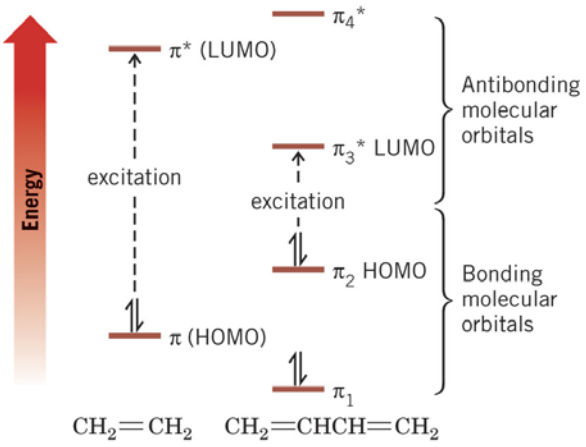


In UV-Vis spectroscopy the electrons are excited from lower to higher energy levels.

- The electron is generally excited from the highest occupied molecular orbital (HOMO, usually _____) to the lowest unoccupied molecular orbital (LUMO, usually_____)

UV-VIS of Alkenes

- Alkenes and nonconjugated dienes have absorptions below 200 nm because the energy difference between the HOMO and LUMO is large.
  - $\downarrow\lambda = \uparrow\Delta E$
- In conjugated dienes these energy levels are much closer together and the wavelengths of absorption are longer than 200 nm.
  - $\uparrow\lambda = \downarrow\Delta E$
- For example:
  - Ethene has λ_{max} at 171 nm and 1,3-butadiene has λ_{max} at 217 nm.



***Note*:**
The longer the conjugated system, the smaller the energy difference between the HOMO and the LUMO

Perceived Color versus Absorbed Color

- β-Carotene has 11 conjugated double bonds and an absorbance maximum at 497 nm which is in the blue-green region of the visible spectrum
- β-Carotene is perceived as red-orange, the complementary color of blue-green

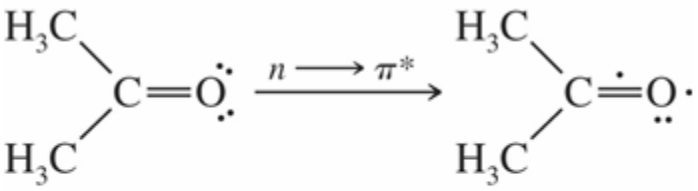
UV-VIS of Carbonyl Compounds

- Two transitions seen in carbonyl compounds:

1)

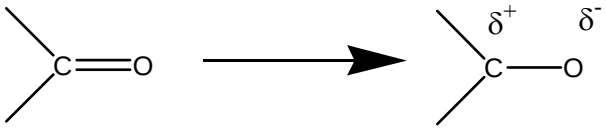
2)

- An unshared (n) electron on oxygen is promoted to a π* orbital

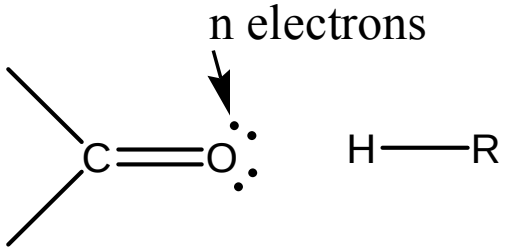


- A bonding pi-electron is promoted to a π* orbital

π (bonding) excited to the antibonding π^*



Solvent Effects on UV-VIS Spectra
The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species.



Effects of increasing solvent polarity on carbonyl spectra.

- $n \rightarrow \pi^*$
  - Hydrogen bonding _____ the net energy of the *n* electrons (thus increasing the energy gap between n and π^*)
  - Absorption undergoes a shift to an absorption of shorter wavelength or a higher energy.

- $\pi \rightarrow \pi^*$
  - Hydrogen bonding _____ the energy levels of ***both*** the excited and unexcited states.
  - However, this effect is greater for the excited state (π^*), and so the energy difference between the excited and unexcited states is slightly reduced resulting in a decrease in energy.
  - Absorption undergoes a shift to a longer wavelength (lower energy)

↑Wave Number = ↑_____

Table 6-3. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ band maxima in the UV/Vis absorption spectrum of benzophenone in solvents of increasing polarity [104].

Solvents	$\tilde{\nu}(n \rightarrow \pi^*)/cm^{-1}$	$\tilde{\nu}(\pi \rightarrow \pi^*)/cm^{-1}$
n-Hexane	28860	40400
Cyclohexane	28860	40240
Diethyl ether	29070	40160
1,2-Dichloroethane	29370	39600
Dimethyl sulfoxide	29370	–
N,*N*-Dimethylformamide	29330	–
Acetonitrile	29540	39920
1-Butanol	29990	39600
1-Propanol	29900	39600
Ethanol	30080	39680
Methanol	30170	39600
Water	ca. 31060 (sh)	38830
	$\Delta\tilde{\nu} = -2200\ cm^{-1}$	$\Delta\tilde{\nu} = 1570\ cm^{-1}$

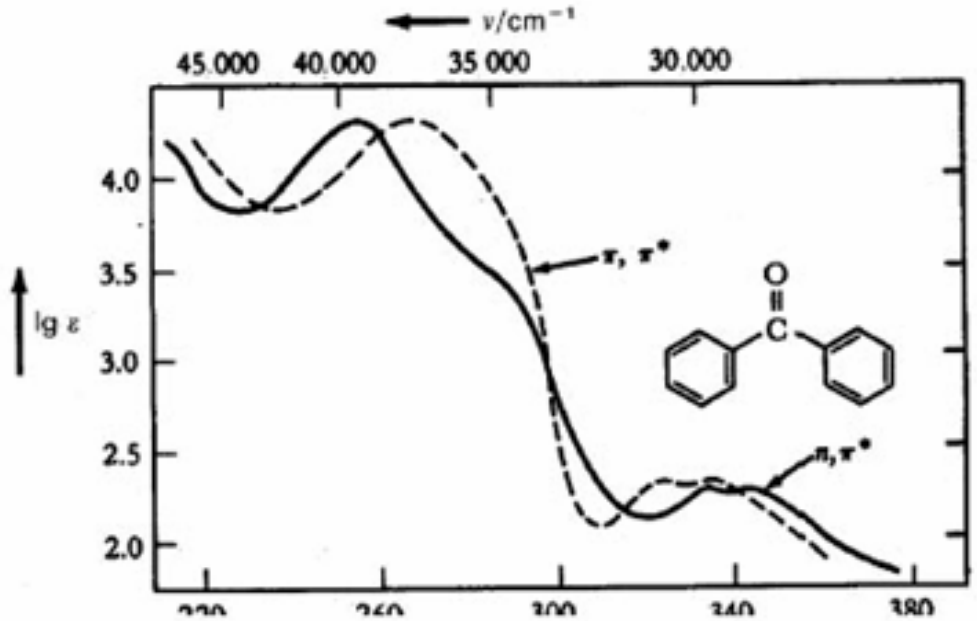


Fig. 6-6. UV/Vis absorption spectrum of benzophenone in cyclohexane (——) and ethanol (- - -) at 25 °C [104, 108].