

Ultraviolet Spectroscopy

Ultraviolet and Visible (UV) Spectroscopy

- Spectroscopy is the study of the interaction between matter and electromagnetic radiation.
- UV/Vis spectroscopy provides information about compounds with conjugated double bonds.
- The Ultraviolet region of the electromagnetic spectrum extends from 200 – 400 nm.

Ultraviolet and Visible (UV) Spectroscopy

- Conjugated compounds can absorb light in the ultraviolet region of the spectrum
- The electrons in the highest occupied molecular orbital (HOMO) undergo a transition to the lowest unoccupied molecular orbital (LUMO)
- The region from $2 \times 10^{-7}\text{m}$ to $4 \times 10^{-7}\text{m}$ (200 to 400 nm) is most useful in organic chemistry
- A plot of absorbance (log of the ratio of the intensity of light in over light transmitted) against wavelength in this region is an **ultraviolet spectrum**

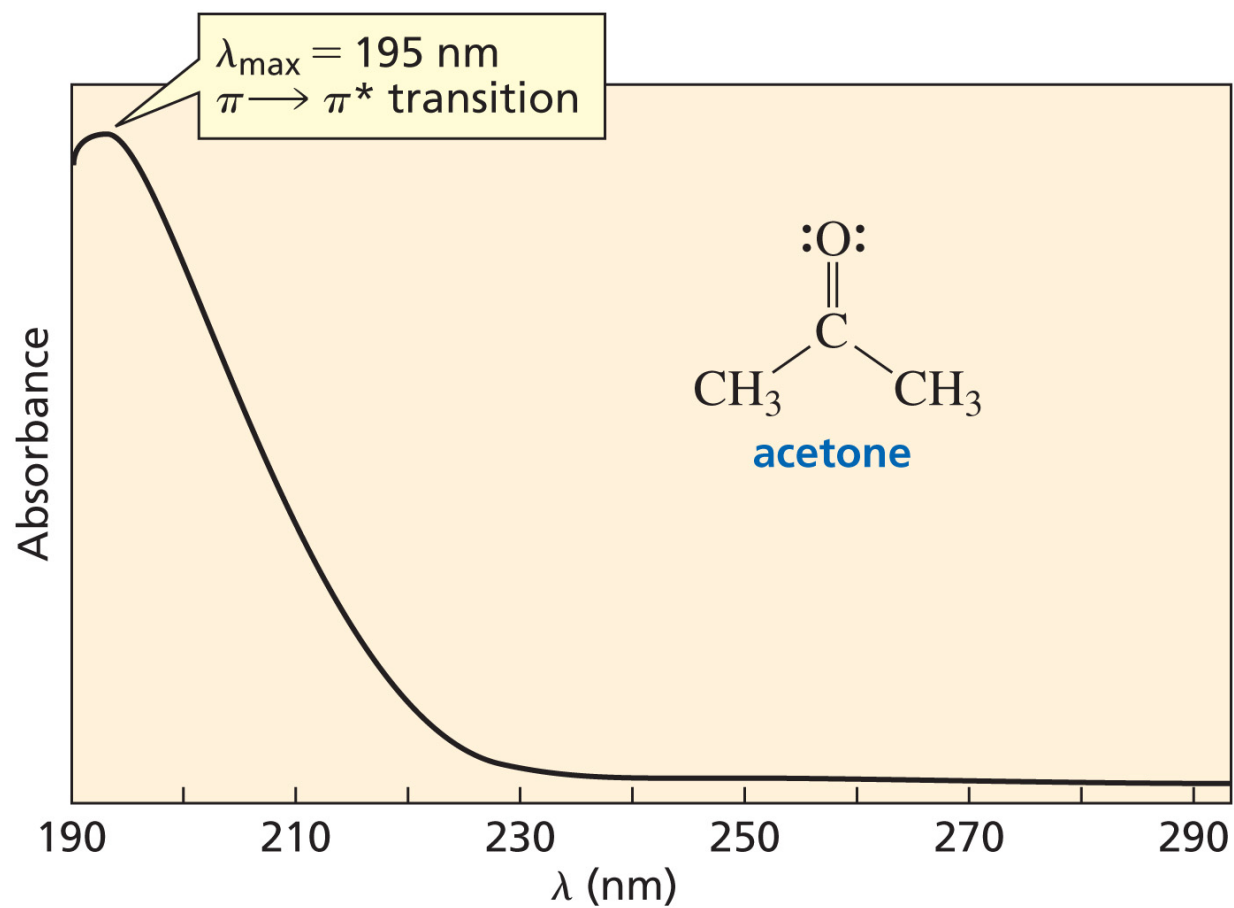
Ultraviolet and Visible (UV) Spectroscopy

- When an organic molecule is irradiated with electromagnetic energy, the radiation either is absorbed by the compound or passes through, depending on the radiation's exact energy.
- When (UV) radiation is used, the energy absorbed by a molecule correspond to the amount necessary to exact energy from one molecular orbital to another.

Ultraviolet and Visible (UV) Spectroscopy

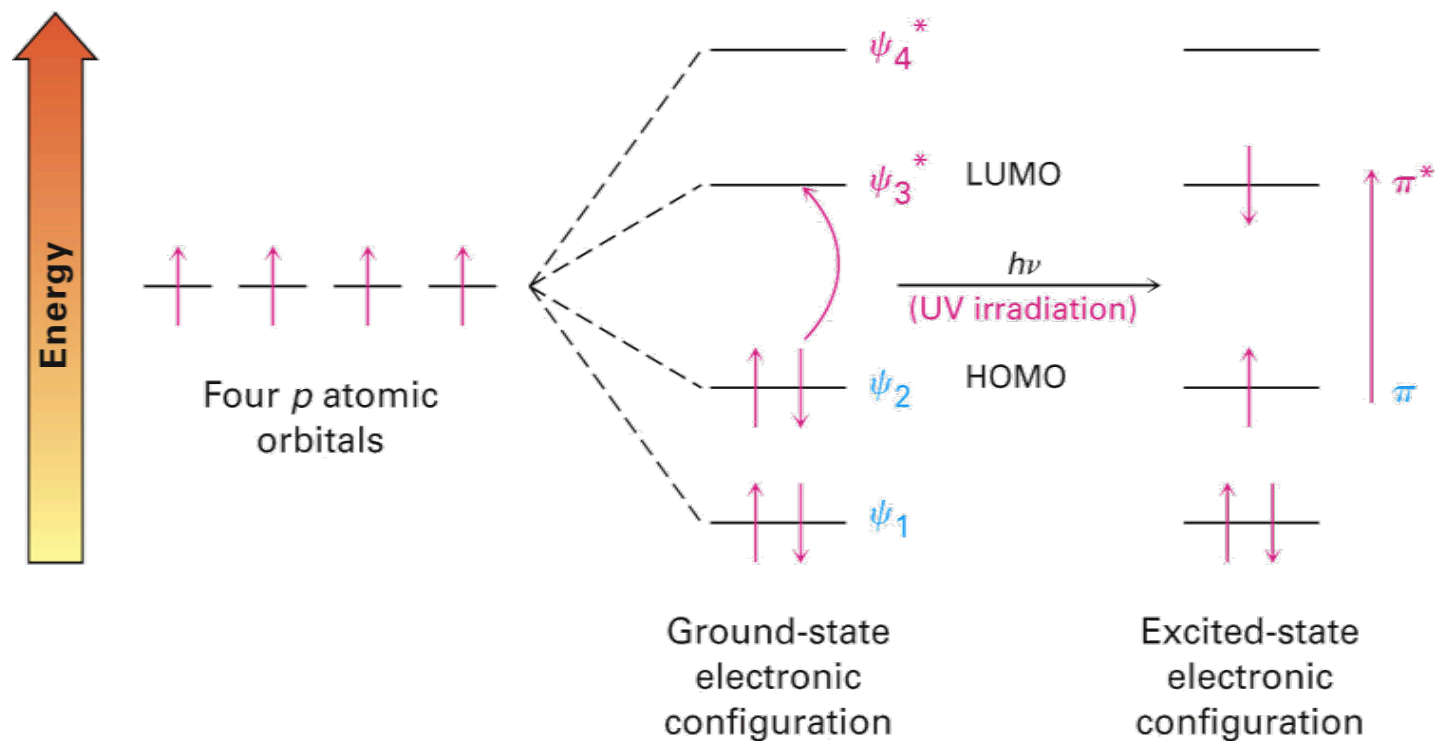
- The UV spectrum is recorded by irradiating the sample with UV light of continuously changing wavelength (200 – 400 nm).
- When the wavelength of light corresponds to the energy level required to excite an electron to a higher level, energy is absorbed.
- Absorption is detected and displayed on a chart that plots λ vs % radiation absorbed.

A UV Spectrum



Ultraviolet Spectrum of 1,3-Butadiene

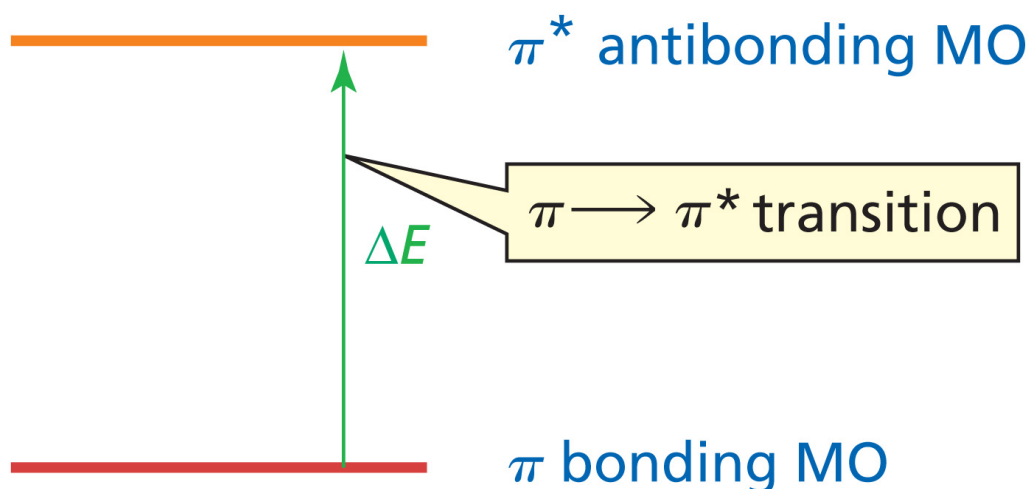
- Example: 1,3-butadiene has four π molecular orbitals with the lowest two occupied
- Electronic transition is from HOMO to LUMO at 217 nm (peak is broad because of combination with stretching, bending)



Interpreting UV Spectra: The Effect of Conjugation

- λ_{\max} : wavelength where UV absorbance for a compound is greatest
- Energy difference between HOMO and LUMO decreases as the extent of conjugation increases
- λ_{\max} increases as conjugation increases (lower energy)
 - 1,3-butadiene: 217 nm, 1,3,5-hexatriene: 258 nm
- Substituents on π system increase λ_{\max}

An Electronic Transition

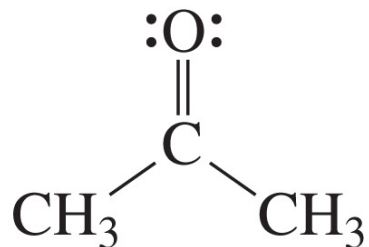


Only organic compounds with π electrons can produce UV/Vis spectra.

A **UV spectrum** is obtained if **UV light is absorbed**.

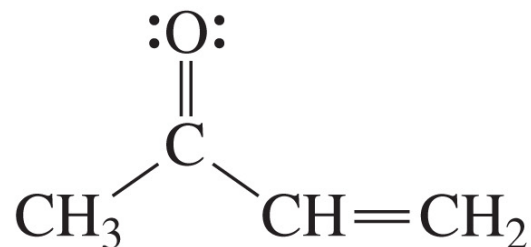
A **visible spectrum** is obtained if **visible light is absorbed**.

The More Conjugated Double Bonds, the Longer the Wavelength



acetone

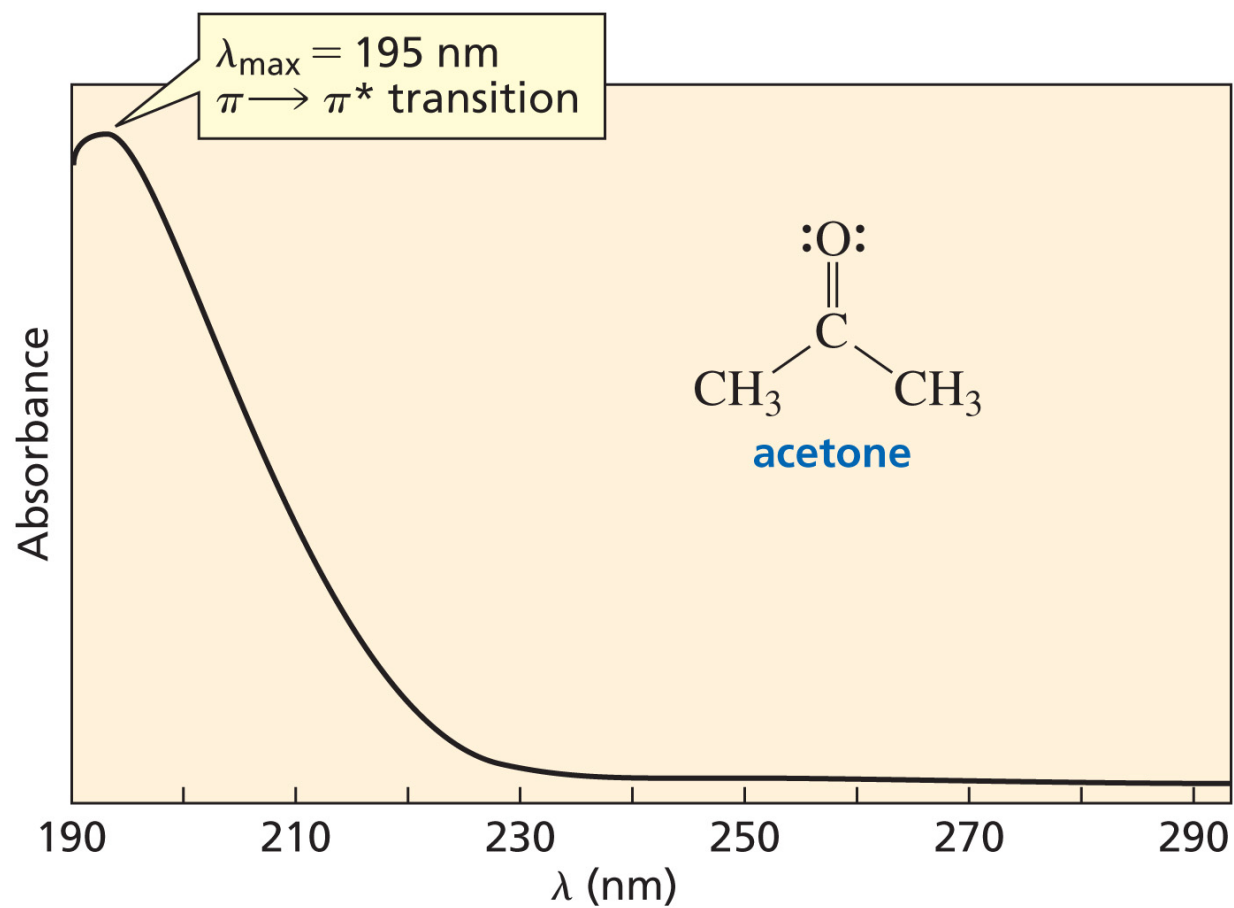
$$\lambda_{\max} = 195 \text{ nm}$$



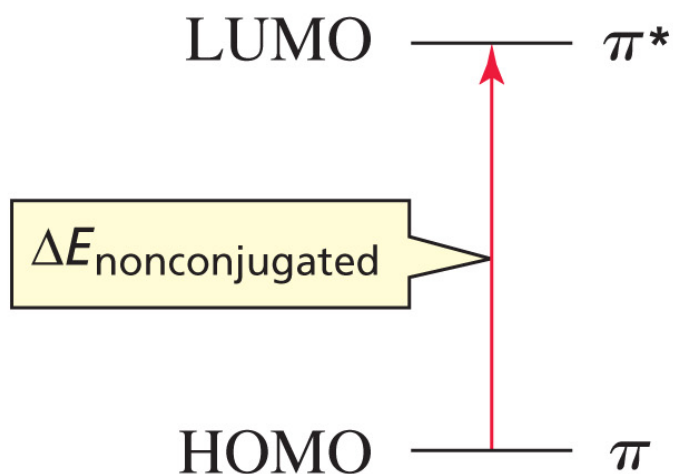
methyl vinyl ketone

$$\lambda_{\max} = 219 \text{ nm}$$

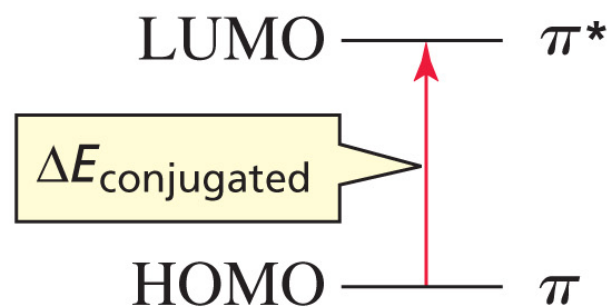
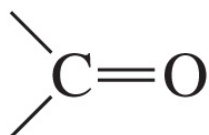
A UV Spectrum



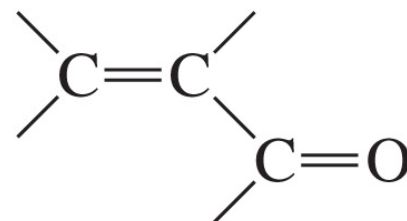
Conjugation Makes the Electronic Transition Easier



nonconjugated π electrons

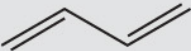






conjugated π electrons

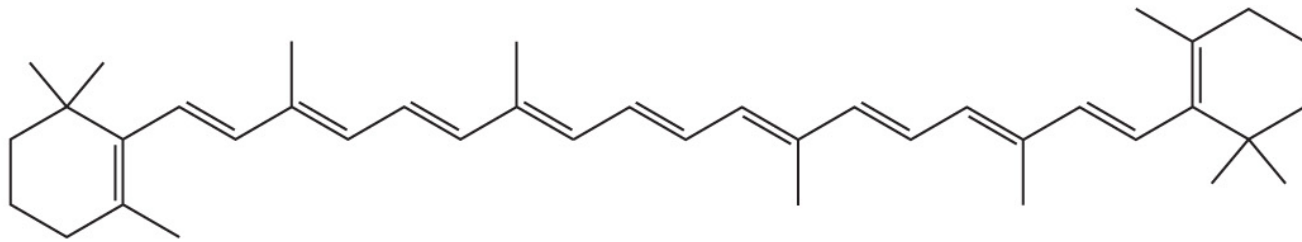


Conjugation Makes the Electronic Transition Easier

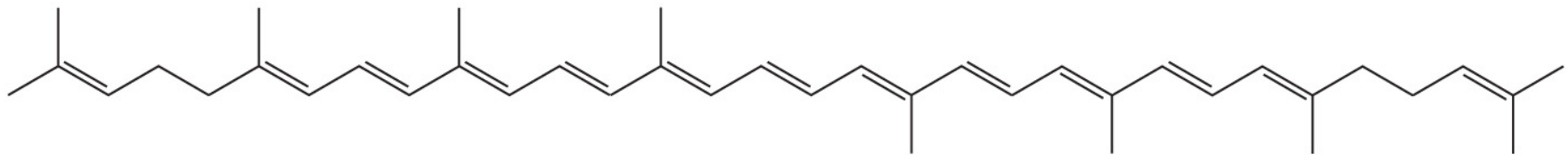
Table 14.6 Values of λ_{\max} and ϵ for Ethylene and Conjugated Polyenes

Compound	λ_{\max} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
$\text{H}_2\text{C}=\text{CH}_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

Colored Compounds Absorb Visible Light (> 400 nm)



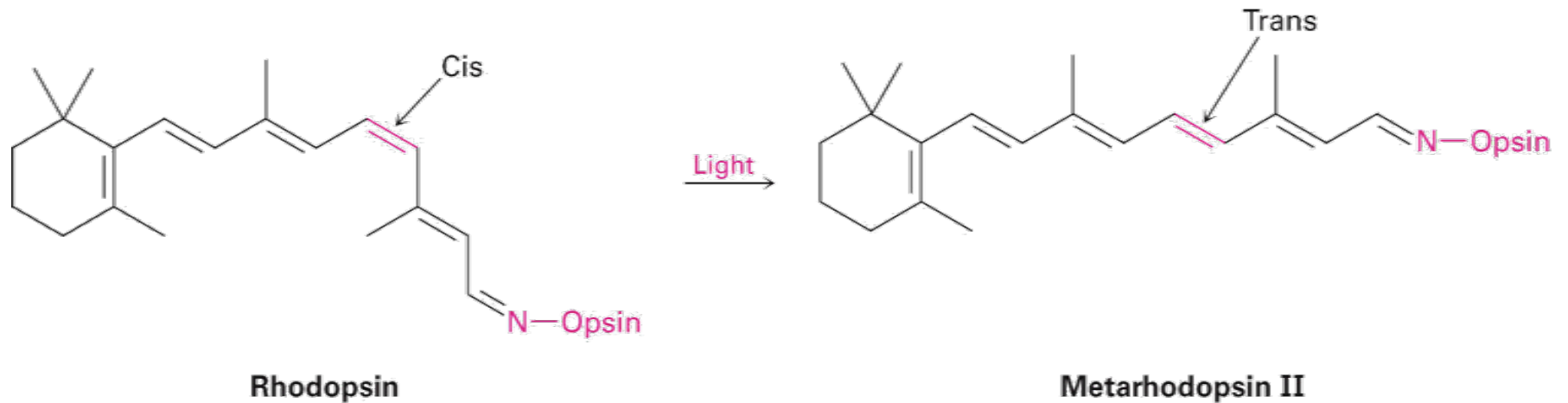
β -carotene
 $\lambda_{\max} = 455 \text{ nm}$



lycopene
 $\lambda_{\max} = 474 \text{ nm}$

Conjugation, Color, and the Chemistry of Vision

- Visible region is about 400 to 800 nm
- Extended systems of conjugation absorb in visible region
- β -Carotene, 11 double bonds in conjugation, $\lambda_{\text{max}} = 455 \text{ nm}$
- Visual pigments are responsible for absorbing light in eye and triggering nerves to send signal to brain



Quantitative Use of UV Spectra

- Absorbance for a particular compound in a specific solvent at a specified wavelength is directly proportional to its concentration
- You can follow changes in concentration with time by recording absorbance at the wavelength
- Beers' law: $\text{absorbance} = \epsilon c l$
 - “ ϵ ” is molar absorptivity (extinction coefficient)
 - “ c ” is concentration in mol/L
 - “ l ” is path of light through sample in cm

The Beer–Lambert Law

$$A = \varepsilon c l$$

A = absorbance of the sample

c = concentration of substance in solution

l = length of the cell in cm

ε = molar absorptivity of the sample

(a measure of the probability of the transition)

UV/Vis Absorption Bands are Broad

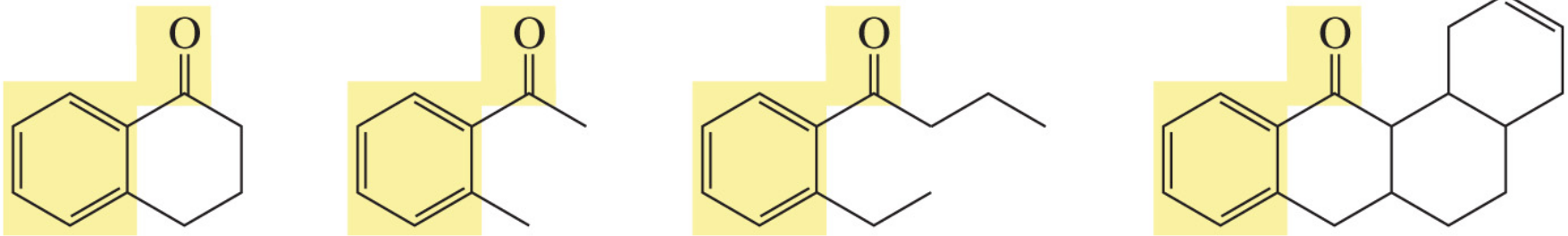
≡≡≡ π^* antibonding MO

vibrational sublevels

≡≡≡ π bonding MO

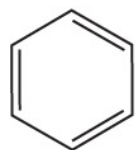
UV/Vis absorption bands are broad
because an electronic state has **vibrational sublevels**.

Chromophore



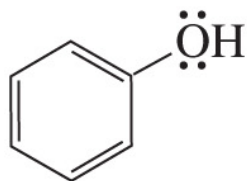
A chromophore is that part of a molecule that is responsible for a UV/Vis spectrum.

Auxochrome



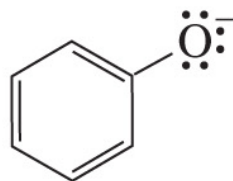
benzene

$\lambda_{\max} = 255 \text{ nm}$



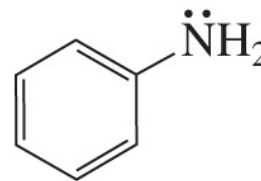
phenol

270 nm



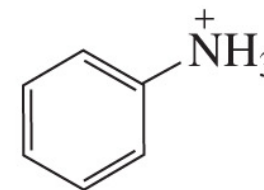
phenolate ion

287 nm



aniline

280 nm



anilinium ion

254 nm

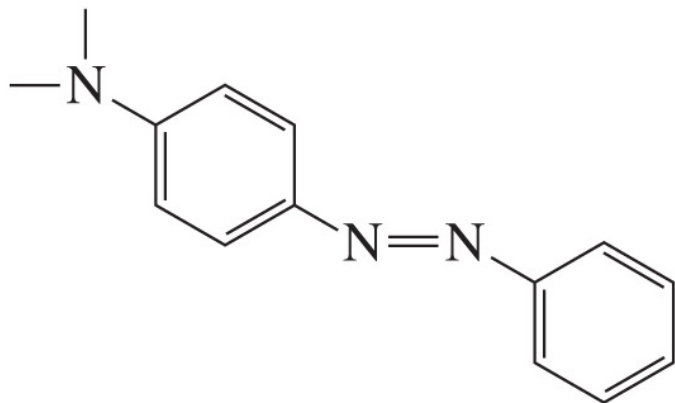
An auxochrome is a substituent that alters
the position and the intensity of the absorption.

The Color Observed Depends on the Color Absorbed

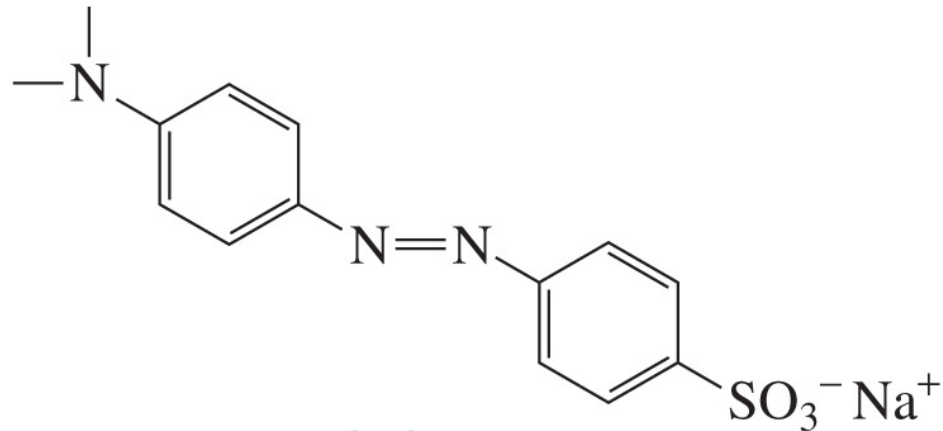
Table 14.7 Dependence of the Color Observed on the Wavelength of Light Absorbed

Wavelengths absorbed (nm)	Color absorbed	Color observed
380–460	blue-violet	yellow
380–500	blue	orange
440–560	blue-green	red
480–610	green	purple
540–650	orange	blue
380–420 and 610–700	purple	green

Common Dyes



butter yellow
an azobenzene



methyl orange
an azobenzene

Terms describing UV absorptions

1. **Chromophores:** functional group(s) of a molecule responsible for the absorption of light.
2. **Auxochromes:** functional group that does not itself absorb in the UV region above 200 nm, but does not effect of shifting chromophore peaks to longer λ . Substituents with unshared pair e's like OH, NH, SH ..., when attached to π chromophore they generally move the absorption maximum to longer λ .
3. **Bathochromic shift:** shift to longer λ or lower frequency, also called **red shift**.
4. **Hysochromic shift:** shift to shorter λ or higher frequency, also called **blue shift**.
5. **Hyperchromism:** increase in ϵ of a band.
6. **Hypochromism:** decrease in ϵ of a band.

Calculating λ_{\max}

Use Woodward-Feiser rules to predict λ_{\max} for:

Benzoyl Derivatives

Unsaturated Acids and Esters

Unsaturated Aldehydes

Enones

Homoannular (cisoid) dienes

Heteroannular (transoid) dienes