UV-Visible Spectroscopy

PUACP

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What is UV-Visible Spectroscopy ?
Molecular spectroscopy that involves study of the interaction of Ultra violet (UV)-Visible radiation with molecules

What is the result of interaction of UV-Vis light and the molecule?
Ultraviolet light and visible light have just the right energy to cause an electronic Transition of electron from one filled orbital to another of higher Energy unfilled orbital
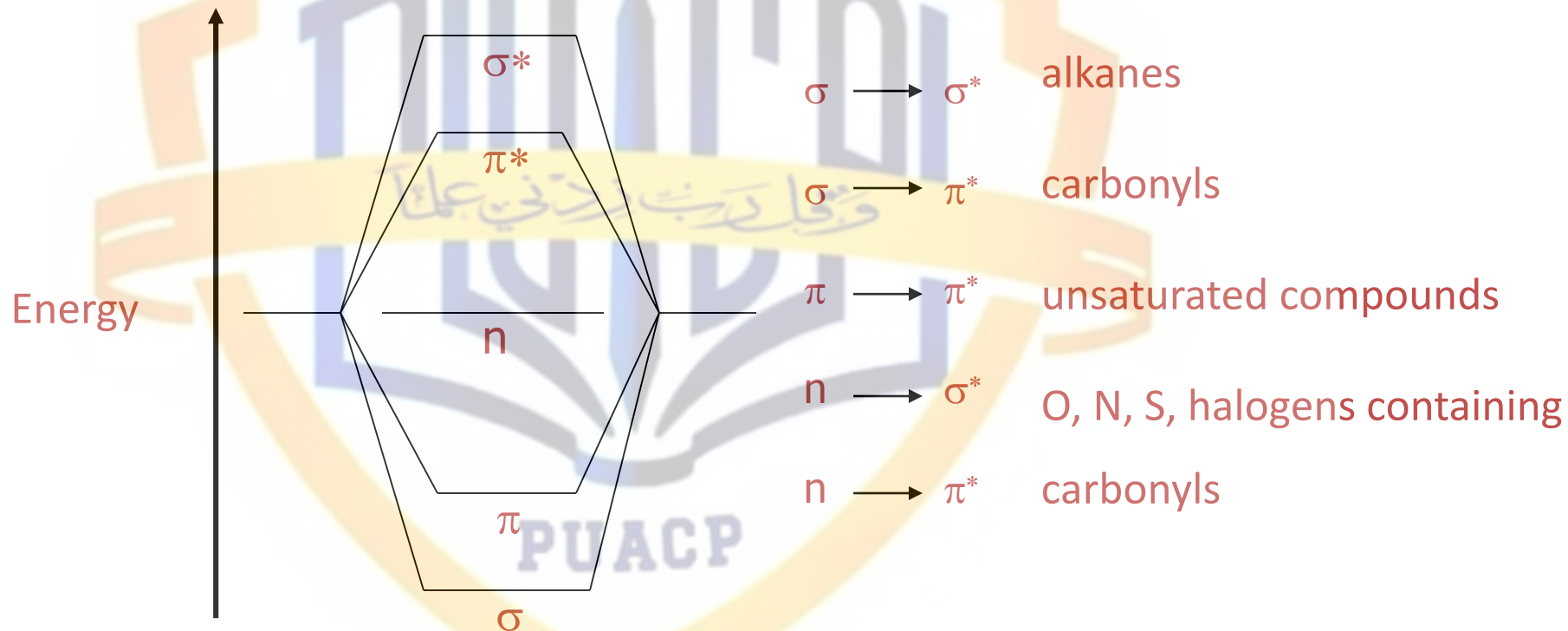
When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in an **excited state**
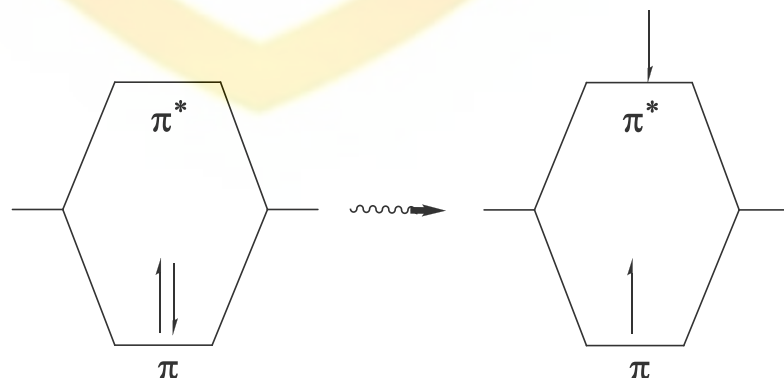
What is the information you get from UV spectroscopy?
The Wave length of absorbed light will provide the information on the energy gap which is related to functional group

UV-Spectroscopy: Possible Transitions Organic Molecules

Energy

σ^*

π^*

n

π

σ

$\sigma \longrightarrow \sigma^*$	alkanes	
$\sigma \longrightarrow \pi^*$	carbonyls	
$\pi \longrightarrow \pi^*$	unsaturated compounds	
$n \longrightarrow \sigma^*$	O, N, S, halogens containing	
$n \longrightarrow \pi^*$	carbonyls	

UV spectra of organic compounds are generally collected from 200-700 nm

$\sigma \longrightarrow \sigma^*$	alkanes	150 nm	
$\sigma \longrightarrow \pi^*$	carbonyls	170 nm	
$\pi \longrightarrow \pi^*$	unsaturated cmpds.	180 nm	√ - if conjugated!
$n \longrightarrow \sigma^*$	O, N, S, halogens	190 nm	
$n \longrightarrow \pi^*$	carbonyls	300 nm	√

UV-Spectrometer: Measurement of Absorbed Radiation
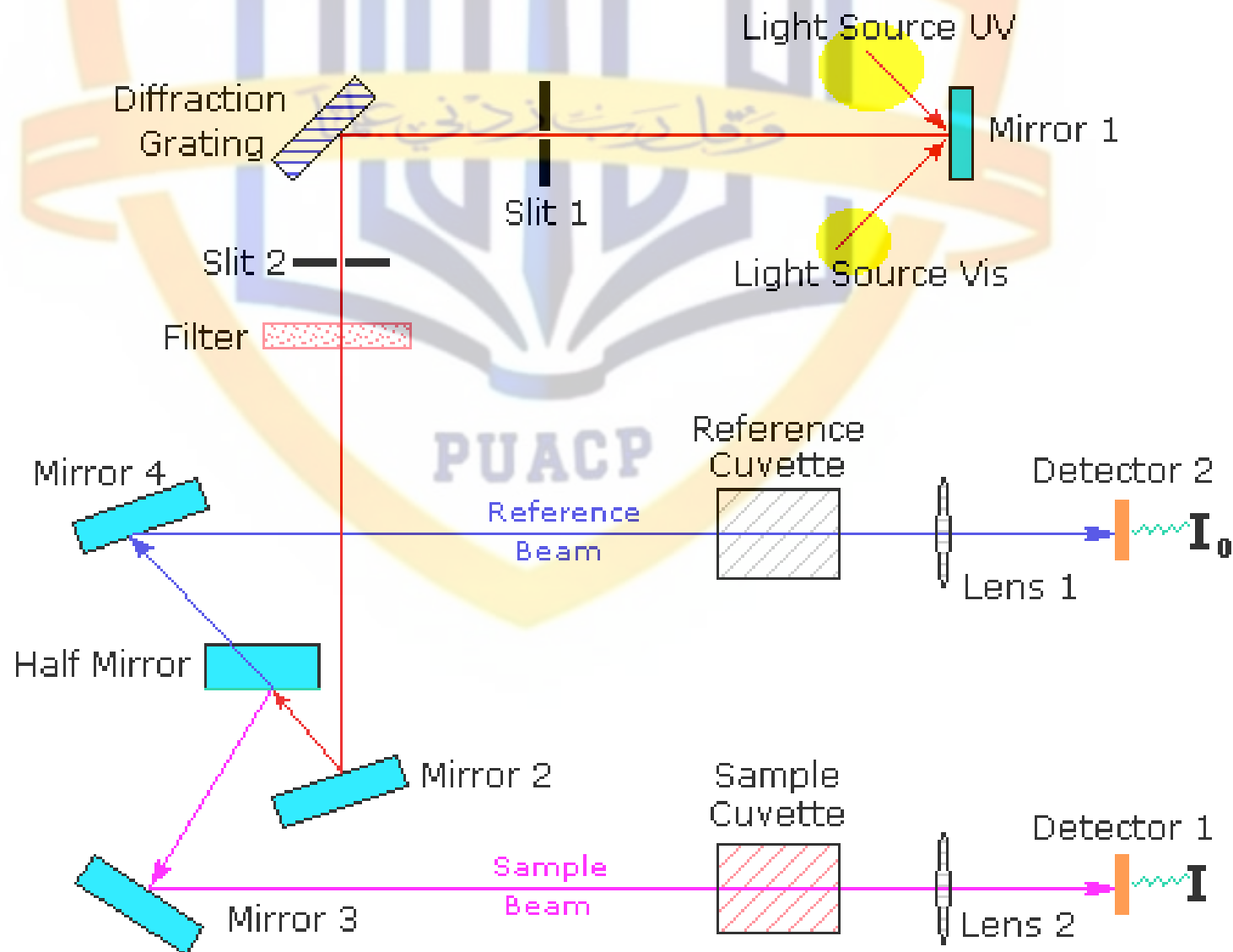
UV-Spectroscopy: Absorption Law

Beer–Lambert law:
At a given wavelength, absorption is proportional to the concentration of absorbing molecules and the path length of the light through the sample

$$A = \varepsilon c l$$

A = absorbance of the sample = $\log_{10} (I_0/I)$

I_0 = intensity of the radiation entering the sample
I = intensity of the radiation emerging from the sample
l = length of the light path through the sample, in centimeters
c = concentration of the sample, in moles/liter
ε = molar absorptivity (liter mol^{-1} cm^{-1} or M^{-1} cm^{-1}) where M = mol L^{-1}

The **molar absorptivity (formerly called the extinction coefficient) of a compound** is a constant that is characteristic of the compound at a particular wavelength

Molar absorptivities may be very large for strongly absorbing compounds (>10,000) and very small if absorption is weak (= 10 to 100)
No absorption gives ε = 0!

UV-Spectroscopy: Absorption Law

Guanosine has a maximum absorbance at 275 nm. $\varepsilon_{275} = 8400\ M^{-1}\ Cm^{-1}$ and the path length is 1 cm. Using a spectrophotometer, you find the that $A_{275} = 0.7$. What is the concentration of guanosine?

$$A = \varepsilon c l$$

$$0.70 = (8400\ \text{M}^{-1}\ \text{cm}^{-1})(1\ \text{cm})(C)$$

$$C = 8.33 \times 10^{-5}\ \text{mol/L}$$

There is a substance in a solution (4 moles/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the absorption coefficient of the substance?

$$-\log\left(\frac{I_t}{I_o}\right) = -\log\left(\frac{0.5}{1.0}\right) = A = 8\epsilon$$

$$\epsilon = 0.0376\ \text{M}^{-1}\ \text{cm}^{-1}$$

PRESENTATION OF SPECTRA

The ultraviolet–visible spectrum is generally recorded as a plot of absorbance versus wavelength

$\lambda_{max} = 195$
$\pi \longrightarrow \pi^*$ transition

:O:
$\parallel$
$CH_3 - C - CH_3$
acetone
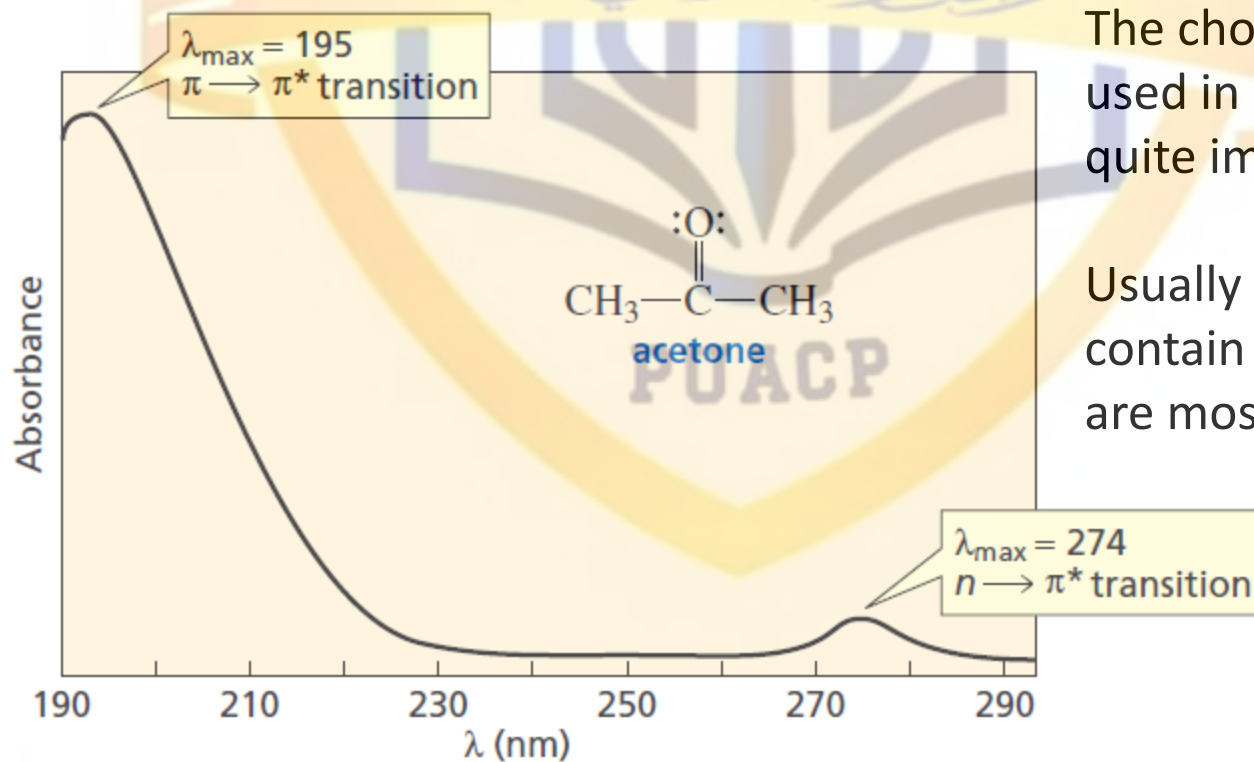
The choice of the solvent to be used in ultraviolet spectroscopy is quite important

Usually solvents that do not contain conjugated systems are most suitable for this purpose

$\lambda_{max} = 274$
$n \longrightarrow \pi^*$ transition

Absorbance

190   210   230   250   270   290
λ (nm)

λ_{max} is the wavelength where maximum absorption occurred

Chromophore

A **chromophore is that part of a molecule that absorbs UV or visible light**

Alkanes: molecules contain single bonds and the only possible transitions are σ to σ*
Absorb ultraviolet energy at very short wavelengths below 200 nm, shorter than the wavelengths that are experimentally accessible (200-700 nm)

Alcohols, Ethers, Amines, and Sulfur Compounds: In saturated molecules that contain atoms bearing nonbonding pairs of electrons, possible transitions of the *n to σ* They are also* high-energy transitions
Alcohols and amines absorb in the range from 175 to 200 nm; Organic thiols and sulfides absorb between 200 and 220 nm
Most of the absorptions are below the cutoff points for the common solvents, so they are not observed in solution spectra.

Alkenes and Alkynes: Possible transitions are **π to π*.** These transitions are of rather high energy (170 nm) as well, but their positions are sensitive to the presence of substitution

Carbonyl Compounds: Unsaturated molecules that contain atoms such as oxygen or nitrogen may also undergo *n to π*transitions (*280 to 290 nm)*.* Carbonyl compounds also have a **π to π*** transition at about 188 nm

Substituent Effects

The attachment of substituent groups in place of hydrogen on a basic chromophore structure changes the position and intensity of an absorption band of the chromophore

Substituents that increase the intensity of the absorption and the wavelength, are called **auxochromes.**
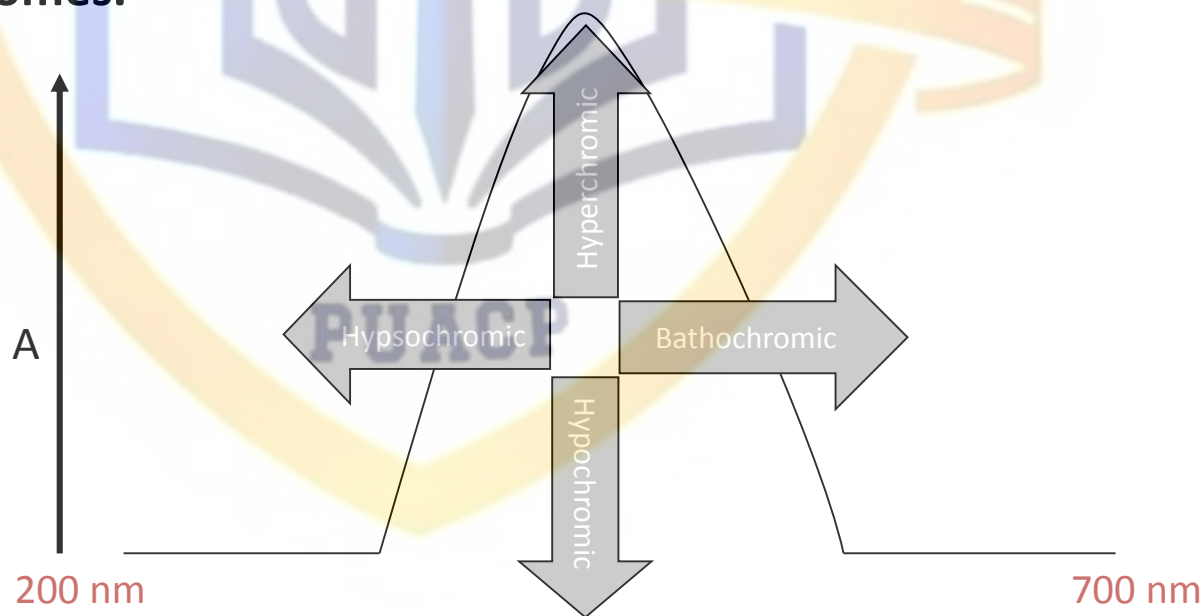
General – Substituents may have any of four effects on a chromophore

 i. Bathochromic shift (red shift) – a shift to longer l; lower energy

 ii. Hypsochromic shift (blue shift) – shift to shorter l; higher energy

 iii. Hyperchromic effect – an increase in intensity

 iv. Hypochromic effect – a decrease in intensity

Effect of Conjugation on λ_{max}

Conjugation raises the energy of the HOMO and lowers the energy of the LUMO

With increase in conjugation the HOMO-LUMO gap will decrease
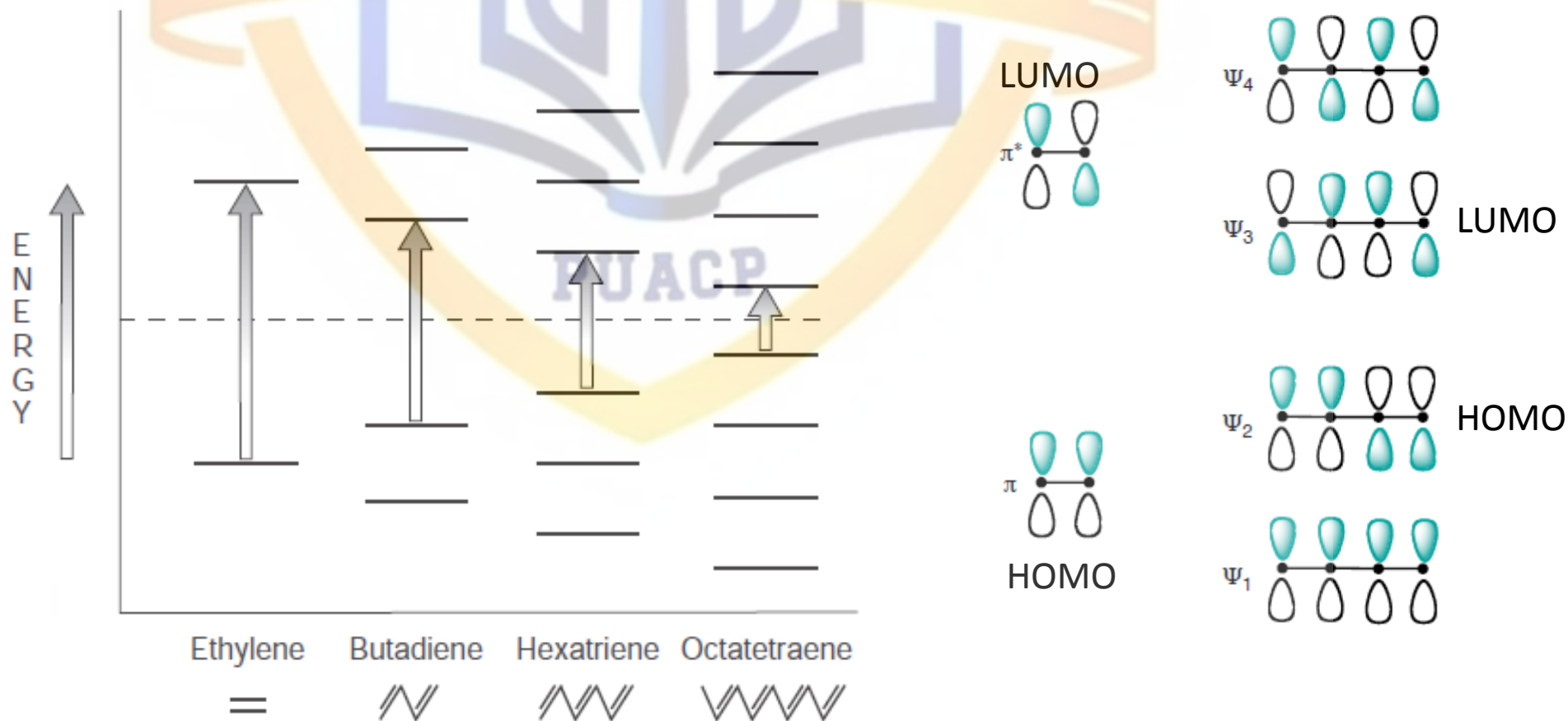
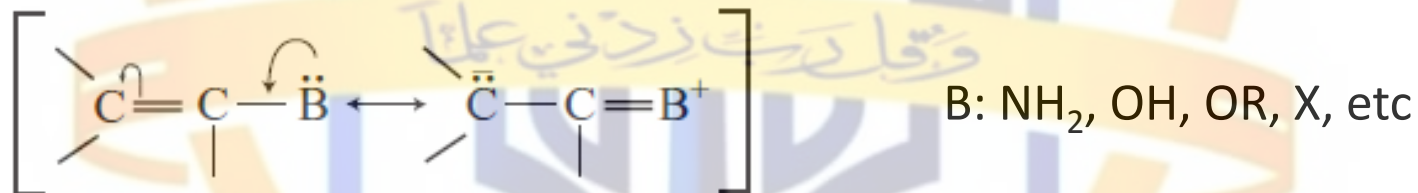Bathochromic shift or red shift – a shift to longer λ; lower energy will be observed

Effect of Conjugation on λ_{max}

Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$H_2C{=}CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

Both λ_{max} and ε (molar absorptivity) increases with the increase in conjugation

Substituent Effects

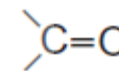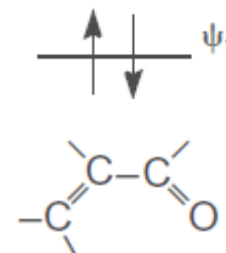auxochromes exert their bathochromic shifts by means of an extension of the length of the conjugated system

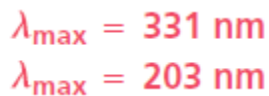$$\left[\quad \overset{\curvearrowright}{C} = C - \ddot{B} \quad \longleftrightarrow \quad \bar{\ddot{C}} - C = B^+ \quad \right]$$
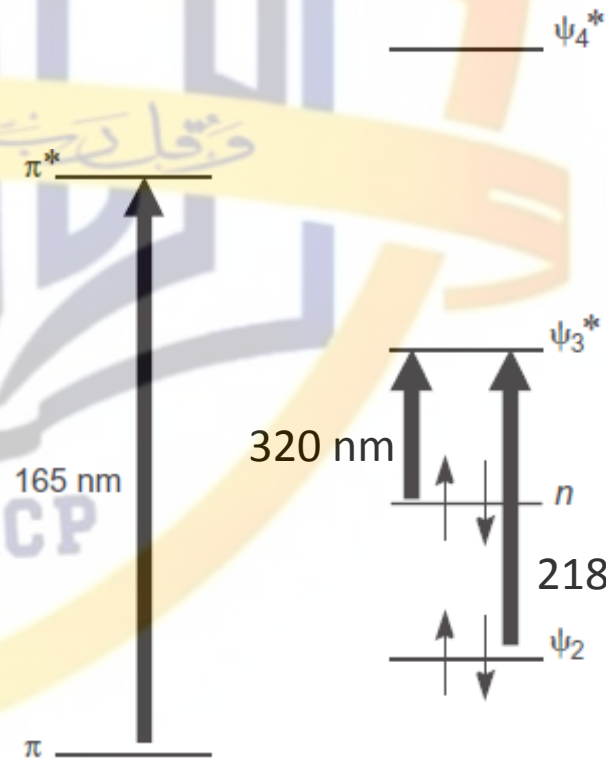
B: NH_2, OH, OR, X, etc

Vs

CH_3
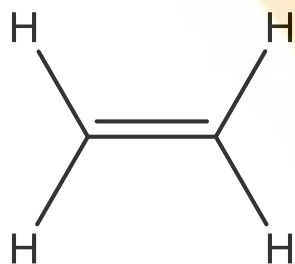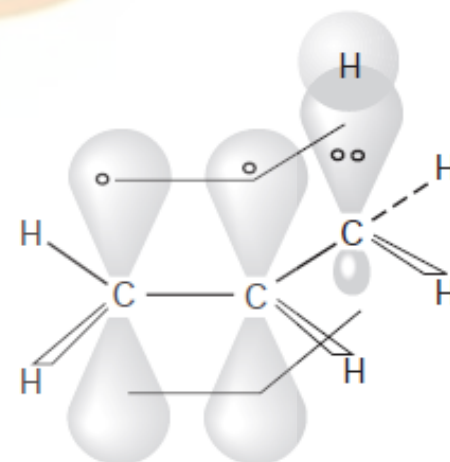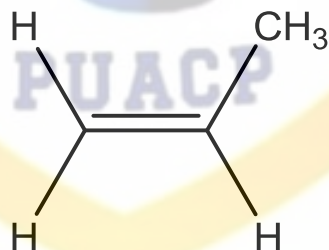
methyl groups also produce a bathochromic shift **Via hyperconjugation**

benzene	phenol	phenoxide ion	aniline	anilinium ion
:ÖH	:Ö⁻	ṄH₂	ṄH₃⁺	

benzene	phenol	phenoxide ion	aniline	anilinium ion
λ_{max} = 255 nm	270 nm	287 nm	280 nm	254 nm
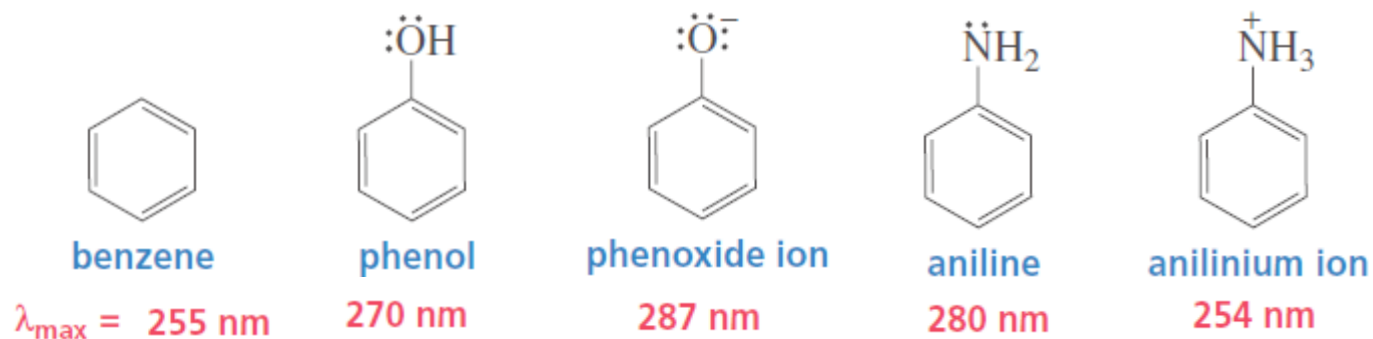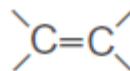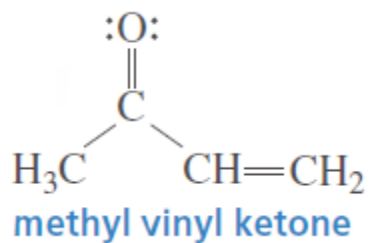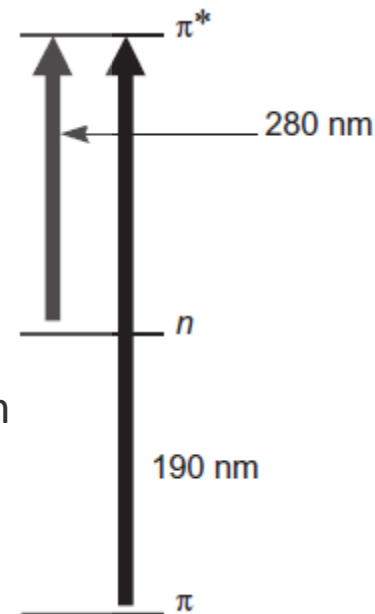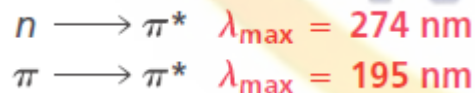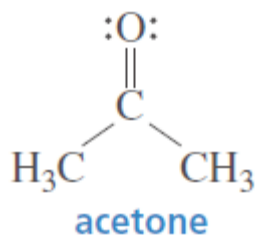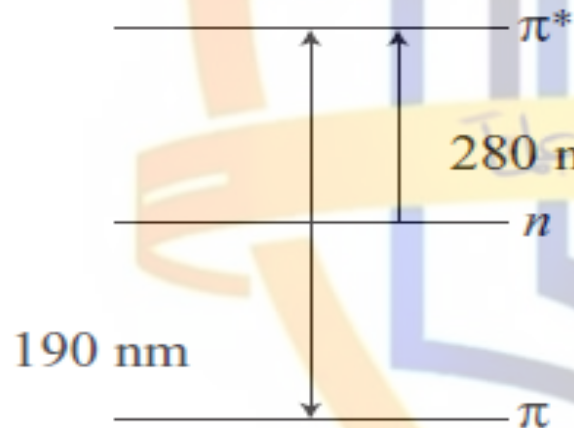
Looking forward

UV spectroscopy:

Unsaturated carbonyls, …

Visible spectroscopy:

Origin of colors of compounds, …