Ultraviolet
and
Visible Spectroscopy

تشخيص المركبات بواسطه الاشعه فوق البنفسجيه

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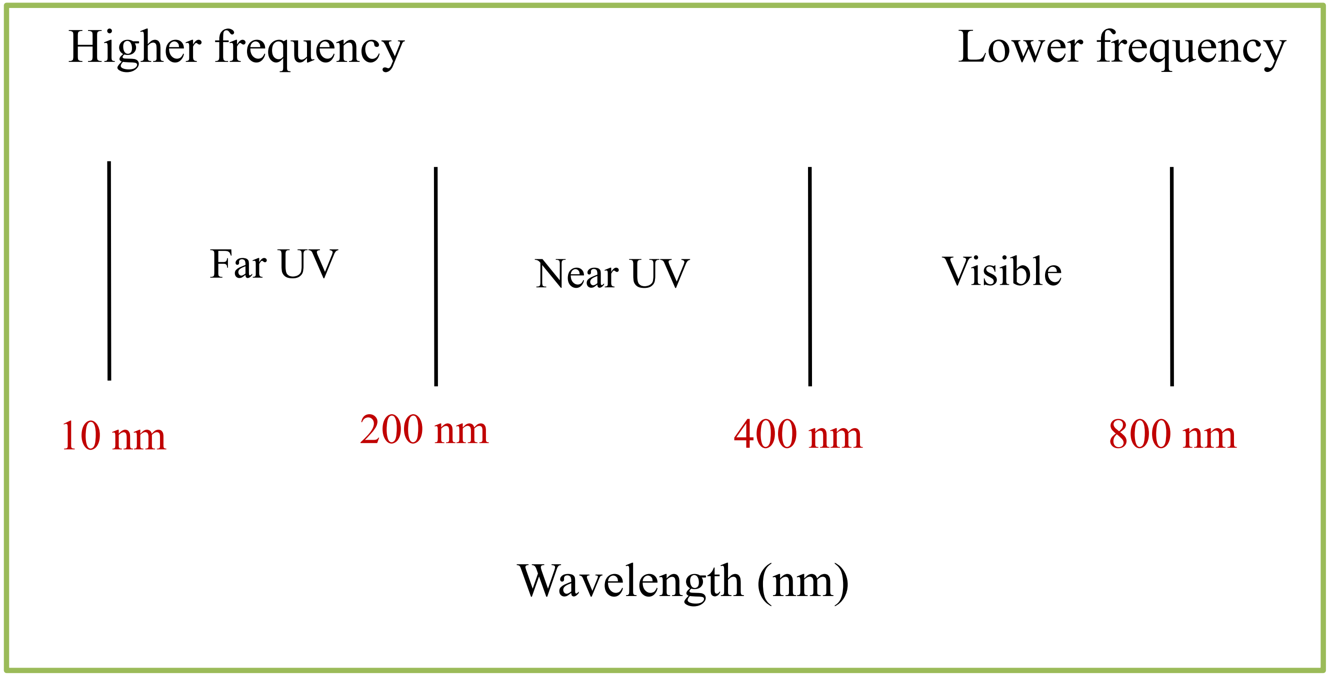
The Ultraviolet and Visible Spectrum



Higher frequency

Lower frequency

Far UV

Near UV

Visible

10 nm

200 nm

400 nm

800 nm

Wavelength (nm)

Ultraviolet and Visible Spectroscopy

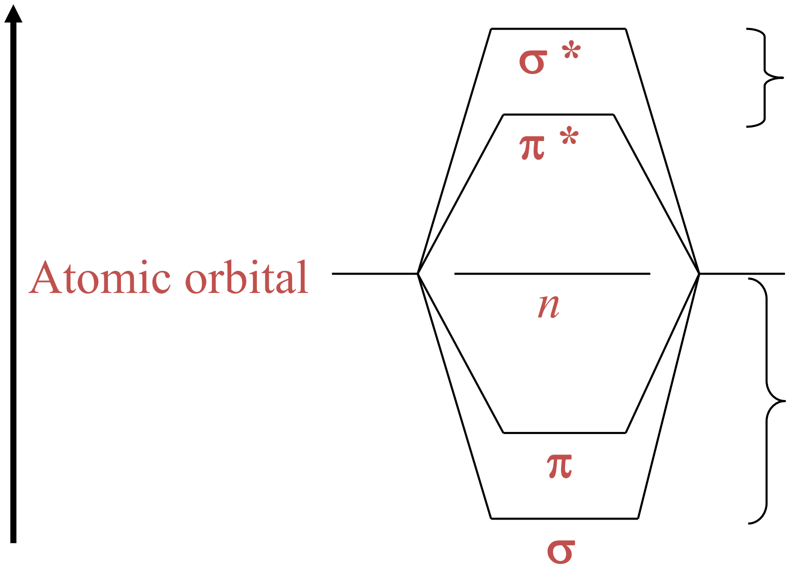
- ☐ The absorption of ultraviolet and visible radiation by molecules is dependent upon the electronic structure of the molecule.
- ☐ So the ultraviolet and visible spectrum is called:

Electronic Spectrum

- ☐ The absorption of light energy by organic compounds in the visible and ultraviolet region involves the promotion of electrons in σ, π, and n-orbitals from the ground state to higher energy states. This is also called

Energy Transition

Electron Transitions



Energy

Atomic orbital

σ *

π *

n

π

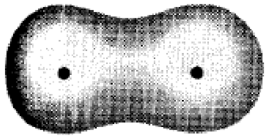
σ

Atomic orbital

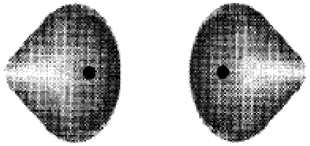
Anti-bonding

Bonding

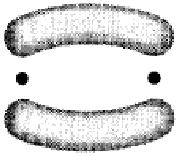
Molecular orbitals



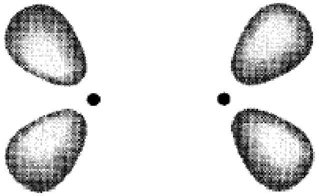
(a) σ orbital



(c) σ* orbital

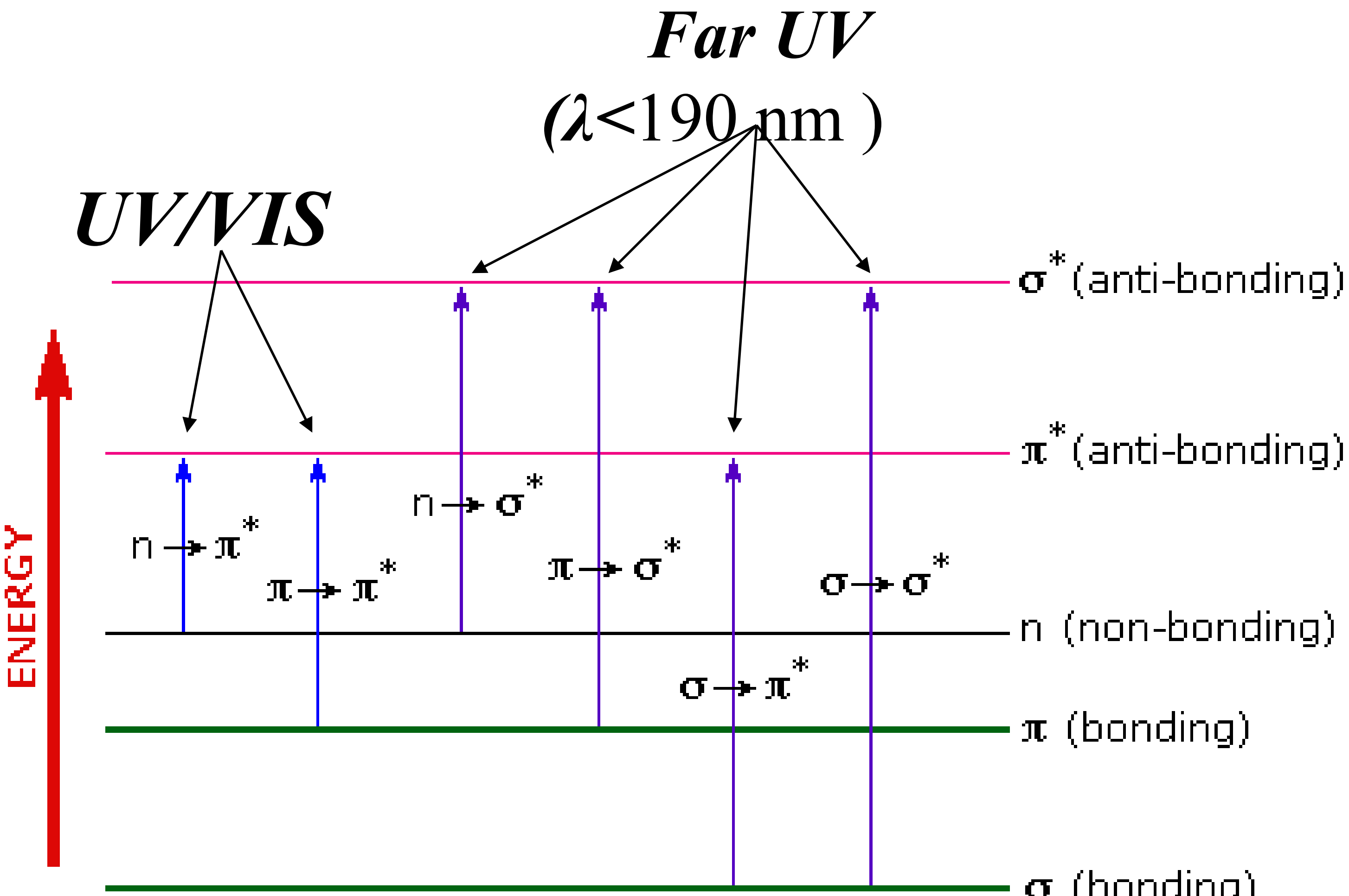


(b) π orbital

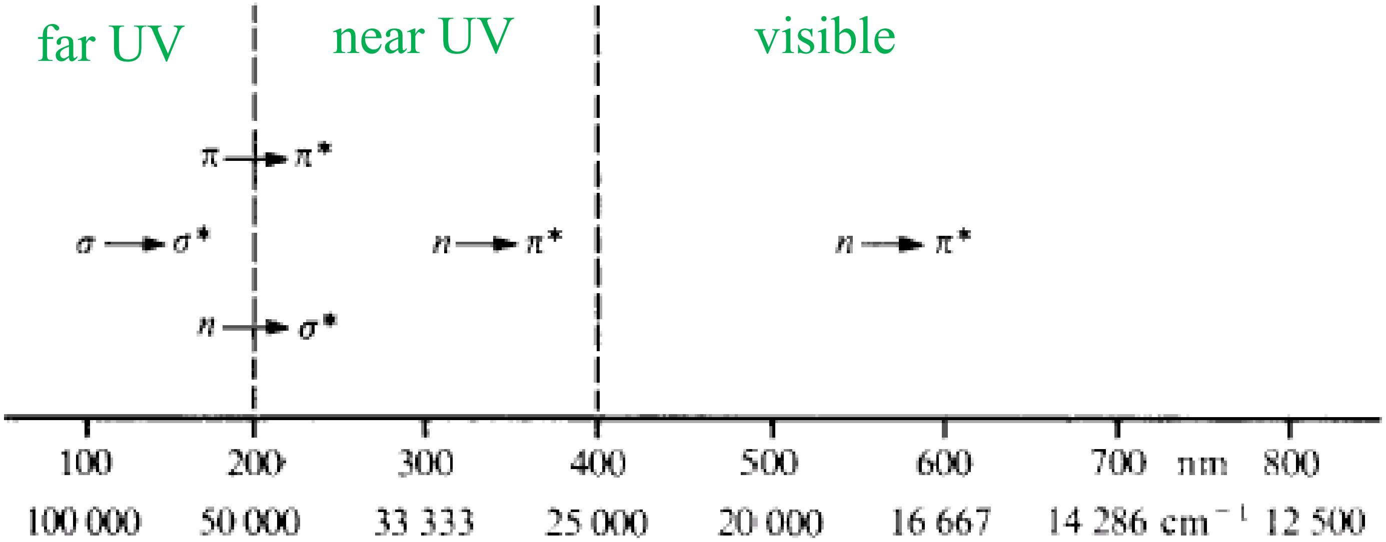


(d) π * orbital

Electron transitions

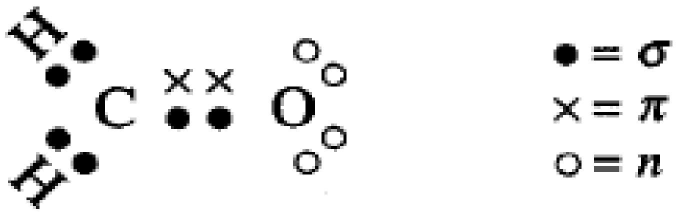


The region of the electronic spectrum and the type of transitions that occur in each.



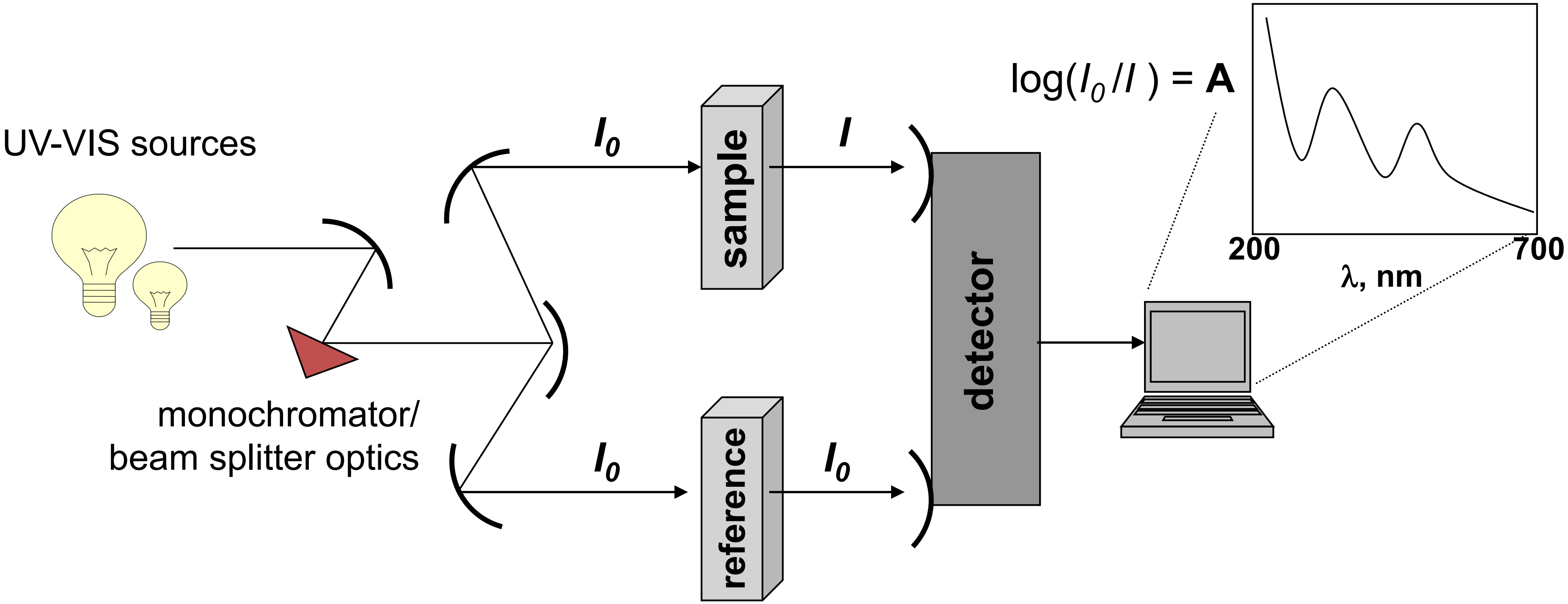
Some of the most important transitions:

$\sigma \longrightarrow \sigma^*$	In alkanes
$\sigma \longrightarrow \pi^*$	In carbonyl compounds
$\pi \longrightarrow \pi^*$	In unsaturated compounds
$n \longrightarrow \sigma^*$	In O, N, S and halogen compounds
$n \longrightarrow \pi^*$	In carbonyl compounds



Spectrometer

An instrument which can measure the absorbance of a sample at any wavelength.



Absorption laws

Beer – Lambert Law

$$\text{Absorbance (A)} = \text{Log}\,\frac{I_0}{I}$$

$$A = ECL$$

I_0 = Original light intensity
I = Transmitted light intensity
E = Molar Extinction Coefficient
C = Concentration (moles/L)
L = Length of sample cell (cm)

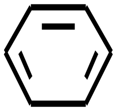
Solvents

Common solvents :

solvent	λ nm
acetonitrile	190
chloroform	240
cyclohexane	195
1,4-dioxane	215
95% ethanol	205
n-hexane	201
methanol	205
isooctane	195
water	190

Terms describing UV absorptions

1. **Chromophores**: functional groups that give electronic transitions.

Group	Structure	nm
Carbonyl	$> C = O$	280
Azo	$-N = N-$	262
Nitro	$-N=O$	270
Thioketone	$-C =S$	330
Nitrite	$-NO2$	230
Conjugated Diene	$-C=C-C=C-$	233
Conjugated Triene	$-C=C-C=C-C=C-$	268
Conjugated Tetraene	$-C=C-C=C-C=C-C=C-$	315
Benzene		261

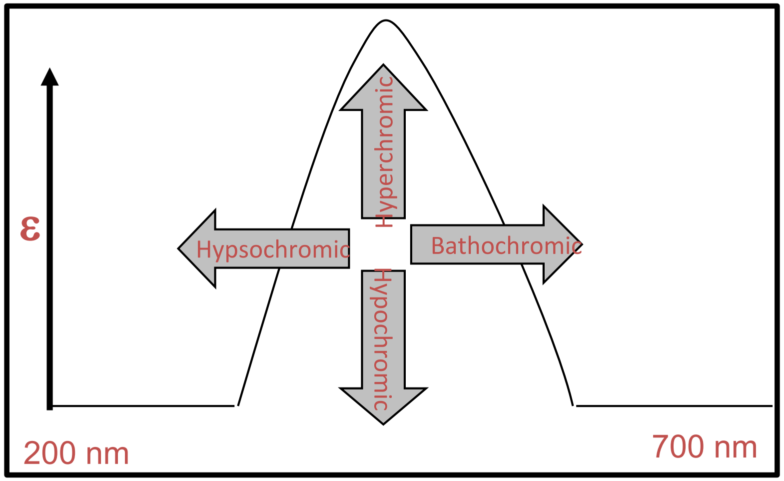
2. **Auxochromes**: substituents with unshared paire's like OH, NH, SH ..., when attached to π chromophore they generally move the absorption max. to longer λ.

3. **Bathochromic shift**: shift to longer λ, also called red shift.

4. **Hypsochromic shift**: shift to shorter λ, also called blue shift.

5. **Hyperchromic effect**: increase in absorption intensity.

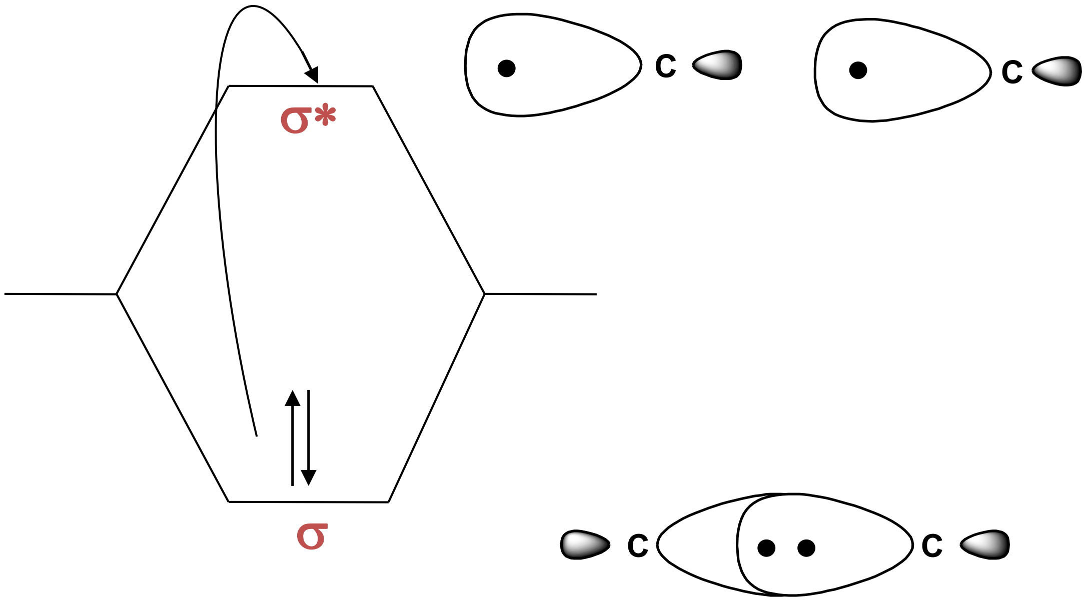
6. **Hypochromic effect**: decrease in absorption intensity.



Absorption of Ultraviolet and Visible Radiation in Organic Compounds

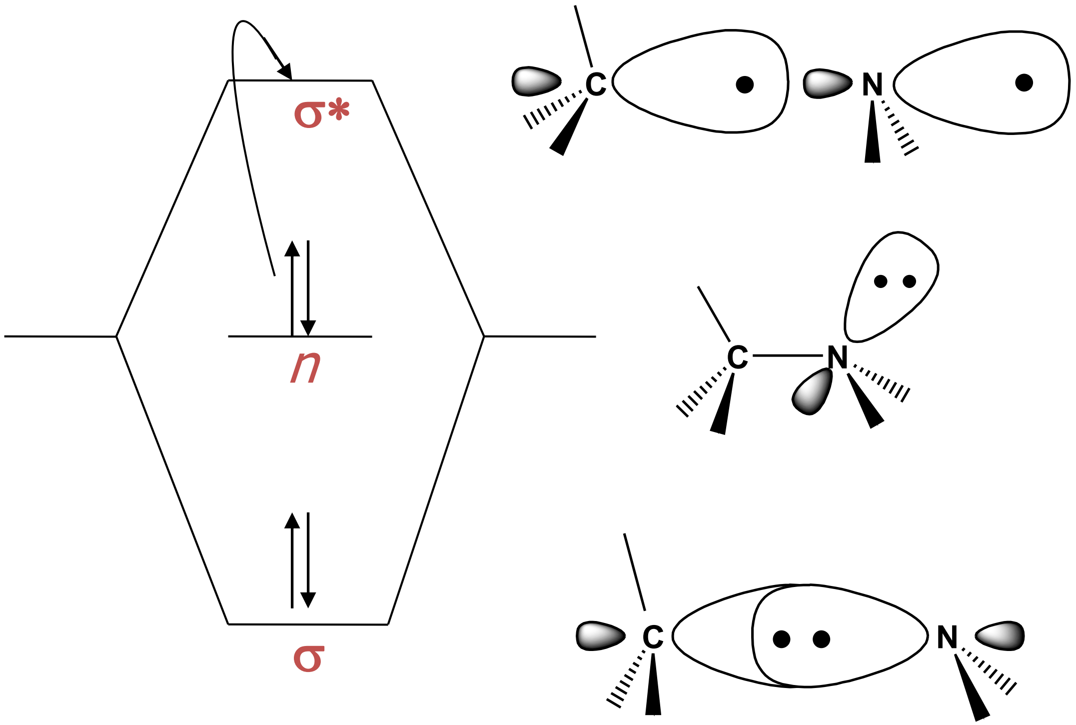
1- Saturated compounds

Alkanes – only posses σ-bonds and no lone pairs of electrons, so only the high energy σ → σ* transition is observed in the far UV.



2. Saturated compounds with unshared e^-

Alcohols, ethers, amines and sulfur compounds – in the cases of simple, aliphatic examples of these compounds the $n \rightarrow \sigma^*$ is the most often observed transition; like the alkane $\sigma \rightarrow \sigma^*$ it is most often at shorter λ than 200 nm.

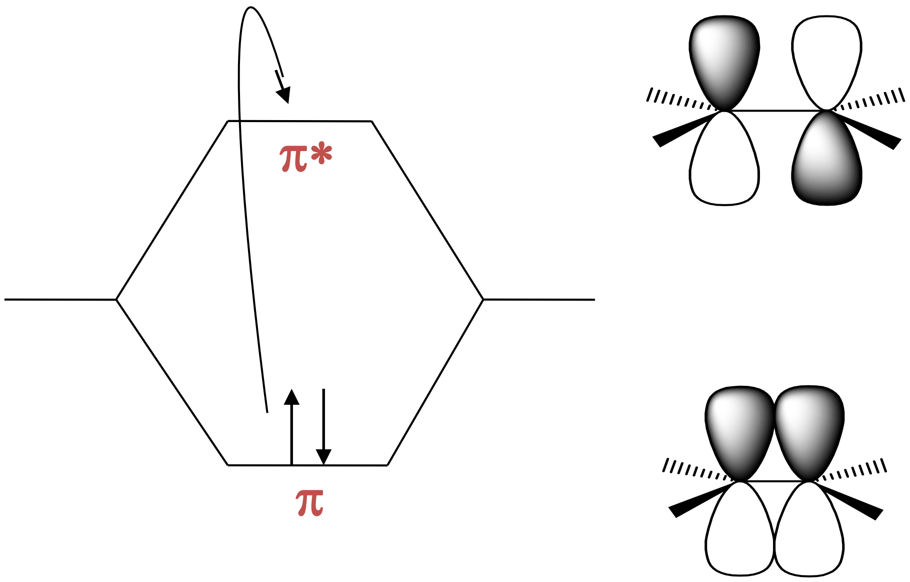


3. Unsaturated compounds

- Alkenes– in the case of isolated examples of these compounds the π → π* is observed at 175 nm.

$CH_2=CH_2$ at 175 nm

- Even though this transition is of lower energy than σ → σ *, it is still in the far UV – however, the transition energy is sensitive to substitution.



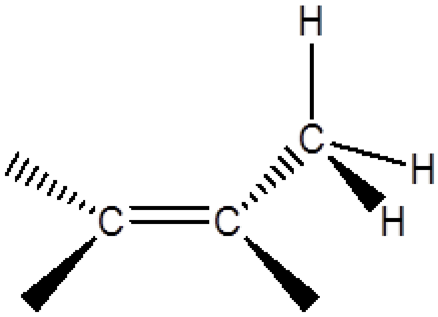
Substituent Effects

CH_2=CHR at 180 nm

cis CHR=CHR at 183 nm

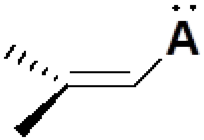
trans CHR=CHR at 180 nm

CR_2=CR_2 at 200 nm

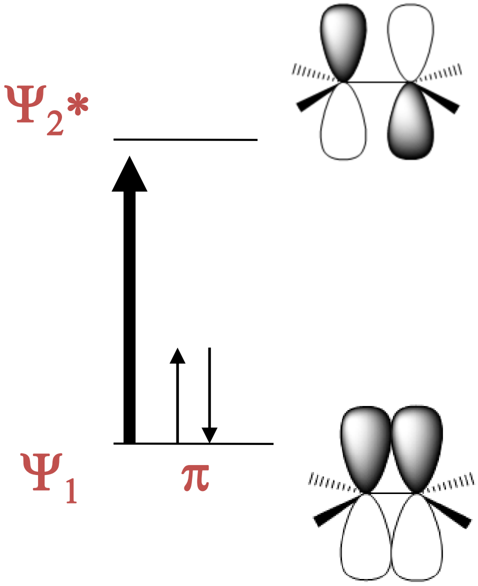


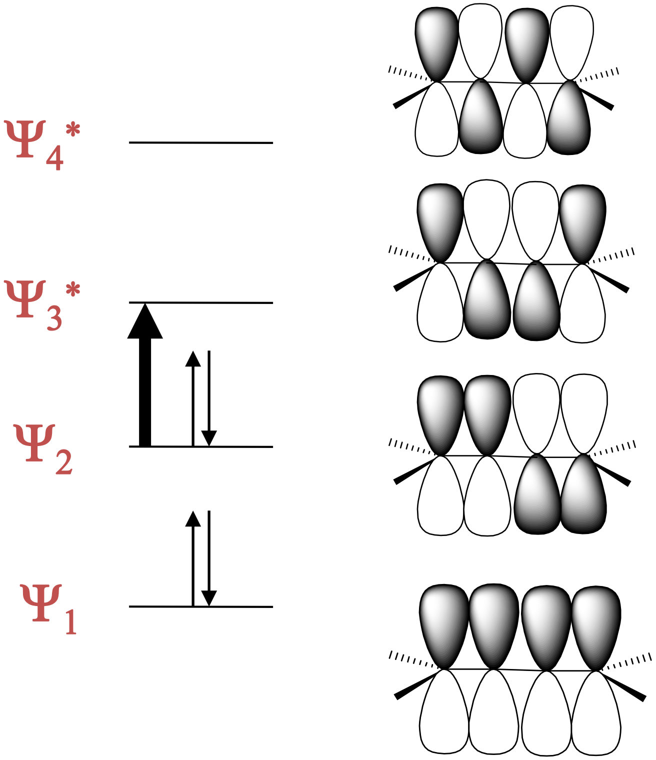
- This effect is thought to be through what is termed "hyperconjugated" or sigma bond resonance
- Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems

Substituent	Increment of Substituent
-SR	45
-NR_2	40
-OR	30
-Cl	5

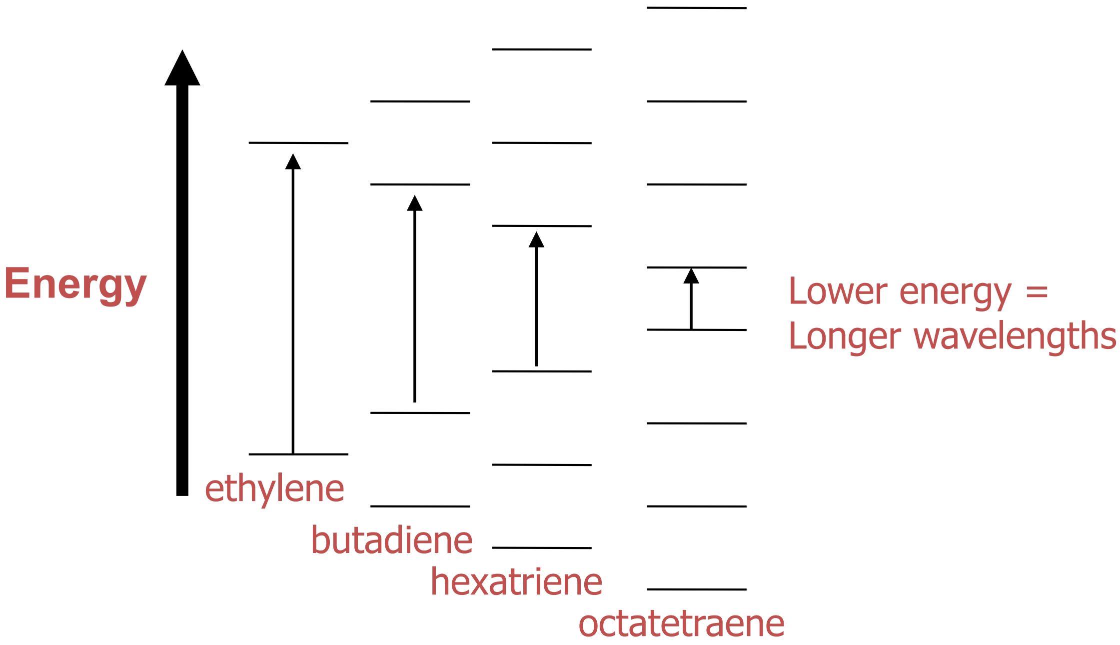


- Dienes– in the case of isolated examples of these compounds the $\pi \rightarrow \pi^*$ is observed in the far UV.
- Conjugated dienes–The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation.

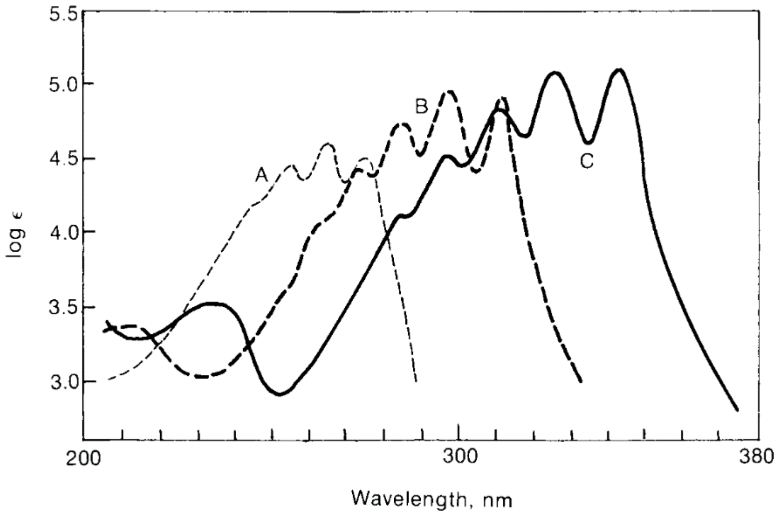




- Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller.

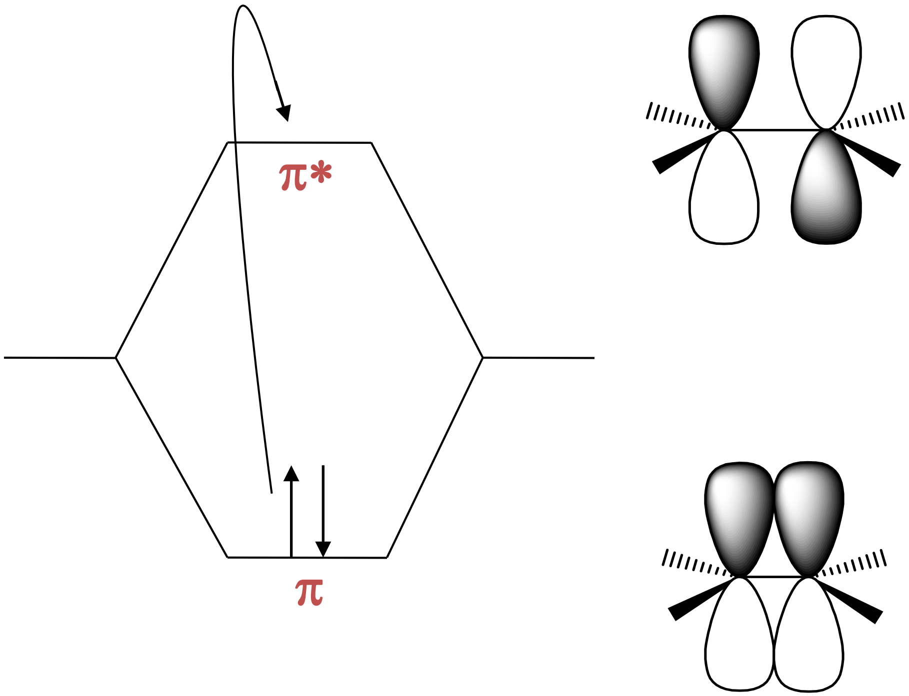


$\pi \rightarrow \pi^*$ is observed in the region from 217 to 245 nm.

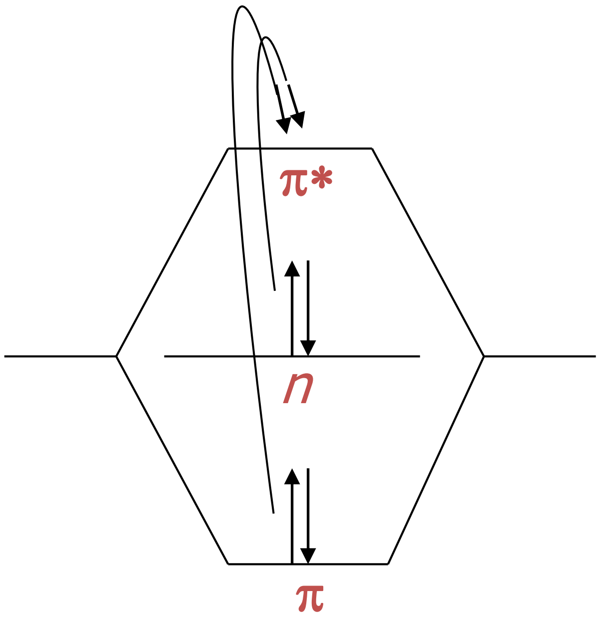


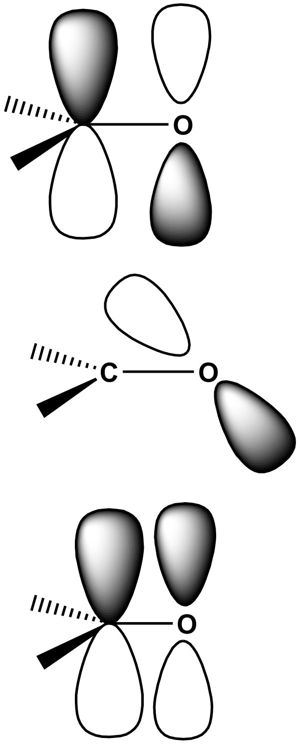
- Alkynes– in the case of isolated examples of these compounds the π → π* is observed in the far UV.

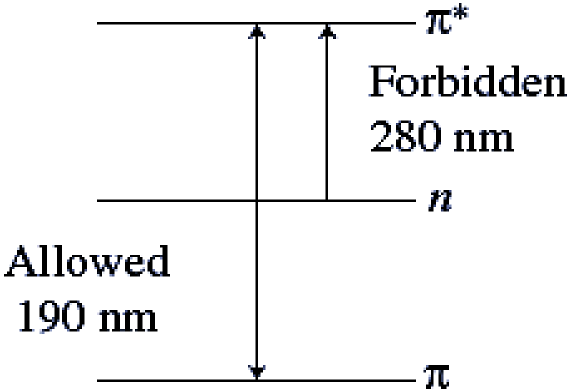
$CH\equiv CH$ at 170 nm



- Carbonyl compounds – unsaturated systems incorporating N or O can undergo $n \rightarrow \pi^*$ transition (~280 nm) in addition to $\pi \rightarrow \pi^*$ transition (190 nm). Most $n \rightarrow \pi^*$ transitions are forbidden and hence are of low intensity.

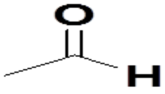




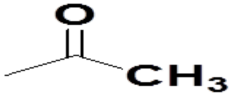


- For auxochromic substitution on the carbonyl, such as –NR$_2$, -OH, -OR, -X, gives a pronounced hypsochromic effect on the *n* → π * transition and a lesser bathochromic effect on the π → π* transition.

Hypsochromic effect on the *n* → π * transition



293 nm



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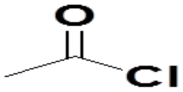

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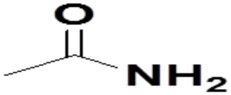

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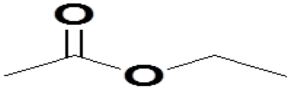

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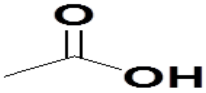
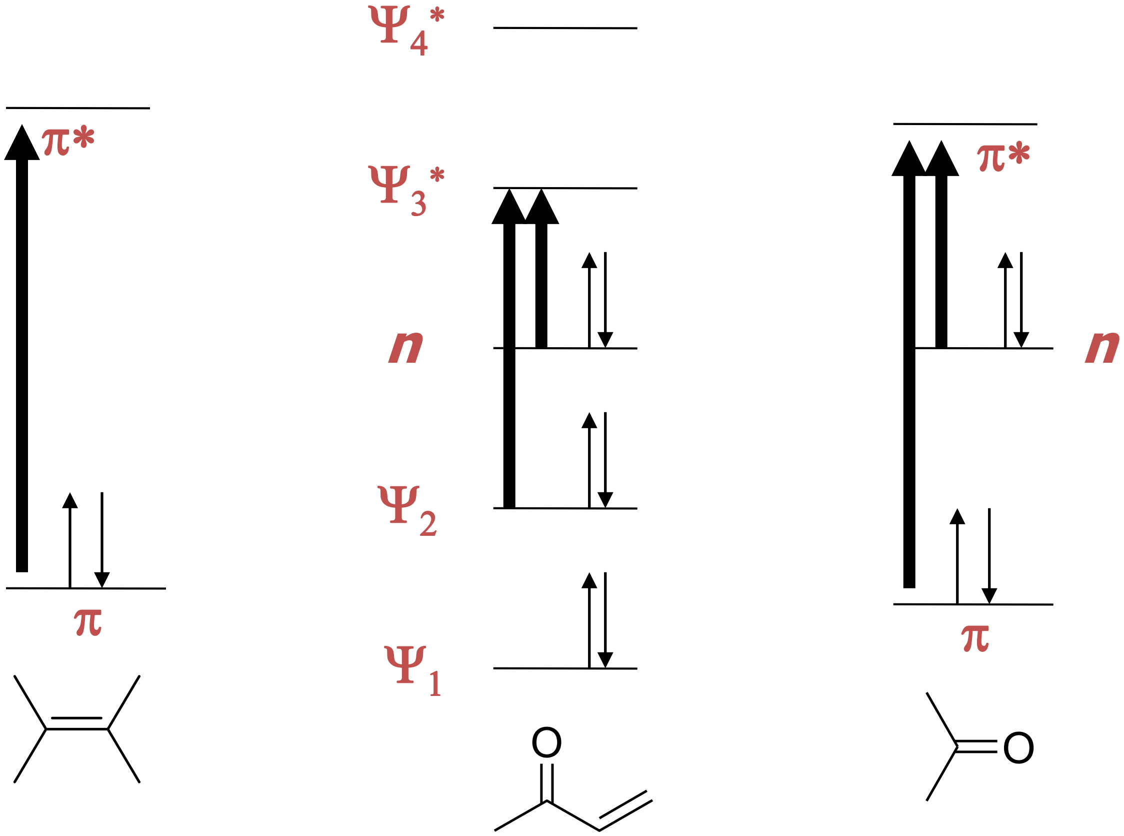


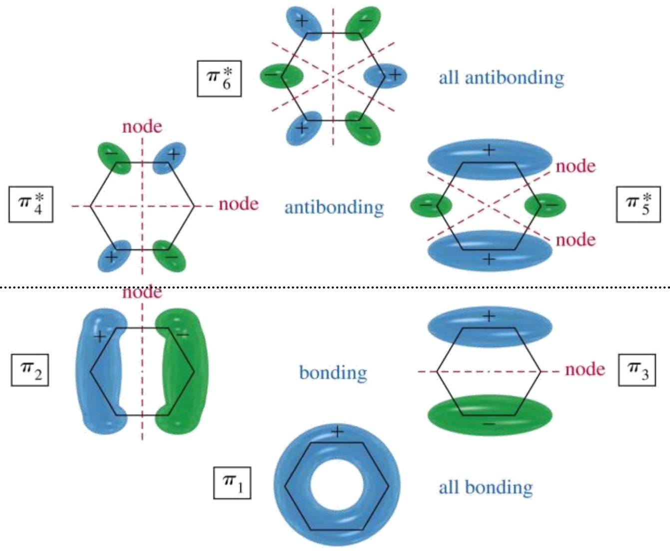
204

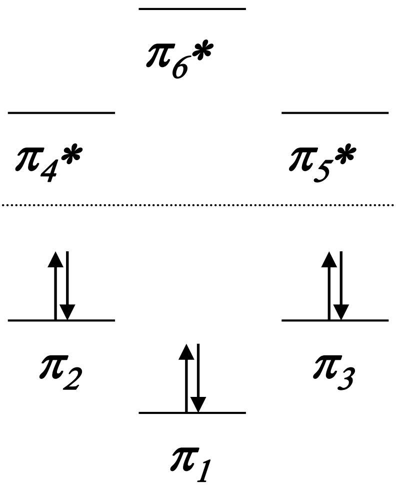
- Enones compounds – Conversely, if the C=O system is conjugated both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are bathochromically shifted.

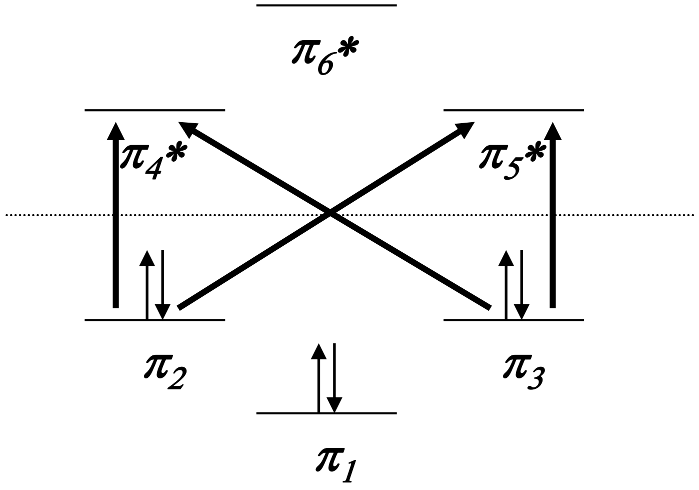


4. Aromatic Compounds

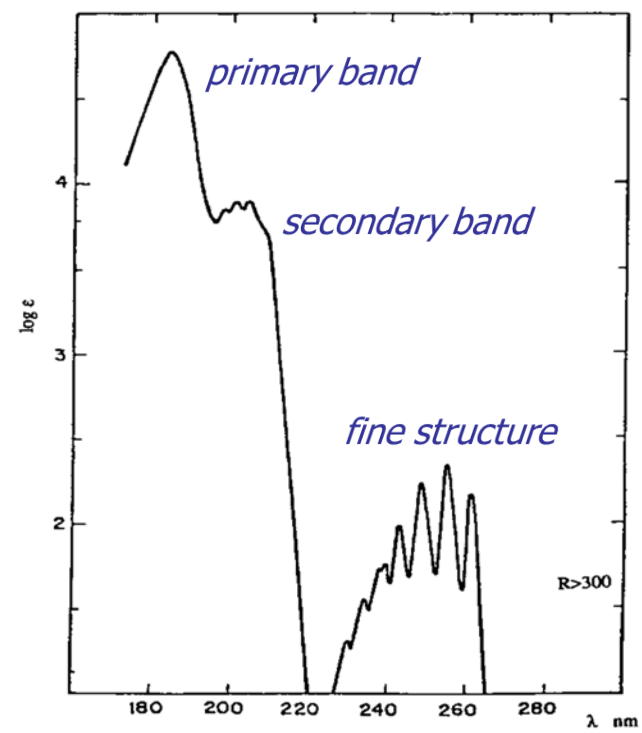
- On first inspection, benzene has six π -MOs, 3 filled π, 3 unfilled π *





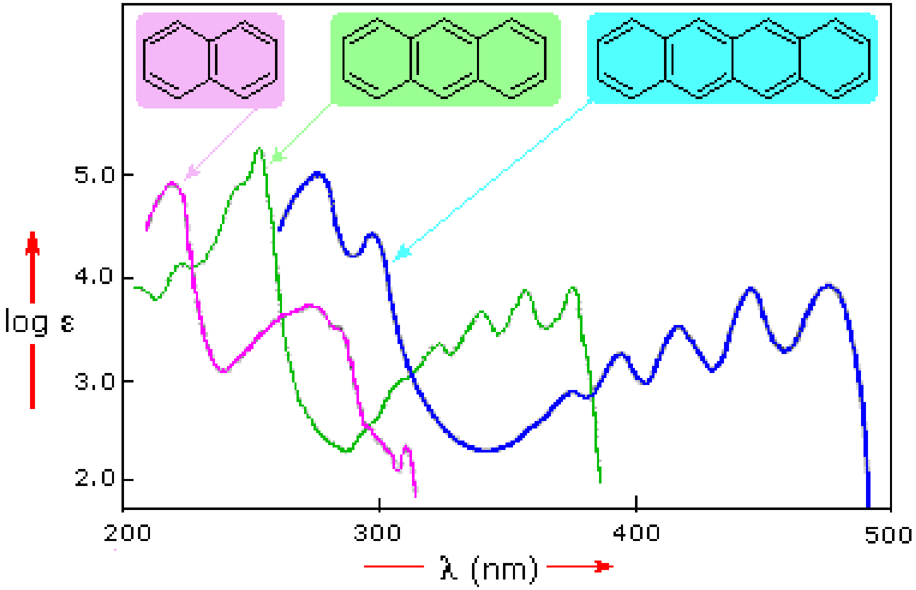


- The spectrum of Benzene has two bands at 204, 254 nm and transition i fleetingly allowed due to the disruption of symmetry by the vibrational energy states, the overlap of which is observed in what is called fine structure



- Substituent Effects
  - Polynuclear aromatics

- When the number of fused aromatic rings increases, the λ for the primary and secondary bands also increase



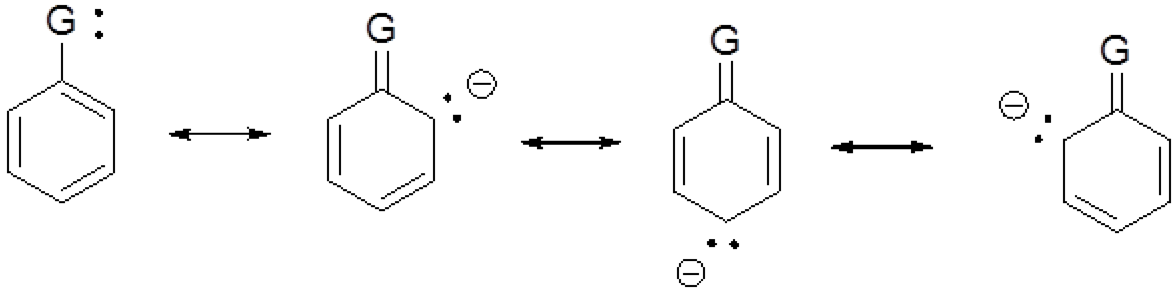
Substituent Effects

Substituents with Unshared Electrons

- If the group attached to the ring bears *n* electrons, they can induce a shift in the primary and secondary absorption bands.

- Non-bonding electrons extend the π -system through resonance – lowering the energy of transition π → π*

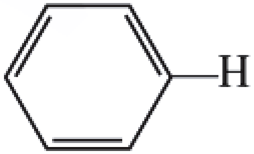
- More available n-pairs of electrons give greater shifts.



- Substituent Effects
  - Electron-donating and electron-withdrawing effects

		Primary		Secondary	
	Substituent	λ_{max}	ε	λ_{max}	ε
Electron donating	-H	203.5	7,400	254	204
	$-CH_3$	207	7,000	261	225
	-Cl	210	7,400	264	190
	-Br	210	7,900	261	192
	-OH	211	6,200	270	1,450
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron withdrawing	-CN	224	13,000	271	1,000
	C(O)OH	230	11,600	273	970
	-C(O)H	250	11,400		
	$-C(O)CH_3$	224	9,800		
	$-NO_2$	269	7,800		

- Substituent Effects
  - pH effects

	Primary		*Secondary*	
Substituent	**λ (nm)**	**ε**	**λ (nm)**	**ε**
	203.5	7,400	254	204
$-OH$	210.5	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
$-COOH$	230	11,600	273	970
$-COO^-$	224	8,700	268	560

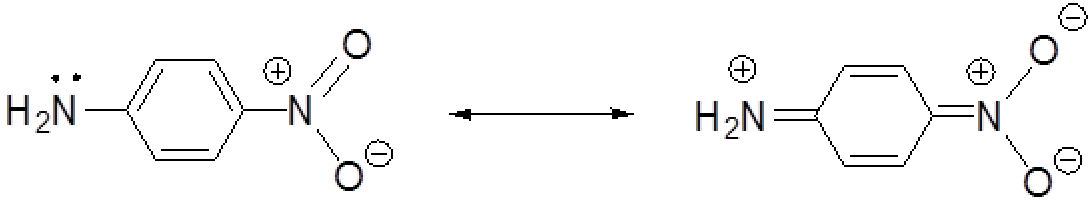
Substituent Effects

Di-substituted and multiple group effects

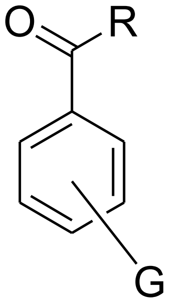
- If the two electonically dissimilar groups are ortho- or meta- to one another, the effect is usually the sum of the two individual effects (meta- no resonance; ortho-steric hind).

- If both groups are electron donating or withdrawing, the effect is similar to the effect of the stronger of the two groups as if it were a mono-substituted ring.

- If one group is electron withdrawing and one group electron donating and they are para- to one another, the magnitude of the shift is greater than the sum of both the group effects



Parent Chromophore	λ_{max}
R = alkyl or ring residue	246
R = H	250
R = OH or O-Alkyl	230



G	Substituent increment *o*	*m*	*p*
Alkyl or ring residue	3	3	10
-O-Alkyl, -OH, -O-Ring	7	7	25
$-O^-$	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHC(O)CH_3$	20	20	45
$-NHCH_3$			73
$-N(CH_3)_2$	20	20	85