Bonga university

Instrumental Analysis II (Chem.2052)

Chapter 5

Uv/visible spectroscopy

2012 E.C

5.1. Introduction

✓**For a long time, experimental work made use of the human eye as the detector to measure the hue and intensity of colors in solutions.**

✓ **However, even the best analyst can have difficulty comparing the intensity of two colors with slightly different hues, and there are of course people who are color-blind and cannot see certain colors**

✓**Thus, instruments like UV-Vis have been developed to perform these measurements more accurately and reliably than the human eye.**

✓Most of the organic compounds are transparent in the portion of electromagnetic spectrum.

✓**UV-Vis spectroscopy involves absorption of UV-Vis light by molecules but not by atoms**.

✓The transition is electronic, therefore it is electronic spectroscopy.

- ✓UV-Vis Spectroscopy (frequently called Electronic Spectroscopy), is the spectroscopy which utilizes the UV and Vis range of electromagnetic radiation.
- ✓The UV-Vis wavelength range is commonly between 190 – 800 nm.
- ✓**Table 5.1.** Ranges of the electromagnetic radiation used in electronic spectroscopy.

Radiation	λ		ν^*
	nm	A^o	cm^{-1}
VIS	400-750	4000-7500	25000-13000
near UV	200-400	2000-4000	50000-25000
Far UV(vacuum UV)	< 200	< 2000	>50000

Ranges of the electromagnetic radiation used in electronic spectroscopy

5.2. Basic Principles

✓**Absorption of radiation in the visible and uv regions of the electromagnetic spectrum results in electronic transitions between molecular orbitals**.

✓Electron is promoted from an occupied molecular orbital to unoccupied orbitals. The unoccupied orbital's are in higher energy than the occupied orbitals.

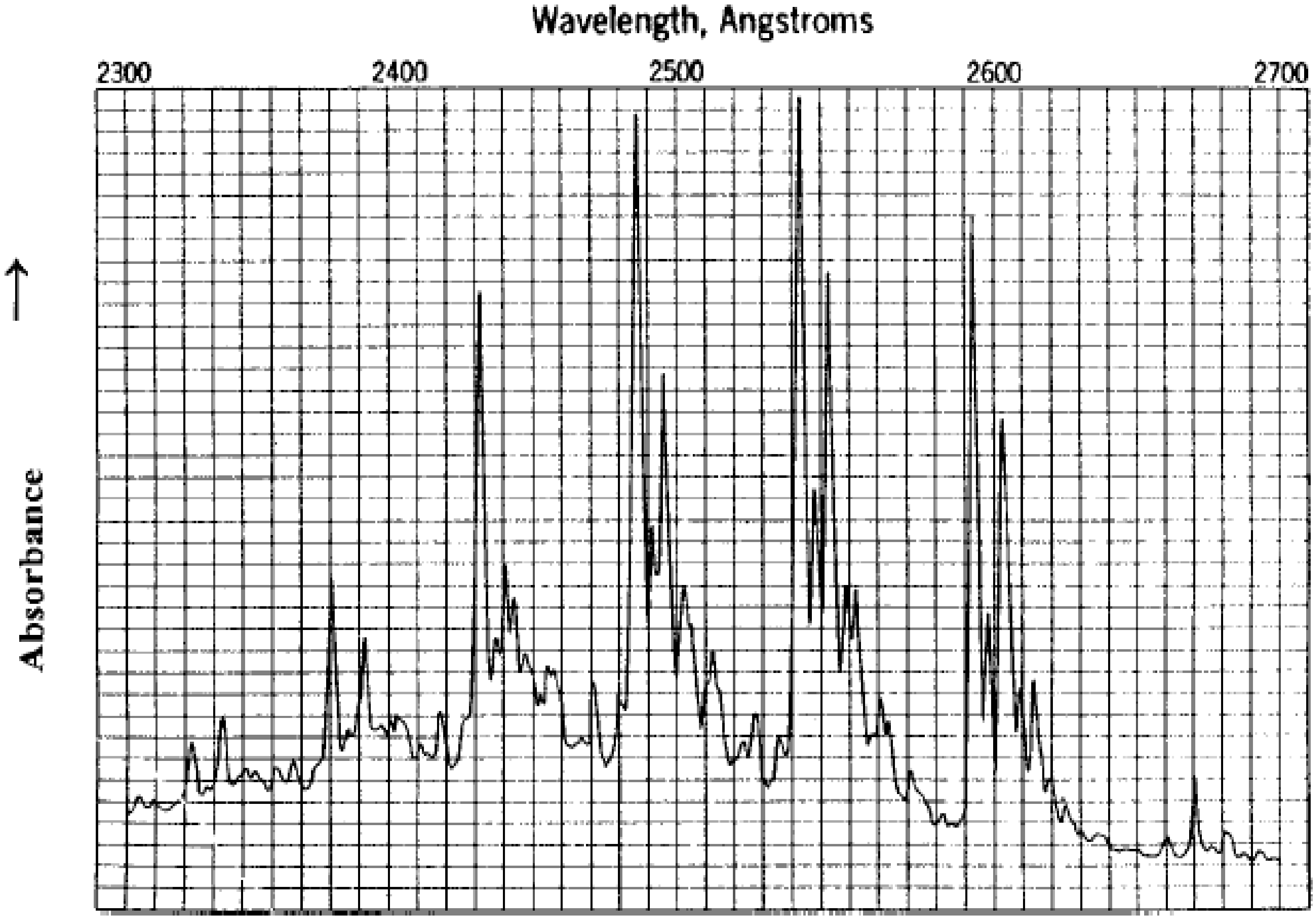
✓ During electronic transition (excitation), there are also absorption processes that cause rotational and vibrational excitations.

Cont…

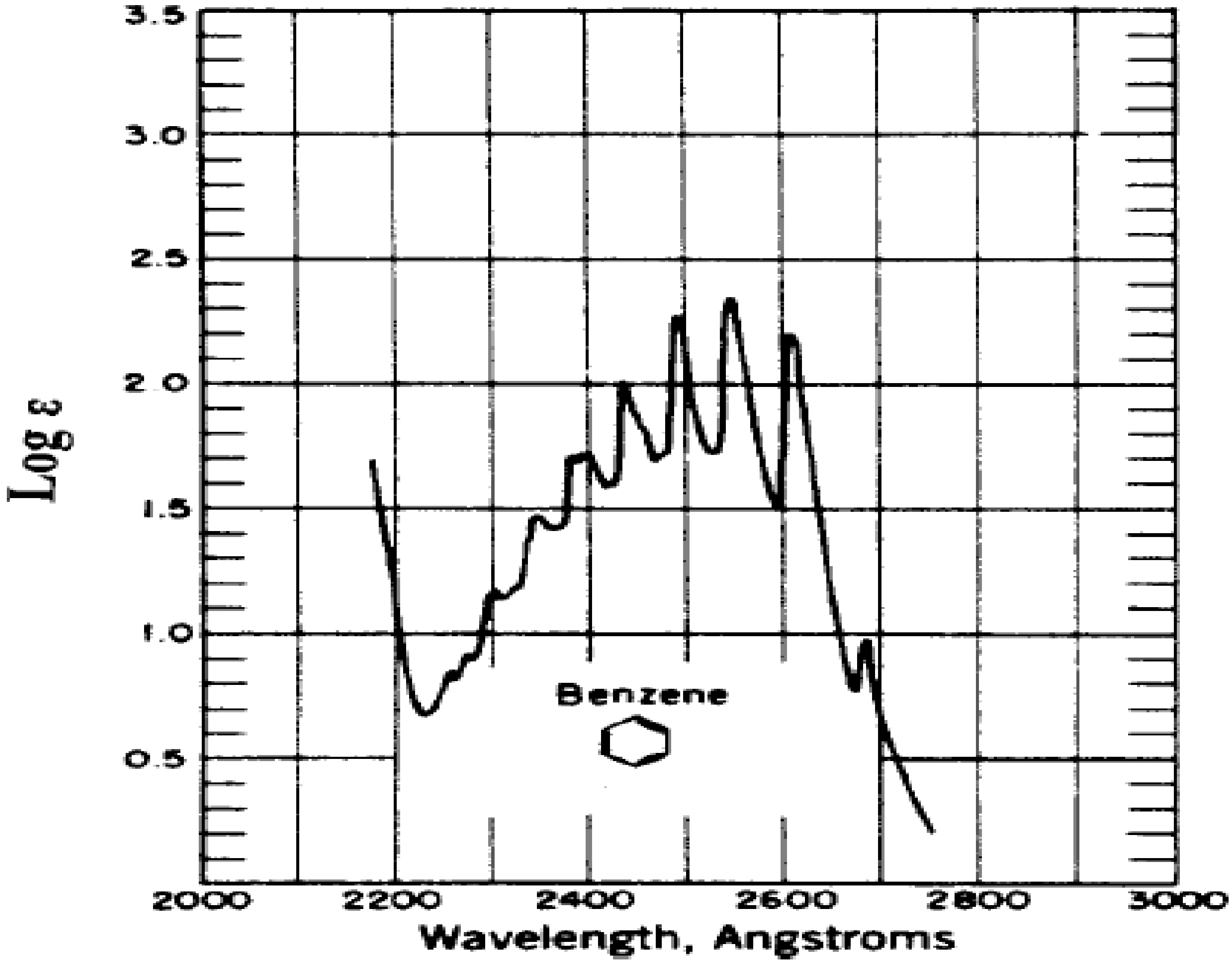
Rotational λ > Vibrational λ > Electronic λ

Energy of electronic > Energy of vibrational > Energy of rotational

- ✓Thus, the rotational and vibrational levels are superimposed on the electronic levels leading to abroad band centered near the λ of the major transitions unlike the band of AAS which is sharp.
- ✓**Example:** the absorption spectrum of benzene in solution and gas phase



samples run in gas



Samples run in solution

Cont….

- ✓**Such vibrational and rotational fine structure lines are not usually observed for samples run in solution because of physical interactions between solute and solvent molecules which cause collisional broadening of the lines.**
- ✓The resulting overlapping bands coalesce to give one or more broad band-envelopes.
- ✓Though the resolution of commercial instrumentation is not high enough to separate these lines, the fine structure due to vibrational and rotational sublevels are never observed in routine UV/VIS spectra.

Cont….

Characteristics Features of UV-Vis Absorption Spectrum

✓is usually recorded as plot of absorption versus λ or ε versus λ at which maximum absorption is observed.

✓An absorption band is characterized by its shape, that is, by its width and intensity.

✓ The shape of the band is determined primarily by the vibrational energy level spacing and the intensity of each vibrational transition.

✓The intensity distribution is related to the probability of the transition to a given vibrational sublevel.

➢The position of the peak is characterized by λ_{max}

➢The intensity of the peak is characterized by ε_{max}

5.2.2. The Magnitude of Molar Absorptivities

✓Empirically, molar absorptivities (ε values) that range from 0 up to a maximum on the order of 10^5 L mol^{-1} cm^{-1} are observed in UV-visible molecular absorption spectrometry.

✓**Commonly ε 10^4–10^5L mol^{-1} cm^{-1} for an allowed transition and is on the order of 10–100 for a forbidden transition.**

✓ **The magnitude of the absorptivity is an indication of the probability of the electronic transition.**

✓ **High values of ε give rise to strong absorption of light at the specified wavelength; low values of ε result in weak absorption of light.**

5.2.3. Types of Electronic Transition

✓Molecules are composed of atoms that are held together by sharing electrons to form chemical bonds.

✓When the molecule becomes excited, an outer shell (valence) electron moves to an orbital of higher energy.

✓**The process of moving electrons to higher energy states is called electronic excitation.**

✓ **For radiation to cause electronic excitation, it must be in the visible or UV region of the electromagnetic spectrum.**

- Generally, there are three types of electronic transitions – namely:

1. **Transition involving** $\sigma, \pi\ and\ n\ electrons$ (in most organic molecules)
2. **Transition involving d and f electrons** (most transition metal ions, lanthanide and actinide series absorb UV or visible light due to d and f electrons transition respectively) and
3. **Transition involving charge transfer electrons** (involving the transfer of an electron between two orbitals one of which is associated predominantly with the ligand and the other with the metal).

Absorbing Species σ, π *and* n *electrons* Containing

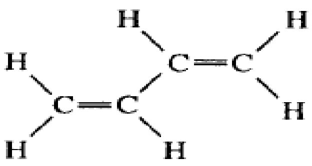
✓Three distinct types of electrons are involved in valence electron transitions in molecules.

1. The electrons involved in single bonds
2. The electrons involved in double and triple (unsaturated) bonds.
3. Electrons that are not involved in bonding between atoms

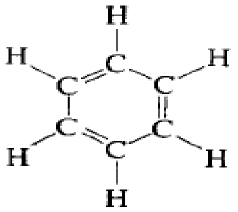
✓These are called n electrons, for nonbonding electrons. In saturated the outer shell electrons of carbon and hydrogen are all involved in bonding; hence these compounds do not have any n electrons.

✓Organic compounds containing nitrogen, oxygen, sulfur, or halogens, however, frequently contain electrons that are nonbonding (Fig. 5.7).

✓Because n electrons are usually excited by UV or visible radiation, many compounds that contain n electrons absorb UV/VIS radiation.



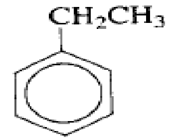
1,3-butadiene



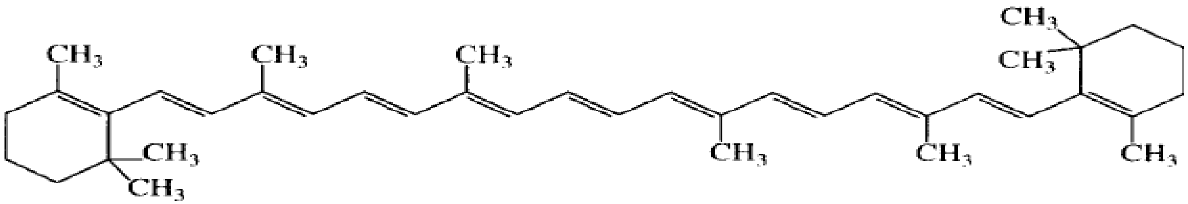
benzene

$H_3C-C\equiv C-H$

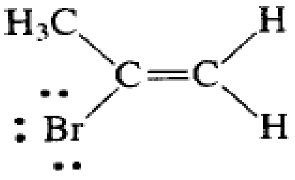
propyne



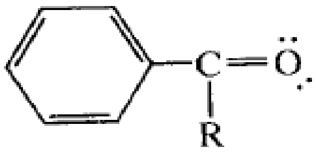
ethylbenzene

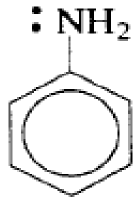


β-Carotene



2-bromopropene





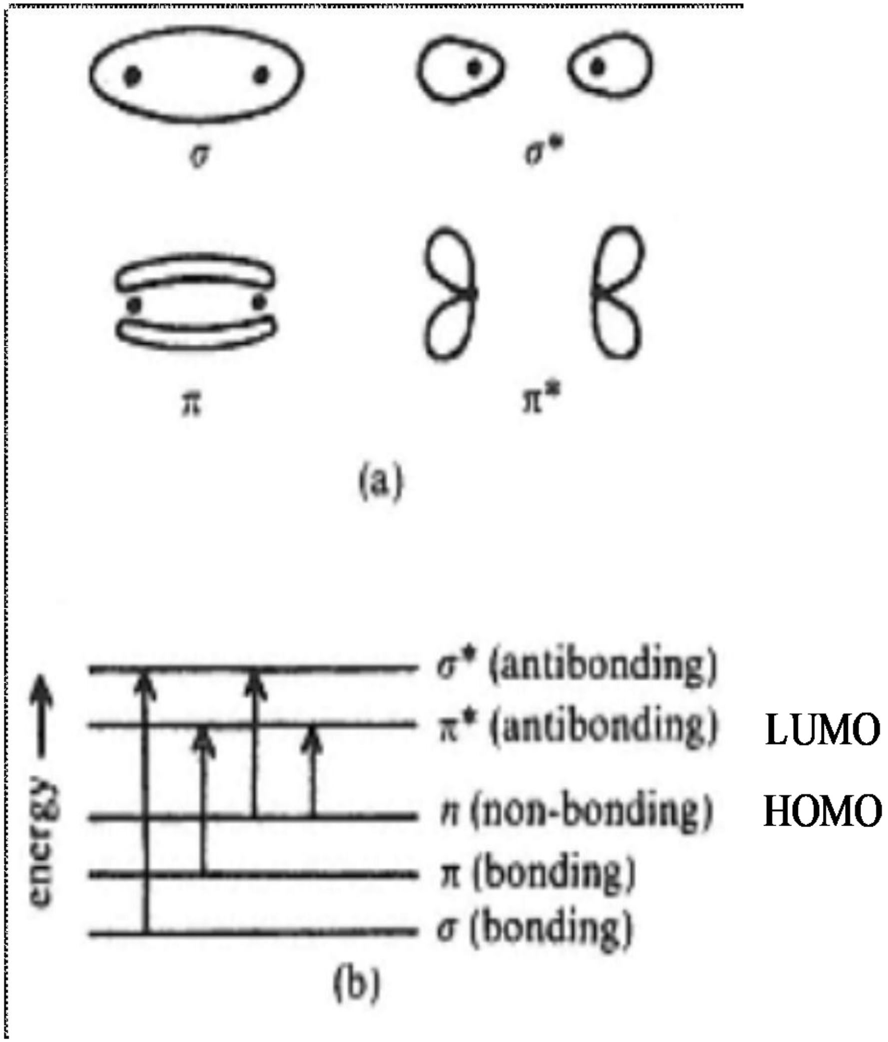
aminobenzene

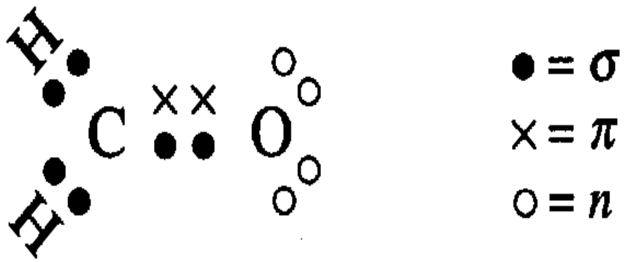
Electronic Transition of Organic Molecules

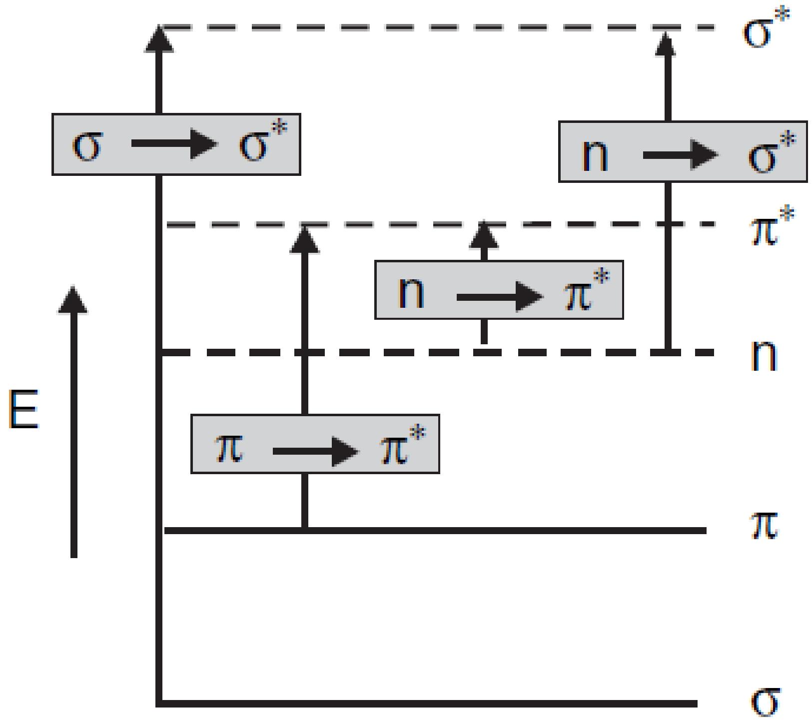
✓According to molecular orbital theory, the interaction of atomic orbitals leads to the formation of bonding and antibonding molecular orbitals.

✓Depending on the nature of the overlapping atomic orbitals, molecular orbitals may be of the σ and π (bonding) or σ * and π * (antibonding) orbitals and n (non bonding orbital).

✓The σ type electron densities are concentrated ***along*** the internuclear axis, and the type, the π electron density is concentrated on ***either side*** of the internuclear axis.

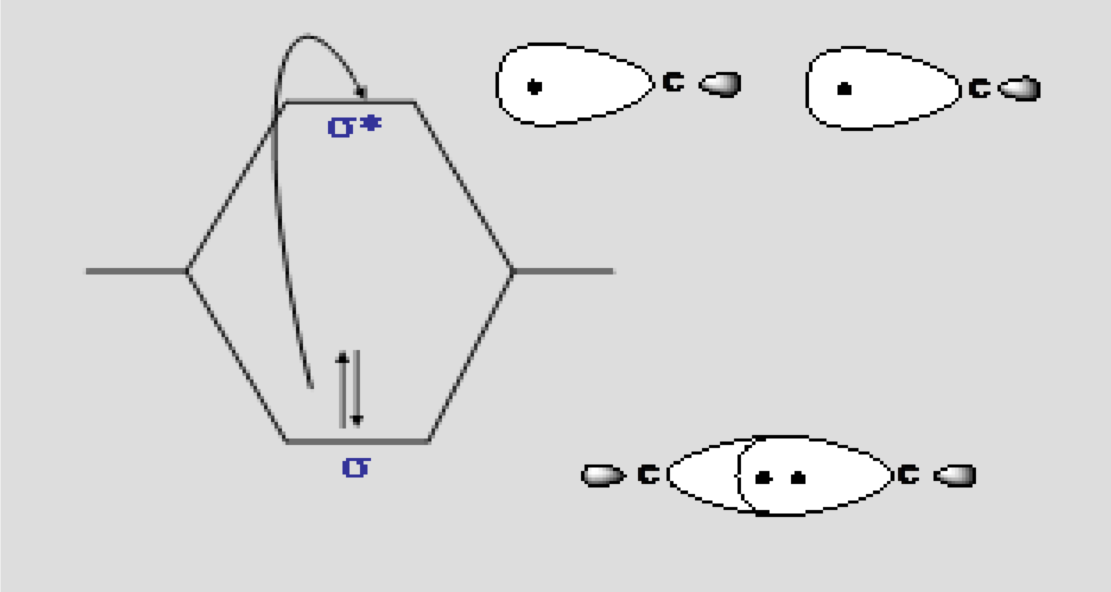

σ
σ*
π
π*
(a)
energy
σ* (antibonding)
π* (antibonding)
n (non-bonding)
π (bonding)
σ (bonding)
(b)
LUMO
HOMO


H
H
C
O
● = σ
× = π
○ = n


E
σ → σ*
n → σ*
n → π*
π → π*
σ*
π*
n
π
σ

- When molecules are electronically excited, an electron moves from the highest occupied molecular orbital (HOMO - n) to the lowest unoccupied orbital (LUMO- π*), which is usually an antibonding orbital.
- Electrons in **π** bonds are excited to antibonding **π***orbitals, and **n** electrons are excited to either σ* or π* orbitals.

i. σ →σ * transition



✓ ΔE large and occurs in vacuum UV region (λ<150 nm), ε =10 - 10,000 L/mol.cm. It is not commonly used for analytical purpose.

✓This is because the component of air like N, O, which absorbs energy, so to avoid them we need to expensive energy.

✓This is the reason for saturated hydrocarbons that only contain this type of bonding being transparent in the near UV. i.e. saturated hydrocarbons contain only single bond (they don’t contain lone pair of electrons or multiple bonds).

Example:

1.methane contains only single C-H bonds exhibits a at λ_{max} =125nm,

2.Ethane has also an absorption peak at 135 nm but here electrons of the C-C appeared to be involved. Because the strength of the C-C is less than that of the C-H bond, less energy is required for excitation: thus the absorption peak occurs at a longer wavelength.

Note: as the length of the hydrocarbon increases the λ will also increases.

ii. $n \rightarrow \sigma^*$ transition

✓Saturated compound containing atoms with unshared electron pairs (nonbonding) are capable of $n \rightarrow \sigma^*$ transition

✓In general these transition requires less energy than the $\sigma \rightarrow \sigma^*$ transition.

✓They can brought about by radiation in the region between 150 and 250 nm, with most absorption peaks below 200 nm (leads to moderate intensity located around 180 nm for alcohol, near. 190nm for ethers or halogen derivatives and in the region of 220nm for amines.

Examples:

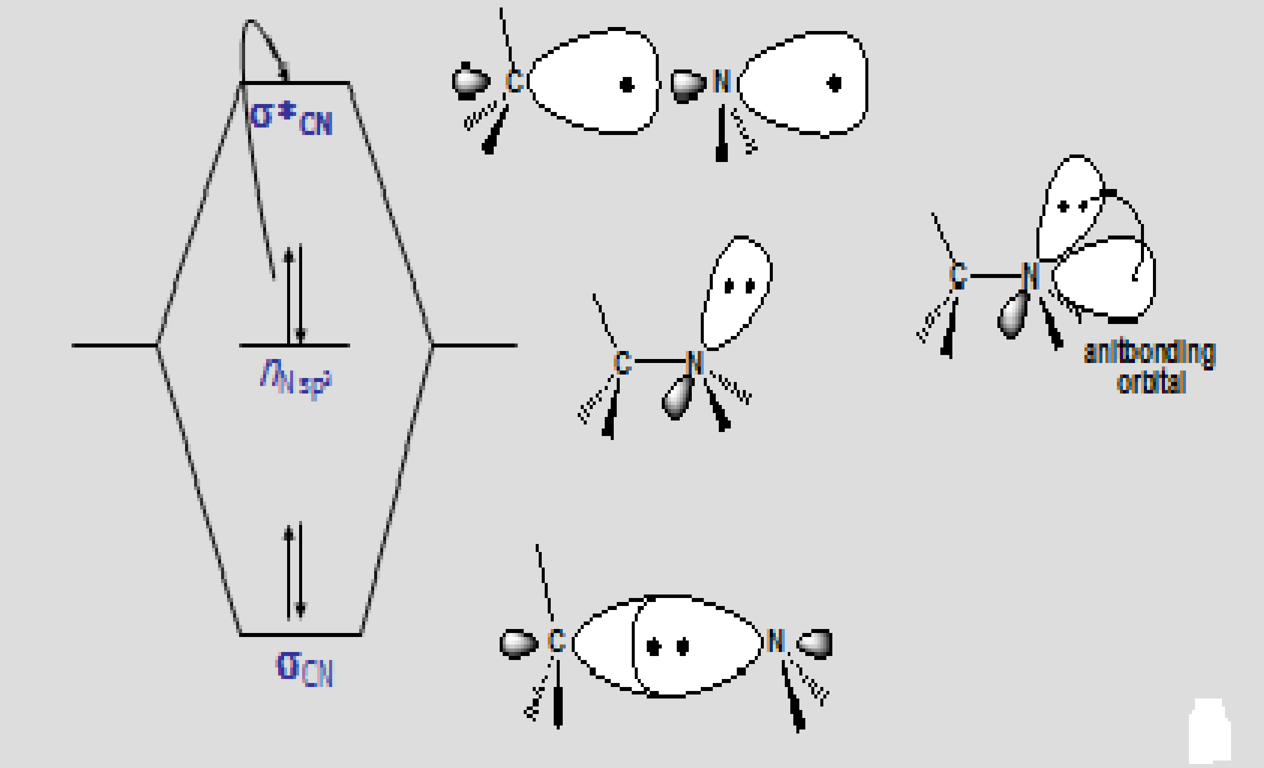
1.methanol: λ_{max} = 183nm (ε = 50) ether: λ_{max} = 190nm (ε = 2000) ethylamine: λ_{max} =210nm (ε =800); 1-chlorobutane: λ_{max} =179nm.

✓Transition depends on the electron negativity of hetroatoms and the nature of the solvents.

✓Examples: 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 than 200 nm

Example: Absorption due to **$n \rightarrow \sigma$ * transition**

Compound	λ_{max}	ε_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S$	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900



✓The molar absorptivity associated with these type of transition are low to intermediate in magnitude and usually ranges between **100** and $\mathbf{300\ L\ mol^{-1}.cm^{-1}}$

iii. $n \rightarrow \pi^*$ transition

✓This transition of low intensity results from the passage of an **n** electron (engaged in a non-bonding MO) to an anti-bonding π^* orbital.

✓This transition is usually observed in molecules containing a *hetero atom carrying lone electron pairs as part of an unsaturated system.*

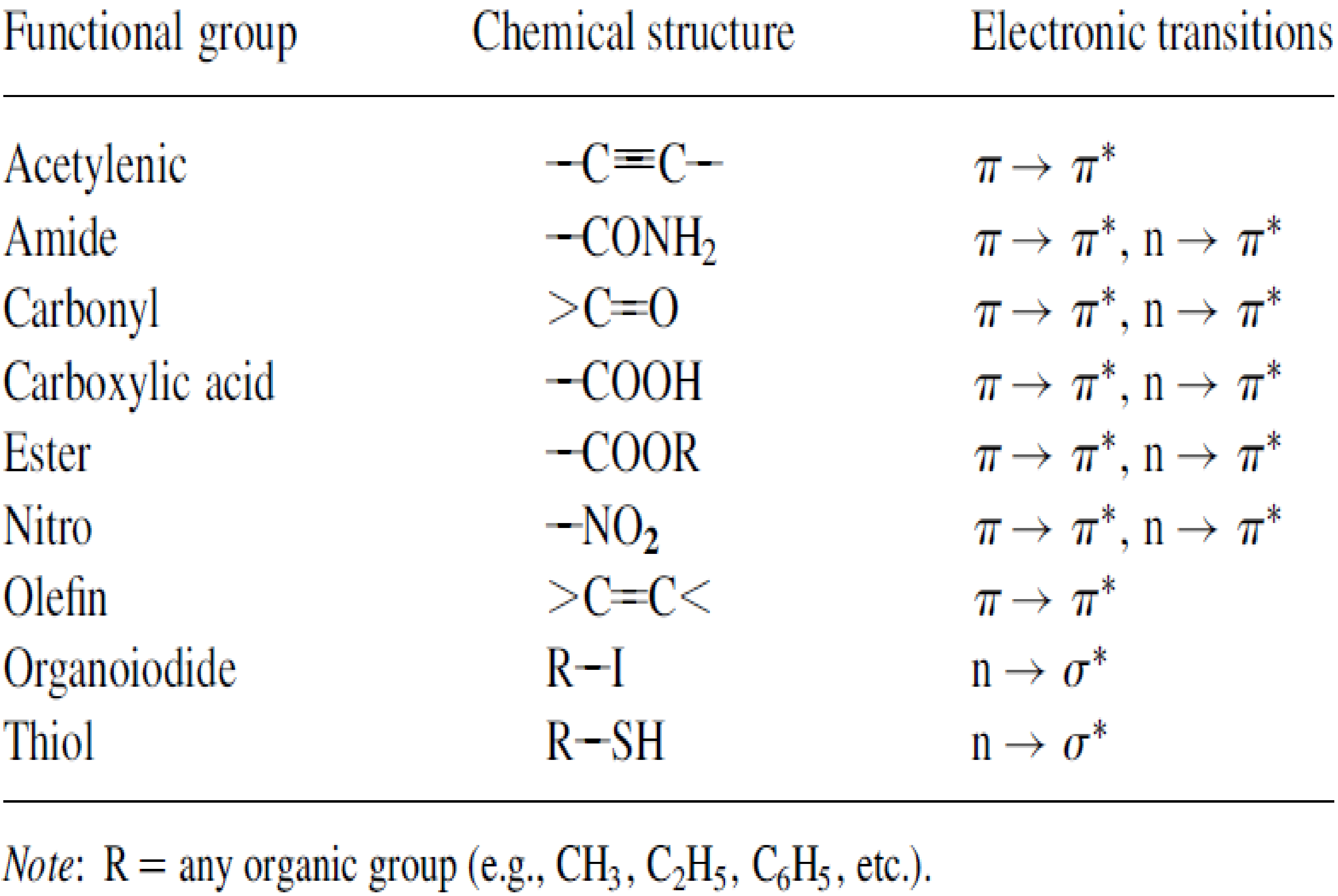
✓The best known is that corresponding to the carbonyl band, easily observed at around 270 to 295 nm. The molar absorption coefficient for this band is weak.

Example: ethanal: λ = 293nm (ε=12, with ethanol as solvent).

- ✓Organic molecules that contain atoms with non bonded electrons should be able to absorb UV/VIS radiation.
- ✓Such atoms include **nitrogen, oxygen, sulfur, and the halogen** atoms, especially Br and I. Table 5.2 presents some typical organic functional groups that serve as chromophores.

Table 5.2. Organic Functional Groups that can Absorb UV/VIS Radiation

Table 5.2



Functional group	Chemical structure	Electronic transitions
Acetylenic	$-C\equiv C-$	$\pi \rightarrow \pi^*$
Amide	$-CONH_2$	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
Carbonyl	$>C=O$	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
Carboxylic acid	$-COOH$	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
Ester	$-COOR$	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
Nitro	$-NO_2$	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
Olefin	$>C=C<$	$\pi \rightarrow \pi^*$
Organoiodide	$R-I$	$n \rightarrow \sigma^*$
Thiol	$R-SH$	$n \rightarrow \sigma^*$

Note: R = any organic group (e.g., CH_3, C_2H_5, C_6H_5, etc.).

✓The molar absorptivity for peaks associated to the **n**,π * state are generally low and ordinarily ranges from ***10 to 100 L mol^{-1}.cm^{-1}***

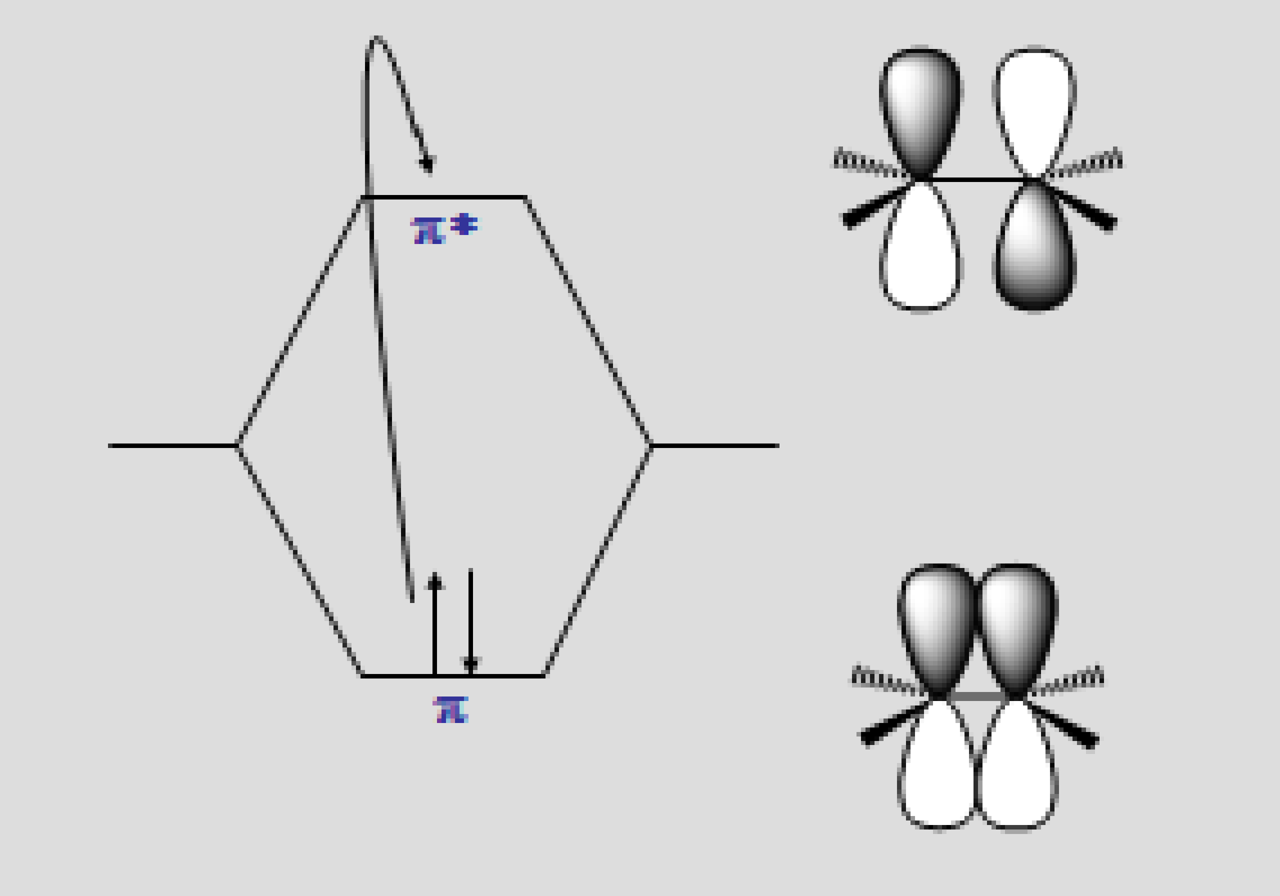
✓Peaks associated with **n$\rightarrow\pi$ * transitions** are generally shifted to shorter λ (a blue shift with increasing polarity of the solvent.

iv. $\pi\rightarrow\pi$* transition

➢This transition to occur, a molecule must possess a chromophore with an ***unsaturated bond***, such as

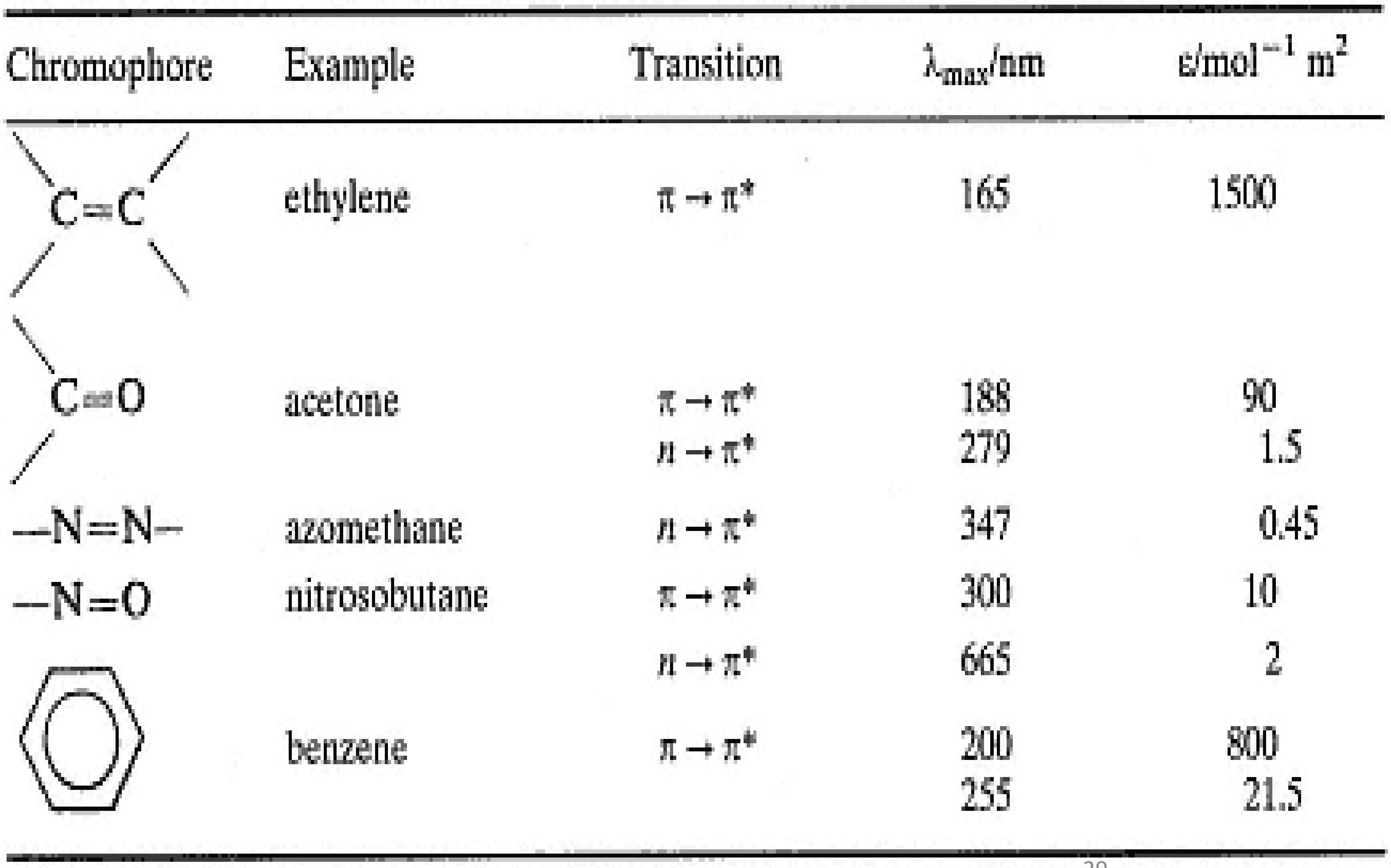
C=C, C≡C, C=O, C=N, N=O,N=N and so on.

Compounds with these types of chromophores include alkenes, amides, ketones, carboxylic acids, and oximes, among others.



- ✓Exhibited by compounds containing multiple bonds like ***alkene, alkyne*** etc.
- ✓Is affected by conjugation, as conjugation increases the wavelength also increases.
- ✓Values of **ε** for **π→ π* transition** fall in the range between **1000** *and* **10,000** ***L*** ***mol***$^{-1}$***.cm***$^{-1}$
- ✓Usually but not always, a red shift is observed for **π→ π* transition** with increasing polarity of the solvent.

Table 5.3 lists types of organic compounds and the wavelengths of their absorption maximum,



Chromophore	Example	Transition	λ_{max}/nm	ε/mol^{-1} m^2
C=C	ethylene	π → π*	165	1500
C=O	acetone	π → π*	188	90
		n → π*	279	1.5
—N=N—	azomethane	n → π*	347	0.45
—N=O	nitrosobutane	π → π*	300	10
		n → π*	665	2
	benzene	π → π*	200	800
			255	21.5

- ✓ In most organic compounds the bonding and non-bonding orbitals are filled and the antibonding orbitals are vacant.
- ✓ The lowest energy and therefore the longest wavelength transitions are from non-bonding orbitals to antibonding π orbitals, i.e. $n \rightarrow \pi^*$. These give rise to bands in the near UV and visible regions.
- ✓ Other allowed transitions in order of increasing energy (shorter wavelength) are $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, which have comparable energies, and $\sigma \rightarrow \sigma^*$. The latter occur in the far UV or vacuum region below 200 nm and are of little use analytically.

✓Of these transitions, the most important are the n→π* and π→π*, because they involve functional groups that are characteristic of the analyte and wavelengths that are easily accessible.

5.3. Absorption characteristics of some chromopores

Definition of some terms:

Chromophore:

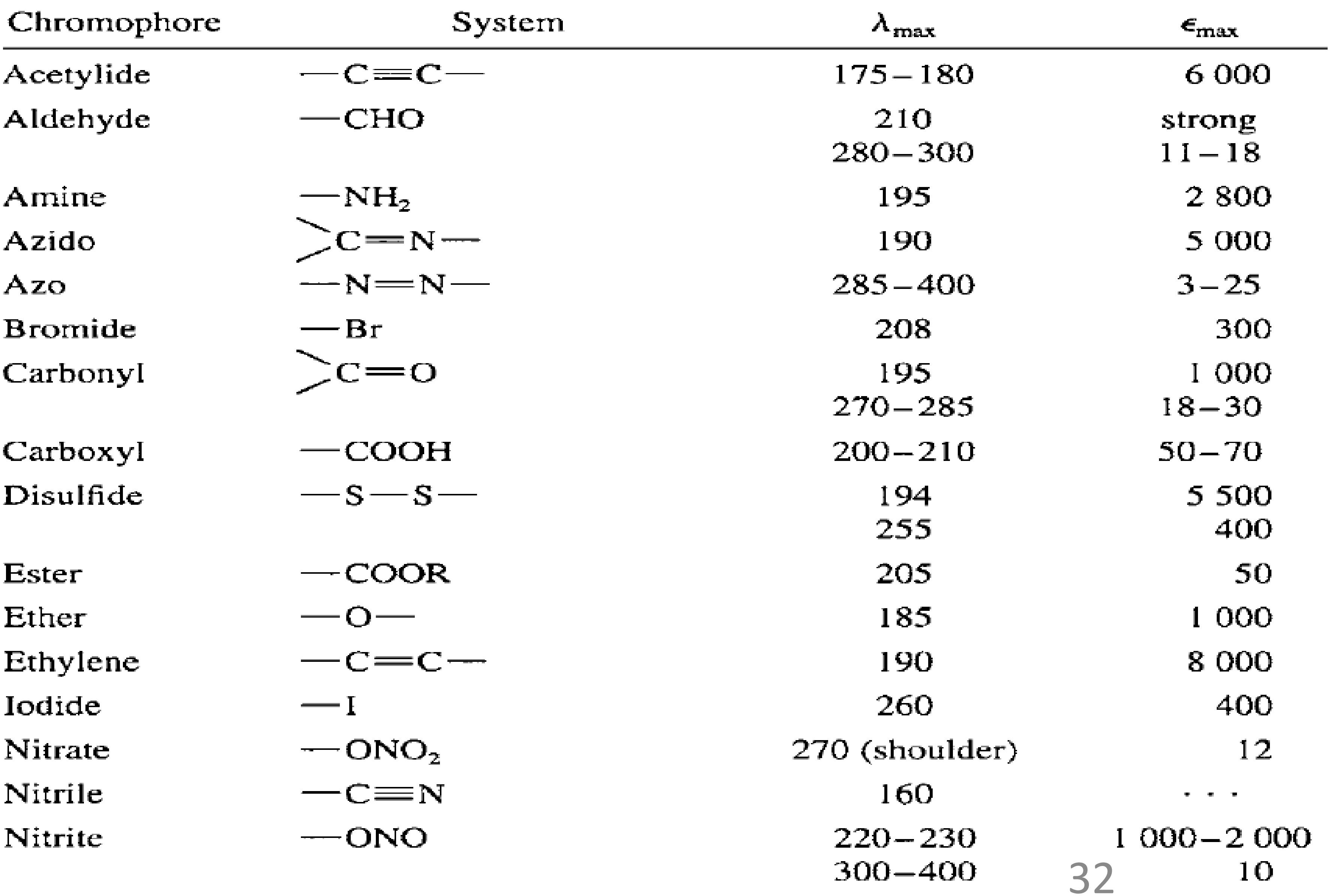
✓is a group of atoms (part of a molecule) that gives rise to an electronic absorption.

✓an identifiable part of a molecule responsible for any spectral features arising from electronic transition.

✓are may be functional groups (like double bond, hydroxyl group, carbonyl...) or single atom within molecule or group (like methyl).

✓The detection of chromphore permits to deduce presence of structural element or fragment in the molecule from which the molecular structure may be built up.

The λ_{max} and ε values for some typical chromophores are given in tables following



Chromophore	System	λ_{max}	ϵ_{max}
Acetylide	$-C\equiv C-$	175–180	6 000
Aldehyde	$-CHO$	210 280–300	strong 11–18
Amine	$-NH_2$	195	2 800
Azido	$>C=N-$	190	5 000
Azo	$-N=N-$	285–400	3–25
Bromide	$-Br$	208	300
Carbonyl	$>C=O$	195 270–285	1 000 18–30
Carboxyl	$-COOH$	200–210	50–70
Disulfide	$-S-S-$	194 255	5 500 400
Ester	$-COOR$	205	50
Ether	$-O-$	185	1 000
Ethylene	$-C=C-$	190	8 000
Iodide	$-I$	260	400
Nitrate	$-ONO_2$	270 (shoulder)	12
Nitrile	$-C\equiv N$	160	· · ·
Nitrite	$-ONO$	220–230 300–400	1 000–2 000 10

Nitro	$-NO_2$	210	strong
Nitroso	$-NO$	302	100
Oxime	$-NOH$	190	5 000
Sulfone	$-SO_2-$	180	. . .
Sulfoxide	$>S=O$	210	1 500
Thiocarbonyl	$>C=S$	205	strong
Thioether	$-S-$	194	4 600
		215	1 600
Thiol	$-SH$	195	1 400
	$-(C=C)_2-$ (acyclic)	210–230	21 000
	$-(C=C)_3-$	260	35 000
	$-(C=C)_4-$	300	52 000
	$-(C=C)_5-$	330	118 000
	$-(C=C)_2-$ (alicyclic)	230–260	3 000–8 000
	$C=C-C\equiv C$	219	6 500
	$C=C-C=N$	220	23 000
	$C=C-C=O$	210–250	10 000–20 000
		300–350	weak
	$C=C-NO_2$	229	9 500
Benzene		184	46 700
		204	6 900
		255	170
Diphenyl		246	20 000
Naphthalene		222	112 000
		275	5 600
		312	175
Anthracene		252	199 000

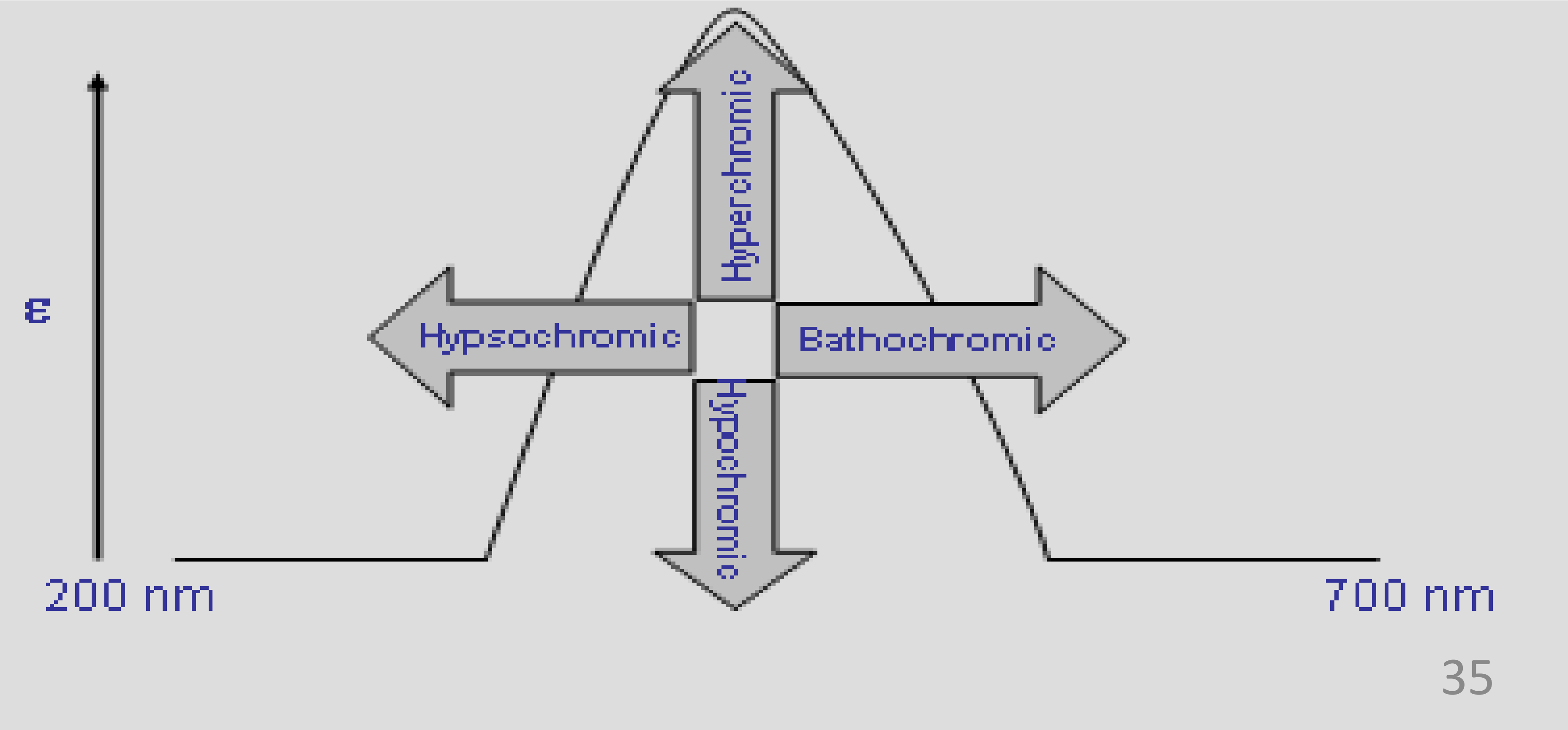
Cont…

Auxochrome (Auxilary chromophores):

- ✓is a substituent that contains unshared (nonbonding) electron pairs, such as OH, NH, and halogens.
- ✓Are groups with very little UV/Vis absorption by themselves, but which often have significant effects on the absorption (both λ_{max} and ε) of chromophore to which they are attached.
- ✓Generally, groups containing heteroatoms with one or more lone pairs like –OH, –Cl, –OR and $–NR_2$, -halogens are auxochromes.

- In general, substituents may have any of four effects on a chromophore:

1. Bathochromic shift (red shift) – a shift to longer λ; lower energy
2. Hypsochromic shift (blue shift) – shift to shorter λ higher energy
3. Hyperchromic effect – an increase in intensity(ε)
4. Hypochromic effect – a decrease in intensity(ε)



Factors affecting the position intensity of the absorption band

✓The positions and intensities of the absorption bands are sensitive to:

1. **substituents close to the chromophore,**
2. **conjugation with other chromophores, and**
3. **Solvent effects**.

1.Effect of Auxochrome (substituents close to the chromophore)

✓In general, auxochromic substitution of chromophores causes bathochromic shifts and increases in intensity for $\pi \rightarrow \pi^*$ transitions, and hypsochromic or blue shifts (to shorter wavelengths) for $n \rightarrow \pi^*$ transitions.

Cont….

- ✓The shifts are explainable in terms of mesomeric (resonance) effects caused by interaction of lone pair electrons associated with such auxochromes as —OH, —Cl, —NH_2 with the π system of the chromophore.
- ✓This leads to increases in the energies of π and π* orbitals, the π being raised by more than the π*, but leaves the energy of the non-bonding orbital unchanged.

Auxochrome

Auxochrome : Substitutent groups which are not themselves optically active in this energy range, but which do interact with other chromophores to **shift both intensity and wavelength**. Associated with redistribution of internal electronic configurations and charge densities

Absorption Characteristics of Pyridine Derivatives

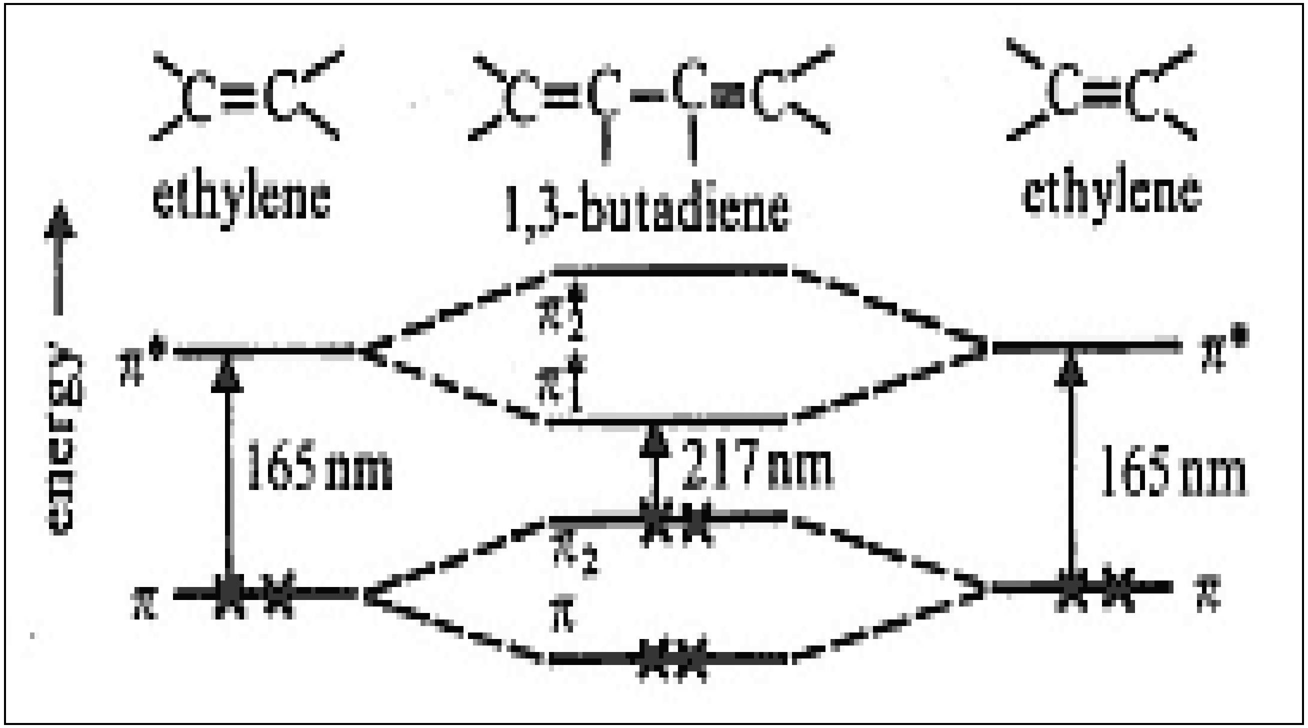
Derivative	λ_{max}	ε_{max}
Pyridine	257	2750
2-CH_3	262	3560
3-CH_3	263	3110
4-CH_3	255	2100
2-F	257	3350
2-Cl	263	3650
2-I	272	400
2-OH	230	10000

2. Conjugation Effects

✓Increase in the amount of conjugated double bonds always significantly shift absorption maxima towards longer wavelength (bathochromic) and usually towards stronger intensity relative to an isolated chromophore.

✓**The shift can be explained in terms of interaction or delocalization of the π and π* orbitals of each chromophore to produce new orbitals in which the highest π orbital and the lowest π* orbital are closer in energy.**

✓**Figure 5.9.** shows the conjugation of two ethylene chromophores to form 1,3-butadiene. The $\pi \rightarrow \pi^*$ transition in ethylene occurs at 165 nm with an ε_{max} value of 1500 whereas in 1,3-butadiene the values are 217 nm and 2100 respectively.



- Red shift of λ_{max} with increasing **conjugation**
  - CH_2=$CHCH_2CH_2CH$=CH_2 λ_{max} = 185 nm
  - CH_2=$CHCH$=CH_2 λmax = 217 nm
  - CH_2=CH-CH=CH-CH=CH_2 (trans) λmax = 263 nm
- Red shift of λmax with **number of rings**
  - Benzene λ_{max} = 204 nm
  - Naphthalene λ_{max} = 286 nm

- ✓ If two unlike chromophores are conjugated and one group has nonbonding electrons, the $n \rightarrow \pi^*$ transition is also shifted bathochromically because the energy of the antibonding orbital is lowered.
- ✓ Thus the weak $n \rightarrow \pi^*$ band in a saturated carbonyl compound is shifted from below 300 nm to above 300 nm with an increase in ε.
- ✓ Conjugation of additional chromophoric groups moves λ_{max} progressively towards the visible region and increases ε.

For example:

- ➢ tetradecahexaene (six double bonds) absorbs at the blue end of the visible region and appears yellow whilst with further conjugation, as in the carotenes (ten or more double bonds), the compound may appear orange, red, purple, or even black.

- ✓The presence of an auxochrome that extends the double bond causes a red shift.

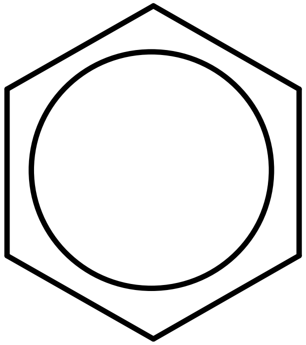
  Example: $H_2C=O$ and $CH_2=CH-CH=O$

  λmax < λmax

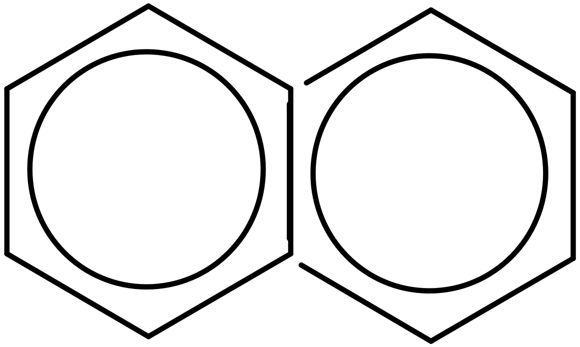
- ✓They have the same functional group why the difference? This is because of conjugation, the larger the conjugation, the larger the λ

Absorption by aromatic compounds

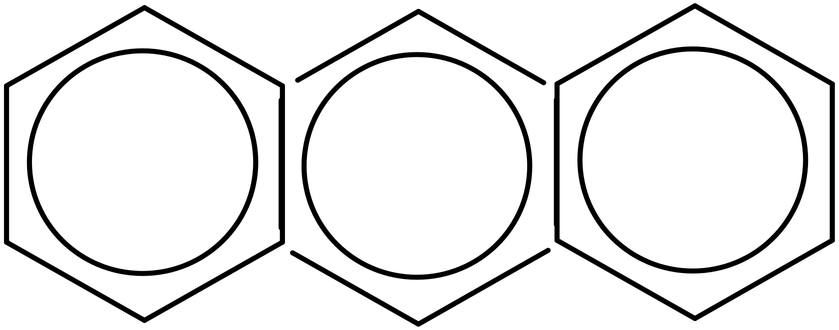
- ❖Absorption of aromatic hydrocarbons are characterized by three sets of bands. Benzene can be regarded as a special case of a conjugated triene. It shows $\lambda \pi \rightarrow \pi^*$ *at* 184, 204 and 254 nm.
- ❖The last one is said to the normal absorption band, which shifts bathochromically and intensifies on chromophoric substitution.
- ❖ Of more importance is that substitution produces a new and intense band between 200 and 300 nm which arises from a $\pi \rightarrow \pi^*$ transition in the extended conjugated system.



254 nm



275 nm



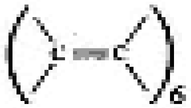
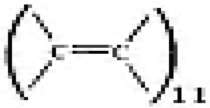
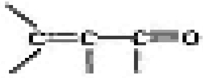
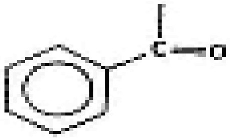
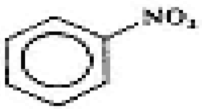
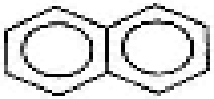
280 nm

- ✓ As the number of the ring increases, the absorption λ also increases why? This is b/c of conjugation.

Example: Substituent effect on benezene absorption maximum

Substituent of benzene	λ_{max}	ε	logε	Substituent of benzene	λ_{max}	ε	logε
none	204 256	7900 200	3.9 2.3	$-NH_2$	230 281	8000 160	3.9 3.2
$-CH_3$	208 261	8000 300	3.9 2.5	-OH	211 270	6300 1500	3.8 3.2
-Cl	216 265	8000 1500	3.9 2.4	$-NO_2$	251 280 330	9000 1000 130	4.0 3.0 2.1
$-OCH_3$	220 272	8000 1500	3.9 3.2	$-CH=CH_2$	244 282	12000 1600	4.1 3.2

Table 5.5. Absorption characteristics of some conjugated chromophores and chromophorically substituted benzenes

Chromophore	Example	Transition	λ_{max}/nm	ε/mol^{-1} m^2
	butadiene	$\pi \rightarrow \pi^*$	217	2100
	tetradecahexaene	$\pi \rightarrow \pi^*$	360	6300
	γ-carotene	$\pi \rightarrow \pi^*$	460	6500
	crotonaldehyde	$\pi \rightarrow \pi^*$	217	1600
		$n \rightarrow \pi^*$	321	2
	acetophenone	$\pi \rightarrow \pi^*$	240	1300
			278	110
		$n \rightarrow \pi^*$	320	5
	nitrobenzene	$\pi \rightarrow \pi^*$	252	1000
			280	100
		$n \rightarrow \pi^*$	333	13
	naphthalene	$\pi \rightarrow \pi^*$	221	10 000
			286	930
			312	28

3. Solvent Effects

✓Solvent polarity changes λ_{max} since polarity changes with the movement of electron from one orbital to another.

✓**Absorption bands arising from $n \rightarrow \pi^*$ transitions suffer hypsochromic shifts on increasing the solvent polarity, whilst those of $\pi \rightarrow \pi^*$ transitions are shifted bathochromically. i.e.**

✓**Polar solvents cause a blue shift (lower λ) due to salvation of the nonbonding electrons lowering the n orbitals But they cause a red shift for stabilizing the π^* orbitals than do the π (polar solvents will stabilize both π and π *but it stabilizes* π^* stronger than π). On the other hand, the reverse is true if the solvent is non polar.**

Explanations:

➢ **The energy of the non-bonding orbital is lowered by hydrogen bonding in the more polar solvent thus increasing the energy of the n to π^* transition, but the energy of the π^* orbital is decreased relative to the π orbital.**

✓Solvent can also induces significant changes in the intensity of peaks.

Hyperchromic – Increase in absorption peak

Hypochromic – Decrease in absorption peak

Example:

1.For acetone, *n to π** transition occurs at 279 nm in n-hexane, 270 nm in ethanol and at 265 nm in water

2. Absorption characterstics of 2 – methylpyridine

Solvent	$\lambda_{\mathbf{max}}$	$\varepsilon_{\mathbf{max}}$
Hexane	260	2000
Chloroform	263	4500
Ethanol	260	4000
Water	260	4000
Ethanol – HCl (1:1)	262	5200

Woodward's Rules or the Woodward–Fieser Rules

- ✓The rule is governed by additive effect of auxochrome substituent.
- ✓The incremental contribution of substituents is added to this base value from the group tables:

Table 5.6 Empirical Rules for Calculating the Absorption

Maxima of conjugated dienes	nm
Absorption of parent diene system C=C−C=C	217
Shift to longer λ	
Double bond extension to diene system	30
Diene system within a ring	36
Exocyclic nature of double bond in conjugated system	5
Each alkyl substituent or ring residue	5
Auxochrome is	
O-acyl	0
O-alkyl	6
S-alkyl	30
N-alkyl$_2$	60
Cl, Br	5

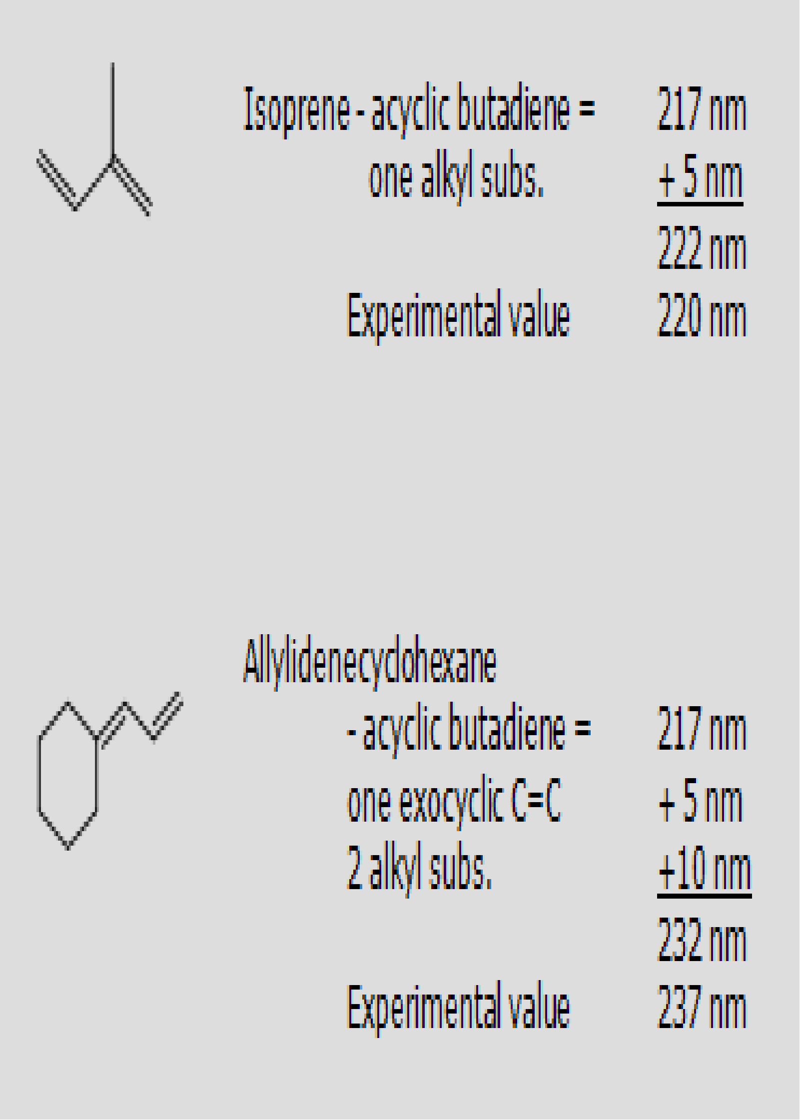
Diens

Homonuclear
(the dien is within
the ring known as Cisoid)

Hetronuclear - This type of Diens can be
Cyclic type or Acyclic type

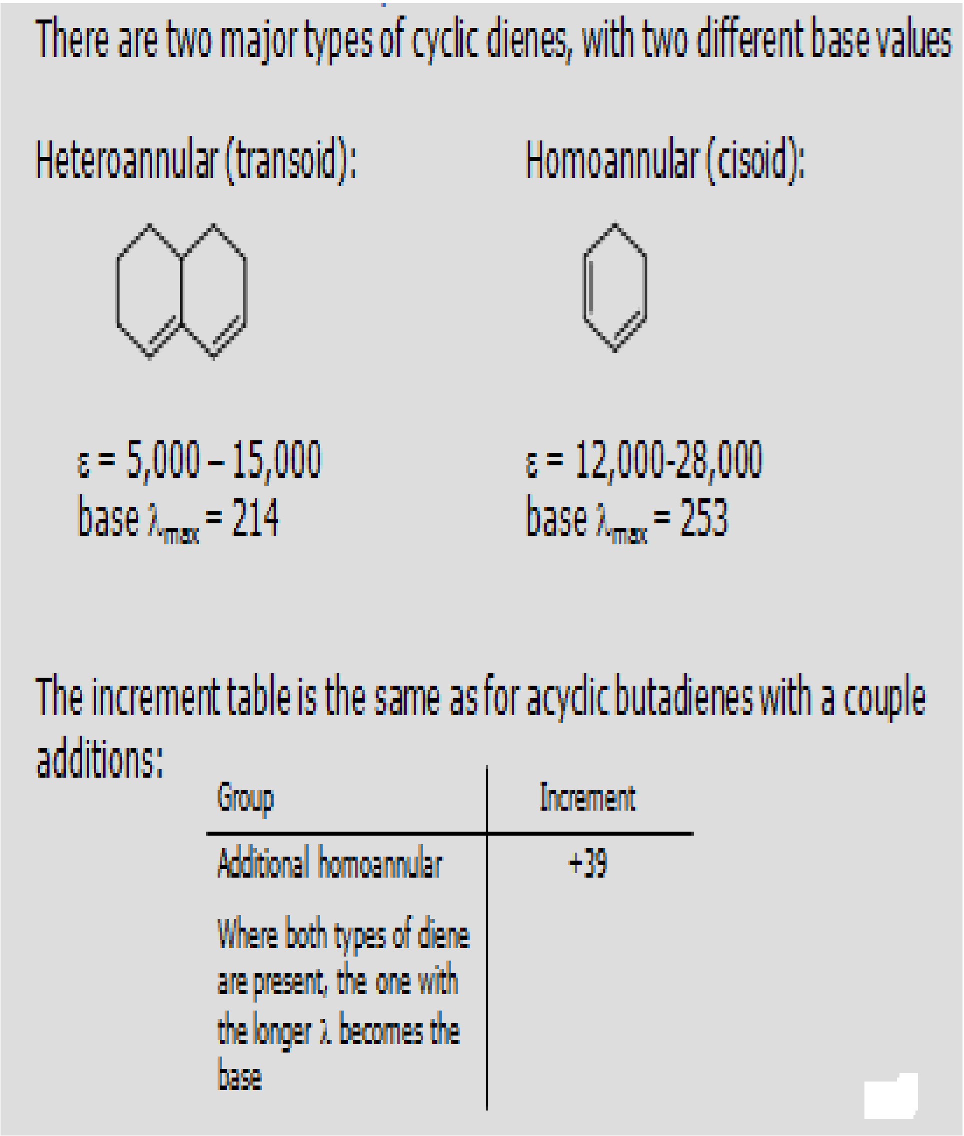
	Homonuclear	Hetronuclear
The parent absorption	$\lambda = 253$ nm	$\lambda = 214$ nm Cyclic $\lambda = 217$ nm Acyclic

Examples



Isoprene - acyclic butadiene = 217 nm
one alkyl subs. + 5 nm
222 nm
Experimental value 220 nm

Allylidenecyclohexane
- acyclic butadiene = 217 nm
one exocyclic C=C + 5 nm
2 alkyl subs. +10 nm
232 nm
Experimental value 237 nm



There are two major types of cyclic dienes, with two different base values

Heteroannular (transoid):
ε = 5,000 – 15,000
base λ_{max} = 214

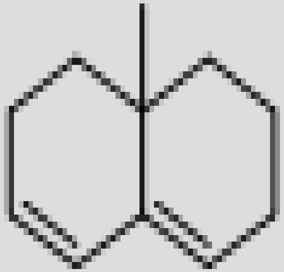
Homoannular (cisoid):
ε = 12,000-28,000
base λ_{max} = 253

The increment table is the same as for acyclic butadienes with a couple additions:

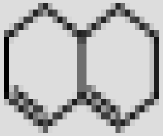
Group	Increment
Additional homoannular	+39
Where both types of diene are present, the one with the longer λ becomes the base	

Woodward-Fieser Rules – Cyclic Dienes

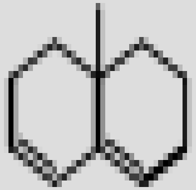
For example:



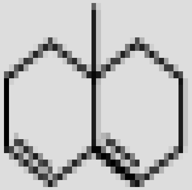
1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene



heteroannular diene = 214 nm



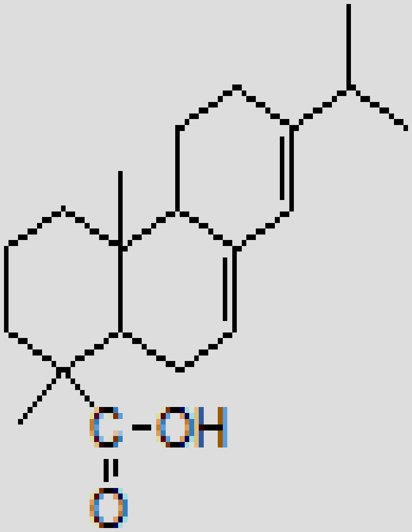
3 alkyl subs. (3 x 5) +15 nm



1 exo C=C + 5 nm

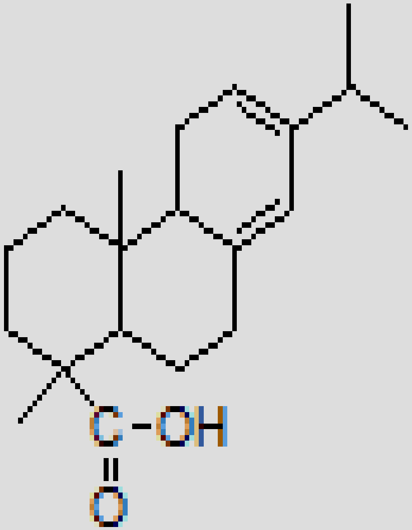
234 nm

Experimental value 235 nm



heteroannular diene =	214 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	<u>+ 5 nm</u>

239 nm



homoannular diene =	253 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	<u>+ 5 nm</u>

278 nm

INSTRUMENTATION FOR UV-VISILE SPECTROSCOPY

✓Spectrometric instruments have a common set of general features. Often, one technique is distinguished from another by differences in these features. Here we look at specific features for the UV/Visible experiment.

1.**Sources:** D2 lamp, W filament (halogen lamp), and Xe arc lamp.

2.**Wavelength Selectors**: Filters and Monochromators.

3.**Sample Containers**: Fused silica, quartz, and glass.

4.**Detectors**: Phototube, PMT, photodiode, photodiode array, CCD array

Application

- ❑ Have Both qualitative and quantitative analysis.

✓Used In analytical chemistry for the quantitative determination of different analytes, such highly conjugated organic compounds, and biological macromolecules.

✓Identification is done by comparing the absorption spectrum with the spectra of known compounds.

✓UV absorption spectroscopy is generally used for characterizing aromatic compounds and aromatic olefins etc.

THANK YOU!