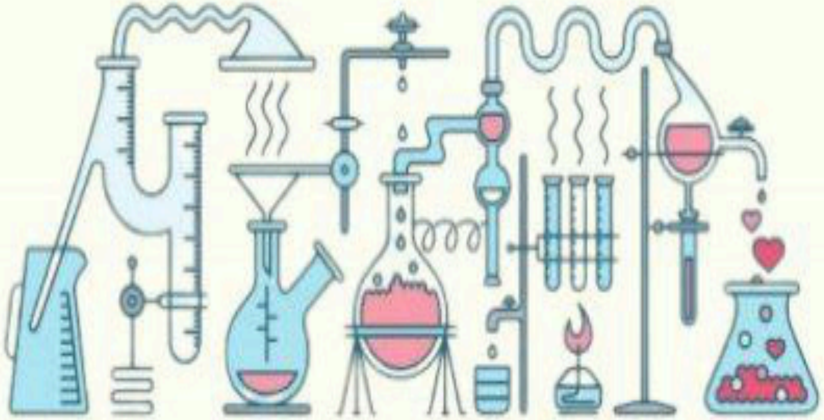
تفريغ تحليل آلي



اسم الموضوع: Application of Ultraviolet/ visible absorption spectrometry

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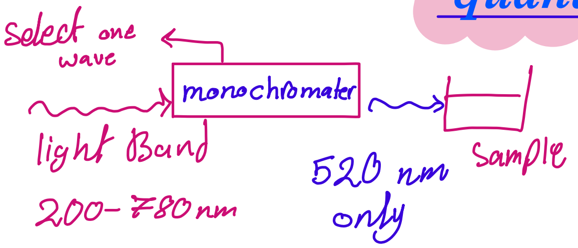
Soul Academy

لجان الدُفعات

Chapter 14
Application of Ultraviolet/Visible Molecular Absorption Spectrometry

$\lambda = 200-780\ nm$

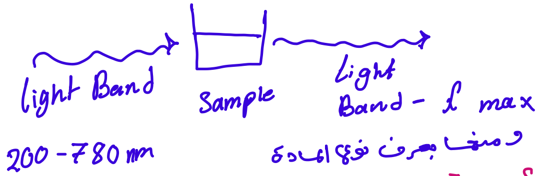
quantitative and qualitative



وبحسب

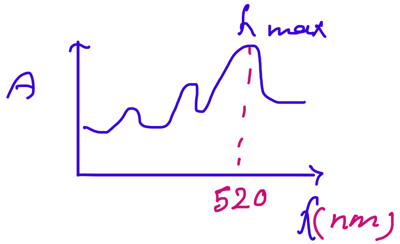
عدد λ ومنها التركيز ← Beer's law

بعدما اتخلص من deviation



ومنها بعرف نوع المادة

[200-780] - {520}



Pure باخذ المادة

Absorption measurements based upon ultraviolet and visible radiation find widespread application for the identification and determination of myriad inorganic and organic species. Molecular ultraviolet/visible absorption methods are perhaps the most widely used of all quantitative analysis techniques in chemical and clinical laboratories throughout the world.

• $C < 0.01\ M$

$< 10^3$: لايمكن استخدام القانون

$> 10^3$: يمكن استخدامها القانون

$[0 < a < 10^5]$

Absorptivity (a or ε)

Defines how much radiation will be absorbed by a molecule at a given concentration and wavelength

- Is termed molar absorptivity (ε) if concentration is expressed in molarity (M, mol/L)

- Can be calculated using Beer’s Law ($A = abc = \varepsilon bc$)

- If units of b is cm and c is M then ε is $M^{-1}cm^{-1}$ or $Lmol^{-1}cm^{-1}$

- Magnitude of ε is an indication of the probability of the electronic transition

e^- $E^0 \rightarrow E^*$

The magnitude of Molar Absorptivities

Molar absorptivities range from zero up to a maximum on the order of 10^5 are observed. The magnitude of ε depends upon the probability for an energy-absorbing transition to occur. Peaks having molar absorptivities less than about 10^3 are classified as being of low intensity. They result from so-called forbidden transitions, which have probabilities of occurrence that are less than 0.01.

لو كانت شدة الامتصاص (عدد الموجات التي تم امتصاصها) اقل من 10^3 يعني ان الـ e^- التي انتقلت من $E_0 \to E_1$ قليلة والاغلب راحوا للـ E_2 وللـ E_3

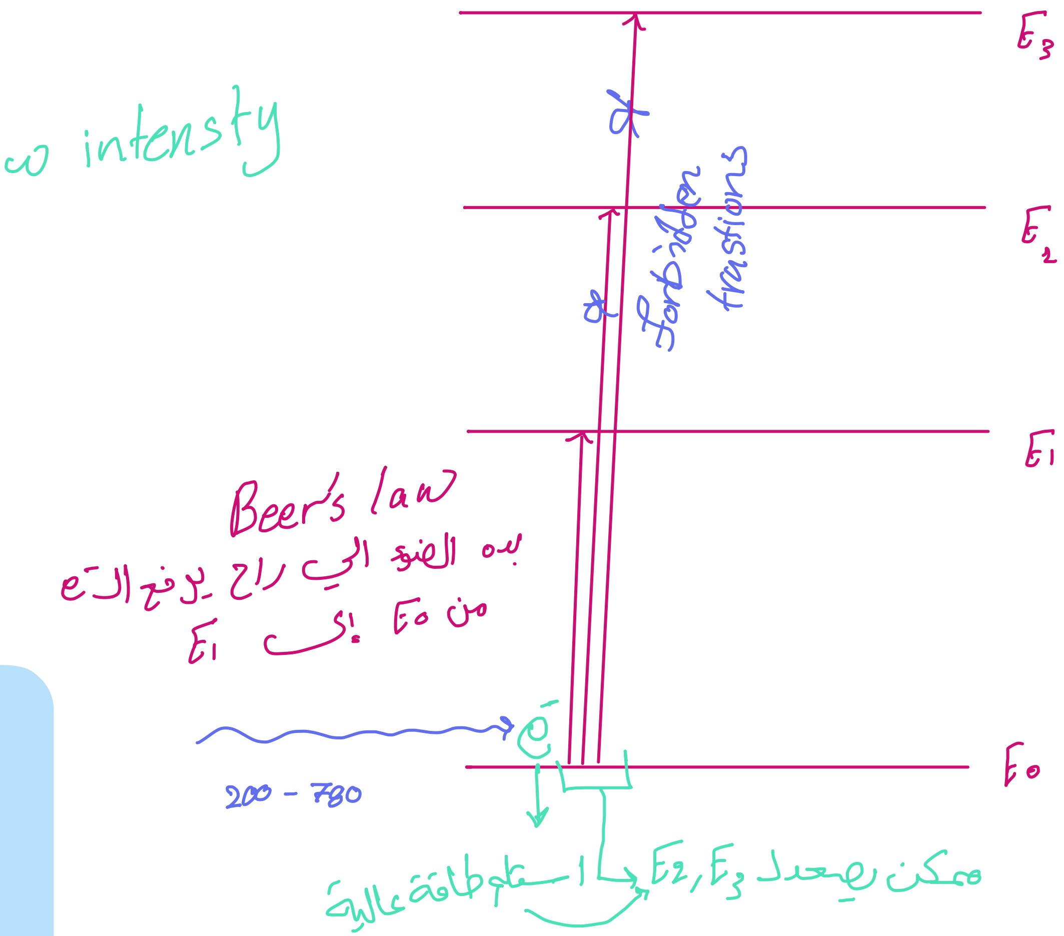
low intensty

لكن لو كانت اكبر من 10^3 يعني الضوء الذي ممتص والضوء الذي امتص كان $E_0 \to E_1$ major

متى اقدر احلل المركب بال UV-Vis لازم يطبق

$$\lambda = 200-780\ nm \ \&\ \varepsilon \geq 10^3\ M^{-1}cm^{-1}$$

الشرطين مع بعض



Beer's law

بده الضوء الي راح يرفع الـ e^- من E_0 إلى E_1

ممكن يصعد E_2, E_3 اذا اعطيتها طاقة عالية

مختص بالمركبات الـ organic ← $\sigma + \pi$

π ← هو الي بتحلل

ABSORBING SPECIES

The absorption of ultraviolet or visible radiation by a molecular species M can be considered to be a two-step process, excitation

$$M + h\nu \longrightarrow M^*$$

The lifetime of the excited species is brief (10^{-8} to 10^{-9} s). Relaxation involves conversion of the excitation energy to heat.

$$M^* \longrightarrow M + \text{heat}$$

The absorption of ultraviolet or visible radiation generally results from excitation of bonding electrons.

Electronic Transitions

There are three types of electronic transitions. The three include transitions involving:

(1) π, σ, and n electrons

(2) d and f electrons

(3) charge transfer electrons.

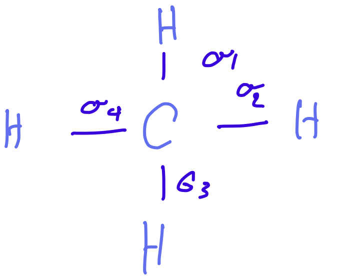
Types of Absorbing Electrons

The electrons that contribute to absorption by a molecule are: (1) those that participate directly in bond formation between atoms; (2) nonbonding or unshared outer electrons that are largely localized about such atoms as oxygen, the halogens, sulfur, and nitrogen. The molecular orbitals associated with single bonds are designated as sigma (σ) orbitals, and the corresponding electrons are σ electrons.

Types of Absorbing Electrons

The double bond in a molecule contains two types of molecular orbitals: a sigma (σ) orbital and a pi (π) molecular orbital. Pi orbitals are formed by the parallel overlap of atomic p orbitals. In addition to σ and π electrons, many compounds contain nonbonding electrons. These unshared electrons are designated by the symbol n.

CH_4



No π Bonds

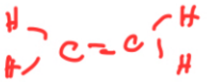
NO non Bonding e^-

only σ Bonds → only sp_3

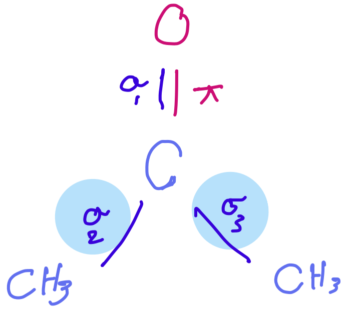
Can't analiezed By UV-Vis why? → المسافة بين σ و σ* كبيرة جدًا ← بحتاج طاقة عالية

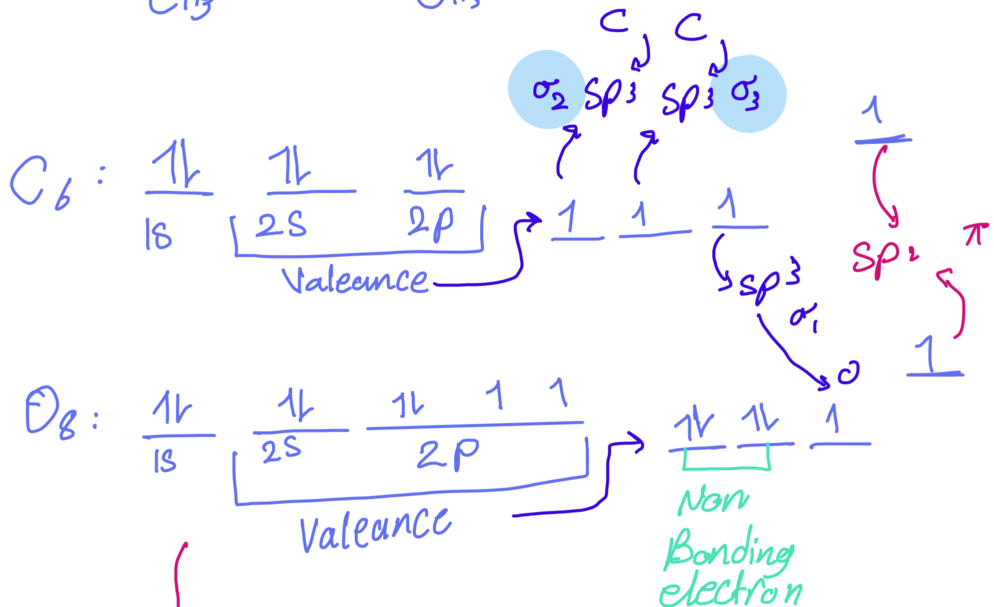
يعني λ اقل من 180 nm ← فهو خارج منطقة UV-Vis

ما بقدر اشوفها ←

$\sigma \to \sigma^*$	$\sigma \to \sigma^*$ $n \to \sigma^*$	$\sigma \to \sigma^*$ $\pi \to \pi^*$	$\sigma \to \sigma^*$, $\pi \to \pi^*$ $n \to \sigma^*$, $n \to \pi^*$
CH_4 $< \lambda_{max}$ 180	 150 – 250 λ_{max} مثل الكحول $\varepsilon = 100 - 3000$ قليلة ممكن اشوفها وممكن لا هك حسب المركب	 $\lambda_{max} \geq 180$ $\varepsilon > 10^3$	

N, S, P كلهم عندهم lone pair



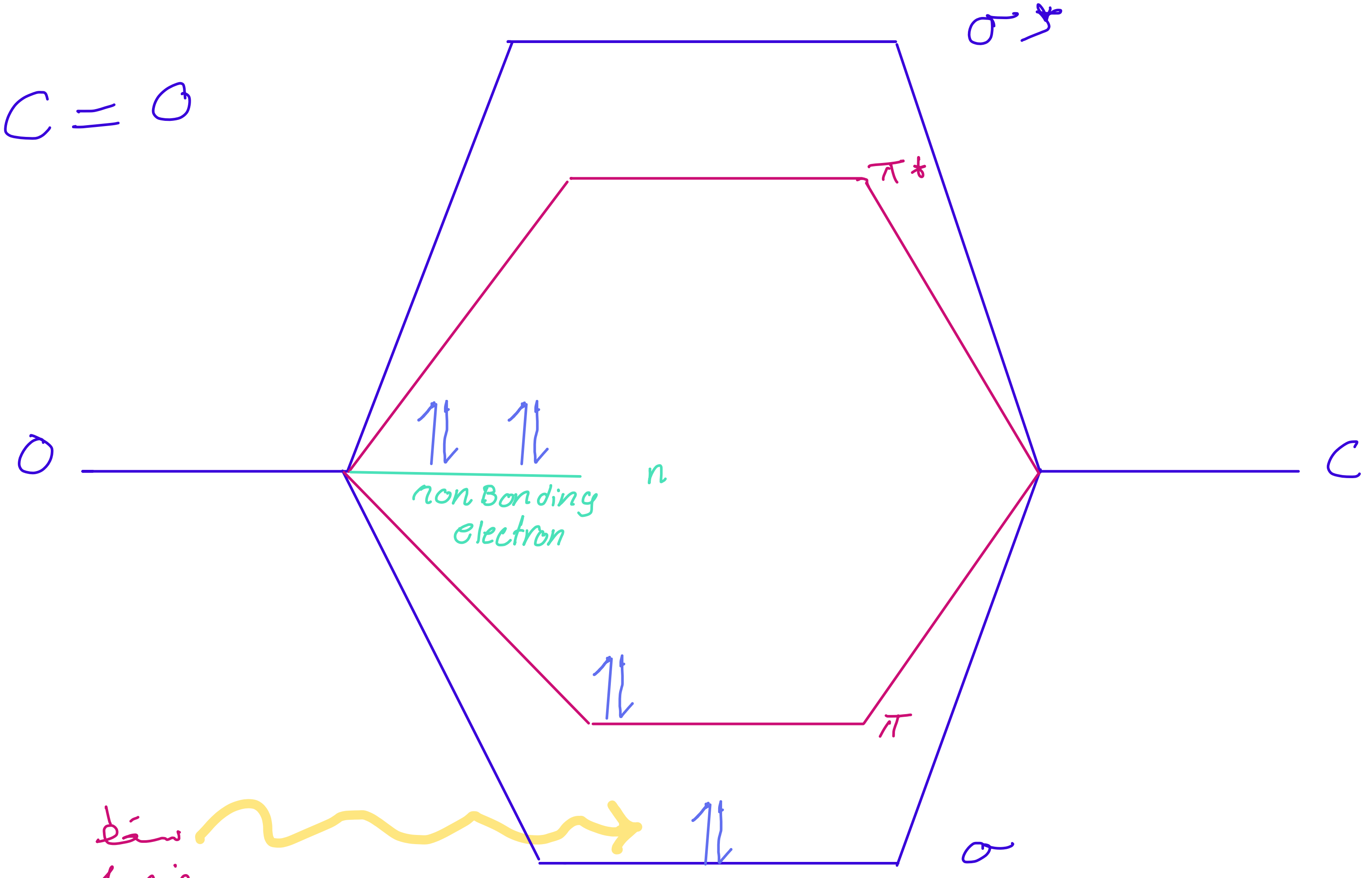


الشرطين لازم يكونوا مع بعض

- $\varepsilon > 10^3$
- $\lambda_{max} > 180$ nm – 780

C = O

بشكل أوضح



سقط
ضوء على C=O

احتمال الانتقالات

1. σ → σ*
2. π → π*
3. n → σ*
4. n → π*

π → σ*
σ → π*

ما بصير

only σ Bonds
saturated
compund

σ → sp^3

π → sp^2

Energy

The energies for the various types of molecular orbitals differ significantly. The energy level of a nonbonding electron lies between the energy levels of the bonding and the antibonding π and σ orbitals. Electronic transitions among certain of the energy levels can be brought about by the absorption of radiation. Four types of transitions are possible:

من حيث الطاقة ، من حيث الاحتمالية

① ② ④ ③

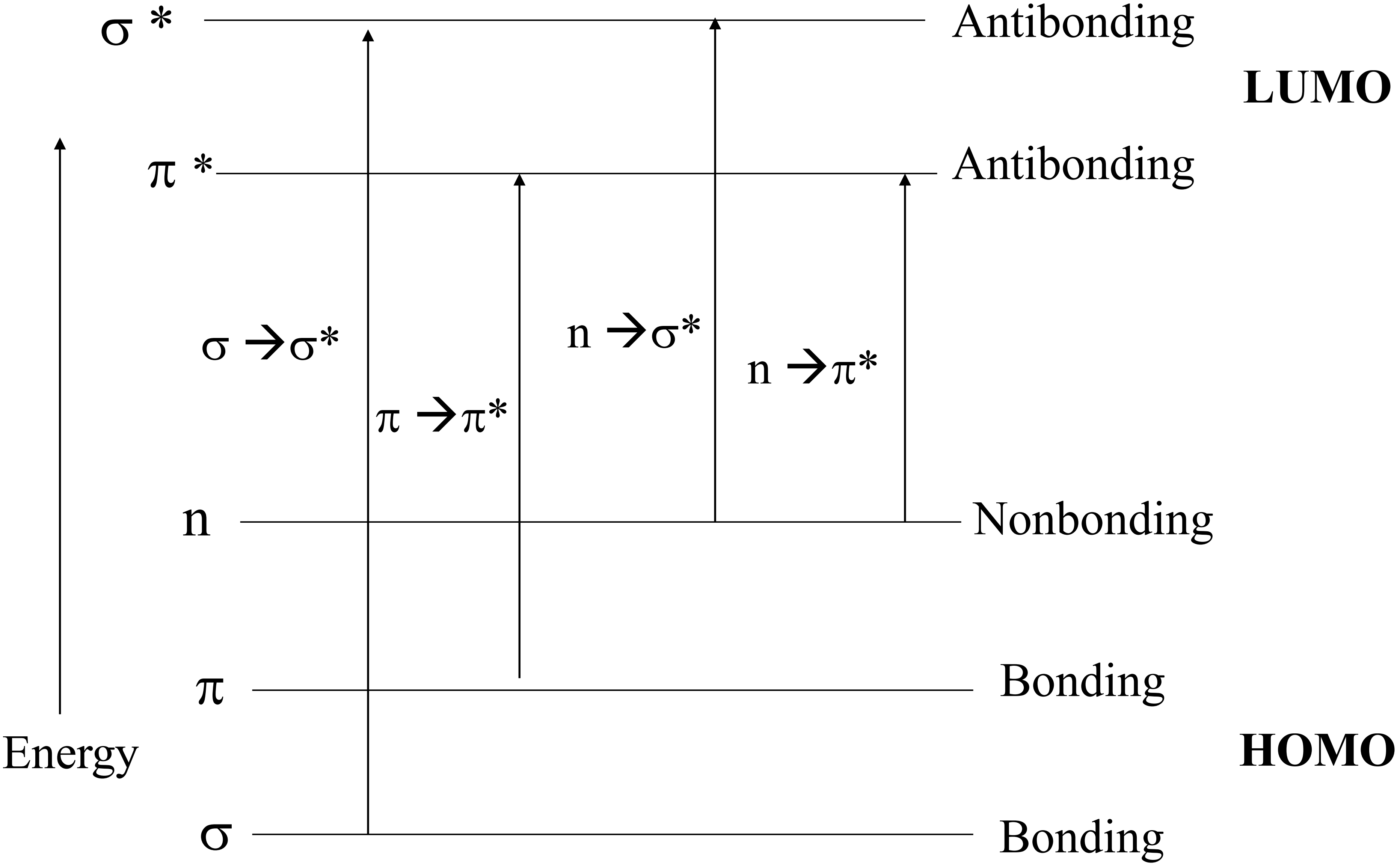
$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$.

أعلى طاقة

أقل طاقة ، ع أقل

احتماليته قليلة

LUMO: lowest unoccupied molecular orbital



σ * Antibonding

LUMO

π * Antibonding

σ →σ*

π →π*

n →σ*

n →π*

n Nonbonding

π Bonding

Energy

HOMO

σ Bonding

HOMO: highest occupied molecular orbital

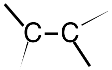
For convenience of reference, definitions of the various spectral regions have been set by the Joint Committee on Nomenclature in Applied Spectroscopy:

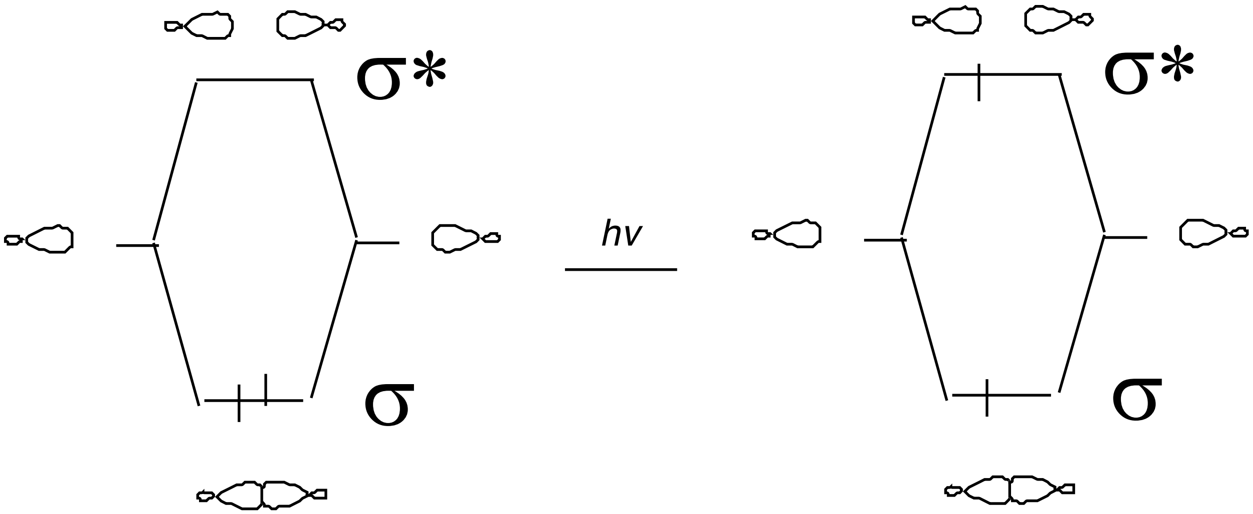
Region	**Wavelength (nm)**
Far ultraviolet	10-200 UVA
Near ultraviolet	200-380 UVB
Visible	380-780
Near infrared	780-3000
Middle infrared	3000-30,000
Far infrared	30,000-300,000
Microwave	300,000-1,000,000,000

σ →σ* Transition

An electron in a bonding σ orbital of a molecule is excited to the corresponding antibonding orbital by the absorption of radiation. The energy required to induce a σ →σ* transition is large. Methane (CH_4) can undergo only σ →σ* transitions, exhibits an absorption maximum λ_{max} at 125 nm. Absorption maxima due to σ →σ* transitions are never observed in the ordinarily accessible ultraviolet region **(Far UV range).**

Ethane





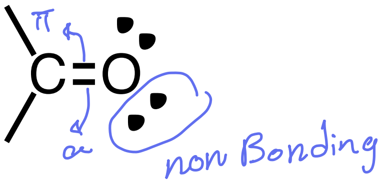
$$\sigma \longrightarrow \sigma^*$$

λ_{max} = 135 nm (a high energy transition)

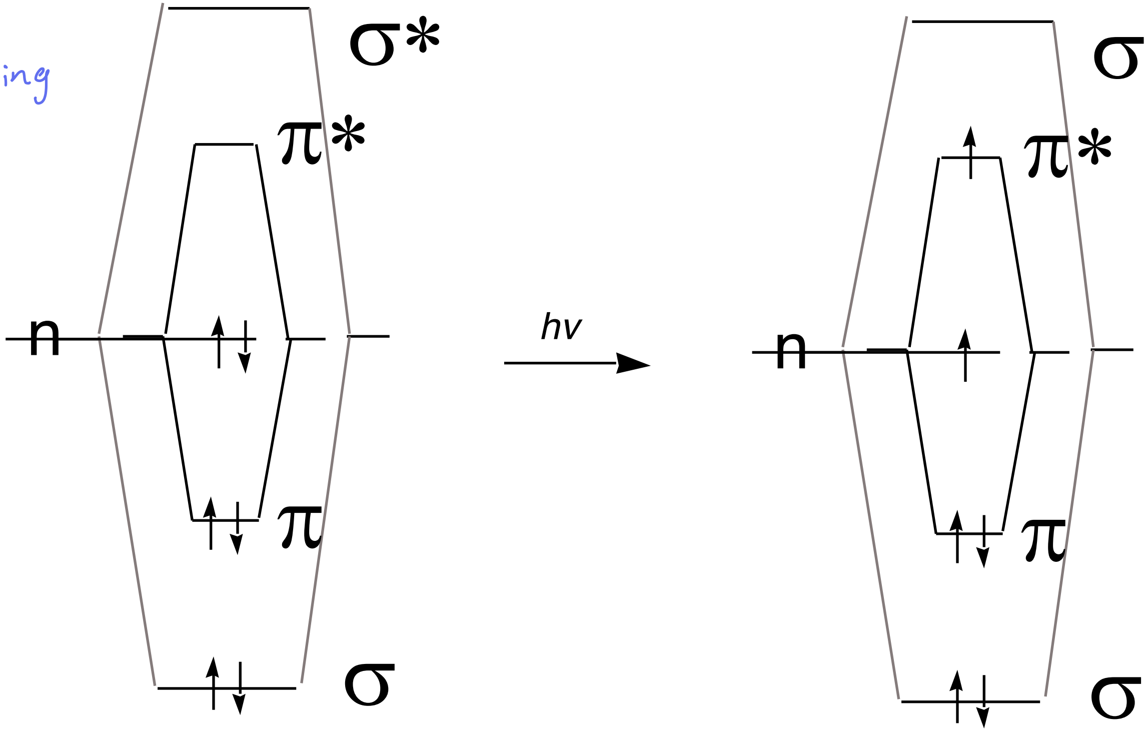
Absorptions having λ_{max} < 200 nm are difficult to observe because everything (including quartz glass and air) absorbs in this spectral region.

n →σ* Transitions

Saturated compounds containing atoms with unshared electrons are capable of n →σ* transitions. These transitions require less energy than the σ →σ* type and can be brought about by radiation in the region of between 150 and 250 nm, with most absorption peaks appearing below 200 nm. The molar absorptivities are low to intermediate in magnitude and range between 100 and 3000 L cm^{-1} mol^{-1}.



على نفس
الذرة
بخلي لـ لونها غامق



n → π*

The n to π* transition is at even lower wavelengths but is not as strong as π to π* transitions. It is said to be "forbidden."

Example:

Acetone: ✓ π–π* λ_{max} = 188 nm ; ε= 1860

n–π* λ_{max} = 279 nm ; ε= 15

حقق الشرطين

قليل

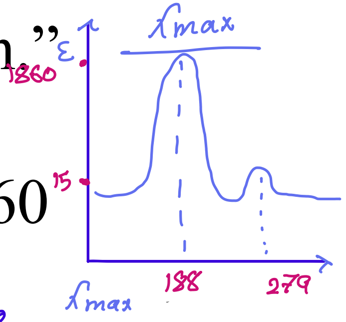


TABLE 14-2 Absorption by Organic Compounds Containing Heteroatoms with Nonbonding Electrons

Compound	**λ_{max}, nm**	**ε_{max}**
CH_3OH	167 ✗ اقل من 180	✓ 1480
$(CH_3)_2O$	184 ✓	✓ 2520
CH_3Cl	173 ✗	200
CH_3I	258	365
$(CH_3)_2S$	229	140
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

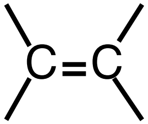
λ ✓

ε ✗

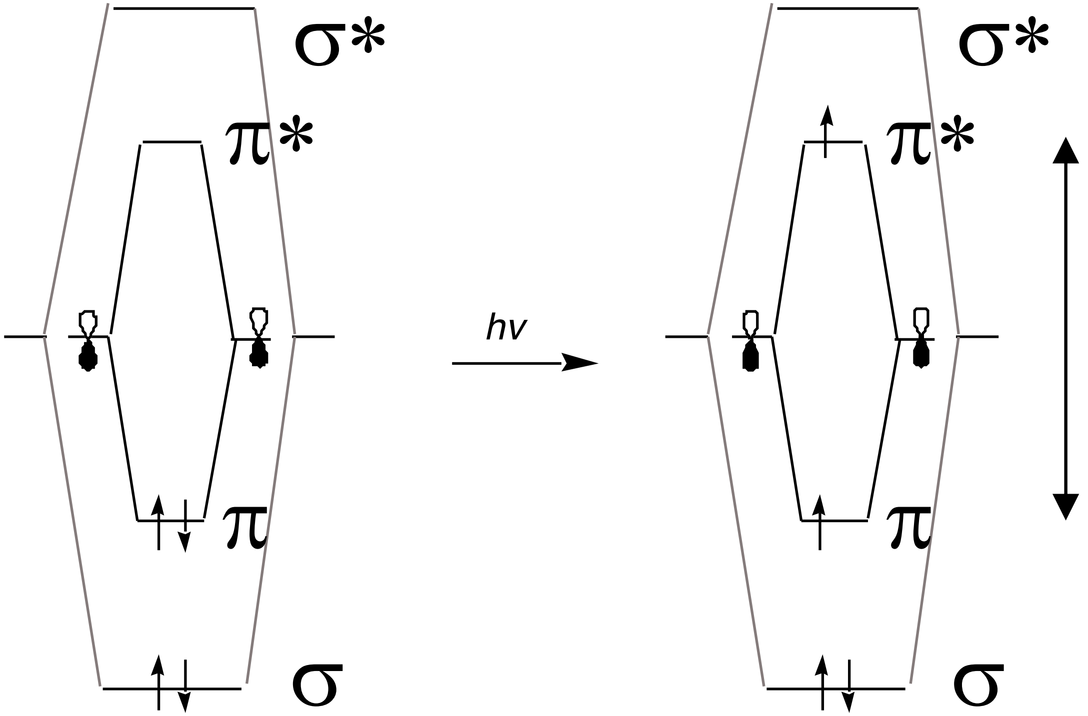
LOW!

n →π* and π →π* Transitions

Most applications of absorption spectroscopy are based upon transitions for n or π electrons to the π* excited state because the energies required for these processes bring the absorption peaks into an experimentally convenient spectral region (200 to 780 nm). Both transitions require the presence of an unsaturated functional group to provide the π orbitals. The molar absorptivities for peaks associated with excitation to the n, π* state are generally low and ordinarily range from 10 and 100 L cm^{-1} mol $^{-1}$; values for π →π* transitions are normally take place in the range between 1000 and 10,000.



C_2H_4



$$\Delta E = h\nu$$
$$= hc/\lambda$$

$\pi \longrightarrow \pi^*$

Example: ethylene absorbs at longer wavelengths:
$\lambda_{max} = 185$ nm $\varepsilon = 10{,}000$

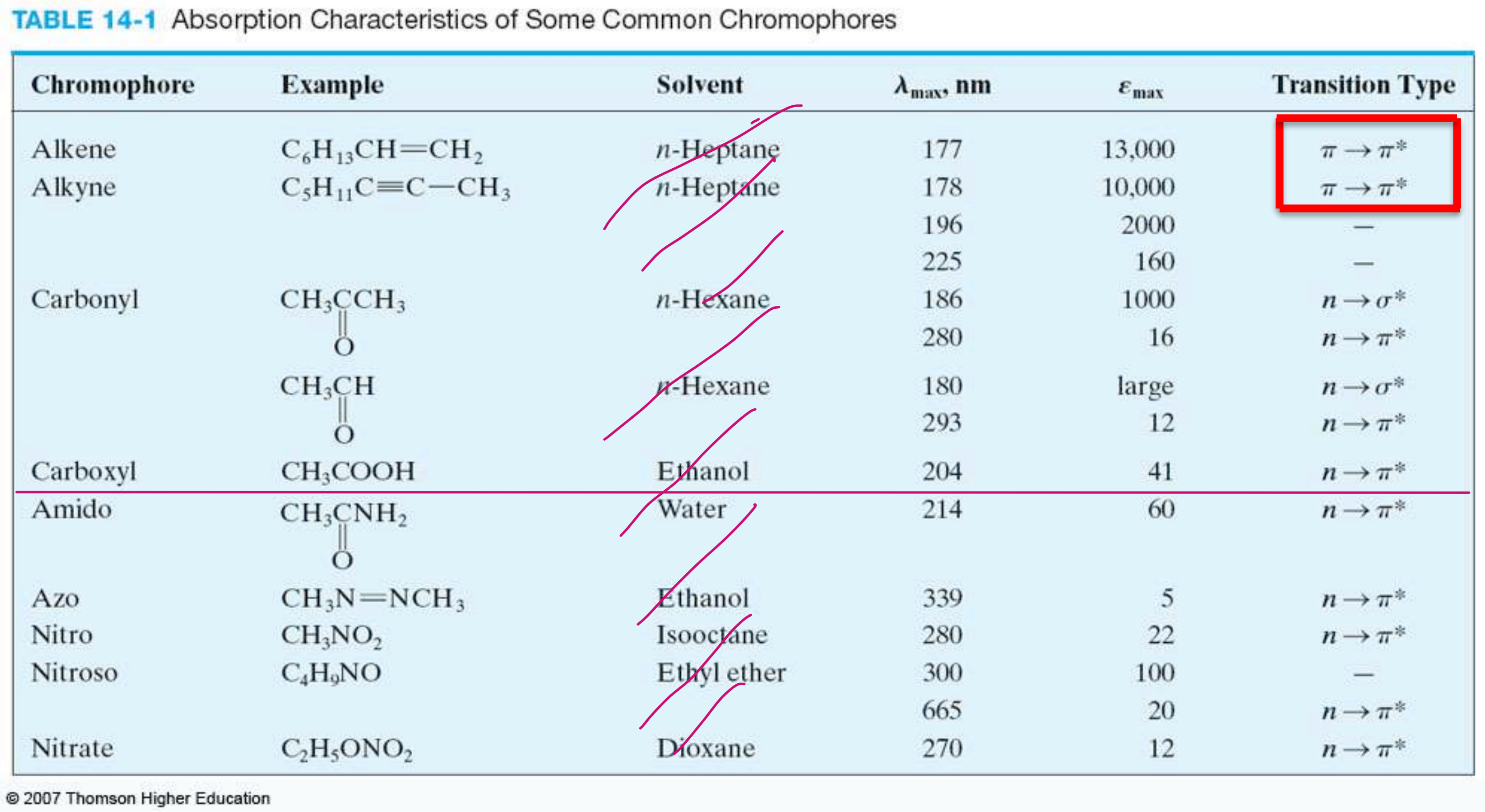


TABLE 14-1 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	λ_{max}, nm	ε_{max}	Transition Type
Alkene	$C_6H_{13}CH{=}CH_2$	*n*-Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$C_5H_{11}C{\equiv}C{-}CH_3$	*n*-Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2000	—
			225	160	—
Carbonyl	$CH_3\underset{\underset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$CH_3\underset{\underset{O}{\|}}{C}H$	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	CH_3COOH	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$CH_3\underset{\underset{O}{\|}}{C}NH_2$	Water	214	60	$n \rightarrow \pi^*$
Azo	$CH_3N{=}NCH_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	C_4H_9NO	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12	$n \rightarrow \pi^*$

Olefins and aromatics

$\sigma \rightarrow \sigma^*$ < 185 nm

$n \rightarrow \sigma^*$ 150-250 nm

$\pi \rightarrow \pi^*$

$n \rightarrow \pi^*$ 200-700 nm

Absorption by Organic Compounds

- All organic compounds are capable of absorbing electromagnetic radiation since all contain valence electrons that can be excited to higher energy levels
- The energies associated with electrons in single bonds are sufficiently high ($\sigma \rightarrow \sigma^*$) that absorption occurs in the Far-UV ($\lambda < 185$ nm). Components of the atmosphere also absorb in this region.
- This is the reason why normal n-alkanes organic compounds can be utilized as solvents in the UV/Vis region.
- Because of experimental difficulties association with the Far-ultraviolet region, most spectrophotometric investigations of organic compounds involves the longer wavelengths ($\lambda > 185$ nm)
- Most applications of Absorption spectroscopy are based on transitions for $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$. (UV/VIS 200-780nm)
- Both $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ require the presence of unsaturated functional groups (double bonds) to provide the π orbitals. Molecule containing these functional groups are also referred to as "chromophores"

اي مركب فيه one or more Pi
π Bond

Absorption Definitions

Chromophore

A group of atoms that gives rise to electronic absorption

Or

A functional group capable of having characteristic electronic transitions is called a **chromophore** (color loving)

$\sigma \to \sigma^*$ & $\pi \to \pi^*$

Or

The **chromophore** is a region in the molecule where the energy difference between two different molecular falls within the range of the visible spectrum

Auxochrome $\sigma \to \sigma^*$ & $\pi \to \pi^*$ & $n \to \pi^*$

SH
PH

I
Br
F
Cl

A substituent that contains unshared electron pairs ($\ddot{O}$H, $\ddot{N}$H, $\dot{X}$)

An auxochrome attached to a chromophore with π electrons shifts the λ_{max} to longer wavelengths

يعني بدي E قليلة حتى اقدر اشوفه فبصير بمرحلة Visible واللون بيغمق

Common functional groups

Compound	λ(nm)	Intensity/ε	transition with lowest energy
CH_4	122	intense	σ-σ*(C-H)
CH_3CH_3	130	intense	σ-σ* (C-C)
CH_3OH	183	200	n-σ* (C-O)
CH_3SH	235	180	n-σ* (C-S)
CH_3NH_2	210	800	n-σ* (C-N)
CH_3Cl	173	200	n-σ* (C-Cl)
CH_3I	258	380	n-σ* (C-I)
$CH_2{=}CH_2$	165	16000	π-π* (C=C)
CH_3COCH_3	187	950	π-π* (C=O)
	273	14	n-π* (C=O)
CH_3CSCH_3	460	weak	n-π* (C=S)
$CH_3N{=}NCH_3$	347	15	n-π* (N=N)

تأثير ال Solvent

Absorption Definitions

Bathochromic

A shift to longer wavelengths or red shift (increase in λ) لون اغمق

افقي
λ بتتغير

Hypsochromic

A shift to shorter wavelengths or blue shift (decrease in λ) لون افتح

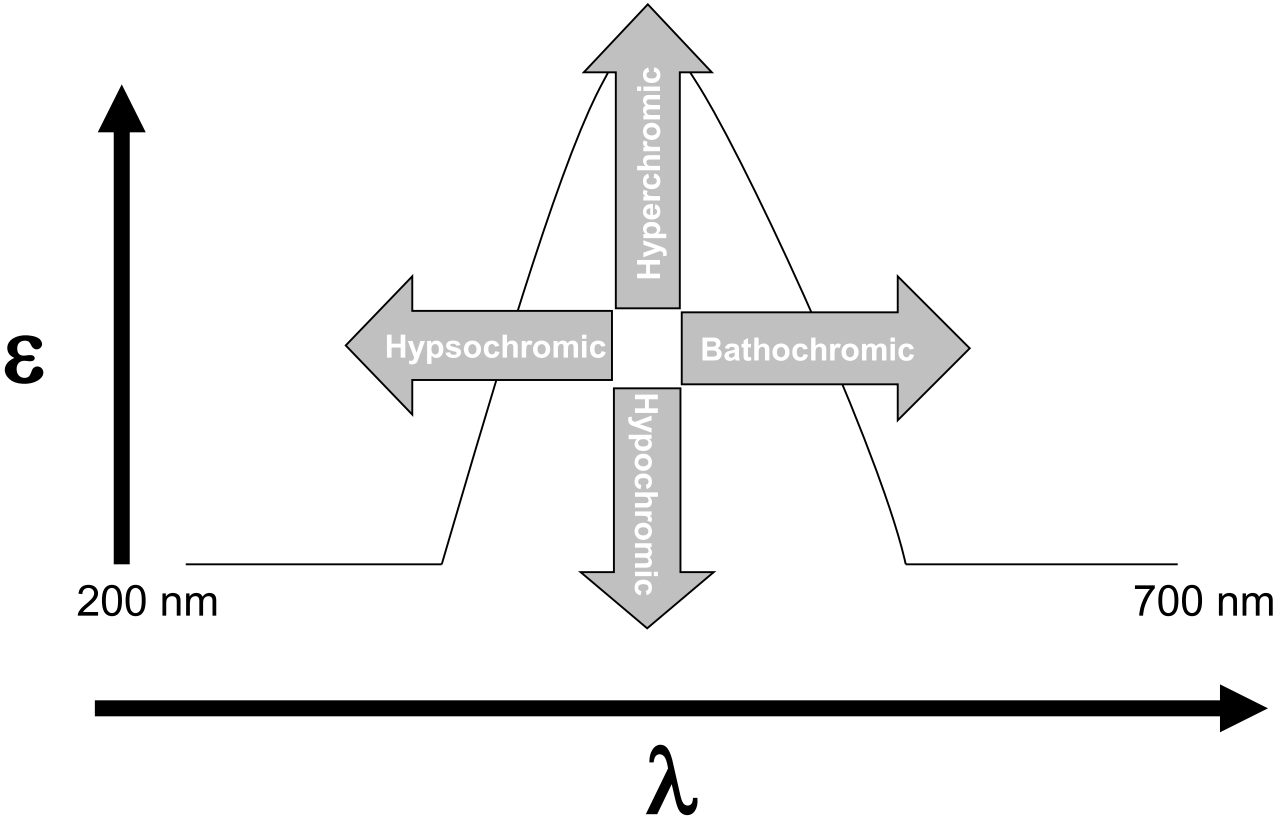
Hyperchromism

عامودي
ε بتتغير

An increase in intensity of an absorption band (increase in ε_{max})

Hypochromism

A decrease in intensity of an absorption band (decrease in ε_{max})


Hyperchromic
ε
Hypsochromic
Bathochromic
Hypochromic
200 nm
700 nm
λ

Solvent Effects

A compound that contains both π and n electrons may exhibit two absorption maxima with change in solvent polarity

- $\pi \rightarrow \pi^*$ transitions absorb ~10 x more strongly than $n \rightarrow \pi^*$ transition

- $n \rightarrow \pi^*$ transition occur at longer wavelengths than $\pi \rightarrow \pi^*$

- Such a compound will exhibit two characteristic peaks in a nonpolar solvent such as hexane

- The two peaks will be shifted closer to each other in a polar and hydrogen bonding solvent such as ethanol

Solvent Effects

Molecules with absorption due to $\pi \rightarrow \pi^*$ transition exhibit red shift when dissolved in polar solvents as compared to nonpolar solvents

- Used to confirm the presence of $\pi \rightarrow \pi^*$ transitions in molecules

Molecules with absorption due to $n \rightarrow \pi^*$ transition exhibit blue shift when dissolved in solvents that are able to form hydrogen bonds

- Used to confirm the presence of n electrons in a molecule

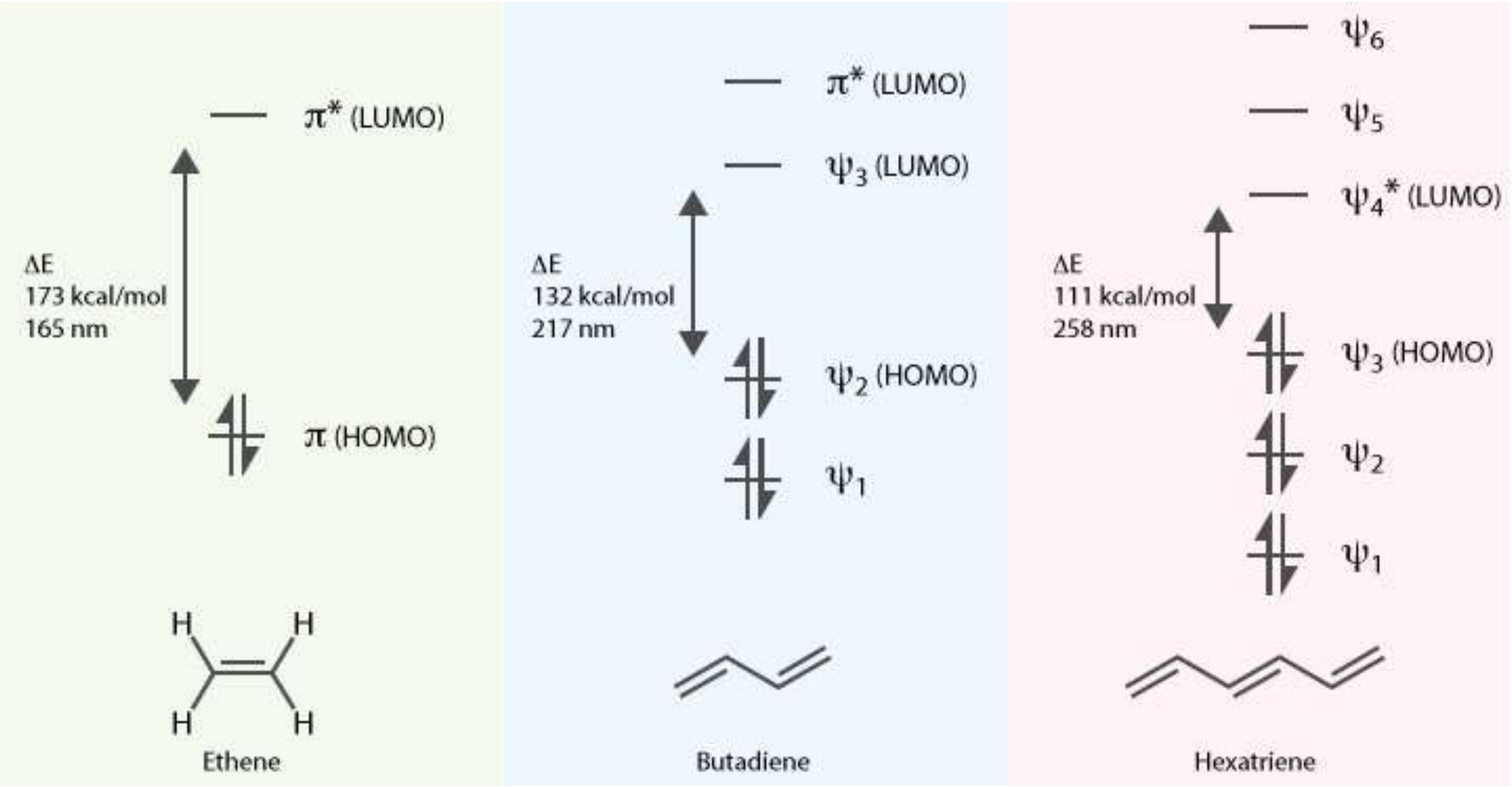
Effect of Conjugation of Chromophores

π electrons are considered to be further delocalized by conjugation; the orbitals involve four (or more) atomic centers. The effect of this delocalization is to lower the energy level of the π* orbital and give it <u>less antibonding character</u>. Absorption maxima are shifted to longer wavelengths as a consequence. Conjugation of chromophores, has a profound effect on spectral properties. 1,3-butadiene, $CH_2=CHCH=CH_2$, has a strong absorption band that is displaced to a longer wavelength by 20 nm compared with the corresponding peak for an unconjugated diene.

$\lambda \uparrow$

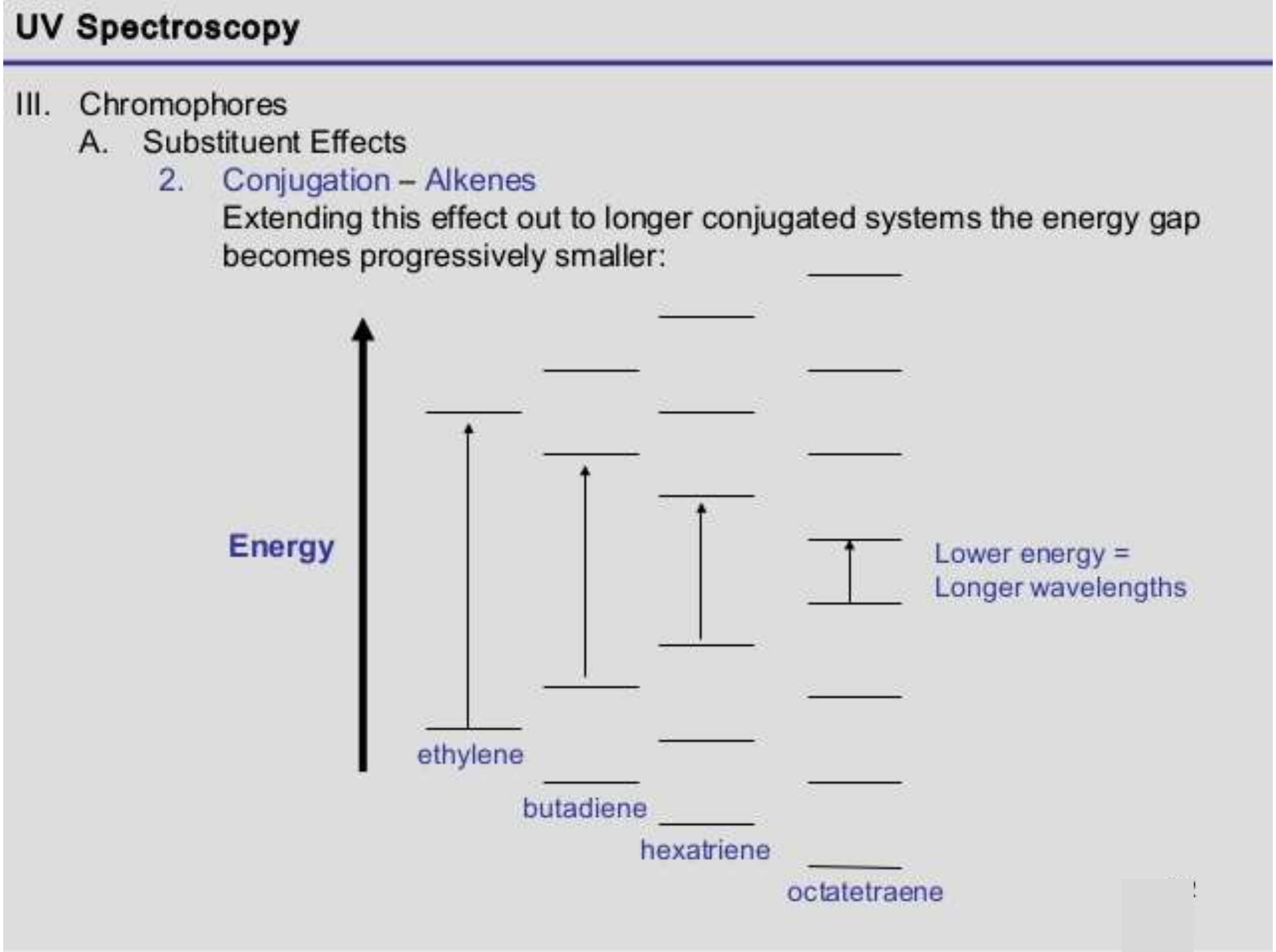
اللون بيوضح

Effect of Conjugation of Chromophores



المسافة بين HOMO و LOMO بتقل

Effect of Conjugation of Chromophores



UV Spectroscopy

III. Chromophores
  A. Substituent Effects
    2. Conjugation – Alkenes
    Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:

Effect of Conjugation of Chromophores

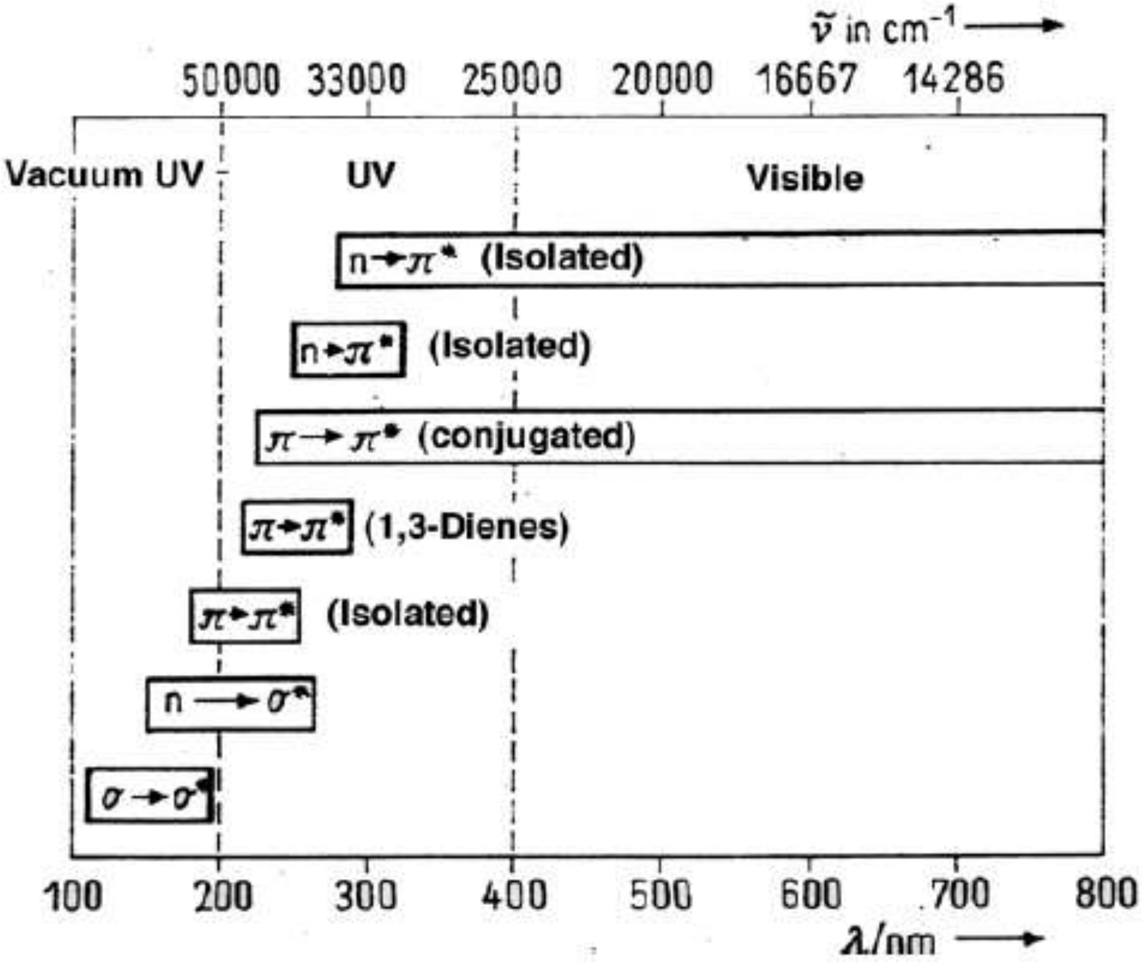
Table 8.3 Values of λ_{max} and ε for Ethylene and Conjugated Dienes

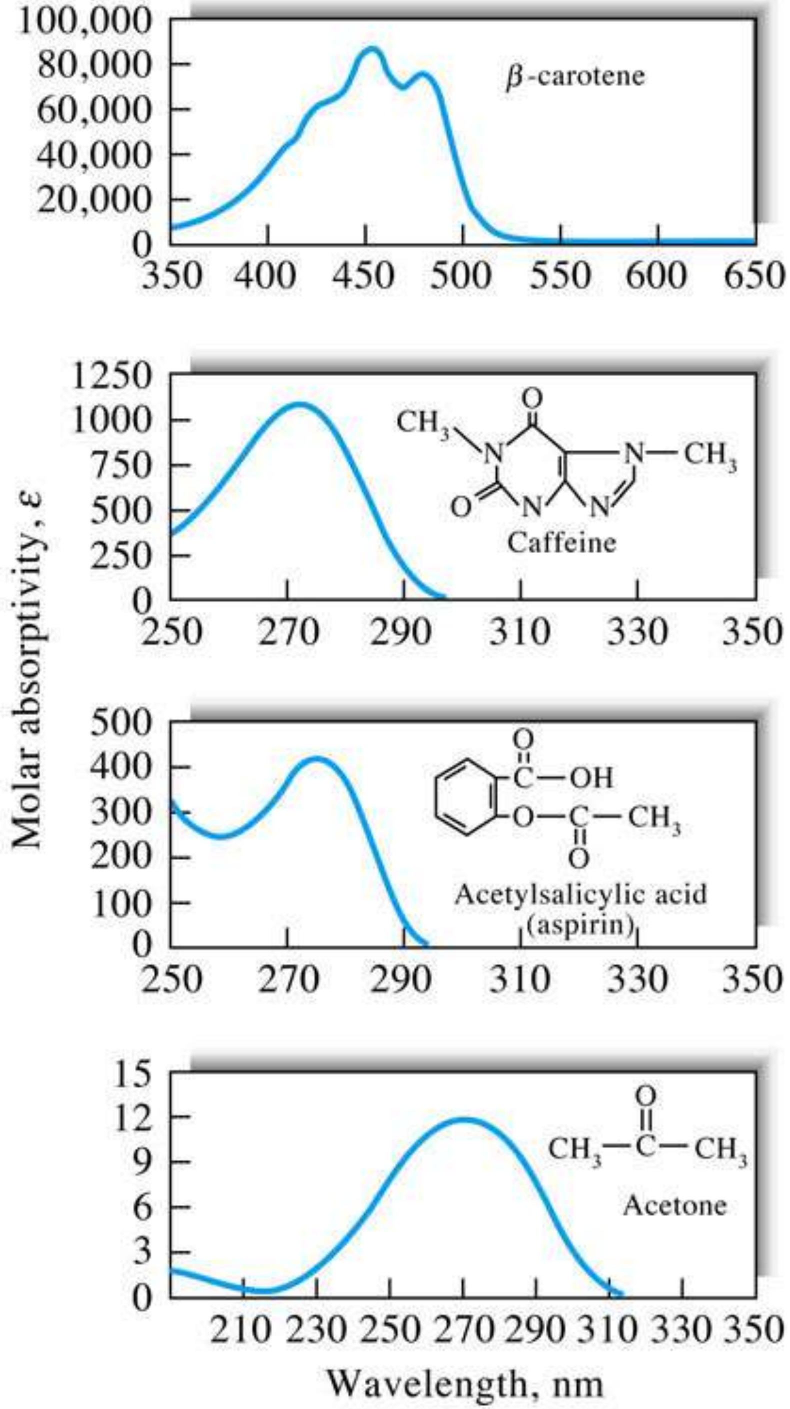
Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$H_2C{=}CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

$\lambda \uparrow$

These transitions correspond to simple bonds and are common to all molecules.

$\pi \rightarrow \pi^*$ transitions depend on the conjugation, so it can reach the visible region of radiation, causing the color of substances.

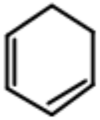



β-carotene
100,000
80,000
60,000
40,000
20,000
0
350 400 450 500 550 600 650
Caffeine
CH3
O
N
N—CH3
O
N
N
1250
1000
750
500
250
0
250 270 290 310 330 350
Molar absorptivity, ε
Acetylsalicylic acid
(aspirin)
O
C—OH
O—C—CH3
O
500
400
300
200
100
0
250 270 290 310 330 350
Acetone
CH3—C—CH3
O
15
12
9
6
3
0
210 230 250 270 290 310 330 350
Wavelength, nm

Empirical Rules for Calculating Uv/Vis Absorptions

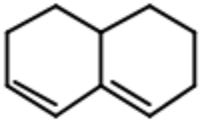
Woodward-Fieser Rules for Calculating the λmax of Conjugated Dienes and Polyenes

- Parent:



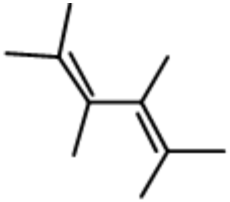
Homoannular

λ=253 nm



heteroannular

λ=214 nm

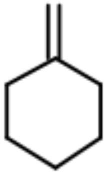


acyclic

=217

- Increments for:

Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5



exocyclic

~~Polar groupings:~~

~~-OC(O)CH_3~~	~~+0~~
~~-OR~~	~~+6~~
~~-Cl, -Br~~	~~+5~~
~~-NR_2~~	~~+60~~
~~-SR~~	~~+30~~

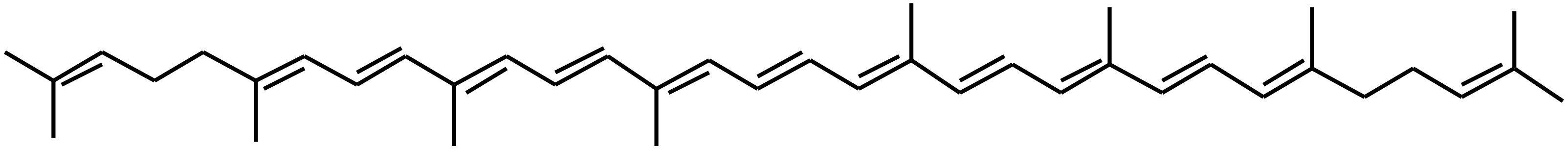
مش مطلوبين

For more than 4 conjugated double bonds:

λ_{max} = 114 + 5(number of alkyl groups) + n(48.0-1.7n)

Example:

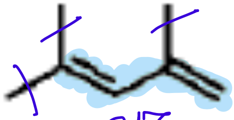
Lycopene:



λ_{max} = 114 + 5(8) + 11*(48.0-1.7*11) = 476 nm

λ_{max}(Actual) = 474.

Example 1:

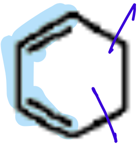


③ alkyl

Transoid:		217 nm
Alkyl groups or ring residues:	3 x 5 =	15 nm
Calculated:		232 nm
Observed:		234 nm

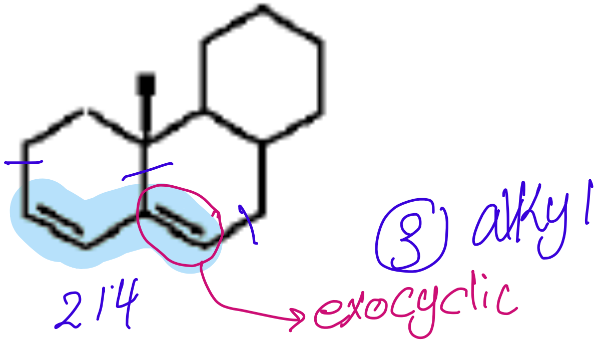
Example 2:

253

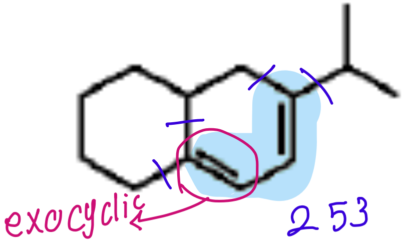


② alkyl

Cisoid:		253 nm
Alkyl groups or ring residues:	2 x 5 =	10 nm
Calculated:		263 nm
Observed:		256 nm



Transoid:		214 nm
Alkyl groups or ring residues:	3 x 5 =	15 nm
Exocyclic double bond:		5 nm
Calculated:		234 nm
Observed:		235 nm



④ alkyl

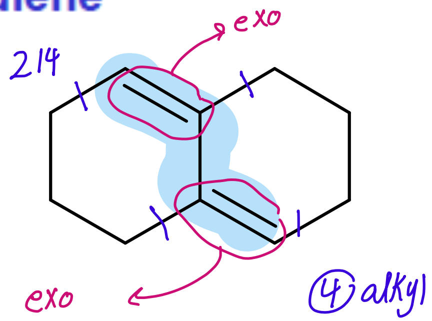
Cisoid:		253 nm
Alkyl groups or ring residues:	4 x 5 =	20 nm
Exocyclic double bond:		5 nm
Calculated:		278 nm
Observed:		275 nm

Example 1

Calculate the λ_{max} for 1,4, dibenzodiene

Solution:

The structure is



Parent heterodiene = 214

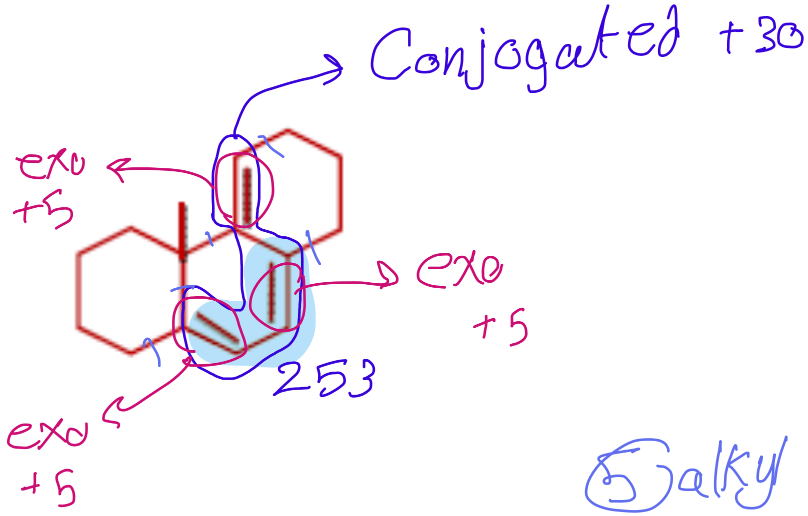
Alkyl substituents (4x5 nm) = 20

Exocyclic double bond 2x5 = 10

λ_{max} = 244 nm (observed 247 nm)

Example 2

Calculate the λ_{max} for



Solution:

The compound is a homoannular diene

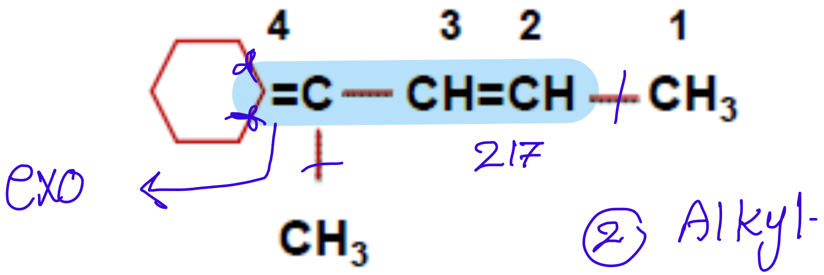
Base value = 253
Ring residues (5x5) = 25
Exocyclic double bond 3x5 = 15
Extended C=C = 30

λ_{max} is 323 nm
observed value is 320 nm.

Example 3

Calculate the absorption maximum for 4 cyclohexenyl 2-pentene

Solution



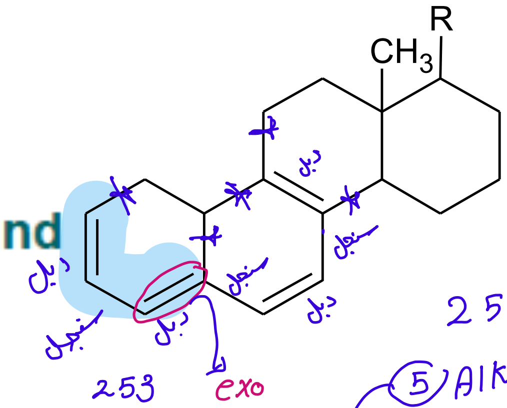
It is a 2, 4 diene system

Base value	217
2 Alkyl substituents 2x5	10
* 2 Ring residues 2x5	10
1 Exocyclic bond	5
	242 nm

Observed value is also 242 nm

Example 4

Calculate the λ_{max} for the compound



Solution

2 5 3

⑤ Alkyl * 5

① exo * 5

② extended * 30

نفسها

Base value	253 nm
2 Extended double bonds (2x30)	60 nm
5 Ring residues (5x5)	25 nm
1 Exocyclic double bond (1x5)	5 nm
Calculated λ_{max}	343 nm
Observed	345 nm

Woodward's Rules for Conjugated Carbonyl Compounds

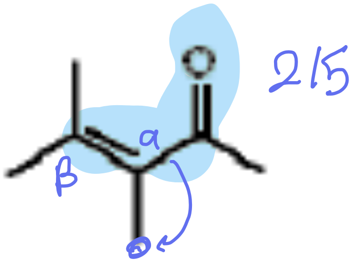
Base values:

X = R	
Six-membered ring or acyclic parent enone	λ=215 nm
Five-membered ring parent enone	λ=202 nm
X = H	λ=208 nm
X = OH, OR	λ=195 nm

Increments for:

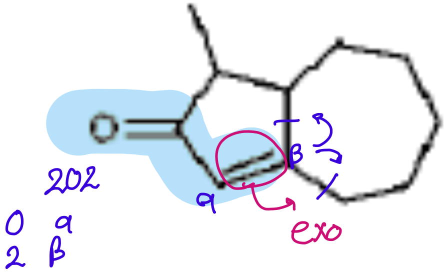
Double bond extending conjugation		30
Exocyclic double bond		5
Endocyclic double bond in a 5- or 7-membered ring for X = OH, OR		5
Homocyclic diene component		39
Alkyl substituent or ring residue	α	10
	β	12
	γ or higher	18

example

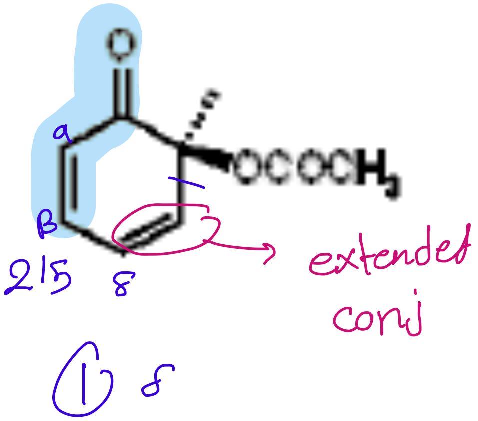


① α
② β

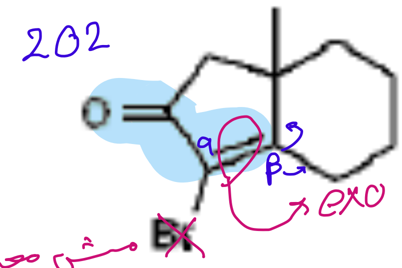
Acyclic enone:		215 nm
α-Alkyl groups or ring residues:		10 nm
β-Alkyl groups or ring residues:	2 x 12 =	<u>24 nm</u>
Calculated:		249 nm
Observed:		249 nm



Five-membered ring parent enone:		202 nm
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Exocyclic double bond:		5 nm
Calculated:		231 nm
Observed:		226 nm



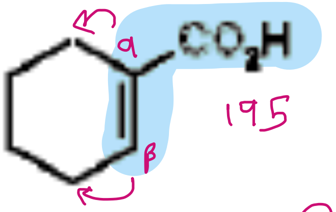
Six-membered ring or alicyclic parent enone:	215 nm
Extended conjugation:	30 nm
Homocyclic diene component:	39 nm
δ-Alkyl groups or ring residues:	18 nm
Calculated:	302 nm
Observed:	300 nm



مش معنا
بس لو اعتبرناه alkyl

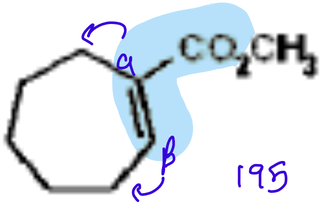
202
① a = 10
② β = 24
① exo = 5

Five-membered ring parent enone:		202 nm
~~α-Br:~~		~~25 nm~~ 10
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Exocyclic double bond:		5 nm
Calculated:		256 nm
Observed:		251 nm



① α
① β

Carboxylic acid:	195 nm
α-Alkyl groups or ring residues:	10 nm
β-Alkyl groups or ring residues:	12 nm
Calculated:	217 nm
Observed:	217 nm

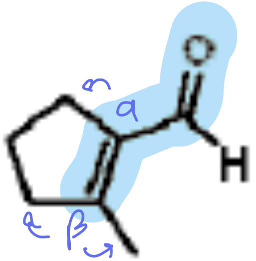


195

① α

① β

Ester:	195 nm
α-Alkyl groups or ring residues:	10 nm
β-Alkyl groups or ring residues:	12 nm
Endocyclic double bond in 7-membered ring:	5 nm
Calculated:	222 nm
Observed:	222 nm

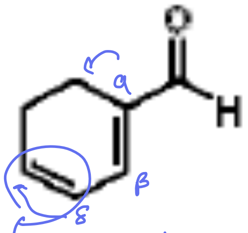


202

① α

② β

Aldehyde:		208 nm
α-Alkyl groups or ring residues:		10 nm
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Calculated:		242 nm
Observed:		242 nm



208

extended conj = 30

① α = 10

① β = 12

Aldehyde:	208 nm
Extended conjugation:	30 nm
Homodiene component:	39 nm
α-Alkyl groups or ring residues:	10 nm
δ-Alkyl groups or ring residues:	18 nm
Calculated:	304 nm
Observed:	302 nm