تفريغ تحليل آلي

اسم الموضوع: Ch4 part 2

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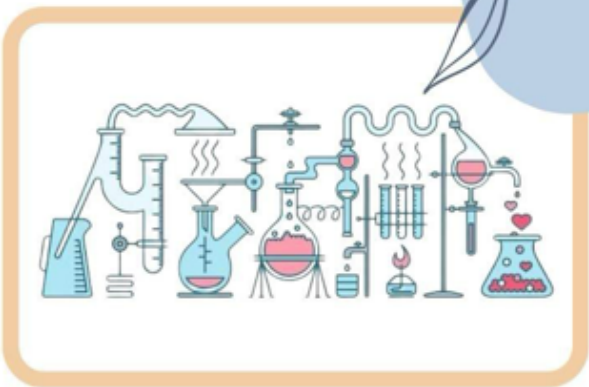
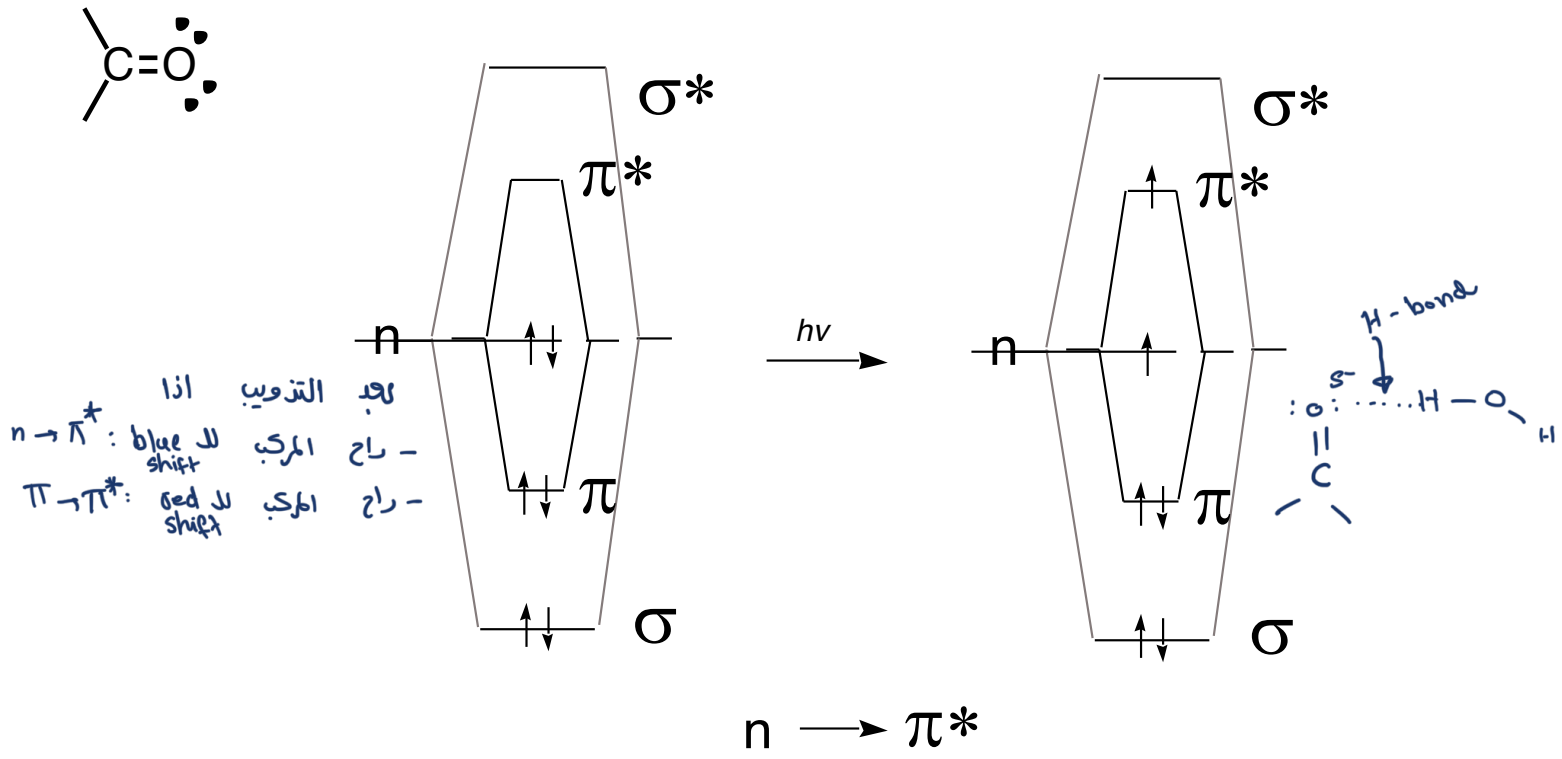


Soul Academy

لجان الدفعات



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

معطيني λmax 2 و molar absorptivity 2 و بحدد منهم مين اللي بصيرله انتقال حسب القيم اللي بتطبق الشروط

اذا ما اعطاني القيم و حكالي هاد المركب اله λmax بتساوي 188 و سأل لمين يعود الانتقال ، من خلال المركب بعرف انه في $\pi \rightarrow \pi^*$ ، $n \rightarrow \pi^*$ ف لمين بعود الانتقال ؟
فلازم هون عشان اعرف ، اعمل test عالمركب عمليًا ، ف اذا اخدت المركب و دوبته ب polar solvent و اله قدرة يعمل H-bond مثل المي و حللت المركب ، اذا الλmax زادت و صار red shift فالانتقال بعود لل$\pi \rightarrow \pi^*$, و اذا قلت الλmax و صار blue shift فالانتقال بعود لل$n \rightarrow \pi^*$ لأنه المركب عمل H-bond مع ال non-bonding اللي عالاكسجين ف بس سقّطت عليها ضوء ضعفت الالكترونات و احتاجت طاقة عالية حتى تنتقل فقلت الλmax و راحت للblue shift

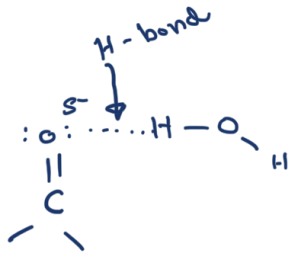


TABLE 14-2 Absorption by Organic Compounds Containing Heteroatoms with Nonbonding Electrons

Compound	λ_{max}, nm	ε_{max}
CH_3OH	167	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

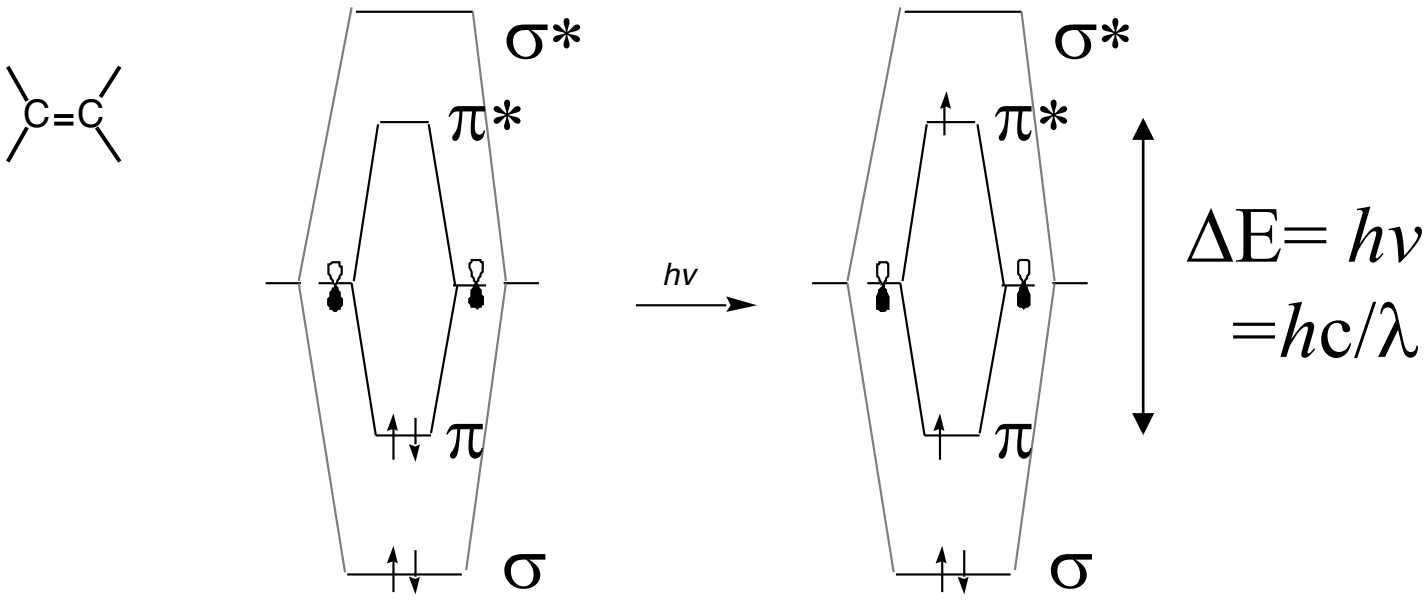
LOW!

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.

$n \rightarrow \pi^*$ → $\lambda_{max} > 180$ nm
→ ε 100 – 3000

$\pi \rightarrow \pi^*$ → $\lambda_{max} \geq 180$ nm
→ $\varepsilon \geq 10^3$



$\pi \longrightarrow \pi^*$

Example: ethylene absorbs at longer wavelengths:

λ_{max} = 185 nm ε= 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_3CCH_3 (=O)	*n*-Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	CH_3CH (=O)	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	CH_3COOH	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	CH_3CNH_2 (=O)	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	$n \rightarrow \pi^*$

المركبات الدوائية مش كلها polar بتدوب بالمي ، و حتى احضّرها و احللها بالUV ما بقدر ادوبها بsolvent polar لأنها مش hydrophilic فلازم اجيب solvent اخر يكون hydrophobic و يدوّب العينة و ما بيمتص طاقة الUV-vis فممكن نستخدم ال(alkanes (organic solvent لأنه بيمتص بمنطقة الuv-vis اما الانتقالات اللي تمتص ال uv-vis اللي هي

Olefins and aromatics

لا يمكن تحليلها و في كتير مواد بتدخل في هاي المنطقة, لذلك منستخدم هاي المواد كsolvent

λ_{max}

$\sigma \rightarrow \sigma^*$ < 180 nm

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

يمكن تحليل $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ 200-700 nm

Conclusion:-

$\pi \rightarrow \pi^*$

$n \rightarrow \pi^*$

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"

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)

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

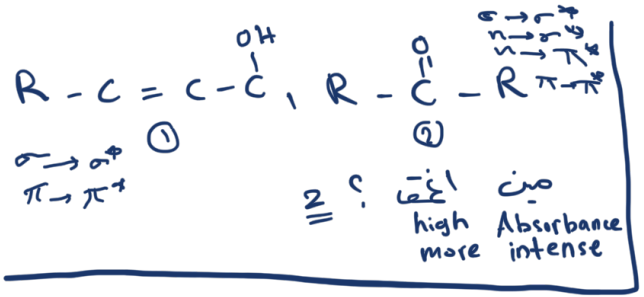
A substituent that contains unshared electron pairs (OH, NH, X)

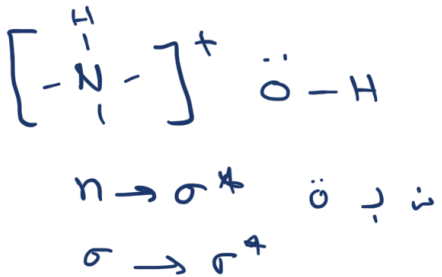
An auxochrome attached to a chromophore with π electrons shifts the λ_{max} to longer wavelengths

المركبات اللي فيها $\pi \rightarrow \pi^*$ هي المركبات اللي فيها chromophores اللي هي المجموعة اللي بتولّد امتصاص بمنطقة الuv ، اللي هي at least one pi (اللي بكون فيها عالاقل 1 π) فالانتقال هاد هو اللي منشوفه بالuv-vis لأنه قيم الλmax و الmolar absorptivity مطابقين للشروط

بسمّوا المركبات هاي color loving لأنه اصبحت تمتص في منطقة الuv-vis

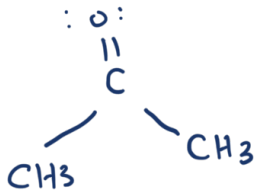
مجموعة الauxochome هي مجموعة اضافية فيها lone pair و فيها OH , N , halogens , S





الπبتمثل الchromophore و الlone pairs بمثلوا الauxochrome و الauxochrome بتزيد ال intensity

المركبين فيهم chromophore و فيهم π بس الفرق وجود الlone pair و ال $n \rightarrow \pi^*$ و هاد الانتقال هو اللي غمق اللون و قرب



$\sigma \rightarrow \sigma^*$

$n \rightarrow \sigma^*$ ← وجوده بنقص الطول

$\pi \rightarrow \pi^*$

$n \rightarrow \pi^*$

$CH_3 - C \equiv N$

لونه غامق لأنه في π ٢

$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

جزيء ما غمقت اللون بيني انا فتت جال vis لأنه بليت تشوف اللون

$CH_3 - CH = CH - \overset{OH}{\underset{|}{CH_2}}$

$\sigma \rightarrow \sigma^*$

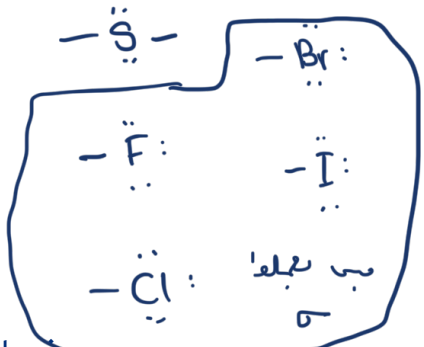
$n \rightarrow \sigma^*$

$\pi \rightarrow \pi^*$

$A - \ddot{O} - H$

$n \rightarrow \sigma^*$

$-\ddot{\underset{|}{N}}-$



فيها 3 lone pairs و auxochromes بولدوا

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)

Absorption Definitions

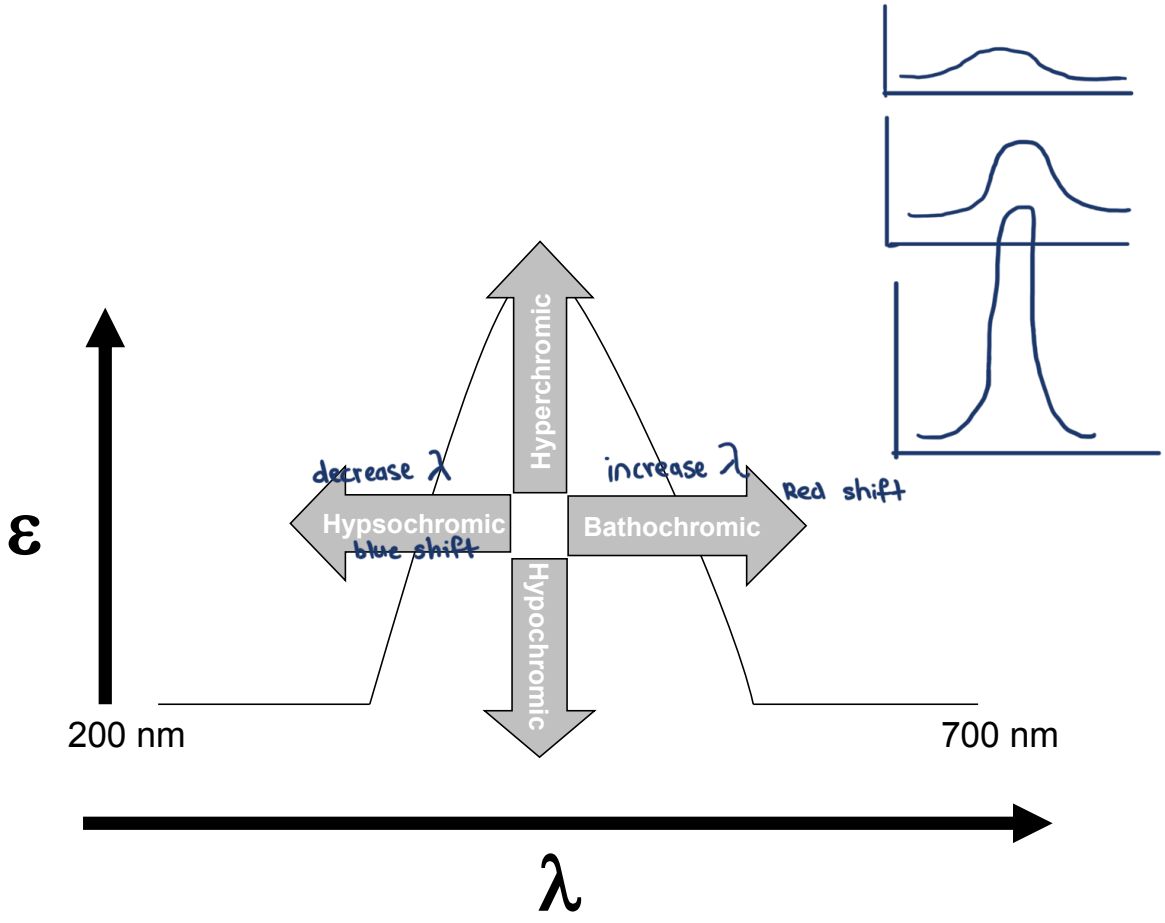
Bathochromic
A shift to longer wavelengths or red shift (increase in λ)

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

Hyperchromism
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})

السولفنت ممكن يغيرلي الwavelength يا بعمل red shift or blue shift و السولفنت ممكن يكون حمض او قاعدة


Hyperchromic
decrease λ
increase λ
Red shift
Hypsochromic
blue shift
Bathochromic
Hypochromic
ε
200 nm
700 nm
λ

الرسمة بتوضح تأثير الsolvent على ال λmax و التأثير عالmolar absorptivity او intensity

ممكن بس احول المركب لsln ، ال. λmax بتتغير او الmolar absorptivity بتتغير

الY-axis بتمثل الmolar absorptivity و الx-axis بتمثل ال. λmax

اذا زادت ال. λmax بسمي التأثير bathochromic او red shift

اذا قلت ال. λmax بسميه hypsochromic او blue shift

اذا زادت الintensity او الmolar absorptivity بسمي التأثير hyperchromism

اذا قلت الintensity او الmolar absorptivity بسمي التأثير hypochromism

Solvent Effects

التأثير على ال λ_{max}

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

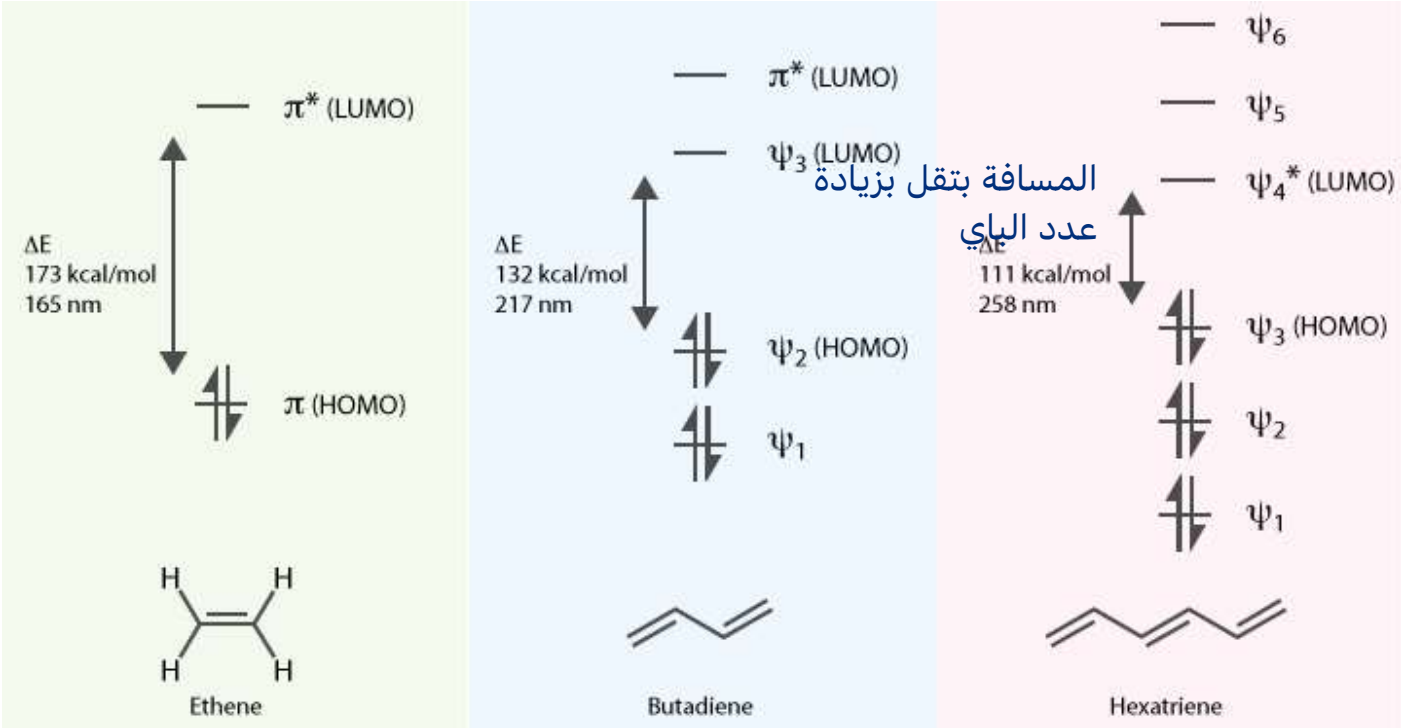
Molecules with absorption due to $n \rightarrow \pi^*$ transition exhibit blue shift when dissolved in solvents that are able to form hydrogen bonds

- 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 less antibonding character. 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.

Effect of Conjugation of Chromophores



اول عامل بأثر عالmolar absorptivity او الintensity هو الconjucation , كل ما تزيد عدد ال π بتزيد الmolar absorptivity و لازم يكونوا conjucated

كل ما زاد الفرق بين الhomo و الlomo , بتقل الintensity و المسافة بتقل بزيادة الchromphore و الauxochrome

كل ما زادت التربل بتزيد الmolar absorptivity و التربل هي extra pi

الauxochrome بزيد الmolar absorptivity

Effect of Conjugation of Chromophores

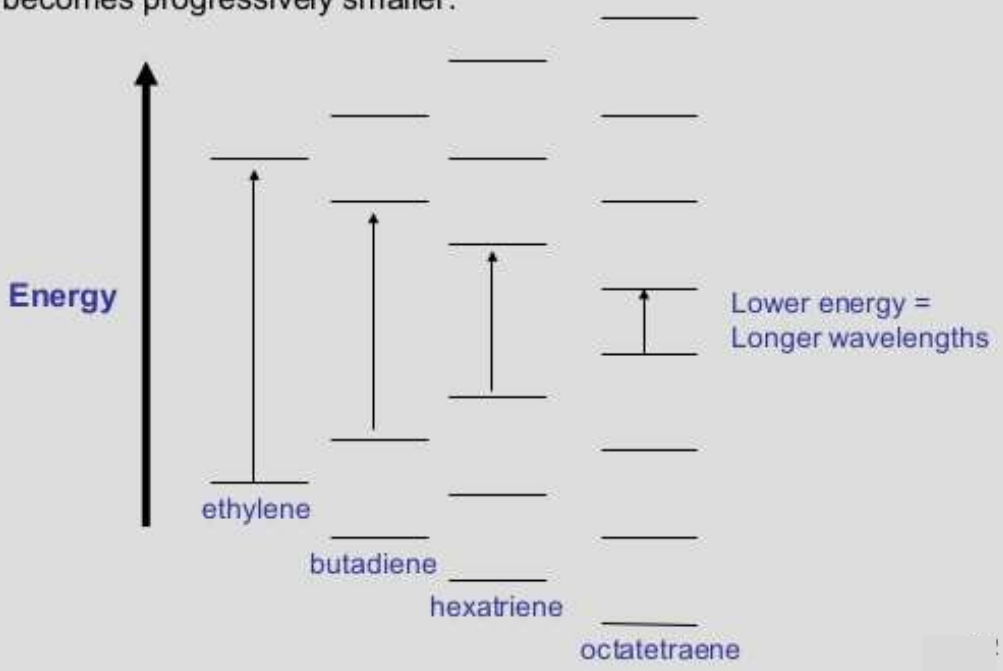
UV Spectroscopy

III. Chromophores

A. Substituent Effects

2. Conjugation – Alkenes

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



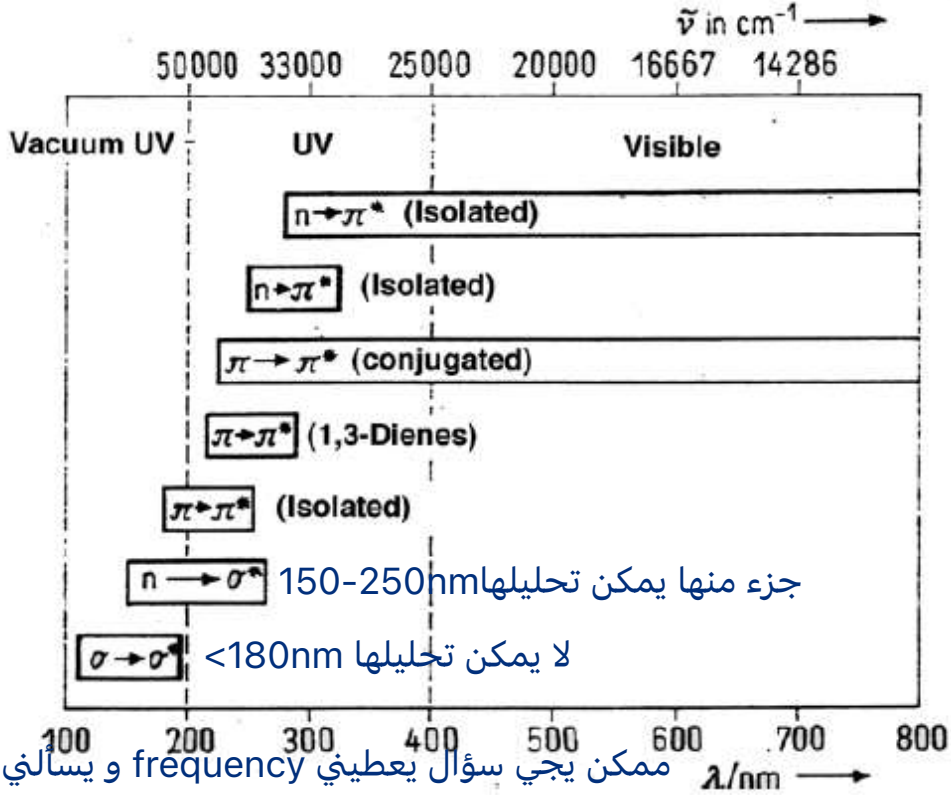
Effect of Conjugation of Chromophores

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

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

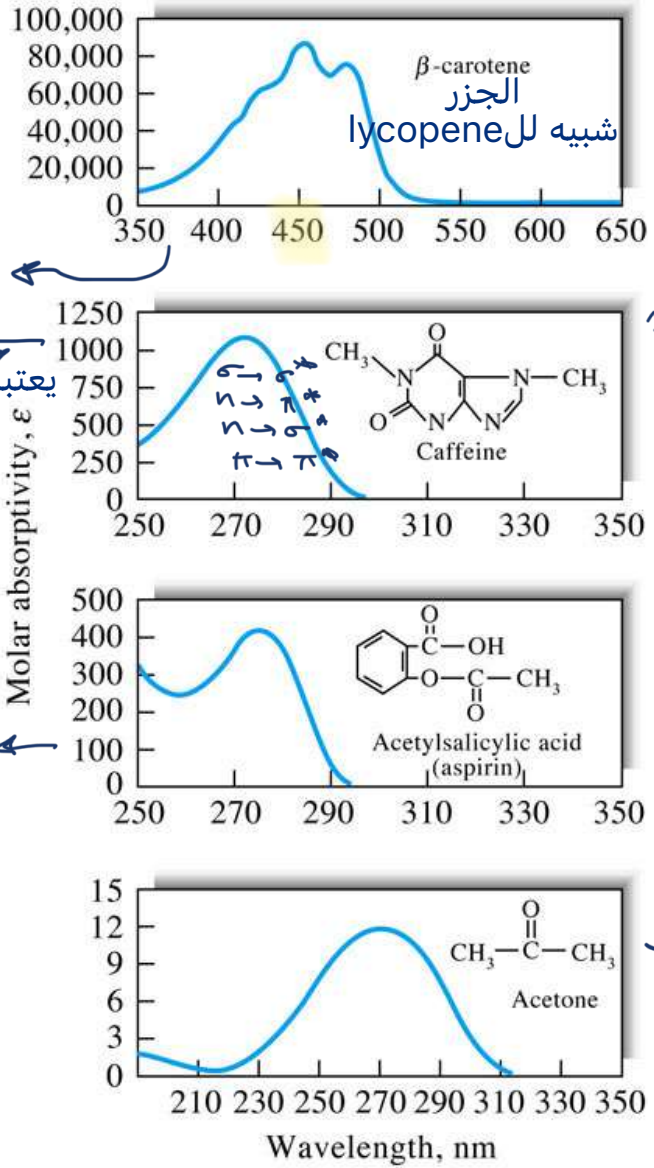
$\pi \rightarrow \pi^*$ transitions depend on the conjugation, so it can reach the visible region of radiation, causing the color of substances.



جزء منها يمكن تحليلها150-250nm

لا يمكن تحليلها <180nm

ممكن يجي سؤال يعطيني frequency و يسألني ب اي منطقة جاي فبحوله ل λ من القانون ، اذا كان اكبر بكتير من الvisible بكون بمنطقة الIR و لازم نكون عارفين انه الfar uv من 10-180 و الnear من 180-380 و الvis من 380-780 و اذا طلع اقل من 10 بكون بمنطقة الx-ray



عندها conjucated pi 11
فهاد بخلي لونه قوي

سؤال
متوقع

الانتقال يعود ل $\pi \rightarrow \pi^*$

الجزر
شبيه للlycopene

يعتبر مركب يمكن تحليله

فيه conjucation و بعطي لون غامق بسبب ال3 pi اللي بحلقة البنزين و الconjucation زاد الintensity

الفرق كان بالy-axis

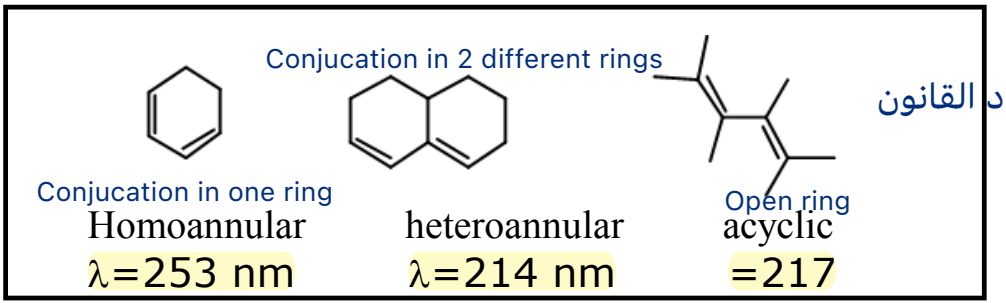
Empirical Rules for Calculating Uv/Vis Absorptions

كيف نحسب الλ_{max} Theoretically

المركبات اللي في one pi بتكون الλ_{max} 188 و يمكن تحليلها بس اللي العالم اللي حط القاعدة حكا بدي ابلش من 2 pi و يكون conjucation حتى اكون بالsafe side

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

- Parent:

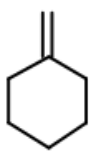


يعني 2-3 pi بستخدم هاد القانون

القانون لهاد السستم ، للمركب اللي فيه 2 pi conjucated و اذا كان اكتر من 3 بروح للقانون التاني

- Increments for:

	Pi تالتة
Double bond extending conjugation	+30
Alkyl substituent or ring residue كل زيادة عالسستم	+5
Exocyclic double bond بضيف 5	+5



exocyclic

اذا اجت الpi عشكل exo رح اضيف خمسة

Polar groupings:

-OC(O)CH3	+0
-OR	+6
-Cl, -Br	+5
-NR2	+60
-SR	+30

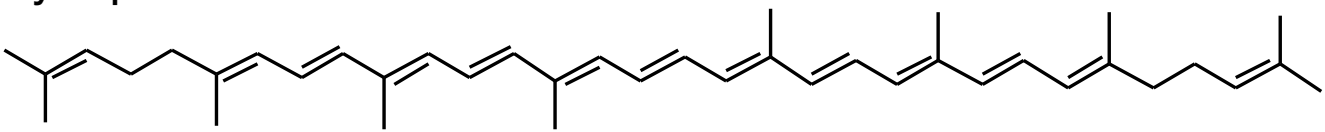
هاد القانون اذا كان اكتر من تلات pi

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.