تفريغ تحليل آلي

اسم الموضوع: Part(1) Application of UV /visible Molecular Apsorption spectrometry

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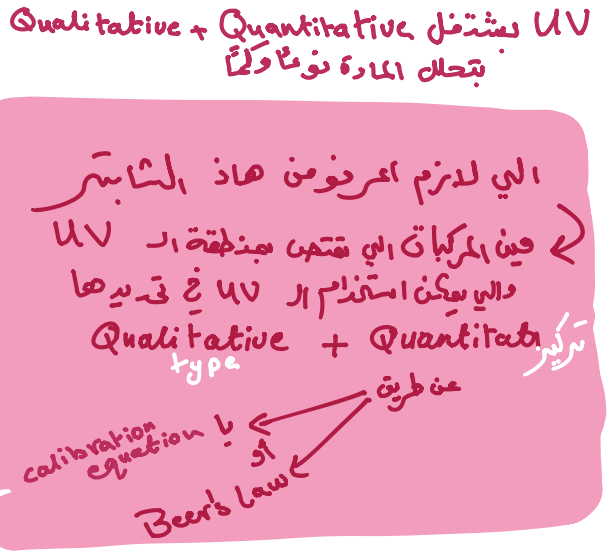
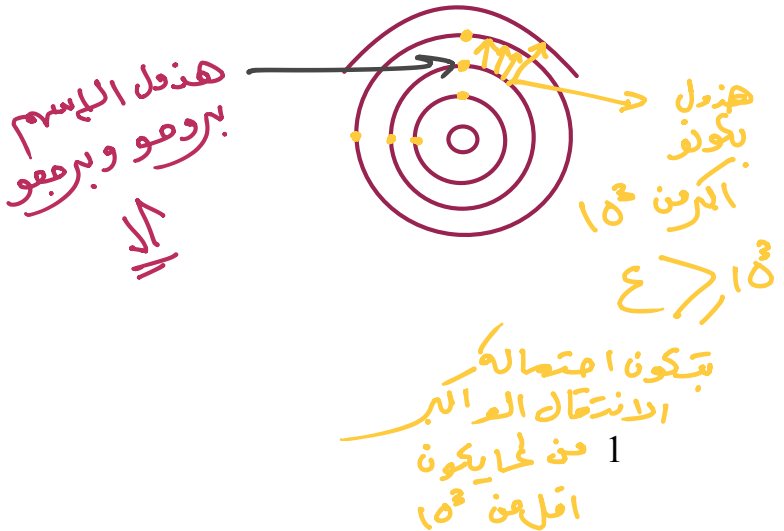
لجان الدُّفعات

Chapter 14
Application of Ultraviolet/Visible Molecular Absorption Spectrometry





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.

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

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.

ABSORBING SPECIES

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

$$M + h\nu \longrightarrow M^*$$ absorption of light

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

$$M^* \longrightarrow M + \text{heat}$$ or حنوء emession of light

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.

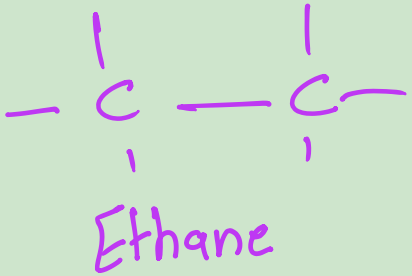
- المركبات اللي بتهمني بتحليل الـ pharmacentical compound هي اللي UU
اللي هي لـ bonded $\bar{e}$ / non bonding / π / σ اللي عاملة Covalent
ما بتهمنيش الـ ionic لأنها موجودة بالملح واستخدام الملح بالأدوية
قليل جدًا اللي برهموني اللي منها organic com. اللي فيها covalent (non/π/σ) bonding

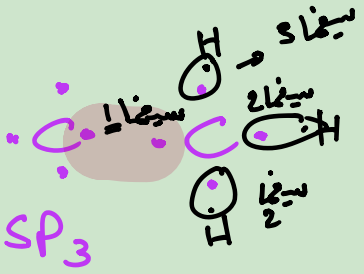
- المركبات اللي فيها عنصر الـ Transition metals الموجودة بالجدول الدوري ما بتهمنيش إلا بحالة واحدة اللي هي Transfer charge اللي هي charged $\bar{e}$
هذول ما برهموني بصناعة الأدوية.

Types of Absorbing Electrons

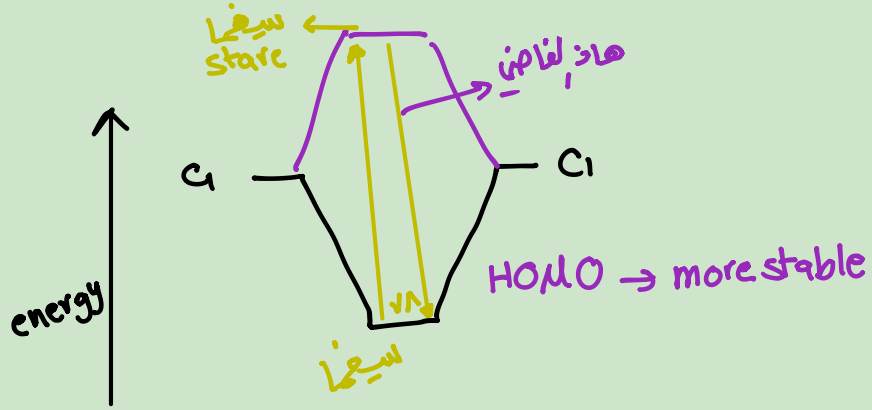
The electrons that contribute to absorption by a molecule are: (1) those that participate directly in bond formation between atoms; (2) nonbonding or unshared outer electrons that are largely localized about such atoms as oxygen, the halogens, sulfur, and nitrogen. The molecular orbitals associated with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

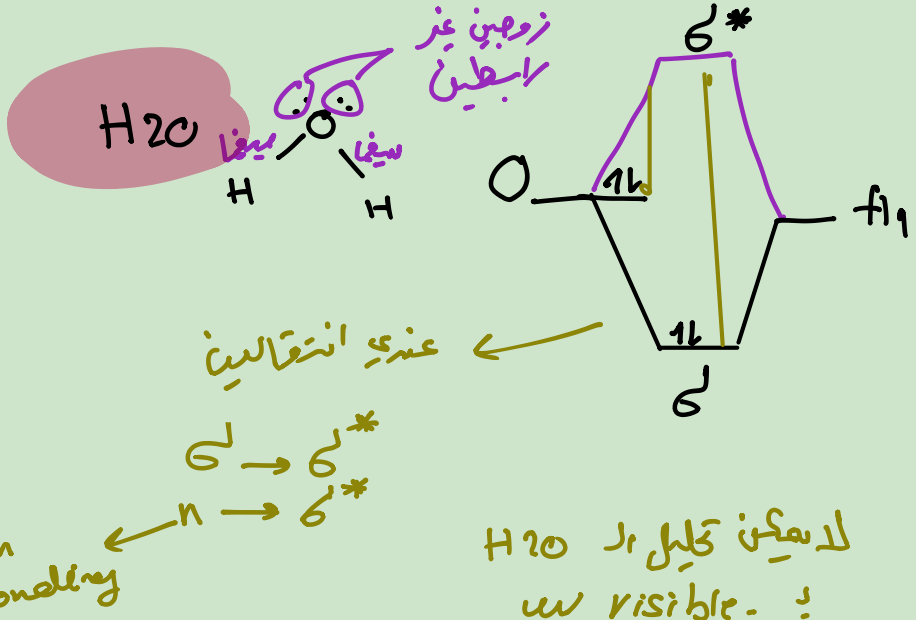
Alcane → مركب بس فيه سيغما

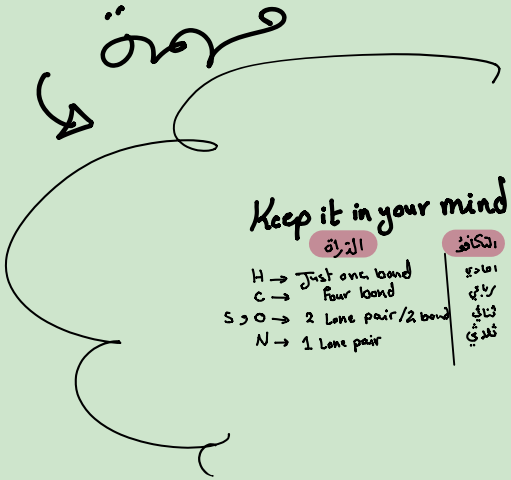




* السيغما بضعف لـ سيغما star بس







Types of Absorbing Electrons

σ و π ← يكون فيها

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.

unshared + nonbonding ال

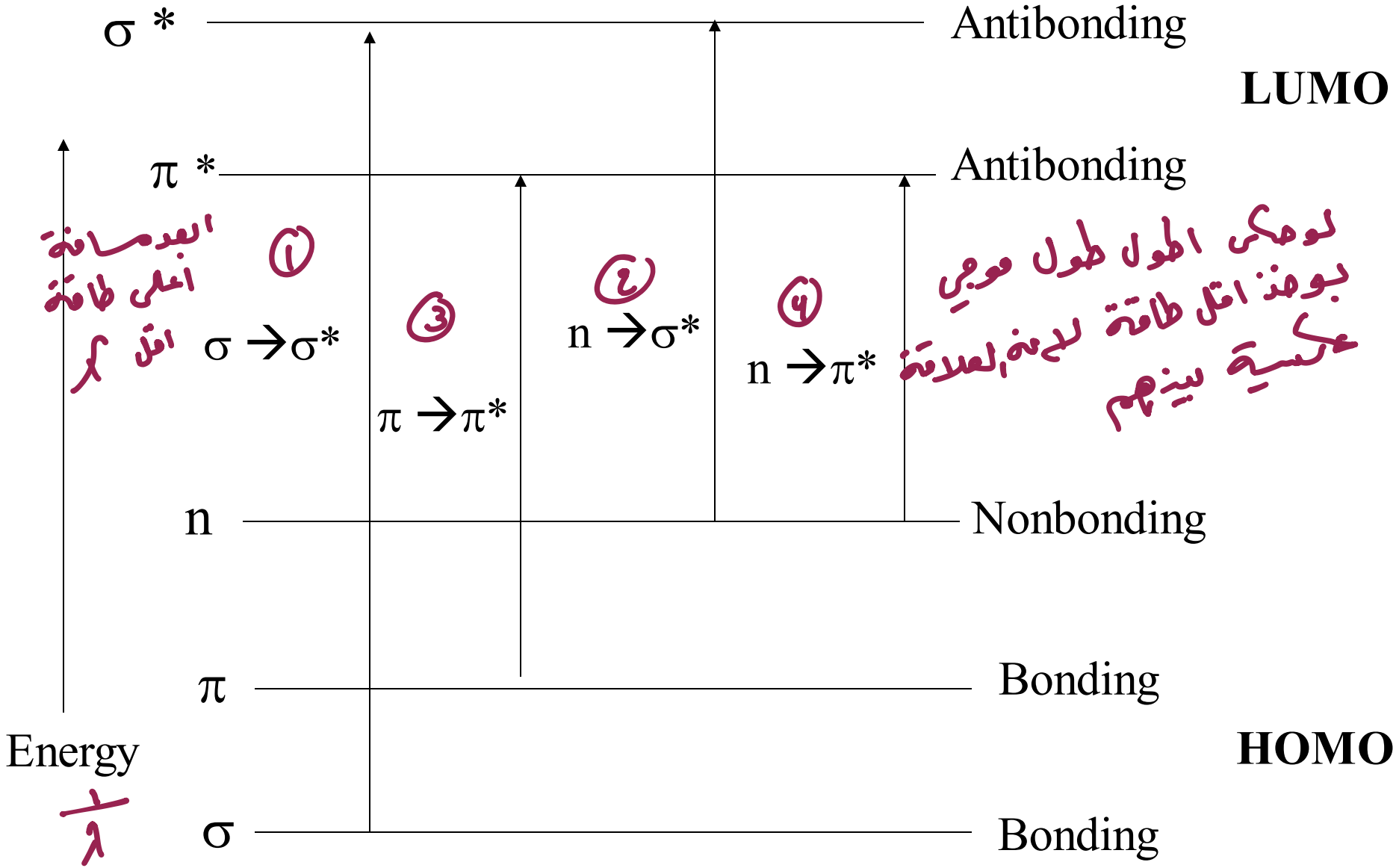
(n) بنعبر عنها بـ

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:

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

LUMO: lowest unoccupied molecular orbital



HOMO: highest occupied molecular orbital

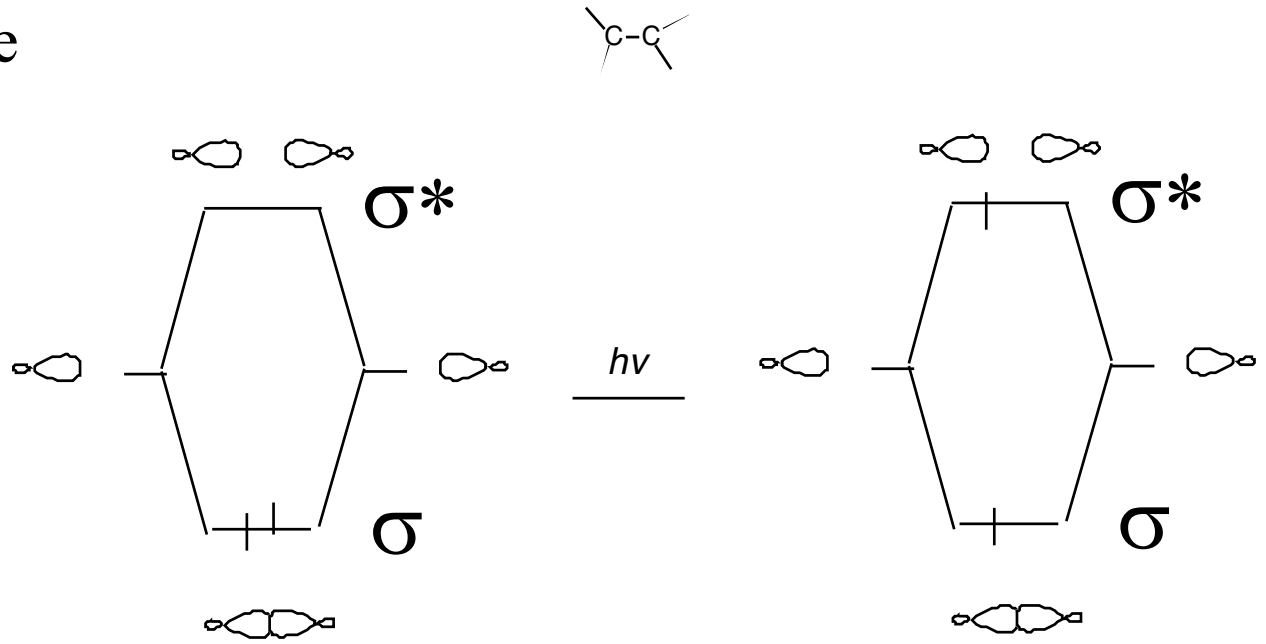
For convenience of reference, definitions of the various spectral regions have been set by the Joint Committee on Nomenclature in Applied Spectroscopy:

Region	Wavelength (nm)
Far ultraviolet	10-200
Near ultraviolet	200-380
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



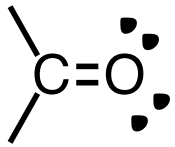
$\sigma \longrightarrow \sigma^*$

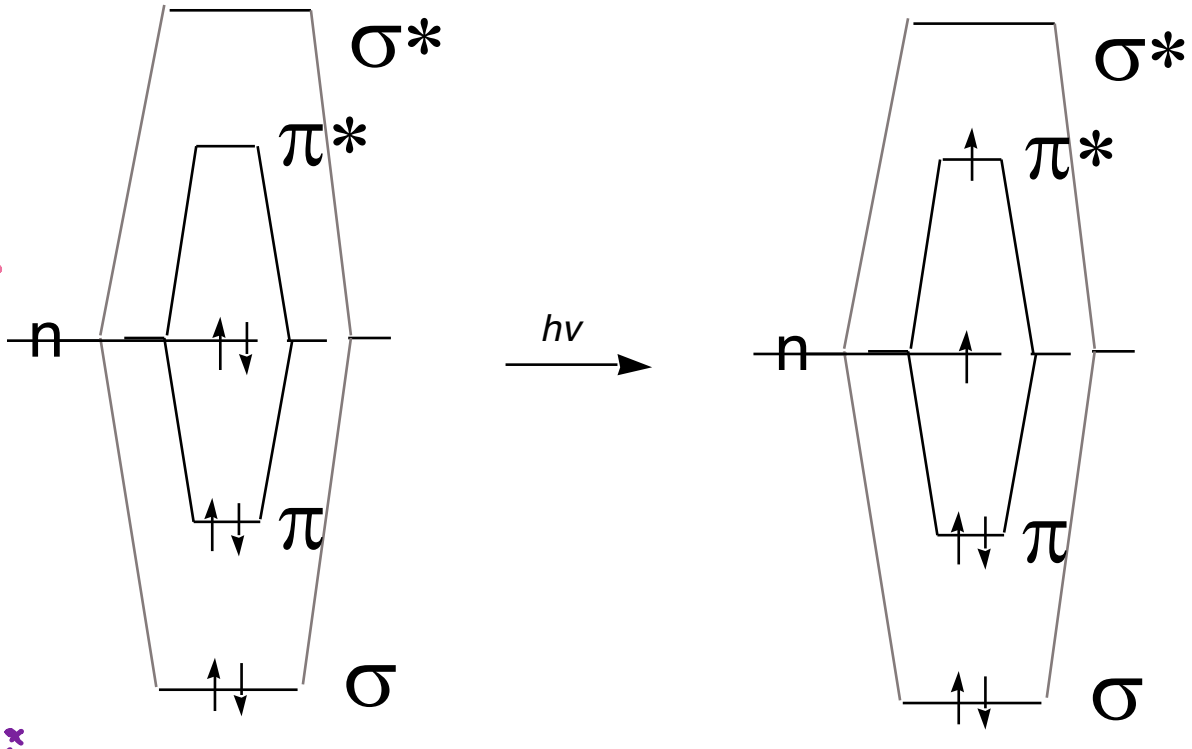
$\lambda_{max} = 135$ nm (a high energy transition)

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}.





عندي اربع انتقالات

$\sigma \rightarrow \sigma^*$

$n \rightarrow \sigma^*$

$\pi \rightarrow \pi^*$

$n \rightarrow \pi^*$

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

$n \longrightarrow \pi^*$

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."

طبقت شرطين

Example:

Acetone: $(CH_3)_2CO$

π–π*	λ_{max} = 188 nm	;	ε= 1860 ✔
n–π*	λ_{max} = 279 nm	;	ε= 15 ✗

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!

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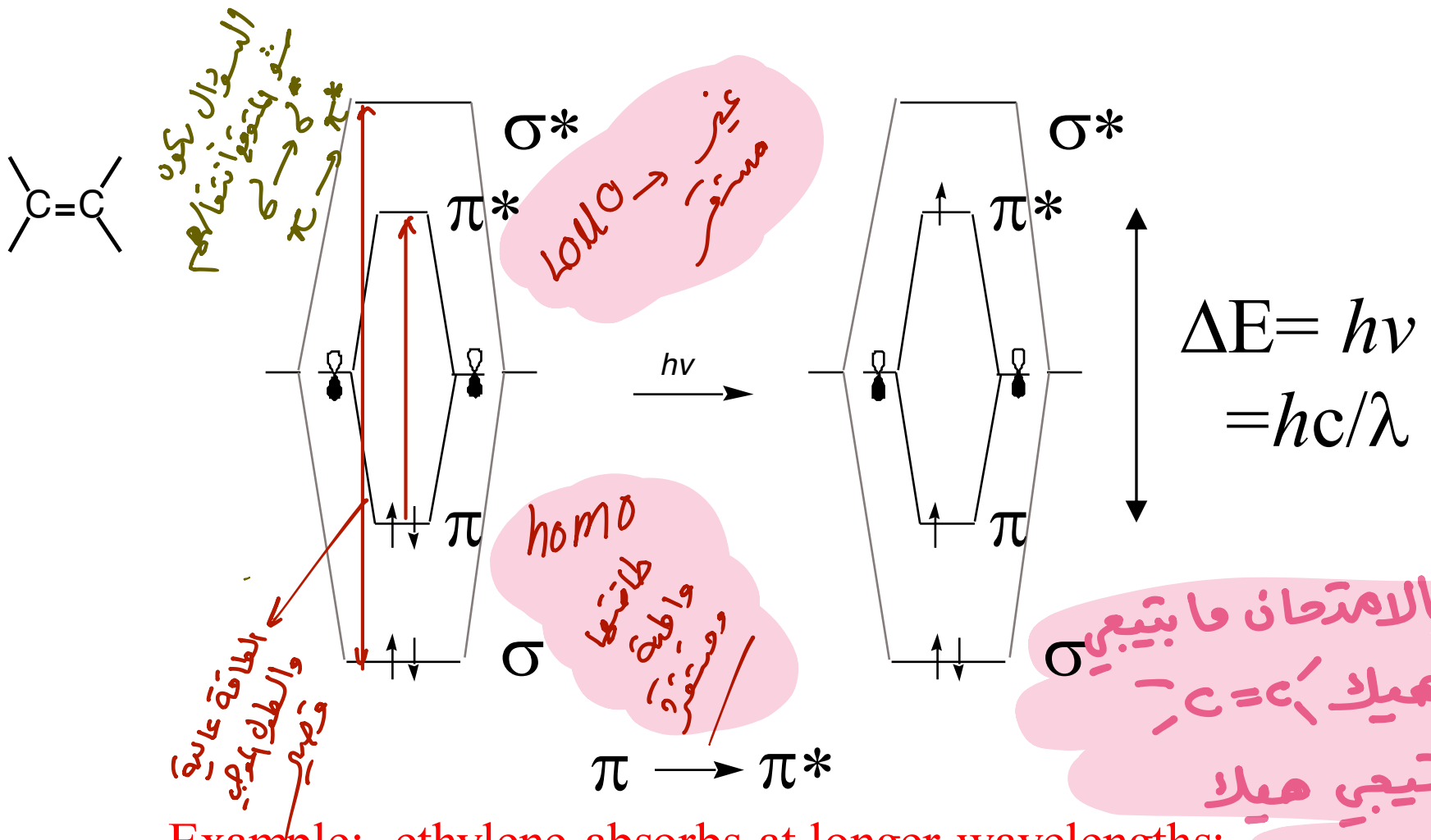
n →π* and π →π* Transitions

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.



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	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$CH_3\overset{\overset{O}{\|}}{C}H$	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	CH_3COOH	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$CH_3\overset{\overset{O}{\|}}{C}NH_2$	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	$n \rightarrow \pi^*$

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ترتيب كـ طاقة

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

Olefins and aromatics

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

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

$\pi \rightarrow \pi^*$

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