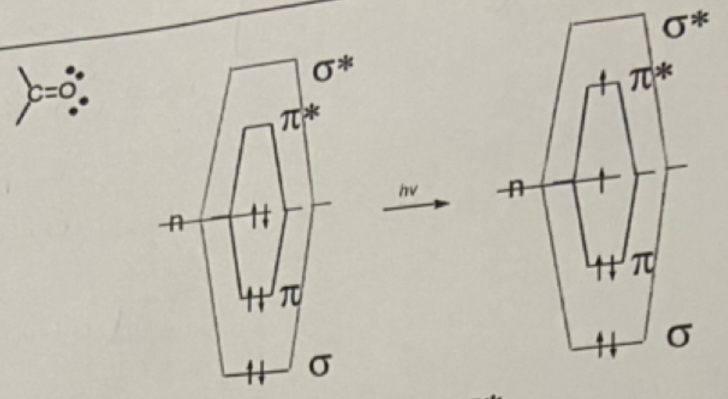


n ⟶ π*

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:

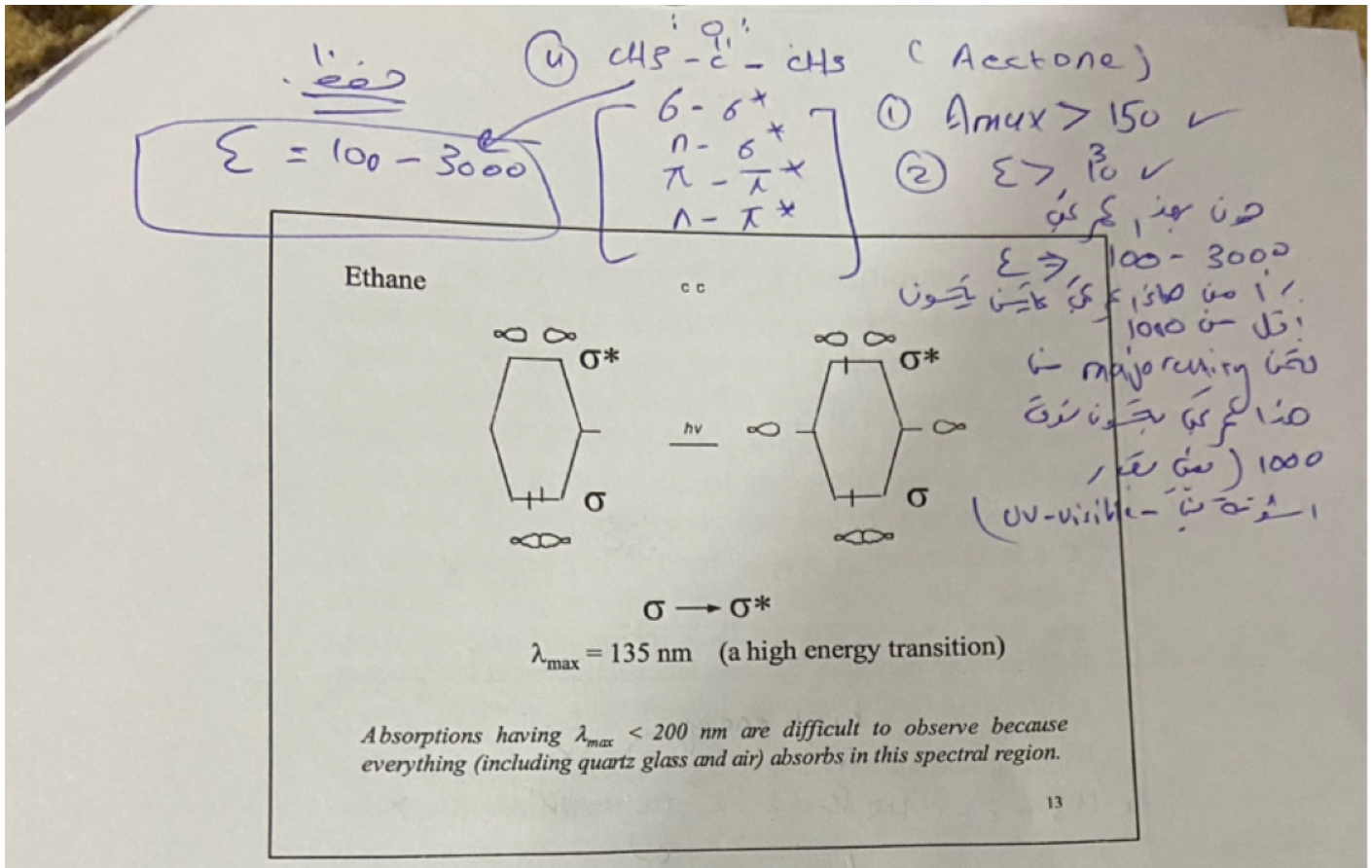
Acetone: π–π* λ_{max} = 188 nm ; ε= 1860

n–π* λ_{max} = 279 nm ; ε= 15

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! (200–900)



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}.

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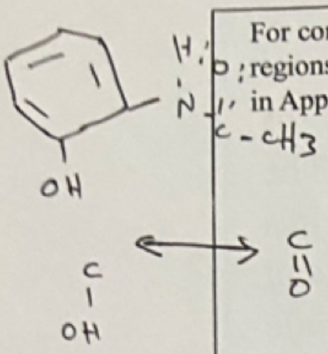
→ paracetamole in (NaOH + H2O), why?
two form not one form



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

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

one pH acidic or basic

high energy
Low λmax

low energy
high λmax

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

λmax > 150
$\varepsilon > 10^3$

① λmax > 150
② $\varepsilon > 10^3$

① Ex: ethane C_2H_6
no see (UV)
λmax = 135

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 (CH4) can undergo only σ →σ* transitions, exhibits an absorption maximum λmax at 125 nm. Absorption maxima due to σ →σ* transitions are never observed in the ordinarily accessible ultraviolet region **(Far UV range).**

② CH_3OH
$\sigma-\sigma^*$
$n-\sigma^*$
λmax > 150 ✓
$\varepsilon < 10^3$ ✗

③ CH_2CH_2
$\sigma-\sigma^*$
$\pi-\pi^*$
λmax > 150 ✓
$\varepsilon > 10^3$ ✓
UV-visible ✓

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:

σ →σ*, n →σ*, n →π*, and π →π*.

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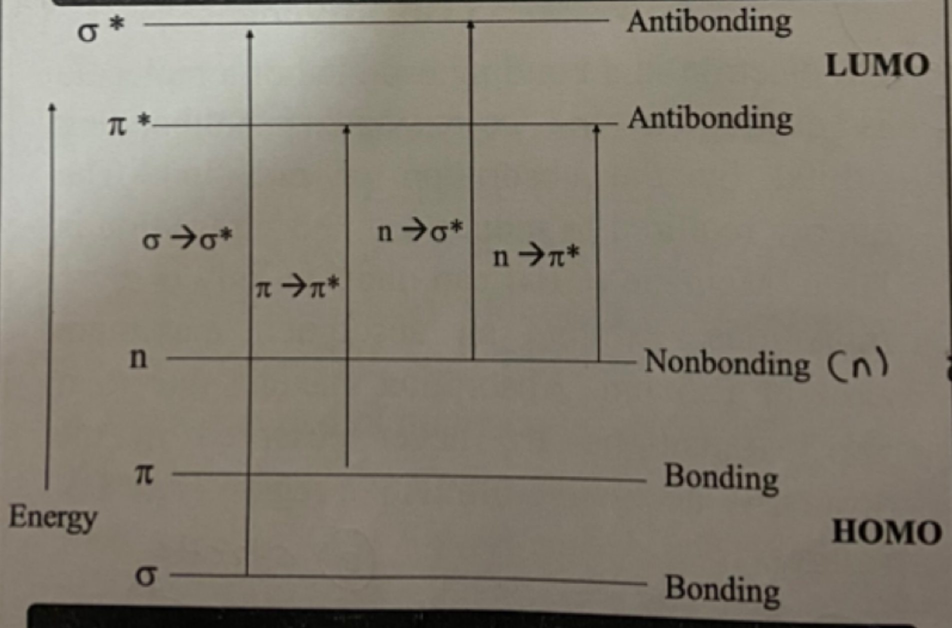
* حتى يصير إنتقال، اقدر اشوفه UV-visible :

① $\lambda_{max} > 150$ nm

② ε (molar observtivity) $> 10^3$

مهم جداً

[redacted]



غير رابطة مع حدا

[redacted]

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* إذا كان مركب معظم يحتوي على σ فقط ما بقدر احلله $\lambda_{max} < 150$ لأنه ما بشوفه UV-visible أقل

* ملاحظة مهمة ① =>

② (صنعة π ← n بقدر احلل)

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})

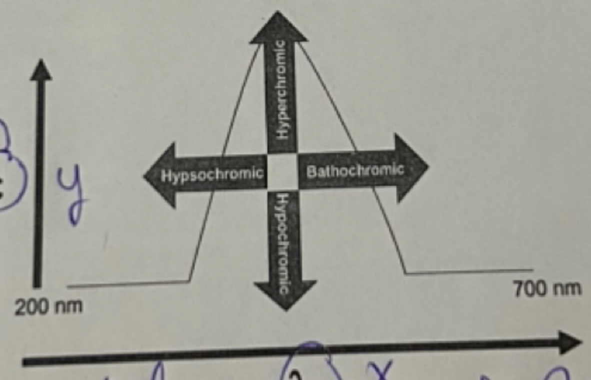
Hypochromism
A decrease in intensity of an absorption band (decrease in ε_{max})

زيادة في إمتصاص جزيئية

* Hyperchromism ⇒ increas intensity, increas Emax
* Hypochromism ⇒ decreas intensity, decrease Emax

نقصان في امتصاص جزيئية

yellow (between them)



intensity عندها زيادة في امتصاص جزيئات

ε y

Low λmax, high energy

high λmax, Low energy

green / Blue-shift ← λ x → Red-shift

λmax < 380 | λmax > 500

λmax = 500 nm

* اذا زادت عن 500 λmax) Red-shift (Bathochromic
* اذا قلت عن 500 λmax) Blue shift (Hypsochromic

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)

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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)
CH_3CSCH_3	273	14	n-π* (C=O)
$CH_3N=NCH_3$	460	weak	n-π* (C=S)
	347	15	n-π* (N=N)

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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 (C=O)	n-Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	CH_3CH (C=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 (C=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	$n \rightarrow \pi^*$

Olefins and aromatics

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

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

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

اذا زادت عدد π بكون اغمق لون . ⇐ note

200   $n-\pi^*$ الاقصى (270)

(1) ethene: H₂C=CH₂ (π, σ) — $\pi-\pi^*$, $\sigma-\sigma^*$

(2) $CH_3-\overset{\cdot\cdot O \cdot\cdot}{\overset{\|}{C}}-CH_3$ acetone — $n-\sigma^*$, $\sigma-\sigma^*$, $n-\pi^*$, $\pi-\pi^*$

اذا السلسلة اغمق ، (2) اغمق زادة منه (Auxochrome $n-\pi^*$

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 (λ< 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 (λ>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”

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.

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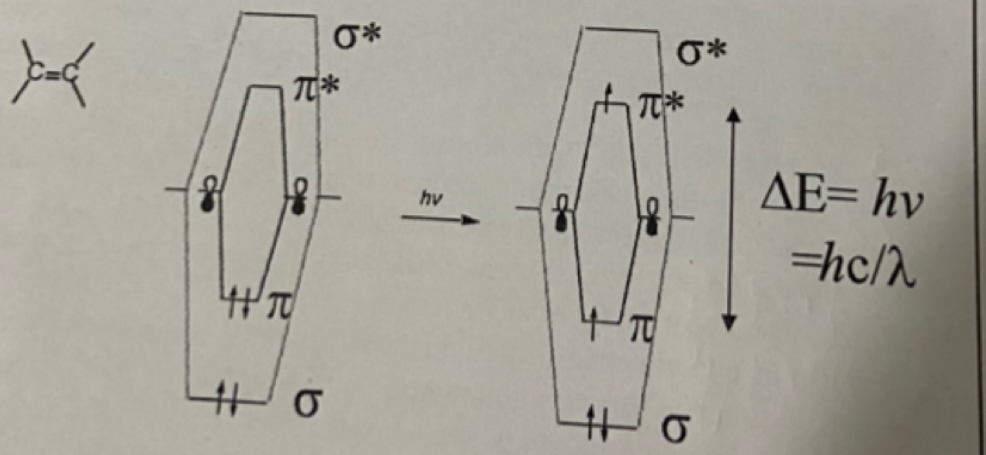

π → π*

Example: ethylene absorbs at longer wavelengths:
λ_{max} = 185 nm ε= 10,000

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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

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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

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