



34:50

start

## Chapter 14

# Application of Ultraviolet/Visible Molecular Absorption Spectrometry

main idea g

molecule absorb light → electron move to a higher energy state (gets excited) → measure Absorption → identify or quantify the compound

$$Y = mX$$

intercept = 0

$$A = \epsilon b c$$

1

$$m = \epsilon$$

في اسئلة فحمه  
check them out  
best of luck

By raneem Al-sayouf

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.

احتمالية حدوث  
والتركيز

# Absorptivity (a or $\epsilon$ )

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

- Is termed **molar absorptivity ( $\epsilon$ )** if concentration is expressed in molarity (M, mol/L)

- Can be calculated using Beer's Law ( $A = \overset{\text{Absorbance}}{\bar{y}} abc = \epsilon bc$ )

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

- Magnitude of  $\epsilon$  is an indication of the probability of the electronic transition *strong absorption*

15. When the path length of the cell is 2 cm, the absorbance of the solution is 0.3 what would be the absorbance if the path length is increased to 4 cm?

- 1) 2
- 2) 0.6
- 3) 0.15
- 4) 0.3

$\lambda_{\max} 188 \leq$   
 $\epsilon 10^3 \leq$   
 أعم شريطة  
 لنقد رتقيست  
 العينة UV in

$0-10^5$

احتمالاً من الانتقال

# 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  $\epsilon$  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.

احتمال حدوثهم  
 $0.01 >$

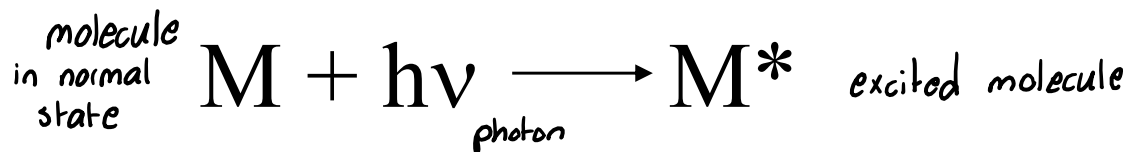
Forbidden transitions

← low intensity  
 أقل من  $10^3$   
 أكثر من  $10^3$   
 strong absorption

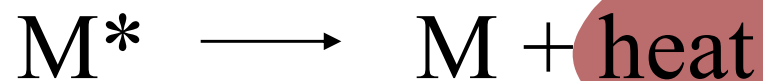


# ABSORBING SPECIES

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



The lifetime of the excited species is brief ( $10^{-8}$  to  $10^{-9}$  s). **Relaxation** involves conversion of the excitation energy to 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)  $\pi$ ,  $\sigma$ , and  $n$  electrons  $\rightarrow$  organic compounds  
covalent bonds

(2) d and f electrons

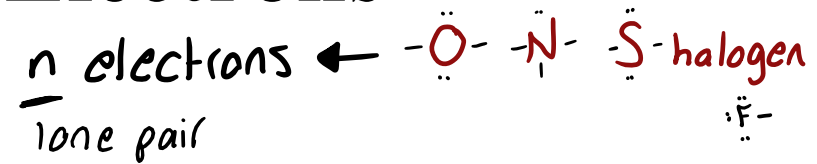
(3) charge transfer electrons.

} inorganic chemistry أملاح  
تأدر لستخدامهم  
بالأدوية  
(ionic bonds)

# Types of Absorbing Electrons

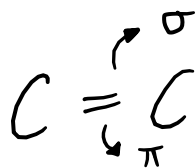
- bonding electrons

- non bonding 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 ( $\sigma$ ) orbitals, and the corresponding electrons are  $\sigma$  electrons.

# Types of Absorbing Electrons



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

*direct overlap head to head*

## sigma ( $\sigma$ ) bond

- every single bond is a ( $\sigma$ )



- head on overlap of atomic orbitals

- require a lot of energy  
to become excited

## $\pi$ bond



- parallel overlap of p orbitals



less energy to absorb light

Absorb UV light ✓

## non bonding (n) electrons

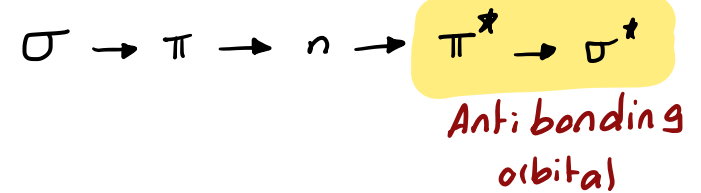
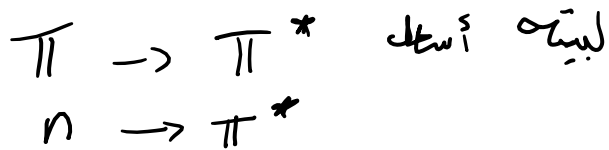
- lone pair electrons



2 lone  
pairs

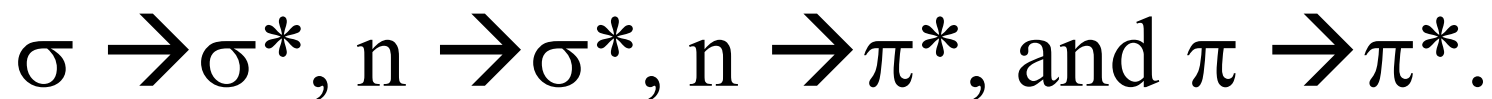
1 lone  
pair

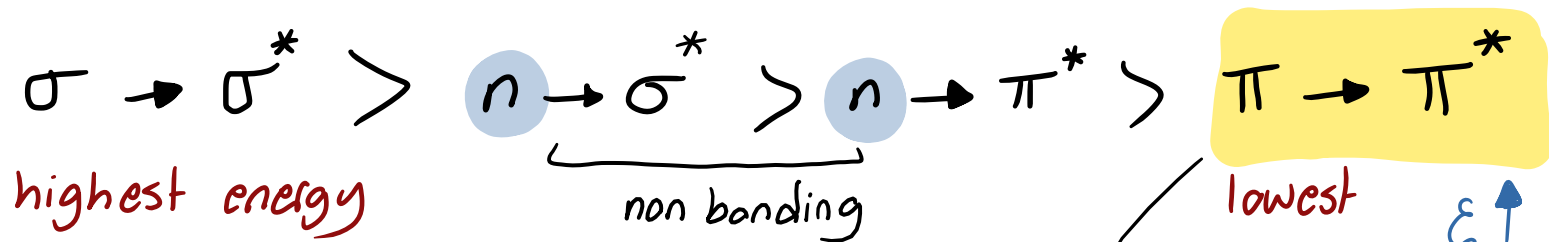
3 lone pairs



# 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  $\pi$  and  $\sigma$  orbitals. Electronic transitions among certain of the energy levels can be brought about by the absorption of radiation. Four types of transitions are possible:





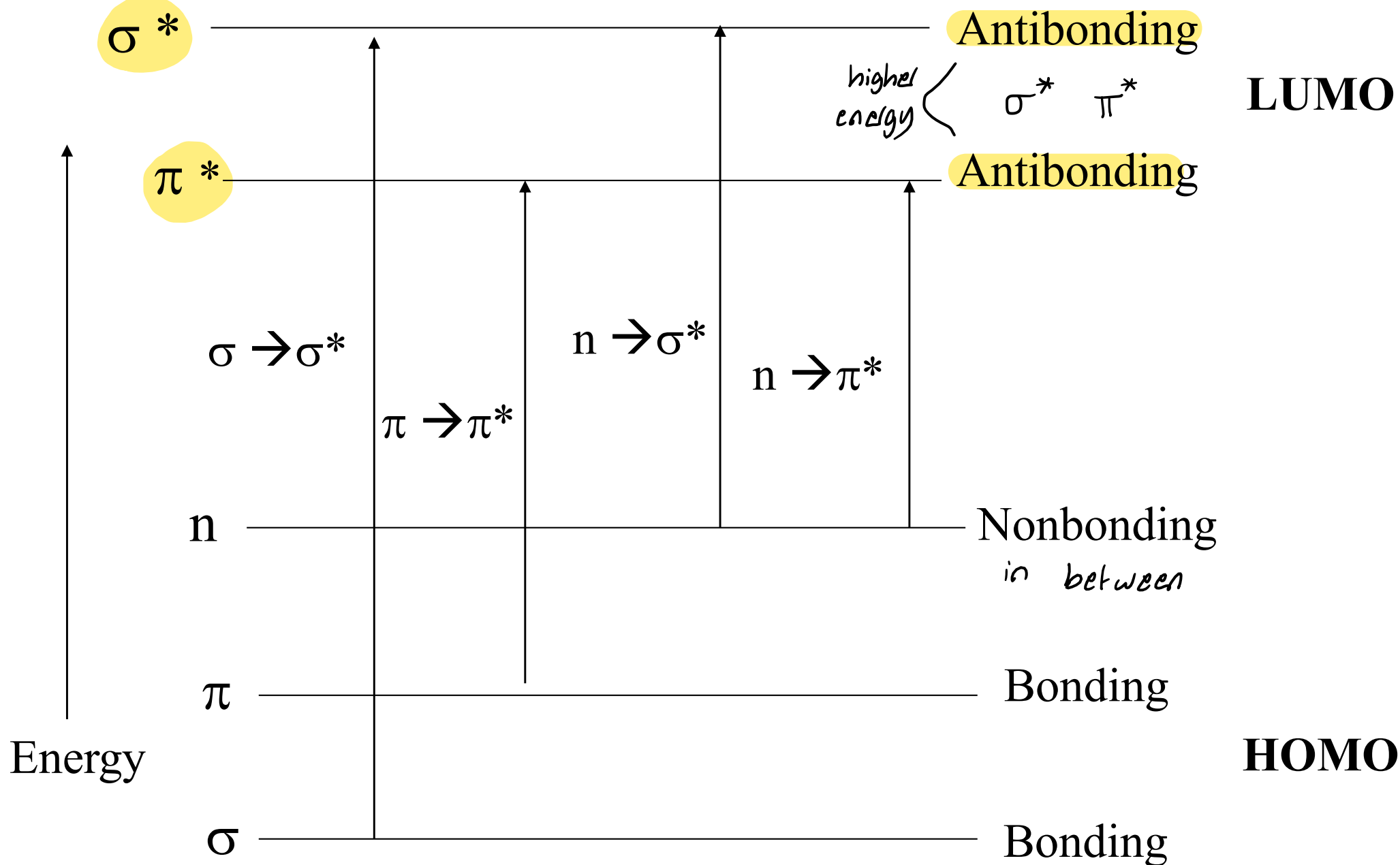
أكثر حدوثاً  
 تكراراً

$\epsilon \uparrow$   
 $\lambda \uparrow$

ترتيبهم حسب  
 الطاقة

العكس  
 wavelength  
 probability ( $\epsilon$ )

**LUMO:** lowest unoccupied molecular orbital



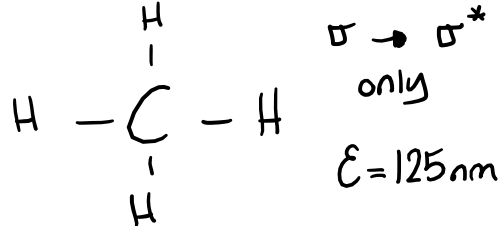
**HOMO:** highest occupied molecular orbital



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 |

↪ high  $\lambda$  low energy



Short Wavelength  $\lambda = 125 \text{ nm}$   
high Energy  $\lambda > 188$  اقل الشرح الاوى

## $\sigma \rightarrow \sigma^*$ Transition

An electron in a bonding  $\sigma$  orbital of a molecule is excited to the corresponding antibonding orbital by the absorption of radiation.

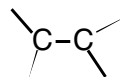
The energy required to induce a  $\sigma \rightarrow \sigma^*$  transition is large. Methane ( $\text{CH}_4$ ) can undergo only  $\sigma \rightarrow \sigma^*$  transitions, exhibits an absorption maximum

$\lambda_{\text{max}}$  at **125 nm**. Absorption maxima due to  $\sigma \rightarrow \sigma^*$  transitions are never observed in the

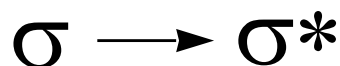
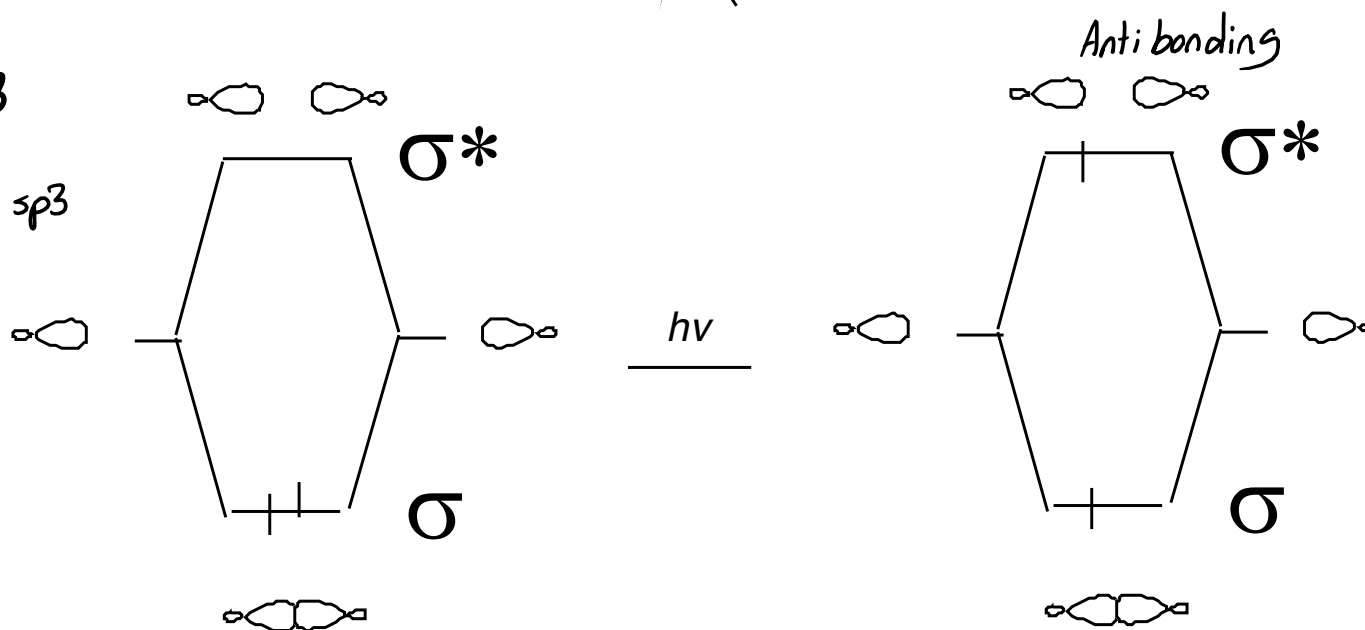
ordinarily accessible ultraviolet region (**Far UV range**).

can't do it in uv light

C-C  
Ethane  
CH<sub>3</sub>CH<sub>3</sub>



saturated sp<sup>3</sup>



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

Far UV region

اعتماداً على الذرات ( 188 nm )

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

Exam tip

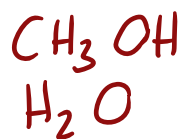
A molecule containing only single bonds (like methane or ethane) usually:

- Has only  $\sigma \rightarrow \sigma^*$  transitions.
- Absorbs below 200 nm.
- Is not usually detected in the normal UV-Vis region (200–800 nm).

34. Material of the cell used in UV spectrophotometer is

- 1) Plastic
- 2) Glass
- 3) Quartz
- 4) Potassium bromide

3



Anti bonding sigma star

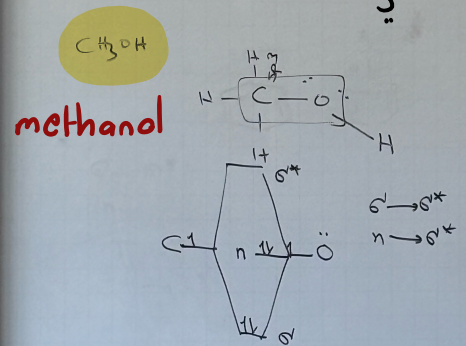
## $n \rightarrow \sigma^*$ Transitions

only single bonds  $\sigma$

lone pair

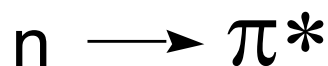
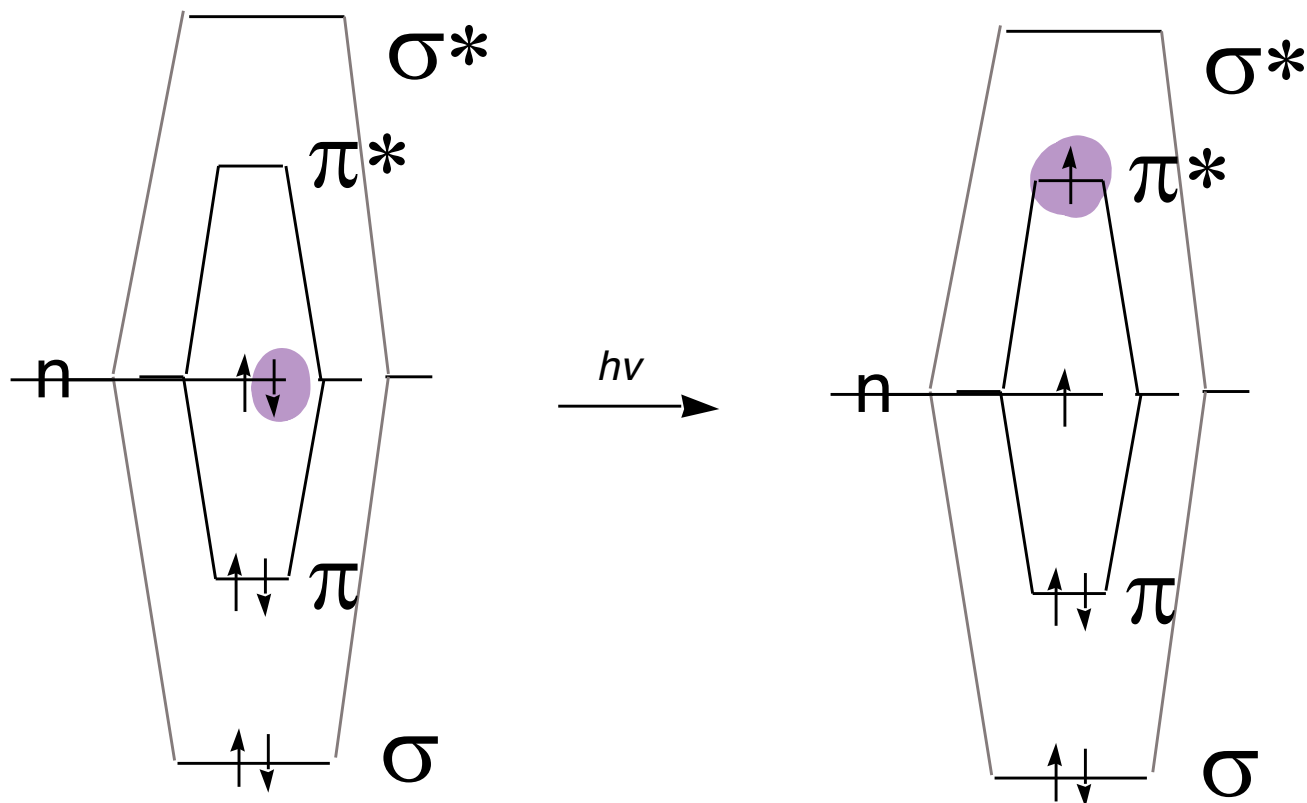
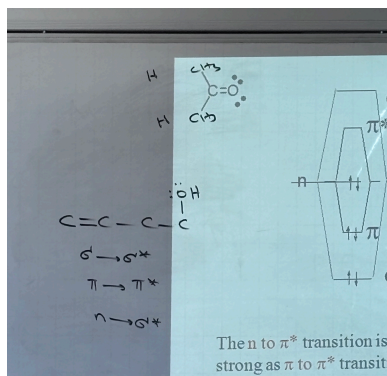
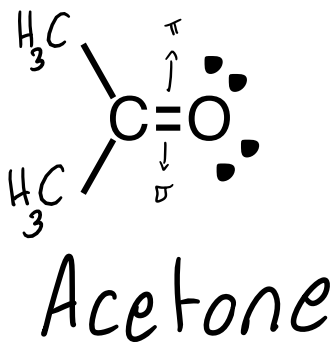
Saturated compounds containing atoms with unshared electrons are capable of  $n \rightarrow \sigma^*$  transitions. These transitions require **less energy** than the  $\sigma \rightarrow \sigma^*$  type and can be brought about by radiation in the region of between **150 and 250 nm**, with most absorption peaks appearing below 200 nm. The molar absorptivities ( $\epsilon$ ) are **low to intermediate** in magnitude and range between **100 and 3000 L cm<sup>-1</sup> mol<sup>-1</sup>**.

الطيف من 188



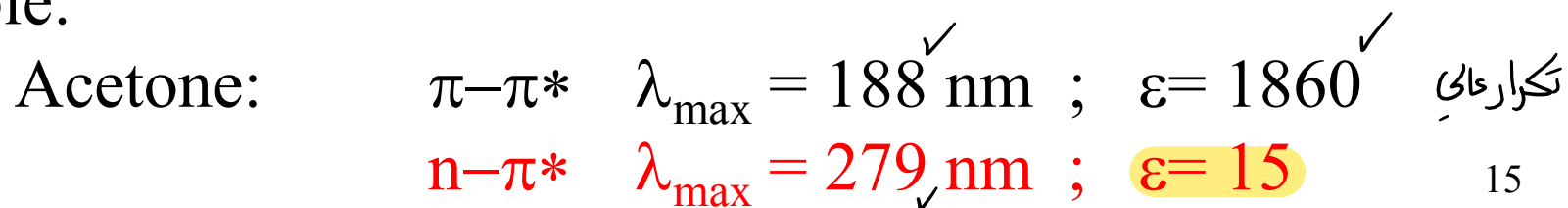
|                                   |                     |
|-----------------------------------|---------------------|
| molar absorptivity ( $\epsilon$ ) | 100 - 3000          |
|                                   | low to intermediate |

That's why UV-Vis spectroscopy is especially useful for compounds containing double bonds ( $\pi$  electrons) and atoms with lone pairs ( $n$  electrons), such as oxygen, nitrogen, and sulfur. Compounds with only single bonds ( $\sigma$  bonds) generally absorb only very high-energy UV light and are usually not detected in the normal UV-Vis range.



The  $n$  to  $\pi^*$  transition is at even lower wavelengths but is not as strong as  $\pi$  to  $\pi^*$  transitions. It is said to be “forbidden.”

Example:



احتمالاً حدوث قلیلیه

37. Acetone shows the UV absorption maximum at 166, 199 and 273 nm. The absorptions are respectively due to

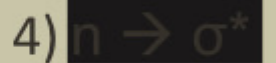
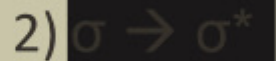
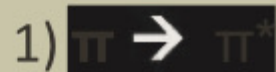
1.  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$
2.  $n \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$
3.  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$  and  $n \rightarrow \pi^*$
4.  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$



②



## 1. The forbidden transition is



$n \rightarrow \pi^*$  is Symmetry-Forbidden:

According to quantum mechanical selection rules (specifically spatial/symmetry rules), a transition is forbidden if the initial and final orbital wavefunctions do not overlap with the correct spatial symmetry. Non-bonding ( $n$ ) orbitals and  $\pi^*$  orbitals lie in perpendicular planes, making this transition **symmetry-forbidden**. Because it is forbidden, its absorption peak is characteristically very weak ( $\epsilon < 100 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).

$\pi \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ , and  $n \rightarrow \sigma^*$  are Allowed:

These transitions meet the symmetry and selection requirements, meaning they are **allowed** transitions with much higher molar absorptivity values.

3

38. The values of  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  of a solution of ethanal in hexane are 290 nm ( $\epsilon_{\text{max}}$  15) and 180 nm ( $\epsilon_{\text{max}}$  10000). Which of the following statements regarding the above observation is not true ?

- 1)  $\lambda_{\text{max}}$  290 nm corresponds to  $n \rightarrow \pi^*$  and  $\lambda_{\text{max}}$  180 nm corresponds to  $\pi \rightarrow \pi^*$
- 2) 290 nm peak is tiny as compared to the one at 180 nm
- 3)  $\lambda_{\text{max}}$  290 nm corresponds to low absorbance and  $\lambda_{\text{max}}$  180 corresponds to high absorbance
- 4) The absorbance at 180 nm needs less energy than the absorption at 290 nm

$$\downarrow E = \frac{hc}{\lambda} \uparrow$$

4

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

| Compound                          | $\lambda_{\text{max}}$ , nm | $\epsilon_{\text{max}}$ |
|-----------------------------------|-----------------------------|-------------------------|
| CH <sub>3</sub> OH                | 167                         | 1480                    |
| (CH <sub>3</sub> ) <sub>2</sub> O | 184                         | 2520                    |
| CH <sub>3</sub> Cl                | 173                         | 200                     |
| CH <sub>3</sub> I                 | 258                         | 365                     |
| (CH <sub>3</sub> ) <sub>2</sub> S | 229                         | 140                     |
| CH <sub>3</sub> NH <sub>2</sub>   | 215                         | 600                     |
| (CH <sub>3</sub> ) <sub>3</sub> N | 227                         | 900                     |

some advanced  
 instruments can  
 absorb it  
 بعض الأمثلة ← ١٨٨

**LOW!**



30. Acetaldehyde shows the transitions

1)  $\sigma-\sigma^*$  and  $\pi-\pi^*$

2)  $n-\pi^*$  and  $\pi-\pi^*$

3)  $\sigma-\sigma^*$  and  $n-\pi^*$

4)  $\sigma-\sigma^*$ ,  $\pi-\pi^*$  and  $n-\pi^*$

$$\lambda \geq 188$$

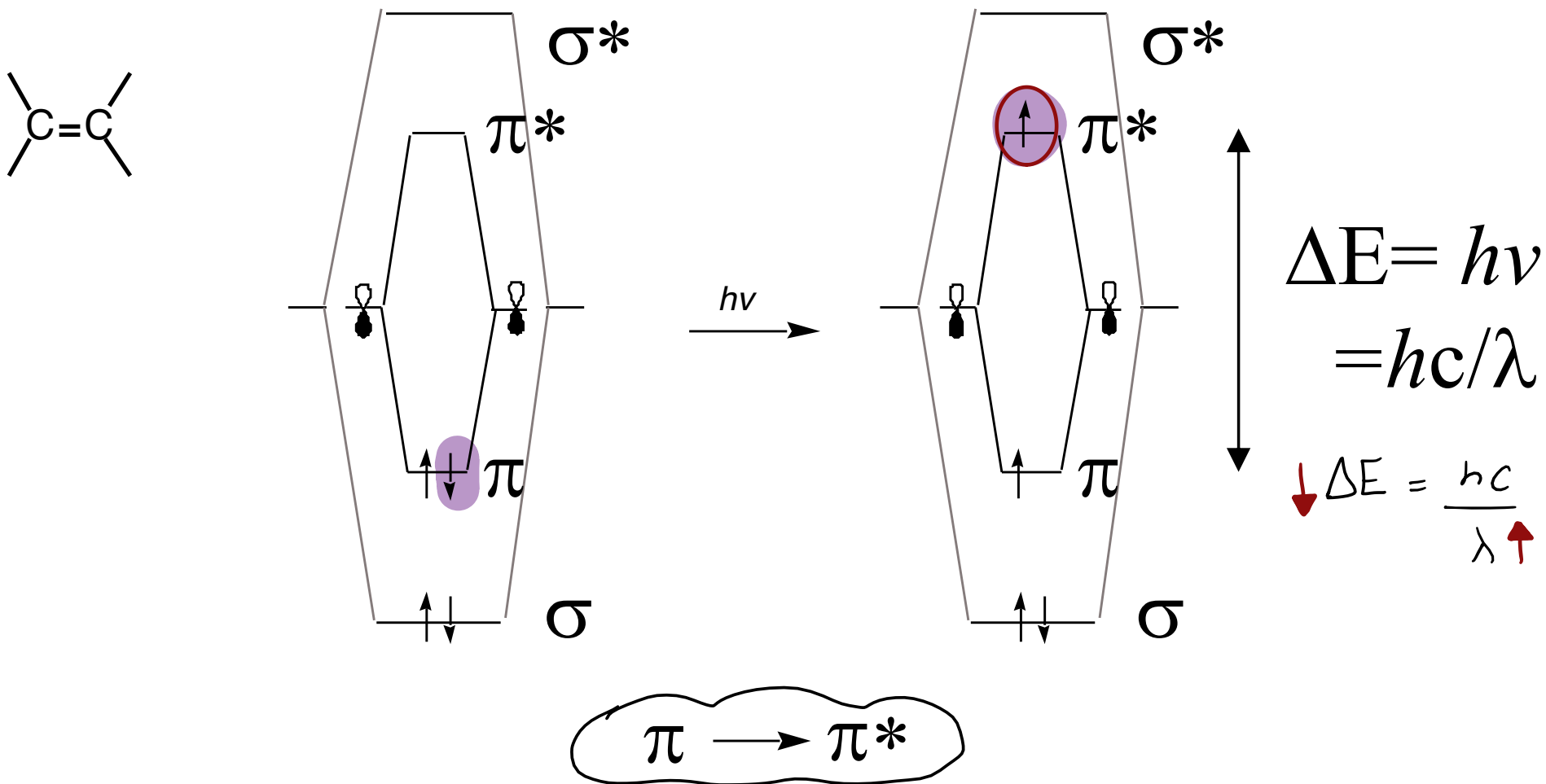
$$\epsilon \geq 10^3$$

## $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most applications of absorption spectroscopy are based upon transitions for  $n$  or  $\pi$  electrons to the  $\pi^*$  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  $\pi$  orbitals. The molar absorptivities for peaks associated with excitation to the  $n, \pi^*$  state are generally low and ordinarily range from 10 and 100  $\text{L cm}^{-1} \text{ mol}^{-1}$ ; values for  $\pi \rightarrow \pi^*$  transitions are normally take place in the range between 1000 and 10,000.

double bond

أكثر صوتاً



Example: ethylene absorbs at longer wavelengths:

$$\lambda_{\max} = 185 \text{ nm } \epsilon = 10,000 \checkmark$$

TABLE 14-1 Absorption Characteristics of Some Common Chromophores

| Chromophore | Example                    | Solvent           | $\lambda_{\max}$ nm | $\epsilon_{\max}$ | Transition Type          |
|-------------|----------------------------|-------------------|---------------------|-------------------|--------------------------|
| Alkene      | $C_6H_{13}CH=CH_2$         | <i>n</i> -Heptane | 177                 | 13,000            | $\pi \rightarrow \pi^*$  |
| Alkyne      | $C_5H_{11}C \equiv C-CH_3$ | <i>n</i> -Heptane | 178                 | 10,000            | $\pi \rightarrow \pi^*$  |
|             |                            |                   | 196                 | 2000              | —                        |
|             |                            |                   | 225                 | 160               | —                        |
| Carbonyl    | $CH_3C(=O)CH_3$            | <i>n</i> -Hexane  | 186                 | 1000              | $n \rightarrow \sigma^*$ |
|             |                            |                   | 280                 | 16                | $n \rightarrow \pi^*$    |
|             | $CH_3CH=O$                 | <i>n</i> -Hexane  | 180                 | large             | $n \rightarrow \sigma^*$ |
|             |                            |                   | 293                 | 12                | $n \rightarrow \pi^*$    |
| Carboxyl    | $CH_3COOH$                 | Ethanol           | 204                 | 41                | $n \rightarrow \pi^*$    |
| Amido       | $CH_3CONH_2$               | 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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## Olefins and aromatics

short wave length  
high Energy

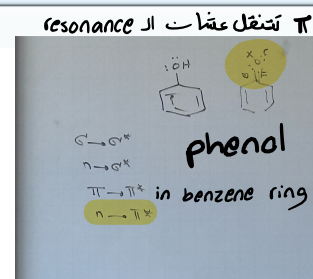
لا يمكن تحليله

$\sigma \rightarrow \sigma^* < 185 \text{ nm}$

$n \rightarrow \sigma^* 150-250 \text{ nm}$

$\pi \rightarrow \pi^*$

$n \rightarrow \pi^* 200-700 \text{ nm}$  ✓



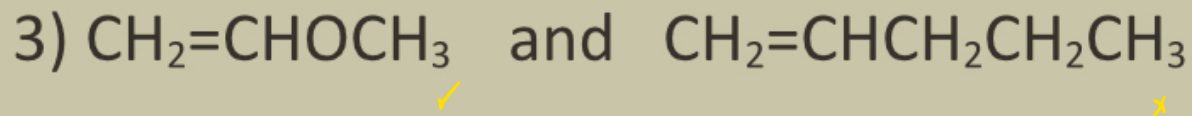
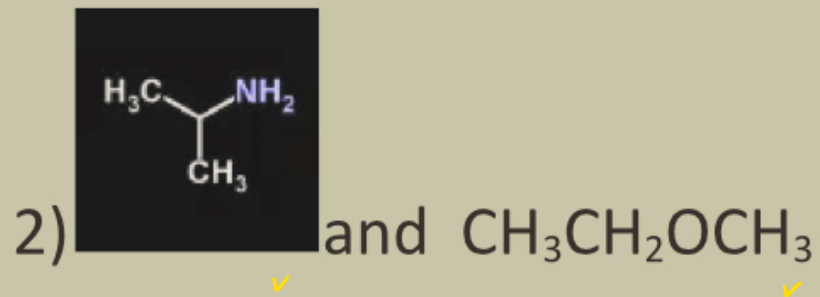
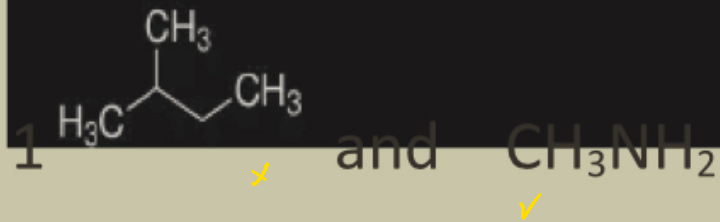
بالمختصات ممكن يجب اسم المركب  
واحد نكوت عارفين ميغته و نفوف  
الانتقالات الى فيه

إجى ايش نوع الانتقالات الموجودة بالH2O

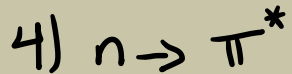
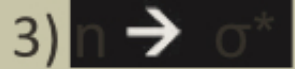
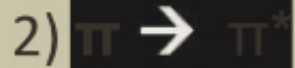
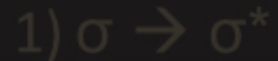
الجواب n الى سيغما\*

و سيغما الى سيغما\*

2. Among the following compounds which pair gives  $n \rightarrow \sigma^*$  as one of the transitions?



5. Which of the following absorptions occurs at shorter wavelength?



$\lambda \downarrow$

Energy  $\uparrow$

①



# 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 ( $\lambda < 185 \text{ nm}$ ).  
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 ( $\lambda > 185 \text{ nm}$ )
- 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 <sup>carbonyl group =</sup> unsaturated functional groups (double bonds) to provide the  $\pi$  orbitals. Molecule containing these functional groups are also referred to as “chromophores”

# Absorption Definitions

HCl polar covalent  
H<sub>2</sub>O

لا يمكن تحليله  
in UV NaOH ionic bond  
used as a solvent

has at least one  $\pi$   
(unsaturated functional group)

**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

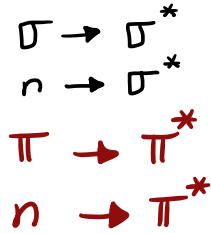
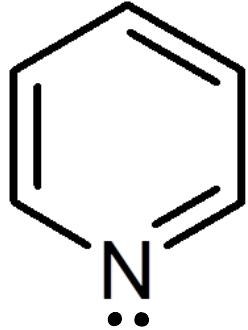
**Auxochrome**  $n \rightarrow \pi^*$

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

An auxochrome attached to a chromophore with  $\pi$  electrons shifts the  $\lambda_{\max}$  to longer wavelengths red shift

4. What is a chromophore \*  
(1 Point)

- ☐ A group of atoms in a colored compound.
- ☒ A colored compound.
- ☐ A group of atoms in a compound responsible for the absorption of electromagnetic radiation.
- ☐ A group of atoms in a compound responsible for electromagnetic radiation
- ☐ None of the above



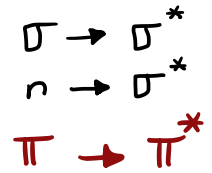
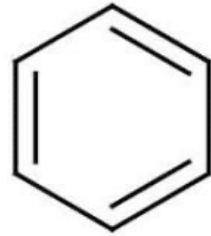
brown

2 chromophore

لون أغمق

vis دخل

$\lambda \uparrow$   $\epsilon \uparrow$   
 Energy  $\downarrow$   
 طاقة أقل



yellow & clear

# Common functional groups

| Compound                           | $\lambda(\text{nm})$ | Intensity/ $\epsilon$ | transition with lowest energy         |
|------------------------------------|----------------------|-----------------------|---------------------------------------|
| $\text{CH}_4$                      | 122                  | intense               | $\sigma\text{-}\sigma^*(\text{C-H})$  |
| $\text{CH}_3\text{CH}_3$           | 130                  | intense               | $\sigma\text{-}\sigma^*(\text{C-C})$  |
| $\text{CH}_3\text{OH}$             | 183                  | 200                   | $\text{n-}\sigma^*(\text{C-O})$       |
| $\text{CH}_3\text{SH}$             | 235                  | 180                   | $\text{n-}\sigma^*(\text{C-S})$       |
| $\text{CH}_3\text{NH}_2$           | 210                  | 800                   | $\text{n-}\sigma^*(\text{C-N})$       |
| $\text{CH}_3\text{Cl}$             | 173                  | 200                   | $\text{n-}\sigma^*(\text{C-Cl})$      |
| $\text{CH}_3\text{I}$              | 258                  | 380                   | $\text{n-}\sigma^*(\text{C-I})$       |
| $\text{CH}_2=\text{CH}_2$          | 165                  | 16000                 | $\pi\text{-}\pi^*(\text{C}=\text{C})$ |
| $\text{CH}_3\text{COCH}_3$ Acetone | 187                  | 950                   | $\pi\text{-}\pi^*(\text{C}=\text{O})$ |
|                                    | 273                  | 14                    | $\text{n-}\pi^*(\text{C}=\text{O})$   |
| $\text{CH}_3\text{CSCH}_3$         | 460                  | weak                  | $\text{n-}\pi^*(\text{C}=\text{S})$   |
| $\text{CH}_3\text{N}=\text{NCH}_3$ | 347                  | 15                    | $\text{n-}\pi^*(\text{N}=\text{N})$   |

# Absorption Definitions

## Bathochromic

A shift to longer wavelengths or red shift (increase in  $\lambda$ )

## Hypsochromic

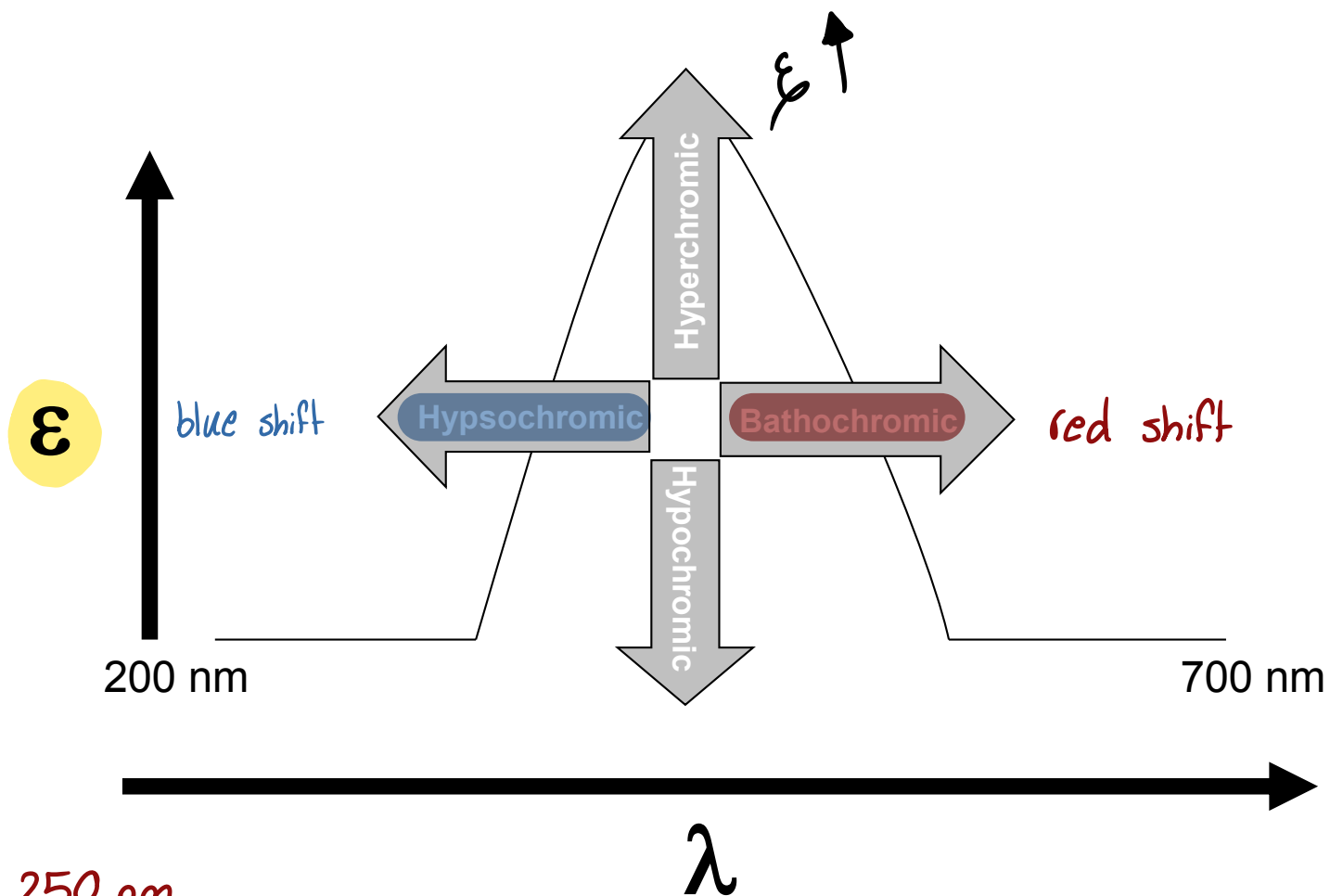
A shift to shorter wavelengths or blue shift (decrease in  $\lambda$ )

## Hyperchromism

An increase in intensity of an absorption band (increase in  $\epsilon_{\max}$ )

## Hypochromism

A decrease in intensity of an absorption band (decrease in  $\epsilon_{\max}$ )



250 nm  
polar solvent

220 nm  
 $n \rightarrow \pi^*$   
blue shift

260 nm  
 $\pi \rightarrow \pi^*$   
red shift

| Transition              | Energy required | Wavelength        | Intensity   |
|-------------------------|-----------------|-------------------|-------------|
| $\pi \rightarrow \pi^*$ | Higher          | Shorter $\lambda$ | Very strong |
| $n \rightarrow \pi^*$   | Lower           | Longer $\lambda$  | Weak        |

strong absorbance  
تكراري  
 $\epsilon \uparrow$

- transparent

protic polar solvent  
 $\text{H}_2\text{O}$

## Solvent Effects

Aprotic non polar  
 $\text{CH}_2\text{Cl}_2$

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

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

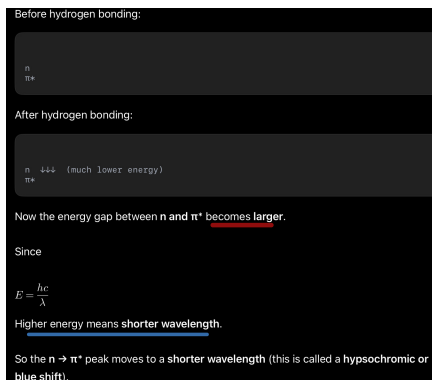
-  $n \rightarrow \pi^*$  transition occur at longer wavelengths than  $\pi \rightarrow \pi^*$

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

- The two peaks will be shifted closer to each other in a polar and hydrogen bonding solvent such as ethanol  $\text{CH}_3\text{CH}_2\text{OH}$







# Solvent Effects

*bathochromic*

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

*hypsochromic*

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

انه ال red shift الناتج من اضافة المركب ب polar solvent دليل على وجود اي انتقال

Q The increase in polarity of the solvent increases the wavelength of absorption

of  $n \rightarrow \pi^*$  transition. *a. True*  
*b. False*

*(b)*

11. Which one of the following is not the most commonly used solvent for ultraviolet spectral absorptions?

1. water
2. 95% ethanol
3. hexane
4. acetone

4

Statement 1 : The absorption of  $n \rightarrow \pi^*$  transition of  $\alpha, \beta$ -unsaturated carbonyl compounds is shifted to shorter wavelength with increasing polarity of the solvent.

Statement 2 : The nonbonding electrons in the ground state are stabilized by hydrogen bonding.

- 1) Both statements 1 and 2 are true and statement 2 is the correct explanation of statement 1.
- 2) The statements 1 and 2 are true but statement 2 is not the correct explanation of statement 1.
- 3) The statement 1 is true and statement 2 is false.
- 4) The statement 2 is true and statement 1 is false.

①

#### Statement 1: True

- In  $\alpha, \beta$ -unsaturated carbonyl compounds, increasing solvent polarity causes a **hypsochromic shift (blue shift)**, meaning the  $n \rightarrow \pi^*$  transition absorption shifts to a **shorter wavelength** (higher energy).

#### Statement 2: True

- Polar, protic solvents form **hydrogen bonds** with the non-bonding ( $n$ ) lone pair electrons on the carbonyl oxygen atom in the ground state.
- This hydrogen bonding lowers the energy of the  $n$ -orbital (stabilizes the ground state).

31. Which type of transition(s) is(are) affected by solvent polarity?

1)  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$

2)  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$

3)  $n \rightarrow \pi^*$

4)  $\pi \rightarrow \pi^*$

2

# Effect of Conjugation of Chromophores

$\pi$  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  $\pi^*$  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,  $\text{CH}_2=\text{CHCH}=\text{CH}_2$ , has a strong absorption band that is displaced to a longer wavelength by 20 nm compared with the corresponding peak for an unconjugated diene.

I delocalization changes the energy levels

$\pi^*$  Antibonding orbital becomes lower in energy  $\downarrow$   $\lambda \uparrow$

energy levels between  $\pi / \pi^*$  becomes smaller  
(gap)  $\lambda_{\max}$  increase

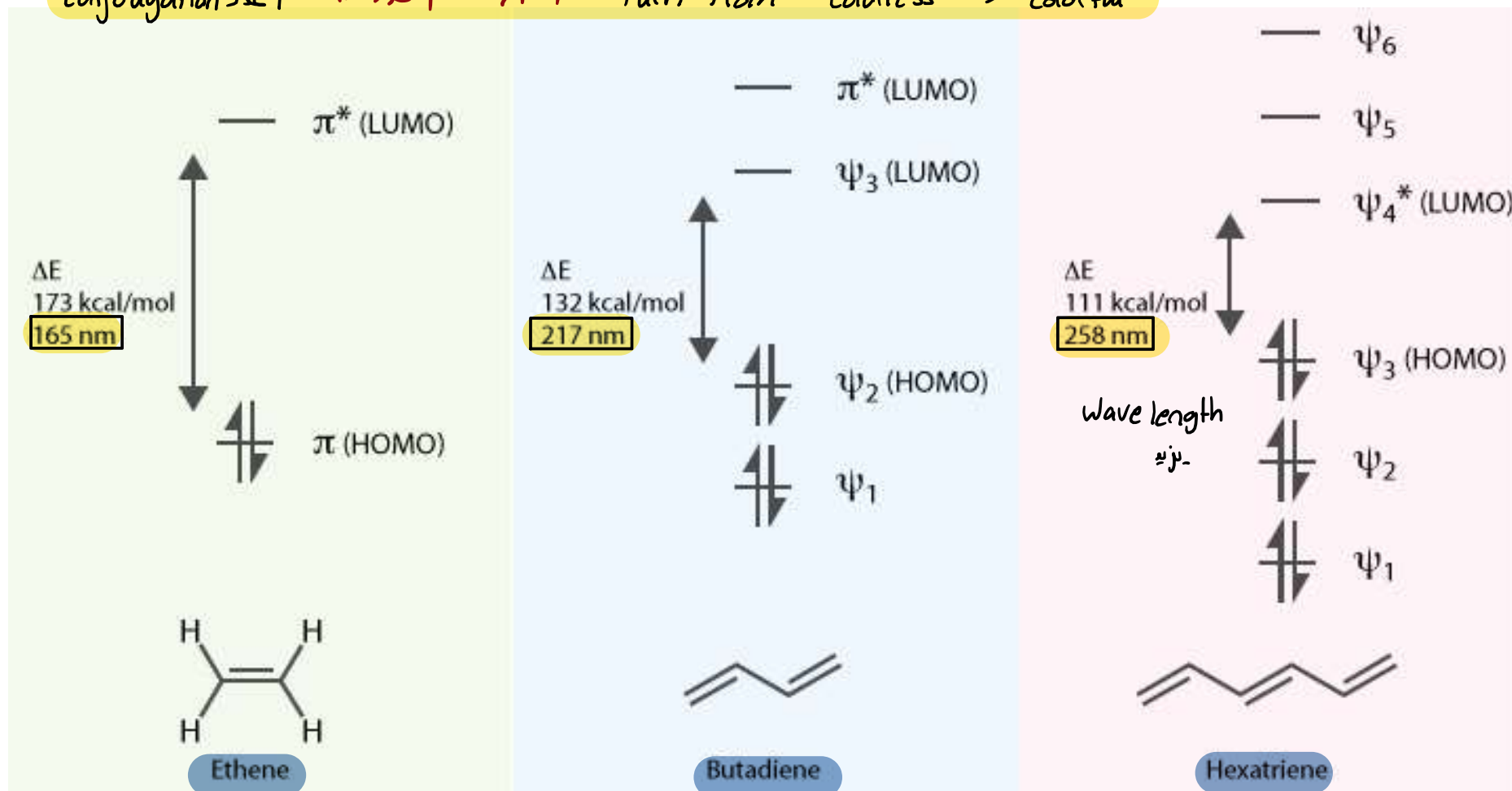
conjugation causes a bathochromic (red shift)

#### High-yield exam points

- Conjugation = alternating single and double bonds.
- Conjugation delocalizes  $\pi$  electrons.
- Delocalization lowers the energy of the  $\pi^*$  orbital.
- The  $\pi \rightarrow \pi^*$  energy gap decreases.
- A smaller energy gap means less energy is required.
- Less energy corresponds to a longer wavelength (higher  $\lambda_{\max}$ ).
- Therefore, conjugation causes a bathochromic (red) shift.
- Increasing the number of conjugated double bonds increases  $\lambda_{\max}$ .

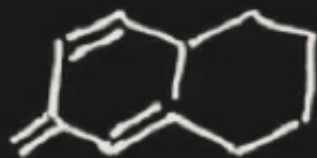
# Effect of Conjugation of Chromophores

conjugation  $\uparrow$   $\pi$   $\uparrow$   $\lambda$   $\uparrow$  turn from colorless  $\rightarrow$  colorful



3. Which of the following compounds does not show absorption in the UV-visible region?

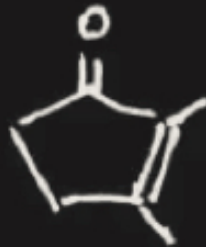
1)



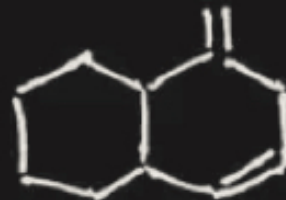
2)



3)



4)





# Effect of Conjugation of Chromophores

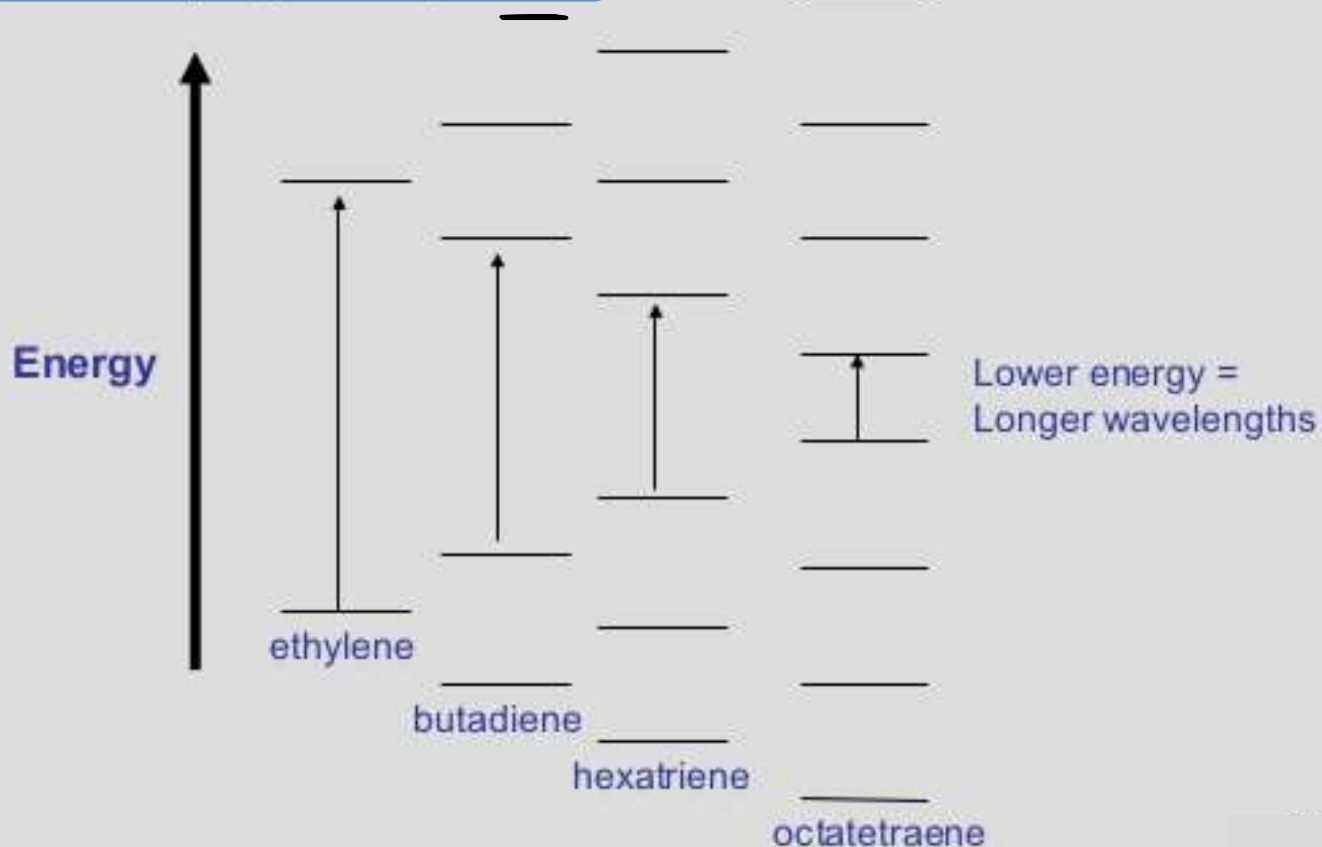
## UV Spectroscopy

### III. Chromophores

#### A. Substituent Effects

##### 2. Conjugation – Alkenes

Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller: *And wavelength larger*



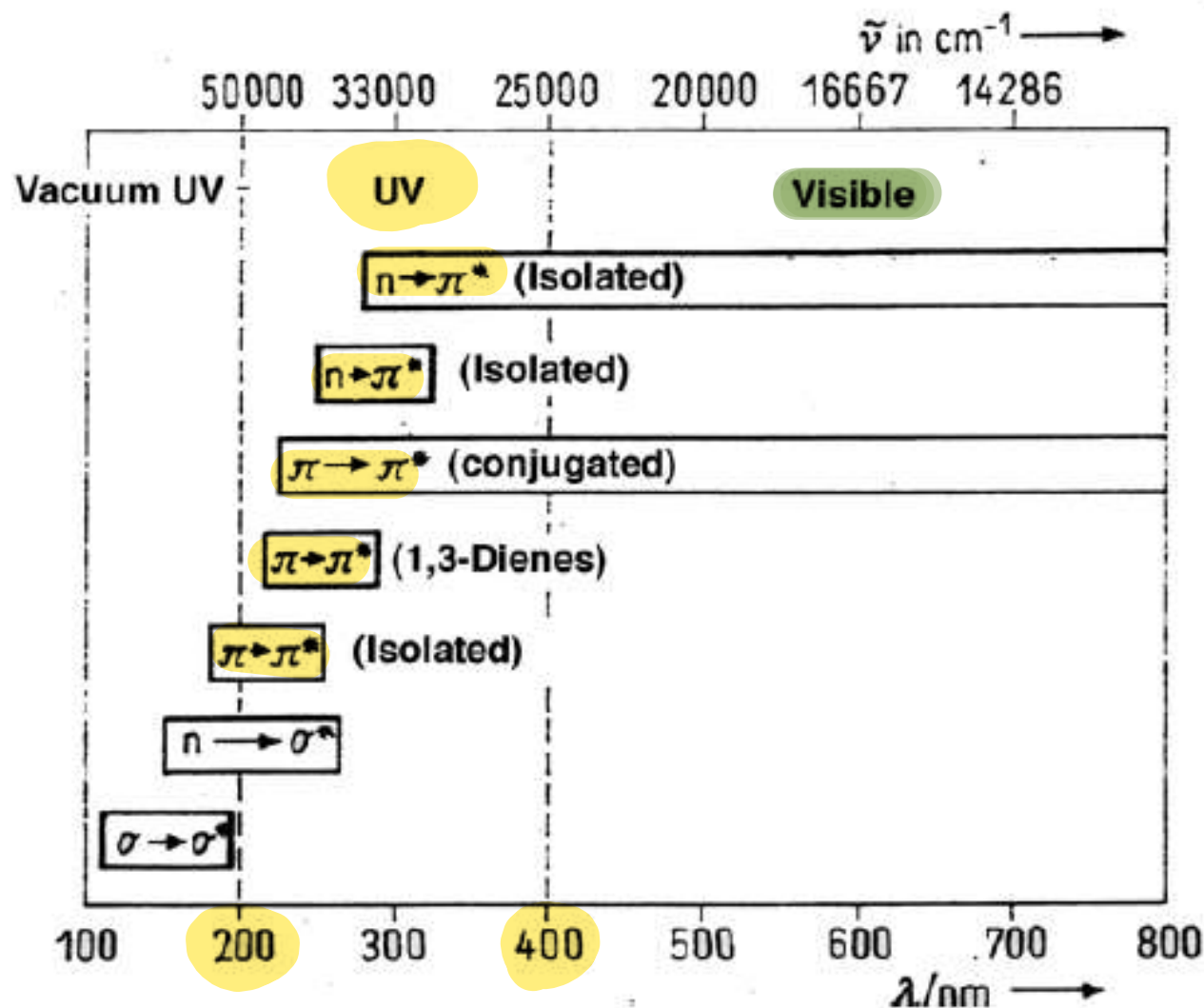
## Effect of Conjugation of Chromophores

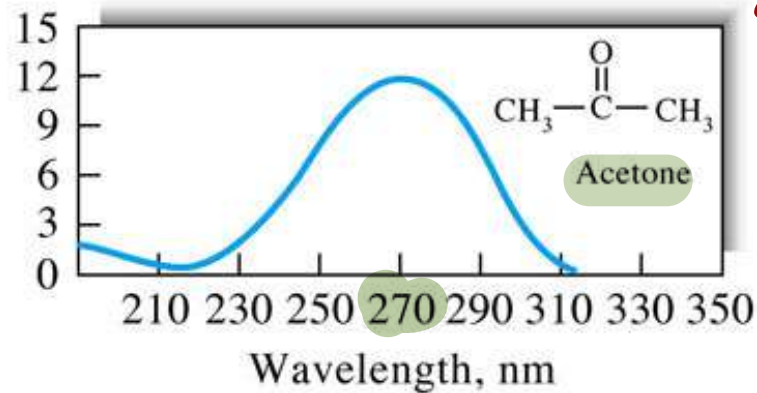
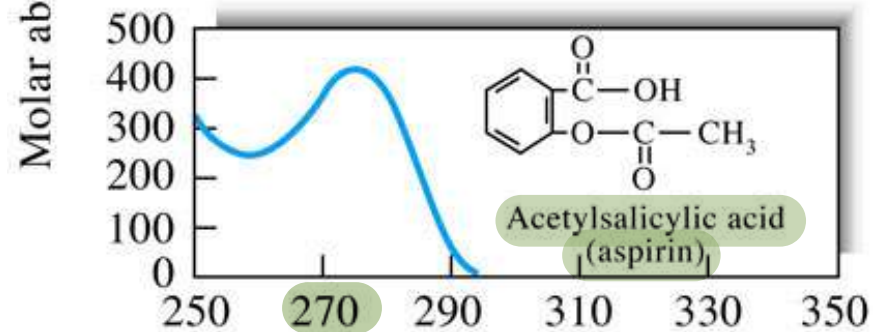
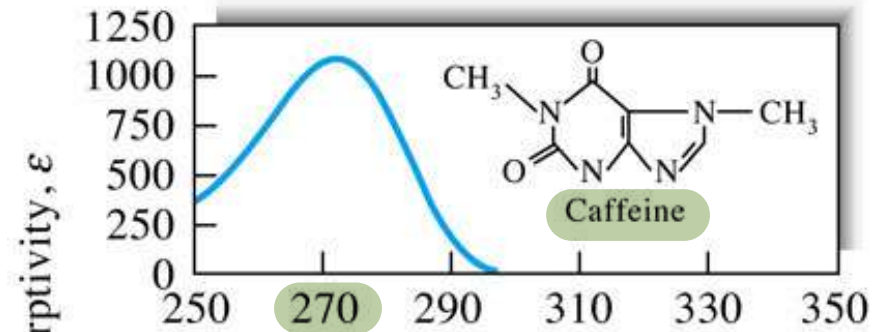
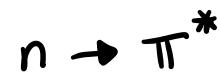
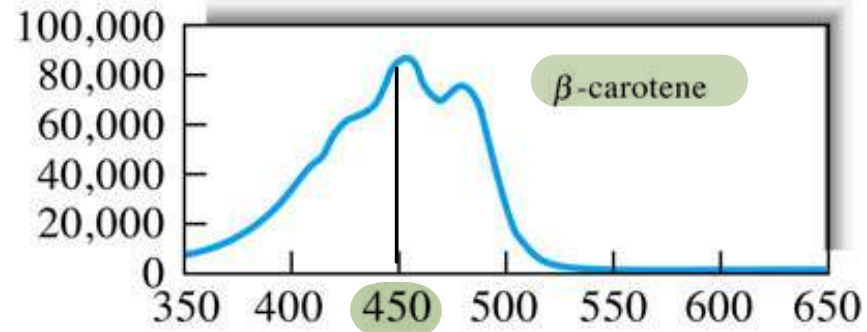
| Table 8.3 Values of $\lambda_{\text{max}}$ and $\epsilon$ for Ethylene and Conjugated Dienes |                             |                                               |
|----------------------------------------------------------------------------------------------|-----------------------------|-----------------------------------------------|
| Compound                                                                                     | $\lambda_{\text{max}}$ (nm) | $\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ ) |
| $\text{H}_2\text{C}=\text{CH}_2$                                                             | 165                         | 15,000                                        |
|             | 217                         | 21,000                                        |
|             | 256                         | 50,000                                        |
|             | 290                         | 85,000                                        |
|           | 334                         | 125,000                                       |
|           | 364                         | 138,000                                       |

increase  
with  
conjugation

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.





شفاف  
نستخدام  
quartz

# **Empirical Rules for Calculating Uv/Vis Absorptions**

# Woodward-Fieser Rules for Calculating the $\lambda_{\max}$ of Conjugated Dienes and Polyenes

At least two double bonds ( $2\pi$ )

- Parent:

3 حالات :

two double bonds in one ring

OR

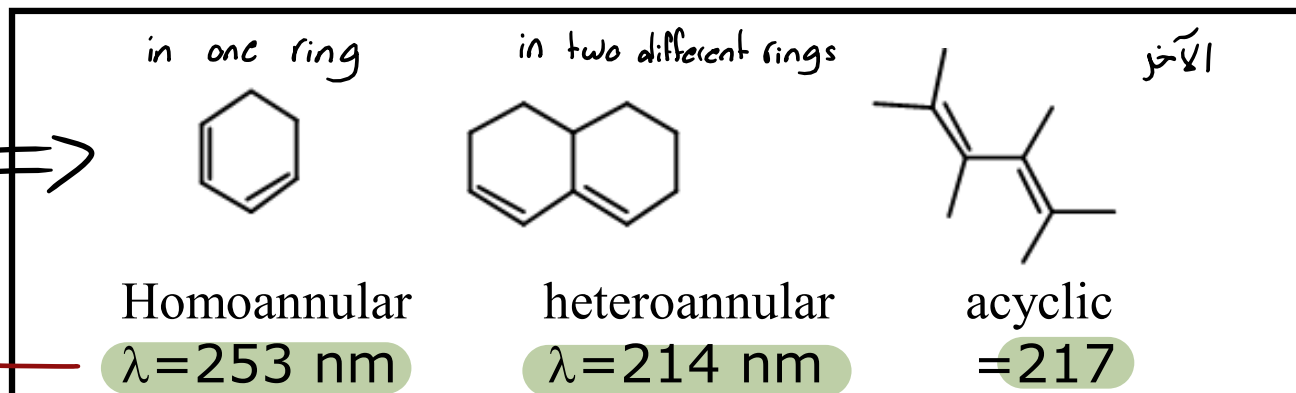
two double bonds in different rings

OR

أي شيء مختلف

( الآخر )

Base  $\Rightarrow$



حفظ

- Increments for:

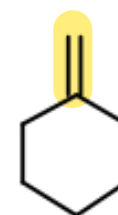
Double bond extending conjugation +30  
Alkyl substituent or ring residue +5  
Exocyclic double bond +5

حفظ

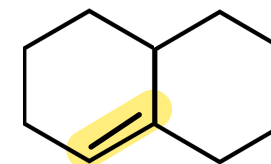
+30

+5

+5



exocyclic



Polar groupings:

-OC(O)CH<sub>3</sub>

-OR

-Cl, -Br

-NR<sub>2</sub>

-SR

+0

+6

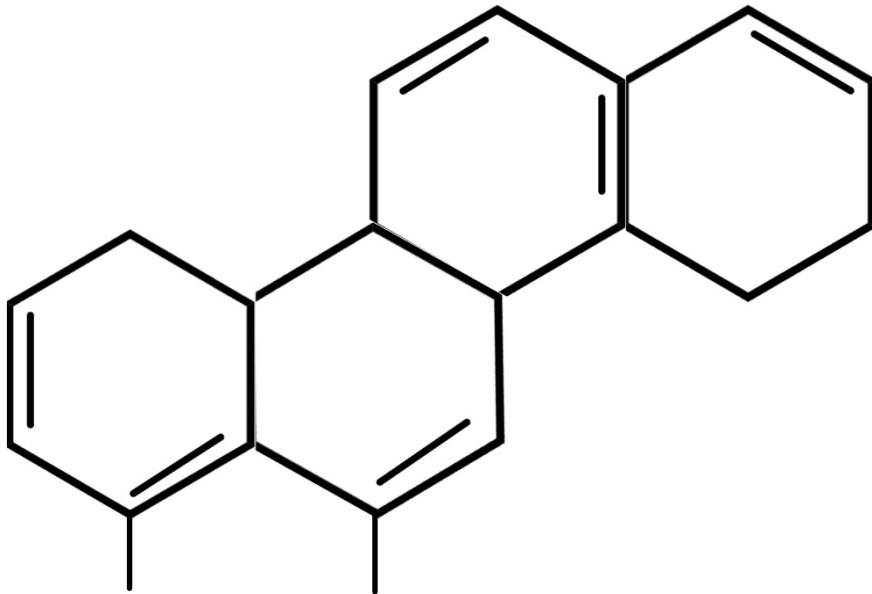
+5

+60

+30

مش مطلوب  
تحفظهم  
للأمتحان

calculate  $\lambda_{\max}$  :



2 two double bond in one ring > in different rings

Base 253 > 214

system 1

system 2

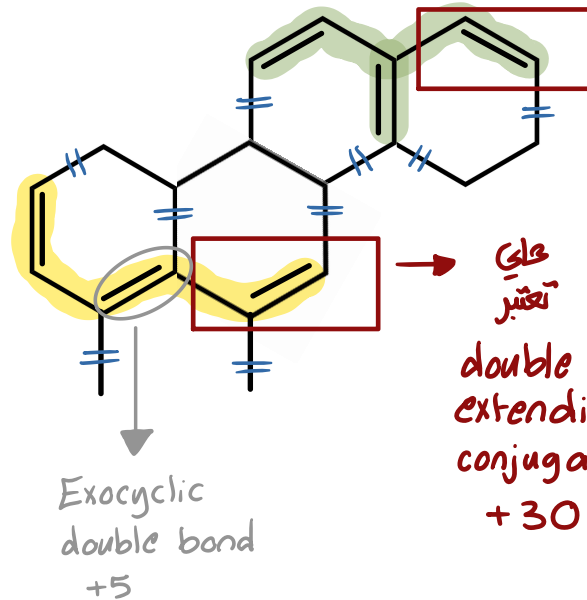
1 two double bond in one ring > in different rings

253 > 214

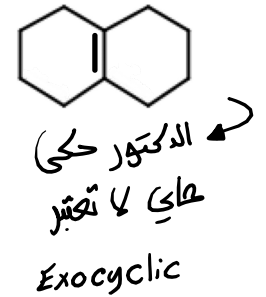
Base

// Alkyl substituent  $+5 \times 5 = +25$

$253 + 30 + 25 + 5 = 313$



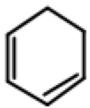
// Alkyl substituent  $+5 \times 4 = +20$



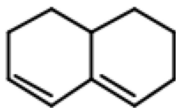
$253 + 30 + 20 = 303$

313 > 303

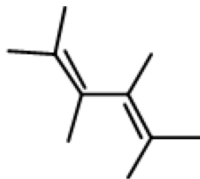
$\lambda_{max}$



Homoannular  
 $\lambda = 253 \text{ nm}$

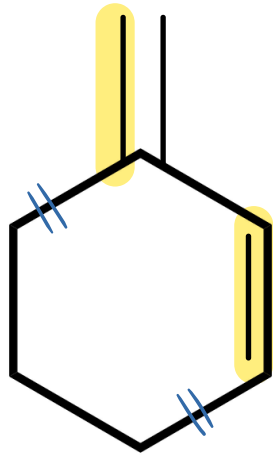


heteroannular  
 $\lambda = 214 \text{ nm}$



acyclic  
 $= 217$





Acyclic تعبر

$$217 + 5 + 10$$

exocyclic

2 AlKyl substituents

$$= 232 \text{ nm}$$

$\lambda_{\text{max}}$

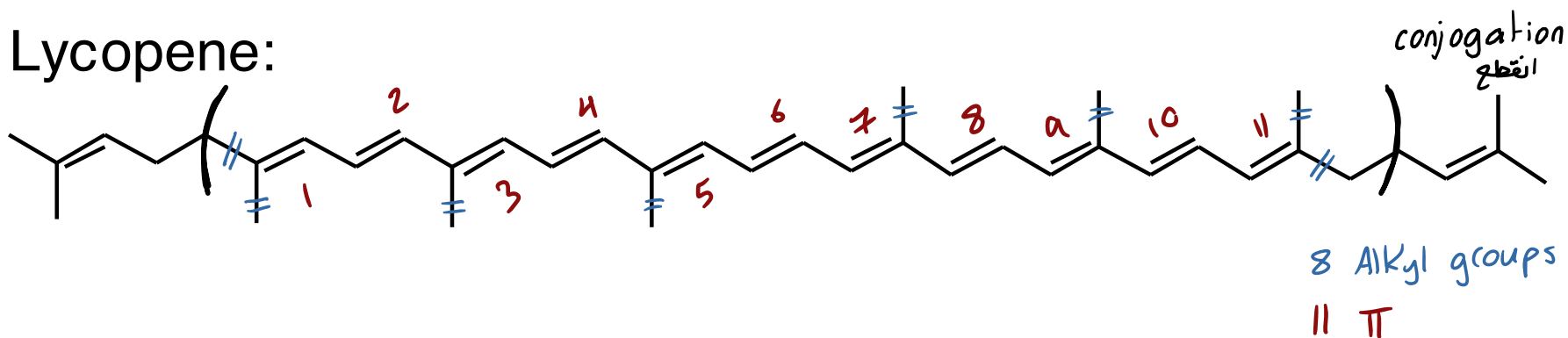
At least two conjugated double bonds

For more than 4 conjugated double bonds:

$$\lambda_{\max} = 114 + 5(\text{number of alkyl groups}) + n(48.0 - 1.7n)$$

Example:

Lycopene:



$$\lambda_{\max} = 114 + 5(8) + 11(48.0 - 1.7 \times 11) = 476 \text{ nm}$$

theory

$$\lambda_{\max}(\text{Actual}) = 474.$$

practical



Example 1:



Transoid: 217 nm

Alkyl groups or ring residues:  $3 \times 5 =$  15 nm

Calculated: 232 nm

Observed: 234 nm

Example 2:

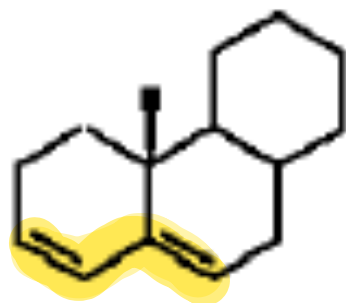


Cisoid: 253 nm

Alkyl groups or ring residues:  $2 \times 5 =$  10 nm

Calculated: 263 nm

Observed: 256 nm



Transoid:

214 nm

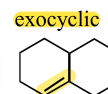
Alkyl groups or  
ring residues:

$$3 \times 5 =$$

15 nm

Exocyclic  
double bond:

5 nm

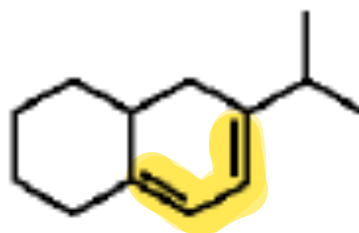


Calculated:

234 nm

Observed:

235 nm



|                                   |         |             |
|-----------------------------------|---------|-------------|
| Cisoid:                           |         | 253 nm      |
| Alkyl groups or<br>ring residues: | 4 x 5 = | 20 nm       |
| Exocyclic<br>double bond:         |         | <u>5 nm</u> |
| Calculated:                       |         | 278 nm      |
| Observed:                         |         | 275 nm      |

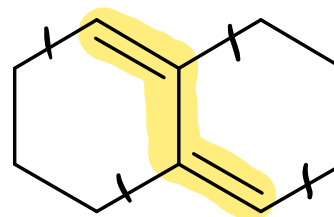


## Example 1

Calculate the  $\lambda_{\text{max}}$  for 1,4, dibenzodiene

Solution:

The structure is



Parent heterodiene = 214

Alkyl substituents (4x5 nm) = 20

Exocyclic double bond 2x5 = 10

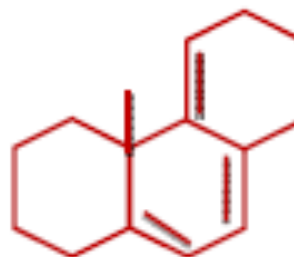
---

$\lambda_{\text{max}} = 244 \text{ nm}$  (observed 247 nm)



## Example 2

Calculate the  $\lambda_{\max}$  for



Solution:

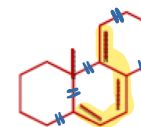
The compound is a homoannular diene

Base value = 253 ✓

Ring residues (5x5) = 25

Exocyclic double bond 3x5 = 15 ✓

Extended C=C = 30 ✓



$\lambda_{\max}$  is 323 nm

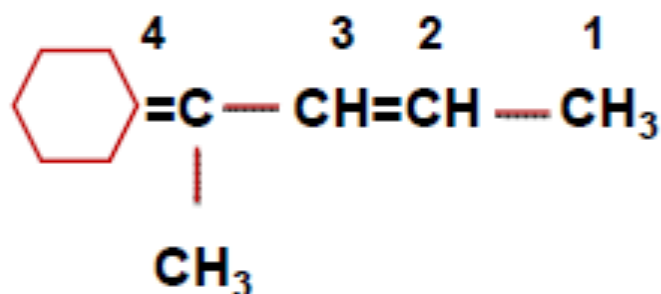
observed value is 320 nm.



### 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

---

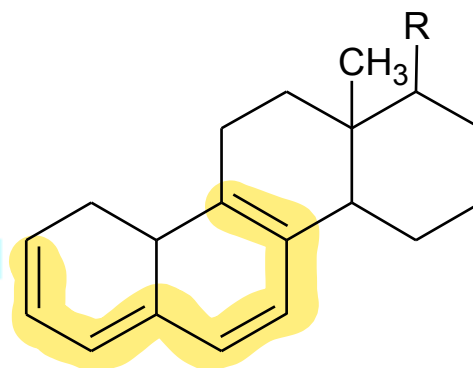
242 nm

Observed value is also 242 nm



### Example 4

Calculate the  $\lambda_{\max}$  for the compound



### Solution

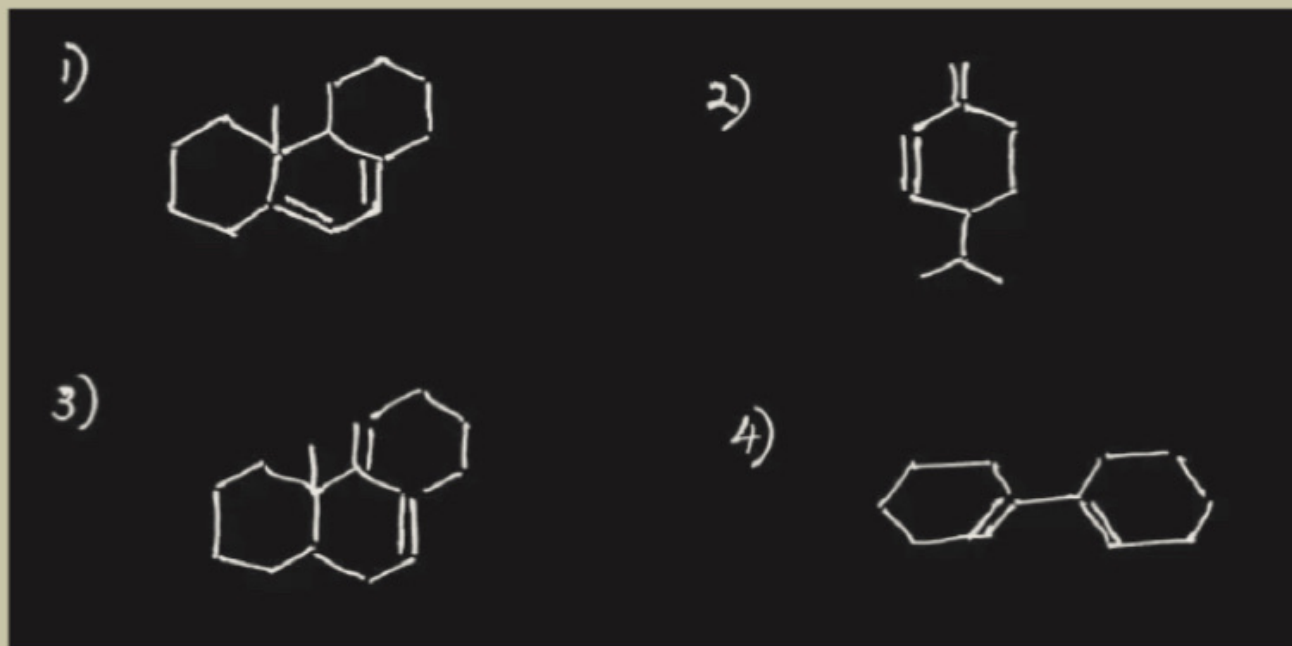
|                                |        |
|--------------------------------|--------|
| Base value                     | 253 nm |
| 2 Extended double bonds (2x30) | 60 nm  |
| 5 Ring residues (5x5)          | 25 nm  |
| 1 Exocyclic double bond (1x5)  | 5 nm   |

---

|                             |        |
|-----------------------------|--------|
| Calculated $\lambda_{\max}$ | 343 nm |
|-----------------------------|--------|

|          |        |
|----------|--------|
| Observed | 345 nm |
|----------|--------|

9. The compound which shows  $\lambda_{\text{max}}$  at 283 nm is



①  $253 + 20 + 10 = 283$

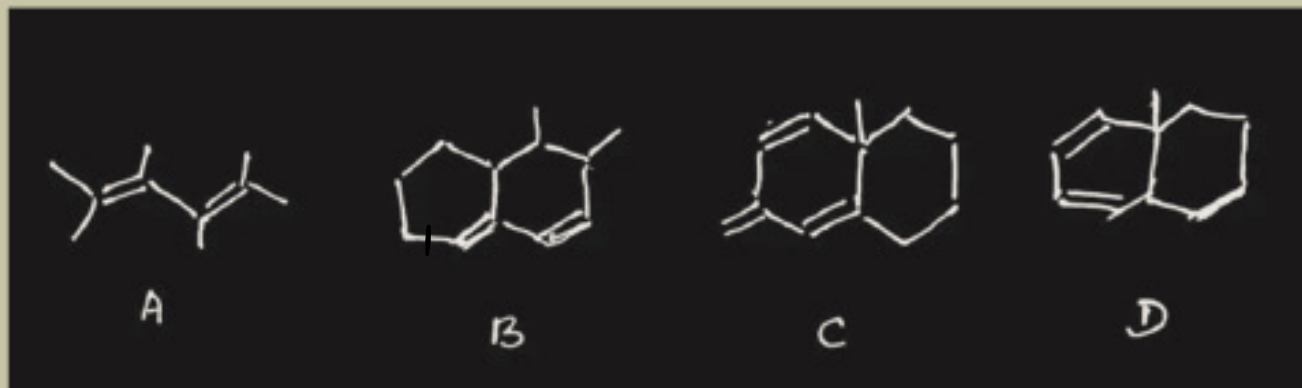
②  $217 + 10 + 5 = 232$

③  $214 + 10 + 20 = 244$

④  $217 + 20 = 237$

①

19. The order of increasing the  $\lambda_{\text{max}}$  in the following compounds is



① ~~B < C < A < D~~  
B < A < D < C

2) C < B < A < D

3) A < D < B < C

4) B < C < D < A

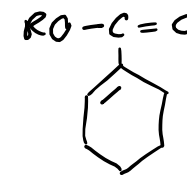
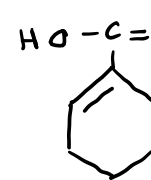
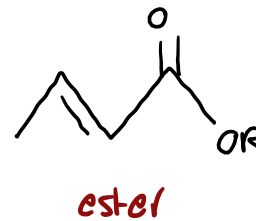
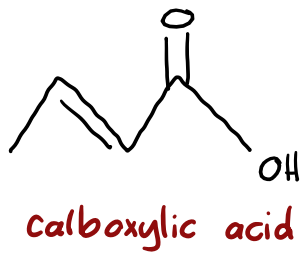
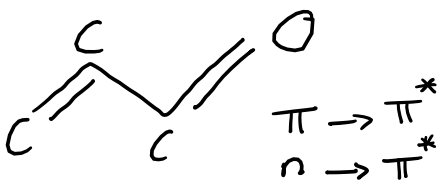
① A  $217 + 30 = 247$

② B  $214 + 15 + 5 = 234$

③ C  $217 + 30 + 15 + 10 = 272$

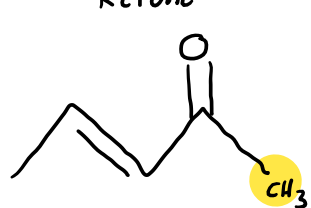
④ D  $253 + 10 = 263$

# Woodward's Rules for Conjugated Carbonyl Compounds

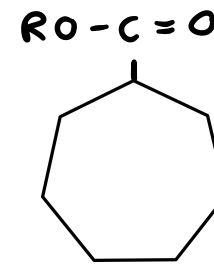
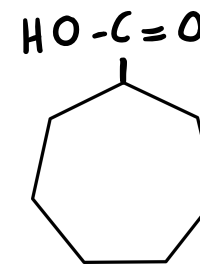
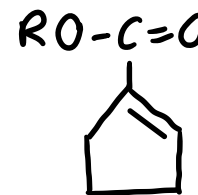
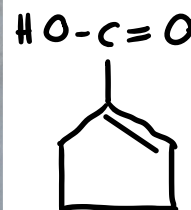
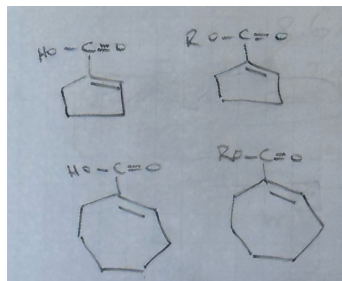
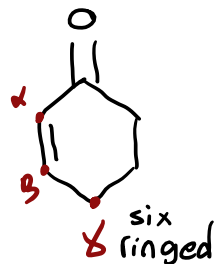


سہاوی  
195

Ketone

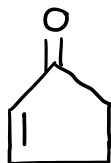


Base 215

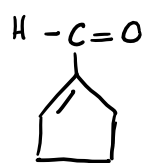
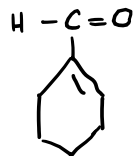
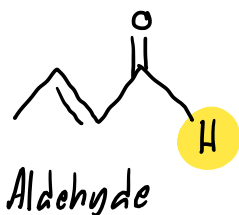


حیاتی + سہاوی

195 + 5

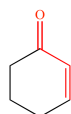


202



208

Base values:



X = R

Six-membered ring or acyclic parent  
**enone**

$\lambda=215$  nm

Five-membered ring parent **enone**

$\lambda=202$  nm

X = H Aldehyde

$\lambda=208$  nm

X = OH, OR ester

سداسي  $\lambda=195$  nm

Increments for:

extension +30   
+69 (rings)

exocyclic +5 in the same rings

substituent

carboxylic acid

Double bond extending conjugation 30

Exocyclic double bond 5

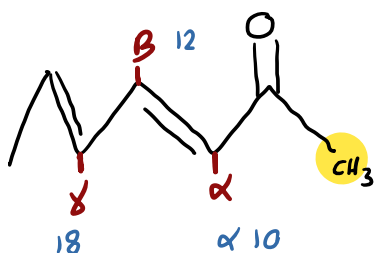
Endocyclic double bond in a 5- or 7-membered ring for X = OH, OR 5

★ Homocyclic diene component 39

Alkyl substituent or ring residue  $\alpha$  10

$\beta$  12

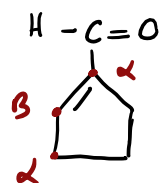
$\gamma$  or higher 18



و ما بعد غاما  
18 ما كذا

# Polar groupings:

|                       |                                 |    |
|-----------------------|---------------------------------|----|
| -OH                   | $\alpha$                        | 35 |
|                       | $\beta$                         | 30 |
|                       | $\delta$                        | 50 |
| -OC(O)CH <sub>3</sub> | $\alpha, \beta, \gamma, \delta$ | 6  |
| -OCH <sub>3</sub>     | $\alpha$                        | 35 |
|                       | $\beta$                         | 30 |
|                       | $\gamma$                        | 17 |
|                       | $\delta$                        | 31 |
| -Cl                   | $\alpha$                        | 15 |
|                       | $\beta, \gamma, \delta$         | 12 |
| -Br                   | $\beta$                         | 30 |
|                       | $\alpha, \gamma, \delta$        | 25 |
| -NR <sub>2</sub>      | $\beta$                         | 95 |



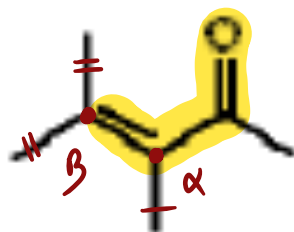
\*Solvent shifts for various solvents:

| Solvent     | $\lambda_{\text{max}}$ shift (nm) |
|-------------|-----------------------------------|
| water       | + 8                               |
| chloroform  | - 1                               |
| ether       | - 7                               |
| cyclohexane | - 11                              |
| dioxane     | - 5                               |
| hexane      | - 11                              |

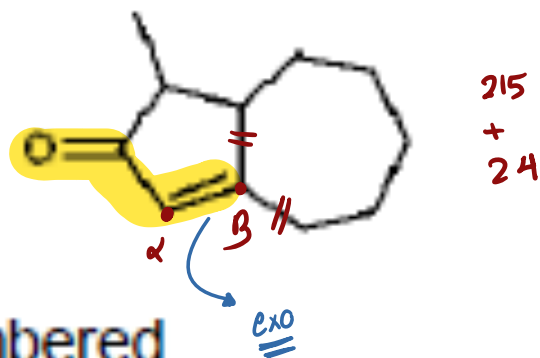




# example



|                                             |                 |              |
|---------------------------------------------|-----------------|--------------|
| Acyclic enone:                              |                 | 215 nm       |
| $\alpha$ -Alkyl groups<br>or ring residues: |                 | 10 nm        |
| $\beta$ -Alkyl groups<br>or ring residues:  | $2 \times 12 =$ | <u>24 nm</u> |
| Calculated:                                 |                 | 249 nm       |
| Observed:                                   |                 | 249 nm       |



Five-membered  
ring parent

202 nm

enone:

$\beta$ -Alkyl groups  
or ring residues:  $2 \times 12 =$

24 nm

Exocyclic  
double bond:

5 nm

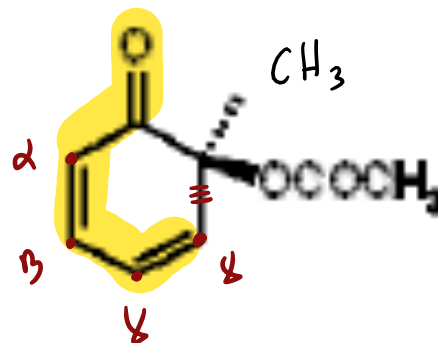
Calculated:

231 nm

Observed:

226 nm

✓



Six-membered  
ring or alicyclic  
parent enone:

215 nm

Extended  
conjugation:

30 nm

Homocyclic  
diene  
component:

39 nm

$\delta$ -Alkyl groups  
or ring residues:

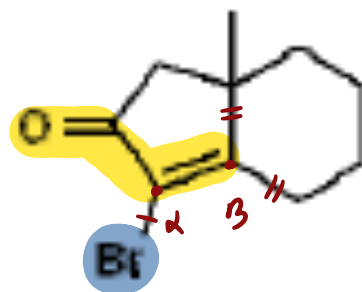
18 nm

Calculated:

302 nm

Observed:

300 nm



Five-membered  
ring parent  
enone:

202 nm

$\alpha$ -Br:

25 nm

$\beta$ -Alkyl groups  
or ring residues:  $2 \times 12 =$

24 nm

Exocyclic  
double bond:

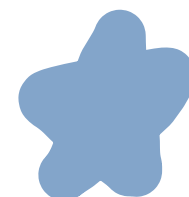
5 nm

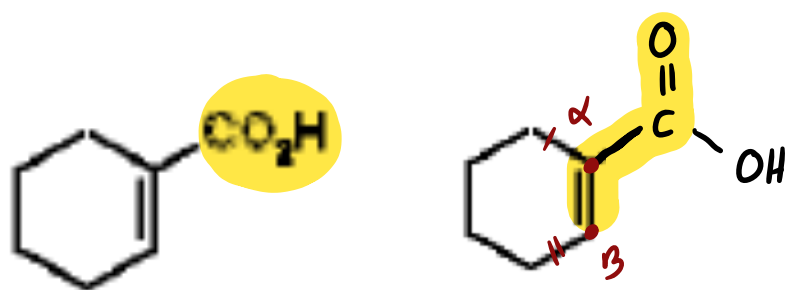
Calculated:

256 nm

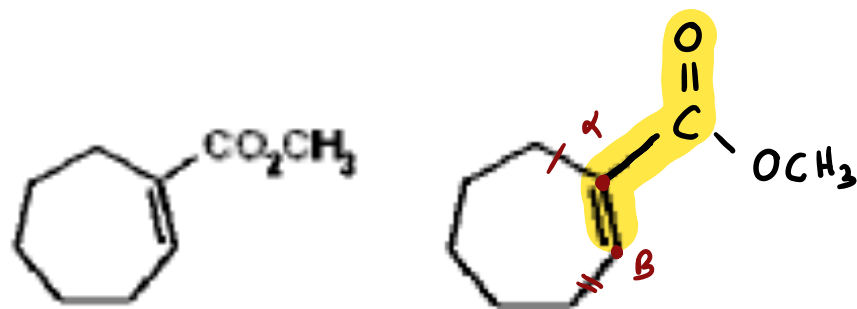
Observed:

251 nm

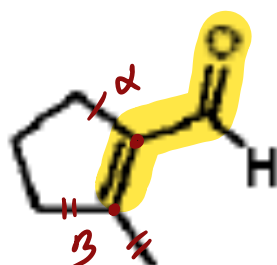




|                                             |               |
|---------------------------------------------|---------------|
| Carboxylic acid:                            | 195 nm        |
| $\alpha$ -Alkyl groups<br>or ring residues: | 10 nm         |
| $\beta$ -Alkyl groups<br>or ring residues:  | <u>12 nm</u>  |
| Calculated:                                 | <b>217 nm</b> |
| Observed:                                   | 217 nm        |



|                                                     |                   |
|-----------------------------------------------------|-------------------|
| Ester:                                              | 195 nm            |
| $\alpha$ -Alkyl groups<br>or ring residues:         | 10 nm             |
| $\beta$ -Alkyl groups<br>or ring residues:          | 12 nm             |
| Endocyclic<br>double bond in<br>7-membered<br>ring: | سباعي <u>5 nm</u> |
| Calculated:                                         | 222 nm            |
| Observed:                                           | 222 nm            |



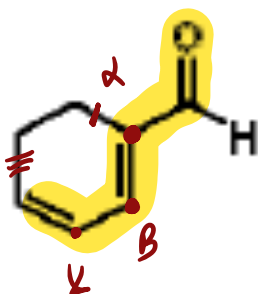
|           |        |
|-----------|--------|
| Aldehyde: | 208 nm |
|-----------|--------|

|                                             |       |
|---------------------------------------------|-------|
| $\alpha$ -Alkyl groups<br>or ring residues: | 10 nm |
|---------------------------------------------|-------|

|                                            |                 |              |
|--------------------------------------------|-----------------|--------------|
| $\beta$ -Alkyl groups<br>or ring residues: | $2 \times 12 =$ | <u>24 nm</u> |
|--------------------------------------------|-----------------|--------------|

|             |        |
|-------------|--------|
| Calculated: | 242 nm |
|-------------|--------|

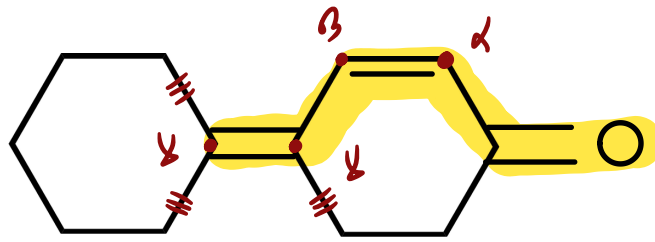
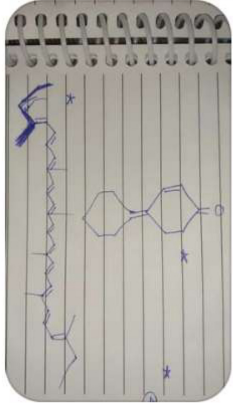
|           |        |
|-----------|--------|
| Observed: | 242 nm |
|-----------|--------|



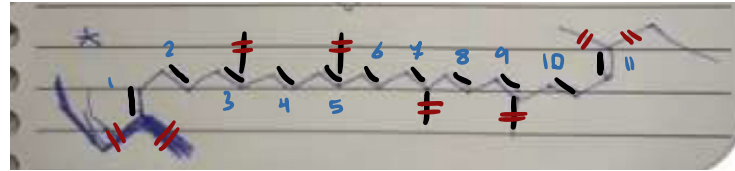
|                                          |               |
|------------------------------------------|---------------|
| Aldehyde:                                | 208 nm        |
| Extended conjugation:                    | 30 nm         |
| Homodiene component:                     | 39 nm         |
| $\alpha$ -Alkyl groups or ring residues: | 10 nm         |
| $\delta$ -Alkyl groups or ring residues: | <u>18 nm</u>  |
| Calculated:                              | <b>305 nm</b> |
| Observed:                                | 302 nm        |



جاء تقريباً هاي المركبات وطلب اللمدا ماكس



$$215 + 30 + 5 + (3 \times 18) = 304$$



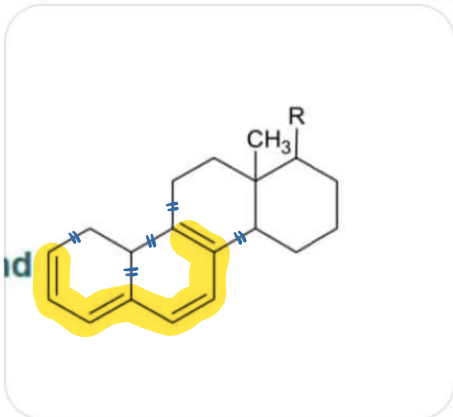
8 Alkyl groups  
11  $\pi$

$$\lambda = 114 + 5 (\text{Alkyl groups}) + n (48 - 1.7n)$$

$$\lambda_{\text{max}} = 114 + 5 \cdot 8 + 11 (48 - 1.7 \times 11)$$

$$\lambda_{\text{max}} = 476 \text{ nm}$$

نحسب ال لمدا ماكس ل هاد الشكل



$$253 + 30 + 30 + 25 + 5 = 343 \lambda_{\text{max}}$$

Alkyl      exo