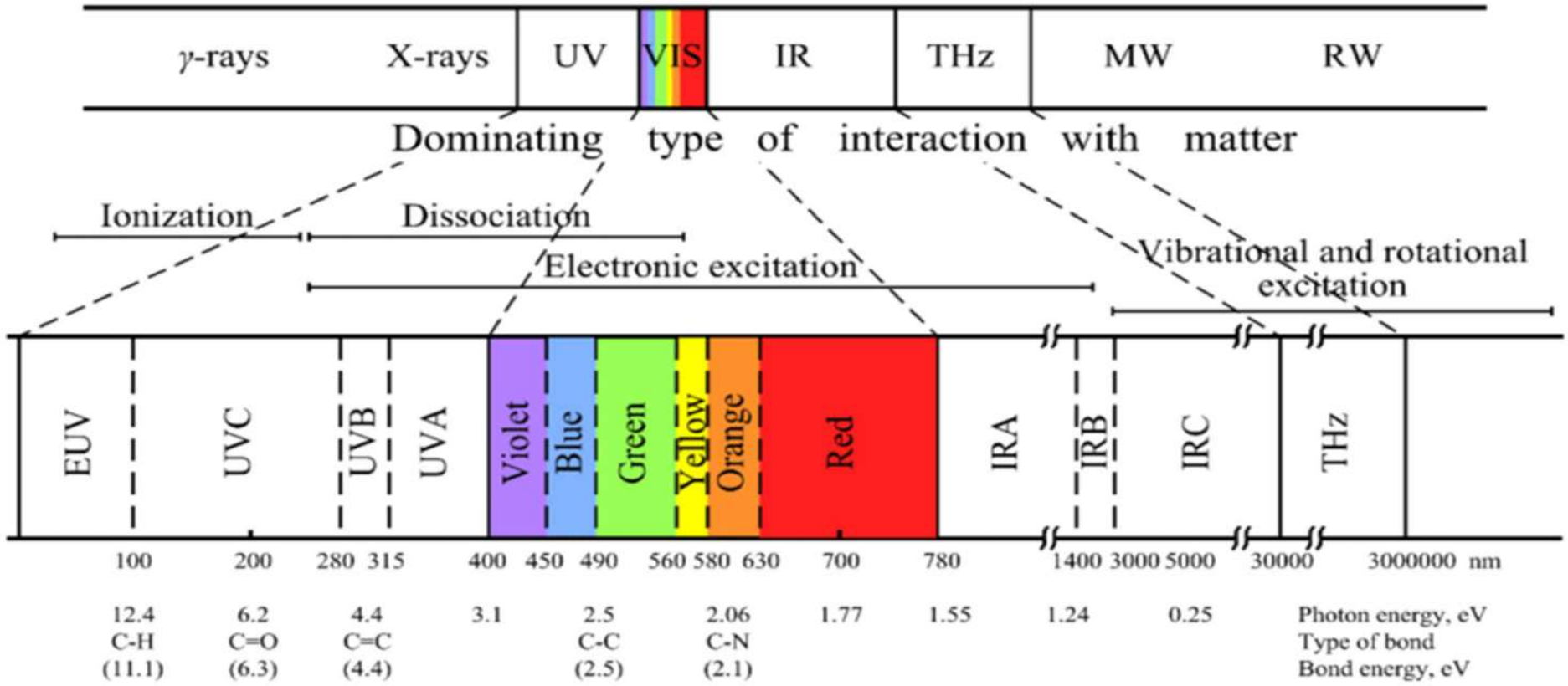
Ultraviolet Spectroscopy "UV"

This chapter includes the following parts:-

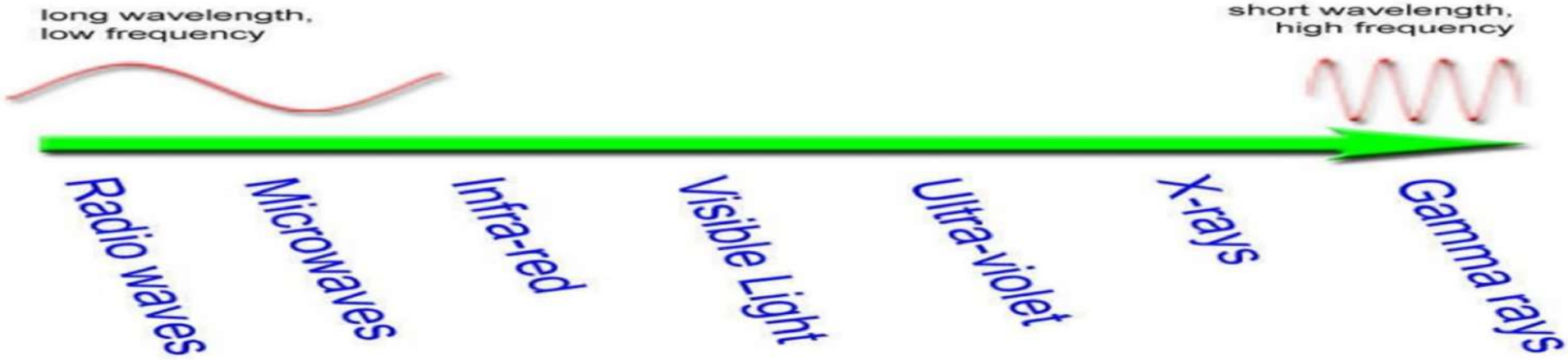
1. Introduction
2. Principles and Electronic transitions. via molecular Orbital theory.
3. λ max and factors affecting its value.
4. UV Important Terminology.
5. calculation of λ max "Woodward-Fieser and Fieser-Kuhn Rules ".
6. Color and Conjugation.

Ultraviolet Spectroscopy "UV"

Part (1)
Introduction



Electromagnetic spectrum

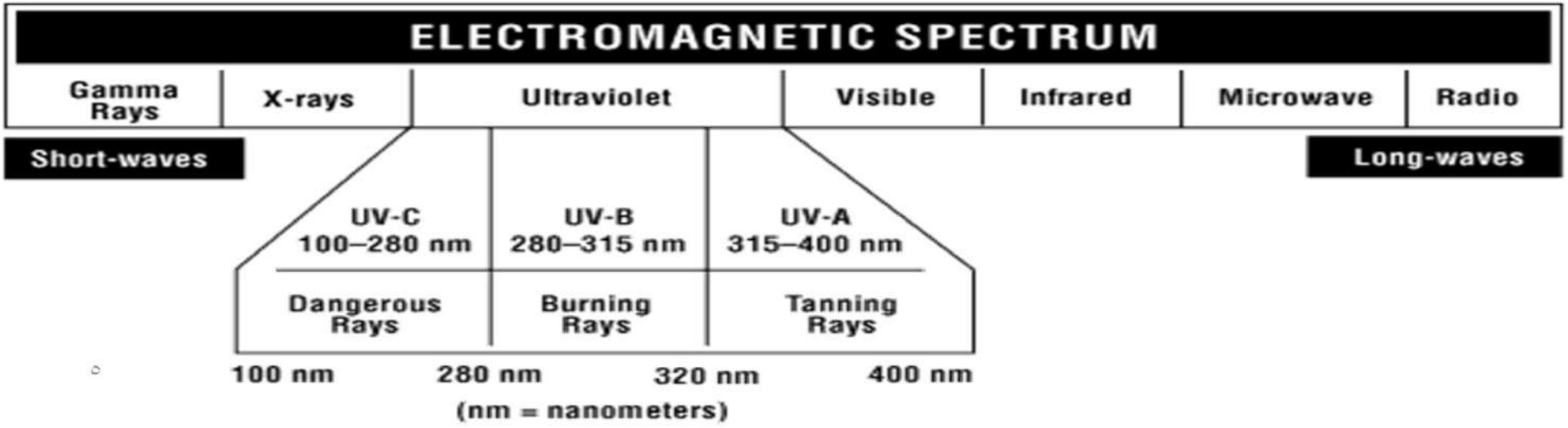


UV is classified by wavelength into three regions:

UVa:-Ultraviolet radiation in the range 315 nm to 400 nm is thought to contribute to premature aging and tanning of the skin and has recently been implicated as a cause of skin cancer.

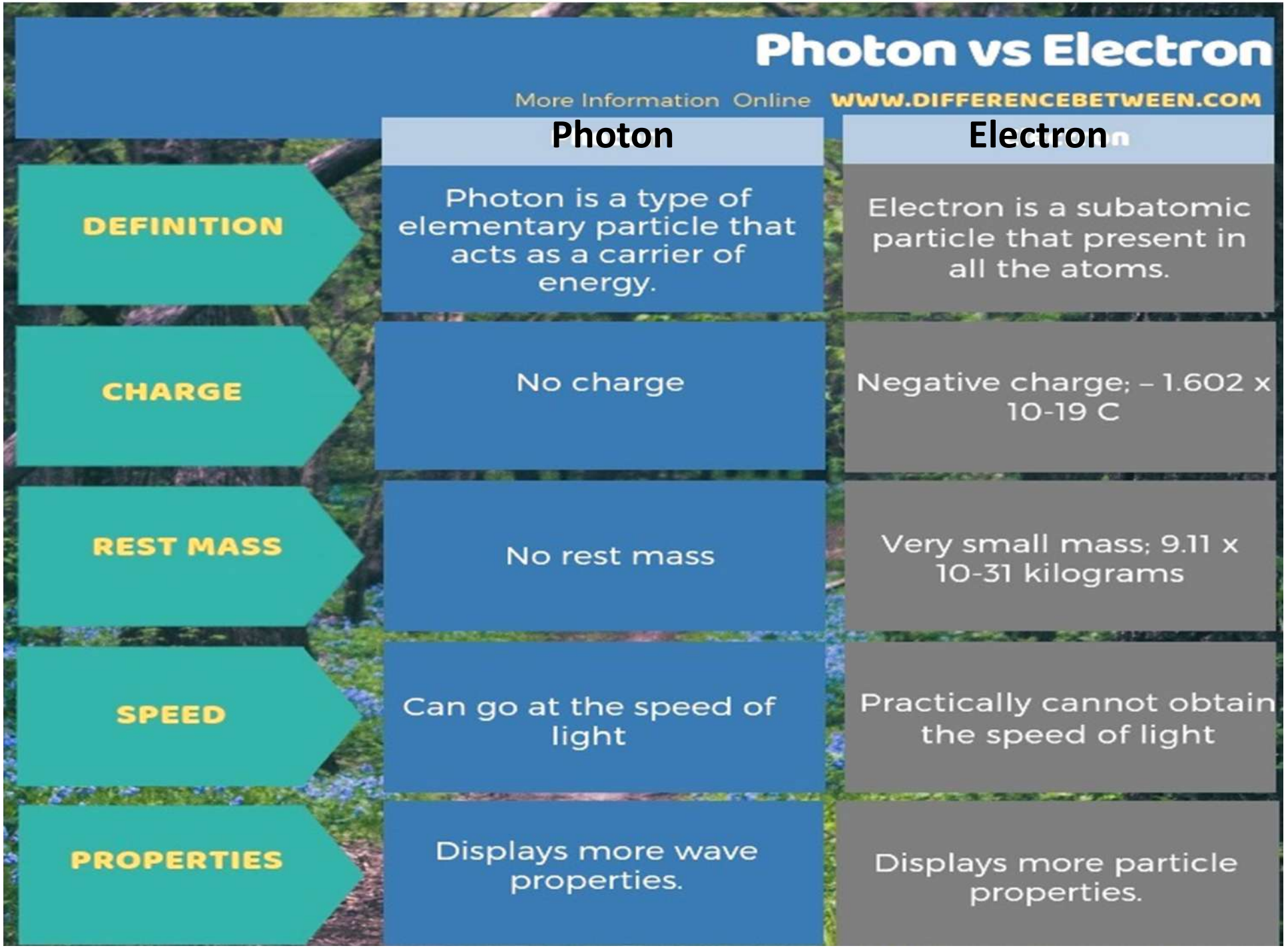
UVb:- Ultraviolet radiation in the range 280 nm to 315 nm is more dangerous than UVA and has been implicated as the major cause of skin cancers, sun burning and cataracts.

UVc:- Ultraviolet radiation in the range 100 nm to 280 nm is extremely dangerous but does not reach the earth's surface due to absorption in the atmosphere by ozone.



Electronic Spectroscopy Ultraviolet (UV) and visible (Vis) spectroscopy:

- **This is the earliest method of molecular spectroscopy by John Ritter 1801).**
- **It is commonly used because of its simplicity, versatility, speed, accuracy and cost-effectiveness.**
- **A phenomenon of interaction of molecules with UV and visible lights leads to absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state to higher electronic states; producing absorption spectra in the range of 200-400 nm**


Photon vs Electron
More Information Online WWW.DIFFERENCEBETWEEN.COM
Photon
Electron
DEFINITION
Photon is a type of elementary particle that acts as a carrier of energy.
Electron is a subatomic particle that present in all the atoms.
CHARGE
No charge
Negative charge; – 1.602 x 10-19 C
REST MASS
No rest mass
Very small mass; 9.11 x 10-31 kilograms
SPEED
Can go at the speed of light
Practically cannot obtain the speed of light
PROPERTIES
Displays more wave properties.
Displays more particle properties.

UV follows the Molecular spectroscopy!!!

Molecular and atomic spectroscopy

Atomic Spectra	Molecular Spectra
1 It occurs from the interaction of atoms and electromagnetic radiation.	It occurs from the interaction of molecules and electromagnetic radiation
2. It is a line spectra	It is a complicated spectra.
3.It is a due to electronic transition in an element	It is due to vibrational, rotational and electronic transition in a molecule

UV Spectroscopy Utility

- First organic spectral method; rarely used as a primary method for structure determination.

- Ultraviolet spectroscopy provides much less information about the structure of molecules than do the spectroscopic techniques studied earlier (infrared spectroscopy and NMR spectroscopy).

- Main contribution is that is can be used to detect the presence of conjugated system like dienes, aromatics, polyenes, and conjugated ketones or aldehydes……etc.

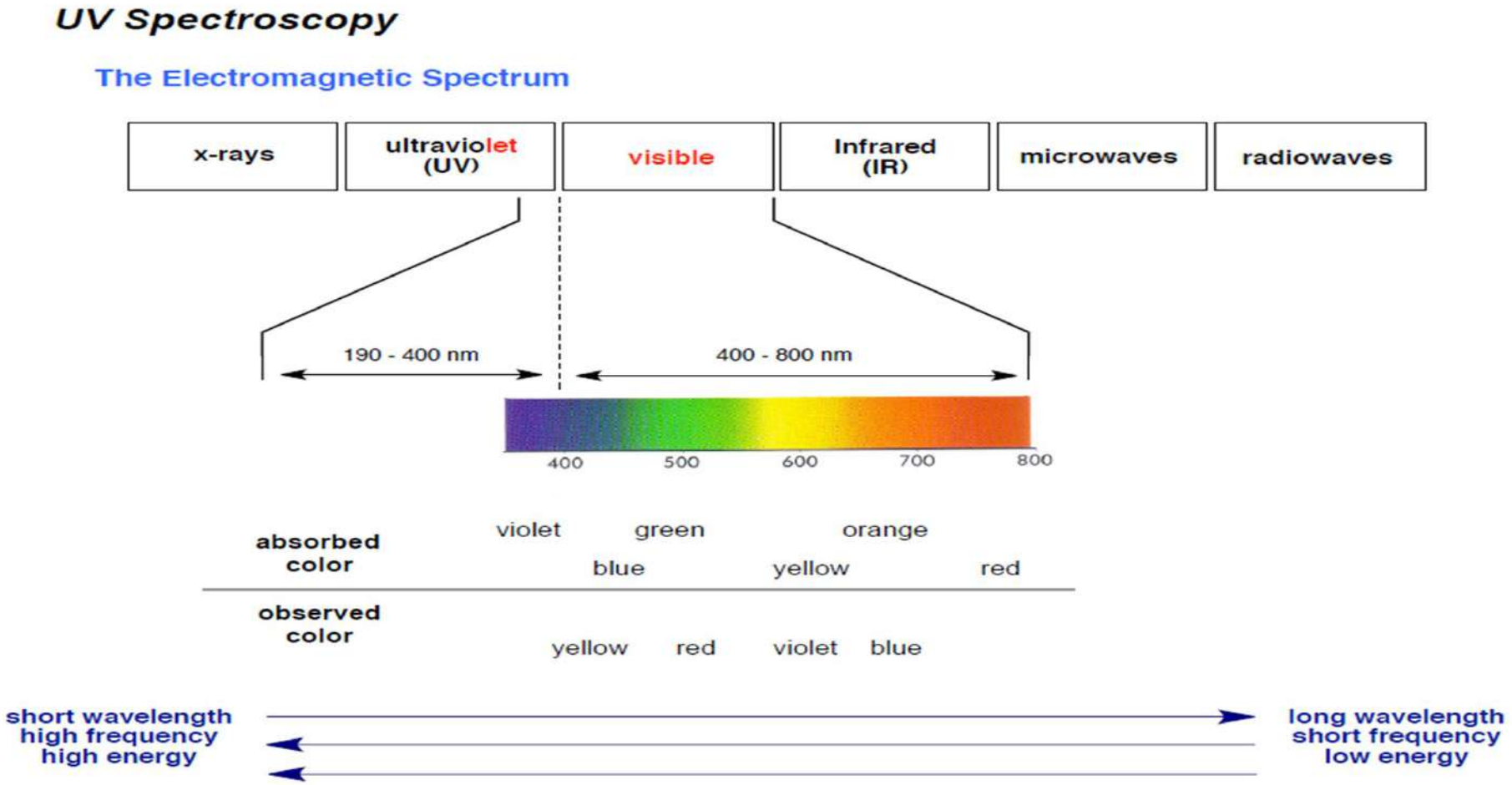
- Can sometimes be used to differentiate double bond isomers.

- In combination with NMR and IR data can use to elucidate unique electronic features not readily apparent from those methods.

- Can be used to monitor reaction kinetics (chemistry, biology, medicine and drug analysis……etc) ATP, DNA…….Metabolic pathway.

What is the difference between UV and Visible EMR?

Both are types of electromagnetic radiation only visible light is at a frequency that the human eye can detect while ultraviolet light is at a frequency that's just beyond what the human eye can detect.



Molecular Absorption

The energy, E, associated with the molecular bands:

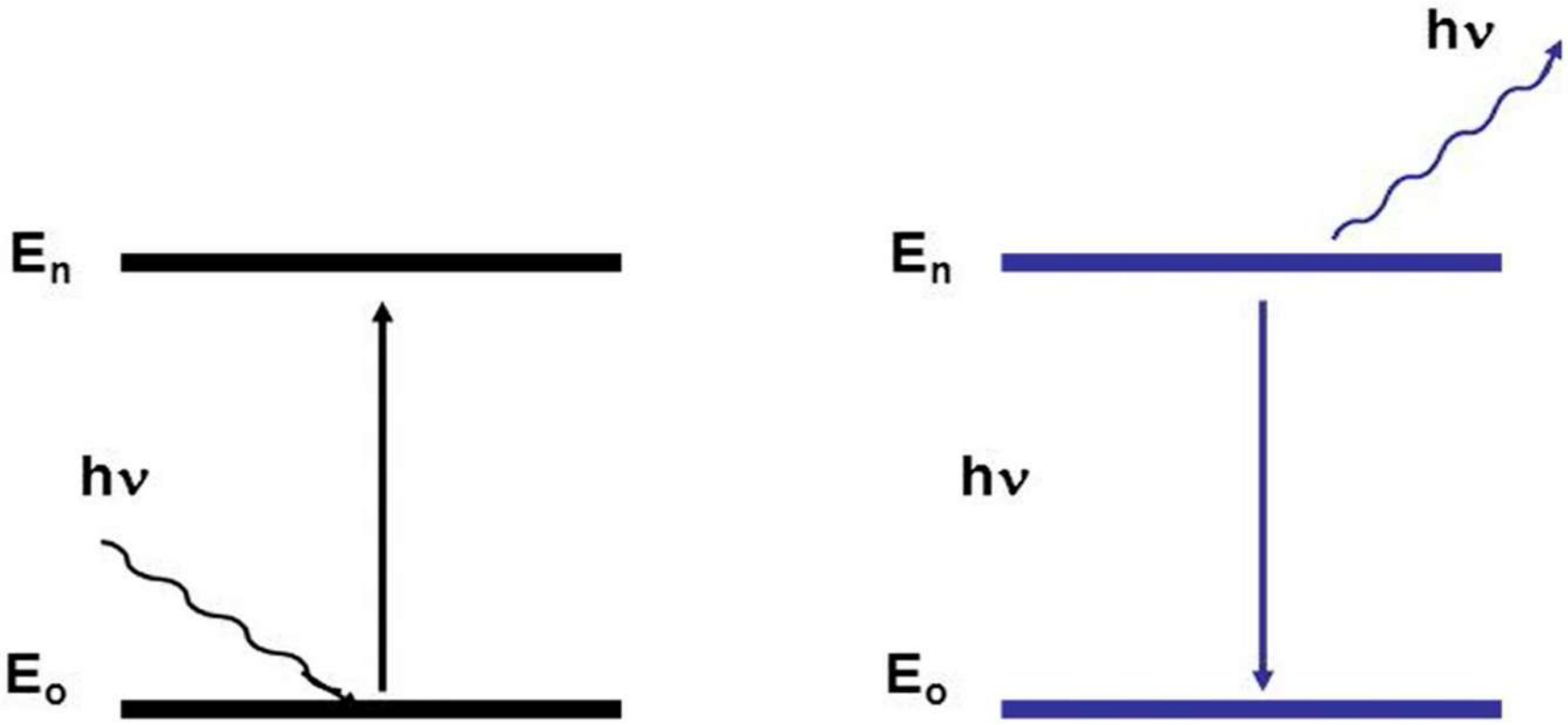
$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational}$$

This is known as Born Oppenheimer Approximation

In general, a molecule may absorb energy in three ways:

- By raising an electron (or electrons) to a higher energy level.
- By increasing the vibration of the constituent nuclei.
- By increasing the rotation of the molecule about the axis.

Absorption vs. Emission



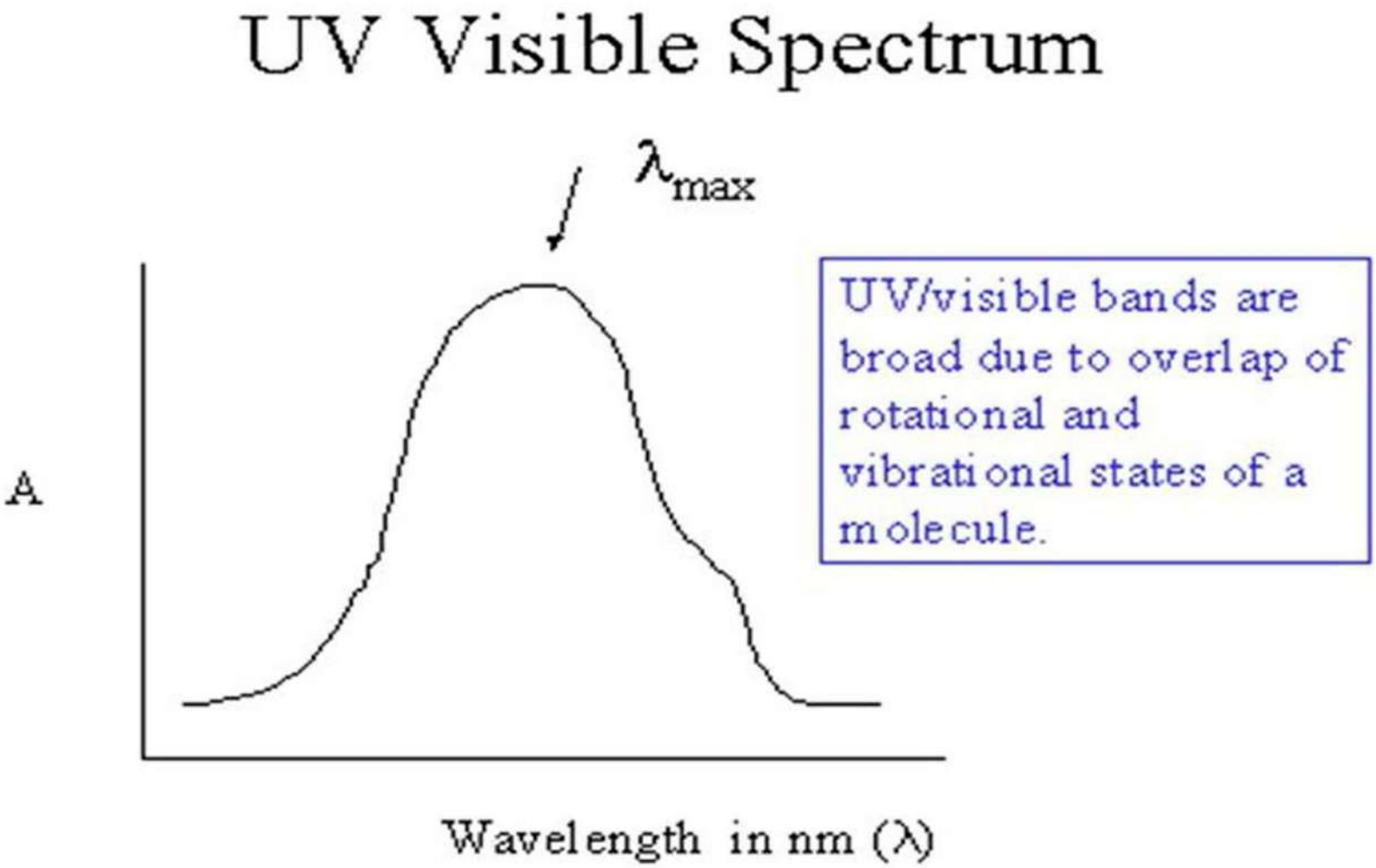
Absorption

Emission

Characteristics of UV spectra of Organic Molecules

- Absorb mostly in UV unless highly conjugated
- Excellent for quantitative Beer's Law-type analyses
- The most common detector for an HPLC.
- Spectra are broad, usually to broad for qualitative identification purposes.
- UV bands are broad due to overlapping of electronic, rotational and vibrational states

Absorption spectrum

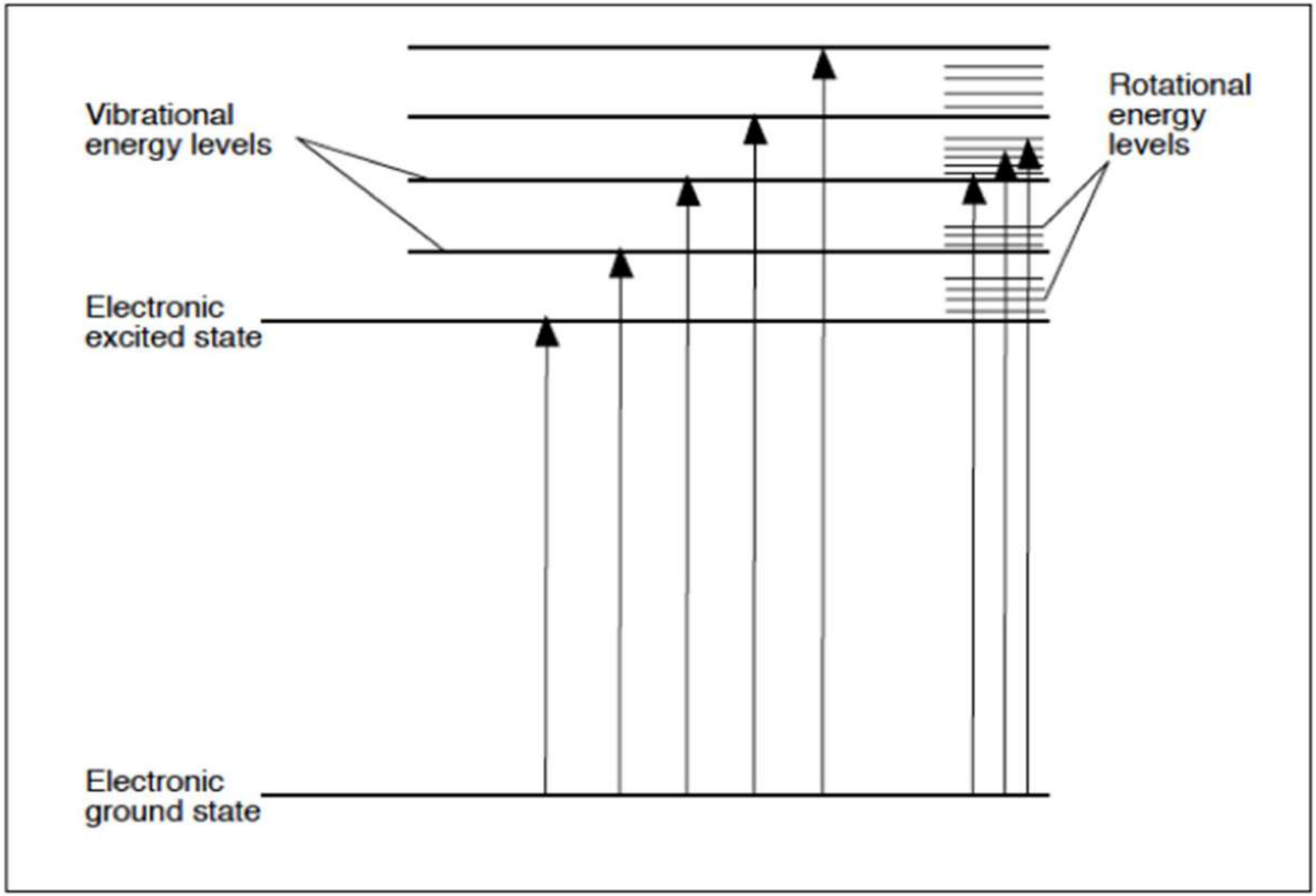


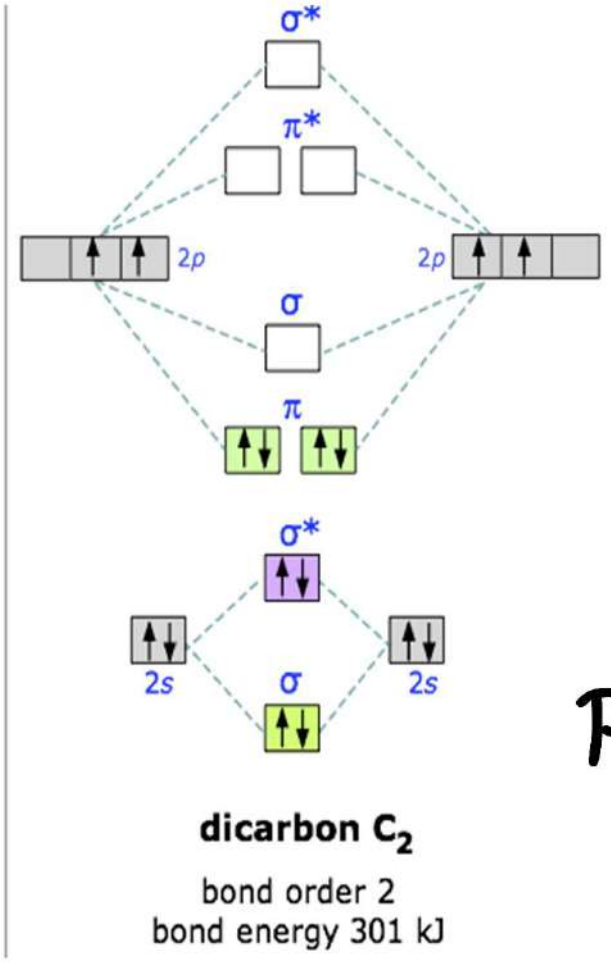
UV Spectroscopy

Spectrum Features

peak broadening

Why UV bands are broad?





Ultraviolet Spectroscopy

"UV"

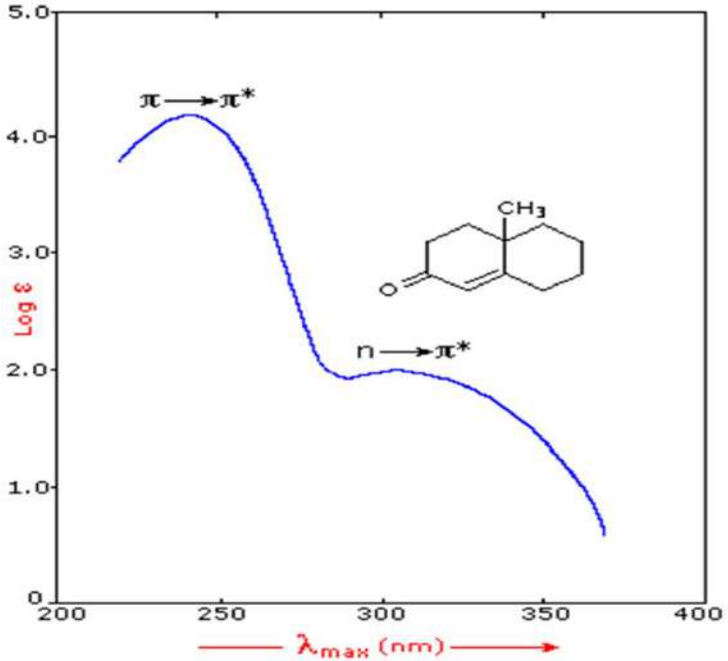
Part (2)

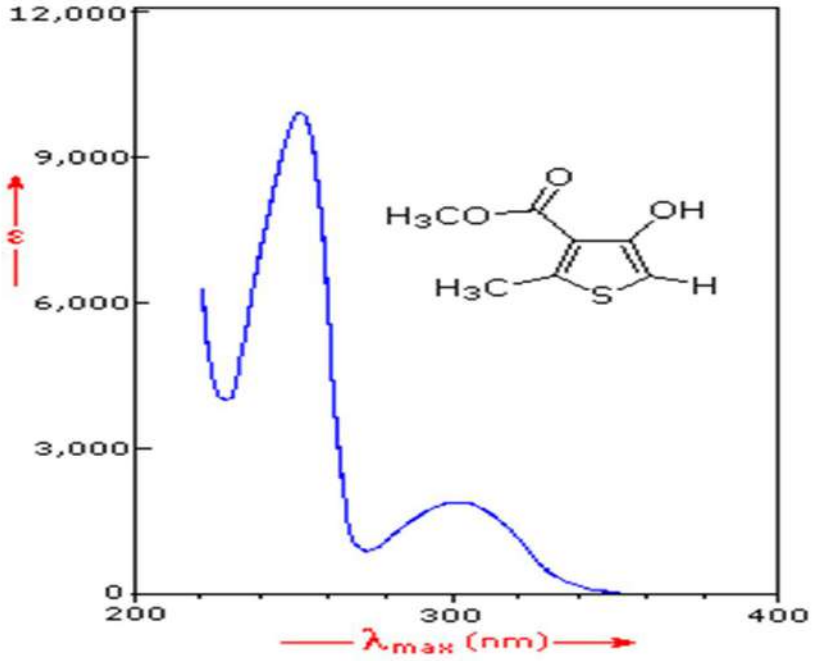
Principles through Electronic transitions via Molecular Orbital theory

Principle of UV spectroscopy

The Spectroscopic Process

1. In UV spectroscopy, the sample is irradiated with the broad spectrum the UV radiation
2. If a particular electronic transition matches the energy of a certain ba of UV, it will be absorbed
3. The remaining UV light passes through the sample and is observed
4. From this residual radiation a spectrum is obtained with "gaps" at the discrete energies – this is called an absorption spectrum





Principle of UV spectroscopy

Origin of electronic spectra Absorptions of UV-Vis light photons by molecule results in electronic excitation of molecule with CHROMOPHORE . The electronic transition involves promotion of electron from an electronic ground state (HOMO) to higher energy state (LUMO).

HOMO and LUMO

They are related to Molecular Orbital Theory ;

HOMO:- Highest Occupied Molecular Orbital

LUMO:- Lowest Unoccupied Molecular Orbital

CHROMOPHORE:

The term chromophore was previously used to denote a functional group which gives a color to compound. For example- Nitro group is a chromophore because its presence in a compound gives yellow color to the compound.

But these days the term chromophore is used in a much broader sense which may be defined as "any group which exhibit absorption of electromagnetic radiation in a visible or ultra-visible region "It may or may not impart any color to the compound. Some of the important chromophores are: ethylene, acetylene, carbonyls, acids, esters and nitrile groups etc. A carbonyl group is an important chromophore, although the absorption of light by an isolated group does not give rise to any colour in the ultra-violet spectroscopy.

Organic Chromophores

Chromophore	Transition	Λ_{max}(nm)	log(ε)
Nitrile (-C≡N)	η to π*	160	<1.0
Alkyne (-C≡C-)	π to π*	170	3.0
Alkene (-C=C-)	π to π*	175	3.0
Alcohol (ROH)	η to σ*	180	2.5
Ether (ROR)	η to σ*	180	3.5
Ketone (-C(R)=O)	π to π*	180	3.0
	η to π*	280	1.5
Aldehyde (−C(H)=O)	π to π*	190	2.0
	η to π*	290	1.0
Amine ($-NR_2$)	η to σ*	190	3.5
Acid (-COOH)	η to π*	205	1.5
Ester (-COOR)	η to π*	205	1.5
Amide ($-C(=O)NH_2$)	η to π*	210	1.5
Thiol (-SH)	η to σ*	210	3.0

Chromophore absorptions

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

Basic Concept

UV light (200 -400 nm)
Visible light (400 – 700 nm)

→ Organic molecules → Electronic Transitions

Excited state/High energy orbitals/LUMO(Lowest Occupied Molecular orbital

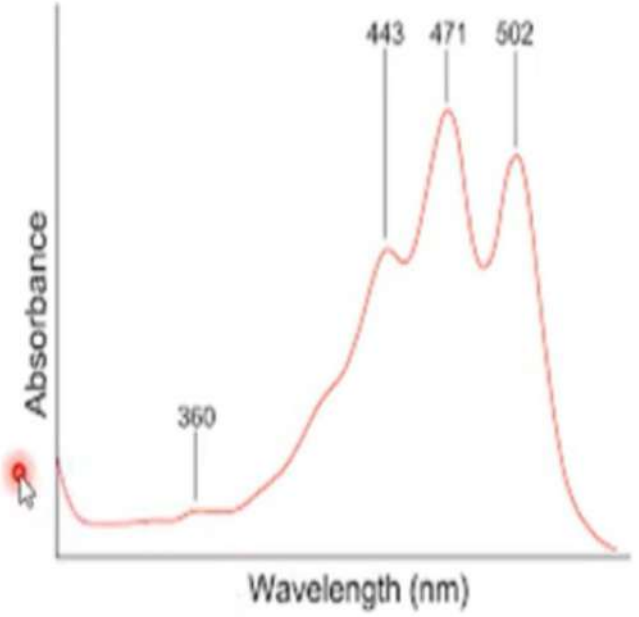
Energy difference

UV light (200 -400 nm)
Visible light (400 – 700 nm

Ground state/Low energy orbitals/HOMO (Highest Occupied Molecular orbital

Excited state/High energy orbitals/LUMO(Lowest Occupied Molecular orbital

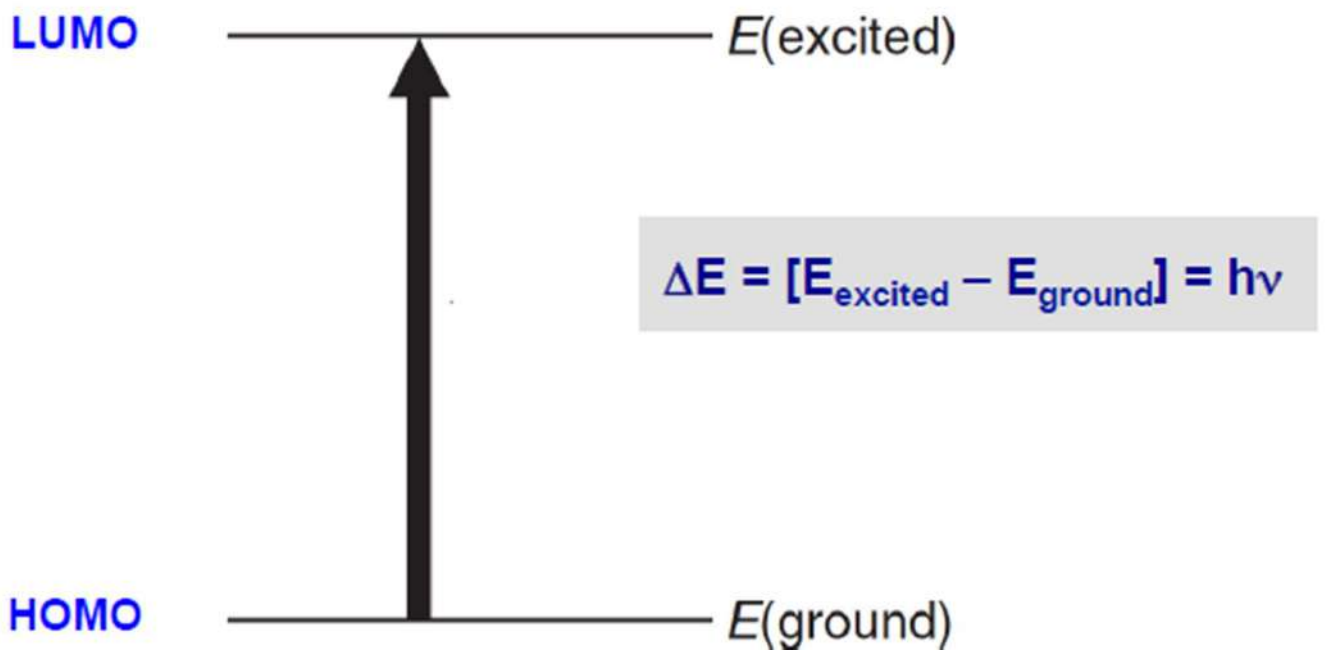
Ground state/Low energy orbitals/HOMO (Highest Occupied Molecular orbital



UV Spectroscopy

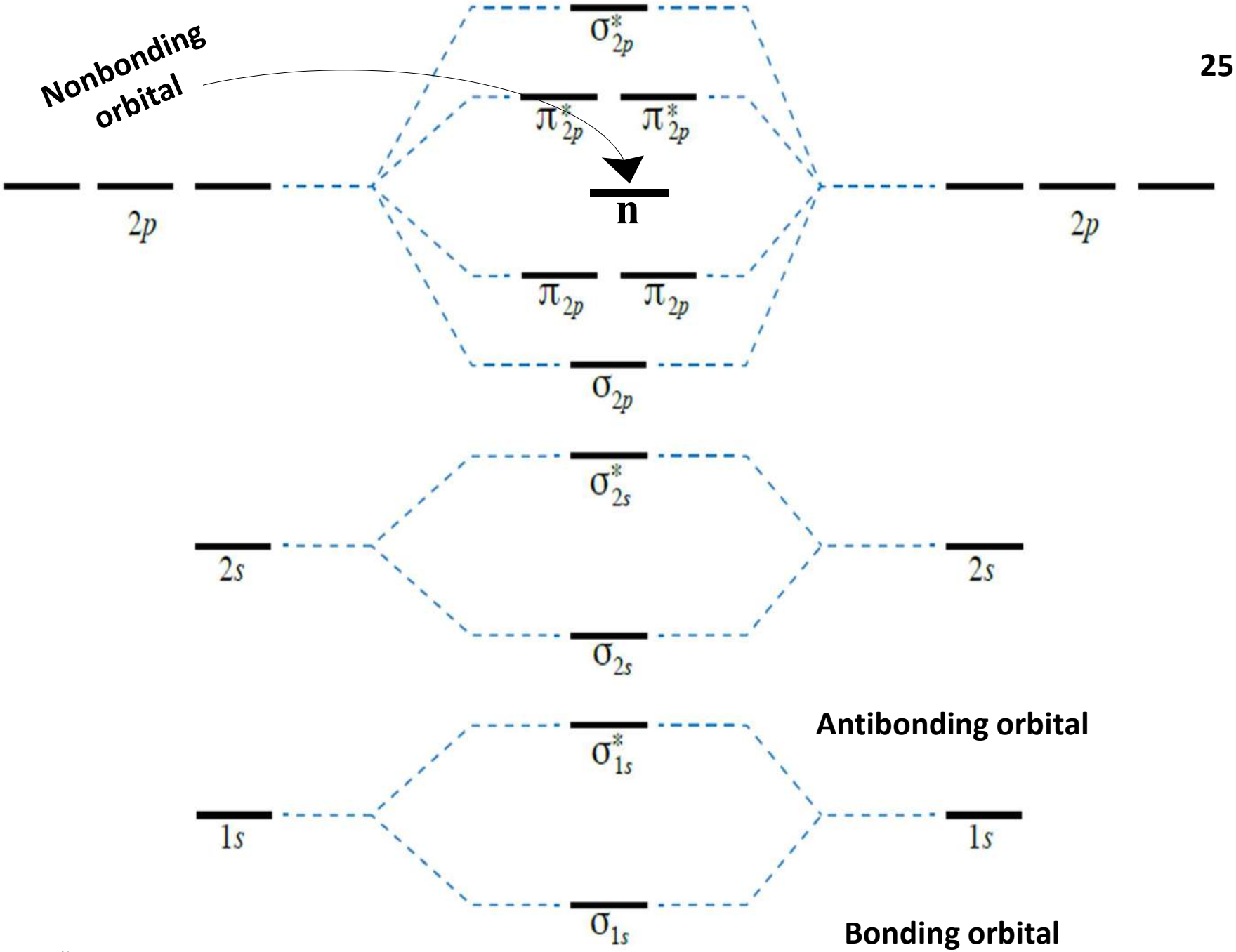
Origin of the Absorption

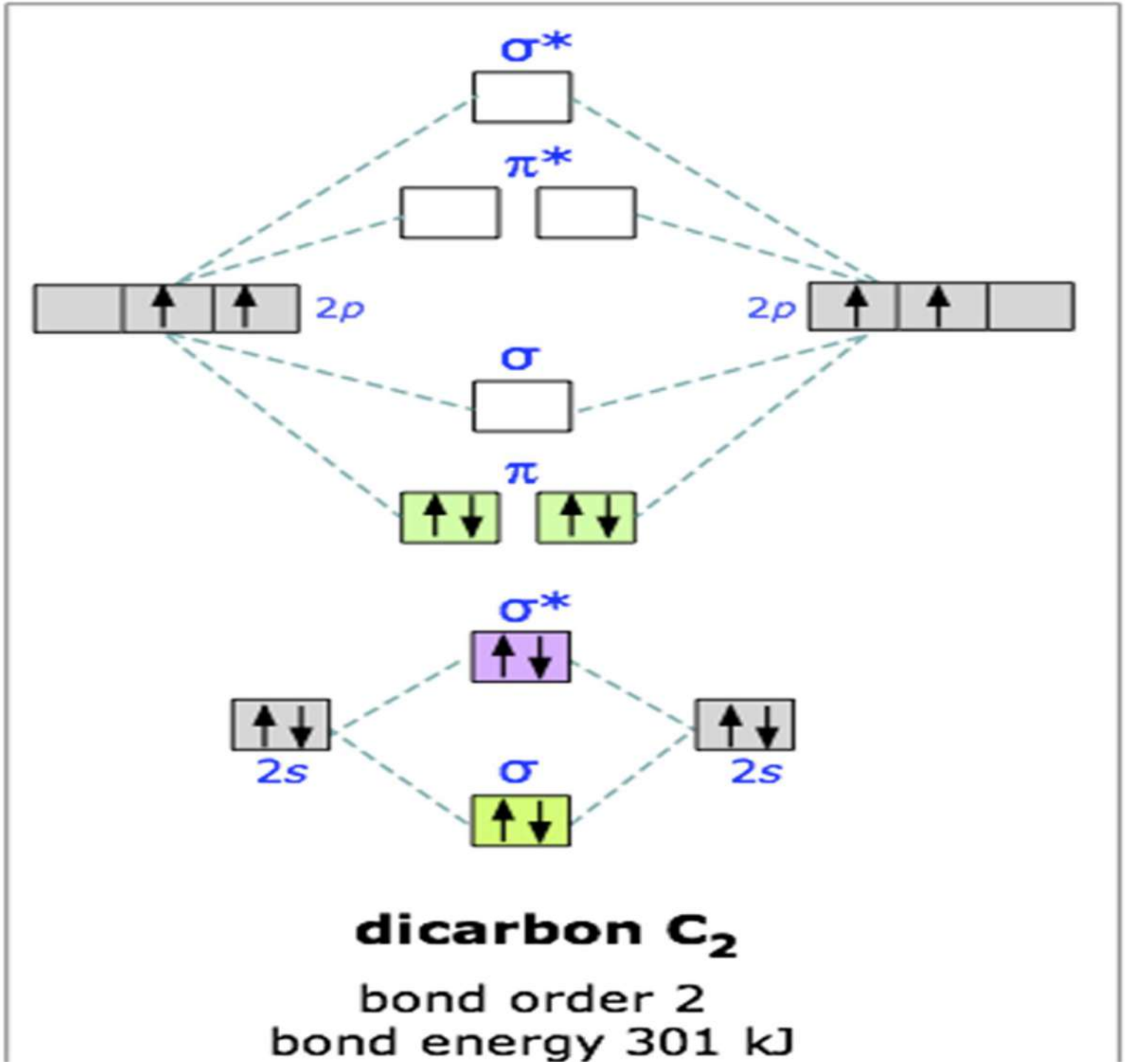
- The absorption of UV or visible radiation corresponds to the excitation of valence electrons
- Valence electrons are typically found in:
  - σ bonding orbitals (single bonds)
  - π bonding prbitals (double or triple bonds)
  - non-bonding orbitals (lone pair electrons)



Molecular Orbital Theory

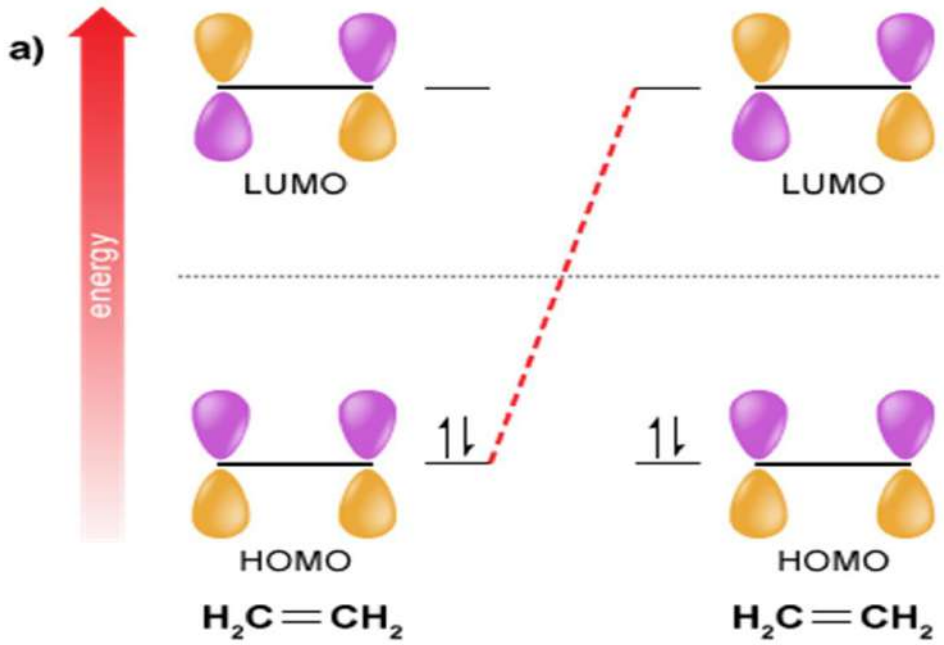
M. O. Theory

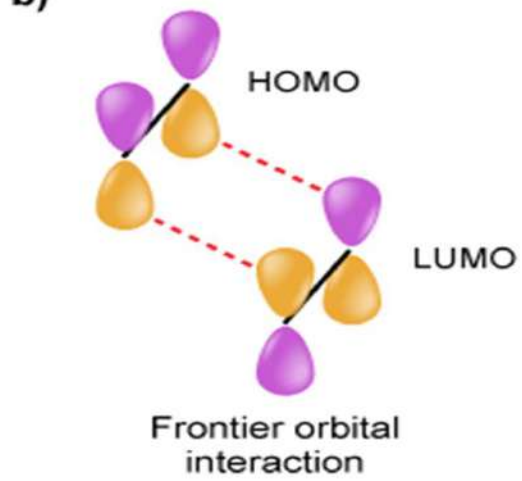

Nonbonding orbital
σ^*_{2p}
π^*_{2p}
π^*_{2p}
n
2p
2p
π_{2p}
π_{2p}
σ_{2p}
σ^*_{2s}
2s
2s
σ_{2s}
Antibonding orbital
σ^*_{1s}
1s
1s
σ_{1s}
Bonding orbital

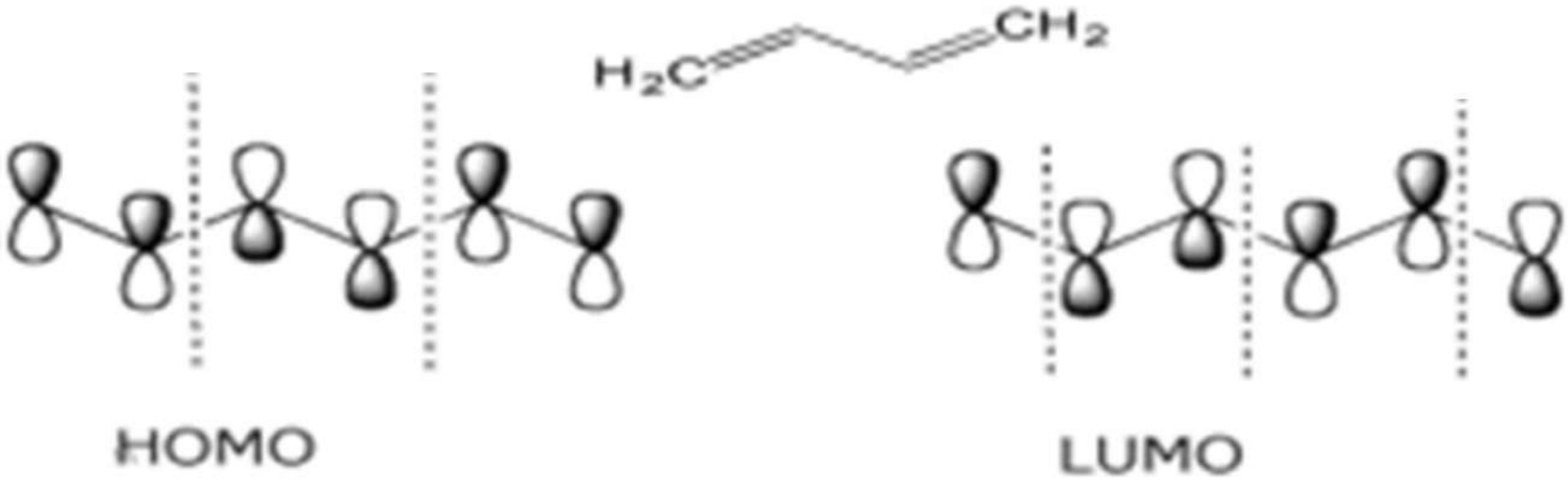


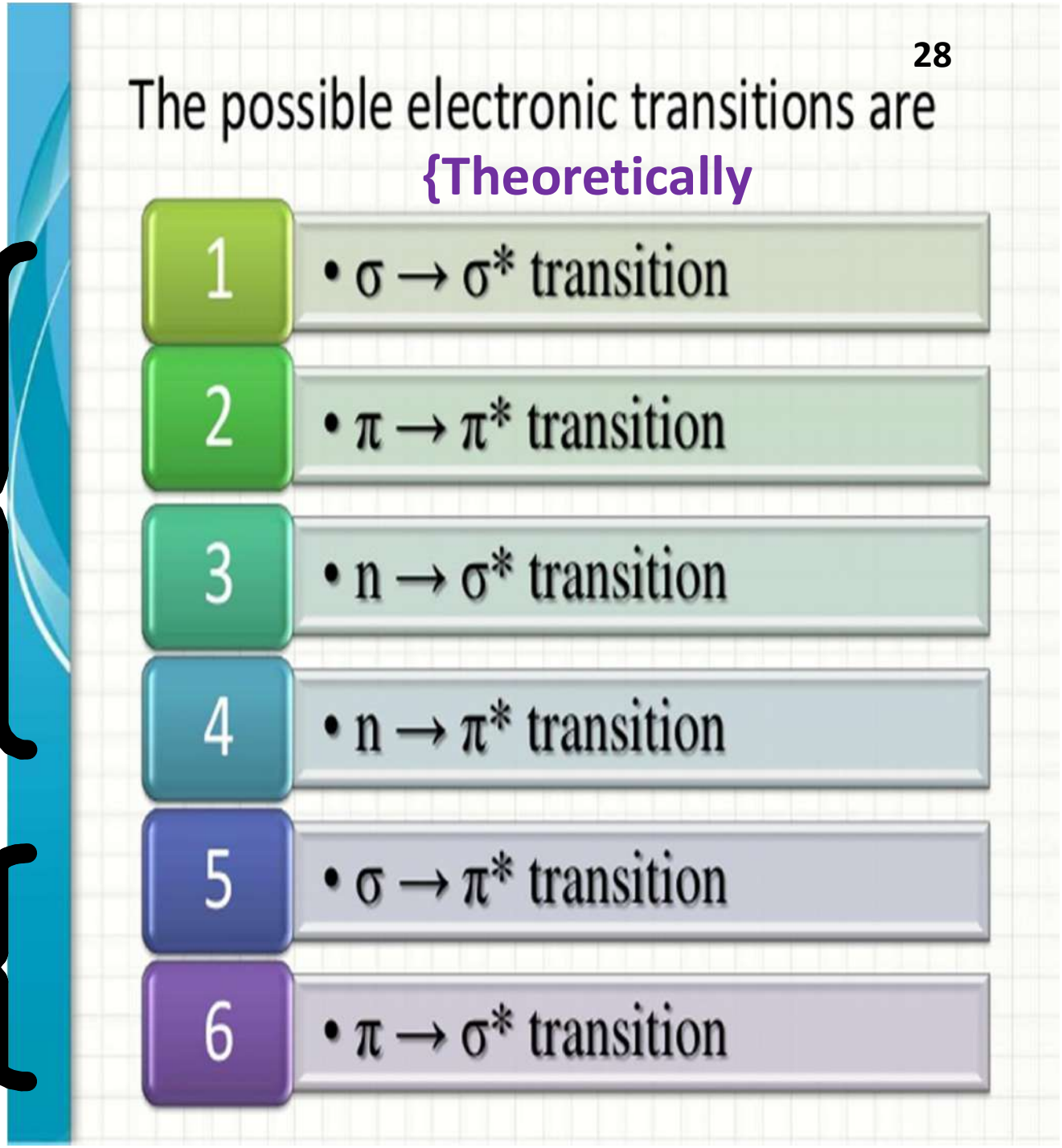
dicarbon C_2

bond order 2
bond energy 301 kJ


a)
energy
LUMO
LUMO
HOMO
HOMO
$H_2C=CH_2$
$H_2C=CH_2$


b)
HOMO
LUMO
Frontier orbital interaction


H_2C
CH_2
HOMO
LUMO



Allowed

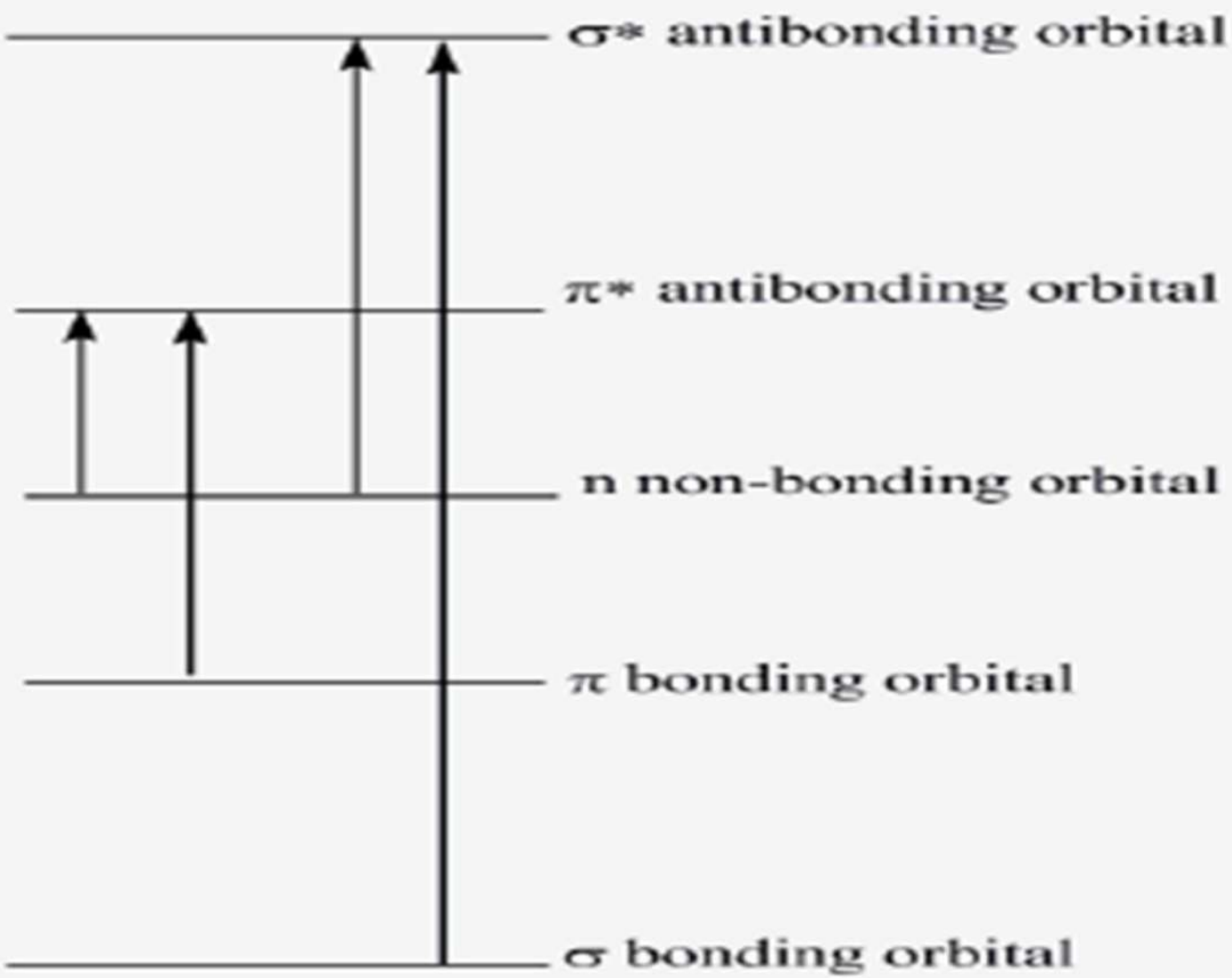
Not allowed

TYPES OF TRANSITIONS:

In U.V spectroscopy molecule undergo 6 electronic transition involving σ, π and n electrons.

- Four types of electronic transition are possible.

i. $\sigma \rightarrow \sigma^*$ transition
ii. $n \rightarrow \sigma^*$ transition
iii. $n \rightarrow \pi^*$ transition
iv. $\pi \rightarrow \pi^*$ transition


σ* antibonding orbital
π* antibonding orbital
n non-bonding orbital
π bonding orbital
σ bonding orbital

1 • σ ⟶ σ* transition

The maximum absorption at (110-125)nm +/-

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.
- The energy required is large for this transition.

2 • π ⟶ π* transition

The absorption region (160-210 nm) +/-

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.

3 • $n \rightarrow \sigma^*$ transition

The absorption region (150-250nm) +/-

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of $n \rightarrow \sigma^*$ transition.

4 • $n \rightarrow \pi^*$ transition

The absorption region ~ 300nm +/-

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.
- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.

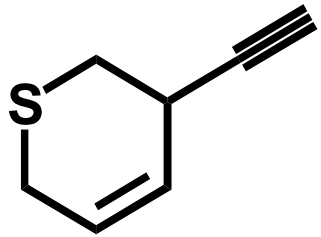
5 • $\sigma \rightarrow \pi^*$ transition

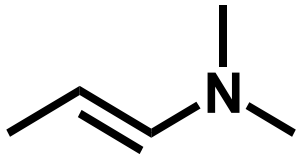
6 • $\pi \rightarrow \sigma^*$ transition

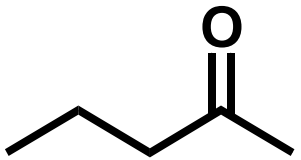
- These electronic transitions are forbidden transitions & are only theoretically possible.

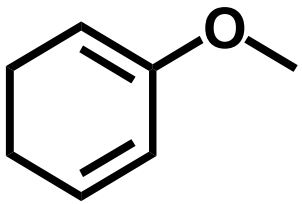
(Selection Rule)

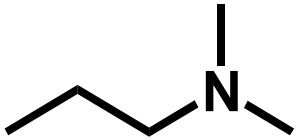
Predict the favorable electronic transitions for each of the following compounds in the UV spectrum (within the allowed four0

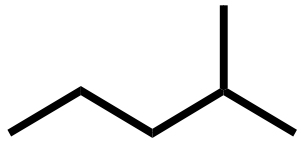
a] 

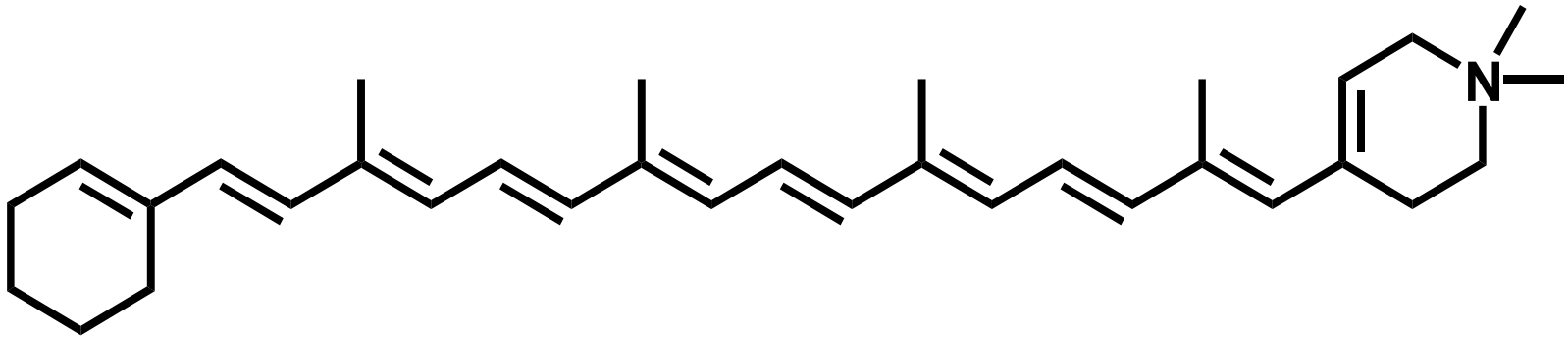
b] 

c] 

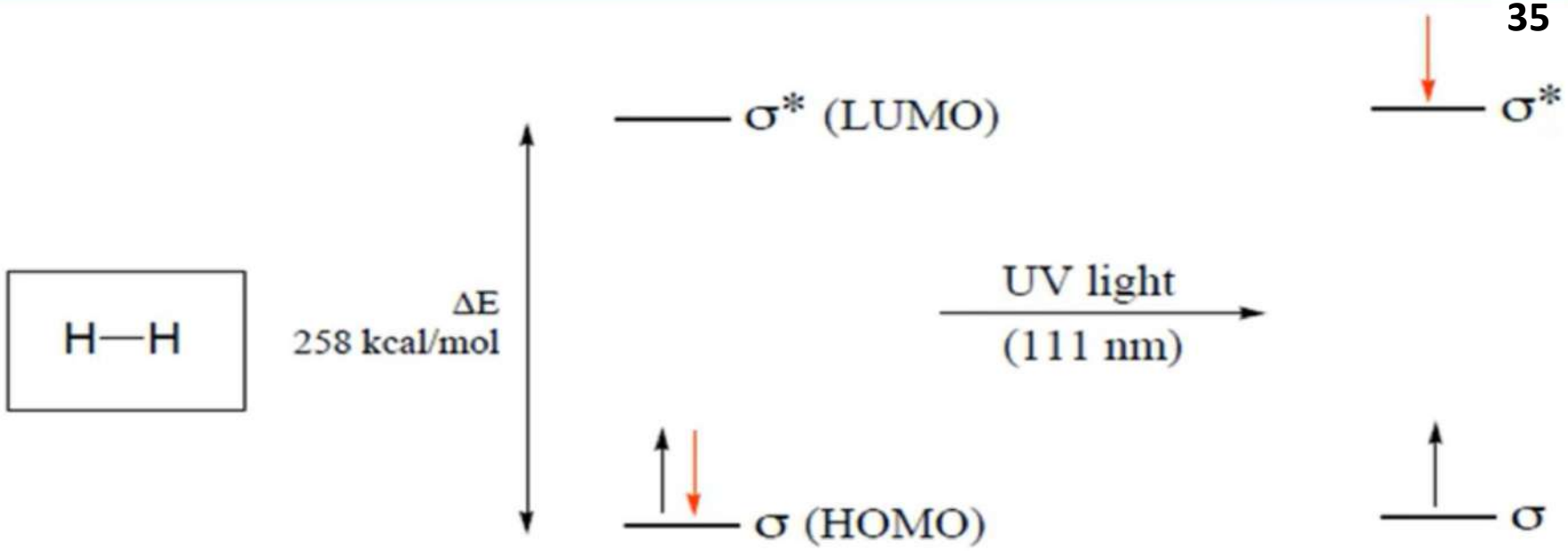
d] 

e] 

f] 

g] 

Interactions of organic molecules with UV/Visible light



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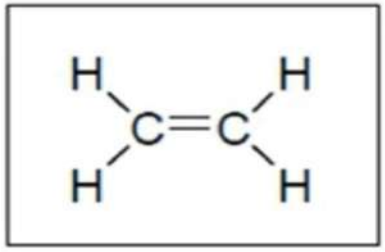
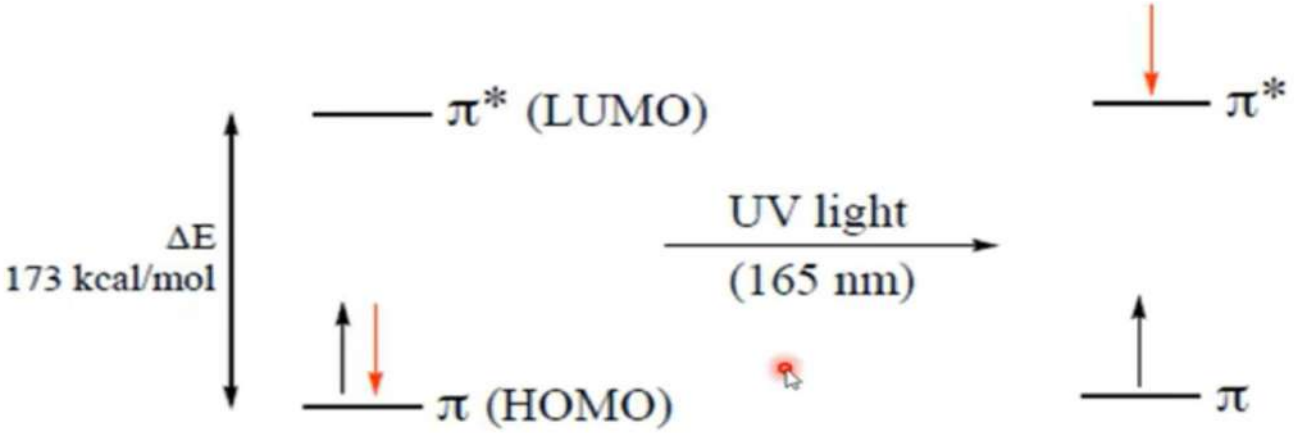
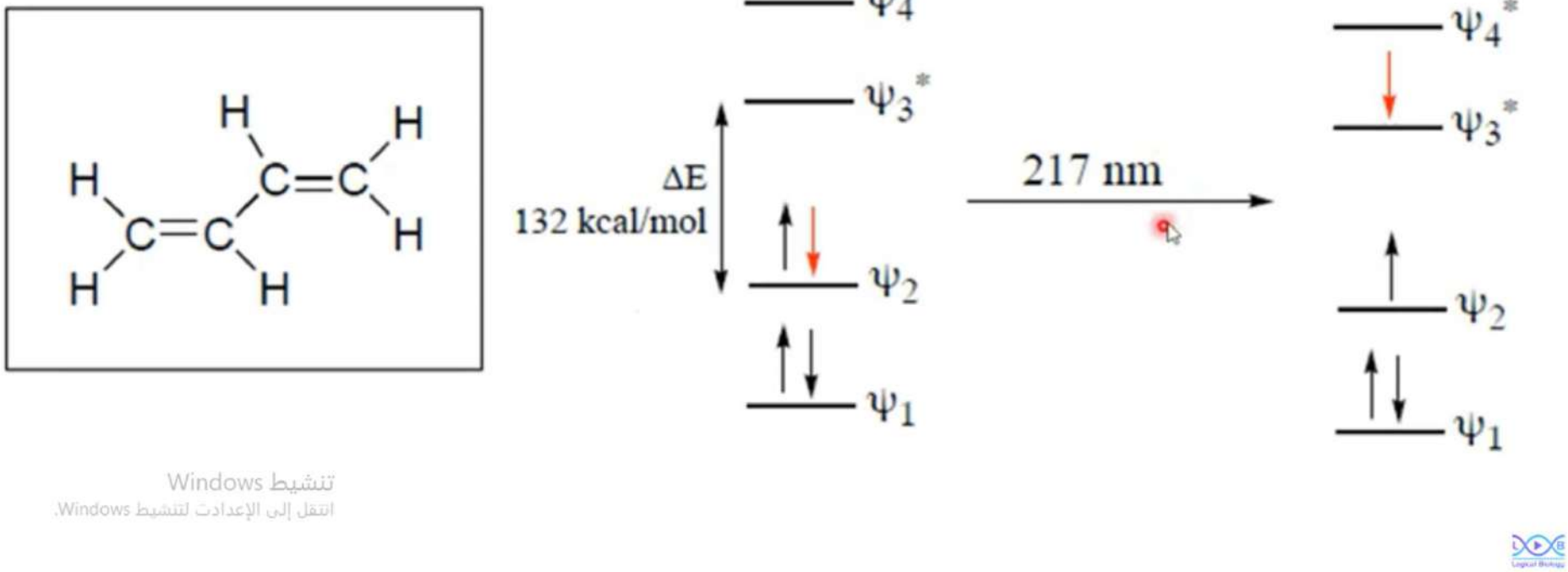
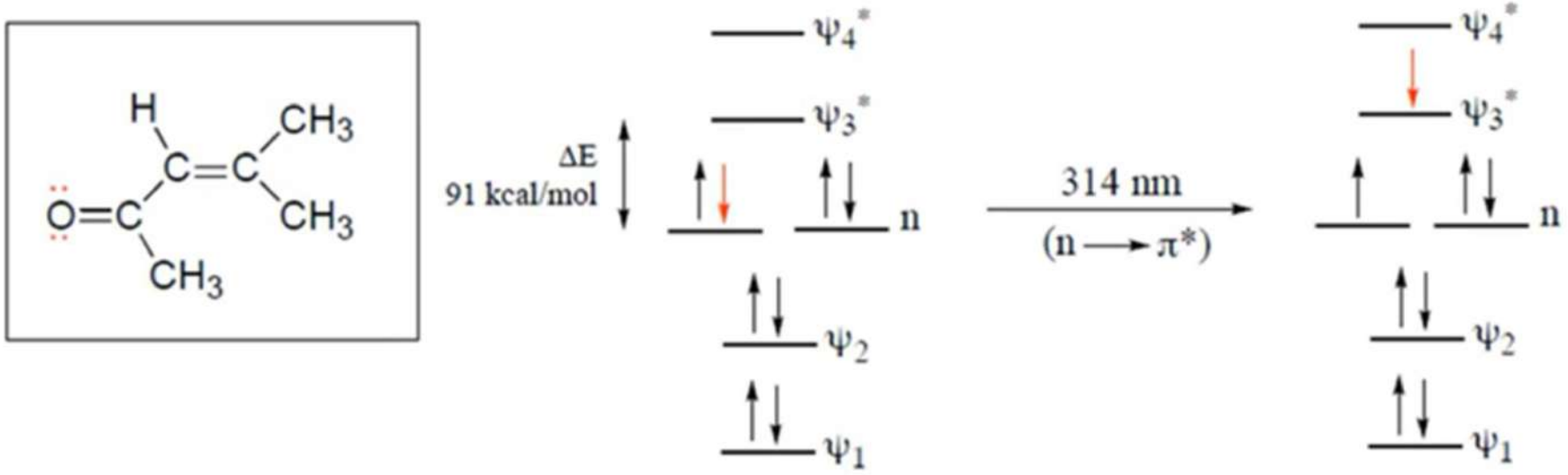




Interactions of organic molecules with UV/Visible light

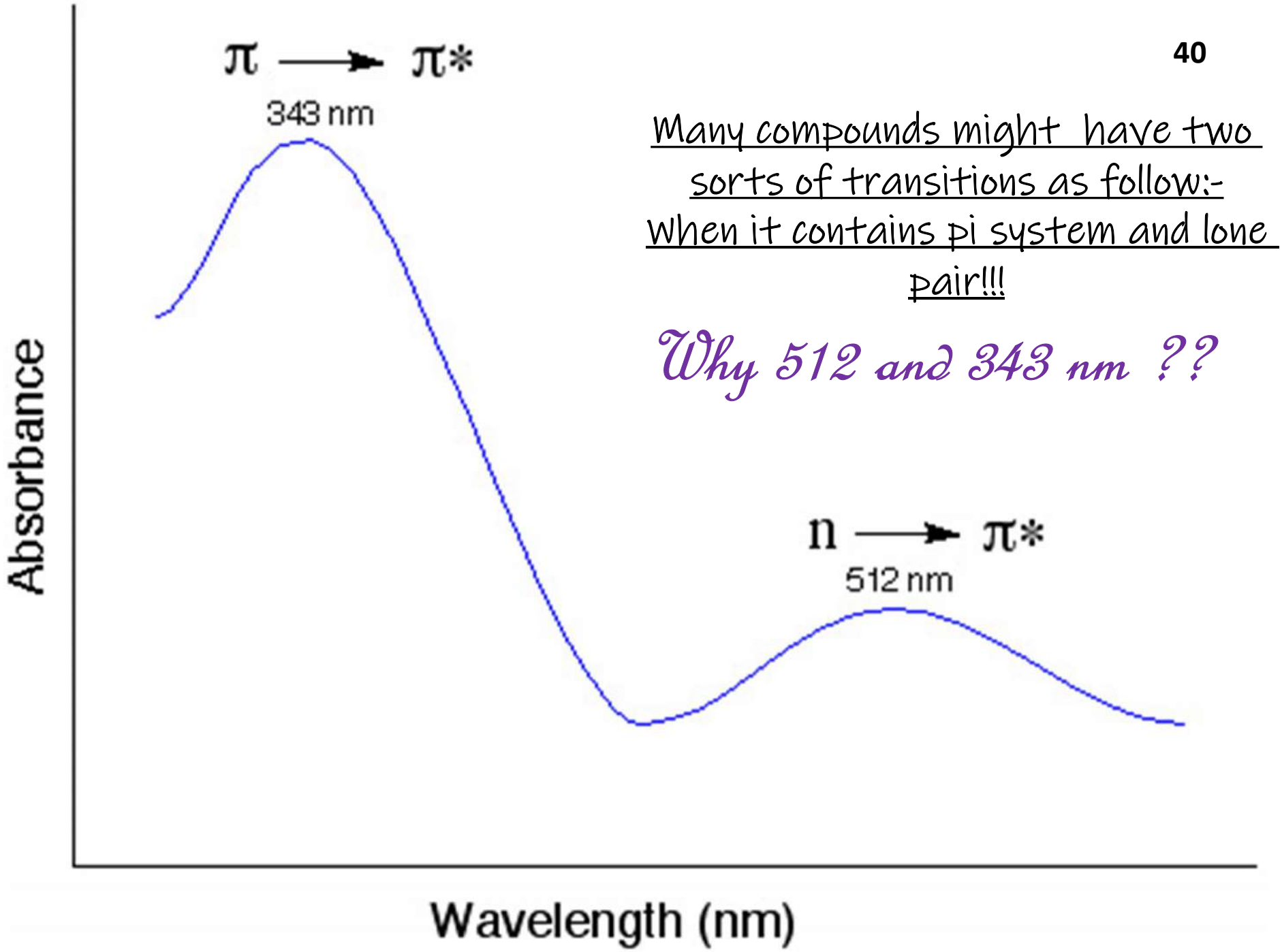


Interactions of organic molecules with UV/Visible light



Wavelength absorbed by functional groups

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

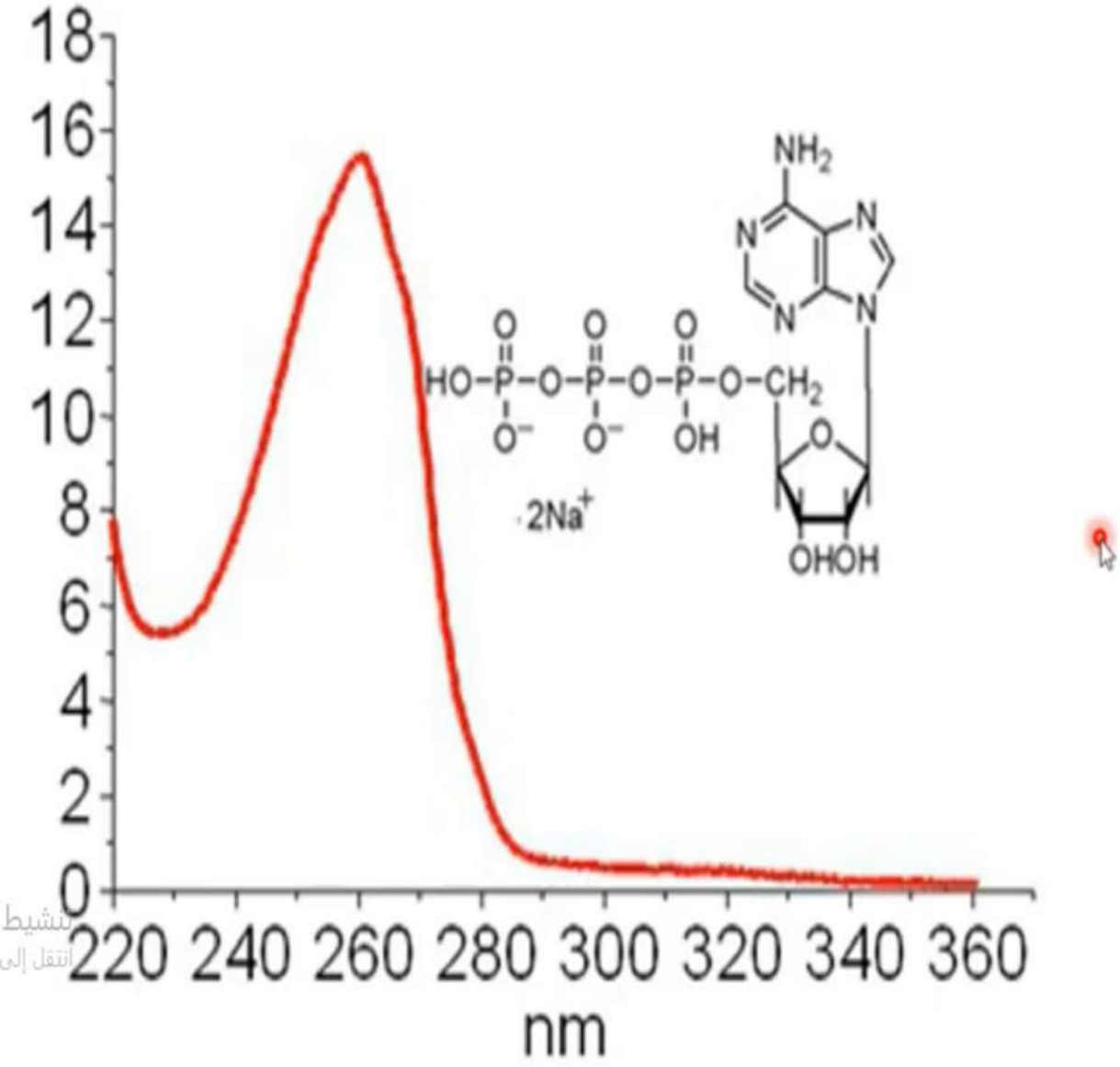


Many compounds might have two sorts of transitions as follow:-
When it contains pi system and lone pair!!!

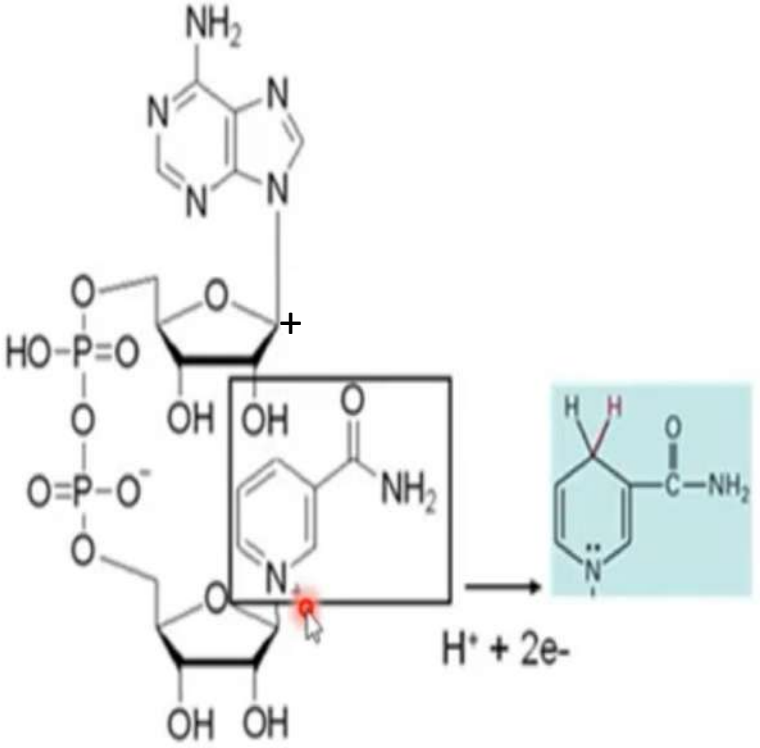
Why 512 and 343 nm ??

UV/VIS Spectra of ATP

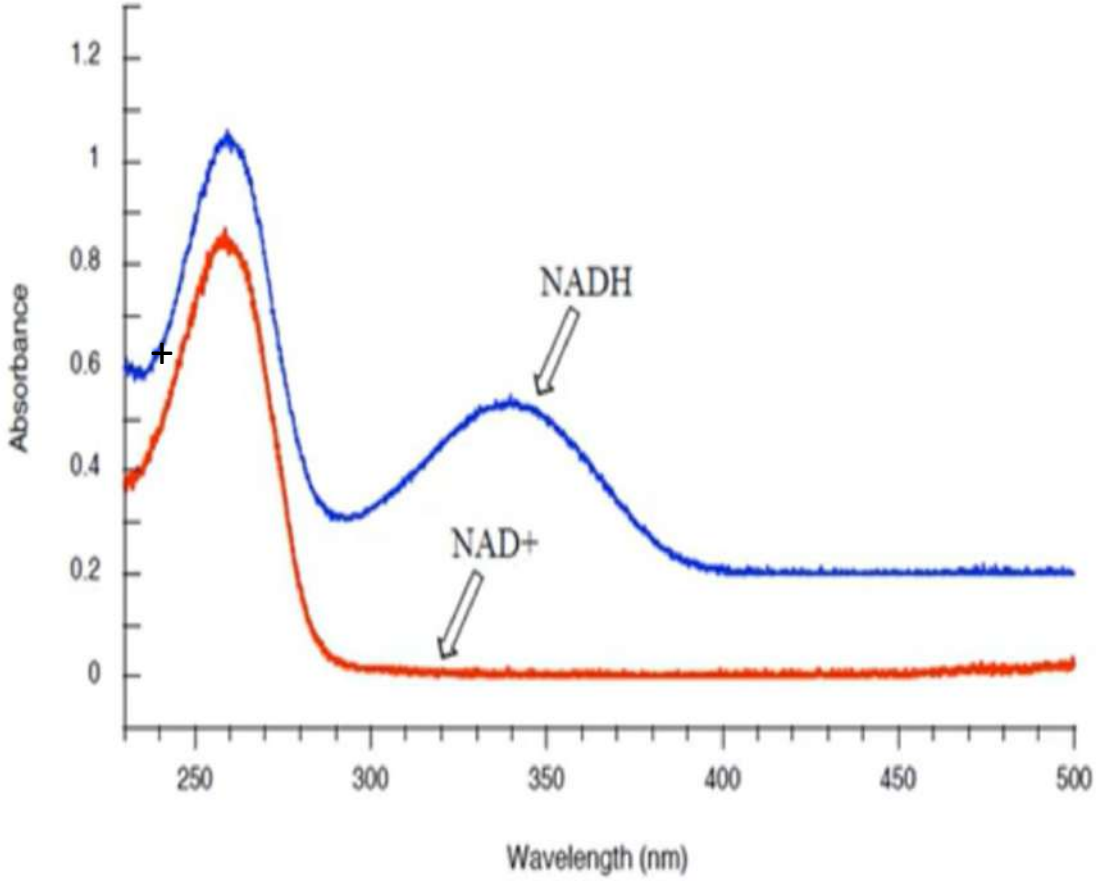
A

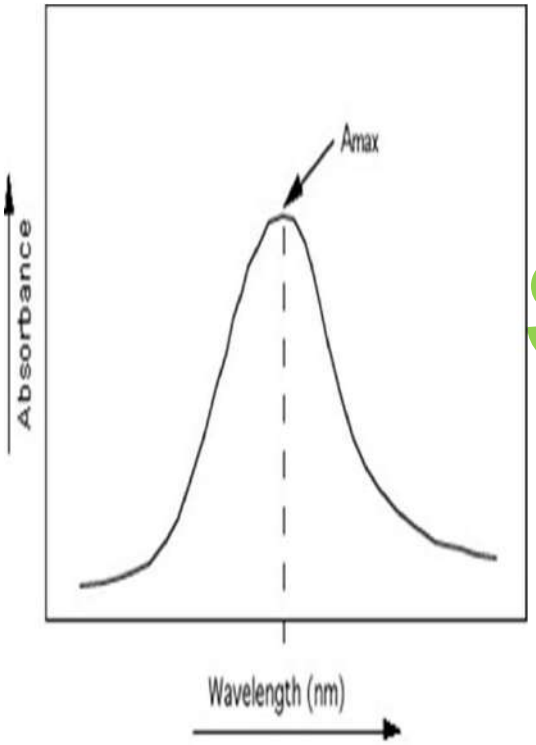


UV/VIS Spectra of NAD+/NADH



NAD+ NADH





Ultraviolet Spectroscopy "UV"

Part (3)

λ max and factors affecting its value

UV-visible spectrum

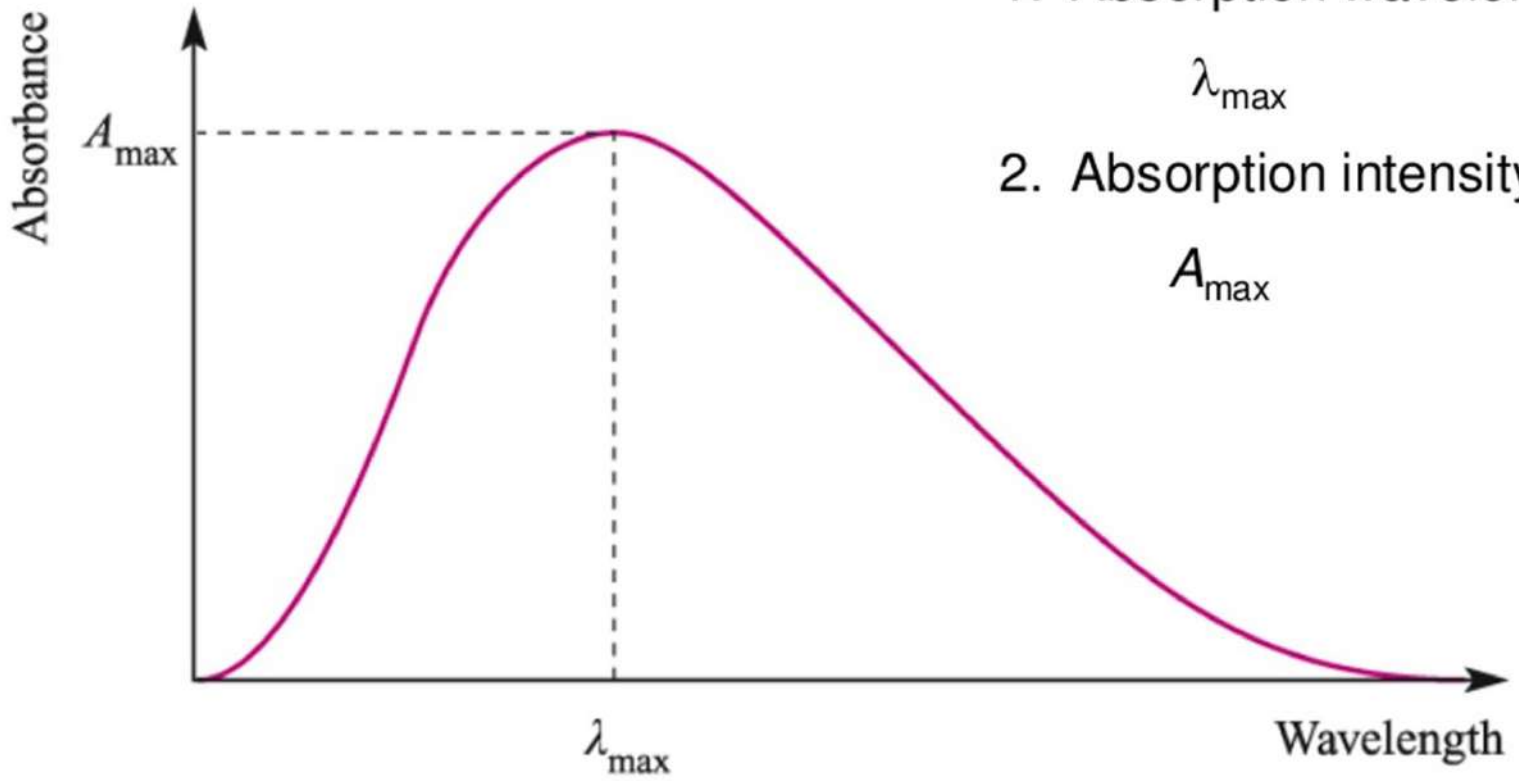
The two main properties of an absorbance peak are:

1. Absorption wavelength

   λ_{max}

2. Absorption intensity

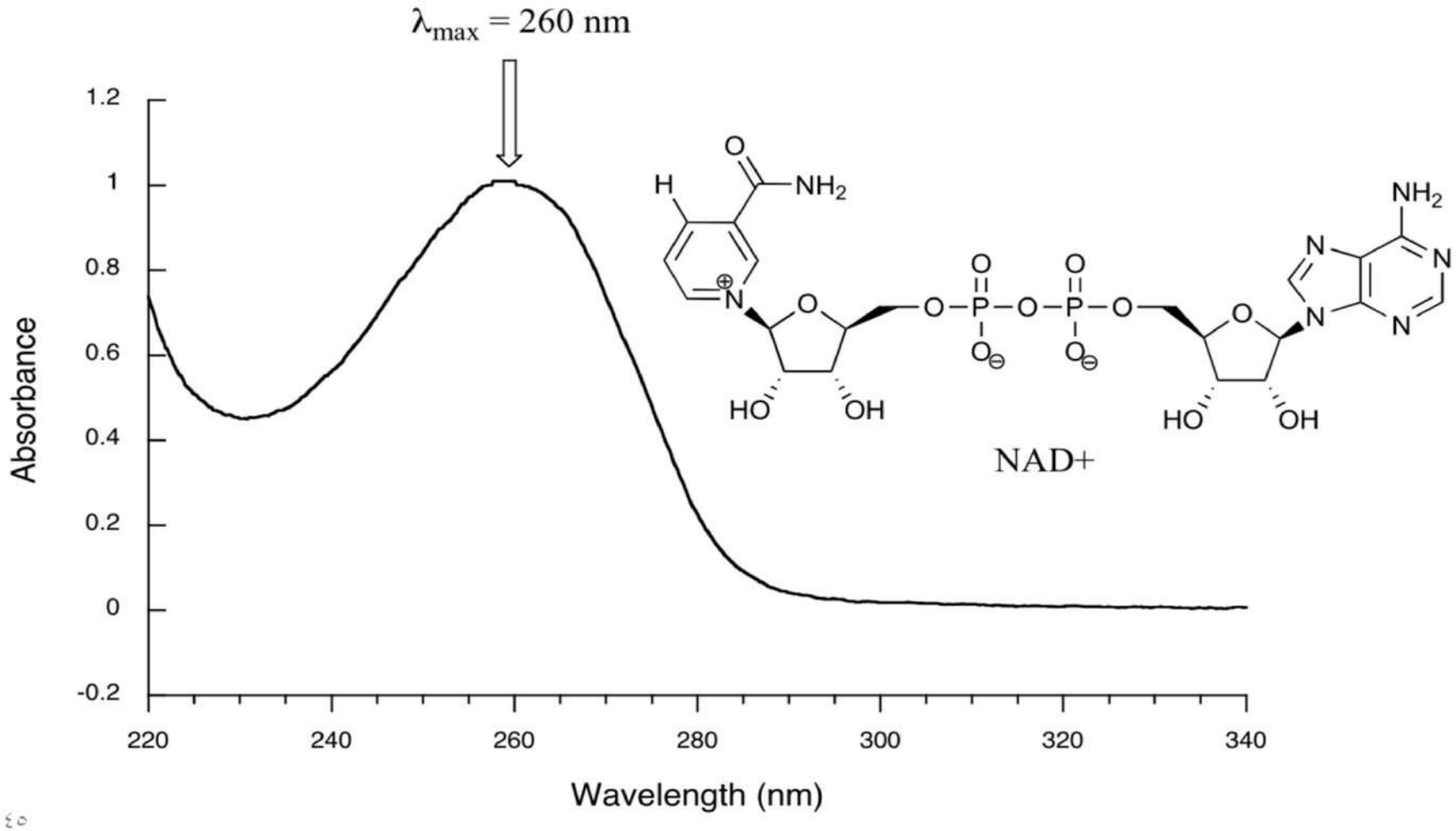
   A_{max}



Housecroft and Sharpe, p. 466

Lambda max, or λ max:-

It identifies which wavelengths achieve maximum absorption



Factors affecting λ_{max}

1- Conjugation
2- Solvent
3- pH Effect

1-Conjugation

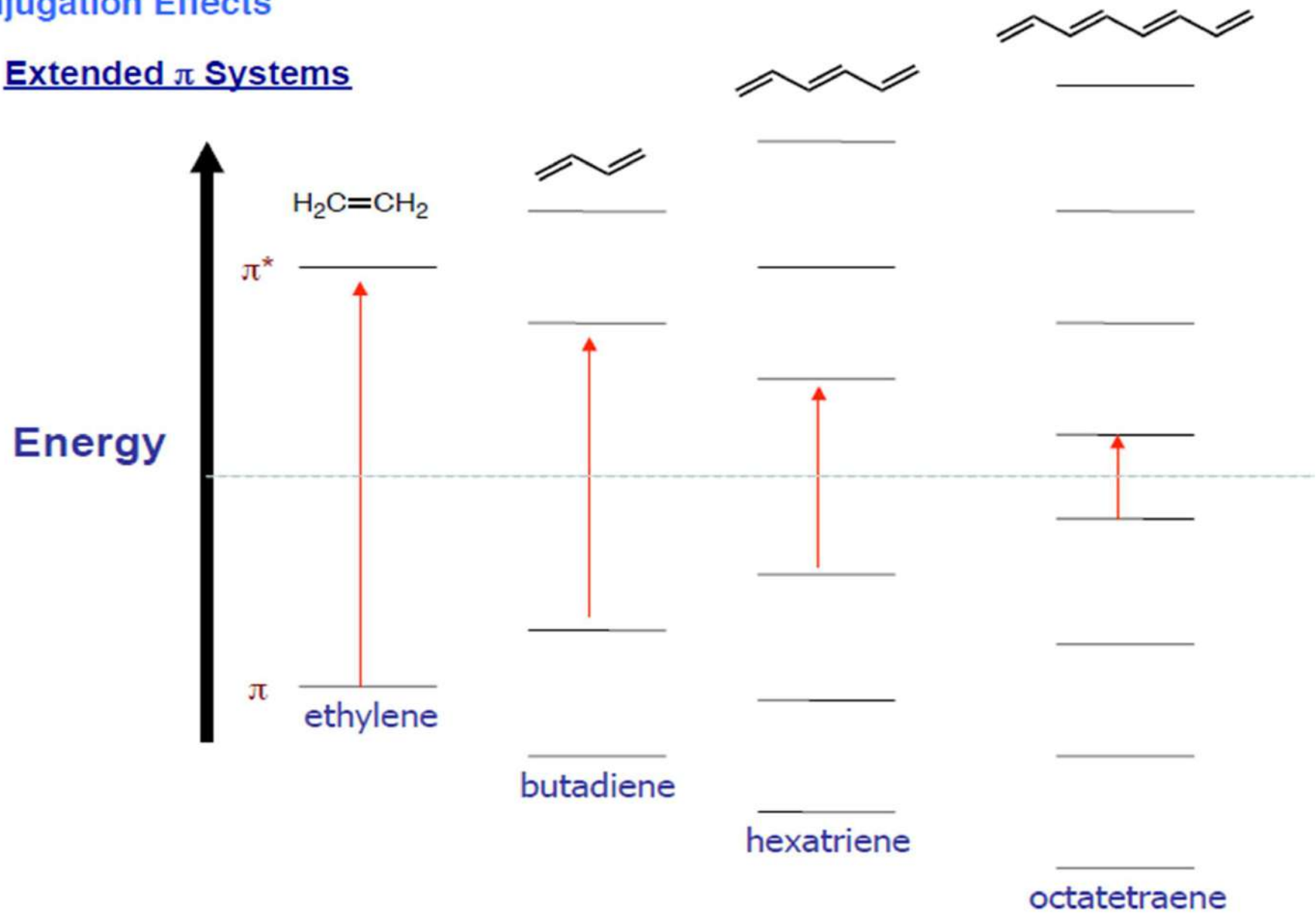
A more conjugated system has a lower HOMO-LUMO energy gap, therefore the λmax will be of a longer wavelength.

λmax	171 nm	180 nm	227 nm

Conjugated alkenes will cause a shift in λ max. As the conjugation increases, the shift will increase

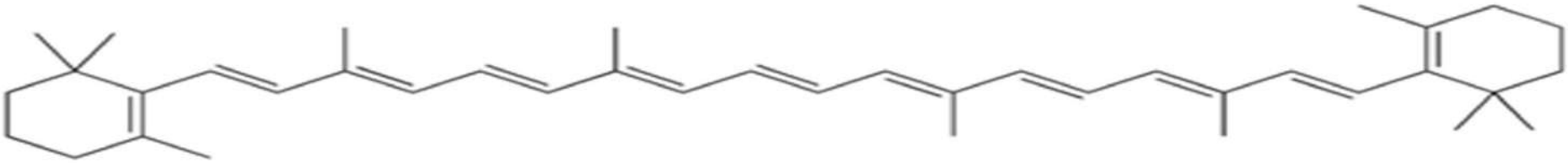
Conjugation Effects

Extended π Systems

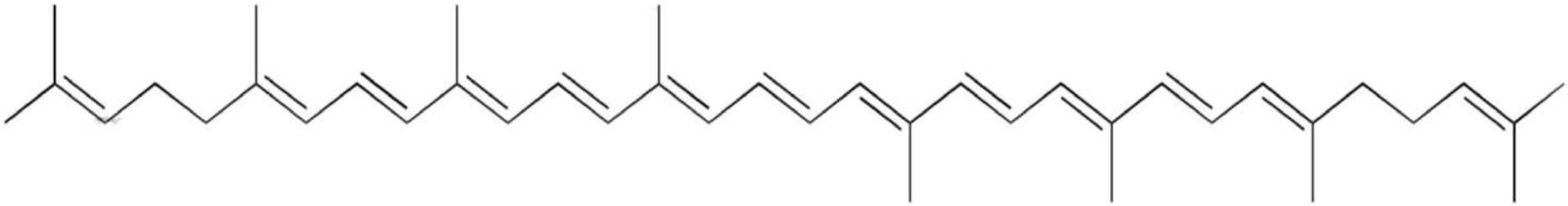


Increasing the conjugation system might lead for colorization

In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.

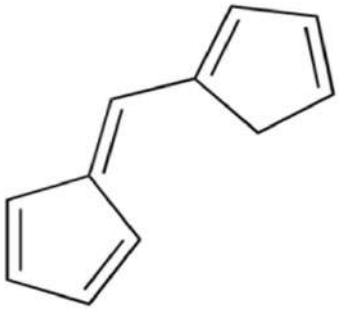


β-carotene

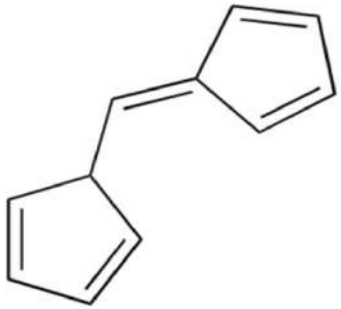


lycopene

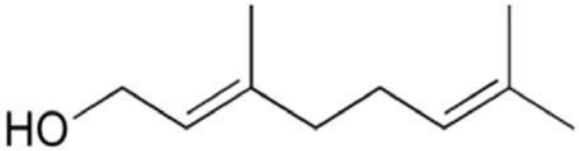
Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.



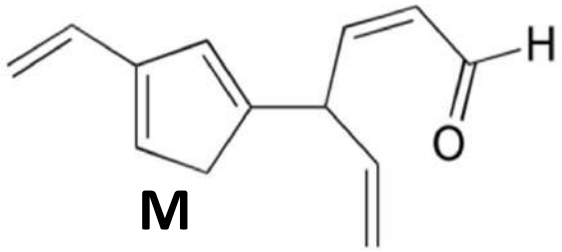
A



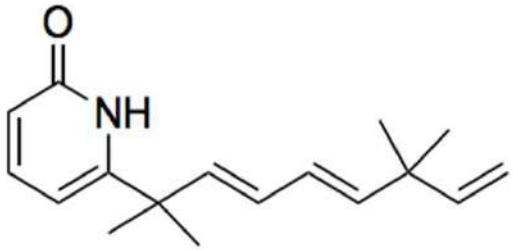
B



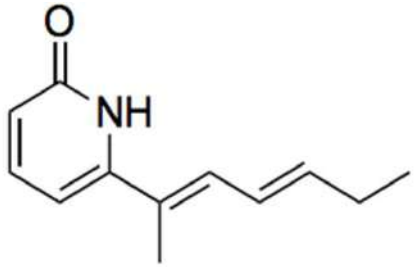
N



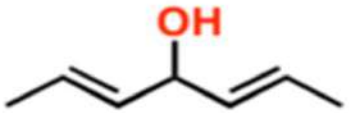
M



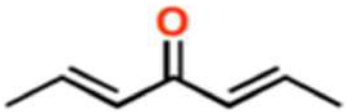
X



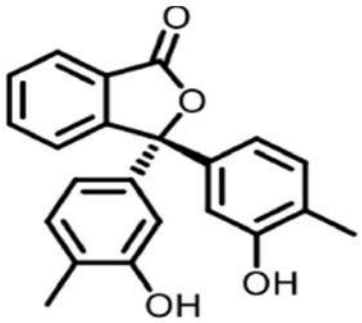
Y



A

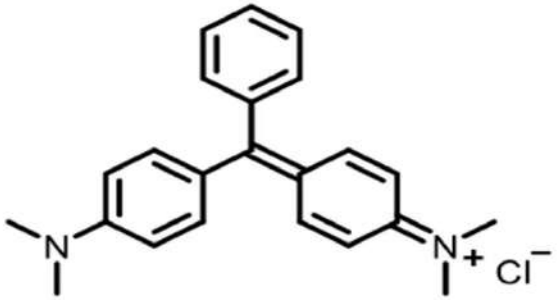


B



cresol red

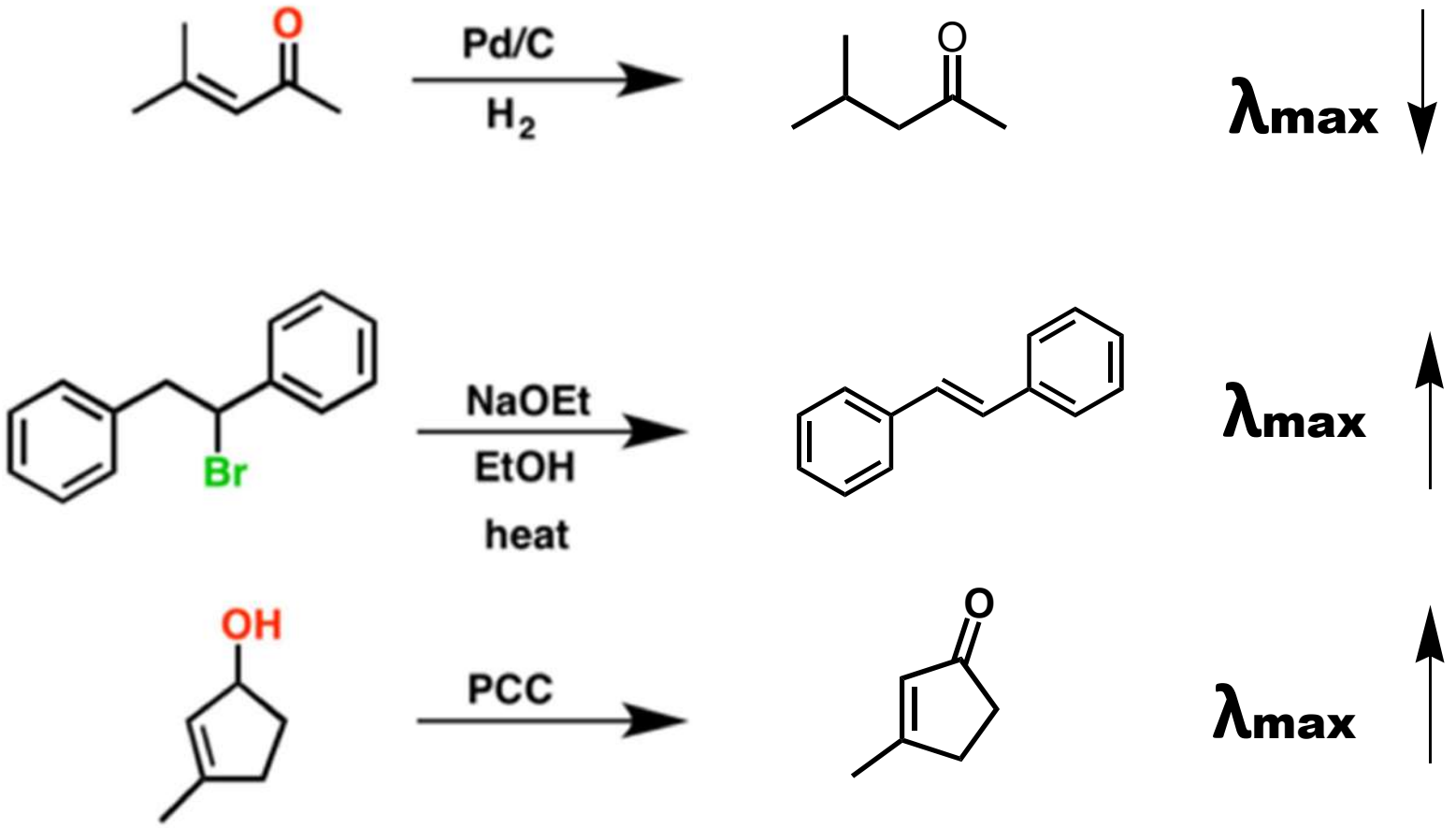
K



malachite green

L

What are the products of these reactions?
Would you expect them to have higher or lower λ_{max} than the starting material?

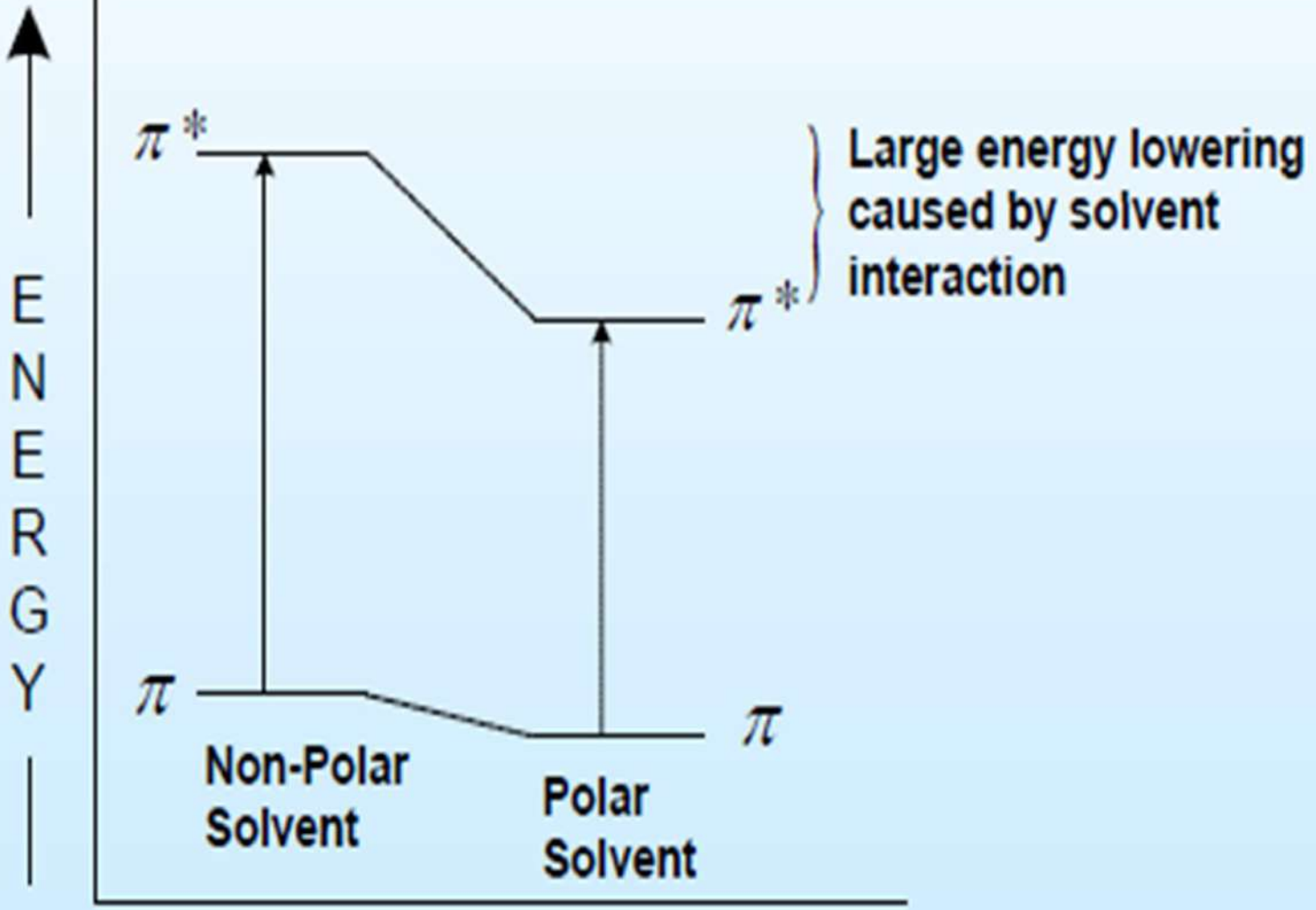


Any factor retards the conjugation; the λmax will be affected negatively

2-Solvent Effect:-

The excited states of most $\pi \rightarrow \pi^*$ transitions are more polar than their ground states because a greater charge separation is observed in the excited state. If a polar solvent is used the dipole–dipole interaction reduces the energy of the excited state more than the ground state, hence the absorption in a polar solvent such as ethanol will be at a longer wavelength (lower energy, hence lower frequency) than in a non-polar solvent such as hexane.

(bathochromic shift, lower energy)



the Effect of a Polar Solvent on a Transition

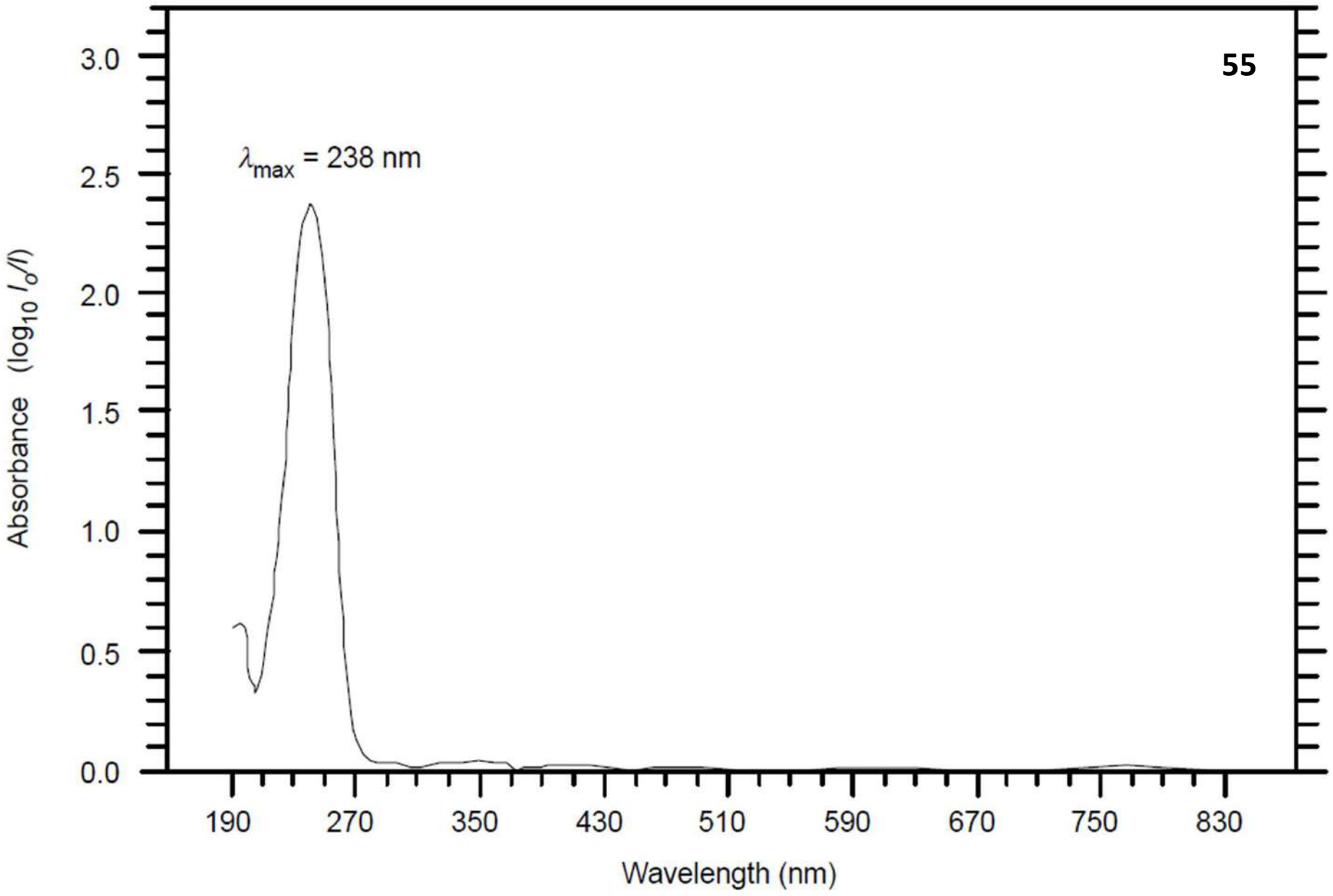


Figure 12b Ultraviolet/visible spectrum of 4-methyl-3-penten-2-one (mesityl oxide) in ethanol

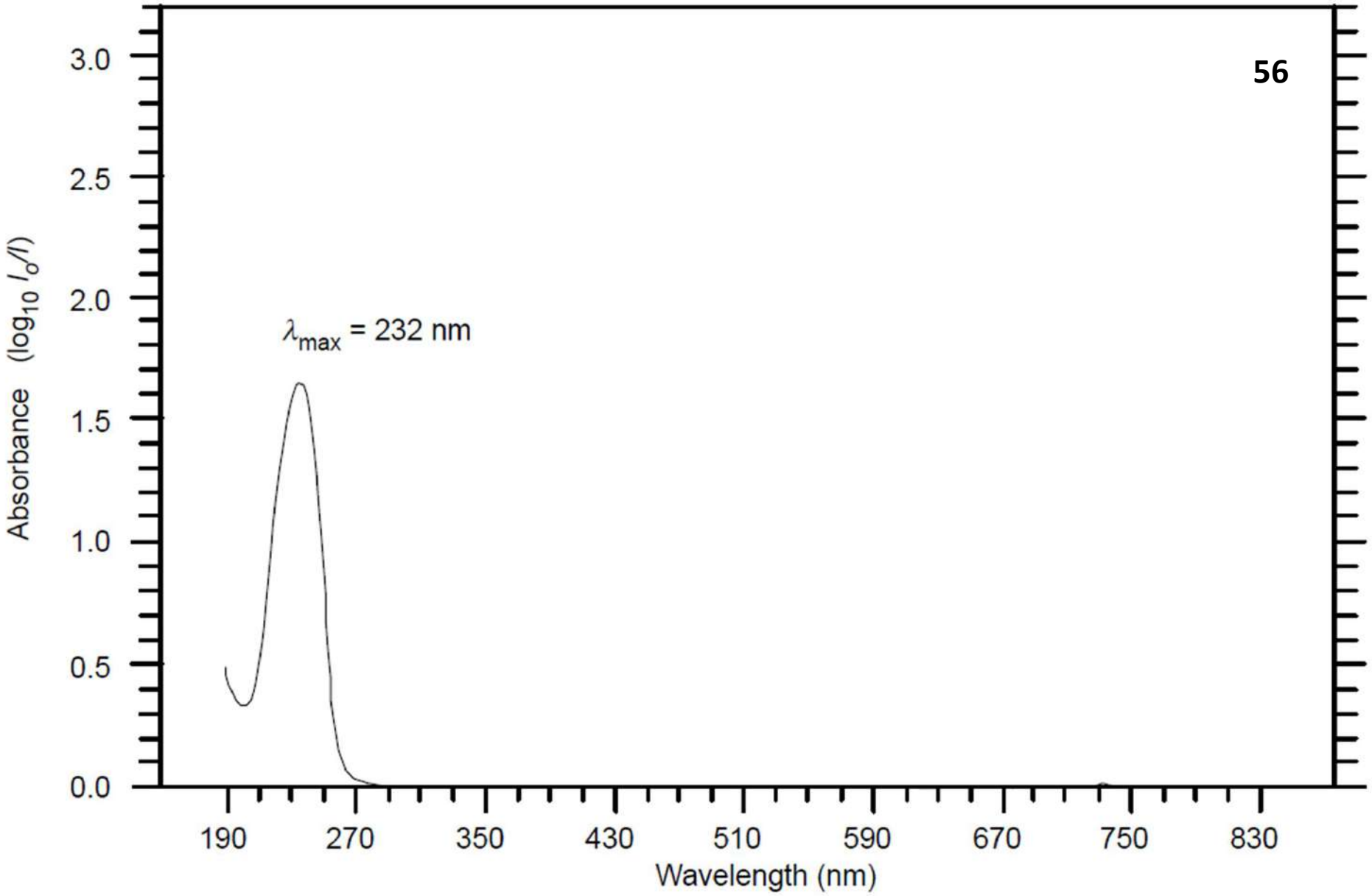
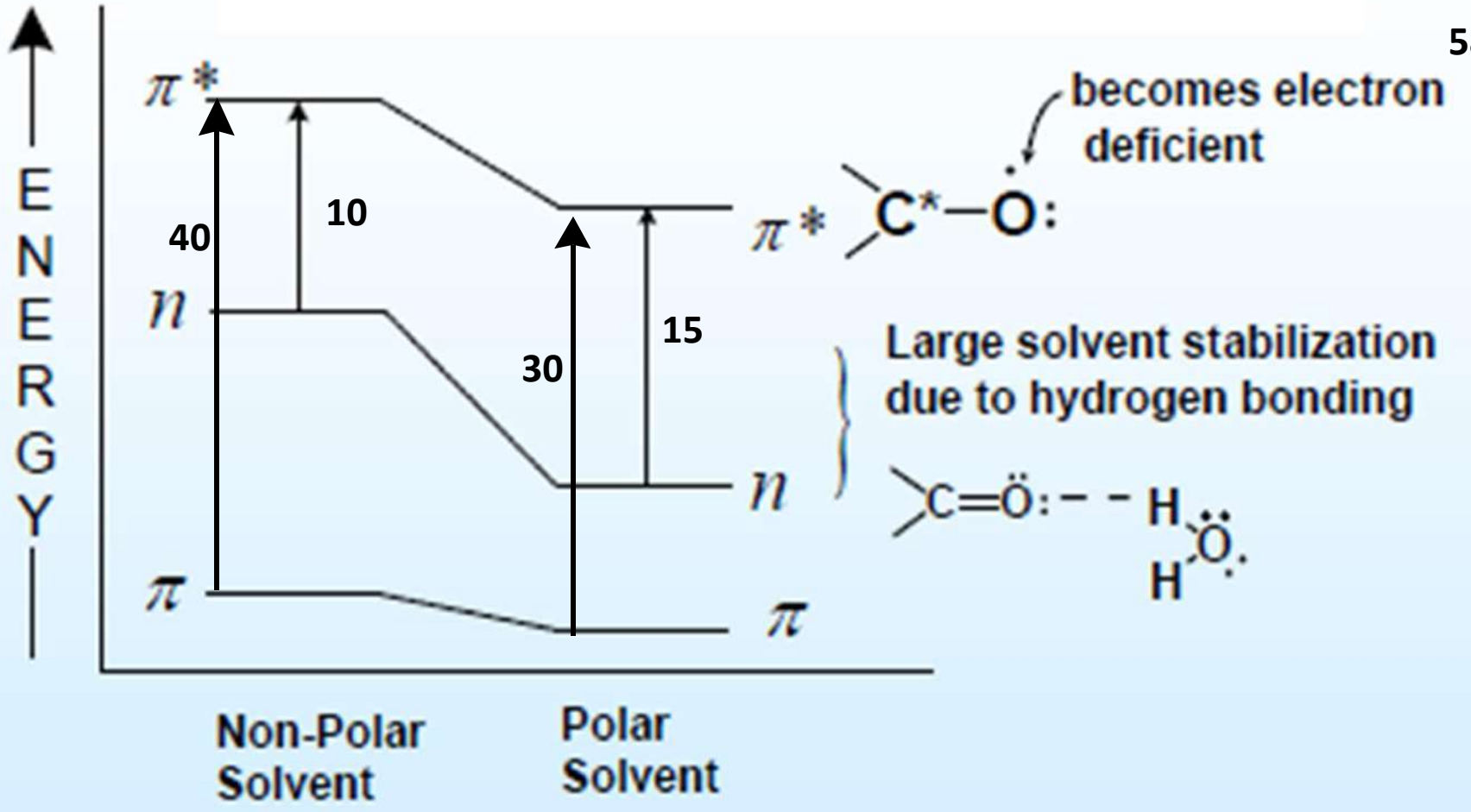


Figure 12a Ultraviolet/visible spectrum of 4-methyl-3-penten-2-one (mesityl oxide) in hexane

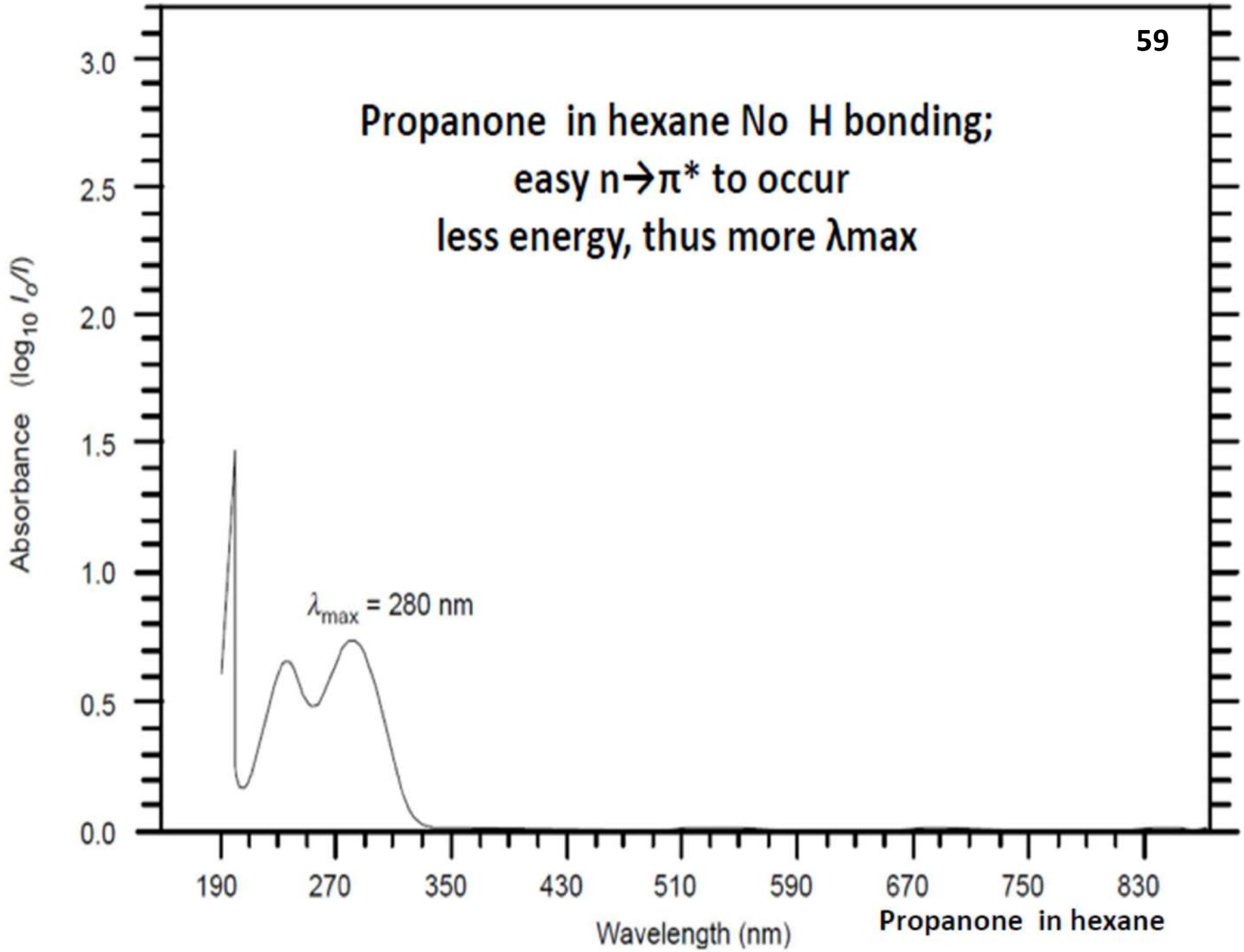
Hydrogen bonding with solvents

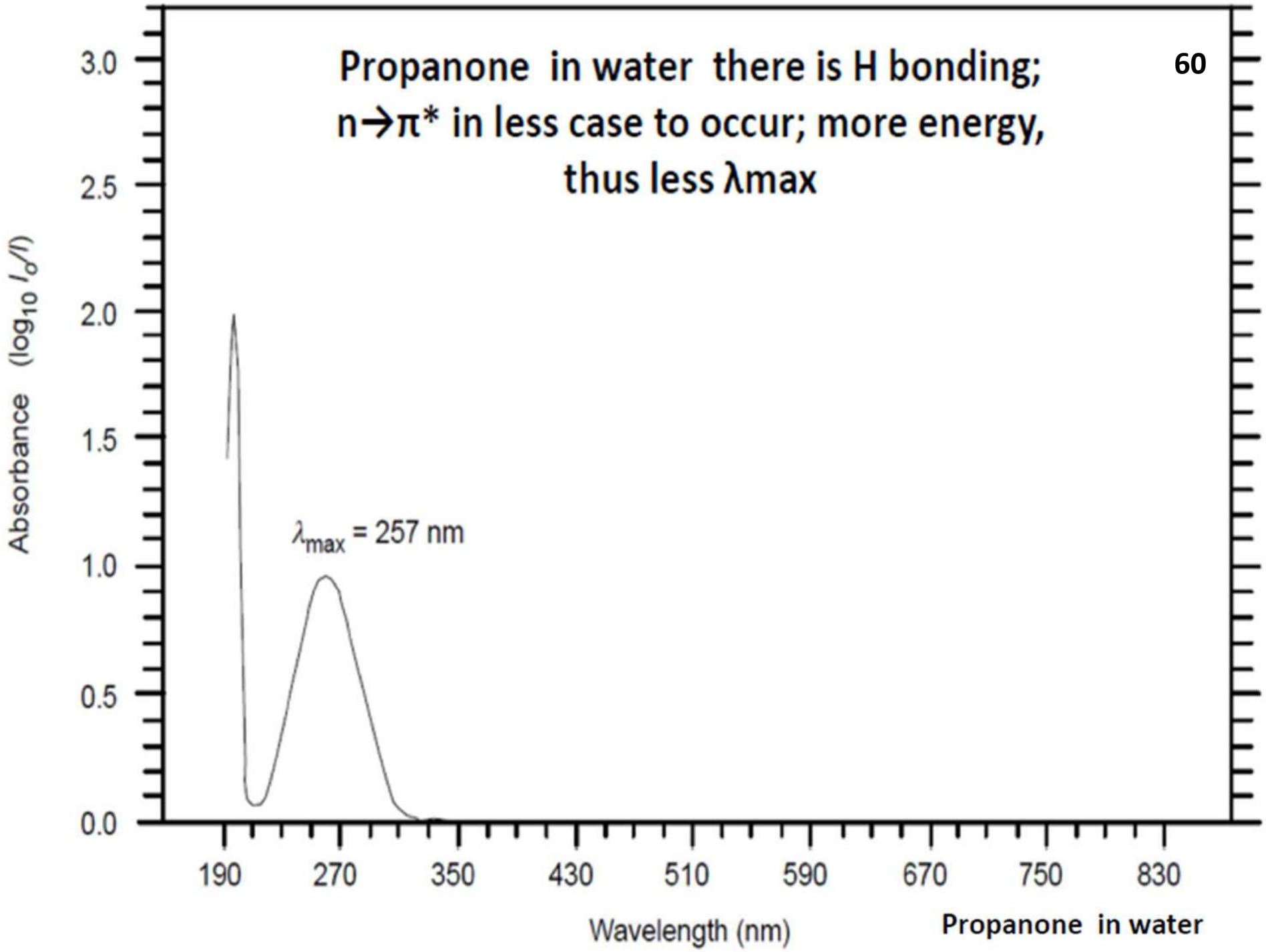
The reverse is also observed if the excited state reduces the degree of hydrogen bonding. This case is clear in the transitions of $n \rightarrow \pi^*$ since carbonyl groups in particular make hydrogen bond with their solvent. For example changing from hexane to water as the solvent for propanone, the absorption maximum moves from 280 to 257nm.



the Effect of a Polar Solvent on an n→π* Transition

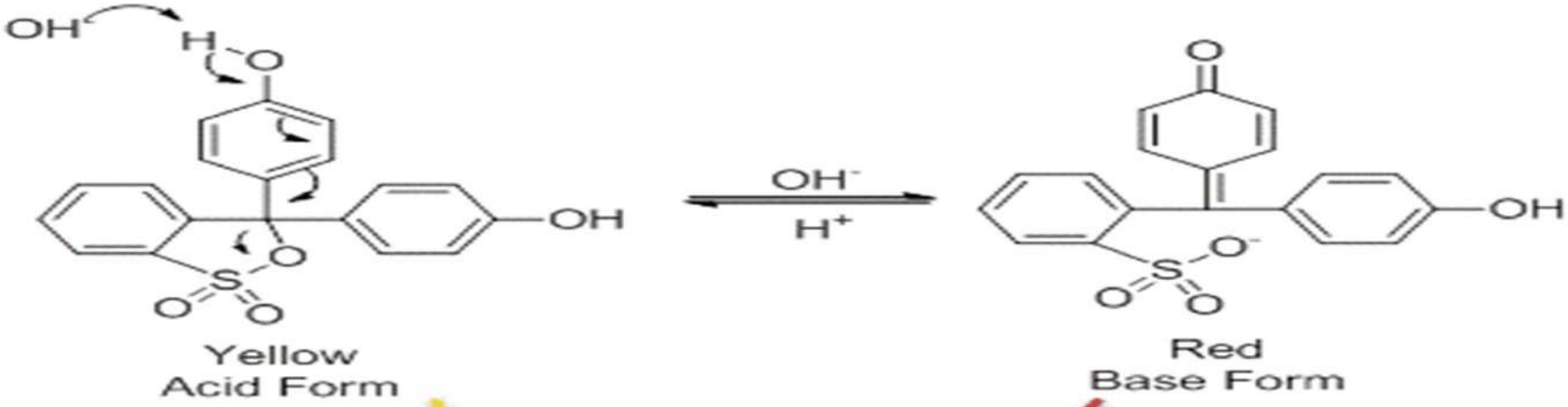
- The ground state is more polar than the excited state.
- Hydrogen bonding solvents interact more strongly with unshared electron pairs in the ground state molecule


Propanone in hexane No H bonding;
easy n→π* to occur
less energy, thus more λmax
Absorbance (log10 Io/I)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
λmax = 280 nm
190
270
350
430
510
590
670
750
830
Wavelength (nm)
Propanone in hexane


Propanone in water there is H bonding;
n→π* in less case to occur; more energy,
thus less λmax
Absorbance (log10 I0/I)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
λmax = 257 nm
190
270
350
430
510
590
670
750
830
Wavelength (nm)
Propanone in water

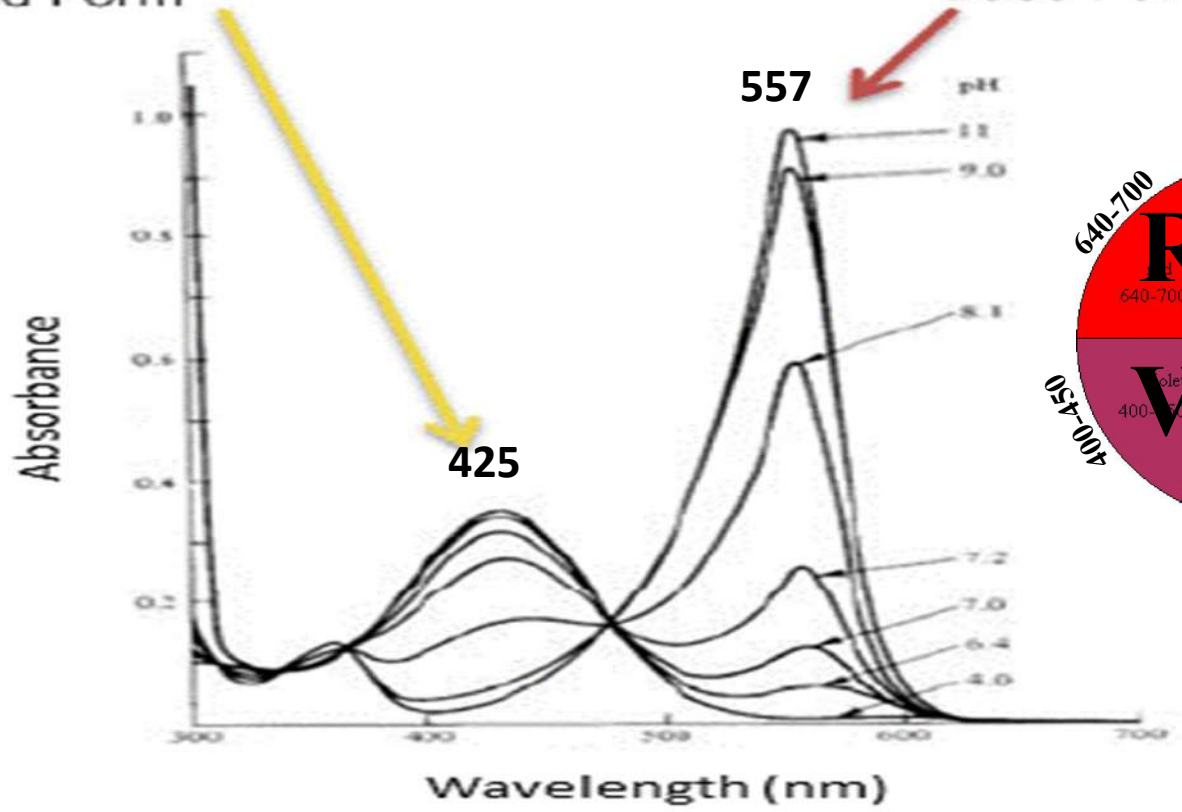
3- PH Effect

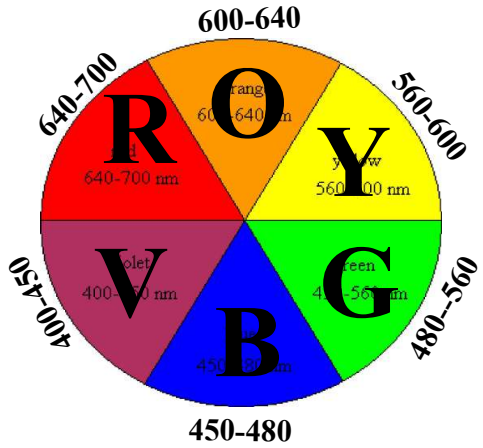
Changing the PH might increase or decrease conjugation



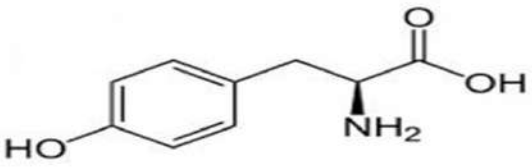
Yellow Acid Form

Red Base Form



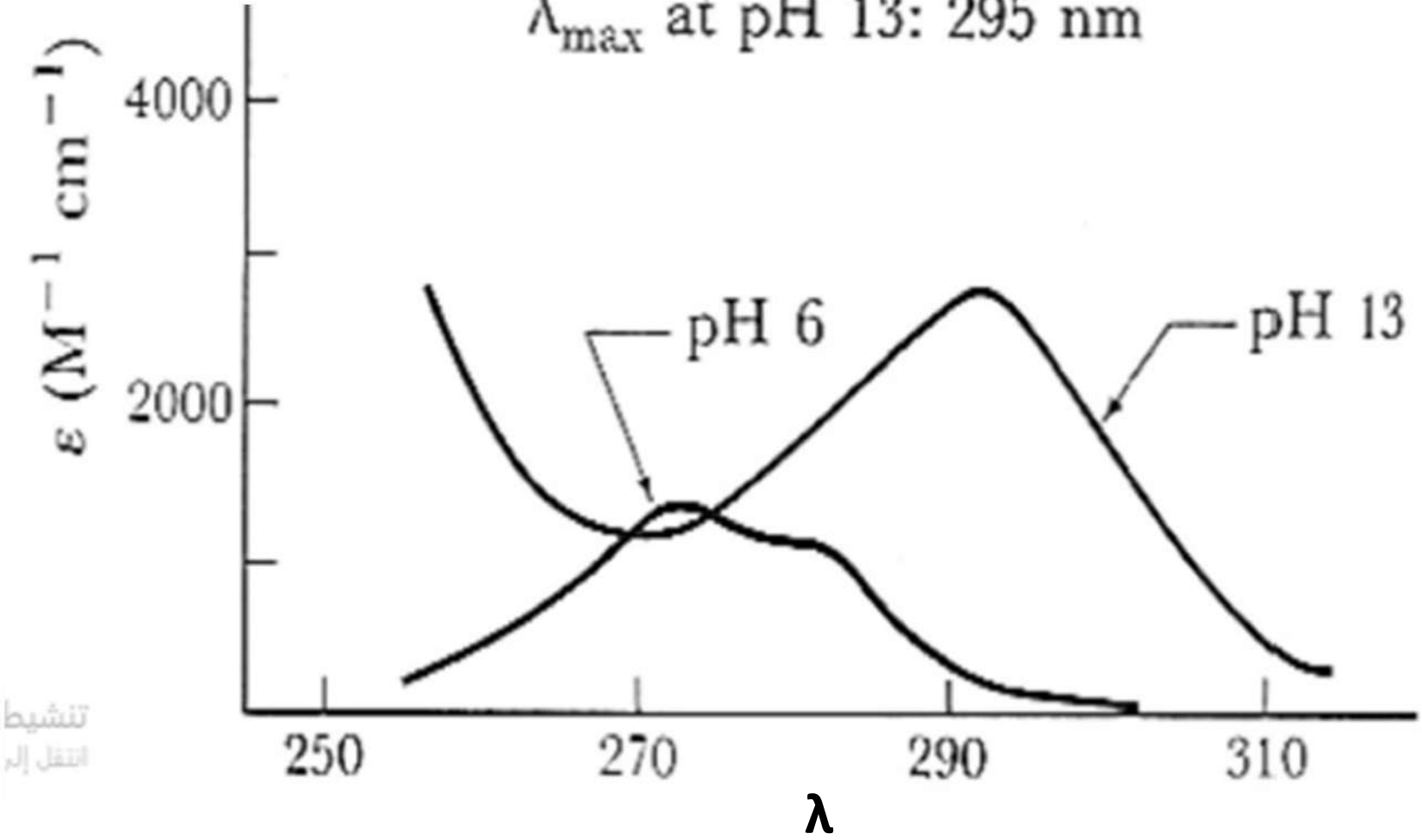


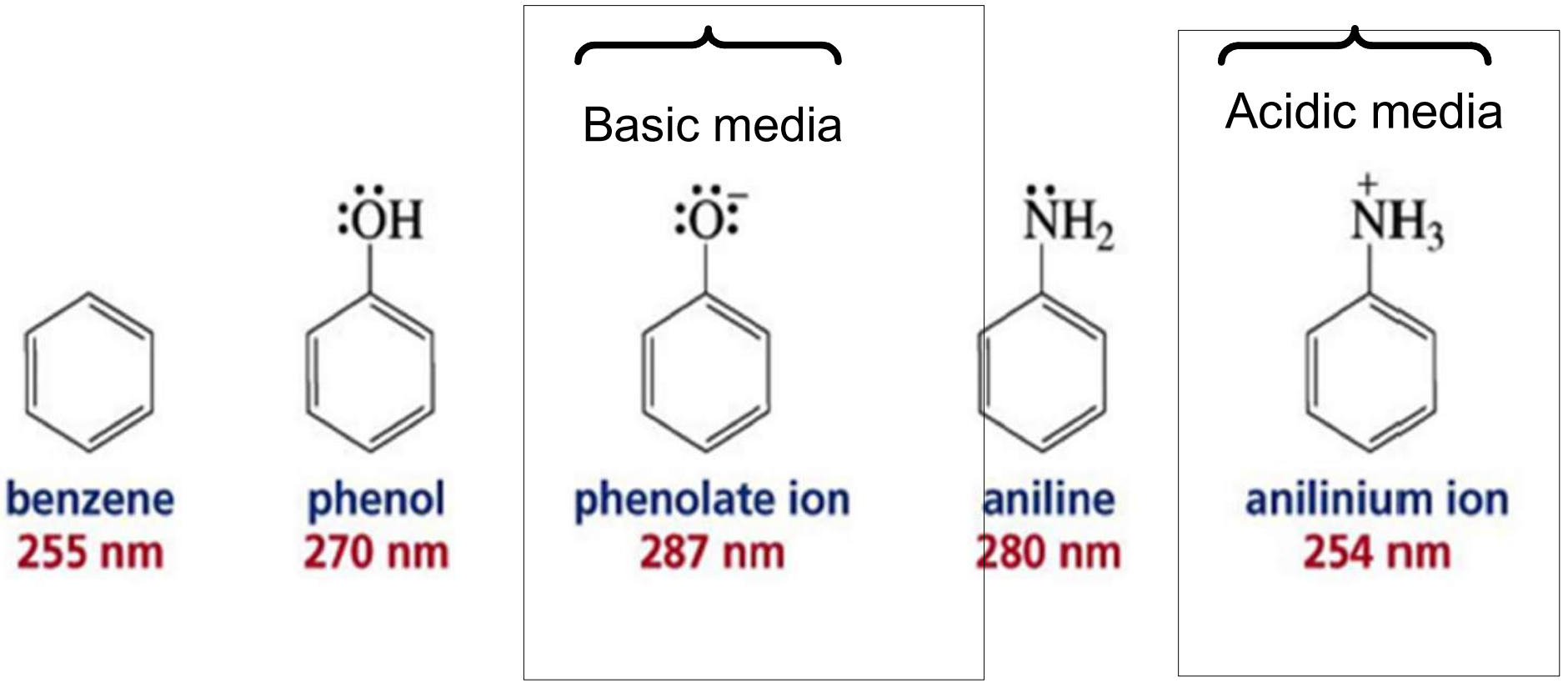
Dependence of tyrosine spectrum on pH



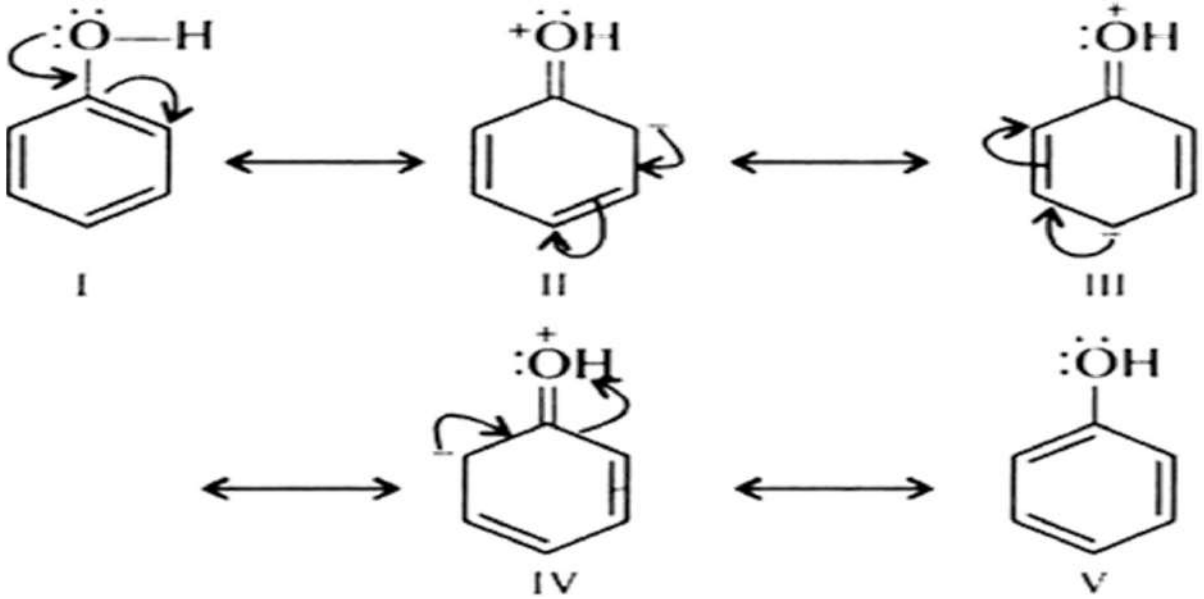
λ_{max} at pH 6: 274 nm

λ_{max} at pH 13: 295 nm

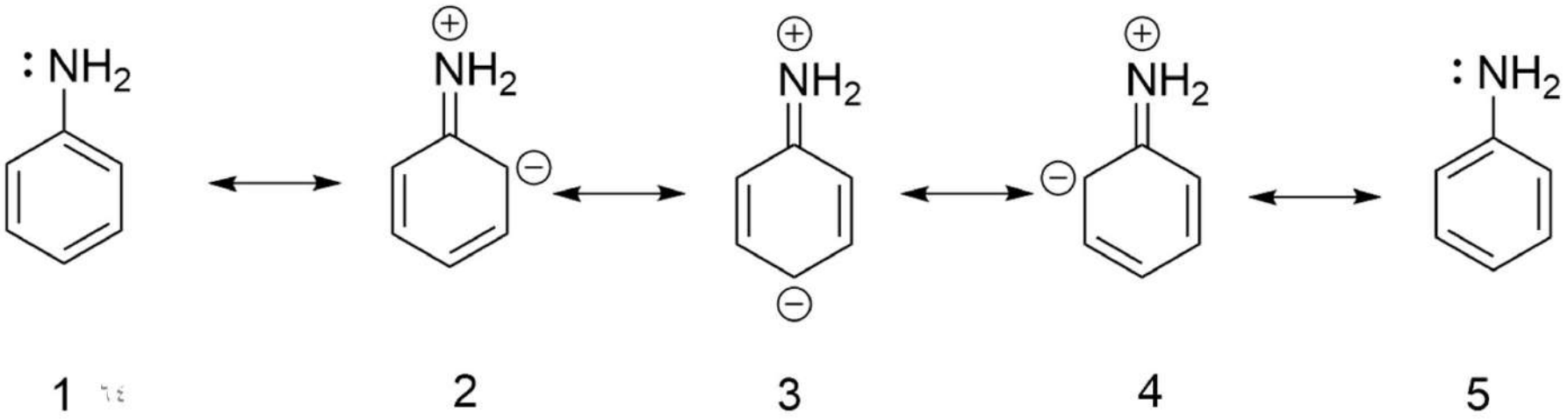



Basic media
Acidic media
:ÖH
:Ö:⁻
NH2
+
NH3
benzene
255 nm
phenol
270 nm
phenolate ion
287 nm
aniline
280 nm
anilinium ion
254 nm

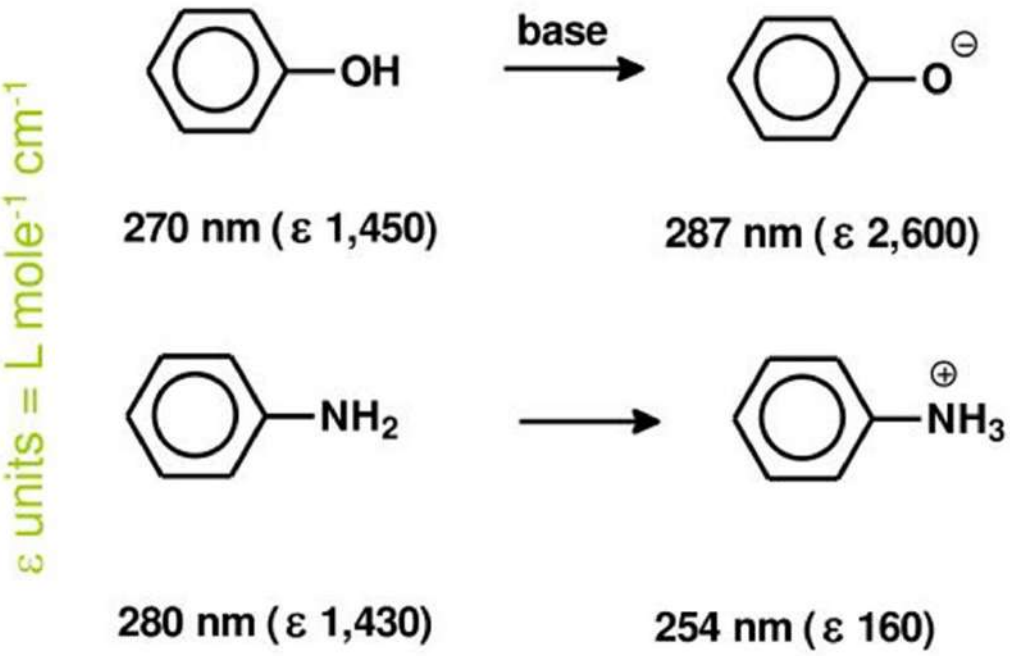
Resonance forms in phenol and its conjugation

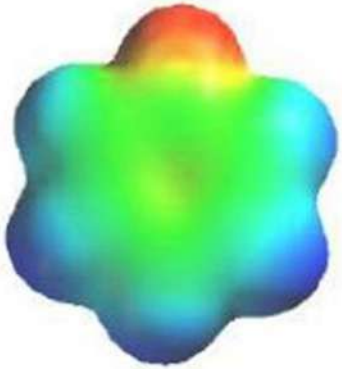


Resonance forms in Aniline and its conjugation

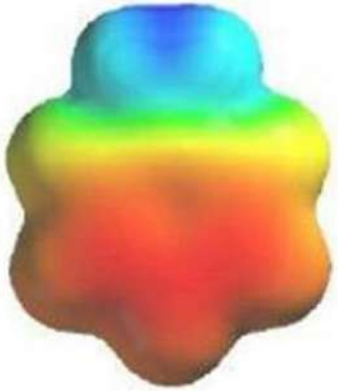


pH Effects on Aromatic Absorptio

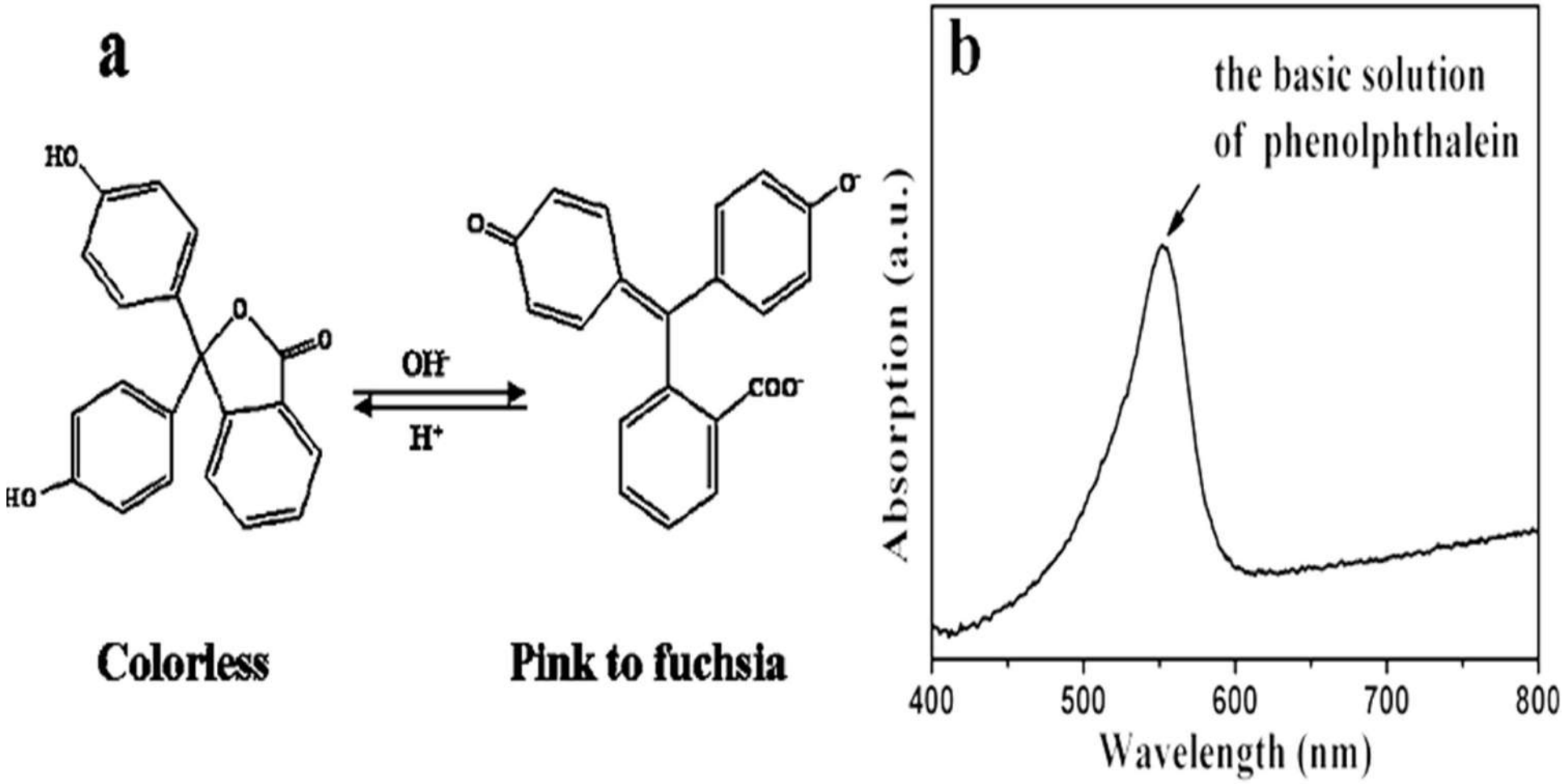




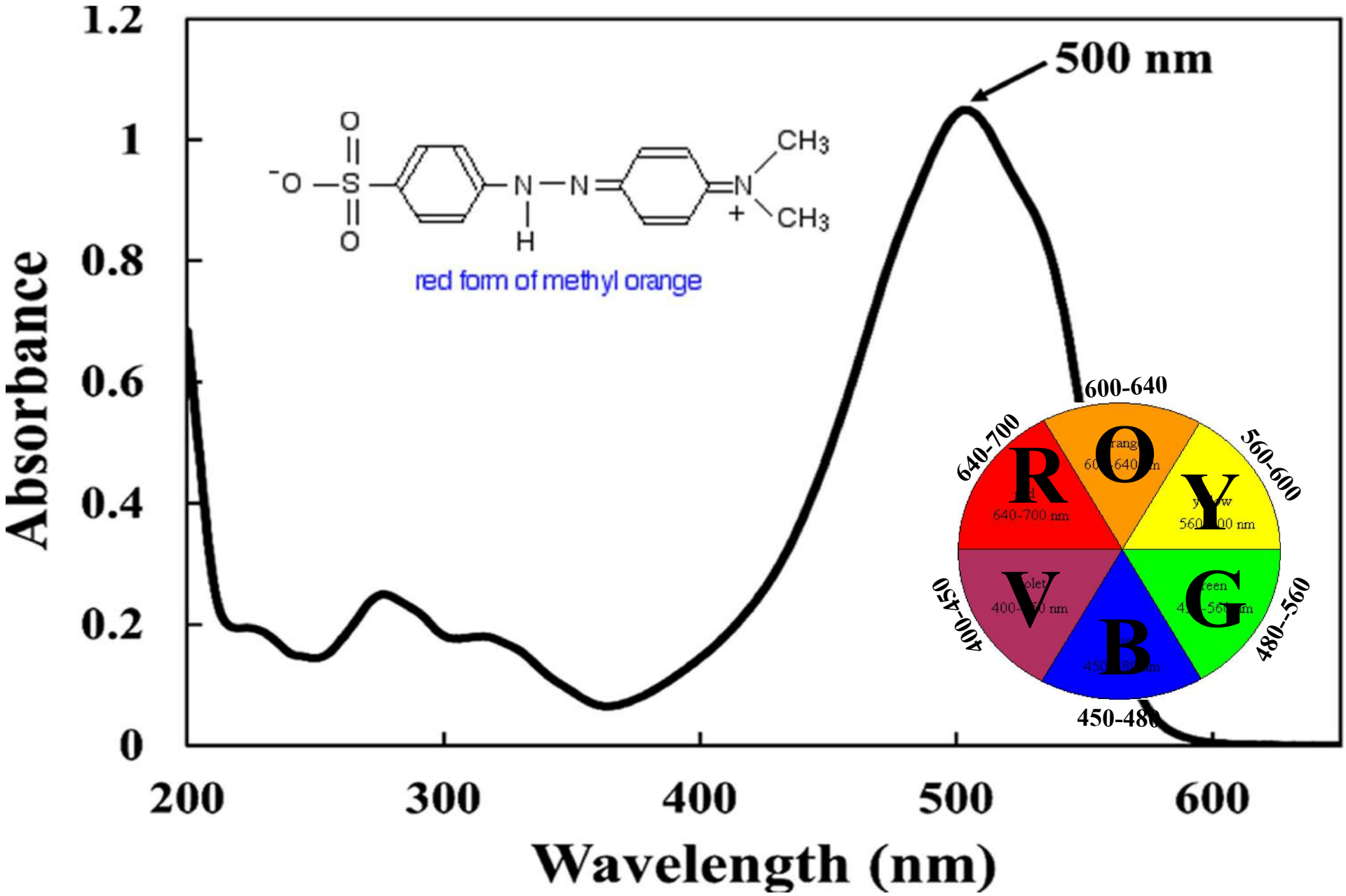
Phenoxide i
electrostatic
potential ma



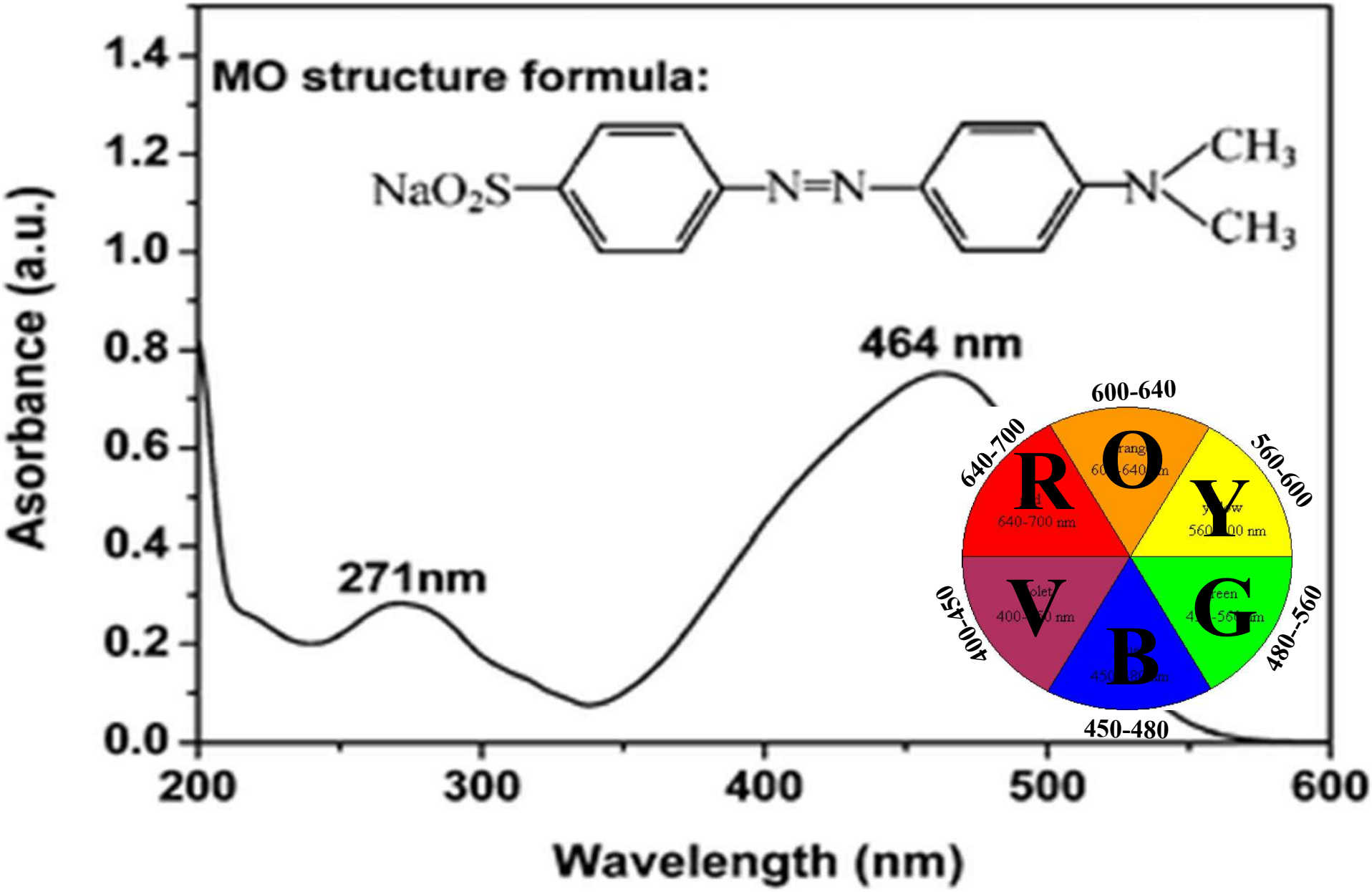
Anilinium ic
electrostati
potential m


a
HO
HO
O
O
OH⁻
H⁺
O
O⁻
COO⁻
Colorless
Pink to fuchsia
b
the basic solution
of phenolphthalein
Absorption (a.u.)
400
500
600
700
800
Wavelength (nm)

The red color is formed at acidic media and has an absorption peak at about 500 nm.



The orange form has an absorption peak at about 460 nm in alkaline media



Ultraviolet Spectroscopy "UV"

Part (4)
UV Important Terminology

CHROMOPHORE:

The term chromophore was previously used to denote a functional group which gives a color to compound. For example- Nitro group is a chromophore because its presence in a compound gives yellow color to the compound.

But these days the term chromophore is used in a much broader sense which may be defined as "any group which exhibit absorption of electromagnetic radiation in a visible or ultra-visible region "It may or may not impart any color to the compound. Some of the important chromophores are: ethylene, acetylene, carbonyls, acids, esters and nitrile groups etc. A carbonyl group is an important chromophore, although the absorption of light by an isolated group does not give rise to any color in the ultra-violet spectroscopy.

UV-VISIBLE ABSORPTION CHROMOPHORES

Chromophore	Example	Solvent	λ_{max}(nm)	ϵ_{max}	Type of Transition
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	2,000	—
			225	160	—
Carbonyl	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1,000	$n \rightarrow \sigma^*$
			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	$CH_3\overset{\overset{O}{\|}}{C}OH$	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	$n \rightarrow \pi^*$

Chromophore absorptions

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

Auxochrome

- The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

TWO TYPES

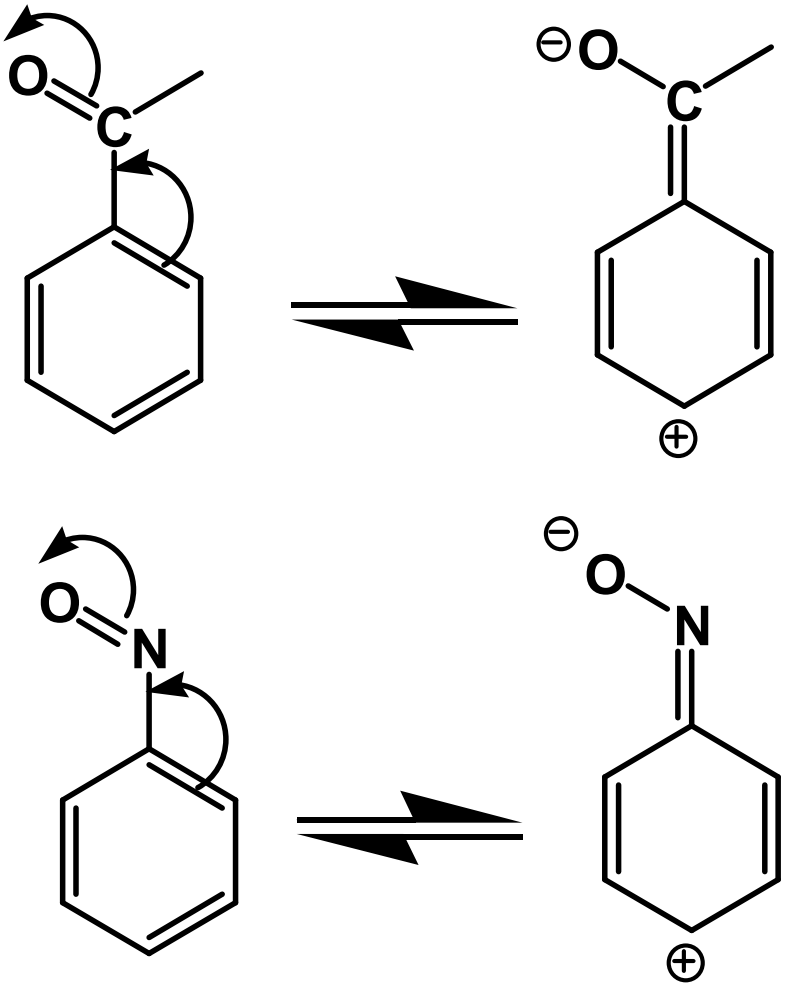
1. Basic or positive auxochromic groups(NH_2,OH)
2. Acid or negative auxochromic groups(NO_2,CO)

Auxochrome

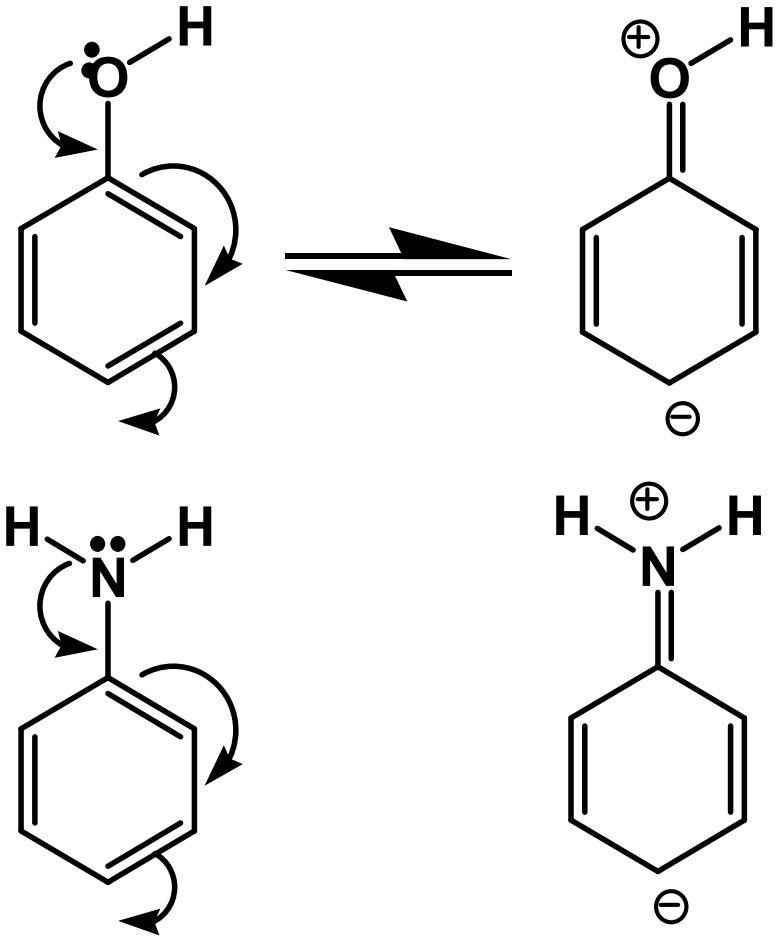
e.g. Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm

Aniline λ_{max} = 280 nm

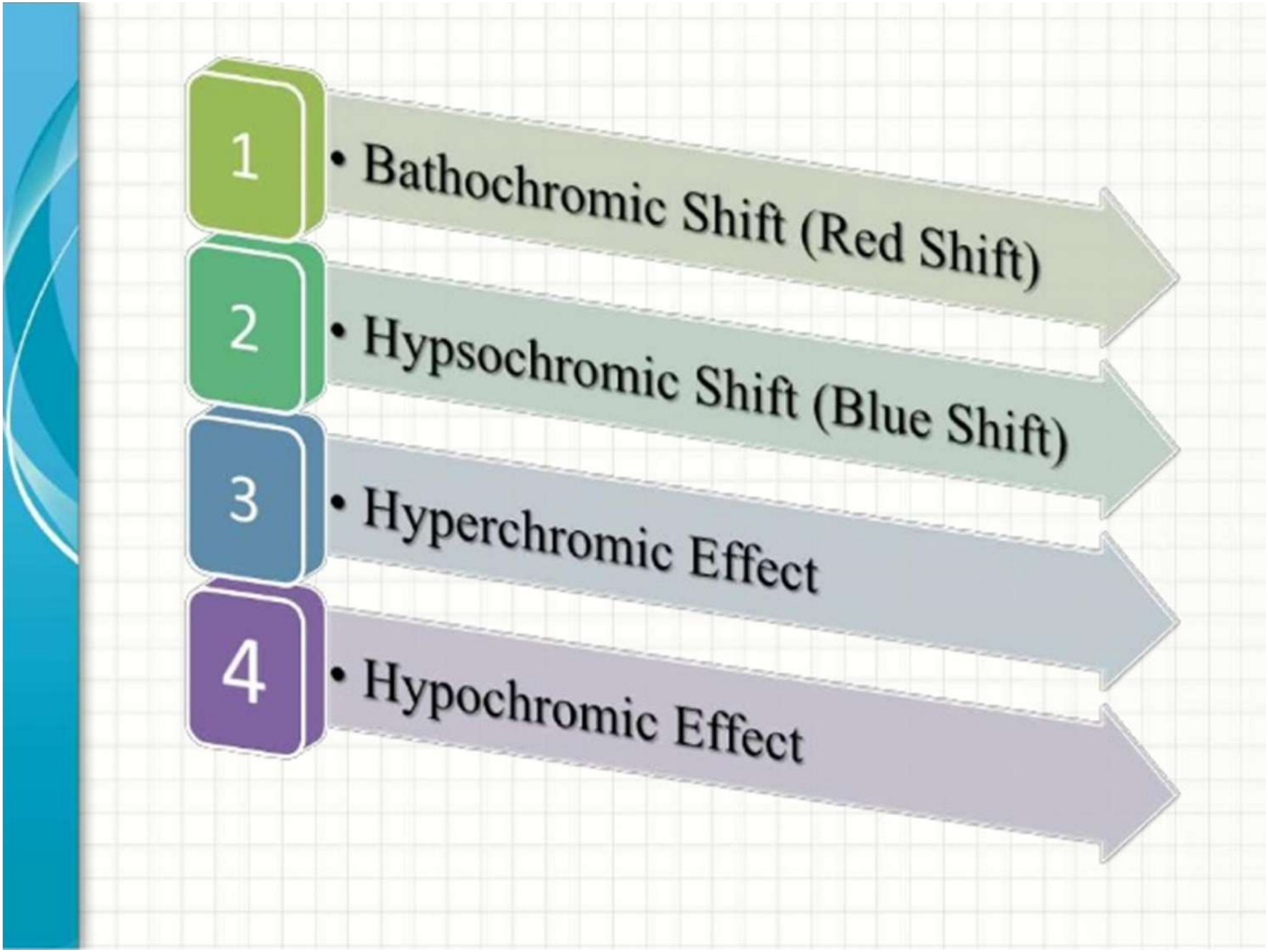


Negative Auxochrome
Acid
- M effect

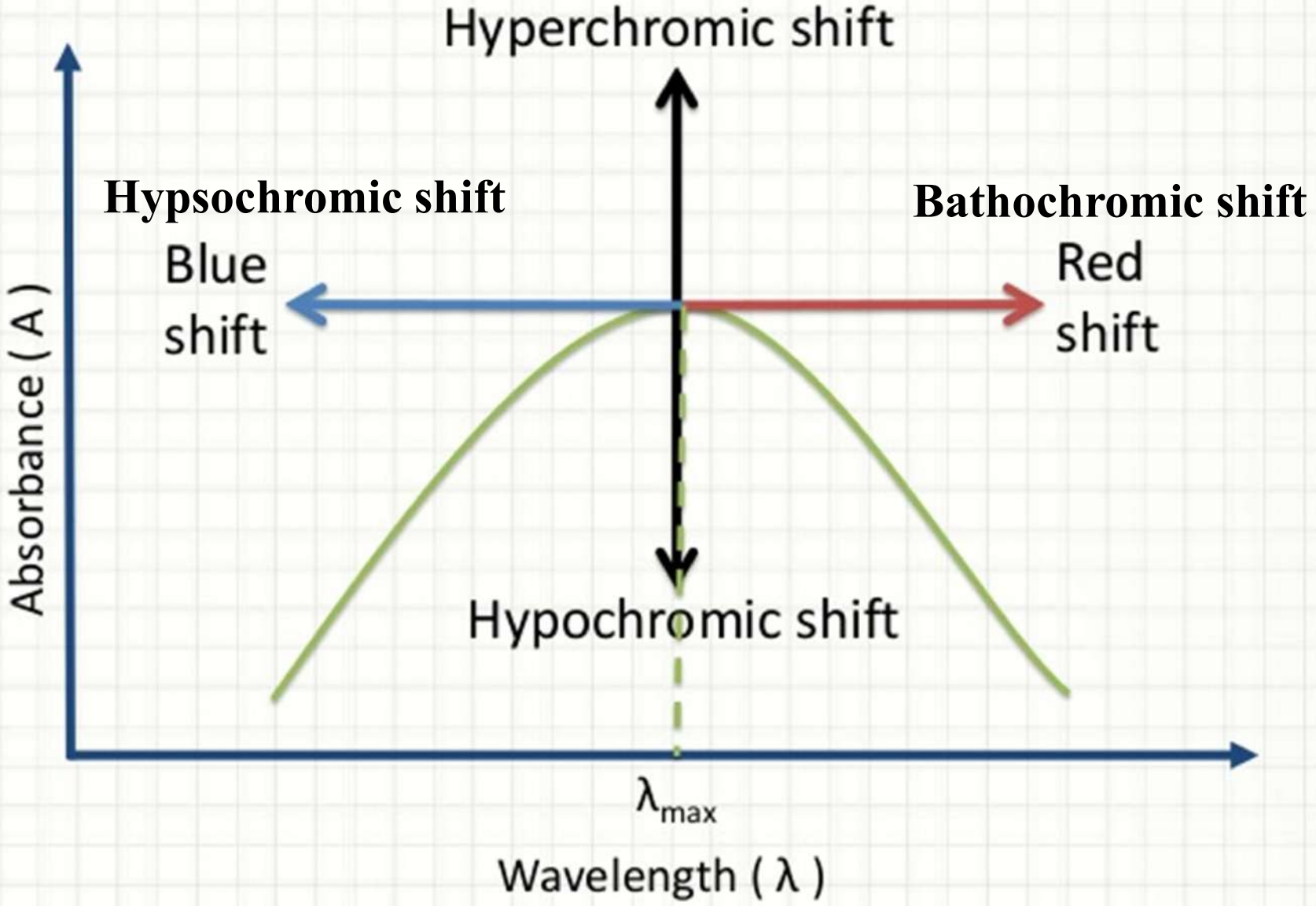


Positive Auxochrome
Base
+ Meffect

Absorption & Intensity Shifts


1
• Bathochromic Shift (Red Shift)
2
• Hypsochromic Shift (Blue Shift)
3
• Hyperchromic Effect
4
• Hypochromic Effect

Shifts and Effects



Some terms related to UV-Vis spectrophotometer:

1- Bathochromic shifts:

Please recall solvent effect on λmax

The shift of absorption to a longer wavelength due to substitution or solvent effect **(red shift)**

2- Hypsochromic shifts:

Please recall solvent effect on λmax

The shift of absorption to a shorter wavelength due to substitution or solvent effect **(blue shift)**

3- Hyperchromic effect:

It is increase in absorption intensity.

4- Hypochromic effect:

It is simply a decrease in the absorption intensity.

Notes:-

- **Conjugation, pH and solvent might cause Hypso or Bathochromic effect.**
- **Change mainly in concentration and structure can cause the effect (Hypo or Hyperchromic). This is due to outright aggregation of the chromophores.**

Ultraviolet Spectroscopy "UV"

Part (5)

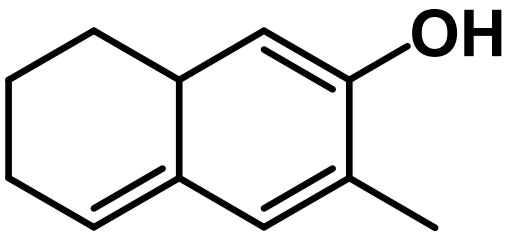
Calculation of λ_{max}

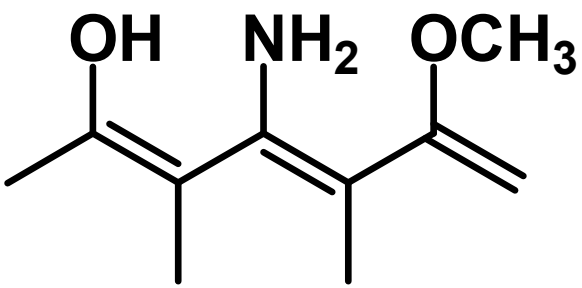
Woodward-Fieser and Fieser-Kuhn Rules

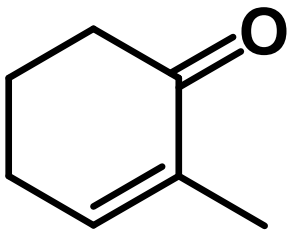
Woodward-Fieser to calculate of λ_{max}

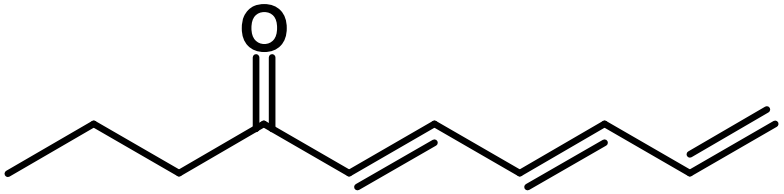
Theoretical and experimental Value of λ_{max}

???



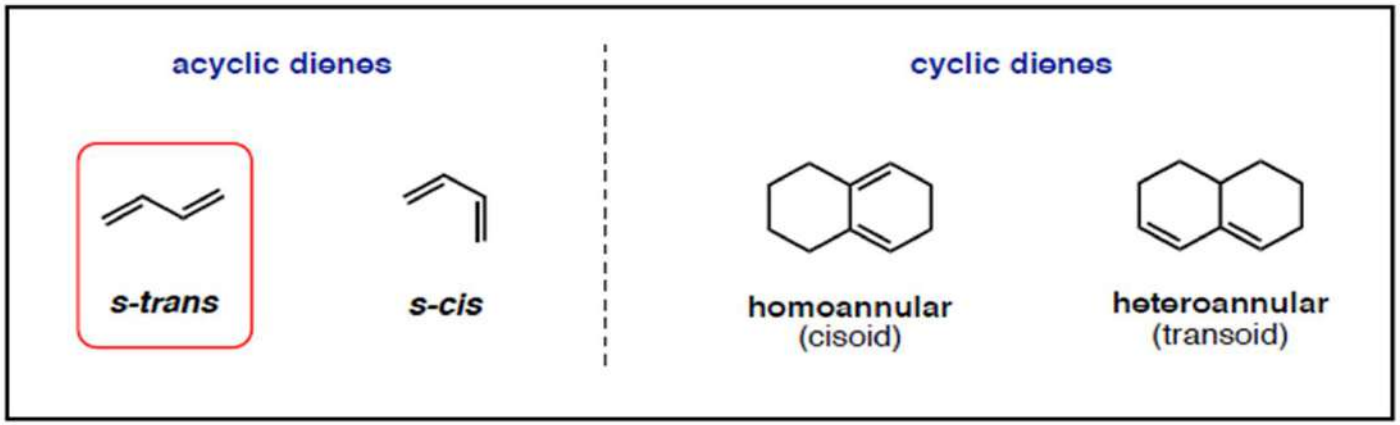






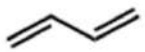
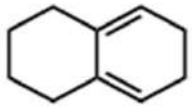
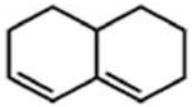
UV Spectroscopy

Woodward Fieser Rules for Dienes



- Woodward & Fieser derived a set of empirical rules for the estimation of wavelength for the low energy $\pi \rightarrow \pi^*$ electronic transition
- Based on empirical observation of known conjugated structures **Base value**
- Can be used to reliably predict absorption wavelength in dienes, enone, and to a lesser extent aromatic systems

Part 1:- Diene

			
	s-trans	**homoannular** (cisoid)	**heteroannular** (transoid)
base values:	**217 nm**	**253 nm**	**214 nm**

Increments:

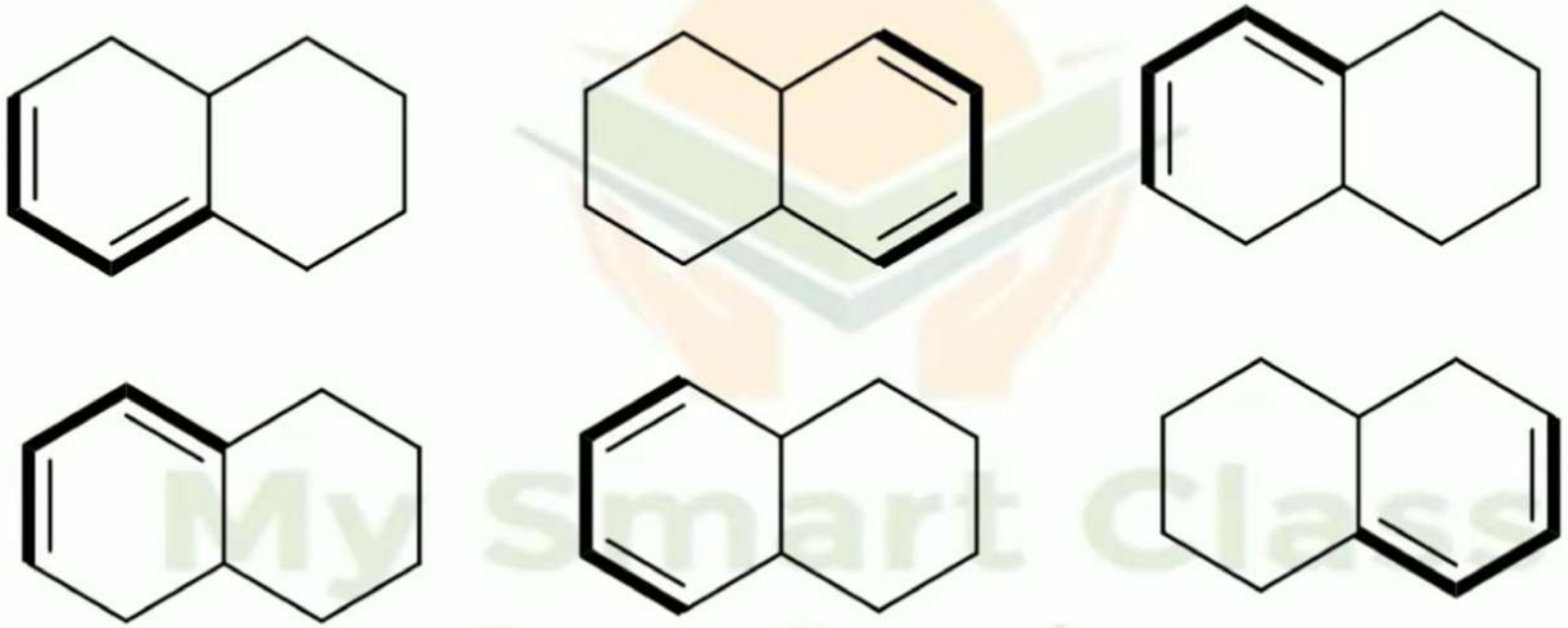
For each additional conjugated double bond		+ 30 nm
For each exocyclic double bond		+ 5 nm
For each alkyl group		+ 5 nm
For each of the following groups:		
	- OR	+ 6 nm
	- O(C=O)R	+ 0 nm
	- Cl	+ 5 nm
	- Br	+ 5 nm
	- SR	+ 30 nm
	- NR_2	+ 60 nm
	- Ph	+ 60 nm

not affected by solvent

Where both types of cyclic dienes are present, the base with the longer λmax is used.

Homo-annular diene: **Cisoid**

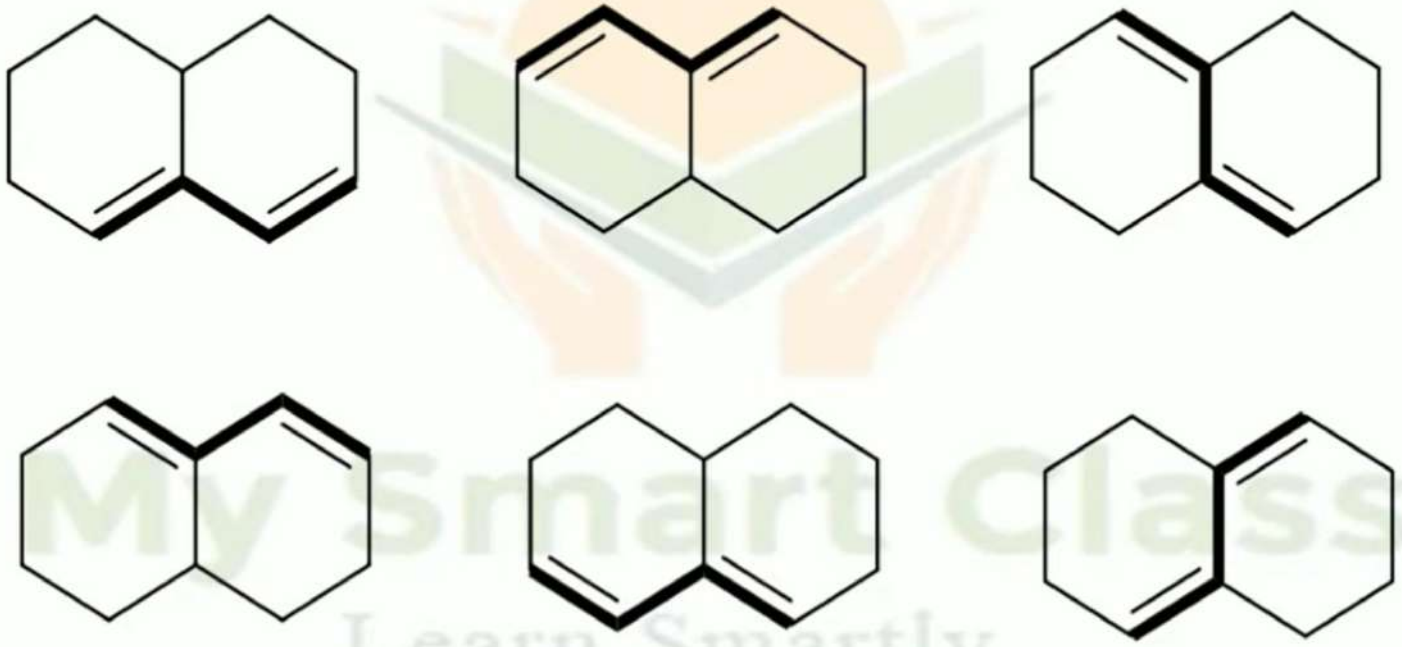
Conjugated double bonds present in the same ring.



Base value for **Homo-annular diene is 253 nm**

Hetero-annular diene: Transoid

Conjugated double bonds which are not present in same ring



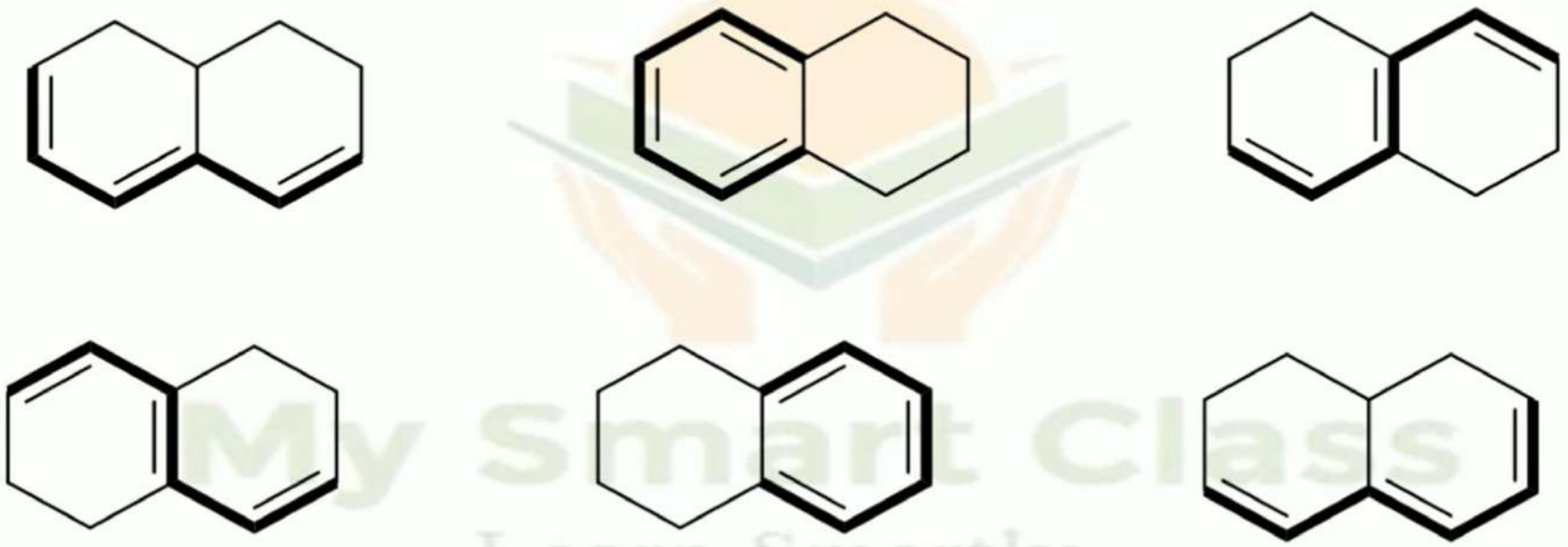
Base value for **Hetero-annular diene is 214 nm**

Whenever there is combination of homo and hetero annular dine consider it "Homo-Annular dine"

Base value for combination of homo and hetero annular dine is **253 nm**

Double bond extending conjugation = Additional conjugated double bond

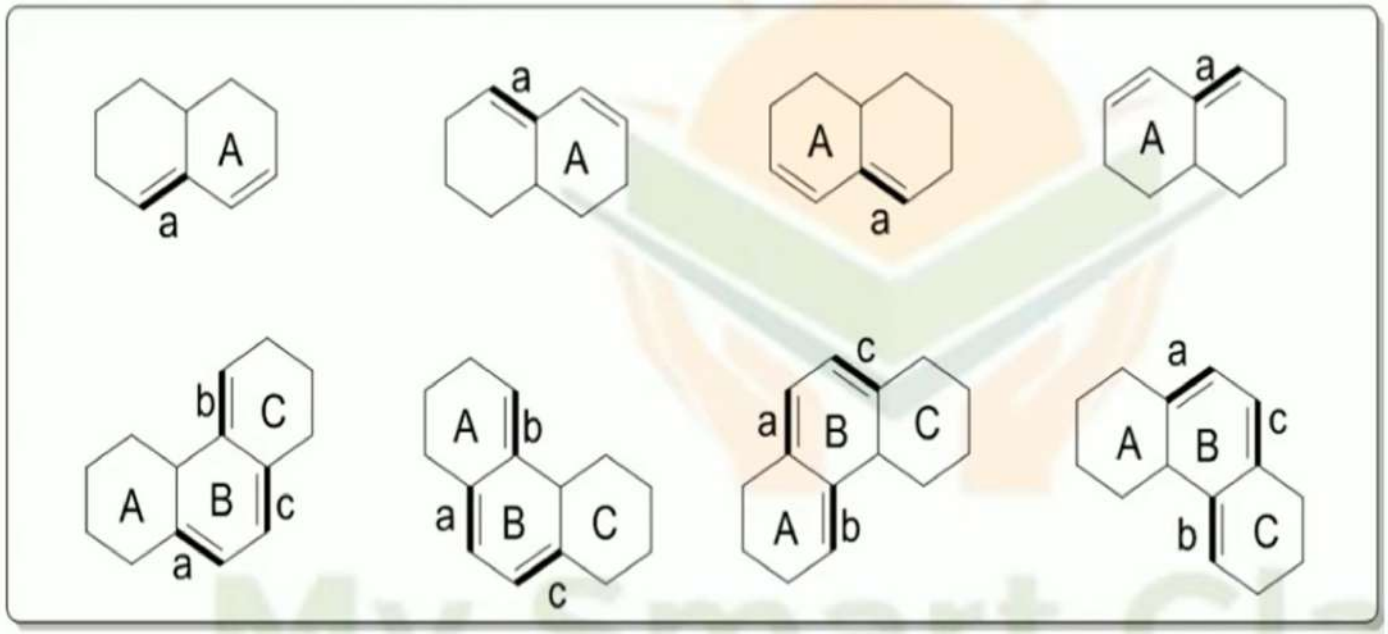
- The remaining conjugated double bond after starting two double bonds are considered as Double bond extending conjugation.

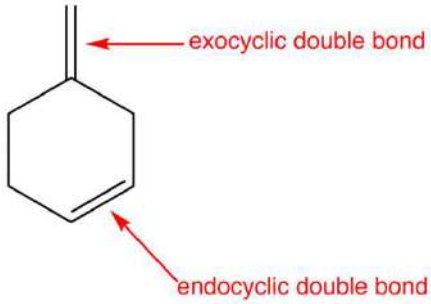


Increment value for Double bond extending conjugation is +30 nm

Exocyclic double bond

- The Exocyclic double bond consist one of the two carbon of double bond is part of one ring and another carbon of double bond is not part of that ring.





A, B. C are symbol for rings

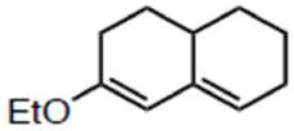
a, b and c are Exocyclic double bonds for ring A, B and C respectively

Increment value for Exocyclic double bond is +5 nm

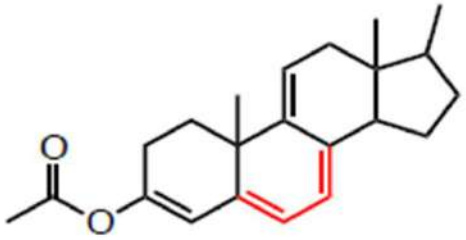
UV Spectroscopy

Woodward Fieser Rules for Dienes

examples



transoid diene	214 nm
3 alkyl subst	15 nm
1 OR subst	6 nm
1 exocyclic db	5 nm
calculated value	240 nm
observed	241 nm

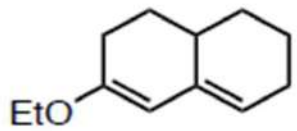


cisoid diene	253 nm
2 conj db	60 nm
5 alkyl subst	25 nm
1 acyl subst	0 nm
3 exocyclic db	15 nm
calculated value	353 nm
observed	355 nm

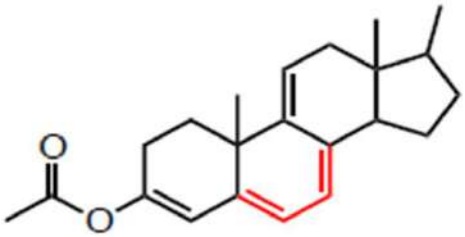
UV Spectroscopy

Woodward Fieser Rules for Dienes

examples

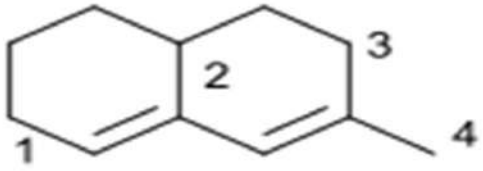


transoid diene	214 nm
3 alkyl subst	15 nm
1 OR subst	6 nm
1 exocyclic db	5 nm
calculated value	240 nm
observed	241 nm

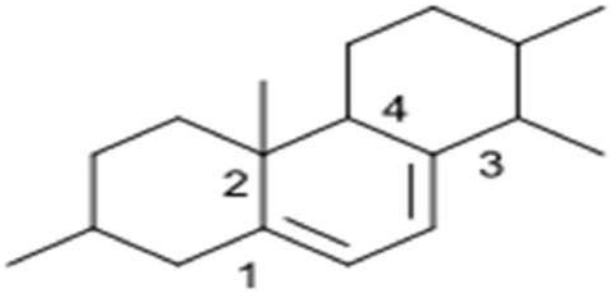


cisoid diene	253 nm
2 conj db	60 nm
5 alkyl subst	25 nm
1 acyl subst	0 nm
3 exocyclic db	15 nm
calculated value	353 nm
observed	355 nm

Absorption maximum : 214 + 20 + 5 = 239 nm



heteroannular diene : 214
alkyl substitutents 4 x 5 = 20
exocyclic double bond : 5



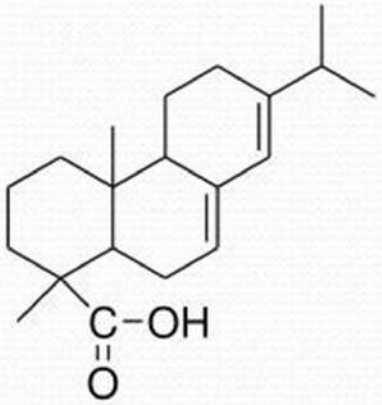
homoannular diene : 253
alkyl substituents : 4 x 5
exocyclic double bond : 2 x 5

Absorption maximum : 253 + 20 + 10 = 283 nm

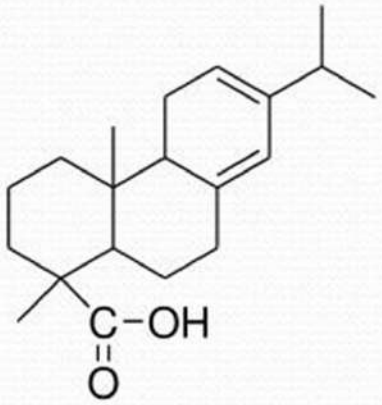
Note:-

In some references you are expected to see alkyl substituent as Ring Residues

Isomers differentiation

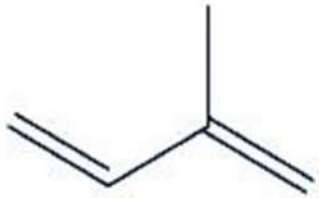


heteroannular diene =	214 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	+ 5 nm
	239 nm

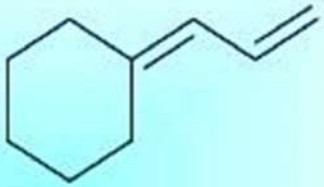


homoannular diene =	253 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	+ 5 nm
	278 nm

For example:



Isoprene - acyclic butadiene =	217 nm
one alkyl subs.	+ 5 nm
	222 nm
Experimental value	220 nm

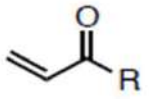
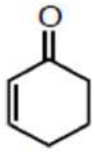
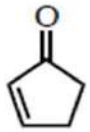
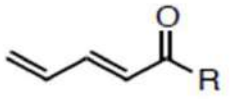


Allylidenecyclohexane

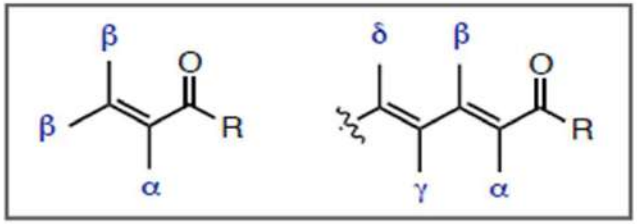
- acyclic butadiene =	217 nm
one exocyclic C=C	+ 5 nm
2 alkyl subs.	+10 nm
	232 nm
Experimental value	237 nm

Part 2:- Enone and Dienone

Solvent Correction	nm
H_2O	+ 8
EtOH	0
$CHCl_3$	- 1
Dioxane	- 5
Et_2O	- 7
Hydrocarbon	- 11

	 acyclic enone	 6-membered ring enone	 5-membered ring enone	 acyclic dienone
base values:	**215 nm**	**215 nm**	**202 nm**	**245 nm**

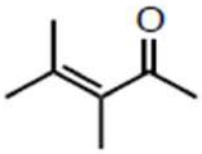
Increments:		α	β	γ	δ and higher
For each additional conjugated double bond		+ 30 nm			
For each exocyclic double bond		+ 5 nm			
For each homodiene component		+ 39 nm			
For each alkyl group **and ring residue**		+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:	- OH	+ 35 nm	+ 30 nm		+ 50 nm
	- OR	+ 35 nm	+ 30 nm	+ 17 nm	+ 31 nm
	- O(C=O)R	+ 6 nm	+ 6 nm	+ 6 nm	+ 6 nm
	- Cl	+ 15 nm	+ 12 nm		
	- Br	+ 25 nm	+ 30 nm		
	- SR	+ 30 nm	+ 85 nm		
	- NR_2	+ 60 nm	+ 95 nm		



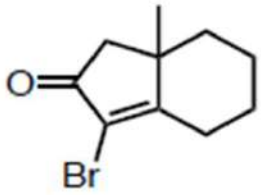
UV Spectroscopy

Woodward Fieser Rules for Enones

examples



acyclic enone	215 nm
1 α alkyl	10
2 β alkyl	24 nm
calculated value	249 nm
observed	249 nm

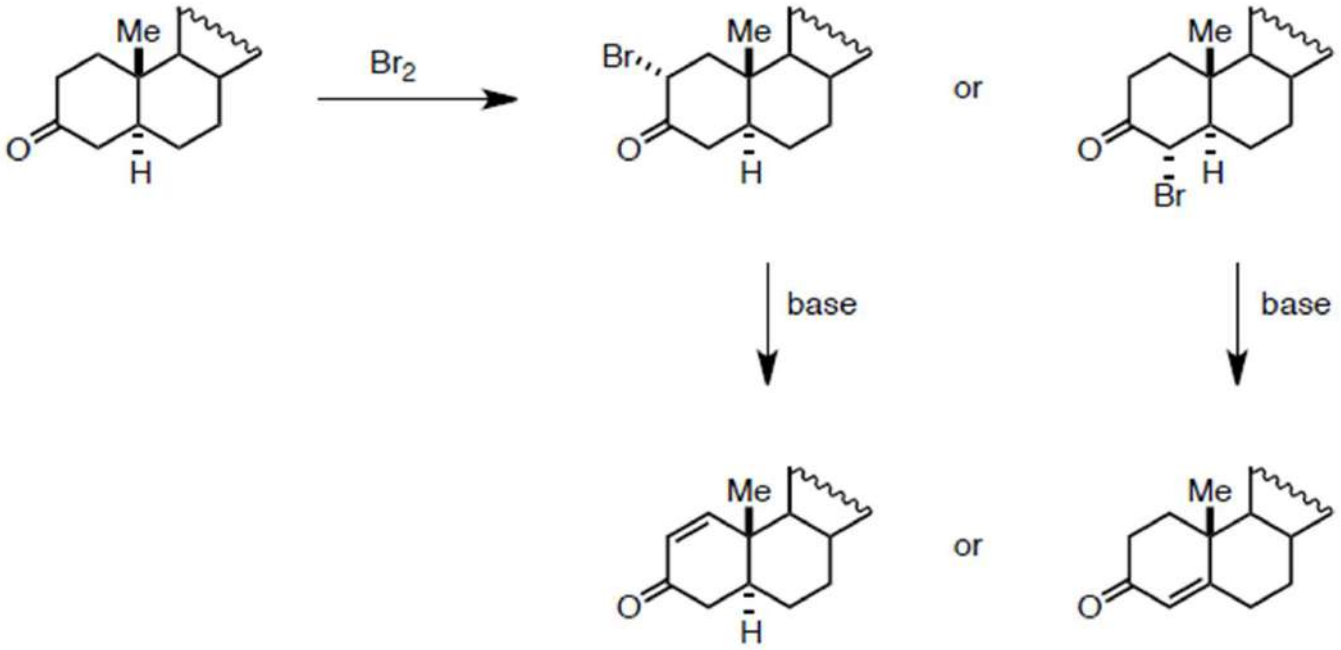


5-membere enone	202 nm
1 α Br	25 nm
2 β alkyl **ring residue**	24 nm
1 exocyclic db	5 nm
calculated value	256 nm
observed	251 nm

UV Spectroscopy

Woodward Fieser Rules for Enones

practice

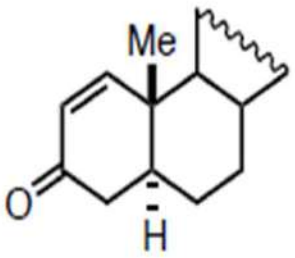


Can you distinguish the two by UV?

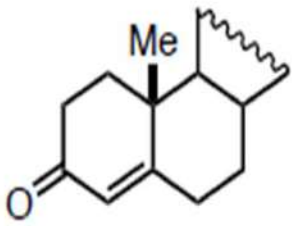
UV Spectroscopy

Woodward Fieser Rules for Enones

practice



vs



6-membered enone	215 nm	215 nm
β alkyl **ring residue**	12 nm	24 nm
exocyclic db		5 nm
	227 nm	244 nm

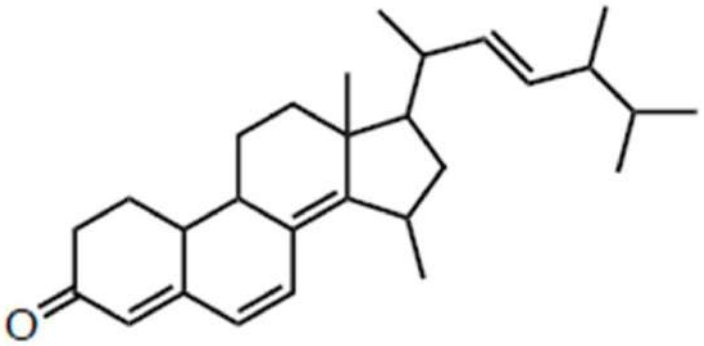
UV Spectroscopy

Woodward Fieser Rules for Enones

practice

The correct λ max is

a) 356
b) 365
c) 563
d) 386
e) None of the above



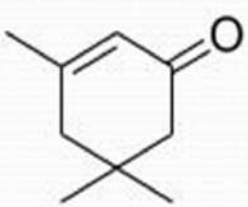
absorbance in EtOH?

and its color is :-

a) violet
b) Green
c) Colorless
d) Blue
e) None of the above.

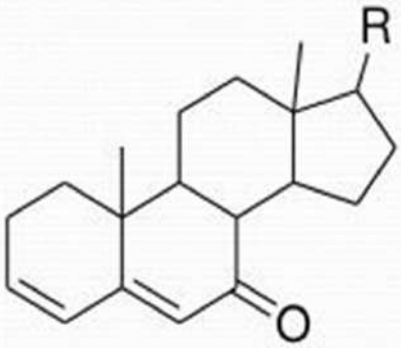
Note:-
In some references you are expected to see alkyl substituent as Ring Residues

Some examples – keep in mind these are more complex than dienes



alkyl sub + ring residue

cyclic enone =	215 nm
2 x β- alkyl subs. (2 x 12)	+24 nm
	239 nm
Experimental value	238 nm

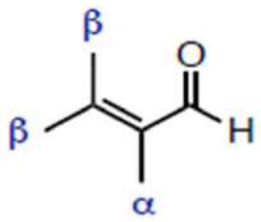
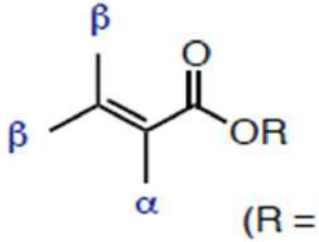


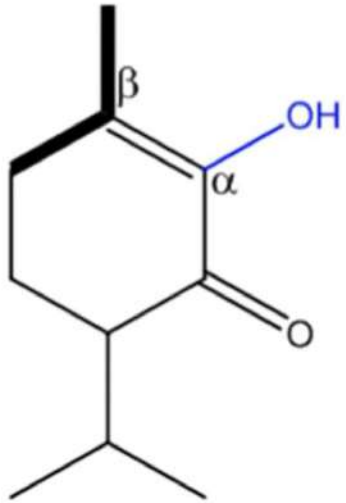
cyclic enone =	215 nm
extended conj.	+30 nm
β-ring residue	+12 nm
δ-ring residue	+18 nm
exocyclic double bond	+ 5 nm
	280 nm
Experimental	280 nm

21

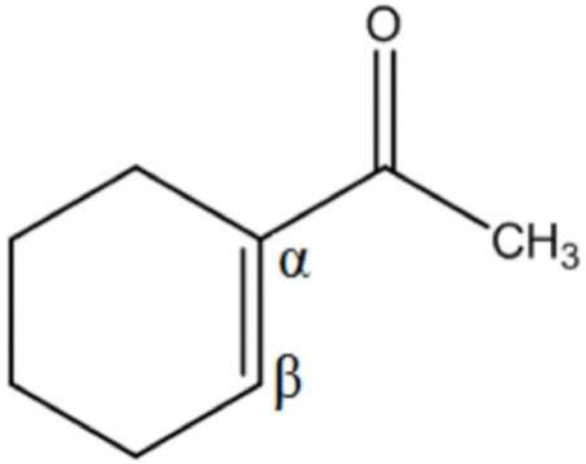
UV Spectroscopy

Woodward Fieser Rules for Other Conjugated Carbonyls

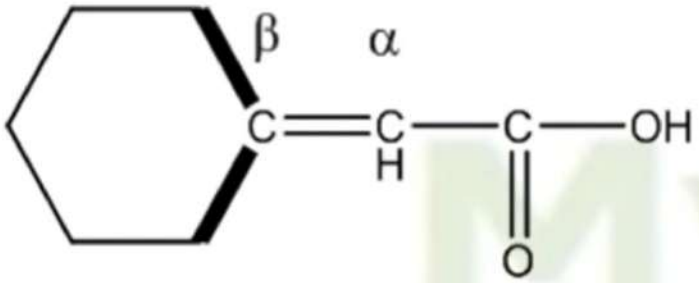
	 aldehydes	 (R = H or R') carboxylic acid or ester
Base Values		
unsubstituted aldehyde or ester	208 nm	193 nm (not observed)
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm
for an exocyclic α,β double bond		+ 5 nm
for an endocyclic α,β double bond in a 5- or 7-membered ring		+ 5 nm



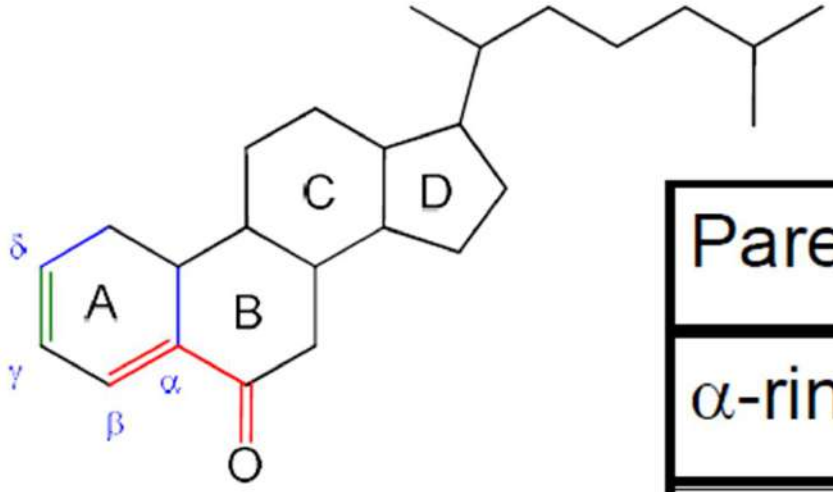
Six membered cyclic α,β-unsaturated ketone				=	215 nm
Beta Ring residue	02	x	12 nm	= +	24 nm
α OH	01	x	35 nm	= +	35 nm
Calculated λ_{max}				=	**274 nm**



Six membered cyclic α,β-unsaturated ketone				=		215 nm
Alpha Ring residue **α-Alkyl**	01	x	10 nm	=	+	10 nm
Beta Ring residue **β-Alkyl**	01	x	12 nm	=	+	12 nm
Calculated λ_{max}				=		**237 nm**

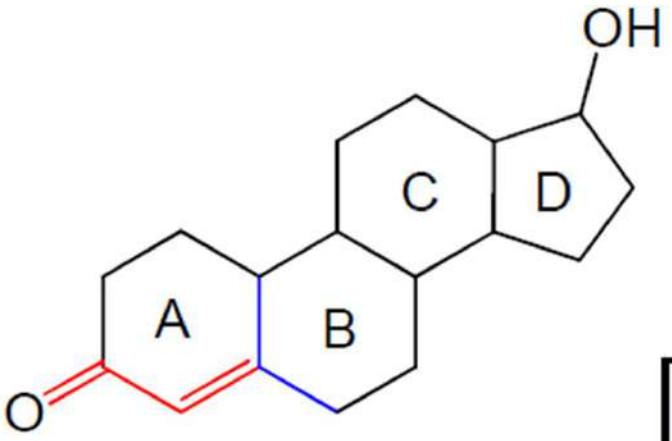


α,β-unsaturated carboxylic acid				=		195 nm
Beta Alkyl subtituent	02	x	12 nm	=	+	24 nm
Exocyclic double bond	01	x	05 nm	=	+	05 nm
Calculated λ_{max}				=		



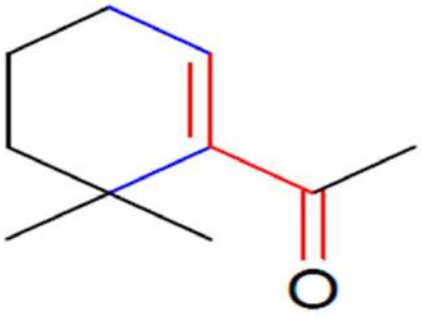
2,4-cholestadien-6-one

Parent chromophore	215 nm
α-ring residue α-Alkyl	10
exocyclic double bond	5
Double bond extending conjugation	30
homodiene	39
δ-ring residue δ-Alkyl	18
Total	**317 nm**
$\lambda_{observed}$	**314 nm**



Testosterone

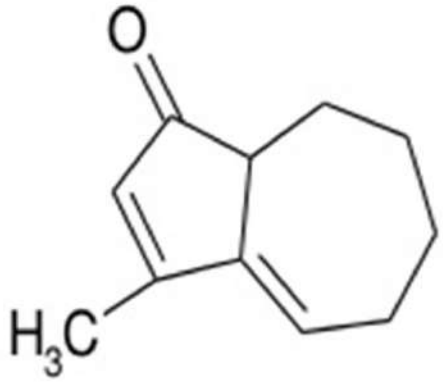
Parent chromophore	215 nm
α-ring residue	0
β-ring residue	2 x 12
exocyclic double bond	5
Total	244 nm
$\lambda_{observed}$	241 nm



1-(6,6-Dimethylcyclohex-1-enyl)-ethanone

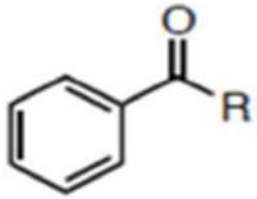
Parent chromophore	215 nm
α-ring residue	10
β-ring residue	12
Total	237 nm
$\lambda_{observed}$	232 nm

4. Calculated the λ max for compound

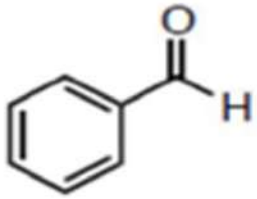


- ά-β unsaturated Cyclopentane =202 mμ
- 1 β alkyl substitution =12 mμ
- 1 Exocylic double bond =5 mμ
- double bond with extending conjugation =30 mμ
- 1γ ring residue =18 mμ
- 1δ ring residue =18 mμ
- Calculated value =285 mμ
- Observed value =285 mμ

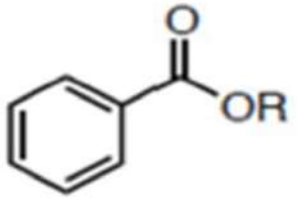
Part 3:- Benzoyl derivatives



aryl ketones
(R = alkyl)



benzaldehydes



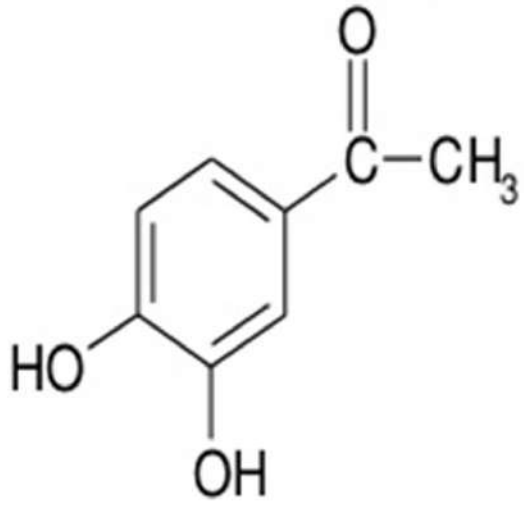
benzoic acids and esters

base values:	**246 nm**	**250 nm**	**230 nm**

Increments:	ortho	meta	para
For each alkyl group	+ 3 nm	+ 3 nm	+ 10 nm
For each OH or OR (R = alkyl)	+ 7 nm	+ 7 nm	+ 25 nm
For each $O^{\ominus}$	+ 11 nm	+ 20 nm	+ 78 nm
For each of the following groups:			
- Cl	+ 0 nm	+ 0 nm	+ 10 nm
- Br	+ 2 nm	+ 2 nm	+ 15 nm
- NH_2	+ 13 nm	+ 13 nm	+ 58 nm
- $NH(C{=}O)CH_3$	+ 20 nm	+ 20 nm	+ 45 nm
- $NHCH_3$			+ 73 nm
- $N(CH_3)_2$	+ 20 nm	+ 20 nm	+ 85 nm

Calculating the absorption maximum for the following compound

- Basic value =246mμ
- OH- substation at para position = 25mμ
- OH - substation at meta position =7mμ
- Calculated value =278 mμ
- Observed value =281mμ



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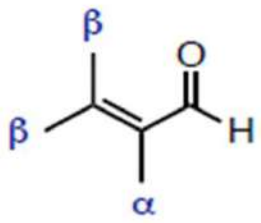
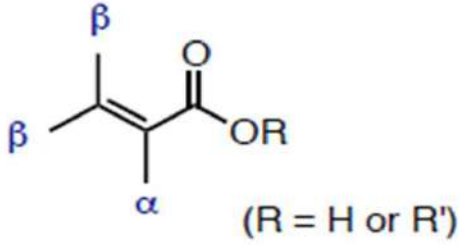
Woodward Fieser Rules for Other Conjugated Carbonyls

صفحة مكررة



aldehydes



carboxylic acid or ester

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for an endocyclic α,β double bond in a 5- or 7-membered ring		+ 5 nm

Fieser-Kuhn Rules to Calculate Wavelength of λ_{max} Absorption of Polyenes

$$\lambda_{max} = 114 + 5M + n\,(48.0 - 1.7\,n) - 16.5(\#R_{endo}) - 10(\#R_{exo})$$

λ_{max} :- is the wavelength of maximum absorption

M:- is the number of alkyl substituents / ring residues in the conjugated system

n:- is the number of conjugated double bonds

R_{endo} **:-** is the number of rings with endocyclic double bonds in the conjugated system

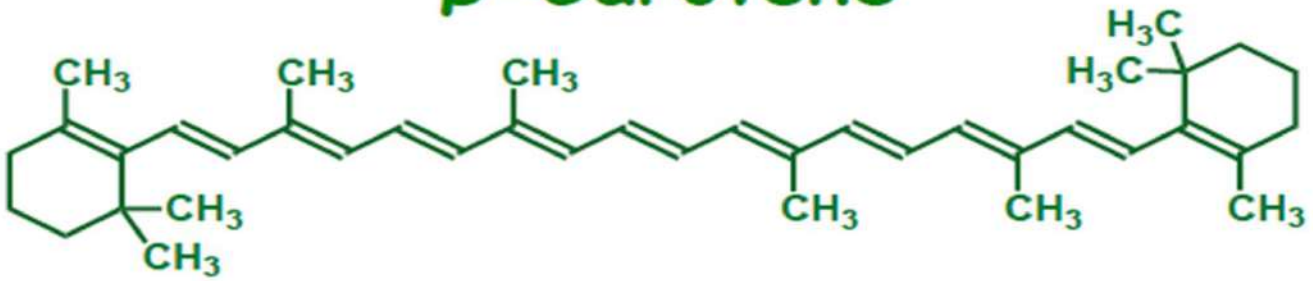
R_{exo} **:-** is the number of rings with exocyclic double bonds in the conjugated system.

Lycopene

λ_{max}^{calc} = 114 + 5(8) + 11[48.0 – 1.7(11)] – 0 – 0
= 476 nm
λ_{max}^{obs} = 474 nm (hexane)

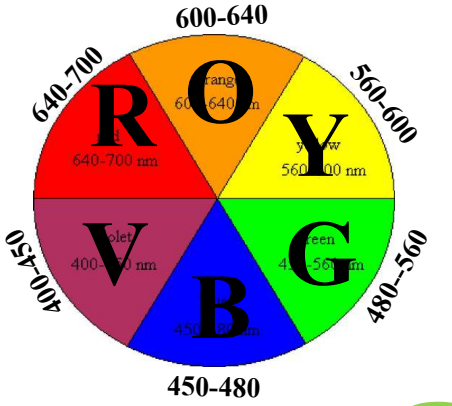
λ_{max} = 114 + 5M + n (48.0 – 1.7 n) – 16.5(#R_{endo})–10(#R_{exo})

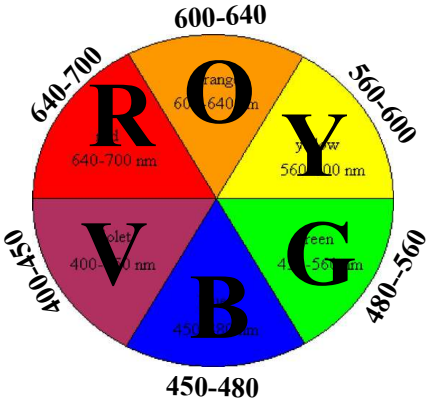
β-Carotene



λ_{max}^{calc} = 453.3 nm
λ_{max}^{obs} = 452 nm (hexane)

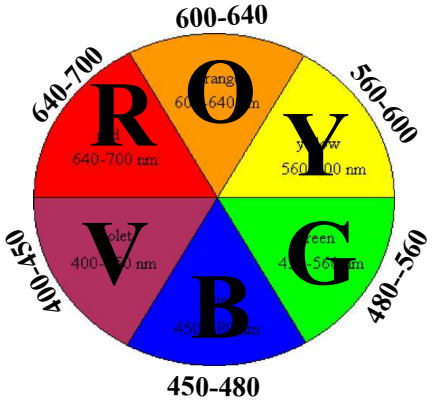
λ_{max} = 114 + 5(10) = 11(48 - 1.7•11) - 16.5(2) - 10(0) = 453 nm
observed: 452 nm

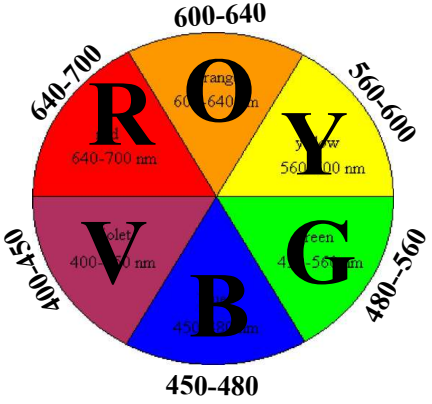




Ultraviolet Spectroscopy "UV"

Part (6)
Color and Conjugation





Color and Conjugation

- **Most simple organic compounds, having few multiple bonds and few functional groups, do not absorb visible light, and thus appear as being colorless or white. More complex molecules, having several multiple bonds that are conjugated appear as being colored. For multiple bonds to be conjugated, they must be in an alternating double bond – single bond –double bond, etc arrangement.**

- **The degree of conjugation determines the actual energy difference between the ground and excited states. The more highly conjugated the system the lower the energy difference and the lower the required energy of light needed to excite the electrons. In other words molecules having more conjugated multiple bonds absorb lower energies of light and higher λ_{max} than do molecules having fewer conjugated multiple bonds.**

How does this affect the actual color of a compound?

1. Energy of visible light increases in the following order: red (low energy), orange yellow, green, blue, violet (high energy).

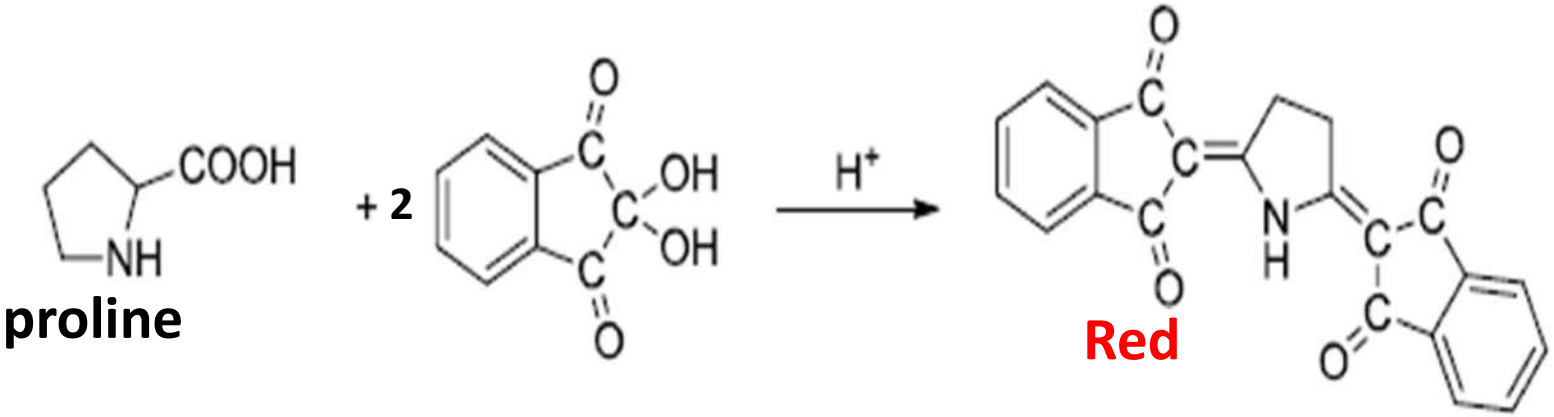
2. A highly conjugated system absorbs the lower energy portions of the light and reflect what is not absorbed; It is this reflected portion that the eye will perceive as the color of that object.

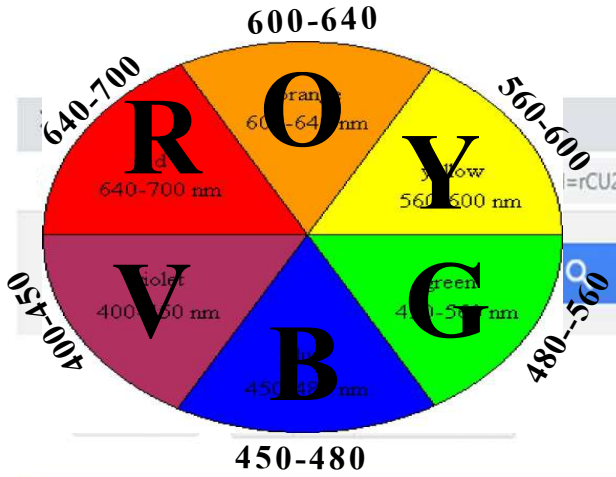
3. A less highly conjugated system will require the absorption of the higher energy part of the spectrum, allowing the lower energy parts to be reflected to the eye.

4. Note that the color that is reflected is the complementary color of the color that is absorbed. For example if the high energy violet portion of the spectrum is absorbed, its complementary color of yellow is what is observed. If the lower energy blue or green colors are absorbed, the colors orange or red would be observed. (color wheel).

Derivatization in pharmaceutical chemistry

- Amines (including α-amino acids) react with Ninhydrin to give a colored product.
- The α-amino acids typically give a blue-purple product.
- Proline, a secondary amine, gives a red product.(λ_{max} =520 nm)
- Blue-purple (λ_{max} =570 nm) and red reaction products positively identify free amino groups on amino acids and proteins. This is due to having different conjugated system leads to different energy and different wave length as a result different color.





proline ninhydrin nm red color

Google

كتب

كتابة مراجعة | إضافة إلى مكتبتي

النتيجة 1 من إجمالي 2 في هذا الكتاب لـ proline ninhydrin nm red color - السابقة التالية - عرض جميع المقتطفات

مجرى البحث

logical and pathological stress conditions. *Free proline is known to play a role in plants under stress conditions*. Though the molecular mechanism has not yet been established for the increased level of proline, one of the hypotheses refers to breakdown of proteins into amino acids and conversion to proline for storage.

Principle

During selective extraction with aqueous sulphosalicylic acid, proteins are precipitated as a complex. Other interfering materials are also presumably removed by absorption to protein-sulphosalicylic acid complex. The extracted proline is made to react with ninhydrin in acidic conditions (pH 1.0) to form the chromophore (red colour) and read at 520 nm.

Materials

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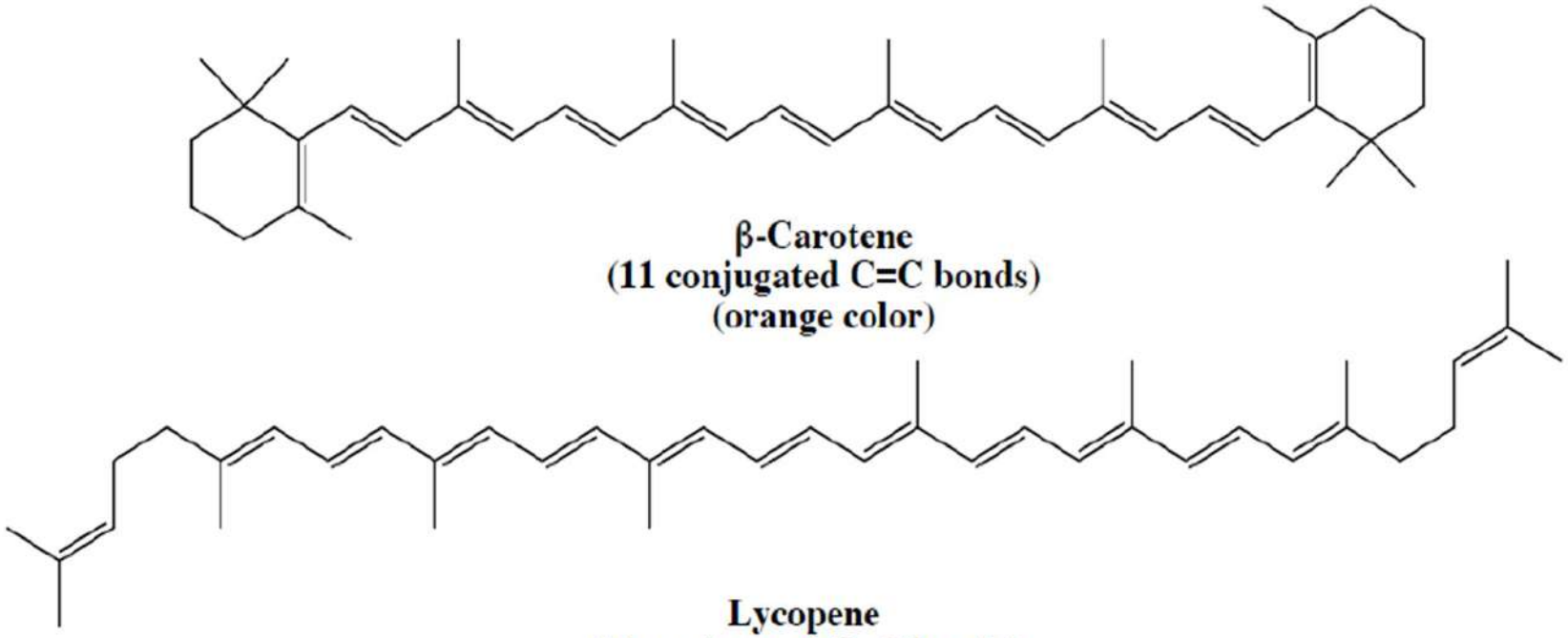
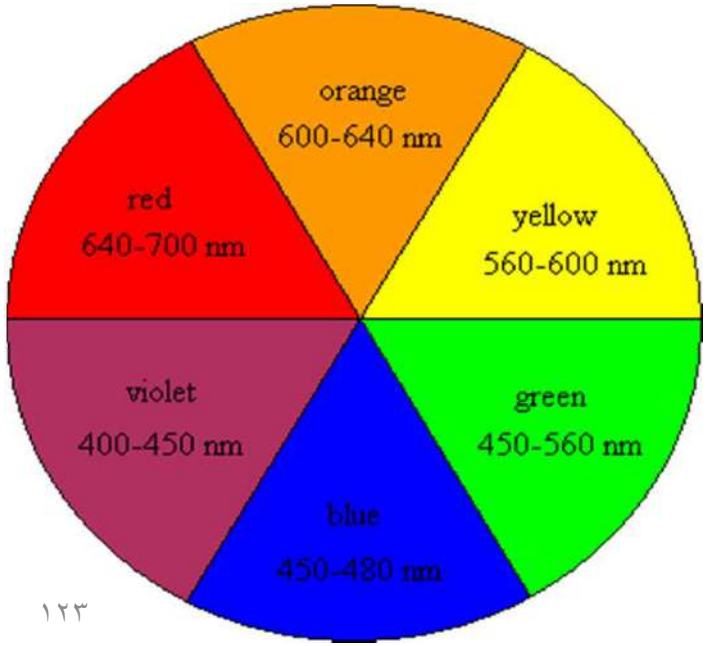
- **To illustrate this, consider the structure of a few molecules. Retinol, or vitamin A, has five conjugated double bonds and absorbs the violet part of the spectrum, thus appearing as yellow.**
- **The more highly conjugated ß-carotene and lycopene, each having eleven conjugated double bonds absorb in the lower energy blue and green portions of the spectrum and appear as orange and red respetively.**

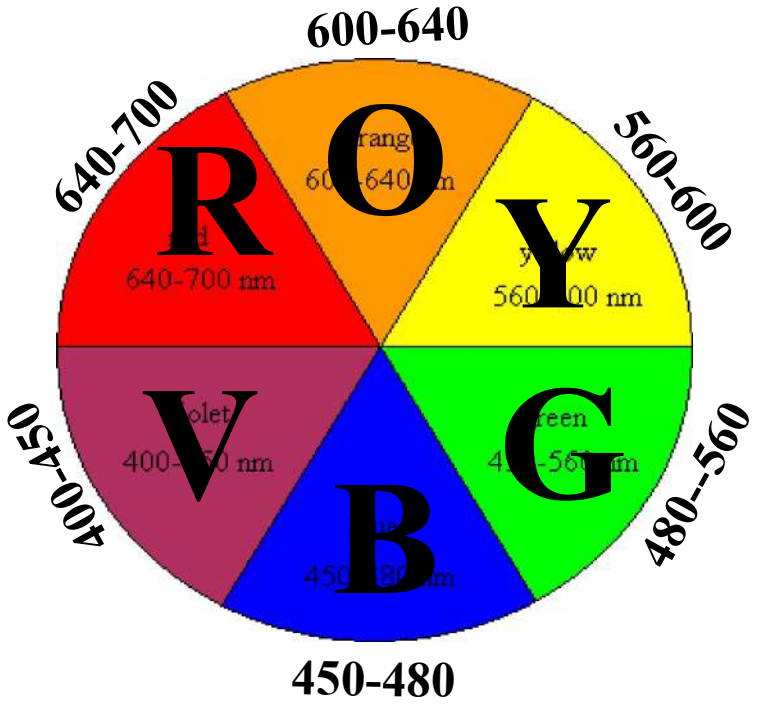


β-Carotene
(11 conjugated C=C bonds)
(orange color)

Lycopene
(11 conjugated C=C bonds)
(red color)

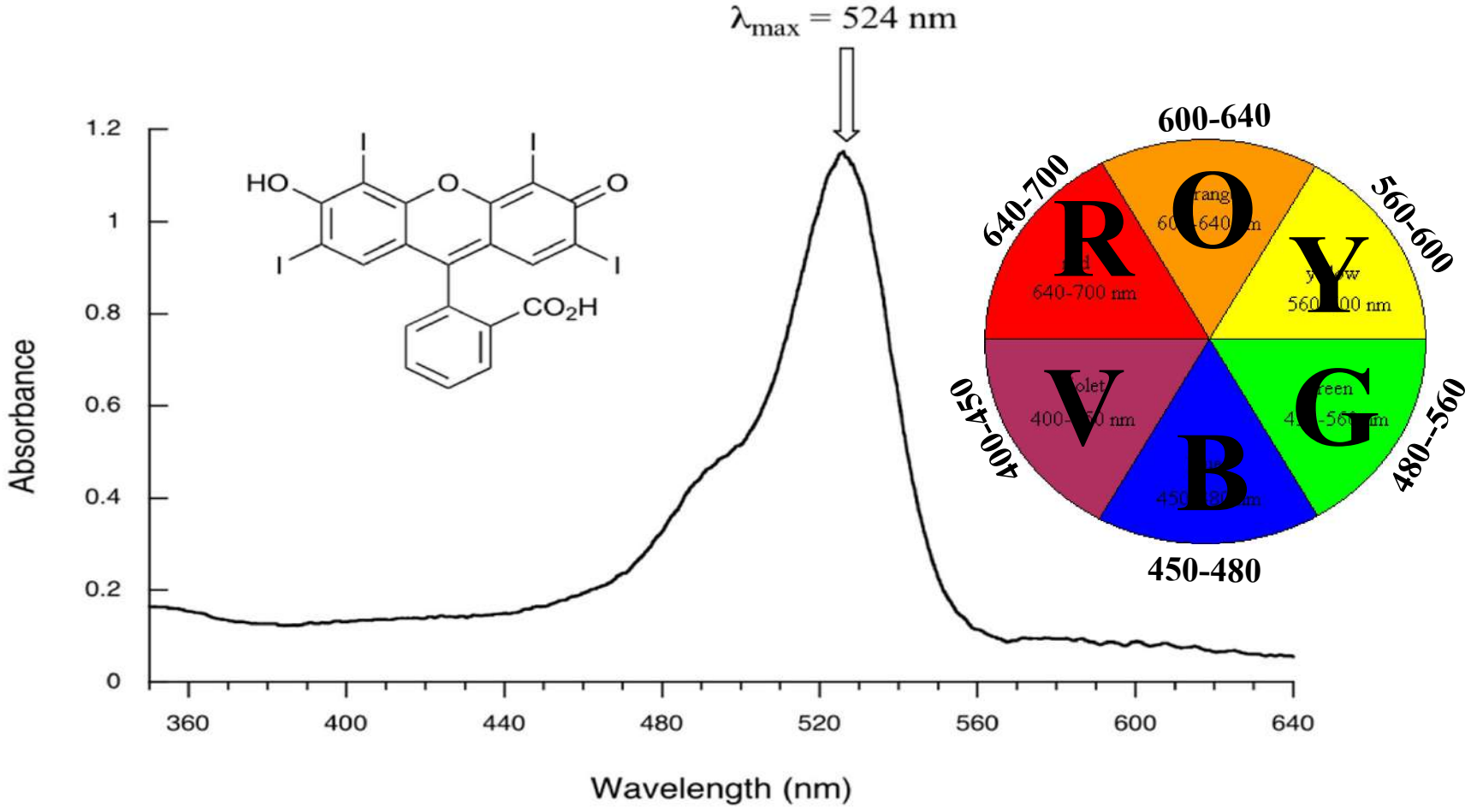
When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red.





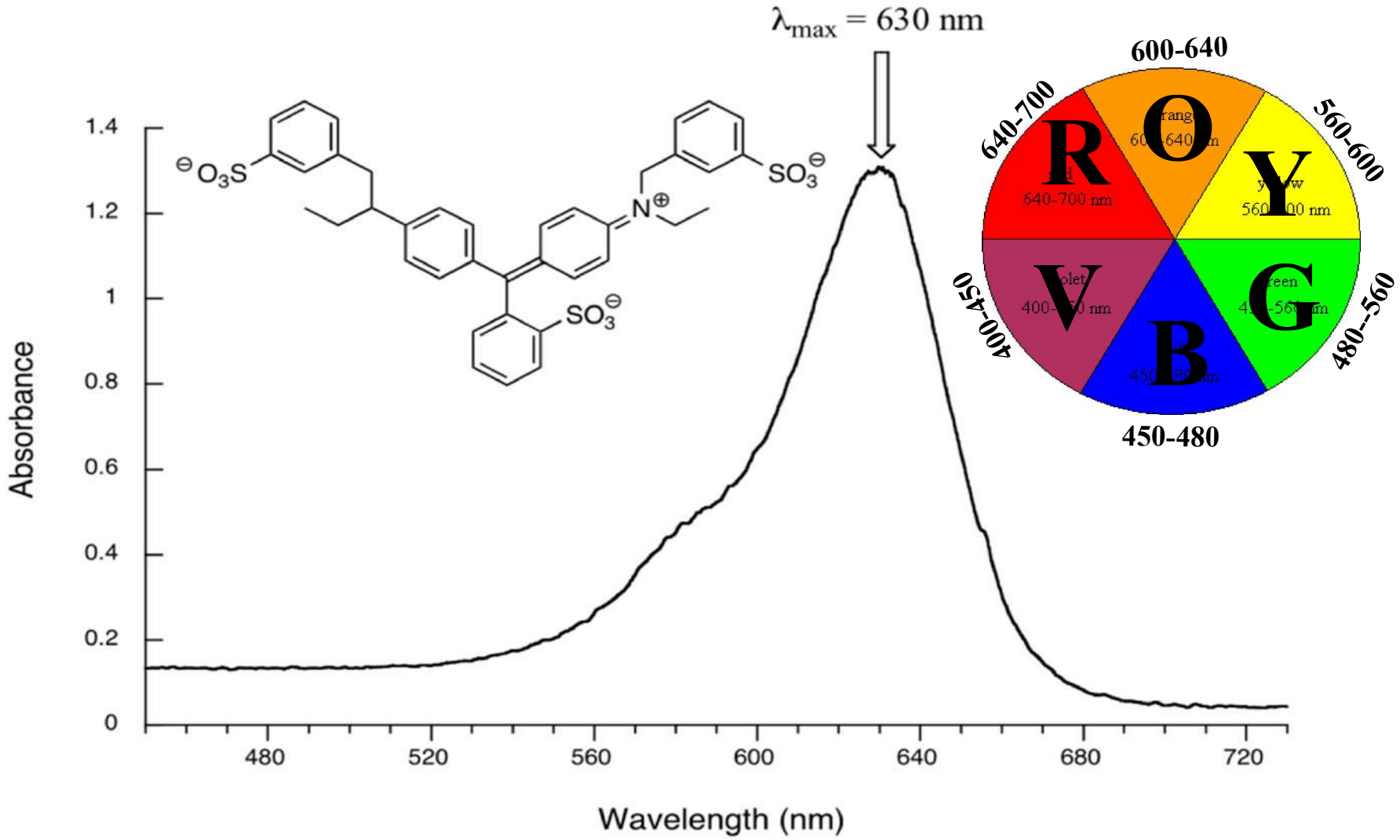
Here is the absorbance spectrum of the common food coloring Red #3:

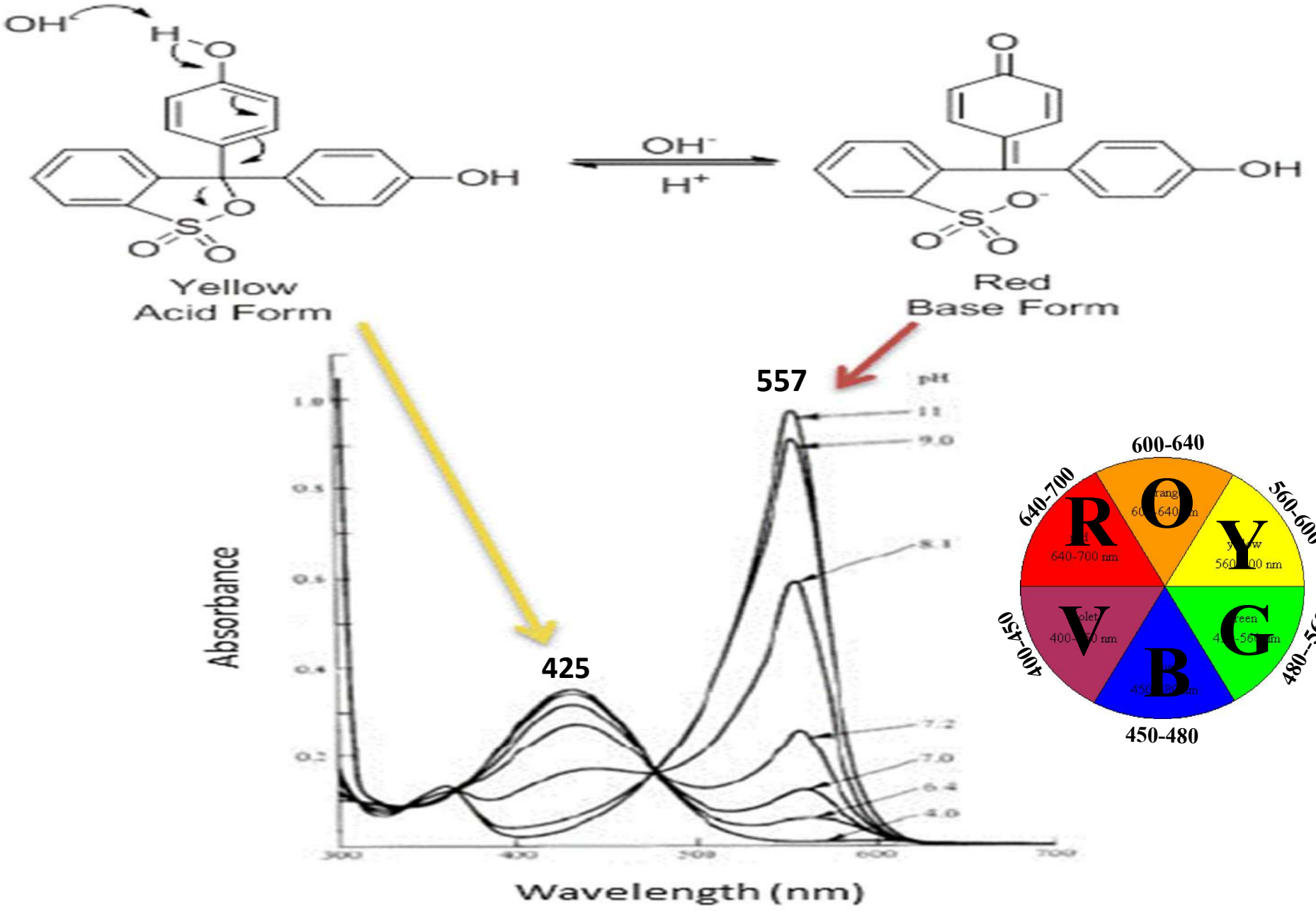
Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound <u>appears red to our eyes.</u>



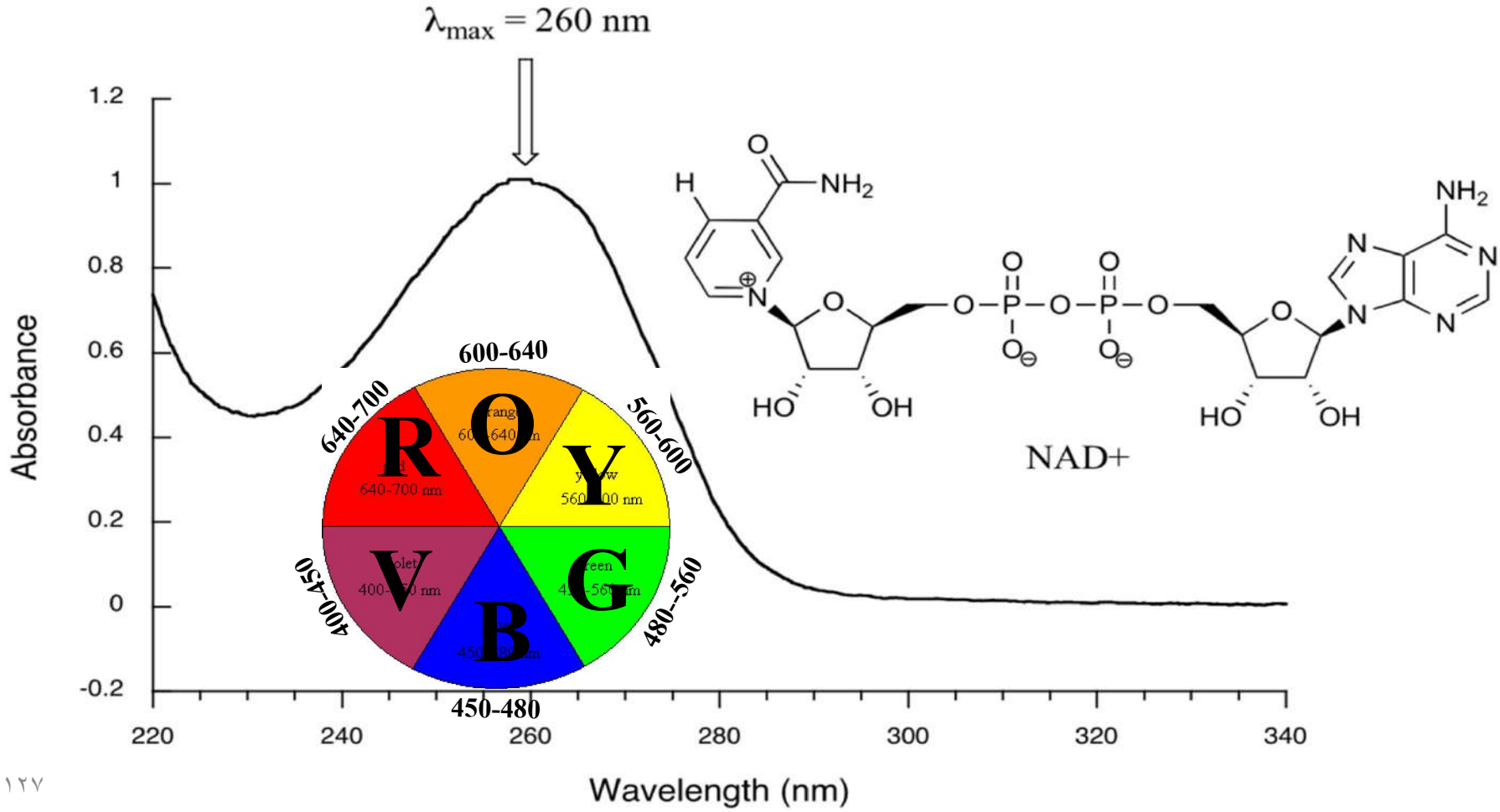
Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound <u>appears blue to our eyes.</u>

:




OH
H
O
OH
O
S
O
O
Yellow
Acid Form
OH⁻
H⁺
O
OH
O⁻
S
O
O
Red
Base Form
557
425
pH
11
9.0
8.1
7.2
7.0
6.4
4.0
Absorbance
Wavelength (nm)
600-640
640-700
560-600
400-450
480–560
450-480
R
O
Y
V
G
B

Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+ This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems but still <u>not colored</u>!!!!!



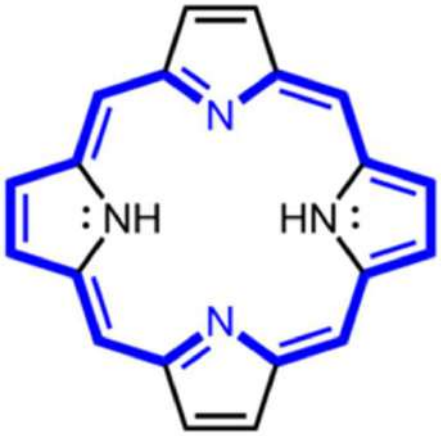
- **This is <u>not to say that aLL highly conjugated molecules ARE colored</u> or that <u>all unconjugated molecules are NOT colored.</u>**

- **There are many other factors that can affect a molecule's color (i.e. many transition metals are colored, NOT due to conjugation).**

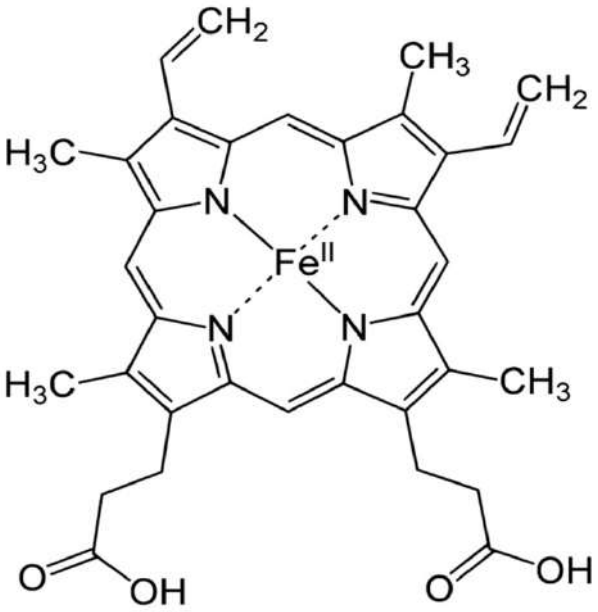
- **When a molecule absorbs a photon of some energy, one electron moves up to a higher energy orbital. Now, there is a gap between that one electron in the higher energy state and the electron in the lower energy state, we call this the HOMO/LUMO gap or ΔE.**

- **This value, ΔE, may correspond to an energy that is absorbed by a photon in the visible light spectrum (shown below). If this occurs, the molecule will be colored. What color you will see is dependent on what wavelength the HOMO/LUMO gap refers to. If it corresponds to 700 nanometers, you would see a green molecule (see complementary colors).**

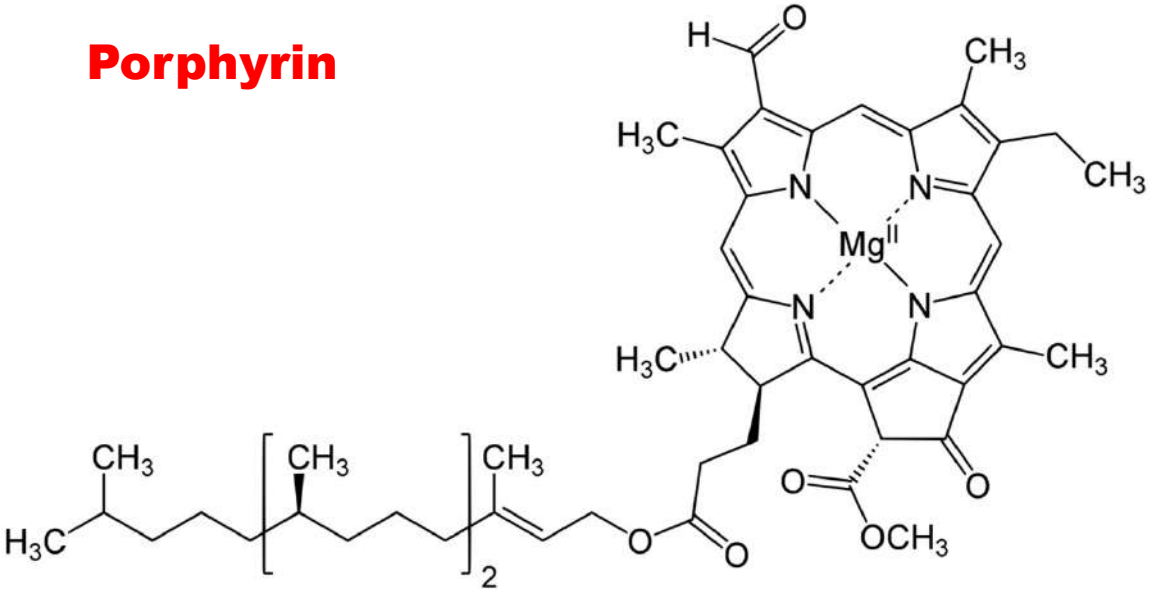
Colors in the bio-system



Porphyrin



Haemoglobin



Chlorophyll