UV SPECTROSCOPY

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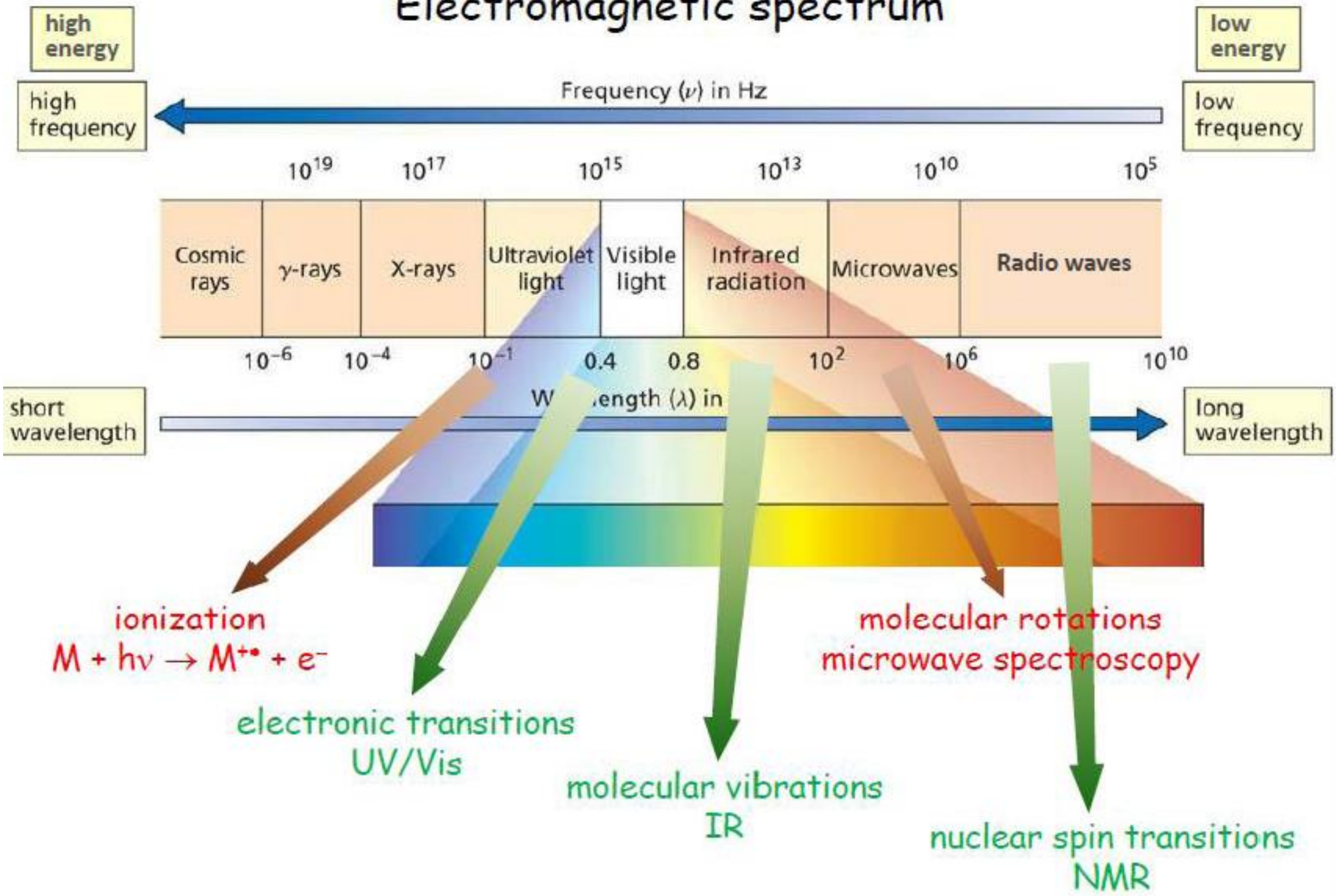
WHAT IS SPECTROSCOPY ?

- Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways.
- Atoms and molecules may absorb and/or emit EMR.
- Absorption of EMR stimulates different types of motion in atoms and/or molecules.
- The patterns of absorption (wavelengths absorbed and to what extent) and/or emission (wavelengths emitted and their respective intensities) are called ‘*spectra*’.
- **spectroscopy** is the interaction of EMR with matters to get ***specta*** ,which gives information like, bond length, bond angle, geometry and molecular structure.

Electromagnetic spectrum



high energy

high frequency

low energy

low frequency

Frequency (ν) in Hz

10^{19} 10^{17} 10^{15} 10^{13} 10^{10} 10^{5}

Cosmic rays | γ-rays | X-rays | Ultraviolet light | Visible light | Infrared radiation | Microwaves | Radio waves

10^{-6} 10^{-4} 10^{-1} 0.4 0.8 10^{2} 10^{6} 10^{10}

W ength (λ) in

short wavelength

long wavelength

ionization

$M + h\nu \rightarrow M^{+\bullet} + e^{-}$

electronic transitions

UV/Vis

molecular vibrations

IR

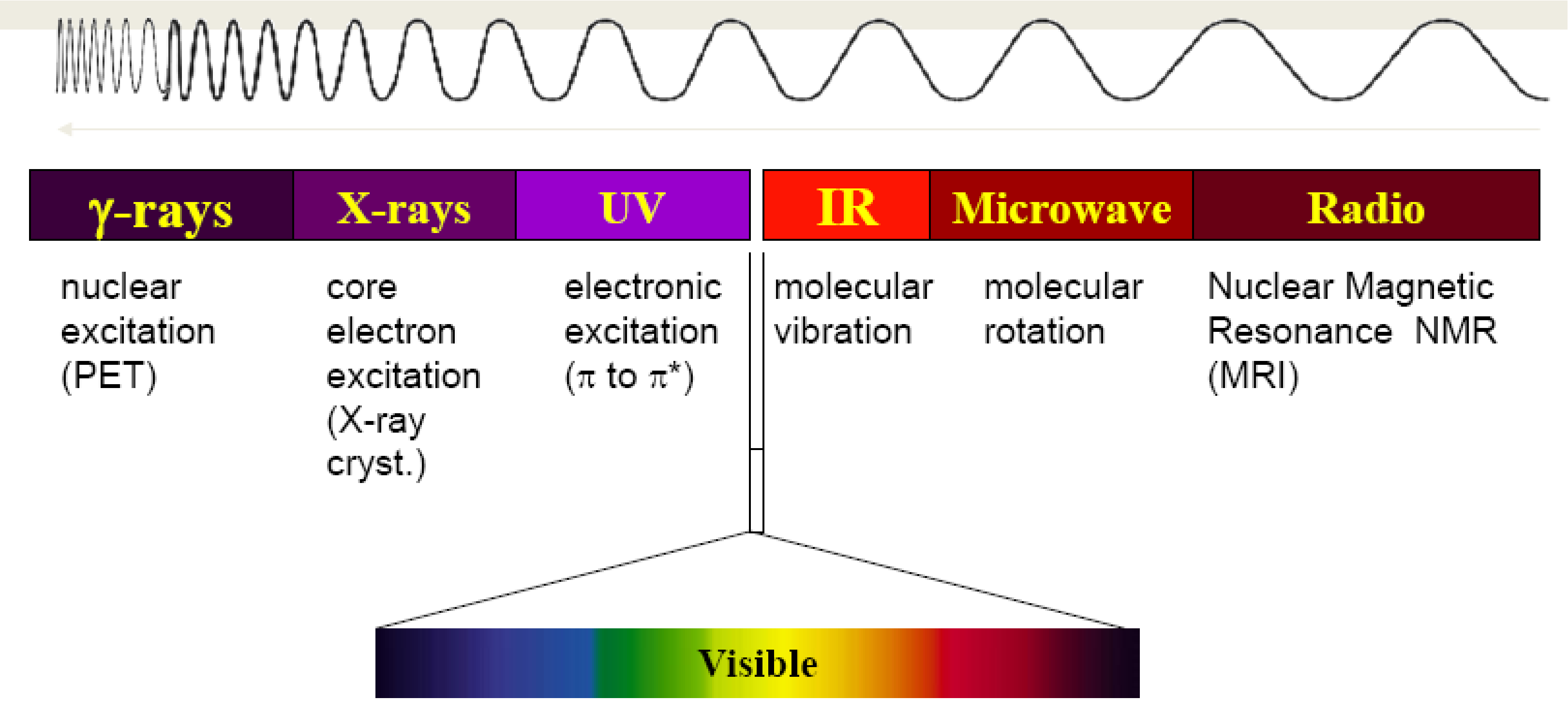
molecular rotations

microwave spectroscopy

nuclear spin transitions

NMR

The entire electromagnetic spectrum is used by chemists:



γ-rays	**X-rays**	**UV**	**IR**	**Microwave**	**Radio**
nuclear excitation (PET)	core electron excitation (X-ray cryst.)	electronic excitation (π to π^*)	molecular vibration	molecular rotation	Nuclear Magnetic Resonance NMR (MRI)

Visible

Electromagnetic radiations, are a form of energy, displays the properties of both ,particles and waves. The particle component is called a ***photon***

The term **"photon"** is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light –

. The important parameters associated with electromagnetic radiation are:

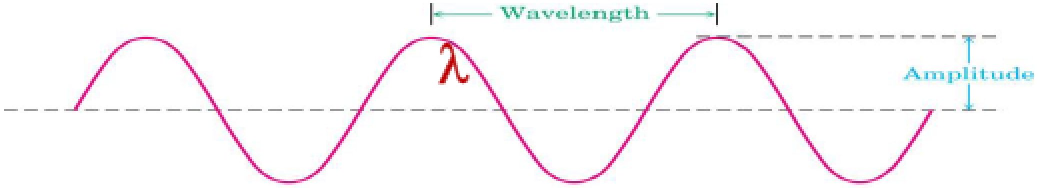
Energy (E):

Frequency (ν)

Wavelength (λ)

$$\mathbf{E = h\nu}$$

Energy is directly proportional to frequency, and inversely proportion to wavelength, as indicated by the equation below



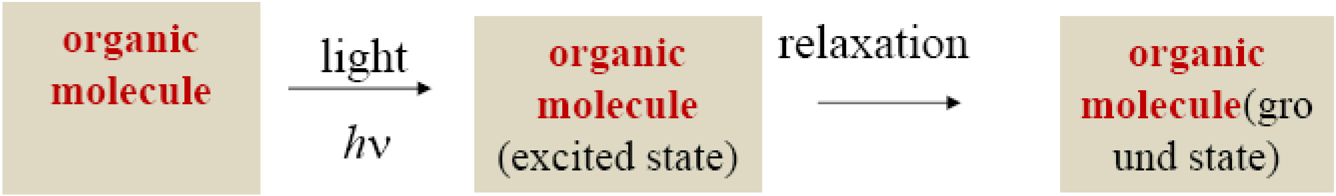
λ = distance of one wave

ν = frequency: waves per unit time (sec^{-1}, Hz)

c = speed of light (3.0×10^8 m • sec^{-1})

h = Plank's constant (6.63×10^{-34} J • sec)

Principles of molecular spectroscopy



organic molecule

light

hν

organic molecule (excited state)

relaxation

organic molecule(ground state)

UV-Vis: **valance electron transitions**

- **gives information about p-bonds and conjugated systems**

Infrared: **molecular vibrations (stretches, bends)**

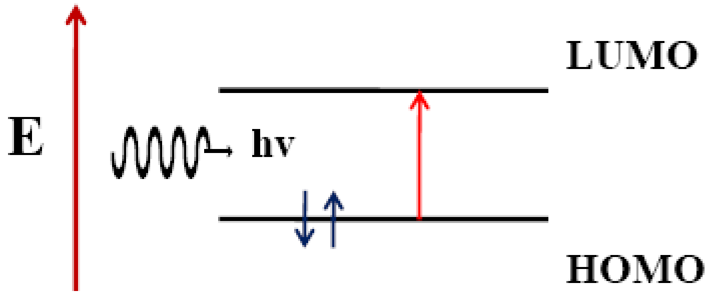
- **identify functional groups**

Radiowaves: **nuclear spin in a magnetic field (NMR)**

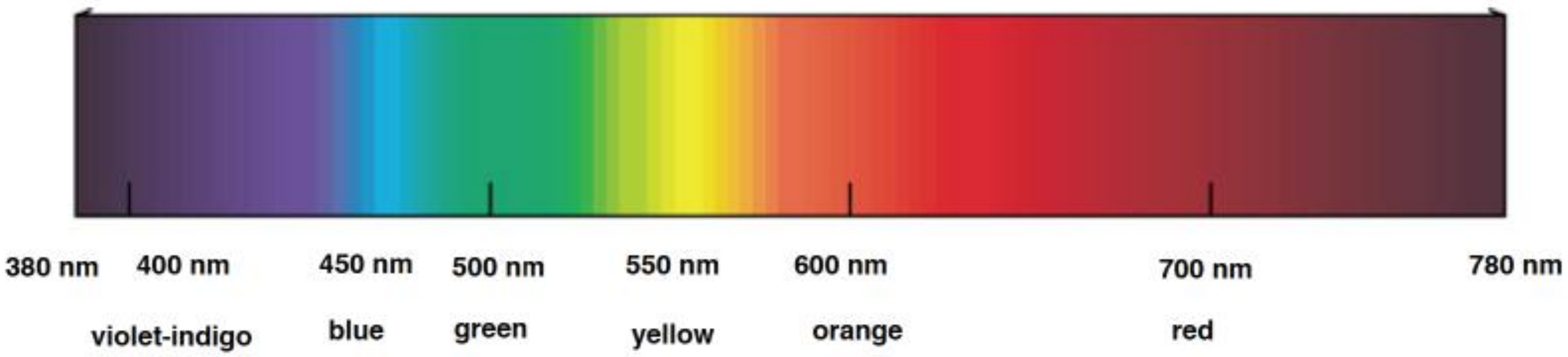
- **gives a map of the H and C framework**

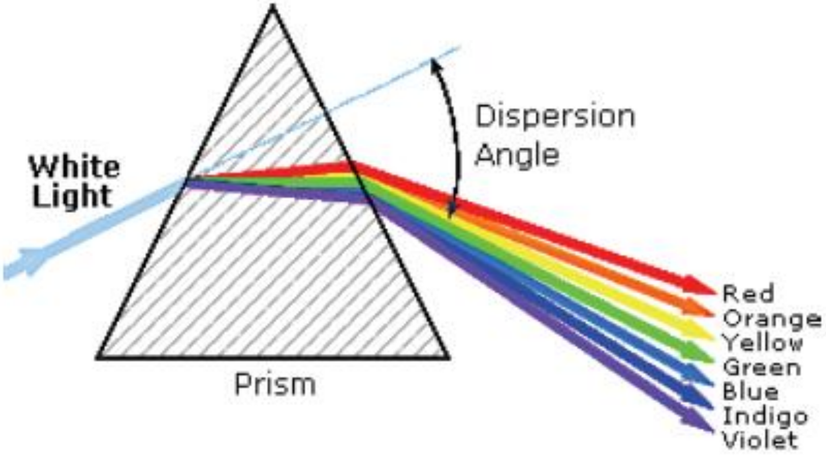
Ultra-Violet Spectroscopy

- It is a branch of spectroscopy in which transition occur due to the excitation of electrons from one energy level to higher one by the interaction of molecules with ultraviolet and visible lights.
- Absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state to higher electronic states.
- Since it involves an electron excitation phenomenon, so, also called as Electronic Spectroscopy.



The Visible Spectrum





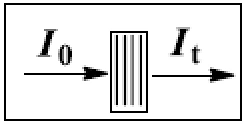
Laws of Photochemistry

- The decrease in intensity of the radiation in its passage through the absorbing medium is governed by two laws - ***Lambert's Law and Beer's Law.***

- **Lambert's Law:** This law states that the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the penetrating radiation. When a monochromatic light is passed through the sample solution, the intensity of the transmitted light decrease exponentially with the thickness of the light absorbing medium. Let us consider, a thin layer of the medium of thickness dl and let I be the intensity of the radiation entering it, then

$$dI/dl = -kI, \text{ on integrating,}$$

$$\ln I_t/I_0 = -kl,$$

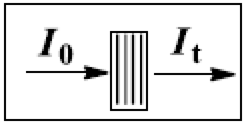


- where I_0 is the intensity at $l = 0$, and I_t, the intensity at distance l. The constant k is called the '***absorption coefficient***' of the substance.

- When the absorbing substance is present in solution, the absorption of light also depends upon the concentration.
- **Beer's Law:** This law states that the rate of decrease in intensity of radiation absorbed is proportional to the intensity of radiation and to the concentration of solute. Hence, using the same symbols,

$$dI/dl = -k'cI \text{, on integrating,}$$

$$\ln I_t/I_0 = -k'cl,$$

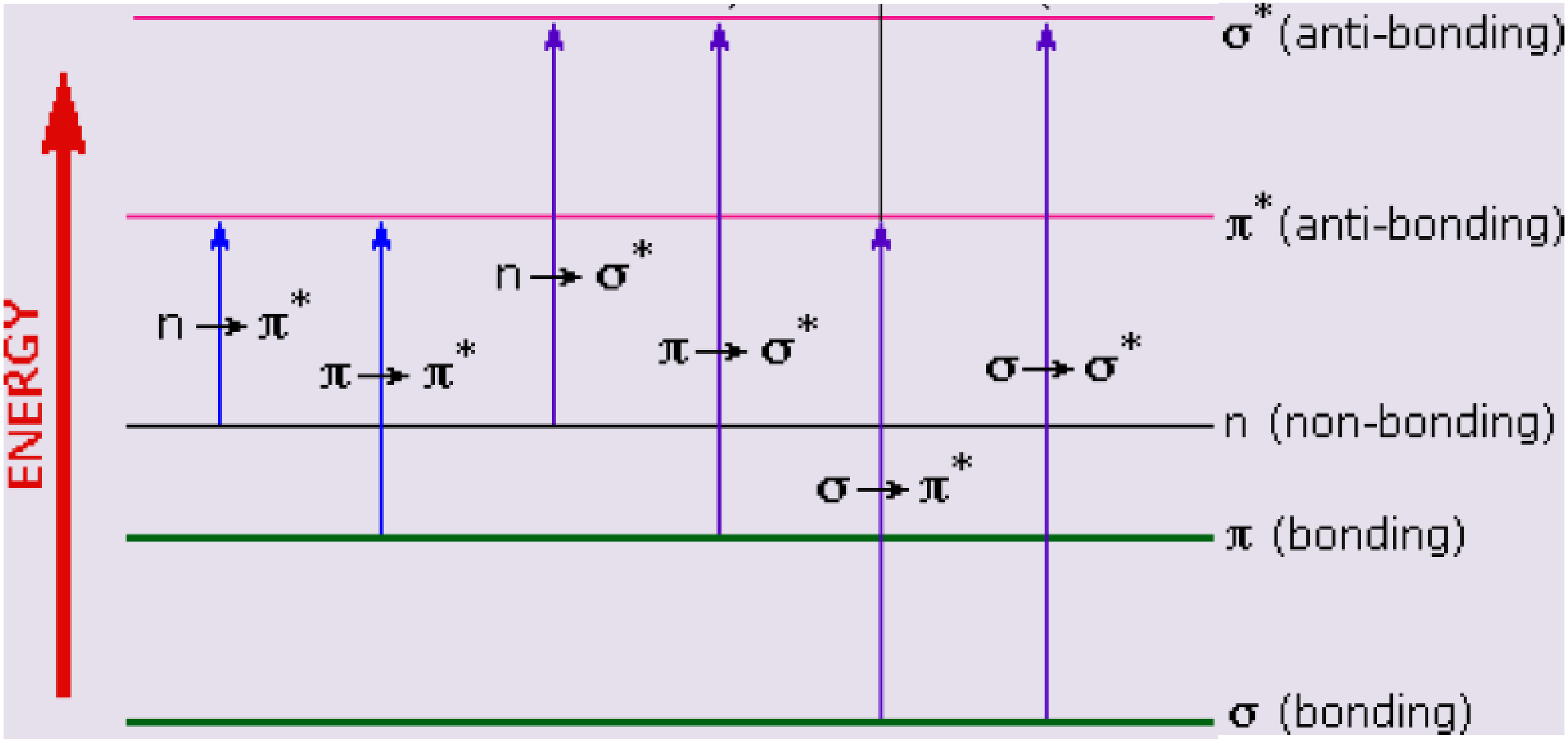


- where c is the concentration, and k' is called the '***molar absorption coefficient***' of the substance.

- Rewriting, $\log I_0/I_t = \varepsilon cl$, where ε is the molar extinction coefficient and is given by $\varepsilon = 0.4343\ k'$. The value of ε is specific for a given substance for a given wavelength of light.

Molar Extinction Coefficient

- The quantity ***$\log I_0/I_t$*** is generally called optical density (or absorbance, *A*). Therefore, ***$A = \varepsilon cl$*.** When *A* **(= *$\log I_0/I_t$*)** is plotted against concentration **(*c*)** of the solution taken in a column of definite thickness a straight line is obtained. The ***molar extinction coefficient*** (ε) is obtained from the slope of the line.


ENERGY
σ^* (anti-bonding)
π^* (anti-bonding)
$n \rightarrow \sigma^*$
$n \rightarrow \pi^*$
$\pi \rightarrow \sigma^*$
$\sigma \rightarrow \sigma^*$
$\pi \rightarrow \pi^*$
n (non-bonding)
$\sigma \rightarrow \pi^*$
π (bonding)
σ (bonding)

Selection Rules

1. Not all transitions that are possible are observed. Only those transitios which follow certain rule ,are called as allowed transitions.

2. For an electron to transition, certain quantum mechanical constraints apply – these are called "selection rules"

3. For example, an electron cannot change its spin quantum number during a transition – these are "forbidden"

   Other examples include:
   - the number of electrons that can be excited at one time
   - symmetry properties of the molecule
   - symmetry of the electronic states

Transitions

$\sigma \rightarrow \sigma^*$

- UV photon required, high energy, shorter wavelength
  - Methane at 125 nm (All saturated comp)
  - Ethane at 135 nm

n-> σ^*

- Saturated compounds with unshared e^-
  N, O, S and Halogens,
  - Absorption between 150 nm to 250 nm
  - e between 100 and 3000 L cm^{-1} mol^{-1}
  - Shifts to shorter wavelengths with polar solvents
  - R-X, R-OH R-NH2

- **n->π* and π–>π***

  - Unsaturated Organic compounds, containing non-bonded electrons (O, N , S) and X
  - wavelengths 200 to 700 nm

    - **n->π*** low e (10 to 100),
    - Shorter wavelengths 200 - 400
      - Shorter wavelengths

    - **π–>π*** higher e (1000 to 10000) , 200- 260

      Longer wavelength as compared to **n->π***

Presentation of U V Spectra

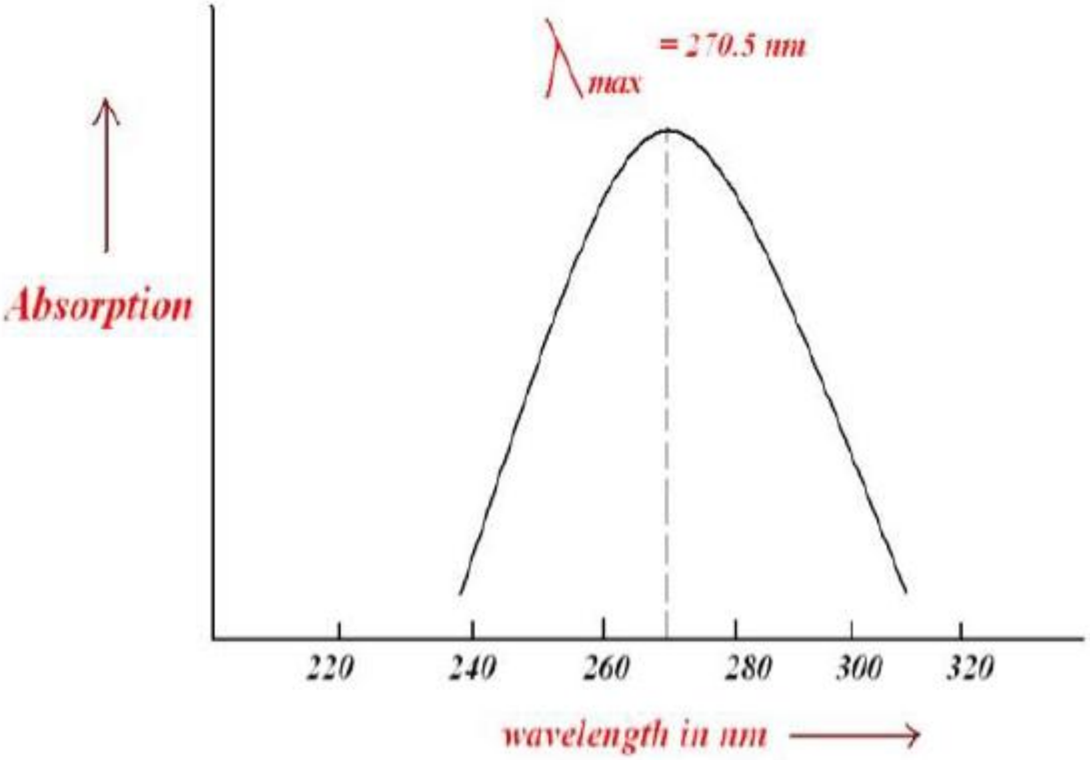


fig:- UV spectrum of acetone

TERMINOLOGIES

Chromophores

- The system containing electrons responsible for absorption is called chromophore. A ***chromophore*** is the part of a molecule responsible for its colour. The part (atom or group of atoms) of a molecular entity in which the electronic transition responsible for a given spectral band is approximately localized.
- The chromophore is a region in the molecule where the energy difference between two separate molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ***ground state*** into an ***excited state***.
- Originally, the term ***chromophore*** was applied to the system responsible for imparting colour to a compound. The term is derived from the *Greek* ***chromophoros***, or ***color carrier***.

- In azo dyes the aryl conjugated azo group (Ar-N = N-Ar) is clearly the principal chromophore. In nitro compounds the yellow color is carried by $-NO_2$, etc.

- The term has been retained within an extended interpretation to imply *any functional group that absorbs electromagnetic radiation, whether or not a 'colour' is thereby produced.* Thus, the carbonyl group is a chromophore in both ultraviolet and infrared terms, even though one isolated C=O group is insufficiently powerful to impart colour to a compound.

- An isolated carbonyl group, as in acetone, absorbs ultraviolet light around 280 nm. Important examples of organic chromophores are listed in **Table 1.**

Table 1: Simple Organic Chromophores

Chromophore	Wavelength (λ_{max}/nm)	Intensity ($\varepsilon_{max}/10^{-2} m^2\ mol^{-1}$)
C=C	165-175	14000
C≡C	170-175	10000
	195	2000
	223	150
C=O	160	18000
	185	5000
	280	15
$R\text{-}NO_2$	200	5000
	274	15
C≡N	165	5
C=C-C=C	217	20000
C=C-C=O	220	10000
	315	30
C=C-C≡C	220	7500
	230	7500
Benzene	184	60000
	204	7400
	255	204

Auxochrome

- ***Auxochrome*** is substituent on a chromophore which shifts the absorption towards longer wavelength. An ***auxochrome*** is a functional group of atoms attached to the chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of the absorption.
- An ***auxochrome*** enhances the color-imparting properties of a ***chromophore*** without being itself a ***chromophore***. The synergist effect of ***auxochromes*** is coupled with their ability to extend the conjugation of a chromophore by sharing of the nonbonding electrons.

- Substituents that increase the intensity of the absorption, and the wavelength, are the ***auxochromes*.** Typical ***auxochromes*** include methyl, hydroxyl, alkoxy, halogen, and amino groups.

- The attachment of substituent groups in place of hydrogen on a basic ***chromophore*** structure changes the position and intensity of an absorption band of the ***chromophore***. The substituent groups may not give rise to the absorption of the ultraviolet radiation themselves, but their presence modifies the absorption of the principal ***chromophore***. **Figure** 🟥 illustrates the terms.

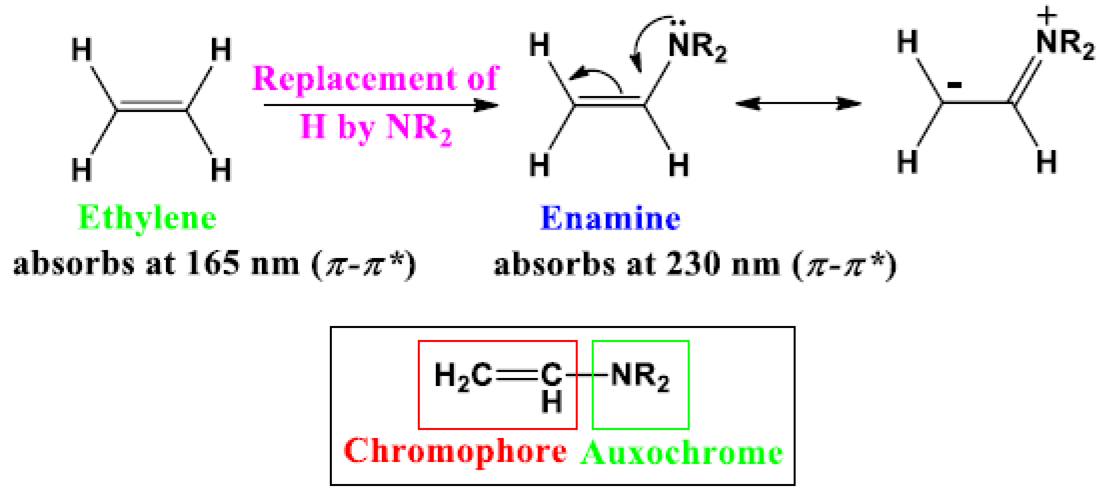


Figure 🟥 **Representation of chromophore and auxochrome**

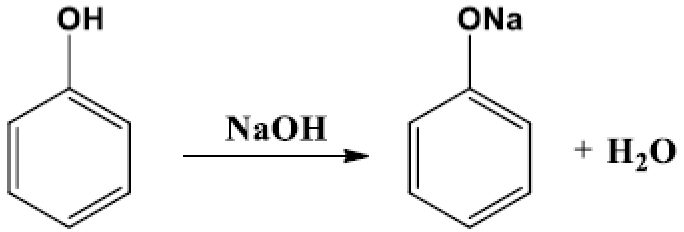
Bathochromic Shift or Red Shift

- The shift of a spectral band (absorption maxima) to longer wavelengths (lower frequencies) owing to the influence of substitution or a change in environment is called ***Bathochromic shift*** (from *Greek* ***bathys***, **“deep”**; and ***chrōma***, **“color”**).

- It is commonly referred to as a ***red shift***. This is because the red colour in the visible spectrum has a longer wavelength than most other colours.

- This shift towards longer wavelength is due to the presence of chromophore which increases conjugation. When this occurs, the energy separation between the ***ground*** and ***excited states*** is reduced and the system absorbs at longer wavelengths and with a greatly increased intensity.

- A shift to the longer wavelength of absorption (bathochromic shift) is observed when an aqueous solution of phenol is made alkaline. In alkaline medium phenol is deprotonated and forms the corresponding anion, the phenoxide ion. Here the negative charge on oxygen atom is delocalized over the benzene ring and consequently the anion gets stabilized more relative to the neutral molecule due to mesomeric effect **(Figure**).



Phenol
λ_{max} = 210 nm, ε_{max} = 6200
E_2-band, $\pi \longrightarrow \pi^*$

Sodium phenoxide
λ_{max} = 235 nm, ε_{max} = 9400
E_2-band, $\pi \longrightarrow \pi^*$

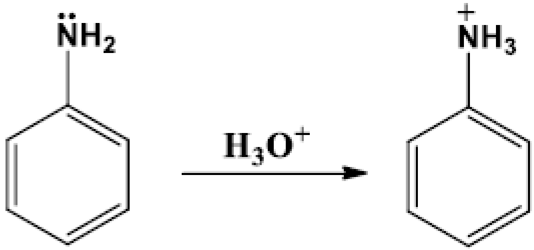
Figure **Bathochromic shift with Hyperchromic effect**

- When an aqueous solution of *p*-nitrophenol is made alkaline, the solution turns yellow/orange due to increased conjugation.

Hypsochromic Shift or Blue Shift

- The shift of a spectral band (absorption maxima) to higher frequency or shorter wavelength upon substitution or change in medium is called hypsochromic shift. This is due to the removal of conjugation.

- It is commonly referred to as blue shift. This is because the blue colour in the visible spectrum has a shorter wavelength than most other colours.



Aniline
$\lambda_{max} = 230$ nm, $\varepsilon_{max} = 8600$
E_2-band, $\pi \longrightarrow \pi^*$

Anilinium ion
$\lambda_{max} = 203$ nm, $\varepsilon_{max} = 7500$
E_2-band, $\pi \longrightarrow \pi^*$

Figure Hypsochromic shift with Hypochromic effect

Hyperchromic and Hypochromic Effects

- The increase in the intensity of a spectral band due to substituents or interactions with the molecular environment is described as hyperchromic effect. ***Hyperchromicity*** is the material's increasing ability to absorb light. It is the increase of absorbance (***optical density***) of a material.

- The decrease in the intensity of a spectral band due to substituents or interactions with the molecular environment is described as hypochromic effect. ***Hypochromicity*** describes a material's decreasing ability to absorb light. It is the decrease of absorbance (***optical density***) of a material.

- Different type of shifts and effects are shown in **Figure**

Representation of Different Shifts and Effects

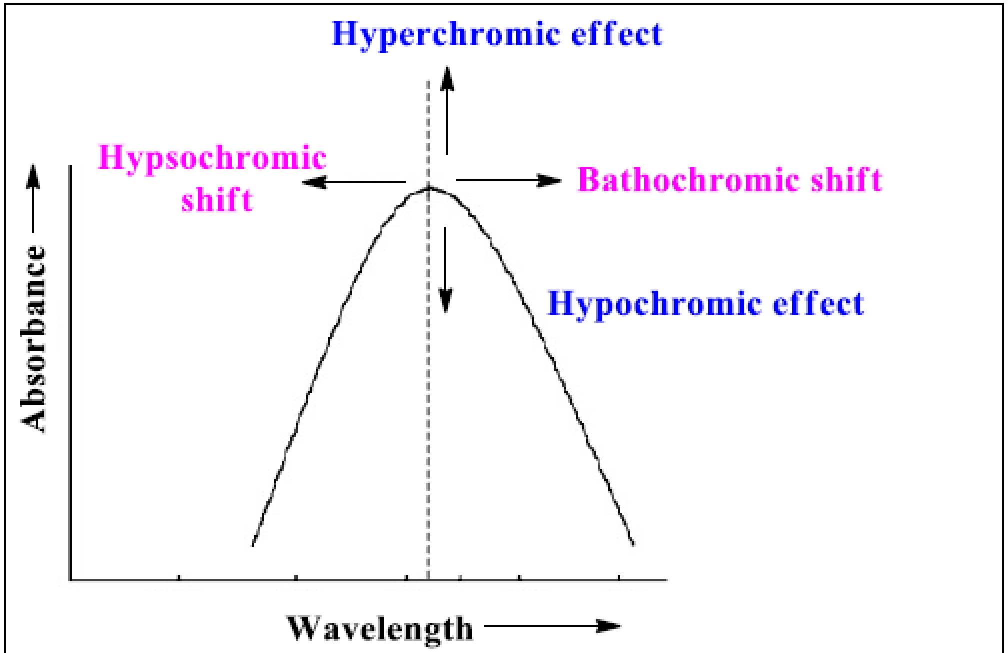
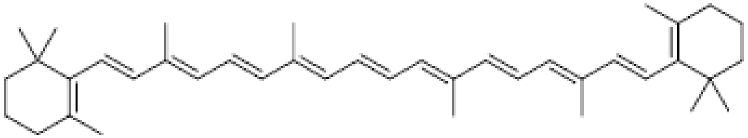
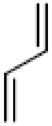
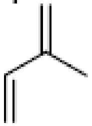
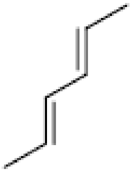
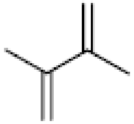
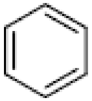
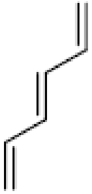


Figure 8: Representation of different shifts and effects

Conjugation And Ethylene Chromophores

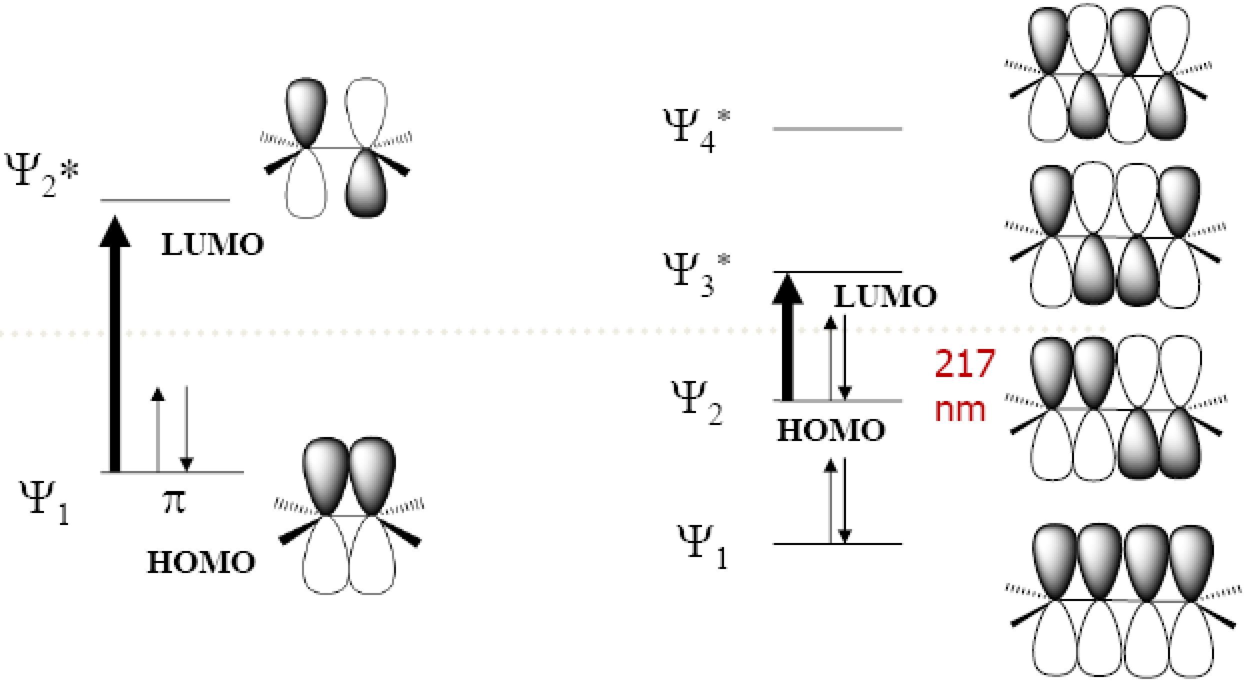
Ethylene absorbs at 175 nm. Presence of either chromophores or auxochromes gives bathochromic shift.

	λ_{max} nm	ε
	175	15,000
	217	21,000
	258	35,000
 β-carotene	465	125,000

							
Λ_{max} =	217	253	220	227	227	256	263 nm

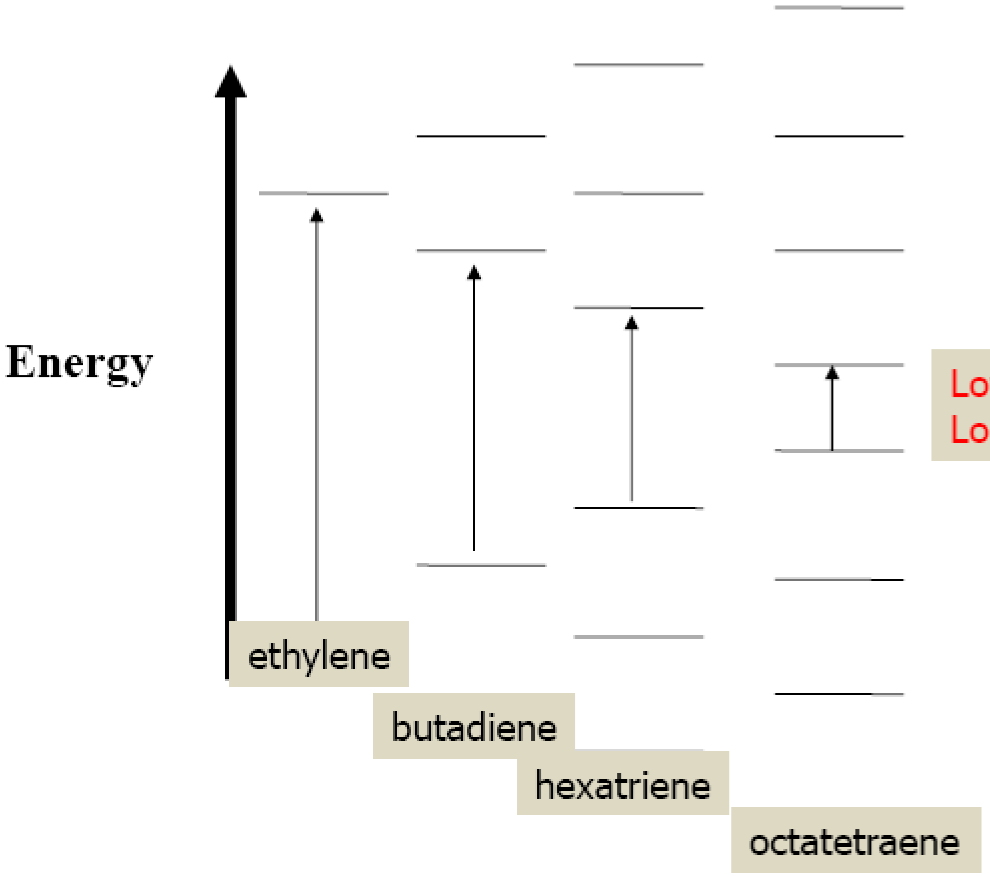
EXPLANATION OF HIGHER WAVE LENHTH FOR CONJUGATION

When we consider butadiene, we are now mixing 4 p orbitals giving 4 MOs of an as compared to ethylene which has only 2 M Os



DE for the HOMO → LUMO transition is reduced So, λ_{max} is increased.

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



Lower energy = Longer wavelengths

Application of Woodward's Rules for Calculation of λ_{max}

- In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure. In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as **Woodward-Fieser Rules**.

- It is used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution of chromophore. By this rule the expected value of absorption maxima (λ_{max}) of cyclic as well as acyclic dienes are calculated.

- Longer the conjugated system, greater is the wavelength of absorption maximum (λ_{max}).

- The intensity of absorption (ε_{max}) also increases with the increase of the ***chromophore***.

- Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***.

- The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br, etc., are added to the basic value to obtain λ_{max} for a particular compound.

- The presence of alkyl group on the double bond (alkyl substituent or Ring Residue) also causes Bathochromic shift. **Ring residue** is a C-C bond, not a part of the conjugated system but attached to any one of the carbon atoms of the conjugated polyene system.

Various Types of Double Bonds in Conjugation

1. **Alicyclic diene or dienes** contained in an open chain system, i.e., where basic unit is butadiene system.

2. **Homoannular conjugated double bonds** are the cyclic diene having conjugated double bonds present in the same ring. It is also called **Homodiene**.

3. **Heteroannular conjugaed double bonds** are the cyclic diene having conjugated double bonds which are present in the different rings.

4. **Exocyclic and Endocyclic conjugated double bonds:** Exocyclic double bond is a double bond, part of the conjugated system, formed by any carbon atom of any ring but present outside the ring. Endocyclic double bond is present inside the ring. The various types of double bonds are shown in **Figure 1**.

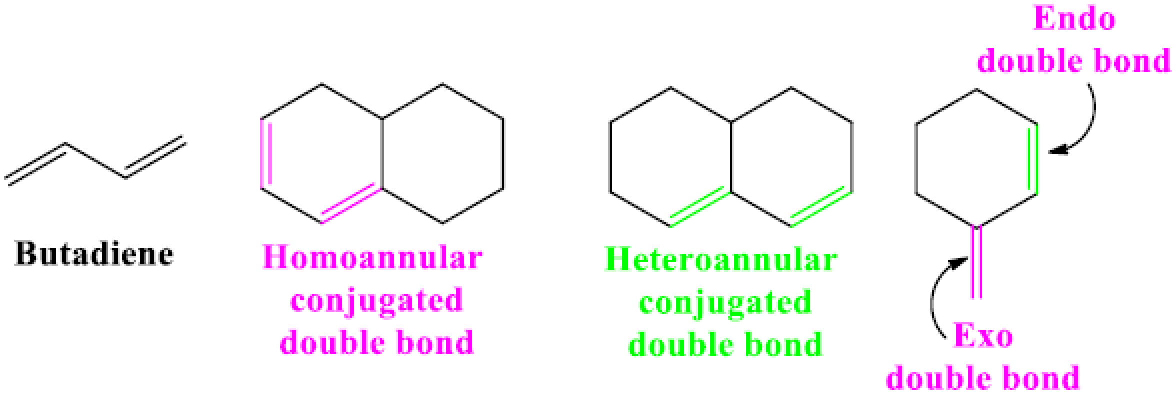
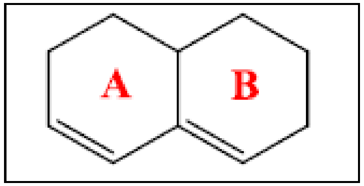
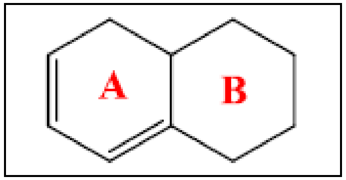


Figure 1: Types of conjugared double bonds



- Here Ring A has one exocyclic and one endocyclic double bond. Ring B has one endocyclic double bond, but no exocyclic double bond.

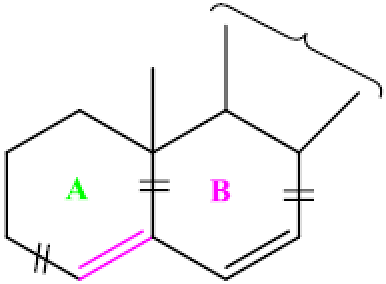


- Here Ring A has two endocyclic double bonds, but no exocyclic double bond. Ring B has one exocyclic double bond, but no endocyclic double bond.

Group Contribution

Base Value			
(i)		Value assigned for parent heteroannular or open chain diene	214 nm (or 217 nm)
(ii)		Value assigned for parent homoannular diene	253 nm
(iii)		Increment for	
	(a)	Each alkyl substituents or Ring Residue	5 nm
	(b)	The exocyclic nature of any double bond	5 nm
	(c)	A double bond extending conjugation	30 nm
		Increment of Auxochromes	
	(i)	- OAc	0 nm
	(ii)	- OR	6 nm
	(iii)	- SR	30 nm
	(iv)	- NR_2	60 nm
	(v)	- Cl, - Br	5 nm

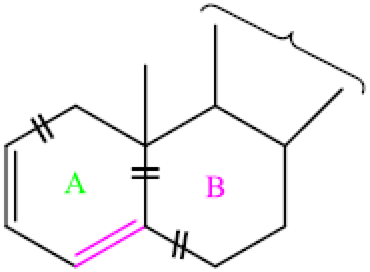
1.



exo d. b.
w. r. to Ring B

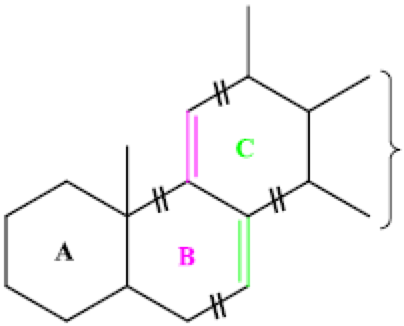
	nm
Parent diene (Heteroannular)	214
Ring residue x 3 (5 nm x 3)	15
Exocyclic double bond x 1	5
Total	234
Observed	235

2.



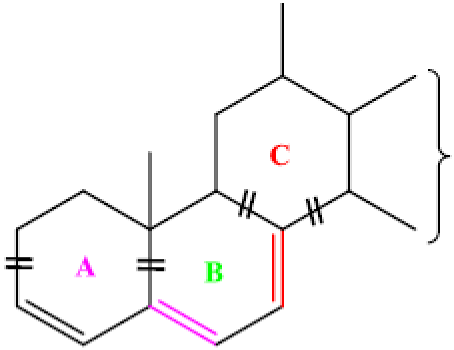
	nm
Parent diene (Homoannular)	253
Ring residue x 3 (5 nm x 3)	15
Exocyclic double bond x 1	5
Total	273
Observed	275

3.



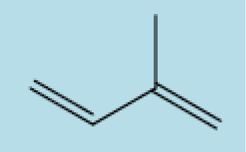
	nm
Parent diene (Heteroannular)	214
Ring residue x 4	20
Exocyclic double bond x 2	10
Total	244
Observed	245

4.

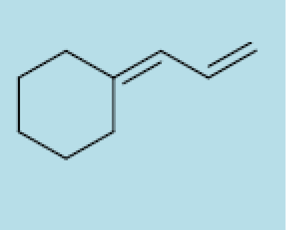


Observed λ_{max} = 315 nm

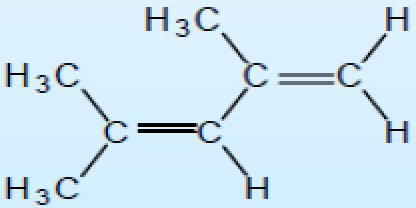
	nm
Parent diene (Homoannular, Ring B)	253
Ring residue x 4	20
Exocyclic double bond x 2	10
Double bond extending conjugation	30
Total	313



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



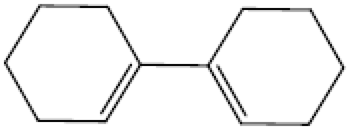
Allylidenecyclohexane
- acyclic butadiene = **217 nm**
one exocyclic C=C **+ 5 nm**
2 alkyl subs. **+10 nm**
232 nm
Experimental value **237 nm**



transoid: **214 nm**
alkyl groups: **3 × 5 = 15**
229nm
observed: 228 **nm**

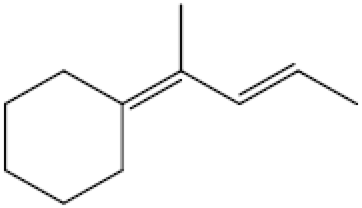
Calculate λ_{max} for the following Compounds

(i)



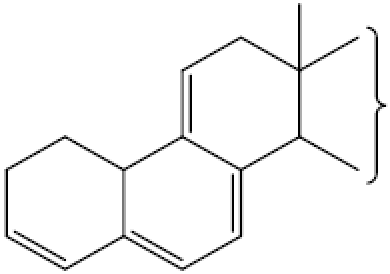
Calculated = 234 nm

(ii)



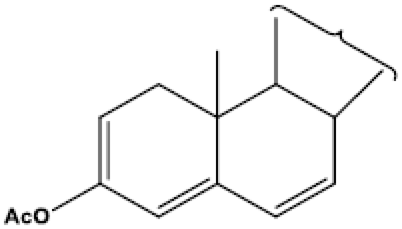
Calculated = 242 nm

(iii)



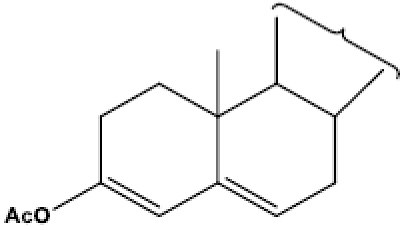
Calculated = 353 nm

(iv)



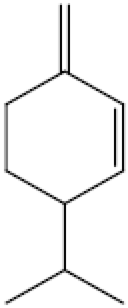
Calculated = 303 nm

(v)



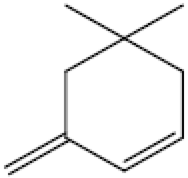
Calculated = 234 nm

(vi)



Calculated = 229 nm

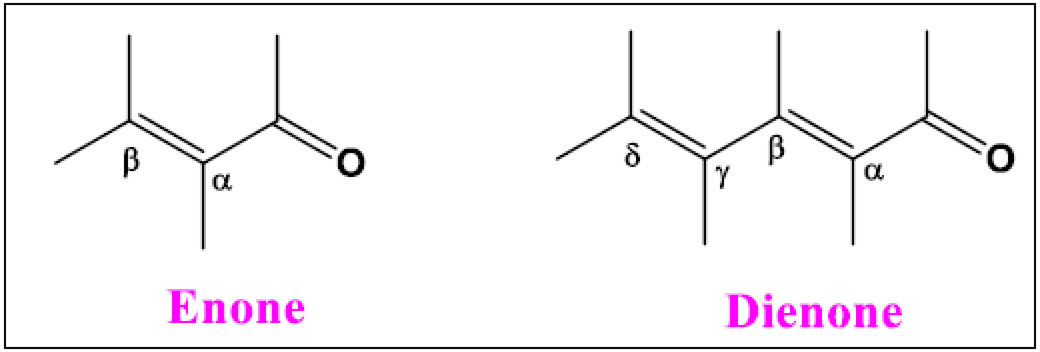
(vii)



Calculated = 229 nm

Woodward's Enone and Dienone Rules for Calculation of λ_{max}

- Woodward and Fieser framed certain empirical rules for calculating the absorption maximum for an **α,β-unsaturated carbonyl** compounds. The rules were later modified by Scott.



Group Contribution

Base Value		
(i)	Value assigned for Acyclic α,β-unsaturated ketone	215 nm
(ii)	Value assigned for 6-membered cyclic α,β-unsaturated ketone	215 nm
(iii)	Value assigned for 5-membered cyclic α,β-unsaturated ketone	202 nm
(iv)	Value assigned for 5-membered cyclic α,β-unsaturated ketone with exocyclic double bond	215 nm
(v)	Value assigned for α,β-unsaturated aldehyde	210 nm

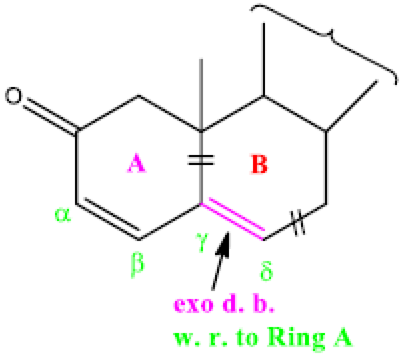
Increment for				
(i)	A double bond extending conjugation	30 nm		
(ii)	The exocyclic nature of any double bond	5 nm		
(iii)	The Homodiene component	39 nm		
(iv)	Alkyl group or Ring residue	α	β	γ or higher
		10	12	18

Increment of Auxochromes

Group	α	β	γ	δ
-OH	35	30	30	50
-OR	35	30	17	31
-OAc	6	6	6	6
-SR	-	85	-	-
-NH$_2$, -NHR, -NR$_2$	-	95	-	-
-Cl	15	12	12	12
-Br	25	30	25	25

Calculation of λ_{max} for Conjugated Carbonyl Compounds

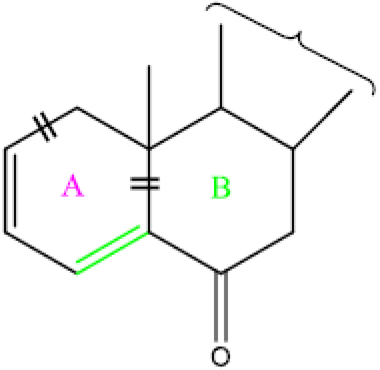
1.



exo d. b.
w. r. to Ring A

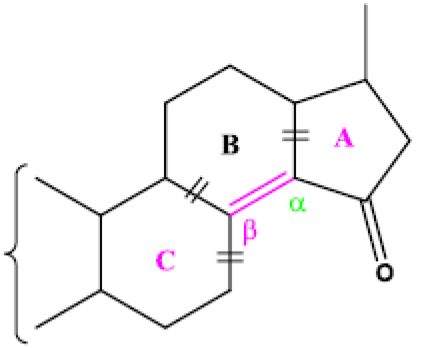
	nm
Basic value for *α*,β-unsaturated ketone	215
Double bond extending conjugation	30
Ring Residues, *γ*-substitution δ-substitution	18 18
Exocyclic double bond	5
Total	286

2.



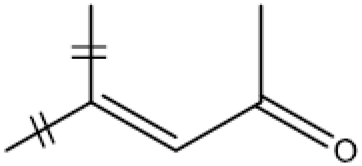
	nm
Basic value for *α*,β-unsaturated ketone	215
Double bond extending conjugation	30
Ring Residues, *α*-substitution δ-substitution	10 18
Exocyclic double bond	5
Presence of Homodiene component	39
Total	317

3.



	nm
Basic value for 5-membered cyclic α,β-unsaturated Ketone *with exo*cyclic double bond	215
Ring Residues, α-substitution β-substitution x 2 (12 x 2 nm)	10 24
Exocyclic double bond x 2 (5 x 2 nm)	10
Total	259

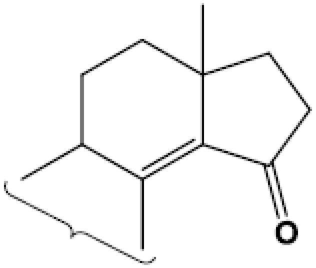
4.



	nm
Basic value for α,β-unsaturated ketone	215
Ring Residues, β-substitution x 2 (12 x 2 nm)	24
Total	239

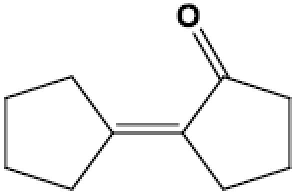
Calculate λ_{max} for the following Compounds

(i)



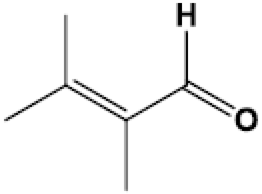
Calculated = 259 nm

(ii)



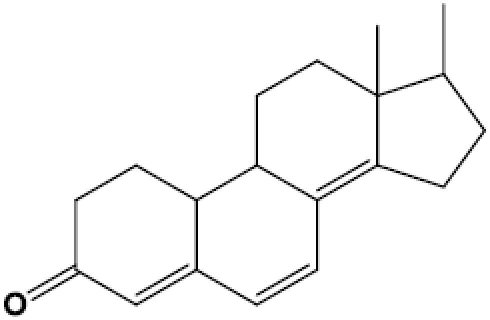
Calculated = 259 nm

(iii)



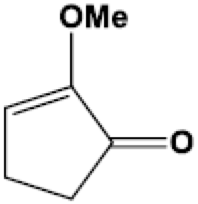
Calculated = 242 nm

(iv)



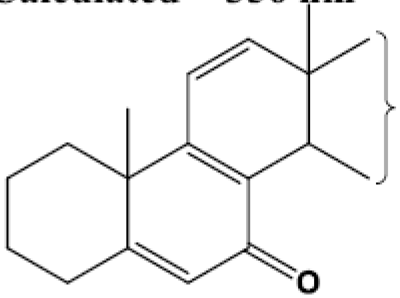
Calculated = 356 nm

(v)



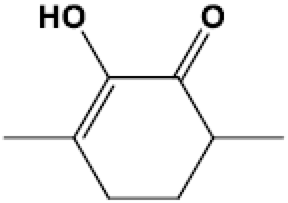
Calculated = 249 nm

(vi)



Calculated = 324 nm

(vii)



Calculated = 274 nm

WOODWARD-FEISER RULE

*Woodward **(1914) :** gave certain rules for correlate with molecular structures with λ_{max} .

*Scott-Feiser**(1959)**:modified rule with more experimental data , the modified rule is known as Woodward-Feiser rule.

*A more modern interpretation was compiled by Rao in 1975 – (C.N.R. Rao, Ultraviolet and Visible Spectroscopy, 3rd Ed., Butterworths, London, 1975)

It is used to correlate the λ_{max} of for a given structure by relating position and degree of substitution of chromophores.

Woodward-Fieser Rules for Conjugated acyclic Dienes

Woodward had predicted an empirical rule for calculating λ_{max} of conjugated acyclic and cyclic dienes based on base value and contribution of different substituent. The equation is:

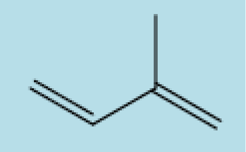
λ_{max} = **Base value + ∑ Substituent's contribution + ∑ Other contribution**

Base value : Take a base value of **214/217** for any conjugated. diene or triene

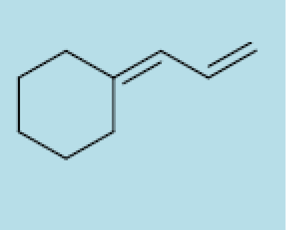
Incrementals: Add the following to the base value

Group	**Increment**
Extended conjugation	+30
Each exo-cyclic C=C	+5
Phenyl group	+60
Auxochromes:	
Alkyl	+5
-$OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
-NR_2	+60

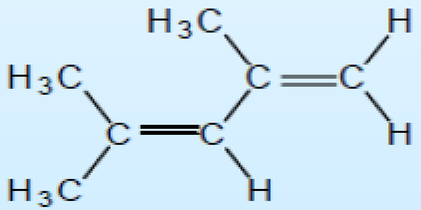
Examples:



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**

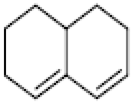


transoid: **214 nm**
alkyl groups: **3 × 5 = 15**
229nm
observed: **228 nm**

Woodward-Fieser Rules – Cyclic Dienes

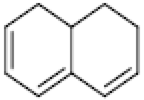
There are two major types of cyclic dienes, with two different base values

Heteroannular (transoid):

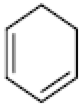


base λ_{max} = 214

Homoannular (cisoid):



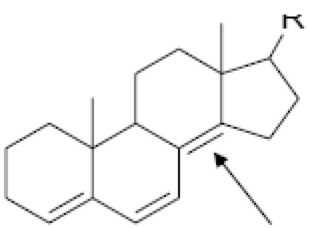
base λ_{max} = 253



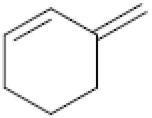
base λ_{max} = 253

Groups	**Increment**
Extended conjugation	+30
Pheny group	+60
Each exo-cyclic C=C	+5
Alkyl / ring residue	+5
-$OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
-NR_2	+60
Additional homoannular	+39

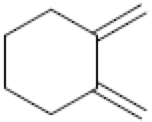
Be careful with your assignments – three common errors:



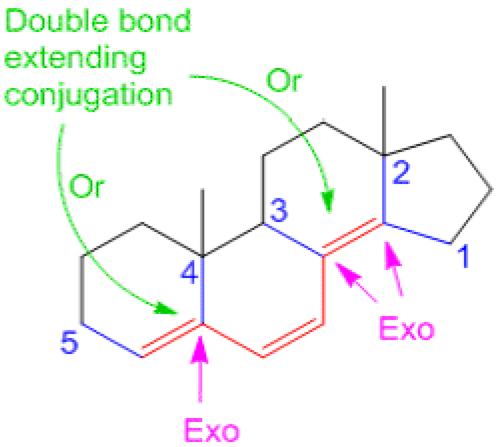
This compound has three exocyclic double bonds; the indicated bond is exocyclic to two rings

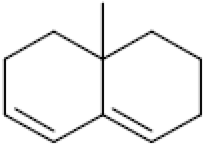


This is not a heteroannular diene; you would use the base value for an acyclic diene

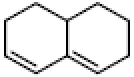


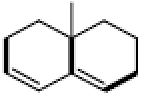
Likewise, this is not a homooannular diene; you would use the base value for an acyclic diene



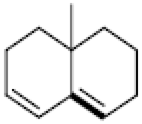


1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene

heteroannular diene =  214 nm



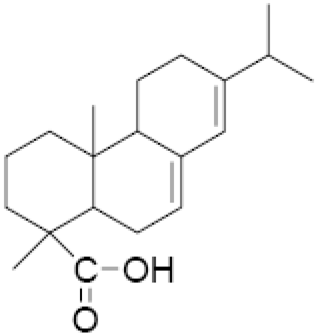
3 alkyl subs. (3 x 5) +15 nm



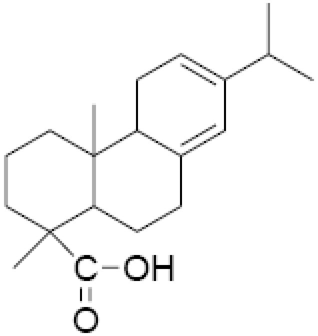
1 exo C=C + 5 nm

234 nm

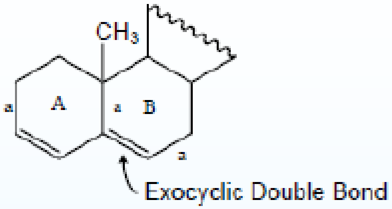
Experimental value 235 nm



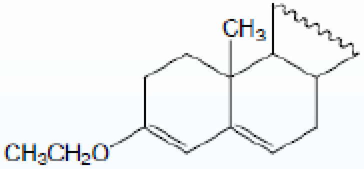
heteroannular diene =	214 nm
1 alkyl subs. (1 x 5)	+ 05
3 RR	+ 15
1 exo C=C	<u>+0 5 nm</u>
	239 nm



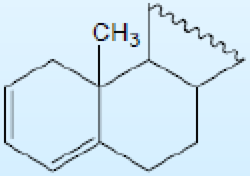
homoannular diene =	253 nm
1alkyl subs. (1x 5)	+05nm
3 RR	+15nm
1 exo C=C	<u>+ 5 nm</u>
	278 nm



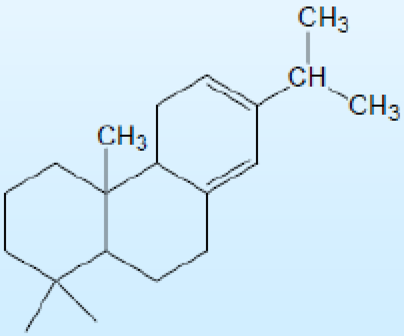
transoid: 214 nm
ring residues: 3 × 5 = 15
exocyclic double bond: 5
234 nm
observed: 235 nm



240 nm
observed: 241 nm

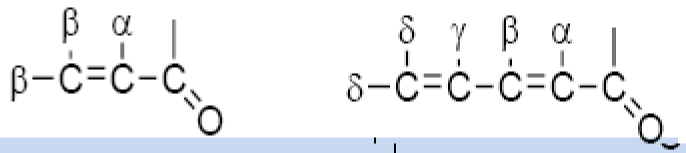


cisoid: 253 nm
ring residues: 3 × 5 = 15
exocyclic double bond: 5
273 nm
observed: 275 nm



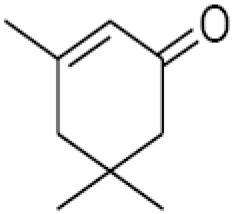
278 nm
observed: 275 nm

Woodward-Fieser Rules - Enones



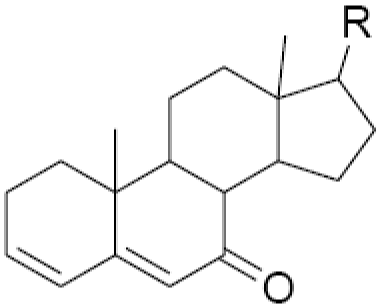
Group		Increment
6-membered ring or acyclic enone		Base 215 nm
5-membered ring parent enone		Base 202 nm
Acyclic dienone		Base 245 nm
Aldehyde,Ester & Acid		Base 208 nm
Substituents:		
Double bond extending conjugation		30
Phenyl group	β	60
Alkyl group or ring residue	α, β, γ and higher	10, 12, 18
-OH	α, β, γ and higher	35, 30, 18
-OR	α, β, γ, δ	35, 30, 17, 31
-O(C=O)R	α, β, δ	6
-Cl	α, β	15, 12
-Br	α, β	25, 30
$-NR_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39

Examples



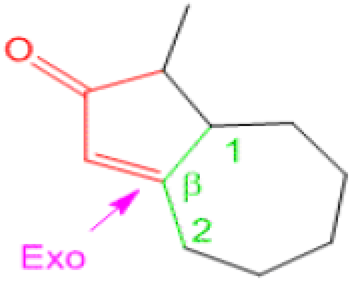
cyclic enone =		215 nm
2 x β- alkyl subs.	(2 x 12)	+24 nm
		239 nm

Experimental value **238 nm**

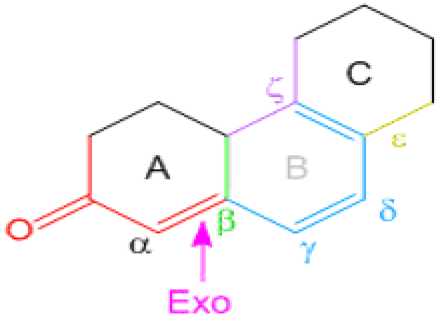


cyclic enone =	215 nm
extended conj.	+30 nm
β-ring residue	+12 nm
δ-ring residue	+18 nm
exocyclic double bond	+ 5 nm
	280 nm

Experimental 280 nm

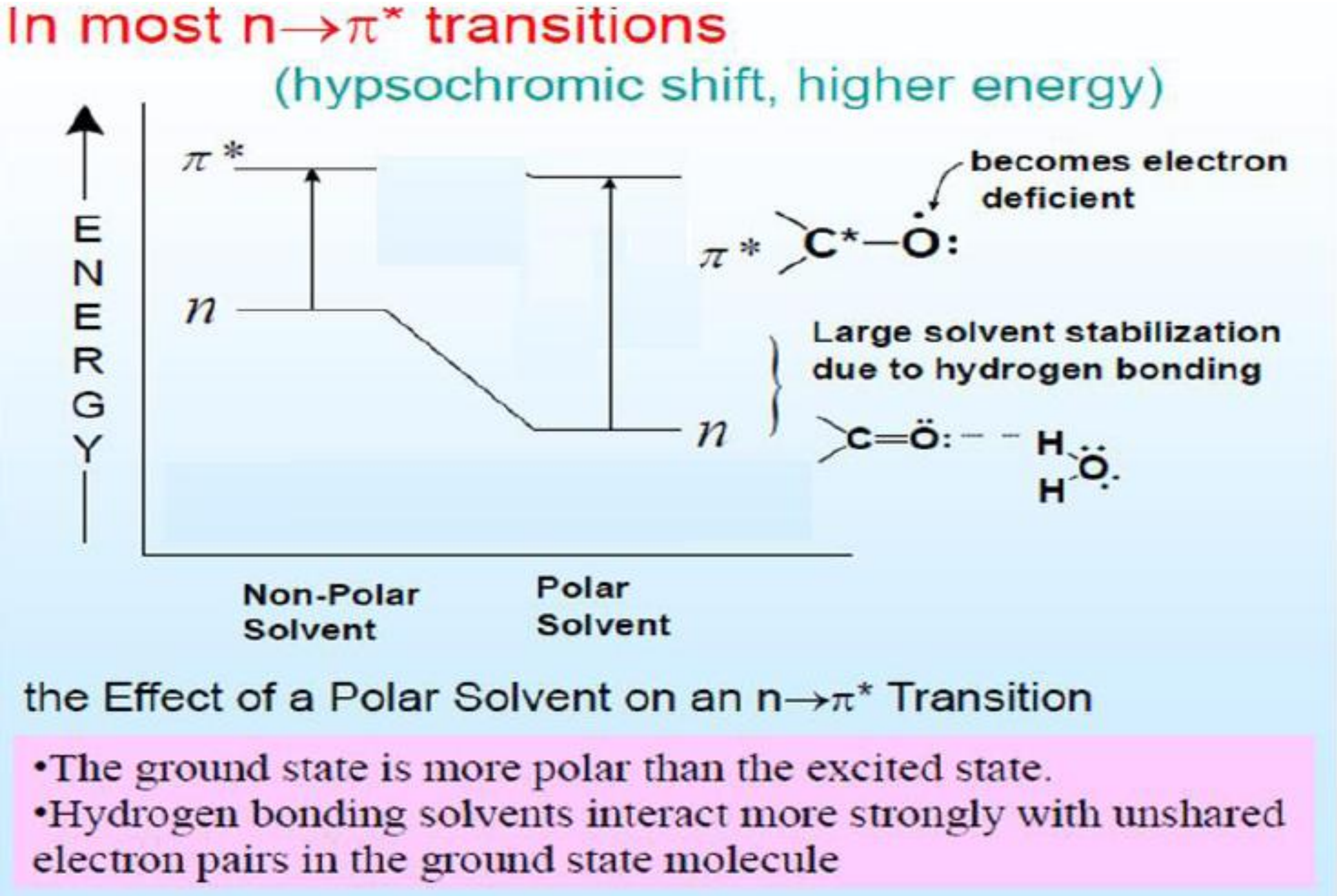


Base - cyclopentenone	+ 202 nm
Substituents at α-position	0
Substituents at β-position- 2 Ring Residue	2 x 12= + 24 nm
Other Effects- 1 Exocyclic Double Bond	+ 5 nm
Calculated λ_{max}	**231 nm**
Observed λ_{max}	229 nm



Base - cyclohexenone	+ 215 nm
Substituents at α-position:	0
Substituents at β-position: 1 Ring Residue	+ 12 nm
Substituents at γ-position	0
Substituents at δ-position:	0
Substituents at ε-position: 1 Ring Residue	+ 18 nm
Substituents at ζ-position: 2 Ring Residue	2 x 18 = + 36 nm
Other Effects: 2 Double bonds extending conjugation Homoannular Diene system in ring B 1 Exocyclic double bond	2 x 30 = + 60 nm + 35 nm +5
Calculated λ_{max}	**381 nm**
Observed λ_{max}	388 nm

Effect of solvent



In most n→π* transitions

(hypsochromic shift, higher energy)

becomes electron deficient

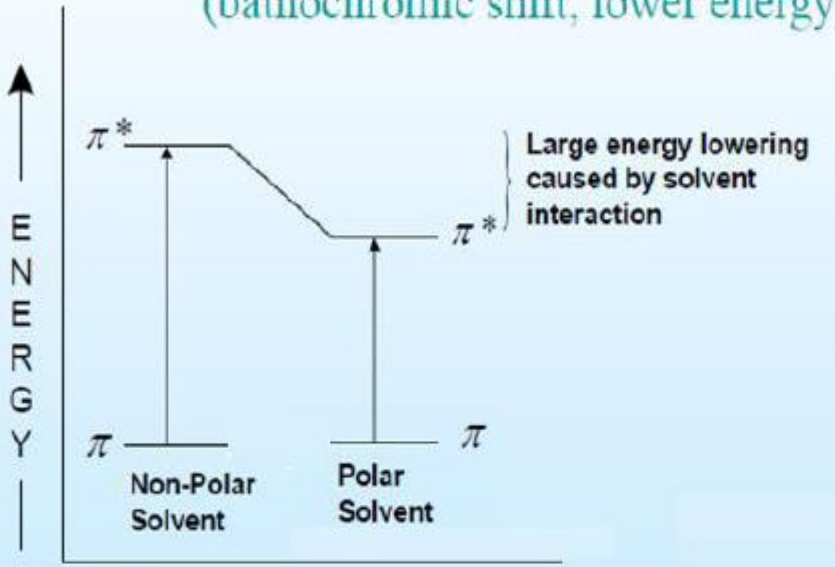
Large solvent stabilization due to hydrogen bonding

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

In most $\pi \rightarrow \pi^*$ transitions

(bathochromic shift, lower energy)



the Effect of a Polar Solvent on a Transition