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L1

Principles of Molecular Spectroscopy

To Understand Spectroscopy We Must Understand Electromagnetic Radiation

Electromagnetic radiation, of which visible light is but one example, has the properties of both **particles and waves**. The particles are called **photons**, and each possesses an amount of energy referred to as a **quantum**. In 1900, the German physicist Max Planck proposed that the energy of a photon (E) is directly proportional to its **frequency** (ν).

$$E = h\nu$$

The SI units of frequency are reciprocal seconds (s^{-1}), given the name ***hertz*** and the symbol Hz in honor of the nineteenth-century physicist Heinrich R. Hertz. The constant of proportionality h is called **Planck's constant** and has the value $h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$

Electromagnetic radiation travels at the speed of light ($c = 3.0 \times 10^8$ /s), which is equal to the product of its frequency ν and its wavelength λ :

$$c = \nu\lambda$$

The range of photon energies is called the *electromagnetic spectrum* and is shown in Figure 1 .

Visible light occupies a very small region of the **electromagnetic spectrum**.

It is characterized by wavelengths of 400 nm (violet) to 800 nm (red). When examining Figure 1 be sure to keep the following two relationships in mind:

- 1. *Frequency is inversely proportional to wavelength* ; the greater the frequency, the shorter the wavelength.**
- 2. *Energy is directly proportional to frequency* ; electromagnetic radiation of higher frequency possesses more energy than radiation of lower frequency.**

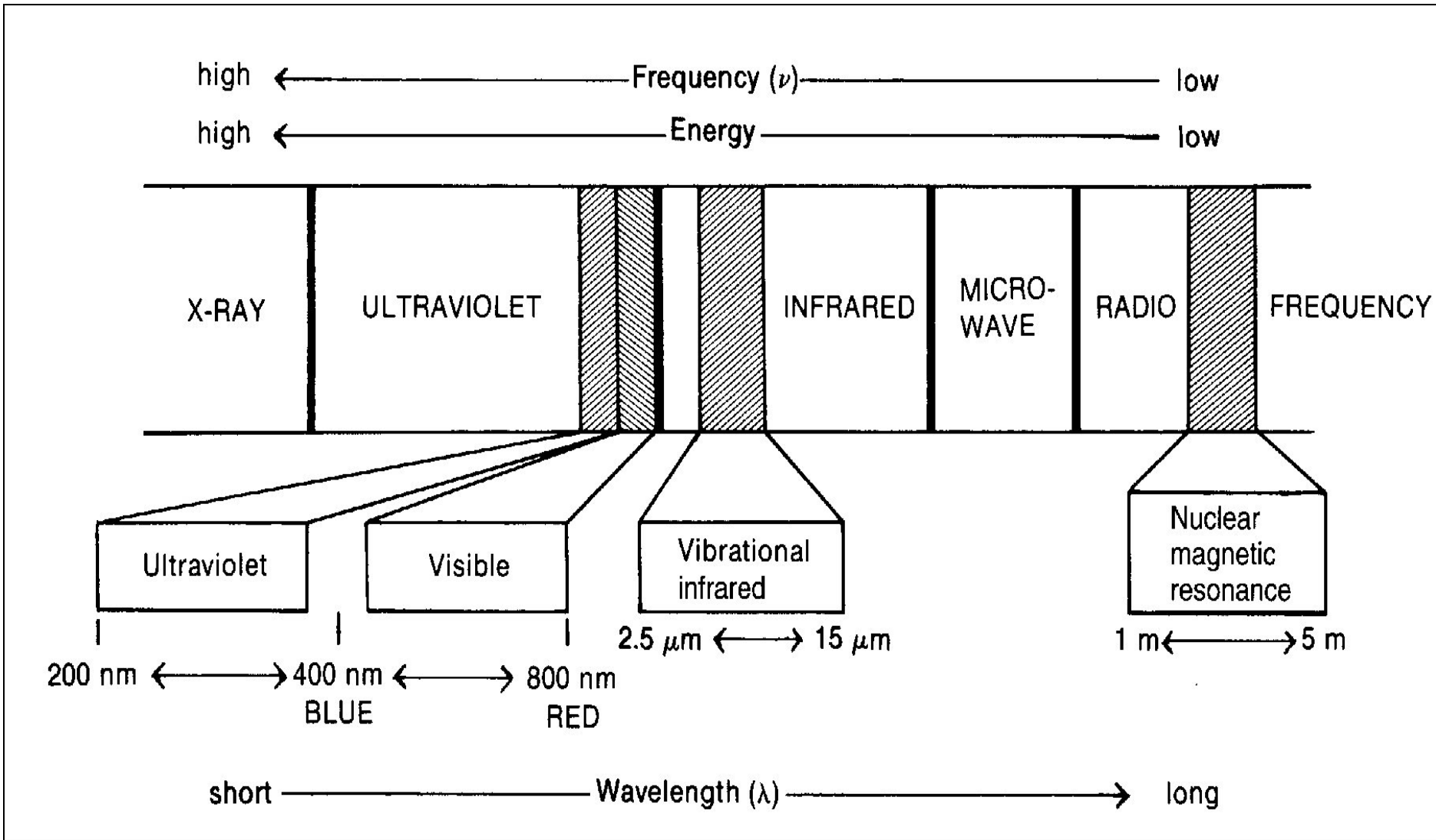
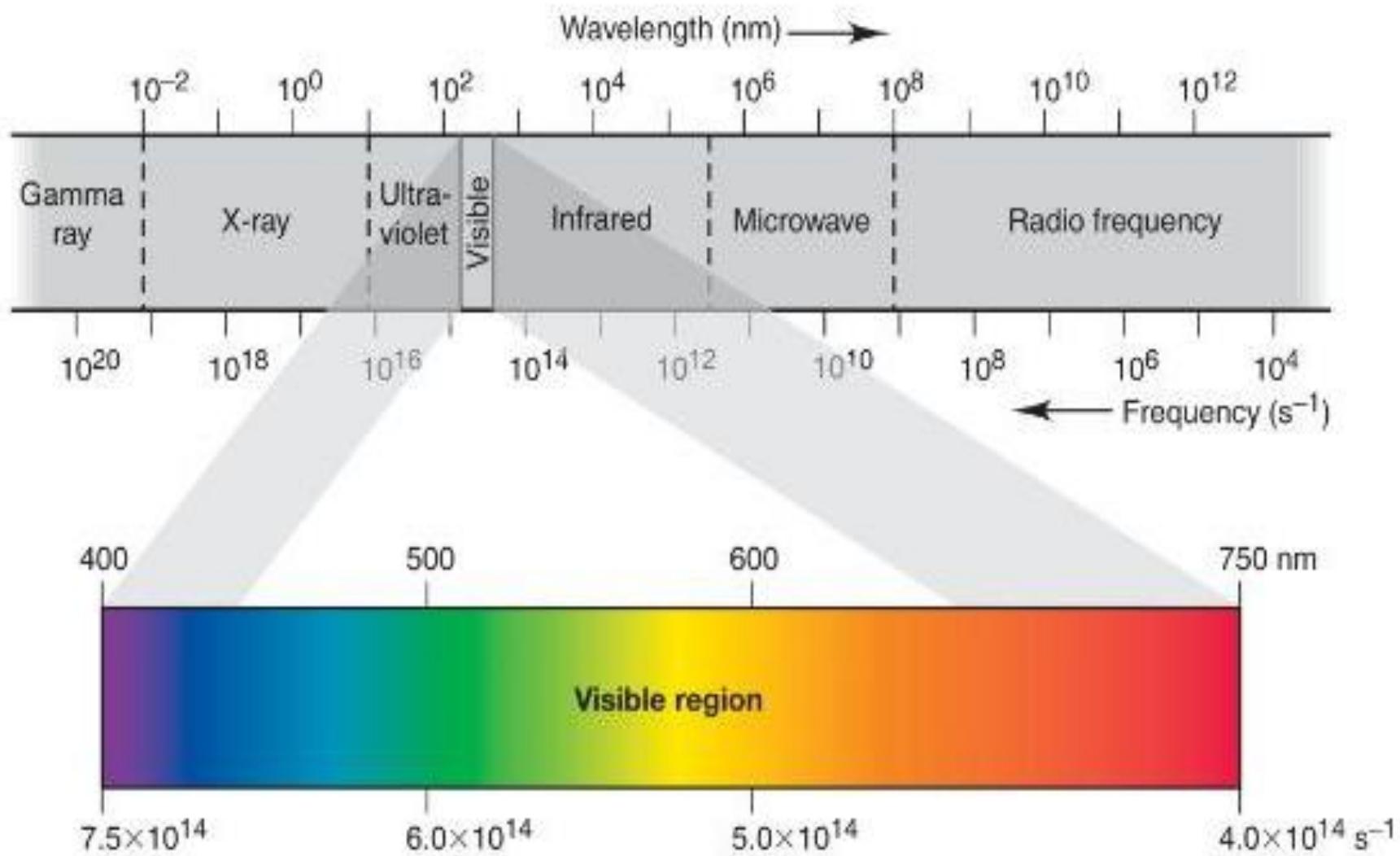


Figure 1: electromagnetic spectrum



Gamma rays and X-rays are streams of very high energy photons. Radio waves are of relatively low energy. Ultraviolet radiation is of higher energy than the violet end of visible light. Infrared radiation is of lower energy than the red end of visible light. When a molecule is exposed to electromagnetic radiation, it may absorb a photon, increasing its energy by an amount equal to the energy of the photon. Molecules are highly selective with respect to the frequencies they absorb. Only photons of certain specific frequencies are absorbed by a molecule. The particular photon energies absorbed by a molecule depend on molecular structure and are measured with instruments called spectrometers. The data obtained are very sensitive indicators of molecular structure.

Principles of Molecular Spectroscopy: Quantized Energy States

What determines whether electromagnetic radiation is absorbed by a molecule? The most important requirement is that the energy of the photon must equal the energy difference between two states, such as two nuclear spin states (NMR), two vibrational states (IR), or two electronic states (UV-VIS).

Qualitative tests and chemical degradation have given way to instrumental methods of structure determination. The main methods and the structural clues they provide are:

■ ■ **Nuclear magnetic resonance (NMR) spectroscopy,**

which tells us about the carbon skeleton and the environments of the hydrogens attached to it.

■ ■ **Infrared (IR) spectroscopy,** which reveals the presence or signals the absence of key functional groups.

■ ■ **Ultraviolet-visible (UV-VIS) spectroscopy**, which probes the electron distribution, especially in molecules that have conjugated π -electron systems.

■ ■ **Mass spectrometry (MS)**, which gives the molecular weight and formula, of both the molecule itself and various structural units within it.

In physics, the term for this is *resonance* the transfer of energy between two objects that occurs when their frequencies are matched. In molecular spectroscopy, we are concerned with the transfer of energy from a photon to a molecule.

Consider, for example, two energy states of a molecule designated E_1 and E_2 in Figure.2.

-UV light can be absorbed by molecules to excite higher energy (most loosely bound) electrons from lower energy states to higher states.

-Such transitions can be studied extensively to understand the binding energy of the corresponding electrons undergoing transition.

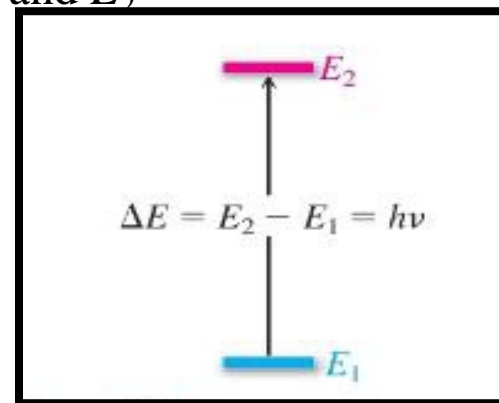


fig 2:Two energy states of a molecule. Absorption of energy equal to $E_2 - E_1$ excites a molecule from its lower energy state to the next higher state.

The energy difference between them is $E_2 - E_1$, or ΔE ., certain energies are possible for electronic, vibrational, and nuclear spin states.

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

These energy states are said to be quantized.

More of the molecules exist in the lower-energy state E_1 than in the higher-energy state E_2 .

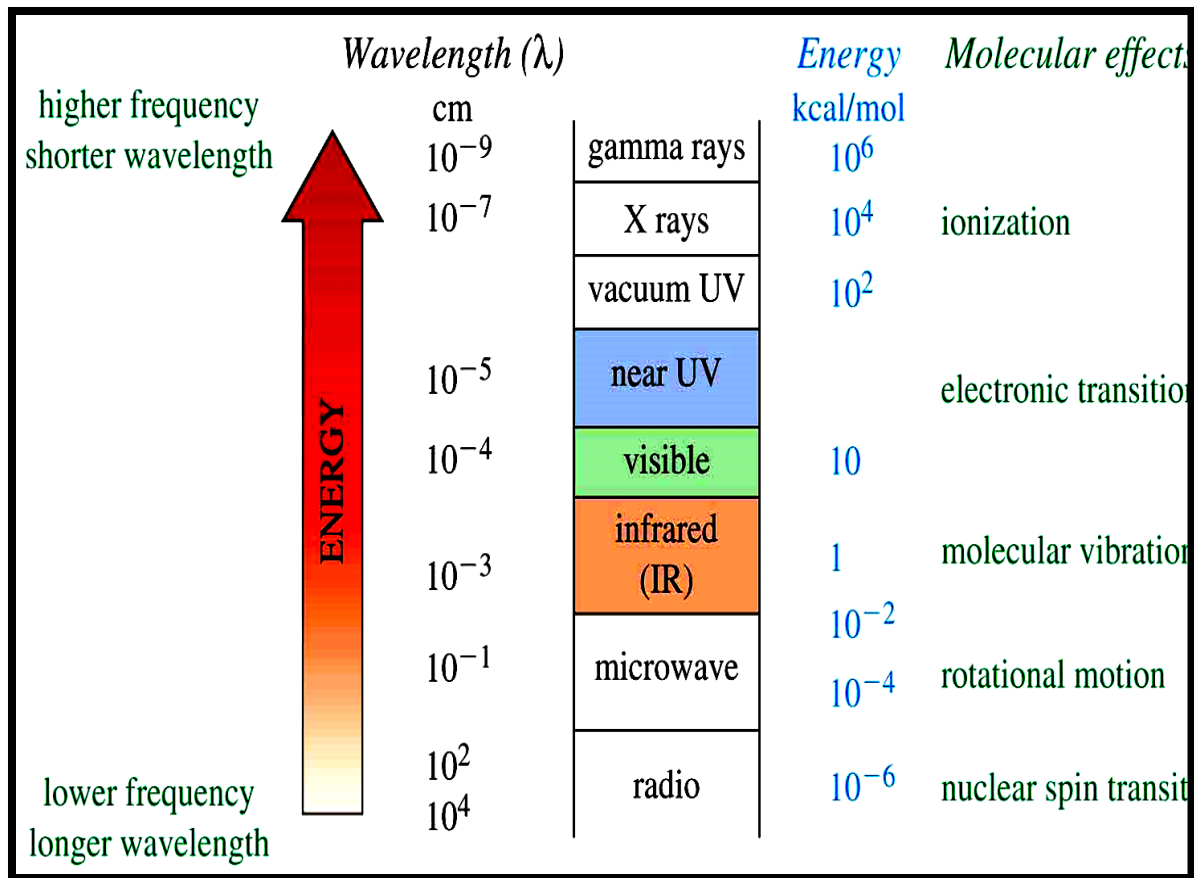
Excitation of a molecule from a lower state to a higher one requires the addition of an increment of energy equal to ΔE . Thus, when electromagnetic radiation strikes a molecule, only the frequency with energy equal to ΔE is absorbed.

Spectrometers: are designed to measure the absorption of electromagnetic radiation by a sample. Basically, a spectrometer consists of a source of radiation, a compartment containing the sample through which the radiation passes, and a detector. The frequency of radiation is continuously varied, and its intensity at the detector is compared with that at the source. When the frequency is reached at which the sample absorbs radiation, the detector senses a decrease in intensity. The relation between frequency and absorption is plotted as a **spectrum,**

Which consists of a series of peaks at characteristic frequencies. Its interpretation can furnish structural information.

Each type of spectroscopy developed independently of the others, and so the data format is different for each one. An NMR spectrum looks different from an IR spectrum, and both look different from a UV-VIS spectrum. With this as background, we will now discuss spectroscopic techniques individually. NMR, IR, and UV-VIS spectroscopy provide complementary information, and all are useful. Among them, NMR provides the information that is most directly related to molecular structure and is the one we'll examine first.

- Ultraviolet: 190~400nm
- Violet: 400 - 420 nm
- Indigo: 420 - 440 nm
- Blue: 440 - 490 nm
- Green: 490 - 570 nm
- Yellow: 570 - 585 nm
- Orange: 585 - 620 nm
- Red: 620 - 780 nm



Internal Energy of Molecules

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{nucl}}$$

E elec: electronic transitions (UV, X-ray) , **E vib:** vibrational transitions (Infrared)

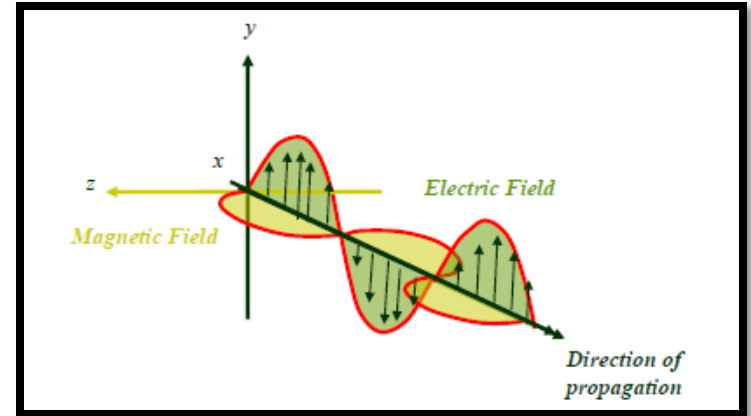
E rot: rotational transitions (Microwave) **E nucl:** nucleus spin (nuclear magnetic resonance) or (MRI: magnetic resonance imaging)

WAVE PROPERTIES.

- EM radiation is conveniently modeled as waves consisting of perpendicularly oscillating electric and magnetic fields , as shown below.

At 90° to the direction of propagation is an oscillation in the **ELECTRIC FIELD**.

At 90° to the direction of propagation and 90° from the electric field oscillation (orthogonal) is the a genetic filed oscillation.



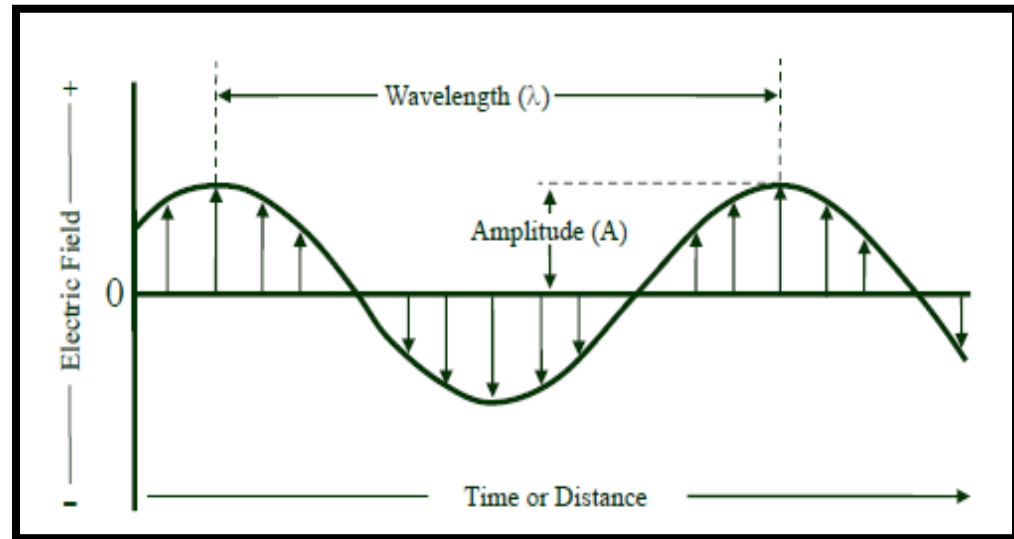
Wave parameters.

We Use Symbols to Designate the Various Properties of Waves .

λ is the wavelength of the waves .

ν is the frequency of the waves .

c is the speed of light .



Period(p)—the time required for one cycle to pass a fixed point in space.

Frequency(ν)—the number of cycles which pass a fixed point in space per second.

Amplitude(A)—The maximum length of the electric vector in the wave (Maximum height of a wave).

Wavelength(λ) The distance between two identical adjacent points in a wave (usually maxima or minima).

Wavenumber $\bar{\nu}$ The number of waves per cm in units of cm^{-1} .

The Spectroscopic Process .

- In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation .
- If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed.
- The remaining UV light passes through the sample and is observed.
- From this residual radiation a spectrum is obtained with “gaps” at these discrete energies —this is called an absorption spectrum.

The UV radiation region extends from 10 nm to 400 nm .

- the visible radiation region extends from 400 nm to 800 nm.
- Near UV Region: 200 nm to 400 nm.
- Far UV Region: below 200nm.

INSTRUMENTATION

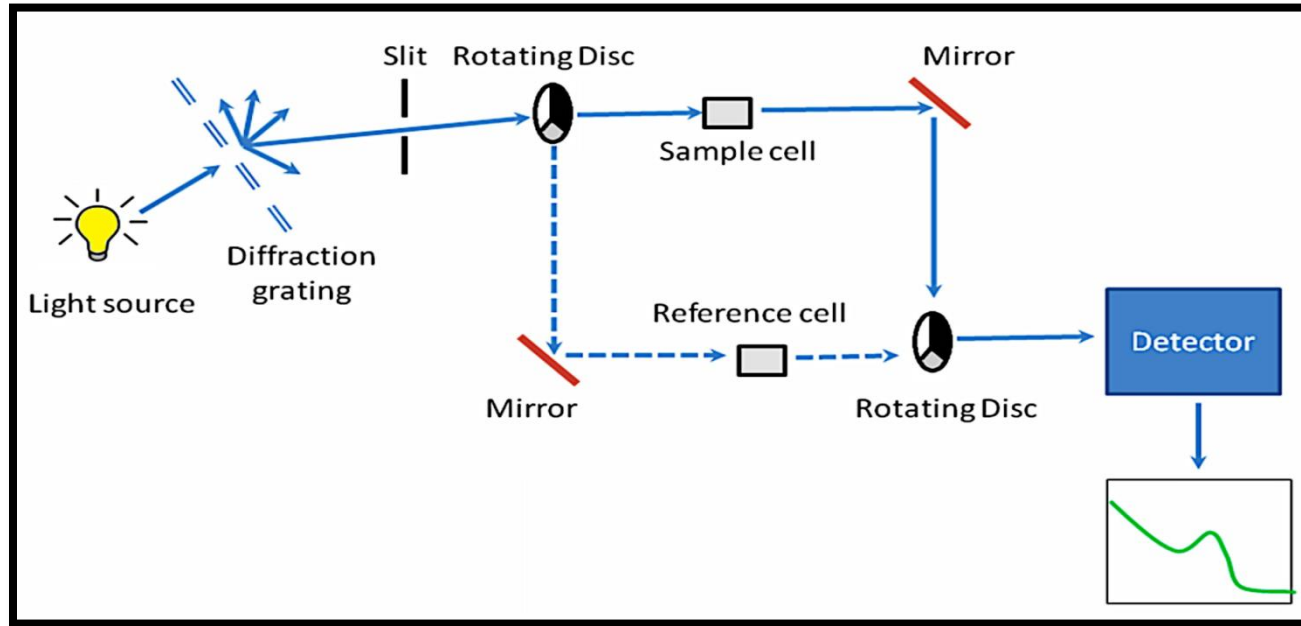
Components of spectrophotometer

1) **Source light** 2) **Monochromator** 3) **Sample compartment** 4) **Detector** 5) **Recorder**

Most spectrophotometers are **double-beam instruments**. The primary source of light is split into two beams, one of which passes through a cell containing the sample solution and the other of which passes through a cell containing the reference solvent.

The spectrophotometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution in the sample beam. Thus, effects owing to absorption of light by the solvent are

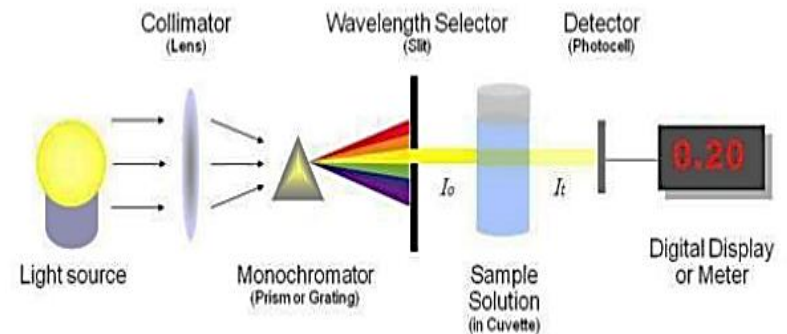
Double Beam UV Spectrometer



Two sources are required to scan the entire (to cover a range of 200-800 nm) UV-VIS band :

- **Deuterium lamp** – covers the UV – 200-330
- **Tungsten lamp** – covers 330-700 (for visible range)

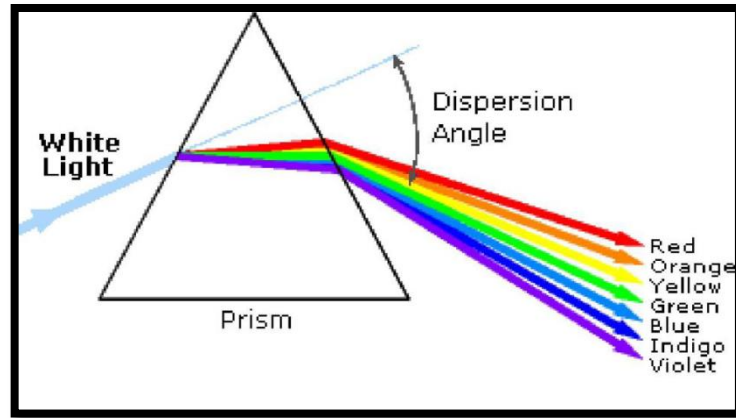
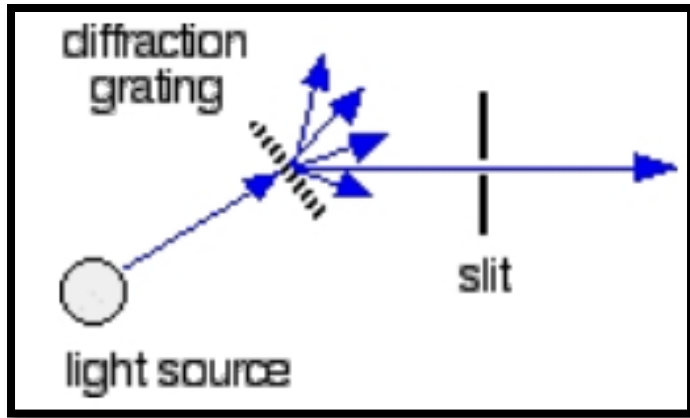
To measure the amount of light that a sample absorbs



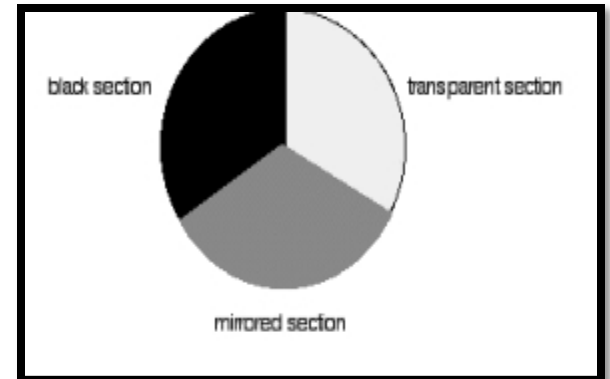
• **Visible spectrophotometer:** uses light over visible range (400 - 700 nm) of electromagnetic radiation spectrum.

Diffraction Grating & The Slit:

- Diffraction grating splits lights to its component colors like a prism
- Slit allows to pass only a narrow range of wavelengths to the rotating disk.



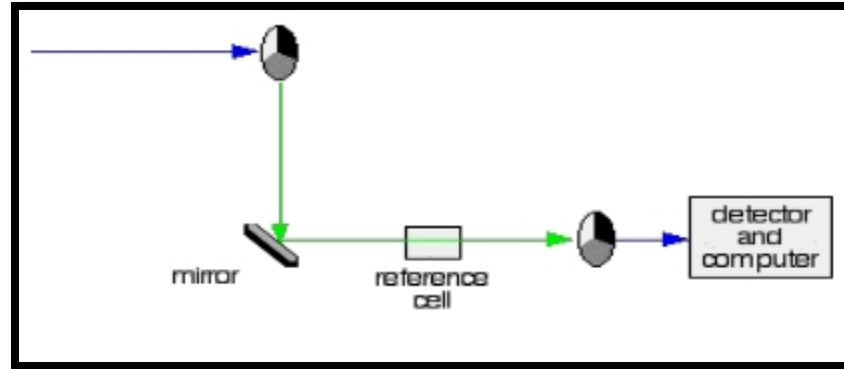
Rotating disks are made of different number of segments Rotating Disks:



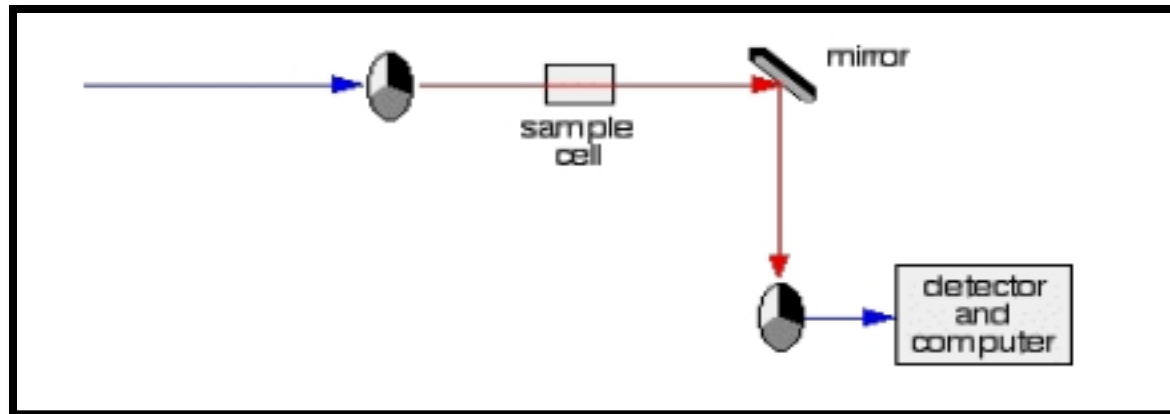
Rotating Disks:

If light hits the mirrored section, it bounces back to a mirror.

The reflected light meets the transparent section of the second disk and passes through it to the detector.



If light hits the transparent section, it will pass through and be bounced by a mirror onto a second rotating disk. Light meets the mirrored section of the second disk and bounces onto the detector.



Sample & Reference Cells .

- Small rectangular glass/quartz containers.
- Designed in such a manner that light has to travel 1cm through the contents

Detector & Computer

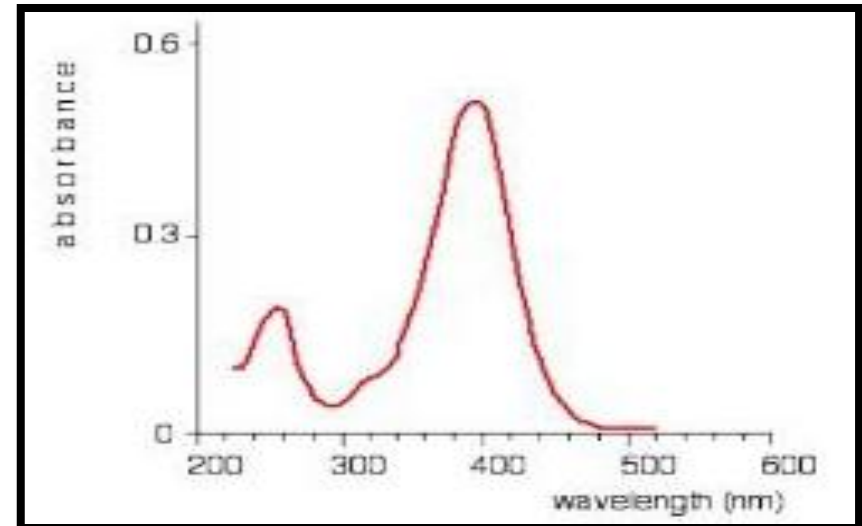
Detector converts light to current. The greater is the intensity of light, the higher is the current.

Intensity of light passing through reference cell = I_0

Intensity of light passing through sample = I

An absorbance (A) could be written as

$$A = \log_{10} \frac{I_0}{I}$$



Lambert-Beer's Law:

$$\log_{10} \frac{I_o}{I} = \epsilon l c$$

Diagram illustrating the components of Lambert-Beer's Law:

- ϵ : Greek letter, epsilon
- l : length of solution the light passes through (cm)
- c : concentration of solution (mol dm⁻³)

Molar absorptivity = Absorbance of 1 mol dm⁻³ solution if cell length = 1 cm

$$A = \log_{10} \frac{I_o}{I} = \epsilon l c$$

molar absorptivities ϵ vary by orders of magnitude:

- values of 10⁴-10⁶ are termed high intensity absorptions
- values of 10³-10⁴ are termed low intensity absorptions
- values of 0 to 10³ are the absorptions of forbidden transitions

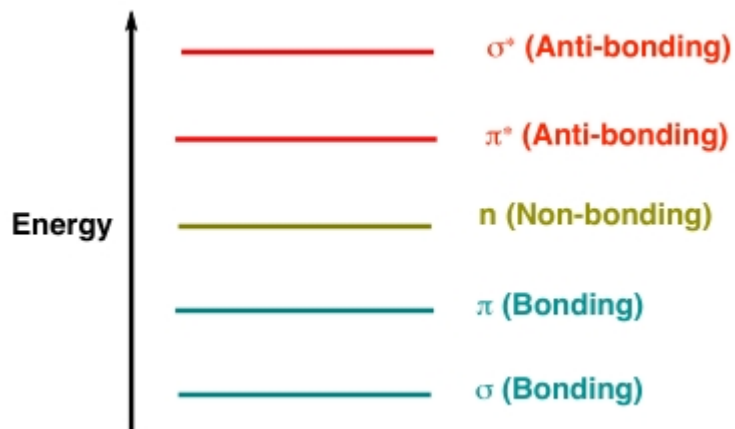
The intensity of an absorption band in UV is expressed as the “molar absorptivity” at maximum absorption ϵ_{max} .

From an experimental point of view, three other considerations must be made:

- a longer path length l , through the sample will cause more UV light to be absorbed –linear effect
- the greater the concentration, c , of the sample, the more UV light will be absorbed –linear effect
- some electronic transitions are more effective at the absorption of photon than others –molar absorptivity

Principle Behind UV Spectrometers

Relative Energies of Various Orbitals.



-These energy gaps are different in different compounds.

-The difference in energy between two orbitals.

$$\Delta E = h\nu = \frac{hc}{\lambda} = h\bar{\nu}c$$

-When light passes through a compound, some of its energy promotes an electron from one of the bonding or non-bonding orbitals to one of the anti-bonding orbitals.

-The frequency (or wavelength) of absorption depends on the energy gaps between those two energy levels

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

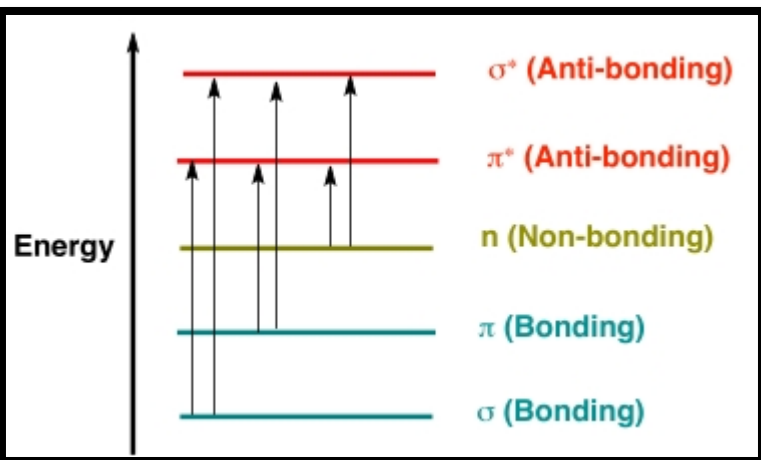
speed of light

frequency
(Greek letter, nu)

$$c = \lambda\nu$$

wavelength

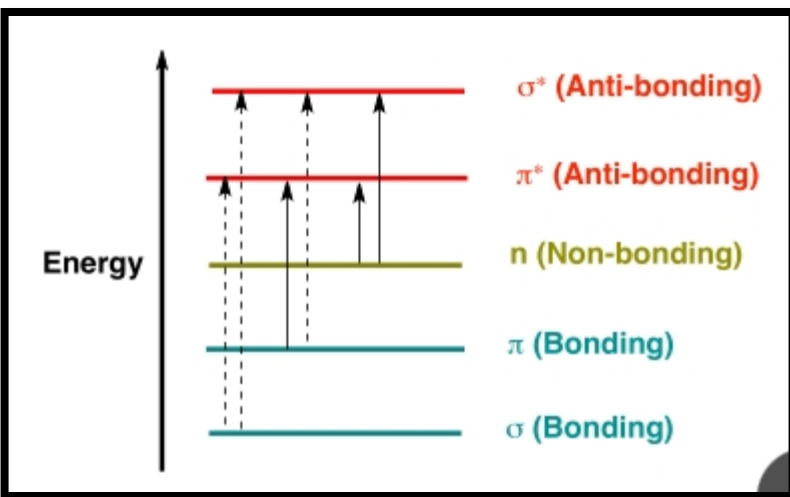
Electronic Transitions



-The higher is the energy gap, the lower is the wavelength of the light absorbed.

-Bigger jumps requires more energy, so absorb light with a shorter wavelength.

Not all electronic transitions are allowed. Certain restrictions should be considered for electronic transitions, called "selection rules"



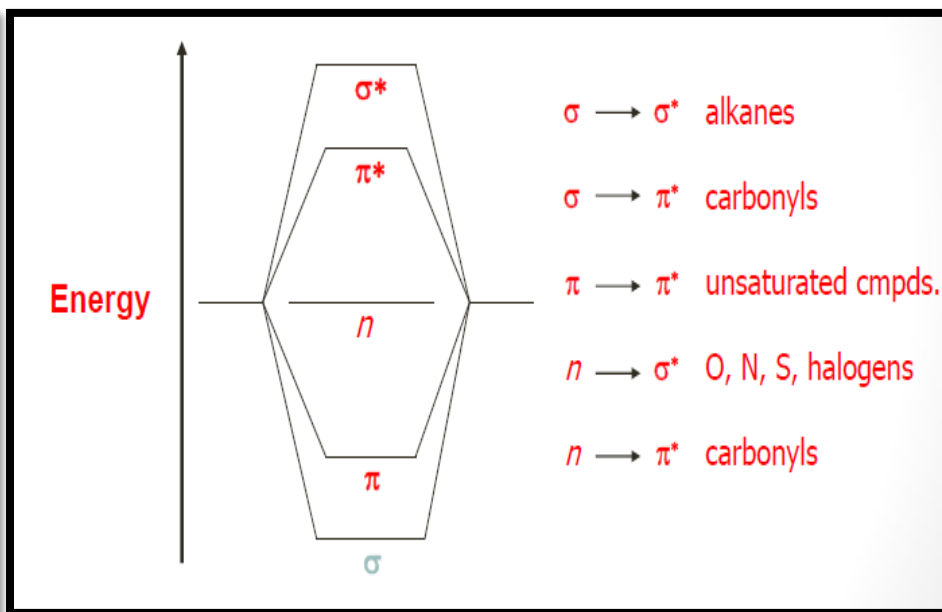
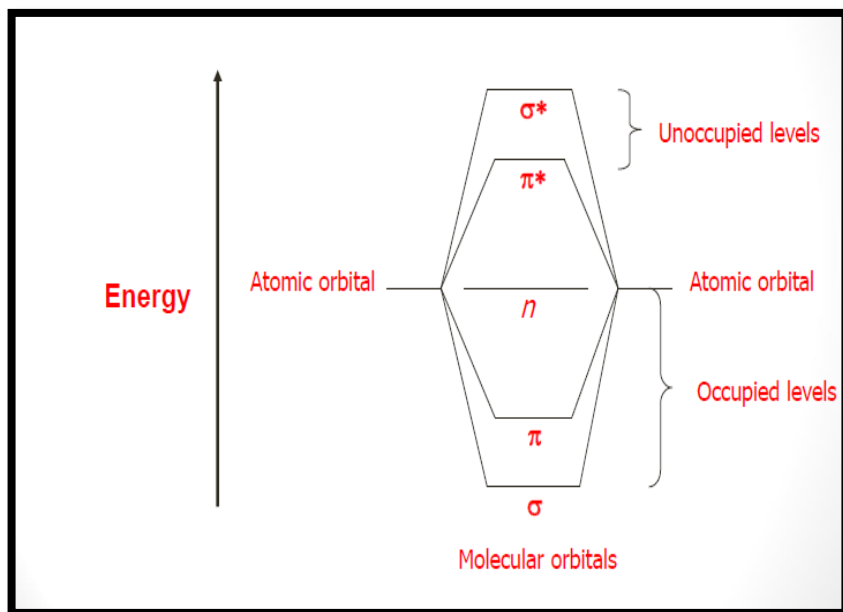
(1) The spin quantum number of an electron should not change during the electronic transition.

(2) The transition between two orbitals should be symmetry allowed.

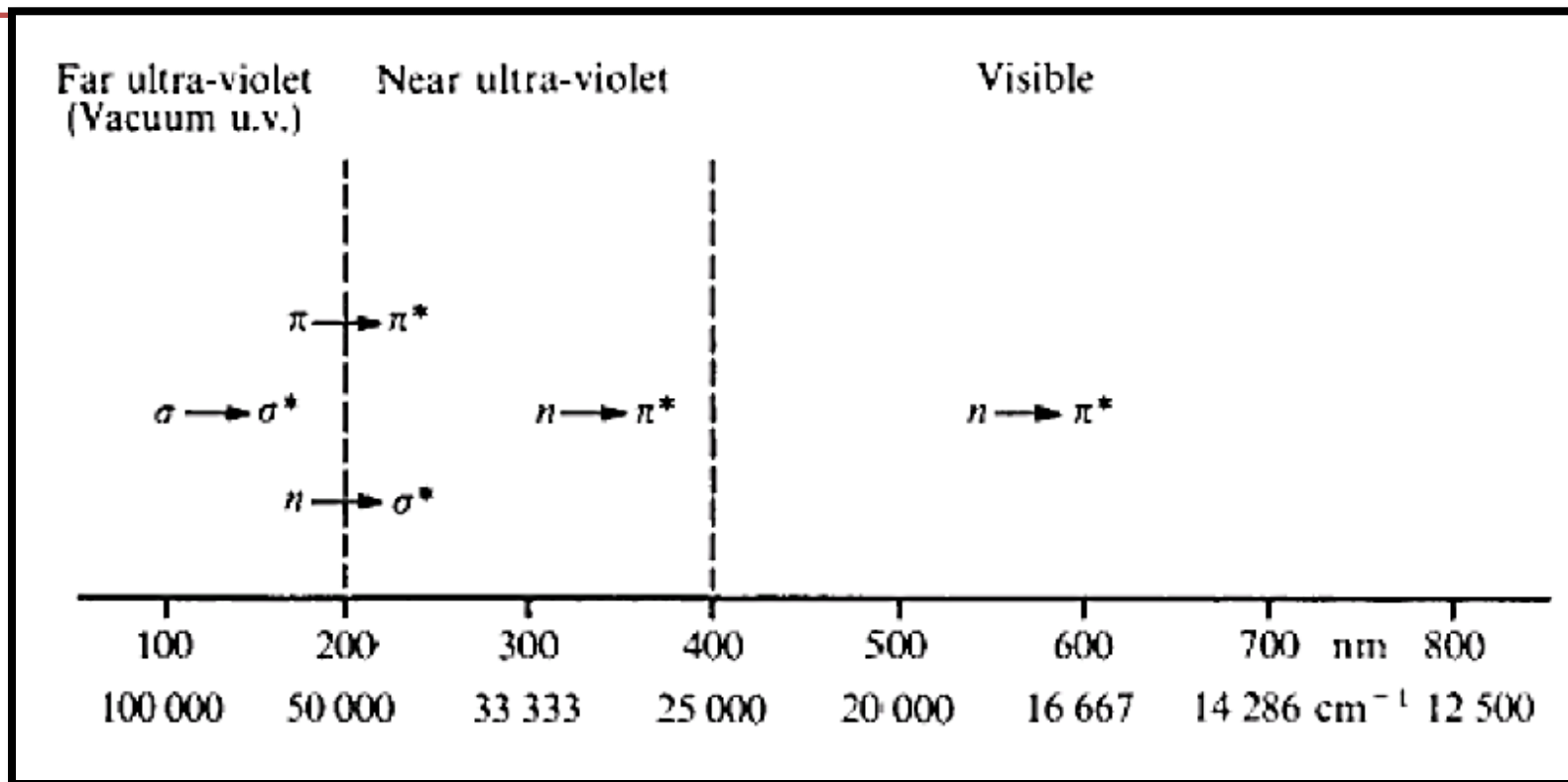
Observed electronic transitions

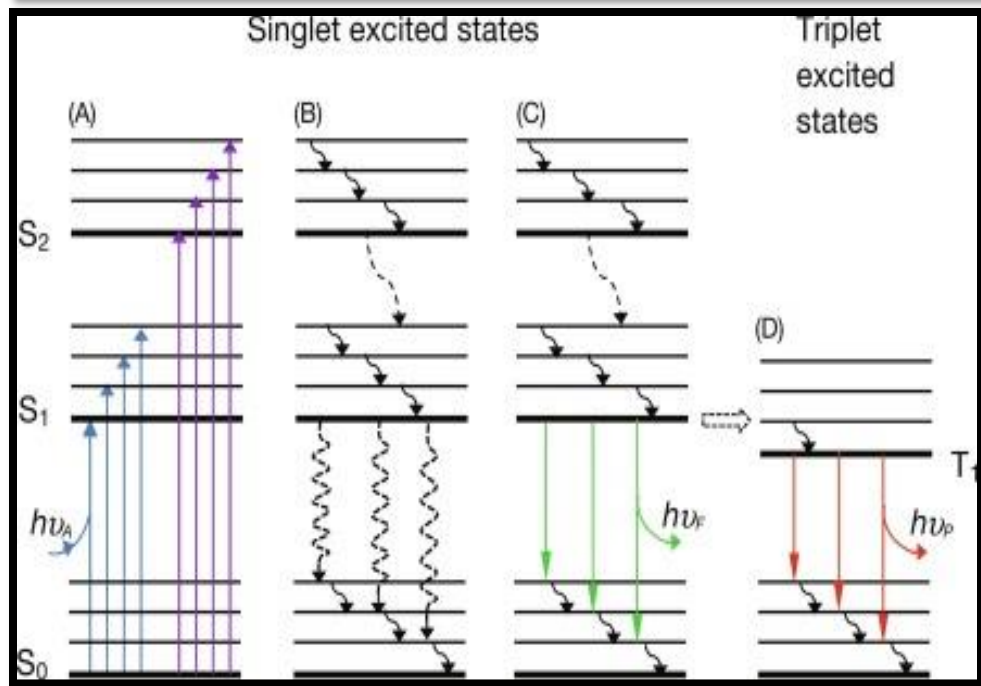
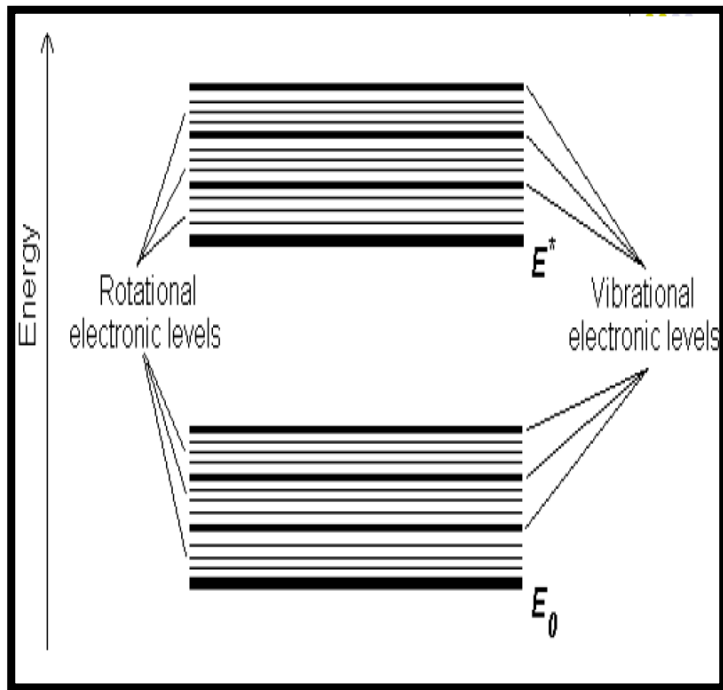
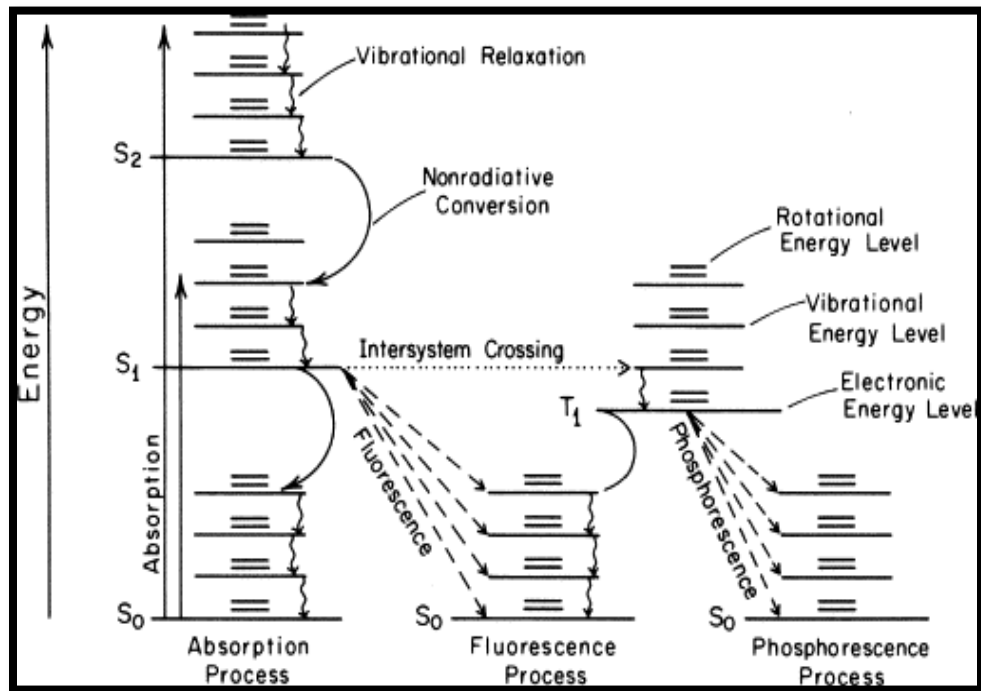
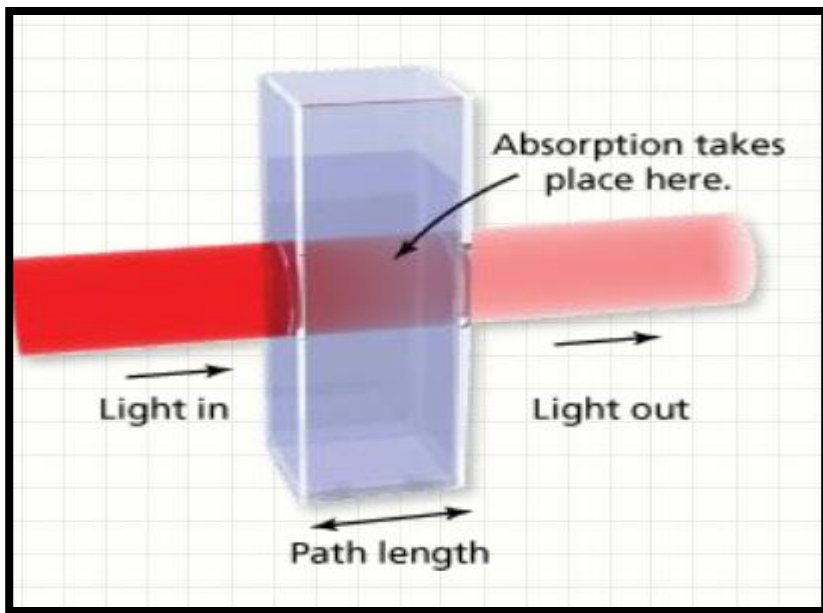
□ The lowest energy transition (and most often obs. by UV) is typically that of an electron in the **Highest Occupied Molecular Orbital (HOMO)** to the **Lowest Unoccupied Molecular Orbital (LUMO)**

□ For any bond (pair of electrons) in a molecule, the molecular orbitals are a mixture of the two contributing atomic orbitals; for every bonding orbital “created” from this mixing (s, p), there is a corresponding anti-bonding orbital of symmetrically higher energy (s*, p*)



From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy:





Selection Rules .

- Not all transitions that are possible are observed
- For an electron to transition, certain quantum mechanical constraints apply these are called “selection rules”
- 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

To further complicate matters, “forbidden” transitions are sometimes observed (albeit at low intensity) due to other factors

Any transition that violates these rules are called “forbidden transition”. Most common “forbidden transition” is $n - \pi^*$.

Important Electronic Transitions

- From π (bonding) orbital to π^* (anti-bonding) orbital ($\pi - \pi^*$).
- From n (non-bonding) orbital to π^* (anti-bonding) orbital ($n - \pi^*$).
- From n (non-bonding) orbital to σ^* (anti-bonding) orbital ($n - \sigma^*$)

-In Alkanes : Electronic Transitions $\sigma - \sigma^*$ or $n - \sigma^*$ Usually weak absorptions

Absorption Characteristics of $n \rightarrow \pi^*$

Compound	λ_{\max}	ϵ_{\max}	Solvent
Methanol	177	200	Hexane
1-Hexanethiol	224 (s)	126	Cyclohexane
Trimethylamine	199	3950	Hexane
N-methylpiperidine	213	1600	Ether
Diethyl ether	188	1995	Gas phase
Methyl chloride	173	200	Hexane
Methyl iodide	259	400	Hexane

In Alkenes.

-In Carbonyls: $\pi - \pi^*$ around 190 nm ($\epsilon = 900$) & $n - \pi^*$ around 280 nm ($\epsilon = 15$).

-In unconjugated alkenes $\pi - \pi^*$ transition takes place around 170 -190 nm.

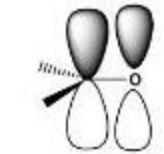
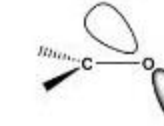
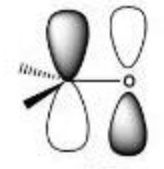
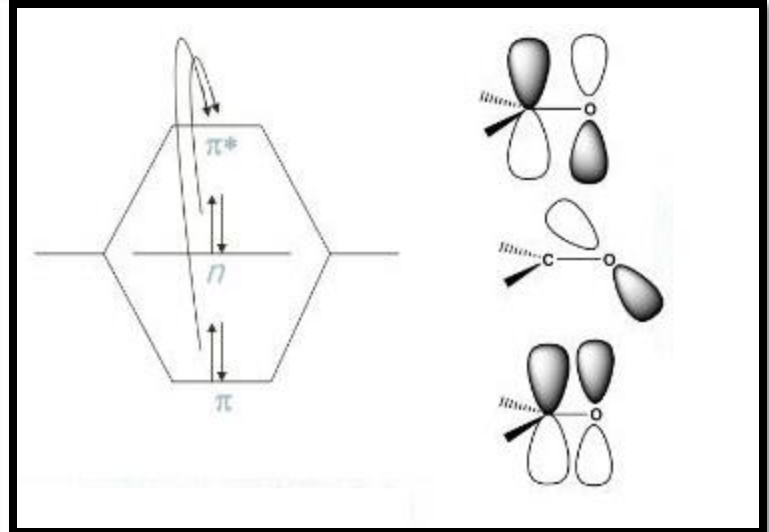
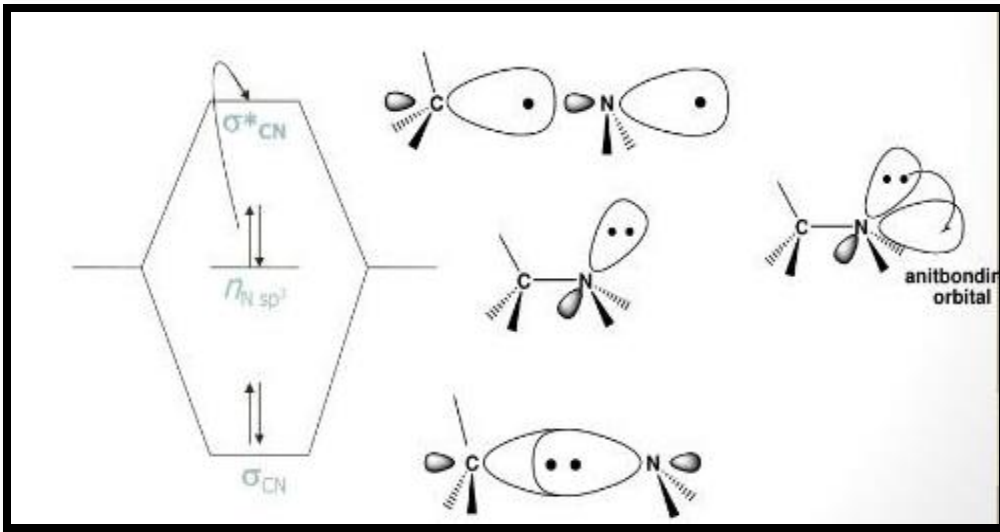
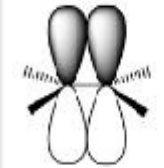
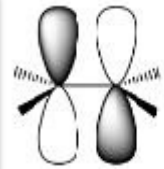
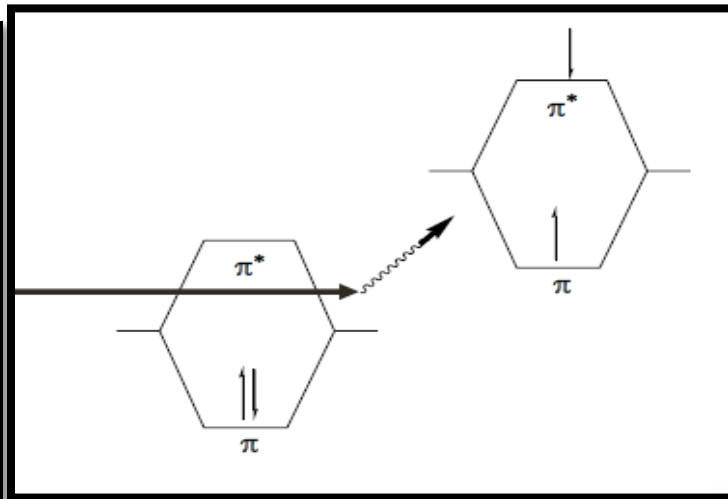
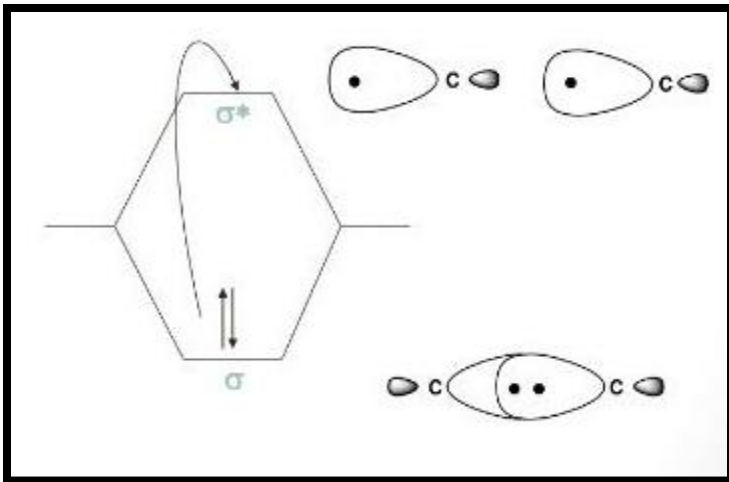
Absorption Data for Conjugated Alkenes ($\pi \rightarrow \pi^*$)

Compound	λ_{\max}	ϵ_{\max}	Solvent
1,3-Butadiene	217	21,000	Hexane
2,3-Dimethyl-1,3-butadiene	226	21,400	Cyclohexane
1,3,5-Hexatriene	253	50,000	Isooctane
	263	52,000	
	274	50,000	
1,3-Cyclohexadiene	256	8,000	Hexane
1,3-Cyclopentadiene	239	3,400	Hexane

In Carbonyls: $\pi - \pi^*$ around 190 nm ($\epsilon = 900$) & $n - \pi^*$ around 280 nm ($\epsilon = 15$)

Since $n - \pi^*$ transition is a symmetry forbidden transition, intensity of this transition is much lower than other allowed transitions.

Chromophore	Example	Excitation	λ_{\max}	ϵ_{\max}	Solvent	
C=C	Ethene	$\pi \rightarrow \pi^*$	165 nm	15,000	hexane	
C \equiv C	1-Hexyne	$\pi \rightarrow \pi^*$	173 nm	10,000	hexane	
C=O	Ethanal	$n \rightarrow \pi^*$	290 nm	15	hexane	
		$\pi \rightarrow \pi^*$	180 nm	10,000	hexane	
N=O	Nitromethane	$n \rightarrow \pi^*$	275 nm	17	ethanol	
		$\pi \rightarrow \pi^*$	200 nm	5,000	ethanol	
C-X	X=Br	Methyl bromide	$n \rightarrow \sigma^*$	205 nm	200	hexane
	X=I	Methyl Iodide	$n \rightarrow \sigma^*$	255 nm	360	hexane



Auxochrome:

A saturated group with non-bonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption (e.g., -OH, -NH₂, -NR₂, -SH etc.)

Chromophore :

A covalently unsaturated group responsible for electronic absorption (e.g., C=C, C=O, esters, amides, -NO₂ etc.).

Bathochromic Shift:

The shift of absorption to a longer wavelength (also known as “red shift”).

Hypsochromic Shift:

The shift of absorption to a shorter wavelength (also known as “blue shift”).

Hyperchromic Effect: An increase in absorption intensity .

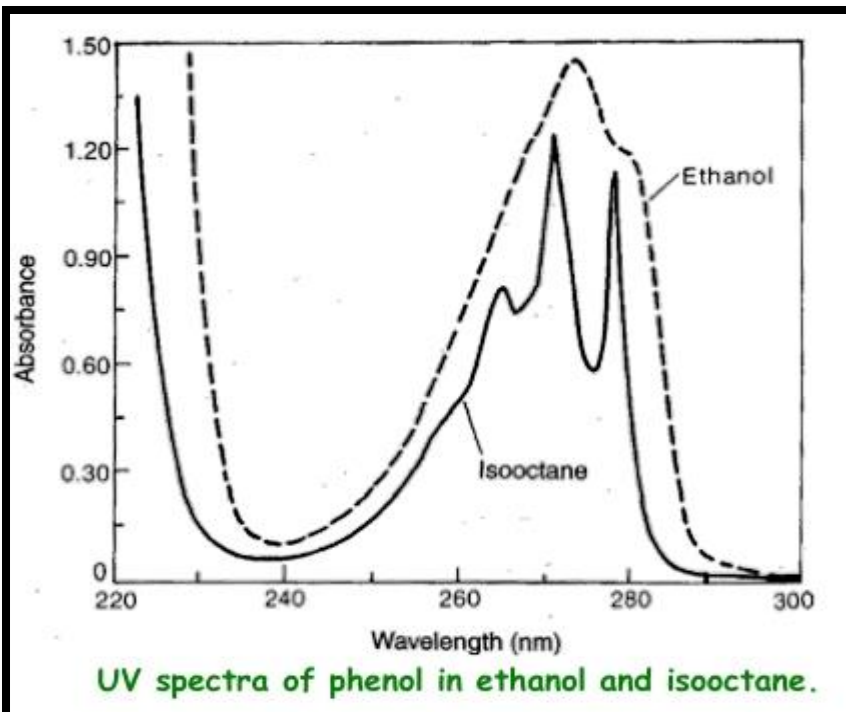
Hypochromic Effect: A decrease in absorption intensity.

Solvents & Solutions

-Solvents should not absorb UV-radiation within same range as the substance.

Acetonitrile	190 nm	<i>n</i> -Hexane	201 nm
Chloroform	240 nm	Methanol	205 nm
Cyclohexane	195 nm	Isooctane	195 nm
1,4-Dioxane	215 nm	Water	190 nm
95% Ethanol	205 nm	Trimethyl phosphate	210 nm

A strong absorbing solvent allows very little amount of light to pass through the sample.



Non-polar solvents do not form H bond with solute, so “fine structure” is often observed.

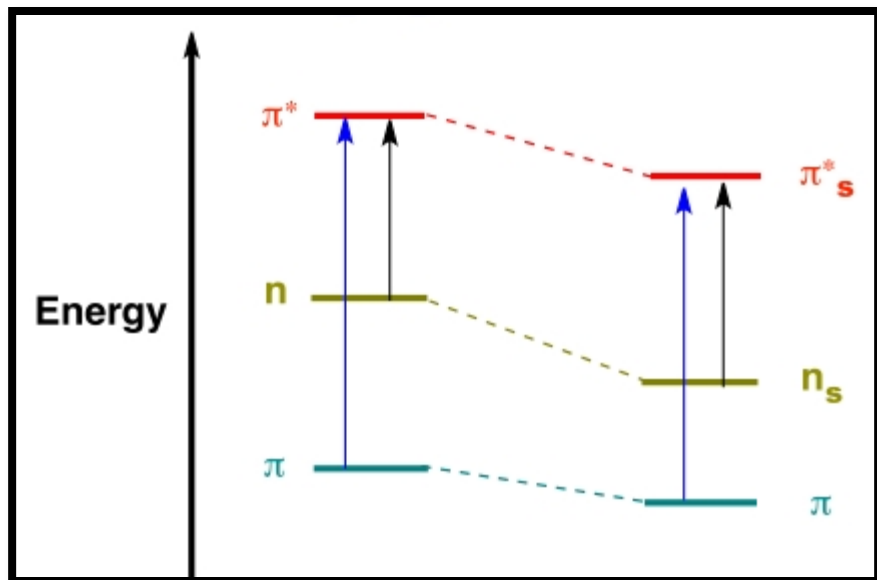
-**Polar solvents** form solute-solvent complexes through H-bonding, hence, “fine structure” may disappear

Solvent Effects

The position and intensity of an absorption band may shift if the spectrum was recorded in different solvents.

Conjugated dienes and aromatic hydrocarbons experience very less “solvent effect”.

α,β -Unsaturated carbonyls show two different shifts in bands for changing solvents from non-polar to a polar protic one.



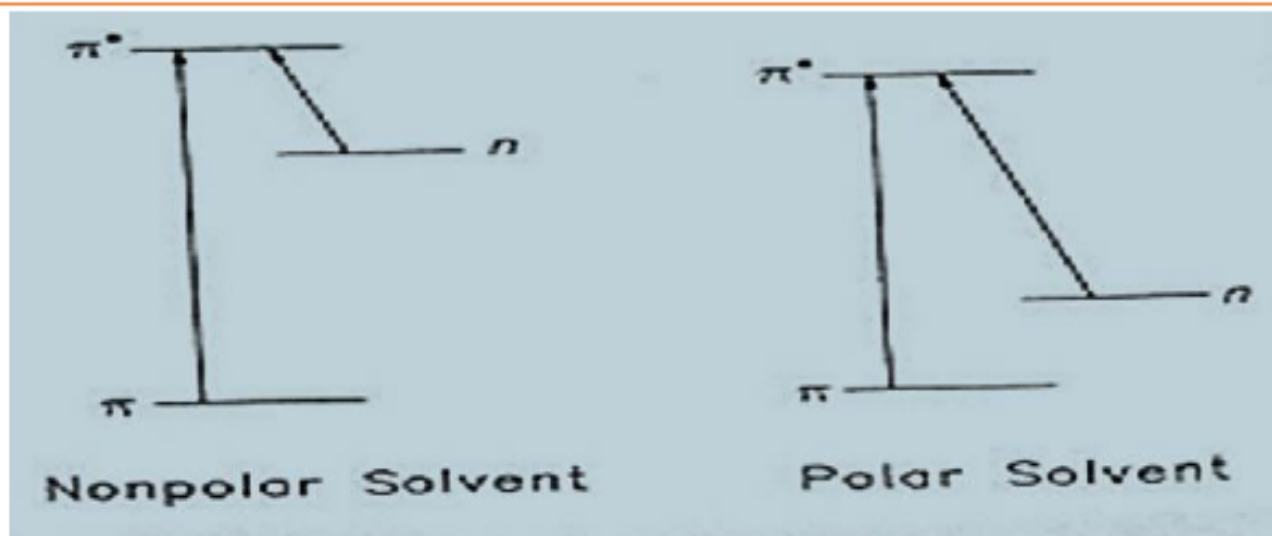
$\pi - \pi^*$ band moves to longer wavelength, $n - \pi^*$ band moves to shorter wavelength.

π^* orbitals get stabilized (due to more polarity) by solvation than π orbitals. n orbitals get stabilized mainly by H-bonding.



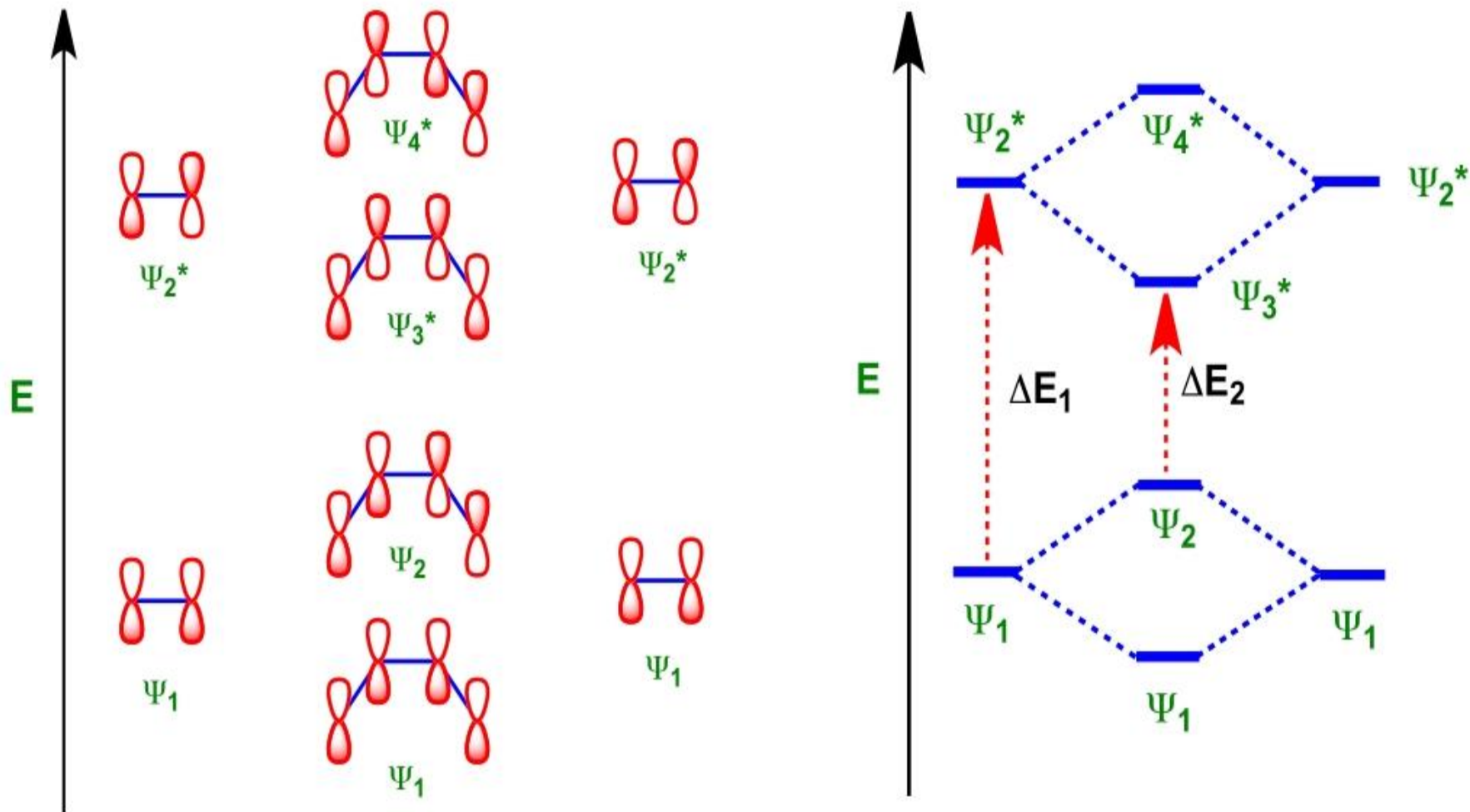
$\pi \rightarrow \pi^*$ transitions leads to more polar excited state that is more easily stabilized by polar solvent associations (H-bonds). The π^* state is more polar and stabilized more in polar solvent relative to nonpolar one, thus in going from nonpolar to polar solvent there is a red shift or bathochromic shift (increase in λ_{\max} , decrease in ΔE).

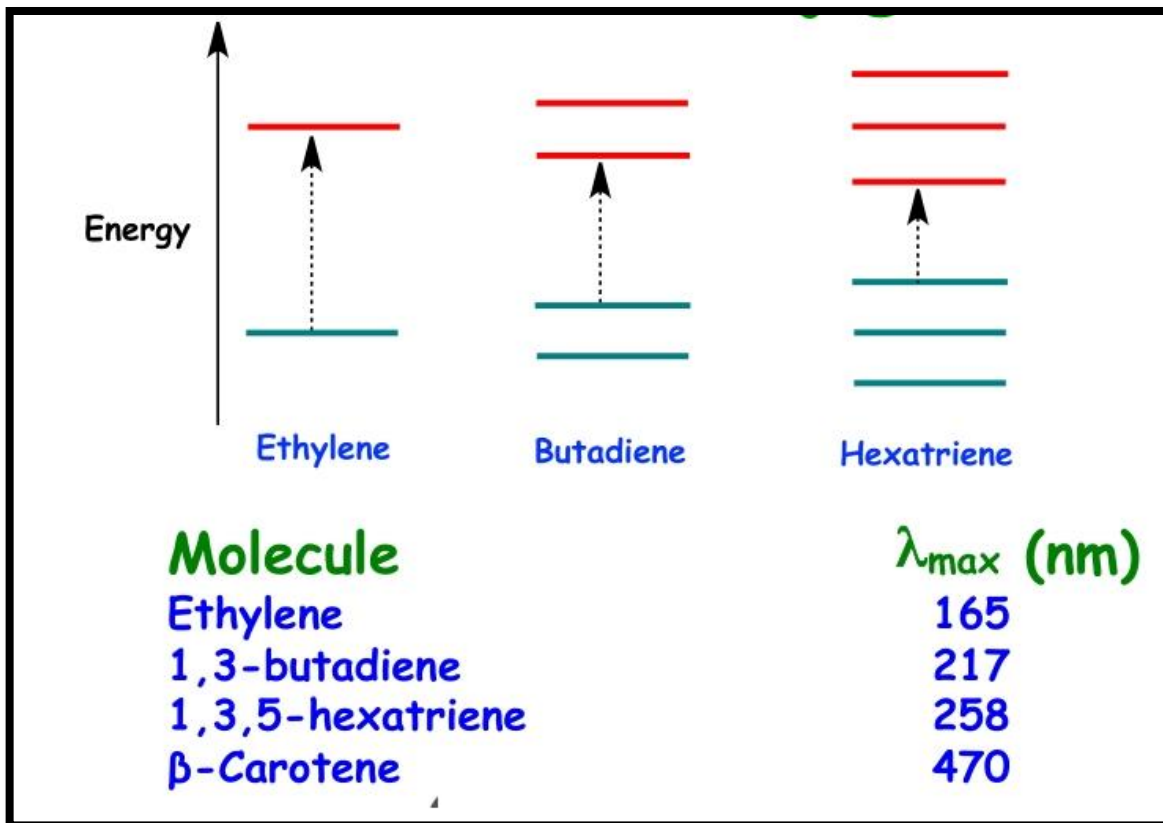
For $n \rightarrow \pi^*$ transition, the n state is much more easily stabilized by polar solvent effects (H-bonds and association-solvation of the lone pair), so in going from nonpolar to polar solvent there is a blue shift or hypsochromic shift (decrease in λ_{\max} , increase in ΔE). (same with $n \rightarrow \sigma^*$ transition)



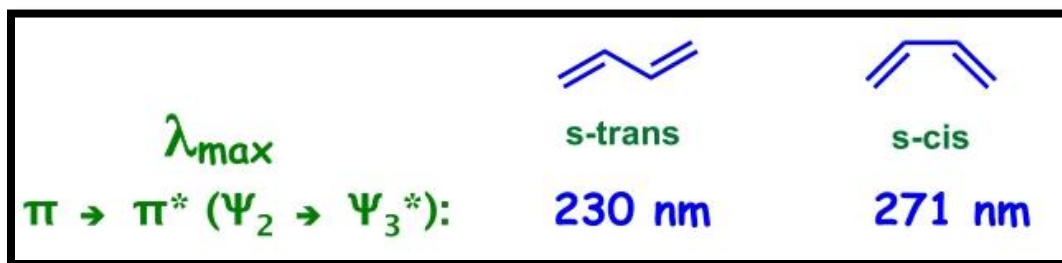
- ❖ Ground state polar > Excited state λ_{\max} decrease with increase solvent polarity.
- ❖ Ground state < Excited state λ_{\max} increase with increase solvent polarity.

Effect of Conjugation

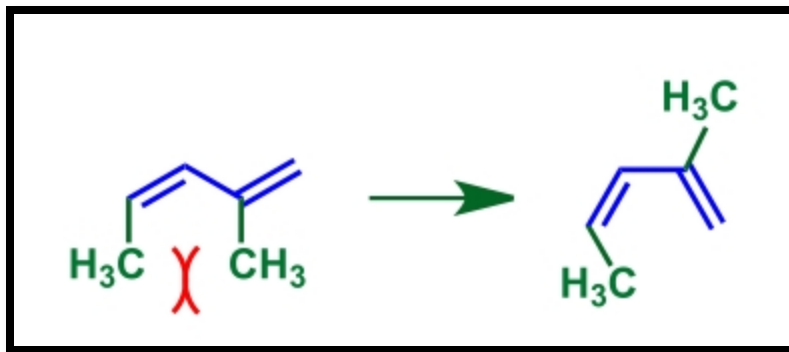




Effect of s-cis & s-trans Conformers:



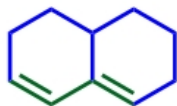
Probably repulsion between terminal lobes of Ψ_2 increases energy of HOMO (Ψ_2) in s-cis form. Hence, less energy (ie. Higher wavelength) is required for $\Psi_2 \rightarrow \Psi_3^*$ transition.



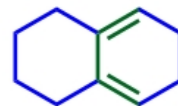
Substitution may force a molecule to take s-cis form, therefore, absorbs energy from a longer wavelength (shows a red shift) than usual s-trans conformer

In cyclic system a double bond is forced to stay in s-cis (Cisoid) form, therefore, shows a red shift with a drop in intensity

Homoannular & Heteroannular Dienes



$\lambda_{\max} = 234 \text{ nm}$
 $\epsilon_{\max} = 12000-28000$



$\lambda_{\max} = 273 \text{ nm}$
 $\epsilon_{\max} = 5000-15000$

Woodward–Fieser Rules for Diene

Woodward (1941) predicted λ max values only for the lowest energy transition ($\pi - \pi^*$) from HOMO to LUMO.

Base values:

Base value for an unsubstituted, conjugated, acyclic or heteroannular diene 214 nm

Base value for an unsubstituted, conjugated, homoannular diene 253 nm

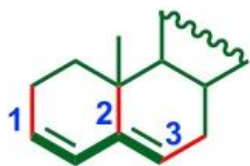
Increments for:

Each extra double bonds in conjugation + 30 nm

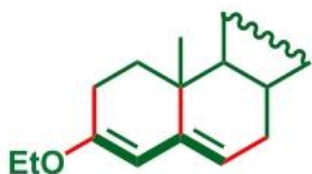
Exocyclic double bond (effect is two fold if the bond is exocyclic to two rings) + 5 nm

Substituent effect:

A. -OCOR or -OCOAr	+ 0 nm
B. Simple alkyl substituents or ring residue	+ 5 nm
C. Halogen (-Cl, -Br)	+ 5 nm
D. OR (R=Alkyl)	+ 6 nm
E. SR (R=Alkyl)	+ 30 nm
F. NR ₂ (R=Alkyl)	+ 60 nm



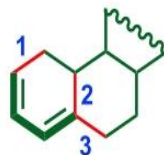
Transoid (base):	214 nm
3 ring residues :	+15
1 exocyclic C=C:	+ 5
Total:	<u>234 nm</u>
Observed:	235 nm



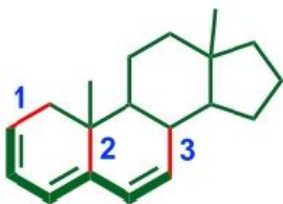
Transoid (base):	214 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
-OR:	+ 6
Total:	<u>240 nm</u>
Observed:	241 nm



Transoid (base):	214 nm
3 Ring residues:	+15
1 Alkyl substituent:	+ 5
1 Exocyclic C=C:	+ 5
Total:	<u>239 nm</u>



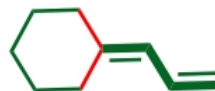
Cisoid (base):	253 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
Total:	<u>273 nm</u>
Observed:	275 nm



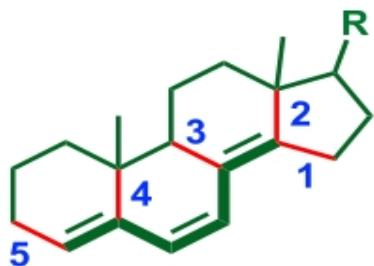
Cisoid (base):	253 nm
3 Ring residues:	+15
1 Exocyclic C=C:	+ 5
Double-bond Extending Conjugation:	+30
Total:	<u>303 nm</u>
Observed:	304 nm



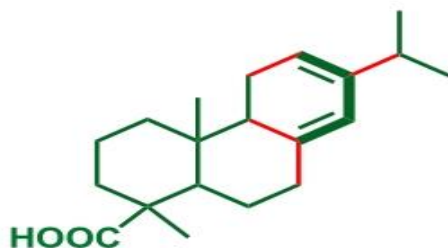
Base value:	214 nm
2 Ring residue	+10
Exocyclic C=C:	+ 5
Total:	<u>229 nm</u>
Observed:	230 nm



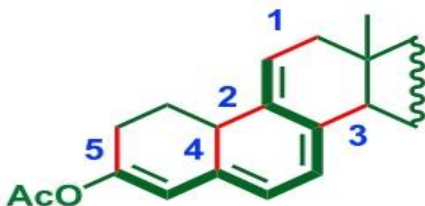
Base value:	214 nm
2 Ring residue:	+10
Exocyclic C=C:	+ 5
Total	<u>229 nm</u>
Observed:	236 nm



Transoid (base):	214 nm
5 ring residues:	+25
1 DEC:	+30
3 exocyclic C=C	+15
Total:	<u>284 nm</u>
Observed:	283 nm



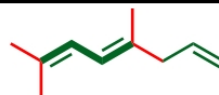
Cisoid (base):	253 nm
3 ring residues:	+15
1 Alkyl subs:	+5
1 exocyclic C=C	+5
Total:	<u>278 nm</u>
Observed:	275 nm



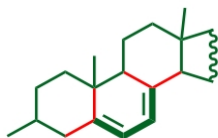
Cisoid (base):	253 nm
5 ring residues:	+25
2 DEC:	+60
3 exocyclic C=C	+15
Total:	<u>353 nm</u>
Observed:	355 nm



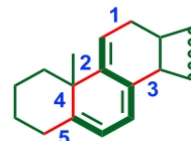
Base value:	214 nm
3 Alkyl grs:	+15
Total:	229 nm
Observed:	232 nm



Base value:	214 nm
4 Alkyl grs:	+20
Total:	234 nm
Observed:	235 nm



Base value:	253 nm
4 Ring residues:	+20
2 Exocyclic C=C:	+10
Total:	283 nm
Observed:	282 nm



Base value:	253 nm
5 Ring residues:	+25
3 Exocyclic C=C:	+15
DEC:	+30
Total:	323 nm
Observed:	325 nm

Base values:

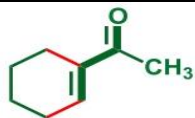
➤ Acyclic α,β -unsaturated ketones	215 nm
➤ 6-membered cyclic α,β -unsaturated ketones	215 nm
➤ 5-membered cyclic α,β -unsaturated ketones	202 nm
➤ α,β -unsaturated aldehydes	210 nm
➤ α,β -unsaturated carboxylic acid & esters	195 nm

Increments for:

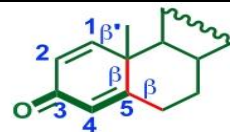
Double bond extending conjugation (DEC):	+30
Exocyclic double bond:	+ 5
Homodiene component:	+39

Increments for:

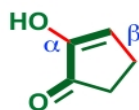
Alkyl group/ring residue: α	+10
β	+12
γ & higher	+18
Polar groups: -OH: α	+35
β	+30
δ	+50
-OAc: α, β, γ	+ 6
-OMe: α	+35
β	+30
γ	+17
δ	+31
-SAlk: β	+85
-Cl: α	+15
β	+12
-Br: α	+25
β	+30
-NR ₂ : β	+95



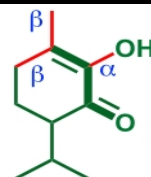
Base value:	215 nm
α substituent:	+10
β substituent:	+12
Total:	237 nm
Observed:	232 nm



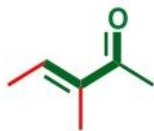
$\Delta^{4,5}$ system (base):	215 nm
2 β substituents:	+24
1 exocyclic C=C:	+5
Total:	244 nm
Observed:	245 nm



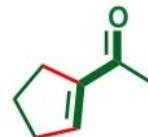
Base value:	202 nm
β substituent:	+12
α -OH:	+35
Total:	249 nm
Observed:	247 nm



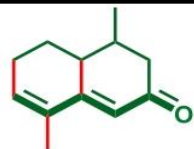
Base value:	215 nm
2 β substituents:	+24
α -OH:	+35
Total:	274 nm
Observed:	270 nm



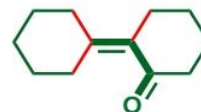
Base value:	215 nm
α alkyl substituent:	+10
β alkyl substituent:	+12
Total:	237 nm



Base value:	215 nm
α alkyl:	+10
β alkyl:	+12
Total:	237 nm



Base value:	215 nm
1 DEC:	+30
Exocyclic C=C:	+ 5
β -alkyl substituent:	+12
γ -alkyl substituent:	+18
δ -alkyl substituent:	+18
Total:	298 nm



Base value:	215 nm
1 α -alkyl:	+10
2 β -alkyl:	+24
2 Exocyclic C=C:	+10
Total:	259 nm

Aromatic Compounds

Parent chromophore: Ar = C₆H₅

Ar-CO-R	246 nm
Ar-CHO	250 nm
Ar-COOH or Ar-COOR	230 nm

Increment for each substituent on Ar:

Alkyl or ring residue	<i>o, m</i>	+ 3 nm
	<i>p</i>	+ 10 nm
OH, OCH ₃ , OAlk	<i>o, m</i>	+ 7 nm
	<i>p</i>	+ 25 nm
NH ₂	<i>o, m</i>	+ 13 nm
	<i>p</i>	+ 58 nm
NHCOCH ₃	<i>o, m</i>	+ 20 nm
	<i>p</i>	+ 45 nm
NHMe	<i>p</i>	+ 73 nm
NMe ₂	<i>o, m</i>	+ 20 nm
	<i>p</i>	+ 85 nm
Cl	<i>o, m</i>	+ 0 nm
	<i>p</i>	+ 10 nm
Br	<i>o, m</i>	+ 2 nm
	<i>p</i>	+ 15 nm



$$\begin{aligned} \text{Calc } \lambda_{\text{max}}^{\text{EtOH}} &= 246 \text{ (parent chromophore)} + 3 \text{ (o-ring residue)} + 25 \text{ (p-OMe)} \\ &= 274 \text{ nm} \end{aligned}$$

$$\text{Obs } \lambda_{\text{max}}^{\text{EtOH}} = 276 \text{ nm}$$



$$\text{Calc } \lambda_{\text{max}}^{\text{EtOH}} = 246 + 3 (\text{o-ring residue}) + 7 (\text{o-OH})$$

$$= 256 \text{ nm}$$

$$\text{Obs } \lambda_{\text{max}}^{\text{EtOH}} = 257 \text{ nm}$$



$$\text{Calc } \lambda_{\text{max}}^{\text{EtOH}} = 246 + 25 + 7 + 3 = 281 \text{ nm}$$

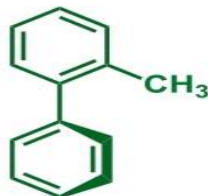
$$\text{Obs } \lambda_{\text{max}}^{\text{EtOH}} = 278 \text{ nm}$$

Violations of Woodward Rules

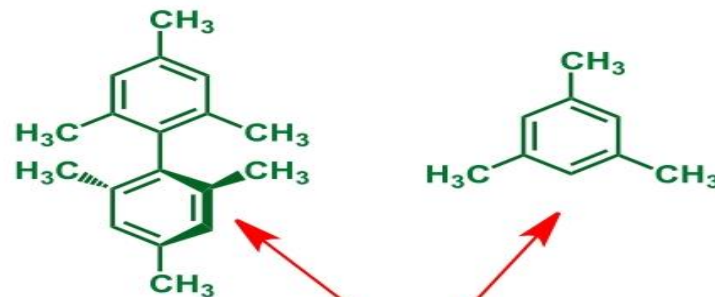
Biphenyls:



250 nm



237 nm



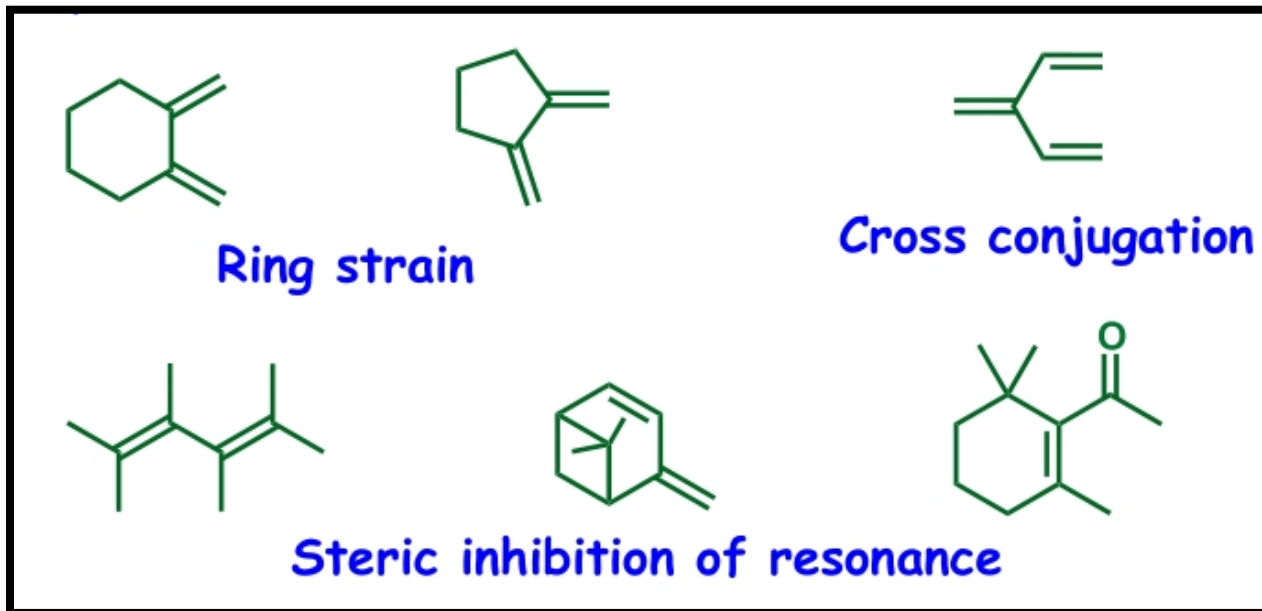
266 nm

Not planar
45 °C angle

Substitutions cause loss of co-planarity of orbitals.
Loss of overlap, blue shift with reduced intensity.

Steric Inhibition of Resonance

- (1) In alkenes, trans isomers exhibit absorption at longer wavelength and high intensity.
- (2) Woodward rules are applicable only if there is no strain around chromophore.



(3) If calculated and experimental values of λ max do not match, one can say that the molecule must have some strain.

(4) Thus UV can be used indirectly to determine if the molecule has any strain

Fieser-Kuhn rules for Conjugated Polyenes

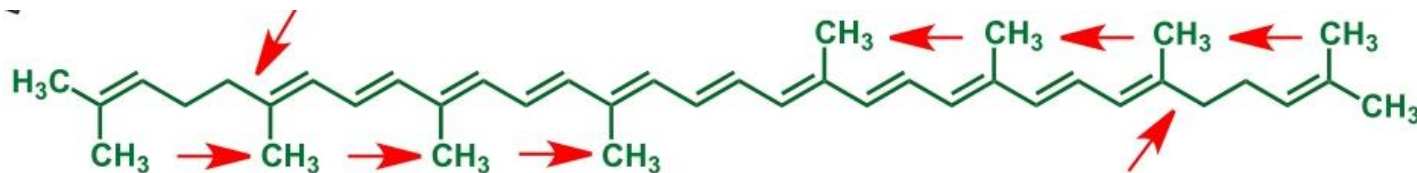
$$\lambda_{\max} = 114 + 5M + n(48.0 - 1.7n) - 16.5R_{\text{endo}} - 10R_{\text{exo}}$$

Where n = number of conjugated double bonds

M = number of alkyl or alkyl like substituents on the conjugated system

R_{endo} = number of rings with endocyclic double bonds in the conjugated system

R_{exo} = number of rings with exocyclic double bonds



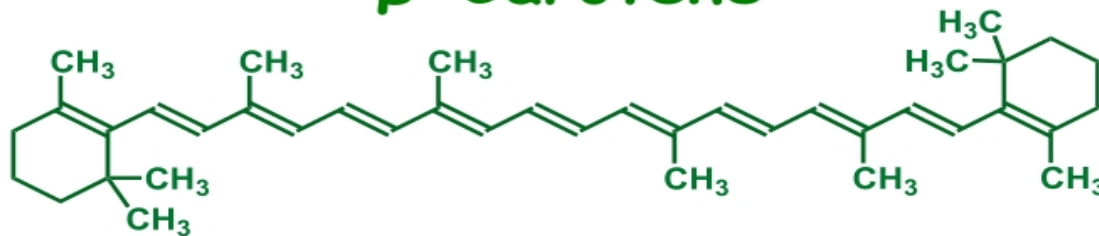
$$\lambda_{\max}^{\text{calc}} = 114 + 5(8) + 11[48.0 - 1.7(11)] - 0 - 0$$
$$= 476 \text{ nm}$$

$$\lambda_{\max}^{\text{obs}} = 474 \text{ nm (hexane)}$$

$$\epsilon_{\max}^{\text{cal}} = 1.74 \times 10^4(11) = 19.1 \times 10^4$$

$$\epsilon_{\max}^{\text{obs}} = 18.6 \times 10^4 \text{ (hexane)}$$

β -Carotene



$$\lambda_{\max}^{\text{calc}} = 453.3 \text{ nm}$$

$$\lambda_{\max}^{\text{obs}} = 452 \text{ nm (hexane)}$$

$$\epsilon_{\max}^{\text{cal}} = 19.1 \times 10^4$$

$$\epsilon_{\max}^{\text{obs}} = 15.2 \times 10^4$$

2. Substituent Effects

A. Substituents with Unshared Electrons

- If the group attached to the ring bears n electrons, they can induce a shift in the primary and secondary absorption bands
- Non-bonding electrons extend the p -system through resonance –lowering the energy of transition p - p^*
- More available n -pairs of electrons give greater shifts

For triplet state: Under the influence of external field, there are three values (i.e. 3 energy states) of +1, 0, -1 times the angular momentum. Such states are called triplet states (T).

□ According to the selection rule, $S \rightarrow S$, $T \rightarrow T$, are allowed transitions, but $S \rightarrow T$, $T \rightarrow S$, are forbidden transitions.

Electronic transitions may be classed as intense or weak according to the magnitude of ϵ_{max} that corresponds to allowed or forbidden transition as governed by the following **selection rules** of electronic transition:

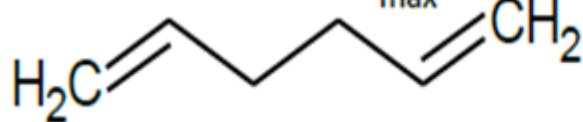
Spin selection rule: there should be no change in spin orientation or no spin inversion during these transitions. Thus, $S \rightarrow S$, $T \rightarrow T$, are allowed, but $S \rightarrow T$, $T \rightarrow S$, are forbidden. ($\Delta S=0$ transition allowed)

Chromophore

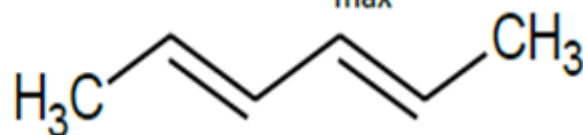
When double bonds are

conjugated in a compound λ_{\max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has $\lambda_{\max} = 178 \text{ nm}$



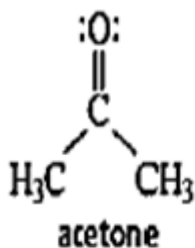
2,4 - hexadiene has $\lambda_{\max} = 227 \text{ nm}$



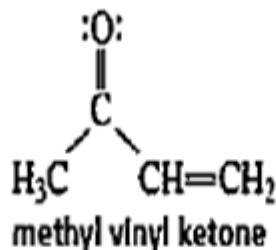
Effect of Conjugation on λ_{\max}

The $n \rightarrow \pi^*$ transition for methyl vinyl ketone is at 324 nm, and the $\pi \rightarrow \pi^*$ transition is at 219 nm. Both λ_{\max} values are at longer wavelengths than the corresponding λ_{\max} values of acetone because methyl vinyl ketone has two conjugated double bonds.

“The λ_{\max} increases as the number of conjugated double bonds increases.”



$n \rightarrow \pi^* \quad \lambda_{\max} = 274 \text{ nm} (\epsilon_{\max} = 13.6)$
 $\pi \rightarrow \pi^* \quad \lambda_{\max} = 195 \text{ nm} (\epsilon_{\max} = 9000)$



$\lambda_{\max} = 331 \text{ nm} (\epsilon_{\max} = 25)$
 $\lambda_{\max} = 203 \text{ nm} (\epsilon_{\max} = 9600)$

The more conjugated double bonds there are in a compound, the less energy is required for the electronic transition, and therefore the longer is the wavelength at which the electronic transition occurs.

Auxochrome

The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of absorption.

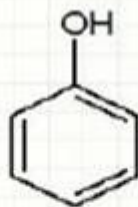
OR

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.

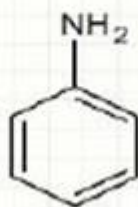
e.g. Benzene $\lambda_{\max} = 255 \text{ nm}$



Phenol $\lambda_{\max} = 270 \text{ nm}$



Aniline $\lambda_{\max} = 280 \text{ nm}$



If the group attached to the ring bears n electrons, they can induce a shift in the primary and secondary absorption bands

Increase λ_{\max} . Of E1 (not appear)

E2 (shorter to appear)

& B with increase E max.

Or stable and loss its fine structure

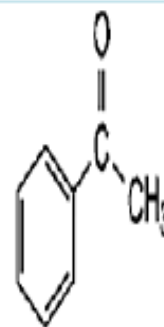


Bathochromic Shift (Red Shift)

Another method of classification uses the symbols:

B	(for benzenoid)	R	(for radical-like)
E	(for ethylenic)	K	(for conjugated)

A molecule may give rise to more than one band in its UV spectrum, either because it contains more than one chromophore or because more than one transition of a single chromophore is observed.



acetophenone

λ_{\max} (nm)	ϵ	$\log_{10}(\epsilon)$	Assignment
244	12,600	4.1	$\pi \rightarrow \pi^*$ K
280	1,600	3.2	$\pi \rightarrow \pi^*$ B
317	60	1.8	$n \rightarrow \pi^*$ R

B band (Benzene band, Benzenoid bands) from the $\pi \rightarrow \pi^*$ transition of Benzene. Broad band with fine structure between 230 - 270 nm. This band can be used to identify aromatic compound.

E band (Ethylenic bands) also from $\pi \rightarrow \pi^*$ transition of ethylenic band in benzene
E1 band and E2 band

R band originated from $n - \pi^*$ transition transition.

The maximum absorption wavelength > 270 nm, $\epsilon_{\max} < 100$

Example: Acetone λ_{\max} 279 nm, $\epsilon_{\max} = 15$

K band (conjugation band, form $\pi \rightarrow \pi^*$ transition.

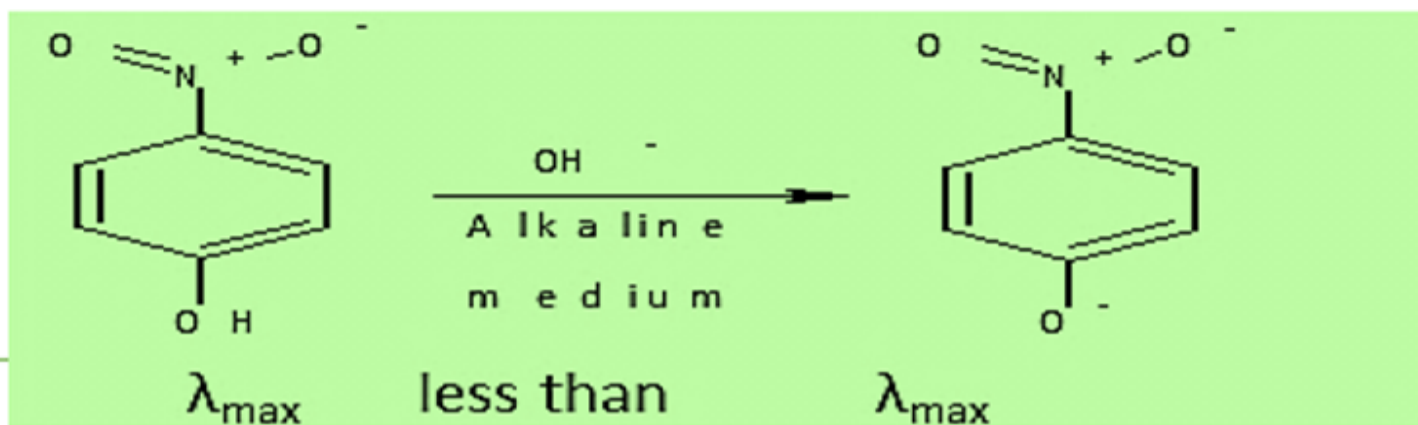
High ϵ_{\max} ($> 10^4$)

Example: Dienes , Acetophenone

1

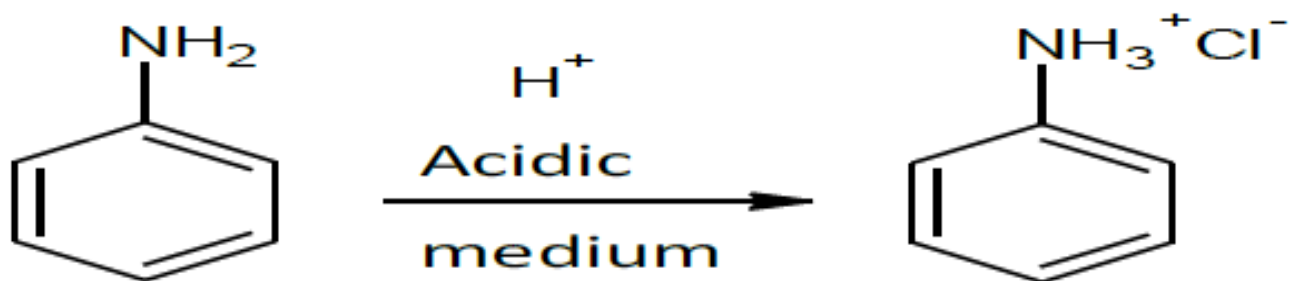
• Bathochromic Shift (Red Shift)

- When absorption maxima (λ_{\max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an **auxochrome** or by the **change of solvent**.
- e.g. An auxochrome group like $-\text{OH}$, $-\text{OCH}_3$ causes absorption of compound at longer wavelength.
- In alkaline medium, *p*-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



2 • Hypsochromic Shift (Blue Shift)

- When absorption maxima (λ_{\max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.
- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.
- **Aniline shows blue shift in acidic medium, it loses conjugation.**



Aniline

$\lambda_{\max} = 280 \text{ nm}$

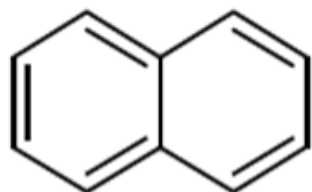
$\lambda_{\max} = 265 \text{ nm}$

3 • Hyperchromic Effect

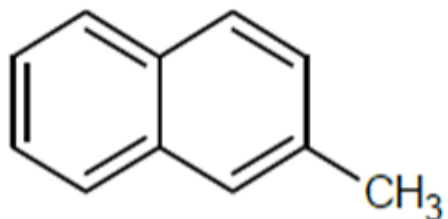
- When absorption intensity (ϵ) of a compound is increased, it is known as hyperchromic shift.
- If **auxochrome** introduces to the compound, the **intensity** of absorption **increases**.

4 • Hypochromic Effect

- When absorption intensity (ϵ) of a compound is decreased, it is known as hypochromic shift.

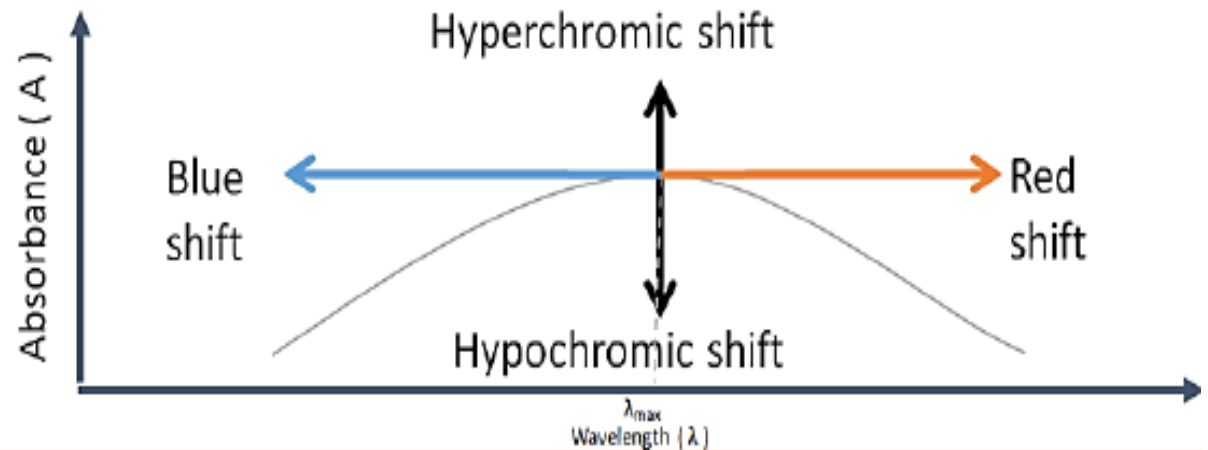


Naphthalene
 $\epsilon = 19000$



2-methyl naphthalene
 $\epsilon = 10250$

Shifts and Effects



Factors affecting UV/Vis absorption :

Biochemical samples are usually buffered aqueous solutions, which has two major advantages.

- Firstly, proteins and peptides are comfortable in water as a solvent, which is also the 'native' solvent. Secondly, in the wavelength interval of UV/Vis (700–200 nm) the water spectrum does not show any absorption bands and thus acts as a silent component of the sample.
- The absorption spectrum of a chromophore is only partly determined by its chemical structure.
- The environment also affects the observed spectrum, which mainly can be described by three parameters :
 - protonation/deprotonation (pH, RedOx).
 - solvent polarity (dielectric constant of the solvent).
 - orientation effects.

❖ Protonation/deprotonation :

- arises either from : changes in pH or oxidation/reduction reactions which makes chromophores pH- and RedOx-sensitive reporters.
- As a rule of thumb, λ_{max} and ϵ increase i.e. the sample displays a bathe- and hyperchromic shift, if a group becomes charged.

Substituent Effects

General - only the weak $n \rightarrow \pi^*$ transition occurs in the routinely observed UV

- The attachment of substituent groups (other than H) can shift the energy of the transition.
- Substituents that increase the intensity and often wavelength of an absorption are called **auxochromes**.
- Common auxochromes include alkyl, hydroxyl, alkoxy and amino groups and the halogens.

Substitution of alkyl group on the benzene ring

B-band

Bathochromic shift (red shift)

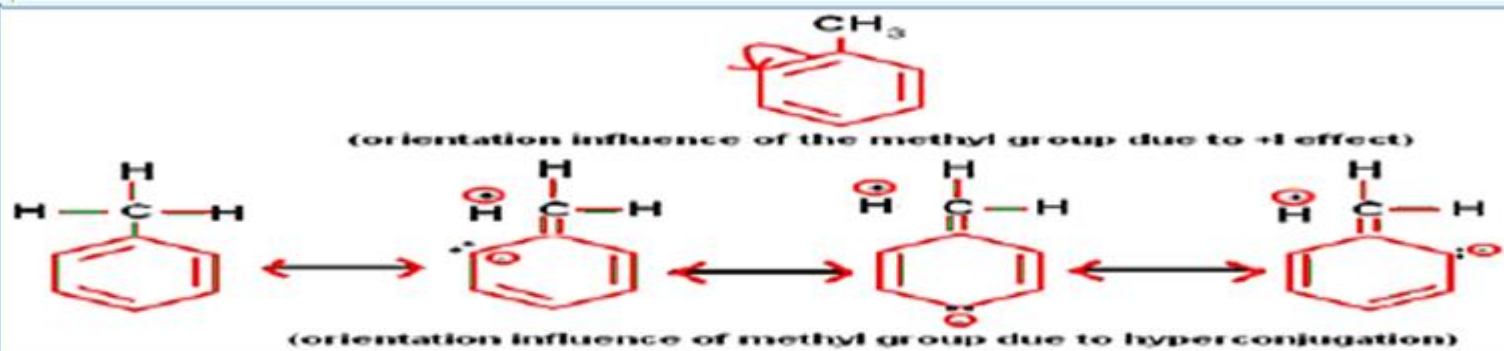
➤ But the effect of alkyl substitution upon the E-band is not clear defined

Q) Why this substitution

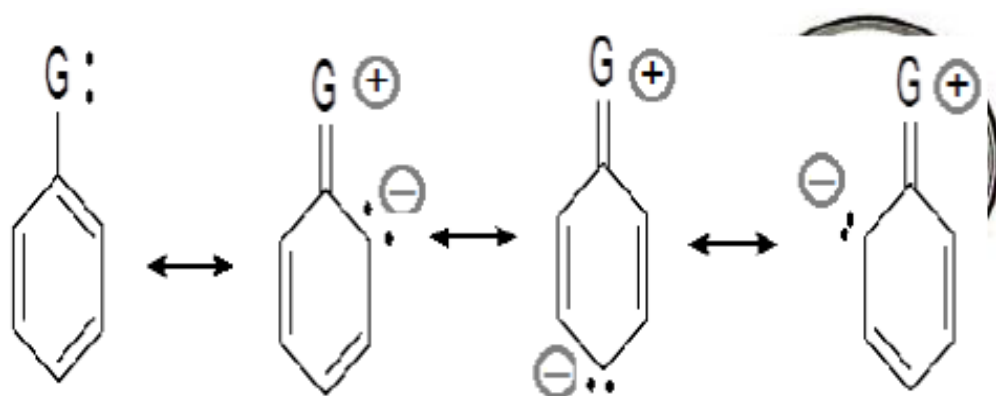
Bathochromic shift (red shift)

Ans.) that due to hyperconjugation in which the σ electrons of alkyl C-H bond participate in resonance with the ring.

Note :- the CH₃ group is more effective in hyperconjugation than other alkyl group



Compound	E2-band		B-band	
	λ_{max}	E max.	λ_{max}	E max.
Benzene	204	7,900	256	200
Phenol	210.5	8200	270	1450
Phenoxide anion	235	9400	287	2600
Aniline	230	8600	280	1430
Anilinium cation	203	7500	254	160



Q) The nonbonding electrons resonance with π bonds of the ring to increase E max. & λ_{max} . Why?

Ans.) as the nonbonding electrons are more available for interaction with the π system to greater the shift will be

- Non-bonding electrons extend the π -system through resonance – lowering the energy of transition $\pi \rightarrow \pi^*$
- More available n -pairs of electrons give greater shifts
- The presence of n -electrons gives the possibility of $n \rightarrow \pi^*$ transitions

o EWG has little effect on B band o EDG shifts B band to longer λ

- Because the unshared of electrons activating the ring by the resonance
- Decrease of excited state to **decreases** required energy for transition (red shift)

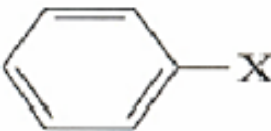
By resonance

The effect of PH :- i.e.

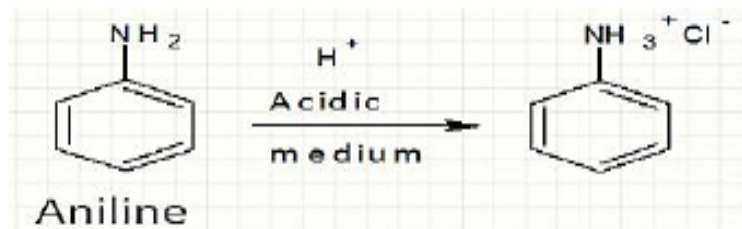
1) Aniline

2) phenol

- In arylamines the interaction of the nitrogen lone pair with the π -electron system of the ring shifts the ring's absorptions to longer wavelengths.
- Tying up the lone pair by protonation causes the UV-Vis spectrum of anilinium to resemble benzene.

	X	λ_{max} (nm)	ϵ_{max}
		E ₂ , B	E ₂ , B
Benzene	H	204, 256	7,900, 200
Aniline	NH ₂	230, 280	8,600, 1,430
Anilinium ion (resemble benzene)	NH ₃ ⁺	203, 254	7,500, 160

protonation of nitrogen eliminates the *n*-pair, raising transition energy

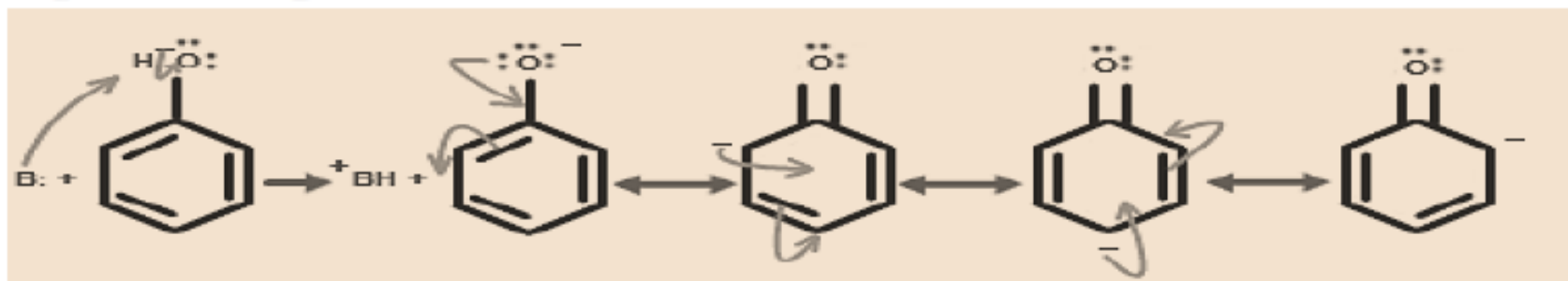


Aniline shows blue shift in acidic medium, it loses conjugation.

the pair of nonbonding electron of aniline is no longer available for interaction with π -electron system of the ring. Its spectrum almost identical to that of benzene result.

Q/ it was found that trimethyl amine in acidic media don't show absorption due to $n \rightarrow \sigma^*$?

- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an auxochrome or by the change of solvent.
- e.g. An auxochrome group like $-\text{OH}$, $-\text{OCH}_3$ causes absorption of compound at longer wavelength.



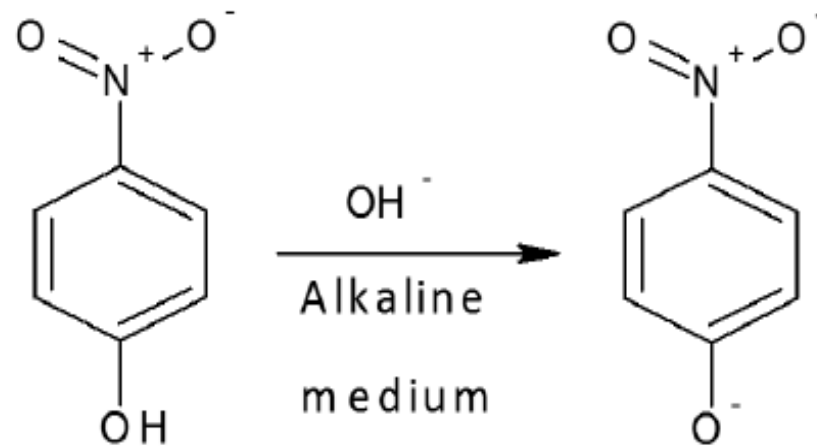
bathochromic shift of the E2 and B-bands and increase in ϵ_{max} .

Compound	E2-band		B-band	
	λ_{max} .	E max.	λ_{max} .	E max.
Benzene	204	7,900	256	200
Phenol	210.5	8200	270	1450
Phenolode anion	235	9400	287	2600

The negative charge of oxygen delocalizes more effectively than the unshared pair of electron

deprotonation of oxygen gives more available n -pairs, lowering transition energy

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.

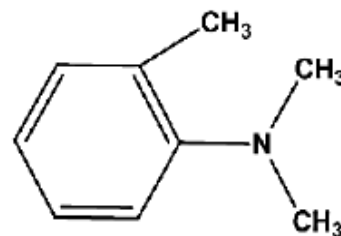
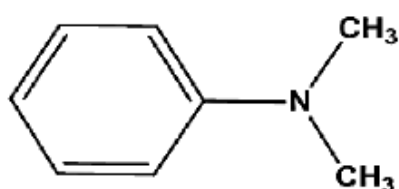


p-nitrophenol

$\lambda_{\text{max}} = 255 \text{ nm}$

$\lambda_{\text{max}} = 265 \text{ nm}$

Thus, bulky substitution in the ortho position of molecules such as N,N-dimethyl aniline cause a hypsochromic (Blue shift) shift in the E2 band & accompanied by a marked reduction E max



ortho

N,N-dimethyl aniline

λ_{max} 251

ϵ_{max} 15.500



2-methyl-N,N-dimethyl aniline

248 \rightarrow λ

6360 \rightarrow ϵ_{max}

\downarrow (the) nonbonding e pair of N not effectively interaction w(with) the π .es of \wedge ring . (not completely parallel)

* This effect in case of O > m >>> P \leftarrow very very \downarrow