UV Spectroscopy

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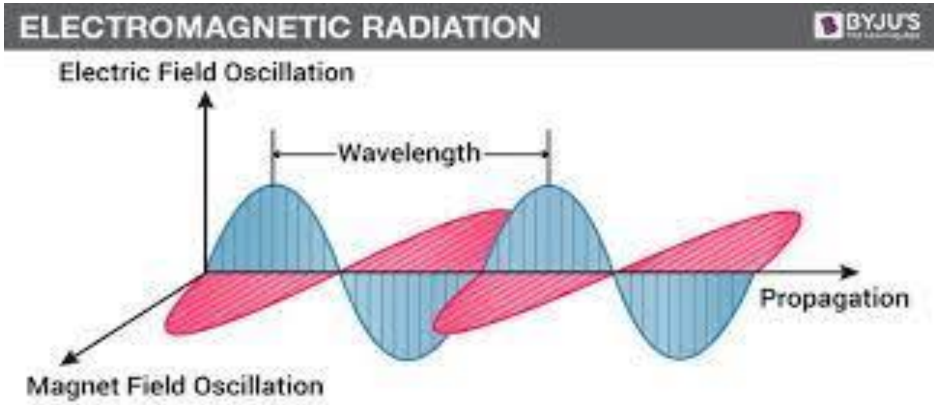
What is Spectroscopy?

The branch of science which describe interactions of electromagnetic radiation with matter known as Spectroscopy.

Electromagnetic Radiation

- *This is a type of energy, described by two complementary theories: wave theory and corpuscular theory and transmitted through space at enormous velocities.*
- *The propagation of this wave involves both electric and magnetic forces and is commonly known as electromagnetic radiation.*

The electric and magnetic vectors oscillates in two mutually perpendicular planes.



These radiations travel with a velocity 2.997x10^8 m/sec

- This type of radiation is described in terms of

i) Wave length (λ): Distance between two consecutive points which are in the same phase. Micron (μ) = 10^{-4} cm; mili micron (mμ)= 10^{-7} cm; 1 nm = 10^{-7} cm; Angstrom = 10^{-8} cm.

ii) **Frequency of radiation:** (ν) Number of wave length in the distance travelled in 1 sec. $\boldsymbol{\nu = c/\lambda}$ cycles/ sec or Hertz

iii) **Energy of Photons (E) :** $E = h\nu$ Electromagnetic radiation consists of a stream of energy packets known as photons, expressed in Joule or K Cal.

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

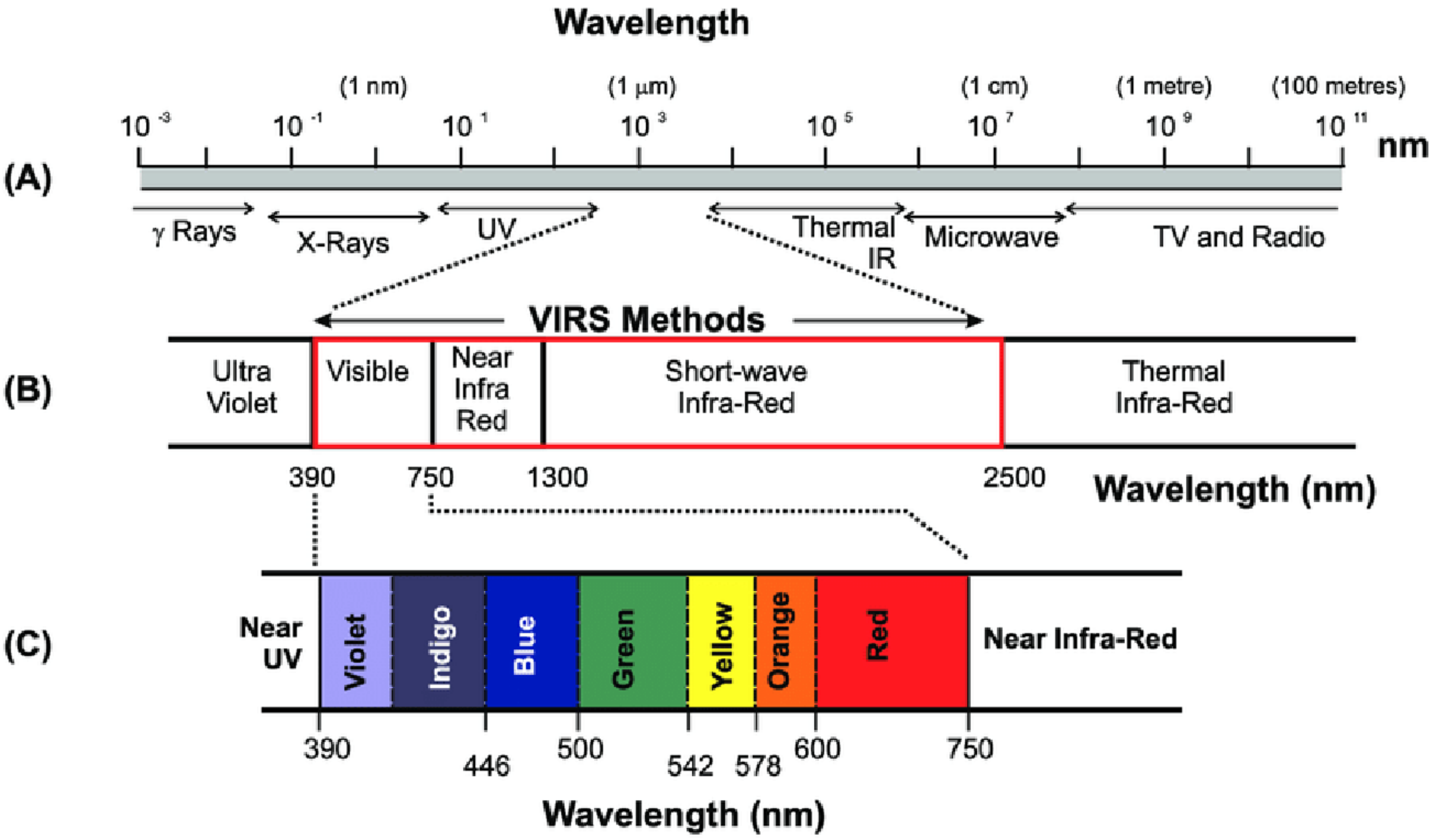
$$\mathbf{E = hc/\lambda}$$

So energy of radiations depend upon frequency and wavelength of radiation.

The total electromagnetic radiations range from short waved cosmic ray to long waved radio frequencies.

The higher the frequency, higher is the energy; longer the wavelength, lower the energy.

Electromagnetic Spectrum



Γ ray : 0.001 -0.1 nm; x-ray: 0.1-100 nm; UV(vacuum): 100-200 nm: UV: 200-400 nm

Types of Spectroscopy and general principle

The fundamental principle of spectroscopy is based on the absorption of certain amount of energy required for transition from a state of lower energy to a state of higher energy. The energy needed is directly proportional to frequency of electromagnetic radiation that causes transition.

Atomic Spectroscopy : Energy absorbed can only be used to raise the energy levels of electrons. Example : Atomic absorption spectroscopy, Flame spectroscopy.

Molecular Spectroscopy: Energy change occurs at molecular level. Example UV, Infrared and rotational Spectroscopy.

UV Spectroscopy: Molecules possess different quantized electronic energy level as a result of specific electronic arrangement under the influence of a set of nuclei. For each molecule there is low energy ground electronic level and different excited electronic levels. Due to absorption of electromagnetic radiation UV region transition occurs between two electronic levels. So UV spectroscpy is known as **Electronic Spectroscopy**

Molecules possess **rotational energy** due to rotation along all the coordinate axis or symmetry axis.

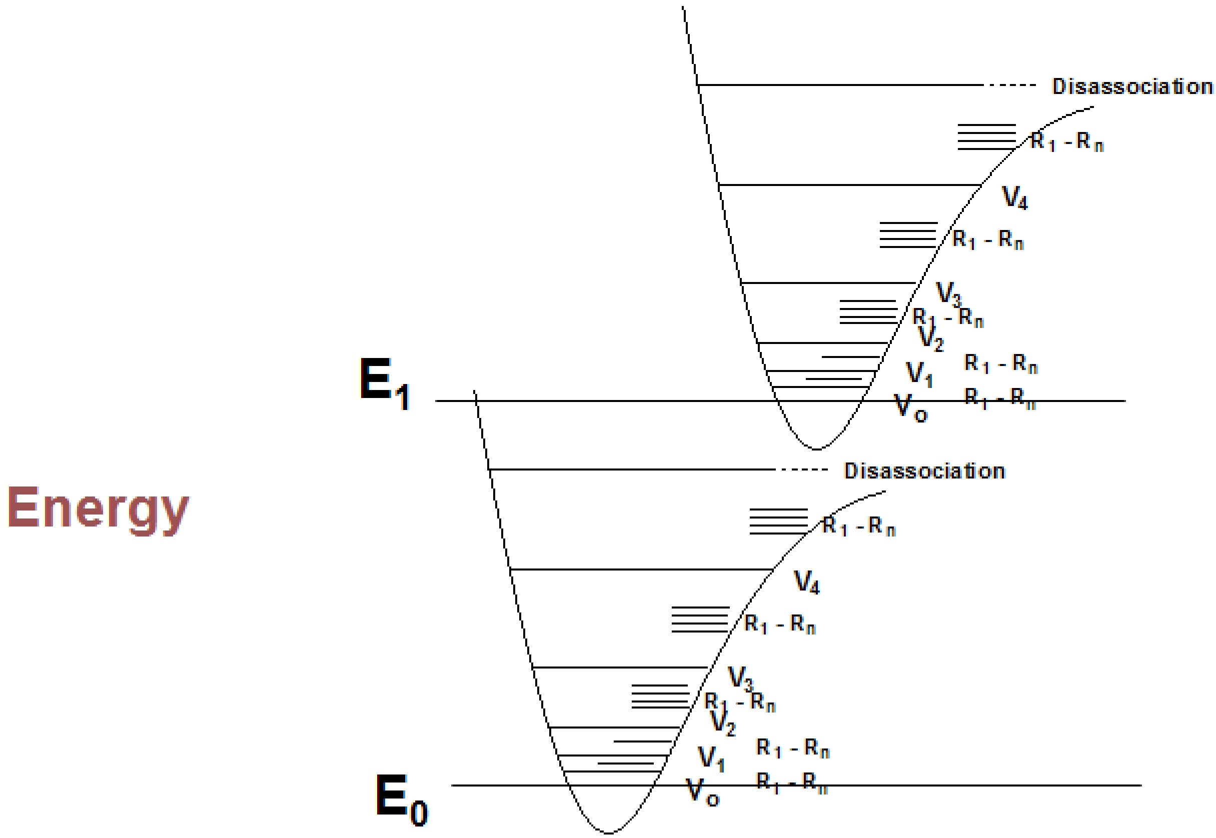
Molecules can also have **energy of vibration** as a result of vibration of its bonds

Molecules possess translational energy due to constant motion in space. According to Quantum Mechanics, molecules which I are confined to move in a small region can have only certain energy levels i.e. energy is quantized.

Total energy of a molecule = Electronic + Vibrational + Rotational

E_0 represents Ground electronic level, E_1 represents first excited state. Each electronic level is associated with number of vibrational levels represented by vibrational quantum no. v. Each vibrational level in each turn is associated with number of sublevels represented by rotational quantum number J. The enegy difference between two electronic levels is highest and much larger than energy difference between two vibrational levels.

UV tend to give wide overlapping **Absorption bands instead of absorption lines.** A change in the electronic energy level is accompanied by a corresponding change in the vibrational, rotational energy levels. Electronic transitions are superimposed by vibrational and rotational transitions so that an envelop of transitions arises.



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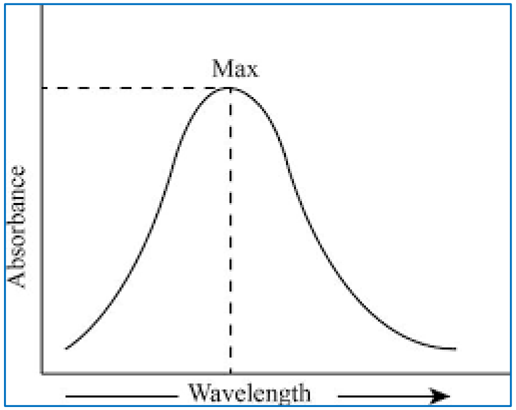
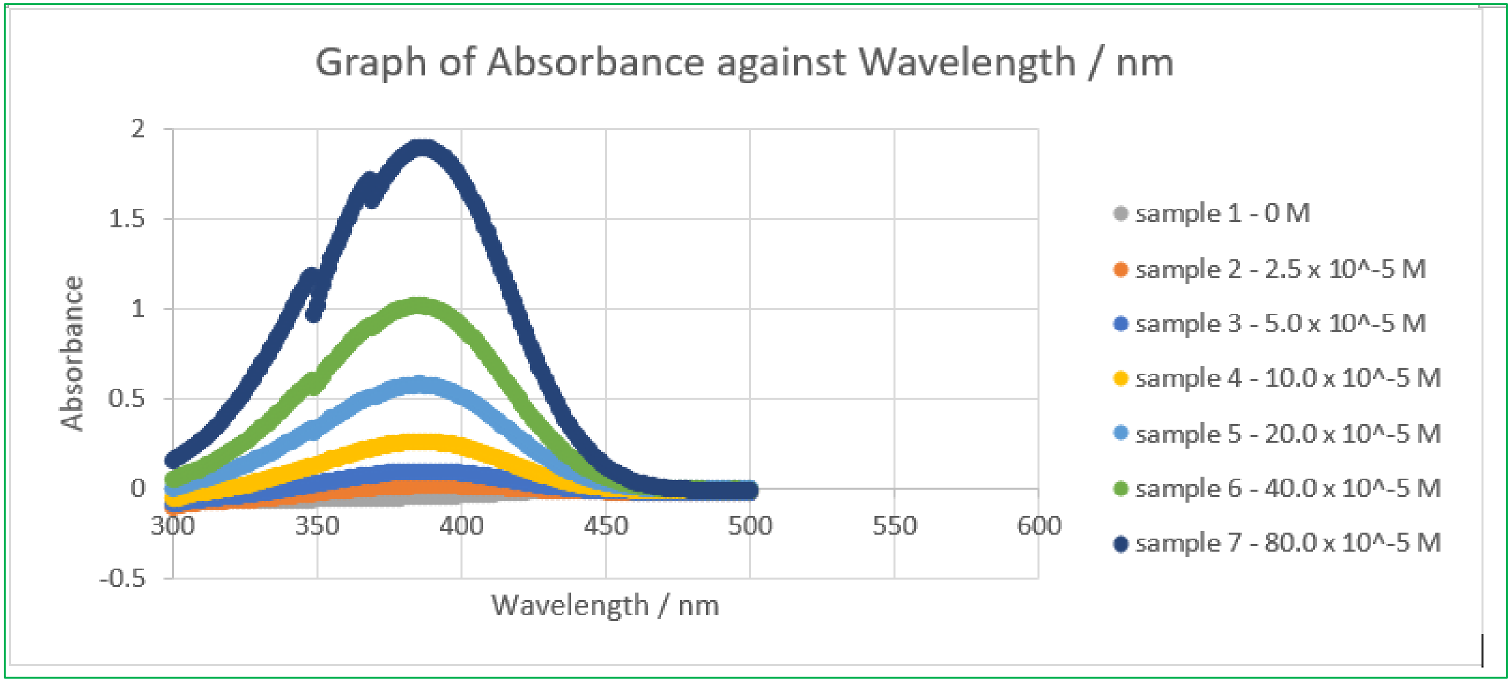
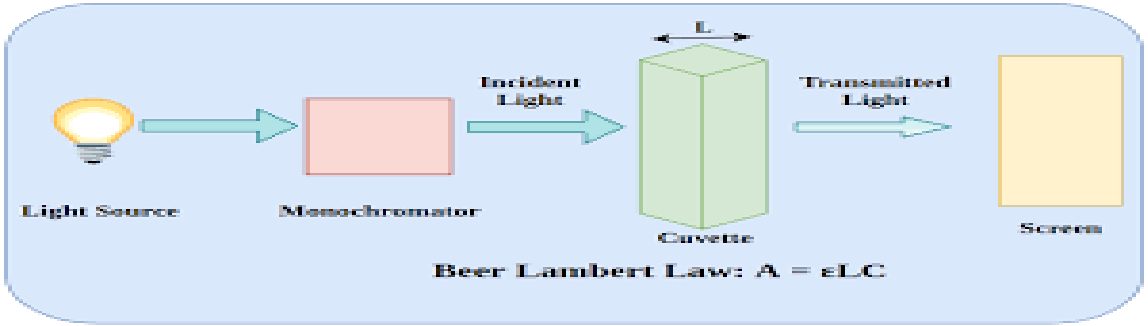
When UV light is passed through a solution of organic substances, intensity of absorption varies with change in the wavelength of the radiation. At a particular wavelength absorption is maximum, known as λmax.





Lambert Beer Law



Lamberts law states that when a monochromatic light is passed through a transparent homogeneous medium of a compound, the intensity of transmitted light decreases exponentially with increase in the thickness of the absorbing medium.

$$\ln I_0/I_t = kl$$

where I_0 = Intensity of the incident light, It = Intensity of the transmitted light.

l = thickness of the absorbing medium.

Beers law states that intensity of the transmitted light decreases exponentially as the concentration of the absorbing medium increases.

$\ln I_0/ I_t = K' C$ where C is the concentration of the absorbing medium.

Combining two equations,

$$\ln I_0/I_t = kk'lC$$

$$\text{Log } I_0/I_t = \epsilon Cl$$

$A = \epsilon Cl$ where ϵ = molar absorptivity or strength of absorption; and A = Optical density or absorbance.

Theory of Electronic Spectroscopy (UV and Visible region)

UV spectroscopy deals with the absorption of Electromagnetic radiation in UV region(200-400 nm) and Visible region (400-800 nm).

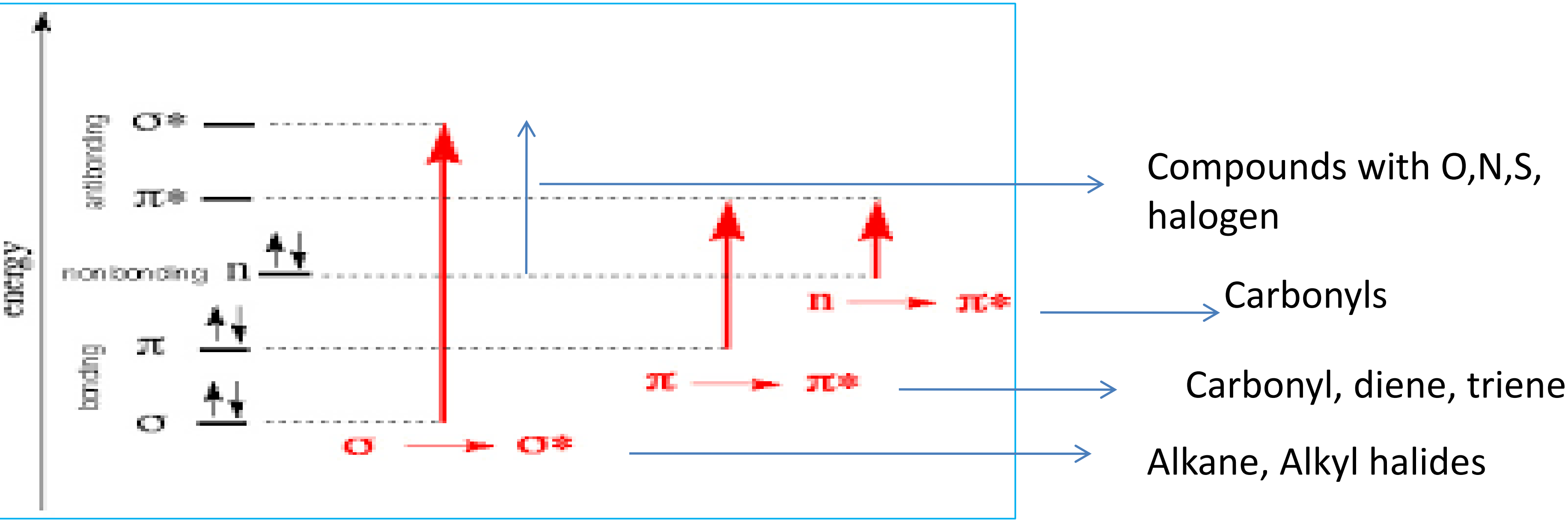
Valence electrons undergo transitions and promoted to higher energy vacant orbitals by absorbing radiation.

The type of absorption depends on th nature of electrons present in a particular molecule.

Types of Transitions

i) σ-σ*
ii) π-π*
iii) n-π*
iv) n-σ*

Probable transitions in UV region

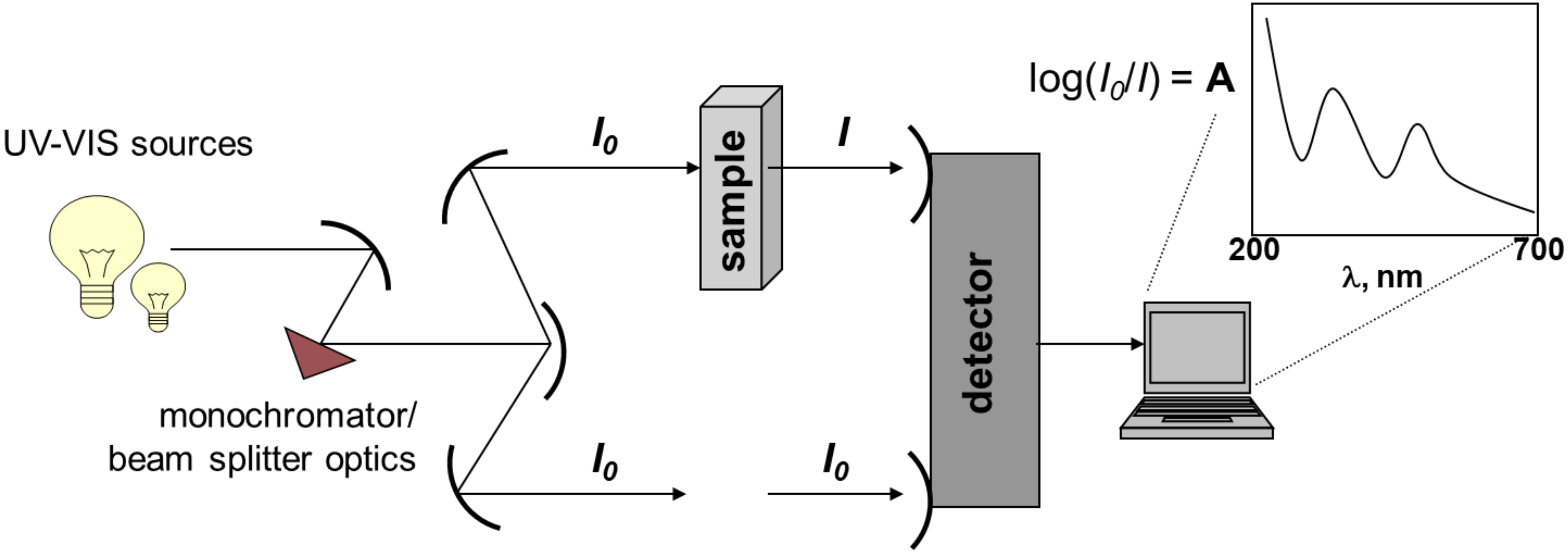


Compounds with O,N,S, halogen

Carbonyls

Carbonyl, diene, triene

Alkane, Alkyl halides



A Spectrophotometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus the instrument compare the intensity of the transmitted light with that of the incident light.

Light sources are Tungsten filament lamp and hydrogen deuterium lamp which cover whole of the UV visible region.

Solvent: 95% Ethyl alcohol is used as solvent. Water and hexane are also used.

Quartz cell is used as container where solution is taken as quartz is transparent in UV region.

σ – σ* transition

- σ electron from bonding orbital is excited to antibonding orbital σ*.

- Energy required for this transition is very high.
-
- This transition is observed with saturated compounds. Eg saturated hydrocarbon
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- The organic compounds where all valence shell electrons are involved in the formation of σ bond do not show absorption in normal UV region. They require high energy radiation below 200 nm where the entire region should be evacuated (vacuum UV region)

- Special equipment to study vacuum UV is needed.

n – σ* transition

- Saturated compounds with hetero atom having non bonded pair of electrons like O, N, S, halogen are capable of showing this transition.

- This transition requires lesser energy than σ – σ* transition.
- The molecules like alcohols, thiols amines and alkyl halides absorb in ordinary UV region. CH_3OH : 183 nm; Me_3N: 227 nm

- In saturated alkyl halides, the energy required for this transition decreases with increase in the size of the halogen atoms.

  Methyl chloride λ_{max} = 173 nm
- Methyl Iodide λ_{max} = 258 nm.

- This type of transitions are very sensitive to hydrogen bonding eg alcohols, amines and require greater energy.

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π –π* Transition

- Observed in molecules with unsaturated centers such as compounds having double and triple bonds, simple alkenes, aromatic compounds, cyanides, azo etc.

- π electrons in a bonding orbital is excited to corresponding antibonding orbital π*.

- Requires still lower energy as compared to n –σ*

- Absorption usually occurs in the ordinary UV region.

- Alkenes generally absorb in the region 170-205 nm and simple carbonyl absorbs at 180 nm.

n – π* transition

- Electrons of unshared pair on hetero atom (n orbital) is excited to π* anti bonding orbital.

- Compounds containing double bonds involving hetero atoms (C=O, N=O) undergo such type of transitions.

- This transition requires minimum energy of all transitions and shows absorption at longer wavelength around 300 nm., but of low intensity. Here the magnitude molar extinction coefficient for a particular absorption is directly proportional to the probability of particular transition. This transition is symmetry forbidden.

Chromophores

A. Definition

1. Previously the term was used to define a system responsible for imparting colour to a molecule or molecule containing a chromophore should be coloured. Examples are azo group, nitro group.

2. Since similar functional groups will have electrons capable of discrete classes of transitions, the characteristic energy of these energies is more representative of the functional group than the electrons themselves

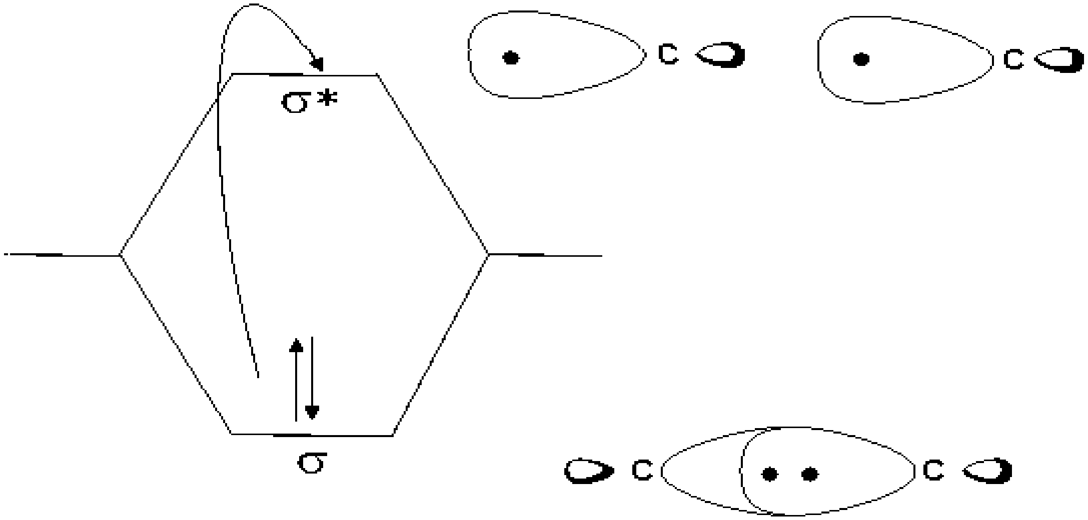
3. Any isolated functional group (covalently unsaturated group) not in conjugation with other groups capable of having characteristic electronic transitions due to absorption electromagnetic radiation in the UV region is called a chromophore (color loving) . Some important chromophores are ethylenic, carbonyls, acids, esters, nitriles etc.

4. Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions

Organic Chromophor

Alkanes – only posses σ-bonds and no lone pairs of electrons

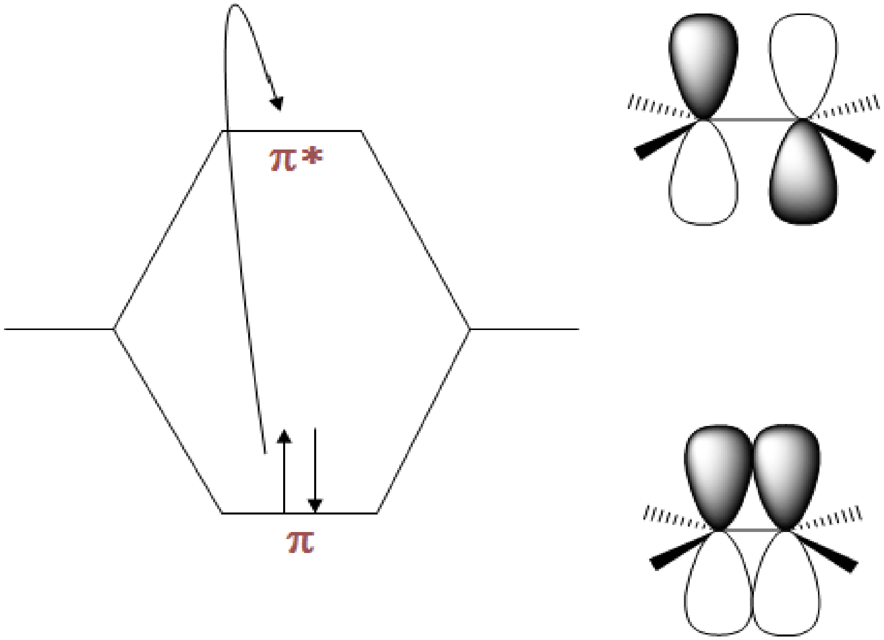
only the high energy σ → σ* transition is observed in the far UV



B. Organic Chromophores

3. Alkenes and Alkynes – in the case of isolated examples of these compounds the π → π* is observed at 175 and 170 nm, respectively

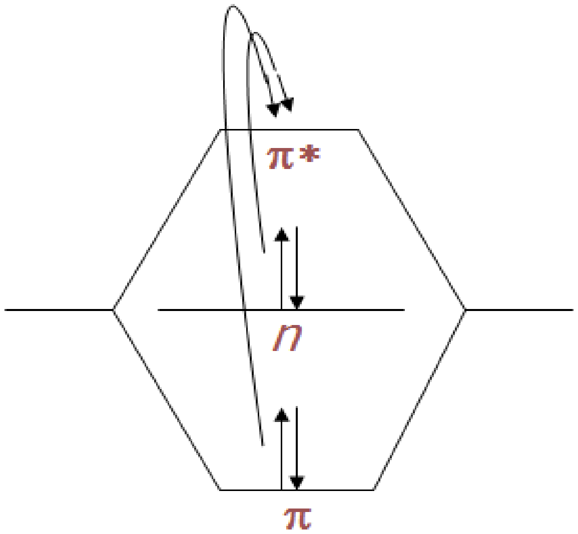
   Even though this transition is of lower energy than σ → σ*, it is still in the far UV – however, the transition energy is sensitive to substitution



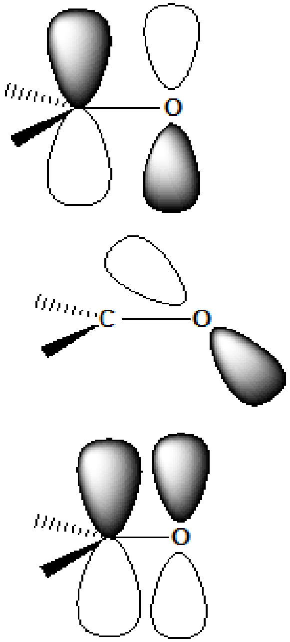
Carbonyls – unsaturated systems incorporating N or O can undergo $n \rightarrow \pi^*$ transitions (~285 nm) in addition to $\pi \rightarrow \pi^*$. Despite the fact transition is forbidden by the selection rules (e = 15), it is the most often observed and studied transition for carbonyls

This transition is also sensitive to substituents on the carbonyl

Similar to alkenes and alkynes, non-substituted carbonyls undergo the $\pi \rightarrow \pi^*$ transition in the vacuum UV (188 nm, e = 900); sensitive to substitution effects



σ_{CO} transitions omitted for clarity



It has been determined from spectral studies, that carbonyl oxygen more approximates sp rather than sp^2 !

Auxochromes

These are coordinately saturated functional groups which do not absorbs radiation in UV region, but when present in conjugation with a chromophore enhances the absorbing properties of chromophore.

Auxochromes include methyl, halogens, -OH, -OR,, $-NH_2$, -NHR, $-NR_2$

Benzene-λ_{max} =255 nm

Phenol-λ_{max} =270 nm

Aniline-λ_{max} =280 nm

Absorption & Intensity Shift

1. **Bathochromic Shift (red Shift)**

   Shift of absorption maximum towards longer wave length and lower enrgy due to increase in conjugation either by the presence of an auxochrome or by the presence of an additional chromophore in conjugation with parent one.

2. **Hypsochromic Shift (blue shift)**

- Shift of absorption maxima towards shorter wavelength or to higher energy caused by removal of conjugation or by changing the polarity of solvent. Aniline has λ_{max} 280 nm but in acid medium the value decreases to 203 nm.

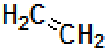
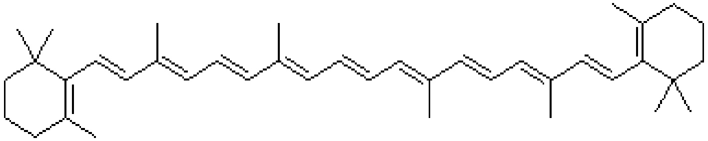
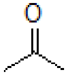
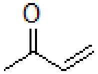
3. **Hyperchromic Shift**

   Intensity of absorption maxima increases. B-band for pyridine at 257nm is shifted to262 nm, ϵ 3560 for2-methyl pyridine. The introduction of auxochrome increases the intensity of absorption.

4. **Hypochromic Shift**

   In this case intensity of absorption maxima decreases. Introduction of group which distorts the geometry of the molecule causes hypochromic effect. Biphenyl has λmax 250 nm and ϵmax 19000 where as 2-methyl biphenyl has λmax 237nm and εmax 10250. The lower values are due to distortion.

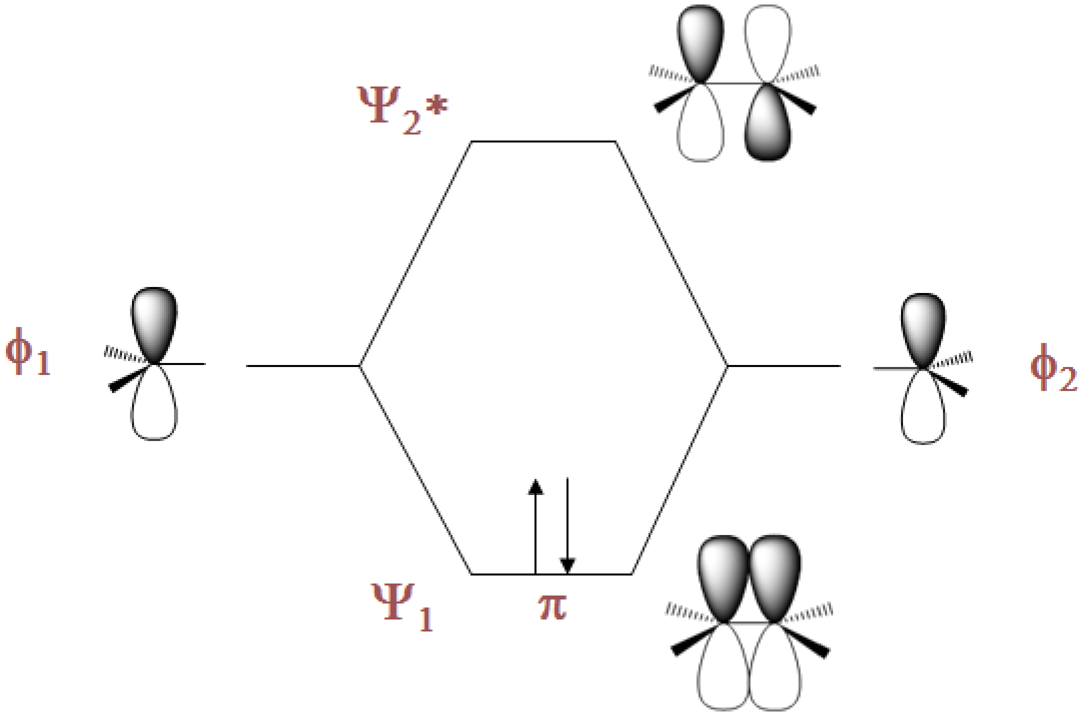
Conjugation is the most efficient cause of bringing Bathochromic shift and hyperchromic shift of an unsaturated chromophore.

		λ_{max}	ϵ
		175	15,000
		217	21,000
		258	35,000
 β-carotene		465	125,000
	$n \rightarrow \pi^*$	280	12
	$\pi \rightarrow \pi^*$	189	900
	$n \rightarrow \pi^*$	280	27
	$\pi \rightarrow \pi^*$	213	7,100

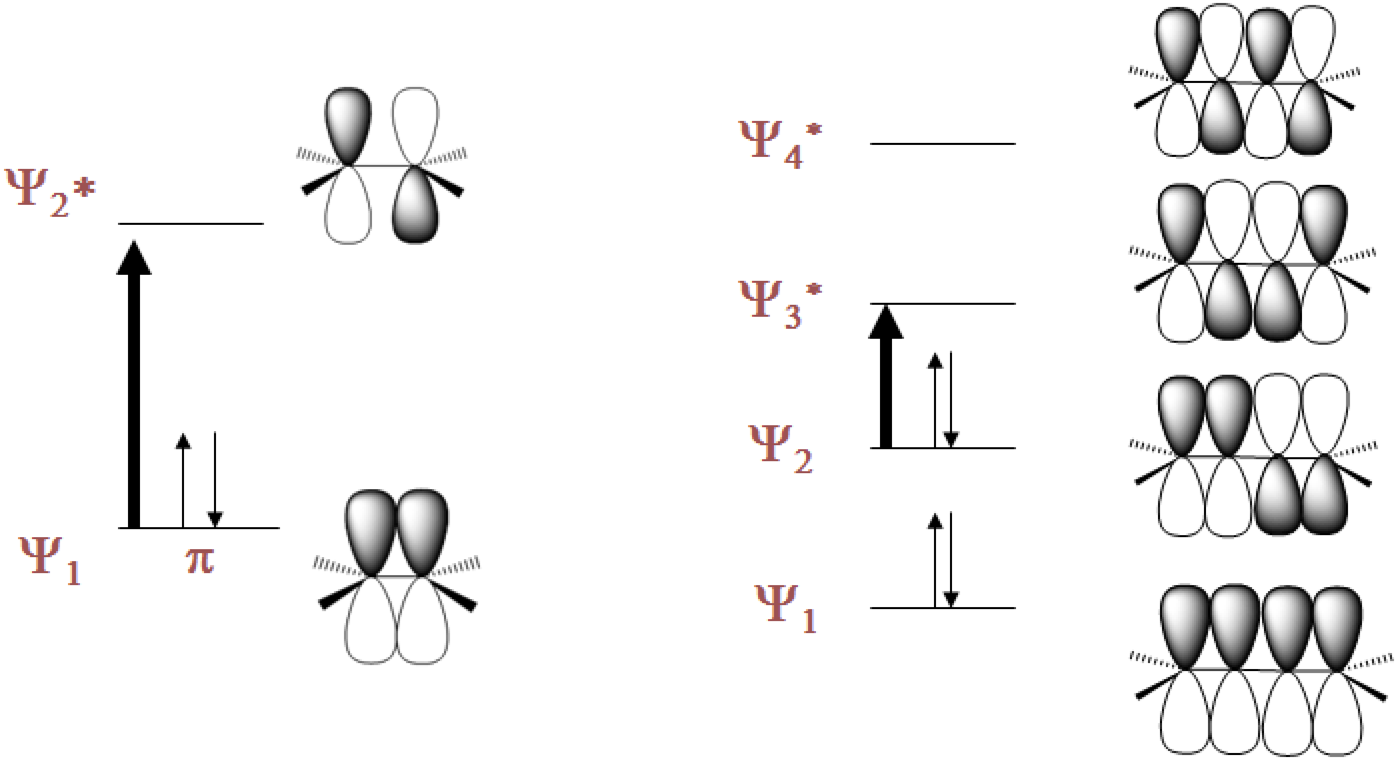
Conjugation

Alkene- The observed Bathochromic shifts from conjugation imply that an increase in conjugation decreases the energy required for excitation of electron.

For ethylene electronic transition occurs from filled MO to antibonding vacant MO.

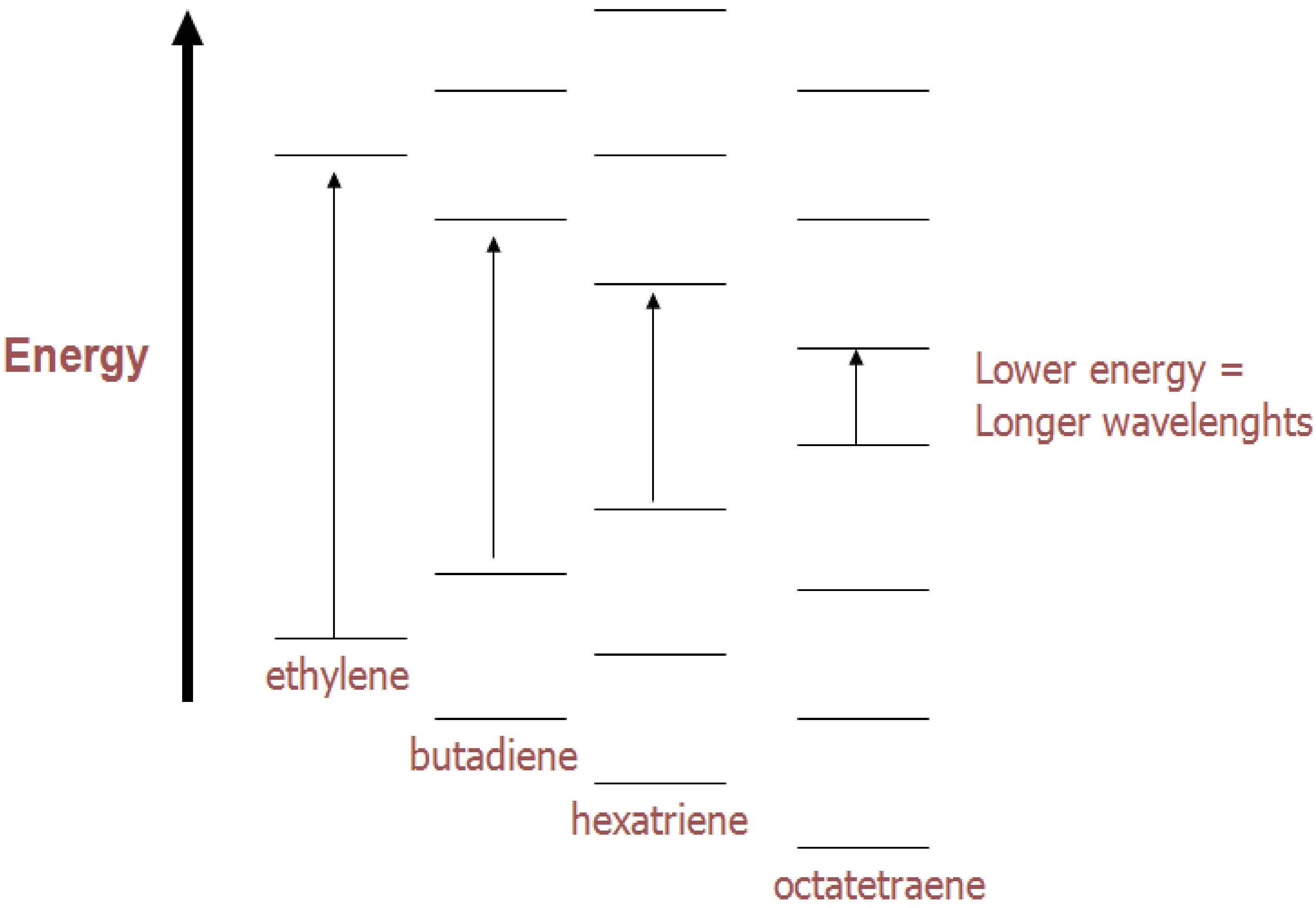


For butadiene 4 p orbitals undergo linear combination to form 4 molecular orbitals. Energy of transition is reduced due to conjugation. Electronic energy levels of a chromophore move closer together. The light wave of longer wavelength is absorbed.

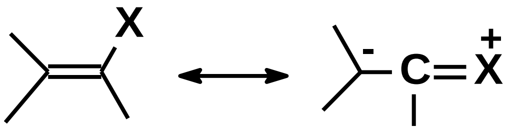


ΔE for the HOMO → LUMO transition is **reduced**

The longer is the conjugated system, the energy gap between HOMO and LUMO is lesser. Vitamin A having five congugated double bonds absorbs at 325 nm (visible region)

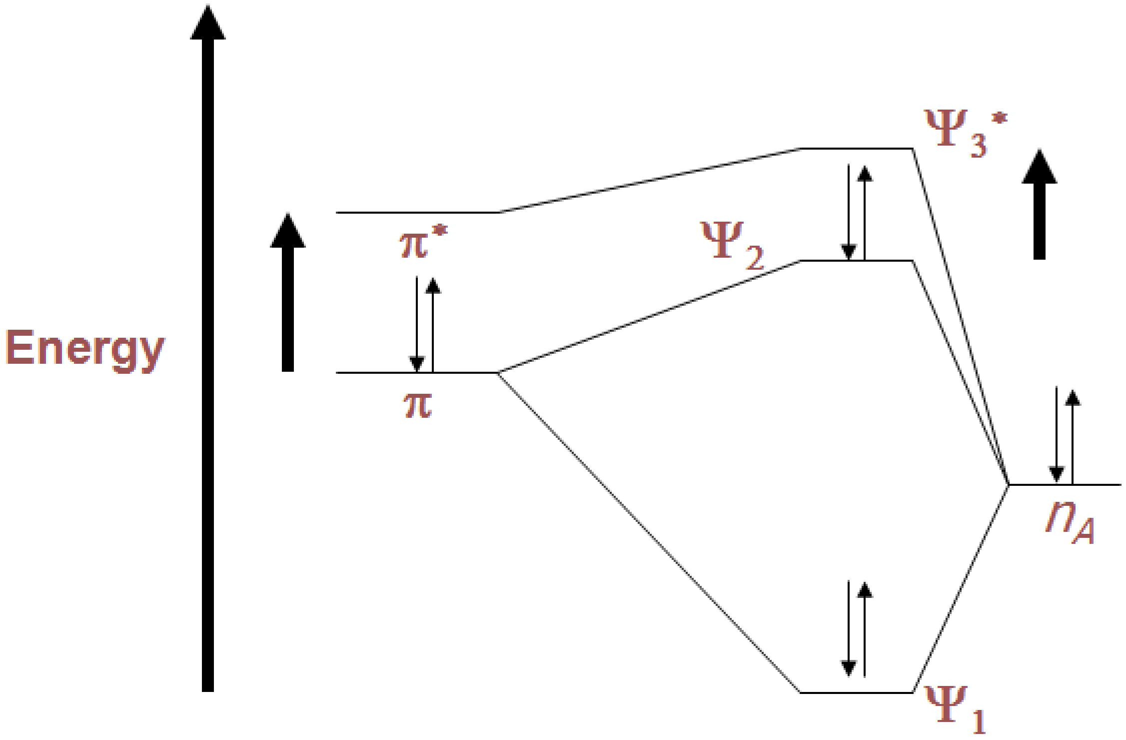


Effect of Auxochrome in Bathochromoc shift

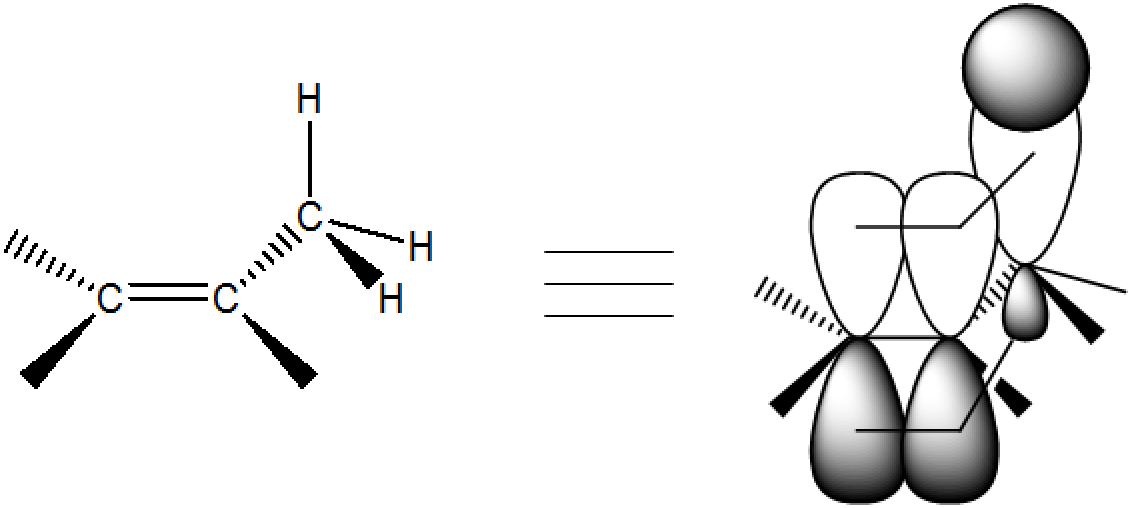


Conjugation is extended due to presence of **Auxochromes**. The lone pair of electrons on N,O, S and halogens can extend conjugated system. Resonance interaction of this lone pair with double bonds increases the length of conjugation.

Here 3 MOs are created though interaction is not strong as in conjugated π system.



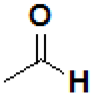
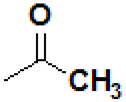
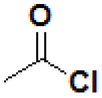
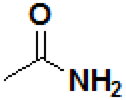
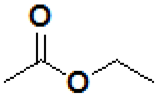
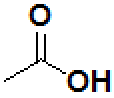
Methyl groups also cause Bathochromic shift through σ-π conjugation, also known as hyperconjugation or sigma bond resonance.



UV Spectra of Carbonyl, Substituted Carbonyl and α,β Unsaturated Carbonyl

Important absorption observed for carbonyl compounds are i) π-π* transition (intense absorption) ii) n-π* transition (weak or forbidden).

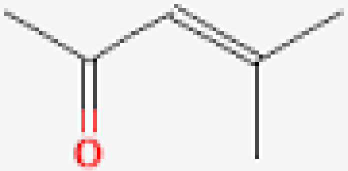
Presence of Auxochrome adjacent to carbonyl gives a pronounced hypsochromic shift of n-π* transition.

	293 nm
	279
	235
	214
	204
	204

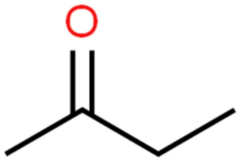
This is explained by the inductive withdrawal of electrons by O,N or halogen from the carbonyl carbon, thereby lone pair of electrons on carbonyl oxygen become tightly held

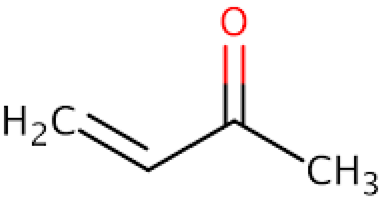
It is important to note that this is different from Auxochromic effect on π-π* which extends conjugation and causes a Bathochromic shift

α, β- Unsaturated Carbonyl Compounds



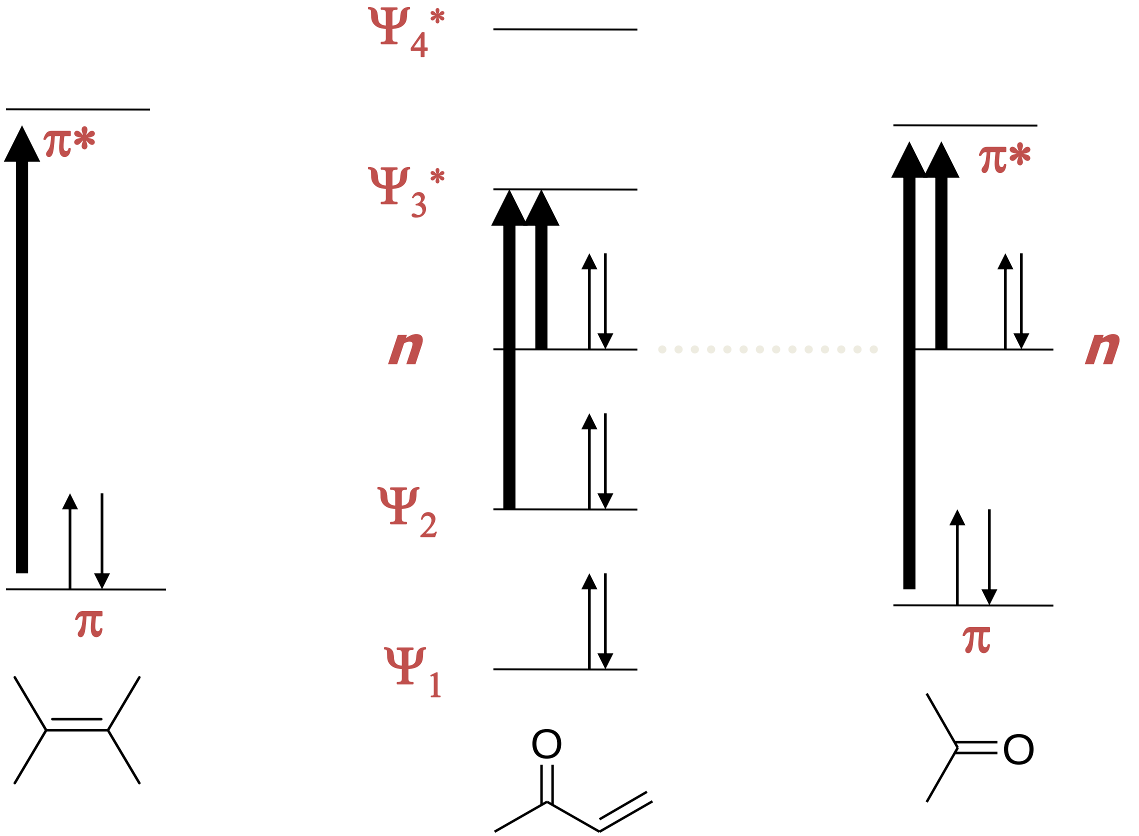
>C=O bond is in conjugation with C=C bond
Energy difference between HOMO and LUMO decreases. So both π-π* and n-π* transitions are at longer wave length than in simple carbonyl compound.



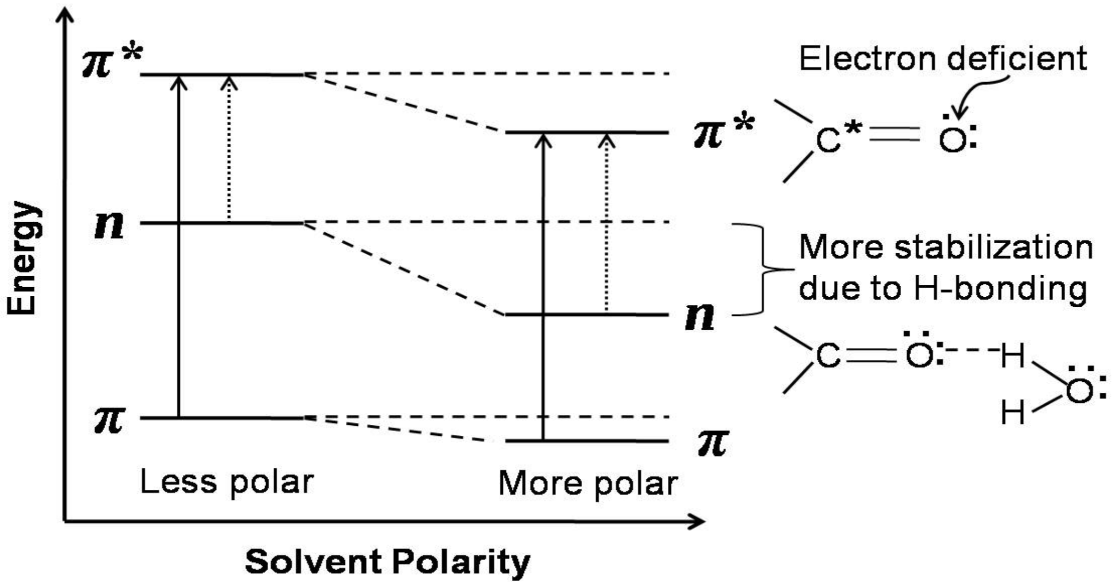


n-π*	λmax : 277nm	λmax: 324nm
π-π*	λmax: 185 nm	λmax: 219 nm

MO diagrams of Alkene, Enone and Ketone



Solvent Effects of Compounds having Polar functional groups.



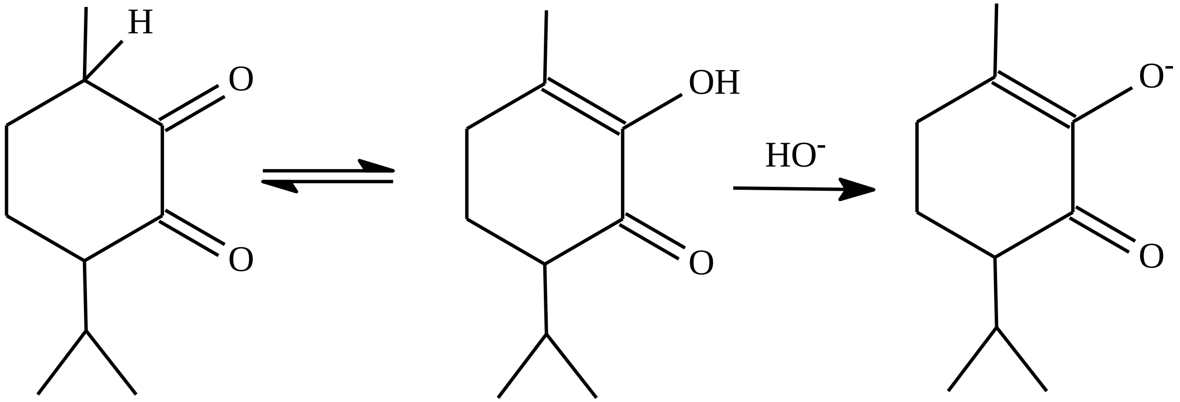
Absorption band is shifted when spectrum is recorded in polar solvent in comparison to non polar solvent.

R band (n-π* transition) is shifted to lower wave length or shows a **Blue shift** on increasing polarity.

K band (π-π* transition) is shifted to longer wave length or shows **Red Shift.**

Mesityl Oxide in n-hexane K band 230 nm(12600); R band 327 nm(98)
in water K band 245 nm(10,000); R band 305 nm(60)

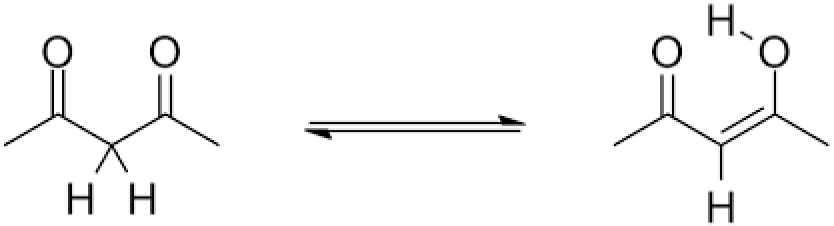
α-Diketones and β-Diketones



Diketo form

Enolic form (more stable)
α,β-unsaturated ketone λmax: 270 nm

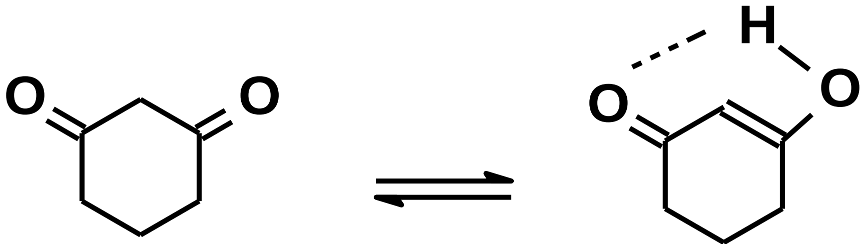
Enolate
λmax : 320 nm



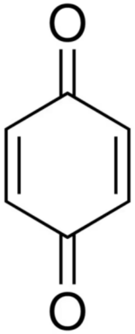
Enol form of β-diketone is stabilised by intramolecular H-bonding.

In H_2O % of Enol : 15%
In non polar solvent %of enol : 91-92%

λ H_2O = 274 nm; ε = 2050
λ(Isooctane) = 272 nm; ε = 12000



This 1,3-diketone exists exclusively in enol form, even in polar solvent due to formation of strong H-bonding. Very strong absorption observed. Λmax : 253 nm and ϵ: 22,000



P-Benzoquinone

Spectrum is similar with that of α,β-unsaturated ketone. A strong K band at 242 nm and a weak R band near 434 nm are observed.

UV Spectroscopy

Band Structure

1. Unlike IR (or later NMR), where there may be upwards of 5 or more resolvable peaks from which to elucidate structural information, UV tends to give wide, overlapping bands

2. It would seem that since the electronic energy levels of a pure sample of molecules would be quantized, fine, discrete bands would be observed – for atomic spectra, this is the case

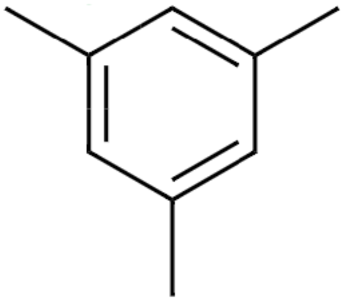
3. In molecules, when a bulk sample of molecules is observed, not all bonds (read – pairs of electrons) are in the same vibrational or rotational energy states

4. This effect will impact the wavelength at which a transition is observed – very similar to the effect of H-bonding on the O-H vibrational energy levels in neat samples

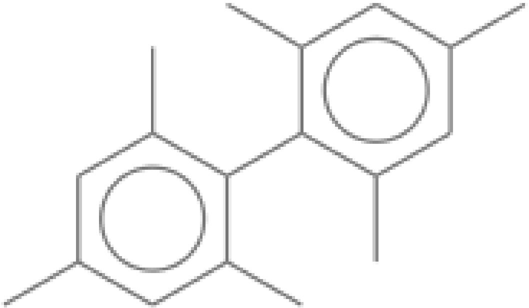
Steric inhibition of Resonance

If a π electron system is prevented from achieving co-planarity, the degree of conjugation decreases and Bathochromic shift is not observed.

λmax 266 nm:
ε: 260

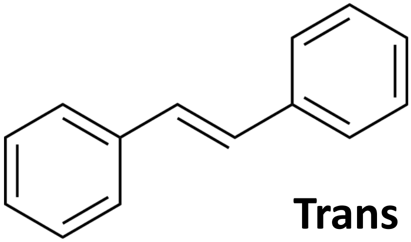


mesitylene



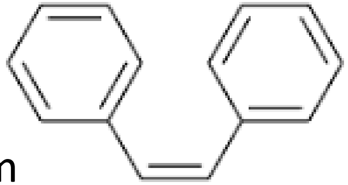
λmax 267 nm:
ε: 545

Bi-mesitylene: one ph nucleus is almost perpendicular to the other to avoid steric hindrance.



Trans Stilbene
λmax 295 nm

Cis Stilbene
λmax 280nm



Ph groups are as far apart from each other, remain in the same plane with C=C linkage. So conjugation is extended.

Non bonded interaction between two ortho H's of Ph ring prevent them to be in the same plane.

Structure Determination

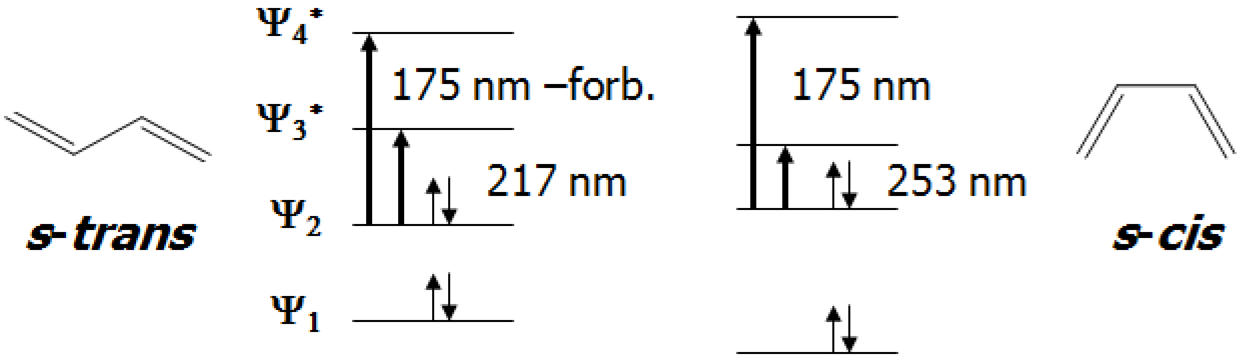
A. Dienes

1. For acyclic butadiene, two conformers are possible – s-cis and s-trans

The s-cis conformer is at an overall higher potential energy than the s-trans; therefore the HOMO electrons of the conjugated system have less of a jump to the LUMO – lower energy, longer wavelength

1. General Feature

Two possible p → p* transitions can occur for butadiene $ϒ_2$ → Y_3^* and Y_2 → Y_4^*



The Y_2 → Y_4^* transition is not typically observed:

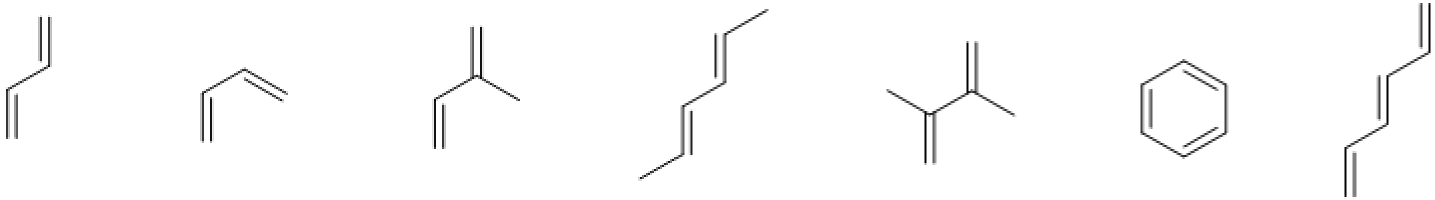
The energy of this transition places it outside the region typically observed – 175 nm

For the more favorable s-trans conformation, this transition is forbidden

The Y_2 → Y_3^* transition is observed as an intense absorption

HOMO- LUMO transition is observed as an intense transition band at λmax 217nm within the observed region of UV.

This band is sensitive to bathochromic or hyperchromic shift due to alkyl substituent or further conjugation.



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

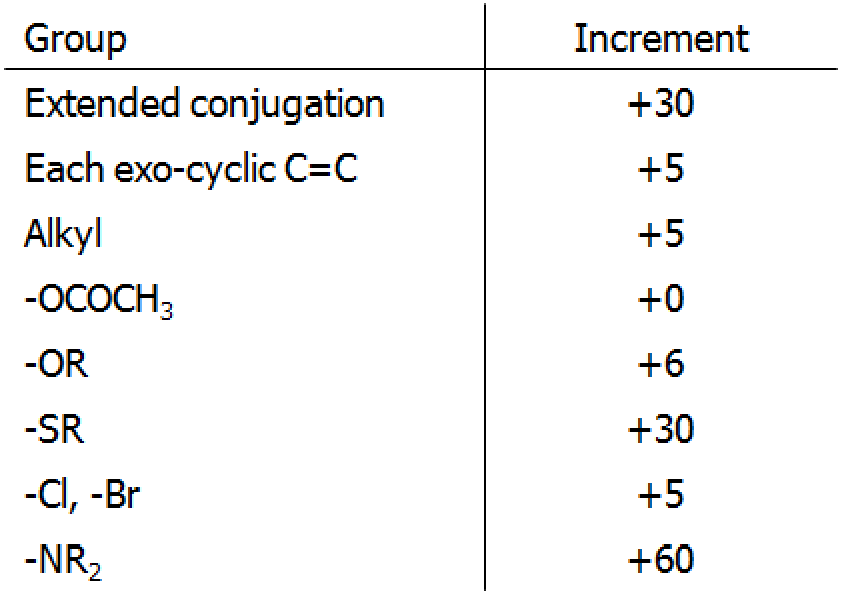
Woodward –Fieser rule for Diene, Triene and cyclic diene , triene

Woodward and Fieser performed extensive studies of terpene and steroidal alkenes and noted that similar substituents and structural features would lead to an empirical prediction of the wave length for lowest energy π-π* transition.

The rule begin with a base value assigned for λmax of the chromophore butadiene (hetero annular or open chain diene) as 217 nm.

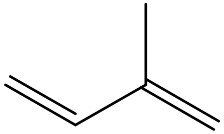
For homoannular diene ,the base value is 253 nm.

The incremental contribution of substituents is added to the base value from the table.



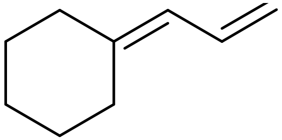
Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
$-OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
$-NR_2$	+60

Examples of Diene systems



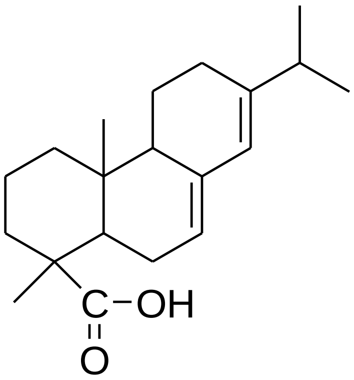
Isoprene
Acyclic Butadiene : 217 nm
One alkyl substituent: +05 nm
Total: 222 nm

Experimental value: 220 nm

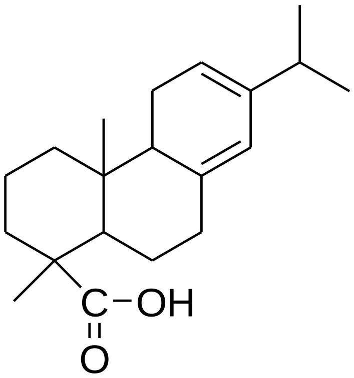


Allylidene Cyclohexane
Acyclic butadiene : 217 nm
One exocyclic double bond: 05 nm
2- alkyl substituents: 10 nm
Total 232 nm
Experimental value 237 nm

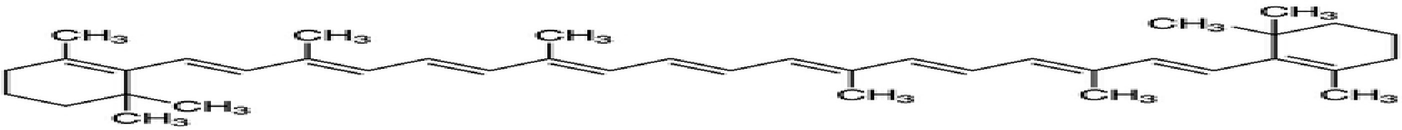
Woodward Fieser Rule : Cyclic Diene



Hetero annular diene :	217 nm
One exocyclic double bond:	05 nm
4- alkyl substituents:	20 nm
Total	239 nm
Experimental value	237 nm



Homo annular diene :	253 nm
One exocyclic double bond:	05 nm
4- alkyl substituents:	20 nm
Total	278 nm
Experimental value	280 nm



Fieser –Kuhn rules are used to calculate λmax for polyene system.

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

ϵmax = $(1.74 \times 10^{4}\ )n$

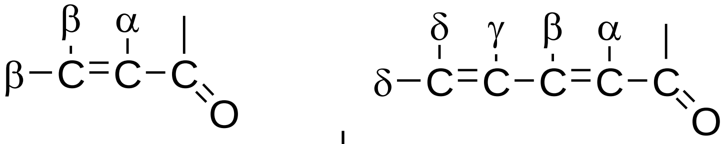
Where n = no. of conjugated double bonds

M= no of alkyl or alkyl like substituents on the conjugated system

R_{eno} = no of rings with endocyclic double bonds in the conjugated system

R_{exo} = no of rings with exocyclic double bonds

Woodward Fieser Rule : Enones



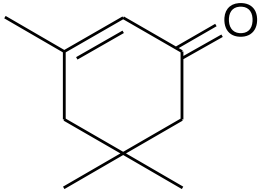
Group		Increment
6-membered ring or acyclic enone		Base 215 nm
5-membered ring parent enone		Base 202 nm
Acyclic dienone		Base 245 nm
Double bond extending conjugation		30
Alkyl group or ring residue	α, β, ϒ and higher	10, 12, 18
-OH	α, β, ϒ and higher	35, 30, 18
-OR	α, β, ϒ, δ	35, 30, 17, 31
-O(C=O)R	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

Base value for acyclic α,β-unsaturated ketone or six membered cyclic unsaturated ketone: 215 nm and for 5- membered cyclic ketone: 202 nm. Aldehydes, acids and esters have different base values

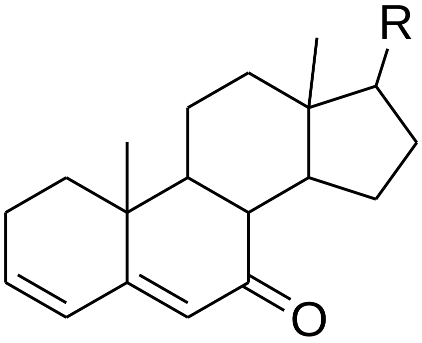
Unsaturated system	Base Value nm
Aldehyde	208
With α or β alkyl groups	220
With α,β or β,β alkyl groups	230
With α,β,β alkyl groups	242
Acid or ester	
With α or β alkyl groups	208
With α,β or β,β alkyl groups	217
Group value – exocyclic α,β double bond	+5
Group value – endocyclic α,β bond in 5 or 7 membered ring	+5

Unlike Conjugated dienes solvent does have effects on λmax. With solvents other than ethyl and methyl alcohols following numerical corrections are to be made.

Solvent correction	Increment
Water	+8
Ethanol, methanol	0
Chloroform	-1
Dioxane	-5
Ether	-7
Hydrocarbon	-11



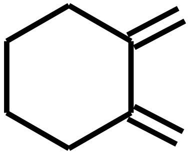
Base value for six membered ketone = 215 nm
2- substituents at β carbon atom = 24 nm
total = 239 nm
Experimental value = 238 nm



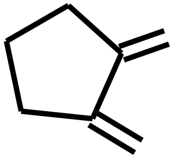
Base value for hetero annular diene= 215 nm
Extended conjugation = 39 nm
ring residue at β carbon atom = 12 nm
ring residue at δ carbon atom = 18 nm
one cexocyclic double bond = 05 nm
Total = 280 nm

Experimental value = 280 nm

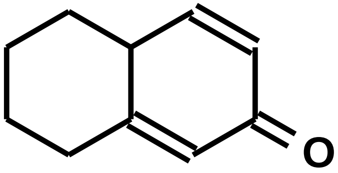
Angular Distortion and Cross-conjugation



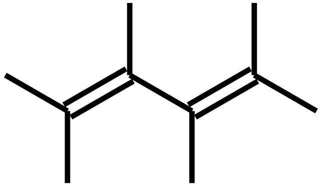
I



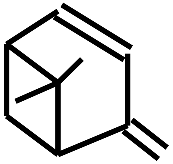
II



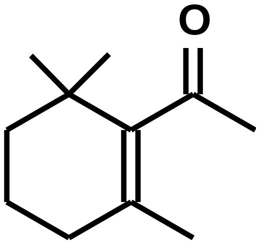
III



IV



V

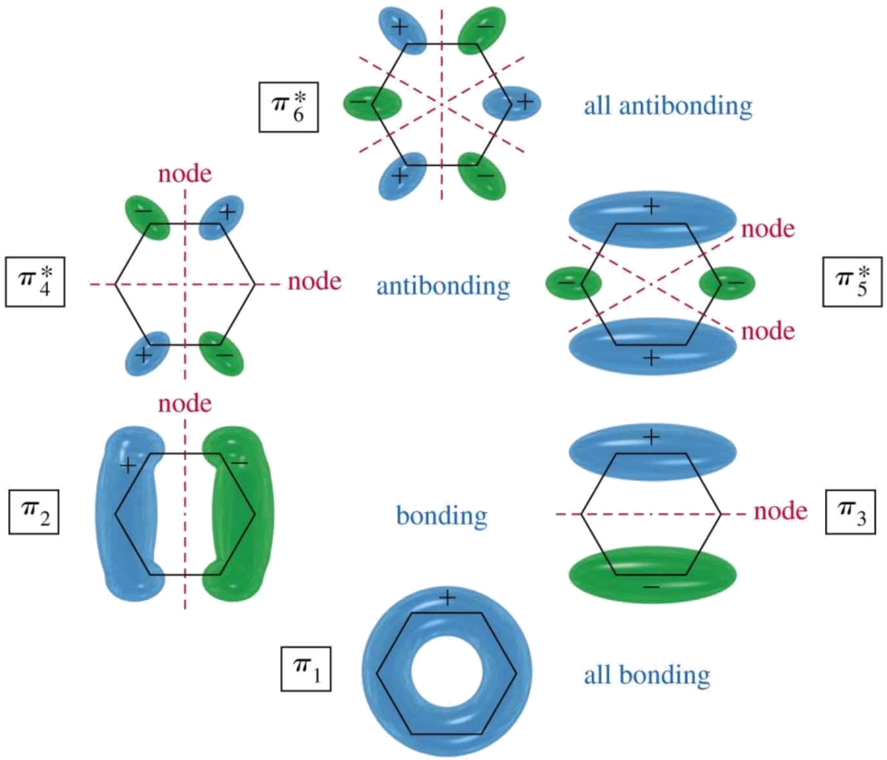


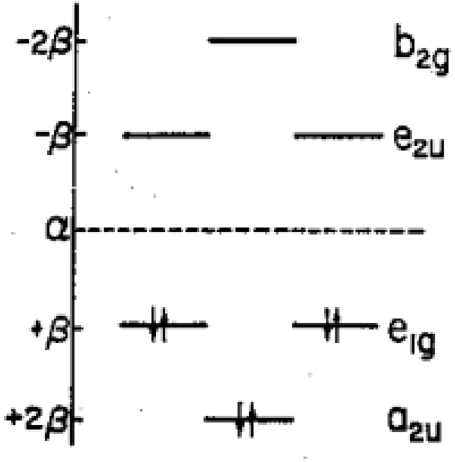
VI

UV spectroscopy is very sensitive to distortion of chromophore which is engendered by ring strain or by the introduction of additional chromophore at the other end. Woodward rule could not satisfactorily predict the spectra of such systems. Observed λmax values are lower than calculated, demonstrating the influence of steric inhibition of resonance.

UV of Aromatic compounds (benzene and substituted benzene)

Although aromatic rings are most widely studied organic chromophores, the absorptions that arise from various electronic transitions are complex in nature. Benzene has six MO’s. Among them 3 filled π and 3 vacant π*.



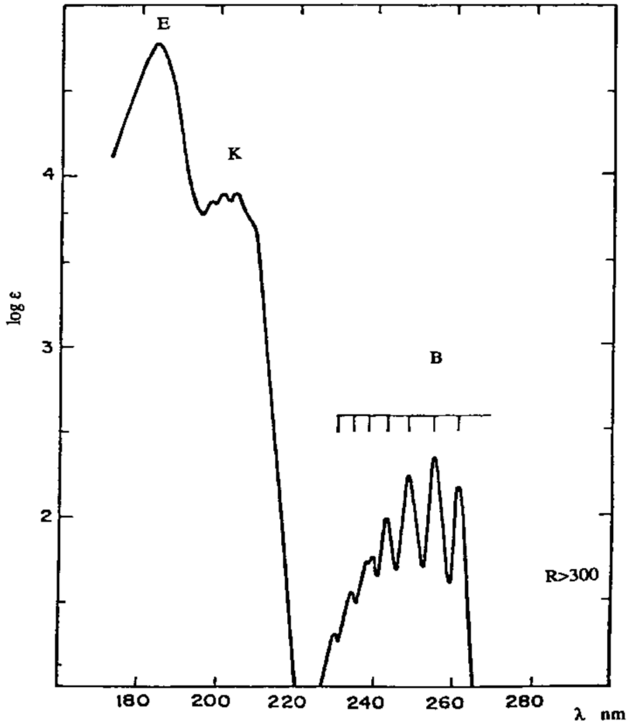


Three absorptions bands are observed due to π-π* transitions.

Among them the first band appears at 184 nm having very high intensity (ϵ 60000) .
Second band is observed near 204 nm, known as primary band (E band) having intensity (ε 7400).

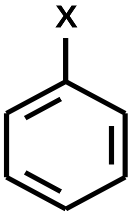
Another band of very weak intensity appears at 254 nm (ϵ 200) which corresponds to asymmetry forbidden transition.

A series of fine structure bands appear in the region between 230-270 nm which originates from transitions between sublevels of vibrational energy levels upon which electronic absorption is superimposed.



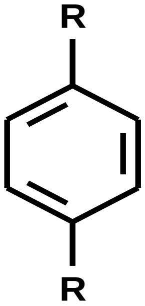
Effect of substitutions on absorption maxima in aromatic system.

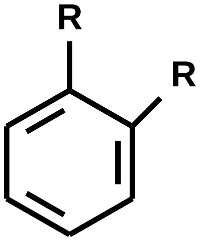
Substituents like alkyl groups, auxochromes or conjugated groups can cause shift of absorptions and intensity of absorbtion



Alkyl group produces bathochromic shift of B band but effect on E band is less. The shift is de to hyperconugation.

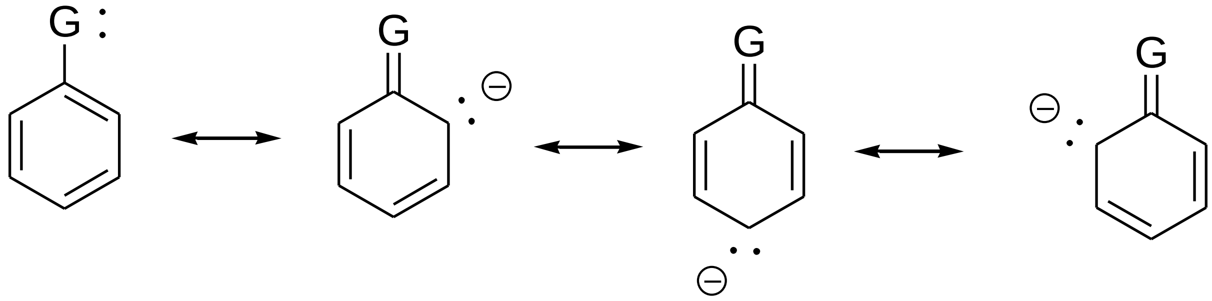
C_6H_5X	Primary Band	B band
X= H	203	256
= CH_3	206	261





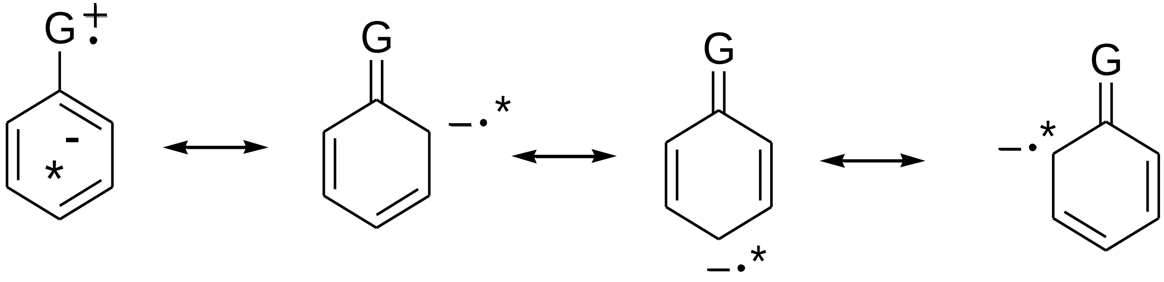
For para dialkyl benzene red shift is more pronounced than in o-disubstituted benzene, later absorps at lower wave length with reduced intensity. Due to steric interaction between two ortho substituents effect of Hyperconjugation is reduced.

Substituents with unshared nonbonded electrons shft absorption maxima of both primary and B bands.



If auxochromes like –NH_2 , -OH, -OMe or halogen having non bonded pair of electrons can induce a shift in the primary and secondary absorption bands. Non bonding electrons can extend the π system through resonance, thereby lowering energy of π -π* transition.

More availability in non bonding pair will give greater shift.



For the substituents with unshared electrons possibility of n-π* transitions arise. The electron now is removed from the substituent to the anti bonding π* orbital of the benzene ring. The state is referred as charge transfer excited state.

Substituents with unpaired electrons show following effects:

i) On changing the pH, nature of substituent can change.
ii) Deprotonation of oxygen gives more available n pairs, lowering transition energies.
iii) Protonation of nitrogen group (amino) removes n pairs, raising transition energy.

	Primary		**Secondary**	
Substituent	$\lambda_{\mathbf{max}}$	ε	$\lambda_{\mathbf{max}}$	ε
-H	203.5	7,400	254	204
-OH	211	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
-C(O)OH	230	11,600	273	970
$-C(O)O^-$	224	8,700	268	560

Substituents capable of π conjugation (chromophore)

Interaction of chromophoric π electrons and benzene π electrons can extend the π electronic system, lowering the transition and shifts the primary band to longer wave length.

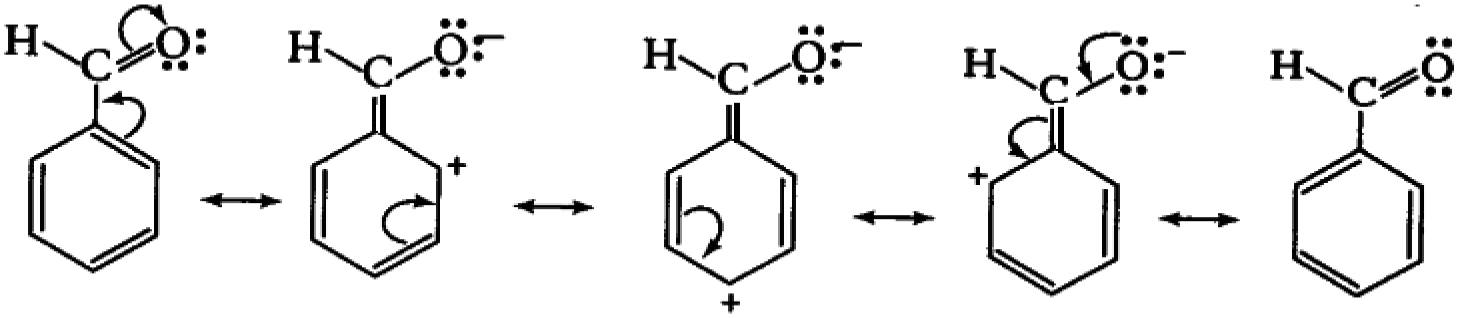


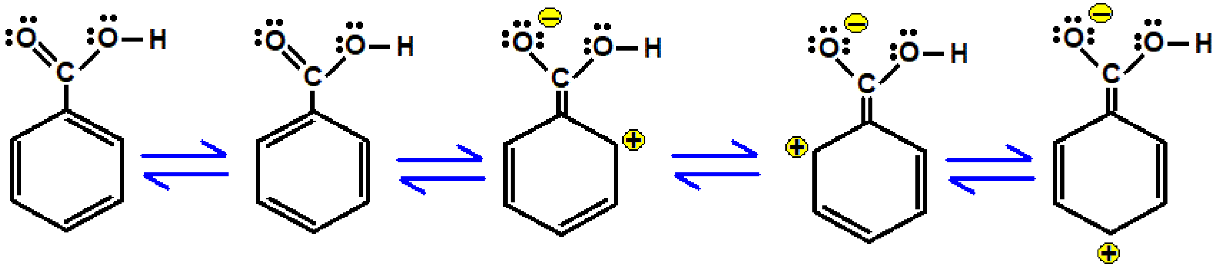
Fig. Resonating structures of benzaldehyde

	Primary Band(E band)	Secondary Band (B band)
X= CHO	249(11400)	-
= NO_2	268.5 (7800)	-
= CN	224 (13000)	271(1000)

With benzoic acid conjugation of the π system of benzene ring with π electrons of substituent can cause an appreciable shift in the primary and secondary band. For benzoate ion the effect is less. The electron transfer is less likely as in parent acid, because functional group already bears a negative charge.

	Primary		**Secondary**	
Substituent	λ_{max}	ε	λ_{max}	ε
-C(O)OH	230	11,600	273	970
-C(O)O$^-$	224	8,700	268	560

The resonance structures of benzoic acid



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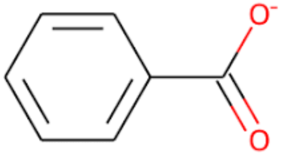
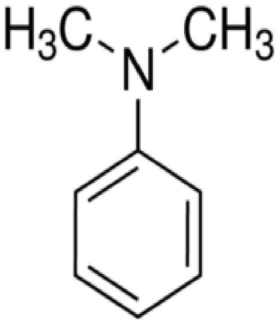
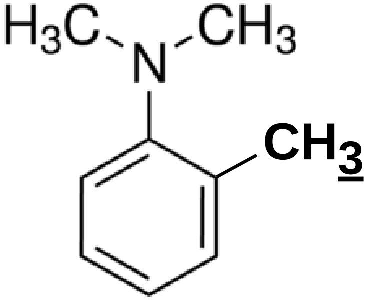




N,N-dimethylaniline

λmax : 251(15000)E-Band

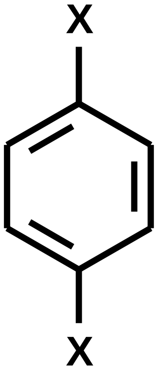


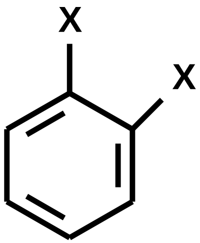
The bulky substituent in ortho position reduces the resonance by twisting the structure. An hypsochromic shift is observed.

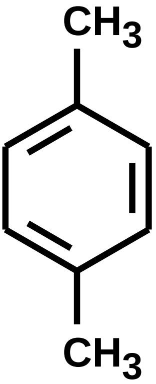
N,N-dimethyl-2-methylaniline

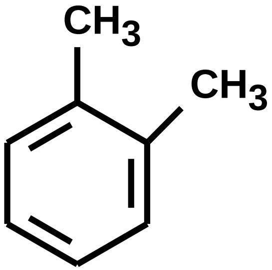
λmax :247 (6300)

Disubstituted System





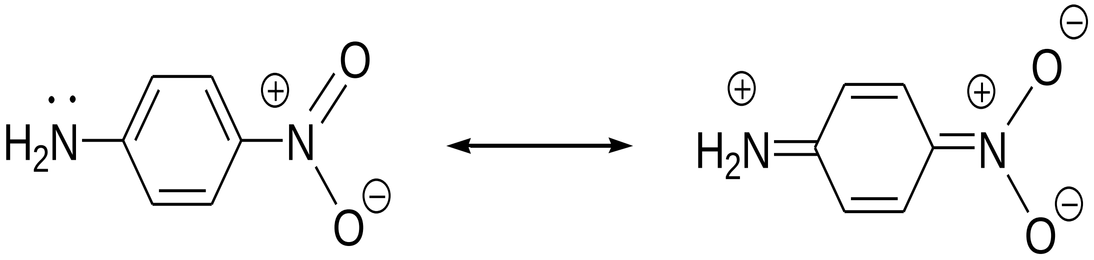




For p-dimethylbenzene bathochromic shift is observed but for ortho isomer hypsochromic shift is observed. Steric interaction between two me groups reduces hyperconjugation

Disubstituted Benzene

If both groups are electron donating or withdrawing, the effect is similar to the effect of the stronger of the two groups as if it were a mono-substituted ring



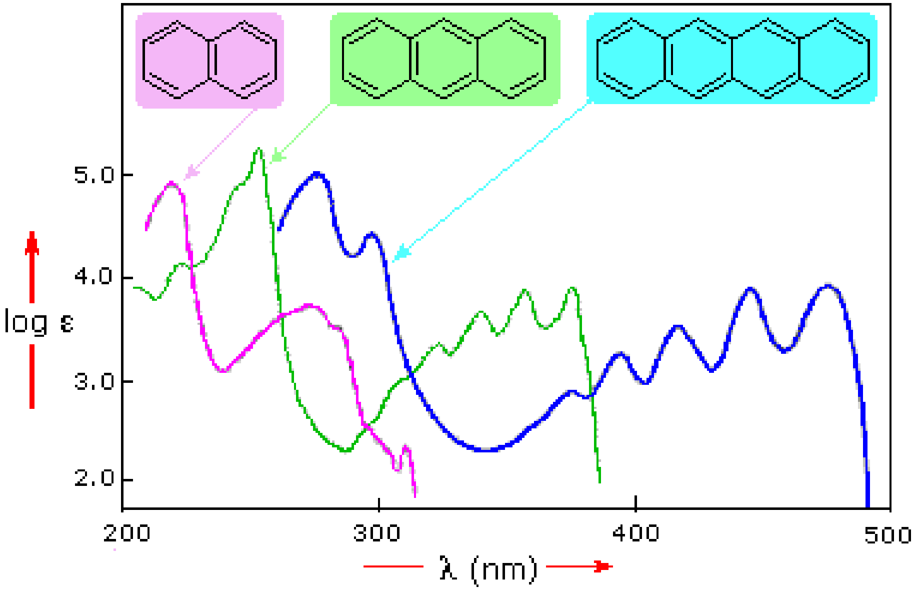
If one group is electron donating and other group electron withdrawing in p-position, a pronounced red shift of E band observed and shift is greater than sum of the shifts of both the groups. (λmax for p-nitroaniline : 381 nm)
λmax for p-nitrophenol is 318nm (K-Band)

If the two electonically dissimilar groups are ortho- or meta- to one another, the effect is usually the sum of the two individual effects (meta- no resonance; ortho-steric hindrance. For ortho and meta nitroaniline no red shift is observed.

Polycyclic Aromatic Hydrocarbons

The spectra of these compounds are characteristic of each aromatic system. As the number of condensed ring increases the absorption moves progressively to longer wavelength until it occurs in the visible region.

	Benzene	Naphthalene	Anthracene	Tetracene	Pentacene
λmax(nm)	254	286	375	477	580



UV spectra of Heteroaromatic Compounds

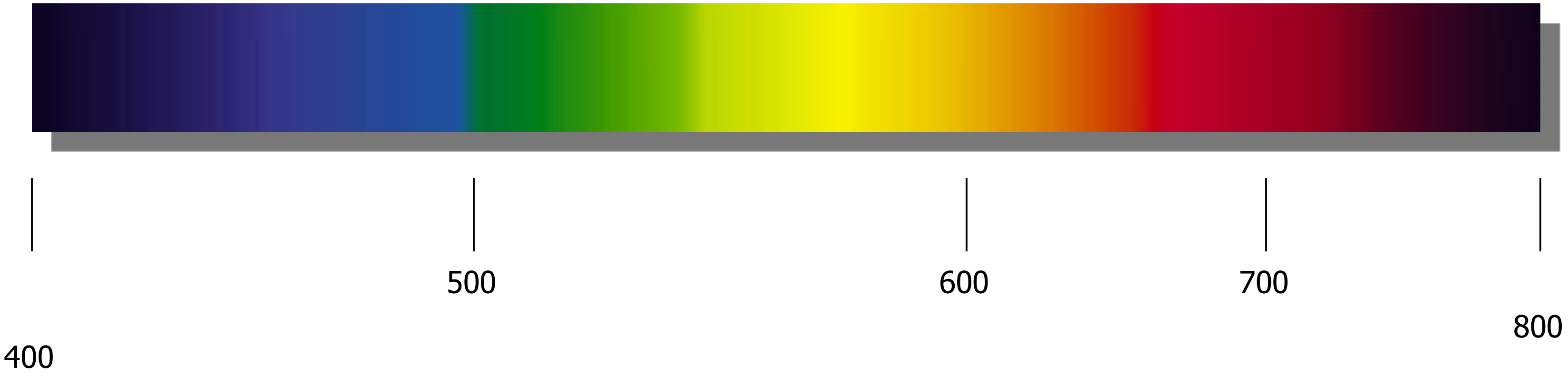
UV absorptions of Five membered heterocycles can be compared to that of Cyclopentadiene.
Aromatic chracter: Cyclopentadiene< Furan< Pyrrole< Thiophene
Auxochromic or Chromophoric substitution causes Bathochromic shift.

	Band-I		Band-II	
	λmax	ϵmax	λmax	ϵmax
Cyclopentadiene	200	10,000	238.5	3400
Furan	200	10,000	252	
Pyrrole	209	6,780	240	300
Thiophene	231	7,100	269.5	1.5
Pyridine	240		320-380	

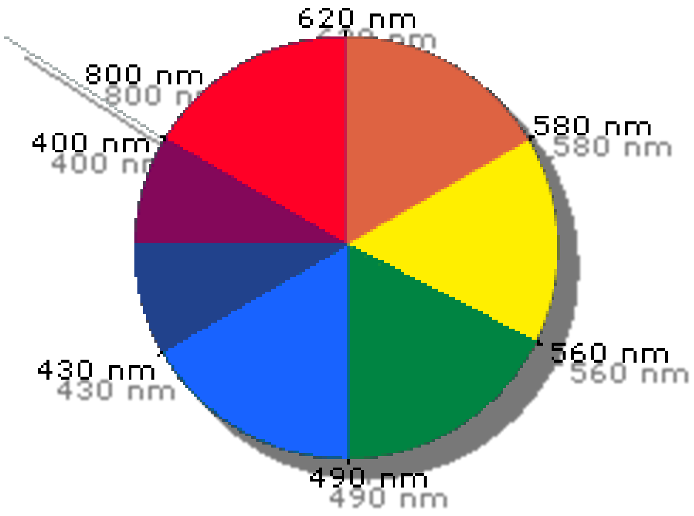
The UV spectra of Pyridine is very similar to that of Benzene. B-band of pyridine is some what more intense and has less intense fine structure than that of Benzene. This transition is allowed for Pyridine and B-band of Pyridine shows a higher intensity with increase in polarity of solvent.

Visible Spectra

The human eye can detect Electromagnetic spectrum in the range between 400 nm-800 nm. When white light passes through a compound, a portion is absorbed and rest is transmitted which is known as complementary colour.



	λ, nm
Violet	400-420
Indigo	420-440
Blue	440-490
Green	490-570
Yellow	57085
Orange	585-620
Red	620-780

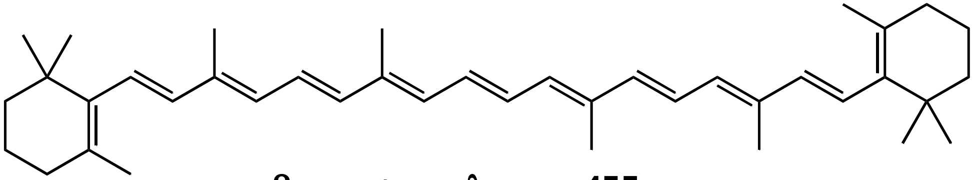


Colour Wheel

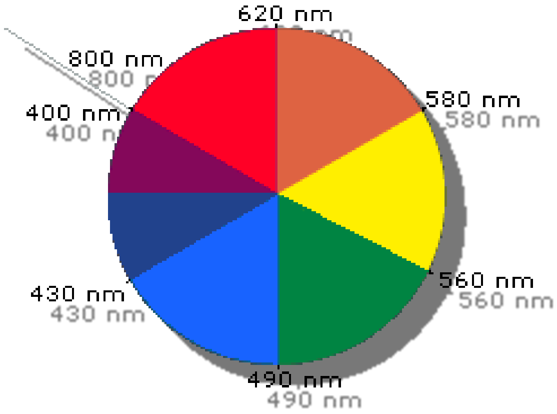
Colour of the Organic Molecules

Organic molecules which are coloured , have extensive conjugation (more than five).

Example: β-Carotene

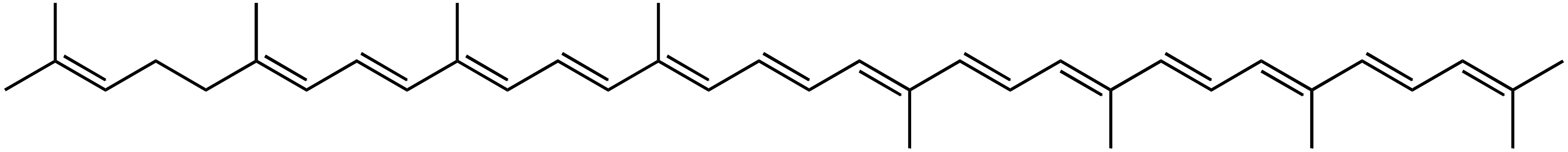


β-carotene, λ_{max} = 455 nm

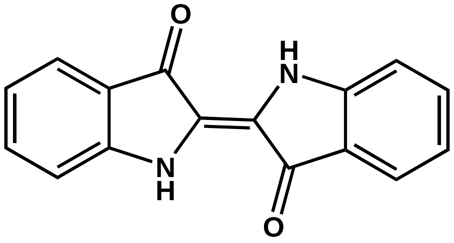


Electomagnetic radiation at λmax 435 nm in the far blue region of the spectrum is absorbed.

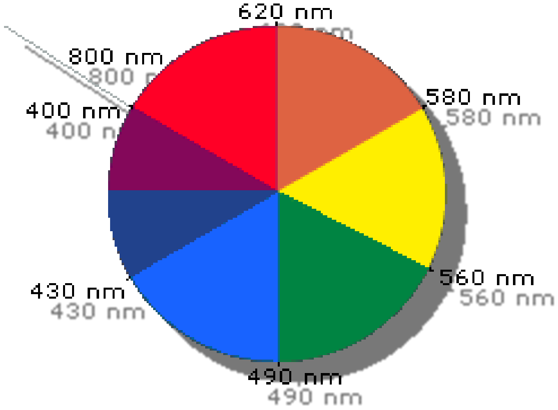
The transmitted light has the complementary colour of orange.



lycopene, λ_{max} = 474 nm



indigo



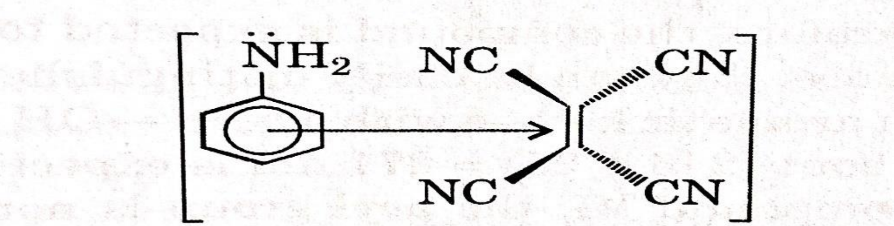
Charge-Transfer Complex

The complex is formed by transfer of electronic charge from an electron rich molecule to an electron deficient molecule is known as Charge Transfer Complex.

In charge transfer complexes the HOMO of the donor molecule interacts with the LUMO of the accepter molecule.
This results in a drop of ΔE value, as a consequence the λ_{max} shifts to the longer wavelength(visible region).
Donar: Anthracene, Aniline, Mesitilene, N,N-dimethyl aniline
Acceptor: Picric acid, TCNE, I_2 , $AlCl_3$

Example:

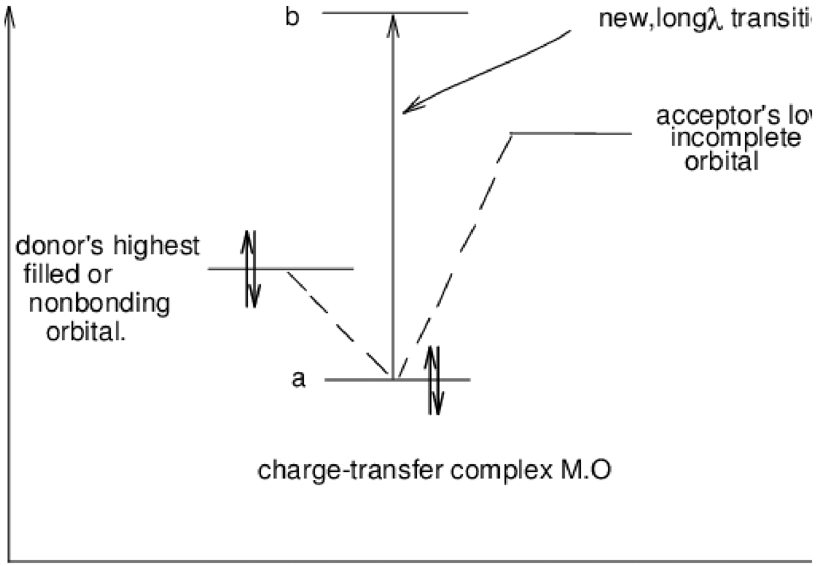
Aniline and tetracyanoethylene compound.
Phenol to picric acid.
Phenol to $AlCl_3$.
Anthracene -Picrate



Charge–transfer complex
(deep blue)

Face-to-face association between donor and acceptor in 1:1 ratio.

Electronic Transitions for Charge-transfer Complex



λmax values for aniline and TCNE are 280 nm and 300 nm respectively
but the deep blue complex has λmax value of 610 nm in visible region.