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- The alternate title for this technique is **Electronic Spectroscopy** since it involves the promotion of electrons (σ , π , n^* electrons) from the ground state to the higher energy state.
- Visible and ultra-violet spectrum, electronic excitations occur in the range **200-800 m μ** and involves the promotion of electrons to the higher energy molecular orbital.
- Since the **energy levels of a molecule** are quantized, the energy required to bring about the excitation is a **fixed quantity**.
- The far ultra-violet region (below 200 m μ) is not much studied due to **absorption by oxygen and nitrogen**.

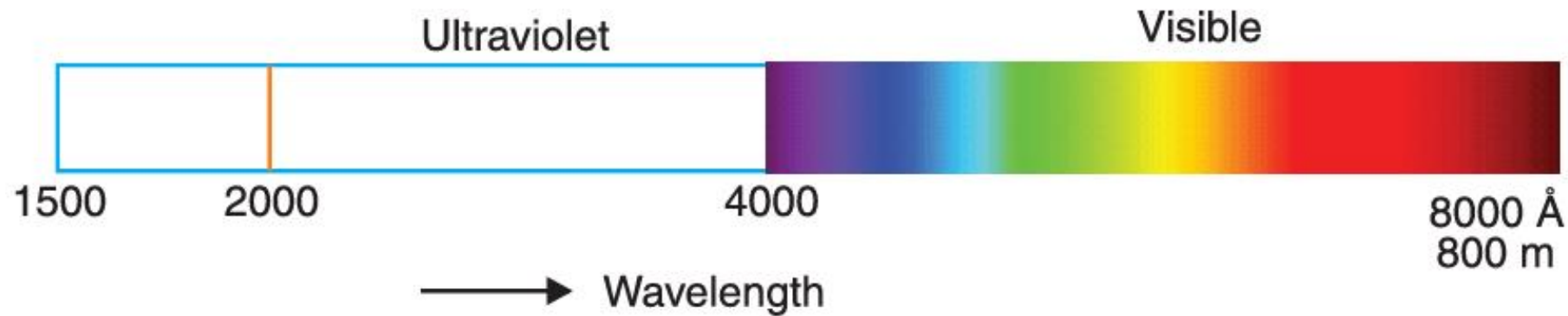


Fig. The range of U.V Visible spectra

$$1 \text{ m}\mu = 1 \text{ nm} = 10^{-7} \text{ cm} = 10 \text{ \AA}$$



- A spectrophotometer is a device that detects the **percentage transmittance of light radiation** when light of a certain intensity and frequency range is passed through the sample.
- Thus, the instrument **compares the intensity of the transmitted light with that of the incident light.**
- **Light Source-** Tungsten Filament lamp and hydrogen-deuterium discharge lamp
- The primary source of light is divided into two beams of equal intensity.
- Before dividing it into two beams, the incident radiation is dispersed with the help of a rotating prism.
- The various wavelengths of a light source are separated with a prism and then selected by slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slits for recording purposes.
- The selected beam is monochromatic which is then divided into two beams of equal intensity.
- One of the beams of selected monochromatic light is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent
- Glass cannot be used since it absorbs strongly in the ultra-violet region.
- Silica cells can be used. These must be properly stored and their optical surfaces should never be handled. Quartz cells also serve the purpose best.
- The spectrometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution
- m1 and m2 are photoelectric cells which receives an intense beam and results in generation of current which is sent to amplifier The amplifier is coupled to a small servomotor, which in turn, is coupled to a pen recorder.

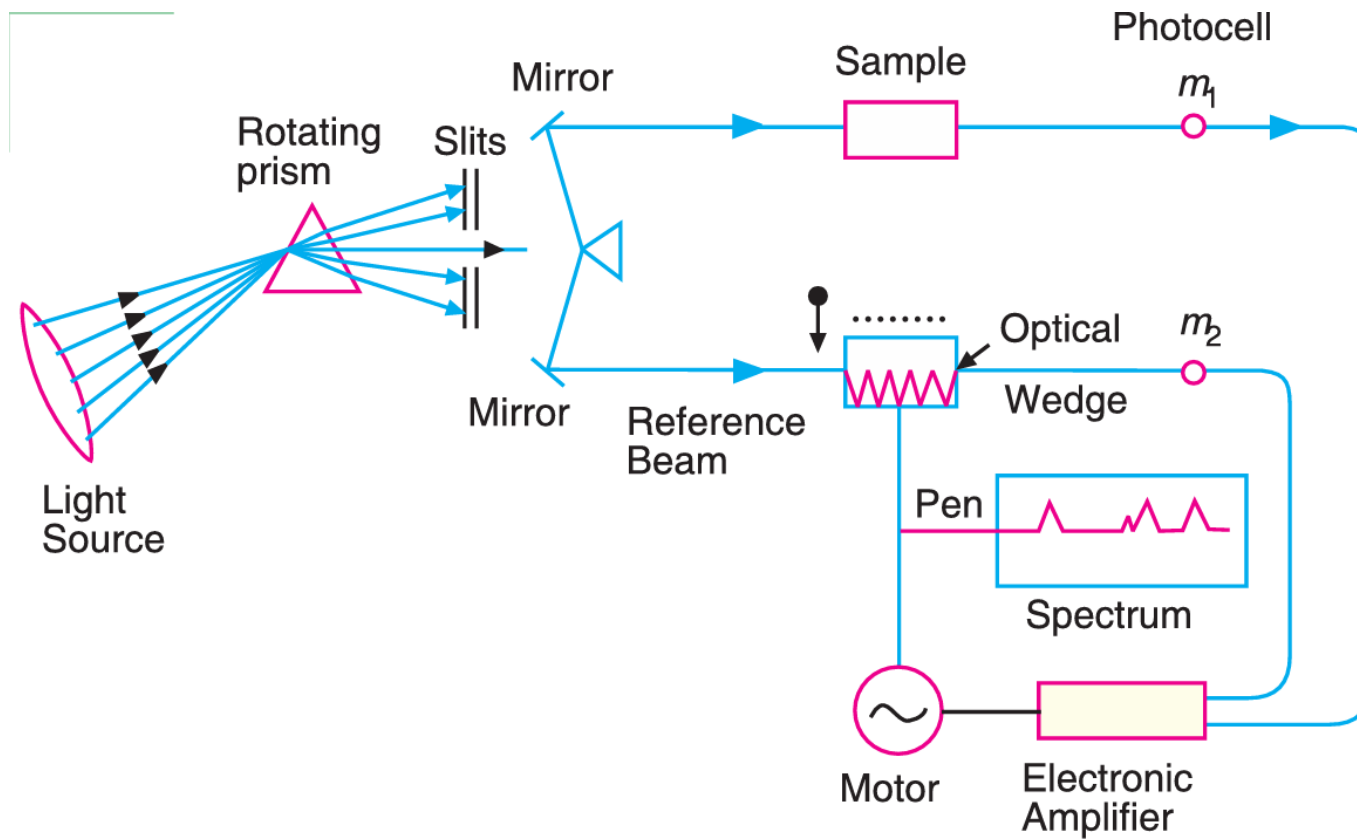
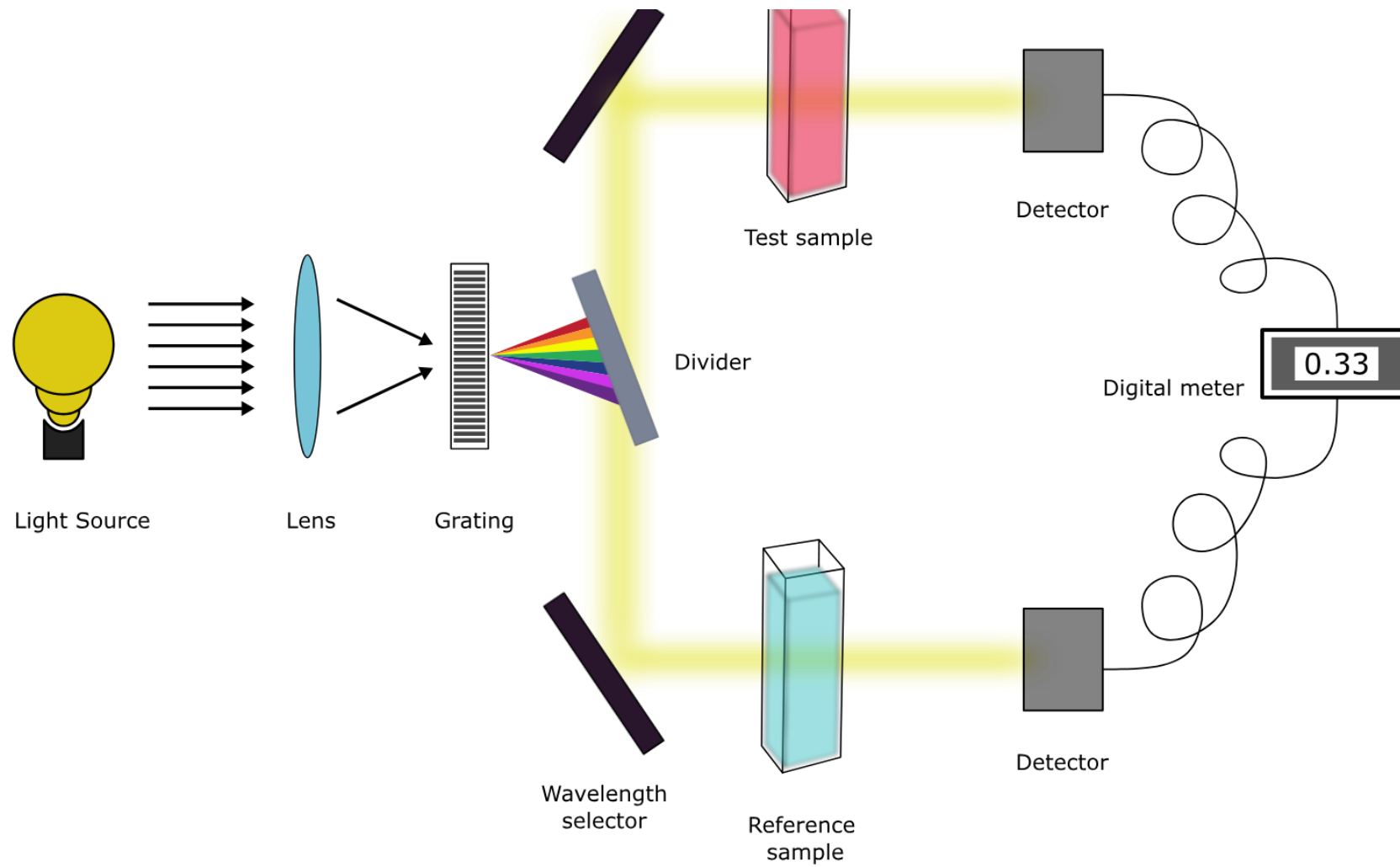


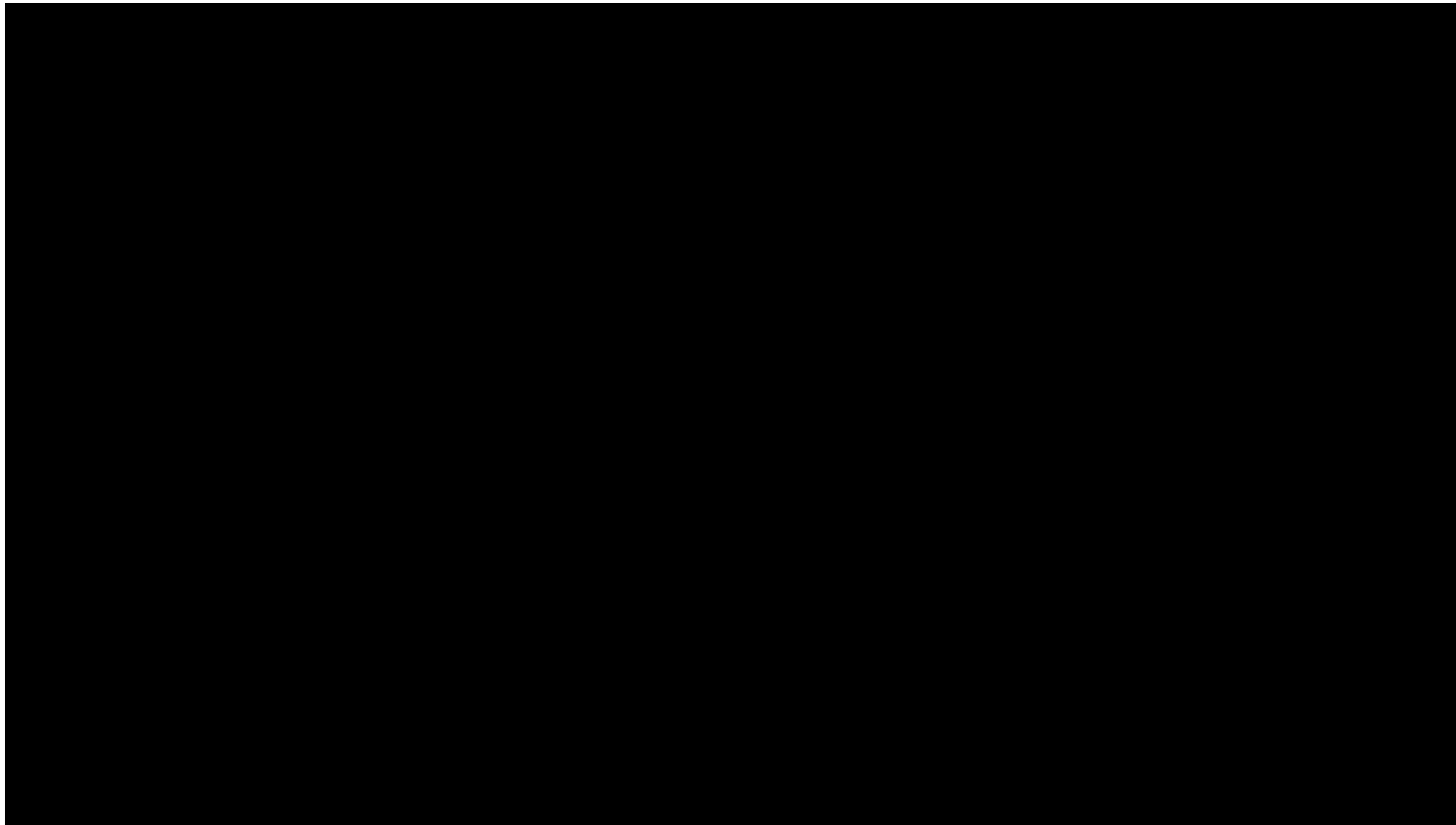
Fig. Ultra-violet spectrophotometer



Double beam spectrophotometer



Working of UV-Visible Spectrophotometer





- There are two laws which govern the absorption of light by the molecules.
- (i) Lambert's law and (ii) Beer's law

(i) Lambert's Law : When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

$$-\frac{dI}{dx} = kI$$

Where;

I = intensity of radiation after passing through a thickness x, of the medium.

dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, of the medium.

$-\frac{dI}{dx}$ = rate of decrease of intensity of radiation with thickness of the absorbing medium.

k = proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.



The Absorption Laws



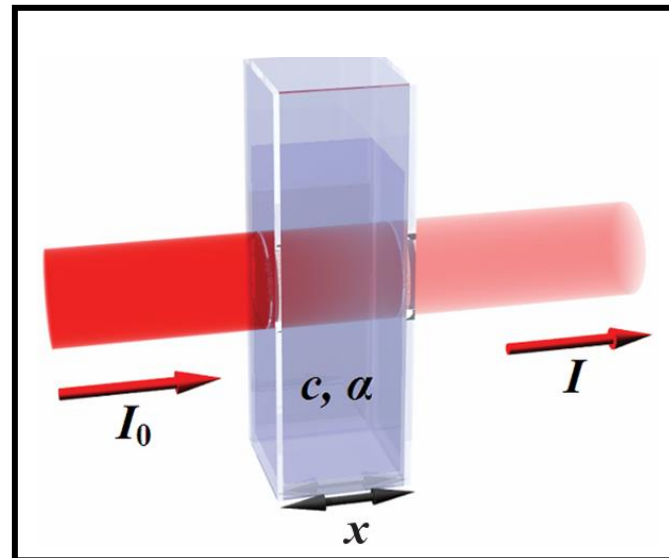
(ii) Beer's law : When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.

$$-\frac{dI}{dx} = k' Ic$$

Where

c = conc. of the solution in moles litre⁻¹.

k' = molar absorption coefficient and its value depends upon the nature of the absorbing substance.



✓ Suppose I_0 be the intensity of the radiation before entering the absorbing solution.

Fig. The Deeper the Glass, the Darker the view, the lesser of the incident Light that gets through 8



- On combining the two laws, the Beer-Lambert Law can be formulated

$$\log \frac{I_0}{I} = \epsilon . c . l = A$$

Where;

I_0 = Intensity of incident light

I = Intensity of transmitted light

c = Concentration of solution in moles litre⁻¹

l = Path length of the sample (usually 1 cm)

ϵ = Molar extinction coefficient (or molar absorptivity)

A = Absorbance

Limitations of Beer Lambert Law :

This law is not obeyed

- (i) When different forms of the absorbing molecules are in equilibrium as in keto-enol tautomer's.
- (ii) When fluorescent compounds are present.
- (iii) When solute and solvent form complexes through some sort of association.



- It may be noted that the intensity of **absorption is directly proportional to the transition probability**. An allowed transition will have ϵ_{max} **value greater than 1000** while those having low transition probability will have its value less than 1000.

Selection Rules :

The various electronic transitions which are governed by certain restrictions are called selection rules.

- (i) The transitions which involve a **change in the spin quantum number** of an electron during the transition do not occur. Thus, singlet-triplet transitions are forbidden.
- (ii) The transitions between orbitals of **different symmetry** do not occur. For example, n to σ^* transition is symmetry forbidden.

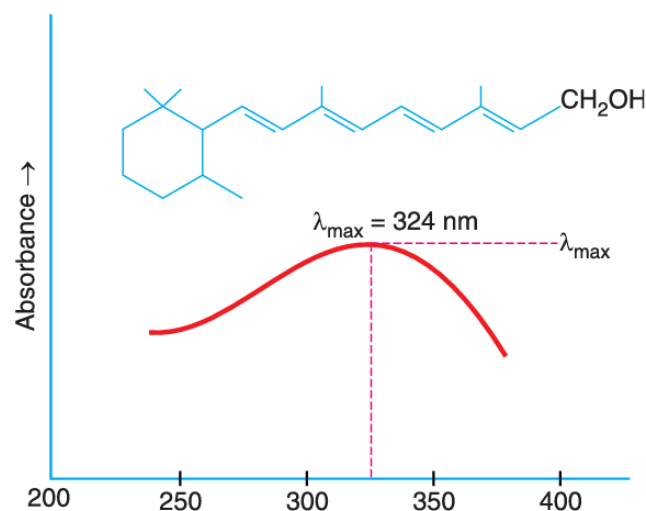


Fig. Ultra-violet spectrum of vitamin A



- When the molecule absorbs ultraviolet or visible light, its electrons get promoted from the **ground state to the higher energy state**.
- In the ground state, the spins of the electrons in each molecular orbital are **essentially paired**, In the higher energy state, if the spins of the electrons are paired, then it is called an **excited singlet state**.
- If the spins of the electrons in the **excited state are parallel**, it is called an **excited triplet state**.
- In the triplet excited state, electrons are farther apart in space and thus, **electron-electron repulsion is minimised**.
- An excited singlet state is converted to excited triplet state with the emission of **energy as light**. The transition from singlet ground state to excited triplet state is **symmetry forbidden**.
- the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled molecular orbital.

Theory of Electronic Spectroscopy

Types of Electronic Transitions: According to the molecular orbital theory, when a molecule is excited by the absorption of energy (UV or visible light), its electrons are promoted from a bonding to an antibonding orbital.

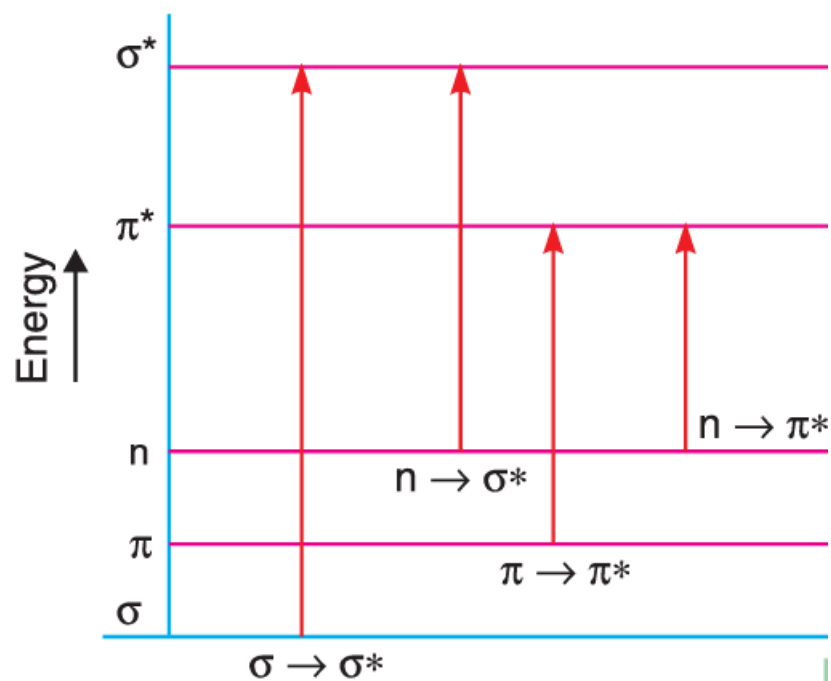


Fig. Electronic excitation energies

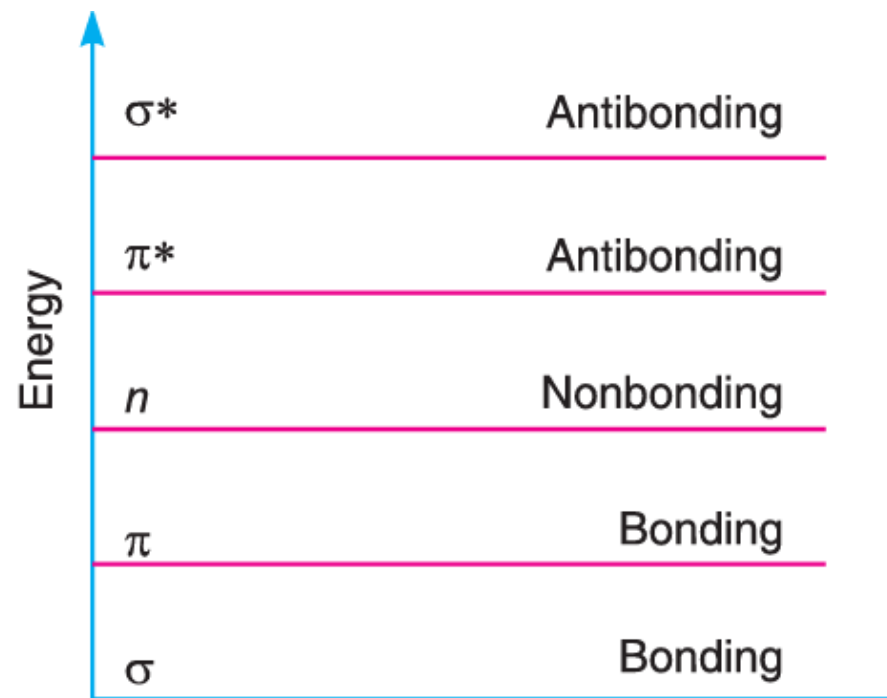


Fig. Electronic excitation energies



➤ Let us now consider the various transitions involved in ultraviolet spectroscopy.



(a) $\sigma \rightarrow \sigma^*$ transitions :

It is a high energy process since **sigma bonds** are, in general, **very strong**. The organic compounds in which all the valence shell electrons are involved in the formation of sigma bonds do not show absorption in the normal ultraviolet region, i.e., **180–400 mμ**.

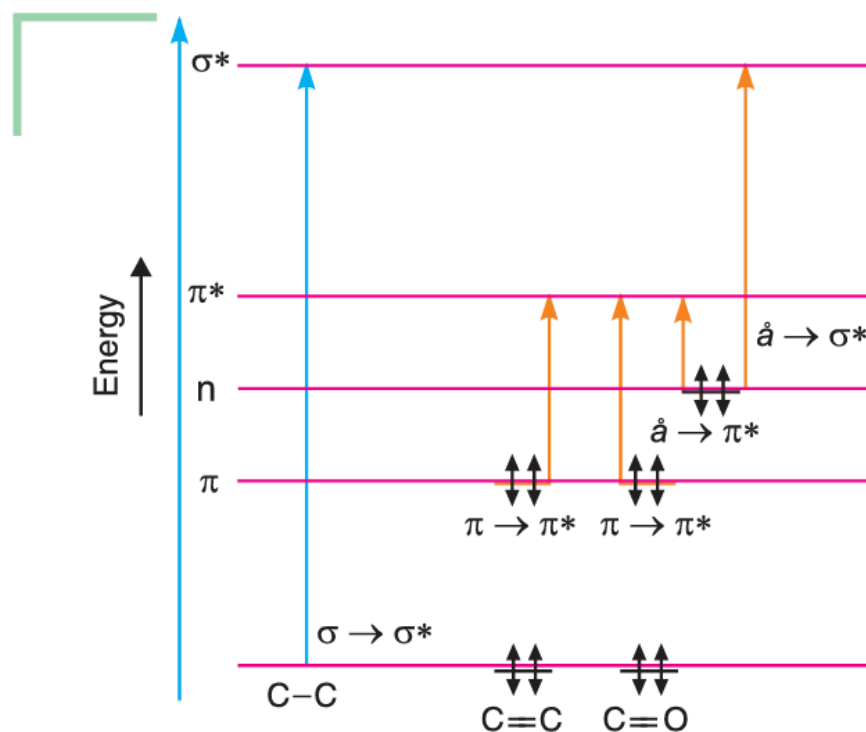
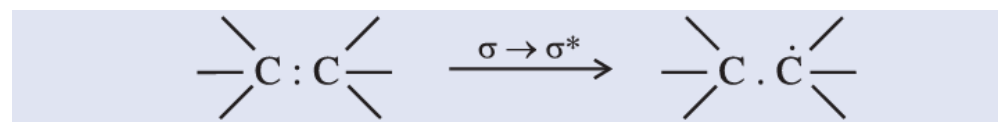
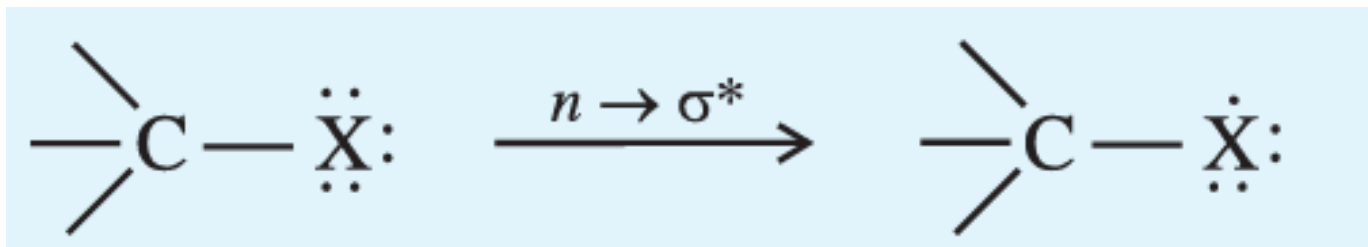


Fig. Various transition involved in Electronic spectroscopy



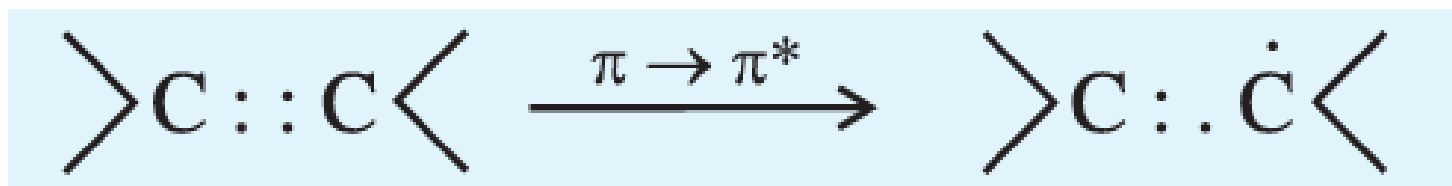
(b) $n \rightarrow \sigma^*$ transitions :

This type of transition takes place in saturated compounds containing **one hetero atom** with **unshared pair of electrons** (n electrons). Some compounds undergoing this type of transitions are saturated **halides, alcohols, ethers, aldehydes, ketones, amines** etc.



(C) $\pi \rightarrow \pi^*$ transitions :

This type of transition occurs in **the unsaturated centres** of the molecule; i.e., in compounds containing double or triple bonds and also in **aromatics**. The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelength. A π electron of a double bond is excited to π^* orbital. For example, **alkenes, alkynes, carbonyl compounds, cyanides, azo compounds** etc.





(b) $n \rightarrow \pi^*$ transitions :

In this type of transition, an **electron of unshared electron pair** on hetero atom gets excited to π^* antibonding orbital. This type of transition requires least amount of energy out of all the transitions discussed above and hence occurs at longer wavelengths.

In **carbonyl compounds**; a high energy n to π^* transition also occurs and is quite intense. Thus, in saturated carbonyl compounds, two types of transitions take place which can be classed as :

(a) High energy transitions

- (i) n to σ^* (intense)
- (ii) π to π^* (intense)

(b) Low energy transition n to π^* (weak)– R^* band

In carbonyl compounds, the shift in the absorption depends upon the polarity of the solvent



- Chromophore was considered any system which is responsible for **imparting colour** to the compound. Nitro-compounds are generally yellow in colour.
- **Nitro group** is the chromophore which imparts yellow colour, similarly, aryl conjugated azo group is a chromophore for providing colour to azo dyes.
- Some of the important chromophores are **ethylenic, acetylenic, carbonyls, acids, esters, nitrile group etc.**
- A carbonyl group is an important chromophore, although, the absorption of light by an isolated group does not produce any colour in the ultraviolet spectroscopy.

There are two types of chromophores :

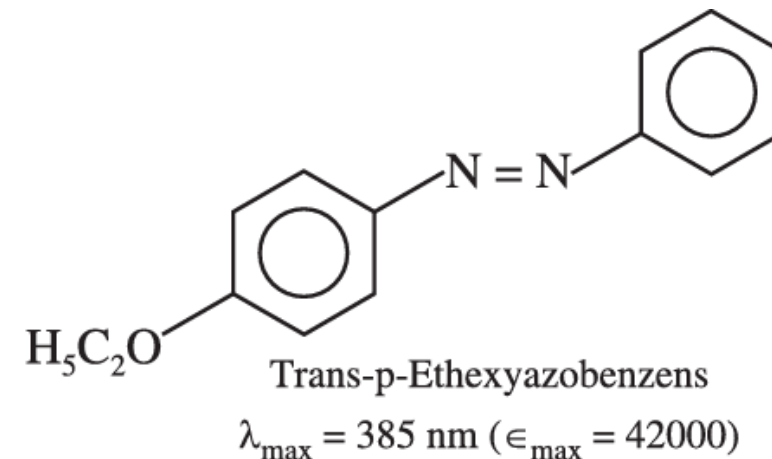
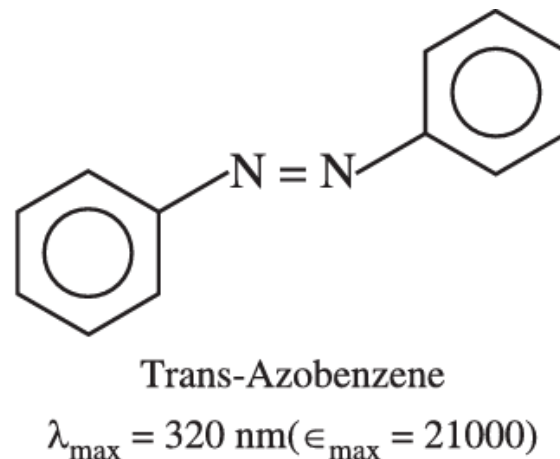
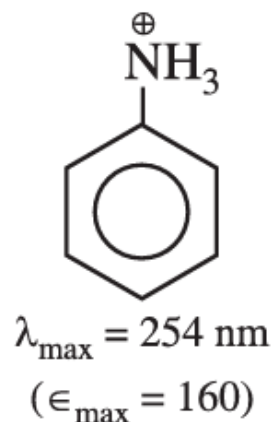
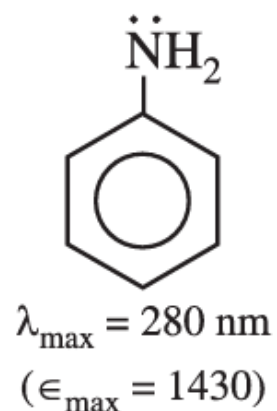
- (a) Chromophores in which the group contains **π electrons** and they undergo **π to π^*** transitions. Such chromophores are ethylenes, acetylenes etc.
- (b) Chromophores which contain both **π electrons** and **n (non-bonding) electrons**. Such chromophores undergo two types of transitions i.e., **n to π^*** and **π to π^*** . Examples of this type are carbonyls, nitriles, azo compounds, nitro compounds etc

Simple Unconjugated Chromophores

<i>Chromophore</i>	<i>Transition</i>	<i>Absorption max (mμ)</i>	ϵ_{max}	<i>Solvent</i>
C=C	$\pi - \pi^*$	~175	~15000	Vapour
		(i) ~175	~10000	Hexane
—C≡C—	$\pi - \pi^*$	(ii) 196	~2000	"
		(iii) 220	~150	"
C=O	$n \rightarrow \sigma^*$	160	18000	"
	$\pi \rightarrow \pi^*$	180	10000	Hexane
	$n \rightarrow \pi^*$	285*	15	
R—NO ₂	$\pi - \pi^*$	~200	5000	Methanol
		$n \rightarrow \pi^*$	~274	15
$\begin{array}{c} \text{—C=O} \\ \\ \text{OH} \end{array}$	$n \rightarrow \pi^*$	204	60	Methanol
—N=N—	$n - \pi^*$	338	~5	Ethanol
—CONH ₂	$n \rightarrow \pi^*$	178	9500	Hexane
	$n \rightarrow \pi^*$	220	63	Hexane



- An auxochromic group is called **colour enhancing group**.
- Auxochromic groups do not show characteristic absorption above 200 mμ. Some common auxochromic groups are **-OH, -OR, -NH₂, -NHR, -NR₂, -SH** etc.
- The effect of the auxochrome is due to its ability to **extend the conjugation** of a chromophore by the sharing of non-bonding electrons.
- For example, benzene shows an absorption maximum at 255 mμ [ϵ_{max} 203] whereas aniline absorbs at 280 mμ [ϵ_{max} 1430]. Hence, amino (-NH₂) group is an auxochrome.





- (a) **Bathochromic effect** : It is an effect by virtue of which the **absorption maximum** is shifted towards **longer wavelength** due to the presence of an **auxochrome**. Such an absorption shift towards longer wavelength is called **Red shift** or bathochromic shift. The **n to π^* transition for carbonyl compounds** experiences bathochromic shift when the **polarity of the solvent is decreased**.
- (b) **Hypsochromic shift or effect** : It is an effect by virtue of which the absorption maximum is shifted towards **shorter wavelength**. The absorption shifted towards shorter wavelength is called **Blue shift** or **hypsochromic shift**. It may be caused by the **removal of conjugation** and also by **changing the polarity of the solvent**. In the case of aniline, absorption maximum occurs at 280 m μ because the pair of electrons on nitrogen atom is in conjugation with the π bond system of the benzene ring. In its acidic solutions, a **blue shift** is caused and absorption occurs at shorter wavelength (~203 m μ).
- (c) **Hyperchromic effect** : It is an effect due to which the **intensity of absorption maximum increases**. For example, the B-band for pyridine at 257 m μ [ϵ_{\max} 2750] is shifted to 262 m μ [ϵ_{\max} 3560] for 2-methyl pyridine (i.e., the value of ϵ_{\max} increases). The introduction of an **auxochrome** usually increases intensity of absorption.
- (d) **Hypochromic effect** : It is defined as an effect due to which the intensity of absorption maximum decreases. The introduction of group which **distorts the geometry** of the molecule causes hypochromic effect. For example, biphenyl absorbs at 250 m μ , ϵ_{\max} 19000 whereas 2-methyl biphenyl absorbs at 237 m μ , ϵ_{\max} 10250 [ϵ_{\max} decreases]. It is due to the distortion caused by the methyl group in 2-methyl biphenyl.

Absorption and Intensity Shifts

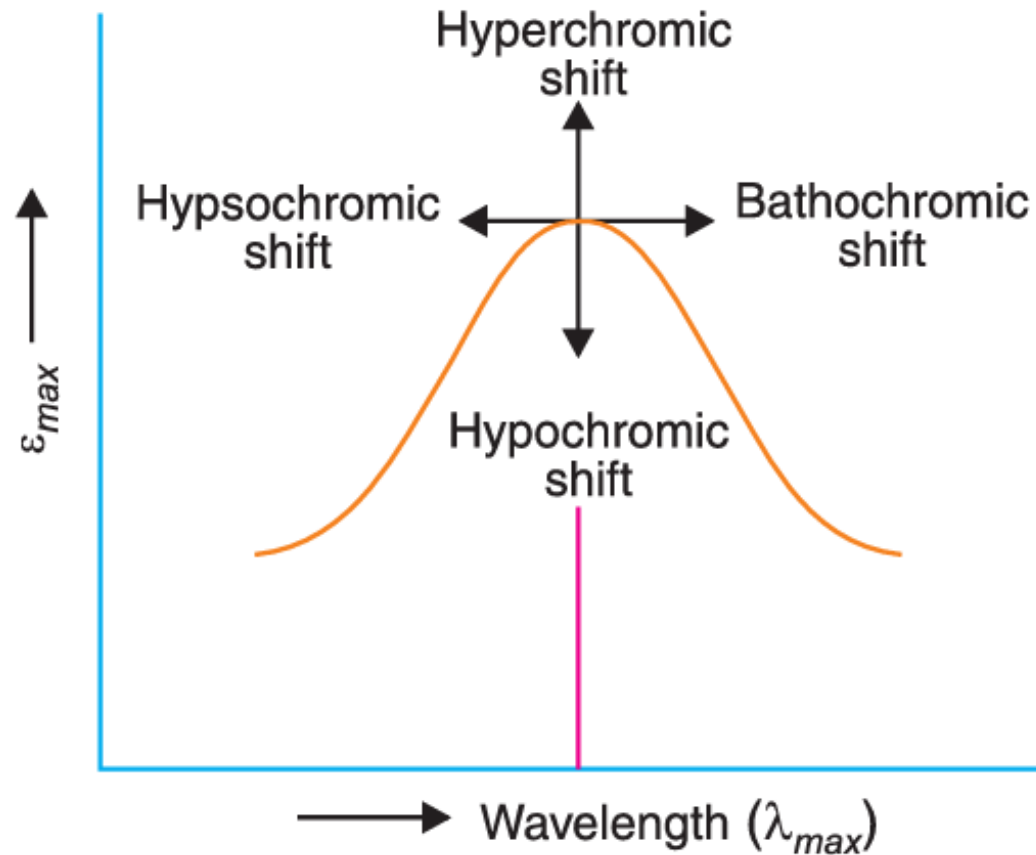


Fig. Absorption and intensity shifts

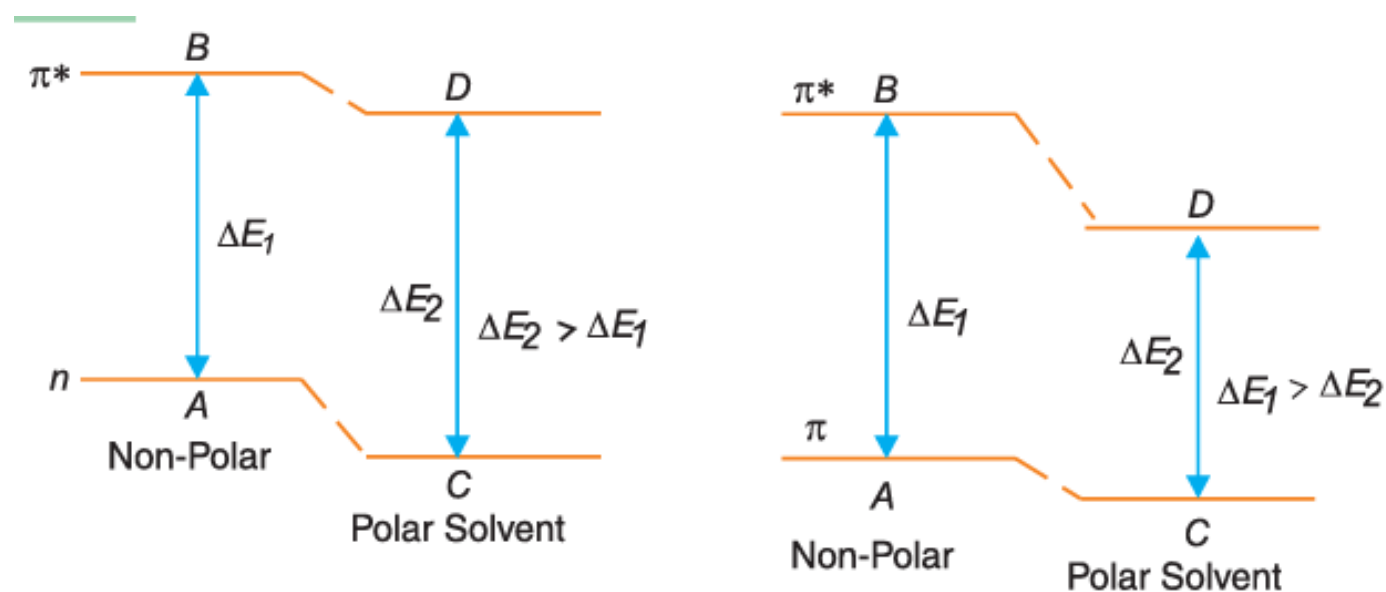


- A most suitable solvent is one that **does not itself absorb** in the region under investigation.
- The most commonly used solvent is **95% Ethanol**. Ethanol is the best solvent as it is cheap and is **transparent down to 210 mμ**.
- **Commercial ethanol** should not be used as it contains **benzene** which absorbs strongly in the ultraviolet region.
- Some other solvents that are transparent above 210 mμ are **n-hexane, methyl alcohol, cyclohexane, acetonitrile, diethyl ether, etc.**
- **Hexane** and other hydrocarbons can be used as these are **less polar and have the least interactions** with the molecule under investigation.
- The position and the intensity of absorption maximum is shifted for a particular chromophore by changing the **polarity of the solvent**.
- **By increasing the polarity of the solvent, compounds like dienes and conjugated hydrocarbons do not experience any appreciable shift.**

<i>Solvent</i>	<i>Upper wavelength limit (mμ)</i>
Ethanol	210
Hexane	210
Methanol	210
Cyclohexane	210
Diethyl ether	210
Water	205
Benzene	280
Chloroform	245
THF (Tetrahydrofuran)	220
Carbon tetrachloride	265



- The absorption maximum for the polar compounds is usually shifted with the change in polarity of the solvents. α , β - unsaturated carbonyl compounds show two different shifts
- In the **n to π^* transition**, the **ground state is more polar** as compared to the excited state. The hydrogen bonding with solvent molecules takes place to a lesser extent with the carbonyl group in the excited state.
- In the case of π to π^* , the absorption band moves to a longer wavelength by increasing the polarity of the solvent.
- The dipole interactions with the solvent molecules lower the energy of the excited state more than that of the ground state



In short, **π^* orbitals** are more stabilised by hydrogen bonding with polar solvents like water and alcohol. It is due to greater polarity of π^* orbital compared to π orbital. Thus, small energy will be required for such a transition and absorption shows a red shift.

$n \rightarrow \pi^*$ transitions are also very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such associations occur due to the presence of nonbonding electrons on the hetero atom and thus, transition requires greater energy.

Fig. Absorption shift with change in polarity of the solvent



- It is known that the **vibrational and the rotational** states depend on temperature.
- As the **temperature is decreased**, the vibrational and the rotational energy states of the molecules are also lowered. Thus, when the absorption of light occurs at a lower temperature, a smaller distribution of excited states results.
- It produces a finer structure in the absorption band than what is noticed at higher temperatures. Consider the UV spectrum of **dodecapentaenoic** acid in ether-alcohol solvent at 20 °C and -195 °C

Solvent effect :

- The solvent used also affects the fineness of the absorption band in the UV spectrum.
- If the **dielectric constant of the solvent is high**, there will be stronger **solute-solvent interactions**.
- Due to this, **vibrational and rotational energy states of molecules increase** and thus, the fineness of the absorption band falls.

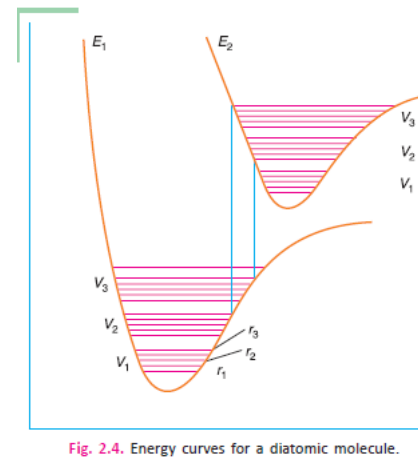
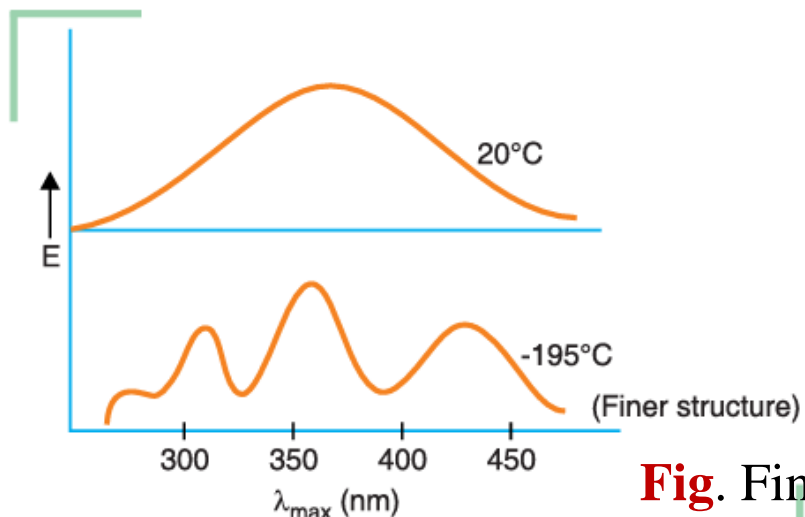


Fig. 2.4. Energy curves for a diatomic molecule.

A molecule in a particular electronic state is also quantised. Clearly a molecule in a particular electronic state is also accompanied by some vibrational and rotational states.

Fig. Finess of the absorption band



Conjugated Dienes



- The wavelength of absorption is **shifted to higher values** (Bathochromic shift), if two or more chromophoric groups are present in conjugation in a molecule.
- For example, ethylene (one double bond) absorbs at 170 m μ (π to π^* transition) while butadiene (two double bonds in conjugation) absorbs at 217 m μ .

<i>Compound</i>	<i>$\lambda_{max}(m\mu)$</i>	<i>ϵ_{max}</i>
Butadiene 1, 3	217	21,000
2,3 dimethyl butadiene	226	21,400
1,3,5, Hexatriene	254	21,400

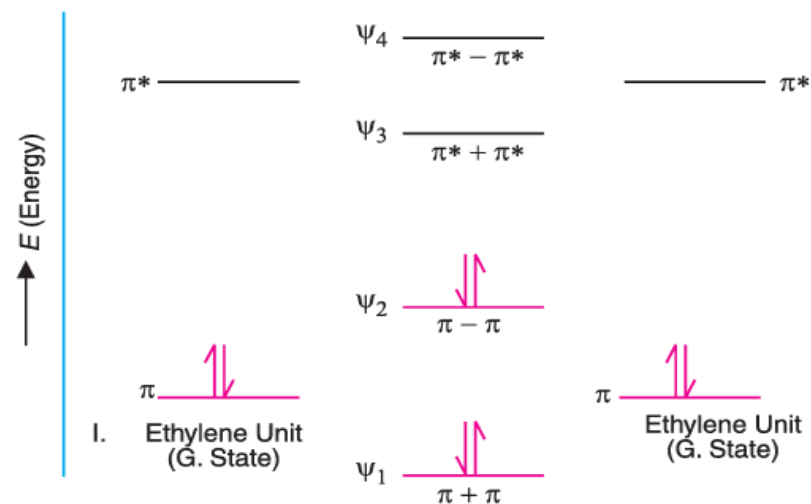


Fig. Electronic excitations in conjugated dienes

- When ethylene molecule gets excited, it gives $\text{CH}_2\text{—CH}_2$ diradical. The electron cloud is spread on two carbon atoms and the absorption maximum occurs at 170 m μ .
- Consider the absorption maximum of butadiene 1,3 ($\text{CH}_2=\text{CH—CH=CH}_2$). It consists of two ethylene units. The various excitations are shown in Fig.
- The two π bonding orbitals, one from each ethylene unit interact or mix up to give rise to two new bonding orbitals

(i) $\pi + \pi = \pi_1$ or ψ_1 —having smaller energy.

(ii) $\pi - \pi = \pi_2$ or ψ_2 —having higher energy.

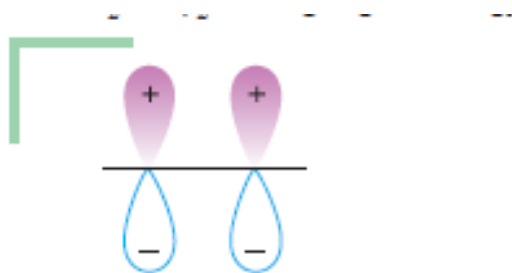


Fig. 2.12. π -bonding orbitals.

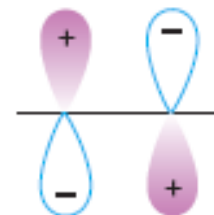


Fig. 2.13. π^* antibonding orbitals

The energy of ψ_1 is less than any one of the two combining atomic orbitals.
Also two π^* orbitals (antibonding) are formed from two ethylene units which are

(i) $\pi^* + \pi^* = \pi_1^* = \psi_3$ having smaller energy.

(ii) $\pi^* - \pi^* = \pi_2^* = \psi_4$ having higher energy.

The energies of ψ_3 and ψ_4 are compared with any one of the two (π^*) antibonding orbitals. Thus, ψ_1 can be represented as shown in the Fig.

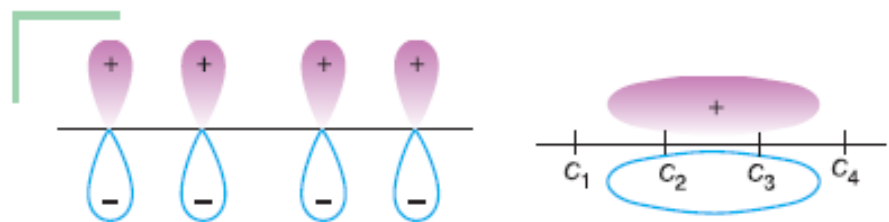


Fig. 2.14. Low energy atomic orbital (ψ_1).

Thus mixing is complete and there is no nodal plane.*

$\pi - \pi = \pi_2 = \psi_2$ can be represented as shown in Figure 2.15.

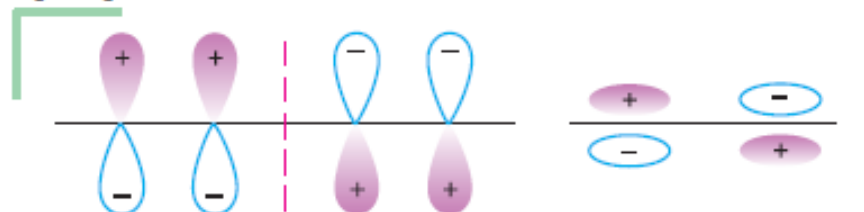


Fig. 2.15. High energy bonding orbital (ψ_2)

In this case, we see one nodal plane.*

Clearly there are double bonds between C_1, C_2 and C_3, C_4 and there is a single bond between C_2 and C_3 .

$\pi^* + \pi^* = \pi_3^* = \psi_3$ can be represented as shown in Fig. 2.16.

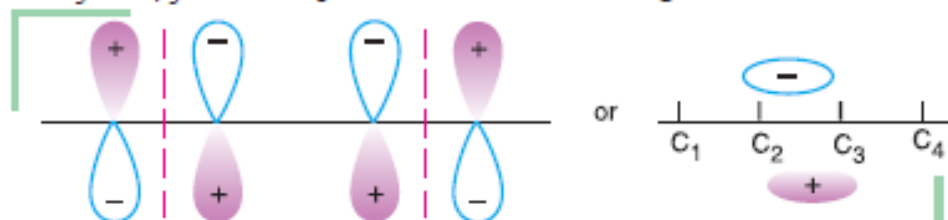


Fig. 2.16. Low energy antibonding orbitals (ψ_3).

In this case, there are two nodal planes and one double bond between C_2 and C_3 .

$\pi^* - \pi^* = \pi_4^* = \psi_4$ can be represented as shown in Fig. 2.17.

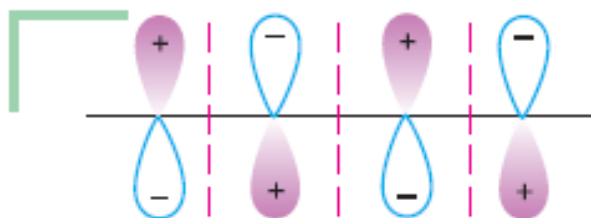


Fig. 2.17. High energy anti-bonding orbital (ψ_4).

This structure corresponds to high energy state since it involves three nodal planes.

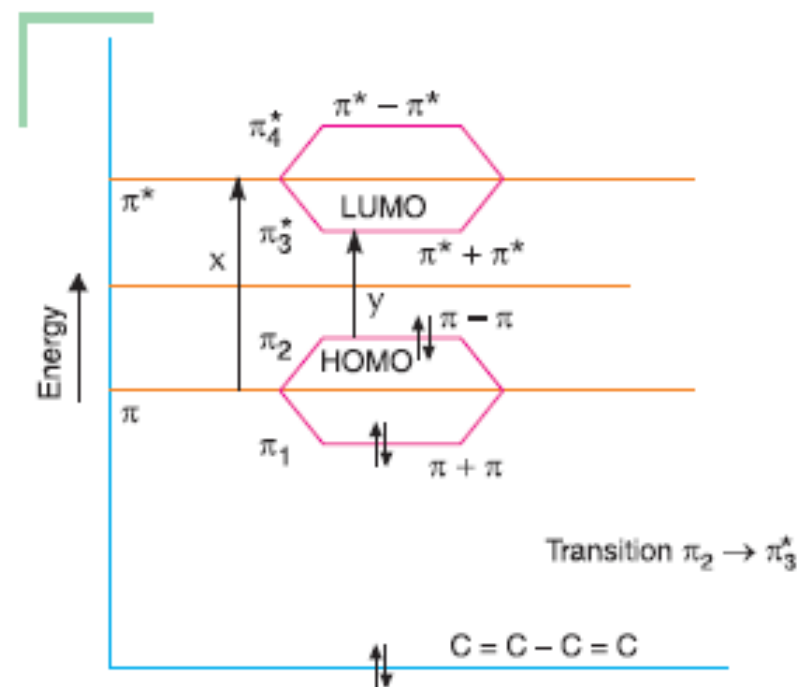


Fig. 2.18. Electronic transition in conjugated diene.

The net result is that when two double bonds are in conjugation, the energy level of higher occupied molecular orbital (HOMO) is raised and that of the lowest unoccupied molecular (antibonding) orbital (LUMO) is lowered

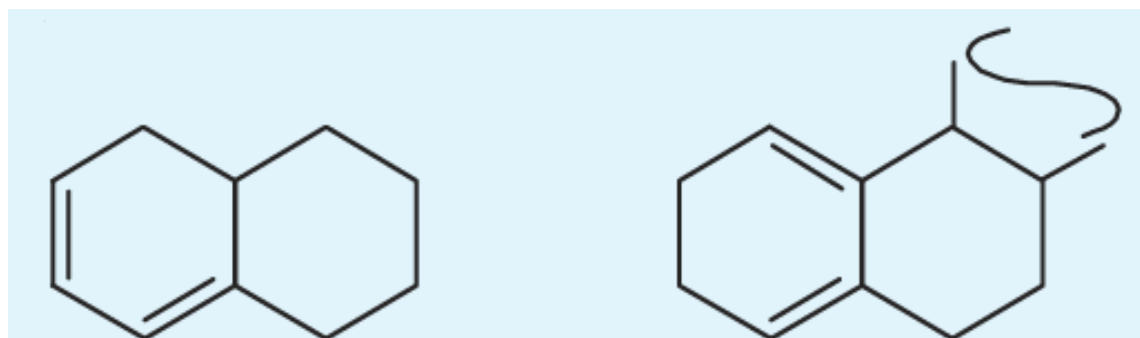


For diene system :

- Longer the conjugated system, greater is the wave-length of absorption maximum. The intensity of absorption [ϵ_{max}] also increases with the increase in the length of the chromophore.
- The conjugated polyene system appears **coloured** to the naked eye if there are **more than five double bonds** in conjugation and absorption occurs around or above 400 m μ .
- The presence of **alkyl group on the double bond** also causes **bathochromic shift**.

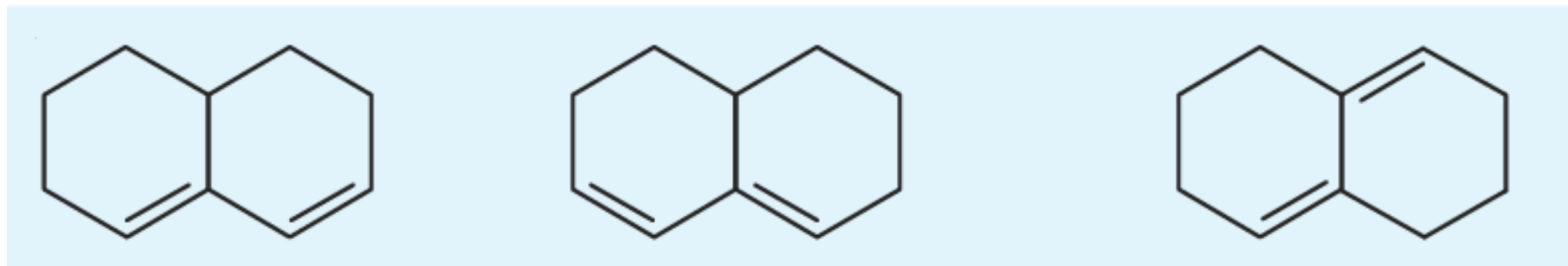
Various types of double bonds in conjugation are described below

- (a) **Alicyclic dienes** or dienes contained in an open chain system, i.e., where basic unit is butadiene system.
- (b) **Homo-annular conjugated double bonds** are the conjugated double bonds present in the same ring. It is also called **Homodiene**.

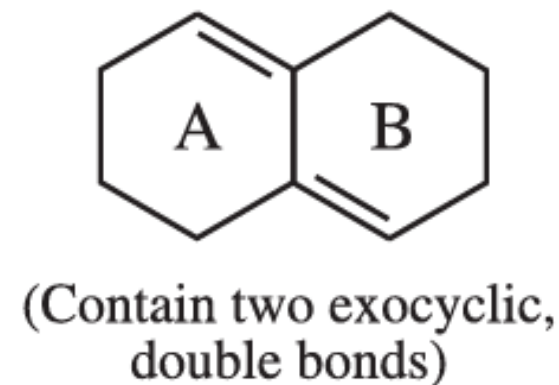
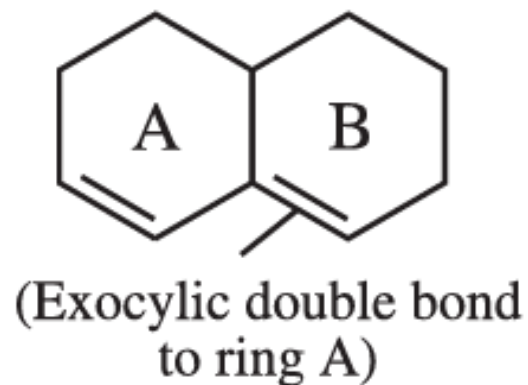
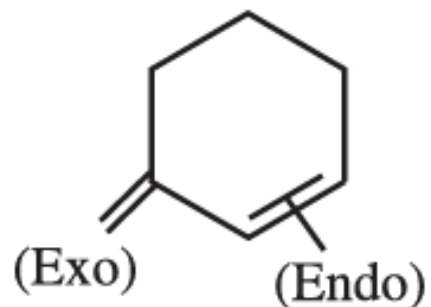




(c) Hetero-annular conjugated double bonds are the conjugated double bonds which are not present in the same ring.



(d) **Exocyclic and Endocyclic conjugated double bonds** : Exocyclic double bond is a double bond, part of the conjugated system, formed by any carbon atom of any ring but present outside the ring. Endocyclic double bond is present inside the ring





Woodward-fieser Rules



- The various rules for calculating the absorption maximum in case of dienes and trienes are summarized in the Table

<i>Solvent—Ethanol</i>	
<i>Transition involved—$\pi \rightarrow \pi^*$</i>	
Parent value for Butadiene system or a cyclic conjugated diene	217 m μ
Acyclic Triene	245 m μ
Homoannular conjugated diene	253 m μ
Heteroannular conjugated diene	215 m μ
Increment for each substituent	
Alkyl substituent or ring residue	5 m μ
Exocyclic double bond	5 m μ
Double bond extending conjugation	30 m μ
Auxochrome	
—OR	+ 6 m μ
—SR	+ 30 m μ
—Cl*, —Br*	+ 5 m μ
—NR ₂	+ 60 m μ
OCOCH ₃	0 m μ



Woodward-fieser Rules



Example: Calculate the absorption maximum in the ultra-violet spectrum of 2, 4- Hexadiene.

Solution: The basic unit in 2, 4. hexadiene is butadiene. There are two alkyl substituents (one on each double bond) on it.

Thus, $(\text{CH}_3\text{---CH=CH---CH=CH---CH}_3)$

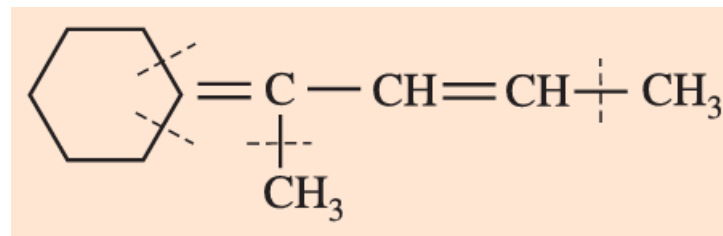
Basic value = 217 m μ

2-alkyl substituents $(2 \times 5) = 10 \text{ m}\mu$

Calculated value = 227 m μ

The observed value* is also found to be 227 m μ .

Example: Calculate the absorption maximum in the UV spectrum of



Solution: The value of absorption maximum is calculated as follows :

Basic value = 217 m μ

2-alkyl substituents $(2 \times 5) = 10 \text{ m}\mu$

2-Ring residues $(2 \times 5) = 10 \text{ m}\mu$

1-Exocyclic double bond Calculated value = 5 m μ

Total = 242 m μ

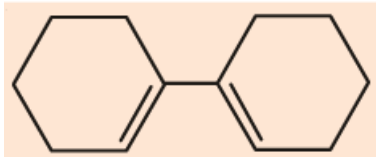
The observed value is also found to be 242 m μ .



Woodward-fieser Rules



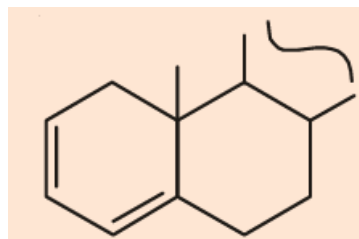
Example : Calculate ϵ_{\max} for



Solution :

$$\begin{array}{rcl} \text{Basic value} & = & 215 \text{ m}\mu \\ \text{Four Ring residues (4} \times \text{5)} & \text{Calculated value} & = 20 \text{ m}\mu \\ \hline \text{Total} & = & 235 \text{ m}\mu \\ \text{The observed value is also found to be} & & 234 \text{ m}\mu, . \end{array}$$

Example : Calculate ϵ_{\max} for



Solution :

$$\begin{array}{rcl} \text{Basic value} & = & 253 \text{ m}\mu \\ \text{3-Ring residues (3} \times \text{5)} & = & 15 \text{ m}\mu \\ \text{1-exocyclic double bond} & \text{Calculated value} & = 5 \text{ m}\mu \\ \hline \text{Total} & = & 273 \text{ m}\mu \\ \text{Calculated value} & \text{Observed value} & = 274 \text{ m}\mu \end{array}$$



Note : In case, both homoannular and heteroannular conjugated diene systems are present in the same compound, then calculations are based on longer wave-length, i.e., for **homoannular conjugated diene system (253 mμ)**.

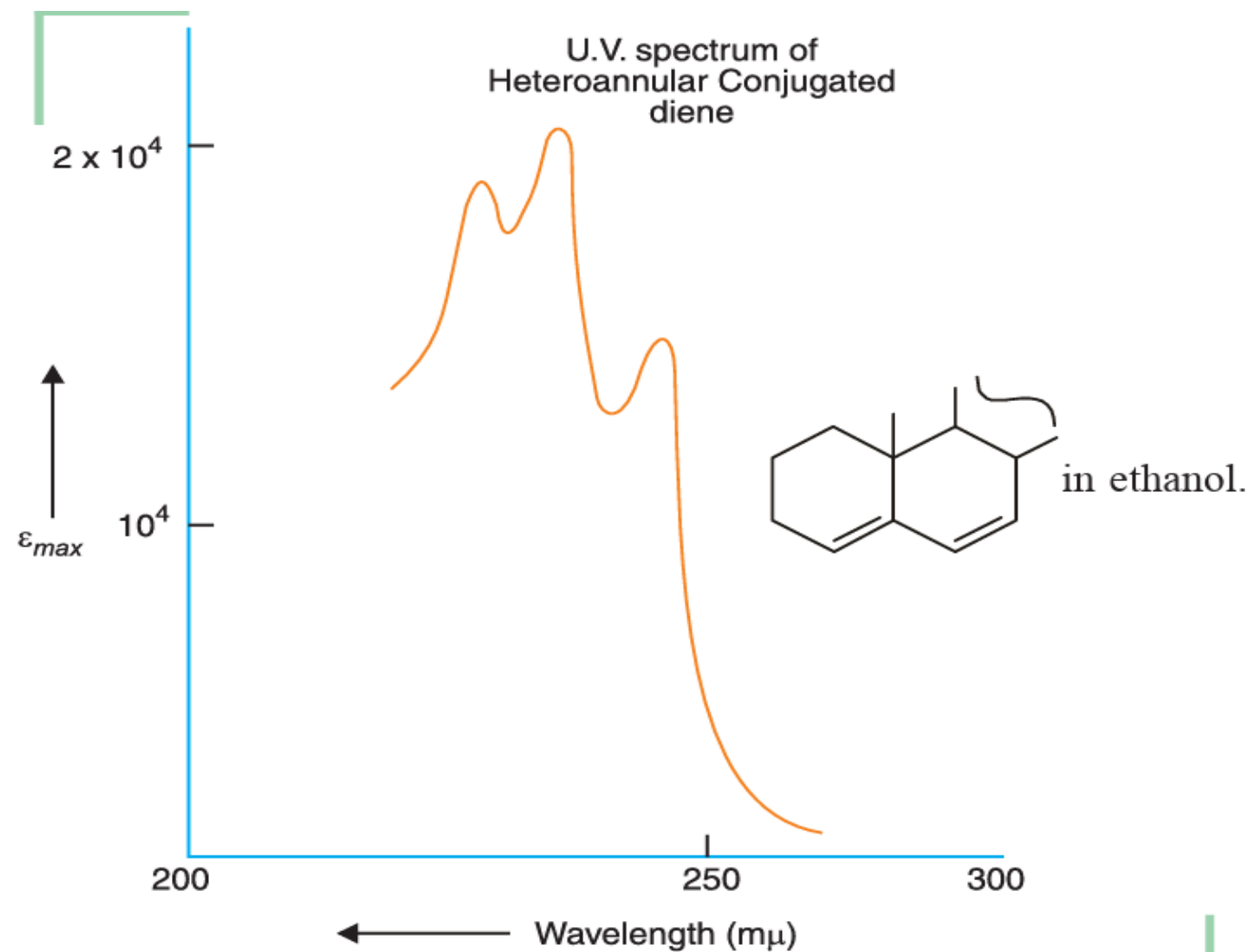
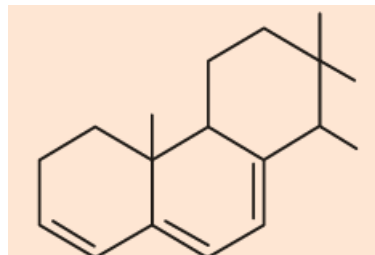


Fig. UV spectrum of heteroannular conjugated diene



Example : Calculate ϵ_{\max} for



Solution :

Basic value = 253 m μ

4-Ring residues (4×5) = 20 m μ

2-exocyclic double bonds (2×5) = 10 m μ

1-double bond extending conjugation = 30 m μ

Calculated value = 313 m μ

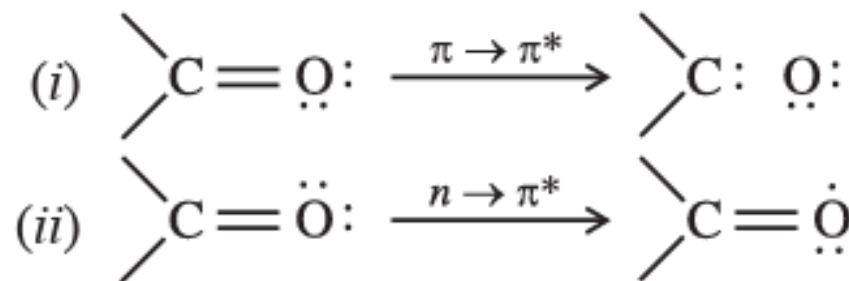
Observed value = 312 m μ



Ultra-violet Absorption in α, β -unsaturated Carbonyl Compounds



➤ For a carbonyl group, two types of transitions occur



- ✓ The first transition involves the promotion of one of the π electrons to an antibonding π^* orbital (π to π^*). It is very intense and corresponds to the shorter wavelength.
- ✓ The second transition (n to π^*) involves the promotion of one of the non-bonding paired electrons to π^* orbital. It is less intense and corresponds to a longer wavelength.

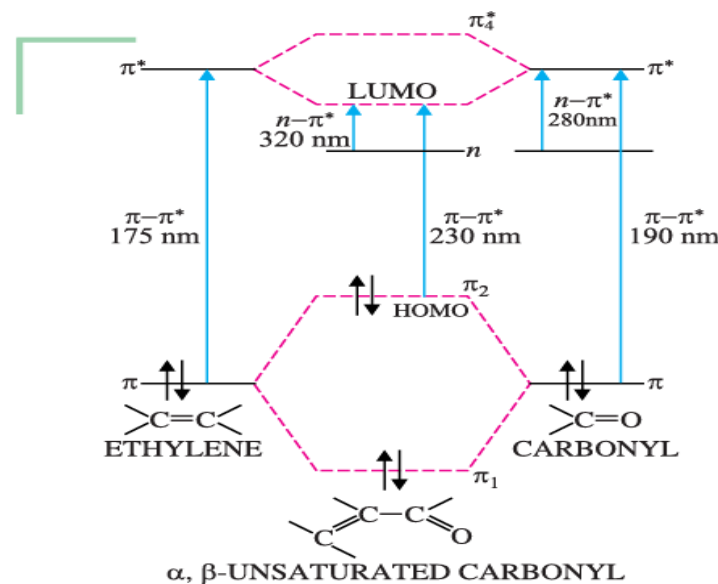


Fig. UV transitions in α, β -unsaturated carbonyl compounds



α , β -unsaturated Carbonyl Compounds :

The structural increments for estimating maximum wavelength for a given α , β , γ -unsaturated Carbonyl compound are as follows :

- (i) For each exocyclic double bond = + 5 m μ
- (ii) For each double bond endocyclic in five or seven membered ring except cyclo-pent-2 enone = + 5 m μ
- (iii) For each alkyl substituent or ring residue at the ;
 - α -position = + 10 m μ
 - β -position = + 12 m μ
 - or γ - or higher position = + 18 m μ
- (iv) For each double bond extending conjugation = + 30 m μ
- (v) For a homoannular conjugated diene = + 39 m μ
- (vi) Increments for various auxochromes in the various α , β , γ - etc. positions are given in the following Table;

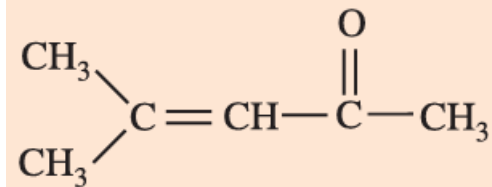
Chromophore	Increment in nm (or m μ) for position w.r.t. the carbonyl group			
	α -	β -	γ -	δ - or higher
—OH	+ 35	+ 30	—	+ 50
—OAc	+ 6	+ 6	+6	+ 6
—Cl	+ 15	+ 12	—	—
—Br	+ 25	+ 35	—	—
—OR	+ 35	+ 30	17	31
—SR	—	+ 85	—	—
—NR ₂	—	+ 95	—	—



Woodward-fieser Rules



Example : Calculate ϵ_{\max} for



Solution :

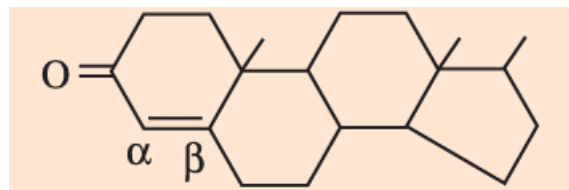
Basic value = 215 m μ

2 β -alkyl substituents (2×12) = 24 m μ

Calculated value = 239 m μ

The observed value is found to be 237m μ

Example : Calculate ϵ_{\max} for



Solution :

Basic value = 215 m μ

2 β -alkyl substituents (2×12) = 24 m μ

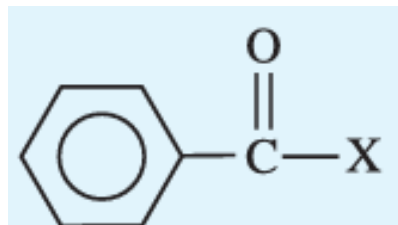
1 exocyclic double bond = 5 m μ

Calculated value = 244 m μ

The observed value is found to be 241m μ



Rules for Calculating Absorption Maximum for Derivatives of Acyl Benzenes



- (i) the basic value is 246 m μ if X is an alkyl group or alicyclic residue.
- (ii) If X is a hydrogen atom, the basic value becomes 250 m μ .
- (iii) the basic value is 230 m μ if X is OH or OR.

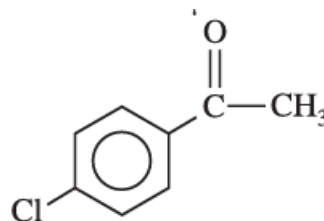
The structural increments in m μ for further substitution on the aromatic ring in the ortho, meta, and para positions are given in Table;

<i>Auxochrome</i>	<i>Increment in mμ Position of the Substituent</i>		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Alkyl	+ 3	+ 3	+ 10
OH, OR	+ 7	+ 7	+ 25
Cl	0	0	+ 10
Br	+ 2	+ 2	+ 15
NH ₂	+ 13	+ 13	+ 58
NHAc	+ 20	+ 20	+ 45
NR ₂	+ 20	+ 20	+ 85
O ⁻	+ 11	+ 20	+ 75



Examples of Absorption Maximum for Derivatives of Acyl Benzenes

Example : Calculate ϵ_{\max} for



Solution :

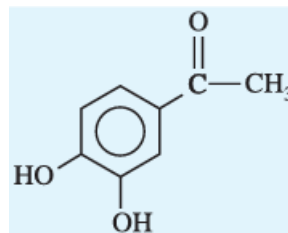
Basic value = 246 m μ

Cl-substitution at para position = 10 m μ

Calculated value = 254 m μ

The observed value is found to be = 256 m μ

Example : Calculate ϵ_{\max} for



Solution :

Basic value = 246 m μ

OH substitution at meta = 7 m μ

OH substitution at para = 25 m μ

Calculated value = 278 m μ

Observed value = 281 m μ



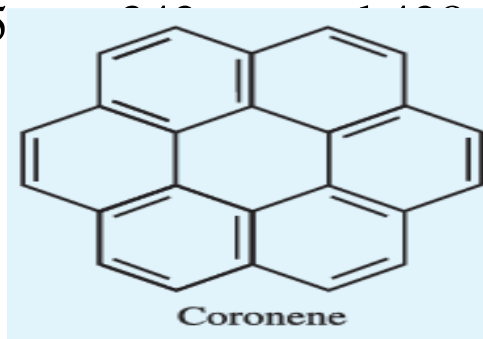
➤ The range of absorption maximum for polycyclic hydrocarbons is very great and spectra are usually complicated

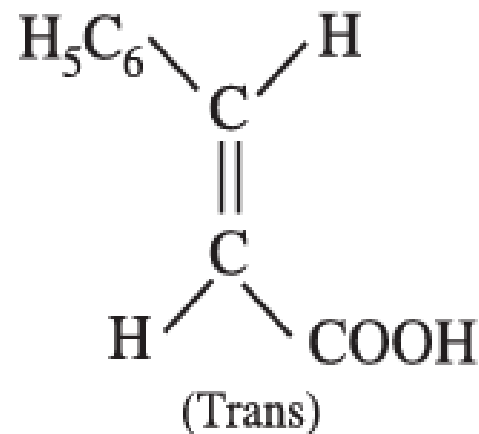
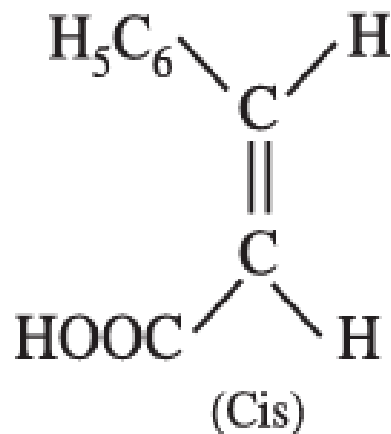
The condensed systems are classified into

- (a) **Cata-condensed system:** In a Cata-condensed system, no carbon atom belongs to more than two rings. Benzene, naphthalene, etc. are the examples.
- (i) Linear cata-condensed compounds. These are Naphthalene, Anthracene, etc.
 - (ii) Bent cata-condensed compounds. These include phenanthrene-type molecules.

The spectra of cata-condensed hydrocarbons resemble benzene. The bathochromic shift is observed with the increase in the number of rings in the structure. For example, benzene absorbs at $254 \text{ m}\mu$ ϵ_{max} 204. Naphthalene absorbs at $312 \text{ m}\mu$ ϵ_{max} 289, while pentacene absorbs in the visible region.

(b) **Peri-condensed system:** In peri-condensed systems, a carbon atom belongs to more than two rings. An example is coronene. Peri-condensed rings show absorptions at longer wavelengths as compared to cata-condensed structures. Coronene shows absorptions at 305 and $480 \text{ m}\mu$.





- Due to greater crowding in cis-form (both bulky groups are on the same side), the geometry of the alkene chromophore is distorted and departure from coplanarity results.
- Thus, π to π^* transition in cis-cinnamic acid takes place at lower wave-length with a lower extinction coefficient.

- (i) Trans-cinnamic acid absorbs at $272 \text{ m}\mu$ ϵ_{max} 15900.
- (ii) (ii) Cis-cinnamic acid absorbs at $268 \text{ m}\mu$ ϵ_{max} 10700.



- Fluorescence is the light of comparatively longer wavelength emitted from a molecule after it has absorbed light of different and short wavelengths.
- Anthracene is a colorless substance and its electronic absorption spectrum lies in the ultraviolet region. However, it is found that pure samples of anthracene when viewed in the ultra-violet light give off a blue-visible light. This light is called **fluorescence**.
- The emission of light or fluorescence stops at once when the irradiating light is removed.
- On the other hand, the phenomenon of phosphorescence is said to occur when the substance continues to emit radiation of a longer wavelength even when the irradiating light is removed.

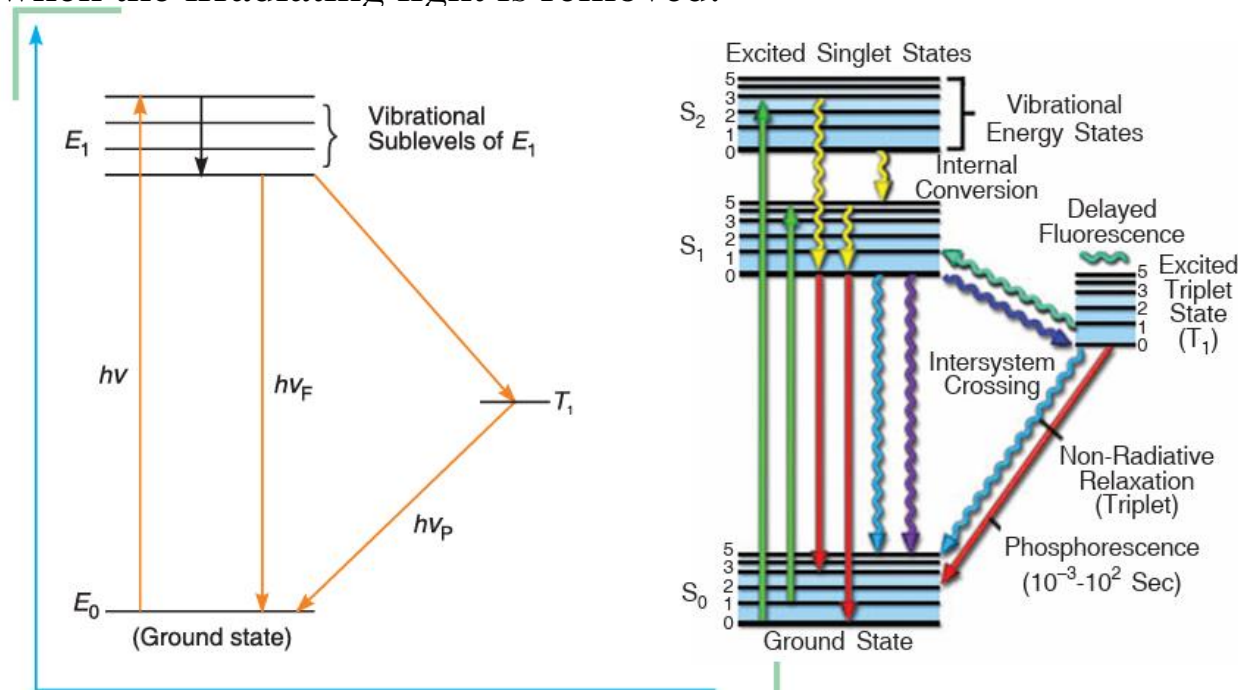


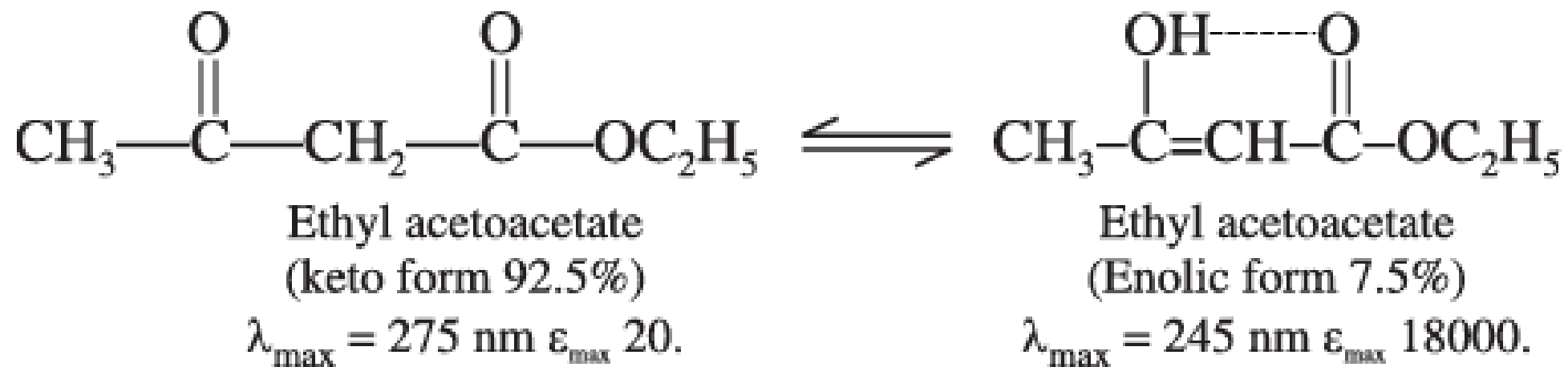
Fig. Mechanism of Fluorescence and Phosphorescence



Study of Keto-enol tautomerism



- Carbonyl compounds containing α -hydrogen exist as keto-enol tautomers.
- β -ketones and β -ketoesters exist as tautomeric mixtures. Their UV spectra show absorption bands which are characteristic of both keto and enol forms.
- Due to the enol form, a strong π to π^* band is observed, and also a weak n to π^* band for the keto group. Consider the case of ethyl acetoacetate ($\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$) in ethanol. A strong band (π to π^*) at 245 nm (ϵ_{max} 18000) is observed and a weak band (n to π^*) is observed at 275 nm (ϵ_{max} 20) due to keto form.





Franck Condon Principle



- According to this principle, “An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.
- This principle is true to the first approximation since the electrons move so much faster than the nuclei that during the electronic transition, the nuclei do not change their positions.
- the molecule in the ground electronic state (E_0) and the first electronic state (E_1).
- Since the bonding in the excited state is weaker than in the ground state, the minimum in the potential energy curve for the excited state occurs at a slightly greater internuclear distance than the corresponding minimum in the ground electronic state

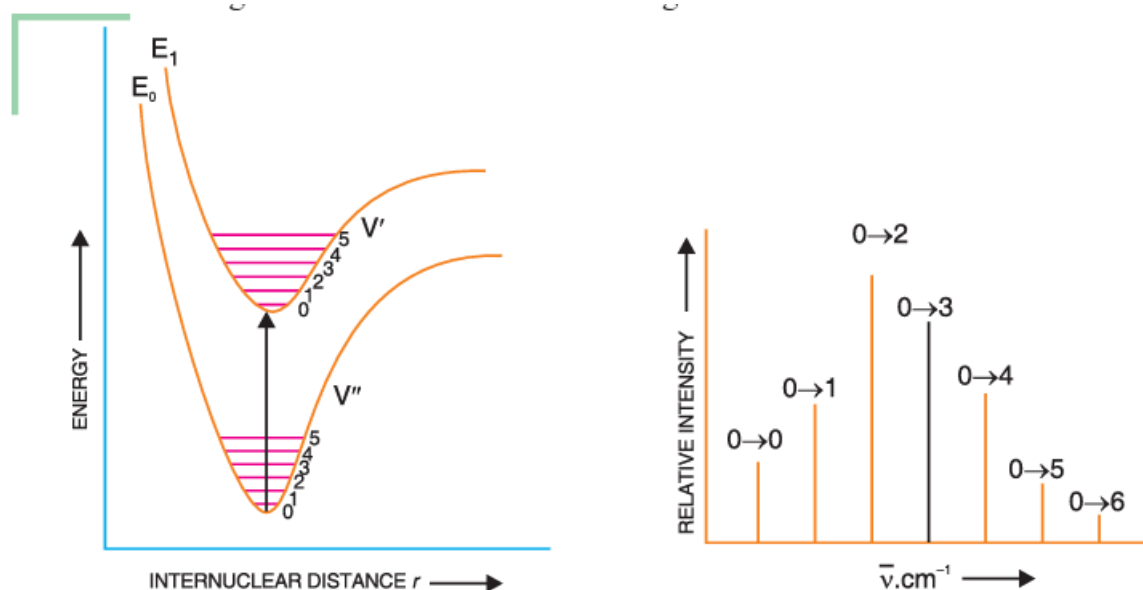


Fig. Electronic transition in diatomic molecule

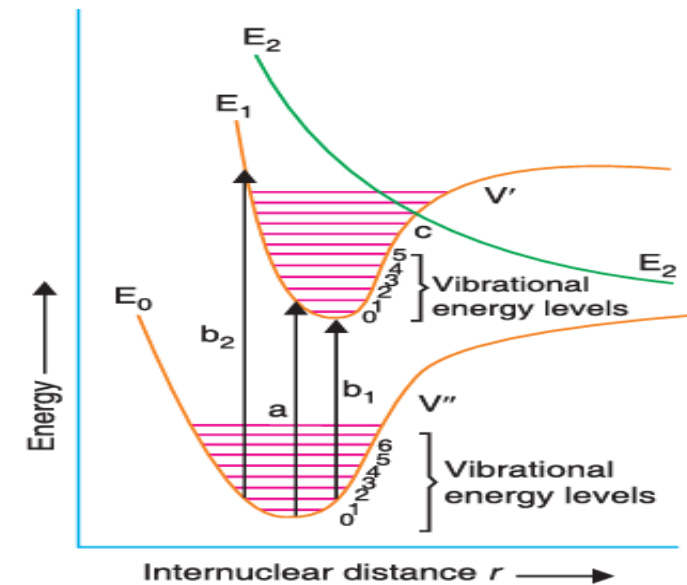


Fig. Potential energy curves for the ground state, two excited states of a diatomic molecule.
The curve crosses the curve E_1



- Ultra-violet spectroscopy has been mainly applied for the detection of functional groups (chromophore), the extent of conjugation, the detection of polynuclear compounds by comparison, etc.
- Some important applications of ultraviolet spectroscopy are as follows :
 - ✓ Detection of functional groups.
 - ✓ Extent of conjugation.
 - ✓ Distinction in conjugated and non-conjugated compounds.
 - ✓ Identification of an unknown compound.
 - ✓ Examination of Polynuclear hydrocarbons.
 - ✓ Elucidation of the structure of vitamins A and K.
 - ✓ Preference over two Tautomeric forms.
 - ✓ Identification of a compound in different solvents.
 - ✓ Determination of configurations of Geometrical isomers.
 - ✓ Determination of strength of hydrogen bonding.
 - ✓ Hindered Rotation and Conformational Analysis.

Thank you

