MODULE - 5

SPECTROSCOPIC TECHNIQUES and APPLICATIONS

Question What is Spectroscopy ? (YMCA)

Spectroscopy is the branch of Scienc which Deals with Interaction between Matter and ELECTROMAGNETIC Radiations (light).

All light measuring devices are based on such Interactions In some of these interactions light behave as Particle and in some other as wave.

Ques- What is the use or application of Spectroscopy ?

1.) Spectroscopic techniques provide a wide Range of Qualitative and Quantitative Information Regarding atomic and molecular Structure, presence of CONJUGATED Double Bonds & their Numbers.

2.) Helps in identification of Conjugated and NON Conjugated System,

3.) Identifying functional groups and Stereochemical arrangements.

Ques - what are Parameter on which spectroscopy is based?

Answer - Two Experimental Paramaters

(a) Absorption or Emission of Energy $(E = h\nu = E_2 - E_1)$

E_1 = Lower energy level

E_2 = Higher energy level

(b) Intensity of spectral lines.

Ques - What are 2 Basic Type of spectroscopy.

Two Basic spectroscopy are

(a) ATOMIC SPECTROSCOPY (b) MOLECULAR SPECTROSCOPY

Ques - EXPLAIN Briefly Atomic & Molecular spectroscopy

(a) ATOMIC SPECTROSCOPY

→ It deals with Interaction of Electromagnetic Radiation with atoms.

→ Absorption of Radiation take place with photons having energy difference equal to $(\Delta E = h\nu)$

ΔE = Energy difference b/w Two Quantized energy level of atom.

→ There is No Vibrational and Rotational Energy levels

→ SPECTRUM is SIMPLE LINE Spectra.

(b) MOLECULAR SPECTROSCOPY

→ It deals with interaction of electromagnetic Radiation with molecules.

→ Electronic, Vibrational and Rotational energy Levels are involved

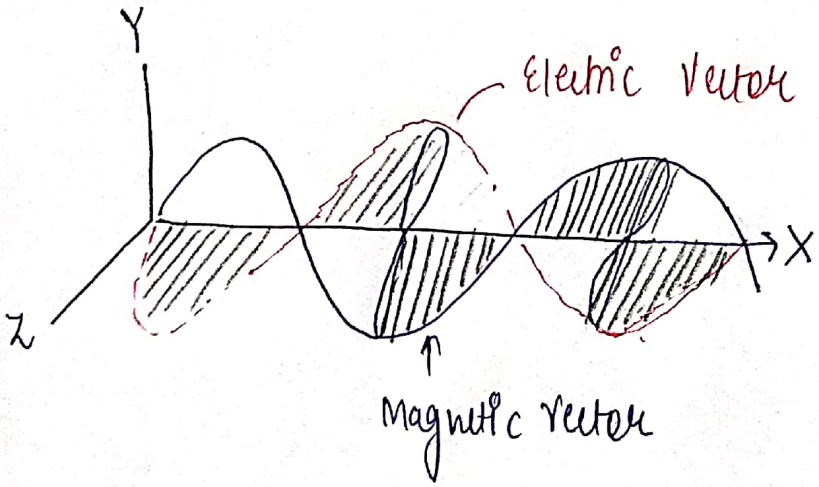
→ SPECTRA is Continious rather than line and is known as BAND SPECTRA

→ Bands are found in Three distinct Regions of electromagnetic Spectrum

- (i) Infrared or Microwave (ii) UV-visible (iii) Near Infrared

→ Spectra provide Information about - shape, size and molecular structure as well as Bond distances, strength and dissociation Energy

Representation of EM Wave



Maxwell Theory of EM Radiation

Light Travels in space in form of an oscillating Electric field which generates Magnetic field perpendicular to itself & direction of Propogation

ELECTROMAGNETIC SPECTRUM

Arrangement of electromagnetic Radiation of various types in order of Increasing (or Decreasing) wavelength or frequencies.

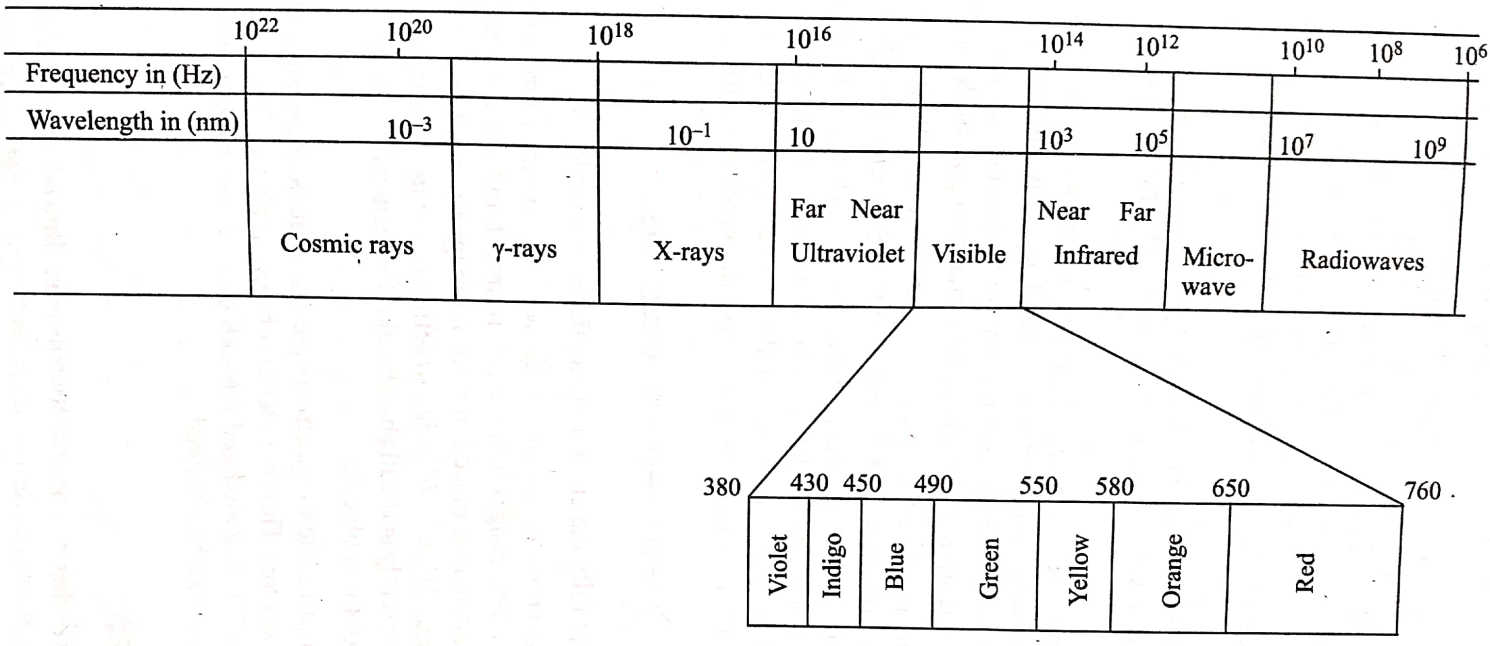


Fig. 2.3 Electromagnetic spectrum

Molecular Spectroscopy

* Molecular spectra arises from three types of Transition (a) Rotational (b) Vibrational and (c) Electronic Transitions.

* Total Energy of molecule is given by Born-Oppenheimer Approximation

$$E = E_{Translational} + E_{Rotational} + E_{vib} + E_{electronic}$$

Where

$$E_{ele} >>> E_{vib} >> E_{rot} > E_{translational}$$

Since $E_{Translation}$ is very small so Neglected

$$\boxed{E = E_{Rotational} + E_{Vibrational} + E_{electronic}}$$

→ Rotational Energy arises when molecule Rotate about an axis Perpendicular to internuclear axis.

→ Vibrational Energy arises due to (to & fro) motion of Nuclei of molecule

→ Electronic Energy is associated with Transition of electron from ground state energy level to excited state on absorption of energy.

→ Electronic Level Consist of Vibrational levels denoted by Quantum No. (V)

→ Vibrational levels consist of Rotational sub levels denoted by Quantum No. (J)

Defination of Spectroscopy

It deals with Transition that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by Quantum Mechanical Selection Rules.

We will study in Detail – Molecular Spectra

MOLECULAR SPECTROSCOPY

* The molecular spectra are governed by so-called SELECTION RULES
* These Rules specify changes in Quantum Numbers accompanying a Particular Transition.

Allowed Transition

The spectral Transition which obey a given Selection Rule are called allowed transition.

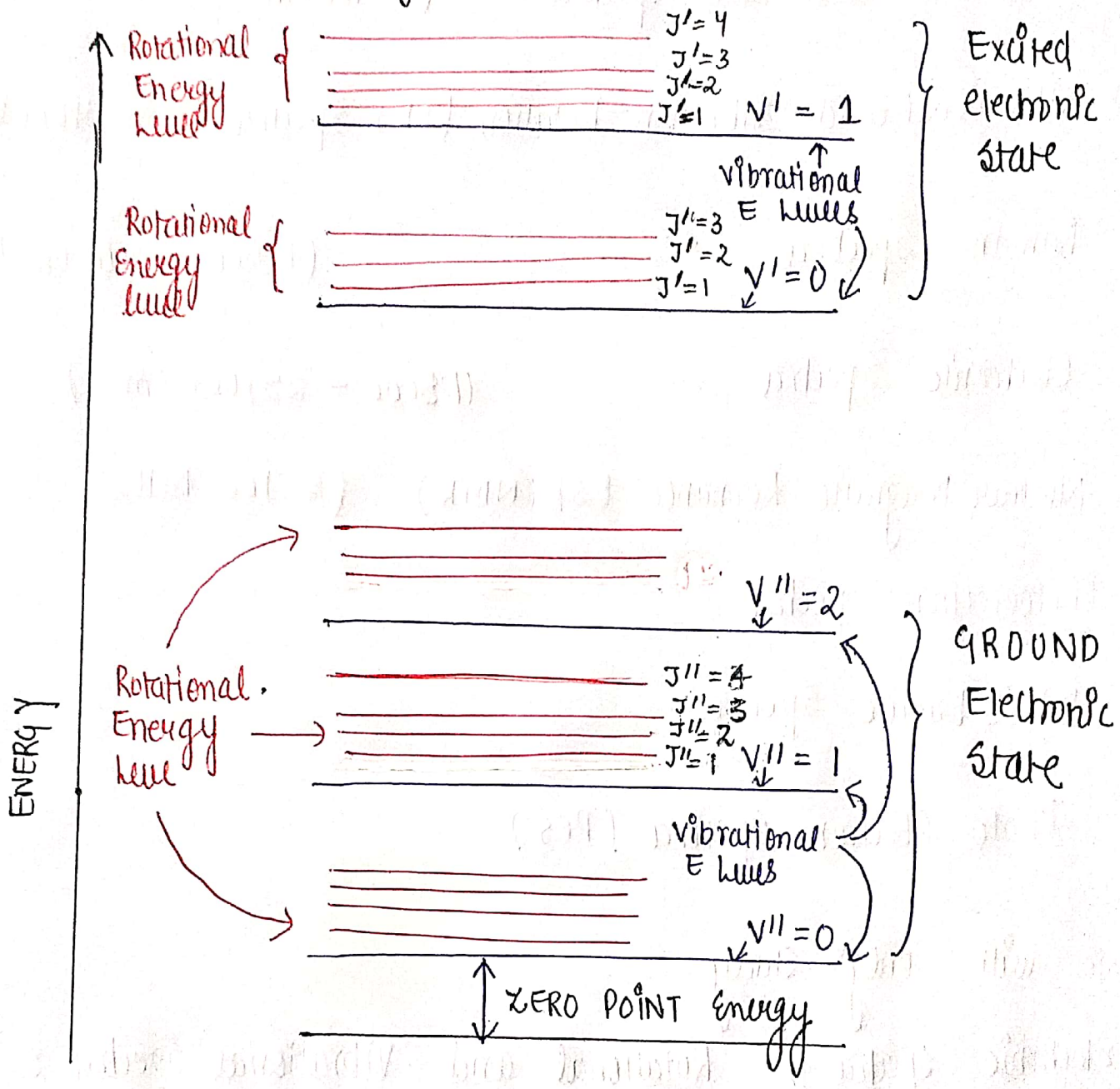
Forbidden Transition

The spectral Transition which Violate a Selection Rule are called Forbidden Transition.

Allowed Transition are More (Intense) Stronger than Forbidden Transitions (weak).

V.V. Imp

ENERGY LEVEL DIAGRAM SHOWING VARIOUS MOLECULAR ENERGIES



Lower Level of Vibrational Energy denoted by V''

Higher " " " " " by V'

Lower Level of Rotational Energy denoted by J'

Higher Level of " " " J''

Transition occurs b/w Vibrationals Levels and Rotational levels Giving Vibrational and Rotational Spectras.

Molecular Spectra Accomodate following Spectras.

(a) Rotational (Microwave) Spectra ($1-100\ cm^{-1}$)

(b) Vibrational and Vibration-Rotation (IR) Spectra ($500-4000\ cm^{-1}$)

(c) Raman Spectra ($12500-25000\ cm^{-1}$)

(d) Electronic Spectra ($12500-25,000\ cm^{-1}$)

(e) Nuclear Magnetic Resonance (NMR)

(f) Photoelectron Spectra

(g) Mossbaeur Spectra

(h) Photo Electron Spectra (PES)

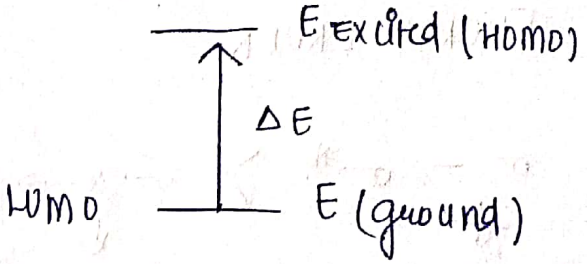
We will only study Electronic spectra, Rotational and Vibrational Spectra & (Nuclear Magnetic Resonance)

ULTRA VIOLET and Visible SPECTROSCOPY

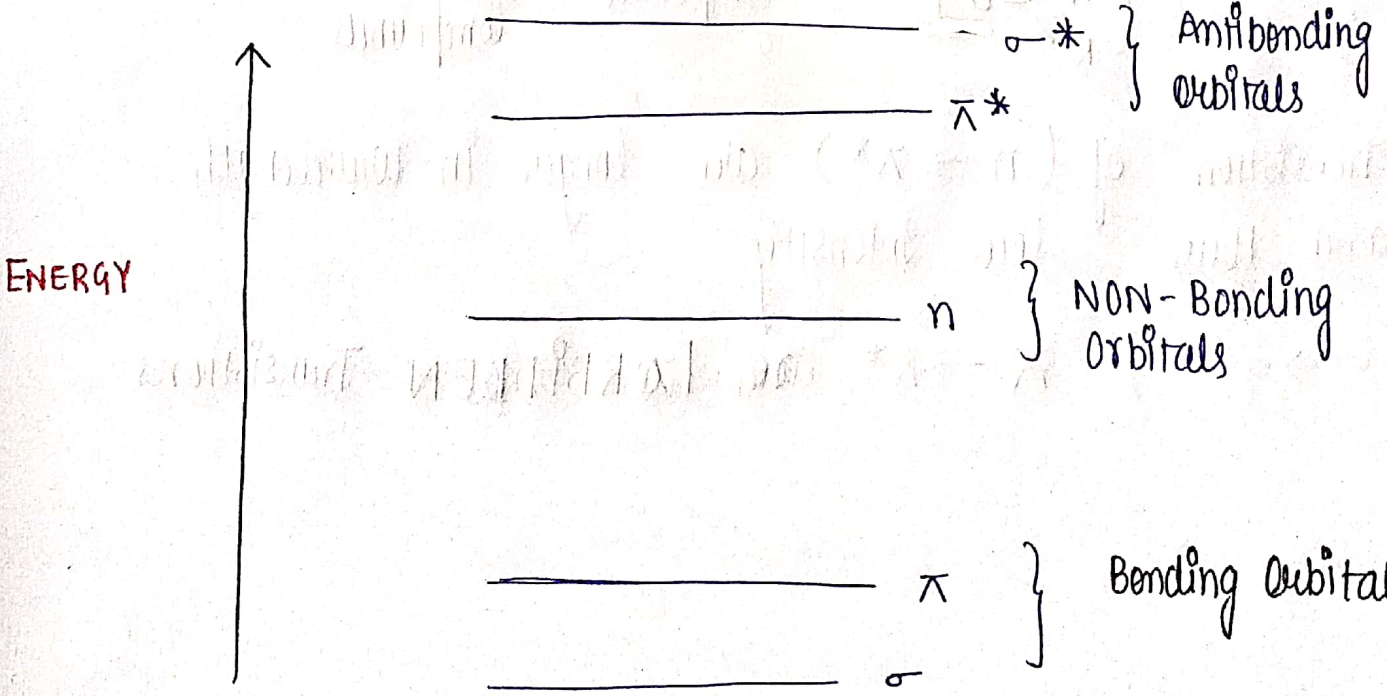
Ultra voilet Region and visible Region lies in between 190 to 800nm.

* UV- visible spectroscopy is based on Electronic Excitations
* In UV- visible Transitions Results from absorption of electromagnetic Radiations b/w electronic energy levels.

$[\Delta E = E(\text{Excited}) - E(\text{ground state})] = h\nu$

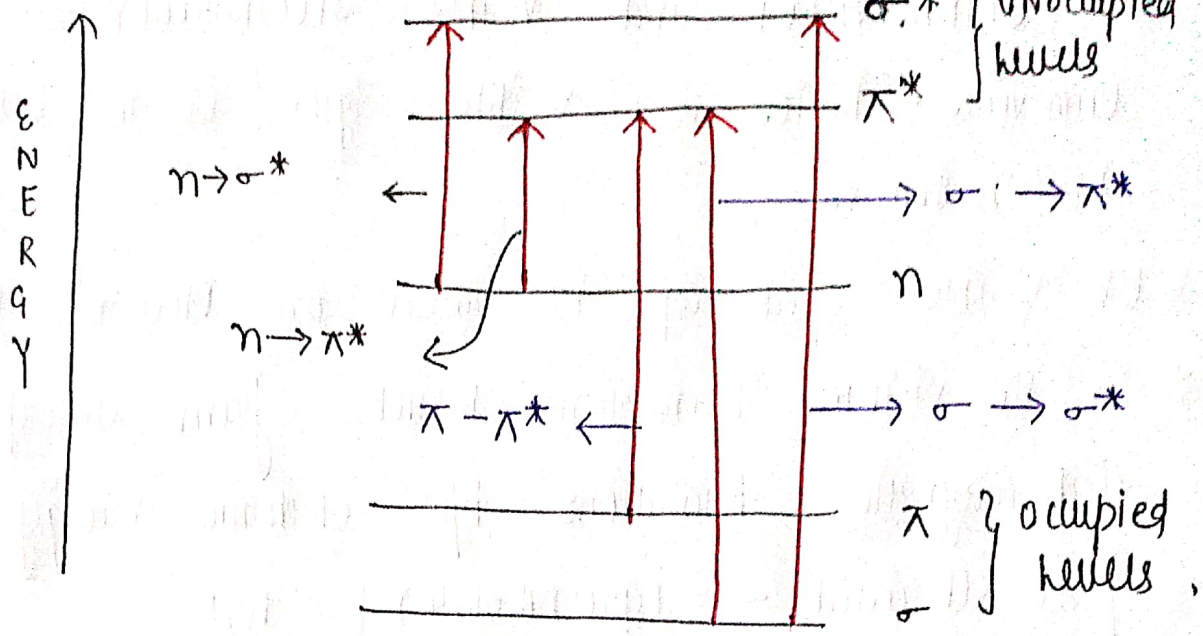


ELECTRONIC ENERGY LEVELS



In absorption of Radiations electrons are promoted from Bonding to Antibonding orbitals.

ELECTRONIC TRANSISTIONS



ENERGY ORDER

$\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$

- $\sigma \rightarrow \sigma^*$: Takes place in alkanes
- $\sigma \rightarrow \pi^*$: Present in Carbonyl compounds ($R_2C{=}O$)
- $\pi \rightarrow \pi^*$: Present in alkynes, azo & carbonyl compound
- $n \rightarrow \sigma^*$: Oxygen, Nitrogen, Sulfur & Halogen compounds
- $n \rightarrow \pi^*$: In carbonyl compounds

* Transistion of ($n \rightarrow \pi^*$) are longer in wavelength and Have low Intensity
* $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ are FORBIDDEN Transistions

Main Features of Transitions

1) $\sigma \longrightarrow \sigma^*$ = Energy Requirment for these Transition is very High and hence occurs at low wavelength

Example → Methane, Ethane and Alkanes

2.) $n \longrightarrow \sigma^*$ = Energy Requirement is less and these Transition takes place in Saturated Compound having Hetro atom (N, O, F, Cl, S) with Unshared pair or NON Bonding Electrons.

Occurs at Longer Wavelength (190-380 nm)

Example → Water, CH_3Cl etc.

3.) $\pi \longrightarrow \pi^*$ ⇒ Occurs in Unsaturated Compound (Double or Triple Bonds) including Aromatic Ring.

Very Small energy Required & Wavelength is very High

4) $n \longrightarrow \pi^*$ ⟹ Shown by Unsaturated atom having hetro atoms like (O, N, S) etc.

Energy Requirement is less and occurs a longer wavelength

Example – Ketones, aldehydes etc.

SELECTION RULES FOR UV – Visible spectroscopy :

(a) Transition involving a change in spin Quantum Number (ΔS) of electrons are Not allowed
They are forbidden Transition
Thus singlet to Triplet Transition are forbidden

(b) Transition between orbitals of different symmetry do not occur
They are symmetry forbidden (Example $n \rightarrow \pi^*$)

LIGHT ABSORPTION BY SOLUTIONS

V.V.Imp (YMCA)

BEER- LAMBERT LAW

Absorption of light in visible and Near Ultraviolet Region by a solution is governed by Beer-Lambert Law

Defination

When a Beam of monochromatic Radiation of suitable frequency passes through a solution, it is absorbed by solution. As a Result Intensity of light when it finally emerges from solution is considerably Reduced.

$$I_a = I_o - I_t \quad — (1)$$

I_a = Intensity of light absorbed I_t = Intensity of Transmitted beam

I_o = " " Incident light

$\frac{dI}{I}$ directly proportional $c\,dx \Rightarrow \frac{dI}{I} = -\alpha c\,dx \quad — (2)$

dI = change in Intensity dx = thickness of solution

α = propotionality constant C = Conunration of solution

Integerating

$$\int \frac{dI}{I} = -\alpha c \int_0^b dx \quad — (3)$$

$$\ln\left(\frac{I}{I_o}\right) = -\alpha c b$$

$$\ln\left(\frac{I}{I_o}\right) = 2.303 \log\left(\frac{I}{I_o}\right) = -\alpha b c \quad — (4)$$

Putting $\frac{\alpha}{2.303} = \varepsilon$ and $\log\left(\frac{I_0}{I}\right) = A$ = absorbance

$$A = \varepsilon b c = \log\left(\frac{I_0}{I}\right)$$

$$A = \log \frac{I}{I_0} = \varepsilon b c$$

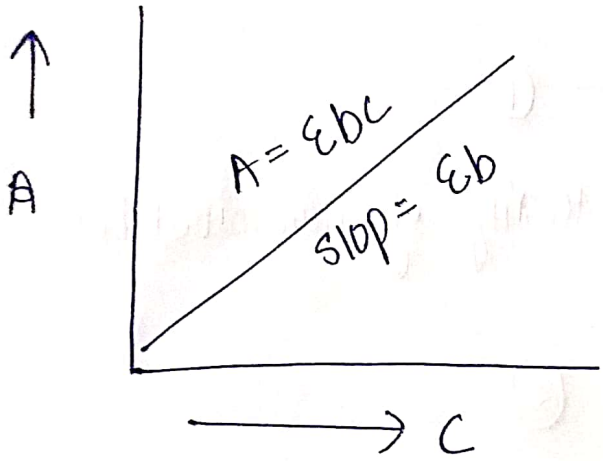
Beer-Lambert Law

A = Absorbance of solution

ε = Molar Extinction coefficient

b = path length

c = Concentration of solution



★ What is molar Extinction coefficient (ε)

It is characteristic of solute and depends upon Nature of solvent, Temperature & wavelength of Radiation employed

It is denoted by (ε)

Q- What is Transmittance

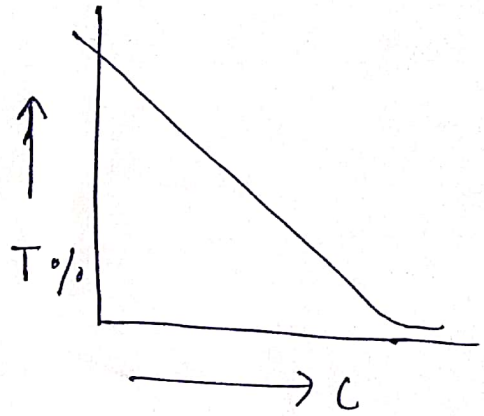
From Beer-Lambert law $A = \varepsilon bc = \log \frac{I_0}{I}$

$T = \frac{I}{I_0}$ So above equation becomes

$$A = -\log\left(\frac{I}{I_0}\right) = -\log T$$

Formula for Transmittance

$$T = 10^{-A} = 10^{-\varepsilon bc}$$



Limitation of Beer-Lamber law.

1. Not obeyed for Radiations which are Not Monochromatic
2. Only applicable for dilute solutions
3. Yeh Applicable only at constant Temperatures

Ques- What are Chromophores ? (YMCA)

Answer - Chromophores are Colour Carrier.

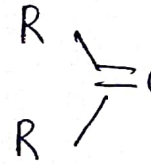
* A group which shows a characteristic absorption in ultraviolet or visible Region spectrum is called chromophore

* They absorb Radiations at wave length greater than 180 nm or longer than 180 nm.

Examples ⇒ (a) Chormophores which shows $\pi \rightarrow \pi^*$ Transition

$C=C$, $C\equiv C$ etc

(b) Chromophores which show $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ Transition



, $-N=N-$, NO_2 group , $C\equiv N$ etc.

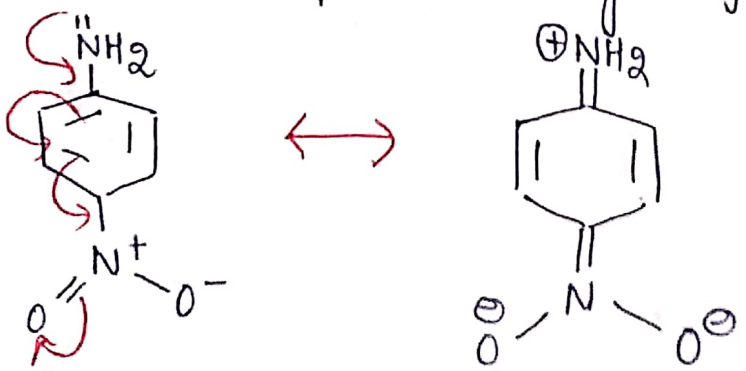
Ques – What are AUXOCHROMES ? (YMCA)

Ans- Auxochromes are the groups which does Not itself act as chromophores but when attached to chromophore it shifts The Absorption Maximum Towards Longer wavelength along with Increase in Intensity of Absorption.

* They causes BATHOCHRMOIC SHIFT and HYPER CHROMIC SHIFT

Examples of Auxochromes — $-\ddot{O}H$, $-\ddot{N}H_2$, $-\ddot{O}R_3$; Halogens , $-CH_3$ etc

* Auxochromes also Helps in extending Conjugation



Ques- What do you mean by BATHOCHROMIC, HYPSOCHROMIC, V.V.Imp HYPERCHROMIC and HYPOCHROMIC SHIFT? (YMCA)

Answer-

(i) BATHOCHROMIC SHIFT → Shifting of λmax (i.e maximum (or RED SHIFT) Absorption) towards Longer wavelength

Bathochromic or Red shift occurs due to Auxochrome or decrease in solvent polarity

(ii) HYPSOCHROMIC SHIFT – Shifting of λmax towards Shorter (or BLUE SHIFT) wavelengths.

Blue shift occurs due to Removal of conjugation or change in solvent Polarity

(iii) HYPERCHROMIC SHIFT – effect due to which There is Increase in Intensity of Absorption Maximum (εmax)

Example

Benzene

λmax = 254
εmax ~ 200

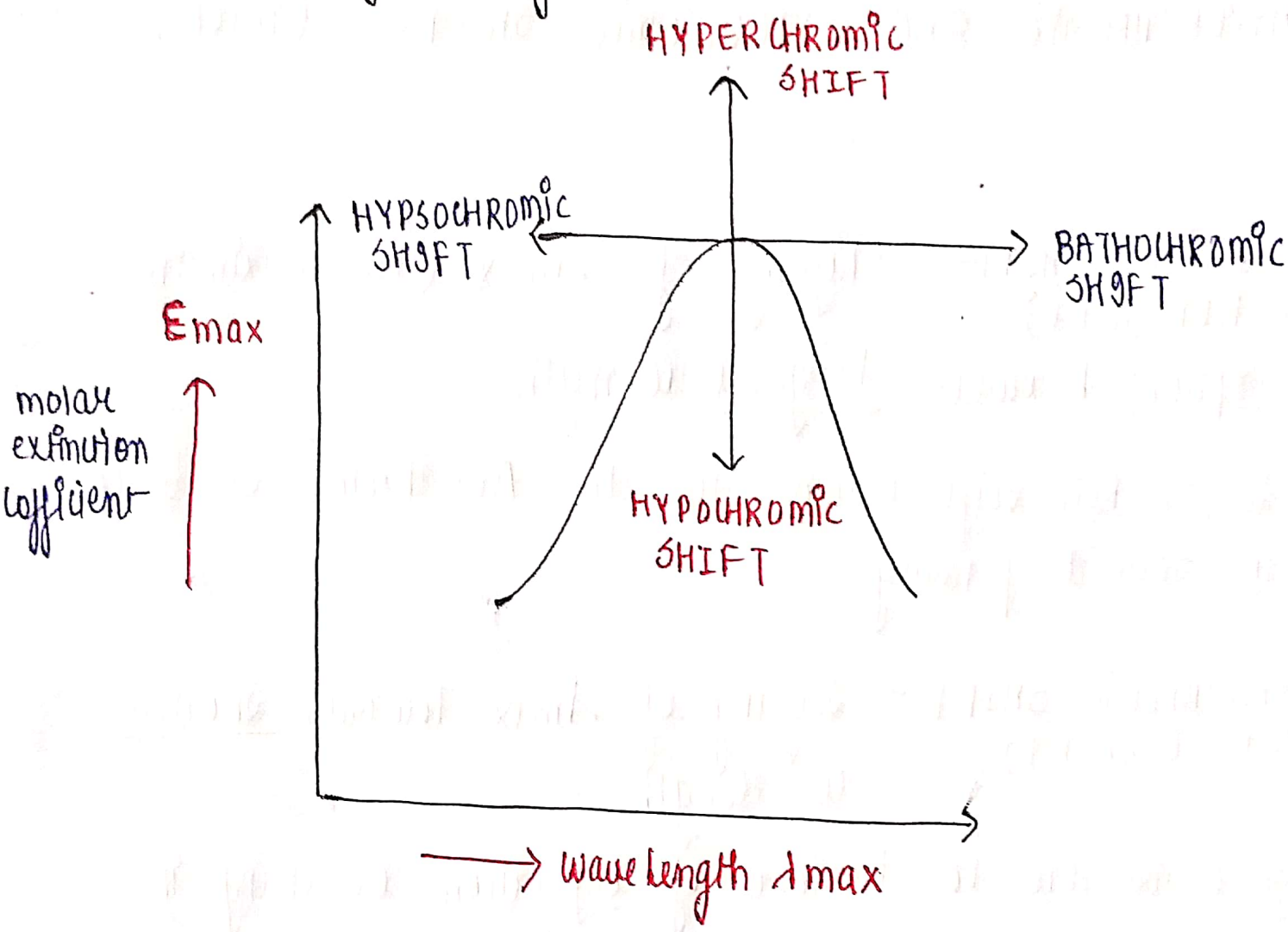
Toluene

λmax = 261
εmax ~ 300

Change of methyl group cause Increase in εmax

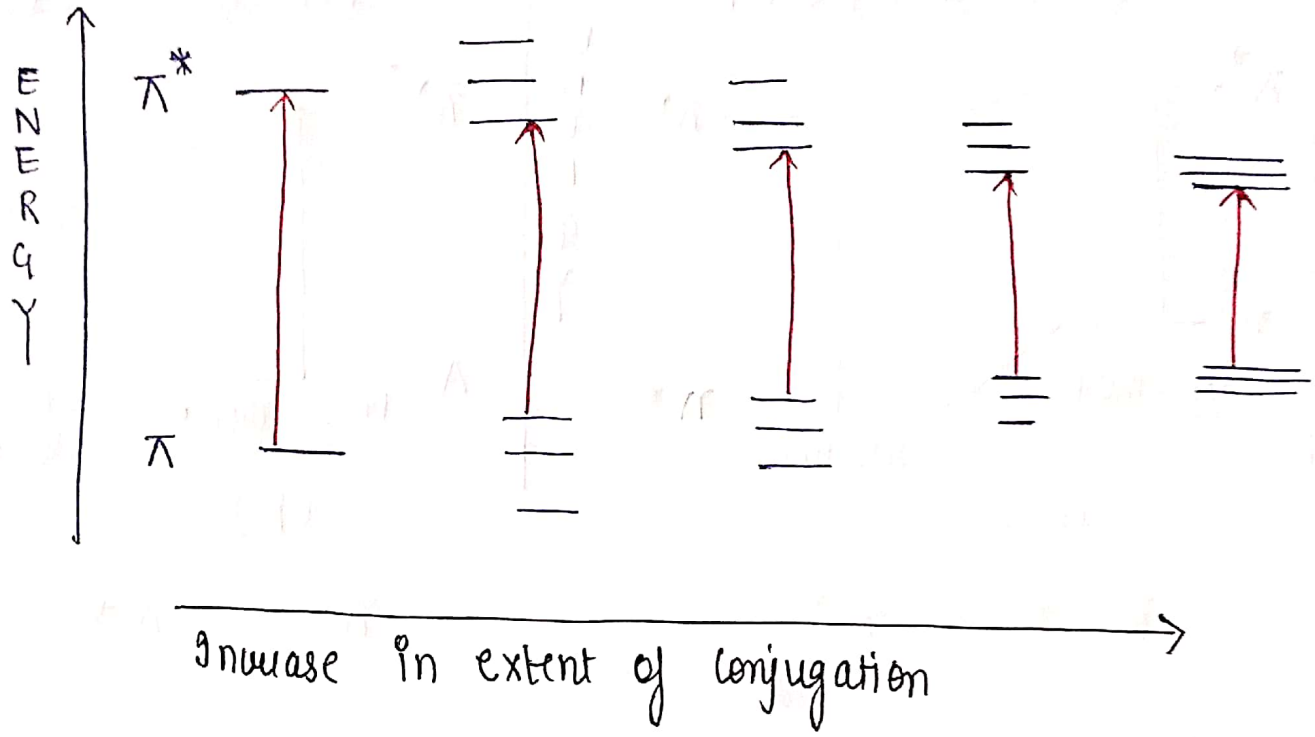
(iv) HYPOCHROMIC SHIFT → effect due to which there is Decrease in Intensity of Absorption Maximum (εmax)

Combined Diagram of All Shifts



What does conjugation have effect on λ_{max} (maximum absorption)

Answer



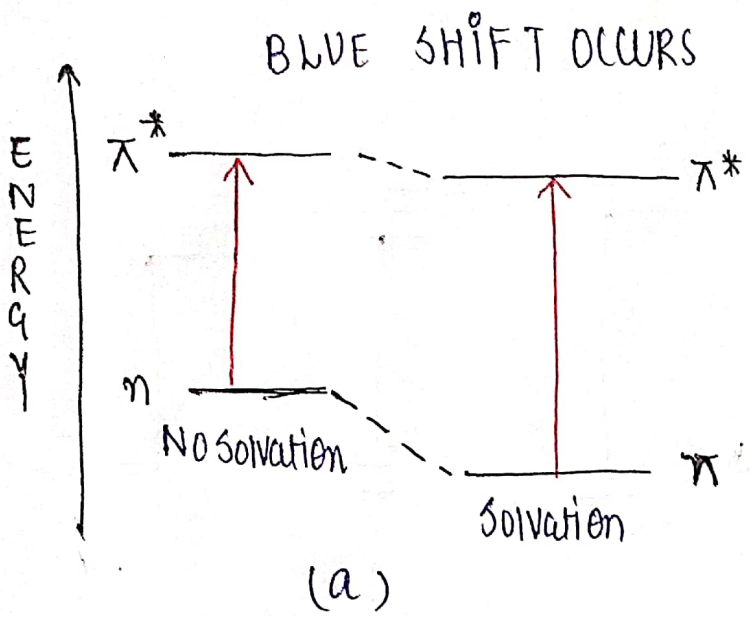
As ABOVE Diagram shows that

$\lambda_{max} \propto$ (directly proportional) to extent of conjugation

Absorption Bands shift towards longer wavelength as extent of conjugation increases.

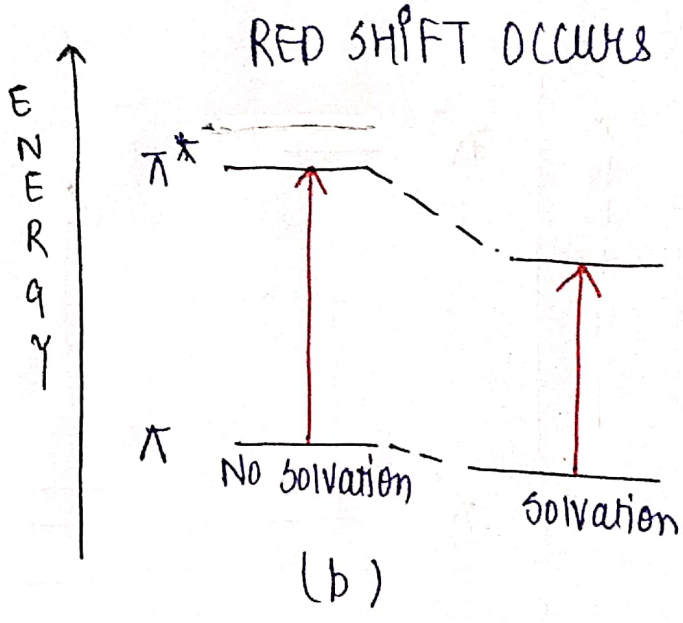
Example → Red colour of carrot is due to highly conjugated system "β-carotene"

What does Solvent Polarity Had effect on $n \rightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ Transition.



(a)

$n \longrightarrow \pi^*$



(b)

$\pi \longrightarrow \pi^*$

* Polar Solvent often stabilizes ground state of $n \rightarrow \pi^*$ transition more than they stabilise excited state causing BLUE SHIFT

* For $\pi - \pi^*$ Transition Excited state is stabilized more than ground state causing RED SHIFT

* Application of UV-visible spectroscopy

1.) Qualitative and Quantitative Analysis of Compounds

2.) Detection of Impurities in Organic Compound

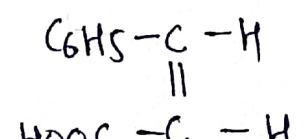
3.) Determination of molecular weight

4.) Determination of dissociation constant of acid & Bases.

5.) Determination of extent of conjugation.

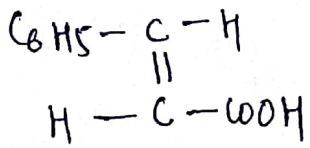
6.) Confirmation of cis and Trans Hydrogen

cis Cinnamic-Acid



Due to steric Repulsion coplanarity lost ($\lambda max = 268$) as conjugation becomes limited

Trans Cinnamic-Acid



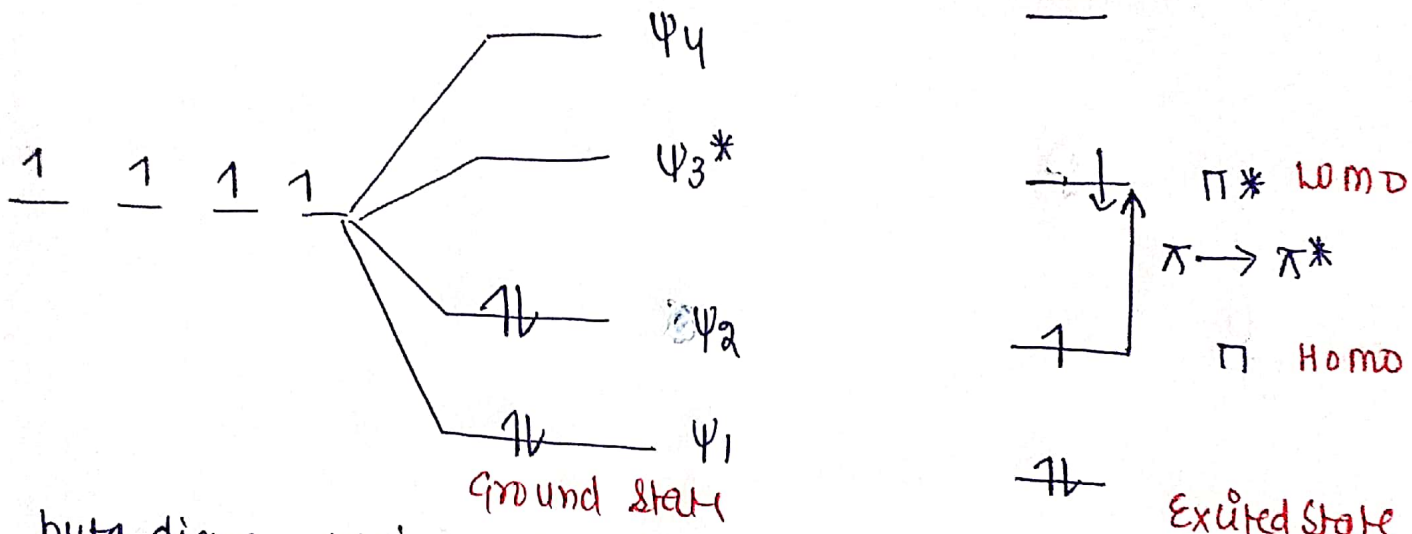
$\lambda max = 272$ nm

Conjugation Not limited.

Ques- Discuss e⁻ spectroscopy with Refrence of Butadiene and Carbonyl compounds. (YMA)

Principle has already Discussed in Notes

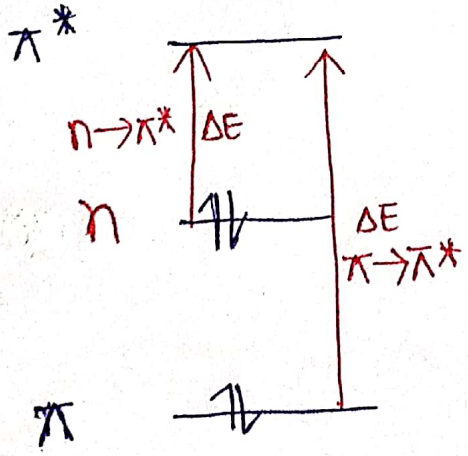
e⁻ spectroscopy in Butadiene



In buta diene maine electronic Transistion are

π → π* Transistion

e⁻ spectroscopy in Carbonyl compound – carbonyl compound has non bonded e⊖



Two Types of Transistion e⁻ are there

n → π* (It Requires less Energy)

π → π* (It Requires More Energy)

Electrons in NON Bonding Has High Energy

σ → σ* & σ → π* are very weak

FRANCK-CODON-PRINCIPLE

Used for Investigating Vibrational structure of Electronic Spectra.

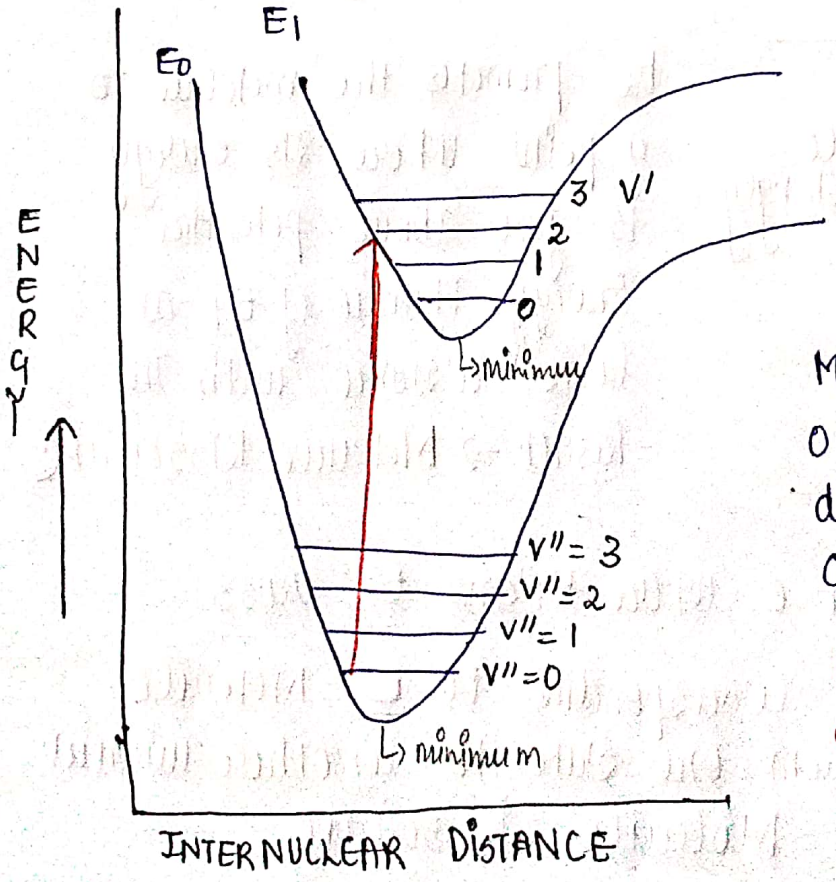
What is Frank-Codon-Principle ?

It states that an electronic Transition takes place so rapidly that a vibrating molecule does Not change its ~~Nuclear~~ InterNuclear distance appreciably during Transition.

electron move much faster in electronic transition and Nuclei do Not change their position.

So-electronic Transition may be Represented by vertical line on plot of potential energy V/s InterNuclear distance.

Franck-Codon Principle For Diatomic Molecule



E_0 = Ground State

E_1 = Exited electronic state

V' = Exited Vibrational states

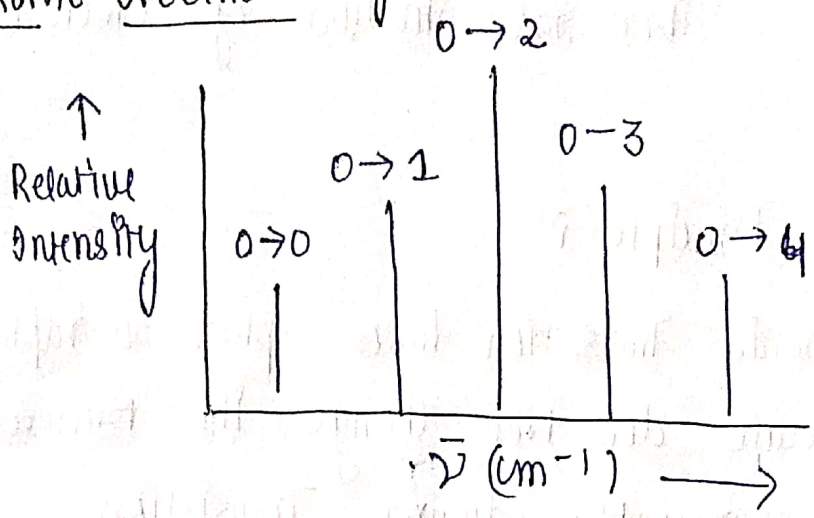
V'' = Ground " "

Minimum in Exited (E_1) state occurs at greater Internuclear distance as compared to Ground state

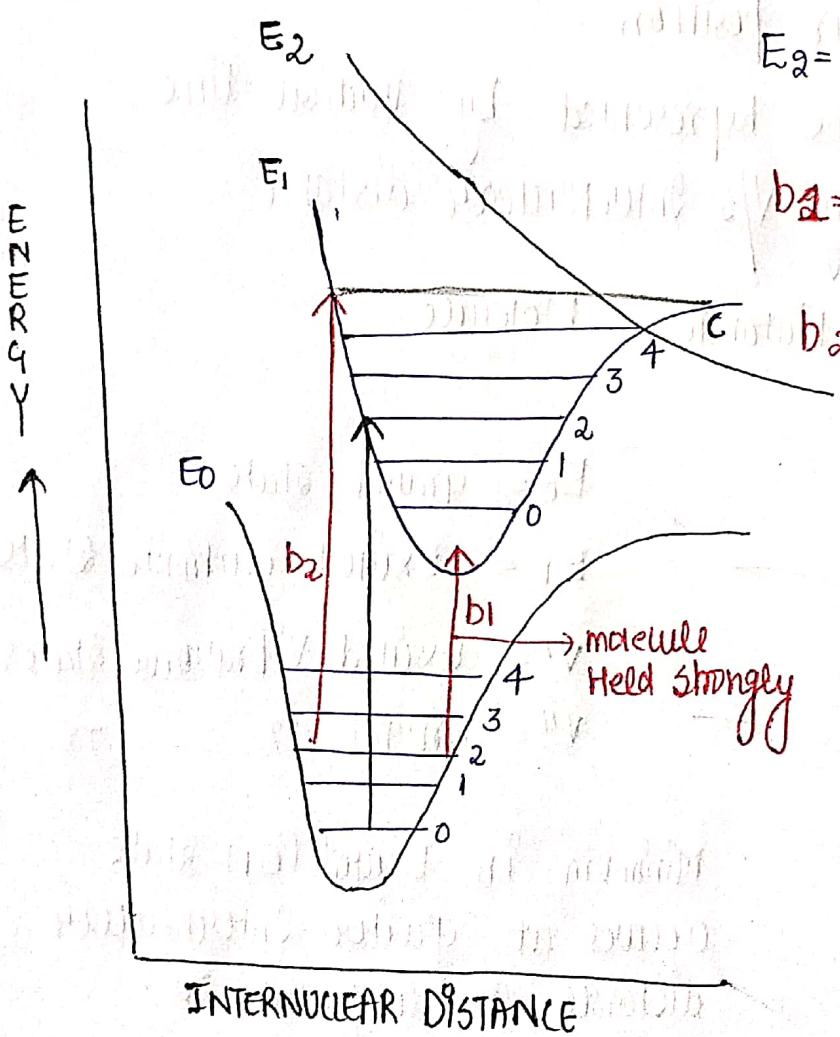
Most probable Transition according To Frank-C-P is

$V''=0 \longrightarrow V'=2$

ELECTRONIC SPECTRUM of Diatomic Molecule



BOND - Dissociation ENERGY



E_2 = Second excited state it does Not have minima

b_1 = Transition ending at lowest Vibrational No. of E_1

b_2 = Transition ending at Highest Vib. No. of E_0

b_2 promotes the molecule to a point where its energy is far above potential Energy Plateau of E_1 at large distance with The Result → Molecule Dissociate

* Molecule dissociate at Point C where E_1 and E_2 cross.
* At an Internuclear distance corresponding to C Molecule may undergo crossover from one state to another without change in Energy and Molecule Dissociate

FLUORESCENCE and Its Application in Medicine

GROTTHUS-DRAPER LAW OF PHOTOCHEMISTRY

Light which is absorbed by a system can bring a photochemical change.

FLUORESCENCE

Light absorbed by a substance may be Re-emitted almost instantaneously in one or more steps (within 10 seconds)
This process is known as FLUORESCENCE

PHOSPHORESCENCE

Light absorbed is given out slowly and even after Removal of source of light. This phenomena is known as Phosphorescence.

The Process of FLUORESCENCE and Phosphorescence is Explained with HELP OF Jablonski-DIAGRAM

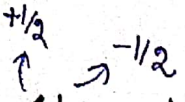
Some Terminologies before Jablonski Diagram

SPIN Multiplicity $\Rightarrow$ $2S+1 = M$

S = Total electron spin

Ques $\rightarrow$ Find S for Antiparallel electrons

$S = -\frac{1}{2} + \frac{1}{2} = 0$



↑↓ and what is M?

$M = 2(0) + 1$

$M = 1$ SINGLET State

Q- what is S for Parallel e^- i.e ↑↑ also find multiplicity

↳ same direction so Both have same spin of $+\frac{1}{2}$

$$S = +\frac{1}{2} + \frac{1}{2} = 1$$

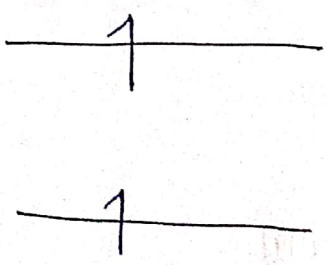
$$M = 2S+1 = 2(1)+1 = 3$$

$\boxed{M = 3}$ so Triplet state

Question what do you mean by Triplet and singlet Excited states

TRIPLET EXCITED STATE

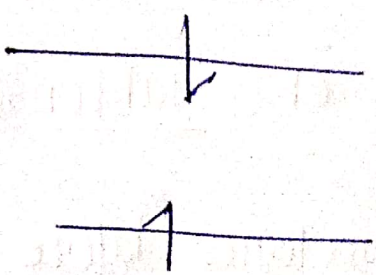
* Multiplicity = 3
* Spins of e^- are in same direction (i.e Parallel)



SINGLET EXCITED State

Multiplicity = 1

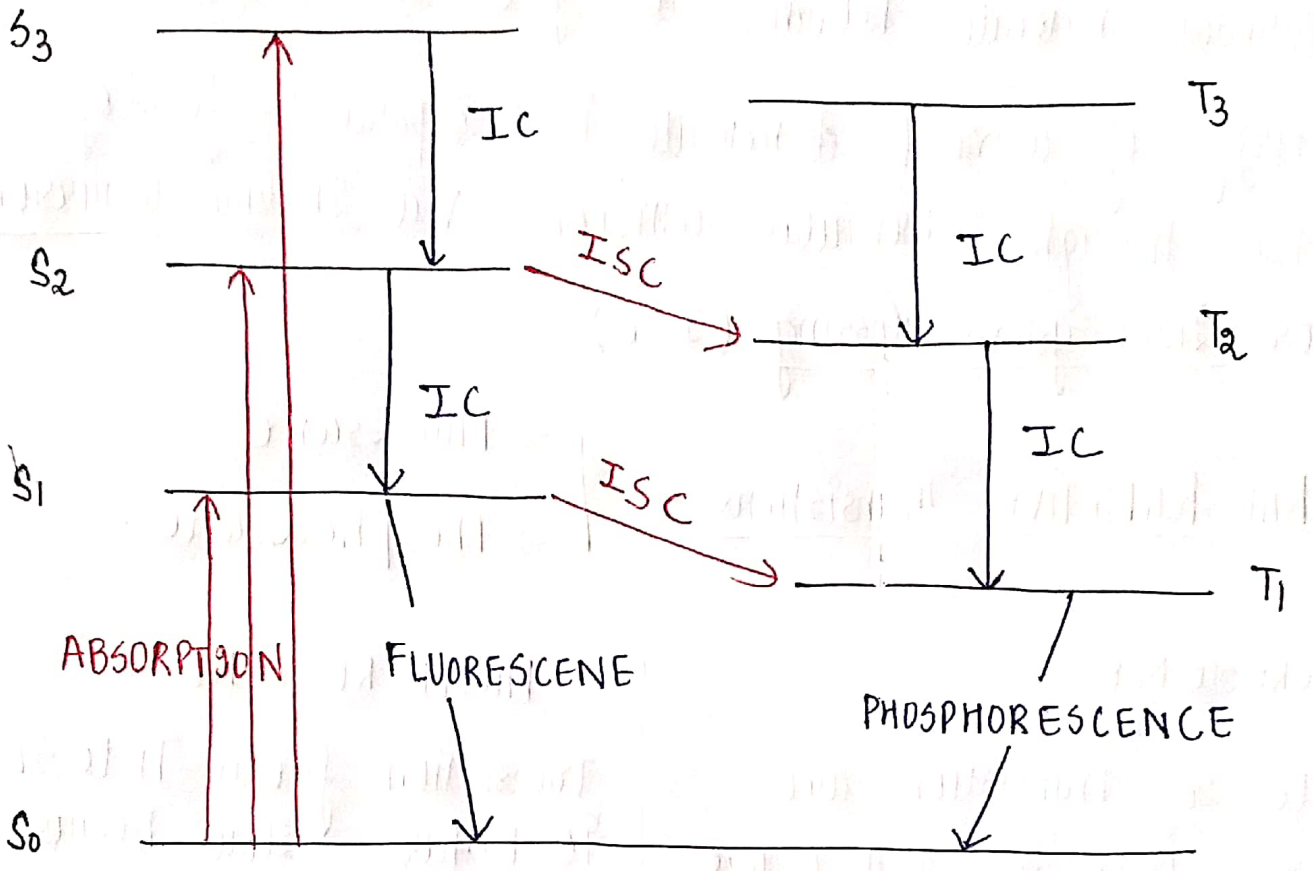
* Spins of e^- are in opposite direction (i.e antiparallel)



V.V.V. Imp

JABLONSKI - DIAGRAM (Ymca)

EXPLANATION OF fluorescene and phosphorescene



S_0 = Ground state , S_1, S_2 and S_3 = 1st, 2nd and 3rd singlet Excited state

T_1, T_2, T_3 are 1st, 2nd and 3rd Triplet Excited state

Energy of $\begin{cases} E_{S1} > E_{T1} \\ E_{S2} > E_{T2} \\ E_{S3} > E_{T3} \end{cases}$

IC = Internal conversion

ISC = Inter System Crossing

On absorption of light photon, electron of absorbing molecule may jump from S_0 to S_1, S_2 or S_3 depending upon energy of light photon absorbed. Molecule in Triplet or singlet state is said to be activated.

molecule in ground state ← $A_0 + h\nu \longrightarrow A^*$ (molecule in excited state)

(i) Non-Radiative Transitions — it is so called (Radiation less Transition)

* No Emission of Radiations
* Activated molecule Return to first excited state S_1 or T_1
* Energy of activated molecule is dissipated in form of Heat through molecular collision via Internal Conversion or Inter system crossing (ISC).

(ii) RADIATIVE Transitions → Fluorescene, Phosphorescene

FLUORESCENE

→ S_1 to S_0 Transition are allowed Transition and occurs in about 10^{-8} seconds

→ Emission of Radiation in this Transition is called fluorescene

→ Emission is very fast

→ No Spin Inversion (Singlet → Singlet)

PHOSPHORESCENE

Transition from T_1 to S_0 is Rather slow because it is a Forbidden Transition

* Emission of Radiation is called phosphorescene

→ Emission is very long (10^{-3} seconds)

→ Spin Inversion occurs. (Triplet → Singlet)

Both fluorescene and phosphorescene emit Radiations of shorter frequencies or Longer Wavelength

APPLICATION OF FLUORESCENE in MEDICINES

* Fluorescene helps in characterization and diagnosis of diseased tissues

For
1.) The analysis of concentration of Riboflavin (Vitamin B_2)

2.) Use of fluorescent Microscopes and fluoroscope used in X-Ray diagnosis help in testing condition of food stuff and detecting Ring Worm.

3.) Wide application of Time Resolved fluorescene to diagnose Pathological condition such as

(a) Diagnosis of cancer in lungs, skin, head, Neck, GI and brain.

(b) opthalmic pathologies (c) atherosclerotic cardiovascular disease

4.) Autofluorescene technique has been used in Treatment of primary brain Tumor.

5.) Analysis of skin physiology, optical biopsy of skin and detection of dermatological disorders.

6.) Used in detection of eye disease & Research

OTHER Application of FLUORESCENE

① Lighting Purposes in fluorescent Tubes

② fluorescent dyes with coloured Paint used in Road sign

Example → Rhodamine 6G

③ used in Televisions

④ Used in Industry for Testing and Identifying materials.

Problem 4. List all the electronic transitions possible for (*a*) CH_4 (*b*) CH_3Cl (*c*) HCHO.

Solution. (*a*) In CH_4, there are only sigma bonds. So the only possible transition is

$$\sigma - \sigma^*$$

(*b*) In CH_3Cl, there are no π or π^* molecular orbitals. So the possible transitions are:

$$\sigma \rightarrow \sigma^* \text{ and } n \rightarrow \sigma^*$$

(*c*) In  , all the bonding, antibonding and π molecular orbitals are available, so the following transitions are possible:

$$\sigma \rightarrow \sigma^*, n \rightarrow \sigma^*, \pi \rightarrow \pi^* \text{ and } n \rightarrow \pi^*$$

Problem 5. The UV spectrum of acetone shows two peaks at λ_{max} = 280 nm, ε_{max} = 15 and λ_{max} = 190 nm, ε_{max} = 100.

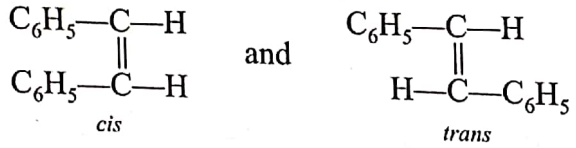
(*a*) Identify the electronic transitions for each and (*b*) which is more intense?

Solution. (*a*) The longer wavelength (280 nm) is associated with smaller energy transition *i.e.*, $n \rightarrow \pi^*$. The transition $\pi \rightarrow \pi^*$ occurs at 190 nm.

(*b*) The larger the value of ε_{max}, the greater the intensity of the transition. Therefore, $\pi \rightarrow \pi^*$ is more intense.

Problem 6. Identify the two geometric isomers of stilbene, $C_6H_5CH = CHC_6H_5$, from their λ_{max} values, 294 nm and 278 nm.

Solution. The two geometric form of the given formula are:



Steric strain would be greater in the *cis* form as compared to *trans* form. The steric strain would prevent full coplanarity of the *cis* phenyl groups and the conjugative effect is attenuated. Thus the higher energy *cis*-isomer has the shorter λ_{max}. The isomer with λ_{max} = 278 nm is *cis* and other is *trans*.

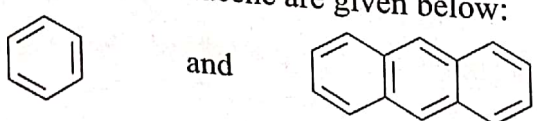
Problem 7. Predict the kind of electronic transitions in (*a*) Cl_2 and (*b*) carbonyl group. Also give their intensity.

Solution. (*a*) The transition in Cl_2 are: (*i*) $\sigma \rightarrow \sigma^*$ (allowed transitions), which is strong in intensity, (*ii*) $n \rightarrow \sigma^*$ (forbidden transition) which is weak in intensity.

(*b*) In C = O group, $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, both are allowed transitions and strong in intensities, whereas $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$, both are forbidden and of weak intensity.

Problem 8. How will you distinguish between benzene and anthracene by UV spectroscopy?

Solution. The structures for benzene and anthracene are given below:



Benzene Anthracene

Anthracene will have higher λ_{max} than benzene. This is because anthracene is more conjugated than benzene.

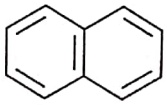
Problem 9. Arrange the following compounds in the increasing order of the their UV absorption maxima.

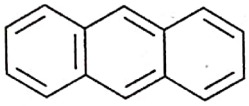
(*a*) Ethylene **(*b*) Naphthalene**

(*c*) Anthracene **(*d*) 1, 3-Butadiene**

Solution. The structures of the given compounds are:

(*a*) $H_2C{=}CH_2$
Ethylene

(*b*) 
Napthalene

(*c*) 
Anthracene

(*d*) $H_2C{=}CH{-}CH{=}CH_2$
1,3-Butadiene

The absorption maxima (λ_{max}) *is directly proportional to the extent of conjugation.* Therefore, the increasing order of absorption maxima of the given compounds would be:

$$(a) < (d) < (b) < (c)$$

Problem 10. Which among $CH_2{=}CH_2$, $CH_2{=}CH{-}CH{=}CH_2$, and trans $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$ can give λ_{max} absorption at about 274 nm? Give reason.

Solution. *Trans* $-CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$, since it is an conjugated triene.

Problem 11. Most of absorption bands in the UV-visible spectra are very broad. Give reasons.

Solution. UV-visible spectra involve transitions between electronic energy level which are associated with vibrational and rotational energy levels. The electronic transition may occur from any of the several vibrational and rotational states of one electronic level to any of the various corresponding states of higher level. *Since a large number of transitions are possible, so a large number of absorptions will take place corresponding to different wavelengths. Hence, spectra are very broad.*

Problem 12. Why does 1, 3-butadiene possess higher λ_{max} value than that of ethene?

Solution. In 1, 3-butadiene $\pi_2 \rightarrow \pi_3^*$ excitation takes place, which requires lesser energy (of higher wavelength) than $\pi \rightarrow \pi^*$ excitation in ethane.

Problem 13. Which of CH_3COCH_3 and $CH_2{=}CHCOCH_3$ exhibit higher value of λ_{max} in the UV-visible spectra?

Solution. $CH_2{=}CHCOCH_3$, since it has two conjugated chromophores (double bond and C=O group), whereas H_3CCOCH_3 has only one chromophore (C=O group).