ELECTRONIC SPECTROSCOPY

In this branch of spectroscopy, information about the molecule under investigation are obtained from the various types electronic transitions taking place. Depending on the types of electrons present i.e. bonding σ, π electrons and nonbonding ***n*** electrons, different types of electronic transitions occur. The term electronic spectroscopy is used for the study of the transitions between different electronic states which lie in visible and ultra-violet region of electromagnetic spectrum. Electronic transitions are also accompanied by Vibrational and rotational energy changes. The rotational energy changes produce rotational fine structure while the vibrational energy changes produce Vibrational coarse structure in electronic spectra. Again, in cases of the molecules containing more than one type of electrons, several transitions may occur resulting in the formation of several bands.

Electronic Transitions

When a molecule absorbs Ultra-violet or Visible light, its electrons get promoted from ground state to the higher excited state. During excitation an electron gets excited from a bonding to an antibonding orbital.

Possible electronic transitions of bonding σ, π electrons and nonbonding ***n*** electrons to antibonding σ^* and π^* orbitals are -

(i) $\sigma \rightarrow \sigma^*$ Transitions

In this type of transitions a bonding σ electron is excited to an antibonding σ*. As the σ bonds are very strong, so this process requires very high energy. This type of transitions requires radiation of very short wavelength.

For example, saturated hydrocarbons like methane (which has only C-H bonds, and can only undergo σ→ σ* transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to σ→ σ* transitions are not seen in typical UV-Vis. spectra (200 - 700 nm).

(ii) **$n \rightarrow \sigma^*$ Transitions**

In this type of transitions a non-bonding n electron is excited to an antibonding σ* orbital. These transitions usually need lesser energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength lies in the range 150 - 250 nm.

For example, Saturated compounds containing atoms with non-bonding electrons i.e. lone pairs are capable of showing $n \rightarrow \sigma^*$ transitions. Organic compounds undergoing this type of transitions are halides, alcohols, ethers, aldehydes, ketones, amines etc.

The absorption maxima of such transitions depend on the electronegativity of the atom containing the lone pair of electrons. If we observe the absorption maxima of CH_3Cl and CH_3I, it can be seen that the absorption maxima of CH_3Cl is around 174 nm while the absorption maxima of CH_3I is around 260 nm. This is because chlorine being more electronegative than iodine, it takes higher energy (lower wavelength) for exciting the non-bonding electrons. The molar extinction co-efficient (ε_{max}) for the molecule is found to be higher in which the $n \rightarrow \sigma^*$ transition takes place readily. Thus out of CH_3Cl and CH_3I, CH_3I will have higher molar extinction co-efficient.

Similarly, amines absorb at higher wavelength in comparison to alcohols as oxygen is more electronegative than nitrogen. Hence, ε_{max} of amines are higher than the alcohols.

(iii) **$\pi \rightarrow \pi^*$ Transitions**

In this type of transitions π electrons are excited to antibonding π* orbital. These transitions require lesser energy than $n \rightarrow \sigma^*$ transitions and hence radiation of longer wavelength can also initiate such transitions.

For example, molecules containing π electrons (unsaturated centres i.e. double or triple bonds and also aromatic rings) show $\pi \rightarrow \pi^*$ transitions. Organic compounds undergoing this type of transitions are alkenes, alkynes, aldehydes, ketones, cyanides, azo compounds etc. The introduction of alkyl groups to the unsaturated centres increases the wavelength of absorption by 3-5 nm per alkyl group.

(iv) n→ π* Transitions

In this type of transitions non-bonding **n** electrons are excited to antibonding **π*** orbital. This type of transitions requires least amount of energy out of all the electronic transitions.

For example, the compounds which involves nonbonding n electrons and **π** electrons show both π → π* and n→ π* transitions. Compounds undergoing this type of transitions are Carbonyl compounds, Nitriles, C=S, N=N, etc. The low energy n→ π* transition occur at longer wavelength than π → π* transition. Usually shorter wavelength transitions are more intense.

The energy order for various transitions can be shown as –

$$\boldsymbol{\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*}$$

Various types of electronic transitions occurring in ultra-violet and visible spectroscopy are shown in **Figure 3.1**.

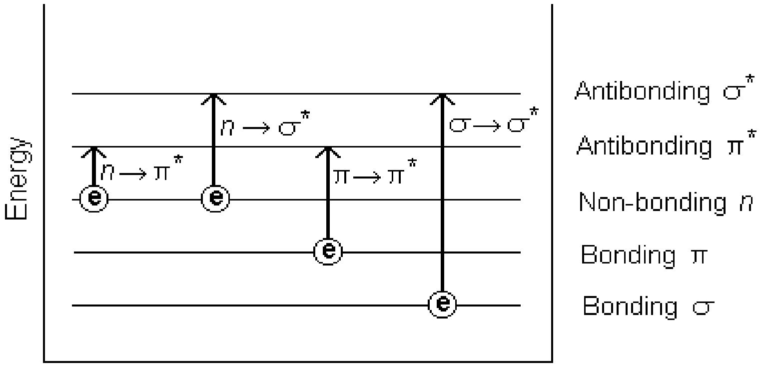


Fig.3.1 Types of electronic transitions

Selection Rule for Electronic Transitions

There are mainly two selection rules which should be followed for an electronic transition to occur. These are -

Laporte Selection Rule

According to this rule, the only allowed transitions are those which involve a change in parity i.e. gerade → ungerade (g→ u) and ungerade → gerade (u→ g) are allowed while gerade→ gerade (g→ g) and ungerade→ ungerade (u→ u) are forbidden.

Spin Selection Rule

According to this rule, the only allowed transitions are those which involve no change in spin state i.e. transitions from singlet → singlet and triplet → triplet are allowed while transitions from singlet → triplet and triplet → singlet are forbidden.

Born-Oppenheimer Approximation

This approximation was proposed in 1927, in the early period of quantum mechanics, by Max Born and J. Robert Oppenheimer and is still indispensable in quantum chemistry.

In this approximation (**Born-Oppenheimer approximation**), it is assumed that the motion of nucleus and electrons in a molecule can be separated. Mathematically, the total wave function (Ψ_{total}) can be written as a product of electronic and nuclear components i.e.

$$\Psi_{total} = \Psi_{electronic} \times \Psi_{nuclear}$$

The complication that arisen while solving for the total wave function, was simplified by Born and Oppenheimer in their approximation. In Born-Oppenheimer approximation two simple steps were used to solve for the Ψ_{total}.

In the first step, nuclei are fixed at a certain configuration (usually equilibrium configuration) and then the electronic Schrödinger equation is solved to get the wavefunction $\Psi_{electronic}$ which depends only on electrons.

In the second step, the nuclear equation is solved to get the wavefunction $\Psi_{nuclear}$ which depends only on nuclei.

Application of Born-Oppenheimer approximation can be discussed taking benzene as an example. Benzene contains 12 nuclei and 42 electrons. It has a total of 162 variables (12x3=36 for the nuclei and 42x3=126 for the electrons). In order to obtain the energy and wavefunction of this molecule, it is necessary to solve the time independent Schrodinger equation. For benzene, this equation is a partial differential eigen value equation in 162 variables that contain the spatial coordinates of the electrons and the nuclei. During solution, in the first step, the nuclei are fixed in equilibrium configuration and then the electronic wavefunction is solved ($\Psi_{\text{electronic}}$). As the nuclei are fixed, so, the wavefunction depends only on 126 electronic coordinates. In the second step only the nuclei is considered, so, the wavefunction depends only on 36 nuclear coordinates. In this way the solution was made simpler in Born-Oppenheimer approximation.

This approximation is an important tool for quantum chemistry as well as molecular spectroscopy. Under this approximation, it is quite easier to get the wavefunctions for large molecules, on the otherhand, if this approximation is not considered then only the wavefunction of the lightest molecule i.e. H_2 can be solved. The success of the BO approximation is due to the large difference between the masses of the nuclei and the electrons.

Vibrational Coarse Structure

The electronic, Vibrational and rotational energies of a molecule are completely independent of each other and hence the total energy of a molecule may be given as –

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} \quad J$$

In terms of wave numbers, the above equation may be written as –

$$\varepsilon_{\text{total}} = \varepsilon_{\text{electronic}} + \varepsilon_{\text{vibration}} + \varepsilon_{\text{rotation}} \quad \text{cm}^{-1} \text{ ………. } (3.1)$$

Thus, a change in total energy of the molecule may be written as –

$$\Delta\varepsilon_{\text{total}} = \Delta\varepsilon_{\text{electronic}} + \Delta\varepsilon_{\text{vibration}} + \Delta\varepsilon_{\text{rotation}} \quad \text{cm}^{-1}$$

The approximate magnitude of changes generated by the electronic, Vibrational and rotational energies are –

$$\Delta\varepsilon_{\text{electronic}} \approx \Delta\varepsilon_{\text{vibration}} \text{ X } 10^3 \approx \Delta\varepsilon_{\text{rotation}} \text{ X } 10^6$$

From the above magnitudes, it can be mentioned here that the Vibrational changes will produce a **coarse structure** while the rotational changes will produce a **fine structure** in the spectra of electronic transitions. Thus, in order to understand the **coarse structure** in the spectra of electronic transitions, it is important to ignore the rotational changes. Hence, without taking the rotational changes into consideration equation (1), may be written as –

$$\varepsilon_{\text{total}} = \varepsilon_{\text{electronic}} + \varepsilon_{\text{vibration}} \quad \text{cm}^{-1} \ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Again the pattern of the Vibrational energy levels can be given as –

$$\varepsilon_{\text{vibration}} = (v+1/2)\,\bar{\omega}_e - (v+1/2)^2\,\bar{\omega}_e\,x_e \quad \text{cm}^{-1} \quad \ldots\ldots\ldots (3)$$

Where v = 0,1,2,3 ……..

$\bar{\omega}_e$ is the oscillation frequency expressed in wavenumbers also called Vibrational wavenumber

X_e is the corresponding anharmonicity constant

Combining equation (3.2) and (3.3), we can write,

$$\varepsilon_{\text{total}} = \varepsilon_{\text{electronic}} + (v+1/2)\,\bar{\omega}_e - (v+1/2)^2\,\bar{\omega}_e\,x_e \quad \text{cm}^{-1} \quad \ldots\ldots\ldots (4)$$

For two arbitrary values of $\varepsilon_{\text{electronic}}$ ($\varepsilon''_{\text{electronic}}$ and $\varepsilon'_{\text{electronic}}$) the Vibrational coarse structure of the band formed during electronic absorption from the ground state (v” = 0) to higher states (v’) are shown in **Figure 3.2**. From the figure, it is clear that the spacing between the upper Vibrational levels are smaller than that between the lower, this is because an excited electronic state generally corresponds to a weaker bond in a molecule and hence a smaller Vibrational wavenumber ($\bar{\omega}_e$). The spacing between the lines decreases with increase in frequency, this is due to anharmonicity of the upper state vibration which causes the excited Vibrational levels to converge.

Conventionally, the transitions are represented as (v’,v”) i.e. (0,0),(1,0), (2,0) etc. under high resolution, the lines formed from different transitions are seen as separate lines, however, under low resolution, a set of lines appear as diffused and broad and hence such a set is called a band. Moreover, in a set of lines as the values of v’ increases by one unit, so, such a set of lines is also called a v’ **progression**.

The study of a band spectrum enables one to get the values of Vibrational wavenumber and anharmonicity constant for both the ground as well as excited electronic state and also the separation between the electronic states.

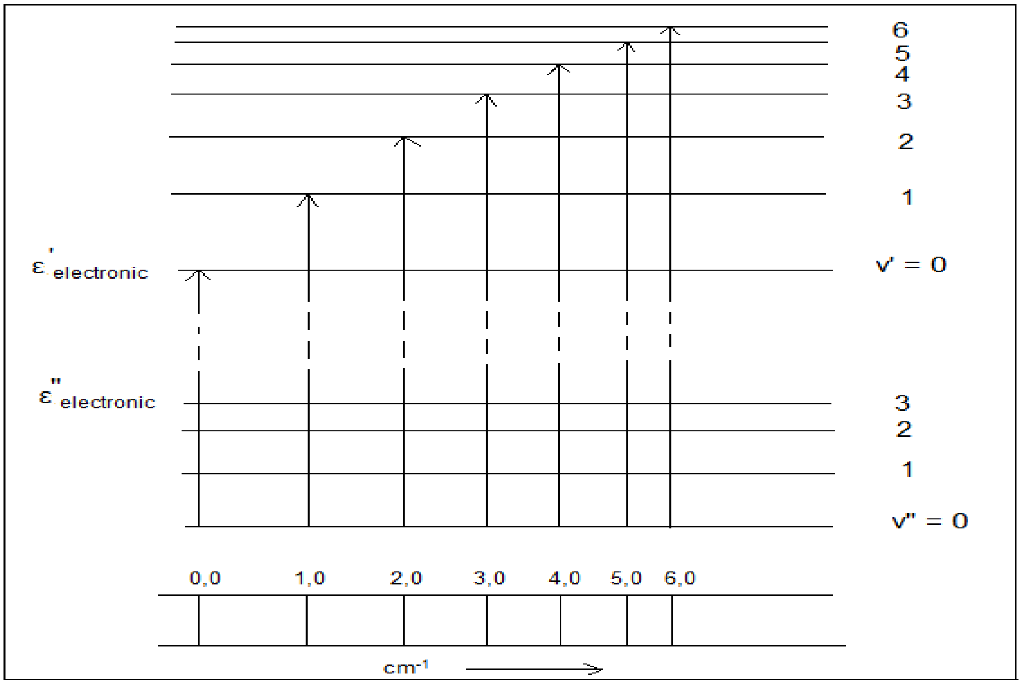


Fig.3.2 Vibrational coarse structure of the band formed during electronic absorption

Franck-Condon Principle

The Franck-Condon Principle describes the intensities of vibronic transitions or the absorption or emission of a photon. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. During an electronic transition, a change from one vibrational energy level to another will be more likely to take place if the two vibrational wave functions overlap more significantly.

As the mass of the nuclei are quite larger than that of the electrons and electronic transitions take place quite faster, so, the nuclear configuration almost remains same during the transition. Thus, the Franck-Condon Principle may be stated as –

An electronic transition takes place so rapidly that a molecule undergoing vibration does not change its internuclear distance significantly during the transition.

Moreover, it may be mentioned here that the most intense vibronic transition is one in which the excited Vibrational state lies vertically above the ground Vibrational state. However, transitions to the other Vibrational levels also occur, but in that cases the intensity of the transitions are found to be quite lower. To understand this fact, let us consider four cases –

Case I

In this case the upper electronic state (ε’) is having slightly less equilibrium internuclear distance (r_e) than the lower electronic state (ε”). Here the transition that occurs vertically is from (v” =0) to (v’=2). So, the most intense line will be (2,0), because in this transition the internuclear distance does not change (**Figure 3.3**).

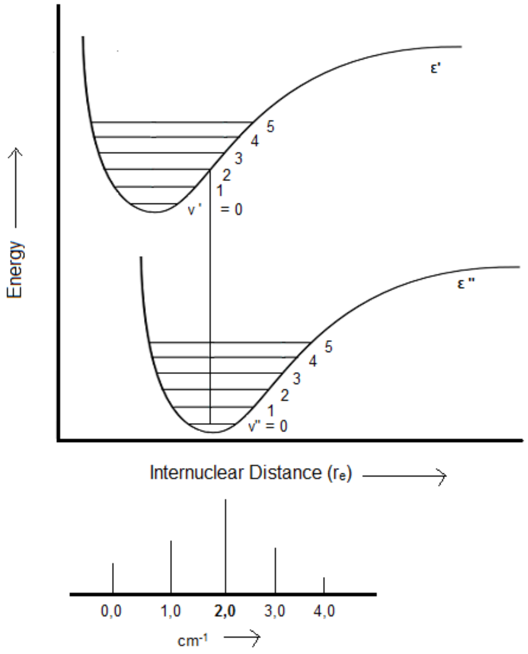


Fig.3.3 Transition in which upper state internuclear distance is less than the lower state

Case II

In this case the upper electronic state (ε’) is having the same equilibrium internuclear distance (r_e) as the lower electronic state (ε”). Here the transition that occurs vertically is from (v” =0) to (v’=0). So, the most intense line will be (0,0), because in this transition the internuclear distance does not change (**Figure 3.4**).

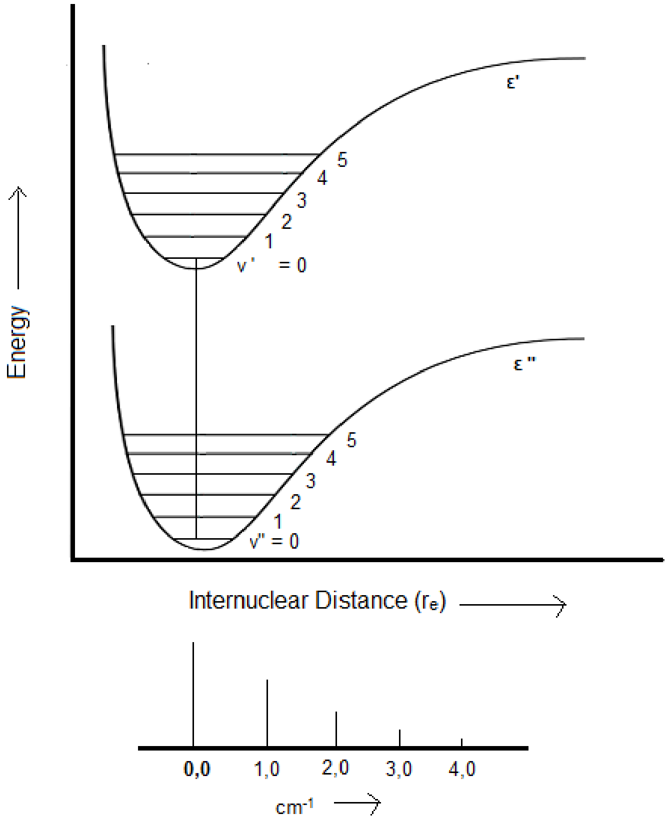


Fig.3.4 Transition in which the internuclear distances are same for both upper and lower state

Case III

In this case the upper electronic state (ε’) is having slightly more equilibrium internuclear distance (r_e) than the lower electronic state (ε”). Here the transition that occurs vertically is from (v" =0) to (v'=2). So, the most intense line will be (2,0), because in this transition the internuclear distance does not change (**Figure 3.5**).

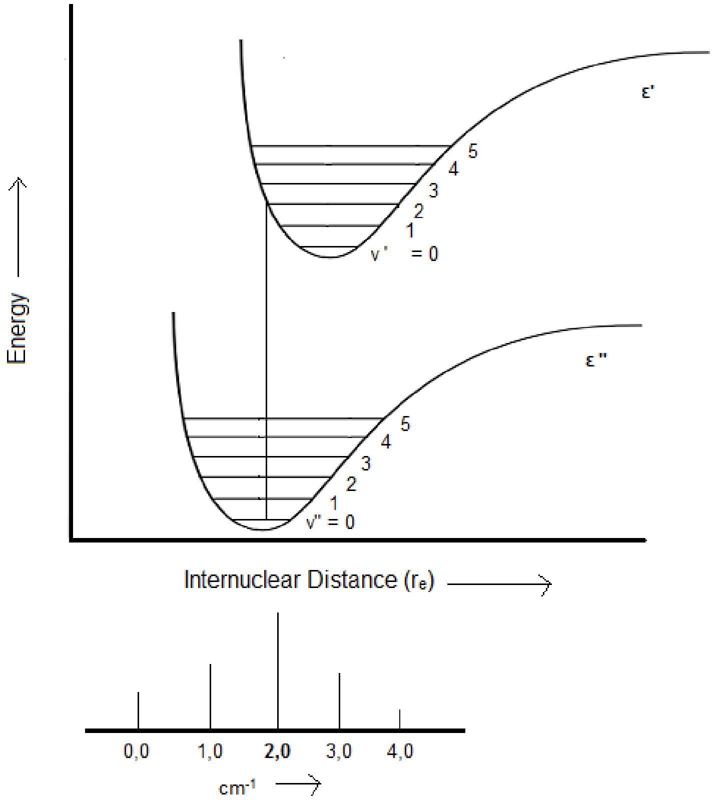


Fig.3.5 Transition in which upper state internuclear distance is greater than the lower state

Case IV

In this case the upper electronic state (ε') is having considerably more equilibrium internuclear distance (r_e) than the lower electronic state (ε"). In this case the observation is somewhat different than that already discussed in the above three cases. Here the Vibrational level to which a transition takes place has a quite high v' value (to get a vertical transition). Moreover, in this case transitions may take place to a state in which the excited molecule has energy in excess of its own dissociation energy. As a result the molecule will dissociate into its constituent atoms without any vibrations. Since the atoms formed may take up any value of kinetic energy, so, transitions are not quantized and results in the formation of a **continuum** (**Figure 3.6**).

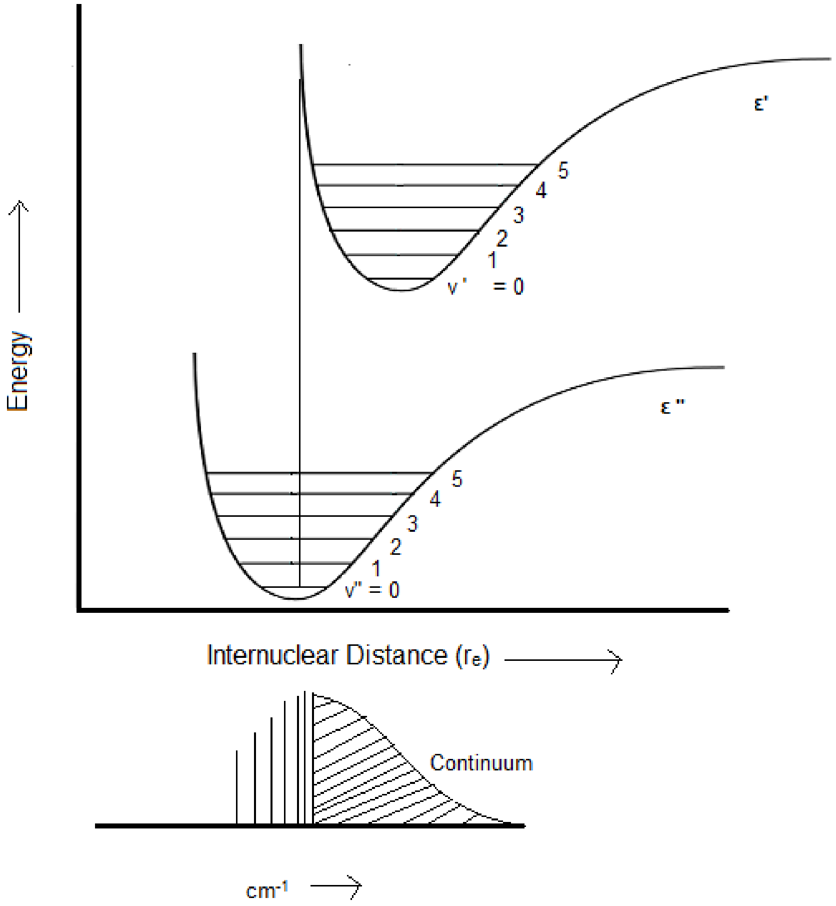


Fig.3.6 Transition in which upper state internuclear distance is considerably greater than the lower state

Problem 3.1: Using the Franck-Condon principle, explain why the intensities of the vibrational lines associated with electronic transitions differ. **[GU 2016]**

Problem 3.2: Discuss Franck-Condon principle to explain intensities of vibronic transitions due to absorption or emission of a photon of appropriate energy. **[GU 2014]**

Problem 3.3: State and explain Franck-Condon principle. Discuss how this principle is applicable to explain the intensity distribution of vibrational bands in electronic transition. **[GU 2013]**

Structure Elucidation by Electronic Spectroscopy

Chromophore

When an electron jumps from a ground state to an excited state, it absorbs radiation of appropriate wavelength. But it is important to note that the nuclei associated with the electrons, play an important role in determining the wavelength of absorbed radiation. The nuclei of an atom determine the strength with which the electrons are bound and hence influence the energy spacing between ground and excited states. Hence, the characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group of atoms rather than that of electrons. The group of atoms responsible for the absorption is called a chromophore.

Thus, *the isolated covalently bonded group that shows a characteristic absorption in the ultra-violet or visible region is known as chromophore.*

Examples of some chromophores with transition and maximum wavelength of absorption are shown in **Table 3.1**.

Table 3.1 Chromophores with type of transition and absorption Maxima

Chromophore	Transition	Absorption Maxima, λ_{max} (nm)
R_2-C=C-R_2	$\pi \rightarrow \pi^*$	175
R-C≡C-R	$\pi \rightarrow \pi^*$	170
R_2C=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	285 188

R-CHO	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	290 190
R-NO_2	$n\rightarrow\pi^*$	271
R-COOH	$n\rightarrow\pi^*$	205
R-$CONH_2$	$n\rightarrow\pi^*$	210
R-COOR	$n\rightarrow\pi^*$	205
R- C≡N	$n\rightarrow\pi^*$	160
R-N=N-R	$n\rightarrow\pi^*$	340

Auxochrome

The position as well as the intensity of the absorption band of a chromophore can be changed by the attachment of certain groups in place of hydrogen to a basic chromophore. Such substituents may not give rise to the absorption, but their presence changes the position and intensity of the absorption band.

Thus, *an auxochrome may be defined as any substituent or group which itself doesnot absorb, but its attachment to the chromophore, increases the intensity of absorption and shifts the absorption band to the longer wavelength.*

Some examples of auxochromes include –OH, -R, -OR, -X, -NH_2 etc.

The effect of the auxochrome is due to its ability to extend the conjugation of the chromophore by the sharing of non-bonding electrons. Hence, by the attachment of auxochrome to the basic chromophore, a new chromophore results which has a different value of the absorption maxima as well as the extinction co-efficient. For example , benzene shows an absorption maxima at 255 nm , while aniline absorbs at 280 nm. So, here amino group act as an auxochrome.

Bathochromic Shift (Red Shift)

The shift of the absorption maxima towards lower energy or longer wavelength due to presence of an auxochrome or by the change of solvent polarity is known as bathochromic shift or red shift.

The n→π* transition of carbonyl compounds show bathochromic shift due to decrease in solvent polarity.

Hypsochromic Shift (Blue Shift)

The shift of the absorption maxima towards higher energy or shorter wavelength due to removal of conjugation or by the change of solvent polarity is known as hypsochromic shift or blue shift.

In aniline, the lone pair of electron shows conjugation with the π – electrons of the benzene ring and hence has absorption maxima at 280 nm. But in acidic solution, due to the formation of anilinium ion, the lone pair of electron on nitrogen is no longer available and as a result the conjugation is lost. Hence, anilinium ion shows absorption maxima at shorter wavelength of 200 nm showing a blue shift.

Hyperchromic Effect

The effect due to which the intensity of the absorption band of a chromophore increases due the presence of an auxochrome is known as hyperchromic effect.

Hypochromic Effect

The effect due to which the intensity of the absorption band of a chromophore decreases is known as hypochromic effect.

Problem 3.4: Define auxochrome. What do you mean by red shift and blue shift of absorption maximum ? [**GU 2016**]

Problem 3.5: "The absorption at longer wavelength in electronic spectroscopy is due to the combination of a chromophore and an auxochrome group." Describe what do you mean by chromophore and auxochrome. Also explain briefly red shift and blue shift. [**GU 2015**]

Absorption due to ethylene chromophore

Woodward's Rules

Woodward gave some empirical rules to calculate the λ_{max} for conjugated dienes, trienes and polyenes. According to Woodward, some basic value is assigned to the parent compound and the increments made by each substituent is added to it. The values of the parent compound as well as various increments for dienes are shown in **Table 3.2**.

Table 3.2: Values of the parent compound as well as various increments for dienes.

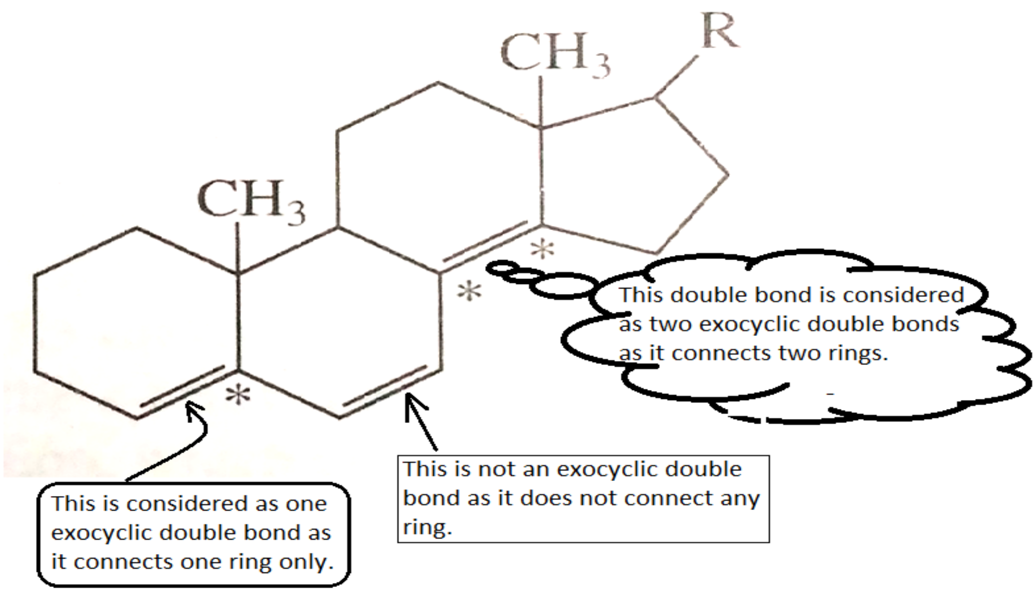
Class	Homoannular (cisoid) (λ nm)	Heteroannular (transoid) (λ nm)
Parent	253	214
Increments:		
Double bond extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Auxochrome:		
-OR	6	6
-Cl, -Br	5	5
$-OCOCH_3$	0	0
$-NR_2$	60	60

NB:

(i) A heteroannular diene means that the two double bonds in conjugation are present in different rings.

(ii) A homoannular diene means that the two double bonds in conjugation are present in same ring.

(iii) A double bond which lies at the junction of two rings is known as an exocyclic double bond. If a double bond connects two rings then it is considered as two exocyclic bonds.



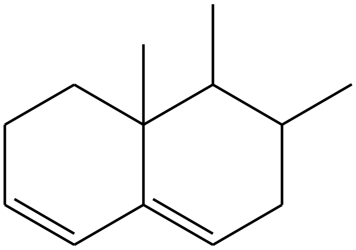
This double bond is considered as two exocyclic double bonds as it connects two rings.

This is considered as one exocyclic double bond as it connects one ring only.

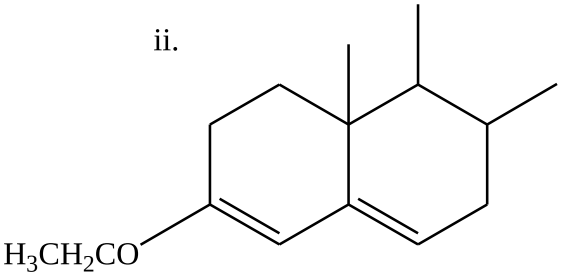
This is not an exocyclic double bond as it does not connect any ring.

Problem 3.6: Calculate the λ_{max} for the following compounds as per Woodward rule –

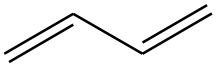
i.



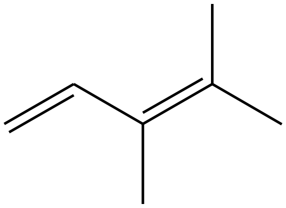
ii.



iii.



iv.



Solution:

(i) Heteroannular Diene (Transoid) = 214 nm

Ring Residue – (3 X 5) = 15 nm

Exocyclic Double Bond = 5 nm

Calculated (λ_{max}) = 234 nm

Observed (λ_{max}) = 235 nm

(ii) Heteroannular Diene (Transoid) = 214 nm

Ring Residue – (3 X 5) = 15 nm

Exocyclic Double Bond = 5 nm

$-OCH_2CH_3$ (-OR) = 6 nm

Calculated (λ_{max}) = 240 nm

Observed (λ_{max}) = 241 nm

(iii) Transoid = 214 nm

Observed (λ_{max}) = 217 nm

(iv) Transoid = 214 nm

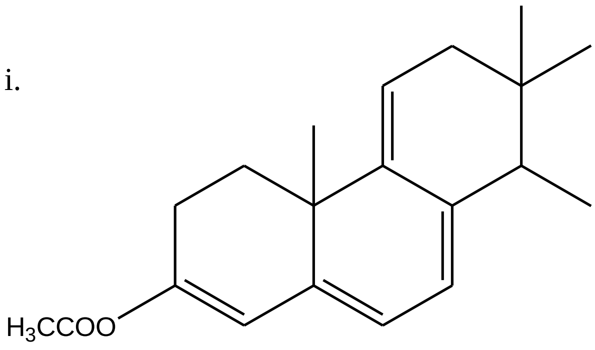
Alkyl groups (3X5) = 15 nm

Calculated (λ_{max}) = 229 nm

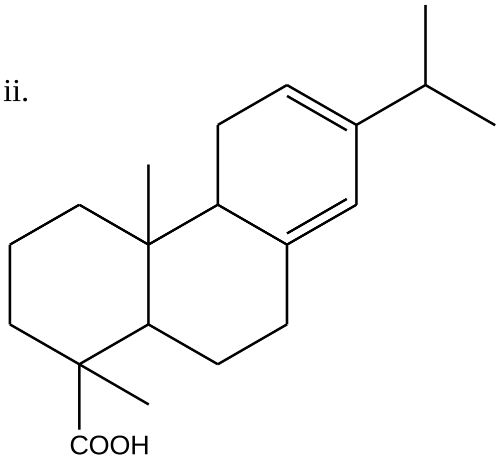
Observed (λ_{max}) = 228 nm

Problem 3.7 : Calculate the λ_{max} for the following compounds as per Woodward rule –

i.



ii.



Solution

(i) Homoannular Diene (Cisoid) = 253 nm

Ring Residue – (5 X 5) = 25 nm

Exocyclic Double Bond -(3X5) = 15 nm

Double bond extending Conjugation - (2 X 30) = 60 nm

Calculated (λ_{max}) = 353 nm

Observed (λ_{max}) = 355 nm

(ii) Homoannular Diene (Cisoid) = 253 nm

Ring Residue – (3 X 5) = 15 nm

Alkyl Substituent = 5 nm

Exocyclic Double Bond - = 5 nm

Calculated (λ_{max}) = 278 nm

Observed (λ_{max}) = 275 nm

The values of the parent compound as well as various increments for enones are shown in **Table 3.3**.

Table 3.3: Values of the parent compound as well as various increments for enones.

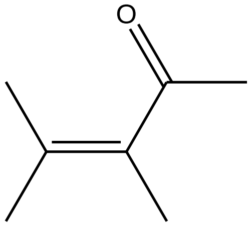
Class		Six membered ring or acyclic parent enone (λ nm)	Five membered ring parent enone (λ nm)	Acyclic dienone (λ nm)
Parent		215	202	245
Increments				
Double bond extending conjugation		30	30	30
Alkyl substituent or ring residue	α	10	10	10
	β	12	12	12
	γ and higher	18	18	18
Exocyclic double bond		5	5	5
Auxochrome				
-OR	α	35	35	35
	β	30	30	30
	γ	17	17	17
	δ	31	31	31
-Cl,	α	15	15	15
	β	12	12	12
-Br	α	25	25	25
	β	30	30	30
-OH	α	35	35	35
	β	30	30	30
	δ	50	50	50
$-OCOCH_3$	α, β, δ	6	6	6

-NR_2	β	95	95	95
Homocyclic diene component		39	39	39

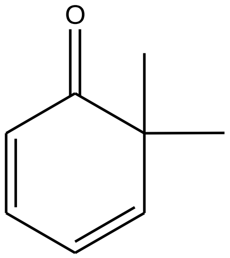
NB. The values are taken from spectroscopy,*Lampman,Pavia,Kriz,Vyvyan*,4th edition

Problem 3.8 : Calculate the λ_{max} for the following compounds as per Woodward rule –

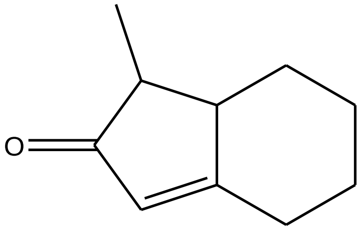
i.



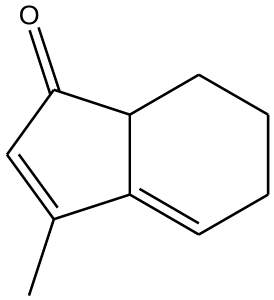
ii.



iii.



iv.
GU,2015



Solution

i. Acyclic enone = 215 nm

Alkyl group at α position(1X10) = 10 nm

Alkyl group at β position (2X12) = 24 nm

Calculated ((λ_{max}) = 249 nm

ii. Six membered enone = 215 nm
Double extending conjugation = 30 nm
Homocyclic diene = 39 nm
Alkyl group at δ position(1X 18) = 18 nm
Calculated ((λ_{max}) = 302 nm

iii. Five membered enone = 202 nm
Ring residue at β position (2X12) = 24 nm
Exocyclic double bond = 5 nm
Alkyl group at δ position(1X 18) = 18 nm
Calculated ((λ_{max}) = 231 nm

iv. Five membered enone = 202 nm
Alkyl group at β position (1X12) = 12 nm
Alkyl group at γ position (1X18) = 18 nm
Exocyclic double bond = 5 nm
Double extending conjugation = 30 nm
Ring residue at δ position(1X 18) = 18 nm
Calculated ((λ_{max}) = 285 nm

Electronic Transitions in conjugated polyenes from particle in a box model

The energy levels for free particles restricted to move in a 1D box are given by –

$$E_n = n^2h^2/8ma^2$$

Where $n=1,2,3,\ldots\ldots$

a = length of the potential box

m = mass of electron

h = Planck's constant

When an electron from the highest filled energy level with quantum number $n = N/2$ is excited to the next higher level with quantum number $n' = N/2 + 1$, energy is absorbed. The difference in energy between these two levels is given as –

$$\Delta E = h^2/8ma^2 \quad [n'^2 - n^2]$$

$$\text{or} \quad \Delta E = h^2/8ma^2 \quad [(N/2 + 1)^2 - (N/2)^2]$$

which on simplification gives,

$$\Delta E = h^2/8ma^2 \quad [N + 1]$$

Thus, the absorption wavelength is given by,

$\Delta E = hv$ where v = frequency of radiation

or $\Delta E = hc/\lambda$ where c = velocity of light, λ = wavelength of radiation

or $\lambda = hc/\Delta E$

or $\lambda = hc\ 8ma^2 / h^2\ [N + 1]$

or $\lambda = 8mca^2 / h\ [N + 1]$ …………………………………… (3.1)

In the above equation, the length of the potential box is not the length of the carbon chain but is taken as the length of the carbon chain plus one extra bond length on each side of the chain, i.e.

$a = (N - 1 + 2)\ l$ where l = carbon- carbon bond length

or $a = (N + 1)\ l$

Putting the value of a in (i), we get

$$\lambda = 8\ m\ c\ [(N + 1)\ l]^2 / h\ [N + 1]$$

or $$\lambda = 8\ m\ c\ (N + 1)\ l^2 / h$$

Which is the wavelength of absorption of conjugated polyene.

NB: For a completely filled conjugated system, the number of π MO's is even. Hence in the ground state of the system the quantum number of the highest filled MO will be N/2, where N is the number of π electrons (or the number of carbon atoms involved).

Effects of Solvents on Electronic Transition

For the analysis, using ultraviolet spectroscopy, it is very important to choose a suitable solvent. The position as well as intensity of absorption maxima is shifted for a particular chromophore by changing the solvent polarity.

A good solvent should show the following characteristics –

Firstly, it should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being studied. Normally, the solvents that donot contain conjugated systems are suitable for this study.

Secondly, it should show fine structure in absorption band. Normally, the fine structure in the absorption band is observed, when the spectrum of the sample is taken in non-polar solvent, as in non-polar solvent the solute doesnot form hydrogen bond with the solvent. But in polar solvent due to the formation of hydrogen bonding between solute and solvent, the fine structure may disappear.

Thirdly, it should have the ability to influence the wavelength of ultraviolet radiation that will be absorbed via stabilization of either the ground or the excited state.

For a particular chromophore, it is possible to change the position as well as intensity of absorption maxima by changing the polarity of the solvent. But there is no any appreciable shift observed on the absorption maxima for non-polar compounds with change in solvent polarity.

Usually, polar solvents form hydrogen bonds readily with the ground states of the solute (polar molecules) in comparison to their excited states. In this case, polar solvents increase the energies of electronic transitions in the molecules and as a result the $n \rightarrow \pi^*$ type of transitions shift to shorter wavelengths. For example, the absorption maxima for acetone in hexane is observed at 279 nm, while in water it is observed at 264 nm.

On the other hand, in some cases polar solvents form hydrogen bonds readily with the excited states of the solute in comparison to their ground states. In this case, polar solvents decrease the energies of electronic transitions in the molecules and as a result the $\pi \rightarrow \pi^*$ type of transitions shift to longer wavelengths. In such case, the absorption maxima will be more in ethanol than in hexane. In case of alcohols and amines formation of hydrogen bonding takes place with solvent molecules. Absorptions in this case occur due to the presence of non-bonding electrons on the heteroatoms ($n \rightarrow \sigma^*$ transition) and thus transition requires greater energy, thereby shifting the absorption maxima to shorter wavelengths.

The shift in the $n \rightarrow \pi^*$ transitions for acetone in various solvents with change in solvent polarity is shown in **Table 3.4**.

For spectral analysis, usually a dilute solution of the sample is prepared. A 95% ethanol is most commonly used as solvent for such spectral analysis.

Thus, it can be concluded that increase in solvent polarity shifts the absorption maxima towards shorter wavelength for $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transition while to longer wavelength for $\pi \rightarrow \pi^*$.transition.

Table 3.4: Shift in the $n \rightarrow \pi^*$ transitions for acetone in various solvents with change in solvent polarity.

Solvent	λ_{max} (nm)
H_2O	264.5
CH_3OH	270
C_2H_5OH	272
$CHCl_3$	277
C_6H_{14}	279

Quantitative Estimation by Spectrophotometry

Spectrophotometric analysis is generally used whenever the sample is coloured. Substances like dichromate, permanganate, cupric, ferric ions etc. can be analyzed directly as such without chemical reactions. As most of the ions are colourless, these are made to react with suitable reagents to form coloured solutions which are then put into analysis. The reagent should be selected such that it reacts with only one ion. It eliminates interference due to the presence of other ions in solution.

Since Beer's law shows variation it cannot be directly applied for analytical problems. The difficulty can be removed by plotting calibration curve between the absorbance and the sample concentration used for preparing calibration curves. For preparing calibration curves a series of standard solutions are prepared. The spectrophotometer is set at that wavelength where the absorption is maximum. This value can be known from the curve between concentration (moles per litre) against absorbance or optical density. After this the absorbance of each solution is measured and then plotted against the concentration of the solution to get a calibration curve.

For measuring the concentration of the unknown solution the absorbance is measured at the wavelength as used for the calibration curve. After this the concentration of the unknown solution can be measured from the calibration curve by observing the value of concentration against the absorbance of the solution. The use of calibration curves is the normal procedure for the quantitative application of spectrophotometry.

EXERCISE

3.1 Explain why absorption maximum (λ_{max}) of CH_3Cl is around 174 nm while that of CH_3I is around 260 nm?

3.2 Aniline shows an absorption maximum at 280 nm. What type of change in the absorption maxima is observed if it is studied in acidic solution?

3.3 Discuss the types of electronic transitions, taking an example in each case.

3.4 If the upper electronic state (ε') is having the same equilibrium internuclear distance (r_e) as the lower electronic state (ε"), then at what point the most intense line will be observed?

3.5 Explain taking an example, how Born-Oppenheimer approximation made it simpler to solve the wavefunction of a system?

3.6 Explain why in case of transitions in which upper state internuclear distance is considerably greater than the lower state, a continuum is observed.

3.7 Derive an expression for the wavelength of absorption of conjugated polyene.

3.8 Discuss how a polar solvent affects the λ_{max} values of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. [**GU 2016**]

3.9 What are the effects of polarity of the solvent on (i) $\sigma \rightarrow \sigma^*$, (ii) $\pi \rightarrow \pi^*$, (iii) $n \rightarrow \pi^*$ and (iv) $n \rightarrow \sigma^*$ transitions ? Show with a diagram the relative frequencies of these electronic transitions. [**GU 2013**]