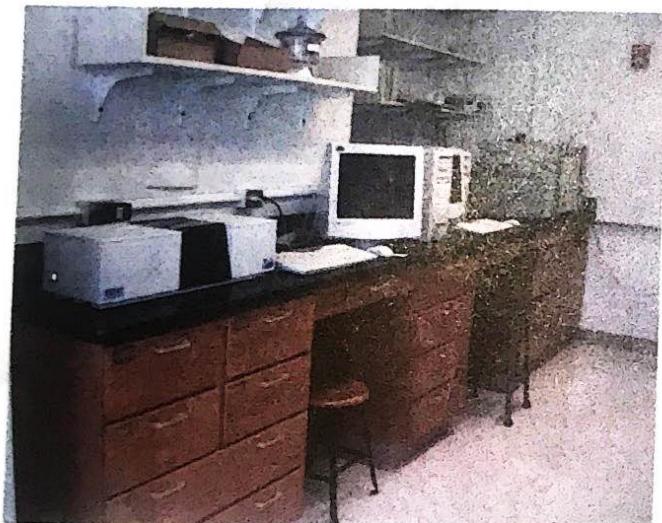


2

Ultra-violet and Visible Spectroscopy



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2.1 Introduction

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. It is very useful to measure the number of conjugated double bonds and also aromatic conjugation within the various molecules. It also distinguishes between conjugated and non-conjugated systems; α , β -Unsaturated carbonyl compounds from β , γ -analogues; homoannular and Heteroannular conjugated dienes etc. For 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 quantised, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. Clearly, if the substance is exposed to radiation of some different value of frequency, energy will not be absorbed and thus, light or radiation will not suffer any loss in intensity. If radiation of a desired or correct frequency is passed or made to fall on the sample of the substance, energy will be absorbed and electrons will be promoted to the higher energy states. Thus, light radiation on leaving the sample after absorption will be either less intense or its intensity may be completely lost.

Substances absorbing in the visible range will appear coloured to the human eye (For visible range – See Fig. 2.1). The wavelength of particular radiation absorbed can also be expressed in terms of frequency or energy in kcal mole $^{-1}$.

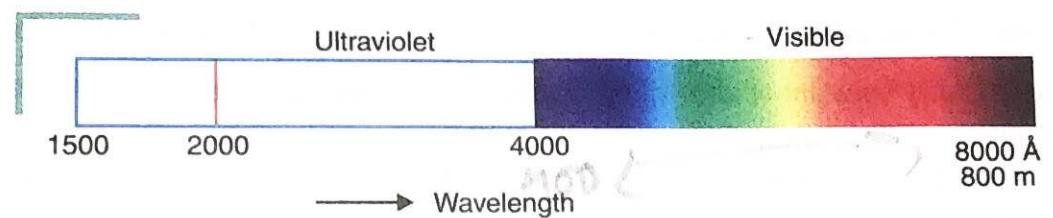


Fig. 2.1. The range of UV-visible Spectra.

$$1\mu = 10^{-4} \text{ cm}$$

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

Let us calculate the energy associated with radiations having wavelength 280 m μ .

$$\lambda = 280 \text{ m}\mu = 280 \times 10^{-7} \text{ cm}$$

We know that

$$E = h\nu$$

$$= h \cdot \frac{c}{\lambda} \quad (h = 6.62 \times 10^{-27} \text{ ergs sec.})$$

Avogadro's number

$$N = 6.023 \times 10^{23}$$

$$4.18 \times 10^7 \text{ ergs} = 1 \text{ calorie}$$

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10} \times 6.023 \times 10^{23}}{280 \times 10^{-7} \times 4.18 \times 10^7 \times 10^3} \text{ kcal mole}^{-1}$$

$$\approx 100 \text{ kcal mole}^{-1}$$

Note. It is not advisable to keep the compounds in ultra-violet radiations except for taking the spectrum.

A record of the amount of light absorbed by the sample as a function of the wavelength of light in m μ or nm units is called absorption spectrum which generally consists of absorption bands.

* Non-bonding electrons.

** nm means nanometers.

The far ultra-violet region (below 200 m μ) is not much studied due to absorption by oxygen and nitrogen. Moreover, studies in these regions require vacuum instruments.

Problem P₂-1. Calculate the energy associated with radiations having wave-length 400 nm. Calculate the answer in keals mole⁻¹.

2.2 The Absorption Laws

There are two laws which govern the absorption of light by the molecules. These are :

(i) Lambert's law and (ii) Beer's law

(i) **Lambert's Law** : It states that :

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.

Mathematically, the law is expressed as

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

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, dx 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.

Let I_0 be the intensity of radiation before entering the absorbing medium ($x = 0$).

Then I , the intensity of radiation after passing through any thickness, say x of the medium can be calculated as :

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k dx$$

or $\ln \frac{I}{I_0} = -kx$ or $\frac{I}{I_0} = e^{-kx}$
 $I = I_0 e^{-kx}$

The intensity of the radiation absorbed, I_{abs} is given by :

$$I_{abs} = I_0 - I = I_0(1 - e^{-kx})$$

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10.

$$I = I_0 10^{-ax}$$

where a = extinction coefficient of the absorbing medium

$$\left(a = \frac{k}{2.303} \right).$$

Note : For ultraviolet spectrum, the region from 200 m μ to 380 m μ (called quartz region) is considered. The molecular absorption in the *UV-VIS* region depends mainly on the electronic structure of the molecule. Depending upon the presence of a ~~common~~ group, the ultraviolet spectrum of a complex compound and that of a simple compound may be almost identical.

(ii) **Beer's Law** : This law states that: 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.

Mathematically, this law is stated as

$$-\frac{dI}{dx} = k' I c$$

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. (when $x = 0$), then the intensity of radiation, I after passing through the thickness x , of the medium can be calculated :

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k' c dx$$

or

$$I = I_0 e^{-k' cx}$$

The above equation can also be written by changing the nature of logarithm to the base 10.

$$I = I_0 \cdot 10^{-a' cx}$$

Here $\frac{k'}{2.303} = a'$ where a' = molar extinction coefficient of the absorbing solution.

Beer's law can also be stated as:

When a monochromatic light is passed through a solution of an absorbing substance, its absorption remains constant when the conc (c) and the thickness of the absorption layer (x) are changed in the inverse ratio.

Alternative expression : On combining the two laws, the Beer-Lambert Law can be formulated as below :

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

where

not true

I_0 = Intensity of incident light

I = Intensity of transmitted light

c = Concentration of solution in moles litre⁻¹

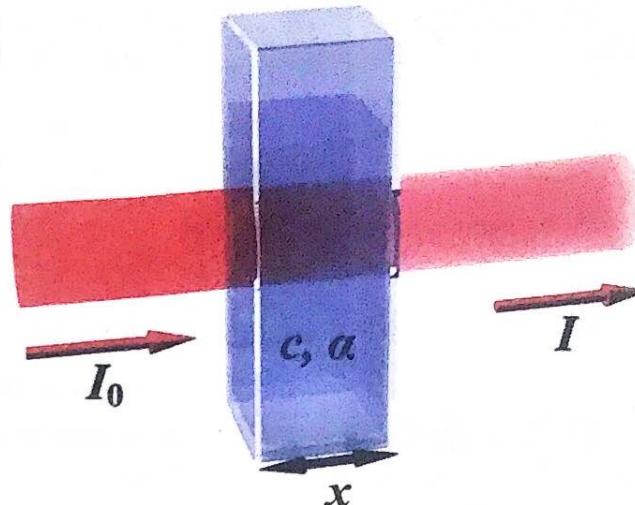
l = Path length of the sample (usually 1 cm)

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 tautomers.
- (ii) When fluorescent compounds are present.
- (iii) When solute and solvent form complexes through some sort of association.



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

$$\frac{I_0}{I} = 10^{-a' cx}$$

$$\log \frac{I_0}{I} = \epsilon \cdot c \cdot x$$

EXAMPLE 1. $2.5 \times 10^{-4} M$ solution of a substance in a 1 cm length cell at λ_{max} 245 nm has absorbance 1.17. Calculate ϵ_{max} for this transition.

$$\text{We know that relation : } \epsilon_{max} = \frac{A}{cl}$$

$$\text{Here } A = 1.17, c = 2.5 \times 10^{-4} M, l = 1 \text{ cm}$$

Substituting the values, we get

$$\begin{aligned}\epsilon_{max} &= \frac{1.17}{2.5 \times 10^{-4} \text{ mol l}^{-1} \times 1 \text{ cm}} = \frac{1.17 \times 10^4 \times 10^3}{2.5 \text{ mol. cm}^{-3} \times 1 \text{ cm}} \\ &= 0.468 \times 10^7 \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

EXAMPLE 2. When a UV light is passed through the given solution, the radiant power is reduced to 50%, calculate the absorbance.

SOLUTION : Let the radiant power incident light (I_0) = $2P$

Then the power of emerged beam (I) = P

Absorbance can be calculated by applying the relation.

$$A = \log \frac{I_0}{I} = \log \frac{2P}{P} = \log 2 = 0.3020$$

EXAMPLE 3. When an incident beam of wavelength 3000\AA was allowed to pass through 2 mm thick pyrex glass, the intensity of radiation was reduced to one tenth of its incident value. What part of the same beam will be transmitted through 1 mm thick same pyrex glass sheet?

SOLUTION. First case. According to Lambert's law:

$$\log \frac{I}{I_0} = -k'x. \text{ Here } I = 10\% \text{ of } I_0 \text{ or } \frac{I}{I_0} = \frac{10}{100} = \frac{1}{10}$$

$$\text{Given } x = 2 \text{ mm} = 0.2 \text{ cm.}$$

$$\text{Thus, } \log \frac{1}{10} = -k'(0.2 \text{ cm}) \text{ or } k' = \frac{1}{0.2 \text{ cm}} = 5 \text{ cm}^{-1}.$$

Second case. Now $x = 0.1 \text{ cm}$

Substituting $k' = 5 \text{ cm}^{-1}$ in the expression for lambert's law, we get

$$\log \frac{I}{I_0} = -5 \text{ cm}^{-1} \times 0.1 \text{ cm} = -0.5$$

$$\text{Taking antilogs, } \frac{I}{I_0} = \text{antilog } (-0.5) = \text{antilog } (\bar{1.05}) = 0.3162$$

$$\text{Thus, } I = 0.3162 \times I_0$$

or Intensity of transmitted light = 31.62% of the intensity of incident light

EXAMPLE 4. When a beam of light (5000\AA) was allowed to pass through 4 mm thick glass sheet, the intensity of transmitted light was reduced to 20% of the initial value. What percentage of light of the same radiation will be absorbed by 2 mm thick glass sheet.

SOLUTION. First case: Given $I_0 = 100, I = 20, x = 4 \text{ mm} = 0.4 \text{ cm.}$

$$\text{Applying Lambert's law: } \log \frac{I}{I_0} = -kx$$

$$\text{Substituting the values: } \log \frac{20}{100} = -k(0.4 \text{ cm})$$

or

$$\log \frac{100}{20} = k(0.4 \text{ cm}) \text{ or } \log \frac{10}{2} = k(0.4 \text{ cm})$$

Thus,

$$1 - \log 2 = k(0.4 \text{ cm}) \text{ or } k = \frac{1 - 0.3010}{0.4 \text{ cm}} = 1.747 \text{ cm}^{-1}$$

Second Case: Given $x = 2 \text{ mm} = 0.2 \text{ cm}$.Substituting $k = 1.747 \text{ cm}^{-1}$ in the Lambert's law expression

$$\log \frac{I}{I_0} = -kx \quad \text{or} \quad \log \frac{I}{I_0} = -1.747 \text{ cm}^{-1} \times 0.2 \text{ cm} = -0.3494$$

Taking antilogs:

$$\frac{I}{I_0} = \text{antilog}(-0.3494) = \text{antilog}(1.6506) = 0.4473$$

Then,

$$I = 0.4473 \times I_0$$

Hence, light absorbed,

$$I_{abs} = I_0 - I = I_0 - 0.4473 I_0 = 0.5527 I_0$$

or

$I_{abs} = 55.27\%$ of the intensity of incident light.

EXAMPLE 5. A 0.01 M solution of a compound transmits 20% of the radiation in a container with path length equal to 1.5 cm. Calculate the molar extinction coefficient of the compound.

SOLUTION. Here $\frac{I}{I_0} = \frac{20}{100} = 0.2$

Where I_0 = Intensity of incident light and I = Intensity of transmitted light.

Also, we know that, absorbance $A = \log \frac{I_0}{I} = \epsilon cl$.

Given $\frac{I}{I_0} = \frac{20}{100} = 0.2$

Substituting the values, $A = -\log \frac{I}{I_0} = -\log(0.2) = \epsilon \times 0.01 \text{ M} \times 1.5 \text{ cm}$

or Extinction coefficient, $\epsilon = \frac{-\log(0.2)}{0.01 \text{ M} \times 1.5 \text{ cm}} = 46.598 \text{ M}^{-1} \text{ cm}^{-1}$

EXAMPLE 6. A substance in a cell length 'l' absorbs 20% of the incident light. What fraction of incident light will be absorbed in a cell of length 5l?

SOLUTION. If I_0 is the intensity of incident light, then the intensity of light absorbed

$$= I_a = \frac{20}{100} I_0$$

Thus, intensity of transmitted light, $I = I_0 - I_a = I_0 - \frac{20I_0}{100} = \frac{80I_0}{100} = 0.8I_0$

Thus, $\frac{I}{I_0} = 0.8$. According to Lambert's law, $\ln \frac{I}{I_0} = -kx$

Where x = thickness of medium = length of the cell containing the substance = l

In the first case, $\ln(0.8) = -k.l$... (i)

In the second case, $x = 5l$. Thus, $\ln \left(\frac{I}{I_0} \right) = -k \times 5l$... (ii)

From (i) and (ii)

$$\ln\left(\frac{I}{I_0}\right)/\ln(0.8) = \frac{-k \times 5l}{-k \times l} = 5$$

or $\ln\left(\frac{I}{I_0}\right) = 5 \times \ln(0.8) = \ln(0.8)^5$

Taking antilogs, the fraction of the transmitted light $= \frac{I}{I_0} = (0.8)^5 = 0.328$

We know that $\frac{I}{I_0} = \frac{I_0 - I_a}{I_0} = 0.328$ or $1 - \frac{I_a}{I_0} = 0.328$

Clearly, the fraction of the incident light absorbed $= 1 - 0.328 = 0.672$

EXAMPLE 7. For a solution of organic ketonic compound ($C_{10}H_{16}O$) in hexane in a 10 cm cell, the absorbance was found to 2.52. What is the concentration of the organic compound? (Given $\epsilon_{max} = 14$).

SOLUTION. Given that : Absorbance (A) = 2.52

$\epsilon_{max} = 14$, cell length, $l = 10 \text{ cm}$

Applying the solution: $A = \epsilon \cdot c \cdot l$.

$$\therefore \text{Concentration, } c = \frac{A}{\epsilon \cdot l} = \frac{2.52}{10 \times 14} = 1.8 \times 10^{-2} \text{ mole L}^{-1}$$

2.3 Measurement of Absorption Intensity

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. These are:

- (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, $n \rightarrow \pi^*$ transition is symmetry forbidden.

The wavelength of light corresponding to maximum absorption is written as λ_{max} . It can be directly read from the horizontal axis as shown in Fig. 2.2. The Figure shows the ultra-violet spectrum of vitamin A with vertical line showing absorbance A which is equal to $\log I_0/I$.

For vitamin A, the absorption maximum (λ_{max}) is observed at 324 nm.

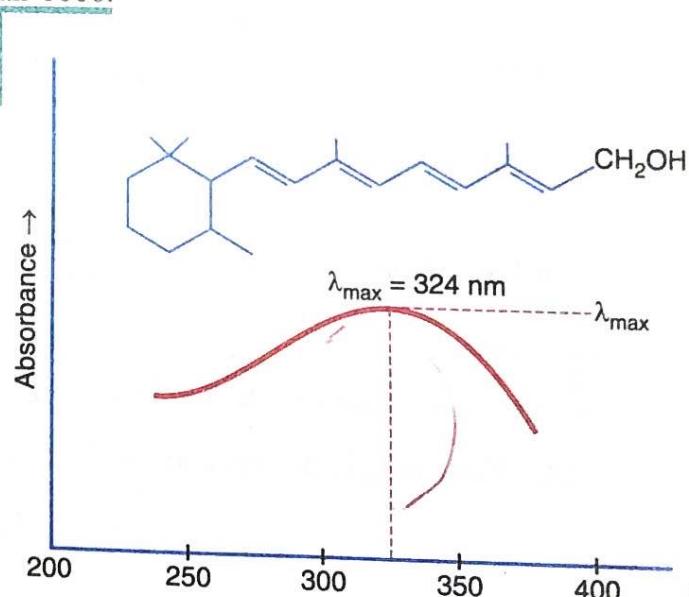


Fig. 2.2. Ultra-violet spectrum of vitamin A.

2.4 Instrumentation

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

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The modern ultra-violet-visible spectrometers consist of light source, monochromator, detector, amplifier and the recording devices. The most suitable sources of light are : **Tungsten Filament lamp** and **hydrogen-deuterium discharge lamp** which cover the whole of the UV-visible region. Tungsten filament lamp is particularly rich in red radiations *i.e.*, radiations with wavelength 375 m μ , while the deuterium discharge lamp covers the region below it. The intensity of the deuterium discharge source falls above 360 m μ . The single source is found satisfactory over the entire UV-VIS region. Ordinary spectrometers cover a range 220-800 m μ . Better instruments cover upto a short wavelength range of 185 m μ . This spectroscopic technique is not useful below 200 m μ (inaccessible region) since oxygen absorbs strongly at 200 m μ and below. To study absorption below 200 m μ , the whole path length is evacuated. The region below 200 m μ is called vacuum ultra-violet region. The low wavelength region can be extended upto 150 m μ by flushing the instrument with nitrogen which absorbs below 150 m μ . Most spectrophotometers are double beam instruments. 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. Dispersion grating can also be employed to obtain monochromatic beam of light from polychromatic radiation (*UV-VIS* radiation). As the dispersion of a single beam or grating is very small, it is not possible to isolate or collimate very narrow band widths. Thus, light from the first dispersion is passed through a slit and then sent to the second dispersion. After the second dispersion, light passes through the exit slit. The main advantage of the second dispersion is that the band width of the emergent light increases and the light passing through the exit slit is almost monochromatic. Also most of the stray light is suppressed.

One of the beams of selected monochromatic light (See Fig. 2.3) is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent. The solvent as well as the solution of the sample may be contained in cells* made of a material which is transparent throughout the region under study.

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. Glass can be used satisfactorily in the visible region. This type of spectrometer is called double beam spectrophotometer. Each absorbance measurement on the solution is accompanied by a simultaneous measurement on the pure solvent.

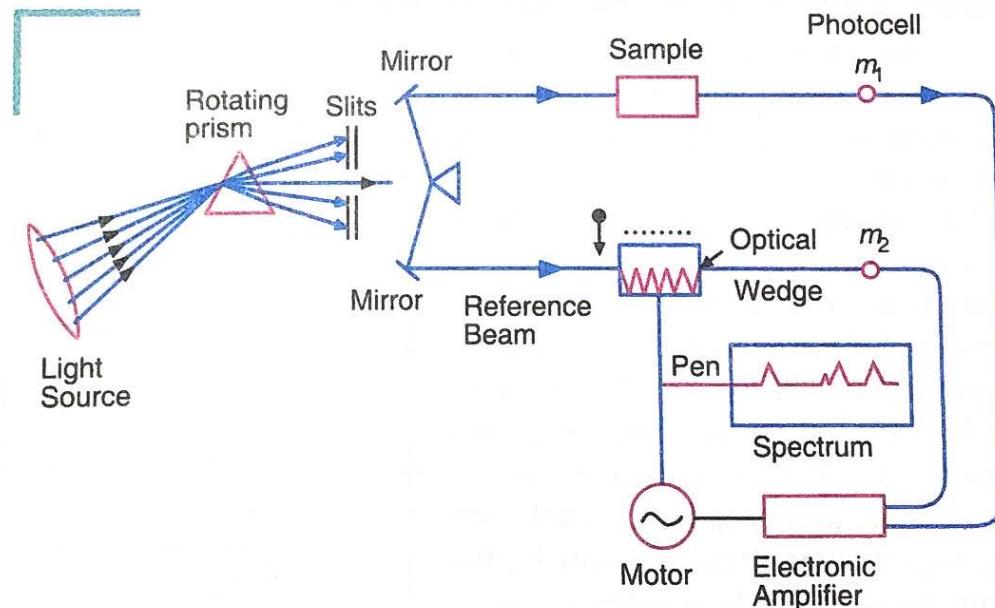


Fig. 2.3. Ultra-violet spectrophotometer.

* Clean cells should be used. These are rinsed many times with the solvent. To remove the last trace of the previous sample, the cell may be cleaned with hot nitric acid or with a detergent.

Usually, samples are scanned in dilute solutions. One mg of the compound under investigation (Molecular weight 100-200) is accurately weighed and dissolved in a suitable solvent to make the solution upto 100 ml volume. A little of this solution is taken in a silica cell. The thickness of the solution in the cell should be 1 cm. When the constitution of the absorbing material is unknown, the absorptivity may be sometimes expressed as $E_{\text{cm}}^{1\%}$. Pure solvent is also taken in an exactly similar cell (Reference cell). These cells are then exposed to the monochromatic beams of equal intensity in the spectrometer. After the beams pass through the sample cell as well as the reference cell, the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. The spectrometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution. Hence, the effects due to the absorption of light by the solvent are minimised. In this way, the absorbance or the transmittance characteristic of the compound alone can be measured. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as absorbance $A (\log_{10} I_0/I)$ against wavelength λ (abscissa). The plot is often represented as ϵ_{max} (Extinction coefficient*) against wavelength.

When the sample absorbs light, its intensity is lowered. Thus, the photoelectric cells P_1 and P_2 will receive an intense beam from the reference cell and a weak beam from the sample cell. This results in the generation of pulsating or alternating currents which flow from the photoelectric cells to the electronic amplifier. The amplifier is coupled to a small servomotor, which in turn, is coupled to a pen recorder. Thus, it records the absorption bands automatically. Actually, the amplifier is coupled to a small servomotor which drives an optical wedge into the reference beam until the photoelectric cell receives light of equal intensities from the sample as well as the reference beams.

2.5 Formation of Absorption Bands

We expect the spectrum to consist of sharp peaks and each peak will correspond to the promotion of electron from one electronic level to another. But, actually sharp peaks are seldom observed and instead, broad absorption bands are recorded. It is due to the fact that the excitation of electrons are also accompanied by the constant vibratory and rotatory motion of the molecules. The vibratory and rotatory modes are also quantised. 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. The differences between two adjacent electronic levels is more as compared to the adjacent rotational levels while the difference between the adjacent vibrational levels has some intermediate value. The electronic excitation is superimposed upon rotational and vibrational levels.

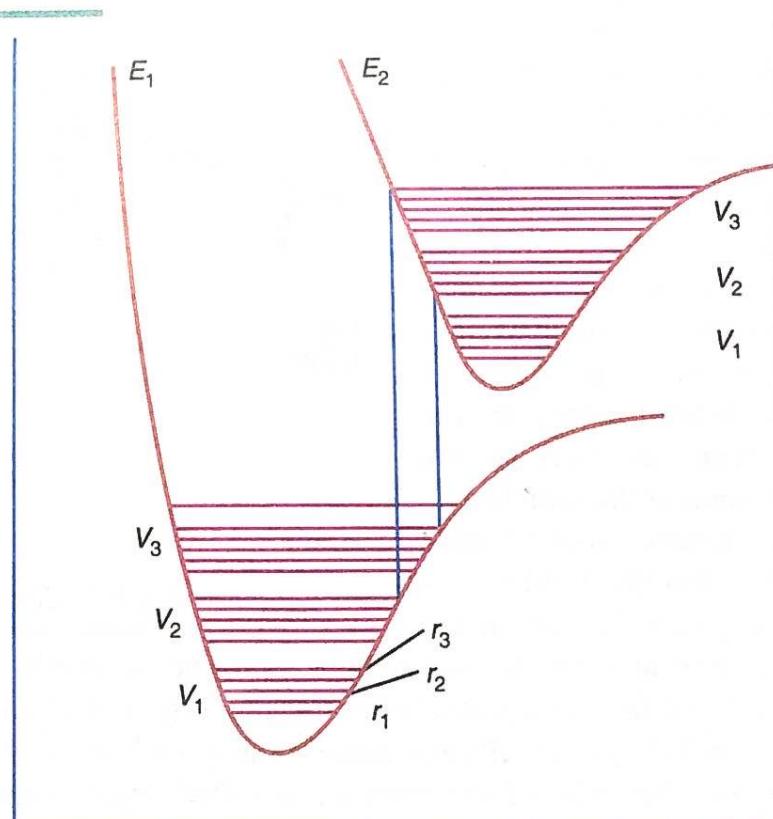


Fig. 2.4. Energy curves for a diatomic molecule.

* It is also called molar absorptivity.

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Clearly, during promotion, the electron moves from a given vibrational and rotational level within one electronic mode to some other vibrational and rotational level within the next electronic mode. Thus, there will be a large number of possible transitions (close together) responsible for change in electronic, rotational and vibrational levels. Hence, not just one but a large number of wavelengths which are close enough will be absorbed resulting in the formation of bands. In more complex molecules which contain a large number of atoms, the multiplicity of vibrational sub-levels and their closeness results in the discrete bands to coalesce and thus, broad bands are observed.

Merges with each other

2.6 Theory of Electronic Spectroscopy

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. On the other hand, if the spins of the electrons in the excited state are parallel, it is called an excited triplet state. The triplet state is always lower in energy than the corresponding excited singlet state. Therefore, triplet state is more stable as compared to the excited singlet state. In the triplet excited state, electrons are farther apart in space and thus, electron-electron repulsion is minimised. Normally the absorption of ultraviolet or visible light results in singlet ground state to excited singlet state transition, i.e., excitation proceeds with the retention of spins. 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 higher energy states are designated as high energy molecular orbitals and also called antibonding orbitals. The highly probable transition due to absorption of quantised energy involves the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled molecular orbital. In most of the cases, several transitions occur resulting in the formation of several bands.

2.7 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.

- The antibonding orbital which is associated with the excitation of σ electron is called σ^* † antibonding orbital. So σ to σ^* transition takes place when σ (sigma) electron is promoted to antibonding (σ) orbital. It is represented as $\sigma \rightarrow \sigma^*$ transition.
- When a non-bonding electron ** (n) gets promoted to an antibonding sigma orbital (σ^*), then it represents $n \rightarrow \sigma^*$ transition.
- Similarly $\pi \rightarrow \pi^*$ transition represents the promotion of π electrons to an antibonding π orbital, i.e., π^* orbital, (See Fig. 2.5)

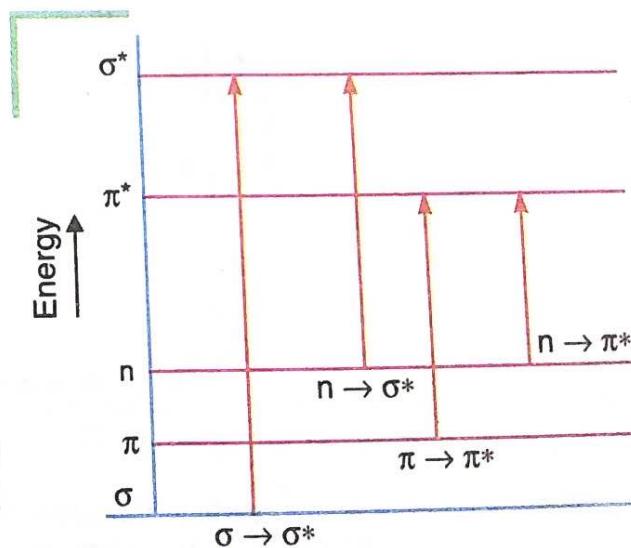


Fig. 2.5. Electronic excitation energies.

* †called sigma asterisk.

** ‡Unshared pair of electrons.

Similarly, when an n -electron (non-bonding) is promoted to antibonding π^* orbital, it represents $n \rightarrow \pi^*$ transition. The energy required for various transitions obey the following order :

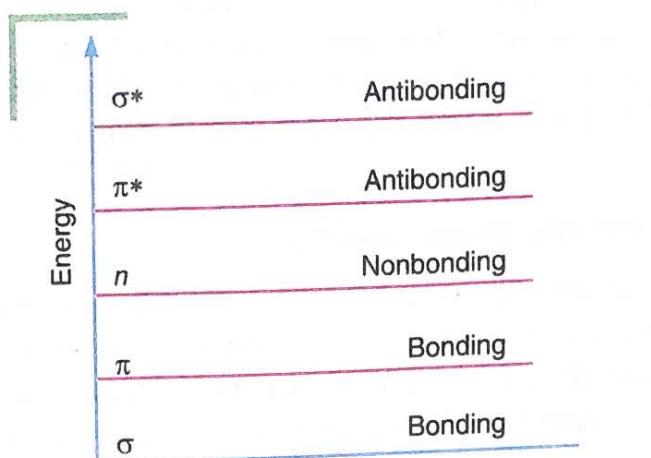
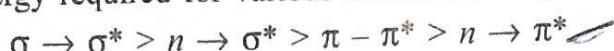


Fig. 2.6. Electronic excitation energies.

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

(a) $\sigma \rightarrow \sigma^*$ transitions. It is a high energy process since σ 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 ultra-violet region, i.e., 180–400 m μ . For saturated hydrocarbons, like methane, propane etc. absorption occurs near 150 m μ (high energy). Consider $\sigma \rightarrow \sigma^*$ transition in a saturated hydrocarbon :

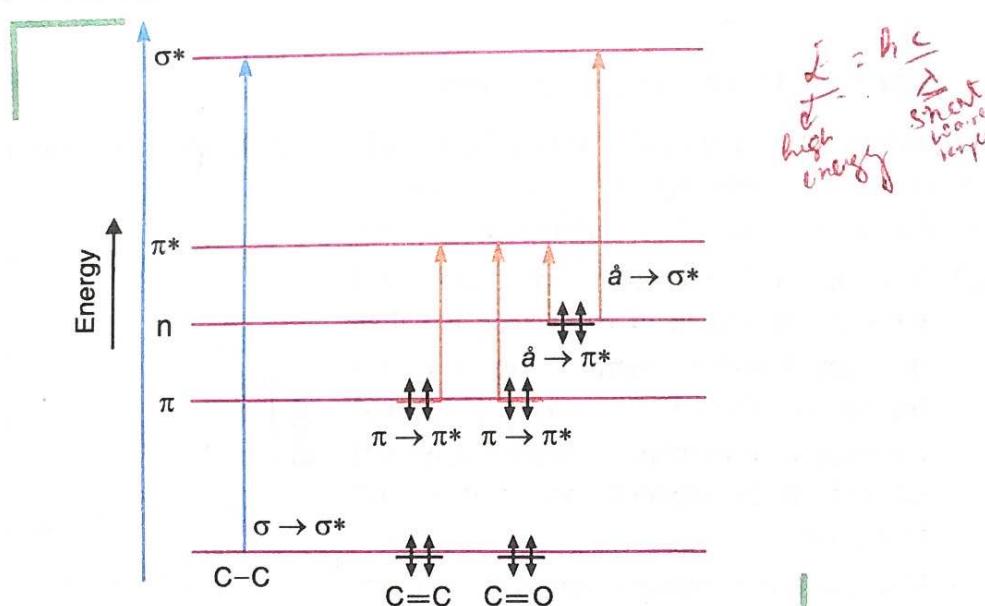
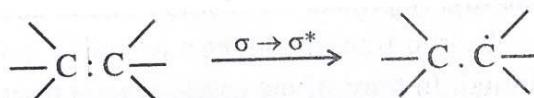


Fig. 2.7. Various transition involved in Electronic spectroscopy.

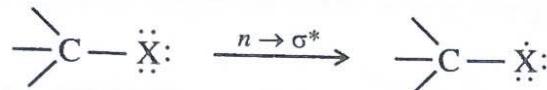
Such a transition requires radiation of very short wavelength (High energy). See Fig. 2.7. The usual spectroscopic technique cannot be used below 200 m μ , since oxygen (present in air) begins to absorb strongly. To study such high energy transitions (below 200 m μ), the entire path length must be evacuated.* Thus, the region below 200 m μ is commonly called vacuum ultraviolet region. The excitation of sigma bond electron to σ^* (antibonding) level occurs with net retention

* Air must be excluded from the instrument so as to avoid absorption due to oxygen.

of electronic spin. It is called excited singlet state which may, in turn, gets converted to excited triplet state. This region is less informative.

(b) $n \rightarrow \sigma^*$ transition. 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. Such transitions require comparatively less energy than that required for $\sigma \rightarrow \sigma^*$ transitions. Water absorbs at $167 \text{ m}\mu$, methyl alcohol at $174 \text{ m}\mu$ and methyl chloride absorbs at $169 \text{ m}\mu$.

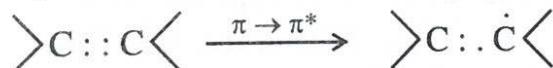
In saturated alkyl halides, the energy required for such a transition decreases with the increase in the size of the halogen atom (or decrease in the electronegativity of the atom).



Let us compare $n \rightarrow \sigma^*$ transition in methyl chloride and methyl iodide. Due to the greater electronegativity of chlorine atom, the n electrons on chlorine atom are comparatively difficult to excite*. The absorption maximum for methyl chloride is $172\text{--}175 \text{ m}\mu$ whereas that for methyl iodide is $258 \text{ m}\mu$ as n electrons on iodine atom are loosely bound. Since this transition is more probable in case of methyl iodide, its molar extinction coefficient** is also higher compared to methyl chloride.

Similarly, amines absorb at higher wavelengths as compared to alcohols and hence the extinction coefficients for amines will be larger. $n \rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus, transition requires greater energy. **Hydrogen bonding shifts the ultra-violet absorptions to shorter wavelengths.** (For details see solvent effects).

(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. show $\pi \rightarrow \pi^*$ transition. Consider an alkene:



This transition requires still lesser energy as compared to $n \rightarrow \sigma^*$ transition and therefore, absorption occurs at longer wavelengths. Absorption usually occurs within the region of ordinary ultra-violet spectrophotometer. In unconjugated alkenes, absorption bands appear around $170\text{--}190 \text{ m}\mu$. In carbonyl compounds, the band due to $\pi \rightarrow \pi^*$ transition appears around $180 \text{ m}\mu$ and is most intense, i.e., the value of extinction coefficient is high. The introduction of alkyl group to olefinic linkage produces a bathochromic shift** of the order of 3 to 5 $\text{m}\mu$ per alkyl group. The shift depends upon the type of the alkyl group and the stereochemistry about the double bond.

(d) $n \rightarrow \pi^*$ transition. 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.

Saturated aldehydes $\left(\begin{array}{c} \text{R} \\ \diagup \\ \diagdown \\ \text{C} = \ddot{\text{O}} : \end{array} \right)$ show both the types of transitions, i.e., low energy $n \rightarrow \pi^*$ and

* Greater the probability of a particular transition, greater the value of its molar extinction coefficient, ϵ_{\max} .

** Shift towards longer wavelength.

high energy $\pi \rightarrow \pi^*$ occurring around $290 \text{ m}\mu$ and $180 \text{ m}\mu$ respectively. Absorption occurring at lower wavelength is usually intense. In simple cases, it is quite easy to tell whether the transition is $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ since the extinction coefficient for the former is quite low as compared to that of the latter. The exact electronic structure of the molecules in the excited state (by the absorption of UV or visible light) is not known but the electronic transition involves the redistribution of electrons within the molecule. In carbonyl compounds; a high energy $n \rightarrow \sigma^*$ 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) $n \rightarrow \sigma^*$ (intense)
- (ii) $\pi \rightarrow \pi^*$ (intense)

(b) Low energy transition

- $n \rightarrow \pi^*$ (weak)-R*band.

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

2.8 Transition Probability

It is not always necessary that the excitation of an electron takes place from a bonding orbital or lone pair to an antibonding or nonbonding orbital when a compound is exposed to UV or visible light. It can be shown that

Extinction coefficient

$$\epsilon_{\max} = 0.87 \times 10^{20} \cdot P.a$$

where

P = transition probability with values from 0 to 1.

a = Target area of the absorbing system, usually called a chromophore.**

It is found that the values of ϵ_{\max} is about 10^5 when the chromophore has a length of the order of 10 \AA or 10^{-7} cm . The chromophore with low transition probability will have ϵ_{\max} value below 1000. Hence, there is a direct relationship between the area of the chromophore and the absorption intensity ϵ_{\max} . In addition, there are some other factors also which govern the transition probability. Depending upon the symmetry and the value of ϵ_{\max} , the transitions*** can be classed as :

(a) Allowed Transitions

(b) Forbidden Transitions

The transitions with values of (extinction coefficient) ϵ_{\max} , more than 10^4 are usually called allowed transitions. They generally arise due to $\pi \rightarrow \pi^*$ transitions. In Butadiene 1, 3, the absorption at $217 \text{ m}\mu$ ϵ_{\max} 21,000 is an example of allowed transition.

The forbidden transition is a result of the excitation of one electron from the lone pair present on the heteroatom to an antibonding π^* orbital. $n \rightarrow \pi^*$ transition near $300 \text{ m}\mu$ in case of carbonyl compounds with ϵ_{\max} value between 10–100, is the result of forbidden transition. The values of ϵ_{\max} for forbidden transition are generally below 10^4 . Consider benzophenone. The two types of transitions observed in this case are :

- | | |
|-------------------------|------------------------------------|
| (i) $252 \text{ m}\mu$ | ϵ_{\max} 20,000 (allowed) |
| (ii) $325 \text{ m}\mu$ | ϵ_{\max} 180 (forbidden). |

Symmetry restrictions in Electronic transitions. The transition (allowed or forbidden) is related with the geometries of the lower and the higher energy molecular orbitals and also on the symmetry of the molecule as a whole. Symmetrical molecules have more restrictions on their electronic transitions than less symmetrical molecules. For example, benzene is a highly symmetrical molecule. Thus, many restrictions apply to the electronic transitions of the benzene molecule and thus, its electronic absorption spectrum is simple. For a totally unsymmetrical molecule, no symmetry

* R-bands (Radikalartig-German).

restrictions apply to the electronic transitions so that transitions may be observed among all of its molecular orbitals except among filled orbitals. Clearly, for such a substance, a complex electronic absorption spectrum will result.

Between symmetrical and totally unsymmetrical extremes, a large number of organic compounds fall which absorb light in the ultra-violet-visible region. To decide whether the transition is allowed or forbidden for such molecules, it is important to consider

- (i) the geometry of the molecular orbital in the ground state
- (ii) the geometry of the molecular orbital in the excited state and
- (iii) the orientation of the electric dipole of the incident light that might induce the transition.

The transition will be an allowed transition if the above three factors have an appropriate symmetry relationship.

2.9 The Chromophore Concept

All those compounds which absorb light of wavelength between 400-800 m μ appear coloured to the human eye. Exact colour depends upon the wavelength of light absorbed by the compound. Originally, a chromophore was considered any system which is responsible for imparting colour to the compound. Nitro-compounds are generally yellow in colour. Clearly, nitro group is the chromophore which imparts yellow colour. Similarly, aryl conjugated azo group is a chromophore for providing colour to azo dyes. Now, the term chromophore is used in a broader way.

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region.

The absorption occurs irrespective of the fact whether colour is produced or not. 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 $n \rightarrow \pi^*$ 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., $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Examples of this type are carbonyls, nitriles, azo compounds, nitro compounds etc.

Note. In compounds of the type $\text{C}=\text{C}$ and $\text{C}=\text{H}$ absorption occurs around 150 m μ (vacuum ultraviolet region) as result of $\sigma \rightarrow \sigma^*$ transition.

For compounds containing such atoms as $-\ddot{\text{O}}-$, $-\ddot{\text{S}}-$, $-\ddot{\text{N}}-$ absorption occurs around 190 m μ as a result of $n \rightarrow \sigma^*$ transition.

There are no set rules for the identification of a chromophore. The change in position as well as the intensity of absorption depends upon a large number of factors. Following points may be helpful :

- (i) Spectrum consisting of a band near 300 m μ may contain two or three conjugated units.
- (ii) Absorption bands near 270–350 m μ with very low intensity, ϵ_{max} 10–100 are due to $n \rightarrow \pi^*$ transitions of the carbonyl group. See table T₂-1.
- (iii) Simple conjugated chromophores such as dienes or α, β – Unsaturated ketones have high ϵ_{max} values, i.e., from 10,000 to 20,000.
- (iv) The absorption with ϵ_{max} value between 1000 to 10,000 shows an aromatic system.

* Although less intense, it is most characteristic of carbonyl group.

Table T₂-1 Simple Unconjugated Chromophores

Chromophore	Transition	Absorption max (m μ)	ϵ_{max}	Solvent
$C=C$	$\pi - \pi^*$	~ 175	~ 15000	Vapour
	(i) $\pi - \pi^*$	~ 175	~ 10000	Hexane "
$-C\equiv C-$	$\pi - \pi^*$	(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
$\begin{array}{c} C=O \\ \\ OH \end{array}$	$n \rightarrow \pi^*$	204	60	Methanol
$-N=N-$	$n - \pi^*$	338	~ 5	Ethanol
	$n \rightarrow \pi^*$	178	9500	Hexane
	$n \rightarrow \pi^*$	220	63	Hexane

When aromatic nucleus is substituted with groups which can extend the chromophore, the absorption occurs at still higher values of extinction coefficients.

Note. The presence of a compound or a functional group can be confirmed by other spectroscopic techniques.

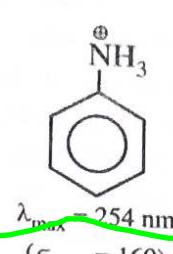
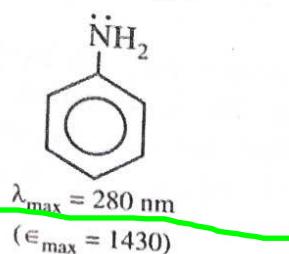
All compounds with the same functional group will absorb at the same wavelength with nearly the same extinction coefficient if the disturbing factors such as conjugation, substituents etc. are absent. Some of the chromophores with their respective absorption maxima and extinction coefficients are given in Table T₂-1.

2.10 Auxochrome

An auxochrome can be defined as any group-which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength). The absorption at longer wavelength is due to the combination of a chromophore and an auxochrome to give rise to another chromophore. An auxochromic group is called colour enhancing group. Auxochromic groups do not show characteristic absorption above 200 m μ . Some common auxochromic groups are $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-SH$ 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. Thus, a new chromophore results which has a different value of the absorption maximum as well as the extinction coefficient. For example, benzene shows an absorption maximum at 255 m μ [ϵ_{max} 203] whereas aniline absorbs at 280 m μ [ϵ_{max} 1430]. Hence, amino ($-NH_2$) group is an auxochrome.

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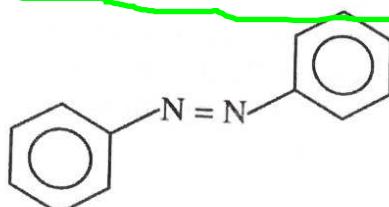
Consider the following :



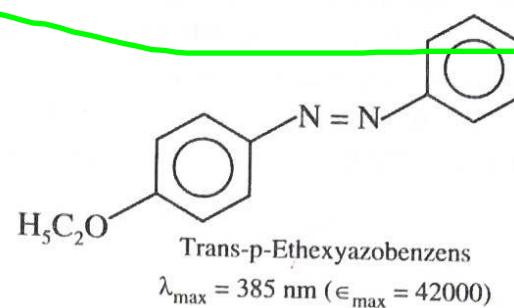
Aniline

In aniline, $-\text{NH}_2$ acts as a chromophore. But in anilinium ion, there is no lone pair on nitrogen atom.

Consider trans-Azobenzene and trans-p-ethoxyazobenzene.



Trans-Azobenzene
 $\lambda_{\max} = 320 \text{ nm} (\epsilon_{\max} = 21000)$



Trans-p-Ethoxyazobenzene
 $\lambda_{\max} = 385 \text{ nm} (\epsilon_{\max} = 42000)$

The presence of $-\text{OC}_2\text{H}_5$ group (an auxochrome) increases the value of λ_{\max} as well as ϵ_{\max} .

Mechanism : All auxochromic groups contain non-bonding electrons. Due to this, there is extension of conjugation of the chromophore by sharing the non-bonding electrons.



2.11 Absorption and Intensity Shifts

(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 or by the change of solvent. (See Fig. 2.8.). Such an absorption shift towards longer wavelength is called Red shift or bathochromic shift. The $n \rightarrow \pi^*$ 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 $280 \text{ m}\mu$ 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 ($\sim 203 \text{ m}\mu$).

In ion formed in acidic solution, the electron pair is no longer present and hence conjugation is removed.

(c) Hyperchromic effect. It is an effect due to which the intensity of absorption maximum increases i.e., ϵ_{\max} increases. For example, the B-band for pyridine at $257 \text{ m}\mu$ $\epsilon_{\max} 2750$ is shifted

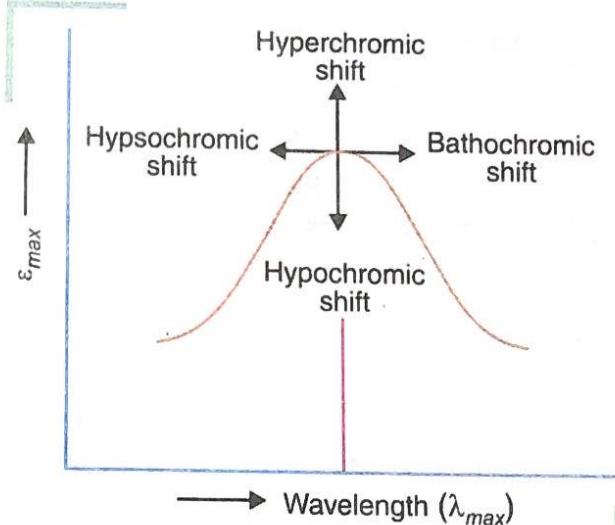


Fig. 2.8. Absorption and intensity shifts.

to $262 \text{ m}\mu \epsilon_{\max} 3560$ 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, *i.e.*, extinction coefficient, ϵ_{\max} decreases. The introduction of group which distorts the geometry of the molecule causes hypochromic effect. For example, biphenyl absorbs at $250 \text{ m}\mu$, $\epsilon_{\max} 19000$ whereas 2-methyl biphenyl absorbs at $237 \text{ m}\mu$, $\epsilon_{\max} 10250$ [ϵ_{\max} decreases]. It is due to the distortion caused by the methyl group in 2-methyl biphenyl.

2.12 Types of Absorption Bands

Following types of bands originate as a result of the possible transitions in a compound.

(a) **K* Bands.** K-bands originate due to $\pi \rightarrow \pi^*$ transition from a compound containing a conjugated system. Such type of bands arise in compounds like dienes, polyenes, enones etc. K-bands also appear in an aromatic compound which is substituted by a chromophore. The intensity of K-band, is usually more than 10^4 . The K-band absorption due to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent.

Table T₂-2 K-band Transitions

Compound	Transition	$\lambda_{\max} \text{ m}\mu$	ϵ_{\max}
Butadiene 1,3	$\pi - \pi^*$	217	21,000
Acrolein	$\pi - \pi^*$	210	11,500
Styrene	$\pi - \pi^*$	214	12,000
Acetophenone	$\pi - \pi^*$	240	13,000
2,3 dimethyl			
Butadiene	$\pi - \pi^*$	226	21,400
Pentadiene 1, 3	$\pi - \pi^*$	223	22,600

(b) **R* band.** Such type of bands originate due to $n \rightarrow \pi^*$ transition of a single chromophoric group and having at least one lone pair of electrons on the hetero atom. R-bands are also called forbidden bands. These are less intense with ϵ_{\max} value below 100.

Table T₂ – 3 R-band Transitions

Compound	Transition	$\lambda_{\max} (\text{m}\mu)$	ϵ_{\max}
Acetone	$n \rightarrow \pi^*$	270	15
Acetaldehyde	$n \rightarrow \pi^*$	293	~ 12
Acrolein	$n \rightarrow \pi^*$	315	14
Acetophenone	$n \rightarrow \pi^*$	319	50
Methyl Vinyl			
Ketone	$n \rightarrow \pi^*$	320	~ 14
Crotonaldehyde	$n \rightarrow \pi^*$	322	~ 14

(c) **B-band.** Such type of bands arise due to $\pi \rightarrow \pi^*$ transition in aromatic or hetero-aromatic molecules. Benzene shows absorption peaks between $230\text{--}270\text{m}\mu$. When a chromophoric group is

Konjugierte-German.

R-band or $n \rightarrow \pi^*$ transition is most characteristic for a carbonyl group of aldehyde or ketone. For aldehydes, it usually appears at higher wavelengths compared to a ketone but at lower value of ϵ_{\max} .

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attached to the benzene ring, the B-bands are observed at longer wave-lengths than the more intense K-bands. For example, K-band appears at $244 \text{ m}\mu$, $\epsilon_{\max} 12000$ and B-band at $282 \text{ m}\mu$, $\epsilon_{\max} 450$. Out of K, B and R-bands which appear in the spectrum of an aromatic compound, R-band appears at a longer wave-length. For example, in acetophenone R-band ($n \rightarrow \pi^*$, forbidden) appears at $319 \text{ m}\mu$ $\epsilon_{\max} 50$ while K and B-bands appear at 240 and $278 \text{ m}\mu$ respectively. The fine spectrum of B-band in case of

- (i) substituted aromatic compounds and
- (ii) by the use of polar solvents
may be missing.

Table T₂-4 B-band Transitions

<i>Compound</i>	<i>Transition</i>	$\lambda_{\max} (\text{m}\mu)$	ϵ_{\max}
Benzene	$\pi - \pi^*$	255	215
Styrene	$\pi - \pi^*$	282	450
Toluene	$\pi - \pi^*$	262	174
Phenol	$\pi - \pi^*$	270	1450
Acetophenone	$\pi - \pi^*$	278	1110
Benzaldehyde	$\pi - \pi^*$	280	1500
Benzoic acid	$\pi - \pi^*$	270	800
Nitro-benzene	$\pi - \pi^*$	280	1000
Naphthalene	$\pi - \pi^*$	312	289
Quinoline	$\pi - \pi^*$	315	2500

(d) E-bands. Such bands originate due to the electronic transitions in the benzenoid system of three ethylenic bonds which are in closed cyclic conjugation. These are further characterised as E_1 and E_2 -bands. E_1 and E_2 bands of benzene appear at 184 and $204 \text{ m}\mu$ respectively. E_1 band which appears at lower wave-length is usually more intense than the E_2 -band for the same compound which appears at longer wavelength.

Table T₂-5 E-band Transitions

<i>Compounds</i>	<i>E₁-band</i>		<i>E₂-band</i>	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
Benzene	(mm)		(mm)	
Benzene	184	50,000	204	79,00
Naphthalene	221	133,000	286	9,300
Anthracene	256	180,000	375	9,000
Pyrrole	234	10,800	288	760
Thiophene	~270	6,300	~294	600
Quinoline	288	40,000	270	3,162

2.13 Solvent Effects

A most suitable solvent is one which does not itself absorb in the region under investigation. A dilute solution of the sample is always prepared for the spectral analysis. Most commonly used solvent is 95% Ethanol. Ethanol is a best solvent as it is cheap and is transparent down to $210 \text{ m}\mu$.

Commercial ethanol should not be used as it contains benzene which absorbs strongly in the ultraviolet region. Some other solvents which are transparent above 210 m μ are n-hexane, methyl alcohol, cyclohexane, acetonitrile, diethyl ether etc. Some solvents with their upper wavelength limit of absorption are given in Table T₂-6.

Table T₂-6 Solvents used in UV-spectroscopy

Solvent	Upper wavelength limit (m μ)
Ethanol	210
Hexane	210
Methanol	210
Cyclohexane	210
Diethyl ether	210
Water	205
Benzene	280
Chloroform	245
THF (Tetrahydrofuran)	220
Carbon tetrachloride	265

Hexane and other hydrocarbons can be used as these are less polar and have least interactions with the molecule under investigation. For ultra-violet spectroscopy, ethanol, water and cyclohexane serve the purpose best.

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. Thus, in general, the absorption maximum for the non-polar compounds is the same in alcohol (polar) as well as in hexane (non-polar). 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.

(i) $n \rightarrow \pi^*$ transition (less intense). In such a case, the absorption band moves to shorter wave-length by increasing the polarity of the solvent. In $n \rightarrow \pi^*$ transition, the ground state is more polar as compared to the excited state. The hydrogen bonding with solvent molecules takes place to lesser extent with the carbonyl group in the excited state. For example, absorption maximum of acetone is at 279 m μ in hexane as compared to 264 m μ in water. (polar)

(ii) $\pi \rightarrow \pi^*$ transition (intense). For such a case, the absorption band moves to 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. Thus, the value of absorption maximum in ethanol will be greater than that observed in hexane.

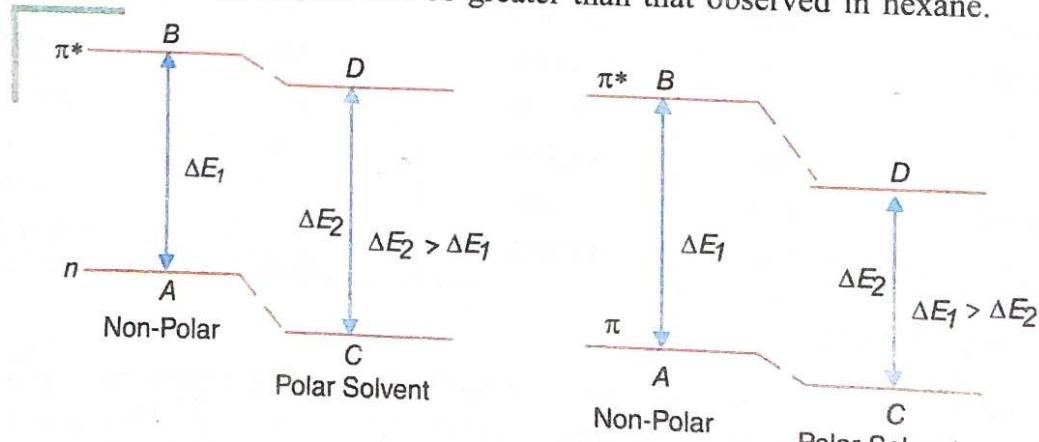


Fig. 2.9. Absorption shift with change in polarity of the solvent.

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.

$n \rightarrow \sigma^*$ 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.

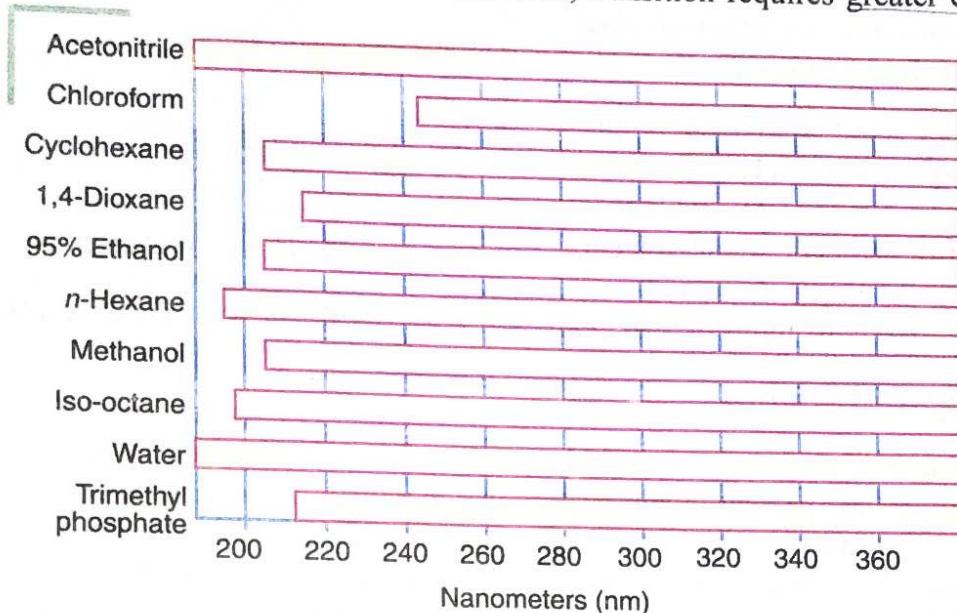


Fig. 2.10. Transparency ranges of useful solvents.

In general, we say that

(a) If the group (carbonyl) is more polar in the ground state than in the excited state, then increasing polarity of the solvent stabilises the non-bonding electron in the ground state due to hydrogen bonding. Thus, absorption is shifted to lower wavelength.

(b) If the group is more polar in the excited state, then absorption is shifted to longer wavelength with increase in polarity of the solvent which helps in stabilising the non-bonding electrons in the excited state.

It has been found that increase in polarity of the solvent generally shifts $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelengths and $\pi \rightarrow \pi^*$ bands to longer wavelengths.

Following points may also be noted in connection with the effect of solvent polarity on the various types of bands.

(i) **K-band.** The K-band absorption due to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent. Usually, K-bands due to conjugated dienes are not effected by changing the polarity of the solvent while these bands due to 'enones' show a red shift by increasing the polarity of the solvent.

(ii) **R-band.** The absorption shifts to shorter wavelength (blue shift) with the increase in polarity of the solvent.

(iii) **B-band.** The position as well as the intensity of the B-band is not shifted by increasing the polarity of the solvent. But in heterocyclic aromatic compounds, a marked hyperchromic shift (increase in ϵ_{max}) is observed by increasing the polarity of the solvent.

2.14 Effect of Temperature and Solvent on the Fineness of Absorption Band

It is known that the vibrational and the rotational states depend on temperature. As the temperature is decreased, vibrational and the rotational energy state of the molecules are also

lowered. Thus, when the absorption of light occurs at a lower temperature, smaller distribution of excited states result. It produces finer structure in the absorption band than what is noticed at higher temperature. Consider the UV spectrum of dodecapentaenoic acid in ether-alcohol solvent at 20 °C and -195 °C.

The solvent used also effects the fineness of absorption band in 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.

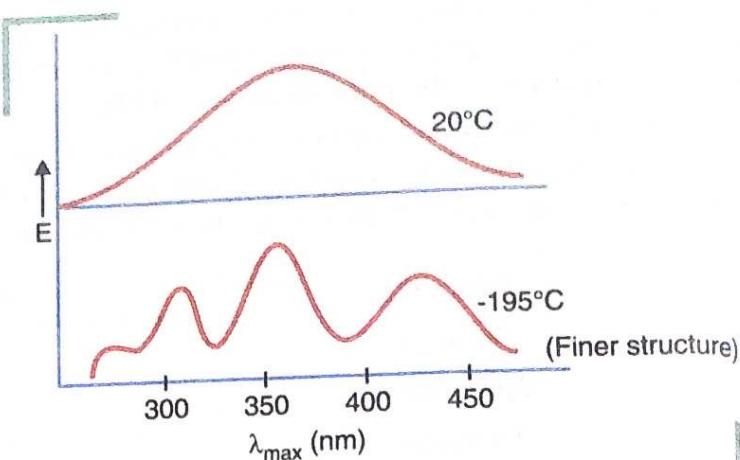


Fig. 2.10(A) Fineness of absorption band.

2.15 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 ($\pi \rightarrow \pi^*$ transition) while butadiene (two double bonds in conjugation) absorbs at 217 m μ . The bathochromic shift is more pronounced if the double bonds are in conjugation as compared to the isolated double bonds in which there is a little interaction between them. The absorption maximum is usually shifted 15–45 m μ towards higher wavelength in conjugated system (compared to unconjugated) as the electron density is spread over at least four atomic centres. The value of extinction coefficient also increases. In conjugated dienes, $\pi \rightarrow \pi^*$ transition results in the formation of a band, called K-band.

Table T₂-7 $\pi \rightarrow \pi^*$ transition (K-band)

Compound	λ_{max} (m μ)	ϵ_{max}
Butadiene 1, 3	217	21,000
2,3 dimethyl butadiene	226	21,400
1,3,5, Hexatriene	254	21,400

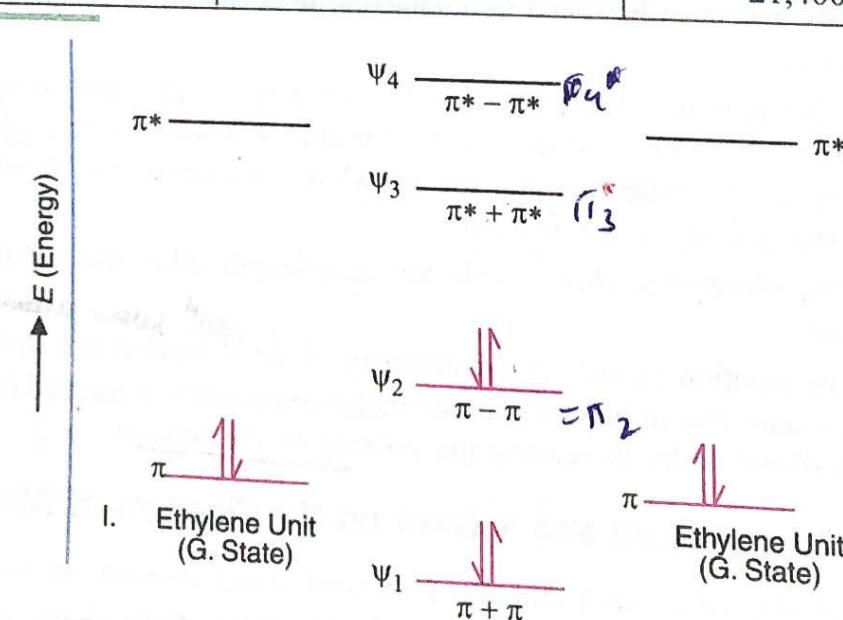


Fig. 2.11. Electronic excitations in conjugated dienes.

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When ethylene molecule gets excited, it gives CH_2-CH_2 diradical. The electron cloud is spread on two carbon atoms and the absorption maximum occurs at $170 \text{ m}\mu$.

Consider the absorption maximum of butadiene 1,3 ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$). It consists of two ethylene units. The various excitations are shown in Fig. 2.11.

The two π bonding orbitals, one from each ethylene unit interact or mix up to give rise to two new bonding orbitals.

(i) $\pi + \pi = \psi_1$ or ψ_1 —having smaller energy.

(ii) $\pi - \pi = \psi_2$ or ψ_2 —having higher energy.

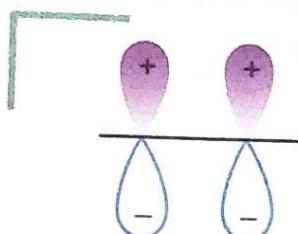


Fig. 2.12. π -bonding orbitals.

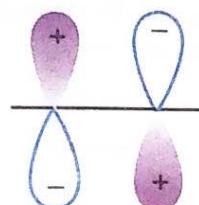


Fig. 2.13. π^* antibonding orbitals

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

(ii) $\pi^* - \pi^* = \psi_4$ 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. 2.14.

In this case, all the four singly filled atomic orbitals have the same spin of electrons.

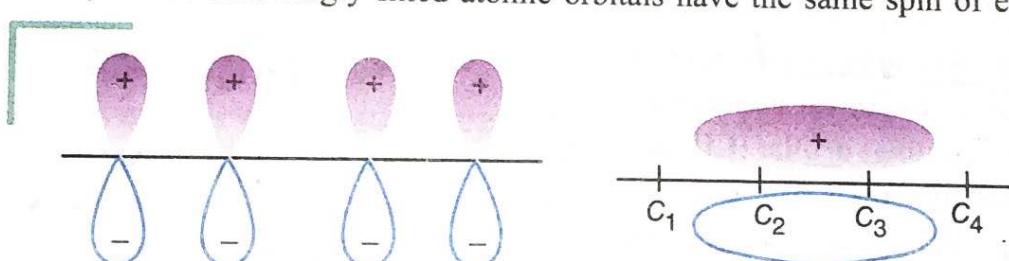


Fig. 2.14. Low energy atomic orbital (ψ_1).

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

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

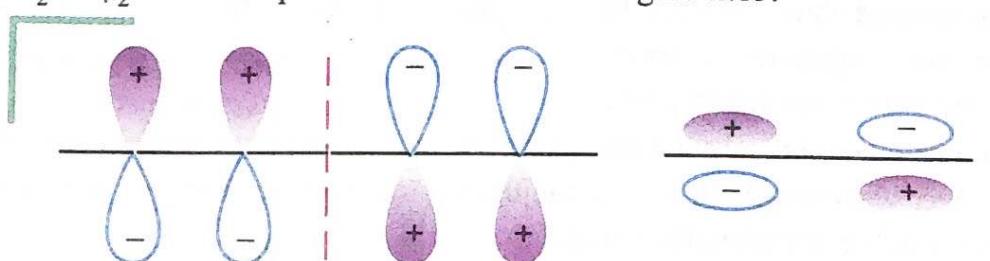


Fig. 2.15. High energy bonding orbital (ψ_2)

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 .

It is defined as an imaginary plane drawn perpendicular to the plane of propagation of the wave where the probability of finding the electron is zero.

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

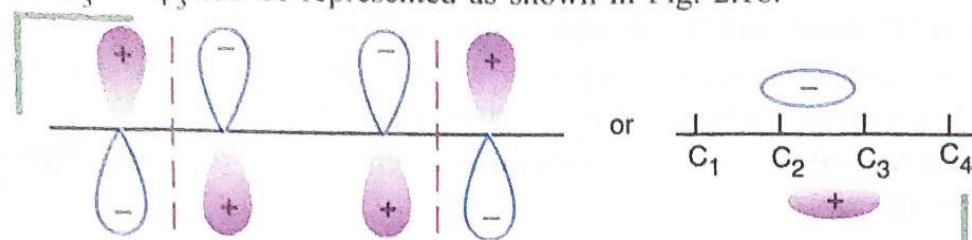


Fig. 2.16. Low energy antibonding orbitals (ψ_3).

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.

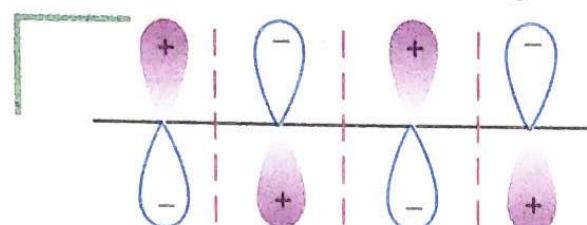


Fig. 2.17. High energy anti-bonding orbital (ψ_4).

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

Thus, in butadiene, four orbitals are involved. On absorption of energy, electron jumps from π_2 to π_3^* . Since the energy difference between π_2 to π_3^* is less, absorption occurs at higher wavelength. This type of transition is called $\pi \rightarrow \pi^*$ transition. 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. (See figure 2.17).

Now this absorption corresponds to the transition y (low energy or higher wavelength). Similarly, when dissimilar chromophores are in conjugation, absorption occurs at longer wavelength as compared to the isolated chromophores. In general longer the conjugated system, smaller will be the energy needed to cause $\pi \rightarrow \pi^*$ transition and therefore, absorption occurs at still longer wavelength. In a long conjugated system like carotene, absorption occurs in the visible region (higher wavelength region).

The values of absorption maximum (λ_{max}) as well as extinction coefficient for conjugated and unconjugated alkenes can be compared from their spectra shown in Fig. 2.19.

The values of λ_{max} and ϵ_{max} are more for conjugated diene as compared to those for an unconjugated alkene. A bathochromic as well as hyperchromic effect are observed when the spectrum of conjugated triene is compared to that of conjugated diene.

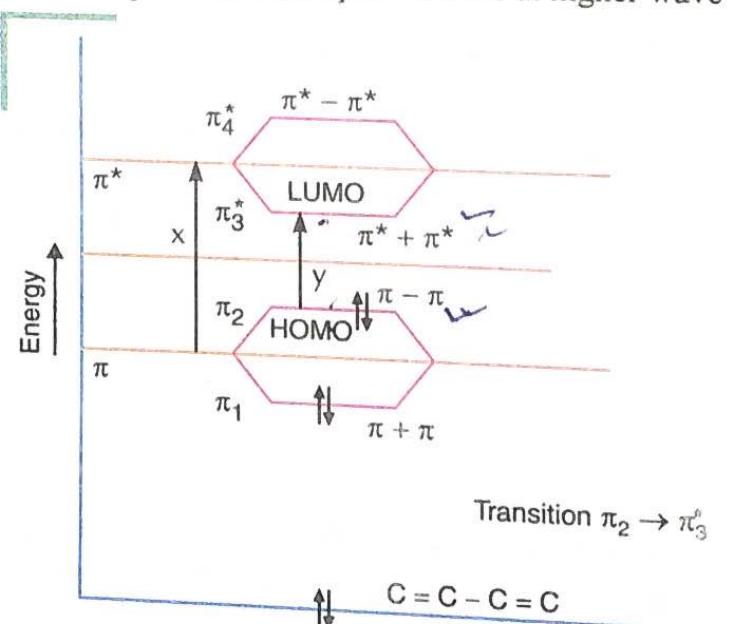


Fig. 2.18. Electronic transition in conjugated diene.

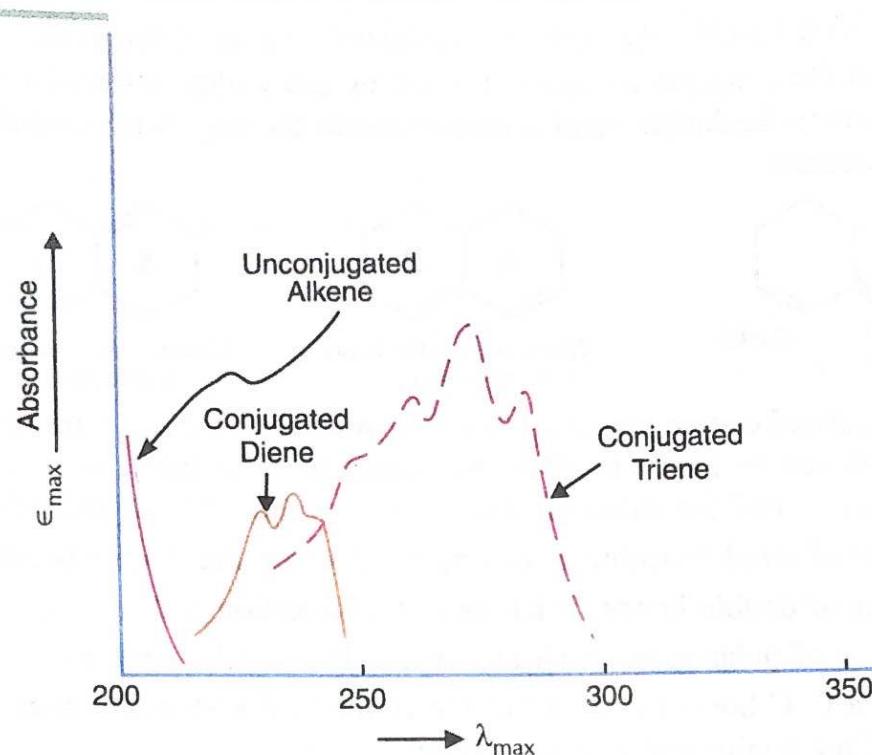


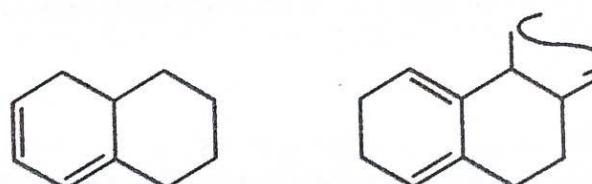
Fig. 2.19. Absorption in conjugated and un-conjugated systems.

It is important to note that greater the number of conjugated double bonds, greater is the bathochromic shift. With continuous increase in conjugation, the absorption may even shift to the visible region. As the conjugation increases, the energy gap between HOMO and LUMO decreases, (See Fig. 2.18). In case of β-carotene which contain eleven double bonds, the absorption bands appear at (i) λ_{max} 478 nm (ϵ_{max} 139000) and (ii) λ_{max} 452 nm (ϵ_{max} 122000).

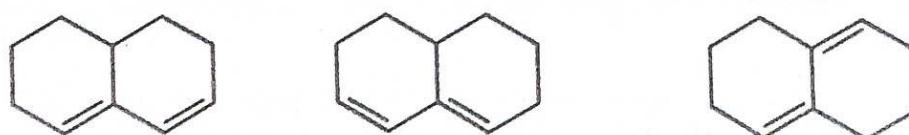
2.16 Woodward-fieser Rules for Calculating Absorption Maximum in Dienes

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 (see Fig. 2.19). 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 (visible region). The presence of alkyl group on the double bond also causes bathochromic shift. Various types of double bonds in conjugation are described below :

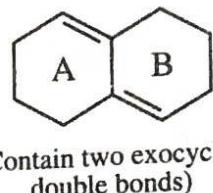
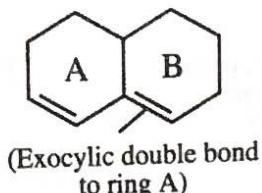
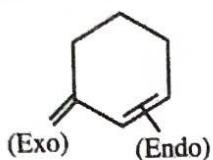
- (a) **Alicyclic dienes or dienes contained in an open chain system**, i.e., where basic unit is butadiene system.
- (b) **Homo-annular conjugated double bonds** are the conjugated double bonds present in the same ring. It is also called **Homodiene**. Some examples of this type are :



- (c) **Hetero-annular conjugated double bonds** are the conjugated double bonds which are not present in the same ring. Some examples of this type are :



(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. Such double bonds are shown in the following examples :



Woodward formulated certain empirical rules for calculating the λ_{max}^* in case of dienes. These rules were later modified by Fieser in 1948. According to these rules, each type of diene has a certain fixed basic value and the value of absorption maximum (λ_{max}) depends upon :

- (i) The number of alkyl substituents or ring residues on the double bond.
- (ii) The number of double bonds which extend conjugation and
- (iii) The presence of polar group such as —Cl, —Br, —OR, —SR etc.

Ring residue is a C—C bond, not a part of the conjugated system but attached to any one of the carbon atoms of the conjugated polyene system.

The various rules for calculating the absorption maximum in case of dienes and trienes are summarised in the Table T₂-8.

Table T₂-8 Conjugated dienes and Trienes.

<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

Some examples illustrating the above rules are as follows :

EXAMPLE 1. Calculate the absorption maximum in the ultra-violet spectrum of 2, 4-Hexadiene.

* Wavelength of absorption maximum.

** In case of a cyclic diene or diene contained in an open chain, 17 m μ are added in the basic value for chlorine as well as for bromine atom.