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## 1. Learning Outcomes

After studying this module, you shall be able to:

- Learn about the important terminologies in UV-Visible spectroscopy.
- Differentiate between the factors causing changes in the UV-Visible spectrum.
- Understand the effect of conjugation on the position and intensity of UV-Visible bands.
- Analyze the effect of solvent on electronic transitions.
- Know about the effect of pH on the UV-Visible absorption band.

## 2. Introduction

Ultraviolet-visible spectroscopy involves the absorption of ultraviolet/visible light by a molecule causing the promotion of an electron from a ground electronic state to an excited electronic state. Although, there are six possible transitions-

$\sigma$ to $\sigma*$, $\sigma$ to $\pi*$, $\pi$ to $\sigma*$, $\pi$ to $\pi*$, n to $\pi*$ and n to $\sigma*$, the most commonly observed transitions in organic molecules are $\pi$ to $\pi*$, n to $\sigma*$ and n to $\pi*$. The $\pi$ to $\sigma*$, n to $\pi*$ transitions usually lie in the UV-Vis region, whereas transitions $\sigma$ to $\sigma*$, $\pi$ to $\sigma*$, $\pi$ to $\pi*$ and $\pi$ to $\sigma*$ lie in the vacuum or far UV region. The lowest energy transition is typically that of an electron in the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Electronic transitions may be as intense or weak according to the magnitude of $\varepsilon_{max}$ that corresponds to *allowed* or *forbidden* transition as governed by the selection rules of electronic transition, which states that the transitions change in their spin states are not allowed. Thus, S→S, T→T, are allowed, but S→T, T→S, are forbidden (where S= Singlet state, T= Triplet state).

## 3. Important terminologies in UV-Visible Spectroscopy

### 3.1 Chromophore
When a molecule absorbs electromagnetic radiation in the ultraviolet/visible range, a transition between different electronic energy levels occurs. Since the wavelength of absorption is a measure of the separation of the energy levels of the orbital concerned. The nucleus holding the electrons together in a bond determine the wavelength of radiation to be absorbed. Thus the nuclei, with which the concerned electrons are bound, affect the energy between the ground and excited states.

Therefore we can say that the energy of transition and the wavelength of radiation absorbed are properties of atoms not the electron themselves. The group of atoms due to which absorption occurs is called chromophore.

*A chromophore is defined as an isolated covalently bonded group that shows a characteristic absorption in UV/Visible region. For example C=C, C≡C, C=O, C=N, N=N, R-NO$_2$ etc.*

If a compound absorbs light in the visible region (400-800 nm), only then it appears coloured to our eyes. Therefore a chromophore may or may not impart colour to a compound depending on whether the chromophore absorbs radiation in the visible or UV region.

There are no standard criteria for the identification of a chromophore because the wavelength and intensity of absorption depend on many factors such as the molecular environment of the chromophore and on the solvent in which the sample is dissolved. Other parameters, such as pH and temperature, also may cause changes in both the intensity and the wavelength of the absorbance maxima. All the compounds having the same functional group will absorb at almost the same wavelength if the other factors such as conjugation, substituents etc are absent.

### 3.2 Auxochrome

The substituents covalently attached to a chromophore which themselves do not absorb ultraviolet/ visible radiation, but their presence changes both the intensity as well as wavelength of the absorption maximum are known as auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes. These are also called colour enhancing groups. The actual effect of an auxochrome on a chromophore depends on the polarity of the auxochrome, e.g. groups like $CH_3$, $CH_3CH_2$ and Cl have very little effect, usually a small red shift of 5-10 nm. Other groups such as $NH_2$ and $NO_2$ show a strong effect and completely alter the spectrum.

Auxochrome generally increases the value of absorption maxima by extending the conjugation through resonance. The extended conjugation brings the lowest excited state (LUMO) closer to the highest ground state (HOMO) and thus permits a lower energy (longer wavelength) transition. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different value of absorption maxima. For example benzene shows $\lambda_{max}$ at 256 nm, whereas aniline shows $\lambda_{max}$ at 280 nm. Hence the $NH_2$ group acts as an auxochrome and causes the shifting of $\lambda_{max}$ to a larger value.
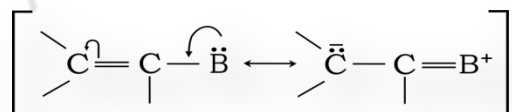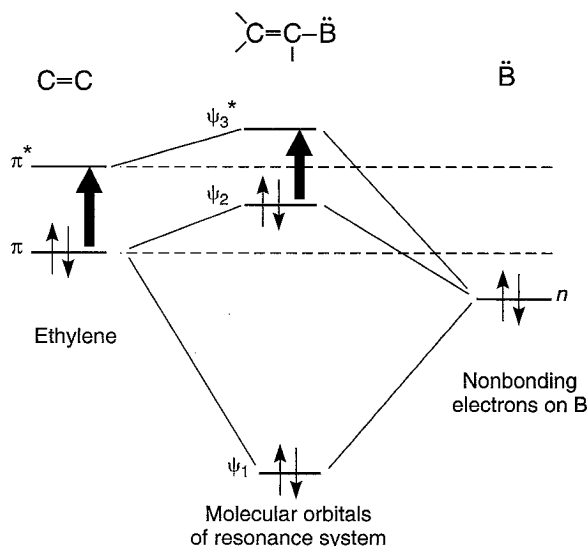
**Figure 1: Molecular orbitals of resonance system showing closeness in HOMO and LUMO**

### 3.3 Bathochromic Shift or Red shift

The shift of an absorption maximum towards longer wavelength or lower energy is called as bathochromic shift. It may be produced due to presence of an auxochrome or in solvent polarity. Because the red color has a longer wavelength than the other colors in the visible spectrum, therefore this effect is also known as red shift.

### 3.4 Hypsochromic Shift or Blue Shift

The shift of an absorption maximum towards the shorter wavelength or higher energy is called hypsochromic shift. It may be caused due to presence of an auxochrome or change in solvent polarity. Because the blue color has a lower wavelength than the other colors in the visible spectrum and hence this effect is also known as blue shift.

### 3.5 Hyperchromic Effect

It is an effect that results in increased absorption intensity. The introduction of an auxochrome usually causes hyperchromic shift. For example benzene shows B band (the secondary band in UV-Vis spectra) at 256 nm and $\varepsilon_{max}$ 200, whereas aniline shows B-band at 280 nm and $\varepsilon_{max}$ at 1430. The increase in the value of $\varepsilon_{max}$ is due to the hyperchromic effect of auxochrome $NH_2$.

### 3.6 Hypochromic Effect

An effect that results in decreased absorption intensity is called hypochromic effect. This is caused by a group which distorts the geometry of the molecule. For example, biphenyl shows $\lambda_{max}$ at 250 nm and $\varepsilon_{max}$ at 19,000, whereas 2-methyl biphenyl absorbs at $\lambda_{max}$ 237 nm, $\varepsilon_{max}$ 10250. The decrease in the value of absorbance is due to hypochromic effect of methyl group which distorts the chromophore by forcing the rings out of coplanarity resulting in the loss of conjugation.
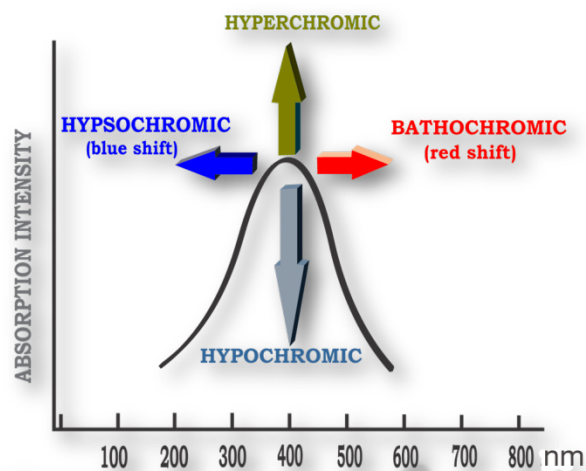
**Figure 2: Effect of substituents on the position and intensity of an absorption band**

The hyperchromic and hypochromic effect can be explained by taking the example of DNA. DNA absorbs in the ultraviolet region of the spectrum due to the conjugated double bond and ring systems of the purine and pyrimidine bases.

The absorption of single strand DNA is higher than the absorbance of double strand DNA. The two strands of DNA are bound together mainly by the stacking interactions, hydrogen bonds and hydrophobic interaction between the complementary bases. The hydrogen bonds between the paired bases in the double helix limit the resonance of the aromatic ring of the bases which results in decrease in the UV absorbance of double strand DNA sample (hypochromic effect). When the DNA double helix is separated into its two fragments, the interaction forces holding the double helical structure is disrupted. As a result, intensity of absorption maxima increases (hyperchromic effect) as the bases are now in a free state and do not form hydrogen bonds with complementary bases. Generally, the absorbance for single-stranded DNA is 37% higher than that for double stranded DNA at the same concentration.

## 4. Factors affecting the position of UV-Visible bands

### 4.1 Effects of Conjugation
When two or more chromophores are conjugated the absorption maxima is shifted to a larger wavelength or shorter frequency. Conjugation increases the energy of the HOMO and decreases the energy of LUMO. As a result less energy is required for an electronic transition in a conjugated system than in a non-conjugated system (Figure 3).
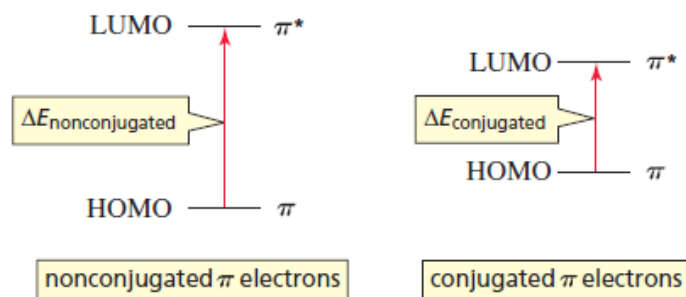
**Figure 3: Effect of conjugation on electronic transition**

Figure 4 shows that as the number of conjugated double bonds increases, the value of $\lambda_{max}$ also increases. The more conjugated double bonds there are in a compound, the less energy is required for the electronic transition, and therefore the longer is the wavelength at which the electronic transition occurs. It is noteworthy that conjugation of two chromophores not only increases the $\lambda$ but also increases the intensity (molar absorptivity). This effect of conjugation can be shown by the spectra of the polyenes $CH_3$-$(CH=CH)_n$-$CH_3$, where n = 3, 4 and 5.
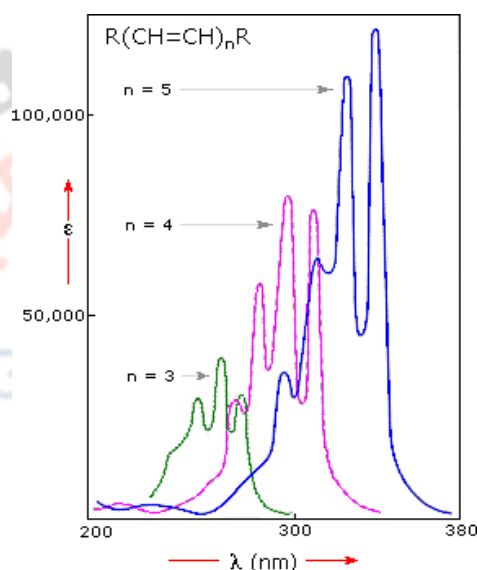


**Figure 4: Electronic transitions in conjugated dienes**

In case of simple alkene (ethylene) we have only two molecular orbitals, one is ground state $\pi$ bonding orbital and the other is excited state $\pi^*$ antibonding orbital. The energy gap between these two is 176 kcal/mol. But in case of conjugated dienes, the $\pi$ molecular orbitals of the two separate C=C groups combine to form two new bonding molecular orbitals designated as $\psi_1$ and $\psi_2$, and two new anti-bonding molecular orbitals designated as $\psi_3^*$ and $\psi_4^*$ (figure 5). It is clear that the transition of lowest energy $\pi$ to $\pi^*$ transition in conjugated system is $\psi_2$ (HOMO) to $\psi_4^*$ (LUMO). Hence we can say that the conjugated dienes absorb at relatively longer wavelength than do isolated alkenes.
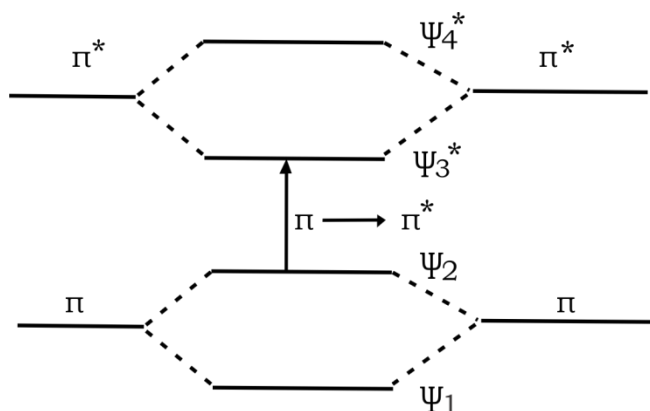
**Figure 5: Energy levels of molecular orbitals in conjugated diene system**

As the number of conjugated double bonds is increased, the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is progressively lowered. Therefore, the increase in size of the conjugated system gradually shifts the absorption maxima ($\lambda_{max}$) to longer wavelength.

If a compound has enough conjugated double bonds, it will absorb visible light and the compound will be colored. The β-carotene, a precursor of vitamin A, has eleven conjugated double bonds (Figure 6) and its absorption maximum gets shifted from ultraviolet to the blue region of the visible spectrum giving it an orange colour.
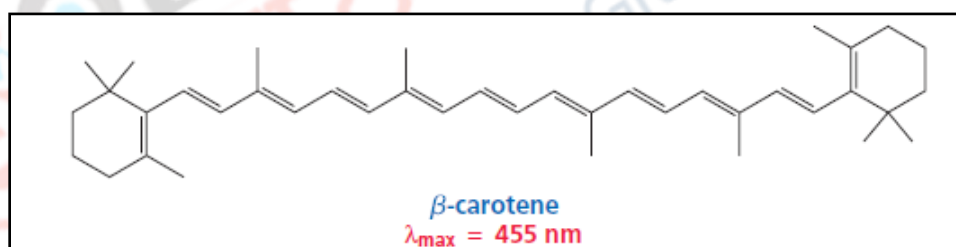


**Figure 6: Extended conjugation in β-carotene**

In a similar fashion, methyl group also produce bathochromic shift. Although methyl group do not have π electron or unshared electrons, it is considered to interact with the π system through its C-H bonding orbitals (hyperconjugation or sigma bond resonance).
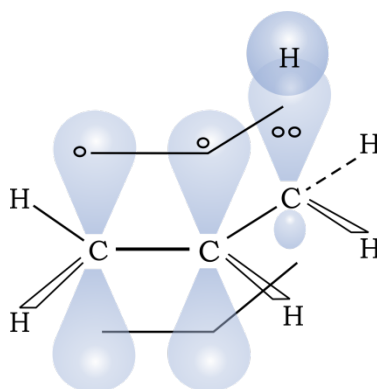
**Figure 7: Extension of π-system by C-H bond through hyperconjugation**

Similarly in case of other conjugated chromophores (conjugation with a hetero atom), the energy difference between HOMO and LUMO is lowered resulting in bathochromic shift.

As discussed above, carbonyl compounds show both π to π* (intense and shorter wavelength) and n to π* (less intense and longer wavelength) transitions. The introduction of polar substituent on the α-carbon of an aliphatic carbonyl do not affect the n to π* transition. But in the case of cyclic ketones, a bathochromic effect is observed. However, this effect is more when the auxochrome is at axial position (10-30 nm) than that when it is present at equatorial position (4-10 nm). Substitution on the carbonyl carbon by an auxochrome with a lone pair of electrons such as amide, acids, esters, acid chloride etc cause the increase in the energy of π* orbital, leaving the n orbital unaffected. As a result, n to π* transition is shifted to shorter wavelength (hypsochromic effect). However, a little bathochromic effect is observed on the transition π to π*. Such bathochromic effects are caused by the resonance interaction between the C=O and lone pair on the other hetero atom.

If the carbonyl group is conjugated with a C-C double bond i.e. α,β-unsaturated carbonyl compounds, both π to π* and n to π* transitions shift to at longer wavelength compared to the un-conjugated carbonyl compounds. However the energy of the n to π* transition does not decrease as rapidly as that of the π to π* band. If the conjugated chain becomes long enough, the n to π* band is buried into the more intense π to π* band system. Figure 8 shows the molecular orbitals of α,β-unsaturated carbonyl system along with the isolated C=C bond and carbonyl group.
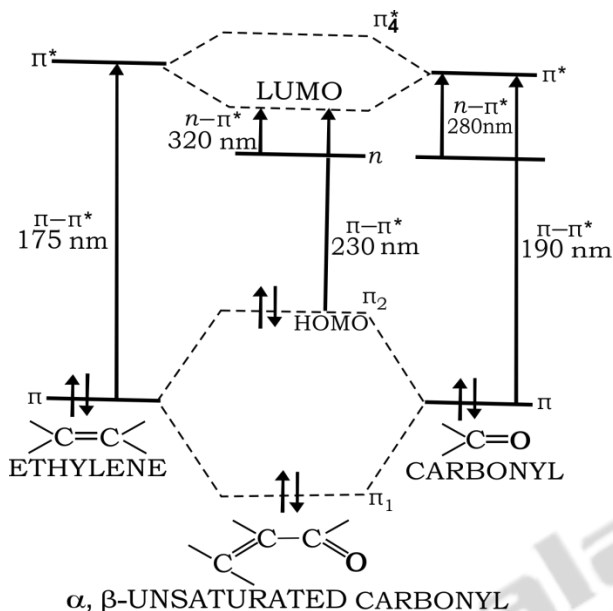
**Figure 8: Electronic transitions in α,β-unsaturated carbonyl compounds**

### 4.2 Effect of Steric hindrance

The UV-spectroscopy is very sensitive to the distortion of the chromophores. We know that the position of absorption maximum and its intensity depend on the length and effectiveness of the conjugative system. Electronic conjugation works best when the molecule is planar in configuration. If the presence of an auxochrome prevents the molecule from being planar then it may lead to the red or blue shifts depending upon the nature of distortion.

For example, the diene I shown below is expected to show absorption maximum at 237 nm (linear 1,3-diene), but distortion of chromophore causes it to absorb at 220 nm. This blue shift is due to the loss of conjugation as the structure is not planar.

Similar trends can also be observed in compounds where geometrical isomerism is possible. It is found that generally the trans-isomers show $\lambda_{max}$ at a longer wavelength and $\varepsilon_{max}$ (molar absorptivity or molar extinction coefficient) is higher than for the cis or mixed isomer. For example the *trans*-stilbene (II) absorbs at longer wavelength with greater intensity ($\lambda_{max}$ = 295 nm, $\varepsilon$ = 27000) than the *cis*-stilbene (III, $\lambda_{max}$ = 280 nm, $\varepsilon$ = 13500) due to steric effects. It is due to the more effective π-π orbital overlapping in the trans-stilbene, which results in achieving coplanarity of π-system more readily than in cis-stilbene. In cis-isomer, due to crowding (bulky groups on the same side of the double bond), planar geometry is distorted.



I      II      III

trans-stilbene      cis-stilbene

Another example of such cases are biphenyl and its 2-methyl and 2,2'-dimethyl analogues. Biphenyl system is not completely planar (two ring being at an angle of $45^0$) and in 2-methyl biphenyl the two rings are pushed even further out of co-planarity resulting in the diminished $\pi$ orbital overlap. As a result, blue shift is observed with less intensity. The biphenyl (IV) has $\lambda_{max}$ at 250 nm ($\mathcal{E}$ = 19000) and 2-methylbiphenyl (V) has $\lambda_{max}$ at 237 nm ($\mathcal{E}$ = 10250).



IV                                                   V

## 4.3 Effect of solvent

The absorption spectrum depends on the solvent in which the absorbing substance is dissolved. The choice of solvent can shift peaks to shorter or longer wavelengths. This depends on the nature of the interaction of the particular solvent with the environment of the chromophore in the molecule under study.

It is usually observed that ethanol solutions give absorption maxima at longer wavelength than hexane solutions. Water and alcohols can form hydrogen bonds which results the shifting of the bands of polar substances. Since polarities of the ground and excited state of a chromophore are different, hence a change in the solvent polarity will stabilize the ground and excited states to different extent causing change in the energy gap between these electronic states. Highly pure, non-polar solvents such as saturated hydrocarbons do not interact with solute molecules either in the ground or excited state and the absorption spectrum of a compound in these solvents is similar to the one in a pure gaseous state. However, polar solvents such as water, alcohols etc may stabilize or destabilize the molecular orbitals of a molecule either in the ground state or in excited state. Therefore, the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

### (i) $\pi$ to $\pi^*$ Transitions

In case of $\pi$ to $\pi^*$ transitions, the excited states are more polar than the ground state. If a polar solvent is used the dipole–dipole interaction reduces the energy of the excited state more than the ground state. Thus a polar solvent decreases the energy of $\pi$ to $\pi^*$ transition and hence the absorption in a polar solvent such as ethanol will be at a longer wavelength (red shift) than in a non-polar solvent such as hexane.

No solvent          Polar solvent
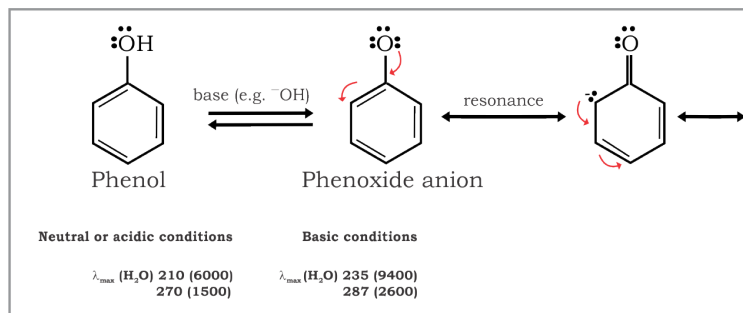interaction         interaction

### (ii) n to π* transitions

In case of n to π* transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Consequently the energy of ground state is decreased which further causes the increase in energy difference between the ground and excited energy levels. Therefore, absorption maxima resulting from n to π* transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity.



No solvent          Polar solvent
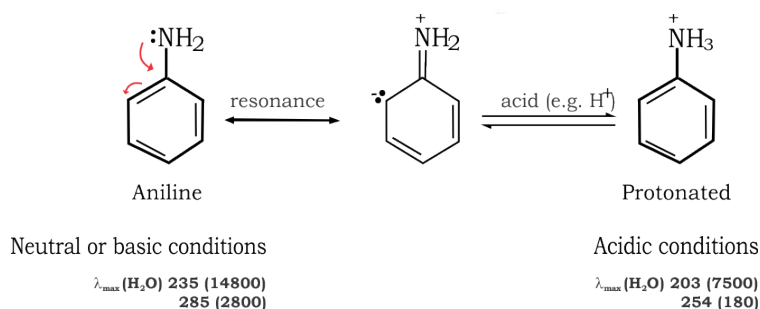interaction         interaction
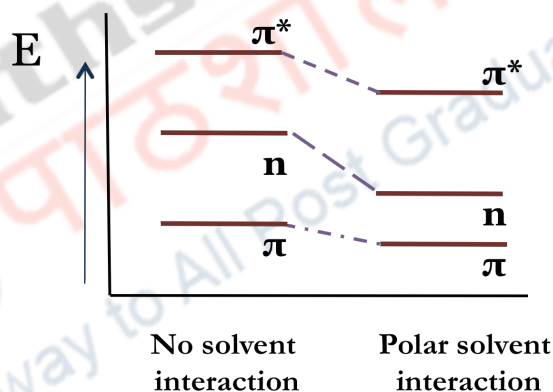
### 4.4 Effect of Sample pH

The pH of the sample solution can also have a significant effect on absorption spectra. The absorption spectra of certain aromatic compounds such as phenols and anilines change on changing the pH of the solution.

Phenols and substituted phenols are acidic and display sudden changes in their absorptions maxima upon the addition of a base. After the removal of the phenolic proton, we get phenoxide ion. In the phenoxide ion lone pairs on the oxygen is delocalized over the π-sytem of the aromatic ring and increases the conjugation of the same. Extended conjugation leads to a decrease in the energy difference between the HOMO and LUMO orbitals, which results in red or bathochromic shift (to longer wavelength), along with an increase in the intensity of the absorption.
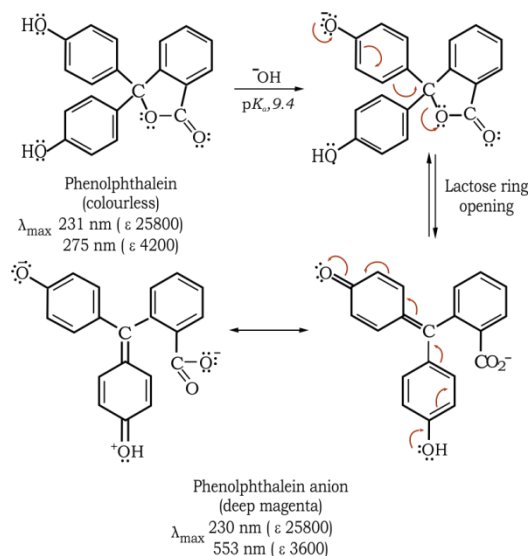
Neutral or acidic conditions     Basic conditions

$\lambda_{max}$ (H$_2$O) 210 (6000)     $\lambda_{max}$ (H$_2$O) 235 (9400)
          270 (1500)                  287 (2600)

Similarly, an aromatic amine gets protonated in an acidic medium which disturb the conjugation between the lone pair on nitrogen atom and the aromatic π-system. As a result, blue shift or hypsochromic shift (to shorter wavelength) is observed along with a decrease in intensity.



Neutral or basic conditions                    Acidic conditions

$\lambda_{max}$ (H$_2$O) 235 (14800)           $\lambda_{max}$ (H$_2$O) 203 (7500)
             285 (2800)                  254 (180)

The acid-base indicators (pH indicators) have their application due to their absorptions in the visible region of the UV-Vis spectrum. A small change in the chemical structure of the indicator molecule can cause a change in the chromophore, which absorb at different $\lambda_{max}$ value in visible spectrum resulting in significant colour change at different pH values.

One such example is phenolphthalein. Phenolphthalein is a weak acid which dissociates in water to give the anion, which results in extension of the negative charge of oxygen atom and leads to a substantial bathochromic shift (to longer wavelength). Thus the anion of phenolphthalein is orange coloured while its non-ionized form is colorless. At acidic and neutral pH, the equilibrium shifts to the left and the concentration of the anions is too low to observe the pink colour. However, under basic conditions, the equilibrium shifts to the right and the concentration of anion increase and we observe the pink colour.

Phenolphthalein
(colourless)
$\lambda_{max}$ 231 nm ( ε 25800)
275 nm ( ε 4200)

Lactose ring
opening

Phenolphthalein anion
(deep magenta)
$\lambda_{max}$ 230 nm ( ε 25800)
553 nm ( ε 3600)

Therefore, UV-Vis spectra of such compounds should be recorded in a suitable buffer solution to maintain the pH at a constant value. The buffer though needs to be transparent over the wavelength range of the measurements. If the buffer absorbs radiation, absorbance readings may be higher than the actual value.

## 5. Effect of temperature and sample concentration on the shape of UV-Visible absorption bands

**5.1 Effect of Sample Temperature**
The effect of temperature is less pronounced. However, simple thermal expansion of the solution may be sufficient to change band intensity. Therefore to get more accurate results the spectrum needs to taken at a specified or constant temperature.

The following three criteria may be given as general effect of temperature on solution spectra.
1. Band sharpness increases with decreasing temperature.
2. Position of absorption maximum does not move or moves very little towards the longer wavelength side, with decreasing temperature.
3. The total absorption intensity is approximately independent of the temperature.
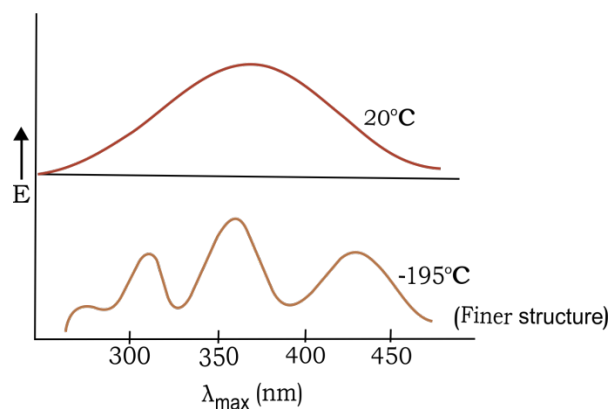


**Figure 10: Effect of temperature on the absorption bands**

We know that the vibrational and rotational states depend on the temperature. As the temperature is decreased, vibrational and rotational energy states of the molecules are also lowered. When, the absorption of light occurs at lower temperature smaller distribution of excited states results, which produces fine absorption bands than that of at high temperature (figure 10). It is also seen that positions of the band maxima do not shift very much with decreasing temperature but tend to move a very little towards the longer wavelength.

### 5.2 Effect of sample Concentration

According to Lambert-Beer law it might be expected that the sample concentration is directly proportional to the intensity of the absorption. But at high concentrations, molecular interactions can take place causing changes to the position and shape of absorption bands. Such effects need to be identified and taken into consideration for quantitative work.

The solvent used also affects the fineness of absorption band in UV-spectrum. It has been observed that polar solvents give rise to broad bands, non-polar solvents show more resolution, while completely removing the solvent gives the best resolution. This is due to solvent-solute interaction. If the dielectric constant of the solvent is high, there will be stronger solute-solvent interaction. For example, a polar solvent like water or ethanol has the ability of hydrogen bonding with the solute if the solute has a hydrogen bonding component, or simply through induced dipole-dipole interactions. The non-polar solvents can also interact though polarizability *via* London interactions but the effect is very less. Depending on the interaction, this can cause the ground state and the excited state of the solute to increase or decrease, thus changing the frequency of the absorbed photon. Due to this, there are many different transition energies that overlap in the spectra and cause the broadening of UV-band.

## 5. Summary

- Chromophore is a functional group which is responsible for the absorption in the UV-Vis region.
- Auxochrome does not absorb itself but increases the value of absorption maxima when covalently attached to chromophore.
- Shifting of the absorption maxima towards longer wavelength is known as red shift, whereas towards shorter wavelength is known as blue shift.
- Hypochromic effect is the decrease in absorption intensity and increase in absorption intensity is called Hyperchromic effect.
- By extending conjugation, the wavelength of absorption is shifted to higher value.
- The position and intensity is greatly affected by the polarity of solvent.
- The temperature, concentration and pH of the sample solution affect the position and shape of UV-Vis absorption bands.
- Recording the spectra at low temperature gives sharp absorption bands, whereas high temperature causes the broadening of UV-bands.
- The change in the pH of the sample solution changes the value of absorption maxima either to higher or lower value.