

# ULTRAVIOLET SPECTROSCOPY

SEM-4, CC-8  
PART-2, PPT-3

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## ULTRAVIOLET SPECTROSCOPY (PART-2, PPT-3)

### Types of Electronic Transitions: $\sigma \rightarrow \sigma^*$ Transition

For molecules, such as alkanes, that contain single bonds and lack atoms with unshared electron pairs, the only electronic transitions possible are of the  $\sigma \rightarrow \sigma^*$  type. These transitions are of such a high energy that they absorb ultraviolet energy at very short wavelengths—shorter than the wavelengths that are experimentally accessible using typical spectrophotometers. **Figure 1** illustrates this type of transition. The excitation of the  $\sigma$ -bonding electron to the  $\sigma^*$ -antibonding orbital is depicted at the right (B).

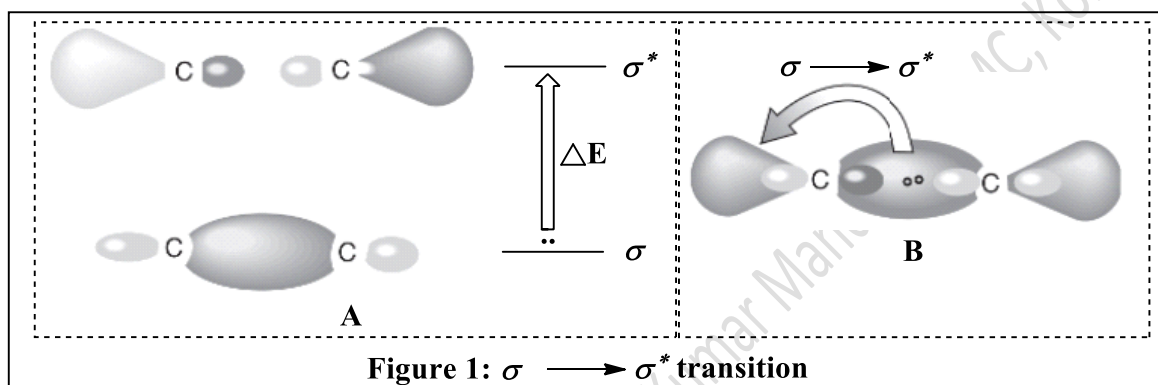


Figure 1:  $\sigma \rightarrow \sigma^*$  transition

The energy required for the  $\sigma \rightarrow \sigma^*$  transition is very high. Consequently, compounds in which all valence shell electrons are involved in single bond formation, such as saturated hydrocarbons do not show absorption in the ordinary UV region. Propane shows  $\lambda_{\text{max}}$  at about 135 nm. An exception is cyclopropane, which shows  $\lambda_{\text{max}}$  at about 190 nm. This is because cyclopropane is under large angle strain and carbon hybridized orbitals are not directed towards one another in the same straight line, and consequently there is a loss of overlap.

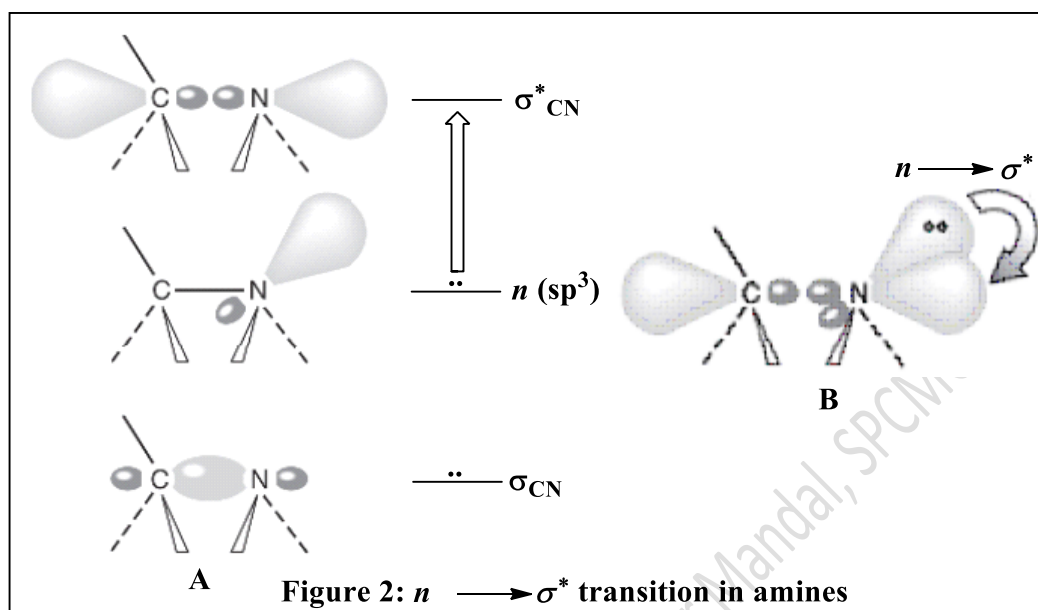
As a result, the C-C bonds in cyclopropane are weaker because of the decreased overlap of the orbitals forming the bonds. Therefore, the energy levels of the *ground state* and first *excited state* are closer together than that of propane. This produces a shift of  $\lambda_{\text{max}}$  towards the longer wavelength region.

### Types of Electronic Transitions: $n \rightarrow \sigma^*$ Transition

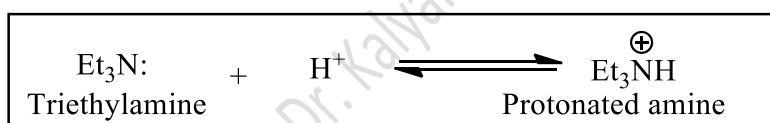
In compounds that contain atoms bearing nonbonding pairs of electrons on oxygen, nitrogen, sulphur and halogen atom, such as in alcohols, ethers, amines, and sulphur compounds, transitions of the  $n \rightarrow \sigma^*$  type become important. Transitions of this type involve the transition of the *non-bonding* electrons (*n*-) of heteroatom to *anti-bonding molecular orbitals*, i.e.,  $\sigma^*$ . They are also rather high-energy transitions, and these transitions are of lower energy than  $\sigma \rightarrow \sigma^*$  transition.

Alcohols and amines absorb in the range from 175 to 200 nm, while organic thiols and sulphides absorb between 200 and 220 nm in non-polar solvents. However,  $\lambda_{\text{max}}$  of  $n \rightarrow \sigma^*$  transition in  $\text{CH}_3\text{OH}$  appears at 183 nm whereas that of  $\text{NMe}_3$  is at 227 nm in vapour phase.

**Figure 2** illustrates an  $n \rightarrow \sigma^*$  transition for an amine. The excitation of the nonbonding electron ( $n$ -) to the antibonding orbital ( $\sigma^*$ ) is shown at the right (**B**). With increasing polarizability of the heteroatom, the absorption maximum moves to longer wavelengths.



In aqueous acidic medium, trialkylamine ( $\text{NR}_3$ ) shows no transition due to a  $n \rightarrow \sigma^*$  transition as the protonated amine ( $\text{R}_3\text{N}^+\text{H}$ ) contains no  $n$ -electrons.

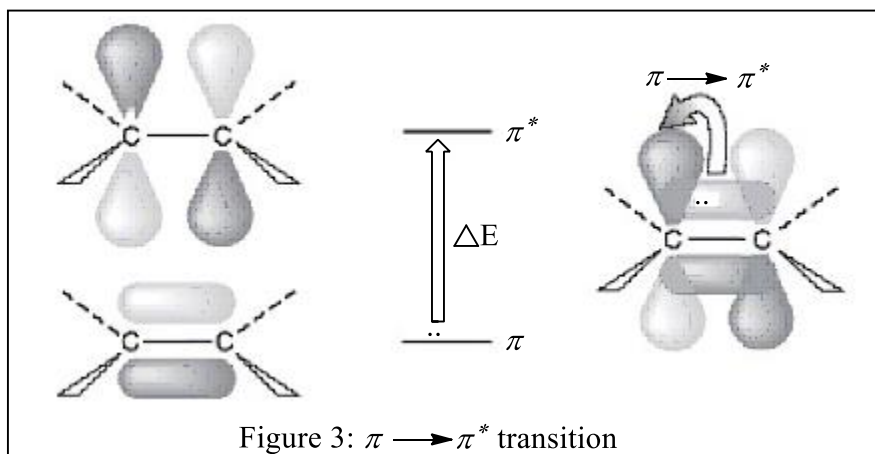


## END TRANSITION

Whether an organic compound contains a particular spectral pattern above 210 nm or not, it will quite generally show some absorption that increases in intensity towards shorter wavelength in this region. The  $n \rightarrow \sigma^*$  transition near 200 nm in UV region due to presence of O, S, N or halogens in an organic compound is called *end absorption*. It is so called as it appears at one end of UV spectrum.

## Types of Electronic Transitions: $\pi \rightarrow \pi^*$ Transition

With unsaturated molecules such as in alkenes, alkynes, carbonyl compounds, etc.,  $\pi \rightarrow \pi^*$  transitions become possible. These transitions are of rather high energy as well, but their positions are sensitive to the presence of substitution directly attached to the unsaturated systems. Alkenes absorb around 165 nm, and alkynes absorb around 170 nm. Figure 3 shows this type of transition.



Absorption of this type is due to the  $\pi$ -electrons absorbing energy and moving from a *bonding molecular orbital* ( $\pi$ -orbital) to an *anti-bonding molecular orbital* ( $\pi^*$ -orbital).  $\pi \rightarrow \pi^*$  transitions (*K*-bands, *German Konjugierte*) are observed for molecules having conjugated  $\pi$ -systems such as butadiene or mesityl oxide. This transition represents the transition of a *bonding  $\pi$ -electron* to an *anti-bonding  $\pi$ -orbital* (i.e.,  $\pi^*$ ). This is a symmetry allowed transition. Thus,  $\pi \rightarrow \pi^*$  transitions are usually characterized by high  $\epsilon_{max}$ ,  $\epsilon_{max} > 10^4$ . The  $\pi \rightarrow \pi^*$  transitions show a red shift with substitution by either electron donating or withdrawing groups and with an increase in the dielectric constant of the solvent. In both cases this may be ascribed to stabilization of the polar *excited state*.

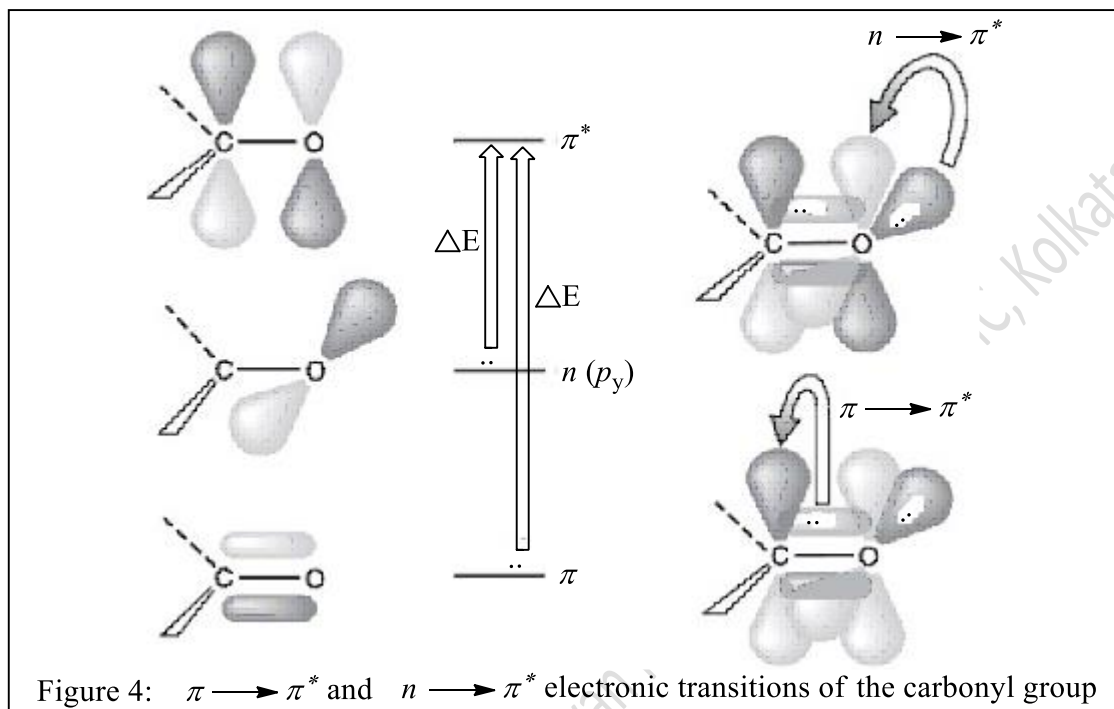
Transitions of this type involve the transition of the *non-bonding* electrons of heteroatoms to vacant *anti-bonding  $\pi^*$ -molecular orbitals*. These absorptions occur at long wavelengths and are of low intensity. These transitions require lowest energy than other transitions, namely  $\sigma \rightarrow \sigma^*$ ,  $n \rightarrow \sigma^*$ , and  $\pi \rightarrow \pi^*$ . This transition is symmetry *forbidden*, low  $\epsilon_{max}$ , less than 100. The  $n \rightarrow \pi^*$  transition shows a hypsochromic (blue) shift in more polar solvents and with electron donating substituents.

$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H}_3\text{C} \\ \text{Acetone} \end{array}$	$\pi \rightarrow \pi^*$	$\lambda$ 166 nm, $\epsilon_{max}$ 16000, Vapour
	$n \rightarrow \sigma^*$	$\lambda$ 188 nm, $\epsilon_{max}$ 900, Hexane
	$n \rightarrow \pi^*$	$\lambda$ 279 nm, $\epsilon_{max}$ 15, Hexane

### $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions in Carbonyl Compounds

The carbonyl group contains, in addition to a pair of  $\sigma$  electrons, a pair of  $\pi$  electrons and two pairs of nonbonding ( $n$ ) electrons. Saturated ketones and aldehydes display three absorption bands, two of which are observed in the far-UV region. A  $\pi \rightarrow \pi^*$  transition absorbs strongly near 150 nm; an  $n \rightarrow \sigma^*$  transition absorbs near 190 nm. The third band (*R*-band) appears in the near UV in the 270-300 nm characterized as a  $n \rightarrow \pi^*$  transition.

The  $R$ -band ( $n \rightarrow \pi^*$ ) is weak ( $\epsilon_{\max} < 30$ ) and results from the forbidden transition of a loosely held  $n$  electron to the  $\pi^*$  orbital, the lowest unoccupied orbital of the carbonyl group. Therefore, most  $n \rightarrow \pi^*$  transitions are of low intensity. Figure 4 shows the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of the carbonyl group.



### $n \rightarrow \pi^*$ Transition: A Forbidden Transition

This band is relatively weak band which means that the transition is a *forbidden* transition. This is a symmetry *forbidden* transition. The reasons for the forbiddenness can be justified by the fact that the  $\pi^*$  orbital, like the  $\pi$ -orbital, is in the  $xz$  plane, while the  $p_y$  orbital containing the  $n$ -electrons is in the  $yz$  plane and hence perpendicular to the  $\pi^*$  orbital. Since the regions in space of the two orbitals overlap so poorly, the likelihood of the transition from one to the other is quite low.

The fact that it occurs at all is probably due to the vibrations of the atoms which include some twisting which in turn increases overlap. Thus, although the symmetry selection rule predicts zero intensity, vibrational interaction makes the transition partially allowed.

### Carbonyl Chromophores

Electronic transitions result in a redistribution of electrons within the molecule. In the *ground state* the structure of the carbonyl group ( $>C=O$ ) contains an important contribution from the polar form  $>C^+-O^-$ . The position of an absorption that involves nonbonding electrons ( $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$ ) is particularly sensitive to the polarity of the solvent used in the determination.

If the group is more polar in the *ground state* than in the *excited state*, the nonbonding electrons in the *ground state* are stabilized (relative to the *excited state*) by hydrogen bonding or electrostatic interaction with a polar solvent. In this case, the absorption is shifted to shorter wavelength (higher energy) with increasing polarity of the solvent.

Conversely, if the group is more polar in the *excited state* than in the *ground state*, the nonbonding electrons of the *excited state* are stabilized (relative to the *ground state*) by interaction with a polar solvent. In this situation, the absorption is shifted to longer wavelength (lower energy) with increasing solvent polarity. Polar solvents generally shift the  $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$  bands to shorter wavelength and the  $\pi \rightarrow \pi^*$  bands to longer wavelength.

The  $\alpha,\beta$ -unsaturated ketone mesityl oxide (4-methyl-3-penten-2-one) shows  $\lambda_{\max}$  230 nm,  $\epsilon_{\max}$  12600 and  $\lambda_{\max}$  329 nm,  $\epsilon_{\max}$  41 in hexane and  $\lambda_{\max}$  243 nm,  $\epsilon_{\max}$  10000 and  $\lambda_{\max}$  305 nm,  $\epsilon_{\max}$  60 in water. This data indicates that the long wavelength  $n \rightarrow \pi^*$  absorption is shifted 24 nm to shorter wavelength (higher energy) in the more polar solvent. Thus, it can be said that the *ground state* would appear to be more polar than the *excited state*.

The *excited state* of the  $n \rightarrow \pi^*$  transition of ketones seems to have major contributions from structures such as  $>C=O$  and  $>C^--O^+$  rather than  $>C^+-O^-$  as in the *ground state*. The shift to longer wavelength (lower energy) observed in the  $\pi \rightarrow \pi^*$  transitions of  $\alpha,\beta$ -unsaturated ketones (13 nm for mesityl oxide) with increasing solvent polarity indicates that the *excited state* in this transition is more polar than the *ground state*. For this transition the data can be interpreted as the promotion of an ethylenic  $\pi$  electron to a carbonyl  $\pi^*$  orbital. Because intramolecular effects such as these involve the transfer of charge from one atom to another, they are frequently called *charge transfer spectra*.

## Chromophores

The system containing electrons responsible for absorption is called chromophore. A *chromophore* is the part of a molecule responsible for its colour. The part (atom or group of atoms) of a molecular entity in which the electronic transition responsible for a given spectral band is approximately localized.

The chromophore is a region in the molecule where the energy difference between two separate molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its *ground state* into an *excited state*. Originally, the term *chromophore* was applied to the system responsible for imparting colour to a compound. The term is derived from the *Greek chromophoros*, or *color carrier*.

In azo dyes the aryl conjugated azo group (Ar-N=N-Ar) is clearly the principal chromophore. In nitro compounds the yellow color is carried by  $-NO_2$ , etc. The term has been retained within an extended interpretation to imply *any functional group that absorbs electromagnetic radiation, whether or not a 'colour' is thereby produced*. Thus, the carbonyl group is a chromophore in both ultraviolet and infrared terms, even though one isolated C=O group is insufficiently powerful to impart colour to a compound. An isolated carbonyl group, as in

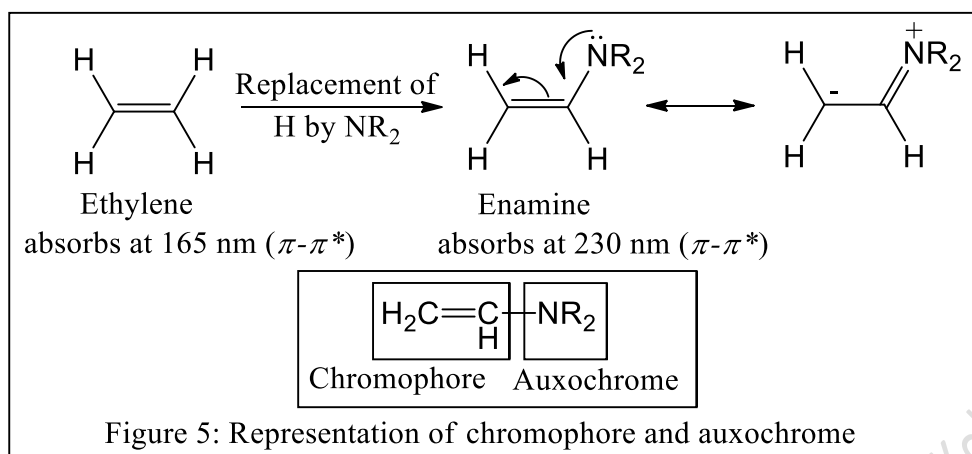
acetone, absorbs ultraviolet light around 280 nm. Important examples of organic chromophores are listed in Table 1.

Table 1: Simple Organic Chromophores		
Chromophore	Wavelength ( $\lambda_{\text{max}}$ /nm)	Intensity ( $\epsilon_{\text{max}}/10^2\text{m}^2\text{mol}^{-1}$ )
C=C	165-175	14000
C $\equiv$ C	170-175	10000
	195	2000
	223	150
C=O	160	18000
	185	5000
	280	15
R-NO <sub>2</sub>	200	5000
	274	15
C $\equiv$ N	165	5
C=C-C=C	217	20000
C=C-C=O	220	10000
	315	30
C=C-C $\equiv$ C	220	7500
	230	7500
Benzene	184	60000
	204	7400
	255	204

### Auxochrome

*Auxochrome* is substituent on a chromophore which shifts the absorption towards longer wavelength. An *auxochrome* is a functional group of atoms attached to the chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of the absorption. An *auxochrome* enhances the color-imparting properties of a *chromophore* without being itself a *chromophore*. The synergist effect of *auxochromes* is coupled with their ability to extend the conjugation of a chromophore by sharing of the nonbonding electrons.

Substituents that increase the intensity of the absorption, and the wavelength, are the *auxochromes*. Typical *auxochromes* include methyl, hydroxyl, alkoxy, halogen, and amino groups. The attachment of substituent groups in place of hydrogen on a basic *chromophore* structure changes the position and intensity of an absorption band of the *chromophore*. The substituent groups may not give rise to the absorption of the ultraviolet radiation themselves, but their presence modifies the absorption of the principal *chromophore*. Figure 5 illustrates the terms.

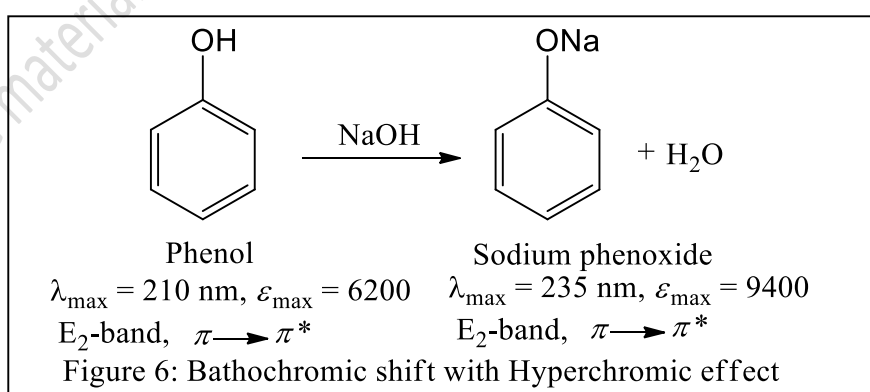


### Bathochromic Shift or Red Shift

The shift of a spectral band (absorption maxima) to longer wavelengths (lower frequencies) owing to the influence of substitution or a change in environment is called *Bathochromic shift* (from *Greek bathys*, “deep”; and *chrōma*, “color”). It is commonly referred to as a *red shift*. This is because the red colour in the visible spectrum has a longer wavelength than most other colours.

This shift towards longer wavelength is due to the presence of chromophore which increases conjugation. When this occurs, the energy separation between the *ground* and *excited states* is reduced and the system absorbs at longer wavelengths and with a greatly increased intensity. A shift to the longer wavelength of absorption (bathochromic shift) is observed when an aqueous solution of phenol is made alkaline.

In alkaline medium phenol is deprotonated and forms the corresponding anion, the phenoxide ion. Here the negative charge on oxygen atom is delocalized over the benzene ring and consequently the anion gets stabilized more relative to the neutral molecule due to mesomeric effect (Figure 6).

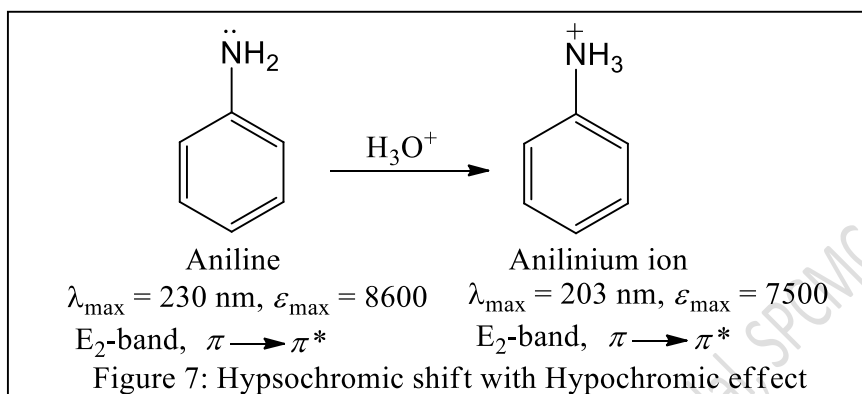


When an aqueous solution of *p*-nitrophenol is made alkaline, the solution turns yellow/orange due to increased conjugation.



## Hypsochromic Shift or Blue Shift

The shift of a spectral band (absorption maxima) to higher frequency or shorter wavelength upon substitution or change in medium is called hypsochromic shift. This is due to the removal of conjugation. It is commonly referred to as blue shift. This is because the blue colour in the visible spectrum has a shorter wavelength than most other colours.



## Hyperchromic and Hypochromic Effects

The increase in the intensity of a spectral band due to substituents or interactions with the molecular environment is described as hyperchromic effect. *Hyperchromicity* is the material's increasing ability to absorb light. It is the increase of absorbance (*optical density*) of a material.

The decrease in the intensity of a spectral band due to substituents or interactions with the molecular environment is described as hypochromic effect. *Hypochromicity* describes a material's decreasing ability to absorb light. It is the decrease of absorbance (*optical density*) of a material. Different type of shifts and effects are shown in Figure 8.

