

## ULTRAVIOLET SPECTROSCOPY

Absorption Spectroscopy measures the absorption of electromagnetic radiation e.g. UV (200 - 400 nm) / Visible (400 - 800 nm) Spectroscopy. UV spectroscopy is the study of absorption of ultra violet radiation (range 200 - 400nm). The plotting of UV spectra is done by recording wavelength  $\lambda$  in nm (horizontal axis) versus absorbance  $\log \epsilon$  (vertical axis). It measures the intensity of the transmitted light after passing through a sample ( $I$ ), and compares it to the intensity of incident light ( $I_0$ ).

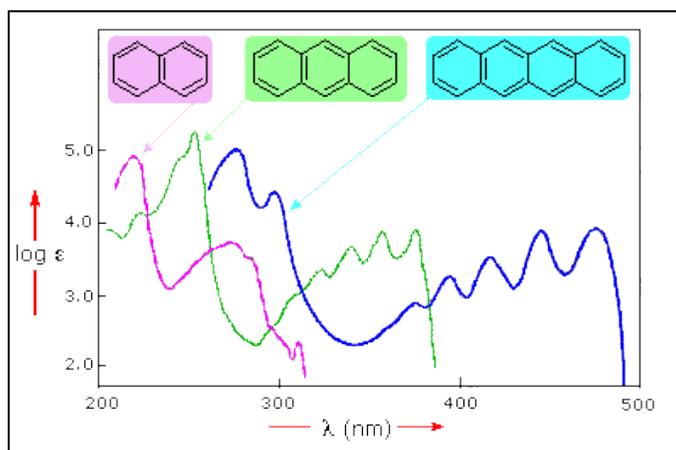
Absorbance (A) of a solution is:  $A = \log (I_0 / I)$

According to the Beer-Lambert law:  $A = \epsilon cl$

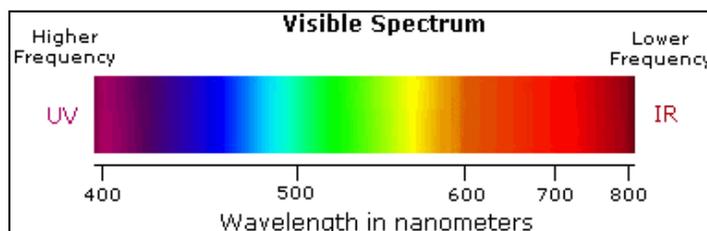
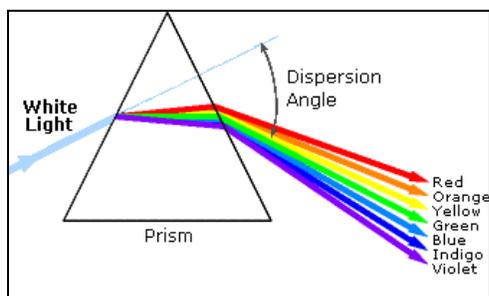
$\epsilon$  = molar extinction coefficient of the sample

$c$  = concentration of the sample

$l$  = path length of the light path through the sample



Far UV Region is below 200 nm (studied under vacuum condition).



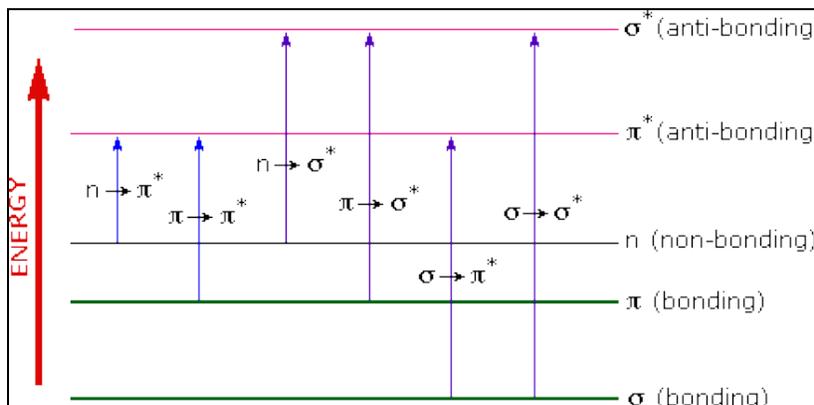
Transition of electron occurs from the occupied bonding ( $\sigma$  or  $\pi$ ) or non-bonding ( $n$ ) molecular orbital of lower energy in the ground state to unoccupied ( $\sigma^*$  or  $\pi^*$ ) antibonding molecular

orbital of higher energy in the excited state. Different kinds of electronic transitions in UV regions are:  $\pi \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ ,  $n \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$ .

Energy order for various transitions are:  $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

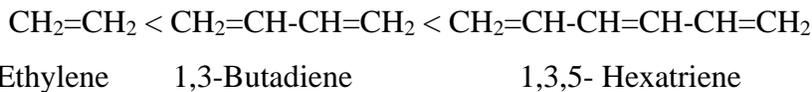
$$\lambda = hc / \Delta E$$

Greater the energy difference ( $\Delta E$ ) between two energy states the shorter is the wavelength ( $\lambda$ ) of light absorbed and vice versa. [ $h$  = Planck constant,  $c$  = velocity of light]

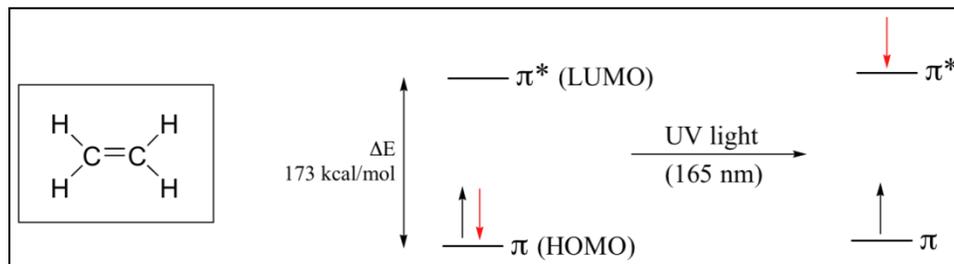


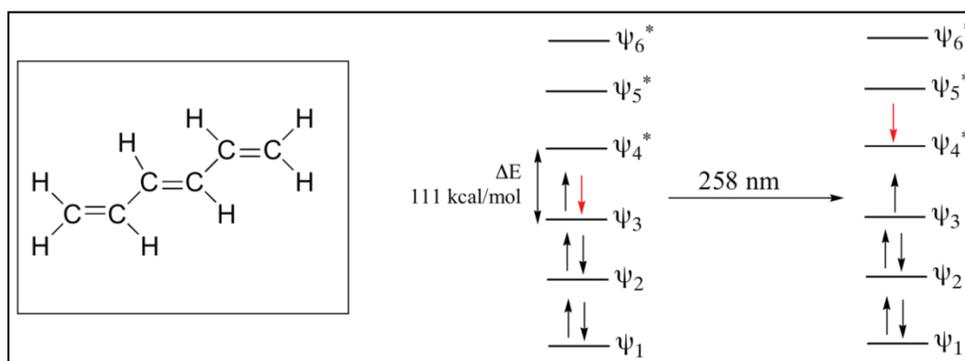
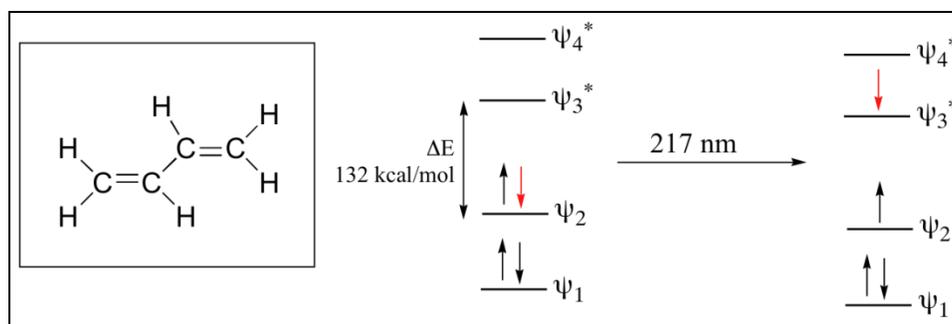
$\pi \rightarrow \pi^*$  transition:

As the conjugation increases, the energy requires to promote an electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital requires lower energy. So wavelength increases in the order:



$\lambda_{\text{max}} (\pi \rightarrow \pi^*)$     165 nm            217 nm            258 nm





Non-conjugated alkenes  $\rightarrow$  intense absorption below 200 nm. Conjugation in a compound shifts the  $\lambda_{\max}$  to longer wavelength. e.g. 1,5-hexadiene has  $\lambda_{\max} = 178$  nm 2,4-hexadiene has  $\lambda_{\max} = 227$  nm. Non-conjugated carbonyl group compound  $\rightarrow$  weak absorption band in the 200 - 300 nm region. Conjugation of C=C and carbonyl group shifts the  $\lambda_{\max}$  of both groups to longer wavelength. e.g. Ethylene has  $\lambda_{\max} = 171$  nm Acetone has  $\lambda_{\max} = 279$  nm. Crotonaldehyde ( $\text{CH}_3\text{-CH=CH-CH=O}$ ) has  $\lambda_{\max} = 290$  nm

**Chromophore** is covalently bonded chemical group that absorbs light at a specific frequency and imparts colour to a molecule. Chromophoric groups (acids, esters) exhibits characteristic absorption in the visible or ultraviolet region. Examples are  $-\text{NO}_2$ ,  $-\text{N=O}$ ,  $-\text{C=O}$ ,  $-\text{C=N}$ ,  $-\text{C}\equiv\text{N}$ ,  $\text{C=C}$  etc.

Chromophores which contains both  $\pi$  electrons and  $n$  (non-bonding) electrons undergo two types of transitions i.e.,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ .

Chromophore	Example	Excitation	$\lambda_{\max}$ (nm)	$\epsilon$	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	Hexane
C $\equiv$ C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	Hexane
C=O	Ethanal	$n \rightarrow \pi^*$	290	15	Hexane
		$\pi \rightarrow \pi^*$	180	10,000	Hexane

N=O	Nitromethane	$n \rightarrow \pi^*$	275	17	Ethanol	
		$\pi \rightarrow \pi^*$	200	5,000	ethanol	
C-X	X=Br	Methyl Bromide	$n \rightarrow \sigma^*$	205	200	hexane
	X=I	Methyl Iodide	$n \rightarrow \sigma^*$	255	360	hexane

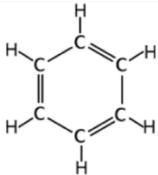
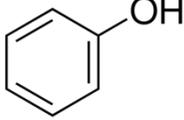
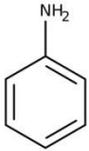
i) Spectrum consisting of a band near 300 nm may contain two or three conjugated units.

ii) Absorption bands near 270-350 nm with very low intensity  $\epsilon_{\max}$  10-100 are due to  $n \rightarrow \pi^*$  transitions of the carbonyl group.

iii) Simple conjugated chromophores such as dienes or  $\alpha, \beta$ -unsaturated ketones have high  $\epsilon_{\max}$  values, i.e., 10,000 to 20,000.

iv) The absorption with  $\epsilon_{\max}$  values between 1000-10,000 shows an aromatic system.

Auxochrome (usually the saturated group with non-bonding electrons) attached to chromophore alters both wavelength (shift of the absorption band towards the red end of the spectrum i.e. longer wavelength) and increasing intensity of absorption. Auxochrome is color enhancing group. Auxochrome extends the conjugation of a chromophore by sharing its non-bonding electrons. Newer Chromophore = Chromophore + Auxochrome. Example: -OH, -NH<sub>2</sub>, -CN, -Cl, -COOH, -NHR etc.

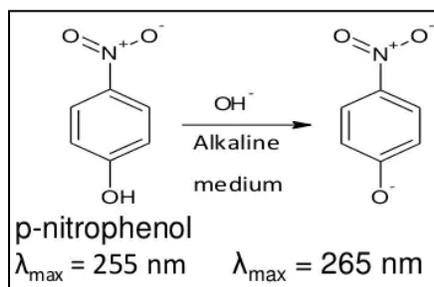
Molecule			
	Benzene	Phenol	Aniline
$\lambda_{\max}$	255 nm	270 nm	280 nm

Nature of Shift	Descriptive Term
The shift of a band to lower energy or longer wavelength	Bathochromic (red shift)
The shift of a band to higher energy or shorter wavelength	Hypsochromic (blue shift)
An increase in the molar absorptivity (to Greater Absorbance)	Hyperchromic effect
A decrease in the molar absorptivity (to Lower Absorbance)	Hypochromic effect

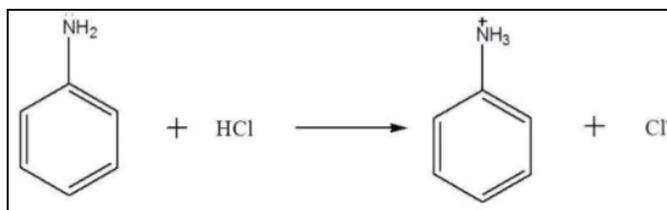
**Bathochromic shift (Red shift):** When the absorption maximum ( $\lambda_{\max}$ ) of compound shifts to a longer wavelength it is known as red shift. The effect is due to the changing the nature of the solvent (polarity), pH of the medium, structure of the substrate or presence of auxochrome.

Example: i) The  $\pi$ - $\pi^*$  transition for  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds experience bathochromic shift when the polarity of solvent is increased.

ii) pH of the medium: The absorption maxima ( $\lambda_{\max}$ ) of *p*-Nitrophenol changes in alkaline medium from 255 nm to 265 nm.



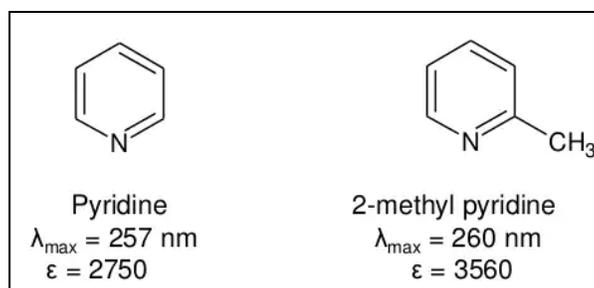
**Hypsochromic shift (Blue shift):** It is an effect due to which the absorption maximum is shifted towards a shorter wavelength i.e. towards the blue end of the spectrum. The effect is due to the removal of conjugation (auxochrome) or by the change of polarity of the solvent. In aniline, the absorption maximum occurs at 280 nm as the pair of electrons on the nitrogen atom is in conjugation with the  $\pi$  bond system of the benzene ring but in acidic solutions, a blue shift occurs at a shorter wavelength (~203 nm). The nitrogen atom of aniline is protonated in an acidic solution, the electron pair is no longer present and hence conjugation is removed.



**Hyperchromic shift/effect:** The increase in the intensity of absorption ( $\epsilon_{\max}$ ) caused by changing the nature of the solvent, pH of the medium, structure of the substrate is known as Hyperchromic shift.

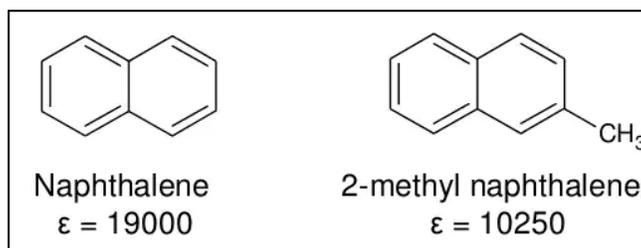
For example, Pyridine shows  $\lambda_{\max} = 257 \text{ nm}$  ( $\epsilon_{\max} 2750$ )

2-Methylpyridine shows  $\lambda_{\max} = 260 \text{ nm}$  ( $\epsilon_{\max} 3560$ ).

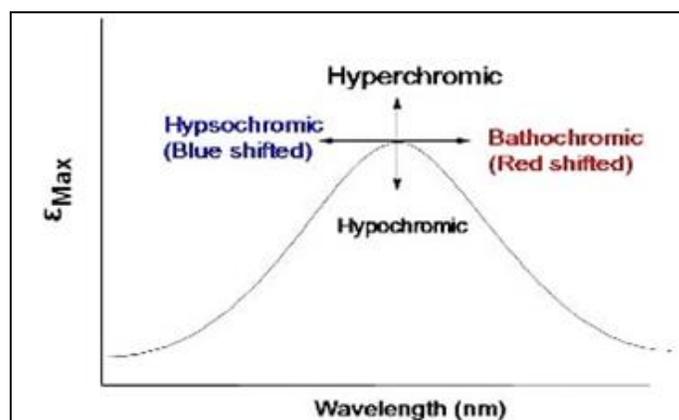


**Hypochromic effect:** The decrease in intensity of absorption ( $\epsilon_{\text{max}}$ ) caused by changing the nature of the solvent, removal of conjugation, pH of the medium, structure of the substrate is known as Hypochromic effect.

Example: Naphthalene absorbs at 250 nm ( $\epsilon_{\text{max}}$  19000) whereas 2-Methylnaphthalene absorbs at 237 nm, ( $\epsilon_{\text{max}}$  10250),  $\epsilon_{\text{max}}$  decreases.



All the four above mentioned effects of Absorption and intensity shifts are summarized below.



#### Absorption and intensity shifts

**Applications:** Qualitative & Quantitative Analysis, characterizing aromatic compounds and conjugated olefins. Useful to find out the molar concentration of the solute. This method is used to detect isomers and impurities in organic solvents. This method is useful to determine molecular weight using Beer's law.

