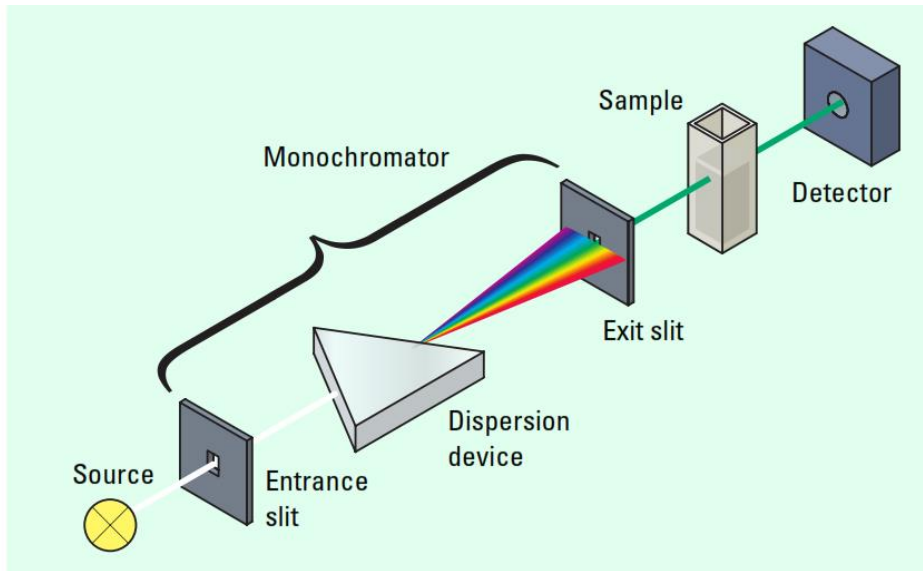


SPECTROMETER DESIGN

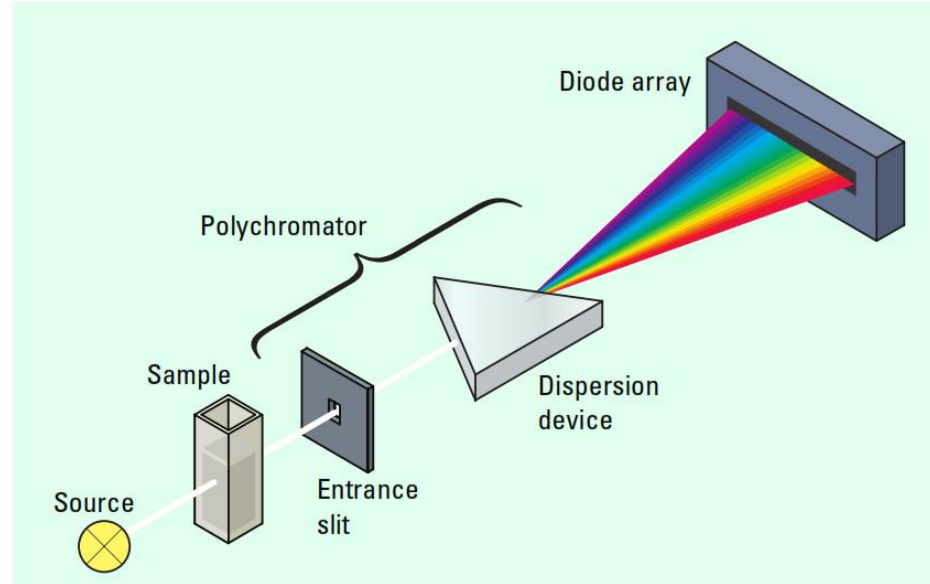


Conventional Spectrometer

Polychromatic source of light falls on an **entrance slit** which transmits a **narrow band** of light.

The light then pass through the **sample** to a detector.

The detector measures the **absorbance** of the sample **by comparing the light that reaches the detector from the sample and the blank (only solvent)**

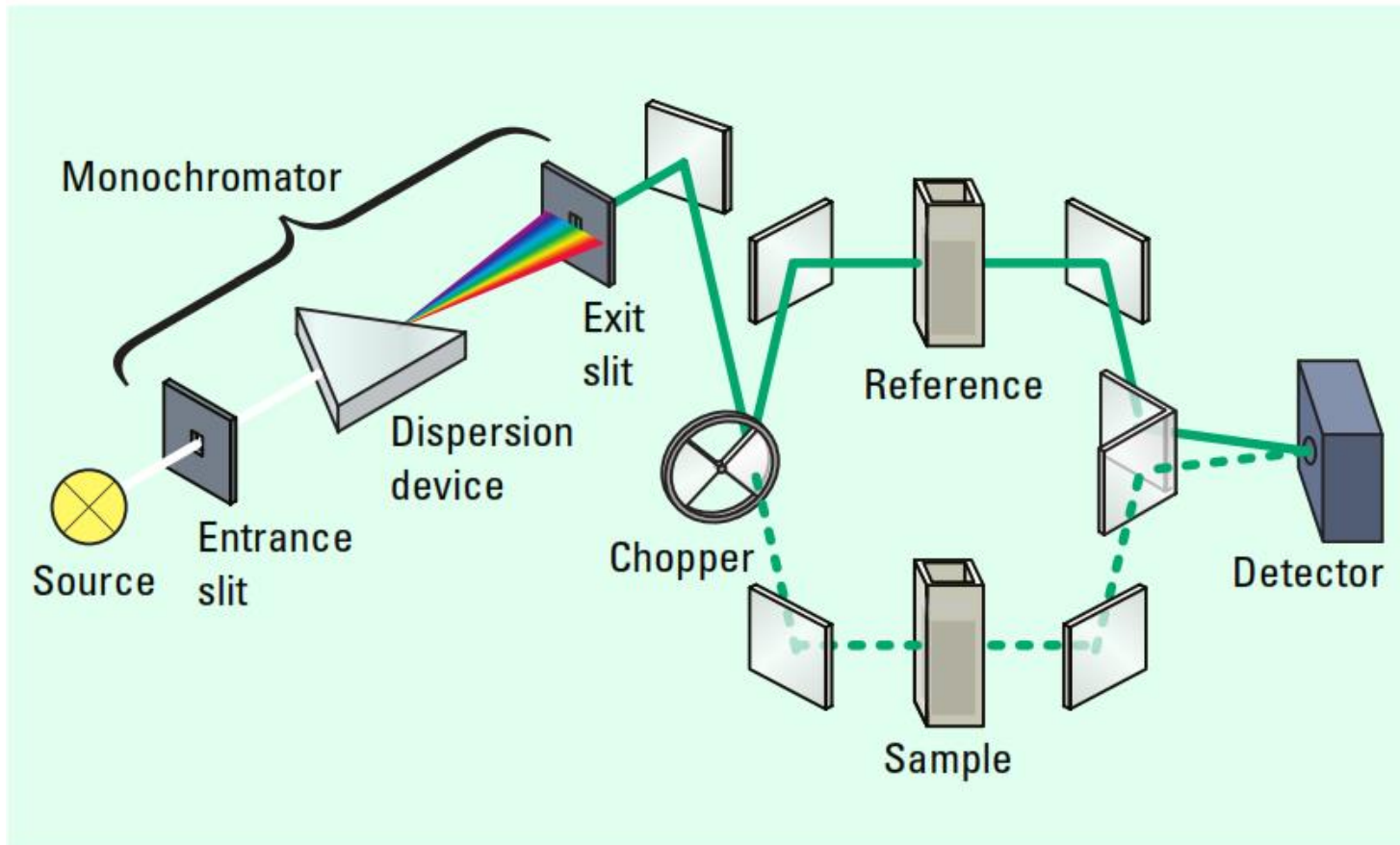


Diode array Spectrometer

Polychromatic source of light falls on a the sample, the transmitted radiation pass through an **entrance slit** of the dispersion device.

The detector measures the **absorbance** of the sample **by comparing the light that reaches the detector from the sample and the blank (only solvent)**

DUAL BEAM SPECTROMETER



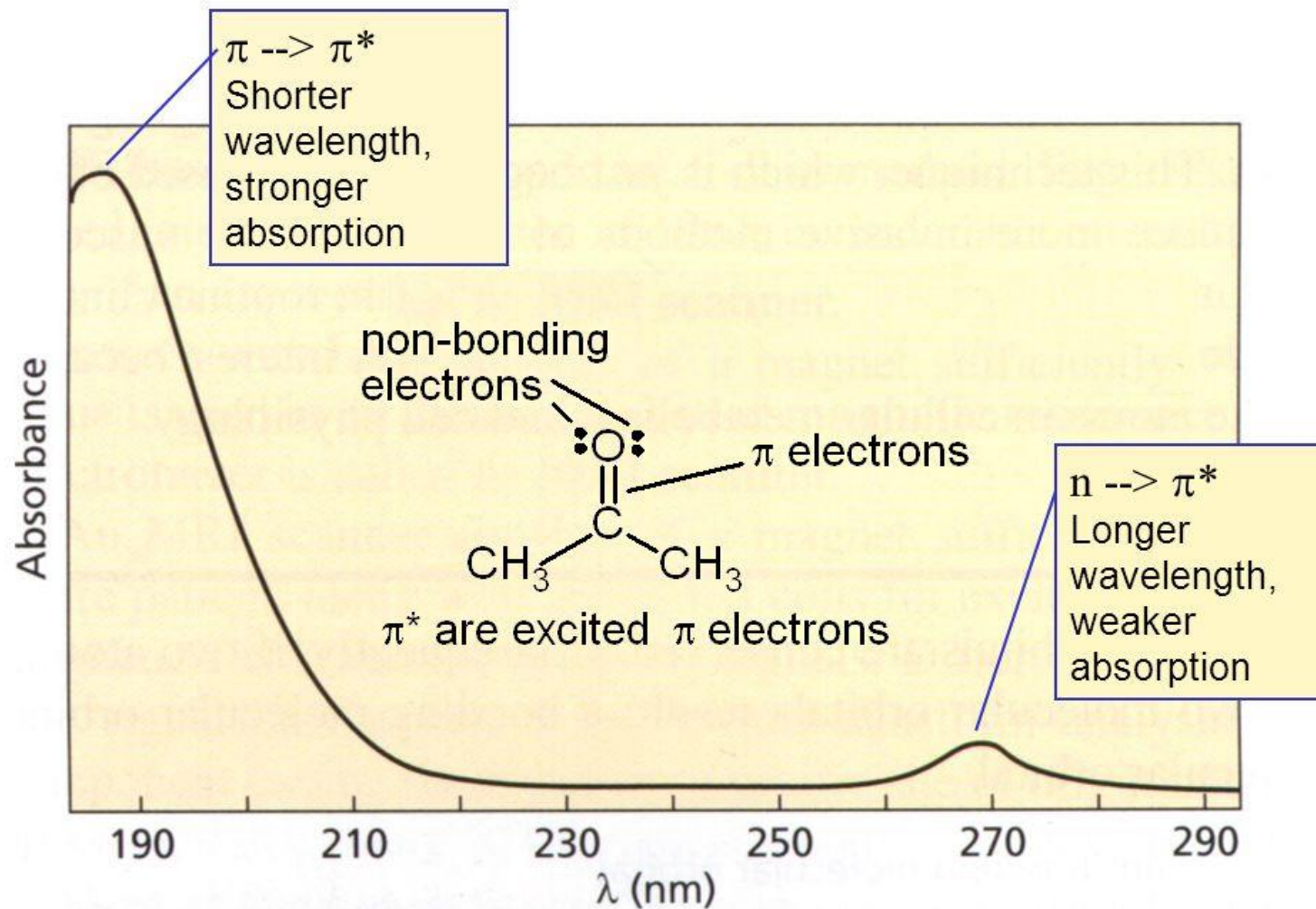
Principle of UV-Visible spectroscopy

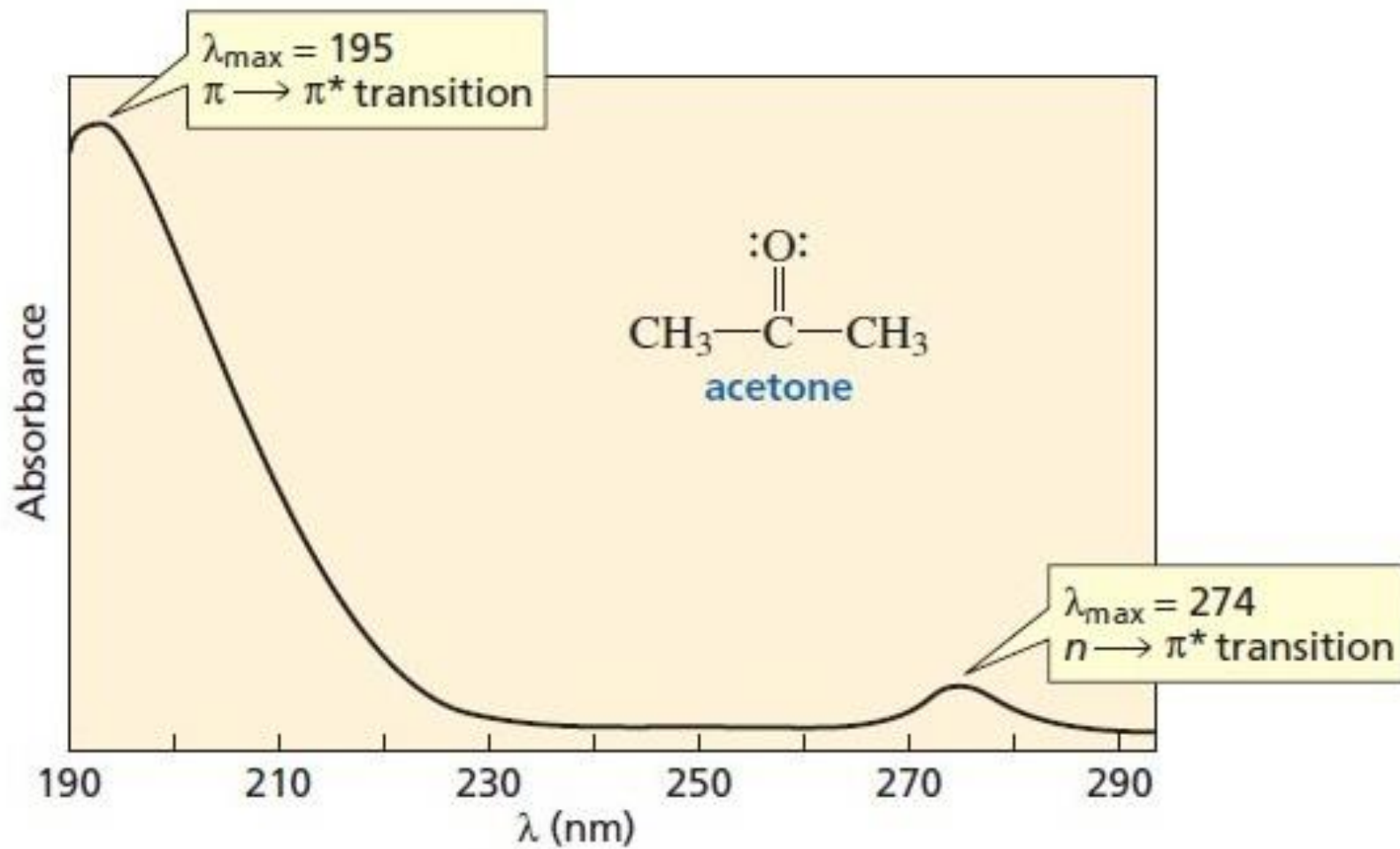
- **Beer-Lambert's law**

$$A = \epsilon c l$$

- A = Absorbance of the sample = $\log_{10}(I_0/I)$
- I = Intensity of the radiation emerging from the sample
- I_0 = Intensity of the radiation incident on the sample
- ϵ = extinction coefficient or molar absorptivity in $M^{-1}cm^{-1}$
- c = concentration of the sample in moles/litr
- l = length of the light path through the sample in cm

UV/Vis of Acetone

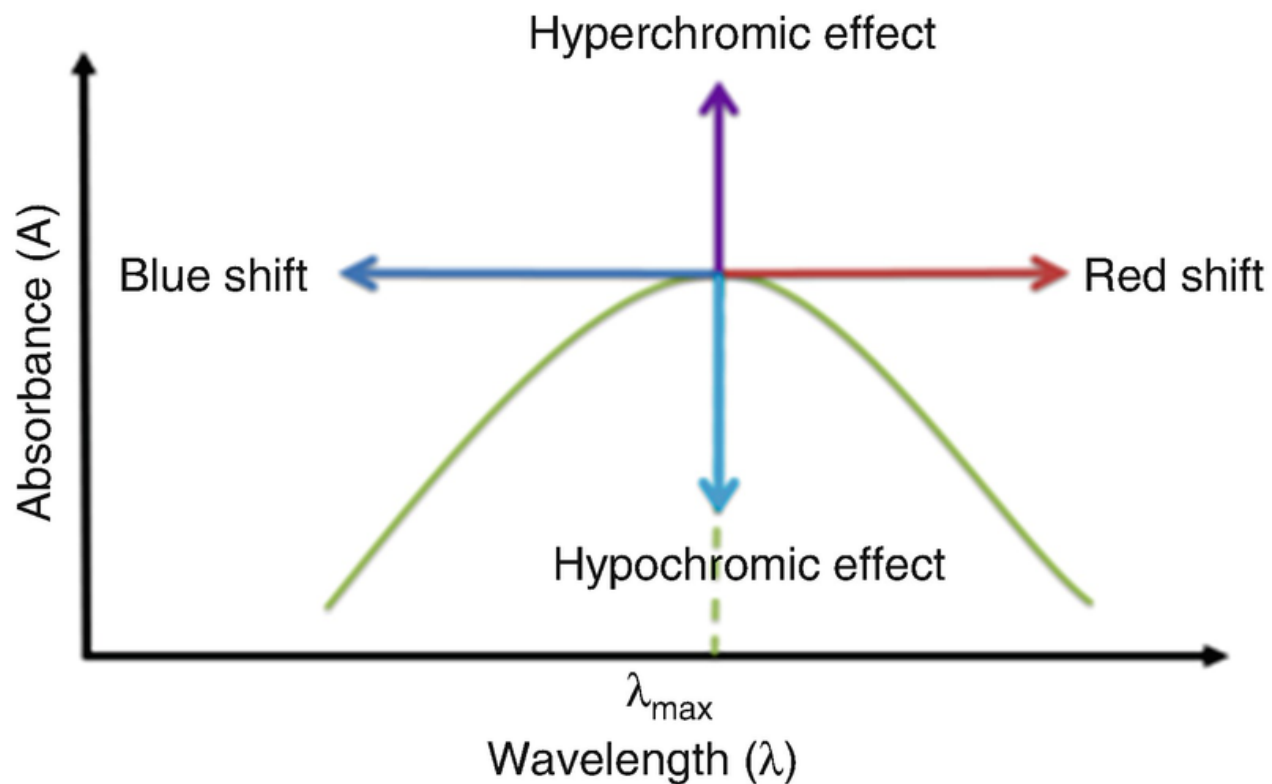




Applications of UV-Vis spectroscopy

Terminology

- **Chromophore:** The **group of atoms** producing an **absorption** is called a 'Chromophore'. Eg. **C=O**, **C=C** etc.
- **Auxochrome:** Groups that helps in **extending the conjugation** by means of the **lone pairs** present. Eg. **NH₂**, **OH**, **OR**, **Cl**, **Br** etc.
- **Hypsochromic shift:** When the λ_{max} of an absorption shift to **shorter** wavelength
- **Bathochromic shift:** When the λ_{max} of an absorption shift to **longer** wavelength.
- **Hyperchromic shift:** When the **absorbance intensity** of λ_{max} shift to **higher** values
- **Hypochromic shift:** When the **absorbance intensity** of λ_{max} shift to **lower** values



Descriptive term	Nature of the shift
Bathochromic shift (Red shift)	Towards longer wavelength
Hypsochromic shift (Blue shift)	Towards shorter wavelength
Hyperchromic effect	Towards higher absorbance
Hypochromic effect	Towards lower absorbance

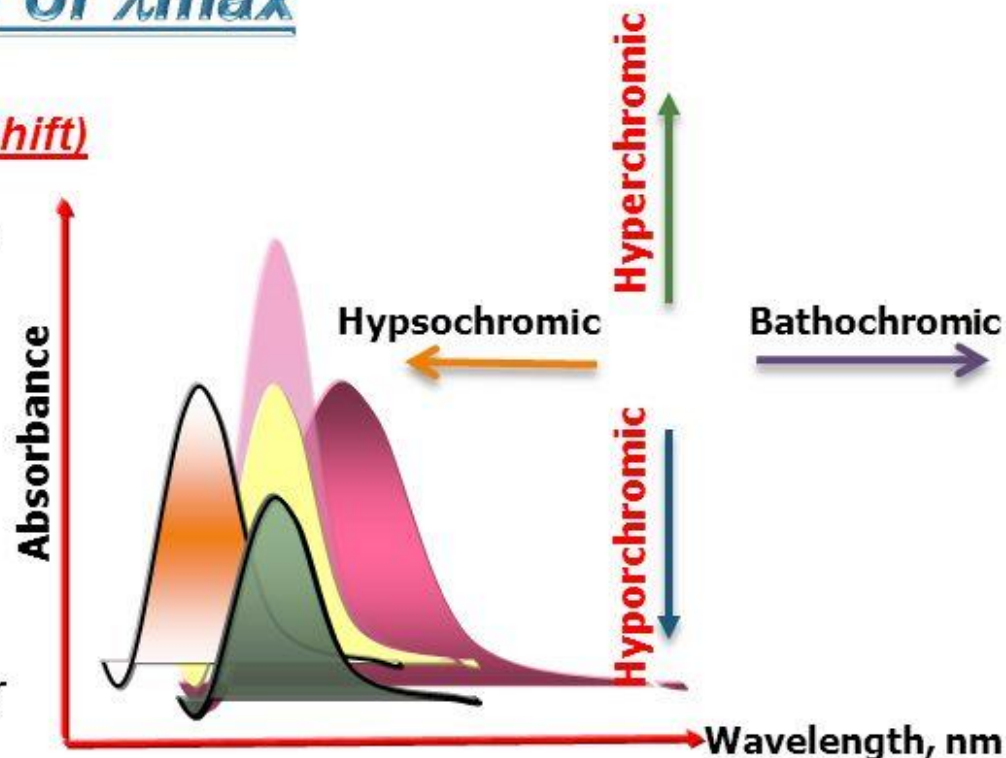
Shifting of λ_{max}

1- Bathochromic shift (or red shift)

It is the shift of λ_{max} to a longer wavelength due to substitution with certain functional groups (e.g. $-\text{OH}$ and $-\text{NH}_2$) and conjugation

2- Hypsochromic shift (or blue shift)

It is the shift of λ_{max} to a shorter wavelength due to removal of conjugation



3- Hyperchromic effect (or shift)

This effect involves an increase in the intensity of absorption. It is usually brought about by introduction of an auxochrome.

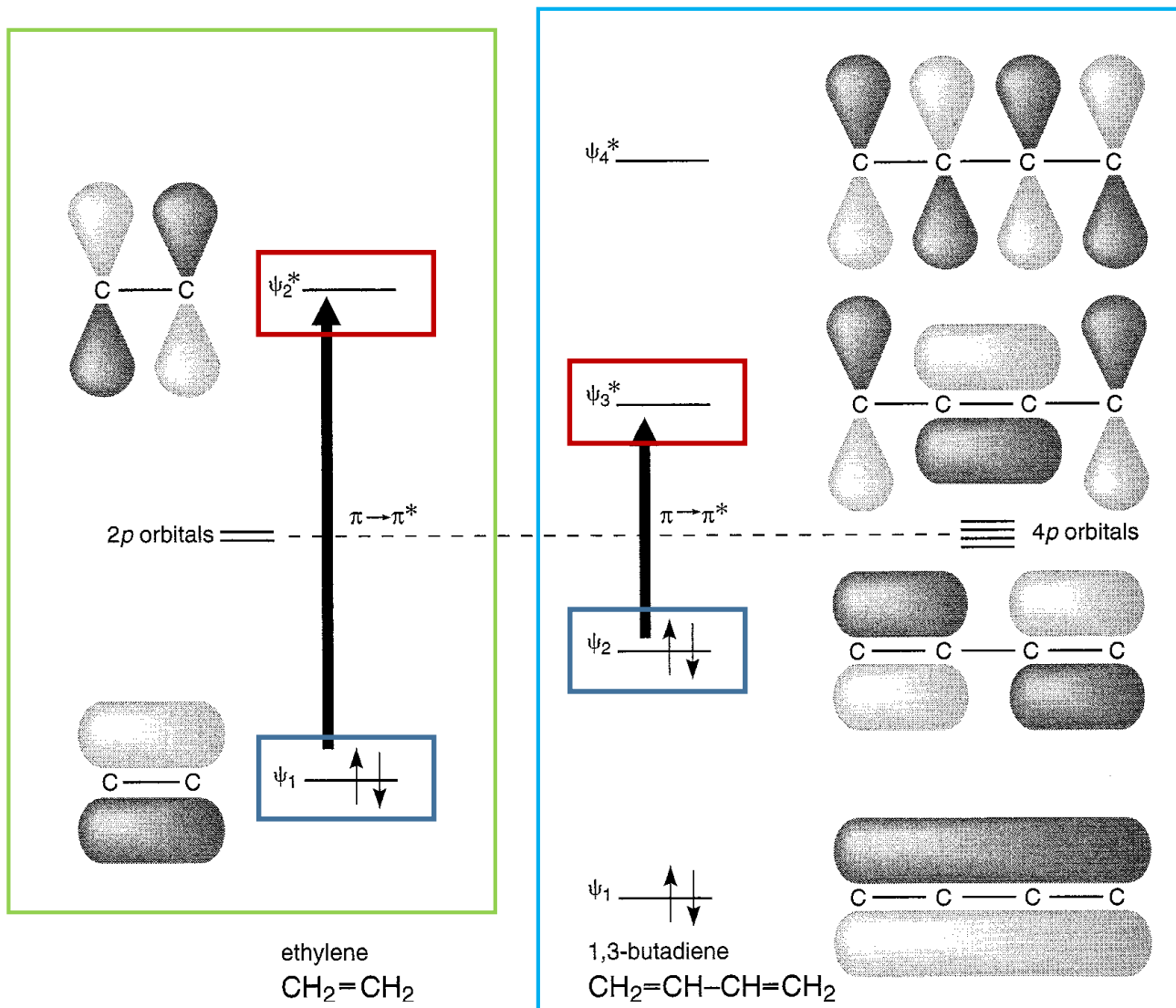
4- Hypochromic effect (or shift)

It involves a decrease in the intensity of absorption

Q. Why wavelength of absorption shift to longer wavelength with increase in conjugation ?

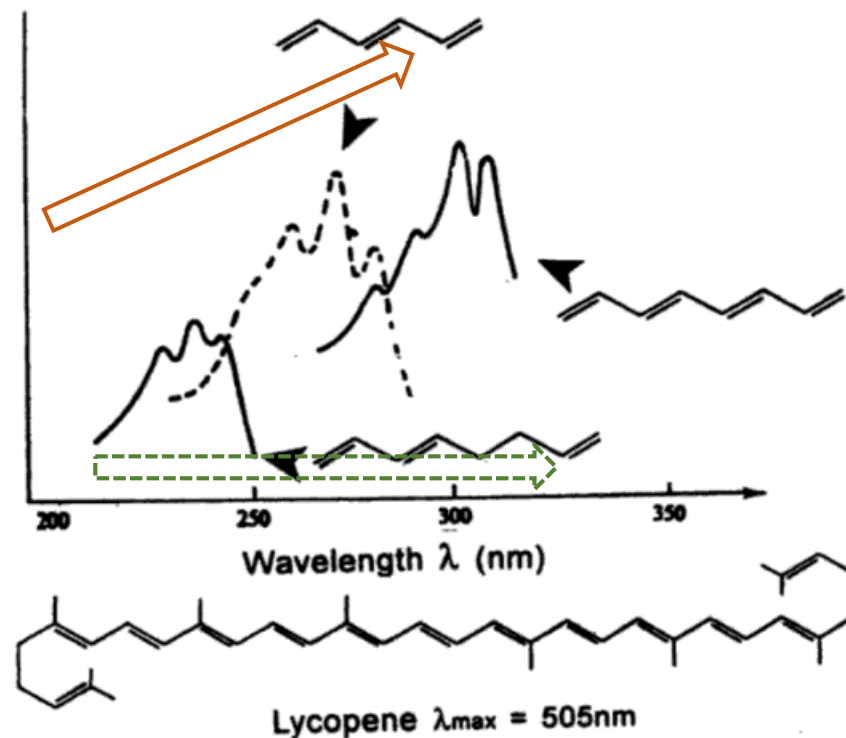
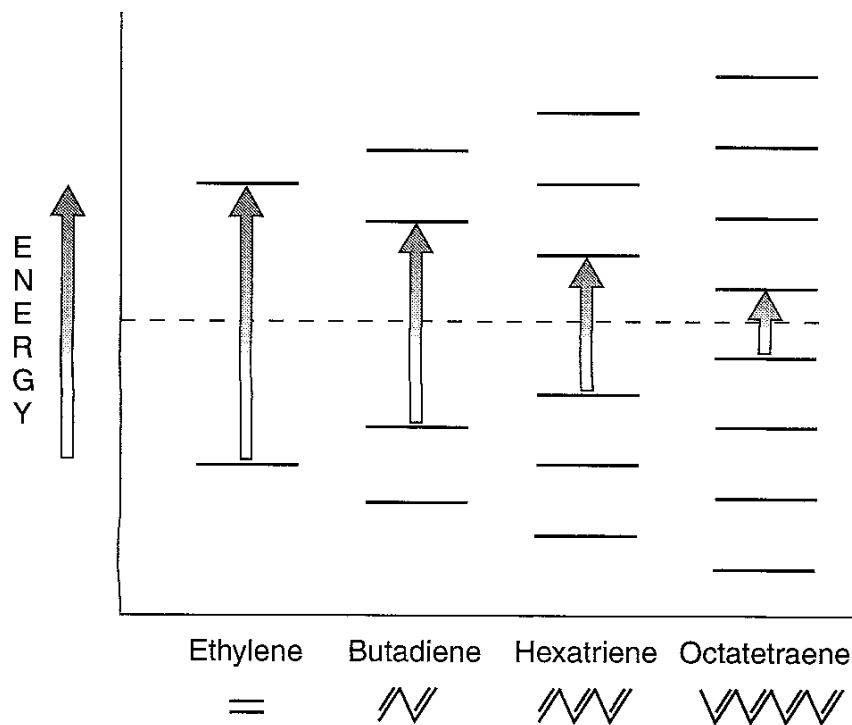
Applications of UV-Vis spectroscopy

Effect of conjugation



Applications of UV-Vis spectroscopy

Effect of conjugation



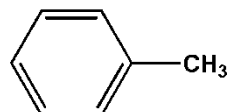
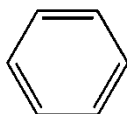
- ✓ Wavelength of absorption shift to longer wavelength with increase in conjugation
- ✓ Molar absorptivity (ϵ) increase with increase in conjugation
- ✓ As the number of conjugated double bonds in polyene increases from 2 – 6, the ϵ increases from $21,000 \text{ M}^{-1} \text{ cm}^{-1}$ to $138,000 \text{ M}^{-1} \text{ cm}^{-1}$

Applications of UV-Vis spectroscopy

Effect of substituents

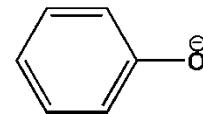
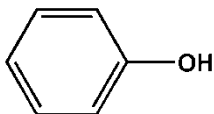
AUXOCHROME

e.g. Benzene $\lambda_{\max} = 255 \text{ nm}$



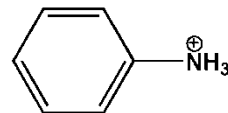
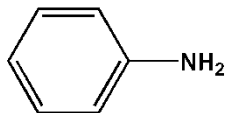
Toluene $\lambda_{\max} = 261 \text{ nm}$

Phenol $\lambda_{\max} = 270 \text{ nm}$



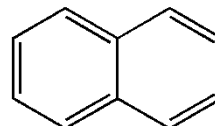
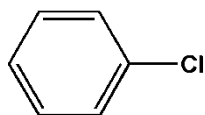
Phenoxide ion $\lambda_{\max} = 287 \text{ nm}$

Aniline $\lambda_{\max} = 280 \text{ nm}$



Anilinium ion $\lambda_{\max} = 254 \text{ nm}$

Chlorobenzene $\lambda_{\max} = 265 \text{ nm}$



Naphthalene $\lambda_{\max} = 312 \text{ nm}$

- ❖ The substituents with lone pair of electrons may undergo conjugation with π -electrons of the phenyl ring causing 'Bathochromic shift'
- ❖ Blocking of the non-bonding pair of electrons by protonation cause 'Hypsochromic shift'

Q.

Cis and trans

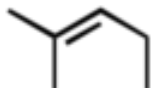
Conjugated systems

Applications of UV-Vis spectroscopy

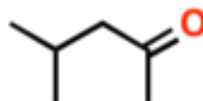
Conjugation in 'enones'

Conjugation of C=O with C-C π bonds results in absorbance at higher wavelengths

Individually, C-C π bonds and C-O π bonds each group absorb at < 200 nm ($\pi \rightarrow \pi^*$)



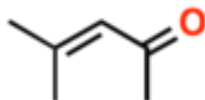
absorption $\lambda_{\max} < 200$ nm



absorption $\lambda_{\max} < 200$ nm (C=O $\pi \rightarrow \pi^*$)

270 nm (C=O $n \rightarrow \pi^*$)
(weak)

When combined in conjugation, absorbance moves to longer wavelengths
(228 nm for mesityl oxide, below)



Mesityl oxide
absorption λ_{\max} 228 nm
($\pi \rightarrow \pi^*$)

Similar to butadiene



absorption λ_{\max} 217 nm

Term Symbol

- Spectroscopic states of Ti^{3+} , V^{4+}
- Electronic configuration in ground state = d^1 ; 1 u.e.
- Spin of the metal ion due to unpaired electron (S) = $\frac{1}{2}$
- Multiplicity of Ground state = $2S+1 = 2 \times \frac{1}{2} + 1 = 2$ (doublet)
- Electronic ground state ^{2S+1}L
- $m_l = 2$, Therefore $L = 2 = D$ [$L = l_1 + l_2 + l_3 = l_n$, $L = 0$ is S, $L = 1$ is P, $L = 2$ is D, $L = 3$ is F]
- Spectroscopic ground state term symbol of $\text{Ti}^{3+} = {}^2D$

Term Symbol

- Spectroscopic states of V^{3+} , Cr^{4+}
- Electronic configuration in ground state = d^2 ; 2 u.e.
- Spin of the metal ion due to unpaired electron (S) = 1
- Multiplicity of Ground state = $2S+1 = 2 \times 1 + 1 = 3$ (triplet)
- Electronic ground state ^{2S+1}L
- $m_l = +2, +1$, Therefore $L = 2 + 1 = 3 = F$ [$L = l_1 + l_2 + l_3 + l_n$, $L = 0$ is S, $L = 1$ is P, $L = 2$ is D]
- Spectroscopic ground state term symbol of $V^{3+} = {}^3F$

Term Symbol

- Spectroscopic states of V^{2+} , Cr^{3+}
- Electronic configuration in ground state = d^3 ; 3 u.e.
- Spin of the metal ion due to unpaired electron (S) = $3/2$
- Multiplicity of Ground state = $2S+1 = 2 \times 3/2 + 1 = 4$ (quartet)
- Electronic ground state ^{2S+1}L (Term symbol of spectroscopic state)
- $m_l = +2, +1, 0$. Therefore, $L = 2 + 1 + 0 = 3 = F$ [$L = l_1 + l_2 + l_3 + l_n$, $L = 0$ is S, $L = 1$ is P, $L = 2$ is D]
- Spectroscopic ground state term symbol of $V^{2+} = {}^4F$