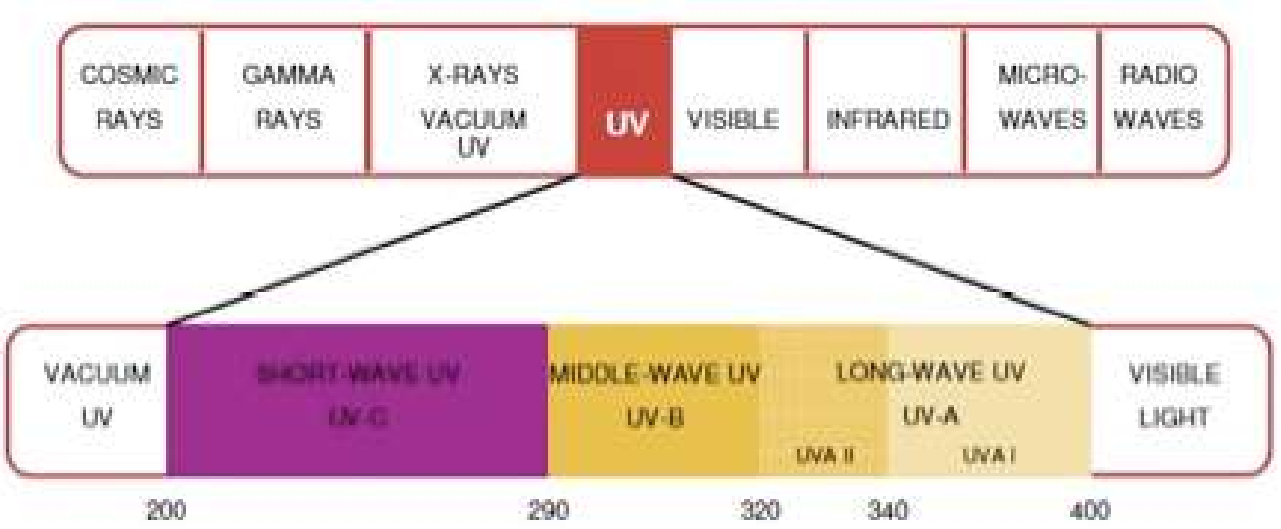
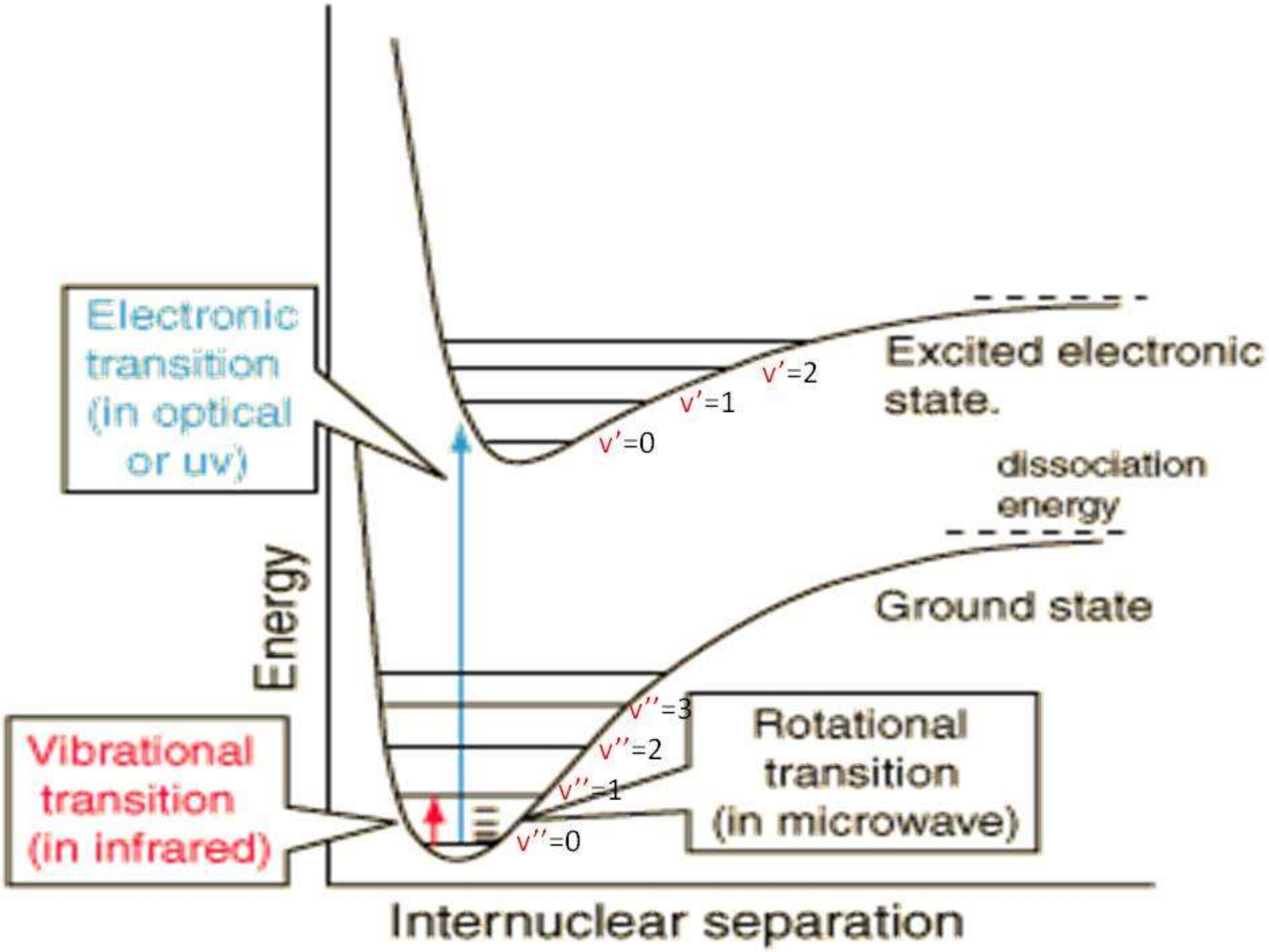
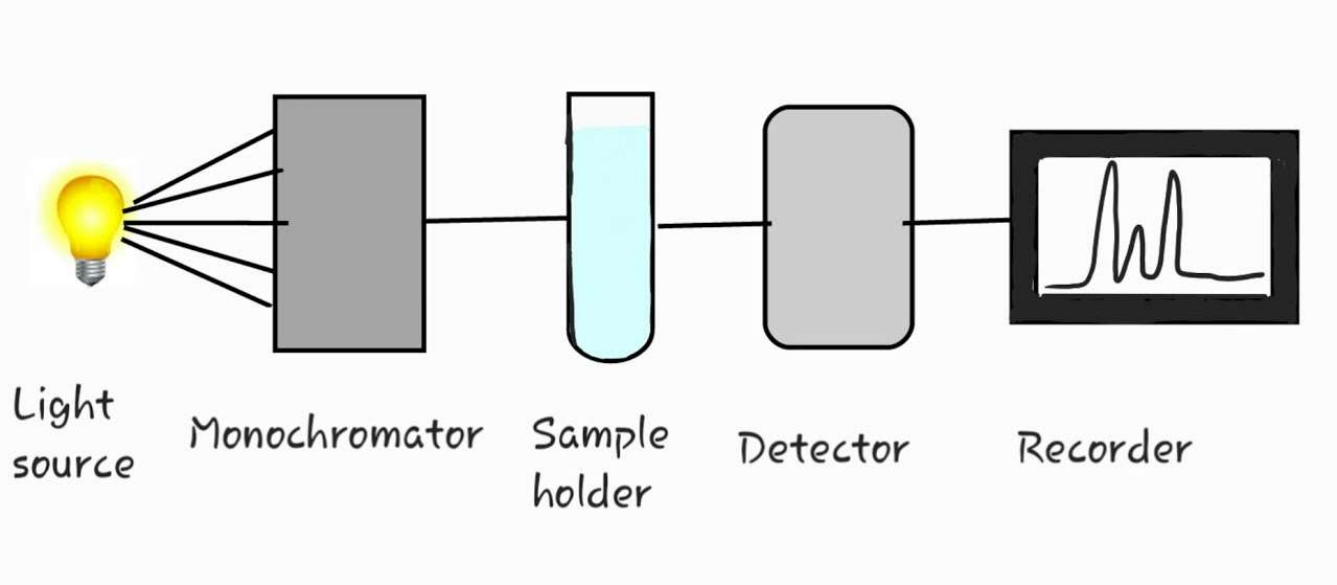
Ultraviolet-Visible Spectroscopy




Electronic transition (in optical or uv)
Excited electronic state.
v'=2
v'=1
v'=0
dissociation energy
Ground state
Energy
v''=3
v''=2
v''=1
v''=0
Rotational transition (in microwave)
Vibrational transition (in infrared)
Internuclear separation

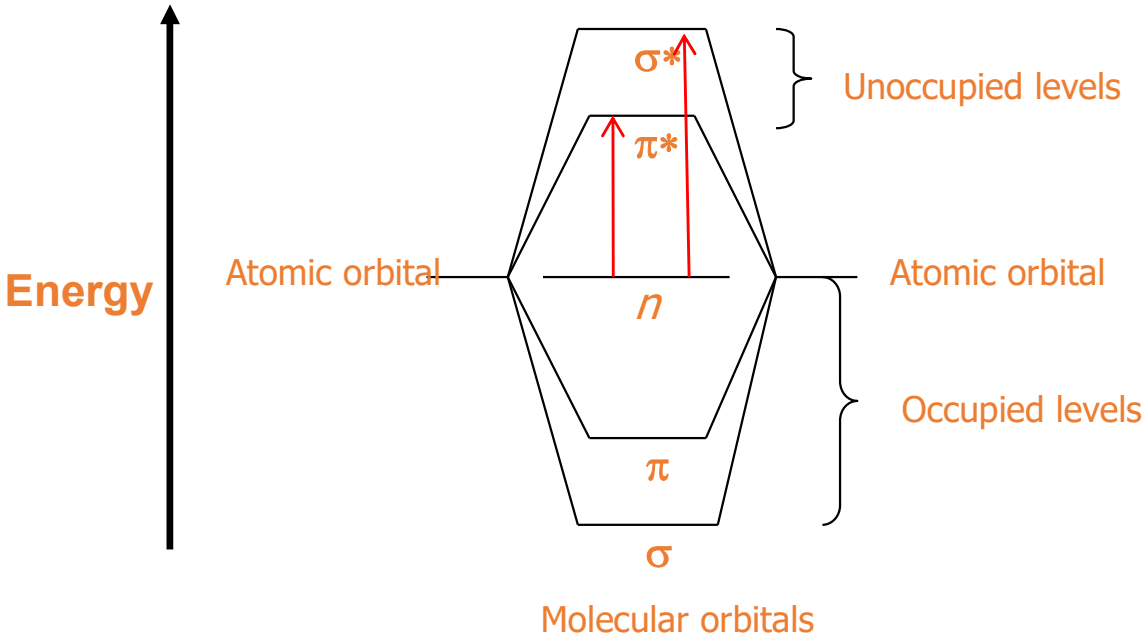
❑ The Spectroscopic Process

1. In UV-vis spectroscopy, the sample is irradiated with the broad spectrum of the UV-vis radiation
2. If a particular electronic transition matches the energy of a certain band, it will be absorbed
3. The remaining light passes through the sample
4. From this residual radiation a spectrum is obtained with "gaps" at these discrete energies – this is called an *absorption spectrum.*



❑ Observed electronic transitions

From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy



$\sigma \rightarrow \sigma^*$ **alkanes**

$\sigma \rightarrow \pi^*$ **carbonyls**

$\pi \rightarrow \pi^*$ **unsaturated compounds**

$n \rightarrow \sigma^*$ **O, N, S, halogens**

$n \rightarrow \pi^*$ **carbonyls**

Transitions

σ–>σ*

- **UV photon required, high energy**
- **Methane at 125 nm (CH_4)**
- **Ethane at 135 nm (C_2H_5)**

n–> σ*

- **Saturated compounds with unshared e^-**
- **Absorption between 150 nm to 250 nm**
- **ε between 100 and 3000 L cm^{-1} mol^{-1}**
- **Shifts to shorter wavelengths with polar solvents**
- **Minimum accessibility**
- **Halogens, N, O, S**

n –> π*, π–>π*

- **Organic compounds, wavelengths 200 to 700 nm**
- **Requires unsaturated groups**
- **n –> π* low ε (10 to 100)**
- **π–>π* higher ε (1000 to 10000)**

INSTRUMENTATION

Spectrometer: An instrument used for measuring transmittance or absorbance of a sample as function of the wavelength of the electromagnetic radiation

Components of a spectrophotometer

Source: It generates electromagnetic radiation

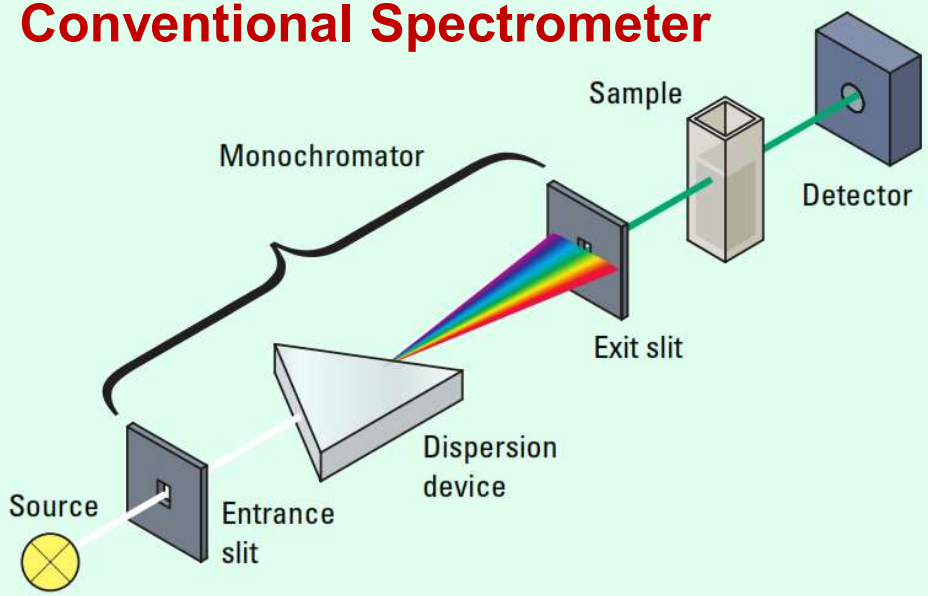
Dispersion device: It select the wavelength required from the broad band of radiation source

Sample area: Where the sample is kept

Detector: One or more detectors that measure the intensity of the radiation

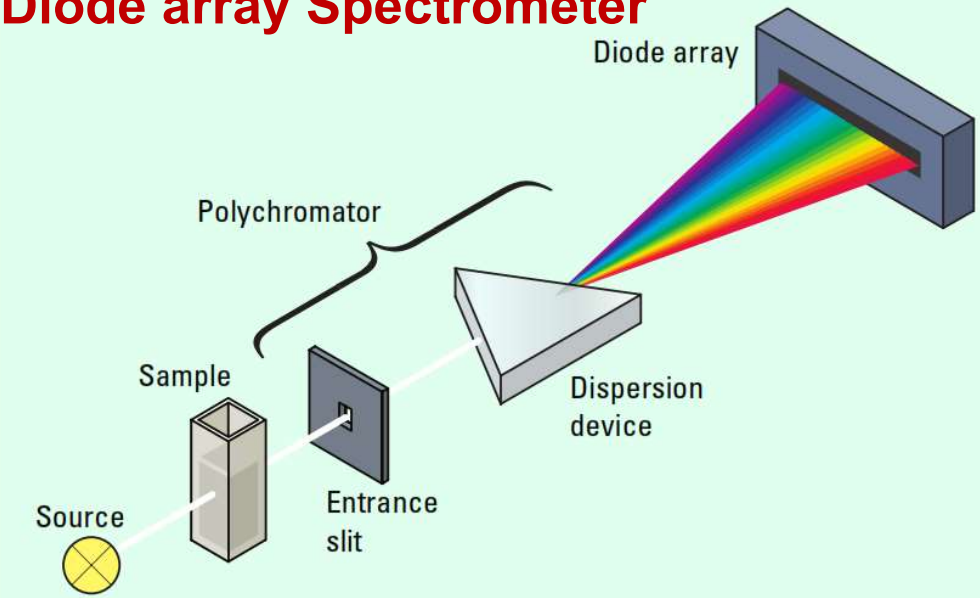
SPECTROMETER DESIGN

Conventional Spectrometer



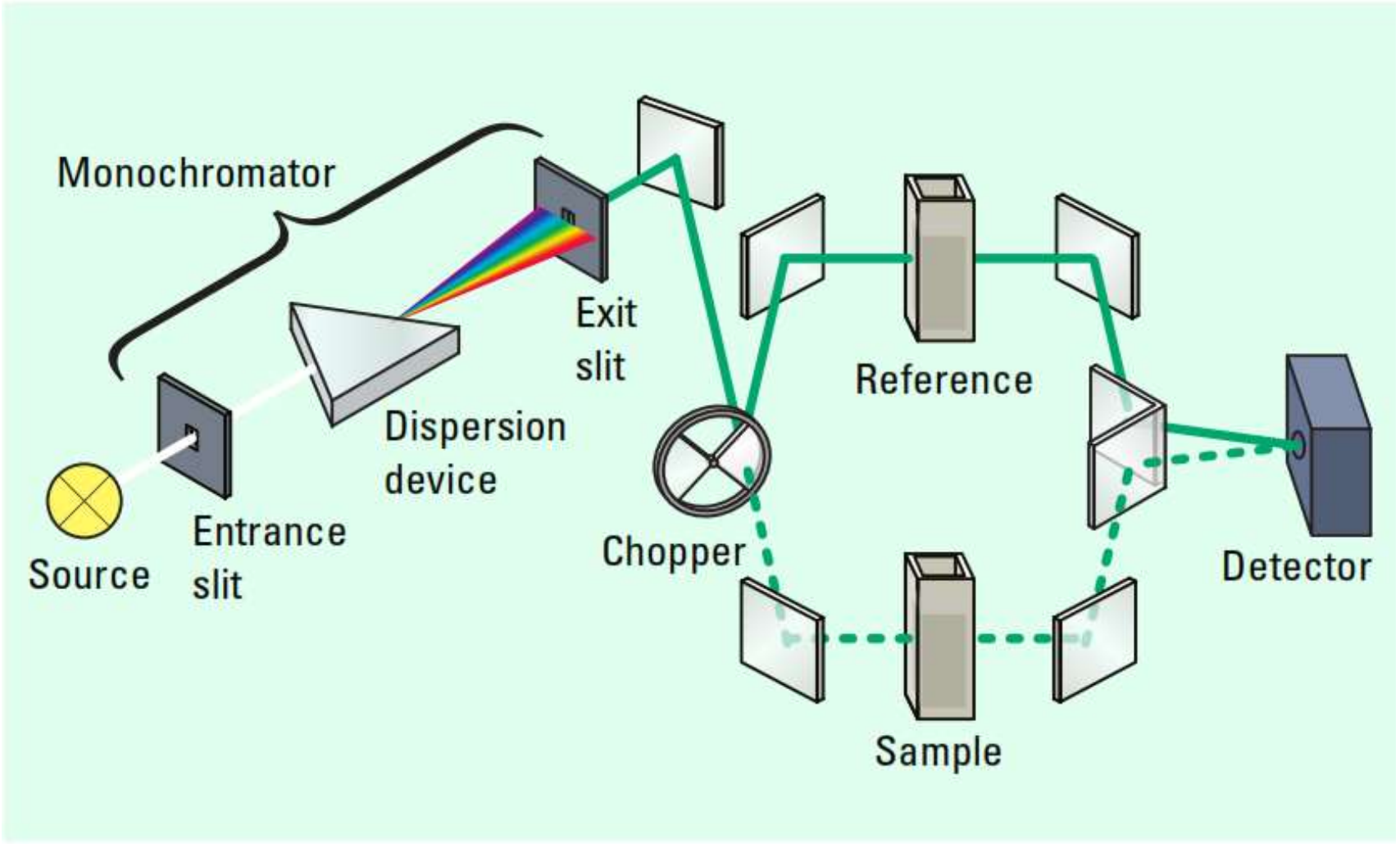
- Polychromatic source of light falls on an entrance slit which transmits a narrow band of light.
- The light then pass through the sample to a detector.
- The detector measures the absorbance of the sample by comparing the light that reaches the detector from the sample and the blank (only solvent)

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



Radiation Sources

Two sources are required to scan the entire UV-Visible band:

- **Deuterium arc lamp– covers the UV – 200-330 (yields a good intensity continuum in the UV region)**
- **Tungsten-halogen lamp – covers 330-700 (yields good intensity over part of the UV spectrum and over the entire visible range)**
- **An alternate light source: Xenon lamp**
  Pros: Yields a good continuum over the entire UV and visible regions.
  Cons: High noise from currently available Xenon lamps compared to deuterium or tungsten lamps

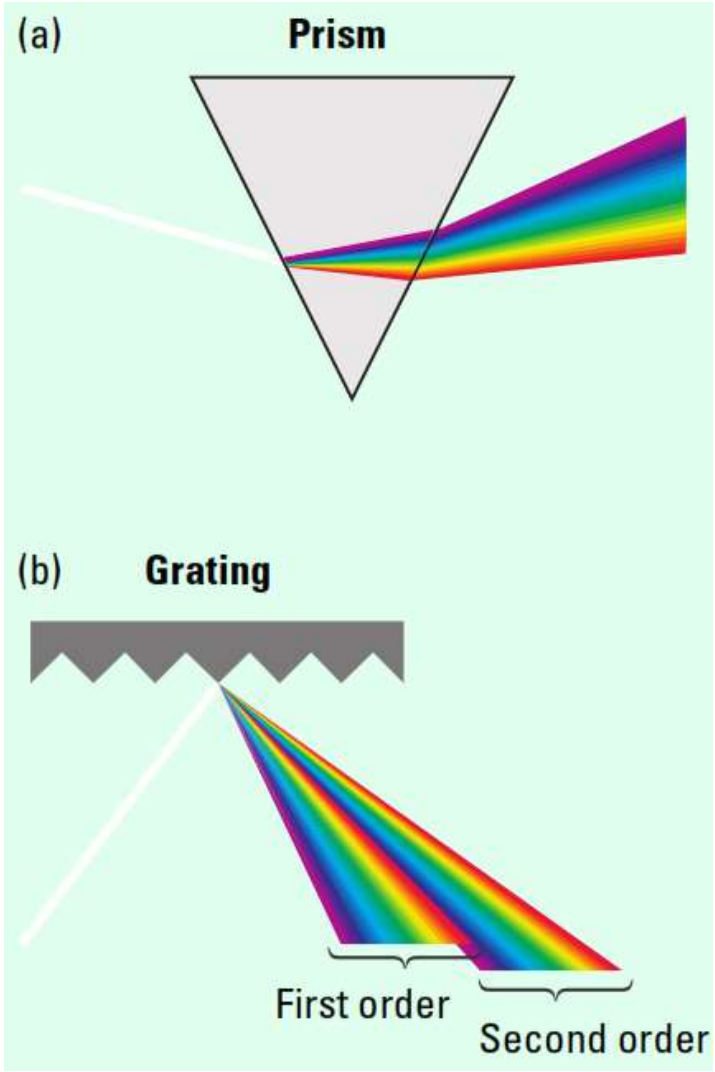
❑ **Monochromator: consists of an entrance slit, a dispersion device, and an exit slit.**

Dispersion devices

- Dispersion devices cause different wavelengths of light to be dispersed at different angles.

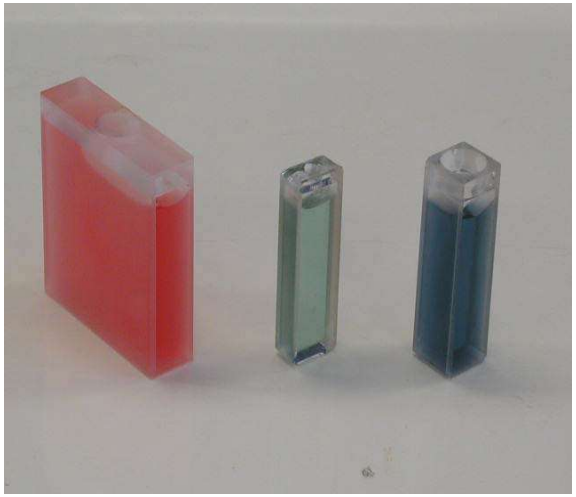
- When combined with an appropriate exit slit, these devices can be used to select a particular wavelength of light from a continuous source.

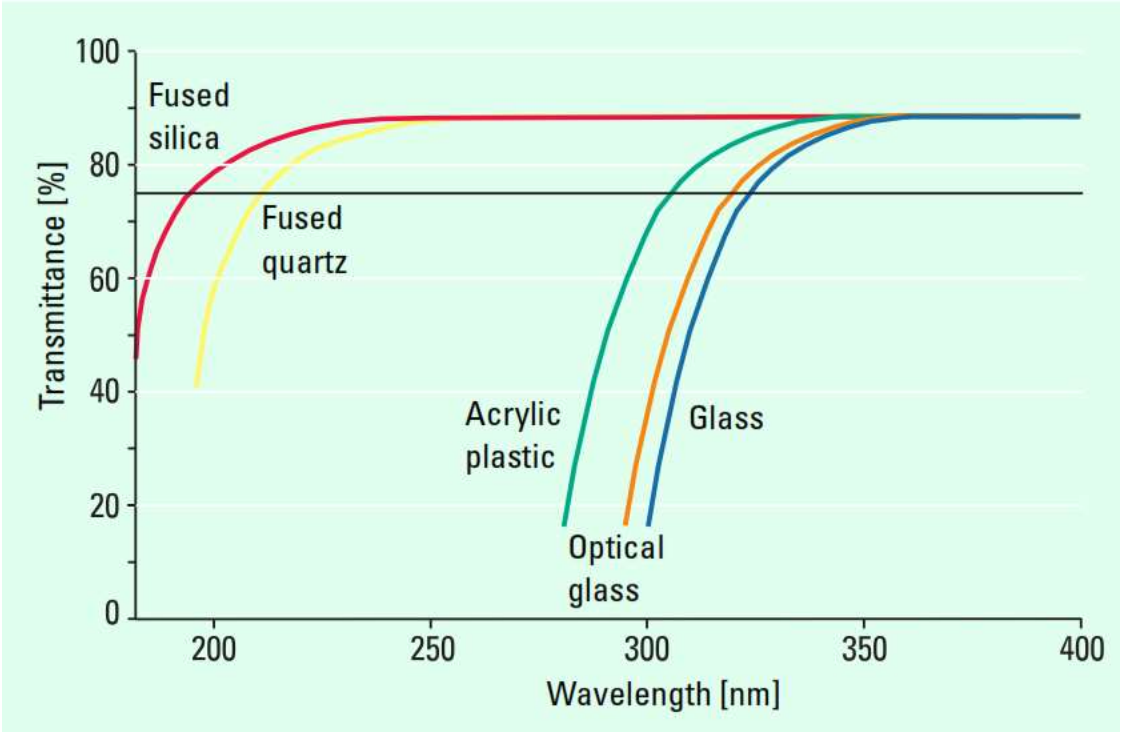
- Two types of commonly used dispersion devices:
  1. Prisms
  2. Holographic gratings



Sample array

1. Sample cells can be made of plastic, glass or quartz
2. Glass absorbs strongly below 320 nm
3. The cells lowest in cost are made of plastic, usually an acrylic. These cells are not resistant to all solvents and absorb strongly below 300 nm
4. Only quartz is transparent in the full 200-700 nm range; plastic and glass are only suitable for visible regions spectra



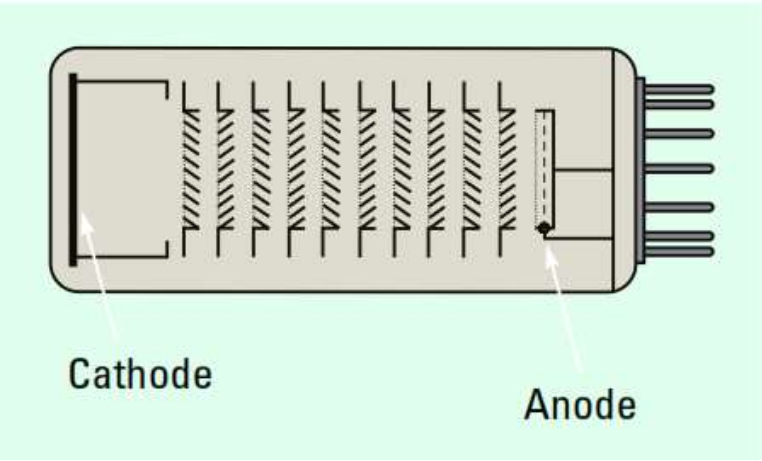


DETECTORS

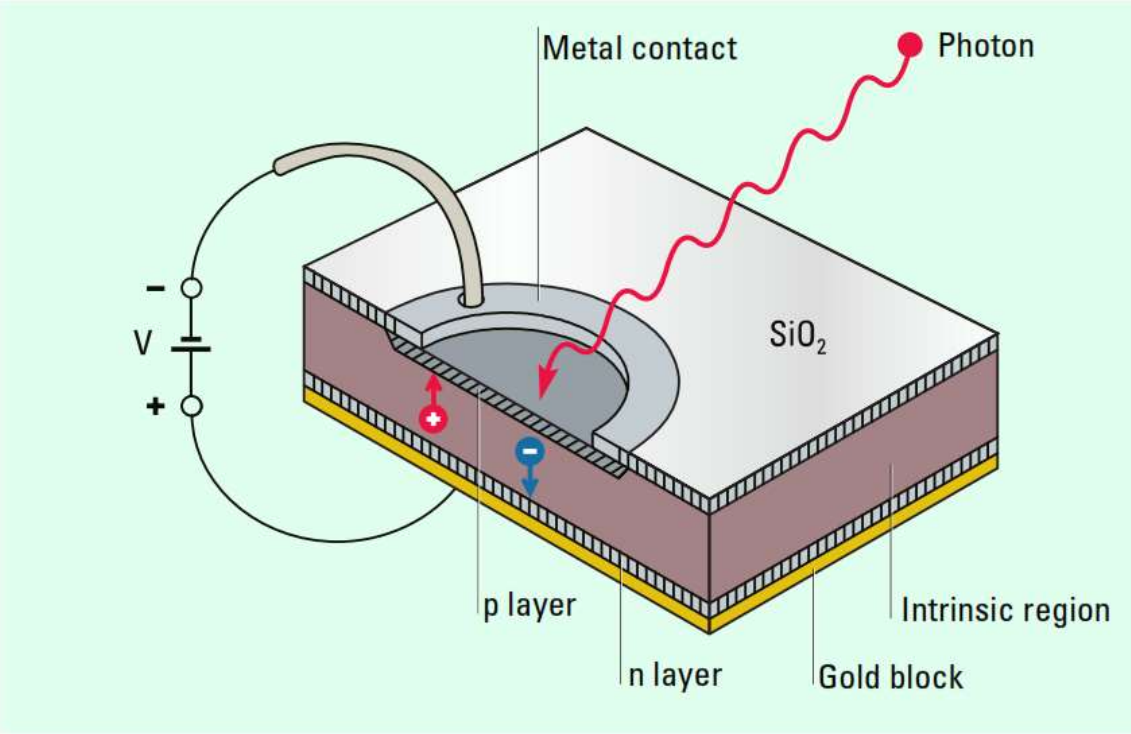
❖A **detector** converts a **light signal** into an **electrical signal.** It gives a **linear response** over a wide range **with low noise** and **high sensitivity**.

❖**Spectrophotometers** normally contain

Photomultiplier tube detector
or a
Photodiode detector.



Photomultiplier tube



Photodiode

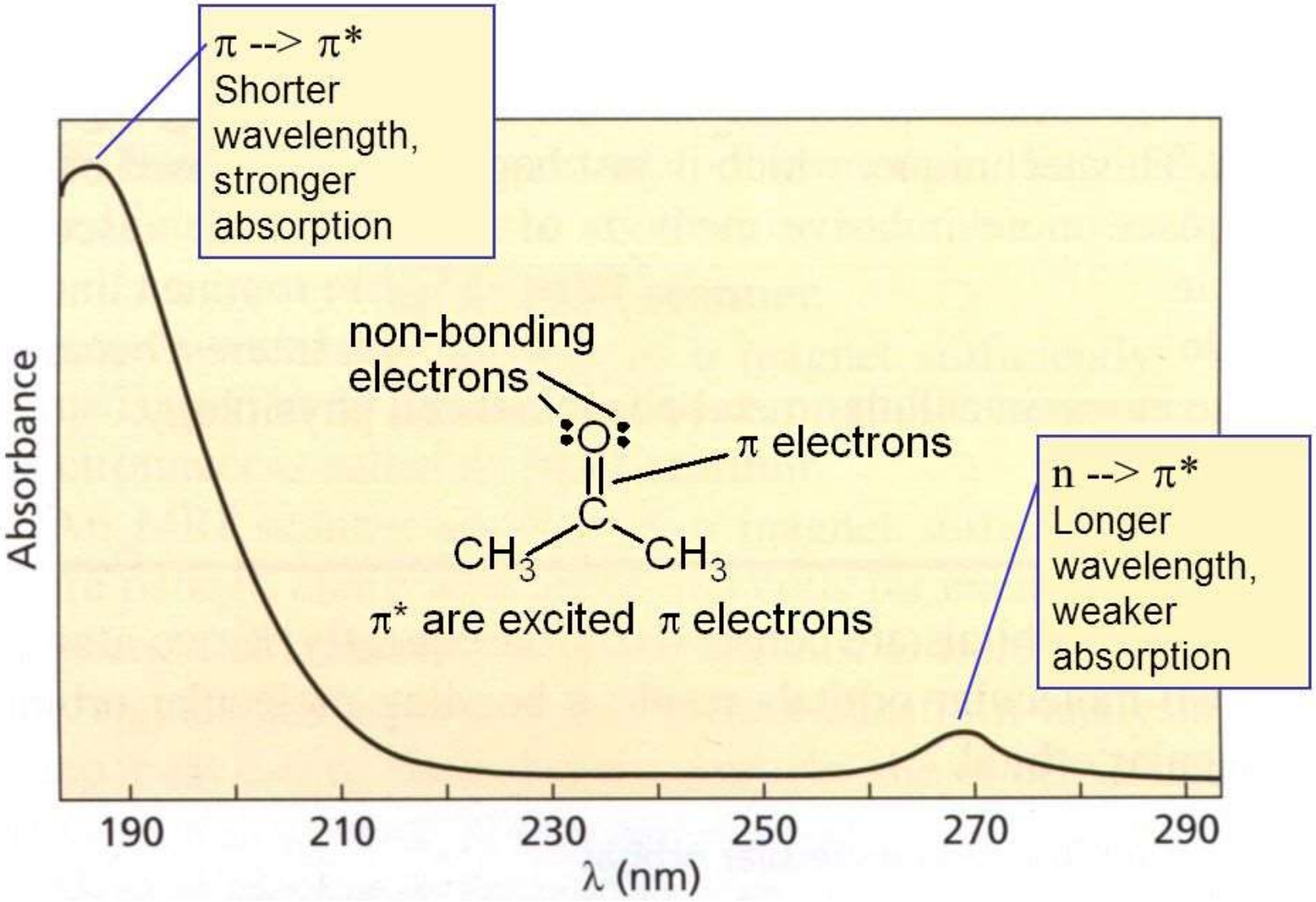
Principle of UV-Visible spectroscopy

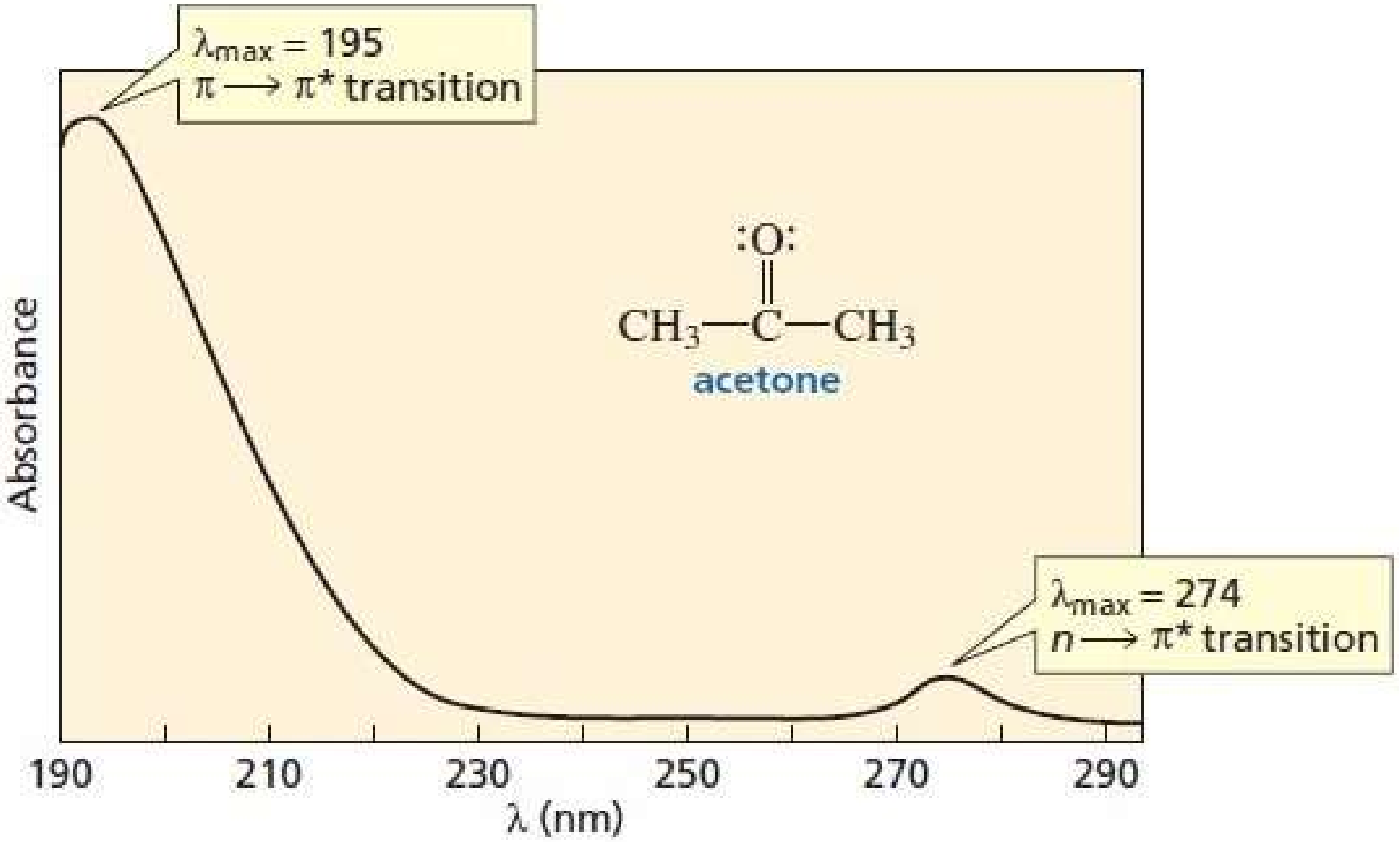
- **Beer-Lambert's law**

$$A = \varepsilon c l$$

- A = Absorbance of the sample = $\log_{10}(I_\circ/I)$
- I = Intensity of the radiation emerging from the sample
- $I_\circ$ = 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

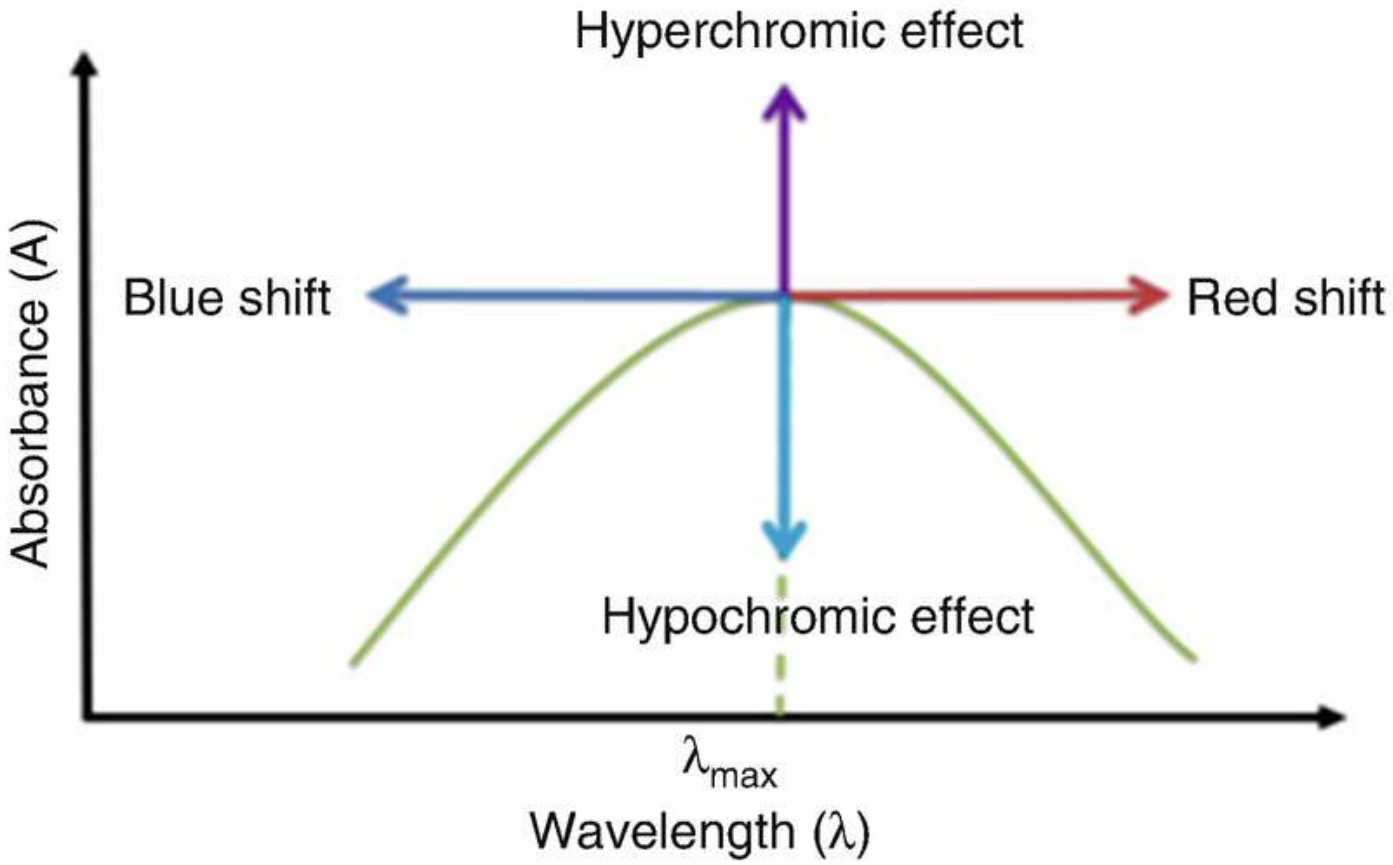



λmax = 195
π ⟶ π* transition
:O:
CH3—C—CH3
acetone
λmax = 274
n ⟶ π* transition
Absorbance
190
210
230
250
270
290
λ (nm)

Applications of UV-Vis spectroscopy

Terminology

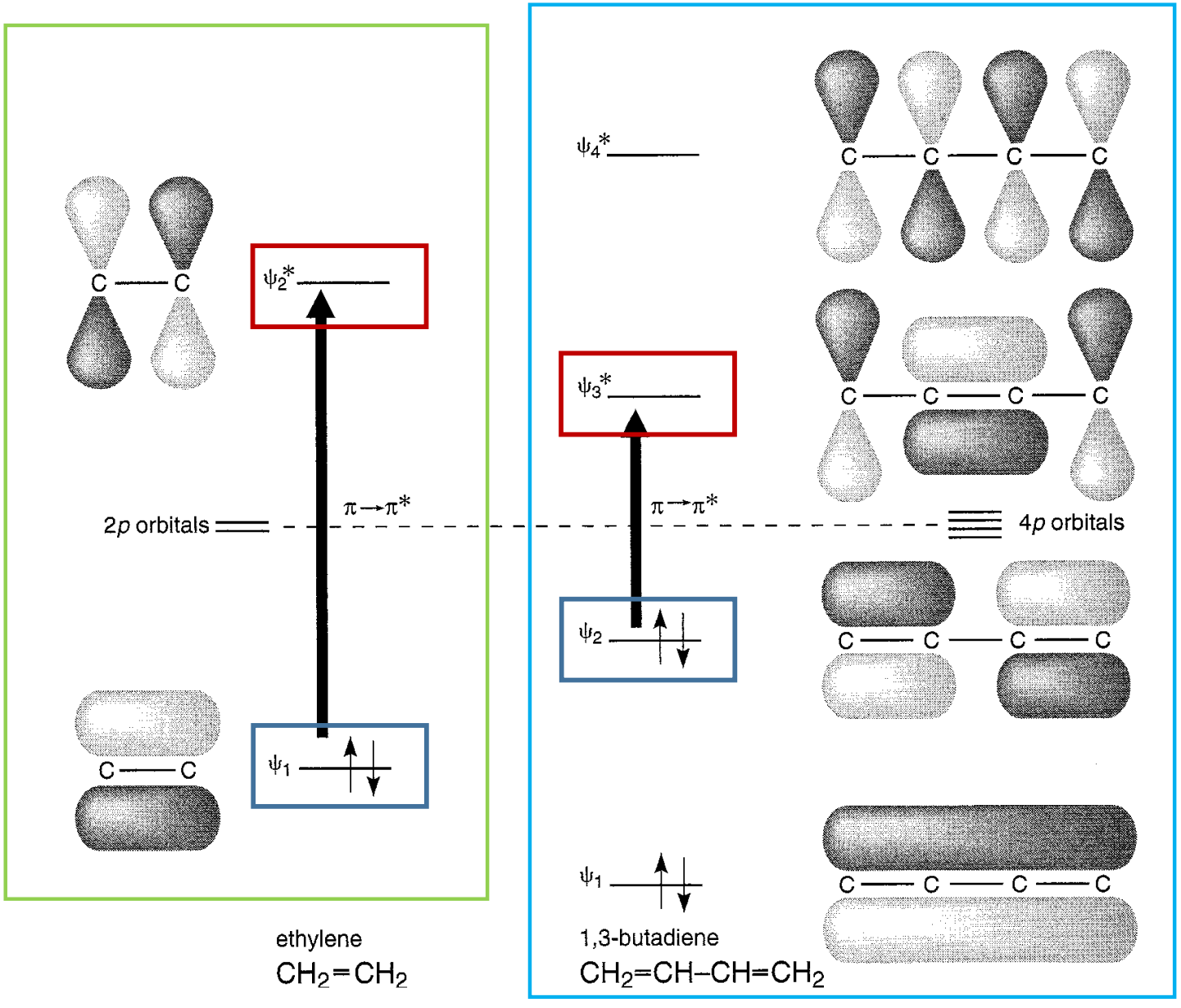
- **Chromophore:** The group of atoms producing an absorption is called a '**Chromophore**'. Eg. C=O, C=C etc.
- **Auxochrome**: Groups that helps in extending the conjugation by means of the lone pairs present. Eg. NH_2, OH, OR, Cl, Br etc.
- **Hypsochromic shift**: When the λ_{max} of an absorption 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

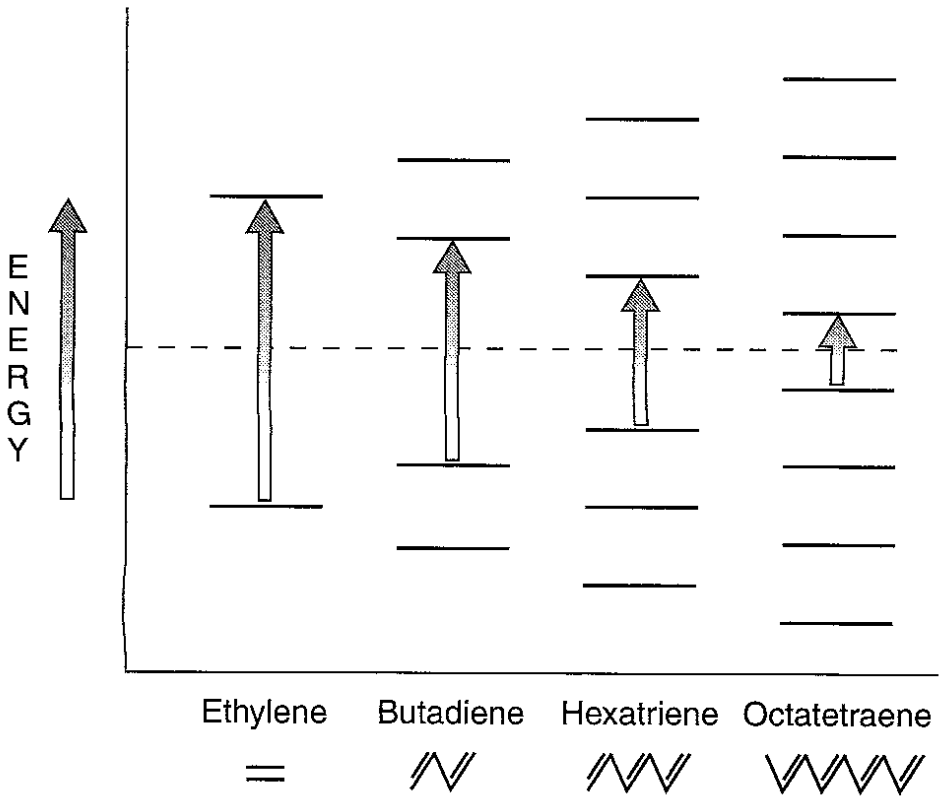
Applications of UV-Vis spectroscopy

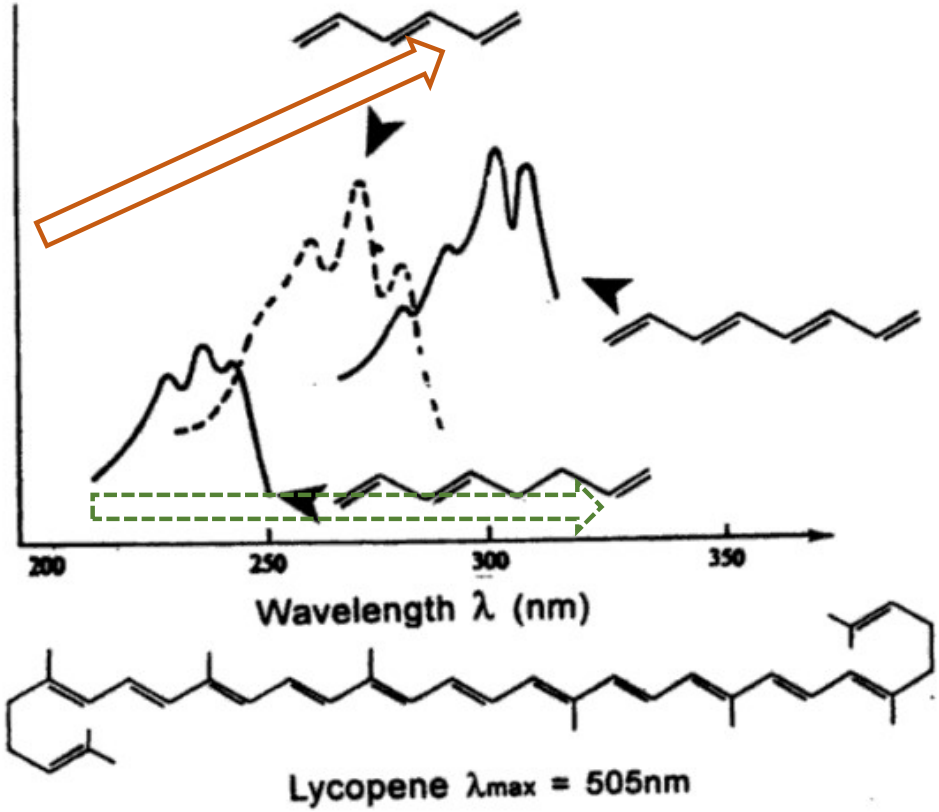
- **Effect of conjugation**



Applications of UV-Vis spectroscopy

Effect of conjugation





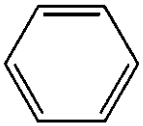
✓ Wavelength of absorption shift to longer wavelength with increase in conjugation

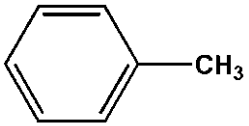
Applications of UV-Vis spectroscopy

Effect of substituents

AUXOCHROME

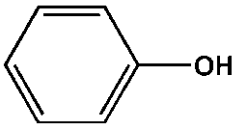
e.g. Benzene λ_{max} = 255 nm

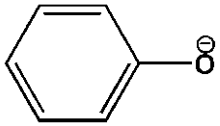




Toluene λ_{max} = 261nm

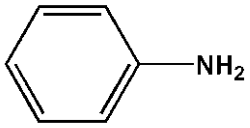
Phenol λ_{max} = 270 nm

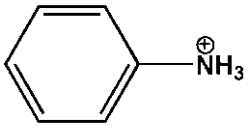




Phenoxide ion λ_{max} = 287nm

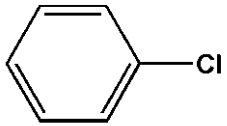
Aniline λ_{max} = 280 nm

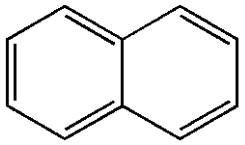




Anilinium ion λ_{max} = 254nm

Chlorobenzene λ_{max} = 265nm





Naphthalene λ_{max} = 312nm

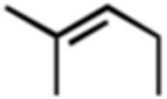
- The substituents with lone pair of electrons may undergo conjugation with π-electrons of the phenyl ring causing '*Bathochromic shift*'
- Blocking of the non-bonding pair of electrons by protonation cause 'Hypsochromic shift'

Applications of UV-Visible spectroscopy

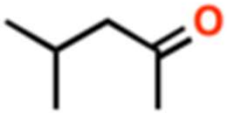
Conjugation in 'enones'

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

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



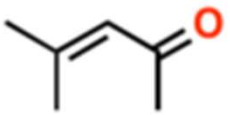
absorption λ_{max} < 200 nm



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

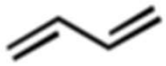
270 nm ($C{=}O$ $n \rightarrow \pi^*$) (weak)

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

❖ Exercises

Q1: A 2.5×10^{-4} M solution of a substance in a 1 cm length cell at λ_{max} 245 nm has absorbance 1.17. Calculate molar extinction coefficient for this transition.

Q2: A 0.01 M solution of a compound transmits 20% of the radiation in a container with a path length equal to 1.5 cm. Calculate molar extinction coefficient of the compound.

Q3: How do you differentiate between Dual beam, conventional, diode array Spectrophotometers?

Q4: What do you understand by Chromophore and auxochrome? Illustrate with one example each.

Q5: What do you understand by bathochromic and hypsochromic shift? Illustrate with one example each.

Q6: Account for the high molar extinction coefficient observed in β-carotene, lycopene and retinal?

Q7: What are different electronic transition possible in Benzophenone, $KMnO_4$?