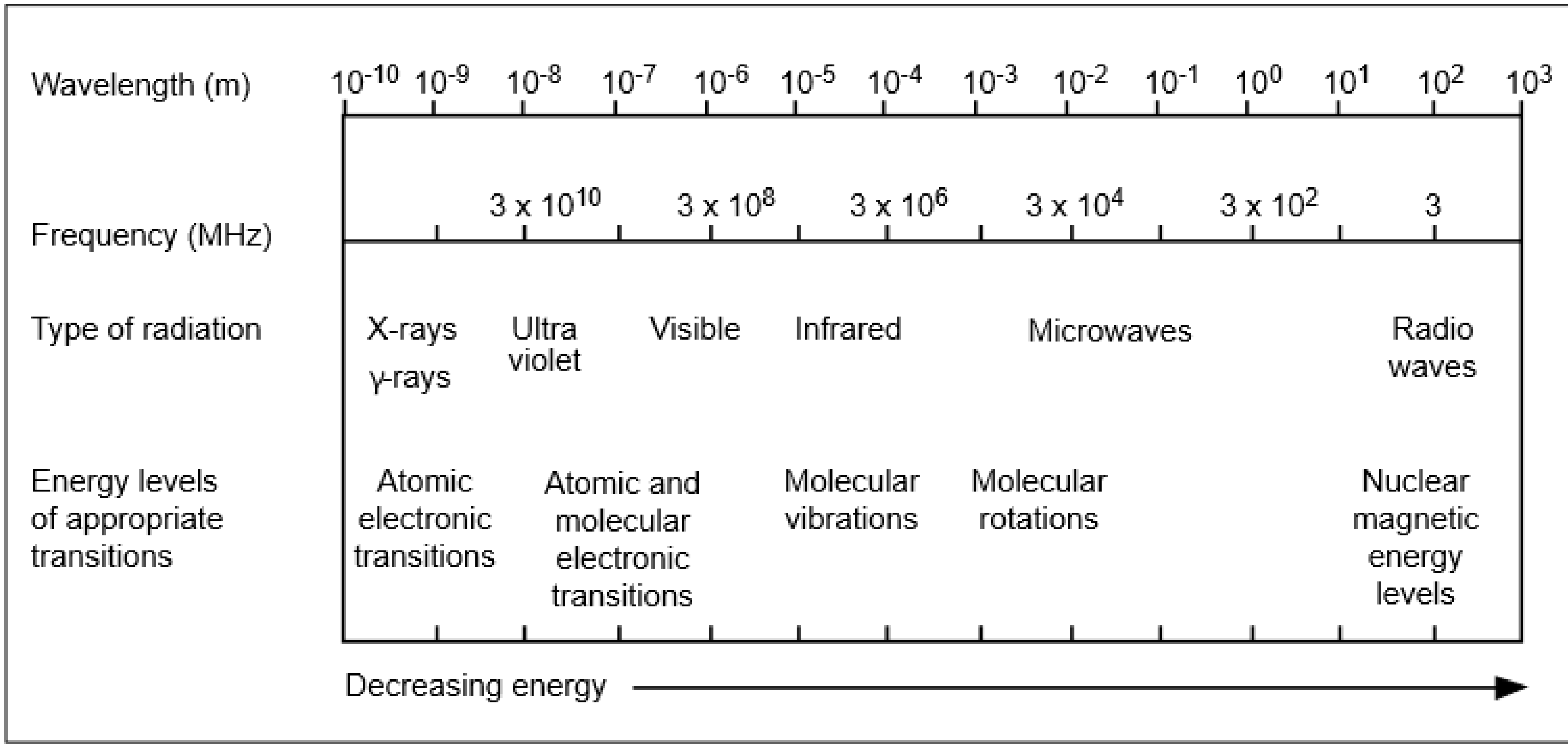
UV-Visible Spectroscopy

Principle of UV- Visible Spectroscopy

- On absorption of UV –Visible radiation molecule undergo **electronic transition**
- **Valence electrons** are promoted from **ground level to higher level**
- Molecule must receive **energy equal to hV** so as undergo electronic transition
- Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).

Electromagnetic regions



UV and Visible Region

- UV region extends from 100-400 nm
- 100-400nm – Far UV
- 190-400 – Near UV
- Visible region – 400-800 nm

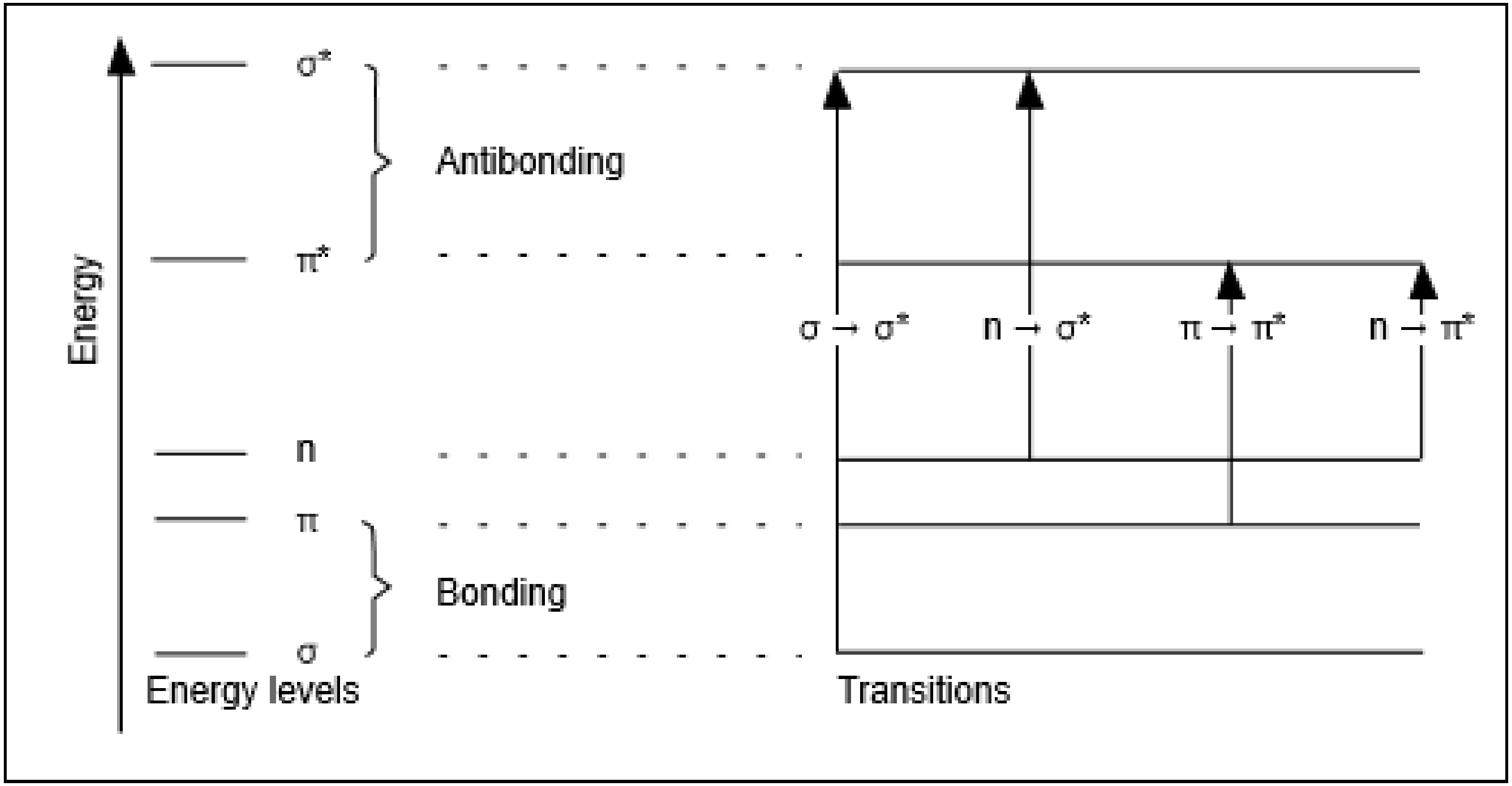
Electronic transitions in molecule

- Total 6 transitions are possible out of that only 4 are practically possible

1) $\sigma \rightarrow \sigma^*$
2) $\pi \rightarrow \pi^*$
3) $n \rightarrow \pi^*$
4) $n \rightarrow \sigma^*$

- $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ are forbidden transitions

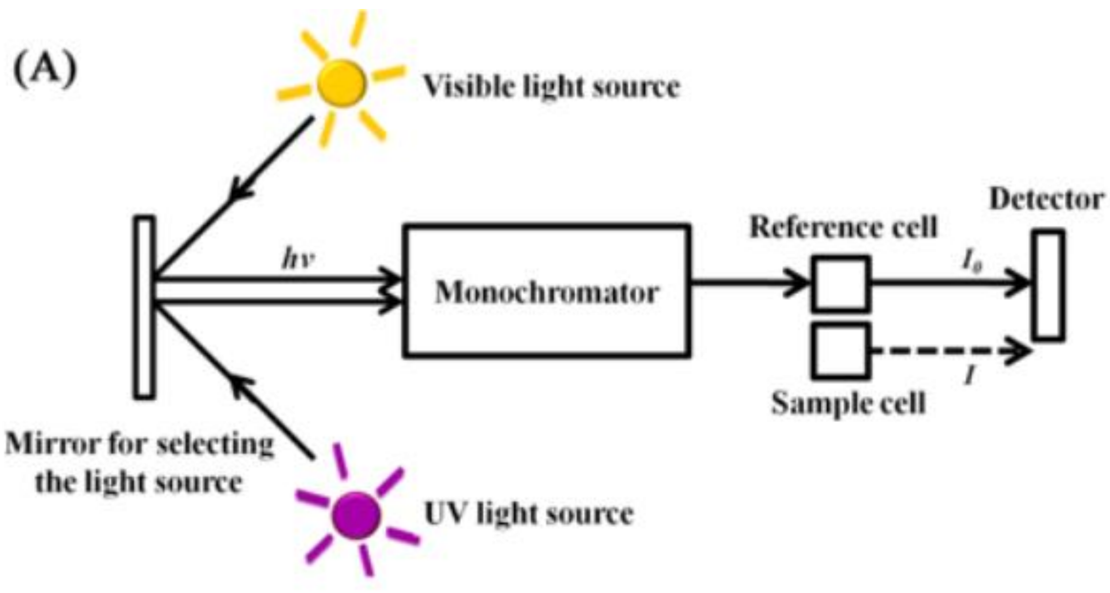
Transition on UV-Visible Absorption



Type of Transitions in Different Molecule

Type of Transitions	Examples
$\sigma \longrightarrow \sigma^*$	Methane , Ethane
$\pi \longrightarrow \pi^*$	Ethylene , Butylene
$n \longrightarrow \pi^*$	Acetone, Formaldehyde
$n \longrightarrow \sigma^*$	Ethanol , Ethyl Thiol

Single Beam Spectrophotometer

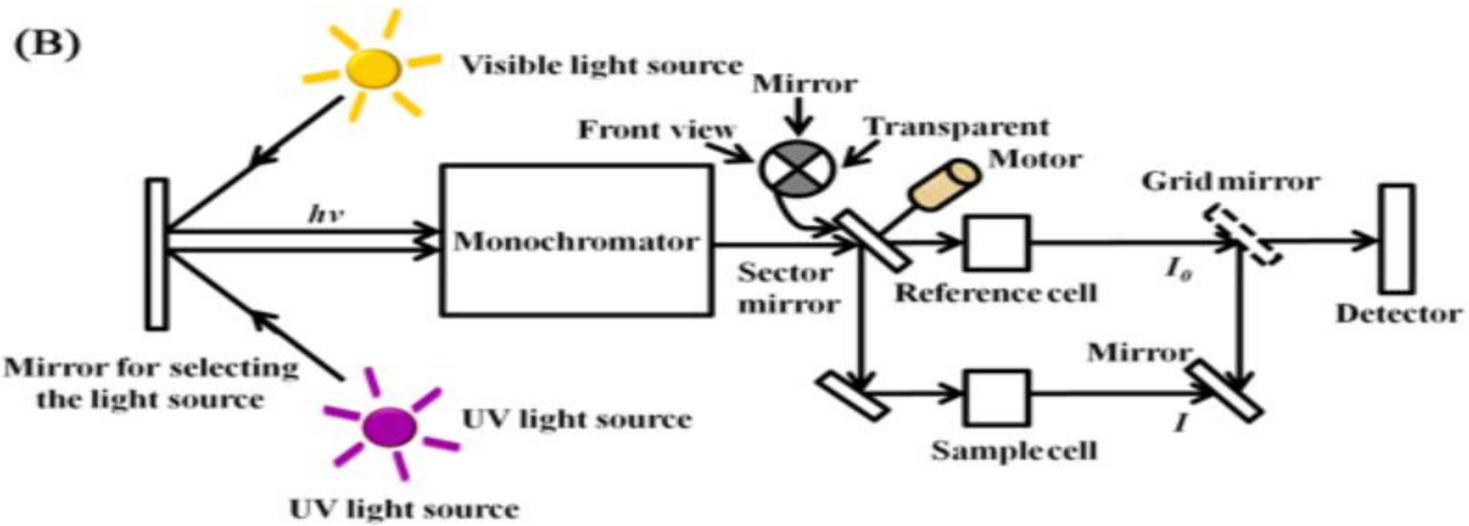


The light enters the instrument through an entrance slit, is collimated and focused on to the dispersing element, typically a diffraction grating. The light of desired wavelength is selected simply by rotating the monochromator and impinged on the sample. The intensity of the radiation transmitted through the sample is measured and converted to absorbance or transmittance

Components in Double Beam UV Visible Spectrophotometer

- Source of radiation
- Monochromator
- Cuvette
- Detector
- Read out device

Double Beam UV-Visible Spectrophotometer



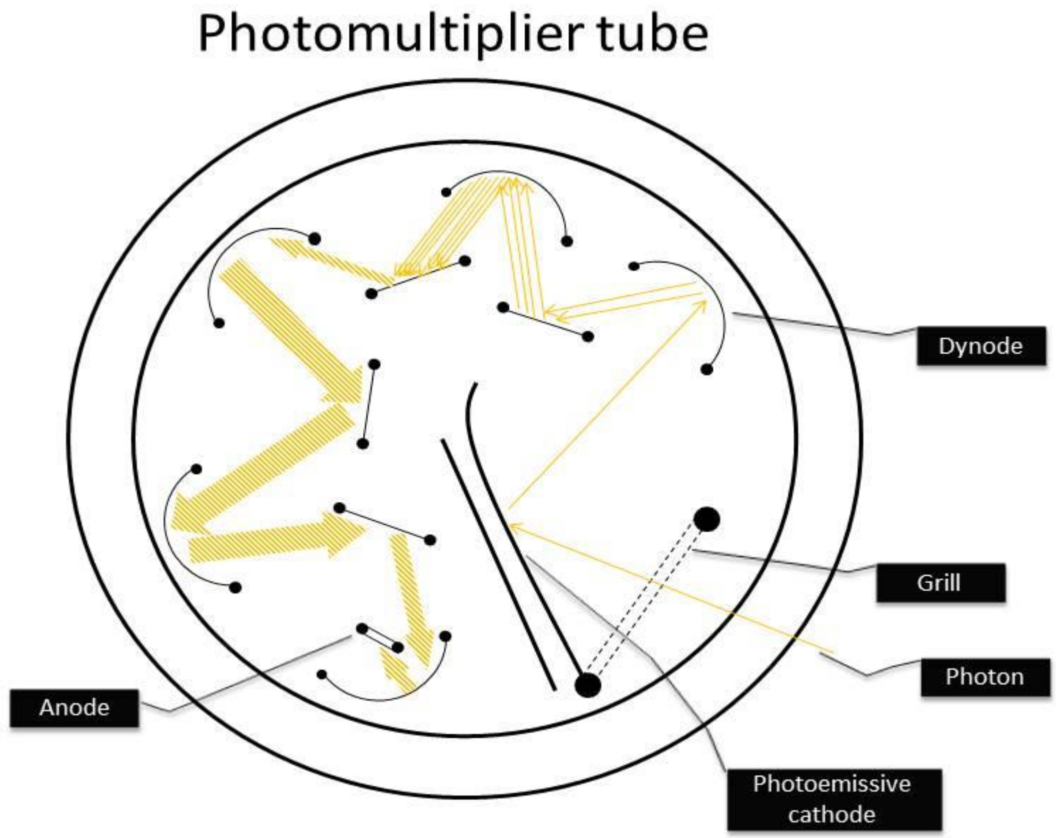
A double beam spectrophotometer has two light beams, one of which passes through the sample while other passes through a reference cell (Figure B). This allows more reproducible measurements as any fluctuation in the light source or instrument electronics appears in both reference and the sample and therefore can easily be removed from the sample spectrum by subtracting the reference spectrum.

Instrumentation :Double beam UV Visible Spectrophotometer

Source: Deuterium Lamp : a continuous spectrum in UV region produced by electrical excitation of deuterium at low pressure

- tungsten Filament lamps : most common source for of Visible radiation
- Function of **monochromator** is convert polychromatic radiation into monochromatic radiation (Multiple wavelength to single Wavelength)
- Grating or Prism or filter work as monochromator
- UV **Sample Cell** should be made up of Quartz material and Glass Cuvette can not be used in UV region as they absorb UV light
- In case of use of visible radiation Cuvette is made from either of glass or plastic material
- Photomultipler tube is used as **Detector**

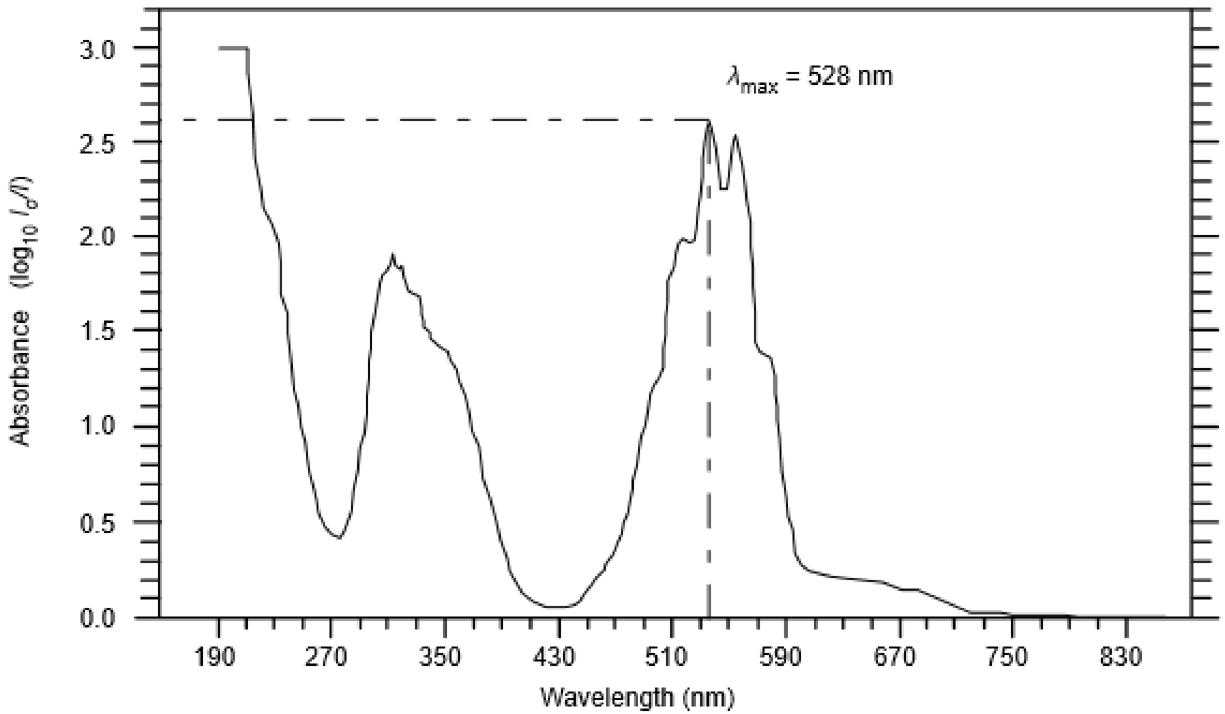
Photomultiplier Tube as Detector



Working of Photomultiplier tube

- Photons enter photomultiplier tube and strikes the cathode
- Electrons are produced due to photelectric effect
- Electrons are directed to dynode (Electron Multiplier)
- Every dynode (total 9) is at More positive voltage (90 V) than previous one
- On striking first dynode more low energy electron are released and these are in turn attracted by greater positive field of next dynode
- Process gets repeated several times and finally electrons reached to anode
- Large number of electrons are emitted due to multiplication
- Resulting current is amplified and measured

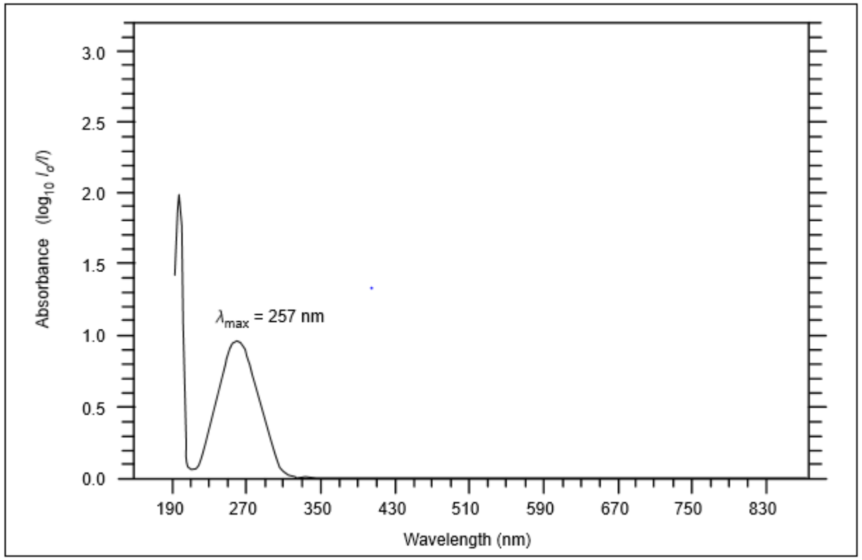
UV Visible spectra of $KMnO_4$



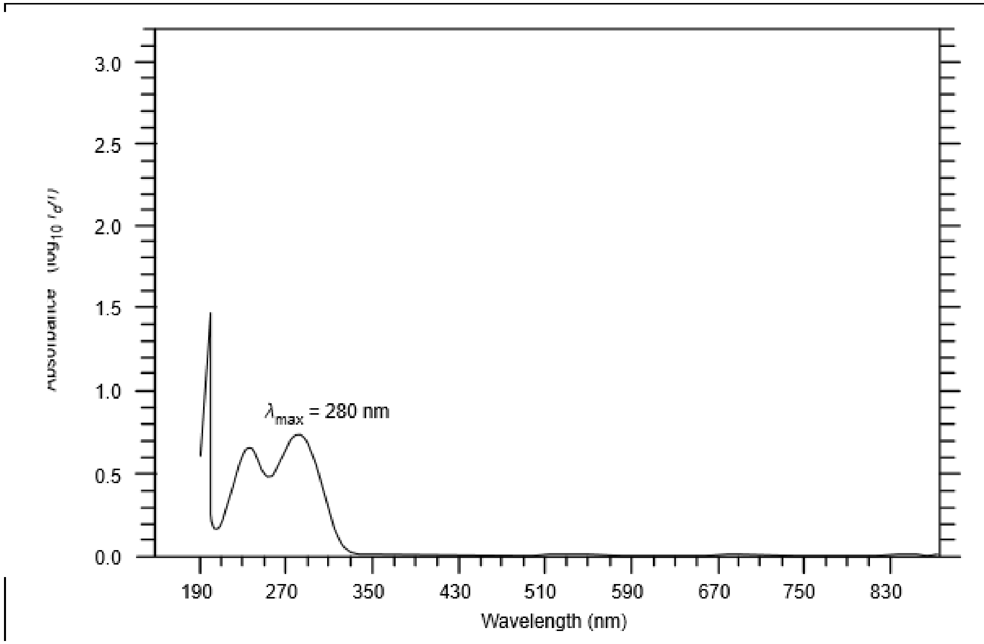
The solution used to obtain this spectrum contained 1.227 mg of potassium manganate(VII) in 5.0 cm^3 of solution. From the spectrum ε is found to be 1.68 x 10^3

Acetone UV Spectra in Different Solvent

Acetone In Water



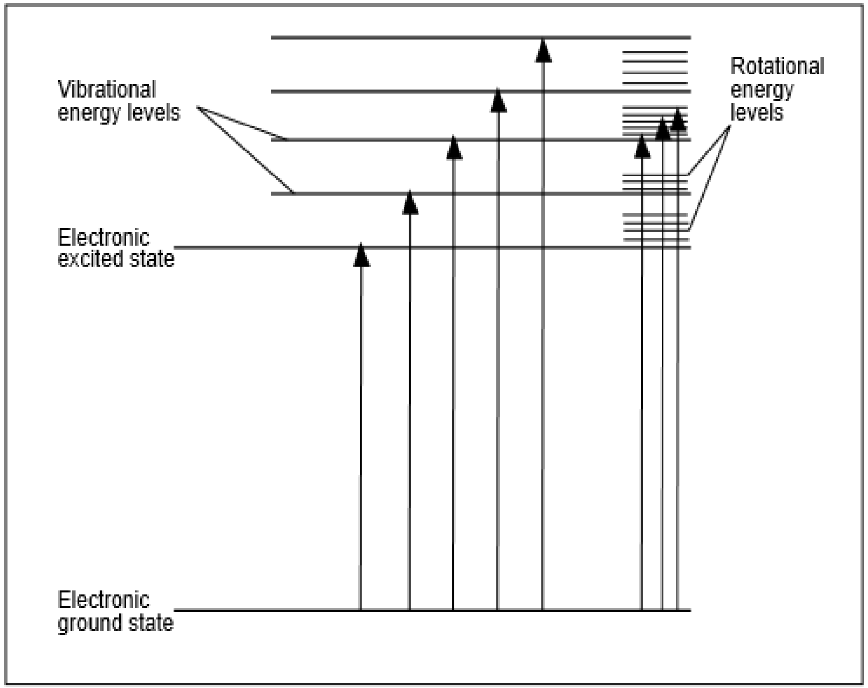
Acetone in Hexane



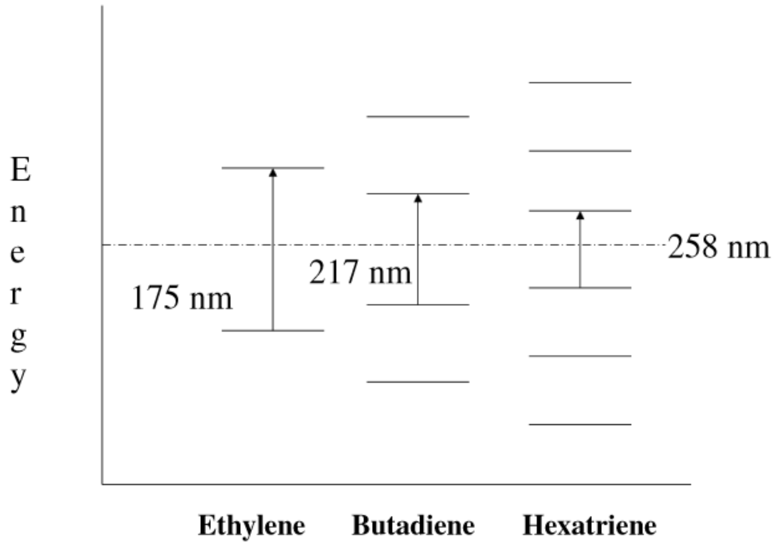
Broad spectra in UV

- Due to a number of vibrational energy levels are available at each electronic energy level, and transitions can occur to and from the different vibrational levels causing peak broadening

- The situation is further complicated by the fact that different rotational energy levels are also available to absorbing materials

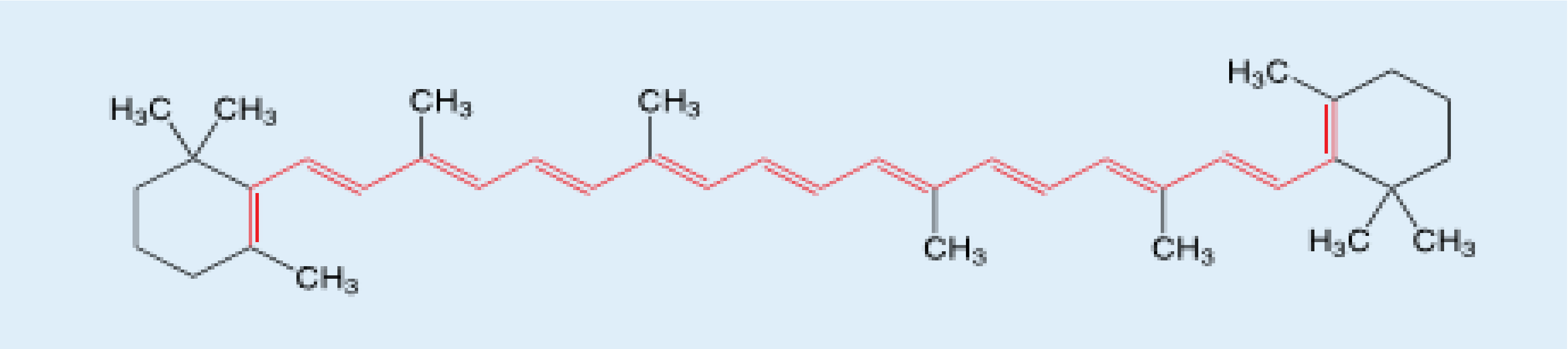


Conjugation and Wavelength



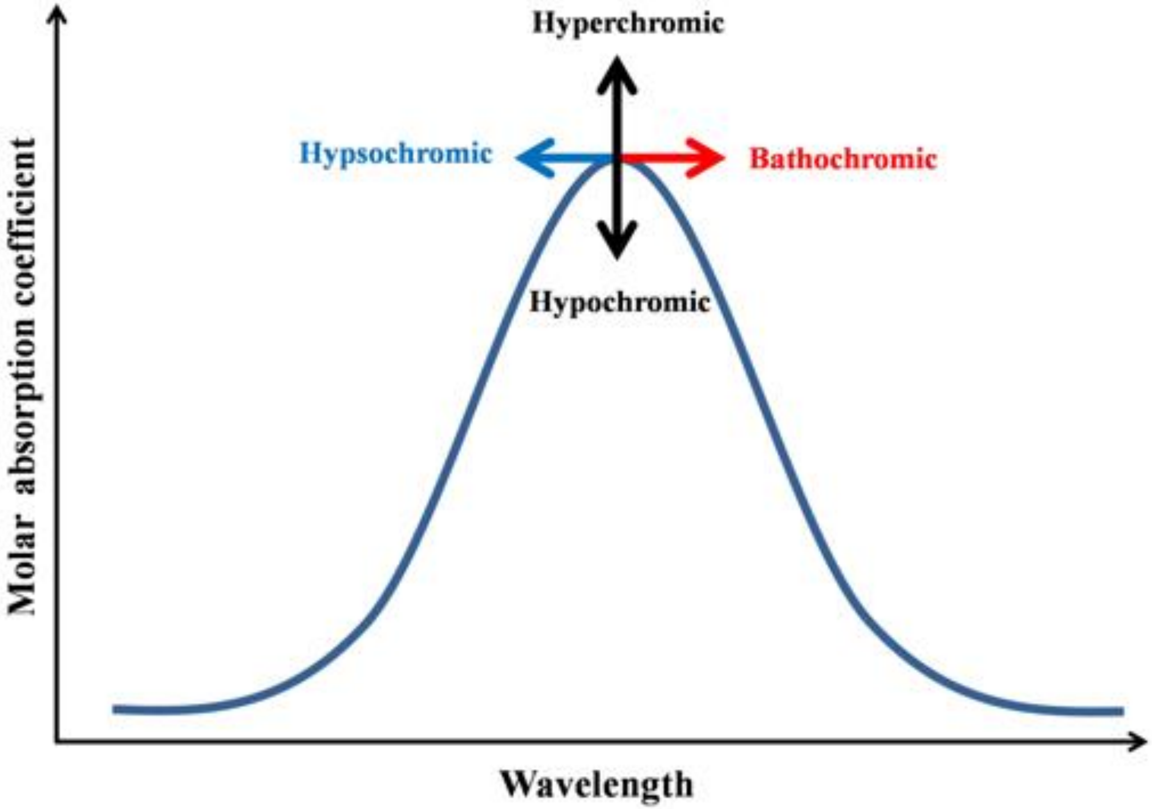
With increase in conjugation Wavelength Increases as conjugation lowers energy require for electronic transition

Effect of Conjugation in case of Carotene



Beta-carotene absorbs throughout the UV region but particularly strongly in the visible region between 400 and 500 nm with a peak at 470 nm.

Terms in UV Spectroscopy



Terms in UV Spectroscopy

- **Bathochromic shift** (Red shift) : Absorption to Longer Wavelength e.g : P-nitrophenol in basic medium
- **Hypsochromic shift** (Blue Shift) : absorption to shorter wavelength e.g Aniline shows Hypsochromic shift in acidic medium (Wavelength decreases due to removal of conjugation)
- **Hyperchromic Shift** : Absorption Intensity Increases
- **Hypochromic shift** : Absorption intensity decreases

Applications of UV- Visible Spectroscopy

- Identification of conjugated and non conjugated compounds
- To distinguish alpha beta diketone from gamma ,delta
- Examination of polynuclear hydrocarbons
- Configuration of geometrical isomers
- Stability of Keto – enol form
- Chemical kinetics