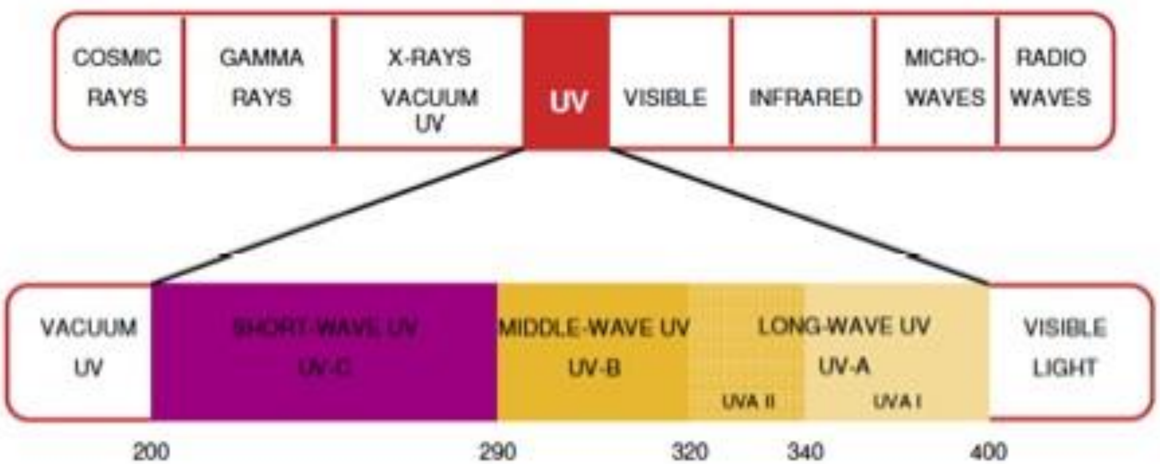
Ultraviolet-Visible Spectroscopy



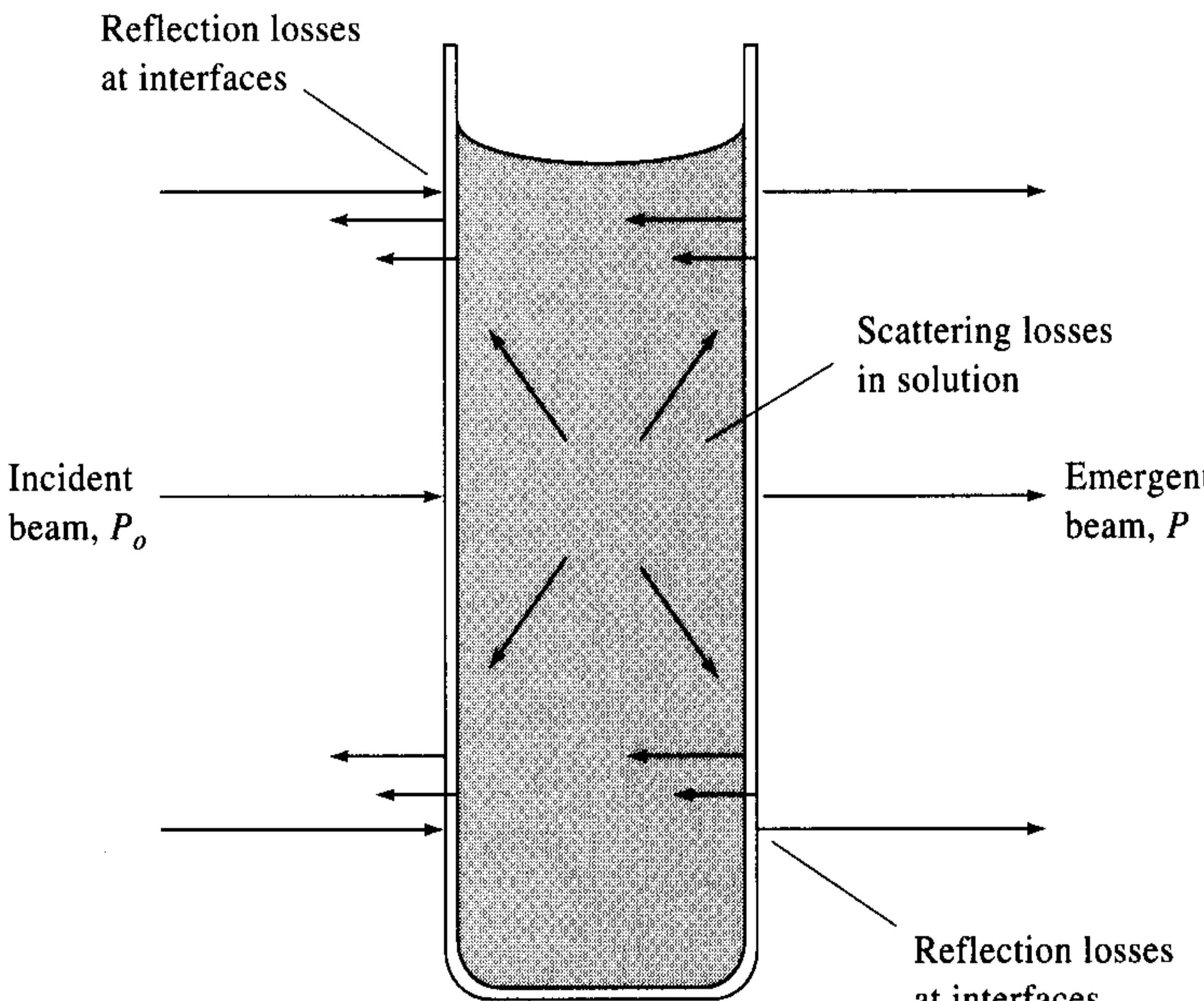


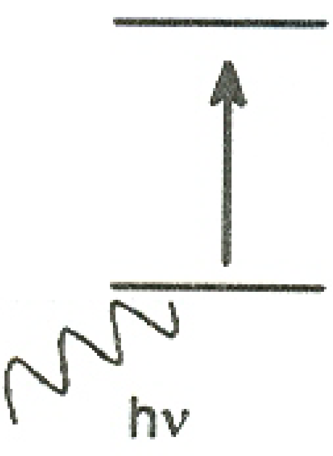
Figure 13-1 Reflection and scattering losses.

NATURE OF ELECTRONIC EXCITATIONS

Absorption: A transition from a lower level to a higher level with transfer of energy from the radiation field to an absorber, atom, molecule, or solid.

Emission: A transition from a higher level to a lower level with transfer of energy from the emitter to the radiation field.

(a)



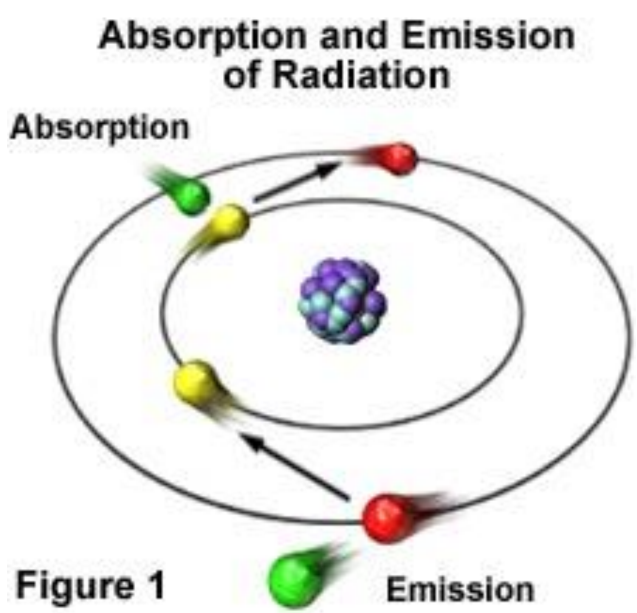
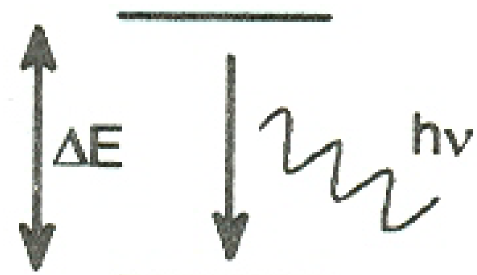
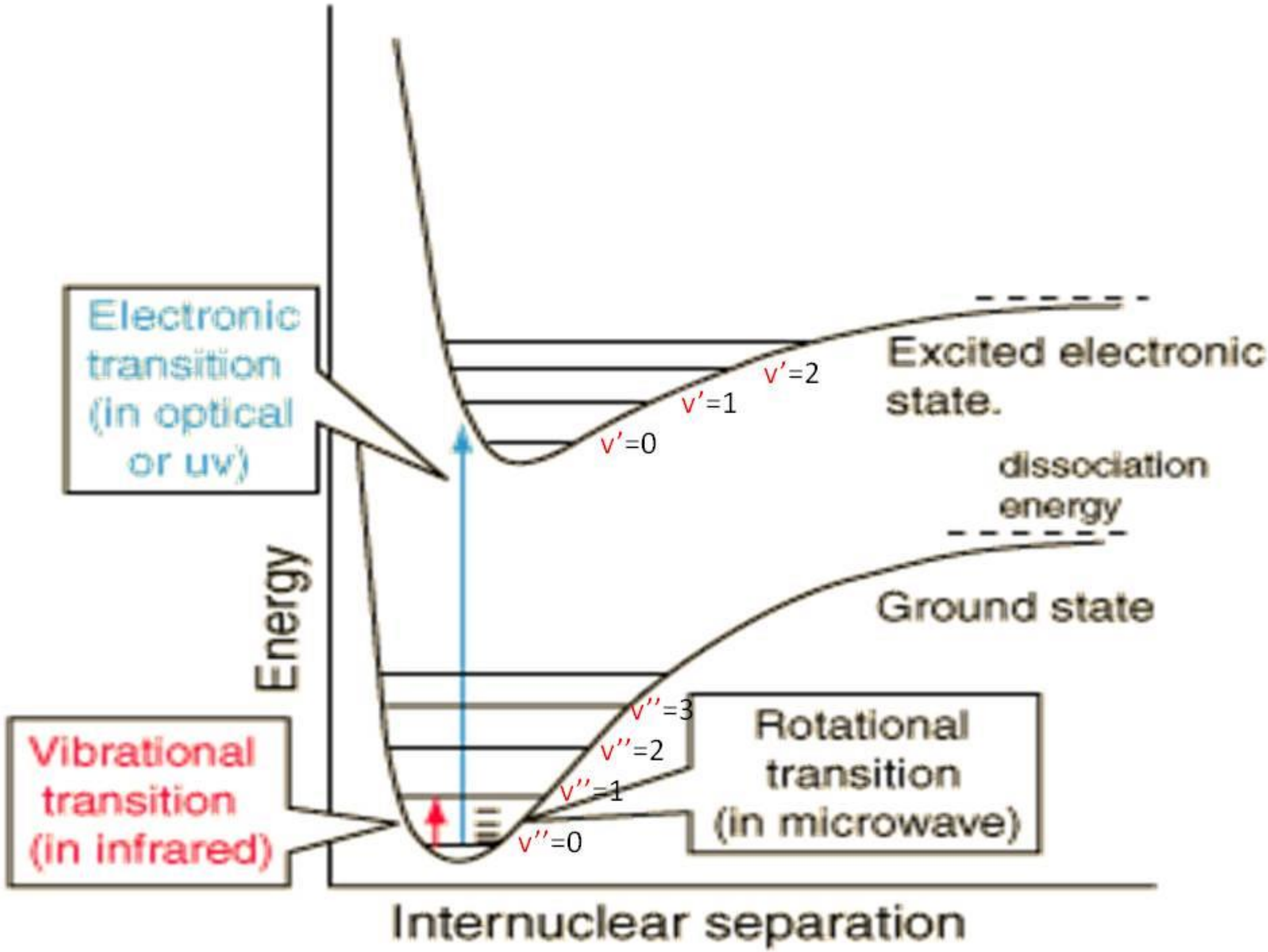


Figure 1

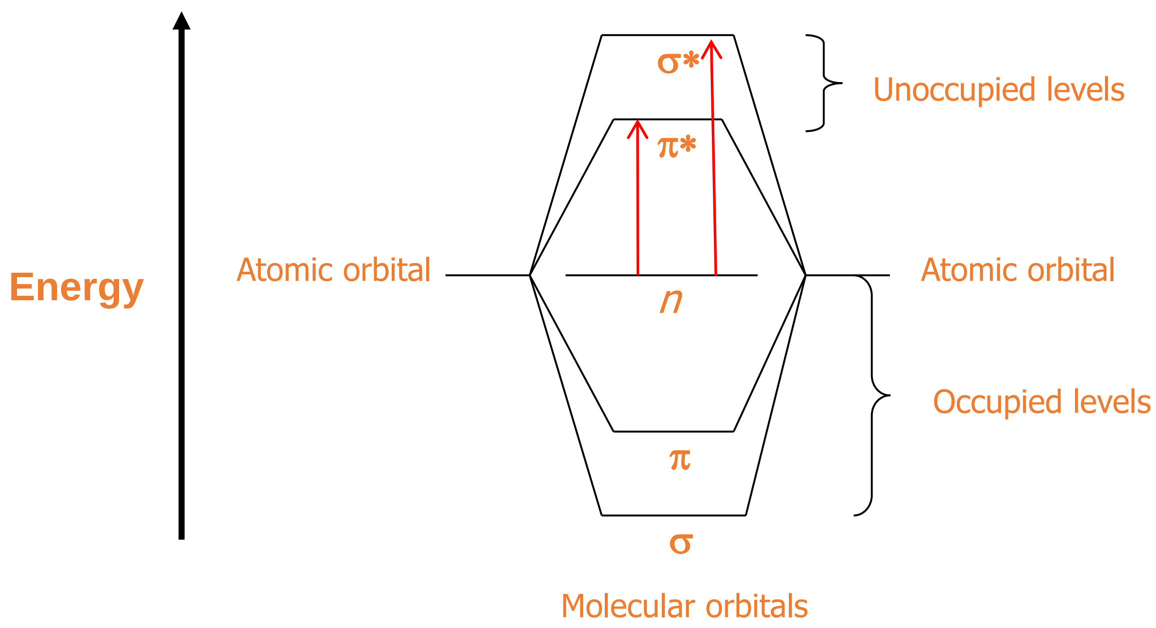
(b)




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

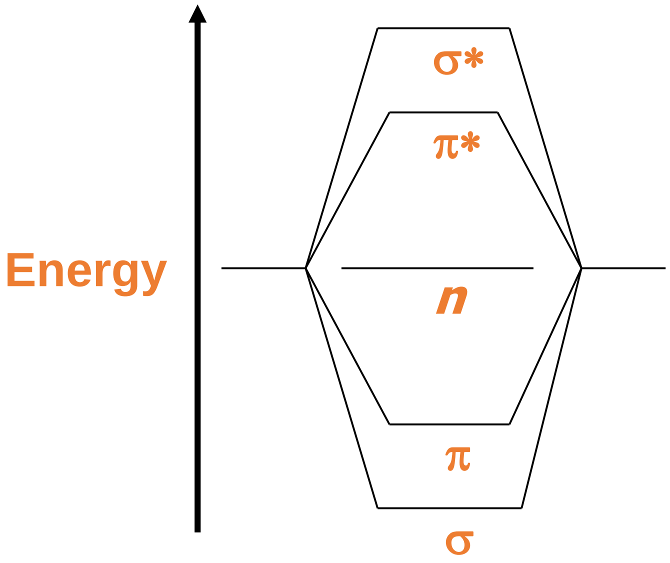
❑ The Spectroscopic Process

1. In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation
2. If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed
3. The remaining UV light passes through the sample and is observed
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)
Shorter wavelengths
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 generate 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

Radiation Sources

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

- **Deuterium arc lamp– covers the UV – 200-330**
- **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

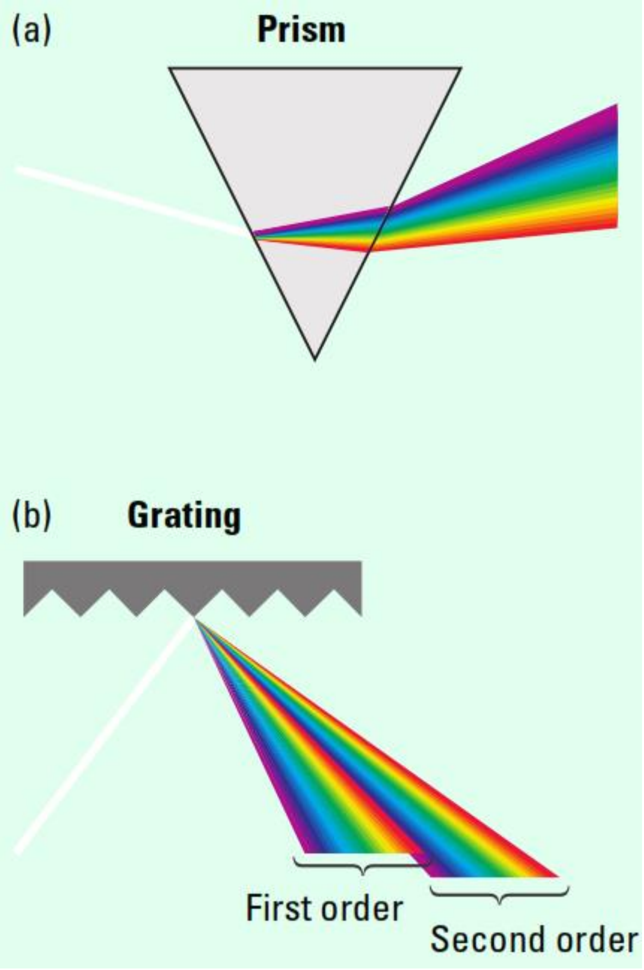
- **Monochromator: consists of an entrance slit, a dispersion device, and an exit slit.**

Dispersion devices

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

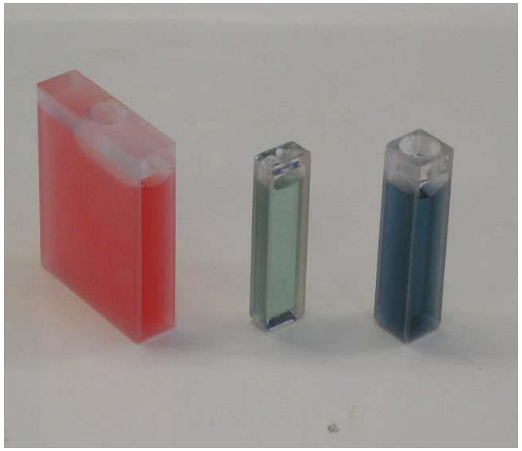
- When combined with an appropriate exit slit, these devices can be used to select a particular wavelength of light from a continuous source.

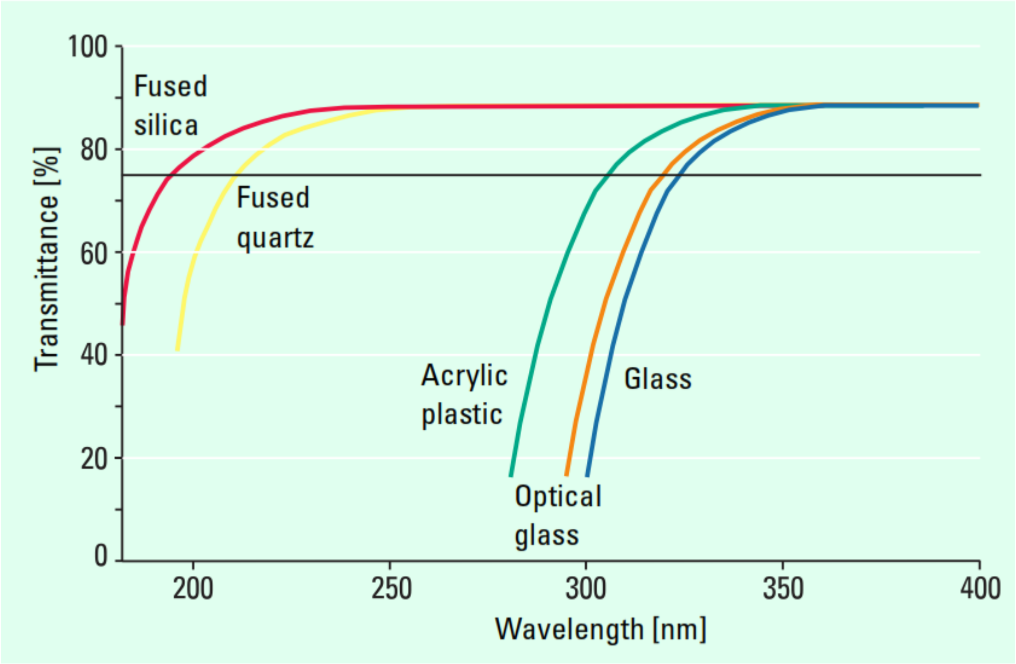
- Two types of commonly used dispersion devices:
    1. Prisms
    2. Holographic gratings



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

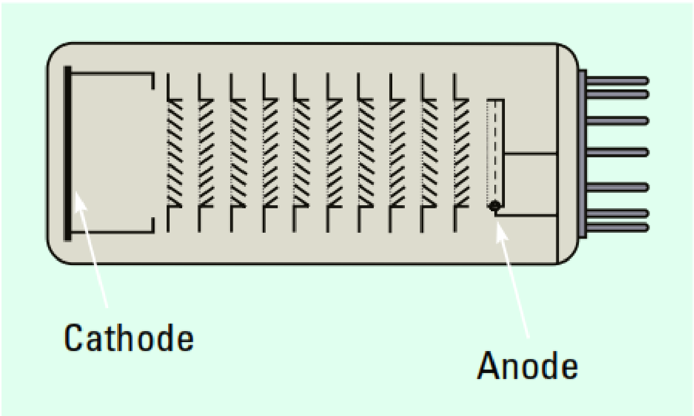




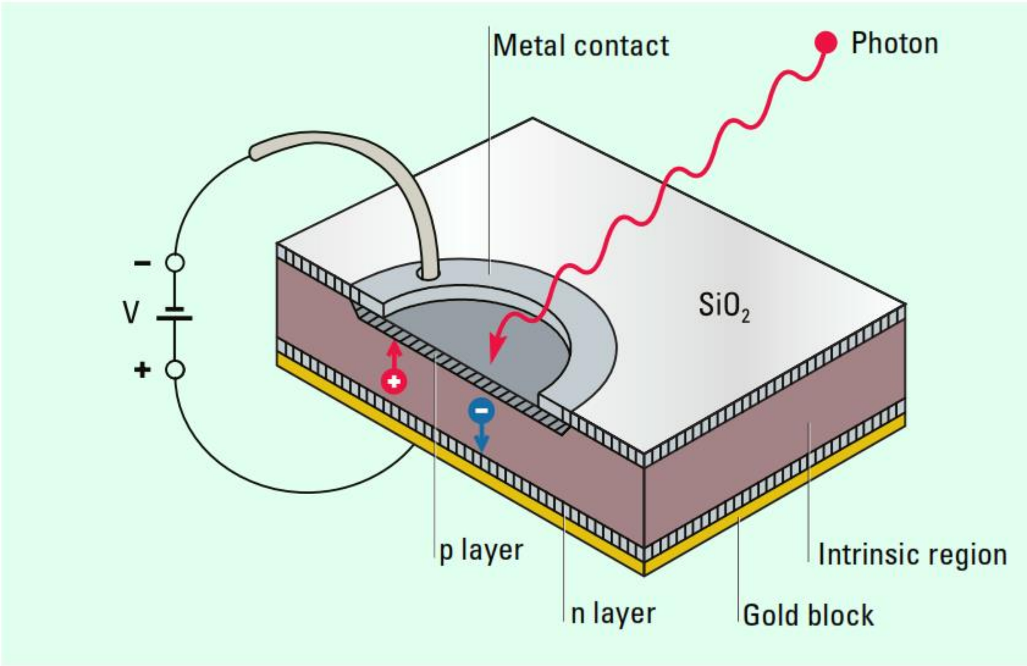
DETECTORS

- ❖A detector converts a light signal into an electrical signal.
- ❖Spectrophotometers normally contain

Photomultiplier tube detector
or a
Photodiode detector.

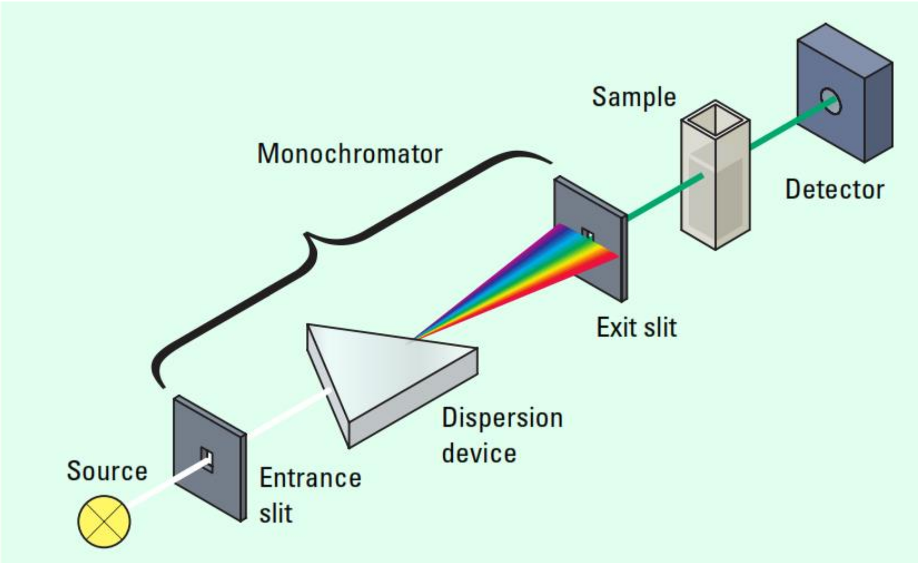


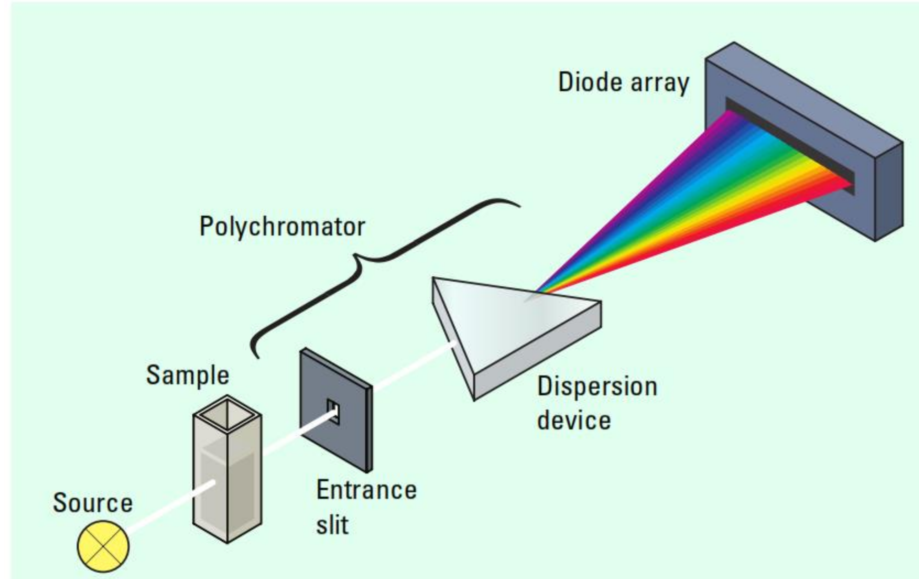
Photomultiplier tube



Photodiode

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)