Molecular Spectroscopy

Visible and UV Spectroscopy

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What is Spectroscopy?

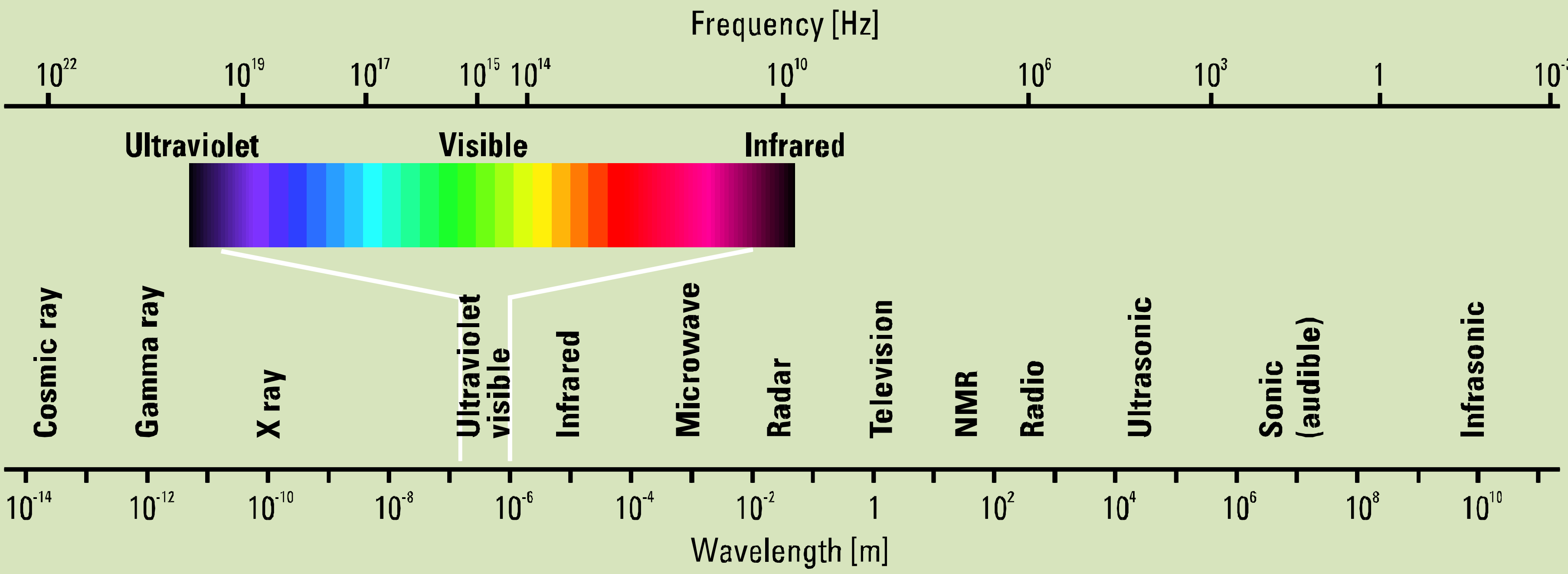
- The study of molecular structure and dynamics through the absorption, emission and scattering of light.

What is Light?

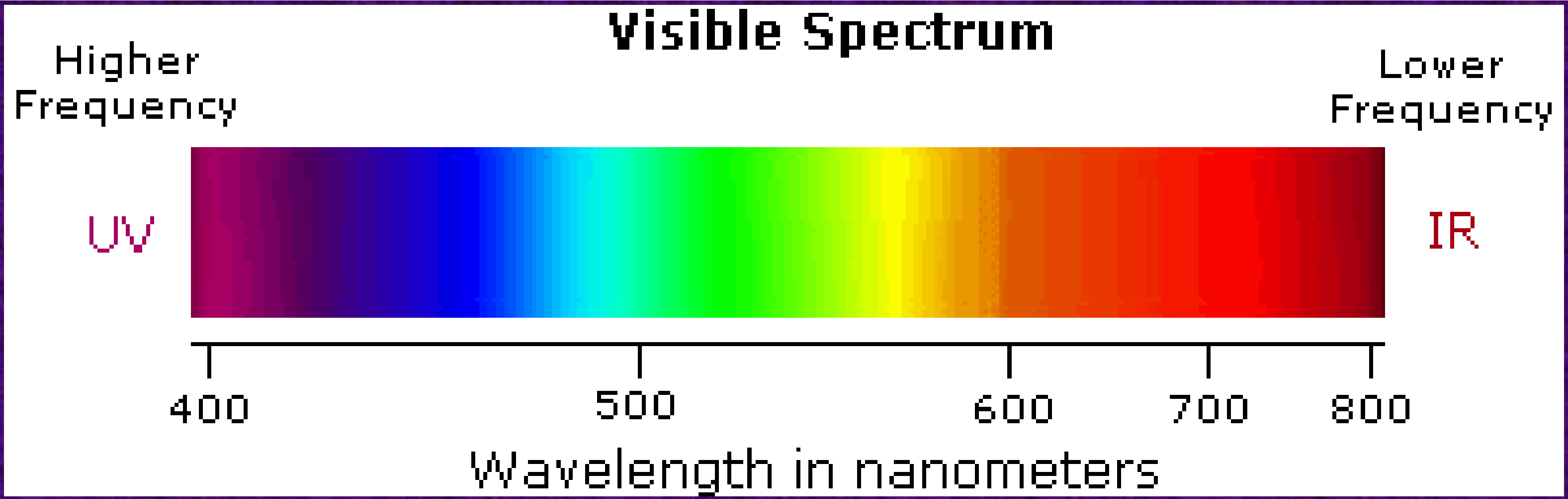
- According to Maxwell, light is an electromagnetic field characterized by a frequency f, velocity v, and wavelength λ. Light obeys the relationship

$$f = v / \lambda.$$

The Electromagnetic Spectrum



$E = h\nu$ $\nu = c / \lambda$



- Ultraviolet: 190~400nm
- Violet: 400 - 420 nm
- Indigo: 420 - 440 nm
- Blue: 440 - 490 nm
- Green: 490 - 570 nm
- Yellow: 570 - 585 nm
- Orange: 585 - 620 nm
- Red: 620 - 780 nm

Spectroscopy

Spectral Distribution of Radiant Energy

Wave Number (cycles/cm)

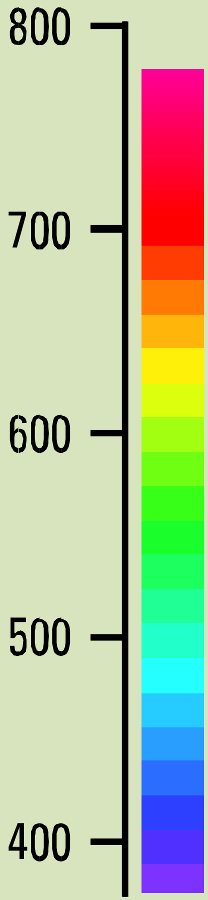
X-Ray	**UV**	**Visible**	**IR**	**Microwave**

200nm **400nm** **800nm**

WAVELENGTH(nm)

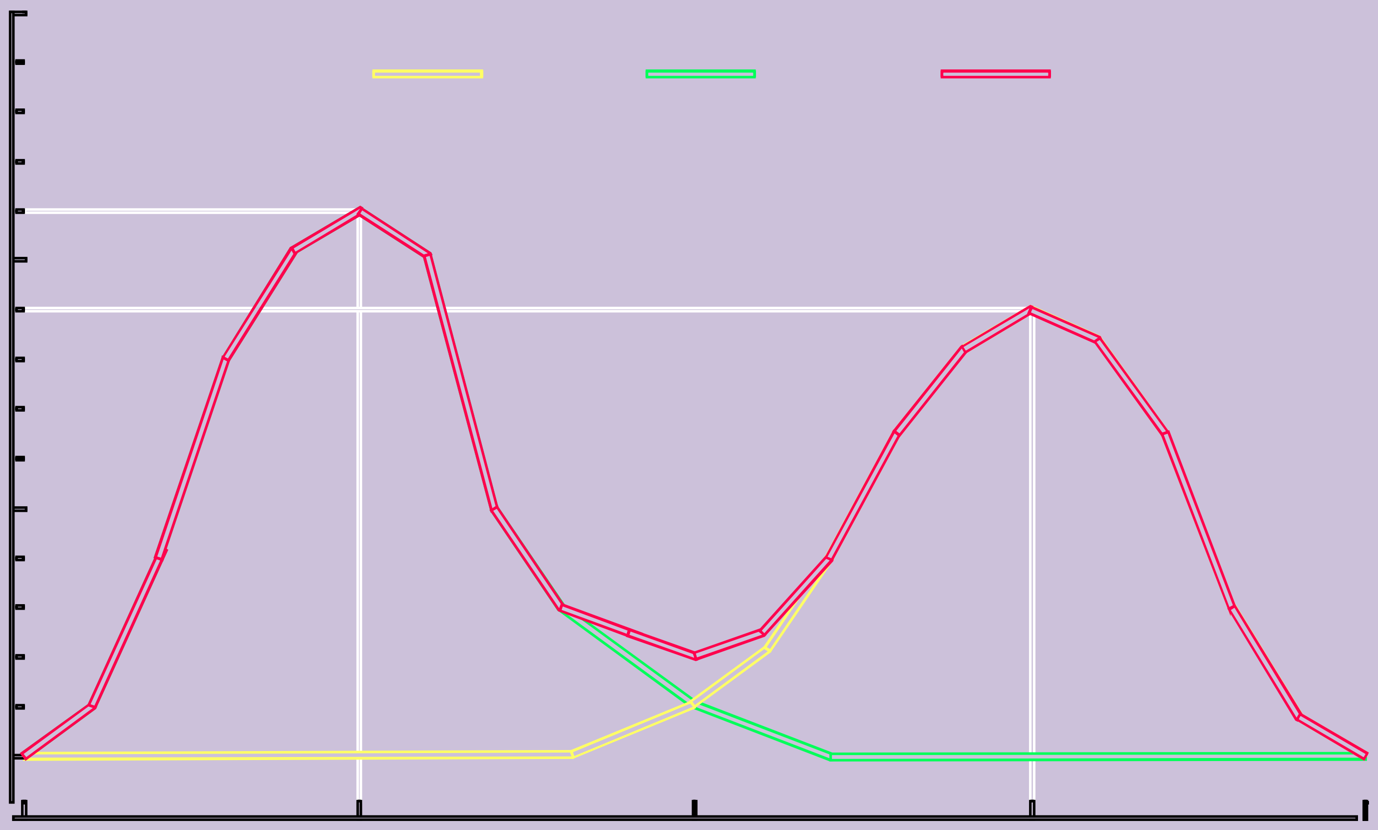
Absorbance and Complementary Colors

The human eye sees the complementary color to that which is absorbed



Wavelength [nm]	Absorbed color	Complementary color
650-780	red	blue-green
595-650	orange	greenish blue
560-595	yellow-green	purple
500-560	green	red-purple
490-500	bluish green	red
480-490	greenish blue	orange
435-480	blue	yellow
380-435	violet	yellow-green

A two-component mixture with little spectral overlap



Ultraviolet-Visible Spectroscopy

- Introduction to UV-Visible
  - Absorption spectroscopy from 160 nm to 780 nm
  - Measurement of transmittance
    - Conversion to absorbance
      - $A = -\log T = \varepsilon b c$
- Measurement of transmittance and absorbance
- Beer's law
- Noise
- Instrumentation

Measurement

- Scattering of light
  - Refraction at interfaces
  - Scatter in solution
    - Large molecules
    - Air bubbles
- Normalized by comparison to reference cell
  - Contains only solvent
    - Measurement for transmittance is compared to results from reference cell

Beer's Law

- Based on absorption of light by a sample
  - $dP_x/P_x = dS/S$
    - dS/S=ratio of absorbance area to total area
      - Proportional to number of absorbing particles
    - dS=adn
      - a is a constant, dn is number of particles
  - n is total number of particles within a sample

$$-\int_{P_o}^{P} \frac{dP_x}{P_x} = \int_0^n \frac{adn}{S}$$

$$-\ln \frac{P_o}{P} = \frac{an}{S}$$

$$\log \frac{P_o}{P} = \frac{an}{2.303S}$$

Beer's Law

- Area S can be described by volume and length
  - S=V/b (cm^2)
  - Substitute for S
  - n/V = concentration
  - Substitute concentration and collect constant into single term ε
- Beer's law can be applied to mixtures
  - $A_{tot}=\Sigma A_x$

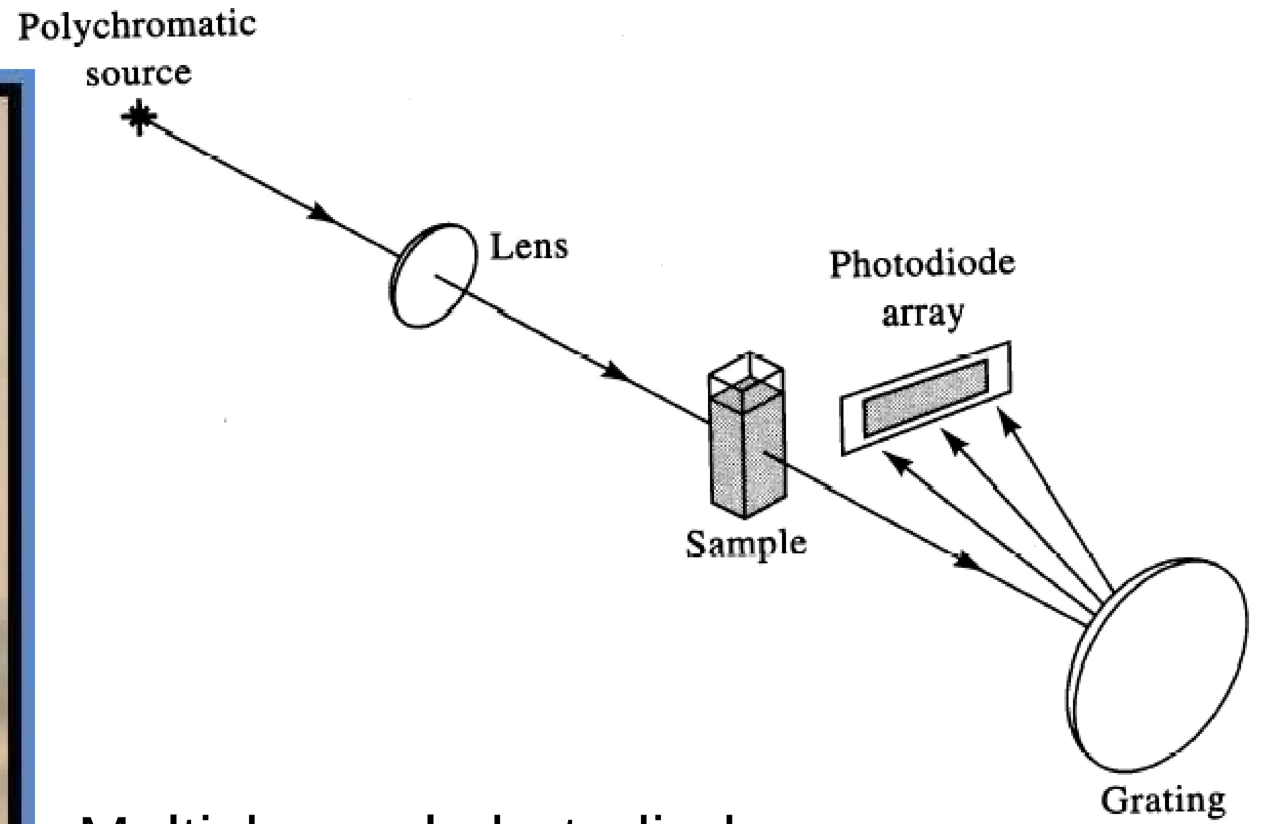
$$\log \frac{P_o}{P} = \frac{anb}{2.303V}$$

Instrumentation

- Light source
  - Deuterium and hydrogen lamps
  - W filament lamp
  - Xe arc lamps
- Sample containers
  - Cuvettes
    - Plastic
    - Glass
    - Quartz

Spectrometer

Dip probe



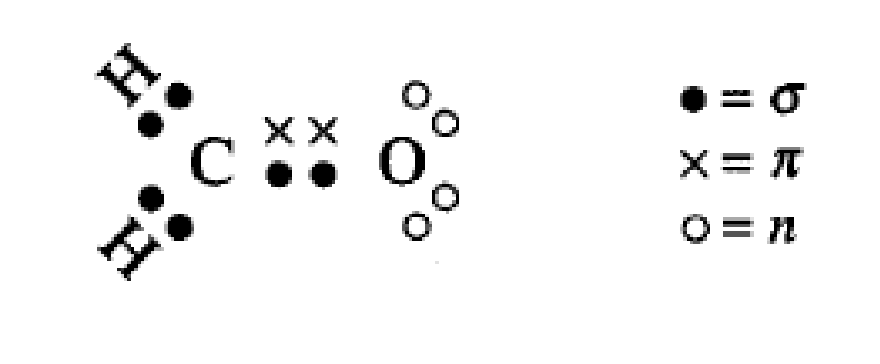
Multichannel photodiode array

UV-Visible Spectroscopy--- Applications

- Identification of inorganic and organic species
- Widely used method
- Magnitude of molar absorptivities
- Absorbing species
- methods

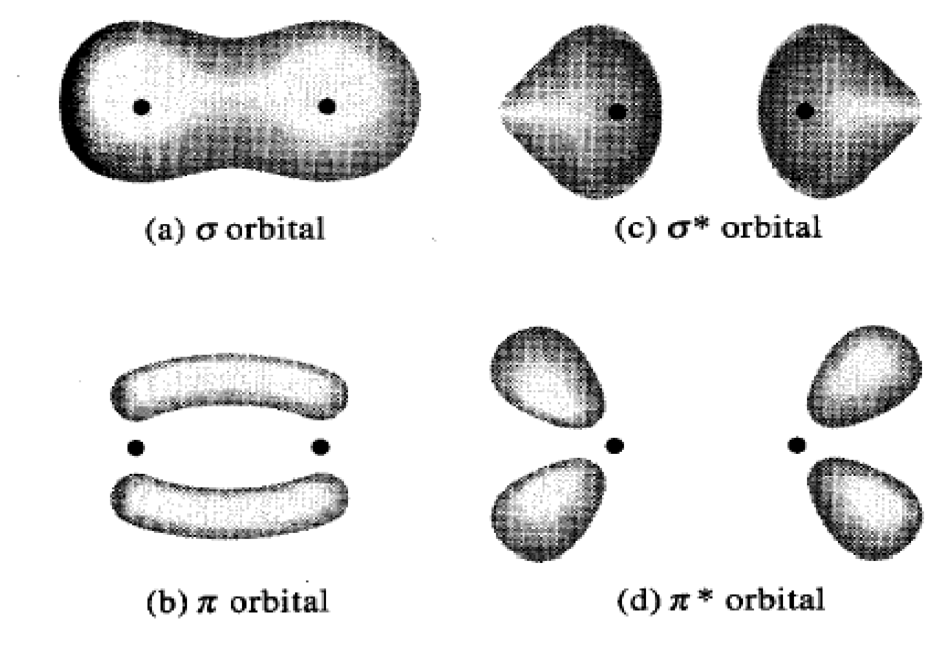
Absorbing species

- Electronic transitions
  - π, σ, and n electrons
  - d and f electrons
  - Charge transfer reactions

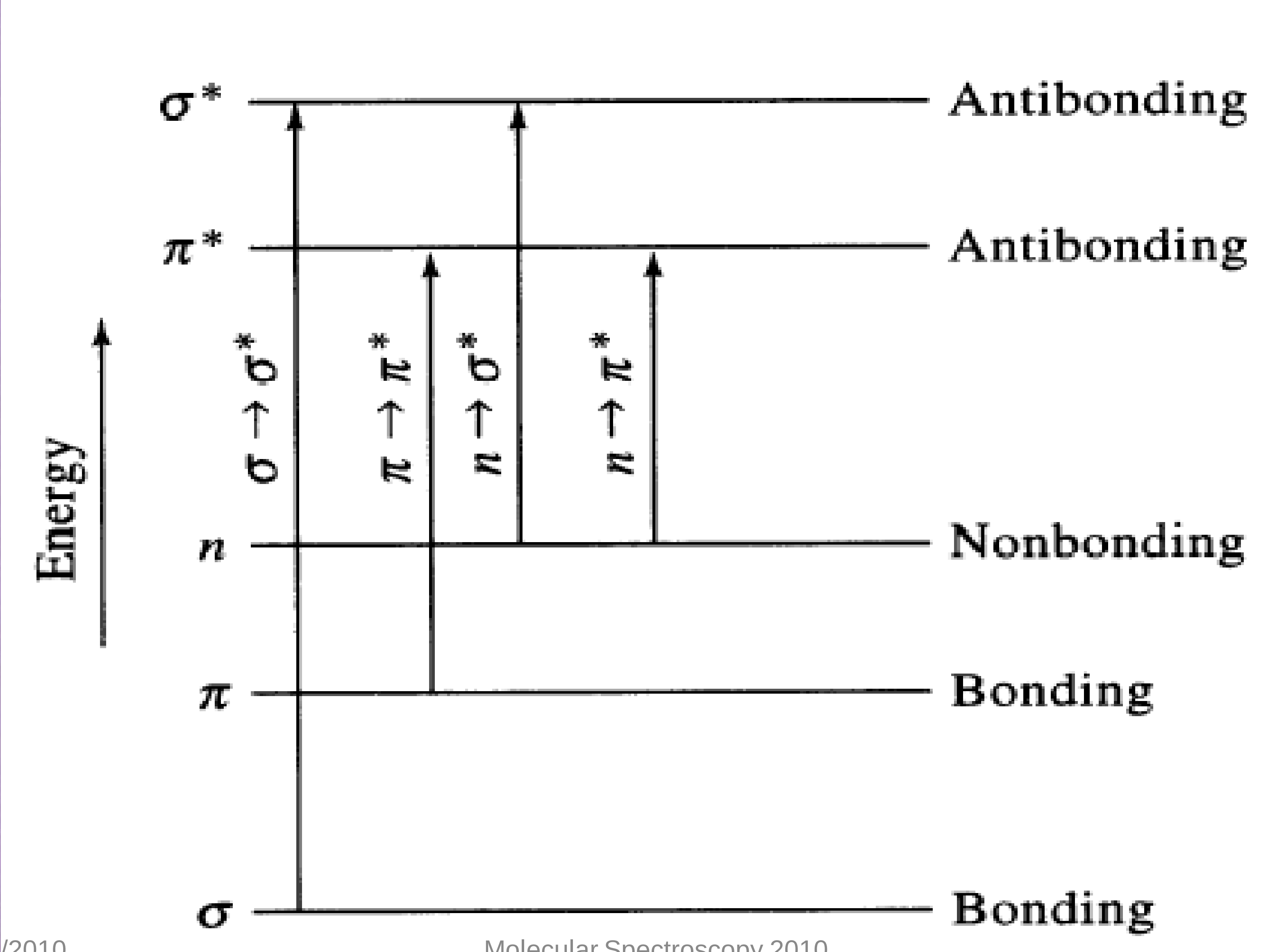


- π, σ, and n (non-bonding) electrons

Sigma and Pi orbitals



Electron transitions



Transitions

- σ–>σ*
  - UV photon required, high energy
    - Methane at 125 nm
    - Ethane at 135 nm
- 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)

Light Sources

UV Spectrophotometer

1. Hydrogen Gas Lamp
2. Mercury Lamp

Visible Spectrophotometer

1. Tungsten Lamp

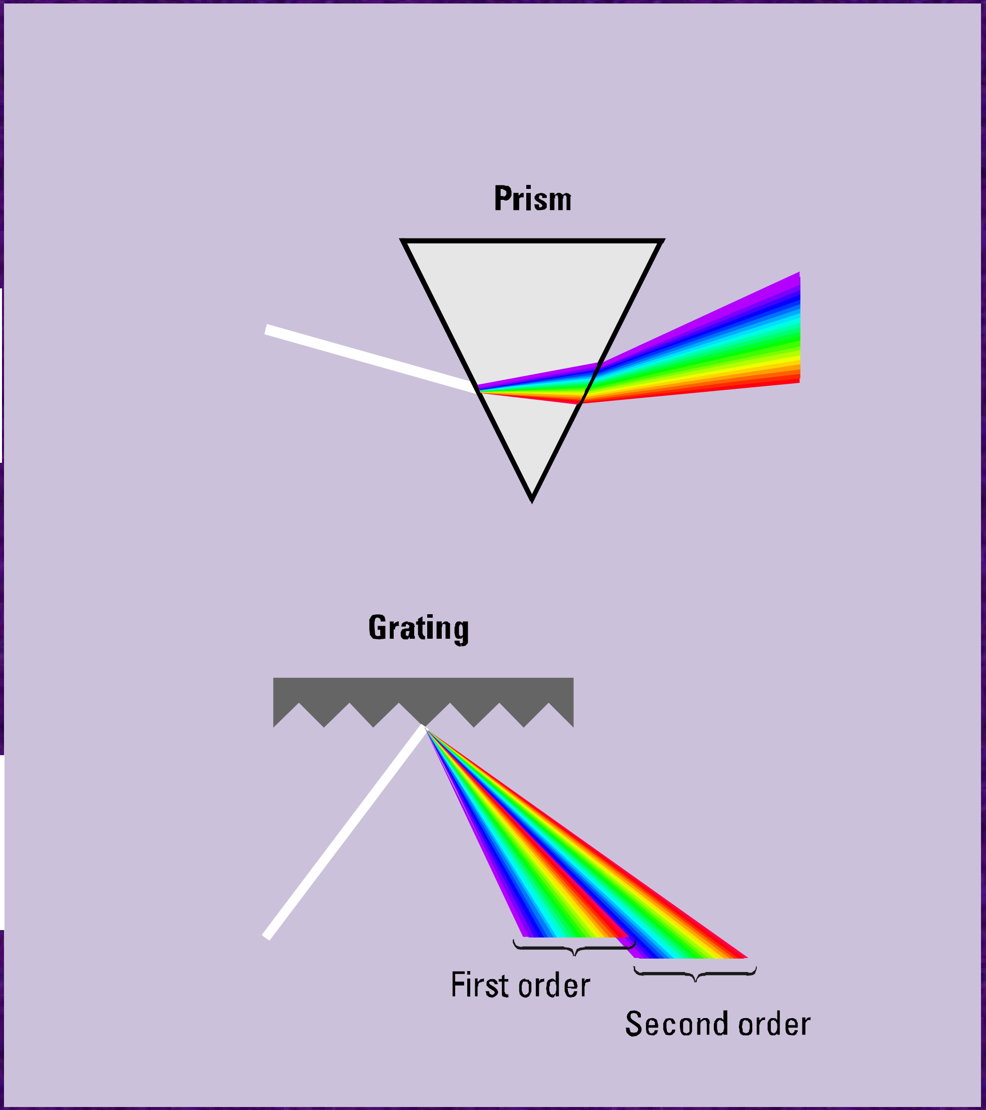
InfraRed (IR) Spectrophotometer

1. Carborundum (SIC)

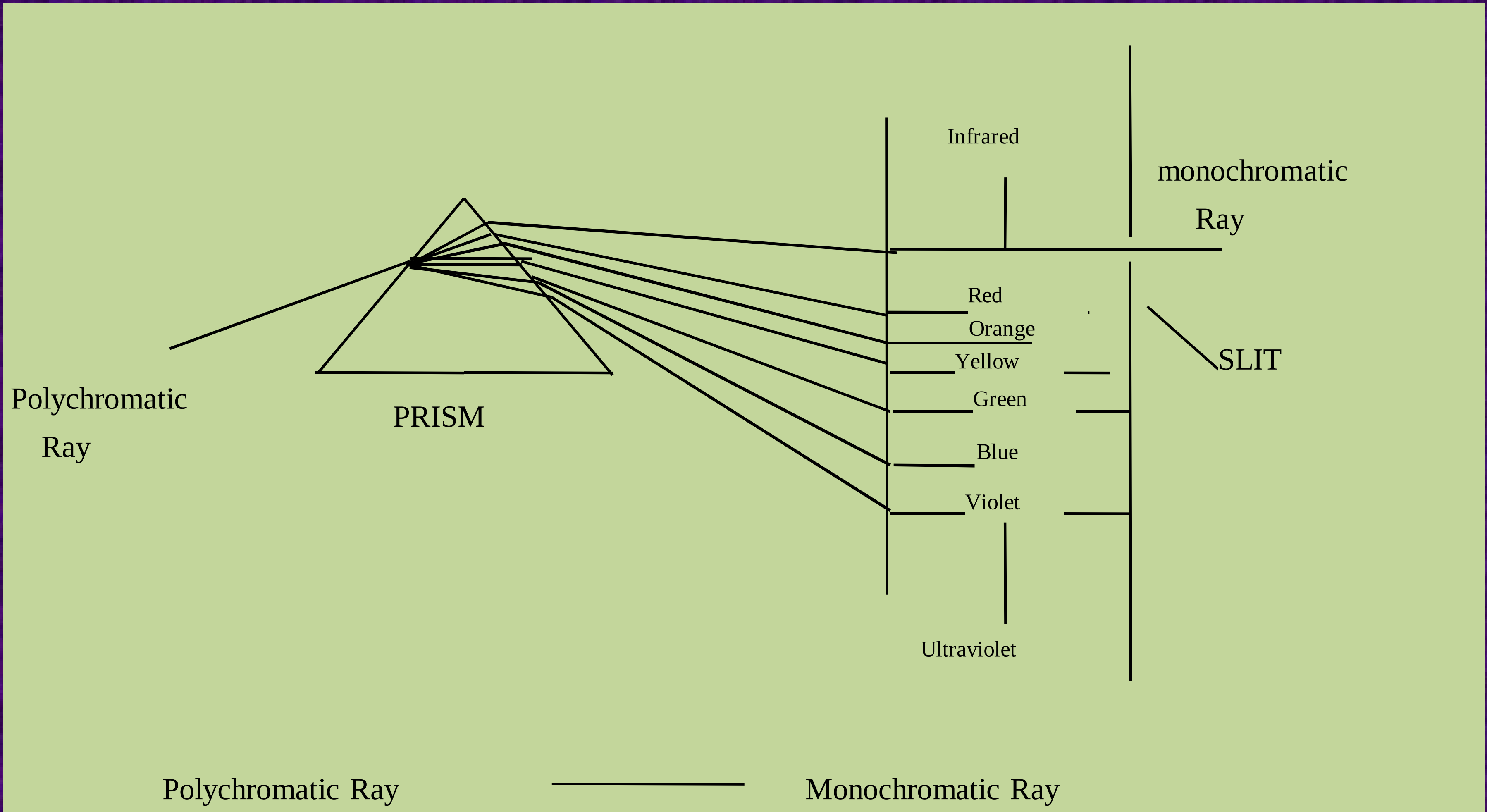
Dispersion Devices

- **Non-linear dispersion**
- **Temperature sensitive**

- **Linear Dispersion**
- **Different orders**



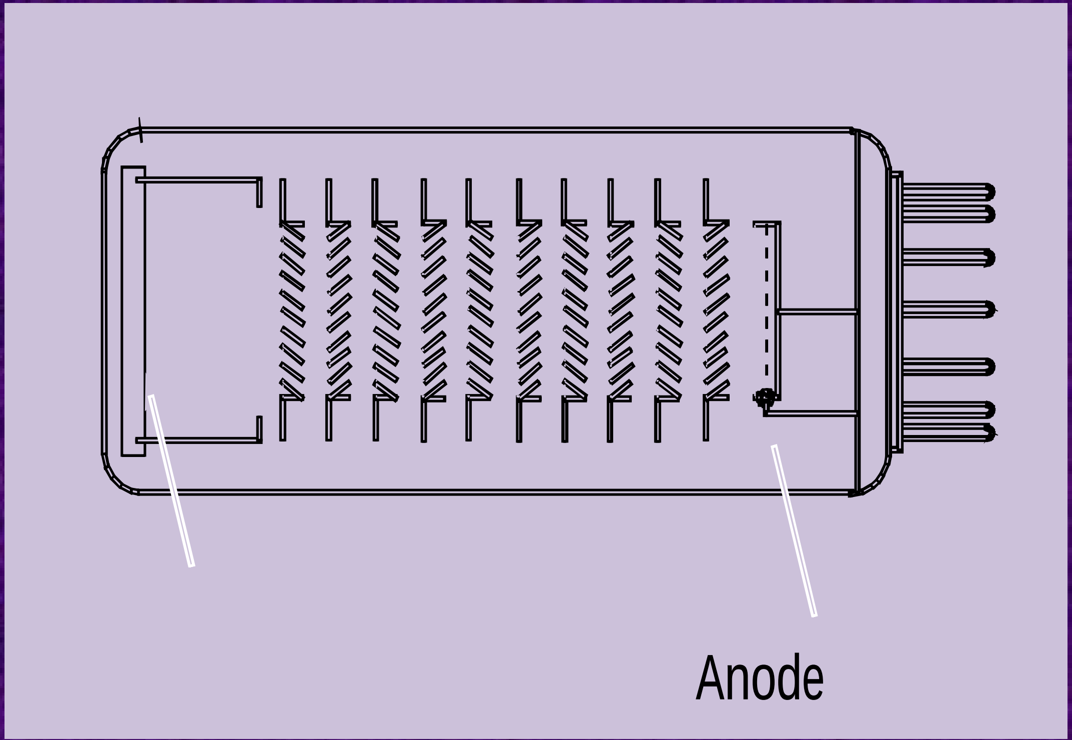
Dispersion of polychromatic light with a prism



Prism - spray out the spectrum and choose the certain wavelength (l) that you want by moving the slit.

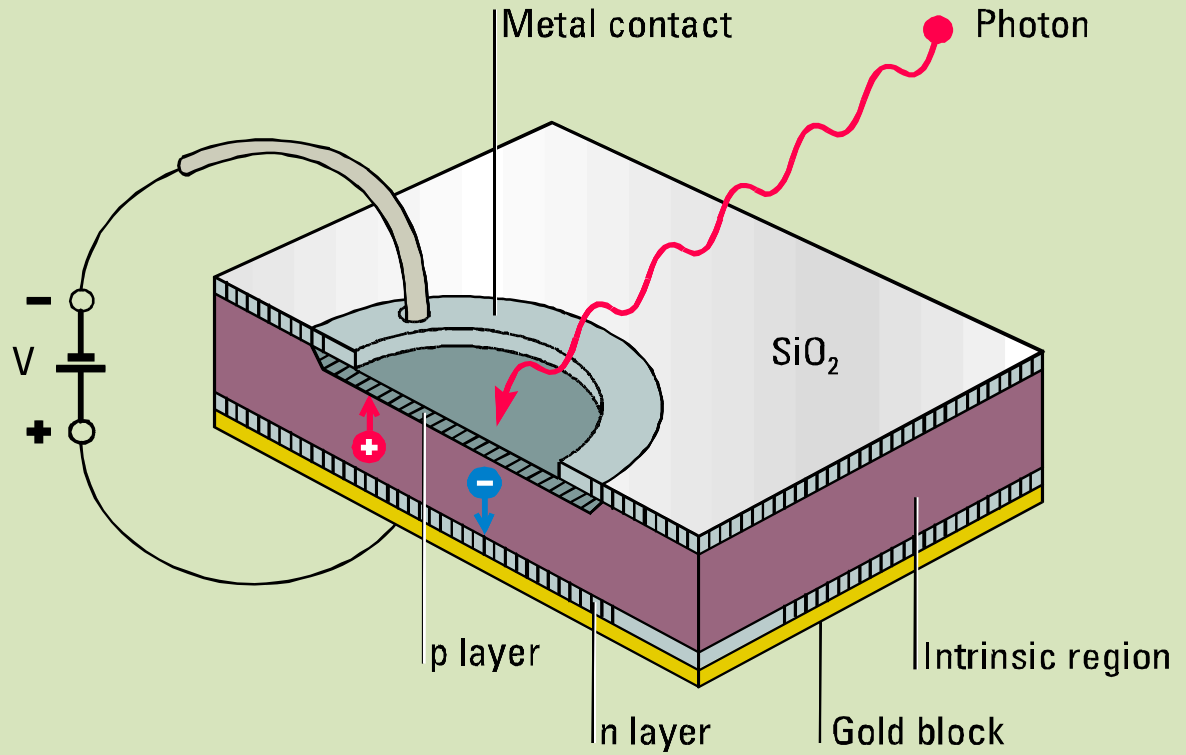
Photomultiplier Tube Detector

- High sensitivity at low light levels
- Cathode material determines spectral sensitivity
- Good signal/noise
- Shock sensitive

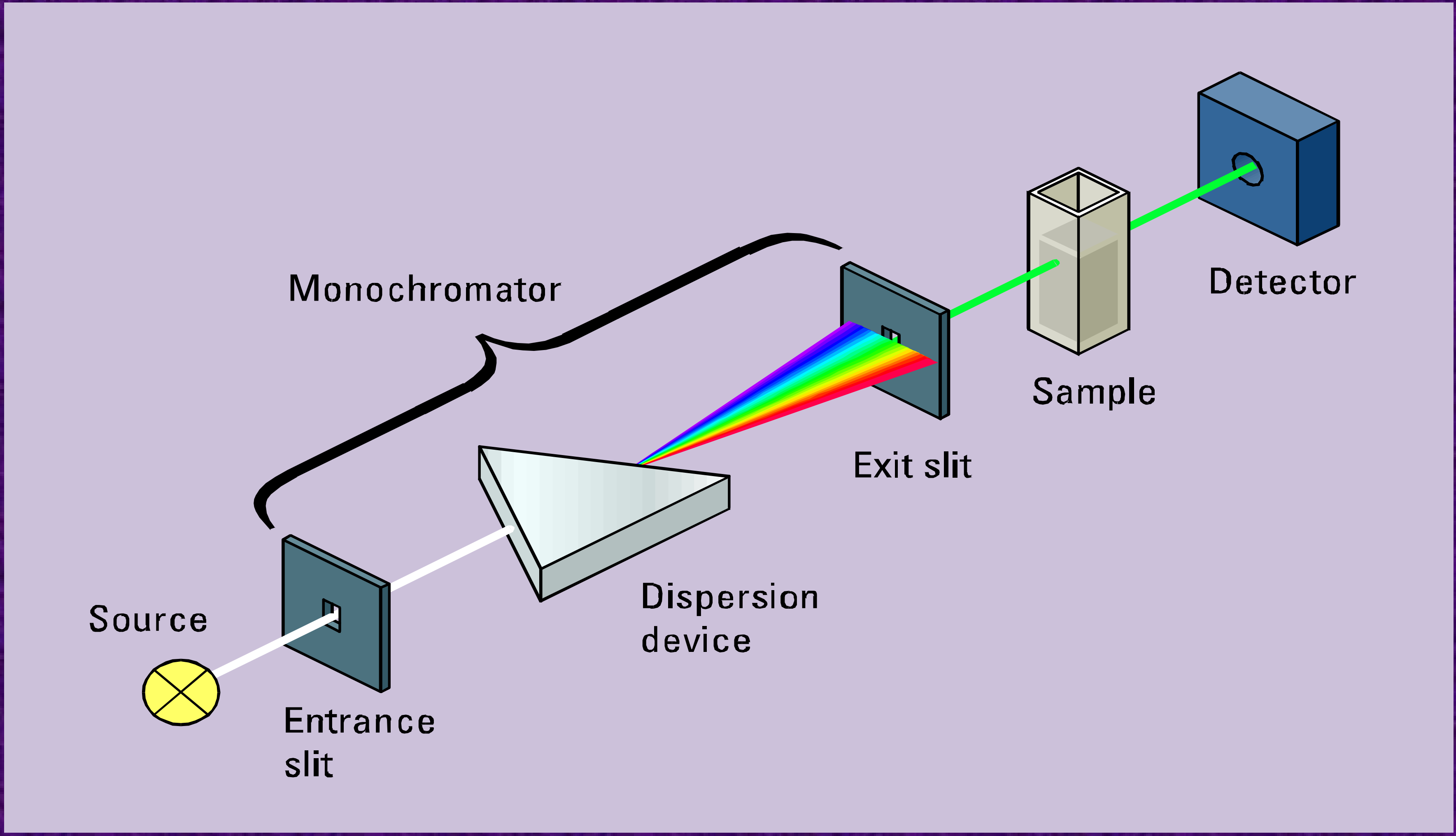


The Photodiode Detector

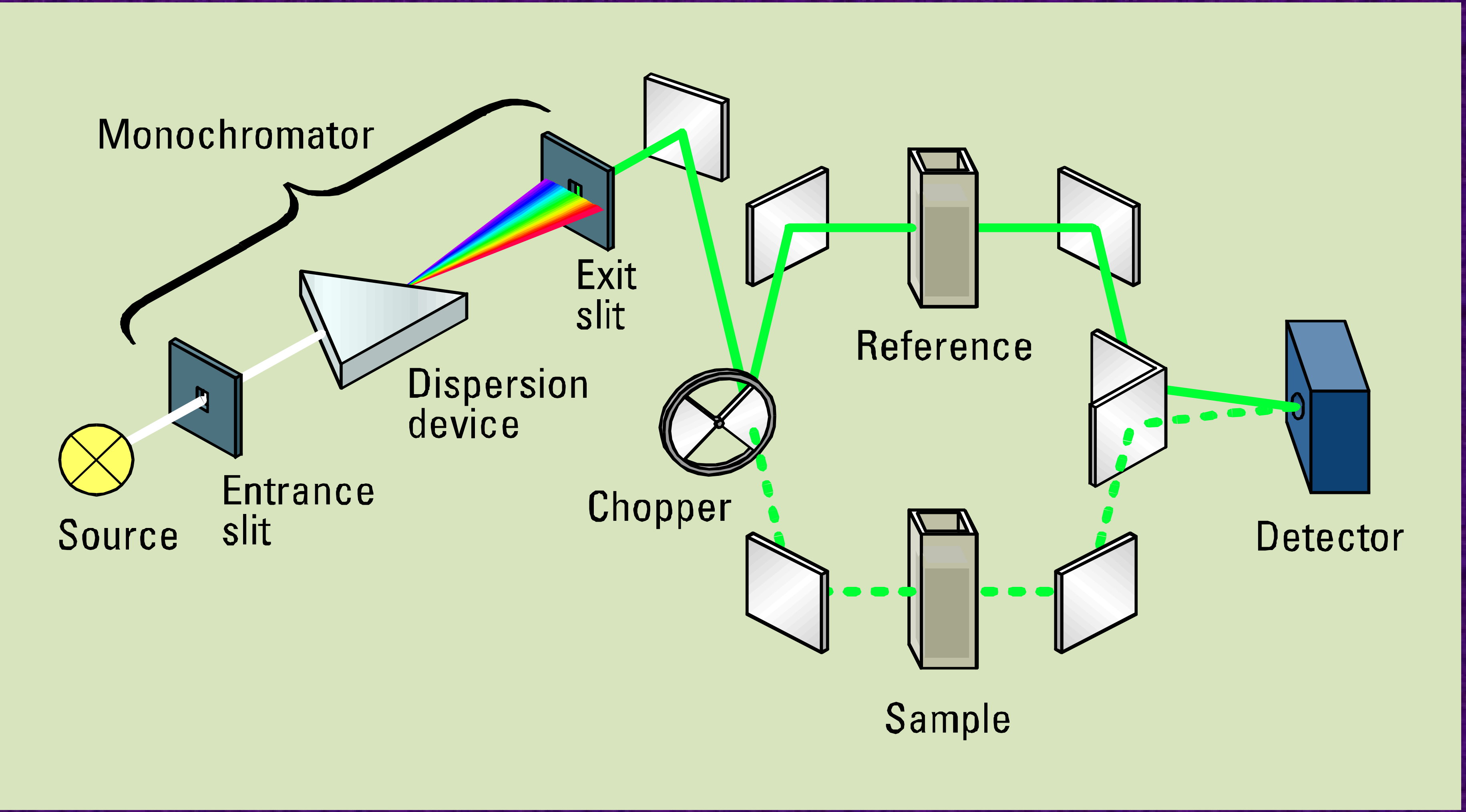
- Wide dynamic range
- Very good signal/noise at high light levels
- Solid-state device



Conventional Spectrophotometer

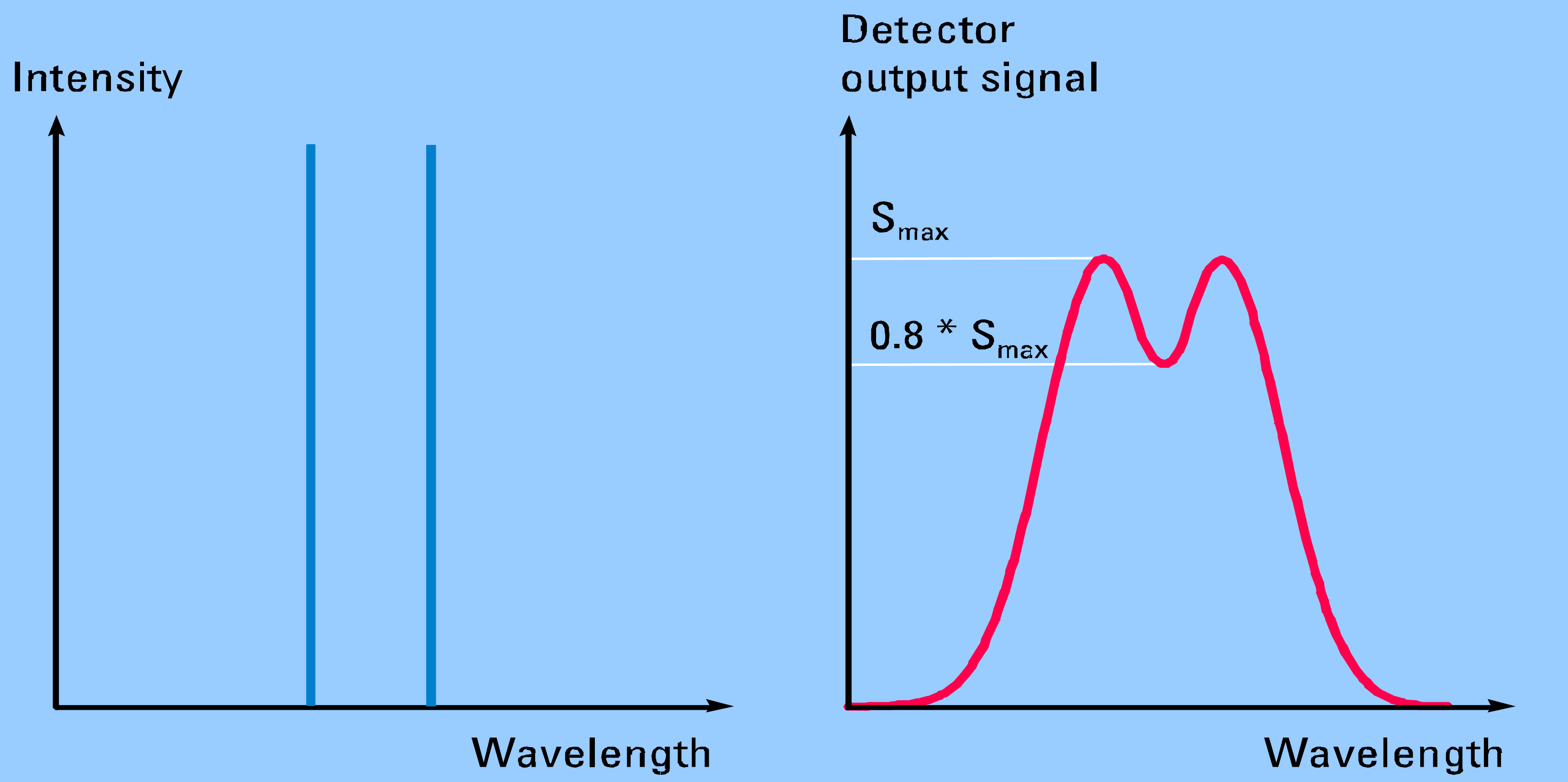


Schematic of a conventional single-beam spectrophotometer



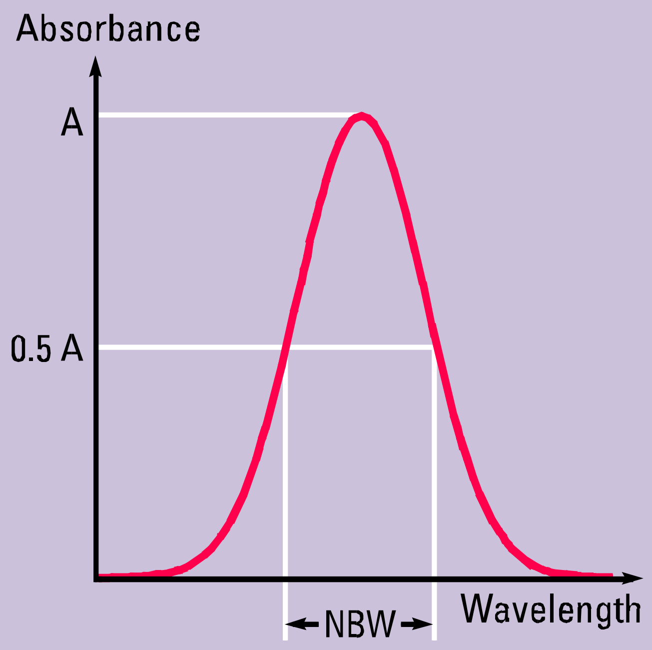
Optical system of a double-beam spectrophotometer

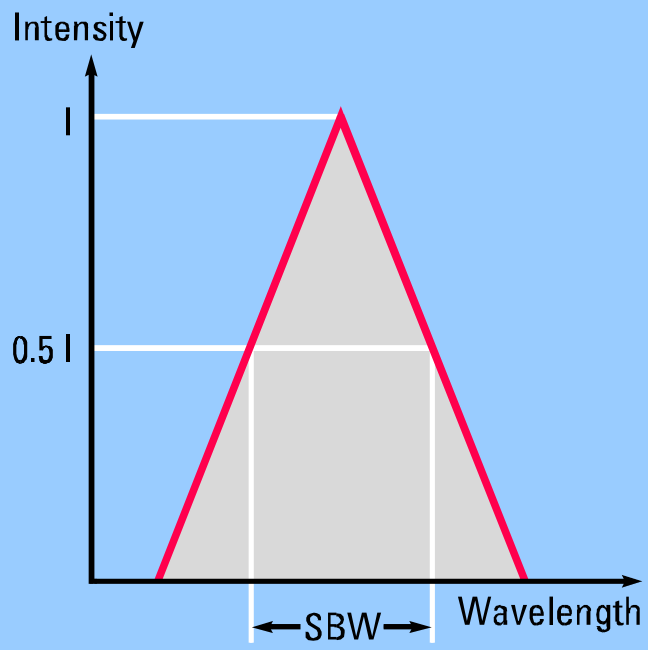
Resolution



Spectral resolution is a measure of the ability of an instrument to differentiate between two adjacent wavelengths

Natural Spectral Bandwidth	Instrumental Spectral Bandwidth





The NBW is the width of the sample absorption band at half the absorption maximum

The SBW is defined as the width, at half the maximum intensity, of the band of light leaving the monochromator

Cells

UV Spectrophotometer

Quartz (crystalline silica)

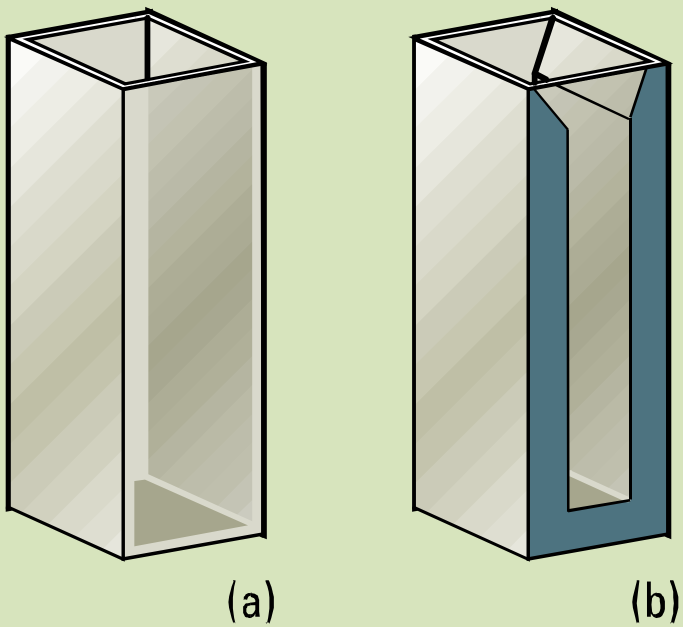
Visible Spectrophotometer

Glass

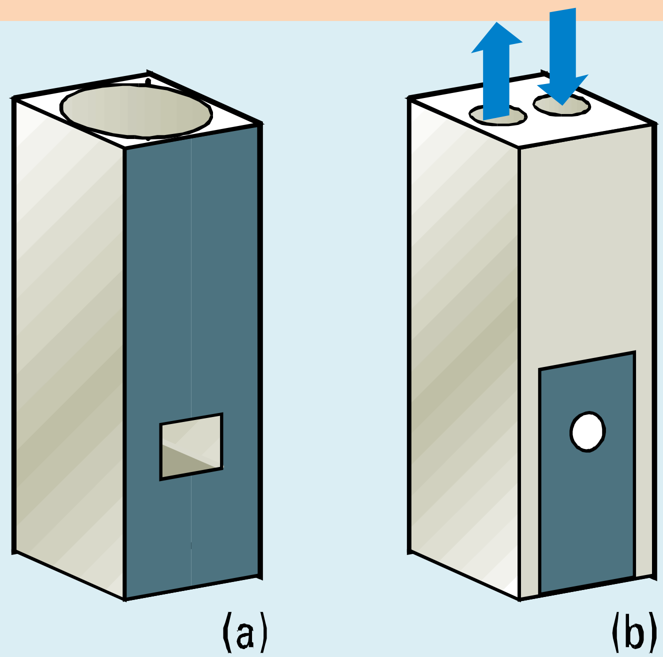
IR Spectrophotometer

NaCl

Cell Types I



Cell Types II

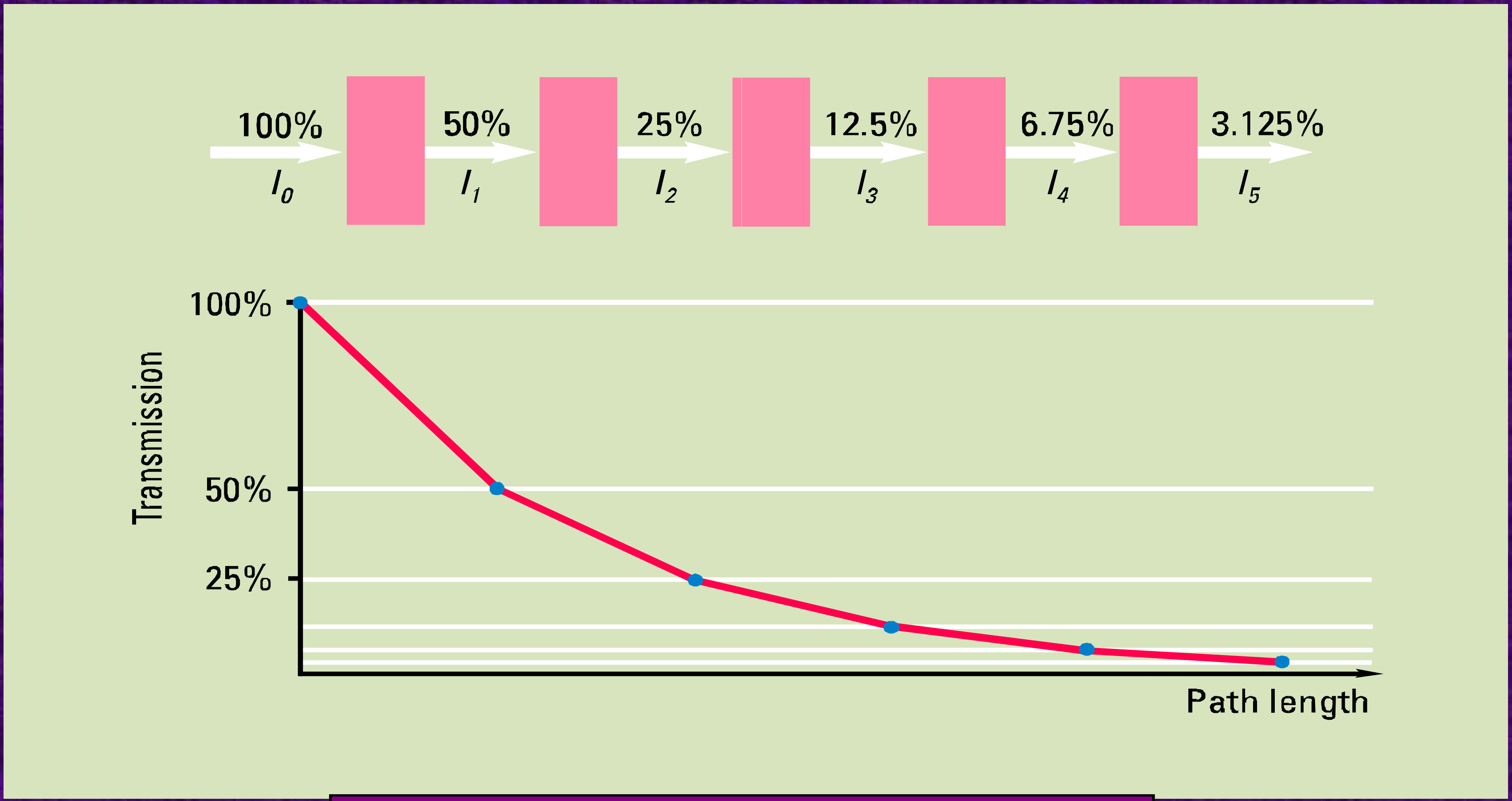


Open-topped rectangular standard cell
(a) an apertured cell
(b) for limited sample volume

Micro cell (a) for very small volumes and flow-through cell
(b) for automated applications

The Bouguer-Lambert Law

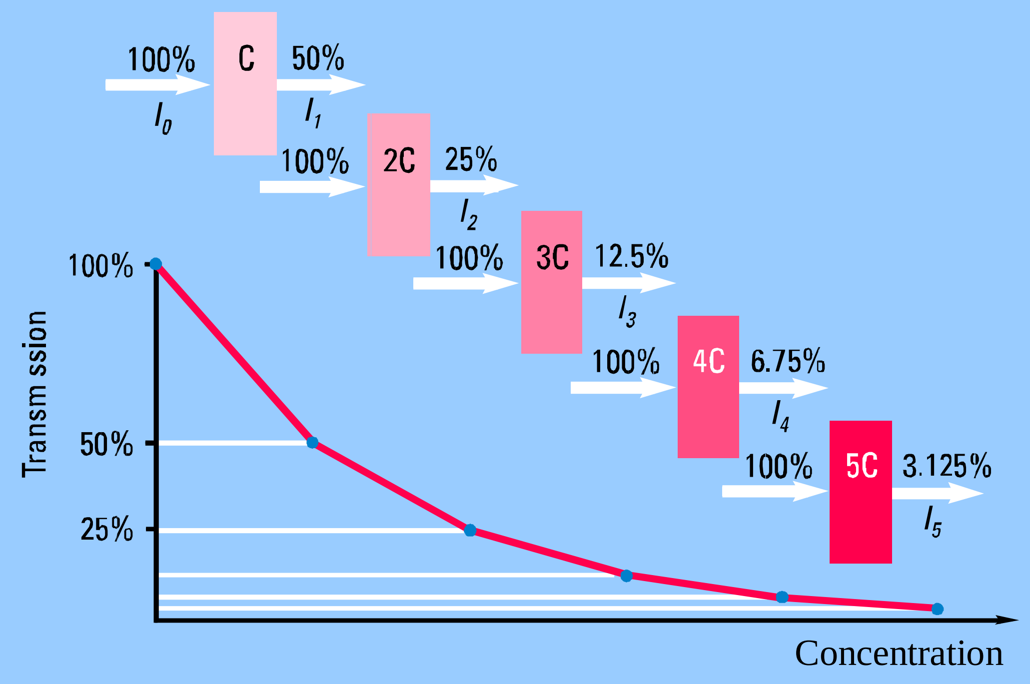
Transmittance and Concentration



$$T = I / I_0 = e^{-Const \cdot Pathlength}$$

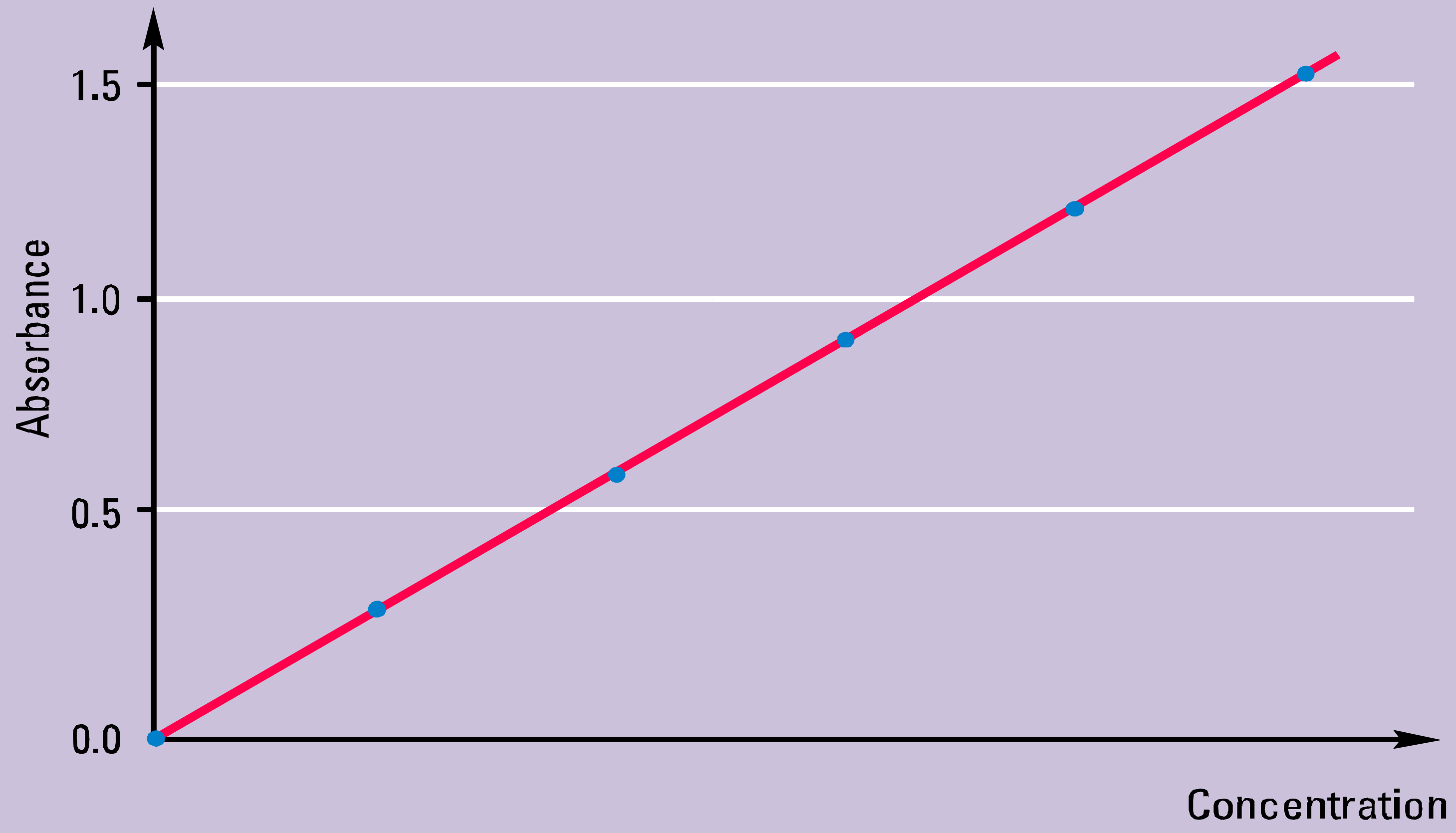
Beer's Law

Transmittance and Path Length



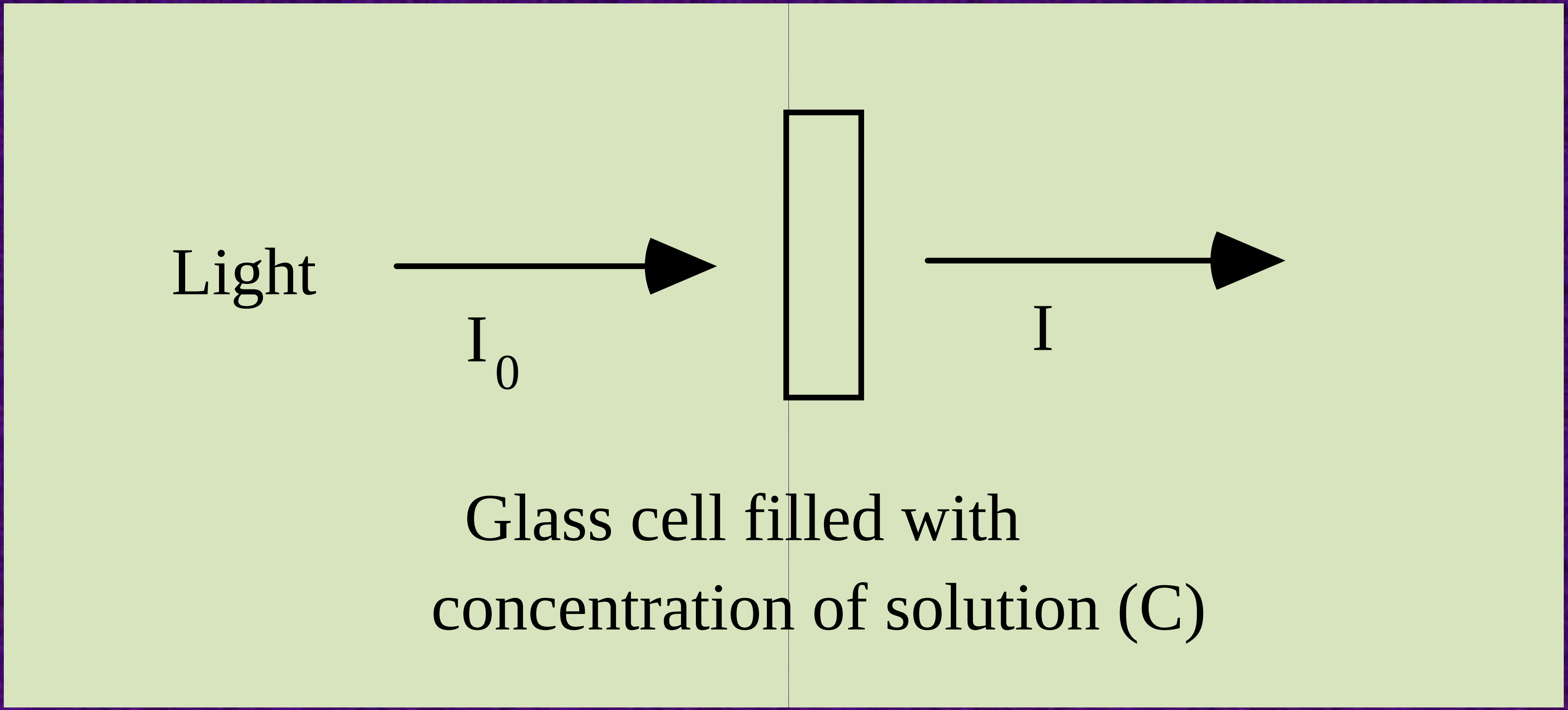
$$T = I / I_0 = e^{-Const \cdot Concentration}$$

The Beer-Bouguer-Lambert Law



$$A = -\log T = -\log\left(I / I_0\right) = \log\left(I_0 / I\right) = \varepsilon \cdot b \cdot c$$

BEER LAMBERT LAW



As the cell thickness increases, the intensity of I (transmitted intensity of light) decreases.