Light

We can use different terms to describe light:

- Color
- Wavelength
- Frequency

Light is composed of electromagnetic waves that travel through some medium.

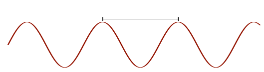
The properties of the medium determine how light travels through it.

In a vacuum, light waves travel at a speed of 3.00 x 10^8 m/s or 186,000 miles/s.

The speed of light in a vacuum is a constant that is tremendously important in nature and science—it is given the symbol, c.

Light (con't.)

Because light behaves like a wave, we can describe it in one of two ways—by its wavelength or by its frequency.



λ

λ = wavelength—distance between two adjacent wave crests. λ has units of distance—frequently nanometers (nm).

ν = frequency—how many times the wave goes up and down in a period of time. n has units of inverse time (1/s $\equiv$ Hz[hertz]).

Light (con't.)

If you know either the frequency or the wavelength, you can calculate the other quantity through the relationship:

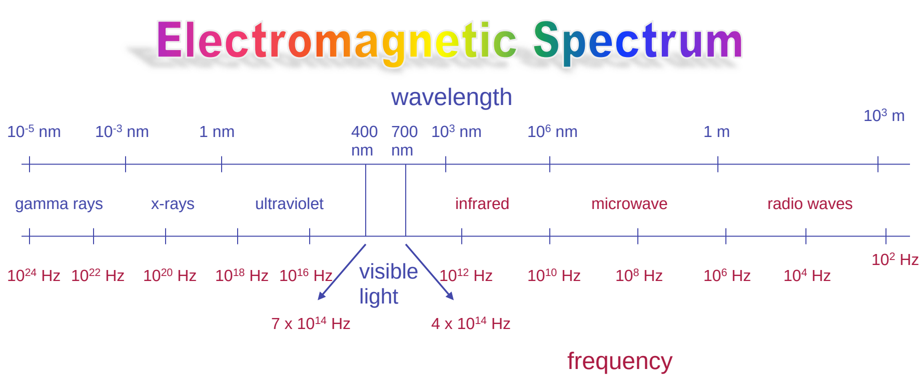
$$c = \lambda \bullet \nu$$

c = speed of light (3.00×10^{8} m/s)
λ = wavelength (m)
ν = frequency (s^{-1})

A "particle" of light is called a photon.

Light (con't.)

The type of light (ultraviolet, visible, infrared, x-ray, etc.) is defined by either its frequency or wavelength:



Light (con't.)

The energy of light can be determined either from its wavelength or frequency:

$$E = \frac{hc}{\lambda} \qquad \text{or} \qquad E = h\nu$$

Planck's constant: $h = 6.626 \times 10^{-34}$ J s

Examples

4.3×10^{13} Hz (ν) light (6980 nm = 6.98 μm):

$E = (6.626 \times 10^{-34} \text{ J s})(4.3 \times 10^{13} \text{ s}^{-1}) = 2.85 \times 10^{-20}$ J

$= 17.2$ kJ mol^{-1}

670 nm (λ) diode laser:

$$E = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{8} \text{ m s}^{-1})}{(670 \times 10^{-9} \text{ m})} = 2.97 \times 10^{-19} \text{ J}$$

$= 179$ kJ mol^{-1}

Examples (con't.)

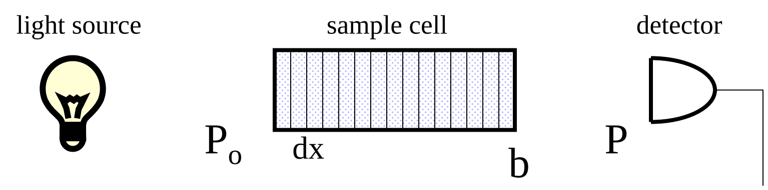
Violet light from a mercury lamp has a wavelength of 436 nm:

$$E = \frac{(6.626 \times 10^{-34}\ \text{J s})(3.00 \times 10^{8}\ \text{m s}^{-1})}{(436 \times 10^{-9}\ \text{m})} = 4.56 \times 10^{-19}\ \text{J}$$

$$= 275\ \text{kJ mol}^{-1}$$

- Atoms and molecules absorb and emit light in the ultraviolet (UV), visible (vis), infrared (IR), and microwave (μwave) regions of the electromagnetic spectrum.
- Absorption or emission of light in the UV and vis regions involves movement of electrons in the atom or molecule.
  - One reason UV light is so damaging is that the light has enough energy to break chemical bonds—biological and chemical systems
    - E (λ = 300 nm) = 399 kJ mol
    - Average bond energy = 380 kJ mol^{-1}

Spectroscopy

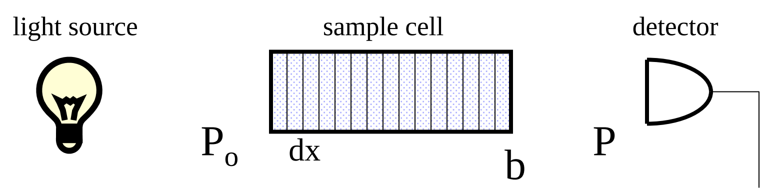


The intensity of light entering the cell is I_o.

Some of the light is absorbed by the sample.

The intensity of light striking the detector is I.

Spectroscopy

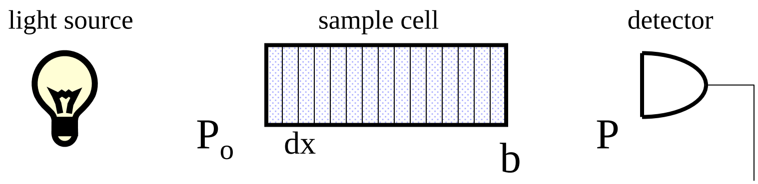


If we look at an infinitesimally small cross section of the cell, dx, the change in intensity across that section is:

$$dP = - P\, k\, dx$$

I is intensity of light entering that cross sectional area

Spectroscopy



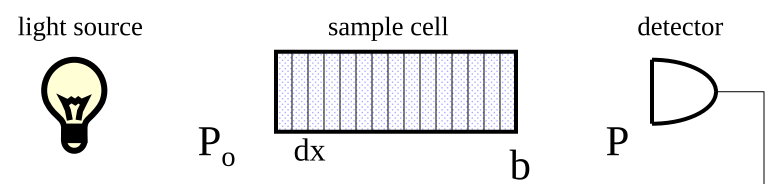
Perform separation of variables:

$$\frac{dP}{P} = -k\,dx$$

Integrating both sides yields:

$$\int_{P_o}^{P} \frac{dP}{P} = \int_{0}^{b} -k\,dx$$

Spectroscopy



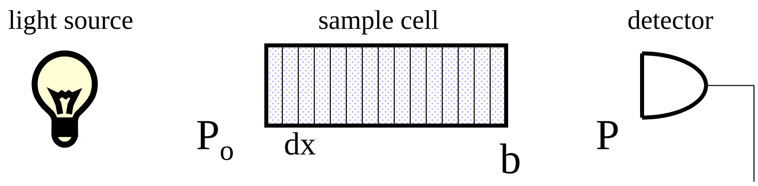
Limits of integration:

intensity goes from P_o to P

distance along the x-axis goes from 0 to b

$$\int_{P_o}^{P} \frac{dP}{P} = \int_{0}^{b} -k\,dx$$

Spectroscopy

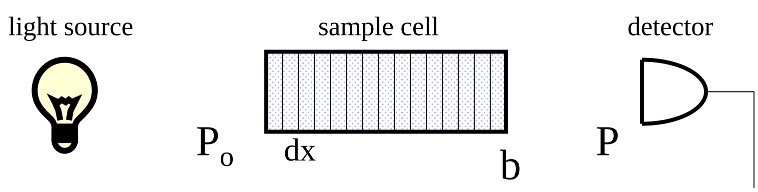


Integrating both sides yields:

$$\ln(P)\Big|_{P_o}^{P} = -kx\Big|_{0}^{b}$$

$$\ln\left(\frac{P}{P_o}\right) = -kb$$

Spectroscopy

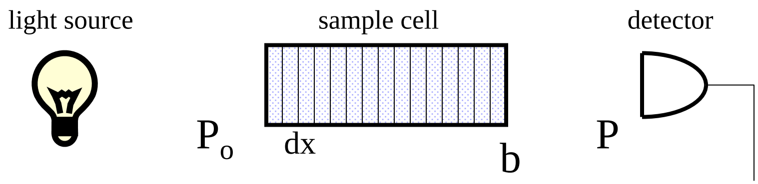


Exponentiating both sides yields:

$$\exp\left\{\ln\left(\frac{P}{P_o}\right)\right\} = \exp\{-kb\}$$

$$\frac{P}{P_o} = \exp\{-kb\}$$

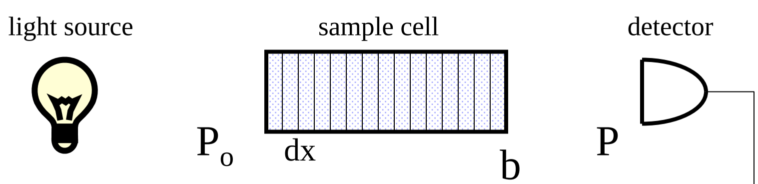
Spectroscopy



Solving for the light intensity striking the detector:

$$P = P_o \exp\{-kb\}$$

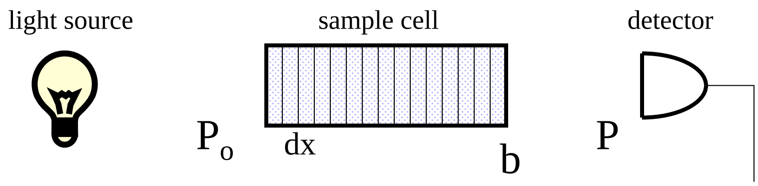
Spectroscopy



The constant k is the product of two quantities from the absorbing species: $k = \varepsilon[C]$

1. The concentration of the absorbing species—the more analyte present, the more light is absorbed
2. The absorption coefficient, $\varepsilon(\lambda)$--this is a measure of how strongly the molecule absorbs light of a certain wavelength. $\varepsilon(\lambda)$ is a function of wavelength and varies significantly over different portions of the electro-magnetic spectrum

Spectroscopy



Transmittance is defined as: $T = P/P_o$

Absorbance is defined as: $A = \log(P_o/P) = -\log(T)$

$$-\log\left(\frac{P_o}{P}\right) = A = \varepsilon[C]b$$

Beer's Law: absorbance is directly proportional to concentration and pathlength

Beer's Law: $A = \varepsilon[C]b$

If we know the pathlength of the absorption cell and the absorption coefficient, then we can determine the concentration of the analyte:

Let $b = 1.00$ cm and $\varepsilon = 2178\ \text{cm}^{-1}\ \text{M}^{-1}$

If $A = 0.482$, find [C]

$$[C] = \frac{A}{\varepsilon b} = \frac{0.482}{(2178\ \text{cm}^{-1}\text{M}^{-1})(1.00\ \text{cm})}$$

$$= 2.21_3 \times 10^{-4}\ \text{M}$$

Beer's Law: A = ε[C]b

We can also use Beer's Law to analyze mixtures to determine the concentrations of the individual components

The total absorbance is the sum of the absorbances from each species:

$A_{tot} = A_1 + A_2 + A_3 + \dots$

$= \varepsilon_1[C_1] + \varepsilon_3[C_3] + \varepsilon_3[C_3] + \dots$

The requirement is that we must measure the total absorbance at as many different wavelengths as the number of unknowns in the sample

Beer's Law: A = ε[C]b

Example:

$\varepsilon_1(400\text{ nm}) = 335.9\text{ cm}^{-1}\text{ M}^{-1}$ $\varepsilon_2(400\text{ nm}) = 2107\text{ cm}^{-1}\text{ M}^{-1}$

$\varepsilon_1(550\text{ nm}) = 879.2\text{ cm}^{-1}\text{ M}^{-1}$ $\varepsilon_2(550\text{ nm}) = 126.4\text{ cm}^{-1}\text{ M}^{-1}$

Total absorbances: $A_{400\text{ nm}} = 0.6775$

$A_{550\text{ nm}} = 0.1083$

b = 1.000 cm

Find $[C_1]$ and $[C_2]$

Beer's Law: A = ε[C]b

Example:

$A_{400} = (335.9)(1.000)[C_1] + (2107)(1.000)[C_2] = 0.6775$

$A_{550} = (879.2)(1.000)[C_1] + (126.4)(1.000)[C_2] = 0.1083$

Rearranging the first equation and then solving for $[C_2]$:

$$[C_1] = \frac{1}{335.9}\left[0.6775 - (2107)[C_2]\right]$$

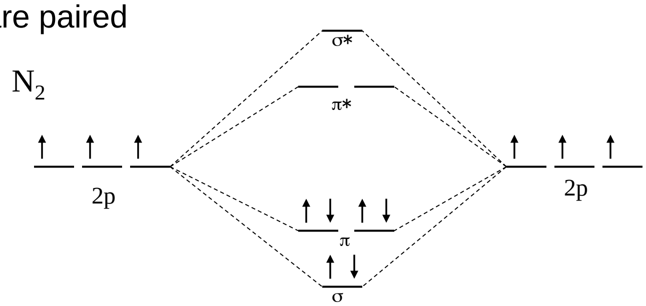
$$\frac{879.2}{335.9}\left[0.6775 - (2107)[C_2]\right] + (126.4)[C_2] = 0.1083$$

$$5388.6[C_2] = 1.6650$$

$$[C_2] = 3.090 \times 10^{-4}\ M \qquad [C_1] = 7.870 \times 10^{-5}\ M$$

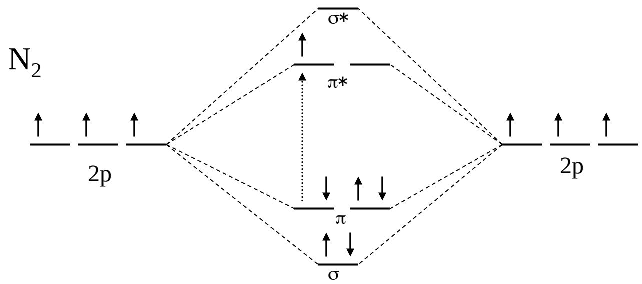
UV/vis Spectroscopy

- Transitions in the UV/visible portion of the spectrum involve movement of electrons between electronic energy states
- Most molecules in their lowest energy state are called singlets—all of the electrons in their molecular orbitals are paired



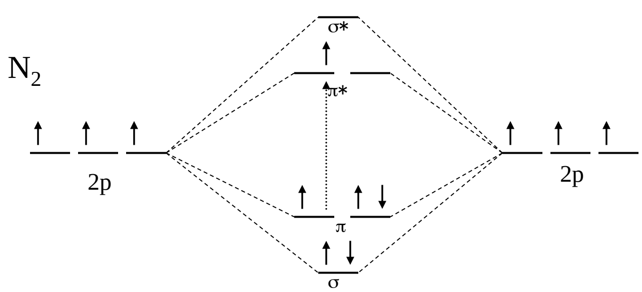
UV/vis Spectroscopy

- When a molecule absorbs light, an electron is promoted to a higher energy molecular orbital
- If the spin of the electron does not change, the transition is a singlet ← singlet transition



UV/vis Spectroscopy

- When a molecule absorbs light, an electron is promoted to a higher energy molecular orbital
- If the spin of the electron flips to the opposite sign, the transition is a triplet ← singlet transition

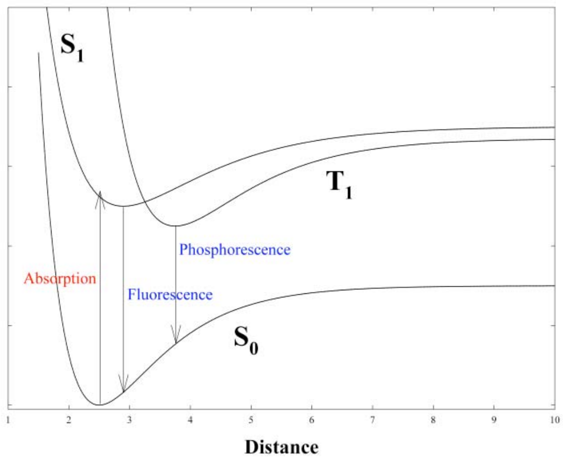


UV/vis Spectroscopy

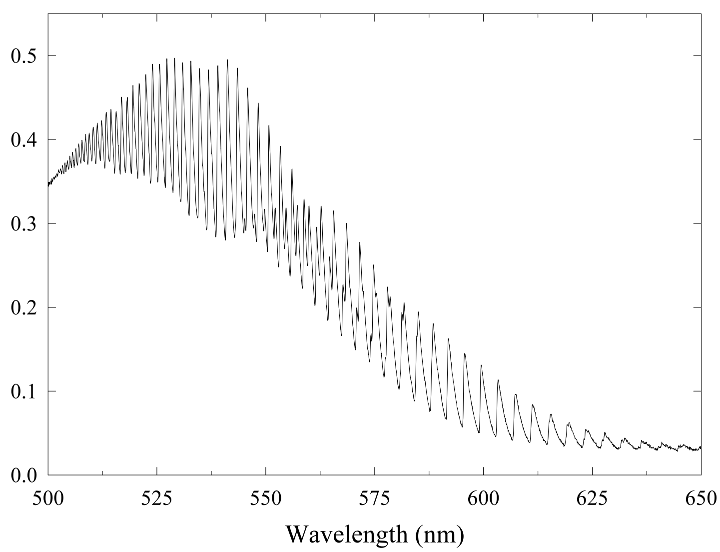
Absorption: excitation of electron to higher energy state

Fluorescence: electron drops to lower energy state without changing spin—fast process

Phosphorescence: electron drops to lower energy state and changes spin—slow process

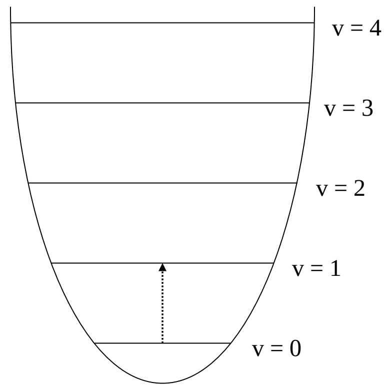


Visible Spectrum of gaseous I_2



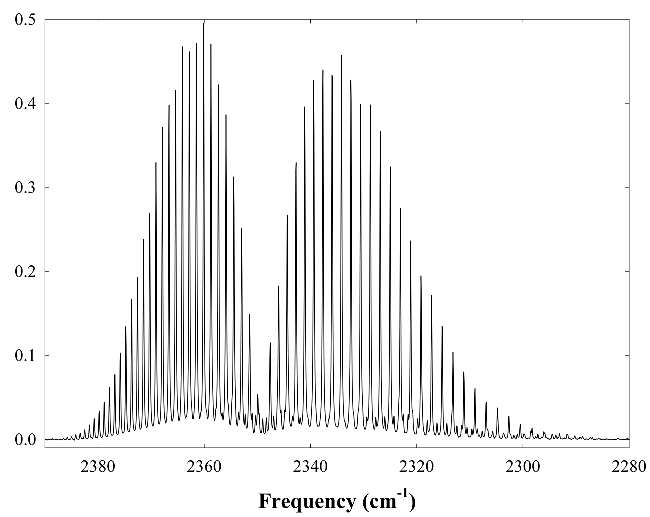
Infrared (IR) Spectroscopy

Superimposed on top of the electronic energy surface of a molecule are the vibration energy states:



When a molecule absorbs IR light, it corresponds to excitation of a vibrational mode in that molecule

Infrared Spectrum of CO_2

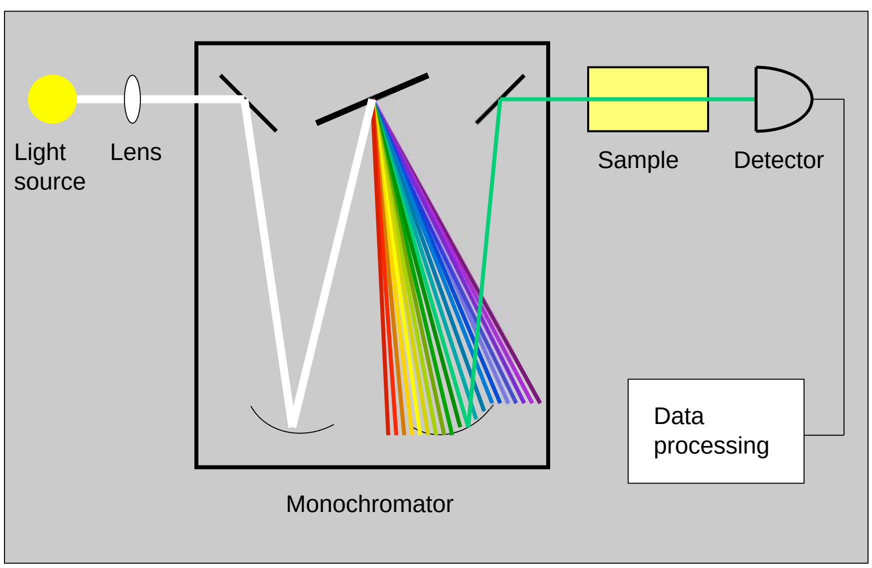


Absorption Spectrometers

Absorption spectrometers have the following necessary components:

- Light source
- Sample compartment
- Wavelength selection
- Detector
- Data analysis computer

Absorption Spectrometer Design



Light Sources

Light sources provide the light that traverses the sample and is detected to produce a signal:

Characteristics of light sources

Bandwidth: the useful wavelength range covered by the lamp

Intensity: the amount of light output

Noise: measure of the random fluctuations in light intensity

Light Sources

UV/visible light sources

- Deuterium lamps—high voltage discharge dissociates D_2 gas: bandwidth = 200 – 350 nm
- Tungsten lamps—current passes through a tungsten filament causing it to heat up and glow: bandwidth = 320 – 2500 nm (UV – near-IR)
- Vapor discharge lamps—high voltage discharge through vapor produces discreet line spectra:

  Hg (nm): 253.6, 365.0, 435.8

  Ar (nm): 427.7, 434.8, 461.0, 472.6, 476.5, 480.6, 488.0

  Ne (nm): 377.7, 585.2, 618.2, 792.7, 794.3, 808.2, …

Light Sources

Infrared light sources

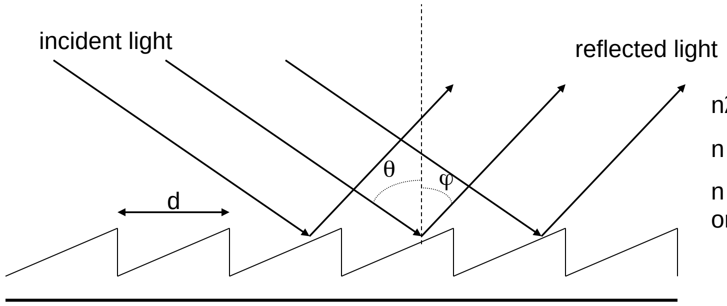
- Globars—a current is passed through a silicon carbide substrate producing broadband light from the near-IR through the far-IR

Other light sources

- Lasers—lasers emit light at a single wavelength with possibly very high intensity
  - Different lasers operate all throughout the UV, visible, and IR regions of the spectrum

Monochromators

- Monochromators are used to select a narrow range of wavelengths from a broadband light source
- The most commonly used monochromators are based on diffraction gratings

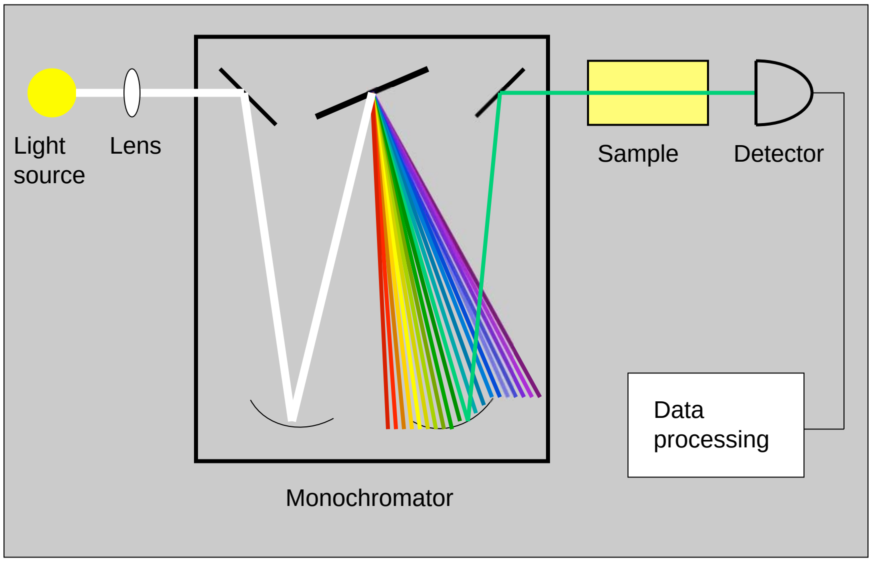


$n\lambda = d(\sin\theta + \sin\varphi)$

$n = \pm 1, \pm 2, \pm 3, \ldots$

n is called the order of diffraction

Absorption Spectrometer Design



Monochromators

- Monochromator figures of merit:
  - Length—the distance between the entrance slit and the grating element
  - Dispersion—the ability to separate light into distinct wavelengths
  - Grating ruling—the number of lines per mm on the grating; the more lines/mm, the greater the dispersion
  - Resolution—the ability of a monochromator to distinguish between closely spaced spectral features; resolution depends on length, dispersion, and the size of the exit slit
  - f#—light gathering power of the monochromator; a function of the entrance lens size and focal length

Detectors

There a number of different types of detectors depending on the wavelength of light to be detected and the desired bandwidth to be covered by the instrument

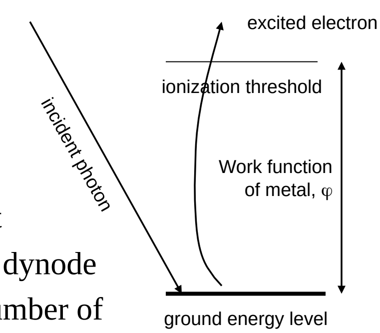
The two primary detectors used for UV/vis instruments are:

- Photomultiplier tubes
- Photodiodes

Detectors

Photomultiplier tubes (see Figure 20-12 for schematic)

- Incident light impinges on a **photoemissive cathode**: a metal substrate that emits an electron when photons of sufficient energy strike the metal
- Photoemissive cathode ejects an electron that is accelerated by high voltage toward a dynode
- When the electron strikes the dynode, it ejects more electrons that are then accelerated toward another dynode
- Each dynode stage multiplies the number of electrons that are finally detected



Detectors

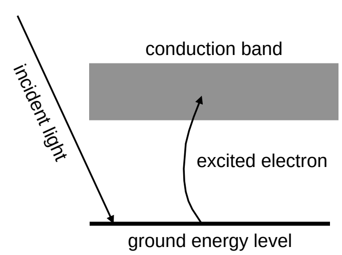
Photomultiplier tubes (see Figure 20-12 for schematic)

- Wavelength response depends on metals used in photoemissive cathode
- Bandwidth can be very narrow or quite large depending on material of photoemissive cathode
- Quantum efficiency of detector (electrons produced per incident photon) can be as high as 40%
- Capable of detecting a single photon and producing signal

Detectors

Photodiodes (see Figure 20-12 for schematic)

- A photodiode is a semiconductor—when the electrons are in the lowest energy state, they are fixed to a specific nucleus in the solid lattice; when an electron is excited to the **conduction band**, it is free to move throughout the solid, thereby conducting current
- Incident light excites and electron to the conduction band producing a current in the detector that is proportional to the amount light striking the photodiode

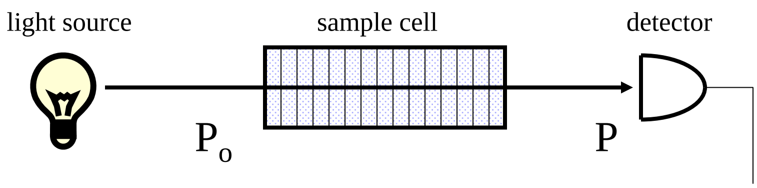


Detectors

Photodiodes (see Figure 20-12 for schematic)

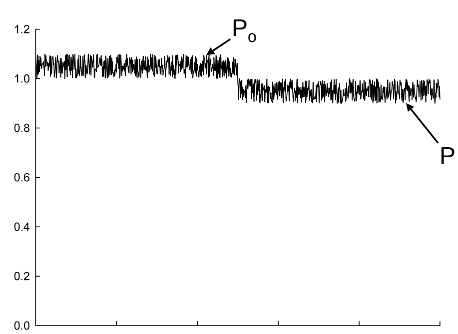
- Useful bandwidth from 200 nm to 900 nm (below 300 nm, photodiode must be enhanced with special material to produce signal)
- Quantum efficiency in the range 10% - 25%
- Very cheap optical detectors
- Photodiode arrays—many photodiode placed side-by-side to create a one-dimensional array—used in some spectrometers to simultaneously detect multiple wavelengths of light—produced entire spectrum in one shot
- Charge-coupled devices (CCDs)—two-dimensional array capable of producing a 2-D image of the incident light

Absorption Spectroscopy



Measure small signal changes on top of a large background signal

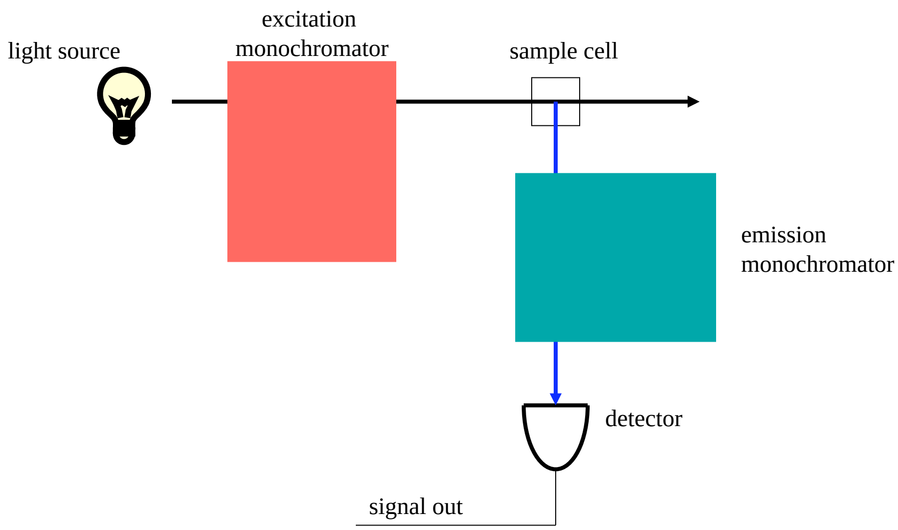
The noise level from the detector determines the detection limits of the analysis



Luminescence Spectroscopy

- Luminescence spectroscopy requires the analyte to be illuminated by some light source to produce an excited state which then relaxes back to the ground state and emits a photon in the process
- Emission process may involve either fluorescence (no spin change in excited electron) or phosphorescence (change in spin of electron during relaxation process)

Luminescence Spectroscopy



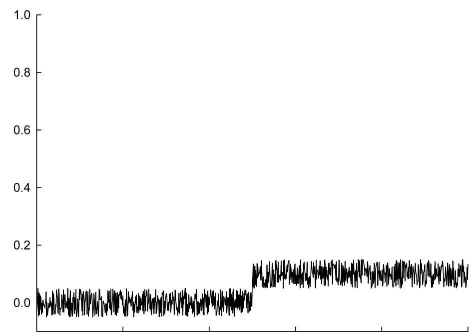
Absorption Spectroscopy

Measure small signal changes on top of a small, nearly zero background signal

Luminescence signal is given by

$I = kP_o[C]$

where k is a collection of constants including the absorption coefficient and pathlength of the excitation light in the sample



Comparison of techniques

Absorption

everything absorbs somewhere in the spectrum—universal technique

small signal on large back-back-ground—poorer detection detection limits

inexpensive, easy-to-use instrumentation

Luminescence

limited to those species that undergo emission

small signal on small ground—better limits

two monochromators require more sophisticated and expensive instrumentation