Ch. 18 Fundamentals of Spectrophotometry

What is Spectroscopy?

- **Spectroscopy:** rely on the interactions of between electromagnetic radiation and matter.
- **Spectrometry and spectrometric methods**:
  -a large group of analytical methods that are based on atomic and molecular spectroscopy
  -the measurement of the intensity of radiation with a photoelectric transducer or other type of electronic device.
- **Colorimetry**: based on absorption of visible light.

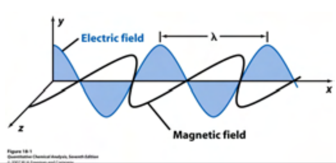
Properties of Electromagnetic Radiation

- Classical sinusoidal wave model
- Particle model

$$\upsilon \times \lambda = c \qquad c = 2.998\times10^{8}\ \text{m/s}$$

$$E = h\upsilon \qquad \upsilon = 6.626\times10^{-34}\ \text{J}\cdot\text{s}$$

- λ, is the distance between crests of a wave; **υ, is the number of oscillations per second (Hz)**



Example: How much is the energy of CO_2 increased per mole when it absorbs IR at 2300 cm^{-1}?

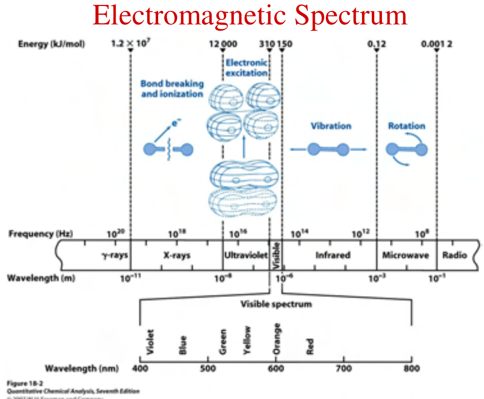
$$\Delta E = h\upsilon = h\frac{c}{\lambda} = hc\tilde{\upsilon}$$

$$= (6.626\times10^{-34}\ \text{J}\cdot\text{s})(2.998\times10^{8}\ \text{m/s})(2300\ \text{cm}^{-1})(100\ \text{cm/m})$$

$$= 4.6\times10^{-20}\ \text{J}$$

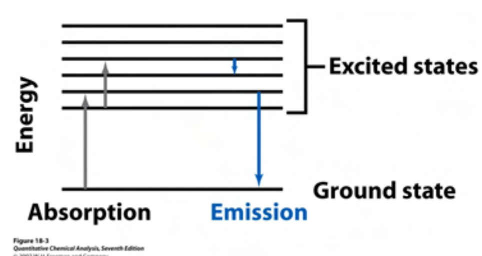
$$(4.6\times10^{-20}\ \text{J})(6.022\times10^{23}) = 28\ \text{kJ/mol}$$

Electromagnetic Spectrum



$$E = hc\tilde{\upsilon} \qquad \tilde{\upsilon} = 1/\lambda \quad \text{(wave number)}$$

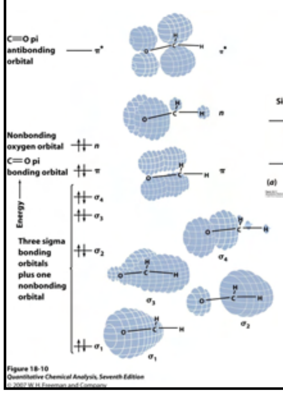
Methods of Interaction

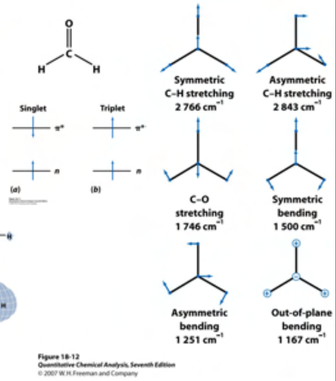


•Absorption of light increases the energy of a substance.

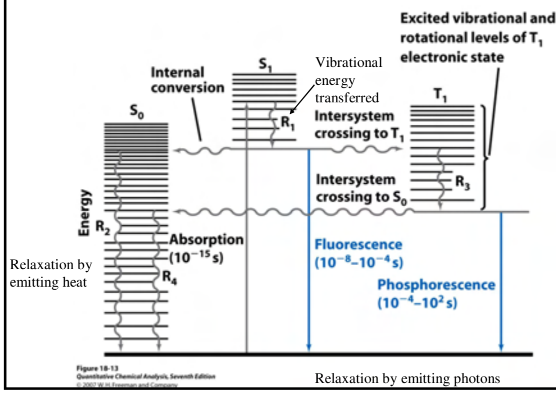
•Emission of light decreases its energy.

Interactions of Radiation and Matter

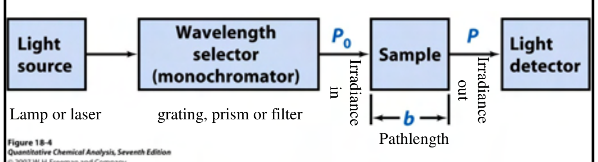




Interactions of Radiation and Matter



Single-beam Absorbance Experiment



Irradiance (P): the energy per unit area in the light beam (W/m^2).

Transmittance (T): the fraction of original light not absorbed by the sample. T = P/P_0

Monochromatic light: consists of "one color" (one wavelength).

Chromophore: the part of a molecule responsible for light absorption

Absorbance and Beer's Law

- **Absorbance** (A): the amount light absorbed by the sample is related to transmittance (T):

$$A = \log\left(\frac{P_0}{P}\right) = -\log T$$

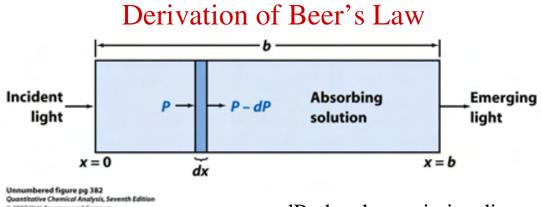
- Beer's law relates the absorbance of a chemical to its concentration:

$$A_\lambda = \varepsilon_\lambda bc$$

b : the pathlength, typically in cm, and *c* is the concentration of the chemical species in M

ε : the molar absorptivity, the unit that tells how much light is absorbed for a given wavelength. ε has units of M^{-1} cm^{-1}

Derivation of Beer's Law



$$dP = -\beta P c dx$$

dP: the change in irradiance
β: a constant of proportionality
c: concentration

$$\frac{dP}{P} = -\beta c dx \quad \Rightarrow \quad \int_{P_0}^{P} \frac{dP}{P} = -\int_0^b \beta c dx$$

Derivation of Beer's Law

$$\int_{P_0}^{P} \frac{dP}{P} = -\int_0^b \beta c dx$$

After integrate both sides:

$$\ln\frac{P}{P_0} = 2.303 \times \log\frac{P}{P_0} = -\beta c b$$

$$\log\frac{P_0}{P} = \frac{\beta}{2.303} cb = \varepsilon cb \qquad -\log T = A = \varepsilon cb$$

Example: Find the absorbance and transmittance of a 0.0220 M solution with a molar absorptivity of 15.5 M^{-1} cm^{-1} in a 2.00 cm pathlength cell

$$A_\lambda = \varepsilon_\lambda bc = (15.5\,\mathrm{M^{-1}cm^{-1}})(2.00\,\mathrm{cm})(0.0220\,\mathrm{M}) = 0.68$$

$$\log T = -A$$

$$T = 10^{-0.68} = 0.21$$

21% of the irradiated light emerges from the analyte sample

Example: Consider a solution of benzene in hexane. If the absorbance of your 1 cm cell is 0.266 at λ=200nm, what is the ε value for benzene (FW: 78.11)?

$$c = \frac{28.8\mathrm{mg}\ C_6H_6}{250\ \mathrm{ml\ sol'n}}\ \frac{1\mathrm{g}}{1000\mathrm{mg}}\ \frac{1000\mathrm{ml}}{1\mathrm{L}}\ \frac{1\mathrm{mol}\ C_6H_6}{78.11\ \mathrm{g}\ C_6H_6}$$

$c=[C_6H_6]=1.321\times10^{-3}M$ $\varepsilon=A/cb=A/c$

$\varepsilon=0.266/1.321\times10^{-3}$

Example: A 22.5 mg sample of anthracene ($C_{14}H_{10}$, MW=178.23) was dissolved in 100 mL ethanol and diluted by 50% four times. The absorbance reading of a 1.0 cm cell of this solution at 266 nm was still 0.93. What is ε?

$$[C_{14}H_{10}] = \frac{(0.0225\,\mathrm{g})/(178.22\,\mathrm{g/mol})}{0.1\,\mathrm{L}} \times \left(\frac{1}{2}\right)^4 = 7.89\times10^{-5}\,\mathrm{M}$$

$$\varepsilon = \frac{A}{bc} = \frac{0.93}{(1.0)(7.89\times10^{-5})} = 1.2\times10^4\,\mathrm{M^{-1}cm^{-1}}$$

Wavelengths and Color

Table 18-1 Colors of visible light

Wavelength of maximum absorption (nm)	Color absorbed	Color observed
380—420	Violet	Green-yellow
420—440	Violet-blue	Yellow
440—470	Blue	Orange
470—500	Blue-green	Red
500—520	Green	Purple
520—550	Yellow-green	Violet
550—580	Yellow	Violet-blue
580—620	Orange	Blue
620—680	Red	Blue-green
680—780	Red	Green

Table 18-1
Quantitative Chemical Analysis, Seventh Edition

Absorption vs. Emission Spectra

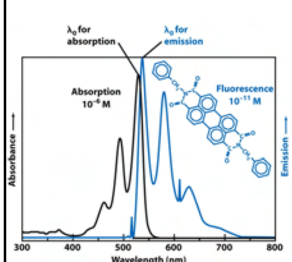


Figure 18-16
Quantitative Chemical Analysis, Seventh Edition

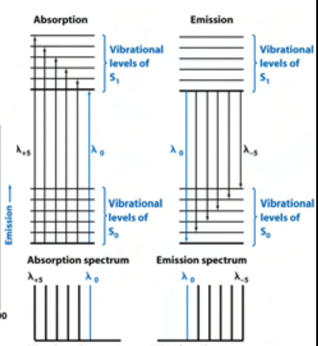


Figure 18-17
Quantitative Chemical Analysis, Seventh Edition

Absorption vs. Emission Spectra

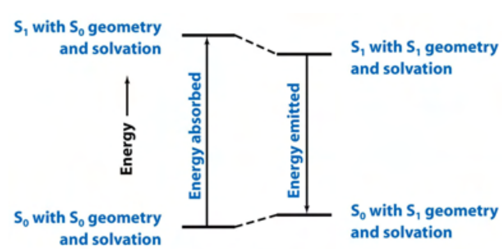
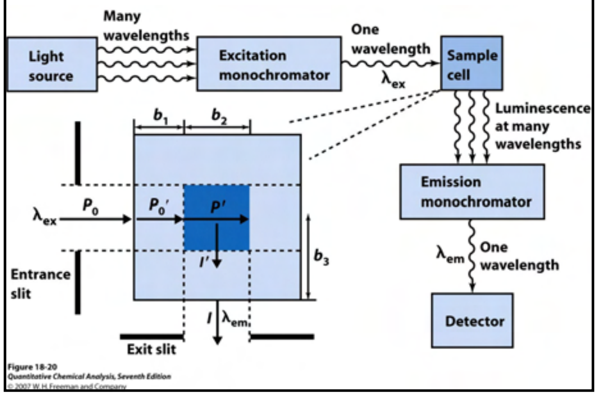


Figure 18-18
Quantitative Chemical Analysis, Seventh Edition

Emission Spectroscopy Experiment



Emission Intensity at Low Concentration

$$A = \log\left(\frac{P_0}{P}\right) = \varepsilon_{ex} bc$$

Irradiance striking central region : $P_0' = P_0 10^{-\varepsilon_{ex} b_1 c}$

Additional distance b_2 : $P' = P_0' 10^{-\varepsilon_{ex} b_2 c}$

Emission intensity is proportional to the irradiance absorbed in the central region of the cell : $I' = k'(P_0' - P')$

Emission intensity emerging from the cell :

$$I = I' 10^{-\varepsilon_{em} b_3 c} = k'(P_0' - P')10^{-\varepsilon_{em} b_3 c} = k'(P_0 10^{-\varepsilon_{ex} b_1 c} - P_0 10^{-\varepsilon_{ex} b_1 c} 10^{-\varepsilon_{ex} b_2 c})10^{-\varepsilon_{em} b_3 c}$$

$$= k' P_0 10^{-\varepsilon_{ex} b_1 c}(1 - 10^{-\varepsilon_{ex} b_2 c})10^{-\varepsilon_{em} b_3 c}$$

$$\because 10^{-\varepsilon_{ex} b_2 c} = 1 - \varepsilon_{ex} b_2 c \ln 10 + \frac{(\varepsilon_{ex} b_2 c \ln 10)^2}{2!} - \frac{(\varepsilon_{ex} b_2 c \ln 10)^3}{3!} + \ldots$$

$\therefore$ At low concentration : $k' P_0 \varepsilon_{ex} b_2 c \ln 10 \Rightarrow$ $\boxed{I = kP_0 c}$