Skoog – Chapter 6
Introduction to Spectrometric Methods

- General Properties of Electromagnetic Radiation (EM)
- Wave Properties of EM
- Quantum-Mechanical Properties of EM
- Quantitative Aspects of Spectrochemical Measurements

Electromagnetic radiation is classified into several types according to the frequency of its wave; these types include (in order of increasing frequency and decreasing wavelength): radio waves, microwaves, terahertz radiation, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. A small and somewhat variable window of frequencies is sensed by the eyes of various organisms; this is what we call the visible spectrum, or light.
Spectroscopy = methods based on the interaction of electromagnetic radiation (EM) and matter

Electromagnetic Radiation = form of energy with both wave and particle properties

EM moves through space as a wave

Sinusoidal wave model: wavelength, frequency, velocity and amplitude

Particle model: frequency of the wave is proportional to the particle's energy

Most interactions of EM with matter are best understood in terms of electric vector
**Relationship between various wave properties**

\[
\nu \lambda_i = \frac{C}{\eta_i}
\]

Where \( \nu \) = frequency in cycles/s or Hz
Determined by source and remain invariant
\( \lambda_i \) = wavelength in medium \( i \)
\( \eta_i \) = refractive index of medium \( i \)
\( C \) = speed of light in vacuum \((2.99 \times 10^{10} \text{ cm/s})\)
Depends upon composition medium

EM slows down in media other than vacuum because electric vector interacts with electric fields in the medium (matter) → this effect is greatest in solids & liquids, in gases (air) velocity similar to vacuum

**Wave Equation**

\[
y = A \sin (\omega t + \phi)
\]

Where \( y \) = magnitude of wavelength at time \( t \)
\( A \) = amplitude of maximum value for \( y \)
\( \omega \) = angular frequency = \( 2\pi \nu \)
\( \phi \) = phase angle
\( t \) = time

For a collection of waves the resulting position \( y \) at a given \( t \) can be calculated by
\[
y = A_1 \sin (\omega_1 t + \phi_1) + A_2 \sin (\omega_2 t + \phi_2) + ...
\]
Interference - amplitude of the resulting wave depends on phase difference $\alpha_1 - \alpha_2$.

At $\alpha_1 - \alpha_2 = 0^\circ$ adding of waves gives Maximum Constructive Interference.

Phase angle difference between Wave 1 & Wave 2 is zero $\alpha_1 - \alpha_2 = 0^\circ$.
When $\alpha_1 - \alpha_2 = 180^\circ$ or $540^\circ$ adding of waves gives Maximum Destructive Interference

![Wave Interference Diagram](image)

- Wave 1
- Wave 2
- Resultant wave

Phase angle difference between Wave 1 & Wave 2 is $180^\circ$ ($\alpha_1 - \alpha_2 = 180^\circ$)

**Diffraction** = EM going past an edge or through a slit (2 edges) tends to spread

- Apparent bending of waves around small obstacles and the spreading out of waves past small openings.

**Diffraction** occurs with all waves, including sound waves, water waves, and electromagnetic waves such as visible light, x-rays and radio waves.

The combination of diffraction effects & interference effects are important in spectroscopy for

1) diffraction gratings
2) slit width considerations

**Difference is a consequence of Interference**
Interference is the addition (superposition) of two or more waves that results in a new wave pattern. Interference usually refers to the interaction of waves that are correlated or coherent with each other, either because they come from the same source or because they have the same or nearly the same frequency.

\[ \delta = \pm K \lambda \]

- \( \delta \) is \( \text{OE-OD} \)
- \( \lambda \) is the wavelength of the light

Light band

\[ \delta = \pm (2K +1) \lambda/2 \]

Maximum destructive

Dark band

**Refraction** = change in velocity of EM as it goes from one medium to another

- Incident ray
- Normal to surface
- Refracted ray
- Original direction
- Medium 1 (air)
  - Velocity larger \( \eta = 1.00 \)
- Medium 2 (glass)
  - Velocity smaller \( \eta = 1.50 \)
- Ray bent toward normal
Equation for Refraction (Snell)

\[
\frac{\sin \Phi_1}{\nu_1} = \frac{\sin \Phi_2}{\nu_2} = \frac{\eta_2}{\eta_1} \quad \text{if medium 1 is air} \quad \eta_i = 1.0
\]

Magnitude of the direction change (i.e., size of the angle depends on wavelength (shown in equation as ν)) this is how a prism works.

Direction of bending depends on relative values of \(\eta\) for each medium. Going from low \(\eta\) to higher, the ray bends toward the normal. Going from higher \(\eta\) to lower the ray bends away from the normal.

**Reflection** = EM strikes a boundary between two media differing in \(\eta\) and bounces back

Specular reflection = situation where angle of incidence (\(\theta_i\)) equals angle of reflection (\(\theta_r\)).

Medium 1 (air) \(\eta = 1.00\)

Medium 2 (glass) \(\eta = 1.50\)
Reflectance = \( R = \frac{I_r}{I_i} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2} \)

Where \( I_i \) and \( I_r \) = incident & reflected intensity

For radiation going from air (\( \eta = 1.00 \)) to glass (\( \eta = 1.50 \)) as shown in previous slide

\[ R = 0.04 = 4\% \]

Many surfaces at 4 % each (i.e., many lenses) can cause serious light losses in a spectrometer. This generates stray radiation or stray light.

Scattering = EM interacts with matter and changes direction, usually without changing energy

This can be described using both the wave or particle nature of light:

1) Wave – EM induces oscillations in electrical charge of matter ⇒ resulting in oscillating dipoles which in turn radiate secondary waves in all directions = scattered radiation

2) Particle (or Quantum) – EM interacts with matter to form a virtual state (lifetime \( 10^{-14} \) s) which reemits in all directions.

Raman effect = when some molecules return to a different state ⇒ change in frequency
Scattering

Incident beam

Scattering Center (i.e., molecule, colloidal or insoluble particle)

Scattered Radiation emitted in all directions

Many types of scattering exist depending on several parameters characterizing the system, we will be concerned with:
Rayleigh Scattering, Large Particle Scattering and the Raman Effect (Raman Scattering or Raman Spectroscopy)

Rayleigh Scattering – scattering by particles whose longest dimension is < 5 % to 10 % of $\lambda$ with no change in observed frequency

\[ I_s = \frac{8 \pi^4 \alpha^2}{\lambda^4 r^2} \left( 1 + \cos^2 \theta \right) I_o \]

Notice the fourth power dependence on wavelength meaning short wavelengths are scattered more efficiently $\Rightarrow$ sky is blue
Polarizability (\( \alpha \)) is a measure of how well a given frequency induces a dipole in a substance. 
\( \alpha \) Tends to be large for large molecules (e.g., proteins).

Large Particle Scattering – particle dimensions < 10 \( \% \) \( \lambda \) to 1.5 \( \lambda \)

* Applies in techniques like turbidimetry and nephelometry.
* Large particles do not act as a point source & give rise to various interference phenomena.
* Forward scatter becomes greater than back scatter.

**Polarization**

EM is said to be unpolarized if its electric vectors and magnetic vectors occur with equal amplitude in all direction.
Linearly polarized light oscillates in one plane only as it moves through space.

Here E vector is vertically polarized and H vector is at 90° in horizontal plane.
Circularly polarized light rotates in either a left-handed or right-handed spiral as it moves through space.

Here E vector is circularly polarized and H vector follows, but is offset by 90°.

Combining equal beams where one is right circularly polarized and the other left, results in linearly polarized radiation.

Polarization is particularly important for studying optically active materials using:
- Optical Rotatory Dispersion (ORD)
- Circular Dichroism (CD)
- Fluorescence Polarization
EM radiation emitted or absorbed, a permanent energy transfer from emitting object or adsorbing media happens. EM need to be treated as discrete particles as photons or quanta.

In spectroscopy (EM interacts with matter), the energy of the transition ($\Delta E$) must correspond to the energy of the light (EM) given by frequency ($\nu$) and Plank's constant ($h$)

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

plank constant = $6.626 \times 10^{-34}$ j·s

This holds for absorption & emission of radiation

Postulates of QM:

1. Atoms, ions and molecules exist in discrete energy states only
   - $E_0$ = ground state
   - $E_1, E_2, E_3$... = excited states
   - Excitation can be electronic, vibrational or rotational
   - Energy levels for atoms, ions or molecules different.
   - Measuring energy levels gives means of identification – spectroscopy

2. When an atom, ion or molecule changes energy state, it absorbs or emits energy equal to the energy difference
   - $\Delta E = E_1 - E_0$

3. The wavelength or frequency of radiation absorbed or emitted during a transition proportional to $\Delta E$
   - $\Delta E = h \cdot \nu = \frac{h \cdot c}{\lambda}$
FIGURE 6-15 Emission or chemiluminescence processes. In (a), the sample is excited by the application of thermal, electrical, or chemical energy. These processes do not involve radiant energy and are hence called nonradiative processes. In the energy level diagram (b), the dashed lines with upward-pointing arrows symbolize these nonradiative excitation processes, while the solid lines with downward-pointing arrows indicate that the analyte loses its energy by emission of a photon. In (c), the resulting spectrum is shown as a measurement of the radiant power emitted $P_0$ as a function of wavelength, $\lambda$.

FIGURE 6-16 Absorption methods. Radiation of incident radiant power $P_0$ can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power $P$. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b). The resulting absorption spectrum is shown in (c).

FIGURE 6-17 Fluorescence and phosphorescence methods. Fluorescence and phosphorescence result from absorption of electromagnetic radiation and then deexcitation of the analyte to state $1$ or state $2$. Once excited, the excess energy can be lost by emission of a photon (fluorescence, shown as solid line) or by nonradiative processes (dashed line). The emission occurs over all angles, and the wavelengths emitted correspond to energy differences between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission, with fluorescence being prompt and phosphorescence being delayed.
Emmission of radiation

Atom: line emission spectra
Molecule:
  vibrational and rotational transitions – band emission spectra
Continuum Spectra:
Line Spectra

Energy level diagram showing Atomic Excitation and Atomic Emission with lifetime~1-100 ns.

\[ \Delta E = 202.8 \text{ kJ/mol} \]
\[ \nu = 5.08 \times 10^6 \text{ Hz} \]
\[ \lambda = 590 \text{ nm} \]

\[ \Delta E = 362.5 \text{ kJ/mol} \]
\[ \nu = 9.08 \times 10^6 \text{ Hz} \]
\[ \lambda = 330 \text{ nm} \]

*Line emission spectra*

Inner shell *(core)* electrons (1s→2p) - x-rays photons

Outer shell *(valence)* electrons (3d→4p) - UV/vis photons

Band Spectra

Energy level diagram showing Molecular Excitation and Molecular Emission with vibrational and rotational transitions.

\[ \Delta E \text{ (Electronic)} > 100 \text{ MJ/mol (x-ray)} \]
\[ \text{to} < 100 \text{ kJ/mol (UV-vis)} \]

\[ \Delta E \text{ (Vibrational)} < 1 \text{ to} < 100 \text{ kJ/mol (IR)} \]

\[ \Delta E \text{ (Rotational)} 10-100 \text{ J/mol (microwave)} \]
Absorption and Emission

Two most interesting and most useful processes when EM interacts with matter

Atoms and molecules can exist in many possible energy states

Consider two states

For absorption of EM

\[ \Delta E = E_2 - E_1 = h\nu \]

Where \( E_1 \) & \( E_2 \) are energies of states & \( h \) is Planck's constant & \( \nu \) is the frequency
**Atomic Absorption** – atoms usually in gaseous state like mercury vapor generated in a flame absorb light & undergo electronic transition

Atomic spectra are simple line spectra because there are no bonds to vibrate or rotate around, just electrons to promote

Example – Na vapor has 2 lines 589.0 nm & 589.6 nm which come from 3s electrons promoted to 2 possible 3p states of different E

Peak at 285 nm from 3s to 5p = more E

UV-vis wavelengths promote outer shell electrons

X-rays promote inner shell e⁻ = much more E

---

**Theory** – The total energy of a molecule can be broken down into several types of energy

For UV-vis must consider:
- electronic energy
- vibrational energy
- rotational energy

Ignore translational energy

**Molecular Absorption** – more complex than atomic absorption because molecules have many more possible transitions

Absorption spectra affected by

1. **number of atoms** in molecule
2. **solvent** molecules

more features
blurred features
Simplified Energy Level Diagram

Electronic Levels (2)

Vibrational Levels (4)

Rotational Levels (5)

For each electronic state - many vibrational states
For each vibrational state - many rotational states

→ many features
**Molecular Absorption** - more complex than atomic absorption because molecules have many more possible transitions

Electronic energy involves changes in energy levels of the outer electrons of a molecule

- these changes correspond to the energy of the ultraviolet-visible radiation
- these changes are quantized (i.e. discrete levels exist corresponding to quanta of light)

\[ \Delta E = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}} \]

Energy change or transition for absorption

Largest energy

Smallest energy

In the IR region of the spectrum the radiation is not energetic enough to cause electronic transitions

\[ \Delta E = \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}} \]

Even less energetic radiation can be used i.e. microwaves and radio waves

Place sample in magnetic field and can observe low energy transitions associated with changes in spin states e.g. NMR, EPR (ESR)
Once the excited state is formed, it will eventually “relax” or go back down to the ground state either by:

1) Nonradiative relaxation = no light (heat)
2) Emission = light emitted that is characteristic of the transition
   1) Large $\Delta E$ then more energetic radiation i.e. shorter wavelength UV, x-ray, etc.
   2) Greater or lesser intensity depending on the number of atoms or molecules involved in the transition
   3) Also a probability factor
Quantitative Aspects of Absorption

Transmittance \( T = \frac{1}{I_0} \)

Percent Transmittance \( \%T = \frac{1}{I_0} \times 100\% \)

Absorbance \( A = -\log T = -\log \frac{1}{I_0} = \log \frac{I_0}{I} \)

Examples:
- \( T=1.00 \) (100 \%T), \( A=0.00 \)
- \( T=0.10 \) (10 \%T), \( A=1.00 \)
- \( T=0.001 \) (0.1 \%T), \( A=3.00 \)

Beer's Law:

Basis for absorbance spectrophotometry

\[ A \propto c \quad \text{and} \quad A \propto b \]

so \( A \propto b \cdot c \)

\[ A = a \cdot b \cdot c \]

proportionality constant \( a \) - units of \( \text{absorptivity} \cdot \text{units of}\)

\[ \text{units of} \quad \text{absorptivity} \cdot \text{units of} \quad \text{L} \cdot \text{g/cm} \]

If units of concentration are M (mol/L) then use \textit{molar absorptivity} \( \varepsilon \)

\[ A = \varepsilon \cdot b \cdot c \]

units of \( \text{L/mol cm} \)

Phenomena used for optical measurements,

1. Absorption
2. Emission
3. Luminescence (Fluorescence, Phosphorescence, Chemiluminescence)
4. Scattering

In all cases, response is proportional to concentration of analyte
Absorbance & Transmittance are unitless

- If C is mol/L & b is in cm then $\varepsilon$ is L/mol-cm
- To minimize the effect of light loses from reflection the procedure followed in UV-vis spectrophotometry is to measure $I_o$ with a reference blank of pure solvent in the light path & then measure I under the same conditions – cuvettes should be optically matched if using 2 & clean, free of scratches, lint, fingerprints, etc.

Effects other than absorption that reduce source intensity (i.e., scattering, reflection) may also be measured as absorbance and must be accounted for when measuring I & $I_o$
Homework 2

- 6-11
- 6-12
- 6-18
- 6-19