CHAPTER 6
INTRODUCTION TO
SPECTROPHOTOMETRIC METHODS

Interaction of Radiation With Matter

• Add to your notes of Chapter 1
• Analytical sensitivity
  – \( \gamma = \frac{m}{s_s} \)
• Homework
  – Problems 1-9, 1-10
  – Challenge 1-12
TOPICS

• General Properties of Light
• Wave Properties of Electromagnetic Radiation
• Quantum-Mechanical Properties of Radiation
• Quantitative Aspects of Spectrophotometric Measurements

A. GENERAL PROPERTIES OF ER

• ER can be transmitted through vacuum
• The behavior/properties of electromagnetic radiations can be fully explained only by its dual nature as a wave and a particle
B. Wave Properties of ER

- Beating/oscillating (sinusoidal) electric and magnetic fields
- Magnetic and Electrical Fields are mutually perpendicular and perpendicular to the direction of propagation

Simplified Picture of a Beam of ER

- Plane polarized
- Monochromatic (Single Frequency)
- Zero phase angle at time = 0
B-1 Wave Characteristics

- **Amplitude** (A): length of electric vector at the maximum in the wave
- **Wavelength** (λ): linear distance between any two equivalent points on successive waves/ distance traveled in one cycle.
- **Period** (p): time in seconds required to complete one cycle (time for passage of successive maxima or minima through a fixed point in space)
- **Frequency** (ν) = 1/p: number of oscillations of the field per second/ number of cycles per unit time. (hertz, Hz = s⁻¹)= 1/p
- **Velocity** of propagation (v) = v = λ x ν
  - In vacuum (independent of wavelength)
    - c = λ x ν = 2.99792 x 10⁸ ms⁻¹ ~ 3.00 x 10⁸ ms⁻¹
  - In medium containing matter: slower due to interactions between electromagnetic field and electrons in matter
  - In Air (0.03 % less than in vacuum)
    \[
    v_{air} \cong c = 3.00 \times 10^8 \text{ ms}^{-1}
    \]

Effect of matter on Velocity and Wavelength
• Wave number (cm$^{-1}$)

$$\nu = \frac{1}{\lambda (cm)} = k \nu$$

- $k$ depends on medium

• Power of radiation ($P$): Energy of beam per second on given area.

• Intensity ($I$) is the power per unit solid angle.

• Solid angle: angle formed at a vertex of a cone.

• $P$ and $I$ are proportional to the square of the amplitude of the electrical field.

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**B-2 The Electromagnetic Spectrum**

![The Electromagnetic Spectrum diagram](image-url)
Spectroscopic Method, Type of ER, and Type of Transition

<table>
<thead>
<tr>
<th>Type of Spectroscopy</th>
<th>Usual Wavelength Range</th>
<th>Usual Wavenumber Range, cm⁻¹</th>
<th>Type of Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma-ray emission</td>
<td>0.005–1.4 Å</td>
<td>—</td>
<td>Nuclear</td>
</tr>
<tr>
<td>X-ray absorption, emission,</td>
<td>0.1–100 Å</td>
<td>—</td>
<td>Inner electron</td>
</tr>
<tr>
<td>fluorescence, and diffraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum ultraviolet absorption</td>
<td>190–1800 nm</td>
<td>1 × 10⁶ to 5 × 10⁶</td>
<td>Bonding electrons</td>
</tr>
<tr>
<td>Ultraviolet-visible absorption,</td>
<td>185–760 nm</td>
<td>5 × 10⁶ to 1.3 × 10⁷</td>
<td>Bonding electrons</td>
</tr>
<tr>
<td>emission, and fluorescence</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infrared absorption and</td>
<td>0.78–300 μm</td>
<td>1.3 × 10⁶ to 3.3 × 10⁷</td>
<td>Rotation/rotation of molecules</td>
</tr>
<tr>
<td>Raman scattering</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microwave absorption</td>
<td>0.73–375 mm</td>
<td>13–0.03</td>
<td>Rotation of molecules</td>
</tr>
<tr>
<td>Electron spin resonance</td>
<td>3 cm</td>
<td>0.33</td>
<td>Spin of electrons in a magnetic field</td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>0.6–10 m</td>
<td>1.7 × 10⁵ to 1 × 10⁷</td>
<td>Spin of nuclei in a magnetic field</td>
</tr>
</tbody>
</table>

B-3 Mathematical Description of a Wave

\[ y = A \sin(\omega t + \phi) \]
\[ y = \text{magnitude} - \text{of} - \text{electric} - \text{field} - \text{at} - \text{time} - t \]
\[ \omega = \text{angular} - \text{velocity} \]
\[ \phi = \text{phase} - \text{angle} \]
\[ \omega = 2\pi \nu \]
\[ y = A \sin(2\pi \nu t + \phi) \]
B-4 Superposition of waves

- Effects of waves traversing the same space are additive

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

- \( y \): electric field
- \( A \): amplitude
- \( \phi \): phase angle
- \( \omega \): angular velocity of the vector

\[ \omega = 2\pi v \]

\[ y = \]

\[ y = A_1 \sin(2\pi v_1 t + \phi_1) + A_2 \sin(2\pi v_2 t + \phi_2) + \ldots \]
Summing waves of same frequency

- Resultant has same frequency
- The larger the phase difference $\Rightarrow$ the smaller the amplitude of the resultant
- Same phase i.e. $\phi_1 - \phi_2 = 0/360^\circ / n \times 360^\circ$ & same frequency $\Rightarrow$ maximum amplitude = maximum constructive interference
- Phase difference = $180^\circ/180^\circ + n \times 360^\circ$ $\Rightarrow$ zero amplitude = maximum destructive interference

Summing waves of different frequencies

- Resultant is not a sin function
- Period of beat

$$P_b = \frac{1}{\Delta \nu} = \frac{1}{(\nu_2 - \nu_1)}$$
Superposition of Waves: Applications

- Any periodic function can be described by a sum of simple sine or cosine terms

- Applications
  1) construction of waves of specific shapes
     - Square wave
     - Fig. 6-6 p.138
     \[ y = A (\sin 2\pi t + \frac{1}{3} \sin 6\pi t + \frac{1}{5} \sin 10\pi t + \ldots + \frac{1}{n} \sin 2n\pi t) \]
  2) De-convoluting a complex periodic function
     - Complex periodic function \( \rightarrow \) Fourier Transform \( \rightarrow \) sum of sin or cos functions

B-5 Diffraction of Radiation

- Bending of a parallel beam radiation as it passes through a narrow opening (slit) or sharp barrier (an edge).
- The slits acts like secondary sources
- Diffraction is a consequence of interference of light that is allowed through small apertures or light that hits sharp edges.
- Slit width \( \equiv \lambda \)

Diffraction of monochromatic radiation

Young’s experiment (1800)
• Constructive interference occur when the difference in path (CF) traveled is an integer multiple of $\lambda$.
• $CF = BC \sin \theta$
• $BC = d$: distance between the two aperture
• $n$: order of interference

$$d \sin \theta = n\lambda$$

**The grating equation**

• Constructive interference occurs when the difference in path (CF) traveled is an integer multiple of $\lambda$.

$$\lambda = \overline{CF} = \overline{BC} \sin \theta$$

$$u = \theta$$

$$n\lambda = \overline{BC} \sin \theta$$

$n$: order of interference

$$d = \overline{BC}$$

$$n\lambda = d \sin \theta$$
Determination of Wavelength

\[ \overline{DE} = \overline{OD} \sin \theta \]

substitute \(- \text{in} \) \((-2)\)

\[ n\lambda = \frac{BCDE}{OD} = \frac{BCDE}{OE} \]

\[ n\lambda = \overline{CF} = \overline{BC} \sin \theta (2) \]

B-6 Coherent Radiation

- Coherent radiation is produced by a set of radiation sources which have
  - identical frequencies
  - constant phase relationships
- Incoherent sources
  - Emission of radiation by individual atoms or molecules results in incoherent light beam: beam of radiation is the sum of individual events (10^{-8}s) (series of wave trains,)
  - Because the motion of atoms and molecules is random, thus phase variation is also random.
- Coherent sources
  - Optical lasers
B-7 Transmission of Radiation

- Propagation of E.R. through a transparent substance.
- The velocity of propagation
  - lower than its velocity in vacuum.
  - This observation led to the conclusion that E.R. interacts with matter.
- The velocity of propagation depends on:
  - composition and structure of matter (atoms, ions, molecules)
  - concentration of substance
- No frequency change \(\rightarrow\) no permanent transfer or energy.
  - Instantaneous (\(10^{-14}\) to \(10^{-15}\)s) dipoles are generated in substance. (temporary deformation of electron clouds/polarization)
  - Interaction leads to scattering in the case of large particle
- Measure of Interaction - Refractive index at a specified frequency:
  \[ n_i = \frac{c}{v_i} \]

Transmission of radiation (Contd)

- Refractive is wavelength dependent!
- Dispersion: variation of refractive index of a substance with wavelength
- Application: selection of materials for optical components
  - Lenses (normal)
  - Prism (near anomalous)
B-8 Refraction

- Change in direction of propagation when radiation traverses at a sharp angle two media of different density, due to difference in velocity in the two media.

\[
\frac{\sin \theta_1}{\sin \theta_2} = \frac{\eta_2}{\eta_1} = \frac{\nu_1}{\nu_2}
\]

\[
(\eta_2)_{\text{vac}} = \frac{(\sin \theta_1)_{\text{vac}}}{\sin \theta_2}
\]

\[
(\eta_2)_{\text{air}} = \frac{(\sin \theta_1)_{\text{air}}}{\sin \theta_2}
\]

\[
\eta_{\text{vac}} = 1.00027 \eta_{\text{air}}
\]
Refractive index of materials

For $\lambda = 589$ nm

<table>
<thead>
<tr>
<th>Substance</th>
<th>Refraction index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1.0000</td>
</tr>
<tr>
<td>Air (STP)</td>
<td>1.0003</td>
</tr>
<tr>
<td>Water ($20^\circ$)</td>
<td>1.33</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.36</td>
</tr>
<tr>
<td>Fused quartz</td>
<td>1.46</td>
</tr>
<tr>
<td>Typical crown glass</td>
<td>1.52</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.55</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>1.63</td>
</tr>
<tr>
<td>Heavy flint glass</td>
<td>1.65</td>
</tr>
<tr>
<td>Diamond</td>
<td>2.42</td>
</tr>
</tbody>
</table>

**A.7.3 Dispersion**

- Spatial separation of E.R. of different wavelengths when refracted due to change of refractive index of medium of propagation with wavelength.
- (rainbow)
- Prism based monochromators exploit this effect.
- Typical dispersion of substances:
  - Normal dispersion region: gradual increase of with frequency
  - Anomalous dispersion region(s): sharp changes in with frequency. Occurs at freq= natural harmonic frequencies of some part of the molecule, ion, atom…absorption of beam occurs
- Important information for the manufacture optical components.
- For lenses: $\eta$ must be high and relatively constant over the wavelength of interest. (Chromatic aberation are minimized)
- For Prism: refractive index must be large and highly frequency dependent. (region of interest approaches the anomalous dispersion region)
B-9 Reflection

- Light/ER bounced off the interface between two media
- When the angle of incidence ($\theta_i$) is close to $90^\circ$ most of the E.R. is reflected.
- Fraction of radiation reflected for a beam entering at right angles

\[
\frac{I_r}{I_0} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2}
\]

\[
\theta_i = \theta_{\text{reflec}}
\]

B-10 Scattering

- Nature of interaction between radiation and matter
  - Electromagnetic field "pushes" electrons around.
  - Polarization of electron densities, i.e. change in electron density distribution.
  - Deformation of electron clouds caused by the alternating electromagnetic field of radiation
  - Energy is momentarily retained $10^{-14}$ to $10^{-15}$ s and reemitted = scattered in all direction.
- Raleigh Scattering
  - Size of particles much smaller than lambda
  - Intensity proportional to
    - $1/\lambda^4$
    - Dimension of particle
    - Square of the polarizability of particles
- Scattering by Large Molecules
  - Radiation scattered is broadened (doppler effect)
  - Used to determine size and shape of colloidal particles
  - Quasi Elastic Light Scattering / Dynamic Light Scattering / Photon Correlation Spectroscopy
Scattering

- Raman Scattering:
  - \( \nu_{\text{scattered}} \neq \nu_{\text{incident}} \)
  - Energy transferred is quantized and corresponds to vibrational energy transitions

B-11 Polarization of Radiation

- Polarization - confinement of the electrical vector in one plane
- Direction of Polarization of a wave is defined by the direction of the electrical vector (E)
- The plane of polarization: defined by the E vector and the direction of propagation of the wave.
- An unpolarized wave: can be thought of as a random superposition of many polarized wave.
  - Ordinary sources: (incandescent bulb, Sun). Atoms behave independently and emit waves with randomly oriented planes of polarization about the direction of propagation
- From non-polarized to polarized
  - Use medium that interacts selectively with radiation in one plane
  - Anisotropic crystals selectively absorb radiation in one plane and not the other.
C. QUANTUM-MECHANICAL PROPERTIES OF RADIATION

• Photoelectric effect
  – Electrons are dislodged from metallic surfaces when irradiated with ER of appropriate frequency
  – Explained by Einstein in 1905

• Wave model with radiation uniformly distributed can not explain ejection of electrons, nor accumulation of energy by electrons to produce instantaneous current observed.

• Radiation = discrete packets of energy = photons
C-1 The photoelectric effect

- Millikan (1916)
- Vacuum phototube
  - Cathode coated with an alkali metal or its compounds
- Radiation $\rightarrow$ electron ejected with different kinetic energies (KE)
- With a negative potential at anode, only electrons with sufficient KE will get into the circuit, and current is observed (photocurrent)
- Stopping voltage: negative voltage required to annul photocurrent (V) corresponds to the Kinetic energy of most energetic electron
  - $KE = e \times V$
- Expt: measure V for different surfaces and at different frequency.

Relationship between Voltage applied and Frequency of radiation

- Observations
  - Photocurrent is proportional to intensity of light at low applied voltages when is $\nu$ constant. More photons more electrons.
  - Stopping voltage depends on frequency for the same photocathode. Radiation must possess enough energy to dislodge electron and impart kinetic energy.
  - Stopping voltage depends on composition of coating on the photocathode.
  - The stopping voltage is independent of the intensity of the incident radiation. Meaning it depends only on the frequency.
The photoelectric effect

\[ E = h \nu = eV + \omega \]

\[ KE_m = h \nu - \omega \]

\[ h = 6.62 \times 10^{-34} \text{Js} \]

\[ \omega = \text{minimum binding energy of electron} \]

C-2 Energy States of Chemical Species

Max Planck (1900) german physicist

- **Two postulates:**
  - Chemical systems exist only in certain discrete energy states and change in energy states occur when atoms, ions, molecules...absorb or emit an amount of energy exactly equal to the difference between the states.
  - The frequency of radiation emitted or absorb is related to the difference in energy of energy states.

\[ E_1 - E_0 = h \nu = h \frac{c}{\lambda} \]
Quantization of Energy States of Matter

- **Atoms, Ions**
  - **Electronic states**
  - Origin of energy of atoms and ions:
    - motion of electrons around positive nuclei
  - Ground state: lowest energy state (room temp. energy state)
  - **Excited states**: higher energy states

- **Molecules**
  - Electronic states
  - Vibrational states
  - Rotational states

Energy States of Matter
C-3 Interactions of Radiation and Matter

- Molecules, ions, atoms can be stimulated by adding
  - Electrical energy
  - Thermal energy
  - Radiant energy
  - Chemical energy
- Absorption of energy can be followed by emission
- Amount and type of energy ($\lambda$) absorbed and emitted reflect the amount and the energy states, respectively, of the analyte.
- Spectrum: representation of type and “amount” radiation absorbed or emitted.
- Spectrum provide information about the analyte and its concentration
Luminescence

- Fluorescence - excitation to short lived Singlet excited state (singlet)
- Phosphorescence – long lived excited state (triplet)
- Photoluminescence – excitation by radiant energy
- Chemiluminescence – excitation by chemical energy

C-4 Emission

- **Methods of Excitation**
  - bombardment with electrons → X-ray
  - electrical ac spark, flame, furnace, dc arc → UV, Vis, or IR
  - electromagnetic radiation → fluorescent radiation
  - Exothermic chemical reaction → chemiluminescence

- **Types of spectra produced**
  - Line
  - Band
  - Continuum
Types of emission spectra

**Line Spectra**

- Produced by individual atomic particles in gaseous phase
- *Narrow*, width of lines ~ $10^{-4}\text{Å}$
- Origin of line spectra: "pure" electronic transitions
- Source of the line spectrum (Uv-vis) of Na ([Ne]3s1) contrasted to molecular emission ($E_1$ and $E_2$ vibrational states omitted)
- Source of X-ray line spectra: excitation of innermost electrons
  - Example: X-ray emission spectrum of Mo metal
Band spectra

- Molecular emission
- Origin: numerous quantized vibrational and rotational levels (omitted in fig.) in the ground state.
- Excited vibrational states are short lived (10^{-15}s): relaxation via collisions to lowest vibrational state of the excited state.
- Relaxation via collisions to electronic state is slower

Continuum spectra

- Produced by hot objects
- Produced by heating of solids to incandescence→ black-body radiation
- Spectrum produced is characteristic of the temperature of the emitting surface. High temperature → higher energy radiation emitted
C-5 Absorption of Radiation

• Absorption of radiation indicates excitation of the absorbing species from the room temperature ground state to higher electronic, vibrational or rotational state.

• The absorption spectrum informs on the nature and amount of absorbing species.

• The appearance of the spectrum depends on the type of absorbing species, the physical state and the environment of the absorbing species.

Atomic versus Molecular Absorption

• Type of absorbing species, physical state and environment determine the appearance of the spectra.

![Graph showing absorption spectra](image-url)
Atomic Absorption

- Monoatomic species
- Few well defined frequencies
- Only electronic transitions involved.
- UV and Visible radiation can cause transition of the outermost electrons only
- X-ray radiation can cause transition of electrons closest to the nuclei of atoms

Molecular Absorption

- Molecular absorption spectra are more complex due to the multiplicity of energy states in a molecules
- UV and visible radiation causes electronic transition of bonding electrons
- Electronic transitions are coupled to vibrational and rotational transitions

\[ E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \]

- In condensed phase: solvent effects broaden the signals
- Pure vibrational absorption (IR)
- Pure rotational spectra in gas phase (ground-state rot. States) (microwave) (0.01 to 1cm)
Absorption Induced by a Magnetic Field

- Applied magnetic field interact with the magnetic moments of electrons and nuclei leading to additional quantized energy levels.
- Method of excitation of nuclei:
  - Radiowaves: 30 MHz ($\lambda = 1000 \text{ cm}$) to 900 MHz or 33.3 cm
  - NMR- most common range: 200 MHz ($\lambda = 150 \text{ cm}$) to 600 MHz ($\lambda = 50 \text{ cm}$)
- Excitation of electron’s magnetic moments:
  - by microwaves ~9500 MHz ($\lambda = 3.16 \text{ cm}$)
  - ESR: electron spin resonance
  - EPR: electron paramagnetic resonance
C-6 Relaxation Processes

• The lifetime of an excited state is generally very short, because several mechanisms for relaxation are available to the system which mediate the return to the ground state
• Categories of Relaxation Processes
  – Non-radiative:
    • loss of energy in small steps via collision
    • Radiant energy converted to kinetic energy
  – Radiative: fluorescence and phosphorescence
• Fluorescence and Phosphorescence

Fluorescence

• From excited singlet state
• Average lifetime: $\sim 10^{-8}$s.
• resonant (atoms in gaseous state)
• non-resonant (molecules in gaseous state and in solution)
• Stokes shift: shift of the fluorescence emission to lower frequencies relative to the excitation frequency
Phosphorescence

– From meta-stable excited state (triplet state)
– Average lifetime: $\sim 10^{-5}$s and longer

C-7 The Uncertainty Principle

- Werner Heisenberg (1927)
- The uncertainty on the measurement of the energy of a particle or system of particles is at least equal to $\frac{h}{\Delta t}$
- $h$: Planck’s constant
- $\Delta t$: duration of measurement
- The longer $\Delta t$ is the higher the precision
- Application: be aware of natural limitations when trying to make improvements to better the precision of measurements

$$\Delta E \times \Delta t = h$$
D. Quantitative Aspects of Spectrophotochemical Measurements

- Signal transduced: radiant power = P
- Signal measured (S): voltage or current
- \[ S = kP + k_d. \]
- \( k_d \): dark current (current detected in absence of radiation)
- \( k_d \) is compensated for in all modern instruments
  \[ S = kP + k_d \]

Absorption Methods

The attenuation of the beam that is related to the concentration

**Transmittance**

\[ T = \frac{P}{P_0} \]

\( P_0 \): power of incident beam
\( P \): power of transmitted beam

**Absorbance**

\[ A = -\log_{10} T = \log_{10} \frac{P_0}{P} \]

**Beer’s Law**

\[ A = abc \]

a: proportionality constant = absorptivity
b: thickness of absorbing medium
c: concentration in moles per liter

\( A = \varepsilon bc \)
c: concentration in moles per liter
b: thickness of absorbing medium in cm
\( \varepsilon (M^{-1}cm^{-1}) \): molar absorptivity
Emission, Luminescence, and Scattering Methods

- \( S = k' \text{C} \)
- \( \text{C: concentration} \)

**TABLE 6-2 Major Classes of Spectrochemical Methods**

<table>
<thead>
<tr>
<th>Class</th>
<th>Radiant Power Measured</th>
<th>Concentration Relationship</th>
<th>Type of Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission</td>
<td>Emitted, ( P_e )</td>
<td>( P_e = k \text{C} )</td>
<td>Atomic emission</td>
</tr>
<tr>
<td>Luminescence</td>
<td>Luminous, ( P_l )</td>
<td>( P_l = k \text{C} )</td>
<td>Atomic and molecular fluorescence, phosphorescence, and chemiluminescence</td>
</tr>
<tr>
<td>Scattering</td>
<td>Scattered, ( P_s )</td>
<td>( P_s = k \text{C} )</td>
<td>Raman scattering, turbidimetry, and particle sizing</td>
</tr>
<tr>
<td>Absorption</td>
<td>Incident, ( P_i )</td>
<td>( \log \frac{P}{P_i} = k \text{C} )</td>
<td>Atomic and molecular absorption</td>
</tr>
</tbody>
</table>

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