Ultraviolet-Visible Spectroscopy

• Introduction to UV-Visible
  ➤ Absorption spectroscopy from 160 nm to 780 nm
  ➤ Measurement of transmittance
    ➤ Conversion to absorbance
      * \[ A = -\log T = \varepsilon bc \]

• 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

$dP_x / P_x = dS / S$

$\Rightarrow dS / S = \text{ratio of absorbance area to total area}$

* Proportional to number of absorbing particles

$\Rightarrow dS = adn$

* $a$ is a constant, $dn$ is number of particles

$n$ is total number of particles within a sample
Beer’s Law

• Area S can be described by volume and length
  - $S = V/b$ (cm$^2$)
  - Substitute for S
  - $n/V = \text{concentration}$
  - Substitute concentration and collect constant into single term $\varepsilon$

• Beer’s law can be applied to mixtures
  - $A_{\text{tot}} = \Sigma A_x$
Beer’s Law Limitations

- Equilibrium shift
  - pH indicators
    - Need to consider speciation
    - Weak acid equilibrium
Beer’s Law Limitation

- Polychromatic Light
  - More than one wavelength

![Graph showing absorbance vs. wavelength and absorbance vs. concentration with different bands and concentration levels.

\[ \varepsilon_1 = 1000 \quad \varepsilon_2 = 1000 \]
\[ \varepsilon_1 = 1500 \quad \varepsilon_2 = 500 \]
\[ \varepsilon_1 = 1750 \quad \varepsilon_2 = 250 \]
Noise

- Limited readout resolution
- Dark current and electronic noise
- Photon detector shot noise
- Cell position uncertainty
  - Changing samples
- Flicker
Instrumentation

• Light source
  • Deuterium and hydrogen lamps
  • W filament lamp
  • Xe arc lamps

• Sample containers
  • Cuvettes
    • Plastic
    • Glass
    • Quartz
Spectrometers
Spectrometer

Time separated double beam
Spectrometer

Polychromatic source

Lens

Sample

Photodiode array

Grating

Dip probe

Multichannel photodiode array
Application of UV-Visible Spectroscopy

• Identification of inorganic and organic species
• Widely used method

• Magnitude of molar absorptivities
• Absorbing species
• methods
Molar Absorptivities

• Range from 0 to 1E5
 ✓ ε=8.7E19PA
  ➤ P=transition probability
  ➤ A=target cross section (cm²)
    * Allowed transitions 0.1>P>1
      ε range 1E4 to 1E5
    * Forbidden transition 0.01

• Absorbing species
  ✰ M+γ->M*
    ➤ M* has a short lifetime (nanoseconds)
    ➤ Relaxation processes
      * Heat
      * Photo emission
        Fluorescence or phosphorescence
Absorbing species

- **Electronic transitions**
  - $\pi$, $\sigma$, and $n$ electrons
  - $d$ and $f$ electrons
  - Charge transfer reactions

- $\pi$, $\sigma$, and $n$ (non-bonding) electrons

![Diagram of electron labels: $\bullet = \sigma$, $\times = \pi$, $\circ = n$]
Sigma and Pi orbitals

(a) $\sigma$ orbital
(b) $\pi$ orbital
(c) $\sigma^*$ orbital
(d) $\pi^*$ orbital
Electron transitions

Diagram showing electron transitions between different energy levels.
Transitions

- $\sigma \rightarrow \sigma^*$
  - UV photon required, high energy
    - Methane at 125 nm
    - Ethane at 135 nm

- $n \rightarrow \sigma^*$
  - Saturated compounds with unshared e-
    - Absorption between 150 nm to 250 nm
    - $\varepsilon$ between 100 and 3000 L cm$^{-1}$ mol$^{-1}$
    - Shifts to shorter wavelengths with polar solvents
      * Minimum accessibility
  - Halogens, N, O, S
Transitions

• 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)
Solvent effects
Transitions

- d-d
  - 3d and 4d 1\textsuperscript{st} and 2\textsuperscript{nd} transitions series
  - Broad transitions
    - Impacted by solution
Transitions
D transitions

- Partially occupied d orbitals
  - Transitions from lower to higher energy levels
    - Splitting of levels due to spatial distribution

Similar

Axial direction

8-22
D transitions

- Binding ligands on axis have greater effect on axial orbitals
D transitions

- Δ value dependent upon ligand field strength
  - <Br-<Cl-<F-<OH-<C2O42-~H2O<SCN-<NH3<en<NO2-<CN-
  - Δ increases with increasing field strength

- f-f
  - 4f and 5f (lanthanides and actinides)
  - Sharper transitions
Figure 2: UV-vis spectra of organic phases for 13M HNO₃ system
Charge-transfer Transitions

- Electron donor and acceptor characteristics
  - Absorption involves e⁻ transitions from donor to acceptor
    - SCN to Fe(III)
      - Fe(II) and neutral SCN
  - Metal is acceptor
    - Reduced metals can be exception
Electronic Spectra

- **Cr(NH$_3$)$_6^{3+}$**
  - d$^3$
  - Weak low energy transition
    - Spin forbidden
  - 2 stronger transitions
    - Spin allowed
    - t$_{2g}$ and e$_g$ transitions
      - Lower energy to higher energy
  - CT at higher energy
    - Ligand to metal transition
Charge transfer bands

- **High energy absorbance**
  - Energy greater than d-d transition
    - Electron moves between orbitals
      * Metal to ligand
      * Ligand to metal
    - Sensitive to solvent

- **LMCT**
  - High oxidation state metal ion
  - Lone pair ligand donor

- **MLCT**
  - Low lying pi, aromatic
  - Low oxidation state metal
  - High d orbital energy
Solvent effect

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Approximate Transparency Minimum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>190</td>
</tr>
<tr>
<td>Ethanol</td>
<td>210</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>195</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>210</td>
</tr>
<tr>
<td>Benzene</td>
<td>280</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>210</td>
</tr>
<tr>
<td>Acetone</td>
<td>330</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>220</td>
</tr>
</tbody>
</table>
Methods

• Titration
  ➤ Change of absorbance with solution variation
    ➤ pH, ligand, metal

• Photoacoustic effect
  ➤ Emission of sound