Absorption or Emission Spectroscopy

![Figure 11-1](image)

\[ B_{ab} = B_{ba} = \left( \frac{2}{3} \right) \left( \frac{\pi}{h^2} \right) \left| \int \phi_b^* \mu \phi_a \, d\mathbf{r} \right|^2 \]

where \( \mu = -|e| \mathbf{r} \) for an electron

or \( \mu = \sum_i q_i \mathbf{x}_i = \sum_i z_i |e| \mathbf{x}_i \) for a molecule

or \( \int \rho(\mathbf{x}) \mathbf{r} \, d\mathbf{v} \)

The above result is from time-dependent quantum mechanics.

The integral \( \int \phi_b^* \mu \phi_a \, d\mathbf{v} \) is called the transition dipole.

\[ = \mu_{ab} \text{ or } \mu_{ba} \text{ for short} \]

This is an important concept or quantity, because unless \( \mu_{ba} \neq 0 \), there is no transition induced by \( \mathbf{E}^* \) of light, or no electric dipole transition.
Selection Rules for Simple Situations

a) Particle in a Box (1D)

\[ \phi_n(x) = \frac{\sqrt{2}}{\sqrt{a}} \sin \frac{n \pi x}{a} \]

\[ W_n = \frac{n^2 h^2}{8 ma^2} \quad (n = \text{integer}) \]

Figure 11-2

\[ \mu_{n \rightarrow m} = \int_0^a \phi_m^*(x) \mu \phi_n(x) dx \]

\[ = -|e| \left( \frac{2}{\sqrt{a}} \right)^2 \int_0^a \sin \frac{m \pi x}{a} \cdot x \cdot \sin \frac{n \pi x}{a} \, dx \]

The integral vanishes unless \( m = n \pm 1, \ n \pm 3, \ n \pm 5 \).

It follows from the symmetry of the problem that:

- \( x \) is an odd function if reflected about \( x = a / 2 \) (middle of box); i.e., it changes sign.
- \( \phi_n(x) \) is an even function for \( n \) odd (antisymmetric function).
- \( \phi_n(x) \) is an odd function for \( n \) even (symmetric function).
- \( \phi_m^*(x) \phi_n(x) \) is an odd function for \( m = n \pm 1, \ n \pm 3, \ n \pm 5 \); it is an even function otherwise.
For the integral not to vanish,

\[ \int \phi_m^*(x) \cdot x \cdot \phi_n(x) \]

must be an even function upon reflection about \( x = a/2 \),
or \( \phi_m^*(x) \phi_n(x) \) must be an odd function to compensate for \( x \) being an odd function

\[ \text{or } m = n \pm 1, \ n \pm 3, \ n \pm 5, \ K \ K \]

Selection rule for electric dipole transitions for a particle in a box.

**Figure 11-3**

(b) **e\(^{-}\)** In a Harmonic Potential or Harmonic Oscillator

**Figure 11-4**

Selection rules for electric dipole transitions: \( \Delta n = \pm 1 \) only.
Note $\Delta n \pm 3, \pm 5$ transitions are allowed by symmetry, but the integrals all turn out to vanish.

(c) **Anharmonic Oscillator with Cubic Anharmonicity**

![Figure 11-5]

Selection rules:
- $\Delta n = \pm 1$ strongest
- $\Delta n = \pm 2$ allowed, but weak
- $\Delta n = \pm 3$

0 $\rightarrow$ 1 transition usually called “fundamental”
0 $\rightarrow$ 2 transition usually called “1st overture”
1 $\rightarrow$ 2 transition usually called “1st hot band”

(d) **Anharmonic Oscillator with Quartic Anharmonicity**

The problem again has symmetry.

Selection rules for electric dipole transitions: $\Delta n = \pm 1, \pm 3, \pm 5$ etc. as for a particle in a box.

(e) **Hydrogen-like Atom**

Quantum states are identified by quantum number $n, l, m_l$.

Selection rules for electric dipole transitions:

- $\Delta n = \pm 1, \pm 2, \pm 3$ no restriction
- $\Delta l = \pm 1$ only $s \leftrightarrow p, \ p \leftrightarrow d, \ d \leftrightarrow f$ transitions only
- $\Delta m_l = \pm 1, 0$
A More Complex Situation: Formaldehyde

2 C—H bonds are formed by carbon hybrid sp² orbital overlapping with hydrogen 1s. The third sp² orbital of carbon overlaps with O 2pₓ orbital to form C—O sigma bond. C 2pₓ and O 2pₓ orbitals form π-bond (π-MO with 2 e⁻'s), and remaining two oxygen electrons are in 2 pᵧ orbital of the oxygen.

**HOMO and LUMO's**

HOMO — highest occupied MO’s

LUMO — lowest unoccupied MO’s

---

**Figure 11-6**

**Figure 11-7**
\[ \pi \rightarrow \pi^* \text{ Transition} \]

\[ \int \phi_{\pi^*}^* \mu \phi_{\pi} \, d\vec{r} = i \int \phi_{\pi^*}^* \mu_x \phi_{\pi} \, d\vec{r} + j \int \phi_{\pi^*}^* \mu_y \phi_{\pi} \, d\vec{r} + k \int \phi_{\pi^*}^* \mu_z \phi_{\pi} \, d\vec{r} \]

Only \( \int \phi_{\pi^*}^* \mu_x \phi_{\pi} \, d\vec{r} \) is nonzero; the others vanish by symmetry.

The result is a transition dipole along the C==O bond or intense absorption can only occur when \( \vec{E}^* \) of the light wave is parallel to the C==O bond; i.e., the transition is polarized along the C==O bond.

\[ n \rightarrow \pi^* \text{ Transition} \]

\[ \int \phi_{\pi^*}^* \mu \phi_n \, d\vec{r} = 0 \text{ for } \mu_x, \mu_y, \text{ and } \mu_z \]

\( n \rightarrow \pi^* \) transition is symmetry forbidden; in practice it can be observable, but is extremely weak. Typically, \( n \rightarrow \pi^* \) absorption has an intensity \(~1\%\) of the \( \pi \rightarrow \pi^* \) transition.

**Absorption Spectrum of Acetone**

![Absorption Spectrum of Acetone](image)
**Biological Chromophores**

Protein Chromophores
- peptide bond
- amino acid side chains (trp, tyr, phe)
- prosthetic groups (hemes, flavins, blue coppers)

Nucleic Acid Chromophores — bases

**Peptide Bond**

Typical models:

![Peptide bond structures](image)

Peptide bond
- $n \rightarrow \pi^*$ absorption
  - 210-220 nm  \( \epsilon_{\text{max}} \sim 100 \) weak
- $\pi \rightarrow \pi^*$
  - 190 nm  \( \epsilon_{\text{max}} \sim 7000 \)

![Typical models](image)

$\mu_{\pi-\pi}$ not along C==O but along a line between O and N in plane of peptide bond — determined by polarized absorption of single crystals

**Amino Acid Side Chains**

<table>
<thead>
<tr>
<th>Table 11-1. Absorption of Amino Acid Side Chains</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trp</strong> (tryptophan); not present in large amounts in proteins</td>
</tr>
<tr>
<td><strong>Tyr</strong> (tyrosine)</td>
</tr>
<tr>
<td><strong>Phe</strong> (phenylalanine)</td>
</tr>
</tbody>
</table>
# Prosthetic Groups

Table 11-2. Absorption of Prosthetic Groups

<table>
<thead>
<tr>
<th>Protein</th>
<th>Prosthetic Group</th>
<th>Longest $\lambda$ Absorption $\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}} \times 10^{-4}$</th>
<th>2nd Longest $\lambda$ Absorption $\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}} \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino acid oxidase (rat kidney)</td>
<td>FMN</td>
<td>455</td>
<td>1.27</td>
<td>358</td>
<td>1.07</td>
</tr>
<tr>
<td>Azurin, P. fluorescene, plastocyanin, spinach stellacyanin</td>
<td>*</td>
<td>781</td>
<td>0.32</td>
<td>625**</td>
<td>0.35</td>
</tr>
<tr>
<td>Ceruloplasmin (human)</td>
<td>8 coppers type 1, 2, 3</td>
<td>794</td>
<td>2.2</td>
<td>610</td>
<td>1.13</td>
</tr>
<tr>
<td>Cytochrome c (reduced) (human)</td>
<td>Fe$^{II}$-heme</td>
<td>550</td>
<td>2.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrodoxin</td>
<td>2Fe$^{III}$,2S$^{-}$cluster</td>
<td>421</td>
<td>0.98</td>
<td>330</td>
<td>1.33</td>
</tr>
<tr>
<td>Flavodoxin (C. pasteurianum)</td>
<td>FMN</td>
<td>443</td>
<td>0.91</td>
<td>372</td>
<td>0.79</td>
</tr>
<tr>
<td>pyruvate dehydrogenase (E. coli)</td>
<td>FAD</td>
<td>460</td>
<td>1.27</td>
<td>438</td>
<td>1.46</td>
</tr>
<tr>
<td>Rhodopsin (bovine)</td>
<td>retinal-lys</td>
<td>498</td>
<td>4.2</td>
<td>350</td>
<td>1.1</td>
</tr>
<tr>
<td>Reubredoxin (M. aerogenes)</td>
<td>(Fe$^{III}$,4 Cys) tetrahedra</td>
<td>570</td>
<td>0.35</td>
<td>490</td>
<td>0.76</td>
</tr>
<tr>
<td>Xanthine oxidase</td>
<td>Fe, Mo</td>
<td>550</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Threonine deaminase (E. coli)</td>
<td>4 pyridoxal phosphates</td>
<td>415</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*blue copper

**Cu$^{II}$ $\longleftrightarrow$ S $^{-}$ charge transfer
Other Protein Chromophores

retinal in bacteriorhodopsin
chlorophylls in reaction centers of cyanobacteria PS I and II
hemes and coppers in cytochrome oxidase (heme $\lambda_{\text{max}}$ 420-600 nm; Cu $\lambda_{\text{max}}$ 830 nm)

Nucleic Acid Bases

In DNA and RNA, absorption is dominated by nucleic acid bases (A, G, T/U, C).

![Figure 11-9](image-url)

$\pi-\pi^*$ transition moments lie in plane of bases

Figure 11-9
**Vibrational Spectroscopy / Rotational Spectroscopy**

Absorption arises from the interaction of the dipole moment of a molecule with $\vec{E}$ of the light wave.

\[
dipole \ moment \ of \ molecule = \nabla \mu(R) \nonumber \\
= \nabla \mu(R) + \sum_i \left( \frac{\partial \nabla \mu}{\partial R_i} \right)_{R_0} (R_i - R_0^i) + K
\]

where $\nabla \mu(R_0) = permanent \ dipole \ moment, \ responsible \ for$ pure rotational spectroscopy

\[
\sum_i \left( \frac{\partial \nabla \mu}{\partial R_i} \right)_{R_0} (R_i - R_0^i) = dipole \ derivative, \ responsible \ for \nonumber \\
(a) \ vibrational - rotational \ spectroscopy \ of \ gases \\
(b) \ vibrational \ spectroscopy \ of \ liquids
\]

**For a Diatomic Molecule**

(a) Rotational Spectroscopy

No absorption unless $\nabla \mu(R_0) = permanent \ dipole \ moment \neq 0$

Selection rule: $\Delta J = \pm 1$

\[
\begin{align*}
H_2 \quad & no \ rotational \ absorption \ spectrum \\
N_2 \quad & no \ rotational \ absorption \ spectrum \\
F_2 \quad & rotational \ absorption \ spectrum \nonumber \\
HCl \quad & rotational \ absorption \ spectrum \\
HF \quad & rotational \ absorption \ spectrum
\end{align*}
\]

(b) Vibrational Spectroscopy

No vibrational excitation unless $\left( \frac{\partial \mu}{\partial R} \right)_{R_0} \neq 0$ (dipole derivative) e.g., H$_2$

Selection rule: $\Delta n = \pm 1, \ (\pm 2, K)$

strong weak
For a Linear Triatomic Molecule

CO$_2$ No $\mu(R_0)$ or permanent dipole moment.

Vibrations:

4 normal modes (normal coordinates $Q_i$)

symmetric stretch $\quad \leftarrow \text{O} \equiv \text{C} \equiv \text{O} \rightarrow \left( \frac{\partial \mu}{\partial Q_i} \right)_0 = 0$

asymmetric stretch $\quad \rightarrow \text{O} \equiv \text{C} \equiv \text{O} \leftarrow \left( \frac{\partial \mu}{\partial Q_i} \right)_0 \neq 0$

bending $\quad \begin{cases} \text{O} \equiv \text{C} \equiv \text{O} \quad \uparrow \\ \downarrow \downarrow \\ \text{O} \equiv \text{C} \equiv \text{O} \end{cases} \left( \frac{\partial \mu}{\partial Q_i} \right)_0 \neq 0$

Accordingly,

symmetric stretch infrared inactive

asymmetric stretch infrared active

bending
For a Peptide Group

Table 11-3. Characteristics of Principal Infrared Absorption Bands

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Hydrogen-bonded Forms*</th>
<th>Non-hydrogen Bonded Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-Helix</td>
<td>β-Sheet</td>
</tr>
<tr>
<td></td>
<td>Frequency</td>
<td>Dichroism</td>
</tr>
<tr>
<td>N—H stretch</td>
<td>3290-3300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cm(^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Amide I</td>
<td>1650-1660</td>
<td></td>
</tr>
<tr>
<td>C=O stretch</td>
<td>( \perp )</td>
<td>( \perp )</td>
</tr>
<tr>
<td>Amide II**</td>
<td>1540-1550  ( \perp )</td>
<td>( \perp )</td>
</tr>
</tbody>
</table>

* α-helix:

\( N\text{—H} \text{——} O\equiv C \) hydrogen bonds \( || \) helix axis

β-sheet:

\( N\text{—H} \text{——} O\equiv C \)

** polarized near C—N bond or \( \perp \) N—H bond

† polarization vector