B.SC. III
CHEMISTRY
PAPER A

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ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES
PART 1
Crystal Field Theory

- Can be used to account for
  - Colors of transition metal complexes
    - A complex must have partially filled d subshell on metal to exhibit color
    - A complex with 0 or 10 d e⁻s is colorless
  - Magnetic properties of transition metal complexes
    - Many are paramagnetic
    - # of unpaired electrons depends on the ligand
Compounds/complexes that have color:
- absorb specific wavelengths of visible light (400 – 700 nm)
- wavelengths not absorbed are transmitted
- color observed = complementary color of color absorbed
Color absorption and observation relationship.
<table>
<thead>
<tr>
<th>Absorbed Color</th>
<th>$\lambda$ (nm)</th>
<th>Observed Color</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>400</td>
<td>Green-yellow</td>
<td>560</td>
</tr>
<tr>
<td>Blue</td>
<td>450</td>
<td>Yellow</td>
<td>600</td>
</tr>
<tr>
<td>Blue-green</td>
<td>490</td>
<td>Red</td>
<td>620</td>
</tr>
<tr>
<td>Yellow-green</td>
<td>570</td>
<td>Violet</td>
<td>410</td>
</tr>
<tr>
<td>Yellow</td>
<td>580</td>
<td>Dark blue</td>
<td>430</td>
</tr>
<tr>
<td>Orange</td>
<td>600</td>
<td>Blue</td>
<td>450</td>
</tr>
<tr>
<td>Red</td>
<td>650</td>
<td>Green</td>
<td>520</td>
</tr>
</tbody>
</table>
For transition metal complexes, Δ corresponds to energies of visible light.

Absorption raises an electron from the lower d subshell to the higher d subshell.
COLORS OF TRANSITION METAL COMPLEXES

Different complexes exhibit different colors because:

- Color of light absorbed depends on $\Delta$
  - Larger $\Delta = \text{higher energy light absorbed}$
    - Shorter wavelengths
  - Smaller $\Delta = \text{lower energy light absorbed}$
    - Longer wavelengths

- Magnitude of $\Delta$ depends on:
  - Ligand(s)
  - Metal
**Beer-Lambert Absorption Law**

\[ A = \varepsilon c l \]

- **A** – absorbance (adimensional)
- **\( \varepsilon \)** – molar absorptivity \( \text{L mol}^{-1} \text{cm}^{-1} \) or \( \text{M}^{-1} \text{cm}^{-1} \)
- **l** – path length through solution (in cm)
- **c** – concentration in M or mol/L

Spectrophotometers plot absorbance vs wavelength.

Other units:

\[ E = h \nu = h c / \lambda = h c \nu \]

- **E** – energy
- **h** – Planck’s constant; \( h = 6.626 \times 10^{-34} \text{ J s} \)
- **c** – speed of light; \( c = 2.998 \times 10^8 \text{ m/s} \)
- **\( \nu \)** – frequency \( \text{s}^{-1} \)
- **\( \lambda \)** – wavelength (often reported in nm)
- **n** = \( 1 / \lambda = \text{wavenumbers} \ (\text{cm}^{-1}) \)
**TERM SYMBOL**

Term symbols are used to indicate the electronic configuration and resultant angular momentum of an atom.

The term symbol for a particular atomic state is expressed as

\[2S+1 \, L \, J\]

Where

- \(S\) = Total spin angular quantum number
- \(L\) = Total orbital angular quantum number
- \(J\) = Total angular momentum quantum number

\(2S+1\) = Spin multiplicity of the state
TERM SYMBOLS

Instead of using numbers for L, we use letters

<table>
<thead>
<tr>
<th>L =</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Term Symbol</td>
<td>S</td>
<td>P</td>
<td>D</td>
<td>F</td>
<td>G</td>
</tr>
</tbody>
</table>

e.g. \( p^2 \uparrow \uparrow \uparrow \) \( S = 1 \)
+1 0 -1 \( L = 1 \)
so, the term symbol for this state = \( ^3P \)
pronounced triplet-P

e.g. \( S = \frac{1}{2} \) and \( L = 4 \) \( ^2G \)
“doublet-G” state

\( S = \frac{3}{2} \) and \( L = 2 \) \( ^4D \)
“quartet-D” state
The total angular momentum, $j$, of an atom can be determined by two methods. These are:

- LS or Russell Saunders Coupling
- JJ Coupling

Out of these two schemes we shall discuss only LS or Russell Saunders Coupling.
ELECTRONIC TRANSITIONS

The interaction of orbital angular momenta ($m_l$ values) and spin angular momenta ($m_s$ values) is called Russel-Saunders or LS coupling.

The lower transition metals (4d and 5d) undergo further coupling (called $j$-$j$ coupling or spin-orbit coupling).
Rules for determining the term symbol according to LS coupling scheme

**LL Coupling**

For two electrons,

$$ L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \ldots |l_1 - l_2| $$

For a $p^2$ configuration, $L = 1+1, 1+1-1, 1-1$. The values of $L$ are: 2, 1 and 0.

$L$ is always positive, and ranges from the maximum value of $\Sigma l$. 
SS COUPLING

For two electrons,
\[ S = s_1 + s_2, \ s_1 + s_2 - 1, \ s_1 + s_2 - 2, ... \mid s_1 - s_2 \mid \]

For a \( p^2 \) configuration, \( S = \frac{1}{2} + \frac{1}{2} , \ \frac{1}{2} + \frac{1}{2} - 1 \). The values of \( S \) are: 1 and 0.
There is also spin-orbit coupling wherein the spin and orbital angular momenta couple with each other.

\[ J = L+S, \ L+S-1, \ L+S-2, \ldots |L-S| \] (no negative values)

\( J \) is a subscript on the right side of the \( L \) quantum #

- Determine the spin-orbit coupling in the \( ^1S \) and \( ^3P \) free-ion terms. Designate these with \( J \).
TO DETERMINE THE STATES (TERMS) OF A GIVEN ATOM OR ION:

1. Write down the electronic configuration (ignore closed subshell electrons)
2. Determine the number of distinct microstates that can represent that configuration. If you have e electrons in a single open subshell of 2l+1 orbitals, this value is
   \[ \text{#microstates(single open subshell)} = \frac{(2(2l+1))!}{e!(2(2l+1)-e)!} \]
3. Tabulate the number of microstates that have a given M_L and M_S
4. Decompose your table into terms by elimination
5. Test the total degeneracy of the resultant terms to account for all the microstates counted in parts 2 and 3
6. Determine the lowest term for the configuration by Hund's Rules.
C \((1s\ 2s\ 2p\ )\) \{lowest electron configuration\}

Calculate the number of possible electron arrangements in the given configuration:

There are \(6!/4!2! = 15\) microstates expected

Write down all these possibilities:
Tabulate the total numbers by ML and MS

<table>
<thead>
<tr>
<th>+2</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>+1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

M_s
Decompose this table into terms

\begin{align*}
\begin{array}{c|cccc}
\text{M}_1 & 0 & 1 & 1 & 1 \\
\text{M}_s & 0 & 1 & 1 & 1 \\
\end{array}
\end{align*}
Absorption of light occurs when electrons are promoted from lower to higher energy states. Interactions between electrons causes more than one peak in the UV/Vis spectra of these complexes. The electrons are not independent of each other, and the spin angular momenta and orbital angular momenta interact.
The interactions produce atomic states called *microstates* that are described by a new set of quantum numbers.

\[ M_L = \text{total orbital angular momentum} = \Sigma m_l \]

\[ M_S = \text{total spin angular momentum} = \Sigma m_s \]
Determining the Energy States of an Atom

A microstate table that contains all possible combinations of $m_l$ and $m_s$ is constructed.

Each microstate represents a possible electron configuration. Both ground state and excited states are considered.
ENERGY STATES

Microstates would have the same energy only if repulsion between electrons is negligible. In an octahedral or tetrahedral complex, microstates that correspond to different relative spatial distributions of the electrons will have different energies. As a result, distinguishable energy levels, called terms are seen.
ENERGY STATES

To obtain all of the terms for a given electron configuration, a microstate table is constructed. The table is a grid of all possible electronic arrangements. It lists all of the possible values of spin and orbital orientation. It includes both ground and excited states, and must obey the Pauli Exclusion Principle.
Consider an atom of carbon. Its highest occupied orbital has a p\(^2\) electron configuration.

Microstates correspond to the various possible occupation of the p\(_x\), p\(_y\) and p\(_z\) orbitals.
Constructing a Microstate Table

\[ m_l = +1 \quad 0 \quad -1 \quad \text{microstate}: \]

Configurations:

\[ \uparrow \quad \uparrow \quad \_ \quad (1^+, 0^+) \]
\[ \_ \quad \_ \quad \uparrow \quad (0^+, -1^+) \]
\[ \_ \quad \_ \quad \_ \quad (1^+, -1^+) \]

These are examples of some of the ground state microstates. Others would have the electrons (arrows) pointing down.
Constructing a Microstate Table

$$m_l = \begin{array}{ccc} +1 & 0 & -1 \end{array}$$

microstate:

Configurations:

$$\begin{array}{ccc} \uparrow \downarrow & \_ & \_ \end{array} \quad (1^+, 1^-)$$

$$\begin{array}{ccc} \_ & \_ & \uparrow \downarrow \end{array} \quad (0^+, 0^-)$$

$$\begin{array}{ccc} \_ & \_ & \_ \_ \_ \end{array} \quad (-1^+, -1^-)$$

These are examples of some of the excited state microstates.
For the carbon atom, $M_L$ will range from +2 down to -2, and $M_S$ can have values of +1 (both electrons “pointing up”), 0 (one electron “up”, one electron “down”), or -1 (both electrons “pointing down”).
Different arrangements of electrons having slightly different energies are called microstates.
**M**<sub>S</sub> Table for \( p^2 \)

<table>
<thead>
<tr>
<th>( M_L )</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2:</td>
<td>1+1-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+1:</td>
<td>1+0+</td>
<td>1+0-</td>
<td>1-0-</td>
</tr>
<tr>
<td>0:</td>
<td>-1+1+</td>
<td>-1+1-</td>
<td>-1-1-</td>
</tr>
<tr>
<td>-1:</td>
<td>-1+0+</td>
<td>-1+0-</td>
<td>-1-0-</td>
</tr>
<tr>
<td>-2:</td>
<td>-1+0-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The table includes **all** possible microstates.
Constructing a Microstate Table

Once the microstate table is complete, the microstates are collected or grouped into atomic (coupled) energy states.
CONSTRUCTING A MICROSTATE TABLE

For two electrons,
\[ L = l_1 + l_2, \ l_1 + l_2 - 1, \ l_1 + l_2 - 2, \ldots \ |l_1 - l_2| \]

For a p² configuration, \( L = 1+1, \ 1+1-1, \ 1-1. \)  The values of \( L \) are: 2, 1 and 0.

\[ L \] is always positive, and ranges from the maximum value of \( \Sigma l \).
CONSTRUCTING A MICROSTATE TABLE

For two electrons,
\[ S = s_1 + s_2, \ s_1 + s_2-1, \ s_1 + s_2-2, \ldots \ | s_1 - s_2 | \]

For a p^2 configuration, \( S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} + \frac{1}{2} -1. \) The values of \( S \) are: 1 and 0.