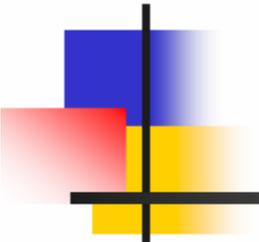


Chapter 11 Coordination Chemistry III: Electronic Spectra

11-1 Absorption of Light

11-2 Quantum Numbers of Multielectron Atoms

11-3 Electronic Spectra of Coordination Compounds



Chapter 11 Coordination Chemistry III: Electronic Spectra

Vivid colors of coordination compound.

Dyes, gems (rubies, emeralds), blood etc.

Transitions between d orbitals of metals.

We will need to look closely at the energies of these orbitals.

The electronic absorption spectrum provides a convenient method for determining the magnitude of the effect of ligands on the d orbitals of the metal.

Absorption of Light

Complementary colors: if a compound absorbs light of one color, we see the complement of that color.

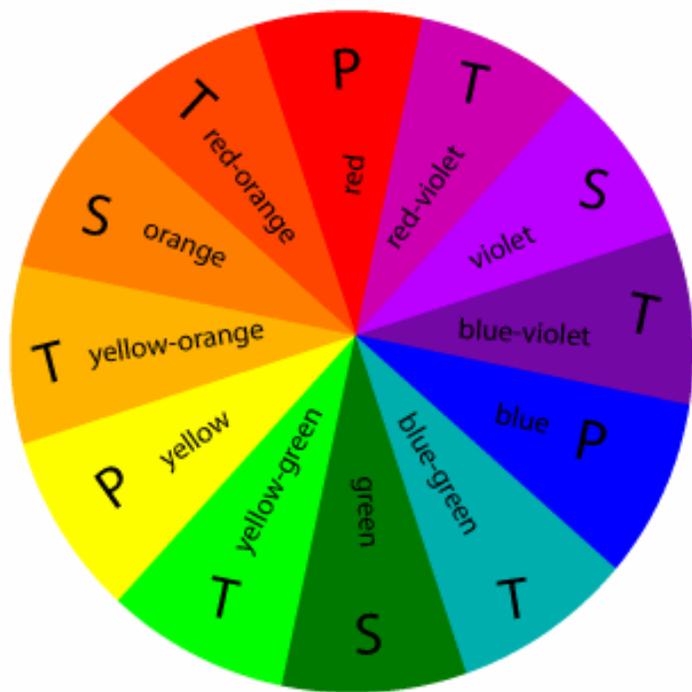


표 11-1
가시광선과 보색

파장 영역 (nm)	파수 (cm^{-1})	색깔	보색
<400	>25,000	자외선	
400-450	22,000-25,000	보라	노랑
450-490	20,000-22,000	파랑	주황
490-550	18,000-20,000	녹색	빨강
550-580	17,000-18,000	노랑	보라
580-650	15,000-17,000	주황	파랑
650-700	14,000-15,000	빨강	녹색
>700	<14,000	적외선	

Absorption of Light

Complementary colors: if a compound absorbs light of one color, we see the complement of that color.

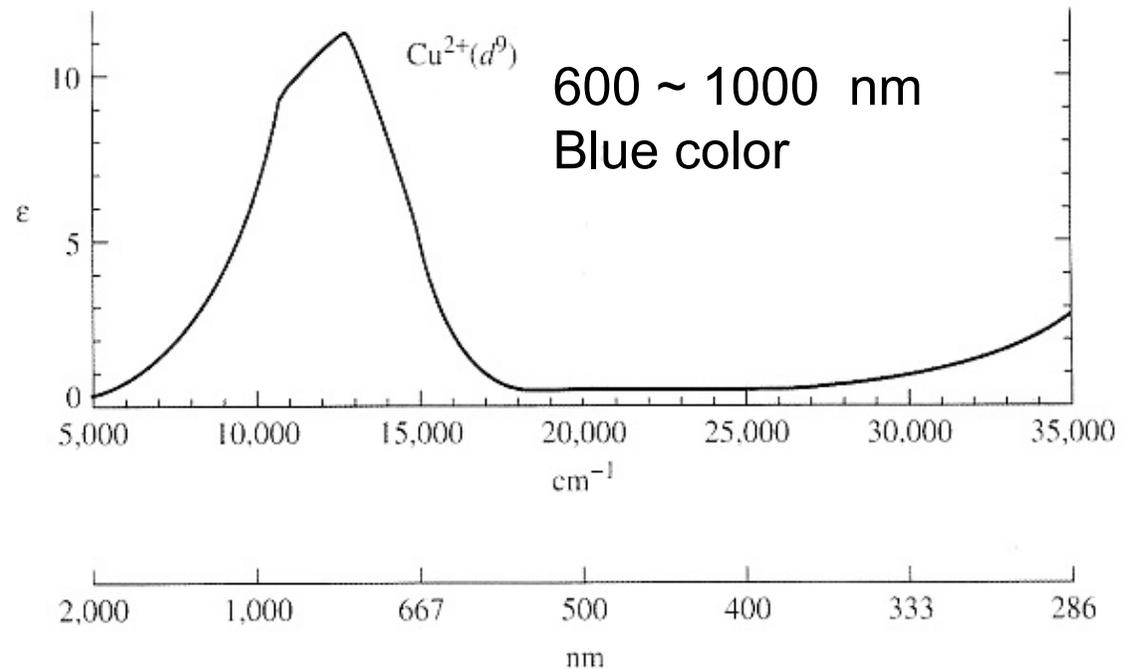


그림 11-1 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ 의 흡수 스펙트럼 (B. N. Figgis, *Introduction to Ligand Fields*, Wiley-Interscience, New York, 1966, p. 221).

Absorption of Light ; Beer-Lambert Absorption Law

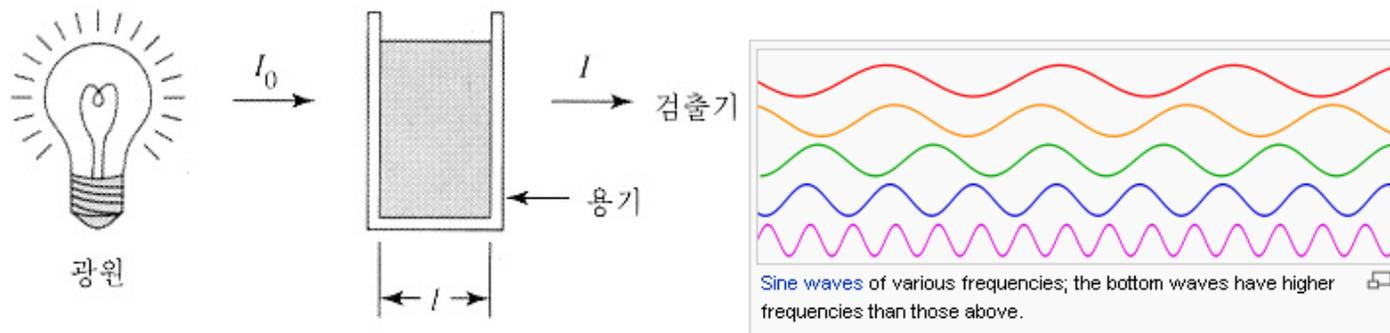
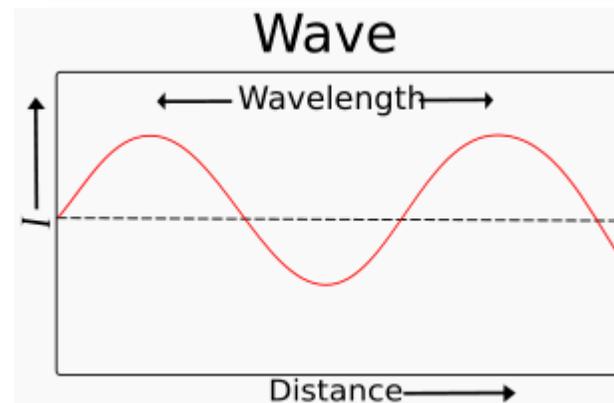
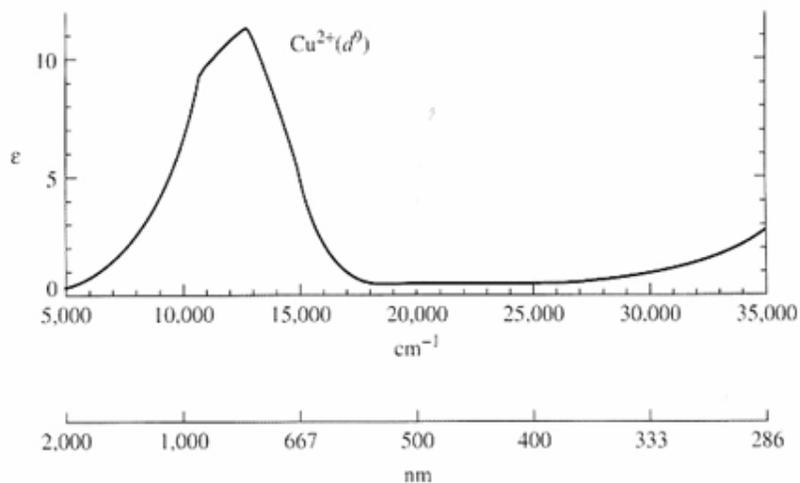


그림 11-2 용액에 의한 빛의 흡수.

Beer-Lambert Law

$$\log(I_0/I) = A = \epsilon lc$$



Wavelength, wavenumber → Energy

$$E = h\nu = hc/\lambda = hc\bar{\nu}$$

Quantum Numbers of Multielectron Atoms

Absorption of light results in the excitation of electrons from lower to higher energy states.

We observe absorption in band with the energy of each band corresponding to the difference in energy between the initial and final states.

We first need to consider electrons in atoms can interact with each other.

Electrons tend to occupy separate orbitals $\leftarrow \uparrow_c$
Electrons in separate orbitals tend to have parallel spins $\leftarrow \uparrow_e$

Quantum Numbers of Multielectron Atoms

Carbon atom

Energy levels for the p^2 electrons → Five energy levels
Each energy levels can be described as a combination of the m_l and m_s values of the $2p$ electrons.

$2p$ electrons

$$n = 2, l = 1$$

$$m_l = +1, 0, \text{ or } -1$$

$$m_s = +1/2 \text{ or } -1/2$$

The orbital angular momenta and the spin angular momenta of the $2p$ electrons interact in a manner called **Russell-Saunders coupling (LS coupling)**.

Quantum Numbers of Multielectron Atoms

Russell-Saunders coupling (LS coupling)

Orbit-orbit coupling

$M_L = \sum m_l \rightarrow L$: total orbital angular momentum quantum number

Spin-spin coupling

$M_s = \sum m_s \rightarrow S$: total spin angular momentum quantum number

Spin-orbit coupling

$J = L + S$: total angular momentum quantum number

How many possible combinations of m_l and m_s values?

One possible set of values for the two electrons in the p^2 configuration would be

First electron: $m_l = +1$ and $m_s = +1/2$

Second electron: $m_l = 0$ and $m_s = -1/2$

Notation 1+0-

2p electrons

$n = 2, l = 1$

$m_l = +1, 0, \text{ or } -1$

$m_s = +1/2 \text{ or } -1/2$

microstate

Quantum Numbers of Multielectron Atoms

Tabulate the possible microstates

1. No two electrons in the same microstate have identical quantum numbers (the Pauli exclusion principle)
2. Count only the unique microstates (1^+0^- and 0^-1^+)

Electronic quantum # (m_l and m_s) to atomic quantum # (M_L and M_S)

표 11-2
 p^2 에 대한 미시적 상태표

microstates

2p electrons

$$n = 2, l = 1$$

$$m_l = +1, 0, \text{ or } -1$$

$$m_s = +1/2 \text{ or } -1/2$$

		M_S		
		-1	0	+1
M_L	+2		$1^+ 1^-$	
	+1	$1^- 0^-$	$1^+ 0^-$ $1^- 0^+$	$1^+ 0^+$
	0	$-1^- 1^-$	$-1^+ 1^-$ $0^+ 0^-$ $-1^- 1^+$	$-1^+ 1^+$
	-1	$-1^- 0^-$	$-1^+ 0^-$ $-1^- 0^+$	$-1^+ 0^+$
	-2		$-1^+ -1^-$	

Quantum Numbers of Multielectron Atoms

Electronic quantum # (m_l and m_s) to atomic quantum #
(M_L and M_S) → **describe states of multielectron atoms**

Russell-Saunders coupling (LS coupling)

Orbit-orbit coupling

$M_L = \sum m_l \rightarrow$ **L: total orbital angular momentum quantum number**

Spin-spin coupling

$M_s = \sum m_s \rightarrow$ **S: total spin angular momentum quantum number**

Spin-orbit coupling

J = L + S : total angular momentum quantum number

Quantum Numbers of Multielectron Atoms

L and S describe collections of microstates.

M_L and M_S describe the microstates themselves.

Atomic States

$$M_L = 0, \pm 1, \pm 2, \dots \pm L$$

$$M_S = S, S-1, \dots -S$$

Individual Electrons

$$m_l = , \pm 1, \pm 2, \dots \pm l$$

$$m_s = +1/2, -1/2$$

Term symbol

표 11-3
원자 상태(자유-이온항)과
양자수의 예

항	L	S
1S	0	0
2S	0	$\frac{1}{2}$
3P	1	1
4D	2	$\frac{3}{2}$
5F	3	2

$$L = 0, 1, 2, 3 \rightarrow S, P, D, F,$$

Term Symbol

$$2S+1 L_J$$

Quantum Numbers of Multielectron Atoms

Electronic quantum # (m_l and m_s) to atomic quantum # (M_L and M_S) → describe states of multielectron atoms

Free-ion terms are very important in the interpretation of the spectra of coordination compounds.

1S (singlet S) :

$$S \rightarrow L = 0 \rightarrow M_L = 0,$$

$$2S+1 = 1 \rightarrow S = 0 \rightarrow M_S = 0$$

The minimum configuration of two electrons

		M_S
		0
M_L	0	0^+0^-

Quantum Numbers of Multielectron Atoms

2P (doublet P) :

$$P \rightarrow L = 1 \rightarrow M_L = +1, 0, -1$$

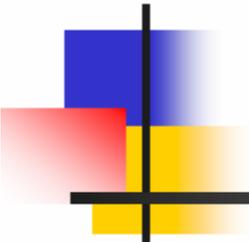
$$2S+1 = 2 \rightarrow S = 1/2 \rightarrow M_S = +1/2, -1/2$$

The minimum configuration of one electron

		M_S	
		$-1/2$	$+1/2$
M_L	$+1$	1^-	1^+
	0	0^-	0^+
	-1	-1^-	-1^+

Six microstates

Quantum Numbers of Multielectron Atoms



M_S

	$-1/2$	$+1/2$
$+1$	X	X
0	X	X
-1	X	X

M_L

Six microstates

The spin multiplicity is the same as the # of microstates

Quantum Numbers of Multielectron Atoms

Reduce microstate table into its component free-ion terms.

The spin multiplicity is the same as the # of microstates.

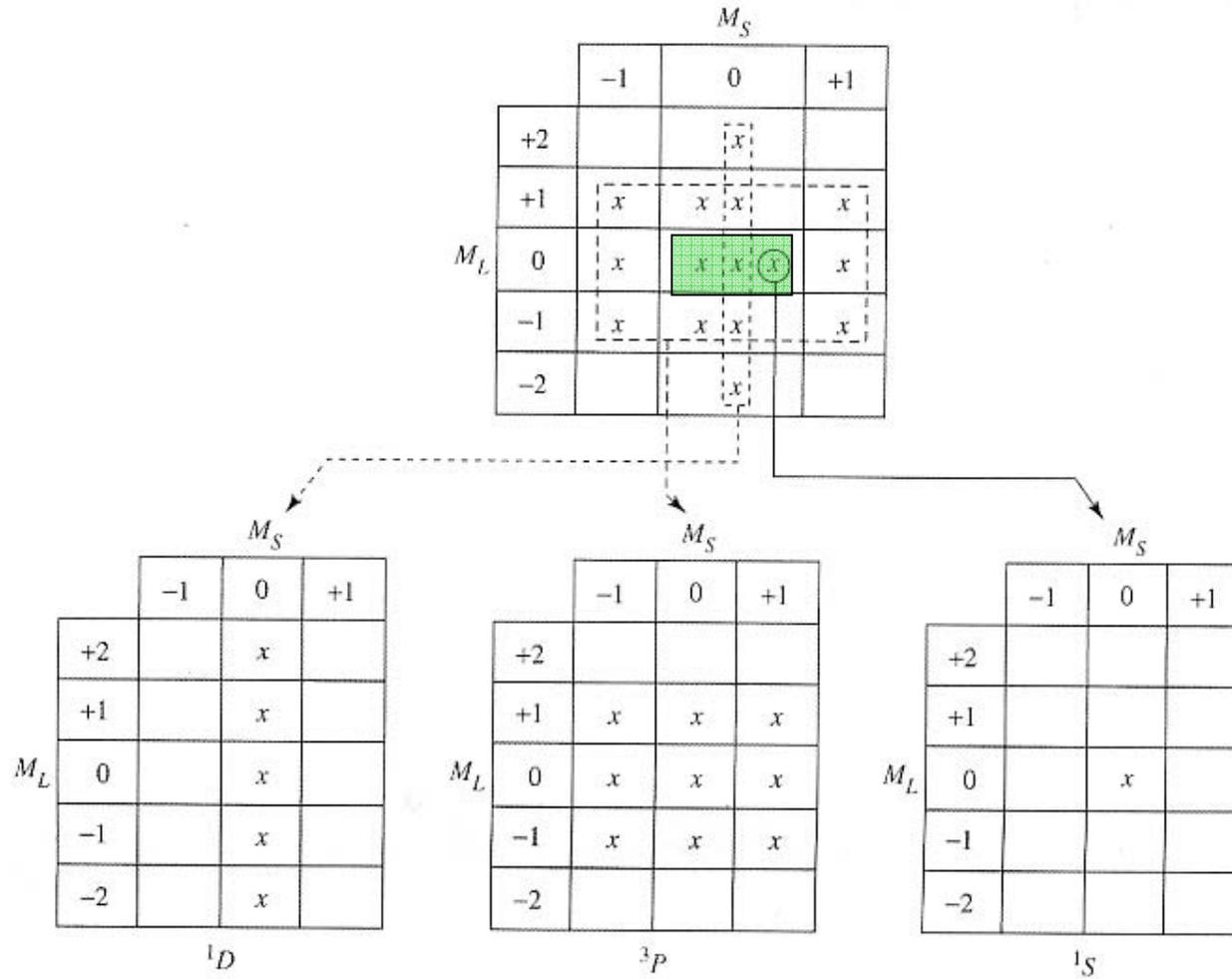
Each term has different energies; they represent three states with different degrees of electron-electron interactions.

Which term has the lowest energy. This can be done by using two of Hund's rules.

- 1. The ground term (term of lowest energy) has the highest spin multiplicity. (Hund's rule of maximum multiplicity)*
- 2. If two or more terms share the maximum spin multiplicity, the ground term is one having the highest value of L.*

Quantum Numbers of Multielectron Atoms

표 11-4
 p^2 에 대한 미시적 상태표와 자유-이온항으로의 변환



주: $1S$ 와 $1P$ 항은 $3P$ 항보다 더 높은 에너지를 갖지만 단일 전자 배치로는 확인할 수 없다. 이들과 같은 보다 높은 에너지를 갖는 항들의 상대적인 에너지도 간단한 규칙만으로는 결정할 수 없다.

Quantum Numbers of Multielectron Atoms

d^2

$l = 2$

$m_l = +2, +1, 0, -1, -2$

$m_s = +1/2$ or $-1/2$

$1S$

$1D$

$1G$

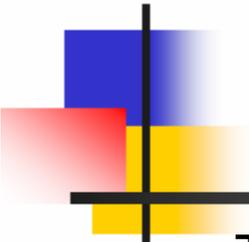
$3P$

$3F$

M_L

M_S

	+1	0	-1
+4		x	
+3	x	xxx	x
+2	x	xxx	x
+1	xx	xxxx	xx
0	xx	xxxxx	xx
-1	xx	xxxx	xx
-2	x	xxx	x
-3	x	xxx	x
-4		x	



Spin-Orbit Coupling

The spin and orbital angular momenta couple each other

→ spin-orbit coupling

J = L + S : total angular momentum quantum number

J may have the following values

$J = L+S, L+S-1, L+S-2, \dots |L-S|$

Term Symbol

$2S+1L_J$

Spin-orbit coupling can have significant effects on the electronic spectra of coordination compounds, especially involving heavy metals.

Spin-orbit coupling acts to split free-ion terms into states of different energies.

Spin-Orbit Coupling

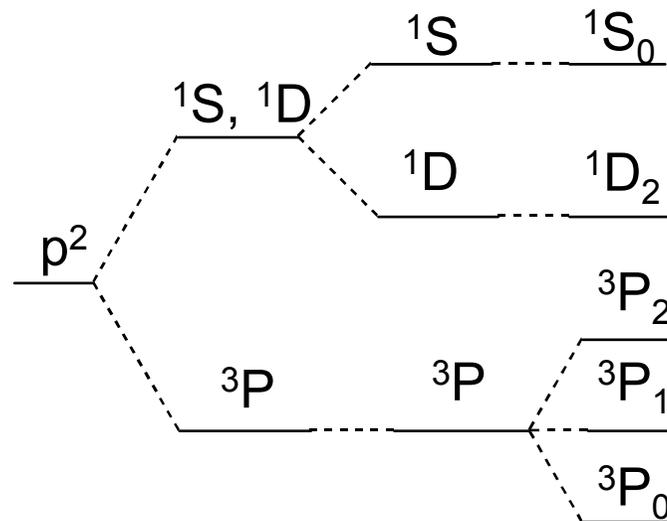
J may have the following values

$$J = L+S, L+S-1, L+S-2, \dots |L-S|$$

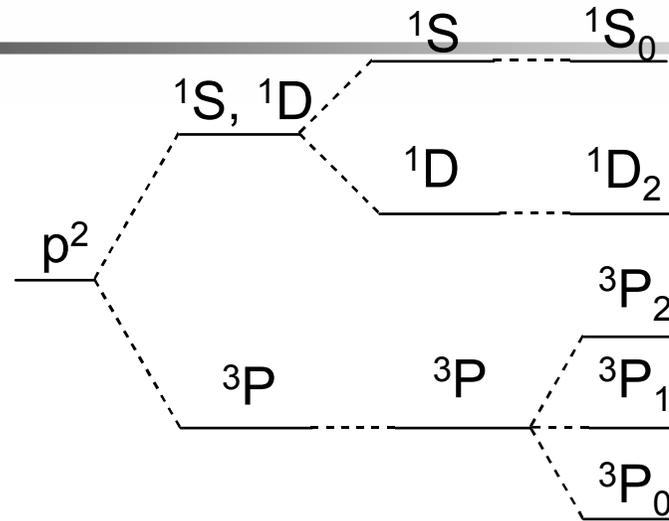
Term Symbol

$$2S+1L_J$$

Spin-orbit coupling acts to split free-ion terms into states of different energies.



Spin-Orbit Coupling



Total energy level diagram for the carbon atom. (five energy states)

The state of lowest energy can be predicted from [Hund's third rule](#).

3. For subshells that are less than half-filled, the state having the lowest J value has the lowest energy.

For subshells that are more than half-filled, the state having the highest J value has the lowest energy.

Half-filled subshells have only one possible J value.