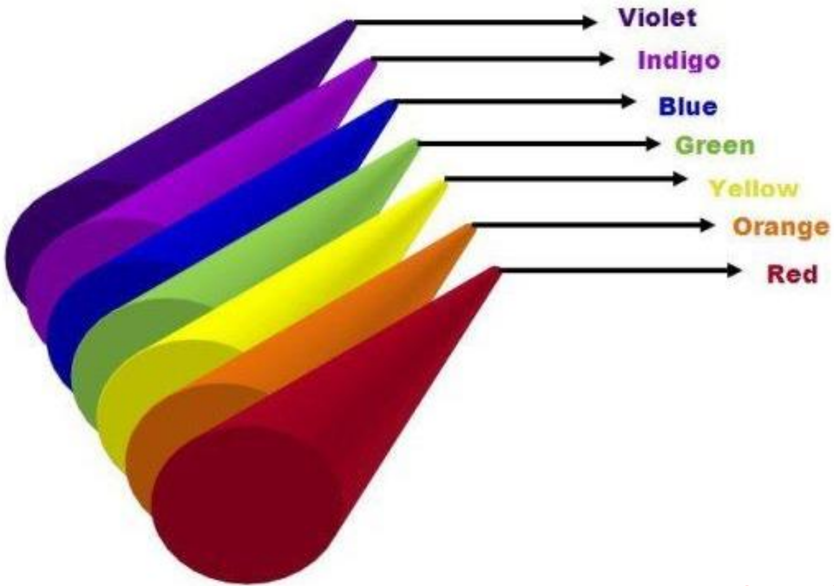
Paper M604

Inorganic Chemistry

Spectra of Coordination Complexes

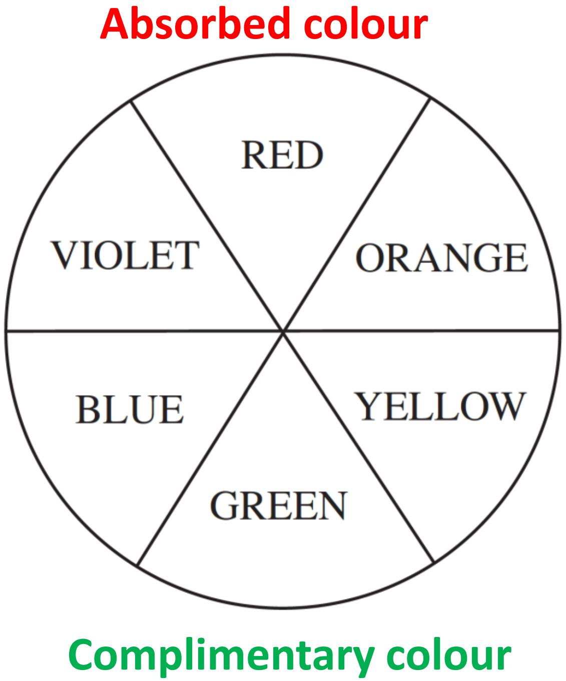
Chemistry of Colours



How do we see colours?

When a compound absorbs a light of specific wavelength it transmits a light of different wavelength which passes through the retina of our eyes and we see the colour.

The transmitted colour is actually known as the complementary colour of the absorbed colour.



Chemistry of Colours

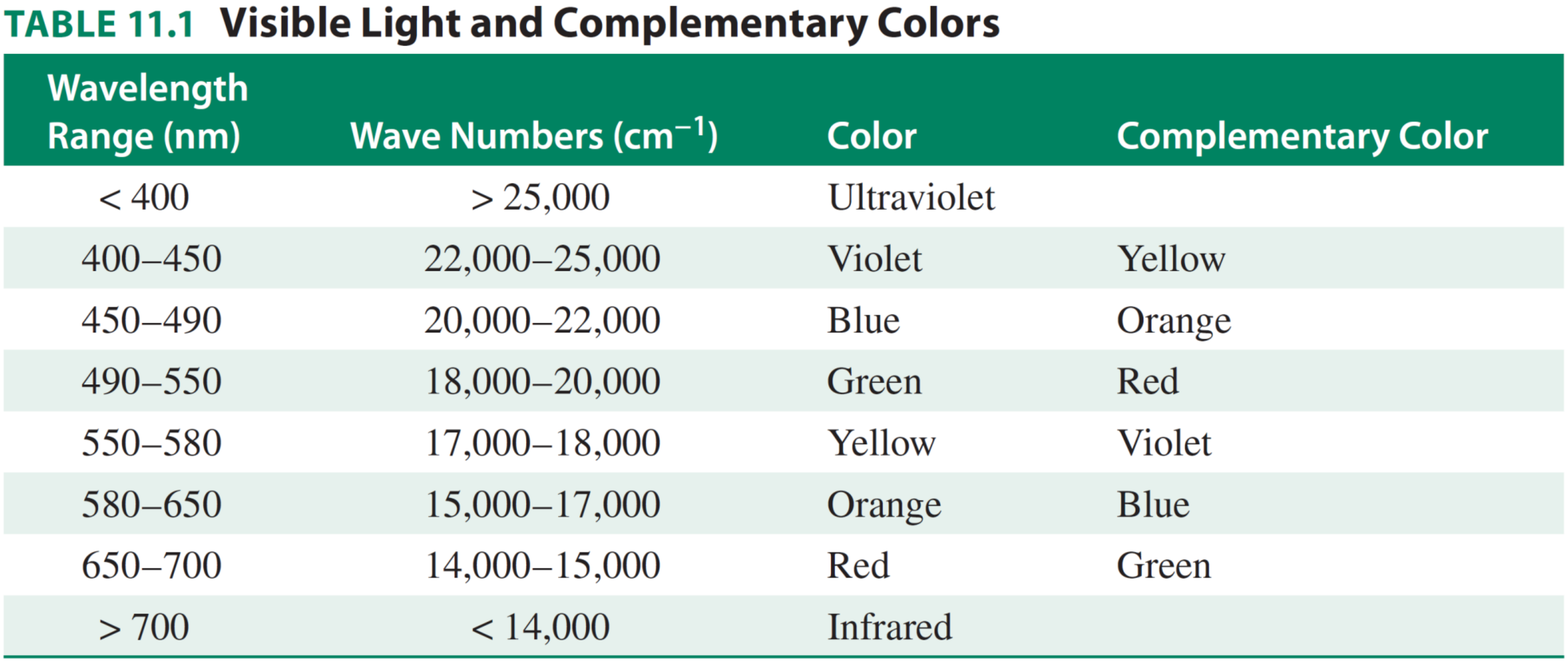


TABLE 11.1 Visible Light and Complementary Colors

Wavelength Range (nm)	Wave Numbers (cm^{-1})	Color	Complementary Color
< 400	$> 25{,}000$	Ultraviolet	
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–550	18,000–20,000	Green	Red
550–580	17,000–18,000	Yellow	Violet
580–650	15,000–17,000	Orange	Blue
650–700	14,000–15,000	Red	Green
> 700	$< 14{,}000$	Infrared	

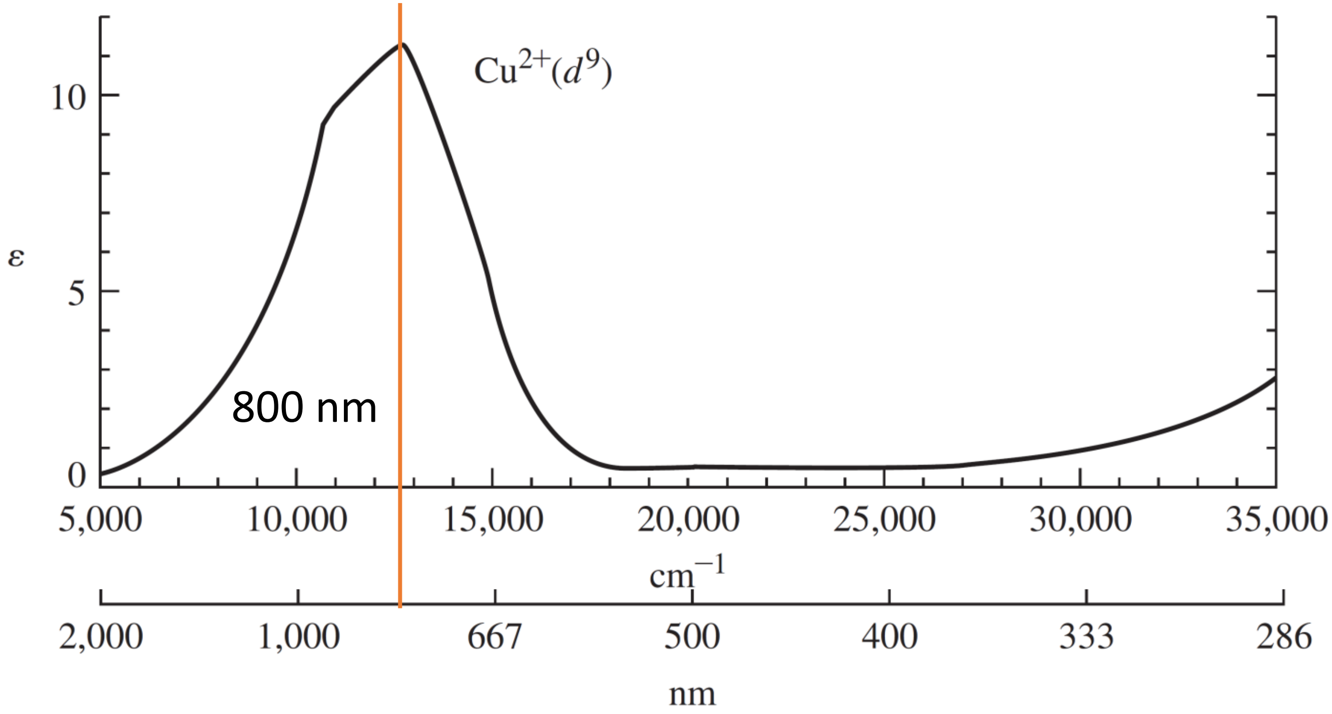
Spectroscopic technique to understand the colour of compounds/complexes:

UV-Visible Spectroscopy: 200 nm to 700 nm

For coordination complexes: 400 nm to 700 nm

An Example: $[Cu(H_2O)_6]^{2+}$

The absorption spectra is shown below:



Complimentary colour: Blue (can see from the naked eyes)

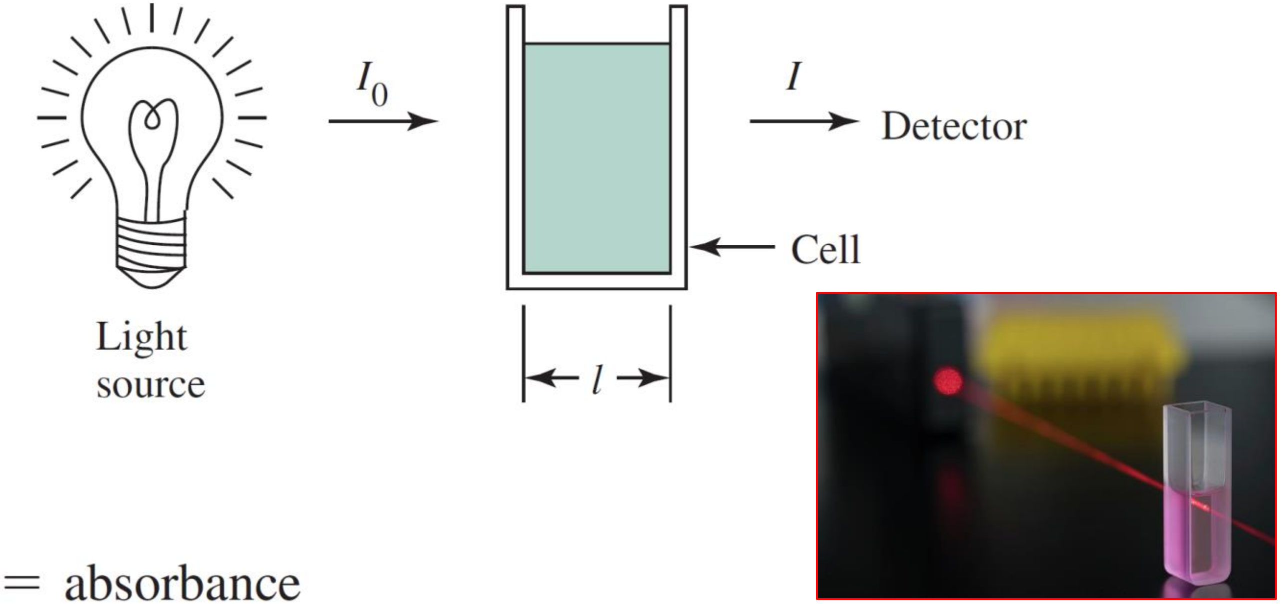
***From the absorption spectra*: It absorbs in the region 600 and 1000 nm**

Conclusion: The color observed, blue,
is the average complementary color of the light absorbed.

Beer–Lambert Absorption Law

The Beer–Lambert law is expressed as:

$$\log \frac{I_o}{I} = A = \varepsilon l c$$



where A = absorbance

ε = molar absorptivity (L mol^{-1} cm^{-1}) (also known as molar extinction coefficient)

l = length through solution (cm)

c = concentration of absorbing species (mol L^{-1})

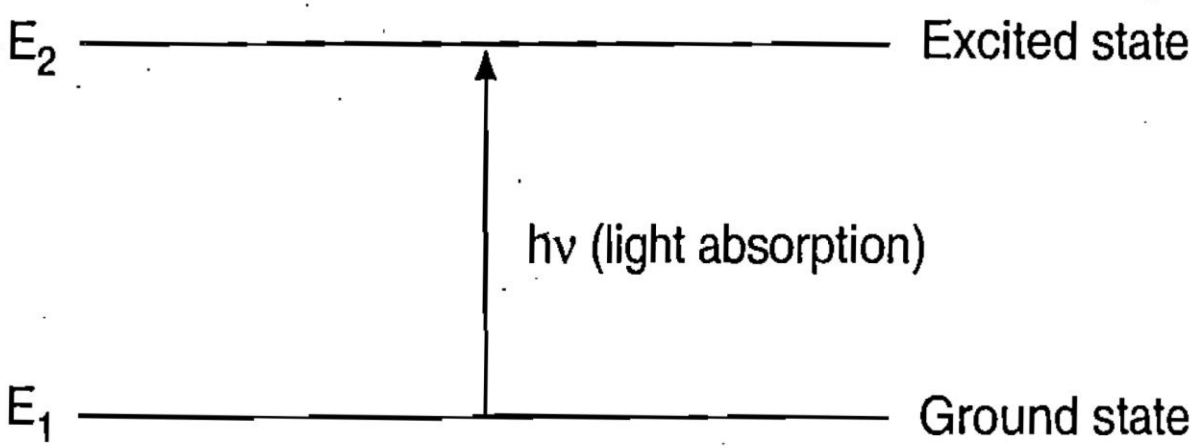
The process of absorption of light by solution

Q: Calculate the % of light absorbed corresponding to absorbance = 1.0 and 2.0?

Electronic Transitions

Electronic transition in complexes: t_{2g} to e_g (for Octahedral complexes)
t_2 to e (for Tetrahedral complexes)

Electronic transitions in transition metal complexes are therefore also called d-d transitions



$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \qquad (\because \ \bar{\nu} = \frac{1}{\lambda})$$

where,

ΔE = energy
h = Planck constant = 6.63×10^{-34} J.s
c = velocity of light = 10^{-10} cm s^{-1}
λ = wavelength of light absorbed (cm)
ν = frequency of light absorbed (s^{-1})
$\bar{\nu}$ = wave number (cm^{-1}) = $\frac{1}{\lambda}$

Importance of Spectral Studies

The spectrum arises due to transitions between states of different energies and can provide valuable information about those states and, in turn, about the structure and bonding of the molecule or ion.

The magnitude of crystal field splitting (Δ) can be measured with the help of wavelength of light absorbed.

Calculation Δ_o for $[Ti(H_2O)_6]^{2+}$ (d^1)

$\Delta E = \Delta_o = 20{,}300\ cm^{-1}$

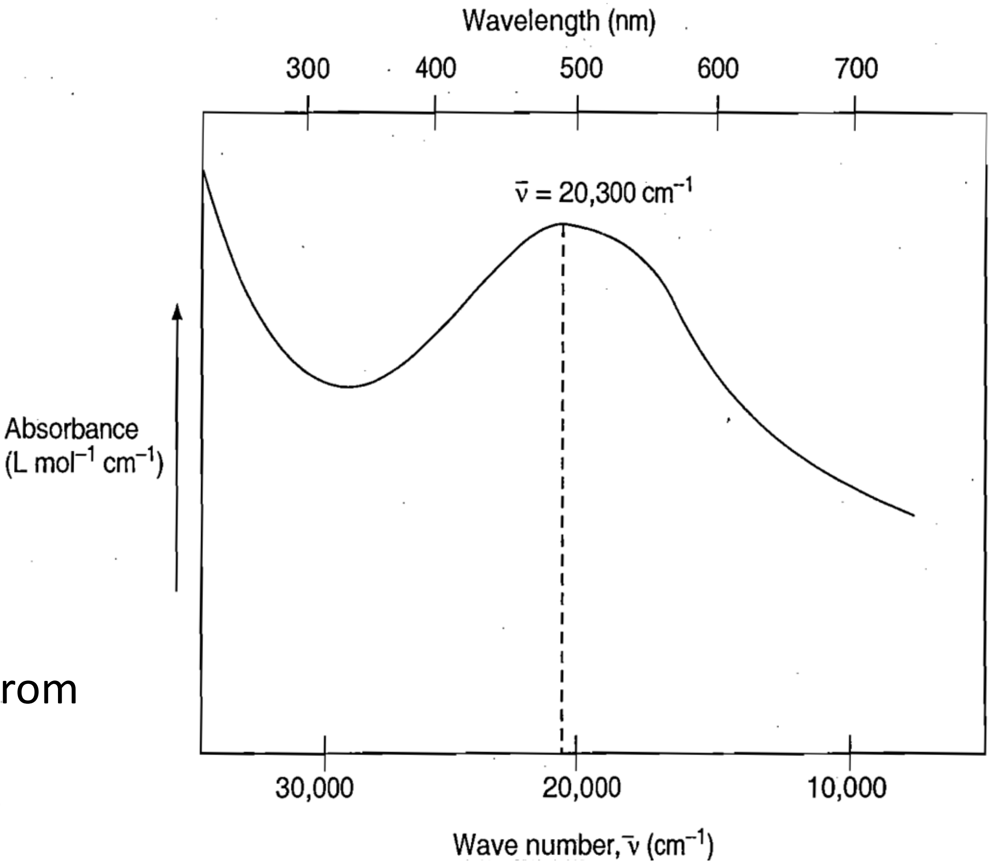
or $= 20{,}300/83.7\ kJmol^{-1}$

or $= 242.53\ kJmol^{-1}$

$\left(\text{Since } 1\ kJ\ mol^{-1} = 83.7\ cm^{-1} \right)$

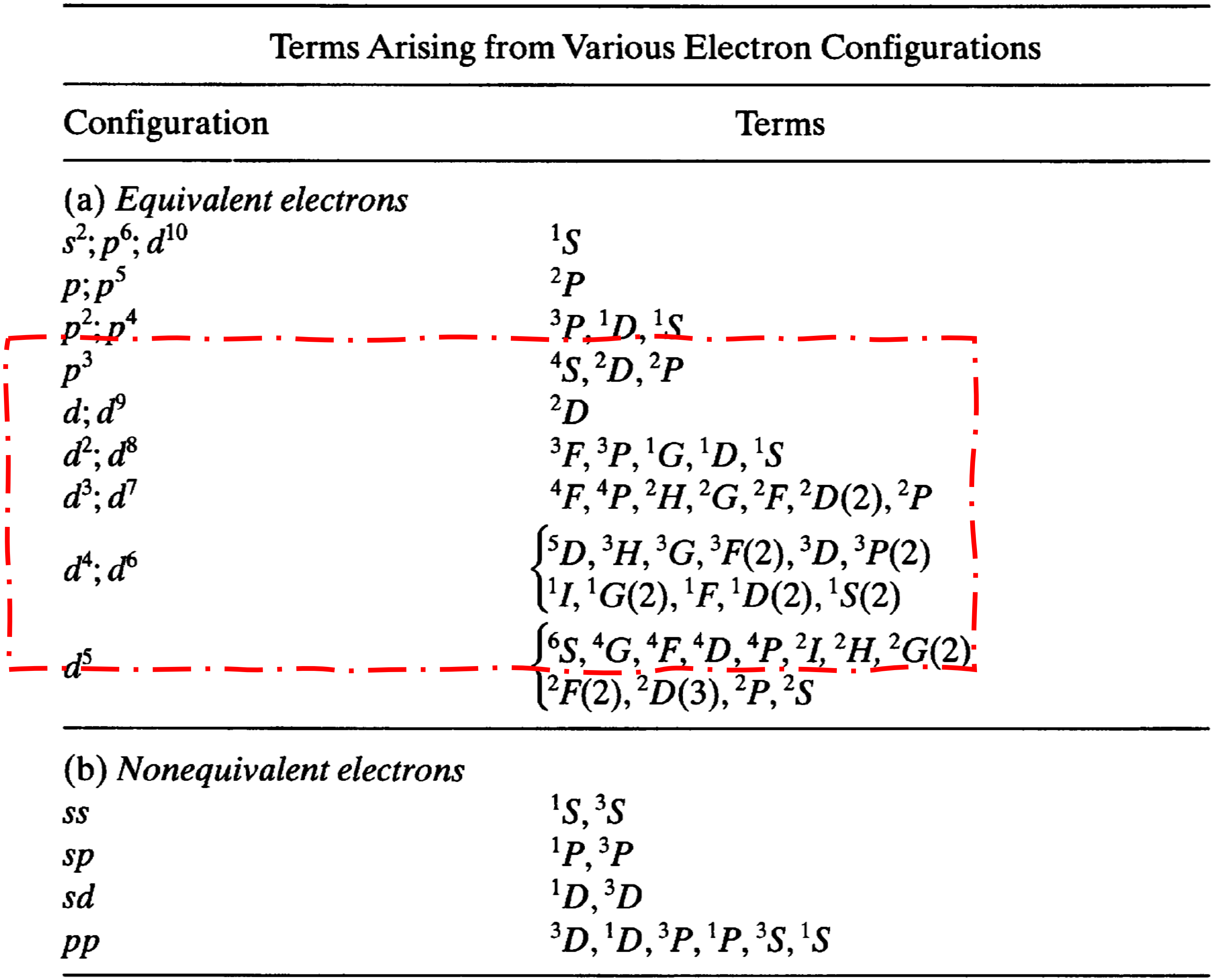
The absorption spectra apparently arises from

a single transition i.e. $t_{2g}^{0}e_g^{1} \longleftarrow t_{2g}^{1}$



Quantum Numbers of Multielectron Atoms

Spectroscopic terms



Terms Arising from Various Electron Configurations

Configuration	Terms
(a) *Equivalent electrons*	
$s^2; p^6; d^{10}$	^1S
$p; p^5$	^2P
$p^2; p^4$	$^3P, ^1D, ^1S$
p^3	$^4S, ^2D, ^2P$
$d; d^9$	^2D
$d^2; d^8$	$^3F, ^3P, ^1G, ^1D, ^1S$
$d^3; d^7$	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$
$d^4; d^6$	$^5D, ^3H, ^3G, ^3F(2), ^3D, ^3P(2)$ $^1I, ^1G(2), ^1F, ^1D(2), ^1S(2)$
d^5	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2)$ $^2F(2), ^2D(3), ^2P, ^2S$
(b) *Nonequivalent electrons*	
ss	$^1S, ^3S$
sp	$^1P, ^3P$
sd	$^1D, ^3D$
pp	$^3D, ^1D, ^3P, ^1P, ^3S, ^1S$

Quantum Numbers of Multielectron Atoms

The classification of microstates

- ❑ The terms of a $3d^2$ configuration are ^1G, ^3F, ^1D, ^3P, and ^1S.
- ❑ The degeneracy of the microstates is given by

_(2L+1)(2S+1)_

Term	Number of states
^1G	$9 \times 1 = 9$
^3F	$7 \times 3 = 21$
^1D	$5 \times 1 = 5$
^3P	$3 \times 3 = 9$
^1S	$1 \times 1 = 1$
Total:	45

- ❑ *Microstates of d^e configuration is given by*

_n!/(e!(n-e)!_

Where, “e” number of electrons to be placed in “n” number of possible orbital positions.

Microstates arising from a $3d^2$ configuration

						m_s= +1/2							m_s= -1/2		
M_L	M_S		m_l =	+2	+1	0	-1	-2		m_l =	+2	+1	0	-1	-2
4	0			↑							↓				
3	0			↑								↓			
2	0			↑									↓		
1	0			↑										↓	
0	0			↑											↓
3	0				↑						↓				
2	0				↑							↓			
1	0				↑								↓		
0	0				↑									↓	
-1	0				↑										↓
2	0					↑					↓				
1	0					↑						↓			
0	0					↑							↓		
-1	0					↑								↓	
-2	0					↑									↓
1	0						↑				↓				
0	0						↑					↓			
-1	0						↑						↓		
-2	0						↑							↓	
-3	0						↑								↓
0	0							↑			↓				
-1	0							↑				↓			
-2	0							↑					↓		
-3	0							↑						↓	
-4	0							↑							↓

Quantum Numbers of Multielectron Atoms

The energies of the terms

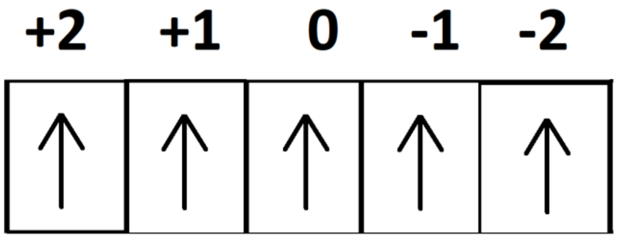
- For a given configuration, the term with the greatest multiplicity lies lowest in energy. For the d^2 configuration, this rule predicts that the ground state will be either ^3F or ^3P.
- For a term of given multiplicity, the term with the greatest value of L lies lowest in energy. for d^2 the rules predict the order: $^3F < {}^3P < {}^1G < {}^1D < {}^1S$
- **The order observed for Ti^{2+} from spectroscopy is $^3F < {}^1D < {}^1G < {}^3P < {}^1S$.**
- *Therefore, the 'greatest L' rule is reliable only for predicting the ground term.*
- The procedure of finding the ground term of an atom or ion is as follows:
  - i. Identify the microstate that has the highest value of M_S.
  - ii. Identify the highest permitted value of M_L for that multiplicity.

For e.g., $3d^5$ of Mn^{2+}

$S = 5 \times 1/2 = 5/2$; $M_S = 2S + 1 = \{2 \times (5/2) + 1\} = 6$

$M_L = 2 + 1 + 0 + (-1) + (-2) = 0$

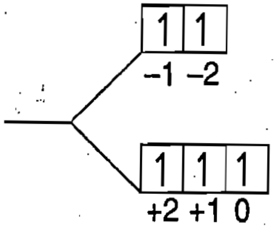
L = 0 corresponds to a S term. So, the ground term is ^6S.



Quantum Numbers of Multielectron Atoms

Identification of G.S. Term in O_h symmetry

(i) High spin d^5 :



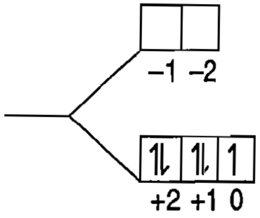
$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{5}{2}$$

$$2S + 1 = 2 \times \frac{5}{2} + 1 = 6$$

$$M_L = 2 + 1 + 0 - 1 - 2 = 0, \quad \therefore\ S \text{ state}$$

$\therefore$ Ground state term = ${}^6S$

(ii) Low spin d^5 :



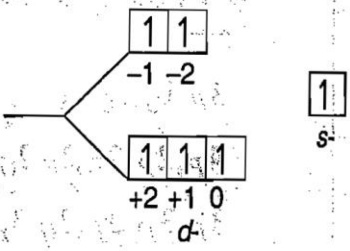
$$M_L = 2 + 2 + 1 + 1 + 0 = 6, \quad \therefore\ I \text{ state}$$

$$S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} + \frac{1}{2} = \frac{1}{2}$$

$$2S + 1 = 2 \times \frac{1}{2} + 1 = 2$$

$\therefore$ Ground state term = ${}^2I$

(iii) High spin d^5s^1 :



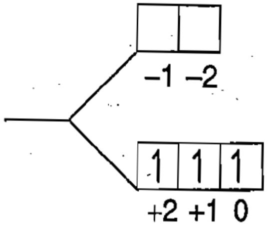
$$M_L = 2 + 1 + 0 - 1 - 2 + 0 = 0, \quad \therefore\ S \text{ state}$$

$$S = \frac{6}{2} = 3$$

$$2S + 1 = 2 \times 3 + 1 = 7$$

Ground state term = ${}^7S$

(iv) d^3-Octahedral Symmetry :



$$M_L = 2 + 1 + 0 = 3, \quad \therefore\ F \text{ state}$$

$$S = \frac{3}{2}$$

$$2S + 1 = 2 \times \frac{3}{2} + 1 = 4$$

$\therefore$ Ground state term = ${}^4F$

Quantum Numbers of Multielectron Atoms

Racah parameters

- The Racah parameters summarize the effects of electron-electron repulsion on the energies of the terms that arise from a single configuration.
- The repulsion energy of any term of a configuration can be expressed as a sum of three quantities denoted A, B, and C are called the Racah parameters.
- The parameter A corresponds to an average of the total interelectron repulsion, and B and C relate to the repulsion energies between individual d electrons.
- The parameters A, B, and C can be used as empirical quantities obtained from gas-phase atomic spectroscopy.
- Each term stemming from a given configuration has an energy that may be expressed as a linear combination of all three Racah parameters.
- Fora d^2 configuration a detailed analysis shows that

$$E(^1\mathrm{S}) = A + 14B + 7C \quad E(^1\mathrm{G}) = A + 4B + 2C \quad E(^1\mathrm{D}) = A - 3B + 2C$$

$$E(^3\mathrm{P}) = A + 7B \quad E(^3\mathrm{F}) = A - 8B$$

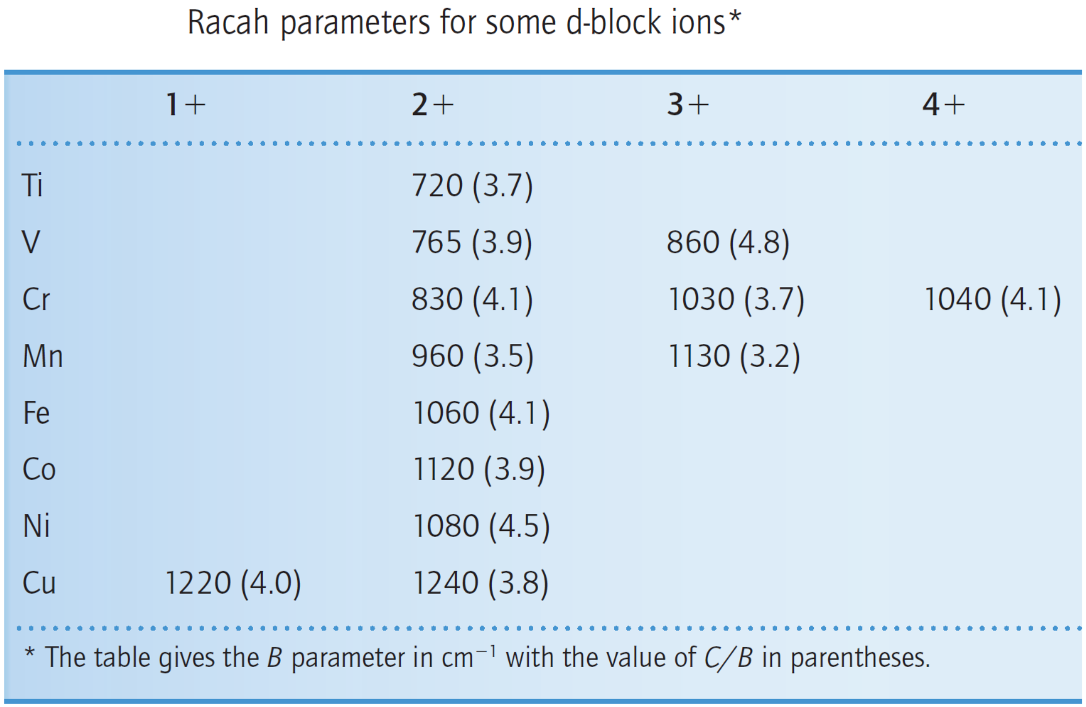
Electronic spectra of complexes

Ligand-field transitions (d-d transitions)

- All three Racah parameters are positive as they represent electron-electron repulsions.
- In case, C > 5B, the energies of the terms of the d^2 configuration lie in the order

$$^3F < {}^3P < {}^1G < {}^1D < {}^1S \text{ (follows Hund's rule)}$$

- However, if C < 5B, the advantage of having an occupation of orbitals that corresponds to a high orbital angular momentum is greater than the advantage of having a high multiplicity.
- The values in parentheses indicate that $C \approx 4B$ so the ions listed there are in the region where Hund's rules are not reliable for predicting anything more than the ground term of a configuration.
- The parameter B is of the most interest.



Racah parameters for some d-block ions*

	1+	2+	3+	4+
Ti		720 (3.7)		
V		765 (3.9)	860 (4.8)	
Cr		830 (4.1)	1030 (3.7)	1040 (4.1)
Mn		960 (3.5)	1130 (3.2)	
Fe		1060 (4.1)		
Co		1120 (3.9)		
Ni		1080 (4.5)		
Cu	1220 (4.0)	1240 (3.8)		

* The table gives the *B* parameter in cm^{-1} with the value of *C*/*B* in parentheses.

Selection Rules

- A spectroscopic selection rule is a statement about which transitions are allowed and which are forbidden.
- An **allowed transition** is a transition with a nonzero transition dipole moment, and hence nonzero intensity.
- A **forbidden transition** is a transition for which the transition dipole moment is calculated as zero.
- The strength of coupling when an electron makes a transition from a state with wavefunction Ψi to one with wavefunction Ψf is measured by the transition dipole moment, which is defined as the integral

$$\boldsymbol{\mu}_{\mathrm{fi}} = \int \psi^*{}_{\mathrm{f}} \boldsymbol{\mu} \psi_{\mathrm{i}} \, \mathrm{d}\tau$$

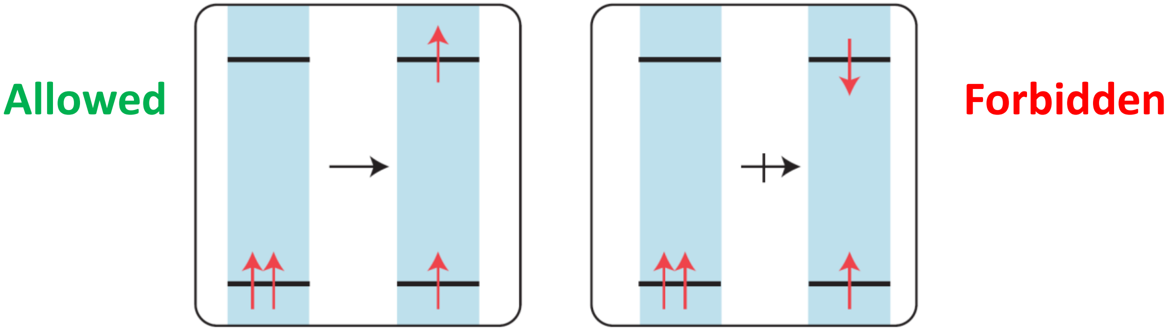
where μ is the electric dipole moment operator, *-er*.

- The transition dipole moment can be regarded as a measure of the impulse that a transition imparts to the electromagnetic field: a large impulse corresponds to an intense transition; zero impulse corresponds to a forbidden transition.
- The intensity of a transition is proportional to the square of its transition dipole moment.

Selection Rules

Spin selection rules

- Transitions between states of different spin multiplicities are forbidden. In other words, the rule ΔS = 0 is for the spin allowed transitions.



- The coupling of spin and orbital angular momenta can relax the spin selection rule, but such spin-forbidden. ΔS ≠ 0, transitions are generally much weaker than spin-allowed transitions.
- The intensity of spin-forbidden bands increases as the atomic number increases because the strength of the spin-orbit coupling is greater for heavy atoms than for light atoms (the **heavy-atom effect**).
- In the 3d series, the spin-orbit coupling is generally weak however, spin-forbidden bands are a significant feature in the spectra of heavy d-metal complexes.
- Metal ions, such as Mn^{2+} ion, have no spin-allowed transitions, and are weakly colored.

Selection Rules

Laporte selection rules

- The Laporte selection rule states that in a centrosymmetric molecule or ion, the only allowed transitions are those accompanied by a change in parity. i.e.

$$g \leftrightarrow u \qquad g \nleftrightarrow g \qquad u \nleftrightarrow u$$

- According to this rule, in a centrosymmetric complex, s-s, p-p, d-d, and f-f transitions are forbidden as there is no change in quantum number l, so there can be no change in parity.
- The intensity of spin-forbidden bands increases as the atomic number increases because the strength of the spin-orbit coupling is greater for heavy atoms than for light atoms (the **heavy-atom effect**).
- Again, since s and d orbitals are g, whereas p and f orbitals are u it follows that s-p, p-d, and d-f transitions are allowed whereas s-d and p-f transitions are forbidden.

The transition dipole moment is proportional to ***r*** *and it changes sign under inversion (and is therefore u)*

Transition	Integral	Remarks
g <-> g	g x u x g = u	Forbidden
u <-> u	u x u x u = u	Forbidden
g <-> u	g x u x u = g	Allowed

Selection Rules

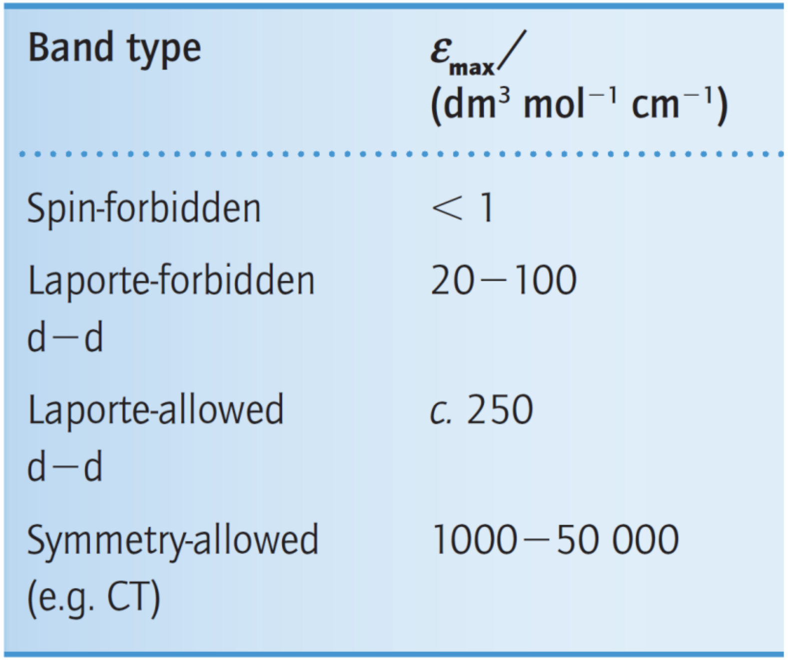
Relaxation of Laporte selection rules

- ❑ Why d-d ligand-field transitions in octahedral complexes occur at all, even weakly?
- ❑ The Laporte selection rule may be relaxed in two ways:
  - i. *First, a complex may depart slightly from perfect centrosymmetry in its ground state, perhaps on account of the intrinsic asymmetry in the structure of polyatomic ligands or a distortion imposed by the environment of a complex packed into a crystal*
  - ii.*Alternatively, the complex might undergo an asymmetrical vibration, which also destroys its center of inversion (Vibronic coupling)*
- ❑ A Laporte-forbidden d-d ligand-field band tends to be much more intense than a spin-forbidden transition.
- ❑ Tetrahedral complexes often absorb more strongly than octahedral complexes of the same metal in the same oxidation state. The mixing of p -orbital character (of u symmetry) with d -orbital character also provides a way of relaxing this selection rule.

Selection Rules

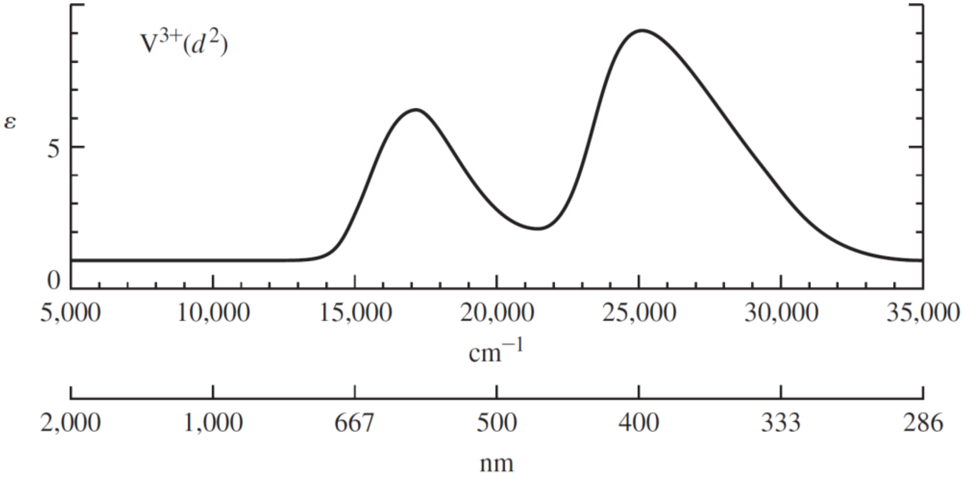
Intensity of Absorption

- Typical intensities of electronic transitions of complexes of the 3d-series elements are as follows:



Band type	**ε_{max}/ (dm^3 mol^{-1} cm^{-1})**
Spin-forbidden	< 1
Laporte-forbidden d–d	20–100
Laporte-allowed d–d	*c.* 250
Symmetry-allowed (e.g. CT)	1000–50 000

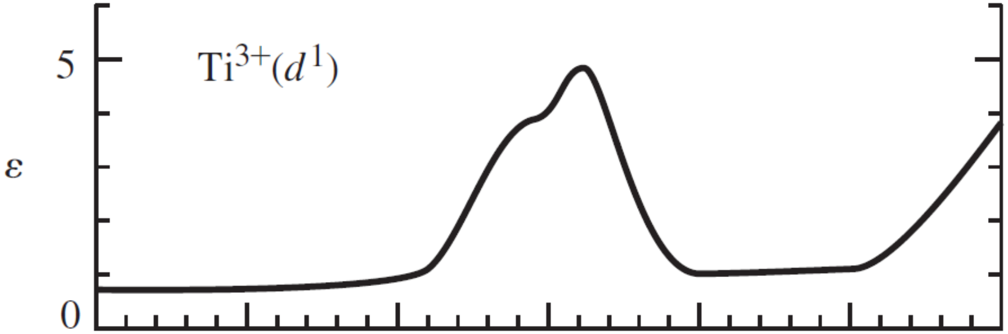
- The width of spectroscopic absorption bands is due principally to the simultaneous excitation of vibration when the electron is promoted from one distribution to another.

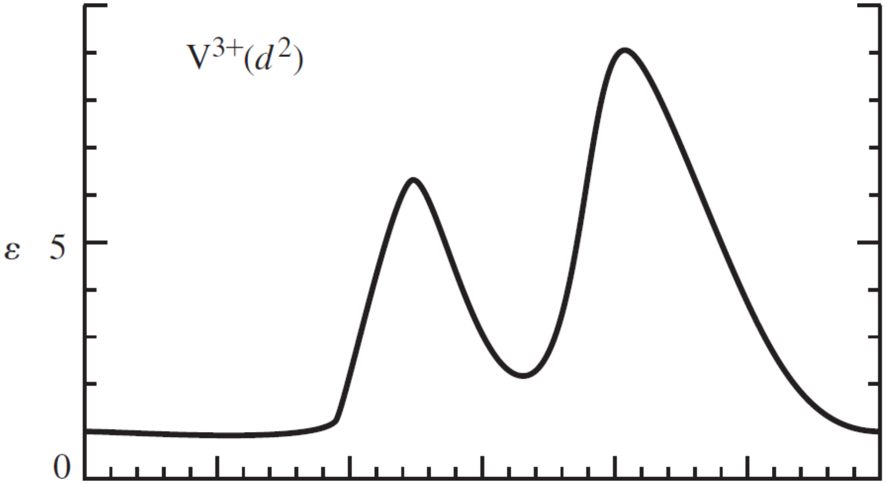


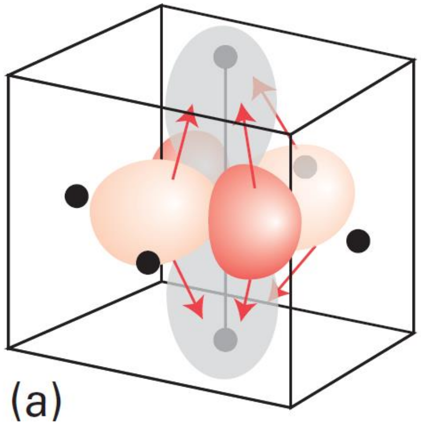
Electronic Spectra of Complexes

Ligand-field transitions

Why the transition gives rise to two bands in a d^2 ion?

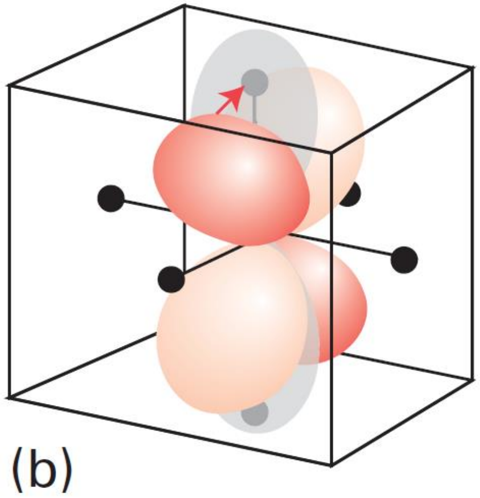






transfer of electron density

e.g.: $d_{z2} \longleftarrow d_{xy}$



relocation of electron density

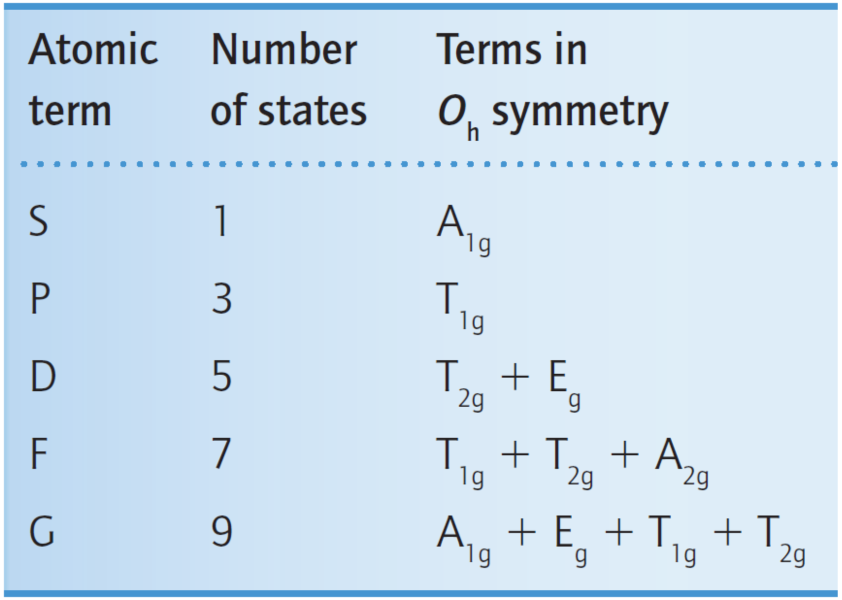
e.g.: $d_{z2} \longleftarrow d_{xz}$

Electronic Spectra of Complexes

The spectroscopic terms

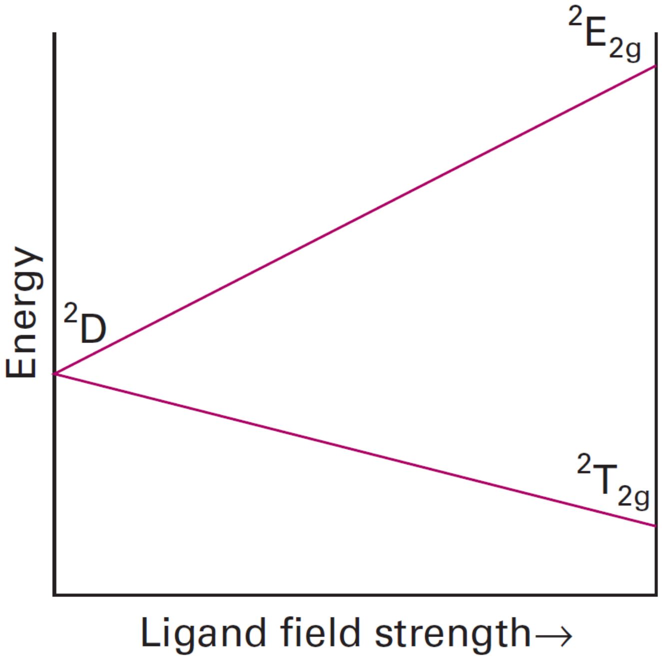
❑ The terms of an octahedral complex are labelled by the symmetry species of the overall orbital state

❑ A superscript prefix of a term represents the multiplicity of the term.



Atomic term	Number of states	Terms in O_h symmetry
S	1	A_{1g}
P	3	T_{1g}
D	5	$T_{2g} + E_g$
F	7	$T_{1g} + T_{2g} + A_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$

The correlation of spectroscopic terms for d electrons in O_h complexes



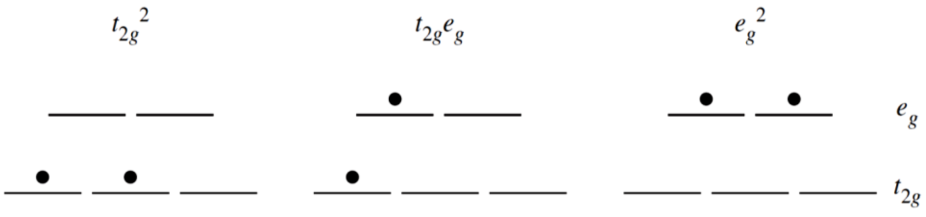
Splitting of a d^1 configuration in O_h field

Electronic Spectra of Complexes

The energies of the terms: weak- and strong-field limits

Correlation diagram

The correlation diagrams illustrate how the energies of electronic states change between the Free ions (no ligand field) and Strong ligand field limits

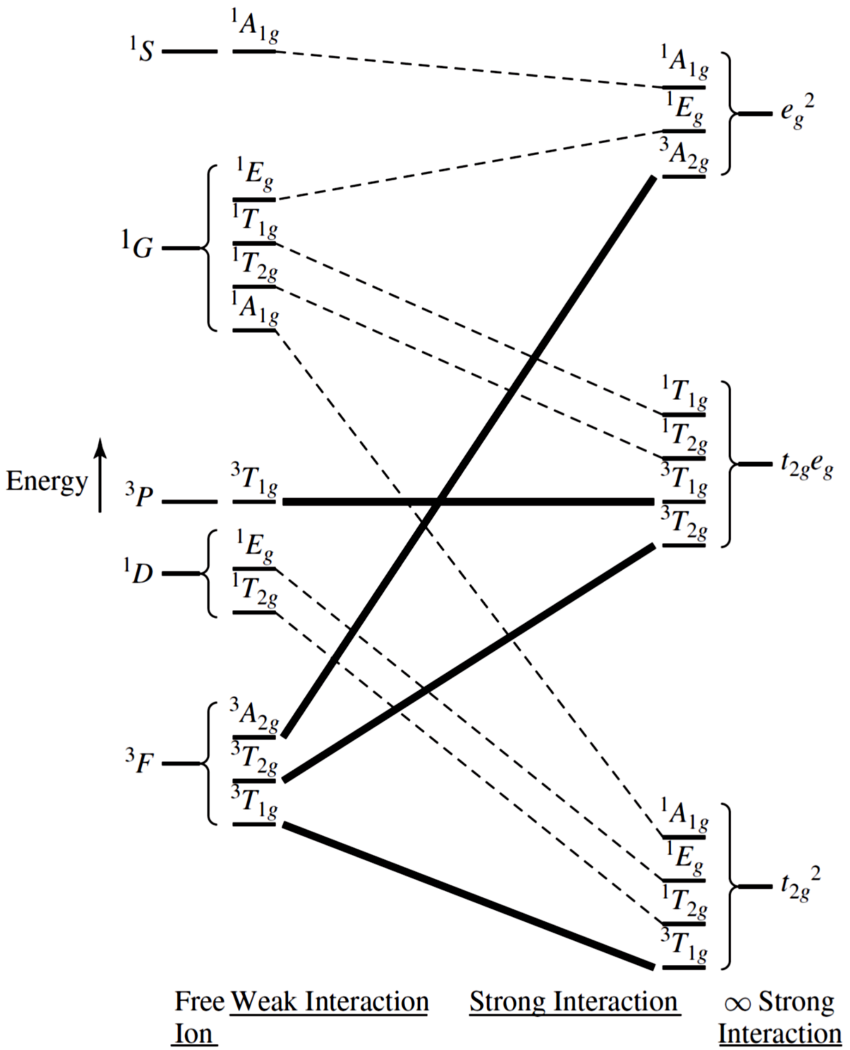


three possible configurations for two d electrons in an octahedral ligand field

Characteristics of the correlation diagram:

1. The free-ion states (terms arising from *LS* coupling) are shown on the far left.

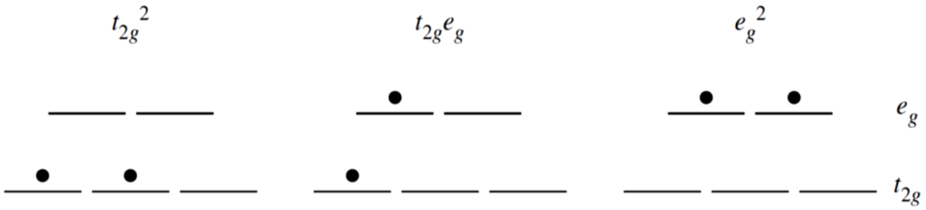
2. The extremely strong field states are shown on the far right.



d^2 in Octahedral Ligand Field

Electronic Spectra of Complexes

Simplified Correlation diagrams: Orgel diagram

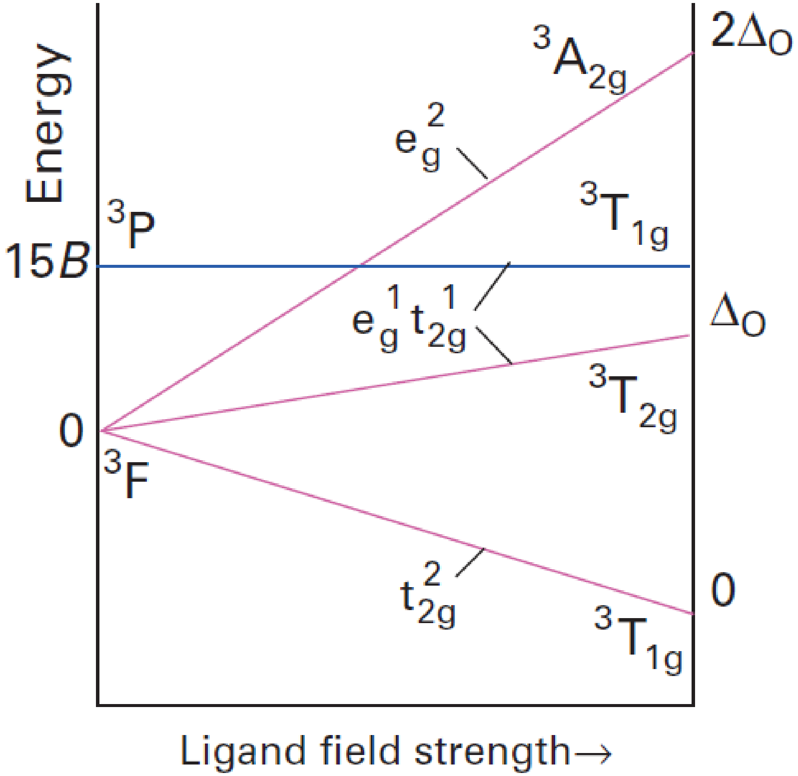


three possible configurations for two d electrons in an octahedral ligand field

$$E(t_{2g}^2) = 2(-\tfrac{2}{5}\Delta_O) = -0.8\Delta_O$$

$$E(t_{2g}^1 e_g^1) = (-\tfrac{2}{5} + \tfrac{3}{5})\Delta_O = +0.2\Delta_O$$

$$E(e_g^2) = 2(\tfrac{3}{5})\Delta_O = +1.2\Delta_O$$



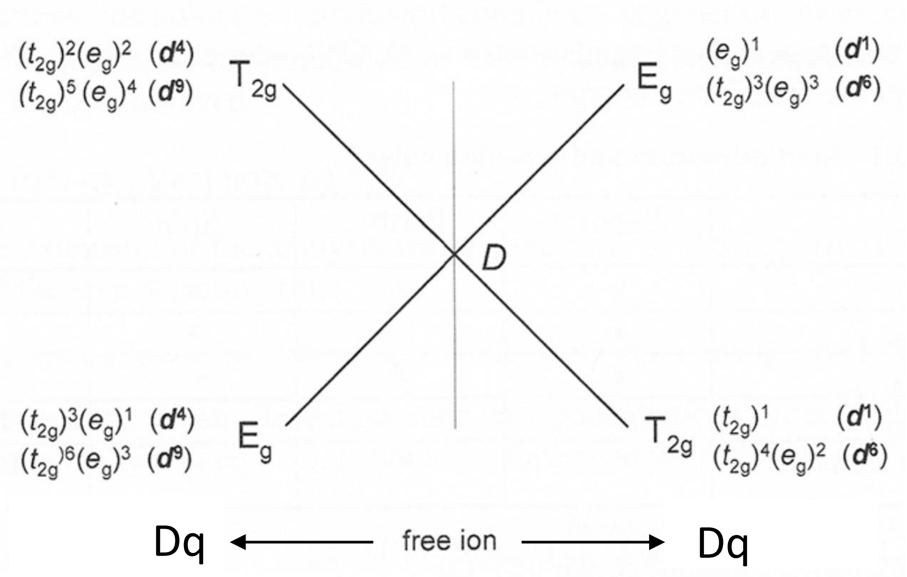
The energies of the terms relative to the ground term are

$$E(t_{2g}^2, T_{1g}) = 0 \qquad E(t_{2g}^1 e_g^1, T_{2g}) = \Delta_O \qquad E(e_g^2, A_{2g}) = 2\Delta_O$$

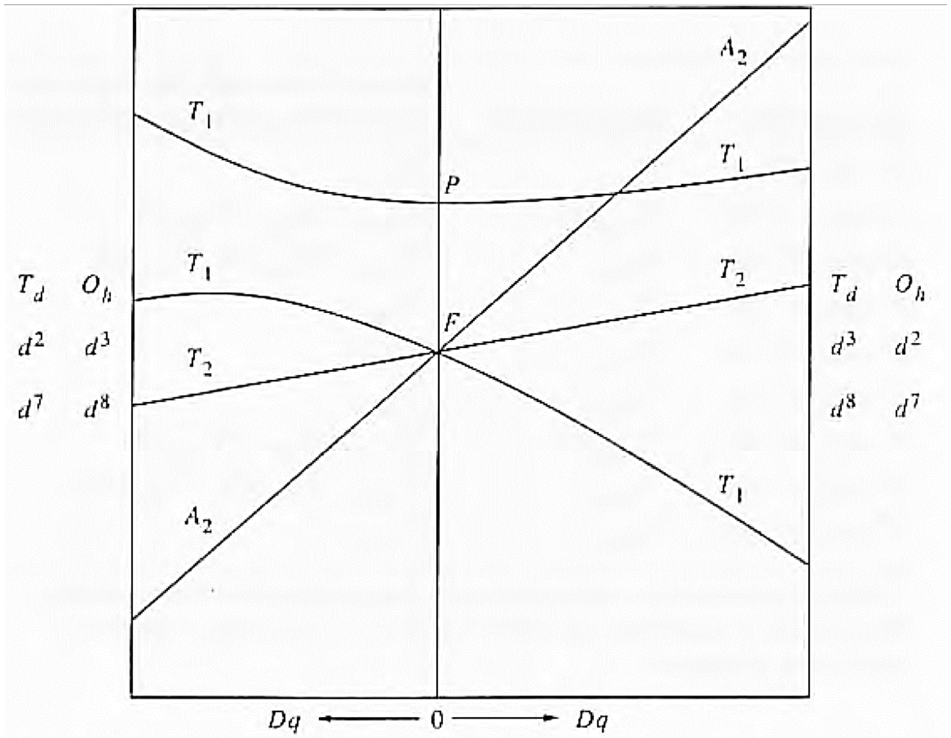
Electronic Spectra of Complexes

Simplified Correlation diagrams: Orgel diagram

NOTE: Orgel diagrams are used to reference the ground state of (*high spin*) transition metal complexes



Orgel diagram for d^1, d^4, d^6, d^9 in O_h field



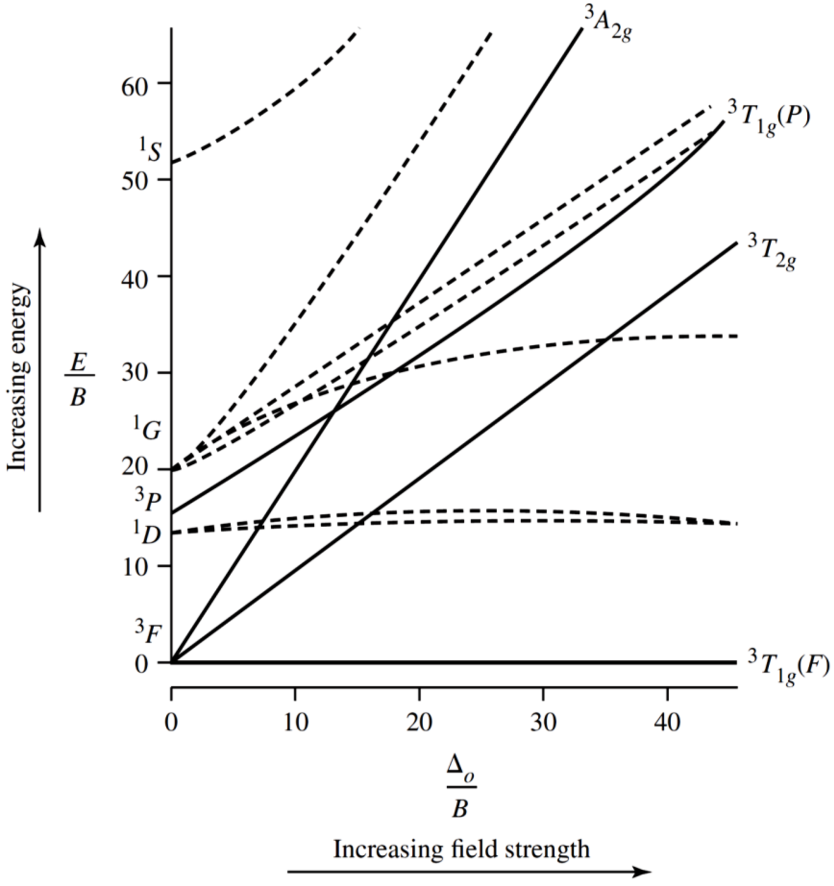
Orgel diagram for d^2, d^3, d^7, d^8 in O_h and T_d fields

Electronic Spectra of Complexes

Tanabe-Sugano Diagram

Tanabe-Sugano diagrams are correlation diagrams that depict the energies of electronic states of complexes as a function of the strength of the ligand field.

- Splitting of all the atomic terms can be seen.
- Energies of the terms are expressed as E/B and plotted against Δo/B, where B is the Racah parameter.
- The relative energies of the terms arising from a given configuration is plotted considering typically setting C ≈ 4B in a single diagram.
- The curved lines represents mixing of terms of the same symmetry type.
- The zero of energy in a Tanabe-Sugano diagram is always taken as that of the lowest term.
- The F in parentheses distinguishes this $^3T_{1g}$ term from the higher energy $^3T_{1g}$ term arising from the ^3P term in the free-ion limit.

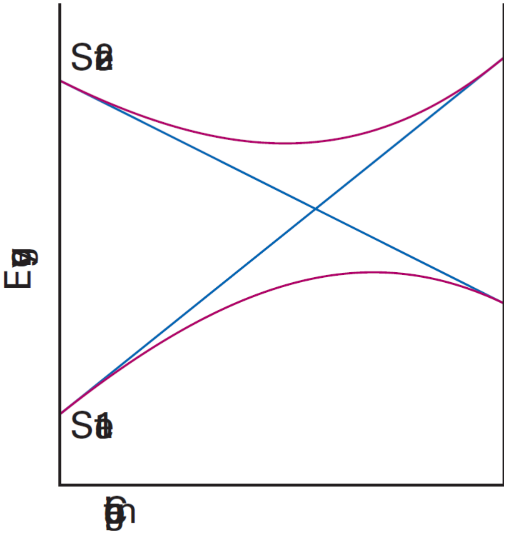


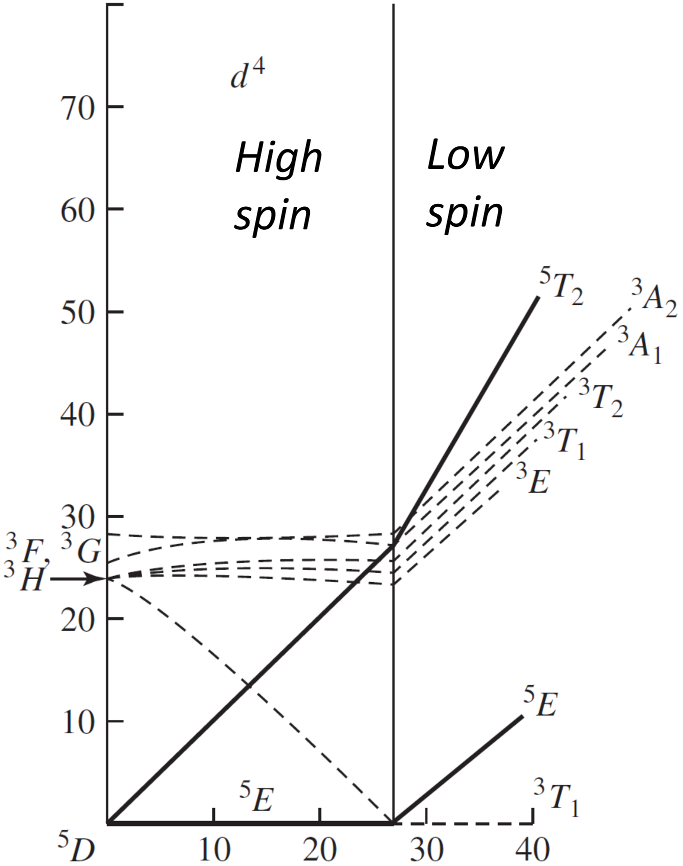
T-S diagram for d^2 configuration

Electronic Spectra of Complexes

Tanabe-Sugano Diagram

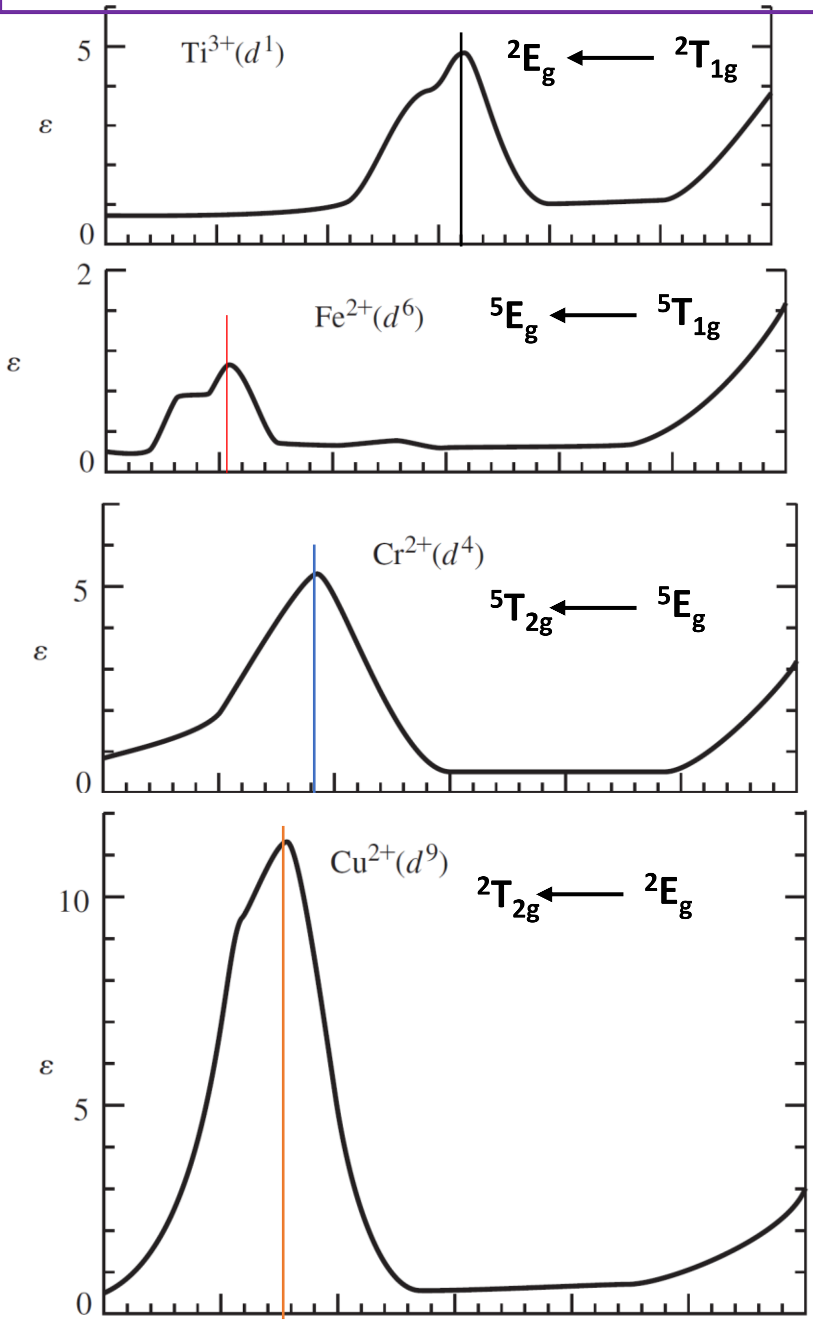
- ☐ Terms of the same symmetry obey the **noncrossing rule**, whic states that, if the increasing ligand field causes two weak-fiel terms of the same symmetry to approach, then they do not cros but bend apart from each other.



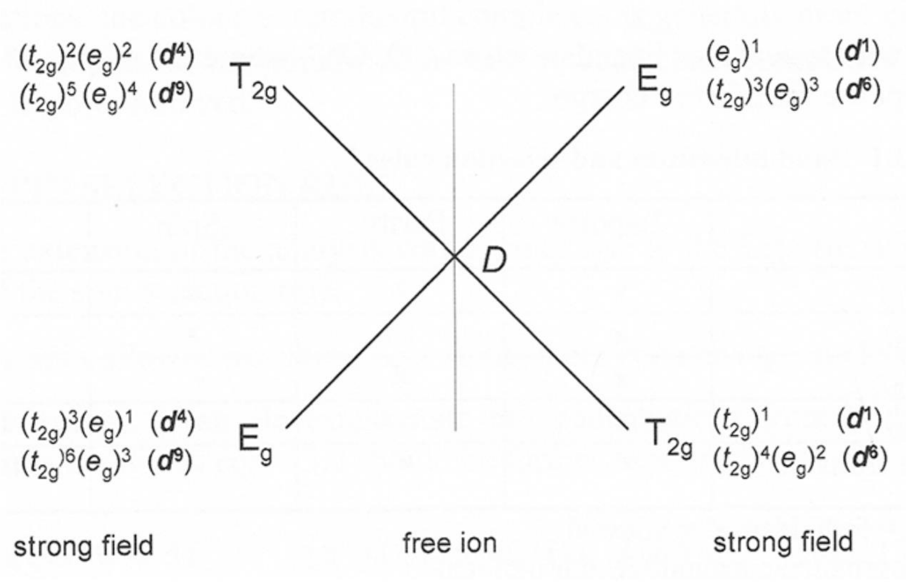


- ☐ The lines in the diagrams have abrupt changes of slope when there is a change in the identity of the ground term brought about by the change from high-spin to low-spin with increasing field strength.
- ☐ USE: To extract the value of the ligand-field splitting parameter from the electronic absorption spectrum of a complex with more than one d electron, when electron-electron repulsions are important.

Electronic Spectra of Complexes



Electronic Spectra of First-Row Transition-Metal Complexes of Formula $[M(H_2O)]^{n+}$ (where M = d^1, d^4, d^6 and d^9 metal ions) in the wavelength range of 2000 nm to 200 nm.



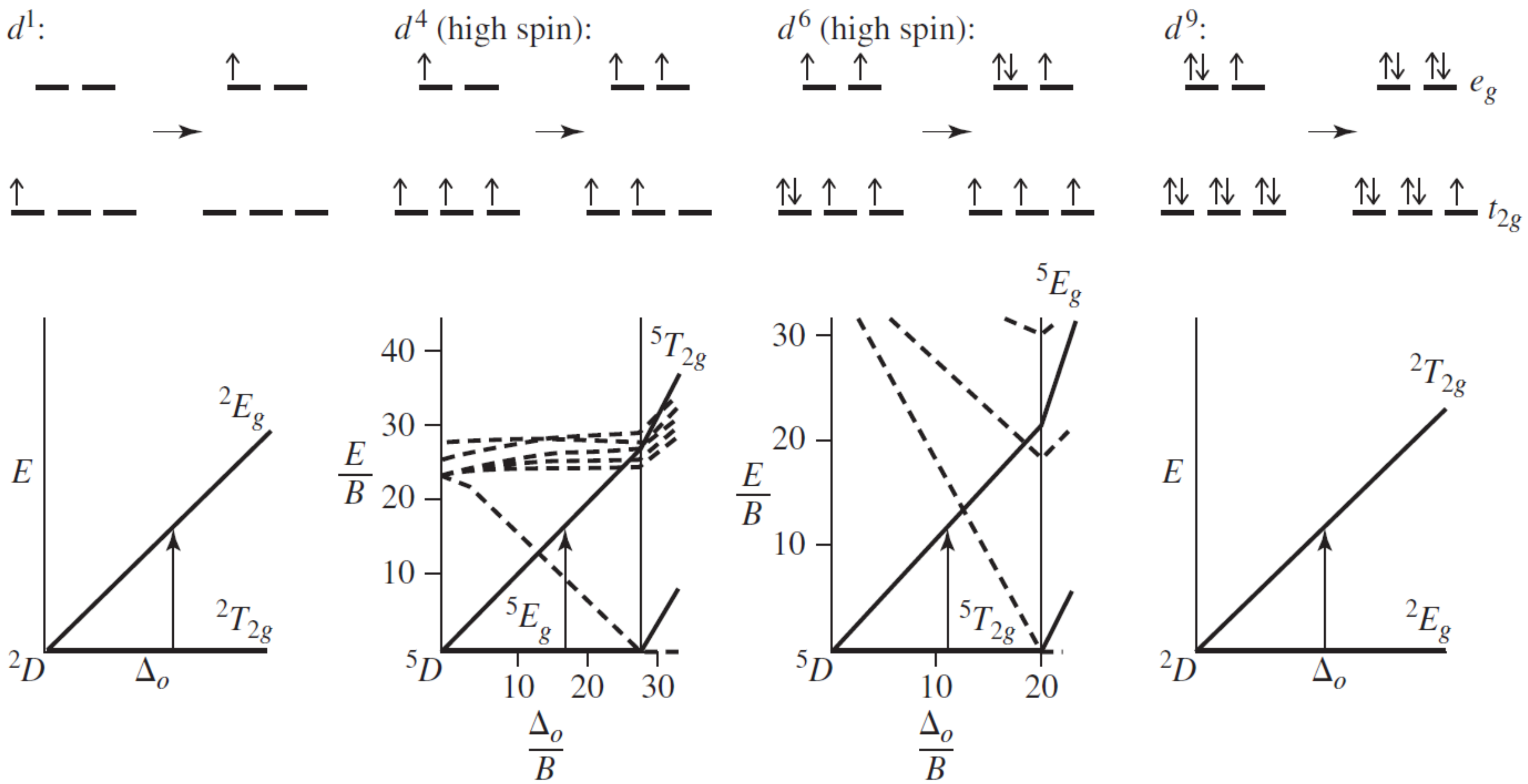
Orgel diagram for d^1, d^4, d^6, d^9 in O_h field

Splitting of band occurs due to Jahn–Teller distortion.

Electronic Spectra of Complexes

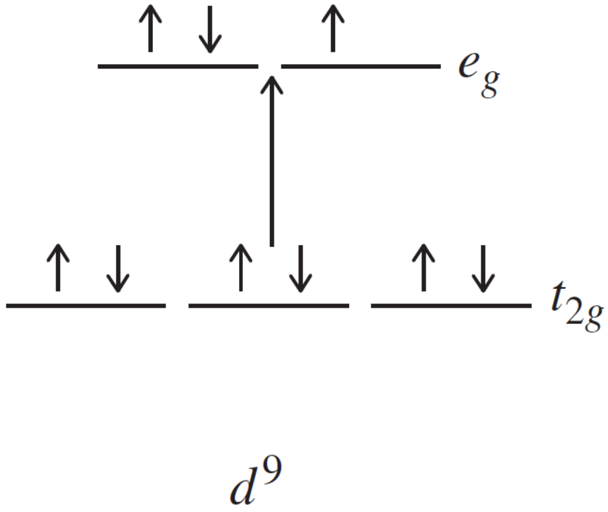
Determining $_o$ for d_1, d_4
(High Spin), d_6 (High Spin),
and d_9 Configurations.

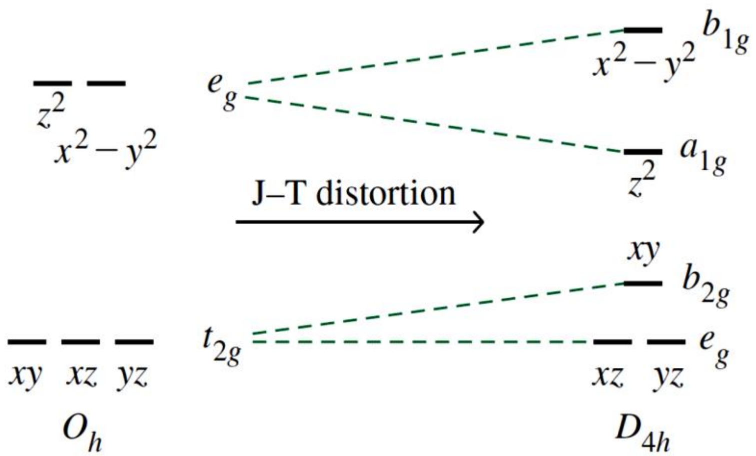
there is a single spin-allowed absorption, with
the energy of the absorbed
light equal to $_o$.



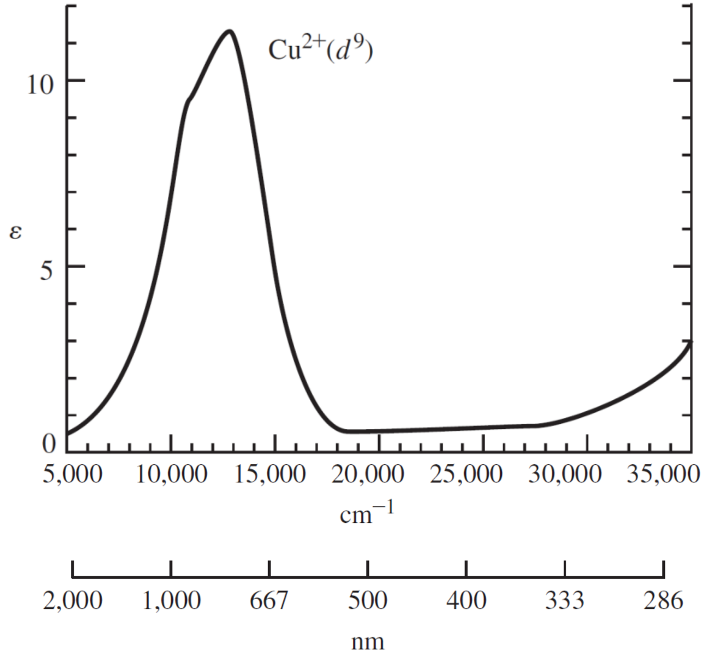
Electronic Spectra of Complexes

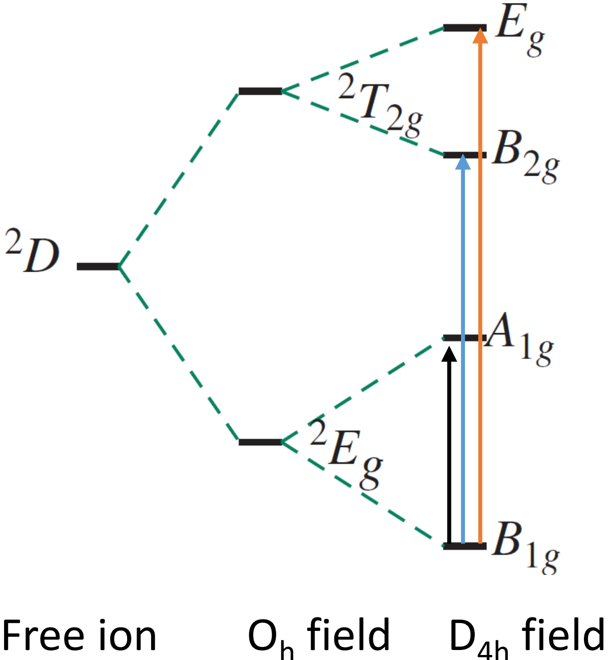
Effect of Jahn–Teller Distortions



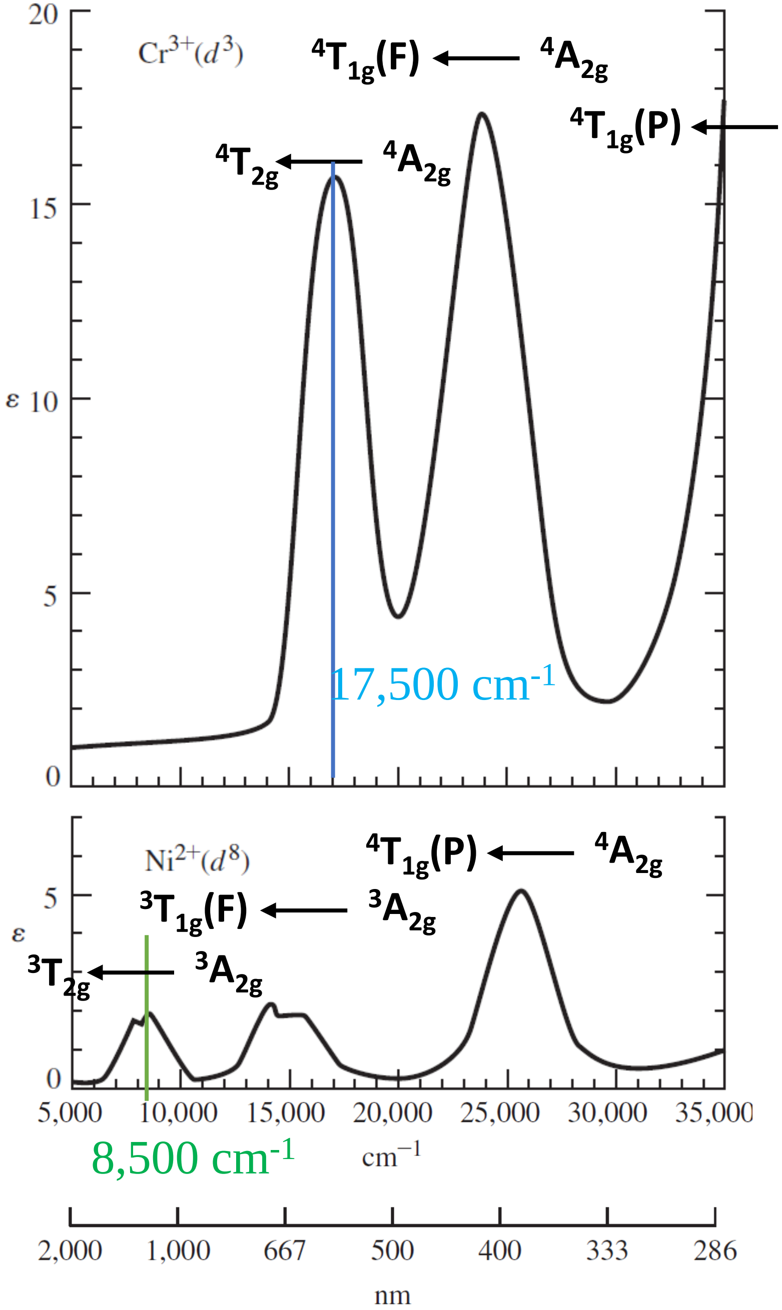


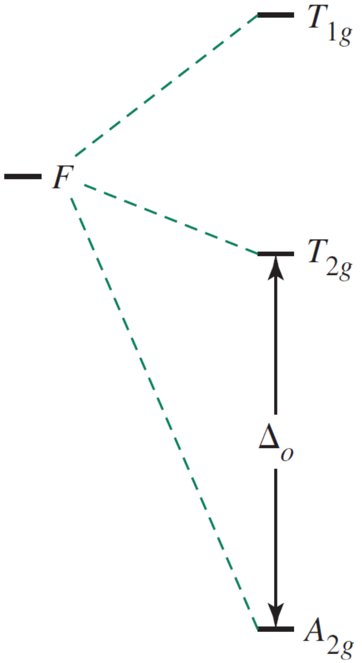
Effect of Jahn-Teller Distortion on d Orbitals of an Octahedral Complex.

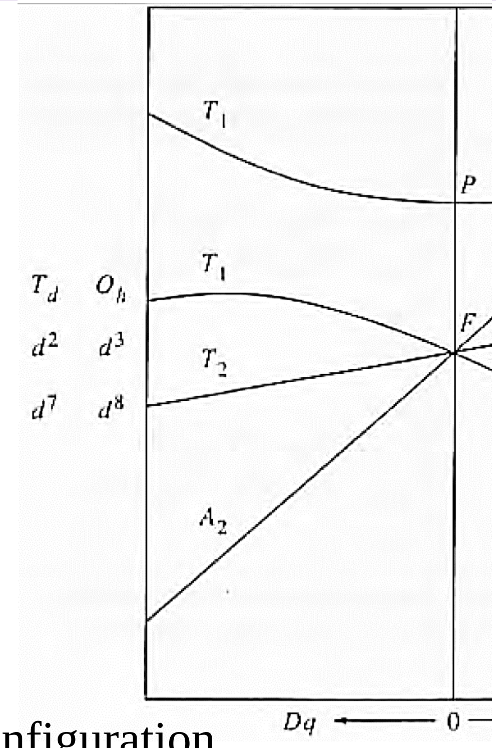




Electronic Spectra of Complexes (d^3 & d^8)







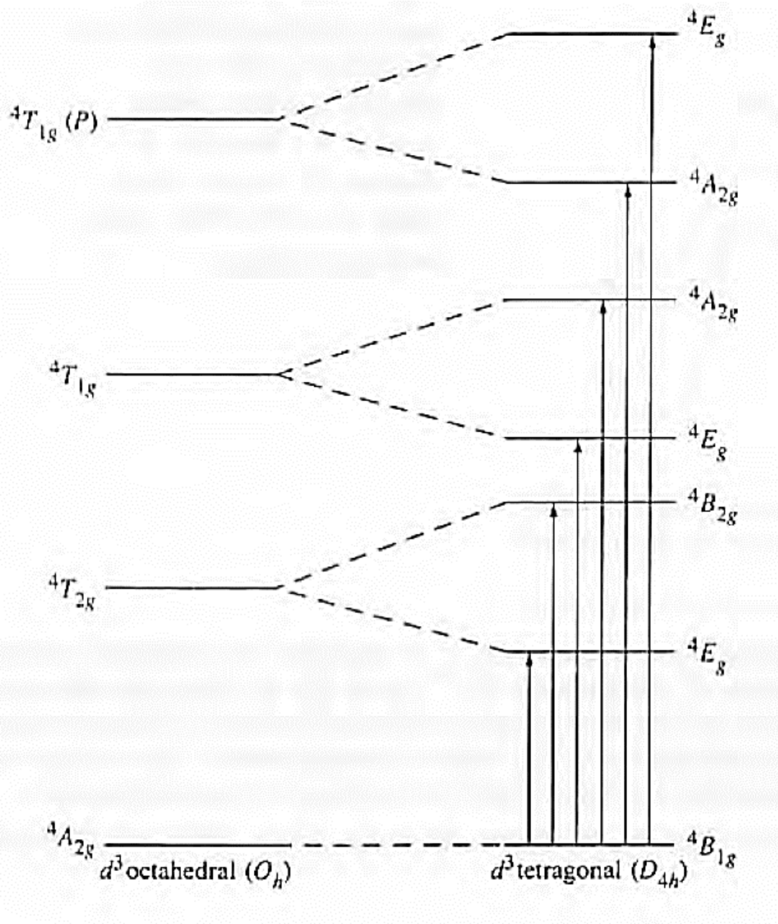
d^3or d^8 Configuration

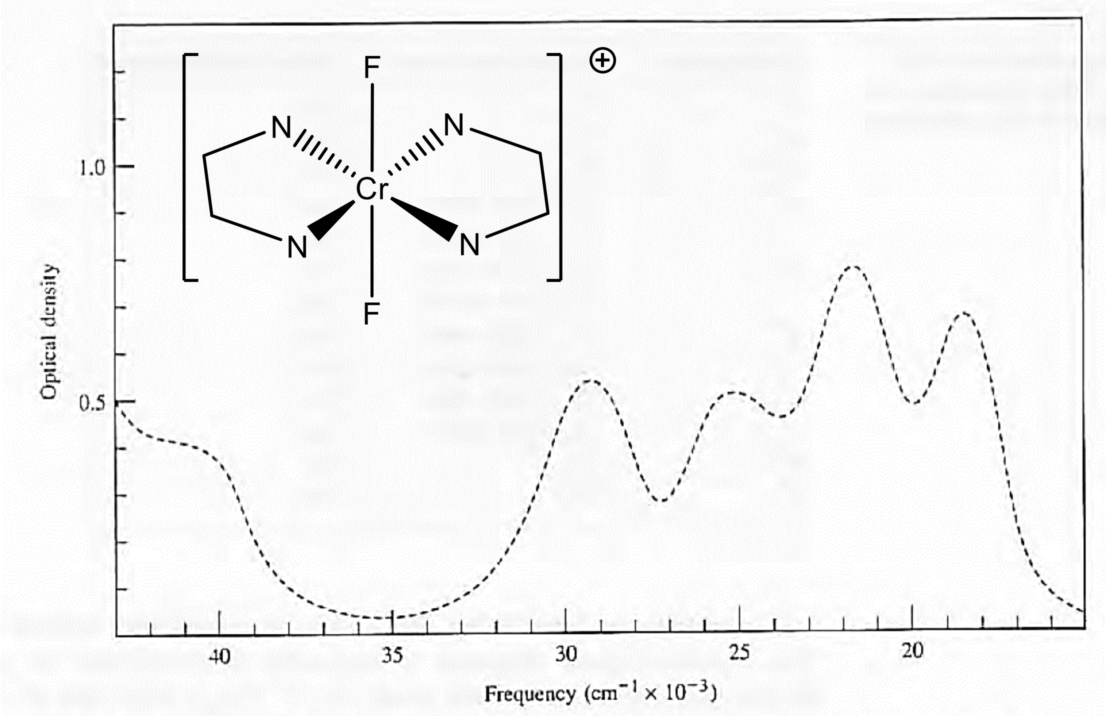
- For these configurations, the difference in energy between the two lowest-energy terms, the A_{2g} and the T_{2g}, is equal to Δ_o.
- B can be calculated from the following relation provided all three transitions are observed.

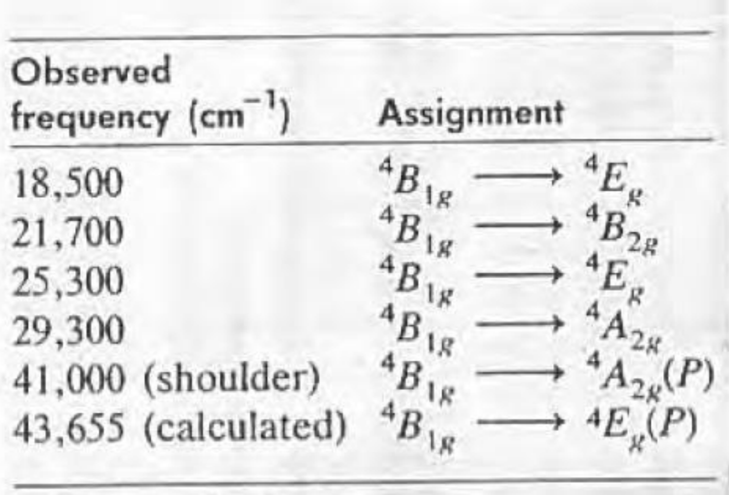
$$\boxed{15B = \nu_3 + \nu_2 - 3\nu_1}$$

Electronic Spectra of Complexes

$[Cr(en)_2F_2]^+$

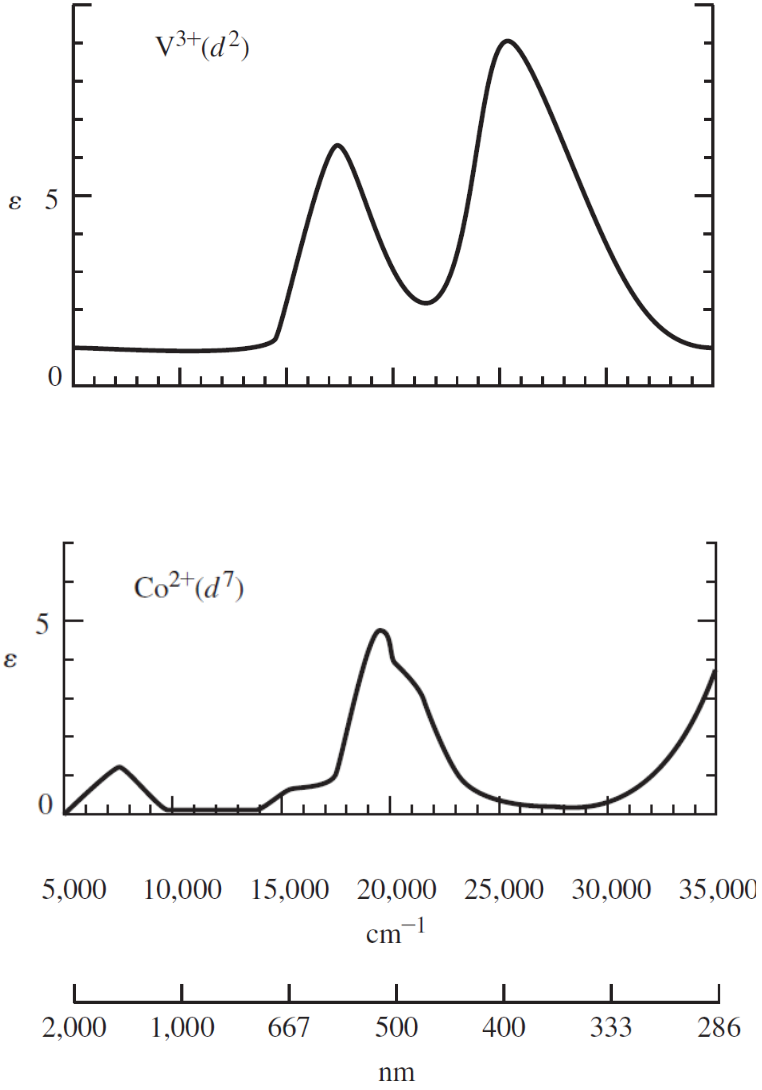


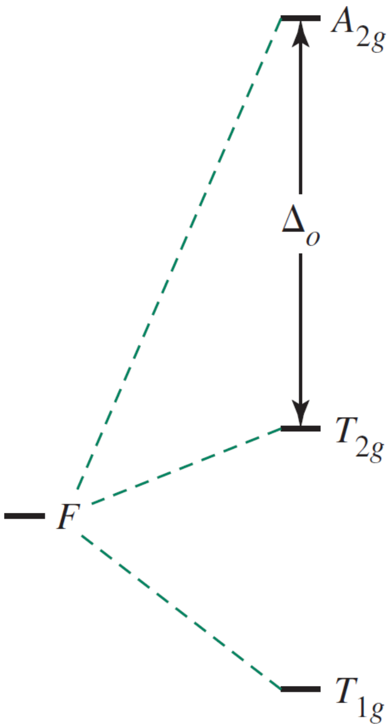


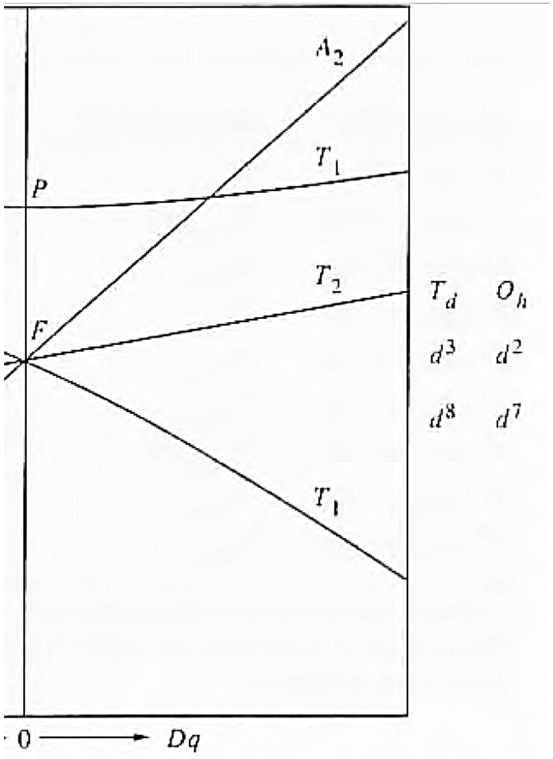


Observed frequency (cm^{-1})	Assignment
18,500	$^4B_{1g} \longrightarrow {}^4E_g$
21,700	$^4B_{1g} \longrightarrow {}^4B_{2g}$
25,300	$^4B_{1g} \longrightarrow {}^4E_g$
29,300	$^4B_{1g} \longrightarrow {}^4A_{2g}$
41,000 (shoulder)	$^4B_{1g} \longrightarrow {}^4A_{2g}(P)$
43,655 (calculated)	$^4B_{1g} \longrightarrow {}^4E_g(P)$

Electronic Spectra of Complexes (d^2 & d^7)







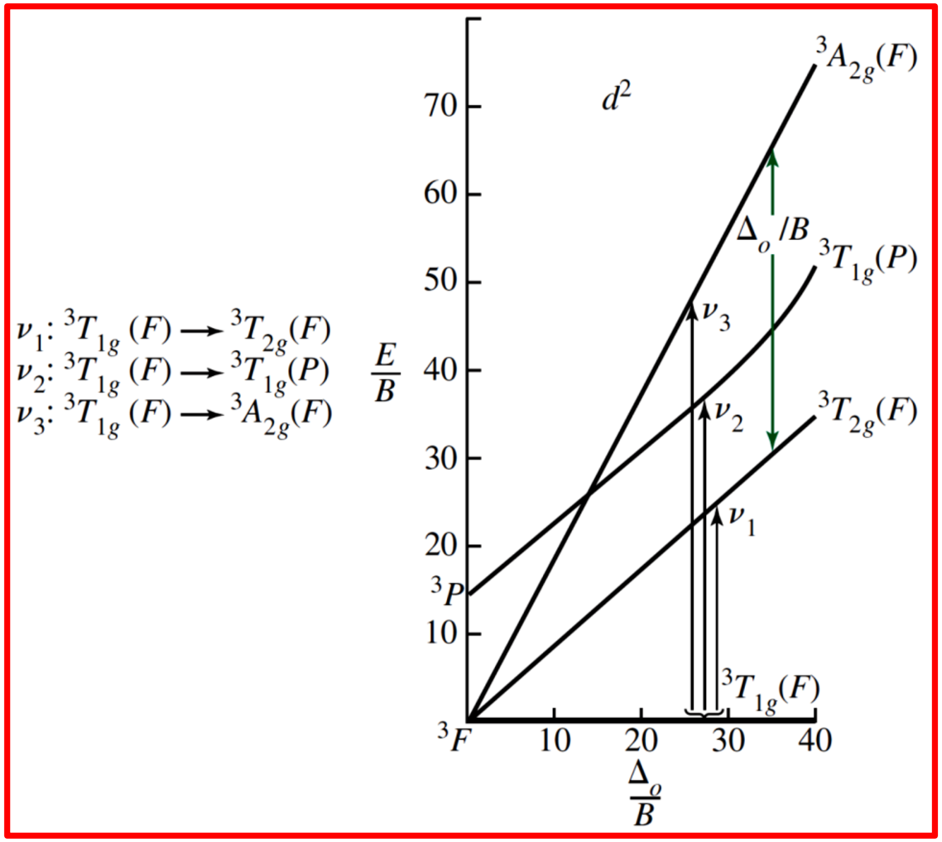
d^2 or *d^7* Configuration

For a d^2 configuration, the ground state is $^3T_{1g}$. It is tempting to simply determine the energy of the $^3T_{2g} \leftarrow {}^3T_{1g}(F)$ band and assign this as the value of Δ_o. This is primarily due to mixing of same symmetry terms.

Electronic Spectra of Complexes

An alternative approach to determine Δ_o is to indirectly measure the difference between $^3T_{2g}$ (for the $t_{2g}e_g$ configuration) and $^3A_{2g}$ (for e_g^2).

$$\begin{array}{r}
\text{energy of transition } {}^3T_{1g} \longrightarrow {}^3A_{2g} \\
-\text{energy of transition } {}^3T_{1g} \longrightarrow {}^3T_{2g} \\
\hline
\Delta_o = \text{energy difference between } {}^3A_{2g} \text{ and } {}^3T_{2g}
\end{array}$$



Q: $[V(H_2O)_6]^{2+}$ has absorption bands at 17,800 and 25,700 cm^{-1}. Using the Tanabe–Sugano diagram for d^2, estimate values of Δ_o and *B* for this complex.

Answer:

$^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ ν_1 (lowest energy)

$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ ν_2

$^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$ ν_3

$\left.\begin{array}{l}\nu_2\\ \nu_3\end{array}\right\}$ (one of the these must be the higher-energy band)

Contd.

Electronic Spectra of Complexes

Determine the ratio of energies of the absorption bands

$$\frac{25{,}700\ \text{cm}^{-1}}{17{,}800\ \text{cm}^{-1}} = 1.44$$

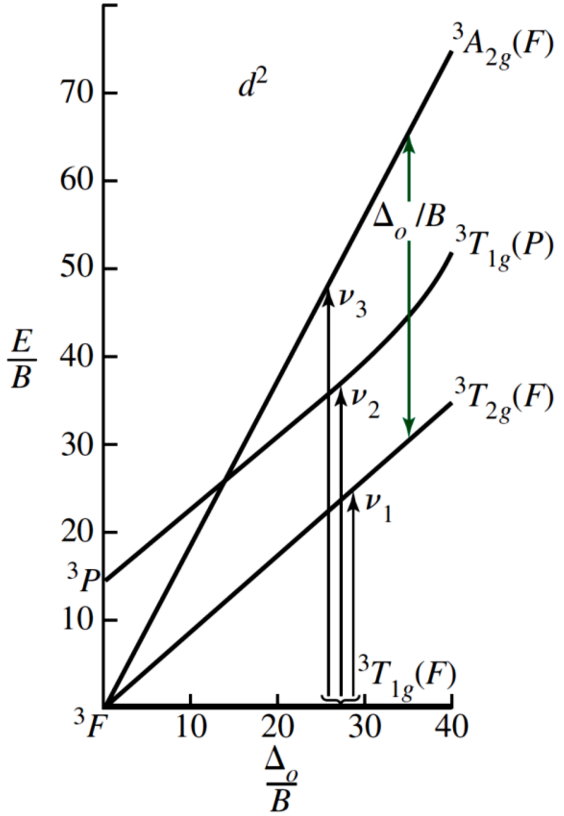
From the Tanabe–Sugano diagram, the ratio of ν_3 to ν_1 is approximately 2, so ν_3 can be eliminated for the band at 25,700 cm^{-1}.

Now, the ratio of ν_2 to ν_1 is approximately 1.44 at $\Delta_o/B = 31$

ν_1: ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$

ν_2: ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$

ν_3: ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$



At $\dfrac{\Delta_o}{B} = 31$,

$$\nu_2: \quad \frac{E}{B} = 42 \text{ (approximately)}; \quad B = \frac{E}{42} = \frac{25{,}700\ \text{cm}^{-1}}{42} = 610\ \text{cm}^{-1}$$

$$\nu_1: \quad \frac{E}{B} = 29 \text{ (approximately)}; \quad B = \frac{E}{29} = \frac{17{,}800\ \text{cm}^{-1}}{29} = 610\ \text{cm}^{-1}$$

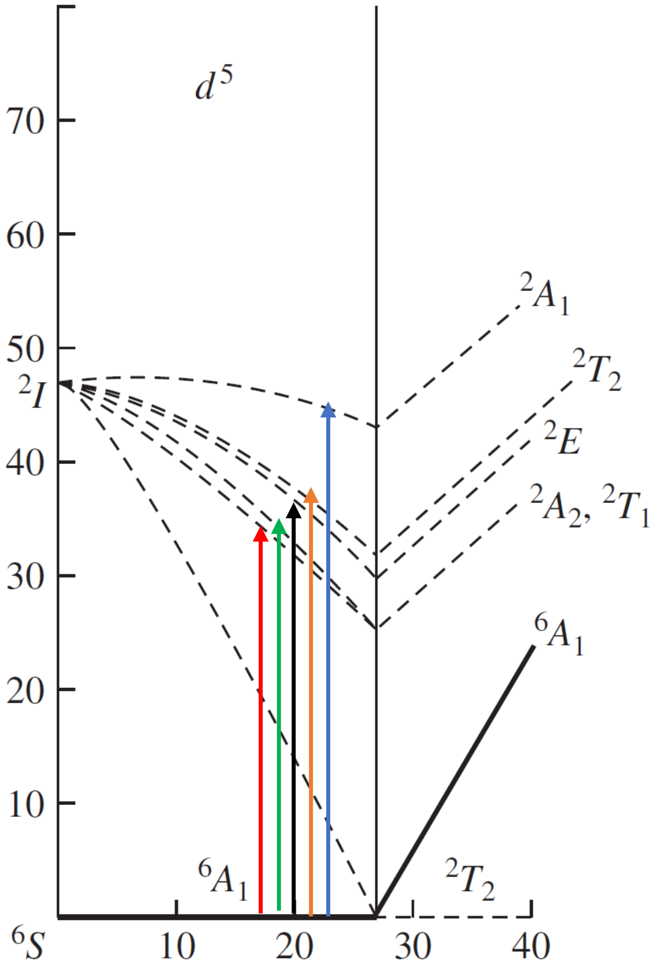
Because $\dfrac{\Delta_o}{B} = 31$,

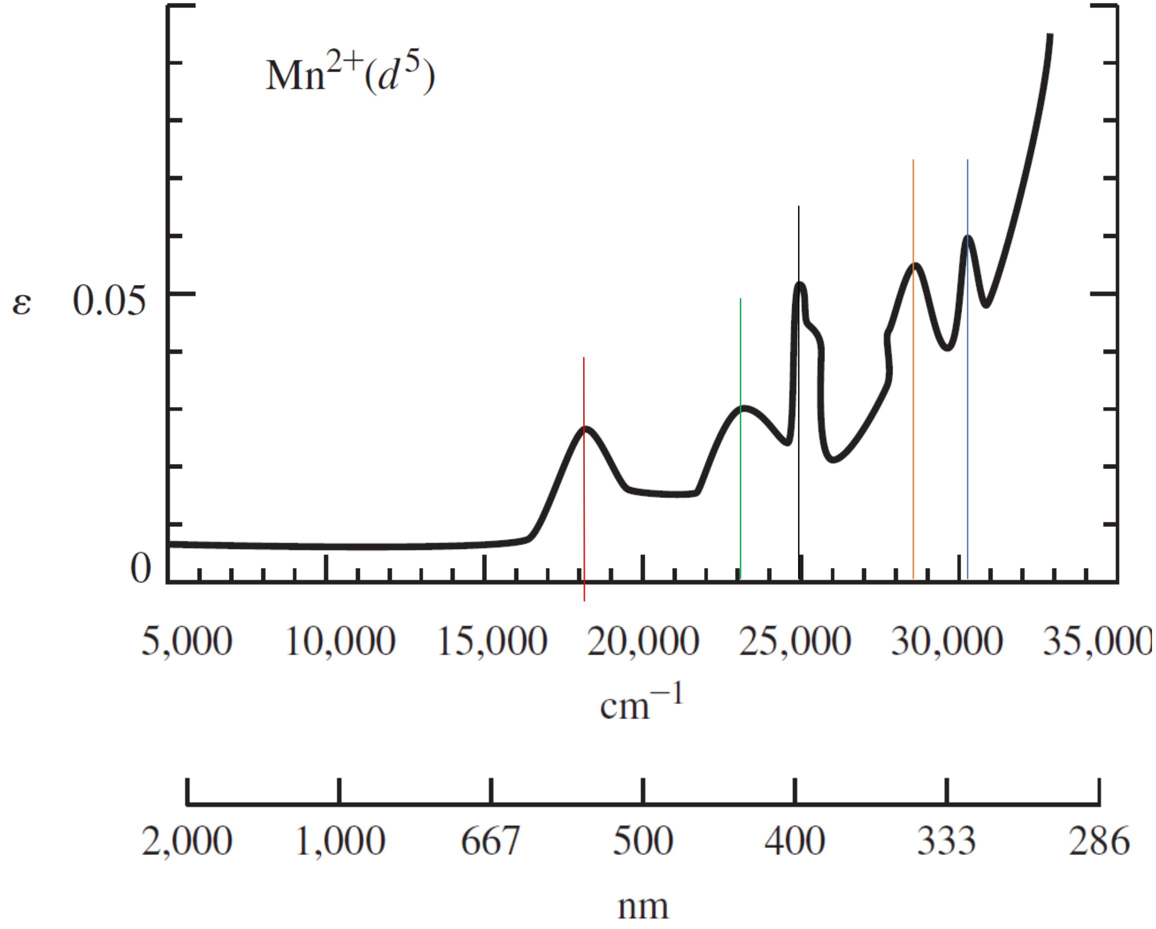
$$\Delta_o = 31 \times B = 31 \times 610\ \text{cm}^{-1} = 19{,}000\ \text{cm}^{-1}$$

This procedure can be followed for d^2 and d^7 complexes of octahedral geometry to estimate values for Δ_o (and B).

Electronic Spectra of Complexes

$[Mn(H_2O)_6]^{2+}$





Q: Assign the corresponding transitions?

High-spin d^5 complexes have no excited states of the same spin multiplicity (6) as the ground state. All the transitions occurred are very week due to spin selection rule.