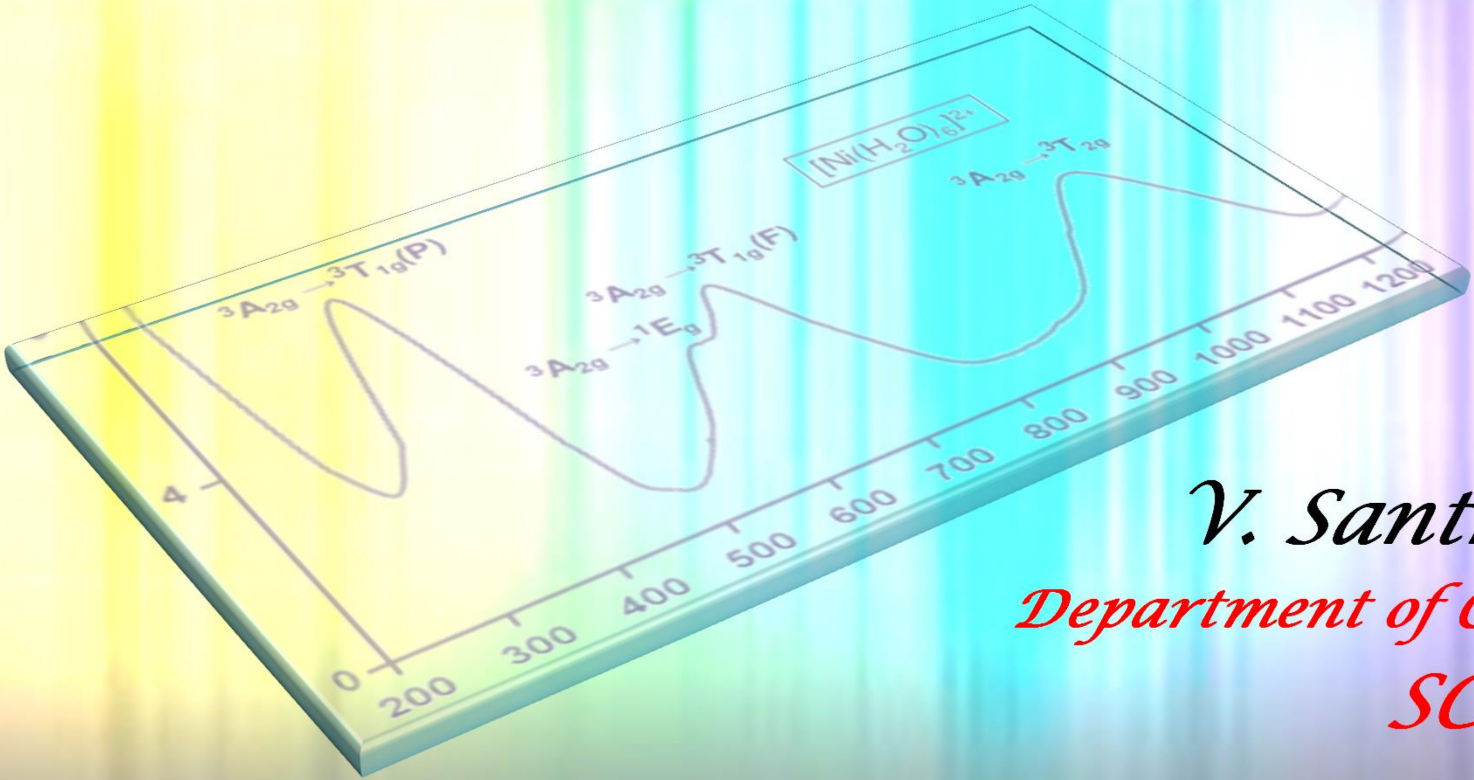
Electronic Spectra of Metal Complexes



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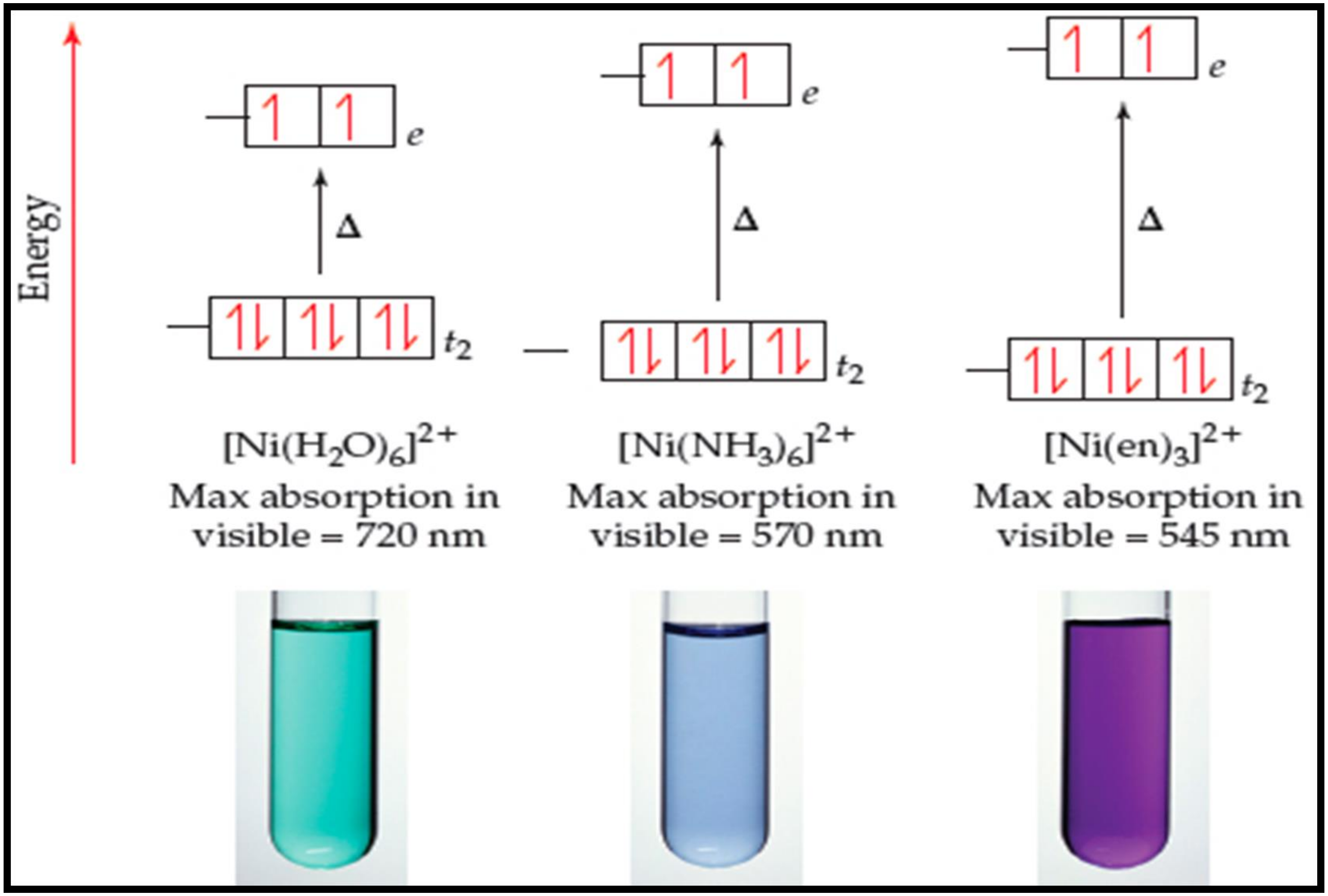
Color of the complexes

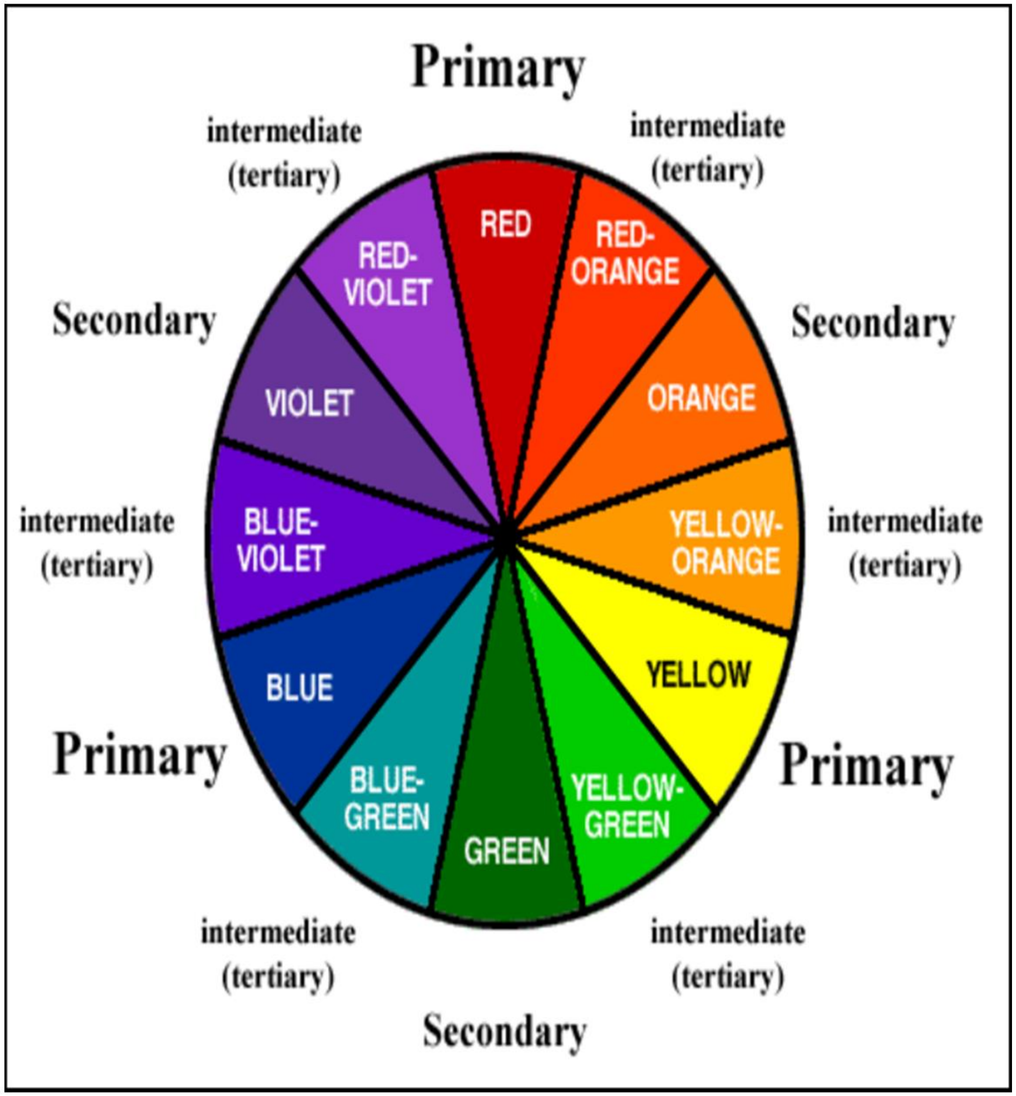


$[Ni(H_2O)_6]^{2+}$
Max absorption in visible = 720 nm

$[Ni(NH_3)_6]^{2+}$
Max absorption in visible = 570 nm

$[Ni(en)_3]^{2+}$
Max absorption in visible = 545 nm

Observed Color	**Light Absorbed**	**Abs Wavelength / nm**
Colorless	UV	< 380
Yellow	Violet	380-450
Orange	Blue	450-490
Red	Green	490-550
Violet	Yellow	550-580
Blue	Orange	580-650
Green	Red	650-700
Colorless	IR	> 700



Use of Electronic spectrum

- **Electronic spectrum – due to d-d transitions.**
- **From the transition energy – energy of d e^- can be got.**
- **The energies of d levels affected by many complicated factors.**

Terms, States and Microstates

- **Energy levels described by quantum numbers.**
  - **Principal quantum number – n**
  - **Azimuthal quantum number – l**
  - **Magnetic quantum number – m_l**
  - **Spin quantum number – m_s**
- **But actual conditions are complicated .**
- **Quantum numbers alone are not sufficient**

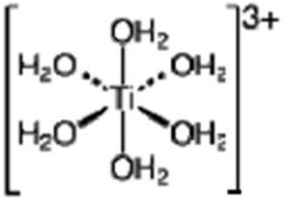
Why ?

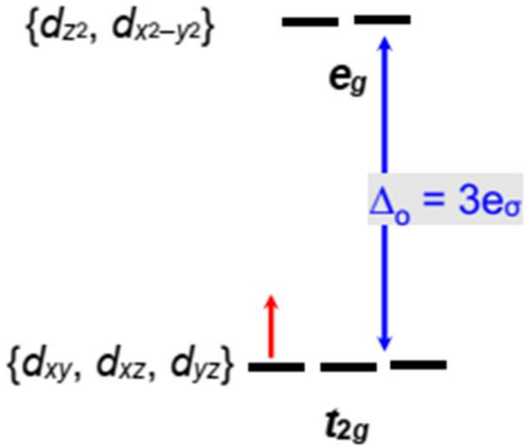
Configuration

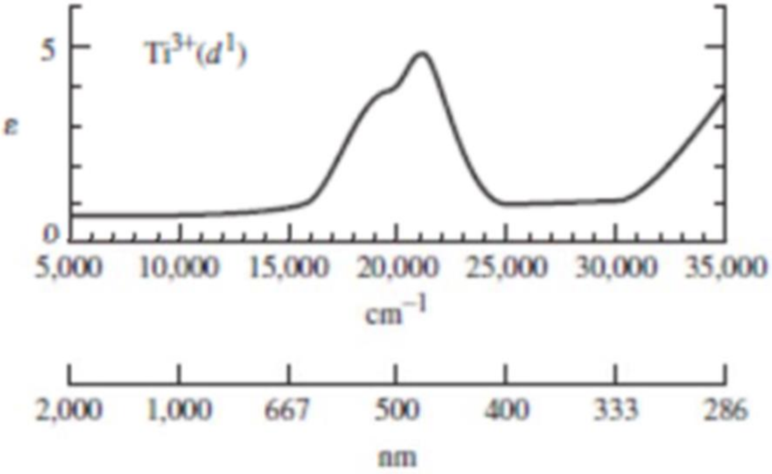
- Arrangement of e^{-}s in an atom or ion
  - The electrons are filled in the increasing order of energy – Aufbau principle
  - If more than one orbital is having same energy, pairing of e- will not take place until all the orbitals are at least singly occupied – Hund's rule
  - No two electrons can have all the four quantum numbers same – Pauli's exclusion principle

$[Ti(OH_2)_6]^{3+}$

Hexaaquatitanium(III) is an octahedral *d*^{1} metal complex.



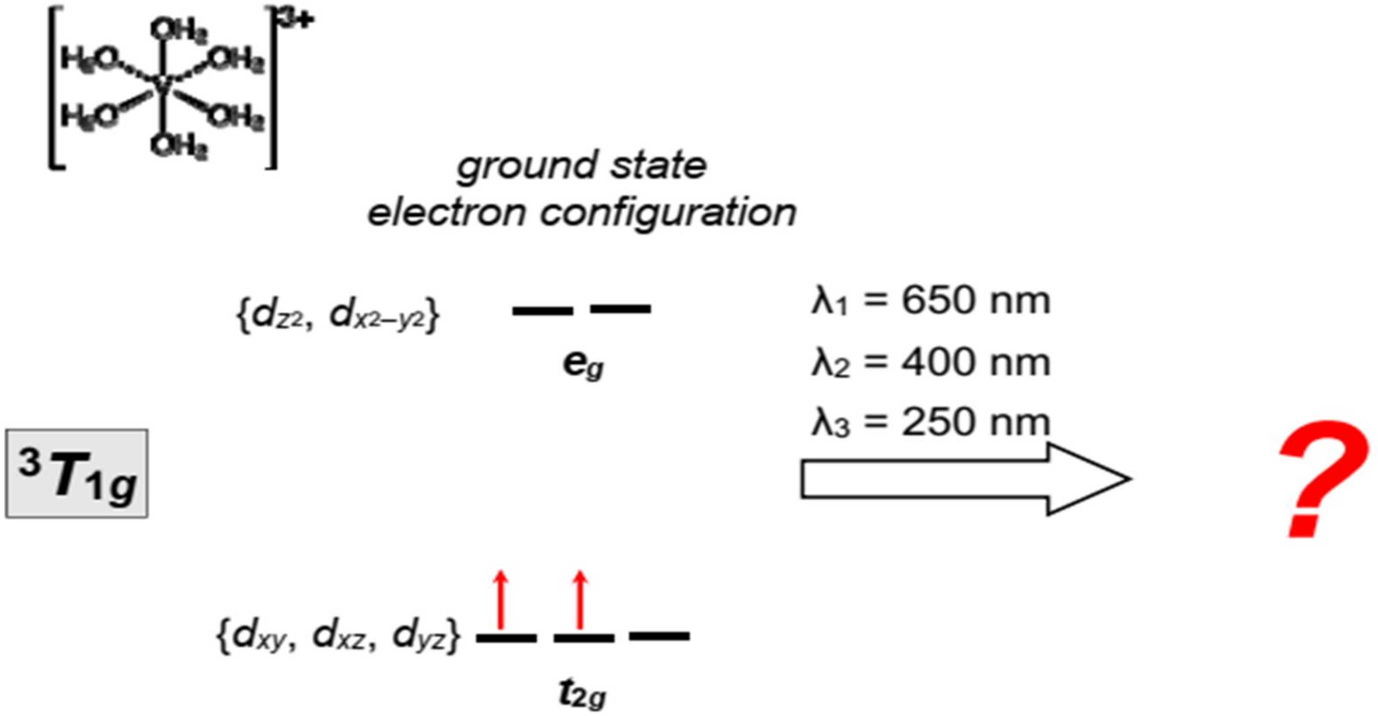




***d-d* transition should give a single peak in the absorption spectrum.**

$[V(OH_2)_6]^{3+}$

Hexaaquavanadium(III) is an octahedral d^2 metal complex.



What's going on?

- It turns out not all electron configurations are equal.
- To understand the absorbance spectrum of $[V(OH_2)_6]^{3+}$ (or any other multi-electron species), we need to do a little work...

Terms

- Energy level of an atomic system specified by an electronic configuration.
- Many terms may arise from a configuration
- Depends on the intrinsic nature of cofig.
- Electrons from filled orbitals have no contribution to energy – Assumption
- Partially filled orbitals decide the energy terms.

Terms … Cont

- **Partially filled orbitals have two perturbations**
  - **Inter Electronic Repulsions**
  - **Spin-Orbit coupling**

Inter-electronic repulsions

- Energy depends on the arrangement of e^-
- The electrons in partially filled orbitals repel each other.
- Repulsion splits the energy levels resulting in many terms.
- Energies of electrons within an orbital itself are slightly different [Pairing and Exchange energies].

Inter-electronic repulsions

Racah Parameters (A, B and C)

- **Racah parameters were generated as a means to describe the effects of electron-electron repulsion within the metal complexes.**

- ***A*** **is ignored because it is roughly the same for any metal center.**

- **B is generally approximated as being 4C.**

Inter-electronic repulsions

- **What *B* represents is an approximation of the bond strength between the ligand and metal.**

- **Comparisons between tabulated free ion *B* and *B* of a coordination complex is called the nephelauxetic ratio (the effect of reducing electron-electron repulsion via ligands).**

- **This effect is what gives rise to the nephelauxetic series of ligands.**

Nephelauxetic Effect

- **Normally the electron repulsion is found to be weaker in complexes than in free ion and this means the value of B for the complex is less than for a free ion.**
- **This is due to the delocalization of the electron over the ligands away from the metal which separates them and hence reduces repulsion.**
- **The reduction of B from its free ion is normally reported in terms of nephelauxetic effet β**

$$\beta = \frac{B'\ \text{complex}}{B\ \text{free ion}}$$

- **Where β is the nephelauxetic parameter and refer to the electron cloud expansion.**

Nephelauxetic series

- The values of β depend on the ligand and vary along the nephelauxetic series. The ligands can be arranged in a nephelauxetic series as shown below. This is the order of the ligands ability to cause d electron cloud expansion.

$I^- < Br^- < Cl^- < CN^- < NH_3 < H_2O < F^-$

- The series tell us that a small value of β means that there is large measure of d- electron delocalization and a greater covalent character in the complex.

Reasons for e- cloud expansion

- This electron cloud expansion effect may occur for one (or both) of two reasons.
  - One is that the effective positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the d-orbitals can expand slightly.
  - The second is the act of overlapping with ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals

Jorgensen Relation

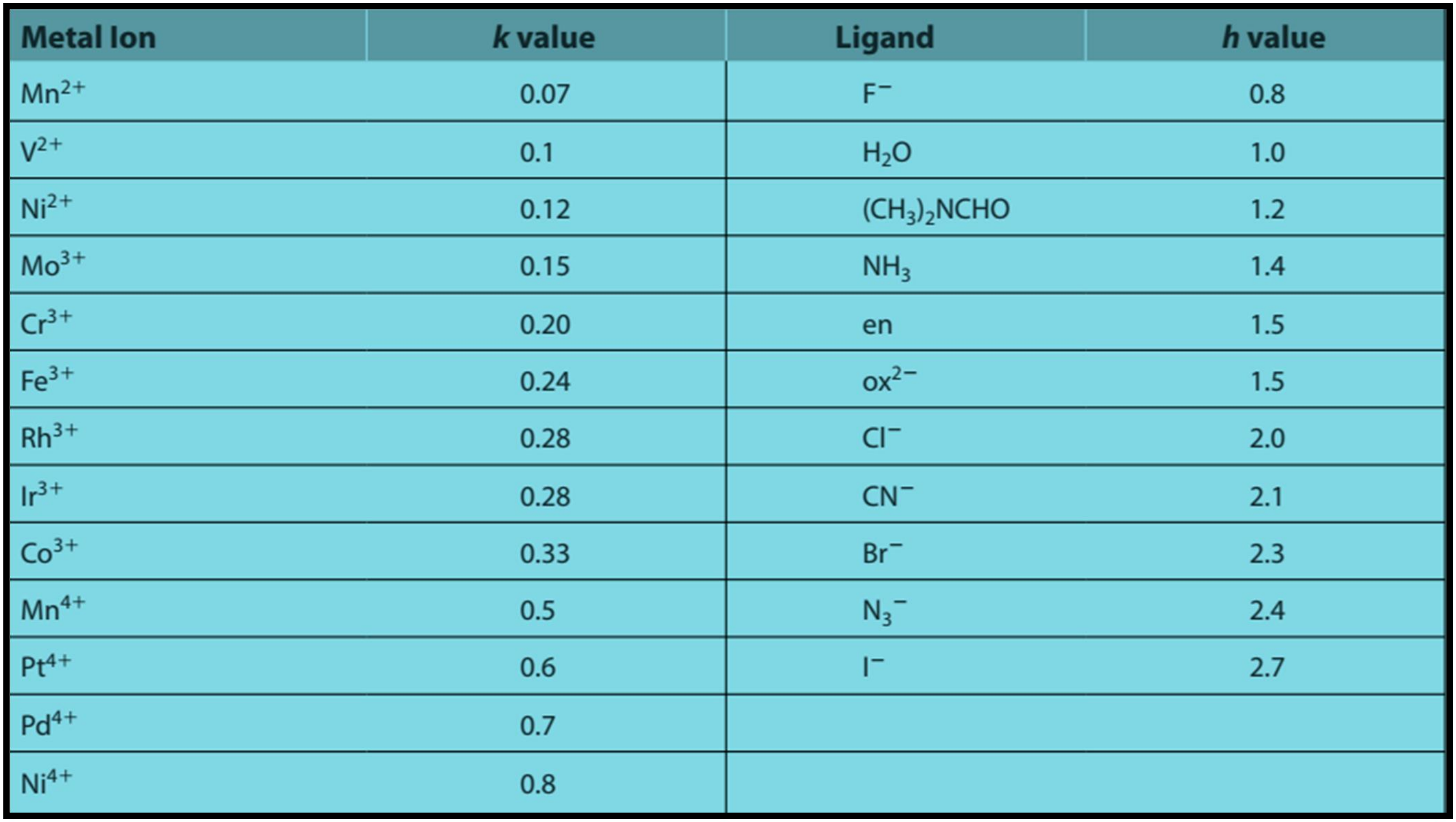
- **We know that** $\beta = \frac{B^*}{B}$
- **C.K.Jogensen derived a relationship for β as**

$(1-\beta) = h.k$

where **h- is ligand parameter**

k- is metal ion parameter

$\beta^* = \beta - \beta h.k$



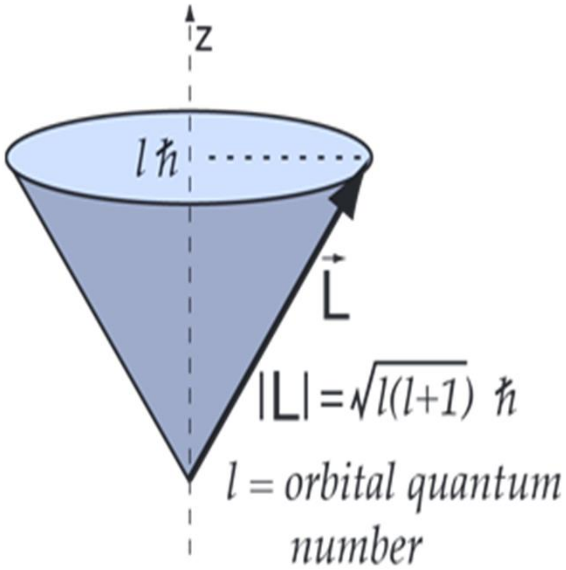
Metal Ion	***k* value**	**Ligand**	***h* value**
Mn^{2+}	0.07	F^-	0.8
V^{2+}	0.1	H_2O	1.0
Ni^{2+}	0.12	$(CH_3)_2NCHO$	1.2
Mo^{3+}	0.15	NH_3	1.4
Cr^{3+}	0.20	en	1.5
Fe^{3+}	0.24	ox^{2-}	1.5
Rh^{3+}	0.28	Cl^-	2.0
Ir^{3+}	0.28	CN^-	2.1
Co^{3+}	0.33	Br^-	2.3
Mn^{4+}	0.5	N_3^-	2.4
Pt^{4+}	0.6	I^-	2.7
Pd^{4+}	0.7		
Ni^{4+}	0.8		

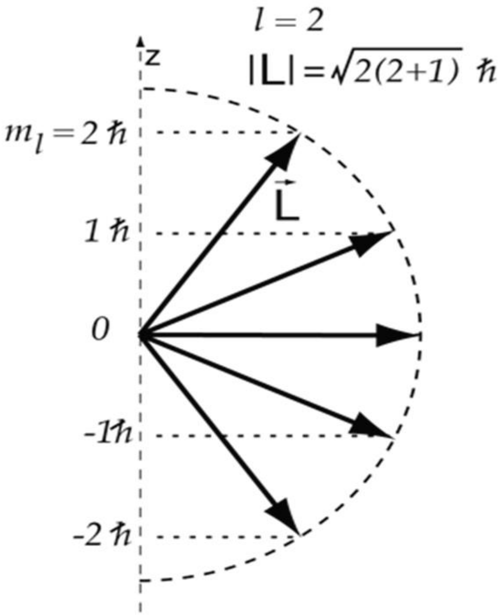
Spin-Orbit coupling

- Responsible for fine structure of spectrum
- e^- has both spin and orbit angular moments and associated magnetic moments.
- These magnetic moments interact weakly to split the energy levels.

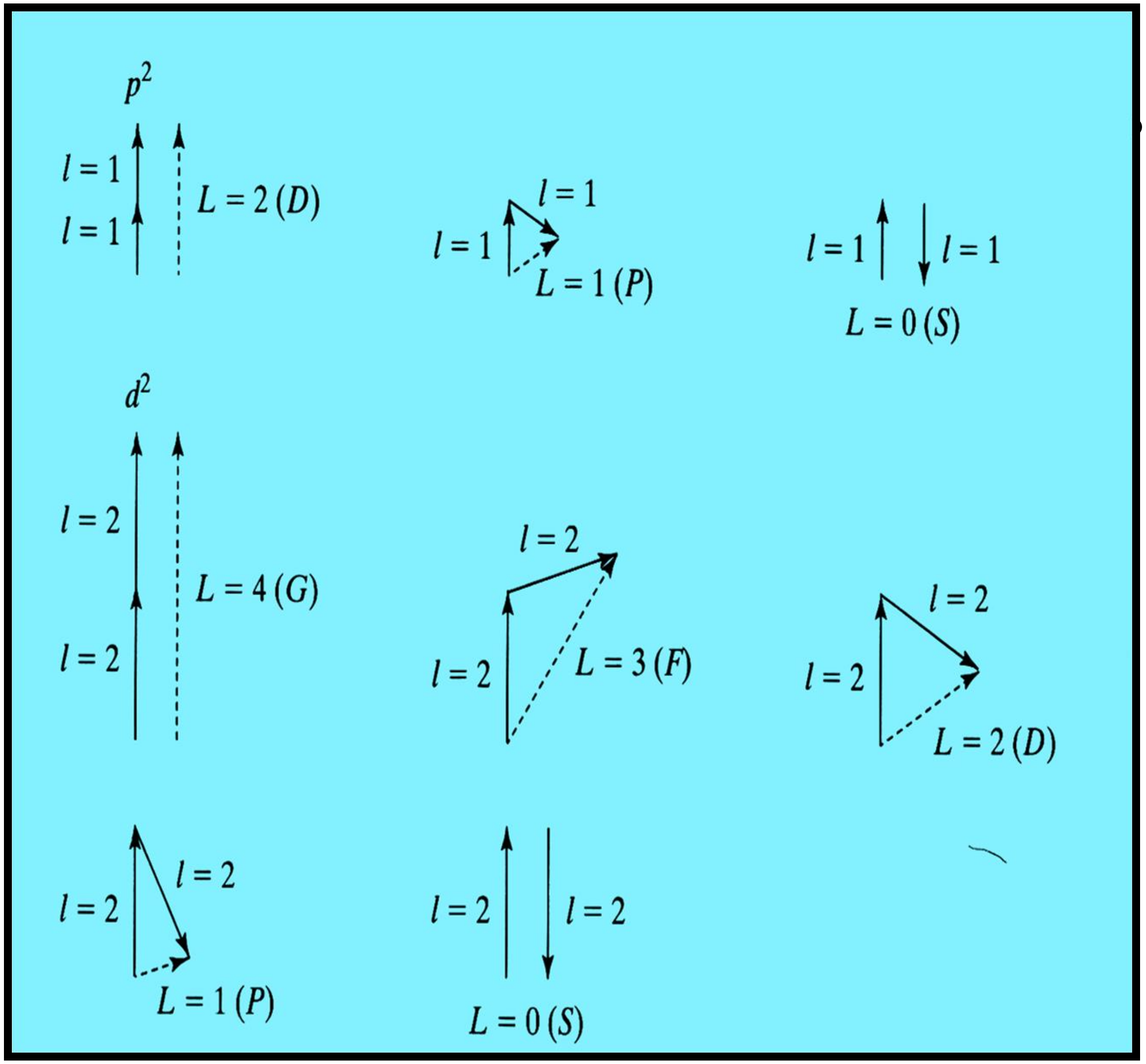
Spin-Orbit coupling

- Microstates can be visualized through the *vector model* of the atom. The vector model associates angular momentum with energy.
- Each electron has an orbital angular momentum *l* and a spin angular momentum *s*.

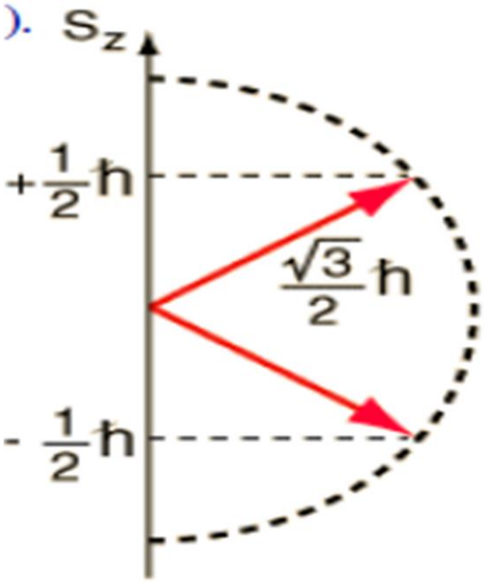




The **single electron orbital angular momentum *l*** (and hence the total orbital angular momentum *L*) can only have certain orientations quantization.



- The **total orbital angular momentum *L*** of a group of electrons in an atom is given by a <u>vector sum</u> of the individual orbital angular momenta *l*.



Modulus $|\vec{s}| = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$

Component along z $s_Z = m_s\hbar$

(with $m_s = \pm\frac{1}{2}$)

$$\vec{\mu}_s = -g_s \frac{e}{2m_0}\vec{s}$$

Spin-orbit coupling / L-S coupling

i) Russel-Saunders for light atoms:

$J = L + S, L + S - 1, \ldots, |L - S|$

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

$S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2|$

Russel-Saunders coupling works well for the light elements up to bromine.

- **Couple all individual orbital angular momenta *l* to give a resultant total orbital angular momentum *L*. ($L = \Sigma l_i$)**
- **Couple all individual spin angular momenta *s* to give a resultant total spin angular momentum *S*. ($S = \Sigma s_i$)**
- **Finally couple *L* and *S* to give the total angular momentum *J* for the entire atom.**

Spin-orbit coupling / L-S coupling

- The extent to which L and S are coupling is called “Spin-Orbit Coupling constant” (ζ)
- The perturbation created by L-S coupling is

$$\zeta\,(l\,.s\,)$$

This value is for single electron of a configuration and always positive

$$\zeta=\left[\frac{z_{eff}\,.e^{2}}{2.m^{2}c^{2}}\right]\left(\frac{1}{r^{-3}}\right)$$

Spin-orbit coupling / L-S coupling

- For convenience, a parameter characteristic of a term is used.
- L-S coupling constant for a term is λ
- The perturbation of energy of a term is $\lambda\left(l.s\right)$

$$\lambda = \frac{\pm\zeta}{2.s}$$

- The λ value is positive for less than half filled and negative if the orbital is greater than half filled.

L-S Coupling continued

- **Each term is split in to states by L-S coupling specified by J values, which differing by unity.**
- **Each L value will have (2L+1) M_L components.**
- **Each S value will have (2S+1) M_S components.**
- **So any term will have a degeneracy of**

(2S+1).(2L+1)

L-S coupling in a p^2 system

Let us consider p^2 configuration

Maximum L value possible is 2

Maximum S value possible is 0

So possible J value is 2

Degeneracy of this state is

((2 x 2)+1) x ((2 x 0)+1) = 5

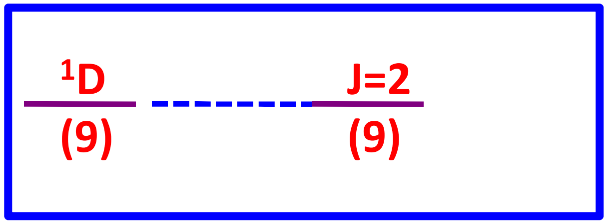
Next maximum L value possible is 1

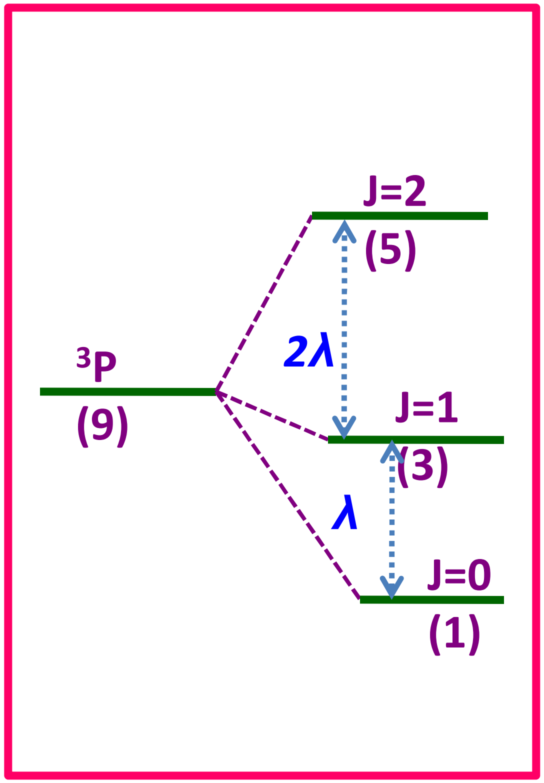
For this L value maximum S value possible is 1

Possible J values are 2, 1, 0

Degeneracy of this state is

((2 x 1)+1) x ((2 x 1)+1) = 9





L-S coupling

- Each L and S combination is having a particular energy.

$$E_J = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

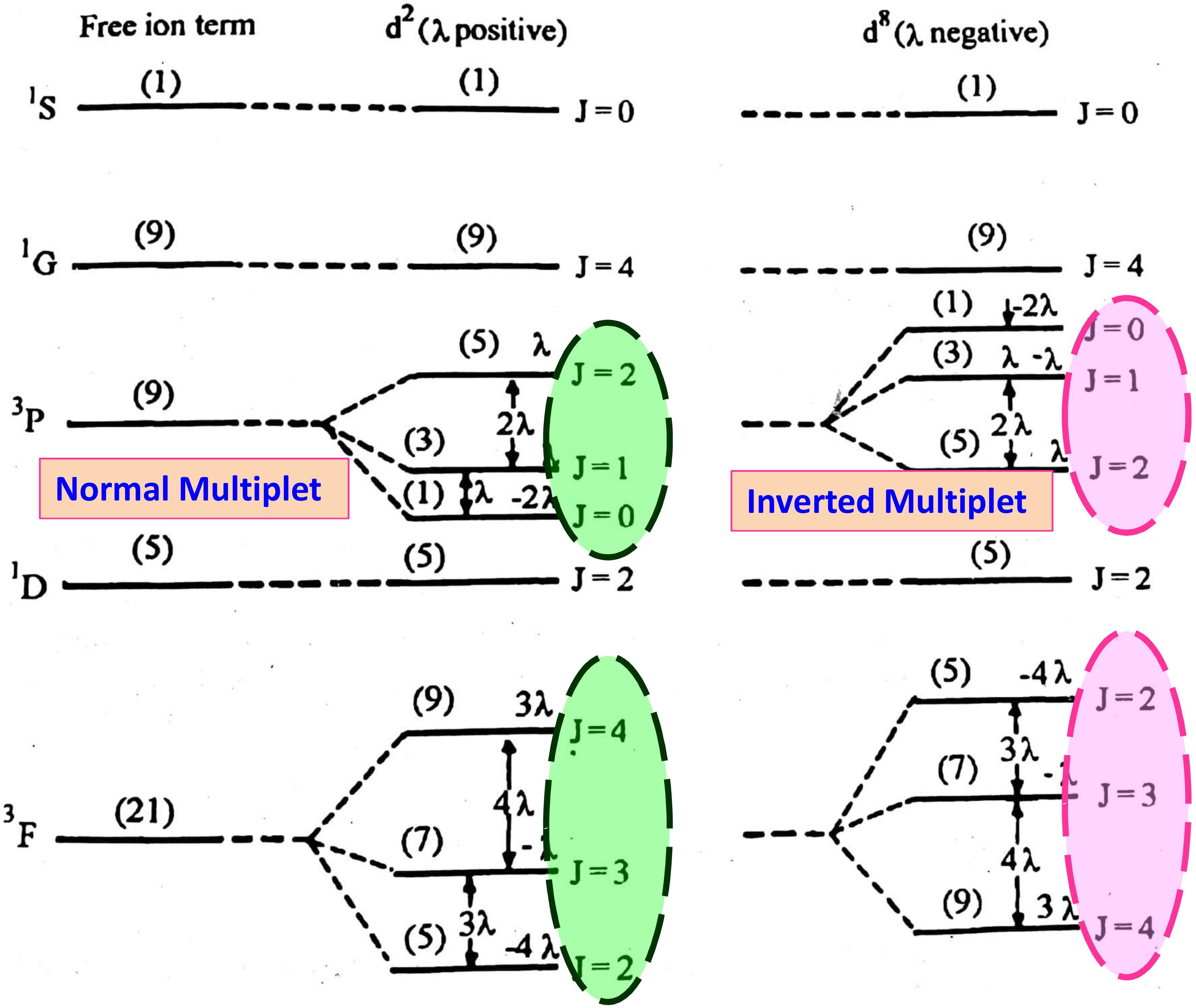
- Total angular momentum quantum number J

  J = |L+S|, |L+S-1|, |L+S-2|,……|L-S|

- J values are of unit difference.
- The energy gap between any two successive J values is

$$\Delta E_{J,J+1} = \lambda(J+1)$$

- For less than half filled, lowest value of J, |L-S| has the lowest energy. (Normal multiplet)
- For more than half filled highest value of J |L+S| has the lowest energy (Inverted multiplet)



Normal Multiplet

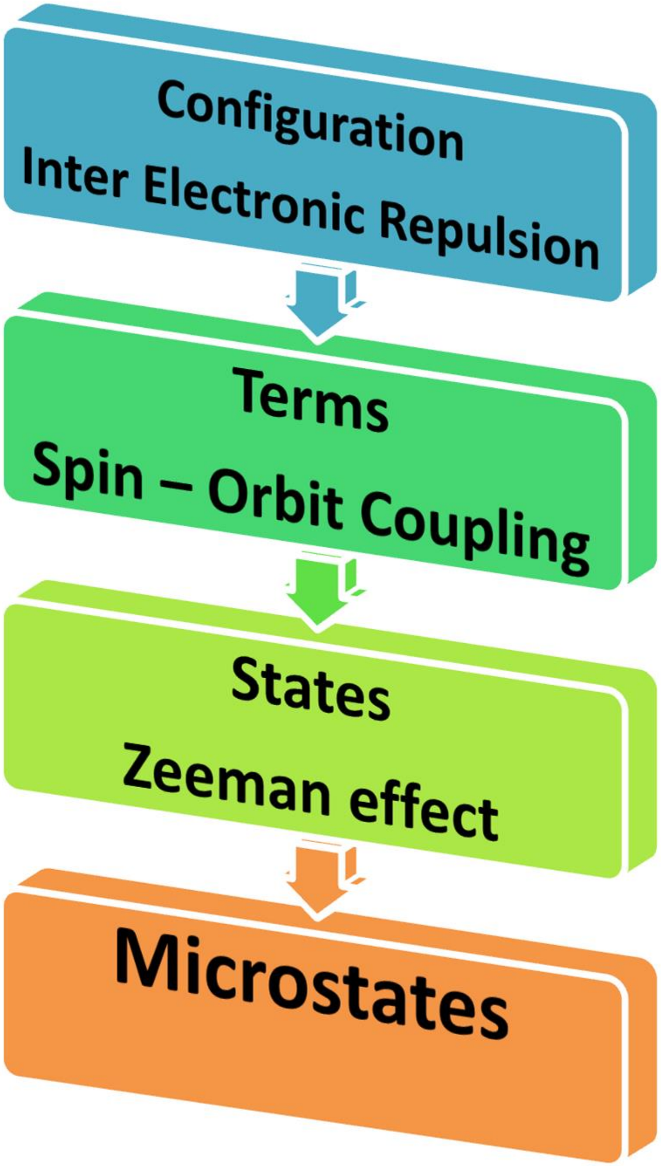
Inverted Multiplet

j-j coupling

- **Couple individual orbital l and spin s angular momenta first to the complete electron angular momentum j. ($j = l + s$)**
- **Couple all j to give the total angular momentum J. ($J = j$)**
- **j-j coupling is much more complicated to treat, but should be used for elements heavier than bromine.**
- **For 4d and 5d series of ions.**

IER Vs SOC

- Both IER and SOC are operating simultaneously.
- Their relative magnitudes are important.
- IER is very high than SOC.
- So the IER causes the splitting first, then splitting by SOC.
- Resulting levels may be further split by magnetic field.



Configuration
Inter Electronic Repulsion

Terms
Spin – Orbit Coupling

States
Zeeman effect

Microstates

Tackling the Multi-Electron Problem

Start by taking a step back

- **first we must treat the V^{3+} ‘free ion’ with no ligands in a spherically symmetric environment**
- **since V^{3+} is d^2, we must consider e^--e^- interactions, spin-spin interactions, and spin-orbital interactions**

Define a few terms

- microstate **– a specific valence electron configuration for a multi-electron free ion**

#spaces

$$\# \, microstates = \frac{i!}{j!(i-j)!} = \frac{10!}{2!(10-2)!} = 45$$

#e–

- atomic state **– a collection of microstates with the same energy**
- term symbol **– the label for a free ion atomic state**

“spin multiplicity”

$$^{\boxed{2S+1}}L$$

L	term symbol label
0	S
1	P
2	D
3	F
4	G

Multi-Electron Quantum Numbers

When we learn about atoms and electron configurations, we learn the one-electron quantum numbers (*n*, *l*, *m_l*, *m_s*)

Multi-electron ions need multi-electron quantum numbers

- *L* **gives the total orbital angular momentum of an atomic state (equal to the maximum value of** *M_L***)**
  - *M_L* **is the *z*-component of the orbital angular momentum of a microstate**

$$M_L = \sum m_l$$

$$M_L \Rightarrow -L, -L+1, \ldots, -1, 0, +1, \ldots, L-1, L$$

- *S* **gives the total spin angular momentum of an atomic state (equal to the maximum value of** *M_S* **(for a given** *L* **value)**
  - *M_S* **is the *z*-component of the spin angular momentum of a microstate**

$$M_S = \sum m_s$$

$$M_S \Rightarrow -S, -S+1, \ldots, -1, 0, +1, \ldots, S-1, S$$

Spin-Orbit Coupling

So far we've considered only e⁻-e⁻ (orbital angular momentum) and spin-spin (spin angular momentum) interactions.

Orbitals and spins can also interact giving rise to spin-orbit coupling

- ***J* is the total angular momentum**

$$J \Rightarrow L+S, L+S-1, L+S-2, \ldots, |L-S|$$

So for the ^3F ground state of a d^2 free ion, we have

$$J \Rightarrow |L+S| = 4$$
$$\Rightarrow L-S = 2$$
$$\text{so } J = 4,\ 3, 2$$

So the ^3F ground state electron configuration of a d^2 free ion splits into $^3F_4$, $^3F_3$, and $^3F_2$.

To determine the lowest energy spin-orbit coupled state:

1. **For less than half-filled shells, the lowest *J* is the lowest energy**
2. **For more than half-filled shells, the highest *J* is the lowest energy**
3. **For half-filled shells, only one *J* is possible**

Number of microstates for a system

$$N = \frac{2y!}{x!(2y - x)!}$$

Where

N= number of microstates possible

y – number of orbitals

X- number of electrons

Number of microstates – p^1 system

+1	0	-1
↑		
	↑	
		↑
↓		
	↓	
		↓

y – number of orbitals - 6

x - number of electrons – 1

$$N = \frac{2.(6)!}{1!.(2.(6-1))!}$$

$$N = \frac{\cancel{2.(1.2.3.4.5}.6)}{1.(\cancel{2(1.2.3.4.5})))}$$

N = 6

Number of microstates – p^2 system

y – number of orbitals - 6

x - number of electrons – 2

$$N = \frac{2.(6)!}{2!.(2.(6-2))!}$$

$$N = \frac{\cancel{2}.(\cancel{1.2.3.4}.5.6)}{(1.2).(\cancel{2}(\cancel{1.2.3.4}))}$$

N = 15

Term Symbols for p^2

- **Maximum L value possible is 2**
  - **Possible M_L values are -L, -(L+1), …, 0 , …, +(L-1), +L**
  - **i.e. -2 , -1 , 0 , +1 , +2**
- **Maximum S value possible is : 0**
  - **Possible M_s value is 0**
- **Considering all possible combinations**

M_L	+2	+1	0	-1	-2
Ms	0	0	0	0	0
Term	^1D				

Term Symbols for p^2

- **Next maximum L value possible is 1**
  - **Possible M_L values are -L, -(L+1), …, 0 , …, +(L-1), +L**
  - **i.e. -1 , 0 , +1**
- **Maximum S value possible is : 1**
  - **Possible M_s value are +1 , 0 , -1**
- **Considering all possible combinations**

M_S	**+1**			**0**			**-1**		
M_L	**+1**	**0**	**-1**	**+1**	**0**	**-1**	**+1**	**0**	**-1**
Term	**^3P**								

Term Symbols for p^2

- **Next L value possible is 0**
  - **Possible M_L value is 0**
- **The only S value possible is : 0**
  - **Possible M_s value is 0**

The term is ^1S

M_S	**0**
M_L	**0**
Term	**^1S**

Term Symbols for d^2

$l_1 = 2; l_2 = 2$

$L = |l_1+l_2|, |l_1+l_2-1|, |l_1+l_2-2| \ldots, 0, \ldots, |l_1-l_2|$

So the possible values for L are

$$L = 4, 3, 2, 1, 0$$

$$s_1 = \frac{1}{2} ; s_2 = \frac{1}{2}$$

So the possible values for S are

$$S = 1, 0$$

Microstates of d^2

Maximum L value is 4

So the possible M_L values are +4, +3, +2, +1, 0, -1, -2, -3, -4

Maximum S value possible is 0

So M_s can be only 0

M_L	+4	+3	+2	+1	0	-1	-2	-3	-4
M_S	0	0	0	0	0	0	0	0	0
Term	^1G (9)								

Microstates of d^2

Next maximum L value is 3

So the possible M_L values are +3, +2, +1, 0, -1, -2, -3

Maximum S value possible is 1

So M_s can be +1, 0, -1

M_L	+3			+2			+1			0			-1			-2			-3		
M_S	+1	0	-1	+1	0	-1	+1	0	-1	+1	0	-1	+1	0	-1	+1	0	-1	+1	0	-1
Term	^3F (21)																				

Microstates of d^2

Next maximum L value is 2

So the possible M_L values are +2, +1, 0, -1, -2

Maximum S value possible is 1

So M_s can be +1, 0, -1

M_L	+2	+1	0	-1	-2
M_S	0	0	0	0	0
Term	^1D (5)				

Microstates of d^2

- Next maximum L value possible is 1
  - Possible M_L values are +1 , 0 , -1
- Maximum S value possible is : 1
  - Possible M_s value are +1 , 0 , -1
- Considering all possible combinations

M_S	+1			0			-1		
M_L	+1	0	-1	+1	0	-1	+1	0	-1
Term	^3P (9)								

Microstates of p^2

- Next L value possible is 0
  - Possible M_L value is 0
- The only S value possible is : 0
  - Possible M_s value is 0

The term is ^1S

M_S	0
M_L	0
Term	^1S (1)

- Five terms obtained: ^1G, ^3F, ^1D, ^3P, ^1S
- Hund's rule for ground state energy:
  - maximum spin multiplicity
  - maximum L value

Ground Term: ^3F

Expected relative energies of microstates

$^3F < {}^3P < {}^1G < {}^1D < {}^1S$

Actual order

$^3F < {}^1D < {}^3P < {}^1G < {}^1S$

Energies of Terms and Racah Parameters

- **Energies of terms**

  Depend on coulombic repulsion between electrons

  Expressed in *Racah* parameters A, B and C

  (all positive, determined from gas phase atomic spectroscopy, Table 13.2)

- d^2 configuration

  $E(^1S) = A + 14B + 7C$

  $E(^1G) = A + 4B + 2C$

  $E(^1D) = A - 3B + 2C$

  $E(^3P) = A + 7B$

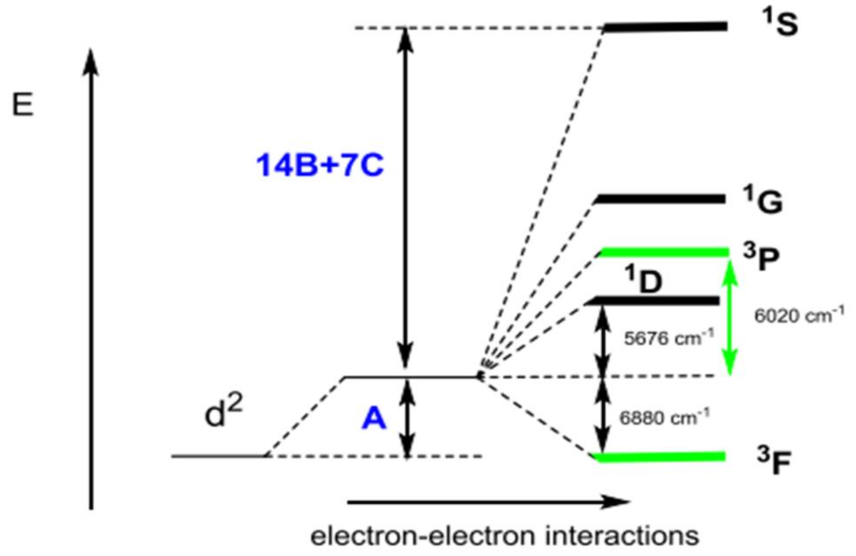
  $E(^3F) = A - 7B$ A: common to all terms

- Energies of terms: depend on C/B ratio. Normally, $C/B \sim 4$.
  When $C > 5B$, $^3F < {}^3P < {}^1G < {}^1D < {}^1S$

  When $C < 5B$, $E(^1D) < E(^3P)$ $^3F < {}^1D < {}^3P < {}^1G < {}^1S$

Energies of atomic terms can be parametrized with Racah parameters. These parameters (i.e. A, B, C) are used to describe the interelectronic repulsion.

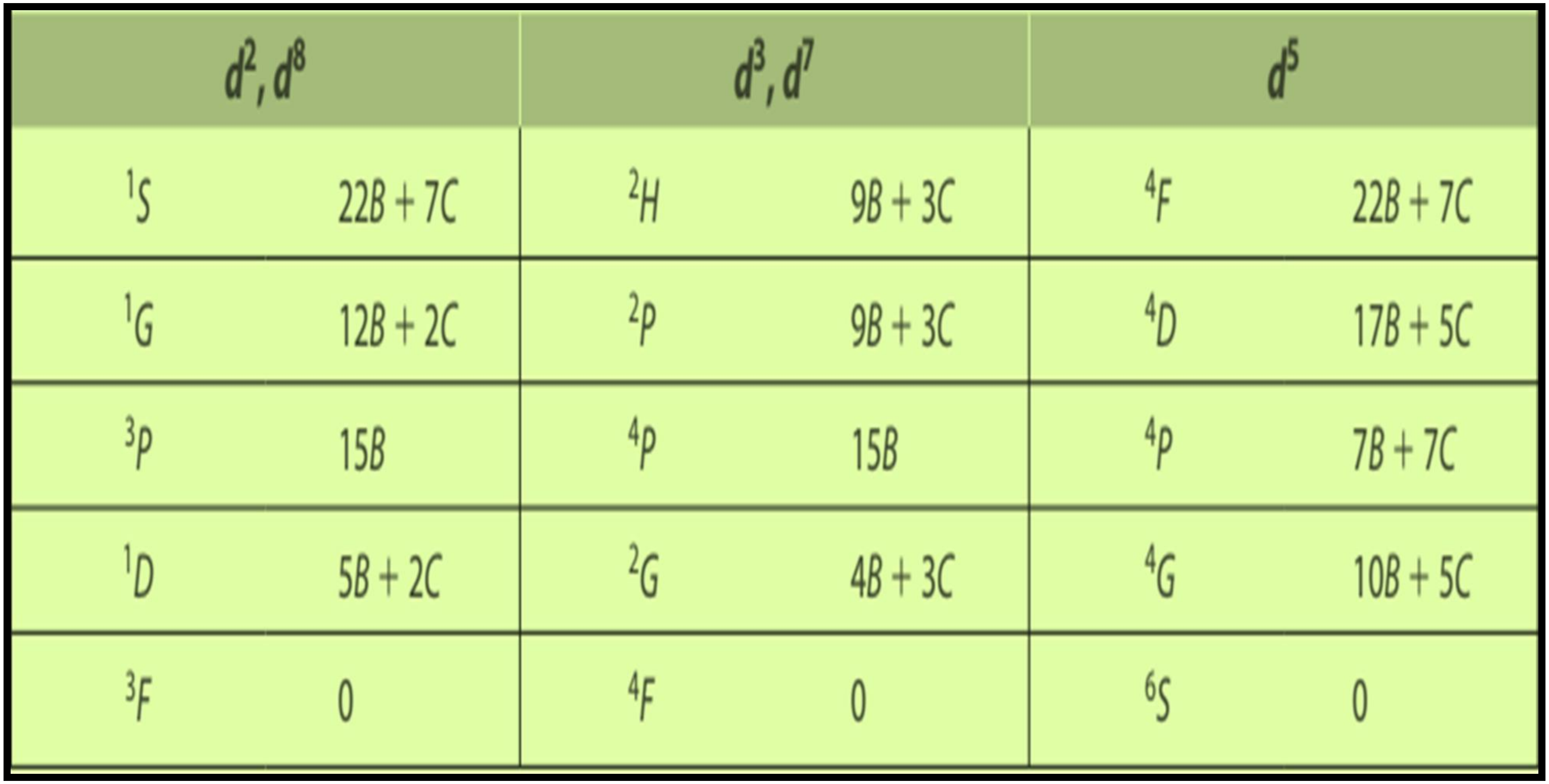
Term	Energy in terms of Racah parameters	Experimental values (scaled to A)
^1S	A+14B+7C	+40936 cm^{-1}
^1G	A+4B+2C	+11696 cm^{-1}
^3P	A+7B	+6020 cm^{-1}
^1D	A-3B+2C	+5676 cm^{-1}
^3F	A - 8B	-6880 cm^{-1}



Advantage of Racah-Parameters: Energy difference between ground and excited terms of same spin-multiplicity depend only on B

e.g. V^{3+} (d^2): B = 860 cm^{-1} (=(6020+6880)/15), C = 4128 cm^{-1}, => C/B = 4.8
Ti^{2+} (d^2): B = 720 cm^{-1}, C = 2664 cm^{-1}, => C/B = 3.7

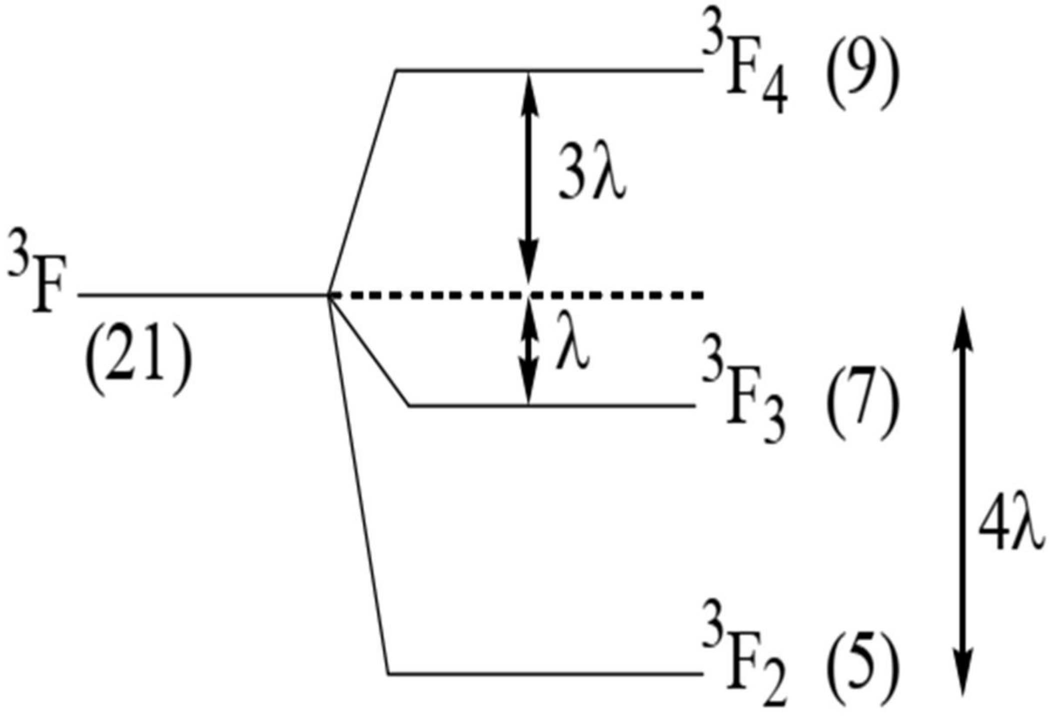
Rule of thumb for free 3d-ions or atoms: C ~ 4·B cm^{-1}, B ~ 1000 cm^{-1}

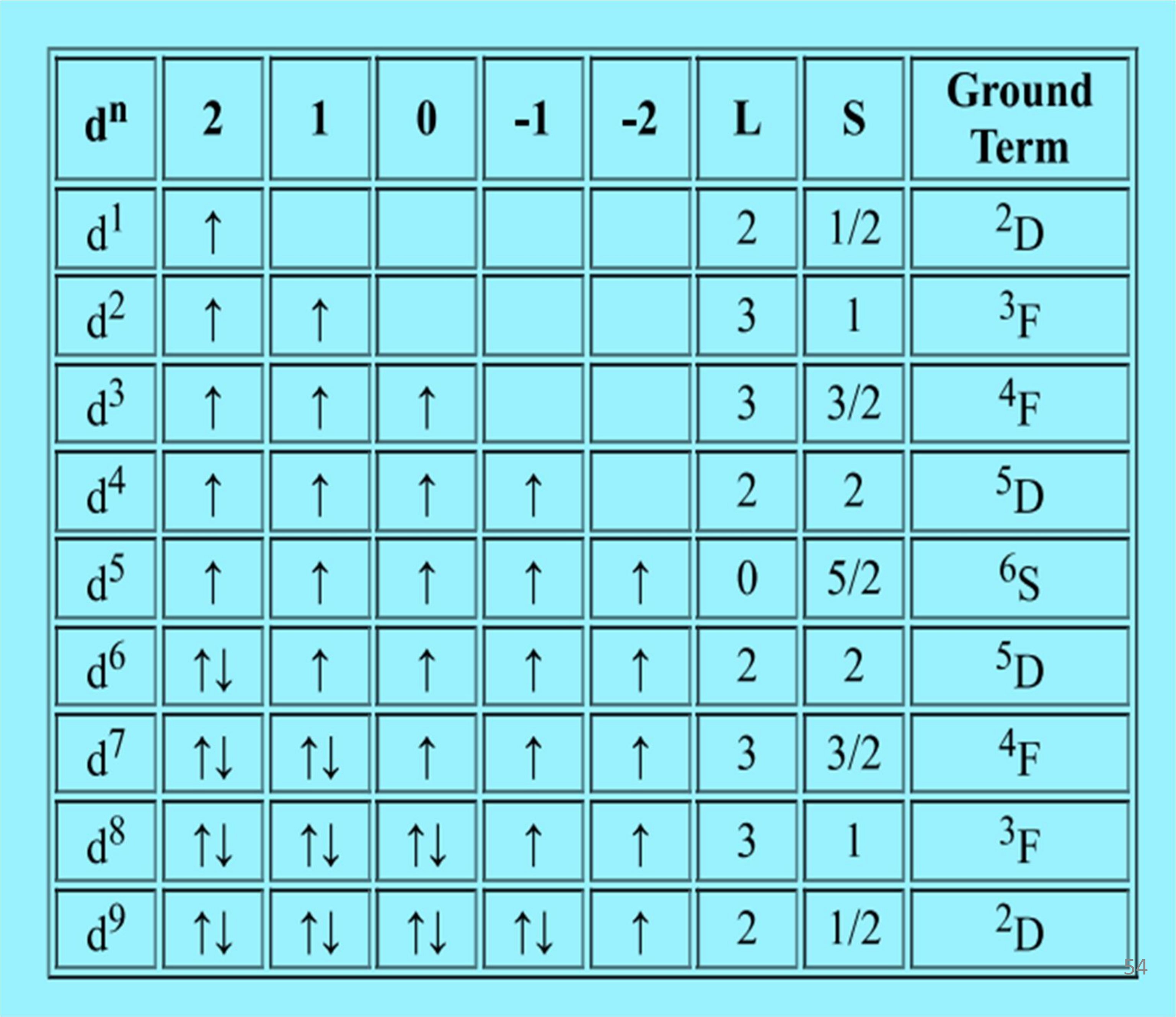


d^2, d^8		d^3, d^7		d^5	
^1S	$22B + 7C$	^2H	$9B + 3C$	^4F	$22B + 7C$
^1G	$12B + 2C$	^2P	$9B + 3C$	^4D	$17B + 5C$
^3P	$15B$	^4P	$15B$	^4P	$7B + 7C$
^1D	$5B + 2C$	^2G	$4B + 3C$	^4G	$10B + 5C$
^3F	0	^4F	0	^6S	0

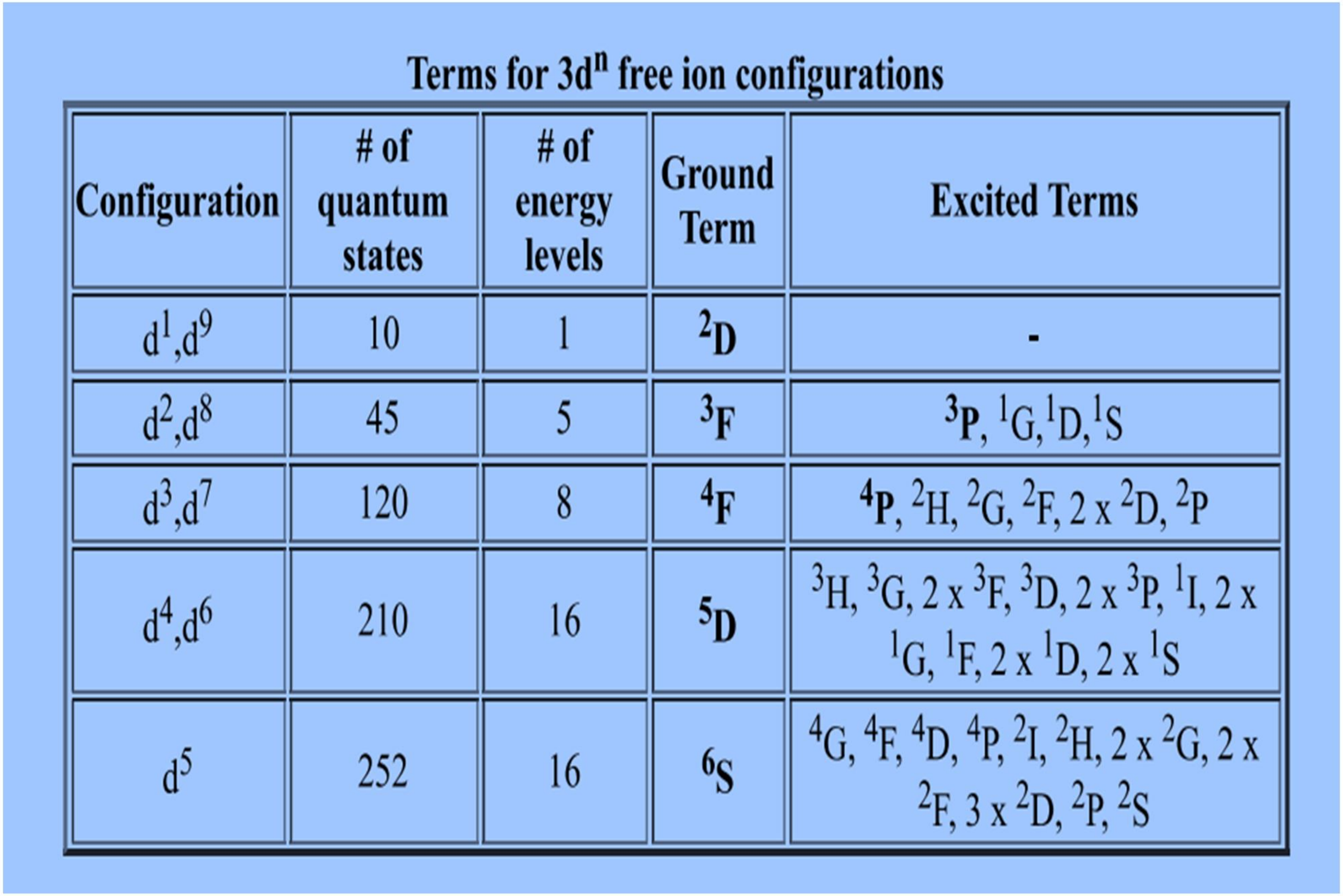
The splitting depends on the size of the spin-orbit coupling constant λ or ζ

Example d^2





d^n	2	1	0	-1	-2	L	S	Ground Term
d^1	↑					2	1/2	^2D
d^2	↑	↑				3	1	^3F
d^3	↑	↑	↑			3	3/2	^4F
d^4	↑	↑	↑	↑		2	2	^5D
d^5	↑	↑	↑	↑	↑	0	5/2	^6S
d^6	↑↓	↑	↑	↑	↑	2	2	^5D
d^7	↑↓	↑↓	↑	↑	↑	3	3/2	^4F
d^8	↑↓	↑↓	↑↓	↑	↑	3	1	^3F
d^9	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	^2D



Terms for 3d^n free ion configurations

Configuration	# of quantum states	# of energy levels	Ground Term	Excited Terms
d^1,d^9	10	1	**^{2}D**	-
d^2,d^8	45	5	**^{3}F**	**^{3}P**, ^{1}G,^{1}D,^{1}S
d^3,d^7	120	8	**^{4}F**	**^{4}P**, ^{2}H, ^{2}G, ^{2}F, 2 x ^{2}D, ^{2}P
d^4,d^6	210	16	**^{5}D**	^{3}H, ^{3}G, 2 x ^{3}F, ^{3}D, 2 x ^{3}P, ^{1}I, 2 x ^{1}G, ^{1}F, 2 x ^{1}D, 2 x ^{1}S
d^5	252	16	**^{6}S**	^{4}G, ^{4}F, ^{4}D, ^{4}P, ^{2}I, ^{2}H, 2 x ^{2}G, 2 x ^{2}F, 3 x ^{2}D, ^{2}P, ^{2}S

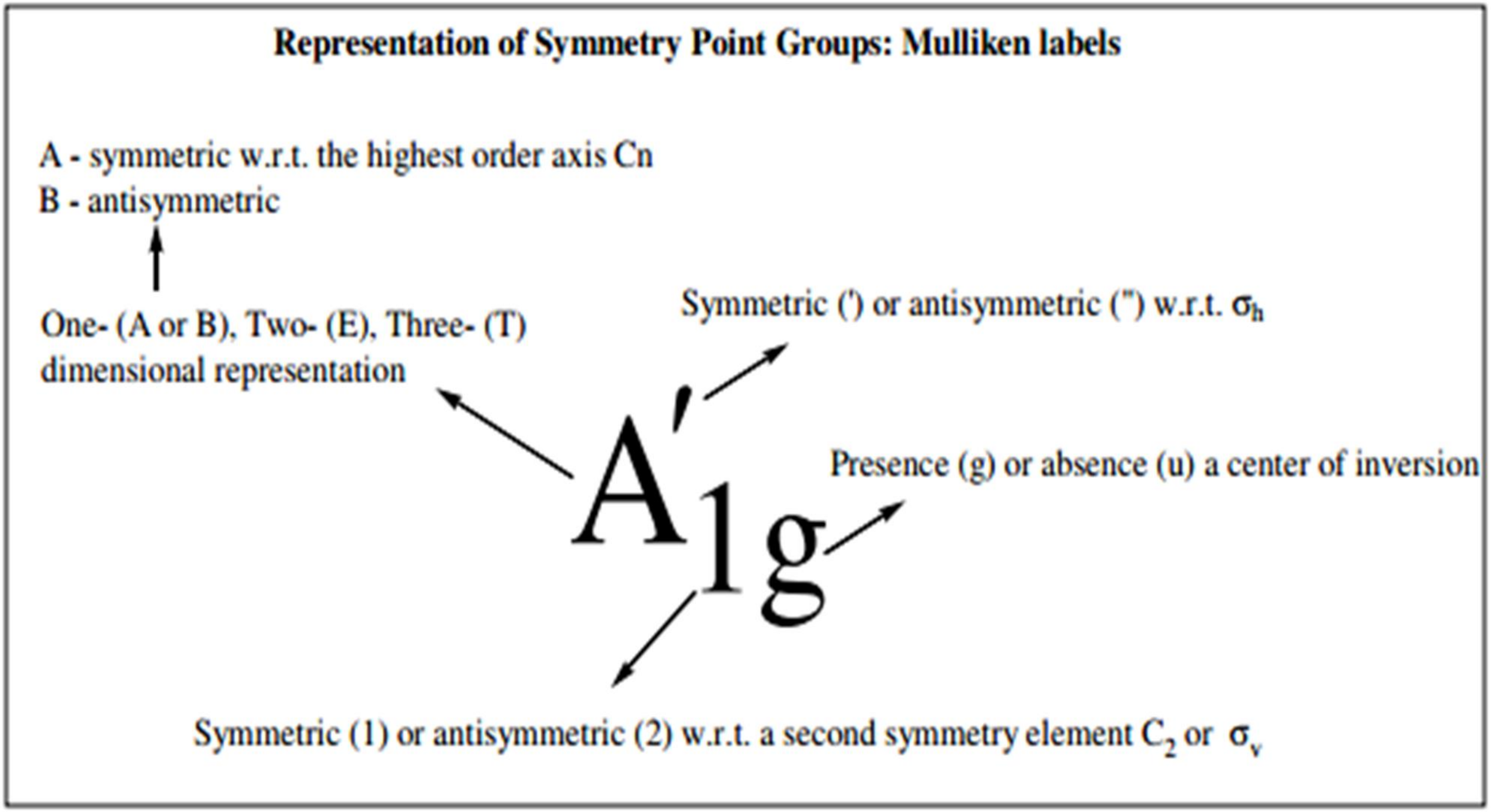
The Crystal Field Splitting of Russell-Saunders terms in weak o_h crystal fields

Russell-Saunders Terms	Crystal Field Components
S (1)	A_{1g}
P (3)	T_{1g}
D (5)	$E_g + T_{2g}$
F (7)	$A_{2g} + T_{1g} + T_{2g}$
G (9)	$A_{1g} + E_g + T_{1g} + T_{2g}$
H (11)	$E_g + T_{1g} + T_{1g} + T_{2g}$
I (13)	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Mulliken Symbols

Mulliken Symbol	Explanation
A	Non-degenerate orbital; symmetric to principal C_n
B	Non-degenerate orbital; unsymmetric to principal C_n
E	Doubly degenerate orbital
T	Triply degenerate orbital
(subscript) g	Symmetric with respect to center of inversion
(subscript) u	Unsymmetric with respect to center of inversion
(subscript) 1	Symmetric with respect to C_2 perp. to principal C_n
(subscript) 2	Unsymmetric with respect to C_2 perp. to principal C_n
(superscript) '	Symmetric with respect to σ_h
(superscript) "	Unsymmetric with respect to σ_h

Mulliken Symbols



Representation of Symmetry Point Groups: Mulliken labels

A - symmetric w.r.t. the highest order axis Cn
B - antisymmetric

One- (A or B), Two- (E), Three- (T) dimensional representation

Symmetric (') or antisymmetric (") w.r.t. σ_h

A'_{1g}

Presence (g) or absence (u) a center of inversion

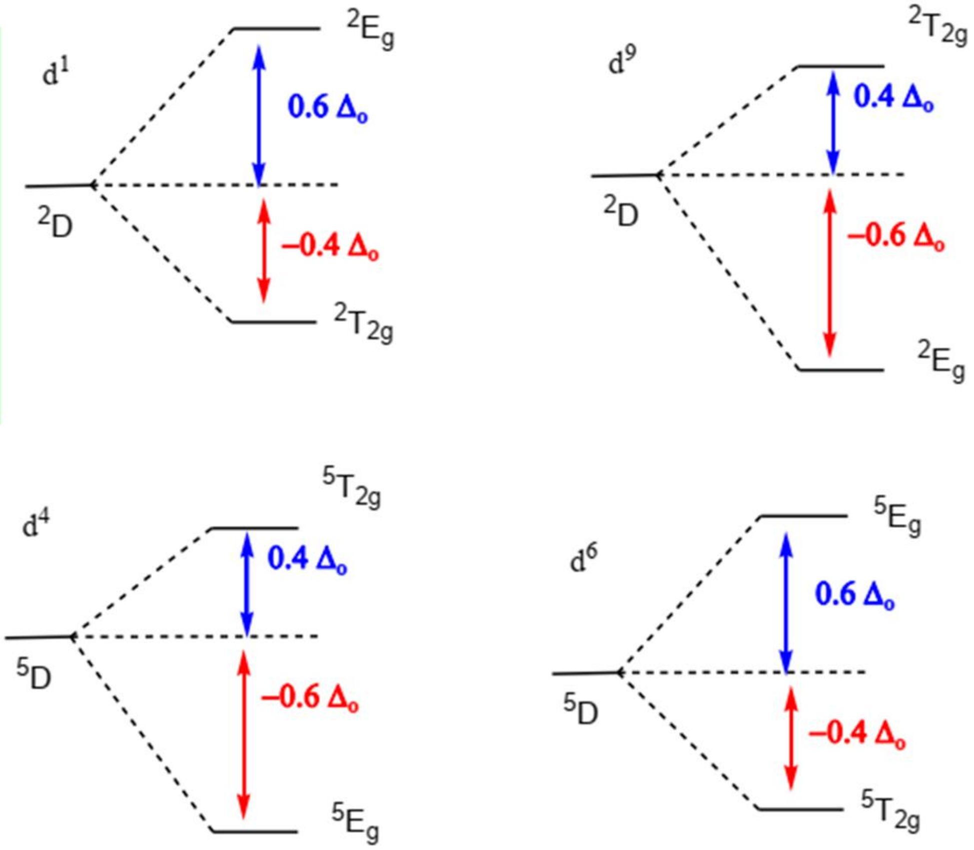
Symmetric (1) or antisymmetric (2) w.r.t. a second symmetry element C_2 or σ_v

Order of energies of crystal field terms

b) Determination of the energies of the upper ligand field terms

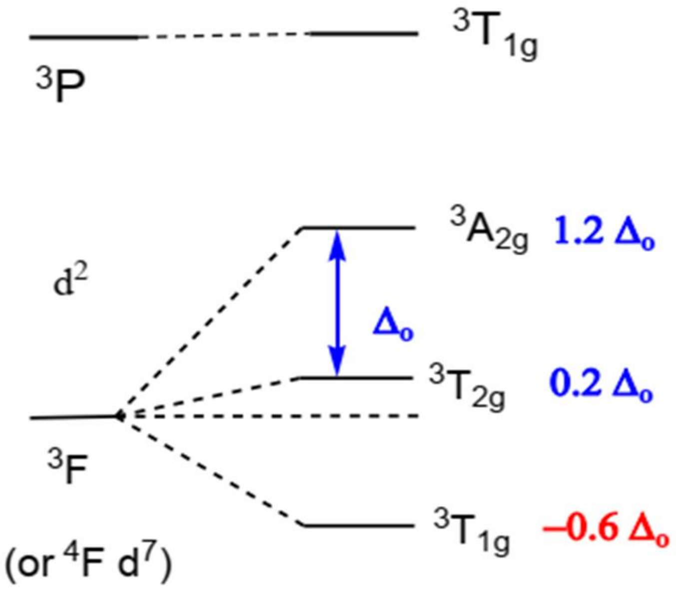
In case of d^1,d^4,d^6 and d^9 systems, the energies of the upper levels are relatively easy to calculate (from the degeneracies of the terms)

T: triply degenerate
E: doubly degenerate term

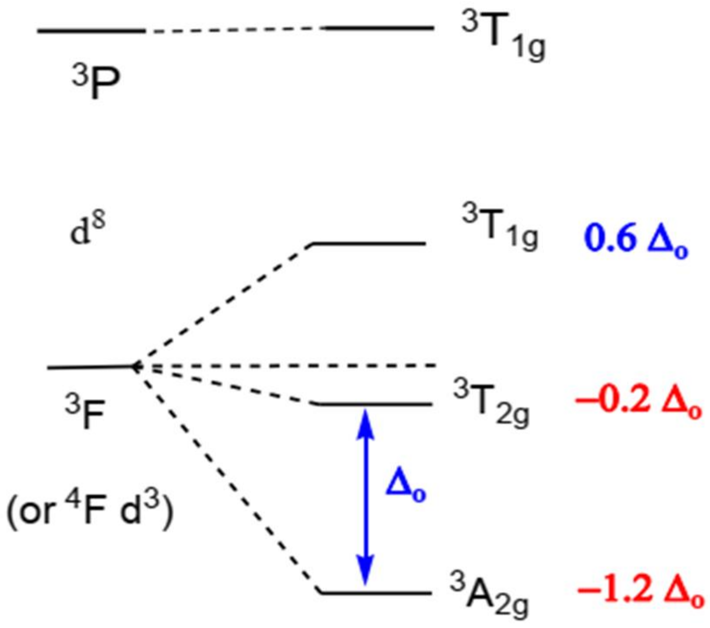


Energies of the crystal field terms: d^2, d^3, d^7, d^8 configuration

- are more difficult to calculate (beyond the scope of this lecture)
- only the results are given here (splitting of the ground terms) (without consideration of the configuration interaction)

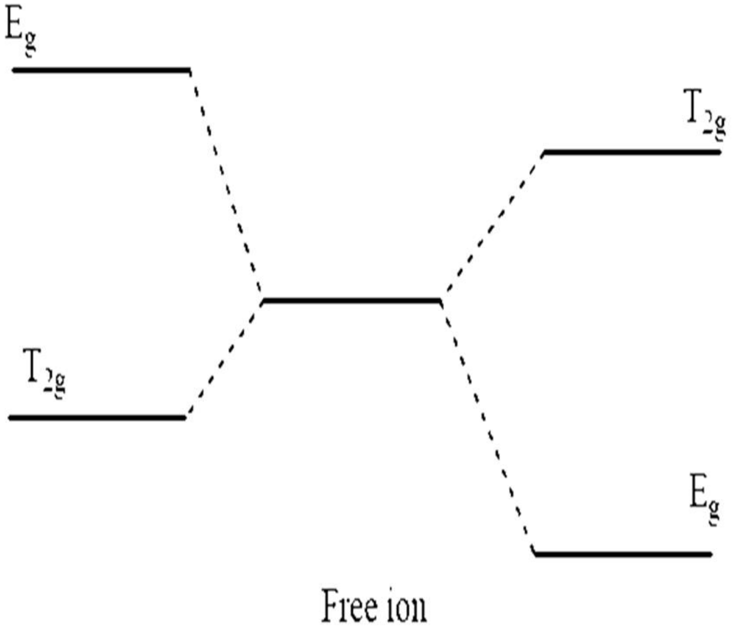


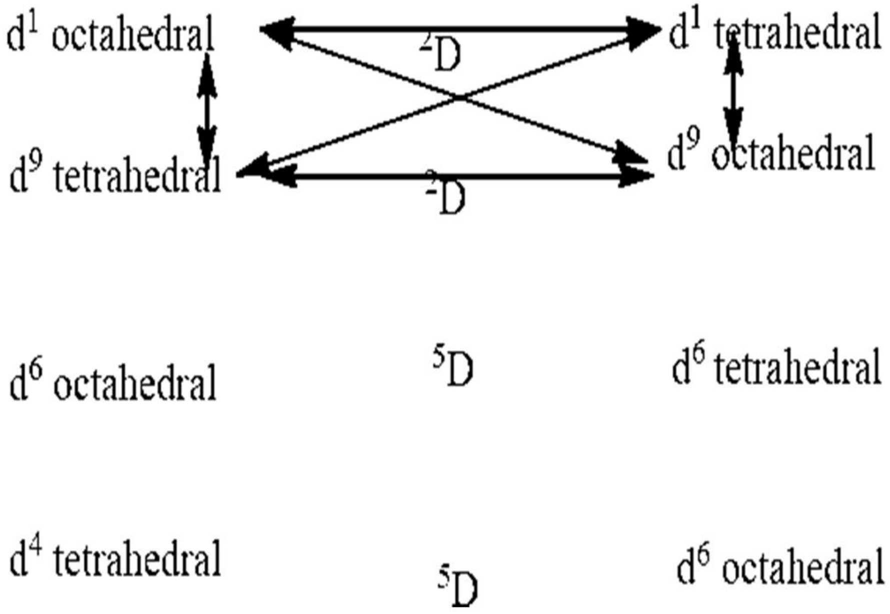
d^2



d^8

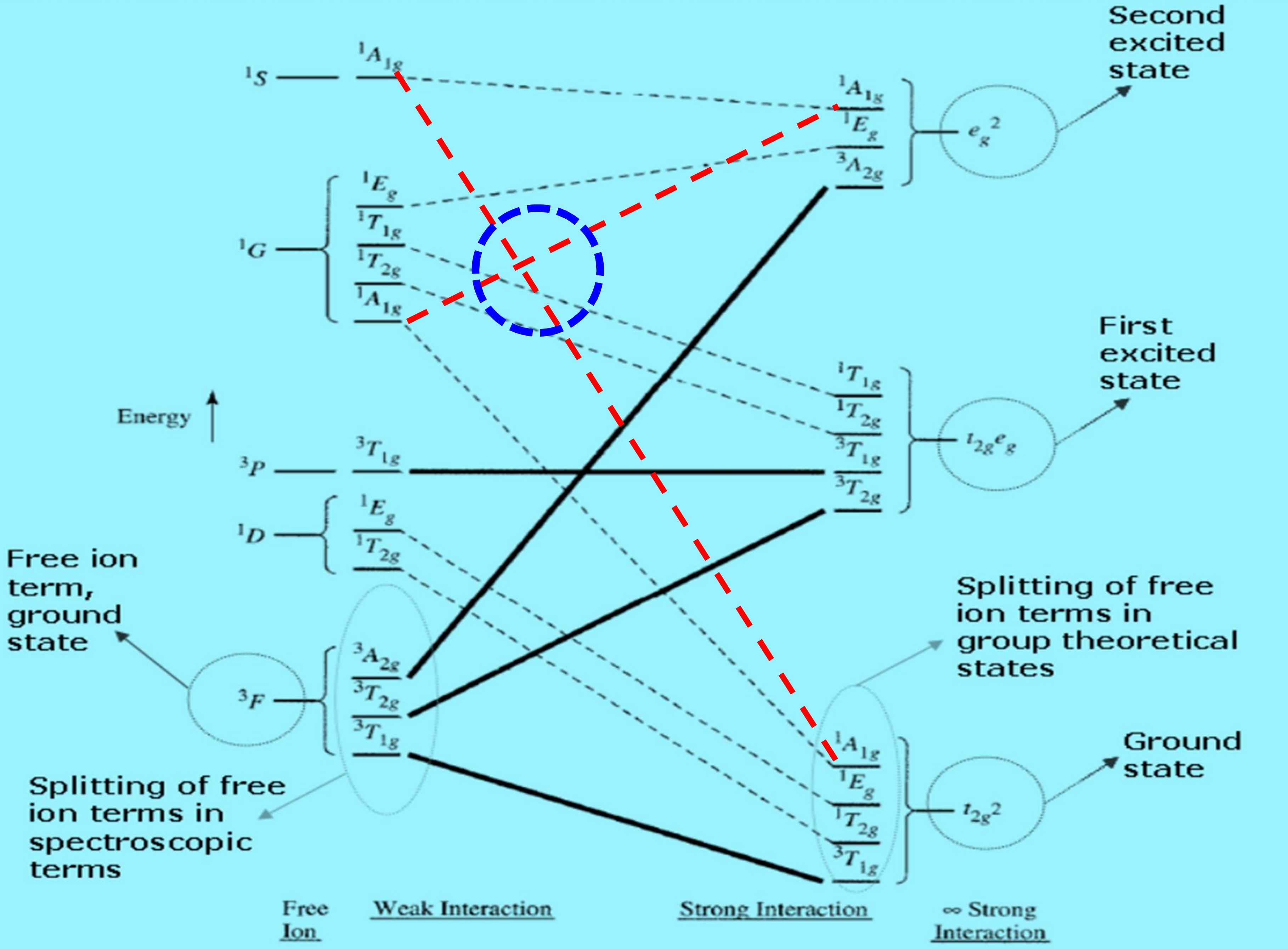
An inverse relation exists between d^n and d^{10-n} systems (hole formalism) and also between octahedral and tetrahedral symmetries. Considering these, the energy level diagrams for the d^n system, strong field configuration is given below. These four diagrams can explain all the seven systems, viz., d^2 to d^8.





Correlation Diagrams
Relating Electron Spectra to Ligand Field Splitting

- **Examine the correlation diagram for a d^2 configuration in an octahedral ligand field.**
  - **Far left (absence of ligand field) – the free-ion terms. On this side, the ligand field has very little influence.**
  - **Far right (strong ligand field) – the states are largely determined by the ligand field.**
- **In real compounds, the situation is somewhere in the middle.**
- **Correlating the states on both sides is done in accordance with the so called " non-crossing rule " .**



Second excited state

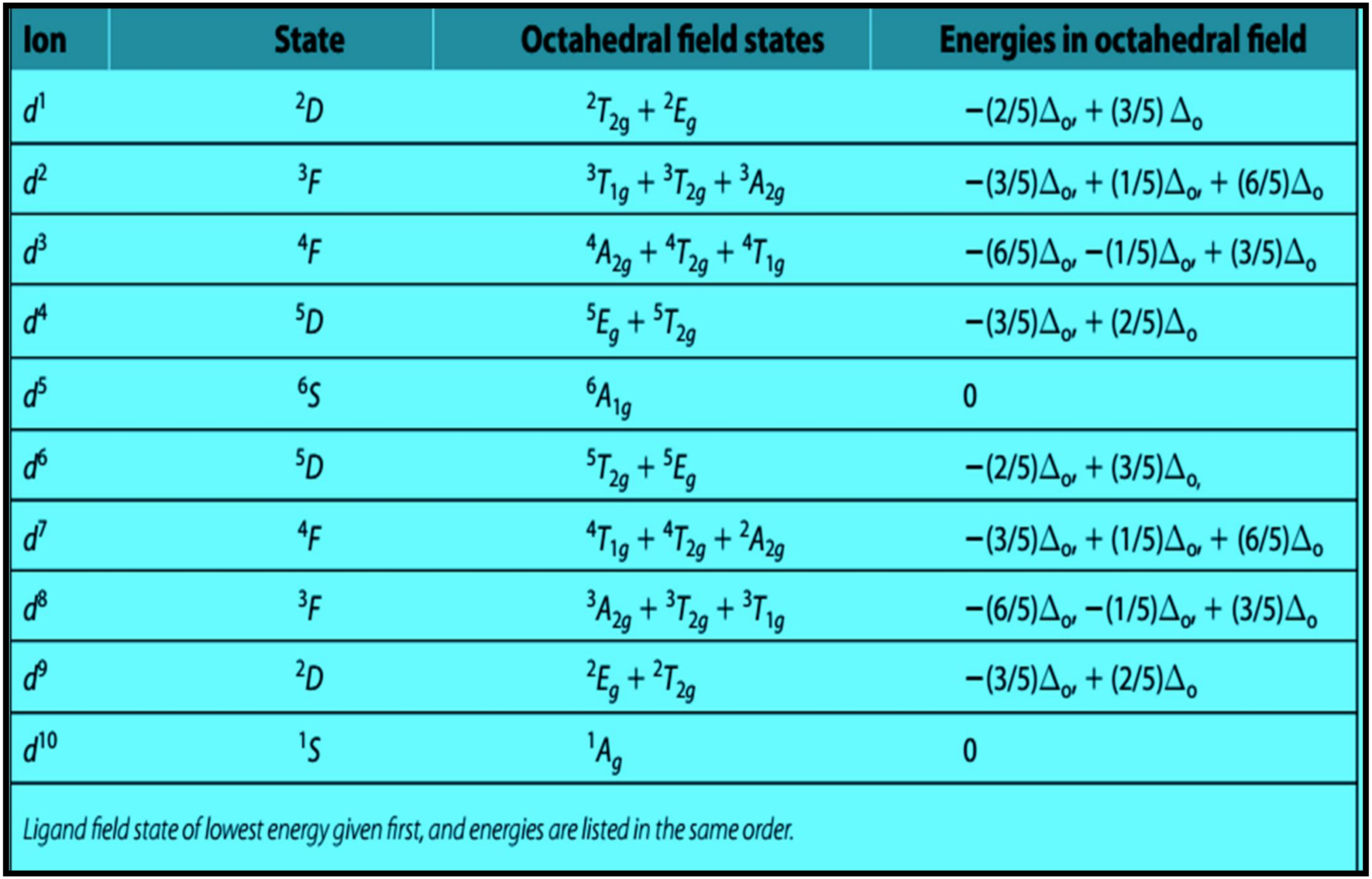
First excited state

Splitting of free ion terms in group theoretical states

Ground state

Free ion term, ground state

Splitting of free ion terms in spectroscopic terms



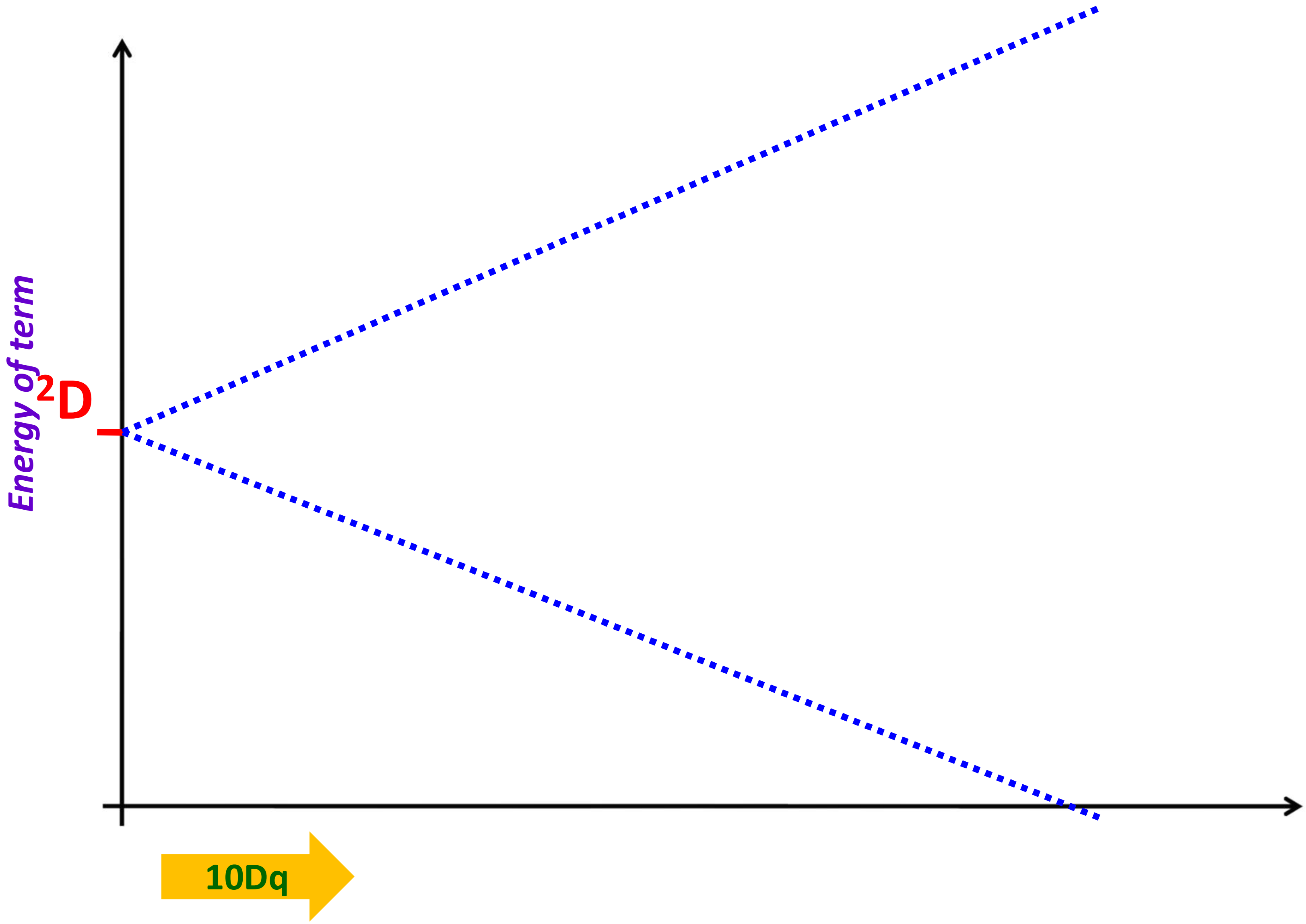
Ion	State	Octahedral field states	Energies in octahedral field
d^1	^2D	$^2T_{2g} + {}^2E_g$	$-(2/5)\Delta_o, + (3/5)\ \Delta_o$
d^2	^3F	$^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$	$-(3/5)\Delta_o, + (1/5)\Delta_o, + (6/5)\Delta_o$
d^3	^4F	$^4A_{2g} + {}^4T_{2g} + {}^4T_{1g}$	$-(6/5)\Delta_o, -(1/5)\Delta_o, + (3/5)\Delta_o$
d^4	^5D	$^5E_g + {}^5T_{2g}$	$-(3/5)\Delta_o, + (2/5)\Delta_o$
d^5	^6S	$^6A_{1g}$	0
d^6	^5D	$^5T_{2g} + {}^5E_g$	$-(2/5)\Delta_o, + (3/5)\Delta_{o,}$
d^7	^4F	$^4T_{1g} + {}^4T_{2g} + {}^2A_{2g}$	$-(3/5)\Delta_o, + (1/5)\Delta_o, + (6/5)\Delta_o$
d^8	^3F	$^3A_{2g} + {}^3T_{2g} + {}^3T_{1g}$	$-(6/5)\Delta_o, -(1/5)\Delta_o, + (3/5)\Delta_o$
d^9	^2D	$^2E_g + {}^2T_{2g}$	$-(3/5)\Delta_o, + (2/5)\Delta_o$
d^{10}	^1S	^1A_g	0

Ligand field state of lowest energy given first, and energies are listed in the same order.

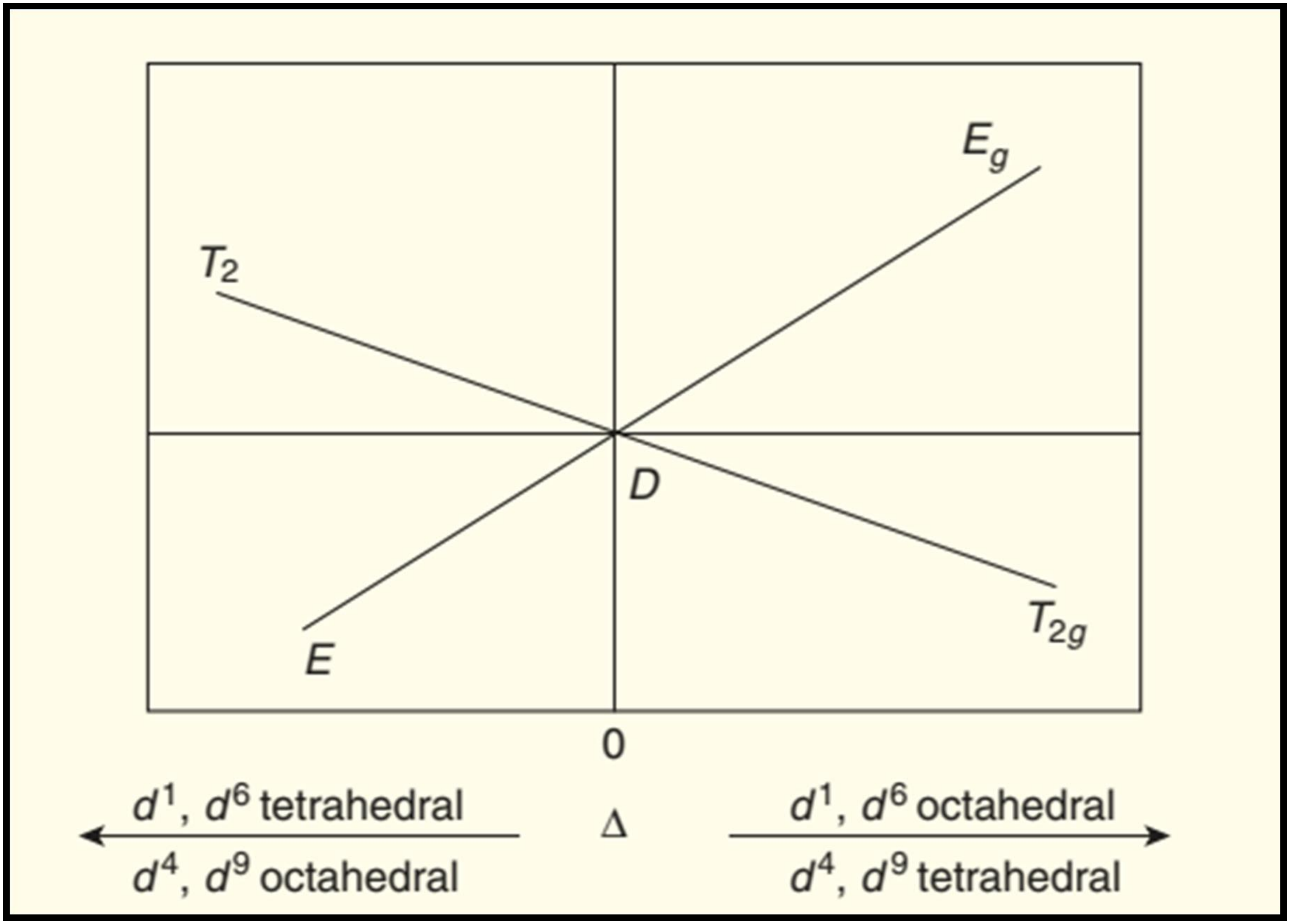
Orgel Diagram

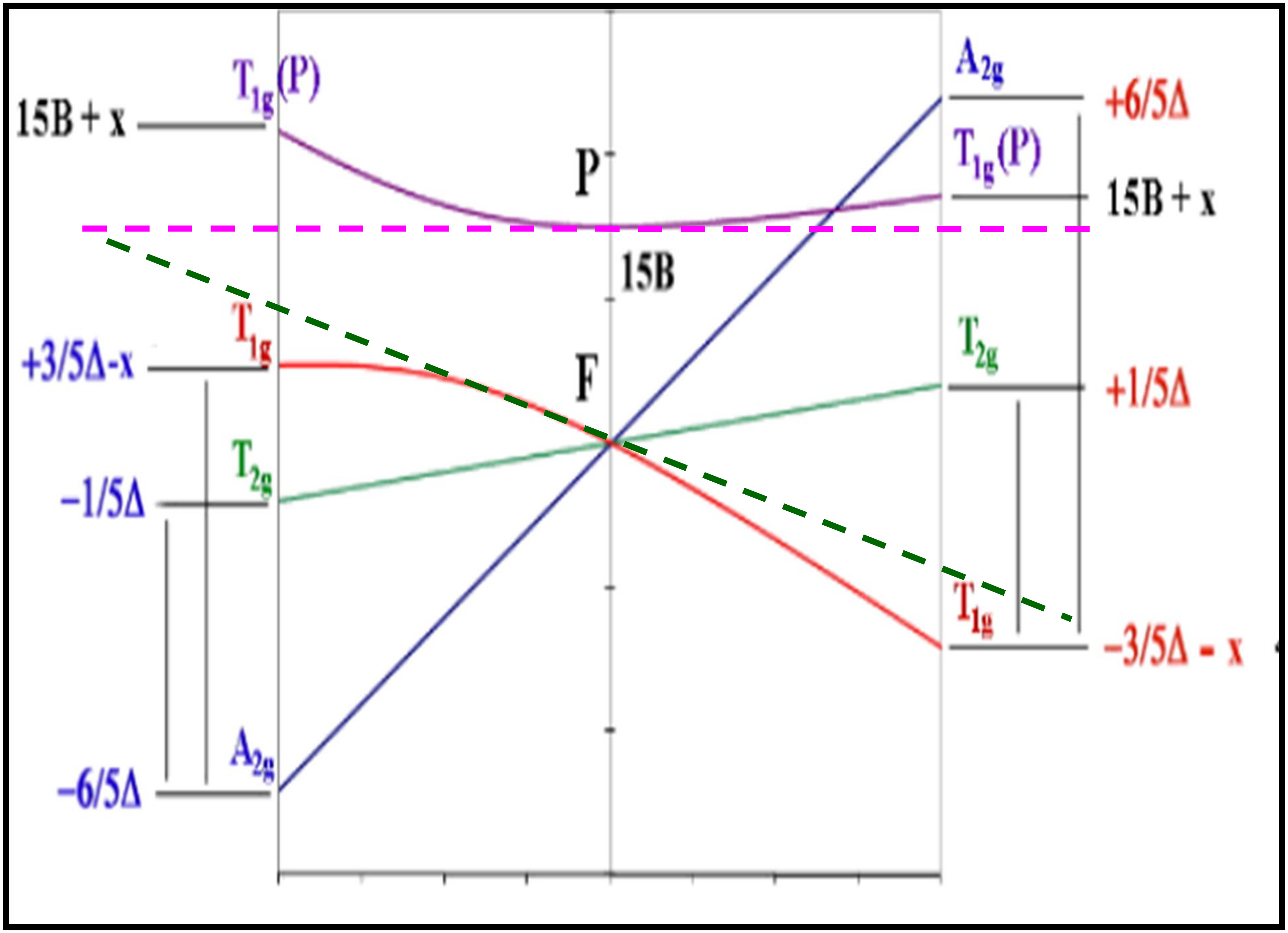
- **Used for interpretation of electronic spectra of metal ion complexes.**
- **Got by plotting the energies of split levels of a term by increasing ligand field strength**
- **Only applicable for weak field cases.**
- **Can predict only spin-allowed transitions.**
- **Transitions are assumed to occur from the lowest energy level.**

Orgel Diagram



Orgel Diagram




$T_{1g}(P)$
15B + x
A_{2g}
+6/5Δ
$T_{1g}(P)$
15B + x
P
15B
T_{1g}
+3/5Δ-x
F
T_{2g}
+1/5Δ
T_{2g}
−1/5Δ
T_{1g}
−3/5Δ - x
A_{2g}
−6/5Δ

For metal ions having d^2, d^3, d^7, and d^8 configurations, the ground state is an *F* state, but there is an excited *P* state that has the same multiplicity. For d^2 and d^7 ions in an *octahedral* field, the spectroscopic states are the same (except for the multiplicity) as they are for d^3 and d^8 ions in *tetrahedral* fields. Therefore, the expected spectral transitions will also be the same for the two types of complexes. The three spectral bands are assigned as follows ($T_{1g}(F)$ means the T_{1g} state arising from the *F* spectroscopic state):

$$\nu_1 T_{1g} \quad (F) \rightarrow T_{2g}$$

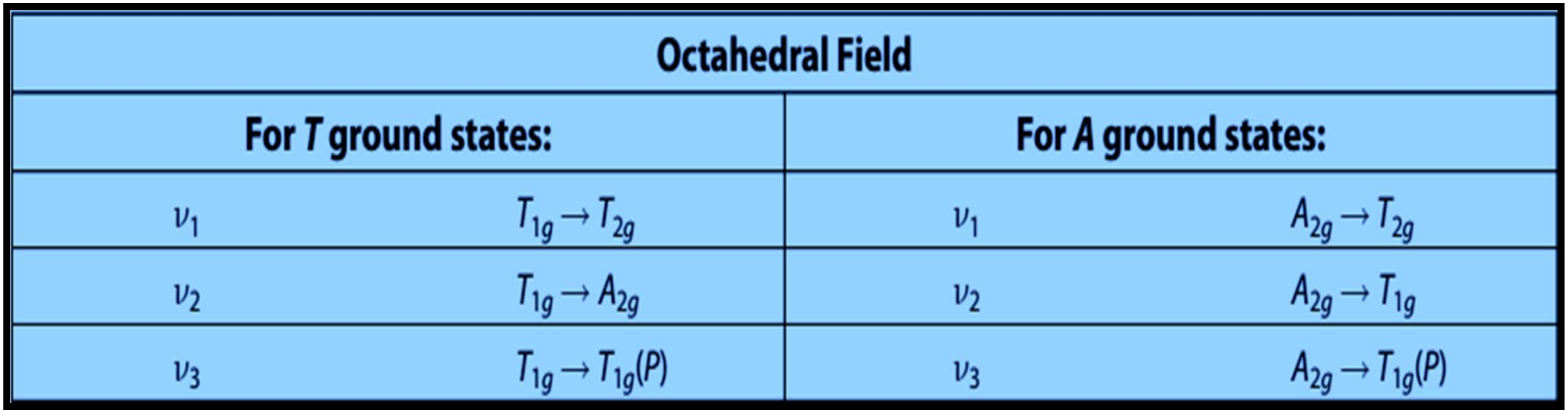
$$\nu_2 T_{1g} \quad (F) \rightarrow A_{2g}$$

$$\nu_3 T_{1g} \quad (F) \rightarrow T_{1g}(P)$$

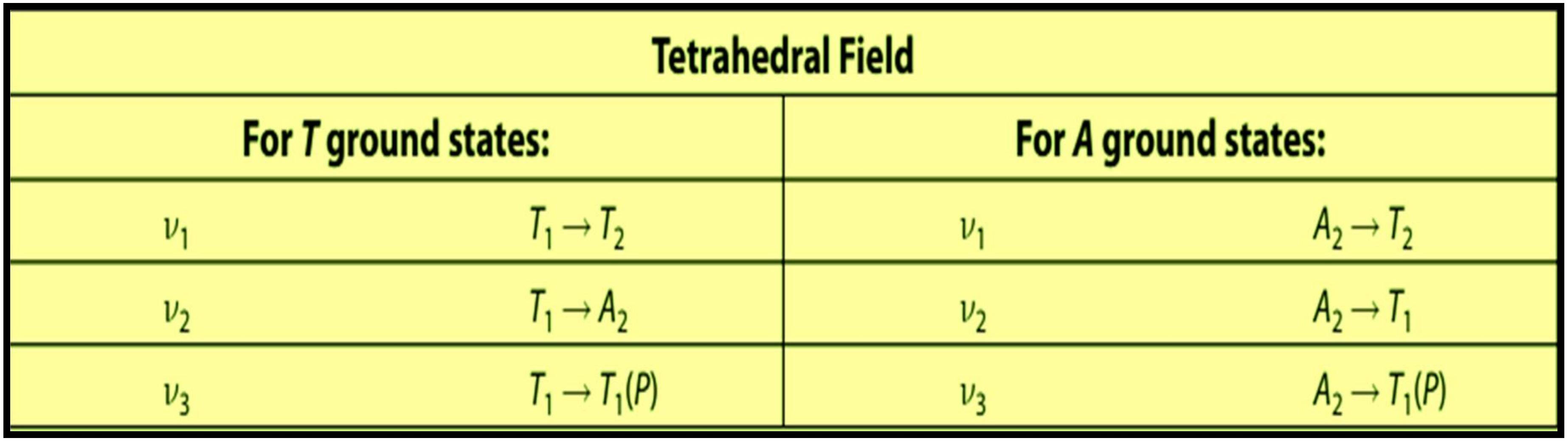
$$E(\nu_1) = 5\mathrm{Dq} - 7.5B + (225B^2 + 100\mathrm{Dq}^2 + 180\mathrm{Dq}B)^{1/2}$$

$$E(\nu_2) = 15\mathrm{Dq} - 7.5B + (225B^2 + 100\mathrm{Dq}^2 + 180\mathrm{Dq}B)^{1/2}$$

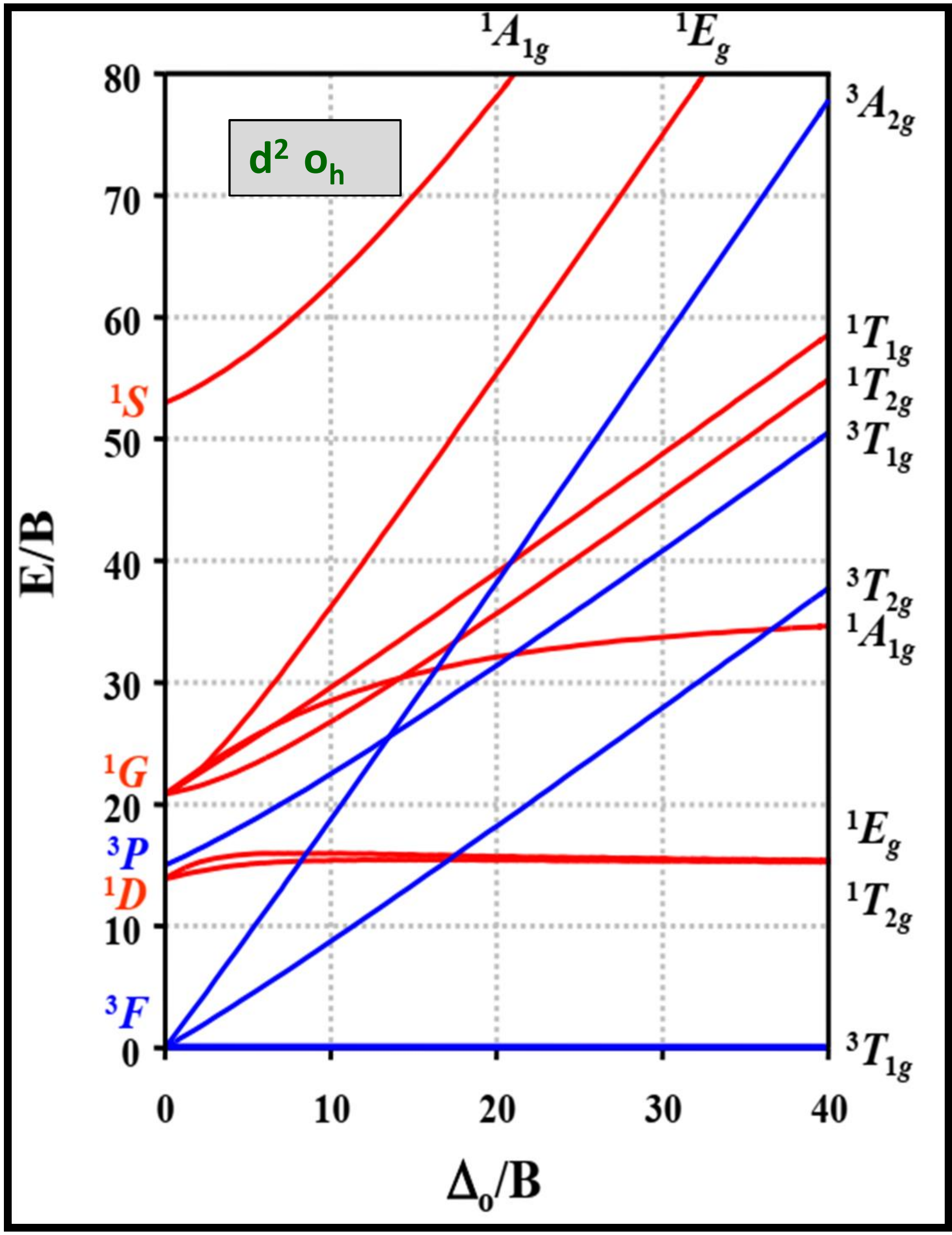
$$E(\nu_3) = (225B^2 + 100\mathrm{Dq}^2 + 180\mathrm{Dq}B)^{1/2}$$

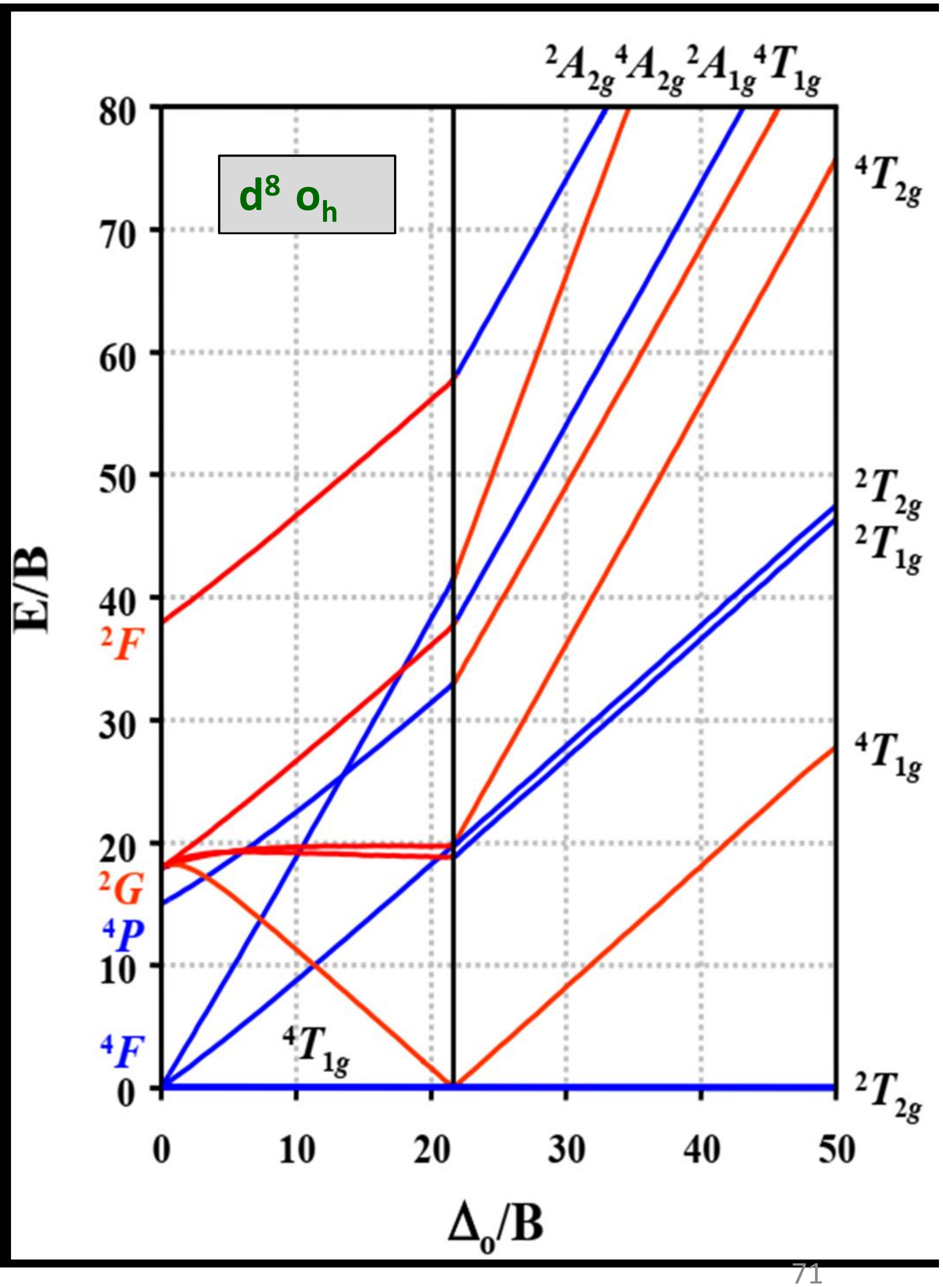


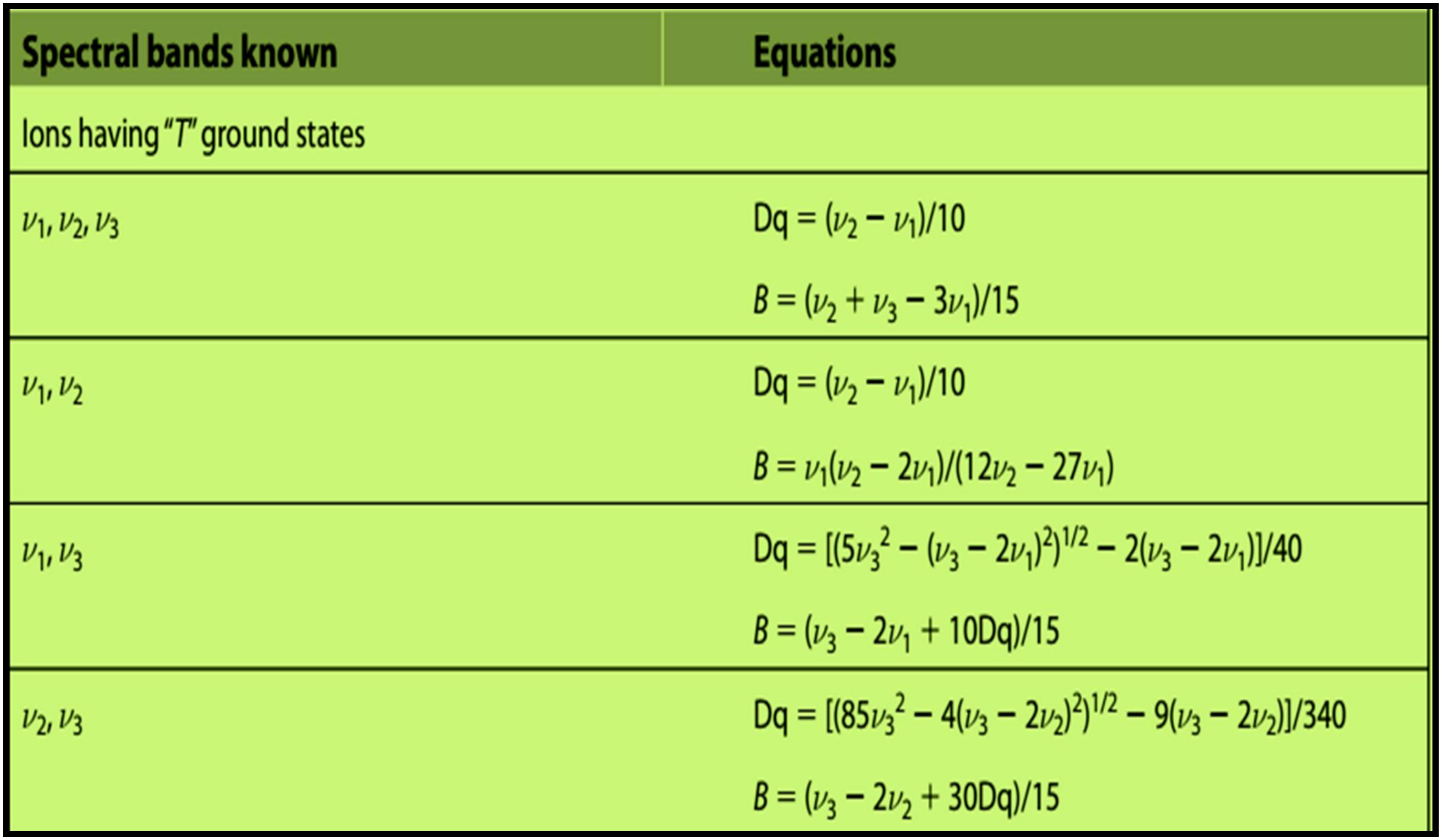
Octahedral Field			
For *T* ground states:		**For *A* ground states:**	
ν_1	$T_{1g} \rightarrow T_{2g}$	ν_1	$A_{2g} \rightarrow T_{2g}$
ν_2	$T_{1g} \rightarrow A_{2g}$	ν_2	$A_{2g} \rightarrow T_{1g}$
ν_3	$T_{1g} \rightarrow T_{1g}(P)$	ν_3	$A_{2g} \rightarrow T_{1g}(P)$



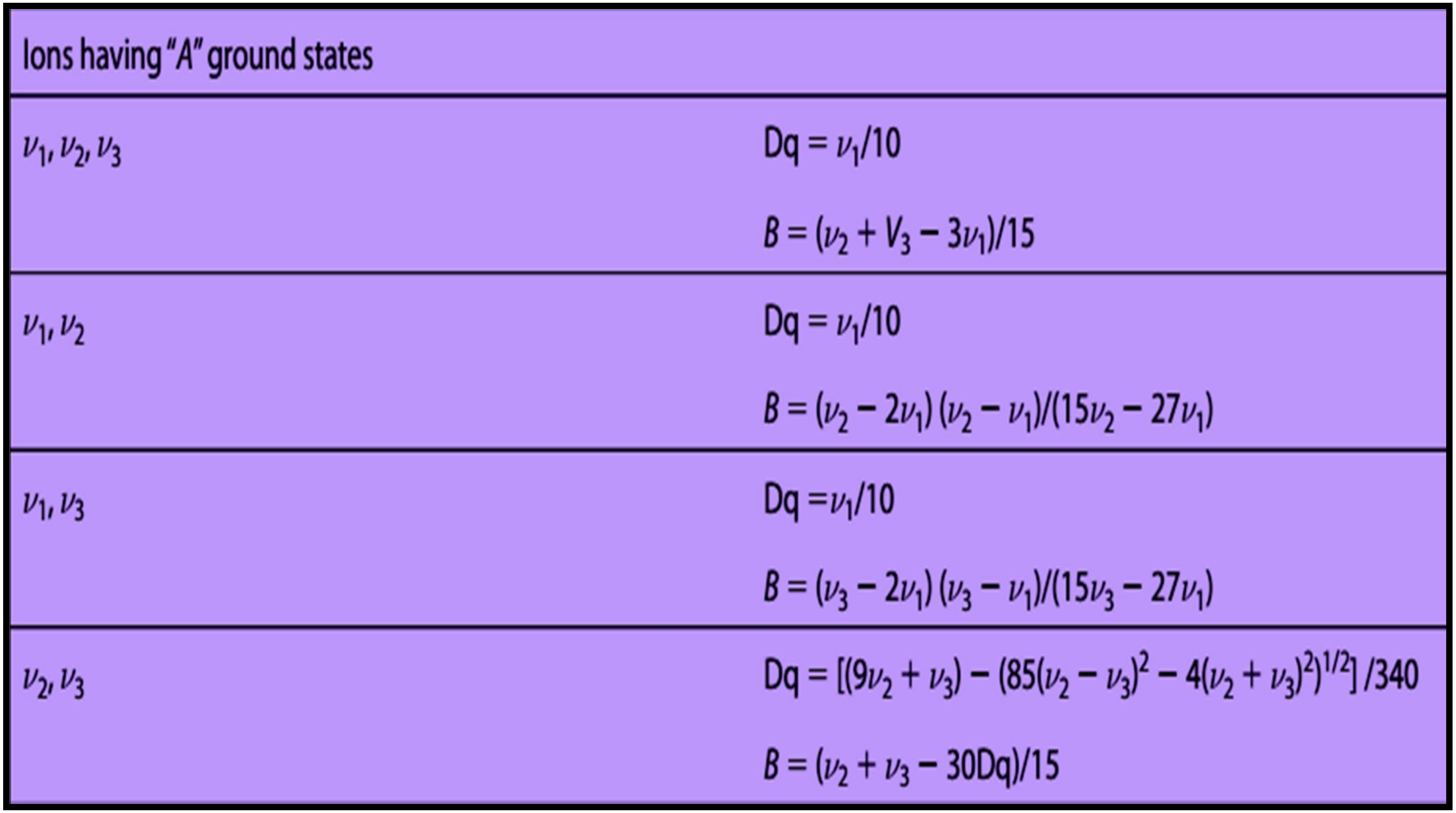
Tetrahedral Field			
For *T* ground states:		**For *A* ground states:**	
ν_1	$T_1 \rightarrow T_2$	ν_1	$A_2 \rightarrow T_2$
ν_2	$T_1 \rightarrow A_2$	ν_2	$A_2 \rightarrow T_1$
ν_3	$T_1 \rightarrow T_1(P)$	ν_3	$A_2 \rightarrow T_1(P)$


d^2 o$_h$
E/B
Δ$_o$/B
0
10
20
30
40
50
60
70
80
0
10
20
30
40
$^1A_{1g}$
^1E_g
$^3A_{2g}$
$^1T_{1g}$
$^1T_{2g}$
$^3T_{1g}$
$^3T_{2g}$
$^1A_{1g}$
^1E_g
$^1T_{2g}$
$^3T_{1g}$
^1S
^1G
^3P
^1D
^3F


d^8 o$_h$
E/B
Δ$_o$/B
0
10
20
30
40
50
60
70
80
0
10
20
30
40
50
$^2A_{2g}$
$^4A_{2g}$
$^2A_{1g}$
$^4T_{1g}$
$^4T_{2g}$
$^2T_{2g}$
$^2T_{1g}$
$^4T_{1g}$
$^2T_{2g}$
$^4T_{1g}$
^2F
^2G
^4P
^4F



Spectral bands known	**Equations**
Ions having "*T*" ground states	
ν_1, ν_2, ν_3	$\mathrm{Dq} = (\nu_2 - \nu_1)/10$ $B = (\nu_2 + \nu_3 - 3\nu_1)/15$
ν_1, ν_2	$\mathrm{Dq} = (\nu_2 - \nu_1)/10$ $B = \nu_1(\nu_2 - 2\nu_1)/(12\nu_2 - 27\nu_1)$
ν_1, ν_3	$\mathrm{Dq} = [(5\nu_3^2 - (\nu_3 - 2\nu_1)^2)^{1/2} - 2(\nu_3 - 2\nu_1)]/40$ $B = (\nu_3 - 2\nu_1 + 10\mathrm{Dq})/15$
ν_2, ν_3	$\mathrm{Dq} = [(85\nu_3^2 - 4(\nu_3 - 2\nu_2)^2)^{1/2} - 9(\nu_3 - 2\nu_2)]/340$ $B = (\nu_3 - 2\nu_2 + 30\mathrm{Dq})/15$



Ions having “A” ground states	
ν_1, ν_2, ν_3	$Dq = \nu_1/10$ $B = (\nu_2 + V_3 - 3\nu_1)/15$
ν_1, ν_2	$Dq = \nu_1/10$ $B = (\nu_2 - 2\nu_1)(\nu_2 - \nu_1)/(15\nu_2 - 27\nu_1)$
ν_1, ν_3	$Dq = \nu_1/10$ $B = (\nu_3 - 2\nu_1)(\nu_3 - \nu_1)/(15\nu_3 - 27\nu_1)$
ν_2, ν_3	$Dq = [(9\nu_2 + \nu_3) - (85(\nu_2 - \nu_3)^2 - 4(\nu_2 + \nu_3)^2)^{1/2}]/340$ $B = (\nu_2 + \nu_3 - 30Dq)/15$

Selection Rules for Electronic Spectra

- When the molecule absorbs electromagnetic radiation, it may be due to interaction of
  - electrical dipole or quadruple with the electrical field of emr – Electrical dipole transitions
  - the magnetic dipole of the molecule with the magnetic field of emr – Magnetic dipole transitions

Electrical dipole >> Magnetic dipole > Electrical quadruple

Transition Moment Integral

$$< M_x >= \int \psi_e^{gs} \mu_x \psi_e^{es} d\tau$$

$$< M_y >= \int \psi_e^{gs} \mu_y \psi_e^{es} d\tau$$

$$< M_z >= \int \psi_e^{gs} \mu_z \psi_e^{es} d\tau$$

- **Probability of any transition is proportional to M_i^2**
- **Allowed transition $M_i \neq 0$**
- **Forbidden transition $M_i = 0$**

Transition Moment Integral

$$\psi_e = \psi_o \psi_s$$

$$< M_i > = \int \psi_o^{gs} \mu_i \psi_o^{es} \, d\tau \int \psi_s^{gs} \psi_s^{es} \, d\tau$$

- For any allowed electronic transition, the M_i value should be non-zero.
- so either first integral or second one should be zero if M_i is zero.
- The dipole moment operator deals with the displacement of atoms and associated dipole moment changes, so the spin part can be isolated.

Odds and evens
Gerade or Ungerade

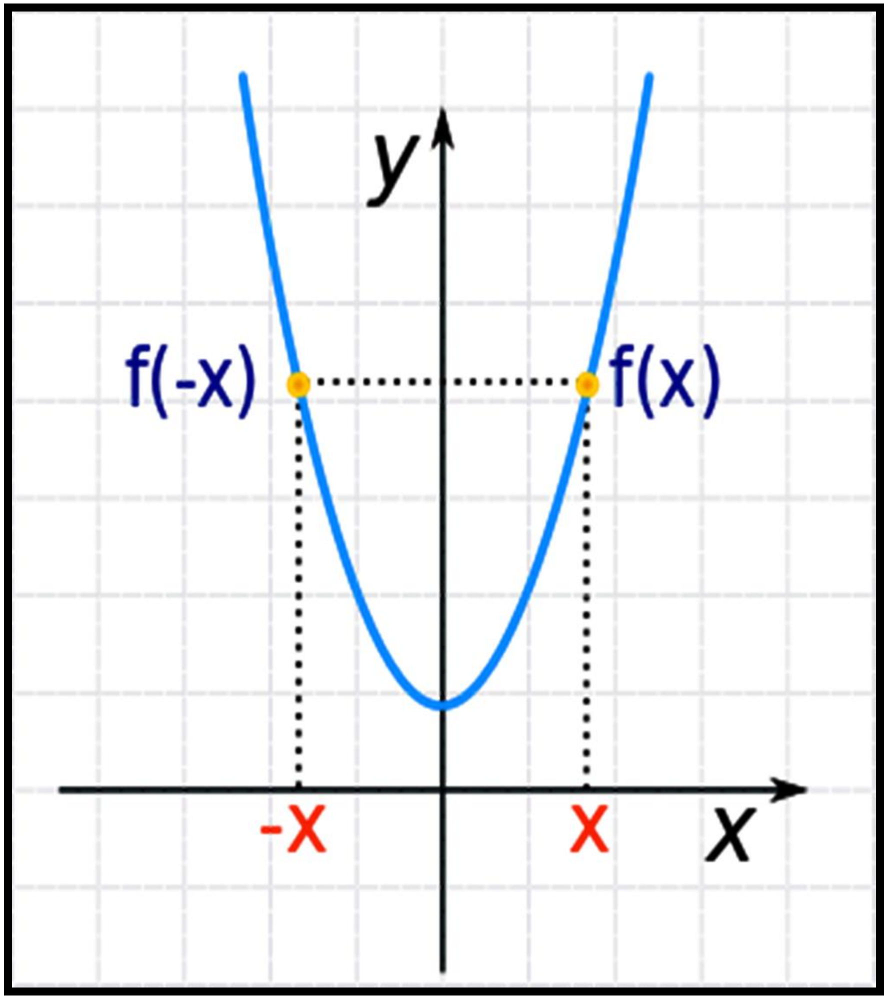
$$\int_{-1}^{+1} x^2 dx = \left[\frac{x^3}{3}\right]_{-1}^{+1} = \left[\frac{(+1)^3}{3} - \frac{(-1)^3}{3}\right] = \left[\frac{1}{3} - \left(\frac{-1}{3}\right)\right] = \frac{2}{3}$$

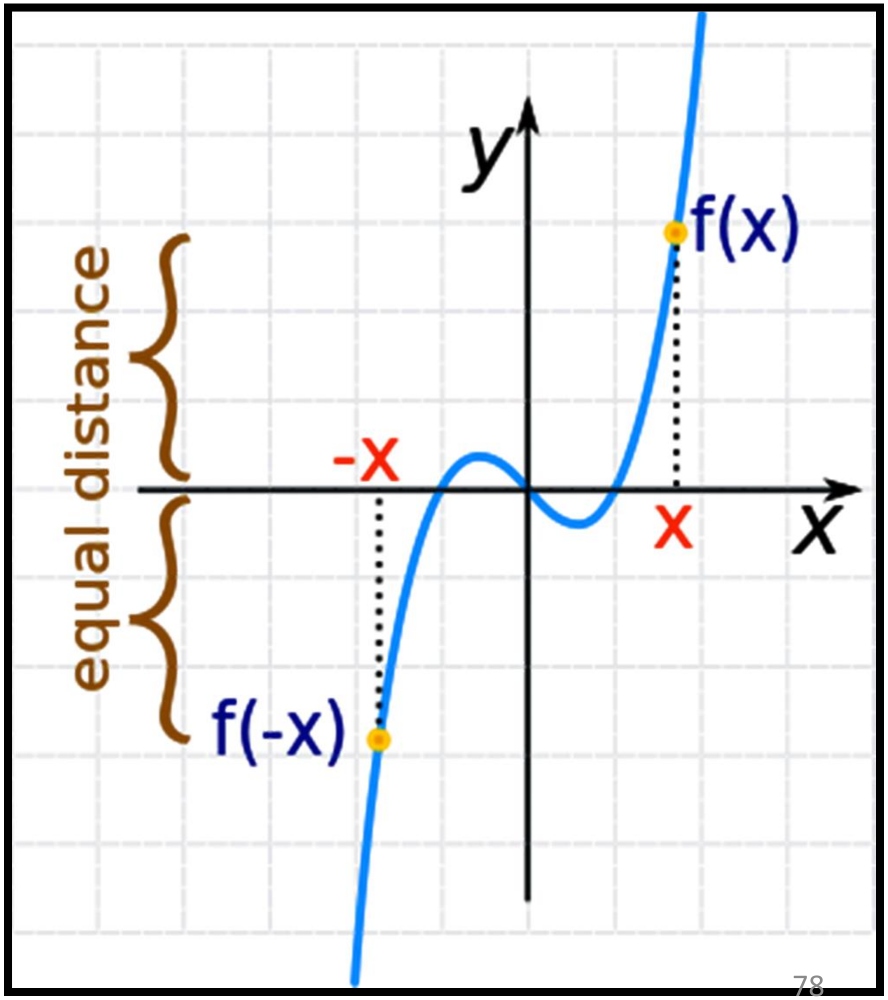
$$\int_{-1}^{+1} x^3 dx = \left[\frac{x^4}{4}\right]_{-1}^{+1} = \left[\frac{(+1)^4}{4} - \frac{(-1)^4}{4}\right] = 0$$

$$f(x) = f(-x)$$

$$f(x) \neq f(-x)$$

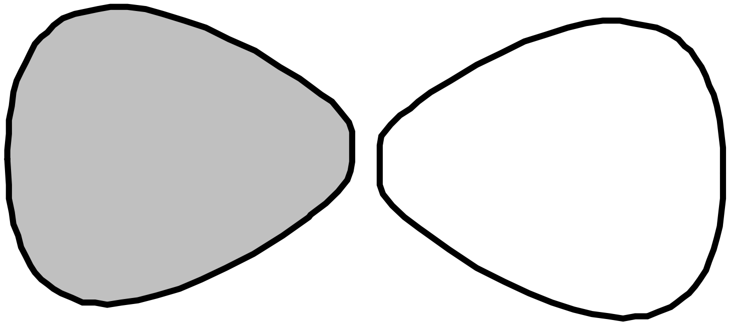
$$f(-x) = -f(x)$$



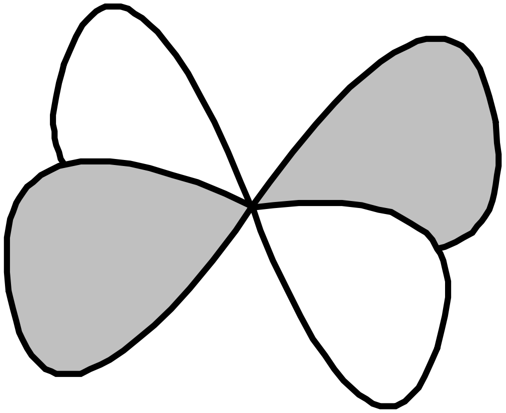


f_1	operator	f_2	Product	$\int_{-\infty}^{+\infty} (productfunction)dx$
x^5	x^3	x^5	x^{13}	Zero
x^5	x^3	x^2	x^{10}	Non-zero
x^2	x^3	x^5	x^{10}	Non-zero
x^2	x^3	x^2	x^7	Zero

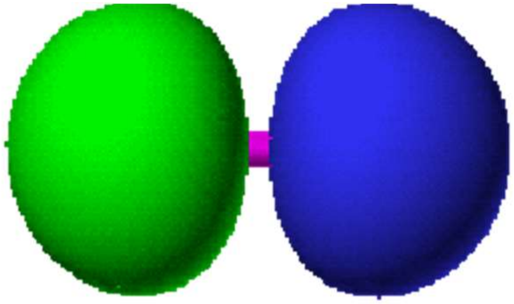
ψ_e^{gs}	μ	ψ_e^{es}	Product	Mi
Odd	Odd	Odd	Odd	Zero
Odd	Odd	Even	Even	Non-zero
Even	Odd	Odd	Odd	Non-zero
Even	Odd	Even	Odd	Zero



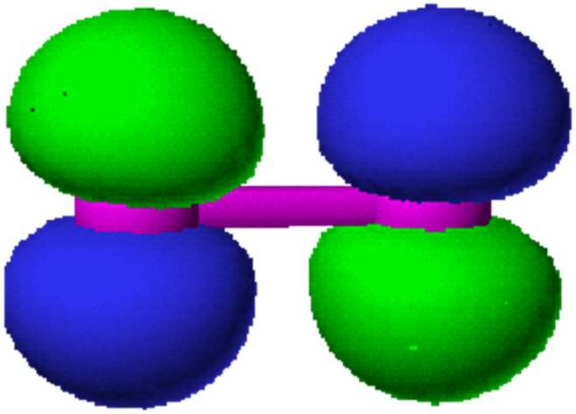
p_x-orbital Ungerade (u)



d_{xy}- orbital -gerade(g)



σ_u molecular orbital



The Laporte Selection Rule

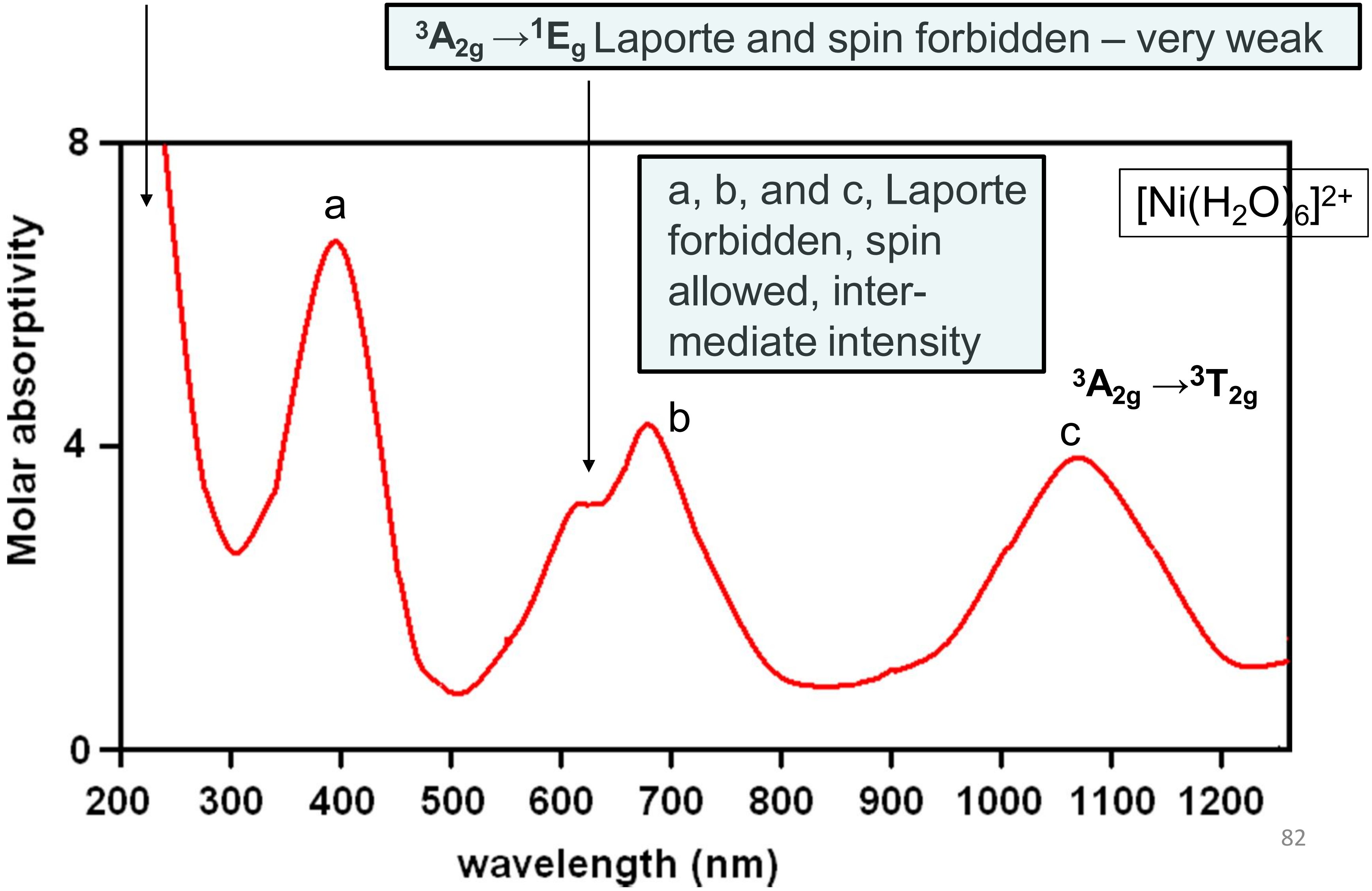
- All transitions within the d-shell, such as $^3A_{2g} \rightarrow {}^3T_{2g}$ are Laporte forbidden, because they are g→g.
- The intensity of the d-d transitions that give d-block metal ions their colors are not very intense.
- Charge transfer bands frequently involve p→d or d→p transitions, and so are Laporte-allowed and therefore very intense.

.

The Selection rules for electronic transitions

Charge-transfer band – Laporte and spin allowed – very intense

$^3A_{2g} \rightarrow {}^1E_g$ Laporte and spin forbidden – very weak



a, b, and c, Laporte forbidden, spin allowed, inter-mediate intensity

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

$^3A_{2g} \rightarrow {}^3T_{2g}$

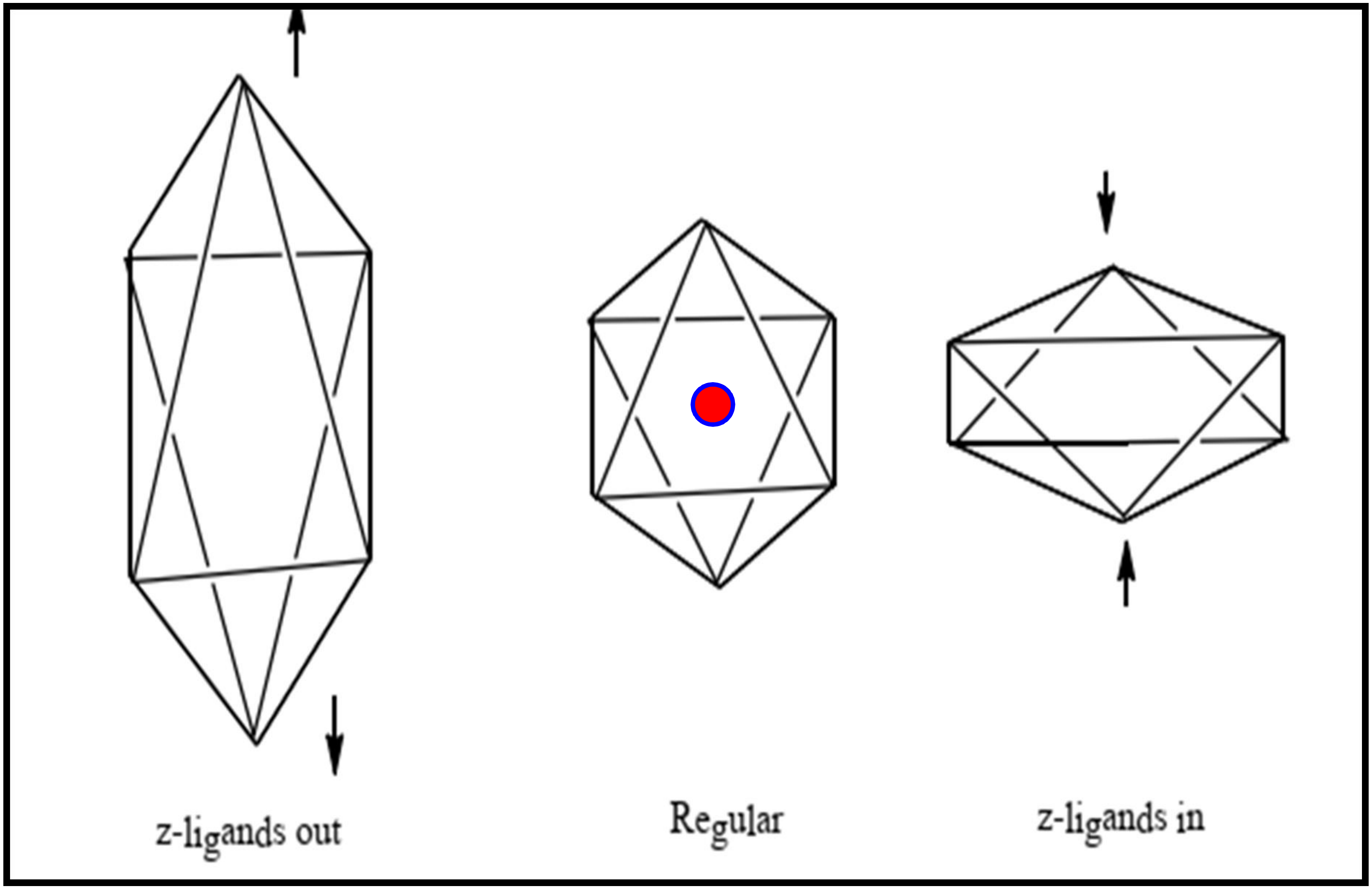
Why the‘forbidden’ transitions occur?

The orbital selection rule or the Laporte selection rule may be relaxed by any one of the following

- ***Departure from cubic symmetry***
- ***d-p mixing***
- ***Vibronic coupling***

Departure from cubic symmetry

- **The orbital selection rule is strictly followed only in perfect cubic symmetries (O_h and cubic)**
- **If the symmetry is lowered, i.e. centre of symmetry is removed either permanently or temporarily, then d-d transitions may become allowed.**
- **T_d complexes are having more intense colors, since the transitions are allowed due to the absence of center of symmetry.**
- **This mechanism may not greatly relax the selection rule, but an useful pathway for transition.**


z-ligands out
Regular
z-ligands in

Mixing of states

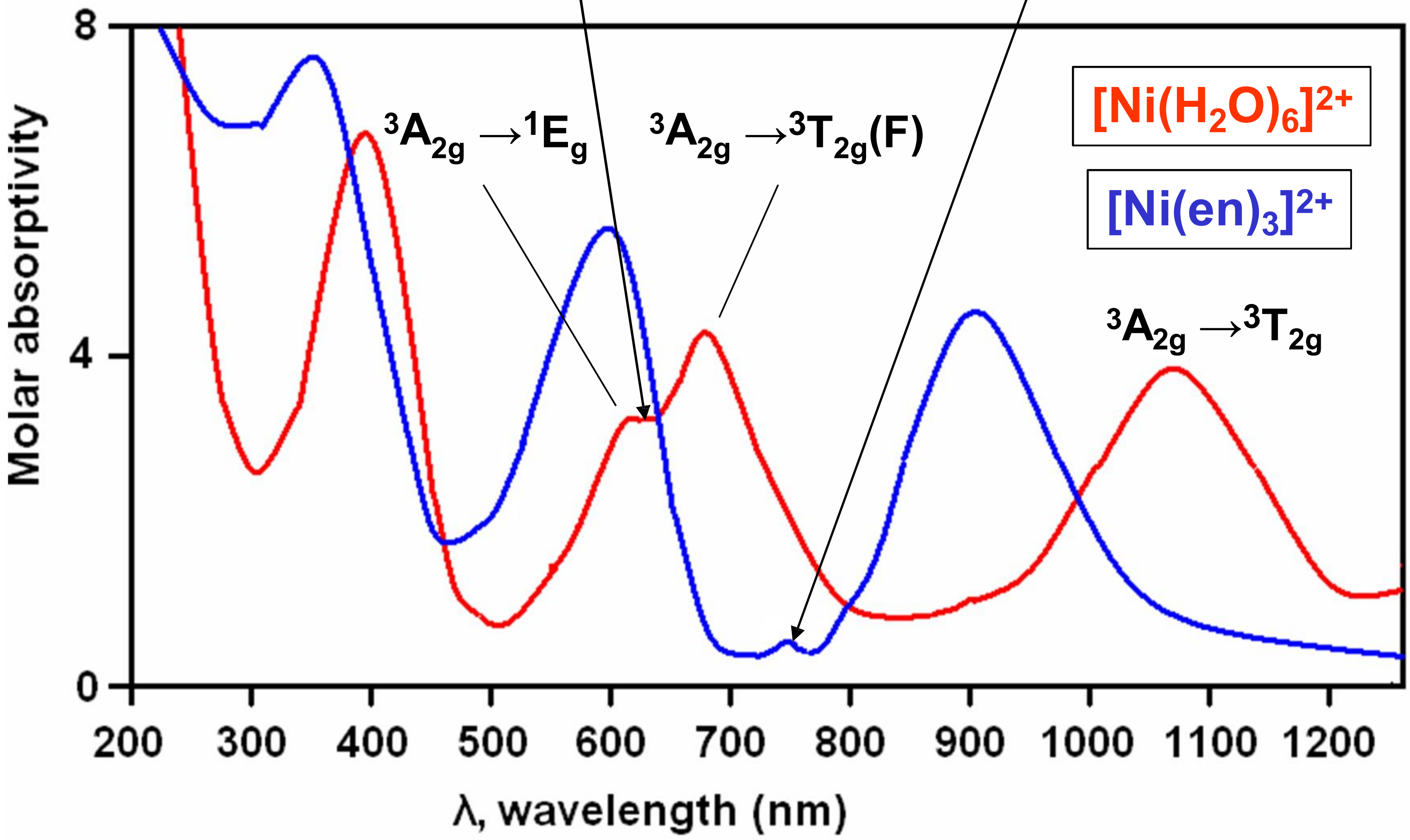
- ***The states in a complex are never pure.***
- ***When two states are energetically too close they may be mixed by thermal vibrations itself.***
- ***Some of the symmetry properties of neighboring states become mixed.***
- ***This makes the transitions partially allowed which are normally forbidden.***

Mixing of states: Comparison of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$:

The spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ is close to the spin-allowed $^3A_{2g} \rightarrow {}^3T_{2g}$(F) and ‘borrows’ intensity by mixing of states

Note: The two spectra are drawn on the same graph for ease of comparison.

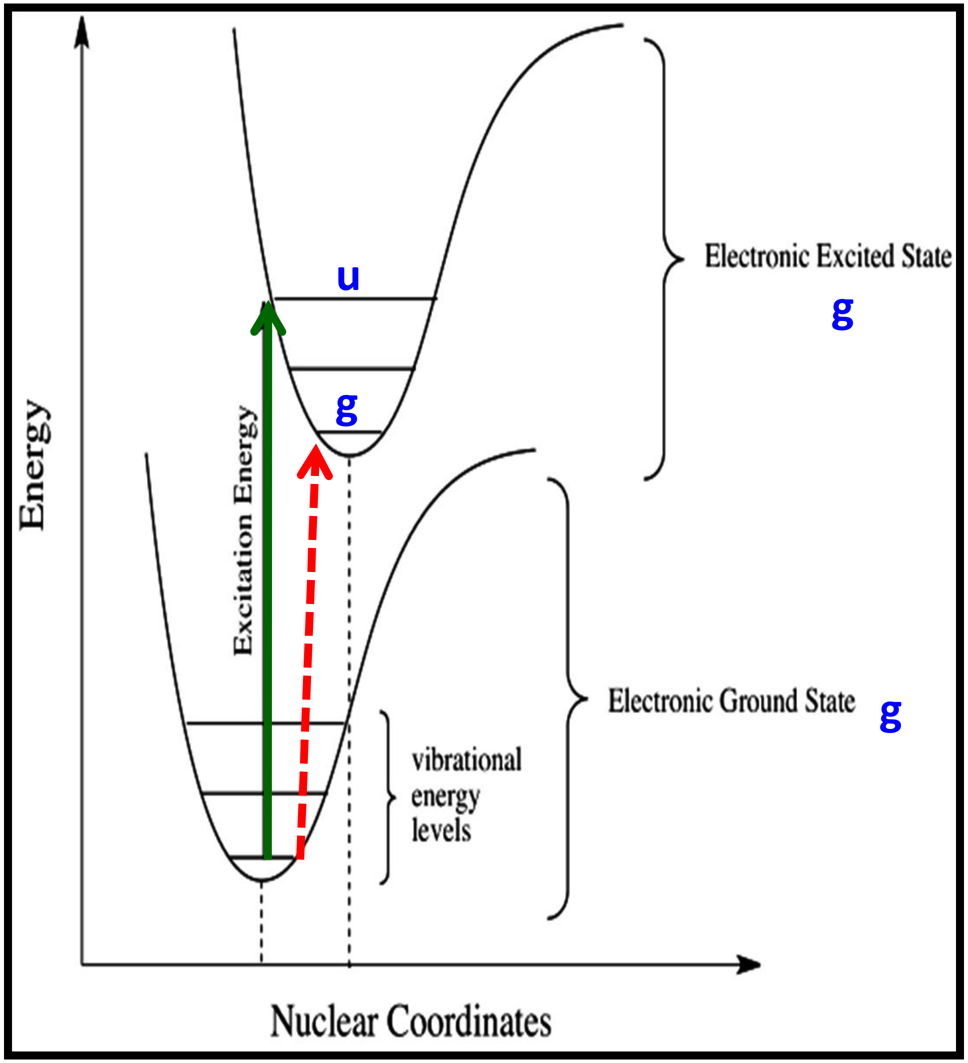
The spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ is not close to any spin allowed band and is very weak



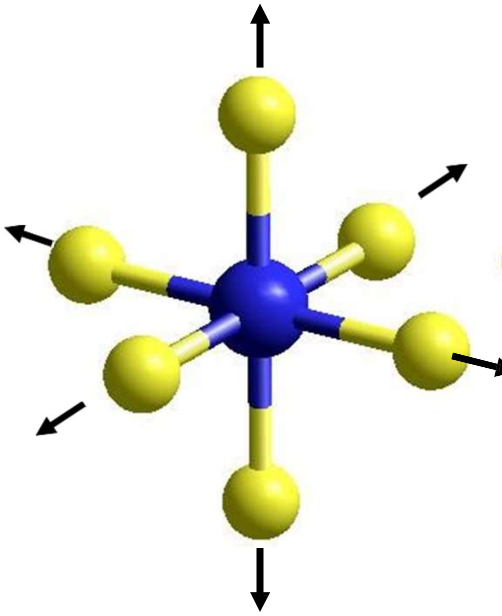
- Electronic transitions are always very broad because they are coupled to vibrations.
- The transitions are thus from ground states plus several vibrational states to excited states plus several vibrational states.
- so the ‘electronic’ band is actually a composite of electronic plus vibrational transitions

Vibronic Coupling

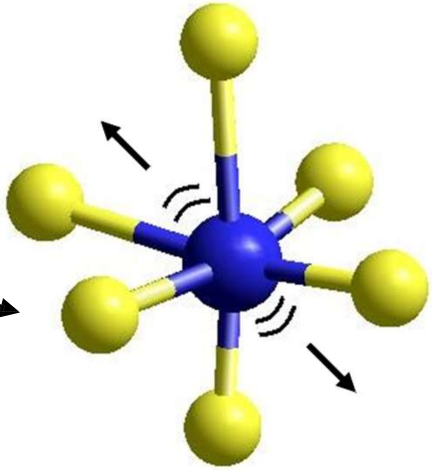
- **The vibrational states may be of opposite parity to the electronic states, and so help overcome the Laporte selection rule**.



Symmetry of vibrational states, and their coupling to electronic states:

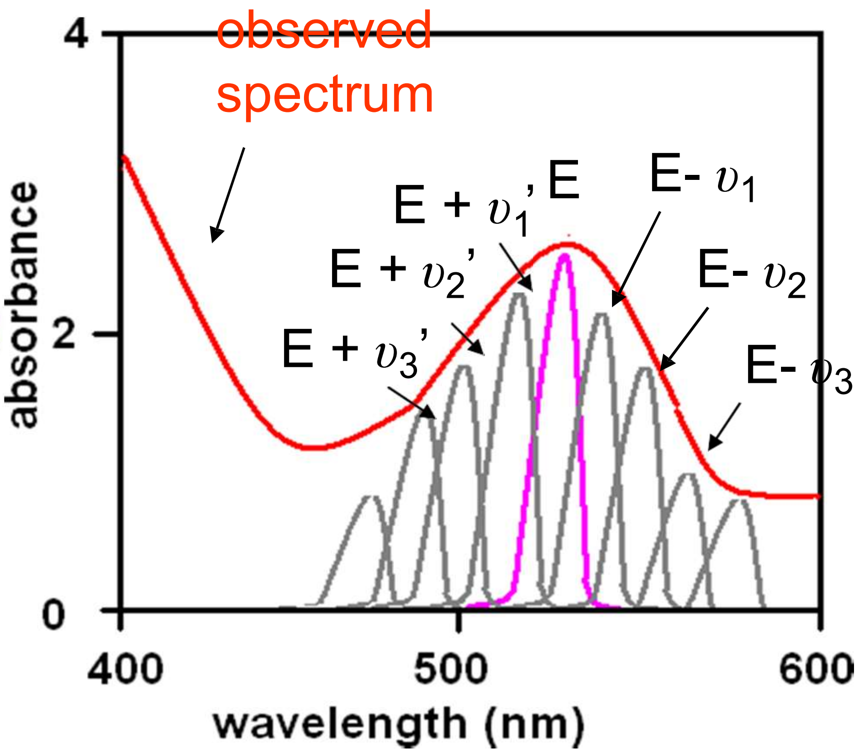


A_{1g}
symmetry
vibration



T_{1u}
symmetry
vibration

(symbols have same meaning for vibrations: A = non-degenerate, T = triply degenerate, g = gerade, u = ungerade, etc.)

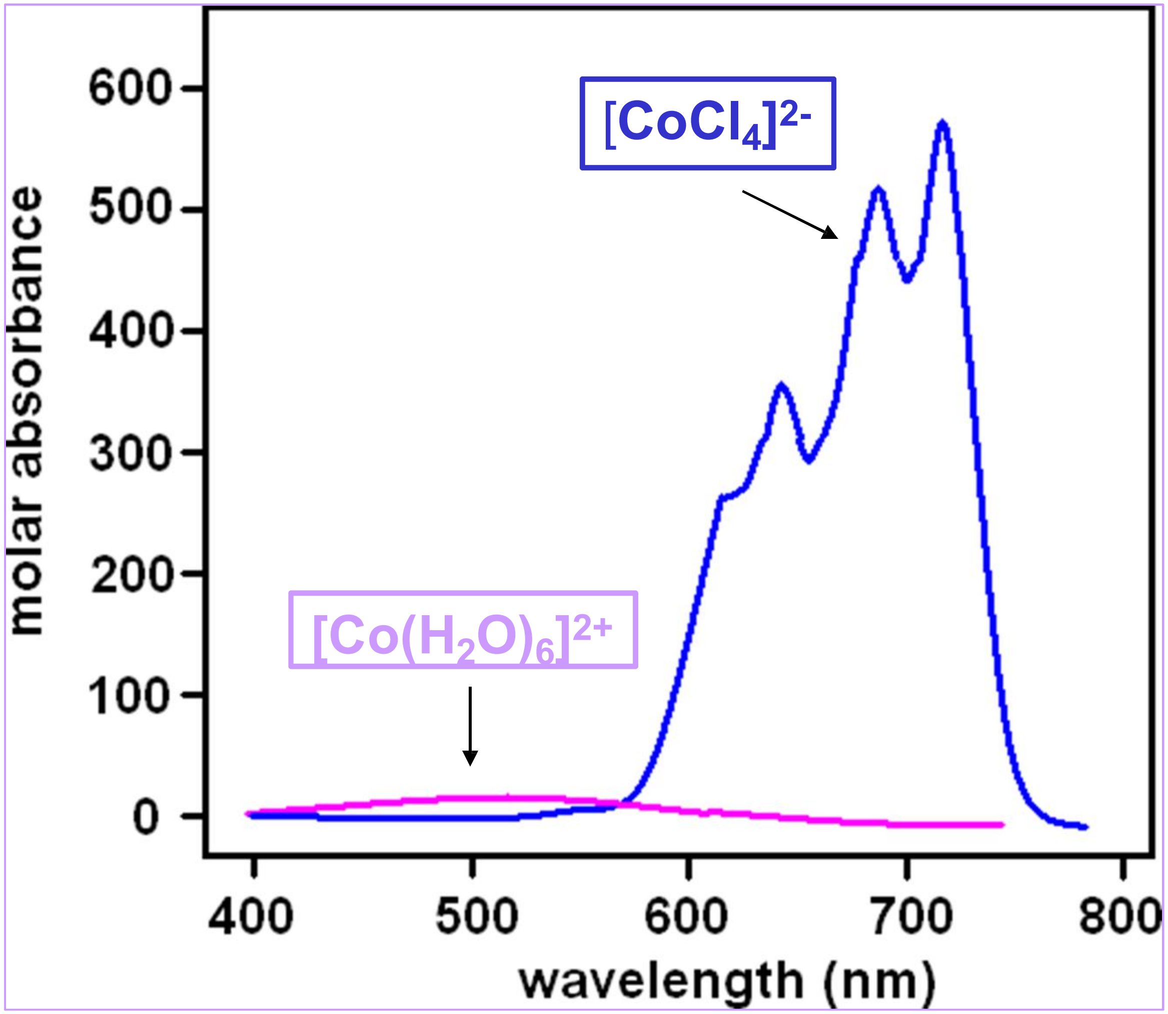


The band one sees in the UV-visible spectrum is the sum of bands due to transitions to coupled electronic (E) and vibrational energy levels (υ_1, υ_2, υ_3)

T_d vs O_h

- **A tetrahedron has no center of symmetry, and so orbitals in such symmetry cannot be *gerade*. Hence the d-levels in a tetrahedral complex are e and t_2.**
- **This largely overcomes the Laporte selection rules, so that tetrahedral complexes tend to be very intense in color.**
- **Dissolving $CoCl_2$ in water produces a pale pink solution of $[Co(H_2O)_6]^{2+}$, but in alcohol forms, which is a tetrahedral $[CoCl_4]^{2-}$ having very intense blue color.**

$[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$



The spectra at left show the very intense d-d bands in the blue tetrahedral complex $[CoCl_4]^{2-}$, as compared with the much weaker band in the pink octahedral complex $[Co(H_2O)_6]^{2+}$. This difference arises because the T_d complex has no center of symmetry, helping to overcome the $g \not\to g$ Laporte selection rule.

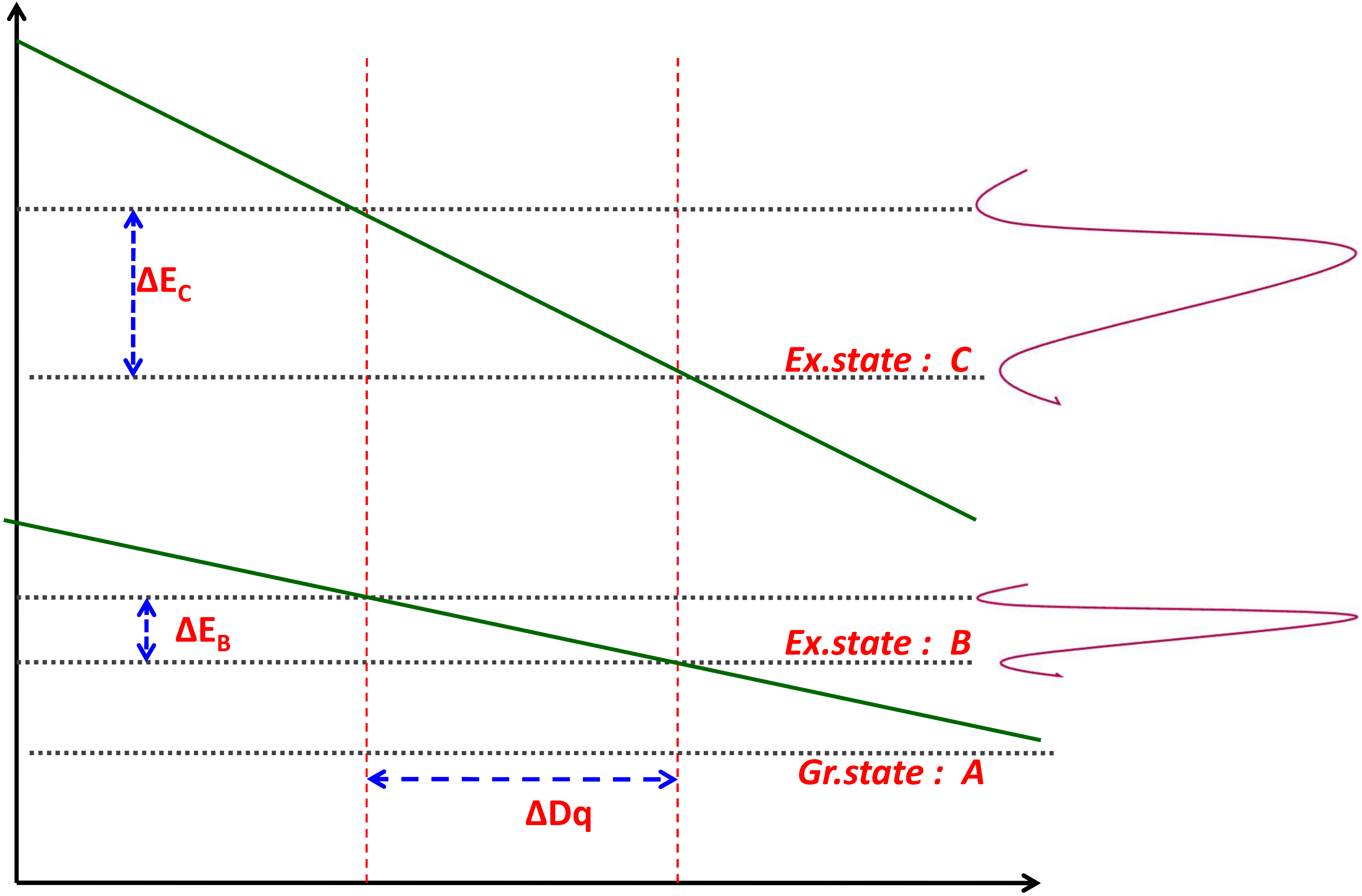
Shape of Electronic bands

- **Variation of 10Dq**
- **Lower symmetry components**
- **Vibrational structure & F.C Principle**
- **Jahn-Teller distortion**
- **Spin-Orbit coupling**

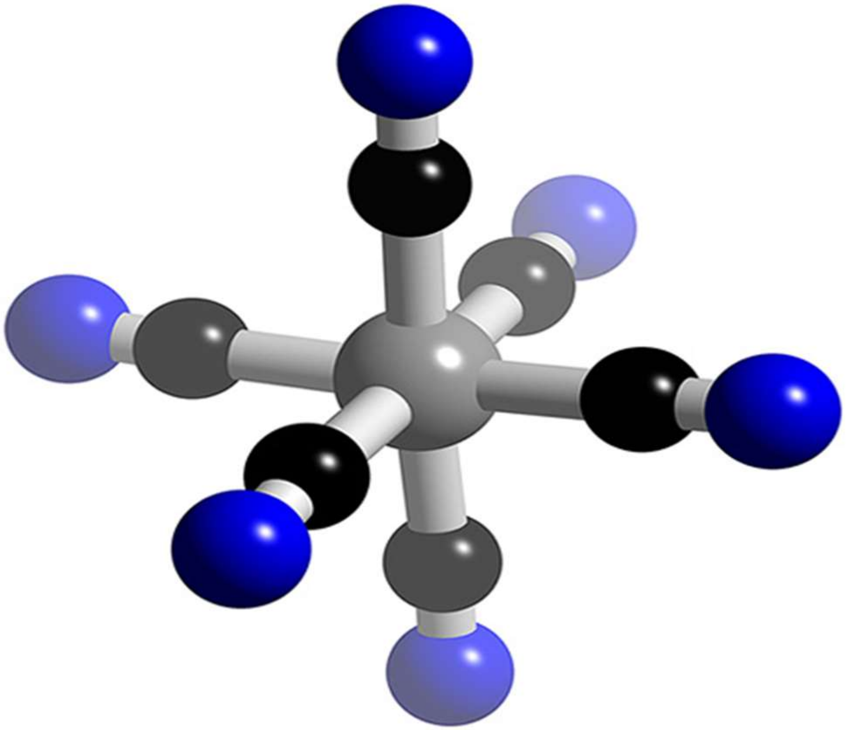
Variation of 10Dq

- **The Dq value is very sensitive to the M-L bond distance.**
- **When the complex molecule vibrates M-L bond length continuously changes, and hence the Dq.**
- **Since transition energy is a function of Dq, the transition occurs over a range of energy, i.e the line broadens.**

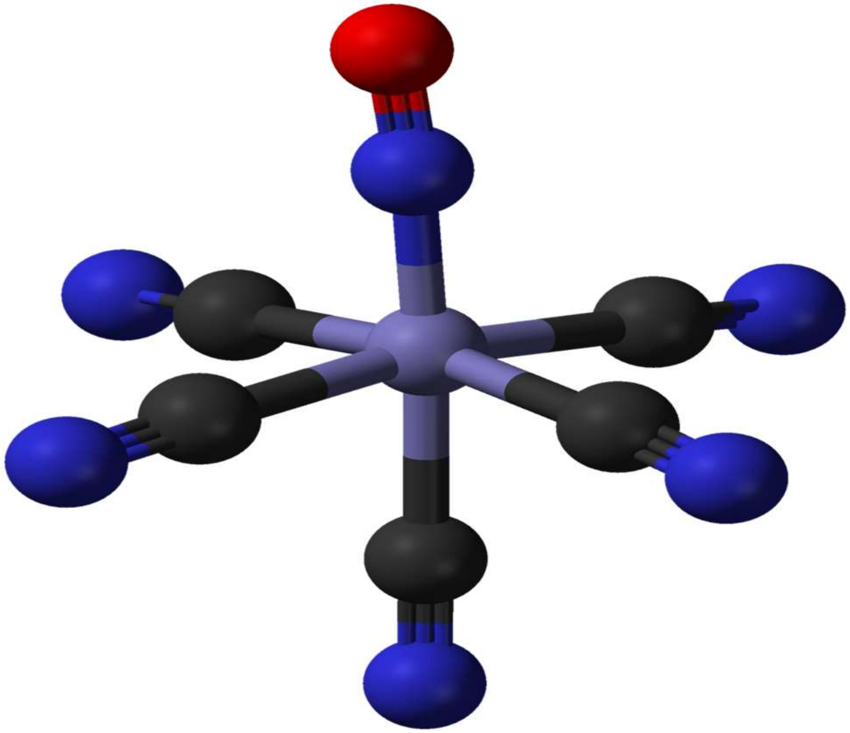
Variation of 10Dq



Lower symmetry components



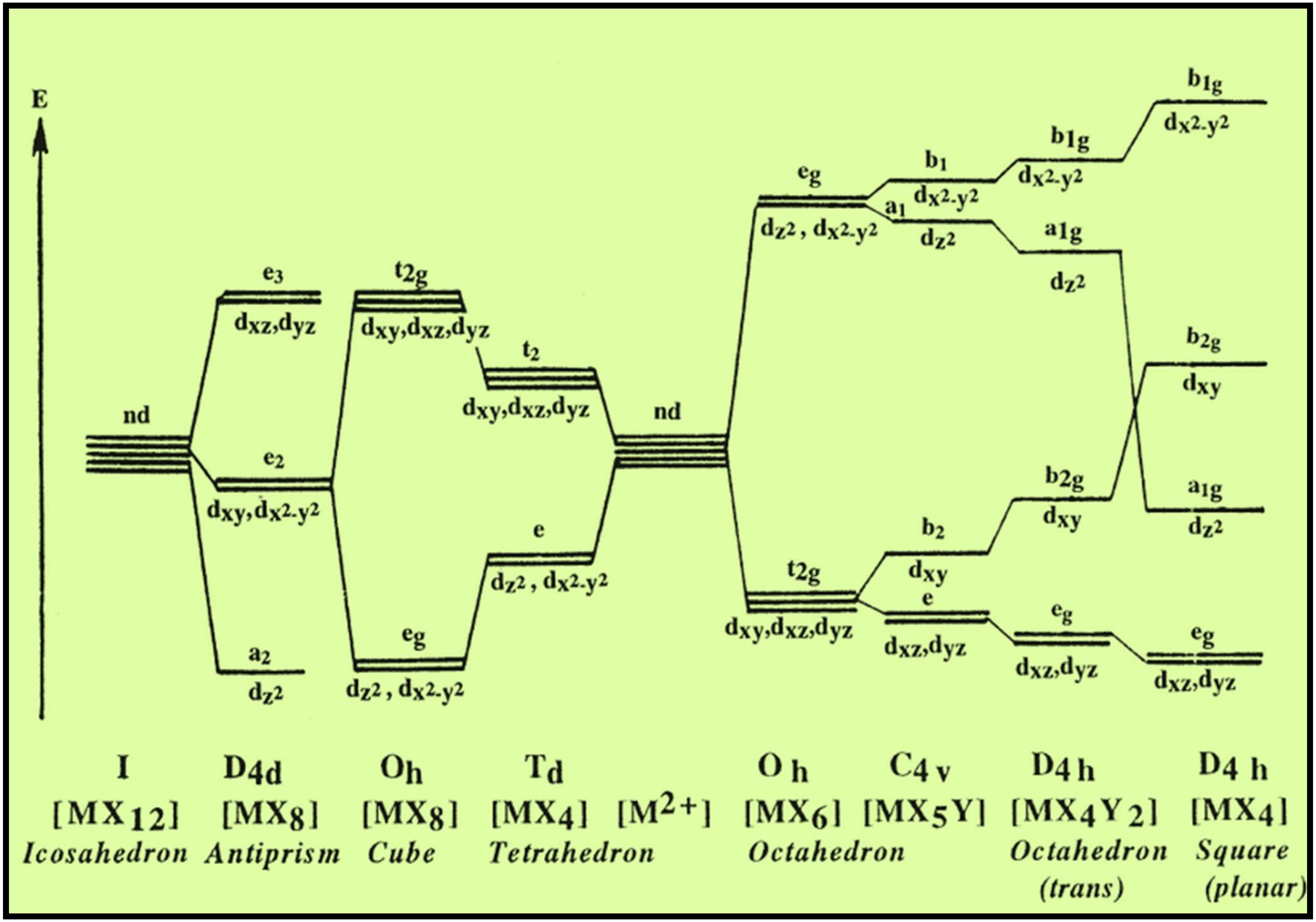
Perfect O_h



Pseudo O_h

Lower symmetry components

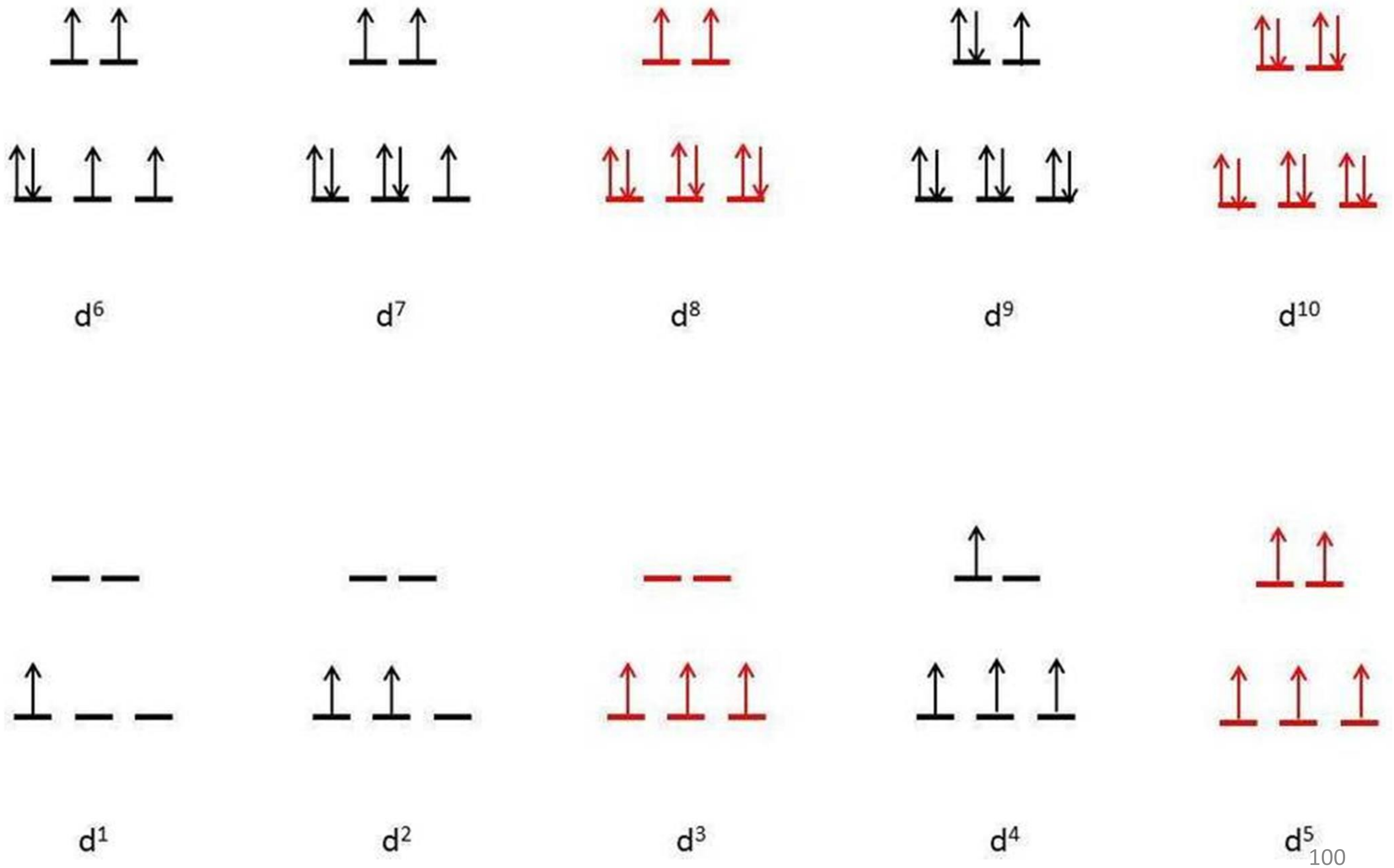
- **Selection rules strictly obeyed in perfect cubic symmetry.**
- **When the ligands are substituted, there is an effective O_h symmetry but not true O_h**
- **This may resolve the electronic states, if the energy gap is more two distinct peaks will appear.**
- **In the case of lesser energy difference broad peaks due to overlap of two lines, may appear.**


E
nd
e3
dxz,dyz
e2
dxy,dx2-y2
a2
dz2
t2g
dxy,dxz,dyz
eg
dz2 , dx2-y2
t2
dxy,dxz,dyz
e
dz2 , dx2-y2
nd
eg
dz2 , dx2-y2
t2g
dxy,dxz,dyz
b1
dx2-y2
a1
dz2
b2
dxy
e
dxz,dyz
b1g
dx2-y2
a1g
dz2
b2g
dxy
eg
dxz,dyz
b1g
dx2-y2
b2g
dxy
a1g
dz2
eg
dxz,dyz
I
[MX12]
Icosahedron
D4d
[MX8]
Antiprism
Oh
[MX8]
Cube
Td
[MX4]
Tetrahedron
[M2+]
Oh
[MX6]
Octahedron
C4v
[MX5Y]
D4h
[MX4Y2]
Octahedron
(trans)
D4h
[MX4]
Square
(planar)

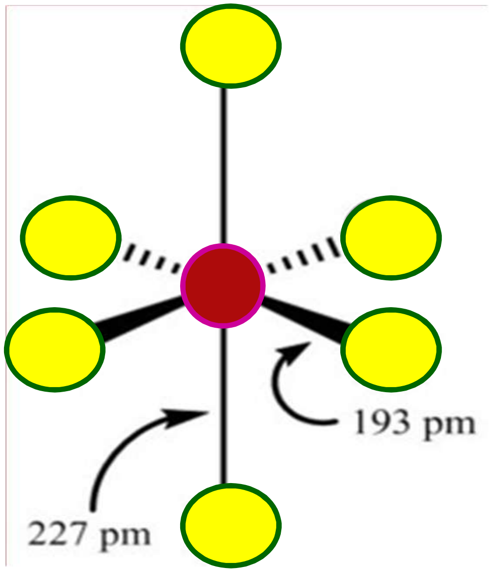
Jahn -Teller distortion

- **In 1937, Hermann Jahn and Edward Teller postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," in regards to its electronic state.**
- **This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry.**
- **“Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy."**

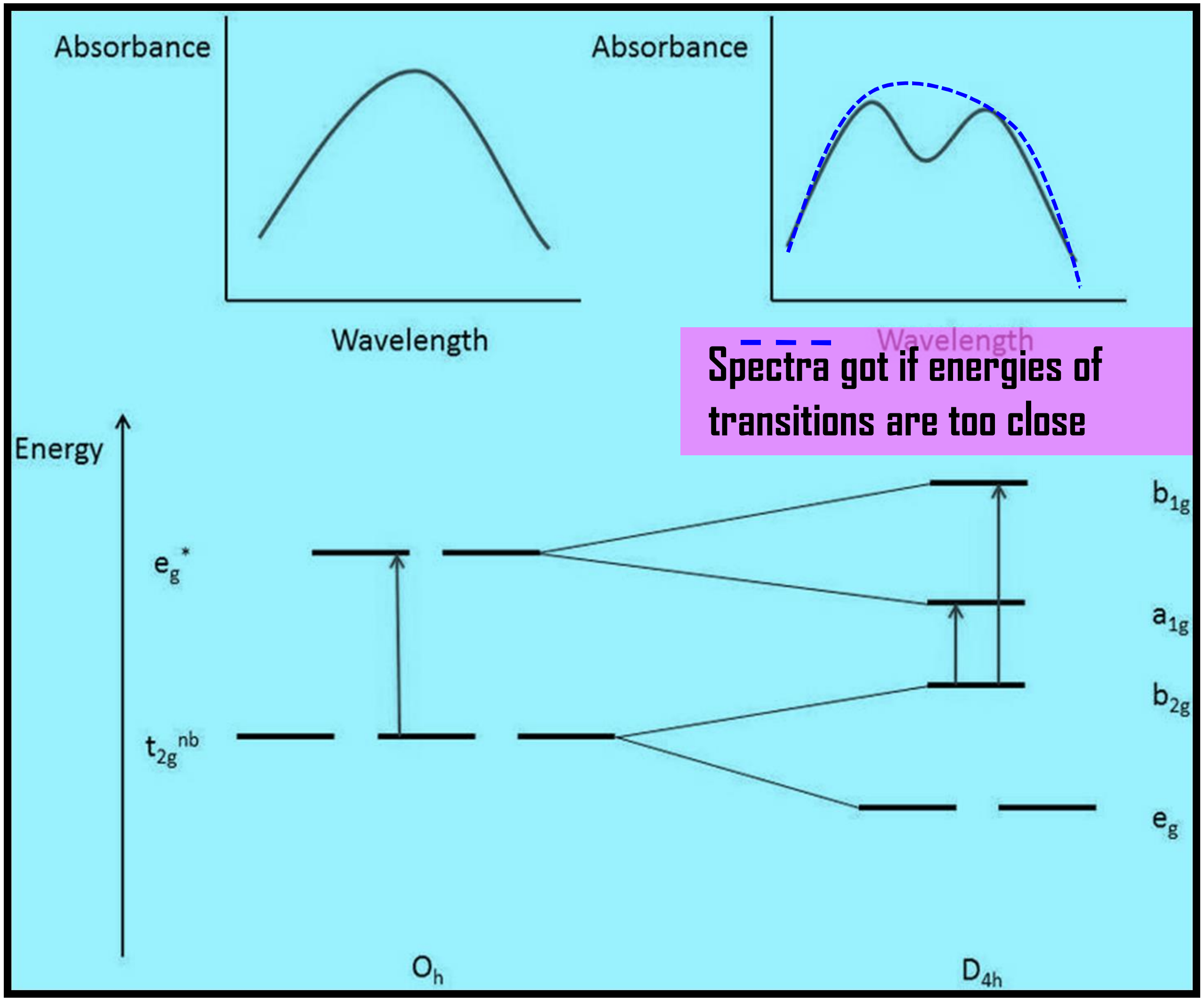
Jahn-Teller distortion



Jahn -Teller distortion



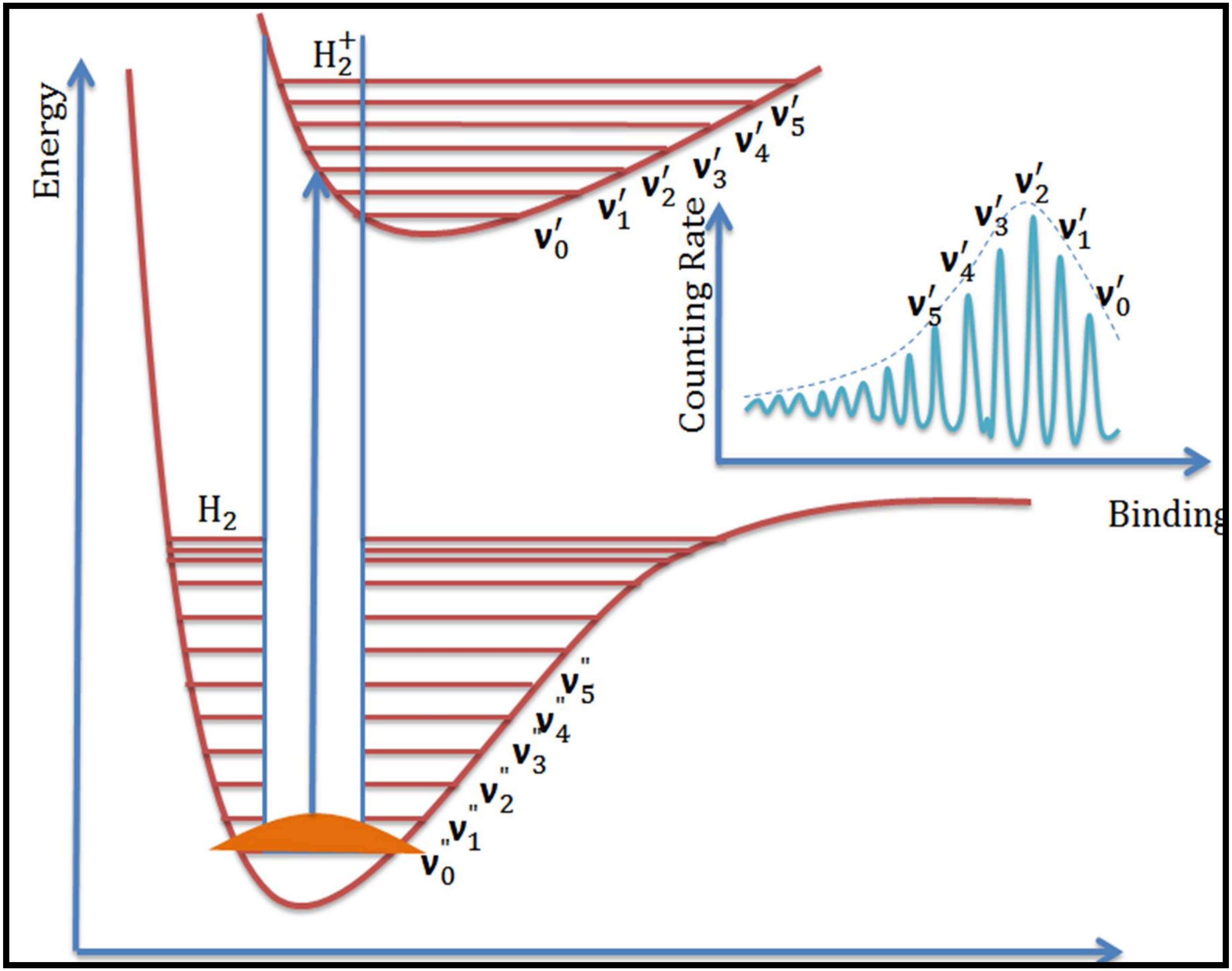
$[CuF_6]^{4-}$



- - - Spectra got if energies of transitions are too close

Vibrational structure
&
Franck-Condon principle

- During an electronic transition, many vibrational transitions may also be simultaneously activated.
- This lead to many closely packed vibrational peak to appear, which make a broad band.
- Under normal temperature many vibartional levels are populated, hence vibartional coarse structure is very common in electronic spectra


Energy
H_2^+
v'_0
v'_1
v'_2
v'_3
v'_4
v'_5
Counting Rate
v'_5
v'_4
v'_3
v'_2
v'_1
v'_0
Binding
H_2
v''_5
v''_4
v''_3
v''_2
v''_1
v''_0

Spin-Orbit coupling

- **Generally spin-orbit coupling is considered as a small perturbation when compared to crystal field. (at least for 3d series).**
- **But n higher elements, the L-S coupling may be stronger, which mix the levels of different spins.**
- **Now S is not a valid quantum number, and many spin-forbidden bands appear leading to broader absorptions.**

Charge-Transfer Bands

- Charge-transfer band arise from the movement of electrons between orbitals that are predominantly ligand in character and orbitals that are predominantly metal in character.

- These transitions are identified by their high intensity and the sensitivity of their energies to solvent polarity.

- Absorption for charge transfer transition is more intense than d–d transitions.

($\mathcal{E}_{d\text{-}d}$=20 L mol^{-1} cm^{-1} or less, $\mathcal{E}_{charge\text{-}transfer}$ =50,000 L mol^{-1} cm^{-1} or greater)

Charge-Transfer transition is classified into:

- Ligand-to-Metal Charge-Transfer transition. ***(LMCT transition)***

If the migration of the electron is from the ligand to the metal.

- Metal-to-Ligand Charge-Transfer transition. ***(MLCT transition)***

If the migration of the electron is from the metal to the ligand .

- *Ligands possess σ, σ*, π, π*, and nonbonding (n) molecular orbitals.*
- *If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals.*
- *LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions.*

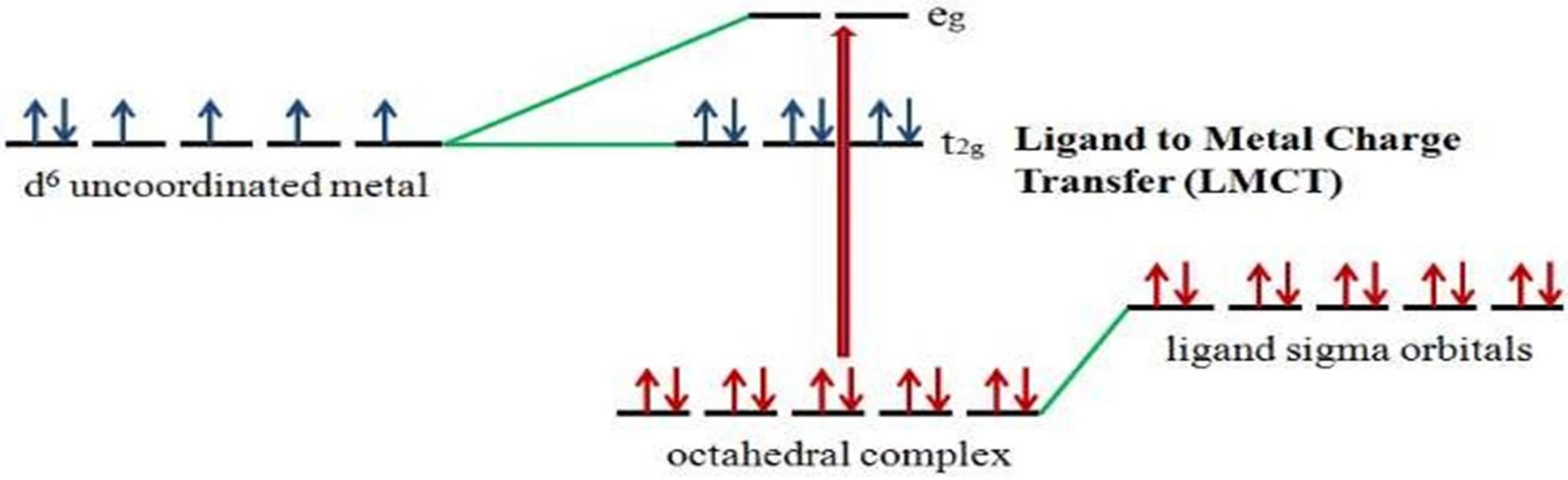


Figure 3. Ligand to Metal Charge Transfer (LMCT) involving an octahedral d^6 complex. (Inspired by reference 3)

MLCT

- ***If the metal is in a low oxidation state (electron rich) and the ligand possesses low-lying empty orbitals (e.g., CO or CN −).***
- ***LMCT transitions are common for coordination compounds having π-acceptor ligands.***
- ***Upon the absorption of light, electrons in the metal orbitals are excited to the ligand π* orbitals.***
- ***MLCT transitions result in intense bands. Forbidden d – d transitions may also occur.***
- ***This transition results in the oxidation of the metal.***

Metal-to-Ligand Charge-Transfer *transition.*

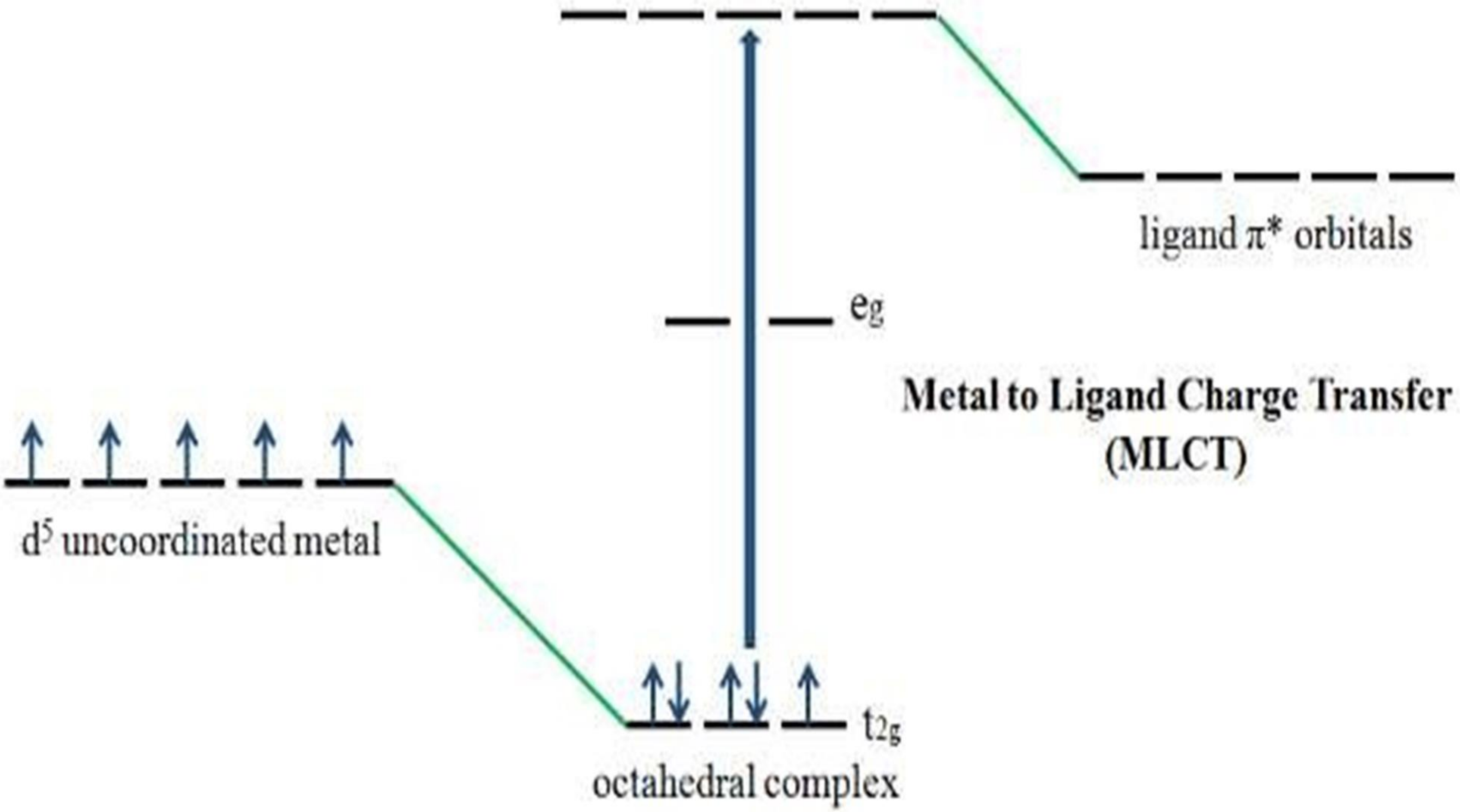
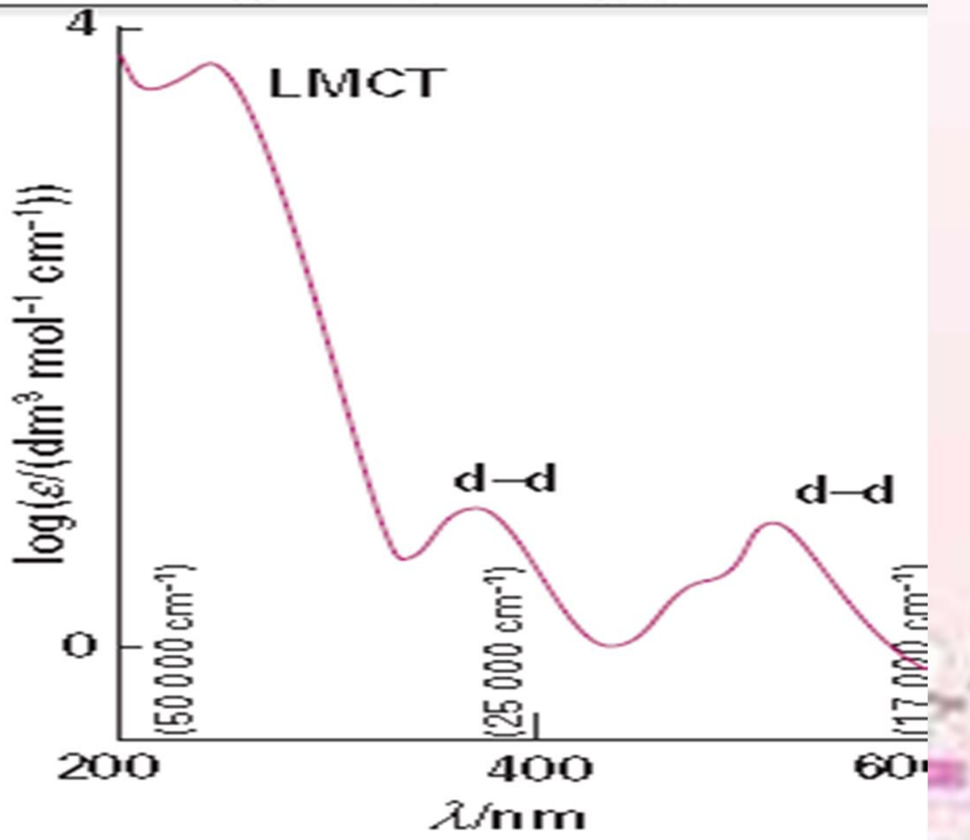


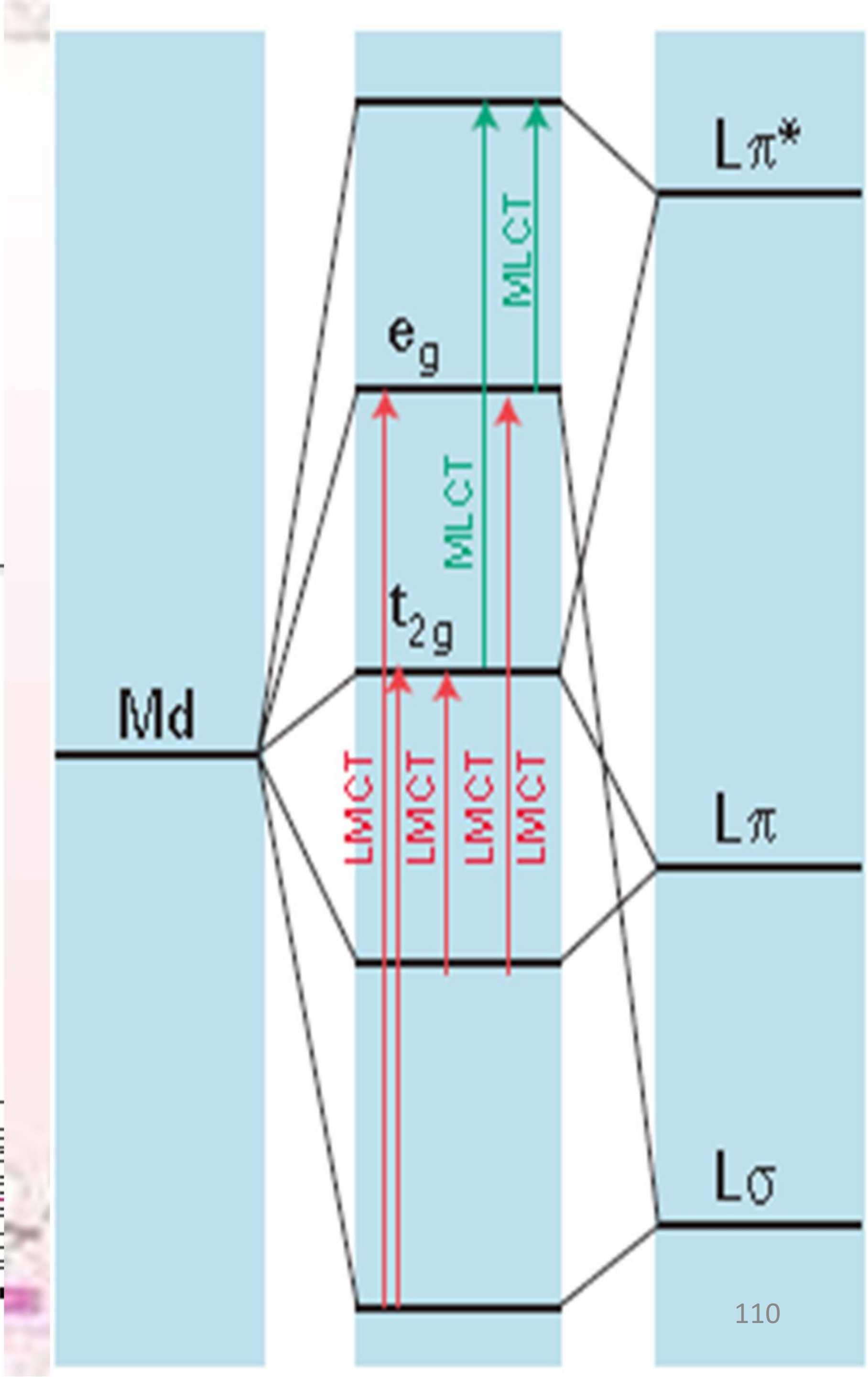
Figure 4. Metal to Ligand Charge Transfer (MLCT) involving an octahedral d^5 complex. (Inspired by reference 3)

NH$_3$
Cr
Cl
2+

5 $[CrCl(NH_3)_5]^{2+}$



4
0
LMCT
d–d
d–d
log(ε/(dm^3 mol^{-1} cm^{-1}))
(50 000 cm^{-1})
(25 000 cm^{-1})
(17 000 cm^{-1})
200
400
60
λ/nm



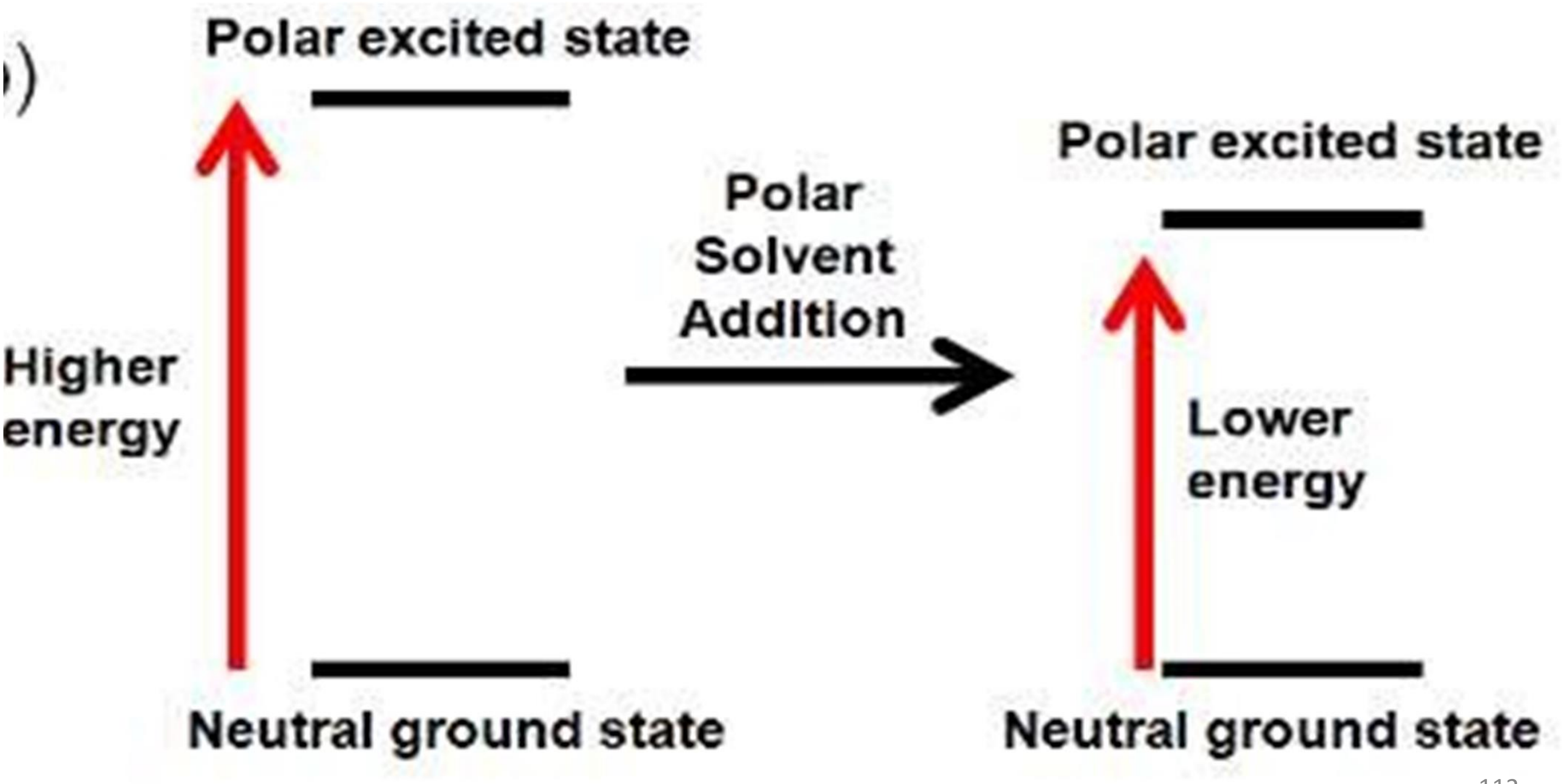
Md
e$_g$
t$_{2g}$
Lπ*
Lπ
Lσ
MLCT
MLCT
LMCT
LMCT
LMCT
LMCT

Effect of Solvent Polarity on CT Spectra

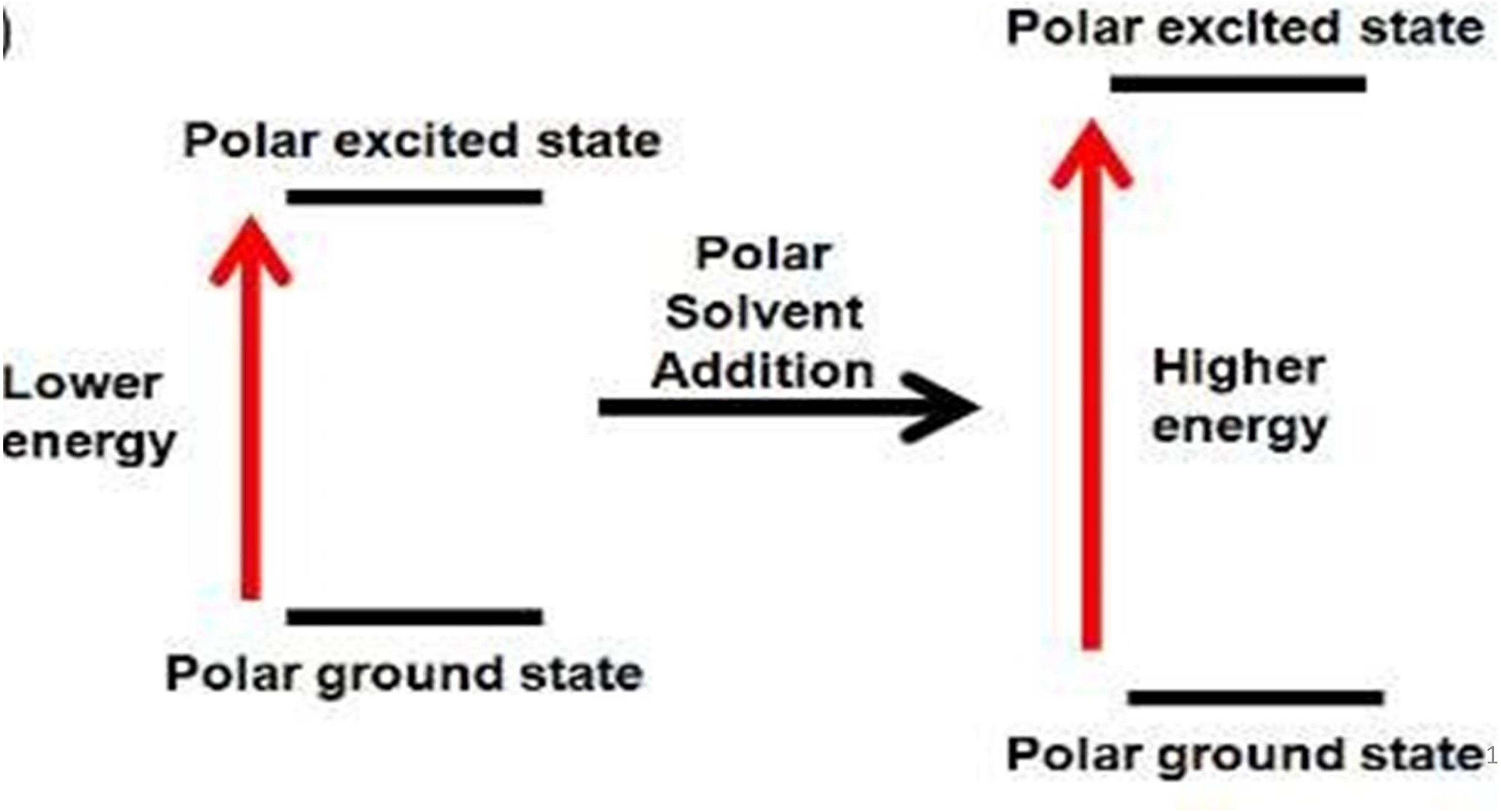
You are preparing a sample for a UV/Vis experiment and you decide to use a polar solvent. Is a shift in wavelength observed when:

- ✓ *Both the ground state and the excited state are neutral .*
- ✓ *The excited state is polar, but the ground state is neutral*
- ✓ *The ground state and excited state is polar*
- ✓ *The ground state is polar and the excited state is neutral*

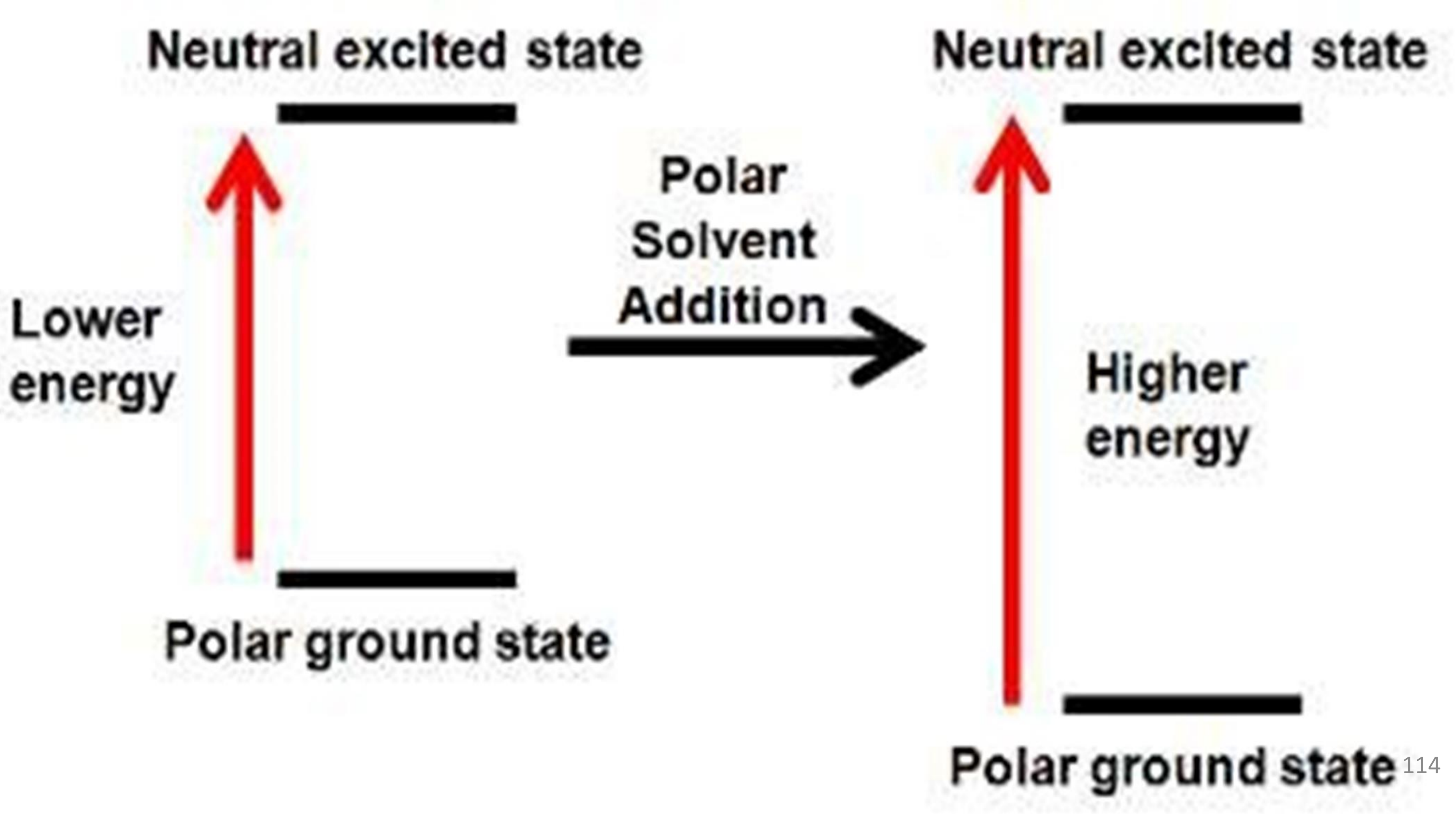
The excited state is polar, but the *ground state is neutral*



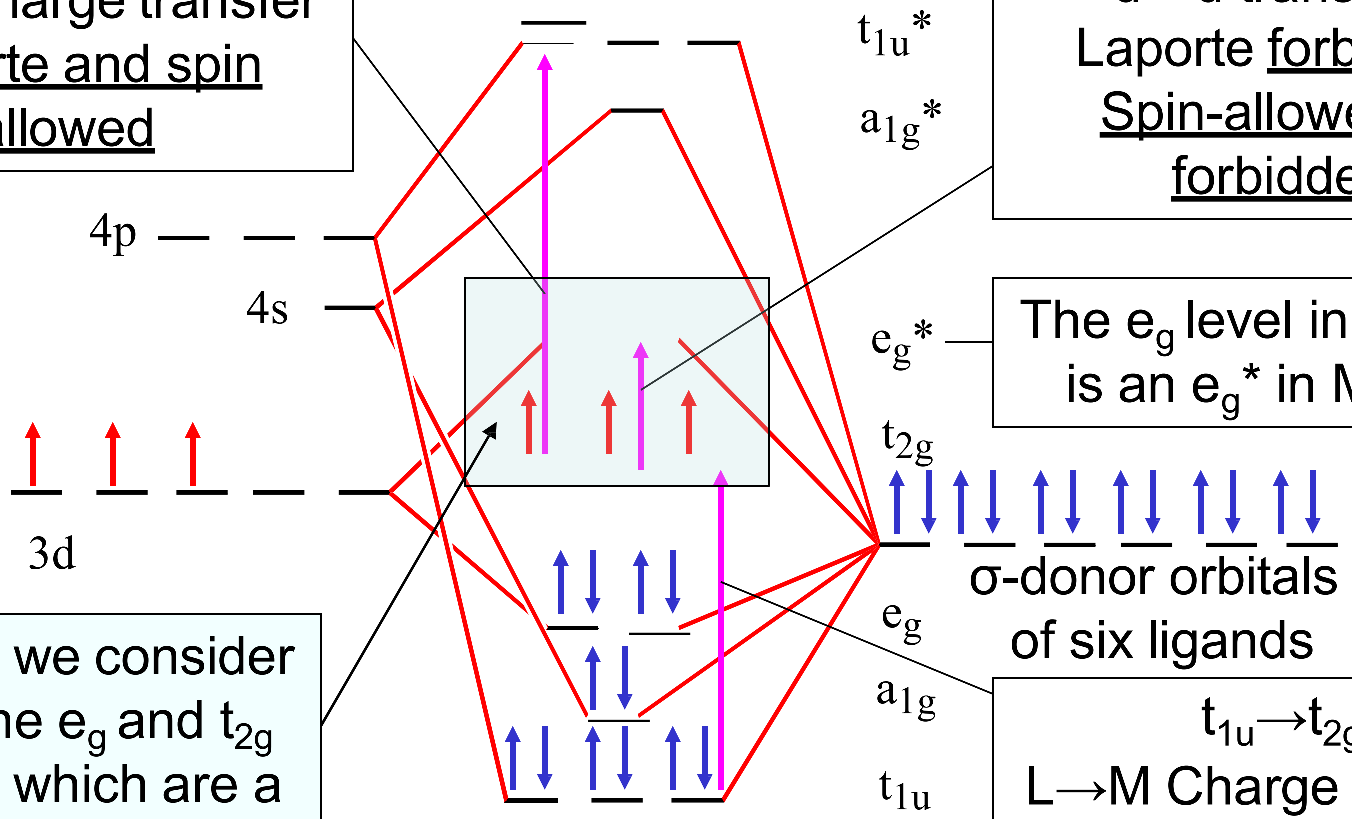
The ground state and excited state is *polar*



The ground state is polar and the *excited state is neutral*



The MO view of electronic transitions in an octahedral complex



$t_{2g} \rightarrow t_{1u}$*

M→L Charge transfer

Laporte and spin allowed

$t_{2g} \rightarrow e_g$

d→d transition

Laporte forbidden

Spin-allowed or forbidden

The e_g level in CFT is an e_g* in MO

In CFT we consider only the e_g and t_{2g} levels, which are a portion of the over-all MO diagram

$t_{1u} \rightarrow t_{2g}$

L→M Charge transfer

Laporte and spin allowed


Thank You!