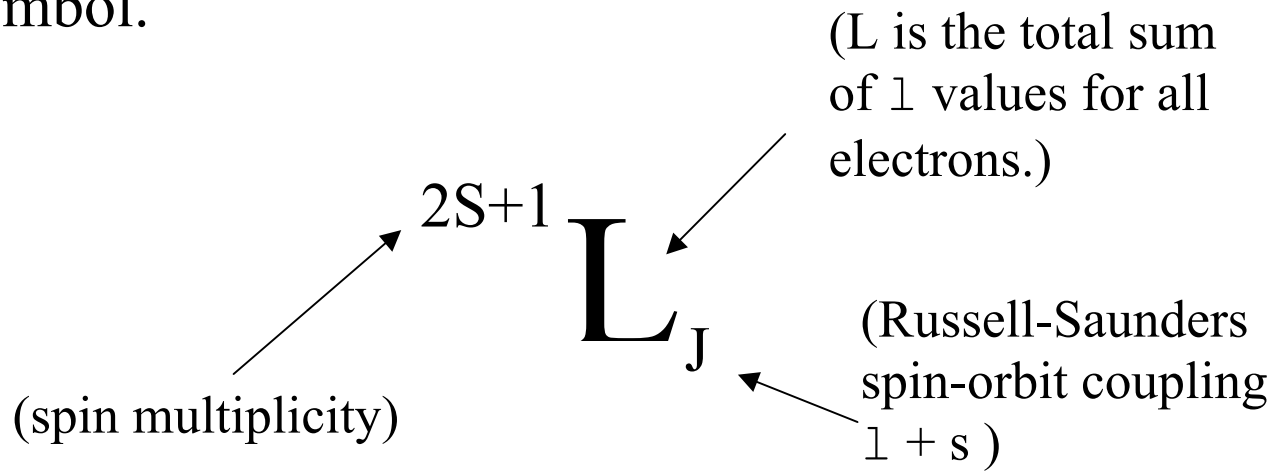
Free ions can easily be assigned a ground state term symbol.



S = 1/2 for one unpaired e^- 2S +1 = 2

S = 0 for zero unpaired e^- 2S + 1 = 1

S = 1 for two unpaired e^- 2S + 2 = 3
Etc.,

L= 0 → S symbol

L = 1 → P symbol

L = 2 → D symbol

L = 3 → F symbol

L total = $(M_{l1}+M_{l2}+M_{l3}+\ldots)$ for each electron

Then, the free ion states symbols have a “one-to-one” correspondence to state symbols derived for orbital configurations

Free ion		Complex
(L = 0) S	→	A_{1g}
(L = 1) P	→	T_{1u}
(L = 2) D	→	$E_g + T_{2g}$
(L = 3) F	→	$A_{2u} + T_{1u} + T_{2u}$

Term symbols for the 11 possible d^n systems are:

d^1 or d^9: ^2D

d^2 or d^8: $^1S, {}^1D, {}^1G, {}^3P, {}^3F$

d^3 or d^7: $^2P, 2^2D, {}^2F, {}^2G, {}^2H, {}^4P, {}^4F$

d^4 or d^6: $2^1S, 2^1D, {}^1F, 2^1G, {}^1I, 2^3P, {}^3D, 2^3F, {}^3G, {}^3H, {}^5D$

d^5: $^2S, {}^2P, 3^3D, 2^2F, 2^2G, {}^2H, {}^2I, {}^4P, {}^4D, {}^4F, {}^4G, {}^6S$

d^0 or d^{10}: ^1S

The last term in each series is the ground state for that system.

Q. How does one know which state is the ground state?

A. Easy. There are three rules to follow

(1) It is the state where all the electrons have maximum <u>Spin Multiplicity</u>

Ex.

d^4 case most stable arrangement is all unpaired e^-

<u>Hund's Rule</u>

(2) It is the state with the maximum orbital angular momentum L (= sum of m_l values)

$m_\perp$	= +2	+1	0	-1	-2

$L_{max} = 2$

This is the best arrangement for L maximized

(3) The J value is L+S for > ½ filled d orbitals and L-S for <1/2 filled

Cr^{3+} free ion

Determine G.S. **$^{2S+1}L_J$ symbol**

(1) 

+2 +1 0 -1 -2 d^3 **$L_{MAX} = 3$**

$L_{MAX} = 3 \rightarrow F$

(2) $S_{MAX} = 3/2 \rightarrow$ $2S + 1 = 4$

(3) $J = L + S = 3 + 3/2 = 9/2$

$J = L - S = 3 - 3/2 =$ $3/2$ < ½ filled

Therefore $^4F_{3/2}$ is g.s.

Q. What about Cr^{3+} complex instead of d^3 free ion?

$[Cr(H_2O)_6]^{3+}$ $t_{2g}^{3}e_g^{0}$

How can we know the ground states for this configuration?

We already said that

$$F \rightarrow A_{2u} + T_{1u} + T_{2u}$$

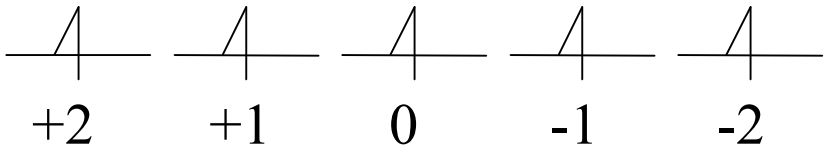
Free Ion	octahedral geometry

therefore in a Cr^{3+} compound d_3 to $t_{2g}^{3}e_g^{0}$ corresponds

to $^4F_{3/2}$: $^4A_{2u}$, $^4T_{1u}$ $^4T_{2u}$

(multiplicity carries but J does not)

Ex. Mn^{2+} free ion



$L_{max} = 0$

$S_{max} = 5/2 \quad 2s + 1 = 6$

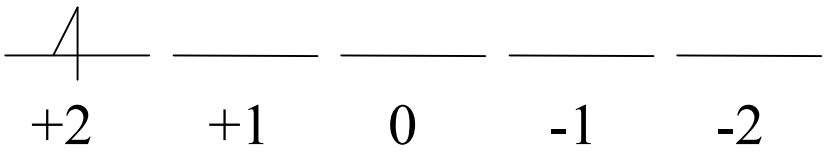
$J = 0 \pm 5/2 = 5/2$

$\rightarrow \quad \boxed{^6S_{5/2}}$

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

free ion state $^6S \rightarrow$ converts to $\boxed{^6A_{1g}}$ in an octahedral geometry

Ex. d^1 case Ti^{3+}



$L_{max} = 2 \rightarrow D$

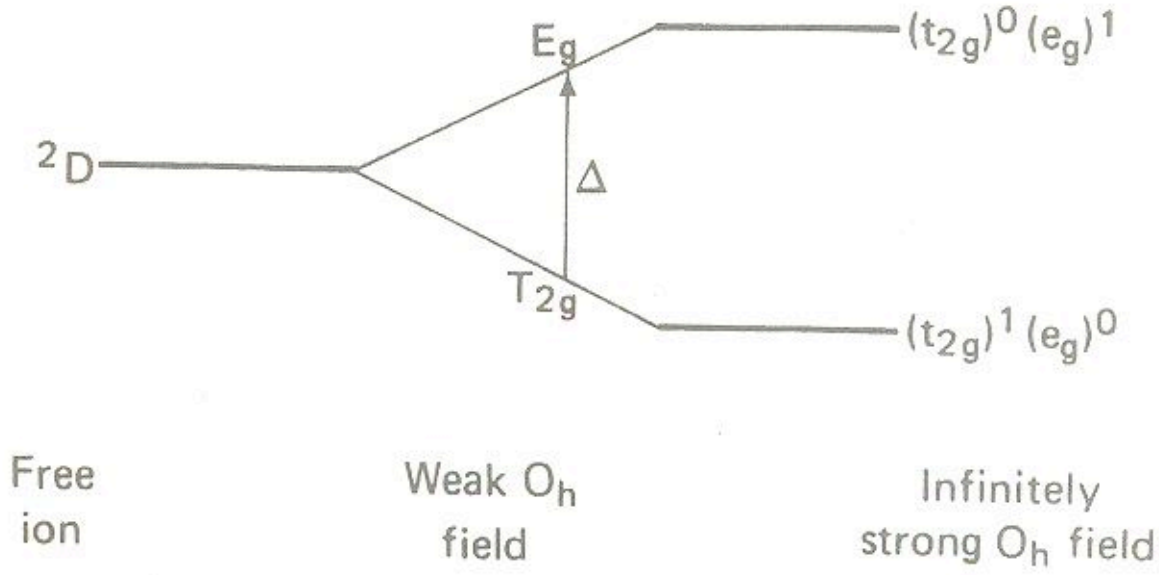
$S_{max} = ½ \rightarrow 2S + 1 = 2$

$J = 2 + ½ = 5/2$

$J = 2 - ½ = 3/2 \leftarrow$

$\boxed{^2D_{3/2}}$

$[Ti(H_2O)_6]^{3+}$ $\quad ^2D \rightarrow {}^2E_g + {}^2T_{2g}$

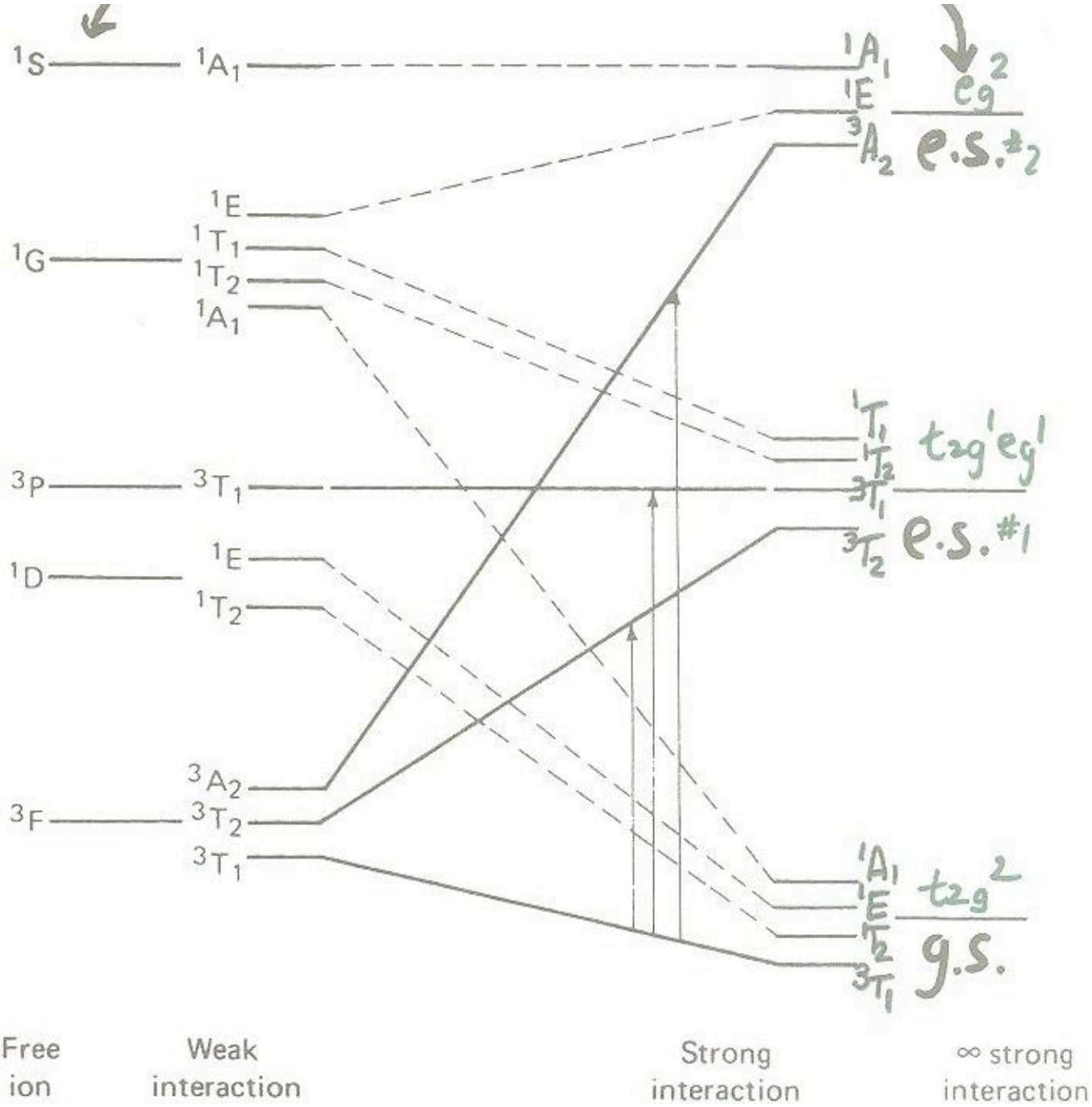


Status arising from electronic configurations in Octahedral, Tetrahedral and square planar

States Arising in Fields of Various Symmetry

Free Ion	*States in Point Groups*		
Term	O_h (octahedral)	T_d (tetrahedral)	D_{4h} (Sq. Planar)
S	A_1	A_1	A_1
P	T_1	T_2	A_2, E
D	E, T_2	E, T_2	A_1, B_1, B_2, E
F	A_2, T_1, T_2	A_2, T_1, T_2	$A_2, B_1, B_2, 2E$
G	A_1, E, T_1, T_2	A_1, E, T_1, T_2	$2A_1, A_2, B_1, B_2, 2E$
H	$E, 2T_1, T_2$	$E, T_1, 2T_2$	$A_1, 2A_2, B_1, B_2, 3E$
I	$A_1, A_2, E, T_1, 2T_2$	$A_1, A_2, E, T_1, 2T_2$	$2A_1, A_2, 2B_1, 2B_2, 3E$

Two electron system d^2
Connecting free ion states to orbital states



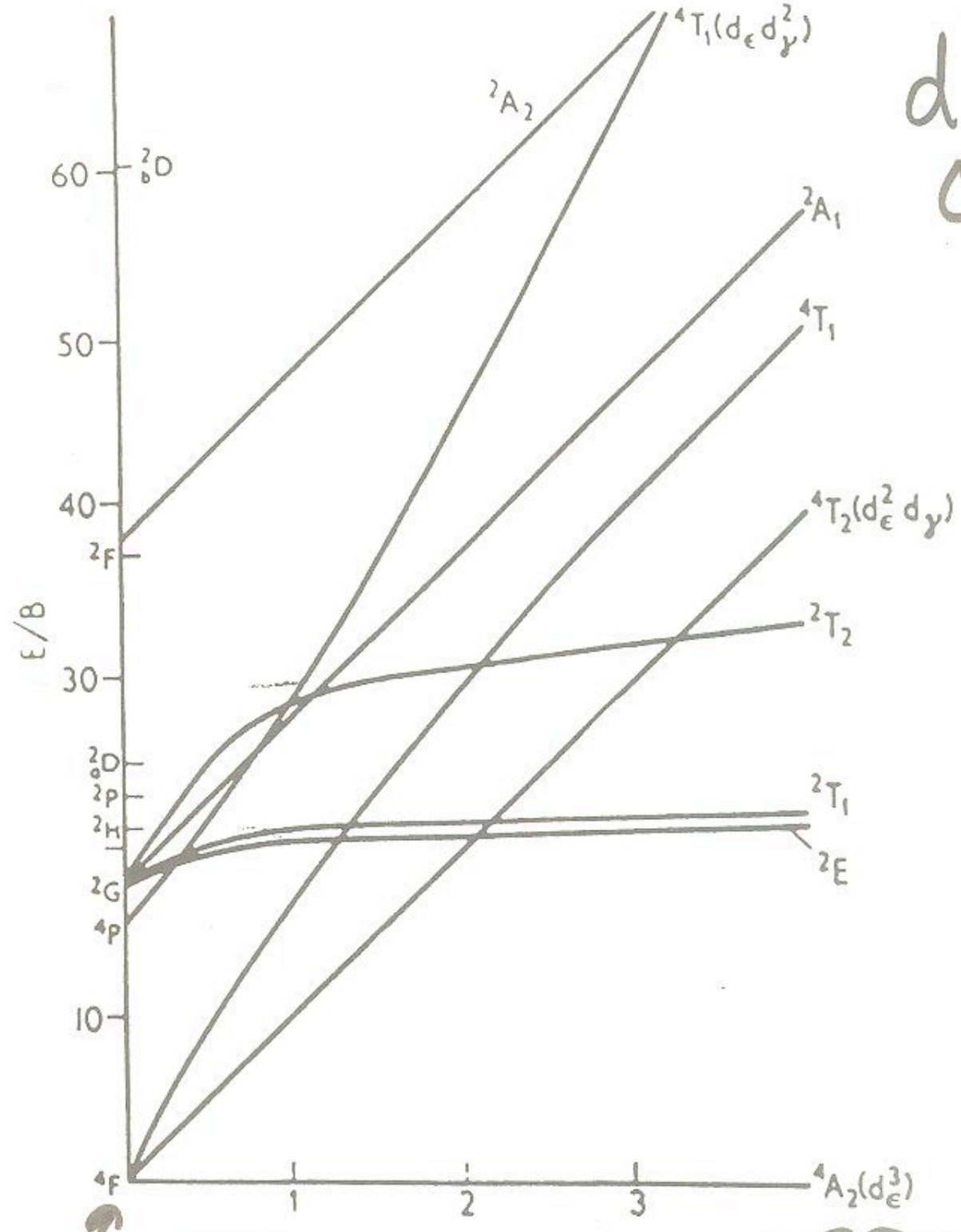
no ligands	weak field ligands	strong field ligands

We call these correlation diagrams Tanabe – Sugano diagrams

Free ions → orbital states

We can use these to help predict spectral transitions

The transitions should be between states with the same multiplicity.



d^3 Cr^{III}

free ion states ~Δ_o

orbital states for the Complex

Energy diagram for the configuration d^3.

Electronic transitions selection rules

a. ^{2s+1}L

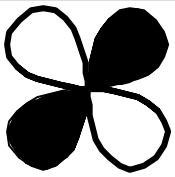
Spin multiplicity must be the same between g.s. and e.s. spin rule

b. orbital in g.s. and orbital in e.s. must have different signs w.r.t. an inversion

p 

When you invert through the center it changes sign.

u → ungerade

d 

When you invert through the center the sign remains the same.

g → gerade

A. **d-d transition in ML_6 octahedral complexes:**

a. Spin-allowed are moderate-to-weak in intensity but spin-forbidden are very weak and often cannot be observed at all unless the concentration is really high

b. they are orbitally or Laporte forbidden always because d → d transitions involve same type of g → g orbital.

B. **Charge-transfer transitions**

M→L (d→p)

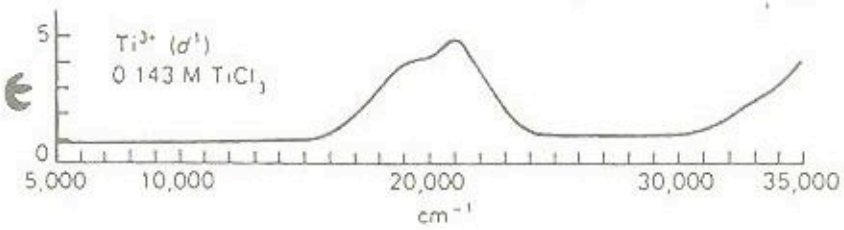
L→M (p→d)

(i.) Spin – allowed

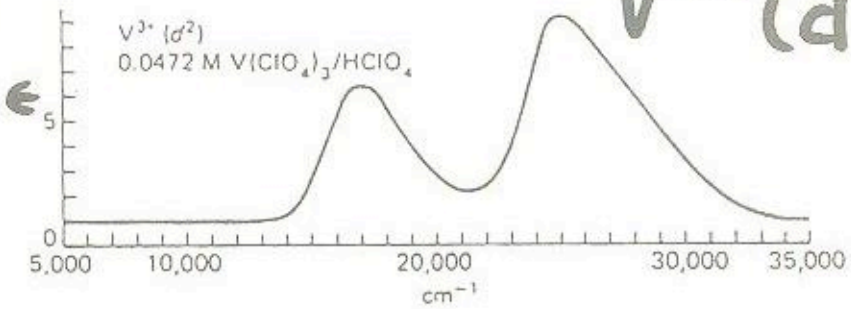
(ii) orbitally allowed g→u or u→g, so much more intense than d→d transitions

(all are six-coordinates)

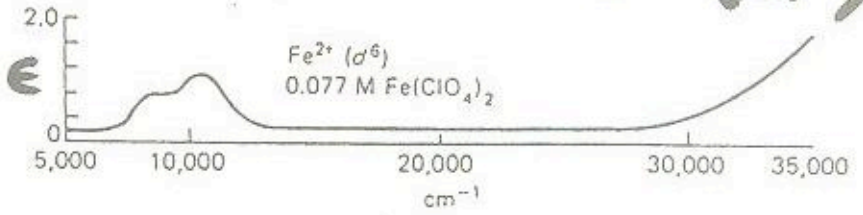
$[Ti^{III}(H_2O)_6]^{3+}$ $TiCl_3$ $Ti^{3+}(d^1)$



$[V^{III}(H_2O)_6]^{3+}$ $V(ClO_4)_3(aq)$ $V^{3+}(d^2)$

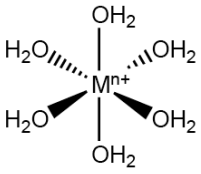


$[Fe^{II}(H_2O)_6]^{2+}$ $Fe(ClO_4)_2(aq)$ $Fe^{2+}(d^6)$



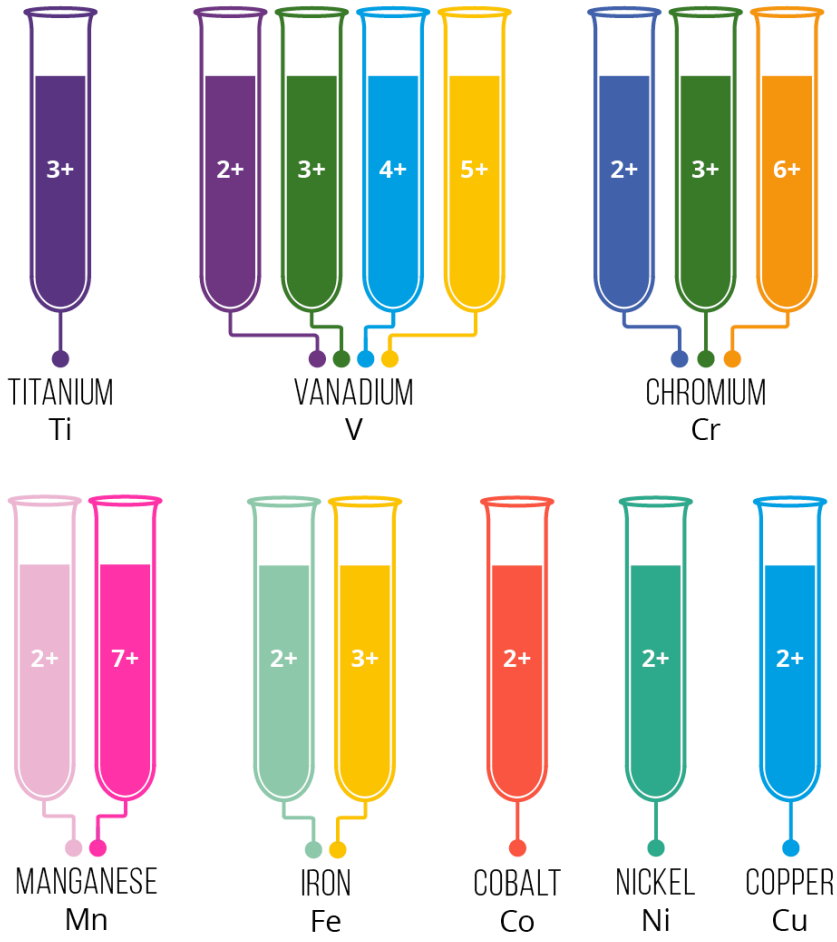
TRANSITION METAL ION COLOURS

Transition metals form coloured compounds and complexes. These colours can vary depending on the charge on the metal ion, and the number and type of groups of atoms (called ligands) attached to the metal ion. In aqueous solutions, the ions form complexes with the colours shown to the right.



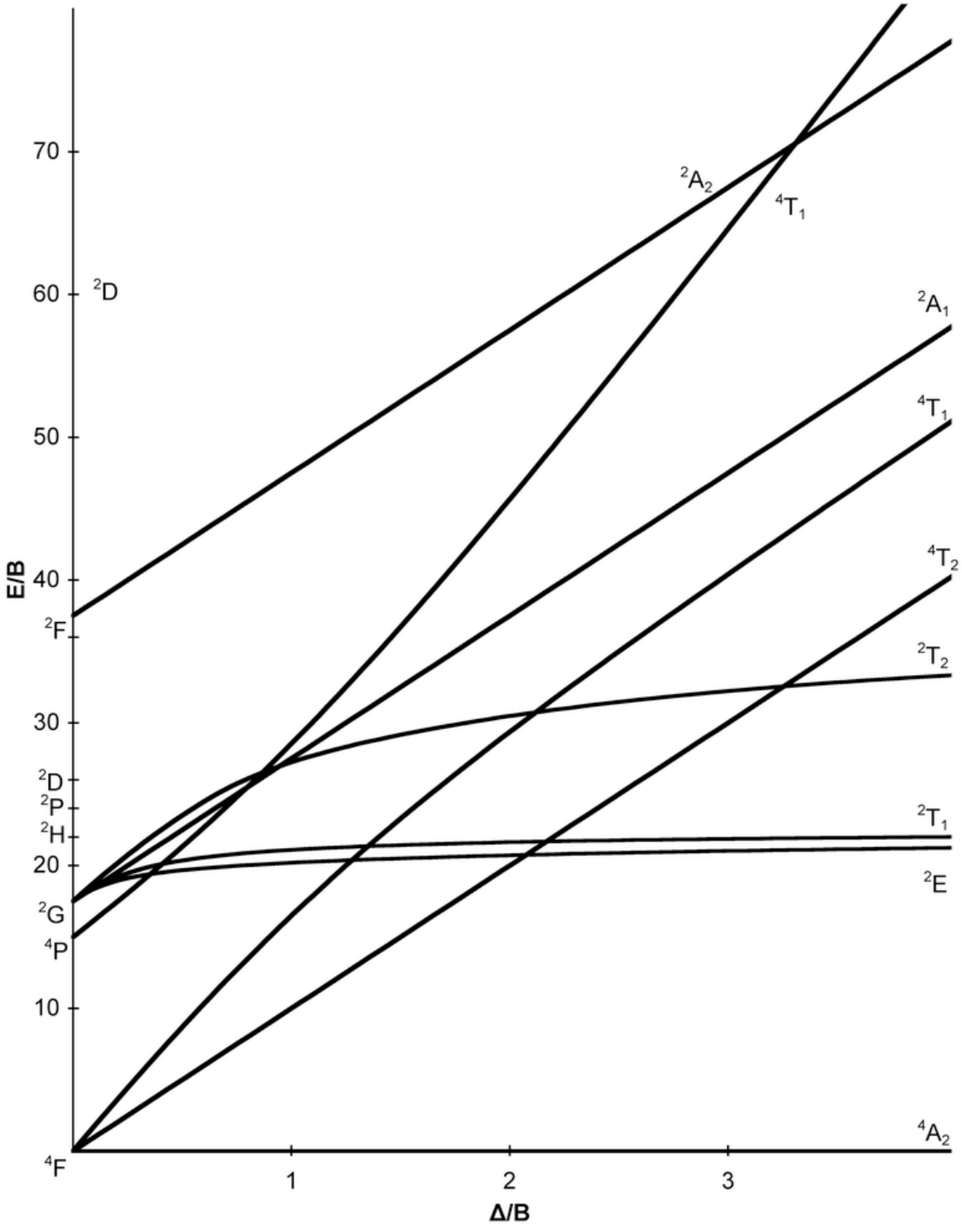
HYDRATED TRANSITION METAL ION

Electrons are arranged around the nucleus of the metal atom in orbitals. Transition metals, unlike other metals, have partially filled d orbitals, which can hold up to 10 electrons. When ligands are present, some d orbitals become higher in energy than before, and some become lower. Electrons can then move between these higher and lower d orbitals by absorbing a photon of light. This absorption of light affects the percieved colour of the compound or complex. The wavelength of the light absorbed is affected by the size of the energy gap between the d orbitals, which is in turn affected by the type of ligand and the charge on the metal ion.

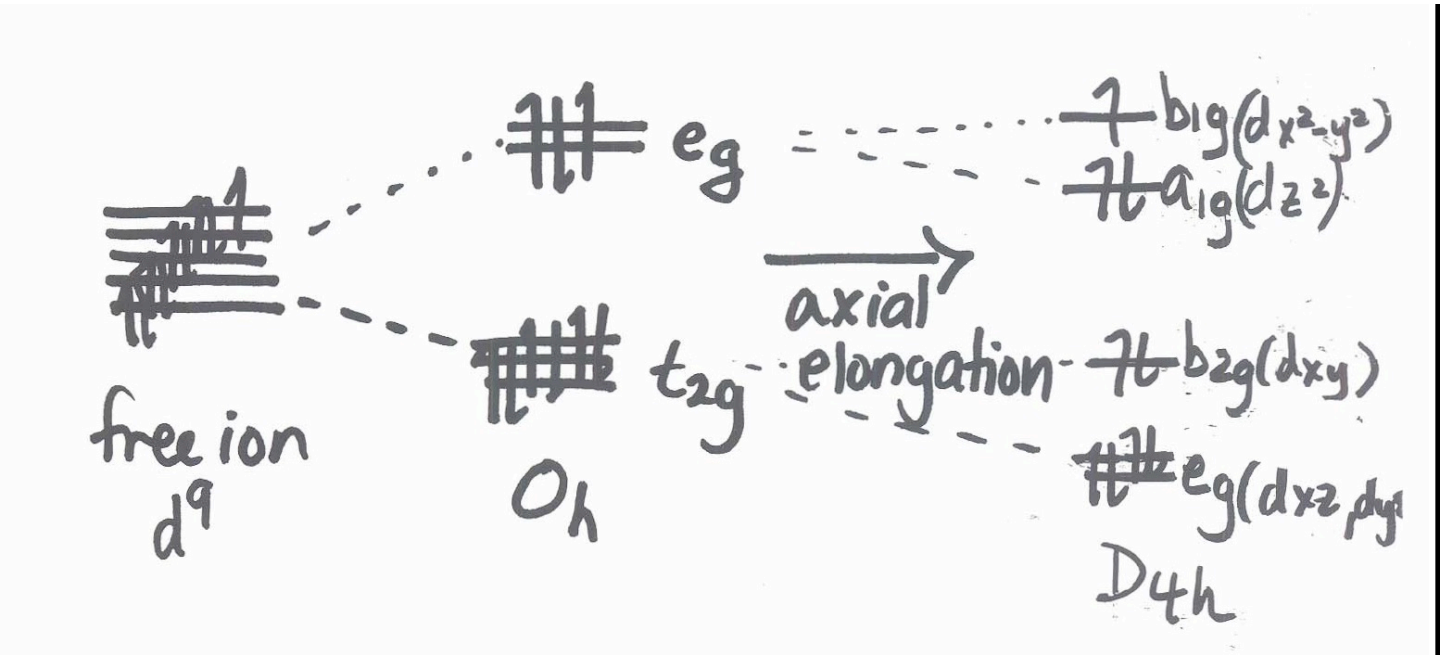


One can use Tanabe – Sugano diagrams to help predict # of spin allowed transitions for a given orbital configuration.

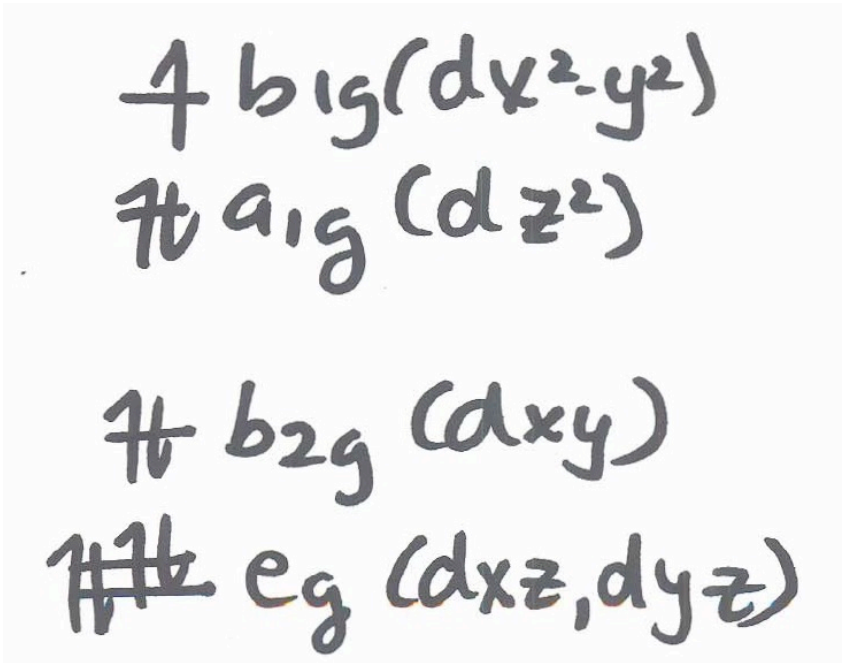
d^2 Tanabe-Sugano diagram



Ex. #2 Cu^{2+}, d^9, blue



Jahn-Teller distortion occurs; the levels move in the particular direction because z-direction is now stabilized


$b_{1g}(d_{x^2-y^2})$
$a_{1g}(d_{z^2})$
$b_{2g}(d_{xy})$
$e_g(d_{xz}, d_{yz})$

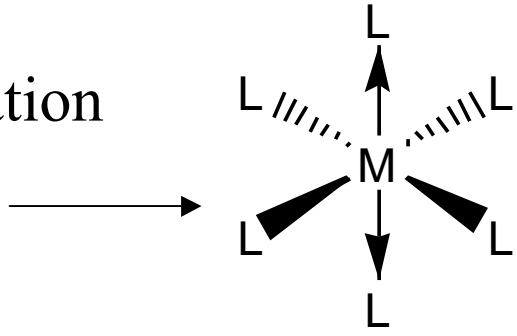
The lower they symmetry, the more transition you will observe. Also, for certain d^n configurations there will be distortions of the molecule from a perfect symmetry to an effectively lower symmetry.

Jahn-Teller Theorem states that for a **non-linear** molecule in an electronically degenerate state, **distortion must occur** to lower the symmetry, i.e. to remove the degeneracy and lower the energy

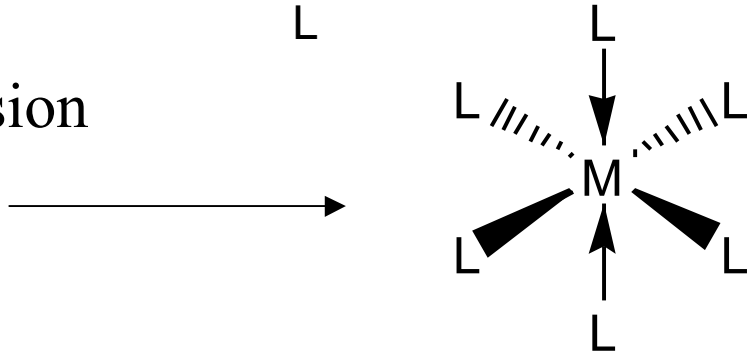
*Note:

The theorem does not predict which type of distortion will take place other than that the center of symmetry will remain. The z-direction ligands can move out or move in.

Tetragonal Elongation

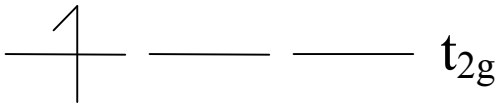


Tetragonal Compression



Consider an ion subject to Jahn-Teller distortion

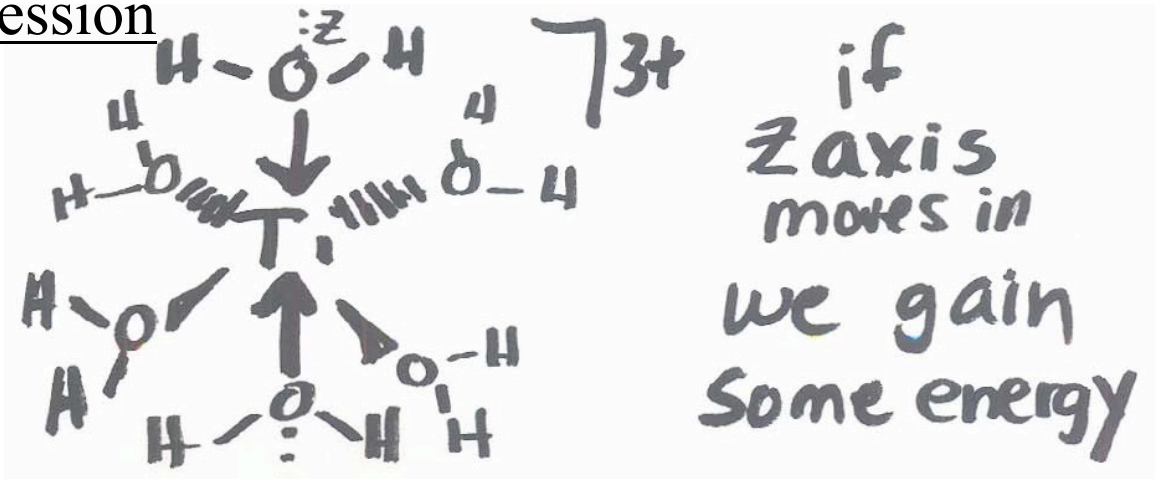
$[Ti(H_2O)_6]^{3+}$ Ti(III) is d^1

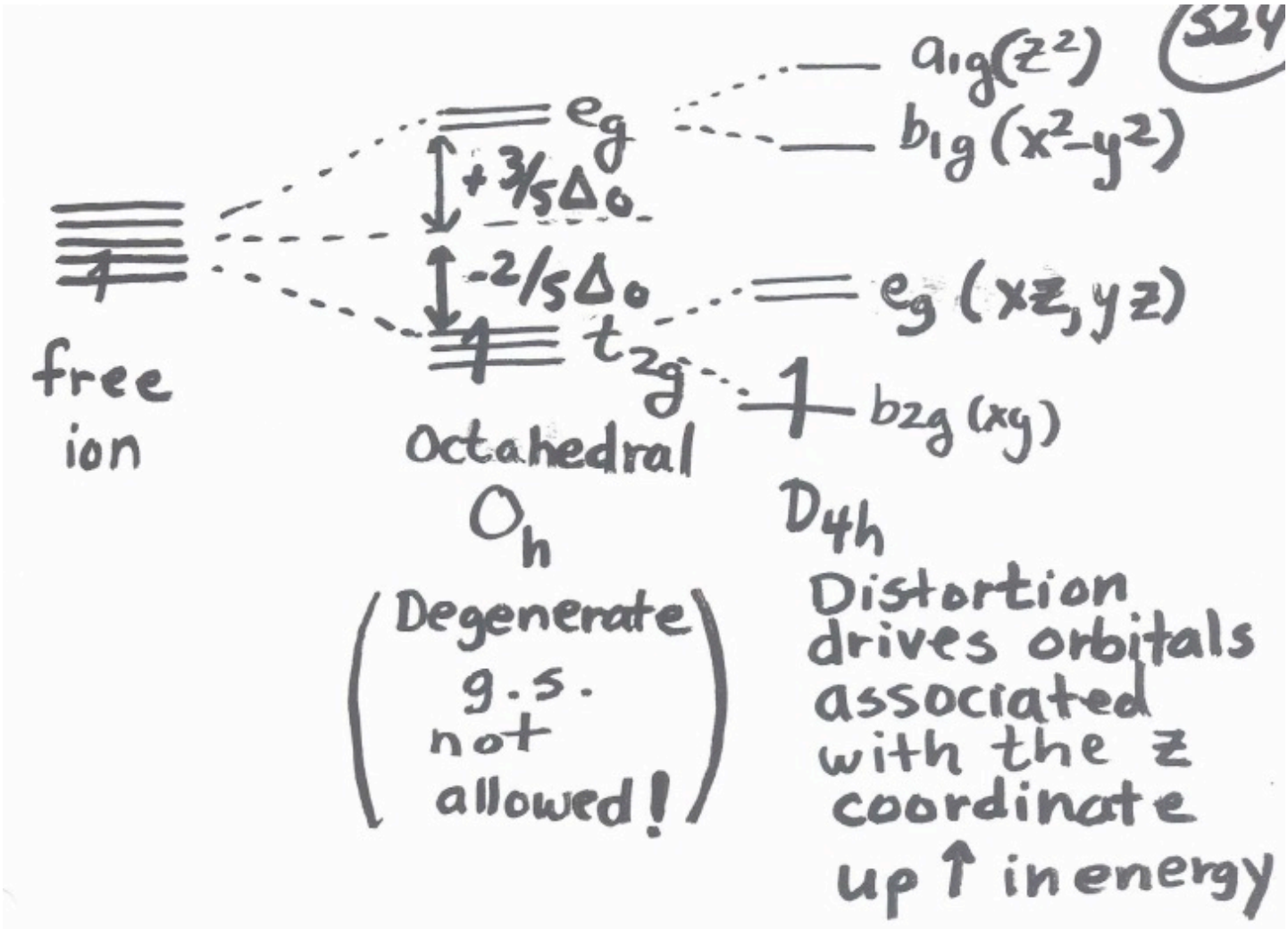


(Jahn-Teller forbids it to be occupied in this manner)

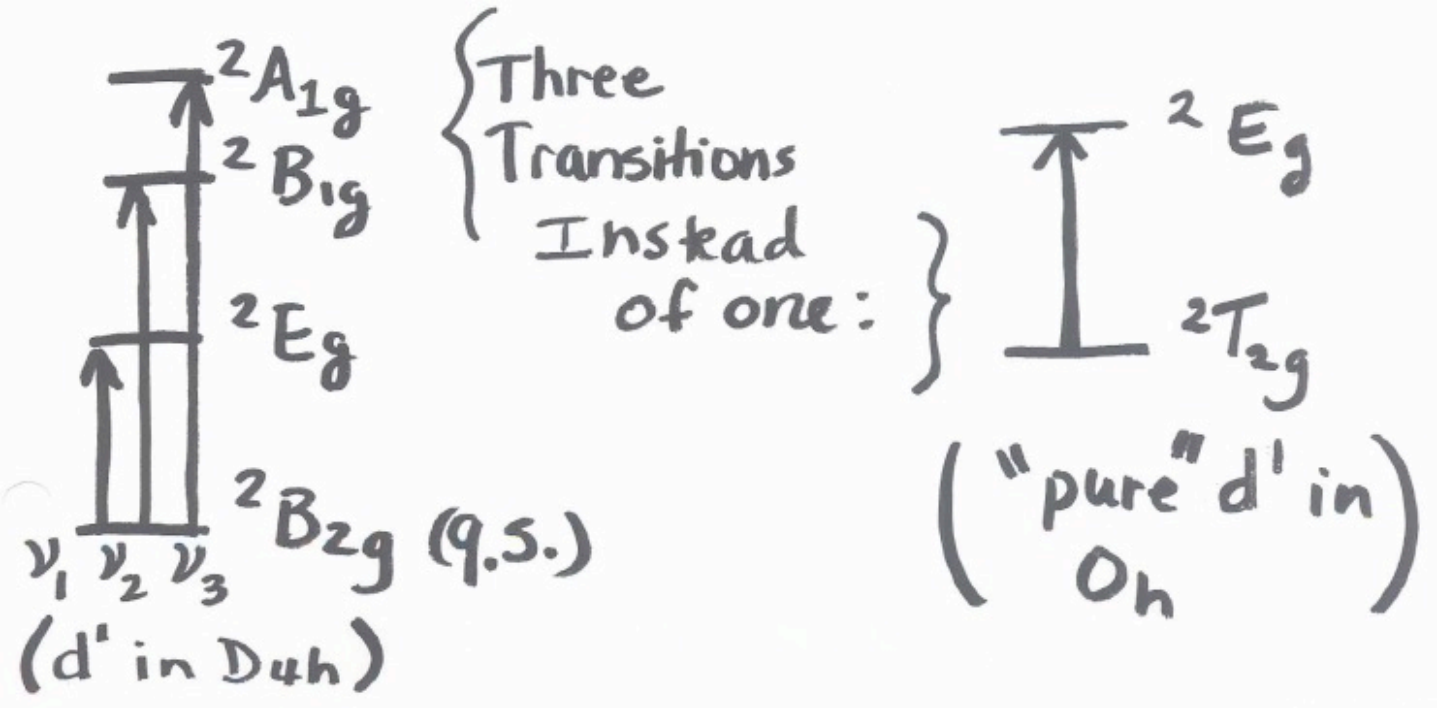
(remember spectrum depicted earlier? Not only one transition. Why?)

<u>axial compression</u>





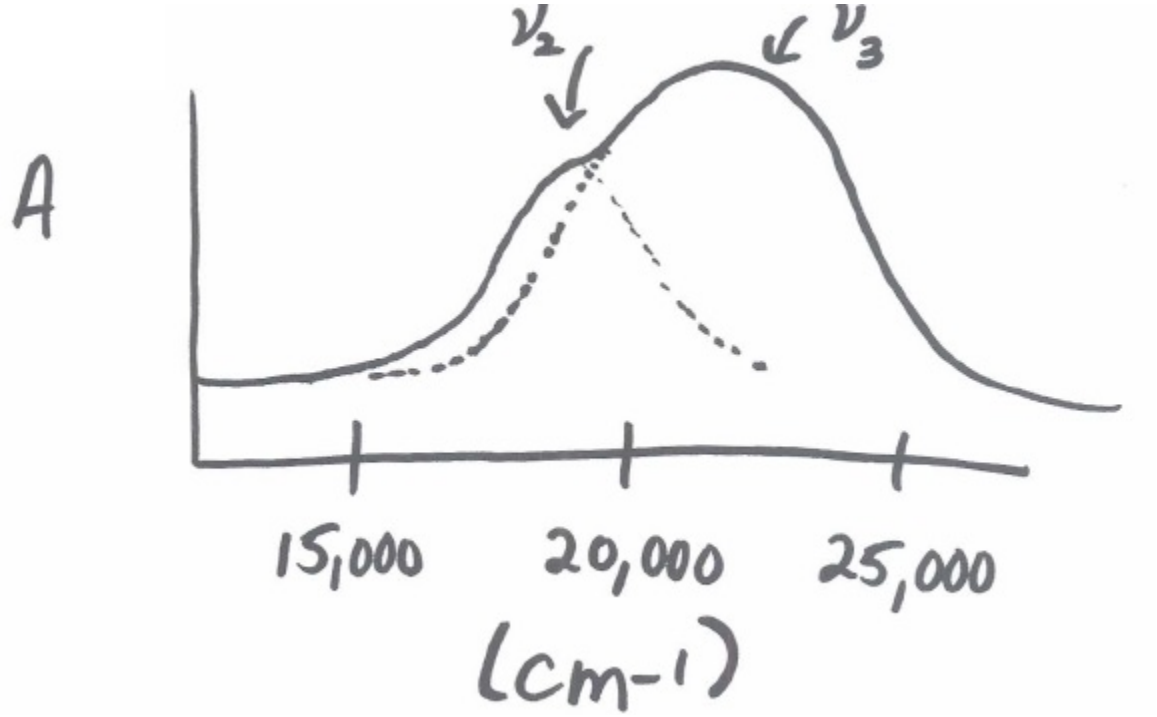
In terms of energy states, the allowed transitions (spin-allowed) are:


$^2A_{1g}$
$^2B_{1g}$
^2E_g
$^2B_{2g}$ (g.s.)
ν_1 ν_2 ν_3
(d' in Duh)
Three Transitions Instead of one:
^2E_g
$^2T_{2g}$
("pure" d' in Oh)

Actual spectrum of $[Ti(H_2O)_6]^{3+}$

Two transitions in uv-visible

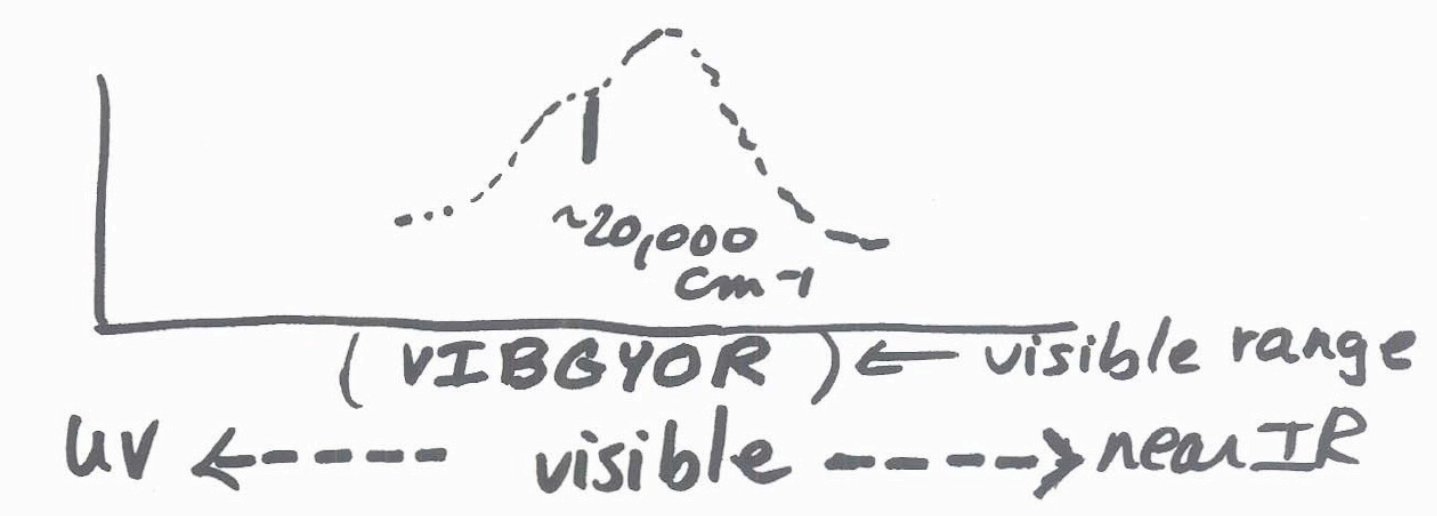
V_1 is too low to observe in this region – it would be found in the IR



Instead of a single Gaussian curve, the absorption peak shows a shoulder due to superposition of two transitions.

Incidentally…

What color would this complex be expected to be?



20,000 cm^{-1} is absorbing in the yellow-green region of the visible spectrum; the colors that are not absorbed are what your eye sees.

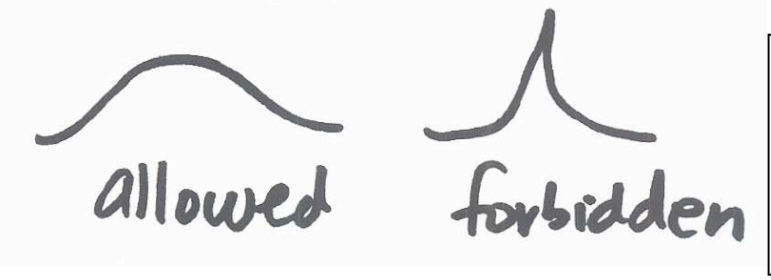
In this case, the $[Ti(H_2O)_6]^{3+}$ ions looks purple (blue and red colors)

In the end, it is still a combination of factors that one must consider in trying to make Spectral Assignments for Simple Transition Metal Complexes.

(1) Intensities (Geometry considerations)

- d-d transitions in O_h are typically weak ($E \sim 0.01 - 100\ M^{-1}\ CM^{-1}$)
  Spin-allowed are easily observed but the spin-forbidden are very weak although sometimes observed.
- d-d transitions in T_d are much more intense than O_h
  T_d point group has no center of symmetry? so it has orbitally allowed (Laporte-allowed) transitions ($E \sim 100\text{-}1000\ M^{-1}CM^{-1}$)

(2) Band Shape – spin allowed transitions are usually broad where as spin-forbidden transitions are sharp.



This should give you a clue when you are assigning transitions.

(3) Shoulders – bands arising from d^1, d^2, d^4 (high-spin), d^7 (low-spin), d^9 have a shoulder due to a

Jahn-Teller distortion (or other transitions due to symmetry lowering)

(4) all of the above deal with ie^- transitions. Two – e^- transitions, while theoretically possible, are 10^{-2} weaker than ie^- and very high in energy

Jahn – Teller Theorem

H.A. Jahn and E. Teller (1937)
Proc. Roy Soc., A161, 220(1937)

A non-linear molecule in an electronically degenerate state will distort to lower the symmetry, remove the degeneracy, and lower the energy.

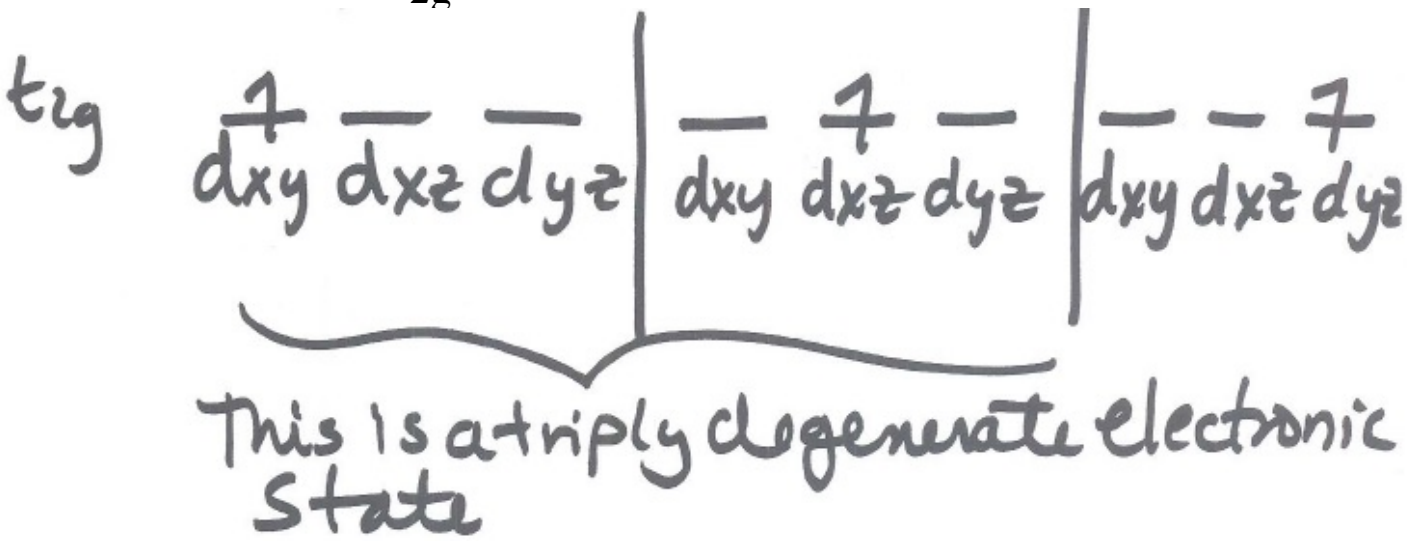
Perhaps it is better to view this in terms of a physical picture than an abstract theorem (more intuitive manner):

(1) non-linear molecule is octahedral, tetrahedral, square planar etc. (anything except small molecules such as diatomics, triatomics)

(2) a degenerate electronic state such as d^1, d^2, d^4, d^5(L.S.), d^6(H.S.), d^7, d^8 is not a spherical distribution of electrons (unlike d^3, d^5(H.S.), d^6(L.S.), d^8)

Ex. #1 Ti^{3+}, d^1 $t_{2g}^{\ 1}e_g^{\ 0}$

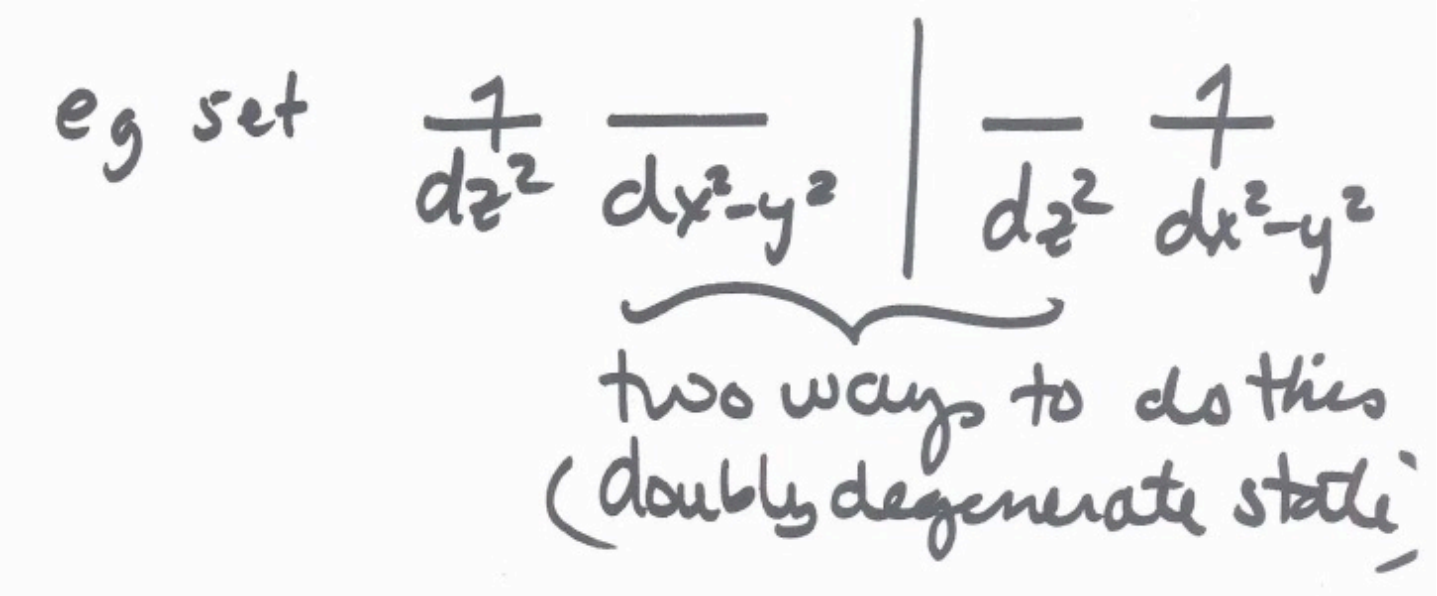
There are three possible ways to arrange the electrons in the t_{2g} set



This is a triply degenerate electronic state

Ex.#2 Cr^{3+}, d^3 $t_{2g}^{\ 3}e_g^{\ 0}$

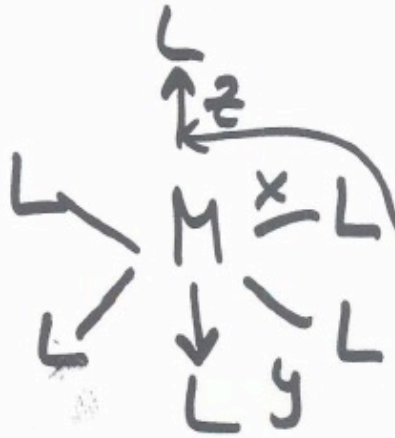
Ex. #3 Co^{2+}, d^7, $t_{2g}^6 e_g^1$



Lets consider the physical reality of placing electrons in d_z^2 versus $d_{x^2-y^2}$ in above case:

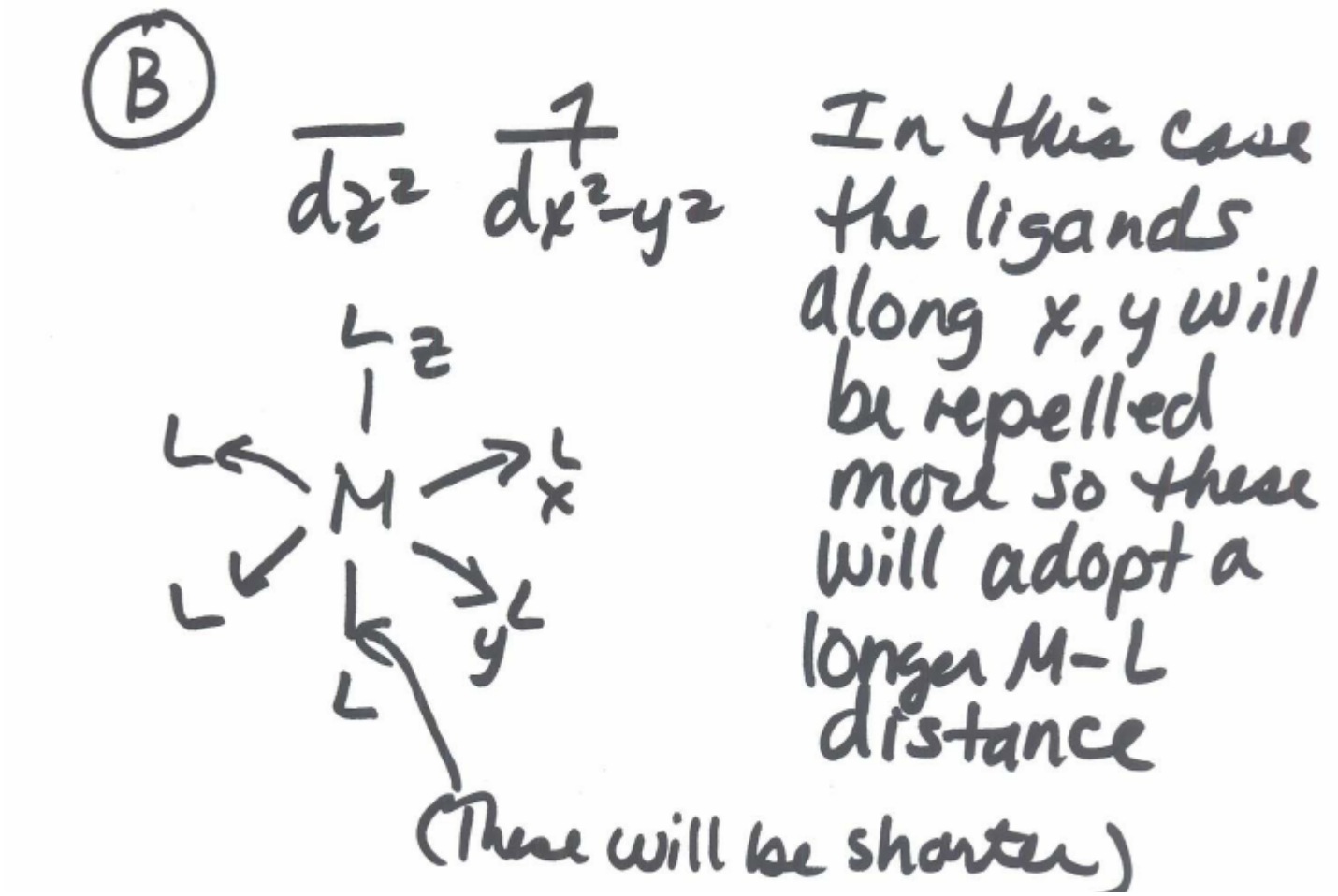
(A)

d_{z^2} — $d_{x^2-y^2}$



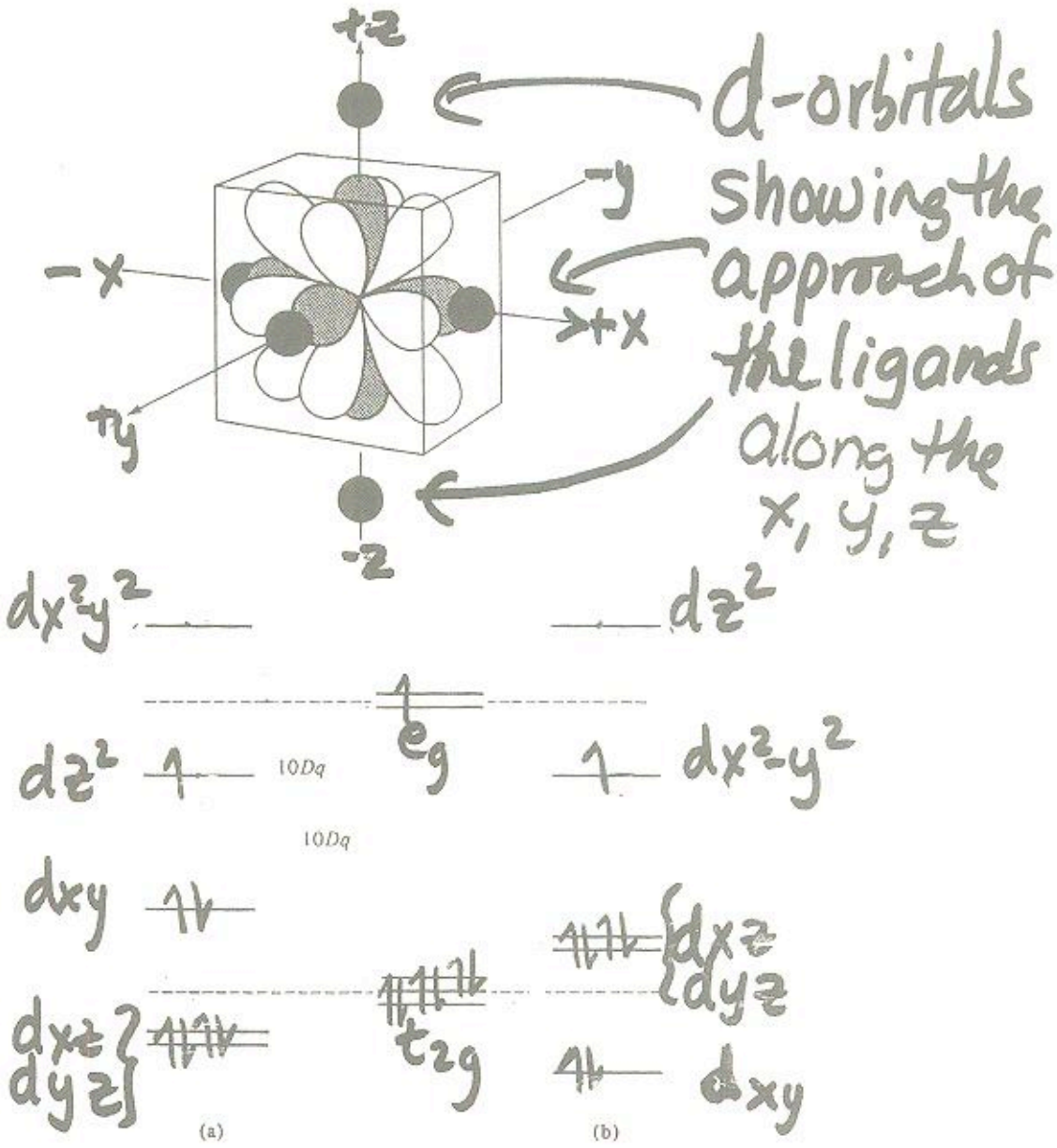
In this case, the ligands approaching along z will be repelled by the electron in dz^2 more than the ligands along x, y direction

These bonds will be longer; the other two types will be shorter



Bottom Line is both are possible!!

a. represents an axial (or tetragonal) elongation
b. represents an axial (or tetragonal) compression



z-Ligands ← Octahedral → z-ligands

“out”	“in”
axial	axial
elongation	compression

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

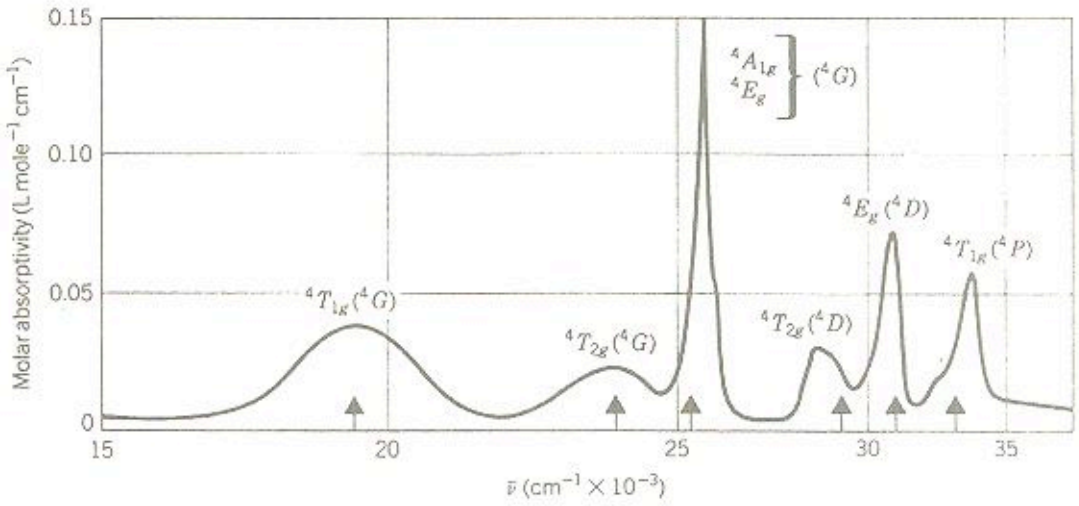
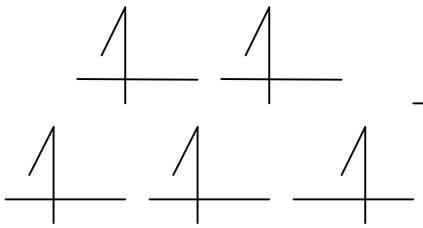


Figure 23-23 The electronic absorption spectrum of $[Mn(H_2O)_6]^{2+}$. Arrows indicate predicted band positions.

All of these transitions are weak (E<0.15) and are spin-forbidden

H.S. d^5



→ No way to promote one electron without changing spin!