Coordination Chemistry III: Tanabe-Sugano Diagrams

Chapter 11

Friday, December 4, 2015

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

We set out to understand the UV-vis-NIR absorbance spectrum of the *d*^{2} ion, $[V(OH_2)_6]^{3+}$

- **We started with the V^{3+} free ion – no ligands, spherical symmetry**
- **Considered two electrons in five equal-energy *d* orbitals to give 45 microstates**
- **Using *L* and *S* we factored these microstates into five atomic states, ^1G, ^3F, ^1D, ^3P, and ^1S**
- **Established that ^3F is the ground state**
  - **maximizes spin multiplicity, and then**
  - **maximizes orbital angular momentum**

If we go back to our selection rules for spectroscopy,

- **spin-allowed transitions occur between states with the same spin multiplicity**
- **Laporte-allowed transition occur between orbitals with different parity**

The important atomic states for describing the absorption spectrum of $[V(OH_2)_6]^{3+}$ must be the ^3F and the ^3P electron configurations.

Visualizing the ^3F and ^3P States (see Table 2.3)

^3F is the ground state with 21 microstates

M_L = -3

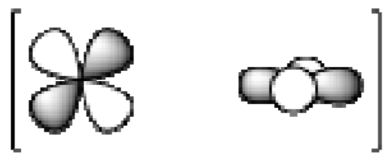
M_L = -2

M_L = 2

M_L = -1

M_L = 1

M_L = 0



M_L = 3

- One electron into each orbital places them as far apart as possible
- For these seven orbital combinations remember that there will be M_S = +1, 0, –1 microstates

^3P is the spin-allowed excited state with 9 microstates

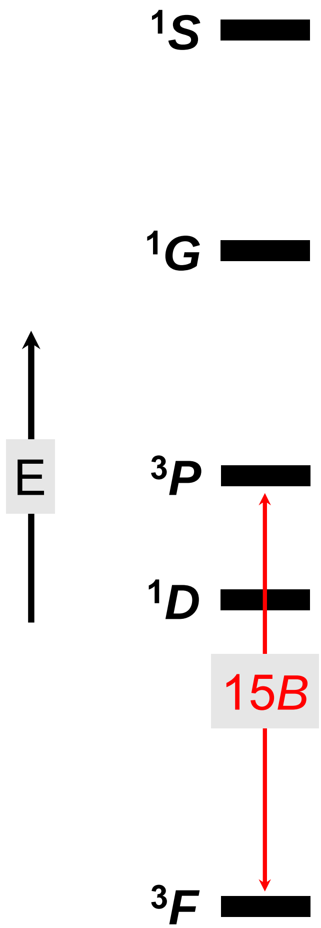
M_L = 0

M_L = 1

M_L = -1

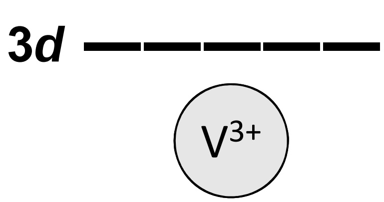
- These microstates put the electrons in the same plane, resulting in greater repulsion
- Again these three orbital combinations will have microstates with M_S = +1, 0, –1

Electronic State Diagram (Correlation Diagram)

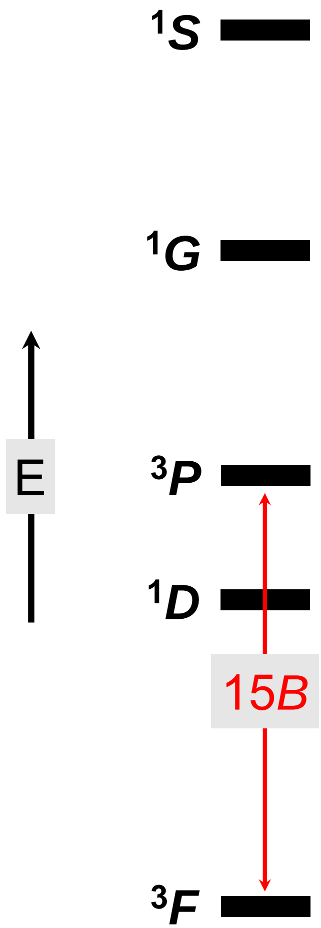


- *The different free ion terms for an electron configuration have different energies due to variations in electron-electron repulsion*
- *The different energies can be expressed using a small number of electrostatic parameters, A, B and C*
  - *These parameters are integrals related to the extent of electron-electron repulsion. The larger they are, the greater the repulsion is*
- *A, B and C are called* ***Racah parameters***

LFT orbital energies



Electronic State Diagram (Correlation Diagram)



Energies of d^2 free ion terms

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

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

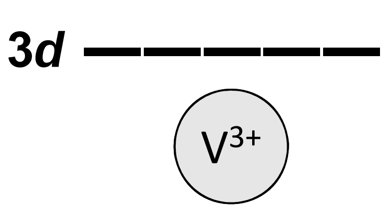
$E(^1D) = A - 3B + 2C$

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

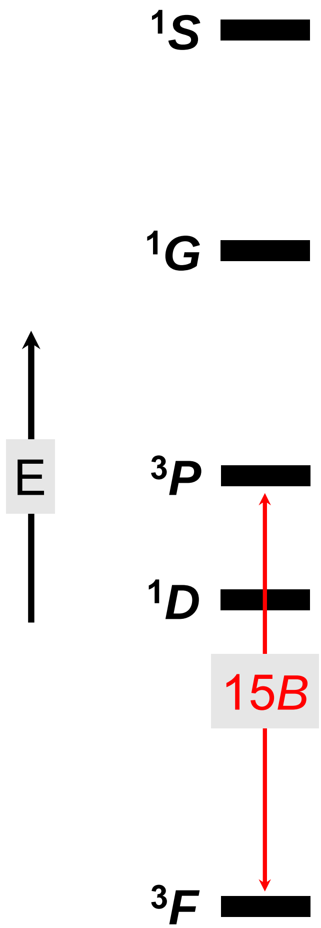
$E(^3F) = A - 8B$

- Note that the difference between any pair of these terms is purely a function of B and C, not A
- If we can measure the energies of two properly chosen spectroscopic transitions between these terms we can calculate B and C
- B = 400-1400 cm^{-1} and depends on ion size. The ratio C/B is almost constant and close to 4.

LFT orbital energies



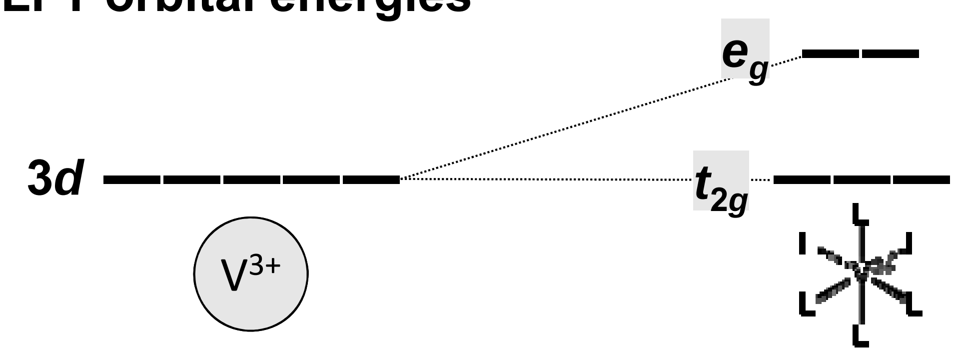
Electronic State Diagram (Correlation Diagram)



These are the electronic states when all the *d* orbitals are at the same energy.

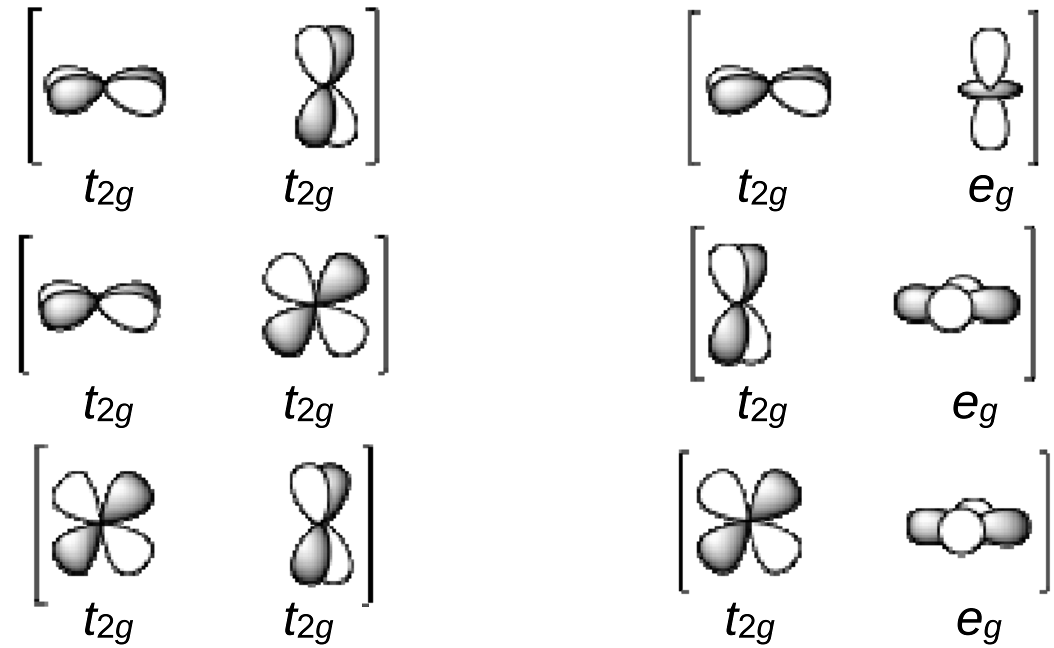
What happens when we impose an octahedral ligand field?

LFT orbital energies



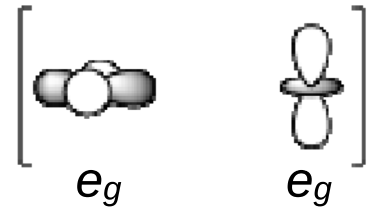
Visualizing the ^3F and ^3P States

^3F is the ground state with 21 microstates



$E = 0\,B + 0\,\Delta_o$

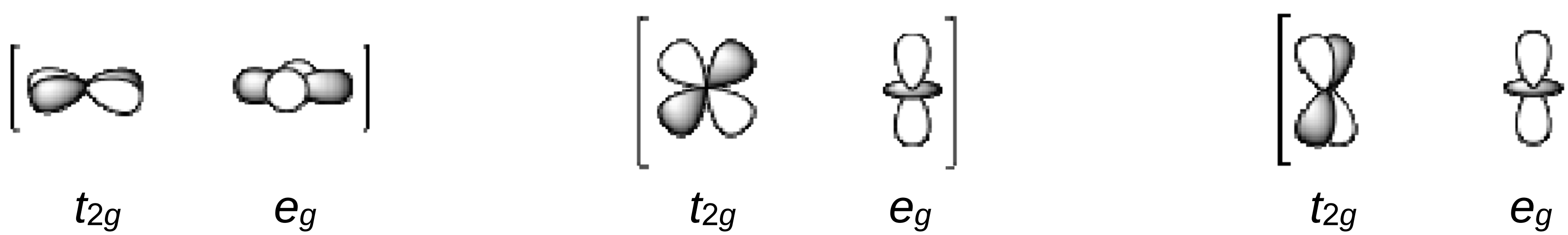
$E = 0\,B + 1\,\Delta_o$



$E = 0\,B + 2\,\Delta_o$

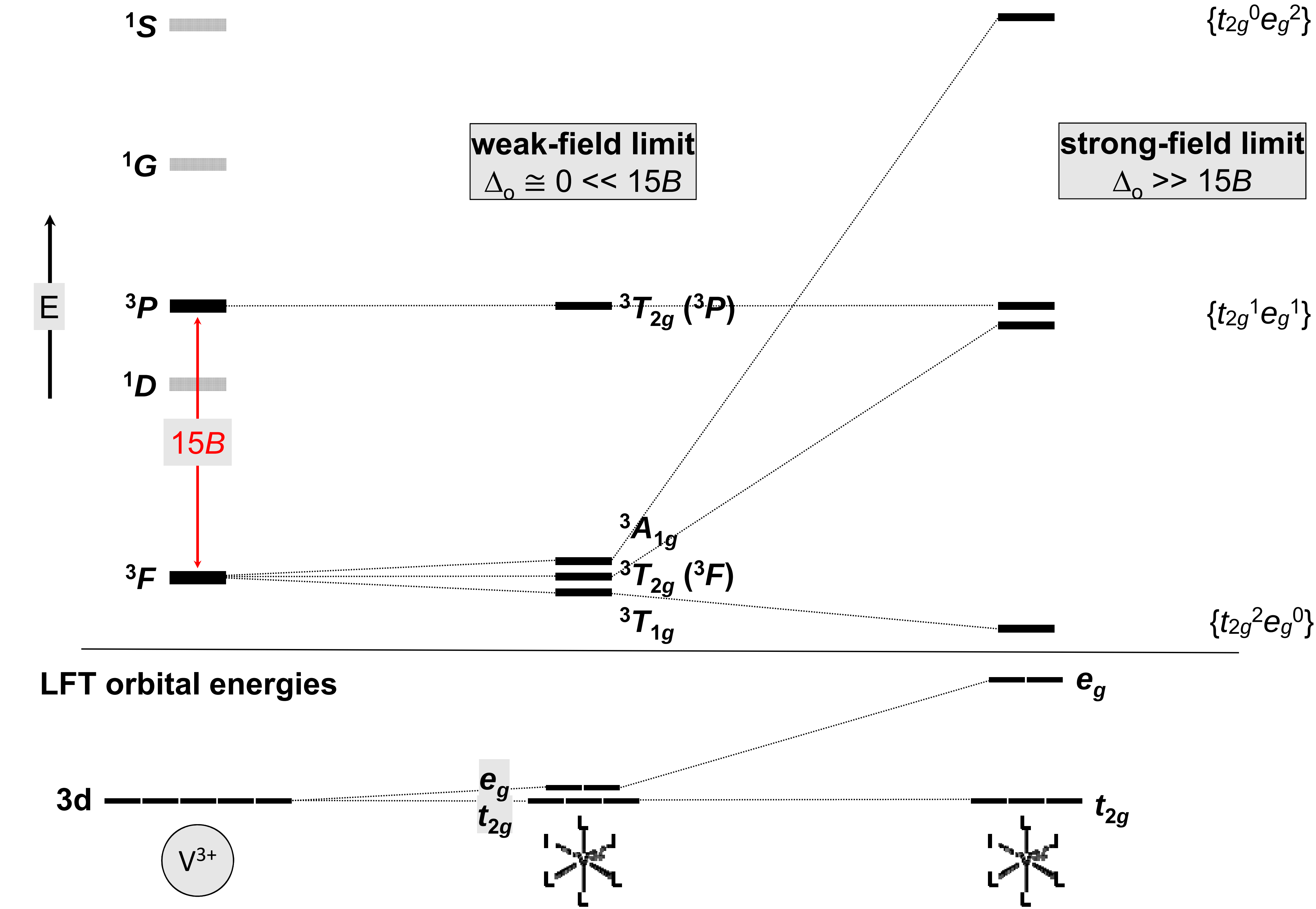
All ^3F microstates are equivalent in the free ion, but what about in an octahedral field?

^3P is the spin-allowed excited state with 9 microstates



$E = 15B + 1\,\Delta_o$

Electronic State Diagram (Correlation Diagram)



Symmetry Labels for Configurations

Free ion terms split into states in the ligand field, according to symmetry:

TABLE 11.6 Splitting of Free-Ion Terms in Octahedral Symmetry

Term	Irreducible Representations
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

The state labels also indicate the degeneracy of the electron configuration:

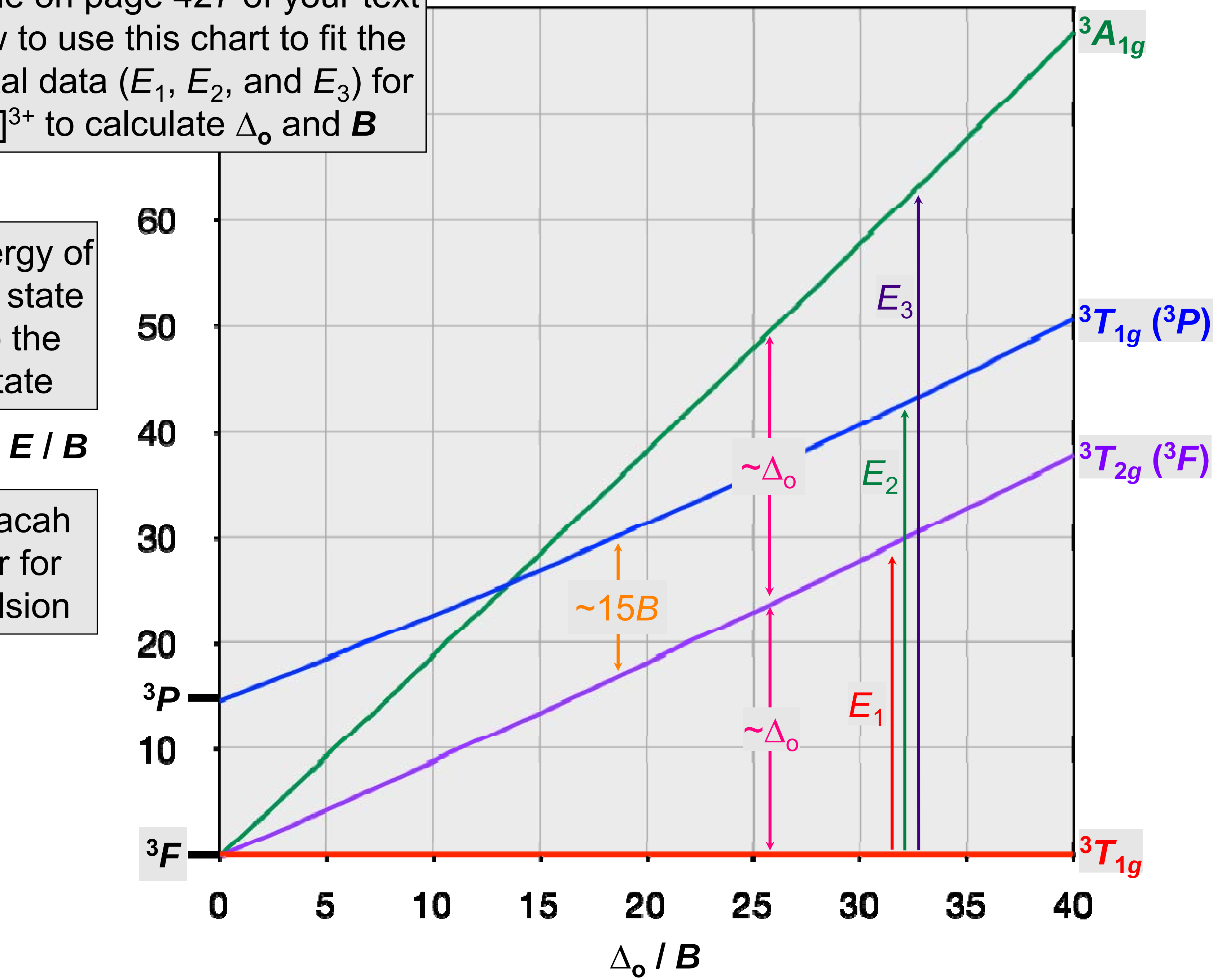
		Examples
T	Designates a triply degenerate asymmetrically occupied state.	
E	Designates a doubly degenerate asymmetrically occupied state.	
A or B	Designate a nondegenerate state. Each set of levels in an A or B state is symmetrically occupied.	

d^2 Tanabe-Sugano Diagram

The example on page 427 of your text shows how to use this chart to fit the experimental data (E_1, E_2, and E_3) for $[V(OH_2)_6]^{3+}$ to calculate Δ_o and ***B***

E is the energy of the excited state relative to the ground state

B is the Racah parameter for e^--e^- repulsion



d^2 Tanabe-Sugano Diagram

E_3 ~ $2.1E_1$

So, E_3 = 37,400 cm^{-1}

very weak

E / B

17800/*B* = 29

So, *B* = 610 cm^{-1}

Δ_o /610 = 31

So, Δ_o = 18,910 cm^{-1}