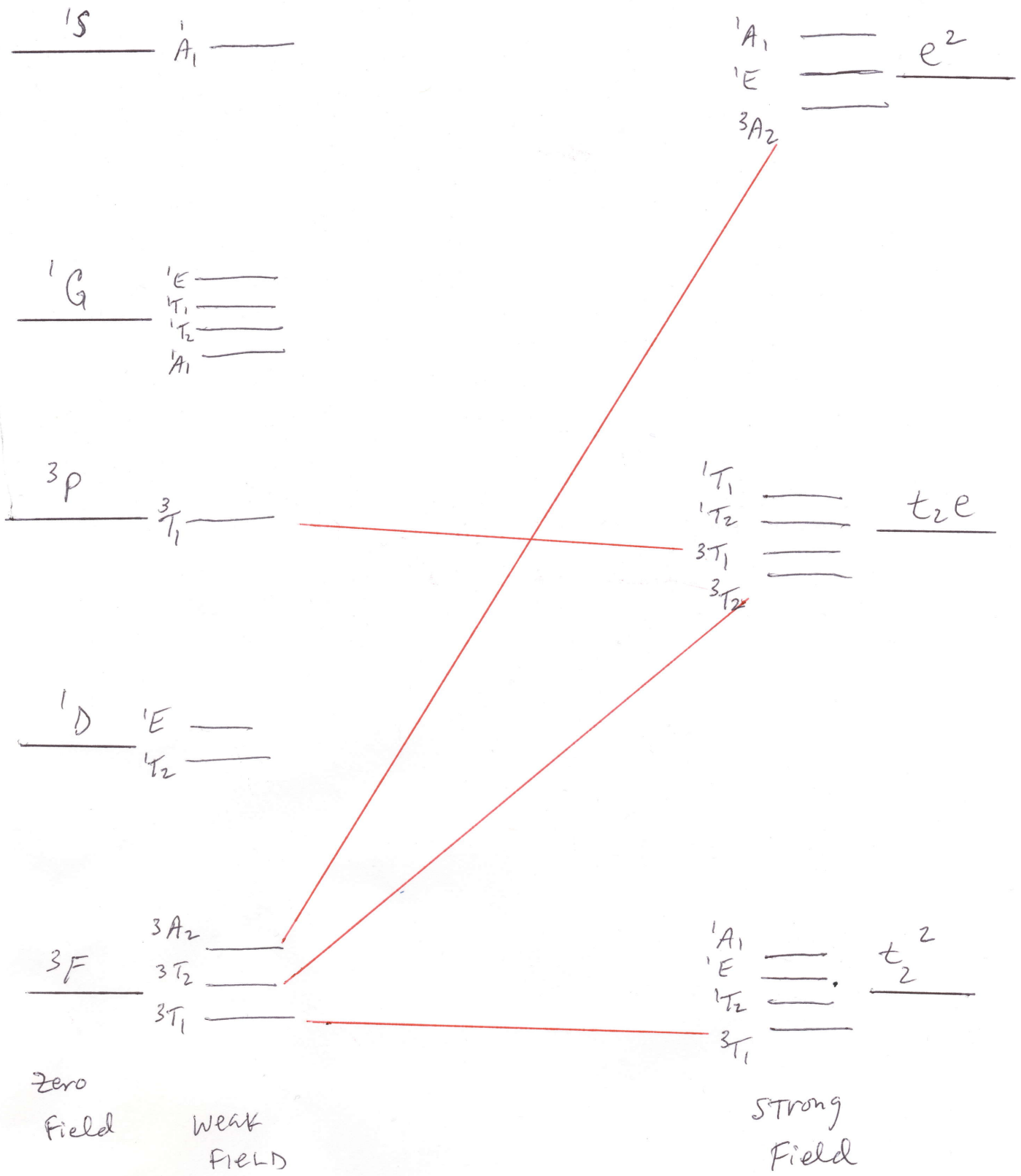


Correlation Diagram:
Energy Levels for a d^2 ion
(g subscripts omitted)

9/17
Tsb

See Wulfsberg Inorganic Chemistry p. 890

Racah Parameters

- Use more than one band to evaluate Δ_o
- Covalency in metal-ligand bonds

Equations for Energies of Free-Ion States

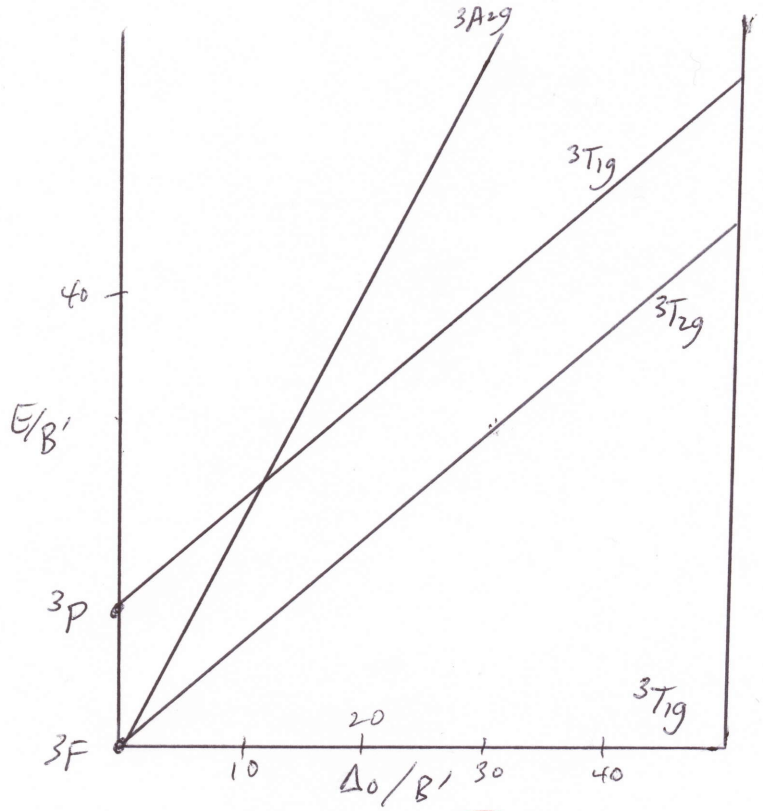
- quantum mechanical treatment of interelectronic repulsions
- Three types of quantum mechanical integrals called Racah parameters A, B, and C.

Racah Parameters for the d^2 case

$$E(^1S) = A + 14B + 7C$$
$$E(^1G) = A + 4B + 2C$$
$$E(^1D) = A - 3B + 2C$$
$$E(^3P) = A + 7B$$
$$E(^3F) = A - 8B$$

For Electronic Transitions

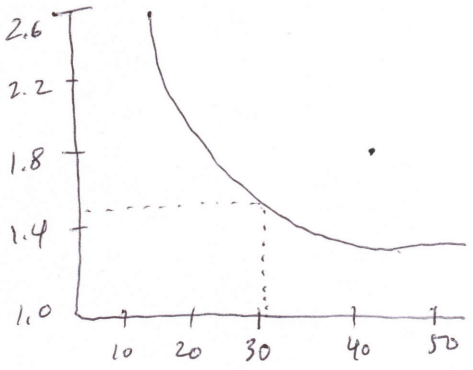
- Differences between state energies so A cancels out
- Differences between triplet states do not involve the C term
- 15 B is the energy difference between ^3P and ^3F
- B' (for weak field O_h) is less than B (for free ion) due to metal-ligand covalent bonding



Tanabe-Sugano Diagram for d^2 (similar to weak-field d^7)

- Here, $\nu_1 \neq \Delta_o$ due to config. interaction between $^3T_{1g}$ (F) and $^3T_{1g}$ (P). Both these states are slightly curved

- From the Tanabe-Sugano diagram, measure and plot the ν_1/ν_2 ratio vs. Δ_o/B':



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

$\nu_1 = 17,800\ cm^{-1}$

$\nu_2 = 25,700\ cm^{-1}$

$\nu_1/\nu_2 = 1.44 \Rightarrow \Delta_o/B = 31$

$\Rightarrow E/B' = 29$

At $\frac{\Delta_o}{B} = 31$

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

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

$\Delta_o = 31 \times B = 19,000\ cm^{-1}$ (pretty different from ν_1)

- d^1, $\nu_1 = {}^2T_{2g} \longrightarrow {}^2E_g$. This energy difference is Δ_o

  d^4 (high spin), d^6 (high spin), d^9

- d^3, d^8 note identical Tanabe-Sugano diagrams (but for the labels)

Value of $\Delta_o = ({}^4A_{2g} \rightarrow {}^4T_{2g})$, ν_1, for d^3

$= ({}^3A_{2g} \rightarrow {}^3T_{2g}) = \nu_1$ for d^8

The two triplet states at higher energy mix (configuration interaction) due to having the same symmetry, but an expression for B' can be derived:

$$15B' = \nu_3 + \nu_2 - 3\nu_1$$

The case of $[Ni(OH_2)_6]^{2+}$

Convert nm into cm^{-1} by dividing into 10^7:

	nm	cm^{-1}
ν_1	1176	8500
ν_2	649	15,400
ν_3	385	26,000

$\Delta_o = 8500\ cm^{-1}$

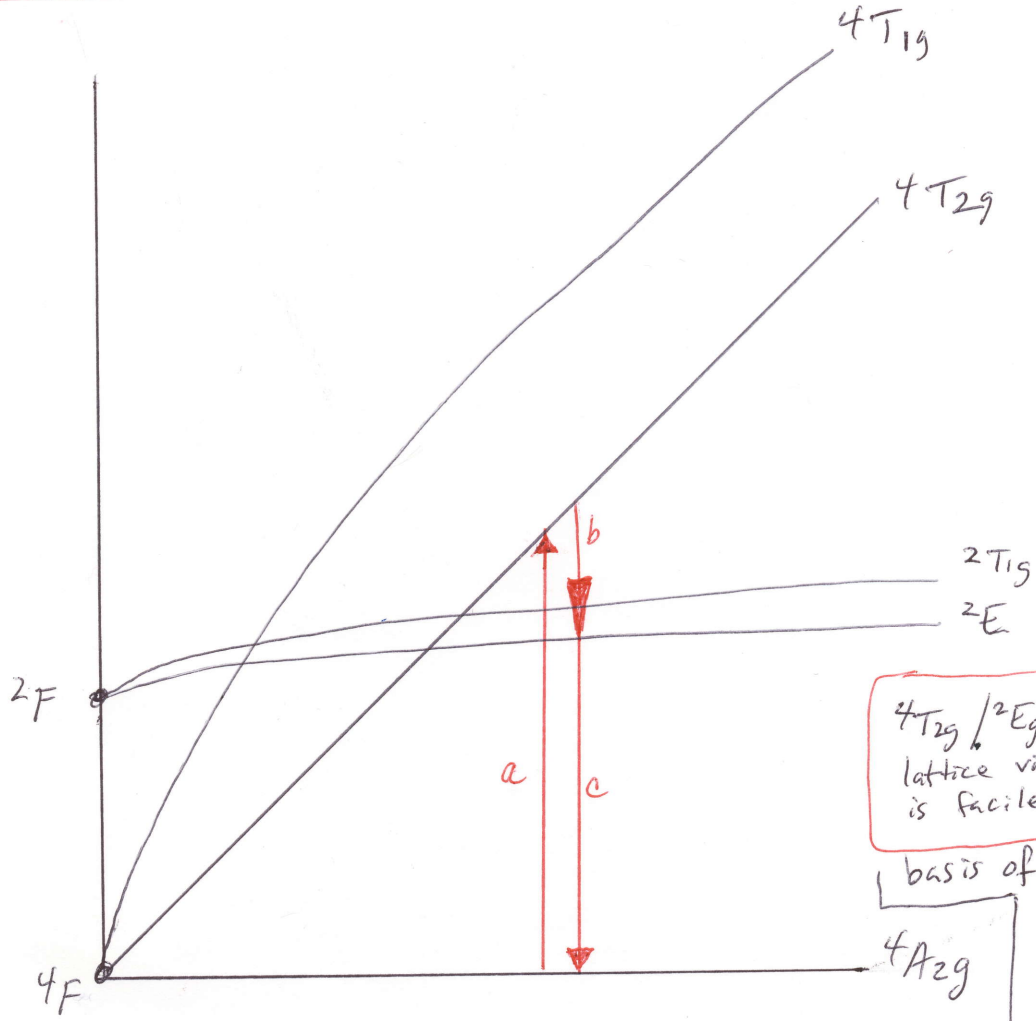
$B' = 1,060\ cm^{-1}$

Luminescence

- fluorescence, excited state is of same multiplicity as the ground state
- phosphorescence, excited state is of different multiplicity from the ground state
  [excited state long-lived in this case]

PARTIAL

Tanabe Sugano Diagram for d^3



$^4T_{2g}$ / ^2E_g gap matches lattice vib. mode so i.s.c. is facile

basis of ruby laser

694.3 nm into 10^7 is

a excitation of Cr^{3+} ion in ruby

b intersystem crossing

c phosphorescent light emission in ruby

ruby: Cr^{3+} substitution into corundum (Al_2O_3)

shorter than normal Cr–O distance

larger than usual Δ_o

$\Rightarrow$ red color

Sapphire: Ti^{3+} in corundum

$\Rightarrow$ blue

emerald: Cr^{3+} into beryl, $Be_3Al_2(SiO_3)_6$

Racah Parameters of Free Ions

		B (cm^{-1})
$3d^2$	Ti^{2+}	718
	V^{3+}	861
	Cr^{4+}	1039
d^3	Sc^{+}	480
	V^{2+}	766
	Cr^{3+}	918
	Mn^{4+}	1064
d^4	Cr^{2+}	830
	Mn^{3+}	1140
d^5	Mn^{2+}	960

Nephelauxetic Parameter β & Nephelauxetic Series

$$\beta = B'/B$$

for H_2O using $[V(OH_2)_6]^{3+}$ $\quad \beta = \frac{610}{861} = 0.71$

- Interelectronic repulsions are less in a complex than in the corresponding free ion

$F^- > H_2O > NH_3 > C_2O_4^{2-} > en > Cl^- > CN^- > Br > I^-$

↖ closest to $\beta = 1.0$.