Orgel Diagram

MSc Chemistry

Postgraduate Department of Chemistry

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- **Orgel diagrams are a special class of correlation diagrams developed by Leslie E. Orgel.**
- **Orgel diagrams are correlation diagrams showing the relative energies of electronic terms in transition metal complexes.**
- **Orgel diagrams are restricted to only weak field (high spin) cases, and offer no information about strong field (low spin) cases.**
- **It provide a convenient means of predicting the number of spin allowed absorption bands in a UV/visible spectrum for a complex along with their respective symmetry designations**
- **Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams.**
- **Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a Tanabe-Sugano diagram.**

Configuration		Term	Ground Term	Excited terms with the same spin multiplicity as ground term
Td	Oh			
d^9	d^1	^2D	$^2T_{2(g)}$	$^2E_{2(g)}$
d^8	d^2	^3F	$^3T_{1(g)}(F)$	$^3T_{2(g)}$, $^2A_{2(g)}$, $^3T_{1(g)}(P)$
d^7	d^3	^4F	$^4A_{2(g)}$	$^4T_{2(g)}$, $^4T_{1(g)}(F)$, $^4T_{1(g)}(P)$
d^6	d^4	^5D	$^5E_{2(g)}$	$^5T_{2(g)}$
d^5	d^5	^6S	$^6A_{1(g)}$	None
d^4	d^6	^5D	$^5T_{2(g)}$	$^5E_{2(g)}$
d^3	d^7	^4F	$^4T_{1(g)}(F)$	$^4T_{2(g)}$, $^4A_{2(g)}$, $^4T_{1(g)}(P)$
d^2	d^8	^3F	$^3A_{2(g)}$	$^3T_{2(g)}$, $^3T_{1(g)}(F)$, $^3T_{1(g)}(P)$
d^1	d^9	^2D	$^2E_{2(g)}$	$^2T_{2(g)}$

Configuration	
Td	Oh
d^9	d^1
d^8	d^2
d^7	d^3
d^6	d^4
d^5	d^5
d^4	d^6
d^3	d^7
d^2	d^8
d^1	d^9

Inverse relationship is viewed here, because a tetrahedral field is a negative octahedral field.

Configuration		Term
Td	Oh	
d^9	d^1	^2D
d^8	d^2	^3F
d^7	d^3	^4F
d^6	d^4	^5D
d^5	d^5	^6S
d^4	d^6	^5D
d^3	d^7	^4F
d^2	d^8	^3F
d^1	d^9	^2D

Table 18.2 Splitting of Spectroscopic States in a Ligand Field[a].

Gaseous Ion spectroscopic state	Components in an octahedral field	Total degeneracy
S	A_{1g}	1
P	T_{1g}	3
D	$E_g + T_{2g}$	5
F	$A_{2g} + T_{1g} + T_{2g}$	7
G	$A_{1g} + E_g + T_{1g} + T_{2g}$	9
H	$E_g + 2\,T_{1g} + T_{2g}$	11
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2\,T_{2g}$	13

[a]*Ligand field states have the same multiplicity as the spectroscopic state from which they arise.*

Configuration		Term	Ground Term
Td	Oh		
d^9	d^1	^2D	$^2T_{2(g)}$
d^8	d^2	^3F	$^3T_{1(g)}$ (F)
d^7	d^3	^4F	$^4A_{2(g)}$
d^6	d^4	^5D	$^5E_{2(g)}$
d^5	d^5	^6S	$^6A_{1(g)}$
d^4	d^6	^5D	$^5T_{2(g)}$
d^3	d^7	^4F	$^4T_{1(g)}$ (F)
d^2	d^8	^3F	$^3A_{2(g)}$
d^1	d^9	^2D	$^2E_{2(g)}$

Hole formalism

A d^9 system can be considered as the inverted d^1 system as far as energy levels can be considered because d^9 system has an electron vacancy, which is called a ' hole'.

Similarly, d^8 system is considered as inverted d^2 system as far as the energy levels are considered. This is called hole formalism.

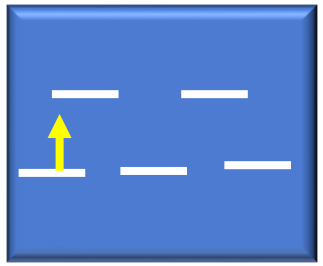
In short, an inverted energy level relationship exists between d^n and d^{10-n} systems.

Hence, with the help of only these two diagrams, all the d^n energy level diagrams can be explained in terms of d^1 and d^2 systems as given below:

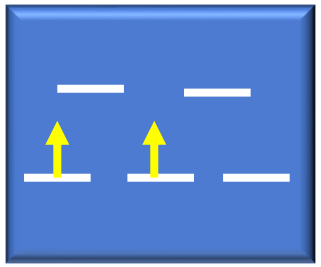
$d^9 = d^{10-1}$ = inverted d^1 system

$d^8 = d1^{0-2}$ = inverted d^2 system

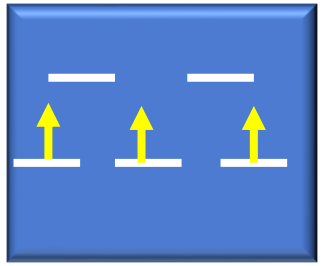
Determination of Ground state



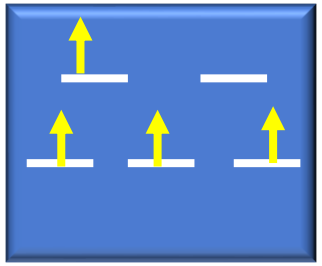
$d^1 = {}^2T_{2g}$



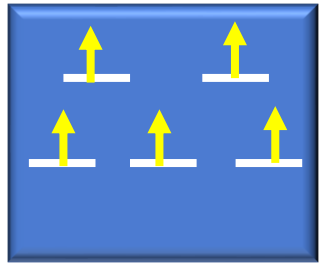
$d^2 = {}^3T_{1g}$



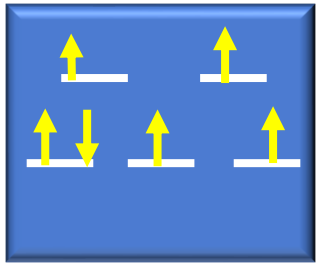
$d^3 = {}^4A_{2g}$



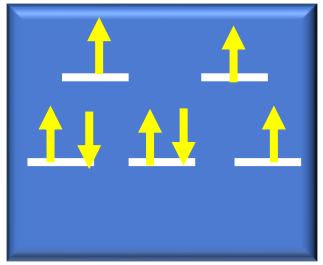
$d^4 = {}^5E_{2g}$



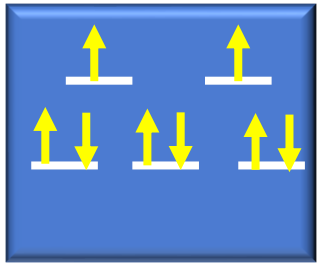
$d^5 = {}^6A_{1g}$



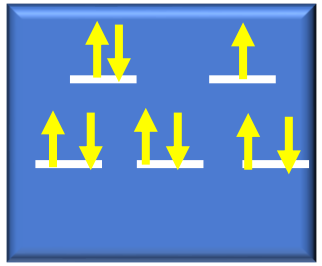
$d^6 = {}^5T_{2g}$



$d^7 = {}^4T_{1g}$



$d^8 = {}^3A_{2g}$

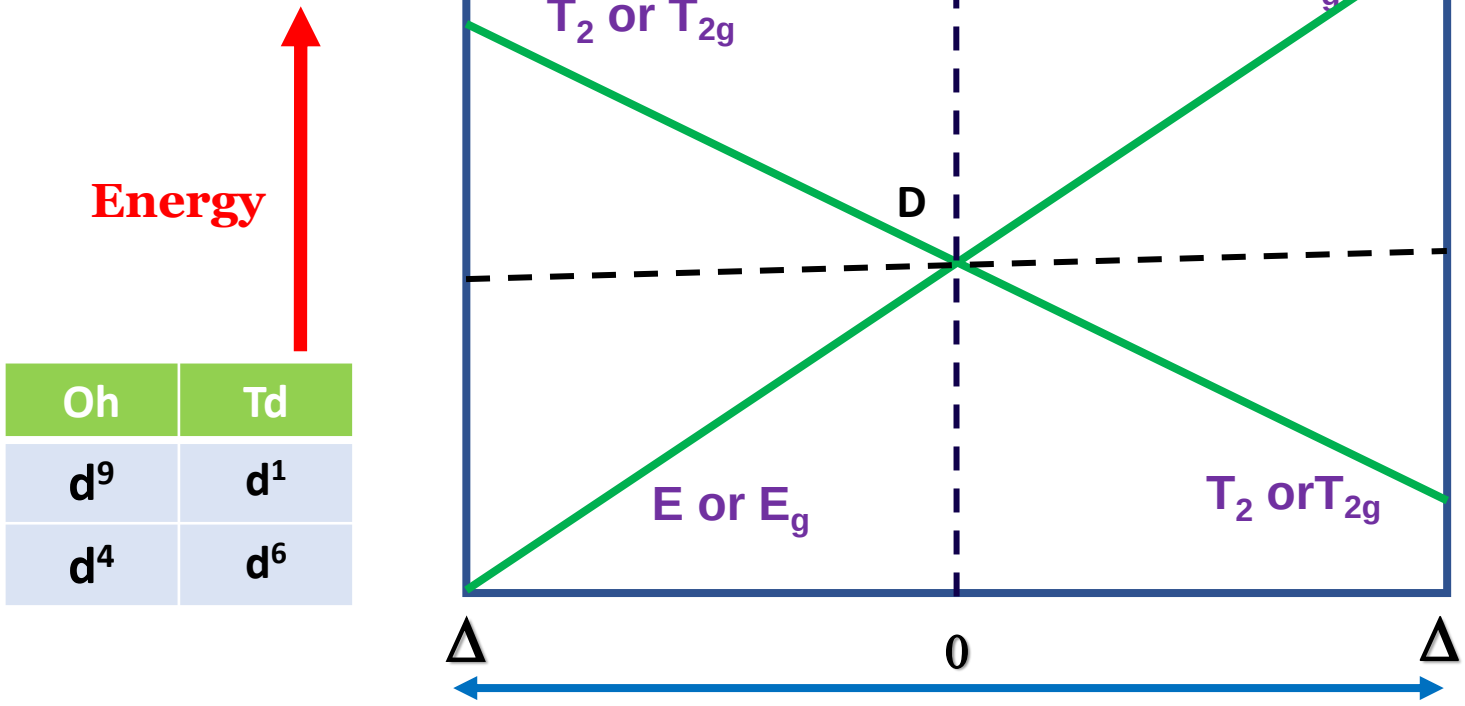


$d^9 = {}^2E_{2g}$

Configuration		Term	Ground Term	Excited terms with the same spin multiplicity as ground term
Td	Oh			
d^9	d^1	^2D	$^2T_{2(g)}$	$^2E_{2(g)}$
d^8	d^2	^3F	$^3T_{1(g)}(F)$	$^3T_{2(g)}$, $^2A_{2(g)}$, $^3T_{1(g)}(P)$
d^7	d^3	^4F	$^4A_{2(g)}$	$^4T_{2(g)}$, $^4T_{1(g)}(F)$, $^4T_{1(g)}(P)$
d^6	d^4	^5D	$^5E_{2(g)}$	$^5T_{2(g)}$
d^5	d^5	^6S	$^6A_{1(g)}$	None
d^4	d^6	^5D	$^5T_{2(g)}$	$^5E_{2(g)}$
d^3	d^7	^4F	$^4T_{1(g)}(F)$	$^4T_{2(g)}$, $^4A_{2(g)}$, $^4T_{1(g)}(P)$
d^2	d^8	^3F	$^3A_{2(g)}$	$^3T_{2(g)}$, $^3T_{1(g)}(F)$, $^3T_{1(g)}(P)$
d^1	d^9	^2D	$^2E_{2(g)}$	$^2T_{2(g)}$

Orgel diagram for d^1, d^4, d^6, d^9 ions in Oh and Td fields

$d^1 \equiv d^6$ $\qquad$ $d^4 \equiv d^9$

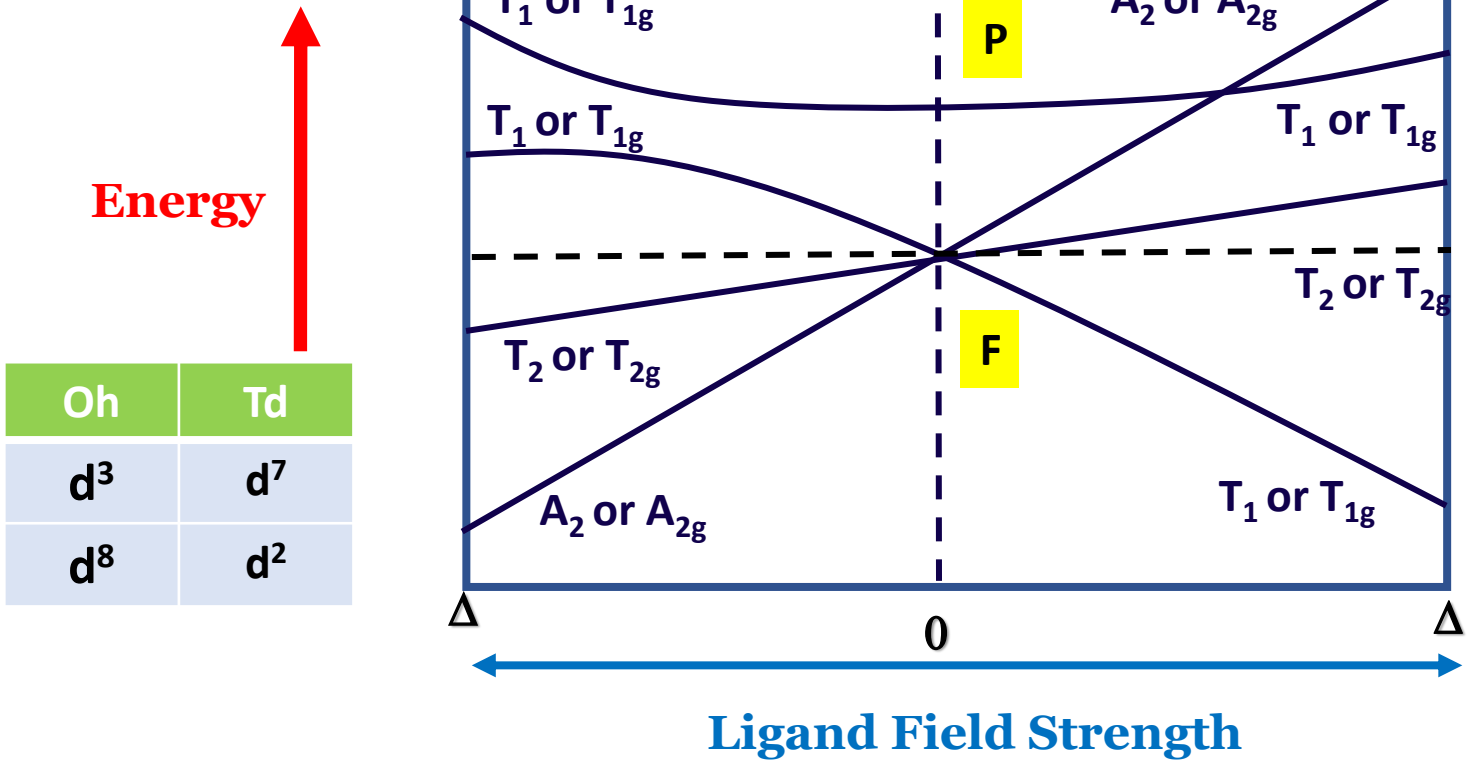


Oh	Td
d^9	d^1
d^4	d^6

Oh	Td
d^1	d^9
d^6	d^4

Orgel diagram for d^2, d^3, d^7, d^8 ions in Oh and Td fields

$d^2 \equiv d^7$ $\qquad$ $d^3 \equiv d^8$

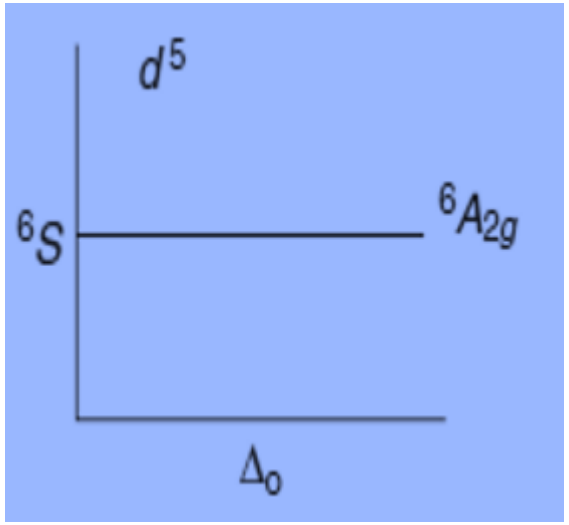


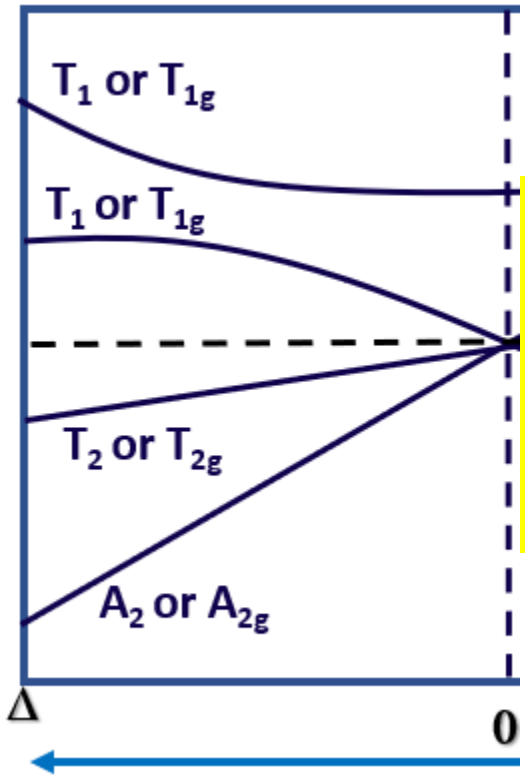
Oh	Td
d^3	d^7
d^8	d^2

Oh	Td
d^2	d^8
d^7	d^3

Special Case of d^5 ion

- The lowest energy term for the free ion is a ^6S ; this splits in a weak oh field to produce $^6 A_{1g}$ ground state.
- This is the only state on the diagram with multiplicity of six.
- This implies that for a d^5 oh complex, all transitions are not only Laporte forbidden, but also spin- forbidden.
- Transitions which are doubly-forbidden produce extremely weak absorption bands & their extinction coefficients are several hundred times smaller than those for singly forbidden transitions.
- This is evidenced by the colourlessness of dilute solutions of Mn^{2+} species.
- Only at high concentrations Mn^{2+} complexes show a faint pink colour ; it is because of vibronic coupling.





- **The lines of T_{1g} (F) and T_{1g} (P) states curve away from each other due to quantum mechanical non crossing rule in the orgel diagram for the d^2 configuration.**
- **Thus the terms of same symmetry will never cross and repel each other**

Q 1

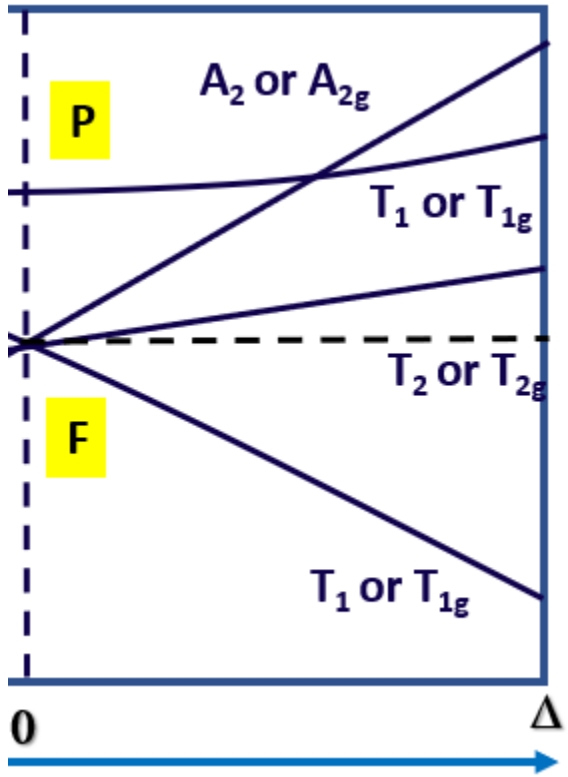
The spectroscopic ground state symbol and the total number of electronic transitions of $[Ti(H_2O)_2]^{2+}$ are

a) $^3T_{1g}$ and 2

b) $^3A_{2g}$ and 3

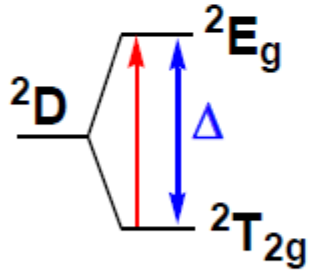
c) $^3T_{1g}$ and 3

d) $^3A_{2g}$ and 3



d^1 Ti^{3+}

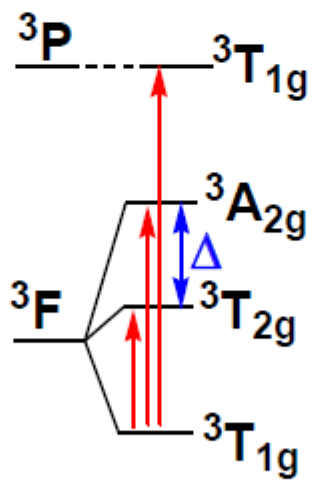
^2D



one transition

d^2 V^{3+}

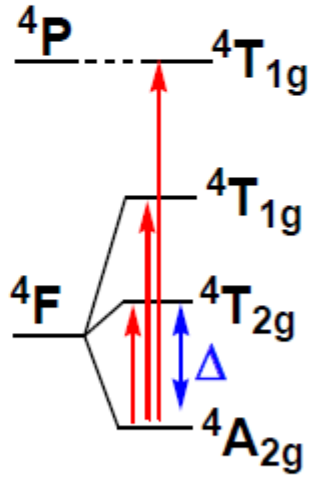
^3F



three transitions

d^3 Cr^{3+}

^4F



three transitions

Exercise: Determine the ground term for d^2, d^6, und d^8 ions in tetrahedral ligand fields!

Solution

Ground terms: $^3F(d^2)$, $^5D(d^6)$, $^3F(d^8)$

The splitting pattern in tetrahedral field is inverted to that in an octahedral field, hence

Splitting :

$^3F \Rightarrow {}^3A_2 < {}^3T_2 < {}^3T_1$

$^5D \Rightarrow {}^5E < {}^5T_2$

$^3F \Rightarrow {}^3T_1 < {}^3T_2 < {}^3A_2$

Exercise: For octahedral $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ one observes the following bands (in cm^{-1}):
$[Ni(H_2O)_6]^{2+}$: 8700, 14500, 25300,
$[Ni(NH_3)_6]^{2+}$: 10700, 17500, 28300

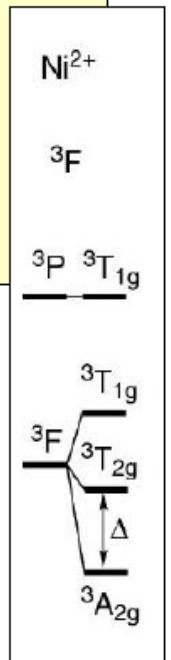
a) Assign the bands
b) Calculate $10Dq$ *(or* Δ_o*)*.
c) Comment on the different position of bands for the two complexes.

Solution:

a) $Ni^{2+} = d^8$, =>		H_2O	NH_3
Laporte-forbidden, spin-allowed bands:	$^3A_{2g} \rightarrow {}^3T_{2g}$,	8700 cm^{-1}	10700 cm^{-1}
	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F),	14500 cm^{-1}	17500 cm^{-1}
	$^3A_{2g} \rightarrow {}^3T_{1g}$(P),	25300 cm^{-1}	28300 cm^{-1}

b) Δ_o refers to the energy of the $^3A_{2g} \rightarrow {}^3T_{2g}$ - transitions
$\Delta_o = 10\ D_q = 8700\ cm^{-1}$, $D_q = 870\ cm^{-1}$ (aqua complex)
$\Delta_o = 10\ D_q = 10700\ cm^{-1}$, $D_q = 1070\ cm^{-1}$ (ammin complex)

c) NH_3 has a stronger ligand field than H_2O.



Assignment

a) What is the ground term for $[Co(NH_3)_4]^{2+}$?
b) How many electronic absorption bands are expected? Assign them?
c) If the band with the lowest energy appears at 7500 cm^{-1}, how large is Δt?
d) Co^{2+} also forms an octahedral complex $[Co(NH_3)_6]^{2+}$. Identify its ground term. How large is Δ_o?

The electronic spectra of an aqueous solution of $[Ni(en)_3]2+$ exhibits broad absorptions with λ max= 325, 550 and 990 nm.