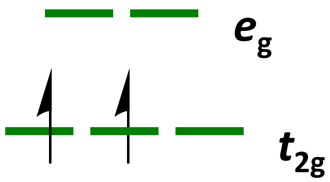
Finding of Ground / Excited Term State for d^n electronic configuration under Octahedral / Tetrahedral Symmetry

d^2 under Octahedral / Tetrahedral Symmetry

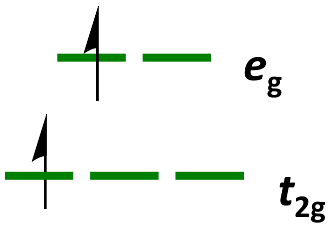
d^n	Ground Term	Splitting (O_h)	Splitting (T_d)	Other Terms
d^2	^3F	$^3T_{1g} + ^3T_{2g} + ^3A_{2g}$	$^3T_1 + ^3T_2 + ^3A_2$	^3P: $(^3T_{1g})$ / $(^3T_1)$

Microstates: $^3F \rightarrow 21 \rightarrow Oh \rightarrow {}^3T_{1g} + {}^3T_{2g} + {}^3A_{2g} \rightarrow 3 \times 3 + 3 \times 3 + 3 \times 1 = 21$

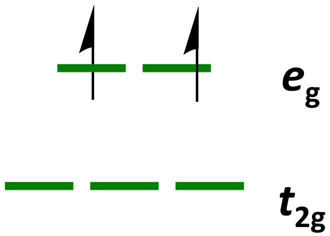
- At first glance, it appears that a *d*² octahedral complex can undergo two electronic transitions



ground configuration



1st excited configuration



2nd excited configuration

number of arrangements: 3 6 1

⇓

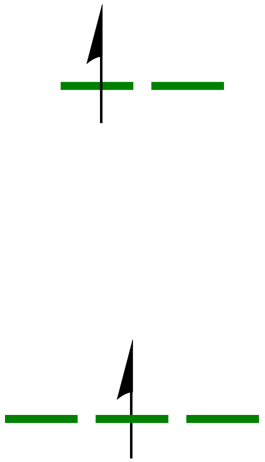
$(d_{xy})^1 (d_{xz})^1 (d_{yz})^0$

$(d_{xy})^1 (d_{xz})^0 (d_{yz})^1$

$(d_{xy})^0 (d_{xz})^1 (d_{yz})^1$

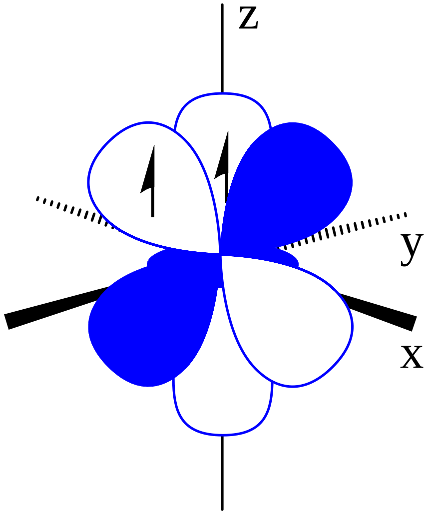
⇒ In an octahedral filed the electronic configuration $t_{2g}^2 e_g$. Thus three arrangements are possible for t_{2g} electron

- However, the 6 arrangements in the 1st excited configuration do not have the same energy
- Consider two arrangements: $(d_{z2})^1(d_{xz})^1$ and $(d_{z2})^1(d_{xy})^1$
    - ➢ they differ in energy due to the repulsion between the d electrons
    - ➢ there is more crowding of the electron density for $(d_{z2})^1(d_{xz})^1$
    - ➢ energy of $(d_{z2})^1(d_{xz})^1 > (d_{z2})^1(d_{xy})^1$

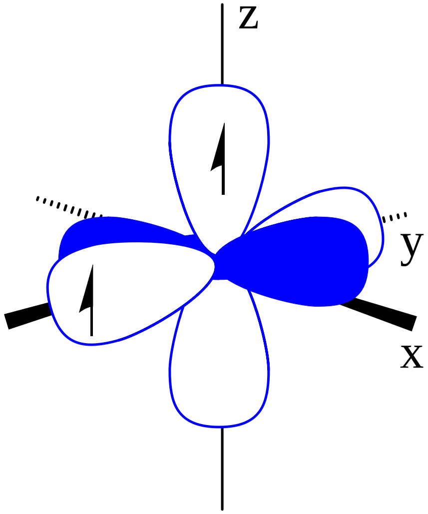


$e_g = d_{z^2}, d_{x^2-y^2}$

$t_{2g} = d_{xy}, d_{xz}, d_{yz}$



$(d_{z2})^1(d_{xz})^1$



$(d_{z}2)^1(d_{xy})^1$

- **The 6 arrangements in the 1st excited configuration can be grouped into two sets – those with low and with high interelectron repulsion**

$(d_{z}2)^1(d_{xz})^1$

$(d_{z}2)^1(d_{yz})^1$

$(d_{x}2_{-y}2)^1(d_{xy})^1$

Electrons are in close proximity lobes overlap, large electron repulsion - Higher energy state ($^3T_{1g}$)

$(d_{x}2_{-y}2)^1(d_{xz})^1$

$(d_{x}2_{-y}2)^1(d_{yz})^1$

$(d_{z}2)^1(d_{xy})^1$

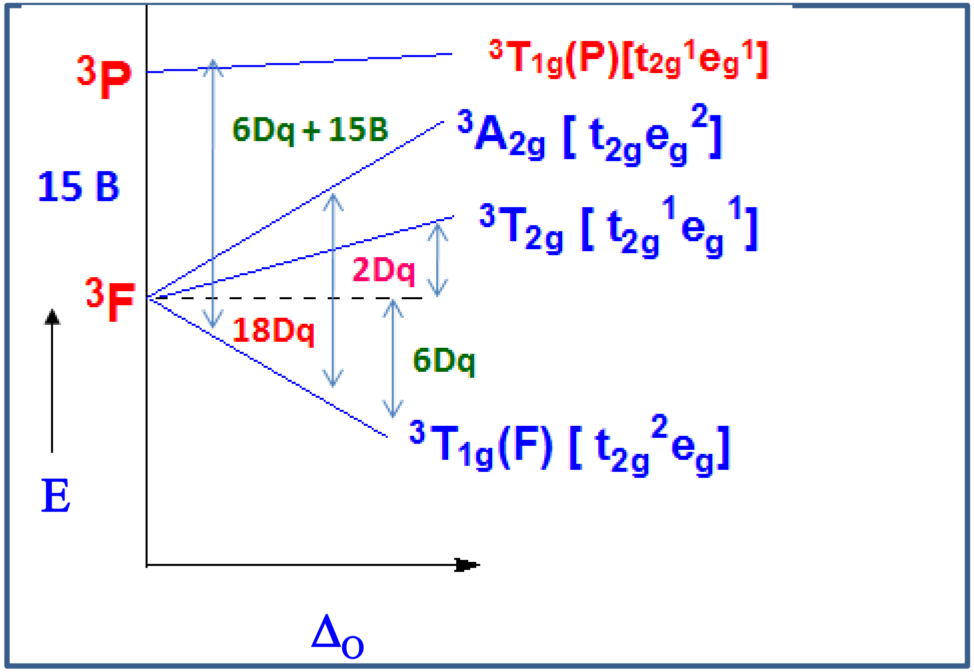
Electrons are nor in close proximity lobes far apart, small electron repulsion – Lower energy state ($^3T_{2g}$)

Thus two triplets ($^3T_{1g}$ + $^3T_{2g}$) are available. Among them the $^3T_{2g}$ is energetically lower that $^3T_{1g}$. It is believed that $^3T_{1g}$ is associated with the ^3P term of the free ion and normally defined as $^3T_{1g}(P)$.

The second exited state will be a singlet state i,e, $^3A_{2g}$. The electronic state associated with $^3A_{2g}$ state is $t_{2g}e_g{}^2$.

So the order of energies of the states : $^3T_{1g}(F) < {}^3T_{2g} < {}^3A_{2g} < {}^3T_{1g}(P)$

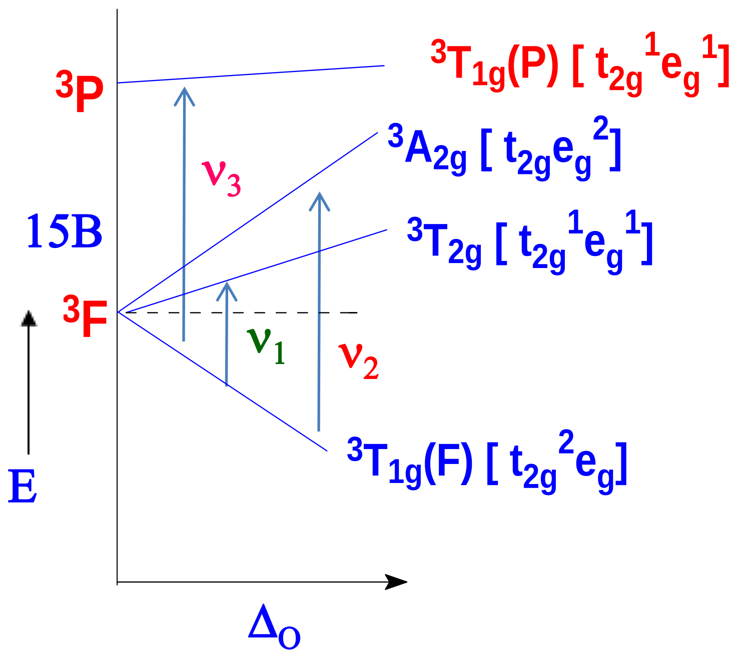
The energy level diagram (simple form)



$E_{3F} - E_{3p} = \Delta E = 15$ B

B is the Racah parameter and is a measure of inter-electron repulsion within the whole ion

Electronic Transitions



1. $\nu_1(^3T_{1g}(F) \rightarrow {}^3T_{2g}) = 8$ Dq
2. $\nu_2(^3T_{1g}(F) \rightarrow {}^3A_{2g}) = 18$ Dq
3. $\nu_3(^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)) = 15B + 6$ Dq

$$\nu_2 - \nu_1 = 10 \text{ Dq}$$

d^2 (Tetrahedral Complex)

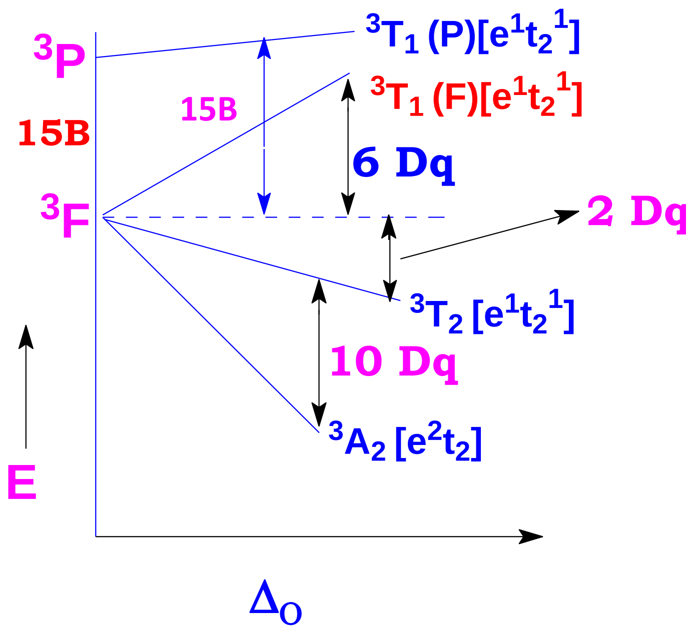
Ground State Configuration: e^2t_2

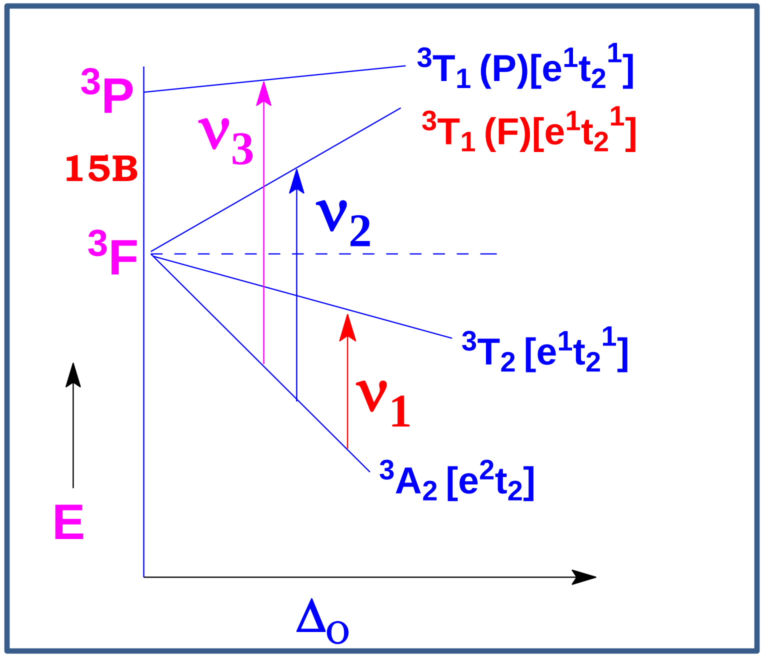
	e^2t_2	$\rightarrow$ $e^1t_2^1$	$\rightarrow$ et_2^2
States	$^3A_2$	$^3T_2 + {}^3T_1(F)$	$^3T_1(P)$

The calculated energy sequence is as follows

$^3A_2 < {}^3T_2 < {}^3T_1(F) < {}^3T_1(P)$

The energy level diagram is shown below



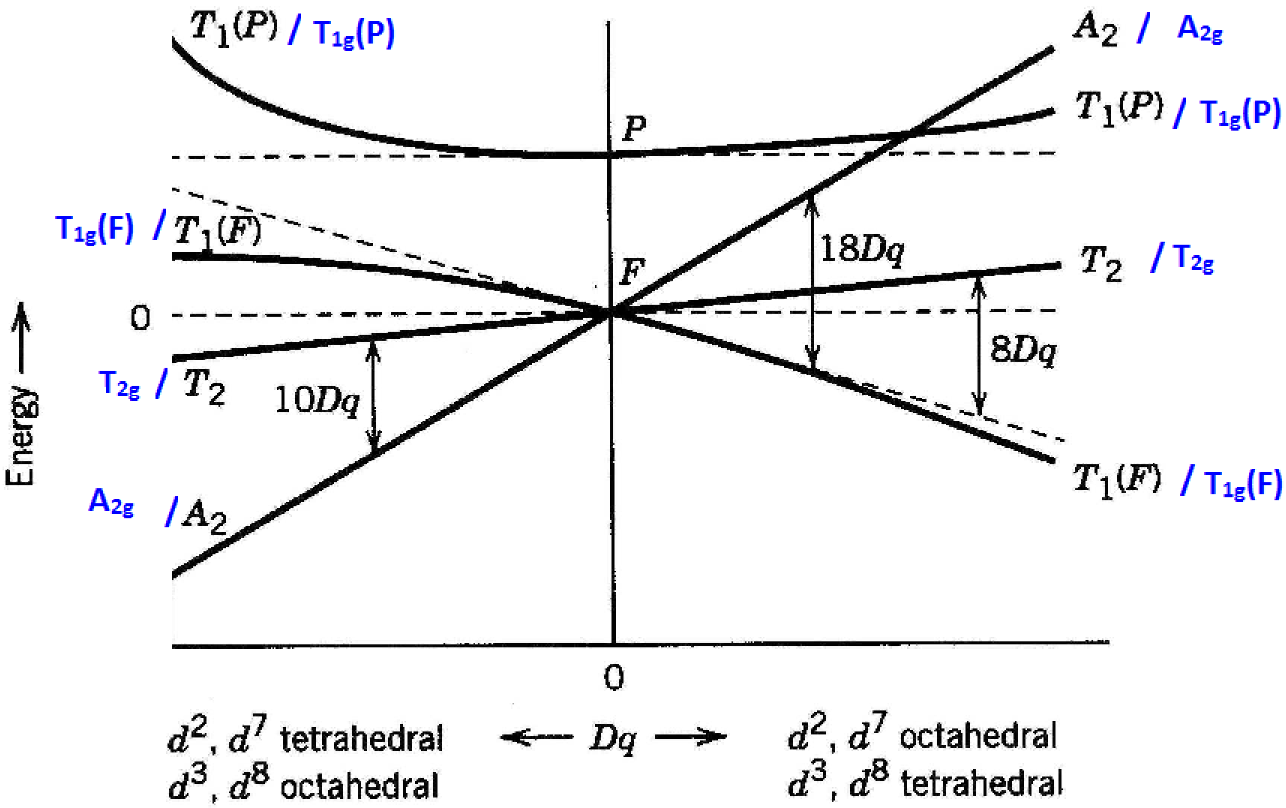


(1). ν_1 ($^3A_2 \rightarrow {}^3T_2$ = 10 Dq

(2). ν_2 ($^3A_2 \rightarrow {}^3T_1$ (F)) = 18 Dq

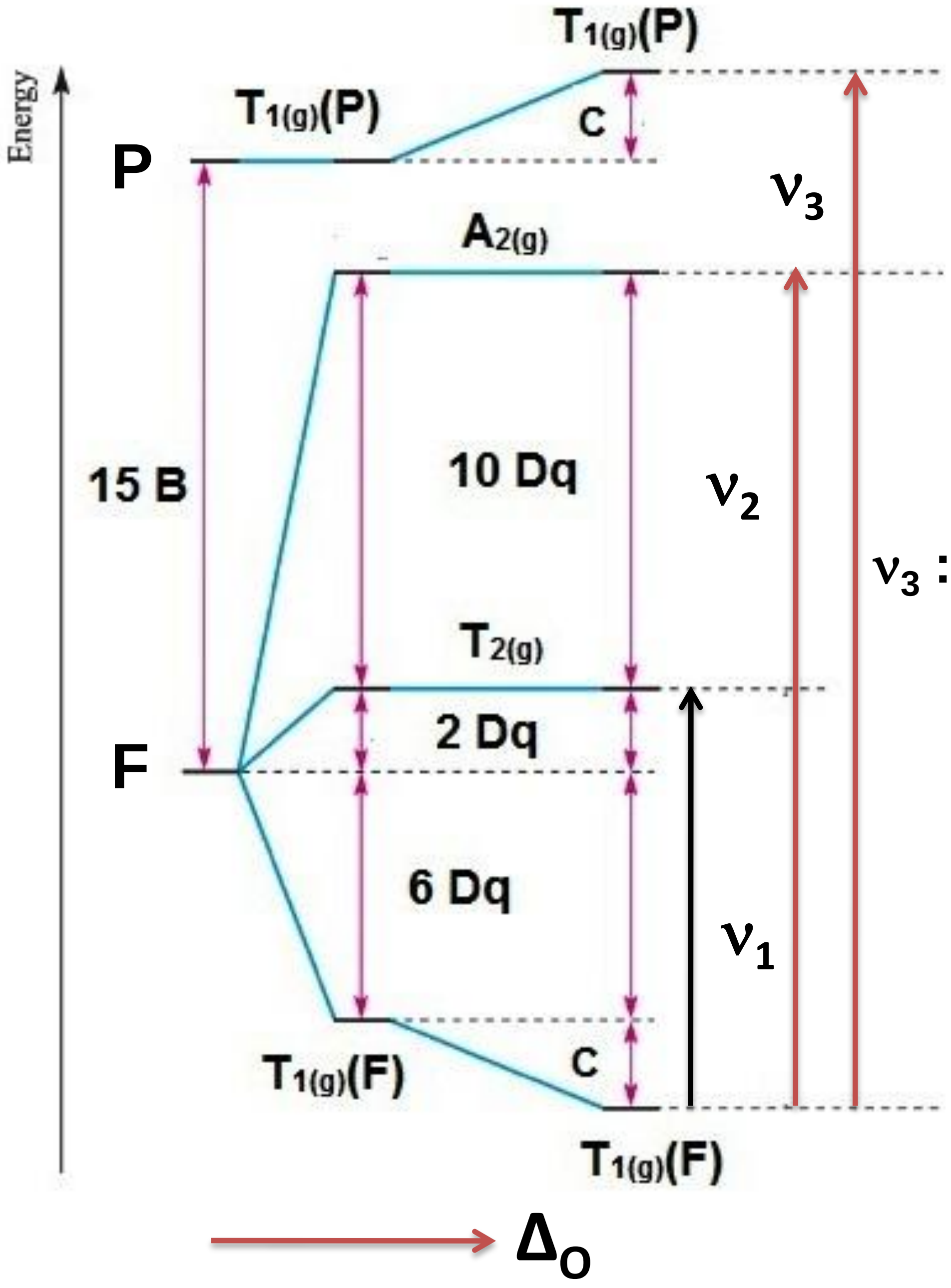
(3). ν_3($^3A_2 \rightarrow {}^3T_1$(P)) = 15B + 12 Dq

d^n	Symm-etry	Ground	One electron Excitation	Two electron Excitation	Energy Sequence
d^2	O_h	$t_{2g}^{2}e_g$	$t_{2g}^{1}e_g^{1}$	$t_{2g}e_g^{2}$	$^3T_{1g}(F) < {}^3T_{2\,g} < {}^3A_{2g} < {}^3T_{1g}(P)$
		$^3T_{1g}(F)$	$^3T_{2g} + {}^3T_{1g}(P)$	$^3A_{2g}$	
d^2	T_d	e^2t_2	$e^1t_2^{1}$	et_2^{2}	$^3A_2 < {}^3T_2 < {}^3T_1(F) < {}^3T_1(P)$
		$^3A_2$	$^3T_2 + {}^3T_1(F)$	$^3T_1(P)$	
d^7	O_h	$t_{2g}^{5}e_g^{2}$	$t_{2g}^{4}e_g^{3}$	$t_{2g}^{3}e_g^{3}$	$^4T_{1g}(F) < {}^4T_{2\,g} < {}^4A_{2g} < {}^4T_{1g}(P)$
		$^4T_{1g}(F)$	$^4T_{2g} + {}^4T_{1g}(P)$	$^4A_{2g}$	
d^7	T_d	$e^4t_2^{3}$	$e^3t_2^{4}$	$e^2t_2^{5}$	$^4A_2 < {}^4T_2 < {}^4T_1(F) < {}^4T_1(P)$
		$^4A_2$	$^4T_2 + {}^4T_1(F)$	$^4T_1(P)$	
d^3	O_h	$t_{2g}^{3}e_g$	$t_{2g}^{2}e_g^{1}$	$t_{2g}^{1}e_g^{2}$	$^4A_{2g} < {}^4T_{2g} < {}^4T_{1g}(F) < {}^4T_{1g}(P)$
		$^4A_{2g}$	$^4T_{2g} + {}^4T_{1g}(F)$	$^4T_{1g}(P)$	
d^3	T_d	$e^2t_2^{1}$	$e^1t_2^{2}$	et_2^{3}	$^4T_1(F) < {}^4T_2 < {}^4A_2 < {}^4T_1(P)$
		$^4T_1(F)$	$^4T_2 + {}^4T_1(P)$	$^4A_2$	
d^8	O_h	$t_{2g}^{6}e_g^{2}$	$t_{2g}^{5}e_g^{3}$	$t_{2g}^{4}e_g^{4}$	$^3A_{2g} < {}^3T_{2g} < {}^3T_{1g}(F) < {}^3T_{1g}(P)$
		$^4A_{2g}$	$^4T_2 + {}^4T_1(F)$	$^4T_{1g}(P)$	
d^8	T_d	$e^4t_2^{4}$	$e^3t_2^{5}$	$e^2t_2^{6}$	$^3T_1(F) < {}^3T_2 < {}^3A_2 < {}^3T_1(P)$
		$^3T_1(F)$	$^3T_2 + {}^3T_1(P)$	$^3A_2$	



1. d^n (O_h) and $d^{n\pm5}$ (O_h) have the same diagram
2. d^n (T_d) and $d^{n\pm5}$ (T_d) have the same diagram
3. d^n, $d^{n\pm5}$ (O_h) is the reverse of d^n, $d^{n\pm5}$ (T_d), and vice versa
4. d^n (O_h) is the reverse of $d^{10\text{-}n}$ (O_h), and d^n (T_d) is the reverse of $d^{10\text{-}n}$ (T_d)

d^3 & d^8 in O_h and d^2 & d^7 in T_d



$\nu_1 : T_{1(g)}(F) \rightarrow T_{2(g)} = 8\ Dq + C$

$\nu_2 : T_{1(g)}(F) \rightarrow A_{2(g)} = 18\ Dq + C$

$\nu_3 : T_{1(g)}(F) \rightarrow T_{1(g)}(P) = 6\ Dq + 15B + 2C$

B = Racah parameter

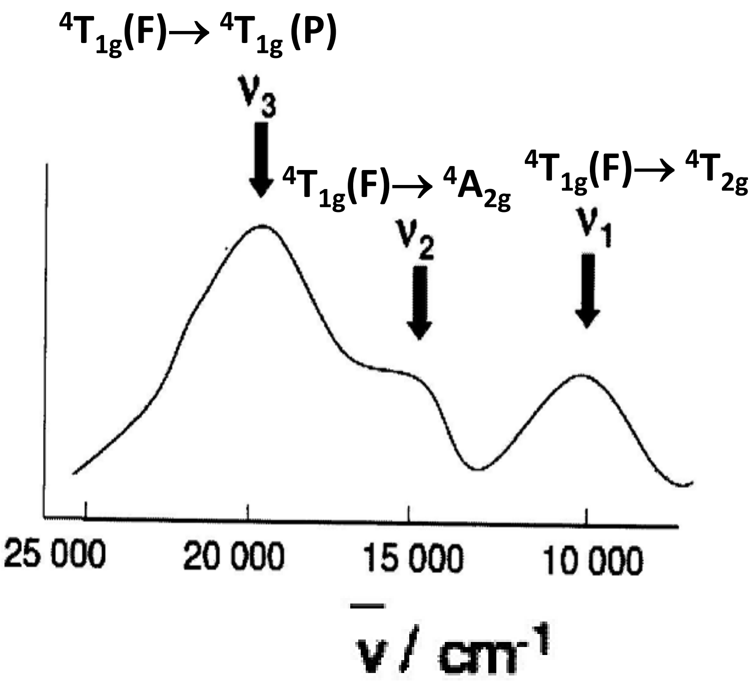
C = Configurational interaction

$\nu_2 - \nu_1 = 10\ Dq$

$\nu_2 - 18\ Dq = C$

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

Spectra of $[Co(H_2O)_6]^{2+}$



In the complex Co^{2+} is a d^7 system. The electronic configuration in high spin octahedral geometry is $t_{2g}^5e_g^2$. Here two electron excitations are possible having the same spin multiplicity

$$t_{2g}^5e_g^2 \rightarrow t_{2g}^4e_g^3 \rightarrow t_{2g}^3e_g^4$$

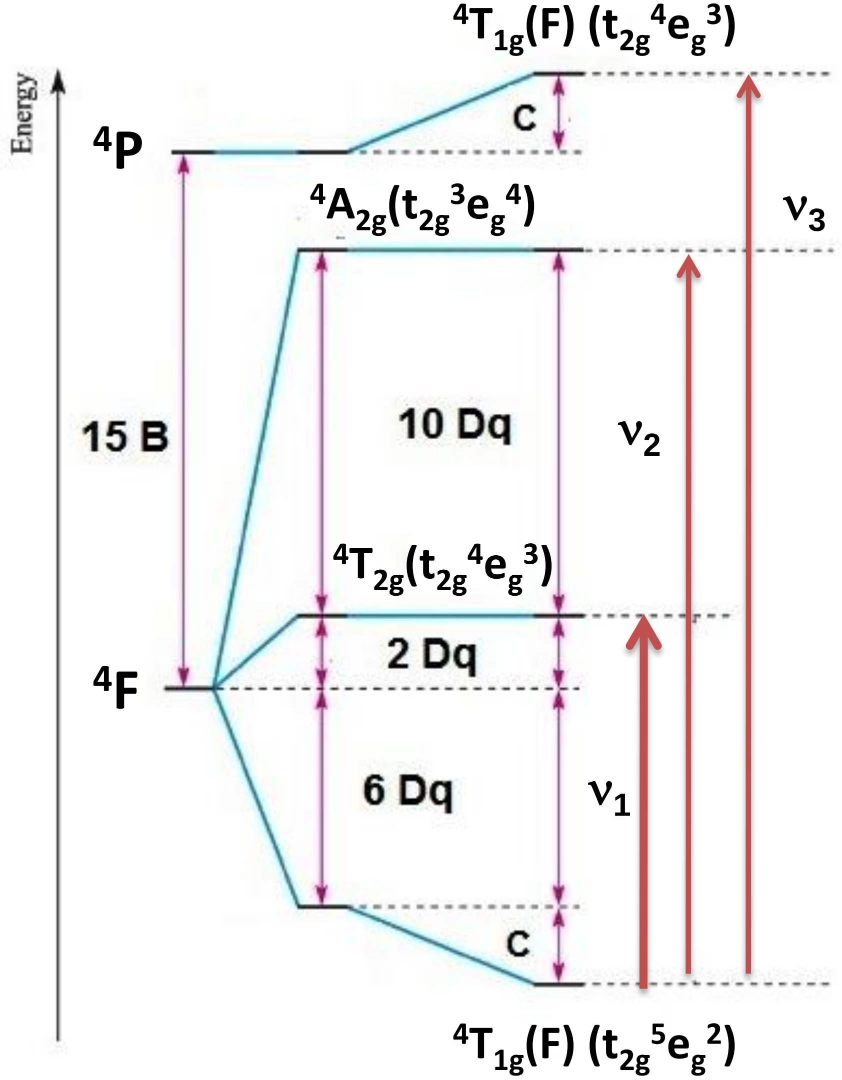
The ground term symbol of free d^7 is ^4F and the other higher energy state is ^4P. In an octahedral field the two terms spilt into $^4T_{1g}$(F) (ground state) and he excited states $^4T_{1g}$(F) (ground state) and he excited states $^4T_{1g}$(F) (ground state) and he excited states $^4T_{2g}$, $^4A_{2g}$ and $^4T_{1g}$(P) respectively. The energy level is shown in the diagram.

Three bands are expected in case of high spin complex. The spectrum consists of three bands found at 8000 cm^{-1}, 16800 cm $^{-1}$ and 20000 cm^{-1} respectively. The bands are assigned as follows

ν_1 : $T_{1(g)}(F) \rightarrow T_{2(g)}$ = 8 Dq + C = 8800 cm^{-1};

ν_2 : $T_{1(g)}(F) \rightarrow A_{2(g)}$ = 18 Dq + C = 16800 cm^{-1}

ν_3 : $T_{1(g)}(F) \rightarrow T_{1(g)}(P)$ = 6 Dq +15B +2C = 20000 cm^{-1}



$$\nu_2 - \nu_1 = 10\,Dq = \Delta_O = 8800\ cm^{-1}$$

$$Dq = 880\ cm^{-1}$$

$$\nu_2 - 18\,Dq = C$$

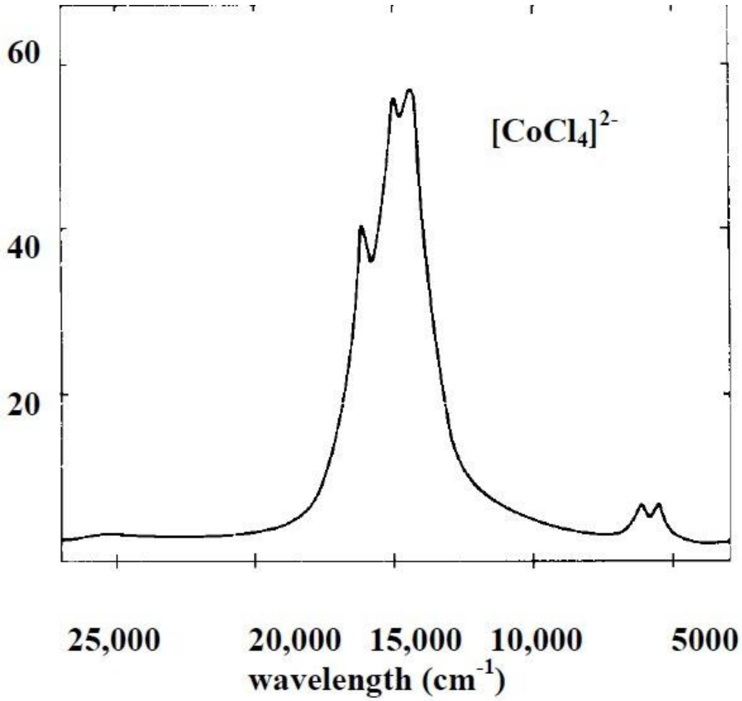
$$16800\ cm^{-1} - (18 \times 880)\ cm^{-1} = C$$

$$C = 960\ cm^{-1}$$

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

$$(20000 + 16800 - 24000)\ cm^{-1} = 15\,B$$

$$B = 854\ cm^{-1}$$



In the tetrahedral case, using Δt =4/9 Δo then we predict that the transition

$$^4T_2 \longleftarrow {}^4A_2$$

should be observed below 4000 cm^{-1}. Only 2 bands are seen and they occur at 5,800 and 15,000 cm^{-1}. (ε value for the 15,000 band is ~60 m^2 mol^{-1}). The first must therefore correspond to

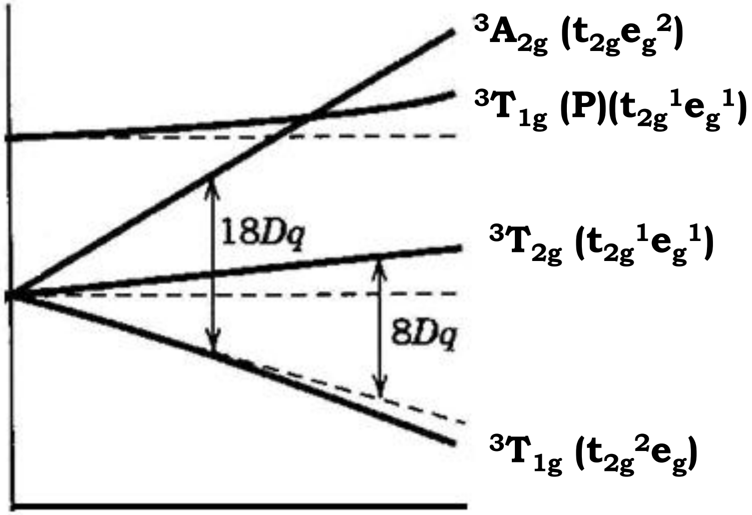
$$^4T_1(F) \longleftarrow {}^4A_2$$

and the second to

$$^4T_1(P) \longleftarrow {}^4A_2$$

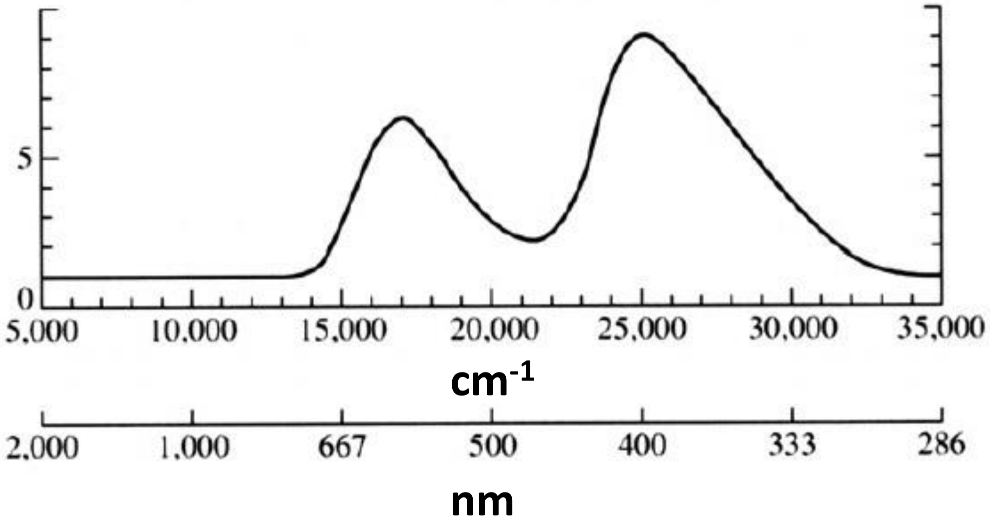
Transitions for $[V(H_2O)_6]^{3+}$, d^2

Complex	$^3T_{1g}(F) \rightarrow {}^3T_{2g}$ (cm^{-1})	$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ (cm^{-1})	$^3T_{1g}(F) \rightarrow {}^3A_{2g}$ (cm^{-1})	Δ_o (cm^{-1})
$[V(H_2O)_6]^{3+}$	17,200	25,000	36,400	19,200



Here H_2O acts a strong field ligands and $^3A_{2g}$ exceed the energy of the $^3T_{1g}$(P) state.

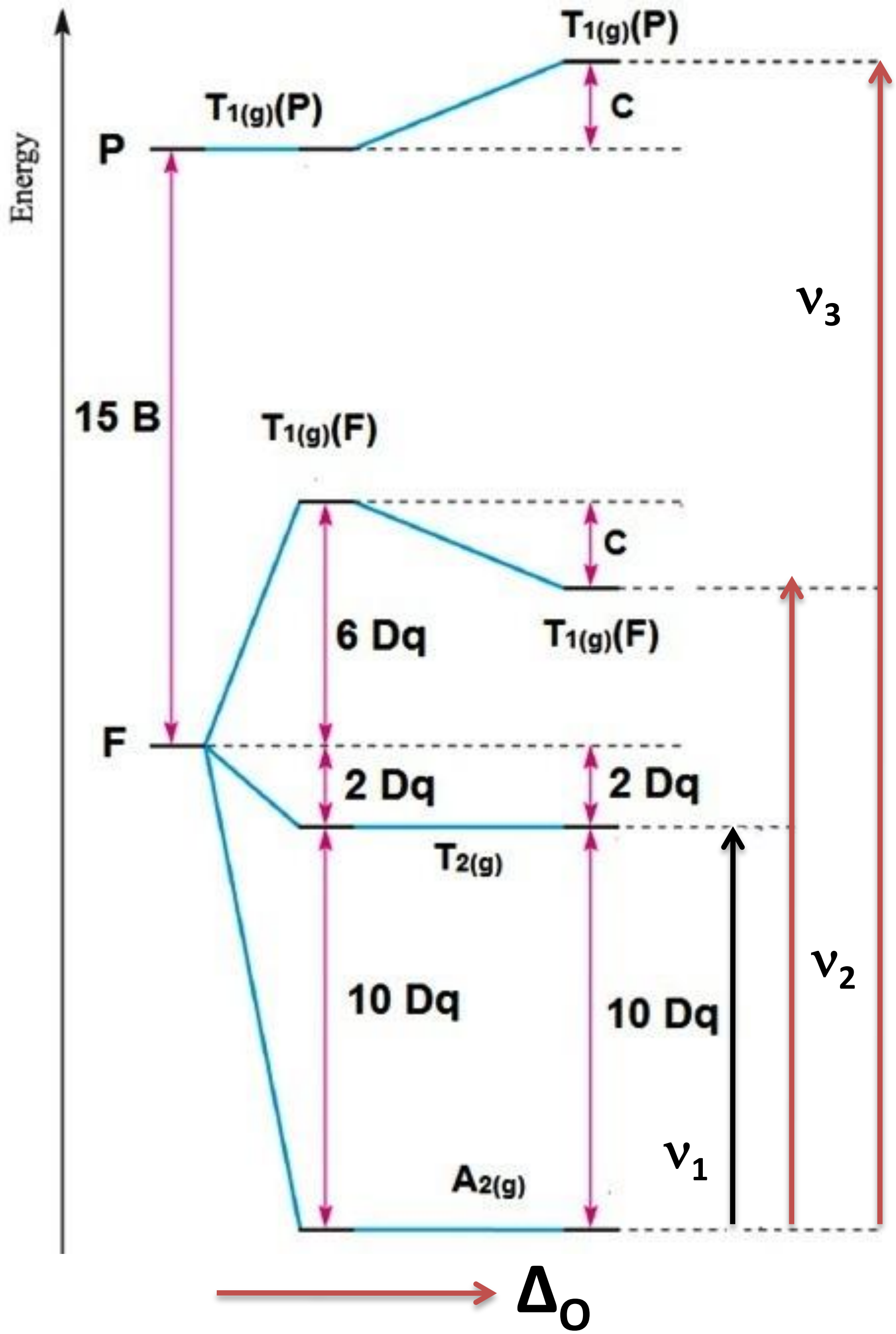
Uv-vis spectrum of $[V(H_2O)_6]^{3+}$



C = (36400 - 34560) cm^{-1} = 1840 cm^{-1}

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

9800 cm^{-1} = 15 B   B = 654 cm^{-1}



d^3 & d^8 in O_h and d^2 & d^7 in T_d

$\nu_1 : A_{2(g)} \rightarrow T_{2(g)} = 10\ Dq$

$\nu_2 : A_{2(g)} \rightarrow T_{1(g)}(F) = 18\ Dq - C$

$\nu_3 : A_{2(g)} \rightarrow T_{1(g)}(P) = 12\ Dq + 15\ B + C$

B = Racah parameter

C = Configurational interaction

In $[CrF_6]^{3-}$

$\nu_1 : {}^4A_{2(g)} \rightarrow {}^4T_{2(g)} = 14900\ cm^{-1} = 10\ Dq$

$Dq = 14900 cm^{-1} / 10 = 1490\ cm^{-1}$

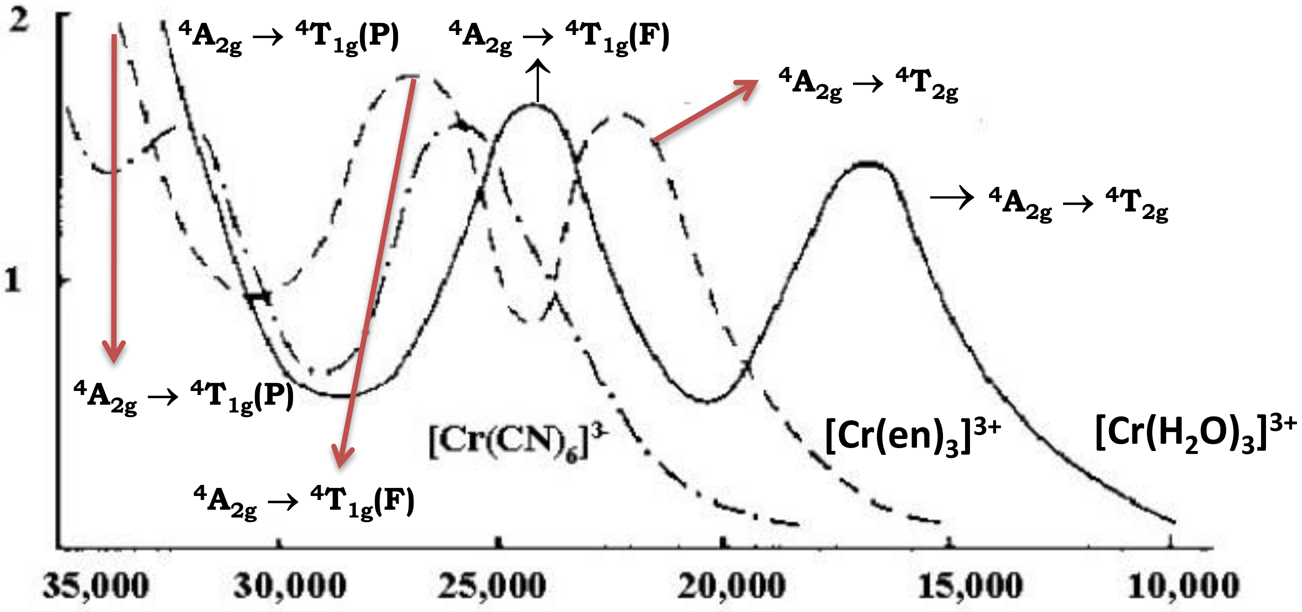
$\nu_2 : {}^4A_{2(g)} \rightarrow {}^4T_{1(g)}(F) = 18\ Dq - C = 22700\ cm^{-1}$

So, $18\ Dq - C = 22700\ cm^{-1}$

$C = (18 \times 1490 - 22700)\ cm^{-1} = 4120\ cm^{-1}$

$\nu_3 : {}^4A_{2(g)} \rightarrow {}^4T_{1(g)}(P) = 12\ Dq + 15\ B + C$
$= (12 \times 1490 + 4120) cm^{-1} + 15B = 34400\ cm^{-1}$

So, $15\ B = 12400\ cm^{-1}$; and $B = 827\ cm^{-1}$



$[Cr(H_2O)_6]^{3+}$

ν_1 : $^4A_{2(g)} \rightarrow {}^4T_{2(g)}$ = 17000 cm^{-1} = 10 Dq; So , Dq = 17000 cm^{-1} / 10 = 1700 cm^{-1}

ν_2 : $^4A_{2(g)} \rightarrow {}^4T_{1(g)}$(F)= 18 Dq – C = 24000 cm^{-1} So, C =18 Dq – 24000 cm^{-1} = 6600 cm^{-1}

ν_3 : $^4A_{2(g)} \rightarrow {}^4T_{1(g)}$(P) = 12 Dq + 15 B + C = (12 X 1700 + 6600) cm^{-1} +15B = 37500 cm^{-1}

So, 15 B = 10700 cm^{-1}; and B = 700 cm^{-1}

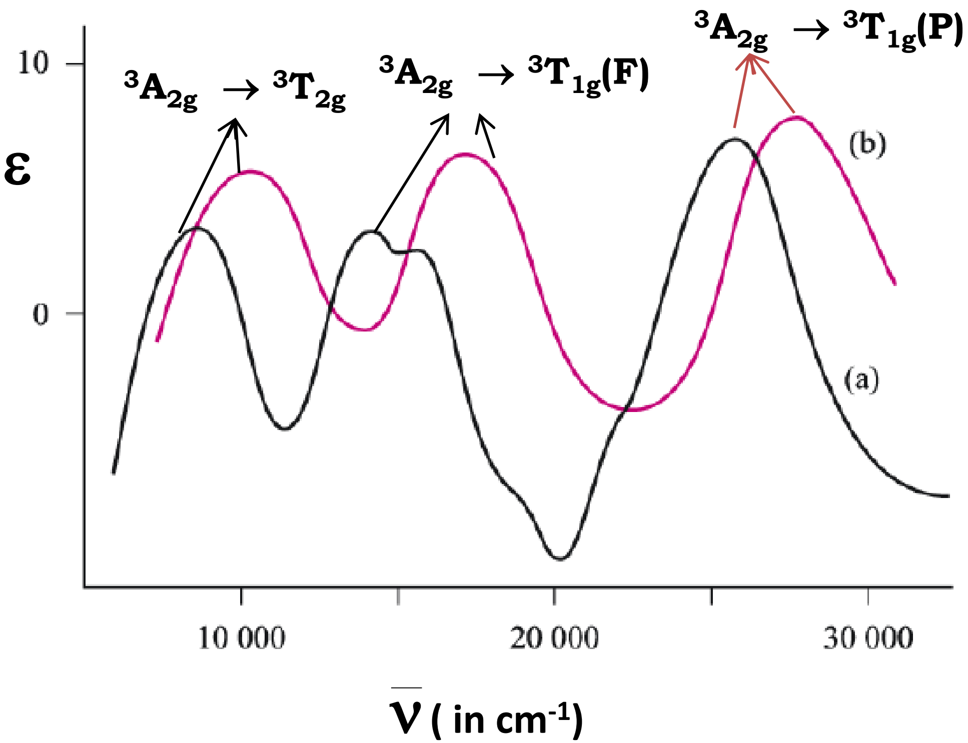
$[Cr(en)_3]^{3+}$

ν_1 : $^4A_{2(g)} \rightarrow {}^4T_{2(g)}$ = 21600 cm^{-1} = 10 Dq; So , Dq = 21600 cm^{-1} / 10 = 2160 cm^{-1}

ν_2 : $^4A_{2(g)} \rightarrow {}^4T_{1(g)}$(F)= 18 Dq – C = 28500 cm^{-1} So, C =18 Dq – 28500 cm^{-1} = 10380 cm^{-1}

ν_3 : $^4A_{2(g)} \rightarrow {}^4T_{1(g)}$(P) = 12 Dq + 15 B + C = (12 X 2160 + 10380) cm^{-1} +15B = 47800 cm^{-1}

So, 15 B = 10700 cm^{-1}; and B = 886 cm^{-1}



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

ν_1 : $^3A_{2(g)} \rightarrow {}^3T_{2(g)}$ = 8500 cm^{-1} = 10 Dq;

So , Dq = 8500 cm^{-1} / 10 = 850 cm^{-1}

ν_2 : $^3A_{2(g)} \rightarrow {}^3T_{1(g)}$(F)= 18 Dq – C
= 13800 cm^{-1}

So, C =18 Dq – 13800 cm^{-1} = 1500 cm^{-1}

ν_3 : $^3A_{2(g)} \rightarrow {}^3T_{1(g)}$(P) = 12 Dq + 15 B + C

Thus ν_3 = (12 X 850 + 1500) cm^{-1} + 15B
= 25300 cm^{-1}

So, 15 B = 13600 cm^{-1}; and B = 907 cm^{-1}

(b) $Ni(NH_3)_6]^{2+}$

ν_1 : $^3A_{2(g)} \rightarrow {}^3T_{2(g)}$ = 10750 cm^{-1} = 10 Dq; So , Dq = 10750 cm^{-1} / 10 = 1075 cm^{-1}

ν_2 : $^3A_{2(g)} \rightarrow {}^3T_{1(g)}$(F) = 18 Dq – C = 17500 cm^{-1} So, C =18 Dq – 17500 cm^{-1} = 1850 cm^{-1}

ν_3 : $^3A_{2(g)} \rightarrow {}^3T_{1(g)}$(P) = 12 Dq + 15 B + C = (12 X 1075 + 1850) cm^{-1} + 15B = 28200 cm^{-1}

So, 15 B = 13600 cm^{-1}; and B = 895 cm^{-1}