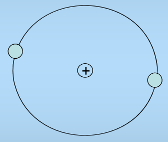
Ligand field theory

$$E = E_{kin} + \sum_{i}^{N} \frac{Ze \cdot e_i}{4\pi\varepsilon_0 \cdot r_i} - \sum_{i,j}^{N} \frac{e^2}{4\pi\varepsilon_0 \cdot r_{ij}} - V_{O_h}$$



one-electron model

e-repulsion
Perturbation1

Ligand field
Perturbation2

P1>P2: weakfield appr.
P2>P1: strongfield appr.

Strong field approximation d^2

Octahedral field: e

One electron model t_2

Symmetry and group theory

E

d^2 electron configuration: $(e)^2$

d^2 split into $(t_2)^1(e)^1$

$(t_2)^2$

Microstates strong field d^2

Allow for inter electronic repulsions in strong field

$(t_2)^2$:

a+ b+	a+ c+	b+ c+	$^3T_1$
a+ b-	a+ c-	b+ c-	$^1T_2$
a- b+	a- c+	b- c+	
a- b-	a- c-	b- c-	
a+ a-	b+ b-	c+ c-	^1E, $^1A_1$

$(t_2)^1(e)^1$: $^3T_1$ $^3T_2$ $^1T_2$ $^1T_1$

$(e)^2$: $^3A_2$ $^1A_1$ ^1E

Octahedral group

The O-group: 5 irreproducible representations:
A_1
A_2
E
T_1
T_2
The O_h-group (with a center of symmetry):
each of these 5 representations as g and u

5.40

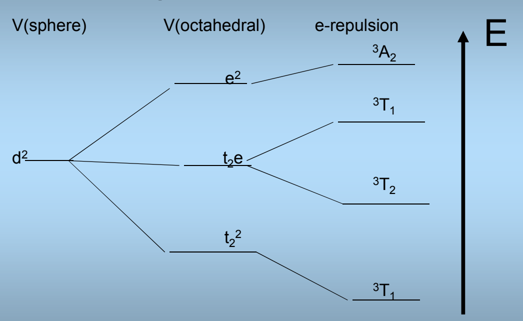
Appendix 3, p 1008

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1
E_u	2	−1	0	0	2	−2	0	1	−2	0
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1

Back two slides

Table 5.4 Part of the O_h character table.

Strong field triplets only



Weak field approximation

Both d electrons have
l = 2, so m_l = 2,1,0,-1,-2;
s=½, so m_s = +½, -½

$M_L = \Sigma m_l$ $\quad M_S = \Sigma m_s$

$$\frac{\{2(2\ell+1)\}!}{2!\{2(2\ell+1)-2\}!} = n$$

= 45 Microstates give

	L	S	n
^1G	4	0	9x1=9
^3F	3	1	7x3=21
^1D	2	0	5x1=5
^3P	1	1	3x3=9
^1S	0	0	1x1=1

Weak field approximation

Both d electrons have
l = 2, m_l = +2,+1,0,-1,-2; s=½, m_s = +½, -½

Example: L=1; S=1 : ^3P

$M_L = \Sigma m_l$ $\quad M_S = \Sigma m_s$

$$\frac{\{2(2\ell+1)\}!}{2!\{2(2\ell+1)-2\}!} =$$

45 microstates

+2	+1	0	-1	-2	M_L	M_S
	↑	↑			+1	+1
	↑		↑		0	+1
		↑	↑		-1	+1
	↓	↑			+1	0
	↓		↑		0	0
		↑	↑		-1	0
	↓	↓			+1	-1
	↓		↓		0	-1
		↓	↓		-1	-1

Weak field approximation

Both d electrons have
l = 2, so m_l = 2,1,0,-1,-2;
s=½, so m_s = +½, -½

$M_L = \Sigma m_l$ $\quad M_S = \Sigma m_s$

$$\frac{\{2(2\ell+1)\}!}{2!\{2(2\ell+1)-2\}!} = n$$

= 45 Microstates give

	L	S	n
^1G	4	0	9x1=9
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^3P	1	1	3x3=9
^1S	0	0	1x1=1

5.40

Appendix 3, p 1008

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	← $x^{2+}+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1	
E_g	2	−1	0	0	2	2	0	−1	2	0	← z^2, x^2-y^2
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	← xy, yz, zx
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	
E_u	2	−1	0	0	2	−2	0	1	−2	0	
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	← x, y, z
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

Table 5.4 Part of the O_h character table.

Weak field

Allow for octahedral ligand field

$^1G \rightarrow {}^1A_1 + {}^1E + {}^1T_2 + {}^1T_1$

$^3F \rightarrow {}^3A_2 + {}^3T_2 + {}^3T_1$

$^1D \rightarrow {}^1E + {}^1T_2$

$^3P \rightarrow {}^3T_1$

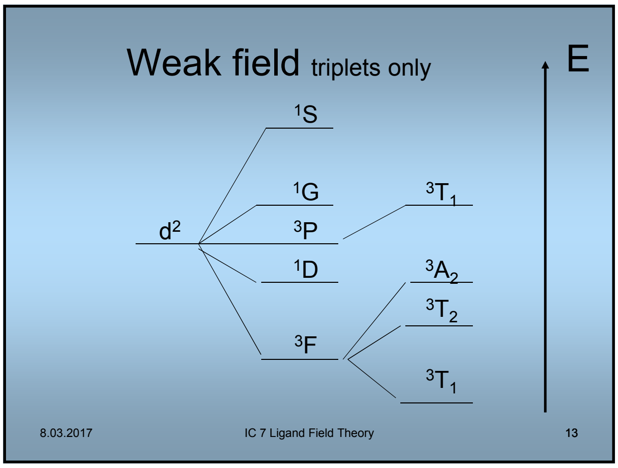
$^1S \rightarrow {}^1A_1$

21.50

Microstates with M_s = +½+½=1

$m_l = +2$	$m_l = +1$	$m_l = 0$	$m_l = -1$	$m_l = -2$	M_L	
↑	↑				+3	^3F (L = 3)
↑		↑			+2	
↑			↑		+1	
↑				↑	0	
	↑			↑	−1	
		↑		↑	−2	
			↑	↑	−3	
	↑	↑			+1	^3P (L = 1)
	↑		↑		0	
		↑	↑		−1	

Table 21.9 A shorthand table of microstates for a d^2 configuration; only a high-spin case (weak field limit) is considered, and each electron has $m_s = +\frac{1}{2}$. The microstates are grouped so as to show the derivation of the ^3F and ^3P terms. Table 21.7 provides the complete table of microstates for a d^2 ion.


Weak field triplets only
E
^1S
^1G
^3P
^1D
^3F
d^2
$^3T_1$
$^3A_2$
$^3T_2$
$^3T_1$
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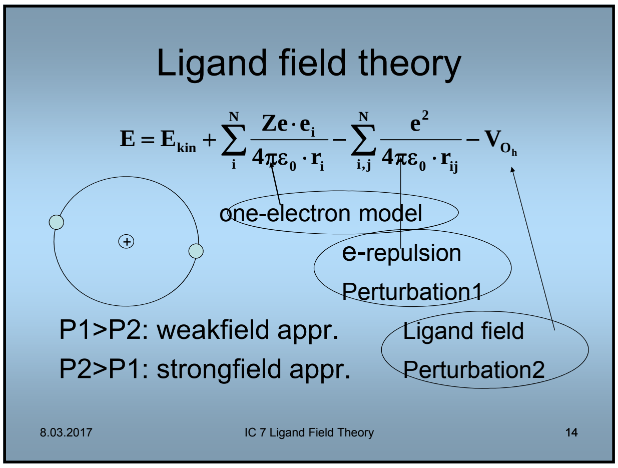
Ligand field theory
$E = E_{kin} + \sum_i^N \frac{Ze \cdot e_i}{4\pi\varepsilon_0 \cdot r_i} - \sum_{i,j}^N \frac{e^2}{4\pi\varepsilon_0 \cdot r_{ij}} - V_{O_h}$
one-electron model
e-repulsion
Perturbation1
Ligand field
Perturbation2
P1>P2: weakfield appr.
P2>P1: strongfield appr.
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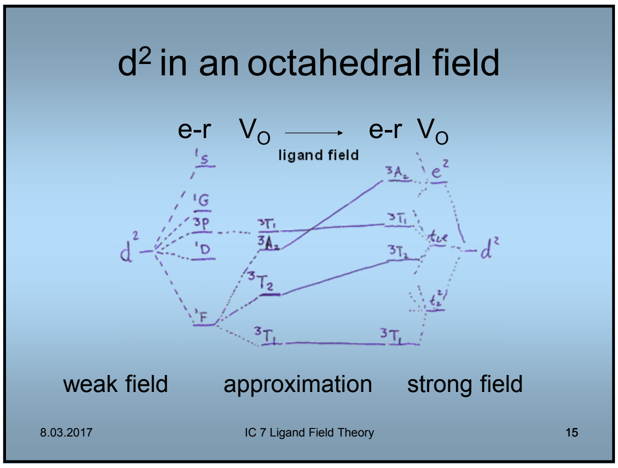
d^2 in an octahedral field
e-r V_O
e-r V_O
ligand field
weak field
approximation
strong field
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21.21

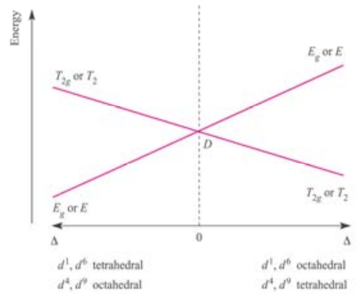


Fig. 21.19 Orgel diagram for d^1, d^4 (high-spin), d^6 (high-spin) and d^9 ions in octahedral (for which T_{2g} and E_g labels are relevant) and tetrahedral (E and T_2 labels) fields. In contrast to Figure 21.18, multiplicities are not stated because they depend on the d^n configuration.

21.22

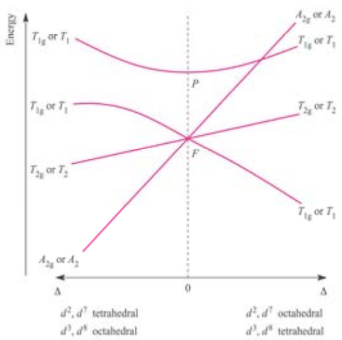


Fig. 21.20 Orgel diagram for d^2, d^3, d^7 and d^8 ions (high-spin) in octahedral (for which T_{1g}, T_{2g} and A_{2g} labels are relevant) and tetrahedral (T_1, T_2 and A_2 labels) fields. Multiplicities are not stated because they depend on the d^n configuration, e.g. for the octahedral d^2 ion, $^3T_{1g}$, $^3T_{2g}$ and $^3A_{2g}$ labels are appropriate.

21.27

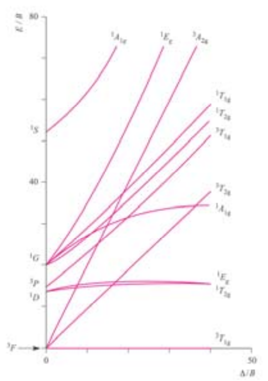
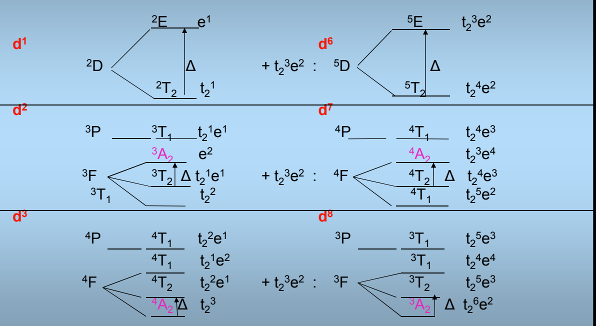


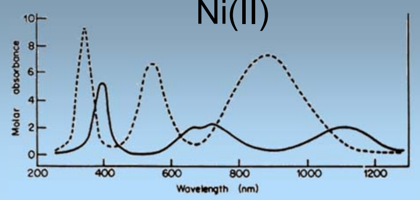
Fig. 21.24 Tanabe–Sugano diagram for the d^2 configuration in an octahedral field.

Summary

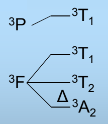


Ni(II)

d8



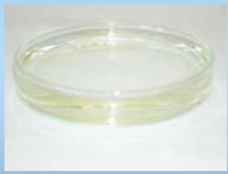
transition	Niaq$_6^{2+}$ λ/nm	σ/10^{-3}cm^{-1}	Nien$_3^{2+}$ λ/nm	σ/10^{-3}cm^{-1}
$^3A_2 \rightarrow {}^3T_2$	1180	8.5	890	11.25
$^3A_2 \rightarrow {}^3T_1$	702	14.0	545	18.4
$^3A_2 \rightarrow {}^3T_1$	400	25.3	345	29.0



Intensity of transitions

	ε	example
ΔS≠0, spinforbidden; d→d	1	$Mn(H_2O)_6^{2+}$, $Fe(H_2O)_6^{3+}$
parity forbidden; d→d centrosymmetric	1-10	$Ti(H_2O)_6^{3+}$, $Ni(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$
parity forbidden; d→d, less or more non-centrosymmetric	10-1000	$Cren_3^{3+}$, cis-[$Coen_2Cl_2$]Cl, $CoCl_4^{2-}$
charge transfer	1000-50000	$FeFe(CN)_6^-$ $Fe(SCN)_3(H_2O)_3$

$Fe(H_2O)_6^{3+}$



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Intensity of transitions

	ε	example
ΔS≠0, spinforbidden; d→d	1	$Mn(H_2O)_6^{2+}$, $Fe(H_2O)_6^{3+}$
parity forbidden; d→d centrosymmetric	1-10	$Ti(H_2O)_6^{3+}$, $Ni(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$
parity forbidden; d→d, less or more non-centrosymmetric	10-1000	$Cren_3^{3+}$, cis-$[Coen_2Cl_2]Cl$, $CoCl_4^{2-}$
charge transfer	1000-50000	$FeFe(CN)_6^-$ $Fe(SCN)_3(H_2O)_3$

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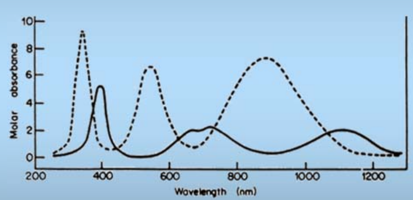
$Ni(H_2O)_6^{2+}$ —— $Nien_3^{2+}$ ----



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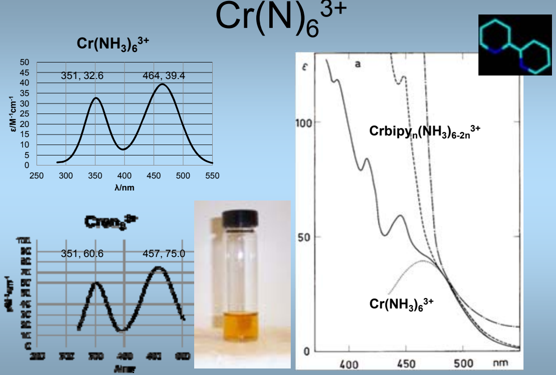
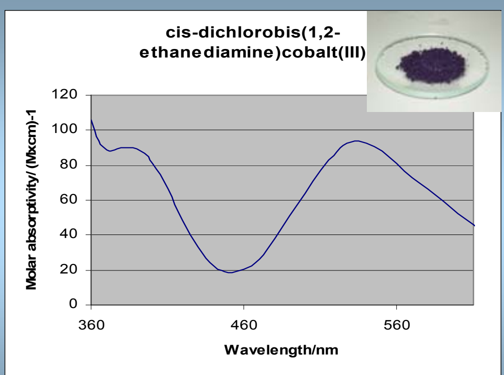
Intensity of transitions

	ε	example
ΔS≠0, spinforbidden; d→d	1	$Mn(H_2O)_6^{2+}$, $Fe(H_2O)_6^{3+}$
parity forbidden; d→d centrosymmetric	1-10	$Ti(H_2O)_6^{3+}$, $Ni(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$
parity forbidden; d→d, less or more non-centrosymmetric	10-1000	$Cren_3^{3+}$, cis-$[Coen_2Cl_2]Cl$, $CoCl_4^{2-}$
charge transfer	1000-50000	$FeFe(CN)_6^-$ $Fe(SCN)_3(H_2O)_3$

$Cr(N)_6^{3+}$





Intensity of transitions

	ε	example
ΔS≠0, spinforbidden; d→d	1	$Mn(H_2O)_6^{2+}$, $Fe(H_2O)_6^{3+}$
parity forbidden; d→d centrosymmetric	1-10	$Ti(H_2O)_6^{3+}$, $Ni(H_2O)_6^{2+}$, $Co(H_2O)_6^{2+}$
parity forbidden; d→d, less or more non-centrosymmetric	10-1000	$Cren_3^{3+}$, cis-$[Coen_2Cl_2]Cl$, $CoCl_4^{2-}$
charge transfer	1000-50000	$FeFe(CN)_6^-$ $Fe(SCN)_3(H_2O)_3$

Fe(III) d^5

spin forbidden

charge transfer

$Fe(H_2O)_6^{3+}$ + $Fe(CN)_6^{4-} \rightarrow FeFe(CN)_6^-$

Fe(III) d^5

- Spinforbidden