Orgel Diagram

(Correlation Diagrams)

Prepared by

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Orgel diagrams for d^1, d^9, d^4, d^6 (and d^2, d^3, d^4, d^6)

Orgel Diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes. They are named after their creator, Leslie Orgel. Orgel diagrams are **restricted to weak ligand fields** (i.e. high-spin complexes). Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams.

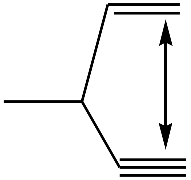
Orgel diagrams only show the **symmetry states** of the highest spin multiplicity instead of all possible terms, unlike a **Tanabe-Sugano** diagram. Orgel diagrams will, however, show the number of spin allowed transitions, along with their respective symmetry designations.

In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side. There are **only two Orgel diagrams**, one for d^1, d^4, d^6, and d^9 configurations and the other with d^2, d^3, d^7, and d^8 configurations.

Recapitulation: Ligand field Theory: Octahedral Complexes

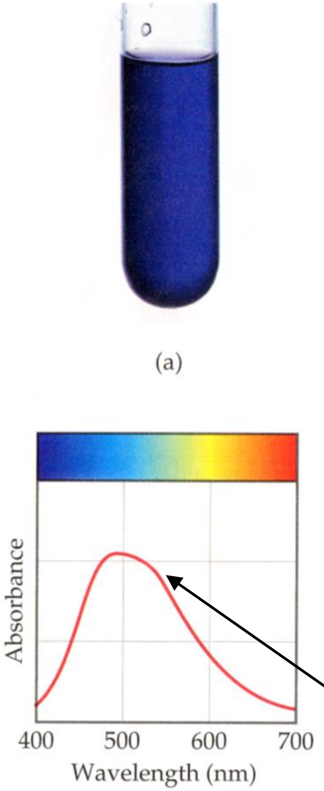
The d^1 configuration …

UV/Vis spectroscopy allows to measure Δ_o directly



$\Delta_o = ch\tilde{\nu}_{max}$

Example: $[Ti(H_2O)_6]^{3+}$ (blue/purple)



(a)

(b)

Figure 24.26 **The color of $[Ti(H_2O)_6]^{3+}$.**
(a) A solution containing the $[Ti(H_2O)_6]^{3+}$ ion.
(b) The visible absorption spectrum of the $[Ti(H_2O)_6]^{3+}$ ion.

$$t_{2g}^{\;1}e_g^{\;0} \xrightarrow{h\nu} t_{2g}^{\;0}e_g^{\;1}$$

$$^2T_{2g} \rightarrow {}^2E_g$$

20000 cm^{-1}
or 500 nm
or 240 kJ/mol

$\varepsilon_{max} < 30\ M^{-1}cm^{-1}$
(Laporte forbidden, spin allowed)

$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}$$

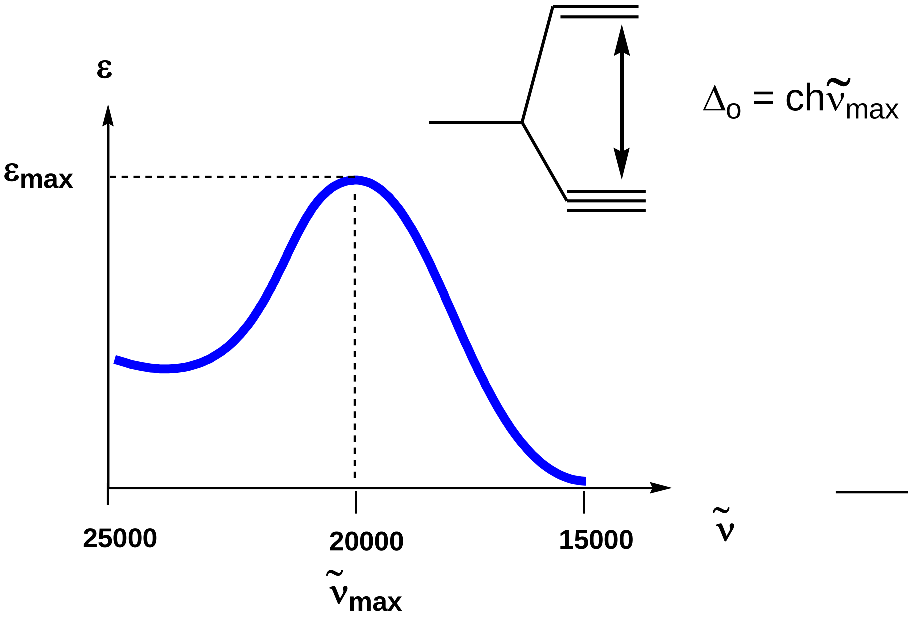
Shoulder
due to Jahn-Teller
effect

The d^9 configuration

Here also: UV/Vis spectr. allows direct measurement of Δ_o

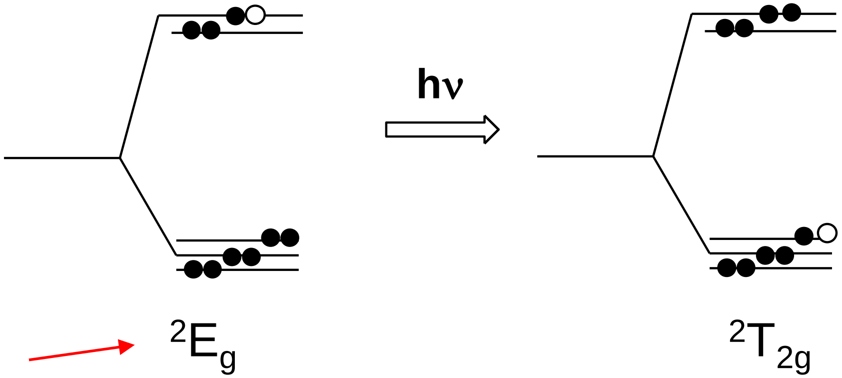
Corresponds to the d^1 case

UV/vis spectrum of $[Cu(H_2O)_6]^{2+}$



$t_{2g}{}^6 e_g{}^3 \rightarrow t_{2g}{}^5 e_g{}^4$

„electron“ – „hole“ analogy



Note that term symbols for ground and excited states are reversed (relative to the d^1 case)

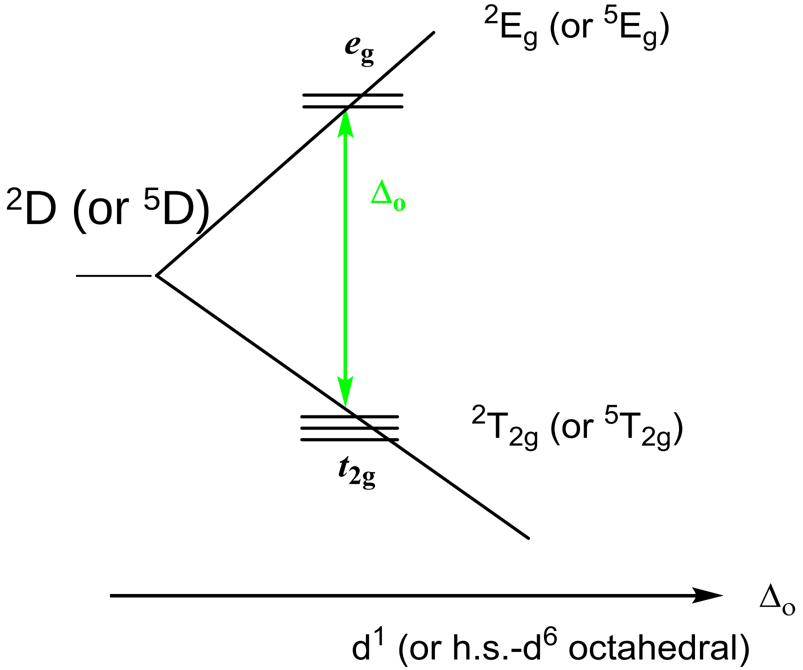
$\Rightarrow$ „electron-hole analogy“ explains also the similar behaviour of h.s.-d^4 and h.s.-d^6 complexes (octaedral as well as tetrahedral ones)

The electron - hole analogy

Electronic absorption spectra of octahedral and tetrahedral complexes with d^1, d^9, d^4, and d^6 configuration

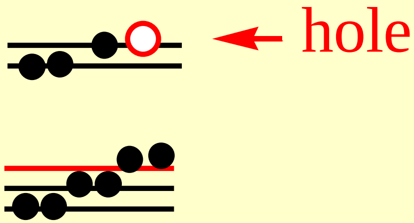
- d^0, d^5, d^{10} analogous
- going from d^5 to d^6 resembles going from d^0 to d^1

configuration	(symbol) of ground term of the free ion	(symbols) of split terms of the complex
d^1, d^9	**^{2}D**	**$^2T_{2g}$, ^2E_g**
d^2, d^8	**^{3}F**	
d^3, d^7	**^{4}F**	
d^4, d^6 (high-spin)	**^{5}D**	**$^5T_{2g}$, ^5E_g**
d^5	**^{6}S**	
d^{10}	**^{1}S**	

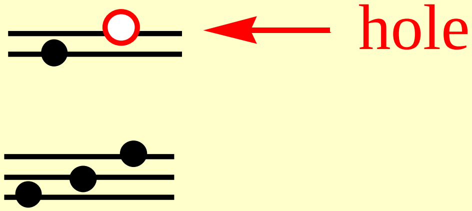


electron hole formalism

- d^0, d^5, d^{10} analogous
- d^5->d^4 resembles d^{10}->d^9 case

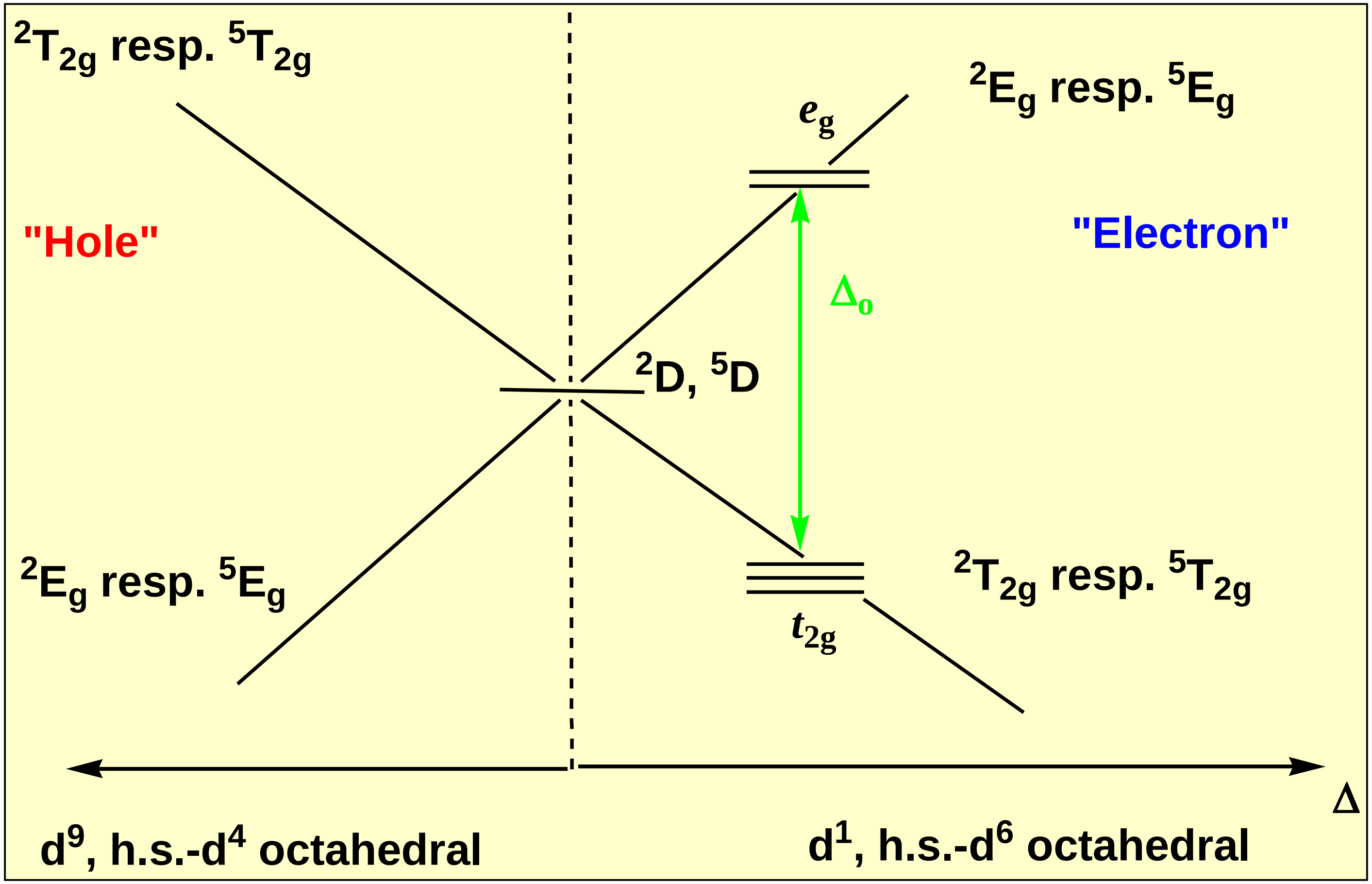


d^{10}->d^9



d^5->d^4

Orgel diagram for d^1, d^9, d^4, d^6



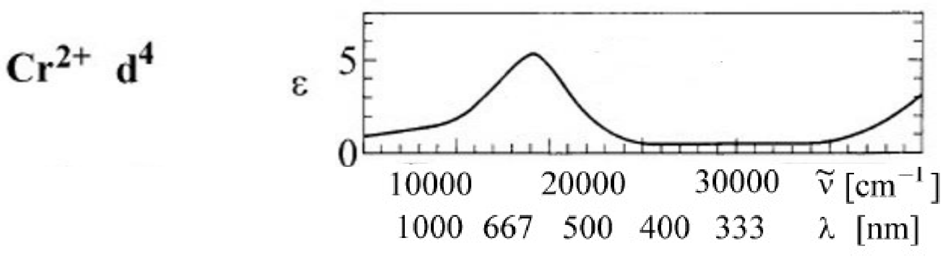
←

term reversal

Similar correlations derivable for tetrahedral complexes (see textbook by C. Housecroft)

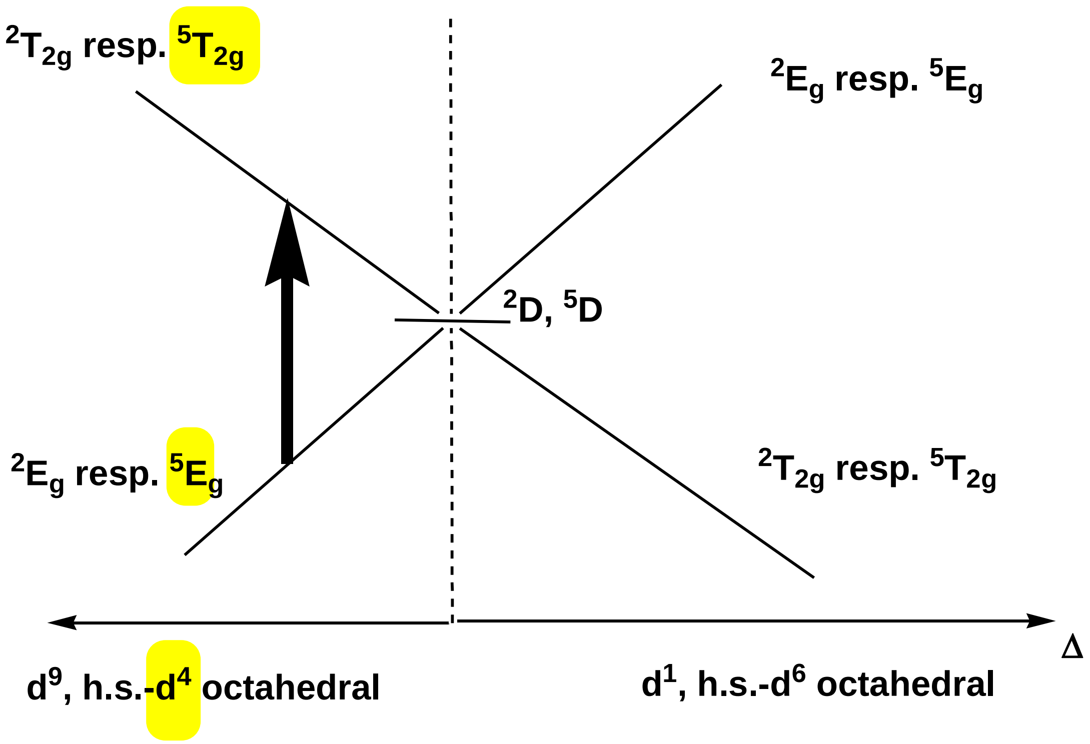
Exercise

The octahedral h.s. complex $[Cr(H_2O)_6]^{2+}$ (d^4) shows one UV/Vis absorption band. Assign the transition! Use an Orgel diagram.



Solution to the above exercise

The octahedral h.s. complex $[Cr(H_2O)_6]^{2+}$ (d^4) shows one UV/Vis absorption band. Assign the transition! Use an Orgel diagram.



We have an octahedral complex with d^4 electronic configuration. So take the left hand side of the Orgel diagram. The ground state is labeled ^5E_g. The excited state is labeled as $^5T_{2g}$. The assignment of the band is thus:
$^5E_g \rightarrow {}^5T_{2g}$

3. Splitting of Terms in Ligand Fields

To understand the electronic spectra of transition metal complexes, one needs to know the **electronic states** of the system.

The following **effects** lead to a **splitting of the energy levels** of transition metal atoms, ions (and complexes):

- Electron-electron repulsion → spectroscopic terms
- Crystal field → spectroscopic terms
- Spin-Orbit Interaction → multiplet
- Spin-Spin Interaction → magnetic states
- Zeeman Effect → magnetic states
- Hyperfine Interaction

Of these, the first two effects are of importance in UV-vis (electron) spectroscopy as they lead to a splitting of the energy levels which are on the same order of magnitude as the energy of the applied UV-vis light.

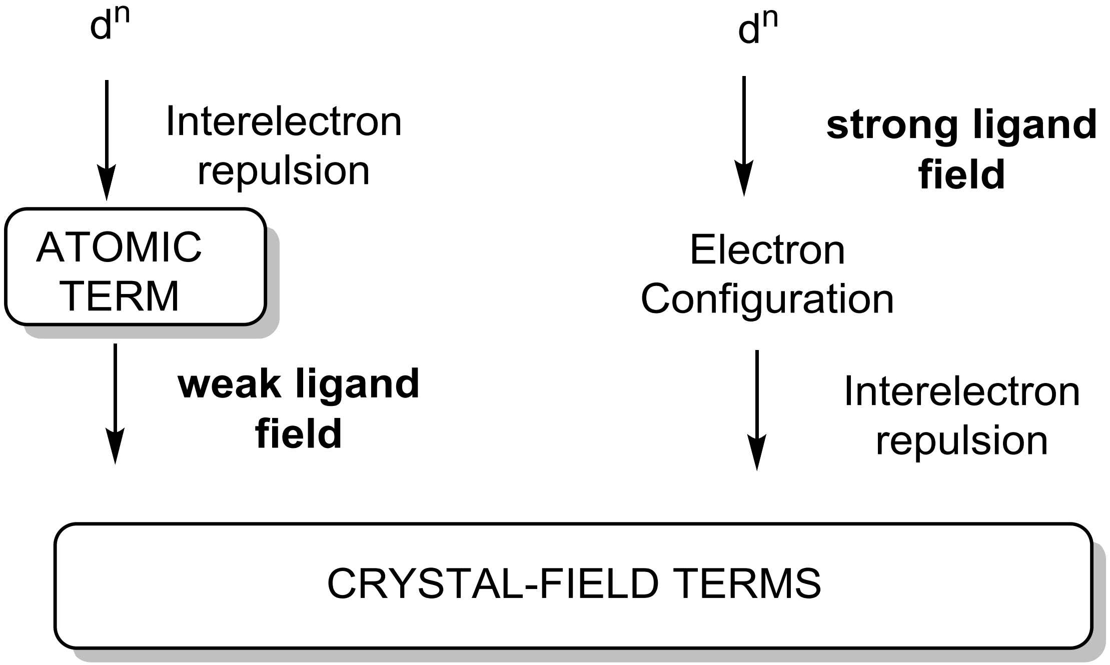
The other effects are of importance in **magnetism** and **EPR spectroscopy**

Weak Field and Strong Field Methods

Coordination compounds can be described by the

- weak field method (the e-e-repulsion more significant) or
- strong field method (crystal field splitting stronger)

(here we concentrate on the **weak field method**, the strong field method is out of the scope of this lecture)



d^n

Interelectron repulsion

ATOMIC TERM

weak ligand field

d^n

strong ligand field

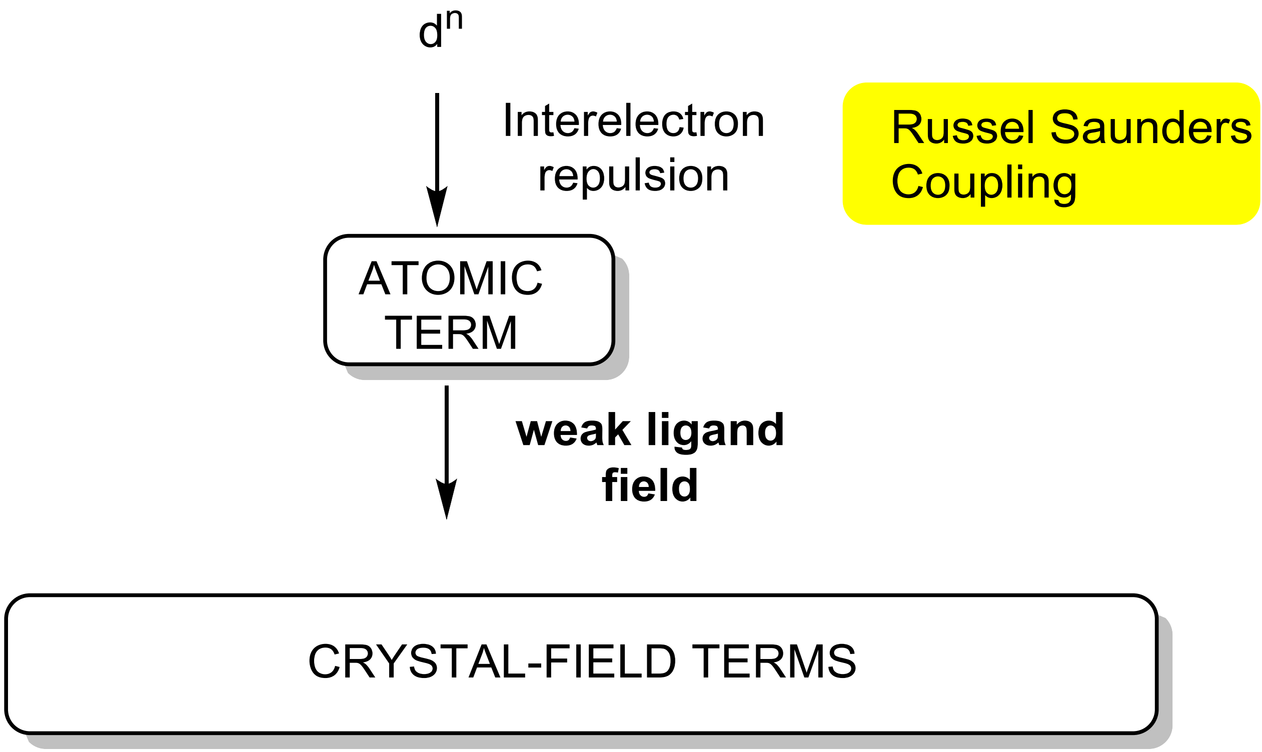
Electron Configuration

Interelectron repulsion

CRYSTAL-FIELD TERMS

Weak field method

The determination of the atomic terms of each d^n configuration is carried out by the Russel-Saunders (LS) coupling method (see appendix, a, b).
The results are shown on the next slide.



d^n

Interelectron repulsion

Russel Saunders Coupling

ATOMIC TERM

weak ligand field

CRYSTAL-FIELD TERMS

The Russel Saunders (atomic) terms of the d^{n} configurations

Terms of the d^{n}-configurations (ground terms in „blue“ color)

configuration	atomic terms
d^{1}, d^{9}	**^{2}D**
d^{2}, d^{8}	**^{3}F**, ^{3}P, ^{1}G, ^{1}D, ^{1}S
d^{3}, d^{7}	**^{4}F**, ^{4}P, ^{2}H, ^{2}G, ^{2}F, ^{2}D
d^{4}, d^{6}	**^{5}D**, ^{3}H, ^{3}G, ^{3}F, ^{3}D, ^{3}P, ^{1}I, ^{1}G, ^{1}F, ^{1}D, ^{1}S
d^{5}	**^{6}S**, ^{4}G, ^{4}F, ^{4}D, ^{4}P, ^{2}I, ^{2}H, ^{2}G, ^{2}G‘, ^{2}F, ^{2}F‘, ^{2}D, ^{2}D‘, ^{2}P, ^{2}S
d^{10}	**^{1}S**

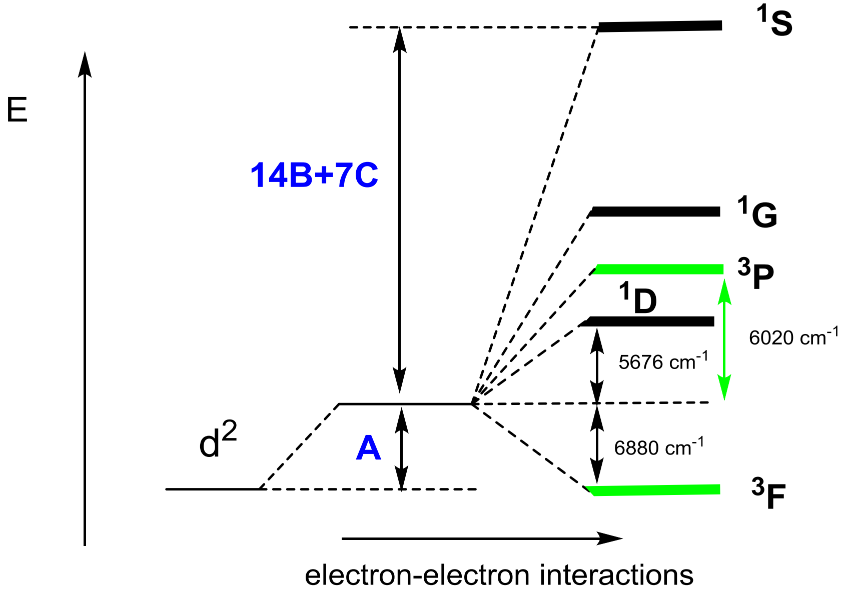
The energies of the terms can be experimentally determined by spectroscopic methods

Hund‘s Rule:
Term with highest spin multiplicity has lowest energy. For terms with same multiplicity, that one with highest value of L is lower in energy (e.g. ^{3}F < ^{3}P for d^{2}, d^{8}), ^{4}F < ^{4}P for d^{3}, d^{7}))

Energy of Russel Saunders (atomic) terms

Energies of atomic terms can be parametrized with Racah parameters. These parameters (i.e. A, B, C) are used to describe the interelectronic repulsion.

Term	Energy in terms of Racah parameters	Experimental values (scaled to A)
^1S	A+14B+7C	+40936 cm^{-1}
^1G	A+4B+2C	+11696 cm^{-1}
^3P	A+7B	+6020 cm^{-1}
^1D	A-3B+2C	+5676 cm^{-1}
^3F	A - 8B	-6880 cm^{-1}



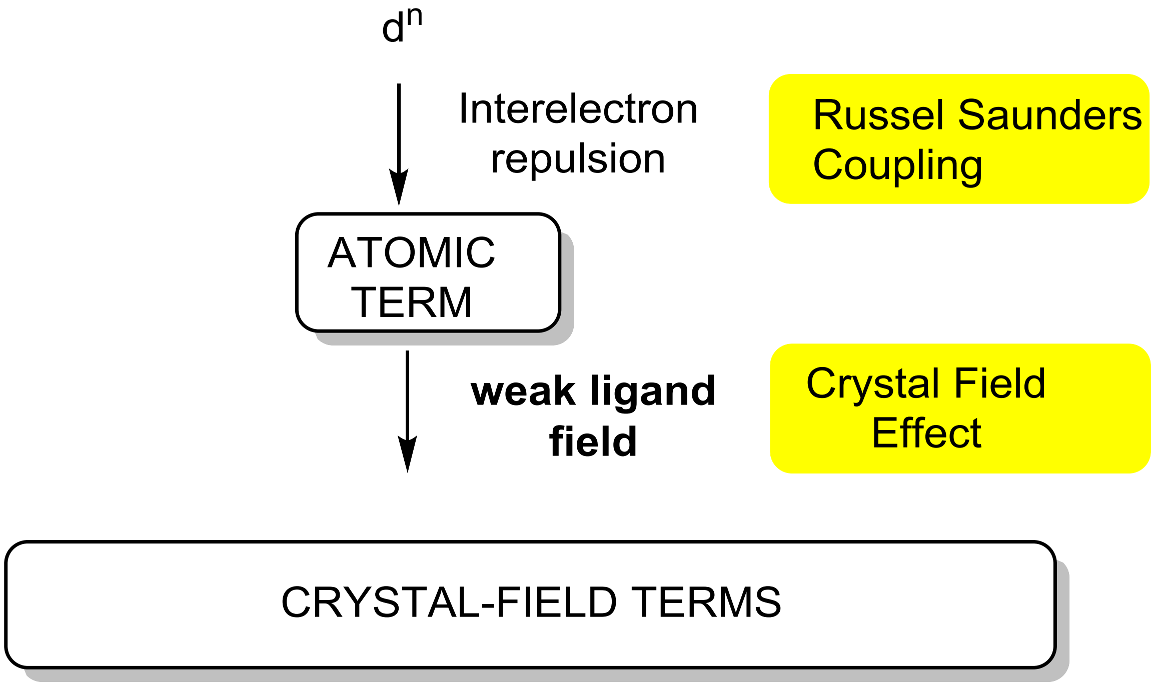
Advantage of Racah-Parameters: Energy difference between ground and excited terms of same spin-multiplicity depend only on B

e.g. V^{3+} (d^2): B = 860 cm^{-1} (=(6020+6880)/15), C = 4128 cm^{-1}, => C/B = 4.8
Ti^{2+} (d^2): B = 720 cm^{-1}, C = 2664 cm^{-1}, => C/B = 3.7

Rule of thumb for free 3d-ions or atoms: C ~ 4·B cm^{-1}, B ~ 1000 cm^{-1}

Crystal Field Effect

It can he demonstrated that a crystal field of a given symmetry splits the atomic terms (S, P, D, etc) like atomic orbitals. The splitting of S, P, D, F terms is shown on the next slide.



d^n

Interelectron repulsion

Russel Saunders Coupling

ATOMIC TERM

weak ligand field

Crystal Field Effect

CRYSTAL-FIELD TERMS

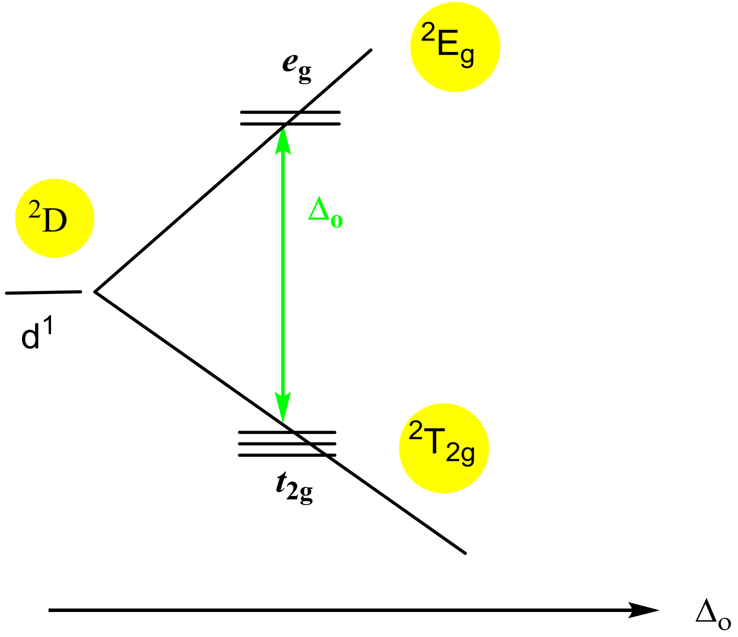
The crystal field splits the atomic terms

Crystal Field Effect

The splitting of S, P, D, F terms in an octahedral crystal field is as follows.

Atomic term	Crystal field term (in O_h symmetry)
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}

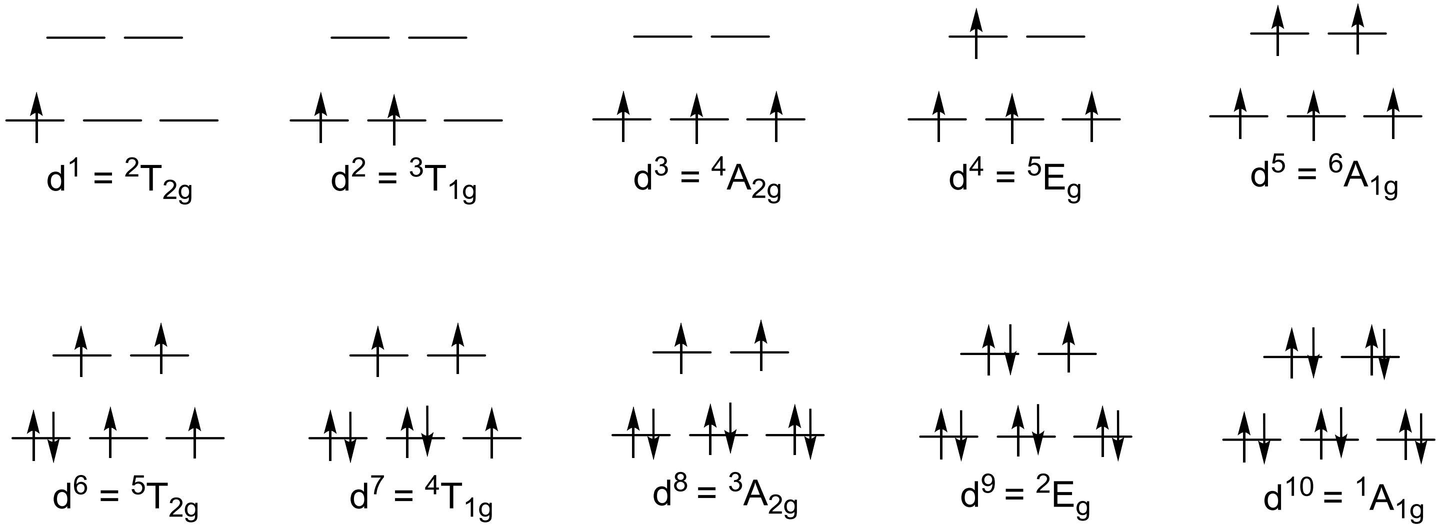
Example: The splitting of the ^2D term in an octahedral crystal field



General points:
- Spin multiplicity is not perturbed by the ligand field
- in centrosymmetric complexes, all split terms are labeled g (gerade)
- g,u symbols not applicable in non-centrosymmetric complexes
- ground terms can be taken from the Tanabe Sugano diagrams
- S and P terms are not split by an octahedral crystal field

Order of energies of crystal field terms

a) Determination of the ground terms



$d^1 = {}^2T_{2g}$ $d^2 = {}^3T_{1g}$ $d^3 = {}^4A_{2g}$ $d^4 = {}^5E_g$ $d^5 = {}^6A_{1g}$

$d^6 = {}^5T_{2g}$ $d^7 = {}^4T_{1g}$ $d^8 = {}^3A_{2g}$ $d^9 = {}^2E_g$ $d^{10} = {}^1A_{1g}$

When there is a single unpaired e^- in the t_{2g} orbitals, $(t_{2g})^1$, the symmetry of the corresponding term is the same as that of the orbital and written in capitals (T_{2g}).

When there are two unpaired electrons in t_{2g} orbitals, three occupations are possible. Therefore it is a triply degenerate term, T. It is not possible to know a priori if it is a T_{1g} or T_{2g} term. It is necessary to perform group theoretical calculations (symmetry descent method). It turns out that the ${}^3T_{1g}$ term is the ground term.

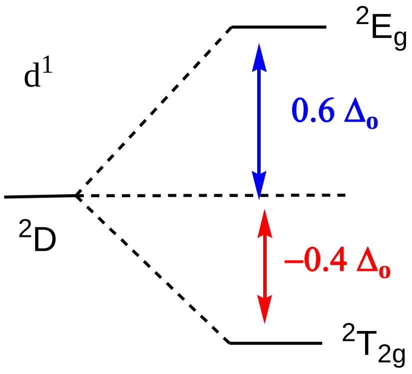
The other ground states are determined in a similar fashion (but this is out of the scope of the present lecture).

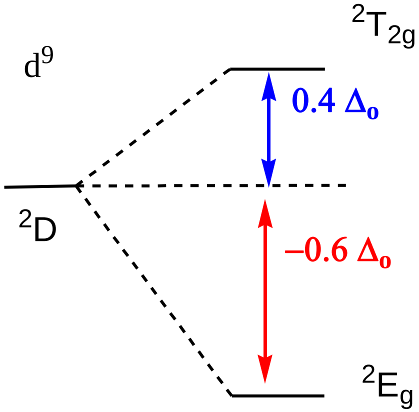
Order of energies of crystal field terms

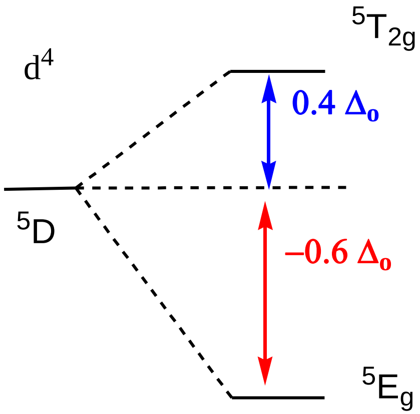
b) Determination of the energies of the upper ligand field terms

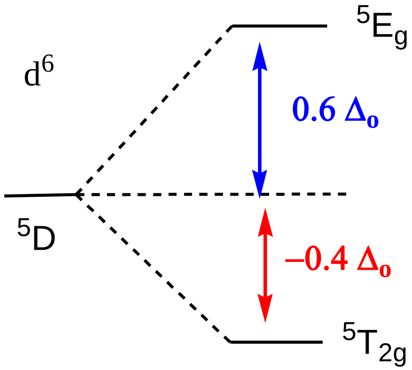
In case of d^1,d^4,d^6 and d^9 systems, the energies of the upper levels are relatively easy to calculate (from the degeneracies of the terms)

T: triply degenerate
E: doubly degenerate term



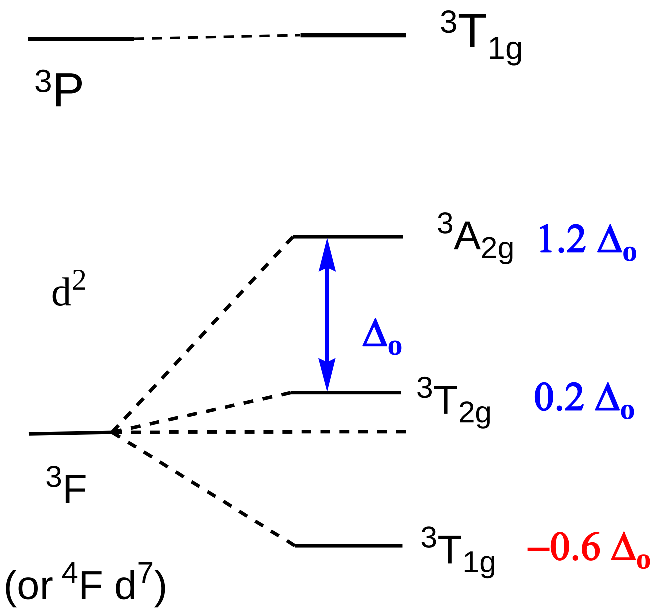




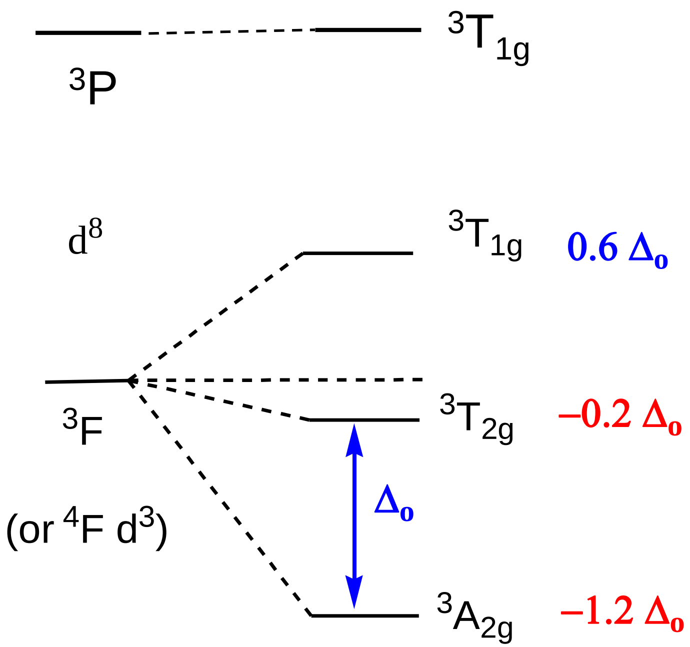


Energies of the crystal field terms: d^2, d^3, d^7, d^8 configuration

- are more difficult to calculate (beyond the scope of this lecture)
- only the results are given here (splitting of the ground terms) (without consideration of the configuration interaction)



d^2



d^8

The Racah Parameter B

B: Racah parameter for a metal ion
B′: Racah parameter for a complex
Racah parameter B′ for a complex is generally smaller than that for the free ion B

$B' < B$

Reason: The e^- - e^- - repulsion is smaller in a complex
this is called the **nephelauxetic effect** (d electrons are delocalized onto ligands; are separated more from each other in a complex, **cloud-expansion**)

The ratio $\beta = B'/B < 1$ is the **nephelauxetic parameter**

β is a measure for covalency of the M-L bonds
- β -> 0 (almost) pure covalent bond
- β -> 1 (almost) pure ionic bond

Example	B/cm^{-1}	B'/cm^{-1}
Cr^{3+}	1030	
$[Cr(en)_3]^{3+}$		622 (=> Tanabe-Sugano-Diagramm)

$\beta = 622/1030 = 0.60$
=> The Cr^{3+}-N-bonds have some covalent character

The Racah Parameter B

Nephelauxetic effect can be factorized (into functions of ligand and metal)
(see textbook by C. Janiak)

nephelauxetic row of ligands

large B‘ → small B‘ (covalency increases)

h_L: $F^- < H_2O < NH_3 < en < ox^{2-} < NCS^- < Cl^- < CN^- < Br^- < I^-$

trend: B‘ decreases with decreasing electronegativity; the less electronegative the ligand, the more it reduces the electron repulsion between d electrons on the metal

nephelauxetic row of TM ions

large B‘ → small B‘ (covalency increases)

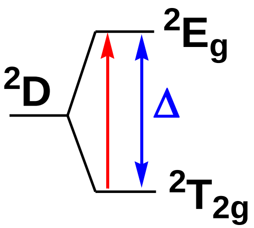
k_M: $Mn^{2+} < Ni^{2+} \sim Co^{2+} < Mn^{3+} < Fe^{3+} < Cr^{3+} < Mn^{4+} < Pt^{4+}$

trend: B‘ decreases from 3d to 5d,
trend: B‘ decreases with oxidation state of M

Electronic transitions

d^1 Ti^{3+}

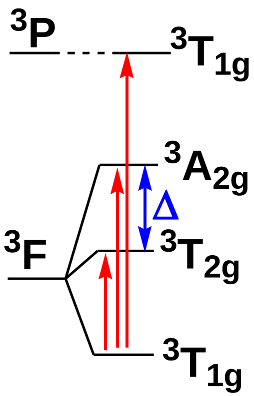
^2D



one transition

d^2 V^{3+}

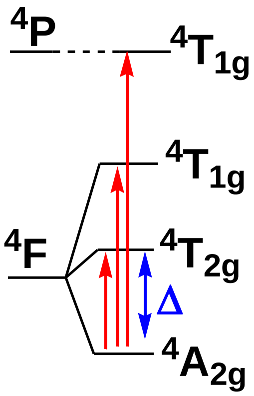
^3F



three transitions

d^3 Cr^{3+}

^4F

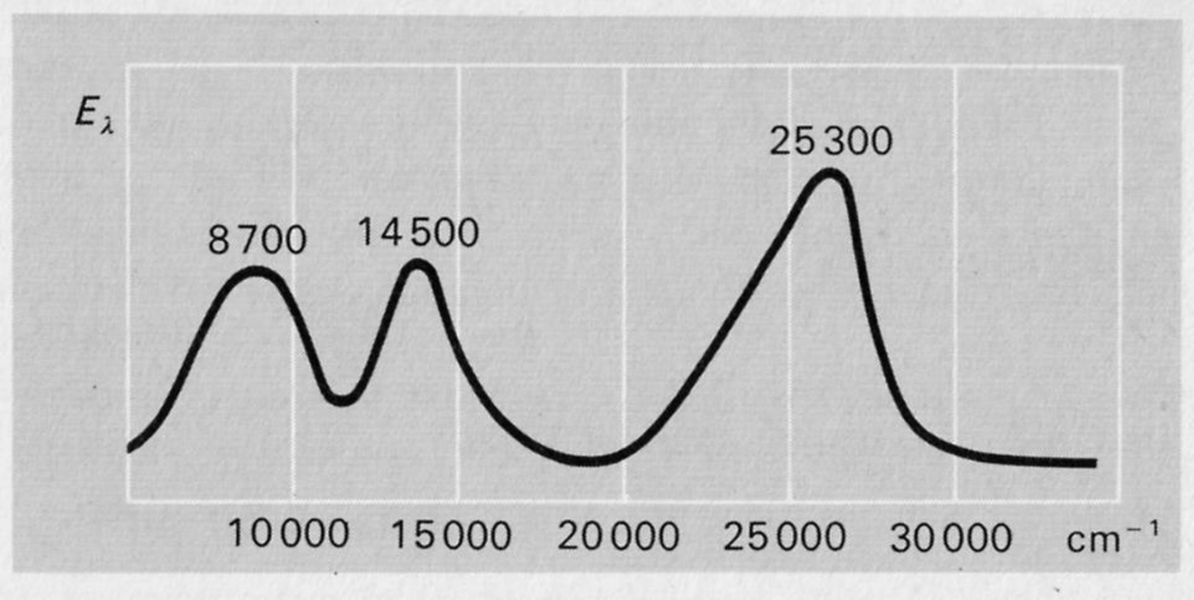


three transitions

… similarly for the other d^n configurations (see the table in Appendix c)

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 10*Dq* *(or* Δ_o*)*.
c) Comment on the different position of bands for the two complexes.



Solution:

a) $Ni^{2+} = d^8$, =>

Laporte-forbidden, spin-allowed bands:

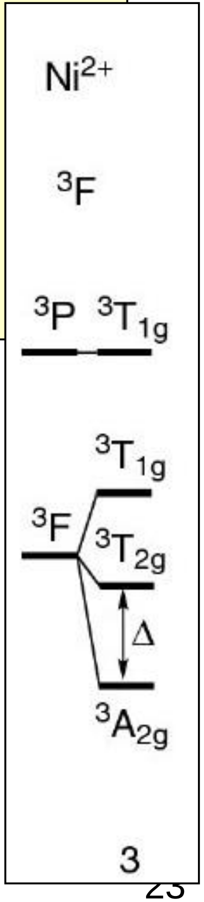
	H_2O	NH_3
$^3A_{2g} \rightarrow {}^3T_{2g}$,	8700 cm^{-1}	10700 cm^{-1}
$^3A_{2g} \rightarrow {}^3T_{1g}$ (F),	14500 cm^{-1}	17500 cm^{-1}
$^3A_{2g} \rightarrow {}^3T_{1g}$(P),	25300 cm^{-1}	28300 cm^{-1}

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.



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

Solution

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

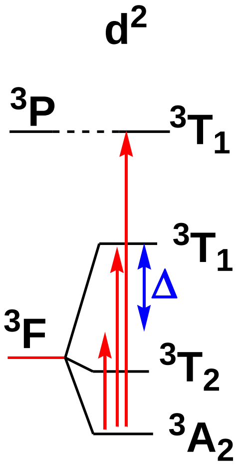
The splitting pattern in tetrahedral field is inverted to that in an octahedral field, hence

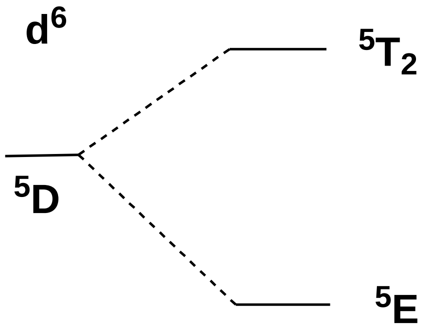
Splitting :

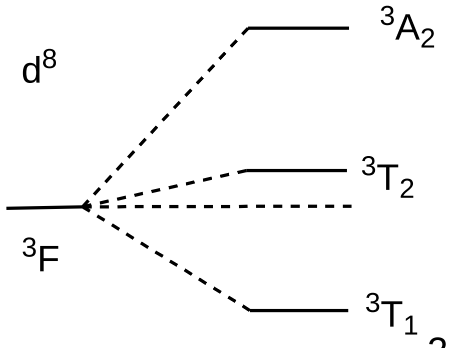
$^3F \Rightarrow {}^3A_2 < {}^3T_2 < {}^3T_1$

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

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







Exercise:

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 Δ_t?

d) Co^{2+} also forms an octahedral complex $[Co(NH_3)_6]^{2+}$. Identify its ground term. How large is Δ_o?

é) What do you expect for the intensity of the bands?

Solution:

a) $Co^{2+} = d^7$. In tetrahedral fields, ground term = $^4A_2$

b) 3 Bands: $^4A_2 \rightarrow {}^4T_2(^4F)$, $^4A_2 \rightarrow 4T_1(^4F)$, $^4A_2 \rightarrow {}^4T_1(^4P)$

c) The energy of the lowest energy transition ($^4A_2 \rightarrow {}^4T_2(^4F)$) relates to Δ_t = 7500 cm^{-1}.

d) $^4T_{1g}$, $\Delta_t = 4/9\ \Delta_o$, => Δ_o = 16875 cm^{-1}.

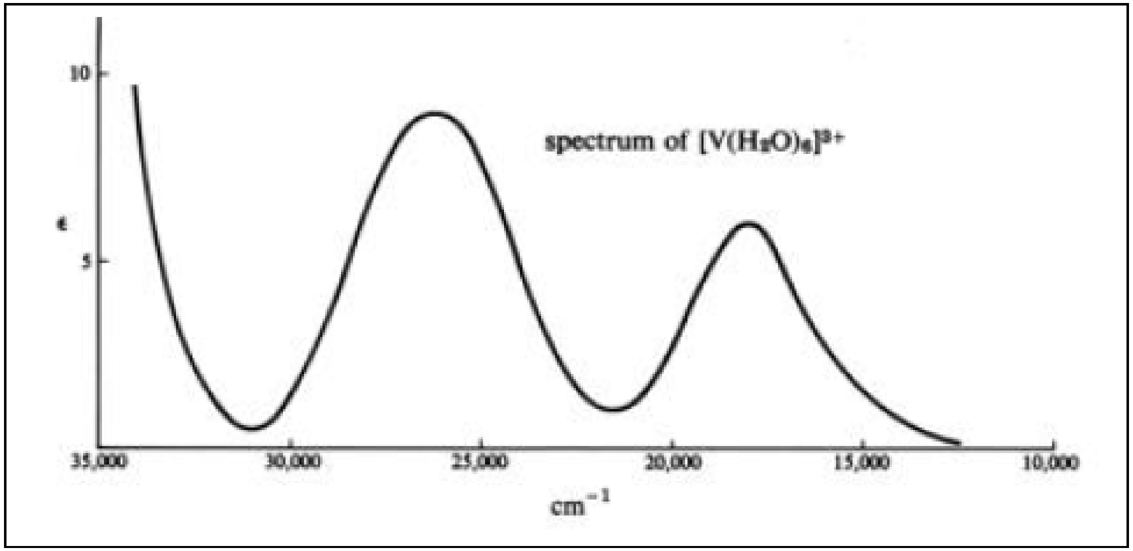
e) The transitions are now Laporte-forbidden, accordingly, the intensity drops (tetrahedral->octahedral). This is experimentally observed.

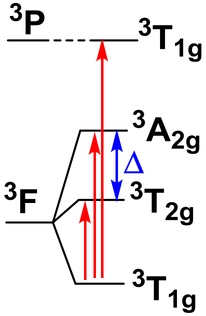
The UV-vis spectrum of $[V(H_2O)_6]^{3+}$

The absorption spectrum of a $[V(H_2O)_6]^{3+}$ solution is shown below, plotted as intensity of absorption (i.e., extinction coefficient) vs. energy (in cm^{1-}).

d^2 V^{3+}

^3F





three transitions

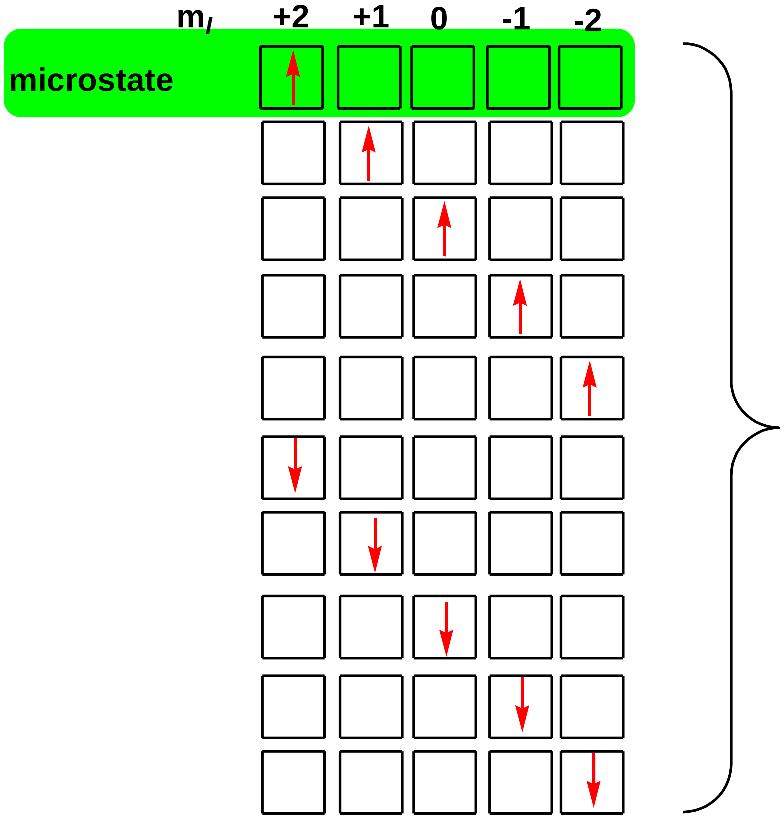
Two bands are observed within the range of measurement. They have maxima at about 17,500 and 26,000 cm^{1-}. The magnitude of the extinction coefficients $(\varepsilon \approx 10)$ suggests these are spin-allowed LaPorte-forbidden d-d transitions.

Appendix a): The Atomic Terms of the d^1 configuration

$l = 2, s = {}^1/_2$ quantum numbers for angular momentum and spin

$m_s = {}^1/_2$ ↑ or $-{}^1/_2$ ↓

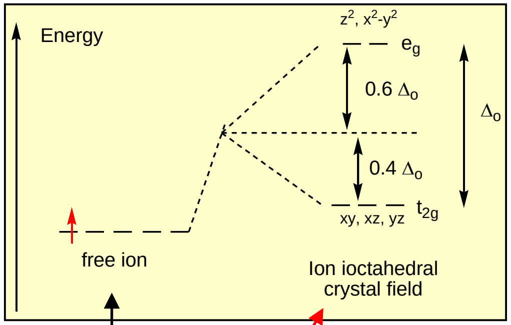
$m_l = 2, 1, 0, -1, -2$



degenerate

degeneracy
$(2l+1)(2s+1) = 5 \cdot 2 = 10$

"Term"

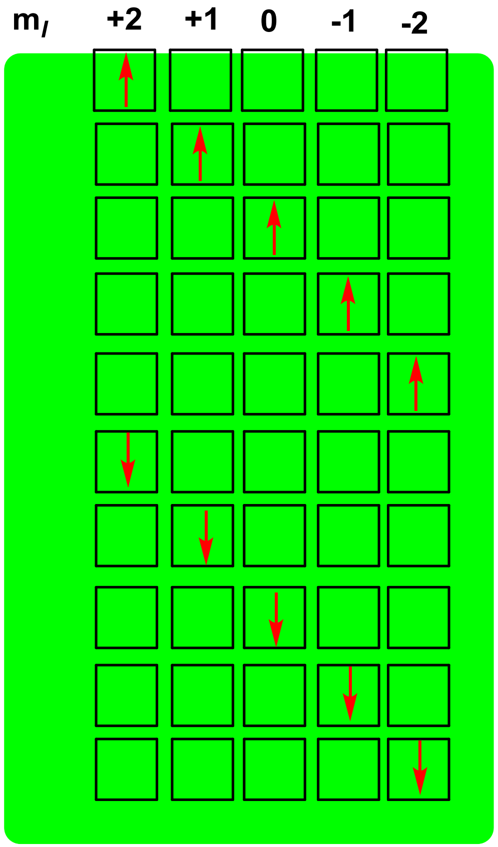


we are here

not here
that is the strong
field method

- a d-electron has 10 possibilities for occupation of the 5 d-Orbitals,
- these **10 microstates** (degenerate) form one **term**
- the d^1 configuration has only one term, a ^2D term
- this ^2D term is also the ground term of the d^1 configuration

Appendix: The Atomic Terms of the d^1 configuration



^2D term

$M_L = L = \sum m_l$	$M_s = S = \sum m_s$
2	1/2
1	1/2
0	1/2
-1	1/2
-2	1/2
2	-1/2
1	-1/2
0	-1/2
-1	-1/2
-2	-1/2

M_L \ M_s	1/2	-1/2
2	x	x
1	x	x
0	x	x
-1	x	x
-2	x	x

Multiplicity = 2 (= $2 \cdot S + 1$)

$L_{max} = 2$ => D-Term

^2D

total degeneracy =

$(2S_{max}+1)(2L_{max}+1) =$

$(2 \cdot 1/2+1)(2 \cdot 2+1) = 2 \cdot 5 = 10$

Appendix b) The Atomic Terms of the d^2 configuration

d^2-configuration of a free ion

⇒ a multi electron system => spin and angular momentum couple

⇒ Russel-Saunders-Coupling

$\binom{10}{2}$ **= 45 micro states**

$L = \Sigma\, l_i$ total orbital momentum

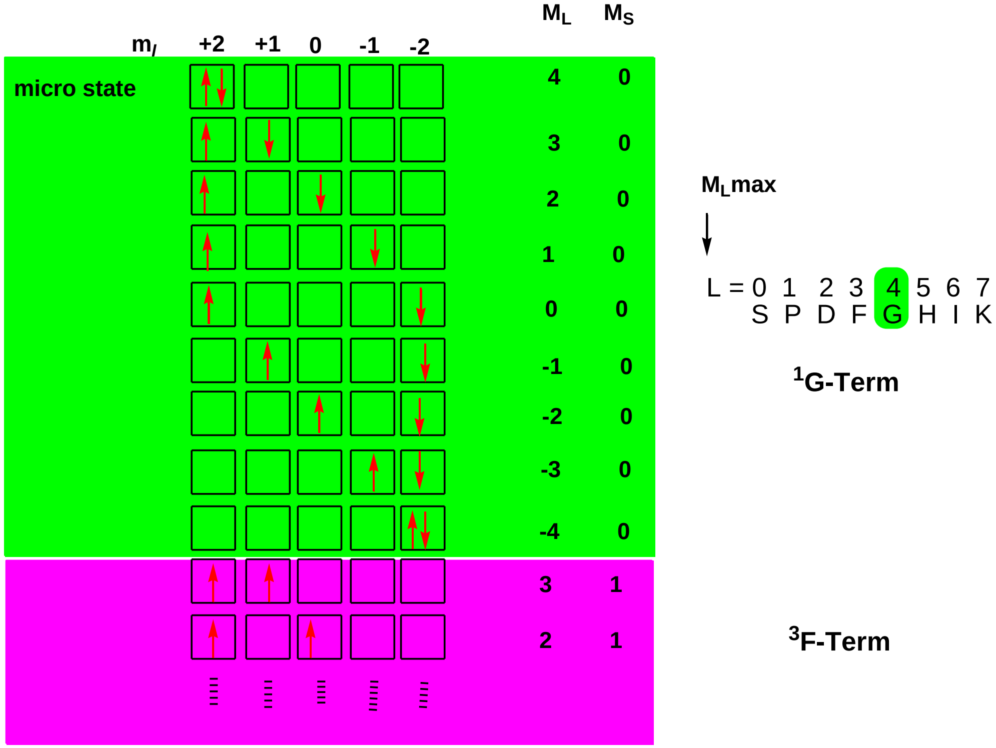
$S = \Sigma\, s_i$ total spin momentum

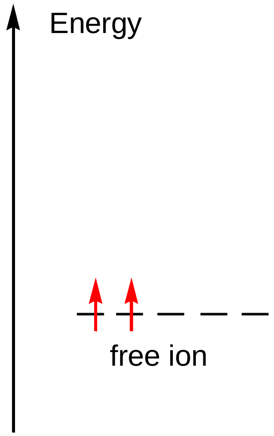
$M_L = +L, +L-1, \ldots -L$
$M_S = +S, +S-1, \ldots -S$

new quantum numbers

⟹ **$L_{max} = 4$, $S_{max} = 1$** (Hund's rule)

⟹ **$M_L = +4, +3, +2, +3, \ldots -4$**
$M_S = +1, 0, -1$





- the two d-electrons have 45 possibilities for occupation of the 5 d-Orbitals
- degenerate microstates form a term
- for d^2 there are 5 terms: ^3F, ^3P, ^1G, ^1D, ^1S with different energies

The 45 microstates of the d^2 configuration

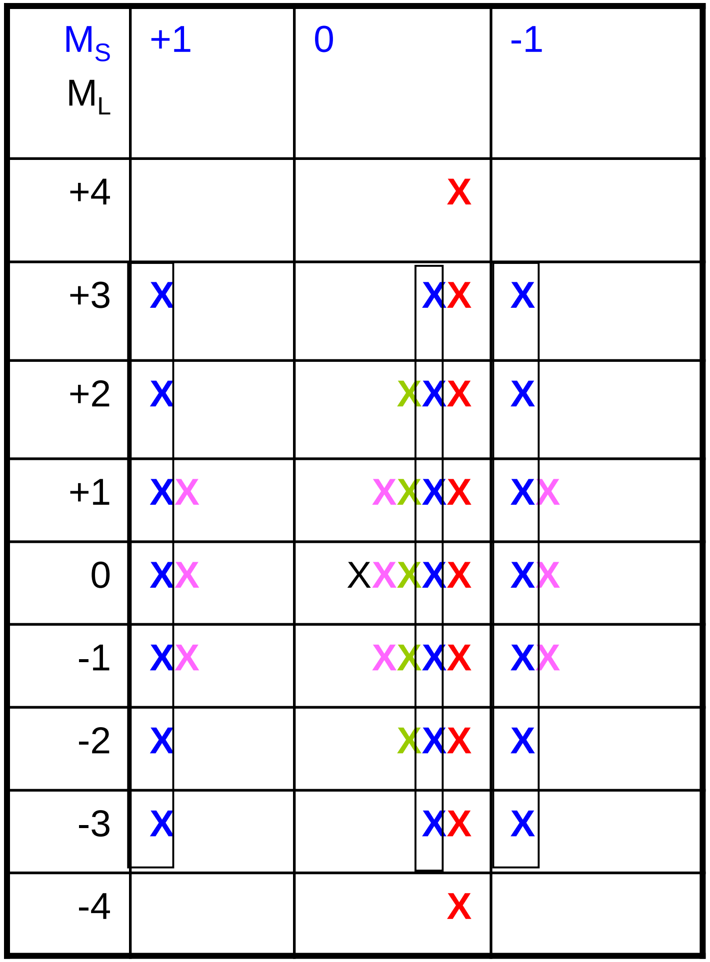
+2	↑↓					↑	↑	↑	↑	↓	↓	↓	↓												
+1		↑↓				↓				↑				↑	↑	↑	↓	↓	↓						
0			↑↓				↓				↑			↑			↑			↑	↑	↓	↓		
-1				↑↓				↓				↑			↑			↑		↓		↑		↑	↓
-2					↑↓				↓				↑			↑			↑		↓		↑	↓	↑
M_S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M_L	4	2	0	-2	-4	3	2	1	0	3	2	1	0	1	0	-1	1	0	-1	-1	-2	-1	-2	-3	-3

+2	↑	↑	↑	↑							↓	↓	↓	↓						
+1	↑				↑	↑	↑				↓				↓	↓	↓			
0		↑			↑			↑	↑			↓			↓			↓	↓	
-1			↑			↑		↑		↑			↓			↓		↓		↓
-2				↑			↑		↑	↑				↓			↓		↓	↓
M_S	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
M_L	3	2	1	0	1	0	-1	-1	-2	-3	3	2	1	0	1	0	-1	-1	-2	-3

↑↓ = ↓↑

The grouping of the 45 microstates of the d^2 configuration into atomic terms

1) Put one cross for each combination of M_L and M_S values into a table:



M_S M_L	+1	0	-1
+4		X	
+3	X	XX	X
+2	X	XXX	X
+1	XX	XXXX	XX
0	XX	XXXXX	XX
-1	XX	XXXX	XX
-2	X	XXX	X
-3	X	XX	X
-4		X	

2) Then check the following:

a) How often is one column type observed =>
=>$2S_{max}+1$

b) What is the value for $M_{L,max}$ (= L_{max})

Example:
The column with blue „crosses“ appears three times
=> Multiplicity = 3 => $S_{max}=1$
=> $M_{L,max} = L_{max} = 3$ => F-Term

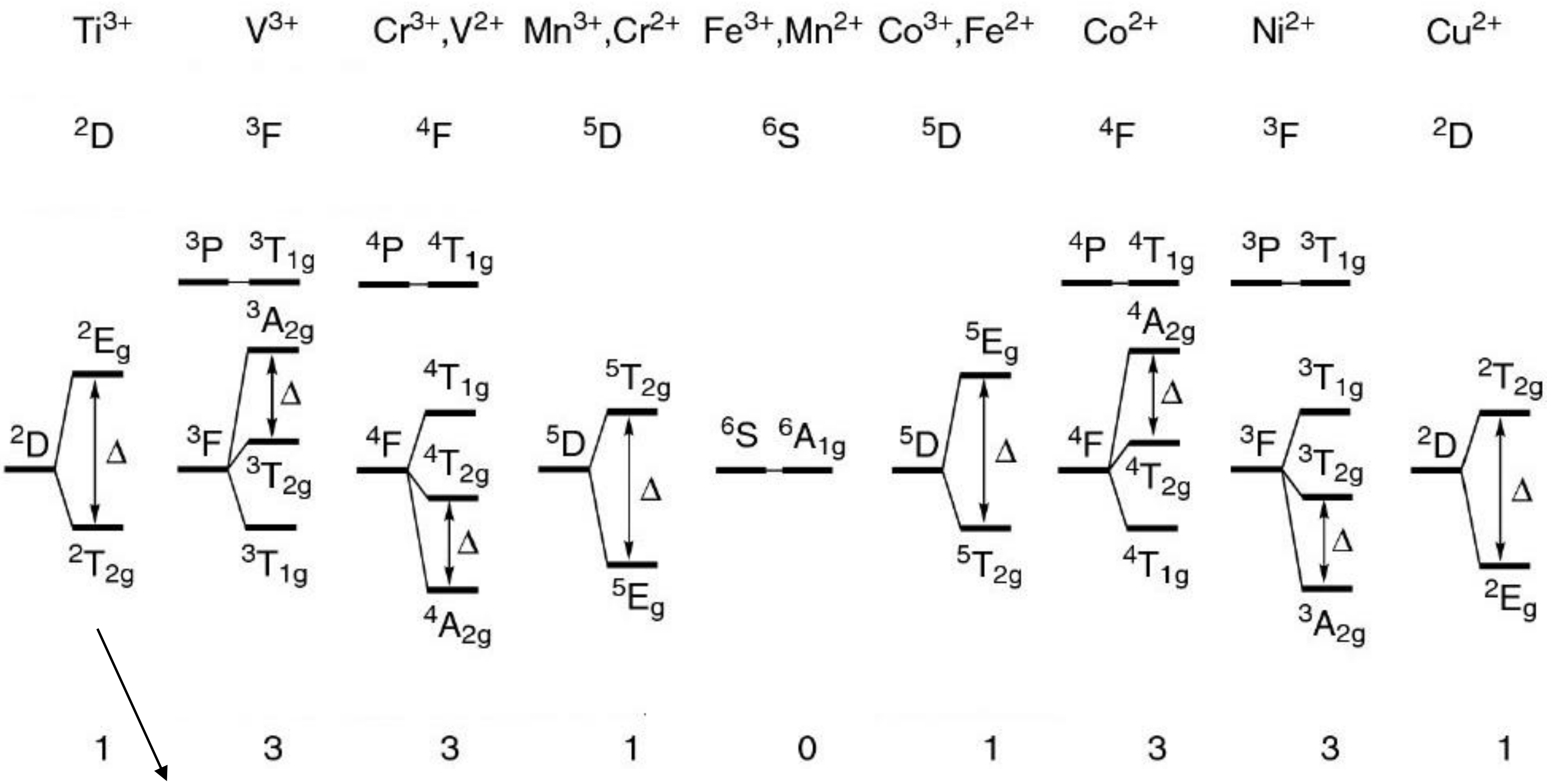
$\Rightarrow$ ^{3}F ^{3}P ^{1}G ^{1}D ^{1}S

$\Rightarrow$ 3·7 3·3 1·9 1·5 1·1 Σ45

Total multiplicity of a term
= spin-multiplicity x orbityl multiplicity
= $(2S_{max}+1)(2L_{max}+1)$

For the F-term: (2·1+1)(2·3+1)=3·7=21

Appendix c) Crystal field terms for high-spin complexes



ground term of complex in the crystal field

=>D ground terms for d^1,d^4,d^6,d^9 => 1 absorption band

⇒ F ground terms for d^2,d^3,d^7,d^3 => 3 absorption bands

⇒ identical splitting patterns for d^n and d^{n+5} (i.e. d^2, d^7); inverted for d^n and d^{10-n} (d^2, d^8)

⇒ inverted diagrams can be used for tetrahedral geometries