

Orgel Diagram

M. Sc. : CC – 3 (Inorganic Chemistry)

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Orgel Diagrams

It is the splitting of term (atomic term) in weak field of complexes.

- It is correlation diagram show the relative energies of electronic terms in transition metal complexes.
- It is named after proposer 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.

Microstate & Ground State Term

The Atomic Terms of the d^n configuration

Electron present in an orbital has several possibilities but stable is only one or few more. It has been calculated by following formula

$$\text{No. of microstates} = n! / (e! (n-e)!)$$

Where n = no. of orientation of orbital

e = no. of electron

But ground stable term is calculated as

The Atomic Terms of the d^1 configuration

m_l	+2	+1	0	-1	-2
	↑				
		↑			
			↑		
				↑	
					↑
	↓				
		↓			
			↓		
				↓	
					↓

2D term

$$M_L = L = \sum m_l$$

2

1

0

-1

-2

2

1

0

-1

-2

$$M_s = S = \sum m_s$$

1/2

1/2

1/2

1/2

1/2

-1/2

-1/2

-1/2

-1/2

-1/2

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

Multiplicity = 2 (= 2·S + 1)

$L_{\max} = 2 \Rightarrow D\text{-Term}$

2D

total degeneracy =

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

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

The Atomic Terms of the d² configuration

d²-configuration of a free ion

⇒ a multi electron system ⇒ spin and angular momentum couple

⇒ Russel-Saunders-Coupling

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

$L = \sum l_i$ total orbital momentum

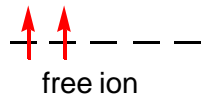
$S = \sum s_i$ total spin momentum

$M_L = +L, +L-1, \dots -L$ new quantum numbers
 $M_S = +S, +S-1, \dots -S$

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

⇒ $M_L = +4, +3, +2, +3, \dots -4$
 $M_S = +1, 0, -1$

Energy ↑



	m_l	+2	+1	0	-1	-2	M_L	M_S
micro state		↑↓					4	0
		↑	↓				3	0
		↑		↓			2	0
		↑			↓		1	0
		↑				↓	0	0
			↑			↓	-1	0
				↑		↓	-2	0
					↑	↓	-3	0
						↑↓	-4	0
		↑	↑				3	1
		↑		↑			2	1
		⋮	⋮	⋮	⋮	⋮		

$M_L \max$



$L = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7$
 S P D F **G** H I K

¹G-Term

³F-Term

- the two d-electrons have 45 possibilities for occupation of the 5 d-Orbitals
- degenerate microstates form a term
- for d² there are 5 terms: ³F, ³P, ¹G, ¹D, ¹S with different energies

Co relationship atomic terms between d^n system

If $d^{n1} + d^{n2} = 10$ then atomic terms are same

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

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

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

Hund's Rule:

Term with highest spin multiplicity has lowest energy.

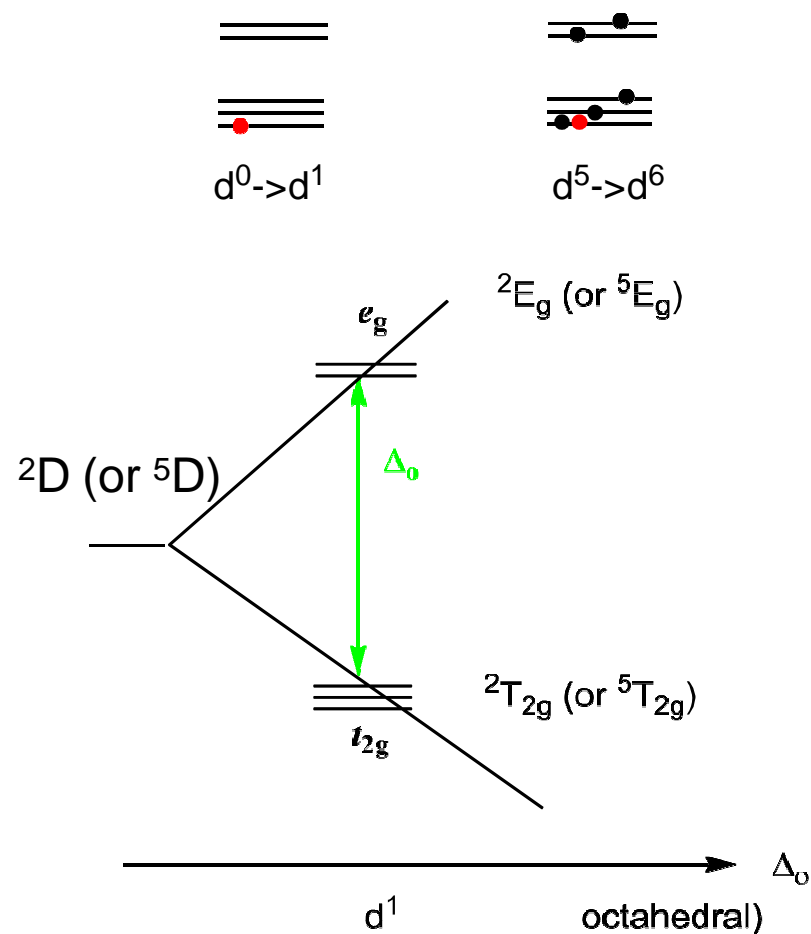
For terms with same multiplicity, that one with highest value of L is lower in energy

e.g. $^3F < ^3P$ for d^2, d^8 ,
 $^4F < ^4P$ for d^3, d^7

Term S & P do not split due to symmetrical shape but term D & F split into smaller crystal field terms depending upon geometry of complexes.

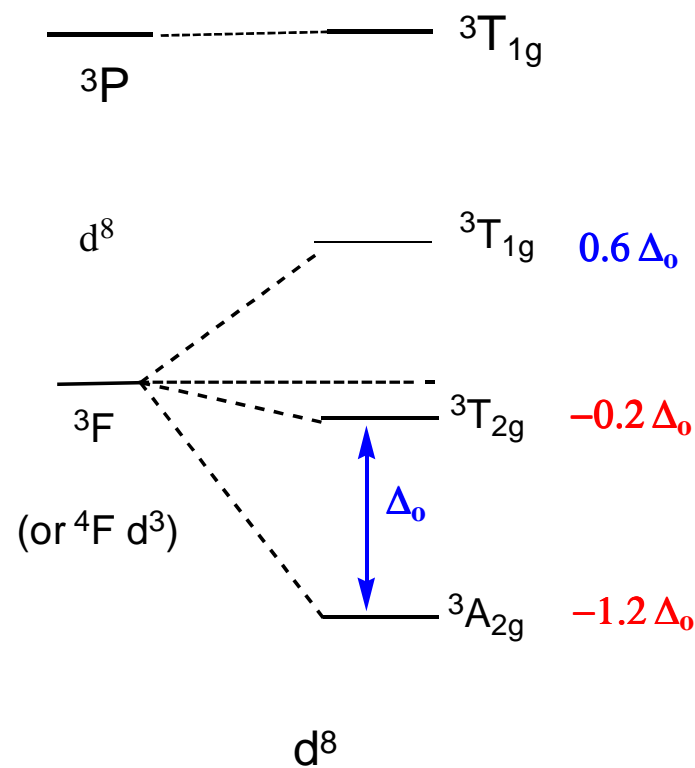
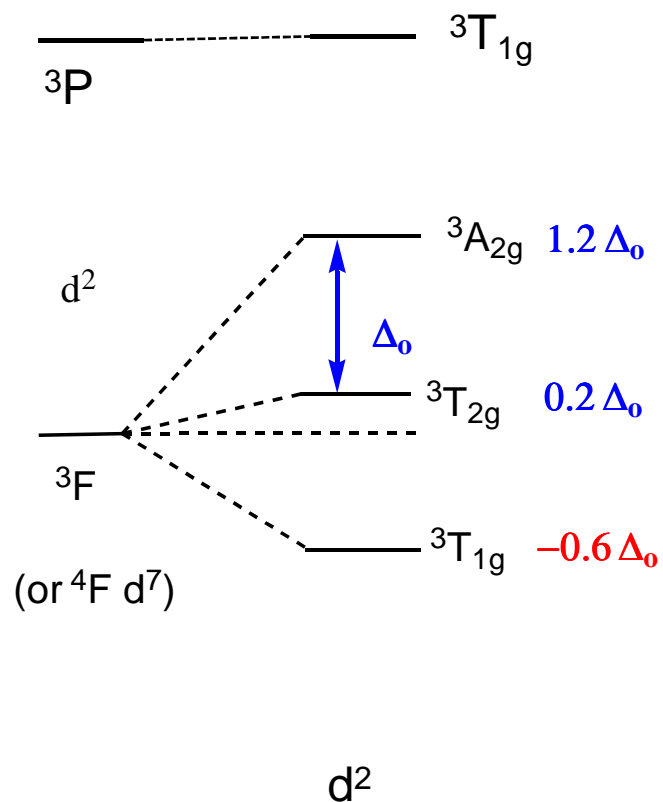
Stable ground term of dn system calculated by following way which also gives idea about Electronic absorption spectra of octahedral and tetrahedral complexes with d^1 , d^9 , d^4 , and d^6 configuration

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

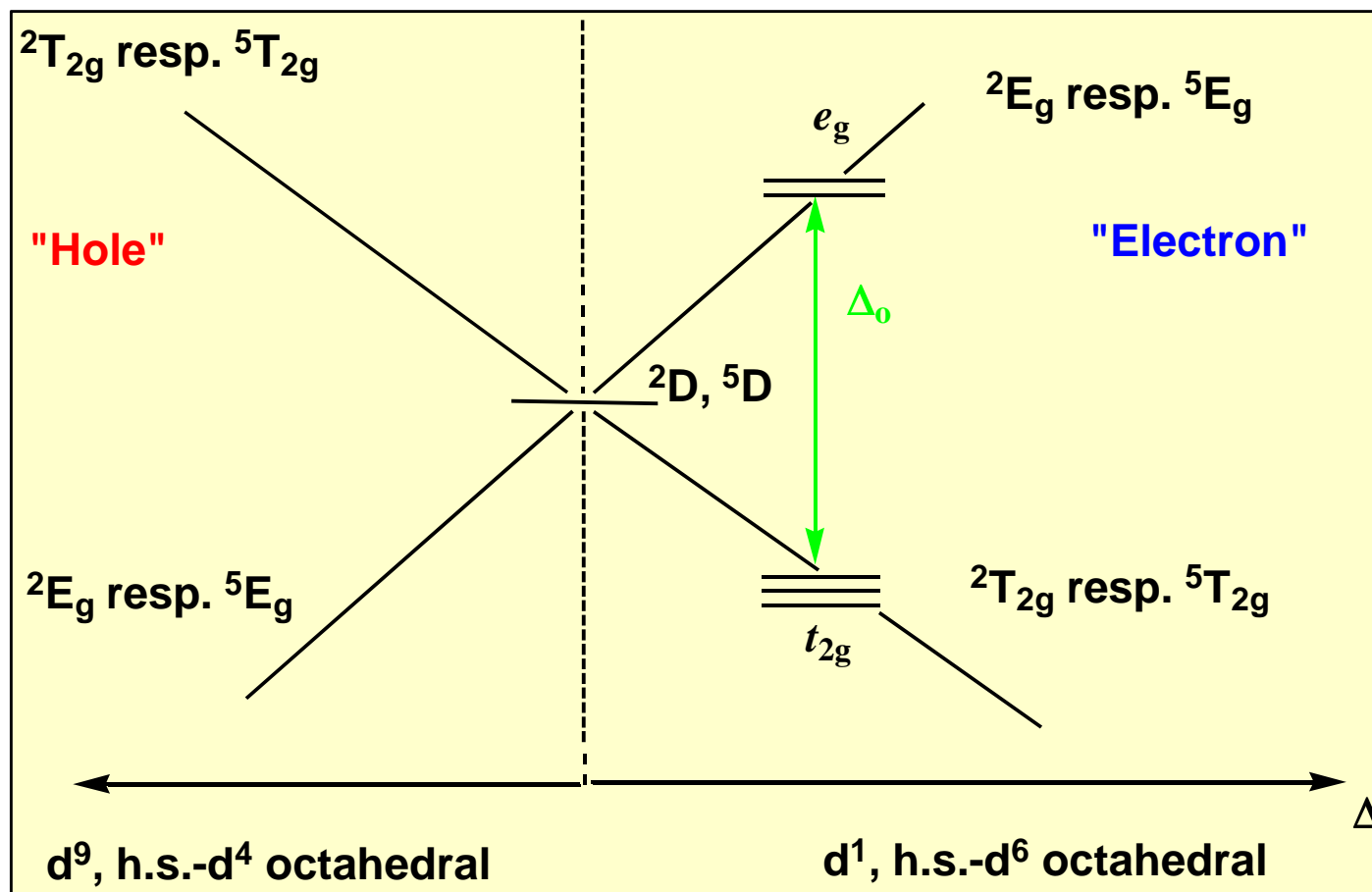


Splitting of atomic term into crystal field terms: d^2 , d^3 , d^7 , d^8 configuration

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



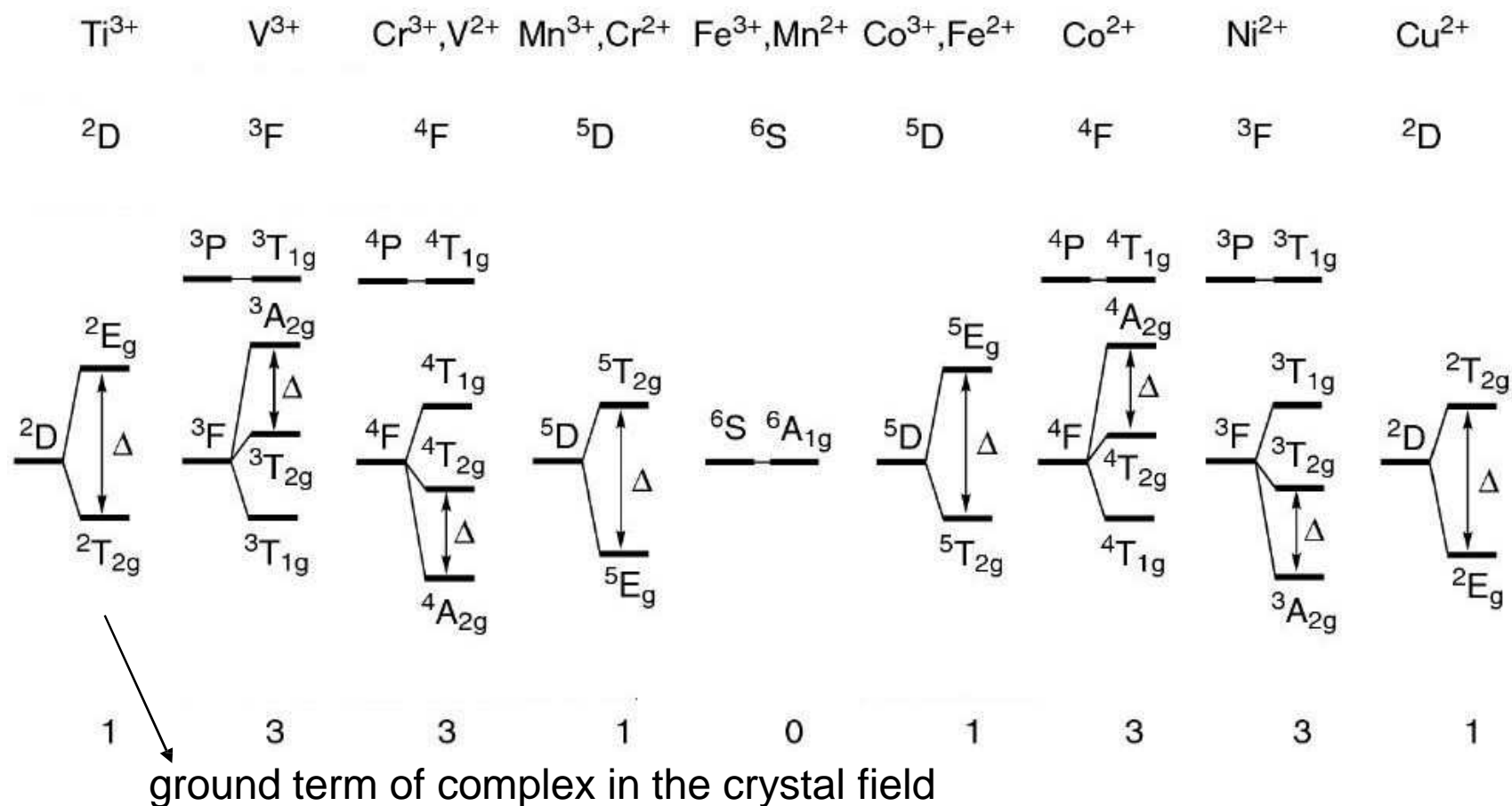
Orgel diagram for d^1 , d^9 , d^4 , d^6



←
term reversal

Similar correlations derivable for tetrahedral complexes

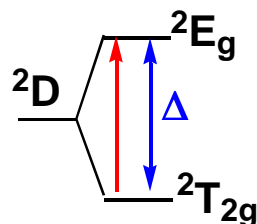
Crystal field terms for high-spin complexes are summarized as



- \Rightarrow D ground terms for $d^1, d^4, d^6, d^9 \Rightarrow$ 1 absorption band
- \Rightarrow F ground terms for $d^2, d^3, d^7, d^8 \Rightarrow$ 3 absorption bands
- \Rightarrow 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)
- \Rightarrow inverted diagrams can be used for tetrahedral geometries

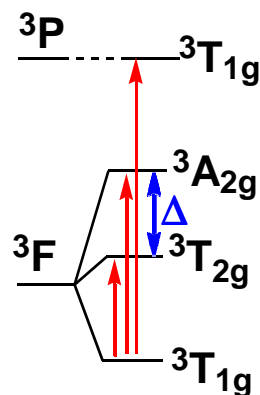
Spectral Peak due to electronic transitions

$d^1 \text{Ti}^{3+}$
 2D



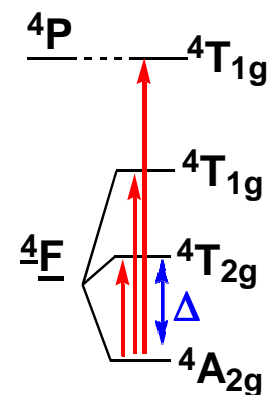
one transition

$d^2 \text{V}^{3+}$
 3F



three transitions

$d^3 \text{Cr}^{3+}$
 4F



three transitions

similarly for the other d^n configurations

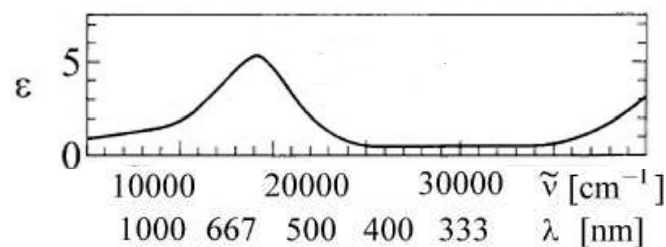
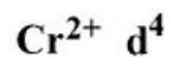
Co relationship of Orgel diagram of d^1 system

If $d^{n1} - d^{n2} = 5$ then diagrams are same.

If $d^{n1} + d^{n2} = 10$ then Orgel diagrams are opposite.

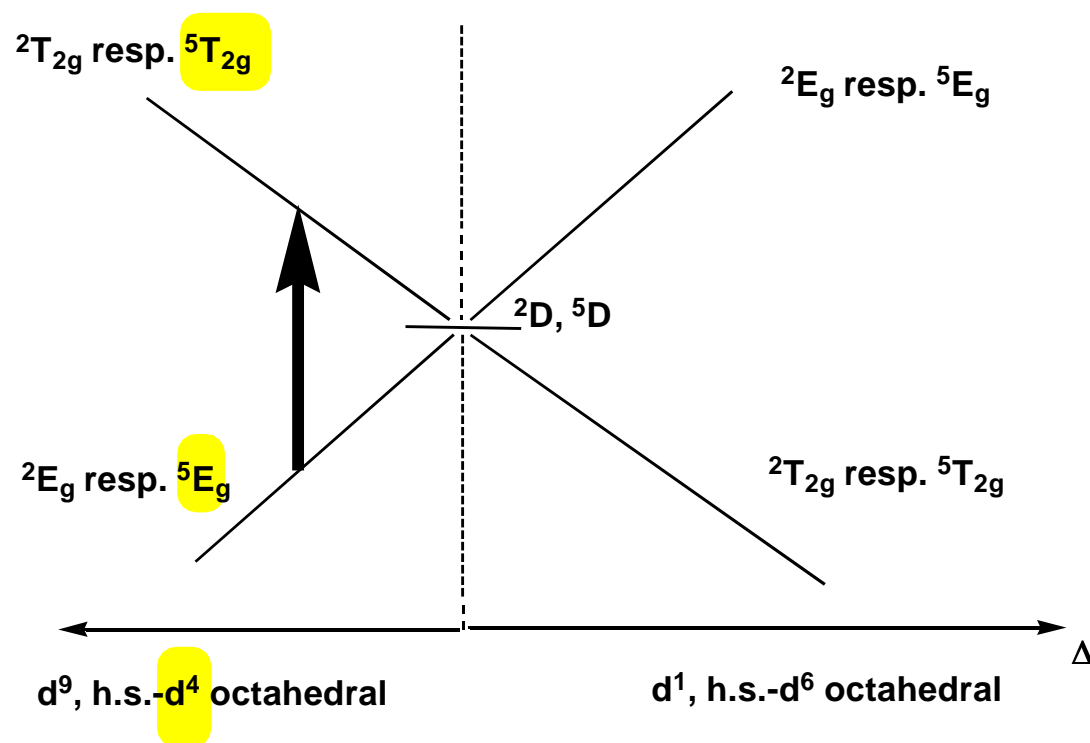
Exercise

The octahedral h.s. complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (d^4) shows one UV/Vis absorption band. Assign the transition! Use an Orgel diagram.



Solution

The octahedral h.s. complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (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:



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

Solution

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

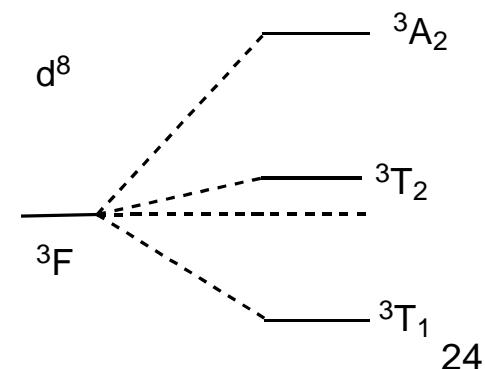
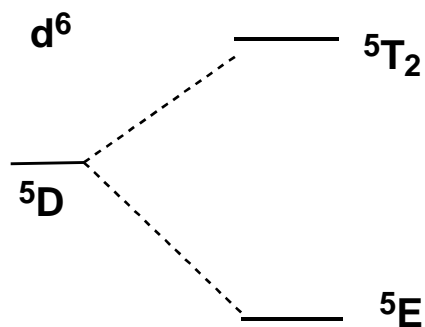
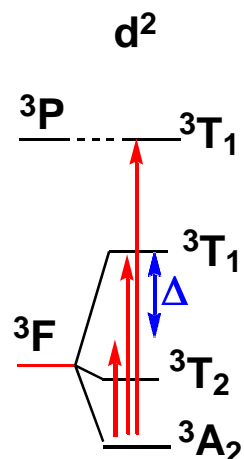
The splitting pattern in tetrahedral field is inverted to that in an octahedral field, hence

Splitting :

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

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

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



Exercise:

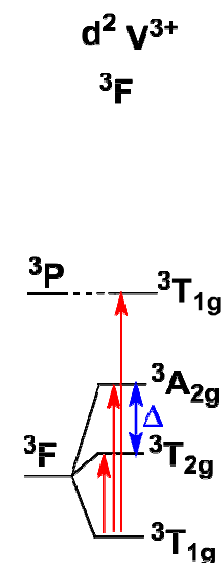
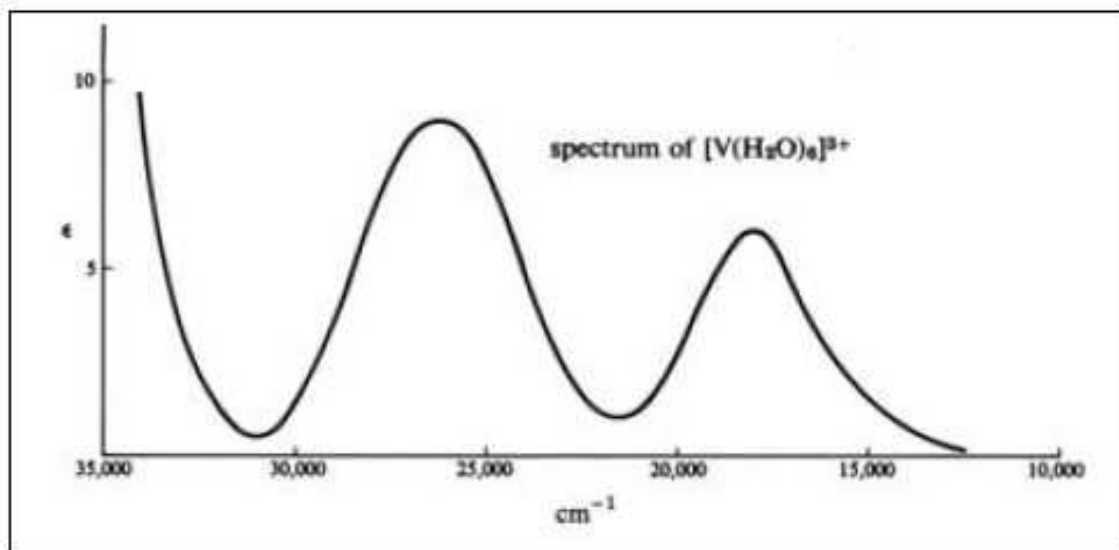
- a) What is the ground term for $[\text{Co}(\text{NH}_3)_4]^{2+}$?
- b) How many electronic absorption bands are expected? Assign them?
- c) If the band with the lowest energy appears at 7500 cm^{-1} , how large is Δ_t ?
- d) Co^{2+} also forms an octahedral complex $[\text{Co}(\text{NH}_3)_6]^{2+}$. Identify its ground term. How large is Δ_o ?
- é) What do you expect for the intensity of the bands?

Solution:

- a) $\text{Co}^{2+} = d^7$. 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 $\Delta_t = 7500 \text{ cm}^{-1}$.
- d) $^4T_{1g}$, $\Delta_t = 4/9 \Delta_o$, $\Rightarrow \Delta_o = 16875 \text{ cm}^{-1}$.
- e) The transitions are now Laporte-forbidden, accordingly, the intensity drops (tetrahedral->octahedral). This is experimentally observed.

The UV-vis spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$

The absorption spectrum of a $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ solution is shown below, plotted as intensity of absorption (i.e., extinction coefficient) vs. energy (in cm^{-1}).



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 ($\epsilon \approx 10$) suggests these are spin-allowed LaPorte-forbidden d-d transitions.



Thank You

