

Electronic Spectroscopy of Transition Metal Ions

- colour is one of the distinguishing features of TM complexes (except d^0 and d^{10} of course!)
- visible and long UV light absorption causes electronic transitions from a filled or partially filled d orbital to a higher energy empty orbital (usually d)

$$\Delta E = h\nu = hc/\lambda$$

- complexes are often pale in colour but there are some notable exceptions:

d→d transitions	Charge transfer (CT) transitions
weak ($\epsilon < 100 \text{ L mol}^{-1} \text{ cm}^{-1}$)	strong ($\epsilon > 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$)
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ d^4 sky blue	MnO_4^- d^0 intense purple
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ d^5 pale pink	$[\text{CoCl}_4]^{2-}$ d^7 deep blue
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ $[\text{Cl}^-]_2$ d^7 pink	
CoCl_2 (s) d^7 blue	

Beer's Law: $A = \epsilon cl$

(A = absorbance; ϵ = molar extinction coefficient or molar absorptivity; c = molar concentration; l = pathlength of light through the solution in cm)

- ϵ ranges from 0-100 (pale colours) to >100,000 (intense colours) due to selection rules (*dealt with later*)
- bands are broad due to **vibronic coupling**: electronic transitions occur on a timescale much shorter than vibrations. Oscillating ligands = different transition energies

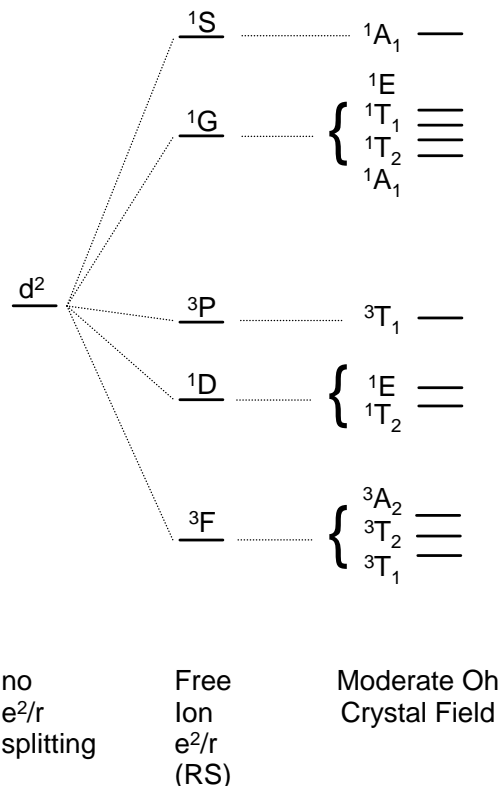
Electronic spectroscopy in multi d electron ions

- in order to understand the spectroscopy of d ions with more than one d electron we must take the effect of $e^- - e^-$ repulsion into account (*we have ignored this so far*)
- each e^- has spin and orbital angular but it is the interaction of the **TOTAL RESULTANT spin and angular momentum** with light that is important
- we can treat the total spin and angular momentum separately OR we can combine them to form a new quantum number J and then come up with a total J ...which is best to use depends on where we are in the periodic table:

Lighter d metal ions: S and L total separately (**Russell-Saunders coupling** – dealt with in this course)

Heaviest d and f metal ions: need to define J states (**jj coupling**)

The energy levels derived from a d^2 ion in an Oh field:



Term symbols: energy differs by **total S and L** for a *'term'*

$$(2S+1)L_J$$

where S = total spin multiplicity, L = total orbital angular momentum and J is combined TOTAL angular momentum (spin and orbital combined which can range from L+S to L-S)

eg. 3F has S = 1 and L = 3

With most TM ions, the **spin-orbit coupling is small** due to electron delocalization onto the ligands so the energy differences between the possible J states are negligible but the possibilities would be J = 4, 3 or 2 giving rise to 3F_4 , 3F_3 and 3F_2 states.

Russell-Saunders coupling scheme for a d^2 ion

- each e^- in a d orbital has $l = 2$ ($m_l = 2, 1, 0, -1, -2$) and $s = \frac{1}{2}$ ($m_s = +\frac{1}{2}, -\frac{1}{2}$)
- combine these into S and L which represent the TOTAL spin and orbital angular momentum
- there are many different arrangements of electrons in d orbitals so this gives rise to many possible states (Russell-Saunders '*terms*') that represent different energies for the system as a whole

eg. d^2 ion

1st electron: any of the 5 d-orbitals and spin up or down gives rise to 10 possibilities

2nd electron: can go in any d orbital but only spin paired in the one already occupied = 9 possibilities

- therefore there are 90 ways to do this but since e^- are indistinguishable, there are actually only 45 unique arrangements (called '*microstates*' of the system)
- but L and S are quantized so an $S = 1$ state has $M_S = 1, 0, -1$ and an $L = 2$ state has $M_L = 2, 1, 0, -1, -2$ thus we need to group these microstates together into the terms with unique L and S that give rise to them

Electronic Spectra and Magnetism of Transition Element Complexes

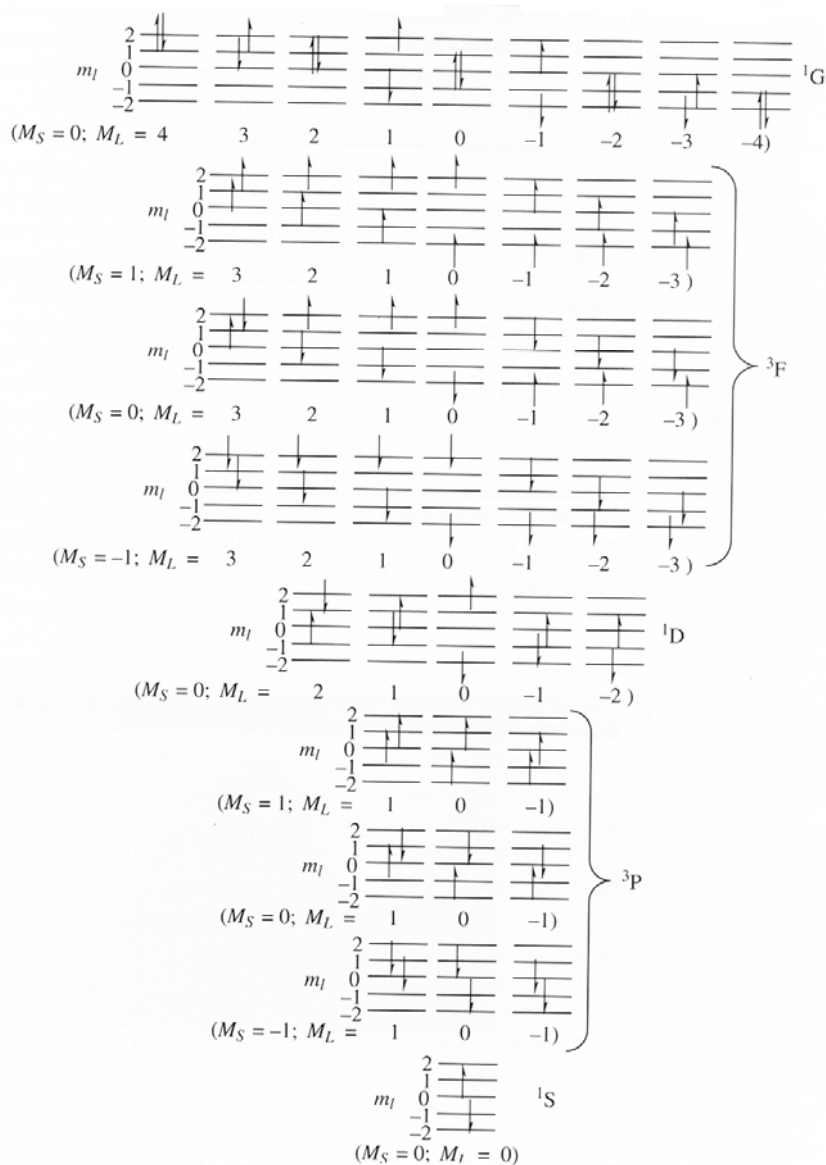


Figure 7.1 Microstates and Russell-Saunders terms for a d^2 transition metal ion.

From: 'd- and f-block Chemistry' by C. Jones, Wiley, 2002.

So the RS terms arising for a d^2 ion are: 1G , 3F , 1D , 3P and 1S but...

which one is lowest in energy (the ground term)?

Hund's rules take care of this:

a) lowest energy term has the largest spin multiplicity

b) if two terms share the same multiplicity, the largest L value is lowest in energy

So that means 3F is lowest for a d^2 ion (Hund's rules only apply to the ground term NOT the order overall)

Here are the complete lists of RS terms for each d electron count:

***d* count RS Terms (ground term listed last in bold)**

d^1, d^9	2D
d^2, d^8	$^1S, ^1D, ^1G, ^3P, ^3F$
d^3, d^7	$^2D, ^2P, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$
d^4, d^6	$^1S, ^1D, ^1G, ^1S, ^1D, ^1F, ^1G, ^1I, ^3P, ^3F, ^3P, ^3D, ^3F, ^3G, ^3H, ^5D$
d^5	$^2D, ^2P, ^2D, ^2F, ^2G, ^2H, ^2S, ^2D, ^2F, ^2G, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

- Since an electron in an empty shell behaves in the same way as an 'electron hole' in a filled shell, the d^1 and d^9 ions have the same set of terms and similarly for the other pairs listed.

Okay, so what happens when we consider crystal field effects?

RS terms (^{2S+1}L) split exactly the same way in a crystal field as do orbitals with the same value of l :

Free ion term	# of states (ML)	Oh crystal field terms
S	1	A_{1g}
P	3	T_{1g}
D	5	T_{2g}, E_g
F	7	T_{1g}, T_{2g}, A_{2g}
G	9	$A_{1g}, E_g, T_{1g}, T_{2g}$

so the 3F ground term for a d^2 ion gives rise to:

$^3T_{1g}, ^3T_{2g}$ and $^3A_{2g}$ states in an Oh crystal field

Simplest case: d^1 ion (like Ti^{3+})

$s = 1/2$ ($m_s = +1/2, -1/2$); $l = 2$ ($m_l = 2, 1, 0, -1, -2$)

therefore: $S = 1/2$ and $L = 2$ which gives only one RS term: 2D

which in an Oh crystal field splits just like a simple d orbital into:

2E_g and $^2T_{2g}$ and the transition observed by spectroscopy is from $^2T_{2g}$ to 2E_g