Electronic Selection Rules (II)

Term Symbols

- now we are finally ready to clearly define our electronic states!

IMPORTANT

- microstates for a particular atomic configuration are grouped into what are called **free ion terms** which are denoted by a **term symbol** $^{2S+1}\{L\}_J$
  - this gives a shorthand for information on the total spin S or actually the multiplicity, the total angular momentum L and the spin-orbit coupling J
  - spin-orbit coupling slightly splits the energy levels of the L states into states of specific J value with 2J+1 degenerate levels corresponding to all the possible M_J values

IMPORTANT

- **Hund's rules** are used to determine the lowest energy ground state
  - the ground state term always has the *highest multiplicity*, and if two terms share the same multiplicity the one with the *highest value of L* is the ground state term
  - the terms arising for a subshell containing n electrons are *the same for those containing n holes*, for example d^2 (2 electrons) and d^8 (2 holes) are the same
  - these rules can occasionally fail for excited states, and should not be used to determine the energy ordering of higher level states
- coming back to our p^2 example which has 15 microstates, we determine the atomic states by assessing the maximum L and S values
  - the largest L must be when both electrons have l=1: L=1+1=2, thus the full set of L values will be 0, 1, 2 giving terms of S P and D
  - the largest S must be when both electrons have the same spin so max S=1/2+1/2=1 and the full set of S values will be 0 and 1, with the corresponding multiplicities of 1 and 3
  - you might think that we could then have states of ^1S, ^3S, ^1P, ^3P and ^1D, ^3D
  - however some of these are forbidden by Hund's rules, and the Pauli principle, the accounting of quantum states can feel very "non-intuitive"
  - for example a state ^3D with L=2 and S=1 is impossible, this would require both electrons to be in the M_L=1 state and both to have M_S=1/2, ie both electrons would be in the same state!
  - the p^2 configuration has allowed ^3P, ^1D and ^1S terms, **Figure 1**

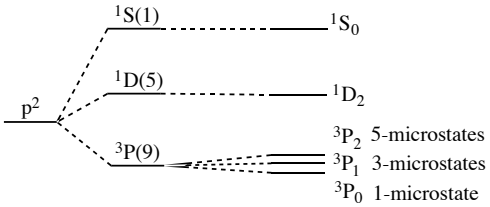


Figure 1 diagram showing microstates for p^2

- determining the free ion states from the atomic configurations $xs^n(x+1)p^n$ is complex!
- the full process is demonstrated in the model answer to the first of the problems at the end of these lecture notes. I also *strongly recommend* looking at the relevant parts of the course text books
- next the J values are evaluated for each of the terms, thus for the ^3P term L=1 and S=1 leading to J=2, 1, 0 and the term symbols are $^3P_2$, $^3P_1$ and $^3P_0$.

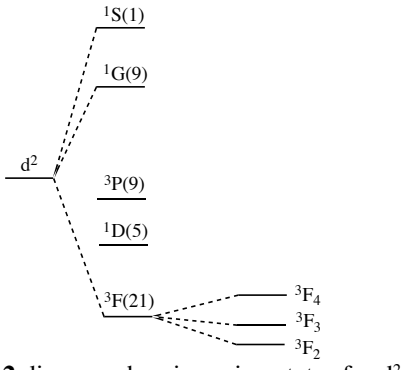


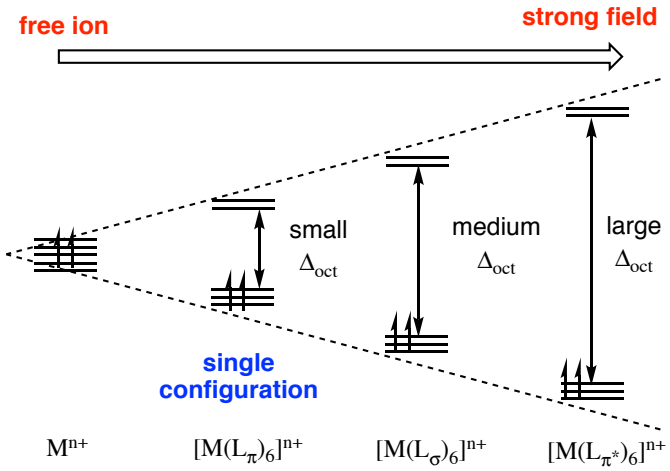
Figure 2 diagram showing microstates for d^2

- the $^3P_2$ term will then be 5 fold degenerate with M_J=-2, -1, 0, 1, 2
- the $^3P_1$ term has J=1 and is 3 fold degenerate with M_J=-1, 0, 1
- the $^3P_0$ term has J=0 and is a single level with M_J=0
- thus the original ^3P term is nine fold degenerate and split slightly into a pattern of 5, 3 and 1

- the dAOs have a very large number of microstates
  - for example for d^2 there are 45 microstates which are divided into the terms shown in **Figure 2**. The number of degenerate states is given in brackets, and the J terms have only been given for the lowest energy state.

Term Symbols in an Octahedral Field

- we have now explored how to define the electronic state for an isolated metal ion or a metal ion in a weak field where the atomic states are only slightly distorted, in this case the **atomic** dAOs form the best basis
- when a transition metal is coordinated by ligands the symmetry is reduced and the ligands substantially distort the local TM environment, there are significant changes, such as the familar splitting into t_{2g} and e_g levels, in this case the **molecular** MOs form the best basis
- this is not an on/off phenomenon, but a graduated scale determined by the ligands and the action of the spectrochemical series, **Figure 3**



OLD way (simplified but useful for those who don't know more)

Figure 3 diagram showing the effects of an increasing ligand field strength on *orbital energies* for a single (d^2) configuration

  - however, we now know that we need to consider more than a single configuration for "d^2", **Figure 4**
  - under an octahedral field the lower symmetry leads to a lifting of degeneracies of the spherical atom and the term symbols become: S=>A_{1g}, P=>T_{1g}, D=>E_g+T_{2g}, F=>A_{2g}+T_{1g}+T_{2g}, G=>A_{1g}+E_{1g}+T_{1g}+T_{2g}
  - note that all the term symbols reduce to gerade symmetries, multiplicities remain unchanged
  - the new pattern of electronic states and term symbols for a set of strong field ligands is very different from that for the atomic states!

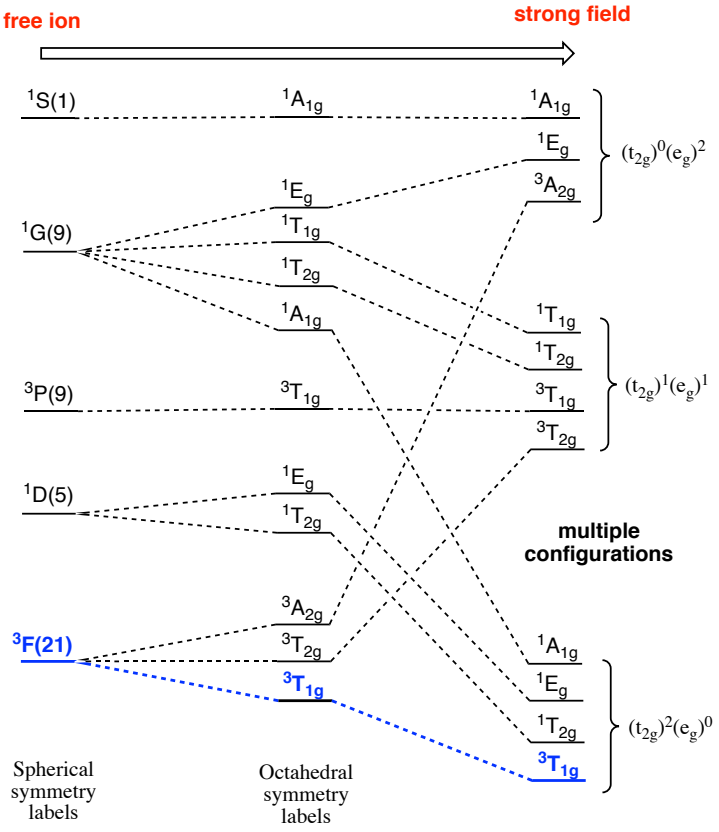


Figure 4 diagram showing the effects of an increasing ligand field strength on (d^2) *configurations*

Term Symbols in Strong Field Limit

- now we will determine the term symbols and possible microstates of an octahedral molecule at the limit of strong field ligands, ie the symmetry labels on the RHS of **Figure 4**
- **Table 1** shows all the possible term symbols and microstate degeneracy for the varying strong field TM-complex dAO dominated MOs.

config	micro -states	Term symbols	config	micro -states	Term symbols
$(t_{2g})^1$	6	$^2T_{2g}$	$(e_g)^1$	4	^2E_g
$(t_{2g})^2$	15	$^1A_{1g}+^1E_g+^3T_{1g}+^1T_{2g}$	$(e_g)^2$	6	$^1A_{1g}+^3A_{2g}+^1E_g$
$(t_{2g})^3$	20	$^4A_{2g}+^2E_g+^2T_{1g}+^2T_{2g}$	$(e_g)^3$	4	^2E_g
$(t_{2g})^4$	15	$^1A_{1g}+^1E_g+^3T_{1g}+^1T_{2g}$	$(e_g)^4$	1	$^1A_{1g}$
$(t_{2g})^5$	6	$^2T_{2g}$			
$(t_{2g})^6$	1	$^1A_{1g}$			

Table 1 Terms associated with dAO configurations

- now we will work through these showing how all the term symbols are derived
- we know in the octahedral environment the dAO dominated MOs split into a t_{2g} and e_g set, we need to consider the potential occupation patterns for filling up these levels

- for $(t_{2g})^1$ there are six microstates (the single electron can occupy any of the $3t_{2g}$ orbitals with spin up or spin down, **Figure 5**.
  - the term symbol is easily established as the symmetry of the state is just the symmetry of the occupied orbital involved $^2T_{2g}$

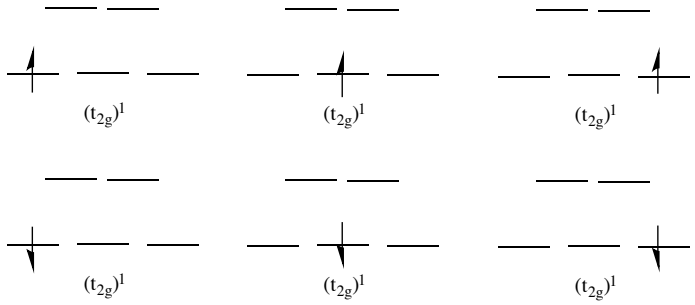


Figure 5 diagram for possible microstates for $(t_{2g})^1$ s=1/2, m_s=+1/2 and m_s=-1/2

- for $(e_g)^1$ the term symbol is also easily established as the symmetry of the $(e_g)^1$ state, this is ^2E_g
- term symbols for the completely full levels $(t_{2g})^6$ and $(e_g)^4$ must be $^1A_{1g}$
- for $(e_g)^3$ and $(t_{2g})^5$ we use the hole formalism, which states that the same number of electrons or holes have the same term symbols. Thus the $(t_{2g})^1$ and $(t_{2g})^5$ configurations will have the same core term symbols, as will $(e_g)^1$ and $(e_g)^3$. $(e_g)^3$ is therefor E_g and $(t_{2g})^5$ is T_{2g}
  - note that I have not explicitly assigned the multiplicity as this can be complex for 5 and 3 electrons respectively, but the multiplicity is given for the term symbols in **Table 1**
- in general for other configurations we can use the same method employed earlier for water and take the direct product of the orbital symmetries for unpaired electrons:
  - for $(t_{2g})^2$ (which is the same as that for $(t_{2g})^4$) we form the direct product of the electrons not paired in a MO:

$$(t_{2g})^2 = T_{2g} \otimes T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$$

  - note that I have again not assigned the multiplicity using the direct product method, as this can be complex, more details can be found in the recommended text

In Notes Activity

- determine the term symbols for the $(e_g)^2$ configuration, draw out the 6 possible microstates for this configuration and identify the multiplicity of each state

Figure 6 diagram of possible microstates for $(e_{2g})^2$

- the direct product method does not work all the time, for example the $(e_g)^3$ and $(t_{2g})^3$ configurations cannot be determined this way

$$(e_g)^3 = E_g \otimes E_g \otimes E_g = \left(A_{1g} + A_{2g} + E_g\right) \otimes E_g = \times$$

$$(t_{2g})^3 = T_{2g} \otimes T_{2g} \otimes T_{2g} = \left(A_{1g} + E_g + T_{1g} + T_{2g}\right) \otimes T_{2g} = \times$$

  - however, we already know the $(e_g)^3$ configuration from the hole formalism
  - the terms for $(t_{2g})^3$ are complex and I will not cover it here, more details can be found in the recommended text
- if we want to connect the strong field ligand configurations with those of the free ion we need to remember that the d^2 configuration includes a number of different strong field configurations: $(t_{2g})^2$ and $(t_{2g})^1(e_g)^1$ and $(e_g)^2$, **Figure 7**

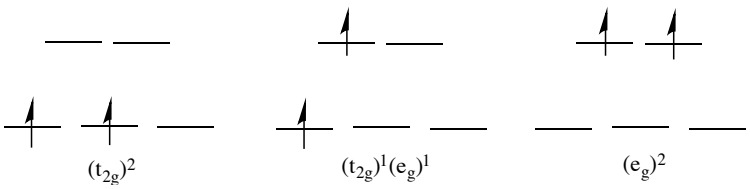


Figure 7 diagram showing contributing configurations for d^2

  - these combinations of irreducible representations or terms can then be matched to the free ion terms as shown in the Error! Reference source not found.

Orgel Diagrams

- we now have a description of the symmetry (term symbols) of the electronic wavefunction for the free-ion and octahedral environments
- we can group relevant information regarding term symbols and the effects of weak through to strong field ligands for various configurations, Figure 8 these are called **Orgel diagrams**
  - this also means we don't need to remember the data in **Table 1** as we can read it off the diagram

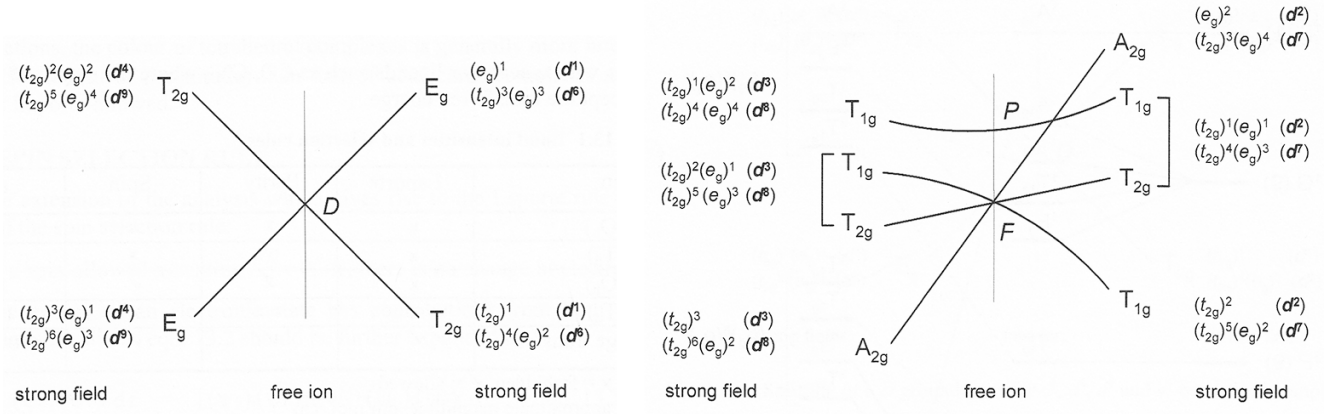


Figure 8 Orgel diagrams.[1]

- Orgel diagrams are used to reference the ground state of (*high spin*) transition metal complexes
  - there is one diagram for D free-ion ground states and one for F free-ion ground states

[1] Figure 13.1 and 13.3 from Group Theory for Chemists by K. Molloy, 2nd edition, 2011, Woodhead Publishing Limited, Cambridge.

IMPORTANT

- you are not expected to be able to generate such diagrams, but you should be able to interpret and use these diagrams.
- we can use Orgel diagrams to determine the ground state symmetry of a TM complex and also to predict possible transitions
- there is a clear reflection relationship between states with n electrons and those with n holes, eg d^2 and d^8, the stability of the states is reversed
- the curvature of the two T_{1g} curves is a result of the **non-crossing rule**, where terms of the same symmetry and multiplicity are not permitted to cross, they mix and appear to "repel" each other.
- tetrahedral states follow very similar patterns but discussing these is outside the scope of this course

Tanabe-Sugano Diagrams

- Orgel diagrams are simplified versions of **Tanabe-Sugano diagrams** which are used to interpret and predict the spectra of TM complexes
  - the Tanabe-Sugano diagram for a d^2 complex is shown in Figure 9, the blue lines represent states of the same multiplicity as the ground state and the red lines represent states of other multiplicity

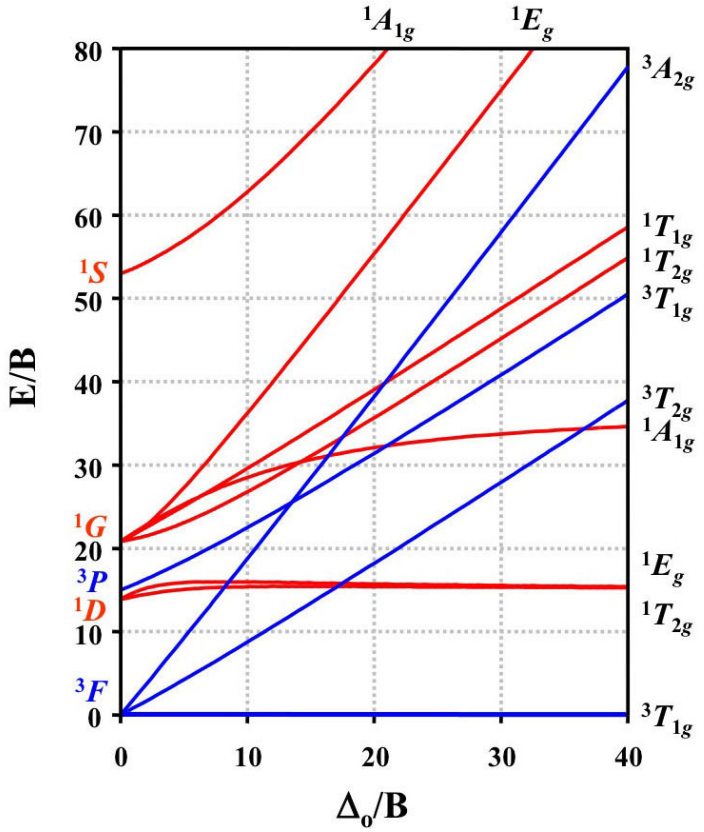
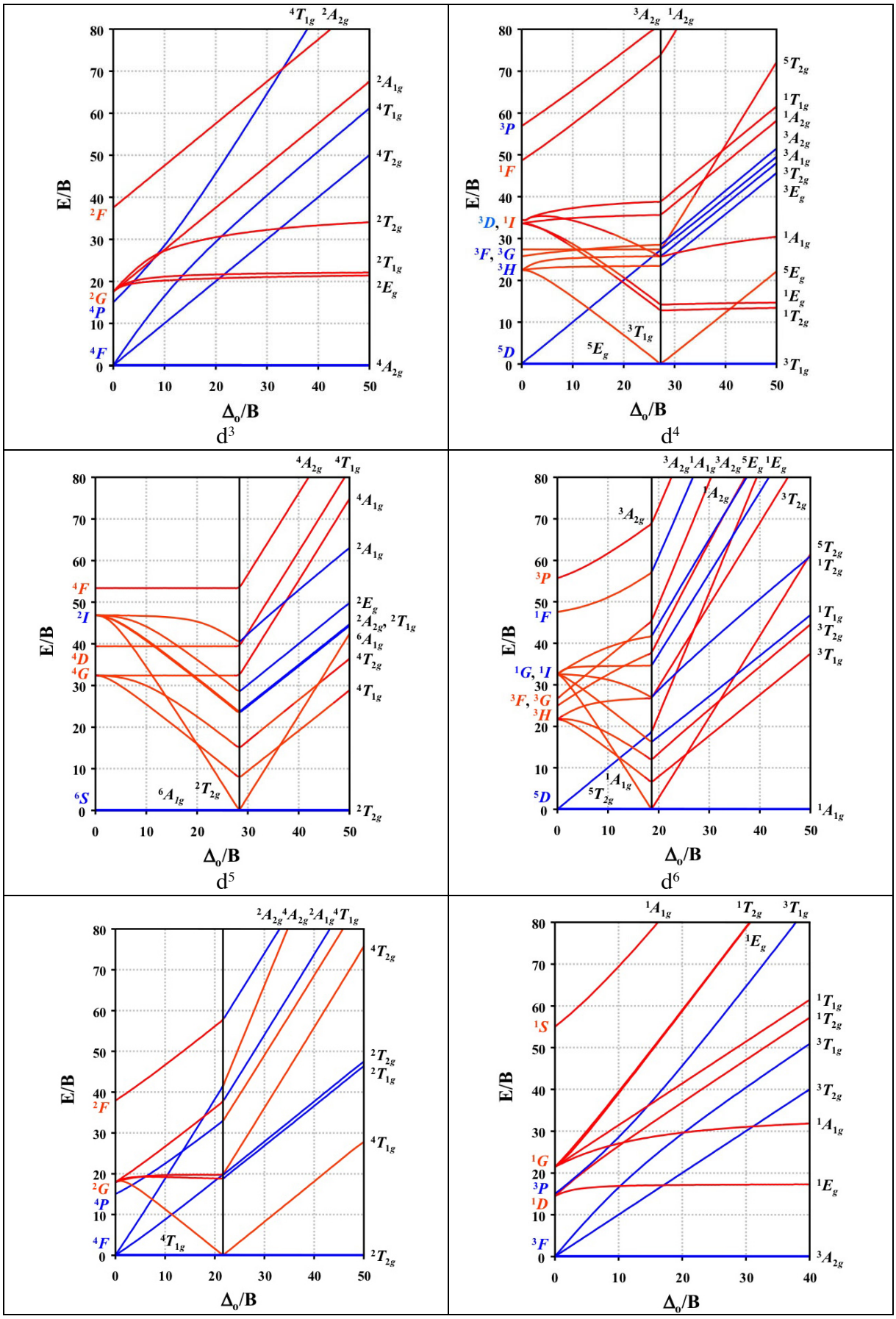


Figure 9 Tanabe-Sugano diagram for d^2.[2]

  - the lowest energy state is plotted horizontally and the vertical distance gives a measure of the energy of the excited states above the ground state (note that the ground state $^3T_{1g}$ is curved in the Orgel diagram but linear in the Tanabe-Sugano diagram)
  - the axes are in units of B or the **Racah parameter** which and represents the extent of repulsion between electrons in dAOs. The vertical axis is energy E/B and the horizontal axis is Δ_{oct}/B

[2] Figure 11.5 from Inorganic Chemistry by G. Miessler and D. Tar, 4th edition, 2011, Prentice Hall, Boston

- a full set of diagrams shown in **Figure 10**, no distinction is made between lines for different spin states and it is assumed that all states are gerade.



d^7	d^8

Figure 10 Tanabe-Sugano diagrams for d^2, d^3, d^4, d^6, d^7 and d^8

- some complexes can undergo a high spin to low spin transition as Δ_o increases, **Figure 11**. This changes the ground state configuration, at the change over point there is a discontinuity in the Tanabe-Sugano diagram, this is shown by a vertical line at the relevant Δ_o.

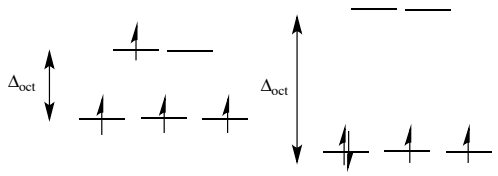


Figure 11 Spin change over as Δ_o becomes large

  - for example the Tanabe-Sugano diagram for d^5 involves only spin forbidden transitions, the ground state is $^6A_{1g}$, until Δ_{oct} is sufficiently large that spin pairing occurs and then the ground state is $^2T_{2g}$.
- there is no Tanabe-Sugano diagram for d^1 as this configuration has only a single free ion electronic state ^2D which is splits into the $^2T_{2g}$ and ^2E_g states in the strong field limit, only a single excitation is possible.
- d^9 is similar but with the reverse stability of states, ie ^2E_g below $^2T_{2g}$ for d^9 complexes there is often there is a shoulder in the spectrum due to a Jahn-Teller distortion (partially occupied degenerate state) which acts to remove the degeneracy and stabilise the molecule overall.
- there is no Tanabe-Sugano diagram for d^{10} because the d-orbitals are all occupied and there can be no transition, the ground state must be $^1A_{1g}$

Predicting Spectra: An Example

- $K_3[VF_6]$ is a bright green solid, assume green light has a wavelength interval of 500-565 nm. What is the ground state term symbol for $K_3[VF_6]$? How many transitions can be expected for the V ion? What are the possible transitions? Sketch a possible UV-vis spectrum. What is the electronic configuration for each state?
- What is the ground state term symbol for $K_3[VF_6]$?
  - V is in group 5 so V^0=>(d^5), F is an anionic ligand, and we have a $[VF_6]^{3-}$ complex, at the V we have 5-6+3=+2 d electrons, ie we have V d^2
  - thus V is in the +3 oxidation state (not so relevant here)
  - this is a standard octahedral complex and so the d manifold is split into t_{2g} and e_g and the electrons will be unpaired and the configuration is $(t_{2g})^2$.
  - using the Tanabe-Sugano diagram for d^2 (**Figure 12b**) the ground state term symbol of the *free ion* is ^3F and in the *strong ligand field* is $^3T_{1g}$
- How many transitions can be expected for the V ion?
  - possible spin allowed transitions are $^3T_{1g}(F)\rightarrow {}^3T_{2g}$, $^3T_{1g}(F)\rightarrow {}^3A_{2g}$ and $^3T_{1g}(F)\rightarrow {}^3T_{2g}(P)$
  - the order of these transitions will depend on the ligand field, for a stronger field ligand the transition order will be $^3T_{2g}$, $^3T_{2g}(P)$ and $^3A_{2g}$, in a weaker field ligand the transition order will be to $^3T_{2g}$, $^3A_{2g}$ and $^3T_{2g}(P)$
  - F is a weak field ligand, and we guess a $\Delta_o/B\approx12$ which will produce a lower energy transition from $^3T_{1g}(F)\rightarrow$ to $^3T_{2g}$ and a higher energy transition to $^3A_{2g}$ and $^3T_{2g}(P)$ which may appear as a broad peak due to overlap.
  - it is possible that there will be weak triplet to singlet transitions to a ^1D (free ion) state or set of ^1E_g and $^1T_{2g}$ states (O_h)

- other weak spin forbidden transitions are possible, the highest energy ones will most likely be in the UV part of the spectrum

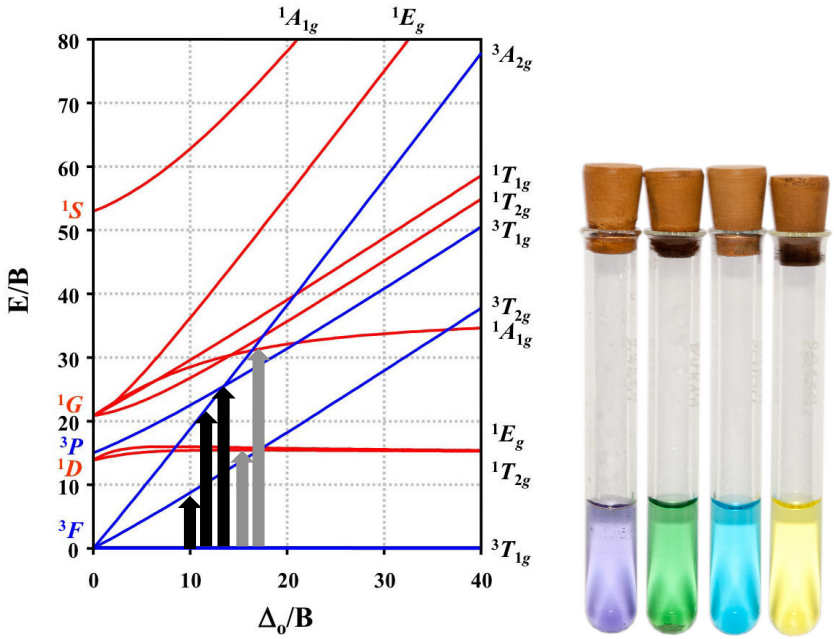


Figure 12 (a)diagram indicating possible transitions, (b) solutions of Vanadium in different oxidation states, green is vanadium in a +3 oxidation state.[3]

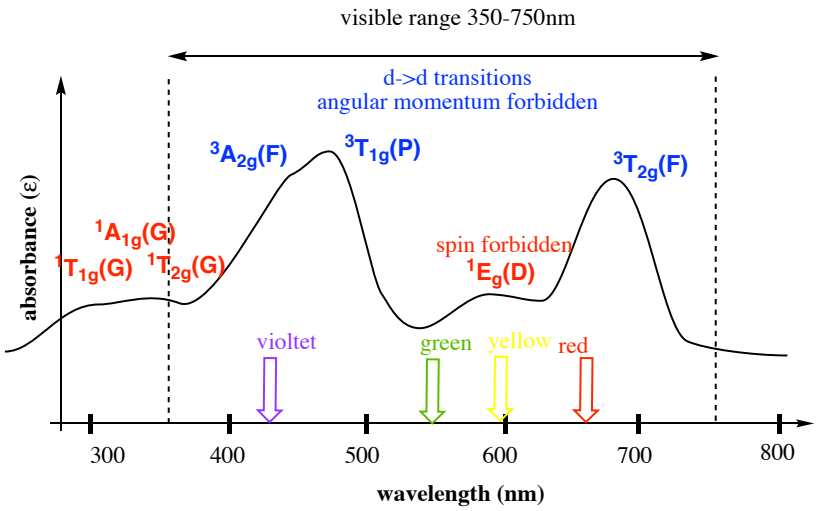


Figure 13 Sketch of a potential UV-vis spectrum of $K_3[VF_6]$

- Sketch a possible UV-vis spectrum.
  - we are told the solid compound is green, therefore the absorbance must be in all other areas of the spectrum, green light has a wavelength interval of 500-565 nm
  - we expect two strong transitions either side of the green region, in the red and blue/violet, there will be a strong overlap of peaks in the higher energy region as the $^3A_{2g}$ and $^3T_{1g}$ transitions are close in energy
  - there will be weaker absorbances due to the spin forbidden transitions, transitions will be hidden under the more intense peaks, and occur in the high energy region (ultra-violet)

[3] picture fron https://commons.wikimedia.org/wiki/File:Vanadiumoxidationstates.jpg by Steffen Kristensen image in the public domain

- vanadium is well known for the range of colours it can produce based on changes in oxidation state, **Figure 12b** is of the aqua complexes lilac $[V(H_2O)_6]^{2+}$, green $[V(H_2O)_6]^{3+}$, blue $[V(H_2O)_5]^{2+}$ and yellow$[V(H_2O)_5]^{3+}$.
- you are expected to be able to produce or interpret a sketch as shown in **Figure 13** and to be able to explain the concepts behind its generation.

IMPORTANT

- What is the electronic configuration for each state?
  - we can associate the transitions identified with specific electronic configurations, the ground state is $(t_{2g})^2$ with multiplicity of 3, using the information from **Table 1** the ground state is easily identified as $^3T_{1g}$

$$(t_{2g})^2 = T_{2g} \otimes T_{2g} = {}^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}$$

  - possible excitations are $(t_{2g})^1(e_g)^1$ and $(t_{2g})^0(e_g)^1$ leading to

$$(t_{2g})^1(e_g)^1 = T_{2g} \otimes E_g = {}^3T_{1g} + {}^3T_{2g}$$
$$(t_{2g})^0(e_g)^2 = E_g \otimes E_g = {}^1A_{1g} + {}^3A_{2g} + {}^1E_{2g}$$

  - thus the transitions to the $^3T_{2g}$ and $^3T_{2g}$ states are single excitations while the transition to the $^3A_{2g}$ state is a double excitation
  - you might want to ask how can a single excitation ($^3T_{2g}$(P)) take more energy than a double excitation ($^3A_{2g}$)? This is because we are near the free ion end of the field rather than at the stronger octahedral field end.

Key Points

- be able to identify term symbols and use Hund's rules to determine the symmetry of the lowest energy (ground) state
- be able to derive the free ion states for 1, 2 and 3 electrons, know what the general notation represents, be able to describe all the terms and be able to identify when 2 states are identical.
- be able predict the term symbols for simple strong field configurations (you will be given those of the $(t_{2g})^3$ if you need them).
- be able to explain the features of Orgel and Tanabe-Sugano diagrams
- be able to predict the ground states and the spectra of TM-complexes

Self-Study / Tutorial / Exam Preparation Problems

- Identify the possible term symbols that arise from the configuration $2p^13p^1$
- Determine the full ground state term symbol for a d^3 free ion configuration (using Hund's rules and determining possible J values), what is the degeneracy of this state?
- How many transitions should be expected for each of the d^1 - d^8 configurations?
- Why is $[Ti(H_2O)_6]^{3+}$ violet? (**Figure 14**)

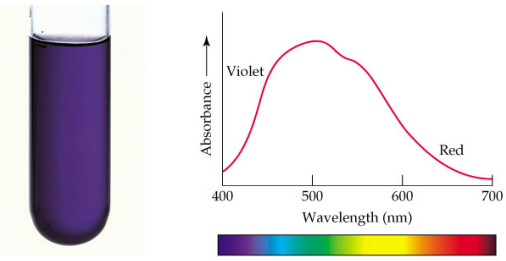


Figure 14 solution and spectrum of $[Ti(H_2O)_6]^{3+}$.[4]

[4] downloaded from http://wps.prenhall.com/wps/media/objects/4680/4793024/ch20_10.htm, 23 Feb 2015