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Interpretation of the spectra of first-row transition metal complexes (textbook problems)

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Abstract.

Introductory courses on coordination chemistry traditionally introduce Crystal Field Theory as a useful model for simple interpretation of spectra and magnetic properties of first-row transition metal complexes. In addition, Crystal Field Stabilisation Energy (CFSE) calculations are often used to explain the variation of their radii and various thermodynamic properties. Such calculations predict that for octahedral systems d^3 and d^8 should be the most stable and for tetrahedral systems d^2 and d^7 would be favoured.

A more detailed interpretation of spectra relies on the development of the concept of multi-electron energy states and Russell-Saunders coupling. Most textbooks [1-9] pictorially present the expected electronic transitions by the use of Orgel diagrams or Tanabe-Sugano diagrams [10], or a combination of both. To this end, nearly all inorganic textbooks include Tanabe-Sugano diagrams, often as an Appendix.

At UWI in the past, we have used Orgel diagrams to cover high-spin octahedral and tetrahedral configurations, except those with a d^2 octahedral configuration or d^5 ions (either stereochemistry). For d^5, no spin-allowed transitions are possible and the Tanabe-Sugano diagram is introduced to help interpret the spin-forbidden bands. For d^2 octahedral, where interpretation is made difficult since generally only 2 of the 3 expected transitions are observed and the lines due to $^3A_{2g}$ and $^3T_{1g}(P)$ cross, we have once again used a Tanabe-Sugano diagram.

To make use of the Tanabe-Sugano diagrams provided in textbooks for all configurations, it would be expected that they should at least be able to cope with typical spectra for d^3, d^8 octahedral and d^2, d^7 tetrahedral systems. **This is not the case**. The diagrams presented are impractical, being far too small. To make matters worse, the diagram for chromium(III) d^3 systems is extremely limited (D/B ~ 30) and for simple NH_3 or acac complexes would require a small amount of extrapolation, whereas for the $[Cr(CN)_6]^{3-}$ ion, D/B corresponds to greater than 50!

No textbooks give Tanabe-Sugano diagrams for tetrahedral systems and any spectral interpretations of cobalt(II) d^7 tetrahedral systems revert to using Orgel diagrams. (Examples of d^2 tetrahedral complexes are not very common.)

A set of UV/Vis spectra (in JCAMP-DX format) as well as spreadsheets and JAVA applets giving the Tanabe-Sugano diagrams will be made available and a comparison of interpretation methods presented.

Note: Viewing the UV/Vis spectra requires the Chime 2.0 plug-in: http://www.mdli.com/support/chime/chimefree.htm (this link opens in a new window).

Introduction

Crystal (and with extension, Ligand) Field Theory has proved to be an extremely simple but useful method of introducing the bonding, spectra and magnetism of first-row transition metal complexes.

To quote from the Preface in the 1969 text by Schlafer and Gliemann[9]:

> "It is hardly possible today to discuss the chemistry of the transition metals, as offered in general lectures on inorganic chemistry, without employing ligand field theory. It is difficult to find a better example of how useful meaningfully chosen models can be for understanding a large body of exceedingly varied experimental results. Nevertheless, only comparatively few basic concepts are required for a first qualitative understanding of the theory".

In the interpretation of spectra, it is usual to start with an octahedral Ti^{3+} complex with a d^1 electronic configuration. Crystal Field Theory predicts that because of the different spatial distribution of charge arising from the filling of the five d-orbitals, those orbitals pointing towards bond axes will be destabilised and those pointing between axes will be stabilised.
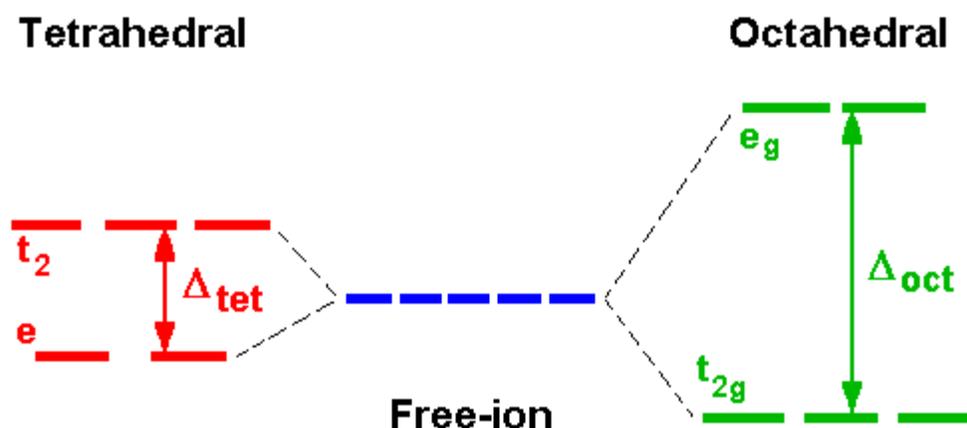
The t_{2g} and e_g subsets are then populated from the lower level first which for d^1 gives a final configuration of $t_{2g}^1 e_g^0$.

The energy separation of the two subsets equals the splitting value D and ligands can be arranged in order of increasing D which is called the spectrochemical series and is essentially independent of metal ion.

For ALL octahedral complexes except high spin d^5, simple CFT would therefore predict that only 1 band should appear in the electronic spectrum corresponding to the absorption of energy equivalent to D. If we ignore spin-forbidden lines, this applies to d^1, d^9 as well as to d^4, d^6.

The observation of 2 or 3 peaks in the electronic spectra of d^2, d^3, d^7 and d^8 high spin octahedral complexes requires further treatment involving electron-electron interactions. Using the Russell-Saunders (LS) coupling scheme, these free ion configurations give rise to F ground states which in octahedral and tetrahedral fields are split into terms designated by the Mulliken symbols $A_{2(g)}$, $T_{2(g)}$ and $T_{1(g)}$.

To derive the energies of these terms and the transition energies between them is beyond the needs of introductory level courses and is not covered in general textbooks[10,11]. A listing of some of them is given here as an Appendix. What is necessary is an understanding of how to use the diagrams, created to display

the energy levels, in the interpretation of spectra.

Two types of diagram are available: Orgel and Tanabe-Sugano diagrams.

Use of Orgel diagrams

A simplified Orgel diagram (not to scale) showing the terms arising from the splitting of an F state is given below. The spin multiplicity and the g subscripts are dropped to make the diagram more general for different configurations.
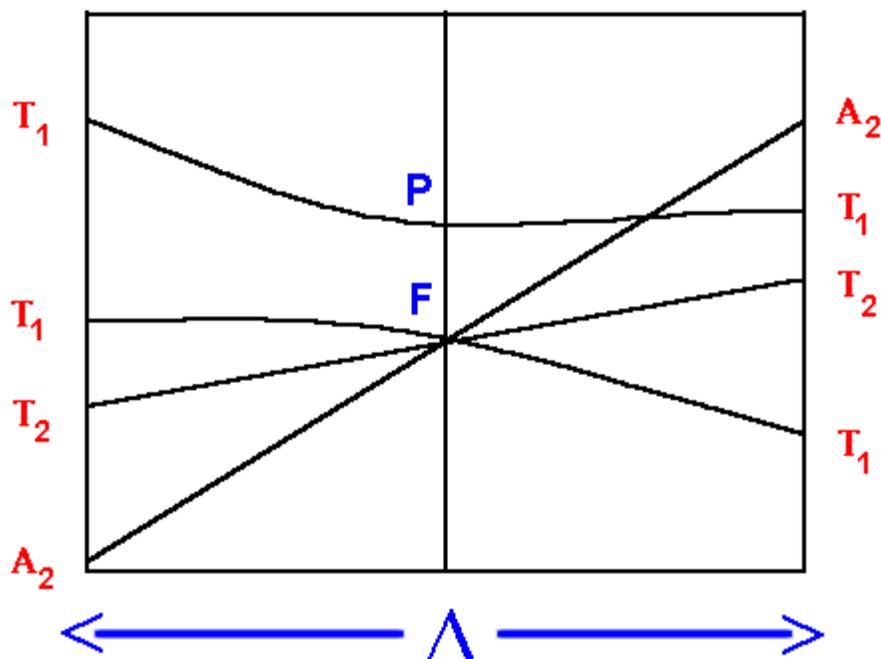
The lines showing the A_2 and T_2 terms are linear and depend solely on D. The lines for the two T_1 terms are curved to obey the non-crossing rule and as a result introduce a configuration interaction in the transition energy equations.

The left-hand side is applicable to d^3 , d^8 octahedral complexes and d^7 tetrahedral complexes. The right-hand side is applicable to d^2 , d^7 octahedral complexes.

Looking at the d^3 octahedral case first, 3 peaks can be predicted which would correspond to the following transitions:

1. $^4T_{2g} \neg {}^4A_{2g}$ transition energy = D
2. $^4T_{1g}(F) \neg {}^4A_{2g}$ transition energy = 9/5 *D - C.I.
3. $^4T_{1g}(P) \neg {}^4A_{2g}$ transition energy = 6/5 *D + 15B' + C.I.

Here C.I. represents the configuration interaction which is generally either taken to be small enough to be ignored or taken as a constant for each complex.

In the laboratory component of the course we measure the absorption spectra of some typical chromium(III) complexes and calculate the spectrochemical splitting factor, D. This corresponds to the energy found from the first transition above and as shown in Table 1 is generally between 15,000 cm^{-1} (for weak field complexes) and 27,000 cm^{-1} (for strong field complexes).

Table 1. Peak positions for some octahedral Cr(III) complexes (in cm^{-1}).

Complex	n1	n2	n3	n2/n1	n1/n2	D/B	Ref
Cr^{3+} in emerald	16260	23700	37740	1.46	0.686	20.4	13
K_2NaCrF_6	16050	23260	35460	1.45	0.690	21.4	13
$[Cr(H_2O)_6]^{3+}$	17000	24000	37500	1.41	0.708	24.5	This work
Chrome alum	17400	24500	37800	1.36	0.710	29.2	4
$[Cr(C_2O_4)_3]^{3-}$	17544	23866	?	1.37	0.735	28.0	This work
$[Cr(NCS)_6]^{3-}$	17800	23800	?	1.34	0.748	31.1	4
$[Cr(acac)_3]$	17860	23800	?	1.33	0.752	31.5	This work
$[Cr(NH_3)_6]^{3+}$	21550	28500	?	1.32	0.756	32.6	4
$[Cr(en)_3]^{3+}$	21600	28500	?	1.32	0.758	33.0	4
$[Cr(CN)_6]^{3-}$	26700	32200	?	1.21	0.829	52.4	4

For octahedral Ni(II) complexes the transitions would be:

1. $^3T_{2g} \to {}^3A_{2g}$ transition energy = D
2. $^3T_{1g}(F) \to {}^3A_{2g}$ transition energy = 9/5 *D - C.I.
3. $^3T_{1g}(P) \to {}^3A_{2g}$ transition energy = 6/5 *D + 15B' + C.I.

where C.I. again is the configuration interaction and as before the first transition corresponds exactly to D.

For M(II) the size of D is much less than for M(III) and typical values for Ni(II) are 6500 to 13000 cm^{-1} as shown in Table 2.

Table 2. Peak positions for some octahedral Ni(II) complexes (in cm^{-1}).

Complex	n1	n2	n3	n2/n1	n1/n2	D/B	Ref
$NiBr_2$	6800	11800	20600	1.74	0.576	5	13
$[Ni(H_2O)_6]^{2+}$	8500	13800	25300	1.62	0.616	11.6	13
$[Ni(gly)3]^-$	10100	16600	27600	1.64	0.608	10.6	13
$[Ni(NH_3)_6]^{2+}$	10750	17500	28200	1.63	0.614	11.2	13

$[Ni(en)_3]^{2+}$		11200	18350	29000	1.64	0.610	10.6	3
$[Ni(bipy)_3]^{2+}$		12650	19200	?	1.52	0.659	17	3

For d^2 octahedral complexes, few examples have been published. One such is V^{3+} doped in Al_2O_3 where the vanadium ion is generally regarded as octahedral, Table 3.

Table 3. Peak positions for an octahedral V(III) complex (in cm^{-1}).

Complex	n1	n2	n3	n2/n1	n1/n2	D/B	Ref
V^{3+} in Al_2O_3	17400	25200	34500	1.45	0.690	30.8	13

Interpretation of the spectrum highlights the difficulty of using the right-hand side of the Orgel diagram above for many d^2 cases where none of the transitions correspond exactly to D and often only 2 of the 3 transitions are clearly observed.

The first transition can be unambiguously assigned as:

$^3T_{2g} \leftarrow {}^3T_{1g}$ transition energy = 4/5 *D + C.I.

But, depending on the size of the ligand field (D) the second transition may be due to:

$^3A_{2g} \leftarrow {}^3T_{1g}$ transition energy = 9/5 *D + C.I.

for a weak field or

$^3T_{1g}(P) \leftarrow {}^3T_{1g}$ transition energy = 3/5 *D + 15B' + 2 * C.I.

for a strong field.

The transition energies of these terms are clearly different and it is often necessary to calculate (or estimate) values of B, D and C.I. for both arrangements and then evaluate the answers to see which fits better.

The difference between the $^3A_{2g}$ and the $^3T_{2g}$ (F) lines should give D. In this case D is equal to either:
25200 - 17400 = 7800 cm^{-1}
or 34500 - 17400 = 17100 cm^{-1}.
Given that we expect D to be greater than 15000 cm^{-1} then we must interpret the second transition as to the $^3T_{2g}(P)$ and the third to $^3A_{2g}$. Further evaluation of the expressions then gives C.I. as 3720 cm^{-1} and B' as 567 cm^{-1}.

Solving the equations like this for the three unknowns can ONLY be done if the three transitions are observed. When only two transitions are observed, a series of equations[14] have been determined that can be used to calculate both B and D. This approach still requires some evaluation of the numbers to ensure a valid fit. For this reason, Tanabe-Sugano diagrams become a better method for interpreting spectra of d^2 octahedral complexes.

Using Tanabe-Sugano diagrams

The first obvious difference to the Orgel diagrams shown in general textbooks is that [Tanabe-Sugano diagrams](#) are calculated such that the ground term lies on the X-axis, which is given in units of D/B. The second is that spin-forbidden terms are shown and third that low-spin complexes can be interpreted as well, since for the d^4 - d^7 diagrams a vertical line is drawn separating the high and low spin terms.

The procedure used to interpret the spectra of complexes using Tanabe-Sugano diagrams is to find the ratio of the energies of the second to first absorption peak and from this locate the position along the X-axis from which D/B can be determined. Having found this value, then tracing a vertical line up the diagram will give the values (in E/B units) of all spin-allowed and spin-forbidden transitions.

N.B. Another approach has been to use the inverse of this ratio, ie of the first to second transition and so both values are recorded in the Tables.

As an example, using the observed peaks found for $[Cr(NH_3)_6]^{3+}$ in Table 1 above then, from the JAVA applet described below, D/B' is found at 32.6. The E/B' for the first transition is given as 32.6 from which B' can be calculated as 661 cm^{-1}. The third peak can then be predicted to occur at 69.64 * 661 = 46030 cm^{-1} or 217 nm (well in the UV region and probably hidden by charge transfer or solvent bands).
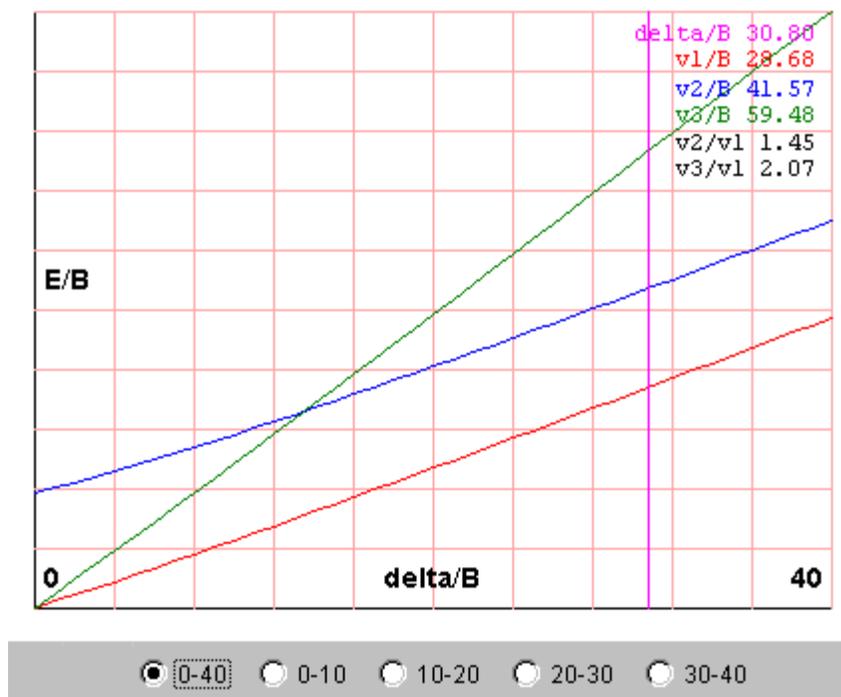

d³ octahedral Tanabe-Sugano diagram

delta/B'	32.60
v1/B'	32.60
v2/B'	43.16
v3/B'	69.64
v2/v1	1.32
v3/v1	2.14

○ 0-60   ○ 0-10   ○ 10-20   ○ 20-30   ◉ 30-40   ○ 40-50   ○ 50-60

For the V(III) example treated previously using an Orgel diagram, the value of D/B' determined from the appropriate JAVA applet is around 30.8.

d^2 octahedral Tanabe-Sugano diagram

Following the vertical line upwards leads to the assignment of the first transition to $^3T_{2g} \leftarrow {}^3T_{1g}$ and the second and third to $^3T_{1g}$ (P) $\leftarrow {}^3T_{1g}$ (blue line) and $^3A_{2g} \leftarrow {}^3T_{1g}$ (green line) respectively.

The average value of B' calculated from the three Y-intercepts is 598 cm^{-1} hence D equals 18420 cm^{-1}, significantly larger than the 17100 cm^{-1} calculated above and shows the sort of variation expected from these methods.

It is important to remember that the width of many of these peaks is often 1000 cm^{-1} so as long as it is possible to assign peaks unambiguously the techniques are valuable.

Use of spreadsheets and JAVA applets

To overcome the problem of small diagrams, it was decided to generate our own Tanabe-Sugano diagrams using spreadsheets. This has been done, using the transition energies given in the Appendix, for the spin-allowed transition expected for:

> **Note:** The following links are to Microsoft Excel worksheets. If your spreadsheet does not read these files, Microsoft provides a free viewer for Excel at: http://officeupdate.microsoft.com/index.htm (this link opens in a new window).

- for d2 (oct)
- for d3 (oct)
- for d8 (oct)
- for d7 (tet)

Even so, the method of finding the correct X-intercept is somewhat tedious and time-consuming and a different approach was devised using JAVA applets.

The JAVA applets display the spin-allowed transitions and when the user clicks on any region of the graph

then the values of n_2/n_1 and n_3/n_1 are displayed. In addition, the values of D/B and the Y-intercepts are given as well. This simplifies the process of determining the best fit for D/B.

The expected ranges for the ratio of n_2/n_1 are:

- for d2 (oct) 2.2 - 1.3 for D/B 10 - 35
- for d3 (oct) 1.8 - 1.2 for D/B 0 - 50
- for d8 (oct) 1.8 - 1.5 for D/B 0 - 18
- for d7 (tet) 1.8 - 1.5 for D/B 0 - 15

These ratios show the need for a certain degree of precision in attempting to analyse the spectra. It has been suggested that instead of using n_2/n_1 that any two ratios can be used and graphs of these plots were produced by Lever in the 1960's[11]. Once again though the diagrams are rather small and so the spreadsheets above contain these charts which can be printed in larger scale. The slopes of the various ratio lines vary greatly and it is useful to examine the region of interest first before deciding on which set of lines should be used for analysis. If only 2 lines are observed then this is not an option.

Changes in JAVA development kits and compilers have meant two different links to the applets are needed although the CLASS files are the same in each case.

Note: The first set of pages use the SUN JAVA plugin 1.2 (this link opens a new window.) which is activated by an HTML EMBED call.

If you have not downloaded the JAVA plugin then use the alternate links to pages which use the embedded runtime JAVA environments in browsers via the HTML APPLET call.

- The first and alternate first can be applied to d3, d8 (oct) d2, d7 (tet) systems.
- the second and alternate second is for d2, d7 (high spin only) (oct), d3, d8 (tet).

Further information for use in laboratory classes is available.

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Appendix

Transitions calculated for spin-allowed terms in the Tanabe-Sugano diagrams.

Octahedral d^3 (e.g. Chromium(III)).

$^4T_{2g} \neg \ ^4A_{2g}$,　　　$n_1/B = D/B$

$^4T_{1g}(F) \neg \ ^4A_{2g}$,　$n_2/B = \frac{1}{2}\{15 + 3(D/B) - \ddot{O}(225 - 18(D/B) + (D/B)^2)\}$

$^4T_{1g}(P) \neg \ ^4A_{2g}$,　$n_3/B = \frac{1}{2}\{15 + 3(D/B) + \ddot{O}(225 - 18(D/B) + (D/B)^2)\}$

from this, the ratio n_2/n_1 would become:

$$\frac{1}{2}\{15 + 3(D/B) - \ddot{O}(225 - 18(D/B) + (D/B)^2)\} / \ D/B$$

and the range of D/B required is from ~15 to ~55

Octahedral d^8 (e.g. Nickel(II)).

$^3T_{2g} \neg \ ^3A_{2g}$,　　　$n1/B = D/B$

$^3T_{1g}(F) \neg \ ^3A_{2g}$,　$n2/B = \frac{1}{2}\{15 + 3(D/B) - \ddot{O}(225 - 18(D/B) + (D/B)^2)\}$

$^3T_{1g}(P) \neg \ ^3A_{2g}$,　$n3/B = \frac{1}{2}\{15 + 3(D/B) + \ddot{O}(225 - 18(D/B) + (D/B)^2)\}$

from this the ratio n_2/n_1 would become:

$$\frac{1}{2}\{15 + 3(D/B) - \ddot{O}(225 - 18(D/B) + (D/B)^2)\} / D/B$$

and the range of D/B required is from ~5 to ~17

Octahedral d^2 (e.g. Vanadium(III)).

$^3T_{2g} \neg \ ^3T_{1g}$,　　　$n1/B = \frac{1}{2}\{(D/B) - 15 + \ddot{O}(225 + 18(D/B) + (D/B)^2)\}$

$^3T_{1g}(P) \neg \ ^3T_{1g}$,　$n2/B = \ddot{O}(225 + 18(D/B) + (D/B)^2)$

$^3A_{2g} \neg \ ^3T_{1g}$,　　$n3/B = \frac{1}{2}\{ 3 (D/B) - 15 + \ddot{O}(225 + 18(D/B) + (D/B)^2)\}$

from this the ratio n_2/n_1 would become:

$$\ddot{O}(225 + 18(D/B) + (D/B)^2) / \ \frac{1}{2}\{(D/B) - 15 + \ddot{O}(225 + 18(D/B) + (D/B)^2)\}$$

and the range of D/B required is from ~15 to ~35

Tetrahedral d^7 (e.g. Cobalt(II)).

$^4T_2 \neg\ ^4A_2$, $n1/B = D/B$

$^4T_1$ (F) $\neg\ ^4A_2$, $n2/B = \frac{1}{2}\{15 + 3(D/B) - Ö(225 - 18(D/B) + (D/B)^2)\}$

$^4T_1$ (P) $\neg\ ^4A_2$, $n3/B = \frac{1}{2}\{15 + 3(D/B) + Ö(225 - 18(D/B) + (D/B)^2)\}$

from this the ratio n_2/n_1 would become:

$$\frac{1}{2}\{15 + 3(D/B) - Ö(225 - 18(D/B) + (D/B)^2)\} /\ D/B$$

and the range of D/B required is from ~3 to ~8.

Acknowledgments