I5 : Electronic Spectroscopy of Transition Metal Compounds

Scope of Lectures: 1) Energy Levels in Multi-Electron Atoms
2) Effects of Ligand Fields on those levels
3) Physical Techniques to study a) Ground States - EPR, magnetism
b) Exited States - Elec Spectra
4) Applications

Books : Kettle, Physical Inorganic Chemistry, Chapter 8
Shriver and Atkins, Inorganic Chemistry, 3rd Edn., Chapter 13
D. Nicholls, Complexes 1st Row Transition Metals, Chapter 6
Solomon + Lever, Inorganic Electronic Spectroscopy. (Reference)

Energy Levels in Multi-Electron Atoms

In determining the energy levels of a central metal ion in a complex we need to know:

1) The energy levels available to the free ion M^{n+}
2) How the energy levels are changed on going from the free ion to the complex

Free Ion Energy Levels

To derive the free energy levels we need to know the resultant angular momentum values available ton that ion. These are obtained by the vectorial addition of the individual electron **Spin Angular Momentum i.e. the *s* values** and the **Orbital Angular Momentum i.e. the *l* values**.

Must first ask which order is the vectorial addition to be carried out ? If we consider just 2 electrons in an incomplete shell:

Which is the stronger coupling : $\mathbf{s_1.s_2}$ **and** $\mathbf{l_1.l_2}$
Or $\mathbf{s_1.l_1}$ **and** $\mathbf{s_2.l_2}$ **?**

This choice gives rise to 2 coupling schemes : a) Russell-Saunders coupling (RS)
b) jj-coupling

Russell-Saunders

Here we assume that the dominant coupling is that the spins of all the electrons couple strongly and the orbital motions couple strongly.

i.e. $\mathbf{s_1.s_2}$ **and** $\mathbf{l_1.l_2}$ > $\mathbf{s_1.l_1}$ **and** $\mathbf{s_2.l_2}$
Then $\mathbf{Ss \rightarrow S}$
and $\mathbf{Sl \rightarrow L}$
with $\mathbf{S.L. \rightarrow J}$ (the total angular momentum)

jj-coupling

Here we assume that the dominant coupling is between the spin and orbital angular momentum of the individual atoms

i.e. $\mathbf{s_1.l_1}$ **and** $\mathbf{s_1.l_2}$ **etc** > $\mathbf{s_1.s_2}$ **and** $\mathbf{l_1.l_2}$
Then $\mathbf{l.s \rightarrow j}$
and $\mathbf{Sj \rightarrow J}$ (the total angular momentum)

Which do we use? As we shall see, coupling between spin and orbital motion of an electron increases appreciably with the atomic number. **RS** scheme is very good approximation for light elements, up to about Cl. **jj** scheme is good for heaviest elements, especially actinides. Between these two for most accurate treatment we would need more complicated approach. However, **RS** scheme normally used, and it works fairly well for 1st transition series. Deviations get worse with increasing atomic number. It is the only one that we shall consider in detail.

Coupling scheme can be simplified by the fact that a filled set of orbitals *e.g.* s^2, p^6, d^{10} *etc.*. contributes zero to the total angular momentum as the vectors of the different electrons cancel out. Therefore we need to consider only *partly filled shells*.

For 2 or more electrons outside closed shells, energy depends on different ways of arranging electrons :

e.g. for p^2  and

will have different energy. Just as for one electron, the energy states are characterised by different values of the angular momentum, and so for several electrons the different energy states are characterised by different values of the resultant angular momentum.

Now, of course, these have all been worked out many years ago and you can look them up in books, but I shall work through the derivation of 2 simple cases for you: a) so you can see the basis of the Russell-Saunders approach, and b) so you can understand the nomenclature used.

DERIVATION OF TERMS FOR TWO EQUIVALENT p-ELECTRONS

m_l			$\Sigma m_l = M_L$	$\Sigma m_s = M_S$	
+1	0	−1			
↑↓			+2	0	△
↑	↑		+1	+1	+
↑	↓		+1	0	△
↓	↑		+1	0	+
↓	↓		+1	−1	+
	↑	↓	0	+1	+
	↓	↑	0	0	△
↑		↓	0	0	+
↓		↑	0	−1	+
↑↓			0	0	×
	↑	↑	−1	+1	+
	↓	↑	−1	0	△
	↑	↓	−1	0	+
	↓	↓	−1	−1	+
		↑↓	−2	0	△

The simplest case for p^2 is shown above. It shows all the possible arrangements. We add together the respective angular momentum vector values. For p^2 there are 15 microstates. These are collected together into **TERMS** starting with the highest value of M_L.

Labelling:

Maximum Values of L = **0, 1, 2, 3, 4 etc…**
S P D F G etc… cf 1-electron case (orbitals)

Maximum Values of S = **0, ½, 1, 1½, 2 etc…**
2S+1 = 1 2 3 4 5 etc… as superscript

TERMS referred to as singlet, doublet, triplet etc. according to value of 2S+1. Denotes Spin multiplicity or spin degeneracy of term.

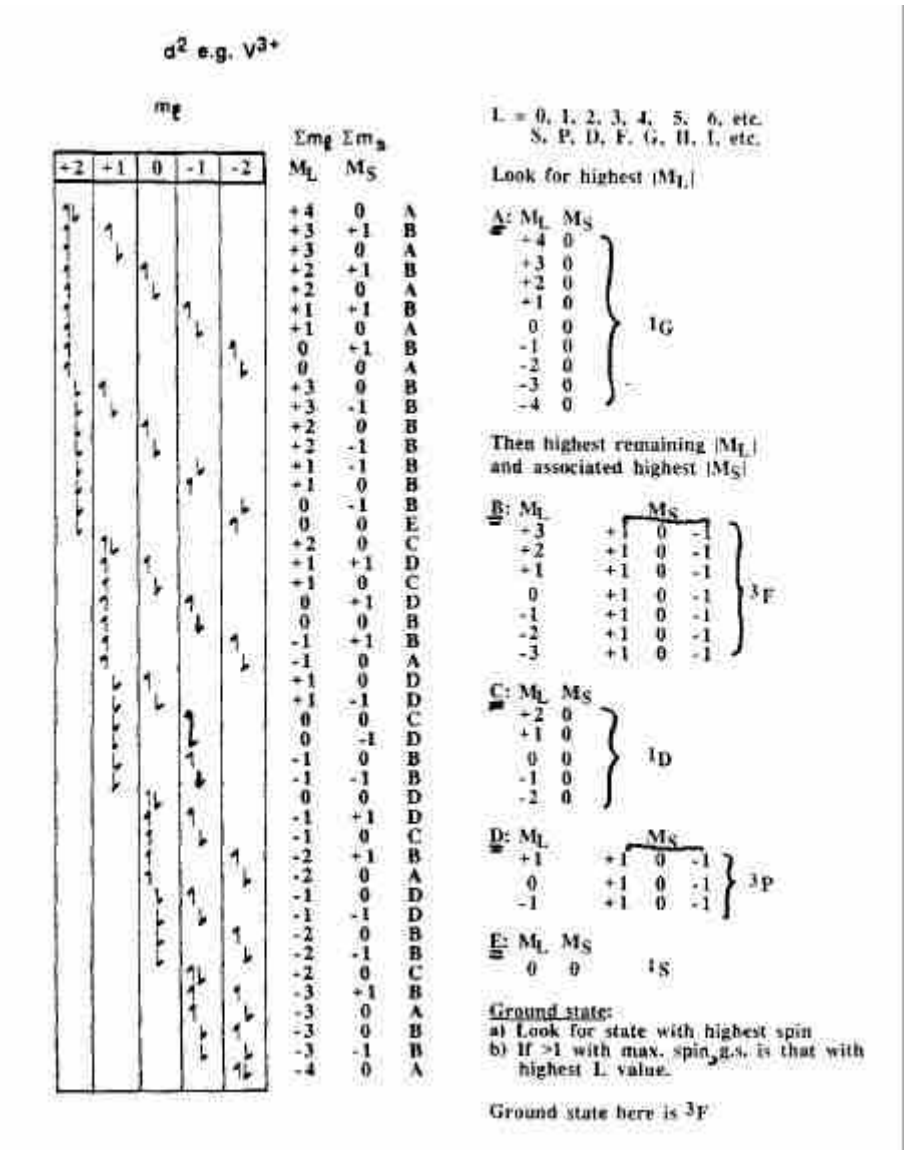
Thus the terms for p^2 can be derived as **^1D, ^3P, ^1S**

The total degeneracy of each term = **(2S+1)(2L+1)**

Thus the original set of 15 microstates for p^2 has become sub divided into 3 terms :

^3P 3x3 = 9
^1D 1x5 = 5
^1S 1x1 = 1
15

Should perhaps note at this point that where 2 or more configurations lead to the same values of M_L and M_S (see table for p^2) we cannot assign a particular one of them individually to one particular term as I have done for simplicity here. Strictly speaking, one should take appropriate linear combinations of the wave functions corresponding to each of the microstates in question. However, that is a point of detail that does not alter our ability to derive and identify the terms arising.



As noted earlier, there is no need to derive these terms each time as they are already available in books, but it is important for you to understand the principles. Thus, you should all attempt one or two derivations yourself. Try p^3.

Next Question to ask is: What are the relevant energies of the spectral terms?

Spectral Terms have different energies because of interelectronic repulsions (see later below). The relevant energies of the terms are found thus:

The ground term (*i.e*. that of the lowest energy) may be predicted by Hund's Rules:

1st Rule: For a given electronic configuration, the term having the highest value of S will be the most stable (*i.e*. that with maximum spin-multiplicity)

2nd Rule: If there is more than one term with the maximum value of S, then of these, the one with the highest value of L will lie lowest in energy.

e.g. For p^2 terms: ^1S ^1D ^3P; the lowest is ^3P
For d^2 terms: ^1S ^1D ^1G ^3P ^3F; the lowest is ^3F

These rules can only be used to decide the ground state term. They do NOT predict the energy order of the excited state terms. These are determined by the magnitude of the

Interelectronic Repulsions

The appearance of several terms for a given electron configuration is caused by repulsion forces between the electrons, which are greater for some arrangements than for others. For any two electrons, the force between them may be separated into two parts, one dependant on the radial part of the wavefunction, the other on the angular part. For a given electron configuration, *e.g*. p^2, the radial part is always the same, regardless of how the electrons are arranged, but the angular part differs. These are conventionally represented by two parameters: **F_0** and **F_2**. These are the **Slater-Condon-Shortley** parameters. They can be calculated by wave mechanics but are beyond the scope of the course.

As the radial part is always the same for a given coordination, the differences between the energies of the terms of p_2 depend only on F_2.

Thus for p^2 **:**

^1S is at $F_0 + 10F_2$
^1D is at $F_0 + F_2$
^3P is at $F_0 - 5F_2$

[The particular values of the parameters differ from one atom to another as they depend on shielding and other effects of the core electrons. If ever needed they can be looked up]

For the d^n electrons, there are two angular parameters and thus use F_0, F_2 and F_4.

See table a over.

Energies of some d^n terms expressed in F parameters

Configuration	Term	Energy
d^1, d^9	^2S	$F_0+14F_2+126F_4$
	^2G	$F_0+4F_2+F_4$
	^2D	$F_0-3F_2+36F_4$
	^2P	$F_0+7F_2-84F_4$
	^2F	$F_0-8F_2-9F_4$
d^2, d^8	^3P	$3F_0-6F_2-12F_4$
	^3G	$3F_0-11F_2+13F_4$
	^3H	$3F_0-6F_2-12F_4$
	^1S	$3F_0-14F_4$
	^1F	$3F_0-15F_2-72F_4$
d^3, d^7	^4P	$6F_0-5F_2-129F_4$
	^4G	$6F_0-12F_2-94F_4$
	^4H	$6F_0-17F_2-99F_4$
	^2D	$6F_0-21F_2-189F_4$
d^4, d^6	^5H	$10F_0-22F_2+30F_4$
	^3H	$10F_0-24F_2-90F_4$
	^3P	$10F_0-28F_2-105F_4$
	^1D	$10F_0-18F_2-225F_4$
	^1F	$10F_0-13F_2-180F_4$
	^1G	$10F_0-25F_2-190F_4$
	^1S	$10F_0-35F_2-315F_4$

Not all the terms are included for d^1, d^4, d^5, d^6, and d^7.

These F parameters are electron repulsion parameters for the d electrons expressed in terms of the radial functions (F_0) and two angular dependent repulsion functions F_2 and F_4.

Table a)

Energy differences between terms of d^n configurations

Configuration	Term interval	Energy gap: F parameters	Energy gap: B and C parameters
d^2, d^8	^1S–^3F	$22F_2-135F_4$	$22B+7C$
	^1G–^3F	$12F_2+10F_4$	$12B+2C$
	^3P–^3F	$15F_2-75F_4$	$15B$
	^1D–^3F	$5F_2+45F_4$	$5B+2C$
	^1S–^1D	$17F_2+90F_4$	$17B+5C$
	^3P–^1D	$10F_2-120F_4$	$10B-2C$
d^3, d^7	^2P–^4P	$9F_2+60F_4$	$9B+3C$
	^2G–^4F	$4F_2+85F_4$	$4B+3C$
	^2H–^4F	$9F_2+60F_4$	$9B+3C$
	^4P–^4F	$15F_2-75F_4$	$15B$
	^4G–^2H	$-5F_2+25F_4$	$-5B$
d^4, d^6	^3D–^3D	$16F_2+60F_4$	$16B+4C$
	^3G–^3D	$9F_2+95F_4$	$9B+4C$
	^3H–^3D	$4F_2+120F_4$	$4B+4C$
	^1D–^3H	$12F_2-60F_4$	$12B$
	^1G–^3H	$5F_2-25F_4$	$5B$
d^5	^4G–^6S	$10F_2+125F_4$	$10B+5C$
	^4F–^6S	$22F_2+135F_4$	$22B+7C$
	^4D–^6S	$17F_2+90F_4$	$17B+5C$
	^4P–^6S	$7F_2+210F_4$	$7B+7C$
	^2I–^6S	$11F_2+225F_4$	$11B+8C$
	^2H–^6S	$13F_2+285F_4$	$13B+10C$

B and C are electron repulsion parameters introduced by Racah such that:

$B = F_2 - 5F_4$ and $C = 35F_4$

Advantage: Energy gaps between ground state and excited states of the same spin multiplicity as the ground state depend only on one parameter B.

Table b)

Racah Parameters

In practice, however, two alternative parameters are used for d^n terms:

$$B = F_2 - 5F_4$$
$$C = 35F_4$$

These are called **Racah** Parameters; Racah recognised that these relationships appeared frequently and thus it is more convenient to use **B** and **C**. See Table b).

Their most important use in attempting to understand d-d spectra is that the energies of the transitions between states having the same spin multiplicity as the ground state depend only on **B.**

e.g. for case of $d^{2/8}$ **3P level at $F_0 + 7F_2 - 84F_4$**

3F level at $F_0 - 8F_2 - 9F_4$ **The gap between the levels is = $15F_2-75F_4 = 15B$**

As we will discuss later, it is these transitions that are most readily observed in the electronic spectra of TM compounds and thus the use of **Racah** parameters is helpful.

Spin-Orbit Coupling

Before moving on to examine the effects of ligand fields on the free-ion terms it is convenient to introduce here the concept of spin-orbit coupling as we shall need it later when we discuss EPR spectra and also some aspects of electronic spectra.

In the Russell-Sunders coupling scheme after allowing for the coupling of the individual spins to give a resultant spin (S) and the individual orbital angular momenta to give a resultant value (L) we can consider spin-orbit coupling (J):

S.L → J (the total angular momentum)

The **J** values are given by**: L + S, L + S - 1,…L - S**

The levels then arising are labelled**:** $^{2S+1}L_J$

For example: consider the ground state term ^3F for d^2.

Here **S = 1, L = 3**; hence **J = 4, 3 ,2**

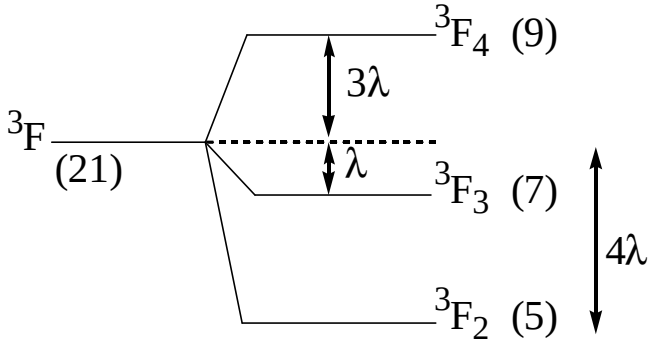
Thus spin-orbit coupling resolves the original ^3F level into three new closely separated levels $^3F_4$, $^3F_3$, $^3F_2$

[Note that the degeneracy of 21 for ^3F (i.e. 3 x 7) is preserved as (2J + 1) = 9 + 7 + 5 =21]

For d^1 - d^4 energy order is $^3F_2 < {}^3F_3 < {}^3F_4$ (normal multiplet)
For d^6 - d^9 energy order is $^3F_4 < {}^3F_3 < {}^3F_2$ (inverted multiplet)

The splitting depends on the size of the spin-orbit coupling constant l or z

Example d^2



The Energies of the J levels relative to the unsplit term are given by:

$$E_J = {}^1/_2[J(J+1) - L(L+1) - S(S+1)]$$

The magnitude of the separation depends on the value of the spin-orbit coupling constant - there are 2 types of such constants (see over)

a) For a single electron designated z always positive (see table over page)

b) For a configuration having more than one unpaired electron it is more common to use l given by $l = \pm z/2\mathbf{S}$

Where **S** is the maximum M_S value of the term concerned; +ve sign used for less than half filled shell d^1-d^4; -ve sign used for more than half filled shell d^6-d^9

[Note that this change of sign is important in the context of magnetism and EPR]

Free ion single electron spin–orbit coupling parameters (ζ_{nd}) for transition elements (cm^{-1}). Values in parenthesis are only estimates.

Metal	Charge → 0	1+	2+	3+	4+	5+	6+
Ti Zr Hf	70	90 (300)	123 (400)	155 (500)			
V Nb Ta	95	135 (420)	170 (610)	210 (800) (1400)	250		
Cr Mo W	135	185	230 (670) (1500)	275 800 (1800)	355 (850) (2300)	380 (900) (2700)	
Mn Tc Re	190	255	300 (950) (2100)	355 (1200) (2500)	415 (1300) (3300)	475 (1500) (3700)	540 (1700) (4200)
Fe Ru Os	275	335	400	460 (1250) (3000)	520 (1400) (4000)	590 (1500) (4500)	665 (1700) (5000)
Co Rh Ir	390	455	515	580	650 (1700) (5000)	715 (1850) (5500)	790 (2100) (6000)
Ni Pd Pt		565 (1300) (3400)	630 (1600)	705	790	865	950
Cu Ag Au			830 (1800) (5000)	890	960	1030	1130

Values of z and l increase with **Z**. Therefore the separation of components increases. If this gets too big then **RS** scheme breaks down.

RS scheme holds well for the light elements. to the end of first row TM series and is the one .you will meet most frequently. The alternative - the **jj**-coupling scheme is valid for the very heavy elements e.g. the actinides, with those in between needing a more complicated approach.

Take an actual example of a 1st row TM series ion: Ni^{2+}

^3F ground state; l ~315 cm^{-1}

Splitting of ground state = 7 l = ~2200 cm^{-1}

This compares with ^3F-^3P separation of ~15000 cm^{-1}

Difference is enough to suggest that the **RS** coupling scheme is a an acceptable approach.

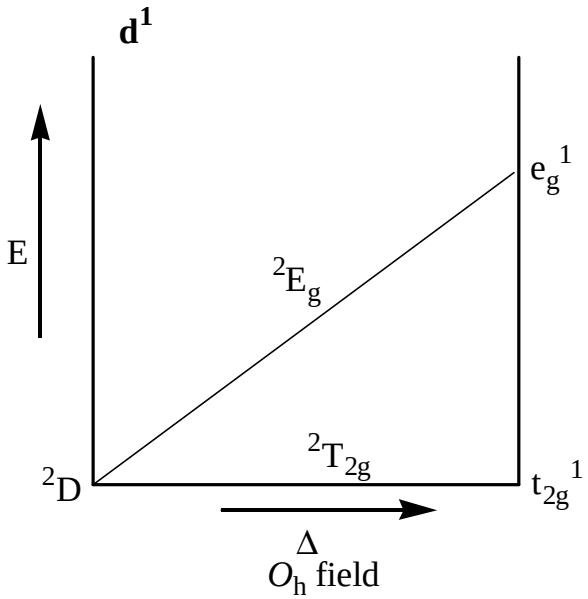
For 2nd and 3rd row TM ions l larger and scheme not so good.

Ligand Field Spectra

So far we have been dealing with the energy levels of isolated atoms or ions. Now we need to consider how these are affected by the presence of surrounding groups such as anions, ligands or solvent molecules. Since we know that orbitals have their energies changed by crystal field, with a tendency to split degeneracies, it is likely that the energy states derived from these will be changed.

If we go back to the simple case of **one electron** in d orbital set the only term arsing is that of ^{2}**D**. We shall ignore spin-orbit coupling for the present. Just as an octahedral field splits the d orbitals into t_{2g} and e_g subsets, the microstates contributing to ^{2}D are no longer all the same in energy - they are also split into the same two groups. The states thus arising are called $^2\mathbf{T_{2g}}$ and $^2\mathbf{E_g}$.

Tanabe-Sugano Diagrams



$^2\mathbf{E_g}$ will be at higher energy than $^2\mathbf{T_{2g}}$ and the difference will be a measure of Δ. Note that the spin degeneracy is unaffected.

Obviously when you consider the cases where you have more than one d electron the result is less trivial.

It is important to introduce forces in order of their magnitude, the largest first. The point at which ligand field effects are introduced depends on its magnitude. With the assumption of **RS** coupling for the free ion we can imagine three cases for the magnitude of the crystal field.

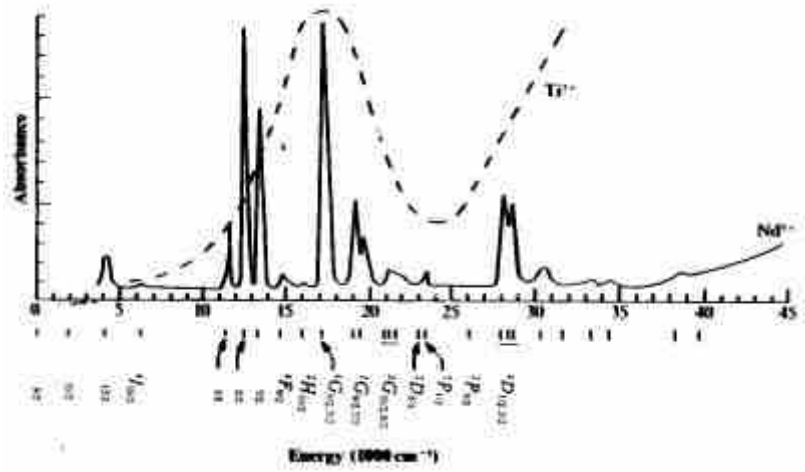
a) Term separation > spin-orbit coupling > crystal field
b) Term separation > crystal field > spin-orbit coupling
c) Crystal field > term separation > spin-orbit coupling

Type a) met in the lanthanides where we are considering transitions between states derived from an incompletely filled 4f shell. Not going into deep detail of Ln spectra, but **note** the main points and compare these with the TM complexes: (see over)

1) The crystal field in lanthanide complexes is weak (~ 100 cm^{-1}) compared with the term separation (1000 - 30000 cm^{-1}) and spin-orbit coupling (~1000 cm^{-1}). Therefore the spectra of lanthanide complexes are **rather like the free ion spectra** - just small perturbations by the crystal field.

2) Because the crystal filed is weak, *i.e*. metal ion is not much perturbed by the ligands, differences between the effects of different ligands are also small. Therefore the **spectrum does not change much** on changing the ligand. All compounds of a given ion give rather similar spectra. This does not mean that the changes that do occur are unimportant, but they are not large.

3) Δ does not change much with small changes in M-L bond length i.e. with bond vibrations. Spectral band energies do not differ much during vibrations and therefore the **bands are sharp.**



Types b) and c) (from page before) are important for ordinary transition elements and they correspond to **Weak** and **Strong** field cases respectively.

Weak Field Approach

This is essentially a perturbation method. Take the energies and types of terms known from atomic spectra and permit them to be perturbed by the crystal field.

Splitting of some terms arising from *d*-configurations for O_h, T_d, and D_{4h} symmetry

Term	O_h	T_d	D_{4h}
S	A_{1g}	A_1	A_{1g}
P	T_{1g}	T_1	$A_{2g}+E_g$
D	E_g+T_{2g}	$E+T_2$	$A_{1g}+B_{1g}+B_{2g}+E_g$
F	$A_{2g}+T_{1g}+T_{2g}$	$A_2+T_1+T_2$	$A_{2g}+B_{1g}+B_{2g}+2E_g$
G	$A_{1g}+E_g+T_{1g}+T_{2g}$	$A_1+E+T_1+T_2$	$2A_{1g}+A_{2g}+B_{1g}+B_{2g}+2E_g$
H	$E_g+2T_{1g}+T_{2g}$	$E+T_1+2T_2$	$A_{1g}+2A_{2g}+B_{1g}+B_{2g}+3E_g$
I	$A_{1g}+A_{2g}+E_g+T_{1g}+2T_{2g}$	$A_1+A_2+E+T_1+2T_2$	$2A_{1g}+A_{2g}+2B_{1g}+2B_{2g}+3E_g$

For example : in an octahedral complex (O_h symmetry)

S is unsplit and gives A_{1g}
P is unsplit and gives T_{1g}
D is split and gives $T_{2g} + E_g$ *Not necessarily*
F is split and gives $A_{2g} + T_{1g} + T_{2g}$ *in this order*

Hopefully you've come across these symbols before ?

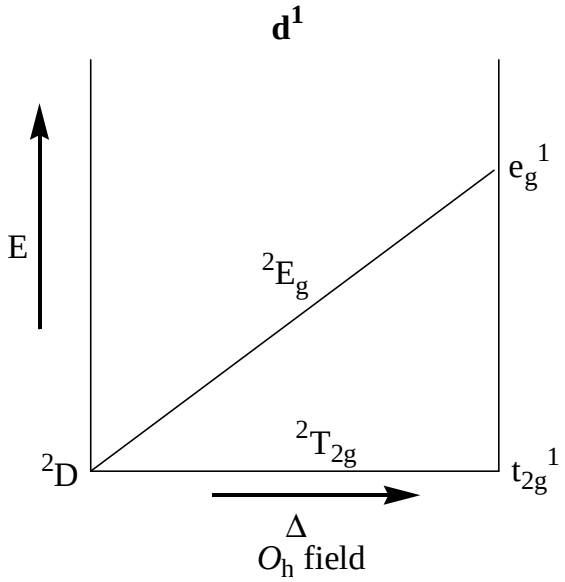
A is orbitally non-degenerate and symmetrical WRT rotation about the principle C_n axis.
B is orbitally non-degenerate and anti-symmetrical WRT rotation about the principle C_n axis.
E is orbitally doubly degenerate
T is orbitally triply degenerate
Subscript 1 symmetrical WRT to C_2 operation perpendicular to the primary axis
Subscript 2 antisymmetrical WRT to C_2 operation perpendicular to the primary axis

Note : Total orbital degeneracy preserved and spin unaffected. Higher terms also split - but can be looked up if needed.

Knowing the symmetry of the ligand field enables one to predict the degeneracies of the derived states but gives no information about their relative energies.

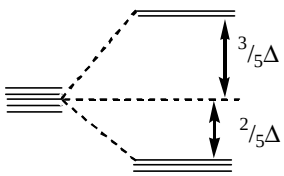
Energy Level Diagrams

Consider d^1 case in octahedral field



At the **strong field limit,** i.e. Ligand Field ≥ term separation, can express as d orbital occupancy [RHS of diagram]

e.g. in O_h orbitals split into t_{2g} and e_g and possible electron arrangements are t_{2g}^1 or e_g^1 with energies $-{}^2/_5D$ and ${}^3/_5D$ WRT to unsplit case.



t_{2g}^1 Ground state has 3-fold orbital degeneracy (and 2 fold spin degeneracy)
e_g^1 Ground state has 2-fold orbital degeneracy (and 2 fold spin degeneracy)

i.e. for d^1 O_h with large Δ, we have 2 arrangements with orbital degeneracies of 3 and 2, while when Δ = 0 we have the free ion term ^2D with orbital degeneracy of 5.

It is conventional to plot free ion terms at left and strong field configurations at right and energy of lowest level at zero (see above). The region in between is know as the **WEAK FIELD** approximation, i.e. apply perturbation on the free ion terms corresponding to the symmetry of the ligand field.

Can look up term splittings from tables.

Now consider d^2 case:

Again in Octahedral field we get t_{2g} and e_g when we have a strong ligand field

Possible arrangements of electrons are	t_{2g}^2	$t_{2g}^1e_g^1$	e_g^2	
Energies	$-^4/_5\Delta$	$+^1/_5\,\Delta$	$+^6/_5\,\Delta$	WRT to unsplit

As we now have > 1 electron we can have spin-pairing but for simplicity we will restrict attention to configurations of Max spin multiplicity (will deal with spin-paired configurations later)

For t_{2g}^2 can have

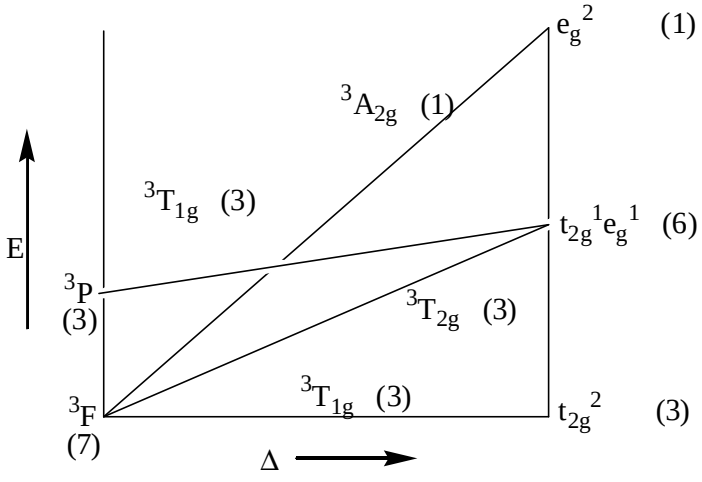
Therefore $t_{2g}^2 \rightarrow {}^3T$ (orbitally and spin triply degenerate - actually $^3T_{1g}$)

Can derive similar permutations for $t_{2g}^1e_g^1$ (6 fold orbitally degenerate) and e_g^2 (orbitally non-degenerate) [for cases with max spin multiplicity]

Therefore for d^2 with large Δ we have 3 arrangements with orbital degeneracy of 3, 6 and 1
And for Δ = 0 have ^3P and ^3F with orbital degeneracy of 3 and 7.

As before:

d^2 in O_h field



In this way we can derive the energy level diagrams for TM ions. When calculated correctly, they show how the energy levels vary as a function of Δ and also B values. All these Tanabe-Sugano diagrams have been worked out.

From these one can find out how many spin-allowed transitions from the ground state to states of the same spin multiplicity would be expected for a given value of Δ. Conversely if we know we have *e.g.* an octahedral complex $[ML_6]^{n+}$, we can evaluate Δ from the observed bond energies.

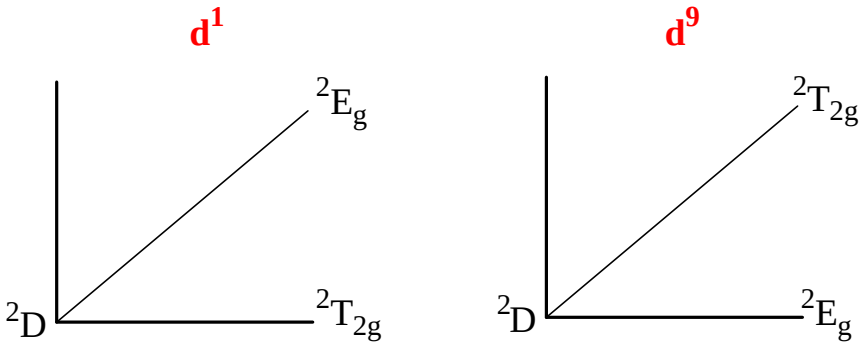
There are several useful relationships between the diagrams for d^1-d^9.

1) *Electron-Hole Inversion*: One "hole" in a d shell (*i.e.* d^9) ≡ d^1, leading to the same free ion terms of maximum spin multiplicity.

d^1 and d^9 → ^{2}D
d^2 and d^8 → ^{3}F and ^{3}P
d^3 and d^7 → ^{4}F and ^{4}P
d^4 and d^6 → ^{5}D

But for the same ligand field symmetry, splittings of each free ion **term are reversed** on going d^n to d^{10-n}.

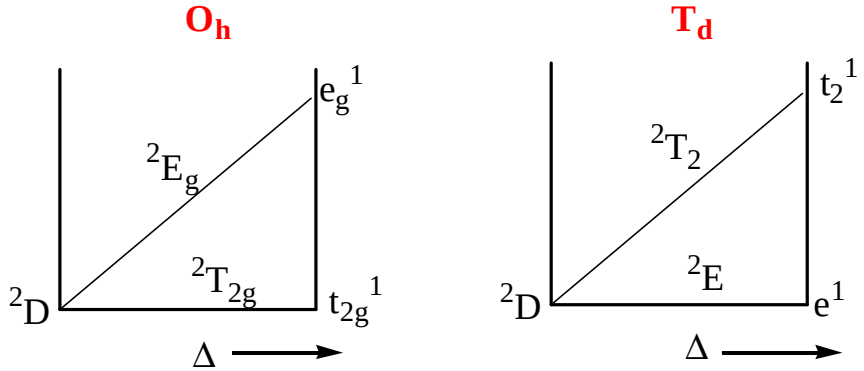
e.g. in O_h field



Do note that the order of the **FREE ION** terms is unchanged.

2) *Octahedral vs Tetrahedral Fields:* As you will recall from 2nd year lectures, the splitting of d orbitals is inverted on changing from an octahedral to a tetrahedral field. So too, although the order of **free ion** terms *remains the same*, the **splittings** of these terms in a weak field will be *inverted* as will the configurations of the strong field limits (d5 unchanged).

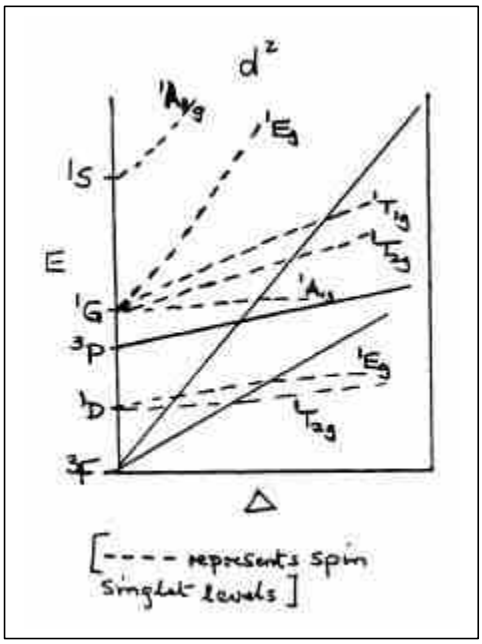
e.g. d^1 case



d^5 is a special case because there is only one way of arranging **5** electrons in a d shell with high spin. In weak field limit ground state is ^6S (unsplit by field) and in strong field limit we have a $t_{2g}^3 e_g^2$ configuration. All excited states have lower spin multiplicity.

Low Spin Levels

For **d^2** the free ion gives (*via* symmetry arguments) the singlet terms ^1D, ^1G and ^1S levels as well as spin triplets.



These singlet terms are also split by crystal field

$^1D \rightarrow {}^1T_{2g} + {}^1E_g$

$^1G \rightarrow {}^1T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}$

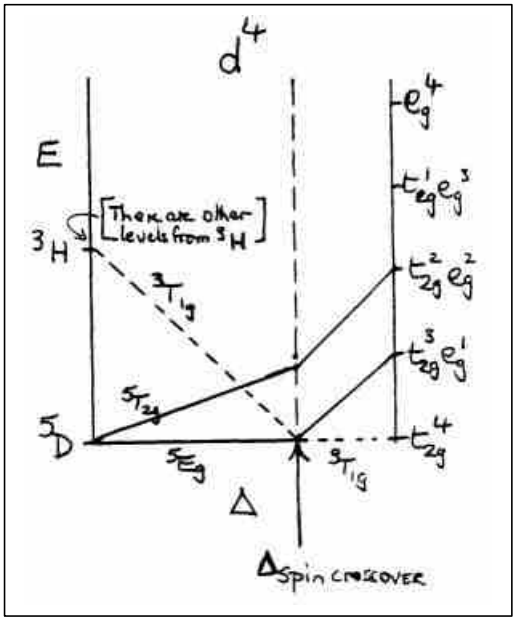
$^1S \rightarrow {}^1A_{1g}$

As with the high spin terms, these low spin terms join up with their corresponding strong field electron configuration counterparts.

Complete diagram is a superposition of singlet and triplet terms.

For d^2 we never need to use the singlet levels because however strong the field no singlet level becomes the ground state, *i.e*. d^2 is always high spin. This is also true for d^3 O_h.

When we reach d^4, however, there is an additional factor.



We know from simple d orbital splitting arguments that in strong octahedral fields it may be favourable to pair the d electrons in the t_{2g} sub-shell.

How does this work out in terms of these energy level diagrams?

The partial d^4, O_h diagram is adjacent.

There are other terms not shown.

Note a) the relevant free ion terms
b) the strong field limit configurations

It is apparent that at some particular value of Δ, $\Delta_{crossover}$, the ground state changes from ^5E_g (arising from ^5D term) to $^3T_{1g}$ (arising from ^3H term).

It is convenient to plot these diagrams so that the lowest energy level is always the base line. The result is that there is an **apparent** sudden change in the line slopes.

d^5, d^6 and d^7 can also be low spin octahedral.

This kind of diagram can be constructed for each d-electron configuration and for any symmetry of the ligand field.

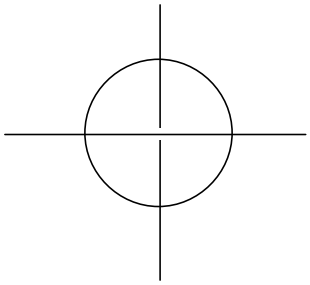
Selection Rules

So far we have deduced the energy levels of the complexed TM ions, but we have not considered the question of the intensities of the spectral bands, i.e. we need to think about the rules governing the transitions between the levels.

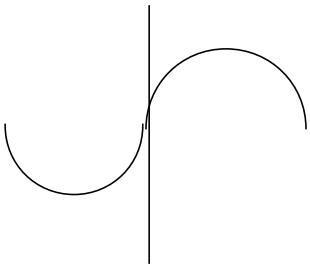
You have probably come across the main ones in other lectures in 1st and 2nd year courses but I shall revise for you the main selection rules, and cases of their apparent breakdown, treating it in a relatively non-mathematical way.

Main selection rules are:

1) **Spin selection rule:** $\Delta s = 0$, i.e. transitions that $\Delta s \neq 0$ are forbidden.
2) **Laporte Rule:** Even parity terms can combine only with odd terms
   Odd parity terms can combine only with even terms



1s



2p

s p d f
g u g u

gerade ungerade

In terms of one electron, hydrogenic orbitals this can be seen very simply on the basis of the symmetry of each orbital type WRT inversion through the nucleus. Orbitals are either gerade (even) or ungerade (odd).

Laporte rule for one electron is thus: g → u or u → g **ALLOWED**
g → g or u → u **FORBIDDEN**

One immediate consequence of the Laporte rule is that all d-d transitions should be forbidden. Why then do we observe "d-d" bands for TM compounds? Requires that

$$\int \Psi_1 . op . \int \Psi_2 . dT \neq 0$$

Where op is the electric dipole operator [**u** symmetry]

Breakdown of the Laporte Rule:

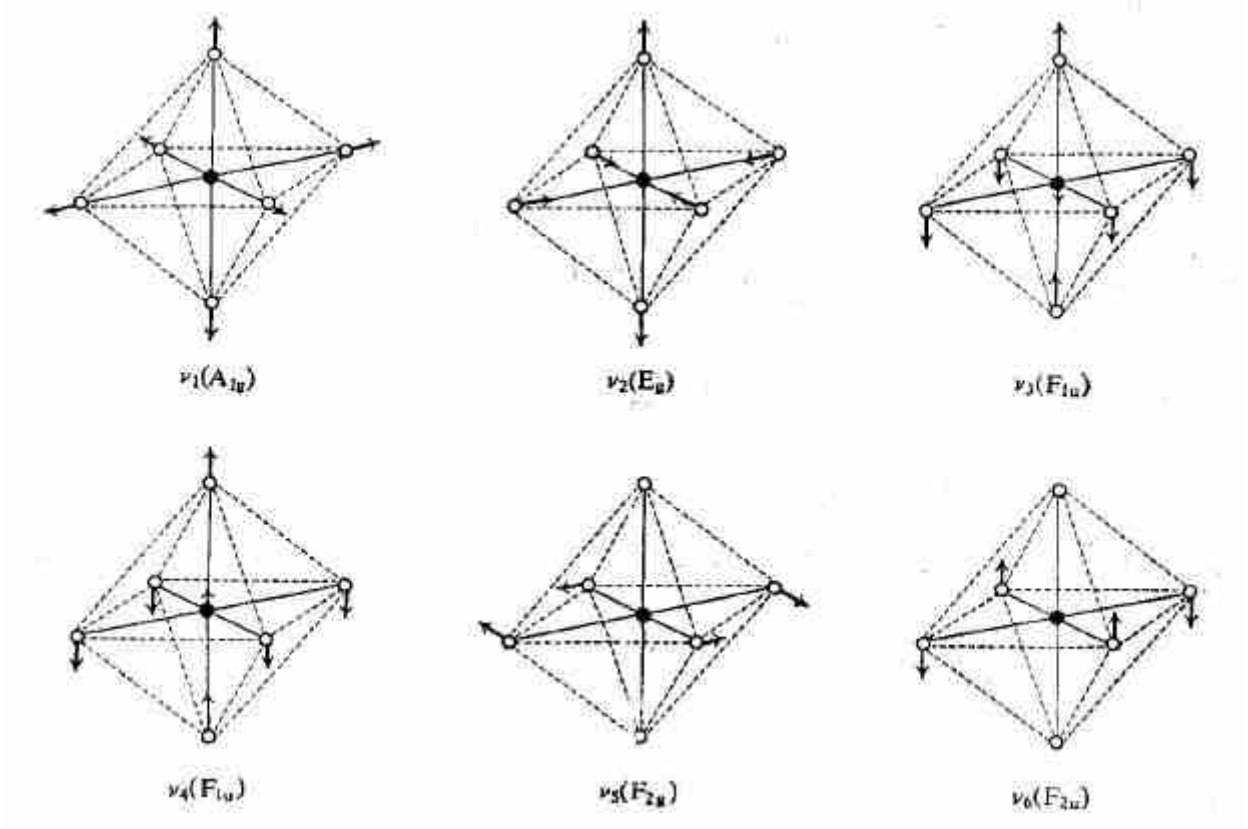
Most common causes are:

1) Interaction between the electronic and vibrational parts of the wave function → ***vibronic*** wave function.

Then if $\int \psi_{1\text{vibronic}}.\text{op}\int \psi_{2\text{vibronic}}.d\tau \neq 0$

the transition between y_1 and y_2 is allowed, at least to some extent.

e.g. If we have an octahedral complex the normal modes of vibration for the primary coordination sphere are:

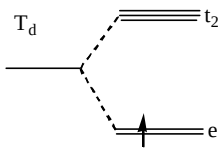


Thus, if the ground electronic state is mixed with a gerade type vibrational mode and the excited electronic state is mixed with an ungerade type vibrational mode or vice versa, then the d-d transition has some odd character and becomes partly allowed by this vibronic mechanism.

2) **d-p orbital mixing**

Take, as an example, "d-d" transitions in tetrahedral complexes.

For simplicity take a one-electron transition for a tetrahedral complex using hydrogenic type d-orbitals e and t_2.



If we consider these only as pure d-orbitals then the Laporte rule predicts that the transition would be forbidden (in the absences of a vibronic mechanism).

But for a tetrahedron, **the t_2 set of orbitals can mix with the metal p-orbitals**.

Therefore, although the **e** set has only d character (even only), the t_2 set has d-p character (some odd character).

Thus transitions of type e → t_2 have some odd character and are partly allowed.

Generally, non-centrosymmetric compounds will have stronger "d-d" bands than their centrosymmetric counterparts.

3) Covalence causes metal d wave function to mix with ligand p → π wave functions, incorporating "odd" character.

The spin-selection rule, Δs=0, is not fully valid in the presence of spin-orbit coupling as then one cannot accurately factorise the total wave function: $\psi = \psi_{space}.\ \psi_{spin}$

which would be required for: $\int \psi_1.op.\ \psi_2 d\tau = \int \psi_{1space}.op\ \psi_{2spin}\, d\tau . \int \psi_{1spin}.op\ \psi_{2spin}\, d\tau$
LAPORTE SPIN

Hence spin-orbit coupling causes "spin-forbidden" bands to appear in spectra. If the spin-orbit coupling constant is small, as for 1st row TM ions, then these bands are very weak, but when it is large, as with the heavier TM ions, their intensities can be much greater.

As an Approx. Guide

	ε_{molar} (approx.)	Example
Spin-forbidden d-d bands are v. weak	0.001-0.1	$Mn(H_2O)_6^{2+}$
Spin-allowed d-d bands	5-30	$Ni(H_2O)_6^{2+}$
Tetrahedral complexes, d-d bands	100-500	$CoCl_4^{2-}$
Electron transfer p → d, M → L etc..	*ca*. 10^3-10^5	Fe^{3+}/NCS^-

Use of Tanabe-Sugano Diagrams

Used mainly for interpreting electronic spectra, but also of value for magnetic properties including EPR of compounds of d^n ions.

In interpreting spectra we must consider:

a) Number of bands
b) Band energies
c) Intensities – i) solutions - ε_{molar}; ii) solids – relative intensities
d) Breadth and Shape

1) *Determination of Stereochemistry and D Values*

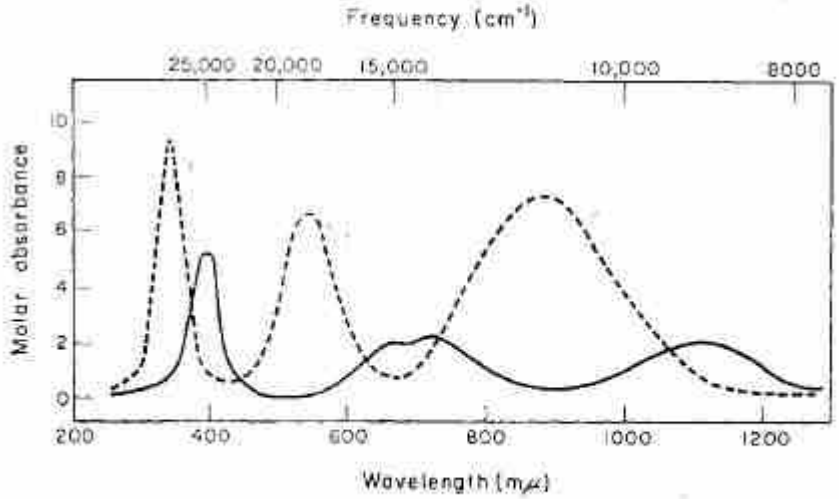
e.g. For a complex ML_6^{n+} it should be possible to find a value of Δ which will explain all the observed d-d bands. Moreover, the value of Δ should be "reasonable" when compared with values for related cases.

(see next page)

Octahedral Ni^{2+} is d^8.

Spectra of Octahedral Nickel(II) Complexes
(Approximate band positions in cm^{-1})

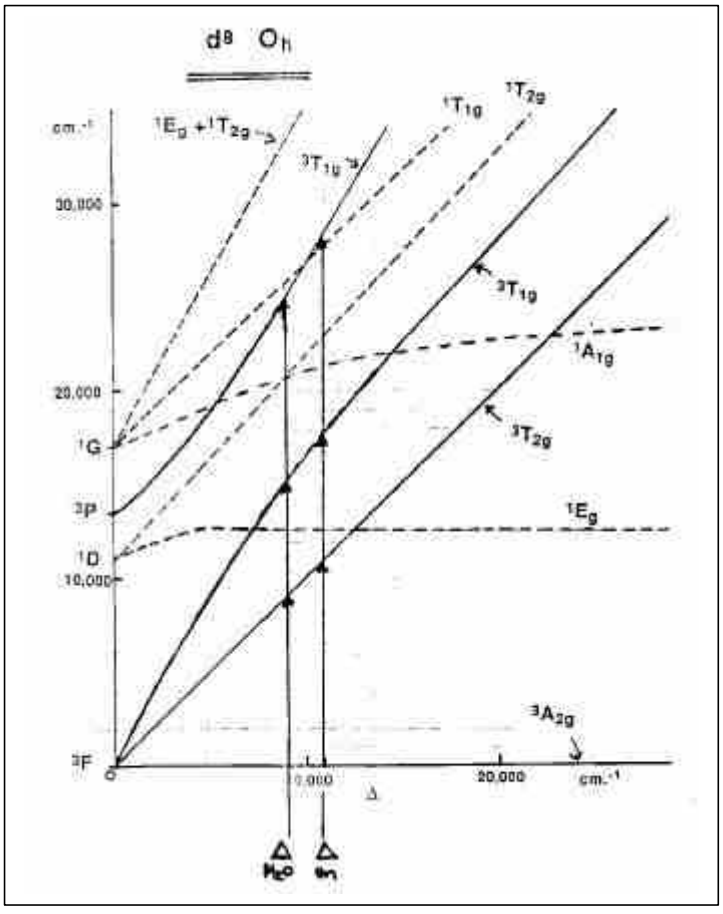
Transition	$[Ni(H_2O)_6]^{2+}$	$[Ni(en)_3]^{2+}$
$^3A_{2g} \rightarrow {}^3T_{2g}$	9000	11,000
$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	14,000	18,500
$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	25,000	30,000



Absorption spectra of $[Ni(H_2O)_6]^{2+}$ (———) and $[Ni(en)_3]^{2+}$ (- - - - - - - -)

Bands are relatively low in intensity.

The Tanabe Sugano Diagram for a d^8 complex in an octahedral field is below.



The band assignments are shown on the figure as arrows.

Δ for en ~ 11000 cm^{-1}
Δ for H_2O ~ 9000 cm^{-1}

Note υ_2 for $Ni(H_2O)_6^{2+}$ involves contribution from ^1E_g (LS Coupling - see later)

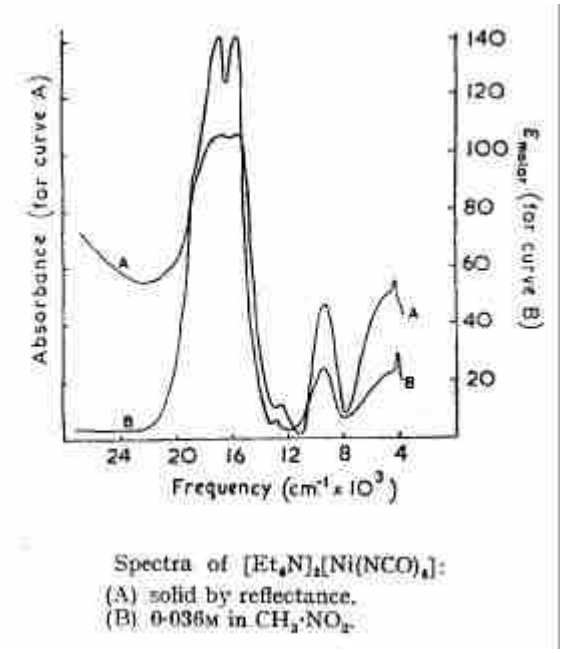
For comparison, solid $KNiCl_3$. What is its structure? It has a similar spectrum to these two compounds with bands at 6700, 12700 and 22000 cm^{-1}. The bands are not very strong. This suggests that the Ni^{2+} is actually surrounded by $6Cl^-$ ligands as in $NiCl_2$ for which bands at 6900, 12900 and 22100 cm^{-1}.

The Δ values form these are reasonable:

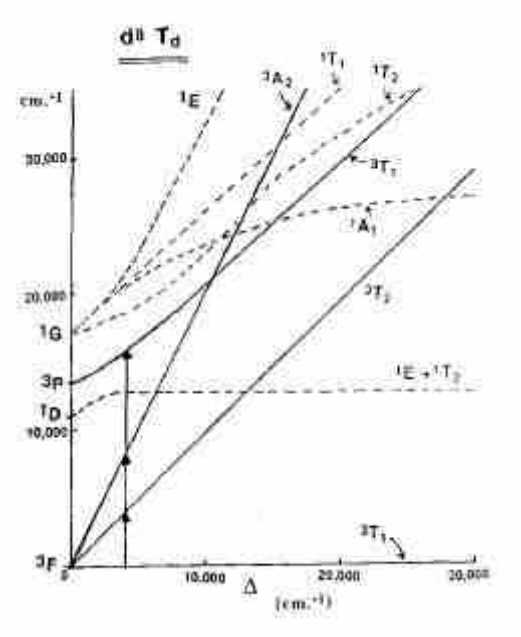
Cl < H_2O < en
~6900 ~9000 ~11000

Agrees with Spectrochemical Series

The spectrum of $(Et_4N)_2[Ni(NCO)_4]$ - paramagnetic compound with 2 upe's.



Spectra of $[Et_4N]_2[Ni(NCO)_4]$:
(A) solid by reflectance.
(B) 0·036M in $CH_3 \cdot NO_2$.



Notes A) Is a spectrum of the solid of the compound by reflectance

B) Is a spectrum of a solution of the compound. Note high ε_{molar} value.

Bands are at 4600, 9500 and ~16200 cm^{-1}.

As the compound is paramagnetic it is not likely to be planar. The Et_4N^+ cannot coordinate but NCO^- ligand could bridge **to give → 6 Coord** or could be monodentate **giving a → tetrahedral** NiN_4 or NiO_4 core? Question is which do we have?

The use of O_h diagram for d^8 would give an abnormally low Δ value of ~4600 cm^{-1} for an NiL_6 system and would predict υ_2 at 8000 cm^{-1} and υ_3 at 18500 cm^{-1}. Therefore it does not fit well for bond energies or intensities.

The use of T_d d^8 diagram, however, gives good agreement with Δ_t ~4600 cm^{-1} - this is quite reasonable as we expect $D_t \sim {}^1/_2 D_{oct}$. Actual structure is NiN_4 from IR data.

See next page

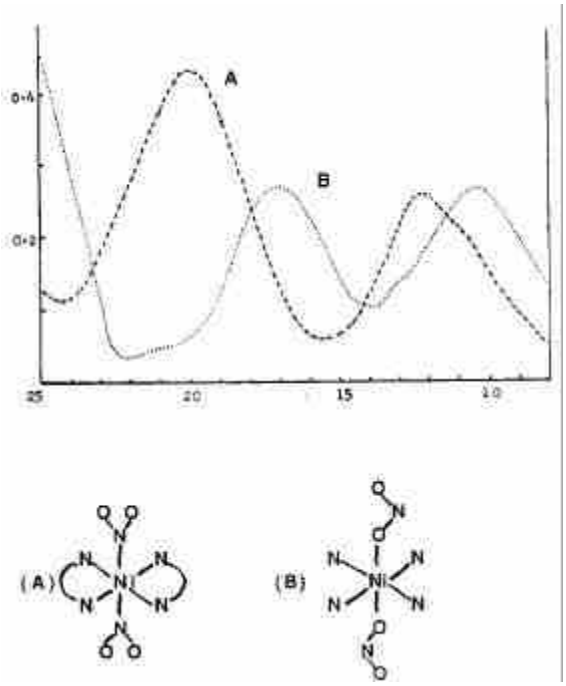
2) Can use spectra to distinguish between various possible donor atom sets (**CHROMOPHORES**)

e.g. NO_2^- can coordinate *via* N or O. D **values differ with N > O**

Electronic Spectra of $Ni(en)_2(NO_2)_2$ and $Ni(4\text{-methylpyridine})_4(ONO)_2$

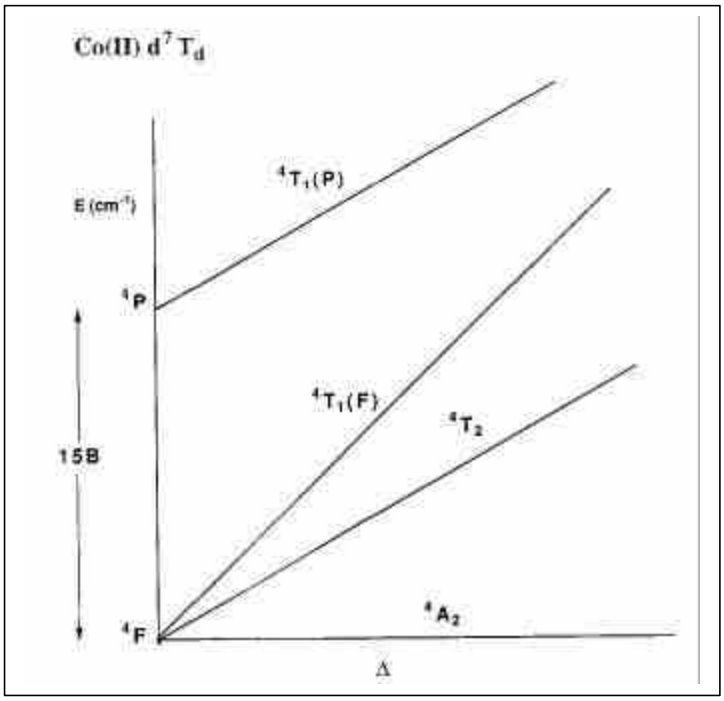
Curve (A) is for $Ni(N\text{-ethylethylenediamine})_2(NO_2)_2$ and curve (B) is for $Ni(4\text{-methylpyridine})_4(ONO)_2$

Both show $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transitions. [In each case there is a further spin-allowed band to $^3T_{1g}(P)$ level above 25000 cm^{-1} not shown in the diagram.]



3) Information about the nature of bonding

Sometimes found that for complexes of a known geometry the energy level diagrams we have constructed using free ion terms in Racah parameters do not fit all the bands. e.g. for tetrahedral Co(II)



Expect three spin-allowed bands.

One at highest energy is:

$^4A_2 \rightarrow {}^4T_1(P)$

for $CoCl_4^{2-}$ observed at 15000 cm^{-1}

for $CoBr_4^{2-}$ observed at 13500 cm^{-1}

for CoI_4^{2-} observed at 12500 cm^{-1}

BUT for free ion (i.e. $\Delta = 0$)

$^4F - {}^4P = 15B = 14540\ cm^{-1}$

Hence need to reduce B, i.e. allow for covalency

Energy of $^4T_1(P)$ increases with Δ

For $CoCl_4^{2-}$ lower two transitions can be fitted with $\Delta \sim 3100\ cm^{-1}$. With this Δ $^4T_1(P)$ predicted at ~16200 – observed at 15000 (if we try to fit this υ_3 band alone, we find $\Delta \sim 400\ cm^{-1}$ – this is unreasonable).

The situation is worse for $CoBr_4^{2-}$ and CoI_4^{2-} as υ_3 at 13700 and 12500 cm^{-1} respectively, i.e. < free ion ^4P ! This is a problem.

We need to take into account covalency in M-L bond. If covalent contributions are present, the metal d electrons will be partly shared by the ligands i.e. will spend < 100% of their time on the metal. If they are spread out more onto the ligands their interelectronic repulsions will be less and the ^4P - ^4F term separation will decrease (thus we modify the diagram to account for this).

The extent to which this is necessary gives an experimental measure of bond covalency. Measured by the required reduction in the Racah parameter B as ^4F - ^4P = 15B and B'< B (expressed as $\beta = {}^{B'}/_{B}$).

For the above three compounds: $CoCl_4^{2-}$ $\beta \sim 0.74$
$CoBr_4^{2-}$ $\beta \sim 0.72$ Thus they are still fairly ionic.
CoI_4^{2-} $\beta \sim 0.69$

<u>Nephelauxetic Series</u>

If the B' values are determined for a number of ligands, keeping the metal constant, they can be arranged in a series of increasing covalency and that series is roughly independent of the metal ion (though the actual B' values will, of course, be metal-dependant). This is known as the **Nephelauxetic Series** (= cloud expanding).

The order found fits in fairly well with what we might expect: fluorides tend to be very ionic, whereas iodides and especially sulfur donors form relatively covalent bonds.

$$F^- < O < N < Cl^- < Br^- < I^- < S$$
→ increasing covalency

<u>4) Distortions from regular symmetry</u>

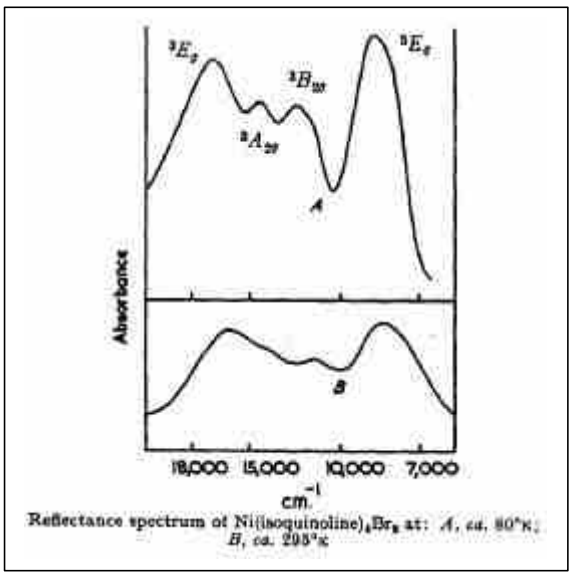
O_h	O	T_d	D_{4h}
A_{1g}	A_1	A_1	A_{1g}
A_{2g}	A_2	A_2	B_{1g}
E_g	E	E	$A_{1g} + B_{1g}$
T_{1g}	T_1	T_1	$A_{2g} + E_g$
T_{2g}	T_2	T_2	$B_{2g} + E_g$
A_{1u}	A_1	A_2	A_{1u}
A_{2u}	A_2	A_1	B_{1u}
E_u	E	E	$A_{1u} + B_{1u}$
T_{1u}	T_1	T_2	$A_{2u} + E_u$
T_{2u}	T_2	T_1	$B_{2u} + E_u$

If the point symmetry at the metal ion is lower than O_h or T_d some of the spectral transitions may be split. We can determine the effects of changing the symmetry upon the orbital degeneracies by using the table of relationships of irreducible representations.

(Refer to descent of Symmetry Handout left).

In a 6-coordinate Ni(II) metal ion all the orbital-triplet states are split by a tetragonal distortion thus in D_{4h} symmetry

$$^3T_{2g} \rightarrow {}^3B_{2g} + {}^3E_g \; ; \; ^3T_{1g} \rightarrow {}^3A_{2g} + {}^3E_g$$

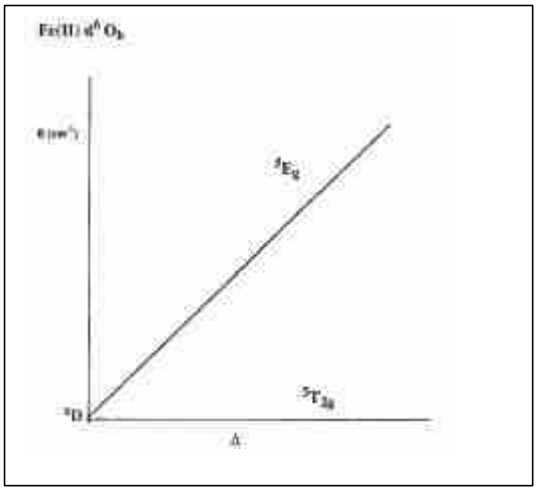


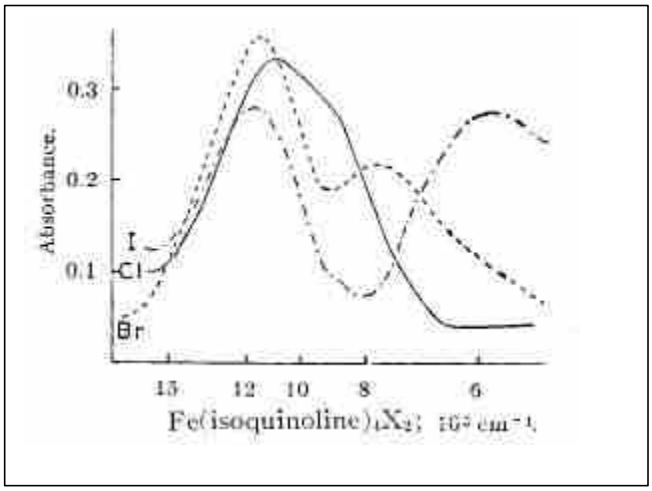
Reflectance spectrum of Ni(isoquinoline)$_4$Br$_2$ at: *A*, ca. 80°K; *B*, ca. 295°K

As an example (adjacent) take NiL_4Br_2 (L = N-heterocycle); structure is "octahedral" with axial Br and bands are split (the *trans* is expected to have ~ twice the splitting of the *cis* isomer).

[NB The Correlation table does not predict the order of the energy].

Similarly for the related Fe(II) complexes (see below)





Fe(isoquinoline)$_4$X$_2$; 10³ cm⁻¹

In O_h expect **1 band**: $^5T_{2g} \rightarrow {}^5E_g$

In D_{4h} ^5E_g becomes $^5A_{1g} + {}^5B_{1g}$ and we therefore expect **2 bands**

Here splitting increases on changing X = Cl, Br I.

Ground state also split (into $^5B_{2g} + {}^5E_g$) but transitions at too low energy to be seen. [Can use **Mossbauer** studies to determine splittings less than 1000 cm^{-1}.]

Problems of Band Resolution

Symmetry arguments tell us only that orbital degeneracies should be split on lowering symmetry. But this may not be by much. This can be overcome by measuring the spectra with **polarized light**.

Polarization Studies

If the ligand field has strictly cubic symmetry e.g. O_h, then transition moment for an allowed transition is isotropic i.e. it has no preferred direction x, y or z. In O_h the electric dipole operator is T_{1u}. In lower symmetry, the electric dipole operator has > 1 component and a given transition may be allowed by one component but not by another and the spectrum may be polarized.

T_{1u} in O_h becomes A_{2u} + E_u in D_{4h}
T_{1u} in O_h becomes A_2 + E in D_3

Hence dipole operators ||z + ⊥z

Selection Rules

If we represent the irreducible representations (e.g. A_1, A_2, E etc.) by Γ then two electronic states Γ_a and Γ_b are connected by the dipole operator Γ_{op} if :

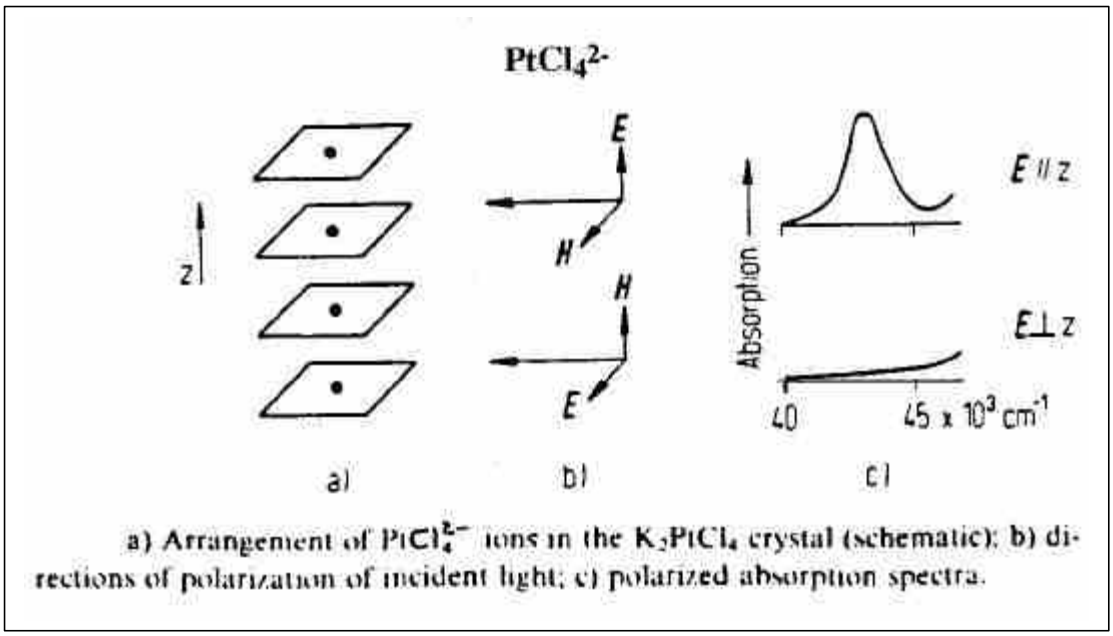
$G_a.G_{op}.G_b$ Ì **A_1 or A_{1g}**

Put another way: $G_a.G_{op}$ Ì G_b

A) Band assignments:

A particularly simple example provided by $PtCl_4^{2-}$ that is low spin d^8 with a $^1A_{1g}$ ground state.

It has a stacked structure as shown below. The point group is D_{4h}.



a) Arrangement of $PtCl_4^{2-}$ ions in the K_2PtCl_4 crystal (schematic); b) directions of polarization of incident light; c) polarized absorption spectra.

The selection rules state T_{1u} becomes A_{2u} and E_u in D_{4h}.

For polarized light ||**z**: A_{1g} x A_{2u} = A_{2u}

i.e. A_{1g} → A_{2u} only will be allowed with ||z

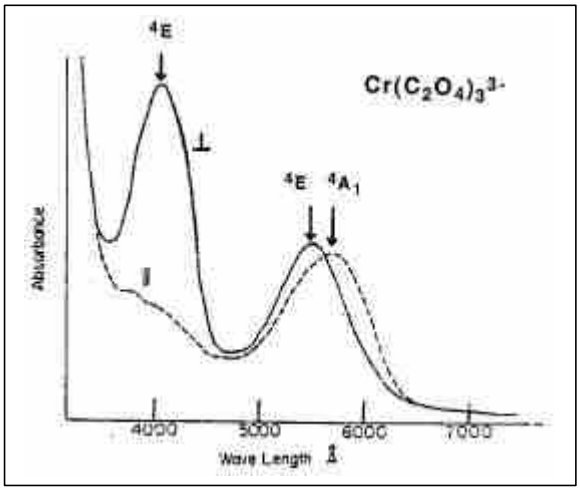
For polarized light ^ **z**: A_{1g} x E_u = E_u

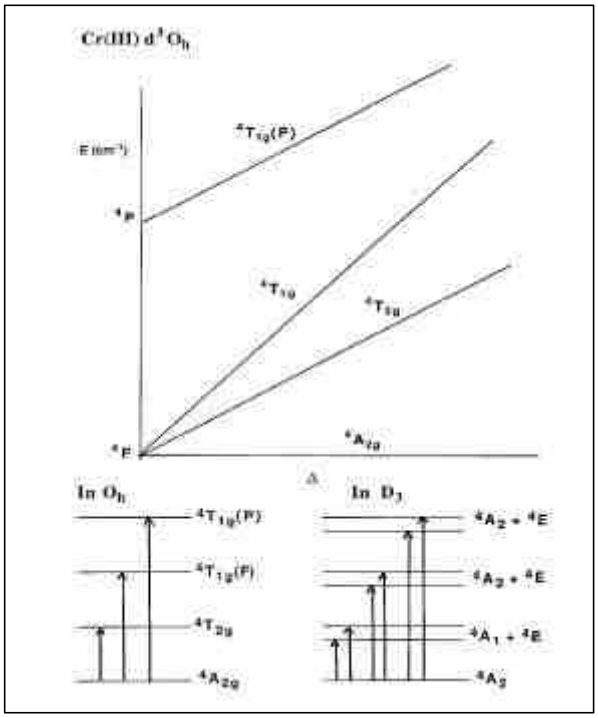
i.e. A_{1g} → E_u only will be allowed with ⊥z

Find experimentally that for $PtCl_4^{2-}$ a strong band at 42500 cm^{-1} allowed only by ||z.
Hence transition is A_{1g} → A_{2u} (probably $5D_z^2$ → $6p_z$).

B) Polarization Studies are useful when crystal field distortions are too small to give well resolved bands with ordinary light.

e.g. $Cr(oxalate)_3^{3-}$





If O_h Cr(III) d^3 would show $^4A_{2g} \rightarrow {}^4T_{2g}$

$^4A_{2g} \rightarrow {}^4T_{1g}(F)$

$^4A_{2g} \rightarrow {}^4T_{1g}(P)$

But ligand field in $Cr(oxalate)_3^{3-}$ has D_3 symmetry.

Using the correct correlation tables: $^4A_{2g}$ becomes $^4A_2$ in D_3

$^4T_{2g}$ becomes $^4A_1 + {}^4E$ in D_3

$^4T_{1g}$ becomes $^4A_2 + {}^4E$ in D_3

Expect band splitting $^4A_2 \rightarrow {}^4A_1, {}^4E_a$

$^4A_2 \rightarrow {}^4A_2, {}^4E_b$

Electric Dipole operator T_{1u} in O_h becomes $A_2 + E$ in D_3

$||z + \perp z$

Apply to $Cr(oxalate)_3^{3-}$ as a single crystal D_3

For spectrum with polarization $||z$ G_{op} **is** A_2 here and ground state G_a **is** A_2

Take product: $A_2.A_2 = A_1$

i.e. for **polarization** $||z$ **only band** $^4A_2 \rightarrow {}^4A_1$ **is allowed** - the others are forbidden.

For polarization $\perp z$ G_{op} **is E** here and ground state G_a **is** A_2 again

Product $A_2.E = E$

i.e. for **polarization** $\wedge z$ **bands** $^4A_2 \rightarrow {}^4E_a$ **and** $^4A_2 \rightarrow {}^4E_b$ **are allowed** - the others are forbidden

[NB Other bands from 4P at higher energy too]. Note also that $^4A_2 \rightarrow {}^4A_2$ forbidden in both polarizations

Measurement of polarized spectrum very useful for making unambiguous band assignments and therefore for determining the bonding leading to a particular energy level set.

Disadvantages of using polarized light:

1) Need to know the crystal structure of the complex so as to be able to mount the crystal correctly WRT the molecular axis and the plane of light polarization.
2) Crystal Size.

Often not as simple as above because of vibrational components.