

ELECTRONIC SPECTROSCOPY

Term Symbols:

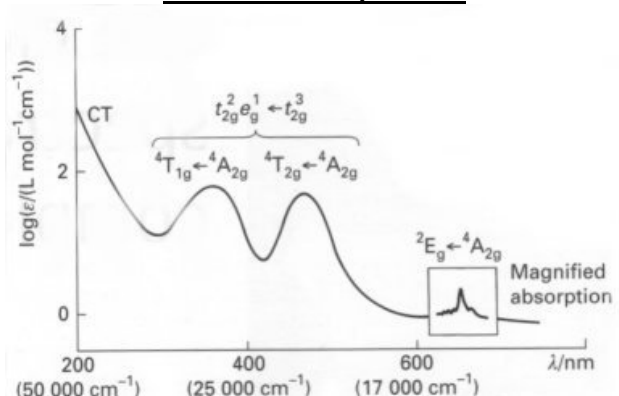
d-count	L	S	J	Term
d ⁰	0	0	0	¹ S ₀
d ¹	2	1/2	3/2	² D _{3/2}
d ²	3	1	2	³ F ₂
d ³	3	3/2	3/2	⁴ F _{3/2}
d ⁴	2	2	0	⁵ D ₀
d ⁵	0	5/2	0	⁶ S ₀
d ⁶	2	2	4	⁵ D ₄
d ⁷	3	3/2	9/2	⁴ F _{9/2}
d ⁸	3	1	4	³ F ₄
d ⁹	2	1/2	5/2	² D _{5/2}
d ¹⁰	0	0	0	¹ S ₀

Spectroscopic Term Symbols –

Spectroscopic Term Symbols are used in the same way as Atomic Term Symbols. Thus ⁴T_{1g} has a multiplicity of 4 (i.e. quartet state with S=3/2, as expected for three unpaired electrons in Cr³⁺).

The letter denotes the symmetry of the overall electronic orbital state. Centrosymmetric properties are also incorporated here for Octahedral complexes. Hence, the rest of the term is T_{1g} (triply degenerate and gerade). For Cr³⁺, this would correspond to t_{2g}²e_g¹, since there are 3 ways of arranging this. Similarly, t_{2g}³ would be A_{2g} (not totally symmetric A_{1g} though).

An Electronic Spectrum



This shows a typical spectrum. This is for the d³ complex [Cr(NH₃)₆]³⁺, and illustrates the features of the rest of these notes – variation in width and magnification, and types of peak (Charge Transfer vs. d-d Transitions).

Types of Transition

Most inorganic electronic spectra are measured in absorption, and thus involve the transitions of electrons from occupied to empty orbitals.

Charge-Transfer Transitions involve ligand- and metal-based levels, and are classified as ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT), LMCT can occur in all complexes including ones with empty or completely filled d shells. MLCT is seen in complexes where the ligands have low-lying empty orbitals (e.g. CO and unsaturated ligands). It is also possible to get intervalence transitions in “mixed valency compounds” such as KFe^{II}Fe^{III}(CN)₆.

Energies

Corresponds to between 3000 and 50000cm⁻¹, 3000 to 200nm, or 0.4 to 6 eV. 14000cm⁻¹ is red, while 25000cm⁻¹ is violet in the visible region.

The colour we see is that of the light transmitted or (in the case of solids) reflected. Light absorbed generally “disappears” as the energy of an electronic excited state is rapidly converted into vibrational energy (and hence ultimately heat); thus the wavelengths absorbed are those we do not see. As transitions are often broad, the relationship between the energies of absorption bands and the colours of a complex are sometimes not obvious.

Intensities

The Beer-Lambert Law governing the amount of radiation transmitted through a sample can be rearranged to give:

$$\log_{10}(I_0/I) = \epsilon c l.$$

Where I_0 is the incident and I the transmitting intensity, c the molar concentration of absorbing species, l the path length, and ϵ is the molar extinction coefficient conventionally given in units of $M^{-1} \text{ cm}^{-1}$. The maximum value of ϵ in a band, ϵ_{max} , is a convenient guide to the absorption intensity, although a better theoretical measure is the integrated value over the band.

The intensity of a transition is governed by **selection rules**.

Selection Rules

There are 3 Selection Rules to consider.

Angular Momentum:

$$\Delta l = \pm 1$$

Thus transitions that involve a change in quantum number by 1 (i.e. $p \rightarrow d$ or $d \rightarrow p$, for instance) are allowed. The important point here is that d-d transitions are **not** allowed.

Spin-multiplicity:

The spin selection rule $\Delta S = 0$, specifies that there should be no change in the number of unpaired electrons. Spin forbidden bands occur weakly through the mediation of spin-orbit coupling.

Transitions between states of the same multiplicity are allowed. Thus, 2T to a 2E are allowed, while 2T to 1T are not. For the electron to change its spin, energy must be expended and so any spin forbidden transitions are usually very weak.

Spin-forbidden transitions are more intense in heavy atoms – larger spin-orbit coupling.

Laporte (parity):

Based on the symmetry of the complex. For centrosymmetric molecules, this forbids a transition between energy levels with the same symmetry with respect to the centre of inversion. So transitions such as $T_{2g} \rightarrow E_g$ are not allowed.

The Laporte selection rule can be circumvented, either due to various ligands around the molecule disrupting the perfect symmetry around the complex, or because the molecule can vibrate to remove the centre of symmetry. The interaction between electronic and vibrational modes is called vibronic coupling and means that d-d transitions are observed. However, they are often not very intense due to energy expended in vibration. The intensity of vibronic bands increases with temperature as vibrational amplitudes increase.

Note that there are several factors to consider here. Firstly, larger transition metals ($2^{\text{nd}}/3^{\text{rd}}$ row) cause a large splitting factor (Δ) which makes the vibronic coupling more efficient.

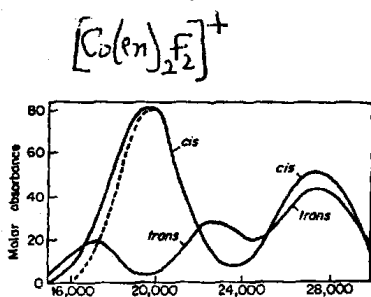
Secondly, complexes with tetrahedral symmetry do not have a centre of inversion, which allows easier mixing of levels to give more intense transitions. This is further magnified by the fact that the t_2 orbitals in T_d complexes have the same symmetry as the $(n+1)p$ orbitals, so $e \rightarrow t_2$ has a

partly d-p character. This means that the Angular Momentum Selection Rule is also partly satisfied, making the intensity even stronger. Note however that some d-d transitions in tetrahedral complexes may be forbidden by symmetry-based selection rules: as in CoCl_4^{2-} below.

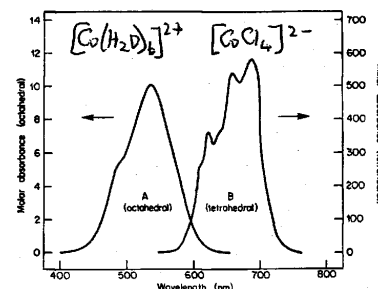
Type of Transition	Example	ϵ_{max}
Spin forbidden d-d f-f	Mn^{2+} (aq) Pr^{3+} (aq)	0.1 1
Spin allowed centrosymmetric d-d	$\text{Co}(\text{H}_2\text{O})_6^{2+}$	10
Spin allowed non-centrosymmetric d-d	CoCl_4^{2-}	100
Fully allowed charge transfer	MnO_4^-	10000

Example:

The very different absorption intensities for octahedral and tetrahedral complexes:



The stronger absorption in $\text{cis-}[\text{Co}(\text{en})_2\text{F}_2]^+$ (no centre of symmetry) compared to the trans complex.



Lanthanides and Actinides, with valence f orbitals, are more contracted and can be seen more as free ion spectra than due to any ligand involvements. This leads to sharper and weaker peaks, since there is weak interaction with the ligands, so more energy is required to cause vibrations or more intense splittings (f-f transitions are of much weaker intensity than d-d). The ionic nature of the lanthanides also increases the energy of Charge Transfers to UV (see below). Hence, the lanthanides are usually pale or non-coloured.

Conversely, for 2nd and 3rd row metals, larger orbitals reduces electron repulsions and reduces the value of B, the Racah Parameter. This gives higher energy transitions. Secondly, the lower energy d-orbitals match better with the ligand orbital energies. This coupled with a better overlap gives a larger value of Δ_o .

More About Mechanisms for Intensity

Magnetic Dipole Intensity

In octahedral sites, pure d-d (and f-f) electronic transitions are forbidden by the Laporte Rule: but the rule is an approximation, based on the dominance of the electric-dipole mechanism. The radiation field also has a magnetic component, perpendicular to the electric component, which can induce transitions between states connected by a magnetic-dipole transition moment. Such transitions generate a rotational displacement of charge.

The ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition of Cr^{3+} , d^3 , is allowed by this mechanism, because the magnetic-dipole operator transforms as T_{1g} in O_h . At low temperatures absorption can only occur from the electronic ground state, and the lowest energy transition is to the pure electronic excited state. All transitions that create vibrational quanta will be at higher energy. In emission, downwards transitions create vibrational energy and occur at lower energy than the pure electronic transition; the only band common to both spectra is the pure electronic transition.

The magnetic-dipole mechanism is also required for natural optical activity, so the intensity of the circular dichroism spectrum of the optical enantiomer $(\Delta)\text{-Cr(en)}_3^{3+}$ is only large in the region where the octahedral analogue has a ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition.

Vibronic Intensity

In the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition of CrCl_6^{3-} , vibrations that enable the electric-dipole intensity mechanism must have ungerade symmetry. In the octahedron there are three such modes, a t_{1u} stretch, a t_{1u} bend and a t_{2u} bend. To test whether the transition is allowed in this way, we determine the overall symmetry of the vibronic states, formed from products of the electronic and vibrational wavefunctions, and require that the direct product derived from these states contain the invariant representation. This condition is satisfied for both types of ungerade mode in this transition. The enabling modes are often said to provide 'false origins' in that they appear to be the first significant transitions in absorption (being so much more intense than the magnetic-dipole allowed pure electronic origin). Intensity enabled in this way is described as vibronic.

The rest of the envelope in the emission spectrum (as well as in absorption) is composed of progressions in two other modes of the octahedron, the a_{1g} symmetric stretch and the e_g mode. These modes cannot themselves enable intensity, but the creation of their quanta in the excited state implies a distortion along their respective coordinates in the excited state equilibrium geometry, and they occur in combination with the intensity enabling ungerade modes.

The activation of the e_g mode is unusual and shows that the excited state has a Jahn-Teller distortion created by the presence of one e_g electron in the $t_{2g}^2e_g$ excited state configuration, as well as the more usual uniform bond-lengthening implied by the progression in the a_{1g} mode. These properties of the excited state help to explain the mechanism of photochemically activated substitution, which is a feature of Cr^{3+} coordination chemistry.


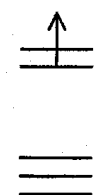
Widths

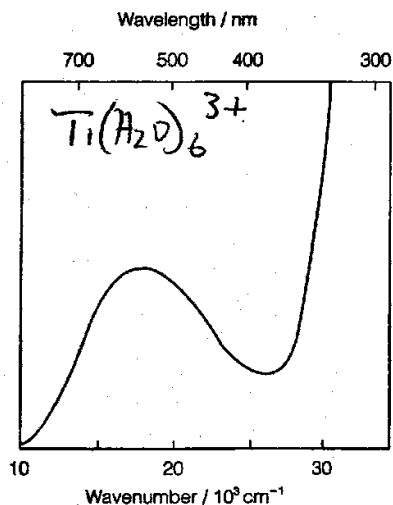
Electronic transitions are often accompanied by vibrational excitation. In some cases (especially in spectra of solids measured at low temperatures) it may be possible to resolve progressions in one or more vibrational modes, but spectra measure in solution are more often simply broadened by unresolved vibrational structure. The extent of broadening can be related to the Franck-Condon Principle and depends on the changes in equilibrium metal-ligand bond lengths resulting from the transition. When there is very little change in the bonding character of the orbitals involved, bands are fairly sharp; examples are f-f spectra and some spin-forbidden d-d bands. On the other hand, charge-transfer transitions are often very broad, as they can involve a large change in bonding.

d-d Transitions in O_h and T_d Fields

The d electrons are treated as though they only occupy d orbitals on the metal. The effect of the ligands is assumed small and comparable in magnitude to the repulsion between pairs of d electrons. The spin-orbit coupling energy is usually small compared with these perturbations, in the first transition series, but can be very significant in the 3rd transition series.

d-d Transitions: spin allowed

${}^2T_{2g}$	2E_g	in an octahedral d^1 complex, we expect one d-d transition from the ground state $t_{2g}^1 {}^2T_{2g}$ to the excited state $e_g^1 {}^2E_g$. the transition energy gives directly the value of the ligand field splitting parameter Δ which (for essentially historical reasons) is sometimes expressed in terms of Dq , where $\Delta = 10Dq$. Thus we see one transition centred on 18000cm^{-1} in the spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, although it is broad and asymmetrical, apparently because the excited state undergoes a Jahn-Teller distortion. Note also the strong charge-transfer band above 25000cm^{-1} .
		



Weak and Strong Field Limits

For most d^n configurations the situation is more complicated because several states can arise. Consider d^2 . There are two approaches. In the strong-field approach we consider the different configurations of t_{2g} and e_g electrons. Group-theoretical arguments predict the following states:

$$\begin{array}{l} t_{2g}^2 \quad \text{gives} \quad {}^3T_{1g}, {}^1A_{1g}, {}^1E_g \text{ and } {}^1T_{2g}. \\ t_{2g}^1 e_g^1 \quad \text{gives} \quad {}^3T_{1g}, {}^3T_{2g}, {}^1T_{1g} \text{ and } {}^1T_{2g}. \\ e_g^2 \quad \text{gives} \quad {}^3A_{2g}, {}^1A_{1g} \text{ and } {}^1E_g. \end{array}$$

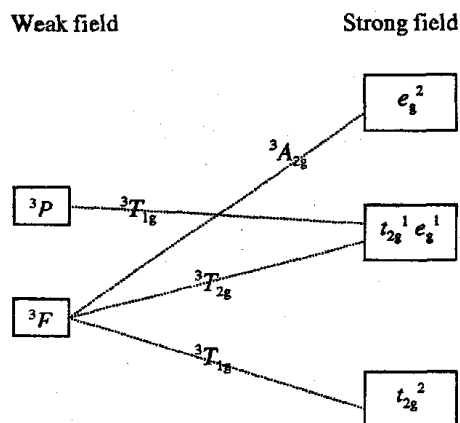
The different states from a given configuration differ in energy because of different degrees of electron repulsion. From Hund's first rule we expect ${}^3T_{1g}$ to be the ground state; as there are three other triplet states we expect to find three spin-allowed transitions, as well as several much weaker spin-forbidden transitions to the singlet states. The strong field limit implies that the ligand field is so strong that electron-electron repulsions can be ignored and energies can be expressed solely in terms of Δ_o .

In the alternative weak field method we start from the states of the free ion with the d^2 electron configuration. Initially ignore the ligand field and find the energies of the free ion terms – this is an atomic problem. Then consider the effect of the ligand field on these terms. We can show that this configuration gives rise to 3F and 3P states as well as several singlets. The weak field limit implies that Δ_o is so weak that only electron-electron repulsions are important and the relative energies of the terms can be expressed as combinations of Racah Parameters.

The energy difference between the states comes again from different electron repulsions. From Hund's first and second rules we expect 3F to be the lowest. Again using group theory, we find that in an octahedral ligand field the following triplet states are predicted:

$$\begin{array}{l} {}^3F \quad \text{gives} \quad {}^3T_{1g}, {}^3T_{2g} \text{ and } {}^3A_{2g} \\ {}^3P \quad \text{gives} \quad {}^3T_{1g} \end{array}$$

Note that the symmetries of the states are the same in both approaches. As only one state each symmetry of ${}^3A_{2g}$ and ${}^3T_{2g}$ is found, their wavefunctions must also be the same. However the two ${}^3T_{1g}$ states are mixed together by the combined effects of electron repulsion and ligand field splitting, and the strong-field wavefunctions will be linear combinations of those arising in the weak-field method. The correlation between the states arising in the two approaches is shown in the diagram:



Weak (ligand) field: i.e. $e^2/r_{12} > \Delta$.
 Strong (ligand) field: i.e. $\Delta > e^2/r_{12}$.

Term Energies for d^2

The terms arising from the $3d^2$ configuration are 1S , 3P , 1D , 3F , and 1G . We calculate the term energies as follows. If $|A\rangle$ is a many electron wavefunction formed from the product of one-electron functions, we need the average value of the inter-electron repulsion energy:

$$e^2/r_{12} = \iint A^* \frac{e^{12}}{r_{12}} A d\tau_1 d\tau_2,$$

which weights the repulsion energy by the probability that the electrons will be separated by the distance r_{12} .

The only difficulty in the theory of electron-electron repulsion (or of electron-ligand repulsion), is the awkwardness associated with the fact that the energy is associated with the distance r_{12} , which is not simply related to the coordinates in which the wavefunctions are cast. So $1/r_{12}$ must be expressed in those coordinates.

Racah parameters come from the method of defining this in the wavefunctions coordinates (actually from the F_n parameters used to adjust to fit the spectrum). With Racah parameters, only B is needed to specify the separation between the ground state and the first excited state with the same spin multiplicity. Since these transitions are spin-allowed, B alone can describe the electron-electron repulsion energy of those excited states that appear intense in the spectrum.

The effect of increasing Z_{eff} on a set of $3d^2$ gaseous ions is that, as the average radii decrease, the mean distance between them also decreases as does their repulsion. Hence there is a relative increase in the parameters B and C, but the relative spacing of the terms is unchanged, because the angular disposition of the electrons is unaffected by the orbital contraction. When a $4d^2$ ion is compared, the separation between excited states decreases by about 25%. This shows the increase in average electron radius in the 4d-shell. In the 5d shell, B and C decrease further. In practice $C \approx 4B$, so approximating the position of all the terms requires just one parameter.

Spin-Orbit Coupling (splits states with S and $L \neq 0$)

Spin-Orbit coupling constant, ξ . ξ is proportional to Z_{eff}^4 . Qualitatively the origin of the strong dependence on Z_{eff} is due to the small average value of the radius of the electron when Z_{eff} is large, and the strong magnetic field associated with orbital motion close to a nucleus with a high charge.

Spectroscopic Consequences of the Spin-Orbit Interaction

- (i) Admixture of states differing in S, allows 'spin forbidden transitions', especially in heavy metal atoms. So these are often observed in the 3rd Transition Series.

- (ii) Splitting of those ligand field states which have orbital angular momentum, i.e. in cubic symmetry, T_1 and T_2 states, but not E states.

Effect of the Ligand Field on the Free Ion Terms

Example: d^2 , 3F (the ground term) in the O_h field.

We want to find how this splits up in the presence of the ligands. Use the 7 M_L components from $L=3$ as a basis for representing the operations of O_h . Work out the characters and reduce them. A general solution exists in the full rotation group, R_3 , for a rotation of angle ϕ .

The result for $L = 3$ tells us the O_h states for 3F (A_{2g} , T_{2g} , T_{1g}) but not their relative energies. These are found by extrapolation to the strong field limit, observing the non-crossing rule. At this limit where, by definition, the electron-electron repulsion is ignored, there are three electron-configurations, t_{2g}^2 , $t_{2g}e_g$, and e_g^2 , with energies, which being the sum of the individual electron energies are $-8Dq$, $+2Dq$, and $+12Dq$ respectively.

Group theory tells us how to find the triplet states in these configurations, using the direct product of the individual electron symmetries. Because the spin part of a triplet wavefunction is symmetric with respect to a permutation of coordinates, the spatial part must be antisymmetric, and for the t_{2g}^2 , and e_g^2 configurations we therefore require the antisymmetric direct product. There is no such restriction for the $t_{2g}e_g$ configuration. The results are $t_{2g}^2 \rightarrow {}^3T_{1g}$, $t_{2g}e_g \rightarrow {}^3T_{1g}$, ${}^3T_{2g}$ and $e_g^2 \rightarrow {}^3A_{2g}$.

It is now possible to construct the correlation diagram connecting the weak and strong field limits. The interconnections for the 3T_1 states are made unambiguous by the non-crossing rule.

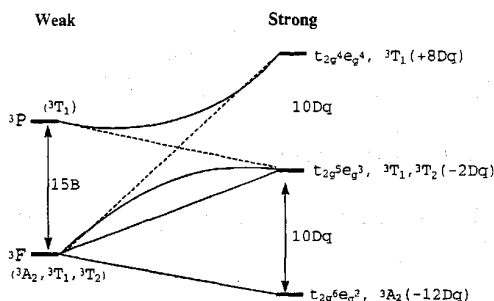
Orgel Diagrams

Similar theory may be applied to other d^n configurations and the results needed for spin-allowed transitions from high-spin ground states are summarised in Orgel Diagrams. The diagrams are applicable to tetrahedral as well as octahedral fields, using the principle that the d orbital splitting pattern of one is the reverse of the other.

These provide a summary of the splitting of the ground free-ion terms in the various cubic fields as well as excited terms with the same spin multiplicity. Because there is a simple relationship between d^n and d^{10-n} cases, and also between tetrahedral and octahedral fields, just two of these diagrams are needed.

Example: d^2 , d^8

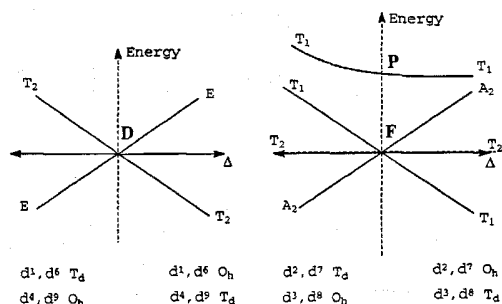
The free ion term energies for these configurations are identical. The angular momentum of the d^8 ion can be considered to arise from two positively charged 'holes' in the closed d^{10} shell (which has no angular momentum). The terms that arise from this angular momentum, and the repulsion energy between the holes, are just the same as for two electrons. However the strong field diagram for d^8 is different. In the octahedral field the configurations are $t_{2g}^6e_g^2$, $t_{2g}^5e_g^3$, $t_{2g}^4e_g^4$. Applying the same methods as for d^2 , there is only one triplet state compatible with $t_{2g}e_g^2$, namely ${}^3A_{2g}$ (notice the absence of any orbital degeneracy in the half-filled e_g set). The d^8 correlation diagram that we get like this is:



Notice how the crossing implied by the dotted lines has been avoided in the actual 3T_1 states whose energies are shown by the full lines. Compared to the d^2 ion the ligand field splitting of the free ion terms has been reversed. We can interpret this as the action of the ligands on the two 'holes' in the filled d^{10} shell. Because they are positively charged, the sign of the splitting is inverted. This result is even simpler for d^1 and d^9 , but is generally true for all high-spin d^n and d^{10-n} ions.

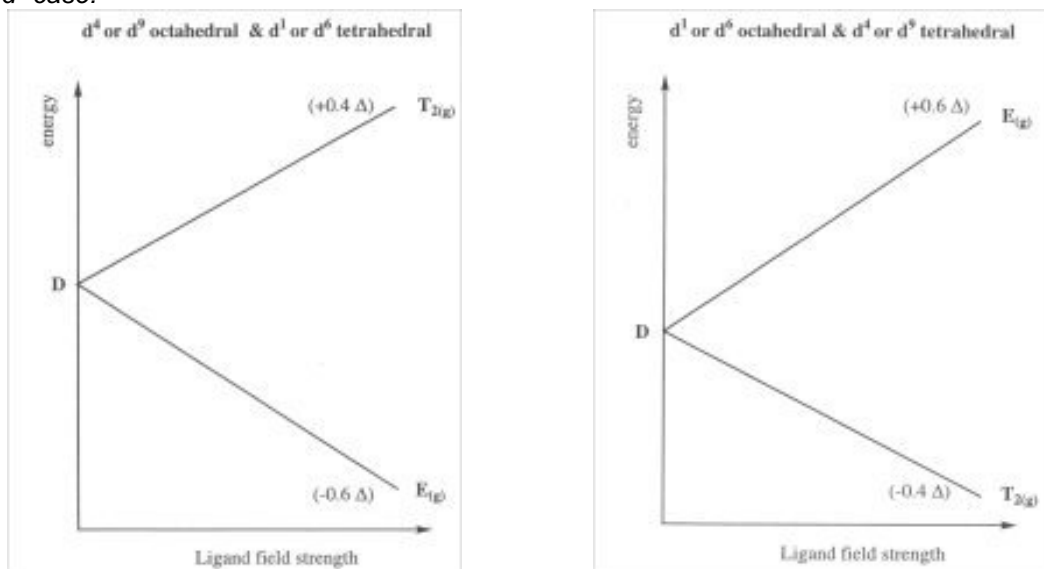
Now replace the octahedral field by the tetrahedral field. The strong field side of all the correlation diagrams inverts because the splitting of the t_2 and e orbitals inverts. Taken with the relationship between d^n and d^{10-n} , this means that the same diagram will describe d^n in an octahedron to be plotted with either sign relative to the free ion term energies, which means that it can describe the four possible combinations of d^n and d^{10-n} ions in tetrahedral and octahedral fields.

Only two Orgel Diagrams are needed to describe most of the states of interest of all the high-spin d^n ions. We can see why by finding the free-ion ground terms for each d^n , but applying Hund's Rules 1 and 2, and using the highest value for M_L got by summing the values of the individual m_l values.



We notice the symmetry of d^n and d^{10-n} . Because S does not split in the ligand field, we only need two Orgel diagrams to cover the D or F/P cases. To check on the sign of the splitting, the symmetry of the ground terms in the strong field limit can be found, using group theory in the manner described previously. With this information the Orgel diagrams can be constructed unambiguously. We have ignored d^5 which has no excited states with $S = 5/2$, and so all its d-d transitions are spin-forbidden.

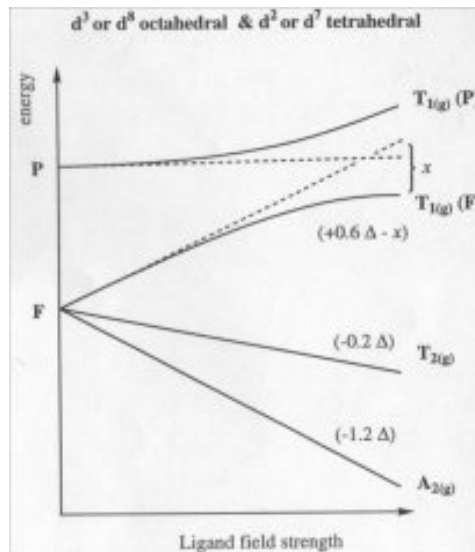
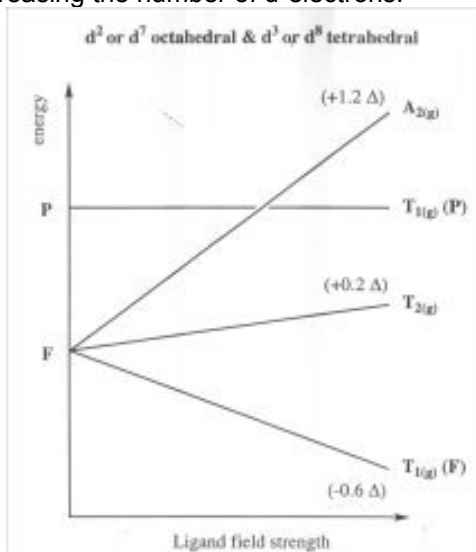
d^1 / d^9 case:



From this, it can be seen that d^1 (right hand side) has a Ground State of T_2 . This implies the t_{2g} energy level.

Thus, for d^1 , there is a single transition from t_{2g} to e_g , written as ${}^2E_g \leftarrow {}^2T_{2g}$. The energy gap corresponds to $1\Delta_o$. The spectra would appear as a single peak, perhaps with some peak-splitting due to Jahn-Teller distortions. However, d^9 (left hand side) has a ground state of E, which corresponds to the e_g level.

Increasing the number of d-electrons:



It can be seen from these that d^2 and d^8 show several transitions, while d^4 is only one. Note also that there is repulsion (bending) between the lines of the same symmetry. This prevents crossing over (non-crossing rule).

$d^4 - {}^5T_{2g} \leftarrow {}^5E_g$ at Δ_o is the only transition, but there will be Jahn-Teller distortions in 5E_g .

d^2 - Several transitions each corresponding to a peak. They are:

${}^3A_{2g} \leftarrow T_{1g}(F)$ at $1.8\Delta_o$.

${}^3T_{2g} \leftarrow T_{1g}(F)$ at $0.8\Delta_o$.

${}^3T_{1g}(P) \leftarrow T_{1g}(F)$. Value here would be dependent on the Racah Parameter.

d^8 - three transitions again.

${}^3T_{2g} \leftarrow {}^3A_{2g}$ at Δ_o .

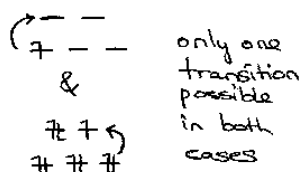
${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$. Would be at $1.8\Delta_o$, but repulsions (bending) alters value.

${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$. This is again Racah dependent.

Hole Formalism

This states that the number of ways of arranging one electron is $2 \times (2l+1)$ states.

Consider comparison of d^1 and d^9 :



Thus there is only one possible transition for each configuration, i.e. they have the same terms.

Mathematically, this makes use of the ${}^n C_r$ function as ${}^{10}C_1 = {}^{10}C_9 = 10$. Thus it is a general trend that d^n has the same terms as d^{10-n} . However, J values are reversed, and energy varies due to shielding differences.

Examples

1. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, Fe^{2+} has the d^6 configuration. The appropriate diagram shows the splitting of a free-ion D state into two states, the lower T_2 and the upper E. the spin multiplicity is not given but we can work this out as high-spin d^6 states must have four unpaired electrons, hence $S = 2$ and $2S+1 = 5$. the full designations of the states are ${}^5T_{2g}$ (which in the strong-field approach comes from the $t_{2g}^4 e_g^2$ configuration) and 5E_g (from $t_{2g}^3 e_g^3$). We expect one spin-allowed transition, which is seen at around 10000cm^{-1} .
2. $[\text{CoCl}_4]^{2-}$. Co^{2+} has d^7 , and we use the other diagram, this time in the "backwards" direction from the scale on the bottom. There are three unpaired electrons so that $2S+1 = 4$ and the states are 4A_2 (the ground state), 4T_1 , 4T_2 and 4T_1 . there are three spin-allowed transitions, which are expected to be more intense than in an octahedral complex. However group-theoretical selection rules tell us that only transitions to T_1 states are allowed in T_d symmetry from an A_2 ground state. The transition to 4T_2 is therefore only vibronically allowed and is considerably weaker.

The most important conclusions to be drawn from Orgel Diagrams concerns the number of spin-allowed d-d transitions expected in high-spin octahedral and tetrahedral complexes. These are summarised:

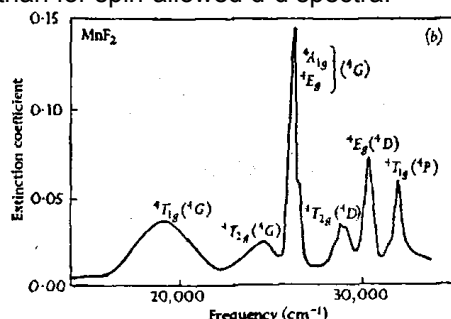
Configuration	Number of Transitions
d^1, d^4, d^6, d^9	One
d^2, d^3, d^7, d^8	Three
d^5	None

Note the following limitations of these predictions:

- a) the expected transitions may not all be seen, either because they are off the scale of the spectrometer (e.g. in the IR) or because they are obscured by much stronger charge-transfer transitions.
- b) The predictions apply to regular O_h and T_d symmetries. When the symmetry is lower the d levels split further and more transitions may be seen.

d-d transitions: spin forbidden

Note also the result for high-spin d^5 . The ${}^6A_{1g}$ ground state from the $t_{2g}^3 e_g^2$ configuration is the only state with five unpaired electrons and so all d-d transitions are spin forbidden. In many other cases spin-forbidden transitions are also possible, but generally they are weak and hard to see. The spectrum of MnF_2 which has the rutile structure with octahedral Mn^{2+} is shown. The intensities are much weaker than for spin-allowed d-d spectra.



Tanabe Sugano Diagrams

These are quantitative version of Orgel diagrams. The relative energies of all the states depends on the relative magnitude of Dq and B , so these diagrams plot the relative energies (in units of B) of the states as a function of the ratio Dq/B . Unlike Orgel diagrams all free ion states are included, and all energies appear relative to the ground state. If the ground state changes, e.g. if Dq is large enough to cause spin-pairing, there is a discontinuity in the slopes of all the lines.

The curvature of the lines indicates the interaction between free ion states under the influence of the field. An approximate method of finding the parameters from a spectrum is to fit the ratios of the energies of the transitions to a vertical section through this diagram. This fit determines Dq/B , while a comparison of any one transition energy with the vertical scale establishes B . Then both parameters are known.

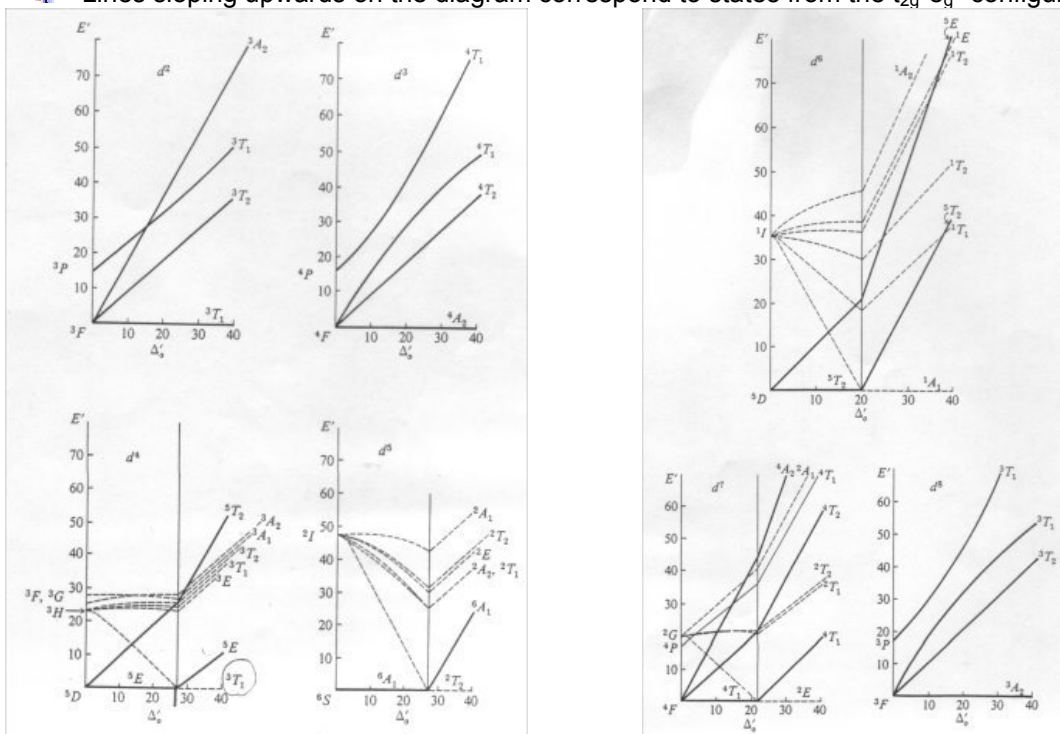
The main limitations of the diagram are:

- 1) It excludes spin-orbit interaction, and
- 2) It assumes that B is a good parameter for all the states.

There are two approximations for all the states. There are two approximations in this. First it assumes $C/B \sim 4.5$, so that the energy of the spin-forbidden states can be determined. More subtly, the free ion electron-electron repulsion parameters assume the same average radius of all d electrons. But in a complex the degree of covalent bonding of the t_{2g} and e_g orbitals is different. The electron-electron repulsion is therefore different for two t_{2g} electrons, two e_g electrons or between a t_{2g} and an e_g electron, and the simple theory is quantitatively unreliable. The errors can be pronounced if the electrons are delocalised, e.g. into an unsaturated π -system on the ligand.

To interpret spin-forbidden transitions such as the ones above for MnF_2 we need a Tanabe-Sugano diagram like those shown below. Note that unlike the case with an Orgel diagram, the ground state energy is drawn at zero. In the weak-field approach the free ion ground state is 6S which gives the single ${}^6A_{1g}$ state in the octahedral field. All other states shown are quartets with only three unpaired electrons. The different slopes of lines in the diagram are important.

- ✚ Lines sloping downwards on the diagram correspond to excited states from the $t_{2g}^4 e_g^1$ configuration. They are of higher energy than the ground state because the spin-pairing energy is greater than Δ .
- ✚ Lines almost horizontal on the diagram correspond to excited states of the same configuration as the ground state. Their energy is therefore independent of Δ . Because there is no change at all in the bonding character of the occupied orbitals, these transitions are sharp.
- ✚ Lines sloping upwards on the diagram correspond to states from the $t_{2g}^2 e_g^3$ configuration.

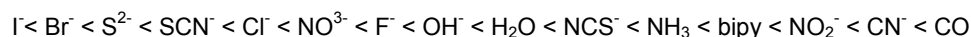


Curving of the lines is due to mixing of terms of the same symmetry type. Still obey non-crossing rule though (bend apart instead).

Spectrochemical and Nephelauxetic Series

Analysis of d-d energies allow the determination of two types of parameter: ligand field parameters represent the splitting of the d orbitals; electrostatic parameters represent the repulsions between electrons in d orbitals and give the energy differences between different terms from the same configuration.

For octahedral and tetrahedral complexes only one ligand field parameter is needed, $\Delta = 10Dq$. For a given metal ion and different ligands, values of Δ follow the order:



This Spectrochemical series of ligands reflects their different bonding properties, the order being:

Weak σ -donor, π -donor < moderate σ -donor < strong σ -donor, π -acceptor.

For a given ligand the corresponding Spectrochemical series of metal ions follows another pattern. There is a general increase in Δ with increasing oxidation state, and a strong increase from 3d to 4d and 5d. within a series Δ tends to decrease from left to right as the d orbitals contract and overlap less well with ligands.

Remember that the Spectrochemical series is largely unrelated to the expectations of the electrostatic model. Even with good metal wavefunctions the magnitude of $10Dq$, calculated with a point charge or point dipole model for the ligand, is about 10 times too small compared to experiment. The missing feature is overlap and MO formation. The most direct evidence for this is:

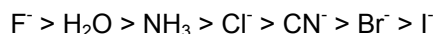
- (a) the distribution of spin density seen by neutron diffraction, and
- (b) hyperfine structure in EPR, where the resonances of unpaired spins, nominally in metal d orbitals, contain fine structure from interaction with the nuclear spin of the ligands.

Electron repulsion between electrons in d orbitals can be expressed in terms of three Racah parameters A, B and C which depend on complicated integrals over the radial distribution. Energy differences between different terms of a configuration depend only on B and C. for example the energy difference between the free ion F and P terms of highest multiplicity in d^2 , d^3 , d^7 and d^8 is $15B$; C is also needed for spin-forbidden transitions but generally the analysis is simplified by assuming a fixed ratio of $C \approx 4B$.

B may be determined for free transition metal ions from analysis of their spectra. It is found that values obtained from analysis of spectra of complexes are invariably smaller than for free ions. This is known as the Nephelauxetic effect (from the Greek meaning "cloud expanding") and reflects the fact that what we call "d orbitals" in complexes are really molecular orbitals involving the ligands as well. The decrease in repulsion arises because electrons in these molecular orbitals are on average further apart than in true d orbitals. It can be quantified by the Nephelauxetic ratio:

$$\beta = B_{\text{complex}} / B_{\text{free ion}}$$

Values of β depend on the metal and the ligand, and for the same metal ion follow the Nephelauxetic series of ligands:



The series reflects the different degrees of covalency found in the metal-ligand bond. This accounts for the difference in electron repulsions between the free ion and a complex. The weakening occurs for the complex because the occupied molecular orbitals delocalise over the ligands and away from the metal.

A small β indicates a large measure of d-electron delocalisation on to the ligand and hence a significant covalent character in the complex.

The nephelauxetic parameter also depends on the location of the electrons. In e_g the overlap of s is usually larger than the p overlap of t_{2g} , so the cloud expansion is larger for e_g .

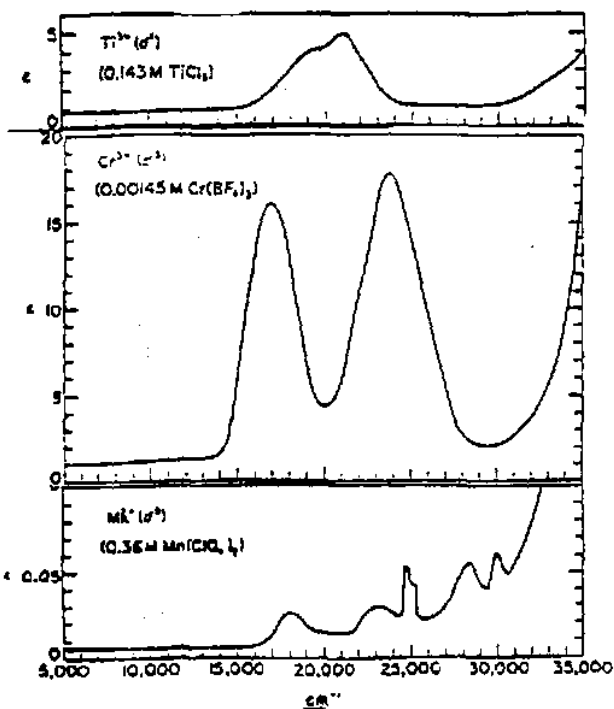
Jahn-Teller Distortions

Indicated by metal-ligand bond lengths not being equal. Is explained by perturbation occurring when there are degenerate sets of orbitals, such that the degeneracy is removed. The consequence is elongation / compression of bonds. Greatest change in length is observed for the orbitals lying on the same axis as the ligands (e_g for O_h).

Thus, in the extreme it is possible to see additional absorption bands in the UV-visible spectra due to reduction in symmetry. Usually though, a splitting of peaks or asymmetric peaks are seen.

Examples – Transition Metal Aquo Ions

The sensitivity of the eye is from $15,000\text{cm}^{-1}$ (red) to $25,000\text{cm}^{-1}$ (violet). A strong absorption band in the red part of the spectrum will make the sample appear blue. A strong absorption band in the blue region makes the sample appear yellow. The eye sees colours from the gaps in the spectrum.



$d^1, \text{Ti}(\text{H}_2\text{O})_6^{3+}$

The absorption in the green, with red and blue transmission gives a purple colour. The presence of two peaks, separated by about 2000cm^{-1} , is peculiar. The spin-orbit coupling constant for Ti^{3+} is 150cm^{-1} and its action in the ${}^2T_{2g}$ ground state, which alone has orbital angular momentum, is too small to explain the splitting. Instead it is attributed to a Jahn-Teller effect in the E_g excited state, in which the single e_g electron creates the same distortion as the e_g^3 configuration does in

the ground state of Cu^{2+} . The two peaks represent vertical transitions to the two potential energy surfaces, which arise from this effect. We can deduce that $10Dq \sim 20,300\text{cm}^{-1}$.

$d^3, \text{Cr}(\text{H}_2\text{O})_6^{3+}$

The solution is purple. The observed transition are: ${}^4A_2 \rightarrow {}^4T_2$, $17,000\text{cm}^{-1}$ ($\epsilon=16$); ${}^4A_2 \rightarrow {}^4T_1(\text{F})$, 24000cm^{-1} ($\epsilon=18$); ${}^4A_2 \rightarrow {}^4T_1(\text{P})$, 37000cm^{-1} (weak). Assignment is simple because from the Orgel or Tanabe-Sugano diagrams the first transition energy is $10Dq$, and the other two transitions give $B = 695\text{cm}^{-1}$ (free ion 1030cm^{-1}). Note the nephelauxetic effect and the weakness of the "two-electron" ${}^4A_2 \rightarrow {}^4T_1(\text{P})$ transition.

d^5, Mn^{2+}

Pale pink. All transitions are spin-forbidden. The Tanabe-Sugano diagram for this configuration shows two types of line. Horizontal lines occur for those states which are derived from the $t_{2g}^3 e_g^2$ configuration; their energies are dependent on the electron-electron repulsion parameters, but are independent of $10Dq$. Since there is no change in orbital occupation in these transitions, there is no change in the equilibrium bond length in the excited state. The transitions are sharp because vertical (Franck-Condon) transitions conserve the vibrational quantum number, i.e. $\Delta v = 0$. Sloping lines correspond to configurations such as $t_{2g}^4 e_g^1$, which become more stable relative to the ground state as $10Dq$ increases. Here the bond lengths shorten in the excited state, and the transitions are broad because Franck-Condon transitions occur between displaced vibrational potential surfaces.

f-f Transitions

f-f transitions in lanthanide complexes are weak and sharp and have energies close to those expected for free lanthanide ions. Together with the magnetic properties, this confirms that 4f orbitals have very little overlap with surrounding atoms. High-resolution spectra measured in crystals at low temperatures do show small ligand field splittings but they are small (of the order of 10cm^{-1}) compared with splittings in transition metal complexes.

Actinides show larger ligand field effects than lanthanides, especially ions early in the series (e.g. U^{4+}). The interpretation of spectra is complicated by strong spin-orbit splitting.

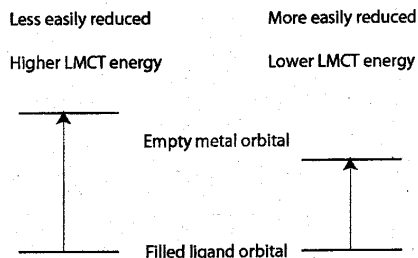
f-f transitions in centrosymmetric complexes are Laporte forbidden as with d-d spectra. Intensities are in the order $4f < 5f < d$ reflecting the order of strength of metal-ligand interactions.

Charge Transfer Transitions

Can be ligand to metal, metal to ligand, and intervalence charge transfer (metal to metal) in mixed valence systems. The occurrence of these is very widespread. Famous examples are $\text{Fe}(\text{SCN})_6^{2+}$ (blood red), $\text{Fe}(\text{phen})_3^{2+}$ (blood red), and Prussian Blue, which are respectively examples of ligand to metal, metal to ligand metal to metal charge transfer.

These transitions are typified by compounds such as MnO_4^- , where there are no d electrons, yet this appears as a deep purple colour.

Ligand-to-metal transitions occur in all complexes, not only transition metals. In complexes with d-d transitions LMCT transitions can often be seen at higher energy and identified by their much stronger intensity. Sometimes they obscure some of the predicted d-d bands. In d^0 complexes such as MnO_4^- they are the only transitions seen. LMCT can be regarded as an internal redox transition, the metal being reduced and the ligand oxidised. It is therefore possible to correlate LMCT energies with the redox properties of metals and ligands. The comparison of two metal ions with the same ligands is shown below. Lowering the energy of empty metal orbitals gives an ion that is more easily reduced hence more strongly oxidising and is expected to correlate with a lower LMCT energy.



For a given ligand LMCT transitions generally follow the trends below:

- (i) Increase $3d < 4d < 5d$ as oxidising power decreases.
- (ii) Decrease with metal oxidation state.
- (iii) Decrease from left to right along the series as Z_{eff} increases.

Exceptions to trend (iii) sometimes occur when there is a change of electron configuration.

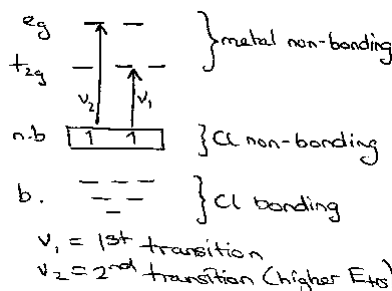


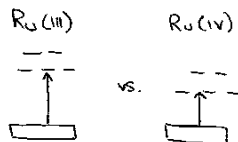
Diagram shows order of transitions (smallest energy first). For 3d transition metals these transitions are usually at much higher energy than d-d transitions (UV end of spectrum).

Variation with Metal –

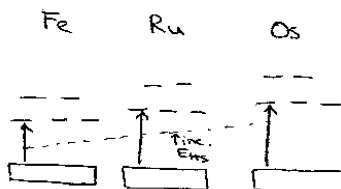
Ability to receive or release electrons is obviously dependent on electron configuration. If the metal has a full t_{2g} then Ligand to Metal Charge Transfer will have to put electrons into the antibonding e_g , which is likely to be very high in energy. Similarly, for the classic MnO_4^- , the d-orbitals are empty so an electron is easily transferred into the lowest energy orbitals.

From this, it is obvious that Ligand to Metal Charge Transfer is more likely to occur for high oxidation state (low d electron count) metals. Similarly, Metal to Ligand Charge Transfer would require many d-electrons, and vacant orbitals on the ligand to receive them (usually π^*).

Comparing metals with different oxidation states, for a higher oxidation state, the d-orbitals are lower in energy, since the increased charge of the nucleus stabilises them. Thus, the energy gap is reduced, and the Transition Energy is lower.

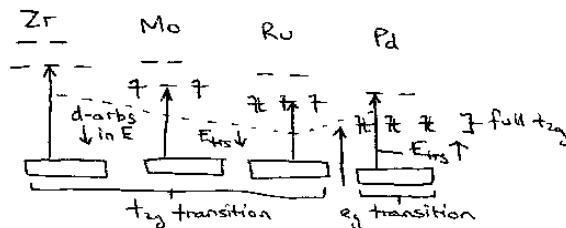


Moving down a Group, 4d and 5d transition metals, the 4d and 5d orbitals are higher in energy and so the Transition Energy is increased.



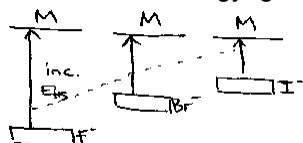
Moving across the Period, the d-orbitals decrease in energy, reducing the Transition Energy. However, d-electrons are increasingly populating these orbitals, and this can have important

consequences. For example, the energy of transition for Pd is higher than for Ru because the electron has to enter an e_g orbital instead of t_{2g} , so the energy gap is larger.



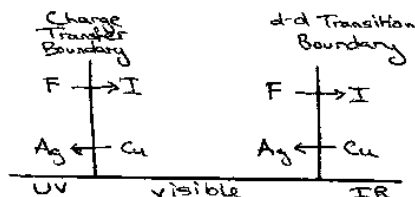
Variation with Ligands

Comparing Ligands, again orbital energy is the key to the transition energies. For example, down the halides, their non-bonding orbitals increase in energy, giving:



Thus, the Transition Energy will decrease for lower halides.

The overall picture for Transition Energies can be summed up in the following diagram:



These processes resemble redox reactions driven by photons, which transfer electrons between atoms. The energies nicely follow the expected redox properties. For a given metal ion, LMCT energies reflect the redox properties of the ligand. A lower LMCT energy corresponds to a more easily oxidising ligand. Thus FeF_3 is light green, because the F and Fe charge transfer occurs in the ultraviolet. However, the colours of FeCl_3 (brown) and FeBr_3 (red-black) and the non-existence of FeI_3 , are indicative of a progressive lowering of the charge transfer energy which eventually becomes possible thermally. There are many examples, e.g. HgCl_2 (white), HgBr_2 (yellow), HgI_2 (red).

Most of the colours used in analytical chemistry are charge transfer transitions, because their high intensity enables the determination of very small concentrations of material. Examples are the use of Ni(IV) in an oxidised dimethylglyoximate complex, which is red, and the determination of platinum metals using sulphur-containing ligands. Apart from Prussian blue, the mixed iron oxides (black), Ag(I)Ag(III)O_2 (brown-black), and $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$ are good examples of mixed valence species.

Energies

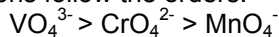
If the orbitals are substantially of one-centre in type, the charge-transfer energies are closely related to the sum of the ionisation energy of the donor centre and the electron-affinity of the acceptor centre.

- The well defined shifts for the series CoX_4^{2-} and NiX_4^{2-} shows the difference between the halides as well as the more oxidising properties of Ni(II) as compared to Co(II) consistent with their effective nuclear charge.
- The series of compounds with the formula $\text{Co(NH}_3)_5\text{X}^{2+}$ demonstrate how large the changes in charge transfer energies are compared to the shifts due to the difference in their ligand field parameters.
- Changes in the metal can have a similarly profound influence. It has been shown that the energy decreases with increasing formal charge on the metal. Higher energies in the

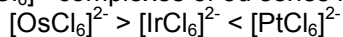
second and third transition series reflect the well-known increase in stability of higher oxidation states of these metals.

EXAMPLE:

- a) LMCT energies of d^0 oxoanions follow the orders:



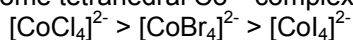
- b) LMCT energies of some $[\text{MCl}_6]^{2-}$ complexes of 5d series metals follow the order:



The ground state electron configurations in these low-spin complexes are t_{2g}^4 , t_{2g}^5 , t_{2g}^6 respectively. In the first two an electron can be excited into a t_{2g} orbital and the order follows the expected trend with increasing Z_{eff} . However in the $[\text{PtCl}_6]^{2-}$ the t_{2g} orbitals are full and the transition is into the higher energy e_g which leads to a reversal of the normal trend.

EXAMPLE:

The energies of LMCT bands of some tetrahedral Co^{2+} complexes follow the order:



as expected from the ease of oxidation of $\text{Cl}^- < \text{Br}^- < \text{I}^-$.

Metal-to-ligand charge transfer occurs in complexes where the ligands have empty antibonding orbitals at relatively low energy, for example in carbonyls and with O and N-donor ligands attached to unsaturated π -systems. Generally they follow the reverse order expected for LMCT, e.g. there is an increase in energy as the metal Z_{eff} increases, because the ions are less easily oxidised.