Electronic spectra

A characteristic feature of many d-block metal complexes is their colours, which arise because they absorb light in the visible region (see Figure below).

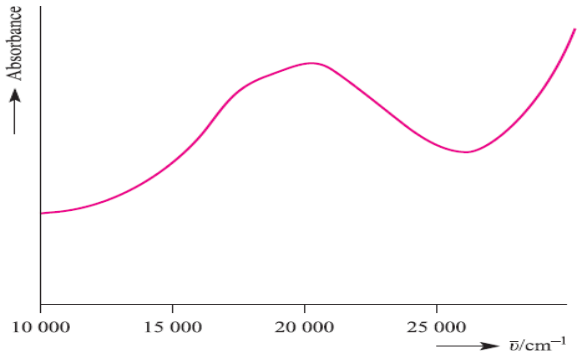


Fig. Shows the electronic spectrum of $[Ti(OH_2)_6]^{3+}$ in aqueous solution.

Studies of electronic spectra of metal complexes provide information about structure and bonding, although interpretation of the spectra is not always straightforward. Absorptions arise from transitions between electronic energy levels:

1) Transitions between metal-centred orbitals possessing d-character („**d–d' transitions**).
2) Transitions between metal- and ligand-centred MOs which transfer charge from metal to ligand or ligand to metal (**charge transfer bands**).

Absorption bands in the electronic spectra of d-block metal compounds are usually broad. The broadness is a consequence of the Franck–Condon approximation which states that electronic transitions are very much faster than nuclear motion (because nuclear mass is far greater than electron mass).

The absorption of a photon of light occurs at ~10^{-18} s whereas molecular vibrations and rotations occur much more slowly. As molecules are vibrating, an electronic transition is essentially a snapshot at a particular set of internuclear distances. It follows that the electronic spectrum will record a range of energies.

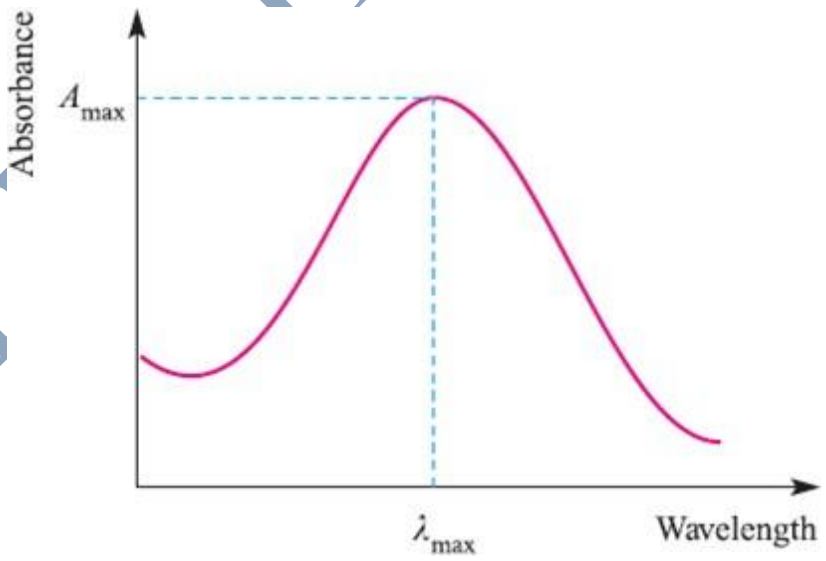
Absorption bands are described in terms of λ_{max} corresponding to the absorption maximum A_{max} (see Figure below). The wavelength, λ_{max}, is usually given in nm, but the position of the absorption may also be reported in terms of wavenumbers, $\bar{\upsilon}$ (cm^{-1}). The molar extinction coefficient (or molar absorptivity) ε_{max} of an absorption must also be quoted; ε_{max} indicates how intense an absorption is and is related to A_{max} by following equation where c is the concentration of the solution and ℓ is the pathlength (in cm) of the spectrometer cell.

$$\varepsilon_{max} = \frac{A_{max}}{c \times \ell} \qquad (\varepsilon_{max} \text{ in } dm^3\, mol^{-1}\, cm^{-1})$$

Values of ε_{max} range from close to zero(a very weak absorption) to >10 000dm^3 mol^{-1} cm^{-1} (an intense absorption).

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

400nm corresponds to 25000 cm^{-1}; 200nm corresponds to 50000 cm^{-1}: (nm cm^{1-} $=10^7$)



Absorptions in the electronic spectrum of a molecule or molecular ion are often broad, and cover a range of wavelengths. The absorption is characterized by values of _λ_{max} and ε_{max}

Some important points are that the electronic spectra of:

1) d^1, d^4, d^6 and d^9 complexes consist of one broad absorption;
2) d^2, d^3, d^7 and d^8 complexes consist of three broad absorptions;
3) d^5 complexes consist of a series of very weak, relatively sharp absorptions.

Charge transfer absorptions

In metal complexes, intense absorptions (typically in the UV or visible part of the electronic spectrum) may arise from ligand-centred n–π* or π– π* transitions, or from the transfer of electronic charge between ligand and metal orbitals.

The latter fall into two categories:

1) Transfer of an electron from an orbital with primarily ligand character to one with primarily metal character (ligand-to-metal charge transfer, **LMCT**).
2) Transfer of an electron from an orbital with primarily metal character to one with primarily ligand character (metal-to-ligand charge transfer, **MLCT**).

Charge transfer transitions are not restricted by the selection rules that govern „d–d " transitions (see later). The probability of these electronic transitions is therefore high, and the absorption bands are therefore intense (Table below).

Table:Typical ε_{max} values for electronic absorptions; a large "max corresponds to an intense absorption and, if the absorption is in the visible region, a highly coloured complex.

Type of transition	Typical ε_{max} / $dm^3\ mol^{-1}\ cm^{-1}$	Example
Spin-forbidden '*d–d*'	<1	$[Mn(OH_2)_6]^{2+}$ (high-spin d^5)
Laporte-forbidden, spin-allowed '*d–d*'	1–10	Centrosymmetric complexes, e.g. $[Ti(OH_2)_6]^{3+}$ (d^1)
	10–1000	Non-centrosymmetric complexes, e.g. $[NiCl_4]^{2-}$
Charge transfer (fully allowed)	1000–50 000	$[MnO_4]^-$

Since electron transfer from metal to ligand corresponds to metal oxidation and ligand reduction, an MLCT transition occurs when a ligand that is easily reduced is bound to a metal centre that is readily oxidized. Conversely, LMCT occurs when a

ligand that is easily oxidized is bound to a metal centre (usually one in a high oxidation state) that is readily reduced. There is, therefore, a correlation between the energies of charge transfer absorptions and the electrochemical properties of metals and ligands.

Ligand-to-metal charge transfer may give rise to absorptions in the UV or visible region of the electronic spectrum. One of the most well-known examples is observed for $KMnO_4$. The deep purple colour of aqueous solutions of $KMnO_4$ arises from an intense LMCT absorption in the visible part of the spectrum as following Figure:

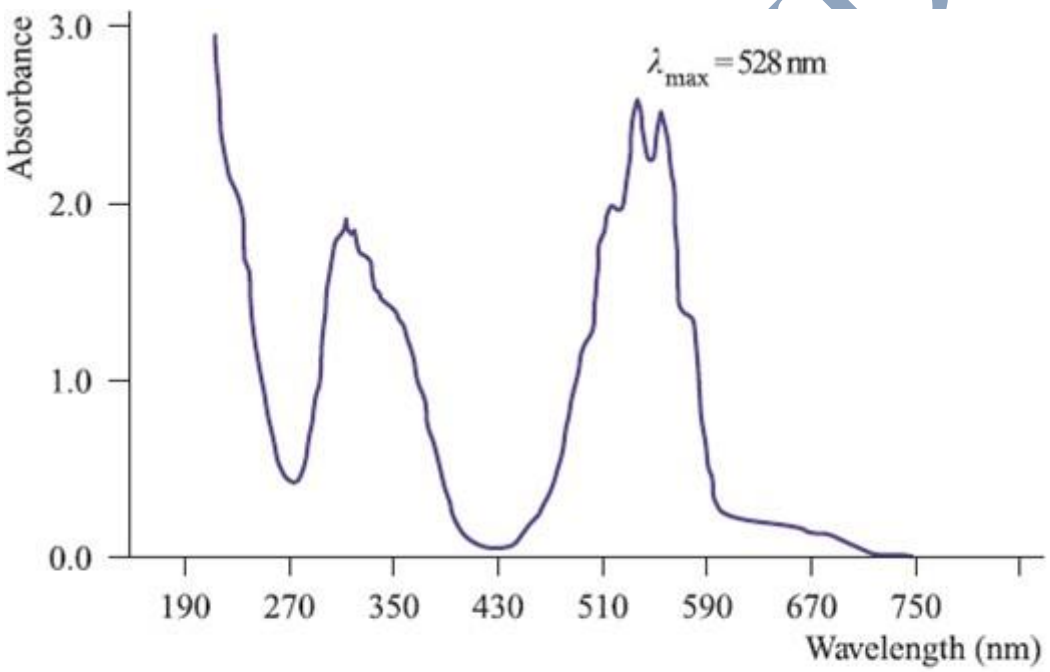


Fig. Part of the electronic spectrum of an aqueous solution of $KMnO_4$. Both absorptions arise from LMCT, but it is the band at 528 nm that gives rise to observed purple colour. Very dilute solutions (here, 1.55×10^{-3} mol dm^{-3}) must be used so that the absorptions remain within the absorption scale.

This transition corresponds to the promotion of an electron from an orbital that is mainly oxygen lone pair in character to a low-lying, mainly Mn-centred orbital. The

following series of complexes illustrate the effects of the metal, ligand and oxidation state of the metal on the position (λ_{max}) of the LMCT band:

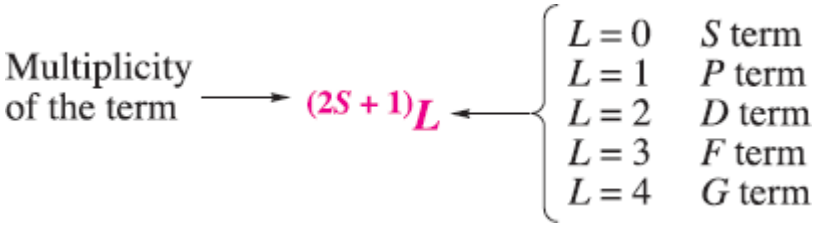
- $[MnO_4]^-$ (528 nm), $[TcO_4]^-$ (286 nm), $[ReO_4]^-$ (227 nm);
- $[CrO_4]^{2-}$ (373 nm), $[MoO_4]^{2-}$ (225 nm), $[WO_4]^{2-}$ (199 nm);
- $[FeCl_4]^{2-}$ (220 nm), $[FeBr_4]^{2-}$ (244 nm);
- $[OsCl_6]^{3-}$ (282 nm), $[OsCl_6]^{2-}$ (370 nm).

Across the first two series above, the LMCT band moves to lower wavelength (higher energy) as the metal centre becomes harder to reduce. The values of the absorption maxima for $[FeX_4]^{2-}$ with different haloligands illustrate a shift to longer wavelength (lower energy) as the ligand becomes easier to oxidize (I^- easier than Br^-, easier than Cl^-). Finally, a comparison of two osmium complexes that differ only in the oxidation state of the metal centre illustrates that the observed ordering of the λ_{max} values is consistent with Os(IV) being easier to reduce than Os(III).

Metal-to-ligand charge transfer (MLCT) typically occurs when the ligand has a vacant, low-lying π* orbital, for example, CO, py, bpy, phen and other heterocyclic, aromaticligands. Often, the associated absorption occurs in the UV region of the spectrum and is not responsible for producing intensely coloured species. In addition, for ligands where a ligand-centred π*←π transition is possible (e.g. heterocyclic aromatics such as bpy), the MLCT band may be obscured by the π*←π absorption. For $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+,}$ the MLCT bands appear in the visible region at 520 and 452 nm, respectively. These are both metal(II) complexes, and the metal d-orbitals are relatively close in energy to the ligand π* orbitals, giving rise to an MLCT absorption energy corresponding to the visible part of the spectrum.

Selection rules

Electronic energy levels are labelled with term symbols. Thus, the term symbol is written in the general form:



Electronic transitions between energy levels obey the following selection rules.

Spin selection rule: $\Delta S = 0$

Transitions may occur from singlet to singlet, or from triplet to triplet states, and so on. Thus the transition is ***allowed***, but a change in spin multiplicity is ***forbidden*** such as singlet to triplet.

Laporte selection rule: There must be a change in parity:

allowed transitions: g ↔ u

forbidden transitions: g ↔g u↔ u

This leads to the selection rule:

allowed transitions are s → p, p →d , d → f ;

forbidden transitions are s → s, p → p, d → d, f → f ,s → d, p →f etc.

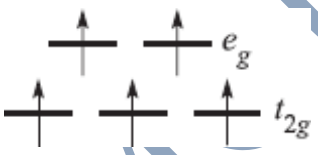
Since these selection rules must be strictly obeyed, why do many d-block metal complexes exhibit „d–d" bands in their electronic spectra?

A spin-forbidden transition becomes „allowed" if, for example, a singlet state mixes to some extent with a triplet state. This is possible by spin–orbit coupling ,but for first row metals, the degree of mixing is small and so bands associated with „spin-forbidden" transitions are very weak (Table pp.73). Spin-allowed „d–d" transitions remain Laporte-forbidden and their observation is explained by a mechanism called ***'vibronic coupling'***. An octahedral complex possesses a centre of symmetry, but molecular vibrations result in its temporary loss. At an instant when the molecule

does not possess a centre of symmetry, mixing of d and p orbitals can occur. Since the lifetime of the vibration ($\approx 10^{-13}$ s) is longer than that of an electronic transition ($\approx 10^{-18}$ s), a „d–d" transition involving an orbital of mixed pd character can occur although the absorption is still relatively weak (Table pp 73). In a molecule which is non-centrosymmetric (e.g. tetrahedral), p–d mixing can occur to a greater extent and so the probability of „d–d" transitions is greater than in a centrosymmetric complex. This leads to tetrahedral complexes being more intensely coloured than octahedral complexes.

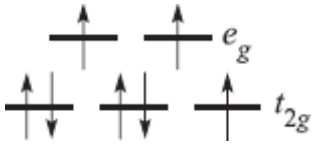
Example: Explain why an electronic transition for high-spin $[Mn(OH_2)_6]^{2+}$ is spin-forbidden, but for $[Co(OH_2)_6]^{2+}$ is spin-allowed.

Sol. $[Mn(OH_2)_6]^{2+}$ is high-spin d^5 Mn(II):



A transition from a t_2g to eg orbital is impossible without breaking the spin selection rule: $\Delta S = 0$, which means that S must remain the same.

$[Co(OH_2)_6]^{2+}$ is a high-spin d^7 Co(II) complex:



A transition from a t_2g to eg orbital can occur without violating the spin selection rule.

NB: Transitions in both complexes are *Laporte- forbidden.*

Electronic spectra of octahedral and tetrahedral complexes

Electronic spectroscopy is a complicated topic and we shall restrict our discussion to high-spin complexes. This corresponds to the weak field limit. We

begin with the electronic spectrum of an octahedral d^1 ion, exemplified by $[Ti(OH_2)_6]^{3+}$. The spectrum of $[Ti(OH_2)_6]^{3+}$ (Figure pp.71) exhibits one broad band. However, close inspection shows the presence of a shoulder indicating that the absorption is actually two closely spaced bands (see below). The term symbol for the ground state of Ti^{3+} (d^1, one electron with L = 2, S = 1/2) is ^2D. In an octahedral field, this is split into ^2T_2g and ^2Eg terms separated by an energy Δ_{oct}. More generally, it can be shown from group theory that, in an octahedral or tetrahedral field, D, F, G, H and I, but not S and P, terms split. (Lanthanoid metal ions provide examples of ground state H and I terms).

Term	Components in an octahedral field
S	A_{1g}
P	T_{1g}
D	$T_{2g} + E_g$
F	$A_{2g} + T_{2g} + T_{1g}$
G	$A_{1g} + E_g + T_{2g} + T_{1g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Similar splittings occur in a tetrahedral field, but the *g* labels are no longer applicable.

The splittings arise because the S, P, D, F, G, H and I terms refer to a degenerate set of d orbitals. In an octahedral field, this splits into the t_2g and eg sets of orbitals (Figure pp.59). For the d^1 ion, there are therefore two possible configurations: $t_2g^1\ eg^0$ or $t_2g^0\ eg^1$, and these give rise to the ^2T_2g (ground state) and ^2Eg (excited state) terms. The energy separation between these states increases with increasing field strength (see Figure below).

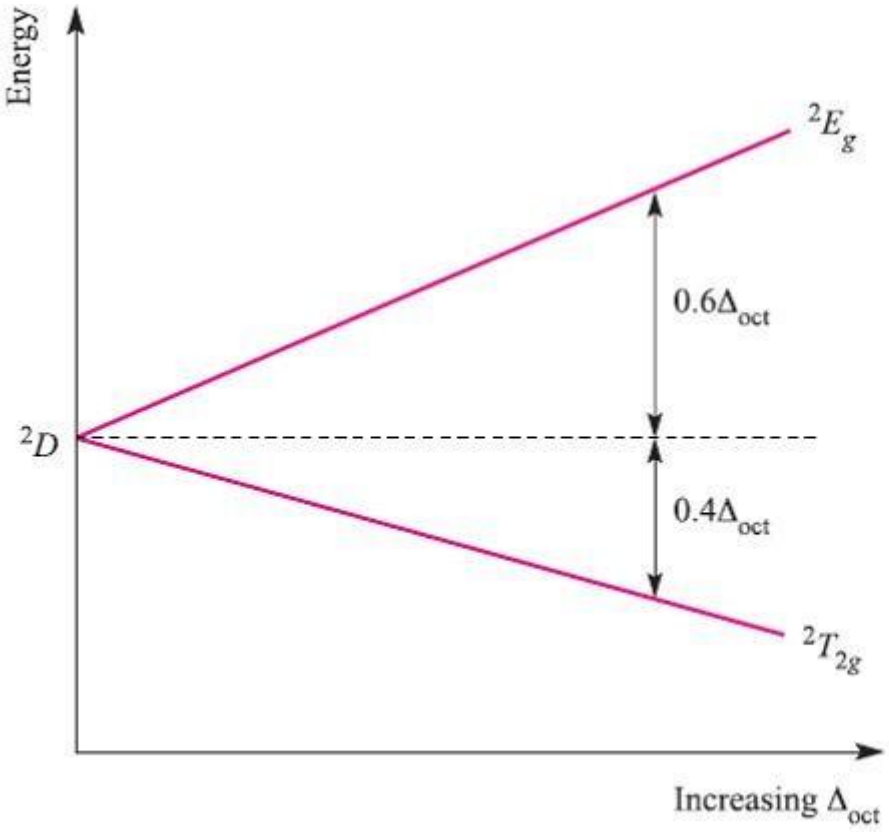


Fig. Energy level diagram for a d^1 ion in an octahedral field.

The electronic spectrum of Ti^{3+} arises from a transition from the T_2g to the Eg level; the energy of the transition depends on the field strength of the ligands in the octahedral Ti(III) complex. The observation that the electronic spectrum of $[Ti(OH_2)_6]^{3+}$ (Figure pp.71) consists of two bands, rather than one, can be rationalized in terms of a Jahn–Teller effect in the excited state, $t_2g^0\ eg^1$.

For the d^9 configuration (e.g. Cu^{2+}) in an octahedral field (actually, a rare occurrence because of Jahn–Teller effects which lower the symmetry), the ground state of the free ion (^2D) is again split into ^2T_2g and ^2Eg terms, but, in contrast to the d^1 ion , the ^2Eg term is lower than the ^2T_2g term. The d^9 and d^1 configurations are related by a positive hole concept: d^9 is derived from a d^{10} configuration by replacing one electron by a positive hole; thus, whereas the d^1 configuration contains one

electron, d^9 contains one „hole“. For a d^9 ion in an octahedral field, the splitting diagram is an inversion of that for the octahedral d^1 ion. This relationship is shown in Figure below (an **Orgel diagram**) where the right-hand side describes the octahedral d^1 case and the left-hand side describes the octahedral d^9 ion. Just as there is a relationship between the d^1 and d^9 configurations, there is a similar relationship between the d^4 and d^6 configurations. The result is that the Orgel diagrams for octahedral d^1 and d^6 ions are the same, as are the diagrams for octahedral d^4 and d^9 (Figure below).

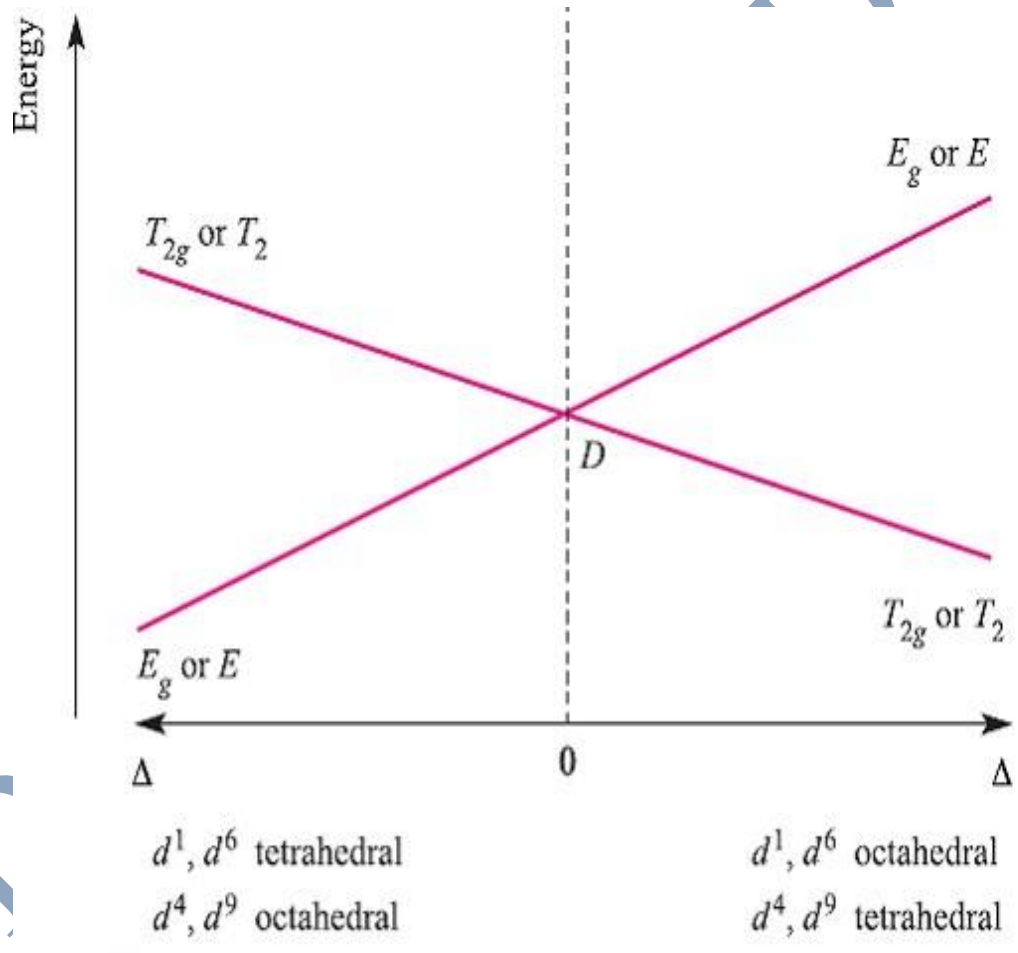


Fig. Orgel diagram for d^1, d^4 (high-spin), d^6 (high-spin) and d^9 ions in octahedral (for which T_{2g} and E_g labels are relevant) and tetrahedral (E and T_2 labels) fields.

Figure above shows that for each of the octahedral and tetrahedral d^1, d^4, d^6 and d^9 ions, only one electronic transition from a ground to excited state is possible:

1) For octahedral d^1 and d^6, the transition is $Eg \leftarrow T_2g$
2) For octahedral d^4 and d^9, the transition is $T_2g \leftarrow Eg$
3) For tetrahedral d^1 and d^6, the transition is $T_2 \leftarrow E$
4) For tetrahedral d^4 and d^9, the transition is $E \leftarrow T_2$

Each transition is spin-allowed (no change in total spin, S) and the electronic spectrum of each ion exhibits one absorption. For sake of completeness, the notation for the transitions given above should include spin multiplicities, 2S+1, e.g. for octahedral d^1, the notation is $^2Eg \leftarrow {}^2T_2g$, and for high-spin, octahedral d^4 it is $^5T_2g \leftarrow {}^5Eg$.

In an analogous manner to grouping d^1, d^4, d^6 and d^9 ions, we can consider together d^2, d^3, d^7 and d^8 ions in octahedral and tetrahedral fields. In order to discuss the electronic spectra of these ions, the terms that arise from the d^2 configuration must be known. In an absorption spectrum, we are concerned with electronic transitions from the ground state to one or more excited states. Transitions are possible from one excited state to another, but their probability is so low that they can be ignored. Two points are particularly important:

1) Selection rules restrict electronic transitions to those between terms with the same multiplicity;
2) The ground state will be a term with the highest spin multiplicity (Hund‟s rules).

In order to work out the terms for the d^2 configuration, a table of microstates (see Table below) must be constructed. However, for interpreting electronic spectra, we need concern ourselves only with the terms of maximum spin multiplicity. This corresponds to a weak field limit. For the d^2 ion, we therefore focus on the ^3F and ^3P

(triplet) terms. These are summarized in (Table below), with the corresponding microstates represented only in terms of electrons with $m_s = +1/2$.

Table A shorthand table of microstates for a d^2 configuration; only a high-spin case (weak field limit) is considered, and each electron has $m_s = +\frac{1}{2}$. The microstates are grouped so as to show the derivation of the ^3F and ^3P terms.

$m_l = +2$	$m_l = +1$	$m_l = 0$	$m_l = -1$	$m_l = -2$	M_L	
↑	↑				+3	
↑		↑			+2	
↑			↑		+1	
↑				↑	0	^3F ($L = 3$)
	↑			↑	−1	
		↑		↑	−2	
			↑	↑	−3	
	↑	↑			+1	
	↑		↑		0	^3P ($L = 1$)
		↑	↑		−1	

The ^3F term is expected to be lower in energy than the ^3P term. In an octahedral field, the ^3P term does not split, and is labelled ^3T_1g. The ^3F term splits into ^3T_1g, ^3T_2g and ^3A_2g terms. The $^3T_1g(F)$ term corresponds to a t_2g^2 eg^0 arrangement and is triply degenerate because there are three ways of placing two electrons (with parallel spins) in any two of the dxy, dyz and dxz orbitals. The ^3A_2g term corresponds to t_2g^0 eg^2 arrangement (singly degenerate).

The ^3T_2g and $^3T_1g(P)$ terms equate with a t_2g^1 eg^1 configuration; the lower energy ^3T_2g term arises from placing two electrons in orbitals lying in mutually perpendicular planes, e.g.$(dxy)^1$ $(dz^2)^1$, while the higher energy $^3T_1g(P)$ term arises from placing two electrons in orbitals lying in the same plane e.g.$(dxy)^1$ $(dx^2\text{-}y^2)^1$. The energies of the $^3T_1g(F)$, ^3T_2g, ^3A_2g and $^3T_1g(P)$ terms are shown on the right-hand side of (Figure below); note the effect of increasing field strength. Starting from this diagram and using the same arguments as for the d^1, d^4, d^6 and d^9 ions, we can derive the complete Orgel diagram shown in (Figure below).

From (Figure below), we can see why three absorptions are observed in the electronic spectra of d^2, d^3, d^7 and d^8 octahedral and tetrahedral complexes. The transitions are from the ground to excited states, and are all spin-allowed, e.g. for an octahedral d^3 ion, the allowed transitions are $^4T_2g \leftarrow ^4A_2g$, $^4T_1g(F) \leftarrow ^4A_2g$ and $^4T_1g(P) \leftarrow ^4A_2g$.

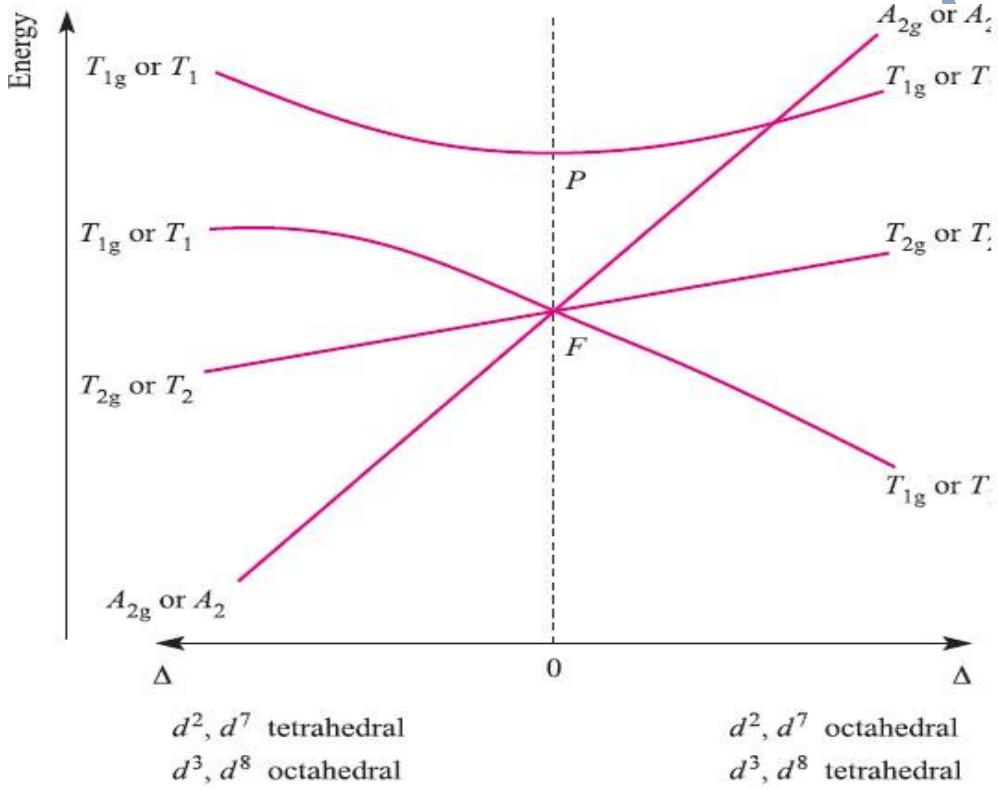


Fig. Orgel diagram for d^2, d^3, d^7 and d^8 ions (high-spin) in octahedral (for which T_{1g}, T_{2g} and A_{2g} labels are relevant) and tetrahedral (T_1, T_2 and A_2 labels) fields. Multiplicities are not stated because they depend on the d^n configuration, e.g. for the octahedral d^2 ion, $^3T_{1g}$, $^3T_{2g}$ and $^3A_{2g}$ labels are appropriate.

Figure below illustrates spectra for octahedral nickel(II) (d^8) complexes. For the high-spin d^5 configuration, all transitions are spin forbidden and „d–d" transitions that are

observed are between the ^6S ground state and quartet states (three unpaired electrons). Associated absorptions are extremely weak.

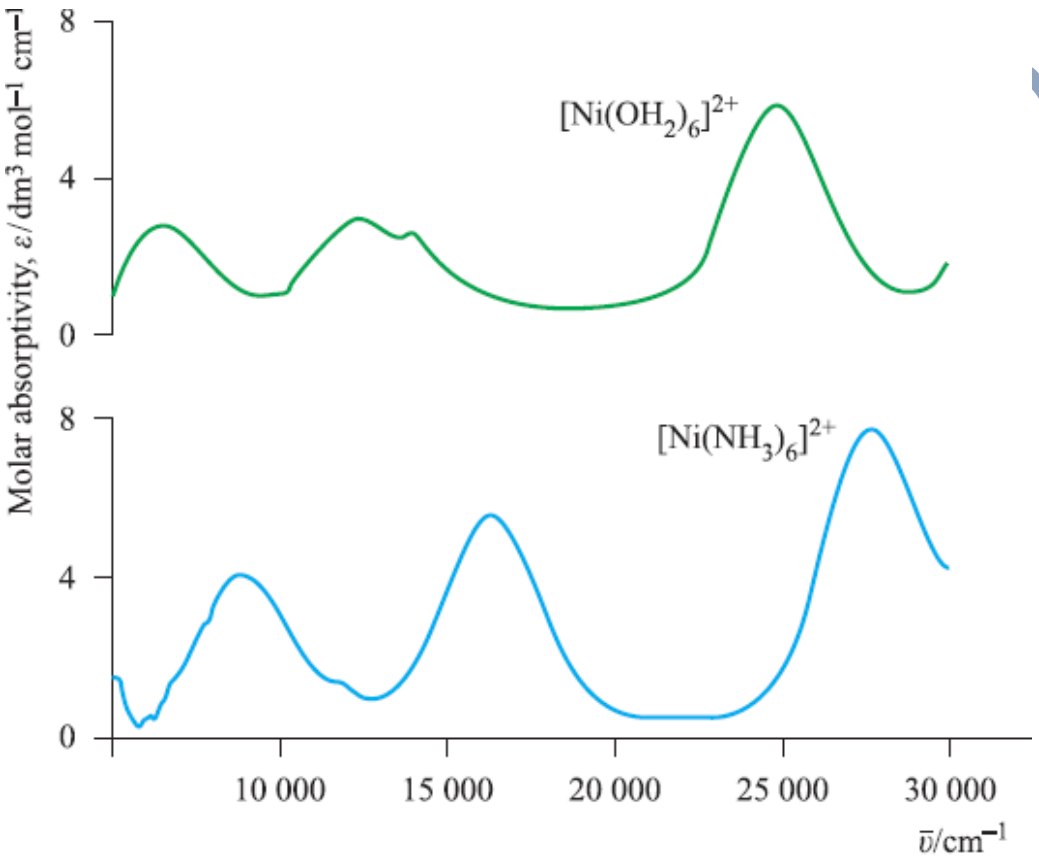


Fig. Electronic spectra of $[Ni(OH_2)_6]^{2+}$ ($0.101\,mol\,dm^{-3}$) and $[Ni(NH_3)_6]^{2+}$ ($0.315\,mol\,dm^{-3}$ in aqueous NH_3 solution) showing three absorption bands. Values of the molar absorptivity, ε, are related to absorbance by the Beer–Lambert law