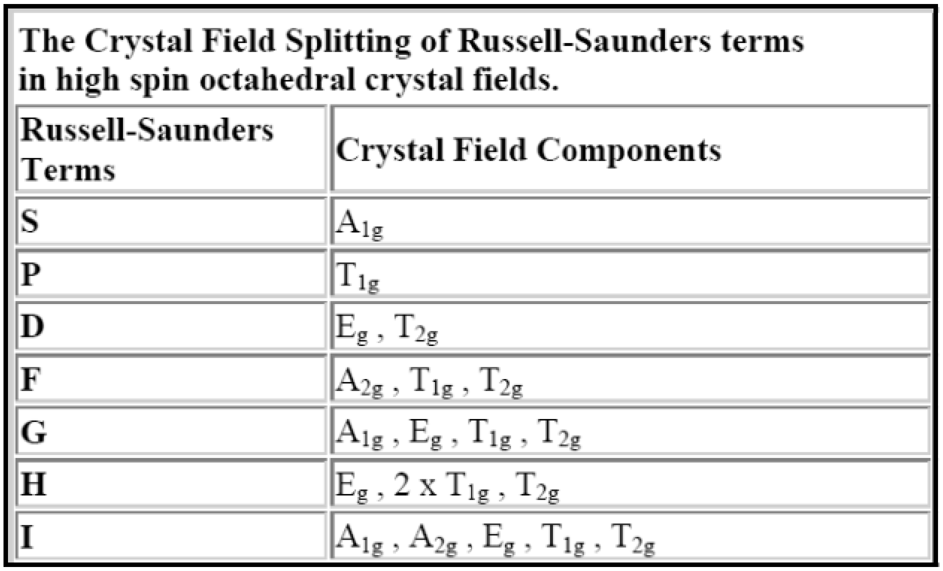
CRYSTAL FIELD SPLITTING OF RUSSEL SAUNDERS COUPLING SCHEME
&
SELECTION RULES

The Crystal Field Splitting of Russell-Saunders terms

The effect of a crystal field on the different orbitals (s, p, d, etc.) will result in splitting into subsets of different energies, depending on whether they are in an octahedral or tetrahedral environment. The magnitude of the d orbital splitting is generally represented as a fraction of Δoct or 10Dq.



The Crystal Field Splitting of Russell-Saunders terms in high spin octahedral crystal fields.	
Russell-Saunders Terms	**Crystal Field Components**
S	A_{1g}
P	T_{1g}
D	E_g , T_{2g}
F	A_{2g} , T_{1g} , T_{2g}
G	A_{1g} , E_g , T_{1g} , T_{2g}
H	E_g , 2 x T_{1g} , T_{2g}
I	A_{1g} , A_{2g} , E_g , T_{1g} , T_{2g}

The ground term energies for free ions are also affected by the influence of a crystal field and an analogy is made between orbitals and ground terms that are related due to the angular parts of their electron distribution. The effect of a crystal field on different orbitals in an octahedral field environment will cause the d orbitals to split to give t2g and eg subsets and the D ground term states into T_{2g} and Eg, (where upper case is used to denote states and lower case orbitals). f orbitals are split to give subsets known as $t_{1g,}$ t2g and a_{2g}. By analogy, the F ground term when split by a crystal field will give states known as T_{1g}, T_{2g}, and A_{2g}.

Note that it is important to recognise that the F ground term here refers to states arising from d orbitals and not f orbitals and depending on whether it is in an octahedral or tetrahedral environment the lowest term can be either A_{2g} or T_{1g}.

18.5 Selection rules:

We have seen that some transitions are not allowed, for example transitions where the spin of the electron in changed are spin-forbidden. This does not mean that such a transition will never occur, but that it is less likely and that the intensity (molar absorption coefficient) of such an absorption band is very low. Whether transitions are allowed or forbidden, and to what degree they may be forbidden depends on selection rules:

(i) Spin selection rule

Electromagnetic radiation usually cannot change the relative orientation of an electron spin. The selection rule states that the overall spin S of a complex must not change during an electronic transition, hence, $\Delta S = 0$.

This selection rule can be relaxed by spin-orbit coupling, i.e., coupling between spin angular momentum and orbital angular momentum. However, spin-forbidden transitions remain generally much weaker than spin-allowed transitions. Spin-orbit coupling is particularly strong for heavy d-metals. In the 3d series, spin-forbidden transitions have εmax = 1 L mol^{-1} cm^{-1}. In an octahedral d^3 transition-metal complex, the 2Eg ← 4A2g transition is spin-forbidden. It is still visible as a very weak absoption band in the UV-visible spectrum (see above).

(ii) Laporte selection rule

The Laporte selection rule is particularly applicable for centrosymmetric molecules, i.e., molecules with an inversion centre. Orbitals and states in such molecules can be described with the symmetry labels g (gerade) and u (ungrerade). Laporte-allowed transitions are accompanies with a change of parity (g and u); this means, transitions from a g-state to a u state and vice versa are Laporte-allowed and transitions from a g- to a g-state and from a u- to a u-state are Laporte-forbidden. All d orbitals are gerade (have g symmetry). Therefore, d-d transitions, e.g., $4T_{2g} \leftarrow 4A_{2g}$ in an octahedral d^3 complex, are Laporte-forbidden.

The Laporte selection rule is relaxed by (a) deviation of perfect centro symmetric symmetry due to ligands of less symmetry or chelate ligands and (b) asymmetric vibrations. While d orbitals are always centrosymmetric by themselves, for a non-centrosymmetric ligand field the Laporte selection rule is strictly not applicable anymore. As a consequence, Laporte forbidden d-d transitions have εmax = 20 to 100 L mol^{-1} cm^{-1}, while Laporte-allowed d-d transitions have εmax = ca. 500 L mol^{-1} cm^{-1}.

(iii) Symmetry-allowed transitions

Transitions which are not governed by symmetry restrictions (e.g. Laporte rule) have much larger intensities in the electronic absorption spectra. Such transitions are usually charge transfer band that give rise to intense colorations.