

Electronic spectra of octahedral and tetrahedral complexes

Orgel diagram:

The Orgel diagram is the quantum mechanically calculated energy of the term level (as ordinate) against an increasing value of field strength, the ligand field splitting parameter.

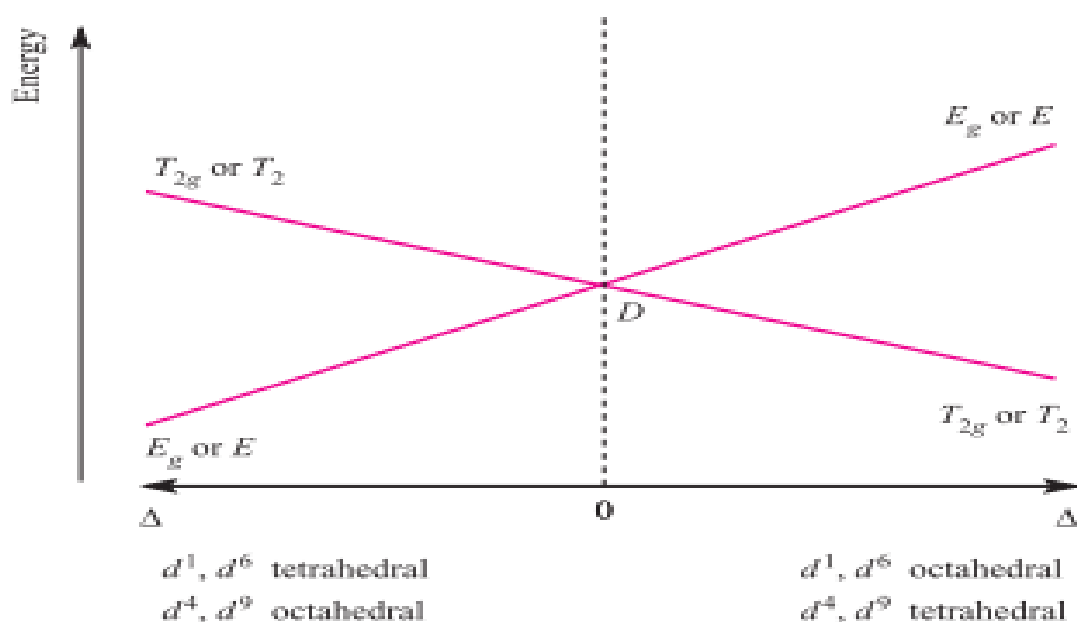


Figure 1: Orgel diagram for d^1 , d^4 (high-spin), d^6 (high-spin) and d^9 ions in octahedral (for which T_{2g} and E_g labels are relevant) and tetrahedral (E and T_2 labels) fields.

For octahedral d^1 and d^6 , the transition is $T_{2g} \rightarrow E_g$.

For octahedral d^4 and d^9 , the transition is $E_g \rightarrow T_{2g}$.

For tetrahedral d^1 and d^6 , the transition is $E \rightarrow T_2$.

For tetrahedral d^4 and d^9 , the transition is $T_2 \rightarrow E$.

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, $2S + 1$.

For example, for octahedral d^1 , the notation is ${}^2T_{2g} \longrightarrow {}^2E_g$, and for high-spin, octahedral d^4 , ${}^5E_g \longrightarrow {}^5T_{2g}$

NOTE: In d^1 case, there is a single electron in the lower t_{2g} level while in the d^9 case there is a single hole in the upper e_g level. Thus, the transition of the d^1 case is the promotion of an electron from t_{2g} to e_g level, while in d^9 ion, it is simpler to consider as the transfer of a hole from e_g to t_{2g} . Thus the energy level diagram for d^9 is therefore the inverse of that for a d^1 configuration.

So, in octahedral Cu(II) complexes we might expect a single absorption band in the visible region corresponding to



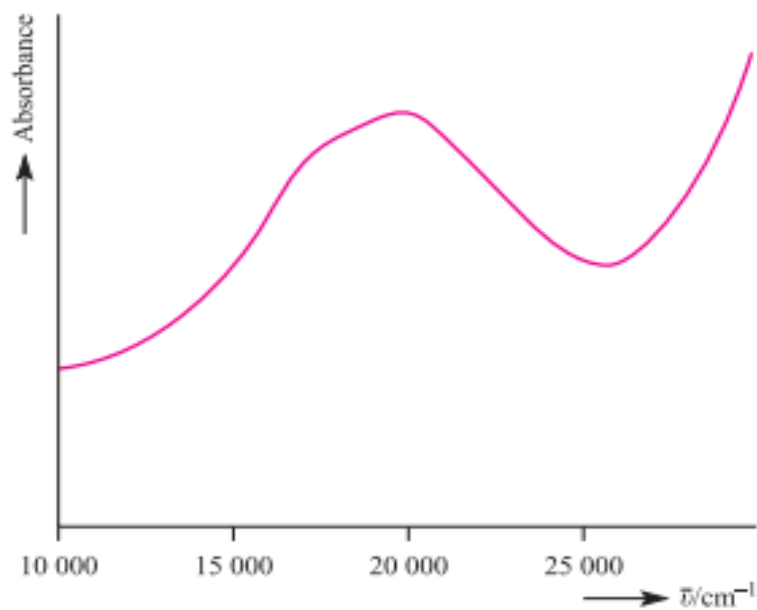


Figure 2a: The electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (d^1) in aqueous solution.

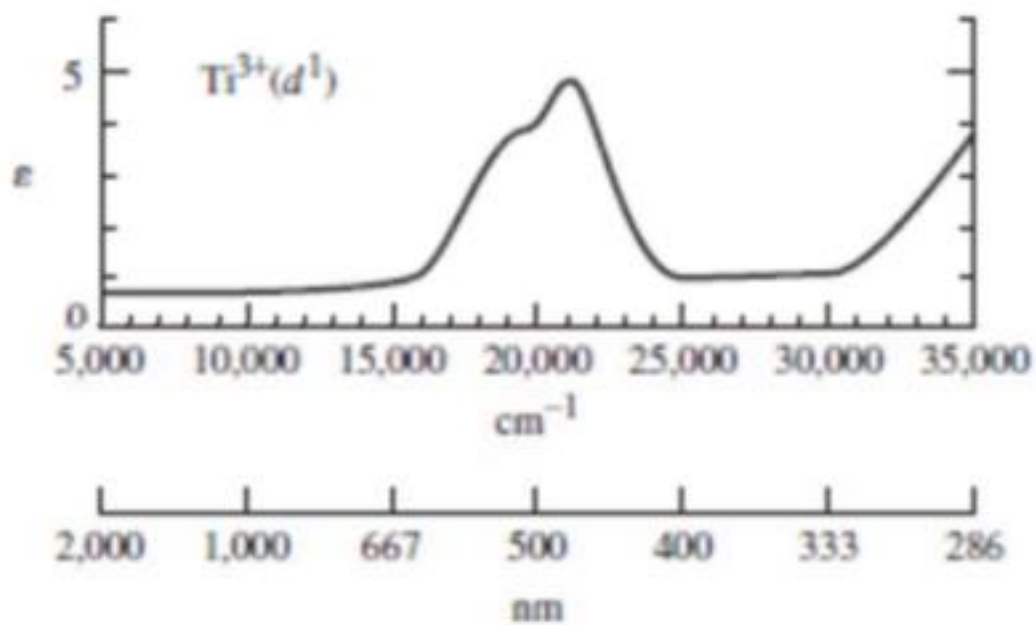


Figure 2b: The electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (d^1) in aqueous solution

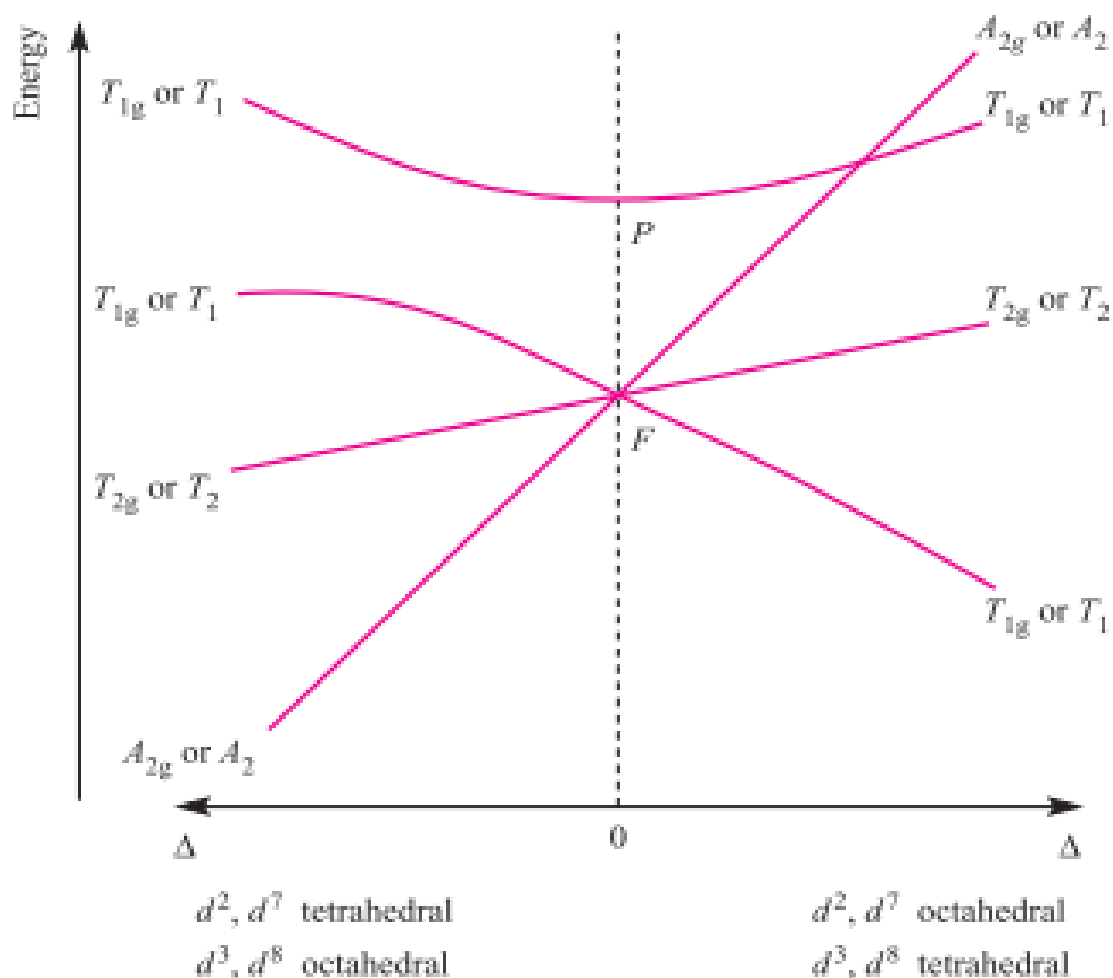
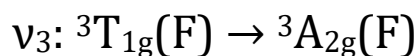
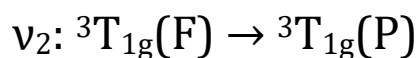
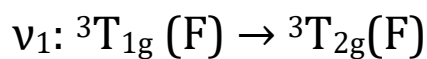


Figure 3: Orgel diagram for d^2 , d^3 , d^7 and d^8 ions (high-spin) in octahedral (for which T_{1g} , T_{2g} and A_{2g} labels are relevant) and tetrahedral (T_1 , T_2 and A_2 labels) fields.

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. Two possibilities and terms arise for the d^2 ion: (i) parallel spin ($2s+1 = 3$) triplet which results to the 3F (ground state) and (ii) anti-parallel spin ($2s+1 = 1$) singlet 3P (excited state).

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 $t_{2g}^2e_g^0$ arrangement and is triply degenerate because there are three ways of placing two electrons (with parallel spins) in any two of the d_{xy} , d_{yz} and d_{xz} orbitals. The $^3A_{2g}$ term corresponds to $t_{2g}^0e_g^2$ arrangement (singly degenerate). The $^3T_{2g}$ and $^3T_{1g}(P)$ terms equate with a $t_{2g}^1e_g^1$ configuration; the lower energy $^3T_{2g}$ term arises from placing two electrons in orbitals lying in mutually perpendicular planes, e.g. $(d_{xy})^1 (d_{z^2})^1$, while the higher energy $^3T_{1g}(P)$ term arises from placing two electrons in orbitals lying in the same plane e.g. $(d_{xy})^1 (d_{x^2-y^2})^1$.

For a d^2 configuration gives 3F ground term, the spectra show three absorption bands corresponding to the following transitions:



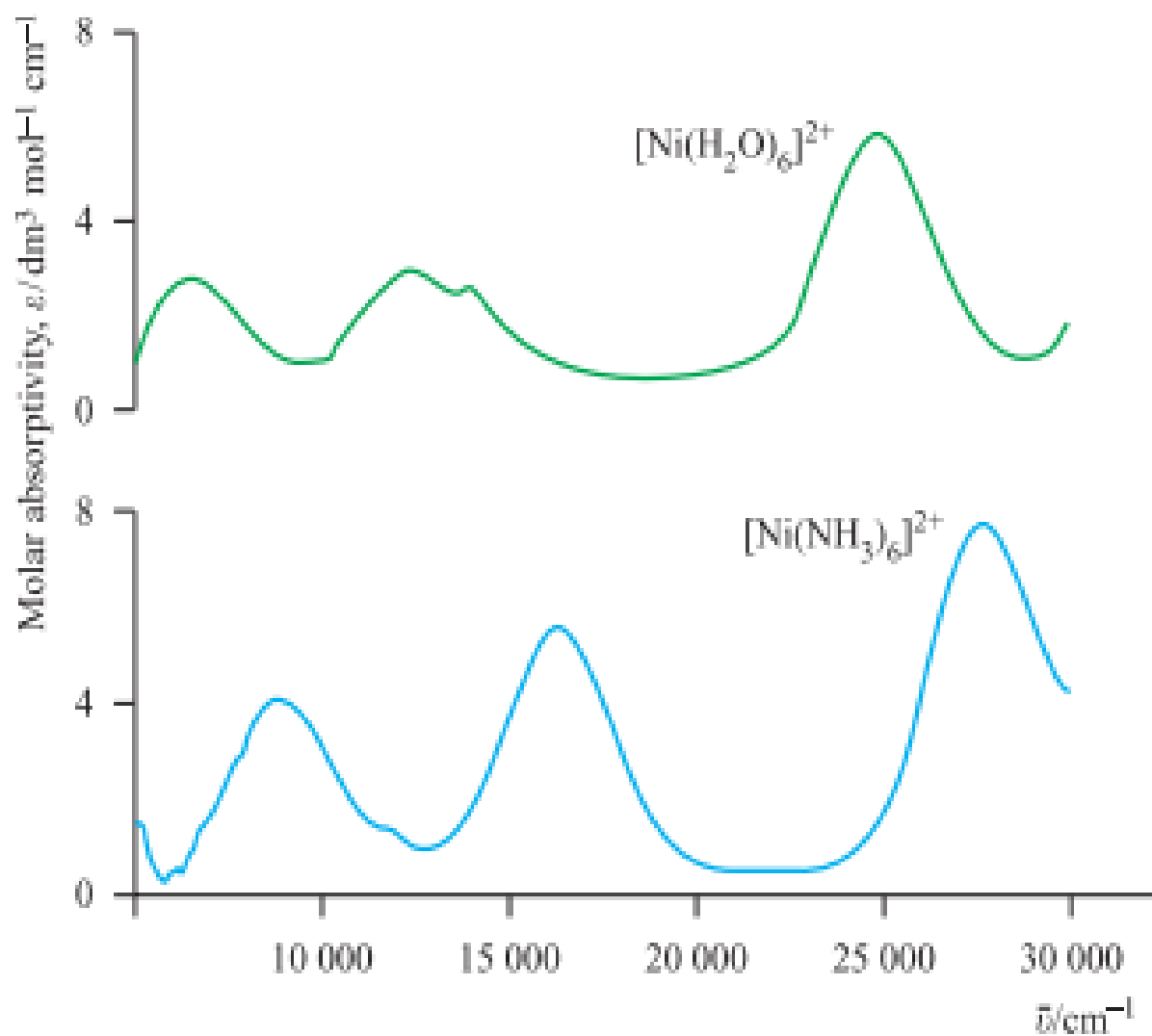
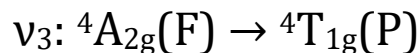
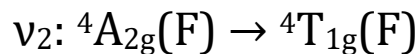
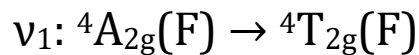


Figure 4: Electronic spectra of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ($0.101 \text{ mol dm}^{-3}$) and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ($0.315 \text{ mol dm}^{-3}$ in aqueous NH_3 solution) showing three absorption bands. Values of the molar absorptivity, ϵ , are related to absorbance by the Beer-Lambert Law.

For a d^3 configuration the ground term is 4F , the spectra show three bands due to the following transitions:



For a d^4 system, the ground term symbol 5D is split into 5E_g and $^5T_{2g}$ with a single transition or absorption band:



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. Example is $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$.

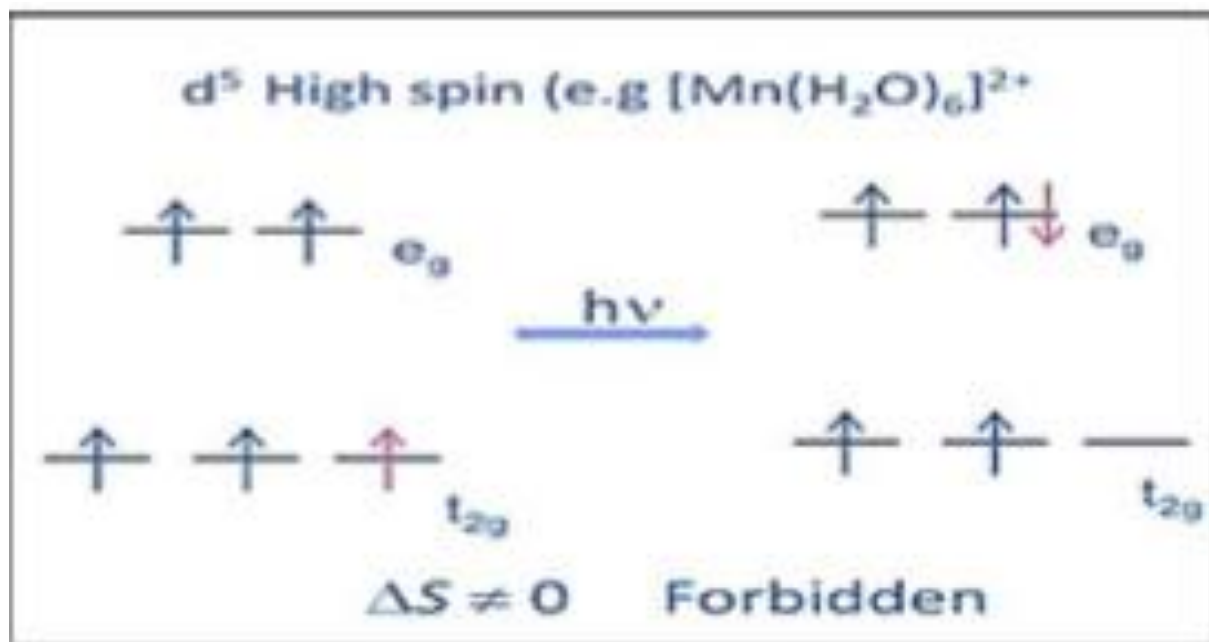


Figure 5: A d⁵ high spin representation showing transition of electron

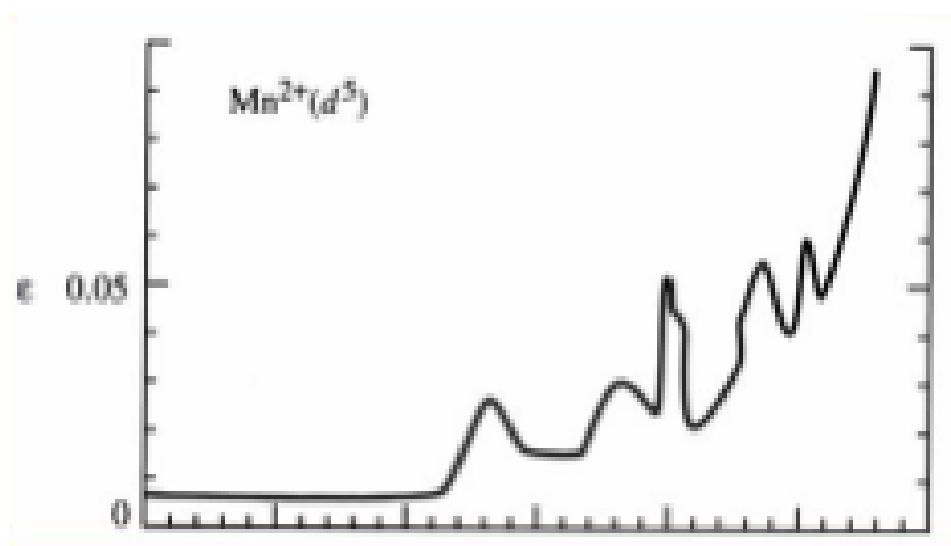
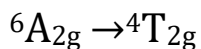


Figure 6: Spectra of a d⁵ high spin configuration

Interpretation: No spin allowed transitions for d⁵ high spin configurations. Extinction coefficients are very low, though the selection rule is relaxed by spin-orbit coupling. So, for high-spin d⁵ ions all possible d-d transitions are **spin-forbidden**.



Tanabe–Sugano diagrams

- ❖ A more advanced treatment of the energies of electronic states is found in Tanabe–Sugano diagrams.
- ❖ The energy of the ground state is taken to be zero for all field strengths, and the energies of all other terms and their components are plotted with respect to the ground term;
- ❖ if there is a change in ground term as the field strength increases, a discontinuity appears in the diagram.
- ❖ Figure 6 shows the Tanabe–Sugano diagram for the d^2 configuration in an octahedral field;
- ❖ notice that the energy and field strength are both expressed in terms of the Racah parameter B .
- ❖ Racah parameters take into account interelectronic repulsion:
- ❖ there are three parameters A , B and C , but only B is mentioned/considered here.

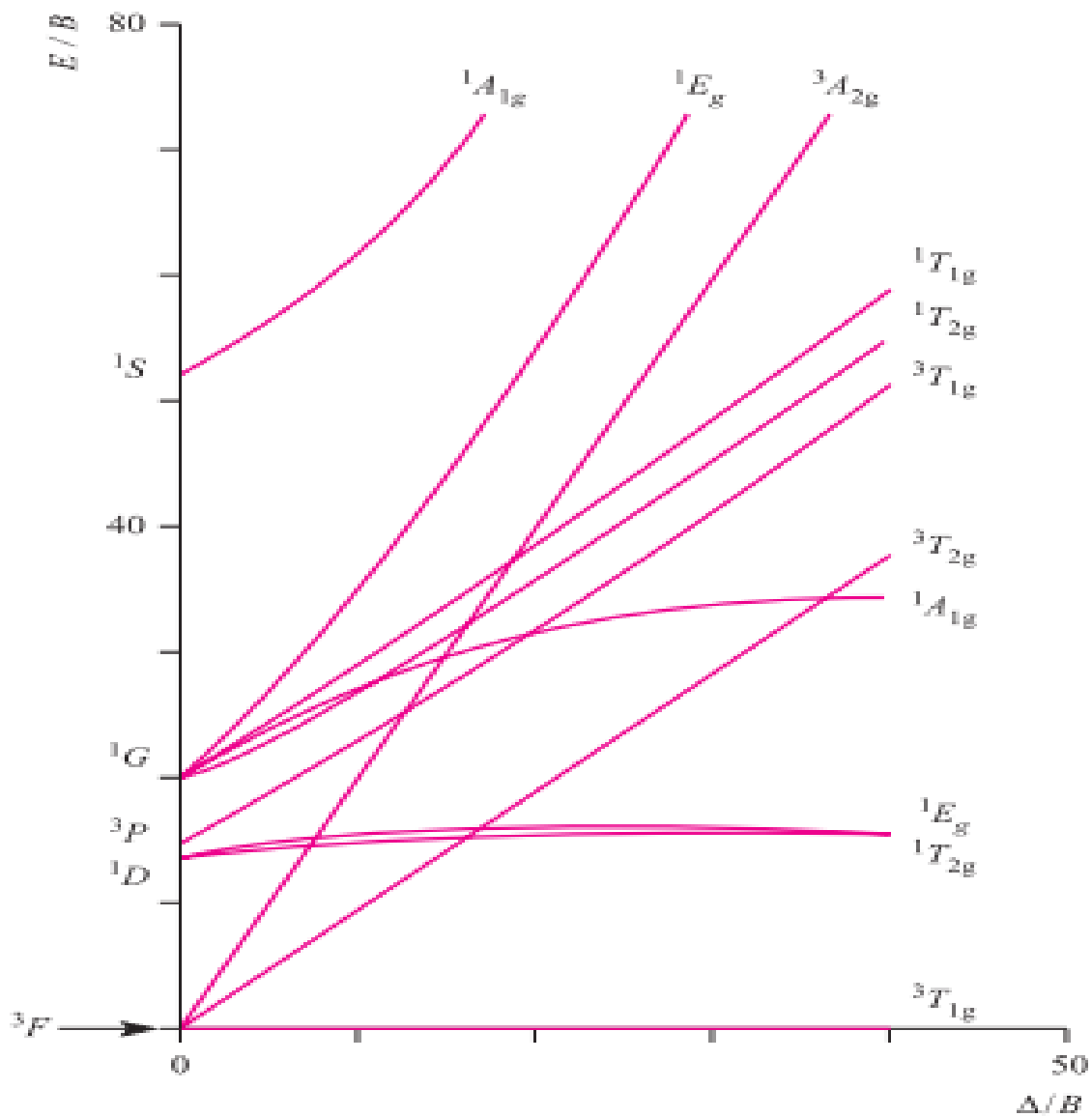
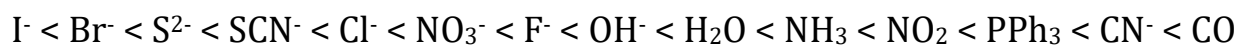


Figure 6: Tanabe–Sugano diagram for the d^2 configuration in an octahedral field

Spectrochemical series

- The magnitude of the ligand field splitting parameter is determined mainly by the identity of the ligands.

- An empirical rule called the spectrochemical series was proposed by a Japanese scientist Ryutarō Tsuchida.
- The rule was constructed from empirical data collected when spectra of complexes that have the same central metal, oxidation state, coordination number, etc. were measured.
- It is noteworthy that ligands with π -acceptor properties are in a higher position in the series.



- Although Δ_o does become larger in this order, it is also dependent on the identity of the central metal and its oxidation state.
- Namely, Δ_o is larger for 4d and 5d metals than for 3d metals and becomes larger as the oxidation number increases.
- The magnitude of Δ_o is closely related to its absorption position in the electromagnetic spectrum, and is a key factor in determining the position of a ligand in the spectrochemical series.
- A π -donor ligand (halogen, aqua, etc.) makes the absorption wavelength longer, and a π -acceptor ligand (carbonyl, olefin, etc.) shorter by contribution from the bond.