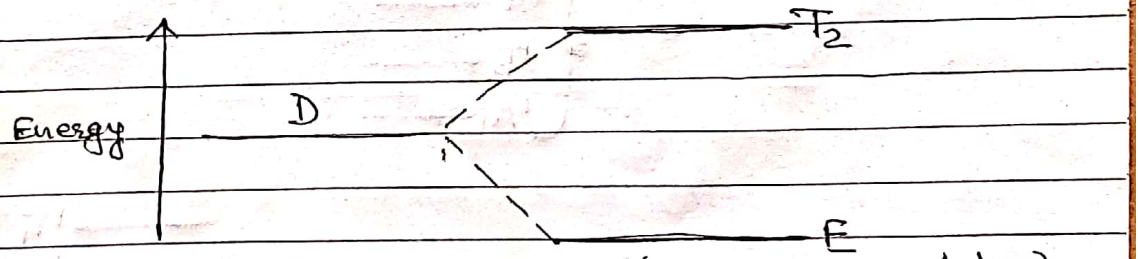
Spectroscopic States and Spectroscopic Ground States in Complexes —

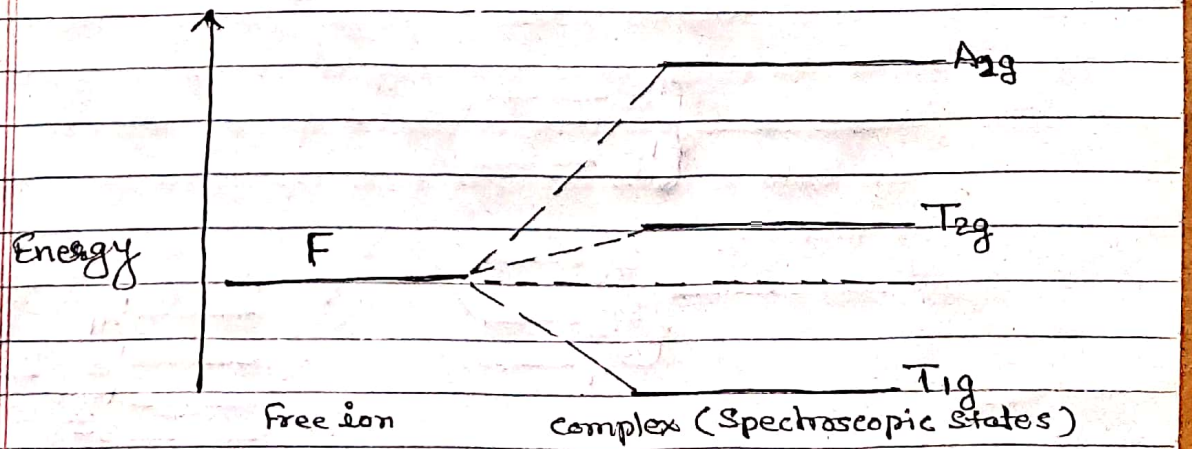
When a metal atom is brought in contact of Ligand, the energy terms of metal ion get split due to crystal field effect. This splitting is affected by geometry of field. In octahedral and tetrahedral field, it is opposite to each other. Spectroscopic states obtained by this splitting are expressed in terms of Mulliken symbols.

S and P energy term are unaffected by crystal field. In octahedral field S and P are shown by A_{1g} and T_{1g} energy levels, also D and F energy term get split into $\underset{E_g}{E_g}$, $\underset{T_2}{T_{2g}}$ and T_{1g}, T_{2g}, A_{2g}. spectroscopic states respectively.

In Fig — the spectroscopic states obtained by D and F energy term under the influence of tetrahedral and octahedral field are shown respectively.



(a) Splitting of D energy term in tetrahedral field state effect



(b) Spectroscopic state obtained by F energy term in Oh field.

Spectroscopic states obtained from S, P, D, F and G energy terms are shown in Table 4 below.

Table 4 Spectroscopic States

Energy step	Spectroscopic States	
	Octahedral field	Tetrahedral field
S	A_{1g}	A_1
P	T_{1g}	T_1
D	$E_g + T_{2g}$	$E + T_2$
F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$	$A_1 + E + T_1 + T_2$

Now we can represent diagrammatically all microscopic states of metal ion having d^2 electronic configuration in octahedral field Fig ——

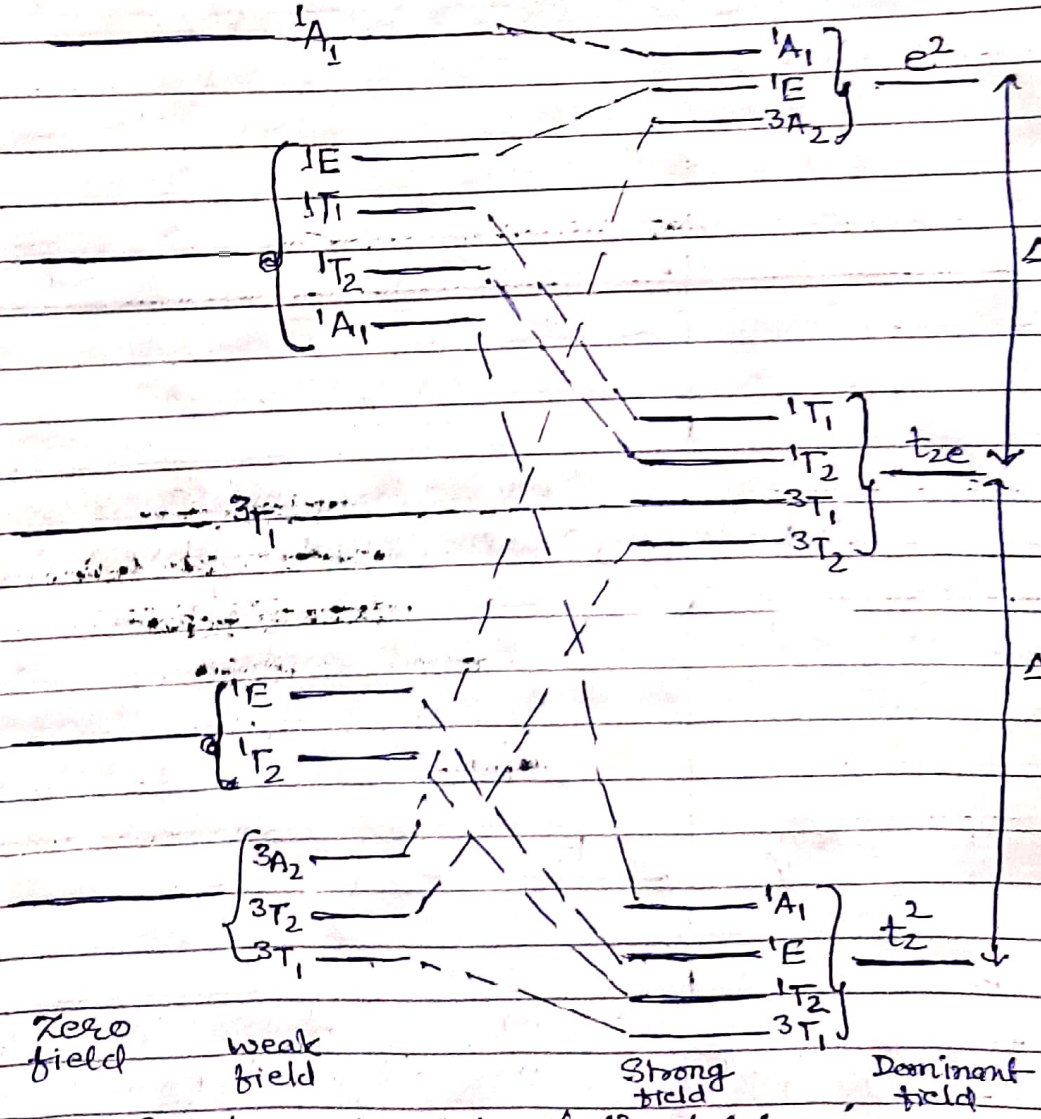


Fig —— Spectroscopic states of d^2 metal ion in octahedral field

Orgel Energy Level Diagram

Two types of energy level diagrams are to explain the electronic spectra of transition metal complexes

1. Orgel energy level diagram – This is used for the lowest extent of weak ligand field.
2. Tanabe – Sugano diagram – This is used for the highest extent of strong ligand field.

In our course only Orgel energy level diagrams. When a graph is plotted between the field splitting energy of energy levels and ligand field strength. It also includes the spin orbit coupling and mixing of different orbitals. These are used to explain the spin permitted absorption band and d-d origin in electronic spectra of transition metal complexes. In spin permitted transitions, the energy level of ground state and excited states have same spin multiplicity. Different d suborbit configuration of free metal ion do not have same multiplicity in ground and all excited states.

Table 5. The Energy level of Metal ions for Ground and Excited states in the same Spin multiplicity

Electronic Configuration	Ground State energy trans	Excited State energy transition
d^1 d^9	^2D	—
d^2 d^8	^3F	^3P
d^3 d^7	^4F	^4P
d^4 d^6	^5D	—
d^5	^6S	—
d^{10}	^1S	—

Spin multiplicity is not changed even after the complex formation. Hence a graph is plotted between the splitting of above energy levels and field strength. This graph is called Orgel energy level diagram, Fig —

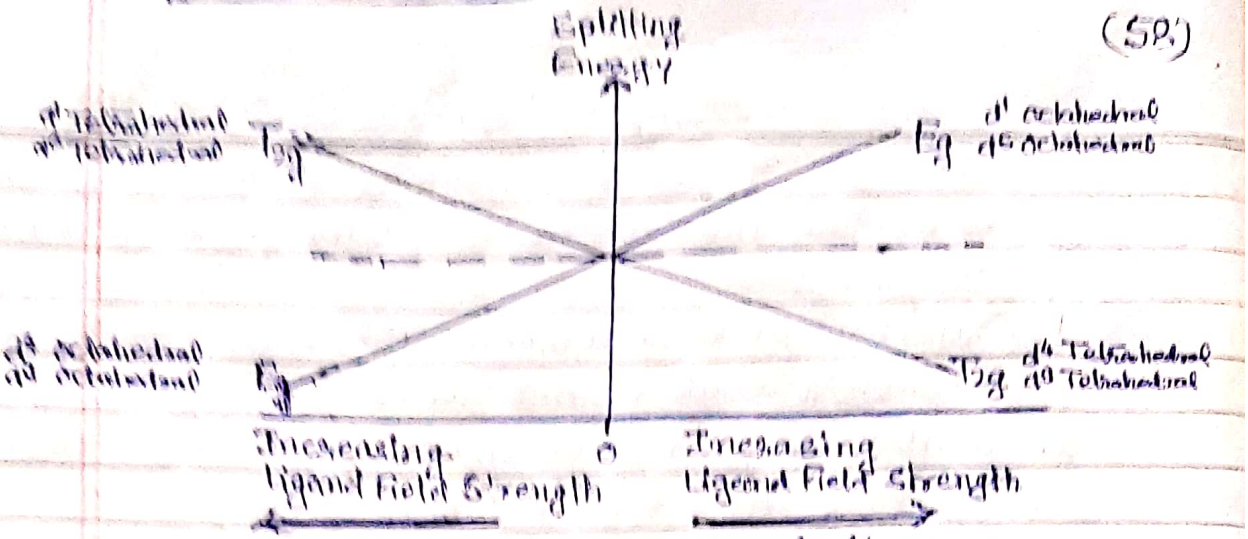


Fig — Orgel energy level diagram

Hence, subscript 'g' will not be used when tetrahedral complexes are considered.

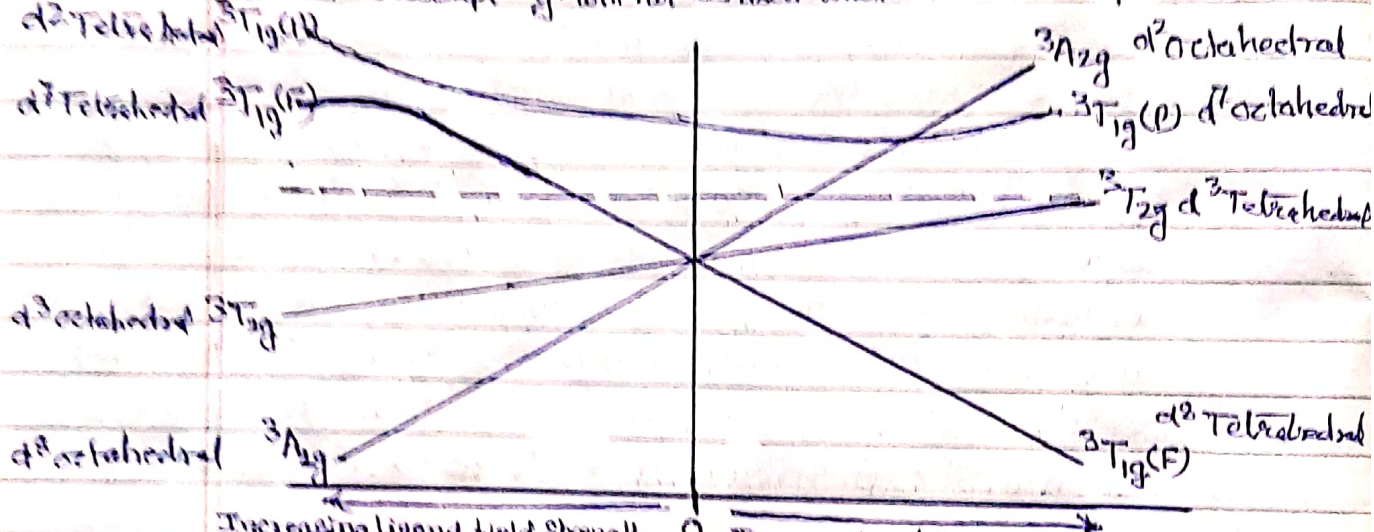


Fig — Orgel energy level diagram.

Above Orgel energy level diagrams are for weak ligand weak. In metal ions having d^1, d^2, d^3, d^8 and d^9 configurations, the field strength of octahedral field does not produce the difference in energy terms. Hence the diagram of above configuration can be used for both weak and strong ligand field in octahedral geometry.