RACAH PARAMETER

M. Sc. : CC – 3 (Inorganic Chemistry)

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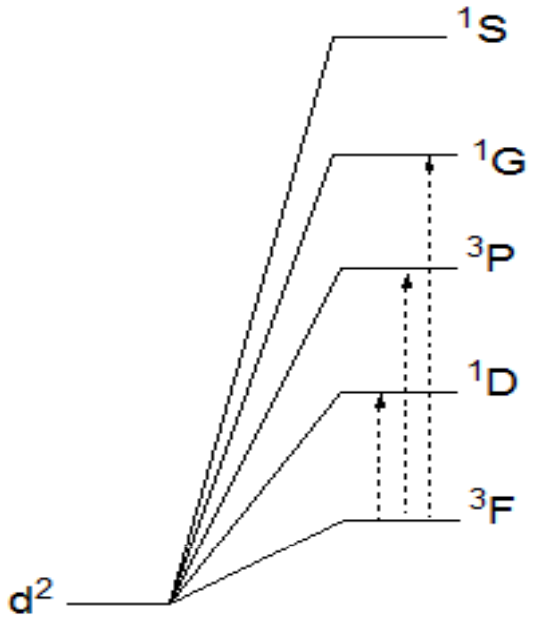
Racah Parameter

- Racah Parameter is the energy gap between two spectroscopic terms due to e-e repulsion.
- It is denoted by B & C.
- Energy gap between two spectroscopic terms of same multiplicity like ^3F, ^3P or ^4F, ^4P etc is expressed by B.
- Energy gap between two spectroscopic term of different multiplicity like ^3P, ^1D or ^4F, ^2D, ^3G etc is expressed by B & C.
- **Racah parameters** after Giulio Racah, who first described them.
- It describes the repulsion energy associated with an electronic term.
- the interelectronic repulsion of a ^3P term is $A + 7B$,
- ^3F term is $A - 8B$,
- $^1D = A - 3B+2C$
- Difference between ^3F & $^3P = (A+7B) – (A-8B) = 15B$.
- Similarly difference between ^3F & $^1D = (A-8B) – (A-3B+2C) = 5B+2C$

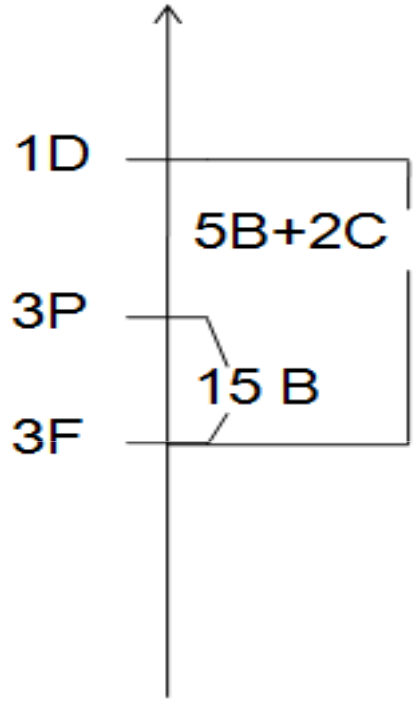
Racah Inter-electronic Repulsion Parameters (B, C)



$E(^3P) = A+7B$

$E(^1D) = A - 3B + 2C$

$E(^3F) = A - 8B$



$^3F \longrightarrow {}^3P = 15B$

$^3F \longrightarrow {}^1D = 5B + 2C$

When ligand approaches to the free metal ion than e-e repulsion is decreased & hence energy gap becomes low & resulting gap also decreased in complex compound i.e. B free ion is greater than B complex.

Reason of Racah Parameter

When an atom has more than one electron there will be some electrostatic repulsion between those electrons. The amount of repulsion varies from atom to atom, depending upon the number and spin of the electrons and its energy level of the orbitals they occupy.

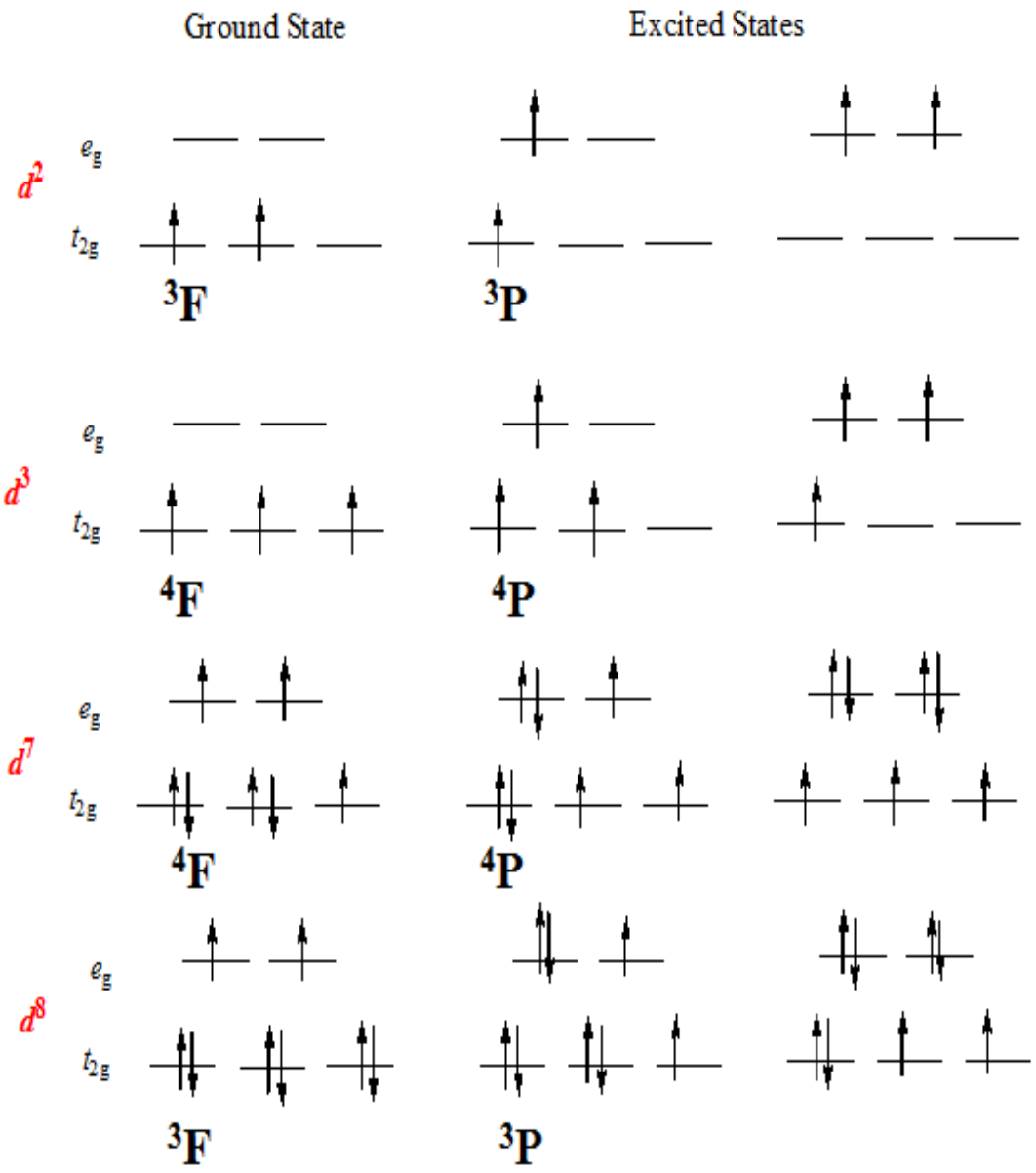
Electronic State & in ground & Excited State

Triple degeneracy of a d^2 ion's $^3T_{2g}$ ground state due to three possible sites for hole in t_{2g} level

Singly degenerate $^3T_{2g}$ ground state. Only one possible arrangement for three electrons in t_{2g} level

Triple degenerate ground state for d^7 Three possible sites for hole in t_{2g} level

Singly degenerate $^3T_{2g}$ ground state. Only one possible arrangement for six t_{2g} electrons.



Configuration	Term symbols
d^1 , d^9	^2D
d^2 , d^8	^3F, ^3P, ^1G, ^1D, ^1S
d^3, d^7	^4F, ^4P, ^2H, ^2G, ^2F, $^2D_2$, ^2P
d^4, d^6	^5D, ^3H, ^3G, $^3F_2$, ^3D, $^3P_2$, ^1I, $^1G_2$, $^1D_2$, $^1S_2$
$_d5$	^6S, ^4G, ^4D, ^4P, ^2I, ^2H, $^2G_2$, $^2F_2$, $^2D_3$, ^2P, ^2S

Repulsion also occurs between the terms of same spin multiplicity & gives different energy level. The total repulsion can be expressed in terms of three parameters *A*, *B* and *C*.

Nephelauxetic Effect/

Electron cloud expension/Nephelauxetic Parameter

- It is electron repulsion found in complexes due to e-e repulsion.
- It is denoted by ß (Nephelauxetic parameter)
- It is expressed by
- ß is always less than 1
- It means B complex is less than B free ion.
- It means energy gap between two terms in free ion is greater than that of its complex form.
- i.e. e-e repulsion between two electrons in free ion is greater than its complex.
- When ligand approaches to the free ion than e-e repulsion is decreased & hence nephelauxetic parameter is decreased.
- It determines covalent character in complex compound.


Thank You