Electronic Transition in non-centrosymmetric system (Tetrahedral system) :-

Tetrahedral Complex

$[CoX_4]^{2-}$, $X^- = Cl^-, Br^-, SCN^-$

Spin allowed Transition

$^4A_2 \rightarrow {}^4T_1$
$^4A_2 \rightarrow {}^4T_2$
} Same spin multiplicity

G.S. : ↑ ↑ ↑ / ↑↓ ↑↓ E.S(1) : ↑↓ ↑ ↑ / ↑↓ ↑

$S = 3 \times \frac{1}{2} = \frac{3}{2}$ $S = 3 \times \frac{1}{2} = 3/2$

$2S+1 = 4$ $2S+1 = 4$

Spin allowed transition

Check for orbitally allowed or not :-

Now, $^4A_2 \rightarrow {}^4T_1$ (Orbitally allowed)

$\Psi_{el}^{gd} \, \mu \, \Psi_{el}^{ex} = \underline{\underline{A_1}} + E + T_1 + T_2$

Totally Symmetric irreducible representation

But $^4A_2 \rightarrow {}^4T_2$ (orbitally forbidden) Since there is no totally symmetric term.

$^{n}A_2 \rightarrow {}^{n}T_2$ in Td Complexes are vibronically allowed.

This is the reason $^{4}A_2 \rightarrow {}^{4}T_1$ transition is 10–100 times higher intense than $^{4}A_2 \rightarrow {}^{4}T_2$ transition.

d-p mixing

In Td Complex,

d-p mixing is more { p ; d_{xy}, d_{yz}, d_{xz} } T_2 representation (No g or u terms)

Oct. system:- p → u-symmetry ; d_{xy}, d_{yz} & d_{xz} → g-symmetry } g → u or u → g (electric dipole allowed transition)

extent of d-p mixing is very very less.

However, due to metal-ligand vibration Center of symmetry lost. Then some extent of d-p mixing occurs.

* extent of d-p mixing ↳ Intensity high

MOT Concept:- Td Complex

Metal — d_{xz}, d_{xy}, d_{yz} & p (T_2 symmetry)

ligand (p) {Group ligand} T_2 Symmetry

anti-bonding (d-p mixing) — — — t_2^* ; some p character

— — e → Nonbonding (pure d-type) (d → dp) g → u

Metal ligand interaction → d-p mixing occurs