Case Study

Vibronic Coupling for the $A_2 \rightarrow T_2$ transition in the noncentrosymmetric T_d system ⇒

Let Suppose, d^7 (tetrahedral system)

↑ ↑ ↑
↑↓ ↑↓ } High Spin Complex

Ground State – A term

$A \times A \rightarrow A$

+2	+1	0	−1	−2
↑↓	↑↓	↑	↑	↑

Total angular momentum Quantum no. $\longrightarrow 2\times2 + 1\times2 + 0 - 1 - 2$

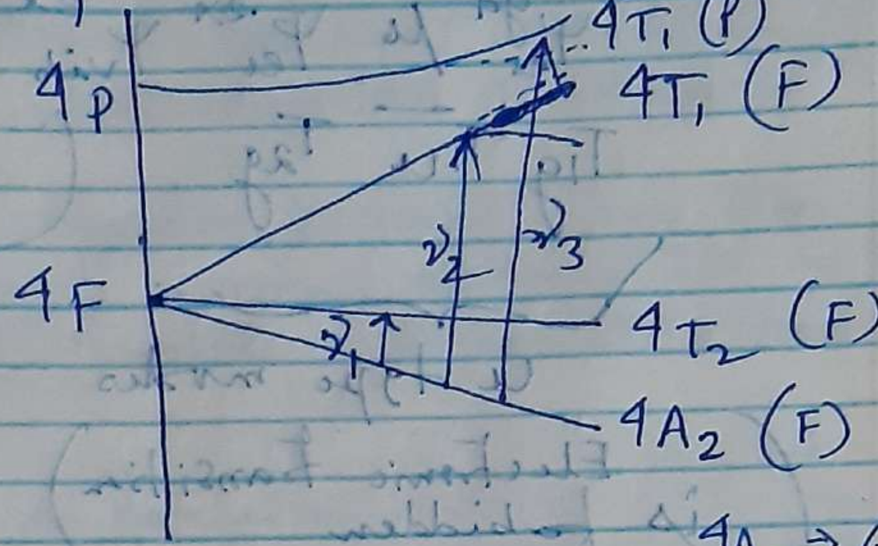
$= 4 + 2 - 3$

$= 3$, F State

F State $\rightarrow A_2, T_2, T_1$

F state ⇒ ORGEL Diagram

No. of unpaired electron = 3. $2S+1 = 4$



$^4A_2 \Rightarrow$ Ground state

$\nu_1 \Rightarrow {}^4A_2(F) \rightarrow {}^4T_2(F)$

$\nu_2 \Rightarrow {}^4A_2(F) \rightarrow {}^4T_1(F)$

But, $^4A_2 \rightarrow T_2$ (forbidden) (How? Think? Homework)

But this transition is vibronically allowed.

$$\int \Psi_{el}^{gd} \mu \Psi_{el}^{ex} \Psi_{vib}^{ex} d\tau \neq 0$$

(Here Ψ_{Vib}^{gd} is totally symmetric i.e, A_1)

From group theoretical calculation:

$A_2 \times \mu \times T_2 \rightarrow A_2 + \underline{E} + T_1 + \underline{T_2}$

Normal modes for T_d group

$A_1 + \underline{E + 2T_2}$

This transition is vibronically allowed. Coupling of E or T_2 can give totally symmetric mode.

Next lecture topic :-

1) d-p mixing (octahedral Vs. Tetrahedral Complexes)

2) peak broadening (spectral line)

3) Electronic Spectra of Ti^{3+} Complexes.

Related questions :-

(1) Why transition from A_2 is considered in Td system?

(2) What is spin multiplicity? What information we get from it?

(3) What is hole formalism?

(4) What is lowering of symmetry in symmetry of complex? What information we get from it?