Selection Rule

M. Sc. Spectroscopy/Inorganic Chemistry

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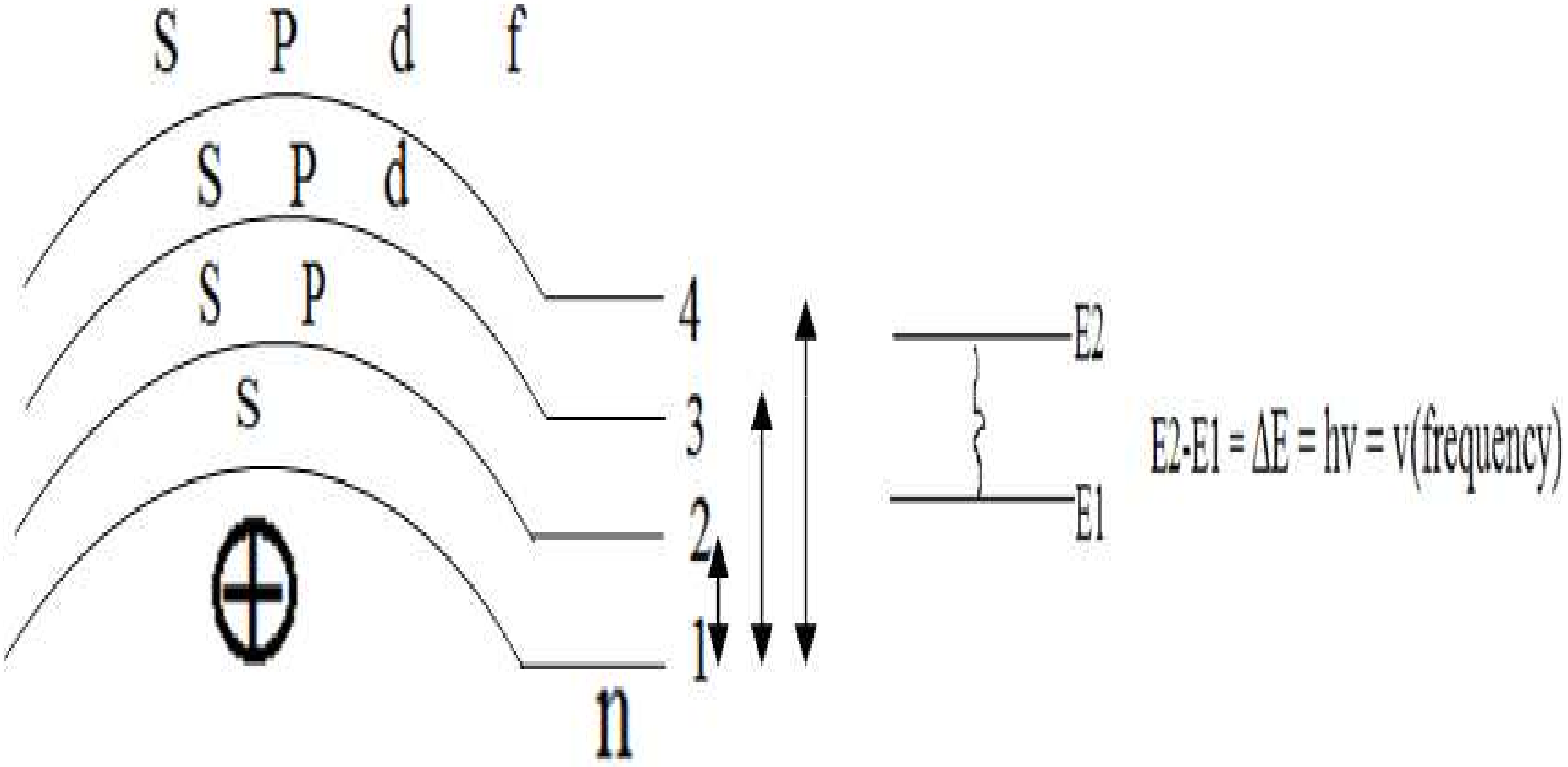
Selection Rule of Electronic Transition (S.R.)

Rule which restrict/allow to transition of electron is called S.R. It helps to determine spectrum of a molecule or atom.

We know that a molecule or atom have electrons in an orbit, suborbit, orbital in several microstate with minimum energy & get stability but when it interacts with EMR then there is change in its energy & transits from one state to another state by absorbing/emitting energy but all transitions are not allowed/restricted. It is guided by selection rule.


S P d f
S P d
S P
S
4
3
2
1
n
E2
E1
E2-E1 = ΔE = hv = v(frequency)

There are two type of transition

(a) **Allowed transition** (more intense) which allow to transition

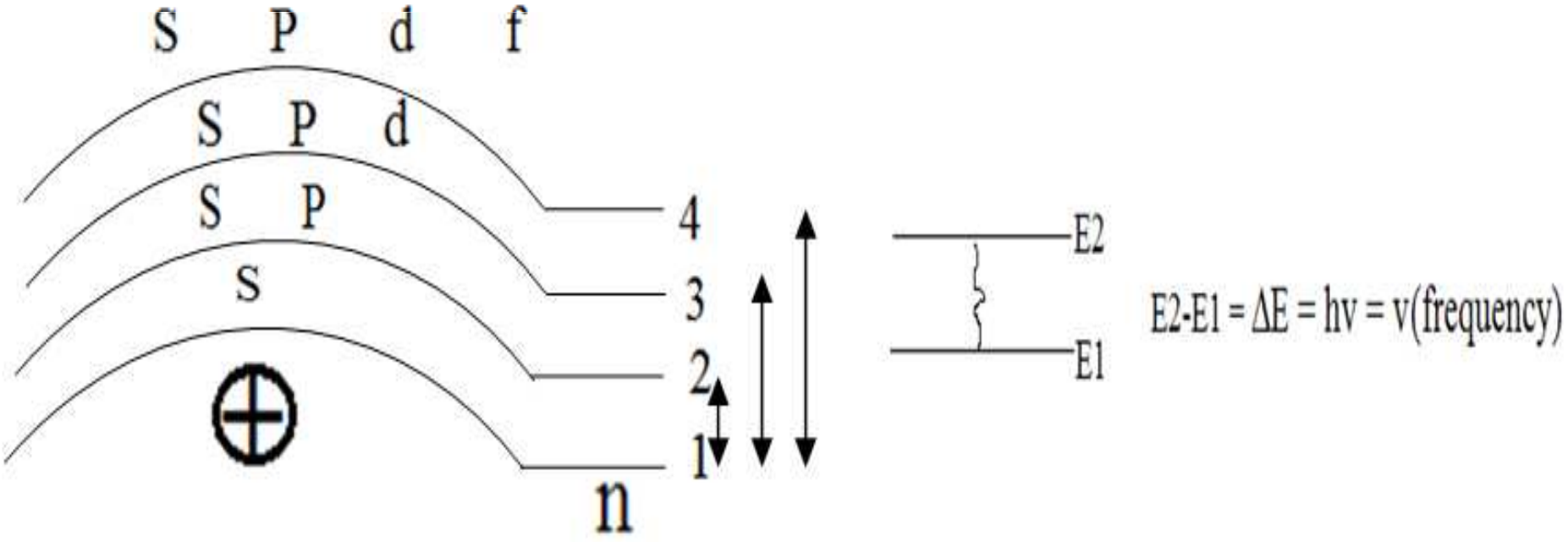
(b) **Forbidden** (less intense) which restrict the transition

Selection Rule

1. Orbit/Energy Selection Rule

Transition of electron one energy level to next higher energy level

$\Delta n = \pm 1, \pm 2, \pm 3 \ldots\ldots$anything allowed

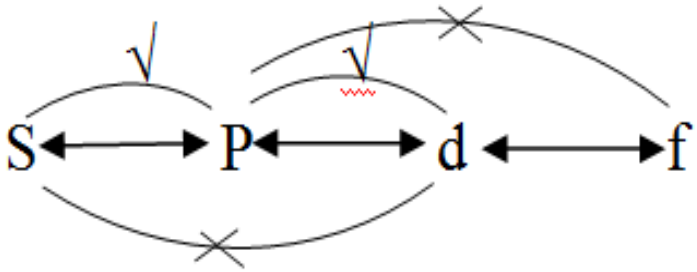


2. Laporte/orbital selection Rule

Overall change in orbital angular momentum by one unit i.e.

$\Delta l = \pm 1$ only. l value of s, p, d, f are 0, 1, 2, 3 respectively

(This rule is Only applied for centro symmetric molecule/orbital i.e. molecule having centre of symmetry or inversion centre like BF_3 is not centro symmetric molecule).



(g) (u) (g) (u)

Here,

g ⟷ u -allowed

u ⟷ g -allowed

but not

g ⟷ g not allowed (forbidden)

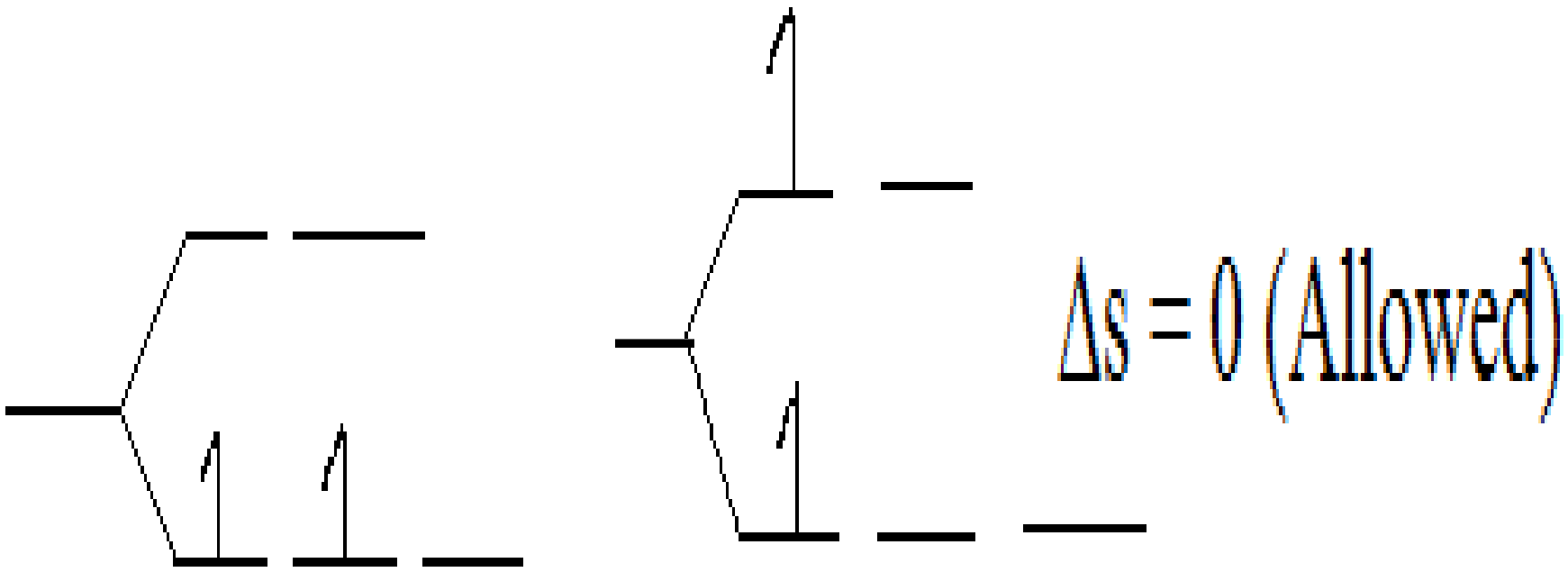
u ⟷ u not allowed (forbidden)

d-d transition $\Delta l = 0$ i.e. it is forbidden transition which absorbs low intensity/low absorbance. But sometimes transition of electron from d to p-d mixing is partially allowed where $\Delta l \neq 0$

3. Spin Selection Rule

$\Delta s = 0$ (allowed transition)

i.e. Total spin quantum no. cannot be change during the transition.



Singlet to Singlet, Doublet to Doublet, Triplet to Triplet are allowed.

4. Change in total angular momentum $\Delta J = 0, \pm 1$ only

Where J = L+S to L-S

L= Total orbital angular momentum

S = Total spin angular momentum = 2s+1

S, L, J value is determine by microstate (term state & symbol)

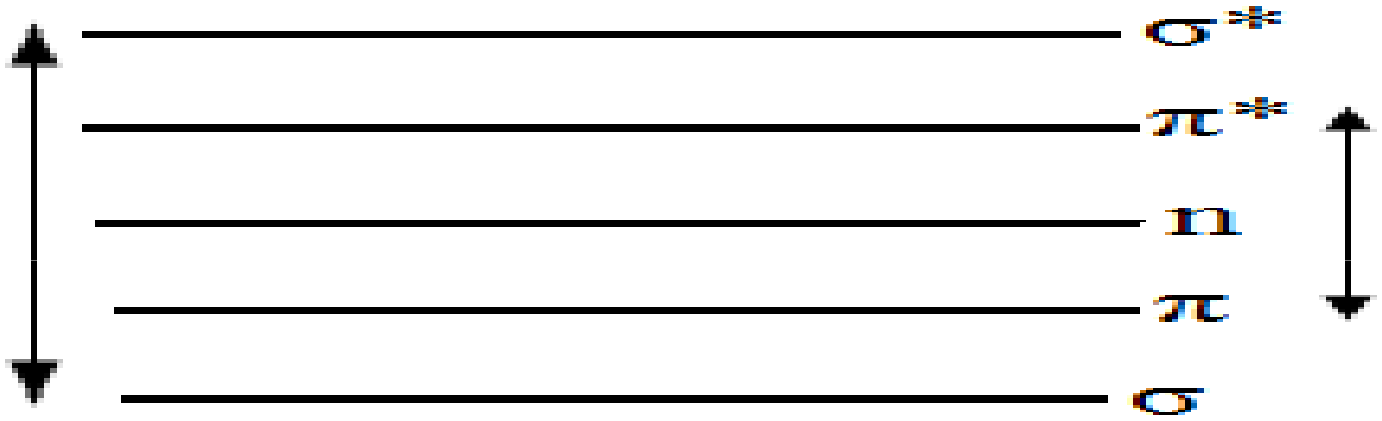
$^2D_{3/2}$ to $^2D_{5/2}$ is possible i.e. allowed

$^3F_{3/2}$ to $^3F_{7/2}$ is not possible i.e. forbidden

5. Symmetry Selection Rule

Transition between different symmetry do not occurs.

We know that a molecule contains BMO, ABMO & NBMO & they are denoted by σ, σ*, π, π* n



σ ⟷ σ* allowed

π ⟷ π* allowed

n ⟷ π* forbidden

Example:

CH_3-CO-CH_3 have σ, π & n electron but all transitions are not allowed.

6. $\Delta M_J = \pm 1$ then transition is allowed

All Selection Rules can be summarized as

Δn = Anything

$\Delta l = \pm 1$

$\Delta S = 0$

$\Delta J = 0, \pm 1$

$\Delta Mj = 0, \pm 1$

Question : Transition of electron is possible or not.

2 to 2

P S

½ ½

Here 2S+1 = Sm = 2-2 = 0 (allowed)

Δl = 1 (for P) – 0 (for S) = 1 (allowed)

ΔJ = ½-1/2 = 0 (allowed)

So transition is allowed (possible)


Thank You