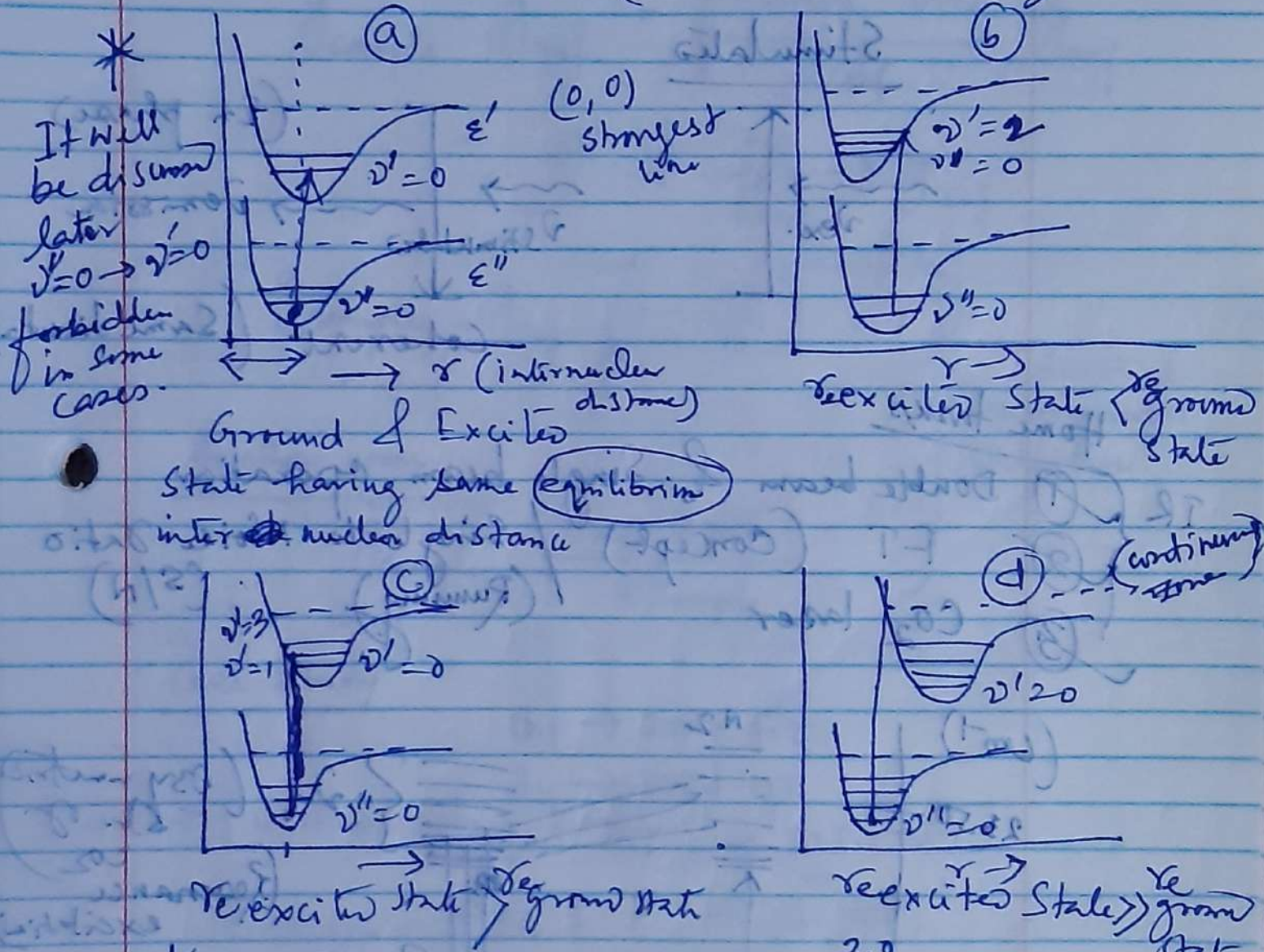


Frank-Condon principle :-

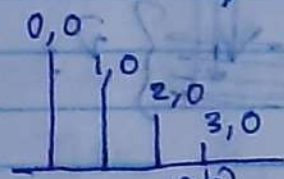
An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance.

4 possibilities (vertical transition)

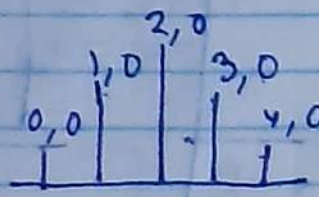


Intensity

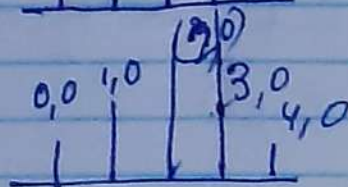
(a)



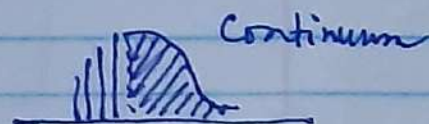
(b)



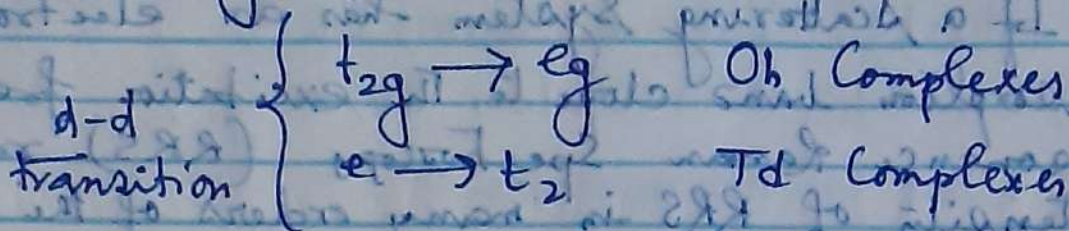
(c)



(d)



Vibronic Coupling (Relaxation of Laporte Selection rule)



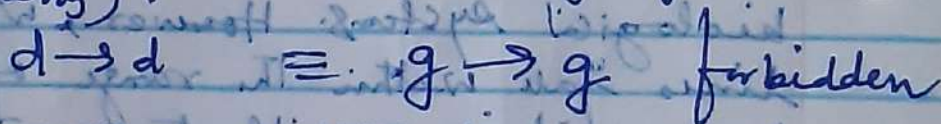
These are Laporte forbidden and they should be colourless.

But in reality many complexes are color.

Laporte Selection rule may be relaxed.

Vibronic Coupling :- (Centrosymmetric system)

In a Centrosymmetric system, all the d orbitals are considered to have the g-symmetry (gerade symmetry).



This restriction can be relaxed through the coupling of electronic and vibrational wave function. This coupling is described as vibronic coupling.

During the vibronic transition, the transition probability between the lower state (say ground state) and upper state (say, excited state) can be determined by considering the vibronic wave functions (Ψ_{vibronic}) of the two states.

$$\Psi_{\text{vibronic}} = \Psi_e \times \Psi_{\text{vib}}$$

Born-Oppenheimer approximation
electronic, rot. and vib. transition

Independently happens

Rotational energy $\approx 1-10 \text{ cm}^{-1}$
Vibrational energy separation $\approx 3000 \text{ cm}^{-1}$

Born-Oppenheimer approximation \Rightarrow (E Total = E electronic + E vib. + E rot.)

But, Total wave function (Ψ) = $\Psi_{el} \Psi_{vib} \Psi_{rot}$

Ψ_{rot} can be treated as independent of the other two wave functions, i.e., Ψ_{el} and Ψ_{vib} . (Born-Oppenheimer approximation)

Then, $\Psi_{vibronic} = \Psi_{el} \Psi_{vib}$

$$[\Delta E_{elec} \approx \Delta E_{vib} \times 10^3 \approx \Delta E_{rot} \times 10^4 \text{ cm}^{-1}]$$

Breakdown of Born-Oppenheimer approximation for vibronic coupling

Electronic transition coupled with vibrational transition

$$I = \int \Psi_{el}^{gd} \Psi_{vib}^{gd} \mu \Psi_{el}^{ex} \Psi_{vib}^{ex} d\tau$$

gd \rightarrow ground state
ex \rightarrow excited state

To make the transition allowed, the above integral must be non-zero. (i.e., the product $\Psi_{el}^{gd} \Psi_{vib}^{gd} \mu \Psi_{el}^{ex} \Psi_{vib}^{ex}$ must be a symmetric function)

Now In a Centrosymmetric system, Ψ_{el} is symmetric

$$\Psi_{el}^{gd} \times \Psi_{el}^{ex} = g \times g = g \text{ (symmetric) (i.e., even function)}$$

dipole moment (μ) is u-symmetric (odd function)

$$\Psi_{el}^{gd} \times \Psi_{el}^{ex} \times \mu = g \times g \times u = u \text{ (odd function)}$$

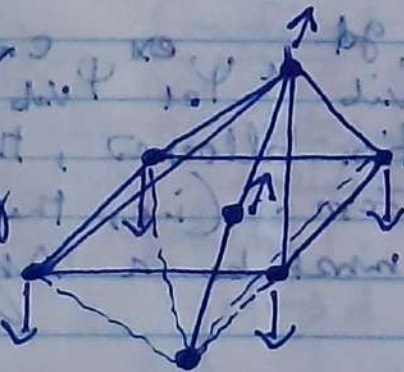
$$\text{Then } \Psi_{vib}^{gd} \times \Psi_{vib}^{ex} = u \text{ function (odd function)}$$

Thus if one vibrational wave function is of g type then the vibrational wavefunction of the other electronic state must be of 'u' type.

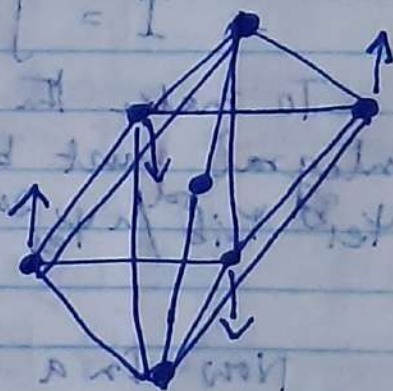
Thus, the transition is possible only when the g type vibration of the ground electronic state is coupled with the u-type vibration of the excited electronic state and vice-versa.

In an octahedral complex, the T_{1u} and T_{2u} normal modes can destroy the center of symmetry i.e., these vibrations are of u-symmetry.

destruction of
center of
symmetry



T_{1u}



T_{2u}

Cartesian Co-ordinates

~~Octahedron~~

Electronic Transition

Normal modes

u-symmetry

If the u-symmetry modes are present

Coupling $\Rightarrow (u \times u = g)$ (even function)
of same term present in each type.
 $\underline{\underline{I}} \neq 0$

In Summary :- (Oh system)

$$\psi_{el}^{gd} \mu \psi_{el}^{ex} \psi_{vib}^{ex}$$

$$T_{1g} \quad T_{1u} \quad T_{2g}$$

u type modes

(Electronic transition)
is forbidden

Irreducible representation
 ${}^1A_{1g}$ (Ground Vibrational level)

→ If the normal modes contain u type with same symmetry & term

$$\boxed{u \times u \rightarrow g}$$

→ Same Symmetry & term (e.g., T_{1u})

(vibronic transition is allowed)