Crystal Field Theory-II

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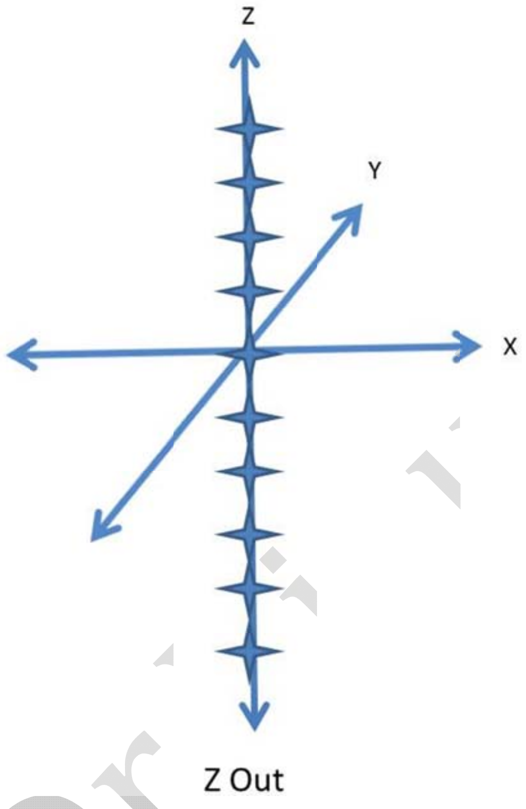
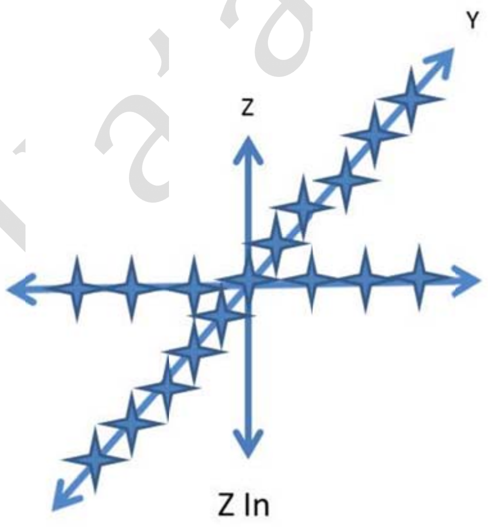
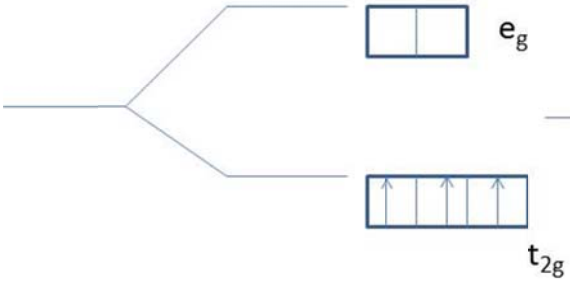
Introduction

- Everything in the world tries to remain in the stable form, and for that it adapts to some kind of geometry.
- The Jahn Teller effect is based upon same kind of phenomenon.
- The Jahn Teller effect observed due to asymmetrical distribution of electron density in the orbitals.
- The electrons density is present over the axis in the orbital.

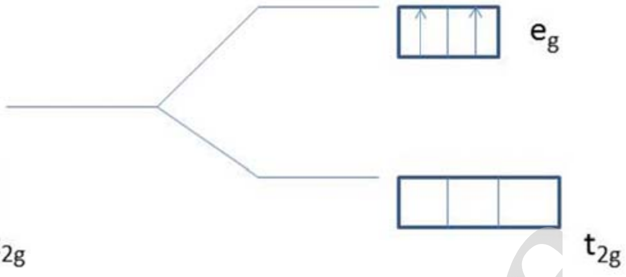




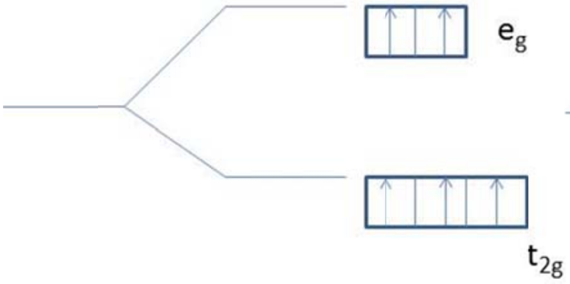
- If the electron density is maximum over z axis than ligands over the z axis will have more attraction hence more repulsion results into large z axis, and the phenomenon is referred as Z OUT.
- If the electron density is maximum over x and y axis than ligands over the x and y axis will have more attraction hence more repulsion results into large x and y axis, and the phenomenon is referred as Z IN.
- Jahn Teller effect is not observed in half filled or fully filled electronic configuration (here consider t_{2g} and e_g as separate orbitals).



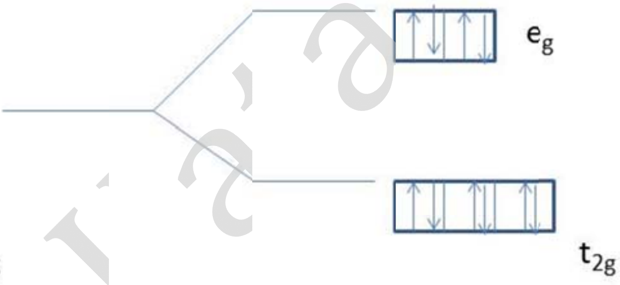
Half filled t2g orbital



Half filled eg orbital

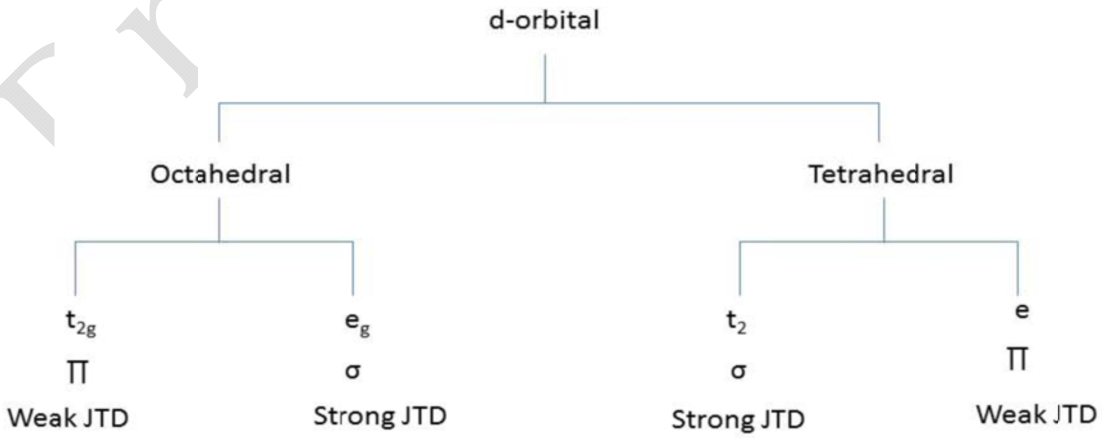


Half filled d orbital



Fully filled d orbital

- Definition: A spontaneous distortion of geometry for non-linear molecules in electronically asymmetric system which results when levels are split to reduce the energy of the overall system.
- The Jahn Teller effect can be strong or weak according to electron from the different orbitals participating in occurrence of distortion.



- Jahn Teller effect in octahedral complexes.

Z in or out	JTD	Strong field	No. of Electrons	Weak Field	JTD	Z in or out

Z in	W	$t_{2g}^{1} e_g^{0}$	d^1	$t_{2g}^{1} e_g^{0}$	W	Z out
Z out	W	$t_{2g}^{2} e_g^{0}$	d^2	$t_{2g}^{2} e_g^{0}$	W	Z out
---	---	$t_{2g}^{3} e_g^{0}$	d^3	$t_{2g}^{3} e_g^{0}$	---	---
Z in	W	$t_{2g}^{4} e_g^{0}$	d^4	$t_{2g}^{3} e_g^{1}$	S	Z out
Z out	---	$t_{2g}^{5} e_g^{0}$	d^5	$t_{2g}^{3} e_g^{2}$	---	---
---	---	$t_{2g}^{6} e_g^{0}$	d^6	$t_{2g}^{4} e_g^{2}$	W	Z in
Z out	S	$t_{2g}^{6} e_g^{1}$	d^7	$t_{2g}^{5} e_g^{2}$	W	Z out
---	---	$t_{2g}^{6} e_g^{2}$	d^8	$t_{2g}^{6} e_g^{2}$	---	---
Z out	S	$t_{2g}^{6} e_g^{3}$	d^9	$t_{2g}^{6} e_g^{3}$	S	Z out
---	---	$t_{2g}^{6} e_g^{4}$	d^{10}	$t_{2g}^{6} e_g^{4}$	---	---

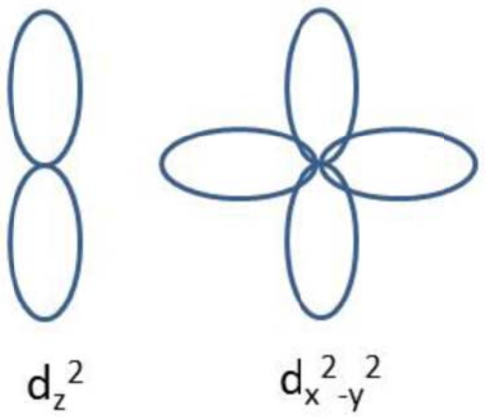
- Jahn Teller effect in tetrahedral complexes.

No. of Electrons	Weak Field	JTD	Z in or out
d^1	$e^1 t_2^0$	W	Z out
d^2	$e^2 t_2^0$	---	---
d^3	$e^2 t_2^1$	S	Z in
d^4	$e^2 t_2^2$	S	Z out
d^5	$e^2 t_2^3$	---	---
d^6	$e^3 t_2^3$	W	Z out
d^7	$e^4 t_2^3$	---	---
d^8	$e^4 t_2^4$	S	Z in
d^9	$e^4 t_2^5$	S	Z out
d^{10}	$e^4 t_2^6$	---	---

Tetragonal complexes or Jahn Teller effect

- The main difference between tetrahedral and tetragonal complex is that in tetrahedral complexes the angle between two ligands is 109˚ 28'. In tetragonal complex the angle between two ligands is any other than 109˚ 28'.
- The Jahn Teller effect owes to asymmetric electron configuration within the orbital which causes higher energy for complex and the complex tries to distort to maintain stability.
- e_g orbitals are equally degenerated while t_{2g} orbitals are triply degenerated.
- t_{2g} orbitals have no role in octahedral complex formation hence it does not produce any Jahn Teller effect as far as tetragonal structure is concerned.
- In octahedral complexes, the six ligands join with the six lobes of e_g orbitals.
- eg orbital is consist of two orbitals (d_{z^2} and $d_{x^2-y^2}$).

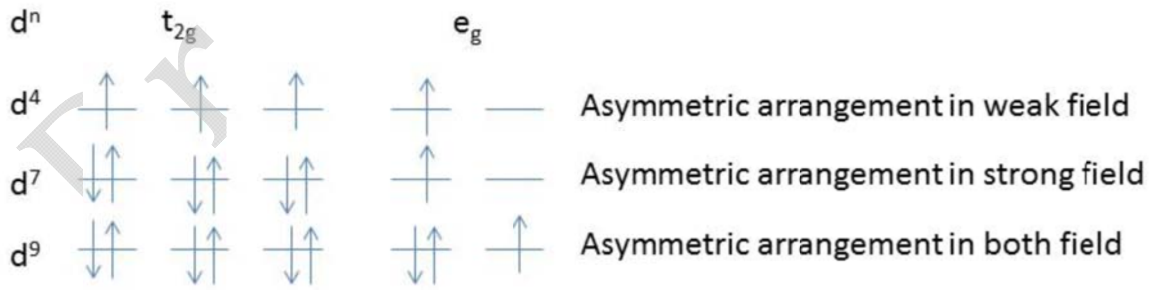
- d_{z^2} orbital has two lobes and $d_{x^2-y^2}$ has four lobes, to which the six ligands join.



- If both the e_g orbitals are filled symmetrically or remain empty than there will not be any Jahn Teller effect and regular octahedral structure forms.
- If the e_g orbital filled asymmetrically than the octahedral structure distorts to form tetragonal structure is formed.

Asymmetric arrangement of electron in e_g orbitals

- If both the e_g (d_{z^2} and $d_{x^2-y^2}$) orbitals are filled with equal number of electrons or remain empty than it will be symmetric arrangement.
- If both the e_g (d_{z^2} and $d_{x^2-y^2}$) orbitals are filled with different number of electrons than it will be asymmetric arrangement that is responsible for Jahn Teller effect.

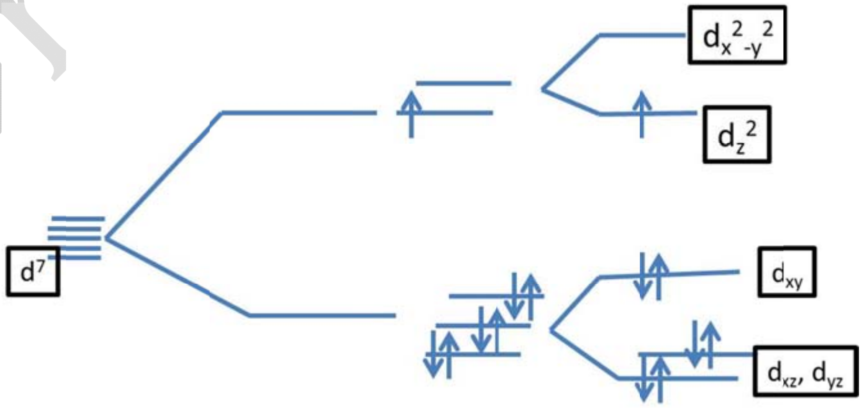


- As shown above, in d4, d7, and d9 systems, e_g orbitals are asymmetric in rest of the cases e_g orbitals filled symmetrically.
- $d_{x^2-y^2}$ orbital has four lobes to which four ligands attach whilst d_{z^2} orbital has two lobes to which two ligands attach.

- Now if the electron density remains higher on x and y axis than $d_{x^2-y^2}$ will have more attraction towards central metal ion (in case of d^4 and d^7) and hence will get more repulsion that results into increased distance from central metal ion compare to z axis (Z in).
- If the electron density is higher on z axis than d_{z^2} will have more attraction towards central metal ion and hence will get more repulsion that results into increased distance from central metal ion compare to x and y axis (Z out).
- In case of Z in, where two bonds on z axis become long and four bonds on x and y axis become short, it results into distortion and octahedral structures distorts to tetragonal structure. Such tetragonal structure is known as compressed tetragonal structure.
- In case of Z out, where two bonds on z axis become short and four bonds on x and y axis become long. It results into distortion and octahedral structure distorts to elongated tetragonal structure.
- The distortion occurs to get the maximum stability.

Splitting of d orbitals

- Due to ligand field effect in octahedral complexes, orbitals splits in to e_g and t_{2g} among which energy of t_{2g} orbital decreased and energy of e_g orbitals increases.
- If e_g orbital filled asymmetrically than further splitting occurs to achieve stability. Energy of $d_{x^2-y^2}$ orbital will increase as it attaches four ligands and energy of d_{z^2} will decrease as it attaches two ligands.

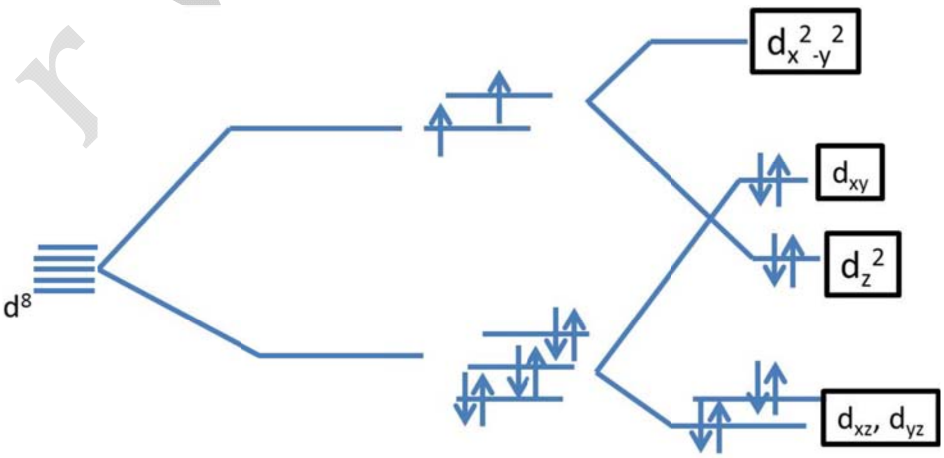


Splitting of d orbitals in square planner complexes

In respect of octahedral field, ligand with its negative charge attacks positively charged central metal ion which produces ligand field effect. As a result of this degeneracy of d orbitals of metal ion loses its degeneracy. It causes splitting of d orbital in two groups.

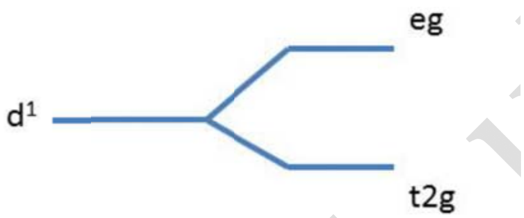
(i) e_g group: ($d_{x^2-y^2}$ and d_{z^2}) (ii) t_{2g} group: (d_{xy}, d_{yz}, and d_{xz})

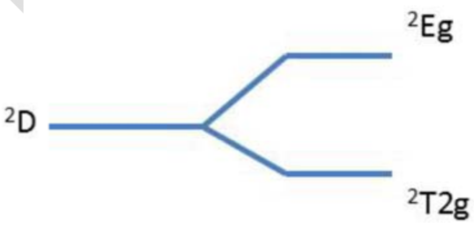
- With reference to octahedral field e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) become excited and energy will be higher while t_{2g} orbitals (d_{xy}, d_{yz}, and d_{xz}) will be stable with lower energy.
- In a system having eight electrons (d8), in presence of weak ligand field or strong ligand field, t_{2g} orbital has six electrons while e_g orbital has two electrons.
- Now, d_{z^2} orbital has two lobes hence there will be little repulsion for one electron as compare to $d_{x^2-y^2}$ as it has four lobes.
- In presence of strong ligand field, energy of d_{z^2} will decrease and energy of $d_{x^2-y^2}$ will increase in same amount to gain stability.
- When energy of $d_{x^2-y^2}$ increases the electron come down to d_{z^2} and four ligands can attach easily to it while d_{z^2} will be repelled the ligands attaching to it due to presence of two electrons.
- It causes exclusion of two ligands to form geometry and square planner structure will form in place of octahedral.

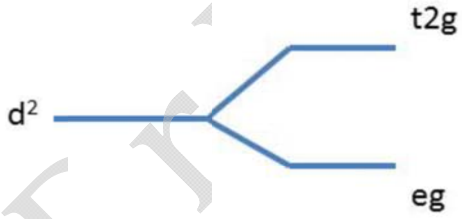


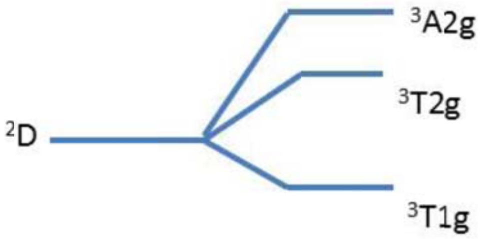
Splitting of ground state terms

- Spectral terms are very useful in understanding the spectra of transition elements and complexes.
- Term symbols obtained by l-l coupling are designated by S, P, D, F….
- In ground state, s orbitals show one, p orbitals show three, d orbital show five and f orbital show seven degenerated layers.
- In case of ground state terms, S term symbol shows one, P term shows three, D
- Ligand field does not affect s & p orbital hence they will not split.
- In presence of ligand field, d orbital splits into t_{2g} and e_g whilst f orbital splits into a_{2g}, t_{2g} and t_{1g}.
- D term splits into T_{2g} and E_g whilst F term spits into A_{2g}, T_{2g}, and T_{1g}.
- A, T and E are Mulliken symbols.
- d orbitals of d^1 and d^2 systems and their spectral terms ^2D and ^3F respectively split in octahedral field as below.









- In tetrahedral field the above splitting got reversed.
- Spin multiplicity (2s + 1) is obtained by S-S coupling and designated as super script on the left side of term symbol.

- Splitting and order of energy of spectral terms are shown in following table.

Term	**Splitting**	**Order of energy of term**	
		Octahedral field	**Tetrahedral field**
S	A_{1g} (one)	A_{1g}	A_1
P	T_{1g} (Three)	T_{1g}	T_1
D	T_{2g} (Three) + E_g (Two)	$T_{2g} < E_g$	$E < T_2$
F	A_{2g} (One) + T_{2g} (Three) + T_{1g} (three)	$T_{1g} < T_{2g} < A_{2g}$	$A_2 < T_2 < T_1$

- E_g and T_{2g} terms are again splits due to Jahn-Teller effect.

Term	Splitting	Order of energy of term	
		Octahedral field	Tetrahedral field
E_g	A_{1g} (one) + B_{1g}	$T_{2g} < E_g$	$E_g < T_{2g}$
T_{2g}	E_g (two) + B_{2g}	$E_g < B_{2g} < A_{1g} < B_{1g}$	$B_{1g} < A_{1g} < B_{2g} < E_g$

Hole Formalism

- In dn and d10-n system of complexes, in presence of same ligand field splitting of Eg and T2g spectral terms will be of reverse of each other. The phenomenon is known as Hole-Formalism.

Spherical charge symmetry of d orbitals

- In d^0, d^5, and d^{10} systems electrons arrange symmetrically and such d orbitals are termed as spherical charge symmetric structures.

Spherical charge asymmetric structures of d orbitals

- Apart from above mentioned systems, all the d orbital electronic structures have different electronic distribution and are known as charge asymmetric structures.

Charge asymmetric structures and Hole formalitic pair

- In d^n and d^{5+n} electrons are more than spherical charge symmetric structures so they are known as excess electron systems.
- In d^{10-n} and d^{5-n} electrons are less than spherical charge symmetric structures and known as less electron systems or positive hole or positron system.
- For example: d^1 system one electron is more than charge symmetric structure while in d^9 system one electron is less than charge symmetric structure, that make one positive hole or one positron system.
- Such pair is known as Hole formalitic pairs.
- The formalistic pairs are depicted below.

Hole	Formalitic Pair	Spectral term
d^n	d^{10-n}	
d^1	d^9	^2D Doublet D
d^2	d^8	^3F Triplet F
d^3	d^7	^4F Quartet F
d^4	d^6	^5D Quintet

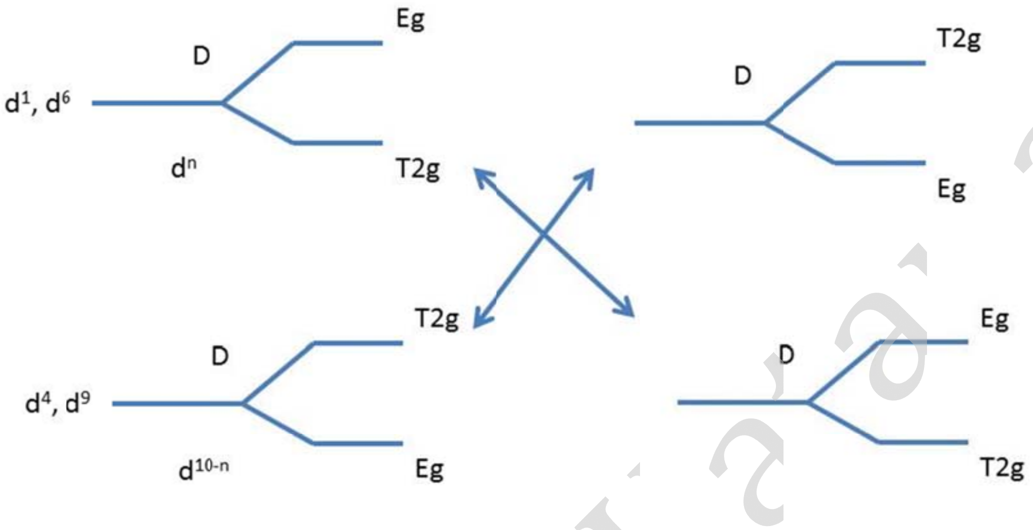
Hole formalism and splitting of spectral term

- d^n and d^{5+n} are excess electron system and in complex formation ligands are attached with metal ion by repulsion forces.
- While in d^{10-n} ligands attach with metal ion by attraction force.
- Thus the d orbital (e_g or t_{2g}) of d^n system with which ligands are attached their energy increases due to repulsion while in d^{10-n} system energy decreases due to attraction forces.
- Thus by attachment of ligands the spectral terms of d^n system show increase in energy, energy of same d orbital spectral term will decrease in d^{10-n} system.
- Thus in same ligand field splitting of spectral terms of d^n and d^{10-n} will be reverse, such pair is known as formalitic pair. It has same spectral term with reverse splitting.

Example

- Spectral term of d^1 and d^9 case is ^2D, in d^1 system in octahedral field energy of T_{2g} decreases while energy of E_g increases.
- In d9 system energy of T_{2g} increases and energy of E_g decreases.
- For tetrahedral field, in d^1 system energy of E_g decreases and energy of T_{2g} increases.

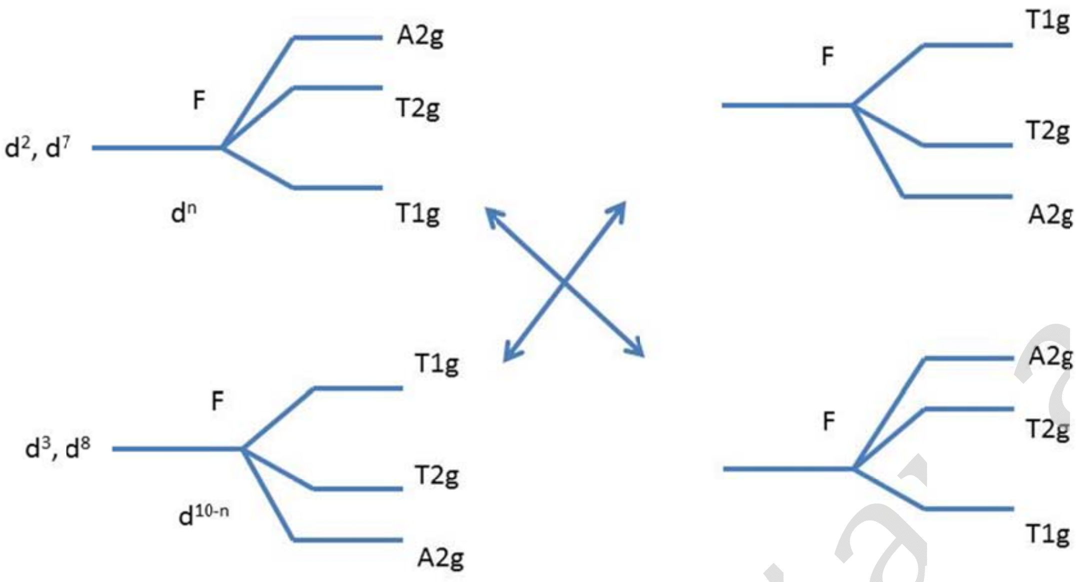
- g is not used in tetrahedral field.
- It can be understood that splitting of d^n spectral term in octahedral field and splitting of d^{10-n} in tetrahedral field is same.



Splitting of D term in Octahedral field

Splitting of D term in Tetrahedral field

- Similarly, d^2 and d^8 has spectral term is F. F term splits as below.



Splitting of F term in Octahedral field

Splitting of F term in Tetrahedral field

Orgel Diagram

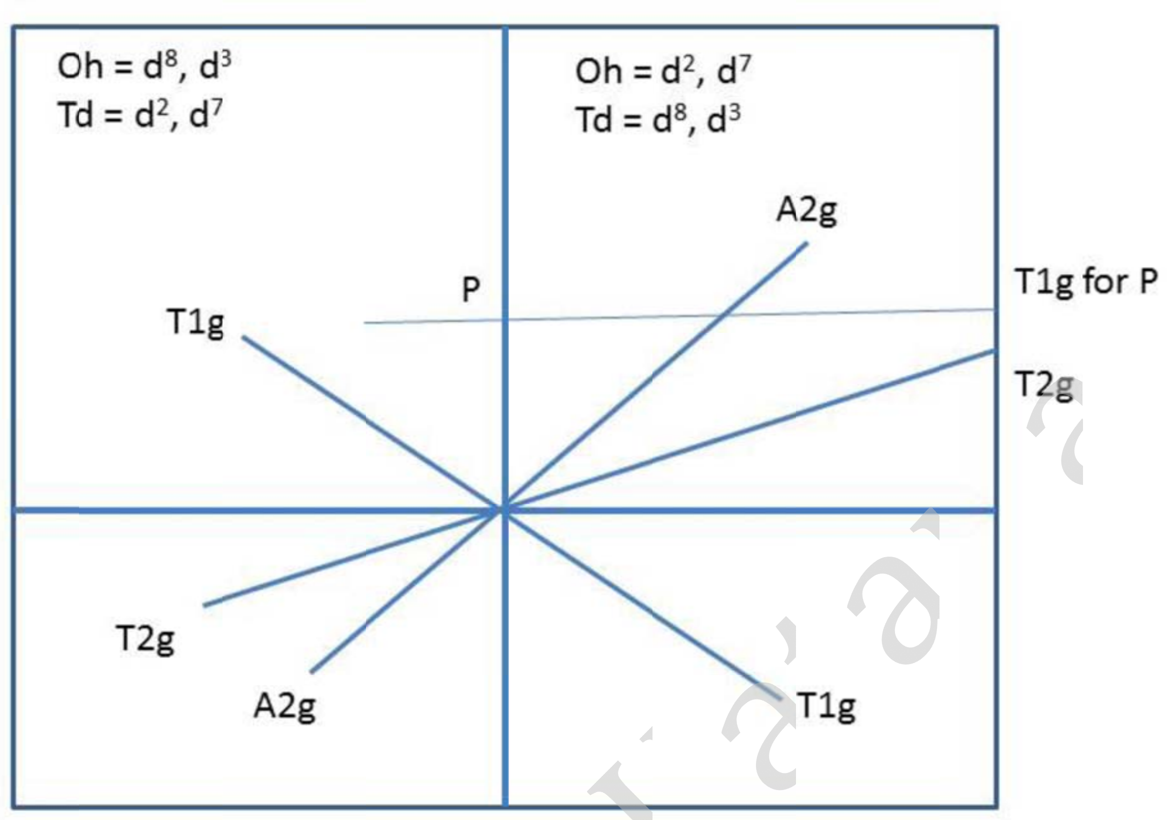
- The spectral terms of various inorganic complexes split in specific manner that can be represented by various diagrams.
- Tanabe-Sugano diagrams are of same kind but difficult to understand and interpret.
- The splitting of spectral terms is important only in weak field and orgel diagram represents same.
- They are easy to understand and interpret.

Splitting of spectral terms and orgel diagrams

- In excess electron systems (d^n and d^{5+n}), ligand attaches to d orbitals by repulsion forces.
- In less electron or positron systems (d^{10-n}), ligand attaches to d orbitals by attraction forces.
- So, in any field, spectral term for d^n and d^{10-n} will be same but splitting will be of reverse.

Example

- d^1 and d^9 has spectral term ^2D.
- In octahedral field for d^1, splitting of ^2D will be in Eg and T2g. energy of Eg will increase and energy of T2g will decrease.
- In octahedral field for d^9, energy of T2g will increase and energy of Eg will decrease.
- In tetrahedral field for d^1, the energy of T2g will increase and energy of Eg will decrease.
- In tetrahedral field for d^9, the energy of Eg will increase and energy of T2g will decrease.
- In same way, spectral term for d^2 and d^8 is 3F.
- In octahedral field for d^2, the splitting and order of energy will be T1g < T2g < A2g.
- In octahedral field for d^8, the splitting and order of energy will be A2g < T2g < T1g.
- There is no effect of ligand field on S and P term as S is spherical and P has all the degenerated orbitals.
- The splitting of d^n and d^{10-n} spectral term is of reverse in same field. However it is same in different field.



- Orgel diagrams are helpful to understand the spectra of complexes in weak ligand field.
- Splitting energy of d orbitals can be explained.

Laporte Selection rules

(A) Orbital Selection rule

- The transition of electron is only allowed if the angular momentum changes by ±1. Change in angular momentum Δl = ±1.
- **Orbital allowed transition:** If the change in angular momentum is ±1 than the transition is called orbital allowed transitions. For example, $2s^2 \rightarrow 2p^1$ is orbital allowed as one electron moves from s orbital to p orbital and the change in angular momentum is 1.
- **Orbital forbidden transition:** if the change in angular momentum is not ±1 then the transition is orbital forbidden transitions. In transition element series d → d transition occurs in which Δl = 0 hence such transitions are orbital forbidden.
- In orbital allowed transitions the value of molar absorption co-efficient (ϵ) is very high and due to this sharp band is observed in uv spectroscopy.

- In orbital forbidden transitions, the value of molar absorption co-efficient (ϵ) is very low and due to this weak and broad band is observed in uv spectroscopy.

(B) Spin Selection rule

- The spin of electron should not be changed in electron transitions. Hence ΔS = 0.
- The spin multiplicity should be same in ground and excited states.
- In other words, no. of unpaired electron should be same in ground and excited states.
- **Spin allowed transition:** If there is no change in spin (ΔS = 0) then such transitions are spin allowed transitions.

- **Spin forbidden transition:** if the ΔS = 0 in electron transition, then such transitions are spin forbidden transitions.

(C) Symmetry Selection rule

- If symmetry of ground state and excited state should be change during electron transition. In other words, the symmetry should be different in ground and excited states.
- For example: transition like g → ug and ug → g are symmetry allowed transitions.
- If symmetry does not change during transition then such transitions are symmetry forbidden transitions.

If above three rules are obeyed during electron transition then the value for molar absorption co-efficient (ϵ) is very high and due to this sharp band is observed in uv spectroscopy. Usually such substances are dark and attractive.

Reasons for forbidden transitions

- Forbidden transitions are very common.
- Spin forbidden and orbital forbidden transitions occur due to L-S coupling.
- l values for ground state and excited states change due to L-S coupling hence orbital forbidden transitions occur.
- Orbital hybridization causes change in symmetry of the orbital (ug converts to g and g coverts to ug) hence symmetry forbidden transitions occur.
- Vibrational levels (V) and rotational levels (J) involves in transitional energy levels due to higher amount energy that causes symmetry changes hence forbidden transitions occur.
- A weak band observed in uv spectroscopy due to forbidden transitions.

Sr. No.	Type of transition	Molar absorption coefficient	Example
1	Spin allowed	10,000	$[Ti(Cl)_6]^{2-}$
2	Spin allowed and orbital partially allowed	500	$[CoBr_4]^{2-}$ and $[CoCl_4]^{2-}$
3	spin allowed and orbital forbidden	8 to 10	$[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$
4	Orbital partially allowed and spin forbidden	4	$[MnBr_4]^{2-}$
5	Spin forbidden and orbital forbidden	0.02	$[Mn(H_2O)_6]^{2+}$

Absorption spectra for transition elements

- The metal salt and complexes are dissolved in appropriate solvent and radiation is passed through.
- Electron transition occurs due to higher amount of energy and accordingly absorption spectra are obtained. The wavelength range is 200 nm to 2000 nm.
- The graph of molar absorption or molar co-efficient against wave number or wave length is plotted, and absorption spectrum can be explained.

- Molar absorption co-efficient is also known as Extinction co-efficient.

$$\epsilon = \frac{A}{c.l}$$

- Where, c = concentration of solution or molarity, and l = length of cell.
- The intensity of absorption band depends upon value of molar absorption co-efficient.

Origin

- Crystal field theory, molecular orbital theory and ligand field theory are the useful means to explain absorption spectra of transition elements.
- In transition elements, d orbitals are degenerated in ground state.
- However in excited state, degeneracy is destroyed and d orbital splits into two groups (t_{2g} and e_g).
- In octahedral complexes, energy of t2g is lower whilst in tetrahedral complexes energy of eg is lower.
- Now in presence of radiation, electron transition occurs from lower energy to higher energy (t2g → eg or eg → t2g).
- Due to such transitions, d → d transition absorption spectra are obtained.

Intensity of absorption band

The absorption bands for transition metal elements are weak, broad and asymmetric due to following reasons.

- d → d transition are orbital forbidden as $\Delta l = 0$.
- d → d transition requires higher amount of energy so some vibration and rotational energy levels are included.
- d orbital is symmetric so the transition will be symmetry forbidden.
- Due to Jahn-Teller effect, t2g and eg orbitals split again hence higher energy levels are produced. So, 2 or 3 maxima are observed and the spectrum gets asymmetric.
- The value for molar absorption co-efficient is very low (1 to 50 cm^{-1}).
- Certain transition metal ions show spectrum with higher intensity due to several other electron transitions.

(a) π → π* transition

- The non-bonding d orbital electrons of transition metal transits to π* anti-bonding bonds of ligands.

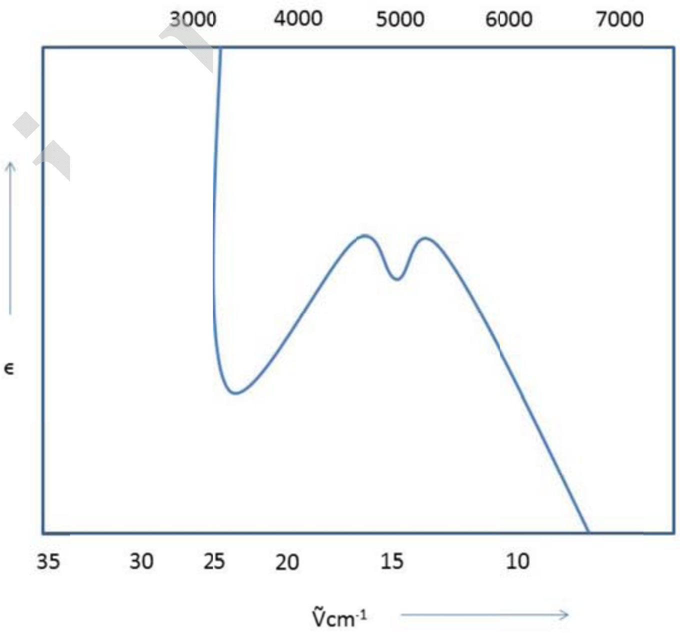
- So, it does not fall into category of d → d or g → g types.
- So, such transition is known as charge transfer transitions.
- Such transition has more intensity and has higher ϵ values (1000 cm^{-1}).

(b) Mixed orbital transitions

- Tetrahedral complexes do not have centre of symmetry.
- In such cases, there are optimum chances of having combination between d and p orbitals.
- Now electrons transit from d → mixed orbitals and hence it is orbital and symmetry allowed ($\Delta l = \pm 1$ and g → ug).
- So, it will be laporte allowed transition that yield intense absorption band.

Absorption spectrum of Ti^{3+}

- The aqueous solution of $TiCl_3$ yields $[Ti(H_2O)_6]^{3+}$
- When radiation passes through solution, certain wavelength absorbed.
- Electron transits from lower energy levels to higher.
  - Plot of A or ϵ versus wavelength or wave number will be as follows.



Position of absorption band

Position of absorption band is found 2000 to 12500 Å.

Position of maxima or peak

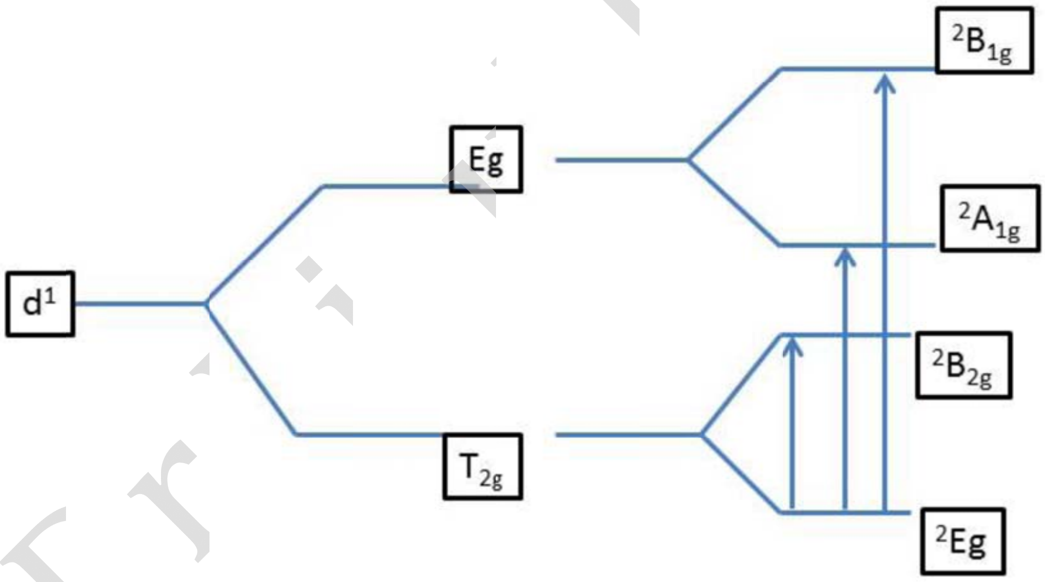
A clear peak is found at 4920 Å which is uv region so colour of complex is light violet.

Position of shoulder

Apart from main peak, one shoulder is found at 5740 Å.

Explanation

- Electronic configuration of Ti^{3+} is [Ar] $3d^1$.
- The spectral term is ^2D.
- $[Ti(H_2O)_6]^{3+}$ is octahedral complex.
- The energy of t2g decreases and energy of eg increases.
- Now due to Jahn-Teller effect the orbitals split again.
- The transitions are found as below.



2Eg -→ 2B1g	4920 Å main peak
2Eg -→ 2A1g	5740 Å shoulder peak
2Eg -→ 2B2g	Peak does not observed

Absorption spectrum of Cu^{2+}

- Cu^{2+} in aqueous solution exist as $[Cu(H_2O)_6]^{2+}$ and blue in colour.
- It represents d9 system.

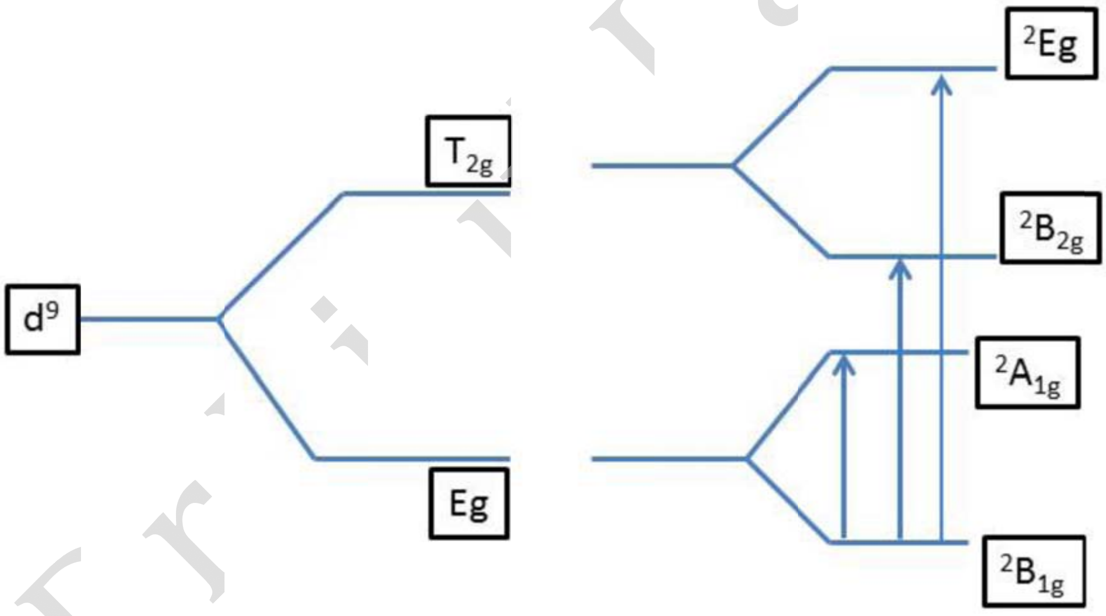
- According to hole-formalism the splitting pattern is reversed in case of d^1 and d^9.
- The spectral term is ^2D.

Range and intensity of absorption spectrum

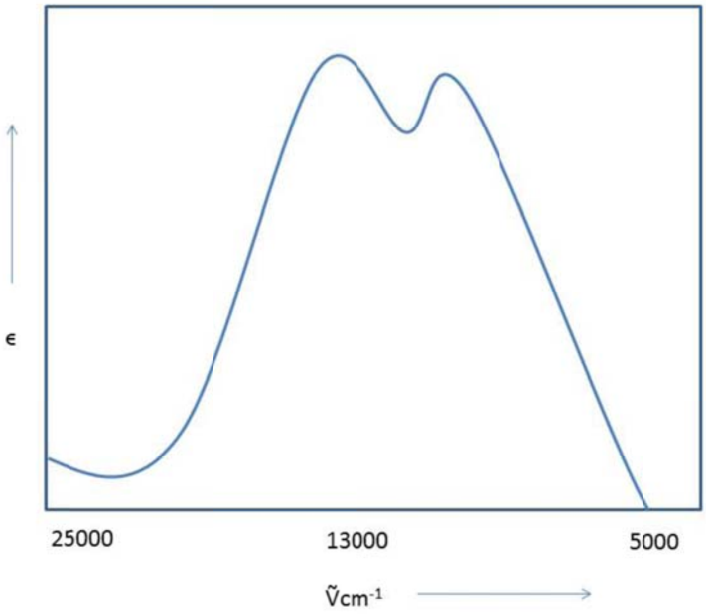
- Absorption spectrum of $[Cu(H_2O)_6]^{2+}$ is between 15000 to 20000 cm^{-1}.
- Spectrum is asymmetric and broad.
- It represents d → d transition and that is laporte forbidden transition.

Position of maxima and peak

- Position of maxima is at 13000 cm^{-1}.
- Shoulder is at 11000 cm^{-1}.
- Spectral term ^2D splits into Eg and T2g.
- Energy of Eg decreases and energy of T2g increases.

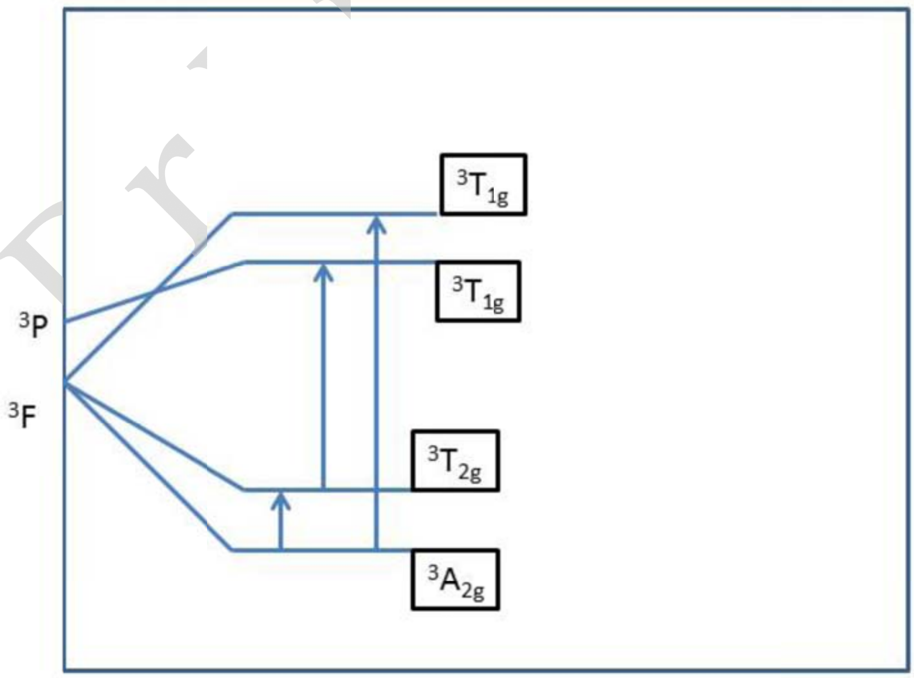


2B1g -→ 2Eg	13000 main peak
2B1g -→ 2B2g	11000 shoulder peak
2B1g -→2A1g	not in visible range

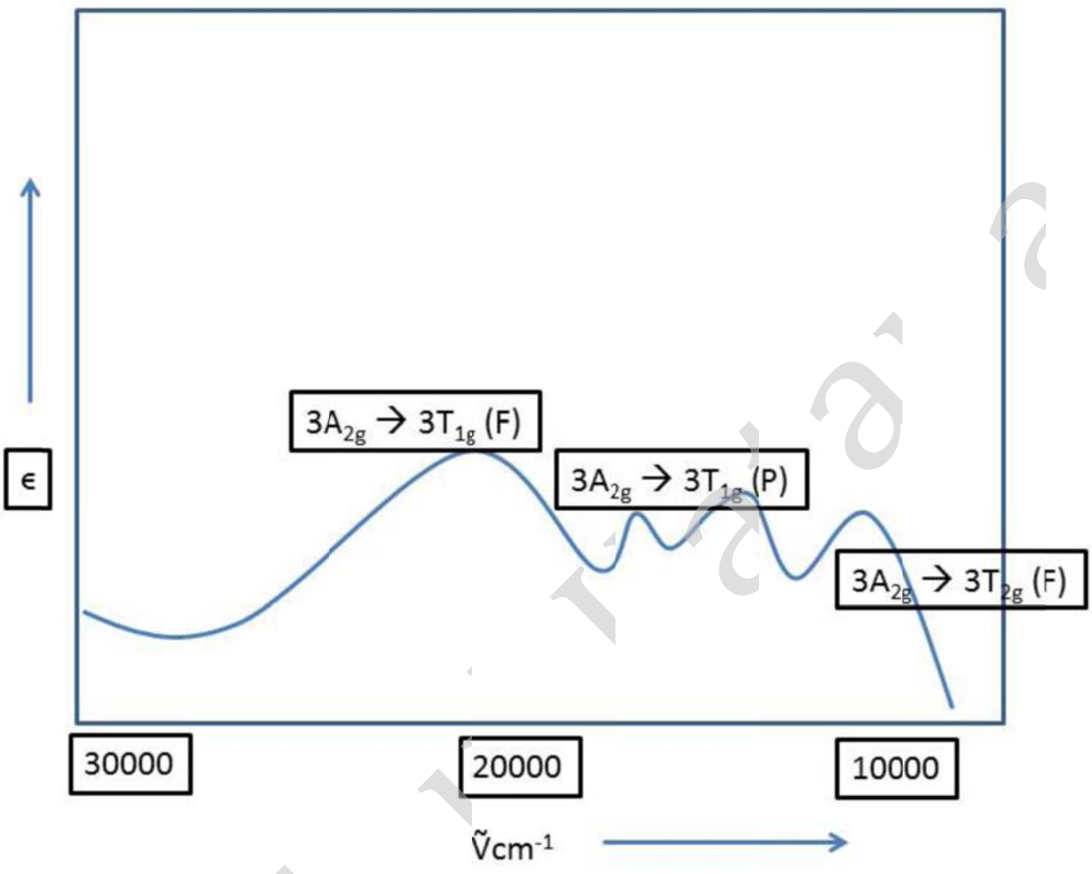


Absorption spectrum of Ni^{2+}

- Ni^{2+} exist as $[Ni(H_2O)_6]^{2+}$ and green in colour.
- Range of spectrum is 50000 to 8000 cm^{-1}.
- Main peak is at 25300 cm^{-1}.
- Shoulder peak is at 14500 cm^{-1}.
- The spectral terms for d8 system are ^3F, ^3P, ^1D and ^1S.
- ^3F is ground state term and ^3P is term for next excited term.



$3A_{2g} \rightarrow 3T_{1g}$ (F)	25300 cm^{-1}
$3A_{2g} \rightarrow 3T_{1g}$ (P)	14500 cm^{-1}
$3A_{2g} \rightarrow 3T_{2g}$ (F)	8700 cm^{-1}



Important Questions

- Explain Jahn-Teller effect in detail.
- Explain Orgel diagram.
- Explain Laporte rule.
- Explain absorption spectra on Ni^{2+}, Cu^{2+} and Ti^{3+}.
- Explain hole formalism.

I have work hard preparing this material……

You also work hard preparing from this material!!!!

Best Luck….