

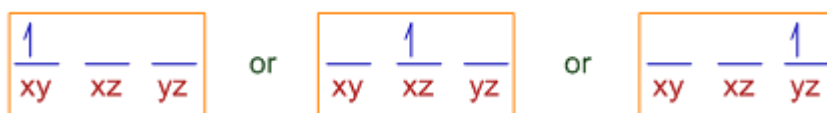
Jahn Teller Distortion

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What is electronically degenerate state?

An electronically degenerate state represents the availability of more than one degenerate orbitals for an electron. In this condition the degenerate orbitals are said to be asymmetrically occupied.

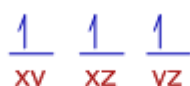
E.g. In octahedral symmetry, the d^1 configuration is said to be electronically degenerate since three t_{2g} orbitals with same energy are available for the electron to occupy. In this condition, the degenerate orbitals are also said to be asymmetrically occupied by electrons.



Electronically degenerate state of d^1 configuration.

The lone electron may occupy any of the degenerate t_{2g} orbitals.

Whereas the d^3 configuration in octahedral geometry is non-degenerate and symmetric. It is not possible to put two electrons in one orbital, which is against of Hund's rule of maximum multiplicity.



Only one arrangement for d^3 configuration is possible according to Hund's rule.

In the electronically degenerate state, the orbitals are said to be asymmetrically occupied and hence get more energy. Therefore, the system tries to get rid of extra energy by lowering the overall symmetry of the molecule i.e., undergoing distortion, which is otherwise known as **Jahn Teller distortion (effect)**.

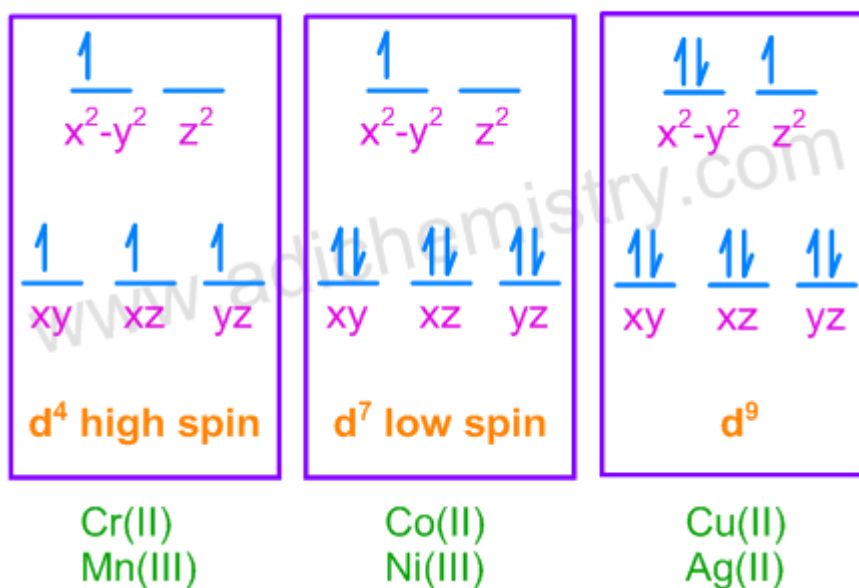
E.g. In case of octahedral d^9 configuration, the last electron may occupy either d_{z^2} or $d_{x^2-y^2}$ orbitals of e_g set. If it occupies d_{z^2} orbital, most of the electron density will be concentrated between the metal and the two ligands on the z axis. Thus, there will be greater electrostatic repulsion associated with these ligands than with the other four on xy plane. This asymmetric distribution of the electron density may increase the overall energy of the system. To get rid of this, the complex suffers elongation of bonds on z-axis and thus lowers the symmetry.

Conversely, occupation of the $d_{x^2-y^2}$ orbital would lead to elongation of bonds along the x and y axes.

* The Jahn Teller effect is mostly observed in octahedral environments. Theoretically, the electronic degeneracy in octahedral symmetry is possible in all the configurations except d^3 , d^8 , d^{10} , high spin d^5 , and low spin d^6 configurations.

However, considerable distortions are usually observed in **high spin d^4** , **low spin d^7** , and **d^9** configurations in the octahedral environment. It is because the Jahn Teller distortion is usually significant for asymmetrically occupied e_g orbitals since they are directed towards the ligands and the energy gain is considerably more.

Configurations with significant JT distortions

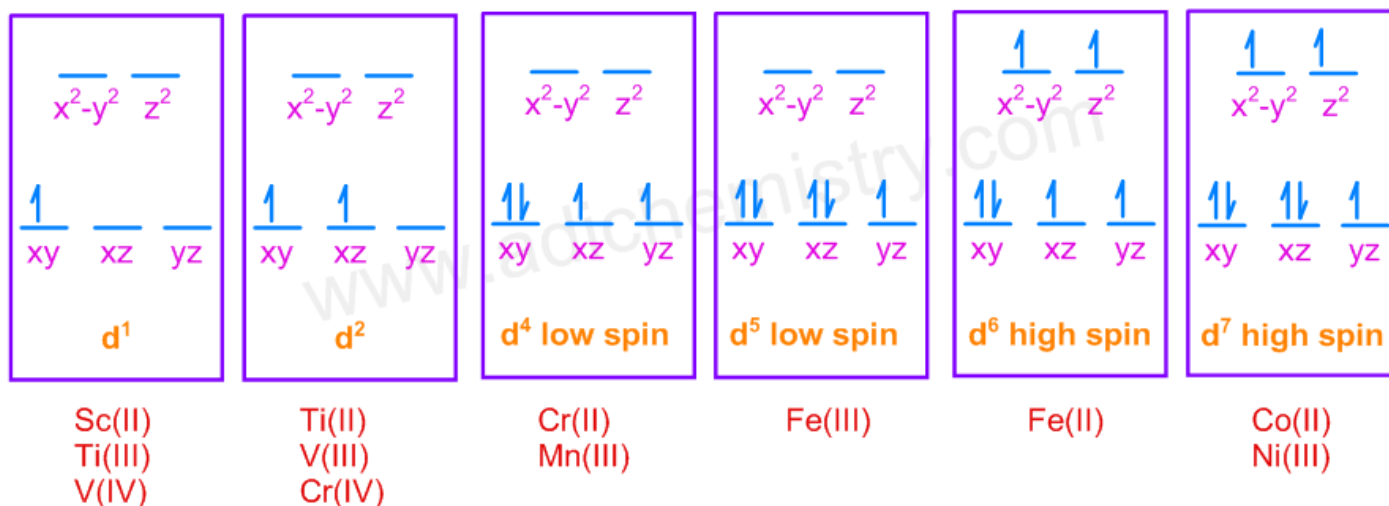


* In case of unevenly occupied t_{2g} orbitals, the Jahn Teller distortion is very weak since the t_{2g} set does not point directly at the ligands and therefore the energy gain is much less.

E.g. d^1 ; d^2 ; low spin d^4 & d^5 ; high spin d^7 & d^7 configurations.

Because of same reason, the *tetrahedral complexes also do not exhibit Jahn-Teller distortion*. Again, in this case also the ligands are not pointing towards the orbitals directly and hence there is less stabilization to be gained upon distortion.

Configurations showing weak JT distortions



The degeneracy of orbitals can be removed by lowering the symmetry of molecule. This can be achieved by either elongation of bonds along the z-axis (Z-out distortion) or by shortening the bonds along the z-axis (Z-in distortion). Thus an octahedrally symmetrical molecule is distorted to tetragonal geometry.

Z-out Jahn-Teller distortion: In this case, the energies of d-orbitals with z factor (i.e., d_{z^2} , d_{xz} , d_{yz}) are *lowered* since the bonds along the z-axis are elongated. This is the most preferred distortion and occurs in most of the cases, especially when the degeneracy occurs in e_g level.

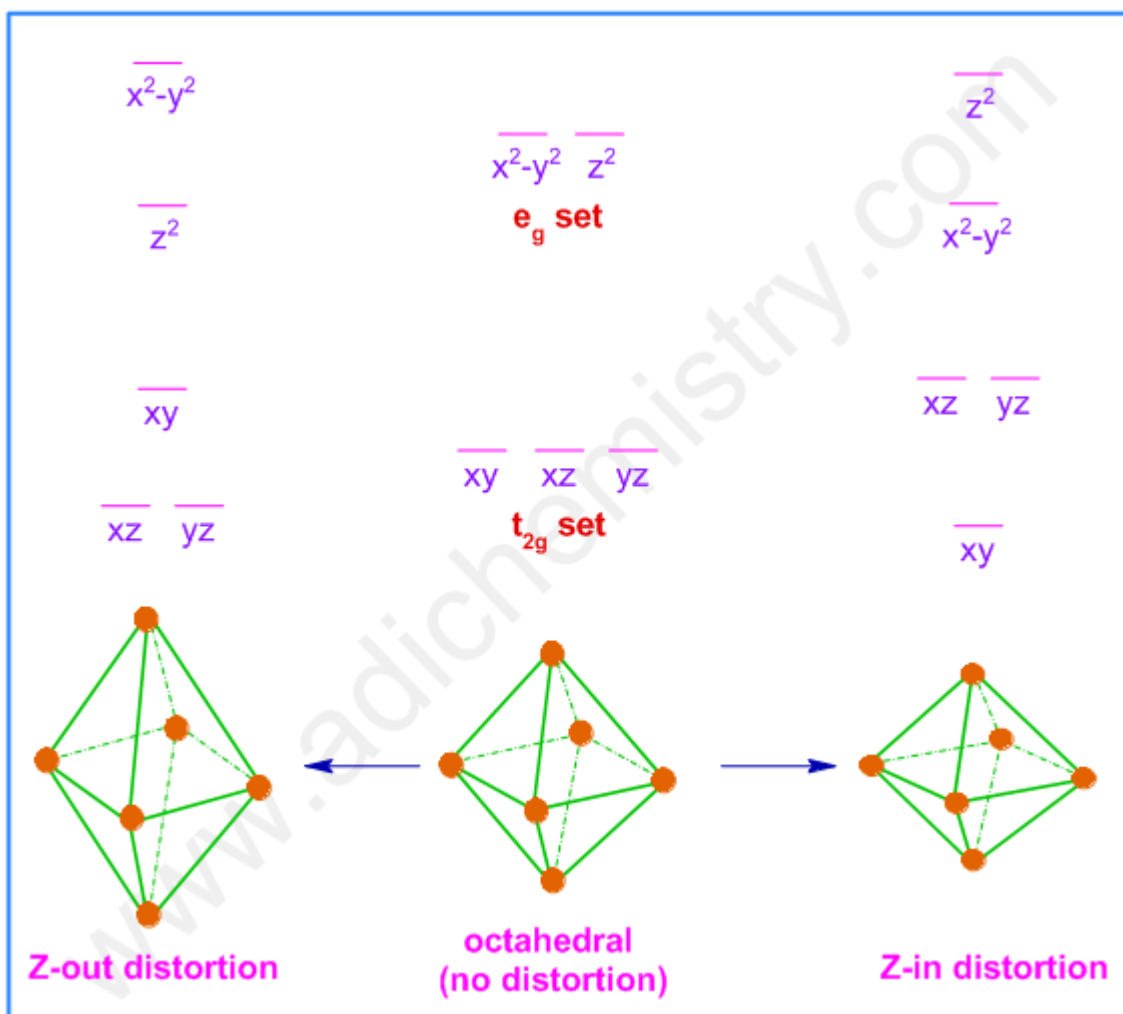
E.g. Usually the octahedral d^2 , d^4 high spin, d^7 low spin, d^8 low spin & d^9 configurations show the z-out distortion.

Theoretically it is not possible to predict the type of distortion that occurs when the degeneracy occurs in e_g level. However it is observed that z-out distortion is more preferred.

Z-in Jahn-Teller distortion: In this case the energies of orbitals with z factor are *increased* since the bonds along the z-axis are shortened. This type of distortion is observed in case of octahedral d^1 configuration. The only electron will now occupy the d_{xy} orbital with lower energy.

E.g. The octahedral d^1 configurations like Ti(III) in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ can show z-in distortion (theoretically?). In this case, the z-out distortion do not remove the degeneracy since even after distortion there are still two degenerate orbitals i.e., d_{xz} and d_{yz} available for the electron to occupy. See the following diagram.

Also remember that the Jahn-Teller theorem does **NOT** predict how large a distortion should occur.



Static Jahn-Teller distortion: Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. It is observed when the degeneracy occurs in e_g orbitals. Hence the distortion is strong and permanent.

Dynamic Jahn-Teller distortion: In some molecules, the distortion is not seen either due to random movements of bonds which does not allow the measurement within a time frame or else the distortion is so weak as to be negligible. However, the distortion can be seen by freezing the molecule at lower temperatures. This condition is referred to as dynamic Jahn-Teller distortion.

E.g.

1) The complexes of the type $M_2PbCu(NO_2)_6$ show dynamic Jahn-Teller distortion.

Here, $M = K, Rb, Cs, Tl$;

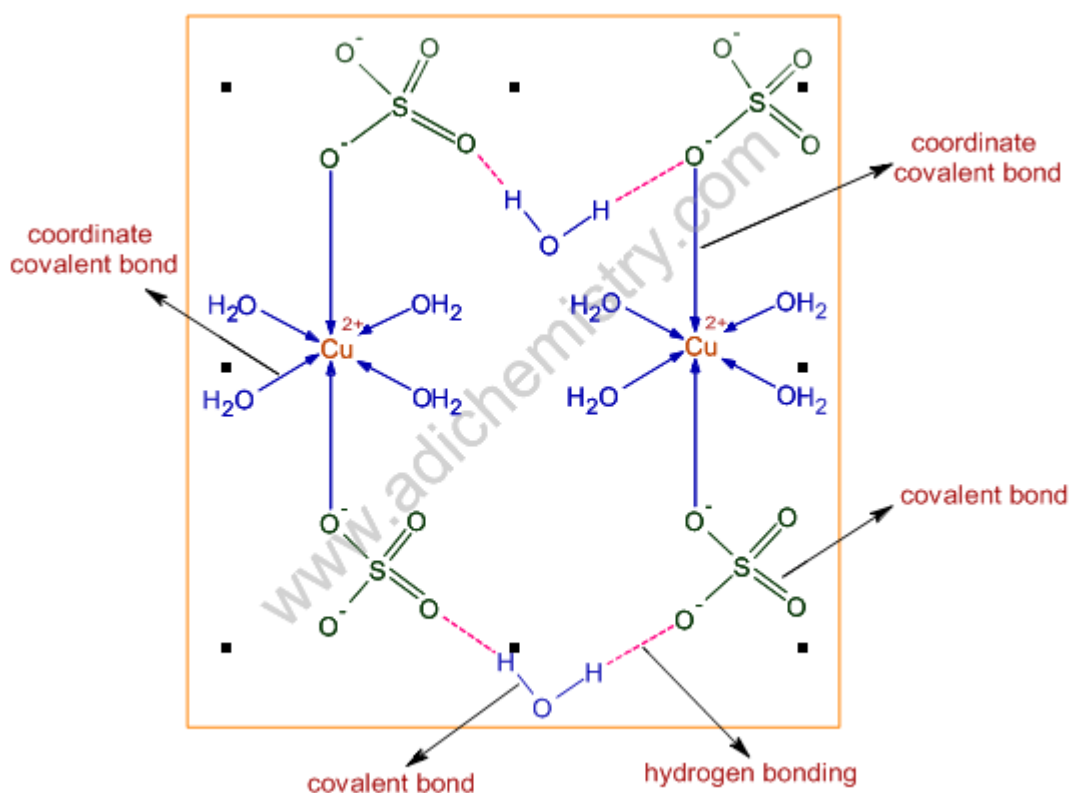
They show tetragonal symmetry at lower temperatures due to static Jahn-Teller distortion. But at higher temperatures, these molecules appear octahedral due to the dynamic Jahn-Teller effect.

2) The complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ shows dynamic Jahn-Teller distortion and appears octahedral. In this case, the distortion is small since the degeneracy occurs in t_{2g} orbitals. Remember Fe^{2+} in above complex is a high spin d^6 system with $t_{2g}^4 e_g^2$ configuration.

1) Jahn-Teller distortion in complexes formed by Cu(II) ions:

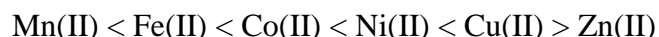
a) **Tetragonal structure of Cu(II) complexes:** The Cu(II) ion is a d^9 system and expected to show Jahn-Teller distortion and depart considerably from octahedral geometry. The Cu(II) ion in the *aqueous medium* is surrounded by six water molecules in tetragonal geometry i.e., four of which are at the corners of square plane and are at shorter distances with stronger interactions, whereas, the remaining two are weakly interacting with the metal ion at distant axial positions.

b) **Structure of hydrated copper(II) sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and other Cu(II) complexes:** In the *solid* $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, the copper ion is surrounded by four water molecules in square planar geometry. There are also weak interactions with the sulphate ions in the axial positions. The 5th water molecule is hydrogen bonded to the sulphate ion. That means the two water molecules on the axial positions are completely eliminated and substituted by sulphate ions while forming the solid.



Note: Due to interactions with these ligands, the d orbitals are split into different energy levels, which makes d-d transitions possible. It absorbs red color and transmits blue color during the d-d transition. But upon heating, all the water molecules are lost, which makes all the d orbitals degenerate again. Hence the anhydrous CuSO_4 is colorless.

c) Extra stability of Cu^{2+} ions: The relative stabilities of complexes formed by high spin divalent first row transition metal ions is given by Irving-Williams series. The stability order is shown below:



The extra stability of Cu(II) ion can be explained by taking into account of Jahn-Teller distortion of this d^9 ion.

d) Other examples: Because of Jahn-Teller distortion:

* In the crystalline KCuF_3 , the two Cu-F distances are at 1.96 \AA and the remaining four Cu-F distances are at 2.07 \AA . It is a case of Z-compression.

* In $[\text{Cu}(\text{hfacac})_2(\text{bipy})]$, there are two short Cu-O bonds and two long Cu-O bonds. (where hfacac = hexafluoroacetylacetonate anion; bipy = 2,2'-bipyridine). It is an example for Z-out distortion.

* Cu(II) cannot form $[\text{Cu}(\text{en})_3]^{2+}$ since JT distortion brings strain into the ethylene diamine molecule that is added along z-axis. Hence only $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ is formed.

2) The splitting of absorption bands in the UV-VIS spectra of complexes due to Jahn-Teller distortion:

E.g. The absorption band in the electronic spectrum of aqueous Ti(III) , a d^1 octahedral system, is not symmetric but rather shows a distinct broad shoulder. It is because of Jahn-Teller distortion.

The Jahn-Teller distortion is negligible in case of degenerate t_{2g} orbitals in the ground state. Hence no distortion in the ground state. But when the electron gets excited, the configuration now becomes $t_{2g}^0 e_g^1$, which is again degenerate. Hence in the excited state, the Jahn Teller distortion is possible. Now the promotion of electron may occur to either of the two non degenerate e_g orbitals, the d_{z^2} and $d_{x^2-y^2}$. Thus, two transitions are possible. But a shoulder appears since the energy difference between two transitions is small.

3) Coordinatively labile nature of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ & $[\text{Co}(\text{NH}_3)_6]^{2+}$:

The $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ undergoes substitution easily since the Cr(II) ion is a high spin d^4 system with one electron in the e_g orbital. Hence it is electronically degenerate and shows Jahn-Teller distortion. Hence the hydrated Cr(II) ion is coordinatively labile.

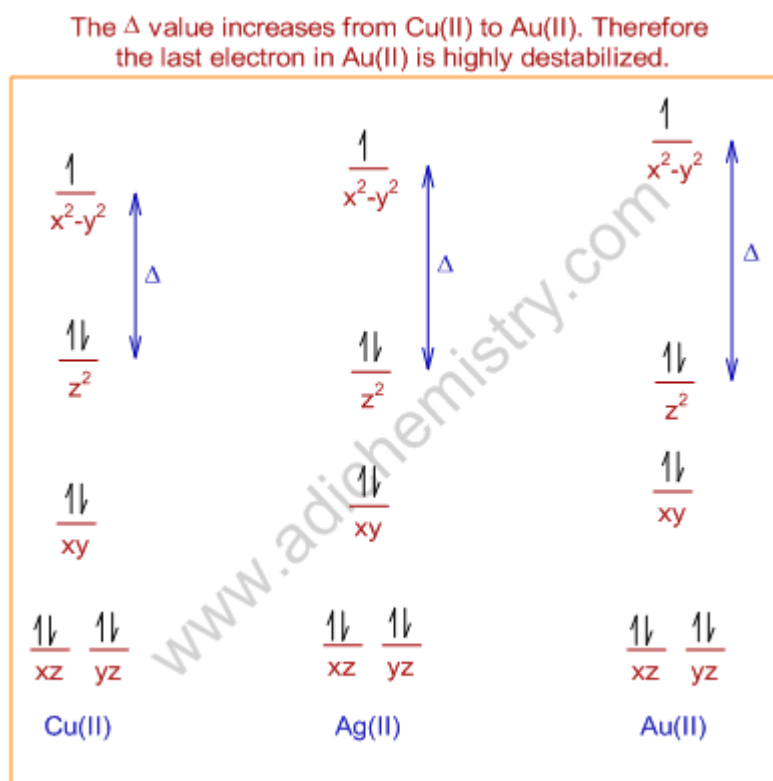
On the same lines, the easy substitution of $[\text{Co}(\text{NH}_3)_6]^{2+}$ by water molecules can be explained. In this case the Co(II) ion is coordinatively labile since it is a low spin octahedral d^7 ion which is degenerate in e_g set. Hence it undergoes J-T distortion and is labile.

4) Disproportionation of Au(II) salts:

Au(II) ion is less stable and undergoes disproportionation to Au(I) and Au(III) even though the Cu(II) and Ag(II) ions are comparatively more stable. One may expect same stability since all are d^9 systems and undergo the Jahn-Teller distortion.

However, the Δ value increase down the group. Hence, in Au(II) ion, it reaches a maximum, which causes high destabilization of the last electron, which is now occupying the $d_{x^2-y^2}$. This makes Au(II) reactive, which may undergo either oxidation to Au(III) , a d^8 system or reduction to Au(I) , a d^{10} system.

The d^8 system, Au(III) is stable as the electron from the $d_{x^2-y^2}$ is removed. Mostly it prefers square planar geometry and more stable than both Au(II) and Au(I). The d^{10} system, Au(I) favors mostly linear geometry with coordination number = 2.



Question-Why do the d^9 systems usually **not** undergo complete distortion to square planar geometry?

Answer: Usually, the d^9 systems are tetragonal with elongated bonds on z-axis and do not undergo complete distortion to square planar. It is because the last electron will be placed in highly destabilized $d_{x^2-y^2}$ if they get square planar geometry. But the low spin d^8 complexes may undergo complete distortion to square planar geometry.

Question-1: Which metal complex ion is expected to be subject to a Jahn-teller distortion?

- A) Cu^{2+}
- B) Ni^{2+}
- C) Ca^{2+}
- D) Cr^{3+}

Answer: A

Question-2: Which of the following does not show octahedral geometry,

- 1) $[\text{Cu}(\text{CN})_4]^{2-}$
- 2) XeF_4
- 3) $[\text{NiCl}_4]^{2-}$

4) All

Answer: 4

Question-3: Strong Jahn-teller distortion is not observed for octahedral complexes of:

- 1) Cu^{2+}
- 2) Low spin Cr^{2+}
- 3) High spin Mn^{3+}
- 4) High spin Cr^{2+}

Answer: 2

Question-4: Which of the following shows strong Jahn teller distortion?

- 1) Fe^{3+}
- 2) High spin Co^{2+}
- 3) Ti^{2+}
- 4) Low spin Co^{2+}

Answer: 4

Question-5: Jahn teller effect is not observed in high spin complexes of:

- A) Mn^{2+}
- B) Cr^{2+}
- C) Cu^{2+}
- D) Fe^{3+}

Answer: A

Question-6: Which metal complex ion is expected to be subject to a Jahn teller distortion?

- 1) Low spin Co^{2+}
- 2) High spin Cr^{2+}
- 3) Ti^{2+}
- 4) All

Answer: 4

Question-7: Which of the following d-configuration shows strong distortion from octahedral geometry?

- 1) d^1
- 2) d^2

3) d^9

4) None

Answer: 3

Question-8: Why does the absorption spectrum of aqueous $[\text{Ti}(\text{OH}_2)_6]^{3+}$ exhibit a broad band with a shoulder?

1) Due to Jahn-Teller distortion in the ground state

2) Due to Compton effect

3) Due to Jahn-Teller distortion in the excited state

4) Due to square planar geometry

Answer: 3