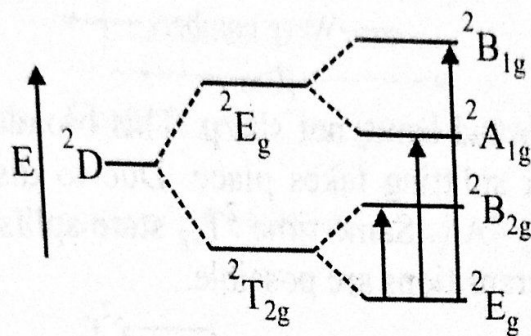
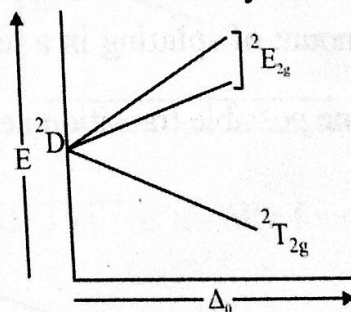


Spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: The absorption band in spectra of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is broad because of **John-Teller Distortion** which splits ${}^2\text{E}_g$ state into ${}^2\text{A}_{1g}$ and ${}^2\text{B}_{1g}$. This splits ground state ${}^2\text{T}_{2g}$ into ${}^2\text{E}_g$ and ${}^2\text{B}_{2g}$ also in some extent.

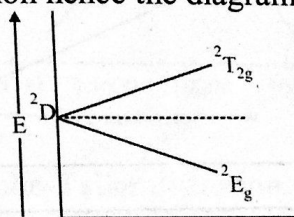


In complex ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorption maximum observed at 20300 cm^{-1} and also the absorption maximum has a shoulder at 17400 cm^{-1} because of John-Teller Distortion. The shoulder is responsible for broad band.

It has also been suggested that the electronic excited state of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has the configuration $t_{2g}^0 e_g^1$ and so in the excited state of complex e_g orbitals are electronically degenerate. Therefore the single electronic transition is really the superposition of two transitions, one from an octahedral ground state ion to an octahedral excited state ion and a lower energy transition from an octahedral ground state ion to a lower energy tetragonally distorted excited state ion. Since these transitions have slightly different energies, therefore the bands overlap one another and can not be resolved. Thus unresolved superimposed band results in an asymmetric broad band.

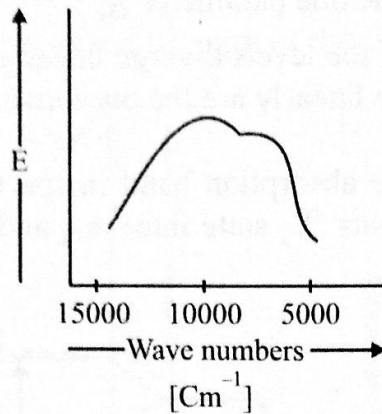


Spectra of d^9 octahedral Complex: In octahedral d^9 complexes the term 2D splitted into 2E_g and ${}^2T_{2g}$. In d^9 octahedral a hole may be considered in e_g orbital. When transition takes place hole moves from e_g to t_{2g} . This is similar to electron transition i.e. ${}^2T_{2g} \leftarrow {}^2E_g$. However hole and electron as moves in opposite direction hence the diagram of d^9 will be inverse of d^1 .

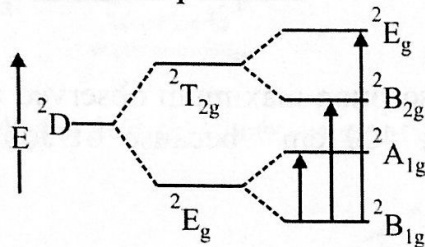


Note: Hence it can be concluded that the Orgel diagrams of d^n and d^{10-n} are inversely related.

Spectra of $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$: The $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$ complex show absorption in visible region at 12000 cm^{-1} and complex is of blue coloured.

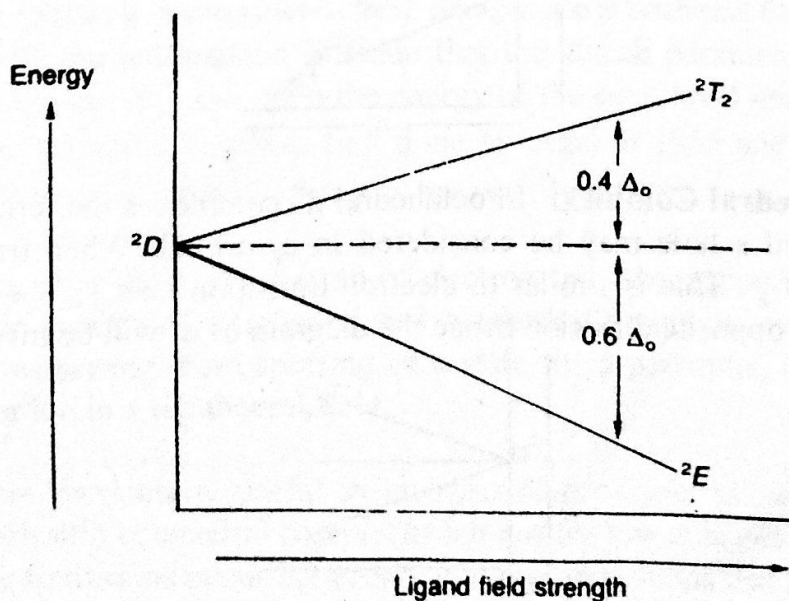


The complex show, intact a broad band, not sharp. This broadening can be explained on the basis that in d^9 system John-Teller splitting takes place. Due to distortion 2E_g states splits into lower energy ${}^2B_{1g}$ and higher energy ${}^2A_{1g}$. Same time ${}^2T_{2g}$ state splits into lower energy ${}^2B_{2g}$ and higher energy 2E_g . Hence now three transitions are possible.



As the splitting is poor, the three absorption bands overlap together showing broad band.

The effect of a tetrahedral ligand field is now considered, the degenerate d orbitals split into two e_g orbitals of lower energy and three t_{2g} orbitals of higher energy. The energy level diagram for d^1 complexes in a tetrahedral field is the inverse of that in an octahedral field, and is similar to the d^9 octahedral case, except that the amount of splitting in a tetrahedral field is only about $\frac{4}{9}$ of that in an octahedral field. There is only one possible transition i.e. ${}^2T_2 \leftarrow {}^2E$



Splitting of energy levels for d^1 configuration in tetrahedral field

Spectra of d^9 in Tetrahedral: In tetrahedral complex of d^9 , the splitting is reverse of d^9 octahedral. The ground state term is 2D which splits into lower 2T_2 and higher 2E . Only one transition is possible.

