Electronic spectra of d^2 – octahedral complexes:

Before discussing the detailed description of orgel diagram for many electron system, it is important to note some more concept about the orgel diagram.

After quantum mechanical calculation, it has been found that

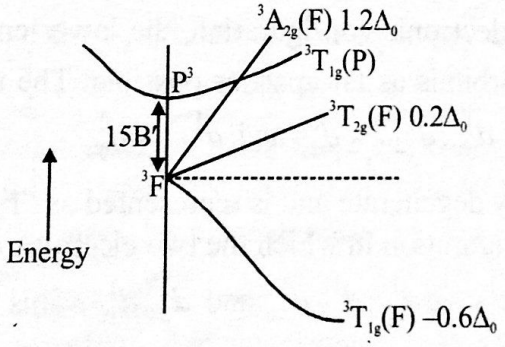
$$E(^3T_{1g}(F)) = -0.6\Delta_0$$

$$E(^3T_{2g}(F)) = 0.2\Delta_0$$

$$E(^3A_{2g}(F)) = 1.2\Delta_0$$

Transitions from $^3T_{1g}$ ground state to any of the singlet states are spin forbidden. Therefore only three absorption bands may appear in spectrum of $[V(H_2O)_6]^{3+}$.

The separation between the ground state $^3T_{1g}$ (F) and the excited states $^3T_{2g}$, $^3A_{2g}$ and $^3T_{1g}$(P) increase with increase in ligand field strength. Thus as the ligand field strength increases, the transitions require higher energies and the absorption bands shift towards the UV region.



Orgel diagram for d^2 octahedral complexes

For $[V(H_2O)_6]^{3+}$ which is a d^2 complex shows only two absorption bands in the visible region corresponding to ${}^3T_{2g} \leftarrow {}^3T_{1g}$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}$ at 17200 cm^{-1} and 25700 cm^{-1} respectively. Theoretically three transition are possible, then why are we getting only two?

This behaviour can be explained by taking into account the concept of cross over point. At or near the cross over point two bands viz ${}^3A_{2g} \leftarrow {}^3T_{1g}$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}$ can overlap each other and thus only two bands are observed. Here v_1 corresponds to ${}^3T_{2g} \leftarrow {}^3T_{1g} = 17200\ cm^{-1}$

Energy of ${}^3T_{2g} \leftarrow {}^3T_{1g} = 17200\ cm^{-1}$

$$0.2\Delta_0 - (-0.6\Delta_0) = 17200\ cm^{-1}$$

$$0.8\Delta_0 = 17200$$

$$\Delta_0 = \frac{17200}{0.8} = 21500\ cm^{-1}$$

Note: In many cases it has been found that the energy of ${}^3T_{1g}(F)$ is not equal to $-0.6\Delta_0$; it further reduces due to phenomenon of configuration interaction. In such case we can do our calculation by putting.

$$E({}^3T_{1g}(F)) = -0.6\Delta_0 - x$$

Similarly, $v_2 = 25200\ cm^{-1}$; which corresponds to the transition between ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$

Unfortunately when third band can not be observed, in such cases a more complicated analysis is required, which will be discussed in Tanabe-Sugano diagram.

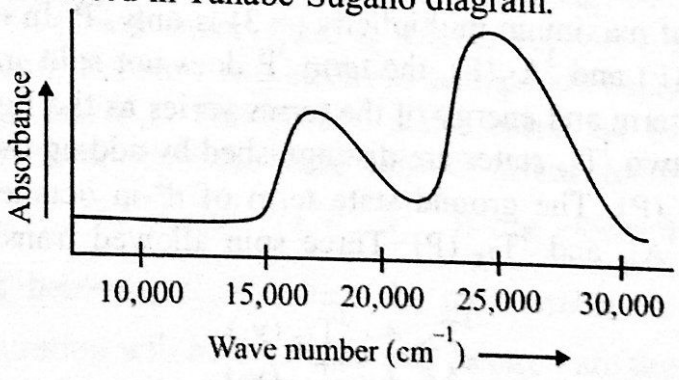


Fig. Absorption spectra for $[V(H_2O)_6]^{3+}$