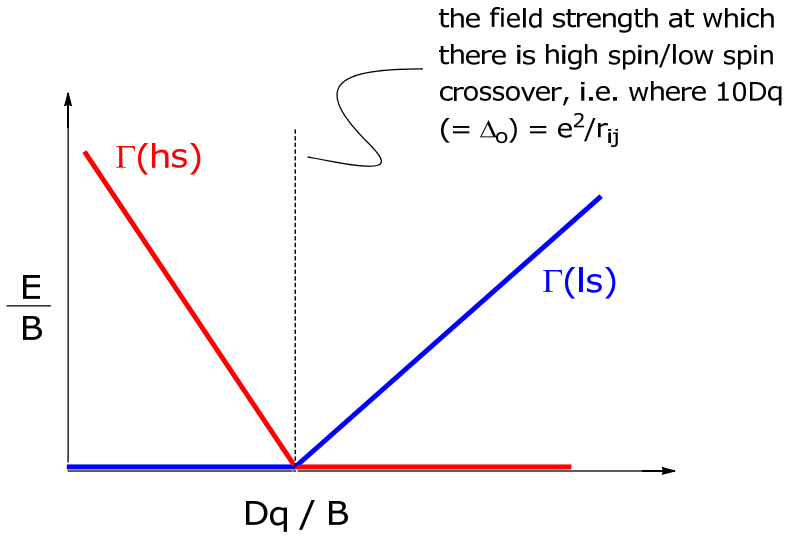
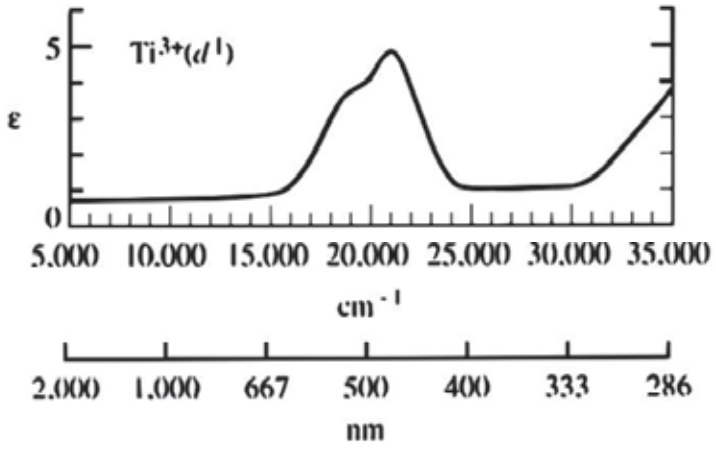
5.04, Principles of Inorganic Chemistry II
Prof. Daniel G. Nocera
Lecture 4 May 11: Tanabe Sugano Diagrams

A Tanabe-Sugano (TS) diagram plots the energy dependence of the various ligand field states (or terms) with field strength. The strength of the ligand field is defined by Dq, which is related to the octahedral crystal field splitting by 10Dq = Δ_o. The energy of the state is given by E. Both the state term energy and field strength are normalized to B, where B is a measure of the two-electron energy. The lowest energy term is set = 0, and all other states are defined energetically relative to the ground state. For d^n counts that can be high or low spin (d^4-d^7), there will be a discontinuity in the TS diagram at the ligand field strength at which there is crossover from high spin to low spin.

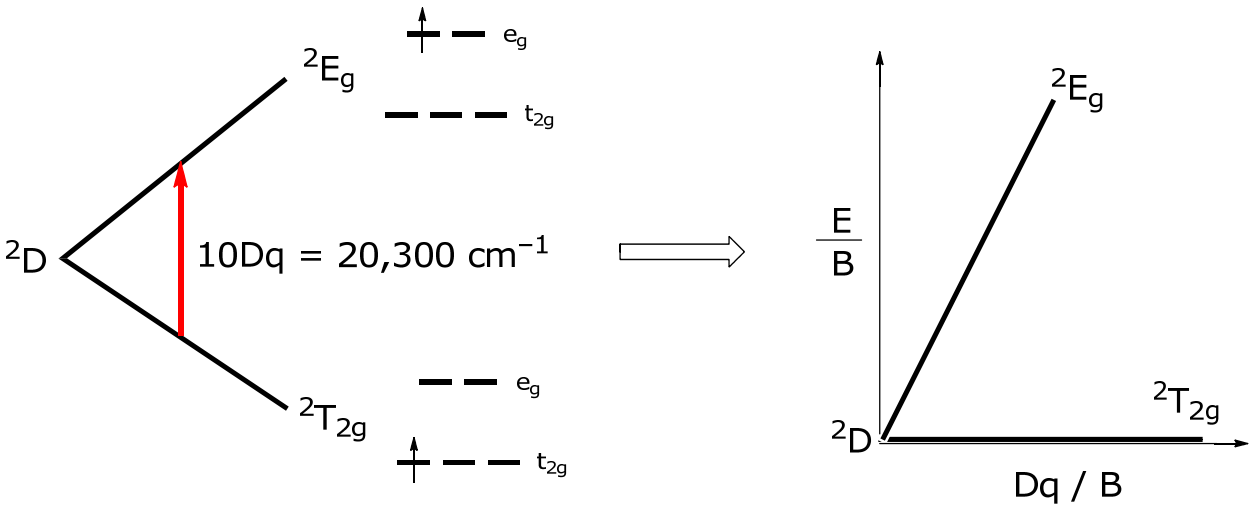


Let's consider electronic spectra of aquo complexes of first row TMs:

d^1, Ti^{3+} (λ_{max} = 20,300 cm^{-1}, $\varepsilon \sim 4$ M^{-1} cm^{-1})

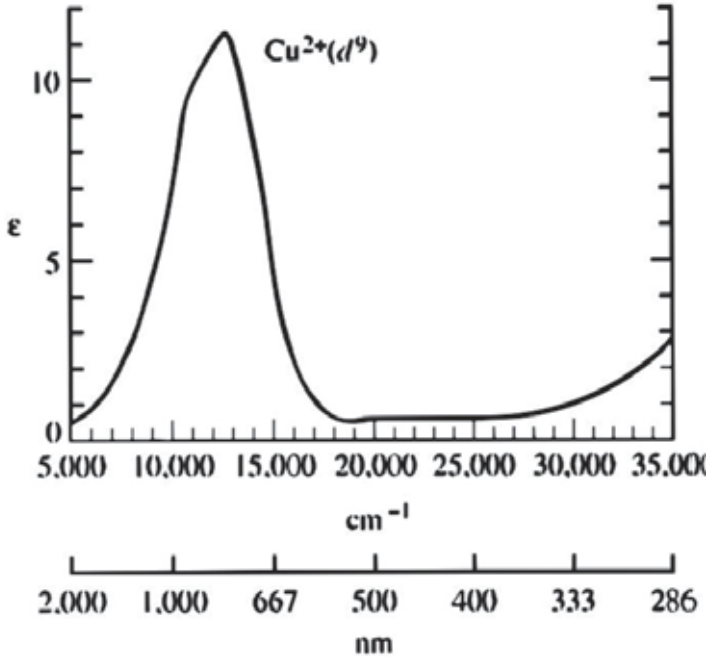


only one transition; the shoulder in the spectrum is due to $Ti(H_2O)_5(OH)^{2+}$

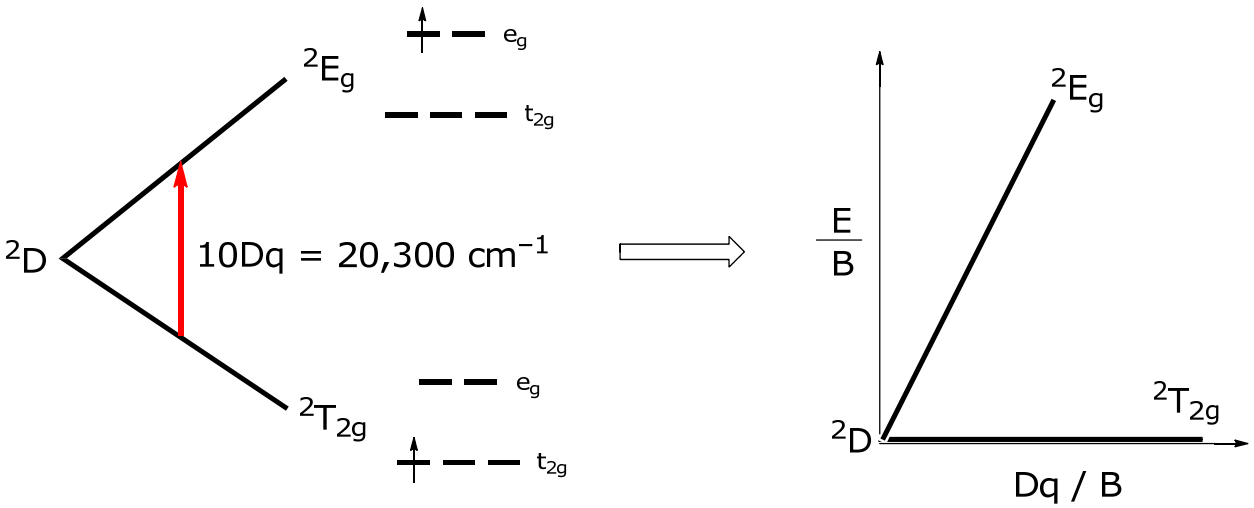


$\frac{E}{B}$ = 10 Dq = 20,300 cm^{-1}, Dq = 2,030 cm^{-1}

d^9, Cu^{2+} (λ_{max} = 12,000 cm^{-1}, $\varepsilon \sim 11\ M^{-1}\ cm^{-1}$)

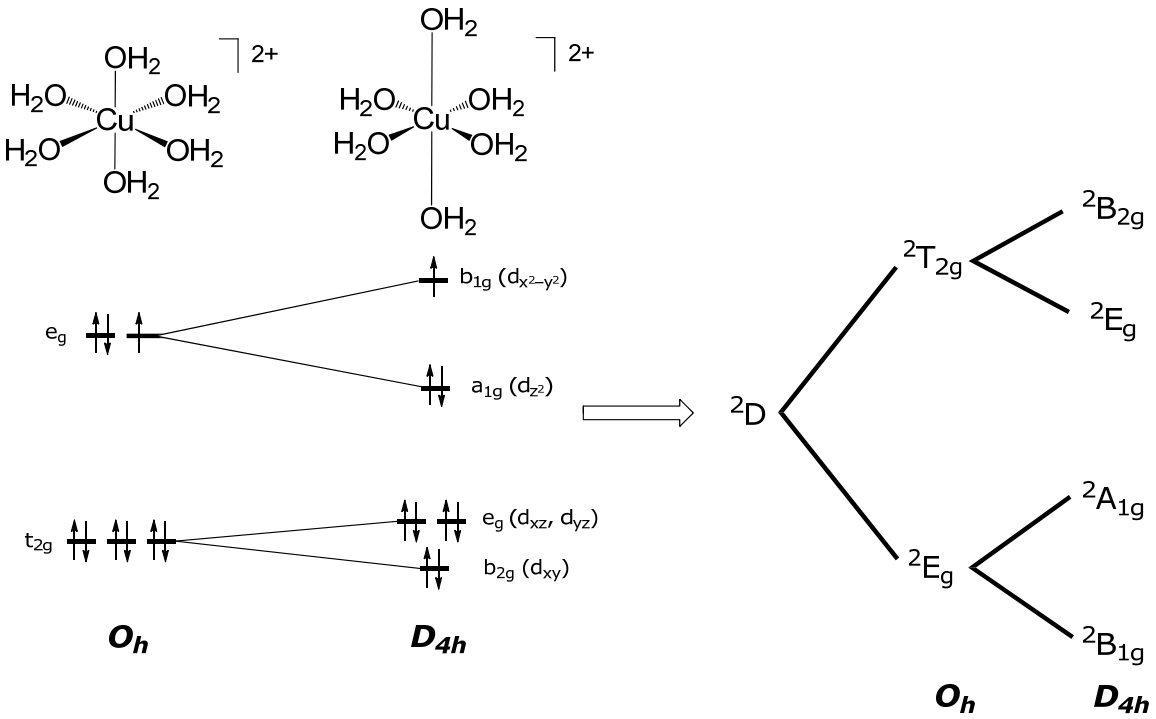


As with d^1 ion, for the d^9 ion, expect only one band, but clearly there is a shoulder. This due to a Jahn-Teller distortion (vide infra)



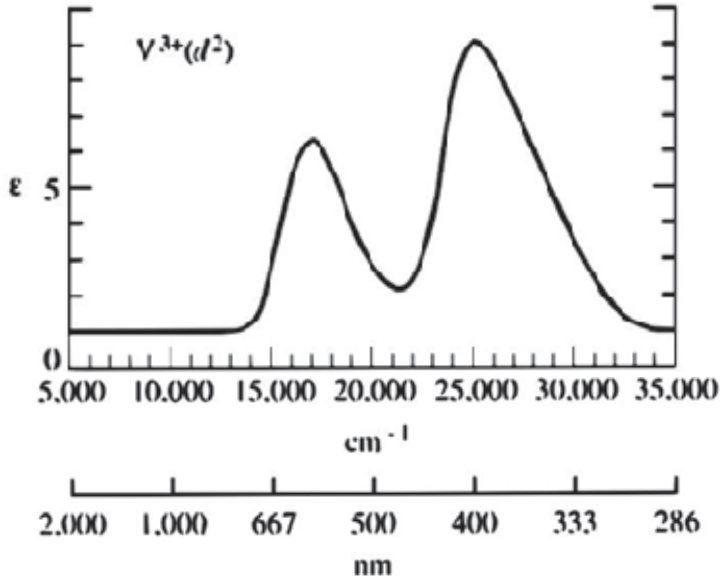
$$\frac{E}{B} = 10\ Dq = 12{,}000\ cm^{-1},\ Dq = 1{,}200\ cm^{-1}$$

The shoulder on the Cu^{2+} absorption band arises from a Jahn-Teller distortion. **Jahn-Teller** effect - a molecule with an orbitally degenerate ground state will distort to remove the degeneracy and consequently lower its overall energy. In the case of $Cu(H_2O)_6^{2+}$, the molecule can axially elongate or compress to remove the degeneracy of the ground state ($O_h \rightarrow D_{4h}$). The JT effect does not say if elongation or compression will occur, only that here will be a distortion. Analyzing $Cu(H_2O)_6^{2+}$ for an axial elongation (note, there will be an equatorial compression since energy cannot be created or destroyed in the distortion),

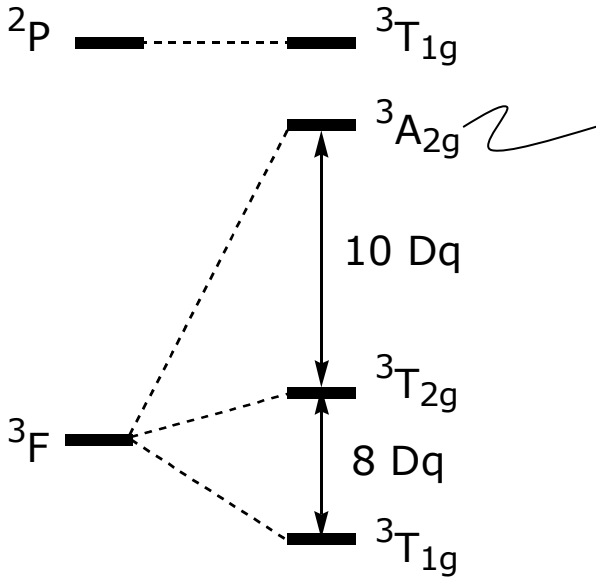


Generally, the JT effect is most pronounced when M–L σ* orbitals are involved. This is why the JT distortion is observed in Cu^{2+} but not in Ti^{3+}, where the JT distortion arises from orbitals which are non-bonding.

d^2, V^{3+} (λ_{max} = 17,200 cm^{-1}, $\varepsilon \sim 6\ M^{-1}\ cm^{-1}$; λ_{max} = 25,600 cm^{-1}, $\varepsilon \sim 8\ M^{-1}\ cm^{-1}$)



From the d^2 configuration, get terms of ^3F, ^1D, ^3P, ^1G and ^1S. Note that spin allowed transitions ($\Delta S = 0$) will prevail (i.e., be the most intense). Thus we will assume that the two transitions observed in the above absorption spectrum arise from the ^3F and ^3P states since the ^3F is the ground state.



this corresponds to a $2e^-$ transition, therefore transitions to this state should be exceptionally weak (due to low absorption cross-section… i.e. isospatial and isotemporal absorption of the two photons needed for the two-electron promotion is very unlikely)

Accordingly, the most reasonable assignments therefore are,

$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ ⟹ 25,600 cm^{-1} transition

$^3T_{1g}(F) \rightarrow {}^3T_{2g}(P)$ ⟹ 17,200 cm^{-1} transition

Note, in a TS diagram, the energy of the transition is not plotted — the transition energy is normalized to B. Thus the transition cannot be fit directly on the TS diagram. However, by taking a ratio of the two transitions, B can be eliminated:

$$\frac{\frac{E\left({}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)\right)}{B}}{\frac{E\left({}^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)\right)}{B}} = \frac{E\left({}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)\right)}{E\left({}^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)\right)} = \frac{25{,}600}{17{,}200} = 1.49$$

From the TS diagram, this ratio of 1.49 is best fit at Dq/B = 2.8 (see next page). At this value of Dq/B, the E/B values for the two states are:

$$\frac{E\left({}^3T_{2g}(F)\right)}{B} = 25.9 = \frac{17{,}200\ cm^{-1}}{B} \quad \text{or} \quad B = 664\ cm^{-1}$$

$$\frac{E\left({}^3T_{1g}(P)\right)}{B} = 38.7 = \frac{25{,}600\ cm^{-1}}{B} \quad \text{or} \quad B = 661\ cm^{-1}$$

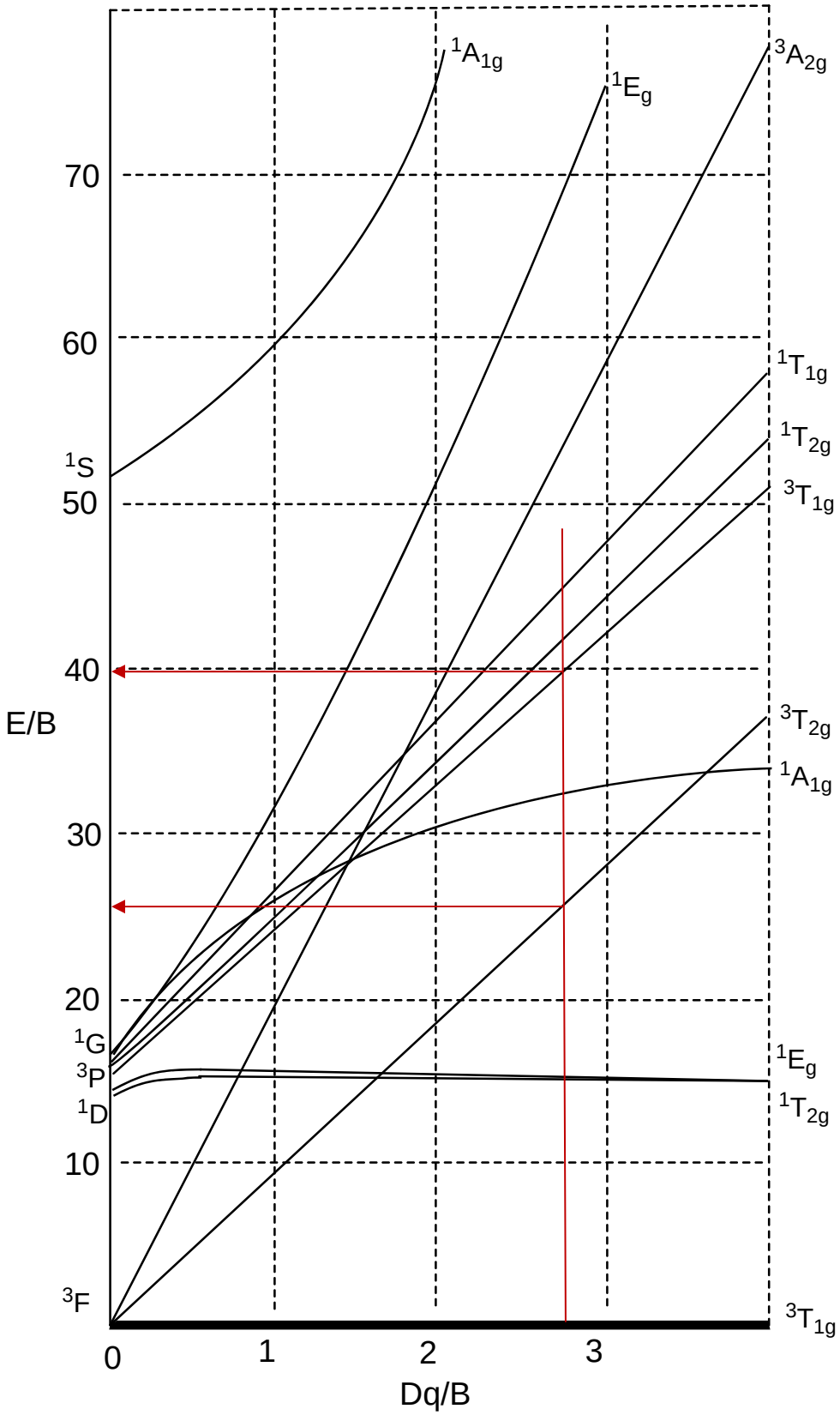
$$B_{avg} = 663\ cm^{-1}$$

With B in hand, Dq may now be evaluated,

$$\frac{Dq}{B} = 2.8 \qquad Dq = 2.8(B) = 2.8(663\ cm^{-1}) = 1{,}860\ cm^{-1}$$

Therefore, $10Dq = \Delta_o = 18{,}600\ cm^{-1}$

d^2 TS diagram



From the fit Dq and B values, may now determine energies of all other transitions (including the spin for bidden ones) of $V(H_2O)_6^{3+}$. The $2e^-$ transition should fall at…

$$\frac{E\left({}^3A_{2g}(F) \leftarrow {}^3T_{1g}(F)\right)}{B} = 54 \quad \text{at} \quad Dq/B = 2.8$$

$E({}^3A_{2g}(F) \leftarrow {}^3T_{1g}(F)) = 54(B) = 54(662\ cm^{-1}) = 35800\ cm^{-1}$

Note: the B value for V^{3+} complexed by H_2O is smaller than the free ion value of 860 cm^{-1}. Remember B is a measure of the interelectronic repulsion… in the complex, the metal d orbitals mix with the ligand orbitals. Owing to the covalency, the spatial dimension of the orbitals in which the d-electrons reside increases… since operator for interelectronic repulsion goes as $\frac{1}{r_{ij}}$… as r_{ij} increases, interelectronic repulsion decreases and hence B decreases.