CHAPTER 11
SOLUTIONS TO SELECTED PROBLEMS

8. Ni^{2+} is a d^8 system. It looks like the lowest transition is not curved, therefore Δ_O should be the energy of the lowest transition, which is about 8700 cm^{-1}.

(the splitting is because of a Jahn-Teller distortion in the excited state, but that isn't particularly important)

9. (a) Cr^{3+} is d^3. From the T-S diagram the lowest energy state is not curved, therefore the lowest energy transition is Δ_O = 17 400 cm^{-1}.

(b) Ti^{3+} is d^1, therefore Δ_O is 18 400 cm^{-1}. Again, splitting is due to the J-T effect in the excited state.

(c) Ni^{2+} is d^8. By the same rationale as #8, Δ_O is 11 200 cm^{-1}.

(d) V^{3+} is d^2. The ground state is curved, so the lowest energy transition is not Δ_O, but instead the difference between the ${}^3A_{2g} \leftarrow {}^3T_{1g}$ and the ${}^3T_{2g} \leftarrow {}^3T_{1g}$ is Δ_O. Because the energy of the third peak is not known, we can't actually solve this question with the information given, because we can't be sure which peaks are the correct ones. We could follow the example in the book (pp. 402-405), but this is beyond the scope of the course.

(e) Another *d*2 ion, which we don't know how to solve (unless we follow the procedure in the book)

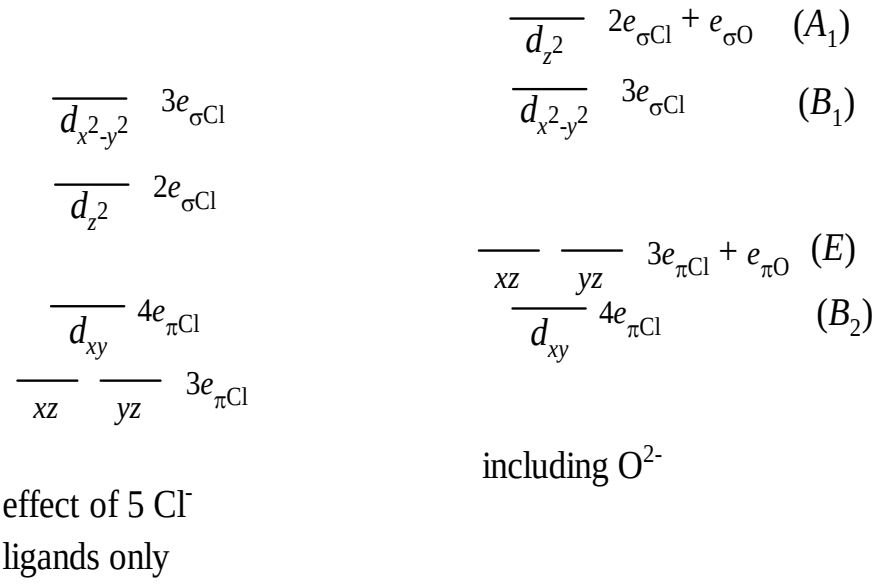
14. I has the highest-energy orbitals ($5p > 4p > 3p$), so is closest in energy to the metal orbitals. Therefore, it is the lowest energy CT-band. 4*p* is further, and 3*p* is further still, so the order is I < Br < Cl.

15. CN^- is a strong field (low spin) ligand. In $Fe(CN)_6^{3-}$, Fe is 3+, and filling in the octahedral *d*-splitting diagram gives a vacancy in both the t_{2g} and the e_g orbitals. CT can occur into either orbital (into the e_g higher in *E* because it is the higher-energy orbital). With $Fe(CN)_6^{4-}$, Fe is 2+ and therefore the t_{2g} set is full of 6 Fe electrons, so only the higher-energy e_g can accept CT electrons.

18. (a) Remember that $\mu = (N(N+2)^{½}\mu_B$, solving for N gives the # of unpaired electrons.
low temperature ($0.65\mu_B$) gives N = 0.19; high temperature ($5.2\mu_B$) gives N = 4.3.
(b) As temperature is raised, more and more electrons will want to be in the excited states. Eventually, a flip from low spin (d^6, 0 unpaired electrons) to high spin (4 unpaired electrons) takes place.

22. $Ni(NO_2)_2$ (*aq*) is actually mostly $Ni(H_2O)_6^{2+}$. H_2O is a low-field ligand, so the absorption is in the red (to make the solution appear green). NH_3 is a higher-field ligand, so the absorption moves into the orange (and the solution appears blue). Finally, en is an even stronger ligand and the absorption moves into the yellow (and sol'n appears purple). This is expected from the spectrochemical series.

16. (a) Assuming the unique axis (the M=O bond) is the *z*-axis, then position #1 contains the O^{2-} (and the Cl^-'s are located at positions 2, 3, 4, 5, 6). All are π-donors, so e_π is *added* to the orbital energies. Assuming the values of e_σ and e_π are larger for O^{2-},

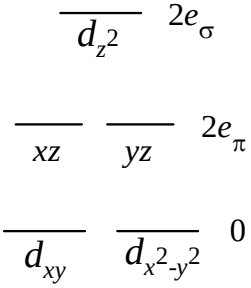


(b) From the C_{4v} character table, the orbitals have symmetries of given in the right-hand diagram above.

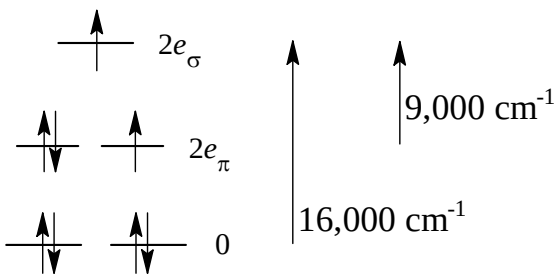
(c) These two metals are putatively 5+, and therefore d^1 metals. The transition in question is identical for the two metals (a *d*1 transition from the d_{xy} to the d_{xz} or d_{yz}). It is a rule in crystal field theory that the heavier the elements, the larger the splitting in the *d*-orbitals in the complex (*e.g.* for O_h complexes, 2nd-transition-metal series are *always* low spin, because Δ_O is always larger for a 2nd-series relative to a 1st-transition-series metal). This is caused by the fact that bonding is stronger for 2nd-transition-series metals, so the bonding/antibonding splits are larger.

19. Linear ML_2 uses positions 1 and 6. O^{2-} is a π-donor (add e_π). Assuming high-spin, Ni^{2+} is d^8.

(a)



(b) according to the reference, the two transitions are as follows:



(c) The 16 000 cm^{-1} transition is $2e_\sigma$, so e_σ = 8 000 cm^{-1}.
The distance to the $2e_\pi$ from the 0 level is 16 000 - 9000 = 7000 cm^{-1}, so e_π = 3500 cm^{-1}