

Magnetism/EPR problems -

1) If μ_{eff} for the Cu^{2+} ion at 298 K is 1.94, then what g value does the ion have?

$$g = \mu_{\text{eff}} / (S(S+1))^{1/2} = 1.94 / (3/4)^{1/2} = 2.24$$

2) $\text{K}_4\text{Mn}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ at 291K has a molar susceptibility $\chi_M = 1906 \times 10^6 \text{ cm}^3/\text{mole}$. What is μ_{eff} ? What electron configuration does this establish in octahedral symmetry? Why does μ_{eff} differ from the ideal spin only value?

$$\mu_{\text{eff}} = 2.827(T \chi_M)^{1/2} = 2.105 \text{ BM}$$

Mn^{2+} octahedral would be either a doublet (low spin octahedral) or a sextet (high spin) ground state. This corresponds to spin-only moments expected of

$$\mu_{\text{eff}} = g (S(S+1))^{1/2} = 2 (3/4)^{1/2} = 1.734 \text{ BM or}$$

$$\mu_{\text{eff}} = g (S(S+1))^{1/2} = 2 (5/2)^{1/2} = 5.484 \text{ BM}$$

Since the ${}^6\text{A}_{1g}$ should have a small orbital contribution, it must be low-spin ${}^2\text{T}_{2g}$ and have a significant contribution from orbital angular momentum, as expected for octahedral T states.

3) What differences would you expect for the g factors of Co^{2+} in O_h vs. T_d coordination environments and in the ability to obtain a spectrum at room temperature?

Case 1) octahedral weak crystal field with a ${}^4\text{T}_{1g}$ ground state (TS diagrams) would be expected to have a first order orbital contribution and $g \sim 4$. Spin orbit splitting of the degenerate T ground state would lead to low lying states, fast electron relaxation, and no EPR spectrum, except at very low temperatures.

Case 2) octahedral strong field with a ${}^2\text{E}_g$ ground state has no first order orbital contribution and g should be near 2 and deviate on the high side from TIP contributions as expected for d-electron counts above 5. Since there is no zero field splitting the spectrum might be observable at room temperature; however, Jahn-Teller splitting could lead to a two state system with faster electron relaxation.

Case 3) tetrahedral, always high spin for first row metals and a ${}^4\text{A}_2$ ground state (TS diagram for hole equivalent). There would be no first order orbital angular momentum, so $g > 2$ expected. Zero field splittings are possible for a quartet state by spin-orbit coupling to the low lying ${}^4\text{T}_2$ state so a spectrum may or may not be observable at room temperature because of relaxation effects.

4) In a frozen glass $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ has $g_{\text{parallel}} = 2.4$ and $g_{\text{perpendicular}} = 2.099$. In aqueous solution a broad absorption centered at 700 nm is observed. Use these data to predict a value for the spin orbit coupling constant and the energy of the next higher electronic transition.

We saw in class that for Cu^{2+}

$$g_{\parallel} = g_e - 8\lambda/\nu_{xy} \text{ and}$$

$$g_{\perp} = g_e - 28\lambda/\nu_{xz,yz}$$

where ν_{xy} is the lowest possible optical transition.

We are given

$$g_{\parallel} = 2.400$$

$$g_{\perp} = 2.099$$

$$\nu_{xy} = 14,286 \text{ cm}^{-1}$$

and we know $g_e = 2.0023$

$$\text{So } \lambda = [(g_e - g_{\parallel})/8] \nu_{xy} = -710 \text{ cm}^{-1}$$

And

The second optical band should be at $\nu_{xz,yz} = 2\lambda/(g_e - g_{\perp}) = 14,689 \text{ cm}^{-1}$, which is nearly the same energy as the first electronic transition. So the broad absorption must contain both electronic transitions.