1) Electronic Spectrum of CsV(SO₄)₂•12H₂O

The UV/Vis absorption spectrum of a single crystal of the CsV(SO₄)₂•12H₂O alum at 16 K is shown at the right.

a) What is the ground-state term symbol for the [V(OH₂)₆]³⁺ ion considering just the VO₆ unit in Oh symmetry (i.e., ignoring H atoms and π bonding)?

b) Propose assignments for the two absorption features in the single-crystal spectrum of CsV(SO₄)₂•12H₂O, assuming Oh symmetry.

c) How would you adjust your assignments if you consider the true S₆ symmetry of the [V(OH₂)₆]³⁺ ion in the alum?

2) Electronic Structure and Spectra of Metal Oxo and Nitrido Complexes

The dπ-orbital splitting for a tetragonal oxo- or nitrido-metal complex is shown above.

The following states arise from the d¹, d², and d³ configurations in this scheme:

\[ d¹: \]
- \( ^2E[(xz,yz)^1] \): \( E = \Delta \pi \)
- \( ^2B_1[(xy)^1] \): \( E = 0 \)

\[ d²: \]
- \( ^3A_2[(xz,yz)^2] \): \( E = 2\Delta \pi + A - 5B \)
- \( ^1A_1[(xz,yz)^2] \): \( E = 2\Delta \pi + A + 7B + 4C \)
- \( ^1B_1[(xz,yz)^2] \): \( E = 2\Delta \pi + A + B + 2C \)
- \( ^1B_2[(xz,yz)^2] \): \( E = 2\Delta \pi + A + B + 2C \)
- \( ^1E[(xy)(xz,yz)^1] \): \( E = \Delta \pi + A + B + 2C \)
- \( ^3E[(xy)(xz,yz)^1] \): \( E = \Delta \pi + A - 5B \)
- \( ^1A_1[(xy)^2] \): \( E = A + 4B + 3C \)
$d^3$:

$^2E[(xz,yz)^3] \quad E = 3\Delta_n + 3A - 3B + 4C$

$^4B_1[(xy)^1(xz,yz)^2] \quad E = 2\Delta_n + 3A - 15B$

$^2B_1[(xy)^3(xz,yz)^2] \quad E = 2\Delta_n + 3A - 6B + 3C$

$^2A_1[(xy)^5(xz,yz)^2] \quad E = 2\Delta_n + 3A - 6B + 3C$

$^2B_2[(xy)^4(xz,yz)^2] \quad E = 2\Delta_n + 3A + 5C$

$^2A_2[(xy)^4(xz,yz)^2] \quad E = 2\Delta_n + 3A - 6B + 3C$

$^2E[(xy)^2(xz,yz)^1] \quad E = \Delta_n + 3A - 3B + 4C$

The absorption spectra of $\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5^{-3}$ and $\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5^{-3}$ are shown below.

In $\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5^{-3}$, the $^2B_2[(xy)] \rightarrow ^2E[(xz,yz)]$ absorption band is at 23,300 cm$^{-1}$.

In $\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5^{-3}$, the $^1A_1[(xy)^2] \rightarrow ^1E[(xy)(xz,yz)]$ absorption band is at 19,400 cm$^{-1}$.

Use the foregoing orbital splitting diagram and the state energies to determine the values of $\Delta_n$ in the Cr and Mn complexes. Assume that $B = 500$ cm$^{-1}$ and $C/B = 4$. 
3) Spin Crossover in $d^2$ and $d^3$ Oxo- and Nitrido Complexes

The value of $\Delta_{\pi}$ is not the same in all of the states of a $d^2$ or $d^3$ nitrido or oxo complex. The $M=N$ (or $M=O$) bond should be longer in a $(xy)^1(xz,yz)^1$ excited state than in the $(xy)^2$ ground state. Consequently, in the relaxed $(xy)^1(xz,yz)^1$ excited state, $\Delta_{\pi}$ will be smaller than it was in the ground state.

You can estimate the change in $\Delta_{\pi}$ from the shape of the absorption band. In $\text{Mn}^3\text{(N)(CN)}_{5}^-$, the parameter $\lambda$ is about $3,400 \text{ cm}^{-1}$. So if $E_{\text{abs}} = 19,400 \text{ cm}^{-1}$, then $E_{\text{em}} = 12,600 \text{ cm}^{-1}$. The energy gap between $^3E$ and $^1A_1$ is $\Delta_{\pi} = 9B - 3C \approx \Delta_{\pi} - 21B$.

For thermal population of a high-spin state, the relevant energy is $E_{\text{TH}}$ (or $E_{00}$), which is less than the vertical energy difference: $E_{\text{TH}} = E_{\text{abs}} - \lambda$. 
a) Find the $\Delta_{\pi}$ values at the high-spin/low-spin crossover points for $d^2$ and $d^3$ tetragonal oxo- and nitrido-metal complexes. Assume that $B = 500$ cm$^{-1}$ and $C/B = 4$.

b) Assume that you have a high-spin/low-spin equilibrium in a $d^2$ tetragonal oxo- or nitrido-metal complex in which $E_{\text{TH}} = 0$. What are the $\Delta_{\pi}$ values for high- and low-spin forms?

c) Assume that you have a high-spin/low-spin equilibrium in a $d^3$ tetragonal oxo- and nitrido-metal complex in which $E_{\text{TH}} = 0$. What are the $\Delta_{\pi}$ values for high- and low-spin forms?

d) What are the relative populations of the high- and low-spin states in problems (b) and (c)?

e) Karl Wieghardt reported (Angew. Chem. Int. Ed. 2005, 44, 2908-2912) that, unexpectedly, the ground-state total spin of the [[cyclam-acetato]Fe$^\text{III}$(N)]$^+$ core is $S=1/2$ and not $S=3/2$. Discuss whether you think that this result is “unexpected”.