Problem Set 3  
Ch 153a – Winter 2021  
Due: 22 January, 2021

1) Electronic Spectrum of CsV(SO$_4$)$_2$•12H$_2$O  
The UV/Vis absorption spectrum of a single crystal of the CsV(SO$_4$)$_2$•12H$_2$O alum at 16 K is shown at the right.

a) What is the ground-state term symbol for the [V(OH$_2$)$_6$]$^{3+}$ ion considering just the VO$_6$ unit in $O_h$ symmetry (i.e., ignoring H atoms and $\pi$ bonding)?

b) Propose assignments for the two absorption features in the single-crystal spectrum of CsV(SO$_4$)$_2$•12H$_2$O, assuming $O_h$ symmetry.

c) How would you adjust your assignments if you consider the true $S_6$ symmetry of the [V(OH$_2$)$_6$]$^{3+}$ ion in the alum?

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

The $d\pi$-orbital splitting for a tetragonal oxo- or nitrido-metal complex is shown above. The following states arise from the $d^1$, $d^2$, and $d^3$ configurations in this scheme:

d$^1$:  
$^2$E[(xz,yz)$^1$] \hspace{1cm} E = \Delta \pi  
$^2$B$_2$[(xy)$^1$] \hspace{1cm} E = 0

d$^2$:  
$^3$A$_2$[(xz,yz)$^2$] \hspace{1cm} E = 2\Delta \pi + A - 5B  
$^1$A$_1$[(xz,yz)$^2$] \hspace{1cm} E = 2\Delta \pi + A + 7B + 4C  
$^1$B$_1$[(xz,yz)$^2$] \hspace{1cm} E = 2\Delta \pi + A + B + 2C  
$^1$B$_2$[(xz,yz)$^2$] \hspace{1cm} E = 2\Delta \pi + A + B + 2C  
$^1$E[(xy)$^1$(xz,yz)$^1$] \hspace{1cm} E = \Delta \pi + A + B + 2C  
$^3$E[(xy)$^1$(xz,yz)$^1$] \hspace{1cm} E = \Delta \pi + A - 5B  
$^1$A$_1$[(xy)$^2$] \hspace{1cm} E = A + 4B + 3C
\[ d^3: \]
\[ ^2E[(xz, yz)^3] \quad E = 3\Delta_\pi + 3A - 3B + 4C \]
\[ ^4B_1[(xy)^4(xz, yz)^2] \quad E = 2\Delta_\pi + 3A - 15B \]
\[ ^2B_2[(xy)^4(xz, yz)^2] \quad E = 2\Delta_\pi + 3A - 6B + 3C \]
\[ ^2A_1[(xy)^4(xz, yz)^2] \quad E = 2\Delta_\pi + 3A - 6B + 3C \]
\[ ^2B_2[(xy)^2(xz, yz)^2] \quad E = 2\Delta_\pi + 3A + 5C \]
\[ ^2A_2[(xy)^1(xz, yz)^2] \quad E = 2\Delta_\pi + 3A - 6B + 3C \]
\[ ^2E[(xy)^2(xz, yz)^1] \quad E = \Delta_\pi + 3A - 3B + 4C \]

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

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

In \( \text{Mn}^{V}(N)(CN)_5^{3-} \), 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 \( \Delta_\pi \) in the Cr and Mn complexes. Assume that \( B = 500 \text{ cm}^{-1} \) 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 \( M=\text{N} \) (or \( M=\text{O} \)) 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 \( \text{Mn}^{\text{V}}(\text{N})(\text{CN})_5^3 \), the parameter \( \lambda \) is about 3,400 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 \( ^3A_1 \) is \( \Delta_\pi - 9B \approx \Delta_\pi - 21B \).

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 $B = 500 \text{ cm}^{-1}$ 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 $E_{TH} = 0$. 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 $E_{TH} = 0$. 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^V(N)]$^+$ core is $S=1/2$ and not $S=3/2$. Discuss whether you think that this result is “unexpected”.