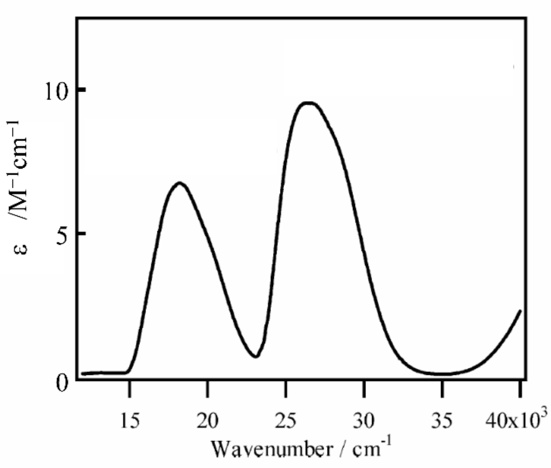
Problem Set 2
Ch 153a – Winter 2022
Due: 14 January, 2022

1) Electronic Spectrum of $CsV(SO_4)_2•12H_2O$

The UV/Vis absorption spectrum of a single crystal of the $CsV(SO_4)_2•12H_2O$ alum at 16 K is shown at the right.

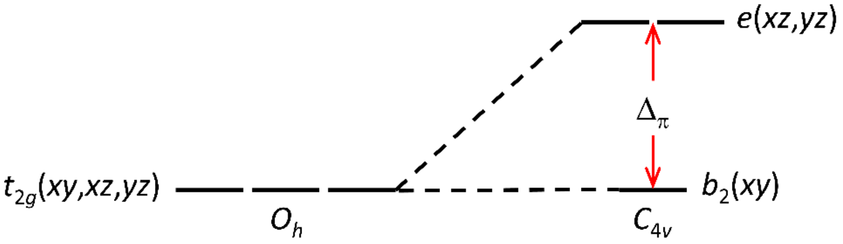


a) What is the ground-state term symbol for the $[V(OH_2)_6]^{3+}$ ion considering just the VO_6 unit in O_h symmetry (*i.e.*, ignoring H atoms and π bonding)?

b) Propose assignments for the two absorption features in the single-crystal spectrum of $CsV(SO_4)_2•12H_2O$, 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:

$^2E[(xz,yz)^1]$	$E = \Delta_\pi$
$^2B_2[(xy)^1]$	$E = 0$

d^2:

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

d^3:

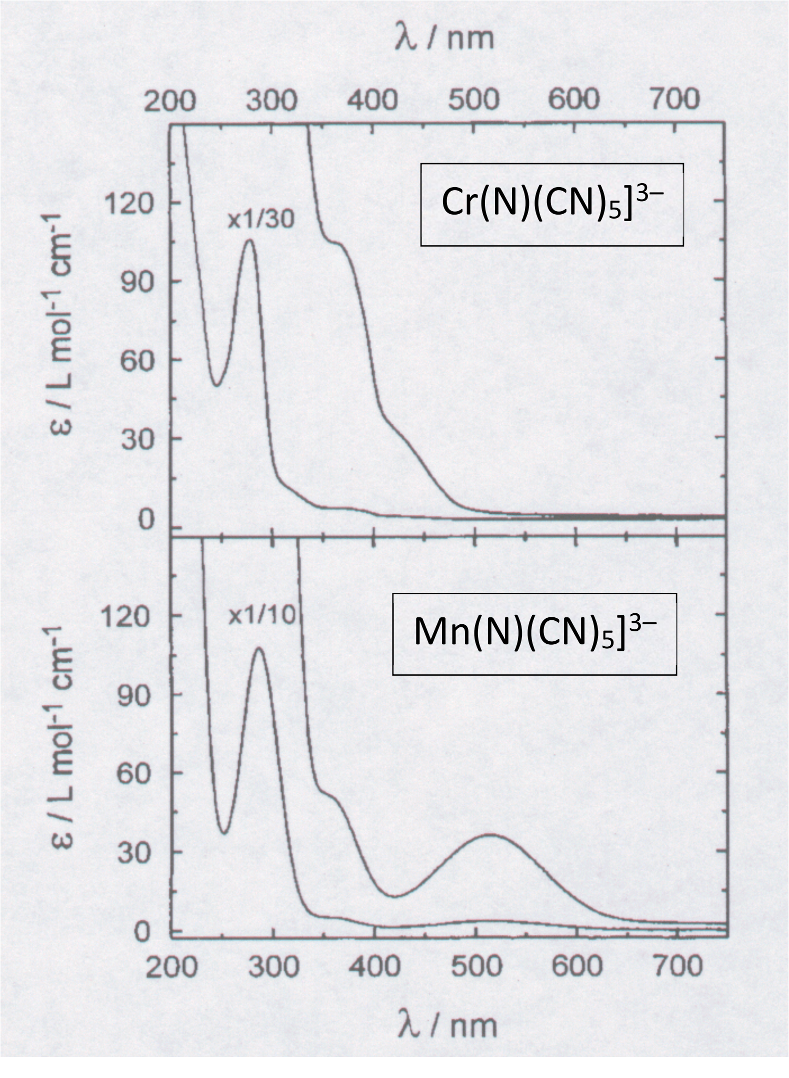
$^2E[(xz,yz)^3]$	$E = 3\Delta_\pi + 3A - 3B + 4C$
$^4B_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 15B$
$^2B_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
$^2A_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
$^2B_2[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A + 5C$
$^2A_2[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
$^2E[(xy)^2(xz,yz)^1]$	$E = \Delta_\pi + 3A - 3B + 4C$

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

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

In $Mn^V(N)(CN)_5^{3-}$, 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 Δ_π in the Cr and Mn complexes. Assume that $B = 500$ cm^{-1} and $C/B = 4$.

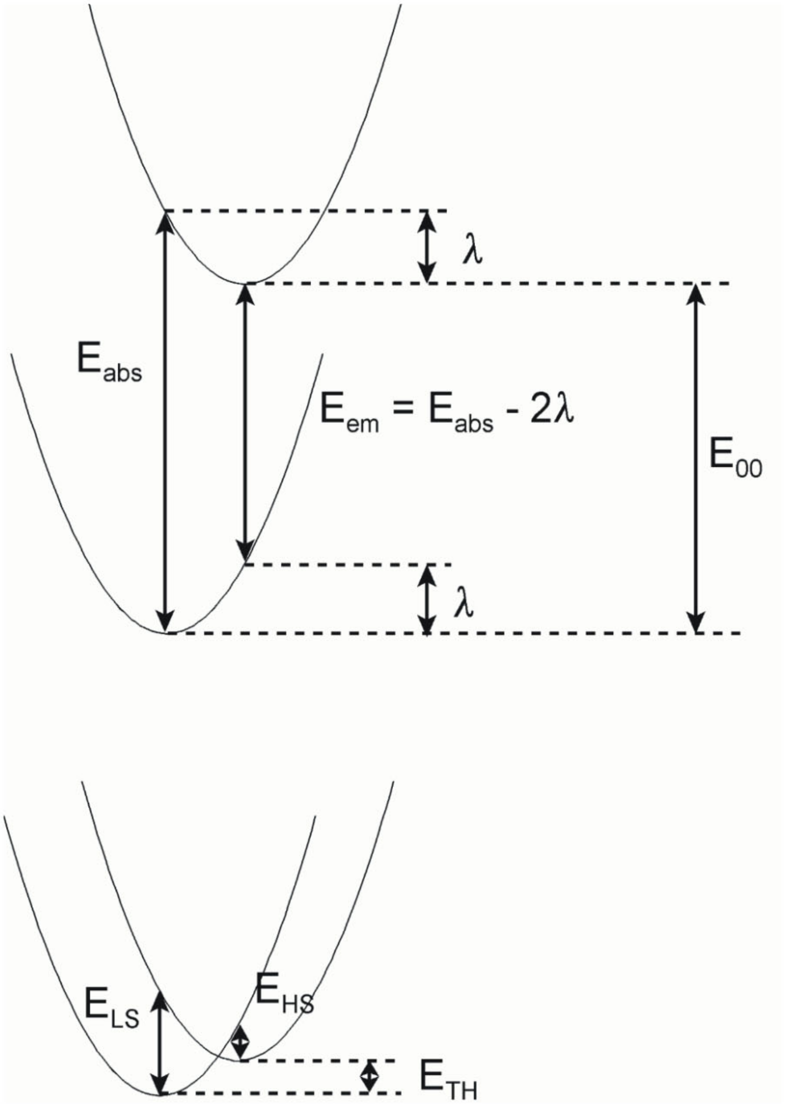


3) Spin Crossover in d^2 and d^3 Oxo- and Nitrido Complexes

The value of Δ_π 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, Δ_π will be smaller than it was in the ground state.

You can estimate the change in Δ_π from the shape of the absorption band. In $\mathrm{Mn^V(N)(CN)_5^{3-}}$, the parameter λ is about 3,400 $\mathrm{cm^{-1}}$. So if E_{abs} = 19,400 $\mathrm{cm^{-1}}$, then E_{em} = 12,600 $\mathrm{cm^{-1}}$. 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_{TH} (or E_{00}), which is less than the vertical energy difference: $E_{TH} = E_{abs} - \lambda$.



a) Find the Δ_π 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_{TH} = 0. What are the Δ_π 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 Δ_π 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".