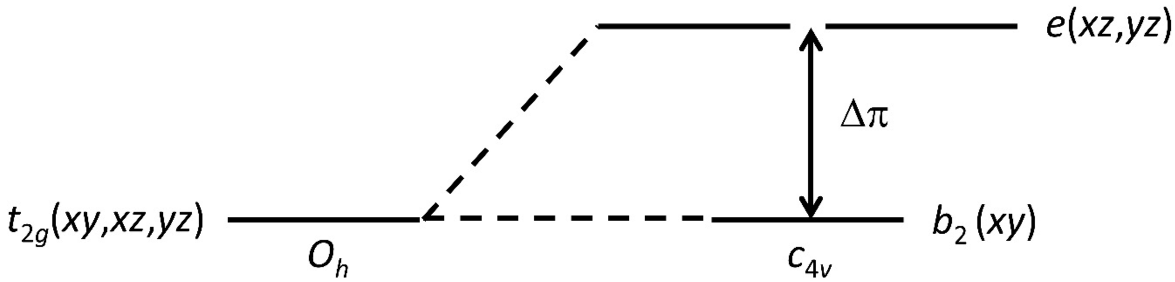
Problem Set 3
Ch153a – Winter 2025
Due: 31 January 2025

1. (50 points) Spin Crossover in d^2 and d^3 Oxo- and Nitrido Complexes

   The $d\pi$-orbital splitting for a tetragonal oxo- or nitrido-metal complex is shown below.



   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.

   The following states and energies arise from the d^2, and d^3 configurations in this scheme:

d^2:

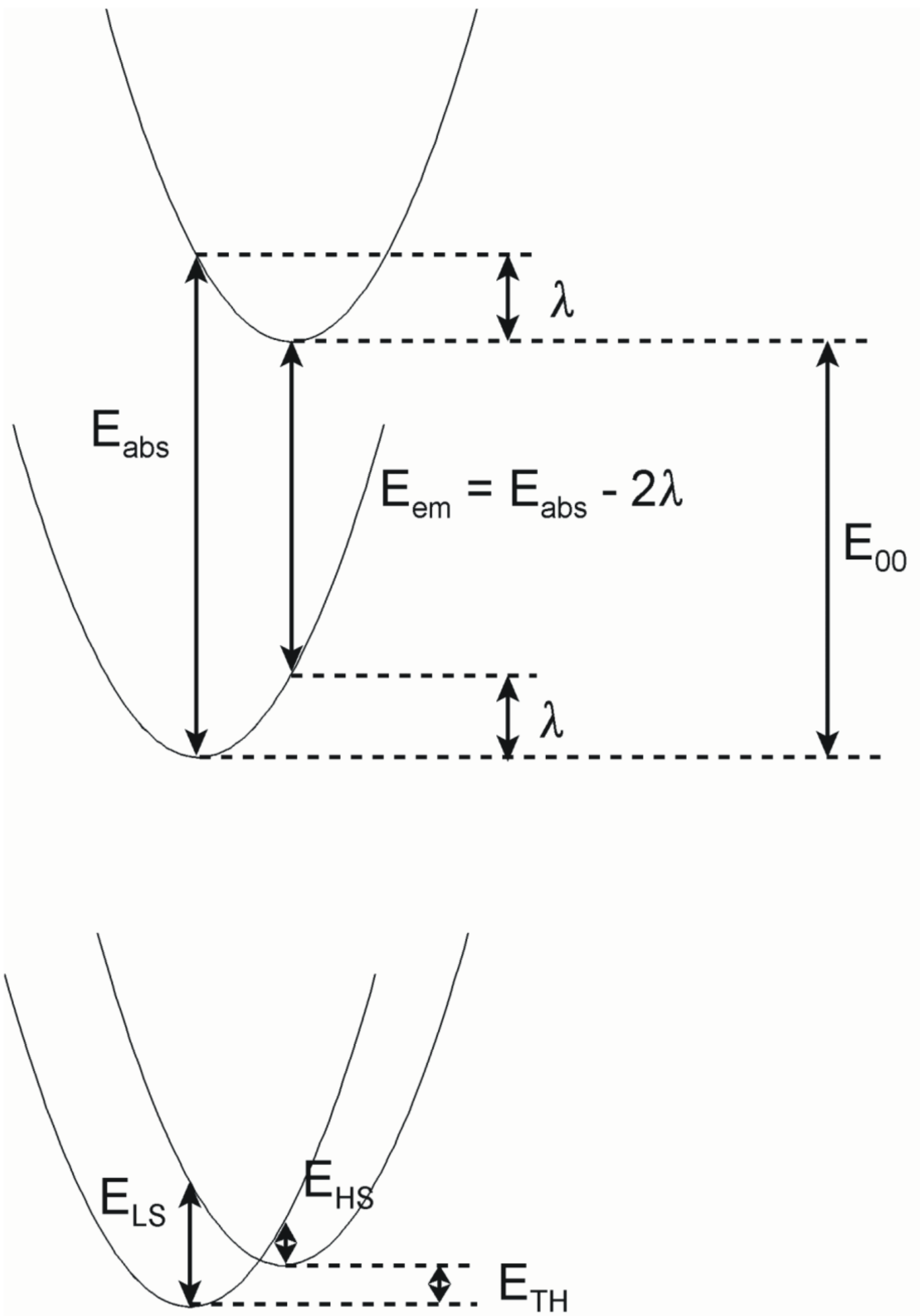
$^3A_2[(xz,yz)^2]$	$E = 2\Delta_\pi + A - 5B$
$^1A_1[(xz,yz)^2]$	$E = 2\Delta_\pi + A + 7B + 4C$
$^1B_1[(xz,yz)^2]$	$E = 2\Delta_\pi + A + B + 2C$
$^1B_2[(xz,yz)^2]$	$E = 2\Delta_\pi + A + B + 2C$
$^1E[(xy)^1(xz,yz)^1]$	$E = \Delta_\pi + A + B + 2C$
$^3E[(xy)^1(xz,yz)^1]$	$E = \Delta_\pi + A - 5B$
$^1A_1[(xy)^2]$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

d^3:

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

You can estimate the change in Δ_π from the shape of the absorption band. In $Mn^{V}(N)(CN)_5^{3-}$, the parameter λ is about 3,400 cm^{-1}. So, if E_{abs} = 19,400 cm^{-1}, then E_{em} = 12,600 cm^{-1}. The energy gap between ^3E and $^1A_1$ is $\Delta_\pi - 9B - 3C \approx \Delta_\pi - 21B$.

Refer to the graphic below. 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".