

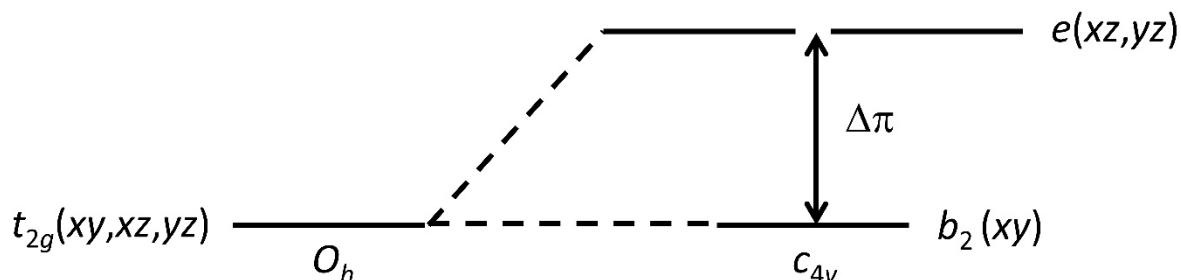
Problem Set 2

Ch153a – Winter 2024

Due: 16 January 2024

1. 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 $\Delta\pi$ is not the same in all of the states of a d^2 or d^3 nitrido or oxo complex. The $M\equiv N$ (or $M\equiv O$) 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.

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

d^2 :

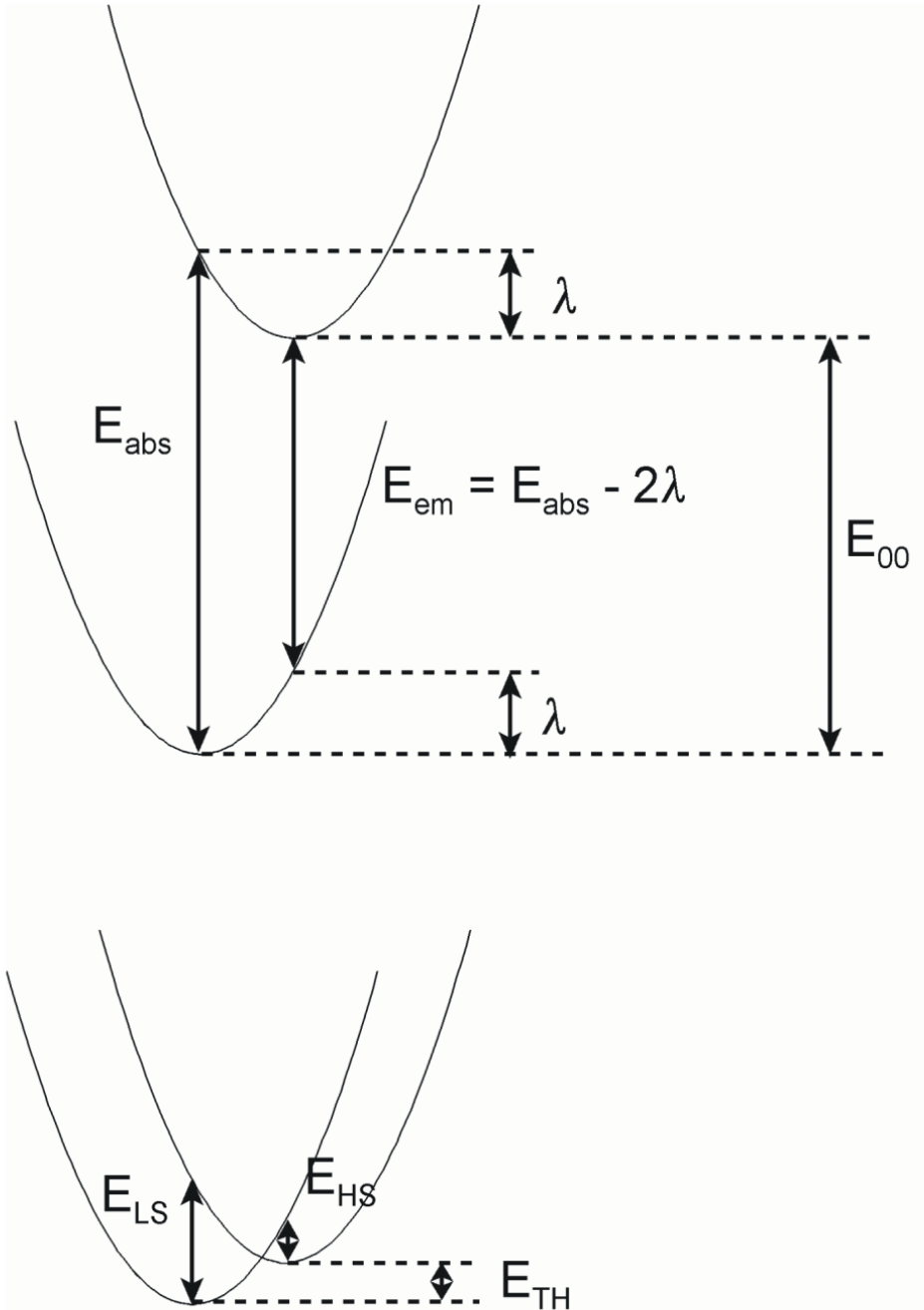
${}^3A_2[(xz, yz)^2]$	$E = 2\Delta\pi + A - 5B$
${}^1A_1[(xz, yz)^2]$	$E = 2\Delta\pi + A + 7B + 4C$
${}^1B_1[(xz, yz)^2]$	$E = 2\Delta\pi + A + B + 2C$
${}^1B_2[(xz, yz)^2]$	$E = 2\Delta\pi + A + B + 2C$
${}^1E[(xy)^1(xz, yz)^1]$	$E = \Delta\pi + A + B + 2C$
${}^3E[(xy)^1(xz, yz)^1]$	$E = \Delta\pi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

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 $\Delta\pi$ from the shape of the absorption band. In $\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5^{3-}$, the parameter λ 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 ${}^3\text{E}$ and ${}^1\text{A}_1$ is $\Delta\pi - 9\text{B} - 3\text{C} \approx \Delta\pi - 21\text{B}$.

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: $E_{\text{TH}} = E_{\text{abs}} - \lambda$.



- 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 $B = 500 \text{ cm}^{-1}$ 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 $E_{\text{TH}} = 0$. 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 $E_{\text{TH}} = 0$. 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".