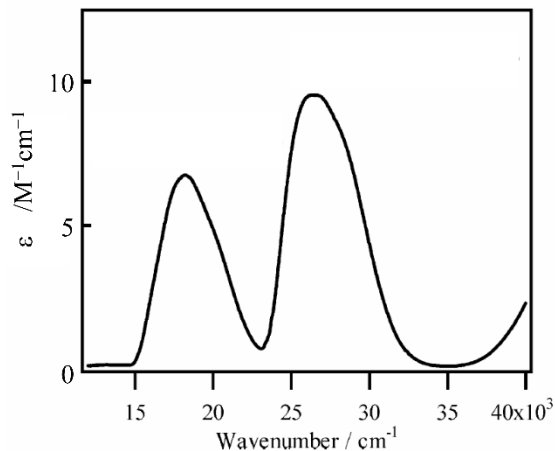


**Problem Set 3**  
**Ch 153a – Winter 2021**  
**Due: 22 January, 2021**

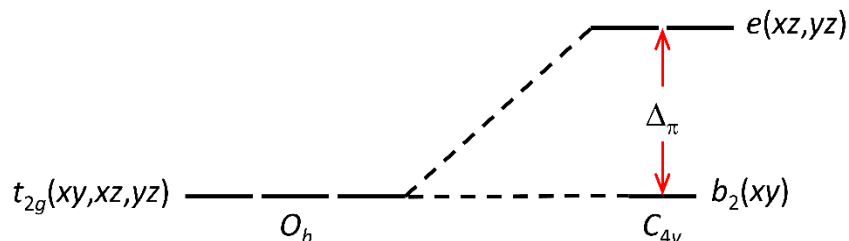
**1) Electronic Spectrum of CsV(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O**

The UV/Vis absorption spectrum of a single crystal of the CsV(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O alum at 16 K is shown at the right.



- What is the ground-state term symbol for the [V(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> ion considering just the VO<sub>6</sub> unit in *O<sub>h</sub>* symmetry (*i.e.*, ignoring H atoms and π bonding)?
- Propose assignments for the two absorption features in the single-crystal spectrum of CsV(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O, assuming *O<sub>h</sub>* symmetry.
- How would you adjust your assignments if you consider the true *S<sub>6</sub>* symmetry of the [V(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> 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 *d*<sup>1</sup>, *d*<sup>2</sup>, and *d*<sup>3</sup> configurations in this scheme:

*d*<sup>1</sup>:

$${}^2E[(xz, yz)^1] \quad E = \Delta_\pi$$

$${}^2B_2[(xy)^1] \quad E = 0$$

*d*<sup>2</sup>:

$${}^3A_2[(xz, yz)^2] \quad E = 2\Delta_\pi + A - 5B$$

$${}^1A_1[(xz, yz)^2] \quad E = 2\Delta_\pi + A + 7B + 4C$$

$${}^1B_1[(xz, yz)^2] \quad E = 2\Delta_\pi + A + B + 2C$$

$${}^1B_2[(xz, yz)^2] \quad E = 2\Delta_\pi + A + B + 2C$$

$${}^1E[(xy)^1(xz, yz)^1] \quad E = \Delta_\pi + A + B + 2C$$

$${}^3E[(xy)^1(xz, yz)^1] \quad E = \Delta_\pi + A - 5B$$

$${}^1A_1[(xy)^2] \quad E = A + 4B + 3C$$

$d^3$ :

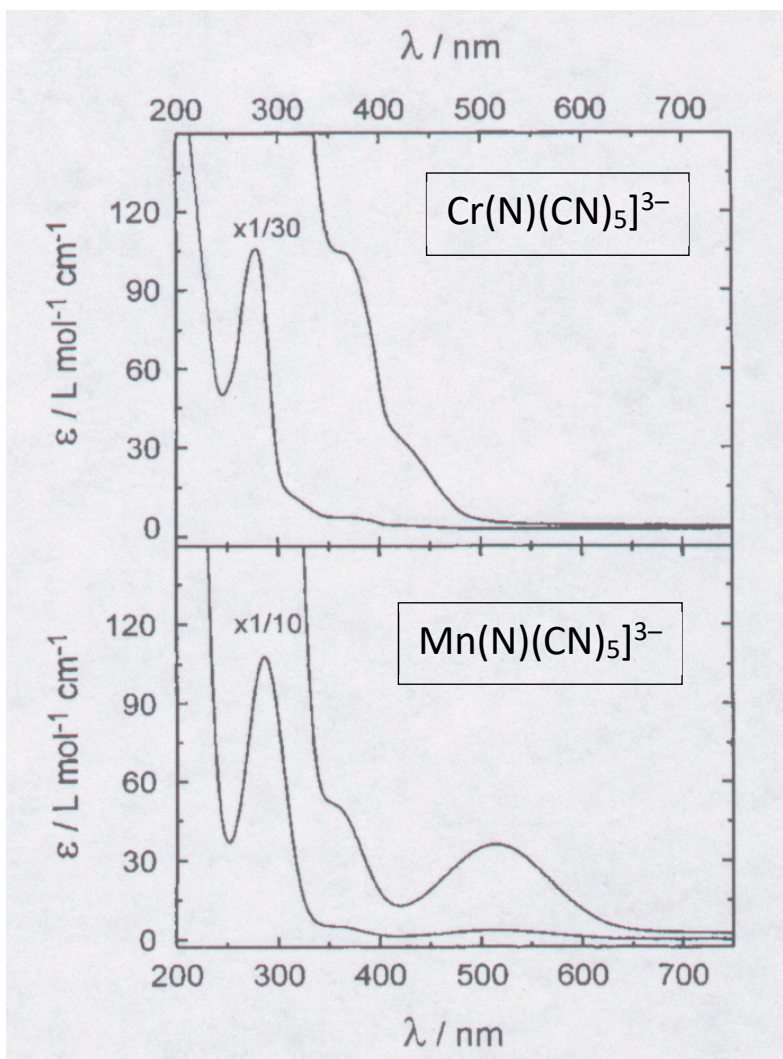
${}^2E[(xz,yz)^3]$	$E = 3\Delta_\pi + 3A - 3B + 4C$
${}^4B_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 15B$
${}^2B_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
${}^2A_1[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A - 6B + 3C$
${}^2B_2[(xy)^1(xz,yz)^2]$	$E = 2\Delta_\pi + 3A + 5C$
${}^2A_2[(xy)^1(xz,yz)^2]$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

The absorption spectra of  $\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5^{3-}$  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  $23,300 \text{ cm}^{-1}$ .

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  $19,400 \text{ cm}^{-1}$ .

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  $C/B = 4$ .

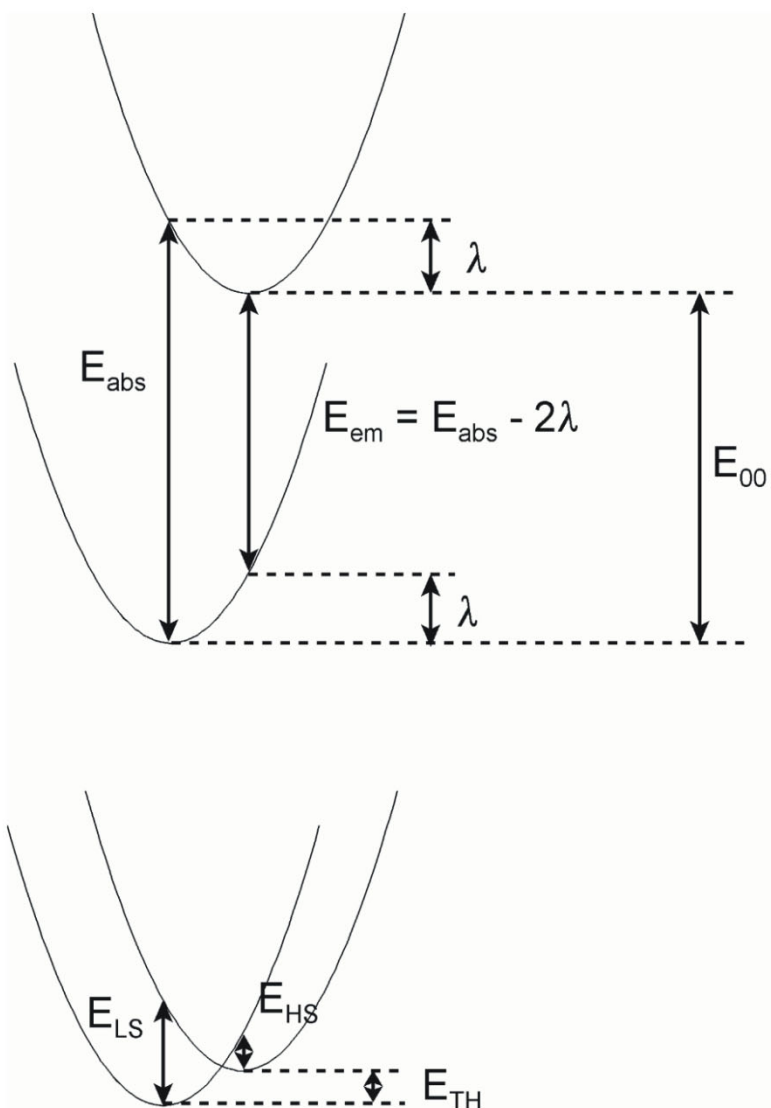


### 3) Spin Crossover in $d^2$ and $d^3$ Oxo- and Nitrido Complexes

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  $M\equiv N$  (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.

You can estimate the change in  $\Delta_\pi$  from the shape of the absorption band. In  $Mn^V(N)(CN)_5^{3-}$ , 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  $B = 500 \text{ cm}^{-1}$  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  $\Delta_{\pi}$  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<sup>V</sup>(N)]<sup>+</sup> core is  $S=1/2$  and not  $S=3/2$ . Discuss whether you think that this result is "unexpected".