

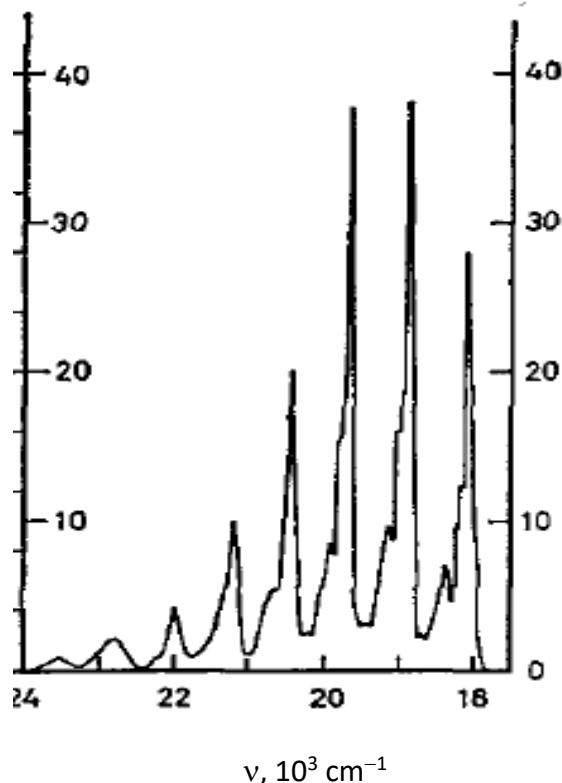
Ch153a

Winter 2020

Due 24 January, 2020

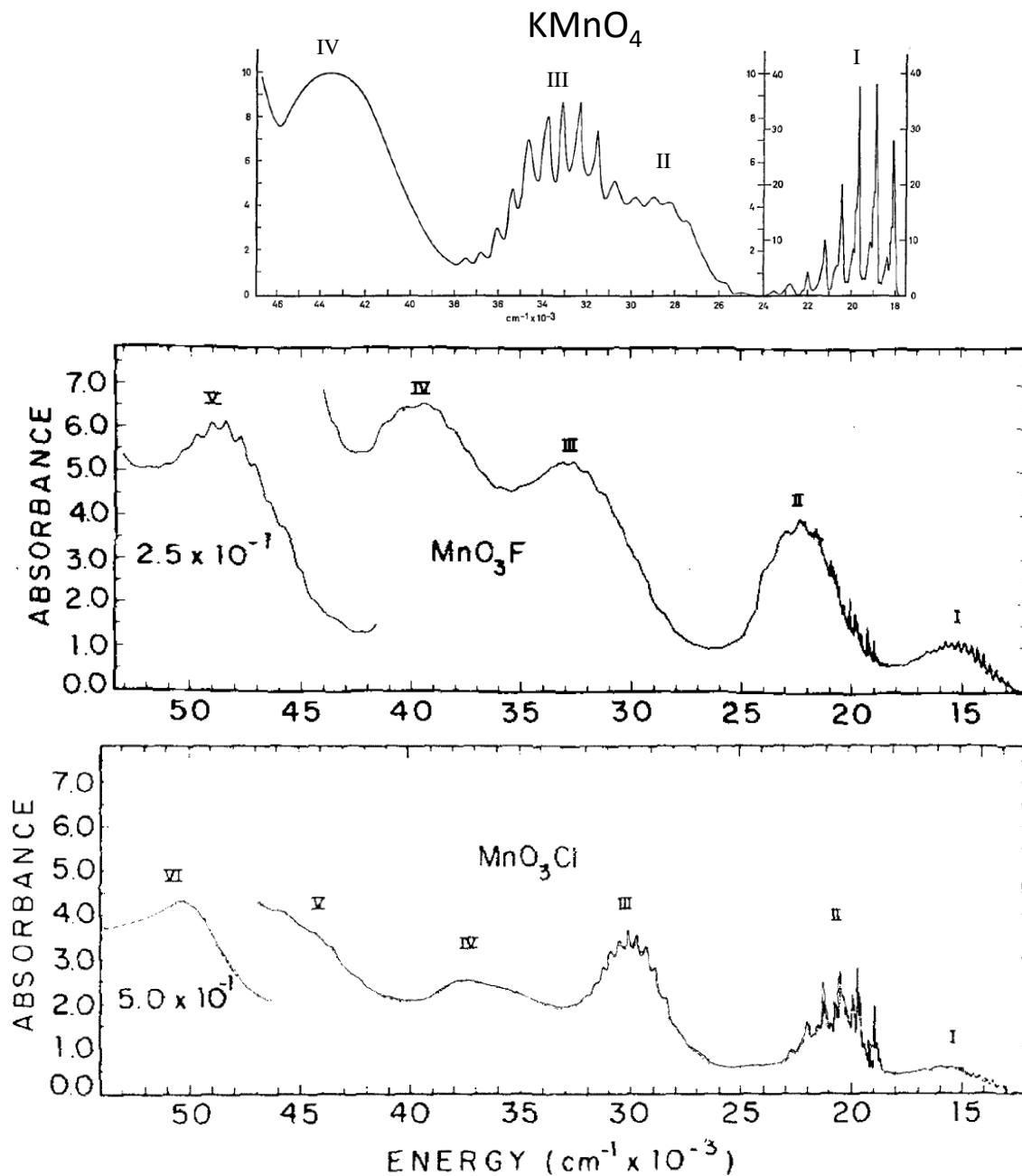
Problem Set 3

1. The 4K single crystal absorption spectrum of KMnO_4 doped into a KClO_4 lattice and a table of peak positions are shown below.



- Perform a Franck-Condon analysis of the vibrational fine structure in the absorption band.
 - What S_{HR} -value gives the best fit to the observed spectrum?
 - If the force constant for the distorting mode is 5.91 mdyne/ \AA , give the magnitude of the distortion in the normal mode (ΔQ).
 - Use group theory to define the normal mode in terms of bond stretching coordinates to estimate the magnitude of the distortion in the individual bonds.
- | Peak Position (cm^{-1}) | Relative Intensity |
|------------------------------------|--------------------|
| 18,072 | 74 |
| 18,842 | 100 |
| 19,602 | 96 |
| 20,380 | 59 |
| 21,145 | 27 |
| 21,915 | 10 |

2. The 4K single crystal absorption spectrum of KMnO_4 doped into a KClO_4 lattice, and the gas-phase absorption spectra of MnO_3F and MnO_3Cl are shown below.

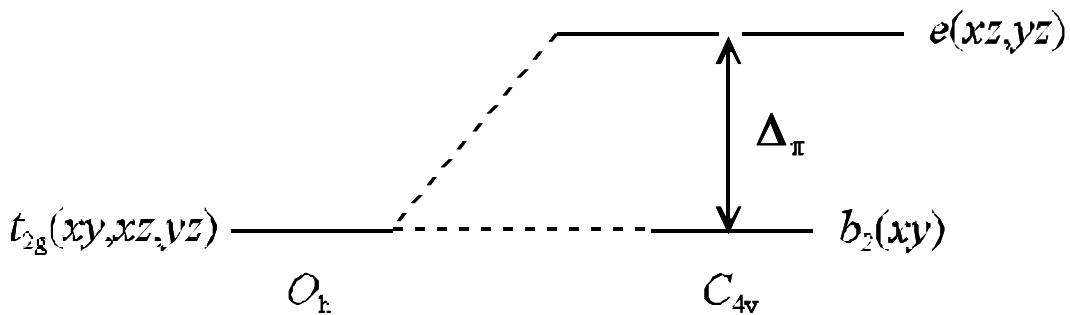


The gas-phase vibrational spectra of MnO_3F and MnO_3Cl exhibit symmetric Mn-O stretches at 905 and 892 cm^{-1} , respectively, and symmetric Mn-X vibrations at 721 ($\text{X} = \text{F}$) and 460 ($\text{X} = \text{Cl}$) cm^{-1} . The vibrational fine structure in bands I-IV of MnO_3X is summarized in the following table.

Band	MnO ₃ F	MnO ₃ Cl
I	851 cm ⁻¹	825 cm ⁻¹
II	819 cm ⁻¹	783 cm ⁻¹
III	653 cm ⁻¹	402 cm ⁻¹
IV	655 cm ⁻¹	618 cm ⁻¹

The assignment of band I in the MnO₄⁻ absorption spectrum was discussed in class. Propose assignments for bands II, III, and IV in MnO₄⁻, and bands I, II, III, and IV in MnO₃F and MnO₃Cl.

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



The following states arise from the d^1 , d^2 , and d^3 configurations in this scheme:

d^1 :

$$\begin{array}{ll} {}^2E[(xz, yz)^1] & E = \Delta_\pi \\ {}^2B_2[(xy)^1] & E = 0 \end{array}$$

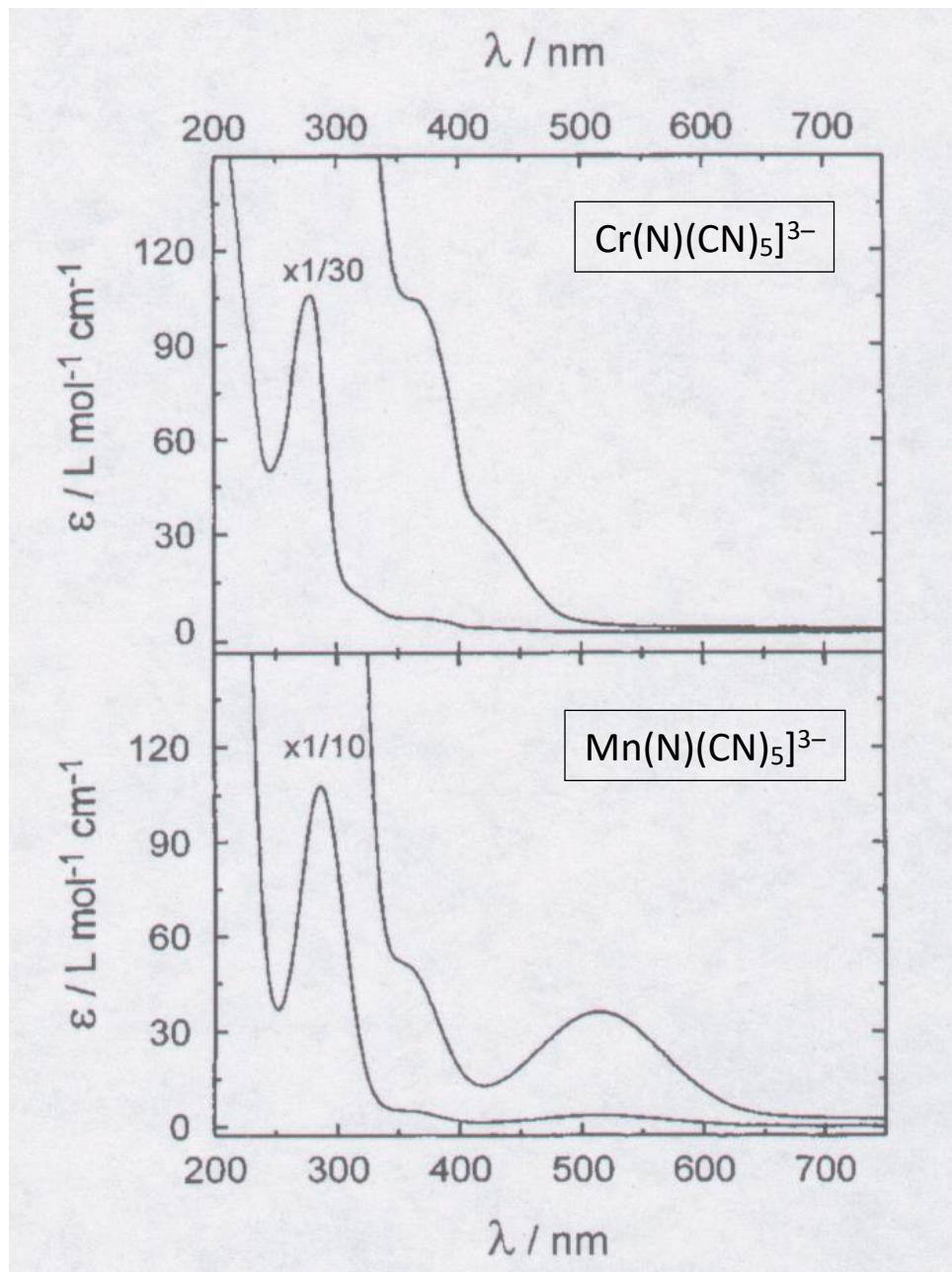
d^2 :

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

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.

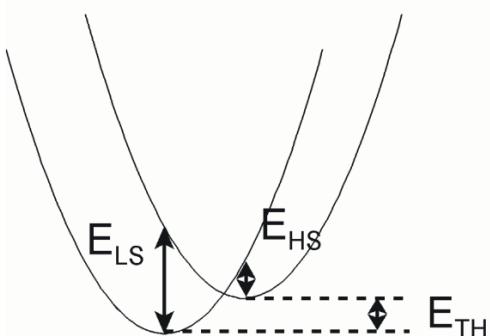
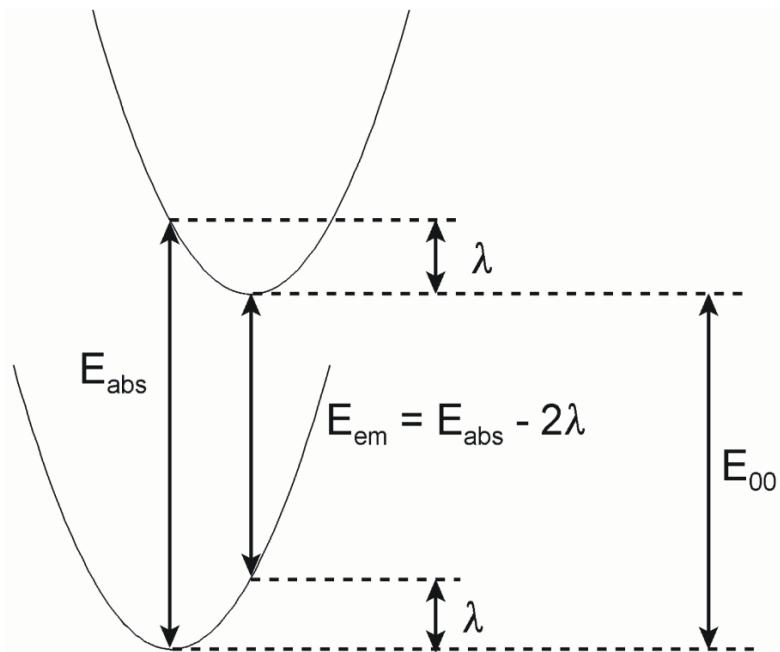


In $\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5^{3-}$, the ${}^2\text{B}_2[(xy)] \rightarrow {}^2\text{E}[(xz, yz)]$ absorption band is at $23,300 \text{ cm}^{-1}$.

In $\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5^{3-}$, the ${}^1\text{A}_1[(xy)^2] \rightarrow {}^1\text{E}[(xy)(xz, yz)]$ absorption band is at $19,400 \text{ cm}^{-1}$.

Use the foregoing orbital splitting diagram and the state energies to determine the values of Δ_π in the Cr and Mn complexes. Assume that $B = 500 \text{ cm}^{-1}$ and $C/B = 4$.

- 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 $\text{M}\equiv\text{N}$ (or $\text{M}\equiv\text{O}$) 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, 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 $\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5^{3-}$, 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 $\Delta_{\pi} - 9\text{B} - 3\text{C} \approx \Delta_{\pi} - 21\text{B}$.

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: $E_{\text{TH}} = E_{\text{abs}} - \lambda$. Find the Δ_{π} values at the high-spin/low-spin crossover points for d^2 and d^3 tetrahedral oxo- and nitrido-metal complexes. Assume that $\text{B} = 500 \text{ cm}^{-1}$ and $\text{C}/\text{B} = 4$.

- a. Assume that you have a high-spin/low-spin equilibrium in a d^2 tetrahedral oxo- or nitrido-metal complex in which $E_{\text{TH}} = 0$. What are the Δ_{π} values for high- and low-spin forms?
- b. Assume that you have a high-spin/low-spin equilibrium in a d^3 tetrahedral oxo- and nitrido-metal complex in which $E_{\text{TH}} = 0$. What are the Δ_{π} values for high- and low-spin forms?
- c. What are the relative populations of the high- and low-spin states in problems (b) and (c)?
- d. Karl Wieghardt reported (*Angew. Chem. Int. Ed.* **2005**, 44, 2908-2912) that, *unexpectedly*, the ground-state total spin of the $[(\text{cyclam-acetato})\text{Fe}^{\text{V}}(\text{N})]^+$ core is $S=1/2$ and not $S=3/2$. Discuss whether you think that this result is “unexpected”.