

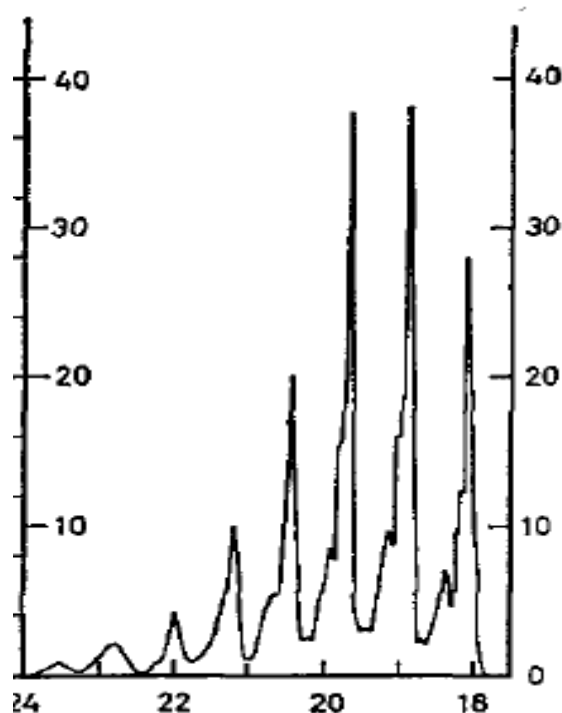
Ch153a

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.



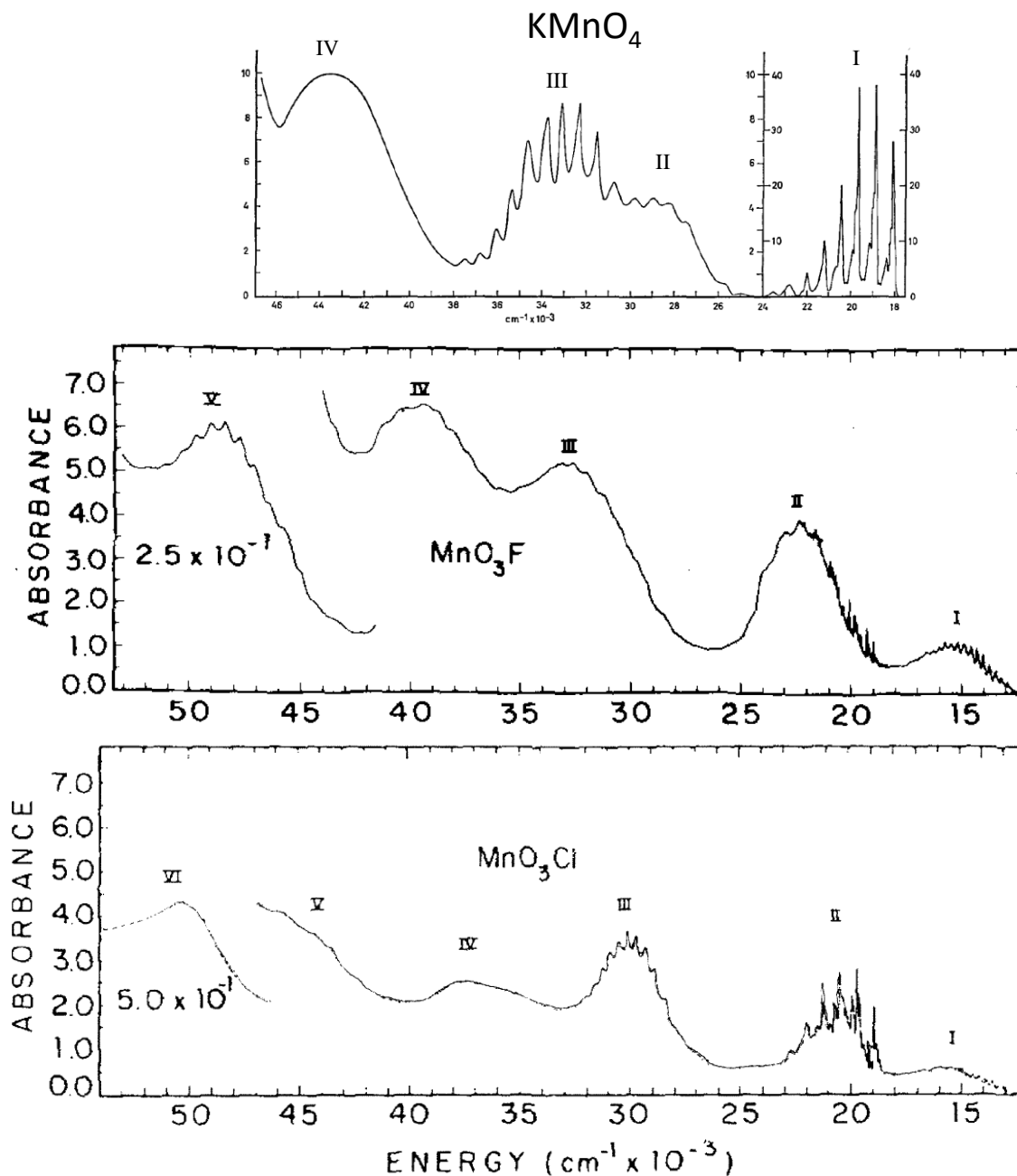
$\nu, 10^3 \text{ cm}^{-1}$

- a. Perform a Franck-Condon analysis of the vibrational fine structure in the absorption band.
- b. What S_{HR} -value gives the best fit to the observed spectrum?
- c. If the force constant for the distorting mode is 5.91 mdyne/\AA , give the magnitude of the distortion in the normal mode (ΔQ).

Peak Position (cm^{-1})	Relative Intensity
18,072	74
18,842	100
19,602	96
20,380	59
21,145	27
21,915	10

- d. 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.

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.

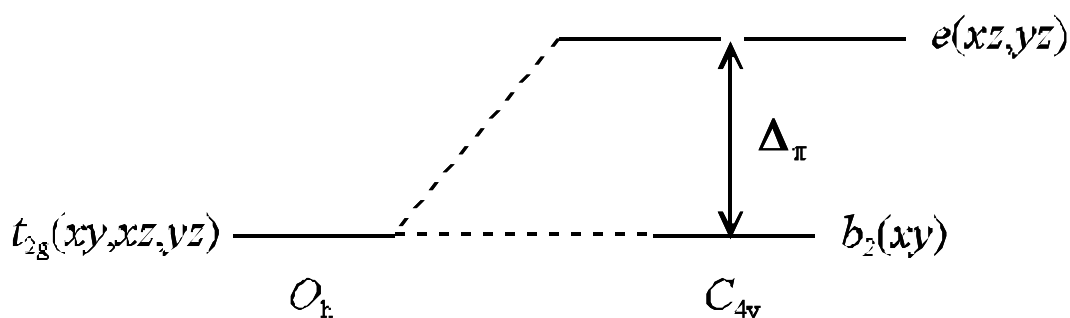


The gas-phase vibrational spectra of MnO_3F and MnO_3Cl exhibit symmetric Mn-O stretches at 905 and 892 cm^{-1} , respectively, and symmetric Mn-X vibrations at 721 (X = F) and 460 (X = Cl) cm^{-1} . The vibrational fine structure in bands I-IV of MnO_3X is summarized in the following table.

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 :

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

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

d^2 :

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

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

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

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

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

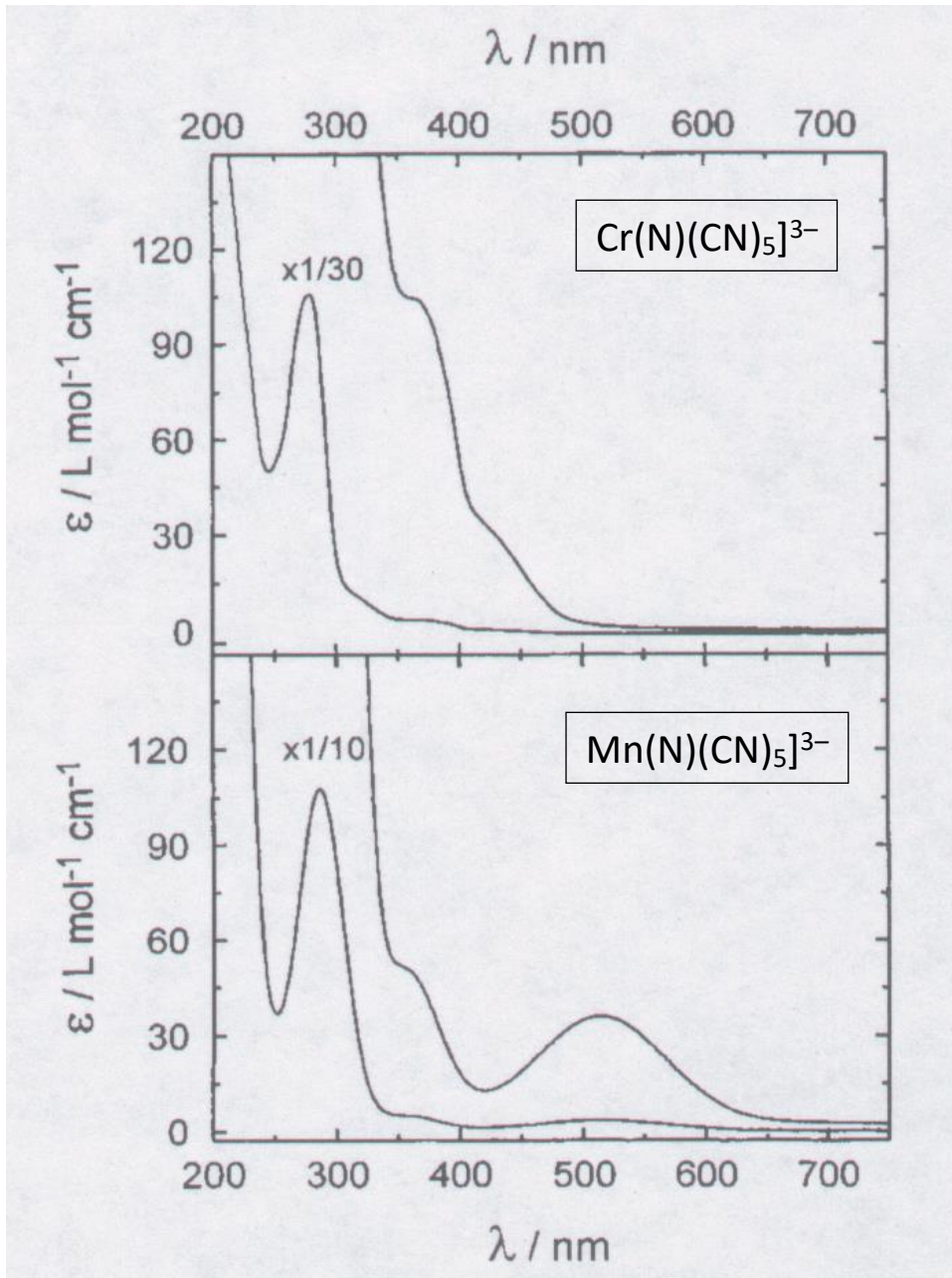
$${}^3E[(xy)^1(xz, yz)^1] \quad E = \Delta_{\pi} + A - 5B$$

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

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.

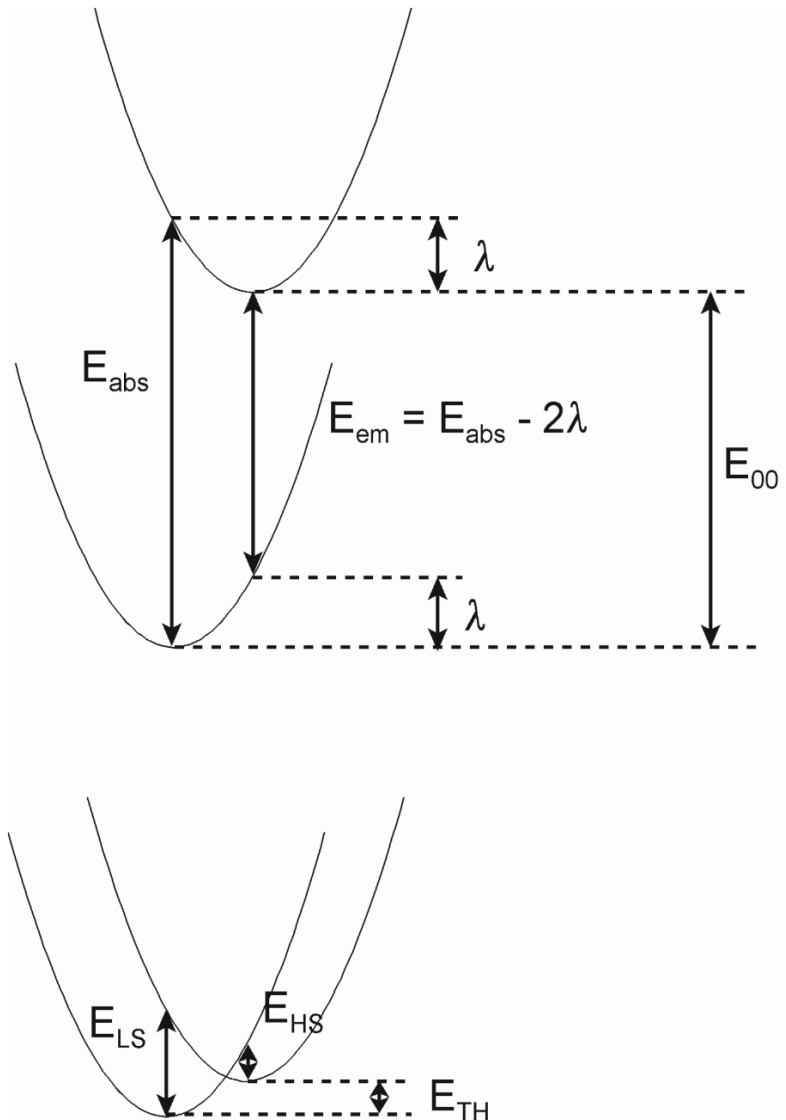


In $\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5^{3-}$, the ${}^2\text{B}_2[(xy)] \rightarrow {}^2\text{E}[(xz,yz)]$ absorption band is at $23,300 \text{ cm}^{-1}$.

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 $\Delta\pi$ 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 $\Delta\pi - 9\text{B} - 3\text{C} \approx \Delta\pi - 21\text{B}$.

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 $\Delta\pi$ values at the high-spin/low-spin crossover points for d^2 and d^3 tetragonal oxo- and nitrido-metal complexes. Assume that $\text{B} = 500\text{ cm}^{-1}$ and $\text{C}/\text{B} = 4$.

- 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?
- 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?
- What are the relative populations of the high- and low-spin states in problems (b) and (c)?
- 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".