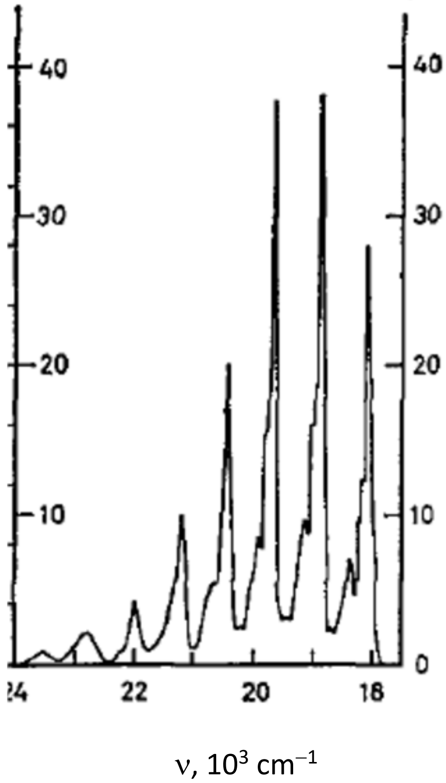
Ch153a
Winter 2019
Due 18 January, 2019

Problem Set 2

(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.

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



(a) Perform a Franck-Condon analysis of the vibrational fine structure in the absorption band.

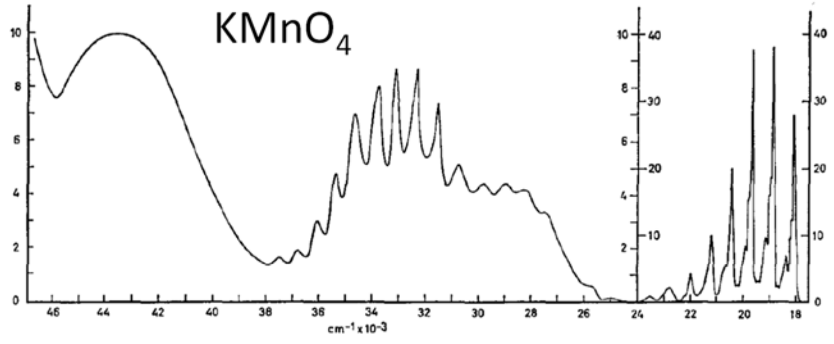
(b) What S_{HR}-value gives the best fit to the observed spectrum?

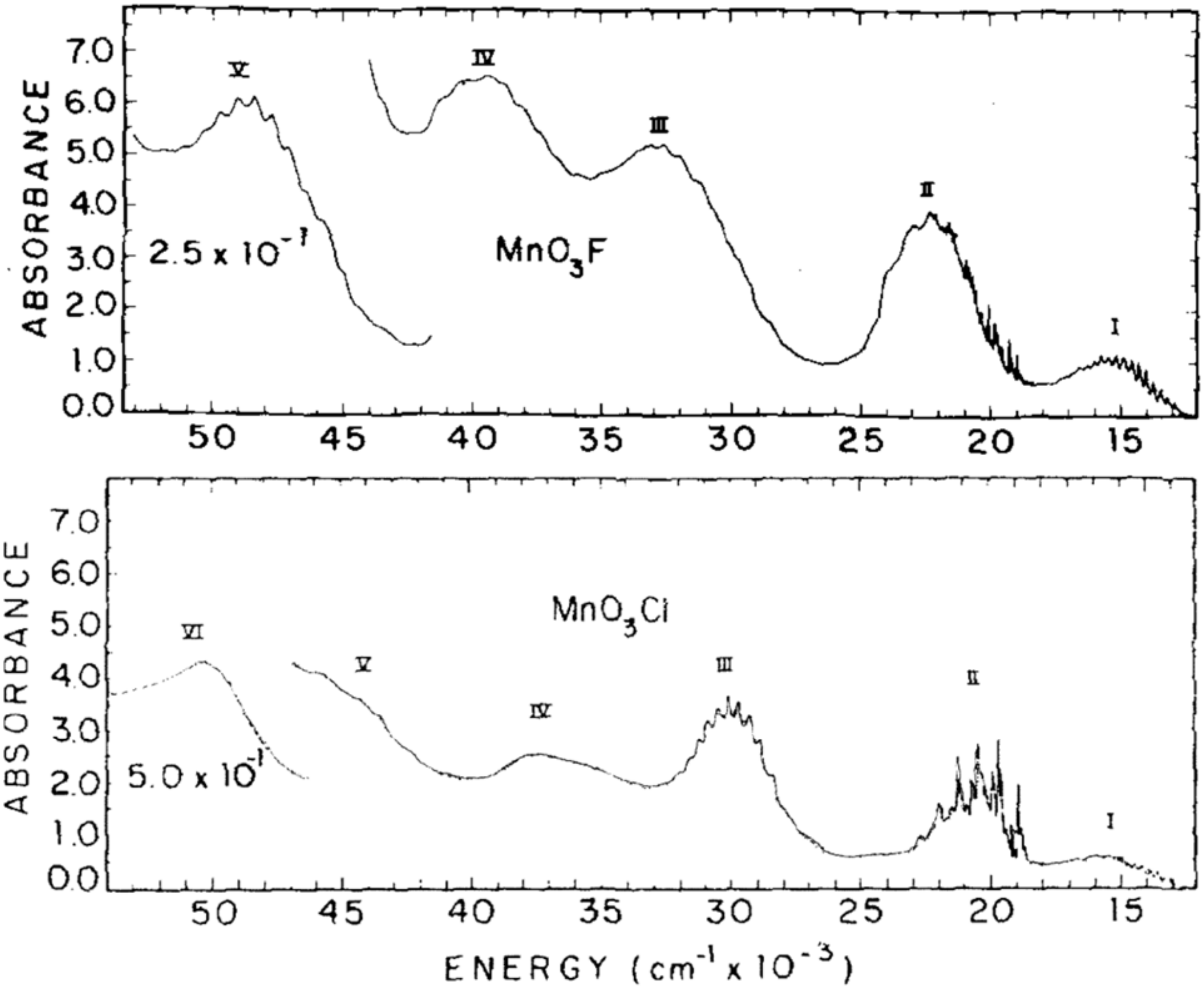
(c) If the force constant for the distorting mode is 5.91 mdyne/Å, give the magnitude of the distortion in the normal mode (ΔQ).

(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) Using the basis functions for T_d coordination with C_3 quantization developed in Problem Set 1, draw a correlation diagram relating the *d*-orbital splitting in a tetrahedral MX_4 molecule to that in a MX_3Y molecule with C_{3v} symmetry (X and Y are strong σ and π donor ligands).

(3) 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 on the following page.





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_3F	MnO_3Cl
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 assignments of the MnO_4^- absorption bands were discussed in class. Propose assignments for bands I, II, III, and IV in MnO_3F and MnO_3Cl.

(4) Consider a hypothetical trigonal (C_{3v}) Co-oxo complex with ancillary ligands L, $Co(O)L_3^{n+}$.

(a) Develop a ligand field splitting diagram for complexes of this type with Co(III) and Co(V) oxidation states.

(b) Predict the ground-state electronic structure (term symbol including spin) for each complex.

(c) Identify the Co-oxo bond order for each complex.