Ge 214 - Homework Problem

Vibrations of SO_4 units in low symmetry environments

Most minerals have structures which are lower symmetry than cubic. As a consequence, symmetrical anions such as SiO_4^{2-} and SO_4^{2-} often find themselves bound in local environments which have lower symmetries than the full symmetry of the tetrahedral anionic unit. In such an environment, the tetrahedral unit will vibrate with energies different from those it would have in a totally symmetric environment. We must learn to deal with the vibrational energies of these units in low symmetry structures.

First, we will consider an isolated SO_4^{2-} unit which has textbook perfect tetrahedral symmetry.

a) Verify that it belongs to the point group T_d.

We will first determine the number of fundamental vibrational modes it has when isolated from the rest of the world. Then we will "place" the group into a series of sites of progressively lower symmetry and calculate how the number and symmetry of vibrational modes should change. Finally, we will compare these predictions with some actual data obtained on a suite of selected sulfate minerals.

Consider the isolated SO_4^{2-} group:

b) The molecule has 5 atoms, each with 3 coordinates along which motion can occur, so there are 15 displacement vectors associated with the vibrations in the molecular group. Three of these potential motions are simply translations along the x,y and z axes. Three of these potential motions are rotations around the x,y and z axes. Thus, there 3n-6 degrees of internal freedom (where n = number of atoms in the molecule) that represent true vibrations.

Onc can use the application of the symmetry operations of T_d upon the five atoms in the SO_4^{2-} to generate the reducible representation: Try this if you want to go more deeply into the principles of the science.

E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
15	etc			

You will end up with the following representation:

E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
15	0	-1	-1	3

c) Next, you need to reduce the representation you determined above into its component symmetry species. Namely,

how many A_{1g}, A_{2g} A_{1u}, A_{2u} modes
how many E modes
how many T1 modes
how many T2 modes

If you are finished with this part of the problem, you may check your answer with the TA before proceeding with the rest of this problem.

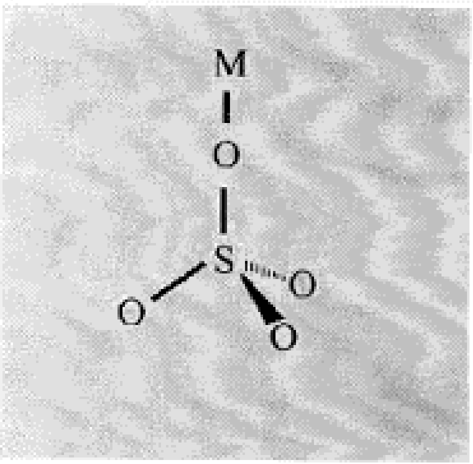
d) The character tables for T_d can be used to determine which of these representations correspond to pure translation and pure rotation. Rotations are represented by Rz for rotation about the (molecular) z-axis, etc. Translations are designated in the same column by the cartesian coordinates x, y, and z. Specifically, the translations in the x, y, and z directions are degenerate and comprise a basis for the representation of T_d.

Subtract out the two representations of translations and rotations from the symmetries of the genuine vibrations. Remember, a T state has 3 components and an E state has 2.

e) Draw a picture of the SO_4^{2-} ion and indicate the direction of motion of the atoms in the A_1 vibration (which is also called ν_1, the symmetric stretch).

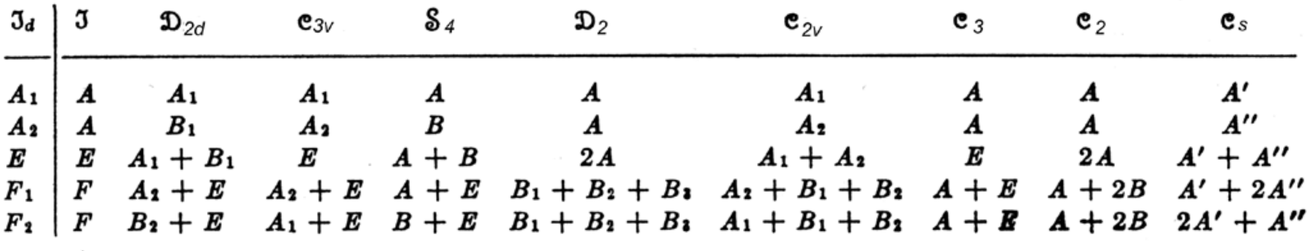
f) From the character tables determine which modes are infrared active. There will be the modes whose symmetry is the same as one of the three coordinates, x, y, and z. Note that some authors call a T mode by the letter F (eg. T_1 becomes F_1.)

g) Next allow one and only one of the oxygens to interact strongly with a cation so as to destroy the effective T_d symmetry.



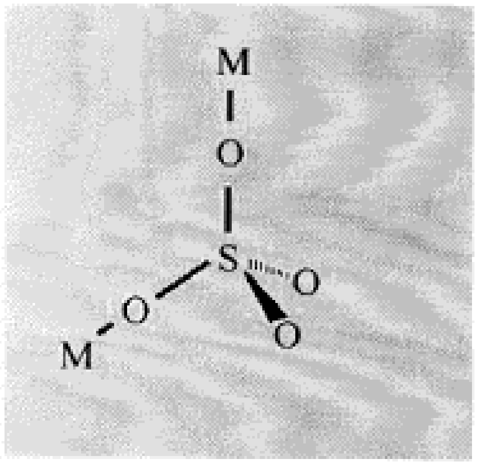
h) Determine the point group of this new unit. Next, determine how many components are generated in the lower symmetry by the splitting of the original bands and the symmetry of each of these individual components.

How many bands are infrared active? You can either work it out completely if you wish, or you may save a lot of time if you use a correlation table such as those in Wilson EB, Decius JC, and Cross PC *(1955)* ***Molecular Vibrations.*** McGraw-Hill. that is on page 340 in my 1980 Dover paperback reprint]. This table tells you what happens to vibrations of different symmetry when you decrease the symmetry of the vibrating unit. A copy of this table for the T_d group follows:



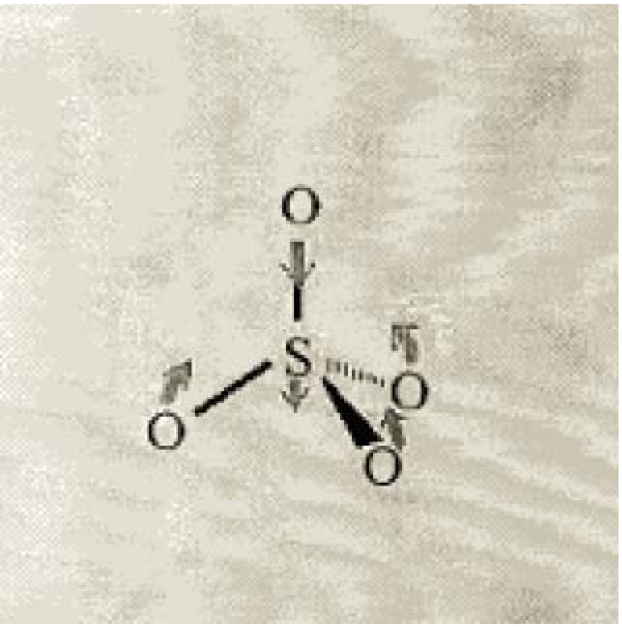
$\mathfrak{T}_d$	$\mathfrak{T}$	$\mathfrak{D}_{2d}$	$\mathfrak{C}_{3v}$	$\mathfrak{S}_4$	$\mathfrak{D}_2$	$\mathfrak{C}_{2v}$	$\mathfrak{C}_3$	$\mathfrak{C}_2$	$\mathfrak{C}_s$
A_1	A	A_1	A_1	A	A	A_1	A	A	A'
A_2	A	B_1	A_2	B	A	A_2	A	A	A''
E	E	$A_1 + B_1$	E	$A + B$	$2A$	$A_1 + A_2$	E	$2A$	$A' + A''$
F_1	F	$A_2 + E$	$A_2 + E$	$A + E$	$B_1 + B_2 + B_3$	$A_2 + B_1 + B_2$	$A + E$	$A + 2B$	$A' + 2A''$
F_2	F	$B_2 + E$	$A_1 + E$	$B + E$	$B_1 + B_2 + B_3$	$A_1 + B_1 + B_2$	$A + E$	$A + 2B$	$2A' + A''$

i) Now let two cations strongly interact with the sulfate group.



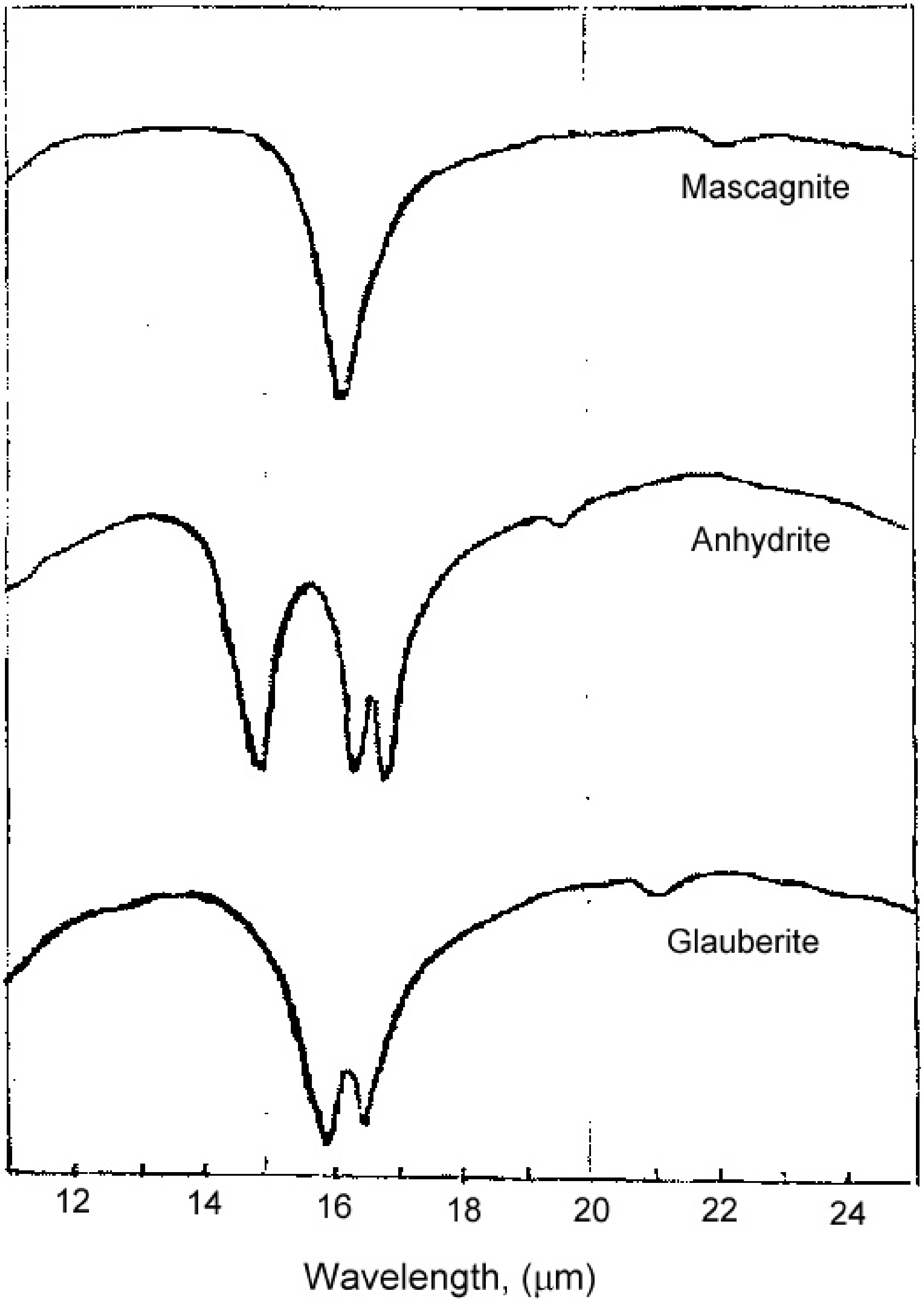
Determine again the manner in which the original tetrahedral bands split.

j) On a following page, you will find three spectra which show the infrared absorption spectrum in the spectral region which corresponds to ν_4 (pictured below), one of the T_2 modes in Td symmetry.



Based on the results of the analysis that you have just completed, explain why the three spectra differ as they do.

The spectra curves below are from Omori and Kerr (1964), Science Report. Tohoku University 9,1.


Mascagnite
Anhydrite
Glauberite
12
14
16
18
20
22
24
Wavelength, (μm)