Solution Set
Problem Set 4 : Vibrations of TO₄ units in low symmetry environments
Ge214 2001

a) Verify SO₄²⁻ unit belongs to T_d point group:
See section 3.12 in Cotton 2nd edition

T_d has the following operations:

E (I think everyone can find this one)
8C₃ : the C₃ axes are along each S-O bond. This makes four C₃’s, but you also have to
count the C₃² (i.e., do C₃ twice) operations under the C₃ operations. That makes 8.
3C₂: These go through the tetrahedron edges. 3C₂ = 3S₄²
6S₄: Again, have 3S₄ and 3S₄³.
6σ_d: Mirror planes- these are the ones that are hard to find unless you have a 3D model.

b) Show the application of symmetry operations of T_d upon the atoms in SO₄²⁻ unit
generates the reducible representation Γ given in homework.

Remember only atoms that don’t move to a new position in space will have on-diagonal
elements in the transformation matrix. So we only have to consider those that don’t
move.

For E: all 5 atoms remain unchanged and all atoms are projected back onto themselves.

For each atom:

x' 1 0 0
y' 0 1 0
z' 0 0 1

trace = 3 x 5 atoms = 15 for molecule. E = 15.

For C₃: One O atom and the S atom project back onto themselves. For these two, two of
their axes are rotated 120 degrees, and the third remains the same. This is the hard one.

For 2 atoms:

x' -1/2 x₃/2 0
y' -x₃/2 -1/2 0
z' 0 0 1

trace = 0 x 2 atoms = 0 for molecule. C₃ = 0.

Similarly, C₂ = -1, S₄ = -1, and σ_d = 3.
Reduce the representation into its component symmetry species. See Cotton, Section 4.3 and equation 4.3-11.

To find h: \( h = 1 + 8(1) + 3(1) + 6(1) + 6(1) = 24 \)

Look at the character table for \( T_d \). We see all of the possible irreducible representations available for this group.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>8C_3</th>
<th>3C_2</th>
<th>6S_4</th>
<th>6\sigma_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A_2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T_1</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>T_2</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

And our reducible rep:

\( \Gamma \)

Using eqn 4.3-11 we find:

\[
A_1 = \frac{1}{24} (1(1)15 + 8(1)(0) + 3(1)(-1) + 6(1)(-1) + 6(1)(3)) = 24/24 = 1
\]

\[
A_2 = \frac{1}{24} (1(1)15 + 8(1)(0) + 3(1)(-1) + 6(-1)(-1) + 6(-1)(3)) = 0/24 = 0
\]

Similarly, \( E = 1; \ T_1 = 1; \ T_2 = 3 \).

So \( \Gamma = A_1 + E + T_1 + 3T_2 \)

d) (I know, no part c). Degrees of freedom = \( 3N-6 = 15-6 = 9 \)

From character table, find rotations Rx, Ry, Rz are \( T_1 \)

Translations x,y and z are \( T_2 \).

Sec. 10.3 in Cotton talks about degenerate modes. Since all 3 of the rotations are degenerate and all 3 translations are degenerate, we just need to subtract one \( T_1 \) (remember, \( T \) means triply degenerate) and one \( T_2 \) from the \( \Gamma \) to get rid of them.

So genuine vibrations are represented by \( A_1 + E + 2T_2 \).

e) The symmetric stretch \( \nu_1 \) just has all S-O bonds stretching and contracting together: (Imagine O’s at ends of arrows):

\[
\begin{align*}
S & \quad \leftrightarrow \\
& \quad \upaarrow \\
S & \quad \dnearrow \\
\end{align*}
\]

f) The 2 \( T_2 \) modes are the only ones that are IR active, using the character table.
g) The key here is to only think about our original 5 atoms: don’t try to include the M atom in the calculation of reducible representations. Its sole purpose in life is to make one of the O atoms different from the others.

The new, less symmetric $\text{SO}_4^{2-}$ has one $C_3$, one $C_3^\perp$, $3\sigma_v$, $E$, and no more $C_2$’s or $S_4$’s. So the group is $C_{3v}$.

The reducible representation only has $E$, $C_3$, and $\sigma_v$ in it now, but if you think about it, the trace for each of these is the same. So

\begin{align*}
\Gamma & \quad E \quad 2C_3 \quad 3\sigma_v \\
\Gamma & \quad 15 \quad 0 \quad 3
\end{align*}

and $h = 1+2+3 = 6$

so figure out irreducible representations:

\begin{align*}
A_1 & = 1/6 \ (1(1)15+2(1)(0)+3(1)(3)) = 4 \\
A_2 & = 1/6 \ (1(1)15+2(1)(0)+3(-1)(3)) = 1 \\
E & = 1/6 \ (1(2)15+2(-1)(0)+3(0)(3)) = 5
\end{align*}

$\Gamma = 4A_1+1A_2+5E$;

Rotations are $A_2 + E$ and translations are $A_1 + E$ so the vibrations left are: $3A_1+3E$, all 6 of which are IR active!

h) Now two cations interact strongly with the $\text{SO}_4^{2-}$ group. We are left with one $C_2$, one $\sigma_v$ and one $\sigma_{v'}$, and $E$. You should recognize this as $C_{2v}$.

We have:

\begin{align*}
\Gamma & \quad E \quad C_2 \quad \sigma_v \quad \sigma_{v'} \\
\Gamma & \quad 15 \quad -1 \quad 3 \quad 3
\end{align*}

so $h = 1+1+1+1 = 4$

\begin{align*}
A_1 & = 1/4 \ (1(1)(15)+1(1)(-1)+1(1)(3)+1(1)(3)) = 5 \\
A_2 & = 1/4 \ (1(15)+1(-1)+-1(3)+-1(3)) = 2 \\
B_1 & = 4 \\
B_2 & = 4
\end{align*}

Subtract Rotations ($A_2 + B_1 + B_2$) and translations ($A_1 + B_1 + B_2$) and we get vibrational motions:

$4A_1 + A_2 + 2B_1 + 2B_2$; all of which are IR-active except $A_2$, so there are 8 IR-active vibrations
i) Summary of results:

<table>
<thead>
<tr>
<th></th>
<th>$T_d$</th>
<th>$C_{3v}$</th>
<th>$C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibrations</td>
<td>$A_1 + E + 2T_2$</td>
<td>$3A_1 + 3E$</td>
<td>$4A_1 + A_2 + 2B_1 + 2B_2$</td>
</tr>
<tr>
<td>IR active vibrations</td>
<td>$2T_2$</td>
<td>$3A_1 + 3E$</td>
<td>$4A_1 + 2B_1 + 2B_2$</td>
</tr>
</tbody>
</table>

We can logically deduce the splitting of the $T_2$ states from $T_d$ to $C_{3v}$ to $C_{2v}$ (or you can use character tables).

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$C_{3v}$</th>
<th>$C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$A_1 + A_2$</td>
</tr>
</tbody>
</table>

Two of these:

$T_2$ | $A_1 + E$ | $A_1 + B_1 + B_2$

So one would expect that each $T_2$ band would be a single band in a $T_d$ environment, would split into two bands in $C_{3v}$ symmetry, and then split into 3 bands in a $C_{2v}$ environment.

Looking at the real mineral data:

**Mascagnite**: (NH$_4$)$_2$SO$_4$ Isolated SO$_4$ tetrahedra with $T_d$ symmetry, see one peak for $\nu_4$.

**Anhydrite**: CaSO$_4$ Chains of alternating edge-sharing S tetrahedral and Ca 8-fold sites. This is closest to the model with 2 M’s attached to tetrahedron, $C_{2v}$, and see three peaks. (Hawthorne and Ferguson, Can Min, v.13, 289-292, 1975)

**Glauberite**: CaNa$_2$(SO$_4$)$_2$ Has SO$_4$ tetrahedra with one S-O-Ca angle relatively close to 180 degrees, so expect this is closest to the model with one M attached to tetrahedron, $C_{3v}$, and see two peaks! (Araki and Zoltai, Am Min v.52, 1272-1277, 1967)