Homework

- confirm for yourself for homework that $\Gamma_{3H}(H_2O) = 3A_1 + 1A_2 + 2B_1 + 3B_2$

$$\begin{array}{c|cccc}
\Gamma(H_2O) & E & \sigma(xz) & \sigma'(yz) \\
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 & -1 \\
\end{array}$$

$$\begin{array}{c|cccc}
\Gamma(H_2O) & E & \sigma(xz) & \sigma'(yz) \\
B_1 & 1 & -1 & 1 & -1 \\
B_2 & 1 & -1 & -1 & 1 \\
\end{array}$$

\[ n_A = \frac{1}{4}[(1\cdot9\cdot1)+(-1\cdot-1\cdot1)+(1\cdot1\cdot1)+(1\cdot3\cdot1)] \]

\[ n_A = \frac{1}{4}[9-1+1+3]=\frac{12}{4}=3 \]

\[ n_B = \frac{1}{4}[(1\cdot9\cdot1)+(-1\cdot-1\cdot1)+(1\cdot1\cdot1)+(1\cdot3\cdot1)] \]

\[ n_B = \frac{1}{4}[9+1+1-3]=\frac{8}{4}=2 \]

\[ n_A = \frac{1}{4}[9-1-1-3]=\frac{4}{4}=1 \]

\[ n_B = \frac{1}{4}[9+1-1+3]=\frac{12}{4}=3 \]

Problem

- determine the symmetry and activity of the vibrational modes of a tetrahedral molecule such as CH₄ or CCl₄
  - first find all the symmetry elements of $T_d$ (this was a tutorial problem from the MOs course)
    - I've reproduced some of the material here
  - The character table for the $T_d$ point group (Figure 1) is shown to the left, and it tells us the key symmetry operations in this group are $E$, $8C_3$, $3C_2$, $6S_4$ and $6\sigma_d$
  - there are three useful ways of thinking about a tetrahedral moleucle, each one emphasises a different aspect of symmetry, Figure 2
    - (a) the $C_2$ axes
    - (b) the $C_3$ axes
    - (c) the cubic structure
    - the "cube" may be less familiar to you, think of the H atoms occupying opposite corners of a cube and the central atom A is at the centre
  - there are 8$C_3$ operations
    - a $C_3$ axis lies along each bond, one $C_3$ axis is shown in Figure 3, the others are easily predicted because the four H atoms are symmetry equivalent, if one has a $C_3$ axis passing through it then they all will, hence there are four $C_3$ axis symmetry elements
    - around each axis there are 3 possible $C_3$ operations: $C_3^1 \ C_3^2 \ C_3^3$, the last operation $C_3^3 = E$ is equivalent to the identity and so is already counted, there are then two symmetry operations associated with each $C_3$ axis and thus there are eight distinct $C_3$ operations in $T_d$: 8$C_3$
- there are 3C₂ operations
  - a C₂ axis lies between each pair of A-H bonds, Figure 4a, bisecting each pair of atoms and through the center of each pair of faces in the cube, Figure 4b, as there are 3 pairs of faces to each cube, there will be 3C₂ axes
  - as we associate only one operation with each C₂ axis there are 3C₂ operations in Td

- there are 6σ_d operations
  - a σ mirror plane passes through each pair of atoms and contains a C₂ axis, i.e., two mirror planes cross each pair of faces, Figure 5, these are dihedral mirror planes σ_d.
  - as there are 3 pairs of faces each with two mirror planes there are 6σ_d operations in Td

- there are 6S₄ operations
  - each C₂ axis has a coincident S₄ axis, consider a rotation of 90° around this axis and then reflection in a plane perpendicular to the axis through the center of the molecule. An example of these elements for the S₄₁ operation is given in Figure 6.
  - notice that neither the C₄ nor the σ_h exist within the T₄ point group as separate elements!!

- S₄₁(Figure 7) is the same as C₄₁ operation and C₂ lies to the left of S₄ and so this operation is not counted with the S₄ operations. In addition the S₄₁ operation is the same as E and so is not counted here either.
thus there are 2S₄ operations per C₂ axis, and as there are 3C₂ axes there must be 6S₄ operations in Tₐ.

- Thus we have shown that there are E, 8C₃, 3C₂, 6S₄, and 6σₐ operations for the Tₐ point group.
- determine the reducible representation, start with the number of atoms lying on symmetry elements, then use the table at the back of your character tables:

<table>
<thead>
<tr>
<th></th>
<th>Tₐ</th>
<th>E</th>
<th>C₃</th>
<th>C₂</th>
<th>S₄</th>
<th>σₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>atoms</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>χ(per atom)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Γ(CCl₄)</td>
<td>15</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

• determine the irreducible representation of the translation and rotation for the whole molecule

\[
\Gamma(T) = T₁
\]
\[
\Gamma(R) = T₂
\]
\[
\Gamma(T + R) = T₁ + T₂
\]

• subtract the translation and rotation from the reduced representation of 3N to obtain the symmetry of the vibrational modes

\[
\Gamma_{vib}(CH₄) = \Gamma(CH₄) - \Gamma(T + R)
\]
\[
= (A₁ + E + T₁ + 3T₂) - (T₁ + T₂)
\]
\[
= A₁ + E + 2T₂
\]

• determine the IR and Raman activity of these modes
• IR have the same symmetry as the translational motions
  \[ \Gamma(T) = T_2 \]
• Raman have the same symmetry as the binary functions
  \[ \Gamma(f) = A_i + E + T_2 \]
• symmetry and activity of the vibrational modes of CCl₄ are
  \[ \Gamma_{vib}(CH₄) = A_i(pol) + E(depol) + 2T_2(IR,depol) \]
• the vibrational modes are:

\[ \nu_1(A_1) \text{ symmetric stretch} \approx 459 \text{ cm}^{-1} \]
\[ \nu_2(E) \text{ symmetric bend} \approx 218 \text{ cm}^{-1} \]
\[ \nu_{3a}(T_2) \text{ degenerate stretch} \approx 793 \text{ cm}^{-1} \]
\[ \nu_{4a}(T_2) \text{ degenerate bend} \approx 314 \text{ cm}^{-1} \]

**Figure 8** vibrational modes of methane

• 3N-6=3\times5-6=9 and thus there are 9 modes 1(A₁)+2(E)+6(T₂)
• which produce 4 peaks in the Raman spectrum and 2 peaks in the IR spectrum
• however a number of the IR peaks are outside the range of normal IR spectrometers (400-4000 cm⁻¹).

**Figure 9** Raman and IR spectra of CCl₄ from web-page: http://ed.augie.edu/~viste/Raman/RamanQuantum.html