Molecular Vibrations

“Bench-Top” Assignment of Vibrational Spectra

- to determine the number and symmetry of the molecular vibrations of a molecule, we must
  1. determine the reducible representation
  2. reduce the representation
  3. determine the symmetry of the CoM motions
  4. determine the symmetry of the vibrational modes
  5. correctly predict the IR and Raman activity
  6. present $\Gamma_{\text{vib}}$ and describe the spectrum

Determine the Reducible Representation

- determining the reducible representation is easily achieved by forming a representation table
- the best way to explain this is by example, Figure 1 shows the representation table for $\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>atoms</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>$\chi(\text{per atom})$</td>
<td>3</td>
<td>$-1$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma(H_2O)$</td>
<td>9</td>
<td>$-1$</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 1 Representation table for $\text{H}_2\text{O}$

- first write out the operations of the point group as the header for the table
- determine the atoms that remain at the same position under each symmetry operation for the row labelled “atoms”
- in Figure 2 the red atoms are those that remain at the same position for each operation

- under $E$ there are 3 atoms that don’t move $\rightarrow 3$
- under $C_2$ there is 1 atom that does not move $\rightarrow 1$
- under $\sigma(xz)$ there is 1 atom which does not move $\rightarrow 1$
- under $\sigma(yz)$ there are 3 atoms which don’t move $\rightarrow 3$
• we then **apply a set of general rules** summarized in **Table 1**,

<table>
<thead>
<tr>
<th>Q</th>
<th>( \chi(Q) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E )</td>
<td>+3</td>
</tr>
<tr>
<td>( i )</td>
<td>-3</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>+1</td>
</tr>
<tr>
<td>( C_n )</td>
<td>( 2 \cos \theta + 1 )</td>
</tr>
<tr>
<td>( S_n )</td>
<td>( 2 \cos \theta - 1 )</td>
</tr>
</tbody>
</table>

**Table 1** contribution to a reducible representation for each symmetry operation.

- at the end of this lecture I will show you how the values in this table are derived, but first I want to show you how to use this information.
- enter this information along the row labelled “\( \chi(\text{per atom}) \)” in representation table, thus
  - under \( E \) each atom contributes 3
  - under \( C_n \) axis each atom contributes \( 2 \cos \theta + 1 \) which for \( \theta = 180^\circ \) is \( 2 \cos(180^\circ) + 1 = (-2) + 1 = -1 \) leading to a total of -1
  - under \( \sigma \) each atom contributes 1

• multiply the numbers in each column to generate the reducible representation \( \Gamma(\text{molecule}) \)
  - \( \Gamma \) (capital Greek gamma) is formal notation for an unknown or undefined symmetry label.

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( \sigma(xz) )</th>
<th>( \sigma(yz) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma(H_2O) )</td>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

**Figure 3** Reducible representation for \( H_2O \)

**In Class Activity**

• determine the reducible representation for a molecule of ammonia

<table>
<thead>
<tr>
<th>( C_{3v} )</th>
<th>( E )</th>
<th>( 2C_3 )</th>
<th>( 3\sigma_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_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>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 4** \( C_{3v} \) point group and symmetry elements

<table>
<thead>
<tr>
<th>( C_{3v} )</th>
<th>( E )</th>
<th>( C_3 )</th>
<th>( \sigma_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi(\text{per atom}) )</td>
<td>( \Gamma(NH_3) )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5** Representation table for ammonia
Reduction of the Reducible Representation

- the reducible representation can then be broken up into contributions from the irreducible representations
  - this is entirely analogous to the way that a vector \( \mathbf{v} = x \hat{i} + y \hat{j} + z \hat{k} \) in Cartesian space can be defined by coefficients \((x, y, z)\) times unit vectors \((\hat{i}, \hat{j}, \hat{k})\) where the unit vectors completely define Cartesian space.
  - a reducible representation can similarly be defined in terms of coefficients times the "unit vectors" or irreducible representations (IR) of the point group, which completely define the space.
  - every reducible representation \(\Gamma_R\) can be written as a sum of the irreducible representations \(\Gamma_{IR}\) of a point group, where \(n_{IR}\) is the number of times a particular irreducible representation occurs:
    \[
    \Gamma_R = \sum_{IR} n_{IR} \Gamma_{IR}
    \]
    \[\text{Equation 1}\]
- the reduction formula is employed to determine the contribution of each irreducible representation to the reducible representation.

**IMPORTANT**

<table>
<thead>
<tr>
<th>The Reduction formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_{IR} = \frac{1}{h} \sum_Q k \cdot \chi_{IR}(Q) \cdot \chi_R(Q))</td>
</tr>
<tr>
<td>(h) = number of operations in the group</td>
</tr>
<tr>
<td>(Q) = a particular class of symmetry operation</td>
</tr>
<tr>
<td>(k) = the number of operations in that class</td>
</tr>
<tr>
<td>(\chi_{IR}(Q)) = the character of the Irreducible Representation under (Q)</td>
</tr>
<tr>
<td>(\chi_R(Q)) = the character of the Reducible Representation under (Q)</td>
</tr>
</tbody>
</table>

**Equation 2**: The reduction formula

- I expect you to know this formula
- component terms of the reduction formula are shown for the \(C_3v\) character table in **Figure 6**
  - \(h\) is the number of operations in the point group and for \(C_3v\) this is 1E+2C3+3\(\sigma_v\)=6 operations

**Figure 6** Components of the reduction formula
• it is best to use a **reduction table** when determining the $n_{IR}$ as it is extremely easy to make simple algebraic errors when performing a reduction
  o below is an example of the reduction process for the $A_1$ IR
  o all molecules possess a totally symmetric stretching vibration, and so we always start by evaluating the number of totally symmetric IRs
  o if you are requested to "**show your working**" the following is expected, **Figure 7**

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma(H_2O)$</td>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$\overrightarrow{\downarrow}$ $\overrightarrow{\downarrow}$ $\overrightarrow{\downarrow}$ $\overrightarrow{\downarrow}$

$n_{h} = \frac{1}{4}[(1 \cdot 9 \cdot 1) + (1 \cdot -1 \cdot 1) + (1 \cdot 1 \cdot 1) + (1 \cdot 3 \cdot 1)] = \frac{1}{4}[9 - 1 + 1 + 3] = \frac{12}{4} = 3$

**Figure 7** Reduction table for the $A_1$ IR

• the process is to work through all the IR one by one for the point group (confirm this for yourself for homework!)
  o in the exam I only expect you to show the long working for one IR
• employing the reduction formula leads to the following for $H_2O$:

$$\Gamma_{3N}(H_2O) = 3A_1 + 1A_2 + 2B_1 + 3B_2$$

**Equation 3**

**In Class Activity**
• reduce the reducible representation for ammonia, show your working

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma(NH_3)$</td>
<td>12</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

**Figure 8** Reduction of the reducible representation of $NH_3$
Removal of the CoM Translations and Rotations

• the reduced representation still includes the collective motions for the translational and rotational motion of the whole molecule. These are not vibrations, and must be subtracted out.

• there are 3 coordinates (x, y, z) contributing for each atom, 3N where N=number of atoms, and we must subtract out the 6 concerted motions (rotation and translation of the centre of mass) for the molecule and hence we arrive at the general rule that:

\[
\text{there are 3N-6 vibrational motions for a molecule with N atoms}
\]

• when the molecule is linear there are 3N-5 vibrational motions

• we have already identified the irreducible representations of the translational and rotational motions for the water molecule (Lecture 1)

  o translation: \( T_x (B_1) \ T_y (B_2) \) and \( T_z (A_1) \)
  o rotation: \( R_x (B_2) \ R_y (B_1) \) and \( R_z (A_2) \)
  o thus the translation and rotational component total to

\[
\Gamma (T \ & R) = 1A_1 + 1A_2 + 2B_1 + 2B_2
\]

Equation 4

• we subtract out the translational and rotational motions which leaves the vibrations for the water molecule

\[
\Gamma (H_2O) - \Gamma (T \ & R) = \left( 3A_1 + 1A_2 + 2B_1 + 3B_2 \right) - \left( 1A_1 + 1A_2 + 2B_1 + 2B_2 \right)
\]

\[
\Gamma_{\text{vib}} (H_2O) = 2A_1 + B_2
\]

Equation 5

• thus the water molecule has 3 fundamental vibrational modes
• however while all of these motions are occurring (and can be computationally determined) they may not all be observable experimentally

Determine the Modes that are IR or Raman Active

• as part of a full assignment we need to identify which vibrational modes are infrared active (IR) and/or Raman active

• IR active modes

  o to be infrared active a vibrational mode must produce a dipole moment change
  o in a later lecture I will explain the mathematics behind this “selection rule” for the moment we will just use it
  o the IR active modes are those that have the same symmetry as the dipole moment (\( \mu \))
  o the dipole moment is a vector with components in the x, y and z directions
  o x, y and z Cartesian functions have the same symmetry as the translational vectors \( \{T_x, T_y, T_z\} \) identified in the character table
  o in the \( C_s \) character table \( \{T_x, T_y, T_z\} \) have \( \{B_1, B_2, A_1\} \) symmetry
  o thus the IR active modes of water must be of \( B_1, B_2, \) or \( A_1 \) symmetry
  o hence all of the water modes are IR active, this is indicated by adding (IR) in brackets after the listing the symmetry of the mode
• Raman active modes
  o to be Raman active a vibrational mode must produce a change in the molecular polarizability (\(\alpha\)) of the molecule
  o in a later lecture I will explain in more detail what the polarizability is and the mathematics behind this “selection rule”
  o \(\alpha\) has the same symmetry as the binary functions \(\{x^2, y^2, z^2, xy, xz, yz\}\)
  o in the C\(_{2v}\) character table the binary functions \(\{x^2, y^2, z^2, xy, xz, yz\}\) span the IRs \(A_1, A_2, B_1\) and \(B_2\)
  o thus the Raman active modes of water are of \(A_1, A_2, B_1\) or \(B_2\) symmetry
  o in addition Raman active modes will leave plane polarised light polarised if they are totally symmetric, otherwise it is depolarised.
  o in a later lecture I will describe Raman spectroscopy in more detail and explain what it means for light to be polarised
  o the Raman activity of \(A_1\) modes is identified by adding (pol) after the listed mode, the activity of other modes by adding (depol)

Describing the Vibrational Assignment
• thus the full description for the vibrational modes of water is:

\[
\Gamma_{vib}(H_2O) = 2A_1(IR, pol) + B_2(IR, depol)
\]

Equation 6

• if you are asked to "determine \(\Gamma_{vib}\)" or to determine the symmetry of the vibrational modes of a molecule, this is the expected expression; identify the number and type of irreducible representations, and if the vibration is IR active or Raman active and if the Raman mode is polarised or depolarised.

• the nature of the vibrational modes is shown in Figure 9, I will show you next lecture how to derive these (“benchtop”). I will also explain how these are calculated in a quantum chemistry code. The IR spectrum of water is shown in Figure 10

\[\begin{align*}
\nu_1 & \quad & \text{symmetric stretch} & \quad & \text{A}\_1 & \text{symmetry} & \approx 3657\text{cm}^{-1} \\
\nu_3 & \quad & \text{asymmetric stretch} & \quad & \text{B}\_1 & \text{symmetry} & \approx 3756\text{cm}^{-1} \\
\nu_2 & \quad & \text{symmetric bend} & \quad & \text{A}\_1 & \text{symmetry} & \approx 195\text{cm}^{-1}
\end{align*}\]

Figure 9 Vibrational modes for water

Figure 10 The IR spectrum of \(H_2O\) and \(D_2O\).\(^1\)

\(^1\) G.E. Walsden, *J. Chem. Phys.* Vol 40 (11), 1964, p3249
In Class Activity

- determine the $\Gamma_{\text{vb}}(\text{NH}_3)$ assignment for ammonia

$$\Gamma_{3N}(\text{NH}_3) = 3A_1 + 1A_2 + 4E$$  \hspace{1cm} \text{Equation 7}

- subtract the IR for the translation and rotation of the whole molecule

- IR have the same symmetry as the translational motions

- Raman have the same symmetry as the binary functions

- symmetry and activity of the vibrational modes of ammonia is:

$$\Gamma_{\text{vib}}(\text{NH}_3) =$$  \hspace{1cm} \text{Equation 8}

---

![Figure 11 Raman spectrum showing the vibrational modes of gaseous ammonia, there is significant rotational fine structure associated with some of the vibrational modes.](image)

---

Determining the Reducible Representation

- what is the reducible representation and where does it come from?
- to determine the symmetry of the molecular vibrations, we must examine the irreducible representations spanned when every atom of a molecule is free to move in any direction, Figure 12.

![Diagram of symmetry elements and coordinate system](image)

**Figure 12** Symmetry elements and the coordinate system

- to determine the overall reducible representation we must determine how each vector x, y or z on every atom transforms under every symmetry operation, Figure 13.

![ matrices for the vibrational assignment of H2O, for clarity components that remain zero not filled in](image)

**Figure 13** Matrices for the vibrational assignment of H2O, for clarity components that remain zero not filled in

- the characters or trace of these matrices can be recorded in a representation table:

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma'(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma{H_2O}$</td>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

- I hope you remember that the numbers in the body of a character table, are the characters. Last term we determined the characters for degenerate orbitals by taking the trace of a transformation matrix.
• the size of these matrices grows as $3N$ and thus they become very large, however we are not interested in the particular matrix representation, but only in the trace, and luckily there are short-cuts for determining the reducible representation

• We can generate a set of general rules:
  o E always has a contribution of $3N$, as no atoms change location
  o when an atom moves it contributes nothing to the trace (look at $H_a$ and $H_b$ for the $C_2$ and $\sigma(xz)$ matrices of water in Figure 13)
  o for each atom on an inversion center the vectors $(x,y,z) \to (-x,-y,-z)$ and thus $\sum \chi_{ii} = -3$

$$
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix} \xrightarrow{i} \\
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{bmatrix}
$$

Equation 9

• for each atom on a mirror plane one vector remains unchanged while the other two are reflected $\sum \chi_{ii} = +1 -1 +1 = +1$

$$
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix} \xrightarrow{\sigma(xz)} \\
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

Equation 10

• for each atom on a rotation axis $\sum \chi_{ii} = \cos\theta + \cos\theta + 1 = 2\cos\theta + 1$

$$
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix} \xrightarrow{C_2(z)} \\
\begin{bmatrix}
\cos(\theta) & -\sin(\theta) & 0 \\
\sin(\theta) & \cos(\theta) & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

Equation 11

$\theta$

$C_2$ 180° $2(-1) + 1 = -1$

$C_3^1, C_3^2$ 120°, 240° $2(-\frac{1}{2}) + 1 = 0$

$C_4^1, C_4^3$ 90°, 270° $2(0) + 1 = 1$

• for each atom on an improper rotation axis $\sum \chi_{ii} = \cos\theta + \cos\theta - 1 = 2\cos\theta - 1$

$$
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix} \xrightarrow{S_3(z)} \\
\begin{bmatrix}
\cos(\theta) & -\sin(\theta) & 0 \\
\sin(\theta) & \cos(\theta) & 0 \\
0 & 0 & -1
\end{bmatrix}
$$

Equation 13

$\theta$

$S_3^1, S_3^2$ 120°, 240° $2(-\frac{1}{2}) - 1 = -2$

$S_3^1, S_3^3$ 90°, 270° $2(0) - 1 = -1$
• summarizing the **contribution per un-shifted atom** to the reducible representation we generate **Table 1**

<table>
<thead>
<tr>
<th>$Q$</th>
<th>$\chi(Q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>+3</td>
</tr>
<tr>
<td>$i$</td>
<td>−3</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>+1</td>
</tr>
<tr>
<td>$C_n$</td>
<td>$2\cos\theta + 1$</td>
</tr>
<tr>
<td>$S_n$</td>
<td>$2\cos\theta − 1$</td>
</tr>
</tbody>
</table>

**Table 1**

**Key Points**
- be able to determine the reducible representation and write out a representation table for a given molecule
- be able to explain how the reducible representation is related to the irreducible representations
- be able to write down the reduction formula and define all the terms
- be able to reduce a reducible representation to its irreducible components
- be able to explain the origin of the 3N-6 rule for vibrations
- be able to determine $\Gamma_{\text{vib}}$ and show your working for this process
- be able to determine with reference to the dipole moment and polarizability which vibrations are IR and Raman active
- be able to explain using a simple molecule and the full matrix representation how to obtain the reducible representation of a molecule
- be able to explain how the characters for the short-cut “table” are obtained

**Self-Study Problems / Exam Preparation**
- determine the symmetry and activity of the vibrational modes of a tetrahedral molecule such as CH$_4$ or CCl$_4$