Determining the Normal Modes of Vibration

Introduction

• vibrational modes of ammonia are shown below

\[
\begin{align*}
&v_1(A_1) & v_2(A_1) & v_{3a}(E) & v_{4a}(E) \\
&\text{symmetric stretch} & \text{symmetric bend} & \text{degenerate stretch} & \text{degenerate bend}
\end{align*}
\]

Figure 1 Vibrational modes

• without carrying out a full normal mode analysis it can be difficult to establish the nature of all the vibrational modes. However, we can determine some of the modes using simple techniques.

• The process is as follows:

1. treat stretches, in-plane bends and out-of-plane bends separately
2. define ALL symmetry elements, identify all symmetry operators
3. define vectors for each motion
4. determine the reducible representation
5. reduce to the irreducible representation (USE short-cuts!)
6. eliminate redundant components
7. use the projection operator to determine the form of the modes
8. add additional movements to ensure the CoM remains stationary

Define ALL symmetry elements, identify all symmetry operations

• identify and label all the conjugate symmetry elements
• each class is expanded in the projection table

\[
\begin{array}{c|cccc}
\sigma_v(3) & C_3v & E & 2C_3 & 3\sigma_v \\
\sigma_v(2) & C_3v & E & C_3 & \sigma_v(1) & \sigma_v(2) & \sigma_v(3)
\end{array}
\]

Figure 2 Defining stretches and symmetry elements

Determine the Form of the Vibrational Modes: Stretches First

• take a vector for each type of bond
• use single arrowheads for stretches
• define them relative to the symmetry elements and individually label them
• s stands for bond stretch vector

Figure 3 define vectors
• determine the reducible representation, and reduce it to the irreducible representation components, use short-cuts!

\[
\begin{array}{c|ccc}
C_{3v} & E & 2C_3 & 3\sigma_v \\
\hline
\Gamma(s_{N-H}) & A_1 \\
\Gamma(s_{N-H}) - A_1 \\
\end{array}
\]

**Figure 4** Setup for the stretching modes

- stretches will always have a totally symmetric mode
- thus we determine
- stretching modes do not usually have redundant components
- use the projection operator to determine the form of the vibration

\[
\begin{array}{c|cccccc}
\hline
C_{3v} & E & C_3^1 & C_3^2 & \sigma_v(1) & \sigma_v(2) & \sigma_v(3) \\
\hline
Q[s_1] & A_1 & 1 & 1 & 1 & 1 & 1 \\
E & 2 & -1 & -1 & 0 & 0 & 0 \\
\hline
\end{array}
\]

- vibrational wavefunctions (= vibrational modes) are:

\[
\text{vibrational modes:} \quad \begin{cases}
\text{A}_1 \\
\text{E}
\end{cases}
\]

- draw out the vibrational modes adding vectors to eliminate the CoM motion
  - the A$_1$ mode is obviously a totally symmetric stretch
  - the E modes are asymmetric stretches
  - arrows are added to the N atom to ensure the CoM does not move.
  - you are only required to find ONE of the degenerate modes

**Figure 5** Final stretching modes

**Consider the Breathing Motions**

- NH$_3$ is not planar so there are no "in-plane" modes, however we can consider the modes that would be in-plane if NH$_3$ were planar, these are sometimes called the breathing motions
- take a vector for each motion (use double arrowheads for breathing or in-plane motions), determine the reducible representation, and reduce it to the irreducible representation components
- define the breathing mode vectors on a diagram, **Figure 6**
  - can be represented as an expansion and contraction of the angles involved

  \[
  \begin{array}{c}
  \text{N-H "in"-plane bends} \\
  \text{\textbf{Figure 6} Setup for the breathing modes}
  \end{array}
  \]

  - it is clear the breathing modes have the same reducible representation as
    the stretches, and hence will span the same IR \( \Gamma(a_{H-N-H}) = A_1 + E \)

- eliminate redundant modes
  - the \( A_1 \) mode is redundant because if the molecule was planar all of the \( \text{H-N-H} \) angles cannot close at once, this leaves only the \( E \) mode
  - this is a common feature of breathing modes; the totally symmetric mode
    is not allowed for physical reasons

- use the projection operator
  - the breathing vibrations have the same reducible representation and
    distribution of vectors as the stretching motions and therefore they will
    have similar wavefunctions, thus it is not necessary to repeat the
    projection process and we can write the equation for the \( E \) mode directly

- the final sketch should contain only single headed arrows
  - the form of these modes can be difficult to "sketch" from the projector
    method functions, this highlights a short coming of this method
  - from the equation we know \( a_1 \) is expanding (doubling) and \( a_2 \) and \( a_3 \) are contracting
  - \( * \text{H} \) feels same forces on both sides and remains stationary, the other \text{H}s
    are moving (breathing) in and out.
  - then to stop the whole molecule translating the \text{N} and \( \text{*H} \) must move.

  \[
  \begin{array}{c}
  \text{\textbf{Figure 7} Final form of the breathing modes}
  \end{array}
  \]
Consider the Umbrella Motions

- take a vector for each motion (use **single arrowheads** for umbrella or out-of-plane motions), determine the reducible representation, and reduce it to the irreducible representation components

\[
\begin{array}{ccc}
C_3v & E & 2\sigma_v \\
\Gamma(b_{x-N-H}) & 3 & 0 & 1 \\
\end{array}
\]

N-H out-of-plane bends

- it is clear that the umbrella vectors have the same reducible representation as the stretches, and hence will span the same IR \( \Gamma(b_{x-N-H}) = A_1 + E \)

- determine the form of the active umbrella motions
  - determine the active mode by considering the modes already identified

- only two E modes are allowed, and we have already found both of them (one is a stretch and the other an "in-plane" or breathing bend).
  - thus the active mode must be the \( A_1 \) symmetric bend.

- use the projection operator
  - because of the similarities with the breathing modes and stretches the form of this mode can be determined directly

**Figure 8** Setup for the umbrella modes

**Figure 9** Final form of the umbrella modes

Complete the Assignment

- we have found the symmetry and vectors for all vibrational modes of \( \text{NH}_3 \)
- we can add further detail to our interpretation of an experimental spectrum or prediction of a spectrum yet to be obtained
- generally when assigning a spectrum:
  - stretches occur at higher wavenumbers than bends (why!)
  - asymmetric modes generally occur at higher energies than symmetric modes (but not always!)
- **group modes**, i.e., those that belong to a functional group remain similar to those of the isolated molecule in the gas phase due to the **local symmetry**
- if the symmetry is strongly broken more modes appear in the spectrum
- **rule of mutual exclusion** molecules which have a center of inversion have no coincidences between the infrared and Raman modes

- all of the information obtained can be summarised in a table and diagram

<table>
<thead>
<tr>
<th>Infrared (matrix, cm(^{-1}))</th>
<th>Activity</th>
<th>Symmetry</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>3378</td>
<td>IR, depol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3223</td>
<td>IR, pol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1646</td>
<td>IR, depol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1060</td>
<td>IR, pol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **describe** the spectrum of NH\(_3\)
  - all vibrations are present in both the Raman and Infrared spectra, the infrared spectrum will contain 4 peaks 2 of which will be degenerate, and the Raman spectrum which will contain 4 peaks 2 of which will be polarised and the other two degenerate

  \[
  \Gamma_{vib}(\text{NH}_3) = 2A_1(\text{IR, pol}) + 2E(\text{IR, depol})
  \]

  - the two highest wavenumber modes belong to the N-H stretches and will have \(A_1\) and \(E\) symmetry, the \(A_1\) mode will be Raman polarised
  - the two lowest wavenumber modes belong to bends. The umbrella motion is totally symmetric and thus will be polarised in the Raman spectrum. The breathing motion is a degenerate asymmetric bend of \(E\) symmetry.

- **IMPORTANT** when you are asked to "Assign the spectrum of \(X\)" you are expected to
  - determine the symmetry and activity of all vibrational modes

  \[
  \Gamma_{vib}(X) = n_1 \Gamma_1(\text{IR, pol}) + n_2 \Gamma_2(\text{IR, pol}) + \cdots
  \]

  - determine the form of the vibrations and provide sketches
  - assign the experimental spectrum supplied (as in the above table), or to describe the expected spectrum (as indicated above).
Computing the Normal Modes

- The vibrational energy levels are determined by solving the HO form of the Schrödinger equation for the nuclear wavefunctions.
- Where did the potential for the HO come from? Consider a Taylor expansion about the equilibrium position (x=0)

\[
V(x) = V(0) + \frac{dV}{dx} \bigg|_{x=0} x + \frac{1}{2} \frac{d^2V}{dx^2} \bigg|_{x=0} x^2 + \frac{1}{3!} \frac{d^3V}{dx^3} \bigg|_{x=0} x^3 + \cdots
\]

- We set \(V(0)=0\) (vertical alignment)
- At equilibrium the first derivative is zero (slope is zero)
- Third order and higher terms are assumed to be very small and are ignored
- This leaves only the second term and we associate the second derivative or curvature of the potential energy with the force constant \(k\):

\[
V(x) = \frac{1}{2} \left( \frac{d^2V}{dx^2} \right)_0 x^2
\]

- So what does this mean? For example, a large force constant indicates a strong bond, and to stretch or contract a strong bond takes a large amount of energy.

The force constants and curvature

- However, the above is a one-dimensional system. In a polyatomic molecule, we have more than one bond distance and we have coordinates in \(3N\) dimensions (x, y, and z), where \(N\) is the number of atoms

\[
V = V(0) + \sum_i \left( \frac{\partial V}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 x_i x_j + \cdots
\]

- We still have that \(V(0)\), the first derivative and the \(3^{\text{rd}}\) and higher order terms are zero
- The second term now is the \textbf{generalised force constant} \(k_{ij}\), and when all these terms are put together in a matrix formulation, the matrix is called the \textbf{Hessian}.

\[
V = \frac{1}{2} \sum_{i,j} k_{ij} x_i x_j \quad k_{ij} = \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0
\]
what this means is that vibrational motions within the molecule are **coupled**, when an atom is displaced via one vibration, this may influence the forces experienced by another atom undergoing a different vibration.

\[
\begin{bmatrix}
k_{11} & k_{12} & \cdots & k_{1(N-6)} \\
k_{21} & k_{22} & \cdots & k_{2(N-6)} \\
\vdots & \vdots & \ddots & \vdots \\
k_{(N-6)1} & k_{(N-6)2} & \cdots & k_{(N-6)(N-6)}
\end{bmatrix}
\rightarrow
\begin{bmatrix}
k_{11} & 0 & \cdots & 0 \\
0 & k_{22} & \cdots & \vdots \\
0 & \vdots & \ddots & \vdots \\
0 & k_{(N-6)(N-6)}
\end{bmatrix}
\]

\[
k_{11} = \left( \frac{\partial^2 V}{\partial x_1 x_1} \right)_0 \quad k_{12} = \left( \frac{\partial^2 V}{\partial x_1 x_2} \right)_0 \quad \text{etc}
\]

\[
k_{11} = \left( \frac{\partial^2 V}{\partial Q_1 Q_1} \right)_0 \quad k_{12} = \left( \frac{\partial^2 V}{\partial Q_1 Q_2} \right)_0 = 0 \quad \text{etc}
\]

ideally we would like to simplify the problem and decouple these "raw" motions, into normal coordinates or normal modes

first we transform to **mass-weighted-coordinates**,

\[
q_i = \sqrt{m_i} x_i \quad V = \frac{1}{2} \sum_{i,j} K_{ij} q_i q_j \quad K_{ij} = \left( \frac{\partial^2 V}{\partial q_i q_j} \right)_0
\]

\[H = T + V\]

\[T = \frac{1}{2} \sum_i m_i x_i^2 = \frac{1}{2} \sum_i q_i^2\]

then we find those coordinates that diagonalise the generalised force constant matrix, these are the **normal coordinates** or **vibrational modes** as you know them, the vector diagrams we have derived are just pictorial representations of the vibrational modes, Q;

thus in computing the normal coordinates (or vibrational modes) the program has diagonalised a large Hessian matrix.

thus a spectrometer is not necessarily required, information can also be obtained from a quantum chemical calculation, see insert below

**Frequencies** tells us the wavenumber of the vibration

vibrations are listed in order of wavenumber and not the assignment number!

**IR Inten** indicates the intensity of the vibration: highest energy vibrations (no. 4-6) are weakest, lowest energy vibrations (no. 1-3) are strongest

the x,y and z coordinates represent the displacement of that atom from its equilibrium position during the vibration

for example the first vibration of A\textsubscript{1} symmetry exhibits large z-coordinate out-of-plane motion, this is the umbrella mode

one of the best advantages of carrying out calculations is that you can animate the vibrations (Gaussview animation in lecture)
Key Points
- be able to determine the form of vibrational modes using the projection method
- be able to use this information to assign and describe a spectrum
- be able to describe, employing appropriate equations, how the normal modes are computed

Problem
- see the worked problem below
- determine the symmetry and activity of the vibrational modes of cis N$_2$F$_2$ and then derive the stretching vibrations using the projector method.
Pd(NH$_3$)$_2$Cl$_2$ Spectrum

- The example from lecture one stated that we could determine which isomer (cis or trans) of Pd(NH$_3$)$_2$Cl$_2$ was present from the IR spectrum. The trans isomer exhibits a single Pd-Cl stretching vibration $\nu$(Pd-Cl) around 350 cm$^{-1}$ while the cis isomer exhibits two stretching modes.

<table>
<thead>
<tr>
<th>$\text{M-X vibrations}$</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-isomer D$_{2h}$</td>
<td>$b_{3u}$</td>
<td>$a_g$</td>
</tr>
<tr>
<td>cis-isomer C$_{2v}$</td>
<td>$a_1$, $b_2$</td>
<td>$a_1$, $b_2$</td>
</tr>
</tbody>
</table>

Table 1 Active M-X stretching modes for ML$_2$X$_2$ complexes

![Figure 10 IR spectra of cis and trans [Pd(NH$_3$)$_2$Cl$_2$]](image)

- Prove this by determining the contribution to the spectrum for the Pd-Cl stretching modes for both the cis and trans complexes.
- Start by determining the contribution of Pd-Cl stretching modes in the trans complex (draw on the diagram below the two stretching vectors)

\[
\begin{array}{c|cccccc}
\Gamma(Pd-Cl) & E & C_2(x) & C_2(y) & C_2(z) & i & \sigma(xy) \\
\hline
- \Gamma & 2 & 0 & 0 & 2 & 2 & 2 & 0 \\
\Gamma(Pd-Cl) - A_g & 1 & -1 & -1 & 1 & 1 & 1 & 1 \\
\end{array}
\]

\[
\sigma(xy) + \sigma(zy) = B_{3u}
\]

- thus $\Gamma_{\text{vib}}(Pd-Cl) = A_g + B_{3u}$

---

• IR active modes have the same symmetry as the translational vectors, thus \( \Gamma(\text{IR}) \Rightarrow \{B_{1u}, B_{2u}, B_{3u}\} \) and the Raman modes have the same symmetry as the binary functions, thus \( \Gamma(\text{Raman}) \Rightarrow \{A_g, B_{1g}, B_{2g}, B_{3g}\} \)

• in addition this molecule has a center of symmetry, and therefore by the rule of mutual exclusion we expect that no modes will be present in both the Raman and IR spectra

• hence \( \Gamma_{\text{vib}}(\text{Pd-Cl}) = A_g(\text{pol}) + B_{3u}(\text{IR}) \)

• thus we expect 1 infrared active mode, and 1 active Raman mode which will be polarized

Then determine the contribution on Pd-Cl stretching modes to the cis complex (draw on the diagram below the two stretching vectors)

Thus for the higher symmetry trans-complex a single mode due to the Pd-Cl stretching vibration is expected in the IR spectrum, and for the lower symmetry cis-complex two modes are expected in the IR spectrum.

Those of you who have carried out the 3rd year computational chemistry lab, may wish to create and optimise a cis and trans molecule and then observe the vibrational modes!