9: Vibrational Spectroscopy
Big picture: spectroscopy

To measure a spectrum, we sweep through a range of frequencies and measure the signal $I(\nu)$ as a function of frequency ($\nu$).

- Quantum number = $\epsilon$
- Quantum number = $J$
- Quantum number = $v$

Diagram showing energy levels, transitions, and quantum numbers.
Identify the vibrational modes of methane and determine whether they are IR or Raman active.

Basis is x,y,z unit vectors on each atom (screen is xz plane).

15 arrows: each operation is a 15x15 matrix.

Use the shortcut to get $\chi$ when possible.

$E$  no change

<table>
<thead>
<tr>
<th>$\Gamma_v$</th>
<th>$\Gamma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_d$</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>8C$_3$</td>
</tr>
<tr>
<td></td>
<td>3C$_2$</td>
</tr>
<tr>
<td></td>
<td>6S$_4$</td>
</tr>
<tr>
<td></td>
<td>6$\sigma_d$</td>
</tr>
</tbody>
</table>

15 arrows: each operation is a 15x15 matrix.
Methane - vibrations

Identify the vibrational modes of methane and determine whether they are IR or Raman active.

Basis is \(x,y,z\) unit vectors on each atom (screen is \(xz\) plane).

\[
C_3 = \begin{pmatrix}
\cos 120^\circ & -\sin 120^\circ & 0 \\
\sin 120^\circ & \cos 120^\circ & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix} = \begin{pmatrix}
x' \\
y' \\
z
\end{pmatrix}
\]

\[
\text{Tr}(C_3) = -1/2-1/2+1 = 0
\]

\[
\begin{array}{c|cccc}
T_d & E & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\
\hline
\Gamma_v & 15 & 0 & \\
\end{array}
\]

For \(C\) and top H: Need rotation matrix.
Identify the vibrational modes of methane and determine whether they are IR or Raman active.

\[ \Gamma_v \]

<table>
<thead>
<tr>
<th>( T_d )</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>( \Gamma_v )</td>
<td>15</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
</tbody>
</table>

\( C_2 \)

- \( z \) (C): 1
- \( x,y \) (C): -1
- all H vectors: swap position: 0
- \( 1-1-1+0+0\ldots = -1 \)

\( S_4 \)

- \( z \) (C): -1
- everything else: 0
Methane - vibrations

Identify the vibrational modes of methane and determine whether they are IR or Raman active.

\[
\begin{align*}
\chi &= 2(-1) + 4(1) + 2(-1) + 6(0) \\
&= 3
\end{align*}
\]

\[
\begin{array}{cccccc}
T_d & E & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\
\hline
\Gamma_v & 15 & 0 & -1 & -1 & 3
\end{array}
\]

\(x,z\) (C): 1
\(\sigma_d\) y (C): -1
\(x,z\) (both in-plane Hs): 1
\(y\) (both in-plane Hs): -1
all other H vectors swapped
Identify the vibrational modes of methane and determine whether they are IR or Raman active.

\[ \Gamma_v = A_1 + E + T_1 + 3T_2 \]

<table>
<thead>
<tr>
<th>Translations</th>
<th>Rotations</th>
<th>Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_2(x,y,z) )</td>
<td>( T_1(R_x,R_y,R_z) )</td>
<td>( A_1, E, 2T_2 )</td>
</tr>
</tbody>
</table>
Vibrational modes

vibrations

$A_1, E, 2T_2$

$A_1$: inactive

$E$: Raman

$T_2$: IR and Raman
IR spectrum of methane
Raman spectrum of methane
Harmonic oscillator energy levels

Potential energy of form \( \frac{1}{2} k x^2 \)

Energy levels:
- \( n=0 \)
- \( n=1 \)
- \( n=2 \)
- \( n=3 \)
- \( n=4 \)

Energy:
- \( E_n = (n + \frac{1}{2}) \hbar \omega \)
- \( E_0 = \frac{1}{2} \hbar \omega \)

Internuclear separation \( x \)

Transition energy: \( \hbar \omega \)

\( x=0 \) represents the equilibrium separation between the nuclei.

http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibspe.html
Vibrational and rotational energy levels

\[ |v, J\rangle \]

\[ |0, J\rangle \rightarrow |1, J-1\rangle \quad |0, J\rangle \rightarrow |1, J-1\rangle \]
IR spectrum of HCl

$v=0, J$ to $v=1, J-1$

P-branch

$v=0, J$ to $v=1, J+1$

R-branch

http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html#c1
Bond length of HCl

$$\Delta f = \frac{4B}{h}$$

$$\approx 1.2 \times 10^{13} \text{ Hz}$$

$$K.E. = \frac{1}{2} I \omega^2 = \frac{J^2}{2I} = \frac{J^2}{2m_{\text{eff}} r^2}$$

spacing between rotational lines = 2B (or 4B for ν=0 to ν=1 transition):

$$\Delta E_J = \frac{2 \hbar^2}{2m_{\text{eff}} r^2}$$

$$2\Delta E_J = 2 \left[ \frac{2 \hbar^2}{2m_{\text{eff}} r^2} \right] = h \left( 0.12 \times 10^{13} \text{ Hz} \right)$$

http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html#c1
Bond length of HCl

\[
\mu r^2 = \frac{2\hbar^2}{h(0.12 \times 10^{13} \text{ Hz})} \frac{21.06 \times 10^{-34} \text{ J} \cdot \text{s}}{(0.9796 \text{amu})(1.66 \times 10^{-27} \text{ kg/amu})\pi(0.12 \times 10^{13} \text{ Hz})}
\]

\[r^2 = \frac{21.06 \times 10^{-34} \text{ J} \cdot \text{s}}{0.9796 \text{amu}(1.66 \times 10^{-27} \text{ kg/amu})\pi(0.12 \times 10^{13} \text{ Hz})}
\]

\[r = 0.13 \text{ nm}
\]

microwave value: 0.127 nm

http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html#c1
Bond length of HCl

If you have the spectrum in wavenumbers:

\[ \Delta \tilde{\nu} = 1 \text{ cm}^{-1} \]

Pick a pair of lines close to the center:

\[ \frac{2865 - 2844}{2} = 10.5 \text{ cm}^{-1} \]

\[ B = \frac{\hbar}{4\pi c I} \quad I = \frac{1.06 \times 10^{-34} \text{ J} \cdot \text{s}}{4\pi \left( 3.00 \times 10^8 \text{ m/s} \right) \left( 1050 \text{ m}^{-1} \right)} = 2.66 \times 10^{-47} \text{ kg} \cdot \text{m}^2 \]

\[ r = \sqrt{\frac{I}{m_{\text{eff}}}} = \sqrt{\frac{2.66 \times 10^{-47} \text{ kg} \cdot \text{m}^2}{(0.9796 \text{ amu})(1.66 \times 10^{-27} \text{ kg} / \text{amu})}} = 1.29 \times 10^{-10} \text{ m} \]
Force constant for HCl

\[ \omega = \sqrt{\frac{k}{m_{\text{eff}}}} \]

\[ 2\pi \left( 8.66 \times 10^{13} \, \text{Hz} \right) = \sqrt{\frac{k}{m_{\text{eff}}}} \]

\[ k = \left[ 2\pi \left( 8.66 \times 10^{13} \, \text{Hz} \right) \right]^2 (0.9796 \, \text{amu}) (1.66 \times 10^{-27} \, \text{kg/amu}) \]

\[ k = 481 \, \text{N/m} \]

http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibspe.html
Force constants

\[ \nu = 0 \text{ to } \nu = 1 \]

<table>
<thead>
<tr>
<th>molecule</th>
<th>frequency $\times 10^{13}$ Hz</th>
<th>force constant N/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>12.4</td>
<td>970</td>
</tr>
<tr>
<td>HCl</td>
<td>8.66</td>
<td>480</td>
</tr>
<tr>
<td>HBr</td>
<td>7.68</td>
<td>410</td>
</tr>
<tr>
<td>HI</td>
<td>6.69</td>
<td>320</td>
</tr>
<tr>
<td>CO</td>
<td>6.42</td>
<td>1860</td>
</tr>
<tr>
<td>NO</td>
<td>5.63</td>
<td>1530</td>
</tr>
</tbody>
</table>
Anharmonic potential

Morse potential:

\[ V = h c \tilde{D}_e \left[ 1 - e^{-a(R-R_e)} \right]^2 \]

\[ a = \left( \frac{m_{\text{eff}} \pi \nu^2}{h c \tilde{D}_e} \right) \]

\[ \tilde{G}(\nu) = \left( \nu + \frac{1}{2} \right) \tilde{\nu} - \left( \nu + \frac{1}{2} \right)^2 x_e \tilde{\nu} \]

\[ x_e = \left( \frac{a^2 \hbar}{4 \pi m_{\text{eff}} \nu} \right) = \frac{\tilde{\nu}}{4 \tilde{D}_e} \]