1. In the IR spectrum of an organic molecule, the fundamental and first overtone for a C-H stretch mode appear at 3034 and 5941 cm\(^{-1}\) respectively.

(a) Calculate the harmonic vibrational frequency and anharmonicity constant for this mode (in cm\(^{-1}\)).

The energy levels for the Morse potential are:

\[ G(v) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e x_e \quad \text{(in cm}^{-1}\text{)} \]

The fundamental corresponds to the transition between \(v = 0\) and \(v = 1\). This occurs at:

\[ G(1) - G(0) = [(1 + \frac{1}{2})\omega_e - (1 + \frac{1}{2})^2\omega_e x_e] - [(0 + \frac{1}{2})\omega_e - (0 + \frac{1}{2})^2\omega_e x_e] \]
\[ = [3/2\omega_e - 9/4\omega_e x_e] - [1/2\omega_e - 1/4\omega_e x_e] = \omega_e - 2\omega_e x_e \]

The first overtone corresponds to the transition between \(v = 0\) and \(v = 2\). This occurs at:

\[ G(2) - G(0) = [(2 + \frac{1}{2})\omega_e - (2 + \frac{1}{2})^2\omega_e x_e] - [(0 + \frac{1}{2})\omega_e - (0 + \frac{1}{2})^2\omega_e x_e] \]
\[ = [5/2\omega_e - 25/4\omega_e x_e] - [1/2\omega_e - 1/4\omega_e x_e] = 2\omega_e - 6\omega_e x_e \]

As these occur at 3034 cm\(^{-1}\) and 5941 cm\(^{-1}\) respectively:

\[ \omega_e - 2\omega_e x_e = 3034 \text{ cm}^{-1} \quad \text{(1)} \]
\[ 2\omega_e - 6\omega_e x_e = 5941 \text{ cm}^{-1} \quad \text{(2)} \]

These are simply two simultaneous equations to solve. Taking \(2 \times (1) - (2)\) gives:

\[ 2 \times [\omega_e - 2\omega_e x_e] - [2\omega_e - 6\omega_e x_e] = (2 \times 3034 - 5941) \text{ cm}^{-1} \]
\[ 2\omega_e x_e = 127 \text{ cm}^{-1} \] or \(\omega_e x_e = 63.5 \text{ cm}^{-1}\)

Substituting this value into (1) gives:

\[ \omega_e - (127 \text{ cm}^{-1}) = 3034 \text{ cm}^{-1} \] or \(\omega_e = 3161 \text{ cm}^{-1}\).

(b) Predict the wavenumber for the second overtone.

The second overtone corresponds to the transition between \(v = 0\) and \(v = 3\). This occurs at:

\[ G(3) - G(0) = [(3 + \frac{1}{2})\omega_e - (3 + \frac{1}{2})^2\omega_e x_e] - [(0 + \frac{1}{2})\omega_e - (0 + \frac{1}{2})^2\omega_e x_e] \]
\[ = [7/2\omega_e - 49/4\omega_e x_e] - [1/2\omega_e - 1/4\omega_e x_e] \]
\[ = 3\omega_e - 12\omega_e x_e \]

Using \(\omega_e = 3161 \text{ cm}^{-1}\) and \(\omega_e x_e = 63.5 \text{ cm}^{-1}\) gives:

\[ G(3) - G(0) = 3\omega_e - 12\omega_e x_e = (3 \times 3161 - 12 \times 63.5) \text{ cm}^{-1} = 8721 \text{ cm}^{-1} \]

(c) The second overtone appears at 8727 cm\(^{-1}\). Explain any discrepancy between this value and your answer to (b).

The predicted value is very close to the observed value. Alongside any experimental uncertainty in the measurement, the main difference is due to the use of the Morse potential which is only an approximation to the potential of the real molecule.
2. Methyl bromide has been widely used as a fumigant. However, its use has been banned in the Vienna amendment to the Montreal Protocol because it is an ozone depleting substance. CH$_3$Br is also a Greenhouse gas, mainly because of the C-Br stretching vibration, which has a frequency of 611 cm$^{-1}$.

(a) How many normal modes of vibration does CH$_3$Br have?

It is a non-linear molecule consisting of 5 atoms: it has $(3N - 6) = 9$ vibrational modes.

(b) Which of the schematic representations of CH$_3$Br vibrational modes overleaf could not be a normal mode? Explain your answer.

In a normal mode:
- the centre of mass cannot move (3 × translations)
- there can be no overall rotation about the centre of mass (3 × rotations)
- all atoms oscillate with the same frequency (though the amplitude of oscillation can be very small for some atoms in the molecule)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>Acceptable? Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>This mode is acceptable as it does not break any of the rules above.</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>This mode is not acceptable. It corresponds to a translation (to the left) rather than a vibration of the molecule.</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>This mode is not acceptable. It corresponds to a (clockwise) rotation of the molecule.</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>This mode is acceptable as it does not break any of the rules above.</td>
<td>Yes</td>
</tr>
</tbody>
</table>

(c) When methyl bromide vibrates in the (CH$_3$) – Br stretching mode it behaves like a pseudo-diatomic molecule because the CH bonds in the methyl group do not vibrate and the whole CH$_3$ group acts like a big atom. The fundamental transition in the (CH$_3$) – Br stretching mode is found at 611 cm$^{-1}$. A weak overtone of the same transition is found at 1215 cm$^{-1}$. Use this information to calculate the harmonic frequency and anharmonicity constant for this mode.

The energy levels for the Morse potential are:

$$G(v) = (v + \frac{1}{2})\omega_x - (v + \frac{1}{2})^2\omega_x\chi$$  
(in cm$^{-1}$)
The fundamental corresponds to the transition between $v = 0$ and $v = 1$. This occurs at:

$$G(1) - G(0) = [(1 + \frac{1}{2})\omega_e - (1 + \frac{1}{2})^2 \omega_e x_e] - [(0 + \frac{1}{2})\omega_e - (0 + \frac{1}{2})^2 \omega_e x_e]$$

$$= \left[\frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e\right] - \left[\frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e\right] = \omega_e - 2\omega_e x_e$$

The first overtone corresponds to the transition between $v = 0$ and $v = 2$. This occurs at:

$$G(2) - G(0) = [(2 + \frac{1}{2})\omega_e - (2 + \frac{1}{2})^2 \omega_e x_e] - [(0 + \frac{1}{2})\omega_e - (0 + \frac{1}{2})^2 \omega_e x_e]$$

$$= \left[\frac{5}{2}\omega_e - \frac{25}{4}\omega_e x_e\right] - \left[\frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e\right] = 2\omega_e - 6\omega_e x_e$$

As these occur at 611 cm$^{-1}$ and 1215 cm$^{-1}$ respectively:

$$\omega_e - 2\omega_e x_e = 611 \text{ cm}^{-1} \quad (1)$$

$$2\omega_e - 6\omega_e x_e = 1215 \text{ cm}^{-1} \quad (2)$$

These are simply two simultaneous equations to solve. Taking $2 \times (1) - (2)$ gives:

$$2\omega_e - 2\omega_e x_e = 2 \times 611 - 1215 \text{ cm}^{-1}$$

$$2\omega_e x_e = 7 \text{ cm}^{-1} \text{ or } \omega_e x_e = 3.5 \text{ cm}^{-1}$$

Substituting this value into (1) gives:

$$\omega_e - (7 \text{ cm}^{-1}) = 611 \text{ cm}^{-1} \text{ or } \omega_e = 618 \text{ cm}^{-1}.$$  

(d) **Using the data from part (c), estimate the bond dissociation energy for the C–Br bond in CH$_3$Br.**

Using $D_e = \frac{\omega_e^2}{4\omega_e x_e}$, the dissociation energy from the bottom of the potential well is given by:

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} = \frac{(618 \text{ cm}^{-1})^2}{(4 \times 3.5 \text{ cm}^{-1})} = 27280 \text{ cm}^{-1}$$

The bond dissociation energy, $D_0$, corresponds to dissociation from the zero point energy. This is the energy of the level with $v = 0$:

$$G(0) = [(0 + \frac{1}{2})\omega_e - (0 + \frac{1}{2})^2 \omega_e x_e] = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e = \frac{1}{2} \times 618 - \frac{1}{4} \times 3.5 \text{ cm}^{-1} = 308 \text{ cm}^{-1}$$

Using $D_0 = D_e - G(0)$ gives the dissociation energy as:

$$D_0 = D_e - G(0) = (27280 - 308) \text{ cm}^{-1} = 26970 \text{ cm}^{-1}$$

(e) **The thermodynamic bond dissociation energy for CH$_3$Br is 276 kJ mol$^{-1}$ (which corresponds to 23,070 cm$^{-1}$). Provide an explanation for the agreement / disagreement between this value and the value you calculated in part d) of this question.**

The predicted value is very close to the observed value. Alongside any experimental uncertainty in the measurement, the difference is due to the use of the Morse potential, which is only an approximation to the potential of the real molecule, and the treatment of the C-Br stretch as a true local mode. A more complete treatment would included the effect of mixing with the other modes in CH$_3$-Br.
3. Using the analogy with the $s$ and $p$ orbitals on N, sketch the form of the three N-H stretching modes in NH$_3$. Which of these modes is IR active?

The analogy replaces the phase of the atomic orbitals used for $\sigma$ bonding with the relative motion of the bonds in the vibration. There are three N-H bonds in NH$_3$ and these will combine to give three stretching normal modes.

The N $s$ and $p_z$ orbitals give the same combination (the ‘breathing mode’):

![Breathing mode diagram]

The combinations corresponding to the N $p_x$ and $p_y$ orbitals are best viewed from the top:

![Pxy modes diagram]

All of the vibrations give rise to a change in the dipole moment so all are IR active. Note, however, that the two $p_x$ and $p_y$ like modes are degenerate: they vibrate at exactly the same frequency.