An Aside: Application of Rotational Motion

Vibrational-Rotational Spectroscopy
Rotational Excited States of a Diatomic Molecule are Significantly Populated at Room Temperature

We can estimate the relative population of the rotational energy states by using the Boltzmann distribution law:

\[
\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-\Delta E/kT}
\]

\[
\Delta E = E_i - E_j
\]

\[
\frac{N_i}{N_j} \quad \text{is the ratio of the molecules in the } i^{\text{th}} \text{ and } j^{\text{th}} \text{ states. The } g^{'s} \text{ are the degeneracies of those states. } k \text{ is Boltzmann's constant and } T \text{ is the absolute temperature in Kelvin.}
\]

The ratio of the number of molecules in the \( \ell \)th rotational state and the ground rotational state is therefore (remember the degeneracy of the rotational states):

\[
\frac{N_\ell}{N_0} = (2\ell + 1)e^{-\frac{\hbar^2}{2\mu r^2 kT}\ell(\ell+1)}
\]
Rotational Spectra

The energy levels of the 3-D rigid rotor are given by:

\[ E_{\ell m} = \ell (\ell + 1) \frac{\hbar^2}{2\mu r^2} \]

\[ \ell = 0, 1, 2, \ldots \]

\[ m = 0, \pm 1, \pm 2, \ldots, \pm \ell \]

Rotational Spectra Selection Rules

Not all transitions are allowed. It can be shown that transitions are allowed only if the following integral is non-zero:

\[ \int Y_{\ell m}^* \mu Y_{\ell' m'} \, d\tau = \int_0^{2\pi} \int_0^\pi Y_{\ell m}^* \mu Y_{\ell' m'} \sin(\theta) \, d\theta \, d\phi \]

for a \( \ell m \rightarrow \ell' m' \) transition

where \( \mu \) is the dipole moment operator (not the effective mass).

\[ \mu = e\vec{r} \]
Using the 3-D rigid rotor wave functions, these integrals are only non-zero when:

\[
\Delta \ell = \pm 1 \quad \Delta m = \pm 1
\]

The diatomic molecules must also have a permanent dipole moment. These are the **selection rules** for rotational transitions.

Since the energy depends only on the quantum number \( \ell \) we have for the transition:

\[
E_\ell \rightarrow E_{\ell + 1}
\]

\[
E_\ell = (\ell + 1)(\ell + 2) \frac{\hbar^2}{2\mu r^2} - \ell(\ell + 1) \frac{\hbar^2}{2\mu r^2}
\]

\[
\Delta E_\ell = \frac{\hbar^2}{\mu r^2} (\ell + 1)
\]

notice the transition energy depends on the quantum number of the initial state.
\[ \Delta E_\ell = \frac{\hbar^2}{\mu r^2} (\ell + 1) \]

For a typical diatomic molecule:

\( \mu = 10^{-25} \) to \( 10^{-26} \) kg. \( \quad r = 10^{-10} \) m

If we use these values in the above equation for the transition energy, starting from \( \ell = 0 \), we find that the absorption frequencies of pure rotational spectra are \( 2 \times 10^{10} - 10^{11} \) Hz

This is in the microwave region of the EM spectrum and the study of rotational transitions in molecules is called **microwave spectroscopy**.

*Microwave ovens actually excite the rotational states of water molecules.*
Microwave spectroscopy has its own Naming Conventions

In the field of microwave spectroscopy, it is conventional to use the symbols $J$ and $M$ for the quantum numbers $\ell$ and $m$, respectively:

$$\ell \rightarrow J \quad m \rightarrow M$$

(We will not use it here, but just be aware of it)

It is also common practice to use the moment of inertia. Recall the definition of the moment of inertia:

$$I = \sum_i m_i r_i^2$$

Distance of the $i^{th}$ particle from the origin.

For our diatomic molecule, the moment of inertia is:

$$I = \mu r^2$$

So the transition energy is commonly written as:

$$\Delta E_\ell = \frac{\hbar^2}{\mu r^2} (\ell + 1) \rightarrow \Delta E = \frac{\hbar^2}{I} (\ell + 1)$$
It is also common practice to write the transition energy in terms of wave numbers (cm\(^{-1}\)) and a rotational constant of the molecule, B.

\[
\Delta \tilde{E}_\ell = \tilde{\nu} = 2\tilde{B}(\ell+1)
\]

Transition energy in wave numbers, cm\(^{-1}\)

\[
\tilde{B} = \frac{h}{8\pi^3 c I}
\]

Rotational constant of the molecule (unique for every molecule)

<table>
<thead>
<tr>
<th>transition involved</th>
<th>frequency of peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ell = 0 \rightarrow \ell' = 1)</td>
<td>(\tilde{\nu} = 2\tilde{B})</td>
</tr>
<tr>
<td>(\ell = 1 \rightarrow \ell' = 2)</td>
<td>(\tilde{\nu} = 4\tilde{B})</td>
</tr>
<tr>
<td>(\ell = 2 \rightarrow \ell' = 3)</td>
<td>(\tilde{\nu} = 6\tilde{B})</td>
</tr>
<tr>
<td>(\ell = 3 \rightarrow \ell' = 4)</td>
<td>(\tilde{\nu} = 8\tilde{B})</td>
</tr>
<tr>
<td>(\vdots)</td>
<td></td>
</tr>
<tr>
<td>(\vdots)</td>
<td></td>
</tr>
</tbody>
</table>
The rigid rotor model predicts that the microwave spectrum of a diatomic molecule should consist of a series of equally spaced lines with a separation of $2\tilde{B}$

The intensity of the lines is given by the thermal distribution of the rotational states.
Rotational-Vibrational Spectra

Recall from our harmonic oscillator model of diatomic vibrations, we had the following selection rules:

$$\Delta n = \pm 1$$

Since the ground state vibrational state is mostly occupied and since the harmonic oscillator model predicts equally spaced energy levels, we predict one strong IR peak that we call the fundamental frequency:

$$\Delta E = E_{n+1} - E_n = \hbar \nu = \hbar \omega = \hbar \left( \frac{k}{\mu} \right)^{\frac{1}{2}}$$

For example, for $H^{35}Cl$ our harmonic oscillator model predicts a fundamental vibrational frequency at 2886 cm$^{-1}$ with a force constant of $k=482$ N/m.

With a low resolution IR spectra this is indeed what we observe, a single strong absorption peak.
Notice the equally spaced peaks on either side of the fundamental frequency.

The vibrational energy level transitions are accompanied by changes in the rotational energy levels. The selection rules for the combined transitions are also 'combined':

\[ \Delta n = \pm 1 \quad \& \quad \Delta \ell = \pm 1 \]

The energy change associated with the allowed transitions is therefore:

\[ \Delta E = \Delta E_{\text{vib}} + \Delta E_{\text{rot}} = \hbar \omega + \frac{\hbar^2}{I} (\ell + 1) \]
At room temperature, it is mostly the ground vibrational state that is populated, therefore, most vibrational transitions will be:

\[ n=0 \rightarrow n=1 \]

\[ \Delta E_{\text{vib}} = \hbar \omega \]

Since many rotationally excited states are occupied at room temperature, there will be both \( \Delta l=+1 \) and \( \Delta l=-1 \) transitions starting from various levels \( l \).

Thus, the total energy of the transitions will be both less than and greater than the fundamental vibrational frequency.

\[ \Delta E = \Delta E_{\text{vib}} \pm \Delta E_{\text{rot}} \]
The shape of each of the branches is again due to the thermal populations of the rotational energy levels governed by Boltzmann’s law.

Shoulders are due to natural abundance of H\textsuperscript{37}Cl, which has larger reduced mass and therefore fundamental vibrational frequency. This is why there is a shift due to the heavier reduced mass.
This is an actual spectrum of HCl taken with a FT-IR instrument.

The isotopic splitting is barely visible on this compressed scale.