Rotational Spectroscopy

Rotational Spectroscopy
- QM model of motion: rigid rotor
- Moments of inertia (16.4)
- Rotational IR, Millimetre Wave and Microwave Spectra (16.5, 16.6)
  i. Diatomic & Linear Polyatomic Molecules
  ii. Symmetric Rotors
  iii. Stark Effect
  iv. Asymmetric Rotors and Spherical Molecules
  v. Applications in Astronomy
- Rotational Raman Spectroscopy (16.7, 16.8)
- Structure Determination from Rotational Spectroscopy
Rigid Rotor: Diatomic Rotation

The **rigid rotor model** is an excellent approximation to the problem of freely rotating molecules. There can be (i) no additional torques, (ii) no angular potential energy dependence, (iii) no significant intermolecular interactions (makes it good for gas phase analysis), (iv) no major energetic contributions from molecular vibrations.

Here \( r = r_1 + r_2 \), and \( r_1 \) and \( r_2 \) are defined such that

\[
m_1 r_1 = m_2 r_2
\]

The **moment of inertia** about this rotation axis is

\[
I = m_1 r_1^2 + m_2 r_2^2
\]

Substituting in the above equation, we write

\[
I = m_2 r_2 r_1 + m_1 r_1 r_2 = r_1 r_2 (m_1 + m_2)
\]

Since \( r_2 = r - r_1 \),

\[
m_1 r_1 = m_2 (r - r_1)
\]

\[
m_1 r_1 + m_2 r_1 = m_2 r
\]
We can now solve for $r_i$:

$$r_1 = \frac{m_2}{m_1 + m_2} r, \quad r_2 = \frac{m_1}{m_1 + m_2} r$$

and finally calculate the moment of inertia:

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

where the reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Thus, the two body rigid rotor can be reduced to a one body problem with a single reduced mass, meaning that we can use one-bodied angular momentum to treat these problems!
Schroedinger Equation for Rigid Rotors

The problem of the rotating diatomic molecule can now be reduced to treating the motion of the particle on a sphere (much like for the hydrogenic wavefunctions). Recall that for translational motion the Schroedinger equation is:

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] \Psi(x,y,z,t) + V(x,y,z,t) \Psi(x,y,z,t) = i\hbar \frac{\partial \Psi(x,y,z,t)}{\partial t}$$

and since the $V = 0$, things are greatly simplified. In one dimension, the kinetic energy operator for linear motion is:

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} = \frac{\hat{p}_x^2}{2m}, \quad \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

and recalling that linear momentum, $p$, and angular momentum, $L$, are related by similar classical equations:

$$\hat{T} = \frac{\hat{L}^2}{2I} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

If $\phi$ is the azimuthal angle in the polar coordinate system, then this operator is for calculating the energy associated with rotation about a ring. If three dimensional rotation is to be examined (i.e., kinetic energy anywhere on a sphere)

$$\hat{T} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\right]$$

If the potential energy is assumed to be zero for the rigid rotor model, the above operators are the total hamiltonians.
**Angular Momentum Review**

The angular momentum of the molecule is directed perpendicular to the plane of rotation, pointing up or down depending on whether rotation is clockwise or counterclockwise (see the **right hand rule**).

Consider angular momentum in the \( x, y \) and \( z \) directions. In turns out that the operators do not commute with one another, implying we cannot simultaneously specify all three components of angular momentum:

\[
[ \hat{A}, \hat{B} ] = \hat{A}\hat{B} - \hat{B}\hat{A}
\]

\[
[ \hat{L}_x, \hat{L}_y ] = i\hbar \hat{L}_z \\
[ \hat{L}_y, \hat{L}_x ] = -i\hbar \hat{L}_z
\]

\[
[ \hat{L}_z, \hat{L}_x ] = i\hbar \hat{L}_y \\
[ \hat{L}_z, \hat{L}_y ] = -i\hbar \hat{L}_x \\
[ \hat{L}_x, \hat{L}_y ] = i\hbar \hat{L}_z \\
[ \hat{L}_y, \hat{L}_x ] = -i\hbar \hat{L}_z \\
[ \hat{L}_z, \hat{L}_x ] = i\hbar \hat{L}_y
\]

However, a special operator, \( \hat{L}^2 \), commutes with all three components of angular momentum:

\[
[ \hat{L}_x, \hat{L}^2 ] = [ \hat{L}_y, \hat{L}^2 ] = [ \hat{L}_z, \hat{L}^2 ] = 0
\]

This means we may specify the **magnitude** (via \( \hat{L}^2 \)) and **one component** (e.g., \( \hat{L}_z \)) of angular momentum. When two operators commute, they share a common set of eigenfunctions. \( \hat{L}_z \) is the simplest form:

\[
\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}
\]

It turns out that the eigenfunctions shared by \( \hat{L}_z \) and \( \hat{L}^2 \) are the **spherical harmonics**, \( Y_{\ell m}(\theta, \phi) \)!
Solution for Rigid Rotors

Since the spherical harmonics are simultaneously eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$, the solutions of the S.E. are

\[ \hat{L}^2 Y_{\ell m} = \ell(\ell + 1)\hbar^2 Y_{\ell m}, \quad \ell = 0, 1, 2, \ldots, n-1 \]
\[ \hat{L}_z Y_{\ell m} = m_\ell \hbar Y_{\ell m}, \quad m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell \]

These operators are of paramount importance in many problems dealing with angular momentum.

The angular momentum vector in a molecule has a particular magnitude:

\[ |\vec{L}| = \sqrt{\ell(\ell + 1)} \hbar \]

and for any value of $\ell$, there are $2\ell + 1$ possible orientations corresponding to the allowed values of $L_z = m_\ell \hbar$. Since the $x$ and $y$ components of angular momentum are unspecified, this means the vector $\vec{L}$ can lie anywhere on a cone making and angle $\theta$ w.r.t. the $z$ axis, with angles

\[ \cos \theta = \frac{m}{\sqrt{\ell(\ell + 1)}} \]

This also implies that $\vec{L}$ cannot coincide with the $z$ direction, as this would impart definite values on $L_x$ and $L_y$ (i.e., they'd be equal to zero!)
Energy Levels of the Rigid Rotor

Schroedinger’s equation is now deceptively simple:

$$\hat{J}^2 \psi = E_J \psi = \frac{J(J + 1)\hbar^2}{2I} \psi$$

Here we have replaced $L$ with $J$, which is a special notation to denote angular momentum of rigid rotors (it is the same as $L$ in every way, with $m_J = 0, \pm 1, \pm 2, \ldots, \pm J$).

Thus, the energy can be calculated as:

$$E_J = \frac{\hbar^2}{2I} J(J + 1)$$

The rigid rotor has quantized angular momentum:

$$|\vec{J}| = \sqrt{J(J + 1)} \hbar$$

Remember, the energy comes from $E_J = \hat{J}^2/2I$. $J$ and $m_J$ define the spherical harmonics, but only $J$ defines the energies ($m_J$ levels are degenerate (same energy) unless in the presence of a magnetic field).

This notation is usually simplified even further, by using the **rotational constant**, $B$:

$$B = \frac{\hbar^2}{2I} \quad \text{(in Joules)}$$

since we know that $I$ will be constant for a given rigid rotor. Then, energy is given by:

$$E_J = B J(J + 1)$$
The spectrum of a pure rigid rotor has transitions evenly spaced by $\Delta E = 2B(J'' + 1)$, where $J''$ is the lower rotational energy level. The selection rule for this model is: $\Delta J = \pm 1$

- There is no zero-point energy, i.e., when $J = 0$ the energy $E_J = 0$ as well.

- The “rotational ladder” of energy levels is not evenly spaced - spacing increases with increasing $J$.

- Spherical harmonic functions can be used as solutions to this Schroedinger equation, since this motion is described by a particle on a sphere.

- Other types of motion (e.g., vibration) can shift these levels and create anharmonicity.
Moments of Inertia

In order to use rotational spectroscopy to study the structure of molecules, they must be classified according to their principal moments of inertia. The moment of inertia, $I$, of any molecule about any axis through the centre of gravity of the molecule is given by:

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

where $m_i$ and $r_i$ are the mass and distance of the atom $i$ from the axis.

There are three principal axes which define the moment of inertia, conventionally labelled $a$, $b$ and $c$, which are all mutually perpendicular. The principal moments of inertia, $I_a$, $I_b$ and $I_c$ are defined such that:

$$I_c \geq I_b \geq I_a$$

There are a variety of molecular shapes for which relative principal moments of inertia can be defined:

- $I_c = I_b > I_a = 0$ linear molecule
- $I_c = I_b > I_a$ prolate symmetric rotor or top
- $I_c > I_b = I_a$ oblate symmetric rotor or top
- $I_c = I_b = I_a$ spherical rotor
- $I_c \neq I_b \neq I_a$ asymmetric rotor
- $I_c \simeq I_b > I_a$ prolate near-symmetric rotor
- $I_c > I_b \simeq I_a$ oblate near-symmetric rotor
Molecules & Principal Inertial Axes

$I_c = I_b > I_a = 0$

$I_c = I_b > I_a$

$I_c > I_b = I_a$

$I_c = I_b = I_a$

$I_c = I_b = I_a$

$I_c > I_b = I_a$

$I_c = I_b > I_a$

$I_c > I_b \neq I_a$

$I_c > I_b \neq I_a$

$I_c \approx I_b > I_a$

$I_c > I_b \approx I_a$
Moments of Inertia, 2

In the example on the right, the centre of mass lies along the $C_3$ axis, and perpendicular distances are measured from this axis.

An asymmetric rotor will have three different moments of inertia, and all three rotation axes coincide at the centre of the molecule.

**Spherical rotors**, which have three equal moments of inertia, include CH$_4$, SiF$_4$ and SF$_6$, and belong to a cubic or icosahedral point group.

**Symmetric rotors** have two equal moments of inertia, include NH$_3$, CH$_3$Cl and CH$_3$CN, and have at least a 3-fold axis of symmetry.

**Linear rotors** have at least one moment of inertia equal to zero, include all diatomic and linear polyatomic molecules.

**Asymmetric rotors** are molecules without a threefold (or higher) axis - other elements of symmetry may exist, but these generally have very complicated sets of energy levels.
Moments of Inertia for Different Molecules

Pictured below are different types of molecules/rotors with their corresponding moments of inertia.

1. Diatomics

\[ I = \frac{m_A m_B}{m} R^2 = \mu R^2 \]

2. Linear rotors

\[ I = m_A R^2 + m_c R'^2 \]
\[ - \frac{(m_A R - m_c R')^2}{m} \]

\[ I = 2m_A R^2 \]

3. Symmetric rotors

\[ I_\parallel = 2m_A R^2 (1 - \cos \theta) \]
\[ I_\perp = m_A R^2 (1 - \cos \theta) \]
\[ + \frac{m_A (m_B + m_C) R^2}{m} (1 + 2 \cos \theta) \]
\[ + \frac{m_c R'}{m} \left[ (3m_A + m_B) R' \right] \]
\[ + 6m_A R \left[ \frac{1}{2} (1 + 2 \cos \theta) \right]^{1/2} \]

\[ I_\parallel = 2m_A R^2 (1 - \cos \theta) \]
\[ I_\perp = m_A R^2 (1 - \cos \theta) \]
\[ + \frac{m_A m_B}{m} R^2 (1 + 2 \cos \theta) \]

\[ I_\parallel = 4m_A R^2 \]
\[ I_\perp = 2m_A R^2 + 2m_c R'^2 \]

4. Spherical rotors

\[ I = \frac{8}{3} m_A R^2 \]
\[ I = \frac{8}{3} m_A R^2 \]
\[ I = \frac{4}{6} m_A R^2 \]

† In each case \( m \) is the total mass of the molecule.
Diatomic & Linear Polyatomic Molecules

Recall that we developed the Schroedinger equation for the rigid rotor in Lecture 6, and found that the rotational energy levels of a rigid rotor (or in this case, a linear molecule) can be written as:

\[ E_J = \frac{\hbar^2}{2I} J(J + 1) \]

where \( I = \mu r^2 \) and \( \mu \) is the reduced mass, equal to

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

and \( J \) is the rotational quantum number, \( J = 0, 1, 2, \ldots \)

In rotational spectroscopy the frequency (\( \mu \)-wave or mm-wave) or wavenumber (far-IR) is measured in practice. The energy levels above can be converted to term values \( F(J) \) which are expressed as frequency (divide above by \( h \)) or wavenumbers (divide above by \( hc \)):

\[ F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I} J(J + 1) = BJ(J + 1) \]

\[ F(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI} J(J + 1) = BJ(J + 1) \]

where \( hcB = \hbar^2/2I \), or \( B = \hbar/4\pi cI = h/8\pi^2 cI \), where \( B \) is known as the rotational constant. The interchangeable use of the symbols \( F(J) \) and \( B \) with frequency and wavenumber is unfortunate, but is a very common symbolism.
Pure Rotational Spectrum of CO

In the picture below, we see the rotational term values, relative populations and transition wavenumbers for CO.

<table>
<thead>
<tr>
<th>$F(J)/\text{cm}^{-1}$</th>
<th>$J$</th>
<th>$(2J+1)$</th>
<th>$\exp\left(-\frac{E_J}{kT}\right)$</th>
<th>$\frac{N_J}{N_0}$</th>
<th>$\frac{\mathcal{P}}{\text{cm}^{-1}}$</th>
<th>$\frac{\hbar^2(2J+1)\exp\left(-\frac{E_J}{kT}\right)}{\text{cm}^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1.00</td>
<td>1.00</td>
<td>14.7</td>
<td>14.7</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0.981</td>
<td>2.94</td>
<td>7.69</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>5</td>
<td>0.945</td>
<td>4.73</td>
<td>11.5</td>
<td>375</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>7</td>
<td>0.893</td>
<td>6.25</td>
<td>15.4</td>
<td>847</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>9</td>
<td>0.828</td>
<td>7.45</td>
<td>19.2</td>
<td>1530</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>11</td>
<td>0.754</td>
<td>8.29</td>
<td>23.1</td>
<td>2410</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>13</td>
<td>0.673</td>
<td>8.75</td>
<td>26.9</td>
<td>3410</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>15</td>
<td>0.590</td>
<td>8.85</td>
<td>30.8</td>
<td>4480</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>17</td>
<td>0.507</td>
<td>8.62</td>
<td>34.6</td>
<td>5480</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>19</td>
<td>0.428</td>
<td>8.13</td>
<td>38.4</td>
<td>6311</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>21</td>
<td>0.355</td>
<td>7.46</td>
<td>42.3</td>
<td>6990</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>23</td>
<td>0.288</td>
<td>6.62</td>
<td>46.1</td>
<td>7340</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>25</td>
<td>0.230</td>
<td>5.75</td>
<td>50.0</td>
<td>7470</td>
</tr>
<tr>
<td>13</td>
<td>13</td>
<td>27</td>
<td>0.180</td>
<td>4.85</td>
<td>58.8</td>
<td>7290</td>
</tr>
</tbody>
</table>
Selection Rules & Conventions

Transition intensity is proportional to the square of the transition moment which is given by

$$ R_r = \int \psi'_r \mu \psi''_r \, d\tau $$

The selection rules for a pure rotational spectrum are:

1. Molecule must have a permanent dipole moment (i.e., $\mu \neq 0$)
2. $\Delta J = \pm 1$
3. $\Delta m_J = 0, \pm 1$ (important if molecule is in an electric or a magnetic field - covered later)

Rule 1:
Transitions are allowed in diatomic molecules such as CO, NO, HF, even $^1\text{H}_2\text{H}$ ($\mu = 5.9 \times 10^{-4}$ D), but not $\text{H}_2$, $\text{N}_2$, $\text{Cl}_2$. Transitions are allowed in polyatomics such as $\text{H-C=N}$, $\text{O=C=S}$, $^1\text{H-C=O=C-}^2\text{H}$ ($\mu = 0.012$ D), not $\text{H-C=C=H}$, $\text{S=C=S}$.

Rule 2:
$\Delta J$ refers to $J'$ - $J''$, which are the rotational quantum numbers of the upper and lower states, respectively. $\Delta J = -1$ really has no meaning, as $\Delta J = +1$ refers to either absorption or emission because $\Delta J = J' - J''$. Transition frequencies or wavenumbers are given by

$$ \bar{\nu} \text{ (or } \nu) = F(J + 1) - F(J) = 2B(J + 1) $$

where unfortunately $J$ is used instead of $J''$ by convention. This means transitions are spaced by an interval of $2B$. 
Rotational Transitions and Spectra

A $J = 1-0$ transition (written conventionally as $J'-J''$) occurs at $2B$. Whether the transition falls in the $\mu$-wave, mm-wave or far-IR region depends upon the values of $B$ and $J$.

Most linear polyatomic molecules have smaller $B$ values and more transitions tend to occur in the $\mu$-wave and mm-wave regions.

The far-IR spectrum from 15 to 40 cm$^{-1}$ with $J'' = 3$ to 9 is shown below.

<table>
<thead>
<tr>
<th>$\nu$/cm$^{-1}$</th>
<th>$J''$</th>
<th>$J'$</th>
<th>$\nu$/GHz</th>
<th>$\Delta\nu_{J''}'$/GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.845 033 19</td>
<td>0</td>
<td>1</td>
<td>115.271 19</td>
<td>115.271 195</td>
</tr>
<tr>
<td>7.689 919 07</td>
<td>1</td>
<td>2</td>
<td>239.537 97</td>
<td>115.266 779</td>
</tr>
<tr>
<td>11.534 509 6</td>
<td>2</td>
<td>3</td>
<td>345.795 90</td>
<td>115.257 026</td>
</tr>
<tr>
<td>15.378 662</td>
<td>3</td>
<td>4</td>
<td>461.040 68</td>
<td>115.244 78</td>
</tr>
<tr>
<td>19.222 223</td>
<td>4</td>
<td>5</td>
<td>576.267 75</td>
<td>115.227 07</td>
</tr>
<tr>
<td>23.005 643</td>
<td>5</td>
<td>6</td>
<td>691.472 60</td>
<td>115.204 85</td>
</tr>
</tbody>
</table>

Frequencies & wavenumbers of rotational transitions of CO observed in the mm-wave region.
Uses of rotational spectroscopy

Very powerful tool for determining:
1. accurate molecular mass
2. relative isotopic abundances
3. extremely accurate bond length determinations
4. identity of molecules (astronomy)

\[
\begin{align*}
{^{12}\text{C}^{16}\text{O}} & : B = 1.92118 \text{ cm}^{-1} \\
{^{13}\text{C}^{16}\text{O}} & : B = 1.83669 \text{ cm}^{-1}
\end{align*}
\]

Superimposed rotational spectra of \(^{12}\text{C}^{16}\text{O}\) and \(^{13}\text{C}^{16}\text{O}\):
Spectral Intensities

Two important factors determine the intensities of the transitions: (1) the numerical square of the transition moment equation (varies little with $J$) and (2) the relative population of the energy levels involved in the transition.

Once again, the **Boltzmann distribution** can be used to determine the relative populations of the rotational energy states, $N_j$, and the ground rotational state, $N_0$:

$$\frac{N_j}{N_0} = (2J + 1)e^{-E_j/kT}$$

where $g_j = 2J + 1$, the degeneracy of the $J$th level (again note that in the absence of electric or magnetic fields, the levels with $m_J = 0, \pm 1$ are all degenerate).

The $2J + 1$ term of course increases as $J$ increases, but the exponential term decreases as $J$ increases - eventually the exponential term dominates at high $J$ values and $N_j/N_0$ approaches zero. As a result, the population is at a maximum value at $J = J_{\text{max}}$:

$$\frac{d(N_j/N_0)}{dJ} = 0, \quad J_{\text{max}} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

for $B$ in cm$^{-1}$.

For CO, $J_{\text{max}} = 7$ (highest population), but the actual spectrum has a maximum intensity at $J'' = 8$, because there are some other factors we have omitted from this analysis.
The number of molecules in the energy levels corresponding to the quantum number $J$ relative to the number of molecules in the ground state is shown as a function of $J$, for three temperatures of 100, 300 and 700 K.

As long as the ratio $N_J/N_0$ increases, the intensity of the lines originating from quantum states with the quantum number $J$ will increase.

The varying intensities can be used to monitor the excited rotational states of molecules of molecules say in flames, other “gaseous objects”, interstellar spectroscopy, etc. which have temperature gradients.
Centrifugal Distortion

There is actually a small decrease in the transition spacings with increasing $J$, so the approximation of treating a diatomic molecule as a rigid rotor is not perfectly valid. A vibrational component must be included which when $J$ increases, the nuclei tend to be thrown outwards by centrifugal forces (i.e., spring stretches, $r$ increases, and therefore $B$ decreases).

This was originally accounted for by changing the term values of the equations to

$$F(J) = B[1 - uJ(J + 1)]J(J + 1)$$

but is now more commonly written as

$$F(J) = BJ(J + 1) - DJ^2(J + 1)^2$$

where $D$ is the centrifugal distortion constant, and is always positive for diatomic molecules. Transition frequencies are modified to

$$\bar{v} \text{ (or } v) = F(J + 1) - F(J) = 2BJ(J + 1) - 4DJ^2(J + 1)^3$$

$D$ depends upon the stiffness of the bond, and can be related to the vibrational frequency, $\omega = (k/\mu)^{1/2}$, from the harmonic approximation:

$$D = \frac{4B^3}{\omega^2}$$

Interestingly, this implies that rotational spectroscopy can be used to estimate vibrational frequencies!
Centrifugal Distortion, 2

Where does the equation below come from?

\[ F(J) = BJ(J + 1) - DJ^2(J + 1)^2 \]

Recall that in the rigid rotor approximation the internuclear distance \( r \) does not change.

But in reality it will increase for higher values of \( J \) due to the centrifugal force:

So in the “rigid rotor” hamiltonian, the kinetic energy term is affected by the moment of inertia, and there is a now a potential energy term of the form \( V = \frac{1}{2}k(r - r_e)^2 \)

We will not attempt the formal proof of this here, but if \( \omega_e = \hbar(k/\mu)^{1/2} \) and \( B = \hbar^2/2I \), then \( D \) comes from:

\[
D = \frac{\hbar^4}{2I^3(k/\mu)} = \frac{\hbar^4}{2I^3(\omega_e^2/\hbar^2)} = \frac{\hbar^6}{2I^3(\omega_e^2)} = \frac{4B^3}{\omega_e^2}
\]
Centrifugal Distortion, 3

Thus the centrifugal forces in the molecule result in narrowing of the spacings between peaks corresponding to higher values of $J$:

$$E_J$$

20$B$

12$B$

6$B$

2$B$

0

rigid rotor spectrum

non-rigid rotor spectrum

$$F(J) = BJ(J + 1)$$

$$F(J) = BJ(J + 1) - DJ^2(J + 1)^2$$
Excited Vibrational States: Vibrotors

Every vibrational level, including the ZP level, have a stack of rotational levels associated with them.

The ratio of the population $N_v$ of the $v$th vibrational level to $N_0$ (ZP level) is

$$\frac{N_v}{N_0} = e^{-\hbar \omega v/kT}$$

where $v$ is the vibrational quantum no.

Since this ratio is only 0.10 for $v = 1$ and $\bar{v} = 470$ cm$^{-1}$, rotational transitions in excited state are generally very weak unless the molecule is quite heavy or the temperature is quite high.

The rotational constants $B$ and $D$ are slightly vibrationally dependent so that the term values and frequencies are:

$$F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2$$

$$\bar{v} \text{ (or } v) = 2B_v(J + 1) - 4D_v(J + 1)^3$$

and the vibrational dependence of $B$ is (to a good approx.):

$$B_v = B_e - \alpha(v+1/2)$$

where $B_e$ is the equilibrium state rotational constant and $\alpha$ is the vibration-rotation interaction constant. To obtain $B_e$, (and therefore $r_e$), $B_v$ must be obtained in two vib. states. If the $v = 1$ state is insufficiently populated, $B_0$ is only obtained. The vibrational dependence of $D_v$ is generally very small (forget it for now) - but we will look at vibrational-rotational spectroscopy later in the course.
Symmetric Rotors

In linear molecules, the rotational angular momentum vector \( \mathbf{P} \) is directed along the axis of rotation, and is quantized in terms of \( J \). In a prolate symmetric rotor, \( \mathbf{P} \) can be oriented in any direction in space (depending upon the molecule), and the molecule rotates about \( \mathbf{P} \).

The component of \( \mathbf{P} \) along the \( a \) axis, \( P_a \), is quantized, taking on values only of \( K\hbar \), where \( K \) is a second rotational quantum number, giving the projection of angular momentum along the principal axis: \( K = 0, 1, ..., J \).

Rotational terms, neglecting centrifugal distortions and the vibrational dependence of rotational constants are given by

\[
F(J,K) = BJ(J + 1) + (A - B)K^2
\]

and these constants are related to \( I_a \) and \( I_b \) by (\( \nu \) units)

\[
A = \frac{\hbar}{8\pi^2 I_a}; \quad B = \frac{\hbar}{8\pi^2 I_b}; \quad C = \frac{\hbar}{8\pi^2 I_c}
\]

In an oblate symmetric rotor (e.g., \( \text{NH}_3 \)):

\[
F(J,K) = BJ(J + 1) + (C - B)K^2
\]

The energy level spacings for these symmetric rotors are somewhat more complicated for than a linear molecule...
Symmetric Rotors, 2

The selection rules for transitions for these molecules are:
\[ \Delta J = \pm 1; \quad \Delta K = 0 \]

and the expression for transition frequencies is:
\[ \bar{v} \text{ (or } v) = F(J+1, K) - F(J, K) = 2B(J+1) \]

Rotational energy levels for (a) a prolate and (b) an oblate symmetric rotor are shown below:

Transitions again show an equal spacing of $2B$, and the requirement that a molecule must have a permanent dipole moment still applied for the symmetric rotors.
Symmetric Rotors, 3

Including the effects of centrifugal distortion for a prolate symmetric rotor, the term value is:

\[ F(J,K) = BJ(J + 1) + (A - B)K^2 - D_J J^2(J + 1) - D_{JK} J(J + 1)K^2 - D_K K^4 \]

where there are now three possible centrifugal distortion constants, \( D_J \), \( D_{JK} \) and \( D_K \). There is an analogous equation for an oblate symmetric rotor. The transition frequencies or wavenumbers for both cases are given by:

\[ \bar{\nu} \text{ (or } \nu) = 2(B_v - D_{JK} K^2)(J+1) - 4D_J (J + 1)^3 \]

The \(-2D_{JK} K^2(J+1)\) term separates the \( J + 1 \) components of each \((J + 1) \leftarrow J\) transition with different values of \( K \).

For example, the eight components of the \( J = 8-7 \) transition of isothiocyanate (\( \text{H}_3\text{Si-N=C=S} \)) are shown below, which has a linear SiNCS chain and is a prolate symmetric rotor.

Here, \( K = 0 \) to 7, and peaks are separated by centrifugal distortion.
Asymmetric Rotors

These molecules form the largest class of molecules - however, there are no closed formulae to generally predict term values and spectroscopic transition frequencies due to their asymmetry.

Term diagonal values can be determined accurately by full matrix diagonalization for each value of $J$. Still, the selection rules $\Delta J = \pm 1$, $\Delta m_J = 0, \pm 1$ still apply, and the molecules must have a permanent electric dipole moment.

Pure rotational spectra of near-symmetric prolate or oblate rotors can be roughly interpreted with

$$F(J,K) \approx \bar{B}J(J + 1) + (A - \bar{B})K^2$$
$$F(J,K) \approx \bar{B}J(J + 1) + (C - \bar{B})K^2$$

where $\bar{B} = (1/2)(B + C)$ and $\bar{B} = (1/2)(A + B)$ for prolate and oblate rotors, respectively. Since the molecules are only approximately symmetric, $K$ is not strictly a good quantum number (i.e., not always integer values).

Dipole moments of asymmetric rotors (components along various inertial axes) can be determined using the Stark effect).
Spherical Rotor Molecules

Spherical rotor molecules, which have no permanent dipole moment, should in theory have no IR, mm-wave or µ-wave rotational spectra.

In CH₄ it is possible that rotation about any of the C₃ axes in the molecule will result in centrifugal distortion of the three H atoms not along the rotation axis, thereby temporarily converting the molecule to a symmetric rotor with a very small dipole moment.

The very small transient dipole moment permits the detection of a very weak rotational spectrum. The far-IR spectrum of silane (SiH₄) is shown below, from which the dipole moment is estimated as $8.3 \times 10^{-6}$ D.

The term values for a spherical rotor are

$$F(J) = BJ(J + 1)$$

and the transition frequencies are:

$$\bar{v} \text{ (or } v) = F(J + 1) - F(J) = 2B(J + 1)$$

which is the same for linear rigid rotors ( spacings: $2B$). $T_d$ molecules give these weak spectra, but $O_h$ molecules do not, since rotation about a $C_4$ axis does not produce a dipole moment (e.g., no rotational spectrum for SF₆).
The Stark Effect

Recall that space quantization of rotational angular momentum (linear molecule) can be expressed as

\[(P_j)_z = m_j \hbar\]

where \(m_j = J, J - 1, ..., -J\). Under normal conditions the \((2J + 1)\) components of each \(J\) level remain degenerate. In the presence of an electric field \(\mathcal{E}\), the degeneracy becomes partially removed: each is split into \(J + 1\) components according to \(|m_j| = 0, 1, 2, ..., J\).

This splitting in an electric field is known as the Stark effect. For a linear molecule, the energy levels \(E_J\) are modified to \(E_J + E_\mathcal{E}\), where

\[
E_\mathcal{E} = \frac{\mu^2 \mathcal{E}^2 [J(J + 1) - 3m_j^2]}{2\hbar BJ(J + 1)(2J - 1)(2J + 3)}
\]

The above expression has \(m_j^2\), so this term is independent of the sign of \(m_j\), and it involves the molecular dipole moment.

Increasingly complicated equations are available for more complicated rotors.

This makes \(\mu\)-wave and mm-wave spectroscopy very powerful techniques for determining the magnitude (not direction) of molecular dipole moments. Studies are normally on volatile species (sometimes at very high temp!)
Applications in Astronomy

Radiotelescopes are used to scan the universe for radiation in the rf EM region, and are used to detect a variety of molecules.

Examples: atomic H, $\lambda = 21$ cm (varying quantities and densities throughout universe), and OH, $\lambda = 18$ cm

Molecules are detected in regions of space where nebulae are found (Milky Way and other galaxies), and in luminous clouds composed of interstellar dust and gas.

Starlight passing through dust clouds is reddened due to preferential scattering, $\propto \lambda^{-4}$, of the blue light of the dust particles (estimated to be 0.2 $\mu$m in diameter on average).

New stars are formed by gravitational collapse in the region of nebulae, which contain the material from which the new stars are formed - this is why they are of interest (e.g., Sagitarius B2, near the centre of our galaxy, is much studied). NH$_3$ was detected in 1963 in Hat Creek, CA, using a radiotelescope designed to detect in the mm-wave region. Emission lines in the $\lambda = 1.25$ cm region were detected indicating the $\nu_2 = 0$ and $\nu_2 = 1$ levels of the inversion vibration of NH$_3$! 
Rotational Spectroscopy: Instellar Molecules

For the molecules below, the transitions detected using radiotelescopes are rotational in nature (except OH and NH$_3$). C$_2$H, HCO$^+$ and N$_2$H$^+$ were detected in space before they were ever detected in the laboratory!!

**Diatomics:** OH, CO, CN, CS, SiO, SO, SiS, NO, NS, CH, CH$^+$, SiC, NH, CP, HCl, CO$^+$, SO$^+$

**Triatomics:** H$_2$O, HCN, HNC, OCS, H$_2$S, N$_2$H$^+$, SO$_2$, HNO, C$_2$H, HCO, HCO$^+$, HCS$^+$, H$_2$D$^+$ (cyclic)

4 atoms: NH$_3$, H$_2$CO, HNCO, H$_2$CS, HNCS, N≡C-C≡C, H$_3$O$^+$, C$_3$H (linear), C$_3$H (cyclic)

5 atoms: N≡C-C≡C-H, HCOOH, CH$_2$=NH, NH$_2$CN, C$_3$H$_2$ (linear), C$_3$H$_2$ (cyclic), H-C≡C-C≡C

6 atoms: CH$_3$OH, CH$_3$CN, NH$_2$CHO, CH$_3$SH, CH$_3$NC, HC$_2$CHO, HC$_3$NH$^+$, C$_5$H

7 atoms: CH$_3$-C≡C-H, CH$_3$CHO, CH$_3$NH$_2$, N≡C-C≡C-C≡C-H, CH$_2$=CHCN, C$_6$H

8 atoms: HCOOCH$_3$, CH$_3$-C≡C-C≡N

9 atoms: CH$_3$OCH$_3$, CH$_3$CH$_2$OH, N≡C-C≡C-C≡C-C≡C-H, CH$_3$CH$_2$CN, CH$_3$C$_4$H

11 atoms: N≡C-C≡C-C≡C-C≡C-C≡C-H

13 atoms: N≡C-C≡C-C≡C-C≡C-C≡C-C≡C-H

Frequencies of such molecules detected in the laboratory are completely unambiguous and accurate - but interstellar spectra must be corrected for the Doppler effect.

C$_2$, N$_2$, O$_2$ and H-C≡C-H cannot be detected with these methods - but the presence of the remarkable cyanopolyacetylenes was a complete surprise!!
At present, more than 120 different chemical species have been detected in interstellar space, primarily in giant gas clouds scattered throughout our Galaxy. One of the primary objectives of our research is to study these molecules and their chemistry via an interdisciplinary approach that involves high resolution molecular spectroscopy in the laboratory, radio astronomical observations, and chemical modeling. Of particular interest are small molecules composed of a metal atom and a simple ligand. These species are also of significance for organometallic chemistry. Small organic molecules related to sugars and nucleic acids are another area of investigation, as part of the NASA Astrobiology Institute.

They have recorded the spectra of a wide range of metal-bearing hydride, hydroxide, cyanide, acetylide, methyl, nitride and carbide radicals, including AlNC, CuCH3, MgCN, CaC, AlH, CoCN, and MnCl.

Almost all of these species have unpaired electrons, and thus their spectra exhibit complex fine and hyperfine splittings. Analysis of such data requires a detailed knowledge of quantum mechanics and the coupling of angular momentum.
Key Concepts

1. Moments of inertia can be calculated accurately for molecules of a variety of shapes. The “rotational shapes” are classified as linear, symmetric, spherical and asymmetric rotors. Symmetric rotors may be prolate or oblate.

2. For all rotors but the asymmetric rotors, exact expressions for energy levels (term values) and rotational transition frequencies can be calculated.

3. The rotational selection rules are: (1) Molecule must have a permanent dipole moment (i.e., \( \mu \neq 0 \)), (2) \( \Delta J = \pm 1 \) and (3) \( \Delta m_J = 0, \pm 1 \) (important if molecule in an electric or a magnetic field)

4. Centrifugal distortion of molecules results in uneven spacing in the pure rotational spectra. The centrifugal distortion constant \( D \) is used to modify the rigid rotor model to accurately predict energy levels and transition frequencies.

5. Rotational spectra of symmetric rotors are further complicated by the second rotational quantum number, \( K \), which quantizes the molecular rotational angular momentum.

6. Rotational transitions are split into multiple peaks in the presence of an electric field: the Stark effect