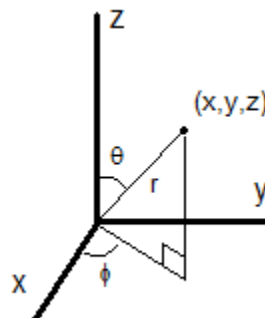


Chapter 5: The Rigid Rotor and Rotational Spectroscopy

One of the most powerful tools for elucidating molecular structure is the analysis of rotationally resolved molecular spectra. These can be observed in the microwave, infrared, and visible/ultraviolet regions of the spectrum. The **rigid rotor** (or rigid rotator) problem provides the idealized model that chemists use to describe the rotational motion of a molecule. In this chapter, we will explore the quantum mechanical model of a rotating body, and apply the results to lay the foundation for an understanding of the rotational structure in molecular spectra. We'll look at the shortcomings of the model when applying it to real molecules (which as we saw in the previous chapter, do not have rigid bonds!) and apply these results to the interpretation of pure rotational spectra (generally found in the microwave region of the spectrum) and rotation-vibration spectra (accounting for the rotational structure that is observed in infrared spectra of molecules.)

Spherical Polar Coordinates

The description of a rotating molecule in Cartesian coordinates would be very cumbersome. The problem is actually much easier to solve in **spherical polar coordinates**. Consider a particle that is located in space at some arbitrary point (x,y,z) . In spherical polar coordinates, the position of a particle is also described by three variables, namely r , θ , and ϕ . These variables are defined according to the diagram. The distance from the origin to the point is specified by r . θ gives the angle formed by the position vector of the point and the positive z -axis. ϕ give the angle of rotation from the positive x -axis of the projection of the position vector into the xy plane. The ranges of possible values for r , θ and ϕ are given by



$$0 \leq r \leq \infty$$

$$0 \leq \theta \leq \pi$$

$$0 \leq \phi \leq 2\pi$$

The coordinates of any point can be transformed from spherical polar coordinates to Cartesian coordinates using the following equations.

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

The coordinates can be transformed from Cartesian coordinates to spherical polar coordinates by these equations.

$$\begin{aligned}r &= \sqrt{x^2 + y^2 + z^2} \\ \theta &= \tan^{-1}\left(\frac{y}{x}\right) \\ \phi &= \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)\end{aligned}$$

Potential Energy and the Hamiltonian

Since there is no energy barrier to rotation, there is no potential energy involved in the rotation of a molecule. All of the energy is kinetic energy. This simplifies the writing of the Hamiltonian.

In Cartesian coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\end{aligned}$$

In spherical polar coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\end{aligned}$$

For the rigid rotor problem, r is taken to be a constant, simplifying the operator.

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The expression μr^2 is the **moment of inertia** for the molecule. This value shows up often in problems involving the rotation of a molecule.

$$I = \mu r^2$$

While the expression for the Hamiltonian in spherical polar coordinates looks considerably more cumbersome than the Hamiltonian expressed in Cartesian coordinates, it will still be simpler to solve the problem describing the rotation of a molecule.

Solution to the Schrödinger Equation

The time-independent Schrödinger equation can be written as follows.

$$\begin{aligned}\hat{H}\psi(\theta, \phi) &= E\psi(\theta, \phi) \\ -\frac{\hbar^2}{2\mu r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi(\theta, \phi) &= E\psi(\theta, \phi)\end{aligned}$$

Since the Hamiltonian can be expressed as a sum of operators, one in θ and the other in ϕ , it follows that the wavefunction should be able to be expressed as a product of two functions.

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

Making this substitution, the equation becomes

$$-\frac{\hbar^2}{2\mu r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \Theta(\theta)\Phi(\phi) = E\Theta(\theta)\Phi(\phi)$$

With minimal rearrangement, the following result can be derived

$$\frac{\Phi(\phi)}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \Theta(\theta) + \frac{\Theta(\theta)}{\sin^2 \theta} \frac{d^2}{d\phi^2} \Phi(\phi) = -\frac{2\mu r^2 E}{\hbar^2} \Theta(\theta)\Phi(\phi)$$

And dividing both sides by $\Theta(\theta)\Phi(\phi)$ produces

$$\left(\frac{1}{\Theta(\theta)\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \Theta(\theta) \right) + \left(\frac{1}{\Phi(\phi)\sin^2 \theta} \frac{d^2}{d\phi^2} \Phi(\phi) \right) = -\frac{2\mu r^2 E}{\hbar^2}$$

This expression suggests that the sum of two functions, one only in θ and the other only in ϕ , when added together, yields a constant. As the two variables θ and ϕ are independent of one another, the only way this can be true is if each equation is itself equal to a constant.

$$\begin{aligned}\frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \Theta(\theta) &= -\lambda_1^2 \Theta(\theta) \\ \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} \Phi(\phi) &= -\lambda_2^2 \Phi(\phi)\end{aligned}$$

where λ_1 and λ_2 are constants of separation (the form of which is chosen for convenience) which satisfy the following relationship.

$$\begin{aligned}
 -\lambda_1^2 - \lambda_2^2 &= -\lambda^2 \\
 &= -\frac{2\mu r^2 E}{\hbar^2}
 \end{aligned}$$

Rotation in the xy plane ($\theta = \pi/2$)

We'll tackle the equation in ϕ first. One way to picture this part of the equation is that it describes the rotation of a molecule in the xy plane only (defined by $\theta = \pi/2$.) Given this constraint, it is clear that the $\sin^2(\theta)$ term becomes unity, since $\sin(\pi/2) = 1$. The problem then becomes

$$\frac{d^2}{d\phi^2} \Phi(\phi) = -\frac{2\mu r^2 E}{\hbar^2} \Phi(\phi)$$

If a substitution is made for the constants on the right-hand side of the equation,

$$-m_l^2 = -\frac{2\mu r^2 E}{\hbar^2}$$

we get

$$\frac{d^2}{d\phi^2} \Phi(\phi) = -m_l^2 \Phi(\phi)$$

which should look like a familiar problem. Instead of using sine and cosine functions this time though, we will use an imaginary exponential function instead.

$$\Phi(\phi) = A_{m_l} e^{im_l \phi}$$

The boundary condition for this problem is that the function $\Phi(\phi)$ must be single valued. Therefore

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

So

$$A_{m_l} e^{im_l \phi} = A_{m_l} e^{im_l (\phi + 2\pi)}$$

Dividing both sides by A_{m_l} and expressing the second exponential as a product yields

$$e^{im_l\phi} = e^{im_l\phi} e^{im_l 2\pi}$$

$$1 = e^{im_l 2\pi}$$

Using the Euler relationship

$$e^{i\alpha} = \cos \alpha + i \sin \alpha$$

we see that

$$1 = \cos(2m_l\pi) + i \sin(2m_l\pi)$$

In order for this to be true, the sine term must vanish and the cosine term must become unity. This is true if m_l is an integer, either positive or negative and including zero.

$$m_l = \dots, -2, -1, 0, 1, 2, \dots$$

Energy Levels

As such, the energy of a rigid rotator limited to rotation in the xy plane is given by

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2\mu r^2} \quad m_l = 0, \pm 1, \pm 2, \dots$$

It is important to note that these functions are doubly degenerate for any non-zero value of m_l as there are always two values of m_l that yield the same energy.

Normalization

The wavefunctions can be normalized in the usual way.

$$\begin{aligned} \int_0^{2\pi} (A_{m_l} e^{im_l\phi})^* (A_{m_l} e^{im_l\phi}) d\phi &= 1 \\ &= A_{m_l}^2 \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} d\phi \\ &= A_{m_l}^2 \int_0^{2\pi} d\phi \\ &= A_{m_l}^2 [\phi]_0^{2\pi} \\ &= 2\pi A_{m_l}^2 \\ \sqrt{\frac{1}{2\pi}} &= A_{m_l} \end{aligned}$$

As was the case with the particle in a box problem, the normalization factor does not depend on the quantum number. The wavefunctions can be expressed

$$\Phi(\phi) = \sqrt{\frac{1}{2\pi}} e^{im_l\phi} \quad m_l = 0, \pm 1, \pm 2, \dots$$

Rotation in three dimensions

We are now ready to tackle the more complicated problem of rotation in three dimensions. Recall the Schrödinger equation as was previously written.

$$\frac{\Phi(\phi)}{\sin\theta} \frac{d}{d\theta} \sin\theta \frac{d}{d\theta} \Theta(\theta) + \frac{\Theta(\theta)}{\sin^2\theta} \frac{d^2}{d\phi^2} \Phi(\phi) = -\frac{2\mu r^2 E}{\hbar^2} \Theta(\theta) \Phi(\phi)$$

We already know the form of the solutions for the $\Phi(\phi)$ part of the equation. However, due to the $1/\sin^2\theta$ term in the Φ equation, it is possible that the solution to the Θ part of the equation will introduce a new constraint on the quantum number m_l .

Energy Levels

The only well-behaved functions (functions that satisfy all of the boundary conditions) have energies given by

$$E_l = \frac{l(l+1)\hbar^2}{2\mu r^2} \quad l = 0, 1, 2, \dots$$

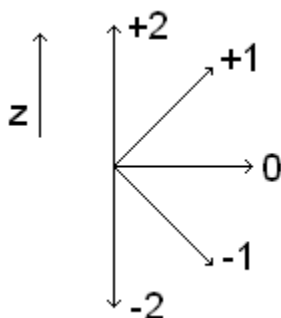
The quantum number l indicated the angular momentum. m_l is the z-axis component of angular momentum. The z-axis is treated differently than the x- or y-axes due to the unique manner in which the z-axis is treated in the choice of the spherical polar coordinate system (since θ is taken as the angle of the position vector with the positive z-axis.) Also, as will be shown later, the operator \hat{L}_z , the z-axis angular momentum component operator, has a special relationship with the Hamiltonian (as does the squared angular momentum operator, \hat{L}^2 .)

Degeneracy

The interpretation of the quantum number m_l is that it gives the magnitude of the z-axis component of the angular momentum vector. And since no vector can have a component with a magnitude greater than that of the vector itself, the constraint on m_l that is introduced by this solution is

$$|m_l| \leq l$$

so for a given value of l , there are $(2l + 1)$ values of m_l that fit the constraint. And since the energy expression does not depend on m_l , it is clear that each energy level has a degeneracy that is given by $(2l + 1)$. That can be demonstrated as in the diagram below for an angular momentum vector of magnitude 2 ($l = 2$).



As can be seen in the diagram, there are five possible values of m_l , +2, +1, 0, -1 and -2. These five values correspond to the $(2l + 1)$ degeneracy predicted for a state with total angular momentum given by $l = 2$ (and therefore $2l + 1 = 5$). When we see the wavefunctions in more detail, there will be a new reason for this constraint on the quantum number m_l .

Wavefunctions

For convenience, we'll first look at the solutions where $m_l = 0$. The wavefunctions under this constraint have two parts, a normalization constant and a **Legendre polynomial** in $\cos(\theta)$. The Legendre polynomials are another set of orthogonal polynomials, similar to the Hermite polynomials that occur in the solution to the harmonic oscillator problem. The Legendre polynomials can be generated by the following relationship

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l$$

The first few Legendre polynomials are given below.

l	$P_l(x)$	$P_l(\cos \theta)$
0	1	1
1	x	$\cos(\theta)$
2	$\frac{1}{2}(3x^2 - 1)$	$\frac{1}{2}[3\cos^2(\theta) - 1]$
3	$\frac{1}{2}(5x^3 - 3x)$	$\frac{1}{2}[5\cos^3(\theta) - 3\cos(\theta)]$

A recursion relation for the Legendre Polynomials is given by

$$(l + 1)P_{l+1}(x) = (2l + 1)xP_l(x) - l P_{l-1}(x)$$

When $m_l = 0$, the spherical harmonic function $Y^m(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ becomes just $\Theta(\theta)$, since the ϕ dependence disappears. The $\Theta(\theta)$ part of the wavefunctions are given by

$$\Theta(\theta) = \left[\frac{(2l+1)}{2} \right]^{\frac{1}{2}} P_l(\cos \theta)$$

The functions are slightly different for $m_l \neq 0$. In this case, the functions involve a set of functions that are related to the Legendre Polynomials called the **associated Legendre polynomials**. These functions are generated from the Legendre polynomials via the following relationship.

$$P_l^{|m_l|}(x) = (-1)^{|m_l|} (1-x^2)^{|m_l|/2} \frac{d^{|m_l|}}{dx^{|m_l|}} P_l(x)$$

Note that for any value of $|m_l| > l$, the derivative of $P_l(x)$ vanishes.

$$\frac{d^{|m_l|}}{dx^{|m_l|}} P_l(x) = 0 \quad \text{for } |m_l| > l$$

And this is the origin of the constraint on m_l .

The associated Legendre polynomials depend on both l and m_l . Also, given the $|m_l|$ dependence, the sign of m_l does not matter. (The only place that the sign of m_l matter is in the $\Phi(\phi)$ function.) The first few associated Legendre Polynomials are given in the table below.

l	$ m_l $	$P_l^{ m_l }(x)$	$P_l^{ m_l }(\cos \theta)$
0	0	1	1
1	0	x	cos(θ)
	1	$(1-x^2)^{1/2}$	sin(θ)
2	0	$\frac{1}{2}(3x^2-1)$	$\frac{1}{2}(3 \cos^2(\theta) - 1)$
	1	$3x(1-x^2)^{1/2}$	$3 \cos(\theta) \sin(\theta)$
	2	$3(1-x^2)$	$3 \sin^2(\theta)$

Spherical Harmonics

The rigid rotor problem was solved using the Schrödinger equation

$$-\frac{\hbar^2}{2\mu r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi(\theta, \phi) = E \psi(\theta, \phi)$$

As it turns out, the solutions to this equation are very important in a number of areas in chemistry and physics. The eigenfunctions are known as the **spherical harmonics** ($Y_l^{m_l}(\theta, \phi)$) and they appear in every problem that has spherical symmetry. The Spherical Harmonics satisfy the relationship

$$\left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) Y_l^{m_l}(\theta, \phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta, \phi)$$

Each function $Y_l^{m_l}(\theta, \phi)$ has three parts: 1) a normalization constant, 2) an associated Legendre polynomial in $\cos(\theta)$, and 3) an imaginary (for $m_l \neq 0$) exponential in ϕ .

$$Y_l^{m_l}(\theta, \phi) = \left[\frac{(2l+1)(l-|m_l|)!}{4\pi(l+|m_l|)!} \right]^{\frac{1}{2}} P_l^{|m_l|}(\cos \theta) e^{im_l \phi}$$

The first few Spherical harmonics are shown in the table below.

l	m_l	$Y_l^{m_l}(\theta, \phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} \cos(\theta)$
	± 1	$\sqrt{\frac{3}{8\pi}} \sin(\theta) e^{\pm i\phi}$
2	0	$\sqrt{\frac{5}{16\pi}} (3 \cos^2(\theta) - 1)$
	± 1	$\sqrt{\frac{15}{8\pi}} \sin(\theta) \cos(\theta) e^{\pm i\phi}$
	± 2	$\sqrt{\frac{15}{32\pi}} \sin^2(\theta) e^{\pm 2i\phi}$

Notice the $(2l+1)$ degeneracy in these functions, due to the $(2l+1)$ values of m_l for each value of l . Also, it is useful to note that these functions all have l angular nodes (values of θ that cause the wavefunction to vanish.) For the $l = 1$ wavefunctions, these nodes occur at $\theta = \pi/2$ for $m_l = 0$ and at $\theta = 0$ for $m_l = \pm 1$. The number of nodes in each wavefunction is a useful property to know when discussing how these functions related to the radial wavefunction in the Hydrogen atom.

Angular Momentum

The Spherical Harmonics are involved in a number of problems where **angular momentum** is important (including the Rigid Rotor problem, the H-atom problem and anything else where spherical symmetry is involved.) Angular momentum is a vector quantity that is given by the cross product of position and momentum.

$$\vec{L} = \vec{r} \times \vec{p}$$

This quantity can be calculated from the following determinant.

$$\begin{aligned}\vec{L} = \vec{r} \times \vec{p} &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k}\end{aligned}$$

Substituting the operators for the components of linear momentum, the operators that correspond to the three components of angular momentum are

$$\begin{aligned}\hat{L}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)\end{aligned}$$

These can be used to determine the square of the angular momentum, which is given by the dot product of \vec{L} with itself.

$$\vec{L} \cdot \vec{L} = L^2 = L_x^2 + L_y^2 + L_z^2$$

Similarly, the operator for the square of the angular momentum is given by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

In spherical polar coordinates, the angular momentum operators are given by the expressions

$$\begin{aligned}\hat{L}_x &= -i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_y &= -i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial^2}{\partial \phi^2}\end{aligned}$$

And the angular momentum squared operator is given by

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

For the Rigid-Rotator problem, it is interesting to note that the Hamiltonian is very closely related to the angular momentum squared operator.

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \frac{1}{2I} \hat{L}^2\end{aligned}$$

The eigenfunctions of the \hat{L}^2 operator are the Spherical Harmonics, $Y_l^{m_l}(\theta, \phi)$. These functions have the important properties that

$$\begin{aligned}\hat{H}Y_l^{m_l}(\theta, \phi) &= \frac{\hbar^2 l(l+1)}{2\mu r^2} Y_l^{m_l}(\theta, \phi) \\ \hat{L}^2 Y_l^{m_l}(\theta, \phi) &= \hbar^2 l(l+1) Y_l^{m_l}(\theta, \phi) \\ \hat{L}_z Y_l^{m_l}(\theta, \phi) &= \hbar m_l Y_l^{m_l}(\theta, \phi)\end{aligned}$$

Seeing as the spherical harmonics are eigenfunctions of all three of these operators, what is implied about the commutator of these two operators?

There are important relationships between the angular momentum operators. Each of the operators corresponding to the components of angular momentum commutes with the \hat{L}^2 operator, but they do not commute with one another. This implies that one can measure the squared angular momentum and only one component of angular momentum. This is generally taken as the z-axis component of angular momentum as the z-axis has special properties due to the manner in which the spherical polar coordinates have been defined.

$$\begin{aligned} [\hat{L}^2, \hat{L}_x] &= [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \\ [\hat{L}_x, \hat{L}_y] &\neq 0; \quad [\hat{L}_y, \hat{L}_z] \neq 0; \quad [\hat{L}_x, \hat{L}_z] \neq 0 \end{aligned}$$

The commutators involving two components of angular momentum are particularly interesting. Consider the commutator between \hat{L}_x and \hat{L}_y .

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x$$

Let's define each term separately and then take the difference.

$$\begin{aligned} \hat{L}_x \hat{L}_y &= (-i\hbar)^2 \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ &= -\hbar^2 \left(y \frac{\partial}{\partial z} z \frac{\partial}{\partial x} - y \frac{\partial}{\partial z} x \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} z \frac{\partial}{\partial x} + z \frac{\partial}{\partial y} x \frac{\partial}{\partial z} \right) \end{aligned}$$

The second, third and fourth terms are easy to simplify as the derivatives do not affect the x or z variables. The first term, however, requires some application of the chain rule.

$$\hat{L}_x \hat{L}_y = -\hbar^2 \left(\left\{ y \frac{\partial}{\partial x} + yz \frac{\partial^2}{\partial x \partial z} \right\} - xy \frac{\partial^2}{\partial z^2} - z^2 \frac{\partial^2}{\partial x \partial y} + xz \frac{\partial^2}{\partial y \partial z} \right)$$

Similarly,

$$\begin{aligned} \hat{L}_y \hat{L}_x &= (-i\hbar)^2 \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ &= -\hbar^2 \left(z \frac{\partial}{\partial x} y \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} z \frac{\partial}{\partial y} - x \frac{\partial}{\partial z} y \frac{\partial}{\partial z} + x \frac{\partial}{\partial z} z \frac{\partial}{\partial y} \right) \\ &= -\hbar^2 \left(zy \frac{\partial^2}{\partial x \partial z} - z^2 \frac{\partial^2}{\partial x \partial y} - xy \frac{\partial^2}{\partial z^2} + \left\{ x \frac{\partial}{\partial y} + xz \frac{\partial^2}{\partial z \partial y} \right\} \right) \end{aligned}$$

Taking the difference will cancel all of the second derivative terms, leaving only the first derivative terms behind.

$$\begin{aligned} \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x &= -\hbar^2 \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \\ &= i\hbar \hat{L}_z \end{aligned}$$

Similarly, it can be shown that

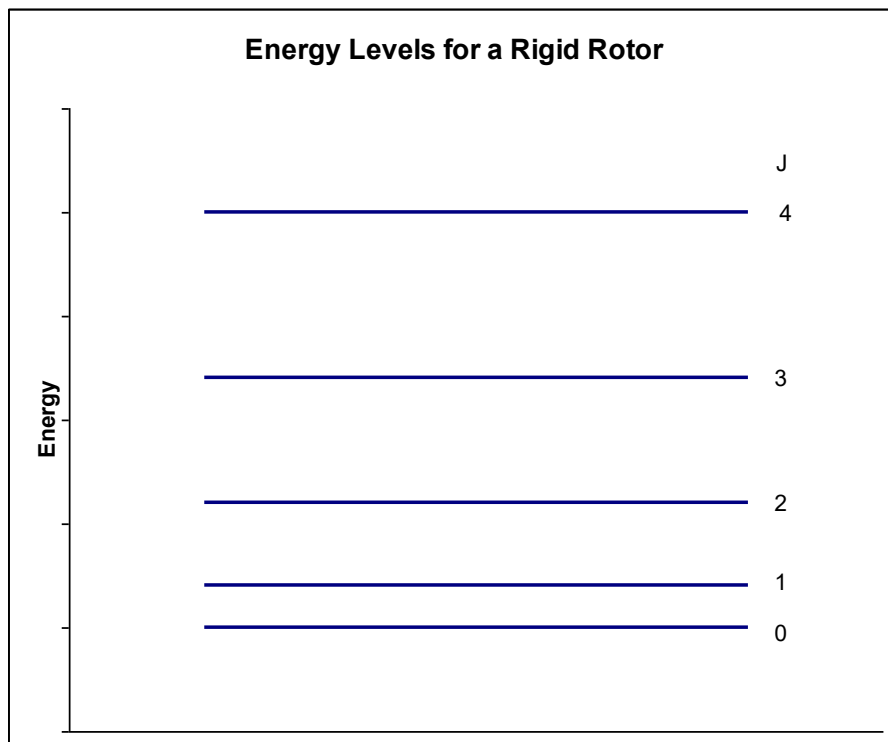
$$\begin{aligned} [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}$$

Application to the Rotation of Real Molecules

While the spherical harmonics are the wavefunctions that describe the rotational motion of a rigid rotator, the names of the quantum numbers are changed to reflect the type of angular momentum encountered in the problem. The quantum number l and m_l should be familiar as these are the ones used in the hydrogen atom problem to describe the orbital angular momentum. However, for rotational motion, these are replaced by J and M_J . The energy levels of the rigid rotator are therefore given by

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

And since M_J does not appear in the energy level expression, each level has a $(2J+1)$ degeneracy. The spacings between energy levels increases with increasing J due to the $J(J+1)$ dependence (which has a J^2 term.) This pattern is shown in the diagram below.



For spectroscopic measurements, the rotational energy (given the symbol F_J) is often expressed in spectroscopic units, such as cm^{-1} . Also, a spectroscopic constant, B , is used to describe the energy level stack.

$$F_J = \frac{E_J}{hc} = B J(J + 1)$$

where the spectroscopic constant B is given by

$$B = \frac{h}{8 \pi^2 c \mu r^2}$$

Thus, by knowing the value of μ , the reduced mass, and measuring the value of B , the rotational constant, one can determine the value of r , the bond length. This is the utility of rotational spectroscopy – it gives us detailed information about molecular structure!

Centrifugal Distortion

As we know, since they vibrate, real molecules do not have rigid bonds. So it is no surprise to learn that the Rigid Rotor is really just a limiting ideal model, much like the ideal gas law describes limiting ideal behavior.

Real molecules, especially when rotating with very high angular momentum, will tend to stretch. In other words, the average bond length will increase with increasing J . And given the inverse relationship between B and bond length (r), it is not surprising that the effective B value is smaller at higher levels of J . In fact, this centrifugal distortion problem is well treated by introducing a “distortion constant” D such that

$$F_J = B J(J + 1) - D [J(J + 1)]^2$$

Naturally, one would expect the distortion constant to be small in the case of a strong, inflexible bond, but larger if the bond is weaker. The approximation of Kraitzer suggests that the distortion constant is determined to a good approximation by

$$D \approx \frac{4B^3}{\omega_e^2}$$

For a well behaved molecule, the distortion constant D is always smaller in magnitude than B . Some molecules require several distortional constants to yield a reasonable description of their rotational energy level stack. If additional constants are needed, they are introduced as coefficients in a power series of $J(J + 1)$.

$$F_J = B J(J + 1) - D [J(J + 1)]^2 + H [J(J + 1)]^3 + \dots$$

The power series is truncated at a point that yields a good fit to experimental observations for a given molecule.

Spectroscopy

The experimental determination of spectroscopic rotational constants provides a very precise set of data describing molecular structure. To see how experimental measurements inform the determination of molecular structure, let's examine what is to be expected in the pure rotational spectrum of a molecule first.

Microwave Spectroscopy

The rotational selection rule in microwave absorption spectra is

$$\Delta J = +1$$

(Selection rules are discussed in more detail in a later section.) The pattern of lines predicted to be observed in a microwave spectrum (a pure rotational spectrum of a mole) can be derived by taking differences in rotational energy levels.

$$\tilde{\nu}_J = F_{J+1} - F_J$$

$$\begin{aligned} F_{J+1} - F_J &= B(J+1)(J+2) - BJ(J+1) \\ &= B(J^2 + 3J + 2) - B(J^2 + J) \\ &= B(J^2 + 3J + 2 - J^2 - J) \\ &= B(2J + 2) \\ &= 2B(J + 1) \end{aligned}$$

This suggests that a pure microwave spectrum should consist of a series of lines that are evenly spaced, the spacing between which is $2B$. It also suggests that a plot of the line frequency divided by $(J+1)$ should yield a straight and horizontal line,

$$\frac{\tilde{\nu}_J}{(J+1)} = 2B$$

The inclusion of distortion yields a slightly different conclusion.

$$\begin{aligned}
 F_{J+1} - F_J &= B(J+1)(J+2) - D[(J+1)(J+2)]^2 - BJ(J+1) + D[J(J+1)]^2 \\
 &= B(J^2 + 3J + 2 - J^2 - J) - D[(J^2 + 3J + 2)^2 - (J^2 + J)^2] \\
 &= B(2J + 2) - D(J^4 + 6J^3 + 13J^2 + 12J + 4 - J^4 - 2J^3 - J^2) \\
 &= 2B(J+1) - D(4J^3 + 12J^2 + 12J + 4) \\
 &= 2B(J+1) - 4D(J+1)^3
 \end{aligned}$$

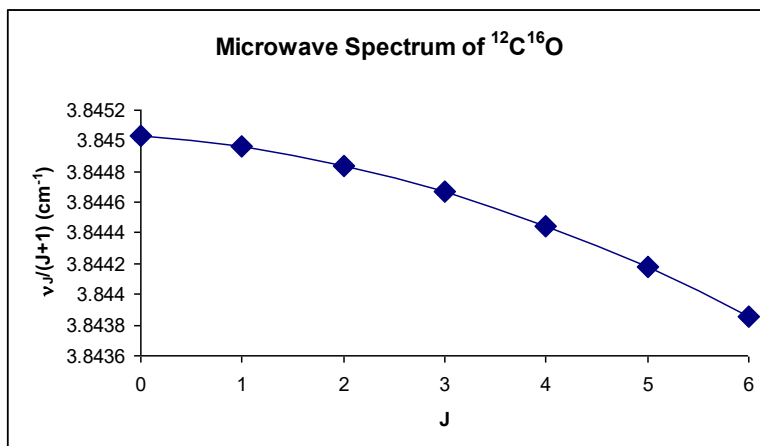
$$\frac{\tilde{\nu}_J}{(J+1)} = 2B - 4D(J+1)^2$$

This suggests that a plot of $\frac{\tilde{\nu}_J}{(J+1)}$ vs. $(J+1)^2$ should yield a straight line with slope $-4D$ and intercept $2B$.

Consider the following set of data for the microwave spectrum of $^{12}\text{C}^{16}\text{O}$ (Lovas & Krupenie, 1974).

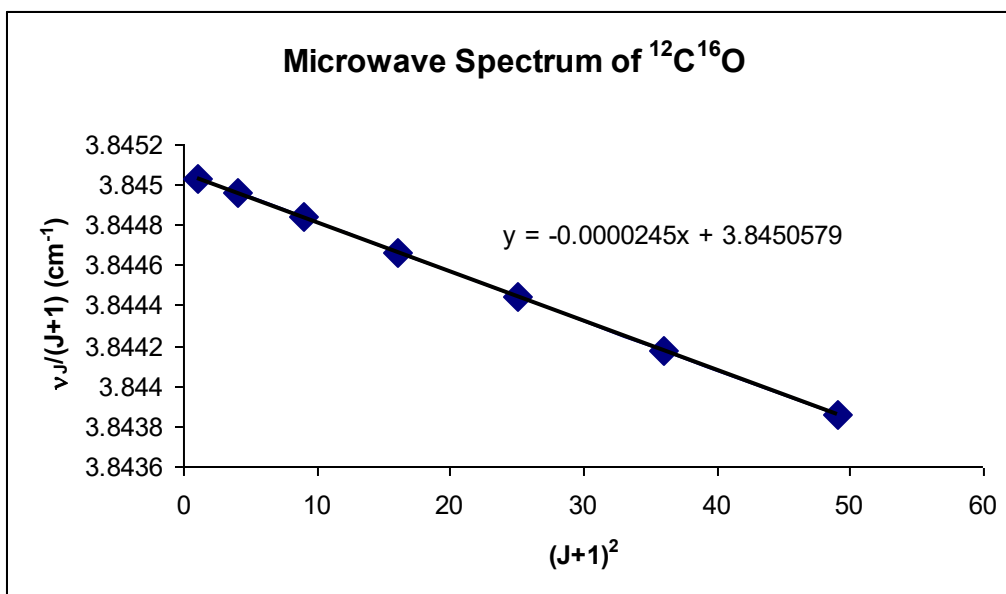
A plot of $\frac{\tilde{\nu}_J}{J+1}$ vs. J yields a plot as the following.

J	$\tilde{\nu}_J$ (cm ⁻¹)
0	3.84503
1	7.68992
2	11.53451
3	15.37867
4	19.22223
5	23.06506
6	26.90701



Clearly, this is not a horizontal line. The conclusion is that centrifugal distortion is not negligible for this molecule. Including distortion suggests that the plot that should be considered would

involve $\frac{\tilde{\nu}_J}{(J+1)}$ vs. $(J+1)^2$. This yields the following:



This does yield a straight line! From the fit, one calculates a B value of 1.92253 cm^{-1} and a D value of $0.00000612 \text{ cm}^{-1}$.

Calculating a Bond Length from Spectroscopic Data

Spectroscopic data (and microwave data in particular) provides extremely high precision information from which bond lengths can be determined. Based on the above data and the masses of carbon-12 (12.00000 amu) and oxygen-16 (15.99491463 amu) (Rosman & Taylor, 1998) a reduced mass for $^{12}\text{C}^{16}\text{O}$ can be calculated as

$$\mu = \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} = 6.85621 \text{ amu} = 1.1385 \times 10^{-26} \text{ kg}$$

Recalling the expression for the rotational constant B

$$B = \frac{h}{8\pi^2 c \mu r^2}$$

The bond length is given by

$$r = \sqrt{\frac{h}{8\pi^2 c \mu B}}$$

Using the data from above, one calculates a bond length for CO to be $r = 1.1312 \text{ \AA}$. This value is actually the average value of the bond length in the $v = 0$ level. The literature value for the equilibrium bond length (the bond length at the potential minimum) is given by $r_e = 1.128323 \text{ \AA}$

(Bunker, 1970) which is slightly shorter (as is to be expected.) The extrapolation of data to determine values at the potential minimum is discussed in a later section.

Rotation-Vibration Spectroscopy

Each vibrational level in a molecule will have a whole stack of rotational energy levels. As such, vibrational transitions will also show rotational fine structure. This fine structure can be analyzed to determine very precise values for molecular structure in much the same ways microwave data for the pure rotational spectrum can be. One method for analyzing this data is that of **combination differences** although direct fitting of the data will give better results mathematically. Before beginning a discussion of combination differences, however, it is necessary to discuss **selection rules**.

Selection Rules and Branch Structure

Selection rules are determined for spectroscopic transitions as those transitions for which the **transition moment** integral does not vanish. This is because the observed intensities of spectroscopic transitions are proportional to the squared magnitude of the transition moment. The transition moment integral is given by

$$\int (\psi')^* \vec{\mu}(\psi'') d\tau$$

and so the intensities of transitions are given by

$$Int. \propto \left| \int (\psi')^* \vec{\mu}(\psi'') d\tau \right|^2$$

where a single prime (') indicates the upper state of the transition and a double prime (") indicates the lower state. The operator $\vec{\mu}$ corresponds to the change in the electric dipole moment of the molecule as it undergoes a transition from a state described by ψ'' to one described by ψ' . Other operators may be used in this expression (magnetic dipole, electric quadrupole, etc.) but these lead to significantly weaker transitions (by a factor of 10^6 or more!) When the electric dipole operator is used, the transitions for which the transition moment is not zero are said to be **allowed transitions**, while all others are said to be **forbidden transitions** by electric dipole selection rules. Since other types of transitions are so weak by comparison, a transition that is said to be allowed or forbidden is assumed to mean by electric dipole selection rules unless specifically stated otherwise.

The selection rules for vibrational transitions are

$$\Delta v = \pm 1$$

For closed-shell molecules (molecules where all of the electrons are paired), the rotational selection rules are

$$\Delta J = \pm 1$$

$\Delta J = 0$ is possible for some open-shell molecules, but this topic will be discussed in more detail in Chapter 7.

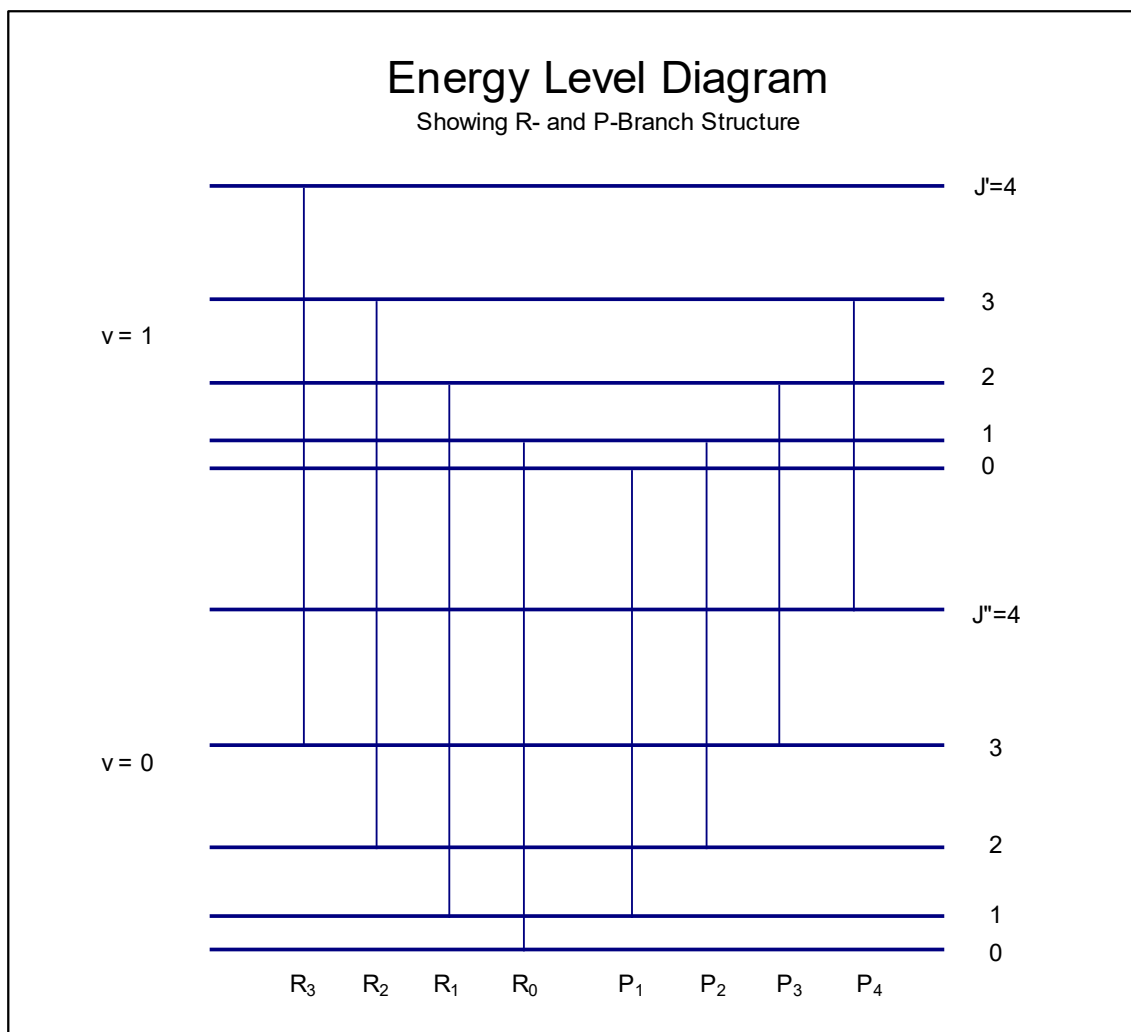
The rotational fine structure of a transition can be separated into branches according to the specific change in the rotational quantum number J .

ΔJ	
+1	R-branch
0	Q-branch
-1	P-branch

In Raman spectroscopy (which is an inelastic light scattering process rather than the direct absorption or emission of a photon, and thus follows different selection rules) O- and S-Branches can be observed with $\Delta J = -2$ and $+2$ respectively.

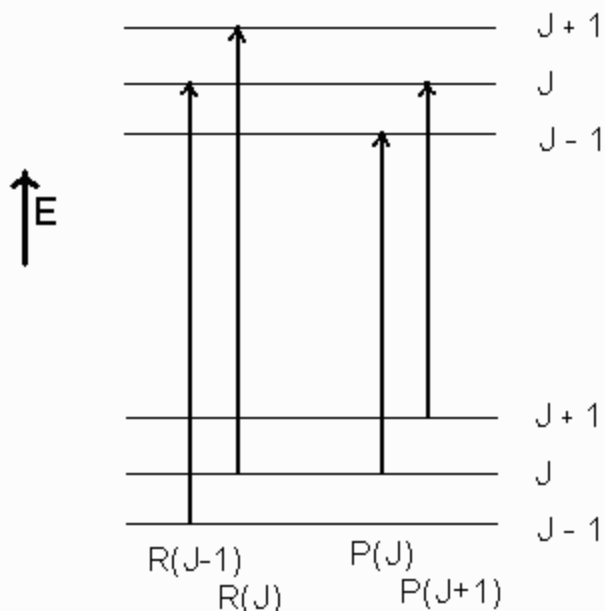
The spectrum of possible branches and transitions that can be observed for all possible molecules can be quite daunting (and take an entire graduate level course in molecular spectroscopy just to scratch the surface!) For the purposes of this discussion, we will limit ourselves for the time being to just closed-shell molecules for which P- and R-branches can be observed.

Consider the following energy level diagram depicting the rotational energy levels in two different states. The diagram shows the expected branch structure for a closed shell molecule. Notice that the transition lines get longer with increasing J in the R-branch, but shorter with increasing J in the P-branch. The largest difference in transition energy is for successive lines in the spectrum is that between the R_0 and P_1 lines. The **band origin** ($\tilde{\nu}_0$) will lie between these two lines, and is at the energy difference between the $J'=0$ and $J''=0$, the two non-rotating levels in the two vibrational levels. Also notice that the rotational energy spacings in the upper state are smaller than those in the lower state. This is due to a smaller B value in the upper state ($v = 1$), which has a larger average bond length than the $v = 0$ level.



Combination Differences

Consider the following partial energy level diagram:



It is clear that since the $R(J)$ and $P(J)$ transitions share a common lower rotational level (F_J), the energy difference between the $R(J)$ and $P(J)$ transitions gives the energy difference between the F_{J+1} and F_{J-1} in the upper state of the transition. Similarly, the difference between F_{J+1} and F_{J-1} in the lower state is given by $R(J-1) - P(J+1)$. Thus, by taking differences of transition energies in the proper combination, dependence on one of the states can be eliminated. Also, the difference $\Delta_2 F(J)$ can be found. This difference is defined by:

$$\Delta_2 F(J) \equiv F_{J+1} - F_{J-1}$$

Using the rigid rotator model,

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

an expression for $\Delta_2 F(J)$ can be easily derived:

$$\begin{aligned} \Delta_2 F(J) &= B(J+1)(J+2) - B(J-1)(J) \\ &= B(J^2 + 3J + 2) - B(J^2 - J) \\ &= B(4J + 2) \\ &= 4B(J + 1/2) \end{aligned}$$

Thus the value of $\Delta_2 F(J)$ that can be found for either the upper or lower states by combination differences from the energies of the spectral lines, can be used to find the spectroscopic constant B .

$$\frac{\Delta_2 F(J)}{(J+1/2)} = 4B$$

And the $\Delta_2 F(J)$ values are determined by the combination differences

$$\begin{aligned}\Delta_2 F'(J) &= R(J) - P(J) \\ \Delta_2 F''(J) &= R(J-1) - P(J+1)\end{aligned}$$

where the single prime (') refers to the upper state and the double prime (") refers to the lower state.

For most molecules, the rotational distortion constants are not negligible. In this case, the rotational term values are given by

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \dots$$

Neglecting terms of higher order than $DJ^2(J+1)^2$ (since these terms are small for most molecules) the combination differences relationship can be derived as

$$\begin{aligned}\Delta_2 F(J) &= B(J+1)(J+2) - D(J+1)^2(J+2)^2 - B(J-1)J + D(J-1)^2J^2 \\ &= B[(J^2 + 3J + 2) - (J^2 - J)] - D[(J^2 + 2J + 1)(J^2 + 4J + 4) - (J^2 - 2J + 1)J^2] \\ &= B(4J + 2) - D(J^4 + 4J^3 + 4J^2 + 2J^3 + 8J^2 + 8J + J^2 + 4J + 4 - J^4 + 2J^3 - J^2) \\ &= 4B(J + 1/2) - D(8J^3 + 12J^2 + 12J + 4) \\ &= 4B(J + 1/2) - 8D(J^3 + 3/2J^2 + 3/2J + 1/2)\end{aligned}$$

It would be convenient if the term involving D could be factored. Recognizing that

$$(J+1/2)^3 = J^3 + 3/2J^2 + 3/4J + 1/8$$

the "cube" can be "completed" by

$$\begin{aligned}\Delta_2 F(J) &= 4B(J + 1/2) - 8D(J^3 + 3/2J^2 + 3/4J + 1/8 + 3/4J + 3/8) \\ &= 4B(J + 1/2) - 8D(J + 1/2)^3 - 8D(3/4J + 3/8) \\ &= 4B(J + 1/2) - 8D(J + 1/2)^3 - D(6J + 3) \\ &= 4B(J + 1/2) - 8D(J + 1/2)^3 - 6D(J + 1/2) \\ &= [4B - 6D](J + 1/2) - 8D(J + 1/2)^3\end{aligned}$$

And by dividing through by $(J+1/2)$

$$\frac{\Delta_2 F(J)}{(J+1/2)} = [4B - 6D] - 8D(J + 1/2)^2$$

So using the spectral data, a plot of

$$\frac{R(J) - P(J)}{(J + 1/2)} \text{ vs. } (J + 1/2)^2$$

or

$$\frac{R(J - 1) - P(J + 1)}{(J + 1/2)} \text{ vs. } (J + 1/2)^2$$

should yield straight lines with slopes of $8D$ and an intercept of $(4B - 6D)$ for the upper and lower states respectively.

Additional Spectroscopic Constants

Since each vibrational level has a different average bond length (increasing with increasing vibrational quantum number for a well-behaved electronic state,) the rotational constant has a dependence on the vibrational quantum number v .

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) + \gamma_e \left(v + \frac{1}{2}\right)^2 + \dots$$

where B_e is the equilibrium value of the rotational constant (and the constant from which r_e is derived), α_e and γ_e are constants that describe how rotation and vibration are coupled in a molecule. Usually this power series in $(v + \frac{1}{2})$ can be truncated at the α_e term (unless data for a great many vibrational levels are known.)

Similarly, the distortional term can be expanded in a power series in $(v + \frac{1}{2})$.

$$D_v = D_e - \beta_e \left(v + \frac{1}{2}\right) + \dots$$

For most molecules, β_e is not determined within experimental uncertainty unless a great many vibrational levels have been included in the fit.

A typical methodology would be to determine B_v for all of the vibrational levels for which data exists. (A single vibration-rotation band analysis provides two values, one for the upper state and one for the lower state.) Then the B_v values are fit to the functional form given by

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) + \gamma_e \left(v + \frac{1}{2}\right)^2 + \dots$$

truncating the power series so as to include the minimum number of adjustable parameters as are needed to yield a good fit to the data. This process yields a value for B_e which can then be used to calculate r_e . These values can then be compared to those found in the literature (if such a value has been measured) or reported in the literature if it has not yet been measured! A similar approach is used for the distortional term(s).

Line Intensity in Rotational Structure

One element that we have not discussed in the subject of rotational spectroscopy (or the rotational fine structure in vibration-rotation spectroscopy) is the intensities of the spectral lines. The intensity will be determined by two factors: 1) the population of the originating state (lower state in absorption and upper state in emission spectra) which is well described for a thermalized sample by a **Maxwell-Boltzmann distribution**, and 2) the **line strength**, which is determined by the quantum mechanical relationship between the upper and lower states of the transition.

the Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution of energy level populations will be achieved by any system that is in thermal equilibrium (usually implying that a sufficient number of molecular collisions occur for a gas phase sample, or that all of the parts of a sample are in thermal contact with one another in condensed phase samples) to ensure thermal uniformity throughout the sample. The distribution is given by the following expression:

$$\frac{N_i}{N_{tot}} = \frac{d_i e^{-E_i/kT}}{q}$$

where N_i/N_{tot} is the fraction of molecules in the i^{th} quantum state, that has an energy given by E_i and a degeneracy given by d_i . The term kT is the Boltzmann constant times the temperature on an absolute scale. The denominator, q , is a partition function, which is part of a normalization factor. The partition function is given by

$$q = \sum_i d_i e^{-E_i/kT}$$

In the case of rotational energy levels for closed-shell molecules, the subscript i can be replaced by the rotational quantum number J .

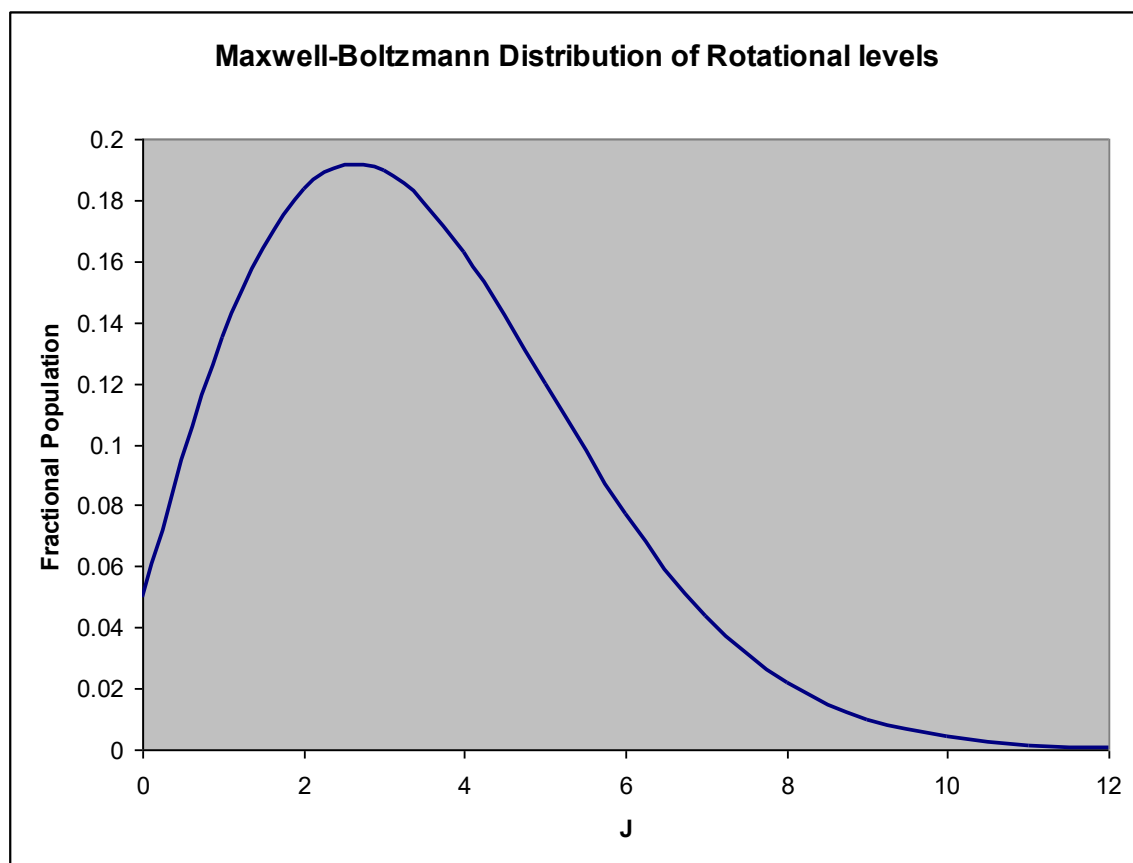
$$q_{rot} = \sum_J d_J e^{-E_J/kT}$$

In this expression, the rotational energy level degeneracies are always given by $(2J+1)$ and the rotational energy levels (if treated as rigid rotor levels) are given by $hcBJ(J+1)$. Thus the expression for the rotational partition function, q_{rot} , is given by

$$q_{rot} = \sum_J (2J+1) e^{-hcBJ(J+1)/kT}$$

It is handy to note that hc/kT has a value of approximately 206 cm^{-1} at room temperature. When the energy E_i exceeds approximately $10 \cdot kT$, the exponential term becomes negligibly small.

Focusing on the numerator of the Maxwell-Boltzmann expression, it is clear that the effect of increasing J is mixed in the expression. As J increases, the degeneracy increases (having the effect of increased fractional population in the level) but also the exponential term gets smaller due to the higher energy (having the effect of a decreased fractional population in the energy level.) A plot of fractional population as a function of J (for HCl at 298 K) is shown below.



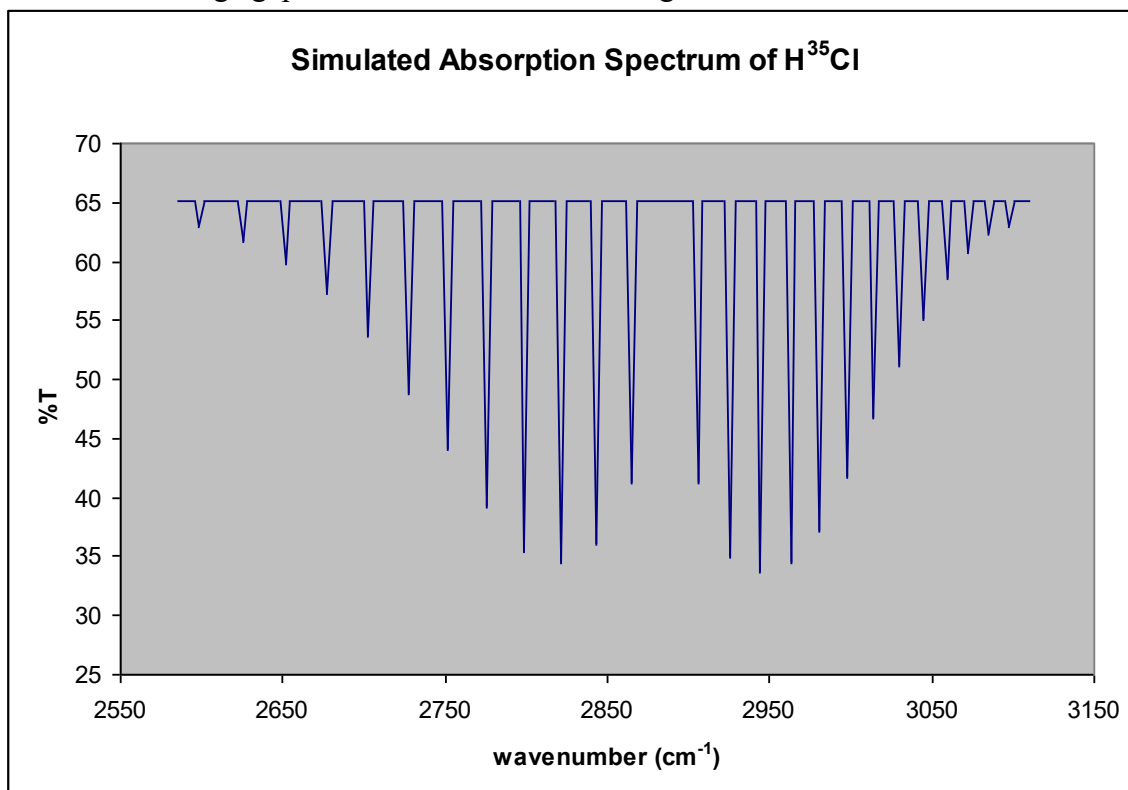
Note that at low values of J , the fractional population increases with increasing J , to a point. Eventually, the exponential term takes over and the population is extinguished. The J value (J_{max}) at which this changeover occurs is a function of the rotational constant B and the temperature, and can be determined by solving the following expression for J .

$$\frac{d}{dJ}(2J+1)e^{-hcBJ(J+1)/kT} = 0$$

The result is

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

The intensity pattern is plainly visible in the rotation-vibration spectrum of HCl. A simulated spectrum of the 1-0 band of H³⁵Cl is shown below, clearly showing the P- and R-branch structure, and the large gap between where the band origin can be found.



Line Strength Considerations

The second major consideration in spectral line intensity is the **line strength**. This is determined by the squared magnitude of the transition moment integral.

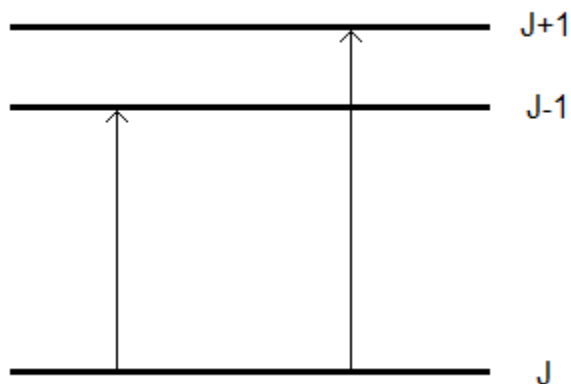
$$Int. \propto \left| \int (\psi')^* \vec{\mu}(\psi'') d\tau \right|^2$$

The rotational contribution, often called the *rotational line strength*, to this expression is a **Hönl-London factor**. For closed shell diatomic molecules, the Hönl-London factors are given by

$$\begin{aligned} S_J &= J+1 && \text{(for R-branch lines)} \\ S_J &= J && \text{(for P-branch lines)} \end{aligned}$$

A good way to think of these expressions is to view them as **branching ratios**. They indicate the relative fraction of molecules in a given level that will undergo an R-branch transition

compared to what fraction will undergo a P-branch transition. The molecules the lower state must “decide” to undergo either an R-branch transition or a P-branch transition. The relative fraction of each type of “decision” is the branching ratio.



Notice that the sum of these two expressions gives the total degeneracy of the rotational level. Given this relationship, it should be clear that the fractions of molecules undergoing each type of transition are given by

$$F_R = \frac{J+1}{2J+1} \quad \text{and} \quad F_P = \frac{J}{2J+1}$$

For open shell molecules, the expressions can be quite a bit more complex, but that is a topic for a more detailed course on molecular spectroscopy. However, some of the details of rotational structure of open shell molecules will be discussed in Chapter 8, as the electronic portion of the molecular wavefunction can affect the rotational structure profoundly.

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Vocabulary and Concepts

allowed transitions	140	associated Legendre polynomials	130
angular momentum	131	branching ratios.....	147

combination differences.....	139	moment of inertia.....	124
forbidden transitions	140	rigid rotor	123
Hönl-London factor	147	selection rules.....	139
Legendre polynomial	129	spherical harmonics	130
line strength.....	145, 147	spherical polar coordinates	123
Maxwell-Boltzmann distribution	145	transition moment	140

Problems

- Consider the data given in the table for lines found in the pure rotational spectrum of $^{12}\text{C}^{16}\text{O}$. Determine an approximate value for B and assign the spectrum (the lower \rightarrow upper state rotational quantum numbers for each line.) Make a graph of $\frac{\tilde{\nu}_J}{(J+1)}$ vs. $(J+1)^2$ and determine the best fit line. Use these results to determine B and D for the molecule. Compare your results to those found in the NIST Webbook of Chemistry for the ground electronic state of CO.

line	$\tilde{\nu}$ (cm^{-1})
1	3.845 033 19
2	7.689 919 07
3	11.534 509 6
4	15.378 662
5	19.222 223
6	23.065 043
- Consider the following data for the rotation-vibration spectrum of H^{35}Cl .
 - Using the differences in frequency, assign the location of the band origin and assign the P- and R-branches accordingly.
 - Using combination differences, fit the data to find B', D', B'' and D''.
 - Use your results to find B_e , α_e and D_e .
 - Based on your value of B_e , find a value for r_e for the molecule.
 - Compare your results to those found in the NIST Webbook of Chemistry.

line	Freq. (cm^{-1})	$\Delta\tilde{\nu}$
1	3085.62	
2	3072.76	
3	3059.07	
4	3044.88	
5	3029.96	
6	3014.29	
7	2997.78	
8	2980.90	
9	2963.24	
10	2944.89	
11	2925.78	
12	2906.25	
13	2865.09	
14	2843.65	

15	2821.49	
16	2798.78	
17	2775.79	
18	2752.03	
19	2727.75	
20	2703.06	
21	2677.73	
22	2651.97	
23	2625.74	
24	2599.00	

3. A recursion formula for the Legendre Polynomials is given by

$$(l + 1)P_{l+1}(x) = (2l + 1)xP_l(x) - l P_{l-1}(x)$$

Based on $P_0(x) = 1$ and $P_1(x) = x$ find expressions for $P_2(x)$ and $P_3(x)$.

4. The function describing the $l = 1, m_l = 0$ spherical harmonic is $Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos(\theta)$
- Show that this function is normalized. To do this, you must use the limits on θ and ϕ of $0 \leq \theta \leq \pi$, and $0 \leq \phi \leq 2\pi$. Also, for the angular part of the Laplacian, $d\tau = \sin(\theta) d\theta d\phi$.
 - Using plane polar graph paper (or a suitable graphing program) plot the square of the function from problem 2 in the yz plane (which gives a cross-section of the probability function for the particular spherical harmonic.) Does the shape look familiar?

5. Based on the given bond-length data, calculate values for the rotational constants for the following molecules:

Molecule	Bond Length (Å)
H^{35}Cl	1.2746
H^{79}Br	1.4144
H^{127}I	1.6092

6. The spacing between lines in the pure rotational spectrum of BN is 3.31 cm^{-1} . From this, find B and calculate the bond length (r_{BN}) in the BN molecule.
7. From your result in problem 6, calculate the frequencies of the first 4 lines in the pure rotational spectrum of BN.