Lecture 34

We now turn to our final quantum mechanical topic, **molecular spectroscopy**. Molecular spectroscopy is intimately linked to quantum mechanics. Before the mid 1920's when quantum mechanics was developed, people had begun to develop the science of molecular spectroscopy. However, its early use was purely qualitative, based solely on the observation that molecules and atoms, when exposed to light, absorbed and emitted it in patterns that were unique to each species. The interpretation of these spectra in terms of the physical parameters that describe the geometries and bonding of the molecules that produce them had to wait until the development of quantum mechanics. The close interrelation between spectroscopy and quantum mechanics is shown by the fact that Robert Mulliken, who was the foremost practitioner and proponent of Molecular Orbital theory in its early years, was spurred on by an attempt to understand the details of molecular spectra. It is further shown by the fact that Gerhard Herzberg, the foremost practitioner of molecular spectroscopy from the middle of the '30s to the 70's, used to keep a bound copy of Mulliken's papers by his desk. In fact, I keep a bound copy of Mulliken's major papers, edited by Norman Ramsey, Herzberg's collaborator, by my desk.

Molecular spectroscopy, which is the study of the interaction of light with atoms and molecules, is one of the richest probes into molecular structure. **Radiation from various regions of the electromagnetic spectrum yields different information about molecules**. For example, **microwave radiation is used to investigate the rotation of molecules** and yields moments of inertia and therefore bond lengths. **Infrared radiation is used to study the vibrations of molecules**, which yields information about the stiffness or rigidity of chemical bonds. **Visible and ultraviolet radiation is used to investigate electronic states of molecules**, and yields information about ground and excited state vibrations, electronic energy levels, and bond strengths. We will do a fairly detailed treatment of rotational and vibrational spectroscopy and a somewhat briefer treatment of electronic spectroscopy. In our treatment we will begin with the basic interpretation of molecular spectra, and finish with the quantum mechanical basis of these interpretations.

The features of the electromagnetic spectrum that are of interest to us are summarized below. The absorption of microwave radiation is due to transition between rotational energy levels; the absorption of infrared radiation is due to transitions between vibrational levels, accompanied by transitions between rotational levels; and the absorption of visible and ultraviolet radiation is due to transitions between electronic energy levels, accompanied by simultaneous transitions between vibrational and rotational levels. The frequency of radiation absorbed is calculated from the energy difference between the upper and lower states in the transition, given by

Region	Frequency/Hz	Wavelength/m	Wave number/cm^{-1}	Energy/ J *molecule^{-1}	Molecular Process
Microwave	10^{9}-10^{11}	$3x10^{-1}$-$3x10^{-3}$	0.033-3.3	$6.6x10^{-25}$-$6.6x10^{-23}$	Rotation of polyatomic molecules
Far Infrared	10^{11}-10^{13}	$3x10^{-3}$-$3x10^{-5}$	3.3-330	$6.6x10^{-23}$-$6.6x10^{-21}$	Rotation of small molecules
Infrared	10^{13}-10^{14}	$3x10^{-5}$-$3x10^{-6}$	330-4000	$6.6x10^{-21}$-$8.0x10^{-20}$	Vibration of flexible bonds
Visible and Ultraviolet	10^{15}-10^{16}	$9 x 10^{-7}$-$3x10^{-8}$	11,000-$3.3x10^{5}$	$2.2x10^{-19}$-$6.6x10^{-18}$	Electronic transitions

$$\Delta E = E_u - E_l = h\nu$$

where E_u and E_l are the energies of the upper and lower states respectively.

For example, if we have an absorption with wavenumber, $\overline{\nu}$ = 1.00 cm^{-1}, we calculate ΔE as follows. Remember that $\overline{\nu} = 1/\lambda(cm)$. Therefore ΔE is related to $\overline{\nu}$ by

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\overline{\nu}$$

and so

$$\Delta E = hc\overline{\nu} = (6.626 \times 10^{-34}\ \text{Js})(3.00 \times 10^{10}\ \text{cm/s})(1.00\text{cm}^{-1}) = 1.99 \times 10^{-23}\ \text{J}.$$

TO WHAT TYPE OF MOLECULAR PROCESS WILL THIS RADIATION CORRESPOND?

We will begin with **molecular rotation**. A rigid rotor is the simplest model of molecular rotation. We discussed the quantum-mechanical properties of a rigid rotor before, but will review the pertinent results here. The energy of rotation of a rigid rotor is all kinetic energy. For a motion with circular symmetry, it is convenient to express this energy in terms of the angular variables L, angular momentum, and I, moment of inertia. The moment of inertia for a diatomic molecule is given by

$$I = \mu R_0^2$$

where μ is the reduced mass of the molecule and R_0 is the bond length of the molecule. The angular momentum L is given by

$$L = I\omega,$$

where ω is the angular frequency. When the Schrödinger equation for this problem is solved, it is found that the angular momentum is quantized according to the equation

$$J^2 = J(J+1)\hbar^2$$

where J is the spectroscopic notation for the total angular momentum of a molecule, and that the angular momentum in the z direction is quantized according to the equation

$$J_z = M\hbar ,$$

where M = J, J-1, ..., -J. The energy of the rigid rotor, in the absence of an external field, depends on J only, is also quantized and is given by

$$E_J = \frac{\hbar^2}{2I} J(J+1), \quad J = 0,1,2,...$$

Since there are 2J+1 values of M for each energy E_J, the energy states are 2J+1 fold degenerate.

When microwave or far infrared radiation shines on a rotating molecule, the J value can either increase or decrease, and the energy of the light absorbed is given by $\Delta E = E_u - E_l$. **An important characteristic of all molecular spectra is that the choice of upper and lower states is not completely free but is in fact extremely limited.** The rules that govern the choices of upper and lower states are called **selection rules**. These selection rules are determined by time dependent perturbation theory. **For the pure rotational transitions of a diatomic rigid rotor the selection rule is ΔJ = ±1.** In other words, when a diatomic rigid rotor absorbs light, its rotational quantum number can increase by 1 or decrease by 1. These are the only possible transitions that occur. (The reason that I specify diatomic rigid rotors is that the selection rules depend in part on symmetry, and molecules with other symmetries have different selection rules.) **In addition, for pure rotational transitions the molecule must have a permanent dipole moment.** Thus molecules like H_2 and I_2 will have no pure rotational spectra, while HI or CO, which have permanent dipole moments, will exhibit rotational spectra. For molecules that do have permanent dipole moments, the larger the dipole moment, the more strongly the molecule will absorb light.

The consequence of this selection rule is that **the rotational absorption spectrum of a rigid rotor is a series of evenly spaced lines in the microwave or far infrared region**. To see this we begin with the energy eigenvalues,

$$E_J = \frac{\hbar^2}{2I} J(J+1), \quad J = 0,1,2,\ldots$$

According to our selection rule, for absorption ΔJ = +1. The energy change for this transition is

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

$$= \frac{\hbar^2}{2I}(J+1), \quad J = 0,1,2,\ldots.$$

The wavenumber change for this absorption is given by

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{h}{4\pi^2 cI}(J+1), \quad J = 0,1,2$$

It is typical in spectroscopy to write the energy in the form

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

where $\bar{B}$, the rotational constant of the molecule, has units of wavenumbers and is given by

$$\bar{B} = \frac{h}{8\pi^2 cI}$$

In this form the wavenumber of the rotational absorptions is given by

$$\bar{\nu} = 2\bar{B}(J+1), \quad J = 0,1,2,\ldots$$

Thus for the lowest energy rotational transition, J = 0 to J = 1, the absorption occurs at a wavenumber of $2\bar{B}$. The second transition, J = 1 to J = 2, occurs at a wavenumber of $4\bar{B}$. The third transition occurs at a wavenumber of $6\bar{B}$ and so on. Thus **the rotational spectrum consists of a series of equally spaced lines separated by 2** $\bar{B}$. [Illustrate] Lets check on our assertion that the rotational spectrum is in the microwave region, by calculating the value of $\overline{B}$ for the rotation of HI.

$$\overline{B} = \frac{h}{8\pi^2 cI}$$

The moment of intertia I is given by μR_0^2, where μ is the reduced mass in kg and R_0 is the bond length in meters. For HI, the reduced mass is given by

$$\mu_{HI} = \frac{m_H m_I}{m_H + m_I} = \frac{1AMU x 127AMU}{1AMU + 127AMU} x 1.66 x 10^{-27} \frac{kg}{AMU} = 1.65 x 10^{-27} kg$$

and the bond length is 160.4 pm, so the moment of intertia is

$$I = \mu R_0^2 = 1.65 \text{ x } 10^{-27} \text{ kg } (160.4 \text{ x } 10^{-12} \text{ m})^2 = 4.25 \text{ x } 10^{-47} \text{ kg m}^2,$$

and $$\overline{B} = \frac{6.6262 x 10^{-34} Js}{(8\pi^2)(3.00 x 10^{10} cm/s)(4.25 x 10^{-47} kg m^2)} = 6.58 cm^{-1}$$

Our first rotational transition will occur at a wavenumber of 2 $\overline{B}$ = 13.16 cm^{-1}, which is in the far infrared region, as predicted.

A more typical application is to determine the value of $\overline{B}$ from the spacing of a rotational spectrum, and use this to determine the moment of inertia and therefore the bond length. For example, the microwave spectrum of ^{39}K^{127}I consists of a series of lines whose spacing is almost constant at 3634 MHz. Calculate the bond length of ^{39}K^{127}I. The rotational spacing for KI is given in Hz, a unit of frequency. Our equation for the rotational wavenumber is

$$\overline{\nu} = 2\overline{B}(J+1)$$

The relation between wavenumbers and frequency is

$$\nu = c\overline{\nu}$$

where c is the speed of light in cm/s. Thus our rotational absorption frequency becomes

$$\nu = 2c\overline{B}\left(J+1\right),$$

and our rotational spacing becomes $\Delta\nu = 2c\overline{B}$. Thus

$$\overline{B} = \frac{\nu}{2c} = \frac{3634x10^{6}s^{-1}}{2x3.00x10^{10}} = 6.05x10^{-2}cm^{-1}$$

From this we can use our formula for $\overline{B}$ to calculate the moment of intertia for KI,

$$I = \frac{h}{8\pi^{2}c\overline{B}} = \frac{6.6262x10^{-34}}{(8\pi^{2})(3.00x10^{10})(.06057)} = 4.618x10^{-45}kgm^{2}.$$

The reduced mass of ^{39}K^{127}I is

$$\mu_{KI} = \frac{39AMUx127AMU}{39AMU+127AMU}x1.67x10^{-27}\frac{kg}{AMU} = 4.983x10^{-26}kg.$$

Thus $R_0 = (I/\mu)^{1/2} = 3.04 \text{ x } 10^{-10}$ M.

Lecture 35-37

The simplest model of a vibrating molecule is the harmonic oscillator. The harmonic oscillator assumes that the potential energy function for the vibration is given by $V = \frac{1}{2}kx^2$, where k, the vibrational force constant, is a measure of the stiffness of the bond. The energy eigenvalues for the harmonic oscillator are quantized and are given by

$$E_n = (n + \frac{1}{2})h\nu, \quad n = 0,1,2,...$$

$$\text{where } \nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}.$$

Transitions between vibrational levels are subject to the selection rules $\Delta n = \pm 1$ and that the dipole moment must change during a vibration. Once again for diatomic molecules this means that homonuclear diatomics will have no vibrational absorption spectrum. The implication of this selection rule together with the formula for the energy eigenvalues of the harmonic oscillator is that the pure vibrational absorption spectrum of a diatomic molecule is a single absorption whose frequency is given by $\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$. To see this note that for absorption $\Delta n = +1$, so

$$\Delta E = E_{n+1} - E_n = (n + 1 + 1/2)\, h\nu - (n + 1/2)\, h\nu = h\nu$$

Thus the spectrum consists of a single line with frequency ν. Determining the infrared frequency allows us to determine the force constant k of the bond. For example, the infrared spectrum of $^{39}K^{35}Cl$ has a single intense line at 378.0 cm^{-1}. What is the force constant? Our first step is to convert the wavenumber to frequency, using $\nu = c\bar{\nu}$. This yields

$$\nu = 378 \text{ cm}^{-1} \times 3.00 \times 10^{10} \text{ cm/s} = 1.134 \times 10^{13} \text{ s}^{-1}.$$

The reduced mass of $^{39}K^{35}Cl$ is

$$\mu_{KCl} = \frac{35AMU x 39AMU}{35AMU + 39AMU} x 1.67 x 10^{-27} \frac{kg}{AMU} = 3.08 x 10^{-26} kg$$

Rewriting our frequency equation to solve for force constant yields

$$k = (2\pi\nu)^2\mu = (2\ \pi\ 1.134 \text{ x } 10^{13})^2 \text{ x } 3.08 \text{ x } 10^{-26} = 156 \text{ N/m.}$$

All of the quantum mechanical systems we have studied so far have the common property that their energies are quantized. Suppose we have a system where the available energies are the set $\{E_J\}$. An example of this would be a diatomic harmonic oscillator, whose energies belong to the set {1/2hν, 3/2hν, 5/2hν, ...} = $\{E_0, E_1, E_2, ...\}$. A question of practical importance is the fraction of the molecules in a gaseous sample that are at a given energy. In other words **if we have N molecules, how many are in E_0, how many in E_1, how many in E_2 and so on**. The answer to this question comes from **statistical mechanics** and says that if N_i is the number of molecules with energy E_i, then

$$N_i = ce^{-E_i/kT}$$

where k is Boltzmann's constant, T is the absolute temperature and c is a proportionality constant. We can evaluate this constant c by summing both sides over all possible energies and recognizing that $\sum_i N_i = N$ This yields

$$\sum_i N_i = N = c\sum_i e^{-E_i/kT}$$

or

$$c = \frac{N}{\sum_i e^{-E_i/kT}}$$

which yields finally

$$N_i = \frac{Ne^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

This equation is called a **Boltzmann distribution** after the German physicist Ludwig Boltzmann, and **governs how the energy levels are populated at any temperature**. Since most of the time we won't know the absolute number of molecules in our sample, a more practical quantity to calculate is **the fraction of molecules in a given state**. This is given by

$$f_i = \frac{N_i}{N} = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

Let’s use this to figure out the fraction of molecules in the ground state of a harmonic oscillator. For the harmonic oscillator, E_i is given by

$$E_i = (i + 1/2)h\nu$$

so our equation for the f_i becomes

$$f_i = \frac{e^{-\frac{(i+1/2)h\nu}{kT}}}{\sum_0^\infty e^{-\frac{(i+1/2)h\nu}{kT}}}$$

The infinite series in the denominator can be evaluated to be

$$\sum_{i=0}^\infty e^{-\frac{ih\nu}{kT}} = \frac{1}{1-e^{-\frac{h\nu}{kT}}}$$

Thus for the harmonic oscillator our equation for f_i becomes

$$f_i = (1 - e^{-h\nu/kT})e^{-ih\nu/kT}$$

Lets apply this equation to calculate the fraction of molecules in the ground vibrational state for HBr at 300 K and 2000 K. The fundamental vibrational frequency of HBr is 7.7 x 10^{13} Hz. The easiest way to begin this is to calculate the quantity hν/kT. At 298 K this is

$$\frac{h\nu}{kT} = \frac{(7.7x10^{13}s^{-1})(6.6262x10^{-34}\,Js)}{(298K)(1.38066x10^{-23}\,JK^{-1})} = 12.3$$

At 2000 K the same type of calculation shows that hν/kT = 1.8. If we substitute i = 0, the quantum number for our ground vibrational state into our equation for f_i, we find that

$$f_0 = 1 - e^{-12.3} \approx 1\,at\,298K$$

while

$$f_0 = 1 - e^{-1.8} = .83\ at\ 2000K.$$

Thus we see that at room temperature practically all of the HBr molecules are in the ground vibrational state, while even at 2000 K the bulk of the molecules are still in the ground vibrational state. Let's look at the effect of vibrational frequency on the ground state population by calculating f_0 for I_2, which has a ground state vibrational frequency of 6.42 x 10^{12} Hz, over a factor of 10 smaller than HBr. Here hν/kT = 1.034, so

$$f_0 = 1 - e^{-1.034} = .6444\ at\ 298K.$$

We see that even at room temperature a substantial fraction of iodine molecules will be in excited vibrational states. We conclude that **either increasing the temperature or decreasing the vibrational frequency will result in an increase in the population of vibrational excited states.**

Molecules simultaneously vibrate and rotate. If we treat the rotations using the rigid rotor approximation, and the vibrations using the harmonic oscillator approximation, then the energy of this vibrating, rotating molecule is given by

$$E_{vib,rot} = (n + 1/2)h\nu_0 + hc\overline{B}J(J+1)$$

where n = 0, 1, 2, ... and J = 0, 1, 2, ... An important feature of these energies is that **the rotational energies are generally much smaller than the vibrational energies, so each vibrational state is accompanied by a large number of rotational states**. For example, for HCl at room temperature, we will find finite populations of molecules with v= 0 and J ranging from 0 to approximately 20. The lowest energy state will be the pure vibration with $E_{nj} = \nu_0/2$. The next energy will be $\nu_0/2 + 2B$, the next will be $\nu_0/2 + 6B$, the next $\nu_0/2 + 12B$ and so on. For HCl, the vibrational frequency is 2885 cm^{-1}, while B is 10.6 cm^{-1}. Thus the first few energies are 1442.5 cm^{-1}, 1463.7 cm^{-1}, 1505 cm^{-1} and so on. Because the energies of the rotations are small compared to the vibrations, vibrational rotational spectra have the appearance of widely separated clusters of rotational lines.

When a diatomic molecule absorbs infrared radiation, the vibrational transition is accompanied by a rotational transition. **The selection rules for absorption of infrared radiation by a diatomic molecule are**

$$\boldsymbol{\Delta n = \pm 1}$$

$$\boldsymbol{\Delta J = \pm 1.}$$

In other words, when an infrared photon is absorbed, the vibrational quantum number goes up by one, and the rotational quantum number either goes up by one or down by one. The wavenumber $\overline{\nu}_{obs}$ associated with the absorption is

$$\overline{\nu}_{obs} = \overline{\nu}_0 + \overline{B}[J'(J'+1) - J(J+1)]$$

where J is the initial rotational quantum number, and J', the final rotational quantum number, can be either J + 1 or J - 1. If J' = J + 1, then

$$\overline{\nu}_{obs}(\Delta J = +1) = \overline{\nu}_0 + 2\overline{B}(J+1), \quad J = 0,1,2,\ldots$$

If J' = J - 1, then

$$\bar{\nu}_{obs}(\Delta J = -1) = \bar{\nu}_0 - 2BJ, \quad J = 1,2,3,\ldots$$

WHY CAN'T J BE ZERO IN THIS CASE? Typically, $\bar{B}$ is on the order of 1 cm^{-1} or less, and $\bar{\nu}_0$ ranges from a few hundred to a few thousand wavenumbers, so the spectrum produced by these two equations typically contains lines between 3700cm^{-1} and 350 cm^{-1} ± integral multiples of 1 cm^{-1}. Notice that according to these equations there is no absorption at $\bar{\nu}_0$. Before the quantum mechanical explanation of molecular spectroscopy, this was considered an inexplicable anomaly. Its explanation was one of the early successes of quantum mechanics.

The infrared spectrum that you measured for HCl is typical of these spectra. [Draw] The gap centered around 2885 cm^{-1} corresponds to the missing line at $\bar{\nu}_0$. On each side of the gap is a series of lines whose spacing is about 10 cm^{-1}. The series toward the high frequency side is called the R branch and is due to rotational transitions with ΔJ = +1. The series toward the low frequency side is called the P branch and is due to rotational transitions with ΔJ = -1.

Let's do an example with rotational-vibrational spectra. The bond length in $^{12}C^{14}N$ is 117 pm and its force constant is 1630 N m^{-1}. Let's predict the vibration-rotation spectrum of $^{12}C^{14}N$.

Our first step is to calculate $\bar{\nu}_0$ and $\bar{B}$. Both quantities require the reduced mass, which is

$$\mu = \frac{(12.0AMU)(14.0AMU)}{(12.0 + 14.0)AMU}(1.66x10^{-27}\frac{kg}{AMU}) = 1.07x10^{-26}kg$$

The fundamental frequency $\bar{\nu}_0$ is given by

$$\frac{1}{2\pi c}(\frac{k}{\mu})^{1/2} = \frac{1}{2\pi(3.00x10^{10}cm/s)}(\frac{1630Nm^{-1}}{1.07x10^{-26}kg})^{1/2} = 2.07x10^{3}cm^{-1}$$

The rotational constant $\overline{B}$ is given by

$$\overline{B} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R_0^2}$$

$$= \frac{(6.626x10^{-34}\,Js)}{8\pi^2(3.00x10^{10}\,cm/s)(1.07x10^{-26}\,kg)(117x10^{-12}\,m)^2} = 1.91cm^{-1}$$

The vibration-rotation spectrum will consist of lines at $\overline{\nu}_0$ ± 2BJ, where J = 1,2,3,.... There will be no line at $\overline{\nu}_0$ and the separation between the lines in the P and R branches will be even at 2$\overline{B}$ = 3.82 cm^{-1}.

If we compare these results with experimental data, we see that there are several features which we are not able to explain with this combination of the rigid rotor and the harmonic oscillator alone. The intensities, or heights, of the lines in the P and R branches show a definite pattern and the spacing of the lines is not equal. Close examination shows that the lines in the R branch are more closely spaced with increasing frequency, and that the lines of the P branch become farther apart with decreasing frequency. We now turn to an explanation of these details.

We turn first to **the intensity pattern of the P and R branches**. We know that Beer's law, A = εlc, holds for all optical spectra, and that therefore **the intensities of the rotational lines in a vibration rotation spectra depend on the population in any given rotational state**. Since this population is proportional to the fraction of molecules in that rotational state, we can use the Boltzmann distribution of rotational energies to explain the general nature of the observed intensities. **We need to modify our Boltzmann equation a bit since the rotational energy levels are 2J + 1-fold degenerate**. If an energy level N_i has a degeneracy g_i, then the number of molecules with energy i becomes

$$N_i = cg_i e^{-E_i/kT}$$

where c is a constant. For rotational energies this becomes

$$N_J = N_T(2J+1)e^{-\frac{hc\bar{B}J(J+1)}{kT}}$$

where N_T is the total population. This allows us to calculate the ratio of the population of the state with quantum number J, to the population of the lowest energy level, and therefore to calculate the ratios of the intensities of the peaks corresponding to these two states. If we plot this equation, we find that it yields the characteristic shape of the P and R branches. Thus we see that the shape of the P and R branches reflects the population of the rotational energy levels.

So far in our treatment of the rotational and vibrational spectra of diatomic molecules, we have used two approximations, that the bond length of the molecule was fixed during rotation, and that the vibrations were governed by a harmonic potential. These approximations yield a crude approximation of the experimental results, but closer examination of these results shows that they are not entirely correct. Let's consider rotations again.

The experimental observation which shows that our rigid rotor model needs to be refined is that the lines in a rotational spectrum are not equally spaced, as the rigid rotor model predicts. You have all seen this with the vibrational-rotational spectrum of HCl, but it is also true for the pure rotational spectrum of HCl. If we examine the first few transitions in the rotational absorption spectrum we can see this clearly.

The Rotational Spectrum of $H^{35}Cl$

The Rotational Absorption Spectrum of $H^{35}Cl$		
Transition	ν_{obs} / cm^{-1}	$\Delta \nu_{obs} / cm^{-1}$

$3 \rightarrow 4$	83.03	
		21.07
$4 \rightarrow 5$	104.10	
		20.20
$5 \rightarrow 6$	124.30	
		20.73
$6 \rightarrow 7$	145.03	

The spacing between the rotational lines varies in these few points between 20.2 cm^{-1} and 21.07 cm^{-1}. The discrepancy can be resolved by realizing that a chemical bond is not truly rigid. As the molecule rotates faster and faster, i.e., as J increases, the centrifugal force causes the bond to stretch. The extent of the stretching of the bond can be determined by balancing the centrifugal force, $\mu R\omega^2$, which causes the stretching, with the Hooke's law force, $k(R - R_0)$ which resists the stretching. Thus we have

$$k(R - R_0) = \mu R\omega^2 = \frac{L^2}{\mu R^3}$$

where R_0 is the bond length when J = 0 and there is no rotation. This yields

$$R - R_0 = \frac{L^2}{\mu R^3 k} \approx \frac{L^2}{\mu R_0{}^3 k} \ .$$

This approximation is valid because in general

$$R - R_0 << R_0 \ .$$

In order to determine the effect of the centrifugal stretching on our rotational spectra, we need to find how this changes our rotational energy. As usual we begin with the classical case and use the correspondence principle to find the quantum analog.

As a result of the stretching the total classical energy of the rotator is made up of a kinetic energy term and a potential energy term:

$$E = \frac{L^2}{2I} + \frac{1}{2}k\left(R - R_0\right)^2$$

Substituting our value for R-R_0 into this equation, and neglecting higher powers of R-R_0 yields

$$E = \frac{L^2}{2I_0} - \frac{L^4}{2I_0^2 R_0^2 k}$$

We obtain the quantum mechanical energy for this stretching rotor by substituting the quantum value for L^2, $\hbar^2 J(J+1)$:

$$E_J = \frac{\hbar^2}{2I_0} J(J+1) + \frac{\hbar^4}{2I_0^2 k R_0^2} J^2 (J+1)^2$$

This is usually written in wavenumbers as

$$\overline{E}_J = \frac{E_J}{hc} = \overline{B}J(J+1) - \overline{D}J^2(J+1)^2$$

By comparing these two equations we find that

$$\overline{D} = \frac{\hbar^3}{4\pi c I_0^2 k R_0^2} = \frac{4\overline{B}^3}{\overline{\nu}^2}$$

$\overline{D}$ is called the **centrifugal distortion constant**, and **results in a lowering of the rotational energy compared with the rigid rotor for all states with J > 0**. Typical values of $\overline{D}$ are much smaller than $\overline{B}$. For $H^{35}Cl$, for example, $\overline{B}$ = 10.395 cm^{-1} and $\overline{D}$ = .0004 cm^{-1}, and therefore the centrifugal distortion term represents a small correction to the rigid-rotator approximation. Note also because the centrifugal distortion term is a function of $J^2(J + 1)^2$, that **the size of the correction increases with J.**

The frequencies of absorption due to a transition from $J \rightarrow J + 1$ are given by

$$\overline{\nu} = \overline{E}_{J+1} - \overline{E}_J = 2\overline{B}(J+1) - 4\overline{D}(J+1)^3,\ J = 0,1,2,\ldots.$$

If we use this equation and the values of $\overline{B}$ and $\overline{D}$ for $H^{35}Cl$, we find that the new calculated values are closer to the experimental values, but are still off by a bit. This is due to the fact that **the bond length also changes because the molecule is vibrating, which affects the rotational energy**. This phenomenon is called vibration - rotation interaction. We will cover this in a moment, but first I would like to consider corrections to our basic picture of molecular vibration.

There is experimental evidence that **our picture of vibrating molecules is only approximately correct.** The most obvious problem is our observation, which we made before, that the harmonic potential does not allow for the possibility of dissociation of the molecule. The deviation of a true potential from a harmonic potential is called the **anharmonicity**. Since the potential is correct only toward the bottom of the potential well, and vibrational frequencies are dependent on the shape of the potential, vibrational frequencies which are based on a harmonic potential will have to be approximate. Note that the harmonic potential is close to the true molecular potential for much of the lower energy part of the curve. This suggests that the easiest way to find the true vibrational energy is to begin with the harmonic frequency and find a correction term.

The easiest way to represent the true potential in a way that lends itself to finding such a correction term is to expand the potential function V(R) in a Taylor series about R_e, the equilibrium bond length, which is also the minimum of V(R). This expansion yields

$$V(R) = V(R_e) + \left(\frac{dV}{dR}\right)_{R=R_e}(R - R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R - R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R - R_e)^3 + ...$$

The second term of the expansion is zero, because the first derivative of V with respect to R will be zero at the minimum of the potential. The derivative in the second term $(\frac{d^2V}{dR^2})_{R=R_e}$ is simply our force constant k. Thus the difference in energy from the potential minimum can be written as

$$V(R)-V(R_e) = \frac{k}{2}x^2 + \frac{\gamma_3}{6}x^3 + \frac{\gamma_4}{24}x^4$$

where x = (R - Re), $\gamma_3 = (\frac{d^3V}{dR^3})_{R=R_e}$, and $\gamma_4 = (\frac{d^4V}{dR^4})_{R=R_e}$.

Notice that if we ignore the last two terms we have a harmonic potential. Therefore the harmonic oscillator approximation consists of keeping only the quadratic term in the Taylor expansion. As we showed earlier, the harmonic oscillator approximation predicts that there will be only one line in the vibrational spectrum of a diatomic molecule. Experimentally it is found that there is indeed one dominant line, called the **fundamental**, but in addition there are lines of weaker intensity at almost integral multiples of the fundamental. These lines are called **overtones**. For example for $H^{35}Cl$, the fundamental occurs at 2885.9 cm^{-1}, while successively weaker bands appear at 5668.0, 8347.0, 10923.1 and 13396.5 cm^{-1}. These bands are called the first, second, third and fourth overtones respectively. They represent transitions from $v = 0 \rightarrow 2$, $v = 0 \rightarrow 3$, $v = 0 \rightarrow 4$, and $v = 0 \rightarrow 5$. Note that all of these transitions are in violation of the harmonic oscillator selection rule of $\Delta n = \pm 1$. The wavenumbers of these bands also do not match the prediction of the harmonic oscillator, which predicts that all of the overtones will occur exactly at integral multiples of the fundamental frequency.

If the terms of higher order than the harmonic terms, called the anharmonic terms, are included in the Hamiltonian operator for the vibrational motion of a diatomic molecule, then perturbation theory yields

$$\overline{E}_n = \overline{\nu}_e(n+1/2) + \overline{\nu}_e\overline{x}_e(n+1/2)^2 + \ldots$$

where $\overline{x}_e$ is called the anharmonicity constant. The anharmonic correction is much smaller than the harmonic term because $\overline{x}_e << 1$. For example, for $H^{35}Cl$, $\overline{\nu}_e$ = 2989 cm^{-1}, while $\overline{\nu}_e\overline{x}_e$ = 52.05 cm^{-1}. For another example, CO has $\overline{\nu}_e$ = 2170.2 cm^{-1}, while it has $\overline{\nu}_e\overline{x}_e$ = 13.46 cm^{-1}.

The effect of the anharmonic terms is that the spacing of vibrational energy levels is not even, and that the spacing decreases with increasing n. [Draw] Notice that the harmonic oscillator approximation is best for small values of n, which are the states which have the highest population at room temperature.

The selection rule for an anharmonic oscillator is that Δn can have any integral value, although the intensities of the $\Delta n = \pm 2, \pm 3, \ldots$ transitions are much less than for the $\Delta n = \pm 1$ transitions. Earlier we showed that for diatomic molecules, most of the population at room temperature is in the v = 0 state. This implies that most vibrational transitions will originate in the v = 0 state. The wavenumbers of the observed $v = 0 \rightarrow n$ transitions will be given by

$$\overline{\nu}_{obs} = \overline{E}_n - \overline{E}_0 = \overline{\nu}_e n - \overline{\nu}_e\overline{x}_e n(n+1), \quad n = 1,2,\ldots$$

Application of this equation to the spectrum of $H^{35}Cl$ results in an agreement with experiment to the fifth significant figure.

Let's work an example of calculating the wavenumbers for the absorptions of an anharmonic oscillator. Given that $\overline{\nu}_e$ = 536.1 cm^{-1} and $\overline{\nu}_e\overline{x}_e$ = 3.83 cm^{-1} for $^{23}Na^{19}F$, calculate the frequencies of the fundamental and the first and second overtones. We use our equation for the wavenumber for a transition of an anharmonic oscillator for all three of these transitions. The fundamental is calculated by letting n = 1 and the overtones are calculated by letting n = 2 and 3. For the fundamental,

$$\overline{\nu}_{obs} = \overline{\nu}_e - 2\overline{\nu}_e\overline{x}_e = 528.44cm^{-1}.$$

For the first overtone

$$\overline{\nu}_{obs} = 2\overline{\nu}_e - 6\overline{\nu}_e\overline{x}_e = 1049.22\ cm^{-1}$$

For the second overtone

$$\overline{\nu}_{obs} = 3\overline{\nu}_e - 12\overline{\nu}_e\overline{x}_e = 1562.3cm^{-1}.$$

Note that the overtones are not integral multiples of the fundamental frequency.

Now we turn to the final correction to our vibrating rotating molecule. Recall that the rigid rotor harmonic oscillator model leads to

$$\overline{E}_{n,j} = \overline{\nu}_0(n + 1/2) + \overline{B}J(J+1).$$

Because the amplitude of vibration increases with the vibrational state, we expect that R_0 should increase slightly with n, and that therefore $\overline{B}$ should decrease with increasing n. Since $\overline{B}$ depends on the vibrational quantum number we now write

$$\overline{E}_{n,j} = \overline{\nu}_0(n + 1/2) + \overline{B}_n J(J+1).$$

The dependence of $\overline{B}$ on the vibrational quantum number is called vibration-rotation interaction. The vibration-rotation interaction affects the P and R branches of a rotational vibrational spectrum differently. The frequencies of the P and R branches are given by

$$\overline{\nu}_R(\Delta J = +1) = \overline{\nu}_0 + (2\overline{B}_1 - \overline{B}_0)J + (\overline{B}_1 - \overline{B}_0)J^2, \quad J = 0,1,2,\ldots$$

and $$\overline{\nu}_p(\Delta J = -1) = \overline{\nu}_0 - (\overline{B}_1 + \overline{B}_0)J + (\overline{B}_1 - \overline{B}_0)J^2, \quad J = 1,2,3,...$$

In both cases J is the initial rotational quantum number. Because $\overline{B}_1 < \overline{B}_0$, the spacing between the lines in the P branch increase with increasing J. You should all either have observed this or will shortly observe this in your spectra of $H^{35}Cl$.

The lines in the R and P branches are labeled by the initial value of the rotational quantum number giving rise to the lines. Thus, the lines for the R branch are labeled as R(0), R(1), R(2), ... and those of the P branch are labeled P(1), P(2), P(3), ... etc. Given the following data,

Line	Wavenumber/ cm^{-1}
R(0)	4178.98
R(1)	4218.32
P(1)	4096.88
P(2)	4054.12

lets calculate $\overline{B}_0$, $\overline{B}_1$, R_0 and R_1. The reduced mass of the molecule is 1.58 x 10^{-27} kg.

If we apply our equations for the R and P branches we find that for the R branch

$$4178.98\,cm^{-1} = \overline{\nu}_0 + 2\overline{B}_1$$

and $$4218.32\,cm^{-1} = \overline{\nu}_0 + 6\overline{B}_1 - 2\overline{B}_0.$$

For the P branch we have

$$4096.88\,cm^{-1} = \overline{\nu}_0 - 2\overline{B}_0$$

and $$4054.12\,cm^{-1} = \overline{\nu}_0 + 2\overline{B}_1 - 6\overline{B}_0.$$

If we subtract the first line of the P branch from the second line of the R branch, we find

$$121.44\,cm^{-1} = 6\overline{B}_1$$

or $\overline{B}_1$= 20.24 cm^{-1}. If we subtract the second line of the P branch from the first line of the R branch, we find

$$124.68\,cm^{-1} = 6\overline{B}_0$$

or $\overline{B}_0$ = 20.81 cm^{-1}. Using our usual equation for $\overline{B}$ we find that R_0 = 92.3 pm and R_1 = 93.6 pm.

The dependence of $\overline{B}_n$ on n is usually expressed as

$$\overline{B}_n = \overline{B}_e - \overline{\alpha}_e(n+1/2).$$

The vibrational spectra of polyatomic molecules are more complicated. This is primarily because of one factor: the larger number of atoms yields a larger number of vibrations, any of which may or may not absorb infrared radiation.

The biggest factor is the **number of vibrations**. There are two simple rules which tell us how many different vibrations a given molecule has. **For a linear molecule, there will be 3N-5 vibrations, where N is the number of atoms in the molecule**. **For a nonlinear molecule there will be 3N-6 vibrations**. Where do these rules come from? Consider a single particle. It can move in space three different independent ways, in the x-direction, the y-direction and the z-direction. We call these independent ways the particle can move **degrees of freedom**, and say that a single particle has three degrees of freedom. Now suppose that we have two different particles moving through space. HOW MANY DEGREES OF FREEDOM WILL THESE TWO PARTICLES HAVE? [6] Now suppose that we have N independent particles moving through space. **How many degrees of freedom will these N particles have?** [3N] Now suppose that we take these N particles and bind them together in a molecule. The interesting thing is that **the number of degrees of freedom is conserved, but now it is divided among three different types of through-space motion: translation, rotation and vibration.**

The way the 3N degrees of freedom are divided between the types of motion depend slightly on whether the molecule is linear or not. Let's consider a nonlinear molecule first. The molecule can move through space only three independent ways in the x, y and z directions, so **of the 3N total degrees of freedom, three are taken up by translation**. This leaves 3N-3 for rotation and vibration. A three dimensional molecule can rotate in three different ways (illustrate). Thus there are **three rotational degrees of freedom**. **This leaves 3N-6 degrees of freedom**, which means that a nonlinear molecule will have 3N-6 independent vibrations. **A linear molecule differs because it has only 2 rotational degrees of freedom (illustrate), and thus will have 3N -5 vibrational degrees of freedom.** As examples, acetylene, which is a linear polyatomic molecule has, 3N-5 or 7 vibrations, while ammonia, which is nonlinear, has 3N-6 or 6 vibrations.

These polyatomic vibrations are crudely divided into two types, **stretching vibrations** and **bending vibrations**. There is a simple rule which determines the number of stretching and bending vibrations - **the number of stretching vibrations is equal to the number of bonds** and the rest are bending vibrations. For example in the case of acetylene, there are three bonds, the two CH bonds and the C≡C bond, and therefore there will be three stretching vibrations and four bending vibrations.

What do these vibrations look like? The main requirement is that the vibrational motions conserve linear momentum (i.e. don't get the molecule translating faster) and conserve angular momentum (i.e. don't get the molecule rotating faster). Vibrations which satisfy these requirements are called normal modes of vibration or **normal vibrations**. Let me illustrate for water and acetylene. [Symmetric and asymmetric stretches, bending, degeneracy for C_2H_2] The way that these vibrations are identified is to group them by symmetry, from most symmetric to least symmetric, and within each symmetry group, number the vibrations starting from the highest vibrational frequency and moving to the lowest. Thus for water, we have two symmetric vibrations, the stretch and the bend. Since these have the highest symmetry they are numbered first. The stretch has a higher vibrational frequency, so it becomes ν_1, and the symmetric bend is labeled ν_2. The asymmetric stretch is labeled last and is called ν_3.

Will we see all of these vibrations? The answer is no. **A critical requirement for a vibration to absorb light is the presence of a dipole derivativ**e, a change in the dipole moment of the molecule due to the vibration. For diatomic molecules, it is trivial to determine whether a the dipole moment of a molecule will change on vibration - **if the molecule is homonuclear, there will be no dipole moment change and no infrared absorption**, while **if the molecule is heteronuclear, there will be a dipole moment change and an infrared absorption** will be observed. Thus HCl, CO or KF will all have dipole derivatives and infrared spectra, while H_2, N_2, and O_2 will not absorb in the infrared. This latter fact is very convenient, since it means that we can take infrared spectra in air without interference from the enormous numbers of nitrogen and oxygen molecules present.

For polyatomic molecules **all polar molecules will have dipole derivatives for all their vibrations**. However, unlike diatomic molecules, nonpolar polyatomic molecules can still have infrared absorptions from some of their vibrations. The general principle here is that for most nonpolar molecules, the lack of polarity is from the dipole moments in polar bonds cancelling due to symmetry. [Illustrate with CO_2] This lack of polarity is retained during a vibration if the vibration doesn't change the symmetry of the molecule. This is easiest to see if you draw the molecule before and after the vibration. [Illustrate with CO_2] Thus the CO_2 symmetric stretch retains the original symmetry, and will not result in an infrared spectrum, while the asymmetric stretch and the bend both break the symmetry and will result in infrared absorptions.

In addition to absorbing electromagnetic radiation as a result of rotational and vibrational transitions, molecules can absorb electromagnetic radiation as a result of **electronic transitions**. The difference in energies between electronic levels are usually such that the radiation absorbed falls in the visible or ultraviolet regions. Just as rotational transitions accompany vibrational transitions, **both rotational and vibrational transitions accompany electronic transitions**. If we draw a series of electronic potentials, we see that each electronic state has a series of vibrational states associated with it. The energies of these vibrational states are small compared to the energies of the electronic states, so **the vibrational levels will appear as fine structure in an ultraviolet-visible (UV-vis) spectrum**. **Each of these vibrational levels, will, in turn, have a set of rotational levels associated with it.**

Lecture 38

According to the Born-Oppenheimer approximation, the electronic energy is independent of the vibrational-rotational energy. If we use the anharmonic oscillator to describe the vibrations of the molecule, and the rigid rotor to describe the rotations, **the total internal energy of a diatomic molecule, i.e., the total energy excluding translation, is in wavenumbers**

$$\overline{E}_{total} = \overline{\nu}_{el} + \overline{\nu}_e(n + \frac{1}{2}) - \overline{\nu}_e\overline{x}_e(n + \frac{1}{2})^2 + \overline{B}J(J + 1)$$

where $\overline{\nu}_{el}$ is the energy at the minimum of the electronic potential energy curve. **The selection rules for vibronic transitions (vibrational transitions in electronic spectra) allows Δn to take on any integral value, unlike the case of vibrational-rotational transitions where Δn = ±1**. Because rotational energies are much smaller than vibrational energies, we shall ignore the rotational term in our equation for the internal energy and investigate only the vibrational substructure of electronic spectra.

In electronic absorption spectroscopy, **the vibronic transitions usually originate from the n = 0 state because that is the only state which is appreciably populated at room temperature**. The frequencies of an electronic transition originating in the n = 0 state are given by

$$\overline{\nu}_{obs} = \overline{\nu}_{elel} + (\frac{1}{2}\overline{\nu}_e^{'} - \frac{1}{4}\overline{\nu}_e^{'}\overline{x}_e^{'}) - (\frac{1}{2}\overline{\nu}_e^{''} - \frac{1}{4}\overline{\nu}_e^{''}\overline{x}_e^{''}) + \overline{\nu}_e^{'}n^{'} - \overline{\nu}_e^{'}\overline{x}_e^{'}n^{'}(n^{'} + 1)$$

The term $\overline{\nu}_{el,el}$ is the difference in energies of the minima of the two electronic potential energy curves [illustrate]. The single primes indicate the upper electronic state and the double primes indicate the lower electronic state. Both the fundamental vibrational frequency, $\overline{\nu}_e$, and the anharmonicity, $\overline{\nu}_e \overline{x}_e$, depend on the shape of the electronic potential energy curve at its minimum and so should differ for each electronic state.