The Rotational-Vibrational Spectrum of HCl

Objective
To obtain the rotationally resolved vibrational absorption spectrum of HCl; to determine the rotational constant and rotational-vibrational coupling constant; to compare the rotational transition intensities with theoretical predictions. NOTE: Bring your textbook to the laboratory. Chapter 13 in McQuarrie is a good reference for this lab.

Introduction
In this experiment you will examine the energetics of vibrational and rotational motion in the diatomic molecule HCl. The experiment involves detecting transitions between different molecular vibrational and rotational levels brought about by the absorption of quanta of electromagnetic radiation (photons) in the infrared region of the spectrum. The introductory discussion consists of three parts:

1. vibrational and rotational motion and energy quantization,
2. the influence of molecular rotation on vibrational energy levels (and vice versa), and
3. the intensities of rotational transitions.

Vibrational Motion
Consider how the potential energy of a diatomic molecule $AB$ changes as a function of internuclear distance. For small displacements from equilibrium (typically the case for molecules at room temperature), a simple approximate way of expressing this mathematically is

$$V(x) = \frac{1}{2} kx^2,$$

where the coordinate $x$ represents the change in internuclear separation relative to the equilibrium position; thus, $x = 0$ represents the equilibrium configuration (i.e., the position with the lowest potential energy). For $x < 0$ the two atoms are closer to each other, and for $x > 0$ the two atoms are farther apart. The constant $k$ is called the force constant and its value reflects the strength of the force holding the two masses to each other. Equation (1) is a consequence of Hooke's law, which states that the force between two linked masses is proportional to the displacement of the two masses from their equilibrium position: $F(x) = -kx$. The minus sign indicates that the restoring force is opposite in direction to the displacement.

Equation (1) is referred to as the harmonic potential, and the application of Newtonian (or classical) mechanics to this problem results in a description of the behavior of the masses called simple harmonic (or periodic) motion. The system is commonly referred to as the harmonic oscillator. The harmonic potential (1) is a parabolic potential with a minimum at $x=0$. (See Figure 5.7 in your text.) According to this model, the steepness of the potential is determined by the force constant, $k$.

(Remember that the force is negative the derivative of the potential. This simple picture of molecular energetics predicts that the potential energy of a diatomic molecule increases symmetrically with respect to bond elongation or compression and does so...
without limit. Chemical or physical intuition suggests that this description cannot be entirely true. It is correct that as the nuclei are brought very close to each other, strong repulsive forces are brought to bear and these forces increase sharply with decreasing \( x \). In contrast, as the nuclei are pulled apart, the chemical bond is weakened and eventually broken, and the potential energy therefore becomes constant (and the restoring force vanished) as the two "free" (i.e., unassociated) atoms are produced. Thus the harmonic potential becomes unrealistic for large internuclear distances. This inadequacy of the harmonic potential is called \textit{anharmonicity} and is discussed below.

The application of quantum mechanics to the harmonic oscillator reveals that the total vibrational energy of the system is constrained to certain values; it is quantized. The expression for these energy levels (or eigenvalues) is:

\[ E_v = (v + 1/2)\hbar \nu_e, \quad \text{(ergs)}, \tag{2} \]

where \( v = 0,1,2,3, \ldots \) is the vibrational quantum number, \( \hbar \) is Planck's constant, and \( \nu_e \), is the harmonic frequency (s\(^{-1}\)), which is equal to \( (1/2\pi)(k/\mu)^{1/2} \). Here, \( k \) is the force constant [see equation (1)], and \( \mu \) is the reduced mass of the oscillator, i.e., \( \mu = m_A m_B / (m_A + m_B) \). Notice that the lowest eigenvalue (i.e., \( v = 0 \), is nonzero: \( E_0 = (1/2)\hbar \nu_e \). This is the \textit{zero point energy} of the oscillator. It represents the residual vibrational energy possessed by a harmonic oscillator at zero degrees Kelvin; it is a "quantum mechanical effect." The eigenvalues represent the levels of total energy (kinetic and potential) of the harmonic oscillator, and can be superimposed on the potential energy function. As indicated by equation (2), these levels are equally spaced with a separation of \( \hbar \nu_e \).

It is convenient to express the harmonic frequency in a unit called the wavenumber, \( \tilde{\nu}_e \) or reciprocal centimeter, cm\(^{-1}\). The wavenumber, which is the frequency, \( \nu \), divided by the speed of light, \( c \), is very widely used in atomic and molecular spectroscopy. Expressed in this unit, the vibrational energy in equation (2) becomes

\[ E_v = (v + 1/2)hc \tilde{\nu}_e, \quad \text{(ergs)}. \tag{3} \]

For diatomic molecules, \( \tilde{\nu}_e \) is typically on the order of hundreds to thousands of wavenumbers. For example, for \( \text{I}_2 \) and \( \text{H}_2 \), \( \tilde{\nu}_e \) values (which represent, roughly, the extremes of the vibrational energy spectrum for diatomic molecules) are 215 and 4403 cm\(^{-1}\), respectively.

Next, let us introduce an important and necessary complication to the harmonic oscillator: anharmonicity. Rather than describing the potential energy function as parabolic [equation (1)], we will use a more realistic potential, the Morse function, which takes, into account molecular dissociation at large values of \( x \). The Morse potential is represented analytically as

\[ V(x) = D_0[1-\exp(-ax)]^2 \tag{4} \]

(The Morse potential is illustrated in Figure 5.6 of your text). Using the Morse potential, the vibrational energy levels become more closely spaced at higher energies. \( D_0 \) is the potential energy (relative to the \textit{bottom} of the well) at infinite \( A-B \) separation \( (x = \infty) \), and \( a \) is a constant that, like \( k \) in equation (1), determines the shape of the potential well and hence reflects the vibrational frequency; in fact \( a = (k/2D_0)^{1/2} \). The use of the Morse potential instead of the harmonic potential results in the following expression for vibrational eigenvalues:

\[ E_v = (v+1/2)hc \tilde{\nu}_e - (v+1/2)^2hc \tilde{\nu}_e \chi_e \tag{5} \]
where $\tilde{\nu}_e$ is the harmonic frequency (as above) and $\tilde{\nu}_e\chi_e$ is called the anharmonicity constant. It is a molecular constant that, for the Morse oscillator, is equal to $h\alpha^2/(8\pi^2\mu c)$. Because the anharmonicity term in the eigenvalue expression (5) is multiplied by $-(v + 1/2)^2$, the spacing between eigenvalues rapidly becomes smaller for higher $v$. As the total energy approaches the dissociation limit, the levels become very closely bunched together. For relatively low excitations (only a few vibrational quanta), the Morse potential provides a good description of molecular vibrations.

**Rotational Motion**

Consider the rotation of the molecule $AB$. In the absence of external electric or magnetic fields, the potential energy is invariant with respect to the rotational coordinates; rotational motion is isotropic (independent of spatial orientation). If the $AB$ bond length is assumed to be constant, i.e., independent of rotational energy, then $AB$ is called a rigid rotator. A quantum mechanical treatment of this simple (but not unreasonable) model gives the eigenvalue expression

$$E_J = J(J+1)hcB_e$$

where $J$ is the rotational quantum number ($J = 0,1,2,...$) and $B_e$ is the rotational constant (unit cm$^{-1}$), which is equal to

$$B_e = h/(8\pi^2cI_e)$$

$I_e$ is a molecular constant called the moment of inertia, which for a diatomic molecule is $I_e = \mu r_e^2$, and $\mu$ and $r_e$ are, in turn, the reduced mass, (see above) and the equilibrium bond length of the molecule $AB$. Note that $r_e$ is the internuclear separation for which $x = 0$ in equations (1) and (4) (i.e., the bottom of the potential well). For the general case in which $r$ is considered a variable, $I = \mu r^2$, and thus the rotational constant is a function of $r$:

$$B = h/(8\pi^2c\mu r^2)$$

Notice that the rotational constant contains structural information about the molecule. In fact, the determination of molecular structure can be achieved with high precision from studies of rotational transitions, usually in the gas phase (microwave spectroscopy).

One complication that must be considered is that molecules are, in fact, not perfectly rigid. If a chemical bond is weak enough so that the nuclei respond to increasing rotational energy by moving farther apart) the molecule experiences centrifugal elongation: $r_e$ increases with increasing $J$. The rotational eigenvalues for the nonrigid rotator are approximated by

$$E_J = J(J+1)hcB_e - J^2(J+1)^2hcD$$

where $D$ is called the centrifugal distortion constant. The effect of nonrigidity is to bring the rotational levels closer together for higher energy states. Although, in principle, this
complication is expected to alter the energy levels implied by the rigid rotator model, the effect is often very small and can be neglected. For example, $D$ is typically several orders of magnitude smaller than $B_e$ and therefore centrifugal distortion is significant only for very highly rotationally excited states (large $J$). $D$ can be expressed in terms of $B_e$ and $\tilde{\nu}_e$:

$$D = \frac{4B_e^3}{\tilde{\nu}_e^2}$$

(10)

**Rotational and Vibrational Motion**

If rotational and vibrational motion were completely separable, that is, if molecular vibrations had no effect on rotational states and vice versa, the total energy of a rotating, vibrating diatomic molecule (i.e., a Morse oscillator) would be expressed as the sum of equations (5) and (9), i.e

$$E_{v,J} = \left( v + 1/2 \right) \hbar c \tilde{\nu}_e - \left( v + 1/2 \right)^2 \hbar c \tilde{\nu}_e \chi_e + J(J+1)\hbar c B_e - J^2(J+1)^2 \hbar c D$$

(11)

In this experiment, we are justified in neglecting centrifugal distortion, and thus we will neglect the last term in equation (11). However, the complete separation of rotational and vibrational motion is not realistic because the mean internuclear separation depends on the degree of vibrational excitation (i.e., $v$), and the rotational constant is a function of $1/r$ [see equation (8)], the "effective" rotational constant for a vibrating molecule will vary with the mean value of $1/r$ for the $v$th eigenstate, i.e., $\langle 1/r \rangle_v$. The rotational constant can be approximated by

$$B_v \equiv B_e - \alpha_e (v + 1/2)$$

(12)

where $B_v$ is the rotational constant taking vibrational excitation into account, and $\alpha_e$ is defined as the rotational-vibrational coupling constant. It turns out that for an anharmonic potential (e.g. the Morse potential), $\alpha_e > 0$, whereas for the harmonic potential, $\alpha_e < 0$. This is evident in the expression for $\alpha_e$:

$$\alpha_e = \left[ \frac{6B_e^2}{\tilde{\nu}_e} \left( \frac{\tilde{\nu}_e \chi_e}{B_e} \right)^{1/2} - 1 \right] \text{ (cm}^{-1}) \right].$$

(13)

Notice that for an anharmonic oscillator, $B_v$ decreases as $v$ increases. Also observe that according to equation (13), $B_v < B_e$, even for the case of no vibrational excitation ($v = 0$). Thus $B_e$ as well as $r_e$ and $\tilde{\nu}_e$ are intrinsic molecular parameters that are referenced to the bottom of the potential well; they are independent of vibrational energy. Finally, in applying this treatment of coupled rotational-vibrational motion, we replace $B_e$ in equation (11) by $B_v$ [equation 12)] and write

$$E_{v,J} = \left( v + 1/2 \right) \hbar c \tilde{\nu}_e - \left( v + 1/2 \right)^2 \hbar c \tilde{\nu}_e \chi_e + J(J+1)\hbar c B_v - \left( v + 1/2 \right)J(J+1)\hbar c \alpha_e \text{ (ergs)}$$

(14)

Equation (14) shows that there is a "pure" vibrational contribution (terms containing only $v$), a "pure" rotational term (containing only $J$), and the vibrational-rotational coupling containing both $v$ and $J$. We emphasize again that equation (14) represents the energy of a vibrating, rotating molecule; furthermore, the molecular constants, $\tilde{\nu}_e$, $\tilde{\nu}_e \chi_e$, $B_e$, and $\alpha_e$ are all expressed in cm$^{-1}$. To make things consistent, we will divide equation (14) by $\hbar c$ and replace $E_{v,J}/\hbar c$ by $T_{v,J}$, so that
\[ T_{v,J} = \frac{E_{v,J}}{hc} = (v + 1/2)\tilde{\nu}_{\epsilon} - (v + 1/2)^2\tilde{\nu}_{\epsilon} \chi_{\epsilon} + J(J+1)B_{\epsilon} - (v+1/2)J(J+1)\alpha_{\epsilon} \quad (\text{cm}^{-1}) \]  

(15)

\[ T_{v,J} \] is called the term value; it is the rotational-vibrational state energy expressed in wavenumbers. Equation (15) is the key expression you will use to explain and analyze the experimental data.

**Experimental Method**

Rotational energy levels are much more closely spaced than vibrational levels. For example, for HCl the spacing between the lowest two rotational energy levels \((J = 0 \text{ and } J = 1)\) is about 20 cm\(^{-1}\), whereas the gap between the lowest vibrational level \((v = 0, \text{ ground state})\) and the next highest one \((v = 1, \text{ first vibrational excited state})\) is about 2900 cm\(^{-1}\). The arrangement of rotational and vibrational levels is shown schematically in Figure 13.1 in your textbook.

Because we wish to examine transitions between different vibrational-rotational levels, the spectrometer must be able to resolve the rotational "fine structure" in the vibrational spectrum. The absorption spectrum involving the lowest energy vibrational transition, \(v = 0 \text{ to } v = 1\), called the fundamental, is observed in the infrared region at about 2900 cm\(^{-1}\), or 3400 nm. [The wavelength of a transition is the reciprocal of its energy in cm\(^{-1}\); the nm (10\(^{-9}\) m) is a common wavelength unit.] Infrared spectrophotometers that are based on dispersive optics, i.e., a grating or a prism used to separate the radiation into narrow wavelength "bands", generally do not possess the required resolution for this experiment. Fourier transform (FT) instruments, however, which operate on a different principle are routinely capable of providing resolution of around 1 cm\(^{-1}\), which is satisfactory for this experiment.

The fundamental relation in spectroscopy is derived by equating the photon energy with the difference in state energies involved in the transition. For the case where radiation of frequency \(\nu\) is absorbed, the energy of the transition (ergs) is

\[ E = \hbar \nu = hc \tilde{\nu} = E'_{v',J'} - E''_{v'',J''} , \]

where \(\tilde{\nu}\) is the photon "frequency" in cm\(^{-1}\) and \(v',J'\) and \(v'',J''\) are, respectively, the vibrational/rotational quantum numbers of the upper and lower energy states involved in the transition. (The use of single and double primes to denote the upper and lower states, respectively, is traditional notation in spectroscopy.) Expressed in wavenumber units, the preceding equation becomes:

\[ \tilde{\nu} = T_{1,J'} - T_{0,J''} \quad (16) \]

in which the fundamental transitions are made explicit by assigning \(v' = 1 \text{ and } v'' = 0\).

Equation (16) implies that the frequencies of the fundamental transitions are not precisely equal to the gap, \(v' - v''\), but are instead altered by the simultaneous changes in rotational energy. Logically, we can anticipate three general possibilities: an increase, decrease, or no change in rotational quantum number. In proceeding further, we
introduce an important (and simplifying) constraint in the way in which $J$ changes as a result of photon absorption. This restriction is called a selection rule, and for pure rotational transitions it states that

\[
\begin{align*}
\Delta J = 0 & \text{ is forbidden,} \\
\Delta J = \pm 1 & \text{ is allowed,}
\end{align*}
\]

and all other changes in $J$ values are forbidden. For vibrational transitions, the selection rule requires that

\[
\Delta v = \pm 1.
\]

This rule is rigorous only for the harmonic oscillator. Anharmonicity causes the vibrational selection rule to break down, and thus the $v'' = 0$ to $v' = 2$ transition is weakly allowed.

Returning to the rotational-vibrational spectrum of HCl, we can group the transitions into two classes. In the first, there is a decrease in rotational quantum number ($\Delta J = -1$, and $J' = J'' - 1$), and in the second case, there is an increase in rotational energy ($\Delta J = +1$, and $J' = J'' + 1$). Remember: the $\Delta J = 0$ transitions are not allowed. A reproduction of the rotational-vibrational spectrum for the fundamental band of the similar molecule, HBr is shown in Figure 13.2 of your text and are illustrated schematically below:

The lines for which $\Delta J = -1$ are all positioned at lower energy, and these are conventionally called the $P$-branch. The lines corresponding to $\Delta J = +1$ are situated at higher energy and are referred to as the $R$-branch. If $\Delta J = 0$ transitions were allowed (they are under some circumstances, and are called the $Q$-branch), they would "pile up" in a narrow grouping of lines between the $P$ and $R$ branches. The $Q$-branch, represented by the dashed lines in the figure above, would appear as a single line only if the rotational constants for the upper and lower vibrational states were identical.

The rotationally resolved fundamental transitions can be expressed as a function of rotational quantum numbers, $J''$ (ground state, $v = 0$) and $J'$ (upper state, $v = 1$). This is done by combining equations (16) and (15). After grouping terms
containing $B_e$ and $\alpha_e$ and utilizing the selection rule $\Delta J = \pm 1$, we can express the wave
numbers of the spectroscopic lines in terms of the values of $J''$. Remember that for the P-
branch, $J' = J'' - 1$, where $J'' = 1, 2, 3, \ldots$ Then, for the P-branch of the fundamental
vibrational transition, we have:

$$\tilde{\nu}(J'') = (\tilde{\nu}_e - 2\tilde{\nu}_e \chi_e) - (2B_e - 2\alpha_e)J'' - \alpha_e(J'')^2 \quad (17)$$

These results show that the energies of the P-branch lines decrease nonlinearly with increasing $J''$.

For the R-branch, $J' = J'' + 1$, where $J'' = 1, 2, 3, \ldots$ and equation (17) reads:

$$\tilde{\nu}(J'') = (\tilde{\nu}_e - 2\tilde{\nu}_e \chi_e + 2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e(J'')^2 \quad (18)$$

Note that the transition energies of the R-branch members increase (also nonlinearly) with increasing $J''$. Above a certain $J''$ value the R-lines will begin to decrease in energy because of the negative coefficient of the $(J'')^2$ term. For HCl, this does not occur until $J'' \approx 27$.

If the Q-branch ($J' = J''$) were observable in this experiment, its components would appear at:

$$\tilde{\nu}(J'') = \tilde{\nu}_e - 2\tilde{\nu}_e \chi_e - \alpha_e(J'' + J''^2) \quad (19)$$

for the fundamental vibrational transition, and would be displaced to lower energies than the R-branch. In the absence of rotational vibrational coupling ($\alpha_e = 0$), the Q-branch would appear as a single line at an energy equal to the gap in the vibrational levels, $v = 0, v = 1$. For convenience, this gap is defined as

$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e \chi_e \quad (20)$$

**Determination of the Molecular Constants**

We see from equations (17) and (18) that the P- and R-branch lines (abbreviated P1, P2, P3, \ldots and R0, R1, R2, \ldots, respectively) are quadratic in $J''$. Thus if we were to fit the observed lines to these equations, we could obtain three constants. These correspond to the coefficients $a$, $b$, and $c$ of the equation

$$Y = a + bx + cx^2$$

The three constants obtainable from the $\tilde{\nu}(J'')$ data are $\tilde{\nu}_0$, $B_e$, and $\alpha_e$. Thus we cannot directly determine the anharmonicity constant, $\tilde{\nu}_e \chi_e$ in this experiment.

We could readily and directly regress the P- and R-branch data (fit) to the second-order equations (17) and (18). Alternatively, we could linearize these equations. One approach is to examine the *successive differences* in energies of the lines in both branches. For example, for the P-branch, we develop the expression for P1 - P2; P2 - P3; P3 - P4; \ldots and have, in general,

$$P(J'') - P(J''+1) = \Delta \tilde{\nu}_P = 2B_e - \alpha_e + 2\alpha_e J'' \quad J'' = 1, 2, 3, \ldots \quad (21)$$

Notice that $\tilde{\nu}(P1) > \tilde{\nu}(P2)$, etc.
Likewise, for the successive differences in the R-branch lines, i.e., R1 – R0; R2 – R1, etc., the result is

\[ R(J'' + 1) - R(J'') = \Delta \tilde{\nu}_R = 2B_e - 5\alpha_e - 2\alpha_e J'' \quad J'' = 0,1,2, \ldots \] (22)

Inspection of equations (21) and (22) reveals that the P-branch lines become more widely spaced farther into the tail of the spectrum; likewise, the R-branch lines should become more closely spaced. Using these equations quantitatively, we can obtain values of B_e and \alpha_e from plots of \Delta \tilde{\nu}_P and \Delta \tilde{\nu}_R vs. J''.

Equations (21) and (22) are redundant because each provides the same information; however, examination of the P- and R-branch data separately indicates how well each set fits the vibrationally coupled rigid rotator model.

To obtain a value of \tilde{\nu}_0, we can simply plot the respective term values of the P-branch vs. \((2B_e - 2\alpha_e)J'' + \alpha_e(J'')^2\) once we know B_e and \alpha_e [see equation (18)]. The intercept is equal to \tilde{\nu}_0. We could also use a similar approach with the R-branch data and equation (19).

**Isotope Effects**

You should note that each of the lines of the HCl spectrum is actually a doublet. One of these lines comes from HCl\(^{35}\) and the other from HCl\(^{37}\). From the relative absorption wavenumbers of each member of each doublet, you should be able to assign each line to either of these isotopes. You should also be able to predict the differences in absorption frequencies based on the reduced masses of the two isotopes.

**Temperature and Absorption Intensities:**

To the extent that each absorption in the HCl fundamental rotational/vibrational spectrum represents equal \textit{a priori} probability, the intensities of each line is related to the population of the initial state \((v=0, J = J')\). From your observations of the relative intensities (approximated by relative peak heights) of each of the lines in the P and R branches, you should be able to deduce the relative populations of each quantum level. Given the degeneracy of each energy level, this is further related through the Maxwell-Boltzmann distribution law, to the temperature of the system. Given that the degeneracy of each state (defined by \(J = J'\)) is \(2J''+1\), one can use the relative absorption intensities to estimate the temperature of the absorbing gas sample.

**Safety Precautions**

a. Safety glasses must be worn during this experiment.

b. The cell used to obtain the infrared spectra is valuable and non-replacable. Handle it with extreme caution. The lenses are made from NaCl and are thus moisture sensitive. Do not touch the lenses with your fingers nor expose them to moisture of any kind. If the cell filled with HCl breaks outside of the fume hood, notify your instructor immediately (and pray for mercy).
Laboratory Procedure

During the laboratory period you will work with your group to obtain your IR spectrum of HCl. While other groups are obtaining their spectra, you will work with your partners in the laboratory to answer the pre-lab questions given below. **You are not required to complete the pre-lab questions before coming to laboratory, but you must submit your answers before you leave the laboratory.**

The laboratory period will begin with a demonstration of the generation of HCl gas by the action of concentrated H$_2$SO$_4$ on solid NaCl. The instructor will demonstrate this process and fill the gas IR cell with HCl for the day’s spectra.

Groups of students will then proceed to obtain an absorption spectrum of HCl under instrumental conditions that reveal splitting in each of the rotationally-resolved features and show at least six members in both the P- and R- branches. Record the spectrum as absorbance vs. cm$^{-1}$. For the fundamental transition, the region 2600-3100 cm$^{-1}$ should be displayed. Label each peak with its associated absorption frequency and use the cursor to label the location of the center of the (non-existent) Q-branch. The spectrum can be subsequently displayed on hard copy using the printer. An instructor will guide you through the use of the Fourier transform IR instrument and obtaining your spectrum.

After you have obtained your spectrum print-out, have an instructor check it to be sure that it is of adequate quality for your data analyses. You may then proceed to finish your pre-lab questions. Once your pre-lab questions are completed and submitted, you may either remain in the laboratory to perform some of the data analyses or complete the data analyses on your own time.

Data Analysis

1. You will notice that each "line" shows two components. This results from the presence of two isotopes of Cl; thus, the sample is a mixture of H$^{35}$Cl (the major component) and H$^{37}$Cl, presumably representing the natural abundance of these isotopes. These two isotopomers have different reduced masses and hence different $B_e$ values. You should at this time determine which isotope corresponds to the higher-energy component of the split features.
2. Tabulate the P- and R-branch components corresponding to H$^{35}$Cl. Assign these features as P1, P2, P3, ..., and R0, R1, R2, .... From the instrument-assigned data associate each transition to a frequency in cm$^{-1}$.
3. From the tabulated data, determine the spectroscopic constants $\tilde{\nu}_0$, $B_e$, and $\alpha_e$ from a linear regression analysis of equations (17) and (18). Also do this by calculation of the consecutive differences in the P and R branch lines (equations (21) and (22)). From these analyses, you should obtain 4 redundant values of $\tilde{\nu}_0$, $B_e$, and $\alpha_e$. Now use the best values to obtain the moment of inertia, I, of H$^{35}$Cl. From the reduced mass, obtain a value for $r_e$.
4. From the two isotopic features of each spectral transition, determine (from the relative heights for several transitions) the relative abundances of the two Cl isotopes. Estimate the atomic mass of Cl assuming that $^{35}$Cl and $^{37}$Cl have masses of 34.968 and 36.956 amu respectively. Compare this with the reported atomic mass of Cl.
5. Using your values of $B_e$ and $\tilde{\nu}_0$, calculate D, the centrifugal distortion constant.
(equation (10)). What must the value of J be for the centrifugal distortion term to be 1% of the rigid rotator term in equation (10)? Does this result justify ignoring D in your experimental results?

6. Assuming that the Q-branch could be represented, if present, by a single line, calculate the frequency of this line from your spectral data and compare this value to the observed (estimated with the cursor) center of the R and P branches in your HCl spectrum.

**Lab Report**

In addition to following the general lab report guidelines, your laboratory report should specifically include a copy of your spectrum, all data tables, graphs and calculations, and clearly indicate your values for the molecular constants described above. Also include answers to questions posed in the data analysis section above.

**Pre-lab Questions**

1. The force constant for H\textsuperscript{35}Cl is 5.1669 x 10\textsuperscript{5} dynes cm\textsuperscript{-1} (ergs cm\textsuperscript{-2}). What are the expected values of \(\tilde{\nu} \) and the anharmonicity constant? (\(D_0\) values are given in Table 13.2 in the textbook.)

2. Assuming rotational-vibrational coupling is negligible, calculate the wavenumber (in cm\textsuperscript{-1}) of the hypothetical Q-branch line of H\textsuperscript{35}Cl using your results from Pre-lab question 1.

3. In general, what accounts for the uneven spacing on the lines in the P and R branches of a vibration-rotation spectrum?

4. Convert a wavenumber of 3000 cm\textsuperscript{-1} to wavelength in micrometers and frequency in reciprocal seconds.