Introduction

In this experiment you will record and analyze the fundamental vibration-rotation absorption spectrum of gas phase HCl and DCl. From your analysis you will deduce numerical values for several important molecular parameters such as the HCl bond length. The spectra fall in the IR and will be recorded with a Perkin-Elmer Model 1605 FTIR spectrophotometer. You will be instructed as to the use of this instrument.

As advance preparation, you should read this writeup carefully. Study of the first two references below (at least—the third is the classic reference in the field for professional spectroscopists) will be particularly useful as you complete your writeup. (As with many spectroscopic experiments, collecting the data takes a small fraction of the time needed to analyze them.)

References:


2. D. A. McQuarrie, Quantum Chemistry, University Science, 1983. Read sections 10-2 and 10-3 (pp. 439–443), scan 10-4 (pp. 443–445), read 10-5 (pp. 445–448), scan 10-6 and 10-7 (pp. 448–452), and read 10-8 and 10-9 (pp. 452–457). (On reserve)

Experimental:

The sample will be prepared for you and contained in a gas sample cell. Note: the windows of the cell are NaCl, which is transparent in the IR. Do not touch them or breath on them! Moisture will fog the windows and reduce their IR transparency!

The gas sample is prepared by bubbling HCl gas through D₂O, causing proton/deuteron exchange. The evolved gas after saturation is a mixture of HCl and DCl which is collected by displacement of air and is dried. Thus, the sample pressure will be about 1 atm, and some small residual amount of air will remain in the cell.

Theory, Calculations, and Discussion:

The energy of any vibrational-rotational state of HCl, expressed in its wavenumber equivalent and measured in cm⁻¹ units, can be written to a good approximation as

\[ E_{v,J} = G(v) + B_v J(J+1) - D_v J^2(J+1)^2 + \ldots \]  

where

- \( v \) = the vibrational quantum number (0, 1, 2, etc.)
- \( J \) = the rotational quantum number (0, 1, 2, etc.)
- \( B_v \) = the rotational constant for vibrational state \( v \)
- \( D_v \) = the centrifugal distortion constant for vibrational state \( v \)
- \( G(v) \) = the vibrational energy

with

\[ B_v = B_e - \alpha_e (v + 1/2) + \text{(smaller correction terms, expressed in a power series in } (v+1/2)) \]  

and

\[ G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \text{(smaller terms)} \]  

where

- \( B_e \) = the equilibrium rotational constant
- \( \alpha_e \) = the vib.-rot. coupling constant
- \( \omega_e \) = the fundamental vibrational constant
- \( \omega_e x_e \) = the first anharmonic correction constant.

Only those expressions and constants in bold type will concern us; for example, \( D_v \) for HCl is \( \sim 5 \times 10^{-5} B_v \), which is so small it alters transition energies by an amount too small to measure on your instrument.

Three criteria must be satisfied to observe an absorption event:

1. the incident photon energy must equal the energy difference between two states with different sets of quantum numbers,
2. the quantum numbers of the two states involved in the transition must be such
as to make the transition "allowed", and

(3) there has to be a sufficient amount of molecules in the sample with the initial quantum numbers of the transition to absorb a measurable amount of the incident radiation.

We look at each of these criteria in turn below.

(1) Energy difference expression
By convention, the quantum numbers of the initial state in an absorption event (the state of lower energy) are expressed with double primes: $v'' J''$, while the final (or upper) state quantum numbers carry single primes: $v' J'$. Thus, from Eq. (1),

$$\Delta E = \text{the absorbed radiation wavenumber}$$
$$= E(\text{final state}) - E(\text{initial state})$$
$$= E_{v',J'} - E_{v'',J''}$$
$$= G(v') - G(v'') + B_{v'}J'(J'+1) - B_{v''}J''(J''+1)$$
$$= \omega_e (v' - v'') - \omega_x (v'^2 + v' - v''^2 - v'')$$
$$+ B_{v'}J'(J'+1) - B_{v''}J''(J'' + 1) \quad (4)$$

(2) Selection rules
To have an allowed vibration-rotation absorption transition in a diatomic with all electrons spin-paired, the quantum number changes (expressed as $\Delta(\text{number}) = \text{final value} - \text{initial value}$) must satisfy the following restrictions, called selection rules:

vibrational quantum number: $\Delta v = 1$ (for the most probable absorption transitions—the "fundamental" transitions)

or $\Delta v = 2, 3, 4, \text{etc.}$, with ever diminishing probability of occurrence (the "overtone" transitions)

rotational quantum number: $\Delta J = \pm 1$

where those transitions with $\Delta J = -1$ are said to be members of the "P branch" and those with $\Delta J = +1$ form the "R branch."

(Note the alphabetic/numeric relationships:

$\Delta J = -1 \quad 0 \quad +1$

corresponds to $P \quad Q \quad R$ branches with the

Q branch not allowed for an all spin-paired diatomic.)

Transitions which are members of a given branch are symbolized by the notation $R(J'')$ or $P(J'')$, i.e., the initial rotational quantum number is given in parentheses.

(Note that there is no P(0) transition! Do you see why?)
(3) Initial state population

An equilibrium sample at some finite temperature has a distribution of populated quantum states, the distribution being governed by the absolute temperature and by the energy spacing between states. The form of the distribution is given by the Boltzmann distribution law, which is introduced on p. 93 of Winn. For our purposes, this law will let us compute that, for example, the ratio of the number of HCl molecules in the \( v = 1 \) state to the number in \( v = 0 \) is \( N_1/N_0 = 6 \times 10^{-7} \) at 300 K. For \( v > 1 \), this ratio is raised to the \( v \) power, to a very good approximation; thus, less than one in a million molecules is in a vibrational state other than \( v = 0 \). This fact, coupled with the \( \Delta v = 1 \) fundamental selection rule, allows us to state that we will observe transitions for which \( v'' = 0 \) and \( v' = 1 \), i.e., a so-called \( 1 \leftarrow 0 \) vibrational transition. The overtones, such as \( 2 \leftarrow 0 \), \( 3 \leftarrow 0 \), etc., can be observed, but with diminishing probability due to other than quantum state population effects. We won't see them here simply because their transition energies lie outside the range of our instrument. We will, however, make use of these transition energies later in the discussion.

Rotational states are much more closely spaced in energy, and as a result, many rotational states (of the \( v = 0 \) vibrational state) are significantly populated at room temperature. We thus expect to see many transitions in both the P and R branches, but with an intensity variation which is characteristic of the sample's temperature. (And we add that modern research techniques exist which allow samples to be studied as individual gas-phase molecules over a temperature range from near 0 K to several thousand K! It is the low temperature limit which is often the more important to achieve, since low T means few states are populated, which thus implies fewer observable transitions and a simplified spectrum.)

Summary

Putting together points (1)—(3) above allows us to simplify Eq. (4) to the form

\[
\Delta E(1 \leftarrow 0) = (\omega_e - 2\omega_{eX_e}) + B_1(J' + 1) - B_0(J'' + 1)
\]

and to summarize the expected transitions in an energy level diagram, as in Fig. 2 on the next page. The task will be to assign each absorption feature in the spectrum to a single transition and to use the assigned quantum numbers and observed transition energies (the \( \Delta E \)'s) in Eq. (5) to deduce first the rotational constants \( B_0 \) and \( B_1 \), then the \( B_e \) and \( \alpha_e \) constants of Eq. (2), and, with the help of data you won't be able to measure (the overtone information), the values of \( \omega_e \) and \( \omega_{eX_e} \). Finally, these constants will be used to derive molecular structure information, and all of your data will be analyzed as to its precision.
**Figure 2.** Schematic vibration-rotation energy level scheme for a simple diatomic with allowed absorption transitions shown for the first few P and R branch transitions. The rotational level spacing is to scale, but the vibrational level spacing is many times greater than shown.

**Analysis of Spectra**

To assign and analyze your spectra, you will make use of cleverly chosen differences between selected transition energies, the so-called "combination differences" in the parlance of a molecular spectroscopist. Note in the Figure above that if you subtract the P(2) transition energy from the R(0) transition energy, you are left with the energy difference between the $J'' = 2$ and $J'' = 0$ states, i.e., you are left with something that has rotational energy information about the $v'' = 0$ level only. From this sort of subtraction, a value for $B_0$ can be found. Similarly, subtracting P(1) from R(1) leaves you with the difference between $J' = 2$ and $J' = 0$ states, a quantity which will yield $B_1$. 
Algebraically, we can define a general quantity $\Delta''(J'')$ where

$$\Delta''(J'') = R(J'') - P(J'' + 2) \quad (6)$$

and a similar quantity $\Delta'(J'')$ where

$$\Delta'(J'') = R(J'') - P(J'') \quad (7)$$

with, in each,

$$R(J'') = (\omega_e - 2\omega_e x_e) + B_1 (J'' + 1)(J'' + 2) - B_0 J''(J'' + 1)$$

and

$$P(J'') = (\omega_e - 2\omega_e x_e) + B_1 (J'' - 1)J'' - B_0 J''(J'' + 1).$$

(These expressions for the P and R branch transition energies are just special cases of Eq. (5) which use the $\Delta J = J' - J''$ relationship appropriate for each branch. Note the two uses of the symbols $P(J'')$ and $R(J'')$. One use is as a simple label for the transitions; the other is as above, in an energy function of $J''$.) With these definitions, the combination difference expressions simplify to

$$\Delta''(J'') = B_0 [(J'' + 2)(J'' + 3) - J''(J'' + 1)] = B_0 (4J'' + 6) \quad (8)$$

and

$$\Delta'(J'') = B_1 [(J'' + 1)(J'' + 2) - (J'' - 1)J''] = B_1 (4J'' + 2). \quad (9)$$

Thus, you can find as many values for $B_0$ and $B_1$ as you have pairs of P and R transitions that satisfy Eq.'s (6) and (7). If there were no experimental errors and if Eq.'s (8) and (9) were exact, all your $B_0$ values and all your $B_1$ values would be the same, but errors (and the approximations made in truncating Eq. (1)) will cause slight variations, but $B_0$ and $B_1$ should still be measurably different. **Tabulate at least 6 values for each rotational constant in a way which indicates the $J''$ value used for each, along with an assigned table of every clearly-resolved transition you observe. Do this and the analysis which follows only for the $^{35}\text{Cl}$ isotope transitions.** (Which ones are these, anyway? Can you resolve the Cl isotopes' transitions in both the HCl and DCl spectra? "Assigned", by the way, means to indicate the quantum numbers of each state involved in each transition.)
Error analysis

One of the hallmarks of spectroscopic measurements is the precision with which transition energies can be measured. One part per million precision is not very difficult, and many methods achieve 1:10^9 or better, depending on the radiation frequency region. In the IR, current laser and interferometric methods can beat the part-per-million barrier at almost any transition energy. Of course, the data you have are not of such precision, but we will treat them with the sort of statistical analysis used in higher resolution studies of more complex molecules. It is not uncommon to measure, assign, and analyze several thousand transitions in a small polyatomic molecule these days, and, of course, computer methods are mandatory for data of such extent. Moreover, methods more sophisticated than combination differences have been devised and incorporated into these computer programs. But however it’s done, what one seeks is some uniform, statistically significant measure of the precision of the final molecular parameters and mechanical or geometric constants derived from the analysis. Thus, if your analysis leads to a bond length of, say, 0.916 808 Å (the HF equilibrium bond length, r_e), you need to know how many of those 6 digits are reliably determined. (For HF, r_e is uncertain by about one part in the last digit.) Since r_e is found from B_e, which comes from B_v values, which come from many assigned transitions, each of which come from a measurement with a particular random, instrumental error, the propagation of errors through all these steps, data → r_e, becomes important to study.

Before we do so, however, notice that we have talked only about the precision of the measurements, not their accuracy. Accuracy is most often a question of reliable calibration. Commonly, one uses a standard molecule, the spectrum of which is recorded along with that of the desired sample. In the visible, the I_2 spectrum is often used, while in the IR, a number of molecules—CO, CO_2, H_2O, N_2O, OCS, etc.—serve as standards for various wavenumber regions. Catalogs of transition energies for these standards exist, as do various experimental and mathematical ways of interpolating among sometimes widely spaced transitions. After you finish the propagation of error analysis described below, qualitatively discuss the effect that calibration error would have on your results.

Now on to propagation of error analysis. Given your various measured values for B_0 and B_1, the first operation is to compute the averages, B_0̄ and B_1̄. (Averaged quantities will be represented by a bar over the symbol.) Thus, for example,

\[ \overline{B_0} = \frac{1}{N} \sum_{i} B_{0,i} \]

gives the average for N measured values of B_0, the B_{0,i}’s. The next operation would be to measure the spread of the measurements about \( \overline{B_0} \) by computing the mean of the squared deviations from the mean, \( s_{B_0}^2 \), (also called the mean square error or the
variance) where (note the denominator is $N - 1$, not $N$)

$$s_{B_0}^2 = \frac{\sum_i (B_{0,i} - \bar{B}_0)^2}{N - 1}.$$ 

It is tempting to report a final value, with error limits, as simply $\bar{B} \pm s_B$, and be done with it, but this overestimates the proper error limits. Intuitively, the proper error limits should depend in some way on $N$, in the sense that the greater the number of measurements made of a randomly distributed variable, the smaller will be the error in the average of those measurements. The variance of any one measurement tells you something about the error in that one measurement, but it does not tell you by itself how the error in the average narrows as more and more measurements are made.

To find the relationship between $N$ and the error in the average, note that $\bar{B}_0$ is a function of the $N$ measured values, $B_{0,i}$, $i = 1, 2, ..., N$, which we will abbreviate as simply $B_i$ for now. If we were to change the $B_i$'s by some small amounts, call them $\Delta B_i$, these changes would alter $\bar{B}_0$ (to first order in these small quantities) by an amount $\Delta \bar{B}_0$ where

$$\Delta \bar{B}_0 = \sum_i \left( \frac{\partial \bar{B}_0}{\partial B_i} \right) \Delta B_i. \quad (10)$$

From the definition of $\bar{B}_0$, we find $(\partial \bar{B}_0 / \partial B_i) = 1/N$. Next we square the $\Delta \bar{B}_0$ expression:

$$\left( \Delta \bar{B}_0 \right)^2 = \frac{\left( \sum_i \Delta B_i \right)^2}{N^2} = \frac{\sum_i (\Delta B_i)^2 + 2\Delta B_1 \Delta B_2 + 2\Delta B_1 \Delta B_3 + \ldots}{N^2}$$

and then average this expression over all expected values of $\Delta B_i$. These expected values are the random variations in $B_i$ from measurement to measurement; they are independent, they vary randomly in algebraic sign, and they are characterized by the variance $s_{B_i}^2$. Since each is independent, the average of any one cross term, such as $\Delta B_1 \Delta B_2$, will equal the product of the averages of each factor. But the average of any one factor ($\Delta B_i$ in general) is zero, since each is uniformly distributed about zero. Hence, all the cross terms above average to zero. We are left with

$$\left( \Delta \bar{B}_0 \right)^2 = \frac{\left( \sum_i \Delta B_i \right)^2}{N^2} = \frac{N (\Delta B_i)^2}{N^2} = \frac{(\Delta B_i)^2}{N} \quad (11)$$

where we have used the fact that each measurement has the same average $(\Delta B_i)^2$. 


There is another way to think about this averaging process which also shows how the cross terms average to zero. (A rigorous proof isn’t very difficult, but the symbology becomes complicated and laden with lots of subscripts and summation signs; we’ll stick to an argument in English.) Imagine repeating the experiment M times. Each repetition gives you a set of N values for B₀ (let’s just call it B), and, at each repetition, these are averaged to give M values for \( \overline{B} \). But suppose you did the experiments in a different way. Suppose you recorded only those transitions giving one of the N possible values of B, such as just the P(2) and R(0) transitions, but you did this in M different experiments. You could average these M values and go on to do another M experiments recording just the P(3) and R(1) transitions, for example, which gives you another average value, and so on. For both types of experiments, the different values of B and their averages could be displayed in a matrix like this:

\[
\begin{array}{cccccc}
N \text{ values per spectrum} & B_{1,1} & B_{1,2} & B_{1,3} & \cdots & B_{1,N} \\
B_{2,1} & B_{2,2} & B_{2,3} & \cdots & B_{2,N} \\
B_{3,1} & B_{3,2} & B_{3,3} & \cdots & B_{3,N} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
B_{M,1} & B_{M,2} & B_{M,3} & \cdots & B_{M,N}
\end{array}
\]

(What you have actually measured is just the first row, i.e., one full spectrum, and you have only the single average, \( B_{1,N} \), shown at the top of the right-hand box. What we are after is the uncertainty in the “grand” average \( \overline{B}_{M,N} \).) Since we could construct the above matrix of measurements row by row (by repeating your experiment M times) or, independently, column by column, you can see how the various \( \Delta B_{i} \) values \((i = 1, 2, \ldots, N)\) are independent. This independence assures that the average of a cross-product such as \( \Delta B_{1} \Delta B_{2} \) equals the average of \( \Delta B_{1} \) times the average of \( \Delta B_{2} \), both of which are zero. Hence we arrive at Eq. (11).

Now what we can show about Eq. (11) is that the averaged squared deviations that appear on both sides can each be related to mean square errors: \( (\Delta B_{i})^2 \) to \( s_{B}^2 \) and \( (\Delta B)^2 \) to \( s_{B}^2 \). It is this latter mean square error that we want; it represents the error in the quantity symbolized \( \overline{B}_{M,N} \) in the matrix of measurements above. To show this relationship, we will start with the final answer and work our way back towards Eq. (11).

The final answer will be
We expand each $s^2$ in terms of its respective definition, canceling factors of $(N - 1)$ common to both:

$$\sum (B_{i,N} - \overline{B}_{M,N})^2 = \sum (B_i - \overline{B})^2$$

On the right, we associate $B_i - \overline{B}$ with $\Delta B_i$ and note that what we called $(\Delta B)^2$ in Eq. (11) is just $(1/N) \sum (\Delta B_i)^2$, while on the left, we associate $B_{i,N} - \overline{B}_{M,N}$ with $\Delta B$ and similarly note that $(\Delta B^2)$ is $(1/N) \sum (\Delta B)^2$. With these associations, you can see how Eq.’s (11) and (12) are equivalent. Equation (12) means that we should report

$$\overline{B} \pm s_B = \overline{B} \pm \frac{s_B}{\sqrt{N}}$$

or, in words, the error in the mean varies as one over the square root of the number of measurements if each measurement is characterized by a common mean squared error.

The importance of this exercise goes beyond the result embodied in Eq. (12). It also shows how to begin a propagation of random errors analysis starting with an expression such as Eq. (10). The next section puts this analysis to work.
Molecular constants

Now we are ready to find the important molecular constants $B_e$, $\alpha_e$, $\omega_e$, $\omega_x e$, $r_e$, and $k_e$, the equilibrium force constant. To find $B_e$ and $\alpha_e$, use Eq. (2) and the fact that we know two $B_v$ values in a simple "two equations—two unknowns" problem. You will find that

$$\alpha_e = B_0 - B_1$$

and

$$B_e = (3B_0 - B_1)/2.$$

Keep in mind that these quantities are derived from an averaging procedure. So what does one report for the uncertainties in $\alpha_e$ and $B_e$?

For a general function of many variables, $F = F(x_1, x_2, x_3, \ldots)$, we write a first-order variation equation analogous to Eq. (10):

$$\Delta F = \sum_i \left( \frac{\partial F}{\partial x_i} \right) \Delta x_i$$

and apply a statistical averaging argument, as we did above, which leads us to

$$(\Delta F)^2 = \sum_i \left( \frac{\partial F}{\partial x_i} \right)^2 (\Delta x_i)^2$$

or, in terms of the mean squared errors,

$$s_{F}^2 = \sum_i \left( \frac{\partial F}{\partial x_i} \right)^2 s_i^2. \quad (13)$$

This is the general propagation of errors expression for which Eq. (12) is a special case. As an example of its use, you should derive that

$$s_{\alpha_e}^2 = s_{B_0}^2 + s_{B_1}^2$$

and then go on to derive an expression for the mean squared error in $B_e$.

Given a value for $B_e$ (and its error), you can calculate a value for $r_e$ (and its error). Note first that of more fundamental importance are the so-called $r_v$ values, derived from
where the < > symbols here indicate a quantum mechanical average over the vibrational wavefunction of state $v$. Physically, this averaging represents the motion of the nuclei over all allowed distances during a measurement. These average distances ($r_0$ in particular) are the primary quantities derived from microwave (pure rotational) spectroscopy, which often probes only the lowest vibrational level. But for $B_e$, we can write

$$r_e = \left( \frac{\hbar}{4\pi c \mu B_e} \right)^{1/2}$$

Use $\hbar = 1.054571596 \times 10^{-34}$ J s (the 1999 adjustment of the physical constants value), and note that $c = 299792458$ m s$^{-1}$ exactly, due to the 1983 re-definition of the meter. Also, use the following reduced masses: $\mu(H^{35}Cl) = 0.97959272$ g mol$^{-1}$, $\mu(D^{35}Cl) = 1.90441364$ g mol$^{-1}$, which are precise nuclear reduced masses based on the $^{12}$C = 12.000.... g mol$^{-1}$ scale. (There is a subtle difficulty associated with these masses, which is discussed in an extra credit problem at the end of this handout.)

Next, you should show that

$$s_{r_e} = r_e \frac{S_{B_e}}{2B_e}$$

by using the propagation of errors expression, and you should **compute the error in** $r_e$. Now for the big question: *are the equilibrium bond lengths for HCl and DCl equal to within your experimental uncertainty? Should they be?* As a check that you’re doing the right thing, the best current values are:

$$B_e(HCl) = 10.593553 \text{ cm}^{-1} \quad B_e(DCl) = 5.448794 \text{ cm}^{-1}$$
$$\alpha_e(HCl) = 0.307181 \text{ cm}^{-1} \quad \alpha_e(DCl) = 0.113291 \text{ cm}^{-1}$$
$$r_e(HCl) = 1.2746149 \text{ Å} \quad r_e(DCl) = ?$$ (We can’t give away everything!)

The last constants of concern are the two vibrational constants of Eq. (3), $\omega_e$ and $\omega_e x_e$, and the force constant, $k_e$. We won’t ask for an error analysis on these constants, but we will compare them between the two hydrogen isotopic variants. The most recent high resolution study of HCl and DCl can be found in the paper by G. Guelachvili, P. Niay, and P. Bernage, *Journal of Molecular Spectroscopy*, **85**, 271–281 (1981). These authors were actually studying the spectra of HI and DI in a Fourier transform high resolution study, but noticed HCl and DCl lines in their spectra (due to HCl and DCl "impurities"); so, they analyzed these spectra as well. (Their HI and DI analysis is published as the paper just before the one cited above.) They observed
the HCl $1 \leftarrow 0$ fundamental transition (as you have) as well as the $2 \leftarrow 0$ and $3 \leftarrow 0$ overtones of both HCl and DCl. They could resolve the $^{35}\text{Cl}$ and $^{37}\text{Cl}$ isotopes easily, (for example, they report the H$^{35}\text{Cl} 1 \leftarrow 0$ R(0) transition at 2906.2474 cm$^{-1}$ and the same transition for H$^{37}\text{Cl}$ at 2904.1111 cm$^{-1}$), and they reported many more mechanical constants than our precision warrants.

For our purposes, satisfactory values of $\omega_e$ and $\omega_e x_e$ can be found from your data and the fact that they observed the $3 \leftarrow 0$ R(0) transition for H$^{35}\text{Cl}$ at 8365.8437 cm$^{-1}$ and for D$^{35}\text{Cl}$ at 6122.5661 cm$^{-1}$. (Should you want to look up their paper, there is a typo in their Table IV which lists $3 \leftarrow 0$ transitions. The top part of the table is for D$^{35}\text{Cl}$, and the bottom is for D$^{37}\text{Cl}$.) Use these data along with your own and appropriate expressions derived from Eq.'s (1)–(4) to find $\omega_e$ and $\omega_e x_e$ values. These authors found

\begin{align*}
\omega_e(\text{H}^{35}\text{Cl}) &= 2990.96638 \text{ cm}^{-1} \\
\omega_e(\text{D}^{35}\text{Cl}) &= 2145.1523 \text{ cm}^{-1} \\
\omega_e x_e(\text{H}^{35}\text{Cl}) &= 52.836415 \text{ cm}^{-1} \\
\omega_e x_e(\text{D}^{35}\text{Cl}) &= 27.173645 \text{ cm}^{-1}.
\end{align*}

(If you look at their paper, you will find these constants in Table V where they are given in terms of the so-called Dunham constants, $Y_{ij}$, with $Y_{10} = \omega_e$ and $Y_{20} = -\omega_e x_e$. The Dunham expansion of the energy is just a power series expansion like Eq. (1), but written in a more general and compact way as

$$E_{v,J} = \sum_{i,j} Y_{ij} \left( v + \frac{1}{2} \right)^i \left( J(J + 1) \right)^j.$$  

It is based on a theoretical treatment of the energy levels of a one-dimensional potential well (i.e., a diatomic chemical bond) first devised by J. L. Dunham in 1932. The fact that Eq.'s (2) and (3) incorporate a minus sign in front of $\alpha_e$ and $\omega_e x_e$ simply reflects the fact that, by so doing, these constants will (almost always) be positive numbers. Anharmonicity, $\omega_e x_e$, (almost always) lowers energies from the harmonic value, as does vibrational-rotational coupling, $\alpha_e$.

Finally, convert your two values of $\omega_e$ into equilibrium force constants, $k_e$, via the relationship (be careful with units: we have $\omega_e$ in cm$^{-1}$ units, and $c$ is stated earlier in m s$^{-1}$ units)

$$\omega_e = \frac{1}{2\pi c} \left( \frac{k_e}{\mu} \right)^{1/2}.$$  

Are the values of $k_e$ different for HCl and DCl? Should they be? (Answer these and other bold font questions and bold font "you should show that" derivations in your write-up.)
Summary of what to do:

1. Record the spectra
2. Tabulate the wavenumbers of observed transitions
3. Assign quantum numbers to these transitions
4. Use combination differences to find $B_0$ and $B_1$ values
5. Average these values and subject them to error analysis
6. Find $B_e$, $\alpha_e$, and $r_e$, along with their errors
7. Find $\omega_e$, $\omega_e\alpha_e$, and $k_e$
8. Answer the questions and derivations in bold font in the handout

Optional problems for up to 10% extra credit

1. As every chemist knows, HCl is an acid, and its electronic structure should be thought of as H+Cl−, indicating the polar nature of the chemical bond. Given that the electric dipole moment of HCl is $3.6975 \times 10^{-30}$ C m, that $r_e$ is $1.274 \times 10^{-10}$ m, and that the elementary charge is $1.602 \times 10^{-19}$ C, a good guess as to the amount of charge transferred from H to Cl is

$$\frac{3.6975 \times 10^{-30} \text{ C m}}{1.274 \times 10^{-10} \text{ m}} = 2.901 \times 10^{-20} \text{ C} = 0.1811 \text{ times the charge on an electron.}$$

In computing $r_e$, we used a reduced mass based on the precise nuclear masses. Now, here's the subtle problem mentioned earlier in the writeup. What spectroscopic resolution is needed to distinguish an $r_e$ based on atomic nuclear masses from one based on partially ionized atomic masses? In other words, is spectroscopy capable of measuring that 0.1811 times the mass of an electron has been transferred from H to Cl, or is this too small an effect to observe?

2. It is easy to see how $B_e$ and $\omega_e$ vary, via $\mu$, with isotopic substitution. How do $\alpha_e$ and $\omega_e\alpha_e$ depend on $\mu$? Do your data agree with the theoretical $\mu$ dependence? (The first dozen or so pages of the first chapter in Microwave Spectroscopy, by Townes and Schawlow, will be of particular help here.)

3. Here's a chance to apply ideas from Chem 72 to this lab. (This problem is doubly optional for those who haven't had Chem 72 yet.) Calculate which J state in the $v = 0$ state has the greatest equilibrium population at 300 K, and then check your spectra to see if transitions originating from that state are the most intense. If they aren't, can you suggest a reason why? Comment in general on the characteristic intensity profile of your spectra.