

## Vibration-Rotation Spectrum of HCl

When a molecule absorbs light, its internal energy increases by the photon energy  $h\nu$  (where  $h$  is Planck's constant and  $\nu$  is the frequency of the light). This energy may be put into rotation, vibration, electronic excitation, or some combination of these. In this experiment, the energy of the infrared photons used will not be sufficient to cause electronic excitation, but will excite both vibration and rotation.

### THEORY

The problem of light absorption by HCl will be approached in the following way. First, the rigid-rotor/harmonic oscillator model will be discussed. This model views the molecule's rotations as if the molecule consisted of two point masses held rigidly apart at a fixed distance (the bond length). The vibrations are assumed to be harmonic; that is, the bond is assumed to follow Hooke's law when stretched, so that the frequency gives the force constant of the bond. This combination of models sounds contradictory, but molecules typically change their bond length by less than 10% as they vibrate back and forth in the lowest allowed energy levels, where they usually have less than 10% of the energy required to dissociate. Corrections to this model are needed to accurately describe the transitions in real molecules: they provide information about the range of vibrational motion and the dissociation energy. Additional sections covering the allowed transitions, spectroscopic conventions, and line intensities are included.

#### The rigid rotor

Solving the Schrödinger equation for the rigid-rotor model of diatomic molecules yields an expression for the possible rotational energies:

$$E_J = BJ(J+1) \quad J = 0,1,2,\dots \quad (1)$$

Here  $J$  is the "rotational quantum number" and  $B$  is the rotational constant for the particular molecule

$$B = \hbar^2/2I \quad (\text{MKS units} = \text{Joules}) \quad (2)$$

Where  $\hbar = h/2\pi$  ( $h$  is Planck's constant) and  $I$  is the molecule's moment of inertia, which depends only on the masses of the atoms ( $M_1$  and  $M_2$ ) and the bond length ( $r$ ):

$$I = \mu r^2 \quad (3)$$

$$\mu = M_1 M_2 / (M_1 + M_2) \quad (4)$$

$\mu$  is called the reduced mass and has units of mass. A measurement of the rotational constant  $B$  thus determines the bond length.

In spectroscopy, it is convenient to specify transition energies and spectroscopic

constants in wavenumbers  $\tilde{\nu}=1/\lambda$  (standard unit  $\text{cm}^{-1}$ ) because they are proportional to energies ( $E=hc\tilde{\nu}$ ) but do not depend on the speed of light,  $c$ , or Planck's constant,  $h$ . This saves effort and allows direct comparison to experiments that used older, less accurate values of these constants. To convert between Joules and wavenumbers, just divide by  $hc$ .

**CAUTION: the same symbols are used for the same quantities even if units are different. In wavenumbers, the equation for the rotational constant becomes**

$$B = h/8\pi^2 cI \quad (B \text{ in } \text{cm}^{-1}) \quad (5)$$

**To calculate B in wavenumbers with Eq. (5), use h and I in MKS units, but c in cm/s.**

Putting equations (3) and (5) into equation (1) gives the relationship between the rotational energy (in wavenumbers), the reduced mass, the bond distance, and the rotational quantum number.

$$B = h/(8\pi^2 c\mu r^2) \quad (6)$$

$$E_J = \frac{hJ(J+1)}{8\pi^2 c\mu r^2} \quad (7)$$

Because a photon has an intrinsic spin angular momentum of  $\hbar$ , and angular momentum is conserved, there is a "selection rule" for angular momentum of  $\Delta J = \pm 1$ . (In more complicated cases with angular momentum about more than one axis,  $\Delta J = 0$  can be allowed.) An HCl molecule in  $J=5$  can only make transitions to  $J=4$  or  $J=6$  by absorbing one photon.

### The Harmonic Oscillator

The solution to the Schrödinger equation for the harmonic oscillator gives us the vibrational energy levels. The harmonic oscillator has a potential energy  $V(x)=(1/2)kx^2$  where  $k$  is the Hooke's law force constant. The classical vibrational frequency for a harmonic oscillator is

$$\omega = (k/\mu)^{1/2} \quad (\text{units} = \text{rad/s}) \quad (8)$$

where  $k$  is the force constant and  $\mu$  is the reduced mass. The classical vibrational period of the oscillator is  $T_{\text{vib}} = 2\pi/\omega$ .

The solutions of the Schrödinger equation for a harmonic oscillator depend on this frequency and a vibrational quantum number  $\nu$

$$E_\nu = \hbar\omega(\nu + 1/2) \quad (\nu = 0, 1, 2, \dots) \quad (9)$$

Note that the vibrational energy can never be zero. This is in agreement with Heisenberg's uncertainty principle, which states that the momentum and position of a

particle can't be simultaneously known with complete precision. If the energy were zero, then we would know the atoms were not moving and that their momentum was zero. The atoms' positions would also be fixed at the bottom of the well, and thus known. The minimum energy of  $(\frac{1}{2})\hbar\omega$  is just enough to keep the atoms wiggling so that the uncertainty principle is satisfied. (Note that zero rotational energy is allowed because there is no rotational potential energy to determine the angular position of the atoms).

Again, it is convenient to introduce a spectroscopic constant with units of  $\text{cm}^{-1}$ . Dividing the energy by  $hc$ , we have

$$E_v = \omega_e(v+1/2) \quad (\text{units} = \text{cm}^{-1}) \quad (10)$$

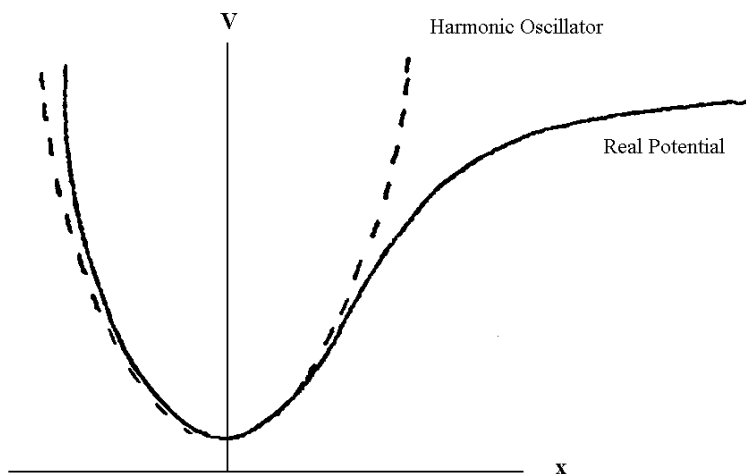
where the spectroscopic constant  $\omega_e = \hbar\omega/hc = \omega/2\pi c$  should not be confused with the angular frequency  $\omega$ . [Eq. (10) will be extended to the anharmonic oscillator below.]

The assumption that the molecular dipole is proportional to bond length leads to a selection rule of  $\Delta v = 0, \pm 1$  for the harmonic oscillator. Real molecules usually fall apart (anharmonic potential) into neutral atoms (zero dipole) at large  $r$ , so this rule is not exact. The extent to which this rule is broken provides information on how charge is shared at different bond lengths.

### Phenomenological corrections to the basic theory

The previous two sections discussed the energy levels of rigid rotors and harmonic oscillators. Real molecules are not described exactly by such models. Spectroscopists use the previously noted equations for the energy levels, but add in additional terms or make some of the "constants" in the expressions dependent upon the energy state.

The true molecular potential energy function for bond stretching is not a harmonic potential. Figure 1 shows a typical potential function for a molecule along with the



**Figure 1 Molecular Potential and Harmonic Oscillator Approximation**

potential function for a harmonic potential. Notice that while the midpoint between classical turning points is unchanged as the energy increases for the harmonic potential, the midpoint moves to the right (longer bond lengths) on the real potential. In a real molecule, the average distance between the atoms almost always increases as vibrational energy increases. What will this do to the rotational energy levels? The rotational constant in Eq. (6) depends on the bond length  $r$ . Since the average bond length changes with vibrational level  $v$ ,  $B$  must change also. Assuming this is a small effect, a first order Taylor series expansion will make  $B$  a linear function of  $v$ . Instead of a single  $B$ , we will have one rotational constant for each value of  $v$ . These are designated  $B_v$ , where the subscript corresponds to the vibrational quantum number.

$$B_v = B_e - \alpha (v+1/2) \quad (11)$$

$B_0$  will correspond to the value of  $B$  for the lowest vibrational level,  $B_1$  for the next vibrational level, and so on. When the subscript  $e$  is used, it will designate the value  $B$  would have if the molecule were at the minimum of the potential well. Thus, using the subscript  $e$  is like discussing the unreachable quantum state corresponding to  $v = -\frac{1}{2}$ . This system of subscripts is used in the same way for other spectroscopic quantities.  $\alpha$  is sometimes called the vibration-rotation coupling constant. We can now write the rotational energy as

$$E_{\text{ROT}(J,v)} = B_v J(J+1) \quad (12)$$

An additional deviation from the idealized rigid rotor model is centrifugal stretching. As the molecule rotates, the atoms feel an apparent “centrifugal force” separating them in much the same way your arms tend to fly out when you spin around. For molecules that rotate faster (high  $J$ ) the vibrational wavefunction is distorted (“centrifugal distortion”) toward larger bond lengths. This centrifugal distortion causes the apparent rotational constant  $B$  to decrease as  $J$  increases.

The anharmonicity of the potential also affects the vibrational energy levels. The levels move closer together as  $v$  increases. Eq. (10) is generalized by adding another term to account for this effect of anharmonicity on the vibrational levels.

$$E_v = \omega_e(v+1/2) - \omega_e x_e (v+1/2)^2 \quad (\text{in cm}^{-1}) \quad (13)$$

$\omega_e x_e$  is generally considered to be a single parameter and is called the anharmonicity.

### Selection rules

The changes in the rotational and the vibrational quantum numbers during a transition are restricted by “selection rules”. Transitions not allowed by the selection rules are termed “forbidden transitions”. The angular momentum and harmonic oscillator selection rules are:

$$\Delta J = \pm 1 \quad \text{and} \quad \Delta v = 0, \pm 1 \quad (14)$$

The case of  $\Delta v=0$  is a pure rotational transition that occurs in a different region of the electromagnetic spectrum (usually the microwave region). When vibrational energy is absorbed or emitted by this “model” diatomic, the vibrational level can only change by one and the rotational level can only change by one. For real diatomic molecules, the  $\Delta J = \pm 1$  rule still holds because it arises from conservation of angular momentum. However, the anharmonic potential and bond length dependent charge distribution of real molecules allow weaker transitions with  $\Delta v = \pm 2, \pm 3$ , etc. These “overtone transitions” are forbidden in the harmonic approximation.

### Energies of Transitions

Now that we are armed with information about possible energy levels and the allowed transitions between them, we may consider what energies of light may be absorbed. The energy of the absorbed photon will be equal to the energy difference between the initial and final states of the molecule. We can write the total energy of a given state as

$$E_{J,v} = E_{\text{ROT}(J,v)} + E_v = B_v J(J+1) + \omega_e (v+1/2) - \omega_e x_e (v+1/2)^2 \quad (15)$$

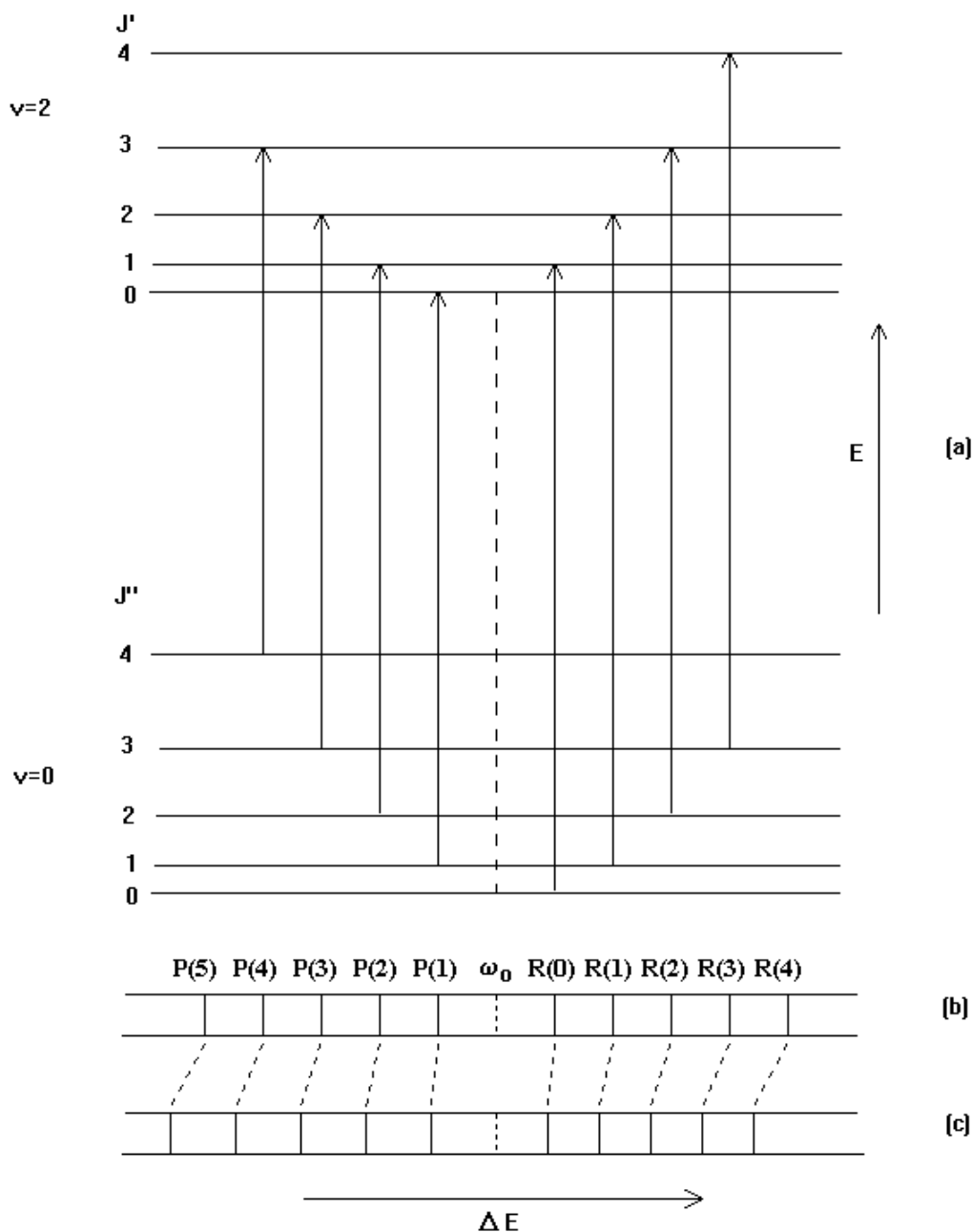
By convention, spectroscopists designate variables for the upper state by single primes and variables for the lower state by double primes. The energy of a transition will be

$$\begin{aligned} \Delta E = E_{J',v'} - E_{J'',v''} = & B_{v'} J'(J'+1) - B_{v''} J''(J''+1) + \omega_e (v'+1/2) \\ & - \omega_e x_e (v'+1/2)^2 - \omega_e (v''+1/2) + \omega_e x_e (v''+1/2)^2 \end{aligned} \quad (16)$$

Also by convention, lines with  $J' = J''-1$  are known as P-branch transitions, and lines with  $J' = J''+1$  are called R-branch transitions. (This labeling scheme produces the same labels for the absorption and emission lines with the same frequency.)

A diagram of energy levels for HCl is shown in Fig. 2. The energy spacing for vibrations is about 100 times as wide as the spacing between rotational levels. The vertical arrows show transitions from  $v = 0$  to  $v = 2$  allowed by the rotational selection rule  $\Delta J = \pm 1$ . The lengths of the arrows correspond to the energies of the transitions. A dotted line is drawn corresponding to the hypothetical  $J' = 0 \rightarrow J'' = 0$  transition, which is forbidden. The wavenumber for this hypothetical transition called the band origin  $\nu_0$ .

The equations for transition energies contain many terms and it might appear to be a nearly impossible job to determine all the spectroscopic constants. Spectroscopists have found the method of “combination differences” simple and accurate. By subtracting the energies of pairs of lines corresponding to transitions with the same initial or with the same final states, most of the terms will drop out. For instance, the difference in energy between the P(1) line and the R(1) line is just  $6B'$ , because both lines start from the same initial state. Using two lines with the same final state allows the determination of  $B''$ .



**Figure 2 Schematic Vibration-Rotation Energy Levels and Schematic Spectrum**  
 (a) Energy level diagram showing first few P and R branch transitions. (b) Idealized vibration rotation spectrum. (c) Actual vibration rotation spectrum taking vibration-rotation coupling into account

### Line Intensities

The intensities of the observed lines in the spectrum are proportional to the number of molecules in the initial state. The principle of spectroscopic stability states that every

initial state has the same total transition probability  $P$  (a fact observed before the development of quantum mechanics). The sum of the transition probabilities from  $J''$  to  $J' = J'' - 1$  and  $J' = J'' + 1$  must thus be proportional to the degeneracy of the level  $J''$ , which is  $2J'' + 1$ . (This degeneracy arises because every rotational energy level  $J$  has  $2J + 1$   $M_J$  sublevels, with  $M_J$  ranging from  $-J, -J + 1, \dots, +J$ . The same degeneracy occurs for the hydrogen atom.) Calling the proportionality constant  $z$ , we have

$$P[P(J'')] + P[R(J'')] = z(2J'' + 1). \quad (17)$$

The principle of microscopic reversibility requires equal forward and backward transition probabilities:

$$P[J \rightarrow J + 1] = P[J + 1 \rightarrow J]. \quad (18)$$

This implies  $P[R(J'')] = P[P(J'' + 1)]$ .\* Since there is no  $P(0)$  transition, Eq. (17) implies  $P[R(0)] = z$ . Using Eq. (18), this leads to  $P[P(1)] = z$ , which upon substitution in Eq. (17) implies  $P[R(1)] = 2z$ . Substitution in Eq. (18) yields  $P[P(2)] = 2z$ , so that Eq. (17) yields  $P[R(2)] = 3z$ . The patterns are:  $P[R(0)] = z$ ,  $P[R(1)] = 2z$ ,  $P[R(2)] = 3z \dots$

$$P[R(J'')] = (J'' + 1)z. \quad (19)$$

$$P[P(J'')] = J''z. \quad (20)$$

The general results can be proved because if one *assumes* that  $P[R(J'')] = (J'' + 1)z$  is true for any  $J''$ , it implies [by Eq. (18)]  $P[P(J'' + 1)] = (J'' + 1)z$ , which implies [by Eq. (17)] that  $P[R(J'' + 1)] = ((J'' + 1) + 1)z$ , thus proving that the same relation is true for  $J'' + 1$ . Since this assumption [Eq. (19)] is actually true for  $J'' = 0$ , it must hold generally.

The Boltzmann distribution may be used to determine the relative populations of the possible initial states, and hence the intensities of transitions from them. The Boltzmann probability of finding a molecule in some state  $J, M_J$  is

$$N(J, M_J) \propto e^{-E_J/kT} \quad (21)$$

where  $E_J$  is the energy of the state  $E_J = BJ(J + 1)$ .

The intensities of P and R branch lines are given by sums of products of transition probabilities and Boltzmann probabilities. Putting Eq. (19) and (20) together with Eq. (21),

$$I[P(J'')] \propto J'' \exp[-BJ''(J'' + 1)/kT]. \quad (22)$$

$$I[R(J'')] \propto (J'' + 1) \exp[-BJ''(J'' + 1)/kT] \quad (23)$$

As expected, these expressions indicate that the lowest allowed P-branch transition is  $P(1)$  while the lowest allowed R-branch transition is  $R(0)$ .

## EXPERIMENTAL

### PART I (Overtone spectrum, $v''=0$ to $v'=2$ )

The Lab Coordinator or TA will have already filled the gas cell with HCl. Run the first overtone spectrum on the Cary 17 spectrophotometer (settings are on a card on the machine). This instrument is capable of giving resolution such that the  $H^{37}Cl$  lines can be resolved from the  $H^{35}Cl$  lines.

### PART II (Fundamental spectrum, $v''=0$ to $v'=1$ )

This spectrum will be done on one of the FTIR instruments available in the lab. First you will take a background spectrum with nothing in the chamber. Then you will take a spectrum of the empty gas cell. Allow the FT-IR to purge itself of any  $CO_2$  and water vapor by waiting 5 minutes to perform a scan after opening the lid. After taking the spectrum of the empty cell, allow a TA or Lab Coordinator to transfer some HCl into the empty cell. Return it to the chamber and take a spectrum. Subtracting the two spectra allows for the isolation of the HCl spectrum. Have the program label the peaks of the spectrum and print out the two branches separately.

## CALCULATIONS

From the fundamental spectrum do the following:

1. Label the transition that corresponds to each line in the HCl absorption spectrum.
2. What is the energy of the  $v'' = 0$  to  $v' = 1$  band origin? Use this value in Part A, #6.

From the first overtone spectrum do the following:

1. Measure the wavelength of each of the lines as accurately as possible. Tabulate the results according to branch,  $J''$ , and isotopic species.
2. Obtain as many values of  $B''$  and  $B'$  as possible, making use of appropriate differences. The ones to use should be obvious from Figure 2. For example,  $R(0) - P(2) = 6B''$  and  $R(1) - P(1) = 6B'$ , etc. Can you notice a slight decrease in  $B$  values as  $J$  increases? If so, what causes this?
3. Assuming  $B$  to be a linear function of vibrational energy, calculate  $B_e$  and the vibration-rotation coupling constant,  $\alpha$ .
4. Calculate the equilibrium internuclear distance for  $H^{35}Cl$  and  $H^{37}Cl$ . Compare with the literature value of  $r_e = 1.2746$  Angstroms.
5. Calculate the  $v''=0$  to  $v'=2$  band origin (the wavenumber for the hypothetical  $J'' = 0$  to  $J' = 0$  transition).

6. Derive an expression for calculating the anharmonicity constant by making use of the band origins for several vibrational transitions. This may be done by manipulating equations for the energies of the  $v''=0$  to  $v'=1$  and  $v''=0$  to  $v'=2$  band origins. Use the results calculated from #5 and the value of the energy for the  $v''=0$  to  $v'=1$  band origin (measured in fundamental spectrum) to calculate  $\omega_e x_e$  for  $\text{H}^{35}\text{Cl}$ .
7. One can estimate the dissociation energy by differentiating the vibrational energy in Eq. (13) to find the vibrational quantum number at which the vibrational energy is a maximum. This extrapolation assumes that no higher order terms [e.g.  $(v+1/2)^3$  terms] are needed to fit the energy levels. It leads to the estimate

$$D = (\omega_e)^2 / 4\omega_e x_e$$

Use this formula to estimate the dissociation energy of  $\text{H}^{35}\text{Cl}$ . Compare this value with the experimental value of  $35,730 \text{ cm}^{-1}$ . What is the dissociation energy in Kcal/mole?

8. For  $\text{H}^{35}\text{Cl}$ , use Eq. (22) and (23) to calculate the relative intensities of the first few rotational lines at  $25^\circ\text{C}$ . Which lines in the P and R branches would you predict to be most intense from this calculation? Which ones are most intense?
9. List the values which you obtained for  $B'$ ,  $B''$ ,  $B_e$ ,  $\alpha$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $r_e$ ,  $D$  and the literature values for  $B_e$ ,  $\alpha$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $r_e$  and  $D$ .

**\*NO ERROR PROPOGATION IS NECESSARY!\***

## DISCUSSION

- Explain the FT-IR source spectrum.
- Explain what an interferogram is.
- Explain what controls the resolution of an FTIR instrument.
- Where do the harmonic oscillator and rigid rotor approximations fail?

## Notes and References

G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 1, Spectra of Diatomic Molecules, D. VanNostrand, Princeton, 1950, Chap. III.

G. M. Barrow, Molecular Spectroscopy, McGraw-Hill Book Company, 1962, Chaps. 2, 3, and 7.

\*We have ignored the change in vibrational quantum number during the transition in making the inference that  $P[v'', J'' \rightarrow v', J' = J'' + 1] = P[v', J' + 1 \rightarrow v'', J'']$  implies  $P[R(J'')] = P[P(J' + 1)]$ . This inference is strictly true only for  $v'' = v'$ , but becomes exact if we neglect the vibrational wavefunction dependence on J (“centrifugal distortion”).

<http://www.dartmouth.edu/~chem81/labs/hcl.html>

<http://webbook.nist.gov/chemistry/name-ser.html>

<http://webbook.nist.gov/cgi/cbook.cgi?Name=hydrogen+chloride&Units=SI&cIR=on&cDI=on>

<http://www.chem.unl.edu/chem484/diatomic/> (some strange idea that real intensity formulas wrong, but gives them. Determines Boltzmann constant from them.)

## Appendix 1:

### The CARY 17

