EXPERIMENT 7

VIBRATION-ROTATION SPECTRUM OF HCl AND DCl

INTRODUCTION

Spectroscopy probes transitions between different energy levels, or states, using light. Light in the infrared region of the EM spectrum can be used to probe vibrational and rotational transitions. The specific rotational and vibrational states are a result of the interactions between the different atoms in the molecule and, since each molecule has a unique arrangement of atoms, it has a unique IR spectrum almost like a fingerprint. In this lab, you will obtain the spectra of HCl and DCl.

When we record a spectrum, all we end up with is a set of lines whose frequencies and intensities we know. What we cannot tell just by looking at the lines is which energy levels are involved in the transition that leads to each line. To find out anything useful from the spectrum, our first step has to be to assign the lines.

By 'assign' we usually mean specifying the quantum numbers of the energy levels involved. There may be more than one quantum number needed to specify the level, depending on the complexity of the problem. The way we go about assigning and interpreting a spectrum is as follows:

· We start with a model for the energy levels. Typically, we use the energy levels available from solving the Schrodinger equation for a simple system, such as the rigid rotor or the harmonic oscillator in the case of radiation in the IR region.

· We then determine the selection rules which apply to these levels and thus predict the form of the spectrum, taking into account that the intensities will be affected by the populations of the energy levels as predicted by the Boltzmann distribution (equation 1).

$$n_j = g_j \frac{N}{q} e^{\frac{-\varepsilon_j}{\kappa T}}$$
(8.1)

- Having done this, we can compare the predicted spectrum with the real spectrum, and see if they can be made to match up. Typically there will be parameters to adjust, such as rotational constants and vibrational frequencies. The process of matching up the experimental and predicted spectra is often aided by looking for patterns, such as repeated spacing of lines.

- If there is reasonable agreement between the two spectra, then the assignment process is complete, as we know the assignment for the predicted spectrum. The values of any parameters used in the model can then be interpreted, for example to obtain bond lengths.

- However, the match between the experimental and predicted spectra is rarely perfect. Usually we need to refine our model for the energy levels in order to obtain a better fit – for example, by introducing the effects of anharmonicity or centrifugal distortion.

The process of assigning and understanding a spectrum is thus one of refining the model in order to obtain the best agreement. The following is a review of the models used in this lab. Students should read Chapter 12 of Atkins and de Paula[1] and Chapters 8 and 9 of Cooksy[2].

Rotational States

The simplest model that considers rotational states is the rigid rotor (RR). This model considers two atoms at a fixed distance that rotate as a unit. A detailed quantum description of the rigid rotor is found in Cooksy [2] and Atkins and de Paula[1]. Here, we will just consider the result.

The quantized energy levels of the rigid rotor are given in equation 2, where I is the

$$E_J = \frac{\hbar^2}{2I} J(J+1) \tag{8.2}$$

moment of inertia shown in equation 3. In the latter, μ is the reduced mass, given in

$$I = \mu r^2 \tag{8.3}$$

equation 4, and r is the distance between the two atoms in the rigid rotor. J is the rotational

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{8.4}$$

quantum number and spans integers from 0 to ∞. The degeneracy of the Jth quantum level is

2J+1 (used in the Boltzmann distribution, equation 1).

Vibrational States

The simplest model for vibrations is the harmonic oscillator (HO). Both Atkins and

de Paula[1] and Cooksy[2] present many details on the derivation of the quantum vibrational

levels for the harmonic oscillator. Again, we will consider only the result. The vibrational

levels for the harmonic oscillator are given by equation 5, where υ spans integers from 0 to ∞

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right) h\nu \tag{8.5}$$

and ν is the frequency of vibration (equation 6; k is the spring constant). Remember that the

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2\pi} \left(\frac{V''(x)}{\mu}\right)^{1/2} \tag{8.6}$$

harmonic oscillator potential is V(x) =½kx² and so the spring constant is directly related to

the curvature, or the second derivative, of the harmonic oscillator potential, V"(x).

Interaction between Rotational and Vibrational States (ro-vibrational spectra)

When a gas-phase molecule undergoes a vibrational transition, the energy of the

absorbed photon may be slightly lower than or slightly higher than the exact energy needed

to change the state of the molecule from υ =0 to υ =1. This excess (or slight deficiency) of

energy can lead to a simultaneous rotational transition provided ΔJ = 0, ±1. These selection

rules were derived using the rigid rotor and harmonic oscillator assumptions. The resulting

ro-vibrational spectra can be divided into three branches. Transitions where $\Delta\upsilon=+1$ and $\Delta J=+1$ are called the "R branch", those where $\Delta\upsilon=+1$ and $\Delta J=-1$ are called the "P branch", and those where $\Delta\upsilon=+1$ and $\Delta J=0$ are the "Q branch". For diatomic molecules the Q branch is a forbidden transition (rotation about the bond axis has no effect on the dipole moment) and is not be observed in a ro-vibrational spectrum.

Figure 1 illustrates the energy levels for the two lowest vibrational states of a diatomic molecule and shows some of the transitions that are allowed between the sublevels. Also shown is a hypothetical IR spectrum of HCl. What you should notice is that the spectrum is separated into two branches, with a gap between them. The gap is where the infrared transitions would be if no change in the J value occurred, *i.e*, $\Delta J=0$. This region is referred to as the Q branch and only involves a change in the vibrational quantum number. The low frequency branch (P branch) consists of $\Delta J=-1$ transitions and the high frequency branch (R branch) consists of $\Delta J=+1$ transitions. Note that the quantum numbers for the lower state in the transition are traditionally labeled as υ" and J" while those for the upper state are labeled υ' and J' (See Lecture 20 notes).

You will notice that as you count away from the center of the spectrum the intensity of individual lines increases, goes through a maximum and then falls off in the wings. This pattern arises from a combination of two effects, the population of molecules in a quantum state and the number of quantum states at a particular energy. Within a band, the intensities are proportional to the population of molecules in the ground vibrational-rotational level. The population in state J is given approximately by equation 7, where κ is Boltzmann's constant,

$$N(J) = N_0(2J+1)e^{\frac{-B_0 J(J+1)}{\kappa T}} \tag{8.7}$$

which must have the proper units so that the argument of the exponential factor is unitless,

and N_0 is the population in the state $\upsilon=0$, J=0. The (2J + 1) factor is the degeneracy of the rotational energy level and arises from the fact that 2J + 1 values of the m_J (orientational) quantum number are possible for each value of J. The exponential factor is called a Boltzmann factor and gives the temperature dependence of the distribution.
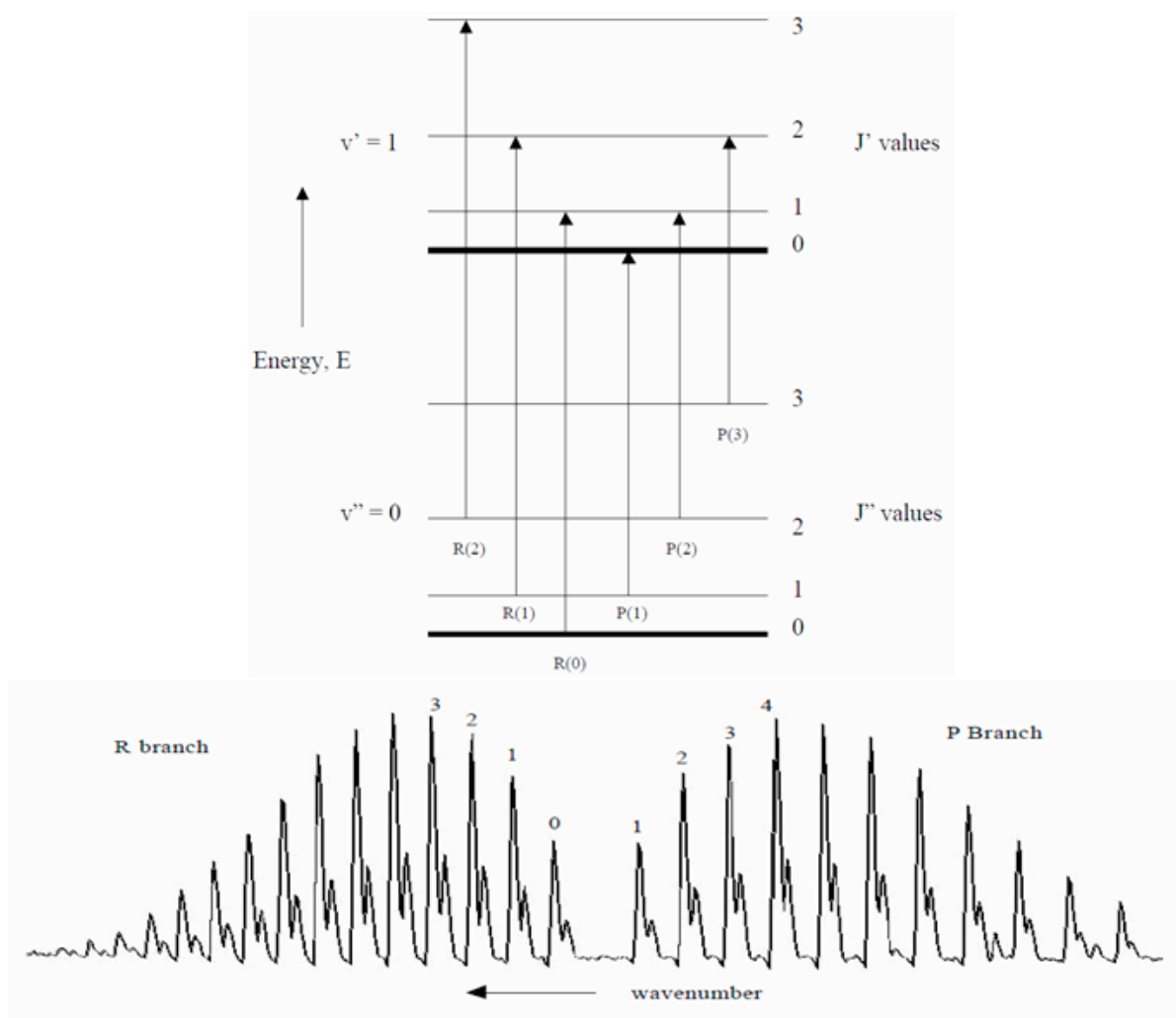

Figure 8.1. Anatomy of a vibration-rotation band showing rotational energy levels in their respective upper and lower vibrational energy levels, along with some allowed transitions. The spectral lines corresponding to these transitions are shown in the spectrum. Note the splitting that arises from the $H^{35}Cl$ and $H^{37}Cl$ isotopic shifts.

As in all quantitative work, using the correct units is vital to avoid extracting nonsense from the spectra. In molecular spectroscopy, it is usually safest to convert everything to cgs units. To make sure you know where to begin, you should decide on consistent units for ν, B, I, r, D, α and κ. The following Table provides values that may be helpful.

Table 8.1. Useful constants and conversion factors.

h	6.626×10^{-27} erg s	6.6261×10^{-34} Js
κ	1.381×10^{-16} erg/K	1.38066×10^{-23} J/K
1 cm^{-1}	1.986×10^{-16} erg	1.98630×10^{-34} J
m$_H$	1.007825 amu	1.672623×10^{-27} kg
m$_D$	2.0140 amu	3.3425×10^{-27} kg
m^{35}Cl	34.968852 amu	5.803558×10^{-26} kg
m^{37}Cl	36.965903 amu	6.135000×10^{-26} kg

If we assume that the vibrational and rotational energies can be treated independently, the total energy of a diatomic molecule (ignoring its electronic energy which will be constant during a ro–vibrational transition) is simply the sum of its rotational and vibrational energies, as shown in equation 8, which combines equation 1 and equation 4.

$$E_{v,J} = \left(v + \frac{1}{2}\right)hv + \frac{\hbar^2}{2I}J(J+1) \tag{8.8}$$

From a pedagogical point of view this provides an excellent framework for exploring quantized vibrational and rotational energy states. The appeal of the HO/RR model arises from the relatively simple mathematical expressions that produce a convenient and solvable

form of the Schrodinger equation. However, you might wonder how well this idealized model works for a real system.

Diatomic molecules are not perfectly rigid rotors. The rotations distort the molecule and change r. The higher the rotational quantum number, J, the longer the molecule becomes. This centrifugal distortion effect is usually very small and important only for very large J values. The harmonic oscillator model also has limitations. The fact that diatomic molecules dissociate makes it clear that they are not perfect harmonic oscillators. A potential that takes into account the fact that diatomic molecules can dissociate is the Morse oscillator potential, equation 9, where D_e is the dissociation energy. The energy levels for a Morse oscillator are

$$V(x) = D_e\left(1 - e^{-ax}\right)^2 \tag{8.9}$$

similar to the harmonic oscillator energy levels but include an anharmonic term. As the vibrational quantum number υ increases, the levels get closer together.

Combining these two corrections, the energies of the rotational-vibrational levels are given, in units of cm^{-1}, by equation 10. The first and second terms account for the vibrational

$$E_{\upsilon,J} = v_e\left(\upsilon + \frac{1}{2}\right) - v_e X_e\left(\upsilon + \frac{1}{2}\right)^2 + B_\upsilon J(J+1) - D_\upsilon J^2(J+1)^2 \tag{8.10}$$

energy, and the third and fourth terms account for the rotational energy. The fundamental vibrational frequency of the molecule is v_e. The first anharmonic correction to the vibrational frequency is $v_e X_e$. B_υ is the rotational constant for a given vibrational level, and D_υ is the centrifugal distortion constant. B_υ may be obtained from the equilibrium geometry of the molecule using the following relationships (equations 11 & 12), where B_e is the equilibrium rotation constant, α is the anharmonicity correction factor to the rotational energy and I_e is the equilibrium moment of inertia.

$$B_\upsilon = B_e - \alpha\left(\upsilon + \frac{1}{2}\right) \tag{8.11}$$

$$B_e(cm^{-1}) = \frac{h}{8\pi^2 c I_e}$$

(8.12)

PROCEDURE[3]

CAUTION! Thionyl chloride is a lachrymator. HCl gas is corrosive and care must be taken to contain it within the optical cell and bubble the excess through water.
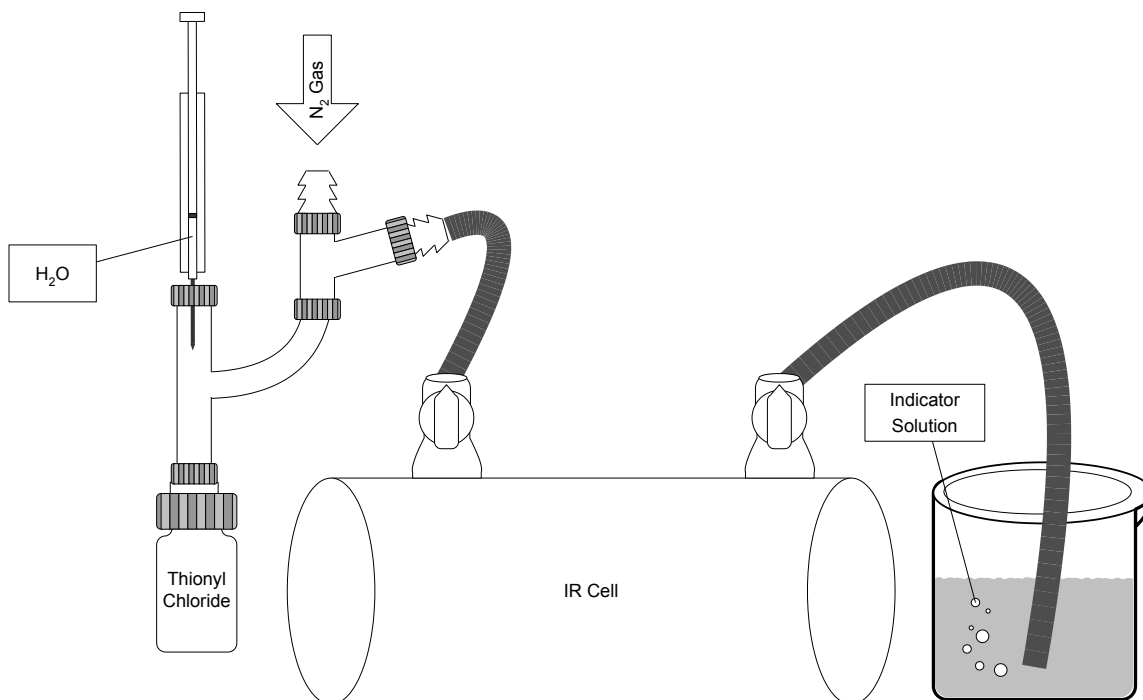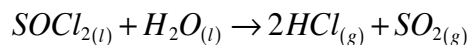
Figure 2: The microscale apparatus used to produce and transfer HCl/DCl gas to an IR gas cell. Adopted from ref. 3.

You will carry out a reaction that involves thionyl chloride and a mixture of water and deuterium oxide to produce HCl/DCl gas and SO_2 gas according to the following reaction:

$$SOCl_{2(l)} + H_2O_{(l)} \rightarrow 2HCl_{(g)} + SO_{2(g)}$$

1. The microscale apparatus is constructed in a fume hood similar to the block diagram shown in Figure 2 (see instructor for details).

2. Approximately three drops of thymol blue is placed into a beaker of water into which is placed the outlet tube from the gas cell.

3. One-half milliliter of thionyl chloride is admitted to the reaction vessel using a microlitre syringe and the entire apparatus is purged with N_2 for 1 minute.

4. Purged the IR cell with N_2, simultaneously close the inlet stopcock and outlet stopcock and move the cell to the FT-IR and collect a background spectrum (See instructor for details) using the following settings:

    a. Resolution: 1 cm^{-1}
    b. No. of Scans: 64
    c. Final format: Absorbance
    d. Correction: None
    e. Background Handling: Choose "collect background before every sample"

5. Return the cell to the microscale apparatus and run N_2 through the apparatus for 1 minute.

6. The N_2 line is then closed with a pinch clamp to prevent HCl/DCl gas from migrating back to the regulator (be careful of any negative pressure).

7. Approximately 1 mL of deuterium oxide and 0.5 mL of deionized water are transferred into a small vial using microlitre syringes.

8. One-half milliliter of the D_2O/H_2O mixture is drawn into a microlitre syringe.

9. The syringe is then inserted through the septum and the water is added to the reaction vessel dropwise until the reaction begins to produce gas as is immediately evident from the bubbles escaping from the outlet tube in the beaker of water. The reaction is allowed to proceed until the thymol blue changes color from yellow to red.

10. Once the reaction has reached the endpoint indicated in Step 9, the inlet stopcock and outlet stopcock are closed simultaneously.

11. Disconnect the inlet and outlet tubes from the cell and immediately place the inlet tube into the beaker of water. Reconnect the N_2 gas to the reaction vessel to relieve any negative pressure.

12. Take the cell to the FT-IR spectrometer and collect a spectrum as instructed.

13. Reconnect the outlet tube and purge the IR cell with N_2 gas for 1 minute.

14. Refill the microliter syringe with deionized water, insert it through the septum and add water to the vessel dropwise until the reaction has gone to completion as evidenced by no more gas bubbles being generated.

15. Since thymol blue changes color over two pH ranges, it can be used to determine when the water in the beaker has been neutralized with 2 M NaOH. Once it has been neutralized, it can be disposed of appropriately.

DATA ANALYSIS

Assigning the Spectrum

The first step in obtaining spectroscopic constants is to assign the spectrum. Several methods may be used but the most obvious way for a diatomic molecule is to count outward from the gap between the R and P branches. Remember that the P(0) line is the $J" = 0 \rightarrow J' = 0$ forbidden transition, so you will not see a peak for it. Next you need to tabulate the transition frequencies of each isotope ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$) for later manipulation.

Finding Rotational Constants, B_υ

A description of the underlying reasoning that is used to obtain the rotational constants for a particular vibrational level is outlined here. First, consider the $\upsilon = 1$ level.

Note that if you subtract the frequency of the P(J") line from the that of the R(J") line, the difference is given by equation 13, where (J") is written as (J) for simplicity. This equation

$$R(J) - P(J) = B_1\left[(J+2)(J+1) - J(J-1)\right] - D_1\left[(J+2)^2(J+1)^2 - J^2(J-1)^2\right] \qquad (8.13)$$

can be simplified to equation 14 and then rearranged into a more useful slope-intercept form (equation 15) so that a plot of $[R(J) - P(J)]/(2J + 1)$ versus $(J^2 + J + 1)$ can be use to obtain B_1

$$R(J) - P(J) = 2B_1(2J+1) - 4D_1(2J+1)(J^2 + J + 1) \qquad (8.14)$$

$$\frac{R(J) - P(J)}{(2J+1)} = 2B_1 - 4D_1(J^2 + J + 1) \qquad (8.15)$$

and D_1. To obtain the rotational constants for the $\upsilon=0$ level, perform the same type of manipulation for $R(J-1) - P(J+1)$, whose difference is given by equation 16, which simplifies to equation 17. These equations apply to both the HCl and DCl species.

$$R(J-1) - P(J+1) = B_0\left[(J+1)(J+2) - J(J-1)\right] - D_0\left[(J+1)^2(J+2)^2 - J^2(J-1)^2\right] \qquad (8.16)$$

$$R(J-1) - P(J+1) = 2B_0(2J+1) - 4D_0(2J+1)(J^2 + J + 1) \qquad (8.17)$$

Finding Molecular Parameters

Using the B_υ values and equation 11, you can obtain B_e for each isotope. Subsequently, you can calculate the equilibrium bond length (combining equation 12 and 3) and the average bond length for each isotope and vibrational level. If the assumptions we have made are all correct, r_e and α should be independent of isotope. Is this true within the precision of the data?

<center>**REPORT**</center>

Results & Analysis	Include a table of B_0, B_1, D_0, D_1, B_e α, and r_e for each isotopomer ($H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$) and all graphs used for obtaining these values
Discussion	Compare your values with those given in references 4-6 (See Experiment #4). You should include percent error calculations assuming the literature value to be correct. 1. Do the values of the spectroscopic constants B_e, B_υ and D_υ

vary with isotope and/or with vibrational level in a way that you would expect?

2. Does r_e change for each isotope? Explain your answers.

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

4. Use the Boltzmann distribution (equation 7) to model what the intensities of the absorption peaks should be for your experimental data. Does your data match this theory? How would the distribution change at higher temperatures?

5. What additional spectroscopic information could be obtained from your data? Be as detailed as possible.

Appendices   Include the data that you obtained experimentally and the spectra with the line positions labeled. Be sure to also include a sample calculation for each type performed.

REFERENCES

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5. D.H. Rank, D.P. Eastman, S. Rao, and T.A.Wiggins, *J. Opt. Soc. Am.* **1962**, 52, 1-7.
6. http://physics.nist.gov/PhysRefData/MolSpec/Diatomic/Html/Tables/HCl.html