Vibrational-Rotational Spectra of HCl and DCl

Dustin Wheeler

Friday 7ᵗʰ February, 2020

Friday 7ᵗʰ February, 2020

This experiment is concerned with the rotational fine structure of the infrared vibrational spectrum of a linear molecule such as HCl. By interpreting the details of this spectrum, it is possible to obtain the moment of inertia of the molecule and thus the internuclear separation. In addition, the pure vibrational frequency determines the force constant that is a measure of the bond strength. By also investigating DCl, the isotope effect can be observed.[1]

[1] Transcribed (with corrections) from Nibler, et al.

Introduction

The infrared region of the spectrum extends from the long-wavelength end of the visible region at $1\,\mu$m out to the microwave region at about $1000\,\mu$m. It is common practice to specify infrared frequencies in wavenumber units: $\tilde{\nu}\,(\text{cm}^{-1}) = 1/\lambda = \nu/c$, where c is the speed of light in cm/s. Thus, this region extends from $10\,000\,\text{cm}^{-1}$ down to $10\,\text{cm}^{-1}$. Although considerable work is now being done in the far-infrared region (below $400\,\text{cm}^{-1}$), the spectral range from $4000\,\text{cm}^{-1}$ to $400\,\text{cm}^{-1}$ has received the greatest attention because the vibrational frequencies of most molecules lie in this region.

Theory

Almost all infrared work makes use of absorption techniques in which radiation from a source emitting all infrared frequencies is passed through a sample of the material to be studied. When the frequency of this radiation is the same as the vibrational frequency of the molecule, the molecule may be vibrationally excited. This results in loss of energy from the radiation and gives rise to an absorption band. The spectrum of a polyatomic molecule generally consists of several such bands arising from different vibrational motions of the molecule. This experiment involves diatomic molecules, which have only one vibrational mode.

The simples model of a vibrating diatomic molecule is a harmonic oscillator for which the potential energy depends quadratically on the change in internuclear distance. The allowed energy levels of a harmonic oscillator, as calculated from quantum mechanics[1], are

$$E(v) = h\nu\left(v + \frac{1}{2}\right), \qquad (1)$$

where v is the vibrational quantum number having integral values $0, 1, 2, ...$; ν is the vibrational frequency in Hz, and h is the Planck constant, $6.626 \times 10^{-34}\,\text{J·s}$.

The simplest model of a rotating diatomic molecule is a rigid rotor or "dumbell" model in which the two atoms of mass m_1 and m_2 are considered to be joined by a rigid, weightless rod. The allowed energy levels for a rigid rotor may be shown by quantum mechanics[1] to be

$$E(J) = \frac{h^2}{8\pi^2 I} J(J+1) , \tag{2}$$

where the rotational quantum number J may take integral values $0, 1, 2, ...$ The quantity I is the moment of inertia, which is related to the internuclear distance r and the reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$ by

$$I = \mu r^2 . \tag{3}$$

Since a real molecule is undergoing both rotation and vibration simultaneously, a first approximation to its energy levels, $E(v,J)$ would be the sum of eqs. (1) and (2). A more complete expression for the energy levels of a diatomic molecule[2, 3] is given below, with the levels expressed as *term values T* in units of cm^{-1} rather than as energy values E in J:

$$T(v,J) = \frac{E(v,J)}{hc} =$$
$$\tilde{v}_e \left(v + \frac{1}{2}\right) - \tilde{v}_e \chi_e \left(v + \frac{1}{2}\right)^2 + B_e J(J+1) \tag{4}$$
$$- D_J J^2 (J+1)^2 - \alpha_e \left(v + \frac{1}{2}\right) J(J+1) ,$$

where c is the speed of light in cm/s, $\tilde{v}_e$ is the frequency in cm^{-1} for the molecule vibrating about its equilibrium internuclear separation r_e, and

$$B_e = \frac{h}{8\pi^2 I_e c} . \tag{5}$$

The first and third terms on the right-hand side of eq. (4) are the harmonic-oscillator and rigid-rotor terms with $r = r_e$. The second term (containing the constant χ_e) takes into account the effect of anharmonicity on the vibrational levels. Since the real potential $U(r)$ for a molecule differs from a harmonic potential U_{HO}[2], the real vibrational levels are not quite those given by eq. (1) and a correction term is required. The fourth term (involving the *centrifugal distortion constant D_J*) accounts for the effects of centrifugal stretching on the rotational levels. Since a chemical bond is not truly rigid but more like a stiff spring, it stretches somewhat when the molecule rotates. Such an effect is only important for high J values, since the constant D_J is usually very small. The last term in eq. (4) accounts for interactions between vibration and rotation. During a vibration, the internuclear distance r changes; this changes the moment of inertia and affects the rotation of the molecule. The constant α_e is also quite small, but this term should not be neglected.
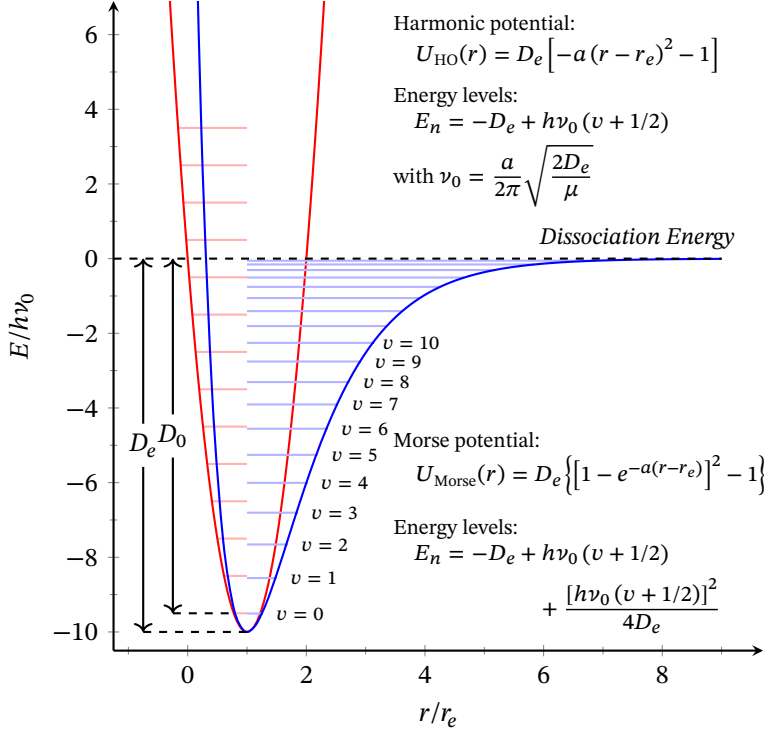
[2] See fig. 1

Figure 1: Schematic diagram showing potential energy curves as a function of internuclear separation, r, for a diatomic molecule. The curve for a harmonic oscillator is depicted in red while the Morse potential is drawn in blue. Vibrational levels are shown for each.

Selection Rules

The harmonic-oscillator, rigid-rotor selection rules[3] are $\Delta v = \pm 1$ and $\Delta J = \pm 1$; that is, infrared emission or absorption can occur only when these "allowed" transitions take place. For an anharmonic diatomic molecule, the $\Delta J = \pm 1$ selection rule is still valid, but weak transitions corresponding to $\Delta v = \pm 2, \pm 3$, etc. (overtones) can now be observed[3]. Since we are interested in the most intense absorption band (the "fundamental"), we are concerned with transitions from various J'' levels of the vibrational ground state ($v'' = 0$) to J' levels in the first excited vibrational state ($v' - 1$). From the selection rule, we know that the transition must be from J'' to $J' = J'' \pm 1$. Since $\Delta E = h\nu = hc\tilde{\nu}$, the frequency $\tilde{\nu}$ (in wavenumbers) for this transition will be just $T(v', J') - T(v'', J'')$. When $\Delta J = +1$ ($J' = J'' + 1$) and $\Delta J = -1$ ($J' = J'' - 1$), we find, respectively, from eq. (4) that

$$\tilde{\nu}_R = \tilde{\nu}_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e J''^2 \qquad J'' = 0, 1, 2, \dots \qquad (6)$$

$$\tilde{\nu}_P = \tilde{\nu}_0 - (2B_e - 2\alpha_e)J'' - \alpha_e J''^2 \qquad\qquad J'' = 0, 1, 2, \dots \qquad (7)$$

where the D_J term has been dropped and $\tilde{\nu}_0$, the frequency of the *forbidden* transition from $v'' = 0, J'' = 0$ to $v' = 1, J' = 0$ is

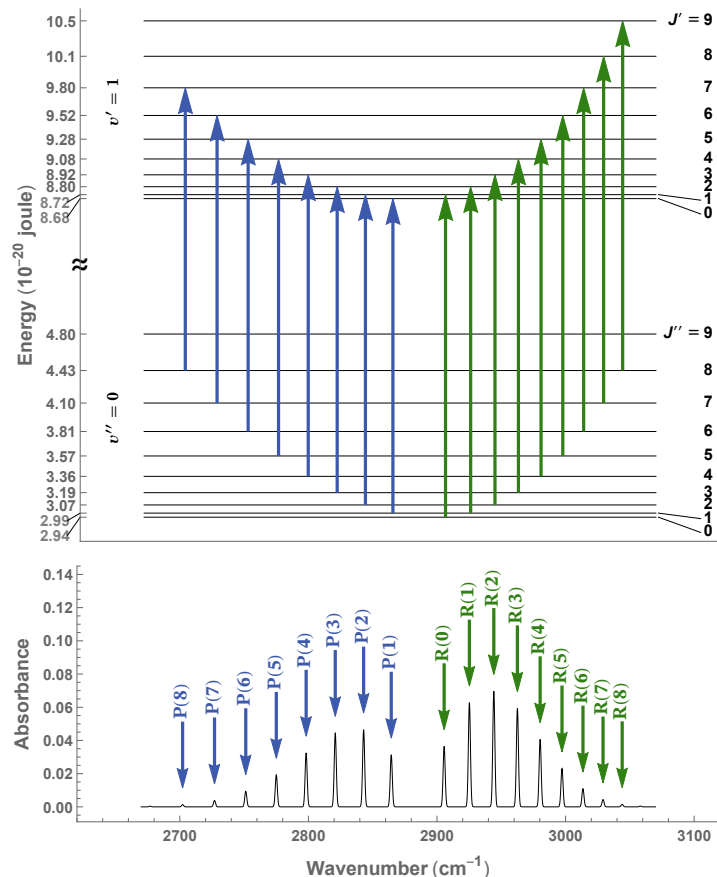$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e \chi_e . \qquad (8)$$

Figure 2: Rotational energy levels for the ground vibrational state ($v'' = 0$) and the first excited vibrational state ($v' = 1$) in a diatomic molecule. the vertical arrows indicated allowed transitions in the R and P branches; the numbers above the arrows index the value J'' of the lower state. Transitions in the Q branch ($\Delta J = 0$) are not shown, since they are not infrared active. Image source code by Whitney R. Hess and Lisa M. Goss, Idaho State University (2011), distributed under a CC BY-NC-SA 3.0 license (via Wolfram Demonstrations Project).

The two series of lines given in eqs. (6) and (7) are called R and P branches, respectively. These allowed transitions are indicated on the energy-level diagram given in fig. 2. If α_e were negligible, eqs. (6) and (7) would predict a series of equally spaced lines with separation $2B_e$ except for a missing line at $\tilde{\nu}_0$. The effect of interaction between rotation and vibration (non-zero α_e) is to draw lines in the R branch closer together and spread the lines in the P branch farther apart, as shown for a typical spectrum in fig. 2. For convenience, let us introduce a new quantity m, where $m = J'' + 1$ for the R branch and $m = -J''$ for the P branch, as shown in fig. 2. It is now possible to replace eqs. (6) and (7) with a single equation:

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)\,m - \alpha_e m^2\,, \tag{9}$$

where m takes all integral values and $m = 0$ yields the frequency $\tilde{\nu}_0$ of the forbidden "purely vibrational" transition. If one retains the D_J term of eq. (4) (which assumes $D'' = D' = D_J$), eq. (9) takes the form

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)\,m - \alpha_e m^2 - 4D_J m^3\,. \tag{10}$$

Thus, a multiple linear regression can be performed to determine $\tilde{\nu}_0$, B_e, α_e, and D_J.

Isotope Effect

When an isotopic substitution is made in a diatomic molecule, the equilibrium bond length, r_e and the force constant, k, are unchanged, since they depend only on the behavior of the bonding electrons. However, the reduced mass, μ, does change, and this will affect the rotation and vibration of the molecule. In the case of rotation, the isotope effect can be easily stated. From the definitions of B_e and I, we see that

$$\frac{B_e^*}{B_e} = \frac{\mu}{\mu^*}, \tag{11}$$

where an asterisk is used to distinguish one isotopic molecule from another.

For a harmonic oscillator model, the frequency $\tilde{\nu}_e$ in wavenumbers is given by

$$\tilde{\nu}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}, \tag{12}$$

which leads to the relation

$$\frac{\tilde{\nu}_e^*}{\tilde{\nu}_e} = \sqrt{\frac{\mu}{\mu^*}}. \tag{13}$$

The ratio $\tilde{\nu}_e^*/\tilde{\nu}_e$ differs slightly from this harmonic ratio due to deviation of the true potential function from a quadratic form, as depicted in fig. 1. A closer approximation to the solid curve can be had by adding cubic and higher anharmonic terms to $U(r)$[3], viz.,

$$U(r) = \frac{1}{2}k(r - r_e)^2 + c_1(r - r_e)^3 + c_2(r - r_e)^4 + \dots \tag{14}$$

Although somewhat complicated, it can be shown[3, 4] that the c_1 and c_2 terms yeild, as the first correction to the energy levels, precisely the $-\tilde{\nu}_e\chi_e(\upsilon + 1/2)^2$ term given in eq. (4). A similar conclusion is reached if $U(r)$ is taken to have the Morse potential form given by[4]

$$U(r - r_e) = D_e\left\{[1 - \exp\{-\beta(r - r_e)\}]^2 - 1\right\}. \tag{16}$$

In both cases, the mass dependence of $\tilde{\nu}_e\chi_e$ is found to be greater than for $\tilde{\nu}_e$ and is

$$\frac{\tilde{\nu}_e^*\chi_e^*}{\tilde{\nu}_e\chi_e} = \frac{\mu}{\mu^*}. \tag{17}$$

Equations (13) and (17) are useful in obtaining the $\tilde{\nu}_0^*$ counterpart of eq. (8),

$$\tilde{\nu}_0^* = \tilde{\nu}_e^* - 2\tilde{\nu}_e^*\chi_e^* = \tilde{\nu}_e\sqrt{\frac{\mu}{\mu^*}} - 2\tilde{\nu}_e\chi_e\frac{\mu}{\mu^*}, \tag{18}$$

and it is seen that a measurement of $\tilde{\nu}_0$ for HCl and DCl suffices for a determination of $\tilde{\nu}_e$ and $\tilde{\nu}_e\chi_e$. Alternatively or course, the latter constants can be determined from overtone vibrations ($\Delta\upsilon > 0$) of a single isotopic

[3] The Morse potential

[4] The parameter β is determined by equating k_e to the curvature of the Morse potential at $r = r_e$, yielding

$$\beta = \sqrt{\frac{k_e}{2hcD_e}}. \tag{15}$$

This three-parameter function has the desired values of $U(r = r_e) = -D_e$ and $U(r = \infty) = 0$. It provides a very good approximation to the real potential energy curve at all distances except $r \ll r_e$, a region of no practical significance.

form[5]. However, such overtones generally have low intensity and the transitions may fall outside the range of many infrated instruments, so the isotopic shift method is used in the present experiment.

Since HCl gas is a mixture of $H^{35}Cl$ and $H^{37}Cl$ molecules, a chlorine isotope effect will also be present. However, the ratio of the reduced masses is only 1.0015,: therefore, high resulution is required to detect this effect. HCl is predominantly $H^{35}Cl$, and for this experiment, we shall assume that the HCl bands obtained are those of $H^{35}Cl$. If deuterium is substituted for hydrogen, the ratio of the reduced masses, $\mu\left(D^{35}Cl\right)/\mu\left(H^{35}Cl\right)$, is 1.946 and the isotope effect is quite large.

Vibrational Partition Function[6–8]

The thermodynamic quantities for an ideal gas can usually be expressed as a sum of translational, rotational, and vibrational contributions. We shall consider here the heat capacity at constant volume. At room temperature and above, the translational and rotational contributions to C_v are constants that are independent of temperature. For HCl and DCl[6], the molar quantities are

[6] diatomic, and thus linear, molecules

$$\widetilde{C}_v\left(\text{trans}\right) = \frac{3}{2}R$$
$$\widetilde{C}_v\left(\text{rot}\right) = R\,. \tag{19}$$

The vibrational contribution to $\widetilde{C}_v$ varies with temperature and can be calculated from the vibrational partition function, q_{vib} using

$$\widetilde{C}_v\left(\text{vib}\right) = R\frac{\partial}{\partial T}\left(T^2\frac{\partial}{\partial \ln q_{\text{vib}}T}\right)\,. \tag{20}$$

The partition function, q_{vib}, of HCl or DCl is well-approximated by the harmonic-oscillator partition function, q_{HO}. Since the energy levels of a harmonic oscillator are given by $\left(v + \frac{1}{2}\right)h\nu$, one obtains[8]

$$q_{\text{HO}} = \sum_{v=0}^{\infty}\exp\left[\frac{-\left(v+\frac{1}{2}\right)h\nu}{kT}\right] = \frac{e^{-h\nu/(2kT)}}{1 - e^{-h\nu/(2kT)}}\,. \tag{21}$$

Combining eqs. (20) and (21), we find

$$\widetilde{C}_v\left(\text{vib}\right) = R\frac{u^2e^{-u}}{\left(1 - e^{-u}\right)^2}\,, \tag{22}$$

where $u = h\nu/(kT) = hc\tilde{\nu}/(kT) = 1.4388\tilde{\nu}/T$.

Safety Precautions

- HCl is a strong acid should be handled cautiously.

- All chemical work should be done in the fume hood and gloves should be worn at all times.

- Always wear safety glasses in the laboratory.

- The cell used to obtain the infrared spectra is valuable and non-replaceable. Handle it with extreme care. The windows are made from NaCl and are moisture sensitive. Do not touch the lenses with your fingers or expose them to moisture of any kind. If the cell filled with HCl breaks outside the fume hood, notify the instructor immediately and clear the area.

Procedure

This experiment must be performed with an IR spectrometer capable of medium to high resolution (> 2 wn resolution). A high-quality grating spectrometer and most FTIR instruments are generally capable of this, and FTIR instruments don't require calibration with external gas standards.

The infrared gas cell is constructed from a short (5 cm to 10 cm) length of large-diameter (4 cm to 5 cm) Pyrex tubing with a vacuum stopcock attached. Infrared-transparent windows are clamped agains O-rings at the ends of the cell or are sealed on the ends with Glyptal resin. For studies concentrating on the region $4000 \, \text{cm}^{-1}$ to $500 \, \text{cm}^{-1}$, NaCl windows will suffice. When the spectrum of interest extends down to $\sim 400 \, \text{cm}^{-1}$, KBr windows are necessary. Both types of salt windows become "foggy" on prolonged exposure to a moist atmosphere and should be protected[7] when not in use. In the present experiment, inert sapphire windows with transmission down to $1600 \, \text{cm}^{-1}$ are particularly convenient and relatively inexpensive.

[7] *e.g.,* stored in a dessicator

Filling the Cell and Recording the Spectra

Before beginning the synthesis, power on the FTIR. A 50-mL two-neck round-bottom flask and a 10-cm air condenser should be washed thoroughly with soap and water followed by several rinses with distilled water. Then, the glassware should be dried in an oven for approximately 10 min at a temperature near 110 °C. While the glassware is drying, purge the 5-cm gas cell (Thermo Fisher) with nitrogen gas to clean out the cell. This can be accomplished by attaching the tubing from the nitrogen tank regulator to one of the glass ports on the gas cell. Open both stopcocks on the gas cell and slowly open the needle valve on the nitrogen tank[8] until a steady stream of gas is exiting the open port of the gas cell. After allowing the

[8] Ask the instructor if you are unfamiliar with the use of a regulator.

gas to flow for 5 min, close the stopcock on the gas cell port releasing the gas and immediately close the stopcock on the port receiving the flowing gas, effectively sealing the gas cell. Immediately close the knob above the regulator nozzle, then close the needle valve controlling the tank's gas flow. Remove the tubing from the gas cell port and take the gas cell to the FTIR to obtain a background spectrum. Return the gas cell to the fume hood for the gas synthesis.

By this time, the glassware in the oven should be dry. Remove the dry glassware and place on a piece of paper towel to cool for another 10 min (or until cool to the touch). Prepare an indicator solution by dissolving 3 to 4 drops of bromcresol green in 300 mL of DI water in a 400-mL beaker. Attach Tygon tubing to the two stems of the gas cell, lubricating with glycerin to help the tubing slide on the glass. Take the end of one tube and submerge it in your indicator solution.[9]

To set up the rest of the apparatus, clamp the two-neck round-bottom flask to a ring stand. Prepare the air condenser by placing a plug of glass wool at the bottom and filling the rest with $CaCl_2$ (approximately 12 mesh). Insert the stem of the condenser into a stopper, again using glycerin for lubrication, and insert the stopper into the vertical neck of the round-bottom flask. Insert the end of the second tube (attached to the gas cell) into another stopper, then insert that stopper into the top of the air condenser. Mix ~5 mL of D_2O with ~5 mL concentrated HCl,[10], then pour the mixture into the round-bottom flask via the second neck. Finally, insert another stopper with a hole into the second neck of the flask.

With a disposable plastic pipette, obtain ~1 mL of concentrated H_2SO_4. Insert the pipette (**carefully** so as not to prematurely inject it) into the hole of the second stopper. Once you have verified that all of the holes are plugged, squeeze 1 to 2 drops of sulfuric acid into the solution. You should see vigorous bubbling in the flask. At this point, open the stoppers on the gas cell. Continue to *slowly* add sulfuric acid dropwise to the flask, watching the bubbles evolving in the indicator. When the indicator changes color, stop injecting acid and close the stopcocks on the gas cell. Carefully remove the tubes from the gas cell and proceed to the spectrometer for analysis.

Make sure the experimental settings are appropriate. The most important change to make is changing the resolution to the smallest possible value. This will allow you to distinguish the individual rotational transitions in the spectrum.

An arrangement for filling the cell is shown in fig. 3.

Theoretical Calculations

The following work will be done during the second week of this lab. You will need to calculate the physical properties of HCl and DCl using

[9] This will fill two roles: as a bubbler, it will prevent atmospheric gases from diffusing back into the cell; and as an indicator, it will show when sufficient HCl has passed through the cell. HCl is highly soluble in water, so the gaseous HCl will quickly acidify the water.

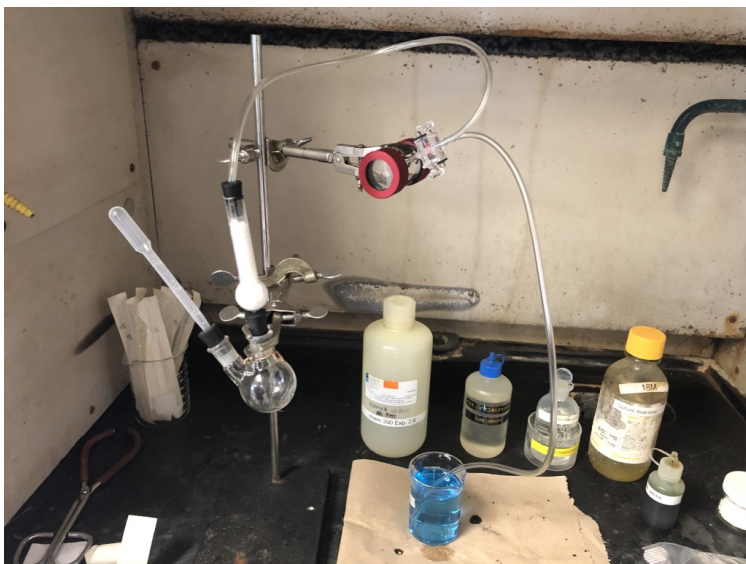[10] this is easiest to do in a small beaker

Figure 3: Glassware setup for generation and capture of HCl gas.

Gaussian[9], including the potential energy, equilibrium bond length, and the predicted vibrational and rotational energies for the molecule.

Using Gaussian, calculate the potential well for the HCl molecule. Because of the methods used for calculation, the mass of the nuclei doesn't influence geometry, so results will be the same for the four iso-topologues. To simplify this process, you can use a modified version of the `run_scan.sh` script from the Introduction to Computational Chemistry lab. These files should be available for you in the `PChem_Lab` folder on the desktop, but a copy is also available on Blackboard. You will need to modify the `run_scan.sh` script (printed below) from it's original distance parameters, set on lines 9 and 19. Reasonable ranges are 0.8 to 2.5 for the first range and 1.15 to 1.41 for the second range.

Contents of Script `run_scan.sh`

```bash
#!/bin/bash

# A simple script to populate a directory tree with instances of
# the input.temp file with substituted values of the DIST variable
# Created by MM / NYC Feb 2019

# Coarse-grained calculations for overall curve shape.
# Sets up and runs calculations for bond lengths from
# 0.7 to 1.3 Angstrom in 0.2 Angstrom steps.
for d in `seq -f "%3.2f" 0.7 0.1 1.3`
do
    echo "running position " $d
    mkdir dist_$d
    sed -e "s/DIST/$d/g" template_input.temp > dist_$d/input.com
```

```
15      cd dist_$d
16      g16 input.com > input.log
17      cd ../
18  done
19
20  # Fine-grained calculations for detailed values near curve minimum.
21  # Sets up and runs calculations for bond lengths from
22  # 0.85 to 0.95 Angstrom in 0.02 Angstrom steps.
23  for d in `seq -f "%3.2f" 0.85 0.02 0.95`
24  do
25      echo "running position " $d
26      mkdir dist_$d
27      sed -e "s/DIST/$d/g" template_input.temp > dist_$d/input.com
28      cd dist_$d
29      g16 input.com > input.log
30      cd ../
31  done
32
33  # Create a file to concatenate distance and energy values
34  printf "%5s%12s\n" dist "E[Ha]" > dist_E.dat
35
36  # Pull calculated energy values from each output file and
37  # append the distance and calculated energy to the data table.
38  for i in dist_[01]*
39      do
40      d=`echo $i | awk -F"_" '{print $2}'`
41      E=`grep "Done" $i/input.log | awk '{printf "%20.8f", $5}'`
42      printf "%5.2f%20.8f\n" $d $E >> dist_E.dat
43  done
```

Once you have calculated the potential energy surface for the molecule, perform an optimization and frequency analysis of the HCl molecule.[11] You only need to do this for $H^{35}Cl$ and $D^{35}Cl$. Here is an example header for the input file for this calculation.

[11] As outlined for H_2O in Problem 3 in the Introduction to Computational Chemistry lab.

```
1   %nproc=4
2   %mem=400MB
3   # MP2 def2qzvpp
4   # opt freq=(anharm,vibrot) scf=tight
5
6   <title information>
7
8   <charge> <multiplicity>
9   <atom1>(Iso=<mass_number>)        <x1>      <y1>      <z1>
10  <atom2>(Iso=<mass_number>)        <x2>      <y2>      <z2>
11  <empty line>
```

Line 3 sets the theory level and basis set to reasonable values for our

computational abilities and time. Line 4 tells Gaussian to optimize the geometry, then do a frequency analysis including anharmonic and vibrational-rotational coupling terms. You will need to replace all items in angle brackets with appropriate data.[12] Note the addition of the (Iso=<mass−number>) option after the element labels. By inserting the relevant value (total number of protons and neutrons) for your isotope (2 for deuterium), you can tell Gaussian to calculate using a different atomic mass.

You will need to search the output file for the relevant information. The vibrational and rotational constants are listed in tables under the heading "Vibrational Energies at Anharmonic Level". You will need to find the *two* values for the first-mode vibrational energy: one calculated using a harmonic analysis, the second incorporating the effects of anharmonicity. In this same section will be equilibrium rotational constants for the two degenerate rotational modes (labeled Ba(y) and Ca(z)) and the energy (relative to the zero-point energy) of the ground state (D_0).[13]

[12] *i.e.,* "*<atom1>*(Iso=*<mass_number>*)" should become "He(Iso=3)" for a ^{3}He atom

[13] All energy values are listed in cm^{-1}.

Data Analysis

1. Select your best HCl and DCl spectra and index the lines with the appropriate m values, as seen in fig. 2. If the ^{35}Cl/^{37}Cl splitting is seen, index the stronger ^{35}Cl lines. Make a table of these m values and the corresponding frequences, $\tilde{\nu}(m)$. Express the frequencies in cm^{-1} to the tenth of a cm^{-1}. Then, list the differences between adjacent lines, $\Delta\tilde{\nu}(m)$, which will be roughly $2B_e$, but will vary with m.

2. Plot $\Delta\tilde{\nu}(m)$ against m and plot the trendline for the series. If any values seem out of line, check the calculation for that cell.

3. Carry out a multiple linear least-squares fit to the data using eq. (9) to determine $\tilde{\nu}_0$, B_e, α_e, and their standard errors. Repeat this fitting procedure using eq. (10), noting that high m transitions will be the most important ones in determining D_J, due to its m^3 dependence.

4. Using your values of $\tilde{\nu}_0$ for HCl and DCl, determine $\tilde{\nu}_e$ and $\tilde{\nu}_e\chi_e$ for HCl. From $\tilde{\nu}_e$, calculate k for HCl.

5. Calculate I_e, the moment of inertia, and r_e, the internuclear distance, for both HCl and DCl. Tabulate your results, along with your estimates of the experimental uncertainty. Compare your results with literature values found in Kerr, Huber, and Herzberg [2].

6. Using your value of $\tilde{\nu}_0$ for HCl, calculate $\widetilde{C}_v$ (vib) at 298 K and at 1000 K from eq. (22). Compare the spectroscopic value $\widetilde{C}_v = 5/2R + \widetilde{C}_v$(vib) with the experimental $\widetilde{C}_v$ value obtained from directly measured values[6, 10] of $\widetilde{C}_p$ and the expression $\widetilde{C}_v = \widetilde{C}_p - R$: $\widetilde{C}_v = 20.80$ J·K/mol at 298 K and 23.20 J·K/mol at 1000 K.

Questions and Further Thoughts

Data Analysis

1. Compute the ratio of B_e^*/B_e and compare with the rigid-rotor prediction of eq. (11). How constant is r_e for HCl and DCl?

2. Compute $B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right)$ for the $v = 0$, 1, and 2 levels of HCl and DCl and, from these, obtain average r_v values for these levels. Comment in your report on the changes in these distances.

3. Compare your $\tilde{\nu}_0^*/\tilde{\nu}_0$ ratio with the ratio $\sqrt{\mu/\mu^*}$ expected for a harmonic oscillator. How anharmonic is the HCl molecule: *i.e.,* how large is χ_e?

4. Use your values of $\tilde{\nu}_e$ and $\tilde{\nu}_e \chi_e$ and eq. (4) to predict the frequencies of the first overtone transitions of HCl and DCl (ignore the rotational terms). Did you observe any evidence of these overtones in your spectra?

5. Do your spectra show any evidence of a $^{35}Cl/^{37}Cl$ isotope effect? Use eq. (11) to calculate the splitting expected for this effect for several P and R branch transitions in HCl and DCl.

6. Compare your experimental results with the values deduced from your theoretical calculations. For each calculation, report the values for total energy (D_e), vibration frequency ($\tilde{\nu}_0$), bond length (r_e), rotation constant B_e, and centrifugal distortion constant D_J. Additionally, you should plot the potential energy curve output by Gaussian against the theoretical Morse potential for the molecule.

Lab Report Guidelines

As previously stated, your lab report should consist of the following parts:

Title, Author and Date

Introduction and Objective A paragraph describing what we hope to find in this experiment, and how.

Experimental Procedure This should be a very brief general outline of the procedure, written out as a paragraph or two. Give the make and model for any major instruments you used, as well as any important settings. For IR spectroscopy, this especially means the spectral resolution and number of scans.

Results and Discussion This should include answers to the questions in the section "Questions and Further Thoughts". This should not be a separate section, but should instead be included organically in the discussion as a way of filling it out.

Conclusion

References

Appendix At the very end of your report, include examples of any calculations that you did by hand. Provide digital copies of the Excel (or other) files that you used to generate your graphs and copies of your Gaussian input files.

References

[1] PW Atkins. *Physical Chemistry*. 5th ed. Oxford University Press, Oxford, 1994, p. 795.

[2] JA Kerr, KP Huber, and G Herzberg. "Molecular Spectra And Molecular Structure: IV. Constants Of Diatomic Molecules". In: *Von Nostrand-Reinhold, New York* (1982). Although out of print, the contents are available as part of the *NIST Chemistry WebBook* at http://webbook.nist.gov.

[3] G Herzberg and JWT Spinks. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*. 2nd. D. Van Nostrand Company, 1989. Chap. 3.

[4] IN Levine. "Molecular spectroscopy". In: Wiley-Interscience, New York, 1975. Chap. 4.

[5] JW Nibler et al. *Experiments in Physical Chemistry*. McGraw-Hill, New York, 2014.

[6] GN Lewis and M Randall. "Thermodynamics". In: 2nd. (revised by KS Pitzer and L. Brewer). McGraw-Hill, New York, 1961, 60 and 419.

[7] DA McQuarrie. *Statistical Thermodynamics*. reprint. University Science Books, Sausalito, CA, 1985.

[8] IN Levine. *Physical Chemistry*. 4th ed. McGraw-Hill, New York, 1995, p. 469.

[9] MJ Frisch et al. *Gaussian 16, Revision B.01*. http://gaussian.com/gaussian16. 2016.

[10] Hugh M. Spencer. "Empirical Heat Capacity Equations of Gases and Graphite". In: *Industrial & Engineering Chemistry* 40.11 (1948), pp. 2152–2154. DOI: 10.1021/ie50467a029.

Further Reading

[1] JI Steinfeld. *Molecules And Radiation: An Introduction To Modern Molecular Spectroscopy*. 2nd. MIT Press, Cambridge, MA, 1985.

[2]   JM Hollas. *Modern Spectroscopy*. 3rd. John Wiley & Sons Inc., New
       York, 1996.

[3]   Peter F Bernath. "Spectra of Atoms and Molecules". In: Oxford
       University Press, Oxford, 1995. Chap. 7.