

Ro-vibrational Spectroscopy of Simple Diatomic Molecules

Introduction

The total energy of a molecule can be partitioned into three components: electronic energy, vibrational energy, and rotational energy. The postulates of quantum mechanics apply to the motion of electrons and atoms and thus the electronic, vibrational, and rotational energies of a molecule are quantized. To a very good approximation, these energies can be treated discretely and we can explore the transitions between quantized levels using spectroscopy. Spectroscopy involves the interaction of light with matter (atoms, molecules) and in all its forms is associated with the transition from one state (one wavefunction) to another state (new wavefunction). When the energy of a photon, E_p , matches the difference in the energy levels of two states of a molecule ($E_2 - E_1$) then energy is transferred from light to matter.

$$E_p = \frac{hc}{\lambda} = E_2 - E_1 \quad (1)$$

The various forms of spectroscopy that you'll encounter in a chemistry degree differ only in the energy (wavelength) of the electromagnetic radiation that interacts with the matter and the type of quantum mechanical transition they probe. These are summarized in Table 1:

Table 1. Spectroscopic quantum mechanical transitions

Type of Spectroscopy	Wavelength of Radiation (nm)	E_p (kJ/mol)	Type of transition
NMR	$\sim 10^9$ (radiowaves)	$\sim 10^{-8}$	Spin change of the nucleus of atoms
Rotational	$\sim 10^5$ (microwaves)	$\sim 10^{-2}$	Change in angular frequency of a molecule
Vibrational	$\sim 10^3$ (IR)	$\sim 10^3$	Change in molecule's vibration quantum number
Electronic	~ 500 (UV-Vis)	$\sim 10^5$	Change in molecule's electronic quantum number

The simplest model of a vibrating diatomic molecule is a simple harmonic oscillator (SHO), for which the potential energy depends quadratically on the displacement of the bond length from the equilibrium bond distance ($r - r_e$).

$$V = \frac{1}{2}k(r - r_e)^2 \quad \text{Potential of molecule (2)}$$

OH

The allowed energy levels for a SHO are

$$E(n) = hf_0 \left(n + \frac{1}{2} \right) \quad (3)$$

where $n = 0, 1, 2, 3, \dots$ is the vibrational quantum number, h is Planck's constant, and f_o is the fundamental frequency of the vibration in s^{-1} . This frequency, f_o , is related to k , the force constant (bond strength) of the vibration, and the reduced mass, μ of the two bonded atoms:

$$f_o = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4)$$

The reduced mass, μ , of the two bonded atoms of mass m_1 and m_2 , respectively, is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (5)$$

Figure 1 shows the relative energies of the first four allowed vibrational energy levels of the quantum mechanical SHO. These levels are quantized and evenly spaced. However, note that even when $n = 0$ that there is energy in the oscillator equal to $\frac{1}{2} h f_o$. This is contrary to what we would expect in a classical oscillator, which could have zero kinetic energy if there is no vibration. We call this the "zero-point energy" for the quantum mechanical harmonic oscillator, and it implies that even when in the lowest energy state that there is still some atomic motion.

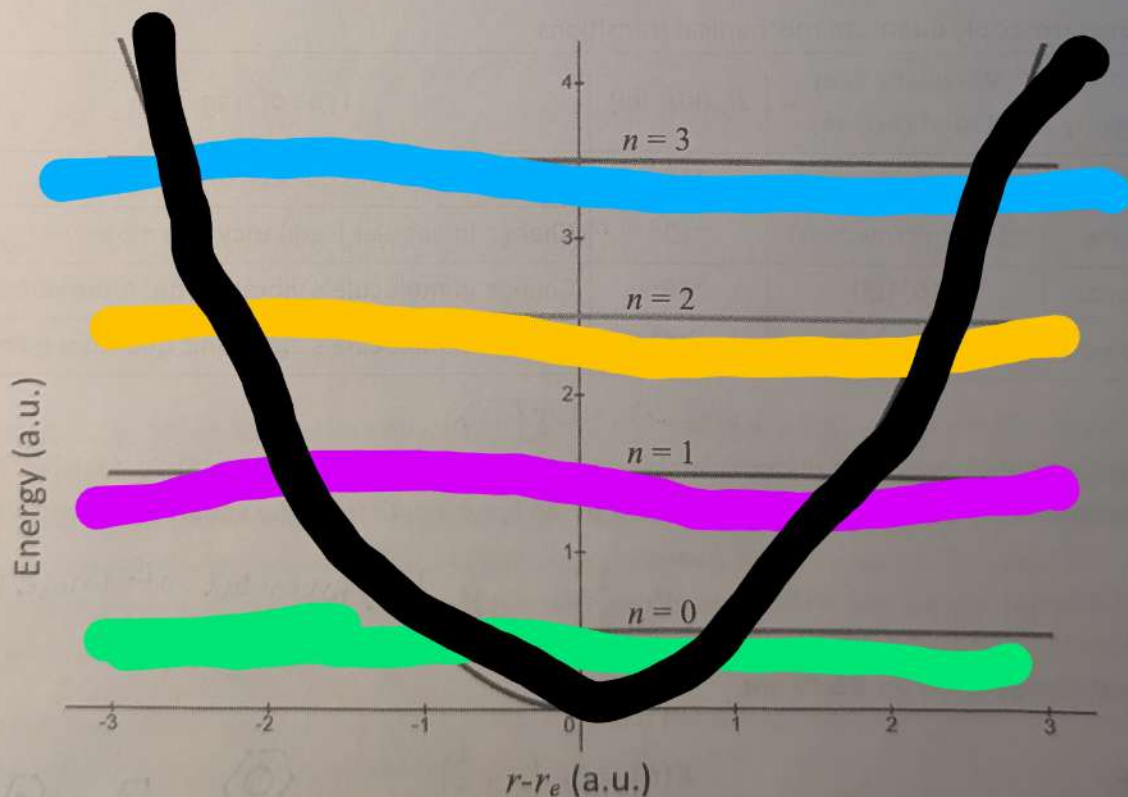


Figure 1. The potential energy curve (black line) for the SHO and the energy levels (green, purple, orange, and red lines) for the first four values of the vibrational quantum number, n .

In class, we will provide a rigorous proof that **the only spectroscopic transitions that are quantum mechanically allowed for the SHO (i.e. the selection rules) are those in which $\Delta n = 1$** . In this experiment, we will be looking at transitions in diatomic molecules which result from the absorption of an infrared photon and a change in quantum number from $n = 0$ to $n = 1$.

You will observe that the spectra that you collect are much more complex than showing a single absorption transition for the $n = 0$ to $n = 1$ vibrational transition. This complexity is largely a result of the fact that not only are the vibrational energy levels quantized, but so, too, are the molecule's rotational energy levels. As you saw in Table 1, the energy required to induce a change in the rotational level of the molecule is much smaller in magnitude than the energy to change the vibrational level. This energetically close spacing results in 'fine structure' observed for each $n = 0$ to $n = 1$ vibrational transition.

In class we will also discuss the rigid rotor which we use as a starting model for a rotating diatomic molecule. This model assumes that the bond between the atoms is entirely rigid and undergoes no distortion upon rotation. The quantum mechanically allowed energy levels for this system are:

$$E(J) = hcBJ(J + 1) \quad (6)$$

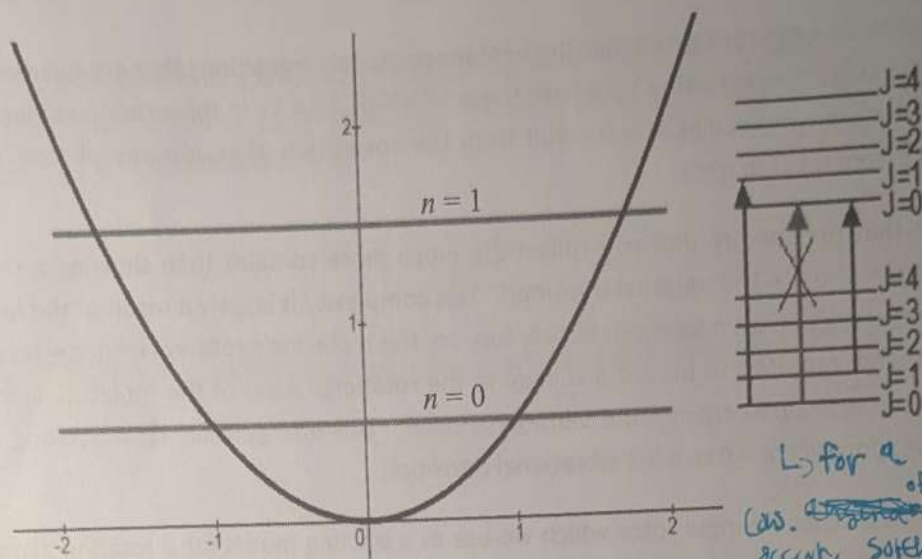
where $J=0, 1, 2, 3$ is the rotational quantum number, c is the speed of light in a vacuum, and B is called the rotational constant. B is given by equation 7:

$$B = \frac{h}{8\pi^2 cI} \quad (7)$$

where I is the moment of inertia of the rigid body and is given by:

$$I = \mu r_e^2 \quad (8)$$

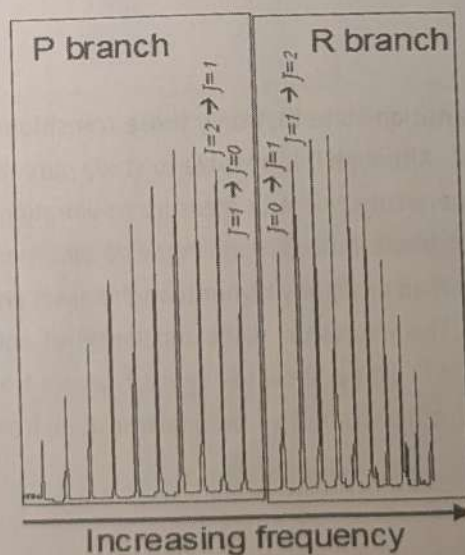
The selection rules for a rotational transition state that **only those transitions where the rotational quantum number, J , changes by ± 1 are allowed**. Although it is possible to study pure rotational transitions (this is often called microwave spectroscopy) it is more convenient to measure ro-vibrational spectra, which is what we are doing in this experiment. 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 $n = 0$ to $n = 1$. This excess (or slight deficiency) of energy can lead to a *simultaneous rotational transition* provided that $\Delta J = \pm 1$. This is shown in figure 2, where transitions from $n=0$ $J=0$ to $n=1$ $J=1$ and from $n=0$ $J=1$ to $n=1$ $J=0$ are allowed, but the purely vibrational transition from $n=0$ $J=0$ to $n=1$ $J=0$ is forbidden.



↳ for a diatomic gas,
 as ~~angular~~ momentum h must
 occur, there must be a
 transition in J

Figure 2. The energy levels for the SHO (coloured lines) and Rigid Rotor superimposed on the same energy axis. Note that the rotational energy levels are actually much smaller and are not equally spaced.

Ro-vibrational spectra can be divided into three branches. Transitions where $\Delta n = +1$ and $\Delta J = +1$ are called the "R branch", those where $\Delta n = +1$ and $\Delta J = -1$ are called the "P branch", and those where $\Delta n = +1$ and $\Delta J = 0$ are the "Q branch". For a diatomic molecule the Q branch is a forbidden transition and will not be observed in a ro-vibrational spectrum. A typical ro-vibrational spectrum with partially labelled changes in J is shown in Figure 3.



P-Q-R
 ↳
 ↳

forbidden
 ∴ must have change
 in momentum
 so will show up as
 blank! (inbetween P/R)

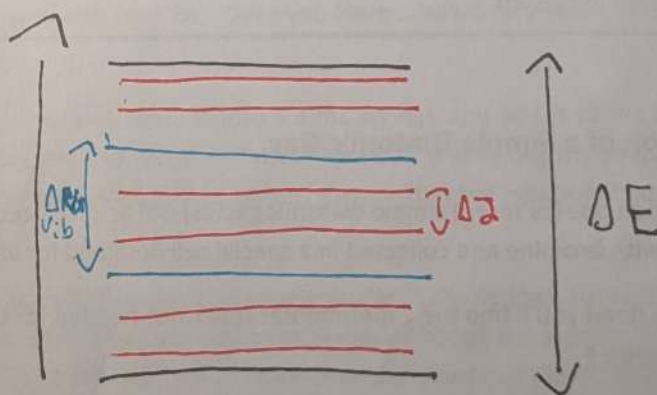
Figure 3. Ro-vibrational spectrum for a simple, heteronuclear diatomic molecule with labelled P and R branches. Note the absence of the Q branch.

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), in Joules, is simply the sum of its rotational and vibrational energies.

$$E_o = hf_o \left(n + \frac{1}{2} \right) + hcBJ(J+1) \quad (9)$$

The E_o indicates that this is the 0th order (simplest) model of our diatomic system. From a pedagogical point of view, this provides an excellent framework for exploring quantized vibrational and rotational energy states. The appeal of the SHO/RR model arises from the relatively simple mathematical expressions which produce a convenient and solvable form of the Schrödinger equation. However, you might wonder how well this idealized model works for a real system. In this experiment you will measure the gas phase, ro-vibrational spectra of simple diatomic molecules. Using the position of the peaks in the mid IR region we will test the applicability of these simple models. We will also add refinements to the SHO/RR in an effort to build "better" quantum mechanical models.

Born-Oppenheimer - Approximation
 ↳ translational motion not accounted for (very large)
 ↳ magnetic ^{and} nuclei very small, ignored!
 ↳ vibrational, electronic, rotational



$$E_{\text{Electronic}} > E_{\text{vibrational}} > E_{\text{rotational}}$$

→ When energy from a photon is absorbed for a vibrational transition, "left-over" energy results in rotational transitions
 ↳ since $\hbar \omega_{\text{rot}} \ll \hbar \omega_{\text{vib}}$, any left-over energy will be used for rotational motion

Experimental Procedure

SAFETY CONSIDERATIONS – READ CAREFULLY

When performing this experiment, use EXTREME CAUTION. The chemicals you are handling and producing are dangerous to inhale and get on your skin.

For this lab, you must wear at all times:

- Protective glasses (NOT just prescription glasses)
- Gloves
- A lab coat

All work must be done in the fume hood with the sash lowered as far as is reasonably possible (i.e., you must still be able to reach in safely to manipulate the apparatus and handle the chemicals). The sash must not be lifted higher than the Maximum Working Height shown on the fume hood. Do not remove the gas IR cell from the fume hood until you are sure it is properly sealed, and you are ready to take it to get the IR measurements. When you are done, dismantle it only in the fume hood.

The apparatus (round bottom flask and stir bar) must be dismantled and cleaned in the fume hood.

When cleaning the Br₂ syringe, please use the following procedure:

1. Carefully remove the needle from the syringe barrel. Rinse the needle inside and out with acetone and dispose of it in the sharps container.
2. Rinse the barrel of the syringe with acetone into the waste container and leave it in the fume hood to dry. The barrel of the syringe may still be a little brown - this is ok.

If you have any questions during the lab, please ask before doing something that might endanger you or another person in the lab.

Preparation of a Simple Diatomic Gas

In this reaction one (or more) simple diatomic gas(es) will be produced as a reaction product(s) from the reaction of toluene with bromine and collected in a special cell designed for gas-phase IR measurements.

In the fume hood you'll find the experimental apparatus needed for the synthesis. Check that it is connected as shown in Figure 4.

Turn on the water to begin circulating through the condenser. It needs to run only at a trickle.

Weigh out 0.1 g of anhydrous FeCl₃ on weighing paper and add it to the three-necked flask via the open port in the flask. Add a small magnetic stir bar to the flask. Place a rubber septum in the open port of the flask.

Before adding the solvent to the flask you must now ensure that the cell is first flushed with nitrogen gas and that the apparatus is not leaking.

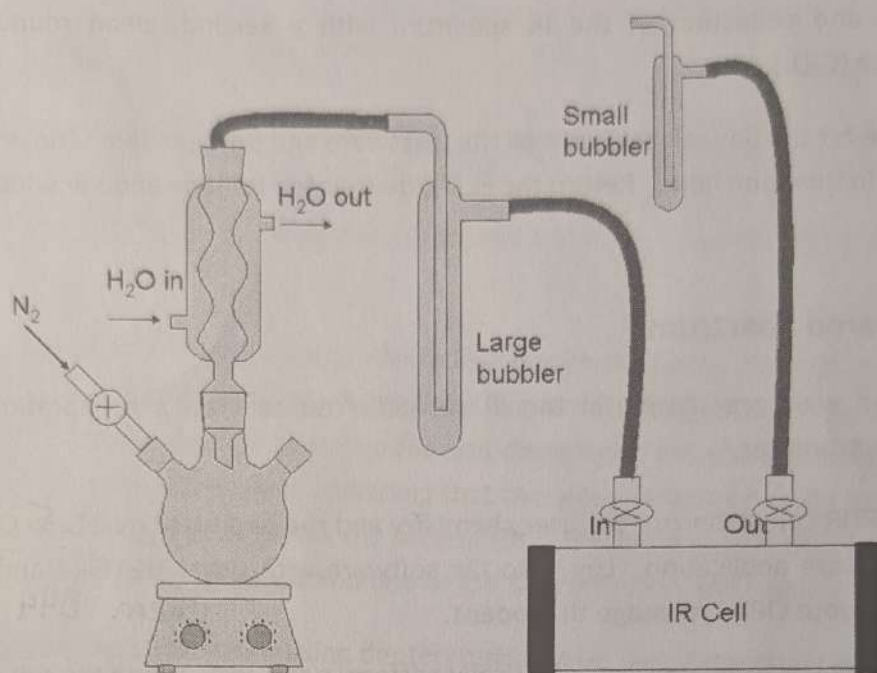


Figure 4. Apparatus used for synthesis and collection of diatomic gases

To check for leaks, ensure that all stopcocks and valves along the nitrogen line and in the apparatus are open and **slowly** open the needle valve on the nitrogen tank until there is clear evidence of bubbling in the large bubbler and the small bubbler. If bubbles are not formed in the first bubbler, there is likely a leak at one of the joints in the apparatus. If bubbles are being formed in the first bubbler but not the second, you may have a leak in your IR cell. If there is any evidence of leaks, check with your TA. Once you have a leak-free system, flush the system for 5 minutes.

Turn on the stirring. Draw 2 mL of non-deuterated toluene into a 3 mL syringe and add it to the three necked reaction flask via the septum while maintaining the nitrogen flush. The FeCl_3 is only slightly soluble in the dry toluene and you will observe the solvent turn a slightly yellow colour. Ensure that the reaction mixture is stirring smoothly.

Draw up 1 mL of bromine into a 3 mL syringe. Attach a short 20-gauge needle to the syringe, turn off the nitrogen flush by closing the needle valve on the nitrogen tank, and insert the syringe through the septum. Add the $\text{Br}_2(l)$ **SLOWLY** (the reaction is very **EXOTHERMIC**) to the reaction mixture over the course of about 30 seconds. You should notice a brownish colour gas (Br_2) appear in the reaction vessel shortly after addition, and gas will begin flowing through both bubblers. The rate of bubbling will wax and wane depending on progress of the reaction. Approximately 30 seconds after the addition of the last of the liquid bromine, close the outlet valve on the IR cell and then the inlet valve. Disconnect the gas cell from the rest of the system.

Important: After you have disconnected the IR gas cell, slowly turn the nitrogen flush back on. You should see bubbling only in the first bubbler. You'll let the system flush with nitrogen while you are taking your IR spectra.

After taking your IR spectra, remove the three-necked flask from the apparatus and leave it to degas safely in the fume hood.

Repeat the reaction and collection of the IR spectrum with a second, clean round-bottomed flask and perdeuterated toluene (C_7D_8).

When you are all done for the day, please leave all the glassware and syringes clean (rinse with acetone) and the gas cell disassembled in the fume hood. Return the $FeCl_3$, deuterated toluene and KBr windows to the dessicator. Wash your hands.

Collecting the Infrared Spectrum

Once you've collected your gas sample in the IR gas cell. You can run a ro-vibrational spectrum using a conventional FTIR spectrometer.

i) To login to the FTIR computer use the user chemistry and the password gwe123. Once in Windows, start the "OPUS" software application. Log in to the software with user CHEM344 and password CHEM344. Click OK on the About OPUS message that opens. Chem 344 Chem 344

ii) When the software starts up, it will automatically perform a self-test. When the self-test is complete, close the message window that opens. If the instrument does not pass the self-test, please inform your TA.

Advanced iii) In the Acquire tab on the left of the screen, click on the downward pointing triangle beside the large Measurement button and click on "Setup Measurement". Load the Experiment "TRANS_chem344.XPM". This method contains information about the method the instrument will use to collect your spectra including the wavelength range and high resolution that we want to use. Click "Accept & Exit". Click background single channel

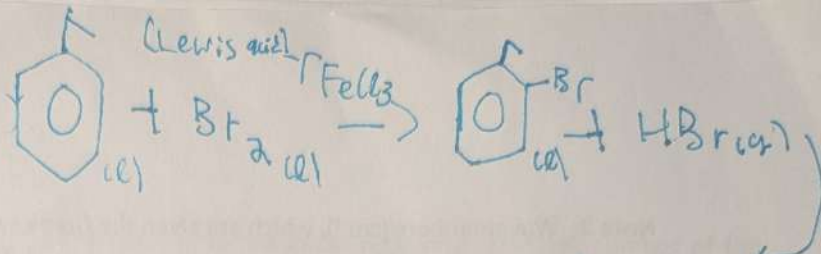
iv) Check that the cell compartment in the instrument is empty. Click on the large rectangular Measurement button. Click on Start Background Measurement. wait until complete

v) When the background measurement is done, place the cell holder and gas cell in the sample compartment. You may need to remove the front panel on the compartment to get the cell to fit. Enter an appropriate short sample name that includes today's date. Click on Start Sample Measurement. The instrument will run and display one scan. If it looks ok (check with your TA), click on Start Measurement at the bottom of the displayed scan. The instrument will run 16 scans in succession.

vi) When the collection is finished, go to File → Save File As. On the Mode tab of the window that opens ensure that Data Point Table is selected then click Save.

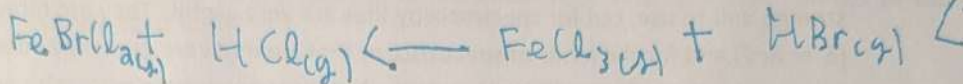
vii) After collecting the spectrum for the reaction with deuterated toluene, remove the gas cell and holder from the instrument, replace the front panel on the sample compartment and close the compartment. Exit the software. The DPT files and screenshots of the spectra will be uploaded to Canvas for you. Log off the computer. Do not turn the instrument off.

1. SE₂ rxn



Analysis and Questions

A. Organic Chemistry



These questions will be done as a group discussion with the TA. You do not need to hand anything in for this part.

1. Consider the reaction of the non-deuterated toluene with the $FeCl_3$. Provide the name of this organic reaction and a chemical equation for the process that is occurring in your experiment. Look carefully at the IR spectrum for the reaction involving the non-deuterated toluene and you should notice two distinct sets of ro-vibrational peaks indicating that two gas-phase species are being generated! Provide a chemical reaction that explains how the second species is produced. Hint: Consider a simple inorganic reaction involving the $FeCl_3$ catalyst and one of the products from the organic reaction.

2. When you repeat the experiment using deuterated toluene, the chemistry is essentially identical. Indicate which two diatomic species you would expect to generate from this process. However, this spectrum will likely reveal four sets of ro-vibrational transitions. Careful inspection will reveal that two of the sets are identical to the experiment you performed with the non-deuterated toluene. This occurs due to isotope exchange between your desired products and H_2O introduced with the very hygroscopic $FeCl_3$.

2. Deuterium: $FeCl_3$ is wet, therefore when water added results in two (4) products; $DBrCl$, $HBrCl$, DCl , HCl

B. Data Analysis (50 marks)

You can use the software of your choice to do the analysis for this experiment. It could be Maple, Excel, Python, Mathematica, Origin, or similar. Anything that will allow you to plot and fit data will work. However, if you're not super comfortable with programming, we suggest that you use Origin even if you have never used it before. It is reasonably user-friendly once you learn a few tips which we will guide you through, it's a valuable tool to have in your toolbox if you're doing any sort of data analysis or presentation, and it's much better than Excel for the kinds of analysis that you'll be doing with this lab. If you are interested in trying to use Maple, there is a Maple version of this lab which will guide you through some of the trickier data importing, peak picking, and plotting. The lab manager can provide this to you if that's the route you'd like to take.

Specifics to include in your answers for each question are given in blue italics.

1. (8 marks) Import and plot the spectral data as absorbance vs. wavenumber for the deuterated toluene experiment. You should see four sets of ro-vibrational peaks should be centred (where the Q branch would appear if that transition was allowed) at approximately 2900 cm^{-1} (species A), 2550 cm^{-1} (species B), 2100 cm^{-1} (species C) and 1850 cm^{-1} (species D). Use the table of estimated spring constants of diatomic molecules provided below to calculate the fundamental frequencies (in wavenumbers) expected for species A, B, C, and D. Use these calculated frequencies as well as the products expected from the organic reaction to help you identify species A, B, C, and D.

Note 1: The calculated frequencies may not perfectly coincide with your observed frequencies.

Note 2: Wavenumbers (cm^{-1}), which are given the Greek symbol nu with a tilde, $\tilde{\nu}$, may seem to be a strange unit to use, but for spectroscopy they are very useful. They are directly proportional to energy ($E = hc\tilde{\nu}$) and for the kinds of spectroscopy that chemists are generally interested in, they give numerical orders of magnitude (1 to 10^5) which are very easy to work with and give a good sense of relative energies. For this report, we'll be using wavenumbers for plotting and analyzing data.

Species	Spring Constant, k (N m^{-1})
H-H	535
D-D	537
D-Cl	480
H-Cl	478
Br-Br	229
Cl-Cl	300
D-Br	384
H-Br	382

In your report, include the plot of the full spectrum with the four species labeled, the calculated fundamental frequencies for Species A, B, C, and D, (show one example calculation in detail), and the assignment of species A, B, C, and D to specific molecules.

2. (4 marks) If you zoom in on species A, you should be able to see that these peaks are split into pairs. Similar splitting can be observed for species C but is absent from species B and D. Splitting results from isotope effects and the differences they produce in the reduced mass, μ , of the diatomic molecule.

Use Equation 5 to explain why peak splitting is seen for species A and C but not B and D. Isotopic information can be found in any general chemistry textbook. What should be the relative intensities of any pair of peaks for species A? How does your data compare with this predicted ratio?

3. (16 marks) Perform a peak pick operation in Origin for **the molecular species assigned to you** to create a table of all the peaks corresponding to the most abundant isotopic form of the molecule (do not round the data as you will need all the significant figures). Index (i.e. for each peak wavenumber maximum, identify and label in another column) the rotational transitions for both the R and P branches for this species using the J value for the *initial* vibrational state of the molecule. Recalling that a peak in the ro-vibrational spectrum corresponds to the *difference* in energy between two successive rotational energy levels, use Equation 9 to show that the positions (in wavenumbers (cm^{-1})) of the peaks in the R branch, $\tilde{\nu}$, are given by

$$\tilde{\nu} = \frac{f_0}{c} + 2B(J + 1) \quad (10)$$

and the position (in wavenumbers (cm^{-1})) of the peaks in the P branch is given by

$$\tilde{\nu} = \frac{f_0}{c} - 2BJ \quad (11)$$

In Equations 10 and 11, the value of J corresponds to the **initial** rotational quantum number of the molecule in its ground vibrational state.

Use Equation 10 to linearize (i.e. plot $\tilde{\nu}$ vs. an appropriate function of J to get a linear relationship) your data and determine the value of the rotational constant B and the fundamental frequency, $\tilde{\nu}_0$ (in cm^{-1}) for the R branch. Perform a similar exercise with Equation 11 to determine the value of the rotational constant B and the fundamental frequency in cm^{-1} , $\tilde{\nu}_0$, for the P branch. Are the two values for B identical? Are the two values of ν_0 identical? Take the average value of B and determine the bond length of your assigned species.

Include:

- A plot zoomed-in on the species assigned to you which has the peak wavelengths picked and labeled with their wavenumber. On this plot, identify the P and R branches, and label at least the first three peaks for each branch with the rotational transitions responsible for those transitions
- A screenshot of the wavenumbers of the peaks in one column with their labeled J values in a second column.
- The derivations of equations 10 and 11
- The linearized plots for the P and R branches, the result of fitting the data to a line, and your calculations of B , $\tilde{\nu}_0$, average B (if the two are not identical) and the calculation of the bond length of your assigned species

4. (6 marks) Your results from question 3 should indicate to you some flaws in the SHO/RR model. Our first refinement will concern the approximation made in the SHO/RR model that the rotational and vibrational energies of a diatomic molecule are uncoupled. Intuitively, this approximation may seem suspect to you if you consider that a rigid rotor assumes that the bond length is always a constant. However, as a molecule vibrates more, the average bond length stretches, therefore the molecule's moment of inertia must change. Therefore, the value of the molecule's moment of inertia must be somehow coupled with the molecule's vibrational motion. We can account for this coupling by writing the following refined expression (1st order approximation) for the energy of the diatomic molecule.

$$E_1(n, J) = hf_0 \left(n + \frac{1}{2} \right) + hcBJ(J + 1) - hc\alpha \left(n + \frac{1}{2} \right) J(J + 1) \quad (12)$$

Inspection of Equation 12 reveals that the first two terms are identical to Equation 9 and only the third term is new. This term introduces the rotational-vibrational coupling constant, α . How does the magnitude of the third term depend on vibrational and rotational quantum numbers? Does this seem intuitive for describing the coupling of the two motions? Explain your reasoning.

Use Equation 12 to derive expressions for the peak positions (in units of wavenumbers) of the ro-vibrational spectra for the P branch and the R branch.

Include written answers for the two questions regarding the third term in equation (12)

Show the derivation of the peak positions for the P and R branches of the spectrum when the coupling term is included.

5. (6 marks) Use the expressions you developed in question 4 to determine B , ν_0 , and α for the R branch and separately for the P branch for the species assigned to you. To do so, you will have to use a second-order polynomial fit in Origin.

Include screen shots of the second-order polynomial fits, and your calculations of B , ν_0 , and α for the R and P branches

6. (6 marks) Our next (and final) refinement accounts for the distortion of the bond length as the molecule rotates. Again, the rigid rotor assumes that this bond length is always constant. However, the bond is really more of a stiff spring and as the atoms rotate this spring will begin to lengthen due to centrifugal force. We can account for this distortion by introducing a second order approximation for the energy of the diatomic molecule.

$$E_2(n, J) = hf_0 \left(n + \frac{1}{2} \right) + hcBJ(J+1) - hc\alpha \left(n + \frac{1}{2} \right) J(J+1) - hc\delta J^2(J+1) \quad (13)$$

The first three terms in Equation 13 are identical to Equation 12 and only the fourth term has been introduced, along with a new constant, δ , which is the centrifugal distortion constant. How does the magnitude of this last term depend on the vibrational and rotational quantum numbers? Does this seem intuitive for describing the centrifugal distortion? Explain your reasoning.

Use Equation 13 to provide an expression for the peak positions (in units of wavenumbers) of the ro-vibrational spectra for $\Delta J = +1$ (Hint make the substitution that $J+1 = m$. Repeat for $\Delta J = -1$).

Include written answers for the two questions regarding the third term in equation (13)

Show the derivation of the peak positions for the P and R branches of the spectrum when the coupling term is included.

7. (4 marks) Use the expressions you developed in question 6 to determine B , ν_0 , α , and δ for the R branch and separately for the P branch for the species assigned to you. To do so, you will have to use a non-linear fit where you specify the four parameters that need to be determined. When you begin fitting your function in Origin ensure that the starting parameters for B , ν_0 , and α are those you obtained from question 5, and that your starting value for δ is appropriate (i.e. do you expect it to be very large?). Comment on whether the centrifugal distortion correction is important for your molecule.

Include the result of the equations of the non-linear fits and the values of the parameters that result as well as a comment on the significance of δ .