Supporting Information

Encouraging Student Engagement by Using a POGIL Framework for a Gas-Phase IR Physical Chemistry Laboratory Experiment

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Student Handbook
What can an IR spectrum tell you about a molecule?
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Pre-experiment Questions: Part 1
1.
  a.   What types of motion can gas-phase molecules exhibit?
  b.   In general, what type of motion allows molecules to absorb infrared radiation?
2.   The frequency of electromagnetic radiation is often reported in units of wavenumbers
       (cm^{-1}). Consider the equation $E = \dfrac{hc}{\lambda}$ and use units as your guide to determine whether
       wavenumbers are directly or inversely proportional to energy.
3.   Consider a hypothetical diatomic gas with a typical harmonic frequency of 2000 cm^{-1}.
  a.   Draw the energy level diagram corresponding to the vibrational energy levels for this
         molecule.
  b.   To which region of the electromagnetic spectrum do transitions between these energy
         levels belong?
  c.   A sample of this diatomic gas is placed in a spectrometer capable of measuring
         absorbance in the range 1000 – 5000 cm^{-1}. Predict the appearance of the spectrum
         (intensity of absorbance vs. frequency). Put frequency (in cm^{-1}) on the x-axis and
         intensity of absorbance on the y-axis. Explain you reasoning.
  d.   Add an arrow to your energy level diagram from 3A to represent each transition drawn in
         your spectrum in 3C.
Experimental protocol: Part 1
A.   Follow the directions from your laboratory instructor to fill a gas cell with either HCl,
       CO, CO$_2$, or another gas.
B.   Acquire an IR spectrum of the gas with the following parameters:
  i.   Wavenumber range: 1000 – 5000 cm^{-1}
  ii. Use absorption mode
  iii. Resolution: As indicated by the instructor.
Thinking About the Data: Part 1
4.   Does the IR spectrum match your prediction from question 3?
5.   In your group, discuss the qualitative features of the spectrum. Compare the properties of
       the experimental spectrum to your predicted spectrum.
6.   Compile a list of qualitative features of the spectrum as a whole class.
7.   Recall or look up the quantum mechanical model system called the harmonic
       oscillator. In your lab notebook:
  a.   Sketch the potential energy function for a harmonic oscillator.
  b.   Record the allowed energy states for a harmonic oscillator (your answer should contain
         quantum number v and harmonic frequency $\tilde{v}$).
  c.   Describe the type of internal motion that is modeled by the harmonic oscillator.
8.   What is the spacing between any two adjacent energy levels in the harmonic oscillator
       model? Your answer should contain the harmonic frequency $\tilde{v}$.
9.   What is the approximate spacing between any two adjacent peaks in your experimental
       spectrum in units of cm^{-1}? To what region of the electromagnetic spectrum does this
       correspond?

10. What type of motion is typically associated with the energy discussed in question 9?
11. As a class come to a consensus for how to qualitatively explain why there are so many peaks in the spectrum and explain your reasoning.
12 Recall or look up the quantum mechanical model system called the rigid rotator. In your lab notebook:
a. What is the potential energy for the rigid rotator?
b. Record the allowed energy states for a rigid rotator (your answer should contain quantum number J and rotational constant B).
c. Describe the type of internal motion that is modeled by the rigid rotator.
13. What is the spacing between any two adjacent energy levels in the rigid rotator model? Your answer should contain the rotational constant B.
14. In the ro-vibrational model, the total rotational and vibrational energy for a given state is:

$$\tilde{E}_{v,J} = \tilde{v}\left(v+\frac{1}{2}\right) + \tilde{B}J\left(J+1\right)$$

(Equation 1)

where v is the vibrational quantum number and J is the rotational quantum number. Complete the following steps to create a model energy level diagram for a hypothetical diatomic molecule with $\tilde{v} = 2000\,cm^{-1}$ and $\tilde{B} = 1\,cm^{-1}$.

a. Draw a horizontal line to represent the ground vibrational state in the ground rotational state. Label this state with quantum numbers v = 0 and J = 0.
b. Draw a horizontal line to represent the first excited vibrational state in the ground rotational state. Label this state with quantum numbers v = 1 and J = 0.
c. Draw the first four rotational levels for each vibrational state. Label the v and J quantum numbers for each energy level drawn. Pay attention to the relative difference between successive rotational energy levels.
d. Use vertical arrows to represent possible absorption transitions in the frequency range scanned by the spectrometer. What is the physical significance of the length of the arrows you've drawn? Explain.
15. The selection rules for ro-vibrational transitions are $\Delta v = \pm 1$ and $\Delta J = 0$ or ± 1. Which of the arrows that you drew in the previous question satisfy these rules?
16. Use the energy level diagram to create a model spectrum for the system described in the last two questions. Include labels for the quantum numbers of the lower and upper states for each feature in your model spectrum.
17. Transitions with $\Delta J = -1$ are part of the P-branch. Transitions with $\Delta J = 0$ are part of the Q-branch. Transitions with $\Delta J = +1$ are part of the R-branch.
a. Label the branches on your experimental spectrum.
b. Are you missing a branch? If so, which branch is missing?
c. Are all of the selection rules given in question 15 applicable for the molecule you are studying? Explain.
18. Use your previous answers to label the quantum numbers of the lower and upper states associated with each feature in your experimental spectrum.

Pre-experiment Questions: Part 2
19. Predict what the spectrum would look like if the instrument was set to a resolution of 10 cm^{-1}. Again, what if the resolution was to 1 cm^{-1}. Draw your predictions in your lab notebook.

Experimental Protocol: Part 2
C.   Acquire IR spectra of the gas at several resolutions. Each group is responsible for the collection of one spectrum. The class should coordinate to ensure that spectra are acquired in the full range of resolutions from the highest possible resolution of the instrument (typically ~ 0.25 cm^{-1}) to a very low resolution (~5 cm^{-1}).

Information: Part 2
        For P-branch transitions, $\Delta v = +1$ and $\Delta J = -1$. Thus, in the ro-vibrational model, the transition energy is

$$\Delta \tilde{E}_P = \tilde{E}_{v+1,J-1} - \tilde{E}_{v,J} = \tilde{v}\left(v + \frac{3}{2}\right) + \tilde{B}\left(J - 1\right)J - \left[\tilde{v}\left(v + \frac{1}{2}\right) + \tilde{B}J\left(J + 1\right)\right]$$ (Model 1)

$$= \tilde{v} - 2\tilde{B}J$$

        Where v and J represent the vibrational and rotational quantum number of the lower state involved in the transition.

Thinking About the Data: Part 2
20.   Share your group's spectrum with the class. As a class, discuss the similarities and differences between the spectra.
21a.   In Model 1, does the J represent the rotational quantum number of the lower state or upper state of the transition? Explain your reasoning.
  b.   Show mathematically how Equation 1 is used to develop Model 1.
  c.   Use sentences and diagrams to describe how Model 1 and Equation 1 relate to your energy diagram.
  d.   Derive an expression analogous to Model 1 for the R branch transitions where $\Delta v = +1$ and $\Delta J = +1$. Call this Model 2.
22.   If you fit your experimental data to Models 1 & 2, what is the independent variable and what is the dependent variable?
23.   It is possible to write Models 1 & 2 as a single equation as
        $$\Delta \tilde{E} = \tilde{v} + 2\tilde{B}m$$ (Model 3)
        Where m is now related to the J values.
  a.   How does m relate to J for P-branch transitions?
  b.   How does m relate to J for R-branch transitions?
  c.   Why doesn't the quantum number v appear in the equation in Model 3? Provide both a mathematical and conceptual rationale for your response.
24.   Fit your data to Model 3 to determine $\tilde{v}$ and $\tilde{B}$. Record your results with appropriate uncertainties in your lab book. Also add your results for $\tilde{v}$ and $\tilde{B}$ to a combined class spreadsheet.
25.   Create a residual plot for your data. It is ideal to have residuals which are normally distributed. They should look random with no obvious trends.
  a.   Are your residuals normally distributed?
  b.   What does this suggest about Model 3 with respect to your data?
26.   What are the limitations of Model 3?
27.   What assumptions have been made in Model 3?
28a.   What physical property of a molecule changes as the molecule gains rotational energy and spins faster?
  b.   How could Model 3 be expanded to better represent this physical process? Explain your reasoning.

Information: Part 3
Model 3 is based on the assumptions that the molecular vibration and rotation are independent and that the rotational constant does not depend on vibrational or rotational state. A more complete model for the rotational and vibrational energy of a molecule is:

$$\tilde{E}_{v,J} = \tilde{v}\left(v + \frac{1}{2}\right) + \tilde{B}J(J+1) - \tilde{D}[J(J+1)]^2 - \tilde{\alpha}\left(v + \frac{1}{2}\right)J(J+1)$$

(Equation 2)

Again, v and J are the vibrational and rotational quantum numbers, respectively.

Pre-experiment Questions: Part 3

29.   What are the differences between Equation 1 and Equation 2?

30a.   What physical property (or properties) of the molecule's motion does $\tilde{D}[J(J+1)]^2$ relate to?

b.   What physical property (or properties) of the molecule's motion does $\tilde{\alpha}\left(v + \frac{1}{2}\right)J(J+1)$ relate to?

c.   Which of the underlying assumptions of Model 3 are modified by including $\tilde{D}$ and $\tilde{\alpha}$?

31.   The energy transitions based on Equation 2 are:

$$\Delta\tilde{E} = \tilde{v} + (2\tilde{B} - 2\tilde{\alpha})m - \tilde{\alpha}m^2 - 4\tilde{D}m^3$$

(Model 4)

Where m relates to J in the same way as in question 21.
Predict what a residual plot will look like if Model 4 is used to fit your data. Explain your reasoning.

32.   In this section of the experiment, you will fit your experimental data with Model 4 to determine the molecular parameters $\tilde{v}, \tilde{B}, \tilde{D}$ and $\tilde{\alpha}$. Predict how the uncertainties of these parameters might vary with the resolution of the instrument used to acquire the experimental data.

Experimental Protocol: Part 3

D.   Open the IR data regression template Excel file. Read the instructions in the instructions tab.

E.   Look at the other tabs and read their contents to familiarize yourself with the document.

F.   Enter the data for the P-branch and R-branch transitions from your experimental spectrum into the appropriate columns of the spreadsheet.

G.   Perform a multiple linear regression on your experimental data based on Model 4.

Thinking About the Data: Part 3

33.   How can $\tilde{v}$ be determined from the regression? Record the value of $\tilde{v}$ with its uncertainty in your lab notebook.

34.   How can $\tilde{\alpha}$ be determined from the regression? Record the value of $\tilde{\alpha}$ with its uncertainty in your lab notebook.

35.   Repeat this process to determine $\tilde{B}$ and $\tilde{D}$. Propagation of error calculations are required for the uncertainties of $\tilde{B}$ and $\tilde{D}$. Carry out the proper derivations to show the propagation of errors for $\tilde{B}$ and $\tilde{D}$ in your lab notebook. Calculate the uncertainties for these values and compare to the values reported in the worksheet.

36. How can the values determined in the previous question be used to determine the bond length of the molecule being studied?

37. As discussed above, a real diatomic molecule is not rigid, and therefore does not have a fixed bond length. What is represented by the bond length found in the previous problem?

38. Share your data (both the values and the uncertainties) with the class in a combined worksheet.

39. As a class, answer the question: How does the resolution affect the values and uncertainties of the empirically determined molecular parameters $\tilde{v}, \tilde{B}, \tilde{D}, \tilde{\alpha}$, and r_e? Are the trends consistent with your predictions from question 28?

40. Create a residual plot based on the fit of your data with Model 4. How does this residual plot compare to the plot in question 23? Which model appears to do a better job fitting the data?

Post-Experiment Questions

41. You likely performed solution-phase FTIR experiments and/or analyzed FTIR spectra in your organic chemistry courses. What are the similarities and differences between those spectra and the spectra you've investigated in this lab? Explain.

42. Explain how the parameters $\tilde{D}$ and $\tilde{\alpha}$ adjust the calculated rotational-vibrational energy levels for a molecule. Use physical intuition to guide your explanation.

43. Look up relevant vibrational and rotational molecular parameters for I_2 and sketch a ro-vibrational energy level diagram for this molecule. Explain how the parameters are used to develop the energy level diagram.

44. A ro-vibrational spectrum for I_2 does not exist. Explain why and propose an explanation for how we have standard values for all the parameters $\tilde{v}, \tilde{B}, \tilde{D}$ and $\tilde{\alpha}$ found in Model 4 for this molecule.

45. In this experiment, we saw a spectrum with features that were spaced by ~4 cm^{-1} or ~20 cm^{-1} (based on the molecule used). However, the features themselves were in the range of ~2000 – 3000 cm^{-1}. We were able to use this information to determine rotational energy levels for the molecule. Reflect on how this approach is similar to and different from using pure microwave spectroscopy. Some questions to consider in your reflections are:

a. Which of the parameters that we determined in this lab ($\tilde{v}, \tilde{B}, \tilde{D}$ and $\tilde{\alpha}$, I, r_e) would also be accessible through pure microwave spectroscopy?

b. Would you expect to see P, Q, and R branches in pure microwave spectroscopy?

c. Would you expect to see the same distribution of relative intensities in a pure microwave spectrum that was observed in this IR experiment?

46. What can an IR spectrum tell you about a molecule?

Part 4 represents 4 possible additions to the experiment.

Part 4A – Isotope Abundance – For HCl Experiments

4A1. The naturally occurring isotopes of chlorine are ^{35}Cl and ^{37}Cl. Use the periodic table to estimate the percent abundances of these two isotopes.

4A2. Based on your answer from the previous question, list the relative abundances of $H^{35}Cl$ and $H^{37}Cl$ in a sample of naturally occurring HCl.

4A3. Does the mass of a molecule have an effect on vibrational energy levels? Use a mathematical expression to support your response.

4A4. How do the vibrational frequencies of $H^{35}Cl$ or $H^{37}Cl$ compare to one another?

4A5. If you haven't already, acquire an absorption spectrum of HCl gas in the frequency range 2500 – 3200 cm^{-1} with the highest possible resolution of your spectrometer. Plot the data in such a way that you can "zoom-in" to various parts of the spectrum. Zoom-in to the frequency range 2800 – 2900 cm^{-1}.

a. Does this spectral range correspond to P, Q, or R transitions?

b. Describe the spectrum in this range qualitatively and specify the total number of peaks seen.

c. Propose an explanation for the pattern observed.

d. Do the relative intensities of the peaks in this range match your expectations based on your response to 4A2? Explain.

Part 4B – Isotopic Substitution

Information: It is possible to synthesize a gaseous mixture of DCl alongside HCl (e.g. from the reaction of KCl and an aqueous solution of D_2SO_4 and H_2SO_4). Beyond the presence of natural isotopic abundances, purposeful isotopic substitution can be incredibly useful in a number of experimental contexts (including, but not limited to, mechanistic studies of catalytic cycles).

4B1.   Discuss with your group members how the HCl and DCl spectra differ from each other.

4B2.   Which substitution has a more dramatic effect on the positioning of the peaks?: H/D or $^{35}Cl/^{37}Cl$? Cite specific evidence from your spectra to support your response.

4B3.   Repeat the multiple linear regression on all new spectra using Model 4.

4B4.   One of the ways to characterize the outcome of isotopic substitution is to compute an *isotope effect*. This is accomplished by taking a ratio of two molecular parameters and obtaining a unitless value. Compute the isotope effect for the reduced mass for $H^{35}Cl$ and $D^{35}Cl$.

4B5.   We will now explore the degree to which the isotope effects manifest themselves in molecular parameters extracted from the spectra.
 a.   In your groups, propose at least two parameters extracted from the regression (Model 4) to compute isotope effects for.

 b.   Compute these isotope effects, and place them in a whole-class spreadsheet.

4B6.   Are there any parameters for which you have computed an isotope effect that can be expressed, explicitly, in terms of the reduced mass isotope effect? If not, make sure that you come up with at least two parameters for which this is possible.

4B7.   As a class, decide whether additional isotope effects should be calculated. If so, decide how the task(s) should be divided among groups.

4B8.   How do the isotope effects you have computed relate to those you calculated based on the reduced masses? Do the results align with what you expect? Explain.

4B9.   Relate these isotope effects back to your qualitative interpretation of the spectra in 4B1. Do your results make sense? Explain.

Part 4C – Overtones

4C1. For the spectra that were fit in Part 3, what were the values for the vibrational quantum number of the lower and upper states involved in the transition?

4C2. Do you see any spectral evidence of a transition with an energy corresponding to approximately two times the fundamental frequency?

4C3. Draw a model energy level diagram to illustrate the transitions that give rise to the peaks observed.

4C4. What do you notice about the intensity of this set of peaks relative to the intensity for the set of peaks observed in Part 3? Provide an explanation for this difference in intensity based on selection rules.

4C5. Using the highest resolution possible, estimate transition frequencies for the **overtone transitions** of your molecule.
Note: Use experimental data for any overtone transitions that you observe experimentally. For overtones that you cannot see in your spectrum, use the data in the table below, which lists several vibrational overtones for $H^{35}Cl$ and CO.

v'	$\tilde{E}_v - \tilde{E}_0$ for $H^{35}Cl$ (cm^{-1})	$\tilde{E}_v - \tilde{E}_0$ for CO (cm^{-1})
2	5667.9841	4259.59
3	8346.782	6350.06
4	10922.81	
5	13396.19	

Table 1: Vibrational overtones of $H^{35}Cl$ and CO.

4C6. Do these overtone transitions equal an integer times the fundamental frequency? In other words, are the overtone transitions evenly spaced?

4C7. To account for the observation that the overtone transitions are not evenly spaced, the equation for vibrational energy (see TATD #8) can be modified. What correction term could be included to make the equation a better model for real molecules? Hint: looking back at the D term in model 4 which was a correction for centrifugal distortion of rotational motion, notice that the correction terms usually come as subtractions of terms proportional to the quantum number squared. Use a process analogous to the D correction to subtract a correction term for vibrations. Use $\tilde{v}\tilde{x}$ as the name of the correction term.

4C8. Generate a general expression for the transition frequency from the v = 0 vibrational energy level to an arbitrary state v based on the energy expression from the previous question. That is, generate a general expression for $\tilde{E}_v - \tilde{E}_0$. To check your formula, you should see that $\tilde{E}_1 - \tilde{E}_0 = \tilde{v} - 2\tilde{v}\tilde{x}$.

4C9. If you were successful in the previous question, you should have derived the equation
$\tilde{E}_v - \tilde{E}_0 = \tilde{\nu}v - \tilde{\nu}\tilde{x}(v+1)v$. Dividing this equation on both sides by the quantum number v gives an equation that is linear in quantum number v.

$$\frac{\tilde{E}_v - \tilde{E}_0}{v} = \tilde{\nu} - \tilde{\nu}\tilde{x}(v+1)$$

a. In this equation, what is the independent variable and what is the dependent variable?

b. How can this equation be used to determine the molecular constants $\tilde{\nu}$ and $\tilde{\nu}\tilde{x}$?

4C10. Use this expression to determine $\tilde{\nu}$ and $\tilde{\nu}\tilde{x}$ with appropriate uncertainties.

Part 4D – Explicit Connection to Statistical Mechanics

4D1. Use the experimental spectra to determine which rotational state is most populated in your sample of gas. State any assumptions.

4D2. Give a possible explanation about why the lowest energy rotational state (J = 0) is not the most populated state. Discuss your answer with your group.

4D3. Write an equation that can be used to calculate the degeneracy of the rotational levels of the molecule that you studied if you know the J quantum number.

4D4. Write an equation that gives the relative population of molecules in two different energy states. Hint, recall or look up the Boltzmann formula.

4D5. Compare your experimental intensities to those predicted based solely on the Boltzmann distribution.

a. Make a spreadsheet with a column for J quantum number, starting with J = 0.

b. Add a column for the rotational-vibrational energy of the state. Calculate the energy using Equation 2 and the experimentally determined values of the molecular constants.

c. Use the Boltzmann formula to calculate the relative population of each J state relative to the J = 0 state.

d. Compare the predicted intensities to the experimental intensities. Try to make a graphical comparison. Be creative.