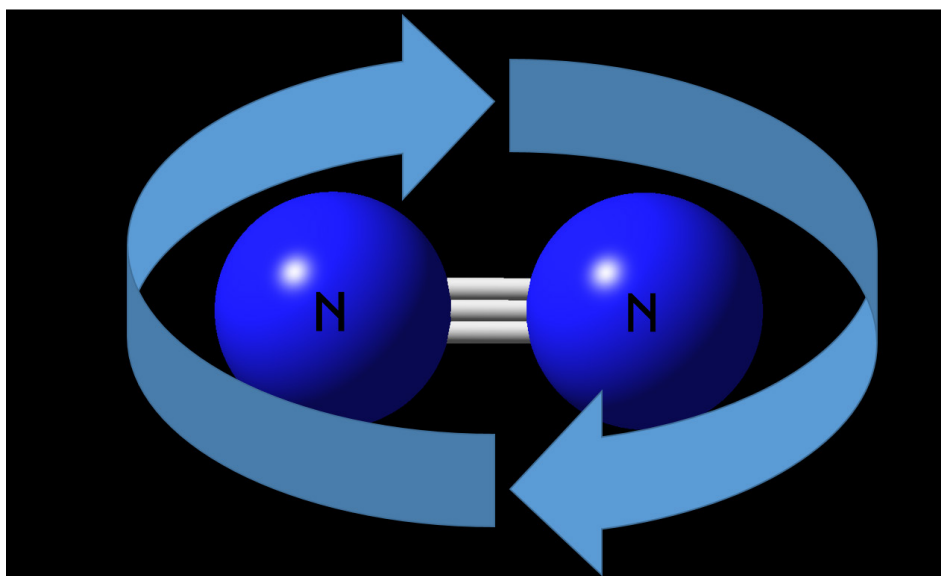# Chemistry 357

Spring 2021

LAB F

<u>Rotational Raman Spectroscopy</u>

<u>of the Atmosphere</u>

TA: Alec Beaton

Pre-Lab Activities

1. <u>Read this entire document.</u> Review the Raman Spectroscopy Overview document that is posted on the CHE357 Blackboard site under "Lab Procedures".

2. Review and practice the exercises contained in the Computational Chemistry Lab Training Handout posted on the CHE357 Blackboard site under "Lab Procedures".

3. Watch (if you have not already) the "Raman Basics" video from Lab C: https://youtu.be/Gok7jRuer1k

4. Watch the "Raman rotation spectroscopy" video: https://youtu.be/DvXX2ijUkkM

5. Optionally, you may want to watch the "Raman scattering" video that is complementary to the previous video: https://youtu.be/1_IqMY6t6w0

Main Learning Objectives

➢ Demonstration of the rigid rotor & non-rigid rotor quantum mechanical models

➢ Application of the Boltzmann distribution to explain spectral intensities

➢ Evaluation of different computational chemistry models for both speed and accuracy

Graded Material

Your grade in each lab is based on your completion of the Post-Lab work and questions that are detailed at the end of each lab procedure.

Text-based questions need to be answered in a narrative style using complete sentences and full explanations. You will be evaluated on accuracy, clarity, and completeness. Keep in mind that adding more text does not necessarily mean you are providing a better answer.

Number-based questions need to be answered numerically with appropriate units, but must also include a clear statement or justification as to how the numbers were determined.

Graphs or plots submitted for grading must be easy to read, have properly labeled axes with units, an overall title, and a legend defining multiple traces. All graphs/plots must include a brief descriptive caption of the represented information.

Tables must be logically organized with column and row labels as appropriate. Units must be specified. All tables must include a brief descriptive caption of the represented information.

Images or figures must clearly and concisely convey information to the reader. Simple figures with clear labeling are most effective. All figures must include a brief descriptive caption of the represented information.

You need to demonstrate in your completed lab reports that you understand the answers you are providing to the questions being posed.

ATTENTION: The written lab procedures serve as guides for lab activities and associated lab reports, but you must interact with the Teaching Assistants to get the most out of each lab. There will always be aspects of lab work that are best conveyed through examples and techniques presented to you by your instructors on a one-on-one basis. Please engage with them early in your work to avoid potential frustration!

ABSTRACT

This laboratory exercise focuses on the analysis of the rotational spectra of atmospheric diatomic molecules, specifically N_2 and O_2, that have been collected using high-resolution Raman spectroscopy. Rigid and semi-rigid rotor quantum models are able to accurately replicate the observed spectral features and provide a measurement of the molecular bond distances through their moments of inertia.

INTRODUCTION

One result of quantum mechanics is the quantization of energy, meaning that energy can only exist or be transferred in discrete increments. One surprising aspect of this is that the **rotational motion (rotational energy levels) of a molecule is quantized**, just like its electronic and vibrational energy levels. The origins of this quantization can be found in the wavefunctions associated with these various energy levels and that **only certain wavefunctions are stable within the boundary conditions defined by the molecule** (by its shape, atom types, etc.).

Rotational energy levels are spaced much closer together than vibrational or electronic levels, and therefore the photons used to connect rotational states are relatively low energy. Pure rotational spectroscopy (based on absorption) is done using microwave radiation with wavelengths spanning roughly 10 to 0.01 centimeters because the microwave photon energies are in resonance with the separation of rotational energy levels.

Instead of using the method of direct microwave radiation absorption to perform rotational spectroscopy, one can use Raman inelastic light scattering to gather information about the same rotational states. The Raman technique used here to study rotational motion in gas-phase molecules is basically the same as the Raman techniques applied for solids and liquids. The exception is **the instrument being used for rotational work has to have much greater spectral resolution (ability to accurately measure closely spaced peaks) and also must have an excellent optical filter to block the laser excitation wavelength.** As you know from previous Raman experiments, the inelastically scattered light from the sample is what is analyzed, and for vibrations, that shift is 1000s of wavenumbers away from the excitation laser center wavelength. But for rotations, the instrument has to have a very good signal-to-noise ratio within 100 cm^{-1} of the laser wavelength and that is not technologically easy and requires specialized instrumentation.

The interpretation of the Raman rotational spectrum of the atmosphere (diatomic N_2 and O_2 molecules) can be readily accomplished using simple quantum models with few inputted

parameters and no advanced mathematics. The standard quantum model for molecular rotation is called the **rigid rotor**.

The rigid rotor model has a few parameters that need to be determined and these parameters must use compatible units (most likely source of error). In a diatomic molecule, the energy of rotational states is determined by two factors: 1) the **moment of inertia**, I, of the molecule and 2) the **rotational quantum number**, J, for the state of interest. The moment of inertia is the most important contributor to the energetic spacing of the peaks in a rotational spectrum and the key for using rotational spectroscopy to determine molecular structure.

$$I = \frac{m_A m_B}{m_A + m_B} R^2$$

Equation 1. Equation for the moment of inertia (kg m^2) of a diatomic molecule using the masses of atom A (m_A, kg) and atom B (m_B, kg) and the bond distance (R, meters)

$$B = \frac{\hbar^2}{2I}$$

Equation 2. Expression for the rotational constant for a diatomic molecule in joules (J). $\hbar$ is pronounced "h bar" and is the reduced Planck's constant or h/2π (1.0546 x 10^{-34} J s)

With the rotational constant (B) determined, the rigid rotor model can be used with the following mathematical form to arrive at the rotational energy levels. The quantum number J can take on integer values of 0, 1, 2, 3, etc.

$$E_J = BJ(J + 1)$$

Equation 3. Equation for the energy levels (E_J) of a rigid rotor with units of joules (J).

The rigid rotor model can be augmented with an additional mathematical factor (distortion constant, D, in joules) to **account for distortion of the diatomic bond with increasing J state**. Increasing J means the molecule is spinning faster, and what is generally called centrifugal force will elongate the bond at high J levels. The nonrigid (or semi-rigid) rotor equation has the following form.

$$E_J = BJ(J + 1) - DJ^2(J + 1)^2$$

Equation 4. Equation for the energy levels (E_J) of a semi-rigid rotor with units of joules (J)

The equations shown so far result in standard energy units of joules, but it is common to find units of wavenumber (cm^{-1}) instead. Rotational constants are easier to write in wavenumber units and easier to relate to the collected spectra. The energy conversion is as follows.

$$\frac{E(joules)}{h(joules \cdot seconds) \times c(m/s) \times 100(cm/m)} = \tilde{E}(cm^{-1})$$

Equation 5. Conversion of energy (joules) to energy (cm^{-1})

With the rotor energy levels calculated, the rotational spectrum can be interpreted by making connections between these levels to represent the transitions that give rise to the spectral peaks. **The specific selection rule for rotational Raman spectroscopy is that ΔJ = +/- 2.** Technically, ΔJ = 0 transitions are also allowed, but they fall under the laser Rayleigh peak and cannot be observed. This means that 0→2, 1→3, 2→5, … are allowed, but for example, 0→1 is forbidden. This is different than the selection rules for pure (microwave) rotational spectroscopy in which ΔJ = +/- 1.

Once all the transition energies have been determined, you have your spectral positions known (your x-axis values), but now need to calculate the peak intensities (your y-axis values). The **primary factor that determines the relative intensities of peaks in a rotational spectrum is the population of molecules** that exist in the lower J state involved in each transition (e.g. the J = 2 state population in a 2→5 transition). These populations are governed by the sample temperature and the population ratios between states can be calculated using the **Boltzmann equation**. The variables in Equation 6 are as previous but be sure to use the correct units for temperature (T, in K) and the Boltzmann constant (k, 1.3806×10^{-23} J/K). If you use the equation, you will find that the populations start out low, then rise to a maximum at a particular J value, before tapering off at higher J levels. This behavior gives a distinctive appearance to the intensity patterns of all rotational spectra that is highly sensitive to temperature.

$$\frac{n_J}{n_0} = (2J + 1)e^{-BJ(J+1)/kT}$$

Equation 6. Boltzmann equation for determining the population in a J state (n_J) relative to the lowest state J = 0 (n_0). The (2J+1) leading factor is due to the 2J+1 degeneracy of each J state.

There is another intensity complication in the case of O_2 and N_2 due to their very high symmetries with identical exchangeable nuclei. For O_2, every other transition has zero intensity. For N_2, every other transition is half the intensity that is otherwise expected. The origin of this strange behavior is not something we will go in to detail about, but it comes from **nuclear spin statistics** which involves wavefunction symmetries and the fermion or boson character of the nuclei (this is the same principle as ortho-hydrogen and para-hydrogen, which you may discuss in lecture).

PROCEDURE

The Raman data provided to you was recorded using a commercial Raman instrument with enhanced sensitivity for low-frequency operation. Some information from the manufacturer is available here about the TR-Bench (with λ=785 nm laser excitation): https://www.coherent.com/lasers/laser/tr-bench It was designed to record inelastically Raman scattered light over a range of ~10 to 250 cm^{-1} away from the central Rayleigh peak (the elastically scattered light). Only the Stokes transitions (ΔJ = +2) are being used in this work since they are more intense than the anti-Stokes peaks and therefore offer a better signal-to-noise ratio. The reason that students are not recording the data themselves is that in order to obtain a rotational Raman spectrum of laboratory air, the spectrometer enclosure has to be removed and the excitation laser beam sent out into the open. The open space laser beam is intense enough to rapidly cause burns and is therefore an extreme eye safety hazard. Only those with special safety training are allowed in the laboratory when these experiments are being performed.

An Excel sheet containing the Raman data and also rigid rotor and semi-rigid rotor calculations is the focus of the lab activity. It can be downloaded from the Blackboard site or you can ask your TA for a copy. The Raman data has already been intensity normalized and baseline corrected using the SpectraGryph software in the same manner you are already familiar with.

You can use the provided Excel spreadsheet to inspect the experimental data and to see how well the simple quantum model of a rigid rotor actually does for reproducing the observations. Feel free to explore how the predicted spectra change when you modify the molecular parameters of mass and bond length, and also the temperature of the experiment. You will need to do some of these calculations yourself to answer the questions contained in the Post-Lab, but you can use the Excel sheet to check your work.

POST-LAB

1. Use the **CRC Handbook of Chemistry and Physics** (https://researchguides.library.syr.edu/az.php?a=c) to determine the experimentally accepted values of the bond distances (referred to as "r_e" values) found in N_2 and O_2. Refer to the **Molecular Structure and Spectroscopy: Spectroscopic Constants of Diatomic Molecules** section of the CRC Handbook. What are the values? Do the relative values make chemical sense based on your knowledge of their bonding interactions? (5 points)

2. The structures of N_2 and O_2 have been studied for many decades, so there are numerous publications listing their bond lengths. Find original literature sources (not the CRC Handbook) for the geometries of N_2 and O_2 from any scientific journal and from any year. Provide citations of the works, the values they report, and the techniques they used to obtain the values. (10 points)

3. Using the information from Step #1 and assuming the diatomics are made from isotopically pure ^{14}N and ^{16}O, calculate the reduced mass (μ), the moment of inertia, and the rotational constant for each molecule. Show your work and units. (10 points)

4. With the values from Step #3, use the rigid rotor equation to calculate the first four (J = 1-4) rotational energy levels of O_2 and N_2. Show your work and units. (20 points)

5. Based on the results of Step #4, provide the wavenumber energies (cm^{-1}) for the first two rotational energy level transitions in both O_2 and N_2. Recall that the selection rule for rotational Raman is $\Delta J = +/- 2$. Show your work and units. (10 points)

6. Isotopes matter a great deal in rotational spectroscopy since they can have a significant influence on the moment of inertia. Repeat Steps #2-5 for $^{15}N_2$. With the increased mass compared to $^{14}N_2$, would the rotational transitions be seen at higher or lower wavenumber? There is no apparent evidence of isotope effects in the provided experimental data. Why? (10 points)

7. Using GaussView/Gaussian, build and optimize the geometries of N_2 and O_2 with a variety of computational approaches. The def2tzvp basis set used in most of these jobs must be entered as a "Custom…" basis set and manually typed into the "Additional Keywords" text area. M062X is a DFT method not found in GaussView and must be entered as a "Custom…" method with "M062X" typed into the "Additional Keywords" box (along with the basis set).

    a. Semi-empirical…AM1 (no basis set is needed for semi-empirical jobs)

    b. Hartree-Fock/def2tzvp

    c. MP2/def2tzvp

      d. DFT…B3LYP/def2tzvp

      e. M062X/def2tzvp

8. Using the Gaussian simulation outputs, construct a table of calculated bond distances for N_2 and O_2, but also include the CRC Handbook published values in the same data table. Calculate the percent errors in the predicted bond lengths for each simulation as compared to the CRC Handbook. Which approach yields the best match with experiment? How much time did each calculation take to run (Look for "Job cpu time:" in the "Results" menu). Did the "best" simulation take the longest time? (20 points)

9. As the rotational quantum number increases, the molecule spins with greater angular momentum. This results in a distortion of the diatomic bond as a function of J state and therefore a deviation in the rotational energy levels occurs away from the pure rigid rotor. The centrifugal distortion term (D) is often used to correct for this distortion by adding a perturbation term to the standard rigid rotor equation. Assume your experimental data has 1 cm^{-1} of spectral resolution. Using the provided Excel simulation sheet, *estimate* what J levels need to be involved for bond distortion to become an issue in your analysis. What are these J values? Given the spectral range of the provided Raman data, is centrifugal distortion a factor that is important in this particular data analysis? Why or why not? (5 points)

10. Using the Excel sheet, *estimate* the temperature of the sample by changing the listed temperature (yellow highlighted cell) until the calculated intensities across the spectral region match as well as possible with the experimental peaks. What is that temperature? If your goal was to measure the centrifugal distortion term (D) for these diatomics, would that be easier to do with a cold sample or a hot sample? Why? (5 points)

11. When inspecting the provided experimental rotational Raman spectrum of our atmosphere, you will find that no matter what temperature is used in the quantum rotor model, the measured O_2 peaks tend to be less intense than the N_2 peaks. Why might this be the case? (5 points)

Lab F: Rotational Raman Spectroscopy of the Atmosphere

Student: XXX

Question 1: (x / 5 pts)

Question 2: (x / 10 pts)

Question 3: (x / 10 pts)

Question 4: (x / 20 pts)

Question 5: (x / 10 pts)

Question 6: (x / 10 pts)

Question 7: (x / 10 pts)

Question 7 + 8: (x / 20 pts)

Question 9: (x/ 5 pts)

Question 10: (x / 5 pts)

Question 11: (x / 5 pts)

Report Total: (x / 100)

General Comments: