

Experiment 3: Bond Strength of Nitric Oxide¹

Prelab:

Reading: Section 10.4 in Olmstead and Williams, *General Chemistry*

To be written in your lab notebook: Refer to the first paragraph in the Procedure section of this experiment to determine the volume of concentrated sulfuric acid needed to make 50 mL of a 2.0 M solution of sulfuric acid in water.

Purpose: Infrared spectroscopy is used to study the bond strength in nitric oxide. The bond strength is compared to the prediction from molecular orbital theory.

INTRODUCTION

This experiment is part of three exercises that study chemical bonding. The purpose of this week's experiment is to generate experimental evidence on the bond strength of nitric oxide, NO. You will make predictions from three theories of chemical bonding and then determine if the predictions agree with your experimental evidence. The theories that you will be testing are Lewis dot structures, qualitative molecular orbital theory, and computational molecular orbital theory. At the end of these exercises we hope to demonstrate that experimental and theoretical approaches are complementary; both are needed to understand the physical world. Bonding in NO will be studied by infrared spectroscopy (IR) in this experiment. The absorption frequencies of the infrared bands of NO will be used to determine the bond order.

Infrared Spectroscopy and Bonding

Infrared spectroscopy is a type of vibrational spectroscopy. Molecular vibrations can be modeled by the vibration of a spring, Figure 1. The two ends of the spring are the two atoms in the covalent bond.

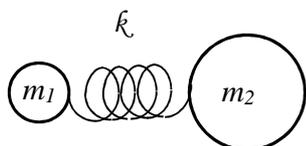


Figure 1. Vibrating molecules can be modeled as two masses on a spring of force constant k .

Vibrational spectroscopy provides a measure of the bond strength for different types of covalent bonds. The bond strength is directly related to the vibrational energy, which is typically expressed in “wavenumber” units (cm^{-1}) in IR spectra. The wave number for a transition, $\tilde{\nu}$, is defined as:

$$\tilde{\nu} = \frac{1}{\lambda}$$

and combining with the energy change for the transition:

$$\Delta E = h\nu \quad \text{with} \quad \nu\lambda = c \quad \text{gives} \quad \Delta E = \frac{hc}{\lambda} = hc\tilde{\nu}$$

So, the wavenumber, vibrational frequency, and vibrational energy are all proportional to each other; when one increases they all increase. The wave number of the IR band for a bond depends on the bond strength, or on the “stiffness” of the spring in the spring model. This stiffness is

characterized by the force constant. The force constant is represented by k and is measured in Newtons per meter, N/m. The relationship between the wave number, $\tilde{\nu}$, and the force constant, k , is given by Equation 1:

$$\tilde{\nu} \text{ (cm}^{-1}\text{)} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 5.309 \times 10^{-12} \text{ s/cm} \sqrt{\frac{k}{\mu}} \quad (1)$$

where c is the speed of light (2.998×10^{10} cm/s) and μ is the reduced mass, which is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (2)$$

where m_1 and m_2 are the masses in kg of the individual atoms forming the covalent bond.

For example, Eq. 1 shows that bonds with larger force constants have higher vibrational wave numbers. So double bonds, other things being equal, have higher vibrational wave numbers than single bonds. However, the bond force constant isn't the complete story; we also need to consider the atomic masses. For equal force constants, bonds with heavier atoms have lower wavenumbers than lighter atoms. This difference is because heavier atoms are harder to move around. The reduced mass takes into account the atom masses. Eq. 2 may seem unfamiliar, so two examples might help. First consider two equal masses on a spring, that is $m_1 = m_2 = m$. From Eq. 2, $\mu = m/2$. In other words, the "effective mass" on the spring is half the mass of one of the atoms, because both atoms are moving at the same time. The case when the atoms have very different masses is a little different. Take HCl as our second example. Then $\mu = m_1 m_2 / (m_1 + m_2) = 1 \times 35 / (1 + 35) \approx 1$ g/mol. In other words, the lighter atom dominates the reduced mass because it is much easier to move the lighter than the heavier atom. Please note that for your calculations, you need the reduced mass in kg per molecule, so you need to divide by N_A and 1000 g/kg: giving $\mu = 1 \times 35 / (1 + 35) / N_A / 1000$ for this example.

Eqs. 1 and 2 show that the force constant of a bond can be determined from the experimental wavenumber of the IR band. The force constant is, in turn, a measure of the bond strength. As bond strength increases, the bond energy and force constant increase, while the bond length decreases. Table 1 lists the values of the bond energies, bond lengths, and force constants for a series of diatomic molecules.²

Table 1. Bond strength characteristics for some diatomic molecules and qualitative bond order predicted using molecular orbital theory.²

	B ₂	C ₂	N ₂	O ₂	F ₂	CO	CN
Bond energy, kJ/mol	289	602	941	494	151	1070	787
Bond length, Å	1.59	1.24	1.10	1.21	1.44	1.13	1.18
k (N/m)	350	930	2240	1140	450	1856	1580
Predicted bond order	1	2	3	2	1	3	

The bond order of diatomic molecules is predicted using molecular orbital theory (see Example 10.9, in Olmstead and Williams). You can clearly see from Table 1 that the bond order varies in a similar trend as the force constant, Figure 2. The correlation of bond force constants and the molecular orbital theory predictions are excellent. The correlation of molecular orbital predicted bond orders and the experimental bond strength parameters validate molecular orbital theory.

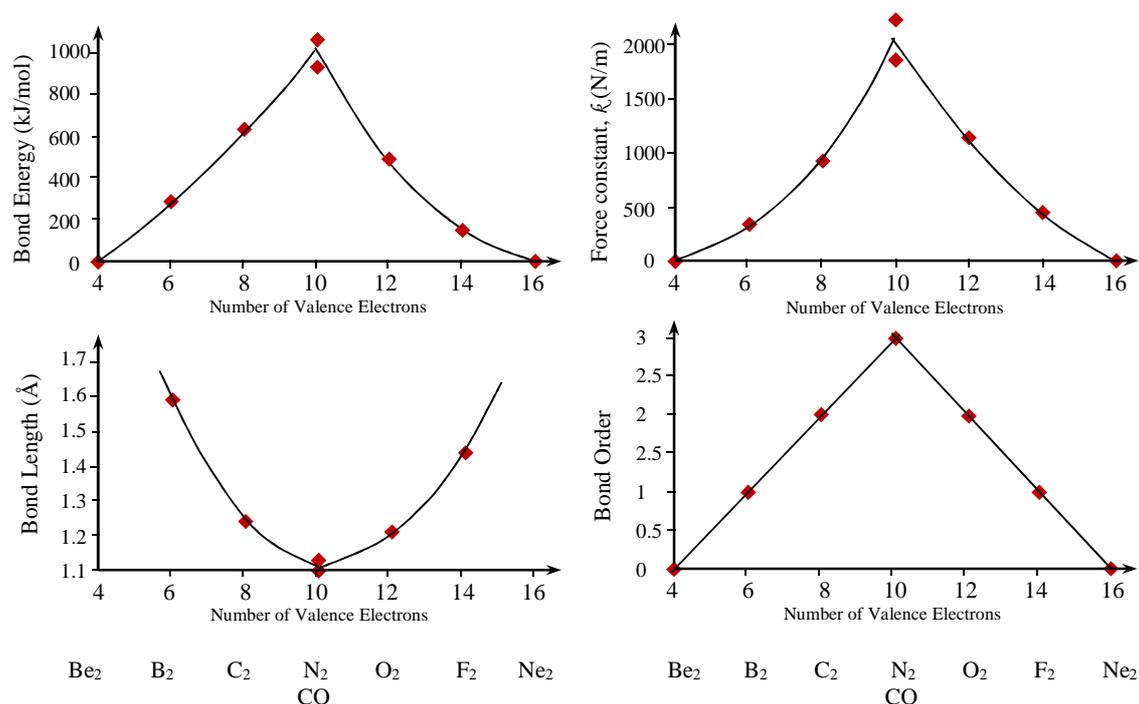


Figure 2: Experimental measures of bond strength correlate with molecular orbital predictions for the qualitative bond order.¹ The plots are with respect to the total number of valence electrons in the diatomic molecule. (The curves are added to guide the eye.)

The vibrational wavenumber can be determined using vibrational spectroscopy in the infrared region of the electromagnetic spectrum. To determine the spectrum, we need a light source, method for varying the frequency of light passing through the sample, and a detector, Figure 3.

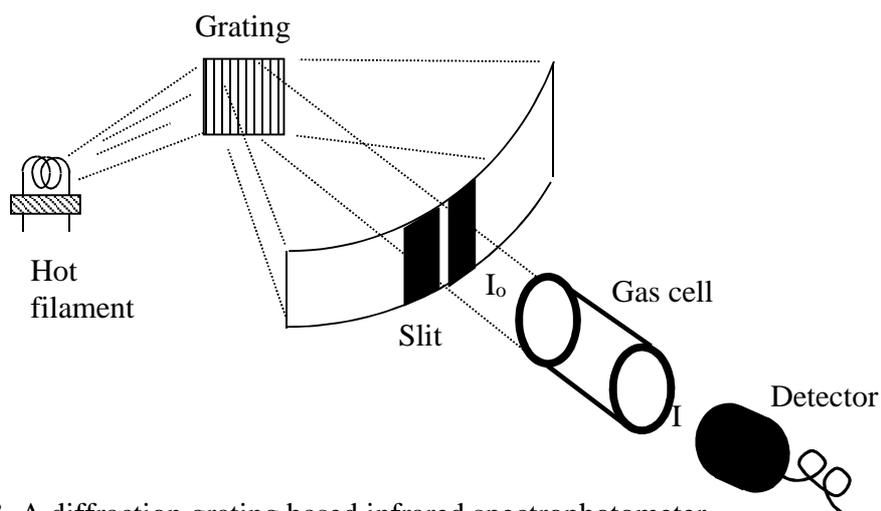


Figure 3. A diffraction grating based infrared spectrophotometer.

The light source is a glowing hot filament or ceramic rod. A grating is used to disperse the light into its different frequency components, and a slit is used to allow a narrow range of frequencies

that pass through the sample. The light intensity is measured by a solid-state detector. The spectrum is determined by scanning the grating and recording the light intensity as a function of frequency of the light passing through the slit. The vertical axis of the spectrum is usually given as percent transmittance, %T, which is the fraction of light that passes through the sample expressed as a percentage, $\%T = (I/I_0) \times 100$. The wavenumber of the transition is read directly from the spectrum. The intensity (absorbance) of the infrared bands of NO can be used to calculate the concentration of nitric oxide. IR spectroscopy is used to measure the levels of gaseous pollutants for environmental problems.

Example–Reduced Mass, Force Constant, and Wavenumber:

Predict the value of the wavenumber of the IR band for carbon monoxide based on the force constant given in Table 1.

Answer: From Eq. 2, the reduced mass for the C-O bond is:

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{M_C M_O}{M_C + M_O} \left(\frac{1}{N_A} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) \quad (3)$$

where M_C and M_O are the atomic masses in g/mol. Given $M_C = 12.0$ g/mol and $M_O = 16.0$ g/mol, Eq. 3 gives:

$$\mu = \frac{12.0 \text{ g/mol} \cdot 16.0 \text{ g/mol}}{12.0 \text{ g/mol} + 16.0 \text{ g/mol}} \left(\frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 1.139 \times 10^{-26} \text{ kg}$$

Note that $1 \text{ N} = 1 \text{ kg m s}^{-2}$ giving $1 \text{ N/m} = 1 \text{ kg s}^{-2}$. The vibrational wavenumber can be calculated from Eq. 1:

$$\begin{aligned} \tilde{\nu} &= 5.309 \times 10^{12} \text{ s/cm} (\kappa/\mu)^{1/2} = 5.309 \times 10^{12} \text{ s/cm} (1856. \text{ kg s}^{-2}/1.139 \times 10^{-26} \text{ kg})^{1/2} \\ &= 2143. \text{ cm}^{-1} \end{aligned}$$

The experimental value from the infrared spectrum of carbon monoxide is identical (2140 cm^{-1}) to this predicted value, within three significant figures.

Example–Correlation of the Force Constant and the Bond Order:

The following example shows how to correlate the bond force constant with the bond order, and how to compare the bond order to the molecular orbital prediction. Do this example as practice to prepare for writing your lab report.

1. Using the force constant from Table 1 and Figure 2, predict the bond order for CN.
2. Predict the qualitative bond order for CN based on molecular orbital theory.

Answer: (1). The plot of the bond force constant is reproduced in Figure 4, based on the data in Figure 2. The bond order as predicted by molecular orbital theory is superimposed on the horizontal axis, as suggested by the correlations in Figure 2. You don't need to do any fancy curve fitting for this question. Given the force constant use the smooth curves in the figure to read off the bond order. Just use a pencil and ruler to extrapolate, as shown below by the dotted line. (For NO use the right-half of the plot.)

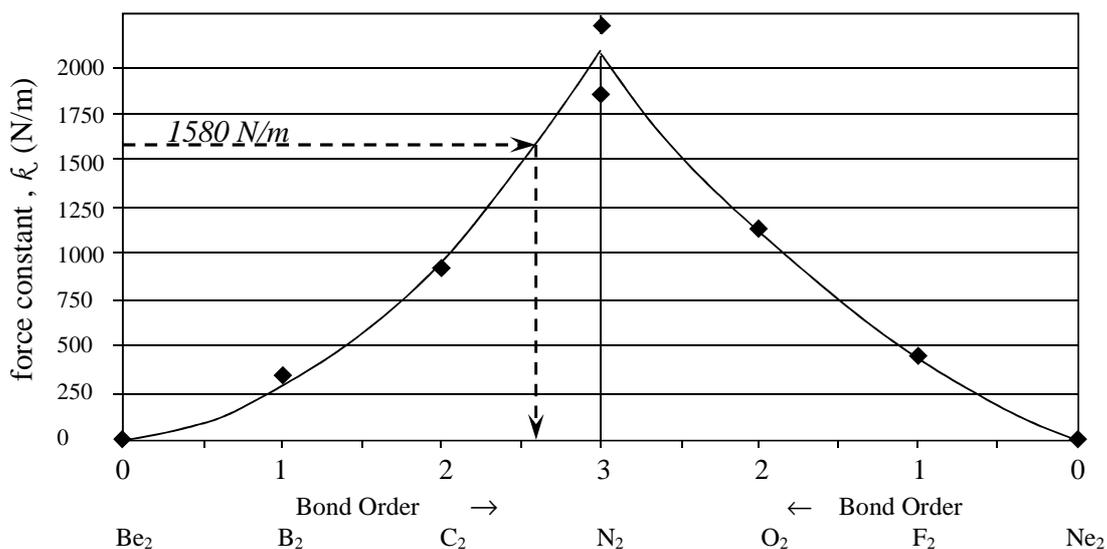
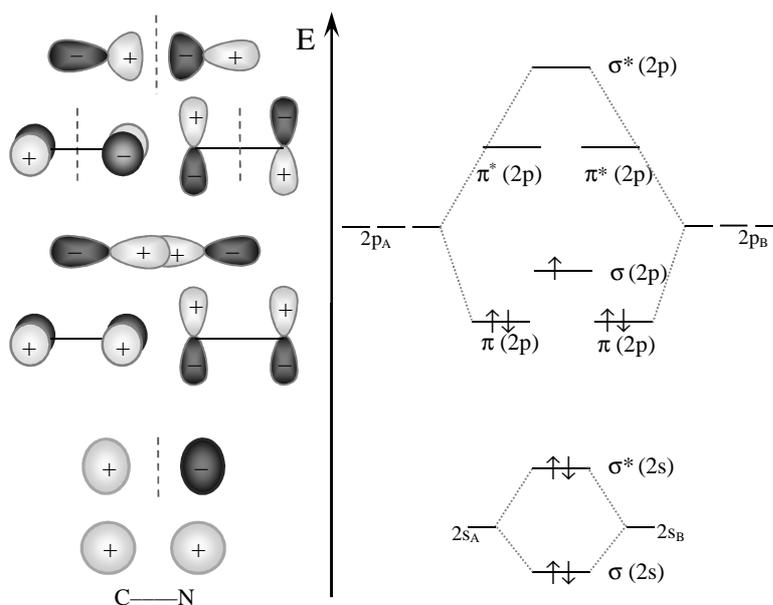


Figure 4: Force constant-bond order extrapolation for CN.

Bond orders can have non-integer values. For qualitative molecular orbital theory, bond orders are restricted to half-integer values, so adjust your extrapolated bond order to the nearest half-integer value (e.g. 1, 1.5, 2, 2.5, 3). The extrapolated bond order from Figure 4 is around 2.6-2.7. The nearest half-integer for CN is 2.5.

2. To predict the qualitative bond order for CN we use the molecular orbital diagram for second period diatomic molecules (see Example 10.9, in Olmstead and Williams). The CN neutral molecule has 9 valence electrons:



The qualitative bond order is:

$$\text{Bond order} = \frac{\# \text{ of bonding electrons} - \# \text{ of anti-bonding electrons}}{2} = \frac{7-2}{2} = \underline{2.5}$$

This value of 2.5 is the same as given by the experimental force constant correlation in the first part of this example. (You don't need to draw the orbitals in your answers.)

PROCEDURE

Safety Information: Concentrated sulfuric acid is highly corrosive and causes chemical burns to the skin on contact. Nitric oxide gas, NO, may cause respiratory irritation and may be absorbed through the skin. NO should be handled in a fume hood.

1. Concentrated sulfuric acid is 96% by mass H₂SO₄ and has a density of 1.84 g/mL. Prepare 50 mL of 2.0 M sulfuric acid. When making this solution, remember to “do as you oughta, add acid to water.” This solution needn't be very accurate. Using the graduations on an Erlenmeyer flask and a graduated cylinder are fine. Make sure to calculate the volume of concentrated sulfuric acid to add to water for a total volume of 50 mL, *before you come to lab.*

Do as you oughta, add acid to watah!

2. Assemble the gas generation system and IR cell as shown in Figure 5. Be careful not to touch the IR cell windows. The windows are made of CaF₂ to allow IR light to pass. (Normally NaCl windows are used for IR spectroscopy, but because NaCl is water soluble we can't use them for this experiment. CaF₂ windows don't work below 1100 cm⁻¹, but NO doesn't absorb in that region, anyway.) Rubber septa are attached to the side arms of the gas sample cell to provide an air-tight seal. Carefully insert two syringe needles through the rubber septa. Add water to the second side-arm flask, but make sure that water won't be able to run into the tubing that goes to the IR cell. Clamp both flasks to a ring stand. Grind about half a stick of sodium nitrite, NaNO₂, in a mortar and pestle. Add 4 g of the powdered sodium nitrite to the first side-arm flask.

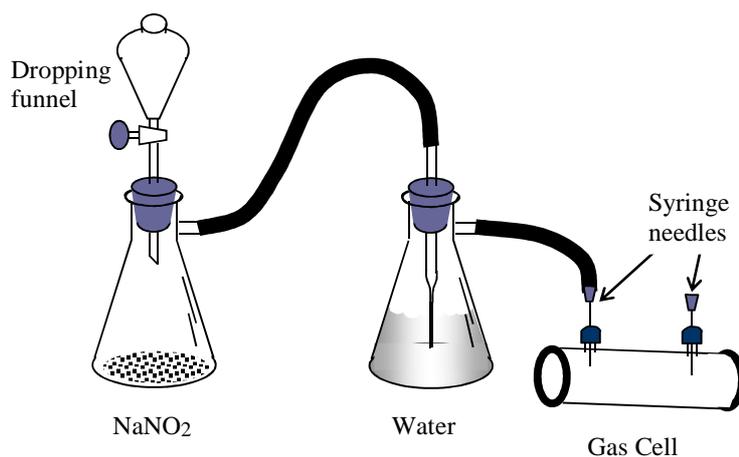


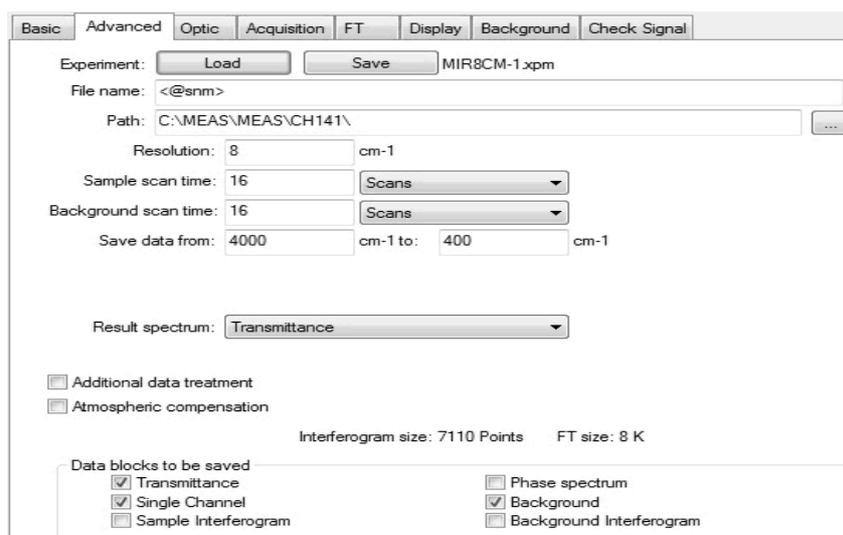
Figure 5. Gas generator setup for nitric oxide. The water bubbler removes NO₂.

The water bubbler removes NO₂ from the gas stream, because NO₂ is soluble in water while NO is not. When NO₂ dissolves in water, nitric acid and NO are produced through disproportionation: $3 \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$

3. Pour 30 mL of 2.0 M sulfuric acid into the dropping funnel. The rubber tubing is attached to the inlet syringe needle through a plastic Luer connector (the lower portion of a syringe barrel). Make sure all the stoppers and tubing are firmly attached. Slowly turn the stopcock until gas evolution begins. The air spaces in the two flasks and the gas cell should turn brown (why?). Allow gas evolution to continue, adding more 2.0 M sulfuric acid as necessary, **until the brown gas has washed out of the gas cell. Be patient!** Don't allow gas evolution to stop to keep O₂ gas from returning into the gas cell through the exit syringe needle. Pull the two needles out of the gas cell, place the gas cell in the provided box, and carry the gas cell to the instrument lab, Keyes 205. Take the IR spectrum in the Instrument Lab as instructed below.

Bruker Tensor 27: Click on the Advanced Measurement Icon: 

In the Measurement dialog, click on the Advanced tab. If the MIR8CM-1.xpm parameter file is not currently loaded, click on the Load button and choose MIR8CM-1. Choose 8 cm⁻¹ resolution with 16 scans. These settings produce a spectrum in less than 10 seconds.



The screenshot shows the 'Advanced' tab of the Bruker Tensor 27 Measurement dialog. The 'Experiment' field is set to 'MIR8CM-1.xpm'. The 'File name' is '<@snm>' and the 'Path' is 'C:\MEAS\MEAS\CH141\'. The 'Resolution' is set to 8 cm⁻¹, 'Sample scan time' is 16 Scans, and 'Background scan time' is 16 Scans. The 'Save data from' is 4000 cm⁻¹ to 400 cm⁻¹. The 'Result spectrum' is set to 'Transmittance'. There are checkboxes for 'Additional data treatment' and 'Atmospheric compensation'. The 'Interferogram size' is 7110 Points and 'FT size' is 8 K. Under 'Data blocks to be saved', 'Transmittance', 'Single Channel', and 'Background' are checked, while 'Sample Interferogram', 'Phase spectrum', and 'Background Interferogram' are not.

Your lab instructor or TA will demonstrate the use of the instrument by taking the spectrum of polystyrene plastic. After the demonstration, take over on your own. The step-by-step instructions follow.

Place the gas cell holder (plate with two horizontal rods) in the cell holder. Please be careful with the sample compartment cover, don't let it fall backwards. Take a background spectrum, without the sample cell present, by completing the following steps.

- Click on the Advanced Measurement Icon: . Click on the Basic tab at the top of the Measurement dialog window. Enter the sample name for your spectrum; include your initials in the name with no spaces. Make sure no sample is in the IR-beam. Click on the Background Single Channel button to take the background scan. The progress of the scan is shown in green at the bottom of the spectrum display window.

- When the background is complete, place the sample in the IR-beam and click the Sample Single Channel button. The sample cell sits on the two long rods. After the scan is complete, click the Close button if the window doesn't close automatically. If the sample holder with the two long rods is not available, the sample can sit on a block of wood.
- Print your spectrum by clicking on the Quick Print icon in the top icon bar at right. The spectrum is printed to the HPLaserJet 4050 PS.
- The spectrum of an empty sample cell is shown in Figure 6 to help you decide which peaks correspond to the NO absorption. Note the positions of the H₂O and CO₂ peaks. The absorption peaks of gases at low resolution show two bands with a shallow dip between the two bands. This shape is caused by the effects of molecular rotation.

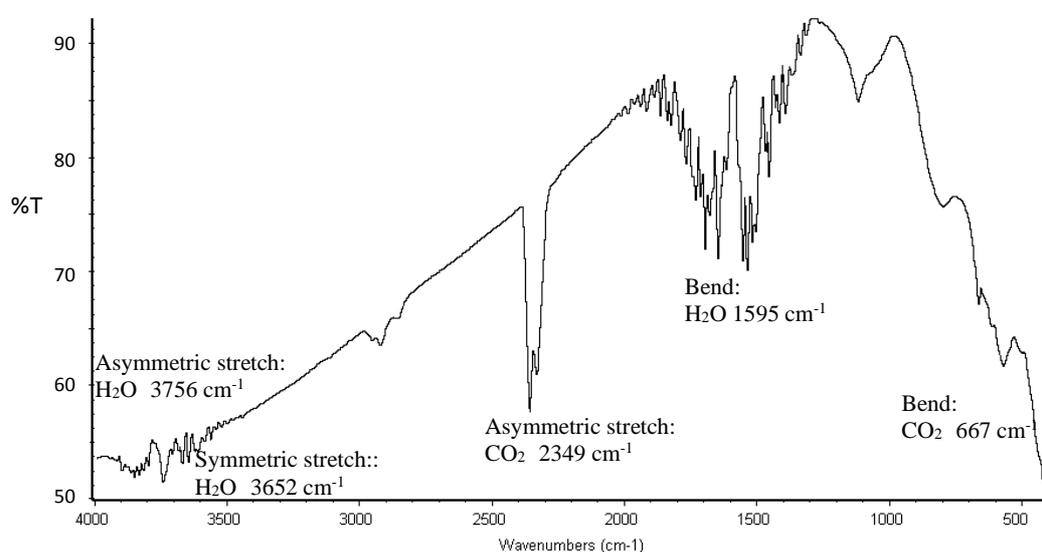


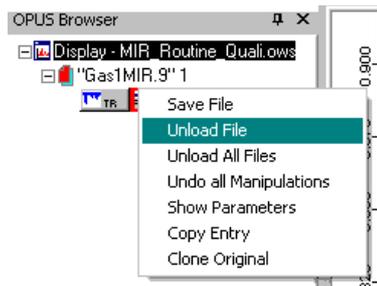
Figure 6: Background IR spectrum of ambient air showing vibrational transitions for CO₂ and H₂O. These transitions are responsible for the bulk of global warming.

To Zoom in around the NO absorption peak (near 1900 cm⁻¹), click on the Zoom In icon: . Left click on the spectrum on the upper left of the zoom region. Double-click the left mouse button on the lower right of the zoom region to expand the X- and Y-scales. You can determine the wavenumber of the peaks by positioning the mouse and reading the wavenumber in the upper-right corner of the spectrum window. If moving the cursor on the screen does not give the wavenumber readout, click right on the spectrum background slide right on Crosshair and choose Follow Data. Record the wavenumbers of the two parts of the NO peak. Average these values to find the vibration wavenumber that you will use for the calculations in the lab report. To exit Crosshair or Zoom mode click right on the spectrum screen.

- To set the Y-axis to full scale, click on the Full Scale Y icon .
- Return the spectrum to full scale by clicking on the  scale button.

Getting Ready for the Next Spectrum:

More than one spectrum can be active at a time. The displayed spectrum is controlled by clicking on the corresponding TR buttons in the Opus browser on the left of the screen. However, it is often less confusing to remove the old spectrum before taking a new spectrum. In addition, if you are finished for the day, you should remove your spectra to prepare for the next student. To remove your spectrum, move the mouse over your spectrum file name in the Opus Browser (not the “Display – “ line that lists the current Opus window system set-up file). Right click and select the Unload File Option.



- NO₂ is present in moderate concentration in your sample, as a contaminant. The NO₂ is produced by the oxidation of NO with residual O₂. To verify that you chose the correct absorption peak for NO, and not the peak for NO₂, pull out one rubber septum for a few seconds, in the hood. The gas in the sample cell should turn brown, showing the oxidation of the remaining NO to NO₂. Take the spectrum again and compare peak heights. Print the spectrum.

You don't need to retake the background again; click on the Advanced Measurement Icon:  and just click the “Sample Single Channel” button.

What should be in your laboratory notebook:

- Write a balanced reaction for your synthesis of NO. Here are some hints: sulfuric acid is just a source of hydrogen ions, any strong acid would do. Sodium nitrite is the salt of a weak acid. The final products of the reaction are NO and HNO₃. (You cannot ask for help on this. Do this part on your own. You may need to review some concepts from previous chapters in the text.)
- Attach a copy of both infrared spectra taken in your notebook.
- Calculate the average vibrational wavenumber, the frequency, the energy in kJ/mol of photons absorbed, the reduced mass, and the force constant of the NO bond.
- The wave number accuracy of the IR spectrometer is excellent. Use your ability to visually read peak positions to determine the number of significant figures to report for your force constant. In other words, how accurately do you think you can estimate the wavenumbers of the vibration bands by eye? The ability to read the wavenumber values is the only significant source of experimental error.

LABORATORY REPORT: Use the Report form for this experiment.

Use complete sentences, the proper number of significant figures, and include units. Equations, reactions, tables, and diagrams can be written by hand. The sections of your report are:

Introduction (2-sentence maximum): State the scientific purpose of the experiment. Describe the method you will use, in a general sense. Do not discuss the experimental procedure details or data analysis steps. Don't include pedagogical goals (e.g to teach us how to use.....).

Procedure: Give one-sentence descriptions of the synthesis and the gas collection method. Reference the lab write-up on the CH145 On-line Laboratory Manual and list any changes. Give the IR cell path length, cell window material, and the manufacturer and model of the IR spectrophotometer.

Data: Give your results for the average vibrational wavenumber, the frequency, the energy in kJ/mol of photons absorbed, reduced mass, and the force constant of the NO bond as a table.

Discussion:

- (a). Purpose accomplished: Restate the purpose of the experiment, but as completed goal.
- (b). Write the balanced half-reactions and overall reaction for your synthesis of NO.
- (c). Using the experimental NO force constant and Figure 4, predict the bond order for NO. (You needn't attach your plot).
- (d). Predict the qualitative bond order for NO based on molecular orbital theory. Show your molecular orbital diagram with the electron filling. Calculate the qualitative bond order.
- (e). Predict the bond order for NO using a Lewis dot structure.
- (f). Do the bond orders determined in parts (c), (d), and (e) agree? Provide the context for your decision.
- (g). Does this experiment provide experimental validation of molecular orbital theory? why?

Literature Cited: Give all literature cited, numbered according to the references in the body of your report.

Attach a copy of both infrared spectra. Identify the NO peak and two other peaks.

References:

1. T. W. Shattuck and M. A. Omary, Colby College, Waterville, Me.
2. G. C. Pimentel, R. D. Spratley, "Chemical Bonding Clarified Through Quantum Mechanics," Holden-Day, Inc., San Francisco, CA, 1969.