Synthesis and Infrared Spectrum of Nitric Oxide

**Purpose**: Infrared spectroscopy is used to determine the force constant of the bond in nitric oxide.

**Prelab:**
**Reading**: Section 6.1 and 6.2 in Brown, LeMay, and Bursten

1. Carbon monoxide absorbs infrared radiation at 2140 cm\(^{-1}\). Calculate the energy associated with this radiation. (Hint: Refer to the example shown on page 3.)
2. What volume of concentrated sulfuric acid is needed to make 50 mL of 2.0 M H\(_2\)SO\(_4\) solution? *For assistance, refer to the first paragraph in the procedure of this experiment.*

**INTRODUCTION**
The purpose of this week's experiment is to synthesize nitric oxide (NO), determine its infrared spectrum (what wavelengths of infrared light are absorbed by NO), and experimentally determine the force constant of its bond.

**Infrared Spectroscopy and Bonding**
Infrared (IR) spectroscopy (literally: the study of matter using infrared light emission/absorption) is a type of vibrational spectroscopy. Molecular vibrations can be modeled by the vibration of a spring (see Figure 1). In our model, the two ends of the spring are the two atoms in a covalent bond.

![Figure 1](image)

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

Vibrational spectroscopy provides a means to evaluate 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 wavenumber (\(\tilde{\nu}\)) for a transition is defined as the inverse of the wavelength:

\[
\tilde{\nu} = \frac{1}{\lambda}
\]

and combining the energy change for the transition (Plank’s equation):

\[
\Delta E = h\nu \quad \text{with} \quad \nu \lambda = c
\]

\[
\Delta E = \frac{hc}{\lambda} = h\tilde{\nu}
\]

So, the wavenumber, vibrational frequency, and vibrational energy are all proportional to each other – when one increases they all increase. The wavenumber of the IR band for a bond depends on the "stiffness" of the spring in the spring model, and this correlates with bond strength. This stiffness is characterized by the **force constant** – a higher force constant corresponds to a stiffer spring/stronger bond. The force constant is represented
by "k" and is measured in units of Newtons per meter (N/m). The relationship between
the wavenumber, $\tilde{\nu}$, and the force constant, $k$, is given by Equation 1:

$$\tilde{\nu} \text{ (cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 5.31 \times 10^{-12} \text{s/cm} \sqrt{\frac{k}{\mu}}$$  \hspace{1cm} (1)

where "c" is the speed of light ($2.998 \times 10^{10}$ cm/s) and "$\mu$" is the "reduced mass," which is
given by Equation 2:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$  \hspace{1cm} (2)

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

For example, Equation 1 shows that bonds with larger force constants have higher
vibrational wavenumbers. So double bonds, other things being equal, will have higher
vibrational wavenumbers 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 is because
heavier atoms are harder to move around. The reduced mass takes into account the atom
masses. Equation 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 Equation 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 $\mu = m_1 m_2/(m_1 + m_2) =
1*35/(1+35) = 1$ 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 1000g/kg: giving $\mu = 1*35/(1+35)/N_A/1000$ for this example.

Equations 1 and 2 show that one can calculate the force constant of a covalent bond if
the wavenumber for the IR band of that bond is determined experimentally. This is what
we will do in this experiment for nitric oxide. The force constant is, in turn, a measure of
the bond strength. Table 1 lists the values of bond energies, bond lengths, and force
constants for a series of diatomic species.\(^2\)

<table>
<thead>
<tr>
<th></th>
<th>B(_2)</th>
<th>C(_2)</th>
<th>N(_2)</th>
<th>O(_2)</th>
<th>F(_2)</th>
<th>CO</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy, kJ/mol</td>
<td>289</td>
<td>602</td>
<td>941</td>
<td>494</td>
<td>151</td>
<td>787</td>
<td>1070</td>
</tr>
<tr>
<td>Bond length, Å</td>
<td>1.59</td>
<td>1.24</td>
<td>1.10</td>
<td>1.21</td>
<td>1.44</td>
<td>1.18</td>
<td>1.13</td>
</tr>
<tr>
<td>$k$ (N/m)</td>
<td>350</td>
<td>930</td>
<td>2240</td>
<td>1140</td>
<td>450</td>
<td>1580</td>
<td>1860</td>
</tr>
</tbody>
</table>

The vibrational wavenumber of the radiation absorbed by a species can be
determined using vibrational spectroscopy in the infrared region of the electromagnetic
spectrum. To determine the spectrum, we need a light source, and method for varying the
frequency of light passing through the sample, and a detector. A schematic of a grating-
based spectrophotometer is diagrammed in Figure 2. 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 to 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/I₀) x 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.

![Figure 2. Schematic of a grating-based infrared spectrophotometer.](image)

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

**Solution:**
From equation 2, the reduced mass for the C-O bond is:

\[ \mu = \frac{m_C m_O}{m_C + m_O} \]

\[ m_C = (12.0 \times 10^{-3} \text{ kg/mol} \times 1\text{ mol}/6.02 \times 10^{23} \text{ atoms}) \times 1 \text{ atom} = 1.99 \times 10^{-26} \text{ kg} \]

Similarly, the mass of an oxygen atom as \( m_O = 2.66 \times 10^{-26} \text{ kg} \)

Substituting in Equation 2 gives:

\[ \mu = \frac{m_C m_O}{m_C + m_O} = 1.14 \times 10^{-26} \text{ kg} \]

The vibrational wavenumber can be calculated from Equation 1:

\[ \tilde{\nu} = 5.31 \times 10^{12} \text{ s/cm } (k / \mu)^{1/2} = 5.31 \times 10^{12} \left( \frac{1860}{1.14 \times 10^{-26}} \right)^{1/2} \]

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

**PROCEDURE**

1. Using concentrated sulfuric acid, which is 96% H\(_2\)SO\(_4\) by mass and has a density of 1.84 g/mL, make up 50 mL of 2.0 M sulfuric acid. When making up this solution, **remember to add acid to water**. This solution concentration need not 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** (see the Prelab assignment).

2. Assemble the gas generation system and IR cell as shown in Figure 3 below. Be careful not to touch the IR cell windows. The windows are made of CaF\(_2\) 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. CaF\(_2\) 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 cell to provide an air-tight seal. Carefully insert two syringe needles through the rubber septa. Add as much water as you can 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, NaNO\(_2\), in a mortar and pestle. Add 3 g of the powdered sodium nitrite to the first side-arm flask.

3. Pour about 20-30 mL of 2 M sulfuric acid into the dropping funnel. 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 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...
O gases from returning into the gas cell through the exit syringe needle. Pull the two needles out of the gas cell, place cell in the provided box and carry this to the instrument lab on the second floor. You will take the required IR spectra with your instructor.

**Mattson 4020 FT-IR Instructions:** The design of this instrument is different than that shown in Figure 2, however, the results are the same. Our instrument is significantly faster than a grating based instrument and is based on a Michelson interferometer. First take a background spectrum without the cell present by completing the following steps. Double click on the Control Panel icon in the lower left-hand side of the computer screen. Click on “Spectrometer Setup”. Choose 4 scans in both the forward and reverse direction and 8 cm\(^{-1}\) resolution. These settings were chosen to produce a spectrum in less than 30 seconds (Normally, for general purpose work more scans and better resolution would be chosen.) Click OK. Make sure the “Background” radio button is selected and then click on the “Scan” button. This step records the background spectrum of the air in the sample compartment.

Next place the gas sample cell in the IR compartment. Please be careful with the sample compartment cover, don’t let it fall backwards. The sample cell sits on top of two wooden blocks. Align the sample cell so that as much light as possible travels through the cell. To do this, note the position of the holes in the side of the sample compartment for the light beam. Double click on the Control Panel icon in the lower left-hand side of the computer screen. Make sure the “Sample” radio button is selected and then click on the “Scan” button. The spectrum should appear in several seconds. When you are asked if you want to replace the spectrum, answer “yes.” Print your spectrum by pulling down the File menu and choosing Plot. Click on the “Plot” button in the Plotting Window and then click on “Done”.

A spectrum of the empty sample cell will be available to help you decide which peaks correspond to the NO absorption. Note the positions of the H\(_2\)O and CO\(_2\) 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. To expand the spectrum use the left mouse button to pull a “rubber-band-box” around the NO absorption peak (near 1900 cm\(^{-1}\)). Print out the expanded spectrum. You can determine the wavenumber of the peaks by positioning the mouse and reading the wavenumber in the lower right-hand border of the spectrum window. 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.

NO\(_2\) will be present in moderate concentration in your sample. The NO\(_2\) is produced by the oxidation of NO with residual O\(_2\). To verify that you chose the correct absorption peak for NO, and not the peak for NO\(_2\), pull out one of one rubber septum for just a second. The gas in the sample cell should turn brown, showing the oxidation of the remaining NO to NO\(_2\). Take the spectrum again and compare peak heights. You don’t need to retake the background again, just do a “Sample” scan.

**Reference:**
1. This is a modified version of the original experiment developed by T. W. Shattuck and M. A. Omary, Colby College, Waterville, ME.

**What should be in your laboratory notebook:**
- Your calculation of the average vibrational frequency for the bond in nitric oxide from your infrared spectrum as instructed in the procedure.
- Your calculation of the energy of the radiation absorbed by the NO bond.
- Your force constant calculation for the bond in nitric oxide from your experimental data using Equations 1, 2.
- Reference citations for the atomic masses.

**What should be attached to your discussion (and put in your notebook later):**
- A balanced reaction for your synthesis of NO. You will have to develop this yourself, but 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 HNO$_3$.
- Both infrared spectra that you obtained with peaks due to H$_2$O, CO$_2$, NO, and NO$_2$ clearly identified.

**What should be in your discussion:**
Address the objectives and report the findings. You don’t have a lot of data for this experiment – so provide and clearly discuss your findings, including the significance for all values that you experimentally obtained/calculated. Be sure to use proper significant figures when presenting values. Include how you determined which IR absorbance was due to the nitric oxide (for your obtained spectra).