Investigation 5: Infrared Spectroscopy and Molecular Modeling

Question:  What do molecules look like and how do they move?  How can we make them vibrate?  Can we model a molecule and its motions?  Can we identify functional groups in an unknown molecule using infrared spectroscopy and modeling?

Pre-lab required reading
Technical Primers:
Keeping a Laboratory Notebook
Infrared Spectroscopy

Safety and Waste Disposal

- Goggles and gloves should be worn while handling organic compounds.
- Some organic compounds are flammable, are mild irritants, or are mildly toxic if ingested.
- All hazardous materials should be placed into appropriate containers after use.

Background

The bonds between atoms are not static, as they are often represented in Lewis structures, but are actually in a state of constant motion called molecular vibrations. They bend, stretch, and vibrate rapidly, and can do so either symmetrically or asymmetrically. Some important modes of vibration are shown in Figure 1.

![Figure 1: Vibrational modes of water. For a moving picture of these modes see:](http://chemwiki.ucdavis.edu/@api/deki/files/7070/=h2ovibrations.gif)

Photons of infrared (IR) radiation are absorbed by the bonds if they have the right amount of energy to cause a vibration. In order for this to happen the frequency of the IR radiation must match that of the vibrating bond. The absorbed radiation then serves to increase the amplitude of the vibrations and thus the kinetic energy of the molecule. Because different bonds vibrate with different frequencies, they will absorb different frequencies of radiation that are unique to them. This is the fundamental idea behind IR spectroscopy.

Using IR radiation to characterize a sample is a highly useful technique for chemists. When a sample is irradiated with IR light, the bonds will absorb only at certain distinct frequencies while the rest of the light passes onto the detector. The detector can determine which wavelengths are hitting it and which are not and it generates a corresponding image, known as a spectrum. One such spectrum, that of 2-butanone is shown in figure 2.
Figure 2: Experimental Infrared Spectrum and structure of 2-butanone.

While the spectrum may look complicated at first a trained chemist could look at this and immediately recognize that this compound contains a C=O bond as well as methyl groups (see primer for a visual reference of major regions). This is possible by the fact that different bonds have very different and distinct absorption frequencies. A typical IR spectrum is organized like the one in figure 2, with % transmittance on the y-axis and wavenumbers (measured in units of cm\(^{-1}\)) on the x-axis. Wavenumbers are a simple way of measuring and reporting the frequency while % transmittance refers to the amount of light that that detector is sensing at each wavelength. At 100%, the detector is receiving all of the light that was initially shown; as the bonds absorb radiation, the amount of light that reaches the detector decreases, generating a “peak” in the spectrum by lowering the % transmittance.

The theoretical or calculated IR spectrum of 2-butanone is shown below (the spectrum is calculated using WebMO/Gaussian computer program that you will use in the lab).

Figure 3: Calculated Infrared spectrum of 2-butanone.
Note that the calculated spectrum does not have the same amount of detail as the experimental spectrum, but the major functional groups (such as the C=O bond near 1700-1800 cm⁻¹ and the C-H stretching near 3000 cm⁻¹) are clearly discernible.

In this investigation, your group will obtain IR spectra of several compounds and observe how the different characteristics of the bond affect the frequency at which it absorbs. A simplistic view of the molecular bond is that of two masses on either side of a spring, shown in figure 4.

**Figure 4:** Illustration of two masses connected by a spring.

The bond is modeled by the spring, while the atoms are represented by the masses. Hooke’s Law describes the relationship between the frequency of the vibration, the masses, and the strength of the spring. Hooke’s Law is:

\[ f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_1m_2}{m_1+m_2} \quad (1) \]

Where \( f \) is the frequency of vibration in Hertz (s⁻¹), \( k \) is the spring constant (representative of the strength of the spring), \( \mu \) is the reduced mass of the system, and \( m_1 \) and \( m_2 \) are the masses of the two objects (or atoms, in this case).

Hooke’s Law can be applied to chemical bonds, and \( k \) can be used as an estimate of bond strength. For example, the nitrogen-hydrogen single bond absorbs at approximately 3350 cm⁻¹ while the carbon–hydrogen single bond absorbs around 3200 cm⁻¹. Using Hooke’s Law these absorption frequencies can be converted into spring constants which can be used to estimate the relative strengths of the bonds.
Procedure

Week one:
Overview

Each lab team will be assigned one of the following sets of three compounds and an unknown. You will then work together to draw Lewis Structures, collect IR spectra and Model the compounds using WebMO/Gaussian.

Table 1: Summary of sets of compounds to be investigated.

<table>
<thead>
<tr>
<th>Compound Set</th>
<th>Compound Name</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td></td>
<td>Heptane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td></td>
<td>Octane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>2</td>
<td>Methanol</td>
<td>CH₃OH</td>
</tr>
<tr>
<td></td>
<td>Methanol-d</td>
<td>CH₃OD</td>
</tr>
<tr>
<td></td>
<td>Methanol-4d</td>
<td>CD₃OD</td>
</tr>
<tr>
<td>3</td>
<td>Methyl tertbutyl ether</td>
<td>CH₃OC(CH₃)₃</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>CH₃C(O)CH₃</td>
</tr>
<tr>
<td></td>
<td>Propionic acid</td>
<td>CH₃CH₂C(O)OH</td>
</tr>
<tr>
<td>4</td>
<td>Octane</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td></td>
<td>Octene</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td></td>
<td>Octyne</td>
<td>CHCCH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>5</td>
<td>DIPEA (N,N-Diisopropylethylamine)</td>
<td>CH₃CH₂N(CH(CH₃)₂)₂</td>
</tr>
<tr>
<td></td>
<td>DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene)</td>
<td>C₉H₁₆N₂ (7-member ring fused with 6-member ring)</td>
</tr>
<tr>
<td></td>
<td>Acetonitrile</td>
<td>CH₃CN</td>
</tr>
<tr>
<td>6</td>
<td>1-chlorobutane</td>
<td>ClCH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td></td>
<td>1, 4-dichlorobutane</td>
<td>ClCH₂CH₂CH₂CH₂Cl</td>
</tr>
<tr>
<td></td>
<td>1-bromobutane</td>
<td>BrCH₂CH₂CH₂CH₃</td>
</tr>
</tbody>
</table>

The groups will rotate through using the IR spectrometer and use either lab computers or laptops to access WebMO/Gaussian.
Part I: Molecular Modeling – Visualizing Molecules with Theory and Models

1. Draw the Lewis structures for the compounds in your group’s assigned set. Use Valence Shell Electron Pair Repulsion Theory to predict the shape around each of the atoms (except hydrogen) in the compounds and label the bond angles. Determine whether each molecule is polar or nonpolar.

2. On a computer, open the ChemDraw Ultra program (It can be downloaded for free at: http://help.allegheny.edu/tutorials/downloads.php). Draw each of the compounds under investigation.

   Use the lasso tool to select each molecule one at a time. From the pull down View menu at the top of the screen select the Show Chemical Properties Window and the Show Analysis Window for each molecule independently. For each, a box will appear that contains information concerning the chemical properties of the structure selected. Record the boiling point and the molecular weight for each compound.

3. From the Chemistry Department web site access the WebMO/Gaussian03 Program. Use the login and password provided by your instructor. From the WebMO Job Manager, start a new job from the pull down menu (Create new job). Build one of the three compounds in your set that your group is investigating. Once the balls (representing carbons) and sticks (representing bonds) of the basic structure have been drawn, the molecule will need to be “cleaned-up” before any calculations are done. Go to the “Clean-Up” pull down menu. First add hydrogens, then go to the “Clean-Up” menu again and click on hybridization. Go to the “Clean-Up” menu again and click on geometry. Go to the “Clean-Up” menu one last time and click on mechanics and choose optimize. At this point the molecule is ready to run the job. To do this, click on the arrow on the bottom right of the window. A new window will appear with a space to name the job and several pull down menus. The appropriate choices for this exercise are:

   - **Name:** actual name of compound plus group identifier
   - **Calculation:** Optimize & vib. freq.
   - **Theory:** B3LYP
   - **Basis set:** Routine: 6-31G(d)
   - **Charge:** 0 (unless your compound is charged – indicate charge here)
   - **Multiplicity:** Singlet.

   A click on the arrow on the bottom right of this window will send the job to the server and return you to the Job Manager window where you may monitor the progress. It will take several minutes to calculate the result. When the job is finished, it will be indicated in the Job Manager. You may then access the data by clicking on the magnifying glass icon under the heading “Actions”. Click here to access the results of the calculation. The structure should appear in the “molecule viewer” window as a three-dimensional ball and stick representation with each atom in the structure numbered.

   To freely rotate the model (the ball and stick representation), select the curvy arrow located on the top of the tool bar. Use this tool to rotate the molecule and view it from different directions. Compare this ball-and-stick representation to the structure made earlier with the model kits. Adjust as necessary until you are sure the representation and the physical model are the same thing.

   Scroll down the page to see the calculated quantities. Near the bottom of the data you can click on the magnifying glass icon next to the Infrared spectrum to view, save and print the spectrum. If you click on the movie icon next to any of the vibrational modes, it will animate the motion in the molecule viewer.

   Repeat the modeling process for the other molecules in your set as advised by your instructor.
Part II: Infrared Spectroscopy
Analyze a sample of each compound in your set (as directed by your instructor) using infrared spectroscopy.

Carefully follow your instructors’ directions when using the infrared spectrometer.
1. Make sure the ATR crystal is clean before using the instrument.
2. Place several drops on the crystal.
3. Collect, save and print the spectrum of your sample.
4. Carefully remove the compound from the ATR crystal and clean with acetone. Dry off completely.
5. Then clean with pentane. Dry off completely.
6. Repeat this procedure with all the remaining compounds in your set.

Week two:

Overview
Spectroscopy can be very useful in identifying unknown compounds. Based on what you have learned in part one of this experiment, you will use infrared spectroscopy and molecular modeling to determine the major functional groups of an unknown compound. Each lab team will be assigned one compound to analyze. You will then work together to draw Lewis Structures, collect IR spectra and Model the compounds using WebMO/Gaussian.

References