Background

The presence or absence of structural units of organic molecules can be identified by infrared absorption spectroscopy. Infrared absorption spectroscopy is the measure of the amount of radiation absorbed by molecules in the infrared region. The energy absorbed causes a molecular vibration, either a stretching or bending between bonds of atoms which in turn is observed as an absorption band or peak in an infrared spectrum. While a typical infrared spectrum will cover frequencies between 600—4500 cm\(^{-1}\) (inverse wavenumbers), bending modes are easier than stretching modes and appear at lower frequencies. The intensity of an absorption can also be seen in the polarity of the bond, and in general, the more polar the bond the greater the intensity of the stretching band. Likewise the greater number of similar bonds will have an additive effect causing a greater intensity of an absorption band or peak to appear.

Infrared spectroscopy is primarily used as an important diagnostic for the identification of structural units of organic molecules. Extensive correlations exist between absorption peaks and the structural units of organic molecules. Characteristic absorbencies are as follows:

<table>
<thead>
<tr>
<th>Specific Functional Group</th>
<th>Observed Frequency Vibration (cm(^{-1}))</th>
<th>Intensity</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonyl C=O stretch</td>
<td>1800-1650</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>O—H or N—H stretch</td>
<td>3600-3300</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>C—O stretch</td>
<td>1300-1100</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>C—H stretch</td>
<td>around 3000 depending on hybridization of C</td>
<td>moderate</td>
<td>variable</td>
</tr>
</tbody>
</table>

Secondly, an infrared spectrum can be thought as a molecular fingerprint. Like fingerprints, a criminologist can prepare a list of possible suspects to a crime by making comparison to prints accessed through the Department of Motor Vehicles and other sources. Likewise, a chemist can make an exact identification of unknown to a known substance since no two molecules will give an identical infrared spectrum. The available of computer and library reference data bases of known standard spectra will allow a chemist to make a final identification an unknown substance by direct comparison to known spectra. Some of my favorite data bases, I find the SDBS (Japanese) site is most useful are linked are linked at [http://www.sdmesa.sdccd.net/~dgergens/spectroscopy_links.htm](http://www.sdmesa.sdccd.net/~dgergens/spectroscopy_links.htm)

Reference spectra are available from a variety of sources:

a. Organic chemistry textbooks, laboratory manuals, and spectroscopy handbooks. Our library has several on reserve.

b. Data from colleagues. Work together, share your data.

c. Spectral libraries. The Aldrich Spectral Library of FTIR Spectra, or Satler Reference Spectra are available in the science library on the campus of USCD or SDSU.

d. Employer reference library. You may already work in a laboratory that has a reference library.

On the next page, is the spectrum of aspirin taken on the FTIR instrument in our laboratory and the spectrum of aspirin taken from a data base found on the internet at the SDBS (Japanese) site.
Correlation Table

<table>
<thead>
<tr>
<th>Specific Functional Group</th>
<th>Observed Frequency Vibration (cm⁻¹)</th>
<th>Intensity</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid O–H</td>
<td>3500-2800</td>
<td>moderate</td>
<td>broad</td>
</tr>
<tr>
<td>ester C=O stretch</td>
<td>1761.7</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>acid C=O conjugated stretch</td>
<td>1693.6</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>C=C conjugated stretch</td>
<td>1617.0</td>
<td>weak</td>
<td>sharp</td>
</tr>
<tr>
<td>C–O stretch</td>
<td>1200.0</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>C–H bend</td>
<td>1472.3</td>
<td>weak</td>
<td>sharp</td>
</tr>
</tbody>
</table>

Experimental FT-IR Spectrum - Aspirin

Actual FT-IR Spectrum - Aspirin

1. [http://aist.go.jp/RIODB/SDBS/sdfs]
Purpose

Infrared spectroscopy is an important tool for recognizing quickly the presence or absence of certain organic structural and functional units by interpreting absorption bands and peaks in an infrared spectrum. In this exercise, you will learn the most useful of these absorption peaks so assignments and deductions for the presence or absence of a structural unit in a given infrared spectrum can be made. The order in which to analyze these absorption peaks in a given spectrum is also very important. You will also learn the correct methods for sample preparation.

Pre-Laboratory

It is recommended that you view the Dr. Gergens' FTIR tutorial and complete the linked handouts before coming to class on the day the FTIR assignment is to begin at

http://www.sdmesa.sdccd.net/~dgergens/chem231L/FTIR/ftir_tutorial_movies_frame.htm

Watch the FTIR tutorial, and take notes by filling in the blanks for important FTIR absorbency frequencies given for each functional group given on the next page. Memorizing the general regions in which an organic structure gives absorption bands or peaks is required for you to do well in this assignment. Additional readings over infrared spectroscopy can also be found in the lecture and laboratory texts.

Exercise

Your laboratory instructor will cover the theory, the workings of an infrared spectrophotometer, the basics of infrared analysis and sample preparation.

Several practice problems are given on the next pages. You are to complete these practice problems and discuss the answers in your laboratory class. Your instructor may assign you individual problems and may ask you to present your answers to the class the following period.

The exercise also asks that you run an infrared spectrum analysis on an unknown organic substance. An explanation for this part of exercise is given on page 17.

Sample Preparation

Just a few words on sample preparation. There are several ways to prepare samples of infrared analysis and a sample will have to be placed in a sample holder, or cell. In general, cells are constructed from materials that do not absorb strongly throughout the infrared region of the spectrum. Typically, ionic substances like sodium chloride or potassium bromide are materials used to construct such cells. NaCl and KBr do not absorb in the 4000 to 650 cm⁻¹ region of a typical spectrum, the region in which we run our infrared analysis. At one time, sodium chloride plates and potassium bromide pellets were the most commonly used cell for routine analysis and are still being used. Now, newer cells consisting of polyethylene film are being used. Polyethylene film, a saturated hydrocarbon and a solid form of liquid mineral oil, is commonly used. Like liquid mineral oil, solid polyethylene film does absorb strongly at 3000 cm⁻¹ for a C—H stretch and 1200 cm⁻¹ for a C—C stretch. We will soon discover these two infrared regions are not the most useful infrared active regions used in an infrared analysis. Why? Most organic substances contain these bonds, thus must substances will absorb in those regions anyway. Still, to assist us in our analysis the absorbencies caused by polyethylene at 3000 cm⁻¹ and 1200 cm⁻¹ will be subtracted out from our final spectrum by having the instrument run a background subtraction.
Use of Polyethylene Cells

To determine the infrared spectrum of a substance, one must place it on a sample holder, or cell. In general, we will use a polyethylene cell in preparing our samples on the Nicolet Impact 400 instrument.

First, before preparing a sample, your cell holder should be clean and a spectrum background of the clean cell taken. To clean a polyethylene cell, methylene chloride, CH$_2$Cl$_2$, is often the solvent of choice. Working under the hood, add enough drops of CH$_2$Cl$_2$ to coat both sides of the cell, then dry the cell by blotting both sides of the cell with a KimWipe. Before running a spectrum background, make sure the cell is clean and dry. Why must the cell be free of solvent when running a background?

Running a spectrum background. A clean dry cell is placed into the instrument. The instrument cover is closed and one selects run background on the instrument. After running a background, the cell is quickly removed, and the instrument sample compartment cover is closed. Working quickly to remove the cell and by closing the sample compartment will assure the atmosphere inside the sample compartment will remain relatively constant while you prepare your sample. Breathing heavily into the sample compartment will affect your analysis. What gases contained in your breath will absorb in the infrared region? Where would those extra absorbencies appear?

Preparing a sample on a cell:

Liquids (Neat). Using an open ended capillary tube, a drop of liquid organic substance is placed directly on one side of the polyethylene cell, and by moving the capillary tube around the cell is coated with sample. Organic liquids have a tendency to evaporate so move quickly. Return the cell to the instrument, and quickly close the cover and select run sample. Can you guess what "neat" means?

Solids: There a three common ways to run solids depending on the sample holder, or cell. Since we will be using polyethylene film as a sample holder, let's consider that first.

A. Polyethylene Thin-Film. Run a background on a clean polyethylene cell. Prepare the solid by placing it on a watch glass and adding a solvent that dissolves the sample. Recall "like dissolves like." Generally, we will use either ethyl acetate or methylene chloride to dissolve the samples on our watch glass. Between these two solvents, can you determine which is more polar? These solvents are volatile. If the solvent evaporates away, just add more. Don't forget to cap the solvent bottle when you done. Then, using an open ended capillary tube, a drop of the dissolved liquid organic substance is placed directly on one side of the polyethylene cell and by moving the capillary tube around, coat the cell with sample. Let the solvent evaporate away from the cell and re-apply more dissolved sample. Between applications, let the solvent evaporate. Apply sample three to five times, evaporating the solvent away from the cell between applications. Finally, air dry the cell. There should be no more solvent on the cell, just a residue of solid. Look to see you have sample on the cell. Then run the sample by returning the cell to the instrument and closing the instrument cover. Can you imagine what would happen if there was still solvent residue on the cell while running your sample?
**B. KBr Pellet.** KBr pellets are prepared by grinding 1 mg of sample in 10 mg of anhydrous KBr, pressing the mixture in a press to make a transparent disk and then running a spectrum of the transparent KBr disk containing the sample in the instrument. Running a background in this method is not required. *Can you think of why running a background in this method is not required?*

**C. Nujol Mull.** Nujol mulls are prepared by grinding 1 mg of sample in 10 mg of mineral oil, and smearing the mixture between sodium chloride salt plates and then running a spectrum of mineral oil containing the sample in the instrument. Running a background is not required but your spectrum will contain more than just absorbencies from your sample. *Can you think of what other absorbencies, besides your sample absorbencies, will appear in the spectrum of a sample prepare using Nujol oil? Where would those extra absorbencies appear?*

**Use of the Instrument and Your Unknown**

Your instructor will demonstrate the use of the instrument. Bring your notebook to the demonstration and take notes. While you are working on this exercise, an unknown liquid or solid will be issued and FTIR spectrum taken. The procedures for running your sample are given in the next experiment, "Unknown Analysis and Write-Up."

**Sign Up Sheet**

The is a instrument sign up sheet. Each sample analysis takes 10 minutes. *Be sure to have a disk, your sample, and a watch glass ready when its is your turn to run your sample. Be considerate. Even if it is your turn, look around, and ask before using the instrument, "Is anyone using the instrument?"* Please ask for help if you need additional assistance in working the instrument. Afterwards, have your instructor inspect and initialize your spectrum.

If you are waiting to use the instrument, make good use of your time. While waiting, review once again Dr. Gergens' tutorial at

http://www.sdmesa.sdccd.net/~dgergens/spectroscopy_links.htm

and, complete the FTIR Problem Set by answering the questions and matching the spectra.
Handout to be completed and discussed in class
Watch Dr. Gergens' IR tutorial

Identify the order of regions in an IR analysis

Identify the Functional Group

Identify the absorbancy value of each indicated bond

X = Cl, Br
Using infrared spectroscopy, how can you tell the difference between:

a. a carboxylic acid and an alcohol?

b. an amide and ester?

c. an aldehyde and a ketone?

d. an alkane and alkene?

e. alkene and a monosubstituted aromatic ring?

f. terminal alkyne and internal alkyne?

g. amine and an alcohol?

h. tertiary amine and ether?
Infrared Spectroscopy Problem Set to be turned in and graded.

NAME: _______________________

1. If you haven't done so already, watch Dr. Gergens' tutorial on infrared analysis. It is linked to the course homepage at http://www.sdmesa.sdccd.net/~dgergens/spectroscopy_links.htm. If you have additional questions and/or suggestions regarding the tutorial, you can e-mail at dgergens@sdccd.cc.ca.us.

Analyzing FTIR Spectra
2. Identifying the most conspicuous peaks.
   a. Draw and label the absorbency peak typically found for a carbonyl stretch, C=O.
   b. Draw and label the absorbency peak typically found for a hydroxyl stretch, O—H.
   c. Draw and label the absorbency peak typically found for a amino stretch, N—H.
   d. Draw and label the absorbency peak typically found for a C—O stretch.

   ![Diagram of Wave Number vs. Absorbency Peaks]

3. Identifying the least conspicuous peaks.
   a. Draw and label the absorbency peak typically found for a hydrocarbon, C—H stretch.
   b. Draw and label the absorbency peak typically found for a hydrocarbon, C—C stretch.
   c. Draw and label the absorbency peak typically found for a hydrocarbon, C—H bend.

   ![Diagram of Wave Number vs. Absorbency Peaks]
4. When an infrared spectrum of an unknown is analyzed, you should concentrate first on trying to establish the presence (or absence) of a few major functional groups. In doing so, you should take a logical approach in analyzing an infrared spectrum. Number in order the absorbency regions your eyes focus in on first, second, third, fourth, etc. when you look at an infrared spectrum? Write these numbers in the regions below.

5. In relationship to your answer in question 4, give approximate values and functionality to each region.

<table>
<thead>
<tr>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
<th>6th</th>
<th>7th</th>
</tr>
</thead>
<tbody>
<tr>
<td>region</td>
<td>1710 cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| functionality | C=O | | | | | |

Stretching Frequencies and Absorption Peaks for the Carbonyl

6. A typical carbonyl of a ketone or aldehyde give an intense stretch at 1710 cm⁻¹.

a. An amide carbonyl stretch will appear at __________ cm⁻¹. Explain why the amide carbonyl appears (less, greater) than a 1710 cm⁻¹.

b. An ester carbonyl stretch will appear at __________ cm⁻¹. Explain why the ester carbonyl appears (less, greater) than a 1710 cm⁻¹.

c. An conjugated carbonyl stretch will appear at __________ cm⁻¹. Explain why the conjugated carbonyl appears (less, greater) than a 1710 cm⁻¹.
7. When preparing a solid sample by the thin-film method, the solvent must completely evaporated from the polyethylene cell and the cell completely dried. However, as the solvent evaporates from the polyethylene plate, the plate cools allowing moisture from the atmosphere to condense onto the plate. If moisture condenses onto the plate with the sample, what erroneous absorbencies will a student observe in his or her spectrum?

8. Thin film versus Nujol mull ample preparation.
   a. What are the major differences between the infrared spectrum of solid prepared by the thin film method of sample preparation relative to the Nujol mull method?

   b. What causes of these differences?

   c. What are appropriate solvents for cleaning an IR salt plate?

   d. What are inappropriate solvents for cleaning an IR salt plate?
9. Examine the following pairs of compounds and pick two definitive frequency regions which you would use to clearly distinguish between them. Use arrows to point to distinguishing features and label important absorbency peaks. Then give a brief discussion.

a. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)  
   ![Diagram of CH₃CH₂CH₂CH₃]  
   1475 1375  
   1475 only  
   Both have C—H bending but butane has a CH₃ which also appears at 1475 cm⁻¹.

g. \( \text{CH}_3\text{C}=\text{OCH}_3 \)  
   ![Diagram of CH₃C=OCH₃]  
   XXXX  

b. \( \text{CH}_3\text{C}^-\text{OCH}_3 \)  
   ![Diagram of CH₃C⁻OCH₃]  
   XXXX  

h. \( \text{CH}=\text{CH}_2 \)  
   ![Diagram of CH=CH₂]  
   XXXX  

i. \( \text{CH}=\text{CH}_2 \)  
   ![Diagram of CH=CH₂]  
   XXXX  

c. \( \text{O} \)  
   ![Diagram of O]  
   XXXX  

j. \( \text{N}^-\text{CH}_3 \)  
   ![Diagram of N⁻CH₃]  
   XXXX  

d. \( \text{O} \)  
   ![Diagram of O]  
   XXXX  

k. \( \text{CH}_3\text{C}=\text{H} \)  
   ![Diagram of CH₃C=H]  
   XXXX  

l. \( \text{CH}_3\text{C}^-\text{CH}_3 \)  
   ![Diagram of CH₃C⁻CH₃]  
   XXXX
10. The following pages contain 16 spectra for compounds that appeared in the ISIS Draw exercise.

a. Report the structure for each substance named below as determined in the ISIS Draw exercise.

b. Predict expected absorbencies peaks to be present in the infrared spectrum for each substance. See letter L as an example. Cut and paste your compound images from the ISIS Draw exercise, and add arrows as needed.

c. Concentrate on trying to establish the presence (or absence) of a few major functional groups in each spectrum. In analyzing an infrared spectrum, what regions do your eyes focus in on first, second, third, fourth...? Watch the Dr. Gergens' IR tutorial again if you are not sure.

d. Separate spectra by functional group by based on your tentative assignments. For example, start by separating those spectra containing a carbonyl absorbency from those without.

e. Match tentative spectral absorbency assignments to your absorbency predictions for each substance.

f. Where your predictions in part b correct? Assign at least two definitive frequency values to each spectrum.

g. Share your results with members of your class.

h. If need be, verify spectral matches by searching for spectroscopic data using links from course home page and/or other sources like Aldrich Spectral Handbook, Satler Reference Spectra at UCSD or SDSU.

<table>
<thead>
<tr>
<th>Letter</th>
<th>Compound &amp; Structure</th>
<th>Letter</th>
<th>Compound &amp; Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ethyl butanoate</td>
<td>9.</td>
<td>ethyl 2-bromo-2-methylpropionate</td>
</tr>
<tr>
<td></td>
<td>ester C=O stretch @ 1765 cm⁻⁻⁻⁻; strong, sharp</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂CH₂C=OCH₂CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>N-ethylaniline</td>
<td>10.</td>
<td>1-phenyl-2-propanone</td>
</tr>
<tr>
<td>3.</td>
<td>4-isopropyltoluene</td>
<td>11.</td>
<td>3,7-dimethyl-6-octenal</td>
</tr>
<tr>
<td>4.</td>
<td>2-methylpropanoic acid</td>
<td>12.</td>
<td>3-methyl-1-butanol</td>
</tr>
<tr>
<td>5.</td>
<td>polyethylene</td>
<td>13.</td>
<td>2-aminotoluene</td>
</tr>
<tr>
<td>6.</td>
<td>3-bromopropyne</td>
<td>14.</td>
<td>3-methyl-3-buten-2-one</td>
</tr>
<tr>
<td>7.</td>
<td>adipoyl chloride</td>
<td>15.</td>
<td>cyclohexanone</td>
</tr>
<tr>
<td>8.</td>
<td>Tylenol</td>
<td>16.</td>
<td>caffeine</td>
</tr>
</tbody>
</table>

8. Tylenol

9. ethyl 2-bromo-2-methylpropionate

10. 1-phenyl-2-propanone

11. 3,7-dimethyl-6-octenal
Purpose

In this experiment, an unknown liquid or solid will be issued for FTIR identification. Since no two molecules of different structure have exactly the same infrared absorption spectrum, the infrared spectrum can be used for molecules much as a fingerprint can be used for humans. By comparing the infrared spectrum of your unknown to an infrared spectrum of a substance thought to be identical, one can establish whether or not they are in fact identical. The unknown will be a substance on a list of possibilities provided in the laboratory.

Procedure

1. RUN your sample. Your instructor will demonstrate the use of the instrument. Bring your notebook during the demonstration and take notes. Please ask for help if you need additional assistance in working the instrument.

2. SCALE the spectrum and do a PEAK PICK.

3. LABEL your spectrum. Use the peak pick function to select an area in the upper left hand corner and input the following: your name, unknown number, date, and how the sample was prepared (i.e., thin film, neat, KBr, Nujol mull).

4. CHANGE the file extension to .tif, and SAVE your spectrum to diskette as a <filename.tif> file. A file name should be less than eight characters long. Your diskette should not be completely full with data when trying to save.

5. PRINT a hard copy of the spectrum.

6. Have your instructor inspect and initialize your spectrum with their approval.

7. PRESS and HOLD the eject button on the disk drive until you diskette ejects.

8. Identify broad visual patterns, stretching frequencies of vibration (cm⁻¹), intensity, and shape. Concentrate on trying to establish the presence or absence of conspicuous peaks. For example, the region at 1710 cm⁻¹ is the first region to consider whether or not there is a carbonyl, C=O. The absence of peaks may also be noted in the correlation table. Have your instructor help you if you are not clear as to how to interpret an infrared spectrum.

9. Record stretching frequencies of vibration (cm⁻¹), intensity, and shape into a correlation table in your notebook. This does not mean you need to record all absorbencies, only pertinent ones.

10. Predict the functional group classification for your compound. Your unknown will be a substance on a list of possibilities provided in the laboratory. By process of elimination, narrow your search to a few possibilities.

11. Research reference spectra for your unknown. Reference spectra are available from a variety of sources:
   a. Organic chemistry textbooks, laboratory manuals, and spectroscopy handbooks. Our library has several on reserve.
   b. The World Wide Web. The SDBS (Japanese) site is most useful. Additional spectroscopy links are located on the organic laboratory home page for this course.
   c. Data from colleagues. Work together, share your data.
   d. Spectral libraries. The Aldrich Spectral Library of FTIR Spectra, or Satler Reference Spectra are available in the science library on the campus of USCD or SDSU.
   e. Employer reference library. You may already work in a laboratory that has a reference library.
   f. Similated spectra. Some spectral data can be generated by spectral simulation programs (i.e., Beaker).

12. Correctly identify your unknown.

13. Complete the post laboratory exercise.
Post Laboratory Exercise

1. Correctly identify the unknown.

2. Apply the word processing skills learned in the previous experiments to complete a data page like the one on page 2. In Microsoft Word, use the <INSERT>, <PICTURE>, <FROM FILE> commands. Scale all images in an appropriate manner. To paste in images, remember the command <PASTE SPECIAL> under <INSERT>:

3. Write a conclusion. Include the following in the conclusion.

a. Begin the conclusion with the following statement and paste an image of your unknown into the report.

   Unknown ___ was a _________ and was correctly identified as __________;
   unk # functional group compound name

   cut & paste or use ISIS draw to add your structure here

   The sample was prepare as a (thin film, neat, Nujol mull), and gave ....

b. Write a spectral interpretation for the unknown compound, BUT don't over do it. In the discussion, interpret the most important spectral features used to correctly identify the unknown.

c. Describe why some functional groups were eliminated while others were retained in the identification.

d. Describe how certain unknowns from the list of possibilities in the laboratory were eliminated.

e. Describe and discuss any anomalies in the appearance of the infrared spectrum for the unknown relative to the appearance for the reference spectrum. The unknown and reference spectra may match, but not exactly. This could be due to differences in sample preparation which may cause slight variances between the appearance of the unknown and reference spectra. Perhaps the reference spectrum was run as a KBr pellet, but your sample was prepared as a thin film. Or, during sample preparation the sample became wet due to moisture in the air. In this case, an O—H stretch at 3500 cm⁻¹ region appears in the spectrum but is absent from the reference spectrum. Discuss these types of notable differences in the conclusion.

f. Give a bibliography and reference all sources for spectral data, and other literature used in the analysis and identification.

Grading of the Unknown - This assignment will be graded with the following criteria in mind:

1. The appearance of your FTIR spectrum of the unknown sample. Did your instructor initialize it?
2. A correlation table with all pertinent absorbencies needed to unambiguously identify the unknown.
3. The correct functional group classification for the unknown.
4. The exact identification of the unknown.
5. A typed conclusion and explanation over the method used in the correct identification of the unknown.
6. The overall appearance of the word processed report.
7. A bibliography of references used in the analysis.
8. Submit the final write-up electronically to me for grading as a Microsoft Word document with the file name <FTIR(your initials here).doc. For example, FTIRddg.doc. Before sending it, scan it for viruses.