ANALYSIS OF ASPIRIN – INFRARED (IR) SPECTROSCOPY AND MELTING POINT DETERMINATION

**Materials:** prepared acetylsalicylic acid (aspirin), stockroom samples of pure salicylic acid and acetylsalicylic acid

**Purpose:** In this laboratory activity you will use the technique of infrared spectroscopy to confirm the identity of your prepared aspirin.

**Introduction:** An important tool of the organic chemist is infrared (IR) spectroscopy. IR spectra are acquired on a special instrument, called an IR spectrometer. IR is used to gather information about compound's structure, assess its purity, and sometimes to identify it.

Infrared radiation is that part of the electromagnetic spectrum between the visible and radio wave regions. The electromagnetic spectrum consists of the family of radiant energy (xrays, UV rays, IR, microwaves, etc.). One of the common features of radiant energy its wave nature. The **wavelength** of a wave is the distance between two crests or two troughs. The **frequency** of a wave characterizes the number of cycles per second. Shorter wavelengths indicate radiant energy of higher frequency and higher energy. In IR spectroscopy, wavelengths are characterized by **wavenumbers**. A wavenumber is simply the inverse of the wavelength as is suggested by wavenumber units 1/cm or cm$^{-1}$. (In spectroscopy, the terms wavenumber and frequency are used interchangeably.)

![Diagram of two waves](image)

**Figure 1 – Diagram of two waves.**

Which is of higher energy, wave “A” or wave “B”? ________
Which is of lower frequency, wave “A” or wave “B”? ________
Which would have the higher wavenumber value, wave “A” or wave “B”? ________

The longer wavelengths of infrared radiation are commonly known as heat. The human eye cannot form images using IR rays. In other words, we can't see heat. Snakes in the pit viper family, like rattlesnakes, have IR sensory pits that are used to image infrared radiation. This
allows the snake to detect warm blooded animals, even in dark burrows. Heat lamps often radiate a reddish light along with heat (infrared radiation). Take a look at the figure below (Figure II) and see if you can explain why.

![Electromagnetic Spectrum](Image)

*Figure II – The Electromagnetic Spectrum*

A molecular compound can be identified by the IR radiation it transmits or absorbs. At specific frequencies, the atoms of the molecule stretch, twist, and bend around the bonds joining them. Radiation of the wavelengths corresponding to those frequencies will be absorbed. The energy absorbed must agree in frequency with the natural frequency of vibration of the molecule.

In using the IR spectrophotometer, a sample of the compound is subjected to varied wavelengths of IR radiation. Certain wavelengths will be readily absorbed by the molecule depending on the structure of the molecule. The various wavelengths absorbed by the compound are measured and recorded graphically. A unique continuous absorption spectrum, an IR spectrum, can be plotted for each molecular compound. Comparison with known spectra will reveal the identity of the compound just as fingerprints reveal the identity of a person.

An IR spectrum is a plot of wave number (X-axis) vs. percent transmittance (Y-axis). Percent transmittance tells us how much IR energy was transmitted through the sample. It can also tell us how much energy was absorbed by the sample. For example, a high degree of transmittance indicates that little IR energy was absorbed and most of the IR energy passed through the sample. The wavenumber scale on the spectrum indicates the energy of the IR incident on the sample.

The IR spectrum of hexanoic acid is shown below (Figure III). Take a minute to look over this spectrum. The deep downward peaks are areas of low IR transmittance and high IR absorbance. Notice that there are areas that are flat areas where very little IR energy was absorbed (nearly 100% transmittance).
Infrared spectroscopy is very useful for qualitative analysis (identification) of organic compounds because a unique spectrum is produced by every organic substance with peaks corresponding to distinct structural features. What is it that causes the absorption of energy? Covalent bonds link atoms together to form molecules. Though these bonds have normal average lengths, the relative positions of the atoms are constantly changing due to bond vibrations such as bending and stretching (Figure IV). A bond can be thought of as a spring with atoms attached to each end.

Each molecular compound has its own infrared spectrum, different from any other compound. Also, each functional group and structural feature absorbs infrared light at a unique frequency (See Figure V and Table I). For example, a carbonyl group, C=O, always absorbs infrared light at 1670-1780 cm\(^{-1}\), which causes the carbonyl bond to stretch. A carbonyl group always absorbs infrared radiation in this frequency range because the bond between the carbon atoms is constantly stretching and contracting within a range of bond lengths. When a molecule is irradiated with infrared radiation, a vibrating bond will absorb energy of the same frequency as its vibration, increasing the amplitude of the oscillation.
The region to the right-hand side of the diagram, the fingerprint region (from about 1400 to 600 cm\(^{-1}\)) usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. It is much more difficult to pick out individual bonds in this region than it is in the “cleaner” region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs and peaks in this part of the spectrum.

IR instruments are used for a variety of purposes. They are used in medical laboratories, crime labs, research facilities, educational institutions, and other installations for the purposes of detecting and identifying particular molecules. Pharmaceutical manufacturers use them to check the purity of their products. They can be used to make quantitative measurements; that is, to find the concentration of a chemical substance in a solution, in a solid, or in a gas. Companies and pollution control agencies use them to monitor gaseous exhaust from smokestacks and automobiles. New medical uses for IR spectroscopy include monitoring cerebral blood flow and non-invasive blood glucose monitoring.

The IR spectra of 1 – butanol is shown below.
Interpreting Infrared Spectra: Characteristic IR Absorption Frequencies

The interpretation of infrared spectra involves the correlation of absorption/transmission bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds. Significant for the identification of the source of an absorption band are intensity (weak, medium or strong), shape (broad or sharp), and position (cm\(^{-1}\)) in the spectrum. Characteristic examples are provided in the table below to assist the user in becoming familiar with the intensity and shape absorption bands for representative absorptions.

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C= N</td>
<td>2260–2220</td>
<td>medium</td>
</tr>
<tr>
<td>C= C</td>
<td>2260–2100</td>
<td>medium to weak</td>
</tr>
<tr>
<td>C= C</td>
<td>1680–1600</td>
<td>medium</td>
</tr>
<tr>
<td>C=N</td>
<td>1650–1550</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>~1600 and ~1500–1430</td>
<td>strong to weak</td>
</tr>
<tr>
<td>C= O</td>
<td>1780–1650</td>
<td>strong</td>
</tr>
<tr>
<td>C= O</td>
<td>1250–1050</td>
<td>strong</td>
</tr>
<tr>
<td>C= N</td>
<td>1230–1020</td>
<td>medium</td>
</tr>
<tr>
<td>O—H (alcohol)</td>
<td>3650–3200</td>
<td>strong, broad</td>
</tr>
<tr>
<td>O—H (carboxylic acid)</td>
<td>3300–2500</td>
<td>strong, very broad</td>
</tr>
<tr>
<td>N—H</td>
<td>3500–3300</td>
<td>medium, broad</td>
</tr>
<tr>
<td>C—H</td>
<td>3300–2700</td>
<td>medium</td>
</tr>
</tbody>
</table>

Table I – Characteristic IR Absorption Frequencies

The melting point of a compound is used by the organic chemist to help establish the identity and purity of a compound. A small amount of material is heated slowly in a special apparatus (Meltemp) equipped with a thermometer, a heating element, and an eyepiece for observing the sample. Two temperatures are noted – the point at which the first drop of liquid forms among the crystals and the point at which the entire sample of crystals turns to a clear liquid. The melting point is recorded by giving this range of melting.
Pure solid substances have a specific and reproducible melting point. Impurities in a solid substance lower the melting point range and make it broader. The more impurities in a solid, the more the melting point will decrease. The table below gives the melting points of several compounds.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic acid</td>
<td>157 - 159</td>
</tr>
<tr>
<td>Acetylsalicylic acid</td>
<td>135</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>75 - 77</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>169 - 172</td>
</tr>
</tbody>
</table>

Procedure:

**Infrared (IR) Spectroscopy**

1. Bring your aspirin sample to the instrument room. Your instructor will help you with acquiring the IR spectra of these samples. Attach your IR spectrum and library search results to this lab.
2. While waiting your turn to use the spectrophotometer, use the procedure below to determine the melting point of your aspirin sample.

**Melting Point Procedure**

1. Use a boiling water bath to calibrate the thermometer in your melting point apparatus as demonstrated by your instructor.

2. Obtain two capillary tubes that are sealed at one end.

3. Load one tube with your synthesized sample as follows. Press the open end gently into a sample of the crystalline material. Crystals will stick in the open end of the tube. The amount of solid pressed into the tube should correspond to a column no more than 2 mm high.

4. To move the solid to the closed end of the tube, drop the capillary tube down a 2/3 meter length of glass tubing, which is held upright on the desk top. The solid will pack down at the bottom of the tube. Repeat this procedure if necessary.

5. Mark the top of this tube with a Sharpie.

6. Repeat this process for the other capillary tube, loading it with a stockroom sample of acetylsalicylic acid.

7. Make identifying marks on the capillary tubes to help you distinguish between the samples.

8. Place the two tubes in the Mel-temp and look at them through the observation window. Record the physical state of each sample (color, crystal size and shape if any, etc.)

9. Begin slowly heating your samples. Be sure to watch the sample closely. Be patient! Don’t miss observing that melting range!! 😊

10. Record the temperature at which the sample first begins to melt and when the entire sample is melted.

11. Your instructor may ask you to calibrate your thermometer before you begin.
IR SPECTROSCOPY AND MELTING POINT OF ACETYLSALICYLIC ACID     Name__________________
Chem 306 Partner’s Name’s ____________________

MELTING POINT OF ASPIRIN – Data and Questions

<table>
<thead>
<tr>
<th>Substance</th>
<th>Physical Appearance</th>
<th>Initial Melting Temp (°C)</th>
<th>Temp at Complete Melting (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Student aspirin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stockroom acetylsalicylic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. How does the melting temperature of your aspirin compare with the stockroom sample.

2. Use the melting point data above to make a statement about the relative purity of your aspirin.

3. What is the most likely impurity in your aspirin? What are two sources of this contamination?

4. Stockroom samples of “pure” acetylsalicylic acid can have melting points below the expected melting point. Why is this so?
IR OF ASPIRIN - Questions

General Questions

1. You are interpreting an IR spectra and find a strong absorption at
   a. 1700 cm\(^{-1}\). What type of bond and which functional groups could be responsible for this absorption?
   b. 3000 cm\(^{-1}\) (very broad). What type of bond and which functional groups could be responsible for this absorption?

2. Which of the IR regions observed in question 1 above requires the most energy for an absorption?

IR Spectroscopy of Alcohol and Pharmaceuticals

1. The IR spectroscopy of alcohol (ethanol) is the basis for some methods of alcohol breath analysis (http://science.howstuffworks.com/breathalyzer.htm).
   a. Draw the structure of ethanol and acetone. Label your structures.
   b. Complete the following table.

<table>
<thead>
<tr>
<th>Bond</th>
<th>C – O</th>
<th>C = O</th>
<th>O – H</th>
<th>C – H</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR Region (cm(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
c. Look at the IR spectra below. One of these spectra is ethanol and the other is acetone. Circle and label the following regions on each spectra where appropriate: C – H unsaturated, C – O, C = O, and O – H. Which spectrum is most likely that of ethanol? Acetone?

Spectrum A = ________________________________

Spectrum B = ________________________________
2. IR spectroscopy is used in law enforcement and forensics to identify substances in body fluids. Look over the structures below.

\[
\begin{align*}
\text{Caffeine} & \quad \text{Morphine} & \quad \text{Heroin} \\
\end{align*}
\]

a. Both heroin and morphine contain C – O bonds. Which other structural features would distinguish the IR spectra of these two structures? How would the IR spectra for these two drugs differ?

b. Would you expect to find a C – O IR absorption for caffeine?

c. Use what you know about IR spectroscopy to assign a drug/substance (caffeine, morphine, or heroin) to each of the given spectra (A, B, and C). Identify (circle and label) two structural features and their characteristic IR regions on each spectra (For example, C – O, C = O, O – H, etc.)

Spectrum A = ________________
Spectrum B = ________________________________

Spectrum C = ________________________________
IR Spectroscopy of Aspirin

1. Draw the structure of aspirin and state the chemical name of aspirin.

2. Indicate the regions (circle and label on your IR spectrum) of your spectrum that correspond to a carbonyl and a hydroxyl functional group. Identify two other regions that correlate with other functional groups/structural features. Indicate these regions on your spectrum (circle and label on your IR spectrum).

3. Use your IR spectrum, melting point data, and FeCl₃ test results to characterize the identity and purity of your sample.

4. Why would the IR spectrum of your aspirin not exactly match the spectrum of a crushed aspirin tablet?

5. Which of the following spectra on page 14 is most likely that of aspirin? Explain your reasoning.

6. Attach your spectra to this report sheet.

7. Turn in your report sheet with your group members. Use a paper clip to bundle the report sheets together.
1. What is IR spectroscopy used for and why it is such an important tool in organic chemistry?

2. What are some uses for IR in medicine and industry?

3. In the space below draw two waves, one with a higher energy than the other. Label your waves.

4. What is a wavenumber and how is it used in spectroscopy?

5. Calculate the wavenumber for an IR wavelength of 0.00125 cm. Include your units. Show your work.

6. What do the peaks represent in an IR spectrum?

7. T or F Two different compounds can have the same IR spectrum.

8. What functional group has a strong peak at 1785 cm⁻¹?

9. What information does melting point data give about a substance?