CHEM 51LB Exp 1
SPECTROSCOPIC METHODS: INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

REACTIONS: None
TECHNIQUES: IR Spectroscopy, NMR Spectroscopy

Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy are two of the most powerful tools chemists use to determine the structures of compounds. In this experiment you will be given a set of unknown compounds. You will need to determine the structures of these unknown compounds using IR and NMR spectra.

READING ASSIGNMENT:
- Review previous techniques.
- Spectroscopy Introduction, Infrared Spectroscopy, and NMR in Making the Connections (2nd ed pg 65-100, 3rd ed pg 65-100, stop at Two-dimensional NMR Spectroscopy)
- Supplementary info can be found in Janice Gorzynski Smith (3rd & 4th ed), Ch 13.5-13.8, Ch 14
- Watch lecture videos on class website!

PRE-LAB ASSIGNMENT:
- Complete all portions of pre-lab ELN work according to guidelines
- Rewrite the procedure in your own words!
- Sapling assignment
- Complete lecture video worksheet. (Complete before class if possible, but can be done in class. Must be complete before you will be allowed to do the experiment.)

CAUTION

The compounds you are assigned may be hazardous if inhaled or absorbed through the skin. Avoid contact and inhalation.

Dichloromethane is toxic, an irritant, absorbed through the skin, and harmful if swallowed. Wear gloves and wash your hands thoroughly after handling it. Avoid contact with skin and eyes. Dichloromethane is a suspected carcinogen when inhaled in large quantities.

EXPERIMENTAL NOTES:

You will be assigned to a team of three to four students. Each team will receive six of the eight total possible unknowns to determine with various functional groups such as alcohol, aldehyde, ketone, carboxylic acid, amine, and alkene.

Four unknowns will be liquid samples and IR spectra must be obtained for these samples during the lab period. Each student in the team must take at least one IR. Proton NMR spectra for
these four unknown liquid samples will be provided. The other three unknowns will have both IR and NMR spectra provided by the stockroom.

<table>
<thead>
<tr>
<th>Six Total Unknowns</th>
<th>IR Spectra</th>
<th>NMR Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four liquid unknowns</td>
<td>Students perform</td>
<td>GIVEN</td>
</tr>
<tr>
<td>Two other unknowns</td>
<td>GIVEN</td>
<td>GIVEN</td>
</tr>
</tbody>
</table>

1. **Obtain IR Spectra for your Unknown Compounds**

Your team will receive a set of the four unknown compound samples and photocopies of three IR spectra of other unknown compounds that are either too toxic or too smelly to be used in the lab. The compounds shown below represent all of the possible unknowns. Obtain an infrared spectrum for all four samples, and make copies for your teammates. Your TA will help you with the IR instrument.

**How might you distinguish these compounds by IR spectroscopy? By NMR spectroscopy?**
2. **Identify the Functional Groups in Your Unknown Compounds:**

Determine the wavenumber of important absorption bands for each compound from its spectrum. Interpret the infrared spectra to determine what kind of bond or group is responsible for each significant IR band. Decide which functional groups are present in each of your unknown compounds and give their names and structures. Use the IR Functional Groups and Frequencies Chart (Table 2-1, page 72 in *Making the Connections* or Table 13.2 in *Smith*) and the table below.

**Table 5.1. Substituted Benzene and their characteristic absorption bands in the aromatic region.**

<table>
<thead>
<tr>
<th>C-H Out-of Plane Bending Vibrations of Substituted Benzenes</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>671</td>
</tr>
<tr>
<td>Monosubstituted benzene</td>
<td>770 - 730</td>
</tr>
<tr>
<td>1,2-Disubstituted</td>
<td>770 - 735</td>
</tr>
<tr>
<td>1,3-Disubstituted</td>
<td>810 - 750</td>
</tr>
<tr>
<td>1,4-Disubstituted</td>
<td>833 - 810</td>
</tr>
<tr>
<td>1,2,3-Trisubstituted</td>
<td>780 - 760</td>
</tr>
<tr>
<td>1,2,4-Trisubstituted</td>
<td>825 - 805</td>
</tr>
<tr>
<td>1,3,5-Trisubstituted</td>
<td>865 - 810</td>
</tr>
<tr>
<td>1,2,3,4-Tetrasubstituted</td>
<td>810 - 800</td>
</tr>
<tr>
<td>1,2,3,5-Tetrasubstituted</td>
<td>850 - 840</td>
</tr>
<tr>
<td>1,2,4,5-Tetrasubstituted</td>
<td>870 - 855</td>
</tr>
<tr>
<td>Pentasubstituted</td>
<td>870</td>
</tr>
</tbody>
</table>

3. **Identify Your Unknown Compounds:**

For each unknown, including the spectra provided by your TA, fill out the IR worksheet provided on the class website.

4. **Use NMR Spectra to Confirm the Identities of Your Unknown Compounds:**

When you have determined the identities of your unknown compounds, confirm them with your TA and ask your TA for the corresponding NMR spectra. For each unknown, including the three IR spectra provided by your TA, fill out the NMR worksheet provided on the class website.
BACKGROUND:

A chemical bond can be compared to a coiled spring. Just as it takes energy to stretch a spring, energy is needed to stretch a chemical bond. A bond stretches and contracts as it vibrates. The frequency of molecular vibrations of organic molecules lies in the infrared region of the electromagnetic spectrum. Infrared light activates these vibrations, a process that consumes energy. In IR spectroscopy, a sample of a molecule is irradiated with light in the IR portion of the electromagnetic spectrum. The energy of the infrared radiation after it has passed through the sample is then measured. A decrease in the energy of a particular wavelength indicates that the molecule has absorbed this energy by undergoing some type of vibration. The energy of the transmitted radiation is plotted as a function of the frequency of the infrared radiation. The plot appears as a series of peaks and is called an infrared spectrum.

Each of these peaks indicates a particular type of vibration that the molecule is experiencing when that frequency of radiation is absorbed. Some of these peaks represent vibrations of the molecule as a whole, but some of them represent vibrations of only particular parts of the molecule. Functional groups tend to absorb at predictable regions of the spectrum. The vibrations of functional groups are so characteristic that a quick glance at an infrared spectrum can give immediate information about the functional groups present in that molecule. The particular frequency of vibration often allows distinctions to be made between functional groups having very similar structures. For example, IR spectroscopy allows one to distinguish between aldehydes, ketones, esters, anhydrides, acid chlorides, etc., all of which are carbonyl-containing compounds.

The frequency of the radiation is conveniently expressed by most chemists in wave numbers, (cm$^{-1}$), a unit which is proportional to the energy of the infrared radiation. The higher the wave number, the greater the energy of radiation needed to activate the vibration. The infrared spectrum normally covered is from 4000 cm$^{-1}$ to about 650 cm$^{-1}$. The functional group region, however, extends from 4000 cm$^{-1}$ to about 1500 cm$^{-1}$. It is in this region that we look for those frequencies that are characteristic of particular functional groups. The 1500 cm$^{-1}$ to 650 cm$^{-1}$ region is called the fingerprint region and is used most often for comparison purposes, but analysis of peaks in this region to identify functional groups is difficult. With some exceptions, no two compounds have identical infrared spectra. Thus, if one wants to verify the structure of a particular compound, a comparison of the infrared spectrum of the compound with the infrared spectrum of the known structure will provide this information. The stronger a bond is, the higher the frequency of vibration of that bond. Triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration. Thus, the C-C single bond in ethane, the C=C double bond in ethene, and the C=C triple bond in ethyne vibrate about 3.6 x 10$^{13}$, 5.0 x 1013, and 6.5 x 1013 times/second, respectively. Meanwhile, the C-O single bond in ethanol (CH3CH2-OH) and the C=O double bond in acetaldehyde vibrate about 3.1 x 10 13 and 5.2 x 10 13 times/second, respectively. The stronger the bond, the more energy is needed to stretch the chemical bond. The frequency of bond vibration is proportional to the energy associated with the vibration, as given by the equation $E=\hbar \nu$. 


Hybridization affects the bond lengths, and bond strength. Bonds are stronger in the order \( sp > sp^2 > sp^3 \), and the observed frequencies of C-H vibration illustrate this nicely.

\[
\begin{align*}
\text{sp} & \quad \text{sp}^2 & \quad \text{sp}^3 \\
\equiv \text{C-H} & \quad \equiv \text{C-H} & \quad \text{C-H} \\
3300 \text{ cm}^{-1} & \quad 3100 \text{ cm}^{-1} & \quad 3000 \text{ cm}^{-1}
\end{align*}
\]

As the atom bonded to carbon increases in mass, the frequency of vibration decreases (\textit{wavenumber gets smaller}):

<table>
<thead>
<tr>
<th></th>
<th>C-H</th>
<th>C-C</th>
<th>C-O</th>
<th>C-Cl</th>
<th>C-Br</th>
<th>C-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm(^{-1})</td>
<td>3000</td>
<td>1200</td>
<td>1100</td>
<td>750</td>
<td>600</td>
<td>500</td>
</tr>
</tbody>
</table>

**Resonance Contributors and the Relative Vibrational Frequencies for C=O Bonds**

In order to determine the relative vibrational frequencies for C=O bonds in different compounds, you may be able to estimate their relative strengths using resonance theory. For example, suppose the carbonyl carbon in a compound is attached to some atom or group, \( Y \), giving the compound the general formula RCO\(_{Y}\). Such a compound will have at least two resonance contributors. When \( Y \) has a lone pair (\textit{as in carboxylic acids, esters, amides, and acid halides}), three resonance structure are possible: \( A \), \( B \), and \( C \). When \( Y \) has no lone pair (\textit{as in aldehydes and ketones}), only two resonance structures are possible: \( V \) & \( X \).
The actual structure of the molecule is neither A nor B nor C (V nor X), but the combination of A, B, & C or V & X in a single structure which is represented by the resonance hybrid (composite structure) shown. The strength of the C=O bond depends on the relative contribution (importance) of the resonance structures. If A, B, & C (or V & X) were of equal importance, the C=O bond of the hybrid would be two parts single bond and one part double bond (or halfway between a double bond and a single bond). This “1/3 double bond (or 1/2 double bond)” would be weaker than a double bond, but stronger than a single bond. Therefore, the bond would vibrate at a lower frequency.

There are two factors to consider:

1. **As Y become more electronegative**, resonance structure B (X) will be less important because the electronegative Y withdraws electrons from the positively charged carbon, making B (X) less stable. Resonance structure C will also be less important because the positive charge will be on the electronegative element Y. Therefore, as Y becomes more electronegative, resonance structure A (V) is more important, and the carbonyl will have more double bond character, and therefore, will vibrate at a higher frequency.

2. **As the ability of Y to donate its electrons increases**, resonance structure C becomes more important. One way to measure how well Y donates its electrons is to look at the basicity of Y. Basicity increases to the left in any row of the periodic table, and increases as you move up any column. The more basic the atom is, the more willing it is to donate its electrons.

Comparing an ester, for example, (Y = O) with an amide (Y = N), nitrogen is more basic and, therefore, has a greater ability donate its electrons. So the resonance structure C will be much more important. **Result:** the C=O will have less double bond character, and will therefore vibrate at a lower frequency. **Conclusion:** An amide will absorb at a lower frequency than an ester.

**Amide:** Resonance structure C is important because N likes to donate its electrons.
Ester: Resonance structure C is less important because \( O \) is less basic than \( N \) and therefore not as willing to donate its electrons.

Note: We can also use the electronegativity argument to compare an ester and an amide. Comparing an ester with an amide, \( O \) is more electronegative than \( N \). An electronegative oxygen destabilizes resonance structure B and C, giving the C=O more double bond character. An ester will therefore absorb at a higher frequency than an amide. This is the same conclusion we reached above. What is the actual frequency of the carbonyl of an amide vs. the carbonyl of an ester?

- Amide C=O: 1650 cm\(^{-1}\)
- Ester C=O: 1725-1750 cm\(^{-1}\)

If \( Y \) is an unsaturated group, such as a vinyl group (CH\(_2\)=CH\(-\)), an additional resonance contributor, C can be drawn. B and C are important resonance contributors because they are allylic cations. This will give the C=O less double-bond character, therefore, it will absorb at a lower frequency.

What is the actual frequency of \( \alpha,\beta \)-unsaturated ketone, vs. a regular ketone?

- Ketone C=O: \(~1710\) cm\(^{-1}\)
- \( \alpha,\beta \)-unsaturated ketone C=O: \(~1680\) cm\(^{-1}\)

The application of resonance theory to the determination of the structure of carbonyl compounds will only provide relative frequencies. It will help us to arrange the assigned compounds in order of their C=O vibrational frequencies, but it will not allow us to determine actual frequencies.

The IR Spectrum: What to look for when examining IR spectra

An infrared spectrometer determines the position and relative sizes of all the absorptions (bands or peaks) in the infrared region and plots them on a piece of paper. This plot of % transmittance
versus wavenumber is referred to as the *infrared spectrum* of the compound. Depending on the functional groups present in the molecule, the spectrum exhibits many strong, medium, and weak absorption bands between 4000 cm$^{-1}$ and 600 cm$^{-1}$. Take notice of frequencies at which an absorption occurs, shapes, and intensities for characteristic bands in the spectrum. The eye must be trained to recognize these features using the IR correlation chart (available in any organic chemistry textbook). Often, when reading the literature of organic chemistry, you will find absorption referred to as strong (s), medium (m), weak (w), broad, or sharp. The author is trying to convey some idea of what the peak looks like without actually drawing the spectrum. You will practice the same for your IR analysis of your unknowns in this experiment.