# 8. Infrared Spectroscopy

## A. Background and Introduction

The purpose of this laboratory experiment is for you to gain hands-on experience in the operation of an infrared (IR) spectrometer and interpretation of IR spectra to elucidate structural details. This experiment will supplement the theoretical aspects of IR spectroscopy discussed in lecture. The information provided below was written to be concise and is meant to be a basic summary of IR spectroscopy. You should refer to your lecture notes and/or textbook for additional details. It is imperative that you develop a firm foundation of IR spectroscopy early in the semester, as we will frequently use IR spectroscopy to characterize the products prepared in the organic laboratory.

Organic chemists typically use infrared (IR) spectroscopy to identify the functional groups present in a molecule. IR spectroscopy takes advantage of light energy in the infrared region of the electromagnetic spectrum. When an organic molecule is irradiated with IR light, the light energy is absorbed if the frequency of light is equal to the vibrational energy associated with a particular bond in a molecule. Covalent bonds are not static, but are rather like springs with atoms attached. These springs (bonds) can stretch (2 atoms separated by a bond) and can bend (3 atoms separated by two bonds) as shown in figure 1. The stretching and bending frequencies for a particular molecule are quantized, thus they occur at discrete energy levels. This fact results in every distinct molecule having its own individual IR spectrum that can be distinguished from that of another molecule.

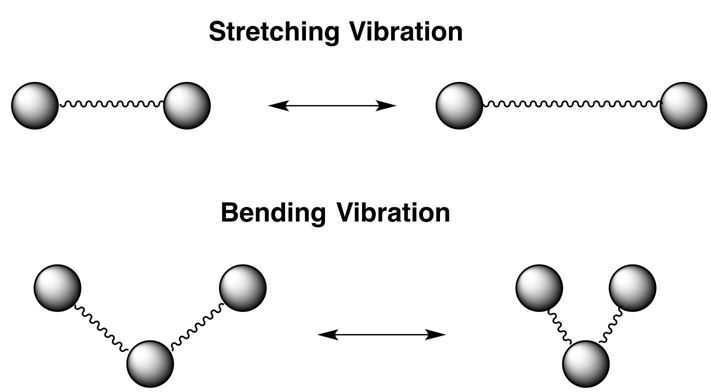



**Figure 1. Stretching and Bending Vibrational Modes**

An IR spectrum is a plot of the percentage of light transmitted (%T) versus the frequency in wavenumbers ($\tilde{\nu}$, $cm^{-1}$). Figure 2 shows the IR spectrum of ethanol ($CH_3CH_2OH$). Notice the typical IR frequency scale ranging from 400 to 4000 $cm^{-1}$. When observing an IR spectrum, it is useful to visualize an imaginary line at 1500 $cm^{-1}$. To the right of this line is the "fingerprint region", which is typically difficult to analyze. To the left of this line is the "functional group region", which is the most useful for our purposes. The leftmost absorption (circled) represents the O-H bond stretch. This absorption occurs at a relatively high wavenumber (3350 $cm^{-1}$). Analysis of this absorption reveals a 10% transmittance of light, which means 90% of the light energy was absorbed by the molecule at that particular frequency.

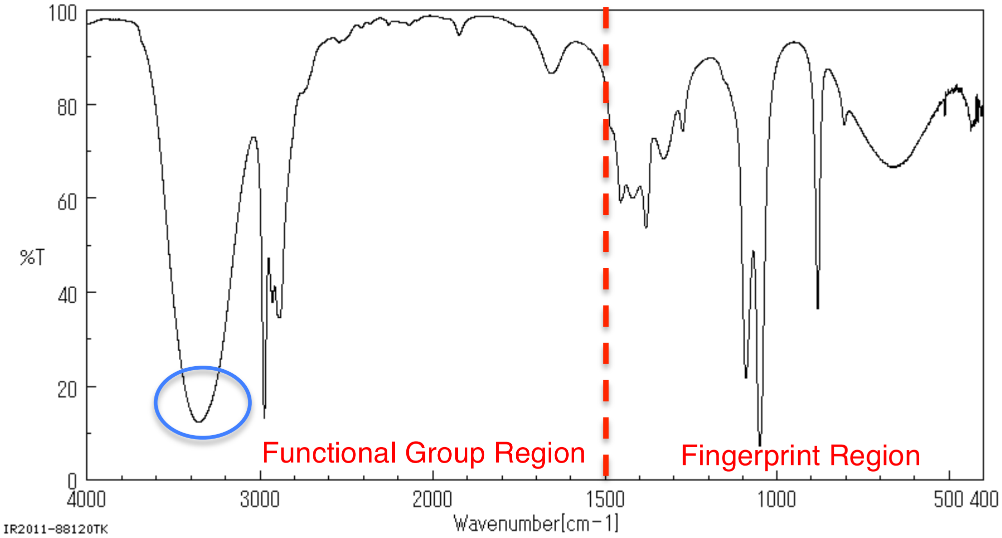
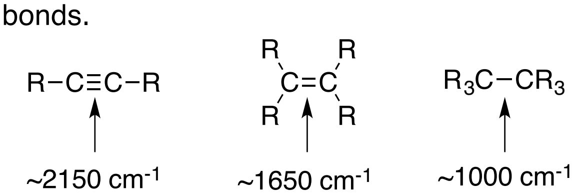



**Figure 2. Sample IR Spectrum (Ethanol)**

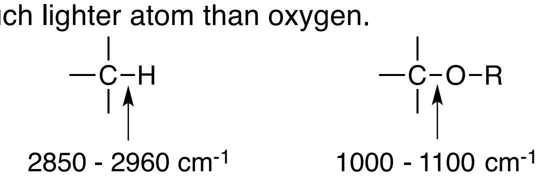
Further application of the spring analogy reveals the relationship between the frequency of IR light absorption, bond strength, and atom mass. Hooke's law describes the motion of a vibrating spring where *k* is a constant, *f* is the force constant, and *m* is the mass.

$$\tilde{v} = k\sqrt{\frac{f}{m}} \qquad \text{(Hooke's Law)}$$

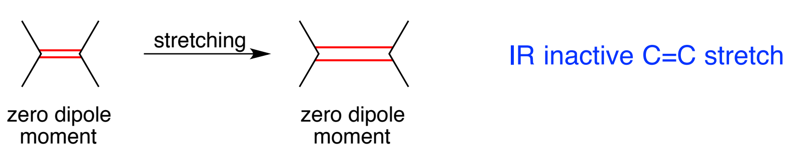
Because the force constant, *f,* represents the strength of the spring (bond), a stronger bond gives rise to a larger ṽ, and thus represents a higher energy absorption. For this reason, triple bonds absorb at a higher wavenumber than double bonds, which absorb at a higher wavenumber than single bonds.




The mass, *m*, of the connected atoms also affects the wavenumber of the absorption. Lighter atoms increase the value of ṽ, which corresponds to a higher energy absorption. For example, the C-H absorption occurs at a higher energy (wavenumber) than does the C-O absorption because hydrogen is a much lighter atom than oxygen.




It is also important to understand that in order for a bond to absorb IR light, there must be a change in the bond's dipole moment during the molecular vibration. For example, 2,3-dimethyl-2-butene has an **IR inactive** C=C bond stretch due to molecular symmetry. During the C=C bond stretch there is no change in the bond's dipole moment.



## Use of the Spectrometer

Our laboratories use an Attenuated Total Reflectance Fourier Transform IR (ATR FT-IR) spectrometer. This type of instrument requires little sample preparation and can easily record the IR spectrum of solids, liquids, and oils. Your TA will show you how to properly use this instrument to acquire an IR spectrum. Although little sample preparation is required, it is important that your sample be free of solvent and other impurities. If your compound of interest contains solvent, and a spectrum is recorded, your spectrum will be contaminated with IR peaks corresponding to the solvent.

## Interpretation of IR Spectra

When given an IR spectrum to interpret, you can use a chart such as the one shown in figure 3 to help you pick out important absorptions corresponding to various functional groups in the molecule. Additionally, the absence of IR absorptions in a particular region gives you important information indicating the absence of certain functional groups.

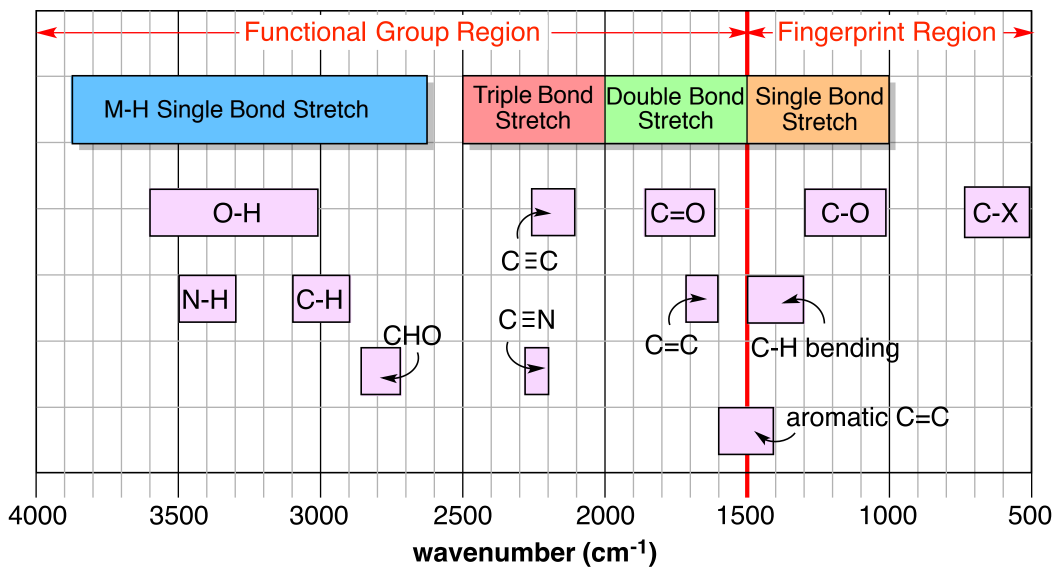



**Figure 3. Some Common IR Regions**

## A Detailed Look at Some Important Absorptions

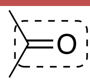
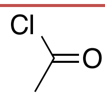
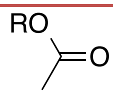
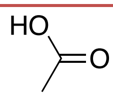
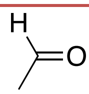
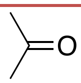
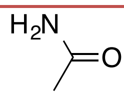
1. Hydroxyl O-H Stretch and Amine N-H Stretch

| Structural Unit | Wavenumber, $cm^{-1}$ | Special Features |
|---|---|---|
| —O–H | **3200-3600 (s, br)** | |
| N–H    —N(H)(H) | **3300-3500 (m)** | $R_2N$-H = one IR stretch<br>$RNH_2$ = two IR stretches |

The hydroxyl O-H stretch is typically broad and strong and appears in the 3200 – 3600 $cm^{-1}$ range. In the case of a carboxylic acid, the O-H stretch is typically very broad and appears in the 2500 – 3300 $cm^{-1}$ range, often overlapping the C-H bond stretches. A carboxylic acid will also have a C=O stretch in the 1700 – 1735 $cm^{-1}$ range.

Amine N-H stretches typically appear in the 3300-3500 $cm^{-1}$ range and are much more narrow and less intense than an –OH stretch. Primary amines have two amine hydrogen and exhibit two N-H stretches. Secondary amines have only one amine hydrogen and exhibit only one N-H stretch. Tertiary amines have no absorption in this region because there are no hydrogen atoms on the amine nitrogen. In the case of an amide, the NH stretches appear in the same 3300-3500 $cm^{-1}$ range. Additionally, look for the amide C=O stretch in the 1650 – 1700 $cm^{-1}$ range.

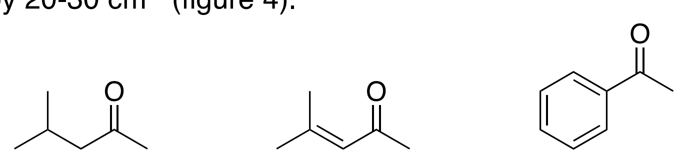
2. Carbonyl C=O Stretch

| Structural Unit | Wavenumber, $cm^{-1}$ | Special Features |
|---|---|---|
|  | **1650-1850 (s)** | Variable depending on the carbonyl functionality (see below) |
|  | **1750-1850** | |
|  | **1700-1750** | Also look for strong $Csp^2$—O stretch between 1200 and 1300 $cm^{-1}$ |
|  | **1700-1735** | Also look for a strong O—H stretch between 2500 and 3300 $cm^{-1}$ |
|  | **1720-1740** | Also look for aldehyde C—H stretches at ~2720 and ~2820 $cm^{-1}$ |
|  | **1680-1750** | Generally around 1720 $cm^{-1}$; Decreased when in conjugation |
|  | **1650-1700** | Also look for N—H stretch between 3300 and 3500 $cm^{-1}$ |

The carbonyl region, 1650-1850 $cm^{-1}$, is one of the most important regions of the spectrum. The table above lists the most common carbonyl containing functional groups and the relative placement of the C=O stretch in each. Use these regions as a guide, but be aware that these cutoffs are not strict and the C=O stretch for one of these functional group may lie outside of the listed range.

Take note of the special features listed for each of the carbonyl containing functional groups, which can be used to help you confirm its identity. For example, it is very difficult to distinguish the C=O stretch of aldehydes and ketones, however, in the case of an aldehyde, there will also be two aldehyde C-H stretches at ~2720 and ~2820 $cm^{-1}$.

When a carbonyl group is **conjugated** with a double bond or benzene ring, the C=O stretch will be decreased by 20-30 $cm^{-1}$ (figure 4).



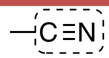
Non-Conjugated — 1717 $cm^{-1}$

C=O Conjugated with C=C — 1690 $cm^{-1}$

C=O Conjugated with Aromatic Ring — 1691 $cm^{-1}$

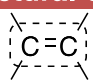
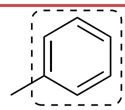
**Figure 4. Effect of Conjugation on Carbonyl Stretching Frequency**

3. Alkyne and Nitrile stretches

| Structural Unit | Wavenumber, $cm^{-1}$ | Special Features |
|---|---|---|
|  | **2200-2300 (s)** | |
|  | **~2150 (v)** | For terminal alkynes, look for C-H stretch at ~3300 $cm^{-1}$ |

The C≡C and C≡N stretches can be very difficult to distinguish because they both appear around 2150 $cm^{-1}$. Terminal alkynes can be distinguished by the additional C-H stretch at ~3300 $cm^{-1}$.

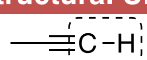
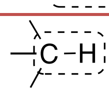
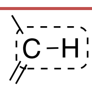
4. Alkene and Aromatic C=C Stretch

| Structural Unit | Wavenumber, $cm^{-1}$ | Special Features |
|---|---|---|
|  | **1600-1700 (v)** | |
|  | **1450-1600 (v)** | Look for 2 or 3 peaks in this region generally at ~1600, ~1500, and <1500 $cm^{-1}$ |

The C=C stretch varies in intensity, but is often rather weak. Typically C=C bond stretches occur between 1600 and 1700 $cm^{-1}$, however, if the C=C is in conjugation with a C=O, the C=C stretching frequency will be lowered by 20-30 $cm^{-1}$.

Aromatic compounds show several C=C absorptions in the 1450 – 1600 $cm^{-1}$ region. Typically you will see absorptions at ~1600, ~1500, and ~1430 $cm^{-1}$. Sometimes you may only be able to see 2 of these absorptions.

5. C-H Stretching and Bending

| Structural Unit | Wavenumber, $cm^{-1}$ | Special Features |
|---|---|---|
|  | **~3300 (s)** | |
|  | **2850-2960 (m)** | Look for $C_{sp3}$—H stretches just below 3000 $cm^{-1}$<br>H-C-H bending just above 1400 $cm^{-1}$<br>$-CH_3$ bending just below 1400 $cm^{-1}$ |
|  | **3000-3100 (m)** | Look for $C_{sp2}$-H stretches just above 3000 $cm^{-1}$ |

The frequency of the C-H stretch has a large dependency on the hybridization of the carbon bonded to the hydrogen. In the case of terminal alkynes, the carbon is *sp*-hybridized and the C-H stretch occurs at ~3300 $cm^{-1}$. The C-H stretch for $sp^2$-hybridized carbon atoms occurs at a slightly lower frequency (3000 – 3100 $cm^{-1}$). Finally, the C-H stretch for $sp^3$-hybridized carbon atoms occurs in the 2850 – 2960 $cm^{-1}$ range. 3000 $cm^{-1}$ is a convenient dividing line to know. Just above 3000 $cm^{-1}$ are the $Csp^2$-H stretches while just below 3000 $cm^{-1}$ are the $Csp^3$-H stretches.

In the case of saturated hydrocarbons, C-H bending vibrations can be observed in the 1375 – 1475 $cm^{-1}$ range. Methyl ($-CH_3$) bending is observed just below 1400 $cm^{-1}$ while methylene ($-CH_2-$) and methine ($R_3C-H$) bending is observed just above 1400 $cm^{-1}$.

6. C-O Bond Stretch

| Structural Unit | Wavenumber, $cm^{-1}$ | Special Features |
|---|---|---|
| —O-C | **$Csp^3$—O: 1000-1100 (m)**<br>**$Csp^2$—O: 1200-1300 (s)** | Common for alcohols and ethers.<br>Common for esters. |

Despite being in the fingerprint region, the C-O single bond stretch is exceptionally useful. The C-O stretch is of medium to strong intensity and appears in the 1000 – 1300 $cm^{-1}$ region. The hybridization of the carbon bonded to the oxygen has a large effect on the C-O stretching frequency. When the carbon is $sp^3$-hybridized such as that in alcohols and alkyl ethers, the C-O stretch absorbs in the 1000 – 1100 $cm^{-1}$ range. When the carbon is $sp^2$-hybridized, however, the C-O stretch absorbs in the 1200 – 1300 $cm^{-1}$ range.

**Analysis of a Sample Spectrum**

In the analysis of IR spectra, it is important to get a feel for the general location of the major functional group absorptions. Then, when confronted with an IR spectrum, such as the one shown below, you will be able to examine it quickly and immediately pick out important absorptions corresponding to various functional groups. This information will allow you to both confirm an expected organic structure and to help elucidate the structure of an unknown molecule.

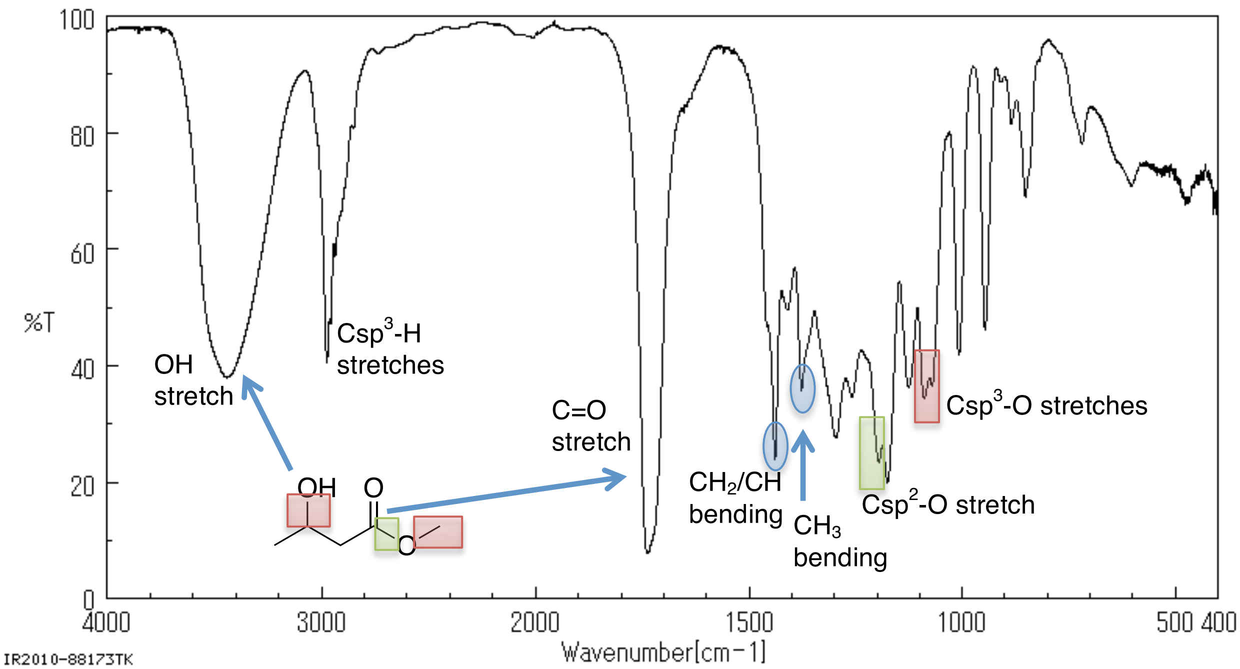



**Figure 5. IR Spectrum of Methyl 3-Hydroxybutanoate**

## B. Experimental Procedure

Your TA will assign you two different unknowns and show you how to operate the IR spectrometer. You should record the IR spectrum of each unknown. Go through each spectrum and identify as many functional groups as possible. In your laboratory notebook make a list of characteristic IR absorptions for each unknown along with the assigned functional group. Using the table of potential unknowns, you should be able to narrow the identity of your unknown down to a maximum of three potential structures (quite possibly two or even one in some cases).

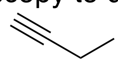
## C. Notebook

The notebook write-up for this experiment is minimal. Prior to lab you should write the experiment number, title, and date as well as the completed pre-lab questions and objective/purpose of this lab. During lab, you should write in the data for you unknowns as described in part B. At the end of the lab period, you should complete the post-lab questions.

## D. Pre-Lab Questions

1. Carbon dioxide ($CO_2$) has two types of bond stretches: symmetrical and unsymmetrical. Classify each one of these stretches as IR active or IR inactive and explain your choice.

2. How could you use IR spectroscopy to differentiate between the two isomers below?



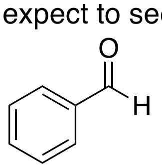
1-butyne

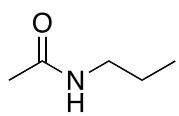


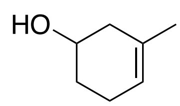
2-butyne

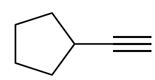
3. Which bond is stronger: the C=O of an ester (1735 $cm^{-1}$) or the C=O bond of a ketone (1715 $cm^{-1}$). Explain your answer.

4. For each compound below, approximate the most important IR absorptions that you would expect to see.



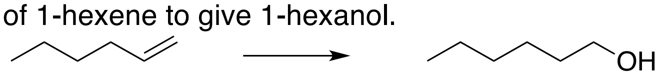



5. For each group of IR frequencies listed below, suggest the functional group that is present.
   a) 1734, 1250, 1080 $cm^{-1}$
   b) 3400 (broad), 1050 $cm^{-1}$
   c) 3050, 1650 $cm^{-1}$

## E. Post-Lab Questions

1. Both TLC and IR can be used to monitor the progress of a reaction (i.e. the oxidation of an alcohol to a ketone). Which technique do you think is most useful? Explain your answer.

2. Explain how IR spectroscopy could be used to monitor the hydroboration-oxidation reaction of 1-hexene to give 1-hexanol.




3. When cleaning the IR crystal between analyses, why is important to ensure that your cleaning solvent has completely evaporated prior to running the next sample?

4. When operating the IR, the instrument provides a % Absorbance spectrum, which you then transformed to a % Transmission spectrum. Explain the difference.

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All IR spectra used in this experiment were taken from SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2016).