Infrared Spectroscopy

Infra-red (IR) spectroscopy is a spectroscopic technique where matter interacts with light in the infrared wavelength range. IR light is lower in energy than that of visible spectroscopy (400-800 nm) and longer in wavelength. The infrared range usually sampled is 2.5-16 μ m (2500- 16000 nm). This energy range is the energy of bond stretching and bending of many bonds found in organic molecules, so the infrared spectrum of a molecule can be considered one type of characteristic energy profile of organic molecules. Comparing and contrasting these energy profiles or IR spectra allows one to characterize the types of bonds present in organic molecules.

The challenges for beginning organic students are several. In the laboratory, students need to learn how to obtain an IR spectrum as well as read or interpret the spectrum obtained. Part of interpreting the IR spectrum obtained is being able to compare and contrast the spectrum to related or known organic compounds. This means that the more IR spectra that you "read" and interpret the better you will be at the compare and contrast challenge and the better you will understand and use this technique. In the interest of full disclosure, this technique has been routinely used by organic chemists since the 1950's so there is two generations of data for you to catch up on. However, each organic compound, you have met that challenge for that compound. In addition, organic compounds that are related by having similar bonds or similar functional groups will have similar IR spectra, so interpreting and understanding one spectra will help you interpret and understand related spectra.

In this laboratory exercise you will run the IR spectrum of an unknown, and identify it from a possible list of unknown compounds. This will help you in the first challenge and to begin meeting the second challenge you will compare and contrast several IR spectra and discuss your interpretation with your laboratory peers. Additionally, reading the IR spectroscopy section of textbooks and following lectures, podcasts, and IR programs such as IR tutor will also help you in this second challenge. Feel free to contact your laboratory instructor and other students in your quest to understand and interpret IR spectra of organic compounds. For chemists, interpreting IR spectra is a skill to be learned just like physicians learn to diagnose given diseases from their symptoms, and detectives learn to solve crimes from forensic evidence. In analyzing IR spectra you will learn to predict specific structural pieces of organic compounds based upon the observed absorptions or peaks in the IR spectrum.

Part 1 Identification of an Unknown from its IR Spectrum

You will run the IR spectrum of your unknown according to instructions in the laboratory. You must record the number of your "Unknown" in your laboratory notebook. (Without a record of your "Unknown number" your experiment is meaningless! Your unknown will be one of the 7 listed in Table 3 (Table 3 is at the end of this experiment.)

IR spectra are record as % transmittance of IR light (%T) on the y axis versus Energy (Frequency) usually referred to as Wavenumber which is reported in cm⁻¹on the x axis. The presence of an absorption, a downward peak from the top (100 % T-90% T (meaning no interaction of IR light and the sample)) to

something lower such as 20% T, indicates that some part of the sample has a bond whose stretching or bending energy is similar to that IR energy.

Part 2 Observation of Several IR Spectra

Initial Investigations and Comparisons

While you are waiting for your turn at the IR spectrometer, look at the following IR spectra of 4 related organic compounds. Guiding questions will help you notice patterns and bonding information from the spectra. In this version you will work in a group of 4 students and look at 4 related compounds. You may share your thinking and reflection with your peers but must write your own answers to your questions. You will also have the opportunity to discuss several questions as a group before looking at more IR spectra. (You should answer the questions on your four IR spectra before you meet with your peers to answer group IR questions.) **Record the answers to your questions in a copy of Table 1 in your notebook.**

Student#1 Compare the IR spectra of the following 4 compounds by answering following questions.

- Compound 1: Cyclohexane
- Compound 2: Cyclohexanone
- Compound 3: Cyclohexanol
- Compound 4: Cyclohexene

Student#2 Compare the IR spectra of the following 4 compounds by answering following questions.

- Compound #1: Cycloctane
- Compound #2: Cycloctanone
- Compound #3: Cycloctanol
- Compound #4: Cycloctene

Student#3 Compare the IR spectra of the following 4 compounds by answering following questions.

- Compound #1: Cyclopentane
- Compound #2: Cyclopentanone
- Compound #3: Cyclopentanol
- Compound #4 Cyclopentene

Student#4 Compare the IR spectra of the following 4 compounds by answering following questions.

Compound #1: Cyclodecane

Compound #2: Cyclodecanone

Compound #3: Cyclodecanol

Compound #4: Cyclodecene

Guided Questions to Answer for Compounds #1, #2, #3, and #4 and their IR Spectra

First look at compound #1 and its IR spectrum. Answer the following questions to make a guess about what you observe. For compound #1 list the 2 types of bonds that are present in compound 1?

How many large absorptions are present in the IR of compound 1?

Recall that bonds between a heavy and a light atom have larger energies (Frequencies). Furthermore, a more polar bond gives a more intense absorption. Which observed frequencies do you assign to each of the two possible types of bonds you observed in compound 1?

(Don't worry if your guess is incorrect, the next analyses may help you correct your assignment.)

Look at compound #4, how is compound #4 different from compound #1? What new types of bonds are observed in compound #4? What types of bonds from compound #1 are still present in compound #4?

Now compare the spectra of compounds #1 and #4. What new absorptions are observed? What absorptions from compound #1 are still present in compound #4? How does the knowledge that bonds between a light and heavy atom give absorptions with higher energies and more polar bonds give more intense absorptions bonds help you assign absorption to specific bonds? Also stronger bonds will have a higher energy (Frequency). Assign each of the new large absorptions present in the IR spectrum of compound 4 to the new types of bonds present in compound 4?

Next compare the structure of compounds #1 and #2. What new types of bond(s) are observed in compound#2? Again what types of bonds from compound #1 are still present in compound #2?

Now compare the spectra of compound #1 and# 2. What new absorption(s) are observed? What absorptions from compound #1 are still present in compound #2? How does the knowledge that bonds between two heavier atoms give absorptions with lower energies and more polar bonds give more intense absorption help you assign absorptions to specific bonds? Assign each of the new large absorptions present in the IR spectrum of compound #2 to the new types of bonds present in compound #2?

Finally compare the structure of compounds #1 and #3. What new types of bond(s) are observed in compound#3? Again what types of bonds from compound #1 are still present in compound #3?

Compare the spectra of compound #1 and #3. What new absorption(s) are observed? What absorptions from compound are still present in compound #3? How does the knowledge that bonds between a lighter and a heavier atom give absorptions with higher energies and more polar bonds give more intense absorptions help you assign absorptions to specific bonds? Assign each of the new large absorptions present in the IR spectrum of compound #3 with the new types of bonds present in compound #3?

Finally how does the structure of compound #2 compare to the structure of compound #3? How does the spectrum of compound #2 compare to the structure of compound #3?

Share your observations, and correlations of observed IR absorptions with your group. How do your assignments of large IR absorptions to specific organic compound bonding patterns compare?

Initial Group discussion question:

If a friend who studies organic chemistry laboratory at another university called you on the phone and said his/her unknown had very sharp absorption at 1718 cm⁻¹, how much could you tell the friend about the unknown? For example: How will this information help you identify the specific compound? Will it help you identify the type of bonding pattern and/or the functional group?

Close this section of the activity by comparing the spectra of cyclohexane to cyclopentane, and/or cyclohexanone to cyclopentanone, cyclohexanol to cyclopentanol, and cyclohexene to cyclopentene. In what part of these spectra do the spectra differ by the greatest amount? Why do you think this region is identified as the "Fingerprint" region identified in textbook discussions?

Observation of Several IR Spectra Part B

In addition to the four initial functional groups (alkane, alkene, ketone, and alcohol) observed in Part A, your unknown might also be an aldehyde, carboxylic acid, ester, amine functional group or contain an aromatic compound. Look at the additional IR spectra of representative examples of these functional

groups and record their characteristic absorptions in a table similar to Table 2 in your notebook. To help you in organizing this spectral information in one place, include compounds #1, #2 #,3, and # 4 of Part A (Table 1) in this table as well, and to help you get started Compounds #1, and #2 have been started for you.

Compound #5: Aldehyde: Cyclohexyl carboxyaldehyde

Compound #6: Carboxylic Acid: Cyclohexyl carboxylic acid

Compound #7: Ester: Cyclohexyl acetate

Compound #8: Amine: Cyclohexyl amine

Compound #9: Aromatic Compound and Ester: Cyclohexyl cinnamate

After recording the IR frequencies observed for these functional groups answer the following questions on the observed IR absorptions.

How does changing the functional group from a ketone C=O to an aldehyde functional group change the observed frequency of the C=O?

In the aldehyde functional group, a C to H bond occurs on the other side of the C=O, where does this C to H stretching frequency show up as unique absorptions(s)?

In the acid and ester functional groups, an O-H and O-C bond are on one side of the C=O bond. First compare cyclohexyl carboxylic acid and cyclohexyl acetate. How does putting the O-H bond on the C=O change the observed absorption of the C=O observed in the ketone? How does putting the O-R bond on the C=O change the observed absorption of the C=O bond?

Next compare cyclohexyl acetate and cyclohexyl cinnamate. What observed difference do you observed in the C=O absorption? What is different about the hybridization of the carbon atoms attached to the carbon side of the C=O? Furthermore, how does this difference change the energy of the C=O observed?

Which functional group is most similar to the amine functional group? How is this similarity reflected in the IR spectrum of cyclohexyl amine?

Look at C-H bonds of cyclohexyl acetate. How does the IR spectrum of cyclohexyl acetate reflect the type of C-H bonds in the cyclohexyl acetate?

Part 3 Identification of your Unknown

Write your known number in your notebook! Your unknown is one of the compounds listed in Table 3. To determine the identity of your unknown, write down the observed absorptions in your IR spectrum of your unknown between 4000 and 1400 cm⁻¹. Which type of bonds do each of these absorptions most likely correspond to? Use the names and structural formulas of the possible unknowns to identify bonding patterns in the possible unknowns. Which of these bonding patterns correspond to absorptions in your unknown? How certain are you of your assignment of your unknown? Explain why?

Group discussion question:

If a friend who studies organic chemistry laboratory at another university called you on the phone and said his/her unknown had very sharp absorptions at 3030 cm,⁻¹ 2920 cm⁻¹ and 2820 cm⁻¹, how much could you tell the friend about the unknown? For example: Could you identify the specific compound? Could you identify the functional group? What other absorptions might you tell the friend to look for in the IR, to help identify the compounds?

Compound #	Compound Name	Functional Group	Bond Type	Observed IR Absorptions	Possible Assignment of Bond Type and Observed IR Absorptions	Comments

Table 1 Answers to Questions on Compounds #1-#4

Table 2 Expanded Table of IR Compounds, Functional Groups and IR Absorptions

Compound #	Functional Group	Observed IR Absoprtion	Bonding Pattern
1	Alkane	2950	С—Н
		2850	С—Н
		1460	CH ₂ —CH ₂
2	Ketone	2950	С—Н
		2850	С—Н
		1715	C=0
		1460	CH ₂ —CH ₂
3	Alcohol		

Table 3 Possible Unknowns

The IR unknowns for this initial investigation are selected from the following compounds:

Acetanilide

Benzaldehyde

Benzophenone

Diphenylmethane

t-Butanol

Phenyl benzoate

o-Toluic Acid