Infrared Spectroscopy (IR)

OBJECTIVE

1. To learn various functional groups encountered in Organic Chemistry
2. To learn of the important role of infrared spectroscopy in the study of structure of organic compounds
3. To develop skill in the recognition of characteristic absorption bands
4. To identify a compound by an investigation of its infrared spectrum

INTRODUCTION

During the course of this year we will study several different classes of compounds including alcohols, alkenes, and ketones. Each of these classes is distinguished by the presence of a “Functional Group”\(^1\) in the molecule. For example, all alcohols contain an ‘O-H’ group attached to an sp\(^3\) hybridized carbon atom. Alkenes contain a carbon-carbon double bond (C=C), and ketones contain a carbon-oxygen double bond (C=O).

As you will learn, IR may actually be thought of as a Functional Group detector.

The quickest and easiest way to determine the presence of one of these “Functional Groups” is to take the IR spectrum of the compound. The technique is simple and can often provide a definitive answer in less than ten minutes. Evidence provided by IR is widely respected. It is commonly used in judicial proceedings as much as fingerprints are used. In fact, the IR of a pure compound bears the same relationship to that compound as fingerprints do to an individual.

To save space, we will not discuss the theory of IR Spectroscopy. Consult the index of your lecture text. Every modern Organic text discusses IR theory in some detail. Be sure to read that section of your text before doing your first IR so that you will understand what you are doing.

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\(^1\)http://en.wikipedia.org/wiki/Functional_group
An IR instrument consists of an IR light source, a sample holder, a means of selecting individual wavelengths or frequencies of the light, some means of detecting the amount of incident light that the sample absorbs, and a device for plotting the amount of light absorbed as a function of wavelength or frequency. This plot is referred to as the ‘IR Spectrum.’ Since IR light is absorbed by most materials, the optics of an IR Spectrophotometer requires special materials. Most frequently they are built of NaCl or KBr — water soluble salts. This requires that the IR spectrophotometers be protected from moisture of any form. The instrument is usually sealed, but the windows, and the sampling devices require special handling. Aqueous samples should never be used, and the sample holders must be cleaned with DRY organic solvents like reagent grade acetone.

![Close-up of the salt plates in the IR instrument, ready to take a sample](image)

**Figure 2:** Close-up of the salt plates in the IR instrument, ready to take a sample

**Sampling**

IR spectra can be determined for solids, liquids, or gases.

IR gas analysis is a common analytical tool for those involved in studies of atmospheric pollution. The only draw-back is that it is very expensive and delicate cells are needed.

IR spectra of solids and liquids are usually obtained by dissolving the sample in a relatively IR transparent solvent such as CCl₄ and using simple liquid cells. A solid could also be ground to a fine paste with NUJOL™ (a mixture of highly purified hydrocarbons) and the resulting ‘mull’ studied directly. The NUJOL exhibits only a very few well defined peaks that can be ignored when examining the spectrum of the mull. Solid spectra may also be obtained by mixing the solid with dry KBr, grinding to a fine, well mixed powder, and then forming a disk of the mixture by applying high pressure in a specially designed device. The resulting ‘KBr Disk’ will produce a spectrum free of almost all extraneous peaks.

Liquids are the easiest to study by IR. A pure sample of the liquid (1-2 drops) may be placed between two disks of pure NaCl or KBr and the resulting ‘sandwich’ placed directly in the sample holder of the spectrometer. Excellent spectra can be obtained in a matter of a few minutes with
minimum expense. This technique is called running a "neat" spectrum, meaning the spectrum is of the pure liquid only, without solvent.

Reference Spectra

The Infrared spectra of thousands of compounds have been determined and compiled by several different companies. Two of the most popular collections are the Sadtler Index of IR Spectra and the Aldrich Library of Infra-red Spectra.

Both collections are easily accessible in 'hard copy' form in most major university libraries. They are also available in computer readable format for rapid searching and spectrum matching. All modern FT-IR spectrometers are controlled by computers. The operating system often has the capability of searching one or more databases of spectra and finding the spectra that most closely match the spectrum that was just run.

It is always a good idea to compare your IR spectrum with an authentic spectrum of the material you think you have.


Figure 3: Methyl formate - An ester
Figure 4: Isopentyl acetate - An ester

Figure 5: 3-Pentanone - A ketone
Figure 6: 2-Octanone - A ketone

Figure 7: 1-Hexanol - An alcohol
Figure 8: 2-methyl-2-propanol

Figure 9: 1,2,4,5-Tetramethylbenzene - An aromatic
Figure 10: Benzene - An aromatic

Figure 11: Cyclooctane An alkane
We have seen that IR is really a “Functional Group Detector.” As such, it will be a valuable tool throughout this year. You should become accustomed to examining an IR spectrum and looking for characteristic bands that indicate the presence of a Functional Group.

This lab manual contains copies of spectra of various compounds. These will serve as the reference spectra for the infrared experiment. Study these spectra and become familiar with the regions that indicate the presence of -OH, C=O, C-H, etc. Where is the “Fingerprint Region” and what is its significance? Consult your lecture text for help with these questions.

Make your own Table of Functional Groups and IR Frequency Ranges. (Consult your lecture text for these important numbers)

Some IR stretching frequencies are located here.²

²../typicalIR.pdf
PRE-LAB

Answer all assigned WebAssign questions.

Questions

1. What part of the electromagnetic spectrum is known as the infrared region? Express your answer in terms of both frequency (wavenumbers) and wavelength (microns). You may need to consult the lecture text on this one.

2. What is the frequency range of the characteristic absorption bands of the following bonds?
   (a) C=O
   (b) O-H
   (c) C=C
   (d) C-C

3. Describe two significant differences between the infrared spectra of ethyl alcohol and ethylene.

4. Material safety data sheets (MSDS) for the chemicals used in the lab can be found in:
   
   http://www.ncsu.edu/ncsu/ehs
   
   From my TA
   
   In the lab

5. In case of fire, the recommended evacuation route is:
   
   Down the nearest stairs to the first floor, meet the rest of the class at the front of the building
   
   Take the elevator to the basement and leave on my own
   
   Take the elevator to the first floor, meet the rest of the class at the front of the building

6. Which region in the IR spectrum could be used to distinguish between butanoic acid and 2-butanone?
   
   (a) 3200-3600 cm⁻¹
   
   (b) 1600 cm⁻¹
   
   (c) 1680-1750 cm⁻¹
   
   (d) 2500-3300 cm⁻¹

7. Which is the order of increasing bond stretching frequency (lowest first)?
   
   (I) C-H
   
   (II) N-H
   
   (III) O-H
   
   (IV) F-H
PROCEDURE

1. After you have carefully listened to the instructions from your instructor and have taken notes on how to operate the instrument, you are ready to take your first IR spectrum. The easiest way to take the spectrum of a liquid is without any added solvent. This is said to be a “neat” sample—a sample with nothing added—just the liquid alone.

2. You can view a short instructional video that explains how to use the IR instruments in our labs.

3. With a Pasteur pipet, add about 2 drops of your dry liquid sample to the center of one face of a clean, dry salt plate. Press a second dry salt plate onto the first to make a “sandwich” of your sample. Hold the plates up and look to see that the liquid has evenly spread between the plates. If there is an uneven film between the plates, take them apart and clean them with a clean, dry Kimwipe. Begin again, using one or at most two more drops than before.

4. Once you have a clear “sandwich,” it may be placed in the SAMPLE beam of the spectrophotometer. Make certain that ALL instructions given by your instructor (or the lab video) have been followed.

5. Take your spectrum, print it, and record on it the wavelength of significant peaks (the most prominent peaks in the spectrum).

6. Remove the plates from the IR instrument, separate the salt plates, rinse them with dry acetone, dry them with a clean Kimwipe, and return them to the desiccator.

7. On your spectrum, record the sample name, date, your name, and other relevant information. Make sure your TA inspects and approves your spectrum before you consider it finished and turn it in with your worksheet.

8. Try to assign at least three of the most prominent bands in the spectrum. Are they consistent with the Functional Group you believe is present in your sample? (Consult the Tables of Characteristic Frequencies in the IR section of your textbook.)

9. If you need help interpreting your IR spectrum, you can view a short video that covers the basics.

IN-LAB QUESTIONS

The laboratory work involves identification of an unknown by recording its infrared spectrum, investigating the major absorption bands, and comparing the spectrum with spectra of a group of known compounds.

Please print the worksheet for this lab. You will need this sheet to record your data.

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3https://www.youtube.com/watch?v=4IYMNSRCqy0
4../typicalIR.pdf
5https://www.youtube.com/watch?v=Ji2BSH-2BdI
Questions

1. Record the number of your unknown ____________

2. Prepare a spectrum of your unknown and attach the spectrum to this report form.

3. Record the characteristic absorption bands for your unknown.

4. Circle the functional group listed below which is suggested as a candidate for identification by a major absorption band in the spectrum of your unknown.

   *alcohols*
   - benzyl alcohol
   - 2-pentanol

   *aldehydes/ketones*
   - acetophenone
   - 2-chlorobenzaldehyde
   - 4-methyl-2-pentanone

   *hydrocarbons*
   - toluene
   - n-hexane
   - 1-hexyne
   - cyclohexene

   *amines/phenols*
   - aniline
   - o-cresol
   - di-n-propylamine

5. Compare the spectrum of your compound with the spectra of the compounds in the functional group that you have circled. Reference spectra may be found in the lecture text or the laboratory manual. Identifying other major peaks may help you isolate the compound. Write the name of the compound you believe your unknown to be.