

# Infrared Spectroscopy

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## Introduction

Infrared (IR) spectroscopy provides a measure of the types of bonds present in an organic molecule. Molecules are constantly vibrating, with bonds stretching, contracting, bending, and twisting. Each kind of vibration has a characteristic frequency, and a molecule will absorb light for each vibrational frequency. These absorptions occur in the infrared region of the electromagnetic spectrum, with wavelengths ranging from  $2.5 \times 10^{-6}$  m to  $1.67 \times 10^{-5}$  m. By convention, IR absorptions are normally given in frequency units called wavenumbers ( $\text{cm}^{-1}$ ), corresponding to the number of wavelengths which will fit into 1 cm. The relationship between wavelength and wavenumber is given by:

$$\text{wavenumber (cm}^{-1}\text{)} = 10^2 / (\text{in m})$$

so that the useful IR range extends from  $600 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ .

The IR spectrum is a plot of absorption as a function of frequency over this range. The absorptions appear as discrete bands, corresponding to the frequencies of the various vibrations in the molecule. The power of IR spectroscopy is that different types of bonds will vibrate with different frequencies, and certain frequency ranges are characteristic for particular kinds of bonds. Therefore, IR spectroscopy can be used to detect the presence (or absence) of certain kinds of bonds, and so it is especially useful for determining the presence (or absence) of functional groups in organic molecules. For example, the C=O double bond of carbonyl compounds has a very characteristic stretching frequency in the range  $1650\text{-}1800 \text{ cm}^{-1}$ . The presence of a strong absorption band in this range is good evidence that the compound contains a carbonyl group. Conversely, if no absorption is seen in this region, it is unlikely that the sample has a carbonyl system.

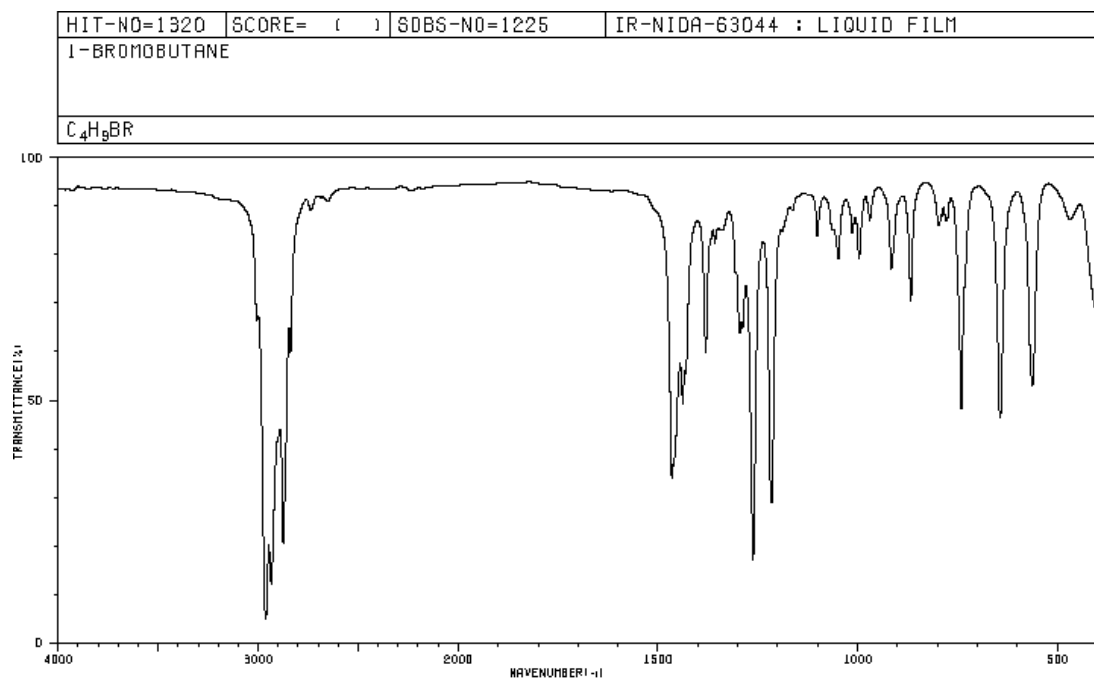
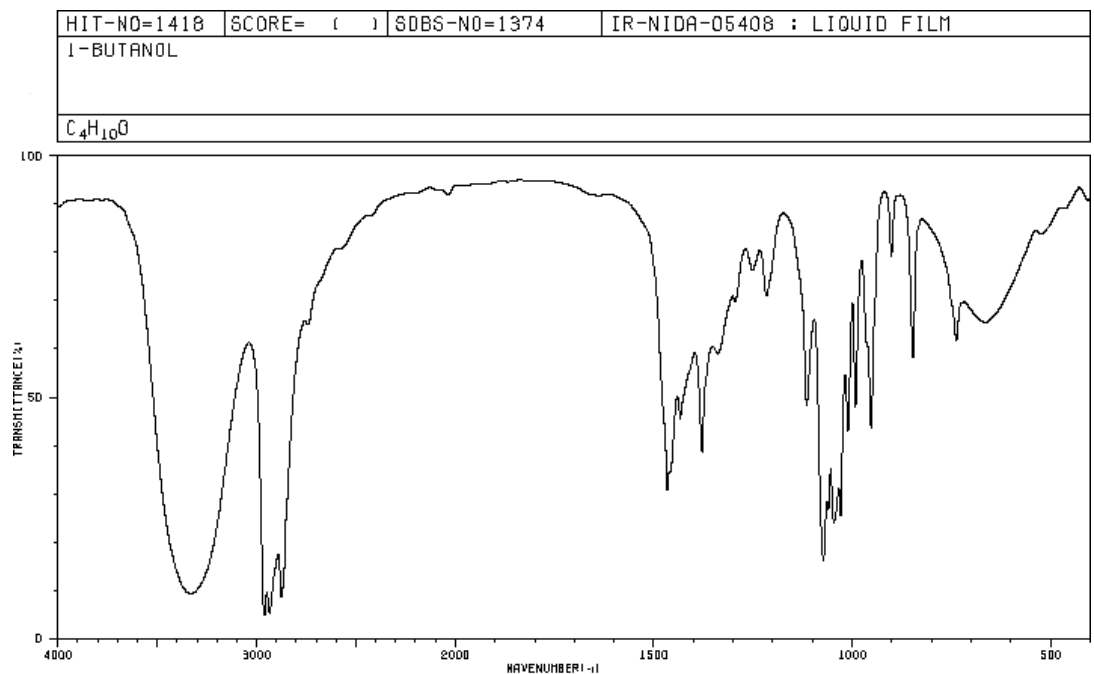
Other parts of the IR spectrum are less diagnostic for particular functional groups. For example, the range from  $1200\text{-}1500 \text{ cm}^{-1}$  includes C-C stretching and C-H bending vibrations, of which there are many in the typical organic molecule, and so this region often has a complicated pattern of absorption bands that is difficult to interpret. While these bands may not be helpful in identifying unique functional groups, it turns out that the exact pattern of absorptions can be used as a 'fingerprint' of the compound in question. If two samples have superimposable IR spectra, it is a good bet that they are identical.

Several tables of characteristic IR absorptions are available. A simplified version is presented in Table 1. This includes IR absorptions which are diagnostic for particular functional groups, and lists the typical frequency range, the type of bond and vibration, representative functional groups, and brief comments regarding each.

The IR spectra of 1-butanol and 1-bromobutane (Figure 1) show the changes in IR absorption characteristic of the functional group change (OH replaced by Br). The O-H and C-O stretching bands for the alcohol are not present in the spectrum of the alkyl bromide, and a band assignable to the C-Br vibration is present in the latter (although this band is not reliable diagnostic). Both spectra show the strong C-H stretch for alkane-type hydrogens, since the absorptions occurs  $< 3000 \text{ cm}^{-1}$ . Vinyl C-H stretches show up at slightly higher frequencies, above  $3000 \text{ cm}^{-1}$ , and this is a very good way to tell vinylic or aromatic C-H's are present.

**Table 1.** Characteristic Group Frequencies.

| Frequency<br>( $\text{cm}^{-1}$ ) | Vibration<br>Mode | Compound<br>Type        | Comments                                                                                                                                         |
|-----------------------------------|-------------------|-------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| 3600-3300                         | O-H stretch       | alcohols, water         | broad, strong band-becomes sharper and moves to higher frequency if no H-bonding; alcohols also have C-O stretch 1200-1000                       |
| 3300                              | C-H stretch       | alkynes                 | strong, sharp band for 1-alkynes (C=C-H)                                                                                                         |
| 3100-3010                         | C-H stretch       | alkenes, benzenes       | medium intensity; vinyl and aromatic C-H stretch is always $>3000$                                                                               |
| 2980-2850                         | C-H stretch       | alkanes                 | strong, present in most organic compounds $<3000$ differentiates from alkene C-H                                                                 |
| 3200-2500                         | O-H stretch       | carboxylic acids        | very broad due to H-bonding; often obscures C-H stretch region; look also for C=O and C-O stretch ( $\sim 1700$ & $\sim 1280$ )                  |
| 2250                              | C N stretch       | nitriles                | strong, sharp band characteristic -C N                                                                                                           |
| 2200-2100                         | C C stretch       | alkynes                 | very weak except for 1-alkynes; the latter also have the band at 3300 (C-H)                                                                      |
| 1800-1650                         | C=O stretch       | carbonyls               | very strong, sharp band; position depends on particular functional group; conjugation shifts to lower freq.<br><i>Typical ranges for C=O:</i>    |
|                                   |                   | anhydrides              | two bands, 1820 & 1760                                                                                                                           |
|                                   |                   | esters                  | 1750-1720, also C-O at $\sim 1250-1150$                                                                                                          |
|                                   |                   | acids                   | 1720-1680, also C-O and O-H                                                                                                                      |
|                                   |                   | ketones                 | 1740-1680                                                                                                                                        |
|                                   |                   | aldehydes               | 1740-1680, also unique C-H at $\sim 2720$                                                                                                        |
|                                   |                   | amides                  | 1650, strong often broad or split                                                                                                                |
| 1650-1600                         | C=C stretch       | alkenes, benzenes       | medium to weak intensity                                                                                                                         |
| 1300-1000                         | C-O stretch       | acids, alcohols, esters | relatively strong band; exact position depends on structure; other weaker bands may also appear in this region<br><i>Typical ranges for C-O:</i> |
|                                   |                   | acids                   | 1300-1280, also has C=O at $\sim 1700$                                                                                                           |
|                                   |                   | esters                  | 1250-1150, often two bands<br>C-O bonds - ester C=O at 1740                                                                                      |
|                                   |                   | alcohols                | 1200-1100, tertiary<br>1150-1090, secondary<br>1100-1050, primary                                                                                |
| 1000-800                          | C-H bending       | alkenes, benzenes       | alcohols also have O-H at 3500-3300<br>out of plane bends, characteristic strong abs. diagnostic for $\text{sp}^2$ C-H                           |
| 600-500                           | C-Br stretch      | alkyl bromides          | usually strong                                                                                                                                   |



**Figure 1.** Infrared transmission spectra of 1-butanol (top) and 1-bromobutane. The spectra were obtained from the SDBS Web site: <http://www.aist.go.jp/RIODB/SDBS/> [accessed 11/30/99].

IR spectra can be used to assess compound purity as well, especially if the potential contaminants are known. You will use IR spectroscopy to check the purity of your product from this experiment. The IR spectrometers you will use are dual beam instruments, meaning that the IR radiation is split into two paths. The sample is placed in one path, with nothing in the other (reference) beam. The instrument then compares the amount of infrared radiation transmitted through the sample with that from the reference beam, and the difference corresponds to the light absorbed by the sample. The beam paths are easily visible in the spectrometer: The one nearest to the front of the instrument is where the sample should go. Since glass absorbs infrared radiation very strongly, it is not suitable as a material for a sample cell. Actually, some of the few substances which does not absorb significantly in the region  $600\text{-}4000\text{ cm}^{-1}$  are simple inorganic salts, and NaCl is commonly used to construct cells for IR samples. For liquid samples, the simplest method is to place the sample between two flat wafers of NaCl. The surfaces of the NaCl plates are polished flat, so that when a drop of liquid is placed on one plate and the other placed on top, the sample will spread to a thin liquid film, and capillary forces will hold the plates securely together. The sample is then placed in a bracket which holds it in the sample beam, and the spectrum recorded. This thin layer of pure (neat) sample is plenty to give a strong IR spectrum.

Solid samples must be handled differently. One method is to dissolve them in a suitable solvent, and to proceed as for liquid samples, but of course this will lead to complication of the IR spectrum due to absorptions by the solvent. If the solvent does not interfere with the bands of interest, this may not be a serious problem. An alternative solution is to make a mixture of the solid (~1%) with powdered KBr. The mixture is ground thoroughly with a mortar and pestle, and the resulting powder compressed to a thin (~0.5 mm) pellet. A clear wafer of KBr containing dispersed sample results, and this can be put in the sample beam. Since KBr does not absorb the IR radiation, the spectrum of the sample can be obtained without interference.

Proper care of the NaCl plates is essential. These are expensive, since they are cut from single crystals of NaCl, and polished to optical smoothness. The main rule is: NO WATER! Water dissolves NaCl, and will destroy the flat surface faster than you can imagine. It goes without saying that water is never permitted on the plates. This includes organic samples that are wet. If your organic liquid is cloudy, then it probably contains water and must not be placed on the salt plates. You will need to redry such a sample with  $\text{CaCl}_2$  or some other appropriate drying agent. Excessive handling or long term exposure to the air will cause the plates to deteriorate – moisture from hands or from the atmosphere will eventually cause clouding of the plate and pitting of the surface. The plates must be handled only by the edges (make certain your hands are completely dry), and the flat surfaces should not be touched. After use, the plates should be rinsed thoroughly with an appropriate solvent (we will use methylene chloride. Acetone is bad news since it inevitably contains dissolved water), patted dry with a clean tissue (Kimwipe®), and placed in a dessicator.

The IR spectrometers are very simple to use. A sheet of chart paper is clamped in the carriage so that the bottom edge of the paper butts against the edge of the carriage, and the mark on the top of the paper (at  $2000\text{ cm}^{-1}$ ) is aligned with the white mark on the carriage. With the scan button off, the carriage can be moved left or right. To record the spectrum, the carriage should be moved to the left-most position, and the scan button pushed (use fast scan speed). Very Important: The carriage must not be moved manually (or even touched!) when the scan button is lit. Problems? Check with your TA.

## How to Obtain Infrared Spectra via the Internet on the World Wide Web

Since the arrival of the Internet, chemists have had access to an extensive amount of information at the click of the mouse. Many web sites have spectral database that are freely accessible by the public. The two spectra shown in Figure 1, for example, were obtained from SDBS Integrated Spectral Data Base System for Organic Compounds. Below are step by step instructions to three different web sites. Find the spectra for 1-butanol and 1-bromobutane on each site and include print-outs of these spectra in your report.

### 1. SDBS Spectral Data Base System (<http://www.aist.go.jp/RIODB/SDBS/>)

#### **Transmittance spectra available.**

- Click on "Web Destinations" in the Chem 212 course web site menu.
- Scroll down to "Chapter 12: Infrared Spectroscopy" and click on it.
- In the "Infrared Spectroscopy" section, click on "SDBS- Integrated..."
- Click on "Search Compounds".
- Type name of compound and click "Query".
- Click "Display".
- Click on the number under SDBSNO.
- You can get a picture of the spectrum by clicking on the IR Spectral Code.
- To print the spectrum, click on the spectrum frame and print.

### 2. NIST Chemistry WebBook (<http://webbook.nist.gov/>)

#### **Both transmittance and absorbance spectra available for most compounds.**

- Click on "Web Destinations" in the Chem 212 course web site menu.
- Scroll down to "Chapter 12: Infrared Spectroscopy" and click on it.
- In the "Infrared Spectroscopy" section, click on "NIST Chemistry WebBook."
- At "NIST WebBook," click on "NIST Chemistry WebBook."
- Under "Search Options" click on "Name."
- Type name of compound, select "Gas Phase IR Spectrum," and click on "Search."
- You can view both transmittance and absorbance spectra.
- To print the transmittance spectrum, click on "View Large Spectrum Image" and print.

### 3. Galactic Industries Corporation Spectral Database (<http://spectra.galactic.com/>)

#### **Absorbance spectra available.**

- Click on "Web Destinations".
- Scroll down to Chapter 12 General Spectroscopy and click on it.
- In section "General Spectroscopy," click on "Galactic Industries Corporation Spectral Database."
- Click on "Search" in the menu on top.
- Click on "Spectra Online."
- Click on "Enter Spectra Online."
- Type compound name and click on "Run Search."
- Find compound in the list and click on the name.
- Print.