

Determination of Unknowns by IR Spectroscopy

An Overview of Today's Experiment

1. Get two unknowns (one liquid and one solid)
3. Show up at IR(Instrument room CPP212) at the assigned time and run IR spectra of unknowns
4. Report results next week. Even though you ran the spectra with a partner, the report should be an individual effort.

Introduction

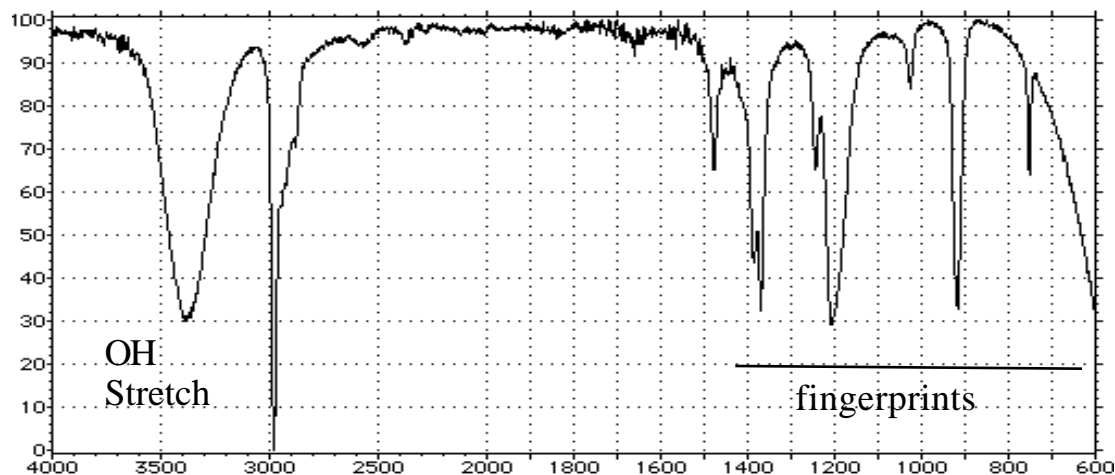
Unlike the chromatographies, which physically separate materials, **infrared (IR) spectroscopy** is a method of determining what you have after you have separated it.

The IR spectrum is the name given to the band of frequencies between 4,000 and 400 cm^{-1} , beyond the red end of the visible spectrum. The units are called wave numbers or reciprocal centimeters (that's what the cm^{-1} means). This range is also expressed as wavelengths from 2.5 to 25 micrometers (μm).

With your sample in the sample beam, the instrument scans the IR spectrum. *Specific functional groups absorb specific frequencies and energies.* And because the spectrum is laid out on a piece of paper, these specific energies become specific places on the chart.

Look at the first two spectra below. Here's an example of a fine pair of alcohols if there ever was one. See the peak (some might call it a trough) at about 3,400 cm^{-1} ? That's due to the **OH** group, specifically the stretch in the O-H bond, the **OH stretch**.

A. t-Butanol

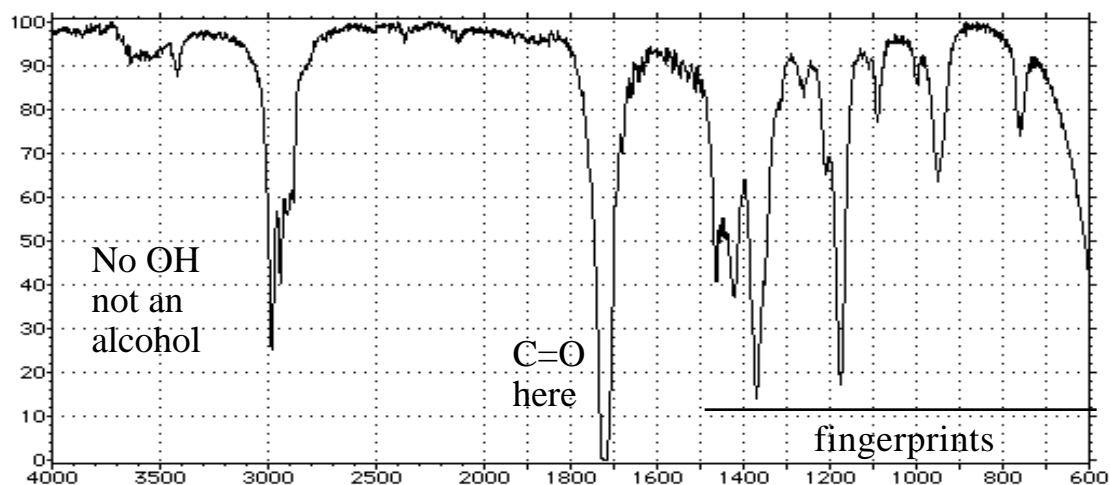


B. Cyclohexanol

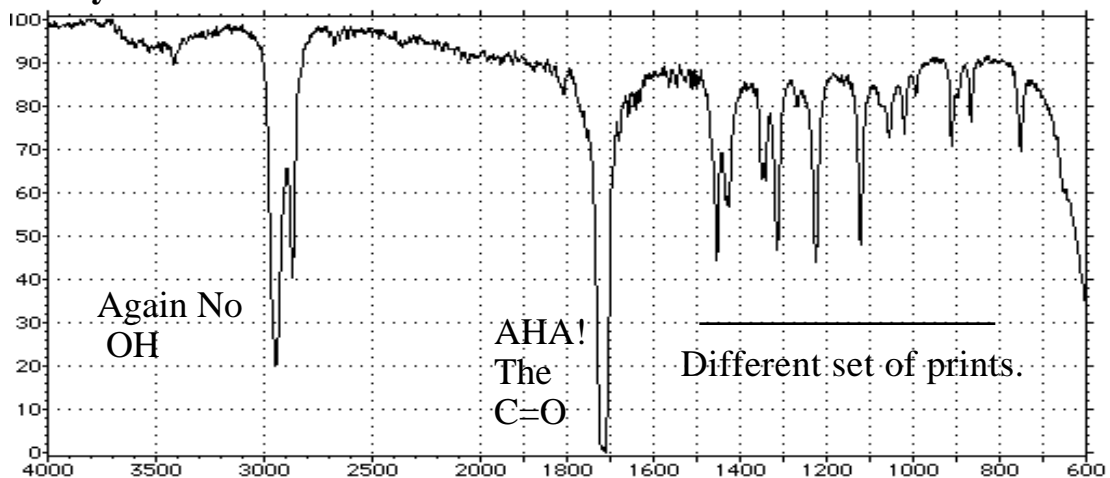


Now consider the spectra of a couple of ketones. Is there an **OH** absorption at 3400 cm⁻¹? Should there be? *Of course not!* But there is a **C=O** and where's that? The peak about 1700 cm⁻¹. It's *not* there for the alcohols, but *is* there for the ketones. Congratulations, you've just interpreted four IR's.

C. 2-Butanone



D. Cyclohexanone



Because the first two have the characteristic OH stretch absorptions of the alcohols they *just might* be alcohols. And the other two *might* be ketones because they have the characteristic C=O stretch absorption at 1700 cm^{-1} in each.

What about the other peaks? Well, you can ascribe some sort of meaning to each of them but it may be difficult. That's why frequency correlation tables exist. They identify regions (frequencies) of the IR spectrum where absorptions for various functional groups show up. See if you can find the C-H stretch absorptions which are in all four spectra; or the C-O stretch absorption which are in two of them.

For you Sherlock Holmes fans, the region between 1500 and 800 cm^{-1} is known as the fingerprint region. *The peaks are due to the entire molecule*, i.e. its fingerprint, rather than being from independent functional groups. And, you guessed it, no two fingerprints are alike.

Take another look at the cyclohexanol, cyclohexanone spectra. Both have very similar structures, only different functional groups of oxygen. Do the fingerprints of these compounds look alike? No. In a similar way the fingerprint regions of both t-butanol and cyclohexanol are very different.

Interpreting IR's

IR interpretation can be as simple or as complicated as you'd like to make it. You have already seen how to distinguish alcohols from ketones by **correlation** of the positions and intensities of various peaks in your spectrum with values listed in **IR Tables**. Two things to watch out for in IR interpretation are:

- 1. Nitpicking a spectrum.** Don't try to interpret every wiggle. There is a lot of information in an IR spectrum. Think about what it is that you are trying to prove.
- 2. Pigheadedness in interpretation.** Usually a case of "I know what this peak is so don't confuse me with the facts." Keep an open mind when examining an IR spectrum. Try not to overlook an important absorption because you don't expect it to be there. On the flip side, try not to see absorptions where there are none, because you think there should be one there.

In this experiment you and a lab partner will be issued two unknown compounds, a solid and a liquid. These unknowns come from a list of possible compounds at the end of this handout. Your mission is to employ IR spectroscopy to determine what your unknown actually is.

IR SAMPLE PREPARATION

You can prepare samples for IR spectroscopy easily, but you must adhere to one very important rule.

NO WATER!

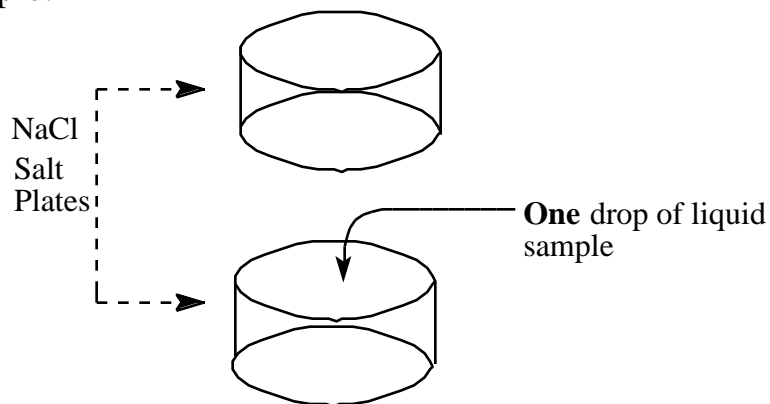
In case you didn't get that the first time

NO WATER!

Ordinarily, you put the sample between two salt plates. Yes. Common, ordinary *water-soluble* salt plates. So, Please keep it dry, folks.

Liquid Samples

1. **Make sure the sample is dry!** There should be no visible water in the sample.
2. Handle the salt plates only by the edges. **Never** touch the face of a plate with your fingers. Wash the face of the salt plates with a few drops of dichloromethane to remove any sample left by the previous user. Dry Gently with a Chem-Wipe.
3. Put some of the dry sample, (one to two drops), on one salt plate, then cover it with another plate. The sample should spread out to cover the entire plate. If it doesn't cover well, try twisting the top plate to spread the sample, or add a drop or two more sample.



4. Place the sandwich in the IR salt plate holder
5. Slided the holder into the bracket on the instrument in the sample beam. To do so you must open the small access door, try to do this as quickly as possible.
6. Run the spectrum.(See how to do so further on)

Solid Samples - The NUJOL Mull

A rapid, inexpensive way to get an IR of solids is to mix them with NUJOL, a commercially available mineral oil. Traditionally this is called "making a NUJOL mull", and is practically idiomatic among chemists.

You want to disperse the sample throughout the oil, making the solid transparent enough that the solid will give a usable spectrum. Since mineral oil is a saturated hydrocarbon, it has an IR spectrum all its own. You'll find C-H stretches and bends in the spectrum, but since you know what and where they are, you'll ignore them. If you are not sure what to look for you can run your own spectrum of pure NUJOL.

1. Put a small(really small) amount of your solid in a mortar and add a few drops of NUJOL oil.
2. Grind the oil and sample together until the solid is a fine powder dispersed throughout the oil.
3. Spread the mull on one salt plat (just a little goes a long way),and cover it with another plate. There should be no air bubbles just an even thin film of the solid in the oil.
4. Proceed as if this were a liquid sample.

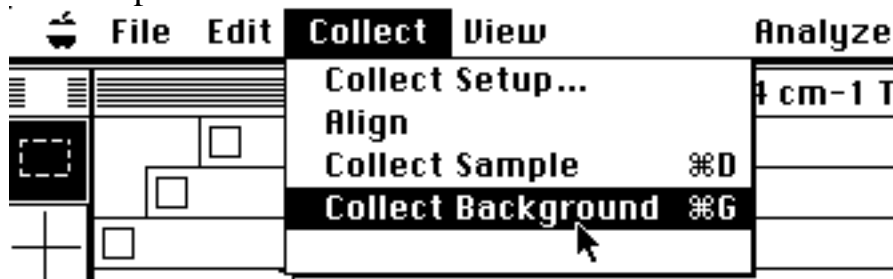
Running the IR Spectrometer

The Nicolet FTIR Spectrometer used in this experiment is an example of a **Fourier Transform (FT) IR Spectrometer**. These instruments operate on a different principle than the double beam spectrometer discussed in class. However, the end result, (which is the IR spectrum of a sample) is identical to what would be obtained with a standard double beam. The theory behind FTIR is complex, *but* the instruments are *very easy* to use. The instrument is interfaced to a Mac computer and is menu driven; all one has to do is move and click the mouse pointer. Anyone with experience using a Mac or Windows based PC should find this familiar and comfortable. This is much easier than what had to be performed back in the bad old days, like five years ago. The operation of the FTIR is **almost** idiot proof, but this does not mean that you have to be an idiot. If you are confused as to what to do, in the words of Dear Abby, "Seek professional help".

I. Collect Background. Many of the gasses in the atmosphere are IR active. Can you guess which ones? We must take these various ir absorptions into account. In a standard double beam IR spectrometer this is no problem since they balance out in the sample and reference beams. However, FTIR spectrometers operate

with a single sample IR beam. The instrument allows us to scan a sample of "background" i.e. an empty beam chamber. The background spectrum is stored, and any peaks are automatically subtracted from the sample spectrum by the computer.

1. Make sure the beam chamber is empty, there should be nothing in the beam
2. Highlight (click mouse on) **Collect** at the top menu bar-drag down until **Collect Background** is highlighted, release mouse. That's it, you have just told the computer to tell the FTIR what to do.



At this point you should see some activity on the screen. What's that funny looking squiggle on the screen, you ask? What you are looking at is called an interferogram; it's how the instrument first collects data. Within a few seconds the interferogram is collected, the computer performs a mathematical operation called a Fourier Transform, and voila, a typical IR spectrum appears. Well, not really typical, in fact it looks funny, but it is a background spectrum. You are now ready for the big time.

II. Collect Sample

1. Open access door on the **top** of the sample compartment and slide sample holder into bracket. **Close Door!**
2. Highlight **Collect** and drag down until **Collect Sample** is highlighted. Release Mouse...watch as the spectrometer slavishly obeys your every command.



III. Print Sample. At this point you want a hard copy of your IR masterpiece

1. Make sure printer is on (look at little switch at left front).

2. Highlight **File**, drag down to **Print** and release. When the printer driver window opens, click on **Print**.

3. Prepare to wait, this printer is SLOOOOW!

IV. Clear Spectrum. When you have printed your spectrum, you will clear your spectrum from the computer.

1. Highlight **Edit**, drag down to **Clear** and release.

V. Clean-up.

1. Remove sample from IR spectrometer. Don't forget to close the access door!

2. Separate salt plates and wash face carefully with dichloromethane (or chloroform). Remember not to touch the faces of the plates with your fingers. Dry with Chem-Wipe.

REPORT

Your grade for this experiment will be based on the correct determination of your unknown and a detailed analysis of your spectra that illustrates how you made your deduction. In your report list all characteristic absorptions observed and how they relate to the compound you have selected.

Possible Liquid Compounds

decane
1-hexanol
mesitylene
n-butylbenzene
t-butylbenzene
cyclohexanol
cyclohexane
acetophenone
benzaldehyde
methyl ethyl ketone
benzonitrile
phenylacetylene
acetonitrile
heptaldehyde
t-butanol
cyclohexanone

Possible Solid Compounds

benzoic acid
p-dimethoxybenzene
p-chlorobenzaldehyde
4-t-butylcyclohexanol
Maleic acid
biphenyl
p-dichlorobenzene
phthalimide

