

Experiment 7

IDENTIFICATION OF AN ORGANIC UNKNOWN. I

Text Topics and New Techniques

Physical properties (density, boiling point, refractive index) and infrared spectroscopy of organic compounds and use of chemistry resources on the Internet.

Discussion

In 1800, Sir William Herschel, an astronomer who was responsible for many important advances including the discovery of Uranus, provided the first evidence for infrared radiation (he called it “invisible light”). It took another 103 years before another physicist-astronomer, William Weber Coblentz demonstrated the potential use of infrared spectroscopy for the determination of structural features of organic compounds. Coblentz founded and then directed the radiometry section of the National Bureau of Standards (currently the National Institute of Standard and Technology, NIST - one of the largest databases of infrared spectra on the Internet). In 1937, Frank Rose demonstrated that group frequencies could be used to determine the functional groups present in a molecule. Finally, it was about 1950 that infrared spectrometers became readily available and organic chemists began to use ir routinely to help with the identification of organic compounds. Before the middle of the 20th century, the identity of previously characterized compounds was confirmed using physical properties of the compound and its derivatives. Determination of the structure of new compounds was accomplished with micro-analytical analysis (empirical formula determination from the quantitative combustion of the compound) and chemical properties. This could involve significant expenditure of time and doubt could still remain about the actual structure. Spectroscopy quickly became a powerful tool for organic chemists.

The use of infrared, nuclear magnetic resonance and mass spectrometers has revolutionized the approach organic chemists use to identify compounds. Interpretation of ir, nmr and ms leads to information on functional groups and the structure of the carbon skeleton. For structure verification, the spectra serve as “fingerprints” for positive identification. In today’s experiment, you will use a combination of physical properties and infrared spectroscopy to identify an unknown organic liquid. In many ways, the approach to this problem is like driving a car; it depends on conditions and what you find out each step of the way. As all of the possible unknowns have been previously characterized, you will want to coordinate the use of experimental results with judicious use of chemistry resources. The general approach for this case should be to determine the ir spectrum, refractive index, density and boiling point of the unknown. The ir spectrum should enable you to determine which functional groups and the class of compound including whether it is aromatic. For this experiment, the unknown will be one of the following: alcohol, aromatic hydrocarbon, ester or ketone. The next step is often to use tables of functional groups that are arranged according to increasing boiling point or refractive index. This will enable you to considerably narrow down the list of possibilities. Then a comparison of the remaining properties and the ir spectrum should lead to a single conclusion. A web site (*Knovel Critical Tables*) that has recently become free (with proper registration) allows arranging of compounds by molecular mass, formula, boiling point, melting point, density or refractive

Fig. 7-1



Sir William Herschel
William W. Coblentz

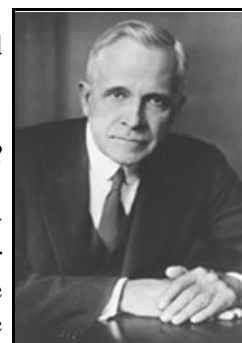


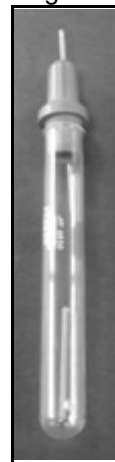
Fig. 7-2

index and should be invaluable for the analysis of unknowns. For the URL, refer to the *Chemistry Resources* section. An alternative but not as educationally valuable method is to enter your information into an Internet site (refer to the *Chemistry Resources* section). These sites compare the data you enter to a computer library of data and give you possible hits.

Techniques

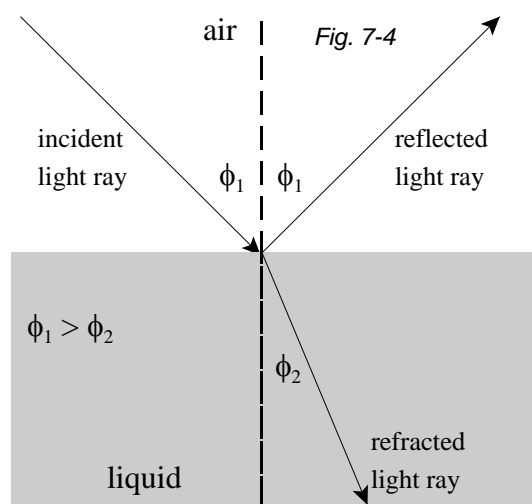
In a future experiment, you will purify a liquid using distillation. You will be able to monitor the **boiling point** of your liquid during the distillation. Unfortunately, distillations require the use of a substantial volume (> 1 mL) of the liquid. Often, this much liquid is not available and other methods have to be used to determine boiling points when only a small volume of sample is available. Transfer about 1 mL of liquid to a 10 x 75 mm test tube. Cut off a melting point capillary tube to about a 2 cm length and insert it up-side-down into the liquid. Insert a prefitted cork with an open ended capillary into the tube. Strap the tube to a thermometer and suspend it into a 150 mL beaker containing mineral oil and a stirring bar. Mount the system on top of a heater-stirrer unit that is on a lab jack. Heat until a continuous stream of bubbles is coming out of the bottom capillary tube. Turn off the heat and lower the lab jack. Now watch the tube carefully. Eventually, the bubbling should stop and the liquid should start rising in the capillary. When the liquid levels inside and outside the capillaries are the same, record the boiling point. (*Why is this the boiling point?*) After recording the boiling point, look at the capillary to be sure the liquid went to the top. If there is an air bubble, the boiling point needs to be redetermined.

Fig. 7-3



Density is another routinely measured physical property. Because the range of values of densities for organic compounds is not huge, densities are limited in their use for distinguishing organic compounds. When more than 1 mL of liquid is available, carefully use a volumetric pipet to transfer 1.00 mL of the liquid to a preweighed container and reweigh. The density is calculated from m/v .

The **refractive index** of a liquid is easy to measure to high precision and is an undervalued property that is extremely useful for identification purposes. Light travels at a speed of 2.998×10^8 m/sec in a vacuum. In liquids, the speed of light is about 24 to 37% slower. When looking at an angle into water, the velocity



difference results in the bending of light with the illusion that objects appear farther away than they actually are. The ratio of the speed of light in a vacuum to the speed of light in a liquid can be measured by determining the angle of refraction of the light. This ratio is called the refractive index. An instrument called

an Abbe refractometer has been designed to very quickly measure the refractive index with a drop or two of liquid. The instrument reads out to 5 significant figures. For example, the refractive index of acetone at 20°C is 1.3588. As the density of a liquid decreases as the temperature increases, the speed of light in the liquid will increase as the temperature increases. As a result, the refractive index decreases with increasing temperature. If your measurement is made at a temperature above 20°C, an approximate correction (so that you can compare it to literature values, most of which are reported at 20°C) is to add 0.0004 to your measurement for each degree your measurement is above 20°C. Because you will have a high degree of confidence in the refractive index to 4 significant figures, the refractive index is very useful for narrowing down a list of possible compounds and for verification of identity. For specific instructions on the use of the refractometer in your lab, either read the instruction book or ask your instructor.

As mentioned earlier, **infrared spectroscopy** is a powerful tool for the analysis and identification of organic compounds. You should start by reading the chapter in your organic chemistry textbook that covers this topic. Your laboratory will probably be equipped with either a dispersive ir instrument or a high technology Fourier Transform Infrared Spectrometer (FTIR). The former takes several minutes to produce a spectrum whereas the latter obtains spectra in seconds with the rate determining factor for hard copy being the printer speed. If used properly, both types of instruments give high quality and essentially identical spectra.

Quickly reviewing some basic principles of spectroscopy, the energy of electromagnetic radiation is proportional to the frequency of the light. The proportionality constant is Planck's constant or $E = h\nu$. Since the speed of light is the product of wavelength and frequency, $c = \lambda\nu$, the energy is inversely proportional to the wavelength, $E = hc/\lambda$. While the position of an ir absorption is sometimes expressed in terms of the wavelength, most chemists prefer to use a property that is proportional to the energy. For this purpose, the inverse of the wavelength is used with the units in reciprocal centimeters (called wavenumbers), $1/\text{cm} = \text{cm}^{-1}$. The fundamental region of infrared and the region normally scanned by lab ir instruments is 4000 cm^{-1} to 400 cm^{-1} . To put this into perspective, refer to the following table:

<u>wave type</u>	<u>wavelength (nm)</u>	<u>energy (kJ/mol)</u>	<u>energy (cm^{-1})</u>	<u>transition</u>
gamma	$10^{-1} - 10^{-3}$	$1.2 \times 10^6 - 1.2 \times 10^8$	$10^8 - 10^{10}$	electronic (ionization)
X-rays	$10 - 10^{-1}$	$1.2 \times 10^4 - 1.2 \times 10^6$	$10^6 - 10^8$	electronic (ionization)
far ultraviolet	$2 \times 10^2 - 10$	$6 \times 10^2 - 1.2 \times 10^4$	$5 \times 10^4 - 10^6$	electronic (ioniz., promotion)
ultraviolet	$4 \times 10^2 - 2 \times 10^2$	$3 \times 10^2 - 6 \times 10^2$	$2.5 \times 10^4 - 5 \times 10^4$	electronic (promotion)
bond energies		$1.5 \times 10^2 - 5.6 \times 10^2$		
visible	$7 \times 10^2 - 4 \times 10^2$	$1.7 \times 10^2 - 3 \times 10^2$	$1.4 \times 10^4 - 2.5 \times 10^4$	electronic (promotion)
infrared	$10^5 - 7 \times 10^2$	$1.2 - 1.7 \times 10^2$	$10^4 - 1.4 \times 10^4$	vibrational, rotational
infrared (fundamental)	$2.5 \times 10^4 - 2.5 \times 10^3$	4.8 - 48	400 - 4000	vibrational
microwaves, radar	$10^8 - 10^5$	$1.2 \times 10^{-3} - 1.2$	$10^{-1} - 10^4$	rotational
radio, mag. res., TV	$10^{12} - 10^8$	$1.2 \times 10^{-7} - 1.2 \times 10^{-3}$	$10^{-5} - 10^{-1}$	nuclear spin

The energy of the visible-ultraviolet region of the spectrum is comparable in energy to bond strengths and also to the difference in energy between the ground and first excited states of molecules. The rather rare occurrence of color is due to the matching of an energy gap between the ground state and the first excited state with the energy of part of the visible region of the spectrum. Much more often the lowest electronic transition is at higher energy in the ultraviolet region and as a result the molecule is colorless. Because the ir region of the spectrum is significantly lower in energy than the visible, there is insufficient energy to promote electrons from one orbital to a higher one. Instead, the infrared region is the appropriate energy to activate vibrational modes in the molecule. Because there are many possible vibrational modes, there are usually many active absorptions in the ir. This means that ir spectra contain considerable information and all we have to do is figure out how to extract it from the spectrum.

Fortunately, most functional groups absorb at distinguishing energies called group frequencies in the infrared region. By learning to read the spectrum, you should be able to determine which functional groups are present and equally important, which ones are not present. In other words, the ir should enable you to determine if a compound is an alcohol or a ketone or some other class of organic compound. The ir also gives information about the presence of double and triple bonds and aromaticity. A list of some group frequencies is below. It would be advisable to do *Exercises 4* and *5* at this point.

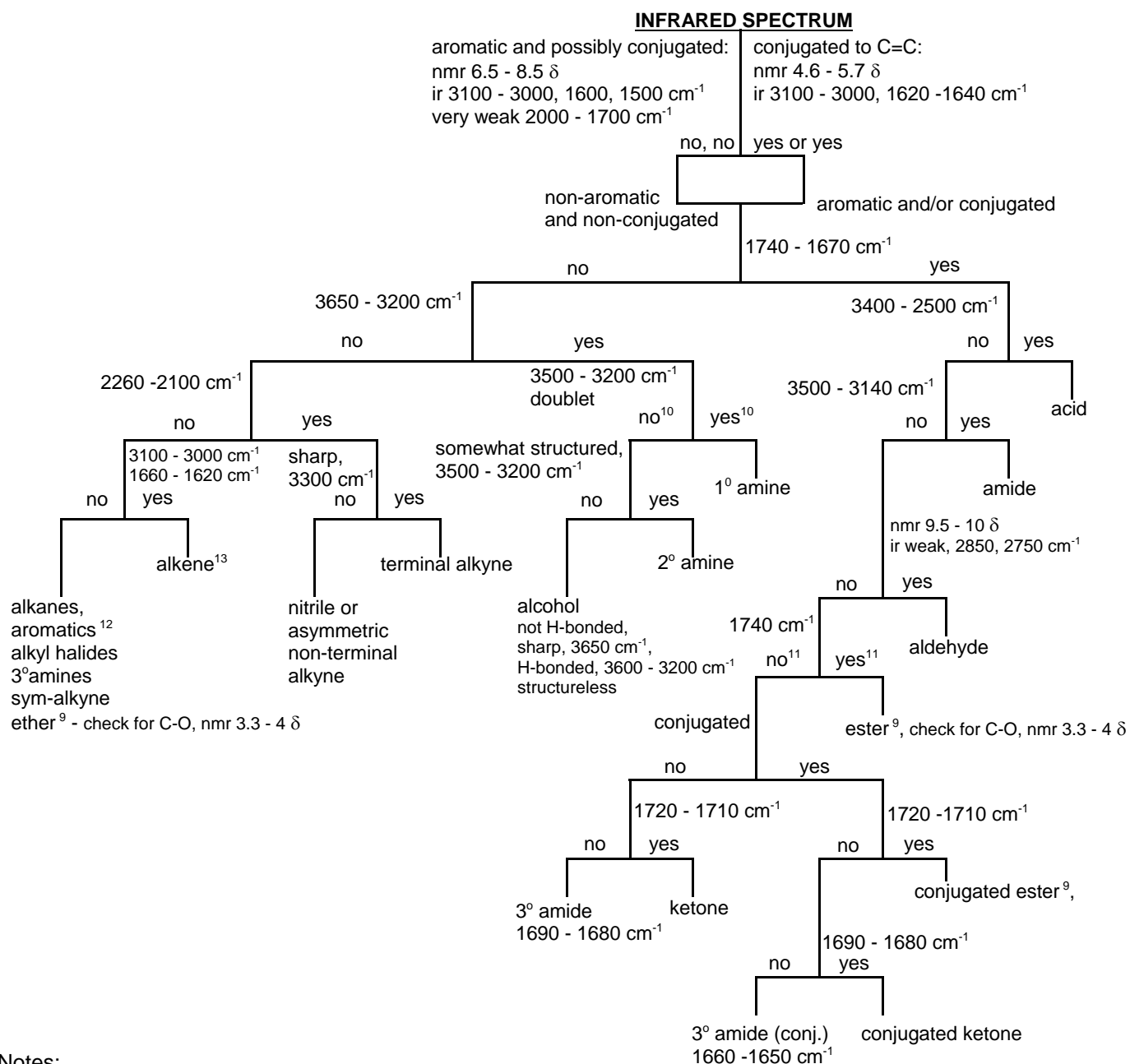
Selected Infrared Group Frequencies

Functional group	wavenumbers (cm ⁻¹)	information
OH	3650 - 3200	strong but broad unless very dilute
NH	3500 - 3200	strong and somewhat sharper than OH, primary amines give 2 peaks
COOH	3400 - 2500	strong and extremely broad with little or no structure
sp CH	3300	strong, sharp
sp ² CH	3100 - 3000	3000 divides sp ² from sp ³
sp ³ CH	3000 - 2850	3000 divides sp ² from sp ³
CO-H	2850, 2750	relatively weak, can be overlooked in dilute solution
C ≡ N	2260 - 2220	strong, sharp
C ≡ C	2260 - 2100	absent if symmetrically substituted
aromatic	2000 - 1700	very weak overtones that can easily be overlooked but can be used to determine orientation on the ring
<u>C=O</u>	<u>1740 - 1670*</u>	
RCOOCOR	1820*, 1760*	
RCOOR	1740*	strong
RCOR, RCOH	1730 - 1700*	strong, 1740 cm ⁻¹ for cyclopentanones
RCOOH	1720 - 1700*	strong but broader than ketones and aldehydes
RCONH ₂	1690 - 1670*	strong
C=C	1650*	moderate
aromatic C=C	1600, 1500	relative intensities of 2 peaks varies considerably
CH ₃	1380	weak, usually a doublet for <i>isopropyl</i> , <i>t-butyl</i> .
C-O	1300 - 1000	highly variable and difficult to distinguish from other absorptions

*Conjugation typically lowers about 25 cm⁻¹

There are many different ways to approach the interpretation of an ir spectrum. The dichotomous key on the next page gives you one possible sequence. It is important to note that some absorptions are strong and if present, provide strong evidence that the functional group is present. If the absorption is not present, the functional group is not present. On the other hand, for weak absorptions such as the aldehydic C - H stretch, the C ≡ C triple bond (for the triple bond, if it is symmetrically substituted, it will not absorb at all), aromatic resonance or methyl C - H bending, the absorptions are weak and the absence of the absorptions shouldn't be taken as definitive evidence that the group is not present. An increase of the concentration or path length might result in the band being observable. Once a tentative identification is made, a match with a literature ir essentially verifies the identity. Expect some differences primarily in intensity due to different concentrations, path lengths or to solvent.

Dichotomous Key for the Analysis of Infrared Spectra of Organic Compounds



Notes:

- Nmr refers to proton magnetic resonance. Carbon-13 resonance could also be useful in many cases.
- Anhydrides, nitro compounds and other less common functional groups were not included in the key.
- The key generally does not consider di or polyfunctional compounds except for those that are aromatic.
- A weak peak at about 3400 cm^{-1} is often an overtone of a carbonyl absorption.
- A weak broad absorption between 3600 and 3200 cm^{-1} is usually due to contamination by water or an alcohol.
- Carbon dioxide absorbs at 2350 cm^{-1} and shows up in spectra if corrections for the CO₂ in the air are not exact.
- Methyl gives a relatively weak absorption at about 1380 cm^{-1} .
- Isopropyl and t-butyl give doublets centered around 1380 cm^{-1} .
- For cases where it says check for C-O, the ir is not very reliable. The nmr 3.3 - 4 δ only applies if a carbon singly bonded to an oxygen has at least one hydrogen. *t*-Butoxy and phenoxy will not give an absorption in this region.
- Alcohols and amines can be difficult to distinguish using ir.
- Esters and ketones can be difficult to distinguish using ir.
- Aromatics are identified in first step. If aromatics make it to this step, there should not be any other functional groups present.
- Alkenes with the C=C stretching frequency between 1640 and 1620 cm^{-1} are probably conjugated.

Whether you use a dispersive ir instrument or a Fourier Transform ir (FTIR), **methods for preparation of samples for the ir** are basically the same. Your goal will be to properly prepare the sample for running the spectrum and the interpretation of the resulting spectrum. As water and glass are essentially opaque in the fundamental region of the infrared, cells cannot be made out of glass and water cannot be used effectively as a solvent.

The best windows for the 4000 - 400 cm^{-1} region are alkali metal halides such as sodium chloride and potassium bromide. This results in another very important reason for avoiding the use of water when running ir spectra; water dissolves the windows. As the NaCl and KBr windows are not inexpensive, **water needs to be strictly avoided**. Also it is best to avoid solvents that contain interfering absorptions and this means that most organic solvents are poor choices for use as solvents for the ir. This experiment will involve determination of the ir spectra of liquids only and the discussion of sample preparation for solids will follow in *Experiment 25*.

For any kind of light spectroscopy, you are probably aware that the absorption of light ($A = -\log T$) is proportional to the product of the path length and the concentration of the compound, $A = \epsilon bc$. In this equation known as Beer's law, ϵ represents the proportionality constant, b the path length and c the concentration of the compound. Generally, when setting up an absorption experiment, an attempt is made to adjust the concentration and path length to give absorptions between about 0.02 and 1.3 or percent transmissions between 95% and 5%. In the ir, absorptions with greater than 95% transmission might go undetected. It is difficult to compare the amount of absorption for peaks with less than 5% transmission as they appear to be full scale. If a couple of drops of liquid are placed on a NaCl window and a second window placed on top, it turns out the thin film of liquid that results has a good $(b) \times (c)$ value for routine ir scans. The use of the neat (pure) liquid also avoids problems associated with the use of a solvent. On the negative side, there is little room for adjusting the path length although slight changes can be made by adjusting how tightly the two windows are held together. Be careful not to make them too tight or the windows can be cracked.

Once an ir spectrum has been obtained, the spectrum should be analyzed for the presence of functional groups. Determine if the compound is an aromatic hydrocarbon, ketone, alcohol or ester. Next, use a reference such as the *Knovel Critical Tables* (see page 10) to narrow down the number of possible unknowns. For the *Knovel Critical Tables*, click the top of the appropriate column to arrange the listing by refractive index, density or boiling point. Using this list coupled with a knowledge of the class of compound from the ir spectrum, it should be possible to select a very few number of possible hits. The next step is to compare all the physical data and your spectrum to literature values and spectra (see *Chemistry Resources* on pages 9 and 10 for online collections of ir spectra). Another option is to enter some of your results into an online site (see page 10) and examine the results to see if any of the hits are consistent with your results.

Fig. 7-7
FTIR



Procedure

You will be given several milliliters of a liquid unknown that will be one of the following:

<u>aromatic hydrocarbons</u>	<u>ketones</u>	<u>alcohols</u>	<u>esters</u>
t-butylbenzene	2-butanone	1-butanol	butyl acetate
ethylbenzene	cyclohexanone	2-butanol	t-butyl acetate
isopropylbenzene	2-heptanone	1-hexanol	ethyl acetate
toluene	3-heptanone	2-hexanol	ethyl butanoate
1,3,5-trimethylbenzene	2-hexanone	2-methyl-1-butanol	ethyl pentanoate
p-xylene	3-hexanone	3-methyl-1-butanol	ethyl propanoate
	3-methyl-2-butanone	2-methyl-2-butanol	isobutyl acetate
	5-methyl-3-heptanone	2-methyl-1-pentanol	isobutyl propanoate
	5-methyl-2-hexanone	4-methyl-2-pentanol	isopropyl acetate
	4-methyl-2-pentanone	1-pentanol	isopropyl butanoate
	2-octanone	2-pentanol	methyl butanoate
	2-pentanone		methyl isobutanoate
	3-pentanone		methyl pentanoate
			propyl propanoate
			propyl acetate

Using the instructions in the *Techniques* section, determine the boiling point, density, refractive index and ir spectrum of your unknown. Use the ir to determine which class of compound (aromatic hydrocarbon, ketone, alcohol or ester) falls in. Then use the ir spectrum coupled with the physical properties and chemical resources to deduce the identity of your compound and if anyone else in your class has the same unknown.

Prelaboratory Preparation - Experiment 7

List all the goals of the experiment.

Observations

Report all relevant observations.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What was the identity of your unknown. Carefully explain the evidence.
3. Who else had the same unknown? Carefully explain the evidence.