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## Experiment #16 – Introduction to IR and NMR Spectroscopy

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**Spectroscopy** studies the light absorbing properties of matter. Since each compound has its unique molecular or ionic structure, its light absorbing properties will also be unique. Spectroscopy is often a quick method to obtain a lot of information about a compound's structure. Sometimes, with sufficient spectroscopic results, the compound's structure can be completely determined.

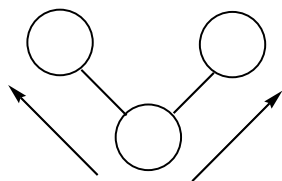
Depending on which region of the electromagnetic spectrum is being used for spectroscopy, the type of information obtained about the compound will vary. For example:

- Visible and ultraviolet spectroscopy: These wavelengths of light cause electrons to be promoted to higher energy orbitals. Thus, information about a molecule's orbitals and bonding can be obtained. You may remember an experiment investigating the visible light emission and absorption of hydrogen, helium, and mercury in your Chem 1A class.
- Microwave spectroscopy: Microwaves cause molecules to rotate. In fact, the microwave oven works by causing the fast rotation of water molecules. This rotational kinetic energy is observed during the heating of the water.
- Infrared spectroscopy (IR): Infrared light causes the bonds in molecules to vibrate.
- Nuclear magnetic resonance (NMR) spectroscopy: NMR spectroscopy uses radiowaves to obtain information about how atoms are connected in compounds.

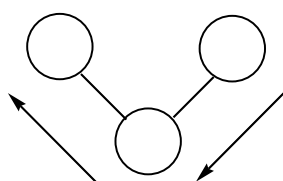
The purpose of this experiment is to use IR and NMR spectroscopy to deduce the structure of a molecule. You will be given a list of possible compounds and structures and you will use the spectra obtained to decide which structure is the correct one while also explaining your reasoning.

The concepts of IR spectroscopy are more straightforward than NMR spectroscopy and they will be discussed first. Fundamentally, each type of bond in a molecule will absorb a characteristic frequency of IR light as it vibrates, and these frequencies can often be used to determine which types of bonds the molecule actually contains. These vibrations fall into several different categories as shown below for a generic three atom system:

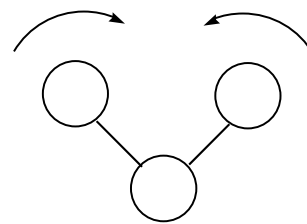
### Modes of Vibration



Symmetric stretching



Antisymmetric stretching



Scissoring

The frequency of light that is absorbed is closely related to the strength of the bonds. An analogy is that of the stretching of a spring. If we imagine each bond as a spring, the frequency of vibration of a spring will be greater if the spring is stiffer. A stiffer spring is equated with a stronger bond; a stronger bond vibrates at a higher frequency.

Planck's equation relates the frequency, wavelength, and energy of light:

$$\Delta E = h\nu = hc/\lambda$$

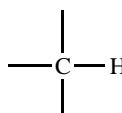
where "h" is Planck's constant ( $6.626 \times 10^{-34}$  J s), "ν" is the frequency of light, "λ" is the wavelength, and "c" is the speed of light ( $3.0 \times 10^8$  m/s). Notice that:

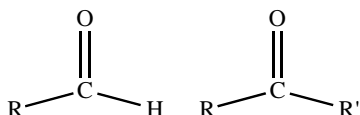
$$\nu = c/\lambda$$

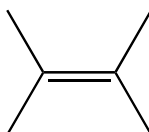
In IR spectroscopy, wavelengths were measured in microns ( $\mu\text{m}$ ) and frequency was measured in  $\text{cm}^{-1}$  (called "wavenumbers"). Your measurements will be made in wavenumbers (note that wavenumbers,  $1/\lambda$  or  $\text{cm}^{-1}$ , and frequency,  $\nu$ , are directly proportional). Some typical frequencies in wavenumbers for the stretching of common types of bonds are given below:

Alcohols RO-H 3200-3650  $\text{cm}^{-1}$

Amines  $\text{R}_2\text{N-H}$  3300-3500  $\text{cm}^{-1}$

Alkanes  2840-3000  $\text{cm}^{-1}$

Carbonyl group in aldehydes and ketones, C=O,  1690-1750  $\text{cm}^{-1}$

Alkenes  1620-1680  $\text{cm}^{-1}$

In general, the symmetric bond stretching frequencies are more clearly shown in the IR spectrum and found in the 4000-1500  $\text{cm}^{-1}$  region. The other types of vibrations, antisymmetric stretches and scissorings, are generally seen in a complex region below 1500  $\text{cm}^{-1}$  called the "fingerprint region." However, since the IR spectrum of each unique molecule should also be unique, the entire spectrum actually serves as a "fingerprint" of the molecule. The spectrum can be used to identify the types of bonds in the molecule, like the examples given above, or, if the spectrum of your compound matches that of a known compound, you can conclude that your compound and the known are the same.

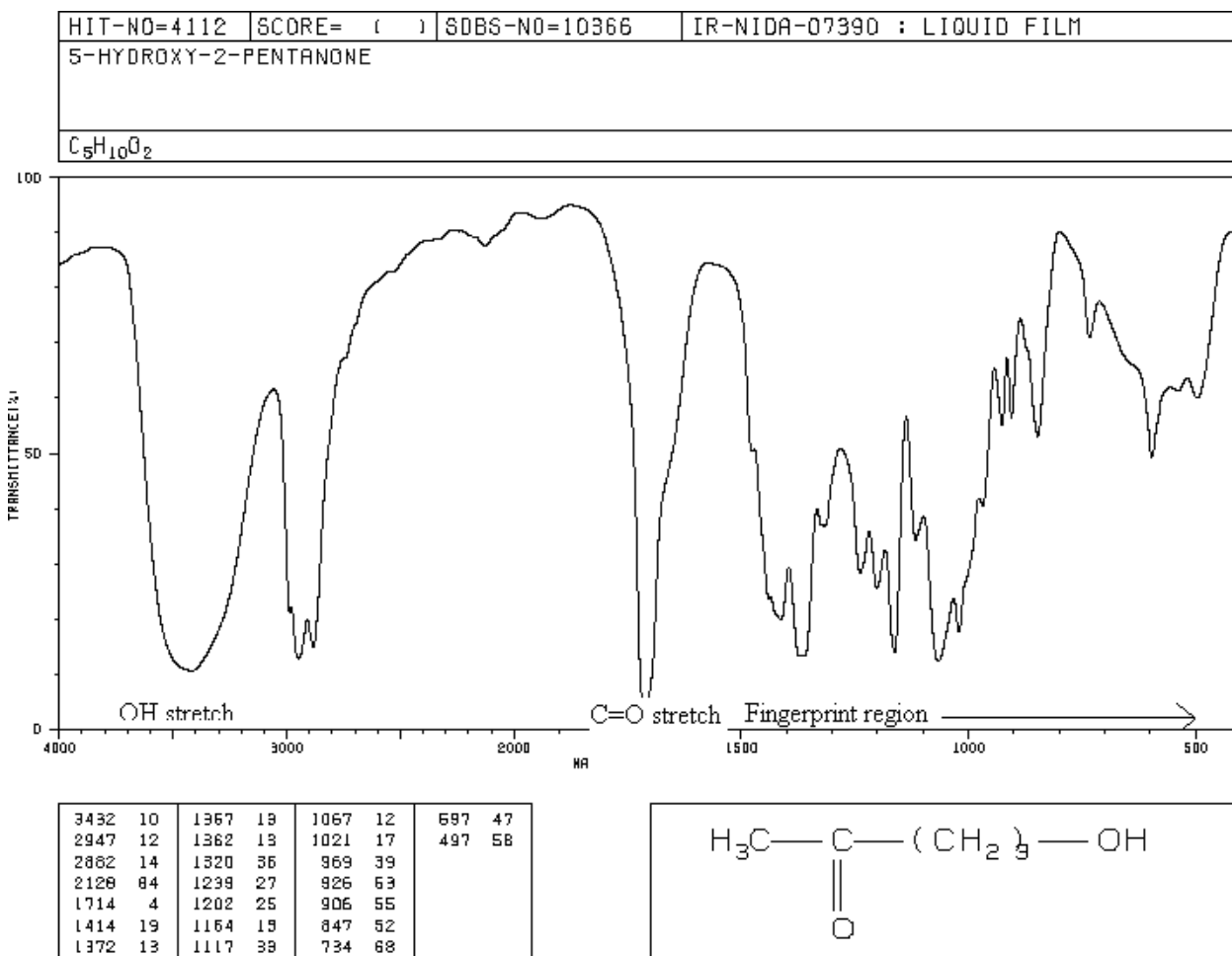
Name: \_\_\_\_\_

Section: \_\_\_\_\_

A website is available which gives thousands of IR and NMR spectra for common compounds. The spectral examples given in this experiment come from that website and its address is:

[https://sdb.sdb.aist.go.jp/sdbs/cgi-bin/cre\\_index.cgi](https://sdb.sdb.aist.go.jp/sdbs/cgi-bin/cre_index.cgi)

Given below is the IR spectrum of the indicated molecule:



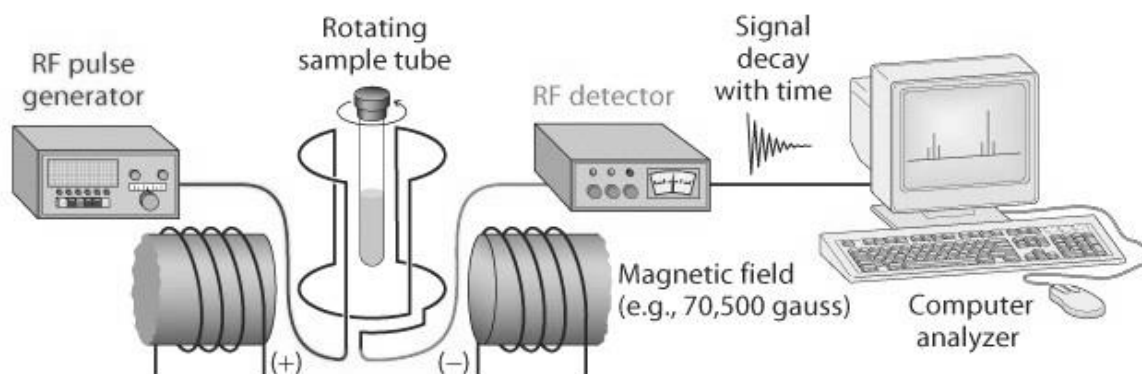
The two most outstanding features of this spectrum are the very broad and strong absorption centered at  $3432\text{ cm}^{-1}$  for the stretch of the O–H bond (the broadness is caused by hydrogen bonding, especially with traces of water) and the carbonyl stretch (C=O), strong and narrow, at  $1714\text{ cm}^{-1}$ . The fingerprint region is shown below  $1500\text{ cm}^{-1}$ .

The compounds that you will be given as unknowns will contain either alcohol bonds, O–H, or carbonyl bonds, C=O, so you should see an absorption similar to one in the spectrum above.

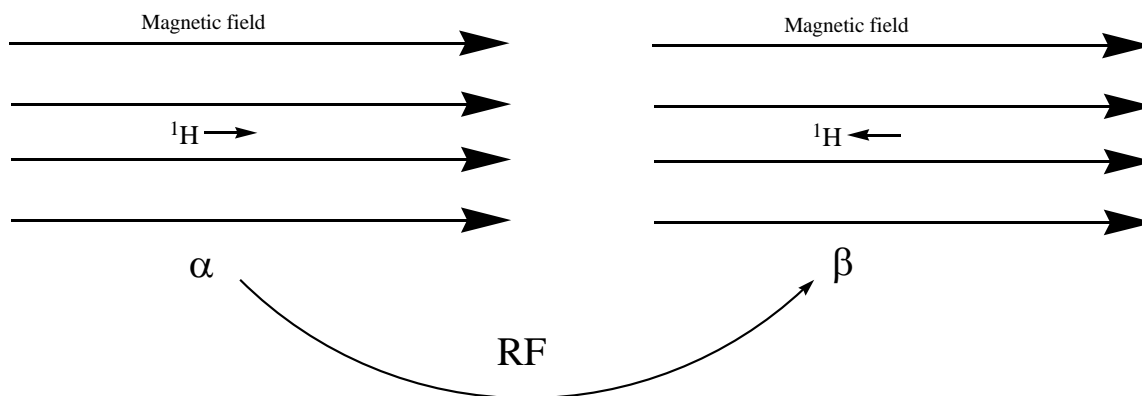
The underlying principles of NMR spectroscopy are much less clear-cut than those of IR spectroscopy. NMR spectroscopy “observes” nuclei that have an overall net spin. The concept of the spin in a nucleus is fundamentally the same as the spin of electrons. Electrons

have spins of  $+\frac{1}{2}$  or  $-\frac{1}{2}$  ( $\uparrow$  or  $\downarrow$ ); protons and neutrons in the nucleus have analogous spins. In each case, spins can be paired or unpaired. Although it is fairly easy to predict the pairing of electrons in an atom, this is not easily done for the pairing of spins in a nucleus. However, any nucleus that has an overall net spin can be observed in an NMR experiment. The most useful nucleus for observation in an NMR experiment is the nucleus of the major isotope of hydrogen,  $^1\text{H}$ , which consists of one proton and, therefore, has a spin of  $\frac{1}{2}$ . It is interesting to note that deuterium,  $^2\text{H}$ , has a spin of 1, i.e., both the proton and neutron in the nucleus contribute spin. Several other important nuclei in NMR spectroscopy are  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  (spins of  $\frac{1}{2}$ ) and  $^{11}\text{B}$  (spin of  $\frac{3}{2}$ ) and  $^{14}\text{N}$  (spin of 1).

The following discussion of the principles of NMR will be given for  $^1\text{H}$ , but a similar explanation can be developed for any nucleus with a spin. A schematic of an NMR spectrometer is shown below (taken from Volhardt and Schore, Organic Chemistry, 4<sup>th</sup> Edition). Pay particular attention to the fact that there is an extremely powerful magnet and a radiofrequency (RF) pulse generator.

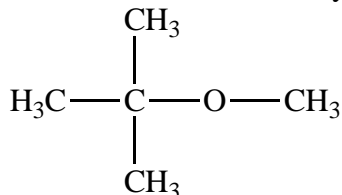


When a compound containing hydrogen is placed in a magnetic field, the spin of the  $^1\text{H}$  nuclei can be aligned parallel to the lines of the magnetic field (lower energy, called  $\alpha$ ) or anti-parallel (higher energy, called  $\beta$ ):

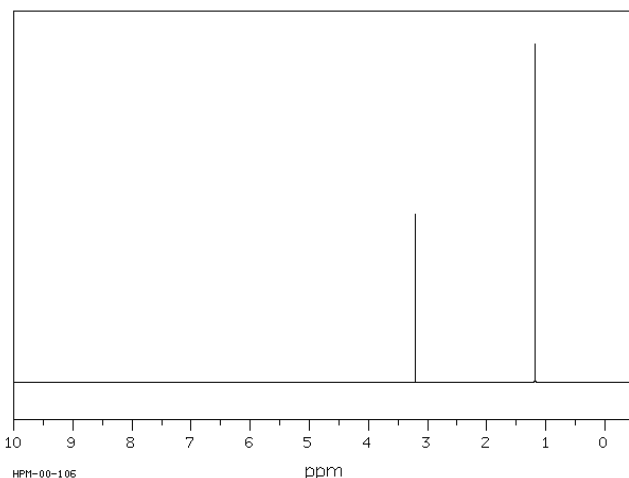


The applied radiofrequency energy from the generator will cause the spins to be promoted to the higher energy state.

Now, consider the fact that a given molecule will generally have several different types of hydrogens in it. For example, consider the molecule methyl t-butyl ether:



There are two types of hydrogen: the three hydrogens bonded to the methyl group ( $\text{CH}_3$ ) attached to the oxygen and the nine H's bonded to the  $\text{CH}_3$  groups attached to the central carbon. These will undergo the  $\alpha \rightarrow \beta$  transition at two different frequencies. In fact, imagine that the molecule is subjected to a pulse of all possible radio frequencies. This causes all  $^1\text{H}$  nuclei to be in the  $\beta$ -state and, once the pulse is ended, they will decay to the  $\alpha$  state and emit their characteristic radio frequencies. These emissions will be picked up by the RF detector. These signals are then manipulated mathematically and plotted, yielding the following NMR spectrum for our compound:



Notice that the scale is labeled “ppm,” commonly called a  $\delta$  (delta) value or “chemical shift.” The zero value on the scale represents the frequency at which a standard compound,  $(\text{CH}_3)_4\text{Si}$  (tetramethylsilane, or TMS), would absorb. This is used as a reference point.

The value of the **chemical shift** ( $\delta$ ) is related to the electron density around the hydrogen atom.  $\delta$ -values are larger if the electron density is lower.

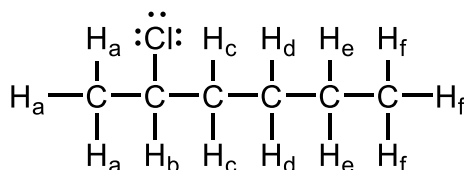
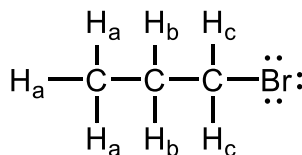
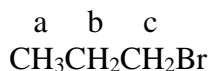
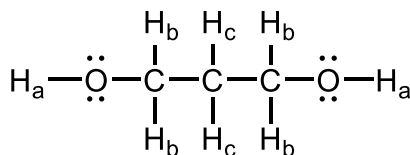
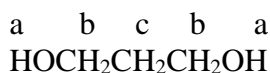
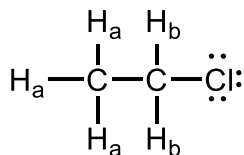
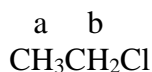
Electronegative atoms or electron withdrawing groups near the carbon to which the hydrogens are bonded will cause a frequency with a higher  $\delta$ -value. In the spectrum above, the peak at 3.4 will correspond to the methyl hydrogens for the group bonded to O.

Some typical chemical shift ranges are shown:

|  |   |
|--|---|
| $\text{RCH}_3$                             | $\delta=0.8-1.0$  |
| $\text{RCH}_2\text{R}'$                    | $\delta=1.2-1.4$  |
| $\text{R}_3\text{CH}$                      | $\delta=1.4-1.7$  |
| $\text{RCH}_2\text{Cl}$                    | $\delta=3.6-3.8$  |
| $\text{RCH}_2\text{OH}$                    | $\delta=3.3-4.0$ (for $\text{CH}_2$ hydrogens, OH hydrogen is often not seen) |
| ROH, if seen,                              | $\delta=0.5$ to $5$ (the large range caused by hydrogen bonding effects)      |
| Ketone, $\text{RCOCH}_3$ ,                 | $\delta=2.1-2.6$  |
| Aldehyde, $\text{RCOH}$ ,                  | $\delta=9.5-10.0$   |
| Aromatic, i.e., H attached to phenyl ring, | $\delta=6.0-9.5$  |

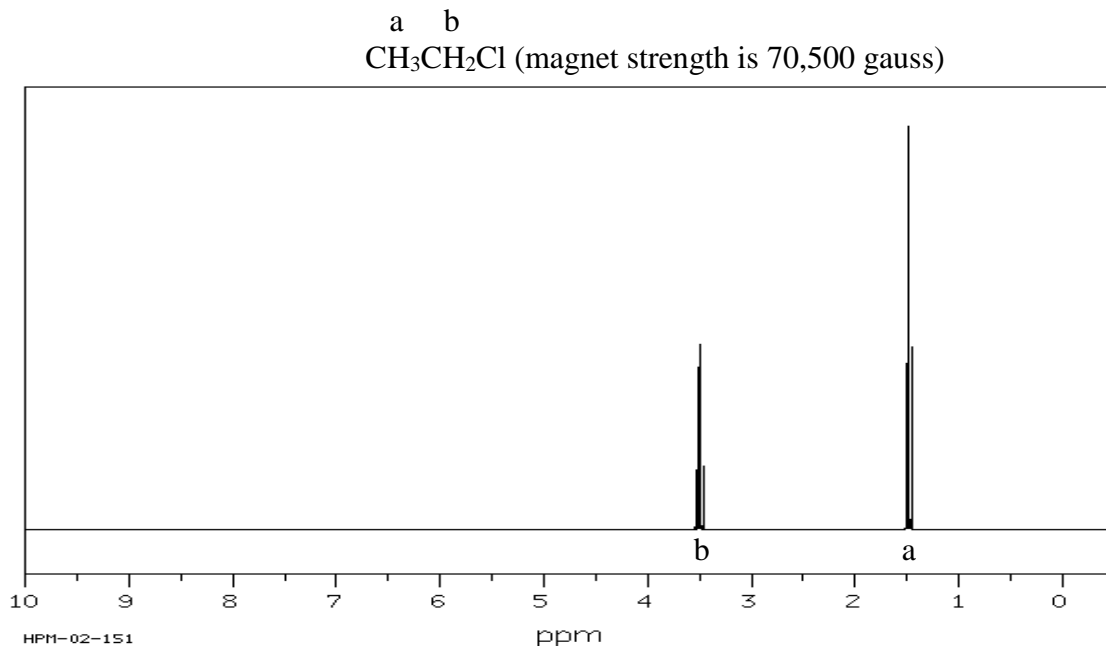
The location in terms of  $\delta$ -values can often give a good idea of what is directly bonded to the carbon on which the observed hydrogen(s) are located.

Although the chemical shift values can give an idea of types of bonds that are present in the molecule—similar to the information obtained in the IR spectrum—even more important is the effect that hydrogens on neighboring atoms will have on the frequencies observed. To see this effect, however, these neighboring hydrogens **must be chemically different**. So, before discussing these effects, you must be able to recognize when hydrogens are the same and when they are different. Four examples are given below, with each unique type of hydrogen labeled with a different letter:

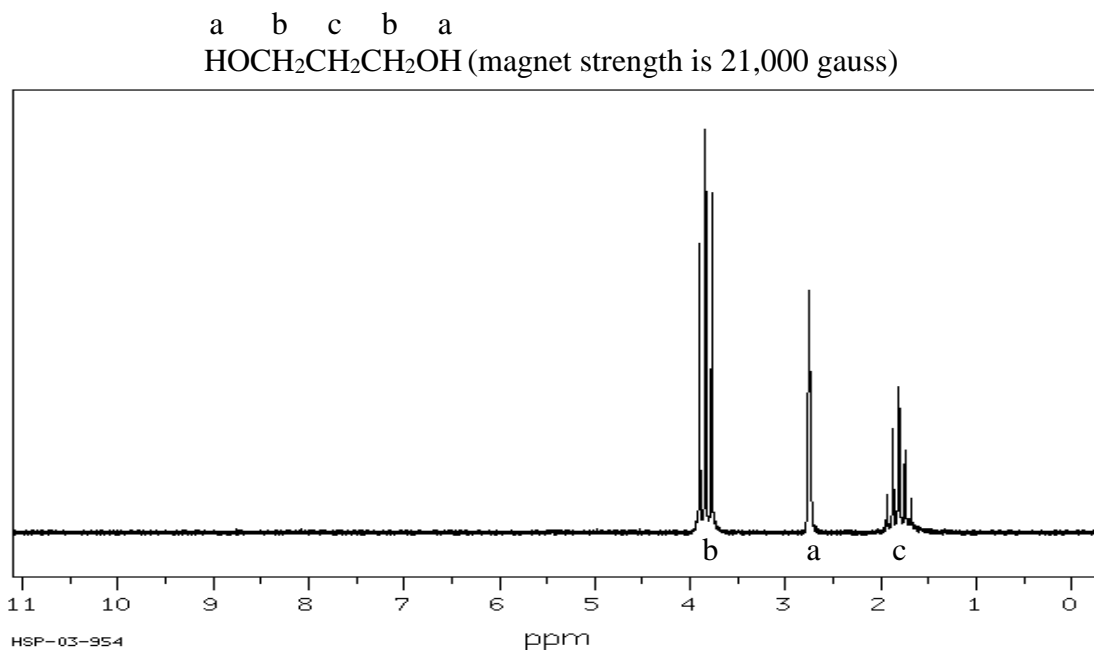


For hydrogens to be the same, they must be in completely equivalent environments. Therefore, in the second example above, the  $\text{CH}_2$ 's are not all the same; the one in the middle is not in the same environment as those labeled at "b" since "b" is immediately adjacent to an OH and "c" is not.

The equivalence or non-equivalence of hydrogens is critical in NMR spectroscopy since the hydrogens on neighboring carbon atoms will split the frequency signal into multiple peaks. If there is one neighboring hydrogen the signal will be split into two peaks, called a doublet; two neighboring hydrogens will split the signal into three peaks, called a triplet; three into a quartet; four into a pentet, etc. These are called, generically, "multiplets." However, the intensities of these split peaks are not equivalent, except for the doublet. A triplet is 1:2:1, a quartet is 1:3:3:1, a pentet is 1:4:6:4:1. If you are familiar with Pascal's triangle, you will see that these intensities follow the triangle's pattern. Some of the corresponding spectra for the compounds follow.



Carefully examine the spectrum above to see the relation of the splitting patterns to the structure of chloroethane. The quartet labeled “b” is caused by the three neighboring hydrogens “a” and the triplet “a” caused by the two neighboring hydrogens labeled “b.”

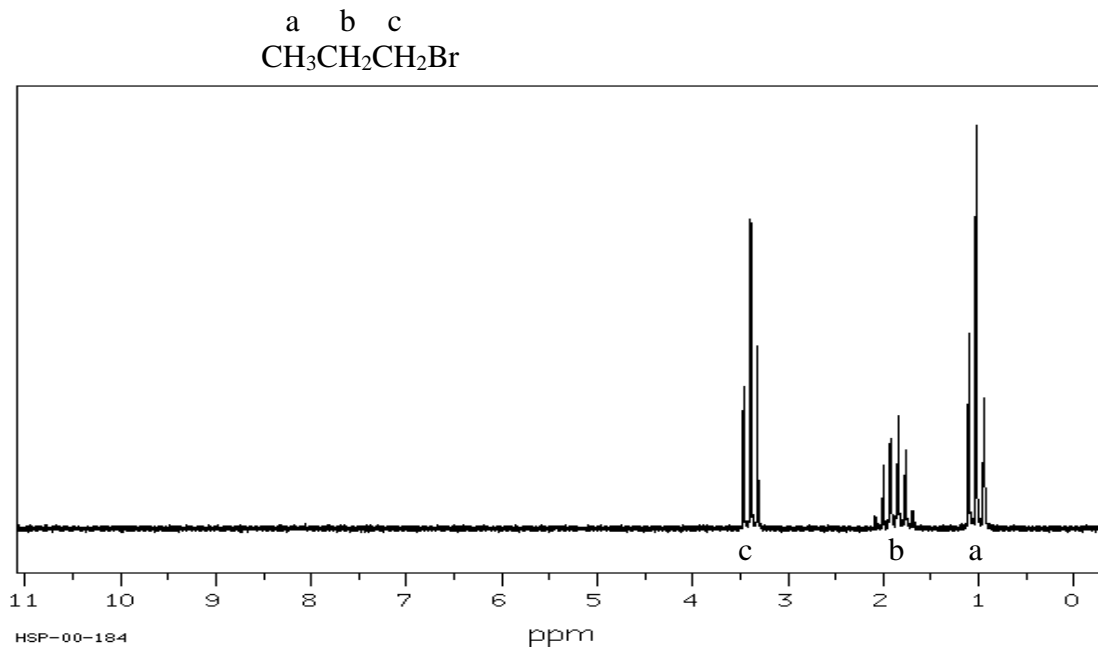


Note that in the spectrum above, the triplet ( $\delta=3.8$ ) is wider than the triplet from the previous spectrum, making it easier to identify the three peaks. This is an effect caused by the lower magnetic field strength. The pentet labeled “c” is caused by the four neighboring hydrogens “b.” Note that the hydrogens labeled “a” form a singlet. As a result of hydrogen bonding, alcohol hydrogens always appear as singlets and do not cause other hydrogens to split.

Name: \_\_\_\_\_

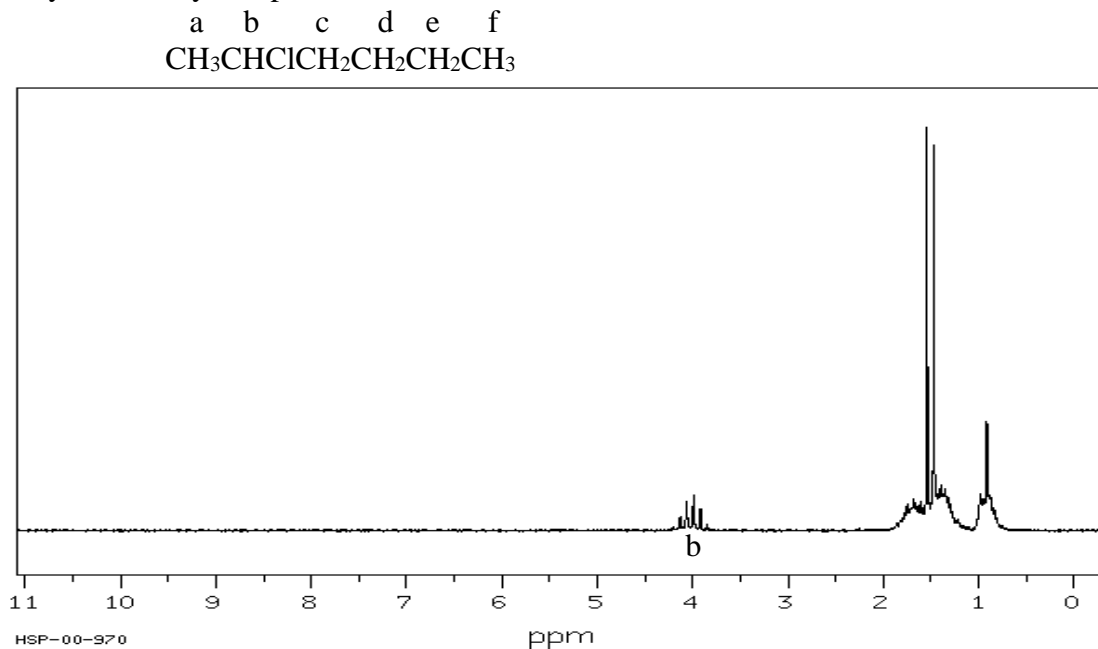
Section: \_\_\_\_\_

Analysis becomes more complex when hydrogens are split by neighboring hydrogens, but the neighbors are non-equivalent. Consider the case shown below:



The hydrogens labeled “b” are split on one side by “a” and then further split by “c,” the overall result being a quartet of triplets or a triplet of quartets, more easily called simply a “multiplet.”

Finally, extremely complex is:



Its interpretation is beyond this experiment, but the hydrogen labeled “b” is found at a value of  $\delta=4$  since there is an electronegative chlorine also attached to the carbon.



Name: \_\_\_\_\_

Section: \_\_\_\_\_

Finally, there are two more issues to discuss concerning the NMR spectra: the area under the signals, called the **integral**, and what **solvents** are used to dissolve samples for analysis.

Each signal in an NMR spectrum represents a certain number of hydrogen atoms. If the area under the entire signal (all of the peaks in a “multiplet”) is measured, this is called the integral and this area is proportional to the number of hydrogens represented by the signal. For example, in the first spectrum above,  $\text{CH}_3\text{CH}_2\text{Cl}$ , the relative integrals would be 2:3 for b:a. The NMR spectrometer will automatically measure the integrals of the signals and list them, but these will not normally be whole numbers. The ratios should be close to the whole number ratios, e.g., you might see 0.386:0.570, close to 2:3, but not exactly equal.

And last of all is the consideration of the solvent. Since NMR solutions are not very concentrated and consist mainly of solvent, any hydrogens in the solvent will give extremely strong NMR signals which may obscure signals from your compound. Fortunately, almost all commonly used solvents can be purchased with deuterium (D) replacing hydrogen and since D is twice the mass of H, the deuterium signal will not appear in your spectrum. For example, deuterated chloroform,  $\text{CDCl}_3$ , is commonly used, a solvent which dissolves most organic compounds and is relatively inexpensive.

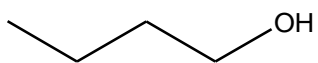
**EXPERIMENTAL PROCEDURE****Paper Unknowns:**

1. Analyze the Paper Unknowns on the next page. Fill in the missing carbon and hydrogen atoms. Identify whether the compound has an alcohol (R–OH) or carbonyl (R–C=O). Label and count the hydrogen atom types starting with “a”, “b”, etc., be aware some hydrogens may have identical neighbors. Predict the expected splitting patterns; singlet, doublet, triplet, quartet, multiplet. Take note of nearby electronegative atoms and expected chemical shifts.
2. Obtain a printout of the IR Spectrum and NMR spectrum of your unknown from your instructor. Analyze the spectrums. Use the list of possible paper unknown compounds and their structures and an analysis of the spectra to decide which compound on the list is your unknown. You will submit a brief analysis which should consist of your choice of the correct compound and a complete explanation of your reasoning involved in coming to that conclusion. This analysis should include interpretation of the splitting patterns in the NMR spectrum, the correspondence of the  $\delta$ -values to the types of hydrogen in the compound, and an interpretation of the IR spectrum, identifying the corresponding absorptions for the functional groups.

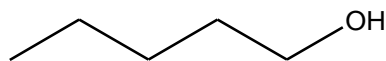
**Liquid Unknowns:**

1. Draw a 3D structural picture for each of the Liquid Unknowns. Identify whether the compound has an alcohol (R–OH) or carbonyl (R–C=O). Label and count the hydrogen atom types starting with “a”, “b”, etc., be aware some hydrogens may have identical neighbors. Predict the expected splitting patterns; singlet, doublet, triplet, quartet, multiplet. Take note of nearby electronegative atoms and expected chemical shifts.
2. Learn how to use the IR instrument in our Organic Chemistry lab room PS 103.
3. Run an experimental IR Spectrum for a drop of your liquid unknown. Clean up after use.
4. Obtain a printed NMR spectrum of that same unknown from your instructor.
5. Analyze the IR and NMR Spectrums. Use the list of possible liquid unknown compounds and their structures and an analysis of the spectra to decide which compound on the list is your unknown. You will submit a brief analysis which should consist of your choice of the correct compound and a complete explanation of your reasoning involved in coming to that conclusion. This analysis should include interpretation of the splitting patterns in the NMR spectrum, the correspondence of the  $\delta$ -values to the types of hydrogen in the compound, and an interpretation of the IR spectrum, identifying the corresponding absorptions for the functional groups.

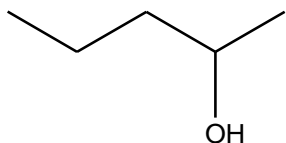
## Part A: Paper Unknowns



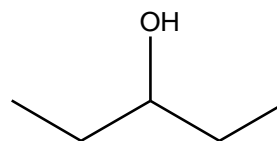
**1-butanol**



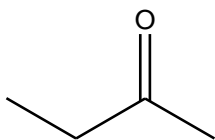
**1-pentanol**



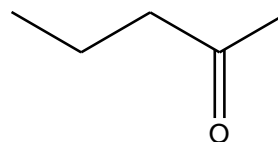
**2-pentanol**



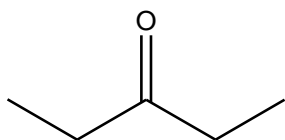
**3-pentanol**



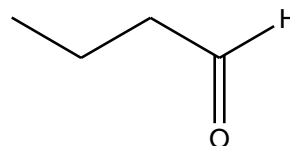
**2-butanone**



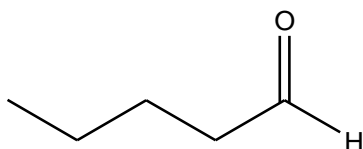
**2-pentanone**



**3-pentanone**



**butanal**



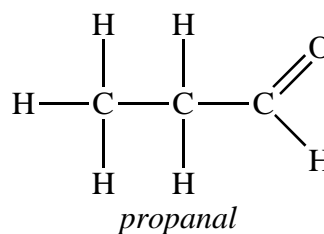
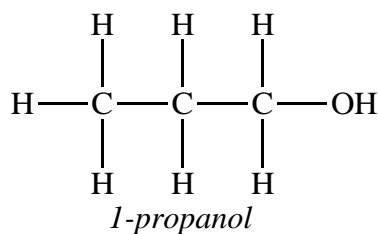
**pentanal**

## Part B Liquid Unknowns

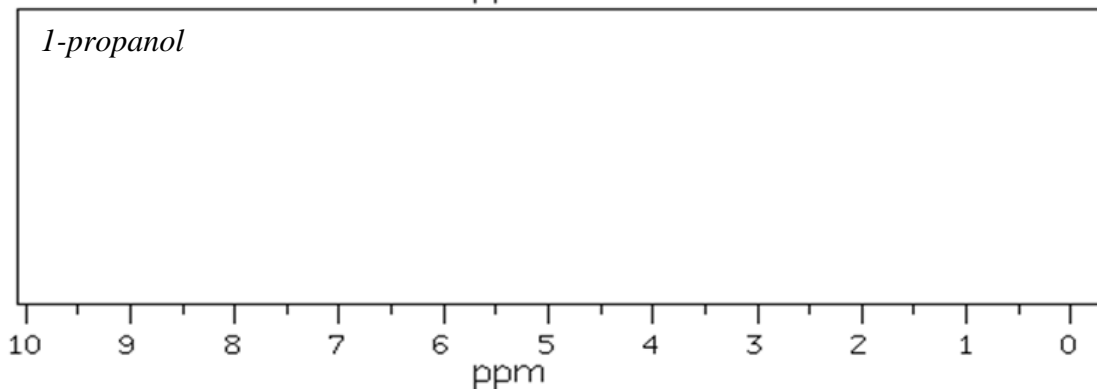
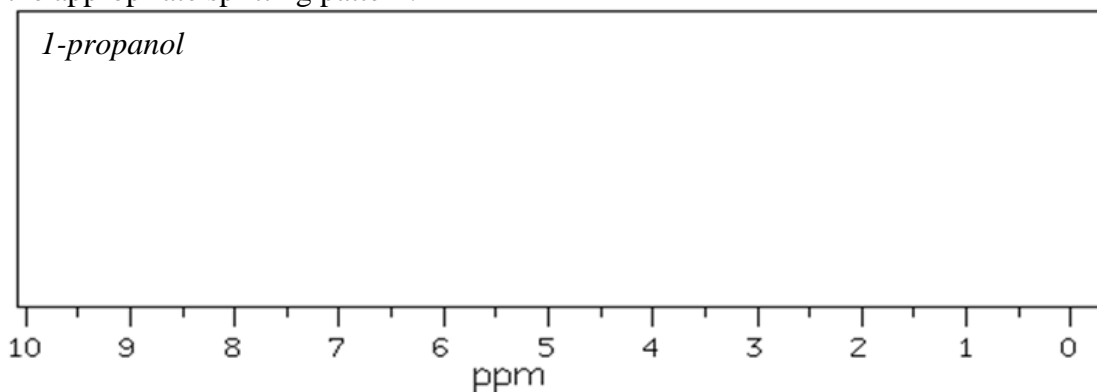
| Name of Solvent                          | Formula     | Draw the 3D structure |
|--|-------------|-----------------------|
| acetone<br>or<br>2-propanone             | $C_3H_6O$   |                       |
| ethyl acetate<br>or<br>ethyl ethanoate   | $C_4H_8O_2$ |                       |
| methanol                                 | $CH_4O$     |                       |
| ethanol                                  | $C_2H_6O$   |                       |
| 1-propanol                               | $C_3H_8O$   |                       |
| 2-propanol<br>or<br>isopropanol          | $C_3H_8O$   |                       |
| methyl acetate<br>or<br>methyl ethanoate | $C_3H_6O_2$ |                       |
| methyl ethyl ketone<br>or<br>2-butanone  | $C_4H_8O$   |                       |

**Post-Lab Questions:** Introduction to IR and NMR

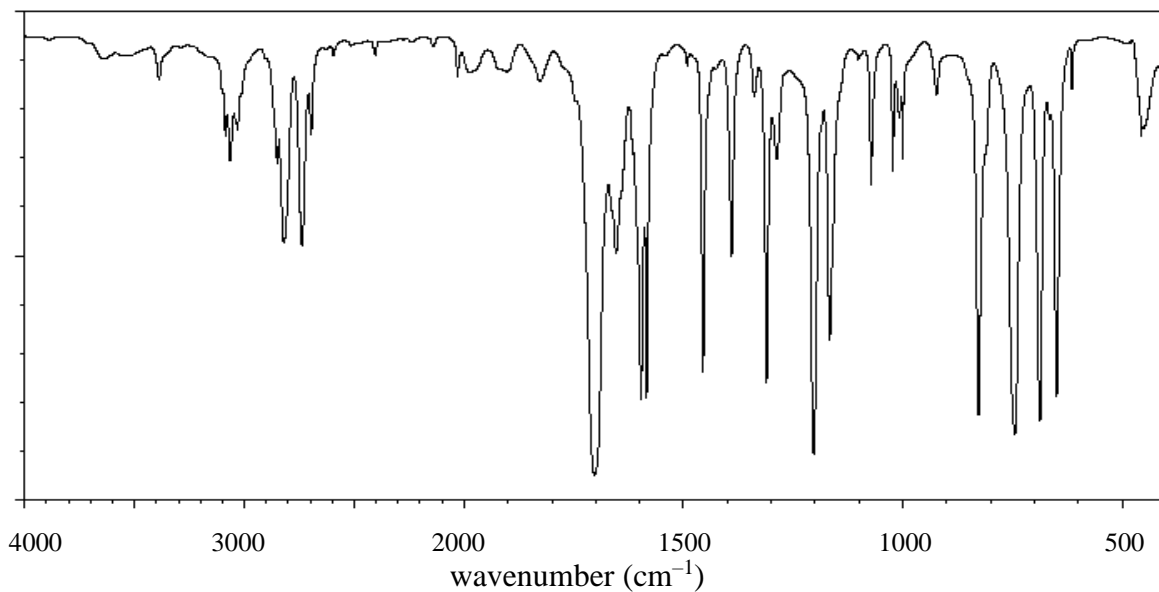
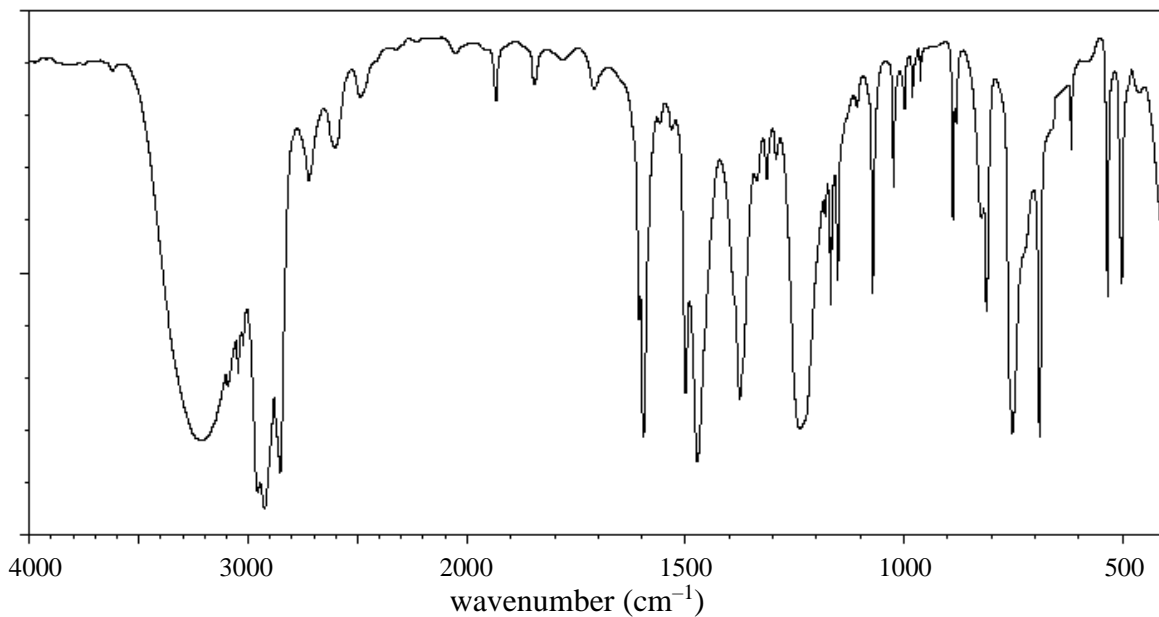
Consider the following two molecules:



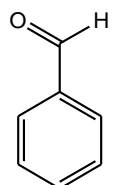
1. What should you see in their infrared spectra that should allow them to be distinguished?
2. Label each of the hydrogen atoms in the molecules above with the letters "a," "b," "c," etc. to indicate all of the different types of hydrogen.
3. For each of the molecules, draw what you would expect the  $^1\text{H}$  NMR spectrum to look like. Label each signal with the letters that you used in question 2 ("a," "b," "c," etc.). Be sure to place the signals in the appropriate chemical shift order and to draw **and label** the appropriate splitting pattern:



4. Consider the two IR spectra shown below. One spectrum is characteristic of benzaldehyde; another spectrum is characteristic of phenol. Which spectrum belongs to which compound? Briefly explain, making sure to identify relevant absorption peaks.

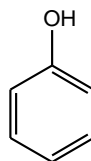


Compound I



benzaldehyde

Compound II



phenol