

Experiment 5
Spectroscopy I: Identification of an Unknown
General Safety Considerations

1. Assume that your unknown liquid is toxic, corrosive and irritating. Wear gloves and goggles continuously while working in the lab today. Though olfactory analysis can be quite a valuable tool when one is identifying an unknown, avoid intentionally inhaling the vapor produced by your unknown. Work with your unknown in the hood. Of course, no flames are allowed in lab.
2. Your unknown can't be flushed down the drain. Consult your instructor/TA before disposing of your liquid.
3. Have your instructor/TA check your set-up before you begin distilling. Do not distill to dryness.
4. Be very careful with the solubility tests using conc. H_2SO_4 and H_3PO_4 . Sometimes a highly exothermic chemical reaction will occur in the test tube. Do these tests in the hood. Point the test tube toward the back of the hood (away from you!).
5. Generally, the acids and bases used in the solubility tests are corrosive. Wear gloves and goggles. Alert your TA should you have a major spill or get any on your skin.
6. Ether is used in the solubility tests. This material is toxic and irritating. It has a very high vapor pressure and is extremely flammable. The fumes from this liquid can cause sleepiness, headaches and nausea. Flames can't be anywhere near ether. Work entirely in the hood. Wear gloves and goggles.
7. If any of the liquid chemicals are spilled on your person, remove clothing in the way and wash the exposed area with cold water for at least fifteen minutes.

Chemistry 211-212

Investigative Experiments

Name

TA Name:

Experiment #

Lab Day:

Unknown #

Section 1 (Pre-lab)	(0 points)
Section 2 (Intro)	(10 points)
Section 3 (E and R)	(68 points)
Section 4 (Disc.)	(72 points)
Section 5 (Post-lab)	(47 points)
Quality of results	(20 points)
References	(13 points)
TOTAL	(220 points)
SCORE	(percent)

This is your report cover. Please fill it out and attach it to your prelab.

Please note that there is a distinction between your keeping of your lab notebook and your lab report. Though you might write your lab report in your notebook, it does not count as keeping your notebook each week.

They are separate and distinct

Please note: This lab is three week lab.

Week One: NMR workshop and run IR

Week Two: All the rest of lab work and work on spectra.

Week Three: work on spectra including GC, work on lab report with group.

First Week NMR Workshop Schedule

Week no. 1

1:00 - 2:00	NMR Lecture - How to Interpret NMR - Room 180
2:00-2:30	Run and interpret the IR of your unknown with your TA
2:30-2:45	Take a break and have a snack
2:45-3:00	Basic NMR Theory
3:00 - 4:30	Interpret a simple NMR with you TA – Room 180 or lab

Week no. 2

All Lockers

1:00 - 1:40	How to solve the unknown, more on NMR interpretation
1:40-5:30	With your group measure the NMR of your unknown (see sign-up sheets), distill your unknown and interpret all assigned spectra. If you have time, work on solving the unknown as a group. Obtain a copy of the Mass Spectrum of your compound and try to figure out molecular weight of your unknown. Note: Alcohols frequently do not give a Mass Ion.

Please note that you will not be allowed to leave lab before you have finished all the required bench work and demonstrated that you can solve NMR spectra. **You must solve at lease three of the assigned spectra before leaving**

ALL LOCKERS

Week no. 3:

All students work on learning how to interpret NMR, IR, MS and work on lab reports.

The following are some readings to help you with interpreting spectra.

Introduction to Infrared Spectroscopy

This Material Must Be Read in Conjunction with the Lab Lecture in Order to Prepare you to solve your Unknown and Assigned Problems.

We will be using IR spectroscopy in many experiments this year. To read more about IR, see your text book.

The major uses we will make of IR are:

- to identify the functional groups present in a molecule
- to confirm that a synthesized or isolated compound is identical to a known compound

Absorption in the IR region of the electromagnetic spectrum arises from the excitation of vibrational modes of chemical bonds. In most cases the energy of the absorbed photon, and thus the frequency of absorbance, can be correlated with specific chemical bonds in the molecule under study. It is this fact that makes IR so useful in identifying the functional groups present in a molecule. In addition to these bond-specific absorbances, an IR spectrum also shows absorbances that are ascribed to the entire molecule. These absorbances are unique to each molecule, and allow us to unambiguously state that two substances are identical if their IR spectra are identical (under identical conditions, of course).

In this brief introduction we will present the practical aspects of how to interpret a spectrum. More theoretical aspects will be covered in the lecture part of this course.

Regions of the IR Spectrum

When approaching an IR spectrum, you should initially focus your attention on six regions of the spectrum that contain absorptions specific to certain types of bonds. These regions are summarized on the next page.

As you study this summary, refer also to the accompanying chart on p. 82 of this manual. In this chart the absorbance ranges that are *diagnostic* of particular bonds have been shaded, while those that are *confirmatory* have been left open. In this context, *diagnostic* means that

- these absorbances are **always present** for a given type of bond
- they are **strong** or **moderate** absorbances, and
- they stand out prominently in the spectrum

Confirmatory means that

- these absorbance are **usually** present for a particular bond
- they may be weak, moderate, or strong, but
- they lie in regions where they are sometimes obscured by other absorbances

Diagnostic IR Absorption Regions

I. $3600 - 3200 \text{ cm}^{-1}$ O-H, N-H strong to medium

There may be two peaks in this region, one from free OH or NH, one from hydrogen-bonded OH or NH.

II. $3000 - 2500 \text{ cm}^{-1}$ Ar-H 3100-3000 weak to medium
COOH (the OH of carboxylic acid) very broad,

usually centered at -3000 cm^{-1}

III. III. $2260 - 2100\text{ cm}^{-1}$ alkyne $-C\equiv C-$ and nitrile $-C\equiv N$ triple bond often weak, but

IV. can be variable.

V. IV. $1750 - 1630\text{ cm}^{-1}$ $C=O$, $C=N$ and $C=C$ weak to strong.

Look for **strong** bands in this region to identify the $C=O$ group. Weak bands in this region can arise from other groups, especially $C=C$ when dipole is weak.

Confirmatory Regions of IR

III. I. $1350 - 1000\text{ cm}^{-1}$ $C-O$ (strong)

C-N (strong to

medium)

This region is usually cluttered with C-H absorbances. Look for strong, distinct bands.

III. II. $1000 - 600\text{ cm}^{-1}$.

Mainly, this region contains the bending vibrations of arenes and alkene C-H bonds, depending on the pattern observed some conclusions (slightly unreliable) can be made about substitution patterns on arenes and alkenes.

We will not be using this much in the first semester. If you wish to explore this, please look at the tables in your text book.

A functional group is almost never identified by a single absorption band. In almost every case we have available *confirming* bands, which are shown on the chart (next page) by the unshaded areas. It is necessary to use confirming bands because in nearly every region of the spectrum there are two or more functional groups that will show absorption. The preceding summary will provide the beginner with a useful starting point.

NMR Slides

The following slides may be used in class to explain NMR theory. If you click on the page number you will link to the webpage that has this teaching tool. It is a good idea to print them (the actual slides) so that you can use them in either lecture or lab. They may or may not be used in lab, but they will be used in lecture this fall.

[Page 1](#)

[Page 2](#)

[Page 3](#)

[Page 4](#)

[Page 5](#)

[Page 6](#)

[Page 7](#)

[Page 8](#)

[Page 9](#)

[Page 10](#)

[Page 11](#)

[Page 12](#)

[Page 13](#)

[Page 14](#)

[Study Aids](#)

The Basics Nuclear Magnetic Resonance Spectroscopy

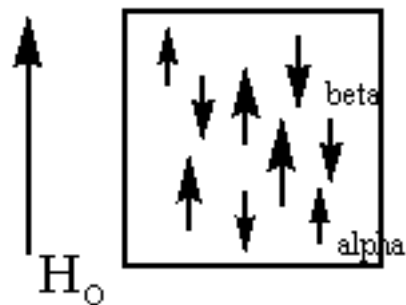
This is a prelab reading and should be completed in conjunction with lecture and to help you solve your NMR problems.

By [Maryellen Nerz-Stormes](#)
[\[Back to Study Aids\]](#)

Nuclei possessing angular momentum (also called spin) have an associated magnetic moment. A few examples of magnetic isotopes are ^{13}C , ^1H , ^{19}F , ^{14}N , ^{17}O , ^{31}P , and ^{33}S . Please note that not every isotope is magnetic. In particular, you should note that ^{12}C is not magnetic. If a nucleus is not magnetic, it can't be studied by nuclear magnetic resonance spectroscopy. For the purposes of this course, we will be most interested in ^1H and ^{13}C . I will limit my discussions to ^1H in this short treatment. Generally speaking, you should think of these special nuclei as tiny, atomic, bar magnets.

Nuclear Magnetic Spectroscopy is based on the fact that when

a population of magnetic nuclei is placed in an external magnetic field, the nuclei become aligned in a predictable and finite number of orientations. For ^1H there are two orientations. In one orientation the protons are aligned with the external magnetic field (north pole of the nucleus aligned with the south pole of the magnet and south pole of the nucleus with the north pole of the magnet) and in the other where the nuclei are aligned against the field (north with north, south with south). The alignment with the field is also called the "alpha" orientation and the alignment against the field is called the "beta" orientation. From my description of the poles, which orientation do you think is the preferred or lower in energy? If you guessed the "alpha", you are correct. It might be worth noting at this point that before the nuclei are placed in the magnetic field they have random orientation



random orientation
outside of field

alpha and beta
orientation in field

Since the alpha orientation is preferred, more of the population of nuclei are aligned with the field than against the field. You might wonder why any spins would align against the field. Realize that we are talking about atomic magnets. These are very, very weak magnets. The energy difference between the alpha and beta orientations is not large. There is enough energy for nuclei to exchange between the two orientations at room temperature, though a slight excess on average is in the lower energy, alpha state.

The nuclear magnetic resonance (NMR) spectroscopy experiment involves using energy in the form of electromagnetic radiation to pump the excess alpha oriented nuclei into the beta state. When the energy is removed, the energized nuclei relax back to the alpha state. The fluctuation of the magnetic field associated with this relaxation process is called resonance and this resonance can be detected and converted into the peaks we see in an NMR spectrum.

What sort of electromagnetic radiation is appropriate for the low energy transition involved in NMR? Well believe it or not, radio waves do the trick. Radio waves are at the very low energy end of the electromagnetic spectrum and are sufficient to induce the desired transition. It is for this reason that NMR is considered to

be a safe method of analysis. The same technology is now used in hospitals in MRI (Magnetic Resonance Imaging - people are afraid of the word nuclear). If you have ever had an MRI done, realize that you were placed in a magnetic field and all your magnetic nuclei lined up in the manner described above. Excess nuclei were pumped to higher energy states as you were exposed to radio waves.

The following are two very, very important points to accept and learn if you are going to understand the rest of the discussion.

- 1. Electric currents have associated magnetic fields.**
- 2. Magnetic fields can generate electric currents.**

If you haven't had physics yet, try to accept these two points. Certainly most people have at least heard of electromagnets and if so, you probably have some idea about the first statement.

The following is a very important NMR relationship. This expression relates the external field to the frequency of resonance.

$$\nu = \mu H_0 / 2\pi$$

In this equation, ν is frequency, μ is the magnetogyric ratio (not needed for this discussion - a constant for each nucleus). The big thing to glean from this equation is that the external field and the frequency are directly proportional. If the external field is larger, the frequency needed to induce the alpha to beta transition is larger. It follows then that in a larger field, higher frequency radio waves would be needed to induce the transition.

In this context, it is relevant to note that different nuclear magnetic resonance spectrometers have different magnetic field strengths. For example, the NMR on the first floor of Park Hall has a relatively high field, superconducting magnet. Because the field is high (high enough to erase bank cards and interfere with pacemakers and watches), the frequency range needed to excite protons is relatively high. It is called a 300 MHz (MHz = megahertz, a hertz is a cycle per second - a frequency unit) spectrometer, referring to the excitation frequency. The NMR on the second floor of Park Hall has a much weaker electromagnet associated with it. It is a 60 MHz instrument. Since different NMRs have different operating frequencies, spectra cannot be compared from different machines if they are reported in frequency units. For this

reason, the universal ppm (parts per million) units are used in NMR. **Please note the following relationship between ppm and frequency. The fact that frequency and ppm are directly proportional is all you need to retain for the future discussion and the course in general.**

$$\text{Chemical shift in ppm} = \frac{\text{peak position in Hz (relative to TMS)}}{\text{spectrometer frequency in MHz}}$$

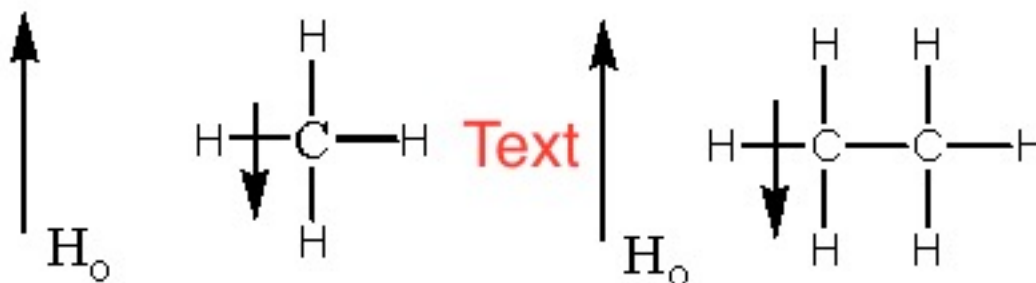
Now let us use these basic ideas to better understand and interpret NMR spectra.

1. Why do we see peaks? When the excited nuclei in the beta orientation start to relax back down to the alpha orientation, a fluctuating magnetic field is created. This fluctuating field generates a current in a receiver coil that is around the sample. The current is electronically converted into a peak. It is the relaxation that actually gives the peak not the excitation.

2. Why do we see peaks at different positions? Realize that in principle, a peak will be observed for every magnetically distinct nucleus in a molecule. This happens because nuclei that are not in identical structural situations do not experience the external magnetic field to the same extent. The nuclei are

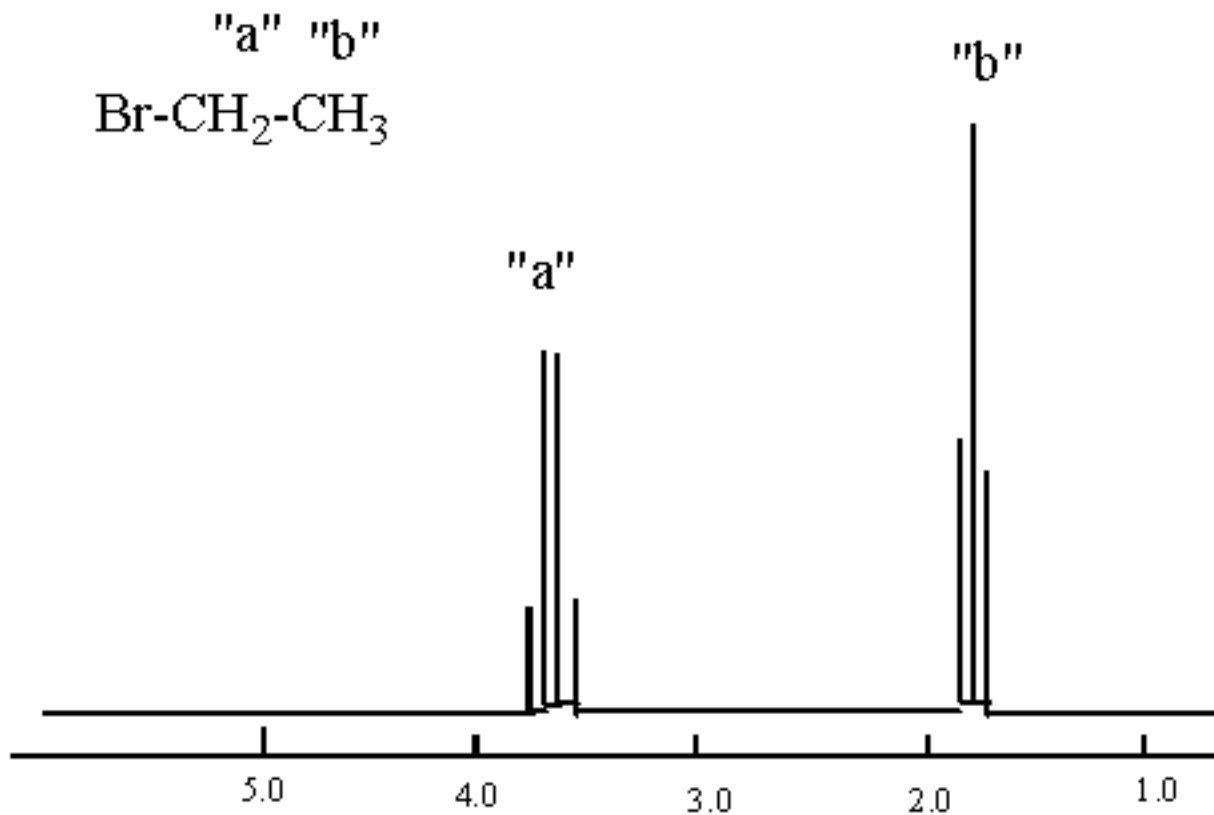
shielded or deshielded due to small local fields generated by circulating sigma, pi and lone pair electrons.

To understand this concept better, consider a "run of the mill" hydrogen like that in ethane or methane. When this sort of hydrogen is placed in a magnetic field, the sigma electrons start to circulate. **Remember : Magnetic fields generate currents.** When the electrons circulate, they generate a small magnetic field that happens to point in the opposite direction to the external field. **Remember: Currents have associated magnetic fields.** Since magnetism is a vector quantity (vector quantities have direction and magnitude), this local field reduces the overall field somewhat. Therefore, the described hydrogen experiences a reduced magnetic field. If we reconsider the important NMR equation given on page two of this document, we can only conclude that if the external field is lower then the frequency of the electromagnetic radiation needed to induce the alpha to beta transition must be lower. **Remember that frequency and ppm are directly proportional.** Therefore, if a hydrogen requires a lower frequency, then it will show up as a peak at a lower ppm value. Hydrogens like those in methane are at around 1.0 ppm in the NMR spectrum.



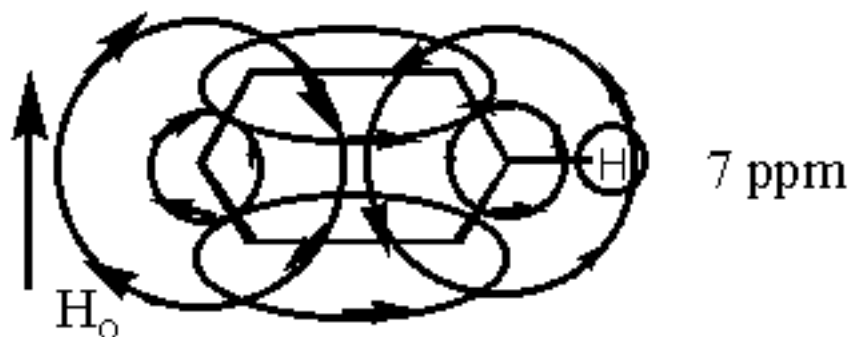
Now consider a hydrogen near a halogen as in bromoethane. This type of hydrogen is in a magnetically altered situation as compared to the hydrogen in methane. Due to its inherent electronegativity, the halogen atom has the effect of pulling sigma electron density away from the hydrogens in the molecule. The effect is largest for the hydrogens closest to the halogen atom. Though the little local opposing sigma field is still generated next to the hydrogens, it is partially pulled away by the electronegative bromine. Therefore, the hydrogens experience less of the local field and more of the external field. In other words, the vector in the vicinity of the hydrogen has been reduced as compared to methane. After you do the vector addition you end up with a larger overall field (again, as compared to methane). So going back to the fact that field and frequency are directly proportional, hydrogens near an

electronegative atom should require a higher frequency to flip from the alpha to beta orientation. Therefore, they should appear at a higher ppm in the spectrum. Hydrogens like those in bromoethane should appear from ca. 2.5-4.0 ppm in the NMR spectrum.



1H NMR Spectrum of Bromoethane

Now as a last example, let us consider the NMR spectrum of benzene. Benzene and aromatics in general are very interesting because their hydrogens appear around 7 ppm even though they have no electronegative atoms. Why is this so? It has to do with the pi electrons. Because benzene and its relatives are aromatic, the p orbitals at each carbon in the ring overlap forming one continuous pi system. When the benzene ring is placed in a magnetic field, the external field induces a current in the pi system and that current generates a secondary magnetic field (or induced magnetic field). Once again, **remember that electric currents have associated magnetic fields and that magnetic fields generate currents.** The secondary magnetic field is such that it adds to the external field in the vicinity of the aromatic hydrogens as diagrammed below.

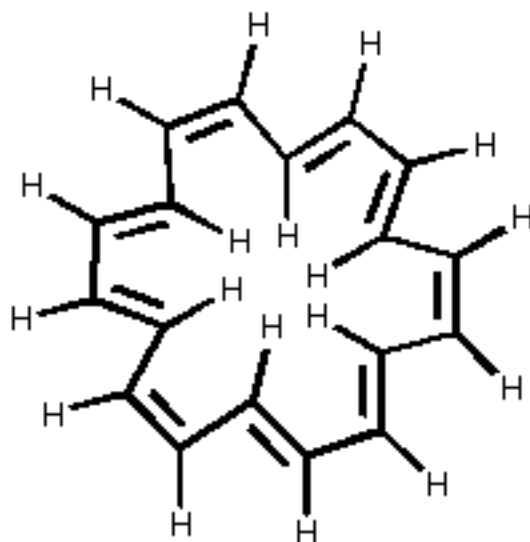


Benzene

If the local field is in the same direction as the external field, the resulting field is larger than the external field. This means that the frequency needed to flip those hydrogens experiencing that field is larger. Larger frequency translates into higher ppm position.

It is really interesting to consider 18-annulene diagrammed below. 18-Annulene is a large enough ring to have both cis and trans double bonds. This means that some of the hydrogens are pointing in toward the center of the aromatic ring. Reconsider the diagram of benzene above. If you look at it carefully, you will see that the magnetic field opposes the external field on the inside of the ring!!! If 18-annulene is aromatic like benzene, the inner hydrogens should absorb at lower frequency (ppm) and guess what? They do - they appear

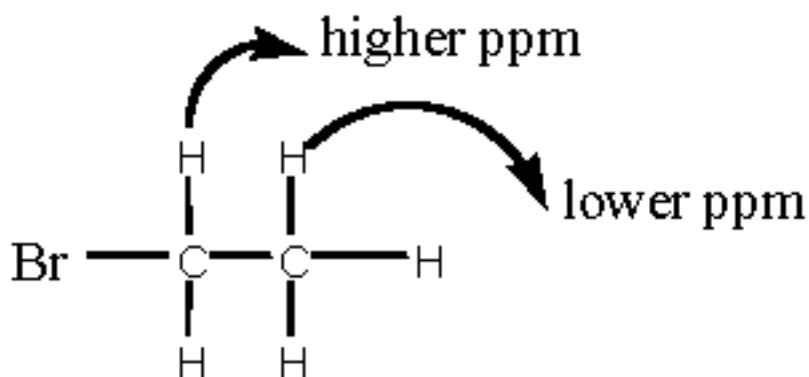
at -1.7 ppm!! Isn't that neat!!



So summing up, the different hydrogens of a molecule appear at different positions because small local magnetic fields are generated when local electrons begin to circulate due to the effect of the external magnetic field. These small fields either add to or subtract from the external field altering the frequency needed for excitation. Some of the effects are due to the circulation of sigma electrons while others are due to the circulation of pi electrons. The pi effects can be the most dramatic as was demonstrated in the preceding examples.

3. What causes splitting?

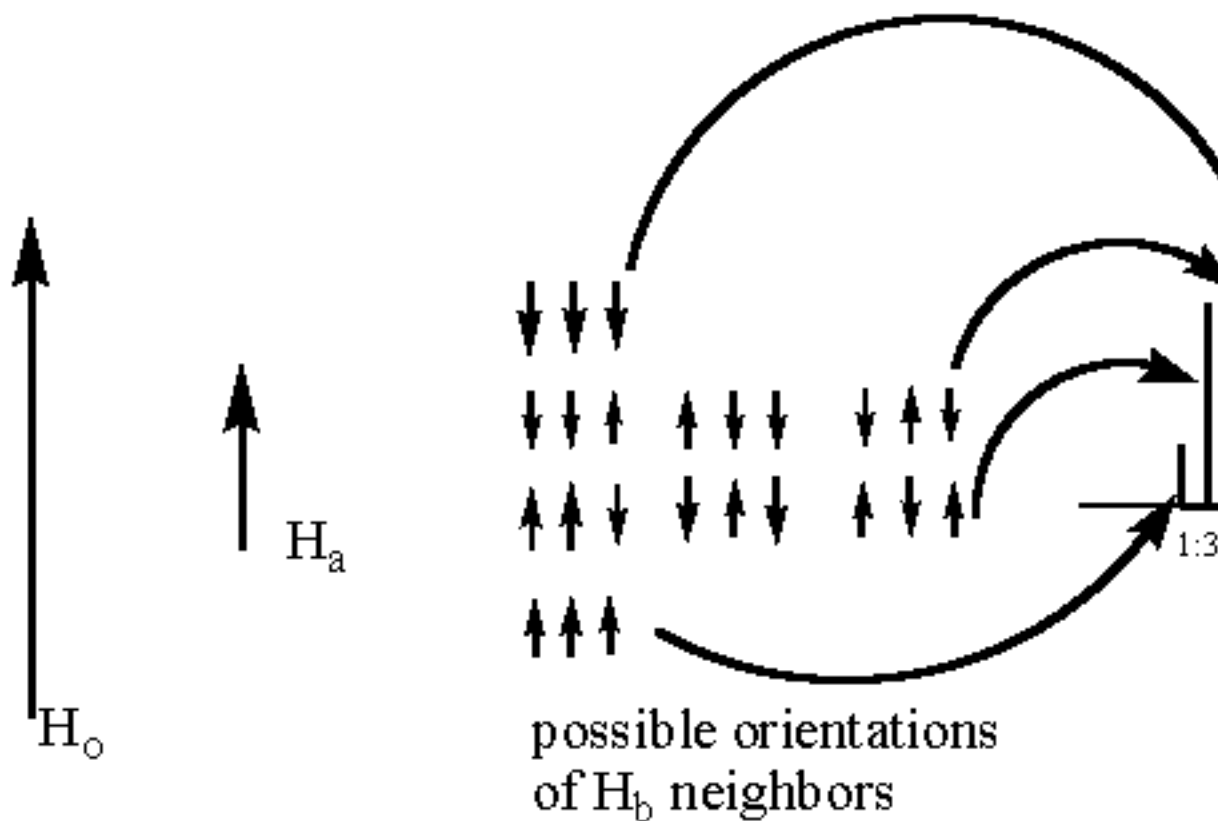
Many peaks in NMR spectra appear as symmetric patterns called doublets, triplets, quartets, quintets, etc. When you see these patterns it tells you about the number of adjacent (usually on the carbon next door to that bearing the absorbing hydrogen(s)), but different hydrogens. In simple spectra such as those we will be studying in organic chemistry lab, the number of peaks you see is one more than the number of adjacent, but different hydrogens. This is the so called **n+1 rule**. Different means that the adjacent hydrogens have a unique magnetic environment and absorb at a distinct frequency compared with the hydrogens in question. For example, consider bromoethane (structure given below).



Bromoethane has two different types of hydrogens so we expect two absorptions in the NMR spectrum. One absorption corresponds to the two hydrogens that are closest to the halogen atom. The other to the hydrogens comprising the methyl group that is farther away. Based on what I described above with regard to chemical shift (the ppm value), the hydrogens nearer the bromine should be at a higher ppm position. The hydrogens further from the bromine should be at lower ppm position.

Anyway, getting back the splitting, the hydrogens closer to the bromine will appear as a quartet because they are near three different hydrogens (the hydrogens on the methyl group). Those adjacent hydrogens are communicating their presence to the hydrogens being flipped. They are saying, "We are your neighbors and there are three of us." The reason they are able to communicate their presence is that they are little magnets

and as such, they either add to or subtract from the external magnetic field depending on their orientation. Since there are many protons in a sample, the following are the possibilities for the neighboring hydrogens during excitation:



Please note that in the above diagram the "a" hydrogens are the ones near the bromine being flipped from the alpha to beta orientation. The "b" hydrogens are the three neighbors. As

shown above, it is possible that a given "a" hydrogen will have three "b" hydrogens nearby that are aligned with the applied field during excitation. It is also possible that the three neighbors could all be aligned against the applied field. More probable is that either two protons will be aligned against the field or two with the field. These situations are more probable because there are more combinations of the three nuclei that give rise to these two possibilities. Since there are three combinations of each of these two, they are each three times more probable than having all three adjacent nuclei aligned with or against the field.

Now let us think about what these neighboring, local magnets do to the overall field. The "a" hydrogens that have all three neighbors aligned against the field have a lower overall magnetic field. Going back to the fundamental nuclear magnetic resonance equation (see page 2), you would conclude that these "a" hydrogens would have a lower frequency requirement for the alpha to beta transition and therefore appear at lower ppm. For the "a" hydrogens having three neighbors with all three "b" hydrogens aligned with the external field, the cumulative local field adds to the external field. This resultant field is larger than the external field so higher frequency electromagnetic radiation is needed to induce the alpha to beta transition. For the "b" hydrogens near two nuclei aligned with the field and one nucleus aligned against the field there is a

slight increase in overall field leading to slightly higher frequency requirements. Similarly, two spins aligned against and one aligned with the field leads to slightly lower frequency requirements. So in the end, the "a" population is divided into four groups appearing at slightly different frequencies. The intermediate frequency peaks are taller than the higher and lower frequency peaks because they reflect more probable situations for local hydrogens. Hence, a quartet is observed.

Now if you understand why the "a" hydrogens give a quartet can you figure out why the "b" hydrogens give a triplet? Try to work it out using vectors as done in the above diagram.

For simple systems like bromoethane, $n + 1$ peaks will be observed for a given absorption, where n = the number of neighboring, but different hydrogens. This formula can be very useful when interpreting simple spectra.

The Interpretation of Simple NMR Spectra

This year, we will abstract the following information from NMR spectra to determine structures of products from organic reactions and isolations.

1. The number of peaks. The number of peaks is directly related to symmetry. If a compound has three significantly different types of hydrogens, it should have three different NMR absorptions.

2. The area under each absorption (the integral). The relative areas (or integrals) of the various absorptions in an NMR spectrum equals the relative number of hydrogens absorbing. If we know the molecular formula of a compound, we can use this ratio to figure out the actual number of each type of hydrogen. From the numbers of each type, we can infer the carbon structure. For example, with bromoethane, the relative areas under the NMR peaks are 2:3. This tells us that there is a group of two hydrogens that are the same and another group of three hydrogens that are the same. With your current knowledge of organic chemistry, it seems most likely that the compound has a methyl ($-\text{CH}_3$) and a methylene ($-\text{CH}_2-$) group. In other words, the most probable way to have three identical hydrogens is on a methyl group. The most probable way to have two

identical hydrogens is in a methylene group.

Suppose you have a compound with the formula $C_5H_{12}O$ and you are told that there are two NMR peaks, having the relative areas of 1:3. Can you come up with the structure of the compound?

3. The splitting pattern. For this semester, we will be using the $n+1$ rule as it applies to the simple structures we will be determining. You will see one more peak than the number of adjacent, but different hydrogens. Therefore, you can look at any peak and automatically know how many neighbors there are. This is crucial information because it allows you to start to hook atoms together in your structure. The problem is that people often confuse integral with splitting. So you must always remember this saying "**Integral tells you what is here and splitting tells you what is near**" This means that the integral tells you about the absorbing hydrogens and the splitting tells you about the neighbors. So what does it mean if you see a quintet with an area of two in a spectrum?

4. The position of the peak or the chemical shift (). This tells you about the electronic environment (the electronic environment directly relates to the magnetic environment) of the absorbing hydrogens. It will tell you if there are pi bonds or electronegative atoms nearby, etc. There are nice tables

available that organize how different groups effect the frequency of absorptions and in lab you will always have these tables available to you. Yes, you will even have them on exams. A good rule of thumb when you are solving spectra is that the closer a hydrogen is to an electronegative atom the higher the ppm position. This little rule only works if the hydrogen is two or more bonds away from the atom. You will soon see the utility of this when you begin your problems in the workshop. It is also useful to keep in your head that aromatic hydrogens absorb at around 7 ppm.

A few tricks of the trade that are generally useful for spectral problem solving.....

1. Always calculate the index of hydrogen deficiency or unsaturation number at the beginning of a problem (you will normally be given the formula of the compound). Determining the unsaturation number is very helpful in regard to knowing which structural elements need to be present in your final solution. The unsaturation number is where you compare the actual formula with the theoretical saturated formula and compute the number of pairs of hydrogens that are missing. This topic should have been covered in class by now.
2. It is a good idea to interpret your IR spectrum before you do the NMR spectrum so that you have an idea about which

functional groups are present in your molecule.

3. Organize your ideas about the structure of the unknown as you go along. For some people it is helpful to set up the following table for the NMR data and conclusions. The important part of the table is the conclusion column in which you are drawing a structural conclusion about the absorbing hydrogens and their neighbors. You should write a structural fragment down as has been done below for bromoethane.

ppm	integral	splitting	conclusion
1.6	3	triplet	$\text{CH}_3\text{CH}_2\text{-}$
3.4	2	quartet	$\text{-CH}_2\text{CH}_3$ near electronegative atom

4. You will notice as we do problems in class that we tend to emphasize and draw the most information from the integral and splitting. Chemical shift (ppm position) in many cases is the last point of interest. There are a few relevant chemical shifts that should be interpreted at the outset of a problem.. One is the aromatic chemical shift. Aromatic hydrogens absorb at ca. 7 ppm. This is a very distinct and characteristic shift and should be interpreted immediately. If you observe a peak at seven chances are you have an aromatic ring. The most common aromatic ring is benzene. Another very distinctive shift is that of the aldehyde functional group. Aldehydic hydrogens appear at

ca. 9 ppm in the spectrum. if you see a shift of nine ppm assume that you have an aldehyde functional group.

5. Solving spectra rapidly involves making good educated guesses. If you get an integral of three there is really only one probable way to have three identical hydrogens - a methyl group. If you get an integral of nine it is most likely three methyl groups that are the same by symmetry. If you get aromatic absorptions, you probably have one or more benzene rings. Always start with the simplest ideas and work your way toward more exotic solutions.

If you want to discuss any of this please feel free to stop by.

[\[Back to Study Aids\]](#)

Mass Spectroscopy: Basic theory and Interpretation

Solubility Tests: How to Carry Them Out and What They Tell You About Structure

Solubility

Solubility classification groups compounds on the basis of their solubilities in water, ether, 5% NaHCO₃, 5% NaOH, 5% HCl and concentrated H₂SO₄. The results of the solubility tests can help classify molecules into categories of functional group. The following flow chart and procedure will help you determine the solubility of your unknown compounds. Realize that while the NMR is the gold standard for structure determination, solubility is probably one of the less useful methods, given the error in the method and the less than objective nature of the observation.

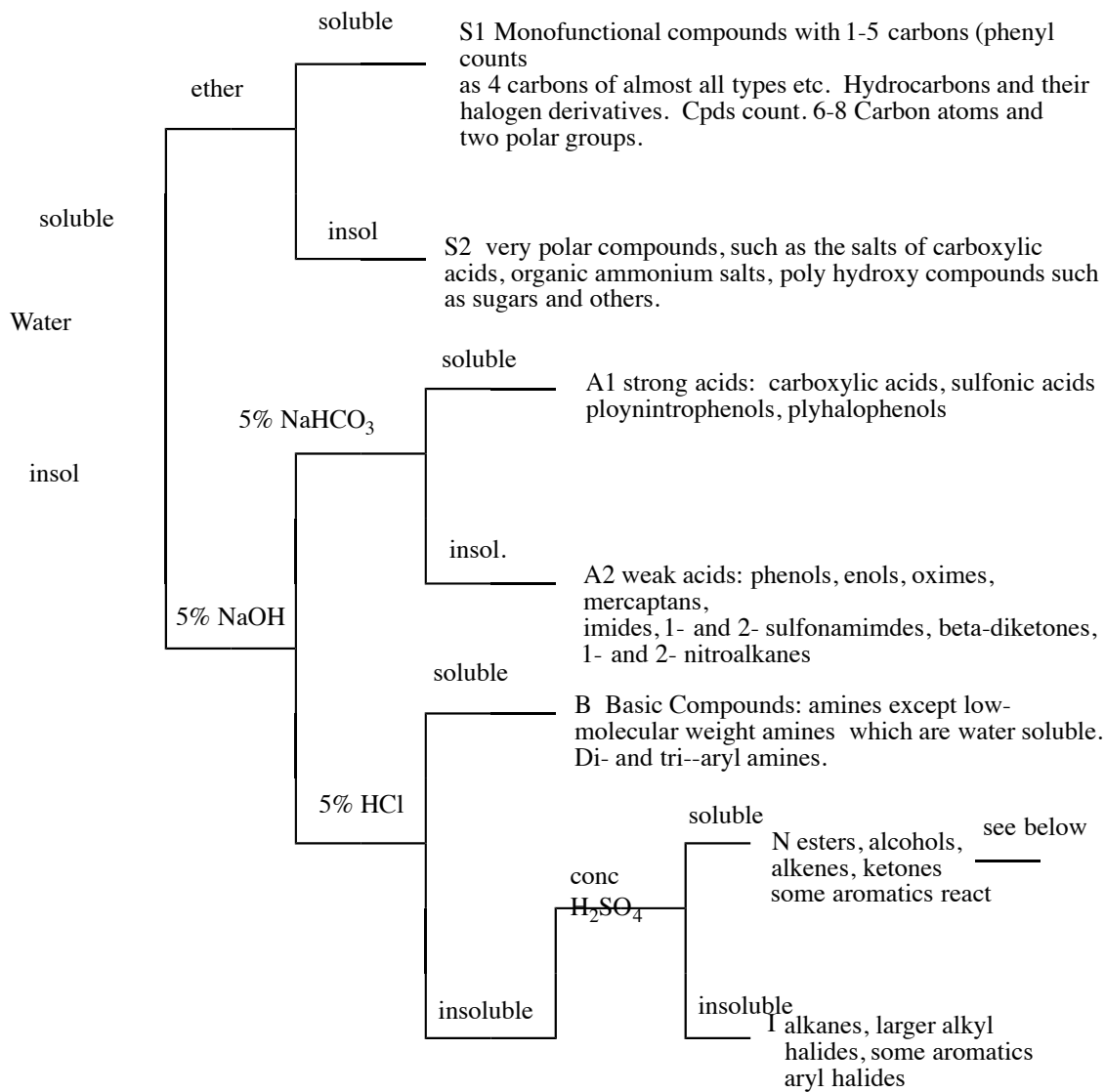
Procedure for solubility tests

Place enough of the solvent being tested to fill the curved part of the special, small test tubes that will be provided for you. Add one drop of your unknown liquid. Always hold the tube with a test tube holder away from you and into the hood. Some of the reactions are very exothermic. Mix the test tube (be careful - especially with the strong acids). Solubility is taken as either a homogeneous appearance (no layers) or a reaction. Please write down any and all observations as the behavior of the compounds even in a class is

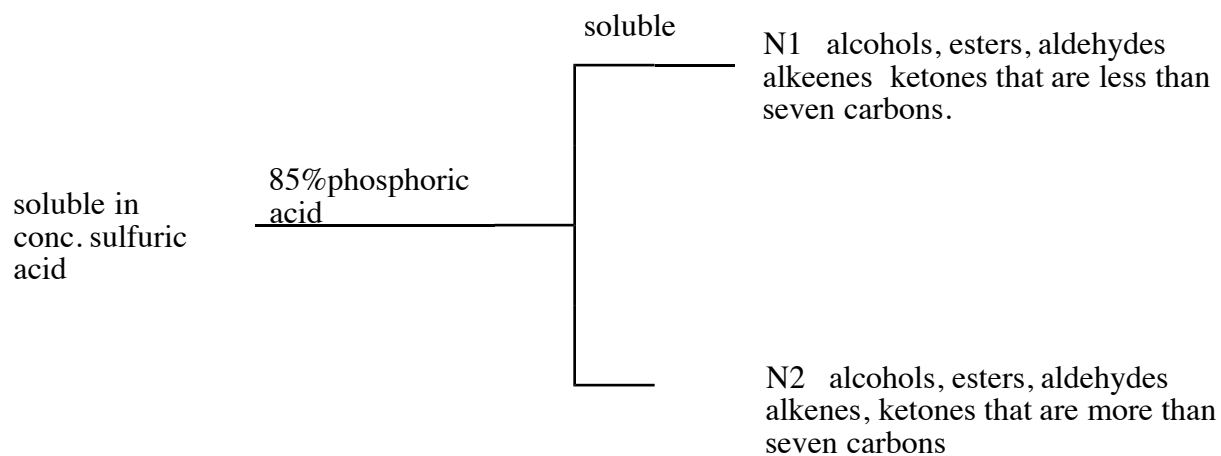
variable.

To carry out a solubility analysis you do not just test all the solvents, you carry out the testing using the following flow chart. Note that solubility in water indicates extreme polarity - meaning few carbons and a polar functional group or many polar functional groups or a charged organic. Solubility in ether means the hydrophobic behavior is dominant, this normally occurs with non charged organics that have more than 5/1 ratio between the number of carbons and the polar functional groups. Compounds that dissolve in dilute acids are bases, usually amines. The compounds themselves are insoluble in the aqueous medium, but the protonated forms are not because they are charged. Think back to the last lab, these tests are very interrelated with what you learned about acid and base extraction. Similarly compounds that are acids will dissolve in dilute bases. Again the acid itself is water insoluble, but the deprotonated acid is an ionic species and is water soluble. It is not expected at this time that you would know the chemistry that is going on with the really strong concentrated acids such as phosphoric and sulfuric, but for the most part we are talking about reactions of the polar functional groups or aromatic chemistry. These later reactions are the ones that can be a bit exothermic. Please keep this in mind.

Solubility Flow Chart - This Will Be Used in Second Week of Lab Please Study and transfer to notebook for second week.



Solubility test for compounds that are soluble in conc. sulfuric acid



[
Experiment 5
Spectroscopy I: Identification of an Unknown

Over the next three weeks of lab you will develop your abilities to run and interpret spectra. As part of this process, you will be assigned a simple unknown liquid to identify. Though you will measure some physical constants and carry out a few chemical tests, most information will be obtained from the IR and ^1H NMR spectra you will be measuring. In preparation for this lab, review chapters 14 and 15 of Bruice. Since this is a rather involved reading, there are no prelab questions assigned this week. Also, read the pre-lab readings associated with this lab and attend the associated lab lecture. This will also be covered briefly in lecture.

Procedure (All of this is done second week, except the IR measurement). The first week is a workshop outlined above where you learn NMR. The third week is used to work on your lab write-up and learn how to interpret NMR, IR and MS.

1. Find two to three other students you would like to work with on the Unknown Identification. First week.
2. You receive the unknown the first week. Record the unknown number. (Second week)
3. Measure the IR spectrum as directed by TA. First week.
4. Distill (simple distillation) your unknown in an effort to purify and determine its boiling point. (Second week)
5. Measure the density of your unknown in the following manner: (Second week)
tare a small graduated cylinder.

fill the graduated cylinder with 10 mL of distilled water.
weigh the cylinder plus 10 mL of water.
measure the temperature of the water.
weigh 10 mL of the unknown in the same cylinder (after drying up water).
calculate the density of unknown as follows:

$$\frac{d \text{ unknown}}{d \text{H}_2\text{O at } x^\circ\text{C}} = \frac{\text{wt. of 10 mL unknown}}{\text{wt. of 10 mL H}_2\text{O}}$$

note: the density of water at X°C can be found in the *CRC Manual*. I am sure it is also available on web. Search density of water at various temperatures.

(Second week)

6. Study the solubility of your unknown in water, 1.5 M NaOH, 0.6 M NaHCO₃, 1.5 M HCl, conc. H₂SO₄. Follow the solubility procedures given in the preceding pages of this manual. (Second week)
7. Sign up to run the NMR spectrum of your unknown. The sign up sheet is outside your instructor's office. Your NMR spectrum will be run during the second week of this lab.(Second week)
8. Run GCMS of unknown, obtain MS data for unknown.
9. Learn more about solving NMR, IR and GC (First, Second and Third Weeks) You will have lots of extra time the third week to learn more.
10. One lab report will be written and submitted by each group. In assigning a structure to the unknown, the discussion in the lab report must include the logic used in determining the unknown's structure, how all the data supports the proposed structure (give references to books used) and a comparison of experimental spectra with literature spectra for the proposed compound (see *Aldrich Library of IR (NMR) Spectra* Collier Library) or the Bryn Mawr College Organic Chemistry website, i.e. websites contained within the virtual library).

(Use the lab time the Third week of the project to learn more about NMR, IR, and MS and work on your lab report with your group).

11. Answer the following post-lab questions.

Explain on a molecular level the solubility behavior of the S2, A2, and I classes of compounds in the appropriate solvents outlined on the solubility flow chart .
(12 points)

Answers to all the NMR problems assigned during workshop. These will be in the textbook Bruice. See the Moodle site for assignment (47 points)

One way to Solve the Spectroscopy Unknown

1. Try to figure out what sort of functional group you have.
 - a. The IR
 - b. The solubility information
 - c. The NMR
 - d. The MS interpretation.
2. When you have a family, try to get a handle on the size of your unknown.
 - a. The boiling point
 - b. The solubility information
 - c. The molecular weight from the MS.
3. Do a search using our libraries extensive data bases by boiling points. Consider compounds +/- 5 degrees of the measured boiling point. There can be a lot of error in boiling points.
4. Think about the sorts of NMRs that the listed compounds would give. Eliminate the compounds that would not give NMRs corresponding to your data.
5. When you think you have it narrowed down to a few compounds, check your spectra vs. the literature. You can use the websites given on my website or you can use the books in the library - see The Aldrich Library of NMR and IR Spectra and links found and in the virtual library on the BMC Organic Chemistry website.. Remember that alcohols and amines are funny for the following reasons.
 - a. Depending on how the NMR is run the hydroxyl hydrogen may not split (or talk to) the neighbors.
 - b. The OH gives a variable chemical shift depending on the concentration of the sample.
 - c. In the IR, there is also a concentration dependence. Highly concentrated solutions give broad strong absorptions at 3400 cm^{-1} . IRs done in the gas phase or high dilution give

sharp, strong absorptions at around 3600 cm^{-1} .

d. Alcohols do not always give a molecular ion in MS. They often exhibit the loss of 18 (water)

This is a total group project - one lab report per group. All group members must be involved in all decisions though the final writing the report can be divided.

Specific Point Breakdown for Experiment 5

Note: this experiment is based on 220 points

Notes for grading lab reports. This is very helpful in ensuring that you have included everything.

I. Pre-lab Exercises (0 points)

II. Section 1 - Introduction (10 points total)

III. Section 2 - Experiments and Results (68 points total)

unknown no.:	6 points
unknown boiling range:	
density data:	6 points
calculation of density:	8 points
solubility of unknown in various solvents:	8 points
IR spectrum:	12 points
NMR spectrum:	16 points
MS spectrum:	12 points

IV. Section 3 - Discussion (72 points total)

interpretation of NMR spectrum:	16 points
Interpretation of IR spectrum:	12 points
Interpretation of MS spectrum:	12 points
interpretation of solubility data:	8 points
Logic leading to unknowns identity of unknown:	
proposed identity of unknown:	12 points
summary of how all data supports proposed	

Identify using references when appropriate: 12 points

IV. Post-lab Questions (*47 points total*)

a. 12 points

b. 35 points

VI. Quality of Results (assigned by TA) 20 points

VI. References: 13 points