Experiment 4
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)   _____ (36 points)

Section 4 (Disc.)   _____ (44 points)

Section 5 (Post-lab)   _____ (47 points)

Quality of results   _____ (20 points)

                           TOTAL   _____ (157 points)

                           SCORE   _____ (percent)

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

Week no. 1 Lockers 1-9

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	See GCMS run with Instructor
3:00 - 4:30	Basic NMR Theory
4:30-5:00	Interpret a simple NMR with your TA - Room 180 or lab

Lockers 10-18

1:00 - 2:00	NMR Lecture – How to Interpret NMR - Room 180
2:00-2:15	Take a break and have a snack
2:15-2:30	See GCMS run with Instructor
2:30-3:00	Run and interpret the IR of your unknown with your TA
3:00 - 4:30	Basic NMR Theory
4:30-5:00	Interpret a simple NMR with your TA - Room 180 or lab

Lockers 19-30

1:00 - 2:00	NMR Lecture – How to Interpret NMR - Room 180
2:00-2:15	See GCMS run with Instructor
2:15-2:45	Run and interpret IR of unknown with TA
2:45-3:00	Take a break and have a snack
3:00 - 4:30	Basic NMR Theory
4:30-5:00	Interpret a simple NMR with your 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. Do the polarimetry exercise.

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

ELECTROMAGNETIC SPECTRUM

Wavelength	Name
$10^{-10}M$	gamma rays
$10^{-8}M$	X-rays vacuum UV near UV
$10^{-6}M$	visible
$10^{-4}M$	Infrared (IR)
$10^{-2}M$	microwave
$10^{0}M$	radiowaves

(left margin: increasing energy, or increasing ν; increasing λ)

$E = h\nu$

ν = frequency = cycles/sec
h = Planck's constant

$E = h\,c/\lambda$

c = speed of light
λ = wavelength

---

wave number $\tilde{\nu} = 1/\lambda\,(cm)$

$IR \cong 4000 \text{ cm}^{-1} \rightarrow 400 \text{ c m}^{-1}$

$\leftarrow$

higher E, ν

$\rightarrow$

longer λ

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* IR spectra are absorbtion spectra
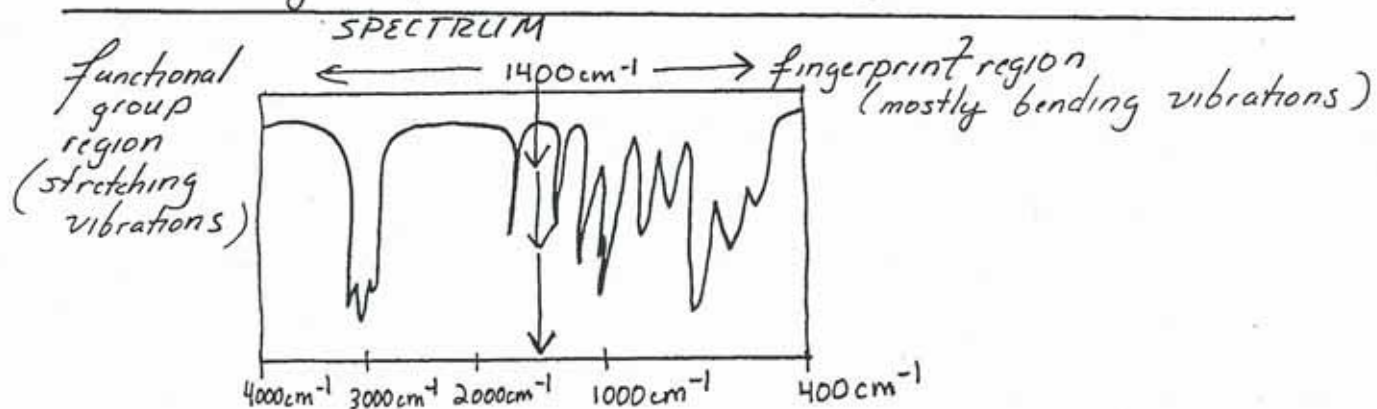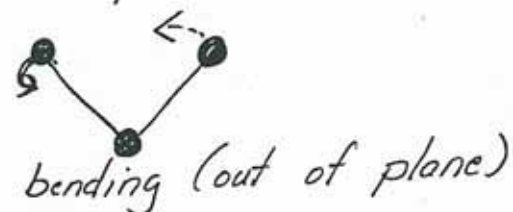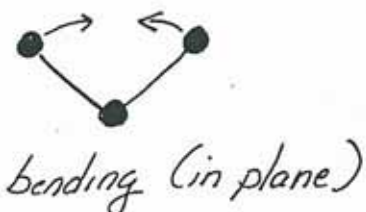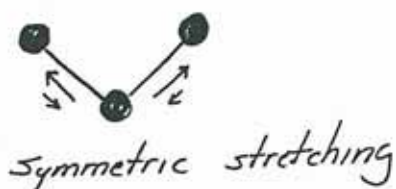* vibrating bonds absorb E = hν when ν = frequency of bond vibration

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What determines frequency of bond vibration?

mass of atoms - smaller = higher frequencies
strength of bond - stronger = higher frequencies
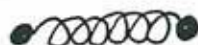
$$\upsilon \sim \sqrt{\frac{k}{m}}$$

TYPES OF BOND **VIBRATION**

Symmetric stretching

antisymmetric stretching

bending (in plane)

bending (out of plane)

SPECTRUM

functional group region (stretching vibrations)

← 1400cm⁻¹ → fingerprint region (mostly bending vibrations)

4000cm⁻¹ 3000cm⁻¹ 2000cm⁻¹   1000cm⁻¹   400cm⁻¹

Bond Stretching Frequencies - Trends

Bond	$v = cm^{-1}$
C-H	3000
C-D	2100
C-C	1200
C≡C	2200
C=C	1660
C-C	1200
C≡N	2200
C=N	1650
C-N	1200
C=O	1700
C-O	1100

SOME CHARACTERISTIC IR FREQUENCIES
Stretching Vibrations

TRENDS

Bond	Bond Energy	$\bar{\nu}$
C-H	100 kcal/mol	3000 cm^{-1}
C-D	100 kcal/mol	2100 cm^{-1}
C-C	83 kcal/mol	1200 cm^{-1}
C-C	83 kcal/mol	1200 cm^{-1}
C=C	146 kcal/mol	1660 cm^{-1}
C≡C	200 kcal/mol	2200 cm^{-1}
C-N	73 kcal/molk	1200 cm^{-1}
C=N	147 kcal/mol	1650 cm^{-1}
C≡N	213 kcal/mol	2200 cm^{-1}
C-O	86 kcal/mol	1100 cm^{-1}
C=O	178 kcal/mol	1700 cm^{-1}

Hydrocarbons

Bond	$\bar{\nu}$
isolated C=C	1640-1680 cm^{-1}
conjugated C=C	1620-1640 cm^{-1}
aromatic C=C	1600 cm^{-1}
C≡C	2100-2200 cm^{-1}
-C-H sp^3	2800-3000 cm^{-1}
=C-H sp^2	3000-3100 cm^{-1}
≡C-H sp	3300 cm^{-1}

Alcohols

O-H	3300 cm^{-1} broad
C-O	1050 cm^{-1} strong

Amines

N-H	3300 cm^{-1} broad with spike
C-N	1200 cm^{-1} strong

Carbonyls

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

1710 cm^{-1} strong

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$
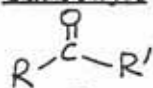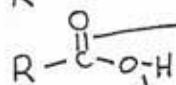
1710 cm^{-1} strong

2500-3500 cm^{-1} broad

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$$
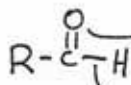
1710 cm^{-1} strong

2700 cm^{-1}, 2800 cm^{-1}

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-=$$
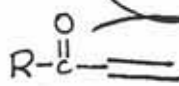
1675-1690 cm^{-1} strong

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-N\overset{-R'}{\underset{-R''}{}}$$
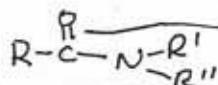
1650 cm^{-1} strong

Other C-N Bonds

C=N   1660 cm^{-1}

C≡N   2200 cm^{-1}
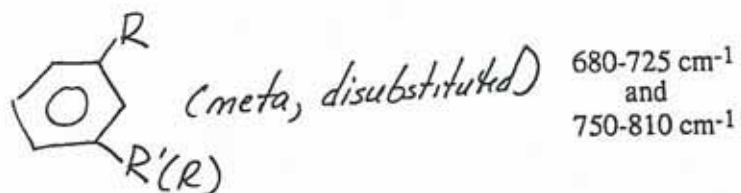
IR Absorption Frequencies[*][+]

Functional group	wavenumber (cm^{-1})	Intensity
Alkanes, alkyl groups		
C-H	2550-2960	medium to strong
Alkenes		
=C-H	3020-3100	medium
C=C	1630-1670	medium
Alkyl halides		
C-Cl	600-800	strong
C-Br	300-600	strong
C=I	300	strong
Alcohols		
O-H	3400-3640	strong, broad
C-O	1050-1150	strong
Aromatics		
	3030	medium
	1600, 1500	strong
Amines		
N-H	3310-3500	medium
C-N	1030, 1230	medium
*carbonyl compounds**		
C=O	1670-1750	strong
carboxylic acids		
- O-H	2500-3100	strong, very broad
Nitriles		
- C≡N	2210-2260	medium
nitro compounds		
- NO$_2$	1540	strong

* acids, esters, aldehydes, and ketones

[+][*] data from McMurry, J. *Organic Chemistry*, third edition, Brooks-Cole, California 1992.

IR DATA Alkene C-H bending	
R-CH=CH$_2$ (mono substituted)	985-1000 cm^{-1} and 905-920 cm^{-1}
R$_2$C=CH$_2$ (geminal disubstituted)	880-900 cm^{-1}
cis-RCH=CHR	657-730 cm^{-1}
trans-RCH=CHR	960-975 cm^{-1}

Aromatic C-H bending

 R (monosubstituted)   690-710 and 730-770 cm^{-1}

 R' (R) (ortho, disubstituted)   735-770 cm^{-1}

 (meta, disubstituted)   680-725 cm^{-1} and 750-810 cm^{-1}

 R (para, disubstituted)   800-840 cm^{-1}
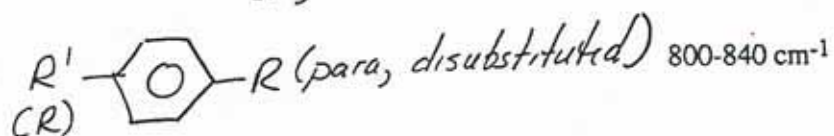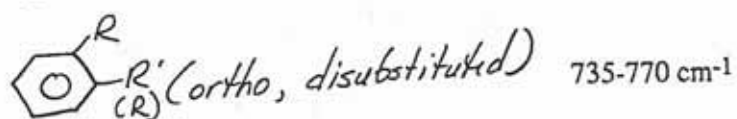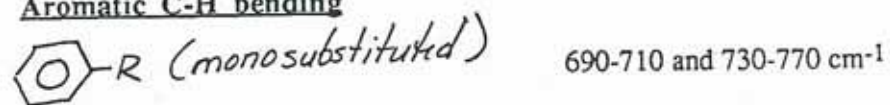
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
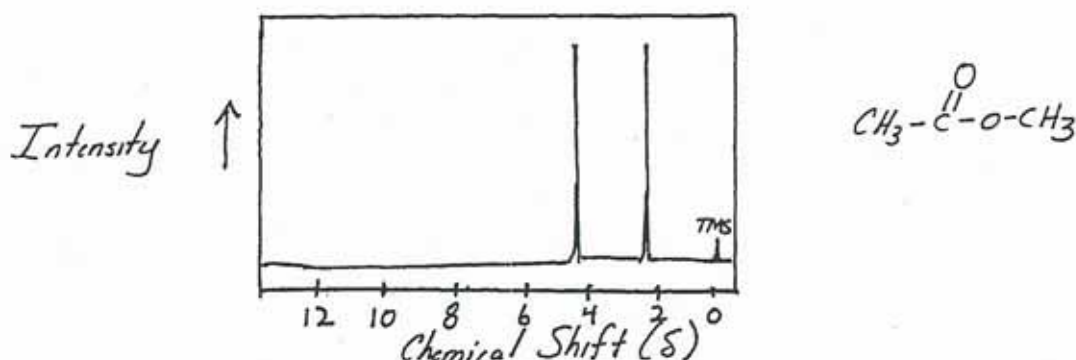
"NMR"

Intro

NMR is based on the fact that some nuclei are magnetic and that magnetic nuclei in molecules can have different magnetic environments.

NMR involves studying molecules containing magnetic nuclei in experiments utilizing both radiowaves (low frequency electromagnetic radiation) and an external magnetic field.

The result is the NMR Spectrum

NMR spectra provide key information regarding the structure of organic, inorganic and biochemical compounds. It is one of the most **powerful** tools **scientists** have!

Using ^1H and ^{13}C in conjunction, one can obtain structural information about the skeleton and periphery of organic molecules.

Information Derived from Spectra

1. *chemical shift* $= \delta =$ ppm = peak position-information about electronic environment of magnetic nuclei resonating at a given position (being observed).

2. *Area under peak of group of peaks* - information regarding the relative number of a given type of magnetic nuclei having a distinct magnetic environment.

3. *Splitting Pattern* = how is a peak split? singlet, doublet, triplet

4. *Coupling Constant* = J value (H_z) = the difference in H_z between lines in a split peak.

3 and 4 give information regarding the numbers (3) and types (4) of distinct magnetic nuclei in the environment of the magnetic nucleus or nuclei being observed at a given peak position
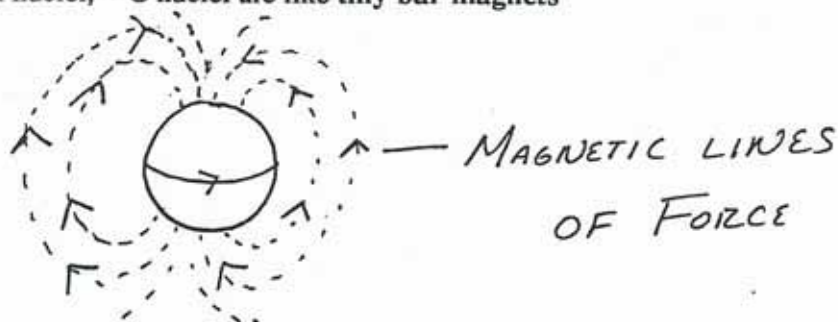

A little background

Where do NMR signals come from?

Some nuclei possess angular momentum and are magnetic
∴ they have spin quantum numbers, I

e.g. ^1H I = 1/2 two spin states +1/2, -1/2
^{13}C I = 1/2 two spin states +1/2, -1/2

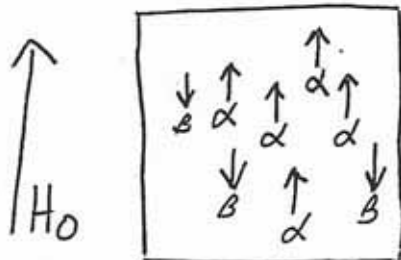
A charged nucleus with spin gives rise to a **small local magnetic** field.
Therefore, ^1H nuclei, ^{13}C nuclei are like **tiny bar magnets**
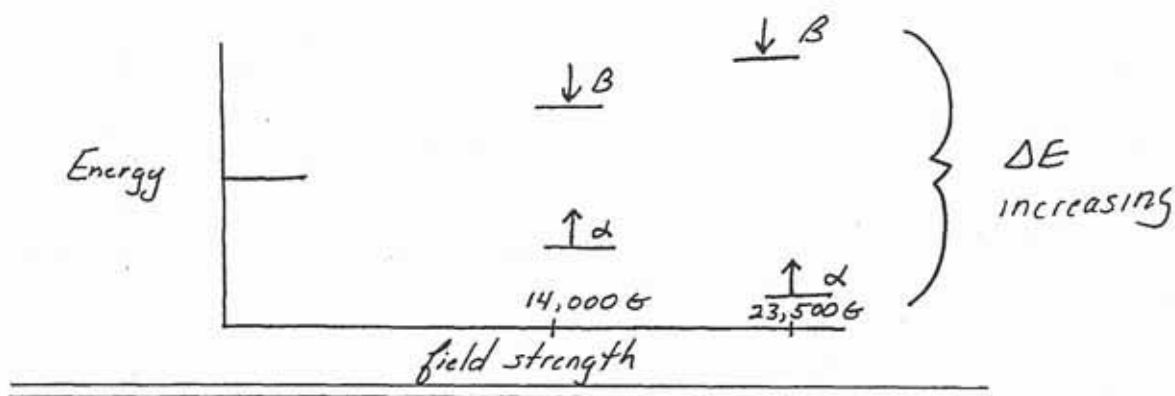

MAGNETIC LINES OF FORCE

In a sample, there are **lots** of **tiny bar magnets** randomly oriented.

Spins in Sample
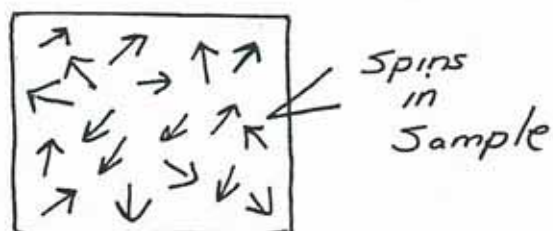
The NMR experiment involves placement of tiny bar magnets in an external magnetic field, H_0.↑

Energy Level of Spin states (α and β) vs. External Magnetic Field Strength

The NMR experiment involves flipping the excess spins in the α (state) $\rightarrow$ β (state). This transformation requires energy provided by radiofrequency electromagnetic radiation. When nuclei flip they are in resonance with the radiofrequency and generate a small electric current in coil surrounding sample giving rise to a signal ⅃.

CHEMICAL SHIFT δ, units = ppm

For ^1H NMR spectrum runs from 0-12 ppm. **What** determines position of signal? For resonance to occur the following condition must be met:

$$\nu = \frac{\mu H_0}{2\pi}$$

$\overline{\nu}$ = r.f.
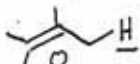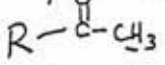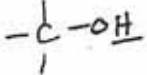
μ = magnetogyrtic ratio
    For ^1H = 26,753
H_0 = strength of external magnetic field

Fortunately, magnetic nuclei in different magnetic environments have different resonance requirements (H_0, ν match). In the old "CW" NMRs, the NMR experiment is carried out holding **r.f.** constant and varying H_0
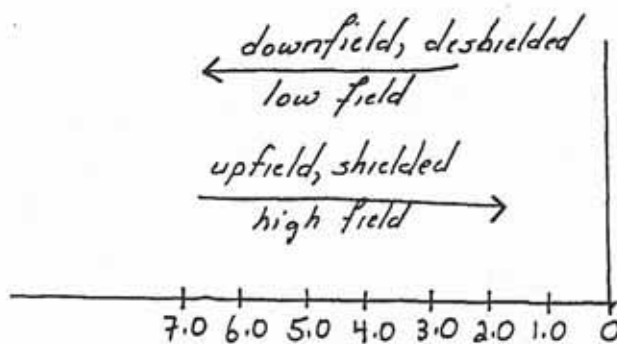
¹H NMR CHEMICAL SHIFT CHART*

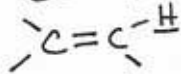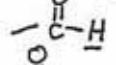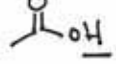| Type of proton	Formula	Chemical shift (δ)
Reference peak	$(CH_3)_4Si$	0
Saturated primary	$-CH_3$	0.7-1.3
Saturated secondary	$-CH_2-$	1.2-1.4
Saturated tertiary	$-\overset{|}{\underset{|}{C}}-\underline{H}$	1.4-1.7
Allylic primary		1.6-1.9
Methyl ketones	$R-\overset{O}{\overset{\|}{C}}-C\underline{H}_3$	2.1-2.4
Aromatic methyl	$Ar-C\underline{H}_3$	2.5-2.7
Alkyl chloride	$Cl-\overset{|}{\underset{|}{C}}-\underline{H}$	3.0-4.0
Alkyl bromide	$Br-\overset{|}{\underset{|}{C}}-\underline{H}$	2.5.-4.0
Alkyl iodide	$I-\overset{|}{\underset{|}{C}}-\underline{H}$	2.5-4.0
		2.0-4.0
Alcohol, ether	$-O-\overset{|}{\underset{|}{C}}-\underline{H}$	3.3-4.0
Alkynyl	$-C\equiv C-\underline{H}$	2.5-2.7
Vinylic	$\overset{}{C}=C\overset{}{}-\underline{H}$	5.0-6.5
Aromatic	$Ar-\underline{H}$	5.6-8.0
Aldehyde	$-\overset{O}{\overset{\|}{C}}-\underline{H}$	9.7-10.0
Carboxylic acid	$\overset{O}{\overset{\|}{C}}-o\underline{H}$	11.0-12.0
Alcohol	$-\overset{|}{\underset{|}{C}}-O\underline{H}$	Extremely variable (2.5-5.0)

Consider the following structures:

CH_3—⟨◯⟩—CH_3

p-xylene

$CH_3\overset{O}{\overset{||}{C}}-OCH_3$

methyl acetate

How many different signals does one expect in the ^1H NMR spectrum of Xylene? _____

of methylacetate? _____

Using table of general ^1H shifts, what are the predicted positions of signals? _____

Question: In **general**, why do certain type of nuclei (^1H) appear (resonate) at certain field positions?

Answer: NEIGHBORING LOCAL MAGNETIC FIELDS!!

MAGNETIC FIELDS

1. Generated by electrons in adjacent bonds (σ)
2. Generated by circulating electrons in π systems = ring current = anisotropy effect

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1. Electrons in adjacent σ bonds, e.g. R⊕H

   These electrons circulate in such a way in H_0 that they produce a local magnetic field that opposes (slightly) H_0. Therefore, the ^1H in question experiences less H_0 and more H_0 must be applied to flip the ^1H. These protons are said to be **shielded**, upfield, highfield, low frequency, low ppm.

   R↓H ↑$_{Ho}$
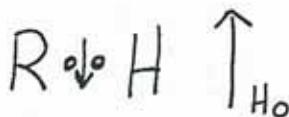
   If an electronegative atom(s) is in the environment of a ^1H, the opposing field due to the J electrons is reduced or deshielded, downfield, lowfield, high frequency, high ppm!

Examples: See SPECTRA

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2. Anisotropy Effects - small magnetic fields operating through space either augmenting or opposing Ho. We will be considering fields produced by the circulation of delocalized π electrons.

a. Ring current - aromatic compounds

Consider Benzene
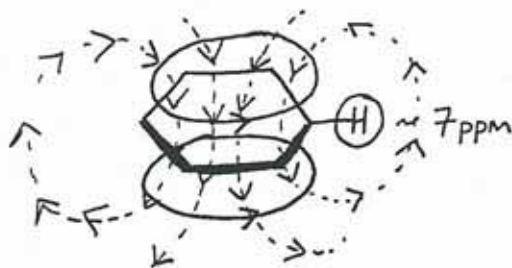
Consider [18]Annulene
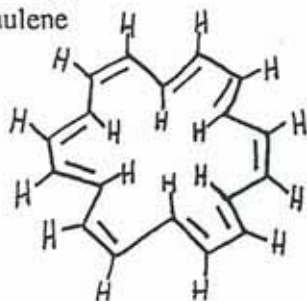
outer hydrogens $\delta = 8.2$ ppm
inner hydrogens $\delta = -1.9$ ppm

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b. Electron Circulation - acetylenes
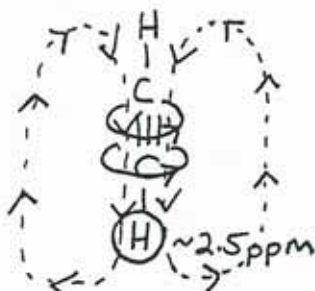
INTEGRALS - the area under a peak or a split peak

The area under a singlet peak or the total area under a split peak is proportional to the number of equivalent nuclei being observed.

Using intergrals, one can calculate **relative** numbers of atoms. Using the molecular formula, one can translate relative numbers of nuclei into absolute numbers.

SPLITTING

In a NMR spectrum (e.g. ^1H) equivalent magnetic nuclei will either appear as an unsplit peak (a singlet) or as a split peak (doublet, triplet, quartet, doublet of doublets, etc.).

Splitting is caused by the magnetic fields of nuclei that are not magnetically equivalent (not equivalent to the nucleus being observed) that are 1, 2, 3 or sometimes 4 bonds away from the observed nucleus.

$$ \sim 1 ppm \quad \sim 4 ppm \qquad\qquad \sim 2 ppm $$

$$ \underset{A}{} \quad \underset{B}{} \qquad \overset{O}{\underset{\|}{}} $$

$$ CH_3CH_2-O-C-CH_3 \qquad\qquad \underline{n+1}\ \text{rule} $$

triplet integrating to 3

quartet integrating to 2

singlet, integrating to 3
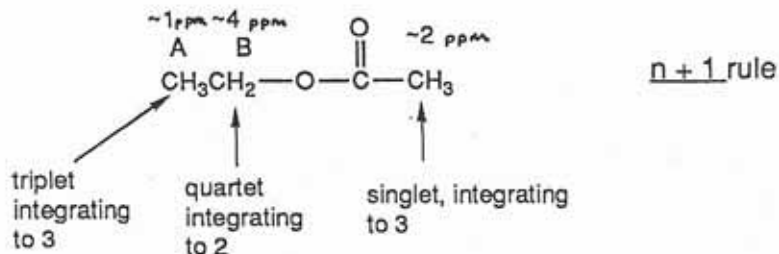
WHY???

Consider A protons

Q: What does each A proton "see" in its local environment?

A: _____

possible orientations of H_B protons at time of excitation

1:2:1 H_A in NMR upfield
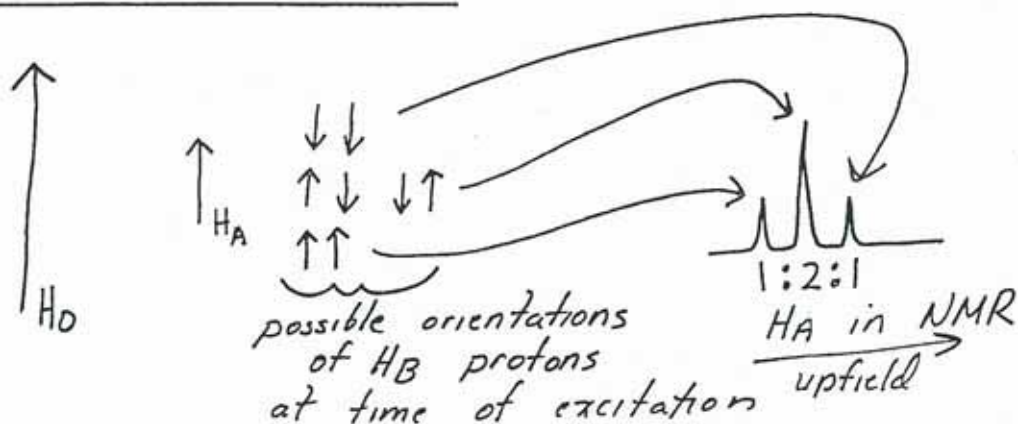
In general, integral tells you about numbers of nuclei being observed. Splitting tells you about numbers of adjacent hydrogens that are different from observed.

Consider B protons

Question: What does each B proton "see" in its local environment??

Answer: _____

possible orientations of H_A protons

1:3:3:1 H_B protons in NMR

4-16
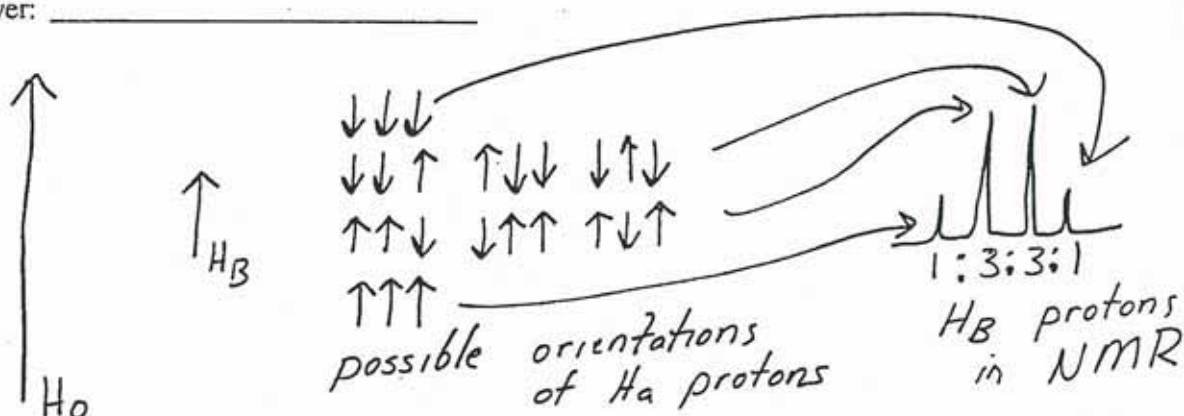
Splitting arises from spin coupling as shown above. The "distance" between the peaks in a multiplet or the difference in frequency is called the coupling **constant**. It is measured in Hz = cycles/sec.
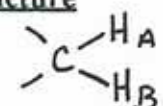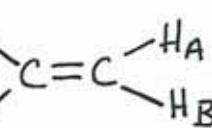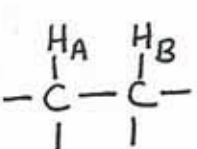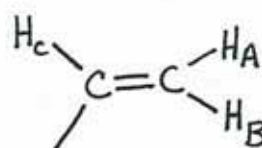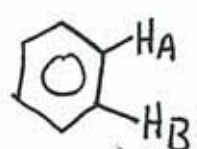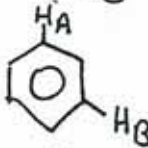
Coupling constants = J values

Important note: $J_{AB} = J_{BA}$!!

Why is this information useful?

The **coupling constant** magnitude can give insight into the types of different protons interacting.

Some typical coupling constants* :

Structure	J value (Hz)
geminal $\Big\{$ $\underset{}{\overset{}{C}}\underset{H_B}{\overset{H_A}{\big<}}$	12-15
$\underset{}{\overset{}{C}}{=}\underset{}{\overset{}{C}}\underset{H_B}{\overset{H_A}{\big<}}$	0.5-3
vicinal $\Big\{$ $-\underset{}{\overset{H_A}{C}}-\underset{}{\overset{H_B}{C}}-$	4.7-9
$\underset{}{\overset{H_c}{\big>}}C{=}C\underset{H_B}{\overset{H_A}{\big<}}$	J_{AC} 4.6-19.3 J_{BC} 12.7-24.0
benzene ring H_A (ortho) H_B	6.5-9.4
benzene ring H_A (meta) H_B	0.8-3
benzene ring H_A (para) H_B	0.4-1

* data taken from Parikh, V.M. *Absorption Spectroscopy of Organic Molecules* Addison-Wesley, Phillipines, 1974.

Introduction to Infrared Spectroscopy

We will be using IR spectroscopy in many experiments this year. To read more about IR, see pages 12.1-2.5 in Loudon.

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

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

Confirmatory means that

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

Diagnostic IR Absorption Regions

I. 3600 - 3200 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 cm^{-1} Ar-H 3100-3000   weak to medium

$$\begin{array}{c} O \\ \parallel \\ C\text{-}\underline{O}\text{-}H \end{array}$$ broad, usually centered at ~3000 cm^{-1}

III. 2260 - 2100 cm^{-1} C≡C and C≡N   strong to variable

IV. 1750 - 1630 cm^{-1} C=O and C=N   strong

Look for **strong** bands in this region to identify the C=O group. Weak bands in this region can arise from other groups.

V. 1350 - 1000 cm^{-1} C-O   (strong)

C-N   (strong to medium)

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

VI. 1000 - 600 cm^{-1} C=C-H

C≡C-H

Ar-H

For alkenes and arenes, various substitution patterns give bands at characteristic frequencies. See a textbook.

Some of these bands can be unreliable, and in any case must be confirmed in the C-H regions.

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.

The Basics Nuclear Magnetic Resonance Spectroscopy

To read more about NMR, please read Chapter 13 of Loudon.

Nuclei possessing angular moment (also called spin) have an associated magnetic moment. A few examples of magnetic isotopes are ^{13}C, ^{1}H, ^{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 ^{1}H and ^{13}C. I will limit my discussions to ^{1}H 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 ^{1}H 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
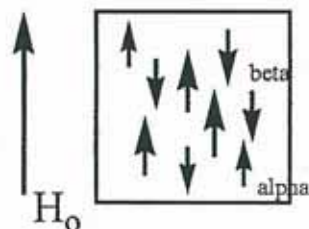
alpha and beta
orientation in field

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 Imagining - 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.

$$\nu = \frac{\mu H_o}{2\pi}$$

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.**

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

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.

methane

bromoethane

4-23
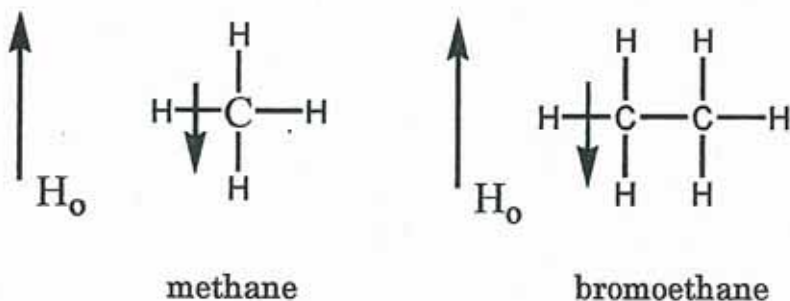
Now consider a hydrogen near a halogen as in bromoethane. This type of hydrogen is in a magnetically altered situation as compared to the hydrogen in methane. Due to its inherent electronegativity, the halogen atom has the effect of pulling sigma electron density away from the hydrogens in the molecule. 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 <u>flip</u> 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.

"a" "b"

Br-CH$_2$-CH$_3$

"b"

"a"

| 5.0 | 4.0 | 3.0 | 2.0 | 1.0 | 0 ppm |
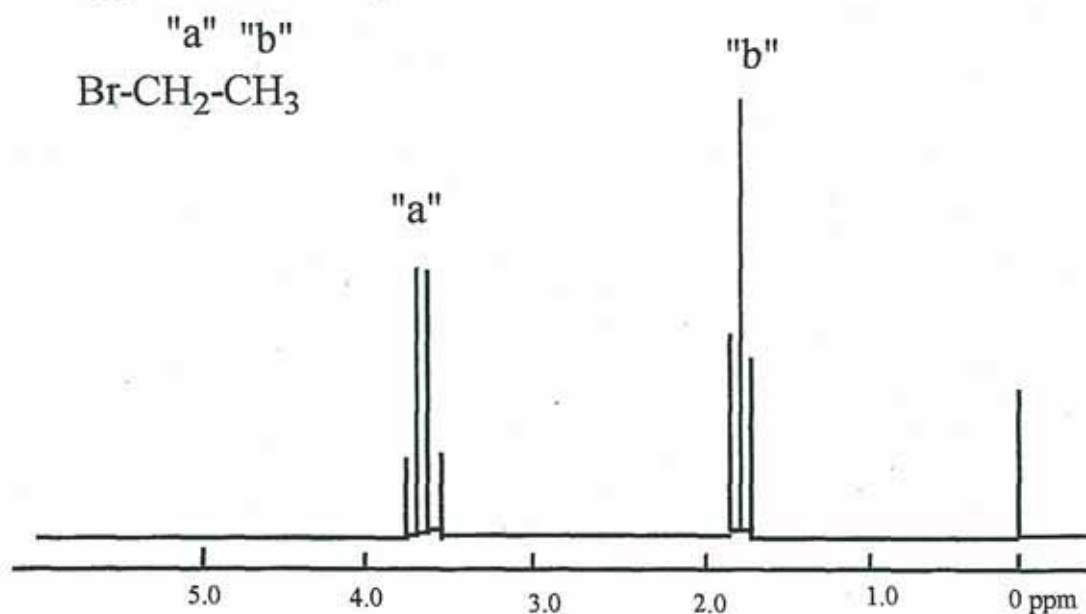
¹H NMR Spectrum of Bromoethane

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.

H_o 7 ppm
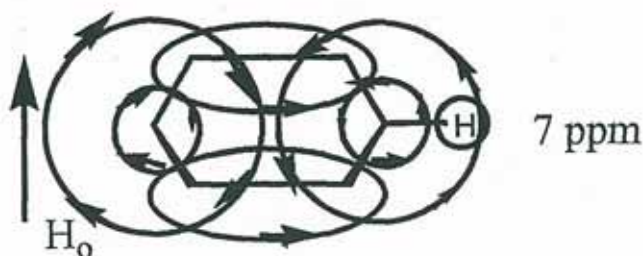
Benzene

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 <u>flip</u> 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!!
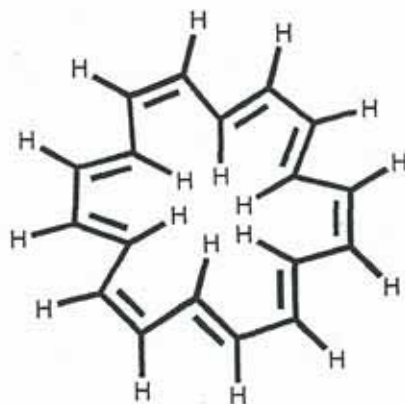
[18]-Annulene

So summing up, the different hydrogens of a molecule appear at different positions because <u>small</u> local magnetic fields are generated when local electrons begin to circulate due to the effect of the external magnetic field. These <u>small</u> 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).

higher ppm

lower ppm
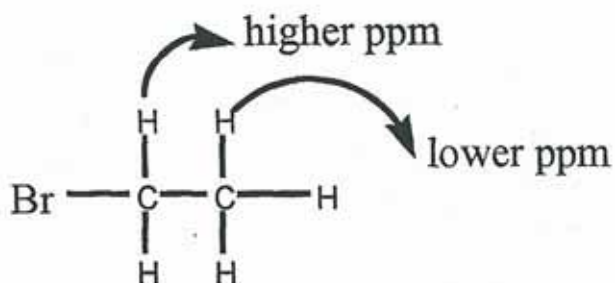
Bromoethane has two different types of hydrogens so we expect two absorptions in the NMR spectrum. One absorption corresponds to the two hydrogens that are closest to the halogen atom. The other to the hydrogens comprising the methyl group that is farther away. Based on what I described above with regard 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:

H_a

H_o

1:3:3:1

possible orientations
of H_b neighbors
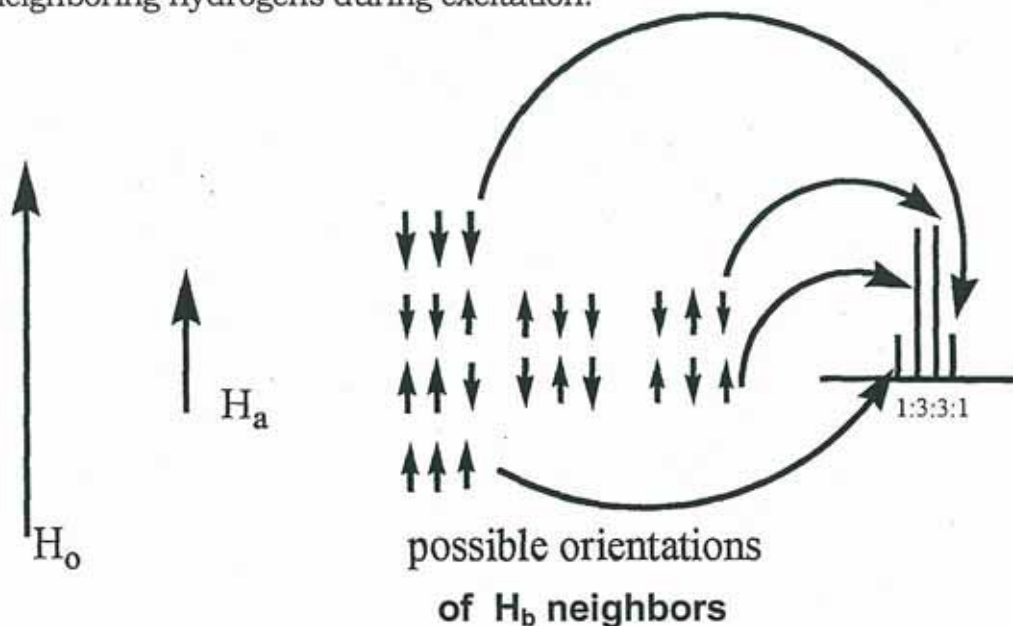
Please note that in the above diagram the "a" hydrogens are the ones near the bromine being flipped from the alpha to beta orientation. The "b" hydrogens are the three neighbors. As shown above, it is possible that a given "a" hydrogen will have three "b" hydrogens nearby that are aligned with the applied field during excitation. It is also possible that the three neighbors could <u>all</u> 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 <u>all</u> 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 <u>all</u> 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 <u>all</u> 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 ($-CH_3$) and a methylene ($-CH_2-$) 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 <u>peak</u> 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 (δ).** 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	CH_3CH_2-
3.4	2	quartet	$-CH_2CH_3$ 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.

Experiment 4
Spectroscopy I: Identification of an Unknown

Over the next two 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 ^{1}H NMR spectra you will be measuring. In preparation for this lab, review chapters 12.1-12.3 and 13 of Loudon. Since this is a rather involved reading, there are no prelab questions assigned this week.

Procedure

1. Find two to three other students you would like to work with on the Unknown Identification.

2. Obtain a liquid unknown from your instructor. Record the unknown number.

3. Distill (simple distillation) your unknown in an effort to purify and determine its boiling point.

4. Measure the density of your unknown in the following manner:

   a. tare a small graduated cylinder.
   b. fill the graduated cylinder with 10 mL of distilled water.
   c. weigh the cylinder plus 10 mL of water.
   d. measure the temperature of the water.
   e. weigh 10 mL of the unknown in the same cylinder (after drying up water).
   f. calculate the density of unknown as follows:

$$\frac{d_{unknown}}{d_{H_2O} \text{ at } X°C} = \frac{\text{wt. of 10 mL unknown}}{\text{wt. of 10 mL } H_2O}$$

   note: d_{H_2O} at X°C can be found in the *CRC Manual.*

5. Measure the IR spectrum of your unknown.

6. Study the solubility of your unknown in water, 1.5 M NaOH, 0.6 M NaHCO$_3$, 1.5 M HCl, conc. H$_2$SO$_4$. Follow the solubility procedures given in the following pages of this manual.

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.

8. 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).

9. Answer the following post-lab questions.

   a) Explain on a molecular level the solubility behavior of the S_2, A_2, and I classes of compounds in the appropriate solvents outlined on the solubility flow chart . *(12 points)*

   b) Answers to all the NMR problems assigned during workshop. *(47 points)*

   (sheets of NMR problems)

Solubility Tests

These tests should be carried out using small test-tubes (8 x 75 mm). These can be obtained from your instructor/TA. Use 0.2 mL of liquid unknown or 0.1 g of a solid unknown - just about enough to fill the rounded bottom part of the test tube. Add 3 mL of the solvent with stirring. Observe carefully during the addition of the solvent. If you obtain a clear, homogeneous (uniform) liquid without globules or cloudiness, the unknown is said to be soluble. If there are two layers or globules of liquid, or if the mixture is turbid, the sample is insoluble. Sometimes, the sample is partially soluble. In that case see whether adding a little more solvent leads to complete solution. Generally, no heat is applied in these tests. However, if the unknown is insoluble in cold water, it may be worth knowing whether it dissolves on heating. If it does, cool and scratch the inside of the test-tube with a stirring rod, and note whether the material precipitates. Also, some acids (which should be soluble in 5% NaHCO₃aq) will not dissolve in dilute sodium bicarbonate unless gently heated.

If the unknown reacts with the solvent chemically (as evidenced by gas evolution, charring, etc.) the unknown is classified as "soluble" in that solvent.
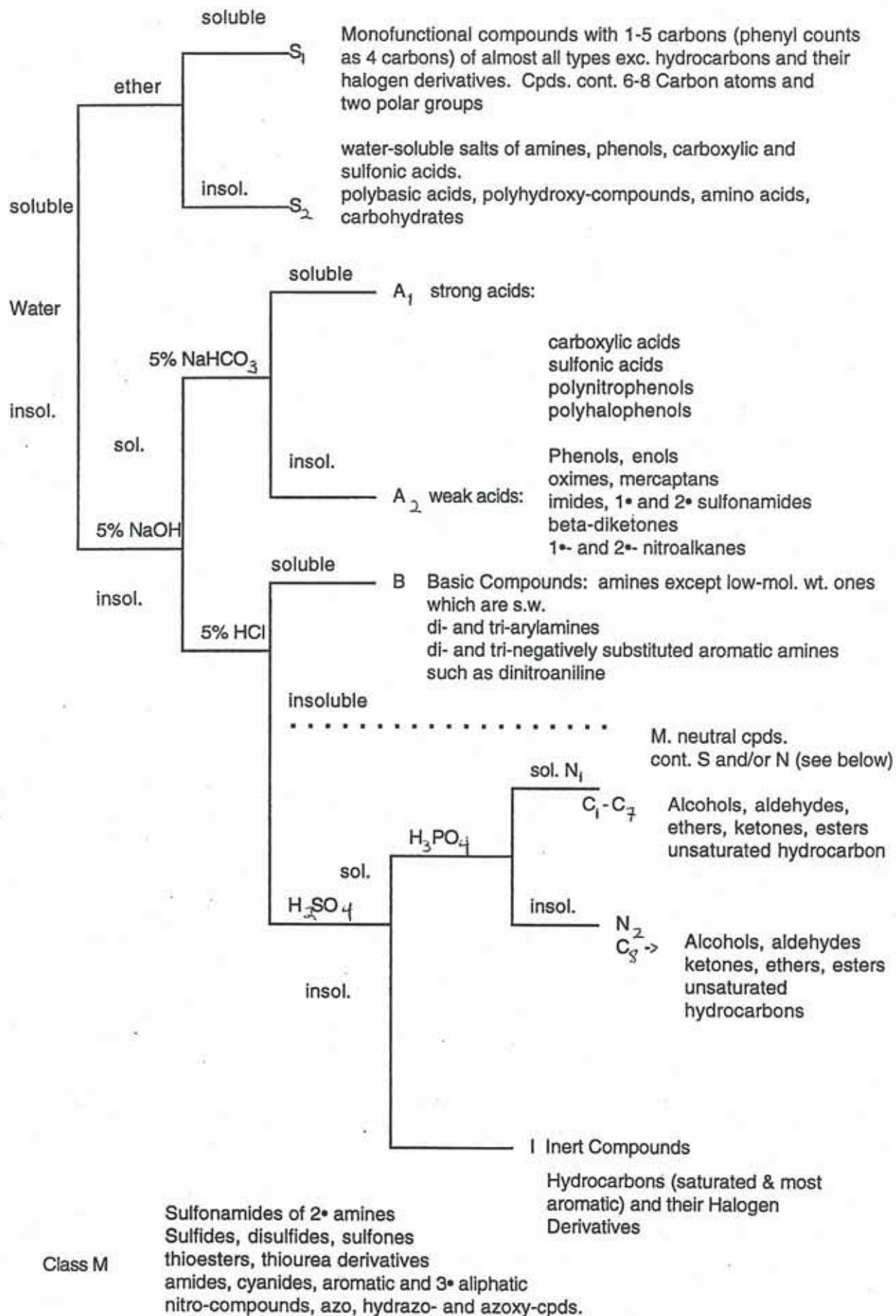
The solvents to be used are (in order): water, ether, 5% NaOH, 5% NaHCO₃, 5% HCl, conc. H_2SO_4, and 85% H_3PO_4. However, not every unknown is tested with every solvent. Rather, testing proceeds in a systematic manner until the unknown has been assigned to a particular solubility class (see schematic outline on next page). e.g., if an unknown is soluble in water, a new sample of the same unknown is tested with ether and that will lead to the unknown being assigned to either class S_1 (soluble in water and soluble in ether) or class S2 (soluble in water and insoluble in ether). In either case no further solubility tests are carried out. If the unknown is insoluble in water, it is next tested with 5% NaOH. If it dissolves a new sample is tested with 5% NaHCO₃, etc.

While most of the assignments to various solubility classes are based only on the pattern of solubilities in various solvents there is one notable exception: water-insoluble, neutral compounds (i.e. compounds insoluble in both 5% NaOH and 5% HCl) are placed in class M if they contain elements other than carbon, hydrogen, and halogens (such as nitrogen or sulfur). Otherwise, they are placed in class N_1, N_2 or I. Here, elementary composition as well as solubility are factors in classifying the unknown.

Assigning an unknown to a particular solubility class is an important step in identifying an unknown, because it tells us to what chemical class the unknown may belong. e.g., a class B compound is an amine; a class I compound is a hydrocarbon or halogen derivative of a hydrocarbon. This type of knowledge, in turn, helps us decide what chemical classification tests should be run on the unknown and what kind of derivative should be prepared.

Water and ether are solvents which act by purely physical means. All other solvents used in this scheme are "reaction solvents" and dissolving in such solvents involves chemical changes (mostly salt formation) as well as physical processes.

If the unknown dissolves in water, the solution should be tested with litmus or pH paper and the results recorded.

soluble — S₁ Monofunctional compounds with 1-5 carbons (phenyl counts as 4 carbons) of almost all types exc. hydrocarbons and their halogen derivatives. Cpds. cont. 6-8 Carbon atoms and two polar groups

ether

insol. — S₂ water-soluble salts of amines, phenols, carboxylic and sulfonic acids.
polybasic acids, polyhydroxy-compounds, amino acids, carbohydrates

Water — **soluble**

insol.

5% NaHCO₃ — **soluble** — A₁ strong acids:

carboxylic acids
sulfonic acids
polynitrophenols
polyhalophenols

sol.

insol. — A₂ weak acids:
Phenols, enols
oximes, mercaptans
imides, 1• and 2• sulfonamides
beta-diketones
1•- and 2•- nitroalkanes

5% NaOH

insol.

5% HCl — **soluble** — B Basic Compounds: amines except low-mol. wt. ones which are s.w.
di- and tri-arylamines
di- and tri-negatively substituted aromatic amines such as dinitroaniline

insoluble
. . . .
M. neutral cpds.
cont. S and/or N (see below)

H₃PO₄ — **sol. N₁** — C₁-C₇ Alcohols, aldehydes, ethers, ketones, esters unsaturated hydrocarbon

sol.

insol. — N₂ C₈ -> Alcohols, aldehydes ketones, ethers, esters unsaturated hydrocarbons

H₂SO₄

insol. — I Inert Compounds

Hydrocarbons (saturated & most aromatic) and their Halogen Derivatives

Class M — Sulfonamides of 2• amines
Sulfides, disulfides, sulfones
thioesters, thiourea derivatives
amides, cyanides, aromatic and 3• aliphatic
nitro-compounds, azo, hydrazo- and azoxy-cpds.

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

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

3. Look in the CRC Handbook of Organic Compound Identification (this is not the normal CRC, it is a slimmer volume found in the library) and all the compounds that boil +/- 5 degrees of your compound. Write their structures out.

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.

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 4
Note: this experiment is based on 157 points

Notes for grading lab reports

I.   Pre-Lab Exercises *(0 points total)*

II.   Section 1 - Introduction *(10 points total)*

III.   Section 2 - Experiments and Results *(36 points total)*

unknown no.:	**2** points
unknown boiling range:	**4** points
density data:	**4** points
calculation of density:	**4** points
solubility of unknown in various solvents:	**8** points
IR spectrum:	**6** points
NMR spectrum:	**8** points

IV.   Section 3 - Discussion *(44 points total)*

interpretation of NMR spectrum:	**14** points
interpretation of IR spectrum:	**6** points
interpretation of solubility data:	**8** points
logic leading to proposed identity of unknown:	**4** points
proposed identity of unknown:	**2** points
summary of how all data supports proposed identity using references when appropriate:	**10** points

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

a)	**12** points
b)	**35** points

VI.   Quality of Results *(20 points total)*

Chirality, Enantiomers and Optical Rotation

In preparation for this polarimetry exercise, please read Chapter 6 of Loudon in addition to the following passages.

As you have no doubt learned in lecture by now, when two molecules are described as enantiomers they have a very close relationship. They are stereoisomers that are nonsuperimposable, mirror images. As hard as it is to believe, the individual molecules that constitute a pair of enantiomers are distinct molecules that can in principle be separated from one another. Once separated, they do not interconvert. Interconversion requires breaking two sigma bonds which is no easy feat since the energies involved in the transformation are rather high.

Each individual molecule in an enantiomeric pair is chiral. Chiral molecules are molecules that are so asymmetric that they are nonsuperimposable on their mirror images. The term chiral can also be used to describe macroscopic objects. Similar to molecules, a macroscopic object is chiral if it can't be superimposed on its mirror image.

As mentioned previously in this manual, chirality is very important in biological systems as it is a fundamental component of molecular recognition. The concept is not unlike the experience a left handed person has in this rather right handed world. Left handed people can have some trouble when they encounter other chiral or handed objects and beings. For example, it is tough for a left handed person to take notes at a right handed desk. Of course, left handed people have no problem when they encounter achiral objects. For example, a left handed person is very comfortable when he or she is sitting at a simple table. This all changes when a righty sits down next to him or her. It is the same for molecules in a living system because living systems are filled with chiral molecules. Enantiomeric molecules interact differently with the chiral molecules they encounter. An example given previously in this course are the two enantiomeric carvones. Remember how dissimilar they smelled? They have distinct fragrances because they interact differently with smell receptors which are chiral.

Like left handed and right handed people, chiral molecules behave the same way when in achiral environments. It is for this reason that enantiomers are tough to physically separate. When they are in an achiral environment, they have exactly the same physical properties. For example, they have the same boiling points, melting points and solubilities. When you think about the comparative structures of enantiomers, it makes sense that they have identical properties. Enantiomers have the same molecular weight, connectivity and dipole moments. This means that they can not be separated directly by any of the conventional versions of techniques you have learned in this course such as distillation, gas chromatography, extraction or recrystallization.

You have probably learned in lecture that chiral molecules have optical rotations and that enantiomers rotate plane polarized light in equal and opposite directions. Plane polarized light is light that has been passed through a polarizer. Light is thought to consist of an infinite number of oscillating electrical and magnetic planes. When light passes through a polarizer, all planes but one are removed.

This behavior upon exposure to plane polarized light is not some magical property that defies the general principles of enantiomers. The reason enantiomers interact differently with plane polarized light is that plane polarized light is chiral. Though polarized light is a planar phenomenon, it is actually comprised of two superimposed helical forms. You can think of the electrical component as oscillating in such a way that there are two electrical vectors rotating in a cork screw fashion in opposite directions away from the source of the propagation at the same rate. Since a helix is a chiral shape , the two versions of the light constitute an enantiomeric pair. If you resolve the vectors of the two superimposed helices, you end up with oscillation in a single plane. This concept will be illustrated in class.

Enantiomers interact differently with the two forms of light. The basic idea is that when plane polarized light encounters enantiomerically pure, chiral molecules, one form of light will slow down more than the other as a consequence of the interaction. This results in one helix coming out of sync with the other. When the vectors are resolved, the resultant plane is rotated with respect to the original position. This change in position is what we mean when we say a compound has an optical rotation.

Since optical rotation is a consequence of asymmetry, several groups of molecules will not exhibit rotations. Obviously, achiral molecules will not rotate plane polarized light Realize that achiral molecules include meso compounds, 50:50 mixtures of enantiomers will not give rotations. Why? The following are optical rotations for a series of natural products.
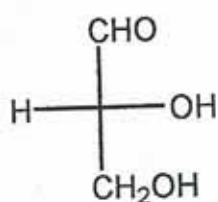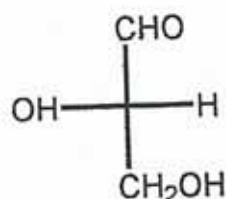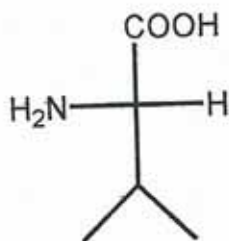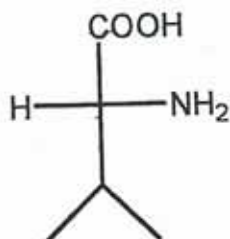

R-Glyceraldehyde   S-Glyceraldehyde

R enantiomer: $[\alpha]_D = +9.4°$ *(C=2, H$_2$O)*

S-valine   R-valine

S enantiomer: $[\alpha]_D = +27.5°$ *(C=8, 6N HCl)*

The important conclusion to draw from the above data is that there is no obvious correlation between the sign of rotation and the absolute configuration (R/S designation). Some R compounds give positive rotations and some negative rotations. There is also no obvious correlation between the magnitude of the rotation and the structure, though there must be a relationship. Once the stereochemistry is established by an independent method, the sign and magnitude of the rotation is a constant for a given chiral compound. Considering this information, can optical rotation be used to establish the absolute configuration of a newly discovered chiral compound?

The numbers reported above are called specific rotations. Since experimentally measured optical rotations are dependent on the nature of the compound, the wavelength of light, the solvent, the temperature and