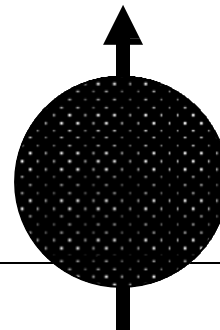# Experiment 14
IR-NMR Exercise

Preparation

Before beginning this experiment, you should have

1. studied 'Structure Determination: Mass and Infrared Spectroscopy' and
2. studied 'Structure Determination: Nuclear Magnetic Resonance'.

You may also wish to read Chapter 29 in J.W. Zubrick's 'The Organic Chem Lab Survival Manual: A Students Guide to Techniques' pp.201-222, and Chapter 30 in J.W. Zubrick's 'The Organic Chem Lab Survival Manual: A Students Guide to Techniques' pp.223-233.

Objectives

Throughout the course, you have been exposed to the technique of 'Infrared Spectroscopy'. This has allowed you to correctly predict or confirm the presence or absence of certain functional groups in organic compounds. The purpose of this experiment is to test your ability to interpret and correlate IR and ^{1}H-NMR spectra data. From this information you will be able to identify functional groups and arrangements of hydrogen atoms within a molecule. Students are encouraged to discuss their approach to interpreting the spectra of the unknowns with their instructor and academic expert.

Introduction to Infrared Spectroscopy: Theory and Practice

Electromagnetic radiation
See 'Infrared Spectra Analysis Review' of the CHEM360 Lab Manual

Infrared radiation
Remember, infrared radiation carries relatively low levels of energy (e.g. ~1-10 kcal/mol) which, when absorbed, result in only bond vibrations - stretching, rotating, bending and scissoring (i.e. deformation).
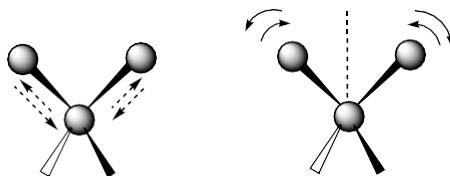
stretching vibration   bending vibration

Every molecule, depending on its makeup, is capable of absorbing infrared photons and increasing the intensity of its molecular motions. Different functional groups within the molecule will absorb photons at different infrared wavelengths. Thus, when a spectroscopic wavelength scan is performed on an organic molecule certain λ will be absorbed while other λ will pass through. Once we have the infrared spectrum of a compound, the spectrum can be analyzed and compared with known infrared absorptions for particular functional groups (see Table 14.1 and Table 14.2).

When analyzing a spectrum, it is important to look at four different regions of the spectrum for the presence or absence of specific absorption peaks. **Note:** you are not required to analyze the fingerprint region.

Table 14.1 Four Regions of the Infrared Spectrum

Wavenumber cm^{-1}

4000	3000	2000	1400	600
N-H O-H	CH	C≡N C≡C	C=C C=O C=N	fingerprint region

Table 14.2   Correlation table of infrared absorption and functional group.

Type of Absorption	Wavenumber (cm^{-1})	Intensity of Absorption	Absorption of:
O-H stretch	3400-3640	strong, broad	alcohol
	2500-3300	strong, very broad	carboxylic acid
N-H stretch	3310-3350	medium ('W' shape)	amine (1°)
C-H stretch	3300	strong	sp C-H of alkyne
	3030	medium	aromatic
	3020-3100	medium	sp^2 C-H of alkene
	2850-2960	medium to strong	sp^3 C-H of alkane
	2750 & 2850	weak-medium ('W' shape)	O=C-H of aldehyde
C≡N stretch	2210-2260	medium, sharp	nitrile
C≡C stretch	2100-2260	medium, sharp	alkyne
C=O stretch	1670-1780	strong, sharp	carbonyl
	1730-1750		ester
	1720-1740		aldehyde
	1705-1725		ketone
	1700-1725		carboxylic acid
	1640-1700		amide
	ca 1800 and 1760		anhydride
C=C stretch	1650-1670	weak-medium, sharp	alkene
	1600, 1500, 1450	strong sharp	aromatic
C=N stretch	1640-1670	medium, sharp	imine
N-H bend	1500-1650	medium to strong, sharp	amine and amide
N=O stretch	1500-1600 (1540) and 1320-1390	strong, sharp	nitro-compound
C-N stretch	1030, 1230	medium	amine
C-O stretch	1050-1150	strong	alcohol
	1250-1310	strong broad	ester-conjugated
	1240	strong, broad	ester-acetates
	1175	strong, broad	ester-unconjugated
C-Cl stretch (terminal)	600-800	strong	alkyl halide
Ar-Cl stretch	1000-1175	medium-strong	aryl halide
C-Br stretch (terminal)	500-760	strong	alkyl halide
C-I (terminal)	500	strong	alkyl halide

Note: when a C=C bond is in conjugation with a carbonyl, the observed carbonyl absorption frequency will be < ~ 30 cm^{-1}.

Calculation of the # degrees of unsaturation in a compound

(*See also 'Alkenes: Structure and Reactivity, Calculating a Molecules Degree of Unsaturation' McMurry 5th ed., p.190-192.

Number of Degrees of Unsaturation = nC +1 + 1/2N - 1/2 nH - 1/2 nX

e.g.,   Therefore, for Compound A, C_7H_{12} = (7) +1 + 1/2(0) - 1/2 (12) - 1/2(0)

= 7 + 1 - 6 = **2** degrees of

unsaturation in Compound A. Note: an aromatic ring = 4 degrees of unsaturation, 1 for the ring + 3 for the 3 double bonds = 4

In this exercise, you will be provided with infrared spectra, and hints to the λ of interest.

NMR Spectroscopy—Theory and Practice

In physics courses you would learn about many properties of electrons including their mass, charge and spin. These properties may appear to be self-evident, but really they are only conceptual models to help describe their complex behaviour. Science trivia experts probably know the following properties of the electron:

diameter = ~10^{-12} cm

rest mass= me=9.109534 × 10^{-31} kg or 0.5110041 MeV or 1/1837 of H nucleus charge= 1.60219 × 10^{-19} C

specific charge= e/me = 1.7588047 × 10^{11} C kg^{-1} magnetic moment= 9.284832 × 10^{-24} J T^{-1}

spin= ½

Note: The property of 'spin' is not exactly like the earth rotating on its axis or a merry-go-round. Rather it tells us what a particle looks like from different directions. A particle of spin =1/2 must go through two rotations to look the same! Remember 'spin' is a quantum number which explains the splitting of spectral lines and that the 'spin' of a particle can line up parallel or anti-parallel with the magnetic field of an atom.

Like the electron, many nuclei also have spin properties (e.g., ^1H, ^{13}C, ^2H, ^{14}N, ^{19}F, ^{31}P). Those that do are all with odd numbered masses or even numbered masses with odd atomic numbers. Those that do have spin properties are known as magnetic nuclei. Thus, nuclei that have even masses and atomic numbers (e.g., ^{12}C, ^{16}O, ^{32}S) are non-magnetic.

Magnetic nuclei will have nuclear spins without a specific orientation, if not in a strong external magnetic field. However, when placed into a magnetic field the nuclei will orient themselves parallel (favoured lower energy state) or anti-parallel (less favoured higher energy state) with the field. Then if the nuclei are exposed to radio waves of the right frequency, energy absorption can occur, and the parallel spin will convert to anti-parallel spin (spin-flip). This spin-

flipping between energy states of the two spin orientations of the nucleus is what is meant by 'nuclear magnetic resonance'.

Nuclear magnetic resonance (NMR) spectroscopy is a very useful tool for organic chemists. Used in conjunction with mass and IR spectroscopy, it allows you to form a framework of the carbon-hydrogen and carbon-carbon bonds in a molecule from which you can infer the structure and identity of a compound.

When you look at a ^{1}H-NMR spectrum you are trying to decipher and correlate four different kinds of information. Because the information in NMR spectra sometimes is very complex, you must develop a systematic approach to analyzing NMR spectra.

1. First the spectrum contains **chemical shift (δ) information** (i.e. the position of the peak) which tells you about the structural grouping to which the H is bound (analogous to relationship between infrared λ and functional groups). Chemical shifts (δ) are measured in **hertz (Hz) or ppm** and are the distance from the center of the signal to a reference signal, usually tetramethylsilane (TMS). Refer to the chemical shifts shown in Table 14.3.

2. Second, the size of or area under a peak (determined by **integration**) tells you about number of identical H in a particular electronic environment.

Table 14.3 ¹H NMR Chemical Shifts (σ, ppm) for Various Functional Groups

|	σ, ppm			σ, ppm
TMS (CH₃)₄Si	0	TMS is used as reference for both ¹H and ¹³C-NMR. It gives rise to a single peak that occurs upfield (farther right) of other absorptions normally found in organic cmpds.	Alcohols, ethers	
Cyclopropane	0.0-0.4		HO—C—H	3.3-4.0
Alkanes				
RCH₃	0.7-1.3		RO—C—H	3.3-4.0
R₂CH₂	1.2-1.4			
R₃CH	1.4-1.7			
Alkenes		Vinylic protons are strongly deshielded by the neighbouring pi bond and therefore absorb in this characteristc downfield position.	Esters	
—C=C—H (vinyl)	4.6-5.9		R—C—O—C—H	3.7-4.1
—C=C—CH₃ (allyl)	1.6-1.9	protons on C next to unsaturated (allylic, benzylic, next to carbonyl) show charact. absorptions in this region, just downfield from other alkane resonance.	RO—C—C—H	2.0-2.6
Alkynes			Carboxylic acids	
—C≡C—H (alkynyl)	2.5-2.7			
—C≡C—CH₃	1.8		HO—C—C—H	2.0-2.6
Aromatic		protons on aromatic rings (aryl protons) are strongly deshielded by the pi orbitals of the ring and show charact. absorptionsin this lower-field range.	R—C—O—H	10.5-12
Ar—H (aryl)	6.5-8.0		Ketones	
Ar—C—H (benzyl)	2.5-2.7		R—C—C—H	2.1-2.4
Fluorides, F—C—H	4.0-4.5		Aldehydes	
Chlorides, Cl—C—H	3.0-4.0	protons on C next to electronegative atoms (X, O, N) are deshielded because of the electron-withdrawing ability of these atoms. Thus the protons absorb in this midfield range.	R—C—H	9.7-10.0
Cl—C—H (with Cl)	5.8		Amides	
			R—C—N—H	5.0-8.0
Bromides, Br—C—H	2.5-4.0	protons on oxygen bearing C atoms are deshielded by the electron-withdrawing effect of the nearby O. Splitting of OH proton not usually observed, therefore usually seen as a broad singlet.	Alcohols R—O—H	2.5-5.0
			Phenols Ar—O—H	4.0-12.0
Iodides, I—C—H	2.0-4.0		Amines R—NH₂	1.0-5.0
Nitroalkanes, O₂N—C—H	4.2-5.6			

6

The integration data may be in the form of **'peak areas'** or an **'integration line'** on the NMR spectrum. If the integration data is in the form of peak areas, the number of protons responsible for signal is easily obtained from the integration by looking at the molecular formula for the unknown and using the following equation:

$$\text{\# of Protons Responsible for Signal} = \text{total \# of protons in molecule} \times \frac{\text{area under signal}}{\sum \text{area under all signals}}$$

e.g., If the molecular formula of the unknown is C_6H_{11}, and has 3 signals with areas of 31, 6, and 20 (sum = 57), then the number of protons responsible for the first signal is $11 \times 31/57 = 5.98 = 6$; and $11 \times 6/57 = 1.15 = 1$ for the second signal; and $11 \times 20/57 = 3.86 = 4$ for the third signal (6 + 1 + 4 = 11).

If the integration data is in the form of an 'integration line' on the NMR spectrum, the number of protons responsible for signal is obtained by measuring the height (h) of each of the integration lines for each of the signals. The **ratio of the signal's heights** is then compared with the molecular formula to determine the number of protons responsible for each signal.

Integration line

h

4   2
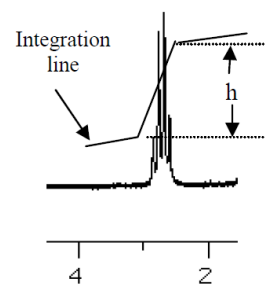
Note: in this experiment, the integration data has been analyzed and given to you.

3. The third type of information you are looking for is called **signal splitting or multiplicity**. This information tells you about the number of neighbouring H and is calculated using the 'n+ 1 Rule'.

$$N = n + 1$$

where N = number of peaks observed, and n = number of equivalent adjacent H (see Table 14.4 for calculating signal splitting).

Table 14.4 Signal Splitting Calculation Using Pascal's Triangle (N=n+1)

N = number of peaks observed for absorbing protons.
n = number of equivalent adjacent hydrogens.

Pascal's Triangle	n+1	n	splitting
1	1	0	singlet
1 1	2	1	doublet
1 2 1	3	2	triplet
1 3 3 1	4	3	quartet
1 4 6 4 1	5	4	quintet
1 5 10 10 5 1	6	5	sextet
1 6 15 20 15 6 1	7	6	septet

4. The last type of information to seek has to do with **coupling constants (J)**.

7

This is the distance between two adjacent peaks in the signal and is measured in hertz. For ideal triplets and quartets, their signal peaks should be symmetrical with relative peaks areas of 1:2:1 and 1:3:3:1 respectively. In actual spectra this is rarely the case, and the peak ratios are distorted.

In Figure 14.5, the peaks of two sets of protons are interacting with each other, i.e., they share the **same** coupling constant (J_{ab}), they are leaning towards each other, and the peaks on the side nearest the other set of signals are higher than predicted.
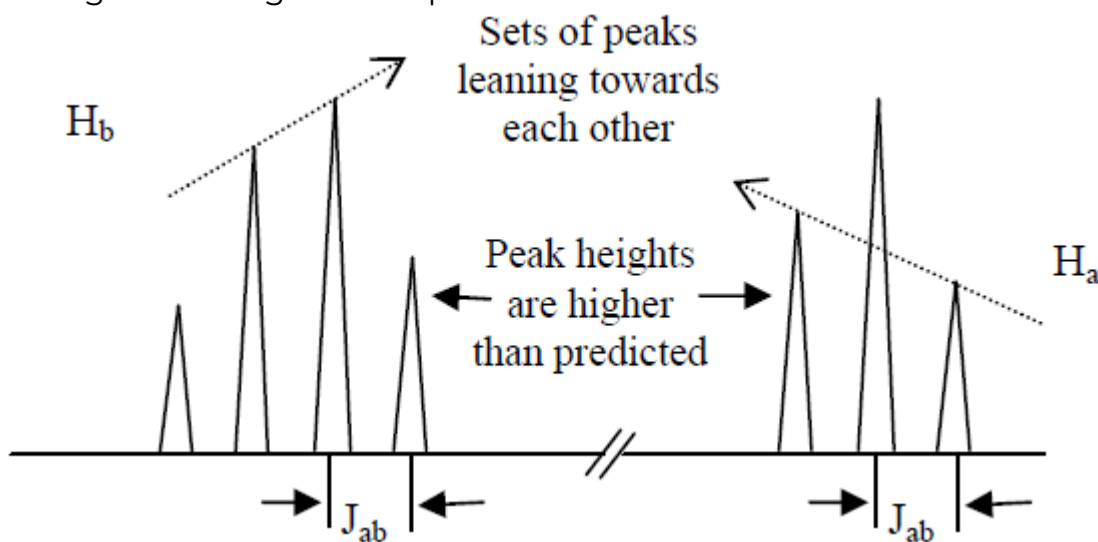

Figure 14.5 Coupling constant (J) for nearest neighbouring H's.

The protons of 'set H_a' have split the protons of 'set H_b' into a quartet and the protons of 'set H_b' have split the protons of 'set H_a' into a triplet. The interacting triplet-quartet peaks of this kind are evidence of the presence of an ethyl group (CH_3CH_2-) in the molecule.

In summary, you must systematically analyze a ^{1}H-NMR and correlate four different kinds of information: the chemical shift, the integration, the multiplicity or signal splitting pattern, and the coupling constants.

Finally, as a chemistry student, is essential that you have a good understanding of the concepts and practice of ^{1}H-NMR. Unfortunately, modern NMR spectrometers are very expensive to own and require a great deal of technical experience to operate. Therefore, in this course you will only be able to gain experience in the theory, interpretation and analyses of ^{1}H- NMR spectra. This exercise, where you are provided with unknown ^{1}H-NMR spectra plus integration data, will allow you learn and practice this important area of chemistry.

Procedure

1. Do the instructor led and practice problems.

2. Obtain 4 unknown samples of organic compounds, and perform melting points or boiling points, and mass, infrared, and ^{1}H-NMR spectroscopy on each of them (This may have been already done for you!).

3. Analyze the provided spectral data and determine the identity and structure of each unknown. (Your instructor will provide you with a handout for each unknown).

4. Calculate the 'Degrees of Unsaturation' present in the molecule.
    Number of Degrees of Unsaturation = nC +1 + 1/2nN - 1/2 nH - 1/2 nX

5. Then analyze the infrared spectrum.

6. It is suggested you analyze your ^{1}H-NMR spectra as follows:

    a) Always survey the spectrum from left (downfield) to right (upfield). As a rule, the further the H signal is shifted downfield, the more electronegative the group to which the H is bound.
    b) Number/code the signals, furthest downfield being #1 or A.
    c) Ask yourself how many hydrogens are giving rise to each signal?
    d) Determine the chemical shift of the signal (δ), in PPM.
    e) Next determine the multiplicity of the signal. Is it a singlet, doublet, triplet, quartet, sextet, septet, multiplet? From this you will be able to say how many H are on the neighbouring carbon.
    f) Now begin to build the framework of C, H, O, and N, which is also supported by the information obtained from the mass and infrared spectra. From this you will eventually obtain the complete structure or the molecule.
    g) Once you have arrived at a structure, confirm the presence (or absence) or the expected peaks such a molecule would give in the Infrared and ^{1}H-NMR spectra. Check to see if the other physical data matches your conclusion (mp or bp, and chemical formula).

7. Submit your answers, along with your reasoning and spectra, in a brief lab report (see 'Write-up Instructions'). If you have any questions about the data, please call your instructor or AE.

How to Interpret an Infrared Spectrum

Step 1   Divide the infrared spectrum into four main areas (use pencil and ruler and take into account any off shift in the spectrum's wavenumbers).
- i)   Above 3000 cm^{-1}
- ii)   Between 3000 and 2000 cm^{-1}
- iii)   Between 2000 and 1400 cm^{-1}
- iv)   Below 1400 cm^{-1} (fingerprint region)

Step 2   Starting at the left of the spectrum, examine the area **above 3000 cm^{-1}**, first looking in the region near 3300 cm^{-1} and record in tabular format the presence/absence of:
- i)   A broad, very strong absorption band of an **'O-H'**. If present, it means you know that your molecule is at least an **alcohol**.
- ii)   A broad, weak to medium strength, double or single absorption band of **'N-H'**. If present it means you have an **amine** (1° or 2°) or possibly an **amide**.
- iii)   A sharp, medium to strong, single absorption band of **'≡C-H'** of a **terminal alkyne**. Note: If present, it means you should also see a 'C≡C' absorption near 2250 cm^{-1}.

After examining the region around 3300 cm^{-1}, look for any sharp, weak to medium absorption just above 3000 cm^{-1} (e.g. 3050 cm^{-1}) resulting from the 'C-H' stretch of a sp^2 hybridized carbon. If present, it means you have a **'C=C-H'** of an alkene or aromatic compound.

Step 3   Next examine the area between **3000 and 2000 cm^{-1}** and record the presence/absence of absorption bands or peaks.
- i)   First look just below 3000 cm^{-1} (e.g. 2850-2950 cm^{-1}) resulting from the 'C-H' stretch of a sp^3 hybridized carbon. If present, it means you are seeing the **'C-H'** stretch of an **-CH$_2$ or -CH$_3$** group. Note: This absorption is not very informative as most organic compounds have -CH$_2$ or -CH$_3$ groups.
- ii)   Then look for the extremely broad peak, starting at 3300 cm^{-1} and extending all the way to ~2500 cm^{-1}, caused by the **O-H dimer** between two **carboxylic acid** molecules (COOH). This absorption is probably the most difficult to see as other absorption peaks may be overlapping the broad peak.
- iii)   Finally look for a sharp, weak to medium peak caused by either **'C≡C'** or **'C≡N'**.
- iv)   If present, then the compound is an alkyne (might also have the 'C-H' of a terminal alkyne, see step 2 above) or a nitrile.

Step 4   Next examine the area between **2000 and 1400 cm^{-1}** and record the presence/absence of absorption bands or peaks.
- i)   First look near 1700 cm^{-1} (e.g. 1680-1750 cm^{-1}) for a sharp, strong peak resulting from the **'C=O'** stretch of a **carbonyl**. Note: <u>This absorption is very informative</u> and will be present if your compound is an aldehyde, ketone, ester, amide, or carboxylic acid.
- ii)   Next look near 1650 cm^{-1} (e.g. 1600-1670 cm^{-1}) for a sharp, weak peak resulting from the **'C=C'** stretch of an **alkene**.

iii) Finally look near 1600 cm^{-1} and 1500 cm^{-1} for a sharp, double peak resulting from the **'C=C'** stretch of an **aromatic ring**.

Step 5 If you dare, you may look in the **fingerprint region (area below 1400 cm^{-1})** and record the presence of absorption bands or peaks.

i) First look near 1200 cm^{-1} for a sharp, strong peak resulting from the **'C-O'** stretch of an **ester**. Note: <u>This absorption is very difficult to see and may or may not be present</u>, i.e. conclusive if present, inconclusive if not present.

ii) If you suspect you have an aromatic ring (absorption bands at ~3030 and 1600 and 1500 cm^{-1} present), you may try to discern the substitution pattern of the benzene ring by looking at the strong absorption bands of the **ring 'C-H'** out-of-plane bending vibrations in the region 680- 900 cm^{-1}.

Benzene Substitution Pattern	Ring 'C-H' Absorption Bands Present (cm^{-1})
monosubstituted	2 sharp peaks, 730-770, 690-710
ortho disubstituted	1 sharp peak, 735-770
meta disubstituted	3 sharp peaks, 860-900, 750-810, 680-725
para disubstituted	1 sharp peak, 800-860
1,2,3 trisubstituted	2 sharp peaks, 760-780, 705-745
1,3,5 trisubstituted	2 sharp peaks, 810-865, 675-730
1,2,4 trisubstituted	2 sharp peaks, 870-885, 805-825

Ref: McMurry, J., 2000. Organic Chemistry, 5th ed, Brooks/Cole, p.578-579, (4th ed, p.559) Nakanishi, K., 1964. Infrared Absorption Spectroscopy, Holden Day p.27.

iii) If you suspect you have a long straight chain (>4 C) alkane, (absorption bands at 28050-2950 cm^{-1} present but not much else), you may try to see the sharp, weak absorption due to the concerted rocking or >4 -CH$_2$ in a chain. It lies in the region 720 ± 10 cm^{-1}.

Step 6 Finally, you will summarize your results by making a statement as to what functional groups you suspect to be present in the molecule or perhaps you will be asked to select from a list of suggested structures, which molecule most likely would generate the spectrum just analyzed.

As tabular format that you might find useful for recording your findings is shown below:

Infrared Data:

	Absorption Band#	Frequency (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm^{-1}					
Between 3000 and 2000 cm^{-1}					
Between 2000 and 1400 cm^{-1}					
< 1400 cm^{-1}					

Functional Group(s) absent:

How to Interpret a ^{1}H-NMR Spectrum

Step 1   Survey the ^{1}H-NMR spectrum from left (downfield) to right (upfield). As a rule, the further the H signal is shifted downfield, the more electronegative the group to which the H is bound. Assign a code # for each signal or group of signals, furthest downfield being #1. Remember, each signal or group of signals represents a proton(s) in a different chemical environment.

Step 2   Determine the **chemical shift** (δ or delta scale, PPM) for each signal, or group of signals, by measuring the distance from the reference TMS peak to the center of the signal or group of signals.

Step 3   Determine the **number of hydrogens** giving rise to each signal or group of signals. This information may be provided (integration data), or you may have to measure the area under the peak(s) of each signal. It is important to check that the sum of the # of protons from each signal adds up to the total number of H indicated in the molecular formula.

Step 4   Determine the **multiplicity or splitting pattern** of the signal or group of signals by counting the number of distinguishable peaks. This may be difficult at times as very weak peaks may be overshadowed by background noise. Also note that you can have irregular signals, and signals that have been split by several other unequivalent protons. In this case, more advanced methods of analysis than shown here are then required to determine the multiplicity.

Step 5   Use the **N = n + 1** rule to determine the number of **neighbouring hydrogens** for each signal. (N = number of peaks observed, and n = number of equivalent adjacent H.)

Splitting Pattern	# of Neighbouring Hydrogens
singlet	0
doublet	1
triplet	2
quartet	3
quintet	4
sextet	5
septet	6

see Table 14.4 for calculating signal splitting

Step 6   Make your **signal assignments** after consulting the Table 14.3 ^{1}H-NMR Shifts for Various Functional Groups.

Step 7   This is the most crucial step in the analysis, and the most difficult. Now you must begin to put together all your results, using the signal assignments, the infrared spectra data, the degrees of unsaturation, and molecular formula to piece together the structure of the unknown organic compound. The tabular format that you will find useful for recording your results is shown below:

Table #X. ^{1}H-NMR Spectral Data:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

In the following pages, we present sample spectrum interpretations for 2-propanol and for 1-propanol.

Sample Interpretation of a ¹H-NMR Spectrum

Use the following examples to understand the step-by-step approach of how to use a ¹H-NMR spectrum to identify an unknown. Please note that the 'degrees of unsaturation' has been calculated, and the infrared spectrum has already been analyzed.

Experiment 14   Student Name: **Earle L. Mier**   AU ID#: 2550100

Unknown #: 360-14-A   Mol. Wt.: 60.1 g/mol   Formula: C_3H_8O BP: 82.4° C

Infrared Spectrum of 360-14-B (thin film) CDCl₃)

¹H-NMR Spectrum of 360-14-B (90 MHz in
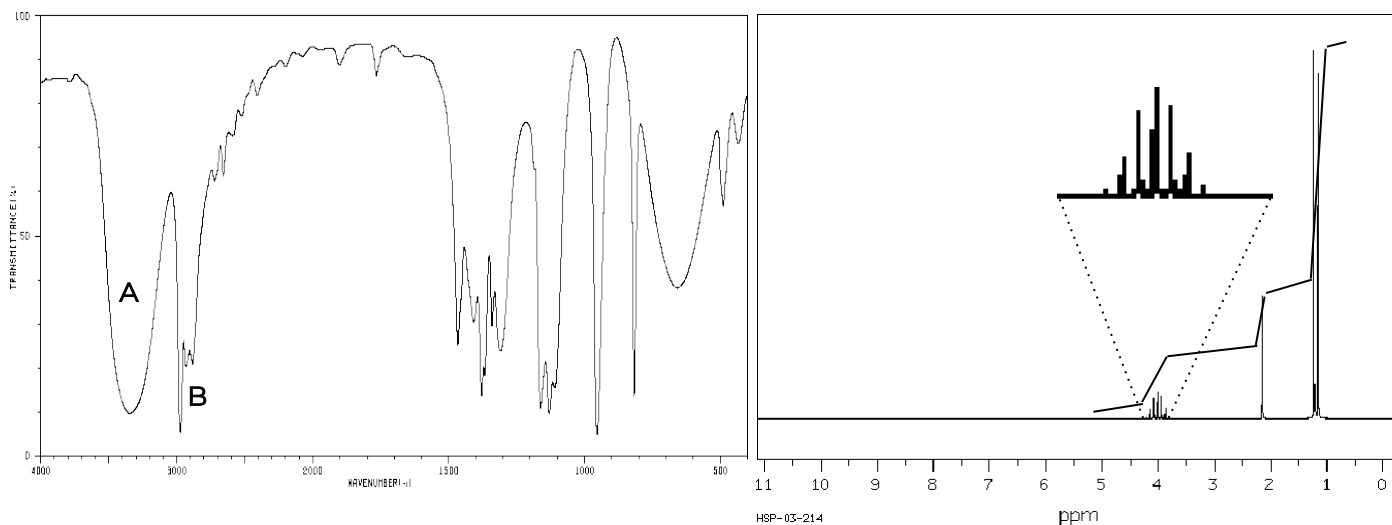
Number of Degrees of Unsaturation   =   nC +1 + 1/2nN - 1/2 nH - 1/2 nX

for Compound 360-14-A, C_3H_8O =   (3) +1 + 1/2(0) - 1/2 (10) - 1/2(0)

=   (3 + 1 + 0 - 4 - 0) = **0** degrees of unsaturation

Infrared Spectrum Data for Unknown 360-14-A:

	Absorption Band	Frequency (cm⁻¹)	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm⁻¹	A	3346	Broad	Strong	O-H stretch of alcohol
Between 3000 and 2000 cm⁻¹	B	2972, 2933, 2884	Multiple, Sharp	Strong	sp³ C-H stretches of alkane
Between 2000 and 1400 cm⁻¹					
< 1400 cm⁻¹					

Functional Group(s) absent: no N-H, C≡C-H, sp² C-H, C≡C, C≡N, C=O, C=C alkene or aromatic

Interpretation of the ¹H-NMR Spectrum for Unknown 360-14-A

Step 1   Survey the ¹H-NMR spectrum from left (downfield) to right (upfield), assigning a code # for each signal or group of signals, furthest downfield being #1. Two proton signals are shifted downfield, indicating they are 'close' to an electronegative group (deshielded). The spectrum also indicates that there are proton(s) in a total of 3 different chemical environment. Note that Signal 1 has been expanded for easier viewing.
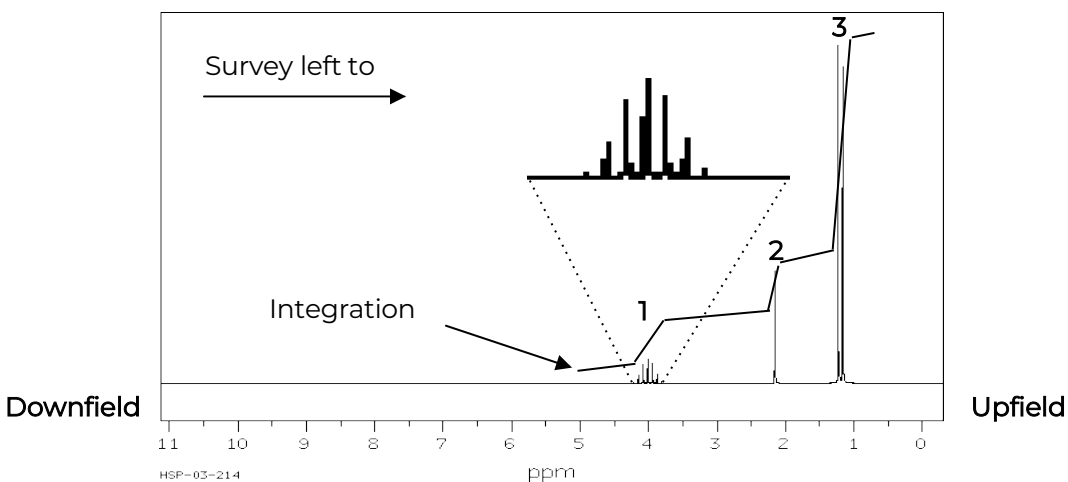
Survey left to →

Integration

Downfield ← → Upfield

11 10 9 8 7 6 5 4 3 2 1 0
ppm

HSP-03-214

.

¹H-NMR Spectral Data for Unknown 360-14-A:

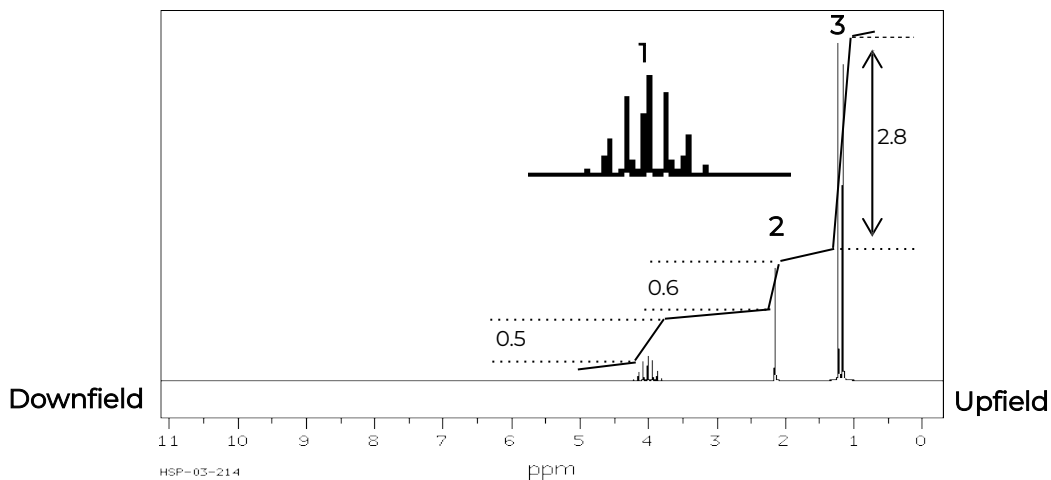| Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1				Shifted downfield		
2				Shifted downfield		
3						

Step 2   Determine the **chemical shift** (δ or delta scale, PPM) for each signal, or group of signals, by measuring the distance from the reference TMS peak (0.0) to the center of the signal or group of signals.

11 10 9 8 7 6 5 4 3 2 1 0
ppm

HSP-03-214
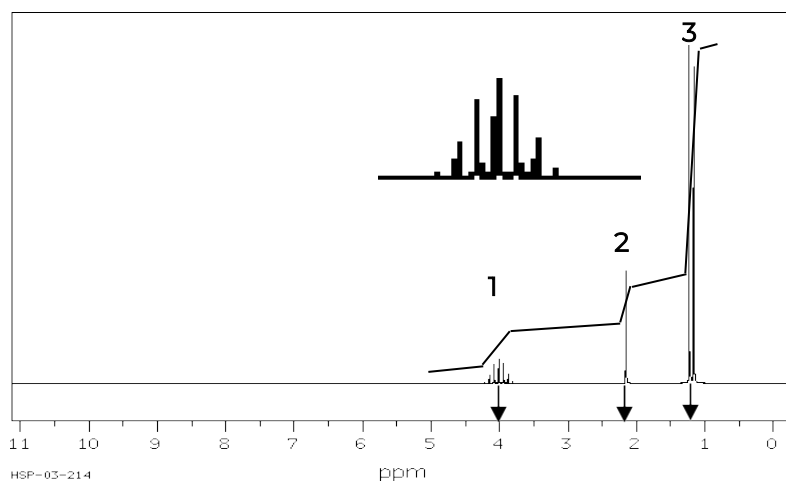
¹H-NMR Spectral Data for Unknown 360-14-A:

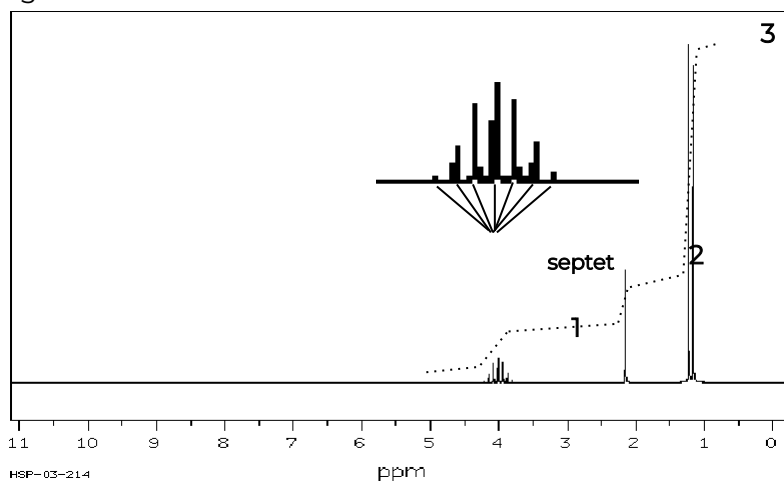| Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	4.0			Shifted downfield		
2	2.15			Shifted downfield		
3	1.2					

Step 3   The **number of hydrogens** giving rise to each signal or group of signals may be provided as integration data, or you may have to determine the ratio of the area under the peak(s) of each signal. Use a ruler to measure the height of each integration line (from left to right = 0.5 cm: 0.6 cm: 2.8 cm). The sum of the # of protons from all signals must add up 8 = the total number of H indicated in the molecular formula. In this case, this is accomplished by multiplying by 2 and rounding off the ratio of heights (from left to right = 1 : 1 : 6) = 8 H total.

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Downfield ... **Upfield**

HSP-03-214

ppm

¹H-NMR Spectral Data for Unknown 360-14-A:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	4.0	1		Shifted downfield		
2	2.15	1		Shifted downfield		
3	1.2	6				

Step 4 Determine the **multiplicity or splitting pattern** of the signal or group of signals by counting the number of distinguishable peaks in each signal. Signal 1 is a septet (as shown on the expanded area below). Signal 2 is a singlet. Signal 3 is a doublet.

HSP-03-214

ppm

¹H-NMR Spectral Data for Unknown 360-14-A:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	4.0	1	septet	Shifted downfield		
2	2.15	1	singlet	Shifted downfield		
3	1.2	6	doublet			

Step 5 Use the **N = n + 1** rule to determine the number of **neighbouring hydrogens** for each signal. (N = number of peaks observed, and n = number of equivalent adjacent H.)
For Signal 1, N = n + 1 = (7 = n + 1), so n = 6. Signals 2-4 # Neighbouring H are calculated the same way.

¹H-NMR Spectral Data for Unknown 360-14-A:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	4.0	1	septet	Shifted downfield	6	
2	2.15	1	singlet	Shifted downfield	0	
3	1.2	6	doublet		1	

Step 6 Make your **signal assignments**, consulting Table 14.3 ¹H-NMR Shifts for Various Functional Groups.

-According to Table 14.3, **Signal 1** (downfield 1H septet at δ 4.0) must be an alkyl halide, an ether, or an alcohol. It can't be an alkyl halide, because there is no halogen in the molecular formula, so it must be an ether, or an alcohol. It is therefore given the signal assignment of R-O-C**H**-R$_2$.

-We know that there is an alcohol in this unknown compound from the infrared analysis (absorption band A). Therefore, we must look to find a decoupled (0 neighbours), deshielded (shifted downfield) signal due to a single proton bonded directly to an oxygen. Only **Signal 2** (singlet, 1H at δ 2.15) could be the H of the hydroxyl group of an alcohol. It is therefore given the signal assignment of R-O-**H**.

-**Signal 3** (6H at δ 1.2) is due to an alkane R-C**H**$_3$ (δ 0.7-1.3), or R$_2$-C**H**$_2$ (δ 1.2-1.4), but not R$_3$-C**H** (δ 1.4-1.7). It is likely that Signal 3 is slightly shifted down field, and so it is more likely the signal assignment should be R-C**H**$_3$.

¹H-NMR Spectral Data for Unknown 360-14-A:

| Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	4.0	1	septet	Shifted downfield	6	R-O-CH-R$_2$
2	2.15	1	singlet	Shifted downfield	0	R-O-**H** of an alcohol
3	1.2	6	doublet		1	R-(CH$_3$)$_2$

Your ¹H-NMR Spectral Data Table is now complete. Proceed to Step 7 on the next page. Please note that you have not been asked to extract information from the spectrum regarding coupling constants (J).

Step 7 Again, this is the crucial step of the analysis. Let's begin to put together all your results by using the signal assignments, the infrared spectra data (O-H in molecule), the degrees of unsaturation (0), and molecular formula (C$_3$H$_8$O).

Rationale:

It was immediately apparent that unknown 360-14-A is an **alcohol**, -OH, due to the broad infrared absorption band O-H at 3346 cm^{-1}, and an downfield lone proton (Signal 2 singlet at δ 2.15).

(Note: 'Atomic Accounting' is now: C$_3$H$_8$O - OH = C$_3$H$_7$).

$$H\!\!-\!\!O\!\!-\!\!\underset{2}{}$$
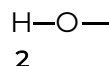
Signal 1 indicates there is a R-O-C**H**- (δ = 4.0, Integration = 1H, splitting pattern = septet) in the molecule. Also this O-C**H**- must have a neighbouring carbons with 6 H on it, so it must be O-CH- (CH$_3$)$_2$. This is confirmed by the presence of a R-**CH$_3$ group** (δ=1.2, Integration = 6H, splitting pattern = doublet). The last piece of the puzzle is that the CH$_2$ group is shifted downfield (δ=3.67) and so must be bonded to the only oxygen in the molecule, i.e. an **O-CH-(CH$_3$)$_2$- group**.

(Note: 'Atomic Accounting' is now: C$_3$H$_7$ - CH = C$_2$H$_6$).

$$\underset{2}{H}\!\!-\!\!O\!\!-\!\!\underset{1}{CH\text{-}R_2}$$
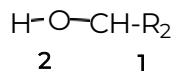
Signal 3 confirms that there are 2 **methyl groups** R-CH$_3$ (δ=1.2, Integration = 6H, splitting pattern = doublet). Also, these 2 -CH$_3$- both have the same neighbouring carbon with a single1 H, so Signal 3 must be due to (C**H**$_3$)$_2$-CH-.
(Note: 'Atomic Accounting' is now: C$_2$H$_6$ - 2(CH$_3$) = 0, all atoms accounted for!).
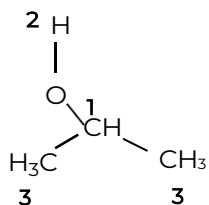
In summary unknown #360-14-A contains an alcohol, and 2 methyl groups. Therefore, the **Unknown #360-14-A** must be **2-propanol**, which also has the correct/matching molecular weight/formula, and boiling point. Also, the ^{1}H-NMR Spectrum shows there are 3 different types of H environments present in the molecule (and all 3 have been accounted for).
Note: The calculation for the 'degrees of unsaturation' in this problem also makes sense. There are 0 degrees of unsaturation present in the unknown.
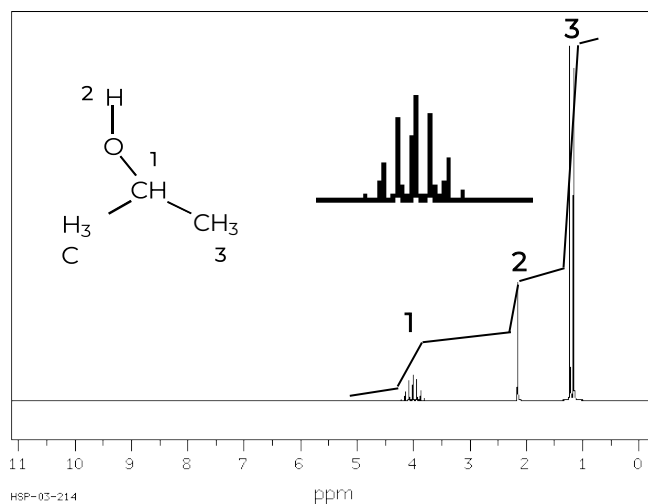
# Another Sample Interpretation of a ^{1}H-NMR Spectrum

Use the following examples to understand the step-by-step approach of how to use a ^{1}H-NMR spectrum to identify an unknown. Please note that the 'degrees of unsaturation' has been calculated, and the infrared spectrum has already been analyzed.

Experiment 14   Student Name: **R.B. Flask**   AU ID#: 2550100

Unknown #: 360-14-B   Mol. Wt.: 60.1 g/mol   Formula: C_3H_8O BP: 97° C

Infrared Spectrum of 360-14-B (thin film) CDCl$_3$)

^{1}H-NMR Spectrum of 360-14-B (90 MHz in
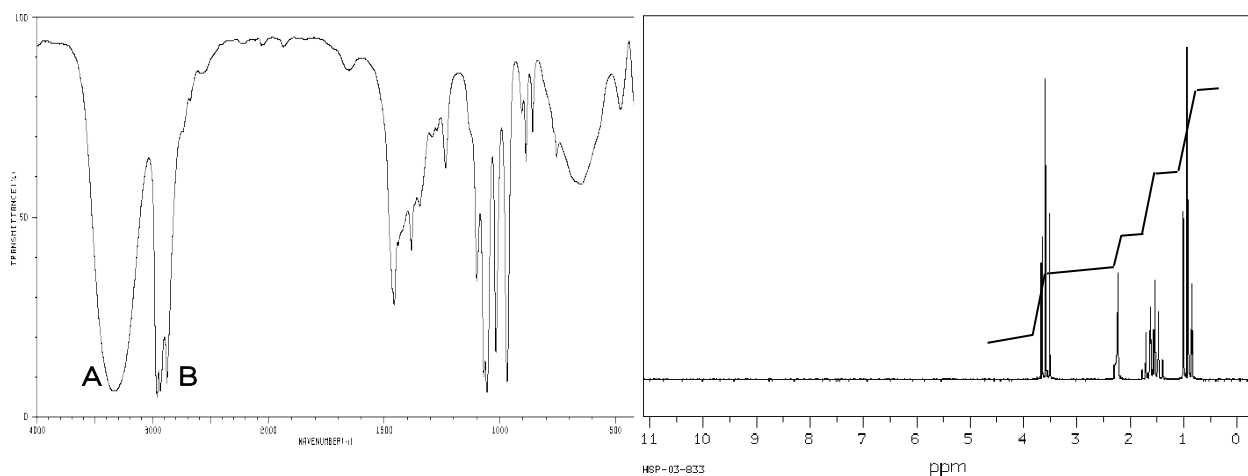
| Number of Degrees of Unsaturation | = | nC +1 + 1/2nN - 1/2 nH - 1/2 nX |
| for Compound 360-14-B, C_3H_8O | = | (3) +1 + 1/2(0) - 1/2 (10) - 1/2(0) |
| | = | (3 + 1 + 0- 4 - 0) = 0 degrees of unsaturation |

Infrared Spectrum Data for Unknown 360-14-B:

	Absorption Band	Frequency (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm^{-1}	A	3333	Broad	Strong	O-H stretch of alcohol
Between 3000 and 2000 cm^{-1}	B	2963, 2938, 2878	Multiple, Sharp	Strong	sp^3 C-H stretches of alkane
Between 2000 and 1400 cm^{-1}					
< 1400 cm^{-1}					

Functional Group(s) absent: no N-H, C≡C-H, sp^2 C-H, C≡C, C≡N, C=O, C=C alkene or aromatic

## Interpretation of the ¹H-NMR Spectrum for Unknown 360-14-B

Step 1   Survey the ¹H-NMR spectrum from left (downfield) to right (upfield), assigning a code # for each signal or group of signals, furthest downfield being #1. Two proton signals are shifted downfield, indicating they are 'close' to an electronegative group (deshielded). The spectrum also indicates that there are proton(s) in a total of 4 different chemical environment.
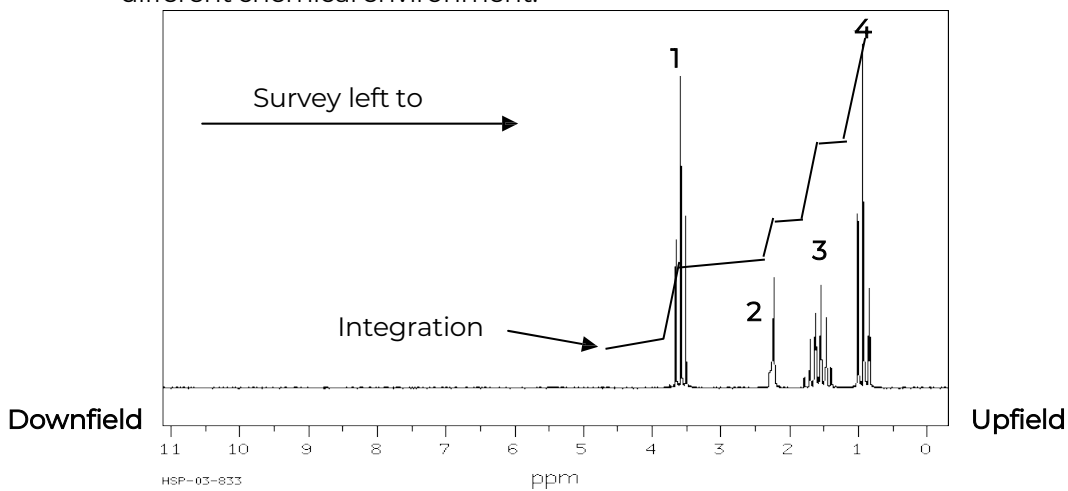
¹H-NMR Spectral Data for Unknown 360-14-B:

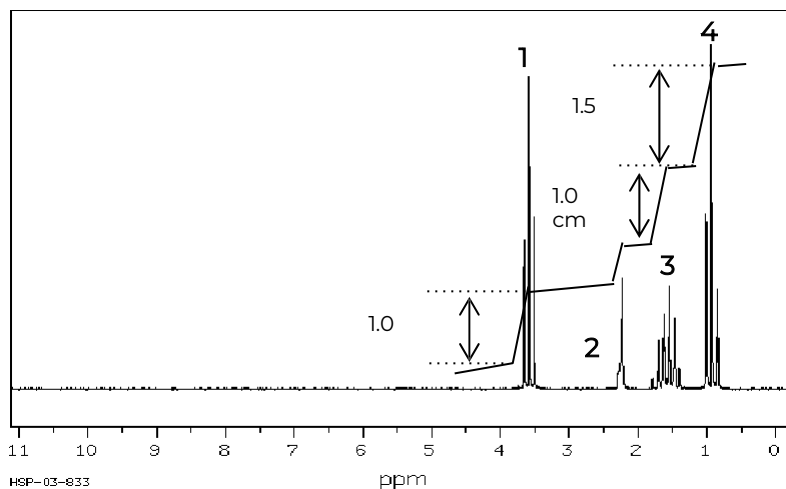| Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1				Shifted downfield		
2				Shifted downfield		
3						
4						

Step 2   Determine the **chemical shift** (δ or delta scale, PPM) for each signal, or group of signals, by measuring the distance from the reference TMS peak (0.0) to the center of the signal or group of signals.

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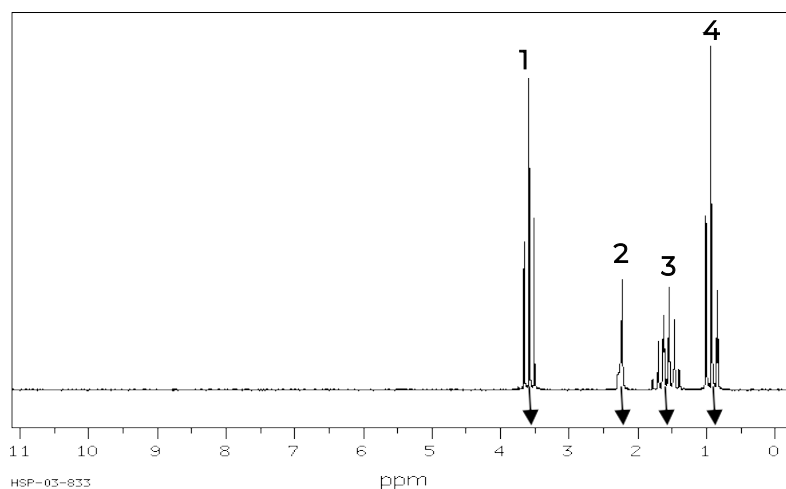
¹H-NMR Spectral Data for Unknown 360-14-B:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	3.6			Shifted downfield		
2	2.25			Shifted downfield		
3	1.6					
4	0.95					

Step 3   The **number of hydrogens** giving rise to each signal or group of signals may be provided as integration data, or you may have to determine the ratio of the area under the peak(s) of each signal. Use a ruler to measure the height of each integration line (from left to right = 1cm: 0.5cm: 1cm: 1.5cm). The sum of the # of protons from all signals must add up 8 = the total number of H indicated in the molecular formula. This is accomplished by multiplying the ratio of heights by 2 (from left to right = 2 : 1 : 2 : 3) = 8 H total.
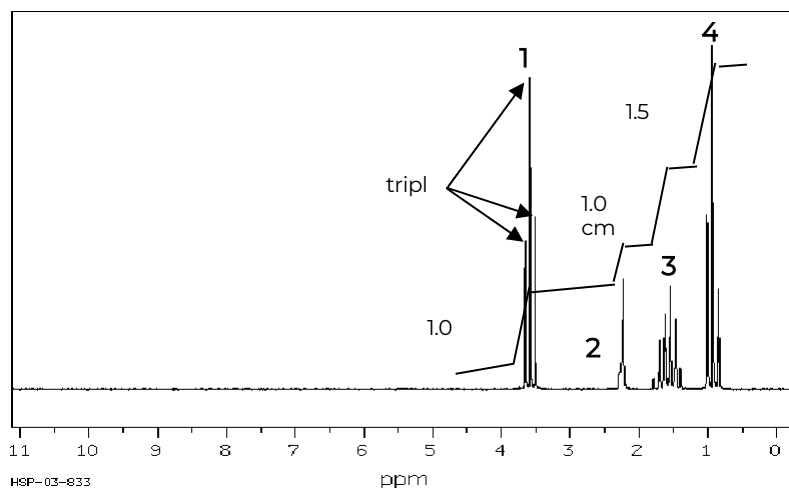

HSP-03-833

¹H-NMR Spectral Data for Unknown 360-14-B:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	3.6	2		Shifted downfield		
2	2.25	1		Shifted downfield		
3	1.6	2				
4	0.95	3				

Step 4   Determine the **multiplicity or splitting pattern** of the signal or group of signals by counting the number of distinguishable peaks in each signal. Signal 1 is a triplet (as shown on the spectrum below). Signal 2 is a singlet. Signal 3 is difficult to interpret, but it is a quintet. Signal 4 is clearly a triplet.

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HSP-03-833

Step 5   Use the **N = n + 1** rule to determine the number of **neighbouring hydrogens** for each signal. (N = number of peaks observed, and n = number of equivalent adjacent H.) For Signal 1, N = n + 1 = (3 = n + 1), so n = 2. Signals 2-4 # Neighbouring H are calculated the same way.

^{1}H-NMR Spectral Data for Unknown 360-14-B:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	3.6	2	triplet	Shifted downfield	2	
2	2.25	1	singlet	Shifted downfield	0	
3	1.6	2	quintet		4	
4	0.95	3	triplet		2	

Step 6   Make your signal assignments, consulting Table 14.3 ^{1}H-NMR Shifts for Various Functional Groups.
-According to Table 14.3, **Signal 1** (2H at δ 3.6) must be an alkyl halide, an ether, or an alcohol. It can't be an alkyl halide, because there is no halogen in the molecular formula, so it must be an ether, or an alcohol. It is therefore given the signal assignment of R-O-C**H**$_2$-.
-We know that there is an alcohol in this unknown compound from the infrared analysis (absorption band A). Therefore we must look to find a decoupled (0 neighbours), deshielded (shifted downfield) signal due to a single proton bonded directly to an oxygen. Only **Signal 2** (singlet, 1H at δ 2.25) could be the H of the hydroxyl group of an alcohol. It is therefore given the signal assignment of R-O-**H**.
-According to Table 14.3, **Signal 3** (2H at δ 1.6) must be due to an alkane or alkene. Since there is no C=C in the molecule (see infrared data, and degrees of unsaturation = 0), it must be due to an alkane R-C**H**$_3$, R$_2$-C**H**$_2$ or R$_3$-C**H**. Of the three possibilities, the table suggests it could be R$_3$-C**H** (δ 1.4-1.7). But what if Signal 3 is near enough to be coupled with protons bonded to a carbon bonded to an oxygen. They might be slightly deshielded as well, due their 'close' proximity to the electron- withdrawing oxygen. So this signal could also be due to R$_2$-C**H**$_2$ (δ 1.2-1.4). This makes more sense, since we are

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dealing with a 2H signal (integration = 2). Thus Signal 3 is given the signal assignment R_2-C**H**$_2$.

-**Signal 4** (3H at δ 0.95) must be due to an alkane R-C**H**$_3$ (δ 0.7-1.3).

^{1}H-NMR Spectral Data for Unknown 360-14-B:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	3.6	2	triplet	Shifted downfield	2	R-O-C**H**$_2$-
2	2.25	1	singlet	Shifted downfield	0	R-O-**H** of an alcohol
3	1.6	2	quintet		4	R_2-C**H**$_2$
4	0.95	3	triplet		2	R-C**H**$_3$

Your ^{1}H-NMR Spectral Data Table is now complete. Proceed to Step 7.
Please note that you have not been asked to extract information from the spectrum regarding coupling constants (J).

Step 7   This is the most crucial step in the analysis, and the most difficult. Now you must begin to put together all your results by using the signal assignments, the infrared spectra data (O-H in molecule), the degrees of unsaturation (0), and molecular formula (C_3H_8O).

Rationale:

It was immediately apparent that unknown 360-14-B is an **alcohol**, -OH, due to the broad infrared absorption band O-H at 3333 cm^{-1}, and a downfield lone proton (Signal 2 singlet at δ 2.25).
   (Note: 'Atomic Accounting' is now: C_3H_8O - OH = C_3H_7).

$$H\text{—}O\text{—}$$
$$\mathbf{2}$$
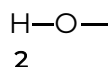
Signal 1 indicates there is a R-O-C**H**$_2$- (δ = 3.6, Integration = 2H, splitting pattern = triplet) in the molecule. Also, this O-C**H**$_2$- must have a neighbouring carbon with 2 H on it, so it must be O- CH_2-CH_2. This is confirmed by the presence of another -**CH$_2$ group** (δ=1.6, Integration = 2H, splitting pattern = quintet). The last piece of the puzzle is that the CH_2 group is shifted downfield (δ=3.67) and so must be bonded to the only oxygen in the molecule, i.e. an **O-CH$_2$-CH$_2$- group**.
   (Note: 'Atomic Accounting' is now: C_3H_7 - C_2H_4 = CH_3).
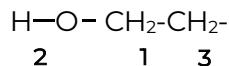
$$H\text{—}O\text{–} CH_2\text{-}CH_2\text{-}$$
$$\mathbf{2} \qquad \mathbf{1} \qquad \mathbf{3}$$

Signal 3 confirms that there is a methylene group R_2CH_2 (δ=1.6, Integration = 2H, splitting pattern = quintet). Also, this -CH_2- has neighbouring carbons with 5 H on it so it must be CH_3- CH_2-CH_2. This is confirmed by the presence of a **CH$_3$ group** Signal 4 (δ=0.95, Integration = 3H, splitting pattern = triplet) thus the CH_2- also has as a neighbour, a carbon with 3 H on it so it must be -CH_2-CH_3.
        (Note: 'Atomic Accounting' is now: CH_3 - CH_3 = 0, all atoms accounted for!).

$$H\text{—}O\text{–} H_2C\text{–} CH_2\text{-}CH_3$$
$$\mathbf{2} \qquad \mathbf{1} \qquad \mathbf{3} \quad \mathbf{4}$$
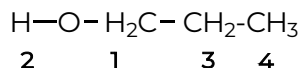
In summary unknown #360-14-B contains an alcohol, and an ethyl group. Therefore, the **Unknown #360-14-B** must be **1-propanol**, which also has the correct/matching molecular weight/formula, and boiling point. Also, the ^{1}H-NMR Spectrum shows there are 4 different types of H environments present in the molecule (and all 4 have been accounted for).

(Note: The calculation for the 'degrees of unsaturation' in this problem also makes sense. There are 0 degrees of unsaturation present in the unknown.)

H — O—H_2C —CH_2- CH_3
2   1   3   4

HSP-03-833
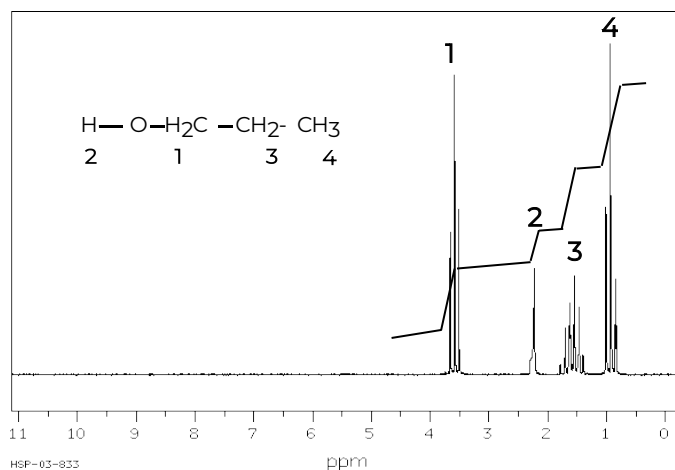
Instructor-Led Group ¹H-NMR Analysis Problems

Use the tables below to record your results of the '¹H-NMR Spectral Analyses' for the following compounds. Remember to label the signals on the spectrum and assign signal codes to each 'H' in the structure.
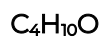
| Problem 1 | C_2H_5I | Degrees of Unsaturation = _____ |

| Structure and name | | Structure Assembly Work Area |

HSP-04-351

¹H-NMR Spectral Data for Instructor-Led Problem 1:   90 MHz (0.04 mL : 0.5 mL CDCl₃)

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
	3.2	2				
	1.8	3				

Problem 2   C₄H₁₀O   Degrees of Unsaturation = _____

Structure and name		Structure Assembly Work Area

10 9 8 7 6 5 4 3 2 1 0
ppm

HPM-00-190
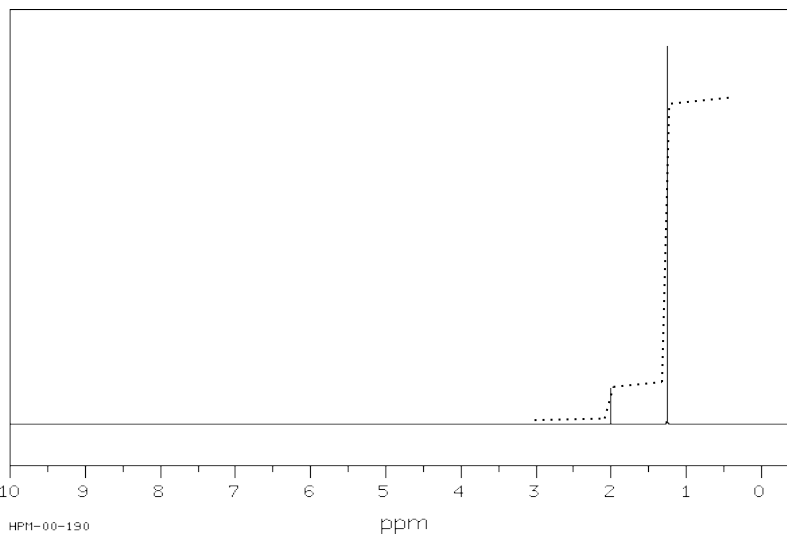
¹H-NMR Spectral Data for Instructor-Led Problem 2:   300 MHz (0.05 g : 0.5 mL CDCl₃

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

Problem 3   C₃H₆O   Degrees of Unsaturation = _____
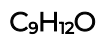
Structure and name		Structure Assembly Work Area

1H   2H   3H

10 9 8 7 6 5 4 3 2 1 0
ppm

HPM-00-450

¹H-NMR Spectral Data for Instructor-Led Problem 3:   90 MHz (0.02 mL : 0.5 mL CDCl₃)

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

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Problem 4 $C_9H_{12}O$ Degrees of Unsaturation = _____

Structure and name		Structure Assembly Work Area

3H   3H

4   2H

11 10 9 8 7 6 5 4 3 2 1 0

ppm

HSP-03-298
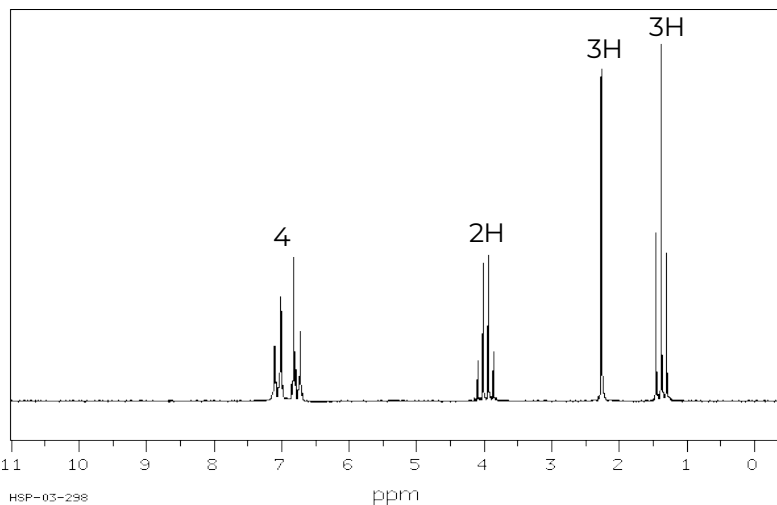
^{1}H-NMR Spectral Data for Instructor-Led Problem 4:   90 MHz (0.04 mL : 0.5 mL CDCl$_3$)

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

^{1}H-NMR Analysis Practice Problems

Use the tables below to record your results of the '^{1}H-NMR Spectral Analyses' of the provided known spectra on this page of the lab manual.

^{1}H-NMR Spectral Data for :

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

^{1}H-NMR Spectral Data for :

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

^{1}H-NMR Spectral Data for :

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

^{1}H-NMR Spectral Data for :

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

Write-up

Use the following example as a guide for reporting your answer for each of the unknowns.

Experiment 14 Student Name: **Phil Terpaper**   AU ID#: **9876543**

Unknown #: 360-14-00 Mol. Wt.: 150.18   Formula: $C_9H_{10}O_2$ MP or BP: 112-113° C

Number of Degrees of Unsaturation = nC +1 + 1/2nN - 1/2 nH - 1/2 nX
for Compound 360-14-00, $C_9H_{10}O_2$ = (9) +1 + 1/2(0) - 1/2 (10) - 1/2(0)
                        = 9 + 1 - 5 = **5** degrees of unsaturation

Structure: (neatly draw the structure and be sure to indicate and label all the hydrogens)
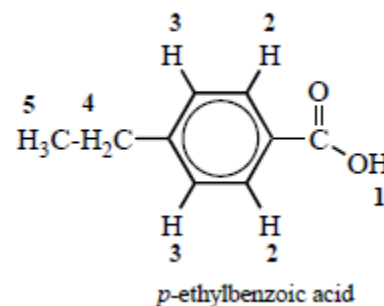
Name of Compound: *p*-ethylbenzoic acid

Table 1. Infrared Spectral Data:

p-ethylbenzoic acid

p-ethylbenzoic acid	Absorption Band#	Frequency (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm^{-1}	A B	2500-3300 3050	v.broad sharp	medium weak	broad carboxylic OH sp^2 C-H stretch
Between 3000 and 2000 cm^{-1}	C	2950	sharp	weak	sp^3 C-H stretch
Between 2000 and 1400 cm^{-1}	D E	1725 1600,1580,1500	sharp sharp	strong med	C = O carboxylic acid C=C aromatic
< 1400 cm^{-1}	F	840	sharp	med-strong	*para* subst.benzene

Functional Group(s) absent: C ≡N, C≡C, N-H

Table 2. ^{1}H-NMR Spectral Data:

| Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	δ 12.1	1H	singlet	(exchanges with D$_2$O)	0	0-**H** of carboxylic acid
2	δ 8.0	2H	doublet	(Signals 2 and 3 could be referred to together as a multiplet, i,e., 4H)	1	Aromatic **H**, para substitution pattern
3	δ 7.3	2H	doublet			
4	δ 2.7	2H	quartet		3	Ar-CH$_2$- (shifted downfield)
5	δ 1.3	3H	triplet		2	CH$_3$-C (methyl group)

Discussion and Conclusions:
It was immediately apparent that Unknown # 360-14-00 was a carboxylic acid, -COOH (absorption bands A and D), and an extremely downfield (deshielded) proton (Signal 1 at δ 12.1). The next functional group indicated was an aromatic ring (absorption bands E and B), and downfield protons (Signals 3 and 4 at δ 7.3 and 8.0). Finally, the ^{1}H-NMR spectrum shows a methyl group (Signal 1). This -CH$_3$- has as neighbouring carbon with 2 H on it, so it must be CH$_3$-CH$_2$. This is confirmed by the presence of a -CH$_2$ group (Signal 2). The last

piece of the puzzle is that the CH_2 group is shifted downfield ($\delta=2.7$), so it is bonded to an aromatic ring, i.e. an $Ar-CH_2-CH_3$ group. In summary unknown #360-14-20 contains a carboxylic acid, an aromatic ring and an ethyl group. The substitution pattern appears to be *para*. Therefore, the **Unknown #360-14-00** is *p*-**ethylbenzoic acid**, which also has the correct/matching molecular weight/formula, and boiling point.

Extra Detailed Answer for this Example:

After analyzing and recording the infrared and ^{1}H-NMR data in Tables 1 and 2 above and consulting the table of 'Chemical Shifts' of the CHEM360 Lab Manual, the following can be deduced. It was immediately apparent that unknown 360-14-00 was a **carboxylic acid**, -COOH, (due to broad infrared absorption bands for C=O and O-H at 1725 and 3300-2500 cm^{-1} respectively), and an extremely downfield proton (δ 12.1).
(Note: 'Atomic Accounting' is now: $C_9H_{10}O_2 - CO_2H = C_8H_9$).

$$\overset{O}{\underset{}{\overset{\|}{C}}}\diagdown OH$$
1
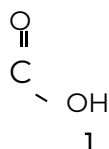
The next functional group apparent in the unknown was an **aromatic ring** (infrared absorption bands for C=C and sp^2 C-H at 1600/1500 and 3050 cm^{-1} respectively), and downfield (deshielded) protons (δ7.3, 8.0). It is also known that the aromatic ring is di-substituted, in a *para* orientation, hence C_6H_4. This is due to the presence of a single infrared absorption at 840 cm^{-1} and the pattern of aromatic H δ at 7.3 and 8.0 (displays anisotropy).
(Note: 'Atomic Accounting' is now: $C_8H_9 - C_6H_4 = C_2H_5$, an 'ethyl group' perhaps?!).

$$\begin{array}{cc} 3 & 2 \\ H & H \end{array}$$
$$\begin{array}{cc} H & H \\ 3 & 2 \end{array}$$
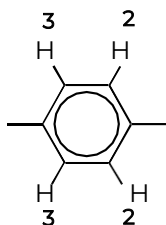
Finally, the spectrum shows a **methyl group** ($\delta=1.3$, Integration = 3H, splitting pattern = triplet). Also this - CH_3- has as neighbouring carbon with 2 H on it so it must be CH_3-CH_2. This is confirmed by the presence of a **CH_2 group** ($\delta=2.7$, Integration = 2H, splitting pattern = quartet) thus the CH_2- also has as a neighbour, a carbon with 3 H on it so it must be -CH_2-CH_3. The last piece of the puzzle is that the CH_2 group is shifted downfield ($\delta=2.7$) and so must be bonded to an aromatic ring, i.e. an **Ar-CH$_2$-CH$_3$ group**.
(Note: 'Atomic Accounting' is now: $C_2H_5 - C_2H_5 = 0$, all atoms accounted for!).

$$\begin{array}{cc} 4 & 5 \end{array}$$
$$-CH_2-CH_3$$
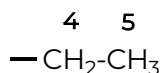
In summary unknown #360-14-00 contains a carboxylic acid, an aromatic ring and an ethyl group. The substitution pattern appears to be *para*. Therefore, the **Unknown #360-14-00** must be *p*-**ethylbenzoic acid**, which also has the correct/matching molecular weight/formula, and boiling point. Also, in the ^{1}H-NMR Spectrum, there are 5 different types of H environments present in the molecule (and all 5 have been accounted for).

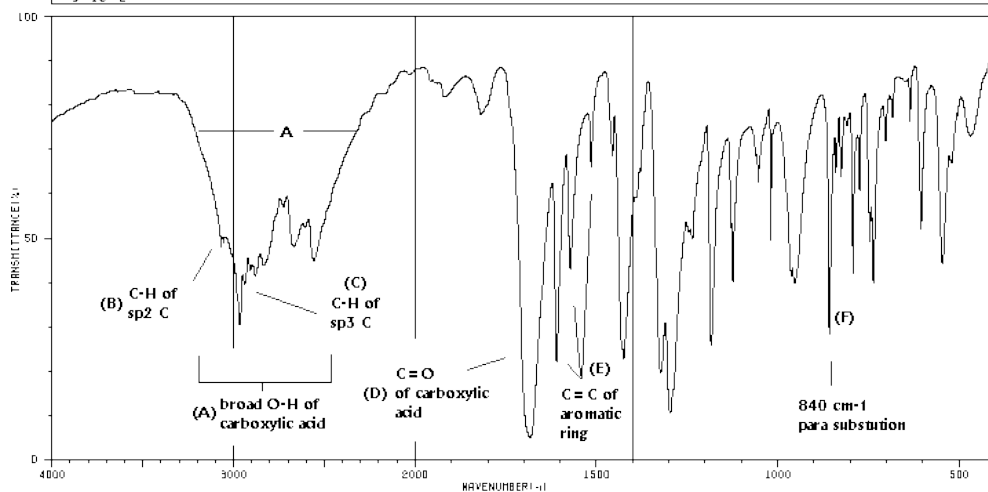$$\begin{array}{cc} 3 & 2 \end{array}$$

27

p-ethylbenzoic acid
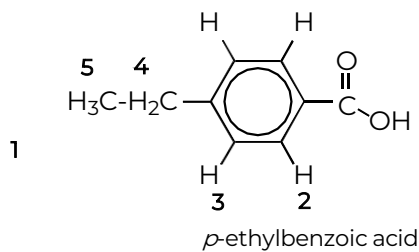
Note: The calculation for the 'degrees of unsaturation' in this problem also makes sense (aromatic ring (4) + carbonyl (1) =5 degrees of unsaturation.

Infrared Spectrum of *p*-ethylbenzoic acid

2977	36	2668	46	1426	21	1064	60	793	41
2966	29	2557	43	1322	18	1020	47	775	58
2940	37	1682	4	1297	10	963	39	747	47
2908	41	1610	21	1236	47	963	38	736	38
2878	39	1572	41	1184	25	858	26	605	50
2856	42	1515	64	1124	38	840	62	547	42
2723	55	1466	66	1061	66	826	60	522	64

¹H-NMR Spectrum of *p*-ethylbenzoic acid (90 MHz in CDCl₃)

p-ethylbenzoic acid

H of carboxylic acid
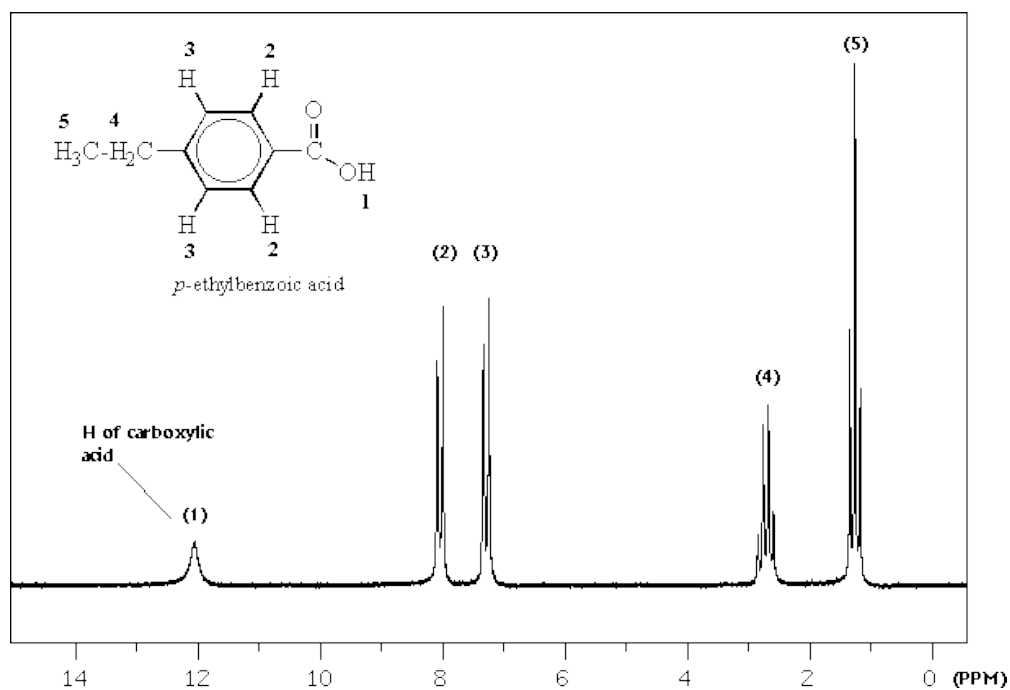
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Answers to Instructor led Group Problems:
Problem 1 iodoethane, 90 MHz (0.04 mL : 0.5 mL $CDCl_3$)   Problem 2 t-butyl alcohol, 300 MHz (0.05 g : 0.5 mL $CDCl_3$)

Problem 3 propanal, 90 MHz (0.02 mL : 0.5 mL $CDCl_3$)   Problem 4 p-ethoxytoluene, 90 MHz (0.04 mL : 0.5 mL $CDCl_3$)