Question # 2 – Where do things show up in the proton NMR? (continued) (7th edition, Chapter 13.5, Table 13.1, 8th edition, Chapter 13.5, Table 3.1, Figure 13.11, 9th edition, Chapter 13.5, Figure 13.8)

We discussed in the last notes where peaks will show up. Peaks usually show up between $0 - 10 \, \delta$. Peaks closer towards 10 are _____ and have less electron density in the carbon-hydrogen bond.

Peaks closer towards 0 are _____ and have more electron density in the carbon-hydrogen bond.

The more electronegative the atom attached to the carbon that bears the hydrogen, the closer the peak is towards _____.

The greater the number of electronegative atoms present on the carbon that bears the hydrogen, the closer the peak is towards _____.

The most electronegative atom in the periodic chart is _____.

However, it will not be included in most proton NMR spectra (at least in this class) because _____ has a spin of _____ which causes coupling similar to hydrogen. This makes the proton NMR spectra of _____ containing compounds MUCH more confusing.

The second most electronegative atom is _____. Many NMR spectra in this class will include _____ which makes protons show up downfield of most other similar protons.

(8th edition, Problem 13.4, 9th edition, same) Identify the most shielded and least shielded protons in the following:

a) 2-bromobutane   b) 1,1,2-Trichloropropane   c) Tetrahydrofuran

Aromatic/Anti-Aromatic Induced Fields and Chemical Shift (8th edition, pgs. 548 – 549, 9th edition, pg. 519)

The definition of an aromatic molecule is defined by being cyclic, planar, able to delocalize the electrons and have a Huckel number of electrons. Another definition of an aromatic molecule is for protons to show up in a different location than expected. The protons on ethene show up around _____. This is the standard position for sp^2-hybridized protons without electron withdrawing groups present.

The chemical shift for benzene's protons is _____. Benzene's protons show up farther downfield. Why? An explanation is an _____.

Benzene will be perpendicular to the applied magnetic field and has pi electrons. These pi electrons cause an _____ _____ which can either shield or deshield the protons. Look at (8th edition, Figure 13.8, pg. 548, 9th edition, Figure 13.9, pg. 519) for a better drawing then the one below. The protons on the benzene ring are in the part of the ring current that reinforces the applied magnetic field causing _____.
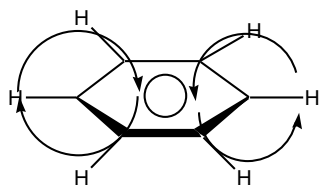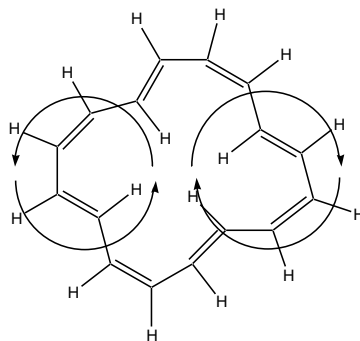
Larger rings can have both shielded and deshielded protons as seen below for [18] and [16]annulene.

(8th edition, Figure 13.10, 9th edition, Figure 13.11)
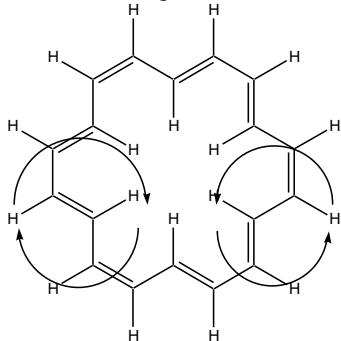
[18] annulene   [16]annulene

The induced field of aromatic molecules is _____ of the bottom of the aromatic rings. This makes the protons on the outside deshielded. The outside protons of [18]annulene show up at 9.3 δ. The inside protons show up at −3.0 δ.

The induced field of anti-aromatic molecules is _____ of the top of the ring. This makes the protons on the outside shielded (5.3 δ) and the protons on the inside deshielded (10.6 δ).

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Alkynes and Induced Field (8th edition, Figure 13.9, 9th edition, Figure 13.10)

Alkynes also have an _____ due to the pi electrons. However, the triple bond lines up parallel to the applied magnetic field instead of perpendicular to it as benzene does. This makes the protons and carbons of the alkyne shielded and they show up farther upfield than expected. An example is shown below.
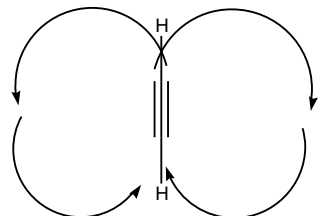
Given below is a table for proton chemical shifts.

TABLE 13.1 Approximate Proton Chemical Shifts

TYPE OF PROTON	CHEMICAL SHIFT, DELTA, PPM
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C=C-CH_3$ with R below	1.6–1.9
Benzylic, $ArCH_3$	2.2–2.5
Alkyl chloride, RCH_2Cl	3.6–3.8
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Ketone, $RCCH_3$ (C=O)	2.1–2.6
Aldehyde, RCH (C=O)	9.5–9.6
Vinylic, $R_2C=CH_2$	4.6–5.0
Vinylic, $R_2C=CH$ with R below	5.2–5.7
Aromatic, ArH	6.0–9.5
Acetylenic, $RC\equiv CH$	2.5–3.1
Alcohol hydroxyl, ROH	0.5–6.0[a]
Carboxylic, $RCOH$ (C=O)	10–13[a]
Phenolic, $ArOH$	4.5–7.7[a]
Amino $R-NH_2$	1.0–5.0[a]

[a] The chemical shifts of these groups vary in different solvents and with temperature and concentration.

3) What do the peaks look like in the proton NMR? (8th edition, Chapter 13.7 - 13.11, 9th edition, same)

Protons interact with the spins of other protons that are near the proton undergoing resonance. This is called _____. The peaks can be identified as the following:

Singlet - _____ Doublet - _____

Triplet - _____ Quartet - _____

Pentet - _____ Sextet - _____

Multiplet - _____ Doublet of Doublets _____

The relationship of the number of peaks and their respective height can be deduced from _____ triangle.

Coupling Constant (8th edition, pg. 557, 9th edition, pg. 528)

How far apart do you draw the peaks?

It depends on the _____ which is shown by the letter _____. You may also see a number attached to the letter _____ and it tells you how far apart the two different NMR active nuclei are. For example, how far apart are the protons shown below?

H   H

^{3}J coupling constants in alkanes can be explained by the Karplus curve which is shown below.

The Karplus curve is J versus the _____. A _____ of 0 or 180° between hydrogens have large coupling constants. A _____ of 90° between hydrogens or NMR active nuclei have a coupling constant of _____. Most alkanes have a dihedral angle of _____ in a staggered conformation which has a coupling constant of about _____.

WHAT DID KARPLUS WIN IN THE FALL OF 2013?

Chemical shift equivalent protons do not couple (8th edition, pg. 557, 9th edition, pg. 527)

How many types of protons does ethane contain? _____

How many types of protons does propane contain? _____

How many types of protons does butane contain? _____

Coupling constants between adjoining atoms is equal (8th edition, Figure 13.21, 9th edition, same)

If the coupling constants between two adjoining atoms are the same, we can use the _____ rule with n = number of NMR active nuclei. Given below is 1-chloropropane with the three hydrogens labeled.
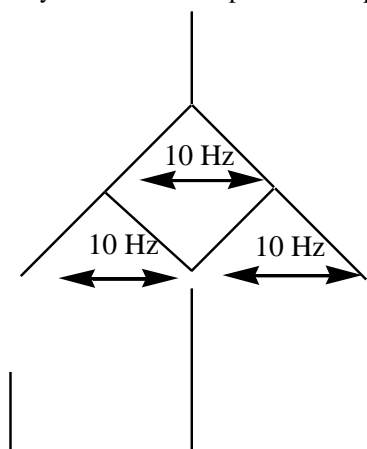
Hb   Hb

Hc

Cl

Hc   Hc Ha   Ha
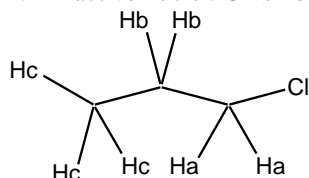
Proton A shows up as a _____.
Proton C shows up as a _____.
If Jab = Jbc, we can use the n+1 rule and proton b shows up as a _____.
Why? Because some peaks overlap and this is shown with the splitting diagram below.

10 Hz

10 Hz   10 Hz

What does the peak for ethane look like in the proton NMR? _____

Assuming the coupling constants are the same for propane, what do the two types of protons look like in the proton NMR? The two CH_3's are a _____. The CH_2 is a _____.

Assuming the coupling constants are the same for butane, what do the two types of protons look like? The two CH_3's are a _____. The CH_2's are a _____.

Coupling constants not equal (8th edition, Chapter 13.11, 9th edition, same)

If J_{ab} is NOT equal to J_{bc}, more than the three peaks are generated AND the _____ cannot be followed. Let us assume that J_{ab} is 10 Hz and J_{bc} is 5 Hz. Instead of the three peaks above, we get a _____ of _____. This is shown with the splitting pattern below.

10 Hz

5 Hz   5 Hz
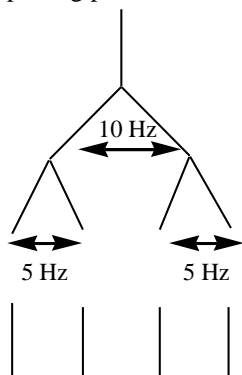
We will assume that the coupling constants are always equal in this class. Is this what exists in most NMR spectra? _____.

Explanation of WHY the n + 1 rule works (8th edition, Figure 13.15, 13.17, 9th edition, same)
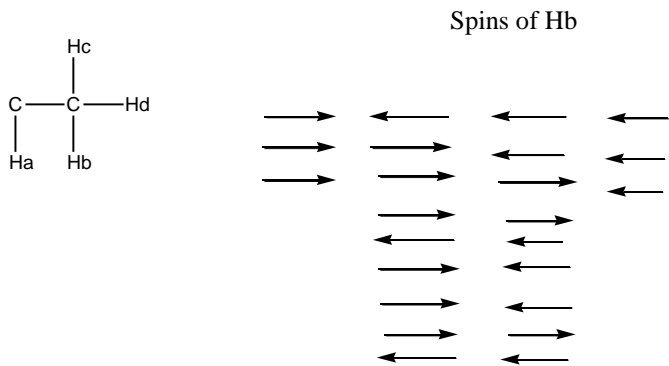
The n + 1 rule works because of the spin of neighboring NMR active nuclei. Let us assume for the molecule below that H_a is in resonance and H_b is the only proton that is influencing proton H_a. The spin of proton H_b can be with the field or against the field. This gives us two equal peaks.

Spins of Hb

```
C —— C
|     |
Ha    Hb
```

→ ←
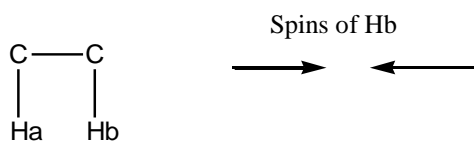
For the molecule below, assume Ha is in resonance and Hb and Hc are the only proton that are influencing Ha. The spin of proton Hb can be either with or against the field. The spin of Hc can be either with or against the field. The possibilities are given below and explain why the triplet is 1:2:1.

Spins of Hb

```
      Hc
      |
C —— C
|     |
Ha    Hb
```

→→   ←←   ←←
→→   →→   ←←

→→
←←
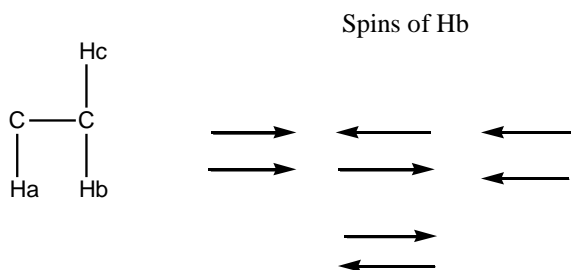
For the molecule below, assume Ha is in resonance and Hb, Hc, and Hd are the only protons that are influencing Ha. The spin of proton Hb, Hc, and Hd can be either with or against the field.

Spins of Hb

```
      Hc
      |
C —— C —— Hd
|     |
Ha    Hb
```

→→   ←←   ←←   ←←
→→   →→   ←←   ←←
→→   →→   →→   ←←

      →→   →→
      ←←   ←←
      →→   ←←
      →→   →→

      →→   ←←
      →→   →→
      ←←   ←←

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Splitting patterns that will be seen (8th edition, Chapter 13.8, 13.9, 9th edition, same)

The ethyl group will be seen as a _____ and a _____.

The isopropyl group will be seen as a _____ and a _____.

(8th edition, Problem 13.11, 9th edition, same) Describe the appearance of the ^{1}H NMR spectrum of each of the following compounds. How many signals would you expect to find, and into how many peaks will each signal be split?

a) 1,2-Dichloroethane

c) 1,1,2-Trichloroethane

b) 1,2,2-Trichloropropane

d) 1,1,2,2-Tetrachloropropane

4) How many protons are causing each peak? (8th edition, pg. 553, 9th edition, pg. 523)

_____ is defined by Carey as "the relative area of a signal in an NMR spectrum. Areas are proportional to the number of equivalent protons responsible for the peak." Integration is shown on spectra by the distance from where the integration trace is flat to where it is flat again. An example is shown below.

Benzene integration

Look at the benzene integration to identify how many substituents are on the benzene ring.

_____ - one substituent on the benzene ring.

_____ - two substituents on the benzene ring. The substituents can be either _____, _____ or _____.
Look for a _____ of _____ for para substitution.

_____ - three substituents on the benzene ring.

Other integration facts

Integration is listed as a ratio. Let's assume the integration is 2 to 1. Some of the possibilities could be four to two or it could be six to three or it could be eight to four. Integration for problems in this class will be given with a number above the peak that is _____.

Carbon NMR(8th edition, Chapter 13.14, 9th edition, same)

Carbon NMR only has three questions that need to be asked instead of the four questions for proton.

1) How many types of carbon does the molecule have?

2) Where do the peaks show up?

3) What do the peaks look like under proton coupled conditions? We do not ask about _____ because carbons cannot be integrated.

   As a general rule, quaternary carbons are very small in carbon NMRs because they relax slowly. The addition of _____ makes the carbons relax quicker. Therefore, CH_3 peaks are usually higher than a CH_2 which are usually higher than a CH but this is not always true.

   Carbon NMR can be taken in three different ways. These ways are listed below.

_____- all of the carbon peaks are given as single peaks.

_____ - all of the carbon peaks are coupled. The _____ rule can also be used in ^{13}C NMR. However, n = number of protons **ON** the carbon not the NMR active nuclei on adjoining carbons as seen in proton NMR.

_____ - quaternary carbon with no hydrogens on the carbon.

_____ - tertiary carbon with one hydrogen on the carbon.

_____ - secondary carbon with two hydrogens on the carbon.

_____ - primary carbon with three hydrogens on the carbon.

_____- Distortionless enhanced polarization transfer gives the substitution pattern of carbons by whether the peaks showing up are sticking up, sticking down, or not showing up. CH and CH_3 groups are _____. CH_2 groups are sticking _____. Quaternary carbons do not show up in the DEPT NMR. The NMR machine at CBU can run DEPT NMR spectra.

Given below is the ^{13}C list of where peaks show up.

TABLE 13.2 Approximate Carbon-13 Chemical Shifts

TYPE OF CARBON	CHEMICAL SHIFT, DELTA, PF
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-\overset{\mid}{\underset{\mid}{C}}-X \left(X = Cl,\ Br,\ or\ \overset{\mid}{N}- \right)$	10–65
Alcohol or ether, $-\overset{\mid}{\underset{\mid}{C}}-O$	50–90
Alkyne, $-C\equiv$	60–90
Alkene, $\diagdown C=$	100–170
Aryl,	100–170
Nitriles, $-C\equiv N$	120–130
Amides, $-\overset{O}{\overset{\|}{C}}-\overset{\mid}{N}-$	150–180
Carboxylic acids, esters, $-\overset{O}{\overset{\|}{C}}-O$	160–185
Aldehydes, ketones, $-\overset{O}{\overset{\|}{C}}-$	185–215

Draw the ^{13}C NMR spectra for the following compounds.

a) Propylbenzene (proton decoupled)

b) Propylbenzene (proton coupled)

c) Propylbenzene (DEPT)

d) 1,2,4-Trimethylbenzene (proton decoupled)

e) 1,2,4-Trimethylbenzene (proton coupled)

f) 1,2,4-Trimethylbenzene (DEPT)

Infrared spectroscopy (8th edition, Chapter 13.20, 9th edition, same)

Infrared spectroscopy identifies _____. IR spectra are taken from 2.5 micrometers to 25 micrometers. _____ are reciprocal centimeters (cm^{-1}) and wavenumbers are taken from 400 to 4000. 4000 is the higher frequency and higher energy part of the spectrum while 400 is the lower frequency and lower energy part of the spectrum. NMR concerned changing spins while IR concerns _____ and _____ of bonds.

There are two factors that determine where peaks show up in the IR and both are related to _____ law.

_____ - If the difference between the atoms in a bond is small, the peak shows up nearer to _____.

If the difference between the atoms in a bond are large, the peak shows up nearer to _____.

_____ - The stronger the bond, the more energy is required to vibrate the bond.

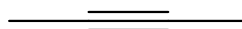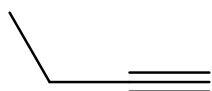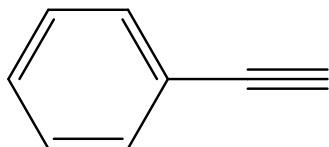For example, a carbon triple bond oxygen shows up at _____ wavenumbers.

A carbon double bond oxygen shows up at _____ wavenumbers.

A carbon single bond oxygen shows up at _____ wavenumbers.

Peaks can be listed as _____ or _____.

Peaks can also be listed as _____, _____, or _____.

What is required for an IR stretch? _____. Circle the molecules below that will have a carbon-carbon triple bond show up in the IR spectrum?

A chart showing where functional groups show up in the IR is below. _____ areas in particular will be required for this class.

TABLE 13.3 Characteristic Infrared Absorptions of Functional Groups

GROUP		FREQUENCY RANGE cm^{-1}	INTENSITY[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m-s)
Isopropyl, —CH(CH$_3$)$_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, —C(CH$_3$)$_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
R—CH=CH$_2$		985–1000	(s)
	and	905–920	(s)
R$_2$C=CH$_2$	(out-of-plane C—H bendings)	880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o-Disubstituted		735–770	(s)
m-Disubstituted		680–725	(s)
	and	750–810	(very s)
p-Disubstituted		800–840	(very s)
E. Alcohols, Phenols, Carboxylic Acids			
OH (alcohols, phenols, dilute solns)		3590–3650	(sharp, v)
OH (alcohols, phenols, hydrogen bonded)		3200–3550	(broad, s)
OH (carboxylic acids, hydrogen bonded)		2500–3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O stretch		1630–1780	(s)
aldehydes		1690–1740	(s)
ketones		1680–1750	(s)
esters		1735–1750	(s)
carboxylic acids		1710–1780	(s)
amides		1630–1690	(s)
G. Amines			
N—H		3300–3500	(m)
H. Nitriles			
C≡N		2220–2260	(m)

[a] Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

_____- A broad peak in this area indicates an OH group. Hydrogen bonding of the OH group weakens the bond to hydrogen and shifts the peak closer to _____. A dilute solution for an OH can give you a _____ peak due to no hydrogen bonding but this is not common.

_____ also show up in this area.

_____- This area can be broken down into peaks above 3000 cm^{-1} and peaks below 3000 cm^{-1}. Peaks above 3000 cm^{-1} (like 3050 cm^{-1}) can be sp^2 C-H stretching. Peaks below 3000 cm^{-1} (like 2950 cm^{-1}) can be sp^3 C-H stretching. sp-hybridized C-H stretching is about 3200 cm^{-1}.

_____- This area indicates a carbonyl group. Acid chlorides show up closer to 4000 cm-1 while carboxylic acids show up closer to 1650 cm-1. Why?

_____ - This area is called the _____. If you think you have a certain molecule, run an IR and compare this region of your unknown to a standard of this molecule. The peaks in the area given above must match _____.

EXTRA NOTES: