

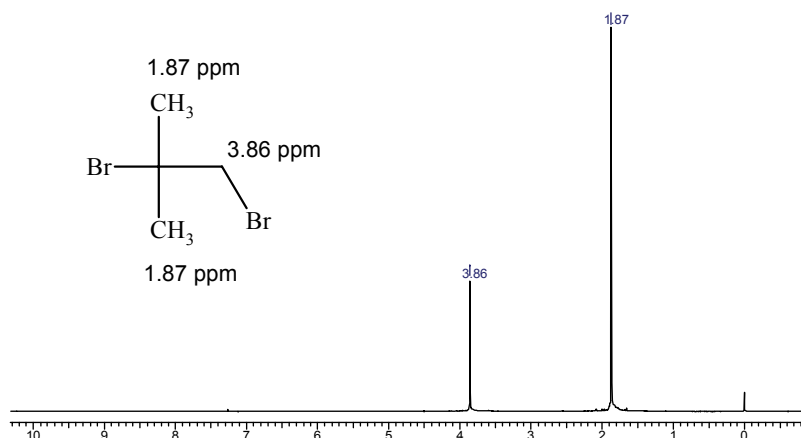
¹H NMR Spectroscopy (#1c)

The technique of ¹H NMR spectroscopy is central to organic chemistry and other fields involving analysis of organic chemicals, such as forensics and environmental science. It is based on the same principle as magnetic resonance imaging (MRI). This laboratory exercise reviews the principles of interpreting ¹H NMR spectra that you should have learned in Chemistry 301. There are four questions you should ask when you are trying to interpret an NMR spectrum. Each of these will be discussed in detail.

The Four Questions to Ask While Interpreting Spectra

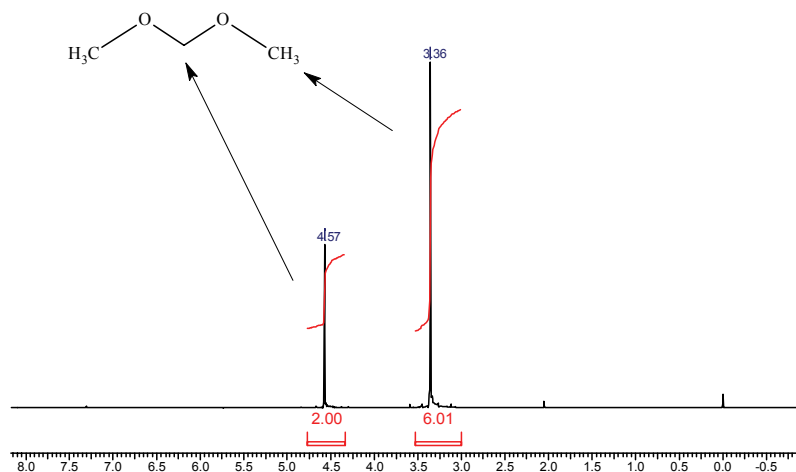
1. How many different environments are there?

The **number of peaks or resonances (signals)** in the spectrum indicates the number of nonequivalent protons in a molecule. Chemically equivalent protons (magnetically equivalent protons) give the same signal in the NMR whereas nonequivalent protons give different signals. For example, the compounds CH₃CH₃ and BrCH₂CH₂Br all have one peak in their ¹H NMR spectra because all of the protons in each molecule are equivalent. The compound below, 1,2-dibromo-2-methylpropane, has two peaks: one at 1.87 ppm (the equivalent CH₃'s) and the other at 3.86 ppm (the CH₂).



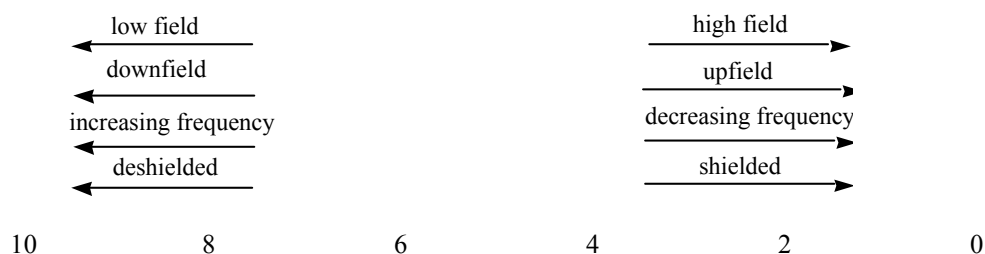
2. How many ¹H are in each environment?

The **relative intensities of the signals** indicate the numbers of protons that are responsible for individual signals. The area under each peak is measured in the form of an integral line. The height of the steps of this line is proportional to the area under the peak and therefore indicates the number of protons. The molecule dimethoxymethane, seen below, has two singlets that have integration areas whose ratio is 2:6. This indicates that there are two equivalent methyl groups ($2 \times 3 = 6$) and one CH₂ group ($1 \times 2 = 2$). A resonance that integrates for three protons indicates a CH₃ group. A resonance that integrates for six protons indicates two equivalent CH₃ groups, which is generally indicative of an isopropyl group. A resonance that integrates for nine protons indicates three equivalent CH₃ groups, which is indicative of a *tert*-butyl group.



3. Are the ^1H 's part of a functional group, or are there functional groups nearby?

The **locations of the peaks (chemical shift, ppm)** indicate the types of protons in the molecule. This results from the fact that the magnetic field at the nucleus varies with the electronic (structural) environment for each type of proton. The greater the electron density around a proton, the weaker the effective field it experiences (shielded) resulting in lower frequency transitions. Shielding can occur in cases where there is extra electron density around a carbon or proton, like in a carbanion. Decreases in the electron density will result in an increased effective magnetic field (deshielded) with these protons resonating at a higher frequency. This deshielding effect can be caused by specific functional groups that withdraw electron density from protons, such as the halogens, amines, alcohols, or those containing carbonyls. We can therefore also gain information on which protons are close to these functional groups. In NMR, the frequency scale is typically displayed from highest to lowest. The designations low field, (downfield) and high field (upfield) are historical designations referring to continuous wave (CW) instrument operations, but are used throughout literature and represent the high frequency and low frequency regions, respectively. These designations are shown below:

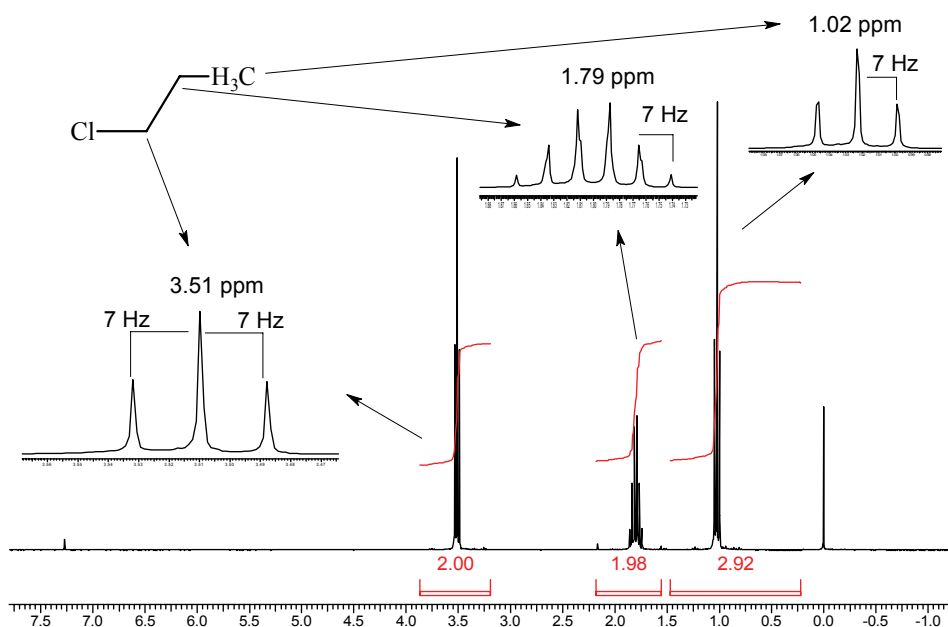


The position at which a proton is located on the bottom axis is its **chemical shift (δ)**. It is commonly expressed in parts per million (ppm) relative to the absorption of the reference signal tetramethylsilane, TMS ($\delta = 0$ ppm). The CH_3 protons of 1,2-dibromo-2-methylpropane are highly shielded and appear upfield at 1.87 ppm. The CH_2Br protons are deshielded due to the electron withdrawing effect of Br and appear further downfield at 3.86 ppm. Likewise, the OCH_3 protons in dimethoxymethane are shifted downfield due to the electron withdrawing effect of oxygen and appear at 3.36 ppm.

4. How many ^1H atoms are there on the neighboring carbon atom?

We can deduce how many ^1H atoms are present on the neighboring carbon atom by **examining the number of lines into which a peak has been split**. Splitting of a peak is the result of a process called “coupling” that occurs between ^1H 's in one environment and those on a neighboring carbon that are in a different environment. In the simplest spectra, such as those we have seen, only singlets are present because there are no nonequivalent ^1H atoms neighboring each other. In the example below, 1-chloropropane, three nonequivalent sets of ^1H atoms are present, at 3.51 ppm, 1.79 ppm, and 1.02 ppm. They are clearly not singlets. The peak at 3.51 ppm has three lines, and it is called a triplet. The peak at 1.79 ppm has six lines; it is a sextet. The peak at 1.02 ppm is another triplet. The triplet at 1.02 ppm is actually the CH_3 . It is a triplet because it is next to a CH_2 . **In general, the number of lines into which a peak is split is given by the formula “ $n + 1$,” where n is the number of ^1H on the neighboring carbons.** The next peak, at 1.79 ppm, is a sextet because it is a CH_2 with five total ^1H neighbors: a CH_3 (3 ^1H) and a CH_2 (2 ^1H), and five plus one equals six, so we see six lines in the peak.

The distance between individual lines in a peak is called the coupling constant (J value). A larger J value means a larger separation between the lines. The J value for the peak splittings observed in the compounds we have examined so far is typically 7 Hz. The CH_3 protons of 1-chloropropane experience a J value of 7 Hz when they couple to the neighboring CH_2 . Likewise, the neighboring CH_2 experiences that same J value of 7 Hz when coupling to the CH_3 and the CH_2 that is bonded to the Cl.

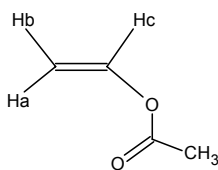


Splitting of peaks into more than one line is observed between nonequivalent protons (different chemical shifts) separated by **three or less bonds**. In some systems, 4 and 5 bond couplings are observed occasionally. For example, the underlined protons in $\underline{\text{H}_2}\text{C}=\text{C}(\text{Cl})\text{CH}_3$ are not equivalent and therefore split each other. The underlined protons in $\underline{\text{H}_2}\text{C}=\text{C}(\text{CH}_3)_2$ are equivalent and do not split each other.

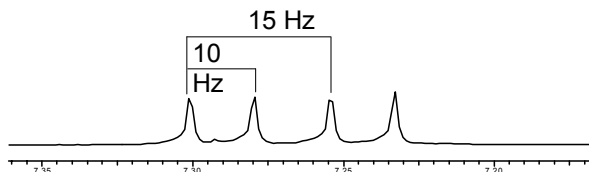
When a peak is split into several lines, **the intensities of the individual peaks follow a predictable pattern**, derived from Pascal's Triangle. The intensities of the peaks of a split signal are 1:1 for a doublet, 1:2:1 for a triplet, 1:3:3:1 for a quartet, 1:4:6:4:1 for a quintet, 1:5:10:10:5:1 for a sextet, 1:6:15:20:15:6:1 for a septet, 1:7:21:35:35:21:7:1 for an octet, and 1:8:28:56:70:56:28:7:1 for a nonet. Note that in a nonet, the outermost lines are only 1/70th the height of the center, most intense line. Therefore, all nine peaks of the nonet are often difficult to see and usually it is mistaken for a septet or even a quintet.

# of splitting protons	Peak Line Intensities									
0						1				
1					1		1			
2				1		2		1		
3			1		3		3		1	
4		1		4		6		4		1
5	1		5		10		10		5	1

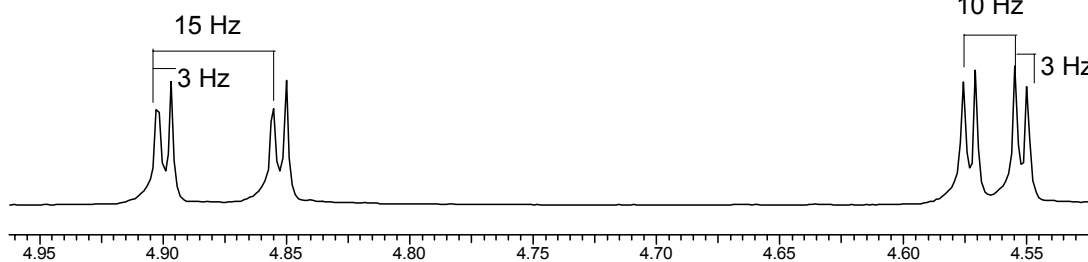
This large value for a coupling constant makes it easy to see splitting of peaks, but there are cases where the splitting of peaks is not so easy to see. It is possible to see more than $n+1$ lines in a peak in ^1H NMR spectra. The line intensities may not follow Pascal's Triangle either. These situations occur when the coupling protons are nonequivalent protons and have different coupling constants (J values). These more complex fine structures for coupling to multiple chemically inequivalent protons can be predicted by introducing the interactions for each group individually. For example, consider the regions of the ^1H NMR spectrum of vinyl acetate, shown below. The three inequivalent protons of the vinyl group, labeled Ha, Hb, and Hc, do not appear as the type of multiplets we saw above. Rather, they are each a **doublet of doublets**, which is a direct result of the J values of each proton. Proton Hc is the farthest downfield proton, at 7.26 ppm, because of the influence of the sp^2 -hybridized carbon to which Hc is attached and the electron-withdrawing effect of the ester oxygen. Hc experiences two different J values. The first is 15 Hz, a result of coupling to the Ha proton that is *trans* to Hc. The second J value is 10 Hz, a result of coupling to the Hb proton that is *cis* to Hc. Similarly, Ha ($\delta = 4.87$ ppm) also has two J values. One must be the same as the value for Hc to Ha, which is 15 Hz. You can see this labeled on the diagram. The other is a new J value of 3 Hz, resulting from coupling between Ha and Hb. You can also see how short the distance is between the lines in the peak for the 3 Hz difference. The most upfield peak, at $\delta = 4.56$ ppm, is generated by Hb. There is a J value for the coupling between Hb and Ha, which is 3 Hz, and a J value for the coupling between Hb and Hc of 10 Hz. The peaks do not appear as quartets because there are two different J values, rather than one J value.



Peak from Hc



Peak from Ha



By answering these four questions, we propose fragments of the molecule that must be present. We combine the fragments to give possible structures. Often, additional data is needed to propose a structure, such as an IR spectrum or ^{13}C NMR spectrum, or other types of NMR experiments, as seen below.

Alcohols and Carboxylic Acids

Alcohols contain an OH that can appear anywhere between δ 0.5-5.5 ppm. The OH sometimes couples to neighboring protons, and sometimes does not. Whether it couples depends on a number of factors. The OH usually appears as a broad singlet, and its chemical shift changes with temperature, solvent, and pH, making it difficult to assign the peak for the OH proton. Fortunately, we can perform a simple experiment to identify the OH. The H on the OH exchanges with other protons; that is, it is only instantaneously associated with a particular O and can be replaced by another H easily. If a small amount of deuterated water (D_2O) is added to the NMR sample and shaken, the OH proton is rapidly exchanged for deuterium (D) and the OH becomes OD, disappearing from the ^1H spectrum. We call this experiment a “ D_2O shake.” This experiment can also be performed with compounds that also have exchangeable protons, such as carboxylic acids, amides, and amines. Carboxylic acid protons appear between 10-13 ppm.

Postlab Questions

You should complete the following assignment in your lab notebook as you would any other postlab report, with the other spectroscopy assignments.

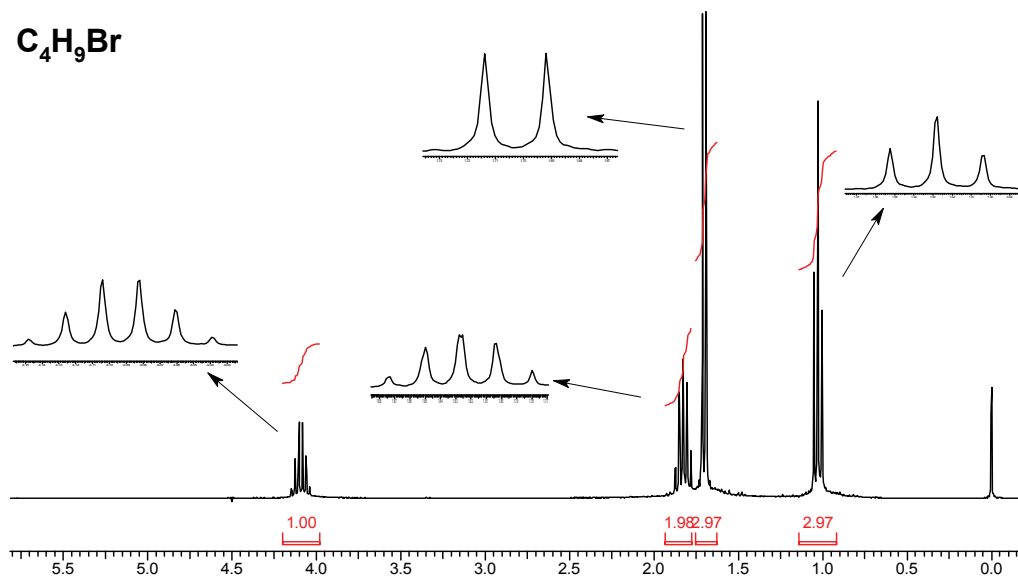
The equation for calculation of the degree of unsaturation from a molecular formula is:

$$\text{d.u.} = \#C - 0.5\#H - 0.5\#X + 0.5\#N + 1 \quad (\text{where } X = \text{F, Cl, Br, or I and } N = \text{nitrogen})$$

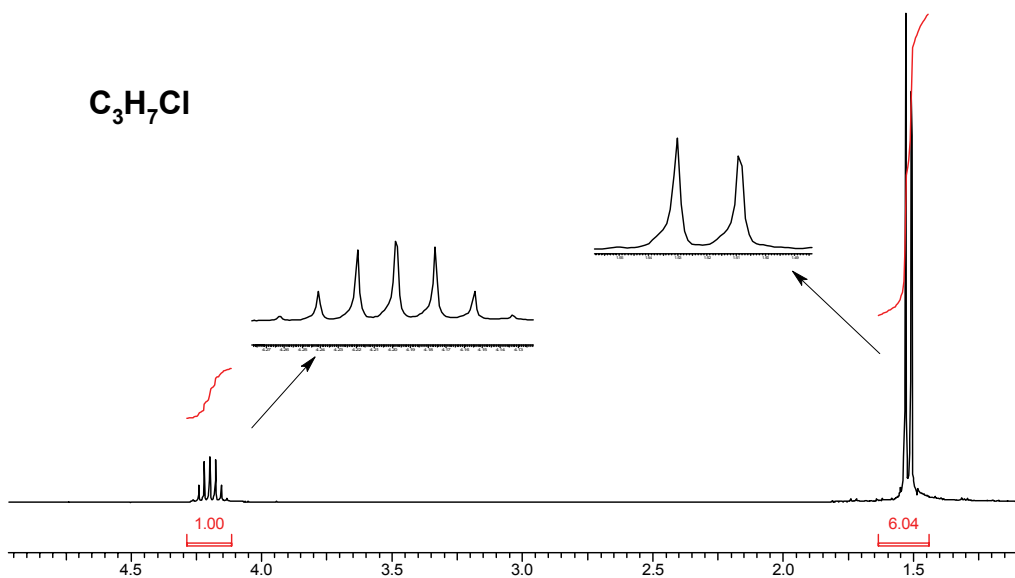
Remember that a degree of unsaturation can be a **pi bond or a ring**. A table of ^1H NMR shifts is located on page 43.

1. Provide structures that are consistent with the following ^1H NMR spectra. Calculate the degree of unsaturation of each compound first. Assign the protons to their respective peaks.

A. $\text{C}_4\text{H}_9\text{Br}$



B. $\text{C}_3\text{H}_7\text{Cl}$



- The ^1H NMR for 2,3-dibromobutane has a doublet at 1.8 ppm and a quartet at 4.5 ppm. Draw the compound and assign the peaks in the spectrum to their respective protons.
- The doublets observed for the alkene protons in the NMR spectra of *trans*-3-chloropropenoic acid and *cis*-3-chloropropenoic acid have the same chemical shift, but the J value for one is 14 Hz and the other is 9 Hz. Which is the *trans* acid and which is the *cis* acid?
- Predict the structure of the compound that gives the spectrum shown below. Upon shaking the sample with D_2O , the doublet at 2.2 ppm disappears from the spectrum and the peak at 3.7 ppm simplifies to a clean sextet. Calculate the degree of unsaturation of the compound. What functional group must this compound contain?

