

Proton NMR Spectroscopy: Split the signals, not your brain!

Before we can understand signal splitting, we have to understand what NMR is. This tutorial will first discuss a few concepts about NMR and then signal splitting.

BACKGROUND ON NMR:

So what exactly is NMR?

-NMR is a technique that is useful for determining the structure of molecules based on the energy required for nuclear spin flip.

What information can be derived from an NMR spectrum?

*For review on these topics, reference the Lecture Supplement and/or other tutorials on the particular topics

*This tutorial will be focused on signal splitting

- 1) the number of signals depends on the number of equivalent protons (hydrogens)
- 2) position of signals (chemical shift)
 - This deals with where the peaks appear on an NMR spectrum (are the protons “shielded” or “deshielded”?)
- 3) relative intensity of signals will give the ratio of equivalent proton types
 - This is known as integration
 - # of hydrogens in molecule divided by the sum of integration=# hydrogen per integration unit
- 4) signal splitting (spin-spin coupling)
 - This deals with how many lines/peaks a particular proton will split into
 - +This depends on the proton neighbors of the proton of interest (this will make more sense later in this tutorial)

Important concepts:

-protons, electrons, and neutrons all have “spin”

+a molecule can have a spin of $I = +1/2$ or $I = -1/2$

-we call $I = +1/2$ parallel to B_0 (external magnetic field) (HIGHER energy)

-we call $I = -1/2$ antiparallel to B_0 (LOWER energy)

-the difference between spin state energies ($I = +1/2, -1/2$) is denoted ΔE

- ΔE corresponds to energy required for a spin flip (when a radio wave photon with energy is added)

+if there is a small magnetic field there will be a small ΔE

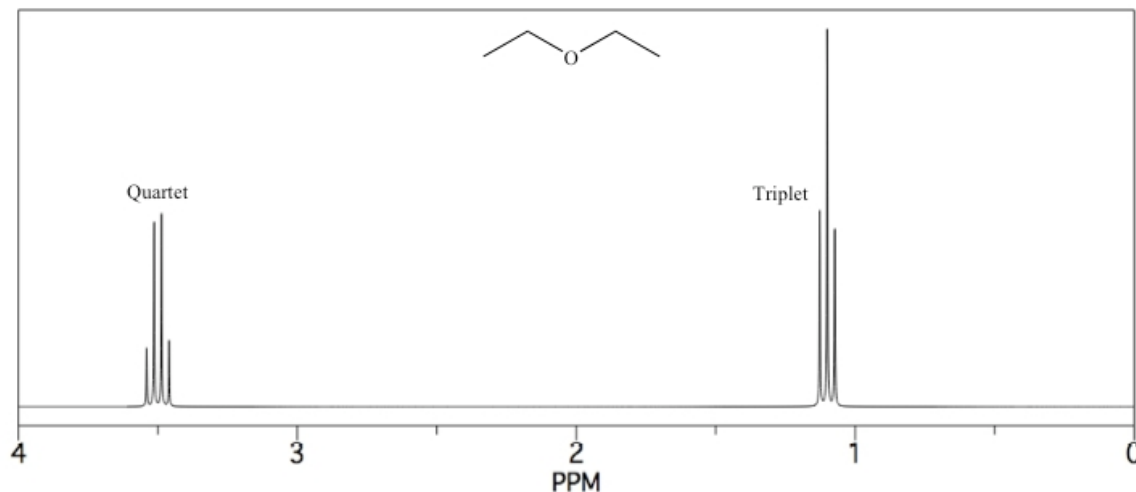
+if there is a large magnetic field there will be a large ΔE

SIGNAL SPLITTING:

Why are there so many peaks all in one area?

This is called signal splitting.

Example: (image from Illustrated Glossary, splitting)



We classify the number of peaks a signal has by certain names:

Singlet

0 equivalent hydrogen neighbors=1 peak

Doublet

1 equivalent hydrogen neighbors=2 peaks

Triplet

2 equivalent hydrogen neighbors=3 peaks

Quartet

3 equivalent hydrogen neighbors=4 peaks

Quintet (Pentet)

4 equivalent hydrogen neighbors=5 peaks

Sextet

5 equivalent hydrogen neighbors=6 peaks

Septet

6 equivalent hydrogen neighbors=7 peaks

Why does spin splitting happen?

-Each line in a signal ...

(a) has a slightly different chemical shift

(b) represents slightly different spin flip energy

(c) represents nucleus with slightly different magnetic environment

(taken from page 149 of Lecture Supplement)

How can a nucleus feel more than one magnetic environment?

-What is important to note is that NMR is done with many molecules of the same conformational structure, however the spin flip of a certain hydrogen may be altered. For instance, suppose we have a structure:



(image from http://w25.indonetwork.co.id/pdimage/29/s_1183029_acetylene-2dcopy.jpg)

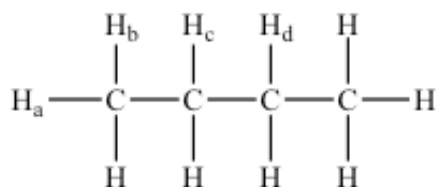
Let's examine the splitting of the hydrogen on the left ...

-Because the hydrogen on the right can either be spin up or spin down, the hydrogen on the left will experience two different magnetic environments.

What does spin-spin coupling mean?

-It involves the different magnetic environments that a specific proton feels due to the presence of other protons that are (generally) attached to adjacent carbons

Example: (image taken from Lecture Supplement)



(A) H_a and H_b *can* couple with H_c but not H_d (H_d is not on an adjacent carbon to H_a and H_b)

(B) The three hydrogens on the methyl group (on the left hand side, looking at the 2-D structure of the molecule on paper) *cannot* couple because they are not attached to adjacent carbons

* A hydrogen cannot couple with itself (or protons that are equivalent to it), meaning that the methyl group hydrogens cannot couple with each other as they all have the same magnetic environment

*Review the general rules listed below to understand which protons can couple

Are there any rules I should follow?

Yes! So far in this tutorial, some of these rules have been introduced, but now they will all be written out explicitly (referenced from the Lecture Supplement).

GENERAL RULE: If a proton has n neighbors (protons attached to adjacent carbons), it will split into $n+1$ lines

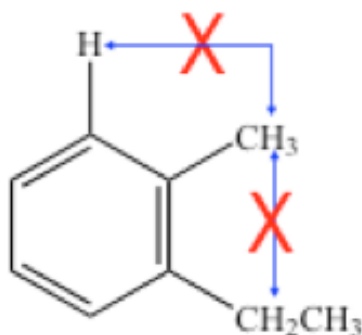
(A) Only nonequivalent protons couple.

*As discussed just before this section, the hydrogens in the CH₃ group cannot couple with each other because they are essentially the same (have the same magnetic environment)

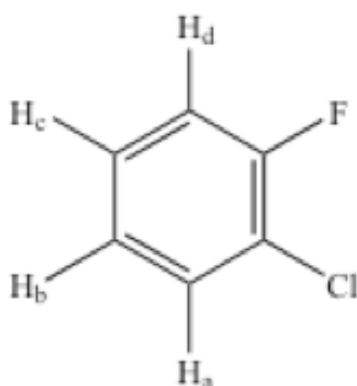
(B) Protons usually only couple with protons attached to adjacent carbons (protons separated by more than three single bonds usually do not couple) *Pi bonds do *not* count toward the limit of three bonds, but J (the spacing in between lines in a splitting pattern on a NMR spectrum) might be too small to observe

*A benzene ring is a “gated community”

+Hydrogens directly attached to a benzene ring can couple with each other, however hydrogens cannot “go through” the benzene ring to couple if attached to other carbons (see diagrams taken from Lecture Supplement)

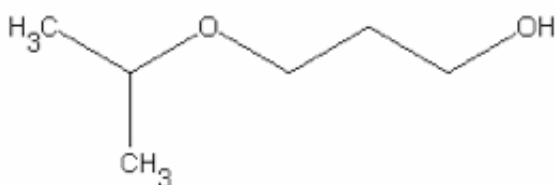


← These hydrogens with the **X** *cannot* couple because they “go through” the benzene ring



← H_a, H_b, H_c, and H_d *can* couple with each other

(C) Alcohol hydrogens (OH) and amine hydrogens (NH) are usually singlets
(image from <http://www.aronis.ru/structure/3-isopropoxy-1-propanol.gif>.)



← This hydrogen attached to the oxygen will not couple with other hydrogens; will expect a singlet

I've heard the term multiplet before. What does this mean?

-Simply put, it is a splitting pattern that is so complex we do not classify it as a singlet, doublet, triplet, etc., but rather as a “multiplet”.

*This is common for benzene rings

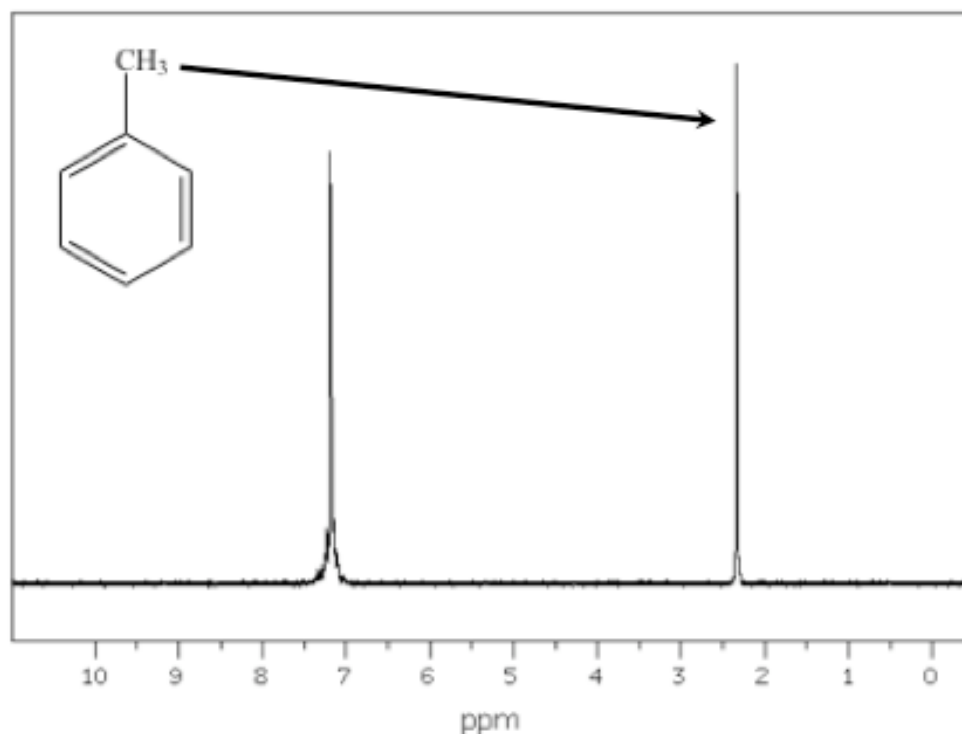
The difference between first order and non-first order splitting:

-First order splitting: If *J* (the spacing in between lines in a splitting pattern) is equal for all lines

-Non-first order splitting: If *J* is not equal for all lines

*For this class (Chemistry 14C), assume that first-order splitting will always be the case ... although there are many exceptions

The benzene ring magic act:



(image taken from Lecture Supplement)

-Looking at the “Characteristic Proton NMR Chemical Shifts (ppm)” chart on the inside cover of the Thinkbook and Lecture Supplement (this information will be given on an exam), we can identify that the benzene-CH₃ will appear at around 2.3 ppm.

-We can also identify that the hydrogens directly attached to the benzene ring (remember: these hydrogens can couple with each other but not the hydrogen in the CH₃ group) appear at 6.5-8 ppm.

-Looking at this spectrum, it looks like there is a singlet at 7.2 ppm.

*This is *not* a singlet! Benzene ring protons are *not* equivalent because they are *not* all symmetric (review equivalency of protons if needed)

*So why does it appear to be a singlet?

+Because *J* is nearing 0, so the splitting pattern disappears

*What do we learn from this?

+Benzene ring splitting signals (and, in general, splitting signals of hydrogens that “go through” pi bonds, a “free spacer” in the counting of 3 bonds between hydrogens that can couple) may correspond with a *J* that is too small to observe

PRACTICE PROBLEM:

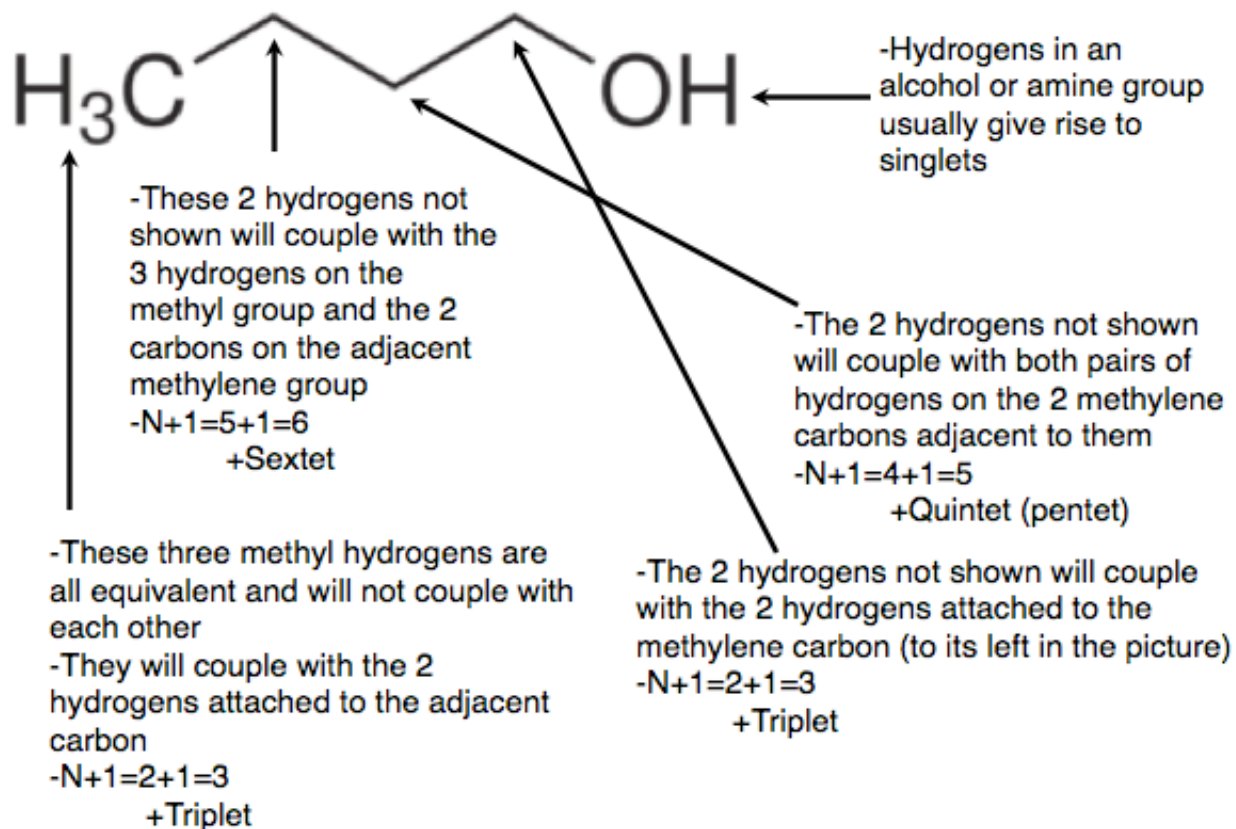
Predict the splitting patterns for this molecule (i.e. classify each proton as splitting into a singlet, doublet, triplet, etc.):



Answer:

(image of the molecule from

<http://www.sigmaaldrich.com/medium/structureimages/64/mfcd00002964.png>, added information written by tutorial writer)



REFERENCES:

- Dr. Hardinger's Chemistry 14C Lecture Supplement, Fifth Edition
- Dr. Hardinger's Chemistry 14C Thinkbook, Ninth Edition
- Illustrated Glossary on Dr. Hardinger's website
- Google images (exact websites of images are listed above or below the particular images used)