## Learning Guide for Chapter 5 - NMR Spectroscopy

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#### I. Introduction to NMR spectroscopy

To introduce you to NMR spectroscopy, we will first compare it to IR spectroscopy.

IR spectroscopy	<u>NMR spectroscopy</u>
type of light:	type of light:
what causes light to be absorbed:	what causes light to be absorbed:

what bands represent:

x-axis:

what we learn about a compound:

what we learn about a compound:

what peaks represent:

x-axis:

Which kind of spectroscopy can distinguish each pair of compounds?



IR

#### NMR

Which type of spectroscopy is more powerful?

What characteristic allows an atom to be detected by NMR?

What elements are commonly found in organic molecules? Which are suitable for NMR?

element: isotopes: NMR?

A typical proton NMR spectrum looks like this:



Each cluster of spikes is called a:

Where can you find each of the following, and what does it tell you about the peak?

chemical shift:

integration:

splitting:

What should you be able to do?

- 1. Assign peaks on a compound to a spectrum.
- 2. Sketch the spectrum of a compound.
- 3. Deduce the structure of an unknown compound from its spectrum.

### **II. Distinguishing Equivalent Hydrogens**

When do we say that two H's are equivalent?

What happens on a spectrum when two H's are equivalent?

Draw in all H's for the following compounds. Circle those that are equivalent, and then count the number of sets.



Rules of thumb:

More exact rule:



How many sets of equivalent H's are present in each of the following molecules?



0

#### **III. Chemical Shift**

What compound is used to establish "0" on the chemical shift axis? Why do you think this would make a good reference compound?

Draw arrows showing the direction of upfield and downfield:

Predict which set of hydrogens will be farthest downfield. When will this rule be useful?

1) CH > CH<sub>2</sub> > CH<sub>3</sub>







Which of the set of H's shown on each compounds will appear furthest downfield?



How many peaks should the following compound have? Which two would be most likely to overlap?



What are some useful ranges to remember?

H's on C next to C=O H's on C with N H's on C with O or X OH or NH in alcohols or amines H's on C=C H's on aromatic ring H's on amides H's on C=O OH in carboxylic acids

13	12	11	10	9	8	7	6	5	4	3	2	1	0
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Give the range at which you would expect to find the following H's:



What H's should stand out on the following compounds?



### **IV. Integration**

What does integration mean, mathematically?

What does the integration tell us on an NMR spectrum?

Why does the area under a curve increase when there are more H's in a peak?

Identify the sets of equivalent H's in the following compound. Which is furthest downfield? Which will have a greater integration?



Compare the integration ratios for the following compounds. Can you tell them apart?

Predict the integration ratio for each of the following compounds.



.CI :

How do we measure the integration?

Identify each set of equivalent H's in the following compound. Give the chemical shifts you would expect. Give the integration. Match up the H's with the peaks in the spectrum.



What does the height of a peak tell you?

#### V. Spin-spin splitting

What does splitting mean?

What happens when H's are separated by more than one atom?



What happens when a set of equivalent H's has one or more neighboring H's?

How can you tell what splitting a peak will have?

Sketch the spectra of the following compounds:



Assign splitting to each set of equivalent H's in the following compounds.



What happens when the chemical shifts of two separate peaks are so similar that they overlap?





When is this common?

What is complex splitting?

What kind of H's commonly show this?

What causes it?

normal complex splitting splitting



Do H's on alcohols and amines usually participate in splitting?

CH<sub>3</sub>OH (regular sample)

#### VI. Deuterium in NMR

What is deuterium?

Why is it useful in NMR?

Why are deuterated solvents needed in NMR?

What are the most common NMR solvents?

Do deuterated solvents show up on an NMR spectrum?

Is there a peak that shows up because of the solvent? Why?

If water is present in the compound or the solvent, where will it appear on the spectrum?

What will happen if  $D_2O$  is added to a sample containing an alcohol?

spectrum before adding D<sub>2</sub>O:

spectrum after adding  $D_2O$ :



What functional groups will have H's that disappear when shaken with  $D_2O$ ?

## VII. Carbon-13 NMR

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Why isn't <sup>13</sup>C NMR as useful as <sup>1</sup>H NMR?

Why isn't integration used?

How is the peak affected by the number of H's attached to the carbon?

Why won't you see any carbon-carbon splitting?

Why is carbon-hydrogen splitting usually eliminated?

What do you call a spectrum with no C-H splitting?





What is the most useful information you can get from a <sup>13</sup>C NMR spectrum?

What are some common chemical shift ranges?

sp3 carbon atoms

C=C in alkenes and aromatic rings

C=O

In the following spectrum of vanillin, assign the carbon atoms to the peaks where possible.



How many peaks would you expect each of the following compounds to have? What chemical shift ranges would they fall in?



Where does the solvent peak appear for CDCl<sub>3</sub>?

# VIII. Practice with NMR spectra

Match the peaks in the following compounds with the H's in the structures shown.



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Sketch the spectrum of the following compounds.





Deduce the structure of the following compounds.







 $C_4H_8Cl_2$ 

1.60 ppm (3H, d) 2.15 ppm (2H, q) 3.75 ppm (2H, t) 4.27 ppm (1H, m(6))