Chem 201 – NMR Handout

I. Coupling Constants
   A. General
      1. The distance (in Hertz) between peaks in a multiplet is the coupling constant.
      2. Hydrogens on neighboring carbons will couple (follow the n + 1 rule)
         a) This is normally a 3 bond coupling constant ($^3J$). There can be 2 bond to 5 bond coupling constants as well. $^3J$ coupling constants are typically what is seen for the n + 1 rule.

Ex - There are three distinct types of hydrogens in (Z)-methylchloroacrylate. Notice that $H_a$ and $H_b$ couple with each other with a $^3J = 9$ Hz value. $H_a$ and $H_b$ are both doublets due to their one neighbor. $H_c$ is too far away to couple with either of them and is thus a singlet. $H_a$ and $H_b$ are both doublets due to their one neighbor.

![NMR spectrum of methylchloroacrylate with peaks at 3.76, 6.18, and 6.88 PPM.]

B. General Values for Coupling Constants

<table>
<thead>
<tr>
<th>Type</th>
<th>Coupling Constant</th>
<th>Type</th>
<th>Coupling Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3J$</td>
<td>7 Hz</td>
<td>$^3J$</td>
<td>8 Hz</td>
</tr>
<tr>
<td>$^3J$</td>
<td>10 Hz</td>
<td>$^4J$</td>
<td>2 Hz</td>
</tr>
<tr>
<td>$^3J$</td>
<td>15 Hz</td>
<td>$^3J$</td>
<td>6 Hz</td>
</tr>
<tr>
<td>$^2J$</td>
<td>2 Hz</td>
<td></td>
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</tbody>
</table>

C. Complex
   1. A hydrogen can be coupled to two (or more) other types of hydrogen with different coupling constants. This will not follow the pattern predicted by the n+1 rule.
a) Say that we have \( H_ACH_BCH_C \). Suppose that \( H_A \) and \( H_C \) were very different from each other. \( H_B \) would be a triplet by the n+1 rule. Instead it is a doublet of doublets since \( ^3J_{AB} \) does not equal \( ^3J_{BC} \).

Example – styrene

Notice that \( H_C \) is not a triplet as predicted by the n+1 rule. Instead it is a doublet of doublets centered around 5.18 ppm. It has both a \( ^3J_{AC} \) and a \( ^2J_{BC} \). \( H_A \) and \( H_B \) are also doublet of doublets as well.

It helps to draw a splitting tree to see what the pattern will look like. \( H_A \) and \( H_C \) are cis to each other and share a \( ^3J=11 \) Hz. \( H_A \) and \( H_B \) are trans to each other and share a \( ^3J=17 \) Hz. \( H_C \) and \( H_B \) share a \( ^2J=1.4 \) Hz.

II. Carbon 13 NMR

A. General Information

1. About 1% of the carbons in an organic molecule are \(^{13}C\), most are the NMR inactive but more common isotope of \(^{12}C\). This means that in order to see a strong signal and interpret it to obtain a spectrum that we need to run the samples as concentrated as possible.

2. The peaks in a \(^{13}C\) spectra can not be integrated relative to one another as in \(^1H\) NMR.
a) CH$_3$ tend to be taller than CH$_2$ which tend to be larger than CH and quaternary carbons peaks will be quite short.

3. TMS is the internal standard as in $^1$H NMR and is set to zero. The chemical shift runs from 250 - 10 ppm.

B. Regions of interest in $^{13}$C.

![Figure 13-41](image)

Table of approximate chemical shift values for $^{13}$C NMR. Most of these values for a carbon atom are about 15 to 20 times the chemical shift of a proton if it were bonded to the carbon atom.

C. Coupling between C and H
1. $^{13}$C and H can and do couple with each other ($^1$J values). The problem is that the carbon atom can couple with the hydrogen attached to itself and the hydrogen on the neighboring carbon. This can make for a very messy spectrum.
   a) $^{13}$C to $^{13}$C coupling is not seen because it would be very unlikely to see two $^{13}$C atoms in the same molecule (remember most of the carbon is $^{12}$C).

D. Different experiments
1. Proton Decoupled Experiment
   a. This is the most common type of spectra for carbon 13.
   b. In this experiment a second radio pulse is used to hit the hydrogens in the molecule so that they can’t couple with the carbons.
   c. Thus **every carbon is a singlet**.

2. Off-Resonance Decoupling
   a. This allows only $^1$J C-H coupling to occur.
   b. The n+1 rule is followed, where n is the # of hydrogen attached to the carbon.
      1) Thus CH$_3$ are quartets, CH$_2$ are triplets and CH are doublets.
   c. Often these values are listed above a peak in a proton decoupled experiment so that both spectra don’t have to be printed out.