**A.** The coupling constants in the 300MHz spectrum are exactly the same as in the
in the 60 MHz instrument, but the sweep width of the 300 MHz spectrum is five
times as large, making the coupling constants appear smaller.

To produce separate signals with *clean* splitting patterns, the difference in
chemical shifts ($\Delta\nu$ in Hz) of two adjacent coupled protons ***must be*** at least 10
times the value of the coupling constant (J).
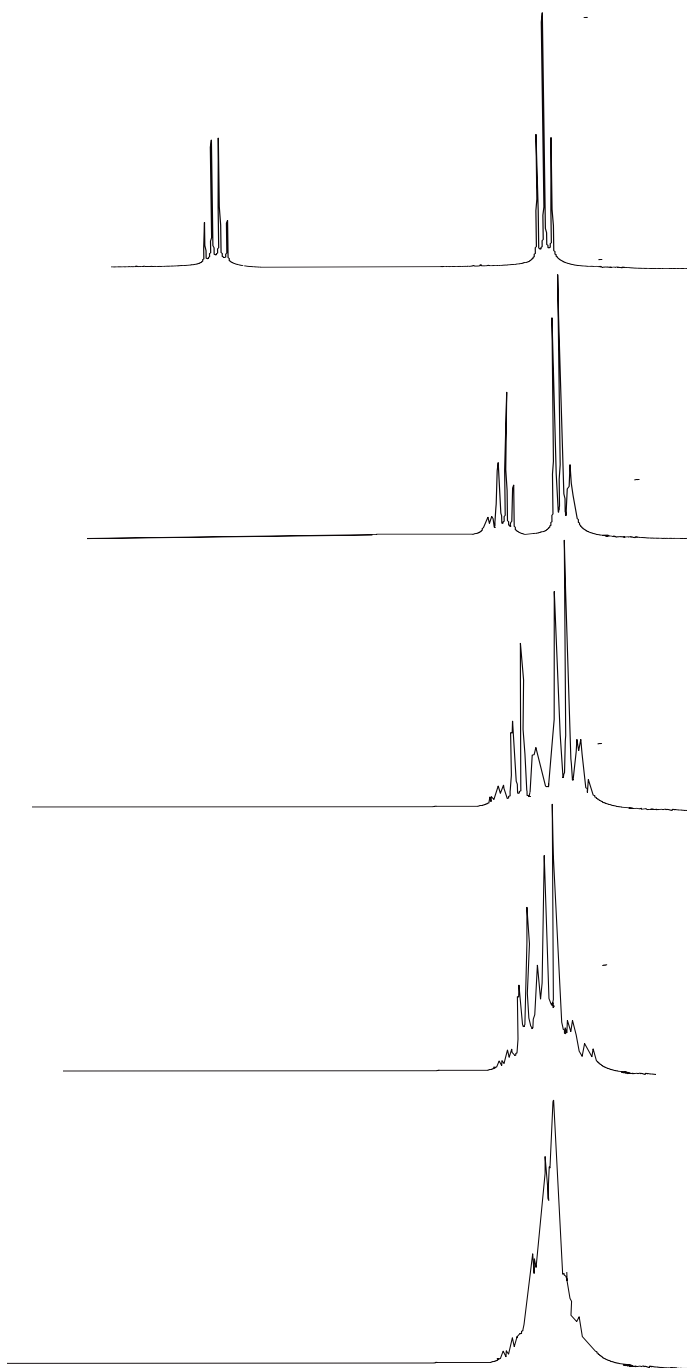
h) Sometimes a signal is split by two or more *different kinds of protons* with *similar coupling constants*. In propyl iodide, for example, the protons on the middle carbon (H_b) are split by two different types of protons (H_a, and H_c). The coupling constants for these two protons are similar ($J_{ab} = 7.3$ Hz and $J_{ac} = 6.8$ Hz.) The spectrum shows the H_b signal as a sextet, almost as though H_b was coupled to 5 equivalent protons. The second trace, enlarged and offset, shows that the pattern is not a perfect sextet. It is actually a quartet of triplets:

$$H_3C-CH_2-CH_2-I$$
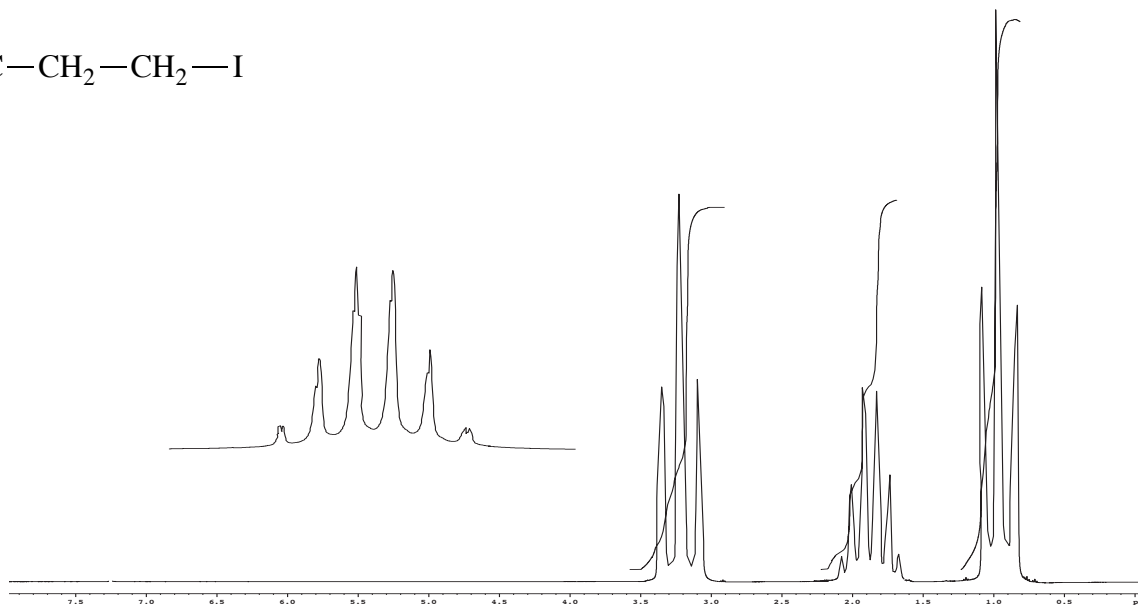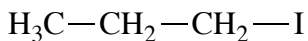
Taking this HNMR on a higher field instrument gives even better resolution:
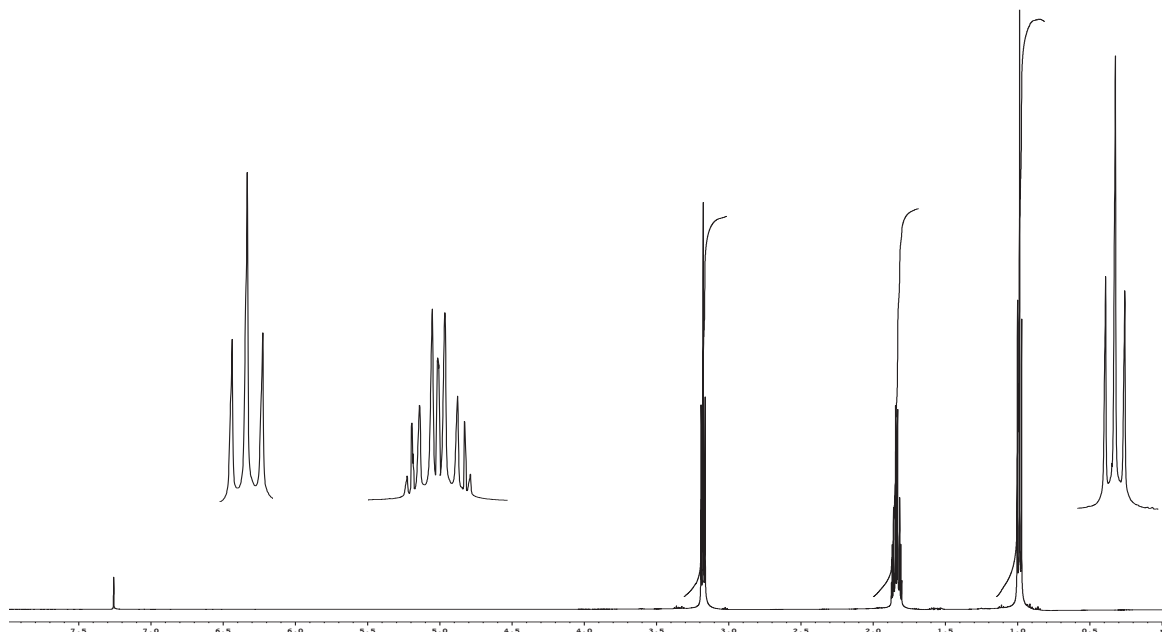
How do you interpret an ^{1}HNMR spectrum?

1) Evaluate the units of unsaturation (as for IR) from the molecular formula.

2) If you have an IR of the compound, analyze the IR spectrum to determine functional groups.

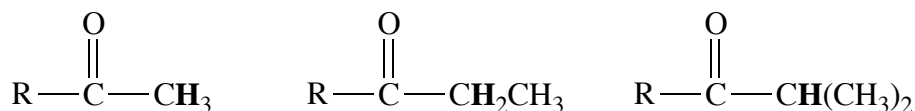3) Look for major features in the NMR first before worrying about details. Consider the following:

   a) Broad singlets are usually due to hydrogens bound to O or N. If a broad singlet appears above 10 ppm, you probably have a carboxylic acid.
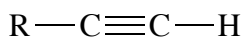
$$—O—H \qquad\qquad —N—H \qquad\qquad \overset{\displaystyle O}{\overset{\|}{—C}}—O—H$$
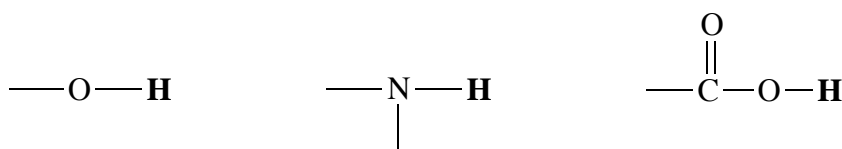
   b) Absorptions around 3 or 4 ppm are typical for hydrogens on carbons bonded to electronegative groups such as halogens or oxygen.

$$Cl—C—H \qquad Br—C—H \qquad I—C—H \qquad —O—C—H$$

   c) Absorptions from about 2.1-2.5 ppm usually mean you have protons adjacent to a carbonyl.

$$\overset{\displaystyle O}{\overset{\|}{R—C}}—CH_3 \qquad \overset{\displaystyle O}{\overset{\|}{R—C}}—CH_2CH_3 \qquad \overset{\displaystyle O}{\overset{\|}{R—C}}—CH(CH_3)_2$$

   d) A sharp singlet at 2.5 ppm is consistent with a proton on a terminal alkyne.

$$R—C\equiv C—H$$

e) Absorptions from about 9-10 ppm are consistent with an aldehyde proton. An aldehyde proton has a *very small* coupling constant with protons on the carbon adjacent to the aldehyde carbonyl, so the peak can often appear as a singlet, especially if the NMR is taken on a lower field instrument.

$$RCH_2 - \underset{\underset{\|}{O}}{C} - H$$
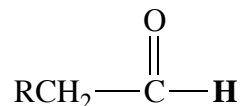
f) Absorptions around 7-8 ppm are typical for hydrogens bonded to aromatic rings.
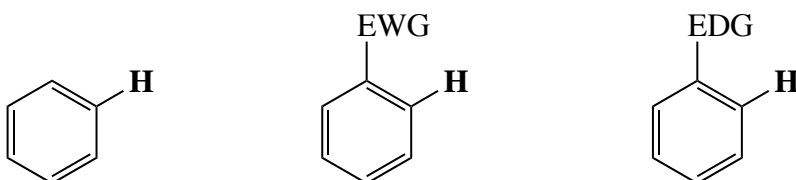
g) Absorptions between 5-6 ppm are consistent with vinyl protons. Coupling constants can be measured and used to determine whether you have a cis, trans, or germinal substitution pattern. If you don't have any units of unsaturation to account for a alkene, you may have a hydrogen on a carbon bonded to *more than one electronegative group*.

or CH_2Cl_2 CH_3OCH_2OH
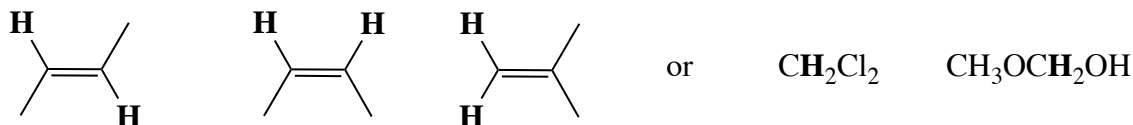
h) Vinylic protons can be moved significantly downfield when electron-withdrawing groups are bonded to the π-system.
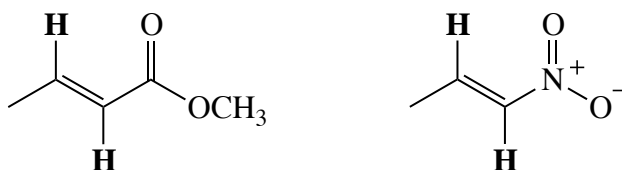
i) Look for common splitting patterns:
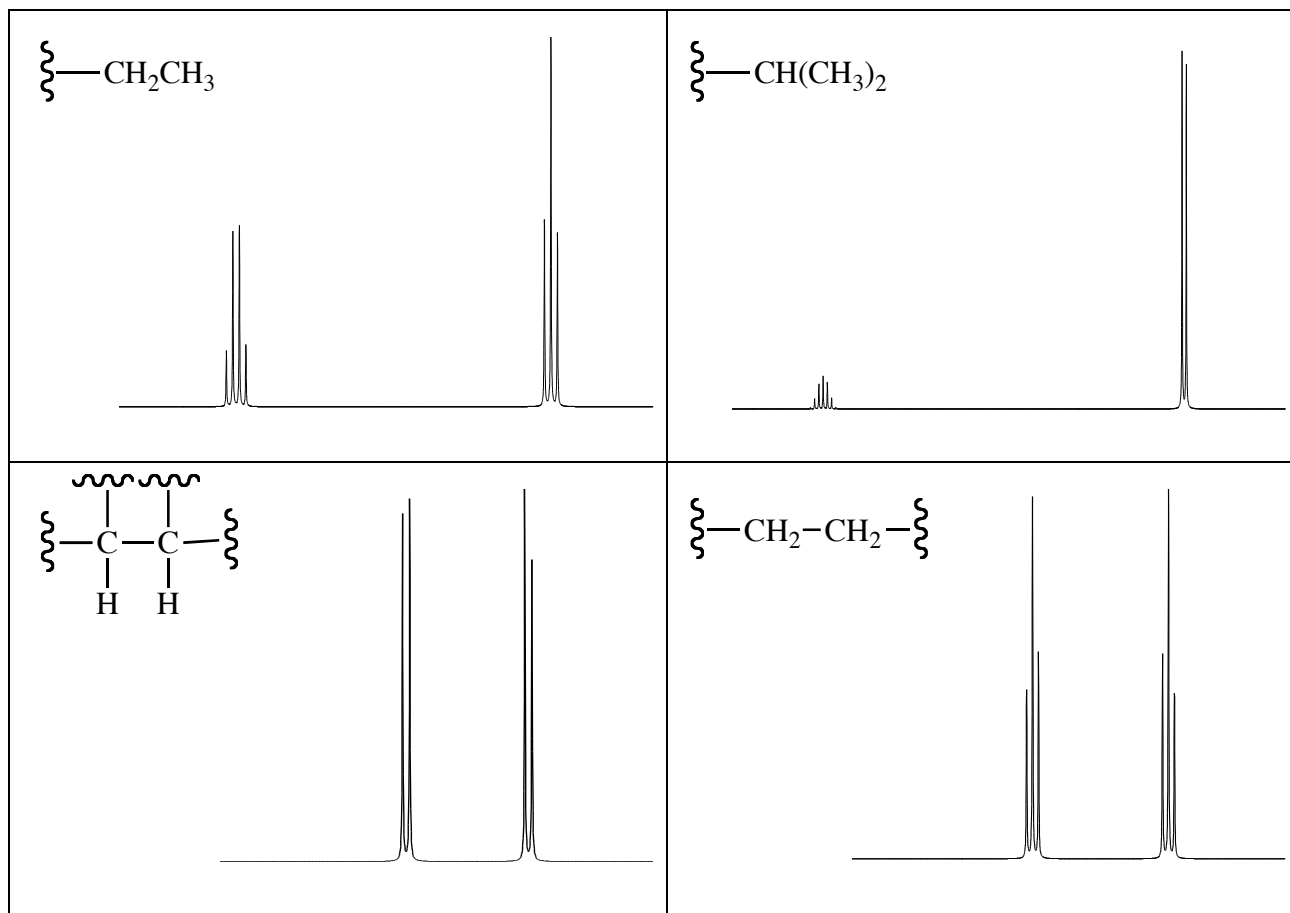
4) Now for the details: Look at the relative integrations to determine how many kinds of hydrogens there are.

5) Correlate H's with diagnostic hydrogens listed in the table given.

6) Propose structures. Correlate the splitting patterns with the structures.

II. ^{13}C Nuclear Magnetic Resonance

Any nucleus with a spin number of $^{1}/_{2}$ can be studied by NMR spectroscopy. The nucleus of ^{13}C has a spin number of $^{1}/_{2}$ just like hydrogen. The natural abundance of ^{13}C, however, is only 1% so there is a **huge** sensitivity problem. A ^{13}CNMR is expected to be about 1% as intense as a ^{1}HNMR spectrum.
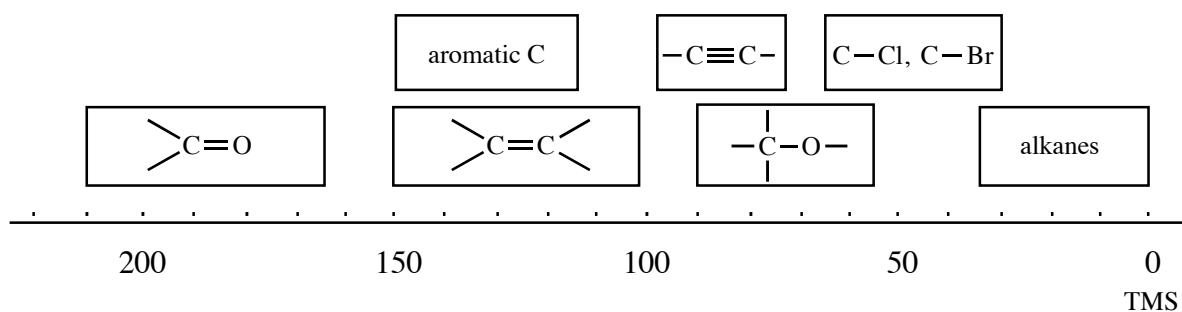
- must use more concentrated samples and/or scan longer to get a comparable spectrum.

The ^{13}C principles are basically the same as ^1HNMR, but some aspects are unique to $^{13}CNMR$:

1) Coupling between carbons is generally not observed. ***Why?***

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$$
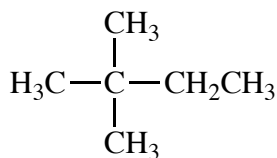
2) The range of chemical shifts is very large compared to ^1HNMR:

| | aromatic C | | $-C\equiv C-$ | C$-$Cl, C$-$Br |
| $>C=O$ | | $>C=C<$ | $-\overset{|}{\underset{|}{C}}-O-$ | alkanes |

```
   200        150        100        50         0
                                              TMS
```

3) Coupling between carbon and hydrogens ($^{13}C - {}^1H$) does occur. This presents its own problems:

- Typical coupling constants are large (20 to 120 Hz for directly attached protons, but longer range coupling is also observed.) Protons on carbons one and two and three carbons away can also cause splitting!
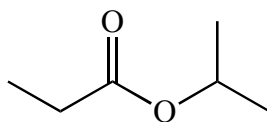
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$$
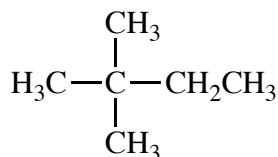
- Typically, the spectra are run **proton-decoupled** to simplify the analysis

4) ^{13}CNMR spectra are not integrated.

5) We will rely on two features of ^{13}CNMR spectra to solve structures in this class:

Sample problem: How many lines are observed in the ^{13}CNMR spectra of the following compound? Which carbon signal would be the furthest downfield?

Compare the ^{1}HNMR and ^{13}CNMR for cholesterol: