Introduction to Spectroscopy IV:
# Interpreting ^{13}C NMR

Basics:
^{12}C has an even number of protons and an even number of neutrons so is not observable in NMR spectroscopy. However ^{13}C has an odd number of neutrons and an odd mass number so is a spin +1/2 nucleus that is observable by NMR. However, ^{13}C is only about 1.1% of naturally abundant carbon so the signal from ^{13}C NMR is much weaker than that of ^{1}H NMR. The physics behind ^{13}C NMR is the same as that of ^{1}H NMR, but due in part to the much lower abundance of carbon, and its lower sensitivity on a per nucleus basis, how we go about analyzing ^{13}C NMR is a bit different.

Chemical Shift:
Chemical shift for ^{13}C NMR works under the same principles as ^{1}H NMR. The more deshielded a nucleus is the more left (downfield) it shifts. ^{13}C has a much larger range than ^{1}H does and chemical shifts for ^{13}C range from about 0-200 ppm. This larger range actually helps analysis as similar chemical environments are spread out over the range so it's uncommon for ^{13}C NMR signals to be at the same chemical shift unless the carbons are chemically equivalent. The values in table 10.6 in Vollhardt+Schore should be remembered.

- A general rule of thumb for ^{13}C NMR is that the *^{13}C chemical shift is 20x that of the ^{1}H NMR chemical shift.* This is not absolutely true, but is close enough to get into the correct zone.
- CH_3 are shielded (right/upfield) compared to CH_2, which are shielded compared to CH.
- sp^3 carbons are shielded and typically below 90 ppm,
- sp^2 carbons are deshielded and typically above 100 ppm.
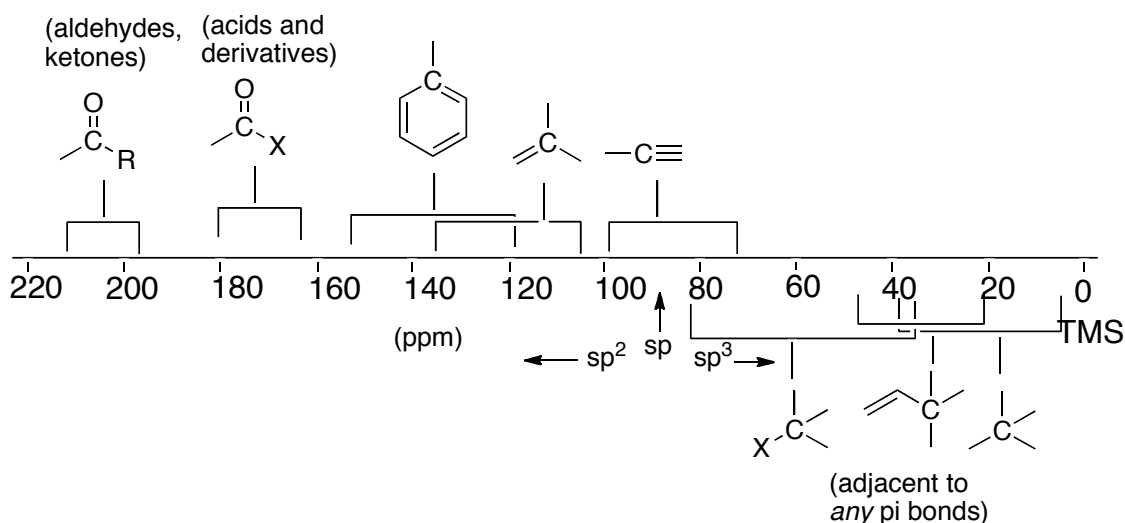
Coupling/Decoupling:

Since the relative abundance of ^{13}C is so small (~1/100 carbons) it's extremely unlikely that two ^{13}C will be adjacent to each other and show coupling as we see it in ^{1}H NMR. The chances of two coupled ^{13}C are approximately 1 in 10,000 so we don't use coupling to determine neighbors.

However, the H attached to a ^{13}C do couple to the ^{13}C nucleus and affect its resonance frequency. A quaternary C will show up as a singlet, a CH will show up as a doublet, a CH_2 as a triplet, and a CH_3 as a quartet if we treat carbon NMR the same as proton NMR. This coupling is inconvenient as it lowers the already weak ^{13}C signal by splitting it into several peaks in a multiplet. Typically carbon NMR is much less sensitive than proton NMR, so when the peak is spread out into a multiplet by coupling, it gets even harder to separate from background noise.

In order to make the signals stronger ^{13}C NMR spectra are decoupled. The radio frequencies are manipulated in a way to prevent the protons from coupling to the attached carbons, so all ^{13}C NMR signals appear as singlets regardless of the number of attached protons. This does result in the loss of some information about number of protons, but allows all ^{13}C NMR signals to be visible in a much shorter period of time.

NOTE: To get an interpretable ^{1}H NMR on a 20 mg sample takes from 30 seconds to 2 minutes in a 400 MHz FT-NMR spectrophotometer (1-16 scans). To get an interpretable ^{13}C NMR spectrum on the same sample with the same spectrophotometer will take 20 minutes to an hour (256-1024 scans) when decoupled and even longer when coupled.

Integration:

Integration does not effectively show the relative number of nuclei in ^{13}C NMR as it does in ^{1}H NMR. The peak area of a single CH_3 nucleus is somewhat larger than that of a single CH_2 or CH nucleus, and quaternary carbons have very small peak areas. The reasons have to do with relaxation effects on the excited states by attached protons and are beyond the scope of this class.
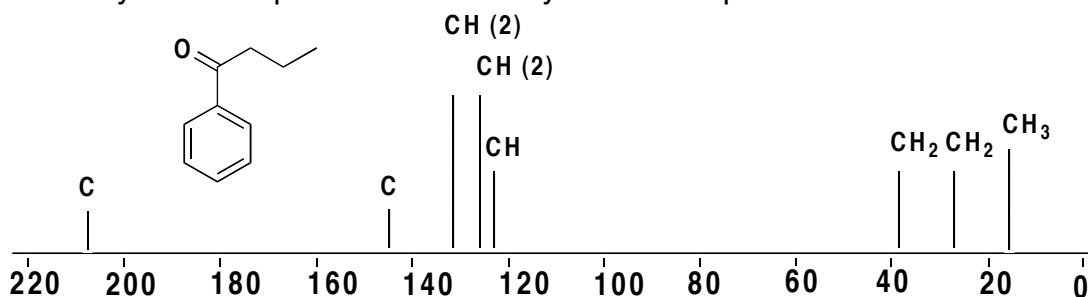

All but two of these signals represent a one carbon singlet and they vary greatly in height. The two CH at 129 and 135 ppm both represent two equivalent carbons and are corresponingly taller than the other $CH/CH_2/CH_3$ signals. Symmetrical carbons do tend to show up as taller peaks and can be picked out with practice. The two quaternary carbons at 208 ppm and 144 ppm are significantly shorter than the $CH/CH_2/CH_3$ signals indicating that they are probably quaternary.

APT/DEPT:

There are 3 possible ways to determine the number of protons bonded to a particular carbon: coupled spectra, APT, and DEPT. While the physics behind the experiments is beyond the scope of this course, the interpretation of the spectra is straight forward if one knows which kind of spectrum one is looking at.

Coupled spectra:

Coupled spectra *don't* decouple the ^1H from the ^{13}C. They show C as singlets, CH as doublets, CH_2 as triplets and CH_3 as quartets. While simple to do, they are not particularly efficient and are not common.
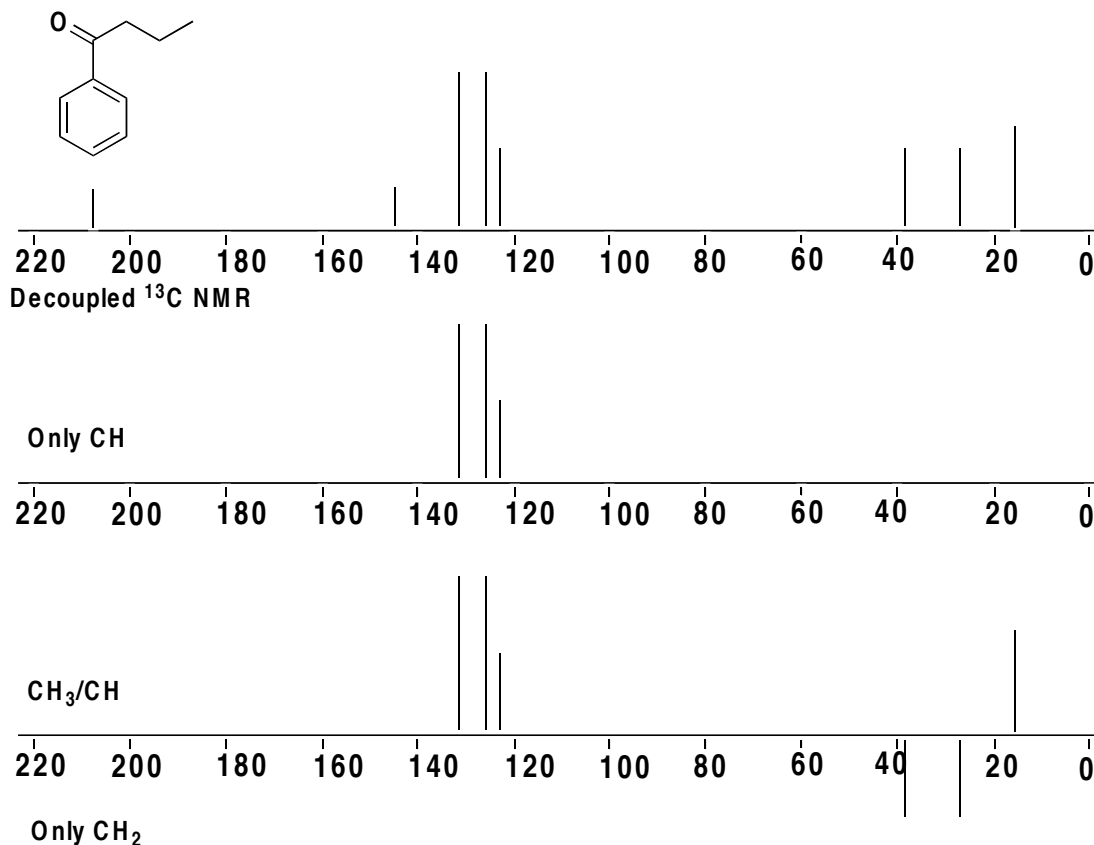

Coupled ^{13}C NMR
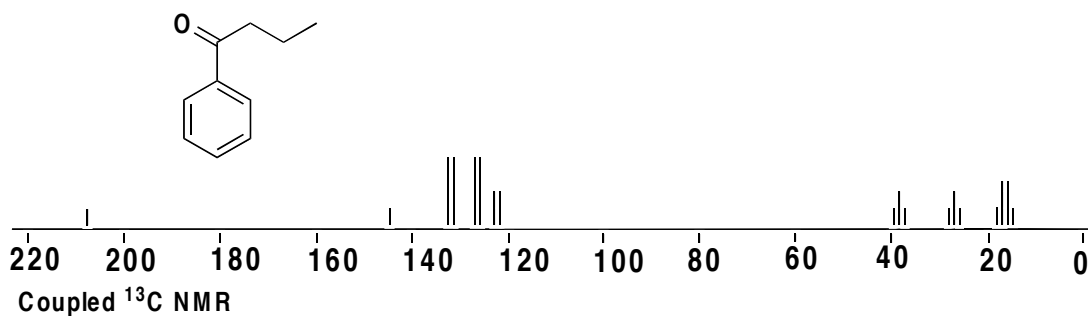
Attached Proton Test (APT):

APT spectra usually consist of two aligned scales with ^{13}C NMR data. One is the normal ^{13}C NMR spectrum, the other shows peaks pointing both up and down. The upward pointing peaks will have odd numbers of H (CH_3 and CH), the downward pointing peaks will have even numbers of attached H (CH_2 and C). Occasionally spectra are phased with the reverse direction odd numbers of H downwards and even numbers of H upwards. When in doubt, look for a signal you're sure of and determine which way it's going, the rest will follow.

Decoupled ^{13}C NMR

CH_3/CH

CH_2/C

24
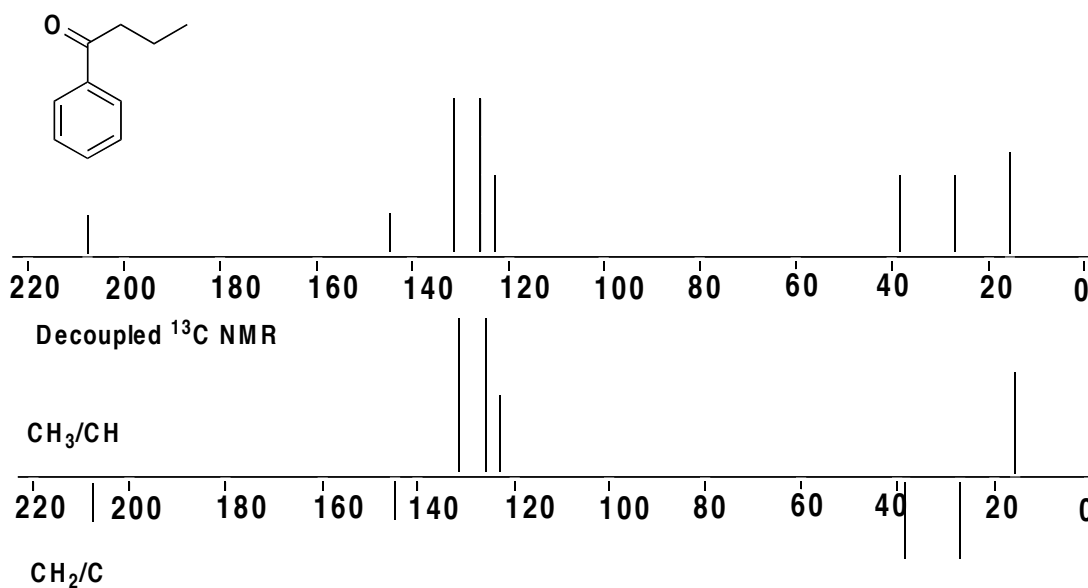
Distortionless Enhanced Polarization Transfer (DEPT):

DEPT experiments show either 3 or 4 scales. The classic experiment shows the normal ^{13}C NMR spectrum, then a DEPT-90 which shows only the CH peaks, then a DEPT-135 which shows the CH and CH_3 peaks as upwards and the CH_2 peaks as downwards (no signals for C). Some printouts will display the normal spectrum, then add and subtract the normal, DEPT-90 and DEPT-135 spectra to show a scale with just CH_3, as scale with just CH_2 and a scale with just CH.

Key Points:

- Carbon NMR only detects ^{13}C (approximately 1% natural abundance).

- ^{13}C chemical shift is approximately 20x the ^1H chemical shift.

- ^{13}C NMR is decoupled so all peaks appear as singlets.

- Peak areas are not an exact ratio of number of equivalent carbons.

- APT and DEPT can differentiate between C, CH, CH_2 and CH_3 signals.