

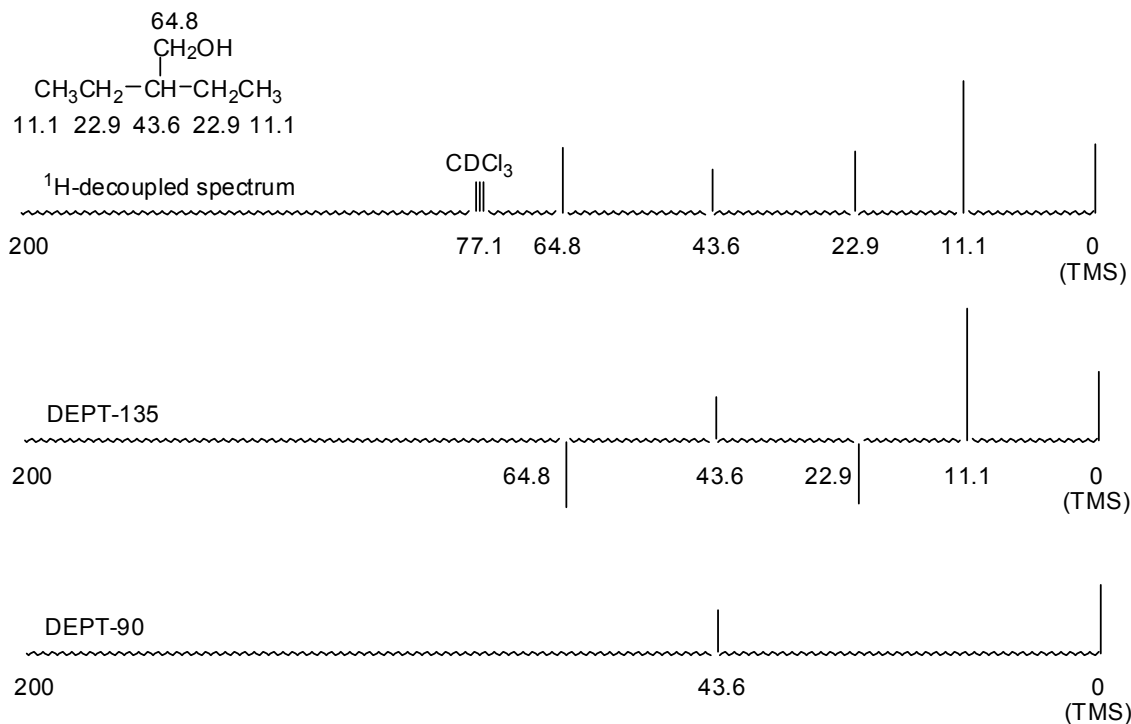
¹³C NMR Spectroscopy (#1d)

Although some special tricks must be employed, ¹³C nuclei can be studied in ways similar to studying the ¹H nucleus. The ¹H nucleus gives a stronger NMR signal than ¹³C because ¹³C has a much lower natural abundance. Only 1% of C atoms are ¹³C. To solve this problem, we employ two modifications to the data acquisition. First, the spectral data is taken many times and added together. Second, we use a mathematical trick called a Fourier transform (FT) to obtain the data more quickly. There are some surprising consequences of using these tricks. Any coupling information that would be present is lost, producing what are known as “proton-decoupled spectra.” Also, the area under the peaks becomes distorted so integration is no longer useful. As a result, peaks in ¹³C spectra appear as singlets. However, we can still obtain the number of different carbon environments and chemical shift information from proton-decoupled ¹³C NMR spectra, which can tell us about functional groups in the molecule.

¹³C NMR spectra cover a wide range, from 0 to about 220 ppm, where carbonyl carbons are found. The degree of substitution on a carbon has about as much effect on its chemical shift position as does the presence of an electronegative atom. Generally, sp³-hybridized carbons appear between 8-60 ppm and sp²-hybridized carbons between 100-150 ppm. Carbonyls appear between 160-220 ppm.

A modern method for obtaining ¹³C NMR spectra involves a complex series of pulses of radio-frequency radiation and delays before the data is acquired. Using this technique, which is called DEPT (Distortionless Enhancement by Polarization Transfer), we can regain the coupling information that is lost in proton-decoupled spectra. Usually, three spectra are obtained: 1. A proton-decoupled spectrum that shows all carbon environments in the molecule; 2. A DEPT-90 spectrum showing only CH protons as upright singlets; and 3. A DEPT-135 spectrum showing CH₃'s and CH's as upright singlets and CH₂'s as *inverted* singlets. By finding the upright peaks in the DEPT-135 that are not found in the DEPT-90, the CH₃'s can be determined. Quaternary carbons are identified by the fact that they appear in the ordinary decoupled spectrum but not in either DEPT experiment. Often, peaks are listed for a ¹³C NMR spectrum with an asterisk listed beside the number. This asterisk is used to denote peaks that are upright singlets in a DEPT-135 experiment: the CH's and CH₃'s.

The example below shows the DEPT and proton decoupled spectra for 2-ethyl-1-butanol. The proton decoupled spectrum at the top shows all of the carbon environments. Note that the solvent peak appears at 77.1 ppm. Even though there are 6 carbons in the formula, note that there are only four different carbon environments in the decoupled spectrum. Therefore, the molecule must contain symmetry. The only CH in the molecule appears in the DEPT-90 spectrum at 43.6 ppm. The DEPT-135 spectrum reveals that there are two CH₂'s, at 64.8 and 22.9 ppm. The only CH₃ environment appears at 11.1 ppm. It appears as a taller peak than the others because it belongs to a CH₃ rather than a CH or quaternary C. Also, note that the carbon bearing the alcohol functional group is shifted farther downfield than the other carbons to 64.8 ppm.

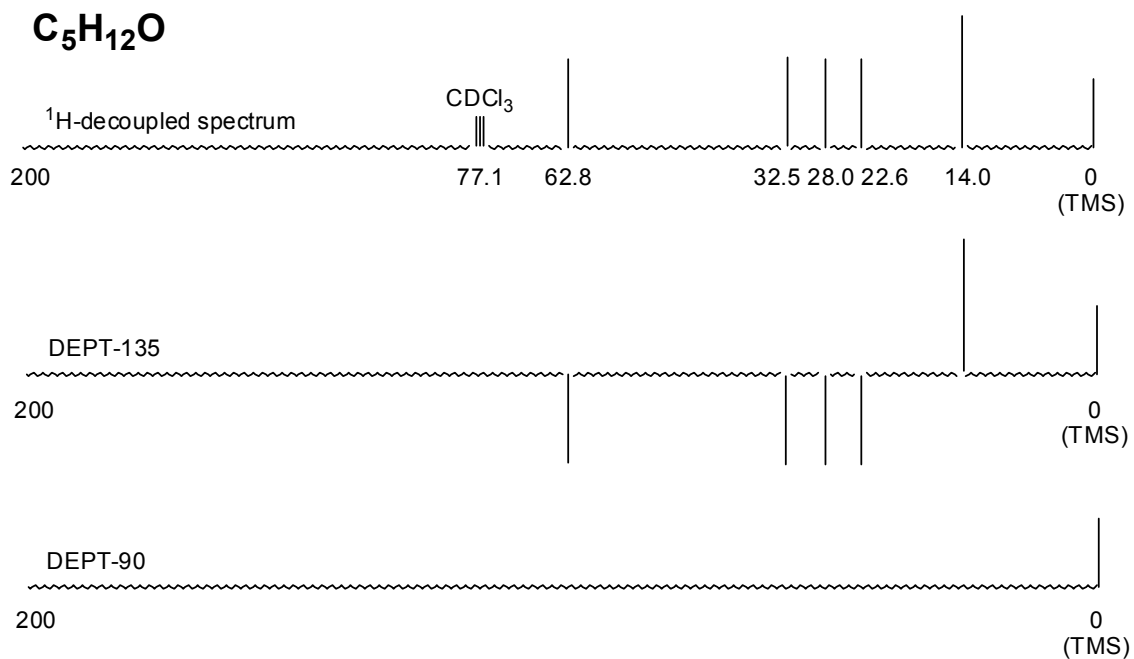


Postlab

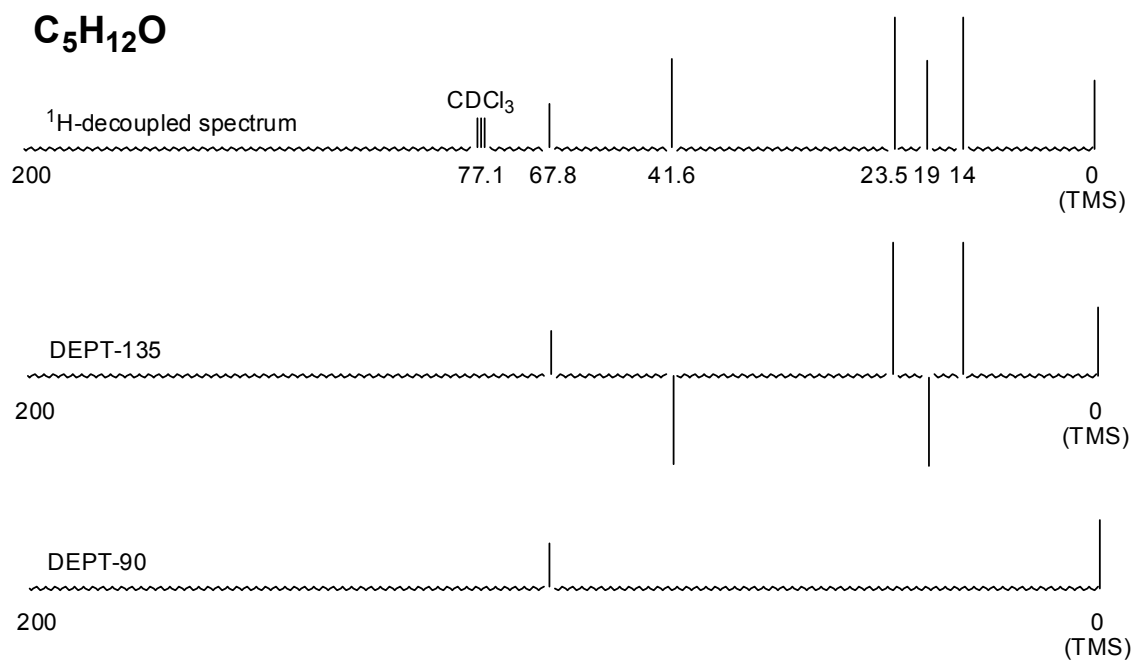
You should complete the following assignment in your lab notebook along with the other spectroscopy assignments.

1. Propose structures for the following isomeric alcohols that give the ^{13}C NMR spectra below. Assign the carbons to their respective peaks. A table of chemical shifts is located on page 42.

A.



B.



C.

