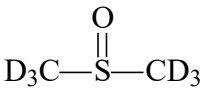
NMR Samples

You will receive a sample of your unknown for this experiment in an NMR tube (it is the same unknown you distilled and characterized last week). The unknown is dissolved in DMSO-d_6. The solvent contains "heavy" hydrogen atoms (^{2}H or D, deuterium) so the solvent's nuclei will not be detected. Trimethylsilane (TMS, $(CH_3)_4Si$)) is the internal standard. Because of the relatively electropositive silicon, the hydrogens on the methyl group absorb far upfield in the NMR spectrum and are assigned a chemical shift of 0 ppm. All other ^{1}H NMR chemical shifts are downfield from TMS.



Your tube may have a small separate layer on top. The top layer is TMS, which has only a low solubility in DMSO-d_6. The solution is probably saturated in TMS and so there is no need to shake the tube.

All tubes have a Teflon vortex plug packed with Teflon tape. It will either be hidden at the top, or lower in the tube so it is visible. This is a device used to slow TMS evaporation from the tube. Ignore it.

Experimental ^{1}H-NMR spectrum interpretation

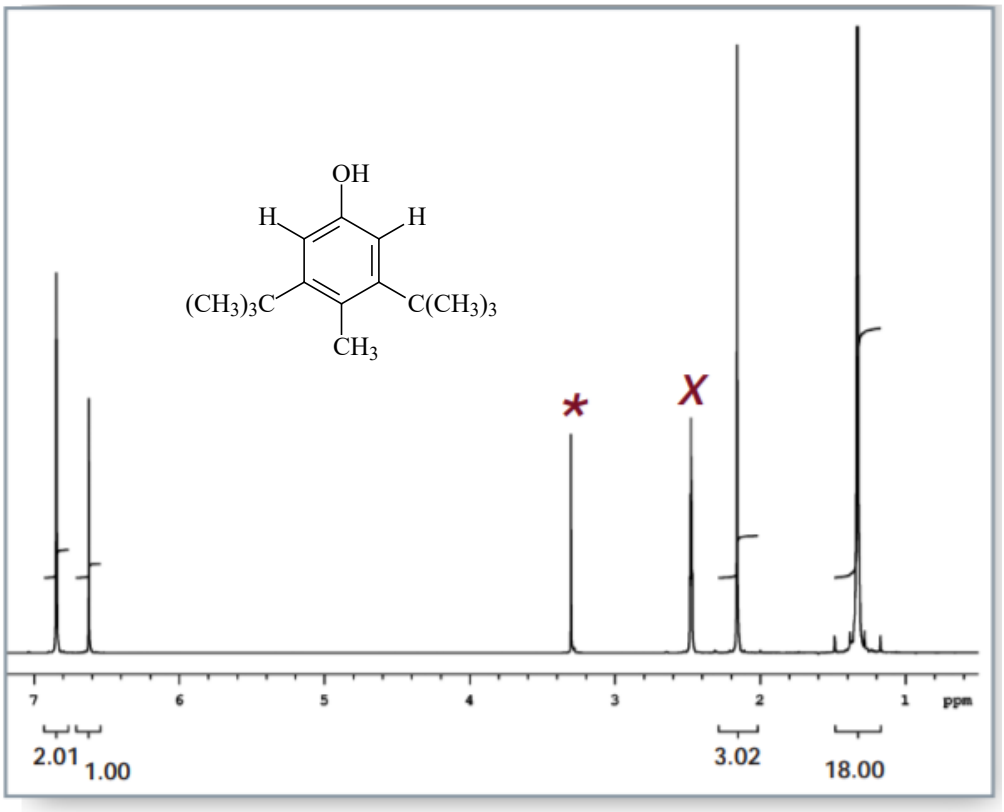
When you obtain your spectrum on the 400 MHz NMR in the GMU NMR Center, it will consist of four pages. On one page there will be the entire spectrum from −1 to +17 ppm. The TMS standard peak appears at 0 ppm. You should very carefully measure the peak integration heights (± 0.5mm) and calculate the ratio of hydrogen atoms present in the unknown. The integration is fairly precise and so you should carefully consider the results in your written analysis.

In the spectrum that is compressed onto one page, it is difficult to discern the splitting patterns. The remaining pages are of the spectrum divided roughly into thirds: 0 - 6 ppm, 6 - 11 ppm, and 11 - 16 ppm. Each of these pages shows the splitting patterns more clearly so that you can analyze them. In addition, the NMR instrument shows the largest peak on each page at full intensity. This may mean that a very small peak in the 1-page spectrum may be very large in the segmented spectrum. You should ignore these differences in intensity. Turn in all pages with your report.

Peaks to be disregarded

- If there are any H atoms in the DMSO solvent that are not replaced by D, they will appear as a peak at **2.5 ppm**. Disregard this peak.
- The spectra taken in DMSO-d_6 have a prominent singlet at **3.3-3.7 ppm** which is due to the presence of H_2O and HOD, both of which absorb in the NMR. You should disregard this peak.

- You may also see a very small, narrow peak at **8.0 ppm**. If it is present, it is due to an electronic artifact and so you should disregard this peak.



[1]H-NMR spectrum of 2,6-di-*tert*-butyl-4-methylphenol in DMSO-d_6. Cambridge Isotope Laboratories, Inc., http://www2.chem.umd.edu/nmr/reference/isotope_solvent.pdf (accessed 5/8/2019).

*-residual water X -residual solvent

Alcohols

When you look at textbook NMR examples of alcohols dissolved in $CDCl_3$ solvent, the H on the hydroxyl –OH appears as a singlet (ideally) because it is rapidly exchanging H^+ with neighboring OH's. This process is catalyzed by stray DCl, which is always present in routine $CDCl_3$ from photolytic free radical reactions.

Alcohol unknowns in DMSO-d_6, in contrast to this, have OH coupled to neighboring alkyls (if there is one) because DMSO-d_6 has no stray acid. This can be confusing until you look at examples of alcohols dissolved in different solvents. The unknown samples in this course are dissolved in DMSO-d_6.

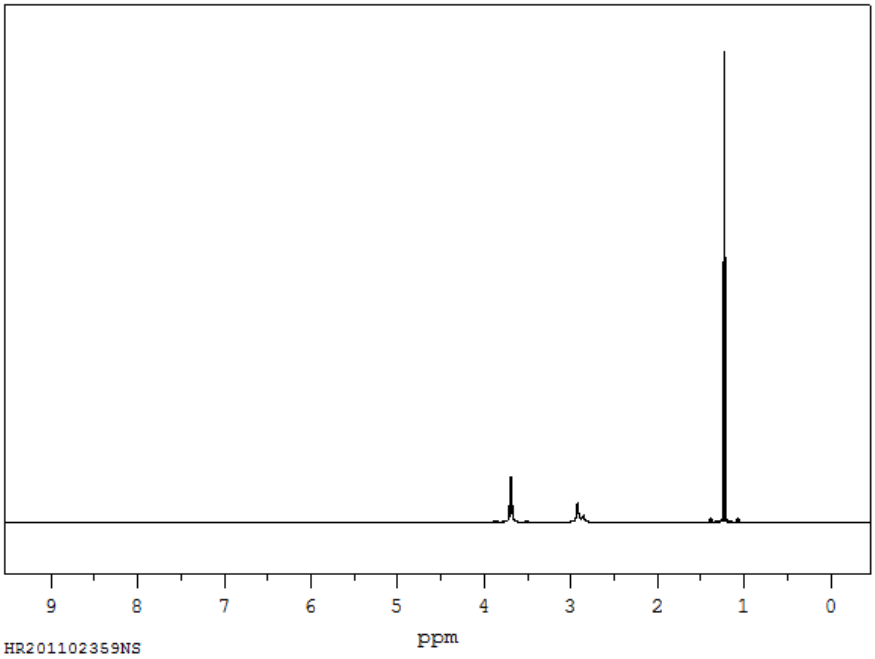


Figure 1 Ethanol in DMSO-d_6

The two figures shown here are both 400 MHz H NMR spectra of ethanol, CH_3CH_2OH. The top spectrum is in DMSO-d_6 And the bottom spectrum is in $CDCl_3$.

First, the chemical shifts for the H's in the different solvent are a bit different. This emphasizes the importance of comparing spectra taken only in identical solvents.

However, the H's bonded to C are in the expected region: the CH_3 hydrogens are upfield, around 1 ppm, and the CH_2 hydrogens are downfield, around 3.5 ppm. They also exhibit the expected splitting patterns: a triplet for the CH_3 methyl group and a quartet for the CH_2 methylene group. The chemical shift of H on the OH hydroxy group varies quite a bit in the two solvents and depends on specific interactions with the solvent.

Furthermore, in DMSO-d_6, the splitting of the H is clearly a triplet at 4.3 ppm. Signal in $CDCl_3$ at 2.9 ppm is a collection of peaks due to H-exchange with the solvent.

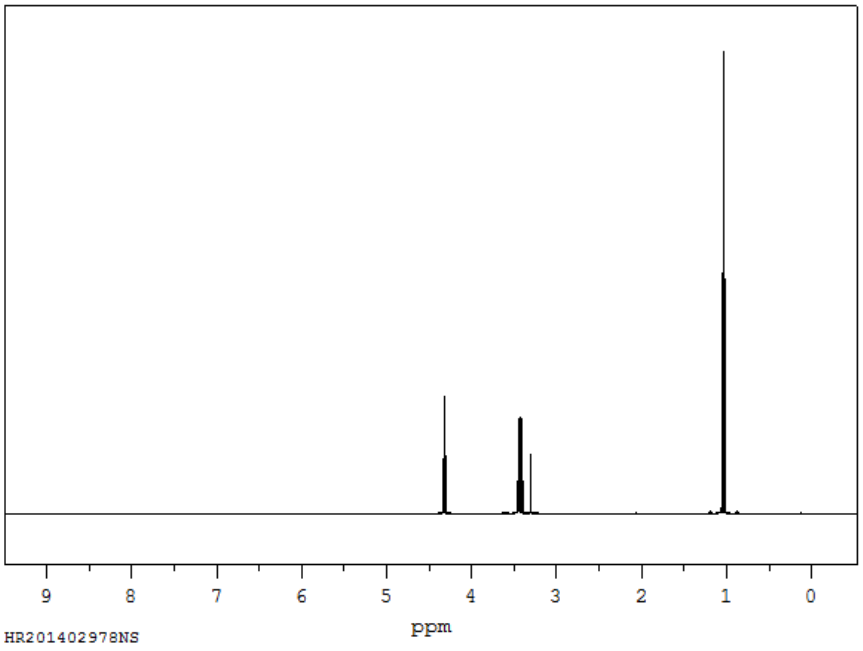


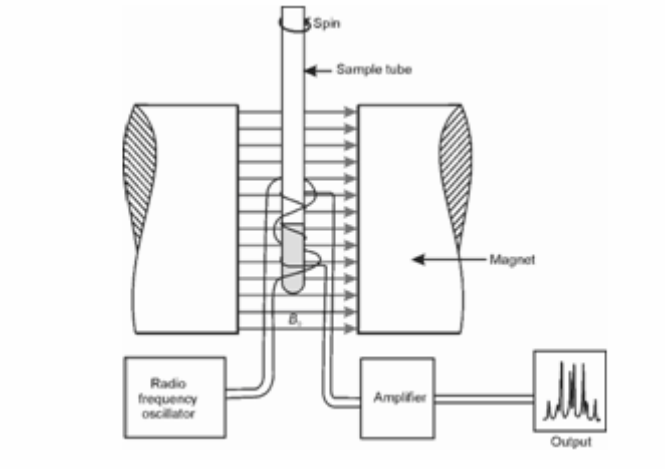
Figure 2 Ethanol in $CDCl_3$

Two important parts of the NMR spectrometer: the magnet and the probe

An NMR spectrometer is a complex system and won't be described in any detail here. However, there is some terminology that you should be familiar with and that supplements the reading in your lab textbook.

The NMR tube holding the sample is inserted into the **probe** which is within the magnet bore. The probe houses the radiofrequency (RF) transmitter that irradiates the sample and the receiver that detects the RF NMR signal from the sample. The probe must be "tuned" in order to reduce noise and increase signal output.

The superconducting **magnet** is cooled with liquid helium (B.pt. 4.2K), which itself is kept cool with liquid nitrogen (B.pt. 77K). The applied magnetic field in the spectrometer may not be homogeneous. Inhomogeneous magnetic fields arise from defects in the magnet itself or from deviations due to the presence of the probe and the sample in the magnetic field. The process of correcting the inhomogeneities is called "**shimming**". If this is not done, the signals in the spectrum are not sharp and splitting patterns might not be discerned. Shimming is performed using small electrical coils that generate a magnetic field within the spectrometer.



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