

Excerpts from <http://www.cis.rit.edu/htbooks/nmr/nmr-main.htm>
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Sample Preparation

NMR samples are prepared by dissolving an analyte in a deuterium lock solvent. Several deuterium lock solvents are available. Some of these solvents will readily absorb moisture from the atmosphere and give water signal in your spectrum. It is therefore advisable to keep bottles of these solvents tightly capped when not in use.

Most routine high-resolution NMR samples are prepared and run in 5 mm glass NMR tubes. Always fill your NMR tubes to the same height with lock solvent. This will minimize the amount of magnetic field shimming required. Figure 1 depicts a sample tube filled with solvent such that it fills the RF coil.

NMR Lock Solvents	
Acetone	CD ₃ COCD ₃
Chloroform	CDCl ₃
Dichloro Methane	CD ₂ Cl ₂
Methylnitrile	CD ₃ CN
Benzene	C ₆ D ₆
Water	D ₂ O
Diethylether(DEE)	(CD ₃ CD ₂) ₂ O
Dimethylether(DME)	(CD ₃) ₂ O
N,N-Dimethylformamide (DMF)	(CD ₃) ₂ NCDO
Dimethyl Sulfoxide (DMSO)	CD ₃ SOCD ₃
Ethanol	CD ₃ CD ₂ OD
Methanol	CD ₃ OD
Tetrahydrofuran (THF)	C ₄ D ₈ O
Toluene	C ₆ D ₅ CD ₃
Pyridine	C ₅ D ₅ N
Cyclohexane	C ₆ H ₁₂

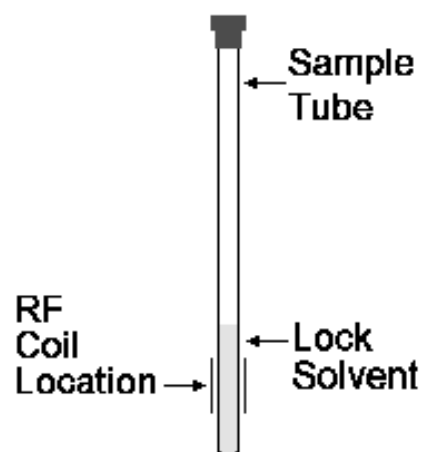


Figure 1

The concentration of your sample should be great enough to give a good signal-to-noise ratio in your spectrum, yet minimize exchange effects found at high concentrations. The exact concentration of your sample in the lock solvent will depend on the sensitivity of the spectrometer. If you have no guidelines for a specific spectrometer, use one drop of analyte for liquids and one or two crystals for solid samples.

The position of spectral lines can be solvent dependent. Therefore, if you are comparing spectra or trying to identify an unknown sample by comparison to reference spectra, use the same solvent. The hydrogen NMR spectrum of ethanol is a good example of this solvent dependence. Compare the positions of the CH₃, CH₂, and OH absorption lines in a hydrogen NMR spectrum

of ethanol in the lock solvents CDCl_3 and D_2O . Notice also that the relative peak heights are not the same in the two spectra. This is because the linewidths are not equal. The area under a peak, not the height of a peak, is proportional to the number of hydrogens in a sample.

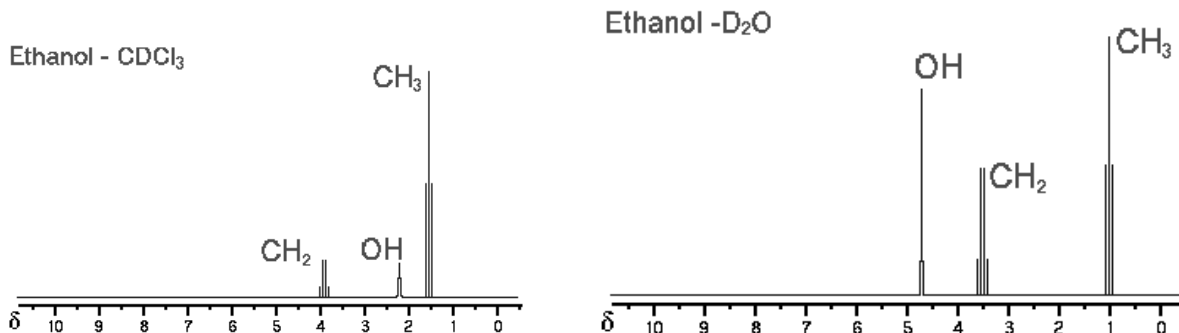


Figure 2

Variations in the polarity and dielectric constant of the lock solvent will also effect the tuning of the probe. The correction of these effects can be achieved by tuning the probe.

Field Shimming

The purpose of shimming a magnet is to make the magnetic field more homogeneous and to obtain better spectral resolution. Shimming can be performed manually or by automatically. It is not the intent of this section to teach you a systematic procedure for shimming, but to present you with the basic theory so that you can (with the aid of the manual) shim your magnet.

Broad lines, asymmetric lines, and a loss of resolution are indications that a magnet needs to be shimmed. The shape of an NMR line is a good indication of which shim is misadjusted. Consider a single narrow NMR line. If we zoom in on this line, we might see the following shape. The following series of spectra depict the appearance of this spectral line in the presence of various inhomogeneities

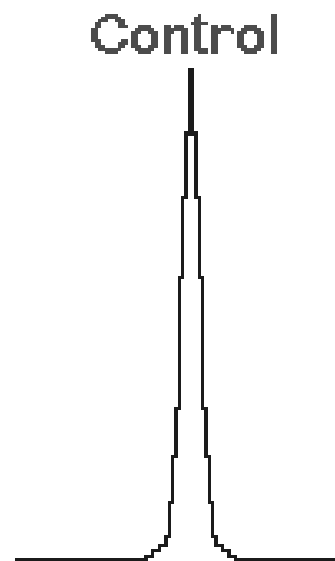
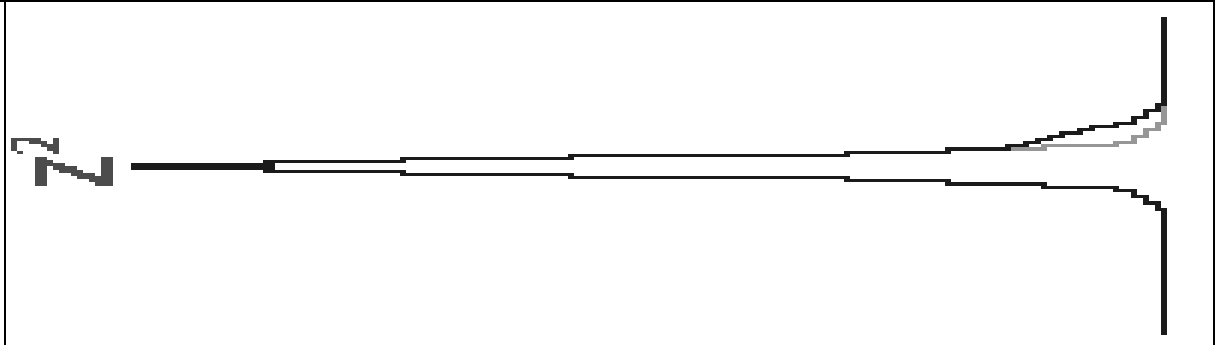
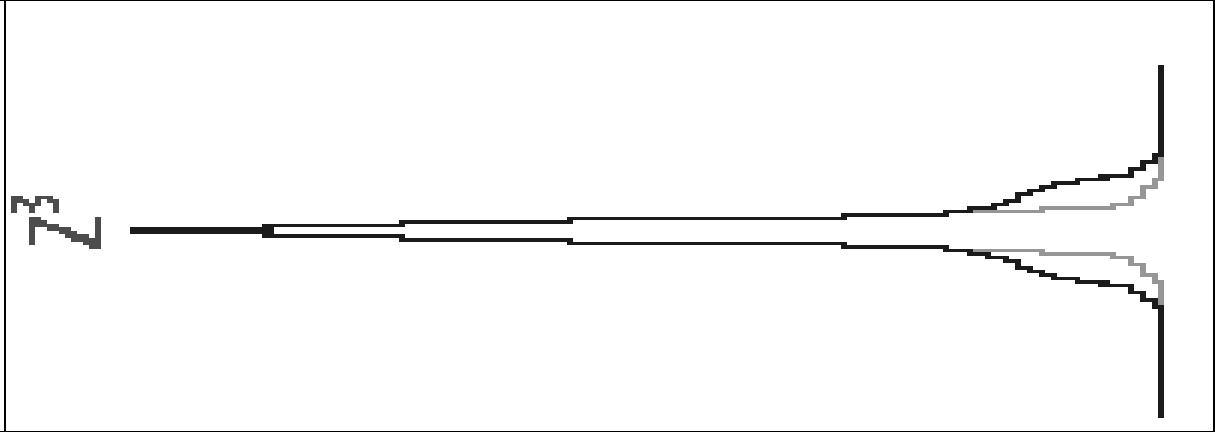
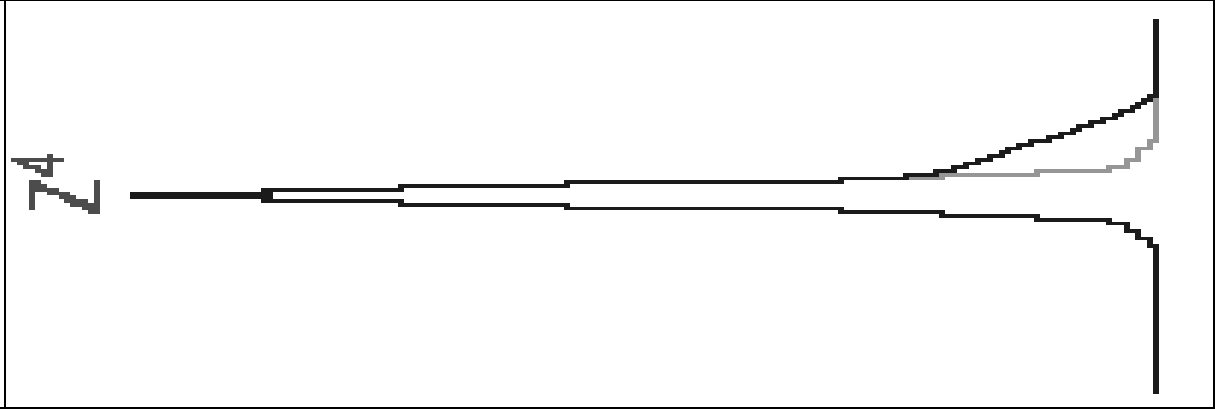
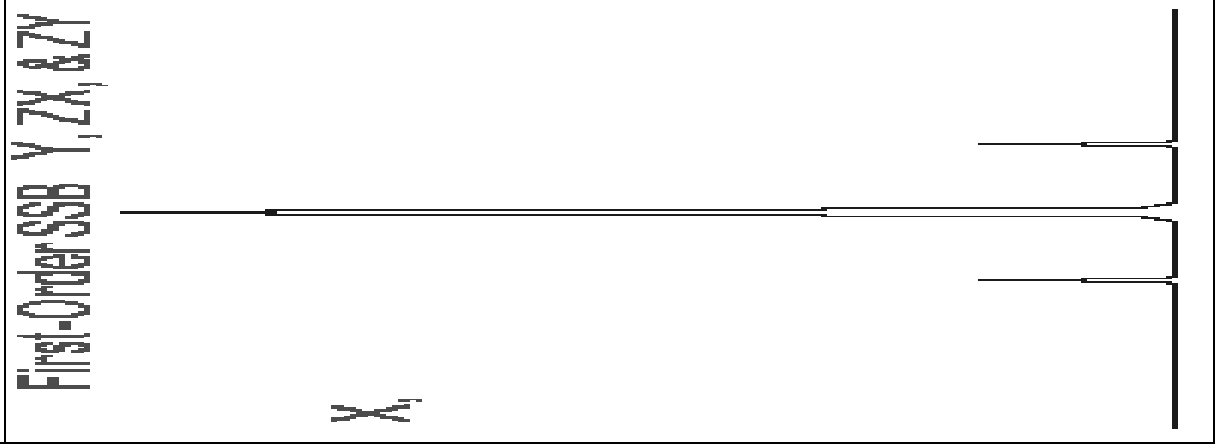
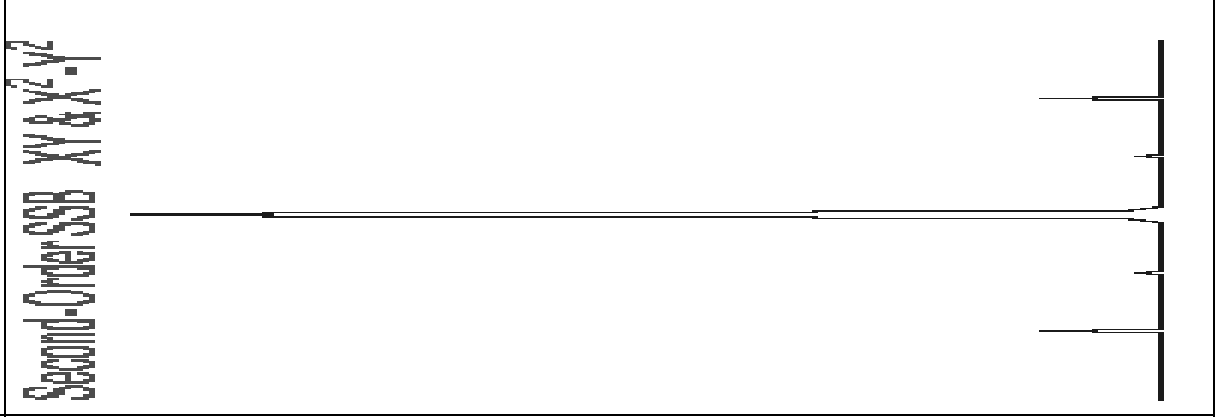


Figure 3

Shim

Z2	Z3	Z4	X, Y, ZX, or ZY	XY or X2-Y2
<p>Z²</p> 	<p>Z³</p> 	<p>Z⁴</p> 	<p>First-Order SSB Y, ZX, & ZY X₁</p> 	<p>Second-Order SSB XY & X²-Y²</p> 

In general, **asymmetric** lineshapes result from mis-adjusted **even**-powered Z shims. This can be seen by looking at the shape of a Z2 shim field. As you go further away from the center of the sample in the +Z or -Z direction, the field increases, giving more components of the spectral line at higher fields. The higher the power of the Z inhomogeneities, the further away the asymmetry is from the center of the line.

Symmetrically broadened lines are from mis-adjusted **odd**-powered Z shims. Consider the shape of the Z3 shim field. The top of the sample (+Z) is at a higher field, resulting in higher field spectral components, while the bottom (-Z) is at a lower field, giving more lower field spectral components. Transverse shims (X,Y) will cause large first order or second order spinning sidebands when the sample is spun. The shape of these inhomogeneities causes the sample, when it is spun, to experience a periodic variation in the magnetic field. Those shims (XY or X2-Y2) causing a spinning sample to experience two variations per cycle will create second order spinning sidebands.