6. MAXIMIZING RESOLUTION AND SENSITIVITY

In this video we'll be concerned about maximizing the resolution and sensitivity of our high-resolution NMR measurement. We know that resolution and sensitivity increase as the magnetic field increases. But, at any field strength, to realize the full potential of the magnetic field being used we'll want to lock and shim on the deuterated solvent signal of our solution. Let's start by explaining lock and shim.

The precession frequencies that we measure by NMR are directly proportional to the external, homogeneous static magnetic field. There are two types of magnetic field deviations that will give us multiple chemical shift values for the same group of protons, not a good thing. One is temporal and the other is spatial. If the magnetic field is not static, meaning it is different from moment to moment (temporally), the precession frequencies will be different from moment to moment. And if the magnetic field is not homogeneous, meaning it is different from place to place (spatially), protons in identical chemical environments, but different locations in the NMR tube will have different precession frequencies. Our aim is for an NMR spectrum where any variations along the x-axis are due to differences in chemical shielding and that each signal correlates with a specific chemical environment.

Lock prevents magnetic field drift. It's a feedback loop that measures the chemical shift of the deuterated solvent in the magnetic field – and if it changes by a little bit, an appropriate corrective field will be applied so that the deuterium chemical shift of the solvent returns to its original place. A good analogy is the feedback loop controlling the temperature in this room, if it starts getting warmer than what we've requested, cooling will be applied, and if it starts getting too cool, the heater will turn on – in this way the temperature of the room remains constant.

To activate the deuterium lock, you should have a per-deuterated solvent at ~ 10% or more of your NMR solution volume. We'll click on three different buttons and wait for the automation routine to finish. You'll notice that if the “sweep” button on the BSMS keypad was lit, it will be automatically turned off once the lock is switched on.

Here we go, instructions number 5a) click on the lock display icon or type lockdisp, #5b) read a shim by clicking this button that says, “rsh qnp” or type rsh qnp – this is a good place to start in terms of decent field homogeneity. Instructions 5c: either type the word “lock” on the command line, or in the lock display window click on this blue icon with a picture of a lock next to a sample tube. Our solvent is cholorform, so we'll click on the CDCl3 line.

We have initialized a ^{2}H NMR experiment. The spectrometer and probe have dedicated channels for the ^{2}H NMR lock. All of our spectrometers in the solution NMR lab have a ^{2}H lock option. Also, when you use the lock routine in this way, you are initializing the automatic chemical shift calibration.

When you see the words “lock finished” appear at the bottom of the screen, then you can go on to the next step. Also notice that the lock button on the BSMS keyboard is lit and NOT flashing. A flashing light means that the lock routine failed. If that happens, you should first try to lock one more time. If that doesn't work, then make sure that you have sufficient signal to noise on the ^{2}H signal by switching off the lock, this will automatically turn on the sweep.

Once the system is locked, the x-axis of the lock display is time. The y-axis is the height (or intensity) of the deuterium NMR signal. Why is the signal intensity constant as a function of time? Because the magnetic field is actively being kept constant as a function of time. If the lock signal is zig-zagging diagonally across the lock display, the lock power is too high and the deuterium signal is saturated. Just

turn down the lock power by clicking the black “lock power” button and turning the dial counter-clockwise. If the signal is too high to see properly, you can make the signal smaller by reducing the lock power, or by reducing the lock gain, or by reducing the lock DC. All of those buttons affect the intensity of the lock signal in a predictable way, the smaller the value (more negative in the case of lock power), the smaller the signal.

The shim system uses a set of coils that allows us to sculpt a compensatory field to cancel out any inhomogeneities in the external static magnetic field.

Let's start our shimming on the ^{2}H signal of the lock display. We'll use two different buttons on the BSMS display to search multidimensional space for the perfect mirror image contour of any distortions in the magnetic field so that the end result can be visualized as perfectly straight magnetic field lines along the length of the sample. Unlike lock power, lock gain, and lock DC, we won't know ahead of time which direction of the dial with increase or decrease the intensity of the deuterium signal. And once we find the correct direction to turn the dial, we might overshoot the optimal value, in which case the signal intensity intensity will go down again. Let's shim already!

First we press Z on the BSMS keyboard. Now we turn the control knob in one direction and look at the ^{2}H signal intensity in the lock display. Does it go up, down, or stay the same? If we push Z again, we will undo any changes to the Z shim gradient. If we push a different button, like STD BY, the current value of the shim gradient will be stored in the memory.
How quickly we can shim effectively is related to the relaxation time of the solvent and not to how quickly I can dial the knob.

Next we'll do the same for Z2 and try to maximize the trace. We'll repeat shimming alternatively on Z and Z2 until there are no further changes.

And that's it.

We're not going to worry too much about making it perfect at this point. We just want to check if we can increase the ^{2}H signal intensity without making any unnecessary changes to the shim file which will make the field homogeneity worse than when we started.

Another thing that I hope is clear is that you must have deuterium nuclei in the NMR tube to use the deuterium lock. You can still do NMR experiments without a deuterated solvent, solid state NMR does this routinely. Just be sure that the magnetic field isn't deliberately being changed as a function of time – which is what the sweep button will do if it is lit. Sweep should be off when you acquire your FID.

The final test for how well the magnetic field has been shimmed is the appearance of the ^{1}H NMR spectrum. We'll have a look at that in the next video and we'll do more shimming on the ^{1}H FID, if it's needed.