

## How to lock when your solvent has multiple deuterium signals

Certain solvents, like methanol, DMF, toluene, and THF, have more than one deuterium signal. This can complicate locking, and can be very confusing to a novice NMR user or an automated locking program. How do you know if you are locked on the correct one?

You typically want to lock on the strongest deuterium signal. To make sure that you are locked on the correct signal, you first want to be sure you have picked the sharper, stronger resonance (the one that has the higher number of equivalent deuteriums). Then, load the proton parameters for your solvent, and run one scan. Check your solvent peaks. If they are in the right place, you have locked on the correct deuterium. If not, chances are you are locked on the wrong one. Relock, run a scan, and check again.

For example, if you have locked onto the wrong deuterium toluene signal, like the aromatic signal ( $\approx 7$ ppm) instead of the methyl signal (2.09ppm), the reference for the spectrum will be off by  $7 - 2.09 \approx 4.9$ ppm. Your spectral window will be shifted to 20 to 0ppm instead of the normal 15 to -5 ppm. If you lock on the wrong methanol signal, the reference will be off by  $4.9 - 3.3$ ppm  $\approx 1.6$ ppm.

In **Figure 1**, you can see the typical Varian Acqi window. The solvent is methanol. The stronger (and correct) deuterium signal ( $-CD_3$ ) can be seen in the overall plateau shape of the line. The second, weaker deuterium signal ( $-OD$ ) can be seen as three "beats" within the overall plateau shape. Note that the Z0 value is close to the correct signal, but is not exactly on resonance (hence the gentle slope to the 'plateau').

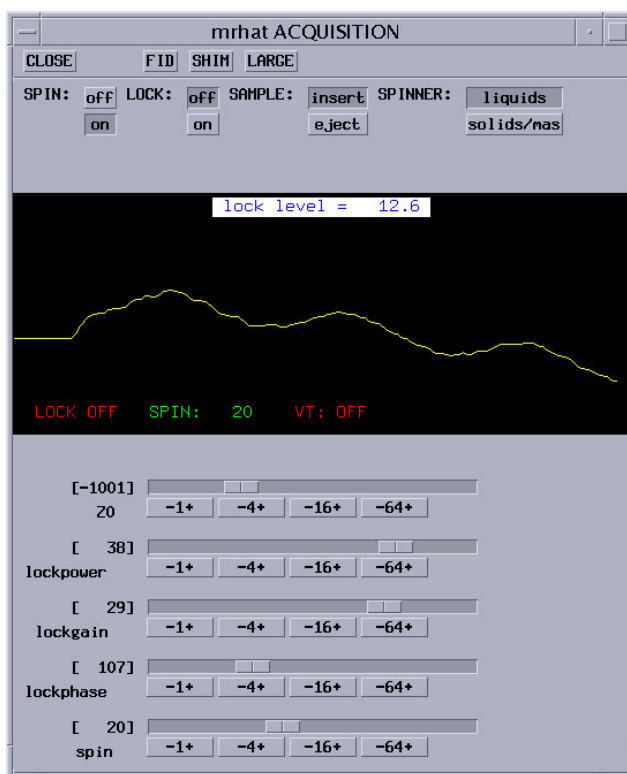


Figure 1

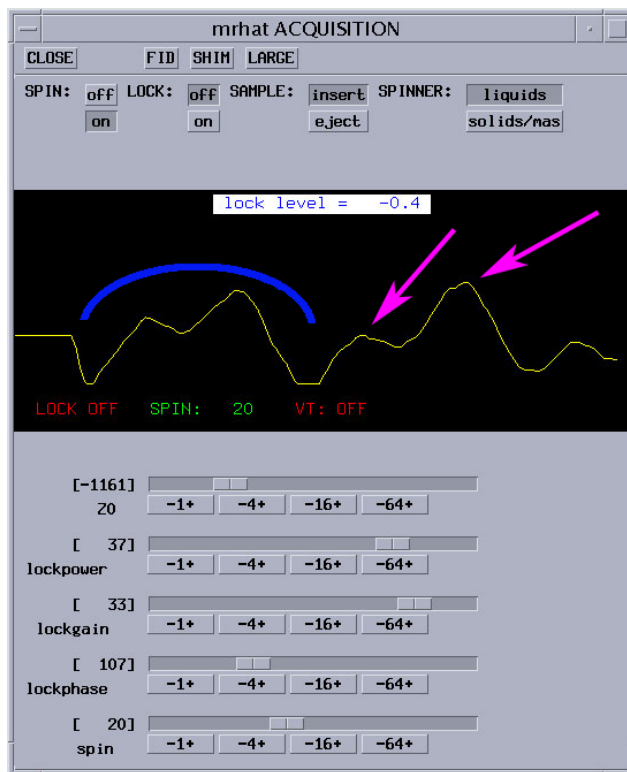


Figure 2

In **Figure 2**, the Z0 value is farther away from being on the correct resonance. The blue arc illustrates a single "beat" in the stronger, correct methanol signal. The two pink arrows point out where the second weaker signal has split this stronger signal into two "sub-beats".

**Figure 3** shows a Bruker lock display window, with methanol as the solvent. It is not hard to distinguish between the stronger, correct signal and the weaker, incorrect one.

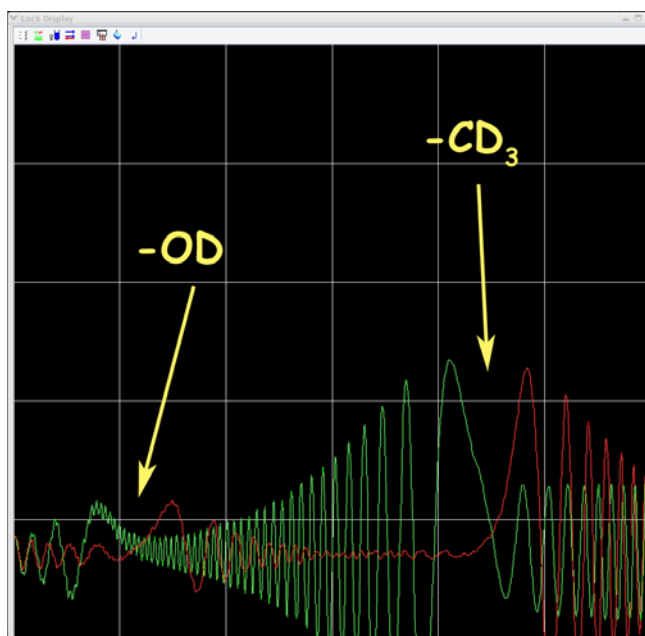


Figure 3

Bruker has an *Autolock* feature that goes through a series of steps that should find and then lock exactly on resonance. However, it is not recommended for use with solvents that have multiple deuterium signals.

If you'd like to lock on a sample with multiple deuterium signals, you need to manually lock using the following procedure:

1. Insert your sample. Make sure that the lock is off, and you can see the sweep "wiggles" (you should see something like Figure 3).
2. Open the BSMS panel, and click on the Lock tab.
3. To adjust the field, press the *Field* button, and using the *Step +* and *Step -* buttons, move the field until the signal you want to lock on is centered in the Lock Display window.
4. Once centered, click the Lock button to engage the lock.

A second way of determining which deuterium signal is the correct one is to look at the Z0 value in relation to other solvents.

For example, let's say you know that the Z0 value for D<sub>2</sub>O (chemical shift 4.8ppm) is around 5050 and the Z0 value for DMSO (chemical shift 2.5ppm) is around 5150. When locked on the correct methanol resonance, the primary methanol chemical shift (-CD<sub>3</sub>) will be around 3.3ppm. Thus, the Z0 value will be between 5050 and 5150, or around 5100 (see **Figure 4**).

Solvent	Chemical shift	Z0 Value
CDCl <sub>3</sub>	7.27	5000
D <sub>2</sub> O	4.80	5050
CD <sub>3</sub> OD	3.31	??
DMSO	2.50	5150

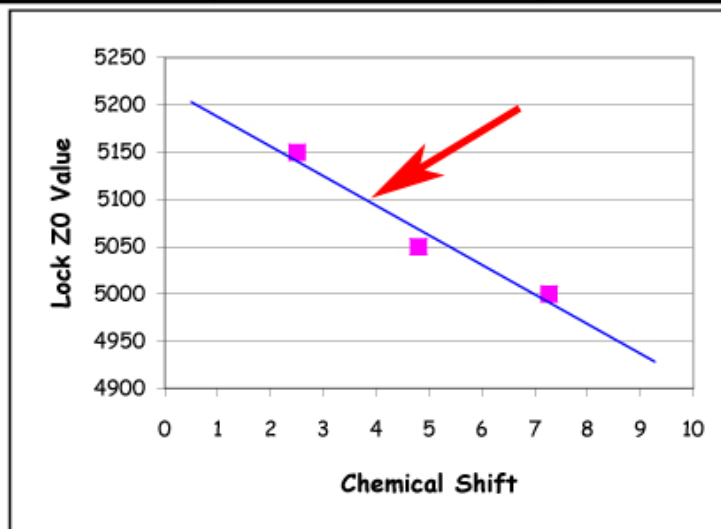


Figure 4