

CSA pattern fitting in ssNake

12th October 2018

1 Introduction

The following will explain how CSA NMR data can be fitted ssNake. The tutorial delivered with the ssNake program is considered as prior knowledge. If you have not yet studied this, please do so before continuing with this example.

In solid state NMR anisotropic chemical shift interactions (CSA) can be a relevant factor in the description of a spectrum. While, using fast magic angle spinning, the isotropic term can be easily established, the size and symmetry of the anisotropy are somewhat harder to determine. As these spectra can be simulated in a straightforward way, fitting the experimental data is a good way to establish these values.

2 Data

The data in this tutorial was recorded on a Varian 300 MHz machine on glycine powder. The spectrum shows the ^{13}C resonance of the carboxyl group of glycine.

3 Fitting a static CSA pattern

Begin by loading the processed data called `GlycineStatic.mat` that is delivered with this tutorial. As this is a chemical shift pattern, we want the x-axis to be in ppm:

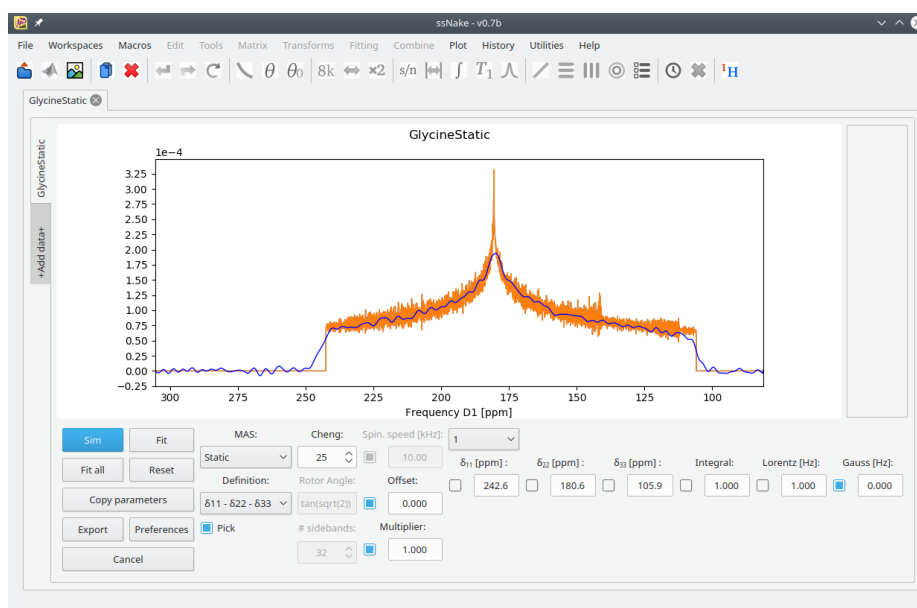
- In the bottomframe, set `Axis` to `ppm`

This should show this:

Before we can be an iterative fit, we must first supply some starting values for the fit. This makes it easier for ssNake to find the best solution. In this CSA fit, this can be easily done by left clicking on the spectrum: each click sets one of the δ -values to the ppm value under the cursor. In this case, these values should be equal to the extremities of the powder pattern, and the ‘peak’ in the center. Left click on the left part of the pattern, the ‘peak’ and the right part. This should set the δ -values to approximately 243, 181 and 106 ppm, which are good starting values.

- Change the Cheng¹ number from 15 to 25

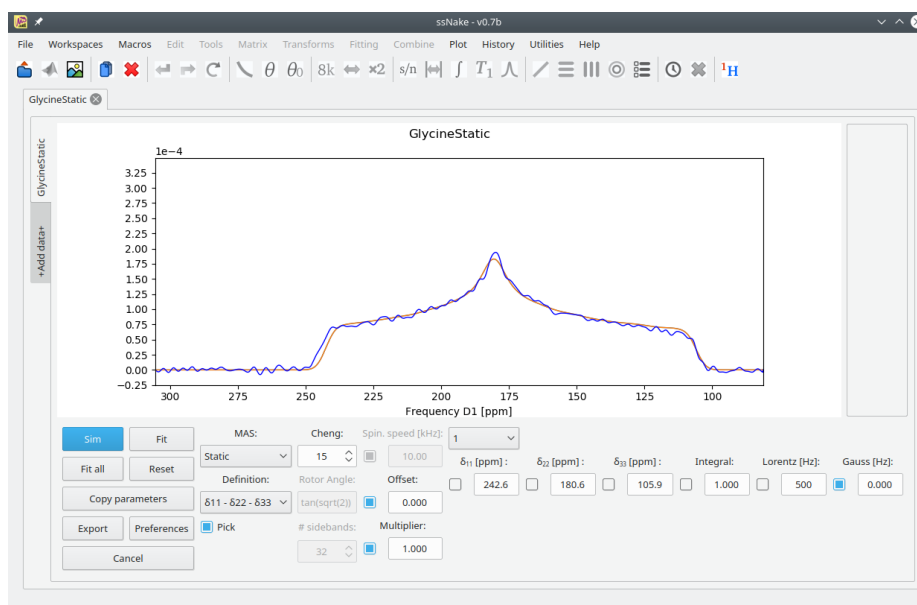
¹The Cheng number represents the number of orientation to be simulated. It is an exponential scale, so it increases quite fast.



which looks a lot more like a powder pattern. However, with Cheng at 25, the simulation starts to become slower due to the high amount of orientations. In this case we actually do not need so many orientations: our actual spectrum is not so precisely defined as there is significant line broadening present (you can see this at the rounded edges of the pattern). Adding line broadening to the simulations also means we need less powder orientations:

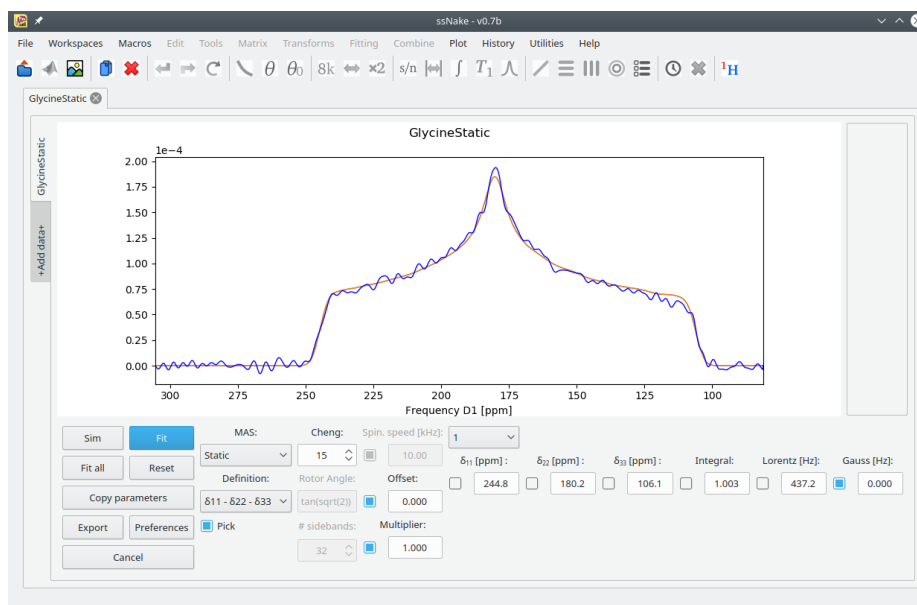
- Set Cheng back to 15
- Set Lorentz at 500 Hz

Pushing 'Sim' gives:



which is quite close to the experimental spectrum.

We are now ready to let ssNake do some iterative fitting, to achieve the best description of our spectrum. Push 'Fit' to let it work its magic. This leads to the final fit:

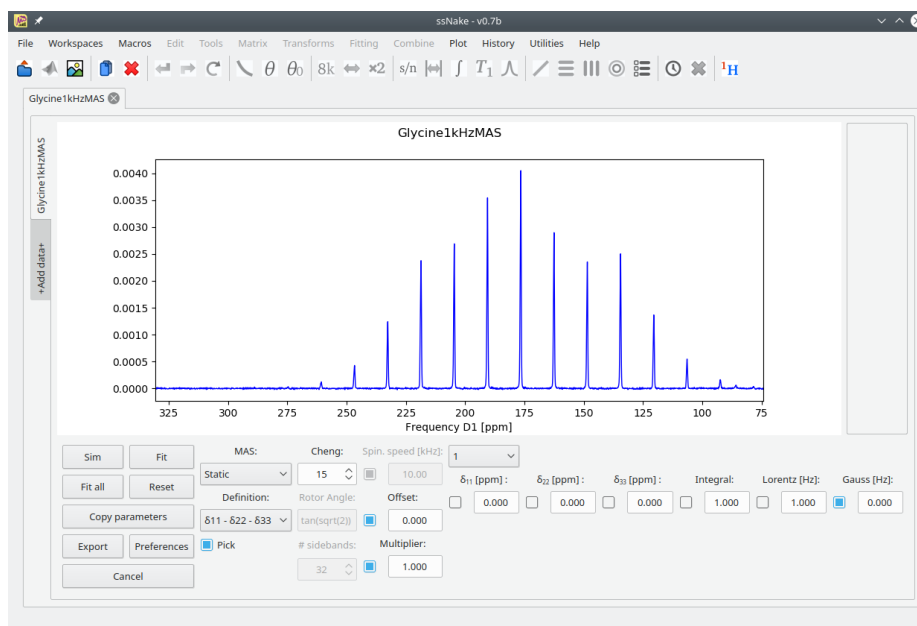


with tensor values 244.8, 180.2, and 106.1 ppm. Often, the CSA tensor values are expressed in another definitions. Common is the iso-aniso-eta definition. We can tell ssNake we need these values by switching the definition from $\delta_{11}-\delta_{22}-\delta_{33}$ to $\delta_{\text{iso}}-\delta_{\text{aniso}}-\eta$. ssNake automatically converts the tensor values on the right. This gives 177.0, -70.93 , and 0.9107 . Using these other definitions can also be convenient during fitting, for example in cases where you know δ_{iso} or η , and you want to fix these values during the fit. Do note that in some definitions the mouse cannot be used to set values by clicking in the spectrum.

4 Fitting a MAS CSA pattern

Naturally, ssNake can also fit a CSA pattern when it has been measured under MAS conditions. This goes large the same way, although there are some extra thing to take notice of.

Start by loading `Glycine1kHzMAS.mat` that is delivered with this tutorial. Again, put the axis on ppm before continuing. Go to the fitting routine via `Fitting` \rightarrow `CSA`. This shows:

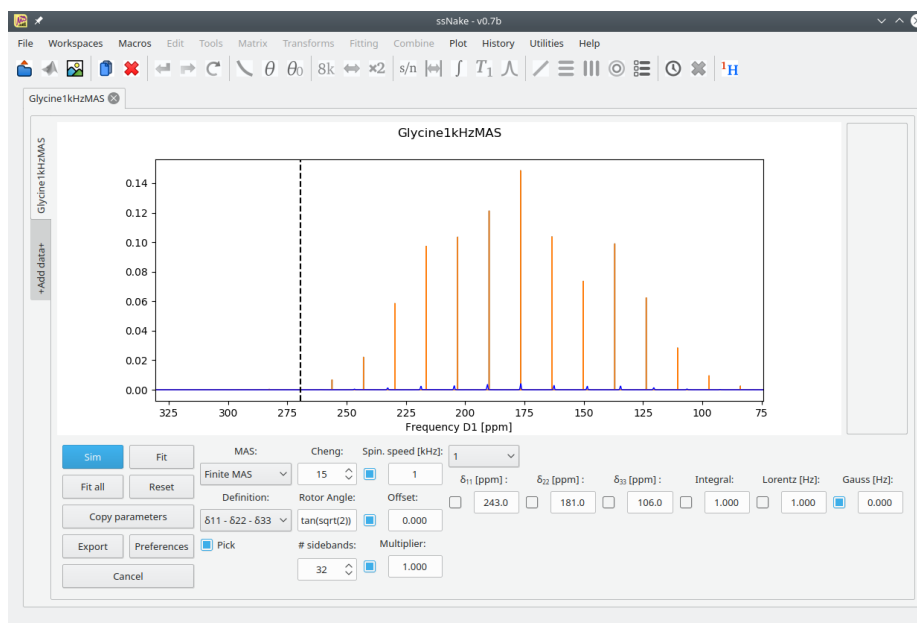


In principal, we could use the mouse again to set the initial values of the tensor values. However, in this spinning spectrum, these values are not really clear. But still, we can give a rough size of the tensor. We can start with the same values as for the static fit: 243, 181 and 106 ppm.

Before we can do a useful simulation, we must tell ssNake that we are using MAS:

- Set MAS to Finite MAS
- Set Spin. speed on 1 kHz

Pushing Sim shows:



By default, the integral is set to the integral of the experimental spectrum. In this case, this looks to big, but this is mostly due to the too low line broadening values. Let's put these to some better values (close to the experimental).

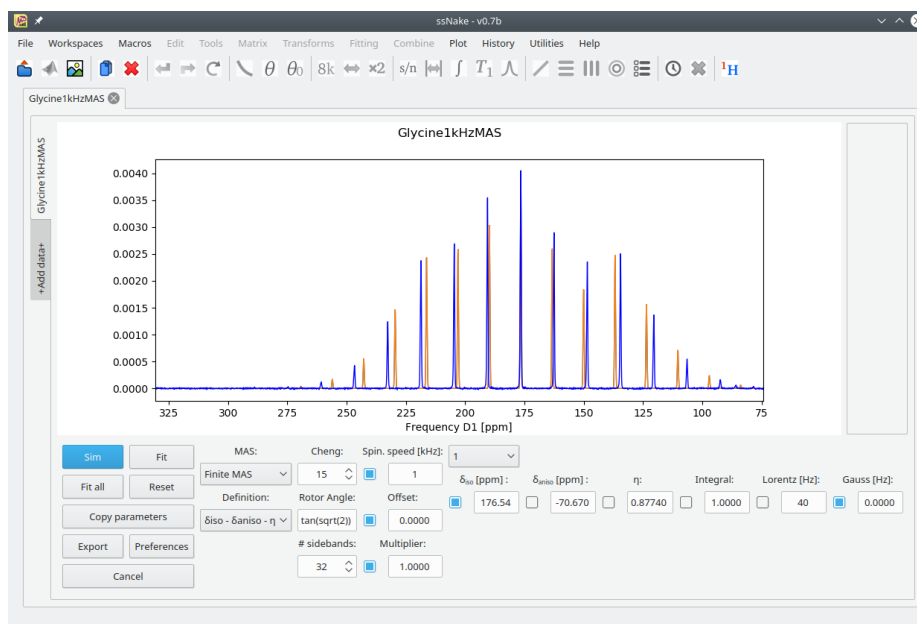
- Put Lorentz on 40 Hz

This gives something more reasonable.

When fitting this spectrum, it is important to realise that it is actually quite a hard fit. The very small lines can be hard to find for the iterative process. It is best that we help the fitting a bit by fixing some values. In this MAS spectrum, the isotropic shift is readily found. In this case, it is at 176.54 ppm. In principle, this value does not need to be fit, as we already know it. So let's fix it at this value:

- Change the definition to iso-aniso-eta
- Increase the number of significant digits to 5 (see Preferences on the left)
- Set δ_{iso} to 176.54 and tick on the left of this value (to fix it)
- Push Sim

This should show:



What is clear from this Figure, is that the spinning speed is not set properly. Clearly, the experimental spectrum was measured with a bit more than 1 kHz MAS. We can manually correct this by looking at one of the peaks further away from the centre, and adjusting the speed till these sidebands overlap.

- Set Spin. speed at 1.0590 kHz

Now, we are ready to fit! Pushing `Fit` optimizes all unticked parameters. This already leads to a reasonable fit. Now that we are close to the optimum, we can also ‘release’ the δ_{iso} and spin speed parameters by unticking their boxes. Pushing `Fit` again optimizes all the values. This should lead to 176.58, -69.457 , and 0.91502 for iso, aniso and eta. Which is pretty close to the values we got for the static spectrum. Note that we did not touch the `# sidebands` parameter. This must always be higher than the number of observed sidebands in the simulation. In this case, the default 32 is sufficient.