

# 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

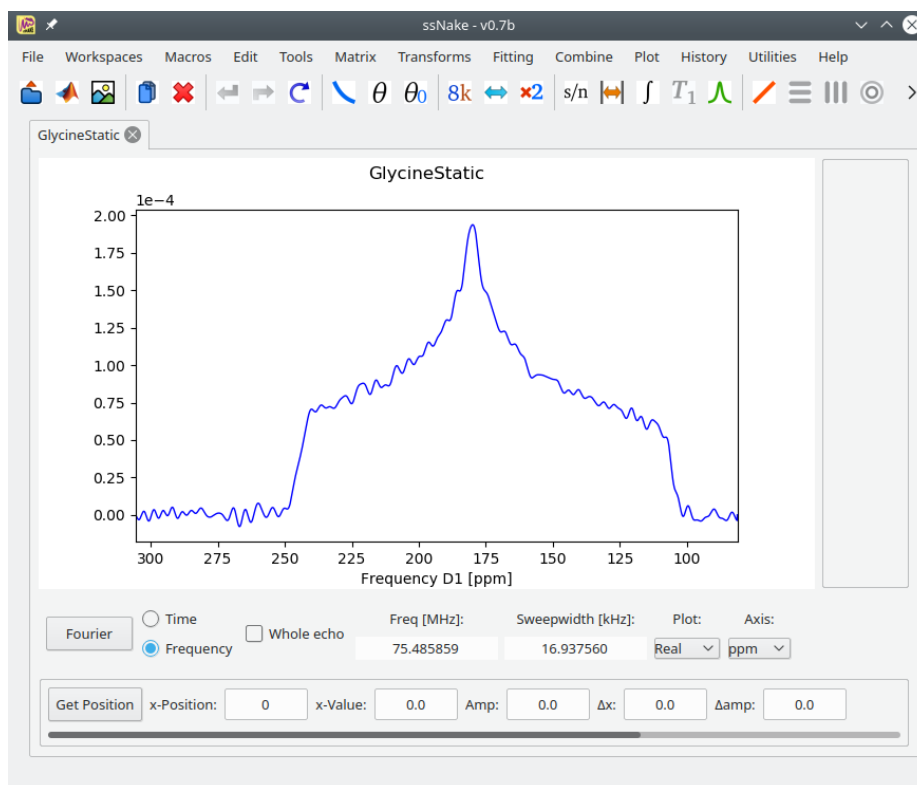
The data in this tutorial was recorded on a Varian 300 MHz machine on glycine powder without the use of MAS. The spectrum shows the  $^{13}\text{C}$  resonance of the carboxyl group of glycine.

## 3 Fitting

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:

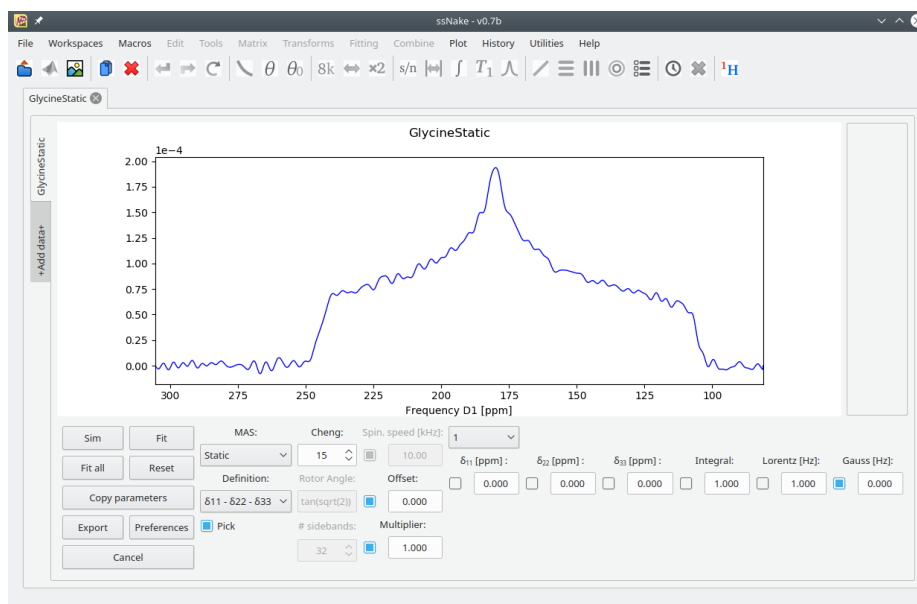
- In the bottomframe, set `Axis` to ppm

This should show this:



Which is a nice CSA powder pattern of a static sample. We now need to fit this data to extract the CSA tensor parameters. Go to **Fitting** → **CSA**.

This show the following window:

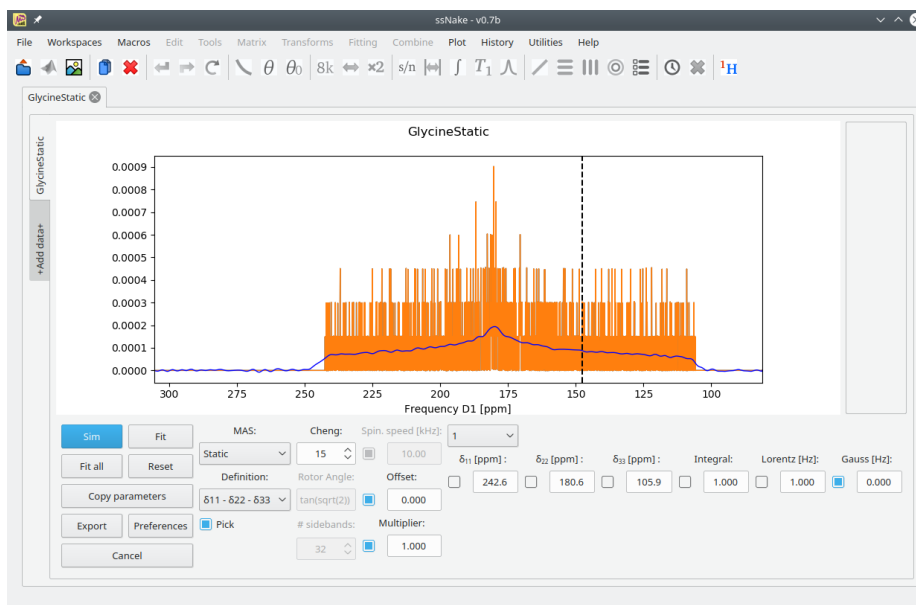


This window has quite some parameters that we can change. The most important are the boxes on the right:  $\delta_{11}$ ,  $\delta_{22}$ , and  $\delta_{33}$  are the CSA tensor values. Also shown are some line broadening parameters (Lorentz and Gauss). The tick boxes next to the input boxes indicate

whether or not the parameters are fixed (checked) or that they may be change during the iterative fitting (unchecked).

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  $\delta$ -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  $\delta$ -values to approximately 243, 181 and 106 ppm, which are good starting values.

Pushing 'Sim' in the left part of the window simulates a spectrum using our current settings. Doing this leads to:

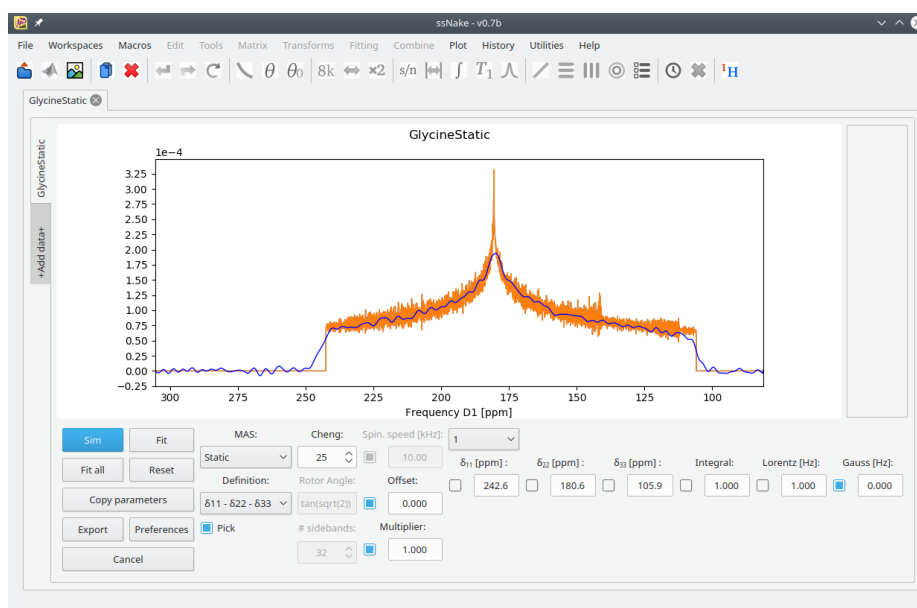


which looks very ugly. Here the orange line represents the simulated spectrum. The reason why it looks like this is because the line broadening is quite low (1 Hz), and we only simulate a finite number of powder orientating. This leads to a series of peaks for each crystal orientation in our synthetic powder, and not a nice pattern. This issue can be overcome by increasing the number of powder orientations.

- Change the Cheng<sup>1</sup> number from 15 to 25

Simulating again shows:

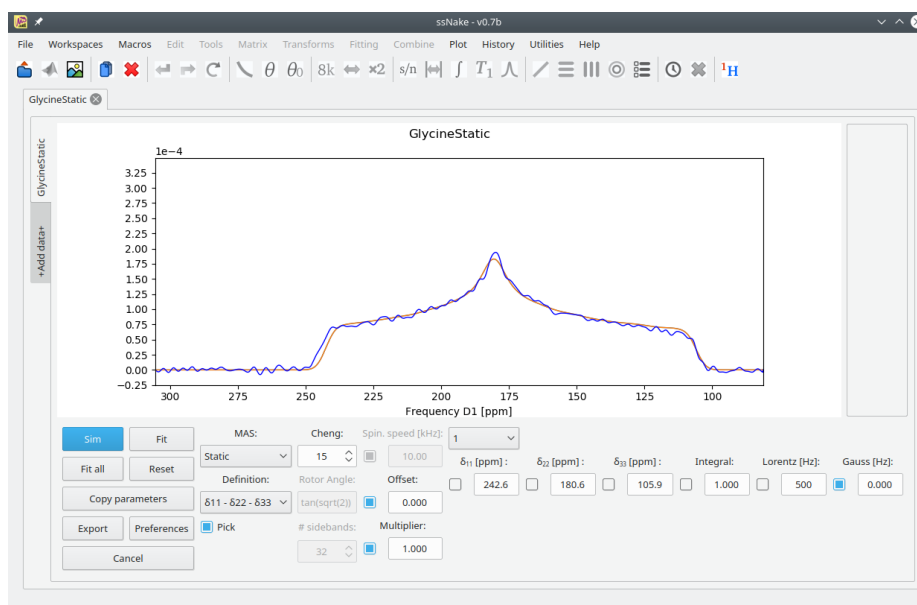
<sup>1</sup>The Cheng number represents the number of orientation to be simulated. It is an exponential scale, so it increases quite fast.



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:

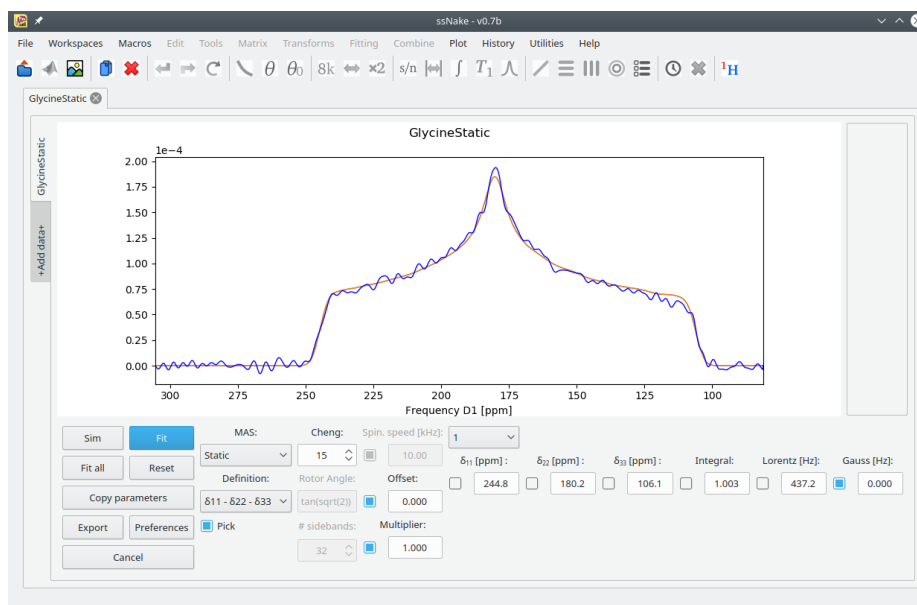
- Set Cheng back to 15
- Set Lorentz at 500 Hz

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  $\delta_{\text{iso}}$  or  $\eta$ , 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.