

Fitting Czjzek spectra distribution in ssNake

8th June 2020

1 Introduction

This tutorial describes how to fit Czjzek and Extended Czjzek quadrupolar lineshapes in ssNake. As this is relatively advanced, it is recommended to study the tutorial on CSA fitting and the single fit part of MultiFitQuadrupole first.

A Czjzek lineshape occurs in case where this is a atomic site in a material with considerable distortions around it. This standard Czjzek model assumes a site with in first instance no quadrupolar coupling ($C_Q = 0$) due to symmetry. However, the distortions in the material break the symmery and introduce a quadrupolar coupling.

Simulating a Czjzek lineshape is a bit more involved than the other fitting routines, as it requires calculation of a whole series of quadrupolar powder patterns (the distortion is different for different positions in the material). Based on the parameters of the Czjzek distribution, the relative intensity of each of these powder patterns changes. To be able to calculate this efficiently in an iterative routine, ssNake pre-calculates the quadrupole powder patterns for a grid of C_Q and η values. To simulate a spectrum, a weighted sum is taken of the quadrupole powder patterns. In the fitting, the Czjzek parameters change, but this leads only to different weights in sum of the powder patterns. The collection of pre-calculated lineshapes is called the ‘library’.

Generating this library can be done by ssNake itself, or supplied by the user from an external source. (In the ssNake paper, we used SIMPSON to calculate lineshape with excitation efficiencies included, for example.) It is in the generation of the library that settings regarding Magic Angle Spinning, inclusion of satellite intensities etc. are relevant.

When generating the library, the grid of quadrupolar parameters (C_Q , η) must be chosen. The larger the grid size that is used, the more accurate the fitting, at the expense of speed. Note that while η is of course always between 0 and 1, C_Q can take any positive value. Generally, Czjzek lineshapes are accurately calculated for $C_Q^{\max} = 4\sigma$, with σ the Czjzek width. As σ can change during the fitting, the choice for C_Q^{\max} should be revisited after the fitting. If this value is unsuitable for the fit results, a new library must be generated and the fitting rerun.

Additional issues can arise if multiple Czjzek sites in the same spectrum are simulated. In this case, the total width of the C_Q range must be wide enough to accommodate the largest of the two σ values, while the step size must be small enough to accurately describe the distribution of the site with the small σ value.

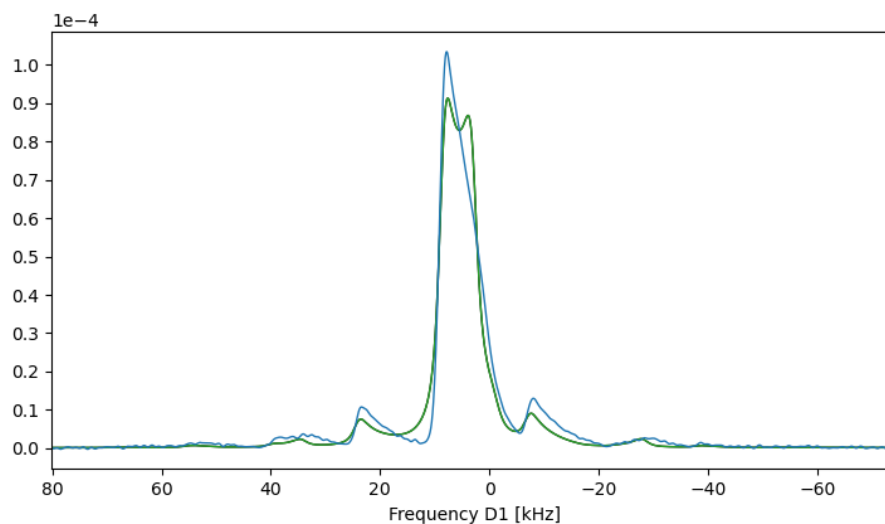
In the following tutorial, we will generate the library and fit an experimental data set with both a regular Czjzek, as well as an Extended Czjzek distribution.

2 Data

The data used in this tutorial is a ^{35}Cl spectrum of ball-milled MgCl_2 with a diisobutyl phthalate adduct. The spectrum was acquired on a 20 T magnet at a spinning speed of 15.625 kHz.

3 Fitting a Czjzek lineshape

Start by loading the data supplied with this tutorial: 'MgCl2.mat'. We observe a central transition with some spinning sidebands. The shape of the central transition is not really clear, indicating it is not just a single quadrupolar site. Fitting it in this way therefore does not lead to a good result:



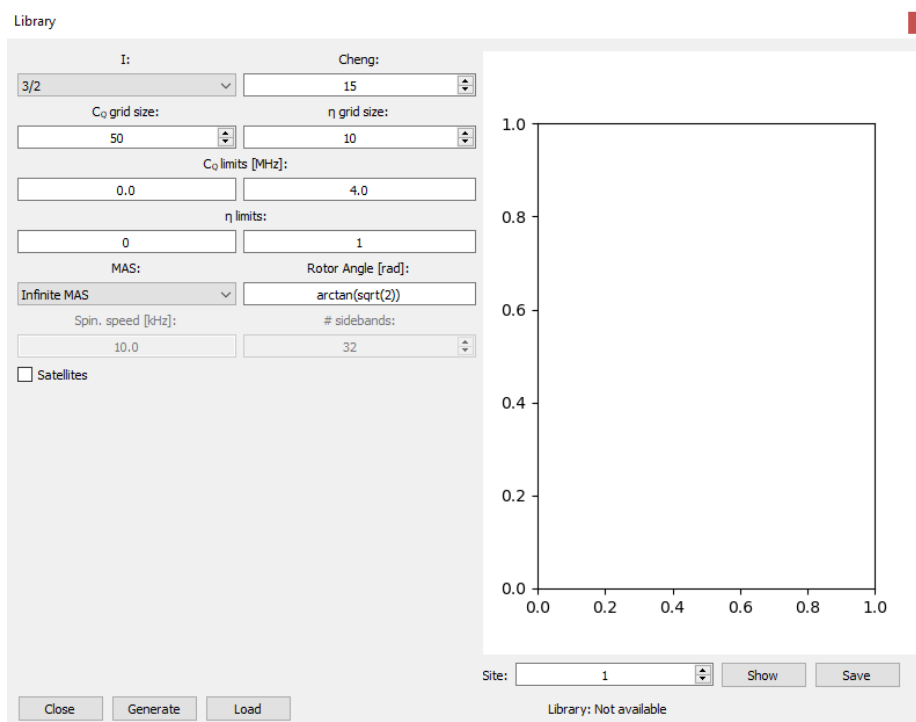
We therefore need something more complicated: the Czjzek routine!.

- Set the x-axis to ppm using the bottom frame.
- Open the Czjzek fitting routine using 'Fitting → Czjzek'.

Firstly, we must generate a library, as was explained above.

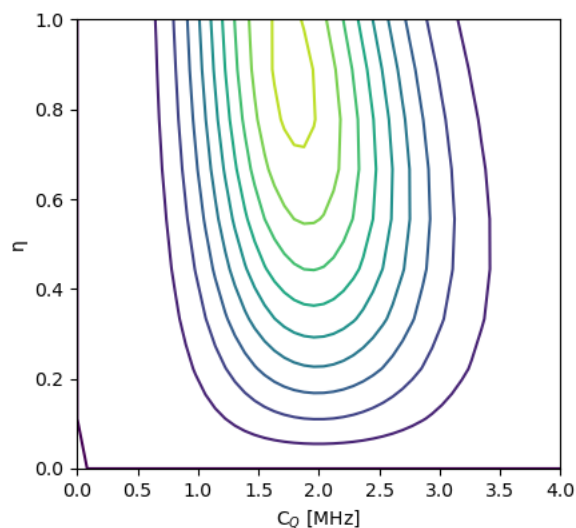
- Click the 'Library' button.

This shows the following:



Here, we can fill in the settings for our library, and generate it. The plot on the right can be used to view a contour plot of the Czjzek weights (per site) on the chosen C_Q - η grid. For this, it uses the largest σ -value that was put in the fitting window. This value is still at its default, so we have no clue about the grid size...

Click the 'Show' button on the right gives the Czjzek intensities for the current σ value:



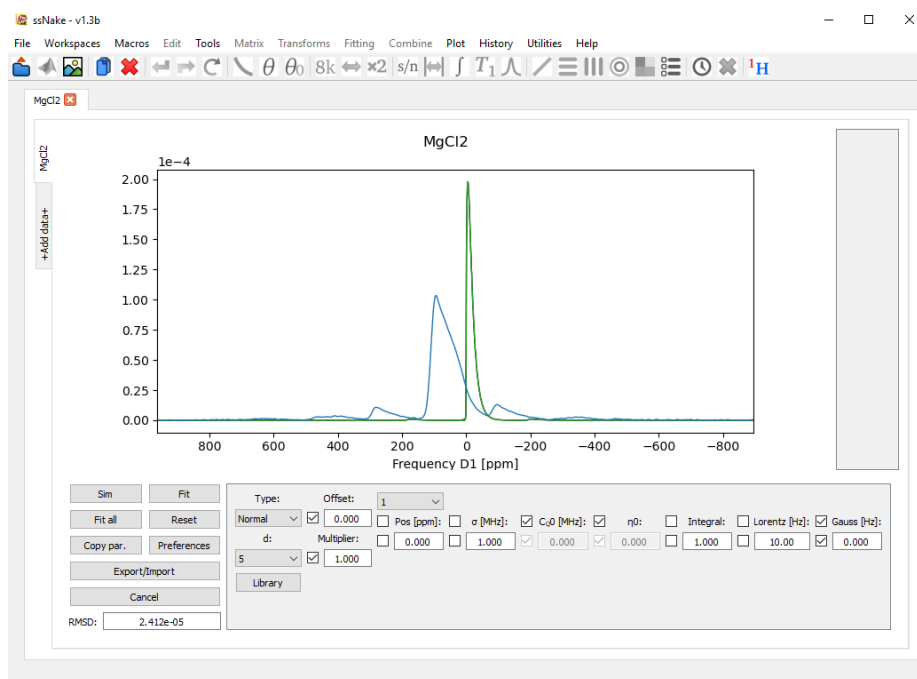
The distribution is nicely centered on the x-axis, so for the current σ this is a good grid. Now, to generate the library, we need a couple of experimental settings:

- Set 'MAS' to 'Finite MAS'.

- Set the 'Spin. Speed' to 15.625 kHz.
- Set the '# sidebands' to 16.

These are all the changes we need for now. Generate the library by pushing 'Generate'. This can take some time. After this, close the window.

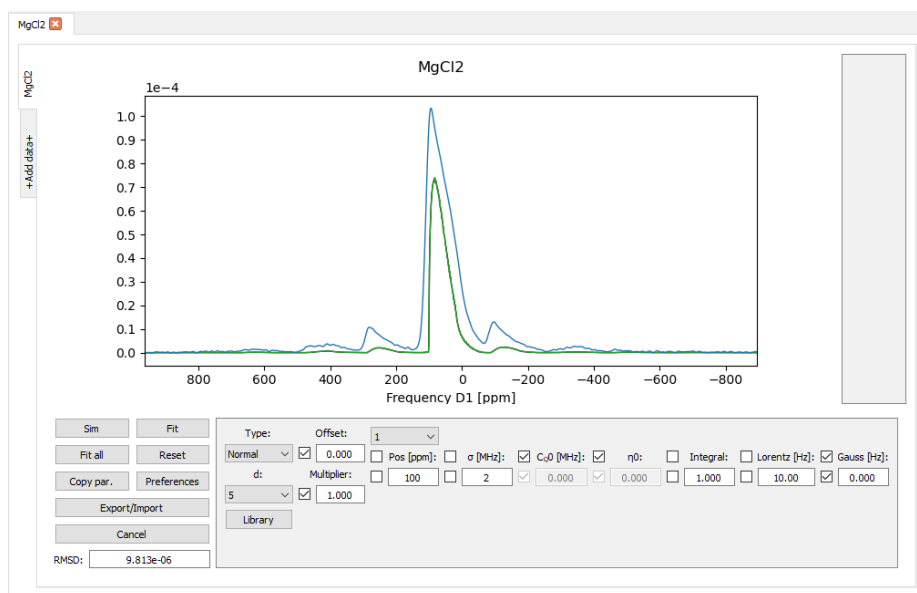
Pushing 'Sim' in the fitting window gives us the following simulated spectrum:



The quadrupolar coupling in the experimental spectrum is a bit larger than in the simulation, so we need to change that. Also, the position is off:

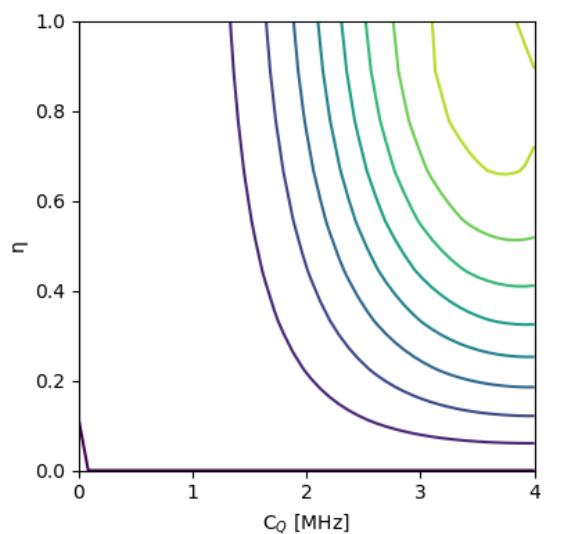
- Set ' σ ' to 2 MHz.
- Set 'Pos' to 100 ppm.
- Push 'Sim'.

This gives:



This looks ok. In most fitting routines, we would now push 'Fit' and be done. However, as we have doubled the σ the library might be wrong! We now need a C_Q range which is twice as large.

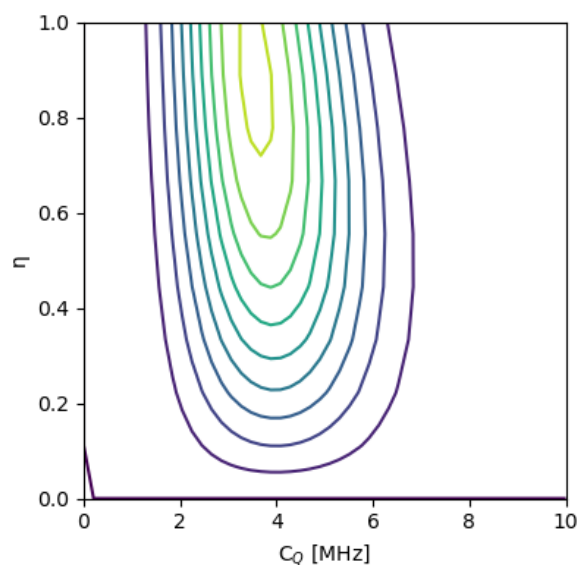
Open the Library window again, and push 'Show' on the right. This shows:



The distribution is now cut off in the C_Q dimension. To fix this, we need a wider range:

- Set the C_Q limit maximum to 10 MHz.

This leads to (after 'Show'):



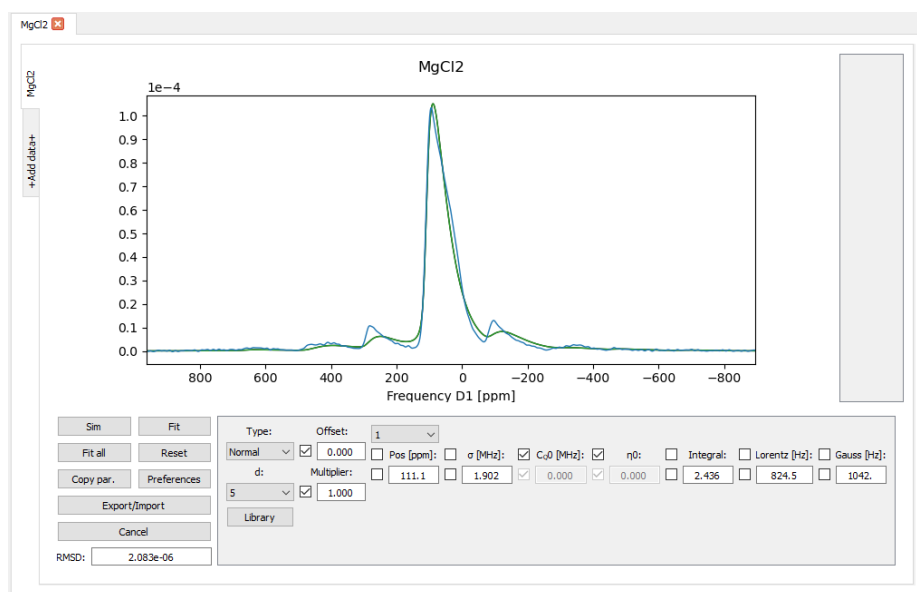
Much better! I put the range a bit more than just times 2, to be able to accommodate larger σ in case this happens during fitting.

- Push 'Generate' to generate the new library.
- Close the window.

Now, let's fit:

- Untick the Gauss value, and set it to 1000 Hz.
- Set 'Integral' to 2.
- Push 'Fit'.

This gives:



Which is much better than the regular quadrupolar fit shown above. However, the result is not that great. The sidebands for example are much ‘sharper’ in the experimental spectrum. . . The reason is that the regular Cjzek model assumes distortions in an otherwise symmetric surrounding ($C_Q = 0$). In this case, the ‘undisturbed’ surrounding is already asymmetric. We therefore require the extended Cjzek model.

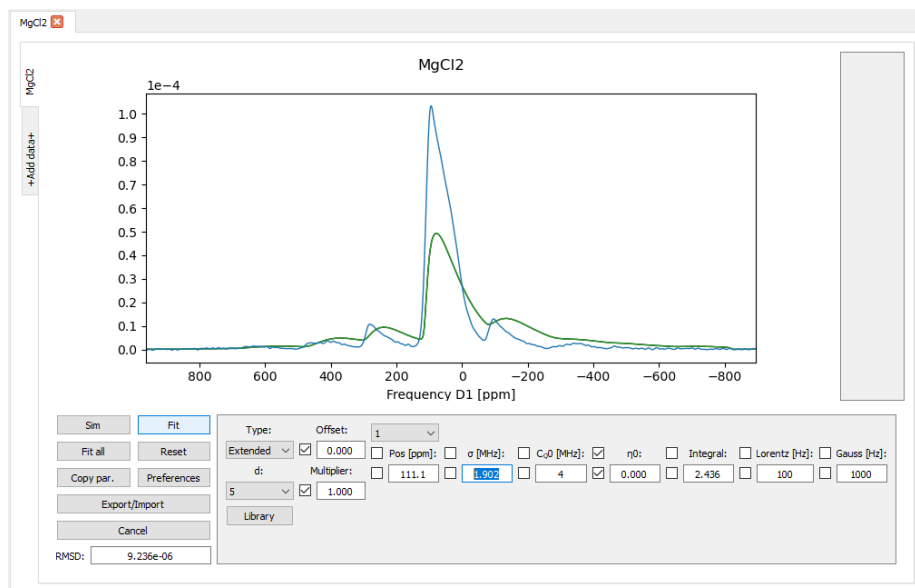
- Change the ‘Type’ to Extended.

This activates two new parameters. C_Q^0 and η^0 . Put these at 4 MHz and 0, respectively. (These are the quadrupole parameters of the undisturbed surroundings of the sites. As the data was recorded on a compound based on MgCl_2 , the values of pure MgCl_2 are a good place to start. Based on this structure we also choose $\eta^0 = 0$.) Also, untick the box at C_Q^0 to let the fitting optimize it.

- Set Lorentz back to 100, and Gauss back to 1000.
- Push ‘Sim’. This will take some time.

Noticed how long that took? This is because the calculation of the Extended Cjzek distribution is quite involved. We have used $\eta^0 = 0$, which means ssNake is actually using an efficient routine! For $\eta^0 \neq 0$ it will be even slower.

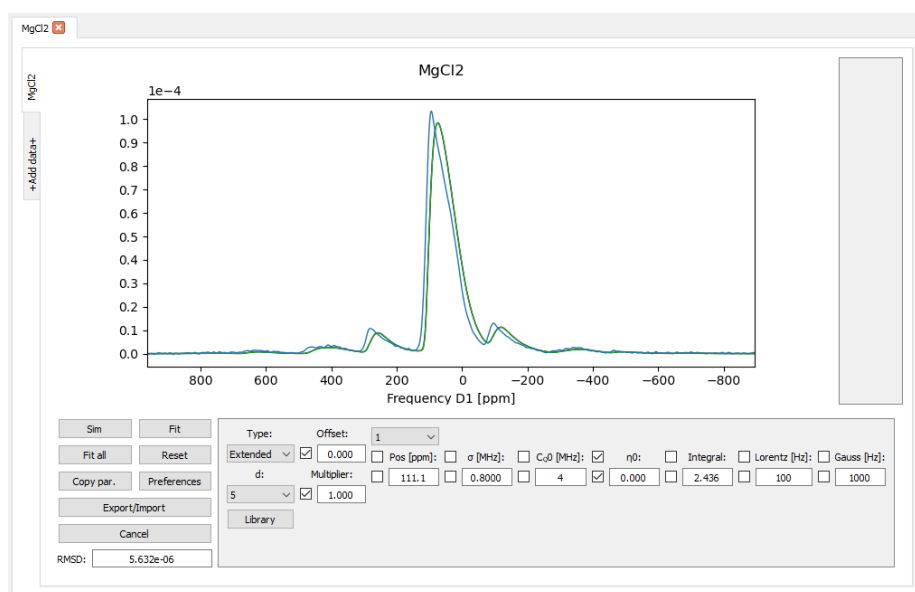
The spectrum we get looks like:



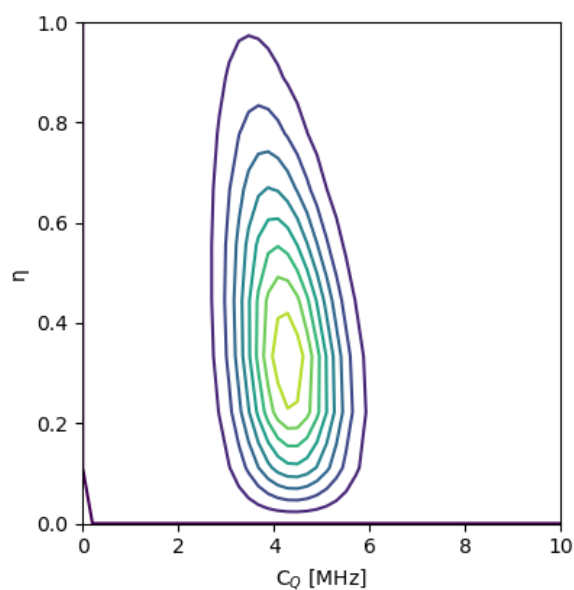
The center line looks a bit too broad and smeared out. Perhaps σ is now too high?

- Set σ to 0.8 MHz.
- Push ‘Sim’.

Much better:



A quick check of the Library shows that we are still in a good regime for the simulation.

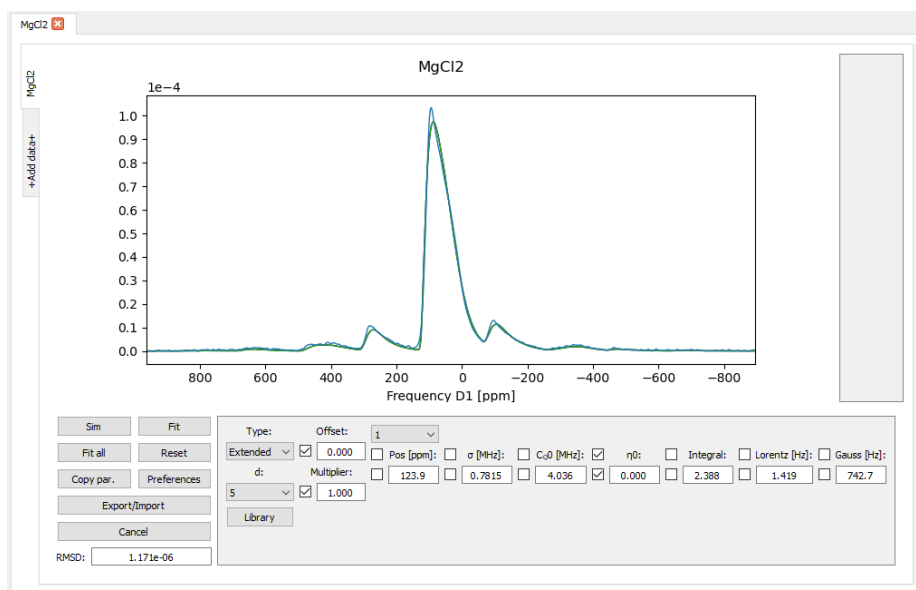


(Notice the different shape of the contours: this is due to the Extended Czek model.)

This means that we can start fitting!

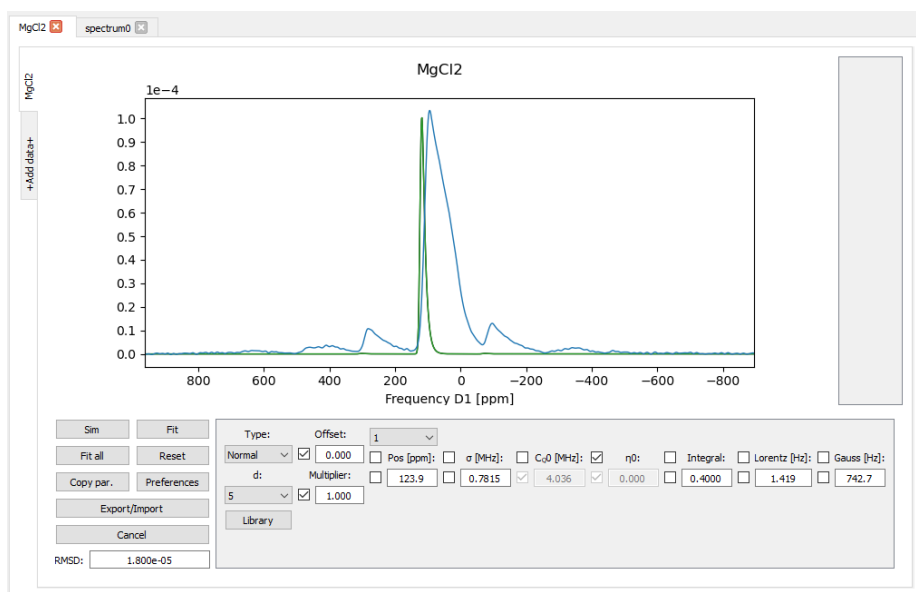
- Push 'Fit'.
- Grab a cup of coffee: this will take some time. The underlying routine is multithreaded, meaning that all your CPU cores will be used. If you have the 'numba' python library installed, the calculations will be a lot faster. (For Windows this is bundled in the ssNake installer.)

After some time we get:



which is a quite good fit. Definitely much better than the quadrupolar or normal Czjzek fit. The fit result can also be found in the data directory of this tutorial.

As a nice trick, we can also return to the regular Czjzek model, and simulate again. This leads to (after lowering the integral a bit):



Clearly, the width of the line is mostly due to the standard quadrupolar broadening. The Czjzek effect is much smaller than we initially had ($\sigma = 2$ MHz). The same broadening of the line can however not be caused by Lorentzian or Gaussian broadening. It really is a distribution in quadrupolar parameters.

This concludes this tutorial. The take home message is that regular Czjzek fitting can be done in a short time, due to the use of a library. Extended Czjzek fitting requires some patience. In both cases, it is important to check, after a change in the parameters, whether the library we use is still correct.