MQMAS processing in ssNake

6th April 2018

1 Introduction

The following will explain how Multiple Quantum Magic Angle spinning (MQMAS) NMR data can be processed in 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.

MQMAS is a 2D experiment for half-integer quadrupolar nuclei which, after proper processing, leads to a spectrum with the regular quadrupolar powder patterns along D2, and peaks at the 'isotropic' value along D1. This allows the separation of multiple overlapping quadrupolar sites on the basis of their 'isotropic' value (which is a combination of the isotropic chemical shift, and the isotropic quadrupolar shift, which is also called the quadrupolar induced shift).

The experiment is almost famously hard to process. Not because of the complication of the steps involved, but due to the high number of different types of MQMAS experiments and the different ways to process these. It is therefore impossible to give a full overview of all the different approaches here, in this tutorial. However, an attempt is made to show a good way for processing the data for both the regular type (shifting echo or z-filter) and the split t1 MQMAS experiment.

2 Data

In this tutorial we will use two data sets, recorded for solid rubidium nitrate ($RbNO_3$). The sets are for ^{87}Rb 3Q MQMAS, with z-filter or and split t1. The data was recorded on a 600 MHz Varian machine using 15 kHz MAS.

3 *z*-filter processing

First, we will look into the processing of MQMAS data recorded using a z-filter experiment (also called three pulse MQMAS). Note that data recorded with a regular two pulse MQMAS (the standard MQMAS experiment) can be processed in an identical way.

Processing the data has the following steps:

- Applying the hypercomplex operation (States)

- Processing of the direct dimensions D2 (zerofill, Fourier, apodize, phase)
- Processing of the indirect dimension D1 (zerofill, Fourier, apodize, phase)
- Shearing the spectrum
- Scaling the spectral width in the indirect dimension
- Referencing both dimensions

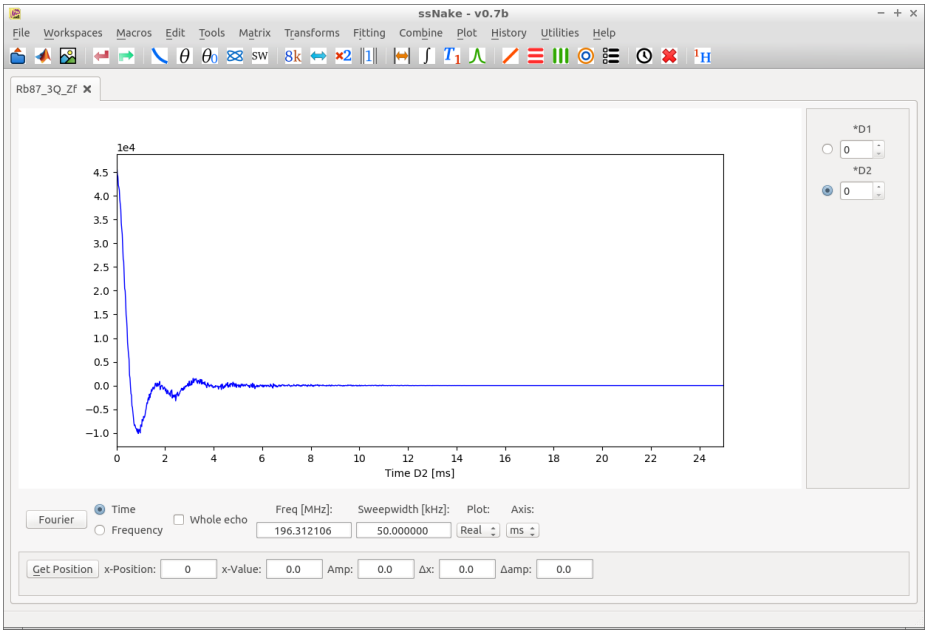
One of the tricky thing of MQMAS processing is that the different traces along D1, have signal starting at different positions in the FID (along D2). When applying apodization, the centre of the apodization widow must be shifted differently for each trace along D1.

- Open the Varian file Rb87_3Q_Zf.fid using File ⟶ Open
- Set the view to D1 (sideframe, radiobutton)
- Convert the hypercomplex data via Tools ⟶ Hypercomplex ⟶ States
- Set the view to D2 (sideframe, radiobutton)

Now, we will apply some apodization. Note that in this case, the position of the echo maximum shift as a function of the D1 time. This must be taken into account when applying the apodization, and is often called 'shifting echo' apodization.

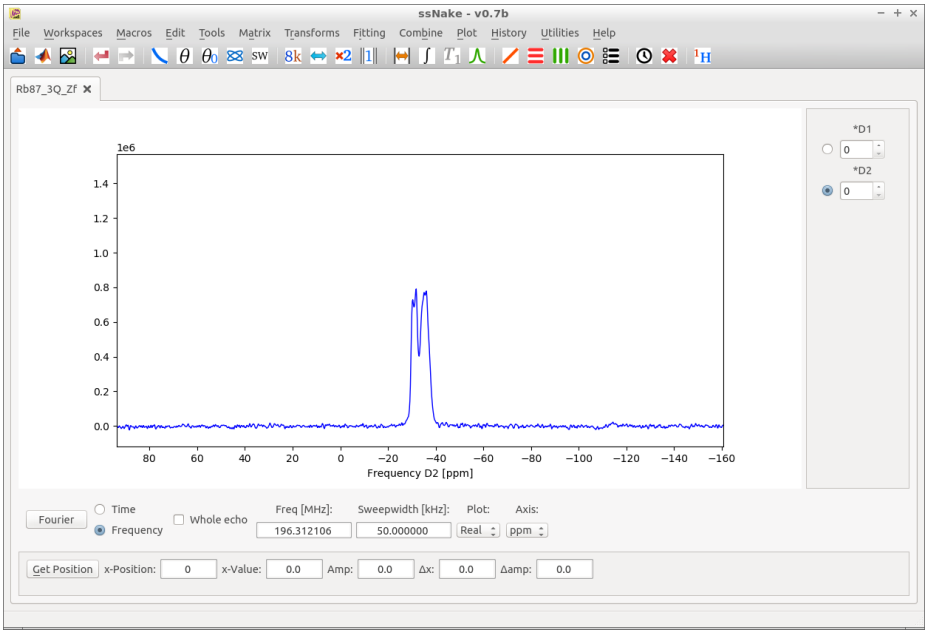
- Open the Apodization window via Tools ⟶ Apodize
- Set Gaussian at 80
- Set Shifting to 'Spin 3/2, -3Q'. This sets the shifting to 7/9 i.e. 0.7778
- Press Ok to apply.

This should show:



- Fourier Transform
- Phase with 2.5 degrees 0 order phasing (Tools ⟶ Phasing)

This should show:



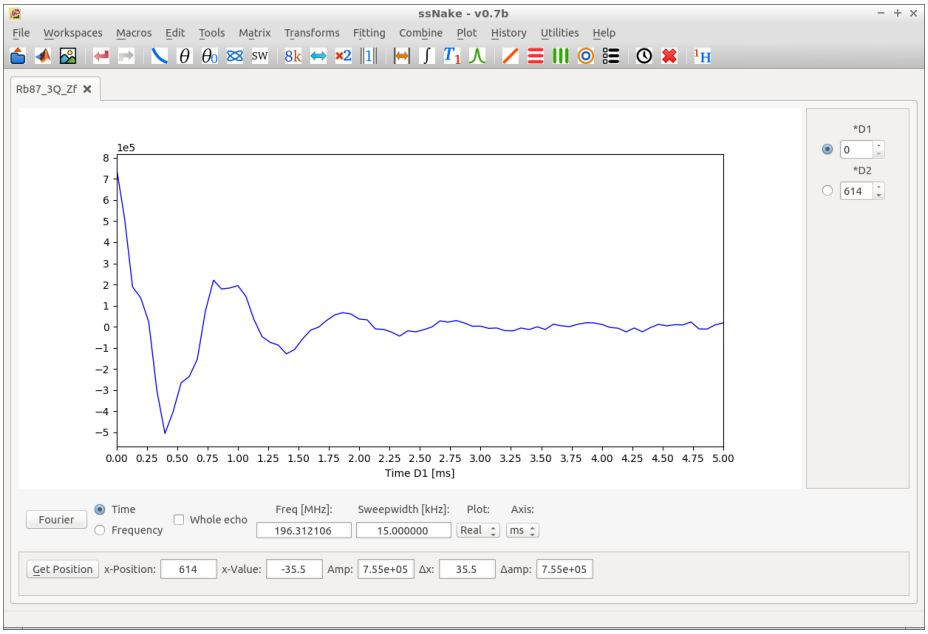
A nice quadrupolar spectrum.

Now, we must process the indirect dimension (D1):

- Switch to D1 (sideframe, radiobutton), and select data point 614 in D2.

- Do a complex conjugate (Tools ⟶ Complex Conjugate)[1]

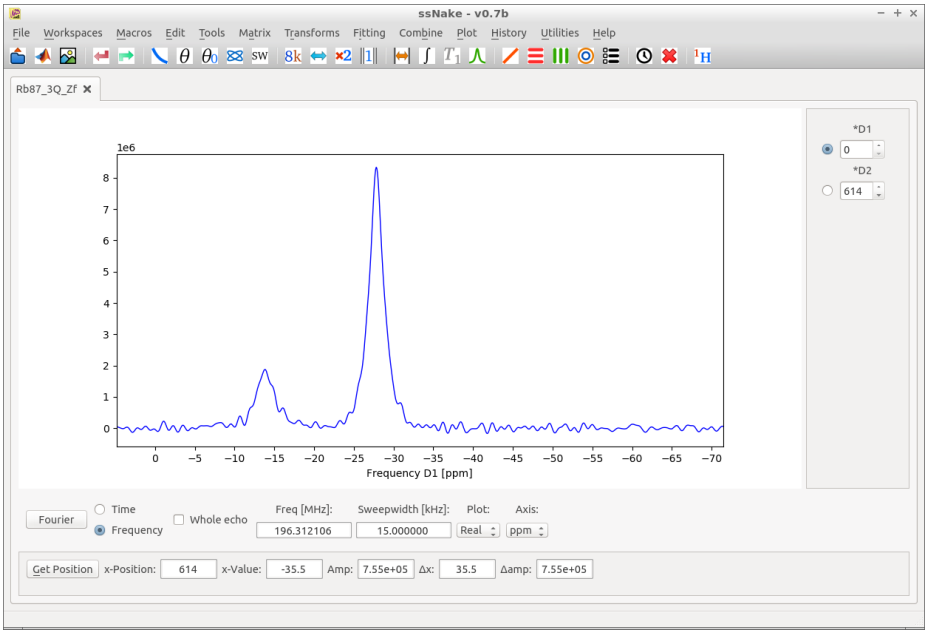
This should show:



Now we need some zerofilling etc.:

- Set the size to 1024 points (Matrix ⟶ Sizing)
- Fourier Transform

This gives the spectrum along D1 for this trace:



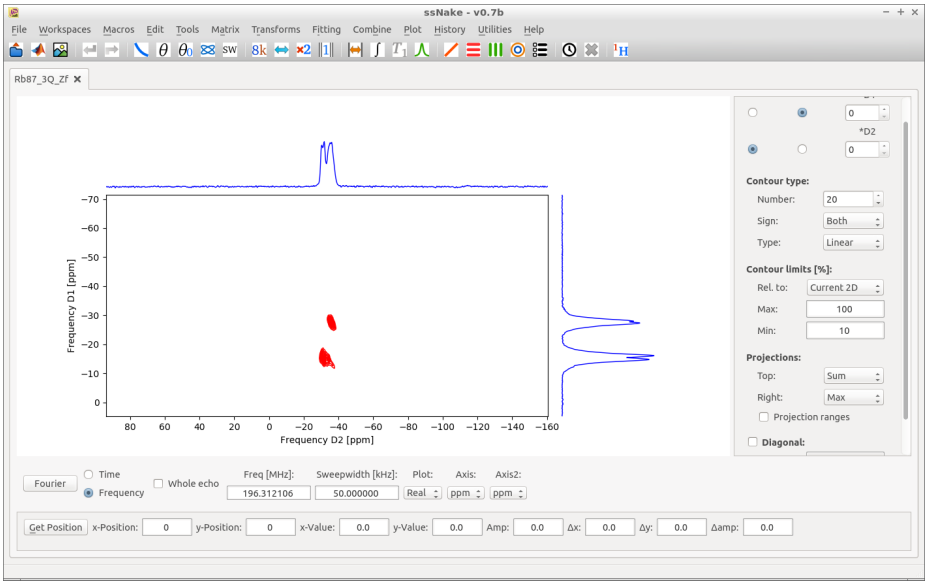
[1]The Varian data we loaded has a different complex definition, so a conjugate in the indirect dimension is nearly always needed.

The phasing looks good, so we do not need to do that.

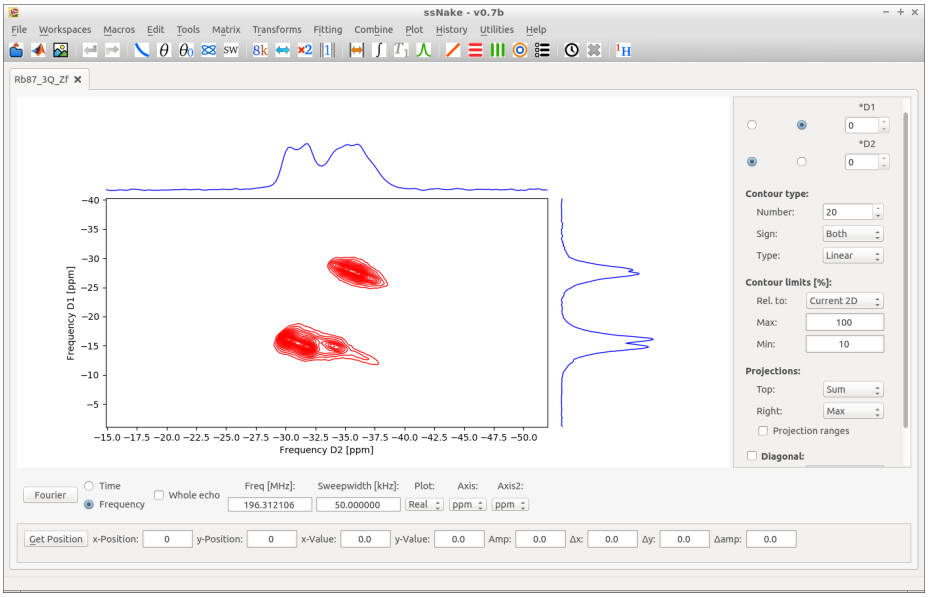
We have now processed both dimensions, so we can view the data as a contour plot:

- Switch to D2 (sideframe, radiobutton)
- Change the view to a contour plot: Plot ⟶ Contour

We now have:



And zoomed:

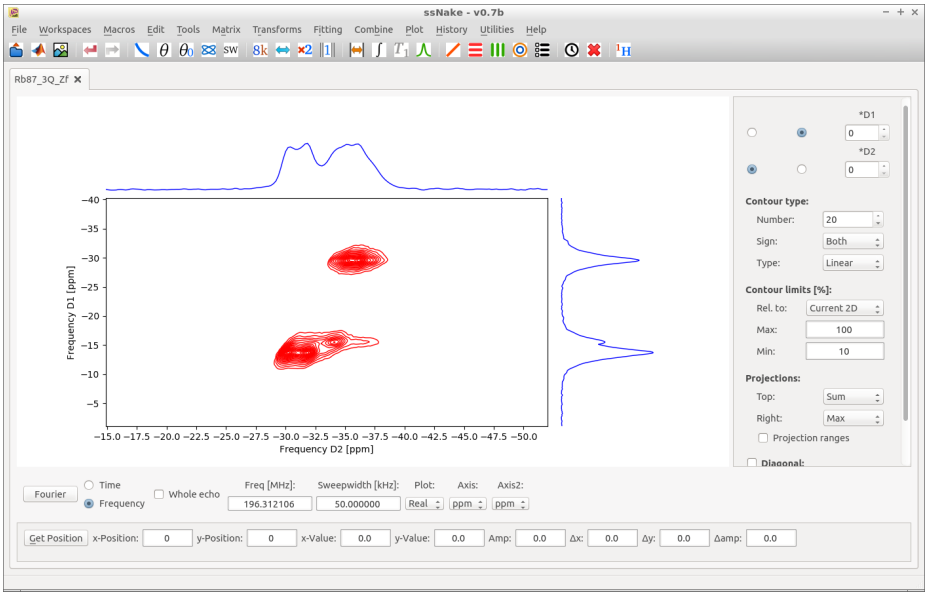


Note that I put the right projection to ‘Max’ instead of the standard ‘Sum’. This gives a skyline projection, which is less influenced by the noise regions of the data.

As can be seen, the different powder patterns are all tilted, going from bottom right to top left. This is normal for a z-filter MQMAS, but needs to be corrected by shearing the spectrum.

- Shear via Matrix ⟶ Shearing, using the ‘Spin 3/2, -3Q’ setting, and direction ‘1’ and axis ’2’

This shows (zoomed):



Which is a nice spectrum! This is the final figure, we now only need to do some work on the axes.

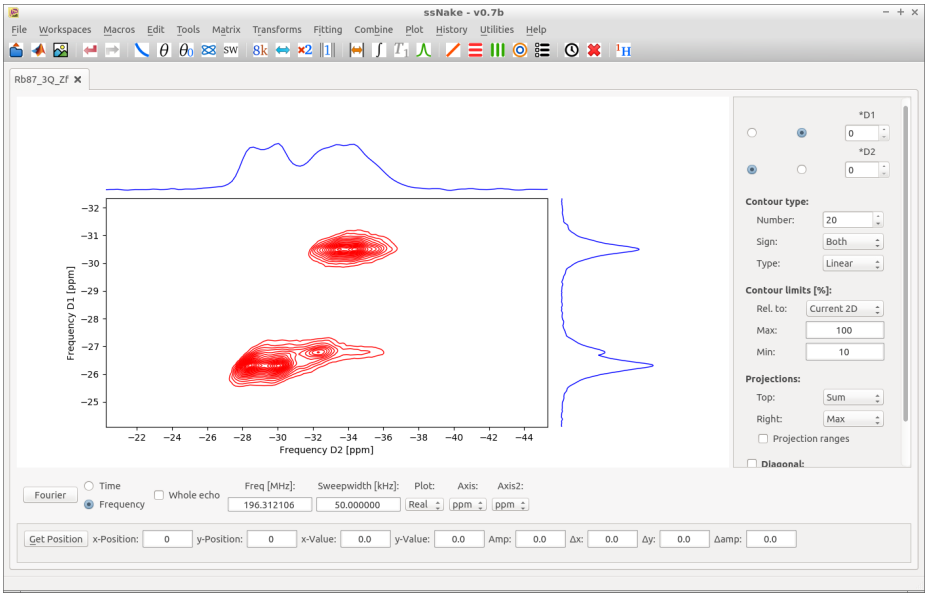
In the view that we have now, the indirect dimension is called the ‘isotropic’ axis. The position along this axis is determined by the scaled isotropic chemical shift, and the scaled quadrupolar induced shift. However, it is more convenient to have in axis with the unscaled isotropic chemical shift. To accomplishing this, we must dived the spectral width by a specific value (which depends on the spin quantum number).

- Switch to D1 (sideframe, click on the upper left radiobutton)
- Use Tools ⟶ Scale SW, and select ‘Spin 3/2, -3Q’ and apply

Now, we have scaled this axis. As a last step, we must apply a chemical shift reference. This was measured using a rubidium nitrate solution. Based on this 0 ppm is at: 196.3182865 MHz.

- Set the reference via Plot ⟶ Reference ⟶ Set Reference, and fill in ‘196.3182865’ in the Frequency box
- Switch to D2 (sideframe, click on the lower left radiobutton)
- Set the reference in the same way

This is the final spectrum, and looks like (zoomed):



This spectrum is also delivered with this tutorial, and named 'Rb87_3Q_Zf_(final_spectrum).mat'. Note that I extracted the relevant region before saving (to lower the file size).

Now, we can fit this spectrum. Either by fitting a specific trace with a regular second order quadrupolar line, or by fitting the whole MQMAS. Another alternative is to only get the isotropic shift and the quadupolar product $P_Q = C_Q\sqrt{1+\eta^2/3}$. For this, we must het the Centre of Mass for each site, in both D1 and D2. This can be going to the relevant slice, and using Fitting ⟶ Centre of Mass. Note that in D1, the peaks are symmetric, so the highest point is the centre in this case.

Site	δ_1 [ppm]	δ_2 [ppm]	δ_{iso} [ppm]	P_Q [MHz]
1	−30.5	−34.17	−31.86	1.89
2	−26.8	−31.96	−28.71	2.24
3	−26.3	−29.76	−27.58	1.83

The last two columns have been calculated using the MQMAS Extraction utility (see the Utilities menu).

4 Split T_1 processing

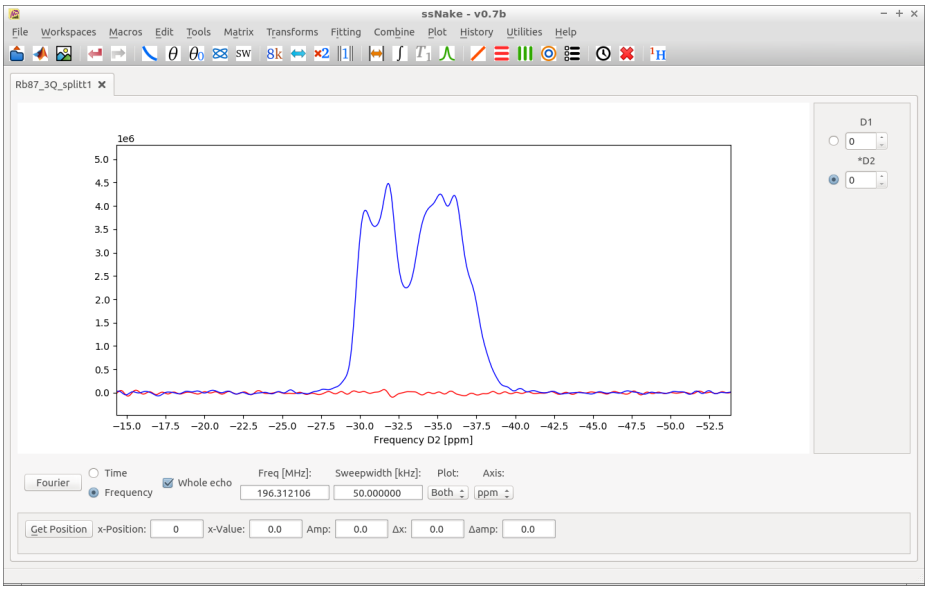
In a split T_1 experiment, the additional shift of the echo is taken into account within the pulse sequence. This leads to regular echo data, were the position of the echo in the time domain is always the same. Due to this, no shearing is required. Also, the data is recorded in such a way that no hypercomplex processing is necessary. The following assumes that you read the information above (about the z-filter processing).

- Open the Varian file Rb87_3Q_splitt1.fid using File ⟶ Open

Now, we must process this data as a whole echo acquisition (see the tutorial on this).

- Swap the echo at position 375 (Tools ⟶ Swap Echo)
- Set the size to 4096 points (Matrix ⟶ Sizing)
- Apply apodization if required (not used in this case)
- Fourier Transform
- Phase the imaginary part to zero (168.9 degrees, via Tools ⟶ Phasing)

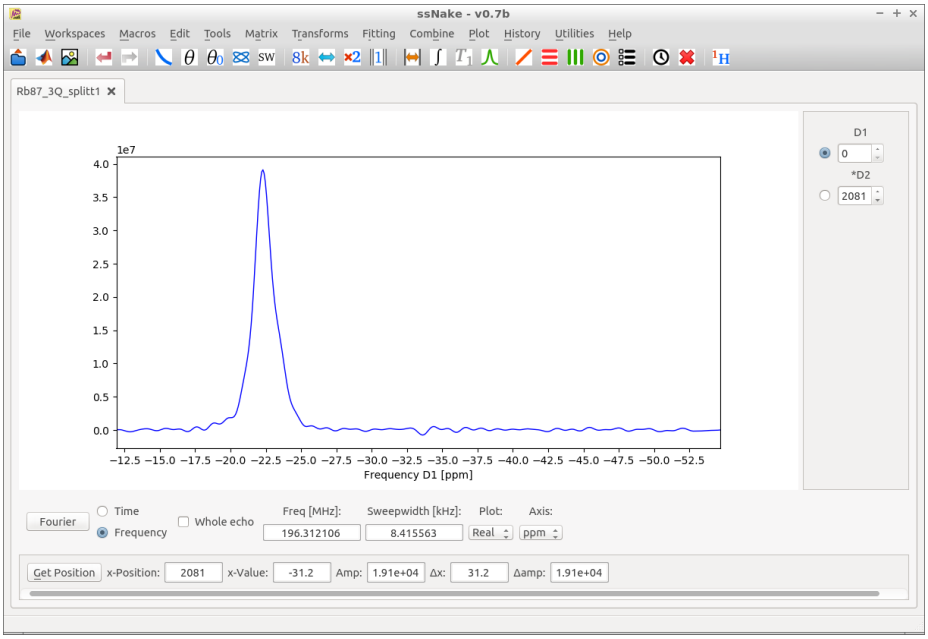
This should show (zoomed):



Now we can process D1:

- Switch to D1 (sideframe, radiobutton)
- View position 2081 along D2
- Tools ⟶ Complex Conjugate
- Set size to 512
- Fourier Transform

This gives:



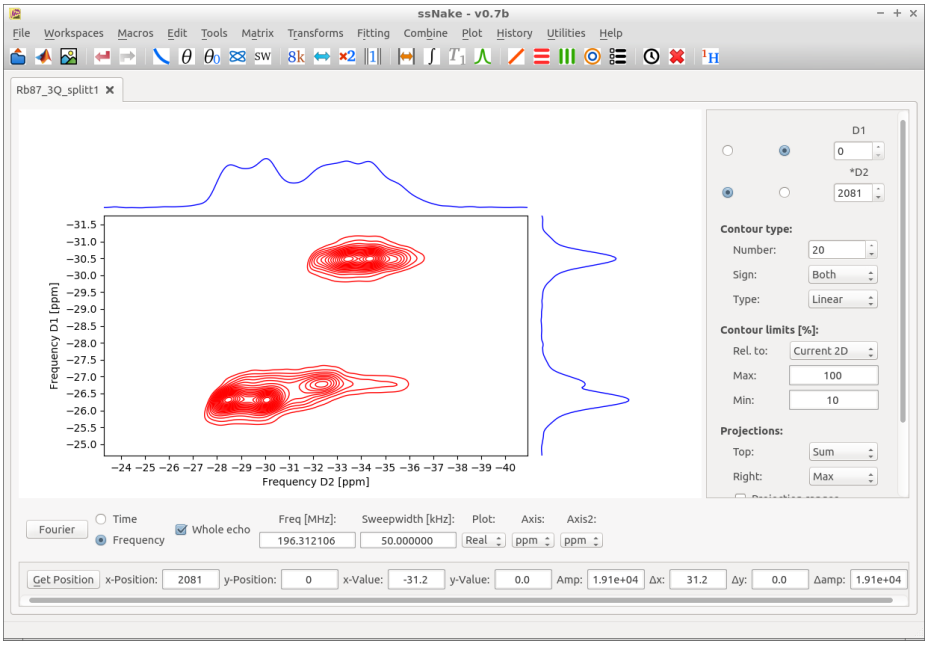
Now, me must scale the spectral width of this dimension, as was described above. However, with this experiment some weird stuff is going on. According to the Varian pulse sequence used to measure this data, the SW that you need to supply must be 9/16 times the desired spectral width. For the processing, this means that this scaling must first be undone.

- Multiply the spectral width by 16.0/9.0 (either via Tools ⟶ Scale SW, or by typing at the SW box in the bottom frame).
- Multiply the SW by the MQMAS scaling value: Tools ⟶ Scale SW, and select ‘Spin 3/2, -3Q’

Now, we must reference the ppm axis in both dimension. As before:

- Set the reference via Plot ⟶ Reference ⟶ Set Reference, and fill in ‘196.3182865’ in the Frequency box
- Switch to D2 (sideframe, click on the lower left radiobutton)
- Set the reference in the same way

Switching to a contour plot gives (zoomed):



This is an equivalent spectrum as obtained above, for the z-filter data. This spectrum is also delivered with this tutorial, and named 'Rb87_3Q_splitt1_(final_spectrum).mat'. Note that I extracted the relevant region before saving this file (to lower the file size).

5 Equations

The following Section will show some equations for the relevant shearing and scaling constant used for MQMAS processing.[2]

These are all included in ssNake in such a way that there is no need to know these values, or to type them in (as the relative input windows know them). However, for the sake of completeness, they are provided here.

The following table summarises the values:

[2]This sections is based on: P. P. Man, *Phys. Rev. B*, **5**, 2764 (1998) and T. Anupõld, A. Reinhold, P. Sarv, A. Samoson, *Solid State Nucl. Magn. Reson.*, **13**, 87 (1998).

I	pQ	k	$1/a$	z
3/2	$-3Q$	7/9	9/34	680/27
5/2	$3Q$	19/12	−12/17	8500/81
	$-5Q$	25/12	12/85	8500/81
7/2	$3Q$	101/45	−45/34	6664/27
	$5Q$	11/9	−9/34	6664/27
	$-7Q$	161/45	45/476	6664/27
9/2	$3Q$	91/36	−36/17	1360/3
	$5Q$	95/36	−36/85	1360/3
	$7Q$	7/18	−18/117	1360/3
	$-9Q$	31/6	6/85	1360/3

Here, k is the shearing factor, $1/a$ the scaling of the spectral width, and z a value necessary to calculate the quadrupolar product P_{Q} from an MQMAS spectrum (see later). The equations are:

$$k = p\frac{36I(I+1)-17p^2-10}{36I(I+1)-27} \tag{1}$$

$$1/a = 1/(k-p) \tag{2}$$

$$z = \frac{1}{\frac{b}{a}-r} \tag{3}$$

With:

$$b = r(k+\lambda) \tag{4}$$

and

$$r = -\frac{3}{10}\frac{I(I+1)-3/4}{[2I(2I-1)]^2} \tag{5}$$

$$\lambda = p\frac{I(I+1)-3/4\cdot p^2}{-I(I+1)+3/4} \tag{6}$$

5.1 Further background

Here, we will quickly derive the relevant equations shown above.

The centre of mass of the MQMAS data in D2 is:

$$\delta_{\mathrm{D2}} = \delta_{\mathrm{iso}} + \delta_{\mathrm{QIS}} = \delta_{\mathrm{iso}} + r\frac{P_{\mathrm{Q}}^2}{\nu_0^2}\cdot 10^6 \tag{7}$$

with

$$r = -\frac{3}{10}\frac{I(I+1)-3/4}{[2I(2I-1)]^2} \tag{8}$$

In D1, before the shearing it is:

$$\delta_{\mathrm{D1}} = -p\delta_{\mathrm{iso}} + \delta_{\mathrm{QIS}} = -p\delta_{\mathrm{iso}} + \lambda r\frac{P_{\mathrm{Q}}^2}{\nu_0^2}\cdot 10^6 \tag{9}$$

with:

$$\lambda = p\frac{I(I+1)-3/4\cdot p^2}{-I(I+1)+3/4} \tag{10}$$

After shearing, this becomes:

$$\delta_{\mathrm{D1'}} = \delta_{\mathrm{D1}} + k\delta_{\mathrm{D2}} = (k-p)\delta_{\mathrm{iso}} + r(k+\lambda)\frac{P_{\mathrm{Q}}^2}{\nu_0^2}\cdot 10^6 \tag{11}$$

$$= a\delta_{\mathrm{iso}} + b\frac{P_{\mathrm{Q}}^2}{\nu_0^2}\cdot 10^6 \tag{12}$$

with the constants:

$$a = k(I,p) - p \tag{13}$$

$$b = r(I)(k(I,p) + \lambda(I,p)) \tag{14}$$

A good way to processes this data, is to divide the spectral width of F1 by a. This leads to a chemical shift axis, were a increase in the isotropic shift of a line leads to an exact same change in the F1 dimension. This leads to:

$$\delta_{\mathrm{D1''}} = \delta_{\mathrm{iso}} + \frac{b}{a}\frac{P_{\mathrm{Q}}^2}{\nu_0^2}\cdot 10^6 \tag{15}$$

When this processing is performed, nuclei that experience a quadrupolar coupling always lay in the lower right part of the spectrum, lower than the diagonal that is. If a lineshape is fully on the diagonal, but stretched along it, there is a chemical shift distribution.

Based on the centre off mass in D1" and D2, the NMR parameters δ_{iso} and P_{Q} can be extracted:

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{D1''}} - \frac{b}{a\cdot r}\delta_{\mathrm{D2}} = \delta_{\mathrm{D1''}} - \frac{k+\lambda}{a}\delta_{\mathrm{D2}} \tag{16}$$

$$= \frac{17\delta_{\mathrm{D1''}} + 10\delta_{\mathrm{D2}}}{27} \tag{17}$$

This result is the same for any I and p.

For P_{Q} the case is more difficult:

$$\delta_{\mathrm{D1''}} - \delta_{\mathrm{D2}} = \left(\frac{b}{a} - r\right)\frac{P_{\mathrm{Q}}^2}{\nu_0^2}\cdot 10^6 \tag{18}$$

$$P_{\mathrm{Q}} = \sqrt{\frac{1}{\frac{b}{a}-r}\cdot 10^{-6}\,\nu_0^2(\delta_{\mathrm{F1''}} - \delta_{\mathrm{F2}})} \tag{19}$$

$$= \sqrt{z\cdot 10^{-6}\,\nu_0^2(\delta_{\mathrm{F1''}} - \delta_{\mathrm{F2}})} \tag{20}$$

With the scaling factor:

$$z = \frac{1}{\frac{b}{a}-r} \tag{21}$$

These depend only on I and are tabulated above. These equation can be used to calculate the isotropic shift and quadrupolar product (P_Q) of a line based on the centre of mass of the line along both dimension. These equations have been included in ssNake in the form of a utility. See the Utilities menu.