

Nutation data analysis using ssNake

17th January 2019

1 Introduction

This tutorial will explain how a standard nutation experiment 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.

A nutation experiment is a series of single pulse NMR experiment with an increasing pulse length (see Figure 1. In this way, the modulation of the signal during the pulse can be studied. When the RF field strength is large, the effects of chemical shift can be ignored during the pulse, which leads to a sine modulation of the signal intensity with a frequency ν_1 : the nutation frequency. Knowledge of the nutation frequency (i.e. the RF field strength) can be used for setting up decoupling sequences, cross-polarization, and so on.

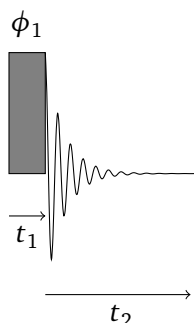


Figure 1: Pulse sequence of a single pulse nutation experiment.

2 Used data

For this example, we will use a Varian data set recorded on a 14.1 T spectrometer. The sample was a saturated solution of KMnO_4 in water, and the ^{55}Mn signal was recorded. In this data set, an array of experiment was performed, with the pulse length starting at $6\text{ }\mu\text{s}$, and increasing with $6\text{ }\mu\text{s}$ with a total of 128 experiments. For the analysis described here, it is required that the step size and initial value are equal.

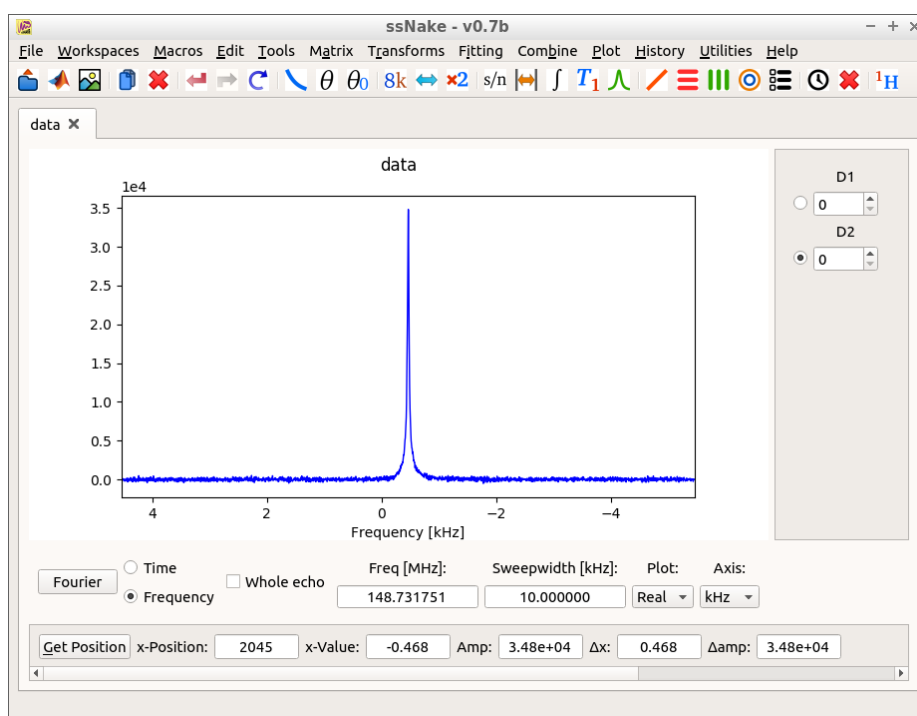
3 Processing

- Open the data file by using File → Open.
- Zero fill the data to 4k points (4096 points) by using Matrix → Sizing, and filling in the value in the Size box.
- Fourier transform using the 'Fourier' button in the bottom frame.

This shows us the spectrum of the first experiment (with a 6 μ s pulse width).

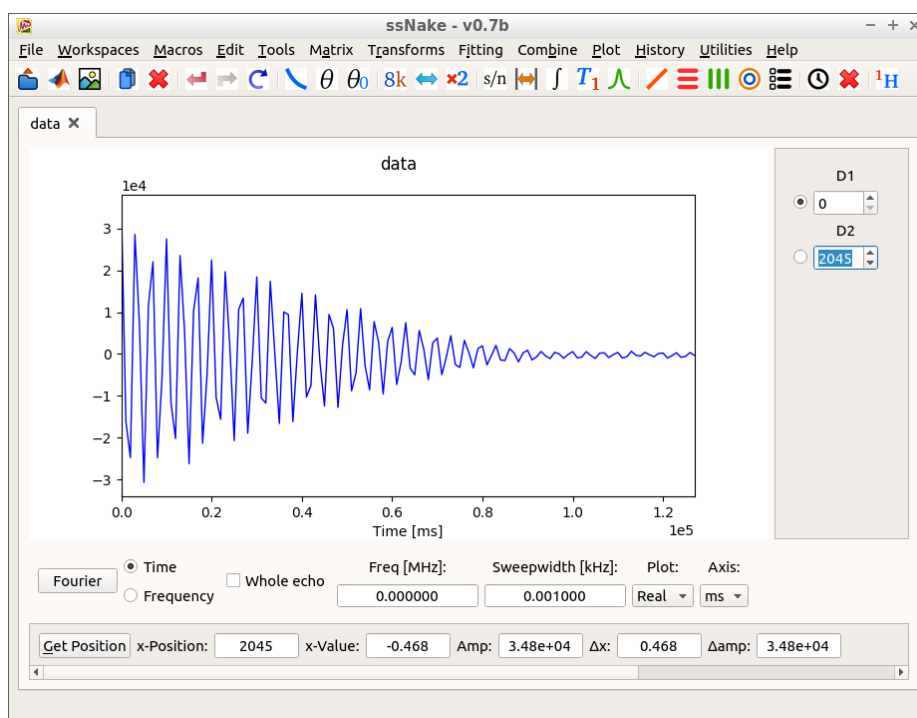
- Phase this spectrum to obtain a nice absorption lineshape.

This results in the following figure:



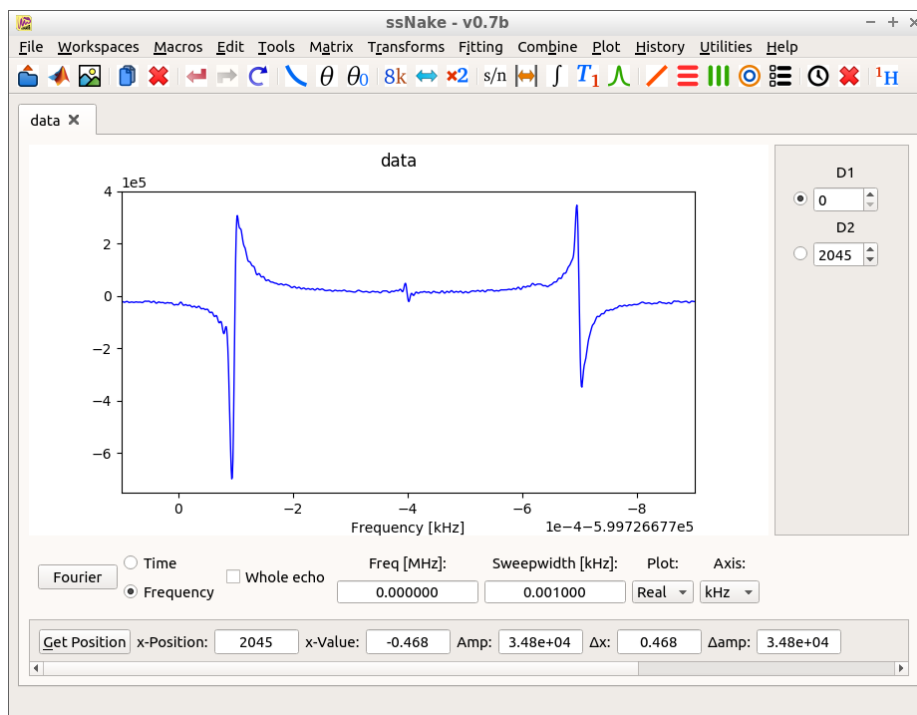
Now we can view the other experiments by increasing the value of the D1 box in the side frame. Note that we want to continue to view the D2 dimension, and therefore keep the bullet next to D2 as the active dimension.

Now we would like to examine the change of the peak height along the D1 dimension. We therefore need to obtain the position of the peak (in data points). Click the 'get position' button in the bottom frame, and select the top of the peak (zoom in for accurate). This should report an x-position of approximately 2045. To view this trace along D1, copy this value into the D2 box, and press enter. This results in the following Figure, which shows a sine oscillation as a function of pulse width:



- Zero fill along this D1 by using Matrix → Sizing and use 1024 points.
- Right shift the data with 1 point by using Matrix → Shift Data, and click the right arrow button once.

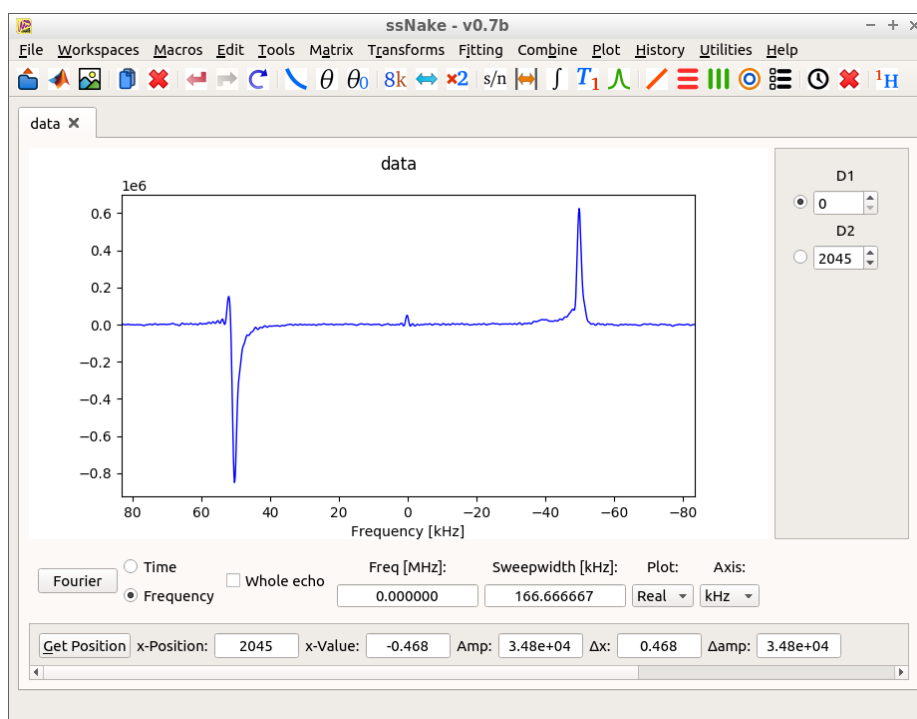
This should result in a figure similar to:



The last step we performed was to add a datapoint in front (with a value of 0) and removing a data point at the end. This shift is required to make our data start at time zero and since a pulse width of 0 should give no signal we can do this by shifting our data by one data point. This way, we artificially made our oscillation start at $t = 0$. For this reason it is convenient to have an initial value which is equal to the step size.

- Transform to a spectrum by clicking the ‘Fourier’ button.
- Phase with -90° to obtain the in-phase spectrum.
- Clear the reference frequency (no reference is required) via Tools \rightarrow Reference \rightarrow Clear Current Reference.

We should now set the sweepwidth to the correct value, so we obtain a sensible axis. In our case, the dwell time of the experiment is the stepsize of the pulse width: $6 \mu\text{s}$. We can therefore type in the sweepwidth box in the bottomframe: ‘1000/6e-6’. ‘1/6e-6’ is the sweepwidth in Hz, and the 1000 is required to convert to kHz. Alternatively, ‘1/6e-3’ could also be used. This results in to the following Figure, which is the final spectrum. It shows an (nearly) anti-symmetric spectrum with a peak at 50 kHz, so $\nu_1 = 50 \text{ kHz}$ in this case.

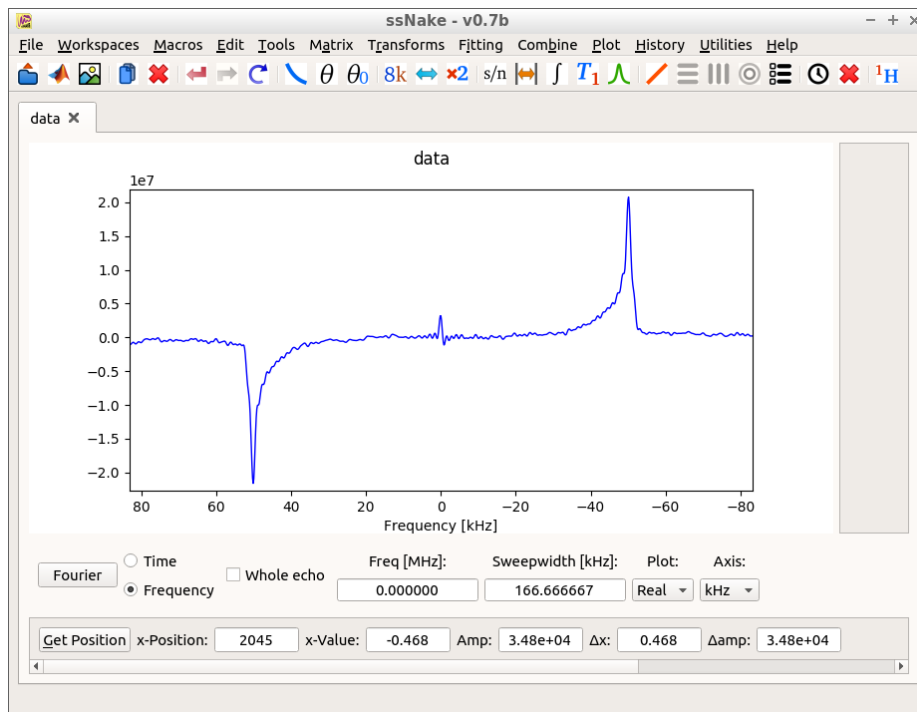


4 Alternatives

4.1 Integrate D2

When having phased the first spectrum in D2, Matrix \rightarrow Region \rightarrow Integrate can be used to integrate the peak. Use the tool by left clicking on the left and right of the peak and press OK.

Continue the steps described above, but notice that the old D2 dimension has now been removed, and only the D1 remains. As there is only one dimension now, the dimension selector in the side frame has disappeared. This results in the following Figure (after 41.5° 1st order phasing):



Note that looks quite different from the 'normal' processed spectrum. This probably means that the nutation frequency varies over the peak. This is probably caused by shimming issues, which result in a correlation between the NMR frequency (D2) and nutation frequency (D1).

4.2 Force symmetry

Ideally, the nutation spectrum has inversion symmetry (the left is -1 times the right). Sometimes it is convenient to force this. This can be done by performing Tools → Real (removing the imaginary part) before the Fourier transform in the D1 domain.

4.3 Correct DC offset

In some cases, the nutation signal does not decay to zero, but to some other value. This will result in a peak at 0 Hz in the nutation spectrum. This can be avoided by subtracting the average of the last part of the nutation time signal from the entire signal. This can be done by using Tools → Subtract Averages. Ideally, this is done before the zero filling the D1 domain.

4.4 2D nutation

When following the method to obtain the nutation spectrum, the spectrum can also be viewed as a contour plot. This can be done through Plot → Contour.