

Supplement: Enhancing the Real-Time Detection of Phase Changes in
Lithium-Graphite Intercalated Compounds Through Derivative Operando
(dOp) NMR Cyclic Voltammetry

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S1 Calculation of lithium concentration and Li-C stoichiometry

From Figure 6 in the main text, the maximum intensity of the peak near 0 ppm was observed at $E_{op} \approx 477$ mV for the second and third cycles of the cell. The first cycle was not used to shift the peak potentials due to the pasivation of the electrodes. From Figure 3B, the integrated charge transferred to the system up to this potential was calculated to be $Q_{op} \approx 0.351$ C and $Q_{op} \approx 0.343$ C for the second cycle and third cycle, respectively.

The amount of lithium ions being transferred were calculated using the following equation:

$$[\text{Li}^+] = \frac{Q}{F}, \quad (1)$$

where Q is the charge in Coulombs and F is Faraday's constant. The resulting lithium ion concentration resulted in $[\text{Li}^+] = 3.637858 \times 10^{-6}$ mol and $[\text{Li}^+] = 3.554945 \times 10^{-6}$ mol for the second and third cycles respectively. Knowing that the amount of carbon in the electrode was 18.06 mg, the corresponding moles of C₆ was $[\text{C}_6] = 1.80338 \times 10^{-6}$ mol. The ratios of Li⁺ to C₆ were then calculated to be 1:68 and 1:71 respectively, which average to 1:69 or a Li-C stoichiometry of LiC₆₉.

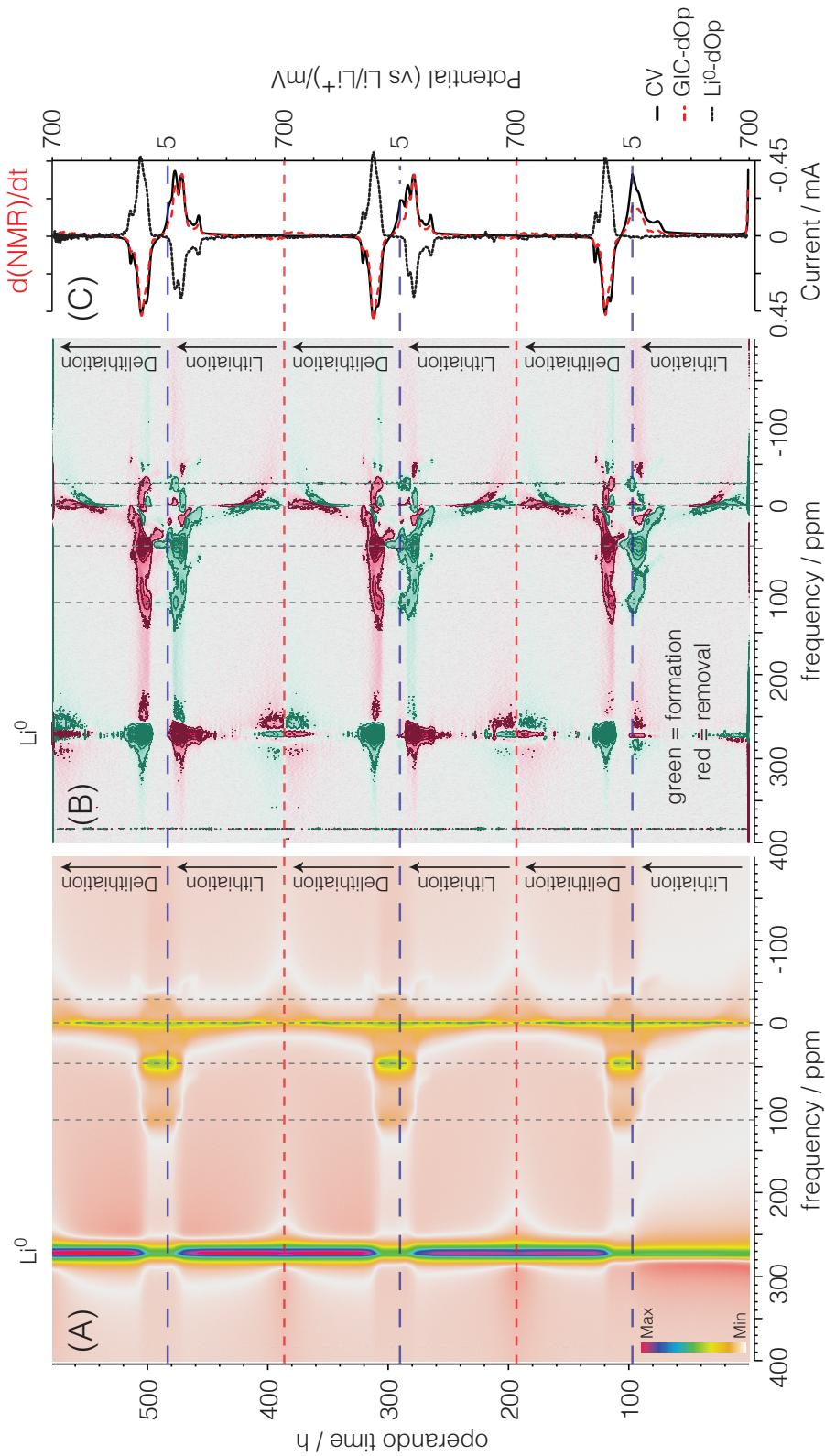


Figure S1: A) Color intensity plot of the operando ${}^7\text{Li}$ NMR spectra of all three cycles of the electrochemical cell. Light colors represent low peak intensities and darker colors represent higher peak intensities. The horizontal axis is the NMR frequency shift in ppm are referenced to 1 M LiCl. The vertical axis is the operando time for the three cycles of the cell. The horizontal blue (dashed) line represents the time at which the current polarity was switched and the red (dotted) line represents the end of a cycle. In (B) is the corresponding bicolor contour plot of the ${}^7\text{Li}$ NMR dOp spectra. Green peaks represent lithium formation (lithiation) and red peaks represent lithium removal (delithiation). In (C) is the corresponding cyclic voltammogram (black line) and the projection of the derivative plot from -200 to 160 ppm (red dashed line), and from 200 to 350 ppm (black dotted line). Peaks labeled A, B, C, D, and E depicted in the second cycle represent the formation of LiC_{36} , LiC_{27} , LiC_{18} , LiC_{12} , and LiC_6 respectively

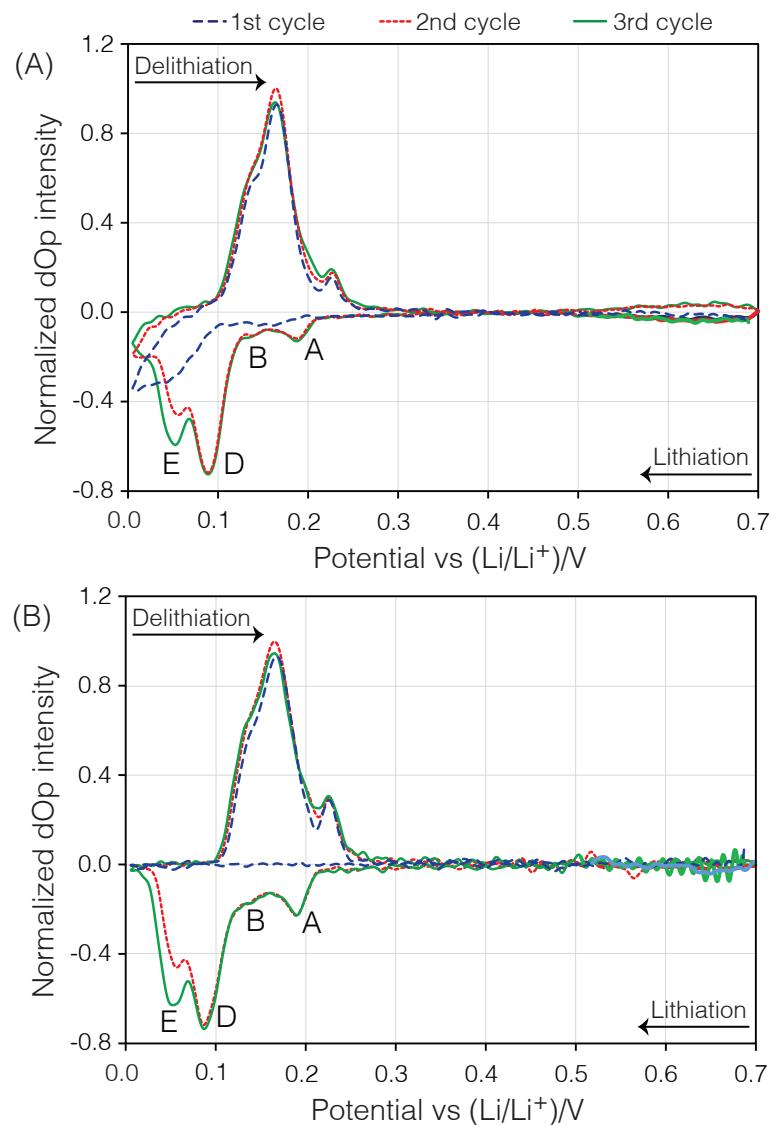


Figure S2: dOp-NMR cyclic voltammogram of the three cycles of the carbon/Li electrochemical cell taken from the projection of the ${}^7\text{Li}$ dOp-NMR signal across (A) the graphite intercalation compounds and (B) the lithium metal. The peaks labeled as A, B, D, and E are described in the text.

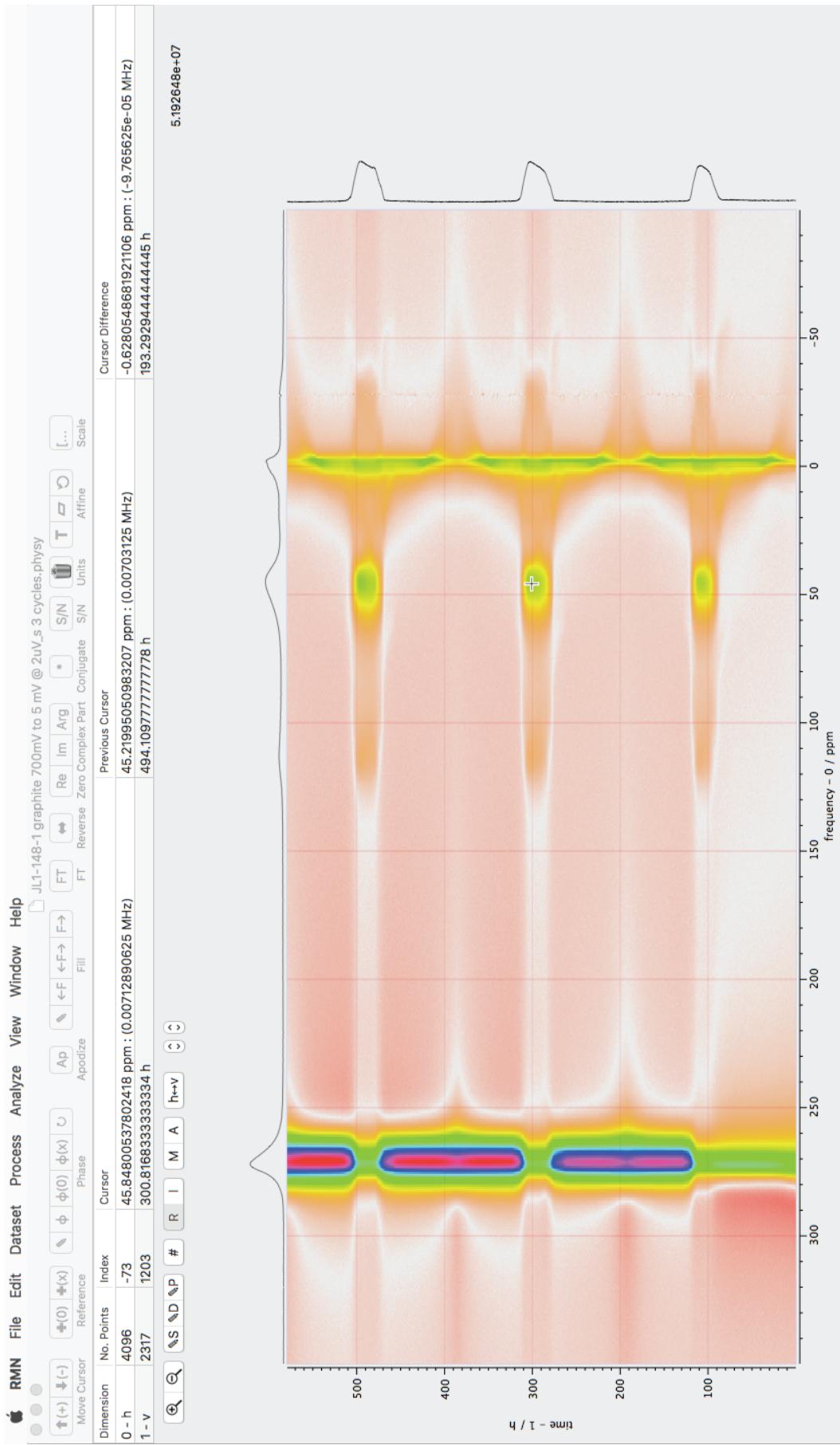
S2 Derivative Processing

Here we give a step-by-step guide to calculating the derivative of the operando signal using RMN. A similar sequence of steps can be taken in other signal processing programs such as Matlab or Mathematica. Taking a derivative through the Fourier derivative theorem consists of applying the following commands in RMN:

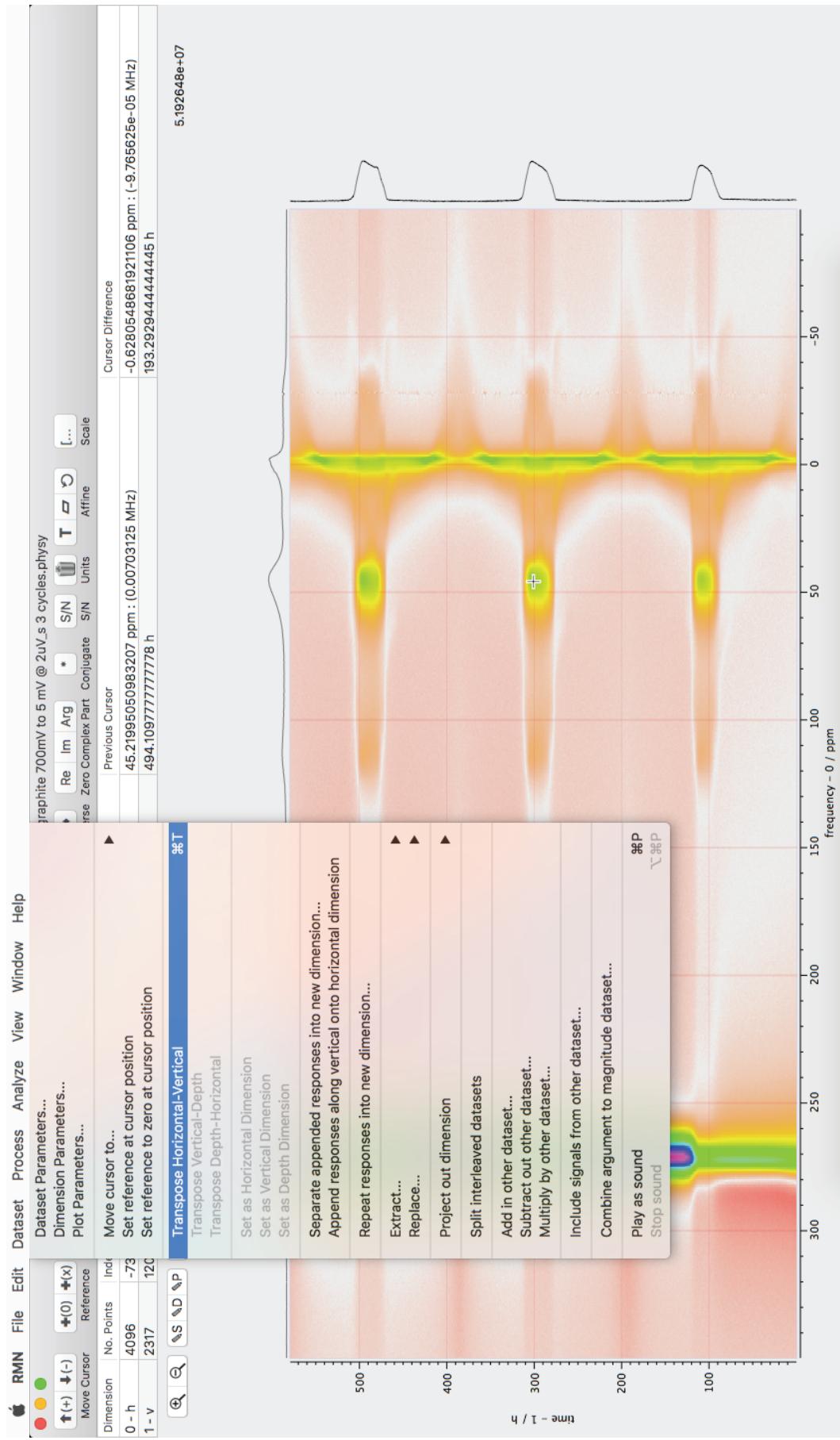
1. Fourier transforming along the operando dimension.
2. Applying the derivative convolution along the operando dimension.
3. Applying a hamming filter along the operando dimension.
4. Inverse Fourier transforming along the operando dimension.

All parameters used in processing the signal are shown.

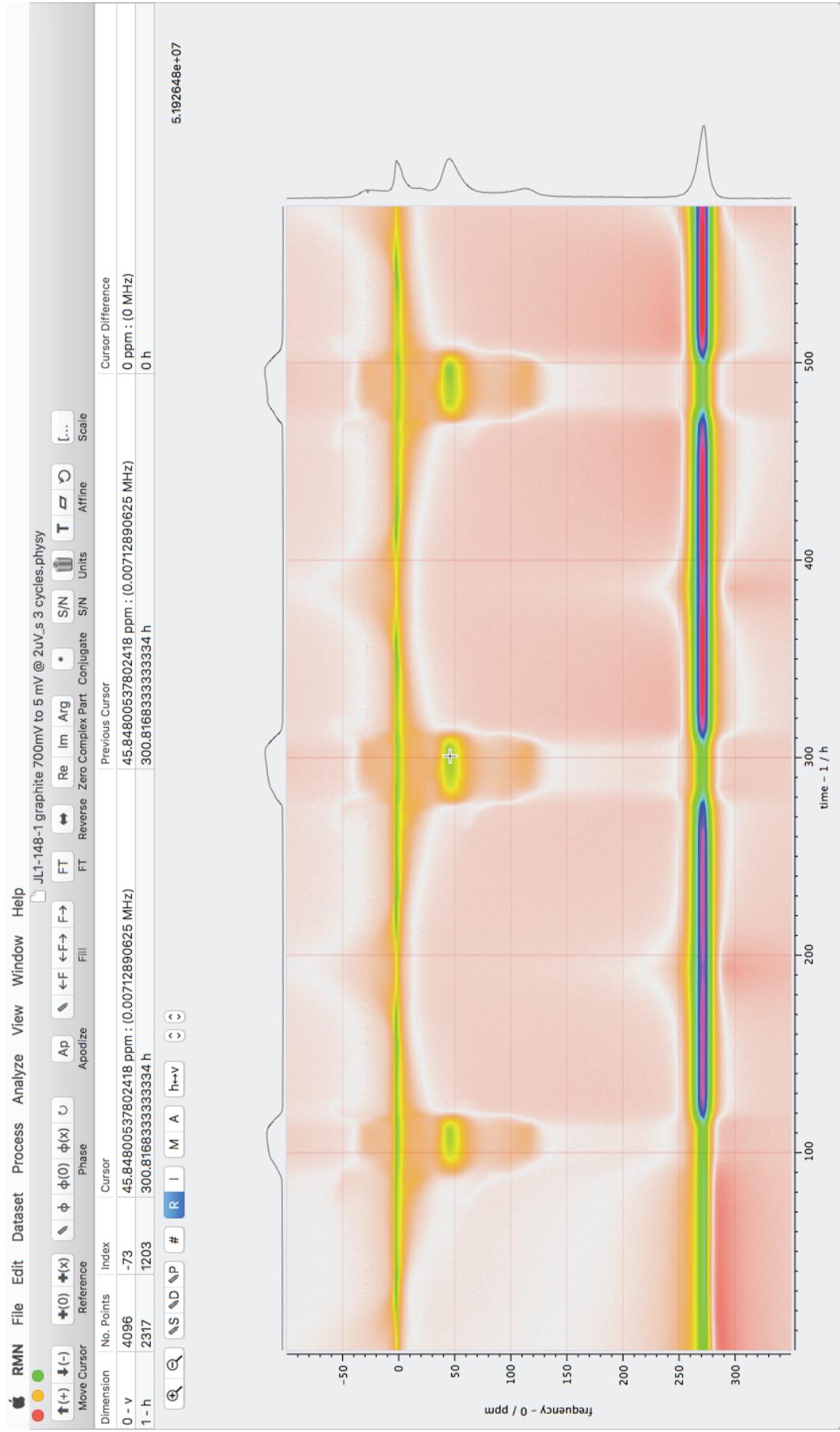
Below is a view of the Operando ^7Li NMR spectra of the three cycles of the electrochemical cell opened in RMN. The second cycle was shown in Figure 3 on the main text.



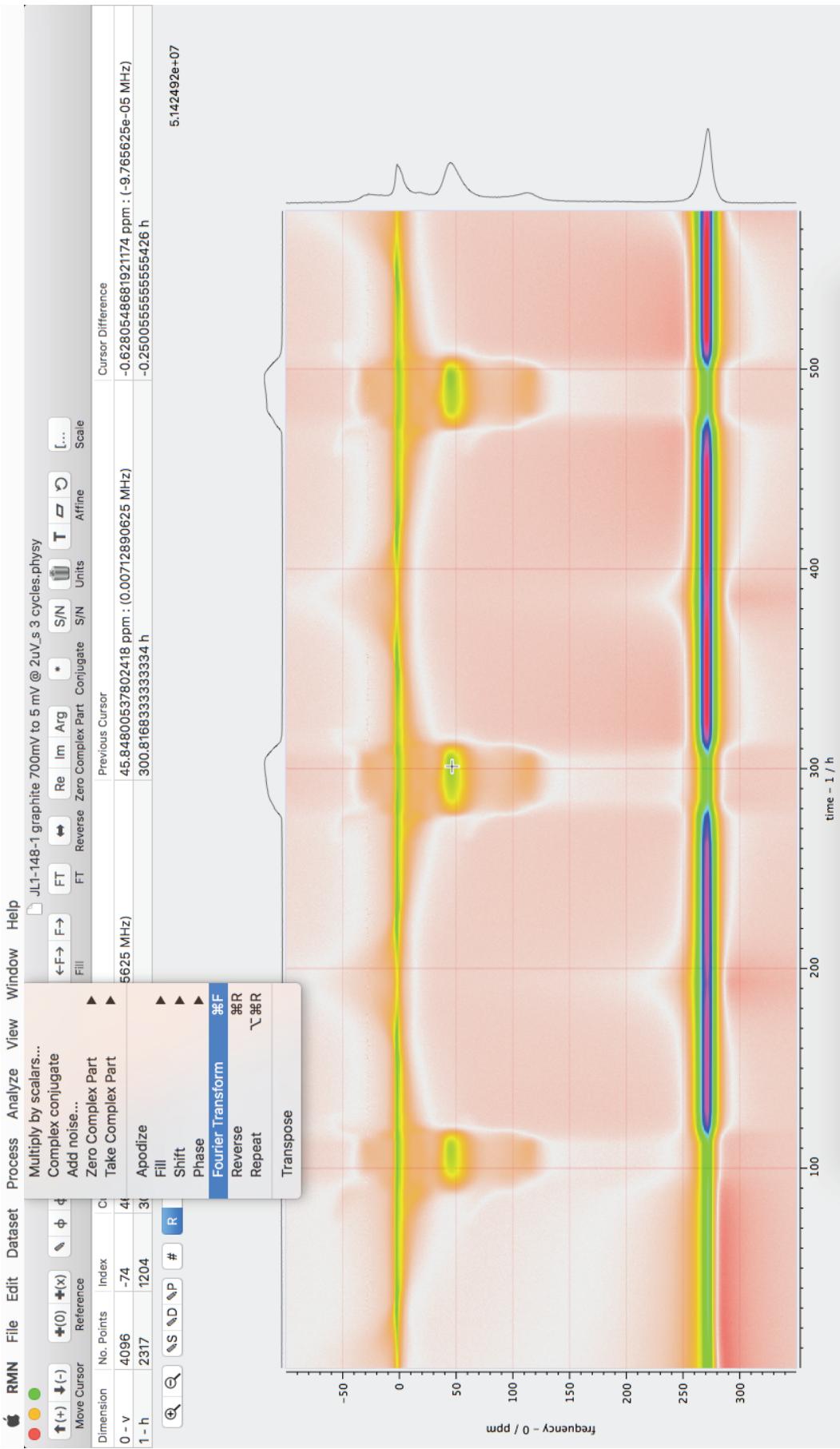
Transpose: All one-dimensional operations in RMN are applied to the signal along the horizontal dimension, therefore, before taking the derivative of the spectrum as a function of operando time, the spectrum is transposed to place the operand dimension along the horizontal. The command to transpose the horizontal and vertical dimensions in RMN are located under the “Dataset” menu.



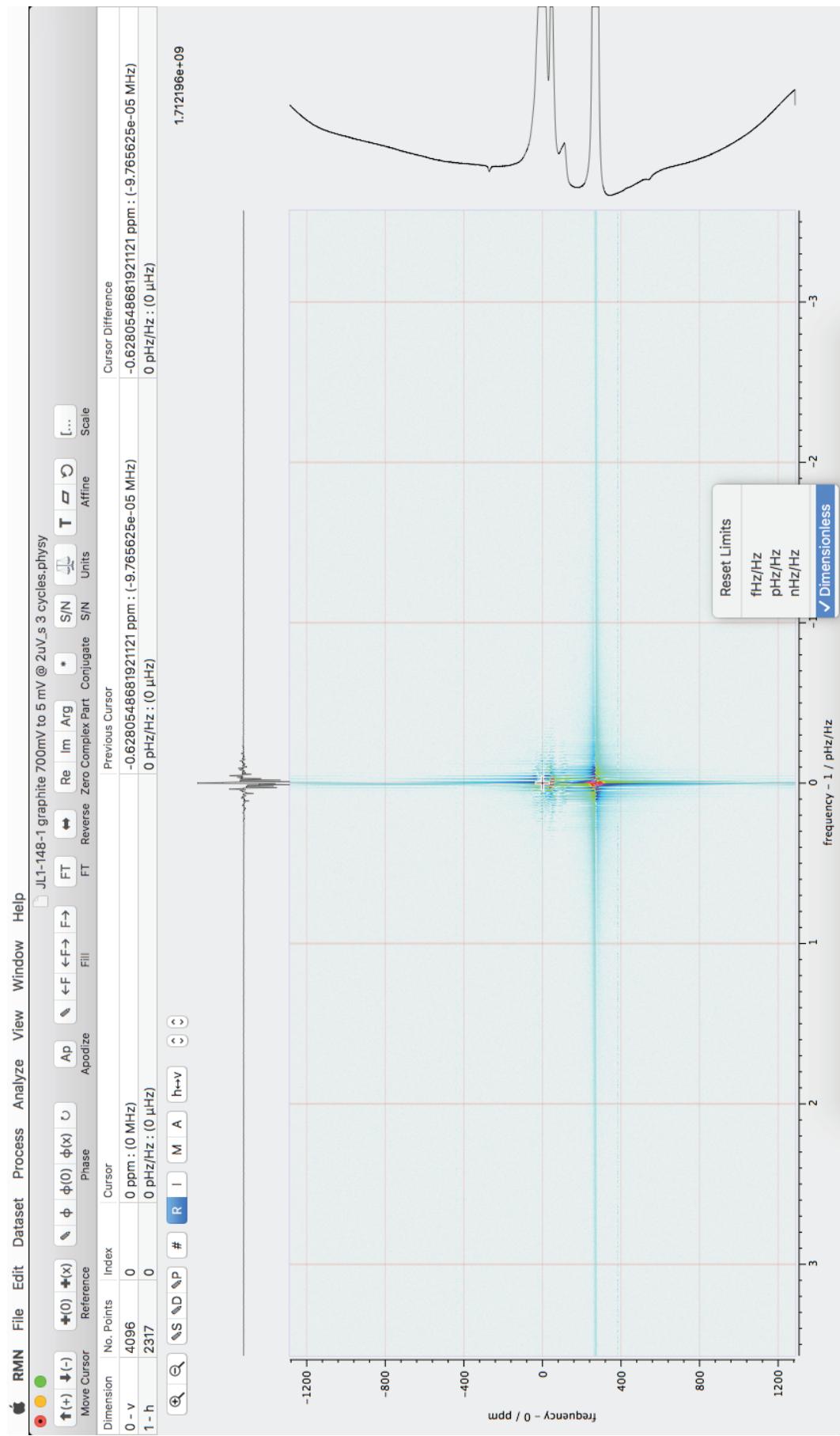
Below is the signal after transposing.



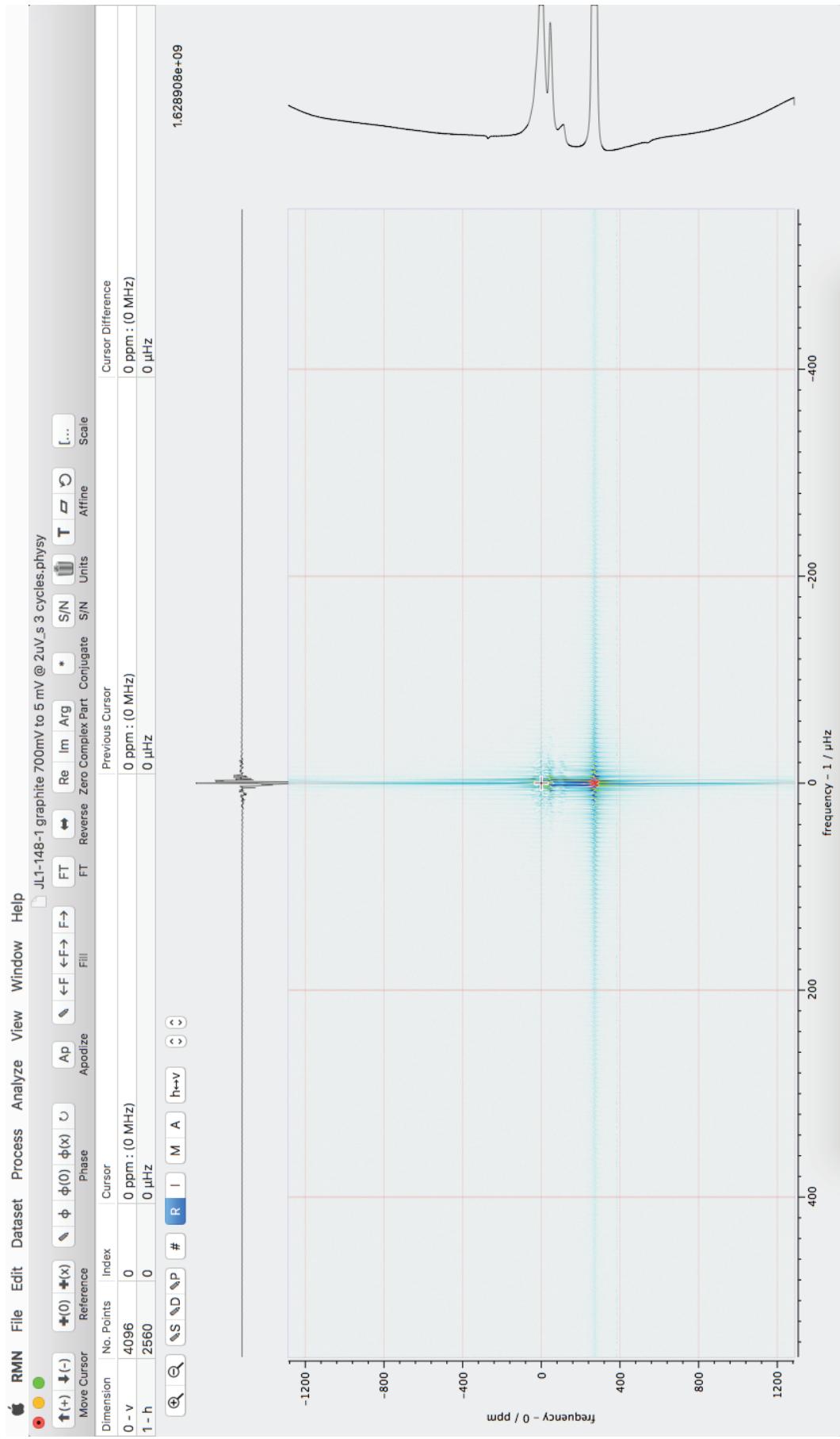
Fourier Transform: Apply a Fourier transform along the horizontal dimension to transform the operand time domain signal into a frequency domain signal. The command to “Fourier Transform” the spectra is located under the “Process” menu as shown below.



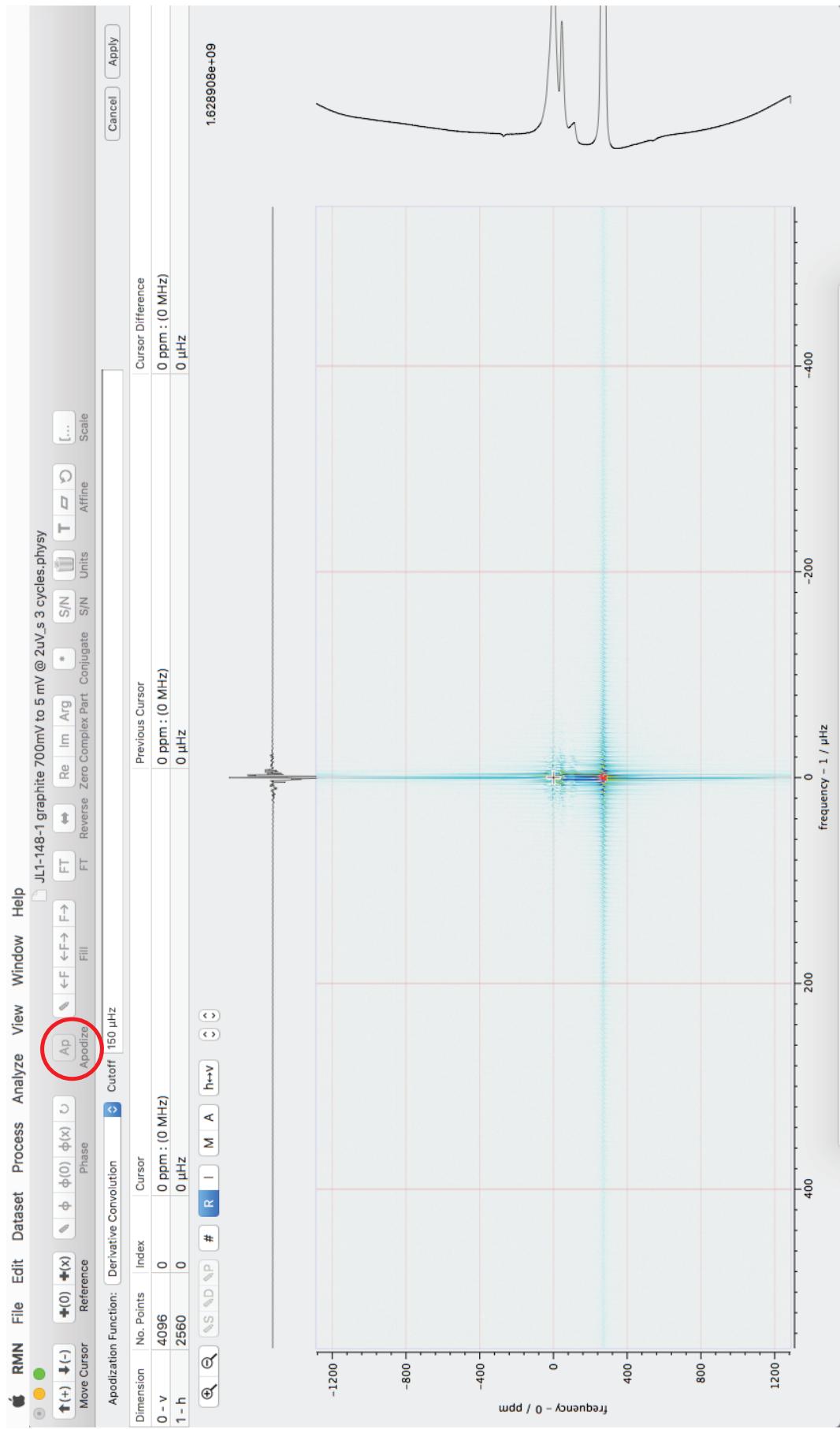
After the Fourier transform we obtain the signal below. Since RMN automatically converts the frequency domain axis of NMR signals into a dimensionless frequency ratio axis is it necessary in this case to convert the horizontal dimension back to units of frequency by clicking anywhere in the horizontal axis and unclicking the Dimensionless flag as shown below.



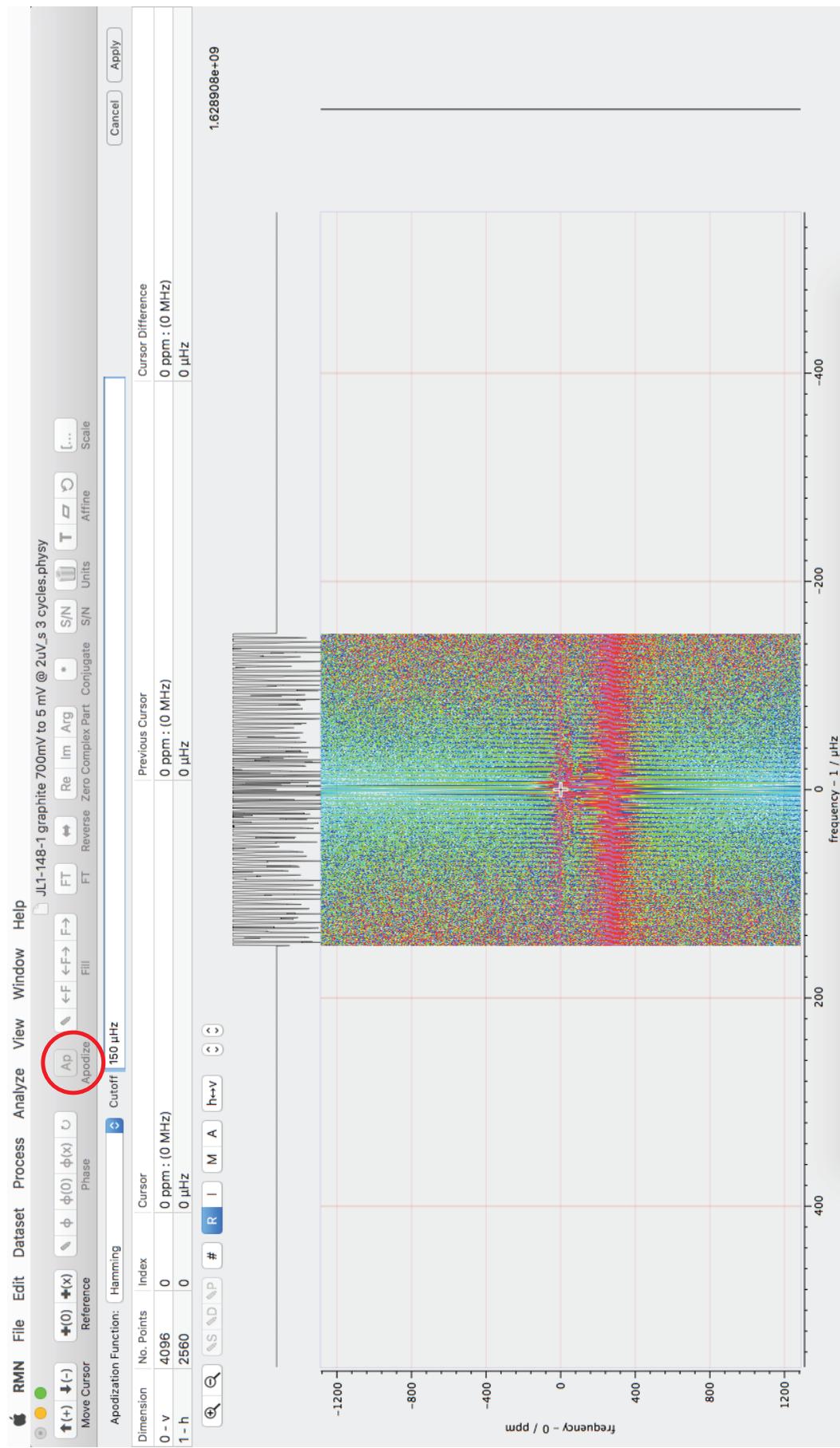
Below is the signal after the Fourier transform with the horizontal axis with units of μHz .



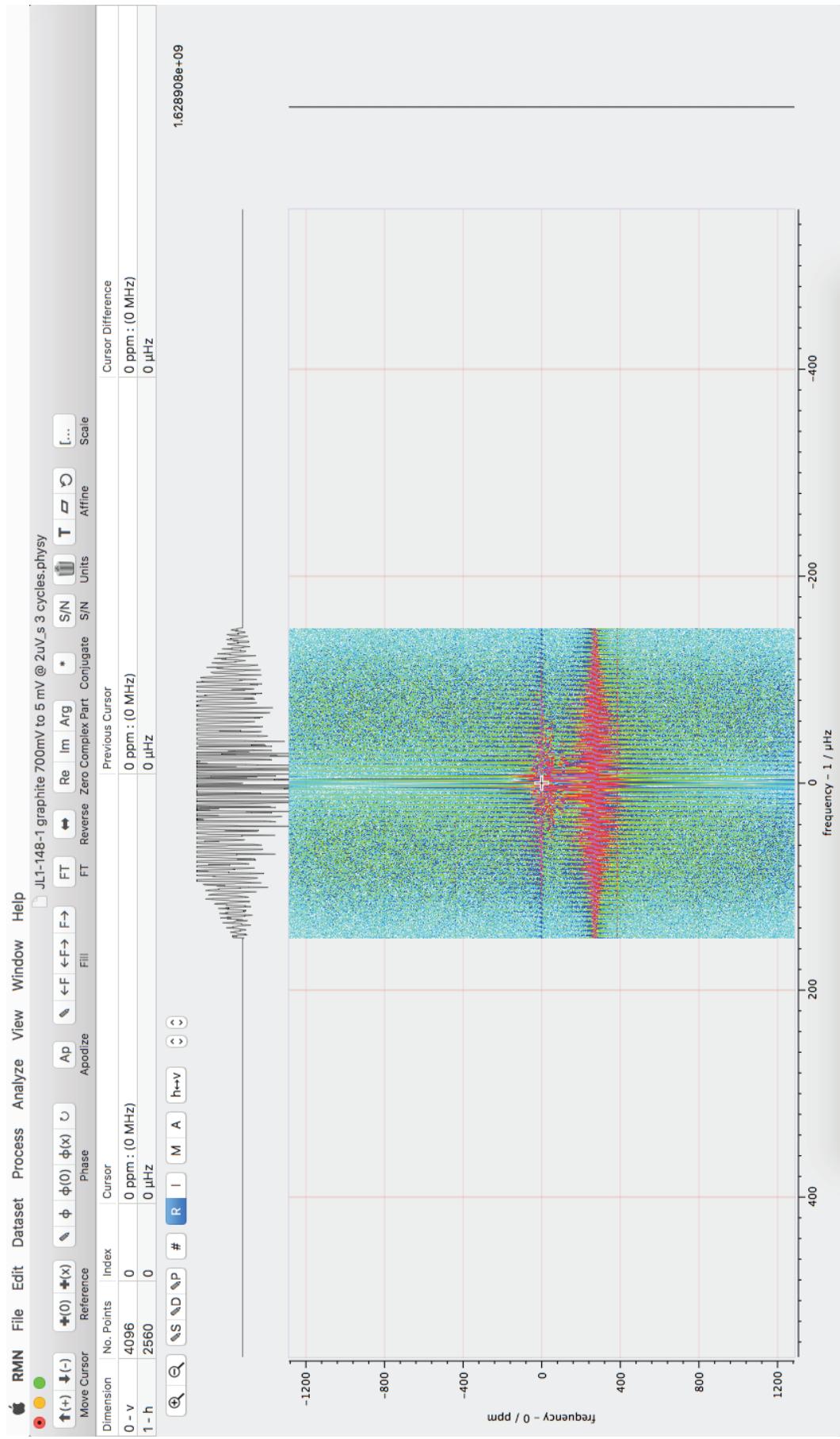
Apply Derivative Convolution: The apodization is done by clicking the Ap button (circled in red) or under the “Process” menu. This will display a dialog with a popup menu displaying available apodization functions. With the popup menu select “Derivative Convolution.” For the cutoff frequency enter a value where the spectra shows mainly noise. In this case, a cutoff frequency of $150 \mu\text{Hz}$ is used. Click the Apply button on the right.



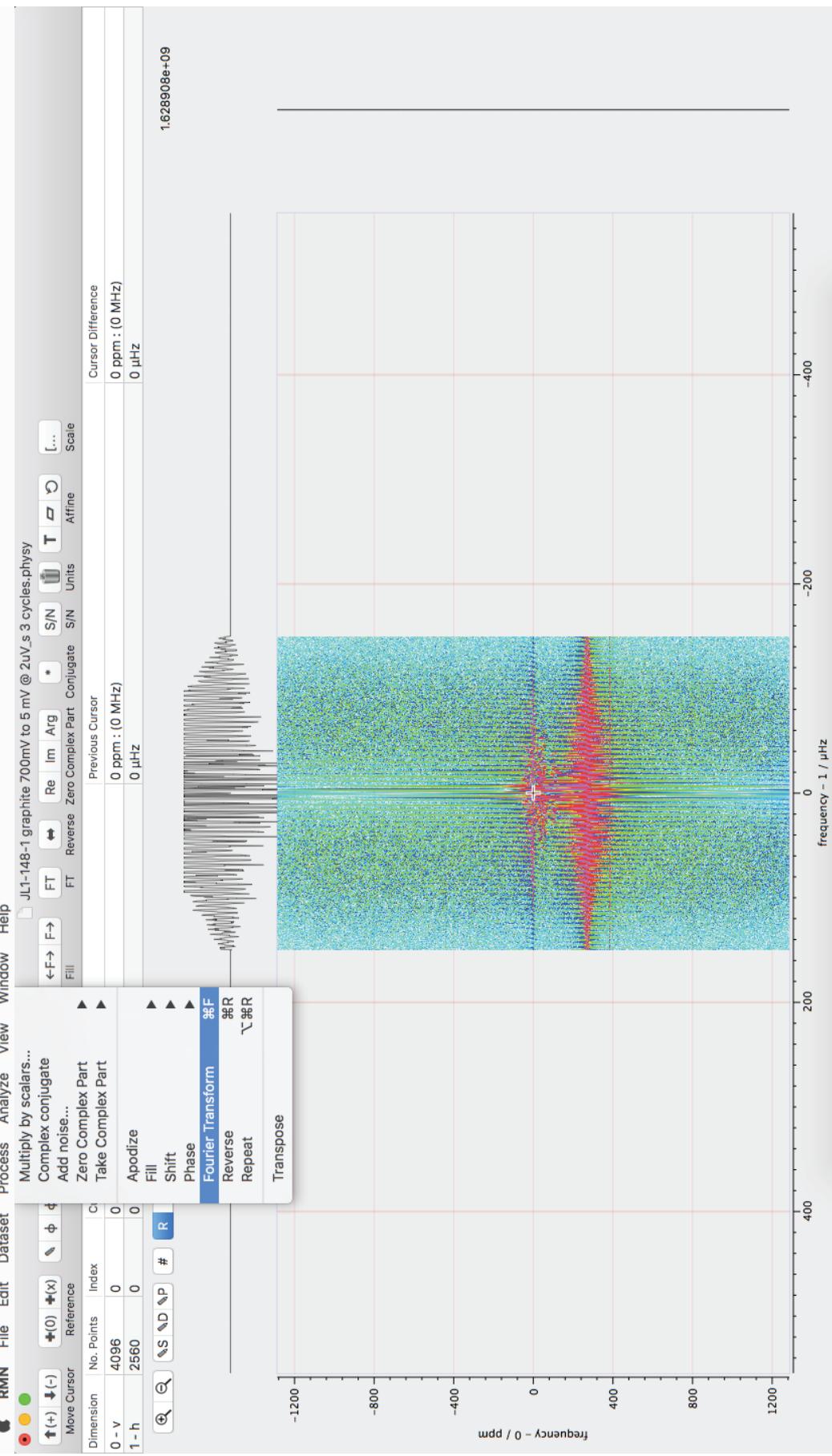
Apply Hamming Filter: To avoid artifacts from using a sharp cutoff frequency an additional hamming filter is applied using the same cutoff frequency. Select the “Hamming” apodization function is selected with the popup menu. Enter a cutoff frequency of 150 μ Hz, and click the Apply button.



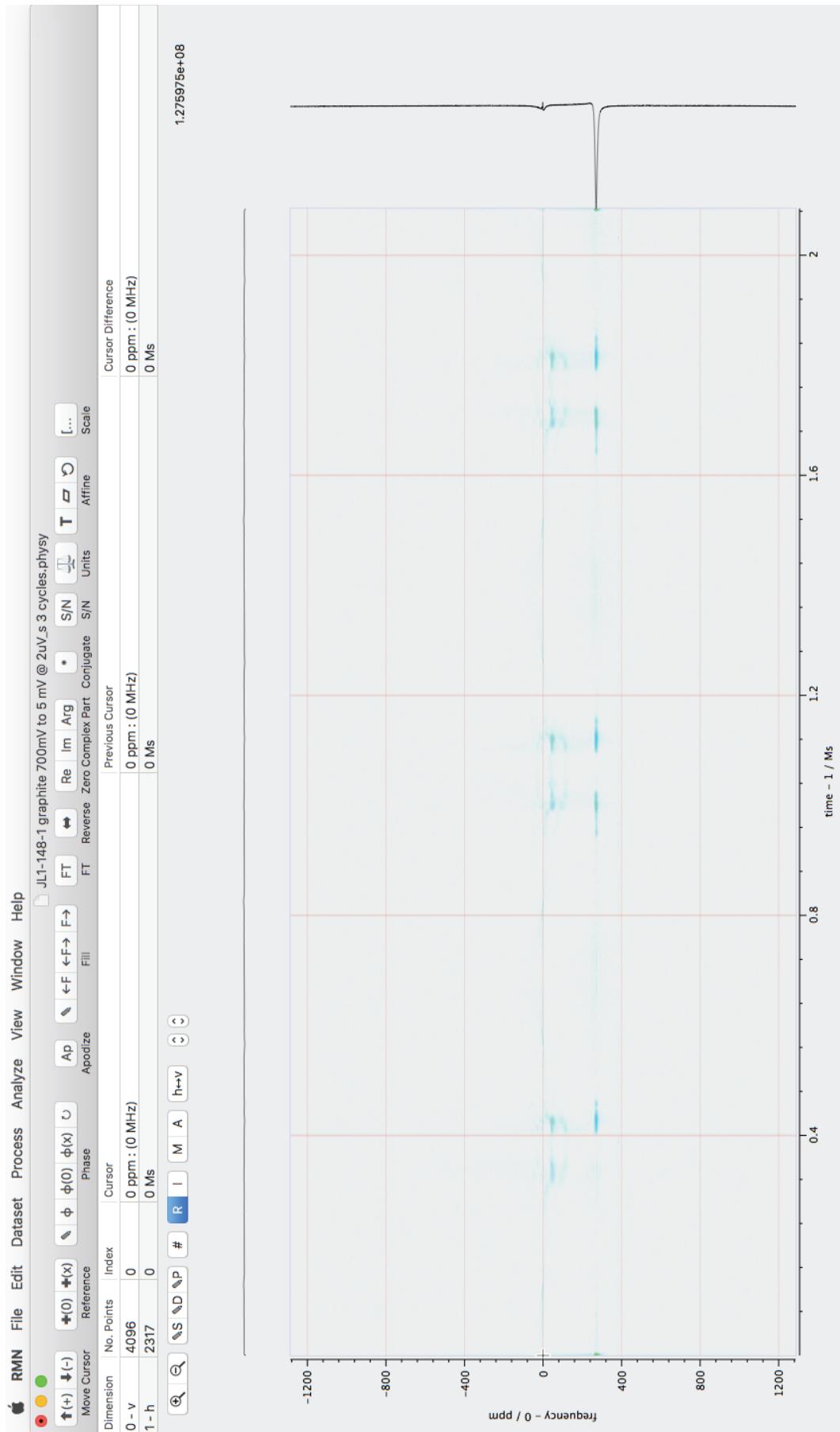
Signal after the hamming function has been applied.



Inverse Fourier Transform: An inverse Fourier transform is then applied to bring the signal back to the operand time domain along the horizontal dimension.



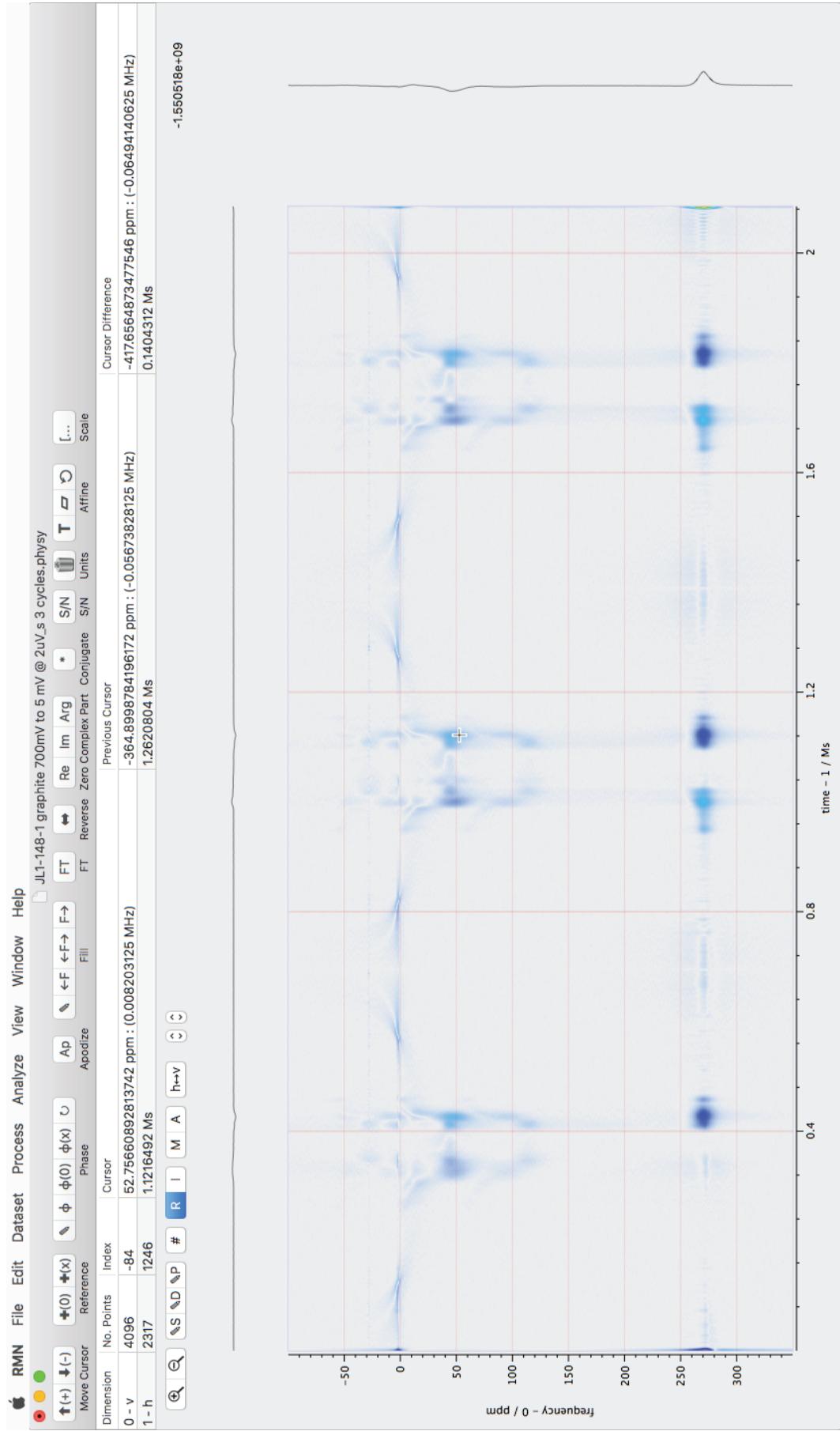
Signal after the inverse Fourier transform. The derivative along the horizontal dimension is complete and the dOp signal is obtained. In the next few steps we adjust the presentation of the signal to match the figure in the main text.



The vertical (NMR frequency) axis is zoomed to show a spectrum within the limits of -100 to 350 ppm. These parameters can be changed by clicking the P circled in red and entering the lower and upper limits for the vertical dimension.



The signal after the vertical zoom.



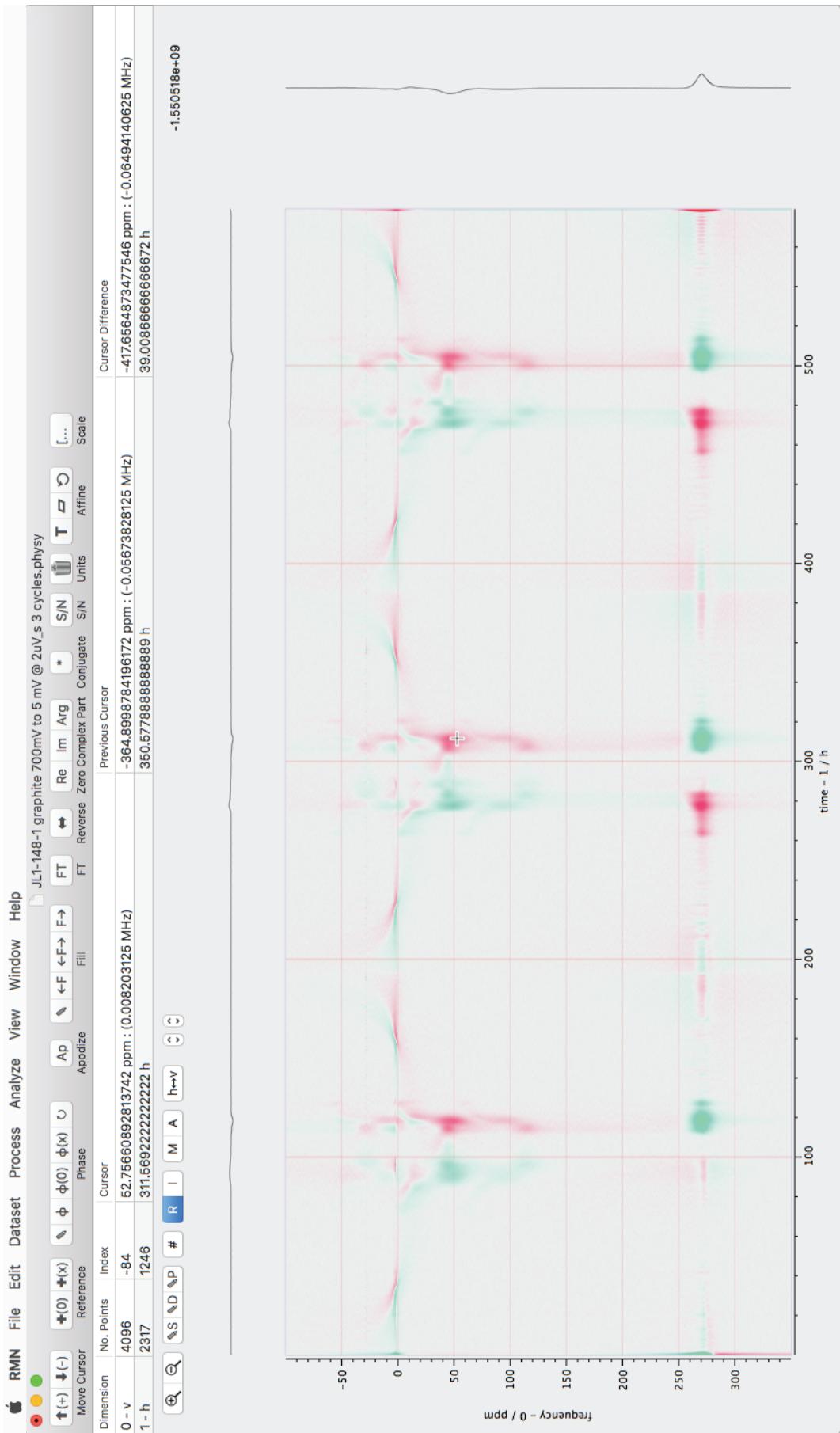
Similarly, the units of the horizontal (operando time) axis are adjusted to show the time in hours.



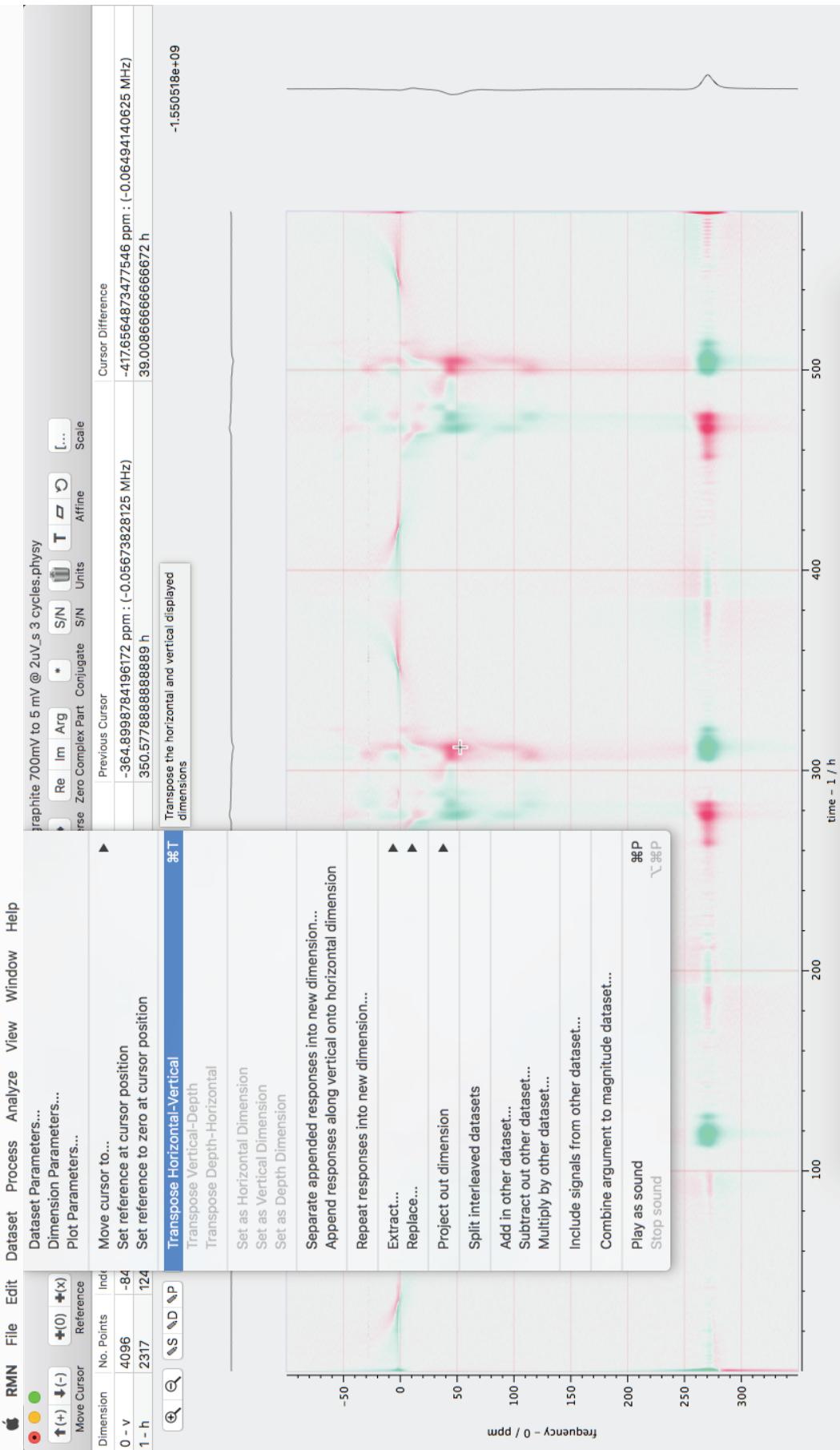
The properties of the plot are then changed to obtain a bicolor spectrum. We choose to represent positive peaks in green to represent formation of lithium species and negative going peaks in red to represent removal of lithium species.



The image below shows a bicolor dOp spectrum. Green peaks represent formation of lithium species and red peaks represent the removal of lithium species.



Next we transpose the signal to placing the NMR frequencies along the horizontal dimension and the operando time along the vertical dimension.



The signal response is then zoomed in to enhance the visibility of the different transitions. A bipolar plot is made by setting the lower and higher signal intensity limits to the same magnitude, with lower limit being -5×10^9 and the higher limit 5×10^9 .



Below is the dOp signal for all three cycles. The second cycle is shown in Fig. 5 and 7 of the main text.

