

REFDCON

- Reference Deconvolution
User Manual
Version 001



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This manual was written by

Frank Decker and Manuela Müller

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1 Introduction

This manual is a reference and training tutorial for using Reference Deconvolution (REFDCON), a simple and effective method to remove distortions caused by field inhomogeneities or modulations in nuclear magnetic resonance spectroscopy.

1.1 Policy Statement

It is the policy of Bruker to improve products as new techniques and components become available. Bruker reserves the right to change specifications at any time.

Every effort has been made to avoid errors in text and figure presentation in this publication. In order to produce useful and appropriate documentation, we welcome your comments on this publication. Support engineers are advised to regularly check with Bruker for updated information.

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1.2 Font and Format Conventions

Type of Information	Font	Examples
Shell Command, Commands, “All what you can enter”	Arial bold	Type or enter fromjdx zg
Button, Tab, Pane and Menu Names “All what you can click”	Arial bold, initial letters capitalized	Use the Export To File button. Click OK . Click Processing...
Windows, Dialog Windows, Pop-up Windows Names	Arial, initial letters capitalized	The Stacked Plot Edit dialog will be displayed.
Path, File, Dataset and Experiment Names Data Path Variables Table Column Names Field Names (within Dialog Windows)	Arial Italics	<i>\$tshome/exp/stan/nmr/ lists expno, procno,</i>
Parameters	Arial in Capital Letters	VCLIST
Program Code Pulse and AU Program Names Macros Functions Arguments Variables	Courier	go=2 au_zgte edmac CalcExpTime() XAU(prog, arg) disk2, user2
AU Macro	Courier in Capital Letters	REX PNO

Table 1.1: Font and Format Conventions

2 Reference Deconvolution

2.1 Algorithm Basics

The quality of spectra is one of the most critical properties of a modern NMR spectrometer. A lot of effort goes into the spectrometer design to ensure that the spectra are free from artifacts or line broadenings. This ensures that the spectra reveal all information they can deliver in principle and that no false information is added which could otherwise result in wrong interpretations of the data.

The most common sources of spectrum imperfections are field inhomogeneities or external field disturbances, mechanical vibrations, temperature variations within the sample and electronic artifacts as phase noise or receiver saturation. Some of these imperfections affect all resonance lines in a spectrum in the same way. The most important ones of this type are field inhomogeneities or modulations. Typically, these have the greatest effect on the spectrum quality. Because they affect all signals in the same way, there is the possibility to remove them from the spectrum if at least one resonance line of the spectrum is very well known and can therefore be simulated mathematically [1,2]. It serves as a reference line. This allows to calculate the distortions by comparing the measured reference line to the ideal simulated one. In a next step, the distortions can be removed from the complete spectrum. This algorithm is called Reference Deconvolution.

The effect of other disturbances may differ for the individual resonance lines of a spectrum. Temperature inhomogeneities belong to this group. They cannot be removed by a Reference Deconvolution.

Reference Model

An ideal high resolution NMR spectrum of a liquid sample consists of one or more Lorentzian shaped resonance lines. The Lorentzian shape results from the fact that the Free Induction Decay (FID) is governed by the loss of intensity due to spin-lattice and spin-spin relaxation. Both lead to an exponential decay of the signal. The Fourier Transform of an exponential decay is a Lorentzian line. Any additional effect such as a field inhomogeneity leads to a broadening of the resonance lines and hence to a faster decay of the FID. This can be described in the time domain as a multiplication of the ideal FID with another decay function which represents the additional loss of phase coherency due to the field inhomogeneity. The effect is analogous to the application of an apodization function to an FID. E.g., a multiplication of the FID with an exponential decaying function in order to improve S/N ratio by suppressing the noise at the tail of the FID **em** leads to a broadening of the resonance lines by the exponential factor **LB**. In the frequency domain, this operation is the convolution of two Lorentzian lines, the resonance line and the Fourier Transform of the exponential decaying apodization function.

Reference Deconvolution works the other way round. It tries to identify the broadening caused by the instrument's imperfections and removes it from the spectrum by multiplying the FID with the inverse of the broadening function. The first step is the determination of the broadening function. As already said, the imperfections we are talking about affect all resonance lines in the same way. Therefore, a well-known resonance line can serve as a reference to derive the information about the additional broadening. One can also choose the protonated solvent line or an additional chemical shift reference compound. The resonance line must be a singlet. This is due to the fact that multiplets generate modulations in the FID. These result in a periodicity of low values of the amplitude of the FID making the mathematical algorithm unstable as the inverse of the model must be calculated.

References

1. Morris GA. *Compensation of instrumental imperfections by deconvolution using an internal reference signal*. J. Magnetic Resonance 1988, 80: 547-552.
2. Metz KR, Lam MM, Webb AG. *Reference Deconvolution: A simple and effective Method for Resolution Enhancement in Nuclear Magnetic Resonance Spectroscopy*. Concepts in Magnetic Resonance 2000, 12: 21-42.

2.2 Working with REFDCON

2.2.1 How to Start REFDCON

To start the reference deconvolution module call the menu item **Process -> Advanced -> Reference Deconvolution** or run the command `.refdcon`.

2.2.2 Interactive Main User Interface

How to define a reference Peak

When starting the interactive reference deconvolution module for the first time, it is necessary to define the region [RDF1, RDF2] including the peak of interest for the reference model calculation. The interval can be defined with a left mouse click and dragging till the end of the desired region. As a consequence a default reference model will be calculated and shown on the screen (see following figure). The default model is a Lorentzian distribution; it is located at the position of the most intense peak contained in the ROI and shares the same intensity and half width of the peak to be modelled.

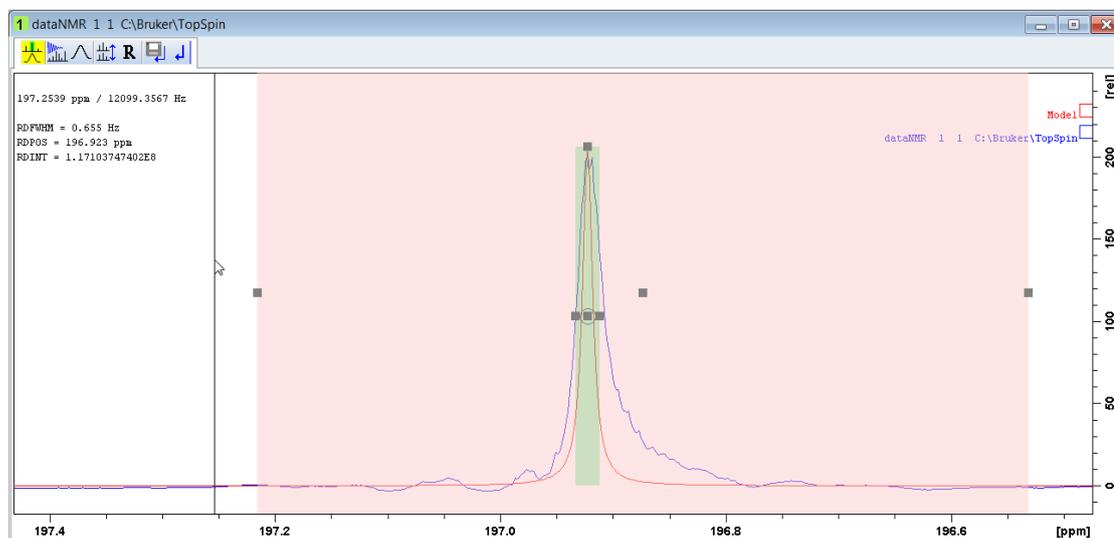


Figure 2.1: Reference deconvolution module example

The user needs to define a region which includes a single and well separated resonance line. The region of interest should be as large as possible because of the long tails of the imaginary part of the reference line. It should also include all artifacts which are attributed to the resonance line under consideration. But it shouldn't include any other resonance lines. Also, the satellites of the resonance line of interest must be excluded in the current version of the module.

The menu bar

-  - Start reference deconvolution of the spectra with the generated reference model.
-  - Recalculate the default reference model in the current region (reset to default).
-  - Change to stacked layout for a better comparison of the results.
- **R** - Reset individual scaling.
-  - Save deconvolved data.
-  - Exit the module without saving the deconvolved spectra (the current parameter will be saved automatically).

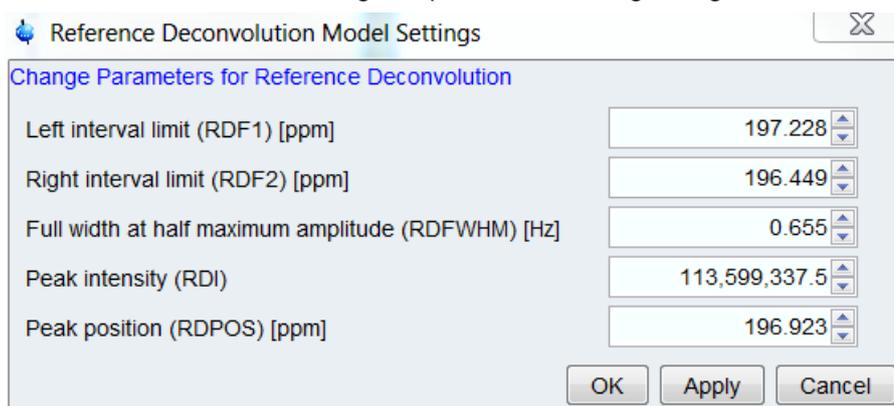
How to change the model

The calculated reference model and the selected region are marked with green and rose-coloured boxes. The drag-handles of the box allow to modify the parameters of both the region of interest and the reference model in real time.

The left and right drag-handles of the model (green box) changes the full width at half maximum amplitude parameter RDFWHM and the handle above adapt the intensity RDINT. The handle in the center changes the peak position RDPOS. The real maximum of the model is aligned with the upper bounding box.

The handles of the rose-coloured drag-boxes allow to adjust the parameters of the region of interest. Dragging either the left or right handle will modify the boundaries RDF1 or RDF2 of the region of interest individually, while relocating the box using the centre handle will apply the identical shift to both boundaries. The reference model will not be modified as long as the selected peak is in the region. By default the maximum peak in the interval is the selected peak.

Another possibility to change the model parameters is by using the parameter dialog. A double click in the selected region opens the following dialog:



Reference Deconvolution Model Settings

Change Parameters for Reference Deconvolution

Left interval limit (RDF1) [ppm]	197.228
Right interval limit (RDF2) [ppm]	196.449
Full width at half maximum amplitude (RDFWHM) [Hz]	0.655
Peak intensity (RDI)	113,599,337.5
Peak position (RDPOS) [ppm]	196.923

OK Apply Cancel

Figure 2.2: REFDCON dialog

How to deconvolve a spectrum

To deconvolve the reference line with the model, press the button  in the menu bar. The region of interest of the spectrum and the model are transferred to their respective FIDs by an Inverse Fourier Transform. For the measured spectrum, this operation acts as a filter function which lets only the FID of the reference line and its artifacts pass. Now, this FID is divided by the model FID (or multiplied with the inverse of it). The result is the broadening function which turns the ideal resonance line into the observed and distorted one. As a last step, the inverse of the broadening function is multiplied to the original full measured FID, thus removing the artifacts and broadenings from the complete spectrum. In the frequency domain, this is a deconvolution of the spectrum with the Fourier transform of the inverse broadening function or a deconvolution with the broadening function itself.

How to compare the result

To compare the result (deconvolved spectrum) with the original spectrum it is possible to switch a stacked layout by pressing  in the menu bar. The button works as a toggle and switched between the spectra overlaid or with separated deconvolved spectra:

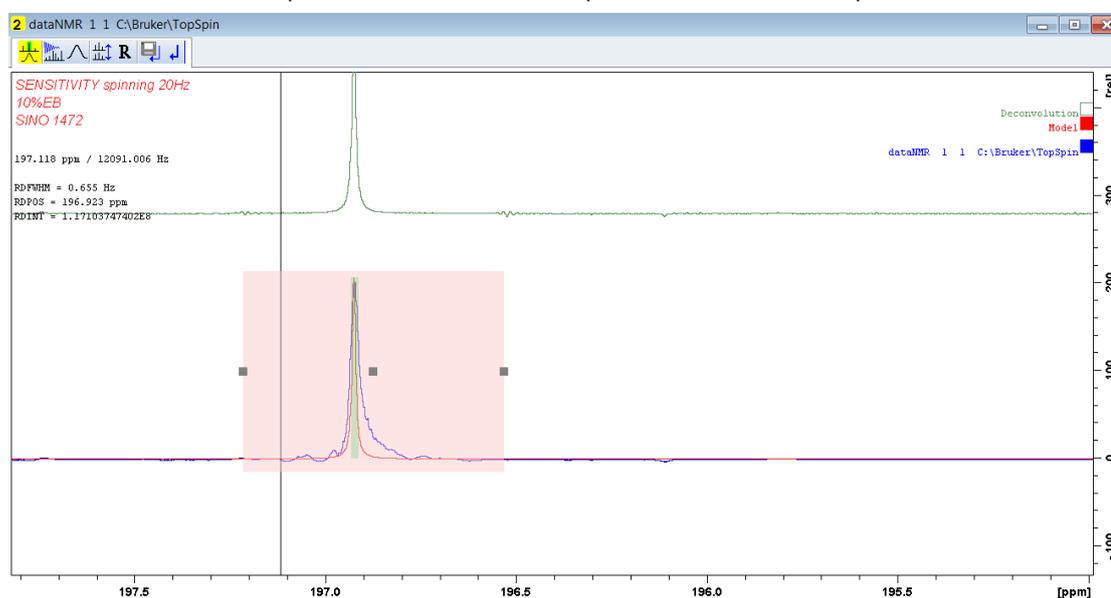


Figure 2.3: Example for a result comparison in a stacked layout

Additional to an individual zooming in the screen it is also possible to scale the spectra individual. By switching in the stacked layout the original spectra with the model is automatically selected. To change the selection to the deconvolved spectra click in the respective spectra on the display. Selection is marked on the upper right shown rectangles next to the spectra name. For an individual scaling use the mouse wheel. Pressing the button **R** will reset the scaling. The reset will also happen if the layout is switched back to the overlaid presentation.

2.2.3 REFDCON Parameters

Reference Deconvolution uses the following parameters to store the Lorentzian model settings with the defined interval:

- RDF1: Left interval limit for region of interest [ppm]
- RDF2: Right interval limit for region of interest [ppm]

- RDINT: Intensity for reference model
- RDPOS Position for reference model [ppm]
- RDFWHM: Full width at half maximum amplitude for reference model [Hz]

If the dataset's Deconvolution processing parameters are set to non-default values, both the region of interest and reference model will be restored accordingly when REFDCON is invoked. However, as long as all parameter values are set to their default value of 0.0, REFDCON will require the user to specify a valid region of interest and create a default reference model.

2.2.4 Additional Information

Zero-filling

It is advised to set the zero-filling at least to a factor of two. The resonance lines after deconvolution are sharper than the original lines resulting in longer FIDs. In addition, the representation of the resonance lines is better if there are more points per line in the spectrum.

Phase Correction

The Reference Deconvolution also removes phase distortions from a spectrum. But it is always a good starting point to apply a phase correction to the spectrum first. It is also important to perform a baseline correction to the spectrum. In the current version, it is not possible to set a baseline offset for the simulated model. Therefore, a baseline offset of the spectrum may lead to artifacts in the deconvolved spectrum.

Region of interest

Great care should be taken not to include signals into the region of interest which are not correlated to the reference line or its artifacts. Otherwise these are transferred to the complete spectrum by the deconvolution and appear as negative signals around each resonance line.

Noise

The algorithm also decreases the noise in the region of interest because noise is just another deviation of the model from the reference line. At the same time, the noise in the rest of the spectrum is slightly increased as the inverse broadening function contains the noise from the region of interest. This is not correlated to the noise in the rest of the spectrum. So, instead of lowering that noise as in the region of interest, it increases the noise outside that region.

Broadening function

A principal problem of the algorithm is the calculation of the broadening function. As this is the division of two FIDs, the result gets unreliable where the two functions are decayed to zero. This typically leads to large erratic numbers. Therefore, a so-called regularization function cuts down this part of the broadening function. The function is automatically applied. Unfortunately, this automatic setting can fail leading to strong artifacts in the spectra. This is related to the mathematics behind the algorithm. In some cases, the parameters of model, mainly the width, must be chosen carefully in order to obtain clean spectra.

Reference model intensity RDINT

In the algorithm of reference deconvolution the intensity of the reference model has no effect to the deconvolved spectra. But it is possible to change the parameter to decide having a better fit in the selected peak shape. The real maximum of the model is aligned with the upper bounding box (green box). In some situations the displayed model seemed to be smaller than the box. This is caused by digitization and is only a visually effect.

2.3 Examples

2.3.1 Using the Lineshape Sample

The lineshape sample was used to demonstrate the effect of REFDCON. The shim of the magnet was changed to broaden the resonance lines. A spectrum has been acquired under sample rotation. It shows the typical rotation sidebands together with a slightly misadjusted on-axis shim.

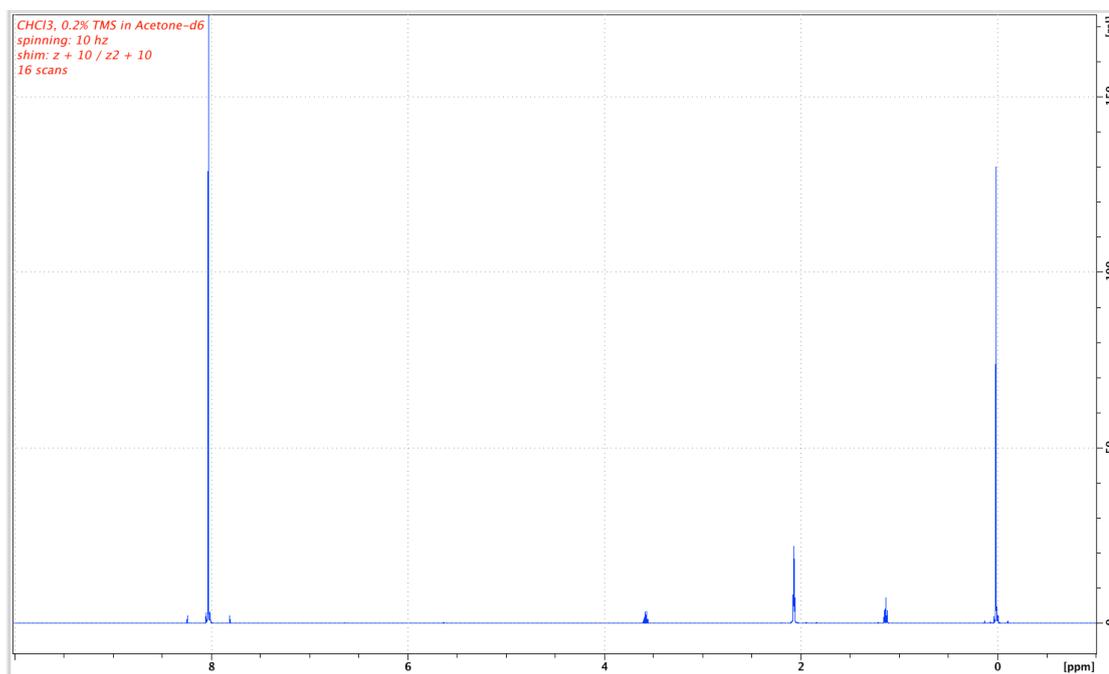


Figure 2.4: Spectrum of the lineshape sample with a bad shim under sample rotation.

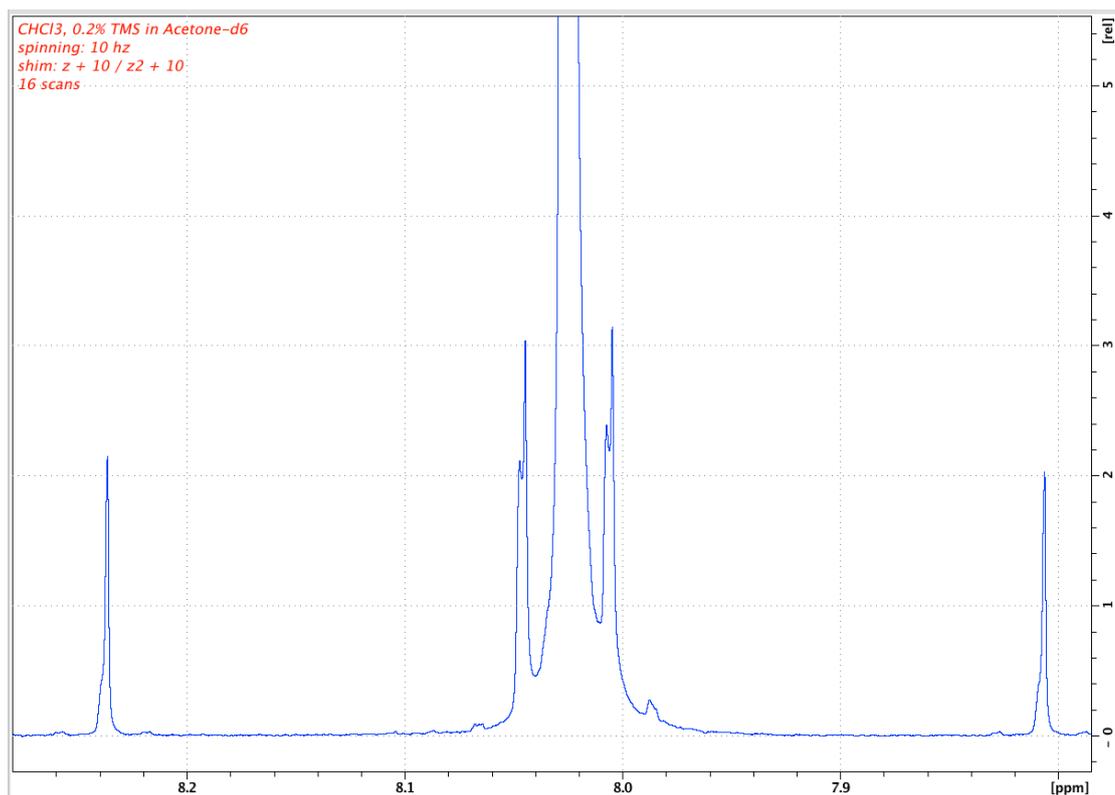


Figure 2.5: The resonance line of chloroform showing the bad shim and the rotation sidebands.

The chloroform resonance line is a singlet and is well separated from other resonance lines. The region of interest is chosen to include all shim and rotation artifacts. It excludes the ¹³C satellites as the current version of REFDCON doesn't include satellites into the model.

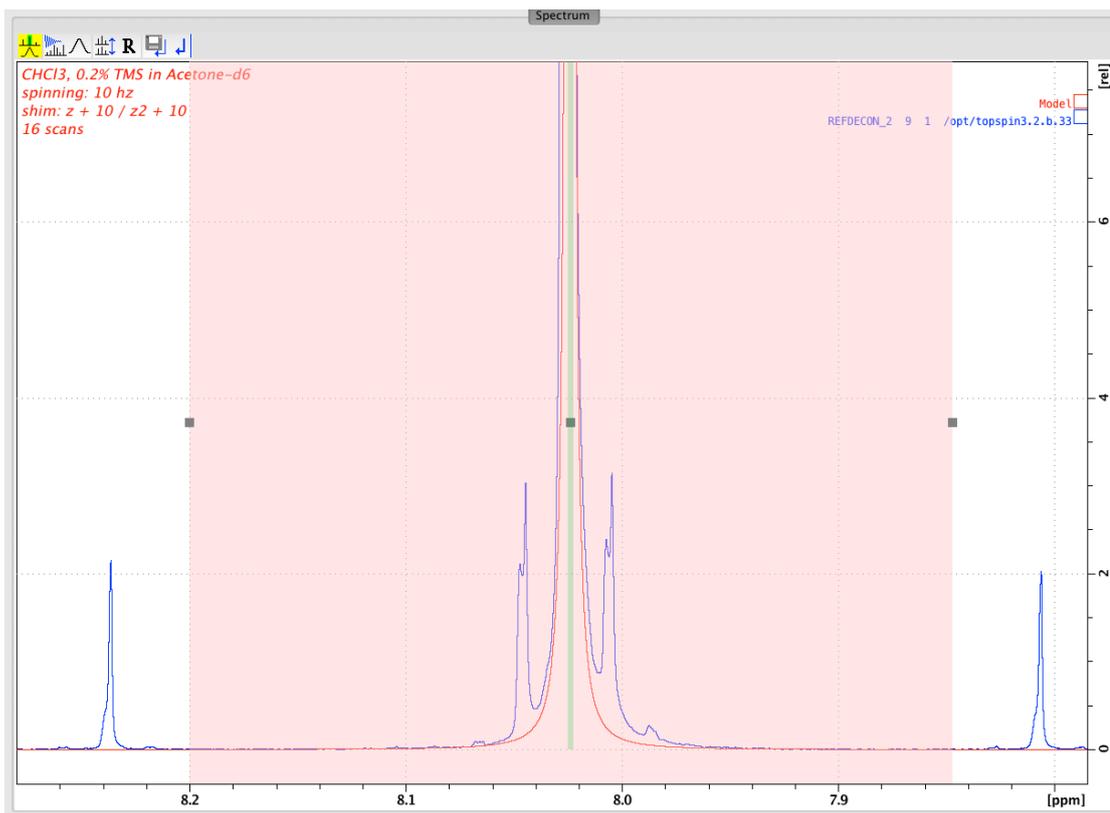


Figure 2.6: Region of interest and model (in red).

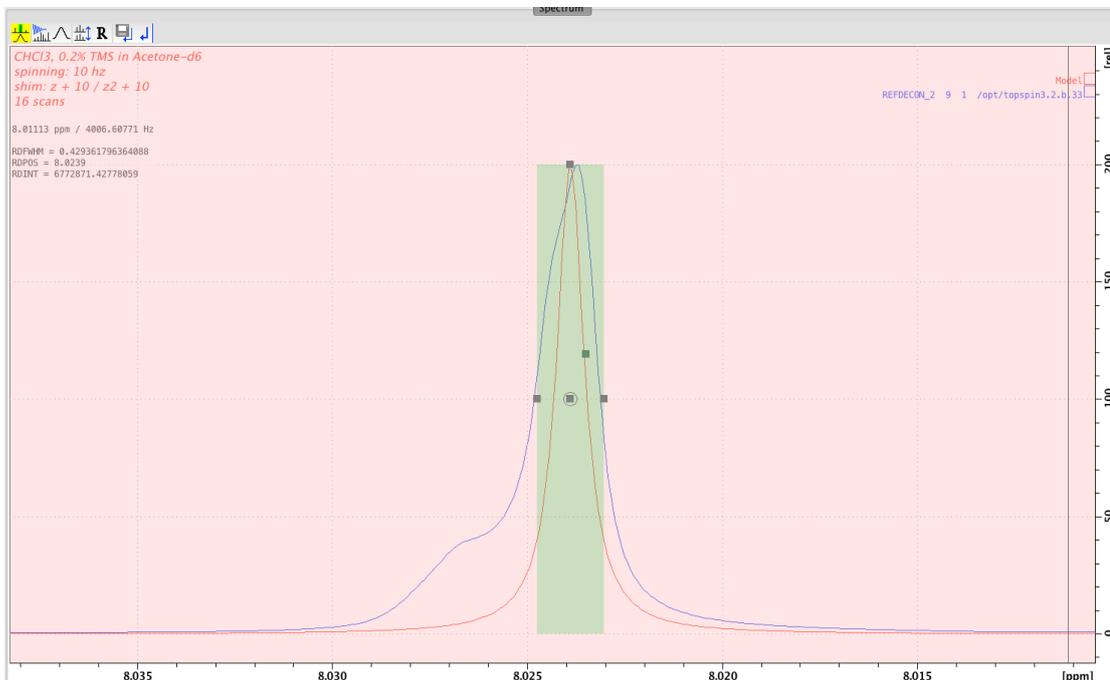


Figure 2.7: A closer look at the model.

The next figure shows the result of the Reference Deconvolution. Note that the chloroform resonance shows a perfect Lorentzian line with almost no noise. This results from the fact that this part of the spectrum was used as a reference.

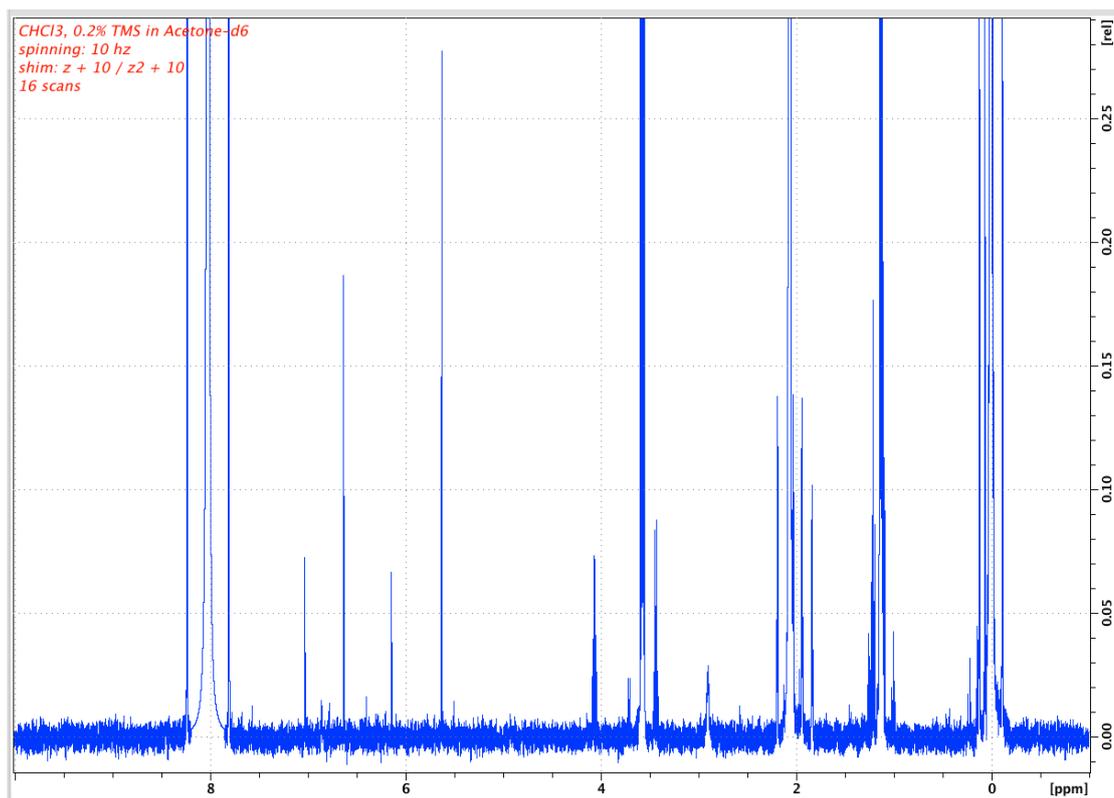


Figure 2.8: The deconvoluted spectrum.

The following figure shows a comparison of the measured TMS signal and the deconvoluted one. The rotation artifacts and the shim problems have been successfully removed from the spectrum.

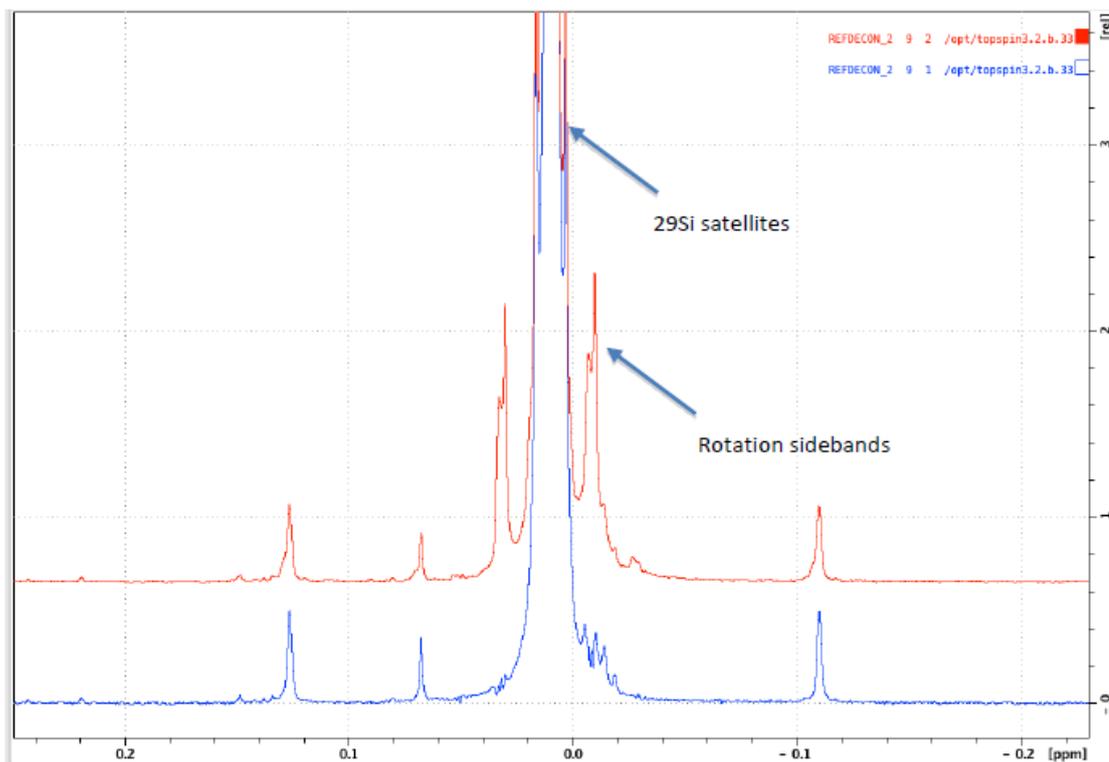


Figure 2.9: The result of the Reference Deconvolution on the TMS signal as an example. The bad shim and the rotation artifacts are almost completely suppressed.

2.3.2 Extreme Examples of Guaiol Spectra

Field modulation

A spectrum of Guaiol was acquired while an external field modulation of 50Hz was intentionally applied in order to test REFDCON.

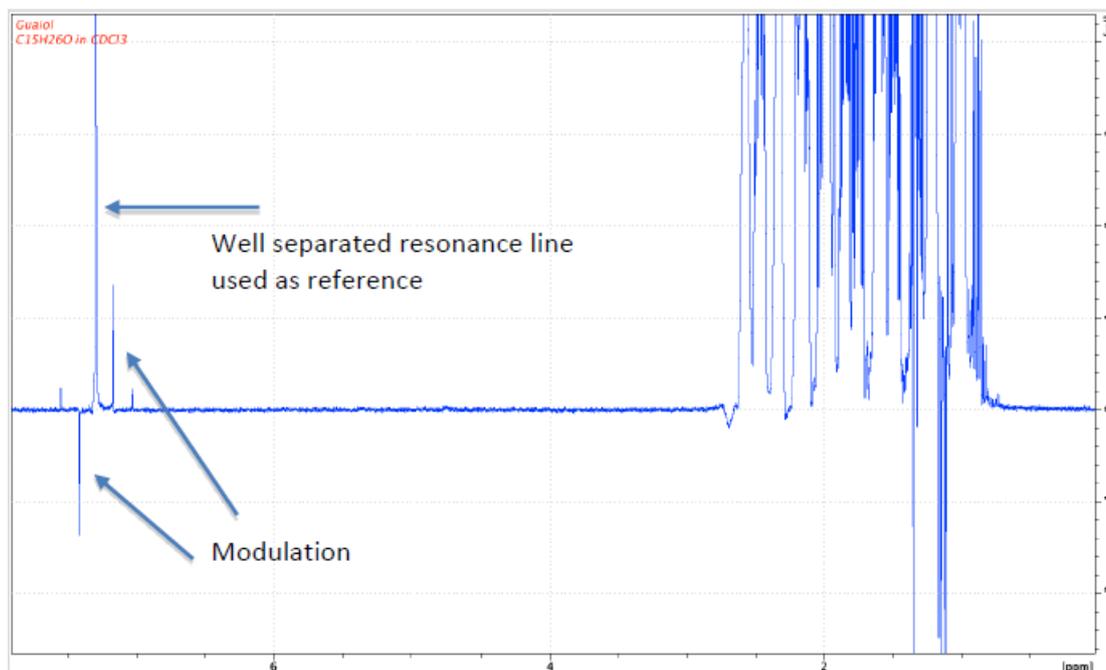


Figure 2.10: Spectrum of Guaiol with strong 50Hz modulation artifacts.

The well separated resonance line at about 7ppm is used as a reference for the algorithm. The following figure shows the region of interest which has been chosen. It includes the modulation artifacts but excludes the ^{13}C satellites.



Figure 2.11: Region of interest used to fit the Lorentzian model.

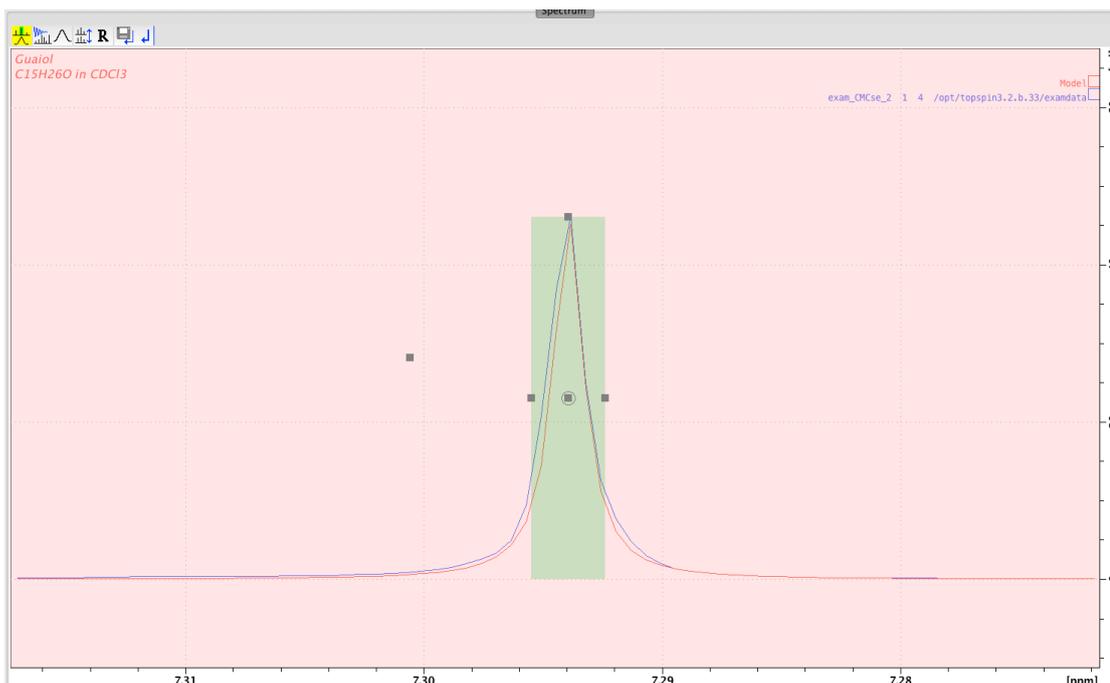


Figure 2.12: A closer look at the reference line and the model.

The result after running the REFDCON algorithm is shown in the high field region of the spectrum. Despite a slightly higher noise, the deconvolved spectrum is identical to a spectrum which was acquired without the external disturbance. The distorted one shows additional signals which obscure some of the real signals.

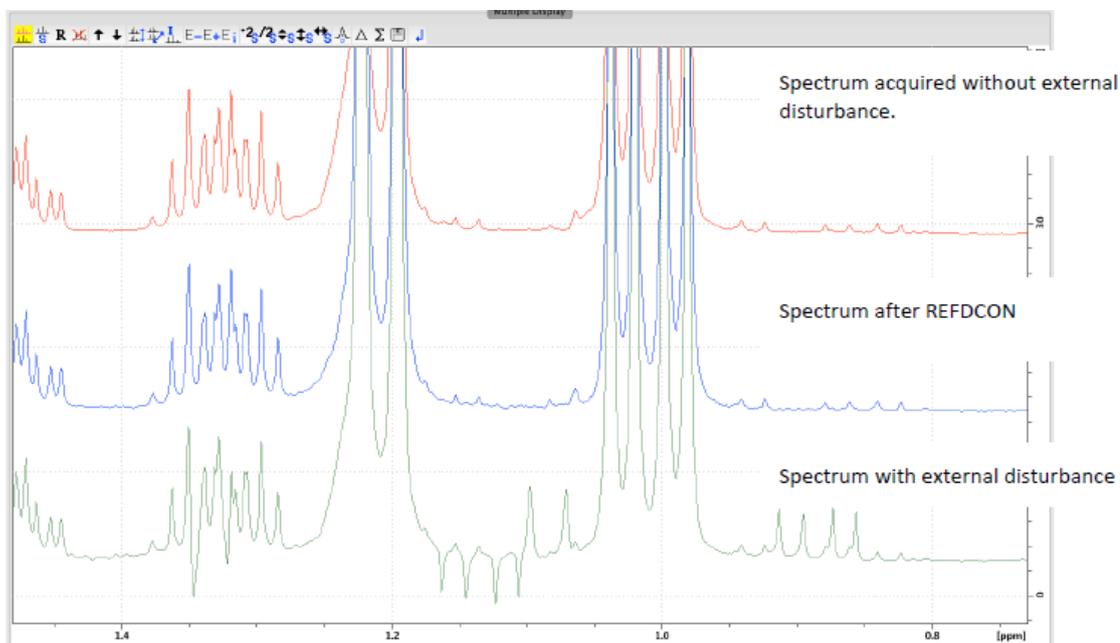


Figure 2.13: A comparison of the undistorted spectrum with the deconvolved and the distorted one.

Field drift

A spectrum of Guaiol was acquired while an external field drift was intentionally applied in order to test REFDCON.

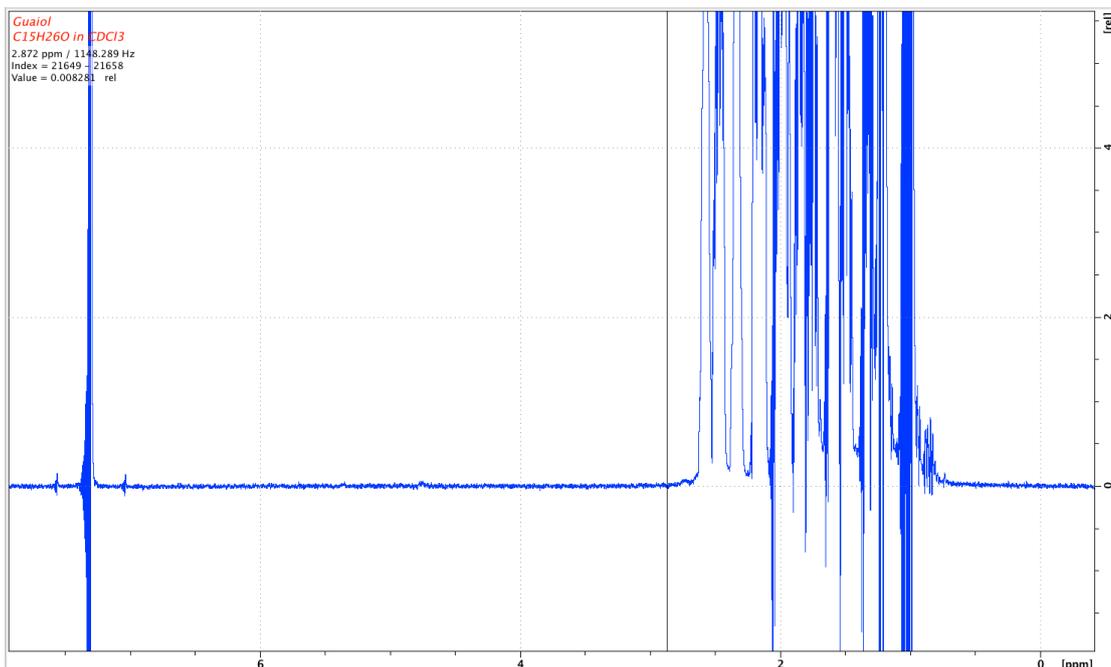


Figure 2.14: Spectrum of Guaiol acquired while applying a field drift Intentionally to test REFDCON.

The same region of interest was chosen.

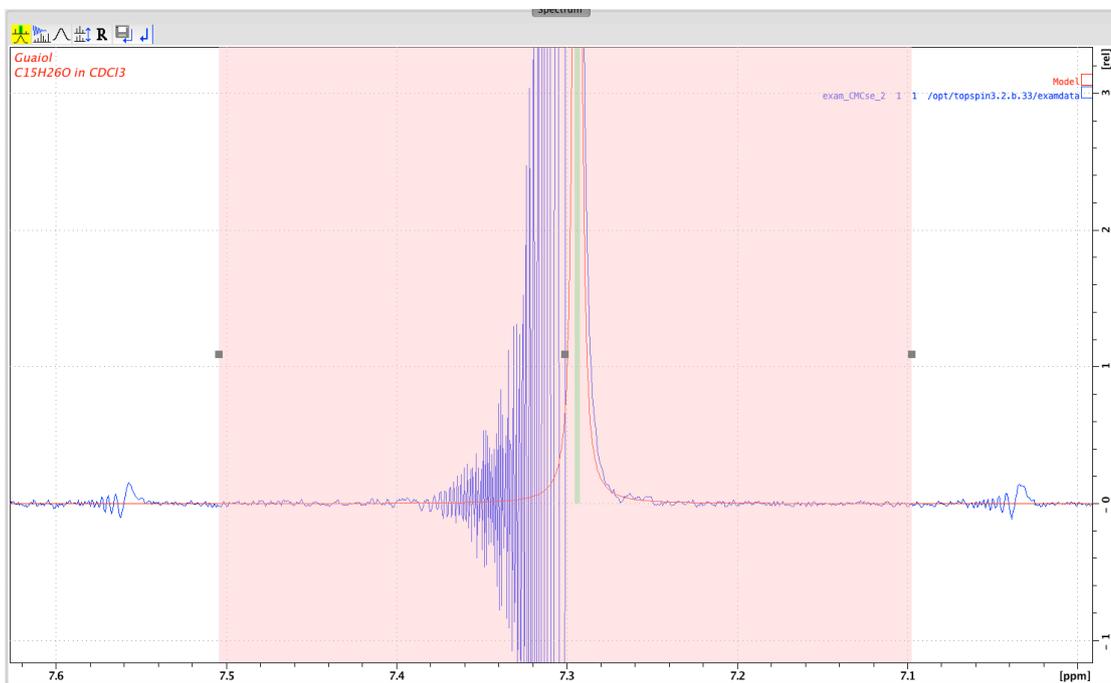


Figure 2.15: Region of interest.

Reference Deconvolution

Instead of letting REFCDON calculate a new model, the model from the example no. 1 was used. This was done because the resonance line in example no. 1 was sharp and only showed the distortion from the modulation. Therefore, the model is close to the ideal resonance line. In the following figure, the extreme effect of the strong field shift on the resonance line can be seen. It is obvious that it would be hard to manually select a good model under these circumstances. So, just using the model we found before is a good approach.

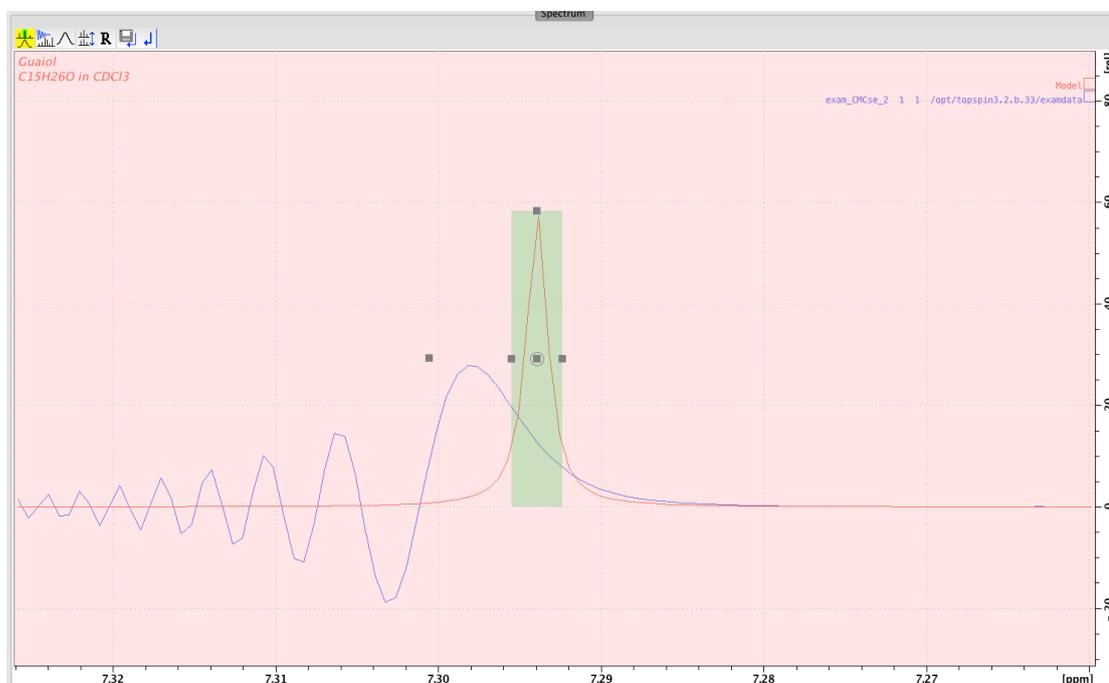


Figure 2.16: The reference line and the model. The parameters for the model have been extracted from the spectrum in example 1.

The following figure shows a comparison of the distorted spectrum, the undistorted and the calculated one. Only the high field part of the spectrum is shown.

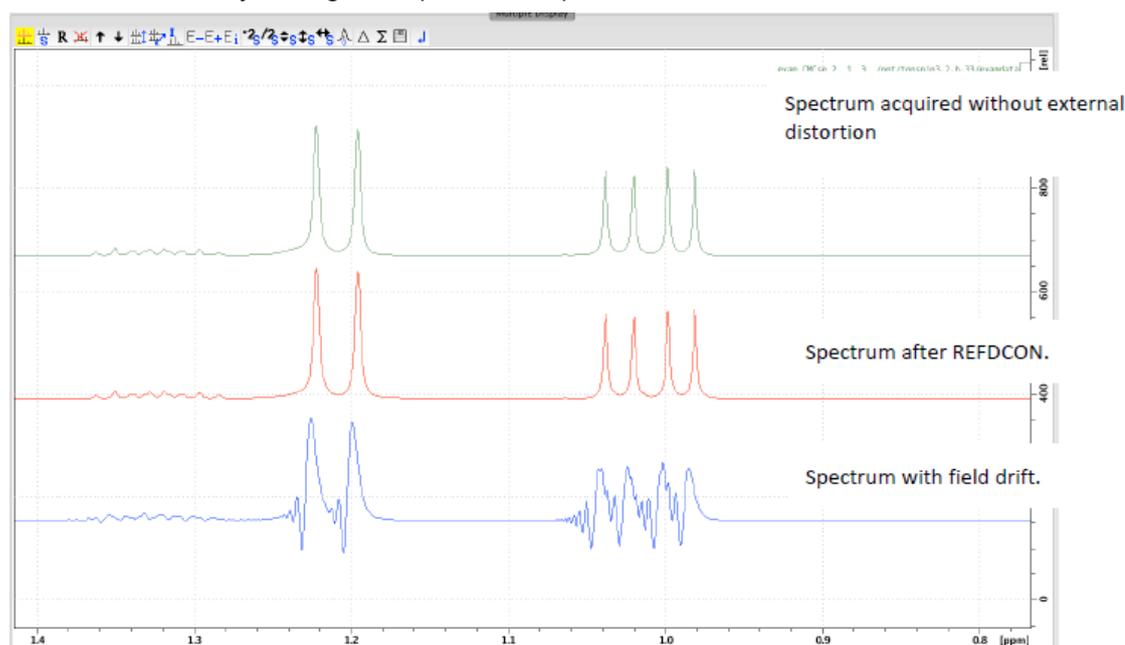


Figure 2.17: Comparison of the high field part of the distorted, undistorted and calculated spectra.

3 Contact

Manufacturer

Bruker BioSpin GmbH
Silberstreifen 4
D-76287 Rheinstetten
Germany
<http://www.bruker.com>

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