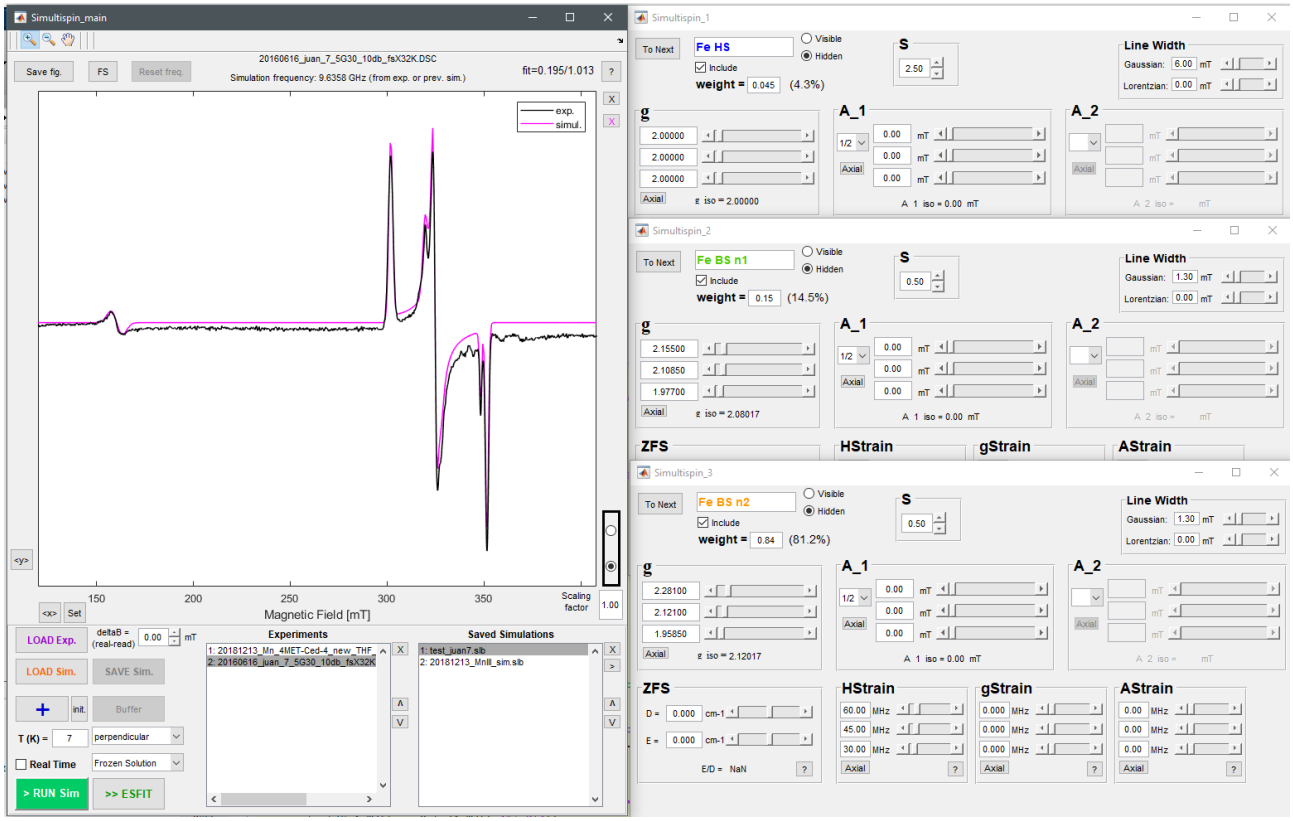
SIMULTISPIN

A user-friendly interface of Easyspin on Matlab for complex cw-EPR spectra simulation

User Guide



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I. Presentation

SIMULTISPIN is a Graphic User Interface (GUI) developed in Matlab. It offers an user-friendly tool for EPR (Electronic Parmagnetic Resonance) simulation and fitting based on the licence-free Easyspin toolbox (Stoll S., J. Magn. Res.,178, 42-45, 2006).

Without coding nor high Easyspin knowledges, SIMULTISPIN helps EPR users to visualize, simulate, fit and compare EPR spectra.

The SIMULTISPIN code is a fork deeply inspired by Simlabel GUI (Etienne E., Magn. Reson. Chem. 2017, 55, 714–719). Whereas Simlabel is dedicated to slow motion system (Site Directed Spin Labeling) and only with electronic spin S of ½, SIMULTISPIN is especially dedicated to frozen solution with the ability to choose the value of S, still in continuous wave EPR.

The following improvements have came to complete SIMULTISPIN to work for a wide type of spectra :

- choice of the experimental temperature,
- choice between perpendicular (classical) or parallel mode (for entire electronic spin like S=2 Mn^{III})
- Zero Field Splitting with D and E parameters for S> ½ systems,
- Strain effects.

It means that SIMULTISPIN will be particularly appropriate to study and simulate metallic complexes or radicals at low temperature, whatever the spin S value. For example: Cu^{II}, low spin or high spin Mn^{II} or Co^{II}, dimer or polynuclear complexes, Fe, etc.

A secondary mode for fast motion is also available.

Some limitations still exist. For example, a maximum of two nuclear spin coupling can be added.

With SIMULTISPIN, users will be able to load experimental spectra then simulate them with different ratios of components if necessary.
The frequency could be manually set up or be automatically picked up from experimental parameters. Simulations can be saved, compared and exported.
Finally an automatic fitting mode is also available from Easyspin and directly integrated in SIMULTISPIN.

II. Installation and launch

To use SIMULTISPIN, it needs first to install Easyspin toolbox and set its path in Matlab. It can be downloaded online at http://www.easyspin.org.

SIMULTISPIN is provided in one zip file. All its content have to be unzip in a folder of your choice.
In Matlab, the path of this folder has to be set: Home menu -> « set path » -> « Add folder ». Select the specified folder and click save to validate, finally close.

Before starting SIMULTISPIN, it is advised to select the local folder corresponding to your workflow folder where your spectra are saved.
Then in the command window of Matlab, type >> simultispin, enter, and the main window interface will pop up ready to use (see fig 1).

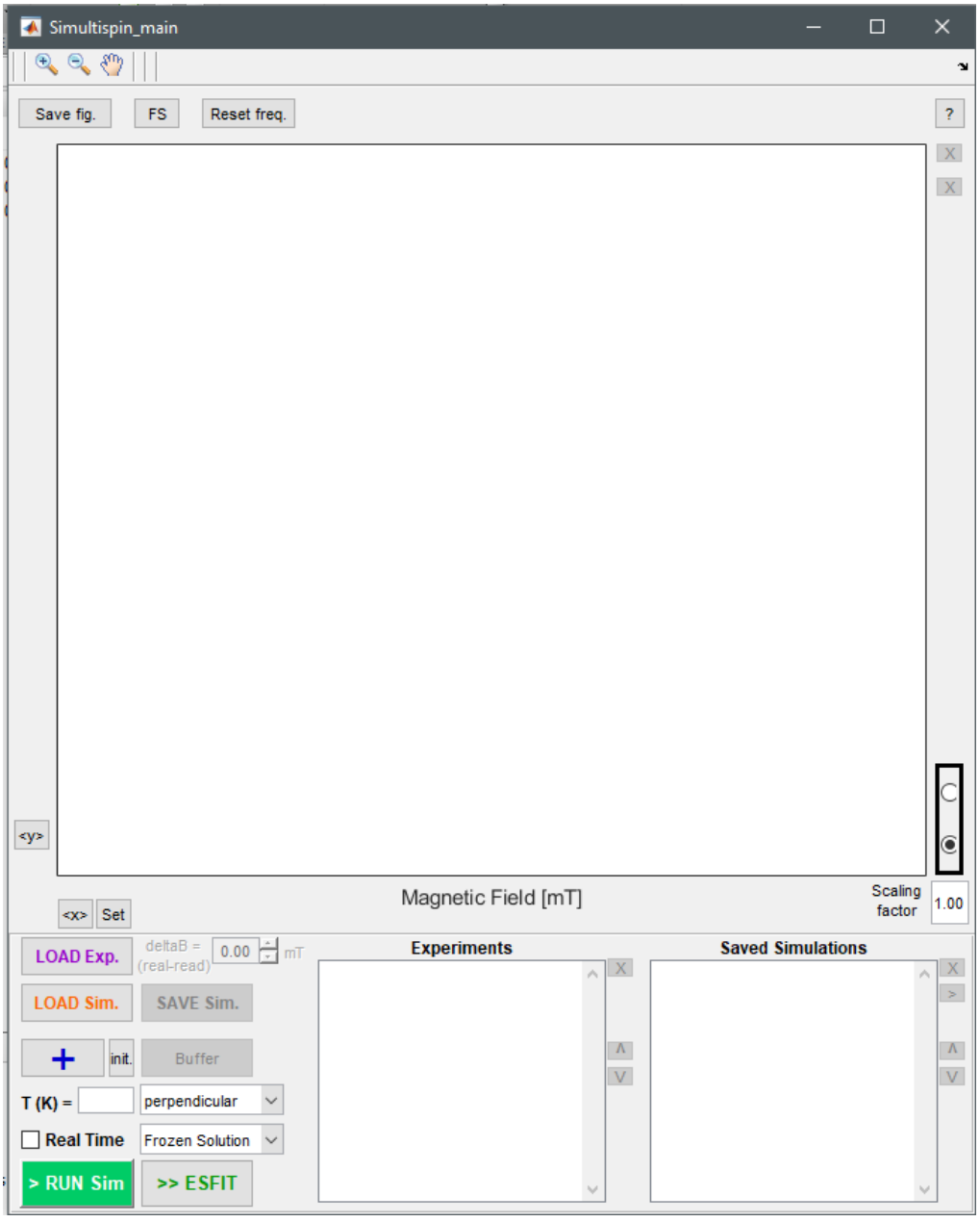


Figure 1: SIMULTISPIN starting window

III. Overview of the main windows

1. Upper Graph section

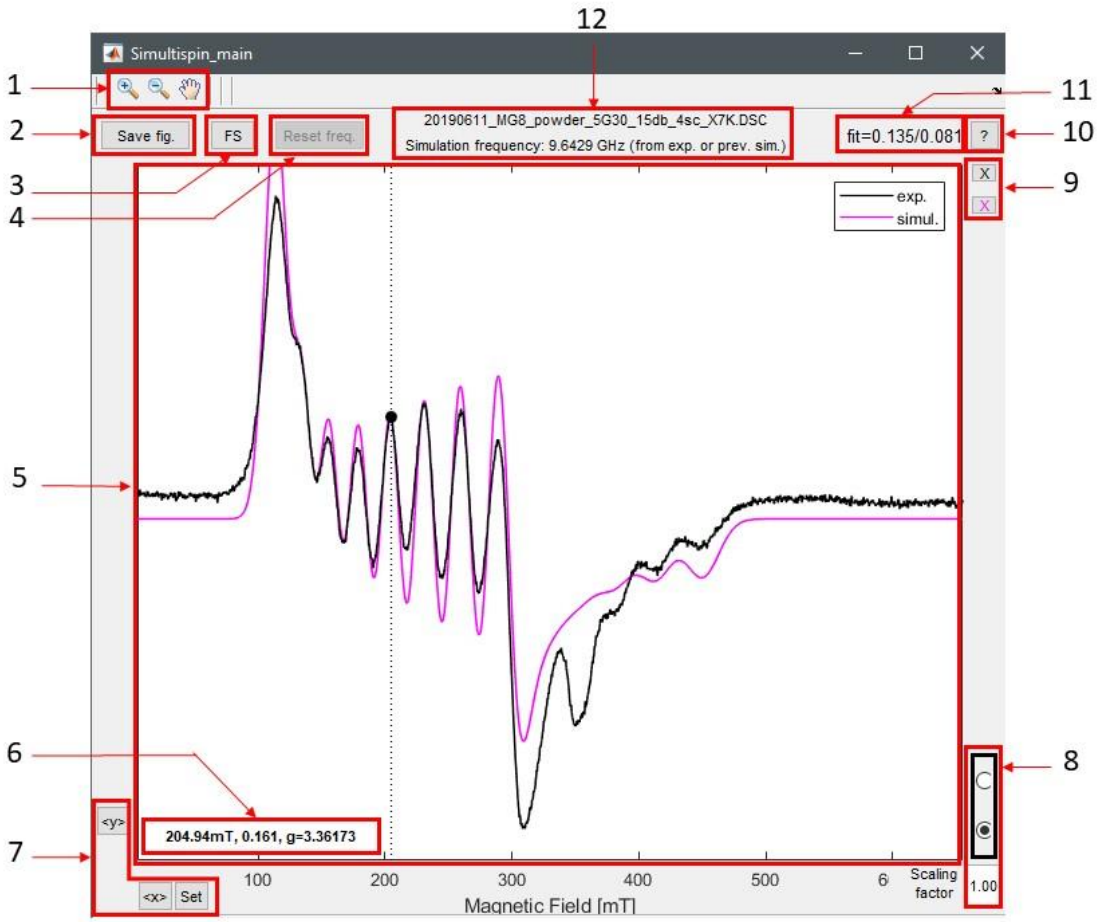


Figure 2: graphic section of the main window

1- Zoom / Unzoom / manual move of the figure.
2- Export the current figure (image file + simulation parameters in .par file).
3- Full scale option optimized for (first click) experimental or (2nd click) simulation spectrum.
4- Reset the current frequency.
5- Main graph window to visualize both experimental and simulated spectra.
6- Click somewhere on a spectrum line to read here the g value corresponding to the pointed magnetic field value. A vertical dot line appears to visualize on the graph.
7- Scale options. Click on the « FS » button to reset the view.
8- Normalization options by integrated intensity or amplitude. Scaling factor normalized to amplitude in order to adjust the intensity of the simulation.
9- Remove experimental spectrum (black) or simulation (pink) from the current figure.
10- Help button to open this pdf document and also the MHz / mT scale converter.
11- Fit indicator.
12- Name of the displayed experimental spectrum and value of the frequency.

2. Lower Menu and lists section

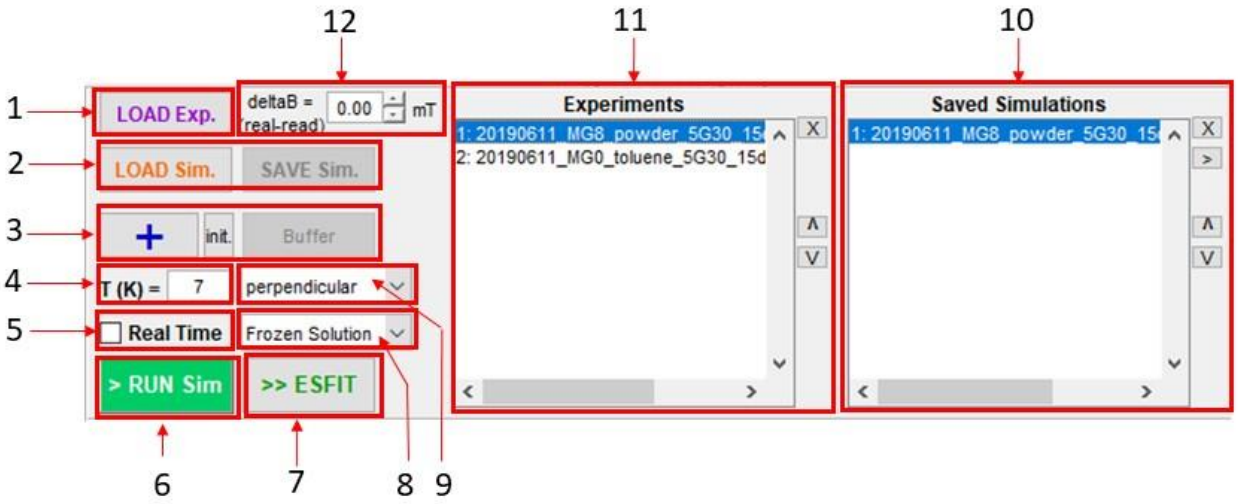


Figure 3: menu and spectra lists sections of the main window

1- Load one or several experimental spectra.
2- Load one or several simulation / Save the selected simulation.
3- « + » button to add one component to simulate. « init » button to set default parameters for the next added components. « Buffer » button to reload last unsaved simulation.
4- Type the experimental temperature in kelvin. The value will be saved at the same time as the simulation is saved. Temperature = 100K by default.
5- Check « real time » to visualize in real time on the figure when one parameter is modified in component windows.
6- Perform global simulation calculated from all parameters.
7- Run the fitting mode. Available only after having saved the simulation.
8- Choose between frozen solution mode (Easyspin Pepper mode) or fast motion mode (Easyspin Garlic mode).
9- Choose between perpendicular mode or parallel mode. It is the direction of the modulating magnetic field compared to the applied field. Perpendicular is the classical mode while parallel can be useful for entire spin S.
10- List of the loaded simulation currently opened. Option to select several spectra at the same time (CTRL+click), remove from the list (X), reorder the list (↑ or ↓) and export (>) data in one .txt file and parameters in one other .par file.
11- List of the loaded experimental spectra currently opened. Same options as for the simulation list except export.
12- Magnetic field shift option.

3. Component window

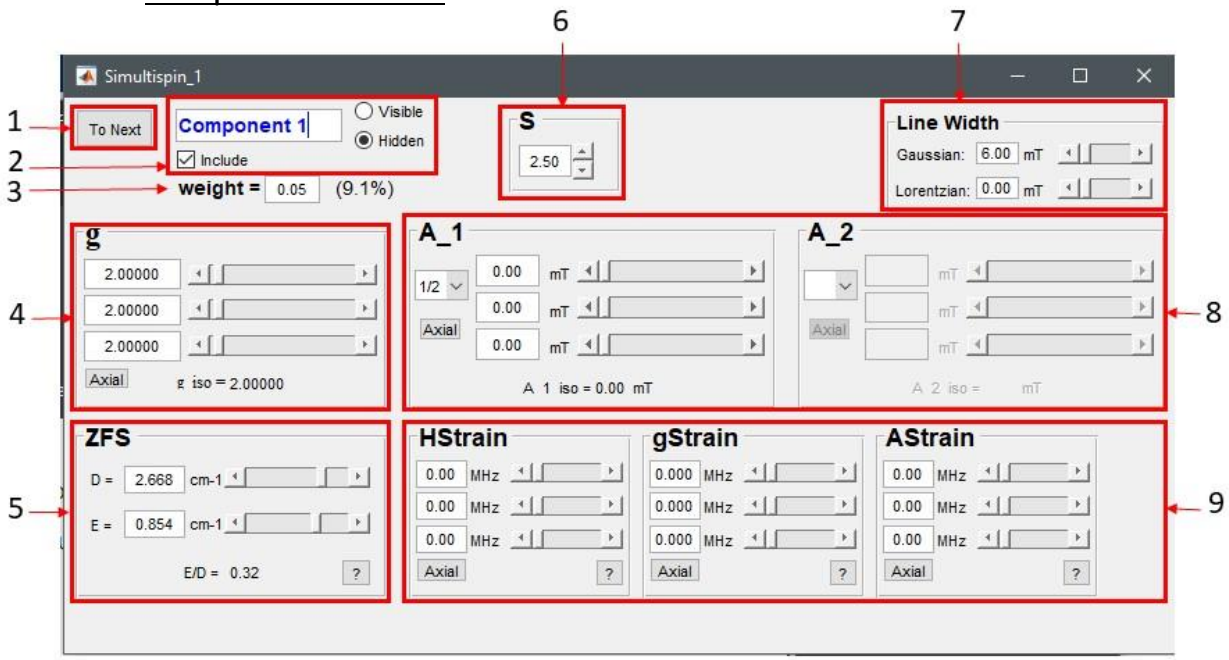


Figure 4: component window

1- Click «To next » to reuse the parameters of this component for a new component window.

2- Type the name of this component (by default is « component X ») and options:
if « Include » is checked, the parameters of this component are taken into account for the simulation.
Choose visible to visualize the simulation of this component independently to the other components. By default hidden will not show the spectrum.

3- Relatice weight of this component in the simulation. Appear only when several components are included in the simulation

4- Selection of the g-values by typing in the boxes or using the sliders.
It can be an isotropic system (3 identical g-values has to be typed), rhombic system (3 different g-values) or axial system. In that last case, the user can select the combination of axis by successively clicking on the « Axial » button. Thus 2 g-values are linked together (perpendicular g-values) represented by vertical black markers, and one keeps independant (parallel g-value).
The average of g values is automatically calculated and shown (g_{iso}).

5- Zero Field Splitting (ZFS) characterized by the parameters D and E. The E/D value is automatically calculated and shown. This section is always available but will have effect only for S > ½.

6- Choice of the electronic spin S with up and down arrows.

7- Choice of the line width. The broadening could be with Gaussian shape or Lorentzian shape or a mix of both.

8- Optionnal selection of hyperfin coupling constants from nuclear spin. Up to two coupling can be applied (A_1 then A_2).

Select the nuclear spin I value in the popup menu then type the coupling constants (or use sliders). Axial setting could be selected with the « Axial » button as for g-value.

A_{iso} is automatically calculated and shown.

Note that axial setting has to be the same as for g, A and Strain (see later). These three sections works in parallel.

If a nuclear spin value is selected but constants stay zero, the contribution for simulation remains zero.

9- Optionnal selection of Strain typing in boxes or with sliders: Hstrain, gStrain or Astrain. Axial setting could be selected with the « Axial » button as for g and A value.

IV. How to run simulation

1. Simulation without experimental spectrum

With SIMULTISPIN, the user can simulate spectra with or without experimental spectrum. In that last case, the fitting mode is not available.

After having opened SIMULTISPIN, follow these steps :

- From the main panel, type the temperature (fig3 n°4. Optionnal, 100K by default), the simulation mode (fig3 n°8. Frozen solution by default) and the field mode (fig3 n°9. Perpendicular by default),
- Click on « + » button (fig3 n°3) from the main window to create a new component parameters window
- Adjust the simulation parameters in the first component window
- To add an other component for simulation, click again on « + » button from the main panel.
- With several components, the user is able to specify the relative weight of each of them in each component window (see fig5).

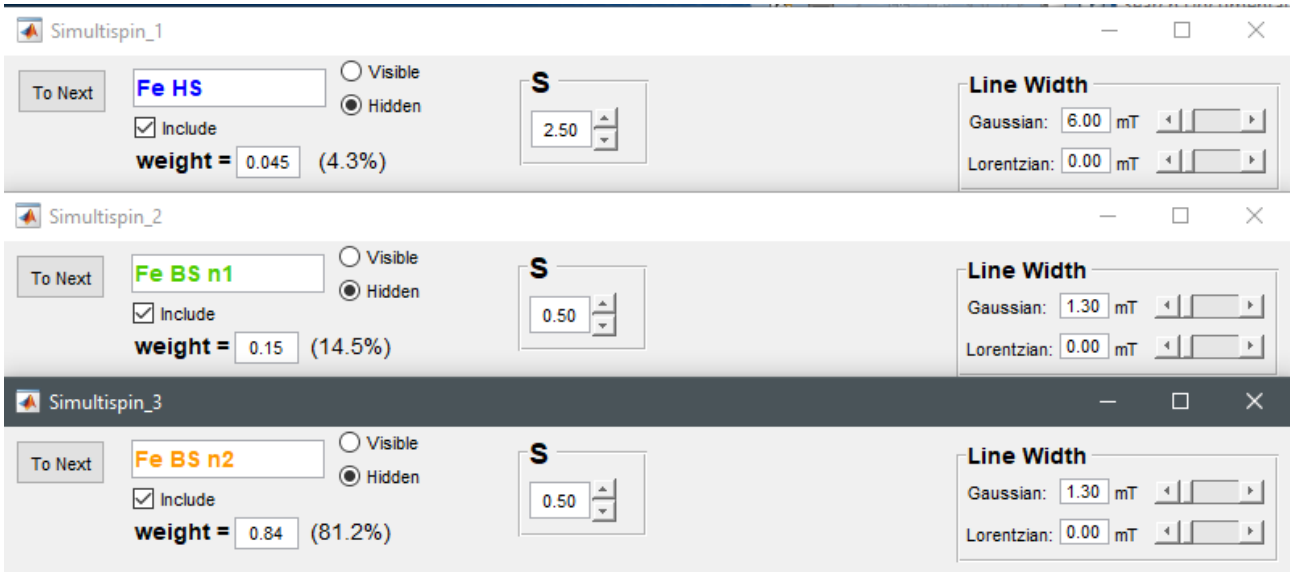


Figure 5: extract of 3 component windows with their relative weight options

- When the parameters have been set, click on « Run Sim » in the main panel (fig3 n°6) to run the simulation.
- A popup window will appear to choose the frequency. Then click ok and visualize the resulting spectrum on the graph.

Note that each time some parameters are changed, the user has to repeat « Run Sim » to update the spectrum.

By checking « Real time mode » box (fig 3 n°5), the user will be able to conveniently visualize in direct each changing of one parameter.

2. Simulation with experimental spectrum

- The first step is to « Load » one or several experimental spectra (fig3 n°1).
- Temperature (fig3 n°4), the simulation mode (fig3 n°8) and the field mode (fig3 n°9) still have to be set.
- One or several component windows can be created and set following instructions detailed in part IV-1.
- Finally when the user will click on « Run Sim » to calculate the simulation, the frequency will be automatically picked up from the experimental parameters of the chosen spectrum (parameters listed in the .DSC Bruker file)

Note that if the user select an other experimental file, « Run Sim » has to be clicked again in order to update the frequency with these data.

V. Automatic fitting mode

1. Requested conditions

To perform the fit, one simulation has to be runned and saved. Then the user should check that both experimental and simulated spectra are highlighted in their respective list (see Fig 6).

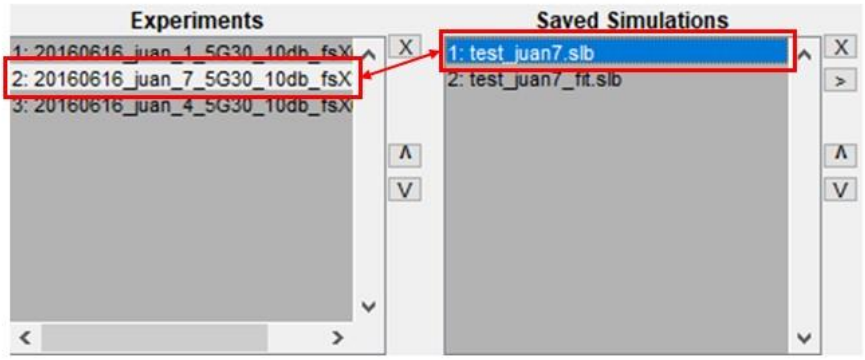
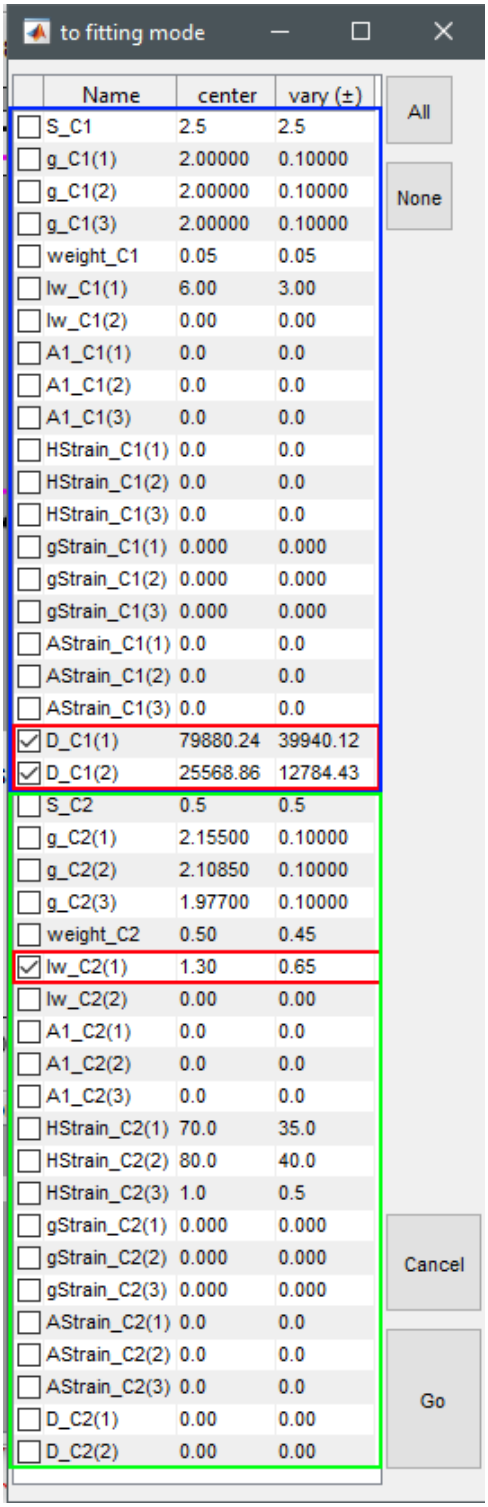


Figure 6: selection of experimental and simulated files to run fitting mode

To obtain a good fitting result, it is necessary to start with parameters already as reliable as possible otherwise the fit could go out of range or maybe even worse the fit could look nice but suggests set of parameters without any spectroscopic reality.

2. Settings of the fitting mode

To launch the fitting mode, click on the « ESFIT » button of the main panel (Fig3 n°7). The following tab (see fig 7) will open. It is summarized all the parameters from the chosen simulation.



Parameters are listed by component : at the top is all the parameters of the 1rst component, then all the parameters of the second component and so on.
The name of each parameters follows this generic code:
« name of the parameter_component number(index of the parameter) ».

For example « g_C1(1) » refers to the g-value « g » of component 1 « C1 » in x-axis « (1) ».

Each parameter that the user wants to make varying during the fit has to be checked.
The center value and the vary value are editable for each of them.

In the example of Figure 7, the fitting will be done for two components (blue and green parts).
The user asks to vary the ZFS parameters of Component 1 and the gaussian line width of Component 2.

Note that for ZFS, D_Cn(1) refers to D and D_Cn(2) refers to E.

When the user is ready, click on « Go » to open ESFIT window.

Figure 7: To fitting mode tab

3. Process the fitting from ESFIT window

ESFIT is an interface from Easyspin called Easyspin Last-Squares Fitting.
In this window (see fig8), the user can click on « Start » to run the fitting process according to the settings selected at the previous step.

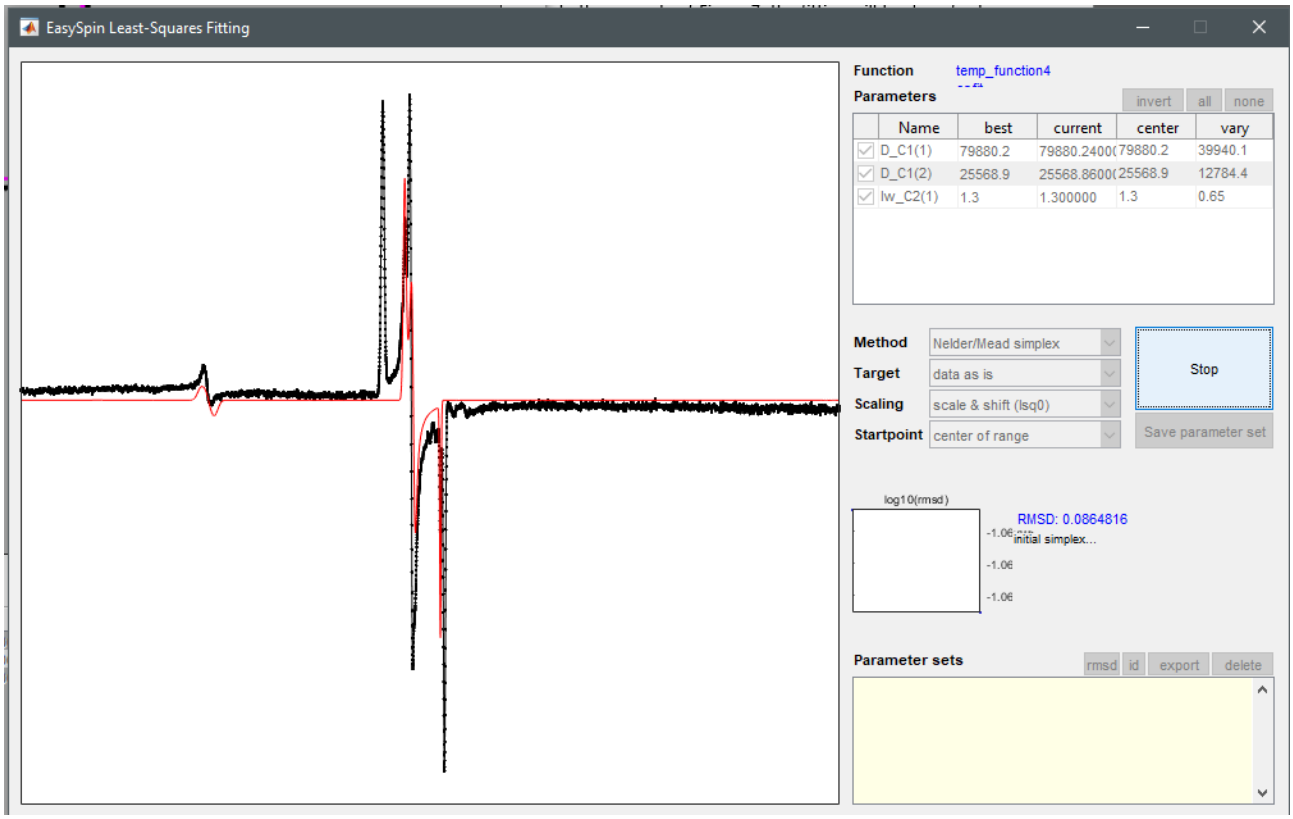


Figure 8: ESFIT window

Several methods and targets are available within the need of the user. Visualization of the fitted spectrum and the best parameters found can be read in real time.
The user can « Stop » the process whenever it wants and keeps on screen the parameters at that time.

4. Exit the fitting mode

To exit the fitting mode, the user can close the window and click on « Esc. Fit M. » on the main panel (fig3 n°7). If nothing else has been done to keep the fitted parameters in memory, they are going to be lost.
A convenient feature consists to automatically export the best parameters in SIMULTISPIN component windows. To do that, the user should click on « Save parameter set » then « Export ».

Then when the ESFIT mode will be closed, SIMULTISPIN will ask to save the new fitted simulation. Thus parameters will be automatically implemented in the component windows.

VI. Additionnal features

1. Comparison of spectra

When the user selects several simulated spectra, they are simultanously plotted on the graph and a window pops up comparing one by one all parameters of each simulation (see fig 9).

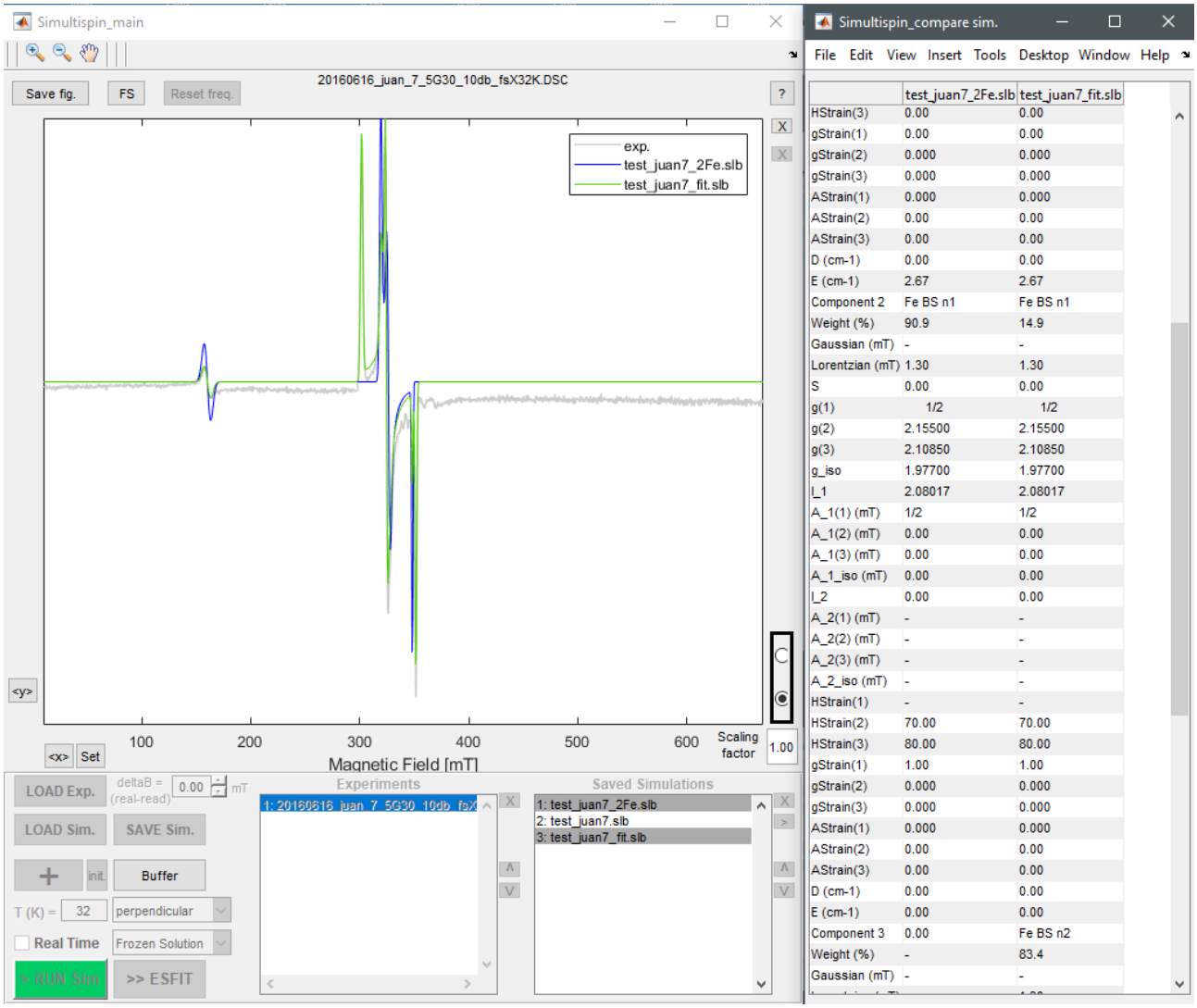


Figure 9: comparison of several simulated spectra

The same action can be done with several experimental spectra. In that case, they are plotted and overlaid on the graph by a g-value axis (see fig 10).

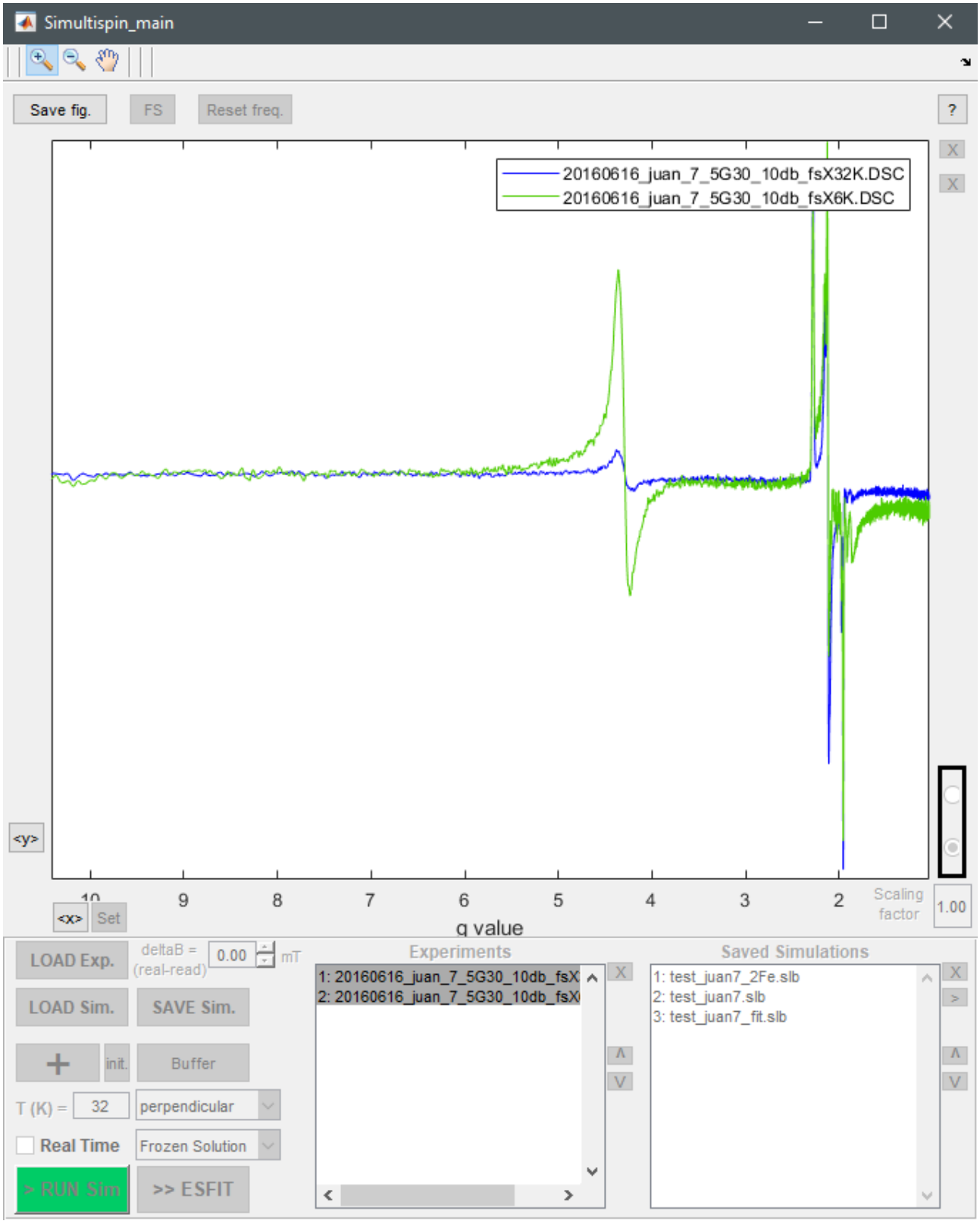


Figure 10: comparison of several simulated spectra

2. Coordinates and g-value

On the graph, by clicking on the point of one spectrum (experimental or simulated), the user can read the coordinates of this point and the corresponding g-value at the bottom left of the figure (see fig 11). This display is removed by clicking on the background.

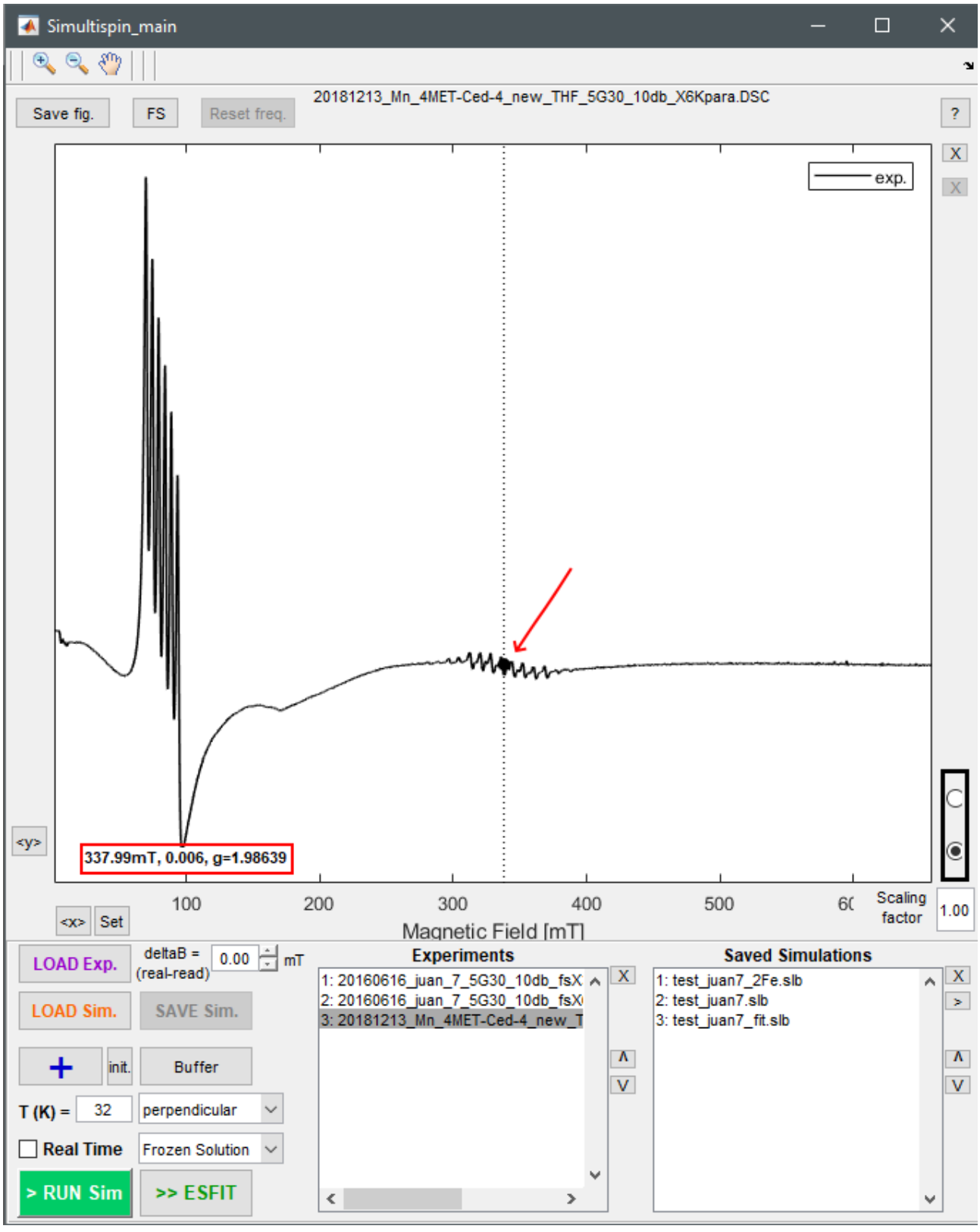


Figure 11: Display the coordinates and g-value of spectrum

3. Help buttons

Several « ? » help buttons are present in SIMULTISPIN :

- In the main panel, it opens this pdf guide documentation and a mT/MHz scale converter.
- In each Strain panel of the component windows, it gives the definition of the corresponding strain referring to Easyspin website.
- In the ZFS section of the component windows, it opens a pdf file with rhombograms helping the user to determine D and E values for S= 3/2 and 5/2 at low field and high field regime (Duboc, C., Chem. Soc. Rev., 2016,45, 5834-5847).

VII. References

1- Etienne, E.; Le Breton, N.; Martinho, M.; Mileo, E.; Belle, V., SimLabel: a graphical user interface to simulate continuous wave EPR spectra from site-directed spin labeling experiments. Magnetic Resonance in Chemistry, 2017,55, 714–719

2- Stoll, S.; Schweiger, A., EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. Journal of Magnetic Resonance, 2006, 178 (1), 42-55.

3- Duboc, C., Determination and prediction of the magnetic anisotropy of Mn ions. Chemical Society Reviews, 2016,45, 5834-5847