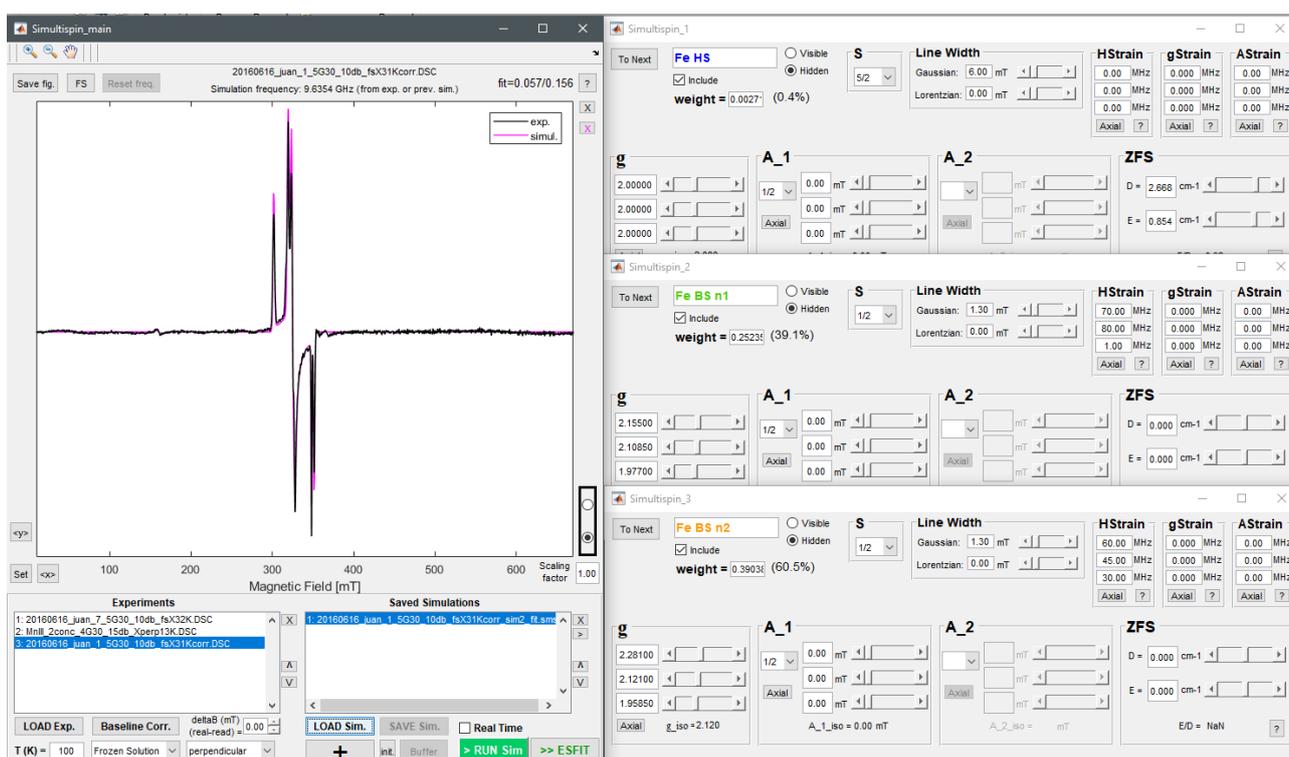


SIMULTISPIN

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 a user-friendly tool for EPR (Electronic Paramagnetic Resonance) simulation and fitting based on the free-of-charge 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 $1/2$, 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 come to complete SIMULTISPIN to work for a wide type of spectra:

- choice of the experimental temperature,
- choice between perpendicular (classical) or parallel modulating magnetic field (for integer electronic spin like $S = 2 \text{ Mn}^{\text{III}}$)
- Zero Field Splitting with D and E parameters for $S > 1/2$ 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, apply a baseline correction, and 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 `>> simmultispin`, enter key, and the main window interface will pop up ready to use (see fig 1).

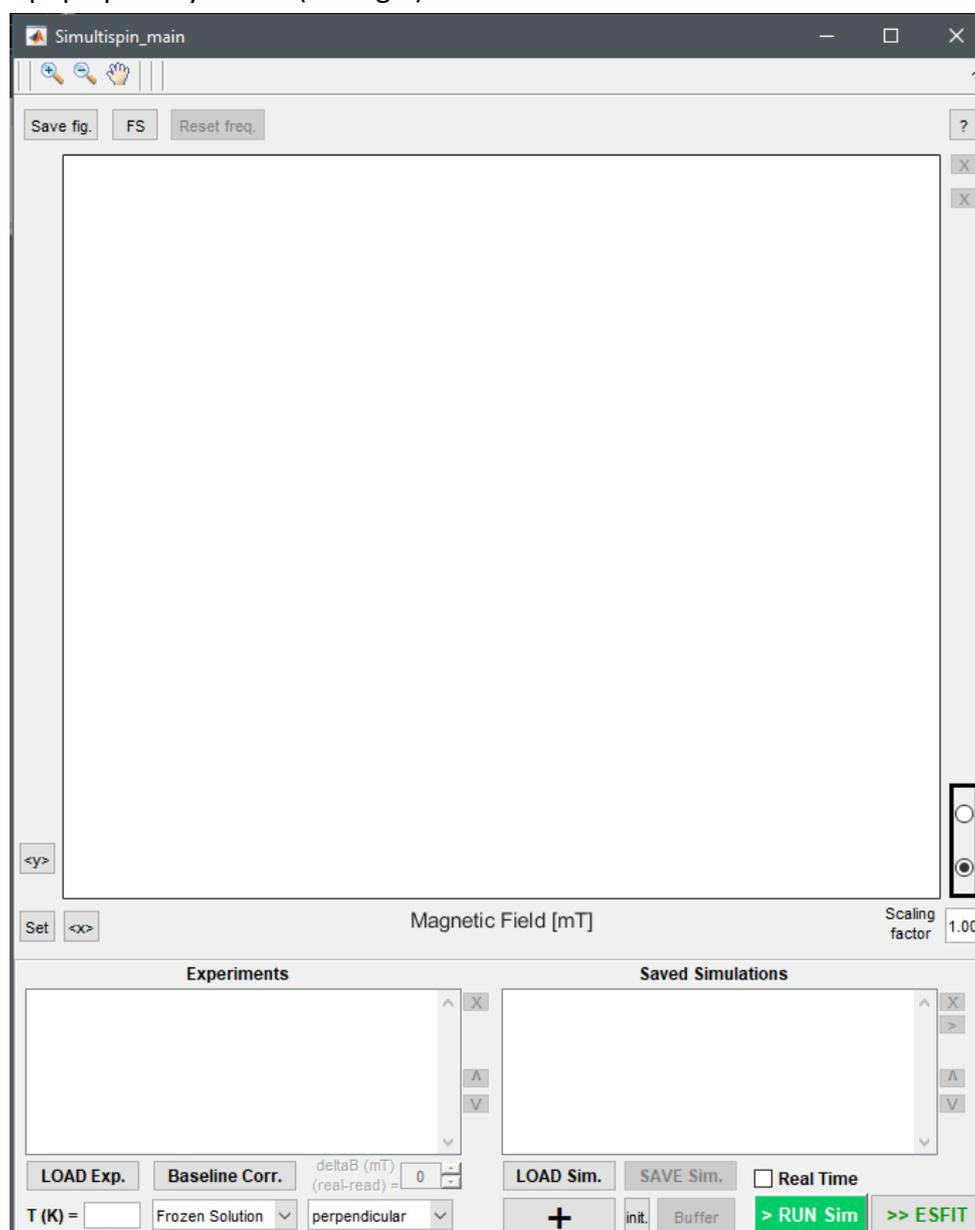


Figure 1: SIMULTISPIN starting window

III. Overview of the main windows

1. Upper Graph section

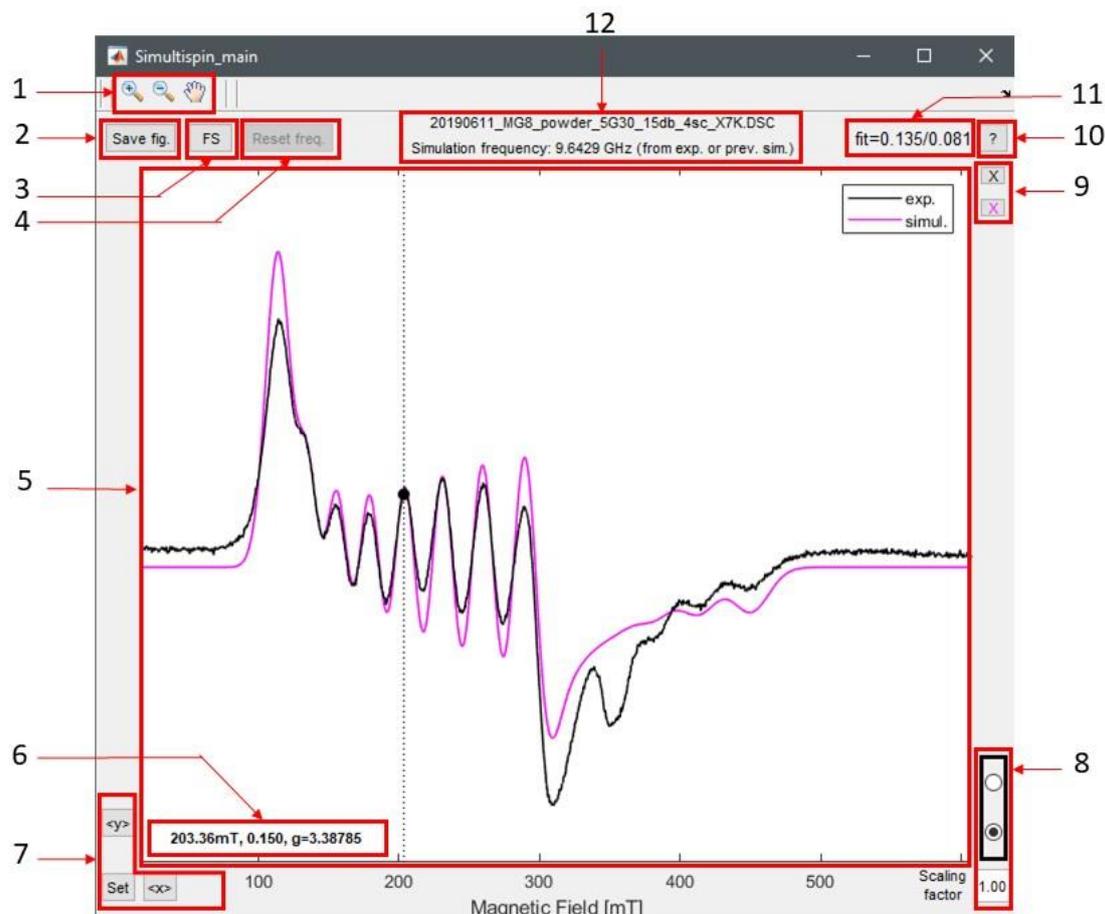


Figure 2: graphic section of the main window

- 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 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

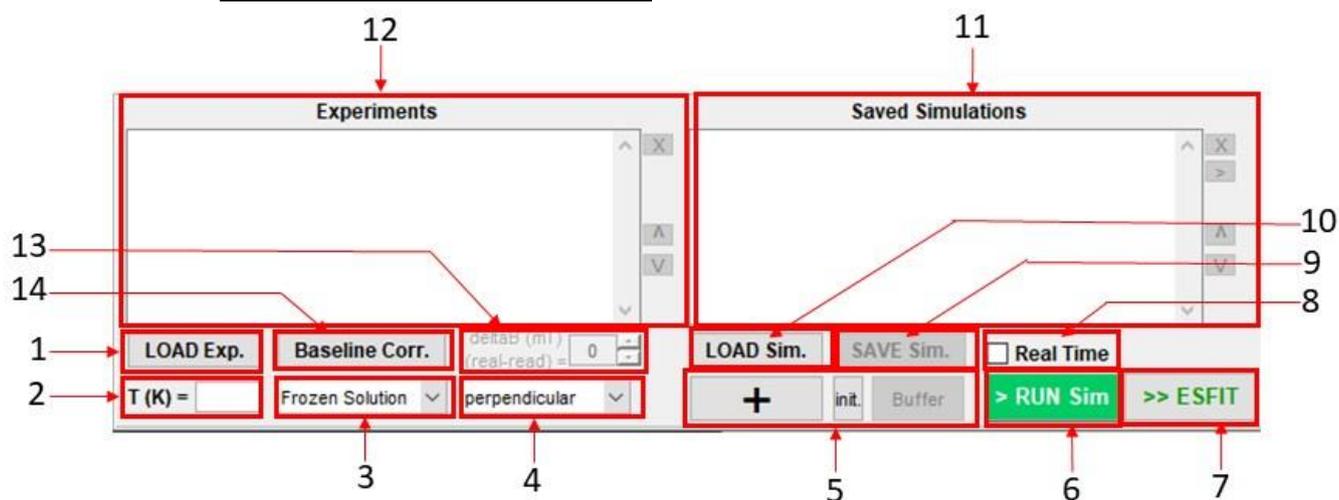


Figure 3: menu and spectra lists sections of the main window

- 1- Load one or several experimental spectra.
- 2- Type the experimental temperature in kelvin. The value will be saved at the same time as the simulation is saved. Temperature = 100K by default.
- 3- Choose between frozen solution mode (Easyspin Pepper mode) or fast motion mode (Easyspin Garlic mode).
- 4- 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 integer spin S.
- 5- « + » button to add one component to simulate. « init » button to set default parameters for the next added components. « Buffer » button to reload the last unsaved simulation.
- 6- Perform global simulation calculated from all parameters.
- 7- Run the fitting mode. Available only after having saved the simulation.
- 8- Check « real time » to visualize in real time on the figure when one parameter is modified in component windows.
- 9- Save the selected simulation.
- 10- Load one or several simulations.
- 11- List of the loaded simulations 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.
- 12- List of the loaded experimental spectra currently opened. Same options as for the simulation list except export.
- 13- Magnetic field shift option.
- 14- Baseline correction tool for the experimental spectrum.

3. Component window

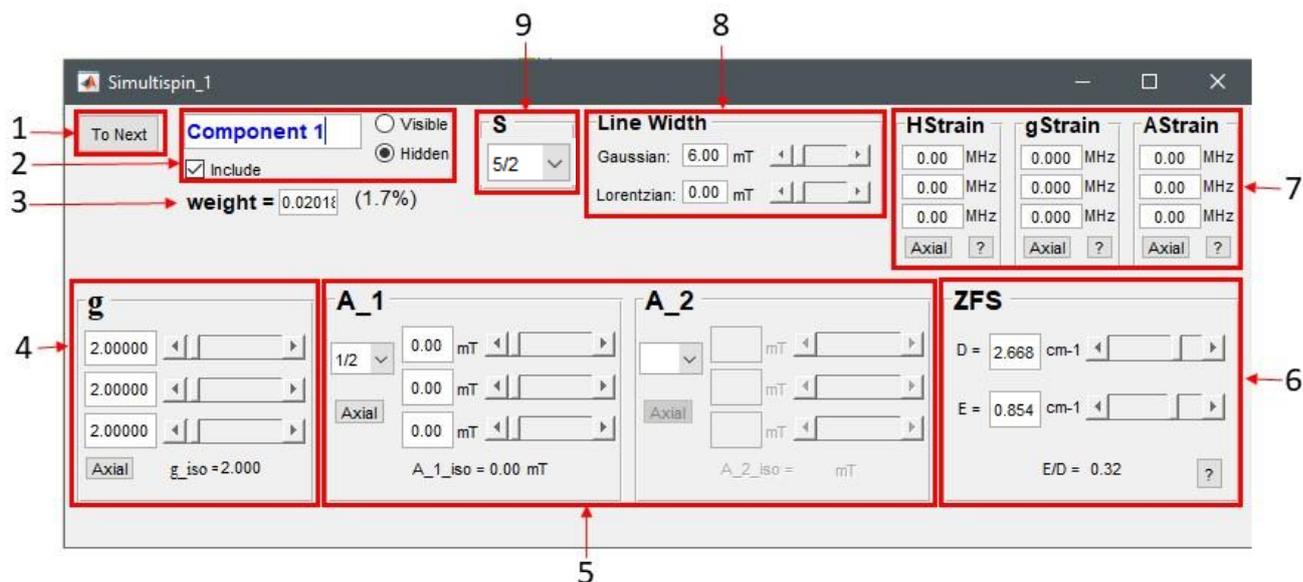


Figure 4: component window

- 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- Relative 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 (three 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 two g-values are linked together (perpendicular g-values) represented by vertical black markers, and one keeps independent (parallel g-value).
The average of g values is automatically calculated and shown (g_{iso}).
- 5- Optional selection of hyperfine 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 the 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 the simulation remains zero.

- 6- 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 $S > \frac{1}{2}$.
- 7- Optional selection of Strain typing in boxes: Hstrain, gStrain or Astrain.
The axial setting could be selected with the « Axial » button as for g and A values.
- 8- Choice of the line width. The broadening could be with Gaussian shape or Lorentzian shape or a mix of both.
- 9- Choice of the electronic spin S with popup menu from 1/2 to 7/2 by steps of 1/2.

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°2. Optional, 100K by default), the simulation mode (fig3 n°3. Frozen solution by default) and the field mode (fig3 n°4. Perpendicular by default),
- Click on « + » button (fig3 n°5) 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).

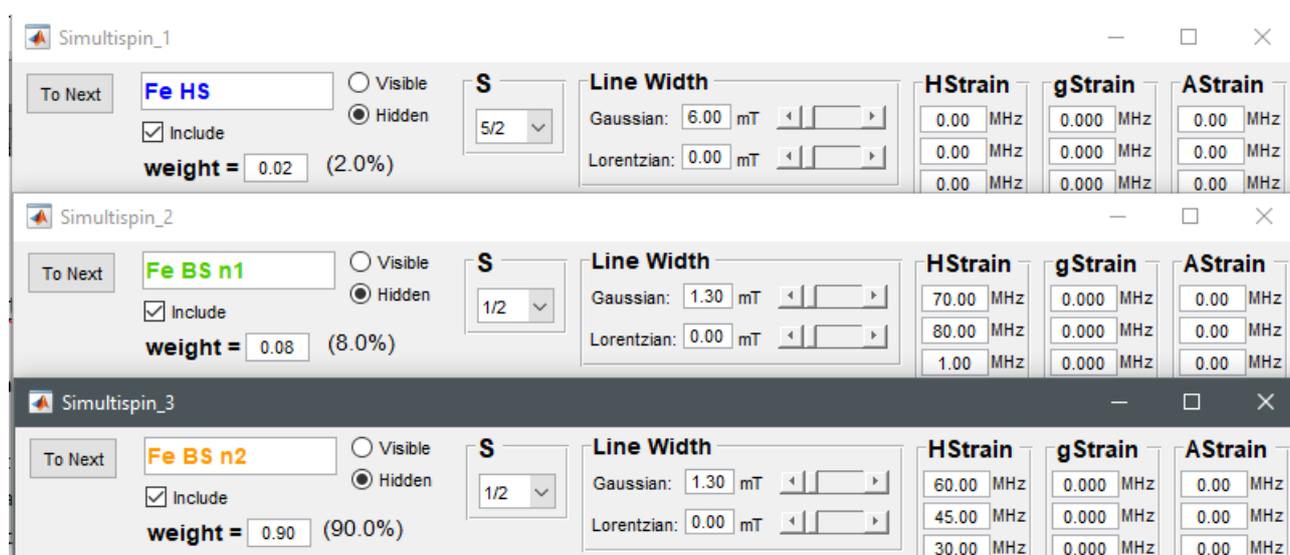


Figure 5: extract of three component windows with their relative weight options

- 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°8), 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°2), the simulation mode (fig3 n°3) and the field mode (fig3 n°4) 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 new 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).

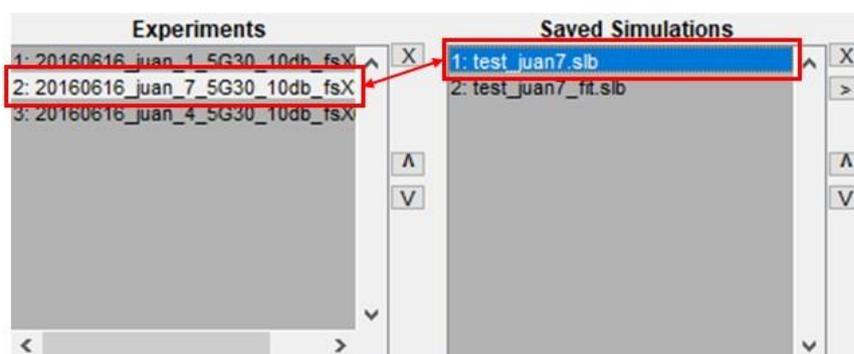
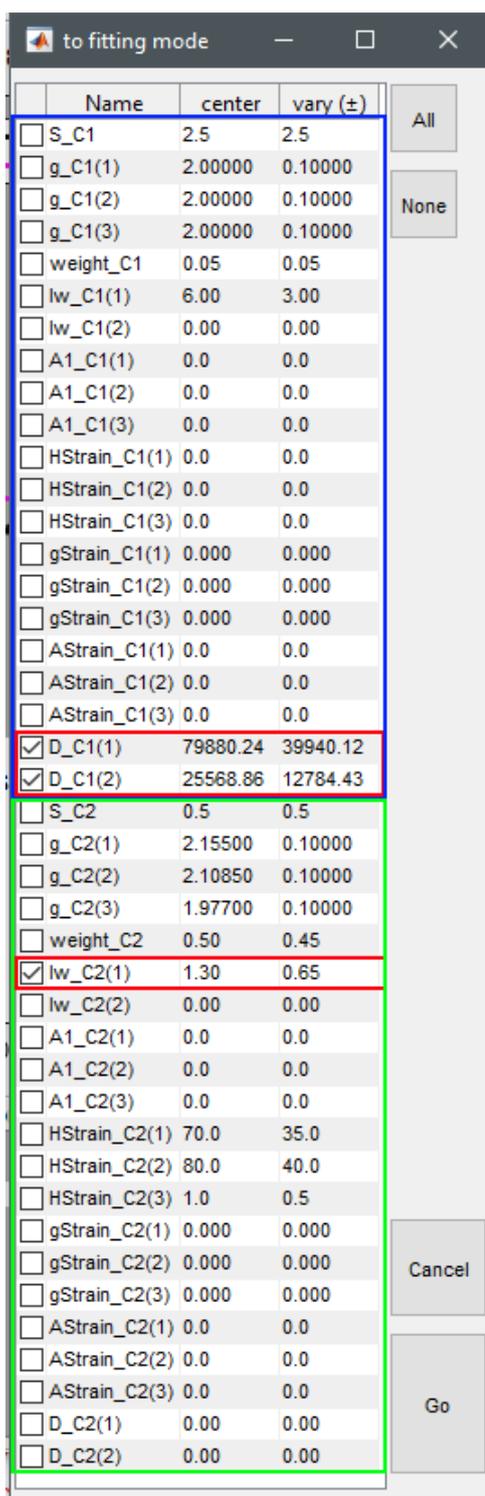


Figure 6: selection of experimental and simulated files to run fitting mode

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 1st 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 named « C1 » for 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 Least-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.

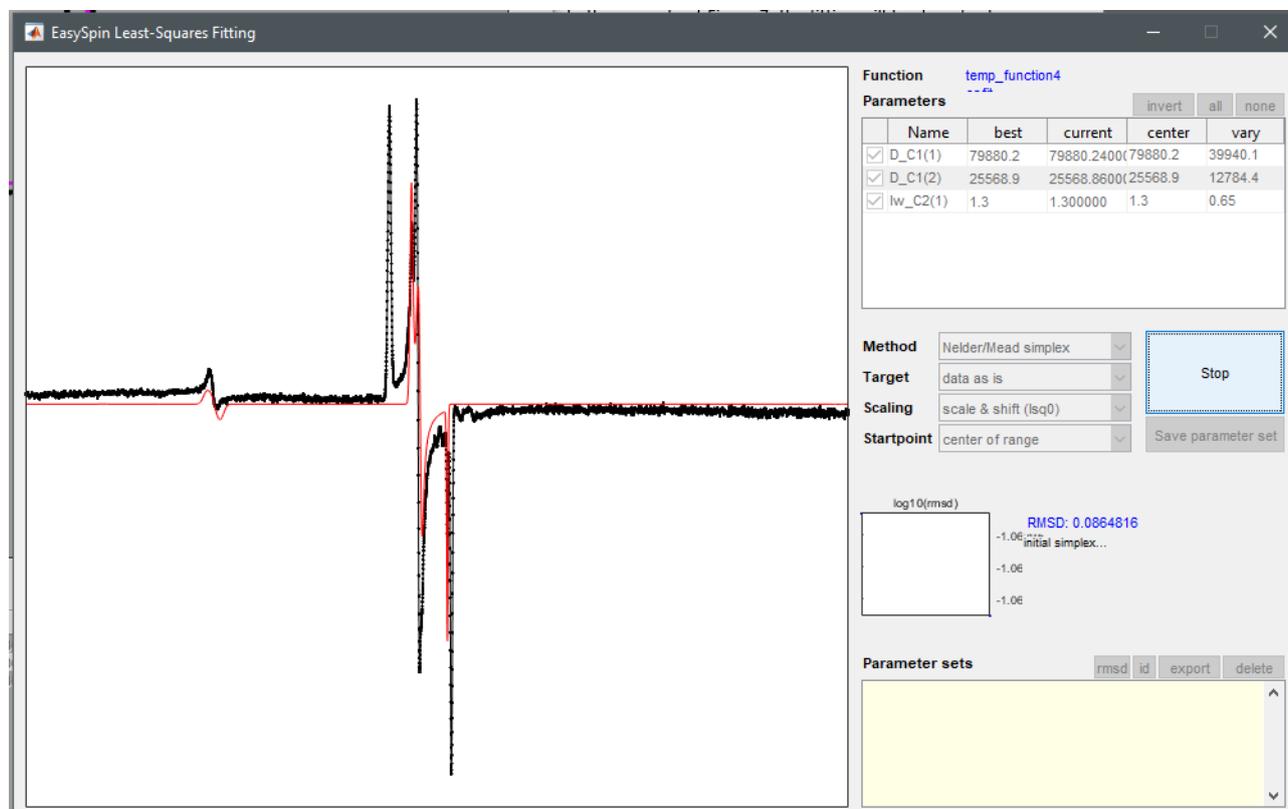


Figure 8: ESFIT window

Several methods and targets are available within the need of the user. The 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

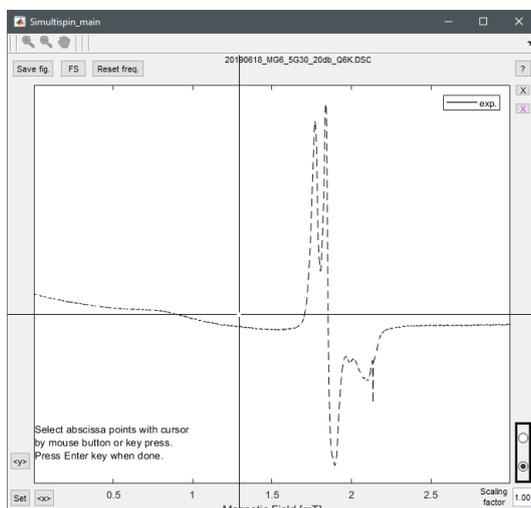
To exit the fitting mode, the user can close the window and click on « Esc. Fit M. » on the main panel (fig3 n°7). If nothing else has been done to keep the fitted parameters in memory, they are going to be lost.

A convenient feature consists to automatically export the best parameters in the 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, the parameters will be automatically implemented in the component windows.

VI. Additional features

1. Baseline correction tool

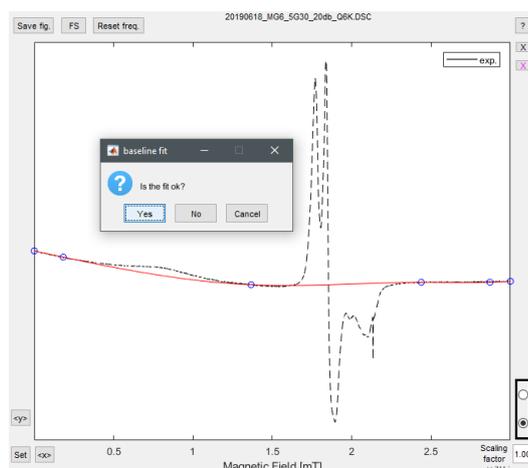
The baseline correction tool is based on the interpolation functions of Matlab. The baseline fit will be subtracted to the experimental spectrum. By default in the program, the spline function is applied. It means that the baseline fit is built by addition of polynomial curves.



When one experimental spectrum is selected, the user can click on the Baseline tool inside the Tool menu (fig 3 n°14). Thus, the spectrum appears in dotted line and a coordinate cross tool is available.

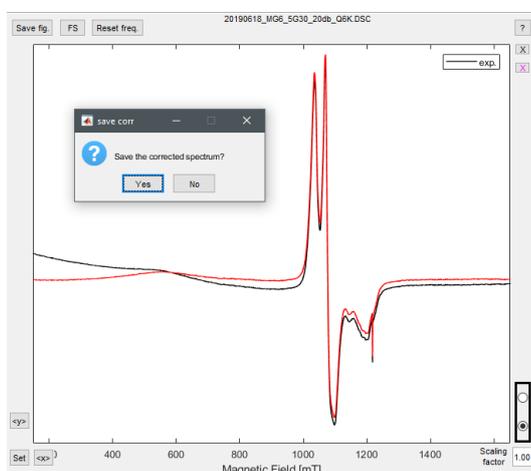
With the cross tool, the user selects the points abscissa of the spectrum to take into account for the baseline fit. They are selected by left mouse click or by key press.

The first and last points of the spectrum are automatically selected and an average of 3 points around the selected points is processed. In case of noisy data, the number of averaged points can be increased in the Matlab code.



When it is done, the user has to press Enter key to validate: the baseline fit is plotted, highlighting the selecting points.

Depending to the result, the user has the choice to accept the fit, redo the points selection or abort.



When the baseline fit is accepted, the corrected spectrum is overlaid in red and the user is invited to save the corrected spectrum in Bruker BES3T format (.DSC and .DTA files). In that case, the frequency is automatically kept in memory and the new spectrum is added to the experimental files list for further simulation.

Figure 9: Baseline correction steps

2. Comparison of spectra

When the user selects several simulated spectra, they are simultaneously plotted on the graph and a window pops up comparing one by one all parameters of each simulation (see fig 11).

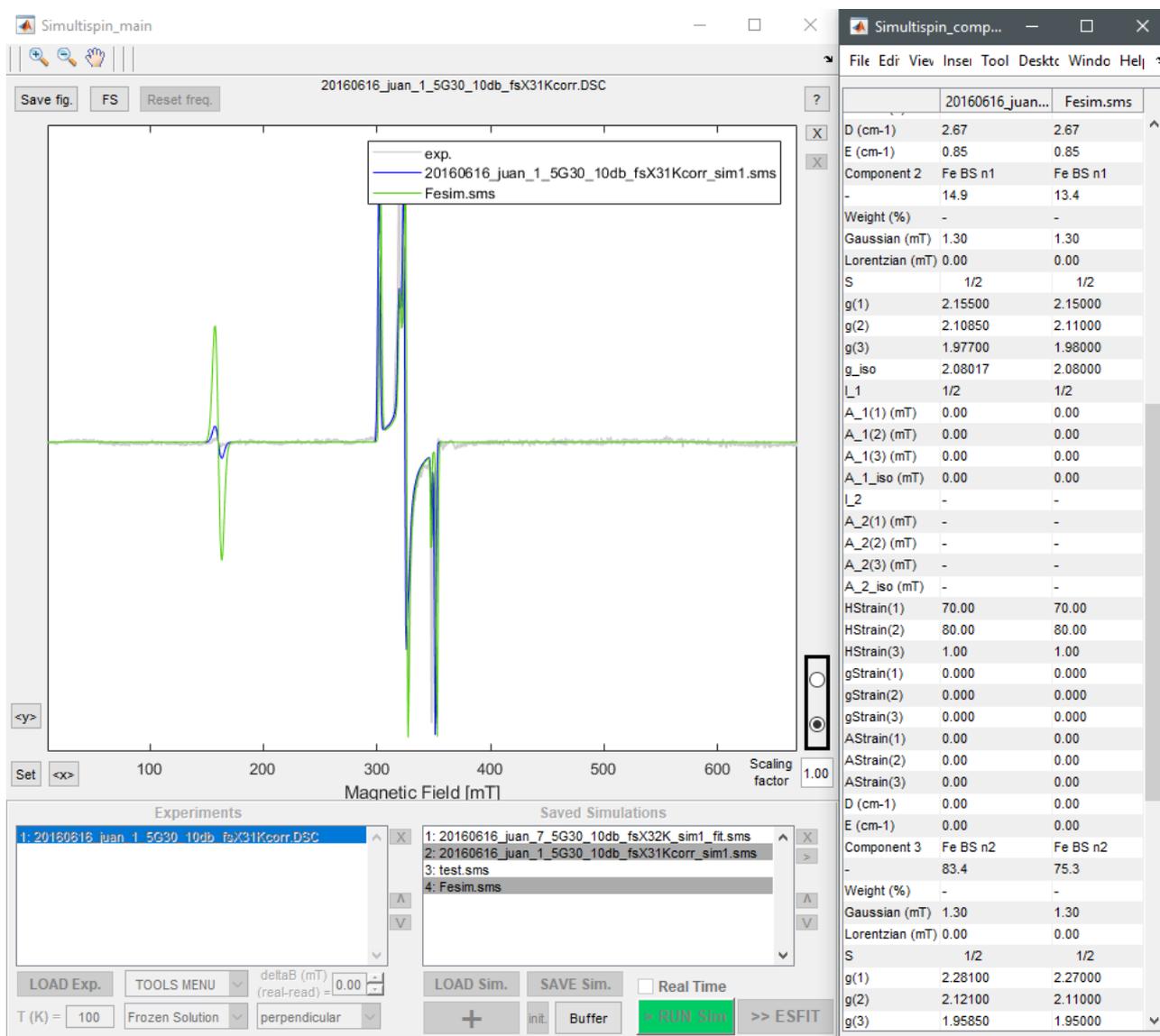


Figure 10: comparison of several simulated spectra

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 12).

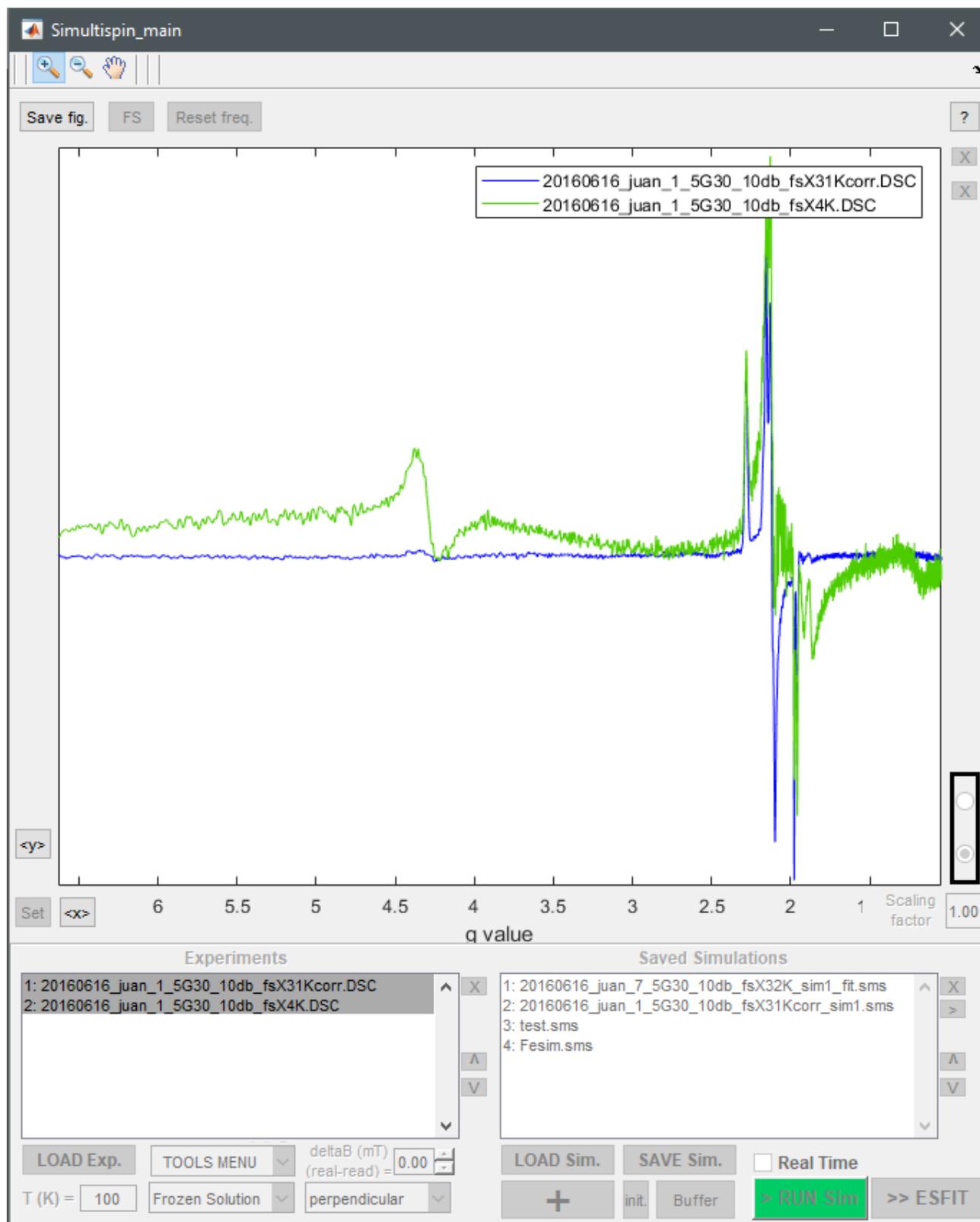


Figure 11: comparison of several simulated spectra

3. 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 13). This display is removed by clicking on the background.

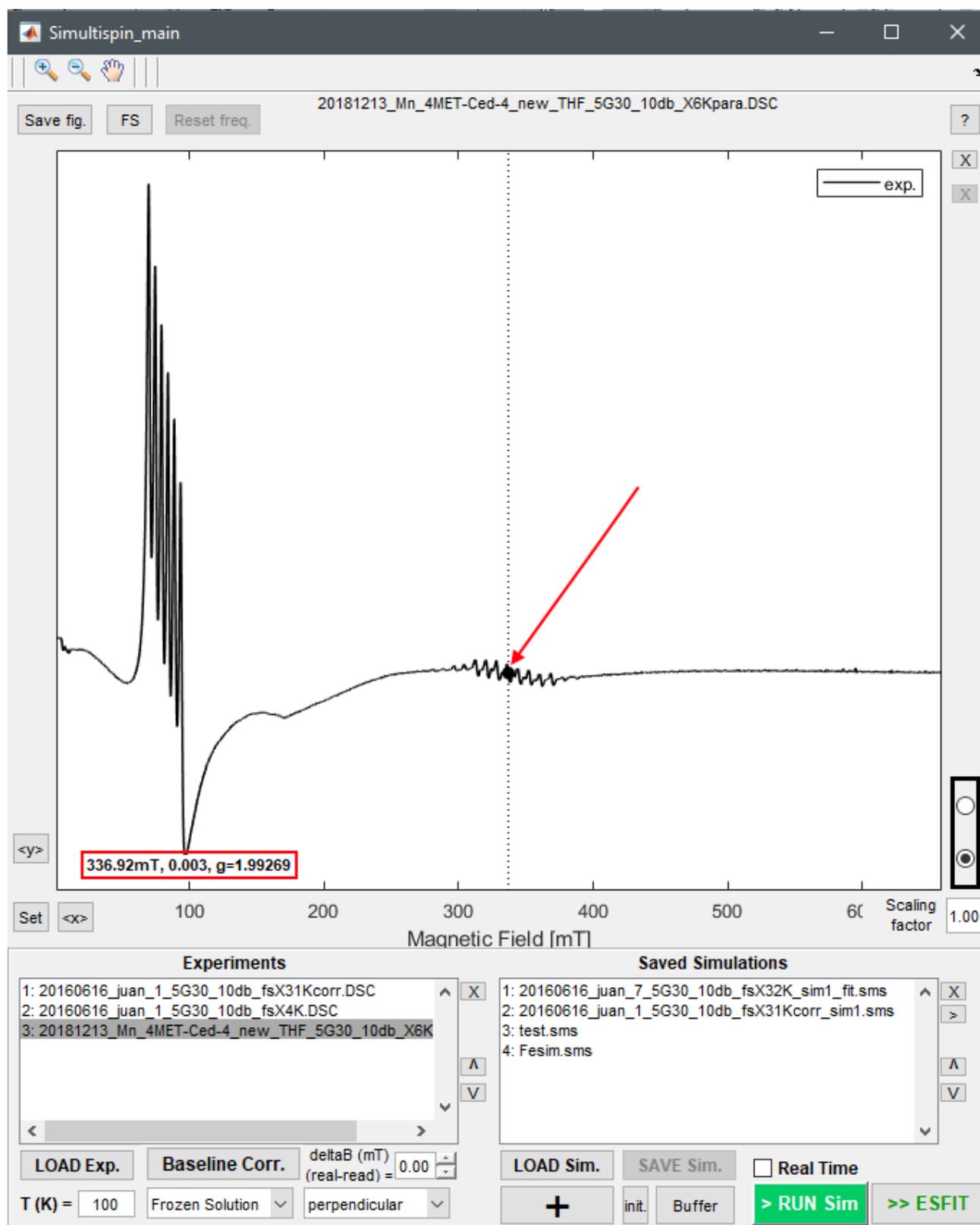


Figure 12: Display the coordinates and g-value of spectrum

4. Help buttons

Several « ? » help buttons are present in SIMULTISPIN :

- At the top right of the main panel, it opens this pdf guide documentation and a mT/MHz scale converter. The version of the GUI is also indicated.
- 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
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- 3- Duboc, C., Determination and prediction of the magnetic anisotropy of Mn ions. *Chemical Society Reviews*, 2016,45, 5834-5847