

# NMR<sub>2</sub>SCO

## *manual*

## Manual to NMR<sub>2</sub>SCO-scripts

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### Introduction

NMR<sub>2</sub>SCO is a collection of 3 Visual Basic scripts to be used for elucidation of solution <sup>1</sup>H-NMR data of Fe<sup>2+</sup>-SCO complexes. They run on every MS Excel implementation provided the Visual Basic extension is installed, that is included even in the student versions. These scripts are not commercial versions and it is not fully tested yet, but was used successfully in preparation of a publication that also provides the background.<sup>[1]</sup> In the following text a short introduction should be given. The source code is included in every file to allow you to modify the program to suit your special requirements. If you use the program we would ask you to cite the following paper/s<sup>[1]</sup>.

### NMR<sub>2</sub>SCO-shifts

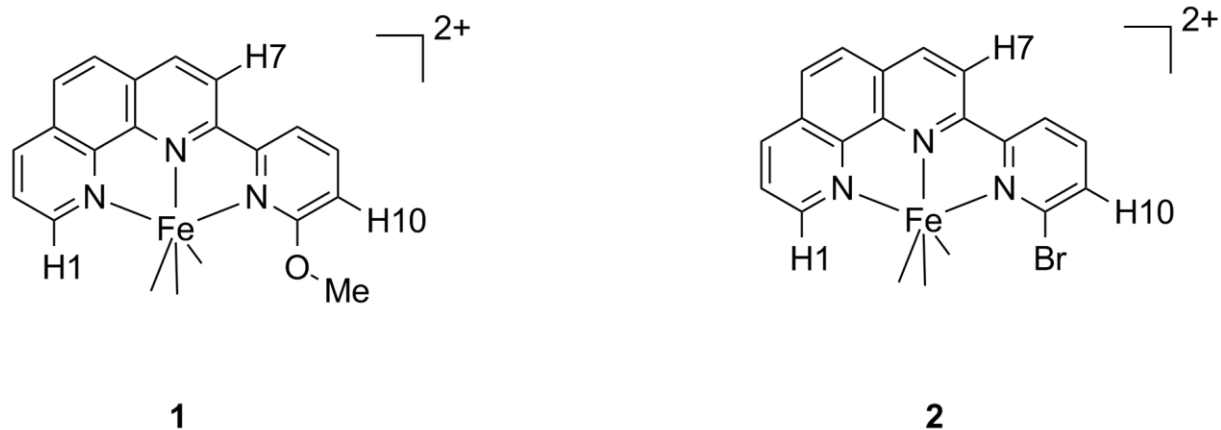


Figure 1: The example files use data for the two complexes 1 and 2. The proton H7 was used for most calculations. Both complexes are air, moisture stable and durable complexes that can be prepared by two step syntheses starting from commercial materials.

The shifts module can calculate the thermodynamic parameters  $\Delta H$ ,  $\Delta S$  and in turn  $T_{1/2}$  of SCO from the temperature dependent chemical shifts. The program assumes that the chemical shifts of the HS state can be calculated by equation (1).

$$\delta_{HS}(T) = C^0T + C^1 + \delta_{dia} \quad (1)$$

In this equation  $C^0$ ,  $C^1$  and  $\delta_{dia}$  are temperature independent. For pure HS complexes  $C^1$  and  $\delta_{dia}$  cannot be separated but for a SCO complex this separation is essential. For SCO systems the program assumes a fast exchange between the HS and LS state. Therefore the chemical shift of a HS complex like **1** can be calculated by equation (2) and (3).

$$\delta_{obs}(T) = (C^0T + C^1 + \delta_{dia}) \cdot \gamma_{HS} + \delta_{dia} \cdot (1 - \gamma_{HS}) \quad (2)$$

$$\gamma_{HS}(T) = \frac{1}{1 + e^{\frac{\Delta_{SCO}H}{R} \left( \frac{1}{T} - \frac{1}{T_{1/2}} \right)}} = \frac{1}{1 + e^{\frac{\Delta_{SCO}H}{R} \left( \frac{1}{T} - \frac{\Delta_{SCO}S}{\Delta_{SCO}H} \right)}} \quad (3)$$

The script calculates for every proton  $C^0$ ,  $C^1$  and  $\delta_{dia}$  (in the following called NMR parameters) and for the given complex a global  $\Delta H$ ,  $\Delta S$  (SCO parameters). It is advisable to estimate reasonable starting values for the SCO and NMR parameters. A simultaneously refinement of all parameters is possible but seldom yields correct and reasonable results. We recommend fixing parameters that can be estimated by other means. This is especially recommended for  $\delta_{dia}$ . Dependent on the data and the temperature range  $C^1$  should be transferred from similar HS complexes or set to 0. For details and justification see<sup>[1]</sup>.

### *How to provide data?*

Prior to refinement the chemical shifts must be collected on an excel sheet. The example sheet "solv\_Me\_a" hold the data for complex **1** in  $d_6$ -aceton solution. The script search for specific keywords: for the SCO data this is solvent, name, dH and dS (here in column B) for the NMR data this is "Proton" (here in column K for Proton H7).

Starting from this position the program reads data from a specific position relative to the key word. For "dH" and "dS" this is the box to the right, data is expected in kJ/mol and kJ/mol-K, respectively. Solvent and name are expect as strings, they are used just for information.

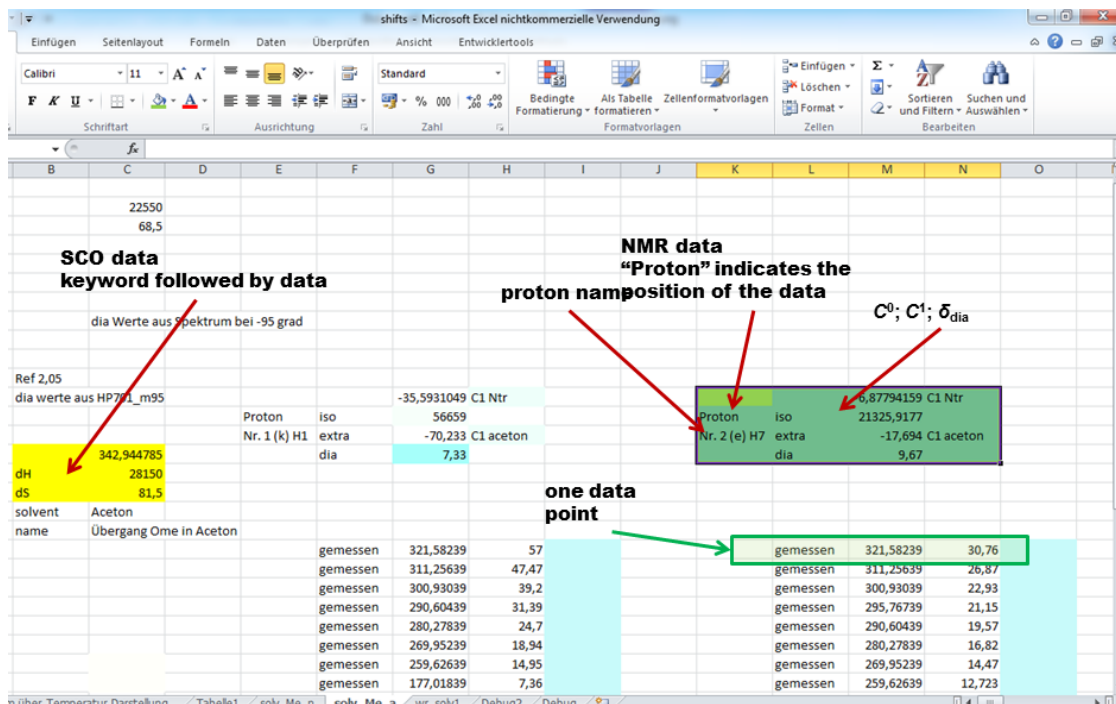


Figure 2: Excel sheet that provides data for the refinement on complex 1.

For "Proton" the program reads the name of the proton directly below the keyword (here "Nr.2(e) H7"). Moreover it checks the column to the right of keyword "Proton" (L for proton H7) for more keywords in this case it search for "dia", "extra" and "iso" and "gemessen". To the right of "dia"  $\delta_{dia}$  in ppm is expected, to the right of "extra" C<sup>1</sup> in ppm is expected and to the right of "iso" C<sup>0</sup> in ppm·K is expected. In the box right to "gemessen" a temperature in K is expected in the next box the observed chemical shift  $\delta_{obs}$  in ppm is expected. In this case it is 321.58 K and 30.76 ppm. All the other fields are ignored so feel free to use this space for comments and other data. This approach also allows you to exclude data from refinement simply by deleting the keyword "Proton" to exclude all data for a specific proton or by deleting gemessen to exclude a specific data point from refinement. If a field is left free the script reads 0. The script sort the data points by the temperature, you do not care about the order. Care must be taken not to write data coincidentally in specific fields.

## Refinement

The script is started by clicking the start button on the sheet "Tabelle1". A new window pops up (Figure 3). This window is used to control the refinement. First you have to tell were the data is stored: write the name of the respective sheet in the box below "read from" here the default is "solv\_Me\_n". Now you can read the NMR data by click on "read NMR data". The protons name should appear in the left window and the bottom turns green. Repeat this for "read dH dS". The refinement is always on all protons that were read, for initial refinement only most shifting should be used to make the process faster. There are two major categories for the refinement, the first is just with fixed  $\Delta H$  an  $\Delta S$ , the other includes refinement of  $\Delta H$  and  $\Delta S$ .

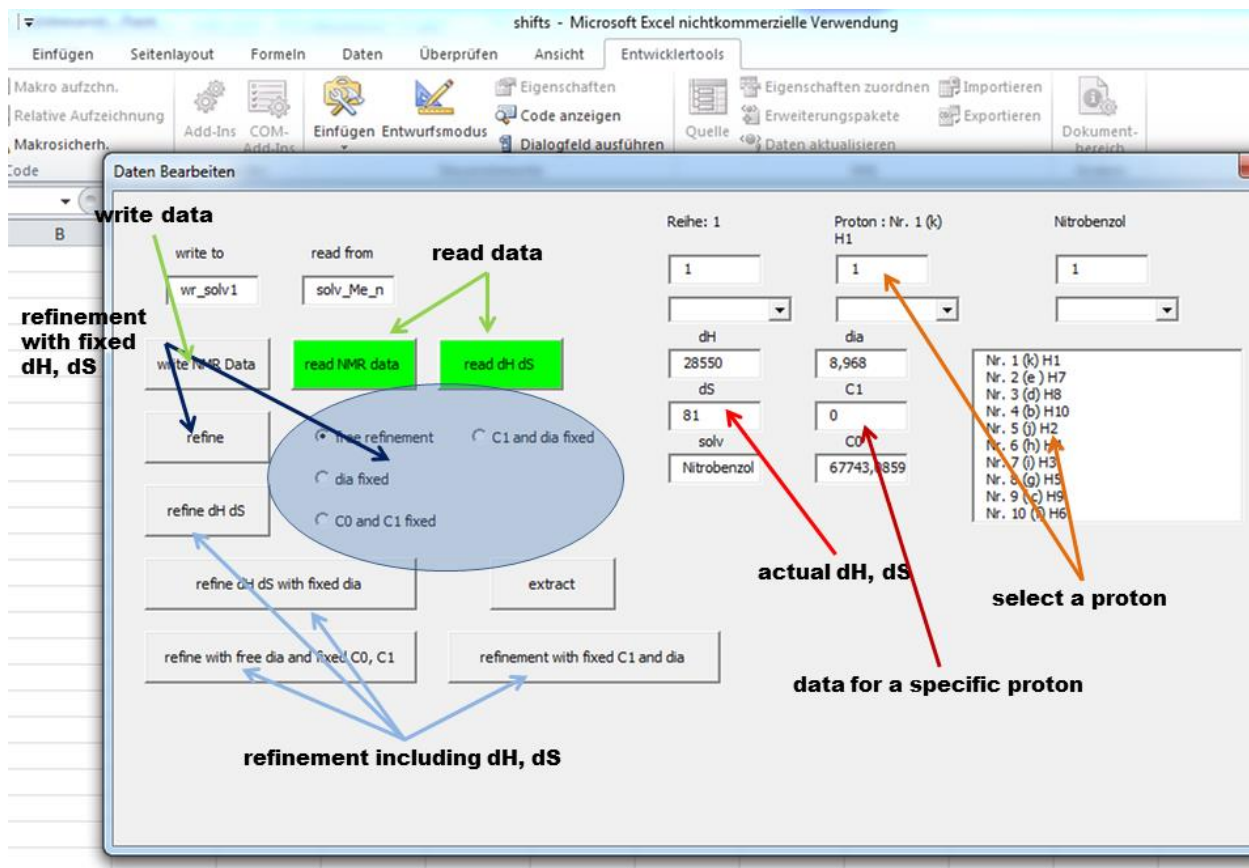


Figure 3: Control-Window for the refinement

For refinement with fixed  $\Delta H$  and  $\Delta S$  values click on refine depending on the option that was chosen the script refines NMR parameters for all protons. With the option button “free refinement”  $C^1$ ,  $C^0$  as well as  $\delta_{dia}$  are refined. Selecting “dia fixed”  $\delta_{dia}$  is left by the value read from the data sheet. Similarly by choosing “C1 and dia fixed” only  $C^0$  is refined, this option must also be selected if  $C^1$  should be fixed to 0. If “C0 and C1 fixed” is chosen then only  $\delta_{dia}$  is refined.

To refine  $\Delta H$  and  $\Delta S$  simultaneously click on the larger buttons “refine dH dS” for full free refinement; “refine dH dS with fixed dia” to fix  $\delta_{dia}$ ; “refine with free dia and fixed C0 and C1” if only  $\delta_{dia}$  should be changed, “refine with fixed C1 and dia” if only  $C^0$  should be changed. In all cases  $\Delta H$  and  $\Delta S$  will be included in the refinement. The algorithm that is used is not the fastest, depending on the number of protons and data points it might take 1h for the full refinement. To speed it up, fix parameters and use only the most significant protons. The refinement is also very sensitive to incorrectly assigned data points. So check the data for this problems and also “fat finger” problems.

The least squares are stored in the memory internally, place 99 is used for the refinement if the refinement is finished in right upper window 99 will appear. To get the best  $\Delta H$  and  $\Delta S$  you must click extract and then write either “2” or “3” in this window then click somewhere in the windows body to

update the window and the best  $\Delta H$  and  $\Delta S$  will appear. These values should then be written on the data sheet and then the NMR parameters should be refined with the new  $\Delta H$  and  $\Delta S$  using the “refine” button.

Clicking on write NMR data will write the data to the sheet given in the box below write to. In this case it is “write\_solv1”. Take care, all cells on this sheet will be cleaned before writing.

### Output

The output sheet provides the NMR parameter as well as the experimental data, shift and temperature, sorted by T and the calculated chemical shifts and the residuals, difference between observed and calculated shift. (Figure 4) Please use your preferred program for graphical representation. To the moment the script cannot calculate standard errors etc. If this is needed you can copy the sorted data to e.g. Origin and do the refinement there with less comfort.

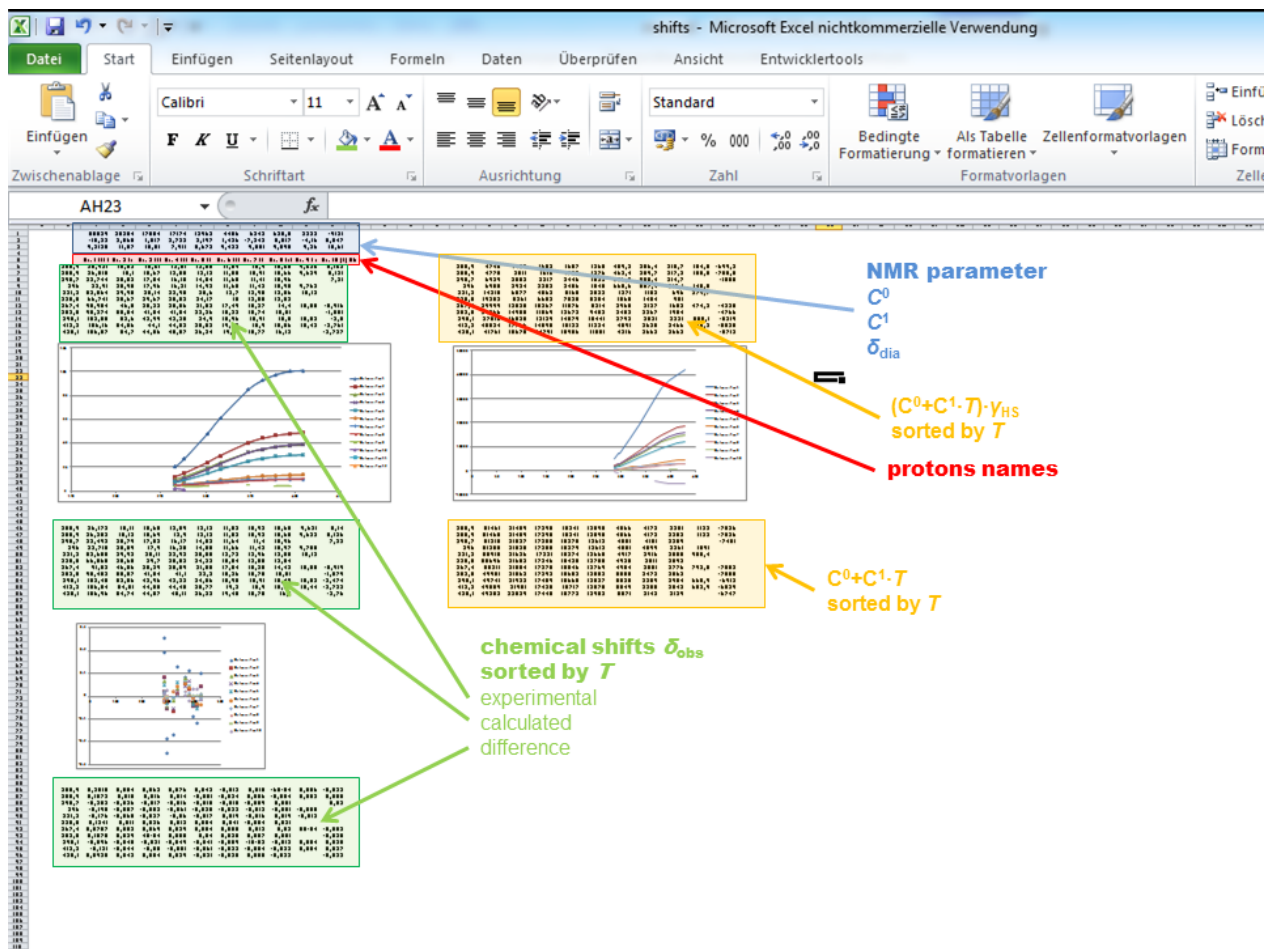


Figure 4: Output of the refinement

## NMR<sub>2</sub>SCO-relaxation

The NMR<sub>2</sub>SCO-relaxation scripts can be used to calculate the relaxivities  $R_1$  and  $R_2$  ( $R_n = 1/T_n = \pi \cdot LW$ ) of a HS  $\text{Fe}^{2+}$  complex. These relaxivities are needed for a correct treatment of the exchange in SCO equilibria. The script calculates this relaxivities on a very simple basis. However our calculations showed that in 95% of the SCO complexes the relaxivities of the HS state does not substantially contribute to the exchange broadening. This satisfies the rather rough treatment. Relaxivities can be calculated from Bloembergen equations. There are three contribution; firstly the dipolar contribution. In octahedral  $\text{Fe}^{2+}$  complexes this contribution dominates  $R_1$  and at ambient temperature  $R_2$ . Dipolar relaxation is caused by the changing magnetic field that comes from the electron spin. The correlation time for the dipolar relaxation is therefore electron spin relaxation time  $\tau_s$ . Secondly the Curie relaxation (Equation (6) and (7)), Curie relaxation is at variance to the dipolar relaxation cause by the static magnetic field that is due to the preferred alignment of the electrons magnetic moment with the  $B_0$  field. This field is much smaller than the magnetic field from the electron spin. However the correlation time for this relaxation is the rotational correlation time  $\tau_r$ . For this reason Curie relaxation contributes about 10% to  $R_1$  but substantially to  $R_2$  especially at lower temperature. The third relaxation mechanism is the scalar relaxation that is due to through bond coupling the correlation time is again the electron relaxation time. However for HS  $\text{Fe}^{2+}$  complexes scalar can be neglected. For this reason the NMR<sub>2</sub>SCO-relaxation script calculates only dipolar and Curie relaxation.

### Dipolar Relaxation

$$\frac{1}{T_1} = \frac{2}{15} \left( \frac{\mu_0}{4\pi} \right)^2 \{ \gamma_I^2 g_e^2 \mu_B^2 S(S+1) \} \left\{ \frac{1}{r^6} \right\} \left\{ \frac{6\tau_s}{1 + ((\omega_I + \omega_S)\tau_s)^2} + \frac{\tau_s}{1 + ((\omega_I - \omega_S)\tau_s)^2} + \frac{3\tau_s}{1 + (\omega_I\tau_s)^2} \right\} \quad (4)$$

$$\frac{1}{T_2} = \frac{1}{15} \left( \frac{\mu_0}{4\pi} \right)^2 \{ \gamma_I^2 g_e^2 \mu_B^2 S(S+1) \} \left\{ \frac{1}{r^6} \right\} \left\{ 4\tau_s + \frac{6\tau_s}{1 + ((\omega_I + \omega_S)\tau_s)^2} + \frac{\tau_s}{1 + ((\omega_I - \omega_S)\tau_s)^2} + \frac{3\tau_s}{1 + (\omega_I\tau_s)^2} \right\} \quad (5)$$

## Curie Relaxation

$$\frac{1}{T_1} = \frac{2}{5} \left( \frac{\mu_0}{4\pi} \right)^2 \left\{ \frac{\omega_I g_e^2 \mu_B^2 S(S+1)}{3kT} \right\}^2 \left\{ \frac{1}{r^6} \right\} \left\{ \frac{3\tau_r}{1 + (\omega_I \tau_r)^2} \right\} \quad (6)$$

$$\frac{1}{T_2} = \frac{1}{5} \left( \frac{\mu_0}{4\pi} \right)^2 \left\{ \frac{\omega_I g_e^2 \mu_B^2 S(S+1)}{3kT} \right\}^2 \left\{ \frac{1}{r^6} \right\} \left\{ 4\tau_r + \frac{3\tau_r}{1 + (\omega_I \tau_r)^2} \right\} \quad (7)$$

The program reads the excel sheet by clicking on the “recalculate” button. The script reads from right to the left and downwards. It looks for key words.

In order to calculate the relaxation the program need to know the diameter of the complex (“radius”) the temperature (“T”) to calculate the rotational correlation  $\tau_r$ , the field strengths magnet in MHz (proton Lamor frequency). The script assumes spectra recorded in acetone, a fit function for the viscosity of acetone is included and used automatically. Moreover the Distance between the Fe and the proton is needed “Fe-H”. Also the correlation time for electron relaxation  $\tau_s$  is needed. The output keyword “R2” and “R1” give the sum of Curie and dipolar relaxivities “CR1” and “CR2” give only the Curie relaxivities.

# NMR<sub>2</sub>SCO-exchnage

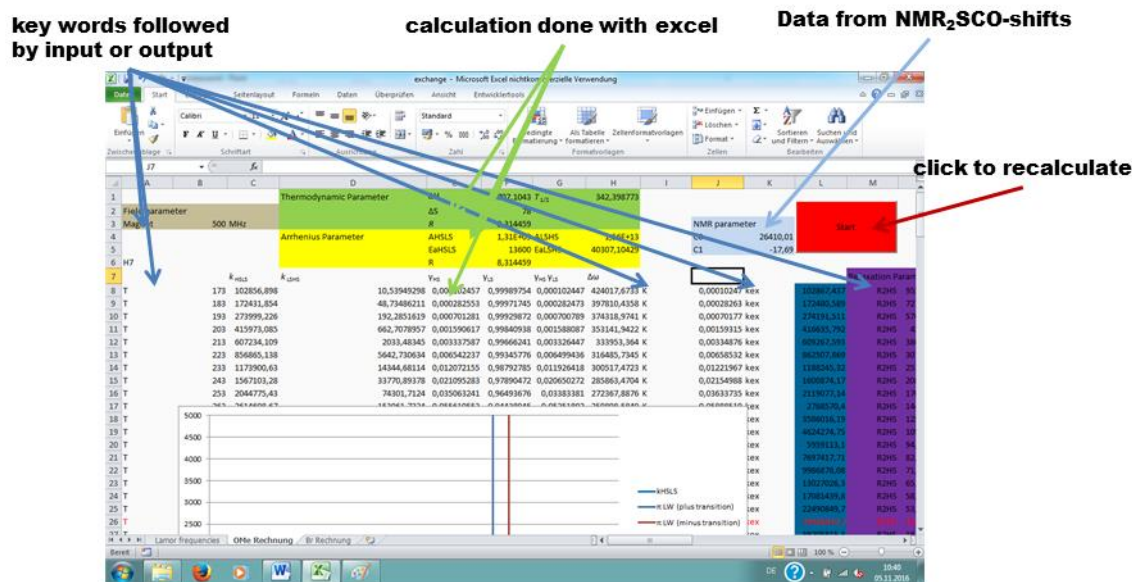


Figure 5: Commented screen shout of the exchange script.

This script calculated the linewidths of a  $Fe^{2+}$  SCO complex using the Bloch equations. As input data it need: the equilibrium constant “K” the correlation time for the exchange “kex” ( $k_{ex} = k_{HSLS} + k_{LSHS}$ ), relaxivities  $R_2$  for the HS “R2HS” and the LS-state “R2LS”; the NMR Parameters “CO” and “C1”, from NMR<sub>2</sub>SCO-shifts, as well as the temperature “T” and the field strengths “magnet” (as proton Lamor frequency) to calculate  $\Delta\omega$  between HS and LS state.  $K$  and  $k_{ex}$  can be calculated by Boltzmann equation and Arrhenius equation as exemplified in the example sheets.

The script collects all data in a matrix and then calculates the solution. It calculates the two “Eigen” values  $\lambda_+$  and  $\lambda_-$  that carry the shifts as imaginary part and the line widths as real part. The four values are outputted after the keywords “Lam\_Rp” – real part of  $\lambda_+$ ; “Lam\_Rm” – real part of  $\lambda_-$ ; “Lam\_Ip” – imaginary part of  $\lambda_+$ ; “Lam\_Im” – imaginary part of  $\lambda_-$ . In order to calculate the real spectrum also the intensity and phase of the two transition must be known. The script assumes that the magnetization at  $t=0$  is equal to the population of the HS and LS state and therefore is calculated from  $K$ . The script provides two coefficients one for  $\lambda_-$  and one for  $\lambda_+$ . Both are complex values therefore four

output keywords are provided. “coeff\_Rp” – real part of  $\lambda_+$ ; “coeff\_Rm” – real part of  $\lambda_-$ ; both give the Lorentzian shaped transition. “coeff\_Ip” – imaginary part of  $\lambda_+$ ; “coeff\_Im” – imaginary part of  $\lambda_-$ . both give the dispersion shaped peak. “coeff\_Ip” and “coeff\_Im” are only close to the coalescence point different from zero. One of the two real parts will quickly go to zero if the fast motion regime is reached.



The line widths are therefore  $\Delta\nu_{\text{Rp}}/\pi$  and/or  $\Delta\nu_{\text{Rm}}/\pi$ . The chemical shifts are  $\Delta\nu_{\text{Ip}}/(2\pi \cdot \text{magnet})$  and  $\Delta\nu_{\text{Im}}/(2\pi \cdot \text{magnet})$ .