Simulation of Second Order Spectra Using SpinWorks

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Introduction

Although we frequently assume that scalar couplings are small compared to the differences in resonance positions due to chemical shifts and analyze spectra in terms of idealized (first order) multiplet structures, this assumption is often violated. It is therefore useful to understand the effects that violation can have on spectra (second order effects). It is also useful to have tools that allow one to extract chemical shifts and coupling constants from spectra in which they cannot be measured directly from positions of multiplet peaks. There are many tools for doing this, including very sophisticated tools based on density matrix calculations (GAMMA, for example, S.A. Smith et. al, J. Magn. Reson.106A, 75-105 (1994)). Here we use a tool based on perturbation theory methods that is part of a general NMR data processing package called SpinWorks. It is far easier to use than GAMMA and it provides an iteration routine that quickly converges to parameters that reproduce experimental spectra.

SpinWorks was written by Kirk Marat at the University of Manitoba for use on Windows systems. There is detailed information and downloading instructions at the University of Manitoba website, http://www.umanitoba.ca/chemistry/nmr/spinworks/index.shtml. There is a detailed manual in pdf format in the Programs/SpinWorks subdirectory on your computer and also downloadable separately from the SpinWorks website. Much of the exercise material included here has been taken from that manual.

SpinWorks has two functions: The first is to provide easy basic off-line processing of 1D NMR and 2D data on personal computers. SpinWorks other function is the simulation and iterative analysis of complex second order spectra including dynamic NMR problems and certain solidstate NMR problems. SpinWorks 2.4 is the forth release of SpinWorks version to contain 2D processing. Full support is included for Bruker (XwinNMR/UXNMR) and Varian (Unix VNMR) data formats. Included F1 detection modes include States, TPPI, States-TPPI, Single Detection (QF), and echo-antiecho.

Simulation Exercise

SpinWorks uses the NUMARIT algorithm as described in: J. S. Martin and A. R. Quirt, J. Magn. Reson. 5, 318 (1971), and modified by Rudy Sebastian and others at the University of Manitoba (who re-named it NUMMRIT). SpinWorks uses a completely original implementation of the NUMARIT algorithm in C++. A small library of sample spin systems is included with the program. In a standard installation these will be located in: C:\Program Files\SpinWorks\SpinSystems. We will also use some new data from a Varian spectrometer located in the Varian subdirectory.

ABX Spectrum Analysis.

1. Start SpinWorks, but do not select any experimental data

2. In the Spin System menu select Edit Chemical Shifts… You will then be presented with a dialog for entering chemical shift and other information describing the spin system. For Group 1, enter 1 for the number of spins, A for the label, proton for the species and 1000 for the chemical shift. For Group 2, enter 1 for the number of spins, B for the label, proton for the species and 1010 for the chemical shift. For group 3, enter 1 for the number of spins, X for the label, proton for the species and 3000 for the chemical shift. (X denotes that a first order calculation should be done, but in genral any symbol can be used)

3. In the Spin System menu select Edit Scalar (J) Couplings… Enter -12 for J(A,B), 2 for J(A,X) and 10 for J(B,X). Note that you must ONLY edit the numerical part of these entries. Do NOT change the coupling labels such as J(1,2) J(A,B) The program needs these labels to identify the couplings.

4. In the Simulation menu select Run NUMMRIT Simulation. In a few seconds, a simulated spectrum will appear on the screen. Zoom in on the X multiplet at ca 6 ppm. (set cursors to the left and right positioning with the mouse, left click for each and select Zo from the menu bar.) Use the cursors to measure the multiplet spacings. (putting a cursor on one line and moving the mouse arrow to the other displays delta in Hz at the bottom) Note that they do not relate all that well to the coupling constants! This is a second-order or virtual coupling effect, and is much more common that one might think.

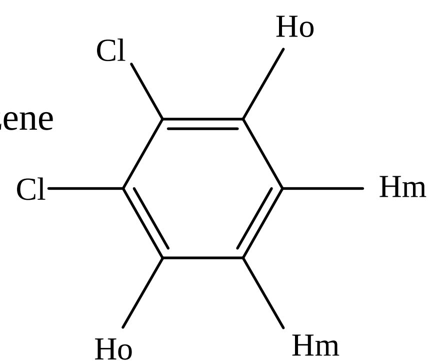
5. Change the J(A,X) coupling to 0. Use Run NUMMRIT Simulation in the Simulation menu again. Note that the X multiplet is still a doublet of doublets, although it is coupled to only one of the other protons. Closer examination of the multiplet shows that there are small satellite peaks (more properly called combination lines) displaced about 16 Hz. from the centre of the multiplet. These lines are an important clue that the spectrum is second order, but are easily lost in baseline noise.

6. Set the B chemical shift to be identical to the A chemical shift (Edit Chemical Shifts…) and re-simulate the spectrum (Run Simulation). The X multiplet looks

like a triplet (with small combination lines) despite the fact that it is only coupled to 1 other proton. How do the measured couplings relate to J(AX) and J(BX)?

Analysis of the Ortho-dichlorobenzene Spectrum.

orthodichlorobenzene



1. Start SpinWorks, and make sure that it is in Varian(VNMR) mode (Options menu, data format)

2. Read the ODCB fid (File: Open...). This is the file is located in C:\Program Files\SpinWorks\varian data\odcb_new. The ODCB fid should now be displayed on the screen. Select ft from the processing menu. The spectrum should now be displayed. Phase it by activating the phasing sliders using the icon with the out-of-phase spectrum on the menu bar. Calibrate the spectrum by putting a cursor on the most upfield peak (left mouse button) and activating the Cal button on the menu bar. Type in 7.3. (Note that there is a check box under Options/preferences that causes auto processing. If you re-open the fid, you may automatically get the processed spectrum)

3. Read in a starting spin system with by loading the odcb_ni file (File: Read Spin System File...). You can examine the starting parameters with the shift and scalar coupling editors if you desire (Spin System menu). Particularly note how explicit two fold symmetry is described with the 2*1 entries in the spins field.

Also note that in a symmetric spin system like AA′BB′, J(A′B′) will automatically be taken to be equal to J(AB) and that

4. Select Edit Simulation Parameters… in the Simulation menu. Set the Display Linewidth (Hz) setting to 0.06 (Yes, really).

5. Run the simulation (Simulation: Run NUMMRIT Simulation). A simulated spectrum somewhat like the experimental will be displayed above experimental spectrum. The vertical offset and scaling of the calculated spectrum can be adjusted with the blue +, -, up-arrow and down-arrow buttons on the toolbar. You can expand the region of interest by setting two cursors at the limits and selecting Zo from the menu bar.

6. The left and right keyboard arrow keys will move a transition cursor across the simulated spectrum. Assign lines to these transitions by pointing to the corresponding experimental peak and clicking with the right mouse button. The peak picking routine is used to find the peak closest to the cursor position. If no peak is found within a reasonable distance of the cursor the transition is assigned to the raw cursor frequency. When a transition is assigned, a red line will be drawn between the transition and it's corresponding peak. Continue assigning all of the lines in the spectrum. A misassigned transition can be deleted with the keyboard "d" key.

7. In the Spin System menu use the Edit Chemical Shifts… and Edit Scalar (J) Couplings… dialogs to check the iterate boxes for both chemical shifts and all four couplings. In the Simulation menu select Edit Simulation Parameters… . Check the Optimize, Autoignore and Autoassign boxes.

8. Run the simulation (Simulation: Run NUMMRIT Simulation). The new spectrum that will be displayed should be a very close match to the experimental. If not, check the simulation output (Simulation: List Simulation Output) for possible clues as to what might be wrong.

9. If the simulation was satisfactory, load the new parameters (Spin System: Load Optimized Parameters) into the spin system editor, and re-run the simulation. Examine the simulation output (Simulation: List Simulation Output). The RMS deviation between the experimental and calculated spectra should be less than 0.005 Hz at this point.

10. Load these final optimized parameters (Spin System: Load Optimized Parameters) and save the new spin system to disk (File: Save Spin System As…) and likewise

save the assigned transitions (File: Save Assigned Transitions As…) for future use.