SPINEVOLUTION Workshop

Problem Set

Problem 1

Simulate a ramped cross-polarization (CP) from ^1H to ^{13}C and study how the degree of polarization transfer depends on the contact time (the duration of the ramp). Try to understand the results. Can this be described using a cross-relaxation matrix approach?

Assume the following conditions for your simulation. Make a linear ramp with the ^{13}C RF field changing in 30 steps from 50 to 56 kHz and ^1H field constant at 63 kHz. Use a spin system of one carbon and three protons: one directly bonded (1.1 Å distance), and the other two from a CH_2 group directly bonded to the carbon (use a z-matrix). Neglect the chemical shifts. Set the spinning frequency to 10 kHz. Run the simulation with the option -t0 to disable the "turbo" algorithm; this will make the computations somewhat faster.

There are at least two ways to simulate this experiment: (1) using a 1D pulse sequence and no scan parameters and (2) using a 0D pulse sequence and a scan parameter. Make both versions. Verify that you get identical results in both cases. Which version works faster? Can you figure out why? Does the answer depend on the duration of the ramp? Make another input file to study the dependence of the polarization transfer on the crystallite orientation for a fixed contact time; use a 2 ms ramp for this simulation.

Problem 2

The main input files in the `examples-jmr/tppmx` directory used to obtain the data to compare the efficiency of SPINEVOLUTION with that of SIMPSON (Table 1 of the JMR paper) are outdated now. In this example, an individual main input file, a coordinates file, and a CSA file are used for each *n* (the number of protons in the system).

Make a single "universal" input file that can be used instead of the individual files to run these simulations for any *n*. This file should load the coordinates from `ch9.cor` and CSA's from `ch9.csa`. Hint: Use the extended molecule functionality and the `-macro` and `-sys` options.

For advanced users. The spin system size cannot be changed within a single simulation, so a separate computation for each *n* must be run even with the file you just created. This can be done manually, from a script, or from some other program. Do this from another SPINEVOLUTION simulation. To be more specific: create an input file that runs such simulations for *n* from 1 to 6, loads the spectra obtained in these simulations, and saves them all in one file. Hints: Define *n* as a scan parameter and run the simulations for different *n* using the `system()` function. You will also need to use the `cat()`, `num2str()`, `eval()`, `save()`, and `load()` functions.

Problem 3

Create an alanine molecule using some reasonable assumptions about its geometry (use a z-matrix). Compute the R^2 (rotational resonance) polarization exchange curves between CO and CA in a [CO,CA]-labeled sample and between CO and CB in a [CO,CB]-labeled sample for n=1 resonance (spinning frequency coincides with the chemical shift difference). Assume a ^1H 500 MHz spectrometer. Include in your simulation as many protons as you have time for to complete the simulation (either 4 or all 7). Assume that the CH_3 and NH_3 groups are hopping infinitely fast. Use a 100 kHz CW ^1H decoupling field during the R^2 exchange. Sample one point per rotor period. Start with the initial density matrix $I_{1z} - I_{2z}$.

Neglect the chemical shifts and CSA's on protons and use the following ^{13}C chemical shift parameters. Isotropic chemical shifts (ppm): 176.8 (CO), 50.9 (CA), 19.8 (CB). Chemical shift anisotropy (ppm): -71 (CO), -20 (CA) -12 (CB). Chemical shift asymmetry: 0.84 (CO), 0.44 (CA), 0.76 (CB). CSA orientation for the CO carbon: the most shielded direction is perpendicular to the sp^2 plane; the least shielded direction is along the CO-CA bond. CSA orientation for the CA carbon: the most shielded direction is perpendicular to the H-CA-CB plane; the least shielded direction is 20° away from the H-CA bond towards the CA-CB bond. CSA orientation for the CB carbon: the most shielded direction is parallel to the CA-CB bond; the least shielded direction can be chosen as you please.

Hint: the most shielded direction coincides with the *z* principal component axis in all three CSA tensors above.

Repeat the simulations with a larger angles set for powder averaging. What can you say about the convergence?

Problem 4

Take-home problem. If you run the `examples-new/quad/quad1_full` example without the `-sz7` option, the results will be noticeably different. Explain why and what you need to do to get the same results again (without using the option).