Dynamic NMR Lineshape Analysis Tool

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Caveat Emptor — not clear that this actually worked, given *k* values presented and lack of actual spectra.

This is a general instruction manual on how to use the dynamic NMR (DNMR) lineshape analysis tool. This tool is useful for simulating temperature dependent NMR spectra to extract rates of exchange (k) which can give insight into exchange mechanisms and the thermodynamic properties of the exchange reaction. This tool interactively defines best-fit model parameters and refines them iteratively.

1. Obtain NMR spectra at various temperatures (VT-NMR). ^{1}H NMR spectra are useful for studying 2-site exchange but this tool can analyze more than 2-site exchange (^{13}C NMR) and provide kinetic data for several spin systems.

2. Open a spectrum. From the "Analysis" drop-down menu, select Line Shape Fitting and go to Dynamic NMR, or type dnmr into the command line.

3. For a 1H spectrum, you need not change anything in the "Parameters" window of the Main tab. Select the "Spectrum" tab.

4. Set the F1P limit to the upper limit of the ppm range you'd like to analyze, set the F2P limit to the lower limit of the ppm range.

5. Go to the "SpinSystem" tab. This is where you will define your spin systems and nuclei. Ex: Propionamide was analyzed where it had two spin systems, one for the molecule and one for the water signal. The molecule had three nuclei, two amide protons and one methyl group. The water has one nuclei.

6. To add a spin system, click the "Add" button once. Click the "Nucleus" tab and click "Add" again to add one nuclei. In the "Nu(iso)" box, you can select the chemical shift that the peak of the nucleus of interest is at, or you can use the Chemical shift button located at the top of the interactive window to line up the simulated peak with the experimental. For a proton nucleus with a spin of ½, your pseudo spin number will be 0.5. If there is more than one spin in the nuclei, this number will need to be increased by increments of ½. The "In Molecule" parameter does not need to be changed. You may also want to adjust the LB and Intensity parameters (also located as interactive buttons at the top of the window) in order to get the best overlap for the nuclei, as well as add coupling constant data (check the J# box and specify a J value in Hz).

7. Add the amount of nuclei needed to complete the spin system and adjust their parameters until you get the highest percentage overlap according to the Best overlap(%) box. After this is complete, click the "Reaction" tab.

8. Check the k box and set an arbitrary k value. This will be adjusted to the correctly simulated one after the iteration takes place. For a two exchange process, the Exchanges parameter should be set to 2. The # 1 From can be set to 1 and the To parameter can be set to 2. The # 2 From can be set to 2 and the To parameter can be set to 1. These parameters adjust the k value according to which nuclei are exchanging in the spin system.

9. The "Molecule" parameters are default for one molecule. These need not be changed unless you are studying the kinetics of a reaction rather than exchange.

10. For each nucleus in the "Nucleus" tab, click on "Step Length". Use "Auto Step" to set the step lengths of the iteration, unless there is a specific one you wish to use, and then click Return. Do the same in the "Reaction" tab for the Exchange parameters.

11. Repeat steps 7 through 10 for each spin system you wish to add.

12. Click on the floppy disk button to save your model and give it a name.

13. Click the "Start the spectrum fit" button. It is bright green with a red arrow inside of it. This begins iteration to refine the parameters.

14. During the iteration, you may click on the Nucleus or Reaction tabs to watch the parameterization.

15. Once iteration is done, the "Log" tab will contain all of the parameters specified before the iteration and then afterwards. To extract the new k value, either go to the REACTION section of the Iteration Result to see k, or go back to the Reaction tab in your spin system and view the value in the k parameter box.

16. You can refine any parameters and step lengths in any of your spin systems to maximize the overlap and extract an exact k value. This program also allows you to save the simulated spectrum by clicking on the "Spectrum" tab and clicking on the "Save Spectrum" and using an empty PROC number. It will save in the same folder as the experimental spectrum.

This program allows one to extract k values at different temperatures to find the rate of exchange for two nuclei at a given temperature and use this to plot an Arrhenius or Eyring equation and extract thermodynamic quantities such as ΔG, ΔH and ΔS.