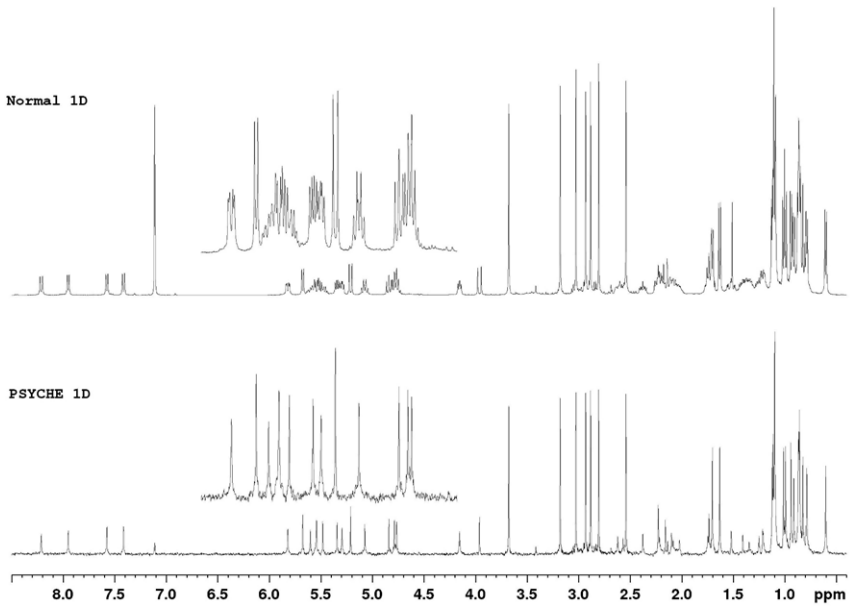
The CBC NMR Laboratory Application Note

Pure Shift NMR Spectroscopy

The pure shift NMR spectroscopy is an emerging NMR technique to produce ultrahigh resolution proton NMR spectrum. Proton NMR spectrum is often overly crowded due to homobuclear proton-proton couplings. While the proton couplings are extremely useful in the molecular structure elucidations, sometime one would wish to have a simplified high resolution spectrum for chemical-shift assignments. The overlapped NMR resonance peaks due to the proton-proton coupling often prevent an accurate measurement and reporting of chemical shifts.

To obtain a "pure shift" spectrum free of the proton-proton couplings, one must decouple so called homonuclear spin-spin couplings while acquiring NMR data. This technique is known as the pure shift NMR spectroscopy, which was first proposed by Zangger and Sterk (ZS)[1] using the spatial frequency labeling method. The ZS method, suffers with a low sensitivity and requires a complex data reconstruction, has been limited its wide application to an open access laboratory. A newly published method PSYCHE (pure shift yielded by chirp excitation) greatly improved the sensitivity[2] and is readily applicable to two-dimensional NMR.[3] This recent development in the pure shift NMR spectroscopy, taking advantage of advanced technologies in hardware and software, made it possible to deploy this very powerful method as a routine experiment in a manual or an automation operation.

We have implemented, tested, and optimized experimental conditions of 1D PSYCHE on AVIII400 and AVIII600 instruments of our laboratory. As an example, a normal and a PSYCHE spectra of cyclosporine in C6D6 are given in the figure below. As it is seen in the figure, in contrast to the normal proton spectrum, all protons appear as *singlet peaks* without spin-spin couplings in the PSYCHE proton spectrum. We also made 2D version of PSYCHE experiments available, however, since the data acquisition of a 2D PSYCHE spectrum is much longer than a routine 2D experiment, we do not recommend to use a 2D PSYCHE experiment in an automation operation.



Operation Instruction

AVIII400 NMR:

On AVIII400 NMR, first acquire a normal proton spectrum, then create a new dataset in experiment number **n**, read "psyche1d" parameter in by a command "*rpar psyche1d*", then start data acquisition by a command "*zg*". The experiment with default parameters takes 6 to 8 minutes. After data acquisition is finished, type "*pshift*", a new reconstructed dataset will be created in a new location (experiment number **1000+n**). In the experiment **1000+n**, process reconstructed NMR data using command "*ef*", then "*apk*". If the sensitivity of the PSYCHE spectrum is not ideal, you may increase number of scans to rerun the experiment.

AVIII600 NMR

On AVIII600 NMR, the PSYCHE experiment is ready to be distributed. A PSYCHE experiment can be added to your user profile upon a request. Data can be further processed on the NMR workstations in 045 BRL using the same steps described above.

References:

(1) K. Zangger, H. Sterk, *J. Magn. Reson*. **1997**, 124, 486-489.

(2) M. Foroozandeh, R. W. Adams, N. J. Meharry, D. Jeannerat, M. Nilsson, G. A. Morris, *Angew. Chem. Int. Ed.* **2014**, 53, 6990-6992.

(3) M. Foroozandeh, R. W. Adams, M. Nilsson, G. A. Morris, *J. Am. Chem. Soc.* **2014**, 136, 11867-11869.

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