PS1D – $^1$H Spectra with Broadband Proton Decoupling

Application Note

Abstract

VnmrJ 3 Software provides easy-to-use, interactive tools for setting up advanced experiments. This allows even novice users to get critical information about their research samples using the most advanced NMR experiments available. This applications note is just one of a series designed to provide step-by-step guidance for setting up sophisticated experiments to collect exactly the data you need for your analyses.

Introduction

One of the attractive features of broadband $^1$H decoupled $^{13}$C NMR spectra is that signals appear as single lines, facilitating the extraction of chemical shifts from a simple line listing. Ordinary $^1$H NMR spectra, however, are typically much more complicated due to homonuclear coupling which can create a number of multiplet components for each proton resonance. Broad or strongly coupled proton multiplets often overlap, seriously compromising the resolution power of proton spectra and making analysis difficult.

Zangger and Sterk published the concept of pure-shift (PS) spectroscopy in 1997 using a 180° pulse that is simultaneously chemical shift and spatially selective. This allows the construction of a synthetic PS1D (Pure Shift 1D) FID piece by piece from the interferograms of a pseudo-2D acquisition. The result is suppression of the multiplet structure, yielding almost an order of magnitude gain in proton spectral resolution. This sequence was rediscovered and modified by Morris and Nilsson, in 2010. The second generation PS1D experiment, which is implemented in VnmrJ 3.2, produces cleaner spectra and is approximately 16 times faster than the original version.
A PS1D Example

Strychnine was used as a test case to demonstrate the utility of the PS1D experiment. Data were collected at 500 MHz on an Agilent DD2 NMR instrument. The $^1$H proton spectrum together with the structure and numbering scheme of strychnine is displayed in figure 1.

The PS1D experiment has only two pulse sequence specific parameters that require consideration. The first is the **Slice Selection Bandwidth** which determines the size of the RF bandwidth of the selective refocusing pulses. The default value of 100 Hz corresponds to 2% of a 10 ppm wide spectral region at 500 MHz. For the optimal decoupling results, the actual bandwidth should not exceed the smallest chemical shift difference expected between any coupled proton pairs. This parameter has a strong inverse relationship to the overall sensitivity of the PS1D spectrum and, in the same time, defines the minimum chemical shift difference where decoupling is still complete.

The second important parameter is the **Pure Shift tau delay**. This parameter has an inverse relationship to the biggest coupling constant to be suppressed; it determines the number of data points used from each acquired element of the pseudo-2D data set to synthesize the final PS1D free induction decay. Larger coupling constants correspond to smaller FID sizes to be concatenated, and will therefore lengthen the overall experimental time to achieve the same line width (2 Hz by default) in the final PS1D spectrum.

The ordinary 1D proton spectrum of strychnine together with two pure-shift proton spectra, collected using 100 Hz and 30 Hz slice selection, is displayed in figure 2. Apart from two regions (indicated by red arrows in figure 2B), most of the signals are

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**Figure 1.** The 500 MHz proton spectrum and the structure of strychnine.

**Figure 2.** The 500 MHz proton spectrum of strychnine (A), with PS1D spectra acquired with 100 Hz (B) and 30 Hz (C) slice selection bandwidth.
completely decoupled even with the default (100 Hz) selectivity. The maximum resolution achievable by the method is clearly illustrated by the expansions in figure 3. In the displayed regions, both PS1D spectra show complete decoupling. The strychnine spectrum between 3.1-3.2 ppm contains three heavily overlapping proton multiplets (H18α, H14, and H11α). The chemical shift difference between H14 and H11α, protons that are not coupled to each other, is only 3.8 Hz, while the width of the two multiplets is about 35 Hz. To achieve the same signal separation between these two protons with the homonuclear couplings retained, one would need a 5 GHz spectrometer.

The expansions in figure 4 are focused on the more challenging regions of the spectra. The chemical shift difference between the aromatic protons H3, H1, and H2 (7.1-7.3 ppm), as well as between the H23αβ geminal proton pair (~4.1 ppm), is well below the 100 Hz bandwidth. As shown in figure 4B, these protons show a complicated, partially decoupled multiplet structure. Reducing the slice selection to 30 Hz (Figure 4C) results in optimal decoupling in the aromatic region, while the H23αβ pair, with a 17 Hz geminal coupling, still exhibits some strong coupling effects. Figures 4B and 4C also demonstrate the sensitivity loss when higher selectivity is required.

Figure 3. Expanded regions of the 500 MHz proton spectrum of strychnine (A), with PS1D spectra acquired with 100 Hz (B) and 30 Hz (C) slice selection bandwidths.

Figure 4. Expanded regions of the 500 MHz proton spectrum of strychnine (A), with PS1D spectra acquired with 100 Hz (B) and 30 Hz (C) slice selection bandwidths.
Experimental Method

The 1D homonuclear broadband-decoupled proton spectrum originates from a pseudo-2D acquisition. While this might sound like a complicated task, in practice it is a simple operation as the necessary tools are either provided in the experiment panels or are executed automatically:

1. Collect a PROTON spectrum as a study in the Study Queue.

2. Load the PROTON spectrum into the current workspace, select Continue Study, and then select Pure Shift 1D from the Experiment Selector (Figure 5).

3. Set the common acquisition parameters and adjust the two sequence specific parameters, if necessary:

   a. **Slice Selection Bandwidth** is set to 100 Hz by default. For optimal decoupling, the actual value should not exceed the smallest expected chemical shift difference between any coupled proton pairs. This parameter has a strong inverse relationship to the overall sensitivity of the PS1D spectrum.

   b. **Pure Shift tau delay**: this parameter has an inverse relationship to the largest coupling constant to be suppressed (8 ms by default, corresponding to a 12.5 Hz coupling constant). Larger coupling constants require shorter tau delays and therefore lengthen the overall experimental time of the PS1D experiment.

4. The experiment is now ready to acquire PS1D data. Use the Submit button in the Study Queue to initiate data collection. When the acquisition is complete, the data are automatically processed and saved.

Conclusions

The PS1D is a very powerful tool for structure elucidation. While it does suffer from limited sensitivity due to slice selective excitation, it provides multiplet-free, or in other words, pure-shift proton spectra. Using PS1D, 1H chemical shifts can be directly extracted, even in crowded spectra, with very high accuracy. The pure-shift concept can be extended to any homonuclear 2D experiments (e.g., NOESY, TOCSY, and more).

References

