Pure shift experiments: 1D Zangger-Sterk. Version 1.0 17th of October 2011

Quick Instructions for setting up a Zangger-Sterk (ZS) pure shift experiment

There are many ways in which you can customize the experiment; these instructions are for a vanilla flavoured experiment, decoupling the entire spectral width. For a detailed description see the list of references.

In order to set up the ZS pure shift experiment you will need to make a few decisions on parameters:

1. The shape/bandwidth of the soft pulse (instruction in a separate section below). Typical shapes are 'rsnob' or 'reburp' with 50-200 Hz bandwidth.[1]
2. The duration of the chunks. This is equal to *sw1*, the spectral width in the indirect dimension, so setting *sw1*=100 Hz gives a chunk duration of 10 ms (1/*sw1*). Typical values of *sw1* are 50-100 Hz. NB *sw*/*sw1* **must** be an integer, or the final pure shift spectrum will contain large artifacts.[2]
3. The number of chunks is equal to *td1*, the number of increments in the indirect dimension; this determines the limiting resolution of the final spectrum (*sw1*/*td1*). Typical values 8-32.[3]

You also need to set the slice-selective gradient, *gpz2*, so that the signal profile under the gradient covers the full range of chemical shifts to be measured. This is most easily done by measuring the spectrum obtained with a single increment of the ZS pulse sequence (*td1*=1) and increasing the amplitude of *gpz2* until the whole spectrum is excited and the relative peak amplitudes are consistent over the full range. An example of a calibration experiment is shown in Appendix 1.

Important acquisition parameters:

Pulse sequence (a graphical representation is given in appendix):

sw1:	Determines the duration of each chunk. *sw*/*sw1* must be an integer[2]. Typical values are 50-100 Hz.
gpz1:	CTP gradient. Typically 50%.
gpz2:	Slice-select gradient. Needs to be calibrated. Typical values 0.25-2%.
spnam2:	Name of soft refocusing pulse. Typically rsnob or reburp.
cnst4:	Number of extra data points to be discarded from the beginning of each chunk, to avoid artefacts caused by DSP. Typically 1-2.
p12:	Duration of soft pulse
p16:	Duration of CTP gradient
sp2:	Power of soft pulse

[1] The bandwidth of the pulse determines the smallest difference in frequency between coupled multiplets that can still be decoupled. A narrower bandwidth lowers the signal to noise by making 'thinner' slices. The shape of the pulse is important for getting clean pure shift spectra. Ideally it should be as square as possible, but 'squarer' pulses are longer and therefore signal loss through T_2 relaxation can get problematic.
[2] If *sw*/*sw1* is not an integer the resulting pure shift FID will contain discontinuities at regular (1/*sw1*) intervals, which will Fourier transform to give sidebands with spacing *sw1*.
[3] The total duration of the resulting pure shift FID is *td1*/*sw1*

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Processing

Raw pure shift data can be processed on different platforms:

TopSpin:
The macro 'pshift' converts the raw data to a new experiment that contains the pure shift FID. This macro detects the dimensions of the experiment and converts 2D→1D or 3D→2D as appropriate. The value of the parameter *cnst4*, as used to define the dropped points in the FID, is used in the reconstruction of the pure shift FID. The 'pshift' macro has been tested for 1D and 2D (DOSY, TOCSY, NOESY and ROESY) ZS pure shift .

The DOSY Toolbox[4]:
Under 'Advanced processing' there is a section (button) that converts raw data into pure shift FIDs for 1D and 2D (DOSY) ZS experiments.

Relevant papers

K. Zangger, H. Sterk, Homonuclear broadband-decoupled NMR spectra, Journal of Magnetic Resonance. 124 (1997) 486-489.

J.A. Aguilar, S. Faulkner, M. Nilsson, G.A. Morris, Pure Shift 1H NMR: A Resolution of the Resolution Problem?, Angew. Chem. Int. Ed. 49 (2010) 3901-3903.

M. Nilsson, G.A. Morris, Pure shift proton DOSY: diffusion-ordered 1H spectra without multiplet structure, Chem. Commun. (2007) 933-935.

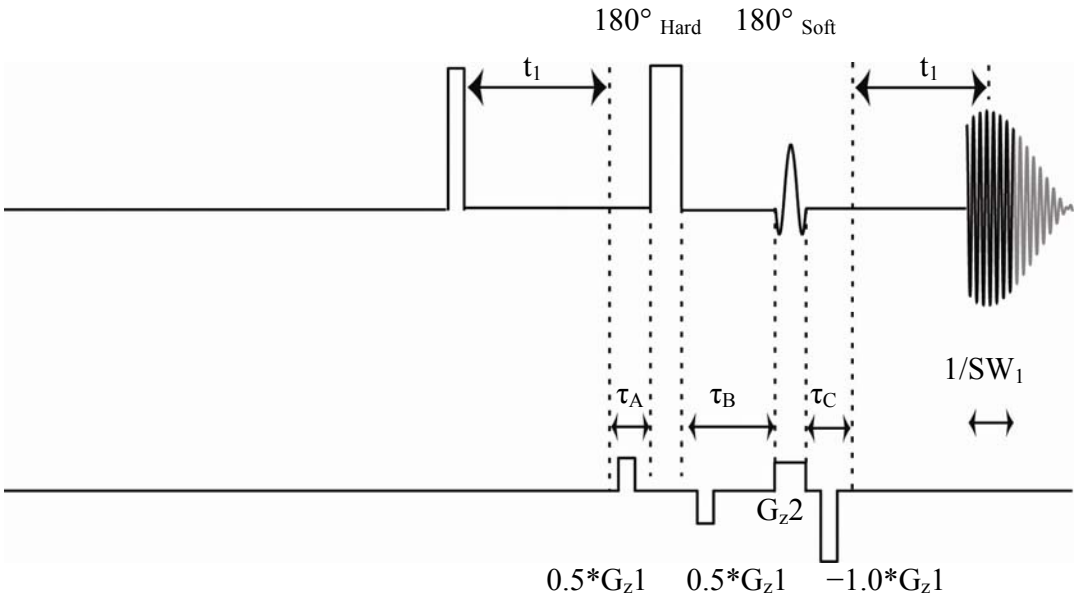
J.A. Aguilar, M. Nilsson, G.A. Morris, Simple Proton Spectra from Complex Spin Systems: Pure Shift NMR Spectroscopy Using BIRD, Angewandte Chemie International Edition. 50 (2011) 9716-9717.

G.A. Morris, J.A. Aguilar, R. Evans, S. Haiber, M. Nilsson, True Chemical Shift Correlation Maps: A TOCSY Experiment with Pure Shifts in Both Dimensions, J. Am. Chem. Soc. 132 (2010) 12770-12772.

[4] More detailed information on the DOSY Toolbox can be found here:
http://dosytoolbox.chemistry.manchester.ac.uk/

Appendix: pulse sequence

Graphical representation of the pure shift pulse sequence



timings **automatically** calculated so that $\tau_A + \tau_C = \tau_B$; $\tau_A = \tau_C$; $\tau_A = 1/4*sw1$

Calibration of selective pulse

'*stdisp*' produces shaped pulse tab.
pick required pulse shape (**spnam2**)
'*calculate bandwidth for refocusing*' – requires pulse name and required selective pulse width (in Hz) and produces a pulse width (**p12**)
'*integrate shape*' – requires pulse length (**p12**), required rotation (180°, in this case), duration of equivalent hard pulse (**p1**) and gives a change in power (add this change to **pl1** to get **sp2**)

Appendix: Calibration of the gradient for slice selection

The strength of the magnetic field gradient applied during the r.f. pulse *p12* to achieve slice selection is set with the parameter *gpz2*. Figures A1 – A3 show the effect of changing *gpz2*. This calibration can be carried out within topspin using the *popt* or *paropt* parameter optimization commands.

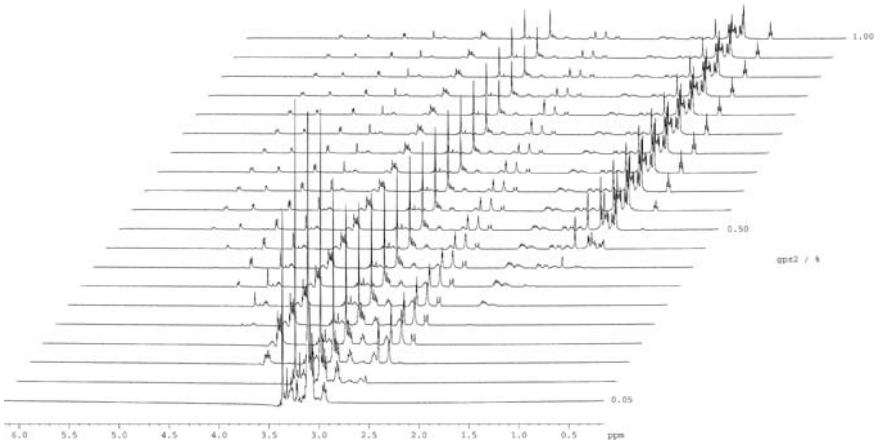


Figure A1: Increasing the strength of the slice selection gradient, *gpz2*, from 0 to 1% of the maximum gradient strength gives an increase in the effective bandwidth of the pulse. *gpz2* should be increased until the outermost signals of interest are observable.

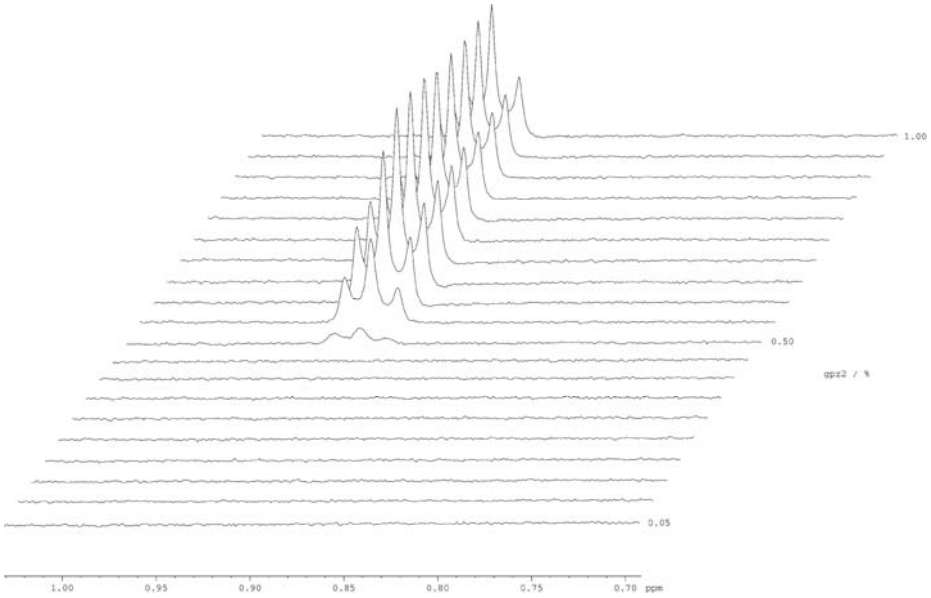


Figure A2: Expansion of figure A1 indicating the rightmost signal. As the gradient strength, *gpz2*, is increased the signal comes within the bandwidth of the pulse and increases in intensity. Further increase in gradient strength results in loss of signal as the effective slice thickness is reduced.

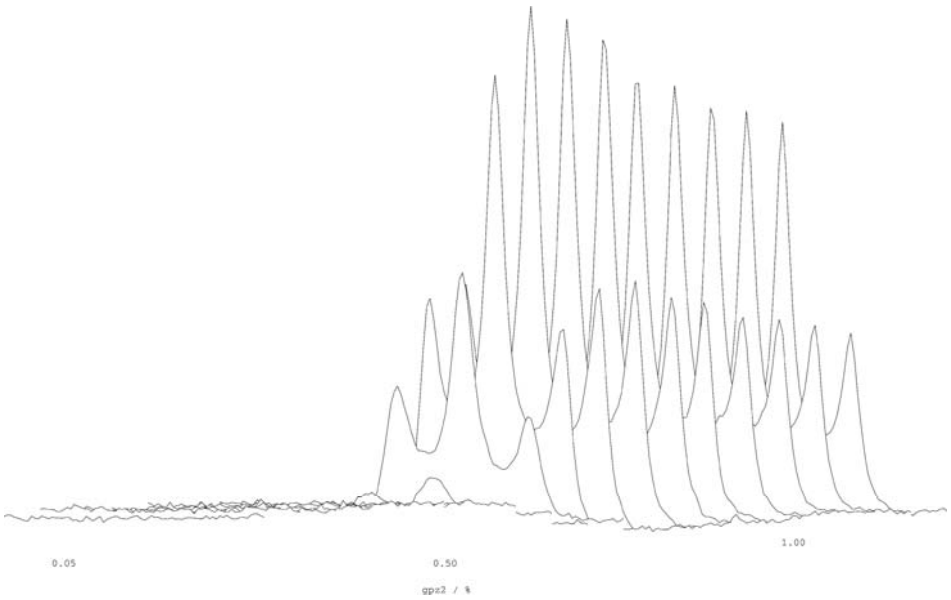


Figure A3: The increase and subsequent decrease in signal intensity of the rightmost signal in the spectrum as the gradient strength, *gpz2*, is increased. Based on these results, *gpz2* would be set to 0.65 – 0.75 % to ensure that all signals are within the bandwidth of the pulse and maximum signal intensity is achieved.