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Direct Polarization Spin Diffusion V.3

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We use this protocol and it's working

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Abstract

Purpose
To obtain 2D spin diffusion spectra in highly correlated protonated systems.

Scope
This protocol describes a very basic implementation of a spin diffusion experiment. It is focused on the case of ^{1}H spin diffusion, *i.e.*, Proton Spin Diffusion (PSD) under fast MAS. This is very straightforward to set up, but provides no mechanism for ^{1}H resolution enhancement via homonuclear decoupling.

Guidelines

This experiment can also be used for the Proton-Driven Spin Diffusion (PDSD) case, for use with X nuclei in protonated systems. The implementation in this sequence is a direct polarization case, and should only be used when direct polarization is preferred over cross polarization. Bruker implements a cross polarization-based experiment in the default **cpspindiff** sequence available in TopSpin.

While labelled as a “spin diffusion” experiment, the **spindiffusion.nmrfam** pulse sequence (and any simple PSD experiment) can also be used to probe chemical exchange dynamics in the same way as an EXSY experiment.

Measuring a PSD build-up curve requires running multiple experiments with different diffusion periods. Interpreting a build-up curve is beyond the scope of this protocol, and for that the user is directed to the literature.

Materials

Definitions:

1. MAS: Magic-Angle Spinning
2. PSD: Proton Spin Diffusion
3. PDSD: Proton-Driven Spin Diffusion

Appendix:

Note that while fast and ultra-fast MAS may be required for sufficient peak resolution in ^{1}H spin diffusion spectra, fast MAS also reduces the rate of spin diffusion. Choose the values of **d21** after careful consideration.

Safety warnings

If proton decoupling is used, user must ensure that the total high-power decoupling time is less than 50 ms or the limit of the probe, whichever is less. This time includes the spin diffusion period.

Before start

User should be familiar with the power, duty cycle, and decoupling limits of the probe.

If proton decoupling is used, user must ensure that the total high-power decoupling time is less than 50 ms or the limit of the probe, whichever is less. This time includes the spin diffusion period.

Expected amount of time SOP will use: 1 to 2 days, depending on sensitivity.

Procedure

1 Load the **spindiffusion.nmrfam** pulse program. Set the following flags and parameters:

1.1 **d1**: Set to 1.3 × previously measured T_1, or 5 × previously measured T_1 for quantitation.

1.2 **ns**: 16∗*n* for full phase cycle; 8∗*n* often suffices.

1.3 **p1**: Previously optimized 90° pulse, using power level **plw1.**

1.4 **plw1**: Previously optimized 90° pulse power, for pulse length **pl1**.

1.5 **d21**: Set to desired spin diffusion time. This will vary from microseconds to seconds depending on the spin system under investigation.

> Note
>
> In ^{1}H spin diffusion, this is typically on the order of milliseconds. For an initial default value for testing with ^{1}H, set to 1 ms.

1.6 If presaturation is desired:
1. Add the **-Dpresat** flag to **zgoptns**.
2. Set **d20**, the presaturation comb delay, to a previously optimized value.
3. Set **l20**, the presaturation comb loop counter, to a previously optimized value.

1.7 If heteronuclear decoupling is desired for X-detect PDSD:
1. Add the **-Dpdsd** flag to **zgoptns**.
2. Set **cpdprg2** to spinal64 or equivalent.
3. Set **pcpd2** and **plw2** to previously optimized decoupling parameters.

> Safety information
>
> Ensure that the acquisition time is below the high-power limit of the probe.

2 Acquire an initial 1D spectrum. Ensure that all expected peaks are present, and that none overlap with the transmitter frequency.

3 Convert to a 2D experiment. Set the following additional parameters:

3.1 **FnMODE:** States-TPPI

3.2 **1 td**: a small value, e.g., 16.

3.3 **1 swh**: sufficiently wide to capture all exchange peaks. This can typically be safely set to the same value as **2 swh**, but can often be much smaller**.**

3.4

Safety information

Decoupling runs through both **2aq**, and **1 aq**. If **-Dpdsd** is set, ensure that the sum of these values is within the high-power decoupling limit of the probe.

4 Acquire an initial 2D spectrum with a minimal number of scans. Ensure that the F1 spectral width is as wide as desired, and that the transmitter is not overlapping with any regions of interest.

5 Adjust **1 td** to ensure sufficient digitization in F1.

6 Adjust **ns** to make best use of available instrument time.

7 Acquire the 2D experiment. If spin diffusion build-up curves are required, repeat with different values of **d21**.

Protocol references

L. Emsley, Spin diffusion in crystalline solids, in: NMR Crystallography, John Wiley & Sons Ltd., 2009.

Bruker Solid State NMR User Manual Z4D10641B, Section 11

Example Data at 1.1 GHz: **usnan.org/ark:/83454/e1b95d684e-aef1-47d6-b03e-71694c493c70**
Example Data at 900 MHz: **usnan.org/ark:/83454/e1e1c3213c-4226-45ae-b1e9-a74327a582ce**
Example Data at 600 MHz: **usnan.org/ark:/83454/e1b2d0f095-3da3-45c1-a919-efb02006da4b**