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Spin-1/2 J-Based DQ-SQ Correlation with Cross Polarization V.2

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We use this protocol and it's working

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Abstract

Purpose

To observe through-bond homonuclear connectivities in protonated systems.

Scope

This protocol uses refocused INADEQUATE with cross polarization (CP-R-INADEQUATE) to probe through-bond connectivities in spin-1/2 systems. As it uses cross polarization, it is best suited to highly protonated systems. For non-protonated systems, refer to the SOP Spin-1/2 J-Based DQ-SQ Correlation with Direct Polarization.

Guidelines

This protocol probes through-bond connectivities. To probe through-space proximities, a pulse sequence using a different double quantum correlation method needs to be used.

DQ-SQ correlation experiments have sensitivity that is inversely proportional to the natural abundance of the nuclide studied. This is in addition to the factor affecting a standard 1D experiment. DQ-SQ correlation experiments on nuclei with low natural abundance (e.g., ^{13}C , ^{29}Si) can require substantial signal averaging. If practical, isotopic enrichment is recommended and sometimes required.

The pulse sequence used by this protocol has high-power proton decoupling during all delay periods. The user must confirm that the total decoupling period, including the acquisition period and all delays, is less than the allowed value for the probe (typically 50 ms). The maximum evolution time, calculated as $0.5 \text{ TD} \times \text{inf1}$, should be included in this calculation.

This experiment is rotor synchronized. For long values of τ , actively triggered rotor synchronization is recommended; however, this is outside the scope of this protocol.



Materials

Definitions:

1. INADEQUATE: Incredible Natural Abundance Double QUANTum Transfer Experiment
2. CP: Cross polarization
3. DQ-SQ: Double quantum-single-quantum
4. FID: Free induction decay

Appendix:

Spinning sidebands can appear in both the single-quantum (MAS) dimension and double-quantum dimension. The user should take care to not assign spinning sidebands as real correlations.

Safety warnings

- ! The pulse sequence used by this protocol has high-power proton decoupling during all delay periods. The user must confirm that the total decoupling period, including the acquisition period and all delays, is less than the allowed value for the probe (typically 50 ms). The maximum evolution time, calculated as $0.5 \text{ TD} \times \text{inf1}$, should be included in this calculation.

Before start

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

User must ensure that the total decoupling period, including all delays, the maximum evolution time, and the acquisition period, is less than the high-power decoupling limit of the probe.

Expected amount of time SOP will use: 1 day

Procedure

- 1 Load the **cp_R-INADEQUATE.nmr** pulse program.
- 2 Set values for the acquisition of an initial spectrum.
 - 2.1 Set the number of scans, **ns**, to a multiple of 32.
 - 2.2 Set the recycle delay **d1** to $1.3 \times T_1(^1\text{H})$, as previously measured.
 - 2.3 Set the ^1H 90° pulse length, **p3**, and pulse power, **plw12**, as previously optimized.
 - 2.4 Set the X channel 90° pulse length, **p1**, and pulse power, **plw11**, as previously optimized.
 - 2.5 Set the X channel CP contact time, **p15**, and pulse power, **plw1**, as previously optimized.
 - 2.6 Set the H channel CP pulse power, **spw0**, and pulse shape, **spnam0**, as previously optimized.
 - 2.7 If used, set the decoupling program, **cpdprg2**, and pulse length, **pcpd2**, to previously optimized values.

Note

Note that the decoupling power uses **plw12**, the same power as the ^1H 90° pulse length.

- 2.8 Set the spinning speed **cnst31** to the MAS frequency in Hz.
- 2.9 Set the acquisition time, **aq**, to the shortest time that captures the full FID.

- 2.10 Set the number of rotor periods for J refocusing, **I5**, such that the J refocusing period, **dtau**, is calculated to be a reasonable value.
1. This should be about $1/4J$, where J is the J -coupling of interest. Note that there is a null point at $1/2J$, and so the value of **dtau** may need to be adjusted if no signal is observed.
 2. A reasonable starting point for optimizing the delay for ^{13}C 1J couplings is 2 ms.

- 2.11 Set the number of rotor periods for the z-filter, **I8**, such that the z-filter period, **dtauz**, is calculated to be a reasonable value. At this point ^1H decoupling during the z-filter is not applied unless the **-Dzdec** flag is set in **zgoptns**.
1. For systems with high isotopic abundance, a reasonable starting value is 2.5 ms.
 2. For systems with low isotopic abundance, this can be 1–3 rotor periods.

3 Acquire an initial 1D spectrum.

4 Optimize the number of rotor periods for J refocusing, **I5**, such that all peaks have adequate intensity.

Note

Note that different environments in the same sample can have different J -coupling values, and so a compromise value that provides adequate, but not optimal, intensity will likely need to be used.

5 Adjust the z-filter settings based on the chemistry of the sample under investigation to minimize anti-phase contributions.

Safety information

In all cases, if the **-Dzdec** flag is set, ensure that the experiment still obeys the high-power decoupling limits of the probe.

- 5.1 If the system has weak proton coupling, a long z-filter (large **I8**) without ^1H decoupling (no **-Dzdec**) can be used, assuming that there is sufficient intensity observed with a given **I8**.
- 5.2 If the system has strong proton coupling and low isotopic abundance, a short z-filter (small **I8**) with ^1H decoupling (**-Dzdec**) can be used.



- 5.3 If the system has strong proton coupling and high isotopic abundance, a moderate z-filter (**I8** set such that **dtau_z** is between 1 ms and 5 ms) without ¹H decoupling (no **-Dzdec**) may be effective, but risks the introduction of proton-driven spin diffusion.
- 5.4 In all cases, antiphase contributions will be more apparent in systems with narrow linewidths.
- 6 Once **I5** and **I8** are adjusted, convert the experiment to a 2D experiment. Set the following 2D parameters:
 - 6.1 **FnMODE**: States, TPPI, or States-TPPI.
 - 6.2 **1TD**: To an appropriate value given the required resolution and T_2 of the samples. Ensure that **1TD** is low enough that the high-power decoupling limit is observed.
 - 6.3 **F1SWH**: An integer multiple of the rotor spinning speed in Hz. Set this value such that the sum of the frequencies of the highest expected connectivity will be included. For ¹³C, 50 kHz to 100 kHz are reasonable starting points.
- 7 Ensure that the total high-power decoupling time ($4 \times \text{dtau} + \text{aq}(\text{F2}) + \text{aq}(\text{F1}) + \text{dtau}_z$ (if **-Dzdec** is set)) is within the acceptable limit of the probe (typically 50 ms). 
- 8 Acquire the 2D spectrum.
- 8.1 To reference the DQ axis, observe a correlation between two peaks with well-determined chemical shifts; the position of this correlation in F1 is the sum of the shifts in F2. 

Protocol references

Lesage, A.; Bardet, M.; Emsley, L. Through-Bond Carbon–Carbon Connectivities in Disordered Solids by NMR. Journal of the American Chemical Society 1999, 121 (47), 10987–10993. DOI: [10.1021/ja992272b](https://doi.org/10.1021/ja992272b).

Cadars, S.; Sein, J.; Duma, L.; Lesage, A.; Pham, T. N.; Baltisberger, J. H.; Brown, S. P.; Emsley, L. The refocused INADEQUATE MAS NMR experiment in multiple spin-systems: interpreting observed correlation peaks and optimising lineshapes. J Magn Reson 2007, 188 (1), 24–34. DOI: [10.1016/j.jmr.2007.05.016](https://doi.org/10.1016/j.jmr.2007.05.016).

Protocol

NAME

CP-Based Saturation Recovery

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Preview

Protocol

NAME

CPMAS

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Preview

Example Data at 1.1 GHz: usnan.org/ark:/83454/e14ebc40f4-e2aa-465f-a01d-01bb74835c82

Example Data at 900 MHz: usnan.org/ark:/83454/e14ed6aa7f-0064-48f2-a967-cc74b19b8862

Example Data at 600 MHz: usnan.org/ark:/83454/e17f4be712-30ec-4ed7-9715-e06f57807e50