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Direct Detect D-HMQC V.3

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We use this protocol and it's working

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Abstract

Purpose
To observe through-space correlations between quadrupolar nuclei and spin-1/2 nuclei.

Scope
The dipolar heteronuclear multiple-quantum coherence (D-HMQC) experiment reveals through-space proximities between two nuclei, facilitating spectral assignments. This implementation is a robust choice for nuclei that are significantly averaged at moderate MAS rates, e.g., 20 kHz. Examples of nuclei pairs which benefit from this experiment are ^{27}Al{^{1}H}, ^{23}Na{^{31}P}, and ^{11}B{^{29}Si}. The indirect-detect, or proton-detect, version of D-HMQC benefits from alternate implementations.

Guidelines

As this implementation of D-HMQC places the dipolar recoupling pulses on the indirect channel, the quadrupolar nucleus should be the one that is detected.

This pulse sequence should not be used for observing the correlations between two quadrupolar nuclei.
This protocol uses the $SR4_1^2$ recoupling scheme.

Materials

Definitions:

1. D-HMQC: Dipolar Heteronuclear Multiple-Quantum Coherence
2. MAS: Magic angle spinning
3. v_r: Magic angle spinning speed
4. v_{rf}: Radiofrequency power
5. X: Direct nucleus
6. Y: Indirect nucleus
7. CT: Central transition

Appendix:

While the $SR4_1^2$ recoupling sequence is robust against minor rf imperfections and MAS instability, in dilute systems this sequence can suffer from t_1 noise. Reducing the **d1** to a very short value (e.g., $0.2 \times T_1$) can mitigate this noise. If doing so, ensure that the overall probe duty cycle is respected.

Before start

Operator should be familiar with acquisition of 2D NMR spectra.

Operator must be familiar with both the MAS spinning limitations of the probe and the RF power limitations of the probe, particularly on the indirect channel.

Operator must be familiar with the duty cycle of the probe.

Expected amount of time SOP will use: 24 hours.

Procedure

1 Identify an appropriate MAS rate, ν_r, for the sample under investigation.

1.1 Note that the Y rf power, ν_{rf}, will need to be set such that $\nu_{rf} = 2\nu_r$.

Safety information

Ensure that this is within the safe limits of the probe.

Note

A MAS speed which returns a rotor period which is an integer number of microseconds can aid in rotor synchronization. E.g., ν_r = 13333.3 Hz, 25000 Hz.

2 Optimize a CT-selective 90° pulse length and power for the X nucleus.

Note

Overly long pulse lengths can cause issues with rotor synchronization.

3 Optimize a Y nucleus 90° pulse width and power that $\nu_{rf} = 2\nu_r$.

Note

For example, an MAS rate of 25 kHz would require ν_{rf} = 50 kHz, *i.e.*, a 5 μs pulse.

4 Load the **dp_d-hmqc_indirect_rec.nmrfam** pulse sequence and set the following parameters:

4.1 **cnst31**: MAS rate in Hz

4.2 **p3**: X channel CT-selective 90° pulse length

4.3 **plw21**: X channel CT-selective 90° pulse power

4.4 **p1**: Y channel 90° pulse length.

Note

This does not have to be the same as in Step 3.

4.5 **plw3**: Y channel 90° pulse power.

Note

This does not have to be the same as in Step 3.

4.6 **plw23**: Y channel 90° pulse power for $SR4_1^2$ recoupling, optimized in Step 3.

Note

This must be the same as in Step 3.

4.7 **p16**: Initial $SR4_1^2$ recoupling time, in µs. 700 µs is a reasonable starting point.

4.8 **d1**: 1.3 × T_1.

5 Acquire an initial 1D spectrum. Repeat with increased **ns** until the signal-to-noise is high enough to allow for optimization.

6 Optimize the value of **plw23** to maximize the signal intensity. This will likely be within 1 or 2 W of the previously optimized value.

7 Optimize the value of **p16** to maximize the signal intensity.

Safety information

The total time used for $SR4_1^2$ recoupling is reported in **p17** in μs. Ensure that this time is short enough to respect the probe duty cycle and maximum sustained high-power pulse limit.

8 Copy the parameters to a new dataset. Convert this dataset to a 2D experiment.

9 Set the following 2D parameters:

9.1 **FnMODE**: States-TPPI

9.2 **F1 TD**: 64, or as appropriate to allow for adequate F1 resolution.

9.3 **F1 SWH**: MAS rate in Hz.

Note

If this spectral window is too narrow, **F1 SWH** can be set to an integer multiple of the MAS rate in Hz.

10 Acquire the 2D spectrum.

Protocol references

Tricot, G.; Trébosc, J.; Pourpoint, F.; Gauvin, R.; Delevoye, L. The D-HMQC MAS-NMR Technique. Annual Reports on NMR Spectroscopy, 2014; pp 145-184. DOI: 10.1016/B978-0-12-800185-1.00004-8

Example Data at 1.1 GHz: usnan.org/ark:/83454/e1df5b48ac-c838-42c2-9a2c-3e7fc6e5bae8
Example Data at 900 MHz: usnan.org/ark:/83454/e178eceb8c-aae4-407d-982f-27f95ca1b4e7
Example Data at 600 MHz: usnan.org/ark:/83454/e1141a31fc-13f2-4a57-9976-8c718eb4e37c

Protocol

NAME

Quadrupole CT-Selective Pulse Width Optimization

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Preview

Protocol

NAME

Quadrupole Non-Selective Pulse Width Optimization

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Preview

Protocol

NAME

Saturation Recovery for Quadrupolar Nuclei

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Preview