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We use this protocol and it's working

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Abstract

Purpose

To probe internuclear distances between a spin-1/2 and spin >1/2 spin pair in a highly protonated system.

Scope

The Resonance Echo Saturation Pulse DObble Resonance experiment with a phase-modulated saturation pulse (PM-RESPDOR) is an effective means of probing through-space internuclear distances between a spin-1/2 nucleus and a quadrupolar nucleus. By using a phase-modulated saturation pulse, it effectively recouples the heteronuclear dipolar interaction over a wide frequency range, and can be used for both integer-spin and half-integer-spin nuclei.

Guidelines

RESPDOR can be used either with direct polarization or, if protons are present, cross polarization. If protons are present, proton decoupling should be applied during both evolution and acquisition. In either case, when considering an X{Y} pair, the preference should be that the Y nucleus has the higher fractional abundance in the sample.

In protonated systems, it can be convenient to calibrate the saturation pulse using a $^1\text{H}\{X\}$ experiment. In this case, SR4_1^2 recoupling is preferred over REDOR recoupling.

The phase modulated pulse can result in significant amounts of reflected power. Care should be taken to avoid excessive reflections.

This protocol is written for the context of highly protonated systems. The procedure for non-protonated systems is broadly similar.

The pulse program **PM-RESPDOR.HXY.i.nmrfam** is written for pseudo-2D acquisition, to allow for better compatibility with queuing experiments and **multizg**. It has flags to adjust between 1D acquisition and pseudo-2D acquisition, to avoid the need to change between different pulse programs.

Materials

Definitions:

1. RESPDOR: Resonance Echo Saturation Pulse DOuble Resonance
2. PM: Phase modulated
3. CP: Cross polarization
4. rf: radiofrequency

Appendix:

If the **zgoptns** flags **-Dsetup_nosat** or **-Dsetup_sat** are not set, the experiment will expect to be run in pseudo-2D mode and will throw the error “td1 symbol not found” if loaded into a 1D experiment. This is normal and can be removed by either setting the above flags, or by changing to a 2D experiment.

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.

Expected amount of time SOP will use: 1 to 3 days, depending on sensitivity.

Procedure

- 1 Load the **PM-RESPDOR.HXY.i.nmrfam** pulse program. Set the following flags and parameters:
 - 1.1 **zgoptns**: -Dsetup_nosat, -DSR421
 - 1.2 **cnst31**: MAS rate in Hz.
 - 1.3 **NUC1**: ^1H
 - 1.4 **d1**: Set to $1.3 \times$ previously measured T_1 .
 - 1.5 **ns**: $64 \times n$ for full phase cycle; $4 \times n$ for optimization if sensitivity permits.
 - 1.6 **CPDPRG1**: SR421.nmrfam
 - 1.7 **p1**: Previously optimized 90° ^1H pulse length, using power level **plw1**.
 - 1.8 **p2**: Previously optimized 180° ^1H pulse length, using power level **plw1**.
 - 1.9 **plw1**: Previously optimized ^1H pulse power for **p1** and **p2**.
 - 1.10 **pcpd1**: Set to a previously optimized 180° ^1H at a rf power of $2 \times \text{cnst31}$

Note

This corresponds to a 180° pulse length of $1/(0.25 \times \text{cnst31})$ if **plw10** is set appropriately.



- 1.11 **plw10**: Set to a previously optimized power level to produce a rf power of $2 \times \text{cnst31}$
- 1.12 **I10**: Set to 3 for full SR4_1^2 supercycling.
- 1.13 **I5**: Set to 1.
- 1.14 **I22**: Set to 1
- 2 Acquire an initial 1D spectrum. Ensure that all expected peaks are present. Save this spectrum, either with wrp or by moving to a new experiment.
- 3 Change **zgoptns** from **-Dsetup_nosat** to **-Dsetup_sat**. Set the following additional parameters:
 - 3.1 **NUC3**: Target nucleus for saturation.
 - 3.2 **CPDPRG3**: modLAREDORphase.nmrfam
 - 3.3 **plw22**: 50 W.
- 4 The saturation pulse is now active. Acquire a spectrum and compare with the spectrum acquired without the saturation pulse. Some dephasing should be observed in the peaks from environments closest to NUC3 atoms.

Note

If there are no protons directly bound to the nucleus of interest, the recoupling block counter **I5** can be increased to a larger value to emphasize the dephasing.
- 5 Optimize **plw22** for maximum dephasing. The dephasing should at first increase with applied power, then reach a plateau.



Safety information

Pay careful attention to probe power limits: the rapidly changing phase of the saturation pulse can lead to power transients.

- 6 If necessary, adjust the saturation pulse length by increasing **I22** by steps of 1.

Note

I22 does not generally need to be greater than 2. Use caution when increasing beyond that length.

- 7 Create a new experiment and load the pulse sequence **cp.PM-RESPDOR.HXY.i.nmrfam**. Load the following parameters:

- 7.1 Adjust the channel routing using **edasp** so that **NUC1** is the detect nucleus, **NUC2** is ^1H , and **NUC3** is the indirect nucleus.
- 7.2 **zgoptns**: remove the -DSR421 flag
- 7.3 Set **cpdprg1** to **redor.nmrfam**.
- 7.4 Set **p2** and **plw1** to a detect nucleus 180° pulse.
- 7.5 Set **pcpd1** and **plw10** to a detect nucleus 180° pulse. This can be the same parameters as above.
- 7.6 Set **I10** to 4.

Note

This sets the the number of REDOR pairs per recoupling increment; 4 implements xy-8 cycling. A lower value of **I10** can be used if the dipolar coupling is very large.

- 7.7 Set **p15** and **plw15** to previously optimized CP contact time and X power.



- 7.8 Set **cpdprg2** to an appropriate decoupling sequence, e.g., **spinal64**.
- 7.9 Set **pcpd2** and **plw12** as appropriate for the optimized decoupling sequence.
- 7.10 Set **p1** and **plw2** to a proton 90° pulse.
- 7.11 Set **spnam0** and **spw0** to a previously optimized CP shape and proton power.
- 8 Acquire an initial pair of spectra, one with and one without the saturation pulse, by using the flags **-Dsetup_nosat** and **-Dsetup_sat**.

Note

If necessary, the recoupling block counter **I5** can be increased to a larger value to emphasize the dephasing.

- 9 Create a new experiment and set it to 2D acquisition mode.
- 9.1 The 2D acquisition mode **FnMODE** must be set to **QF**.
- 9.2 Remove the **-Dsetup_nosat** and/or **-Dsetup_sat** flags.
- 10 Set **1td** appropriately to sample a sufficiently long recoupling time.

Note

This is inherently a sample-dependent quantity.

Note

The recoupling time can be calculated as **d10** × (**1td**) when **I5** is set to 1.



- 11 Adjust **ns** to best use available experiment time.

Note

Remember that the data at longer recoupling times will have lower S/N ratios. The number of scans should be set to ensure sufficient S/N at the later points.

- 12 Ensure **I5** is set to start sampling at the desired portion of the recoupling curve.

Note

To sample at the beginning of the recoupling curve, set **I5** to 1.



- 13 Acquire the pseudo-2D experiment. The data will be stored in alternating rows, first with no saturation, then with saturation.

- 14 Process the RESPDOR curve.



Protocol references

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Protocol

NAME

CPMAS

CREATED BY

NMRFAM Facility

Preview

Example Data at 1.1 GHz: usnan.org/ark:/83454/e11dd7e5d4-6b72-406d-be8b-e1317dbccb63

Example Data at 900 MHz: usnan.org/ark:/83454/e1345bf973-2811-401c-96e4-3ffe1a4c0064