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We use this protocol and it's working

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Abstract

Purpose
To probe internuclear distances between either two spin-1/2 nuclei, or a spin-1/2 nucleus and a quadrupolar nucleus with a small quadrupolar coupling constant.

Scope
The Resonance Echo DOuble Resonance (REDOR) experiment is an effective means of probing through-space internuclear distances between nuclei. It is limited to systems where both nuclei are spin-1/2, or where one nucleus is spin-1/2 and the other is a half-integer-spin quadrupole where you can obtain good spectra via magic angle spinning (e.g., ^{11}B, ^{23}Na, ^{27}Al). For systems where the quadrupole is integer spin (*e.g.*, ^{14}N), or has a large quadrupole coupling constant (*e.g.*, ^{139}La), or where both nuclei are quadrupoles, the Resonance Echo Saturation Pulse DOuble Resonance (RESPDOR) experiment is preferred.

Guidelines

When considering target X{Y} pairs of nuclei, the preference should be that the Y nucleus has the higher fractional abundance in the sample to allow for more dynamic range in the REDOR curve. If both abundances are similar, the direct nucleus should be the one with more favourable spectral properties, particularly sensitivity per unit time and peak resolution. Note that in cases where the Y nucleus is sparsely abundant, REDOR dephasing will be challenging to observe.

In protonated systems, heteronuclear decoupling should be applied during both evolution and acquisition periods. Care must be taken to ensure that the total decoupling time and power does not exceed probe limits.
When a quadrupole is the indirect nucleus, it is important to minimize the number of pulses on the indirect channel. The appropriate flag must be set when the quadrupole is the indirect nucleus.

The pulse program **REDOR.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 during setup.

Materials

Definitions:

1. REDOR: Resonance Echo DOuble Resonance

Appendix:
If the **zgoptns** flags **-Dsetup_norec** or **-Dsetup_rec** 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.

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 REDOR evolution 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 REDOR evolution period.

Expected amount of time SOP will use: 1 to 4 days, depending on sample sensitivity.

Procedure

1 Load the **REDOR.HXY.i.nmrfam** pulse program as a **1D** experiment. Set the following flags and parameters:

1.1 **zgoptns:** -Dsetup_norec.

1.2 **NUC1**: Direct/observed nucleus.

1.3 **cnst31**: MAS rate in Hz.

1.4 **d1**: Set to 1.3 * previously measured T_1.

1.5 **ns**: 64∗*n* for full phase cycle; 4∗*n* for optimization if sensitivity permits.

1.6 **l5**: Set to 1.

1.7 **l10:** Number of REDOR pulse pairs per recoupling block.

> Note
>
> Set to 4 for xy-8 phase cycling; set to 1 for the shortest possible recoupling block.

1.8 **p1**: Previously optimized excitation X pulse, using power level **plw1.**

1.9 **p2**: Previously optimized 180° X pulse, using power level **plw11.**

> Note
>
> If the X nucleus is a quadrupole, this should be a central-transition-selective 180° pulse.

1.10 **plw1**: Previously optimized X pulse power for excitation pulse **p1**.

1.11 **plw11**: Previously optimized X pulse power for 180° X pulse **p2**.

2 If the indirect nucleus is quadrupolar, add the **-DI_quad** flag to **zgoptns** and set the following additional parameters:

2.1 **CPDPRG1**: redor.nmrfam

2.2 **pcpd1**: Set to a previously optimized direct nucleus 180° pulse length, using power level **plw10**.

2.3 **plw10**: Set to a previously optimized direct nucleus 180° pulse power.

2.4 **NUC3**: Indirect quadrupolar nucleus.

2.5 **o3**. Ensure that the indirect nucleus frequency is set such that the resonances of interest will be irradiated.

3 If heteronuclear decoupling is desired, add **-Ddec** to **zgoptns**. Set the following additional parameters:

3.1 **NUC2**: Heteronuclear decoupling nucleus, typically ^{1}H.

3.2 Set **cpdprg2** to an appropriate decoupling sequence, e.g., **spinal64**.

3.3 Set **pcpd2** and **plw12** to previously optimized decoupling pulse length and power.

3.4

Safety information

Ensure that the total decoupling time does not exceed the high-power decoupling limit of the probe, typically 50 ms. Decoupling is active during both **d10** periods, both **d18** periods, **d16**, **d19**, and **aq**.

4 If presaturation of the direct nucleus is desired, add **-Dpresat** to **zgoptns**. Set the following additional parameters:

4.1 Set **d20** to a previously optimized presaturation comb delay.

4.2 Set **l20** to a previously optimized presaturation comb loop count.

5 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.

6 Change **zgoptns** from **-Dsetup_norec** to **-Dsetup_rec**. This enables the REDOR recoupling.

7 If the indirect nucleus is spin-1/2 and the **-Dl_quad** flag is not active, set the following additional parameters:

7.1 **NUC3:** Indirect spin-1/2 nucleus.

7.2 Set **cpdprg1** to redor.nmrfam.

7.3 Set **p3** to a previously optimized indirect nucleus 180° pulse length, using power level **plw10**.

7.4 Set **plw10** to a previously optimized indirect nucleus 180° pulse power.

7.5 **o3**. Ensure that the indirect nucleus frequency is set such that the resonances of interest will be irradiated.

8 If the indirect nucleus is quadrupolar and the **-DI_quad** flag is active, set the following additional parameter:

8.1 Set **plw11** to the power for a previously optimized CT-selective 180° pulse; this is the power level for **p3** for a quadrupole.

9 The REDOR recoupling is now active. Acquire a spectrum and compare with the spectrum acquired without the recoupling (**Step 5**). Some dephasing should be observed in the peaks from environments
closest to NUC3 atoms.

9.1 If no dephasing is observed, the recoupling block counter **l5** can be increased to a larger value to increase the dephasing. If **l5** is increased, an additional spectrum with the flag **-Dsetup_norec** must also be acquired to ensure an accurate comparison is made.

10 It is important to ensure that some dephasing can be observed before proceeding with the protocol. If dephasing is not observed with an increased **l5**, double-check all parameters, but particularly 180° pulse lengths, **cnst31**, and **o3**.

11 Once dephasing has been confirmed, create a new experiment and set it to 2D acquisition mode. Set the following parameters:

11.1 The 2D acquisition mode **FnMODE** must be set to **QF**.

11.2 Set **l5** to 1.

12 Set **1 td** appropriately to sample a sufficiently long recoupling time.

> Note
>
> The recoupling time can be calculated as **d10 × (1 td)** when **l5** is set to 1.

> Note
>
> This is inherently a sample-dependent quantity.

12.1 Remove the **-Dsetup_rec** and **-Dsetup_norec** flags from **zgoptns**.

13 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.

14 Ensure **l5** is set to start sampling at the desired portion of the recoupling curve.

Note

To sample at the beginning of the recoupling curve, set **l5** to 1.

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

16 Process the REDOR curve.

Protocol references

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Chan, J. C.; Eckert, H. Dipolar coupling information in multispin systems: application of a compensated REDOR NMR approach to inorganic phosphates. Rotational echo double resonance. *J. Magn. Reson.* **2000**, *147* (2), 170-178. DOI: 10.1006/jmre.2000.2191

Protocol

NAME

Quadrupole CT-Selective Pulse Width Optimization

CREATED BY

NMRFAM Facility

Preview

Protocol

NAME

Saturation Recovery

CREATED BY

NMRFAM Facility

Preview

Example Data at 1.1 GHz: usnan.org/ark:/83454/e1d014354b-fc7d-4014-850b-7ad5c2eef781
Example Data at 900 MHz: usnan.org/ark:/83454/e13d5e9240-d3c4-46a9-92eb-a43b214b9c95
Example Data at 600 MHz: usnan.org/ark:/83454/e1b33966ec-f84a-4f5f-b2f8-7d0c859b7c2b