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We use this protocol and it's working

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Abstract

Purpose

To collect a cross-polarization spectrum of a spin-1/2 nucleus under slow magic-angle spinning conditions.

Scope

This protocol is focused on acquiring cross-polarization (CP) magic-angle spinning (MAS) spectra at comparatively low spinning rates (generally less than 20 kHz). Under these conditions the Hartmann-Hahn condition is reasonably easy to satisfy, and generally requires less stringent matching parameters than under fast MAS rates (greater than 20 kHz, becoming more complicated as spinning speeds increase).

Guidelines

This protocol is written under the assumption that the polarization source nucleus is ^1H (i.e., $X\{^1\text{H}\}$ CPMAS), as this is by far the most common use case. It would function equally well if the polarization source nucleus is ^{19}F . However, it is not suitable for cases with partial fluorination where ^1H decoupling is desired during acquisition.

This protocol is not intended for the optimization of CPMAS where the detected nucleus is quadrupolar. In general, cross-polarization involving quadrupolar nuclei is complicated and rarely recommended.

Due to the possible differences in CP enhancement between different chemical environments, cross-polarization is not considered to have generally quantitative relative integrated intensities. However, in cases where chemistries are very similar between samples, it may be possible to rely on qualitative intensity differences. When highly reliable quantitative relative intensities are required, Bloch decay experiments are recommended.

The pulse sequence associated with this protocol (**cpmas.nmrfam**) has multiple flags allowing for extended functionality. In the absence of any flags, the sequence functions as a $X\{^1\text{H}\}$ CPMAS sequence with ^1H decoupling during acquisition. This protocol only describes that use case. The additional flags allow for the sequence to function as a Bloch decay experiment with ^1H decoupling, a “cp90” sequence (involving an X flip pulse after CP contact), and a cross-polarization Hahn echo sequence.

The pulse sequence associated with this protocol (**cpmas.nmrfam**) uses target radiofrequency (rf) fields to allow for powers to be optimized using kHz, not W or dB. This requires that both accurate calibrated pulse widths and powers be provided, and that the amplifiers in use be properly linearized. If either the amplifier linearization or the input parameters are not accurate, some optimization may be required even with the use of kHz.

In the cases of highly dynamic systems, or with very low dipolar couplings, it may be challenging to obtain CP signal at all.



Materials

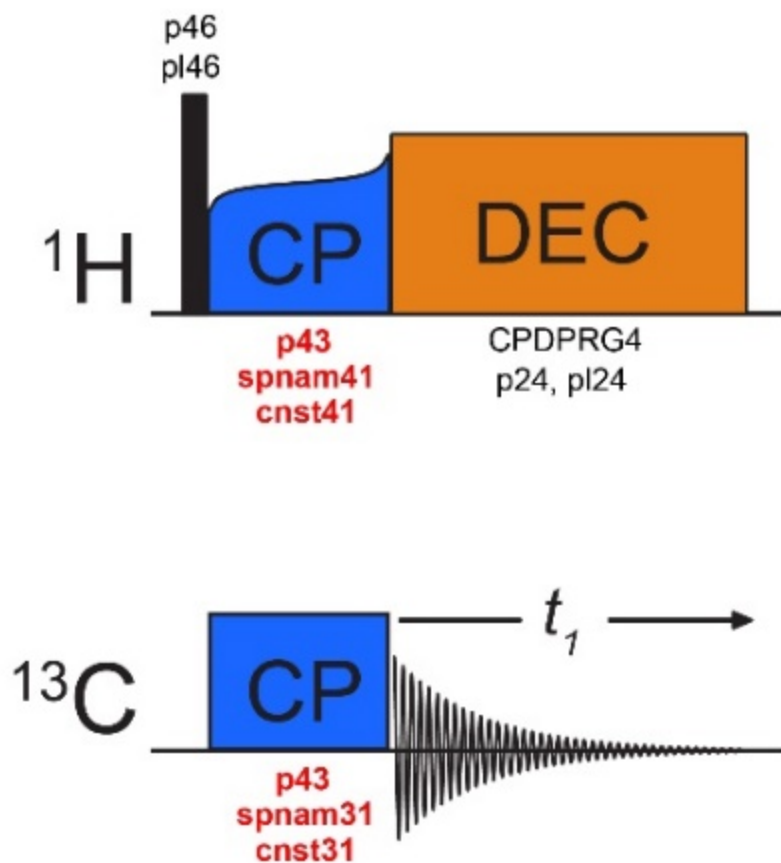
Definitions:

1. CP: Cross Polarization
2. MAS: Magic Angle Spinning
3. rf: Radiofrequency
4. HH: Hartmann-Hahn
5. ω_r : Spinning Rate
6. ω_H : ^1H rf field
7. ω_X : X rf field
8. HORROR: HOmonucleaR ROtary Resonance

Appendix:

The pulse sequence attempts to calculate powers upon every compilation, including when it is first loaded. If **p13** or **p14** is set to 0 (a common default parameter), TopSpin will throw a division by zero error and refuse to proceed. To avoid this, immediately after loading **cpmas.nmrfam**, set **p13** and **p14** to any non-zero pulse length, e.g., 5 μs .

^1H decoupling in **cpmas.nmrfam** uses **p24** and **plw24**. Any decoupling shape can be used as long as it relies on these two parameters. This can be done by prepending **0.5u pl=p124** to the beginning of the cpd file, and changing **pcpd** to **p24**.



Safety warnings

- ⚠ This protocol assumes the use of high-power ^1H decoupling. As such, a long acquisition (50 ms) protection limit is set. This protection limit should not be disabled while high-power decoupling is in use.

Before start

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

Unless low-power proton decoupling is used, user must ensure that the total high-power time is less than 50 ms or the limit of the probe, whichever is less.

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

Procedure

- 1 Begin with at least a roughly optimized ^1H pulse width and power, and similarly a roughly optimized X pulse width and power. Beginning with optimized powers will reduce the need for later parameter optimization; however, these parameters can be revised during this protocol.
- 2 Set the following initial parameters:
 - 2.1 **aq**: Set to 50 ms or less. This is required for the safety of the probe.
 - 2.2 **d1**: Set to $1.3 \times T_1(^1\text{H})$; if quantification is being attempted, instead use $5 \times T_1(^1\text{H})$. If $T_1(^1\text{H})$ is not known, 1 s is often adequate for an initial parameter. Ensure that the time is at least 20 times longer than **aq**; for example, if **aq** is 50 ms, **d1** should be at least 1 s.

Note

See the Warnings section for discussion of quantification and cross-polarization.
 - 2.3 **o1**: Set the X transmitter frequency to the desired center of expected chemical shift range.
 - 2.4 **o2**: Set the ^1H transmitter frequency to the center of the ^1H chemical shift range.
- 3 Ensure the sample is spinning at an appropriate MAS rate (ω_r).
- 4 Set the following calibrated pulse input parameters:
 - 4.1 **p13**: Set to the previously optimized X pulse width.
 - 4.2 **plw13**: Set to the previously optimized X pulse power.

- 4.3 **p14:** Set to the previously optimized ^1H pulse width.
- 4.4 **plw14:** Set to the previously optimized ^1H pulse power.
- 5 Set the ^1H decoupling parameters.
 - 5.1 **p24:** Set to an appropriate pulse width for the decoupling sequence being used.
 - 5.2 **cnst24:** Set to the desired ^1H decoupling strength in kHz. When setting this value, ensure that the resulting calculated power level (**plw24**) is within the acceptable probe power limits.
 - 5.3 **cpdprg4:** Set to an appropriate decoupling sequence. Standard Bruker decoupling sequences may require a modification to function with **cpmas.nmrfam**; see Appendix for details.
- 6 Set the cross-polarization excitation parameters.
 - 6.1 **p46:** Set the ^1H excitation pulse width. A good default value for this is the same value as p14.
 - 6.2 **plw46:** Set the ^1H excitation pulse power. A good default value for this is the same value as plw14.
- 7 Set the following cross-polarization shape parameters:
 - 7.1 **spnam31:** Set to the desired shaped pulse for the X contact pulse. If not using a shaped pulse on X, set to **cw** for a square pulse.
 - 7.2 **spnam41:** Set to the desired shape for the ^1H contact pulse. A ramped pulse is generally recommended to provide a broader HH match condition.
- 8 Set an initial CP condition.

- 8.1 Set the CP contact time, **p43**, in microseconds. If a reasonable contact time is not known ahead of time, set to 1000 μs for an initial condition.
- 8.2 The CP rf fields should satisfy either the zero quantum ($\omega_{\text{H}} - \omega_{\text{X}} = n \cdot \omega_{\text{r}}$) or double quantum ($\omega_{\text{H}} + \omega_{\text{X}} = n \cdot \omega_{\text{r}}$) HH condition. The zero quantum condition is typically preferred for slow spinning speeds, while the double quantum is preferred for fast spinning speeds. In either case, HORROR conditions (ω_{H} or $\omega_{\text{X}} = 0.5 \cdot \omega_{\text{r}}$) or general rotary resonance conditions (ω_{H} or $\omega_{\text{X}} = n \cdot \omega_{\text{r}}$) should be avoided.
- 8.3 Typical values for both ω_{H} and ω_{X} are $n/2 \cdot \omega_{\text{r}}$ ($n = 3, 5, 7, 9$), usually with ω_{H} being higher. For example, $\omega_{\text{H}} = 9/2 \cdot \omega_{\text{r}}$ and $\omega_{\text{X}} = 7/2 \cdot \omega_{\text{r}}$ would be a typical starting point.
- 8.4 The power of a shaped pulse (e.g., a ramped pulse used for **spnam41**) set in TopSpin (e.g., **spw41**, calculated using **cnst41**) refers to the highest power point in the shaped pulse. To ensure that the ramp sweeps symmetrically over the HH condition, divide the appropriate constant (e.g., **cnst41**) by the ramp midpoint fraction. Ensure that the resulting power (e.g., **spw41**) is within the probe power limit.
1. For example, in a tangent ramp from 70 to 100, divide **cnst41** by 0.85. Ensure that **spw41** is less than the probe ^1H power limit.
- Safety information**

If the required power for $n/2 \cdot \omega_{\text{r}}$ would exceed the probe limit, reduce the target field to $(n-1)/2 \cdot \omega_{\text{r}}$.
- 9 Acquire an initial spectrum using a small number of scans. Ensure that the spectrum is phased appropriately.
- 10 If the sensitivity is adequate at this point, increase the number of scans and collect the final spectrum. If not, proceed to the next steps for further optimization.
- 10.1 Calibration of the ^1H calibration pulse can be performed by optimizing the ^1H excitation pulse **p46** and observing the nutation curve for the intensity maximum, or preferably the first null point. After optimizing this pulse, update the value in **p14**.
- 10.2 Calibration of the X calibration pulse can be performed by using **p36**, either with direct polarization via the **-Ddirect** flag, or with a CP flip pulse via the **-Dflip** flag. After calibration of **p36**, update the value in **p13**.
- 10.3 The CP contact condition can be refined by optimizing **cnst31** or **cnst41**. Before running the array, check to see that the highest power in the array is within probe power limits.





Typically only one of **cnst31** or **cnst41** needs optimization.

- 10.4 Optimize the CP contact time **p43**. 1 ms is typically sufficient to obtain signal, but will not necessarily provide the optimal signal.

Note

It is important to note that the optimal contact time will vary with the $T_{1\rho}$ of the individual environments in the sample. The optimal contact time for one environment may be a very poor choice for another environment. Compromises may need to be made for optimal overall sensitivity.

Safety information

The contact time **p43** typically uses high-power rf. In general, the contact time should be less than 10 ms. Longer times are rarely required, but can be necessary; in these cases, be sure to reduce the acquisition time **aq** to ensure that less than 50 ms of high-power rf is being applied per scan.

- 11 If desired, optimize the CP pulse shape. There are no available pulse sequence parameters to do this; pulse shape optimization requires use of the Shape Tool available in TopSpin (**stdisp**), or advanced tools external to TopSpin, both of which are beyond the scope of this protocol.
- 12 Increase the number of scans appropriately for desired S/N ratio, or available experimental time.
- 13 Acquire the optimized spectrum.

Protocol references

Rovnyak, D. Tutorial on analytic theory for cross-polarization in solid state NMR. *Concepts in Magnetic Resonance Part A* 2008, 32A (4), 254-276. DOI: [10.1002/cmr.a.20115](https://doi.org/10.1002/cmr.a.20115).

Hediger, S.; Meier, B. H.; Kurur, N. D.; Bodenhausen, G.; Ernst, R. R. NMR cross polarization by adiabatic passage through the Hartmann—Hahn condition (APHH). *Chemical Physics Letters* **1994**, 223 (4), 283-288. DOI: [10.1016/0009-2614\(94\)00470-6](https://doi.org/10.1016/0009-2614(94)00470-6).

Example Data at 1.1 GHz: usnan.org/ark:/83454/e1ef4b21b5-226f-416c-973f-78b44b7ba8ab

Example Data at 900 MHz: usnan.org/ark:/83454/e1fdfe4465-73f8-4519-aeb5-d75fa253f9c1

Example Data at 600 MHz: usnan.org/ark:/83454/e1c2c6092c-8d24-4e71-a89c-2010c886c18d