

Manual for the ROSMAS script

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1 Requirements

The analytical ROSMAS script was created using Matlab R2016b. Earlier versions are not guaranteed to work.

1. Larmor frequency ω_L (MHz)
2. Spinning frequency ω_R (Hz). Must be less than the chemical shielding anisotropy.

3. The fiber angle deviation from the rotor frame β_1 (rad)
4. The complete Chemical shielding/shift sensor i.e. the principal axis components σ_{11} , σ_{22} , σ_{33} (ppm) and the Euler angles α_0 , β_0 , γ_0 (rad)

2 Introduction

Molecular orientation distributions of partially oriented fibers/solids can be investigated using ROSMAS NMR spectroscopy. The manual describes how to use ROSMAS Matlab script and includes a run through of the theory and experiment setup. The experimental method is that of Harbison and Spiess^[5] For more information on the theoretical background, please consider the referred articles.^[1-10]

ROSMAS relies on the principal that a theoretical intensity can be calculated from the chemical shielding anisotropy and experimental parameters in relation to a specified orientation distribution function (ODF). Harbison et al.[5] used the well established Legendre polynomial function, which is an infinite sum of linear function with decreasing contributions called the order parameter $\langle P_\ell \rangle$.

$$f(\beta) = \sum_{\ell=0}^{\infty} \left(\ell + \frac{1}{2} \right) \cdot \langle P_\ell \rangle \cdot P_\ell(\cos \theta) \quad (1)$$

$$P_\ell(\cos \theta) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d \cos^\ell \theta} (\cos^2 \beta - 1)^\ell \quad (2)$$

The ODF is then introduced to the ROSMAS experiment model so the order parameters can be calculated using Equation (3).

$$(I_{M,N})_{exp} = \sum_{\ell=0}^{\infty} \langle P_\ell \rangle (I_{\ell,M,N})_{calc} \quad (3)$$

In practice, an infinite sum is not used. Depending on the quality of the spectrum, P_2 , P_4 , P_6 and P_8 are likely to be the the only order parameters that can be measured.

2.1 Experimental

Anisotropic chemical shielding is spatially dependent although is often too broad to analyze effectively on static anisotropic samples. By rotating the sample at high speeds, chemical shielding will average out and therefore anisotropic information is lost. Rotating the sample at slow speeds will produce several spinning sideband peaks, separated by the rotation frequency. Peaks can be individually evaluated nevertheless, the essential molecular orientation can not be derived exclusively from a typical cross polarized spectrum. The underlying cause is our rotating anisotropic source is sampled at essentially random starting positions, making the CSA effect only shown as an rotational average. To device a pulse sequence with the CSA orientation dependency intact, a rotational dependence is implied by starting a cross polarization pulse sequence with a tachometer trigger, hence preserving the information of the CSA starting position. Figure 1 shows a pulse sequence where t_1 is sampled n times over a rotor period with $\Delta t_1 = 1/(f \cdot n)$. Svenningsson et al. sampled $n = 10$ times and Harbison et al.[5] sampled $n = 16$ times. High n sampling is only beneficial if the spectrum is well resolved with high degree of molecular order. The resulting data set is sequentially Fourier transformed on both directions. After the Fourier transform, the ω_1 axis is denoted by integers of M . The side bands of a single CSA source are denoted on the ω_2 axis by their periodic integer N , which has the shift $N\omega_R$ from its center band. The resulting two dimensional absorption spectrum is phase shifted in the M direction to account for the initial position of the sample in the rotor.

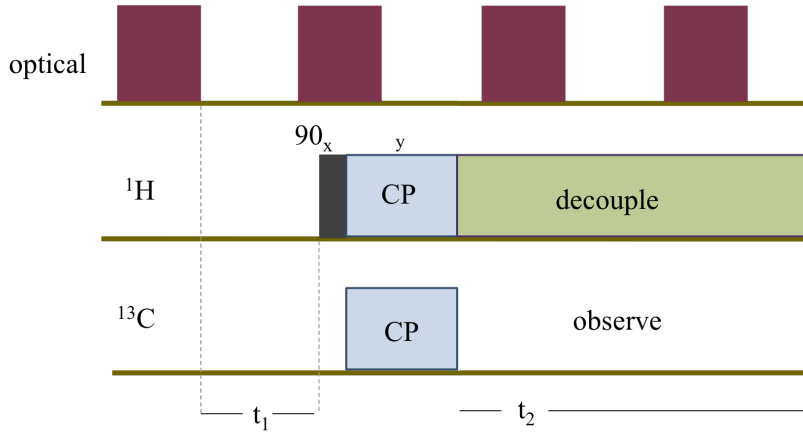


Figure 1: Rotor synchronized MAS (ROSMAS) pulse sequence scheme.

2.2 Sample Preparation

A sample of oriented fibers that physically fits in the NMR rotor has to be made in order to produce spectra with molecular orientation dependence. Therefore, a bundle of fibers is spun around a flat spool and a layer of glue is applied. Pieces of glued fiber films are cut out and stacked to produce a cuboid that fits in the rotor. Remaining spaces are filled with inert silica powder. Since glue does not have a preferred molecular orientation, it will not contribute to the more sensitive $M \neq 0$ sidebands of the oriented spectra. Figure 2 shows such an oriented fiber bundle with an angle $\beta_1 = 60^\circ$. The optimal angle can usually be found somewhere between $30^\circ - 60^\circ$. No orientation dependence is produced for $\beta_1 = 0^\circ$ since fiber orientation is symmetrical with the rotation of the rotor. For $\beta_1 = 90^\circ$ the experiment is limited with information only located at even M only.[5]

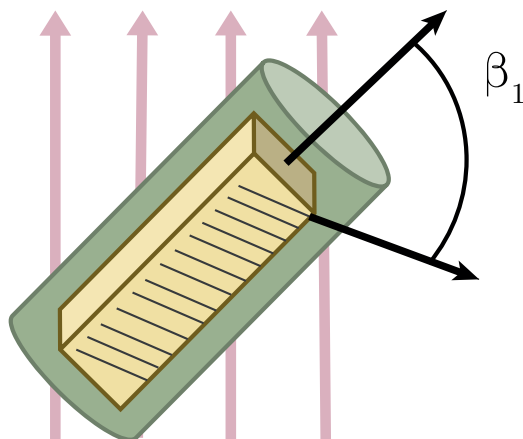


Figure 2: Rotor filled with aligned fiber bundle with the rotor at the magic angle and the fiber bundle with fibers at an angle $\beta_1 = 60^\circ$ from the rotor axis.

3 Tutorial

Steps necessary to calculate a ROSMAS spectrum are referred to Figure 3.

```

1 clear all
2 tic
3 %%%%%
4 randN=1000000;           % number of Monte Carlo samples for a 5 dimensional integral
5 err_est=1;               % error estimation (0 disabled) (1 enabled) may increase computaion time/memory
6 %%%%%
7 L=2;                     % Legendre number
8 M=1;                     % Rotation slice in the M row
9 N=1;                     % Number of N peaks calculatd from -N to N
10 %%%%%
11 omegal = 125.8;          % Larmor frequency MHz
12 omegaR =1500;            % Spinning frequency Hz
13 %%%%%
14 betal =60*pi/180;        % Director frame to rotor frame (radians)
15 %%%%%
16 sigmaPAS=zeros(3,3);    % Empty CSA tensor matrix
17 sigmaPAS(1,1)=-122.21;   % Chemical shielding/shift anisotropy sigma_11 (ppm)
18 sigmaPAS(2,2)=-108.42;   % Chemical shielding/shift anisotropy sigma_22 (ppm)
19 sigmaPAS(3,3)=-90.96;    % Chemical shielding/shift anisotropy sigma_33 (ppm)
20 %%%%%
21 alpha0=0*pi/180;         % Euler rotation angle alpha0 (radians) for Principal Axis System to Molecular Frame
22 beta0=0*pi/180;          % Euler rotation angle beta0 (radians) for Principal Axis System to Molecular Frame
23 gamma0=0*pi/180;         % Euler rotation angle gamma0 (radians) for Principal Axis System to Molecular Frame
24 %%%%%
25
26 %Input ends here

```

Figure 3: Input parameters in the ROSMAS.m file.

- Line 4, *randN*: The number of Monte Carlo samples used to calculate

the 5 dimensional integral. The number is increased or decreased for accuracy or speed, respectively. ROSMAS.m supports multiple cores and uses your personal settings as a reference for the number of active cores.

- line 5, *err_est*: turn error estimation on (1) or off (0).
- line 7, *L*: The legendre polynomial number used to calculate a sub-spectrum. Remember, the calculated intensity is only reflecting the contribution of a specific Legendre polynomial and not the entire ODF.
- line 8, *M*: The slice in the rotor phase dimension (ω_1).
- line 9, *N*: The number if peaks in the chemical shift dimension (ω_2).
- line 11, *omegaL*: Larmor frequency (MHz) the nuclear spin in a specific magnet.
- line 12, *omegaR*: Rotational frequency (Hz) of the MAS rotor.
- line 14, *beta1*: Angle between the fiber and the rotor as shown in Figure 2.
- line 17-19, *sigmaPAS*: Principal axis components of the chemical shielding/shift tensor given in negative ppm.
- line 21-23, *alpha0*, *beta0* and *gamma0*: Euler angles of the chemical shielding/shift tensor.

When all of the prerequisite parameters are filled to your experimental desires, run the scrip by pressing "run". The results are shown in the terminal or as a vector of your chosen number of *N* values saved as "ILMN" in the workspace with the -N value in vector position one.

4 ODF Reconstruction

The ODF reconstruction file "ODFreconstruction.m" will by default take a P_2 value and reconstruct it using the wrapped Lorentzian function. Other functions, like the Gaussian and the most probable function, are disabled

by default. The current version of Gaussian and most probable ODF reconstruction require both P_2 and P_4 values. The fitting parameters is calculated numerically by minimizing the function:

$$\sum \left(\langle P_\ell \rangle - \frac{\int_0^\pi P_\ell(\cos \theta) \cdot f(\theta) \cdot \sin \theta \, d\theta}{\int_0^\pi f(\theta) \cdot \sin \theta \, d\theta} \right)^2 = 0 \quad (4)$$

5 FAQ

Does the ROSMAS script calculate the order parameter of the Legendre polynomials?

No, a easy to use one size fits all solution has not been made so far. Different materials produce spectra of many qualities, of which the number of peaks that can be used for calculating the order parameter differ allot. Therefor we recommend using Equation (3) with a standard linear solver or the method used by Harbison et al.[5]. A very simple technique can be used when only calculating P_2 with for example $P_2 = \frac{(I_{2,1,x})_{exp} \cdot (I_{0,0,y})_{calc}}{(I_{2,1,x})_{calc} \cdot (I_{0,0,y})_{exp}}$ where x and y is the best peak in the $M = 1$ and $M = 0$ slice respectively.

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