Advanced MQMAS processing in ssNake

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1 Introduction

This tutorial will make a review of MQMAS experiment principles and will present several ways to process and fit Multiple Quantum Magic Angle spinning (MQMAS) NMR data using ssNake. We will present several representation of MQMAS (or STMAS) spectra: unsheared (3Q/SQ)/sheared/Q-sheared. The tutorial delivered with the ssNake program is considered as prior knowledge and having done MQMAS tutorial is advized. If you have not yet studied this, please do so before continuing with these examples.

This tutorial is assuming ssNake version 1.5 to be used. There is a change on sign of shearing and scaling with respect to previous versions depending on spin I and MQ level. ssNake v1.5 calculations for shearing and scale assume an evolution on $-pQ$ (p =3, 5, 7 or 9 for MQMAS and $p = 1 or 2$ for STMAS and DQ-STMAS. While previous versions assume a coherence pathway such that quadrupolar echo is shifting towards positive t_2 time.

2 MQMAS principles

MQMAS is a 2D experiment for half-integer quadrupolar nuclei which is used to obtain isotropic information from nuclei broadened by the second order quadrupole interaction. This allows the separation of multiple overlapping quadrupolar sites on the basis of their 'isotropic' value (which is a combination of the isotropic chemical shift, and the isotropic quadrupolar shift, which is also called the quadrupolar induced shift).

The experiment can be quite difficult to process. Not because of the complication of the steps involved, but due to the large number of different MQMAS experiments and the various ways to process these. This advanced tutorial will give several examples of MQMAS processing in various cases and give hints on parameters that must be considered to run processing in the proper way. Moreover, it will explain how to simulate different kind of processing.

The principle of MQMAS is to correlate $-pQ$ coherence ($p = 3$, 5, 7 or 9) during t_1 evolution with the observable $-1Q$ coherence. The total signal phase evolution during t_1 and t_2 is

$$\omega_Q(-pQ) \cdot t_1 + \omega_Q(-1Q) \cdot t_2$$

for quadrupolar interaction and

$$\omega_{CS}(-pQ)\cdot t_1 + \omega_{CS}(-pQ)\cdot t_2$$

for chemical shift interaction.

The dephasing can cancel at a point in t_2 evolution when $t_2 = -\frac{\omega(-pQ)}{\omega(-pQ)}t_1$. The ratio of dephasing occuring during $-pQ$ and $-1Q$ is

$$R = \frac{\omega_Q(-pQ)}{\omega_Q(-1Q)}$$

for the second order quadrupolar interaction and

$$\frac{\omega_{CS}(-pQ)}{\omega_{CS}(-1Q)} = p$$

for the chemical shift interaction.

The reason for MQMAS to be working is that ratios R and p are independant of C_Q/η_Q and chemical shift amplitudes respectively, and these ratio are different ($R \neq p$) which allows to separate their contributions along different axes. Depending on p and spin S, the ratio R of quadrupolar dephasing can be positive or negative. For chemical shift the ratio is $+p$. A negative ratio means that dephasing in t_1 and t_2 are canceling leading to the formation of an echo at positive time ($t_2 = -R\cdot t_1$). A positive ratio means that dephasings are cumulative in t_1 (evolution on $-pQ$) and t_2 (evolution on $-1Q$). The echo is shifting to negative t_2. Note that a positive R will result in a spectrum correlation with slope $F_1 = R\cdot F_2$, but a quadrupolar echo that shifts with $t_2 = -R\cdot t_1$.

Depending on the dominating interaction one can observe the formation of an echo at position $t_2 = -R\cdot t_1$ if the quadrupolar interaction is strong or at $t_2 = -3\cdot t_1$ if chemical shift distribution is dominating.

Z-Filter MQMAS is acquired in hyper-complex mode (for example State): echo and anti-echo are recorded simultaneously so a signal is always observed at positive t_2. The way quadrature is implemented (within the pulse sequence and hardware) will select the $\pm pQ$ pathway (more often the expected $-pQ$). A full echo MQMAS only selects one pathway. It can be $\pm pQ$ depending on the pulse sequence implementation and on the requirement to have signal in positive acquisition time (t_2). Indeed very often the pulse sequence will select the pathway for which an echo shifts towards increasing t_2 times ($R < 0$). If $+pQ$ is selected by the pulse sequence, then one will need to perform a Complex conjugate operation on D1 time domain, or a flip Left/Right operation on D1 frequency domain to flip the spectrum (indeed $\omega(pQ) = -\omega(-pQ)$).

Therefore, apodization should be done along $-R$ axis (or ±R axes for Z-Filter MQMAS when echo and anti-echo are selected). In some experiments the dominating interaction is chemical shift distribution. In that case, the echo is mostly appearing at $t_2 = -p\cdot t_1$. Then the slope for shifting should be ±p. Eventualy one should look at the FID to determine the best apodization and slope.

Shearing process aligns the correlation peaks horizontally instead of along the R slope by rolling each column (in D1 dimension). Shearing should always be done relative to the carrier frequency to get proper scale (the column at the carrier in D2 remains unchanged). In time domain shearing is equivalent to make the quadrupolar echo be positioned at $t_2 = 0$ (time when second order quadrupolar dephasings are canceled).

Once shearing is done, a universal scale can be designed that will make the peaks appear at the same position (in ppm) whatever p is used (3QMAS, 5QMAS, or even STMAS). There are two way to achieve such scale:

- Scale the spectral window (SW).
- Scale the carrier and reference frequencies used to calculate ppm scale).

When using SW scaling, the spinning sidebands will appear at scaled spinning speed in kHz. When using carrier and reference scaling, the spinning sideband separation remains at the spinning speed in kHz, however the Chemical Shift axis slope is scaled (due to shearing operation) and is 1 only when both axis are in ppm unit.

2.1 Split-t1 experiments

Split-t1 MQMAS experiments are designed to refocus the second order quadrupolar anisotropy at a fix time in D2. This corresponds to applying a shearing processing operation. It is usually done by defining a delay τ, on $\pm 1Q$ quantum level, which duration depends on t_1 (pQ coherence evolution) such that $\tau = R \cdot t_1$ before the acquisition during t_2.

Therefore, one just need to deal with such experiment just the same as a pQMAS experiment. The experiment does not need be sheared, and should be scaled as pQMAS experiment with t_1 evolution defined as evolution time on pQ.

3 ssNake tools for MQMAS processing

Note that current ssNake tools assume that the quadrupolar echo is shifting towards positive t_2 time. For example, for spin 5/2 3QMAS, it will use a ratio $R = 19/12$ corresponding to $R = \frac{\omega_Q(+3Q)}{\omega_Q(-1Q)}$ that is evolution on $+3Q$ during t_1. It will apply the corresponding ratio for shearing. Since in that case the spectrum in D1 is reversed, the Scale SW tool will propose to use a negative factor (-12/17) that will reverse the D1 axis (instead of the data as when using Flip L/R tool or using complex conjugate in time domain before FT).

Fitting of MQMAS will also The simulation procedure calculate the frequency of $-pQ$ and $-1Q$ for each crystallite. The 'Auto' button calculates the the shear and Scale SW parameters adequately.

4 Data

In this tutorial we will use several datasets:

- a Z-filter 3QMAS of 5/2 spin nucleus (^{27}Al).
- an unconventional split-t1 full echo 3QMAS of 3/2 spin nucleus (^{35}Cl).
- a Z-filter STMAS recorded with NUS of 3/2 spin nucleus (^{87}Rb).

5 Z-Filter MQMAS processing

First, we will look into the processing of MQMAS data recorded using a Z-Filter experiment (also called three pulse MQMAS). Note that data recorded with a regular two pulse MQMAS (the standard MQMAS experiment) can be processed in the same way.

Open the '3QMAS-Z' dataset. This is a ^{27}Al 3QMAS experiment of AlPO VPI-5 mesoporous sample. It has been recorded in States-TPPI mode on a 18.8 T spectrometer at 20 kHz MAS rate.

Be careful that some information in the dataset may be wrong or unexpected. Especially the carrier and reference frequencies in dimension D1 may be already scaled (if xfshear has been applied under Topspin) or even correspond to a wrong nucleus. In the worst case, the SW could be wrong. This could happen if actual t_1 evolution increment (on Bruker this would often be parameter IN0) does not correspond to declared spectral window (parameter SW_h in Bruker).

Processing of the data is performed in the following steps:

- Remove digital filter.
- Set the view to D1 (sideframe, radiobutton).
- Convert the hypercomplex data via Transforms ⟶ Hypercomplex ⟶ selecting 'States-TPPI'.
- Set the view back to D2 (sideframe, radiobutton).
- Apodize in D2 using a gaussian apodization (50 Hz), with shifting (select 'Spin 5/2 3QMAS' which enter a Value or 19/12).

Note the shifting option. We chose to shift apodization along the quadrupolar echo slope. But in some spectra, chemical shift distribution could be dominant and a slope of 3 would be better. One can also choose a compromise that is a slope in between the two.

The FID should now look like this:

Continue with the following processing steps.

- Zero-fill (Matrix ⟶ Sizing) 2048 points. (FID will be shortened).

- Fourier Transform D2 (ctrl-F shortcut), and phase the first slice.
- Optional baseline correction in D2 ('Tools' ⟶ 'Baseline Correction') + Hilbert transform or HT ('Transform' ⟶ 'Hilbert Transform'). HT is required after operations that only affect the real part but not the imaginary.
- Set the view to D1 (in sideframe radiobutton).
- Processing of the indirect dimension D1 (zerofilling 512 points, apodizing (50 Hz Lorenztian broadening), Fourier transform, phasing).

At that point we have several options for processing:

- whether to shear the spectrum.
- whether to scale the spectral width or the carrier and reference frequencies in the indirect dimension.

5.1 3Q-1Q representation

First we can choose to represent the spectrum in 3Q-1Q scale. To do that we need to adjust the reference frequency to $3 \cdot Ref - 2 \cdot Car$ where Ref is D2 dimension reference frequency and Car is the carrier frequency in D2 (and D1). Indeed this will ensure that the center of the spectrum will correspond to ppm coordinates $(F1, F2) = (p, 3p)$. First we need to ensure that D1 Carrier and Reference frequencies in D1 correspond to D2. This may not be necessary but as said before they may not be correct. Go to menu 'Tools' ⟶ 'Reference' ⟶ 'Set Reference'. Give name 'D2' and validate. Copy (crtl-C) the carrier frequency shown in D2 dimension. Select dimension D1 Paste the Carrier Frequency from D2. Go to menu 'Tools' ⟶ 'Reference' ⟶ 'Apply'. Select 'D2'. Go to menu 'Tools' ⟶ 'Reference' ⟶ 'Set Reference', then apply the operation $3 \cdot Ref - 2 \cdot Car$ for the reference frequency (There you can also 'Paste' the Carrier frequency that was copied above to write the equation).

This results in the following spectrum:

One can fit such spectrum with MQMAS model. There are 3 sites with main parameters summarized in table 5.1. The fourth site at about 5 ppm is actually an impurity that will not be considered in the following.

Site	δ_{iso} [ppm]	C_{Q} [MHz]	η_{Q}
1	-10.10	3.448	0.8992
2	41.74	1.274	0.4267
3	43.69	2.292	0.8697

Open a MQMAS fitting window (menu 'Fitting' ⟶ 'MQMAS'). You can then import '3QMAS-Z_unsheared_fit.txt' file.

If you click on 'Sim' button you won't see any simulated curve. The reason is that all correlations that are visible are folded. To be able to simulate these sites one needs to enable folded sites. This is done by checking the 'D1 Fold' check button. Click on 'Sim' again and all sites should be appear correctly.

5.2 Q-shearing

However folded spectra are not quite easily understandable. Q-shearing operation will allow to unfold the spectrum. The principle is to shear the spectrum to align the chemical shift axis horizontally. After shearing the peaks won't be folded anymore (unless the SW is too small to accomodate for the C_Q spread). Then one zerofills in the frequency domain to obtain an apparent SW three times larger. One can then shear back to an unfolded regular 3Q/1Q spectrum.

To do this proceed as such:

1. Shear the spectrum: Menu 'Matrix' ⟶ 'Shearing'. Set 'User defined' shearing constant to −3.
   The line at −20 ppm is too close to the bottom edge and almost aliased. We need to shift the spectrum up a little bit.

2. Select D1 dimension then menu 'Matrix' ⟶ 'Roll'. Roll to the right by 30 points.
   Now we will pad the spectrum with zeroes on both sides. This will be done by regriding the spectrum in D1. To make things easier, we will extend spectrum each side by one SW. So check that displayed unit is kHz.
   3) Check that D1 unit is kHz and copy the current sweepwidth dispayed in kHz.

3. select menu 'Matrix' ⟶ 'Regrid'. substract SW to the 'Min [kHz]' and add SW to the 'Max [kHz]. This will result in a new sweepwdith three times larger. To keep the spacing between two subsequent points (Hz per point) we need to multiply the number of point by three: '# of points' 256*3.

4. We should revert the spectrum shift done in step 2. Since we kept the spacing per point the same, we can simply use the same tool: Roll to the left by 30 point (−30 in the Roll entry).

5. At that point one should apply a Hilbert transform (HT). Indeed, shearing requires the use of imaginary part. And the imaginary part that contains the dispersive peaks is initialy truncated (does not fit within the initial SW) then padded with zeros. One hence need to rebuild the imaginary signal in the zerofilled spectrum parts.

6. We can now unshear, reverting the shear done in step 1) using a 'User defined' shearing constant of +3.

TADA!

5.3 Sheared (isotropic) representation

Another more common representation is to shear the spectrum in order to display purely isotropic information on D1 axis. Any second order quadrupolar broadening is only in D2 direct MAS dimension. Isotropic information corresponds to isotropic chemical shift and second order quadrupolar induced shift (also called QIS).

For this processing we'll start from the common processing described in 5 (right before 5.1).

1. Let's shear the spectrum using menu 'Matrix ⟶ Shearing'. One can choose the preselected ratio from the Drop down menu 'spin 5/2, 3QMAS'.

2. Now one should scale SW: 'Tools ⟶ Scale SW'. Use the same drop down menu choice.

The spectrum is sheared and scaled. For fitting (menu 'Fitting' ⟶ 'MQMAS') you can reload the previous file '3QMAS-Z_unsheared_fit.txt'. But the simulation must be also sheared and scaled. Click the 'Auto' Button to automatically select the right Shearing and scaling ratios (they depend on I and MQ parameters).

Note: Bruker xfshear procedure scales the Carrier and Reference frequency to get the correct ppm scale. So processing step 2) above can be replaced by 'Tools ⟶ Scale Car/Ref' and select the same drop down menu choice.
Finally for fitting panel in that case one must choose shearing ratio as set by Auto button, but scale must remain 1.

6 Unconventional split-t1 full echo 3QMAS of 3/2 spin nucleus (^{35}Cl)