Resolution enhancement of 2D MQ/MAS NMR spectra: A new processing approach based on biaxial shearing

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Introduction

2D Multiple Quantum Magic Angle Spinning (MQ/MAS) **NMR experiments** significantly enhance spectral resolution of quadrupolar nuclei. Since 75% of all magnetically active naturally occurring isotopes are quadrupolar nuclei (e.g. ^{11}B, ^{23}Na, ^{27}Al) and their abundance and gyromagnetic ratio is relatively high, measurements of their NMR spectra is very advantageous. On the other hand, quadrupolar nuclei exhibit asymmetric distribution of the nuclear charge which complicates measurements and interpretations of NMR spectra (signals are asymmetric and very broad). Consequently, significant effort in solid state NMR is now directed toward the methods for the observation of high resolution spectra of such nuclei.

Measuring of nuclei with quadrupolar character by MQ/MAS NMR usually provides 2D data matrix. 2D MQ/MAS NMR spectrum is obtained after processing and contain contributions of **C**hemical **S**hift (**CS**), **Q**uadrupolar **I**nduced **S**hift (**QIS**) and **A**nisotropic quadrupole broadening (**A**). These contributions have a variety of values, if one of these contributions (CS, QIS, A) is parallel to one's projection, thus the second projection obtains better resolution. Traditional approach of processing makes the **A**nisotropy of quadrupolar splitting axis parallel to F_2 and thus the projection F_1 is highly resolved. If distinct chemical sites are well resolved, shearing by **A** appears to be the best choice. Another approach is to shear the indirect dimension instead with **CS** slope. This procedure makes the **CS** axis parallel to F_2 and thus the projection F_1 is pure quadrupolar.

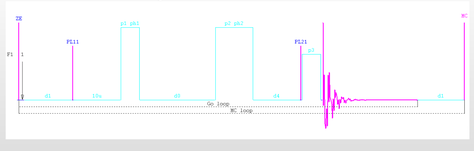
Problem comes with interpretation of 2D MQ MAS NMR spectra when two different contributions act against themselves. Basic knowledge of each contribution provides detailed information about local geometry and nonequivalent sites, therefore, it is very important and advantageous to separate these contributions by **biaxial shearing**. This means that in first step the 2D MQ/MAS NMR spectra are traditionally processed and sheared and during subsequent step are sheared in the second dimension. In this way new structural features are highlighted and specific structure motifs identified.

Aim of work

Amorphous Inorganic Polymers (AIP) possess great potential as special heat-resistance or buildings materials with wide range using. On the other hands, amorphous or disordered materials typically give a distribution of chemical shift and/or quadrupolar parameters, consequently difficult to interpret 2D MQ/MAS NMR spectra to identify distinct chemical sites. Therefore, sophisticated methods of 2D MQ/MAS NMR spectra processing had to be used to obtain detailed structural information. In this contribution we applied the procedure called as biaxial shearing to find structural parameter from ^{27}Al MQ/MAS NMR spectra of amorphous AIP system.

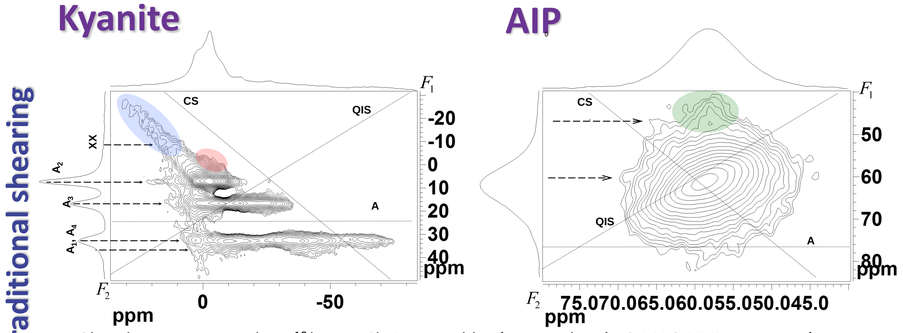
Pulse sequence

MQ/MAS z-filter NMR



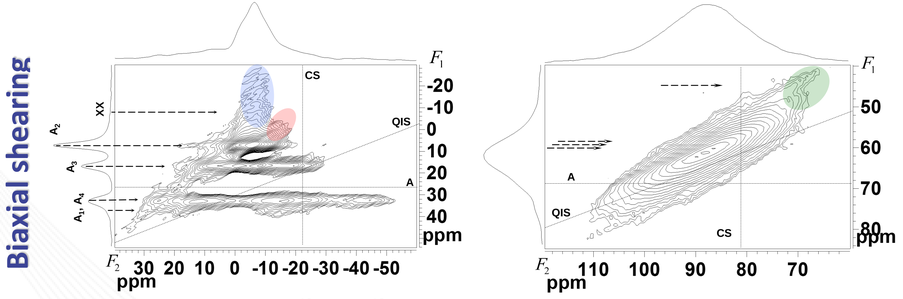
^{27}Al MQ/MAS NMR Spectroscopy

Traditional shearing



Shearing parameters (ν_{3Q}= $^{19}/_{12}$;ν_{1Q}= 0); F_2 - provides `conventional 1Q MAS NMR spectrum`;
F_1 - provides the spectrum without anisotropic axis, and show better resolution of structural units;
δcs- the chemical shift is now given by: $\delta cs(ppm) = {}^{10}/_{27}\,F_2 + {}^{17}/_{27}\,F_1$

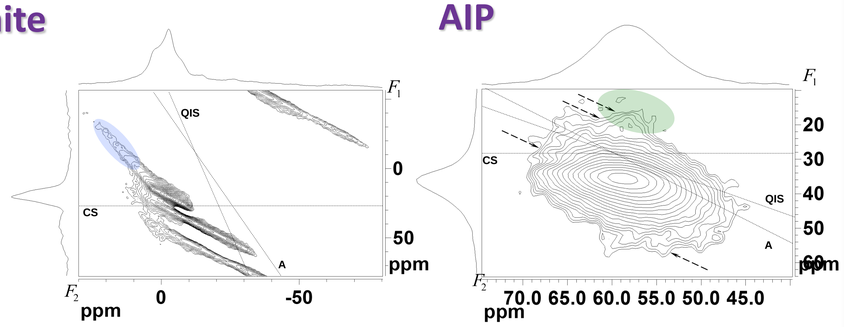
Biaxial shearing



Shearing parameters (ν_{3Q}= $^{19}/_{12}$;ν_{1Q}= $^{12}/_{17}$); F_2 - provides `pure quadrupolar projections`;
F_1 - provides the spectrum without anisotropic axis, and show better resolution of structural units;

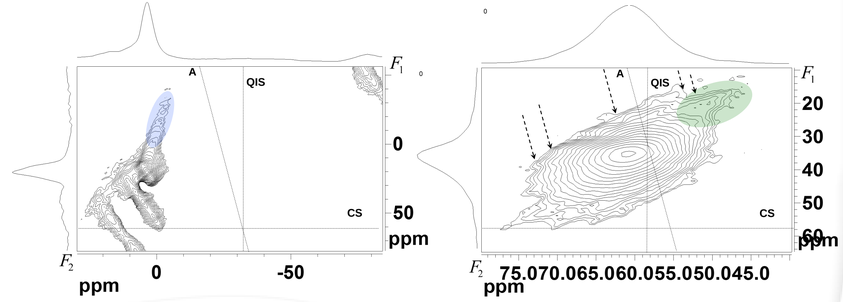
- Traditional shearing is suitable for **crystalline materials** ,however, biaxial shearing helps to separate the contributions of chemical shift and quadrupolar chemical shift and to determine influence of both the contributions on resulting spectra (blue and red areas spectra of Kyanite, green area spectrum of AIP).
- Biaxial shearing uncovers more easily chemically and structurally distinct sites, that are represent by arrows in spectra. The sample of Kyanite indicates clearly A_1 sites, that was hardly detected, by traditional shearing. Similarly, three new signals are detected in the biaxial sheared 2D MQ/MAS NMR spectra of AIP sample.

Q - shearing



Shearing parameters (ν_{3Q}= 3;ν_{1Q}= 0), does not fully eliminate the anisotropic quadrupole broadening, but does eliminate all broadening and other effects of the isotropic chemical shift from F_1 projection. Thus, line-shape slices along F_1 can be used to asses distribution of quadrupole coupling parameters alone;

Biaxial shearing



Shearing parameters (ν_{3Q}= 3;ν_{1Q}= $^{4}/_{9}$), does eliminate broadening of the isotropic chemical shift from F_1 projection and eliminate all effects of the quadrupolar chemical shift from F_2 projections.

- The Q - shear transformation gives a simple and unified representation for MQMAS spectra, especially for **disordered samples** for which traditional shearing does not yield high spectral resolution.
- Biaxial Q - shearing uncover new structural units and is completing all possible of shear transformations.

Shearing Parameters

Slopes of NMR parameter axes after shearing in v_{3Q}, v_{1Q} dimension with factors a,b respectively, for spin I = $^{5}/_{2}$ (eg. ^{25}Mg, ^{27}Al, ^{85}Rb)

	$^{19}/_{12}$; 0	$^{19}/_{12}$; $^{12}/_{17}$	3; 0	**3**; $^{4}/_{9}$
CS	$^{-17}/_{12}$	**1**	0	**0**
QIS	$^{5}/_{6}$	$^{85}/_{162}$	$^{-9}/_{4}$	**1**
A	0	**0**	$^{-17}/_{12}$	$^{-153}/_{40}$

Conclusion

Four possible schemes was demonstrated on this poster which may be valuable for shearing 2D MQ/MAS NMR spectra. Examination of peaks contours under different shearing schemes helps to interpret the 2D MQ/MAS NMR spectra. In practice, several combinations of shearing factors could be explored for spectra displaying broad lines, to lend confidence to the final interpretation and peak assignment.

The general principle presented here may also readily be adapted and applied in the various referencing and scaling conventions used in practice for representation of 2D MQMAS NMR data.

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