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. 11B, 19F, 17O) 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 matrix data. 2D MQ/MAS NMR spectrum is obtained after processing and contain contributions of Chemical Shift (CS), Quadrupolar Induced Shift (QIS) and Anisotropic 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 Anisotropy of quadrupolar splitting axis parallel to F₁ and thus the projection F₂ 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 F₂ and thus the projection F₁ is pure quadrupolar. Problem comes with interpretation of 2D MQ MAS NMR spectra when different contributions act and overlap 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 MQMAS 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 2DAl MQ/MAS NMR spectra of amorphous AIP system.

Pulse sequence
MQ/MAS 2-filter NMR

Shearing Parameters
Slopes of NMR parameter axes after shearing in ¥F₂, ¥CS dimension with factors a,b respectively.

<table>
<thead>
<tr>
<th></th>
<th>¥CS</th>
<th>¥F₂</th>
<th>¥QIS</th>
<th>¥A</th>
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</thead>
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<tr>
<td>CS</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>QIS</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
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Shearing Parameters (ν₁ = 3ν₂ = 0), does not fully eliminate the anisotropic quadrupole broadening, but does eliminate broadening and other effects of the isotropic chemical shift from F₁ projection. Thus, line-shape slices along F₁ can be used to assess distribution of quadrupole coupling parameters alone.

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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