

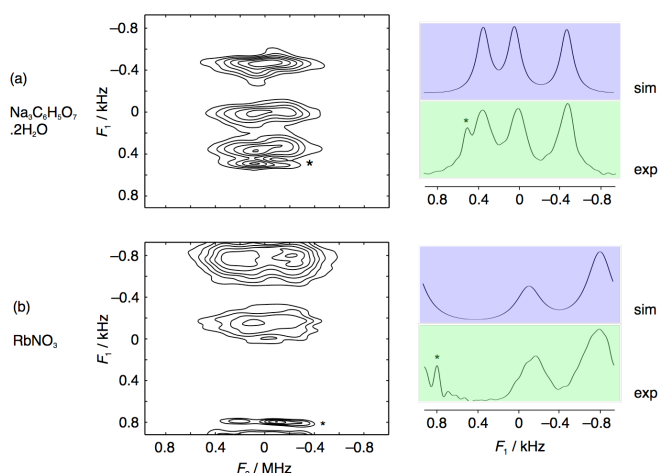
# High-Resolution NMR of Quadrupolar Nuclei: New Methods for Studying Structure and Dynamics

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In NMR of spin  $I \geq 1$  nuclei in powdered solids, it is routine to use magic angle spinning (MAS) to remove the inhomogeneous line-broadening arising from the first-order effects of the quadrupolar interaction. However, for many nuclei, this is not sufficient to obtain truly high-resolution spectra as a significant second-order quadrupolar line-broadening remains. For half-integer spin quadrupolar nuclei ( $I = 3/2, 5/2, 7/2$ , etc.), four basic methods are currently in use for removing the residual second-order broadening and hence achieving an "isotropic" spectrum: DOR,<sup>1</sup> DAS,<sup>2</sup> MQMAS<sup>3</sup> and STMAS.<sup>4</sup> The first two methods involve spinning the sample at two different angles with respect to the static magnetic field. They therefore require specialist probe hardware, while the use of more than one rotation axis means that spinning rates can be limited compared with MAS. In contrast, the second two methods, MQMAS and STMAS, are purely MAS-based and can be performed on standard probe hardware. They achieve removal of the second-order quadrupolar broadening by sequential correlation of different transitions:  $|+3/2\rangle \leftrightarrow |-3/2\rangle$  triple-quantum coherence (usually) with  $|+1/2\rangle \leftrightarrow |-1/2\rangle$  central-transition coherence in the case of MQMAS and  $|+3/2\rangle \leftrightarrow |\pm 1/2\rangle$  satellite-transition coherences (usually) with  $|+1/2\rangle \leftrightarrow |-1/2\rangle$  central-transition coherence in the case of STMAS.

We are developing new approaches to obtaining high-resolution NMR spectra of quadrupolar nuclei and to using existing techniques in combination with *ab initio* calculations of NMR parameters to study structure and dynamics in a range of materials. We will present a small selection of our recent work in this area, which includes: (a) development of an "ultrafast" method for obtaining high-resolution NMR spectra of spin  $I = 3/2$  nuclei, which we call STARTMAS<sup>5</sup> (see **Figure 1**); (b) the use of high-resolution NMR methods to study structure and dynamics in aluminophosphate framework materials;<sup>6</sup> and (c) the use of <sup>17</sup>O NMR and *ab initio* calculations to study structure and dynamics in superdense silicate phases that model those believed to make up much of the Earth's mantle.<sup>7,8</sup> Our collaborators in this work include Dr Sharon E. Ashbrook (St Andrews, UK), Dr Andrew J. Berry (Imperial College, UK), Dr Stefan Steuernagel (Bruker, Germany) and Dr Richard I. Walton (Warwick, UK).



**Figure 1.** Two-dimensional (a) <sup>23</sup>Na ( $I = 3/2$ ) STARTMAS NMR spectrum of sodium citrate dihydrate,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ , and (b) <sup>87</sup>Rb ( $I = 3/2$ ) STARTMAS NMR spectrum of rubidium nitrate,  $\text{RbNO}_3$ , and corresponding experimental and simulated (using literature NMR parameters)  $F_1$  projections. The asterisks mark a "spike" that arises as a result imperfections with the experimental implementation.

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