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Recent advances in solid-state nuclear magnetic resonance spectroscopy of quadrupolar nuclei

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Quadrupolar nuclei, that is, those with nuclear spin quantum number $I > 1/2$, account for over 75% of all nuclear magnetic resonance (NMR)-active nuclides and are the only option for NMR studies of many elements. These nuclei are important in a wide range of solids, from biomaterials through to energy materials, minerals, molecular materials, nanomaterials and microporous solids, and other systems that have industrial, technological, medicinal and societal importance. The quadrupolar interaction, that is, that between the nuclear quadrupole moment and the electric field gradient at the nucleus, has the potential to provide detailed information on the local atomic-scale environment, as it is sensitive to the number, type and arrangement of proximate atoms. The magnitude of this interaction is often considerable, usually much larger than the dipolar and chemical shift anisotropy (CSA) interactions, and often leads to anisotropic broadening of spectral lineshapes over many hundreds of kHz or MHz. Although this offers high sensitivity to small changes in local geometry, it hinders resolution, limiting the site-specific information that can be extracted. Furthermore, the complex angular dependence of second-order quadrupolar broadening means that it cannot be completely removed by magic-angle spinning (MAS), and more complex experiments are required to achieve isotropic spectra. These experiments can be technically challenging to implement (e.g. dynamic angle spinning [DAS] and double rotation [DOR]) or have inherently low sensitivity (e.g. multiquantum magic-angle spinning [MQMAS]). Although the twin challenges of sensitivity and resolution direct much research focus in NMR spectroscopy, this is never truer than for quadrupolar nuclei.

There have been significant advances in this field over the past decade. A deeper theoretical understanding of the spin dynamics in the complex multilevel spin systems has led to the development of new NMR methodology, with multinuclear and multidimensional experiments, often at high magnetic fields, now able to provide detailed quantitative, rather than simply qualitative, information, such as bond distances between a quadrupolar nucleus and its neighbours. Significant gains in sensitivity have been enabled through the use of new technologies, including ultra-high magnetic fields (up to 35 T), and dynamic nuclear polarization (DNP), with the latter now more widely available and benefitting from an increased understanding of the magnetisation processes in direct and indirect DNP. Other researchers have used isotopic enrichment both to improve sensitivity for quadrupolar nuclei with low natural abundance and to exploit the chemical information that the position or rate of enrichment can provide. There has been increased interest in using computation alongside experiment to interpret the complex spectral lineshapes that are seen for quadrupolar solids, particularly for

systems exhibiting significant disorder or dynamics. The improvements described have led to NMR spectroscopy of quadrupolar nuclei being employed in a wide range of complex chemical systems, increasing the ability of the spectroscopist to provide complementary information to other analytical techniques such as X-ray diffraction and to aid the detailed characterisation of the structure and reactivity of solids over different timescales and lengthscales.

In this special edition, we have brought together a set of articles that highlight the current state of the art in the field of quadrupolar NMR, illustrate the recent developments and advances in all areas of the field and point to the remaining challenges and areas of future interest. These articles discuss advances in methodology; a number focus on improvements in magnetisation transfer, both to and between quadrupolar spins; another investigates field-stepped wide-line NMR experiments on static samples; and a further article explores ^2H relaxation measurements to study amyloid fibrils. A set of articles are focussed on the applications of quadrupolar NMR, including the use of ^{17}O NMR to study disordered ceramics for waste encapsulation and phase transitions in porous metal–organic frameworks (MOFs), ^{87}Rb NMR of Rb-ionophore complexes, ^{115}In and ^{209}Bi NMR of functional oxides, multinuclear NMR analyses of hybrid organic–inorganic nanoparticles composed of an Al-nanoMOF core, polymorphism in aluminium coordination compounds, ^{35}Cl NMR of HCl salts of amino acids and pharmaceuticals and ^{43}Ca NMR of bone-related biomaterials. A number of these exploit isotopic enrichment (e.g. of ^2H , ^{43}Ca and ^{17}O) to improve sensitivity, to provide additional chemical information or to help develop new high-resolution correlation experiments, and some make use of periodic computational approaches to help understand the spectral lineshapes observed. The collection also includes two reviews: one focussed on the recent progress in solid-state NMR of low- γ quadrupolar nuclei (i.e. nuclei with a Larmor frequency below that of ^{15}N) in inorganic solids and one describing the evolution of the application of the REDOR experiment to quadrupolar nuclei.

We believe this collection of articles illustrates some of the recent exciting progress in this field and highlights the potential of quadrupolar NMR spectroscopy and the role it can play in understanding solid-state structures in the future. Finally, we would like to thank all of the contributors to the special edition and the reviewers who assisted in the publication of these articles. We would also like to thank Professor David Rovnyak and Paul Trevor for the advice and support they gave us as Guest Editors.