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New frontiers for solid-state NMR across the periodic table: a snapshot of modern techniques and instrumentation

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Selected highlights of the recent literature on solid-state NMR of some of the lesser studied nuclei are provided. The roles of ultrahigh magnetic fields, radiofrequency pulse sequences, dynamic nuclear polarization, isotopic enrichment, and nuclear quadrupole resonance in opening up the periodic table to in-depth study are discussed.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a widely applied tool across the chemical, physical, and biomolecular sciences. While NMR of solutions is commonplace in synthetic chemistry laboratories, solid-state NMR still typically requires special training and expertise for the proper and optimal recording and interpretation of data. Solid-state NMR provides the ability to analyze substances such as crystals, glasses, and powders in their native states, without the need to dissolve them in a solvent. The analysis of solids by NMR can also succeed in cases where solution NMR fails, *e.g.*, for some quadrupolar nuclei where fast relaxation broadens the lines in solution. Solid-state NMR spectroscopists also have at their disposal a vast toolbox of pulse sequences and techniques to provide bonding information, internuclear distances, and in favourable cases, complete crystallographic structural models akin to those derived solely from diffraction data. NMR crystallography is a burgeoning field which has been recognized by the International Union of Crystallography;[1,2] there are a variety of approaches to gain structural and crystallographic information *via* NMR crystallography, but these typically rely on a combination of data gleaned from NMR, diffraction, and computational methods. NMR crystallography approaches relying on ^{1}H SSNMR data have proven to be particularly successful,[3,4] and several groups have applied NMR crystallographic approaches to a wider range of nuclei across the periodic table including *e.g.*, ^{11}B, ^{17}O, ^{95}Mo, ^{23}Na, ^{27}Al, ^{43}Ca, ^{25}Mg, *etc.*[2,5–11]

Indeed, the vast majority of elements in the periodic table have isotopes amenable to analysis by solid-state NMR. Historically, many spin-active nuclei remain understudied due to one or more technical challenges associated with recording or interpreting the data. Such challenges may include low natural abundances, low resonance frequencies, large nuclear electric quadrupole moments (Q), long spin–lattice relaxation time constants (for spin-1/2 nuclei in particular), or some combination of these. Roughly 75% of the spin-active isotopes are quadrupolar (nuclear spin quantum number, I, $>\frac{1}{2}$). Low sensitivity stemming from the Boltzmann distribution of nuclear spins is only further exacerbated by low isotopic natural abundance; this issue becomes increasingly problematic if one wishes to characterize surface species.

The purpose of this Frontier article is to highlight some of the recent advances in instrumentation, pulse sequences, and

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related techniques which are rendering accessible much more of the periodic table to solid-state NMR on a more routine basis. This overview by definition is not exhaustive and the reader is referred to a recent related review article by our group on "*Recent Advances in Solid-State Nuclear Magnetic Resonance Spectroscopy of Exotic Nuclei*".[12] Below, we will elaborate on the advantages gained through the use of increasingly high applied magnetic fields in solid-state NMR spectroscopy, and contrast this with the utility of nuclear quadrupole resonance (NQR) spectroscopy. Examples from our own group and from the literature are discussed. Next, we discuss the advantages offered through improvements in pulse sequences including the use of broadband excitation and indirect detection in two-dimensional NMR. Selected applications using dynamic nuclear polarization (DNP), a signal-enhancement technique which is revolutionizing solid-state NMR, will be discussed. Finally, I will touch on a few other methods which are also contributing to the increasing accessibility of 'difficult' nuclei across the periodic table including, *e.g.*, mechanochemical isotopic enrichment techniques.

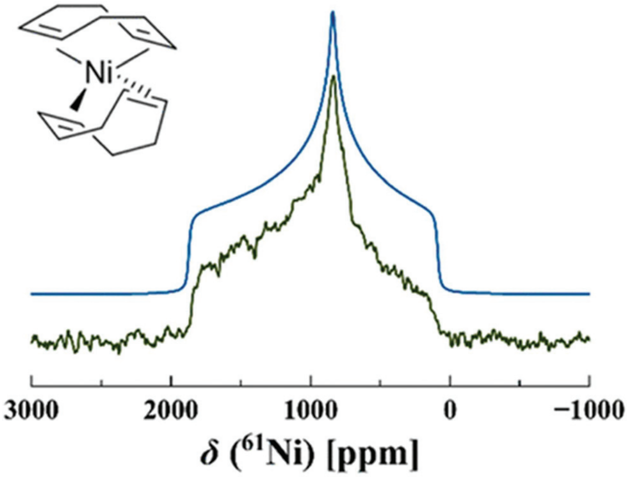

Fig. 1 ^{61}Ni solid-state NMR spectrum of $Ni(cod)_2$ acquired in a magnetic field of 21.1 T. The spectral simulation is shown above the experimental spectrum. Reproduced from *Inorg. Chem.*, 2017, **56**(16), 9996–10006. Used with permission of the American Chemical Society.

(Ultra)high (and low) magnetic fields

Since the early days of NMR, there has been a continued push for higher and higher external applied magnetic fields. Higher fields are advantageous for sensitivity reasons, as a result of the more favourable Boltzmann distribution and higher Larmor frequencies. Improved spectral resolution is also obtained in many cases. For solid-state NMR, further advantages are realized at higher fields especially for quadrupolar nuclei. A quadrupolar nucleus is subject to a coupling between its nuclear quadrupole moment and the electric field gradient at the nucleus. This quadrupolar coupling leads to an orientation-dependent spectral broadening. Broadening arising from second-order quadrupolar coupling (and higher-order terms) is reduced as the external applied magnetic field is increased. Thus, in higher applied magnetic fields, one may be able to observe the spectrum of a quadrupolar nucleus which was 'invisible' for practical purposes at lower field, due both to the increased sensitivity and to the spectral line-narrowing.

Our own recent work at 21.1 T (900 MHz proton frequency) has resulted in $^{35/37}$Cl and $^{79/81}$Br solid-state NMR of halogen-bonded cocrystals.[13,14] These quadrupolar isotopes benefit from very high applied magnetic fields. The 900 MHz system also enabled the first systematic ^{59}Co solid-state NMR study of cobalt in the +1 oxidation state.[15] For a series of fumarate-based organocobalt(I) [CoCp(CO)(fumarate)] catalysts it was established that the ^{59}Co chemical shift anisotropy and the ^{59}Co quadrupolar coupling constant are both very sensitive indirect measures of the Fu–Co–Cp bond angle, thereby providing a link between these ^{59}Co NMR parameters and the catalysts' structures. More recently, our group reported the first ^{61}Ni solid-state NMR study of diamagnetic compounds.[16] Shown in Fig. 1 is the ^{61}Ni solid-state NMR spectrum of $Ni(cod)_2$ [cod = 1,5-cyclooctadiene] acquired in a magnetic field of 21.1 T. This work provided a demonstration that SSNMR, in conjunction with computational studies, is invaluable in characterizing disordered organometallic systems, specifically explaining the solid-state behavior of $Ni(PPh_3)_4$ and providing insight into the crystal structure of $Ni[P(OPh)_3]_4$.

These are but a few examples of the types of compounds and isotopes which are now amenable to study by solid-state NMR thanks to the availability of high applied magnetic fields. We have recently used solid-state NMR of various quadrupolar isotopes to gain insight into multiple bonds between metals. For example, ^{95}Mo ($I = 5/2$) WURST-QCPMG (Wideband Uniform Rate Smooth Truncation Quadrupolar Carr Purcell Meiboom Gill) solid-state NMR of $Mo_2(O_2CMe)_4$ and $Mo_2(O_2CCHF_2)_4$ in a magnetic field of 21.1 T provided a direct NMR description of molybdenum–molybdenum quadruple bonds; they are characterized by particularly anisotropic molybdenum chemical shift tensors spanning 5500 ppm.[17] New experimental understanding into the nature of metal–metal bonds in digallium compounds was obtained *via* two-dimensional ^{71}Ga *J*/*D*-resolved NMR experiments which provide a direct measurement of $J(^{71}\text{Ga},^{71}\text{Ga})$ spin–spin coupling constants.[18,19] The high field of 21.1 T was essential for sensitivity and resolution purposes. In the context of established experimental data for analogous singly, doubly, and triply bonded carbon spin pairs or boron spin pairs, the ^{71}Ga NMR data point to a different bonding model in the gallium systems. These findings were found to be consistent with an increasing importance of classical or slipped π-type bonding orbitals across the supposed gallane–gallene–gallyne series.

Magnets with proton frequencies of 800 to 900 MHz are now relatively commonplace around the world, at least in specialized NMR centres. Several commercial 1 GHz instruments are also now in use or have been ordered. Bruker very recently announced their superconducting 1.1 GHz system in 2019 at the Experimental NMR Conference in Pacific Grove, California.[20] Bruker is also currently producing a 1.2 GHz (^{1}H) magnet for NMR spectroscopy.[21] Dedicated magnet laboratories in Japan and in the USA, for example, also continue to push the limits in terms of applied magnetic field strength. The availability of a 36 T series-connected hybrid (SCH) magnet at the National High Field Magnet Laboratory (NHFML) in Tallahassee, Florida, has further revolutionized the field of solid-state NMR. In particular, quadrupolar nuclei and nuclei with low resonance frequencies and/or low natural abundances will benefit tremendously from this infrastructure. Sub-ppm field homogeneity and stability mean that this magnet can be used for high-resolution solid-state NMR spectroscopy, including multidimensional experiments. An initial proof-of-principle report in late 2017 included demonstrations of field stability and homogeneity *via* ^{27}Al MAS NMR spectra of $9Al_2O_3{\cdot}2B_2O_3$, ^{17}O quadrupole central transition (QCT) spectra of [3,5,6-^{17}O]-D-glucose in glycerol, two dimensional ^{17}O MQMAS spectra of benzoic acid, a ^{15}N/^{1}H separated-local-field spectrum of dimeric ^{15}NGly2-^{15}NAla3 labeled gramicidin-A in liquid crystalline lipid bilayers, and two-dimensional ^{13}C DARR spectra of protein GB1.[22] Since then, the NHFML has been accepting user applications for SCH magnet time. To our knowledge, fewer than ten papers featuring NMR results have been published to date.[23–28] Our work presented the comparative merits of carrying out ^{35}Cl solid-state NMR spectroscopy of covalently-bonded halogens relative to using ^{35}Cl nuclear quadrupole resonance (NQR) spectroscopy (Fig. 2).[23] Griffin and coworkers demonstrated the value of the SCH magnet for ^{17}O MAS NMR correlation spectroscopy,[24] and for the resolution of structural water molecules *via* ^{17}O SSNMR.[28] Bonhomme *et al.* showed nicely the resolving power and sensitivity that is achieved in ^{43}Ca ultrahigh-field solid-state NMR.[27] Wu and coworkers described a quadrupole-central-transition ^{17}O NMR study which provided experimental evidence of cross-correlation between the second-order quadrupolar interaction and magnetic shielding anisotropy.[25] Finally, the value of ultrahigh magnetic fields in ^{14}N overtone NMR spectroscopy was also recently demonstrated by Gan *et al.*[26] These early examples only begin to hint at what can be achieved in the 36 T SCH magnet; it will be exciting to see what new developments and applications emerge in the coming years.

Due to the very strong electric field gradients at nuclei in low-symmetry environments, as well as large nuclear quadrupolar moments, solid-state NMR spectroscopy of certain quadrupolar isotopes will remain impractical even in the highest available magnetic fields mentioned above. Even if isolated examples of success may be found,[29–31] solid-state NMR of isotopes like ^{197}Au, ^{121}Sb, ^{175}Lu, ^{235}U, and ^{229}Th, for example, will remain largely out of reach for the foreseeable future. For this reason, NQR spectroscopy should be considered as a complementary technique for probing the local chemical and elec-

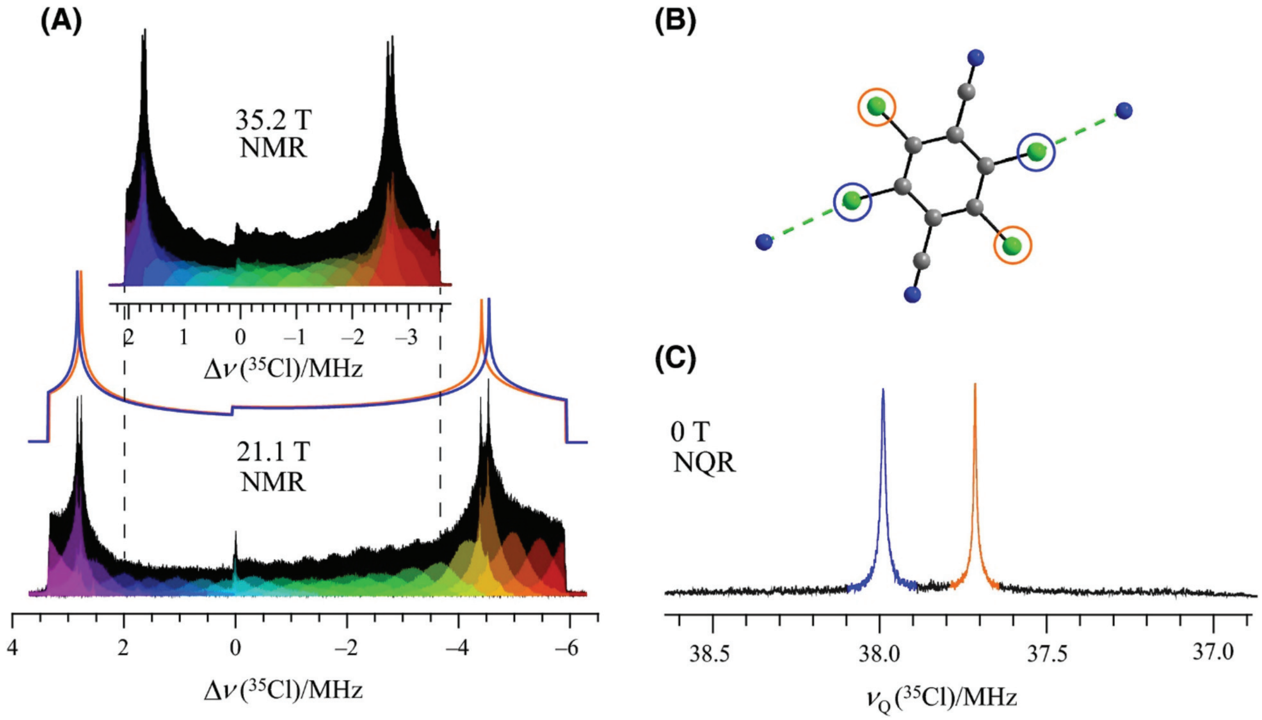

Fig. 2 (A) ^{35}Cl solid-state NMR spectrum of tetrachloroterephthalonitrile acquired at 35.2 T (upper) and 21.1 T (lower). Simulated spectra for each of the two crystallographically distinct sites at 21.1 T are shown in blue and orange. (B) The crystal structure of tetrachloroterephthalonitrile, showing the distinct chlorine sites in blue and orange. (C) The ^{35}Cl NQR spectrum of tetrachloroterephthalonitrile. Reproduced from *Concepts Magn. Reson., Part A*, 2016, **45**, e21412. Used by permission.

tronic environment of such elements. The reader is referred to our recent *Concept* article on the complementarity of solid-state NMR and NQR spectroscopies, with a focus on the quadrupolar halogens $^{35/37}$Cl, $^{79/81}$Br, ^{127}I.[23] While it can be tedious to search for NQR frequencies, new auto-tuning probe technology[32] may help to overcome this limitation in the near future.

Two further recent examples serve to highlight the utility of NQR in the context of studying strongly quadrupolar isotopes. Cerreia Vioglio *et al.* reported on the use of $^{79/81}$Br NQR spectroscopy to characterize halogen bonds in supramolecular assemblies.[33] In supramolecular assemblies constructed from 1,4-dibromotetrafluorobenzene and nitrogen-containing heterocycles, they demonstrated that the bromine quadrupolar coupling constants increased upon halogen bond formation. These increases are on the order of MHz and correlate linearly with the halogen bond distance. This work also showed that $^{79/81}$Br NQR was able to distinguish between crystallographically non-equivalent bromine atoms in halogen bonds. This sensitivity to the local chemical and crystallographic environment surpassed what was possible using routine ^{13}C and ^{15}N MAS NMR in this work.

A more recent example is that of $^{121/123}$Sb NQR of antimony atoms participating in pnictogen bonds.[34] Leroy *et al.* demonstrated frequency shifts on the order of 0.1 to 10 MHz upon the formation of pnictogen bonds to SbF_3 and to $SbCl_3$. Interestingly, decreases in the quadrupolar coupling constants (on the order of 400 to 500 MHz for ^{121}Sb) were noted rather than the increases associated with halogen bonding. This work also explored the impact of the type and number of electron donors interacting with antimony. The value of the $^{121/123}$Sb NQR frequencies was further established by implementing an NQR crystallography protocol to refine the structure of $SbCl_3$·trioxane, which was previously unknown.

Instrumentation, pulse sequences, sample preparation

In this section, I touch briefly on some highlights in instrumentation and pulse sequences as they relate to the scope of this article. The WURST QCPMG[35] sequence continues find widespread application in the area of solid-state NMR of quadrupolar nuclei.[36] It is also a promising technique to speed up the search for NQR frequencies.[37] Broadband adiabatic inversion pulses for cross polarization (BRAIN CP)[38,39] is another valuable method which has been developed by Schurko *et al.* to enable broadband signal enhancement. Improved methods for transferring magnetization to quadrupolar nuclei from protons have been described by Giovine *et al.*[40] The external automatic tuning/matching (eATM) robot described by Grey and coworkers,[32] and related designs, could have several important applications including NQR spectroscopy. Others include scanning wide NMR frequency ranges associated with paramagnetic systems, and the possibility of acquiring data for multiple nuclides in a 'single' spectrum.

Perras, Rossini, Pruski, and coworkers have recently reported on indirect detection of spin-1/2 and quadrupolar nuclei for which direct detection can be challenging.[41–43] Indirect detection *via* ^{1}H spins increases the sensitivity of the experiment by up to 1 or 2 orders of magnitude and thus reduces the overall experimental time. Their results demonstrate that proton detection and fast magic-angle spinning offers a general approach to enable and accelerate solid-state NMR experiments on low-γ nuclei in particular. For example, Perras *et al.* merged fast-magic-angle-turning (MAT) and dipolar heteronuclear multiple-quantum coherence (D-HMQC) experiments to allow for rapid acquisition of 2D solid-state spectra that correlate ^{1}H chemical shifts to an indirectly detected isotropic "infinite-MAS rate" spectrum of heavy spin-1/2 nuclides.[41] The method was successfully applied to acquire a high-resolution MAS ^{195}Pt SSNMR spectrum of a Pt-impregnated MOF. Li *et al.* have similarly reported on the indirect detection of broad spectra using interleaved DANTE trains, with particular applications to ^{195}Pt and to ^{14}N.[44]

Rossini and coworkers demonstrated the value of proton detection for the indirect acquisition of the spectra of half-integer quadrupolar nuclei including ^{17}O, ^{27}Al, ^{35}Cl, and ^{71}Ga.[44] In particular, they showed how proton detected D-RINEPT (dipolar refocused insensitive nuclei enhanced by polarization transfer) benefits from the short longitudinal relaxation time constants normally associated with quadrupolar nuclei. Rossini and his group further showed how indirect proton detection enables and greatly accelerates the acquisition of spectra for very low-γ spin-1/2 nuclei including some very impressive work on ^{89}Y, ^{103}Rh, ^{109}Ag, and ^{183}W (Fig. 3).[43] They rightly speculate that the combination of indirect detection with modern DNP methods could lead to significant further improvements in sensitivity and open the door to new applications.

Dynamic nuclear polarization continues to revolutionize the field of NMR spectroscopy. Briefly, DNP works by transferring electron spin polarization to nuclear spins, thus overcoming the intrinsic low Boltzmann sensitivity inherent to NMR. I mention here some of the most recent developments and applications related to nuclei which have thus far not been extensively studied using modern high-field DNP techniques. Rossini has reviewed the recent applications of DNP solid-state NMR in the area of materials chemistry; nuclei studied include ^{27}Al, ^{29}Si, and ^{119}Sn, for example.[45] Most DNP experiments on heteronuclei rely on an initial transfer of electron polarization to abundant protons, following by a second transfer to the heteronucleus. For example, Kobayashi *et al.* have reported on the use of ^{207}Pb DNP-BRAIN-CP-WCPMG experiments, involving cross-polarization from protons to lead, to observe ^{207}Pb NMR signals from the basic lead carbonate phase in lead white pigment used in paintings.[46] Recently, Emsley and coworkers have described how relayed DNP can work *via* homonuclear spin diffusion for low-γ proton-free samples.[47] For example, they report a factor of 50 gain in sensitivity for the ^{119}Sn NMR spectrum of powdered SnO_2, corresponding to an acceleration by a factor of over 2500 in acquisition time. This is an exciting

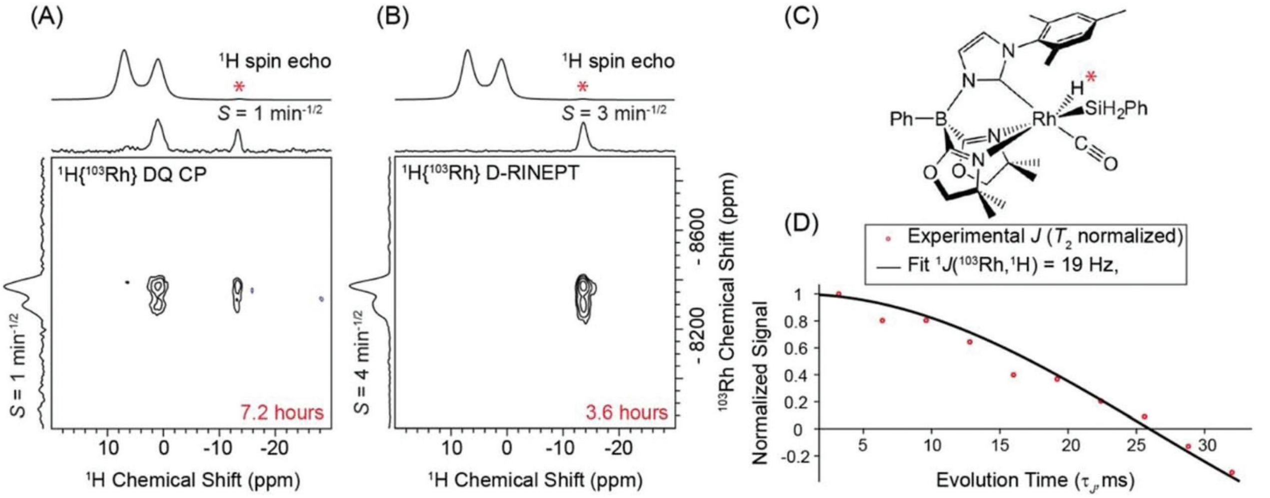

Fig. 3 ^1H and ^{103}Rh solid-state NMR spectra of an organometallic rhodium complex. Proton detected (A) 2D $^1H\{^{103}Rh\}$ double-quantum cross-polarization spectrum and (B) 2D $^1H\{^{103}Rh\}$ D-RINEPT spectrum. (C) Structure of the organometallic rhodium complex. (D) Plot showing the results of a *J*-resolved experiment. Reproduced from *J. Phys. Chem. A*, 2018, **122**(25), 5635–5643. Used by permission.

development which could create new opportunities to study samples which have traditionally been considered impractical candidates for DNP enhancement.

The foregoing describes the roles of ultrahigh magnetic fields, dynamic nuclear polarization, other instrumentation and pulse sequences in facilitating and accelerating solid-state NMR spectroscopy of a broad range of nuclei from across the periodic table. However, sometimes something as simple as the method of sample preparation can be of equal (or greater) importance in acquiring information-rich spectra. Isotopic enrichment is an obvious method which is frequently used in NMR spectroscopy to increase sensitivity and/or to enable particular experiments or spectral editing. Isotopic enrichment can, however, be expensive and cost-prohibitive in some cases, particularly if one is interested in nuclei past the first couple of rows in the periodic table. The report of Métro *et al.* on mechanochemical isotopic enrichment is therefore particularly exciting, as the method minimizes the amount of isotopically enriched material required for the synthesis and minimizes any waste or losses of this material.[48] Their report focusses on the efficient use of ^{17}O-labelled water to produce ^{17}O-labelled organic and inorganic compounds; however, one can easily envision a more expansive application of mechanochemistry to efficiently incorporate a broader range of isotopes of interest to NMR spectroscopists. Sample preparation for DNP NMR experiments is also often crucial to success. Perras *et al.* have recently described optimal sample formulations for DNP SENS experiments specifically for alumina, silica, and ordered mesoporous carbon materials.[49]

Concluding remarks

This *Frontier* article has aimed to provide a snapshot of some of the most exciting applications as well as technological and methodological developments enabling the acquisition of solid-state NMR spectra of nuclei which are typically understudied. Nuclei from across the periodic table can be difficult to study by NMR for a variety of reasons including low isotopic natural abundances, low gyromagnetic ratios, and large quadrupole moments. All three of these issues are mitigated by using the highest possible applied magnetic fields. However, there is a technical and cost limitation at any point in time on the field strengths that can be generated in a commercial NMR magnet; furthermore, the effects of chemical shift anisotropy may become problematic in very large fields. Alternative methods to enhance sensitivity and/or to handle spectral broadening are needed. The most promising of these include dynamic nuclear polarization and novel radiofrequency pulse sequences to improve broadbandedness and to enable proton detection for quadrupolar nuclei and low-γ spin-1/2 nuclei. Older methods including NQR spectroscopy and brute-force isotopic enrichment should not be forgotten, and can sometimes offer the easiest route to the desired spectroscopic and chemical information.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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