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Perspectives on high-field and solid-state NMR methods of quadrupole nuclei

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ABSTRACT

High magnetic field can dramatically increase the spectral resolution and sensitivity of quadrupole nuclei S > 1/2 by the reduction of the second-order quadrupole broadening. A brief overview and outlook on spectral acquisition, the importance of high magnetic field, inter-nuclei distance measurement, various 2D separation and correlation methods of quadrupole nuclei are presented. The complications and consequences of spin dynamics under *rf* irradiation for the (2S + 1) level system and level-crossing with the satellite transition frequencies under magic-angle spinning are discussed. There is a scaling down of (S + 1/2) to the efficiency of many experiments in comparison with a spin-1/2 due to the fact that only two central transition spin states out of the (2S + 1) levels contribute to polarization transfer and spin correlation.

The majority of the elements in the Periodic Table have nuclear spins >1/2. From nuclear theory these nuclei possess electric quadrupole moments that can interact with the electric-field-gradient (EFG) at the nuclei site and give rise to the spin interaction of quadrupole coupling. This quadrupole interaction often in the order of MHz is much larger than the chemical shift and spin-spin couplings. We call generally all spins >1/2 quadrupole nuclei to distinguish them from spins =1/2 nuclei of which the quadrupole interaction is absent. The large quadrupole interactions and the many-level spin-systems of spins >1/2 complicate the acquisition of NMR spectra in terms of spectral resolution, sensitivity and pulse sequences. Numerous technical advancements and applications of quadrupole nuclei have been published in the Journal of Magnetic Resonance in the past 50 years. For this special issue celebrating 50 years of this Journal, I present some personal perspectives or "crystal-balls" looking into the future of solid-state NMR of quadrupole nuclei with a brief overview on where we stand, the challenges we face and the advances that may occur in the near future especially on the importance of high magnetic fields and method development. The first half gives an overview for the case of a single quadrupole spin on spectral acquisition and the 2D methods for separating various broadening and interactions. The second half presents the methods for probing the interactions between two spins and focuses experiments that measure the dipolar interaction, spin correlation, indirect detection and polarization transfer.

Large quadrupole interactions lead directly to broad NMR lines for solid powder samples. The Carr-Purcell Meiboom-Gill (CPMG) pulse sequence is the method of choice searching for NMR signals and acquiring wide-line spectra [1–3]. The CPMG pulse sequence is robust to pulse width calibration with the nulls of bandwidth

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determined only by the inverse of the refocusing pulse length [4]. Frequency-swept pulses can be employed to broaden the bandwidth further and flatten the frequency profiles, and therefore can be particularly useful to compose ultra-wide spectra by stepping the transmitter frequency [5–7]. For powered magnets, stepping the magnetic field can be implemented conveniently for acquiring and composing ultra-wide spectra without the need of adjusting probe tuning [8].

Majority of the quadrupole nuclei are half-integer spins with their central single-quantum transition broadened by the quadrupole interaction in the second-order. The second-order broadening can be further reduced but not completely averaged by magic-angle spinning. A complete averaging of the high-rank second-order anisotropic broadening directly requires a double-axial rotation (DOR) probe [9]. Innovative methods like multiple-quantum magic-angle spinning (MQMAS) [10] and later satellite-transition magic-angle spinning (STMAS) [11] have been invented to obtain isotropic spectra in a two-dimensional manner similar to that of the dynamical angle spinning (DAS) method [12–14] but using the fixed-axis sample rotation of MAS probes. The robust MQMAS in particular has since become widely used for resolving crystalline sites and mapping out the distributions between chemical shift and quadrupole broadening in disordered samples. The efficiency of the multiple-quantum excitation and conversion depends critically on and goes up more than linearly with the *rf* field strength γB_1 [15]. The overall efficiency ranges from a few percents up to 20%, depending on the magnitude of the quadruple couplings, using improved excitation and conversion schemes and balanced probe circuits capable handling high *rf* power. Applying MQMAS to low-γ nuclei is more challenging due to their intrinsic low sensitivity and low γB_1. Using high magnetic fields, CPMG multiple echo acquisition and polarization enhancement like DNP, the scope of MQMAS applications has been extended to insensitive low-γ nuclei.

A variant of MQMAS using the single-quantum satellite transitions namely STMAS can be in principle more efficient than MQMAS [11]. However, STMAS requires extremely precise magic-angle setting and stable spinning making it less robust than MQMAS for practical applications. Nevertheless, the idea on averaging out the large first-order quadrupole coupling of satellite transition has been extended to integer spins such as ^{14}N via indirect detection [16,17]. Furthermore, STMAS is complimentary to MQMAS as the relaxation properties can be very different between the satellite and multiple-quantum transitions [18].

Quadrupole couplings can become very large exceeding tens of MHz or even GHz for heavy atoms with large quadrupole moment in asymmetric environments. Nuclear Quadrupole Resonance (NQR) at zero magnetic field can become advantageous for large quadrupole couplings without the anisotropic broadening [19]. The main challenge of NQR is the search of the narrow NQR lines without prior knowledge where the resonance frequency is. Wide line NMR at high magnetic fields and quantum chemical calculations can help to predict the NQR frequency and narrow down the search.

For the cases where the MAS line width is narrower than the spinning frequency, MAS should be used for the resolution and sensitivity enhancement. The MAS removes about two third of the quadrupolar broadening and averages completely the CSA interaction yielding a peak with a width proportional to the $C_q^2(1 + \eta_q{}^2/3)/\omega_0$ and a shape determined by the asymmetry parameter η_q. Once knowing the quadrupole couplings, analyses of the static line shape allows for the determination of chemical shift anisotropy (CSA) parameters. Varying the magnetic fields changes the relative scale between quadrupole and CSA broadening, and therefore is often useful for the extraction of quadrupole coupling and CSA parameters including their relative tensor orientations.

When the anisotropic line width is larger than the MAS speed, 2D methods can be applied to separate the modulated and the averaged parts of the anisotropic broadening under MAS in two dimensions. Two methods, namely QMAT [20] and QPASS [21], were introduced independently for quadrupole nuclei from their counterparts of spin-1/2: namely magic-angle turning (MAT) [22] and phase-adjusted sideband separation (PASS) [23,24]. Both experiments use nine π-pulses required for the high-rank second-order quadrupole broadening and they project infinite-speed like MAS spectra to one dimension and the sideband manifolds to the other dimension. Due to *rf* field inhomogeneity and frequency offsets, the overall efficiency from the nine π-pulses typically compound to about 25% with a bandwidth up to a few hundreds of kHz.

The polarization of half-integer spins can be manipulated prior to the excitation pulse to enhance the signal. In the *rf* Hamiltonian $\gamma B_1 I_x$, only the central-transition elements connect the upper and lower halves of thermo-equilibrium polarization $\omega_0 I_z$. Thus any irradiation without perturbation to the central transition mixes the population within two sub-brackets of the spin states and consequently increases the polarization between $m = +1/2$ and $-1/2$ states for the central transition. Assuming a complete saturation within the sub brackets equalizing the populations, the enhancement to the central transition would be $S + 1/2$. For static powder samples, an inward frequency-sweep inverting spin states adiabatically from the outer to the inner satellite transitions would ideally enhance the polarization by the maximum factor of S [25]. The sweep of the satellite transitions on both sides of the central transition can be applied simultaneously leading to a pure amplitude-modulated pulse, namely double-frequency sweep (DFS) [26]. In the case of magic-angle spinning, the sweep of satellite transition frequency across a constant *rf* frequency far off from the central transition occurs naturally under sample rotation for polarization enhancement [27]. A small sweep across just one spinning sideband has been found to help the spin-state inversion for higher enhancement than a fixed frequency [28]. Furthermore, as the selective excitation of the central transition does not deplete the polarization of the satellite transitions, the polarization transfer and enhancement from satellite transitions can repeated rapidly without waiting for full T_1 relaxation recovery allowing more time saving and signal enhancement [29]. In all cases, the *rf* frequency needs be sufficiently away from the central transition to avoid any mixing between the two central-transition spin states. It should also be noted that this kind of polarization enhancement is not applicable to MQMAS which excites directly from the multiple-quantum polarization.

High magnetic field plays an important role in solid state NMR of quadrupole nuclei. Besides the gains on spectral sensitivity and resolution, the high fields vary the scale between the chemical shift (B_0) and the second-order quadrupole shift (B_0^{-1}) for the separation and determination of EFG and chemical shift parameters. For samples with spectral broadening dominated by the second-order quadrupole effect, the sensitivity and resolution gains from high fields can be very dramatic [30]. The National High Magnetic Field Laboratory of the United States has recently commissioned a 36 T series-connected-hybrid powered magnet for researchers worldwide. The 36 T field with proton resonance frequency above 1.5 GHz, >50% increase over the highest superconducting NMR magnets commercially available today, is well suited for solid-state NMR of quadrupole nuclei [31].

Looking into the future, combining all the approaches of polarization enhancement, CPMG multiple echo-acquisition and efficient probes with strong B_1 field will expand the scope solid-state NMR of quadrupole nuclei and enable applications to insensitive low-γ nuclei and samples [32]. The high magnetic fields from the next generation NMR magnets and the use of other polarization enhancing techniques like dynamic nuclear polarization (DNP) will facilitate the use of various 2D separation methods such as isotropic vs anisotropic quadrupole shifts, chemical vs quadrupole shifts, and MAS averaged vs MAS modulated shifts to insensitive nuclei. These advanced techniques will provide more resolution and precision for measuring site-specific EFG and chemical shift parameters of complex systems. With the advent in *ab initio* calculation, the prediction of EFG and chemical shift parameters have been becoming more and more precise, reliable and applicable to larger and more complex molecules. The EFG and chemical shift parameters along can be used for peak assignment and provide valuable information on the molecular structure. In compliment with diffraction methods, increasing amount information from NMR parameters including those of quadrupole nuclei will allow the so-called NMR crystallography for molecular structure determination using polycrystalline samples [33].

Now let us switch the topic to the traditional methods of correlation spectroscopy, distance measurement and polarization transfer between two spins for spectral assignment and structure determination for samples containing quadrupole nuclei. The development for quadrupole nuclei has been lagging behind relatively to that for spin-1/2 due to several factors. First, not all but only one related to the central transition of the (2S + 1) level spin system, is manipulated by *rf* pulses and participates in the spin correlation and polarization transfer due to the limited *rf* field relative to the large quadrupole couplings. This generally leads to a reduction of (S + 1/2) in the efficiency as compared to the fully contributing two-level system of a spin-1/2. Second, the spin dynamics under *rf* irradiation for the (2S + 1) level system is more complex especially under MAS. Indeed, sample rotation induces level-crossings between the satellite transitions and the *rf* frequency. As the result, coherence can leak from central to satellite transitions during the brief crossings causing signal losses as first demonstrated by A. Vega in the seminal work on spin-lock under MAS published in JMR [34]. This effect often prevents the use of strong and windowless *rf* pulses for decoupling, recoupling and cross-polarization and consequently puts serious constrains in the use and design of pulse sequences for quadrupole nuclei. Let us first consider cross-polarization transfer which is widely used in solid-state NMR for enhancing signals by transferring polarization from ^{1}H to low-γ nuclei and for establishing hetero-nuclear correlation (HETCOR). For half-integer quadrupole nuclei, the traditional Hartmann-Hahn transfer confronts several problems and issues. First, the polarization transfer usually occurs to the central transition. The proton polarization can be considered as product spin operators which consist of one part with the two central-transition states and the other for the rest. The latter does not contribute to polarization transfer to quadrupole nuclei [35]. Second, the spin-lock during Hartmann-Hahn cross-polarization is complicated by the level-crossing of the satellite transition with the *rf* frequency induced by the sample rotation as mentioned previously. In order to minimize coherence leakage to the satellite transitions, low-*rf* or rotor synchronized pulsed spin-lock has to be used. The low *rf* not only limits the bandwidth needed for covering frequency offsets but also forces the lowering of the ^{1}H spin-lock *rf* field in order to match the Hartmann-Hahn condition under MAS $\gamma_H B_{1H} = -\gamma_Q B_{1Q}(S + 1/2) + n\omega_r$ [35]. ^{1}H spin-lock near the rotary resonance is usually inferior than spin-lock under strong *rf* field, consequently affecting the transfer efficiency [36]. In addition, the difference in T_1 relaxation properties between quadrupole nuclei and protons plays unfavorably for cross-polarization in term of recycle delay. These limitations make cross-polarization rarely used for the purpose of signal enhancement. Instead, its usages are mostly for establishing HETCOR under MAS [37].

An alternative to Hartmann-Hahn CP is dipolar-based INEPT transfer sometimes also called TEDOR transfer [38,39]. Dipolar interaction can be reintroduced under MAS with the PRESTO or RINEPT sequences, where the recoupling is preferably applied to the spin-1/2 considering the *rf* spin dynamics issue for quadrupole nuclei. The PRESTO method [40,41] has been designed specifically using a minimal number of *rf* pulses for quadrupole nuclei [40,41]. The refocused-INEPT method employs two more refocusing pulses. One unique feature about PRESTO is that a zero-crossing for the transfer can be observed and it allows the determination of the dipolar coupling and inter-nuclear distances [41]. It should be mentioned that for both methods the ^{1}H T_2 under the dipolar recoupling is usually shorter than $T_{1\rho}$ under spin-lock therefore often limiting the length of contact time for long-range transfer. The main problem which has rarely been mentioned is the (S + 1/2) reduction in transfer efficiency as compared to spin-1/2. Only two central transition spin states out of (2S + 1) energy levels are involved and contributing to the polarization transfer.

Distance measurement is a powerful tool for structure determination for example with the REDOR method under MAS [42]. When measuring the dipolar coupling from a spin-1/2, the spin states can be fully inverted using a π-pulse resulting in a REDOR difference curve $(S_0 - S)/S_0$ plateaued at $\sim$100%. Dipolar recoupling is usually applied to the indirect spin for robustness to reintroduce only the desired heteronuclear dipolar interaction. In the case of an indirect quadrupole spin, the dipolar recoupling sequence is preferably applied to the spin-1/2 for the reason mentioned above. Such a rearrangement automatically reintroduces the chemical shift anisotropy (CSA) of the directly observed spin. It relies on the spin-echo to refocus the CSA for the REDOR measurement which requires extremely stable spinning and perfect timing between the dipolar evolution and refocusing periods of the long spin-echo to avoid the t_1-noise problem. The other complication for REDOR experiment with quadrupole nuclei is the inversion pulses. Ideally, a complete inversion of all spin states would give the maximum difference curve but this is usually not possible with $\omega_Q \gg \omega_1$. Let us consider the first case of an integer spin-1 such as ^{14}N. It is practically not possible for a strong and short pulse to invert the spin states in the presence of the large quadrupole coupling. The REAPDOR method uses a longer pulse instead, typically lasting about 1/3 of a rotor period. It relies on the adiabatic-passage level-crossing mechanism to invert the spin states yielding difference curves plateaued about 2/3 [43]. When a longer pulse is applied with the aim of saturating all transitions, the RESPDOR [44] method can also achieve similar fractions. For a pair with a half-integer quadrupole spin, the two central-transition spin states can be inverted selectively resulting to the same REDOR curve as a spin-1/2 but scaled by 1/(S + 1/2) as the spin states other than the central transition are unperturbed. Saturating or inverting the satellite transitions using long and strong pulses yields faster dephasing curves and higher plateau values [45].

A unique recoupling method for quadrupole nuclei is to simply blasting *rf* irradiation pulse to the quadrupole spin during the long dipolar evolution. The passages from the rotationally induced level-crossing between the satellite transitions and the *rf* frequency perturb the spin states at the same periodicity of the spinning frequency. The matching frequency introduces the dipolar recoupling which can be measured using the spin-echo difference method. This so-called TRAPDOR method [46,47] is robust though spin dynamics for the recoupling mechanism is complex and quantitative analysis usually requires numerical simulations.

The hetero-nuclei multiple-quantum correlation (HMQC) using dipolar recoupling extends the REDOR experiment with indirect frequency encoding. It replaces the inverting pulse with a pair of frequency-encoding pulses such that pair-wise spatial proximities can be probed. It is an alternative to cross-polarization for establishing HETCOR with quadrupole nuclei and indirect detection of insensitive low-γ nuclei [48,49]. The HMQC method has several attractive features. It allows the use of a minimum number of two *rf* pulses to encode the quadrupole nuclei including integer spins such as ^{14}N. The dipolar recoupling can be applied exclusively on the observing spin-1/2. The signal is originated from and ended up for signal detection with the spin-1/2 nucleus such as ^{13}C taking the advantages of narrower line width and cross-polarization enhancement from ^1H. The HMQC also has a few drawbacks. First, the T_2 relaxation of the observing spin-1/2 contributes the line width of the indirectly detected quadrupole nucleus. Fortunately this additional broadening is usually negligible as the line width of the quadrupole nucleus is often large. Second, the HMQC experiment may prong to t_1-noise as the recoupling applied to the observing nucleus automatically reintroduces the CSA. Small timing errors between the excitation and conversion periods cause imperfect refocus of the CSA and t_1-noise [50]. Third, the HMQC suffers a loss of efficiency due to the spin number of the quadrupole spin. The indirect frequency encoding applies only to the central transition out of all (2S + 1) states, a scale of 1/(S + 1/2) to the efficiency as compared to a spin-1/2.

Double-quantum correlation spectroscopy is a robust method to probe spatial proximity among homo-nuclear spins. The double-quantum filtration eliminates the strong diagonal peaks often seen in single-quantum correlation spectra and allows the measurement even between two indistinguishable equivalent spins. When applying the DQ method to half-integer quadrupole spins, the dipolar recoupling for generating inter-spin DQ coherence is usually restrict to the central transitions. Similar to HMQC, this scales down the DQ efficiency by (S + 1/2). As for the recoupling, strong and windowless pulses which inevitably cause coherence leaks to satellite transitions should be avoided. Low-power recoupling such as the HORROR method [51] is preferred. Consequently, frequency offset often becomes an issue at high fields. Furthermore for spins >1/2, single-spin DQ coherence can exist hence passing through the DQ filtration. A central transition selective π-pulse is useful for its elimination because it converts the single-spin and two-spin DQ coherences differently, $|\Delta p| = 4$ for two-spin central-transition DQ coherence and $|\Delta p| = 2$ for single-spin DQ satellite-transition coherence. Despite suffering from the low efficiency and offset issues, the DQ method has been becoming more frequently used for probe spatial proximity among quadrupole nuclei [52].

In summary, powerful methods commonly used for spin-1/2 based correlation, distance measurement and indirect detection have been developed and becoming more frequently used for quadrupole nuclei. The main complication and drawback as compared to spin-1/2 come from two facts: coherence leakage when applying *rf* under sample rotation and a factor of (S + 1/2) loss associated with most of the polarization transfer and correlation experiments. New ideas and methods will be developed to address these issues. Recently, the polarization enhancement method has been applied to the HMQC experiment converting the heteronuclear multiple-quantum coherence of satellite transitions to the central transition to accelerate the HMQC coherence transfer [53]. The multiple-quantum coherence with the satellite transitions also has been used for the acquisition of the satellite-transition HMQC spectra simultaneously with the central transition [54]. These development step out the boundary of the central transition. Multiple-pulse methods and super cycles were developed to broaden the bandwidth of low *rf* dipolar recoupling [55]. The development along this direction will improve the efficiency of advanced NMR techniques enabling their applications to various materials containing quadrupole nuclei for the elucidation of spectral and structural information.

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