

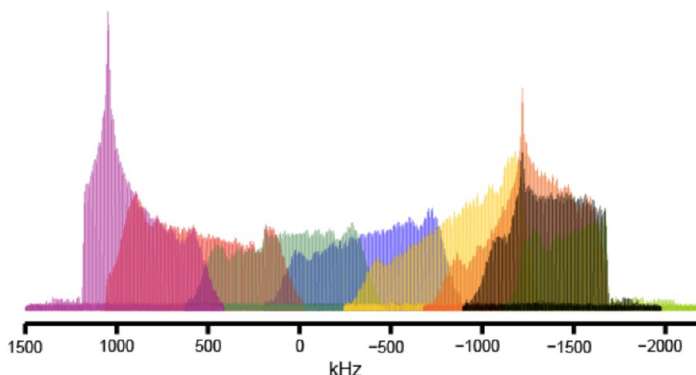
Ultra-Wideline Solid-State NMR Spectroscopy

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CONSPECTUS



- Ultra-wideline NMR:
- Frequency-Stepping
 - CPMG Trains
 - WURST Pulses
 - Broadband CP

Although solid-state NMR (SSNMR) provides rich information about molecular structure and dynamics, the small spin population differences between pairs of spin states that give rise to NMR transitions make it an inherently insensitive spectroscopic technique in terms of signal acquisition. Scientists have continuously addressed this issue via improvements in NMR hardware and probes, increases in the strength of the magnetic field, and the development of innovative pulse sequences and acquisition methodologies. As a result, researchers can now study NMR-active nuclides previously thought to be unobservable or too unresponsive for routine examination via SSNMR. Several factors can make it extremely challenging to detect signal or acquire spectra using SSNMR: (i) low gyromagnetic ratios (i.e., low Larmor frequencies), (ii) low natural abundances or dilution of the nuclide of interest (e.g., metal nuclides in proteins or in organometallic catalysts supported on silica), (iii) inconvenient relaxation characteristics (e.g., very long longitudinal or very short transverse relaxation times), and/or (iv) extremely broad powder patterns arising from large anisotropic NMR interactions.

Our research group has been particularly interested in efficient acquisition of broad NMR powder patterns for a variety of spin-1/2 and quadrupolar (spin > 1/2) nuclides. Traditionally, researchers have used the term “wideline” NMR to refer to experiments yielding broad ^1H and ^2H SSNMR spectra ranging from tens of kHz to ~ 250 kHz in breadth. With modern FT NMR hardware, uniform excitation in these spectral ranges is relatively easy, allowing for the acquisition of high quality spectra. However, spectra that range in breadth from ca. 250 kHz to tens of MHz cannot be uniformly excited with conventional, high-power rectangular pulses. Rather, researchers must apply special methodologies to acquire such spectra, which have inherently low S/N because the signal intensity is spread across such large spectral breadths. We have suggested the term ultra-wideline NMR (UWNMR) spectroscopy to describe this set of methodologies.

This Account describes recent developments in pulse sequences and strategies for the efficient acquisition of UWNMR spectra. After an introduction to anisotropically broadened NMR patterns, we give a brief history of methods used to acquire UWNMR spectra. We then discuss new acquisition methodologies, including the acquisition of CPMG echo trains and the application of pulses capable of broadband excitation and refocusing. Finally, we present several applications of UWNMR methods that use these broadband pulses.

1. Introduction

Solid-state NMR (SSNMR) spectroscopy continues to be one of the most valuable methods of studying molecular-level structure and dynamics in a vast array of systems.

Many elements have NMR-active nuclides which are unresponsive to the NMR experiment, largely due to low natural abundances or low gyromagnetic ratios. In many SSNMR experiments, this problem is compounded by anisotropic

broadening of powder patterns, which serves to drastically reduce S/N. Spectra featuring broad powder patterns ranging from 250 kHz to tens of MHz in breadth cannot be easily acquired with conventional experiments utilizing rectangular high-power pulses, largely because of their limited excitation bandwidths. A variety of methodologies are available for acquiring such patterns, which are grouped in the category of *ultra-wideline NMR* (UWNMR) spectroscopy.^{1,2}

UWNMR spectra can arise from three different anisotropic NMR interactions, including (i) the quadrupolar interaction (QI), (ii) the chemical shift anisotropy (CSA), and (iii) anisotropic broadening from unpaired electrons (e.g., paramagnetic or conduction electrons, as in the case of Knight shift anisotropy, KSA). Generally speaking, the broadening of powder patterns associated with direct dipolar and indirect nuclear spin–spin coupling interactions is very small by comparison, and is omitted here. Herein, discussion is largely limited to diamagnetic systems with large QIs or CSAs, which are the most prevalent; however, studies crucial in the development of UWNMR methods have been conducted on systems exhibiting KSA (*vide infra*).

The QI arises from the interplay of the nuclear quadrupole moment (NQM) with the local electric field gradients (EFGs) with their origins at the nucleus. The local EFG is described by a traceless, symmetric second-rank tensor with principal components defined as $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. The magnitude of the quadrupolar interaction is given by the quadrupolar coupling constant, C_Q :

$$C_Q = eqeQ/h = V_{33}eQ/h \quad (1)$$

where $eq = V_{33}$ is the component with the largest absolute magnitude and Q is the NQM. Since the EFG tensor is traceless, a second dimensionless parameter, the asymmetry parameter, η_Q , completes the definition of the QI:

$$\eta_Q = (V_{11} - V_{22})/V_{33} \quad (2)$$

There is much interest in determining the values of these parameters from SSNMR spectra, since they lend insight into local Platonic or “spherical” symmetry (C_Q) and the axial symmetry (η_Q) of the local ground-state electronic environment.

SSNMR spectra of half-integer spin quadrupolar nuclei are influenced by first- and second-order QIs (FOQI and SOQI). The frequency shifts associated with the FOQI are much larger than those of the SOQI; in many cases, patterns influenced by the FOQI are broadened beyond all hope of detection. The FOQI does not influence the *central transition* powder pattern (i.e., $+1/2 \leftrightarrow -1/2$, CT), but only the outer

satellite transitions (e.g., $\pm 3/2 \leftrightarrow \pm 1/2$, etc., ST). The SOQI affects both the CTs and STs, and its complex orientation dependence is often observed in the CT powder patterns. Integer spin quadrupolar nuclei, of which there are few NMR-active species (e.g., ^{14}N ($I = 1$) and ^{10}B ($I = 3$)), do not have a CT; hence, their SSNMR spectra are almost always composed of broad STs dominated by the FOQI (subtle effects of the SOQI can sometimes be seen under conditions of magic-angle spinning, MAS).³

The CSA is described by a second-rank tensor with principal components defined such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ (δ_{11} and δ_{33} represent the directions of lowest and highest nuclear magnetic shielding, respectively). The CS tensor is not traceless, and the average of the three principal components is equal to the isotropic chemical shift, δ_{iso} . In the case of spin-1/2 nuclides, a number of heavier metals are known to have large CSAs which give rise to UWNMR powder patterns (e.g., ^{119}Sn , ^{195}Pt , ^{199}Hg , and ^{207}Pb). Several half-integer quadrupolar nuclides have broad powder patterns influenced by both the QI and CSA, as well as the relative orientation of the EFG and CS tensors (e.g., ^{59}Co). However, in most of the examples discussed herein, the QIs are so large in comparison to the CSAs that the broadening effects of the former make detection of the latter nearly impossible.

2. UWNMR Methodologies

There are a number of strategies available for acquiring high-quality UWNMR spectra which can be divided into several classes: (i) stepped spectral acquisition/excitation, (ii) signal enhancement via acquisition of Carr-Purcell Meiboom-Gill (CPMG) echo trains, (iii) the use of chirped/adiabatic pulses, (iv) cross-polarization (CP) techniques, and (v) the use of specialized hardware. Only the first four topics are covered herein; readers are referred elsewhere for more information on probes, microcoils, hardware, and so forth for use in UWNMR experiments.²

2.1. “Stepped” Acquisitions and Historical Considerations. In the early years of FT NMR, it was realized that certain SSNMR powder patterns could not be uniformly excited with a single rectangular pulse, nor were they amenable to acquisition with conventional CW NMR experiments. A solution to this problem was to acquire the spectrum in “pieces” by either *sweeping* the field or *stepping* the transmitter.

In a seminal series of papers by Slichter and co-workers,^{4–6} ^{195}Pt ($I = 1/2$) NMR spectra of Pt nanoparticles (NPs) were acquired by utilizing a fixed transmitter frequency ($\nu_0(^{195}\text{Pt}) = 74$ MHz) and varying the magnetic field from 80 to 85 kG.

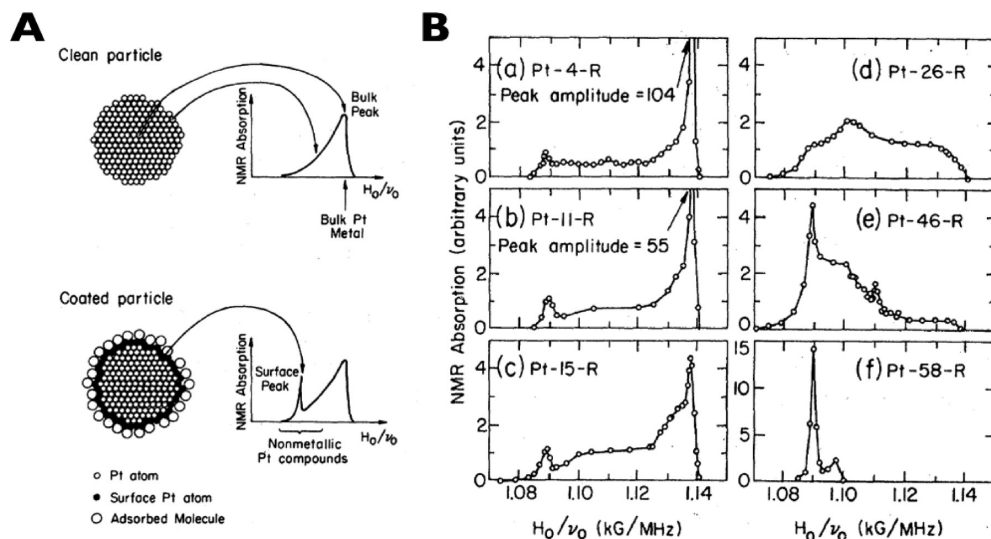


FIGURE 1. (A) Theoretical patterns expected for clean (top) and coated (bottom) Pt nanoparticles (NPs). (B) ^{195}Pt NMR spectra of six NPs of varying size acquired by stepping the magnetic field at 77 K and $\nu_0(^{195}\text{Pt}) = 74$ MHz. Adapted from ref 4.

The ^{195}Pt patterns are extremely broad due to ^{195}Pt KSA; hence, spin-echo experiments were utilized, which can refocus the effects of inhomogeneous broadening. The magnetic field was incremented in steps across the pattern, and the echo intensities were plotted as a function of magnetic field (Figure 1). They reported the acquisition of 50 000+ transients for each echo; the high degree of coherent noise was eliminated by using an "add-subtract" echo strategy. In the end, they were able to examine NPs of varying sizes, differentiate Pt sites in bulk phases from those in the NP core and surface regions, and examine surface interactions with gases.

Bastow et al. conducted many of the early UWNMR studies on half-integer quadrupolar nuclei. One series of papers describes the differentiation of multiple phases of zirconia utilizing ^{91}Zr ($I = 5/2$) NMR, via the CT powder patterns.⁷⁻⁹ Their experiments were conducted at a fixed field of 9.4 T ($\nu_0(^{91}\text{Zr}) = 37.21$ MHz). Spin-echo experiments were conducted at evenly incremented transmitter frequencies, and the NMR probe retuned for each "step" (Figure 2). The final SOQI-dominated CT powder patterns were formed by plotting the spin-echo intensity as a function of transmitter frequency.

The major problems with these methodologies are the long time periods required for spectral acquisition and the limitation of spectral resolution by the number of increments in magnetic field or transmitter frequency. While these patterns clearly reveal information on anisotropic NMR interactions, higher resolution versions of these experiments are necessary for cases in which there were multiple patterns with similar sets of NMR parameters, or where the

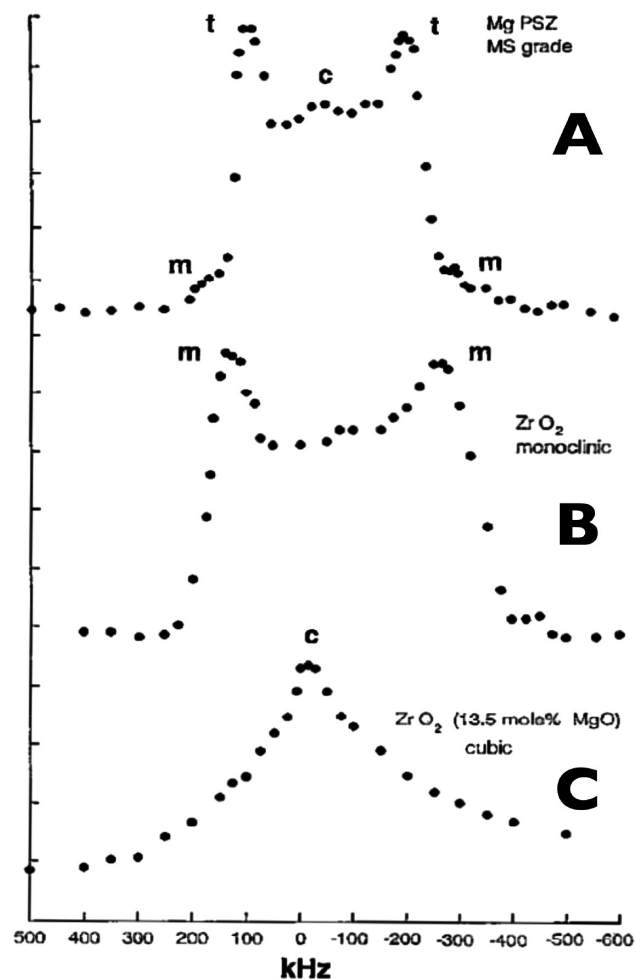


FIGURE 2. ^{91}Zr NMR spectra of (A) t-phase ZrO₂ in MS grade MgPSZ (9.3 mol % MgO); the minor peak from the residual c- and m-phase are marked c and m; (B) pure m-phase ZrO₂; (C) magnesia fully stabilized cubic ZrO₂ (13.5% MgO). Adapted from ref 9.

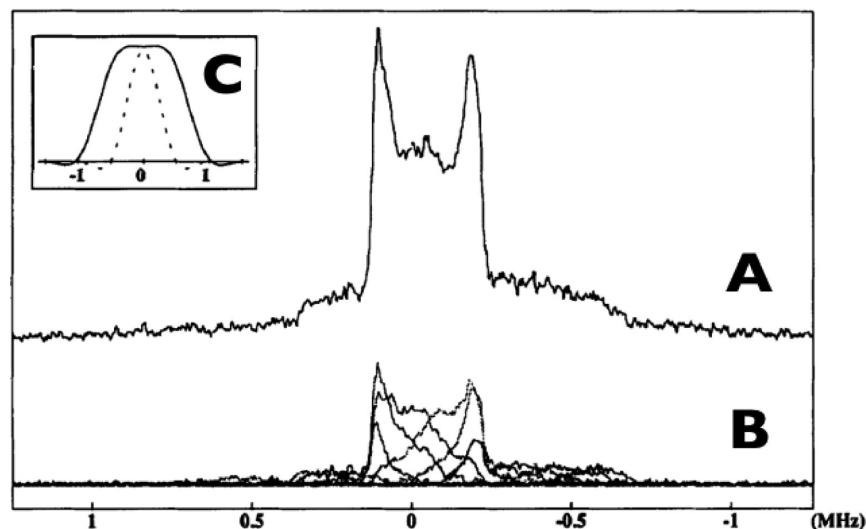


FIGURE 3. (A) Total ^{69}Ga ($l = 1/2$) VOCS NMR spectrum of $\beta\text{-Ga}_2\text{O}_3$ acquired at 7.0 T. (B) Nine subspectra from which the total spectrum is produced. (C) Total irradiation bandwidth of 1 MHz (dashed line shows contribution from a single transmitter frequency). Adapted from ref 10.

powder patterns are influenced by both anisotropic QI and CS interactions.

Massiot and co-workers proposed an interesting solution to the problem of resolution: similar to Bastow, they acquired $^{69/71}\text{Ga}$, ($l = 3/2$) SSNMR spectra at a fixed magnetic field by stepping the transmitter across the pattern.¹⁰ However, instead of plotting echo intensities as a function of transmitter frequency, individual FIDs were FT'ed to produce frequency-domain subspectra, which were then coadded to yield the overall CT patterns (Figure 3). They dubbed this technique the “*variable-offset cumulative spectra*” (VOCS) method. Importantly, (i) fewer “steps” are needed to acquire the entire pattern and (ii) the spectral resolution of the broad pattern is determined by the dwell time used in the spin–echo experiment.

Frydman et al. utilized the VOCS method to acquire ^{59}Co ($l = 7/2$) NMR spectra of cobalt(III)phthalocyanines.¹¹ They focused on the optimization of spectral acquisition, ensuring maximum S/N gain while verifying uniformly excited spectra. They point out that broad CT patterns can be severely distorted, due to the strong interdependence of the rf field strength, ν_1 , and the orientation dependent quadrupolar frequency, ν_Q . The best choice for obtaining undistorted CT patterns is the use of weak rf fields (e.g., 5–10 kHz) combined with short pulses to ensure broadband excitation. If nutation frequencies are too low, S/N does not build up quickly, so a balance must be struck between rapid spectral acquisition and the desire for undistorted patterns. They also suggest the use of full-echo acquisition and processing, as well as short interpulse delays to reduce signal loss from rapid T_2 decay.

It is important to note that all of the aforementioned experiments were conducted upon static samples, and not under MAS conditions. It has been demonstrated for spin-1/2 nuclides with broad CSA patterns that it is very difficult (or impossible in some cases) to uniformly excite the entire spinning sideband (SSB) manifold in both direct excitation and CP experiments.¹² In such cases, individual SSB intensities are not representative of the MAS-averaged CS tensor, rendering useless its determination via Herzfeld-Berger analysis. Frequency-stepped MAS experiments have been conducted in few cases, since only a qualitative estimate of the CS tensor can be obtained.¹³

2.2. Acquisition of CPMG Echo Trains for Enhancement of S/N. In 1997, Larsen et al. reintroduced the idea of using CPMG echo trains for the purpose of enhancing S/N in the SSNMR spectra of half-integer spin quadrupolar nuclei.¹⁴ CPMG enhancements had previously been used for signal enhancement for variety of spin-1/2 nuclides including ^{13}C ,¹⁵ and in earlier ^2H ($l = 1$)¹⁶ and ^{87}Rb ($l = 3/2$)¹⁷ NMR studies. The quadrupolar CPMG (QCPMG) sequence involves the repeated refocusing and acquisition of spin echoes (the collection of more spin echoes leads to higher S/N, Figure 4A). The FID is dependent upon the nucleus under investigation having a suitably long T_2 , and can be processed in two general ways: (i) FT the entire echo train FID, leading to a so-called “spikelet” spectrum whose manifold represents the idealized powder pattern, or (ii) shift and add the echoes into a single echo FID, followed by its FT. Larsen demonstrated the effectiveness of QCPMG in yielding high quality ^{87}Rb and ^{59}Co CT powder patterns with S/N enhancements of up to 30 times compared to conventional

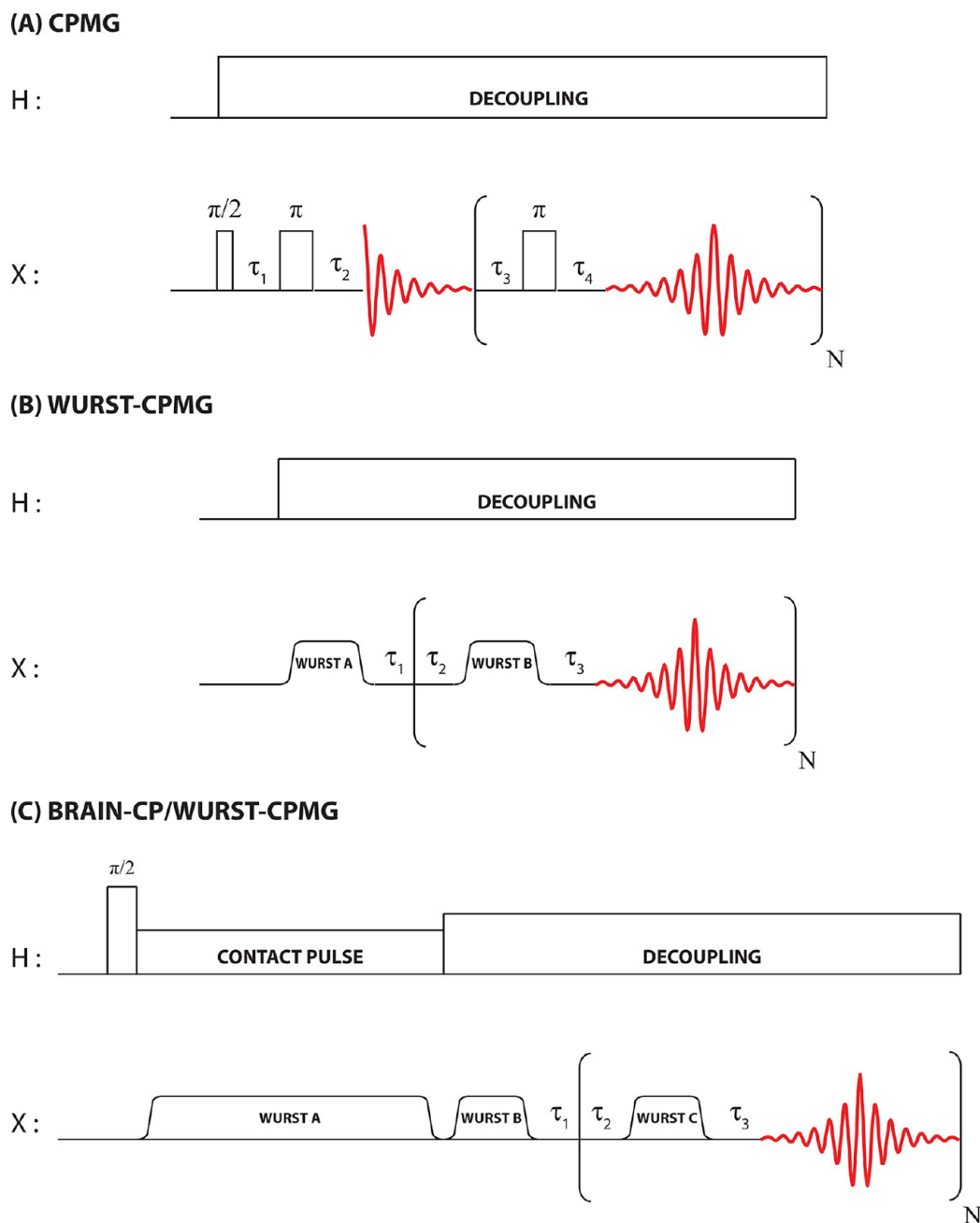


FIGURE 4. (A) Quadrupolar CPMG (QCPMG) pulse sequence. (B) WURST-CPMG pulse sequence for broadband excitation. (C) BRAIN-CP pulse sequence (WURST A and WURST B pulses), with a WURST-CPMG acquisition train (WURST C pulse).

spin-echo spectra. Ellis, Lipton and co-workers applied a combination of the VOCS method with the QCPMG pulse sequence to acquire ^{67}Zn ($I = 5/2$) UWNMR spectra of a series of model compounds for biological molecules¹⁸ as well as Zn^{2+} ions in biological systems.^{19,20} They found that low temperature conditions (i.e., 10 K) and CP were both beneficial for experiments on samples with low Zn^{2+} concentrations.²¹

Around this time, my research group was using similar methods for ^{91}Zr ($I = 5/2$) UWNMR of metallocenes and

zirconia NMR rotors,²² and ^{27}Al ($I = 5/2$) UWNMR of trigonal planar aluminum complexes (Figure 5).²³ To ensure the production of distortionless UWNMR spectra, we proposed a simple method of optimizing the spacings between the transmitter frequency steps, and noted the importance of setting the transmitter offsets to multiple integer values of the spikelet spacings. Since this time, there have been many modifications to QCPMG acquisition and processing,²⁴ as well as numerous applications to both quadrupolar and spin-1/2 nuclei.²

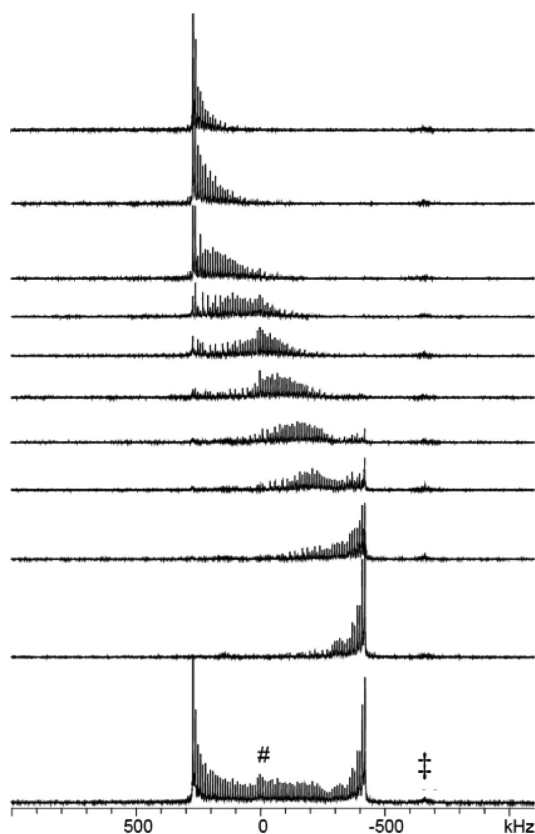


FIGURE 5. Frequency-stepped ^{27}Al QCPMG NMR spectra of trimesityl-aluminum (bottom) produced from coaddition of the individual sub-spectra (top). ‡ indicates FM radio signal interference, and # denotes minor impurities. Adapted from ref 23.

2.3. Broadband Excitation. It is challenging in many instances to obtain a uniformly excited UW powder pattern, since nuclei in individual crystallites with unique orientation dependent NMR interactions may experience different nutation frequencies. Notably, for CT patterns of half-integer nuclei, there are only two regimes where orientation-dependent nutation is minimized. If $\nu_1 \gg \nu_Q$, the nutation frequencies for all of the spins are effectively equal, and a uniformly excited pattern can be produced. However, this *nonselective* case only holds for small QIs. More often, $\nu_1 \ll \nu_Q$; in this case, CT *selective* pulses are often applied, where $\tau_{\text{sel}} = \tau_{\text{nonselect}}/(l + 1/2)$. Again, if low rf fields are used with short selective pulses, uniform excitation is obtained, but sometimes at the expense of S/N.¹¹

Chirped pulses, which have modulated amplitudes and phases, are an excellent alternative to standard rectangular pulses. Many chirped pulses have been developed for use in NMR, including, for improved refocusing in solution NMR experiments,²⁵ and for control of MQ coherences in experiments on quadrupolar nuclei.²⁶ The chirped pulses used by my research group in UWNMR experiments belong to the

WURST (wideband uniform-rate smooth-truncation) class,²⁷ which features a simple amplitude modulation and a complex phase modulation (the latter is responsible for making an effective frequency sweep while irradiating at a constant transmitter frequency).

Bhattacharya and Frydman suggested the use of Hahn-echo like pulse sequences comprising two WURST pulses, the first for excitation and the second for refocusing, for the acquisition of quadrupolar CT patterns.²⁸ The WURST pulses are highly effective in providing broadband excitation, as well as refocusing the inhomogeneous interactions into spin echoes or a frequency-encoded time domain pattern. In the former case, the spin echo can be FT'ed to yield a CT pattern; in the latter case, the FID can be magnitude processed (no FT) to produce a frequency-encoded time domain pattern.

This work inspired us to develop a simple sequence that can be employed to acquire a single spin echo or CPMG train of echoes (Figure 4B).²⁹ Two WURST-80 pulses are applied for excitation and refocusing, followed by a train of WURST-80 pulses interlaced with acquisition periods. The two initial pulses are identical in terms of amplitude and phase modulation, and feature the use of relatively low rf fields to ensure that the spin polarization remains near the effective field. The pulse sequence, called WURST-CPMG, requires very little in the way of optimization or parametrization, and was utilized for the acquisition of ^{71}Ga , ^{91}Zr and ^{59}Co CT powder patterns.

We also found that the WURST-CPMG sequence could be used in frequency-stepped experiments for nuclides exhibiting extremely broad powder patterns.³⁰ We were able to acquire high quality ^{35}Cl and ^{65}Cu ($l = 3/2$) CT patterns of $(\text{C}_5\text{H}_5)_2\text{ZrHCl}$ (Figure 6) and $(\text{PPh}_3)_2\text{CuO}_2\text{CCH}_3$, respectively, the combined ^{59}Co CT and total ST patterns of $\text{Co}(\text{acac})_3$, and the total ^{10}B ($l = 3$) ST patterns for $\nu\text{-B}_2\text{O}_3$. In systems with protons, we found that strong ^1H decoupling is generally necessary to eliminate or reduce the contribution of dipolar coupling to the T_2 , and to ensure that the CPMG echo train continues for as long as possible. We also demonstrated that this sequence can be applied for the acquisition of broad patterns of spin-1/2 nuclides with large CSAs;³¹ however, in cases of long T_1 's, CP experiments are a better choice (vide infra).

2.4. Broadband CP and UWNMR. Cross-polarization (CP) is one of the most widely used techniques in SSNMR.³² CP is normally applied for purposes of signal enhancement, producing transfer of polarization from abundant, high- γ nuclei (e.g., ^1H , ^{19}F , etc.) to dilute, lower- γ nuclei. In typical CP experiments on spin-1/2 nuclides, the generally shorter

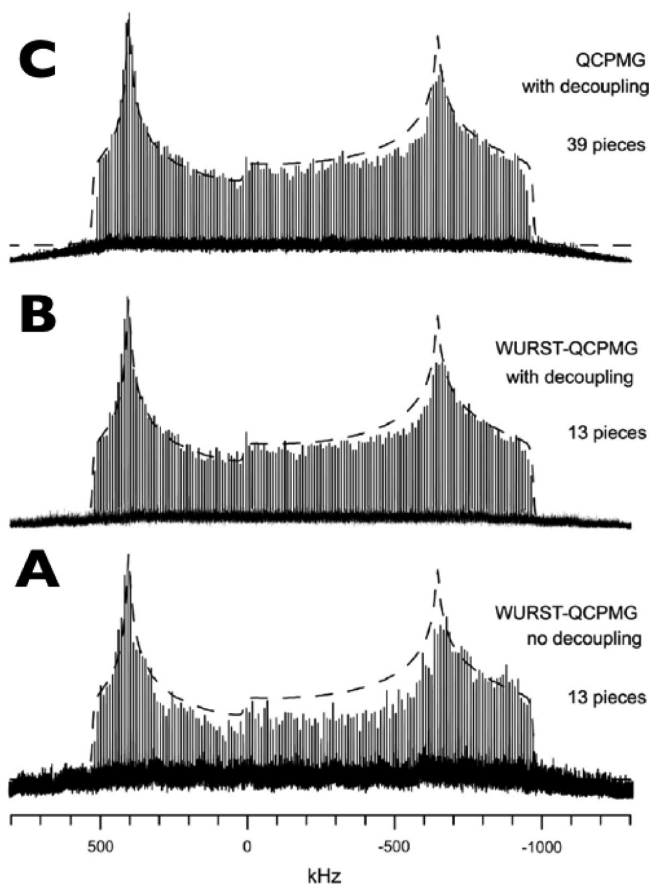


FIGURE 6. ^{35}Cl CT spectra of Schwartz's reagent, $(\text{C}_5\text{H}_5)_2\text{ZrHCl}$, obtained at 9.4 T utilizing (A) WURST-CPMG without ^1H decoupling, (B) WURST-CPMG with ^1H decoupling, and (C) QCPMG with decoupling. High-power ^1H decoupling increases the effective $T_2(^{35}\text{Cl})$, leading to longer CPMG trains and higher S/N. In comparing WURST-QCPMG to QCPMG, the former produces a higher S/N in fewer experiments. Adapted from ref 30.

$T_1(^1\text{H})$ values allow for shorter recycle delays and reduced experimental times compared to direct excitation experiments.

There have been very few reports of UWNMR CP experiments. Ellis et al. utilized ^1H - ^{67}Zn CP experiments run at 10 K to yield ^{67}Zn NMR spectra of a variety of biological model compounds and enzymes.²¹ Wasylishen et al. and our research group have both explored the application of CP for the acquisition of CPMG spectra of heavier spin-1/2 nuclides with large CSAs, including ^{109}Ag , ^{113}Cd , ^{119}Sn , ^{195}Pt , ^{199}Hg , and ^{207}Pb .^{33,34} CP/CPMG experiments are utilized to construct UWNMR spectra by stepping the X-channel transmitter, and are facile to implement; however, one major limitation is the very restricted excitation bandwidth on the X-channel, requiring that numerous CP experiments be conducted with limited distances between steps.

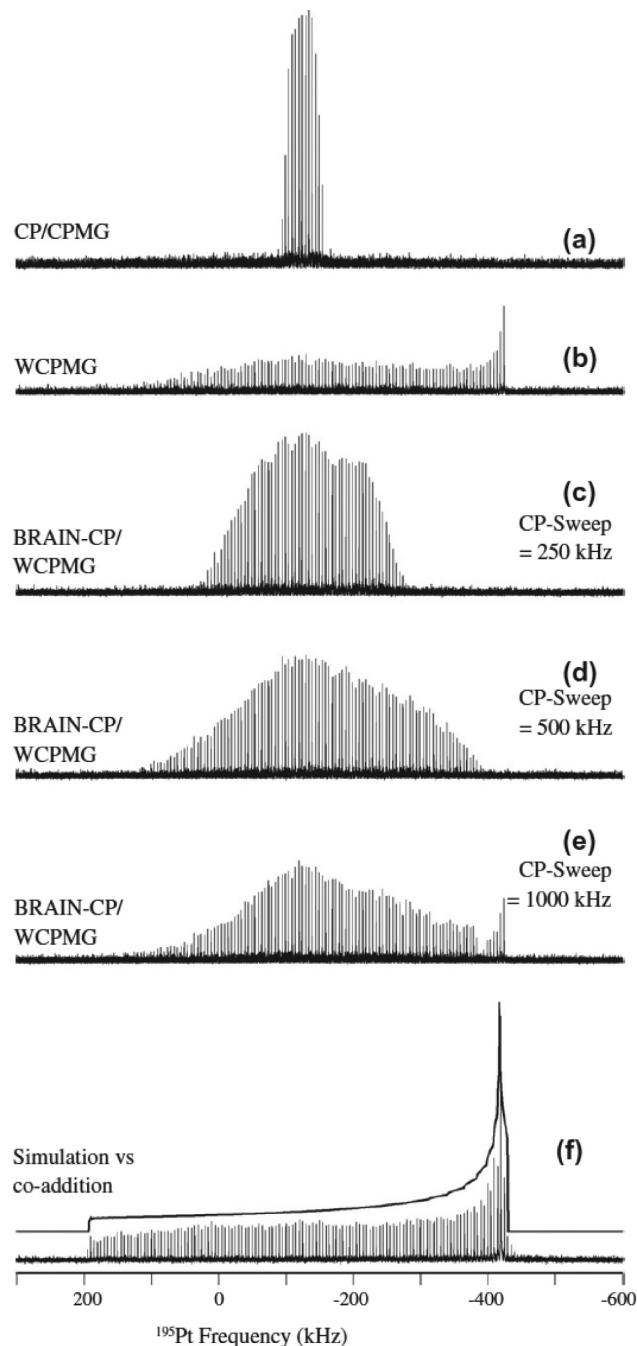


FIGURE 7. Experimental and simulated ^{195}Pt NMR spectra of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$. Experimental spectra acquired with (a) CP/CPMG, (b) WURST-CPMG, (c) BRAIN-CP/WURST-CPMG (250 kHz CP sweep), (d) BRAIN-CP/WURST-CPMG (500 kHz CP sweep), (e) BRAIN-CP/WURST-CPMG (1000 kHz CP sweep), (f) final coadded spectrum (bottom, from five subspectra) and idealized simulation (top). Adapted from ref 35.

We recently published a paper describing a broadband CP pulse sequence, dubbed as Broadband Adiabatic INversion (BRAIN) CP (Figure 4C).³⁵ On the ^1H channel, the sequence is identical to conventional CP. However, on the X-channel, there are several key differences. First, during the contact

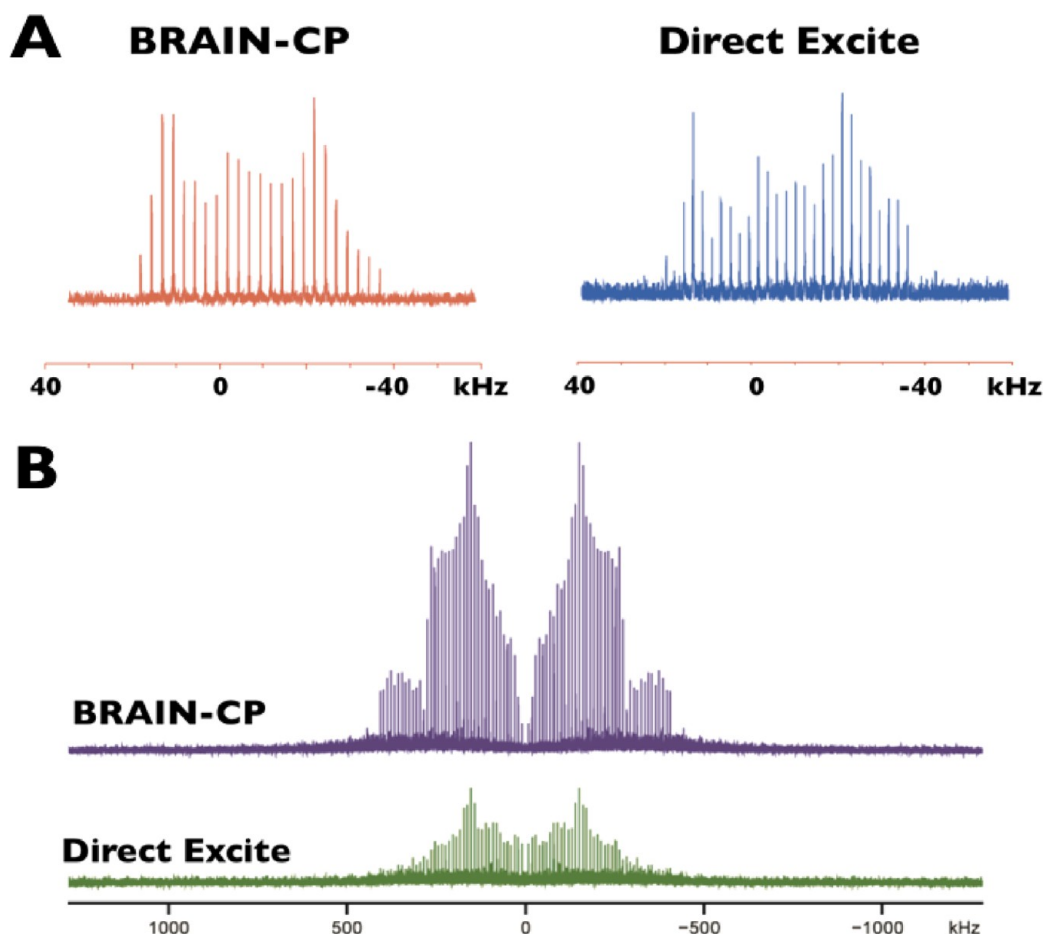


FIGURE 8. (A) ^{39}K UWNMR spectrum of CpK acquired at 9.4 T with BRAIN-CP/WURST-CPMG (left, 10 min) and (i.e., QCPMG) CPMG (right, direct excitation of ^{39}K , 21 h). (B) ^{14}N powder patterns of trigonelline HCl acquired with BRAIN-CP/WURST-CPMG (top, 120 min) and WURST-CPMG (bottom, 480 min). See Supporting Information for experimental details.

period, a frequency swept WURST-80 *inversion pulse* is applied to transfer polarization to the dilute nuclei, and to store this polarization as $-I_z$. Second, a *conversion pulse* is applied to rotate the inverted spin polarization into the transverse plane for detection. Finally, one may acquire a single spin echo, or utilize the aforementioned WURST-CPMG pulse sequence to acquire an echo train. To obtain the maximum polarization along the $-z$ direction, we found that the use of low rf fields on the X channel is crucial; this turns out to be a great advantage for acquiring CP NMR spectra of low- γ nuclei, which normally require long contact times and relatively strong ^1H rf fields. We were able to demonstrate the efficacy of BRAIN-CP for the acquisition of ^{119}Sn , ^{207}Pb , ^{119}Hg , and ^{195}Pt UWNMR spectra, both in terms of broadband excitation and signal enhancement (^{195}Pt UWNMR, Figure 7).³⁵ Interestingly, the CP bandwidths seem to be limited by the excitation bandwidth of the probe, and not the pulse sequence itself.

We have recently been applying BRAIN-CP to different quadrupolar nuclei. Due to their complex relaxation and CP

behaviors, the signal enhancement is not always optimal; however, broadband excitation is possible. In Figure 8, two instances of efficient broadband CP for quadrupoles are shown. A ^{39}K UWNMR spectrum of the CT pattern of CpK can be acquired in a single experiment in approximately 10 min at 9.4 T ($\nu_0 = 18.67$ MHz), compared to ca. 21 h utilizing a direct excitation CPMG experiment. ^{14}N SSNMR spectra of trigonelline HCl, a pharmaceutical compound, acquired utilizing broadband CP and DE methods, reveal that not only is there a significant S/N gain from CP, but certain spectral regions are more efficiently excited.

3. Applications of Broadband Pulses in UWNMR

Over the past 10 years, the development of the aforementioned methodologies, combined with the increased availability of high field NMR spectrometers (e.g., 18.8 T or higher) and improvements in NMR hardware, have resulted in numerous UWNMR studies on a variety of different nuclides

of elements across the periodic table. Since these studies are too numerous² to discuss fully herein, attention is focused in this last section to some select studies by our group and others.

3.1. Main Group Elements and Transition Metals. Our early studies on metallocenes and other organometallics utilized frequency-stepped QCPMG to acquire ^{91}Zr and ^{65}Cu SSNMR spectra.^{22,36} By comparison, the use of the WURST-CPMG in our later work on ^{65}Cu NMR of bis-(triphenylphosphine) copper(I) species³⁷ and comprehensive ^{91}Zr NMR study of zirconocenes,³⁸ greatly reduced experimental times and yielded spectra of superior S/N and higher resolution. This sequence has enabled us to study nuclides which are commonly avoided due to their broad patterns and/or unreceptive natures, including ^{209}Bi ($l = 9/2$) NMR of inorganic periodic and molecular systems,³⁹ ^{137}Ba ($l = 3/2$) NMR of simple inorganic salts,⁴⁰ and ^{195}Pt NMR of vapochromic compounds.⁴¹ A variety of materials have been studied by other groups using UWNMR methodologies, including ^{87}Sr ($l = 9/2$) NMR of pharmaceutical compounds and bioactive glasses,⁴² ^{33}S ($l = 3/2$) NMR of elemental sulfur,⁴³ ^{73}Ge ($l = 9/2$) NMR of organogermanes,⁴⁴ ^{67}Zn NMR of zeolitic imidizolate frameworks and MOFs,⁴⁵ and ^{139}La NMR of $\text{LaLi}_{0.5}\text{Fe}_{0.2}\text{O}_{2.09}$, a material of importance in Li batteries.⁴⁶

3.2. Halogens. The most commonly probed nuclides of the halogens, ^{35}Cl ($l = 3/2$), ^{79}Br ($l = 3/2$), and ^{121}I ($l = 5/2$), all possess sizable NQMs, and correspondingly broad CT patterns in most cases. The only exception are Cl anions, which have narrow CT patterns that are easily acquired.⁴⁷ To date, there are only three ^{35}Cl UWNMR studies of chlorines in bridging or terminal covalent bonding environments. In practice, such spectra can be acquired at standard field strengths (though sometimes with lengthy experimental times); however, high fields enable rapid spectral acquisition, not only due to the proportionality of the signal to the B_0^2 , but also the inverse dependence of the breadth of the CT patterns on B_0 . Our group acquired ^{35}Cl SSNMR spectra of Cl-containing metallocenes, and demonstrated the sensitivity of the ^{35}Cl QIs to both subtle and drastic structural differences (Figure 9).⁴⁸ Bryce and Chapman used similar experiments to acquire ^{35}Cl UWNMR spectra of group-13 chloride salts⁴⁹ and organic compounds featuring terminal C–Cl bonds.⁵⁰ Bryce and co-workers have also been successful using these methods to acquire ^{79}Br , ^{81}Br and ^{121}I UWNMR spectra.^{51,52}

3.3. Nitrogen-14. There are two NMR-active isotopes of nitrogen, ^{14}N ($l = 1$) and ^{15}N ($l = 1/2$). While the former has a

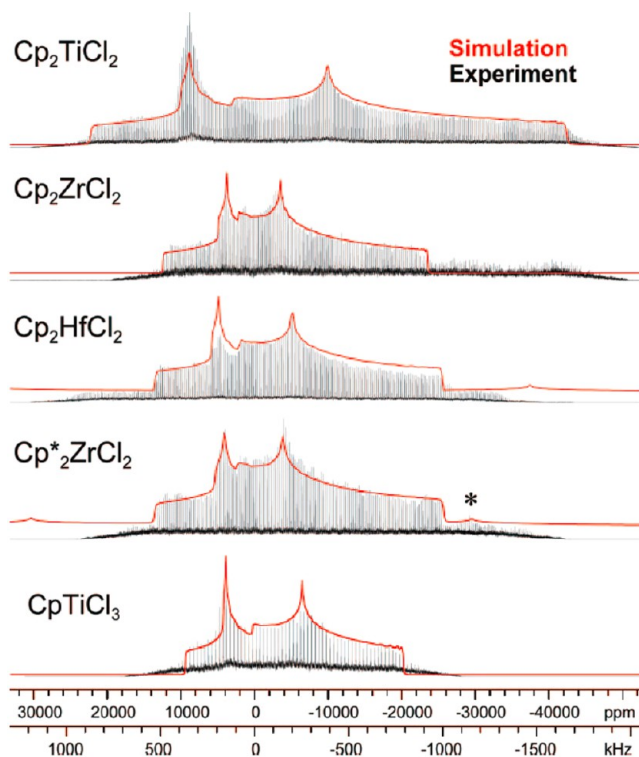


FIGURE 9. ^{35}Cl QCPMG SSNMR spectra and analytical simulations of the spectra (solid traces) for a series of chlorinated metallocenes ($\text{Cp} = \text{C}_5\text{H}_5^-$, $\text{Cp}^* = \text{C}_5\text{Me}_5^-$). In the spectrum of $\text{Cp}^*_2\text{ZrCl}_2$, the asterisk indicates a discontinuity from a ST. Adapted with permission from ref 48. Copyright 2009 American Chemical Society.

much higher natural abundance (99.63%), the latter is the focus of most SSNMR studies. This is because ^{14}N has a nuclear spin of 1, meaning that there are no CT patterns but rather two overlapping ST powder patterns that are spread over large frequency ranges (in most instances). The low S/N that results from spectral broadening and the low $\gamma(^{14}\text{N})$ make ^{14}N SSNMR experimentation very challenging for all but the most simple cases. There have been numerous ^{14}N SSNMR studies featuring specialized techniques such as overtone NMR, stable MAS at very accurately set angles, or on single-crystal or oriented samples; however, none of these techniques is routinely applied today.³

We have published a series of papers describing the use of WURST-CPMG for the acquisition of ^{14}N UWNMR spectra of many different systems with distinct nitrogen structural motifs. Our work on inorganic nitrates demonstrated that it is possible to obtain signal enhancements in ^{14}N powder patterns by population transfers that are dependent upon the sweep direction.⁵³ This work was followed up by a study of several amino acids, where we demonstrated the acquisition of ^{14}N SSNMR spectra of RNH_3^+ moieties faster than any previously reported techniques.⁵⁴ It is possible to resolve

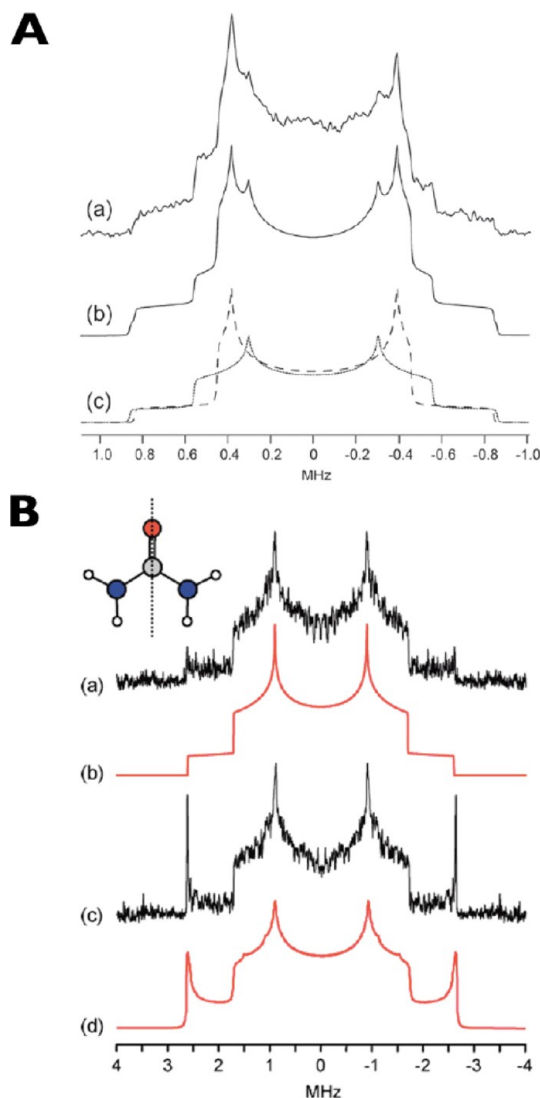


FIGURE 10. (A) Experimental and simulated ^{14}N spectra of L-leucine: (a) Experimental WURST-QCPMG spectrum (processed by coaddition of echoes), (b) idealized two-site simulation, and (c) separated contributing patterns. (B) ^{14}N NMR spectra of urea- d_4 : (a) WURST-echo spectrum and (b) simulation; (c) the WURST-QCPMG spectrum and (d) a simulation. The latter spectrum and simulation demonstrate dynamical rotations about the C=O bond. Adapted from refs 54 and 55 (Copyright 2011 American Chemical Society).

sites with similar quadrupolar parameters (Figure 10A), and high-power ^1H decoupling and/or deuteration is crucial for increasing the effective T_2 and maximizing the S/N. We also investigated a variety of nitrogen environments with powder patterns ranging from several hundred kHz to ca. 6 MHz in breadth (Figure 10B).⁵⁵ O'Dell and Ratcliffe have reported an investigation of the influence of dynamical motions on ^{14}N UWNMR spectra,⁵⁶ and we probed NH_3 groups in square-planar Pt complexes.⁵⁷ The WURST-CPMG pulse sequence and BRAIN-CP/WURST-CPMG combination (see section 2.4 above) make ^{14}N SSNMR

an exciting option for the characterization of nitrogen-containing systems.

4. Conclusions

Ultra-wideline SSNMR holds much promise for the study of unreceptive nuclides across the periodic table. Further developments in swept pulses and broadband CP promise regular access to many more NMR-active nuclides. This, in tandem with the increased access to high magnetic fields and continued development of NMR probes and hardware suited for such experiments, will enable the study of elements in many materials important in organic, inorganic, materials, and biological chemistry.

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Supporting Information. Methods used to acquire the spectra presented in Figure 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

BIOGRAPHICAL INFORMATION

Robert Schurko (Winnipeg, Manitoba, Canada, 1970). He obtained his B.Sc. and M.Sc. at the University of Manitoba (supervisor: Ted Schaefer) and his Ph.D. at Dalhousie University (supervisor: Roderick Wasylishen). He did two PDFs, one with Clare Grey (SUNY, Stony Brook) and one with Lucio Frydman (UIC, Chicago). He is currently a Professor of Chemistry at the University of Windsor, where he works on development and application of NMR techniques for studying inorganic, organic, and organometallic solids.

FOOTNOTES

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