PCCP



PAPER

View Article Online



Cite this: Phys. Chem. Chem. Phys., 2024, 26, 5081

Accelerated acquisition of wideline solid-state NMR spectra of spin 3/2 nuclei by frequencystepped indirect detection experiments†

Sujeewa N. S. Lamahewage, ab Benjamin A. Atterberry, ab Rick W. Dorn, ab Eunbyeol Gi, Dab Maxwell R. Kimball, Dahat Blümel, D* Javier Vela Dab and Aaron J. Rossini 🕩 *ab

73% of all NMR-active nuclei are quadrupolar nuclei with a nuclear spin I > 1/2. The broadening of the solidstate NMR signals by the guadrupolar interaction often leads to poor sensitivity and low resolution. In this work we present experimental and theoretical investigations of magic angle spinning (MAS) ¹H(X) double-echo resonance-echo saturation-pulse double-resonance (DE-RESPDOR) and Y(X) J-resolved solid-state NMR experiments for the indirect detection of spin 3/2 quadrupolar nuclei (X = spin 3/2 nuclei, Y = spin 1/2 nuclei). In these experiments, the spectrum of the quadrupolar nucleus is reconstructed by plotting the observed dephasing of the detected spin as a function of the transmitter offset of the indirectly detected spin. Numerical simulations were used to investigate the achievable levels of dephasing and to predict the lineshapes of indirectly detected NMR spectra of the quadrupolar nucleus. We demonstrate ¹H, ³¹P and ²⁰⁷Pb detection of 35 Cl, 81 Br, and 63 Cu (I=3/2) nuclei in $trans-Cl_2$ Pt(NH $_3$) $_2$ (transplatin), (CH $_3$ NH $_3$)PbCl $_3$ (methylammonium lead $chloride,\ MAPbCl_3),\ (CH_3NH_3)PbBr_3\ (methylammonium\ lead\ bromide,\ MAPbBr_3)\ and\ CH_3C(CH_2PPh_2)_3Cul\ (1,1,1-1)_3Cul\ (1,1,1-1)_3$ tris(diphenylphosphinomethyl)ethane copper() iodide, triphosCul), respectively. In all of these experiments, we were able to detect megahertz wide central transition or satellite transition powder patterns. Significant time savings and gains in sensitivity were attained in several test cases. Additionally, the indirect detection experiments provide valuable structural information because they confirm the presence of dipolar or scalar couplings between the detected nucleus and the quadrupolar nucleus of interest. Finally, numerical simulations suggest these methods are also potentially applicable to abundant spin 5/2 and spin 7/2 quadrupolar nuclei.

Received 18th October 2023, Accepted 15th January 2024

DOI: 10.1039/d3cp05055f

rsc.li/pccp

Introduction

High-resolution magic angle spinning (MAS) solid-state nuclear magnetic resonance spectroscopy has played a pivotal role in determining the molecular structure and dynamics of inorganic materials, organic solids, and biomolecules within crystalline and amorphous systems. 1-3 However, many NMR-active nuclei remain understudied due to technical difficulties in recording or interpreting their NMR spectra. For example, low natural abundances, low gyromagnetic ratios, large nuclear electric quadrupole moments (Q), long spin-lattice relaxation time constants (particularly for spin 1/2 nuclei), or some combination of these properties make acquisition of solid-state NMR spectra challenging. Approximately 73% of all NMR-active isotopes are quadrupolar nuclei, with the vast majority having half-integer spins (I = 3/2, 5/2, 7/2, or 9/2). Quadrupolar nuclei often give rise to extremely broad solid-state NMR spectra due to the first and second order quadrupolar interactions. When the second order quadrupolar interaction (SOQI) is sizable, only the central transition (CT) is typically observable, and the satellite transitions (ST) are usually broadened beyond detection. In such cases, the NMR spectrum of the central transition could be several megahertz broad, necessitating the use of wideline solid-state NMR techniques. 6-9

Slichter first reported the frequency-stepped acquisition of wideline solid-state NMR spectra for 195 Pt (I = 1/2) by recording the intensity of Hahn echoes at variable frequency offsets. 10 Following this work, additional wideline NMR studies on halfinteger quadrupolar nuclei were performed for nuclei such as

^a US Department of Energy, Ames National Laboratory, Ames, Iowa, 50011, USA. E-mail: arossini@iastate.edu; Tel: +1-515-294-8952

^b Iowa State University, Department of Chemistry, Ames, IA, 50011, USA

^c Texas A&M University, Department of Chemistry, College Station, Texas, 77842, USA. E-mail: bluemel@tamu.edu; Tel: +1-979-845-7749

[†] Electronic supplementary information (ESI) available: Shows additional solidstate NMR spectroscopy spectra, PXRD patterns and numerical simulations. Raw NMR data associated and SIMPSON simulation files associated with the main text figures are available for download at DOI: https://doi.org/10.5281/zenodo. 10014989. The CCDC 2250183 contains the supplementary crystallographic data for the copper complex $CH_3C(CH_2PPh_2)_3CuI$ (triphosCuI) for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi. org/10.1039/d3cp05055f

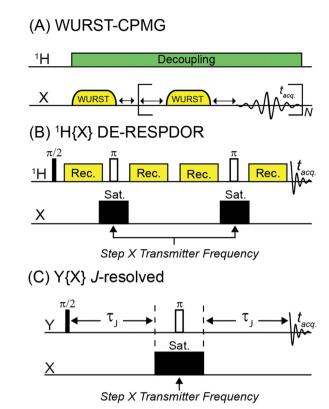


Fig. 1 Pulse sequences used in this work. (A) WURST-CPMG pulse sequence used for direct detection of ³⁵Cl and ⁸¹Br solid-state NMR spectra. (B) ¹H{X} DE-RESPDOR pulse sequence used for indirect detection of ³⁵Cl and ⁸¹Br. (C) Y{X} Heteronuclear spin echo (*J*-resolved) pulse sequence used for ²⁰⁷Pb(³⁵Cl) and ³¹P(⁶³Cu) NMR experiments. The frequency of the saturation pulse(s) in the DE-RESPDOR or J-resolved experiments can be varied in order to map the frequency dependence of the dephasing and reconstruct the solid-state NMR spectrum of the indirectly detected spin 3/2 nucleus. Phase cycles for pulse sequences are given in Table S1 (ESI†).

⁹¹Zr, ^{11,12} ^{69/71}Ga, ⁹ and ⁵⁹Co. ⁸ More recently, the quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) pulse sequence has found widespread application for acquisition of solid-state NMR spectra of nuclei such as ⁸⁷Rb and ⁵⁹Co, ^{13,14} and low-γ quadrupolar metal nuclei such as ⁶⁷Zn, ^{15,16} ⁹⁵Mo, ¹⁷ ¹⁴N, ¹⁸ ⁹¹Zr, ^{18,19} ³⁹K, ²⁵Mg, and ⁸⁷Sr.^{13,14} CPMG techniques have also been used to probe halogens like $^{35/37}$ Cl (I = 3/2), 20 127 I (I = 5/2), 21 and 79 Br (I = 3/2), 22 in organic and inorganic materials.²³ O'Dell and Schurko introduced the Wideband Uniform Rate Smooth Truncation (WURST)-QCPMG pulse sequence (Fig. 1A) and used it to obtain wideline solid-state NMR spectra of a variety of quadrupolar nuclei. 6,19,24 WURST-CPMG offers improved excitation and refocusing bandwidths as compared to conventional QCPMG experiments with rectangular excitation and refocusing pulses.

Unfortunately, direct detection wideline solid-state NMR methods often suffer from inadequate sensitivity and long measurement times.^{8,11–15,17,22,25,26} An alternative to these direct detection methods is to use indirect detection experiments where the NMR signal from a sensitive "spy nucleus" that offers a narrow linewidth and/or high sensitivity is exploited. Indirect detection has been applied to a variety of quadrupolar nuclei. There are two ways of performing indirect detection. In

the first approach, a standard two-dimensional (2D) NMR experiment is performed where a series of 1D NMR spectra are acquired with incrementation of the indirect dimension evolution time delay (t_1) . Fourier transformation of the indirect dimension time domain free induction decay yields the spectrum of the indirectly detected nucleus. For example, Gan and Bodenhausen et al. independently demonstrated the use of Heteronuclear Multiple Quantum Correlation (HMQC) pulse sequences²⁷ for the indirect detection of ¹⁴N MAS quadrupolar powder patterns by ¹³C.^{28–30} With the advent of fast MAS probes, ¹H{¹⁴N} HMQC solid-state NMR experiments have become routine. 31-35 In the second approach, the transmitter offset of the pulses applied to the indirectly detected spin are incremented. The NMR spectrum of the indirectly detected spin is then reconstructed by plotting the response of the detected nucleus as a function of the pulse offset. This approach is especially useful for the quadrupolar nuclei because it can be applied even when the spectrum of the quadrupolar nucleus is megahertz broad, and it is not possible to coherently excite magnetization from the quadrupolar nucleus. These types of indirect detection experiments have been performed with pulse sequences such as Static Echo DOuble Resonance (SEDOR), 36-38 TRAnsfer of Population in DOuble Resonance (TRAPDOR),³⁹ Rotational Echo Adiabatic Passage DOuble Resonance (REAPDOR), 40,41 Resonance Echo Saturation Pulse DOuble Resonance (RESPDOR), 42-46 and PROgressive Saturation of the Proton Reservoir (PROSPR). 47,48 These experiments have been used to indirectly detect NMR spectra of quadrupolar nuclei such as 14N, 27Al, 17O, 33S and 35Cl using 1H or 13C as the detected nucleus. We note that some of the examples cited above described acquisition of wideline solidstate NMR spectra of spin-1/2 nuclei broadened by chemical shift anisotropy (CSA). 36-38,46 Recently, we showed that CT wideline ³⁵Cl solid-state NMR spectra of partially Cl-terminated 2D silicon materials could be detected by plotting the dephasing observed in a ¹H{³⁵Cl} DE-RESPDOR experiments (Fig. 1B) as a function of the 35Cl pulse offset.42 Notably, for the 2D silicon materials, we were unable to observe a direct 35Cl WURST-CPMG signal, presumably due to an unfavorable T_2 for the ³⁵Cl nuclei. ⁴²

Here we provide a detailed investigation of frequencystepped RESPDOR experiments for the detection of wideline solid-state NMR spectra of I = 3/2 nuclei, using ³⁵Cl, ⁸¹Br and ⁶³Cu as representative examples. We apply numerical SIMPSON simulations to investigate saturation pulse conditions that can be used to map out CT and ST wideline solid-state NMR spectra of I = 3/2 nuclei. We also simulate frequency-stepped dipolar dephasing experiments for higher spin quadrupolar nuclei.

Results and discussion

Pulse sequences used for direct detection and indirect detection solid-state NMR experiments

The most common pulse sequence used for direct detection of wideline solid-state NMR spectra of quadrupolar nuclei is WURST-CPMG (Fig. 1A).19 We used WURST-CPMG to acquire ³⁵Cl and ⁸¹Br solid-state NMR spectra of transplatin (trans-

Cl₂Pt(NH₃)₂), MAPbCl₃ ((CH₃NH₃)PbCl₃), and MAPbBr₃ ((CH₃NH₃)-PbBr₃). Fig. 1B illustrates the ¹H{X} DE-RESPDOR pulse sequence. ⁴⁹ DE-RESPDOR is preferred over a conventional RESPDOR experiment because it is more robust to experimental MAS frequency fluctuations. 49 We used DE-RESPDOR to perform 1H detected 35Cl and 81Br solid-state NMR experiments. The Y{X}-heteronuclear spin echo (J-resolved) pulse sequence shown in Fig. 1C was used to indirectly detect ³⁵Cl and ⁶³Cu NMR spectra, using ²⁰⁷Pb and ³¹P as the spy nucleus, respectively. In both the DE-RESPDOR experiments and the J-resolved experiments, solid-state NMR spectra are reconstructed by plotting the dephasing as a function of the pulse offset as illustrated below.

Numerical simulations of dephasing in ¹H{³⁵Cl} DE-RESPDOR experiments

Prior to showing experimental NMR data, we have used SIMPSON⁵⁰⁻⁵² to simulate ³⁵Cl solid-state NMR spectra and illustrate how DE-RESPDOR can be used for indirect detection of ³⁵Cl. Fig. 2A shows the SIMPSON simulated static ³⁵Cl solidstate NMR spectra for transplatin with $C_{\rm O}$ = 37.0 MHz, $\eta_{\rm O}$ = 0.12 and an applied magnetic field of 9.4 T. Fig. 2B illustrates a spectrum simulated with the same parameters but with a magic angle spinning frequency of 50 kHz. In this case, the width of the central transition (CT) MAS powder pattern (ca. 5 MHz) greatly exceeds the MAS frequency (50 kHz), consequently, overlap of the CT MAS powder pattern with its spinning sideband powder patterns yields a spectrum that is nearly identical in appearance to a conventional static spectrum. Comparison of Fig. 2A and B suggests that MAS NMR experiments can provide the same spectrum and line shape as static NMR experiments, provided the width of the quadrupolar powder pattern greatly exceeds the MAS frequency.

Fig. 2C and D show SIMPSON simulated DE-RESPDOR dephasing heat maps. In the heat maps the offset of the saturation pulses

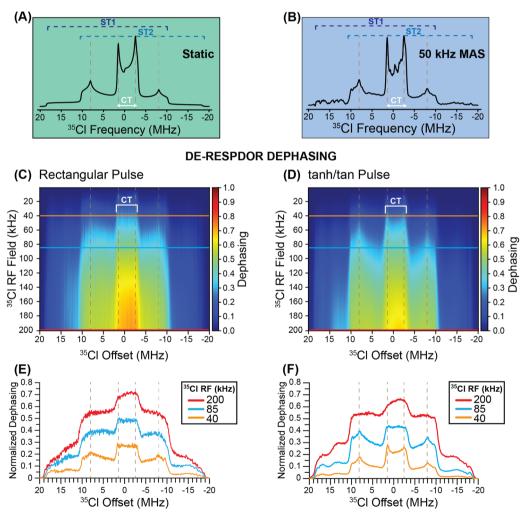


Fig. 2 SIMPSON simulated 35 Cl solid-state NMR spectra of transplatin ($C_{\rm Q}$ = 37 MHz and $\eta_{\rm Q}$ = 0.12) shown for (A) a static (stationary) sample and (B) for a 50 kHz magic angle spinning (MAS) frequency with a magnetic field of 9.4 T. (C) and (D) Heat plots showing the simulated dephasing for ¹H(³⁵Cl) DE-RESPDOR experiments as a function of the ³⁵Cl saturation pulse RF field and pulse offset. Simulations are shown for (C) conventional rectangular pulses 80 μ s in duration and (D) frequency-swept tanh/tan pulses ($\xi = 20$, $\theta = 180^{\circ}$) using a frequency sweep of 5 MHz and 40 μ s duration. All simulations used a 1 H $^{-35}$ Cl spin system with a 2 kHz dipolar coupling constant. Dephasing profiles extracted from the heat plots for the 35 Cl saturation pulse RF fields 200 kHz, 85 kHz, and 40 kHz with (E) rectangular saturation pulses and (F) tanh/tan pulses.

is varied on the x-axis and the RF field of the saturation pulses is varied on the y-axis, while the color indicates the extent of dephasing. The dephasing is shown as a function of ³⁵Cl pulse power and offset with 80 µs (4 rotor cycles) rectangular pulses (Fig. 2C) and 40 μs frequency-swept tanh/tan pulses⁵³ with a 5 MHz sweep width (Fig. 2D). In Fig. 2E and F RESPDOR dephasing profiles are shown for ³⁵Cl saturation pulses with radiofrequency

fields (RF) of 200, 85, and 40 kHz. The heatmaps and dephasing profiles illustrate that the plot of the dephasing as a function of the offset can roughly trace the CT and ST powder patterns. Because the CT is narrower than the ST, it is more easily saturated, resulting in enhanced dephasing in the RESPDOR experiments and a contrast between the CT and ST powder patterns. However, increasing the saturation pulse RF field increases the dephasing for both CT and ST, but also reduces the contrast between the CT and ST. The use of higher RF field saturation pulses also results in a rounding of the powder pattern discontinuities. It is well known in NMR experiments such as CEST,54 that the saturation bandwidth will increase as the saturation pulse RF field is increased, resulting in broadening of the indirectly detected peaks. It is therefore unsurprising that the features in the dephasing profile become more rounded as the saturation pulses can create dephasing more effectively across the entire powder pattern when higher RF fields are used. Another interesting observation from Fig. 2 is that if shorter duration ³⁵Cl saturation pulses are used, then the discontinuities or "horns" associated with the ST are sharper than when rectangular pulses are applied. The tanh/tan pulses employed in Fig. 2D had a pulse length of 40 µs (two rotor cycles). Additional simulations with 40 µs rectangular saturation show similarly sharp features in the RESPDOR dephasing profile as were seen for the tanh/tan pulses (Fig. S3, ESI†). The 40 µs tanh/tan pulses use less RF power due to their hyperbolic tangent amplitude profile, and thus could be preferred experimentally.

In summary, it is evident from Fig. 2 that the RESPDOR dephasing profiles roughly map out the MAS solid-state NMR spectrum, including both the CT and ST regions of the powder pattern. Therefore, the simulations suggest that RESPDOR experiments can be used to indirectly detect wideline solidstate NMR spectra of spin 3/2 nuclei.

Experimental comparison of ¹H{³⁵Cl} DE-RESPDOR and direct WURST-CPMG for acquisition of the 35Cl solid-state NMR spectrum of transplatin

Fig. 3A shows $^1H\{^{35}Cl\}$ DE-RESPDOR dephased spectrum (red, S) recorded with 35Cl saturation pulses and the control spectrum (black, S_0) recorded without saturation pulses. All NMR spectra were acquired at $B_0 = 9.4$ T, with a 35 Cl saturation pulse that was four rotor cycles in duration (80 µs) with an 80 kHz RF field, and 3.84 ms of SR4² dipolar recoupling⁵⁵ applied to the ¹H spins. The NMR spectra shown in Fig. 3A were obtained with a 35 Cl pulse offset of 1.2 MHz. Control (S_0) and dephasing (S) ¹H NMR spectra show signal-to-noise ratios of 60 and 18 with eight scans, respectively. The difference spectrum (S_0-S, cyan) illustrated below has a signal-to-noise ratio of 30, which is adequate for indirect detection of 35Cl in transplatin. We did not optimize the total recoupling time to obtain optimal

sensitivity for the ¹H{³⁵Cl} DE-RESPDOR experiments for transplatin. Fig. S2 (ESI†) illustrates how to choose the optimal recoupling duration using ¹H{³⁵Cl} DE-RESPDOR experiments, using MAPbCl₃ as an example. In brief, the recoupling duration that maximizes the difference signal ($\Delta S = S_0 - S$) should be used. This optimal recoupling time can be found by making a plot of ΔS as a function of the recoupling duration (Fig. S2, ESI†).

¹H{³⁵Cl} DE-RESPDOR experiments on transplatin were performed where the offset of the ³⁵Cl saturation pulse was varied in steps of 400 kHz over a range of +3.4 to -4.6 MHz (Fig. 3B). For each ³⁵Cl pulse offset the probe needed to be manually retuned. Plotting the normalized signal dephasing $(\Delta S/S_0)$ as a function of the ³⁵Cl saturation pulse offset enables the reconstruction of the MAS 35Cl CT quadrupolar powder pattern for transplatin. Notably, the ¹H detected central transition ³⁵Cl solid-state NMR spectrum of transplatin was acquired in only ca. 27 minutes at $B_0 = 9.4$ T. Numerical simulations of the ¹H{³⁵Cl} DE-RESPDOR dephasing profile suggest that the ³⁵Cl $C_{\rm O}$ is ca. 37 MHz (with $\eta_{\rm O}$ = 0.1), in good agreement with 35 Cl $C_{\rm Q}$ value of 36.6 MHz previously reported by Lucier et al. 56 Note, that in order to fit the experimental RESPDOR saturation profile we must scale the simulated dephasing data. Scaling of the simulated dephasing is needed since we use two-spin simulations that assume 100% abundance of the quadrupolar nucleus and furthermore, the values of the ¹H-³⁵Cl dipolar coupling constants are unknown and challenging to measure. The variable offset cumulative spectrum (VOCS) 35Cl WURST-CPMG spectrum of transplatin (black) was constructed by coadding 21 individual sub-spectra (Fig. 3C). The analytically simulated (ssNake) 57 spectrum indicated the 35 Cl $C_{\rm O}$ was 37 MHz with $\eta_{\rm O}$ = 0.12. The co-added VOCS WURST-CPMG spectrum took 3 hours of spectrometer time to acquire (Fig. 3C).

The comparison of experimental time between indirectly detected ¹H{³⁵Cl} DE-RESPDOR experiments and directly detected 35Cl WURST-CPMG experiments shows six-fold timesaving in indirect detection using ¹H as a spy nucleus. The signal-to-noise ratio was also 1.5 times higher in indirectly detected ³⁵Cl NMR spectra compared with the direct detection experiment. The gains in sensitivity obtained are even more impressive if one considers the amounts of sample used in the two types of experiments. ¹H{³⁵Cl} DE-RESPDOR experiments were performed with a 1.3 mm rotor that holds approximately 5 μL of sample, while the static ³⁵Cl WURST-CPMG experiments used ca. 100 µL of sample packed into a 4 mm rotor. Additionally, the ¹H T₁ determines the optimal recycle delay for the DE-RESPDOR experiments, while the 35 Cl T_1 determines the optimal recycle delay in the WURST-CPMG experiments. For transplatin we measured a 1 H T_{1} of 17 s and used a recycle delay of 5 s for DE-RESPDOR experiments, while an experimentally optimized 35Cl recycle delay of 0.5 s was used for 35Cl WURST-CPMG experiments. Thus, samples with shorter and more favorable ¹H T_1 should show even higher gains in sensitivity for the indirect detection DE-RESPDOR NMR experiments.

One trade off with the wideline RESPDOR experiments is that the CT powder pattern discontinuities in the RESPDOR dephasing profiles are not as sharp as those seen in the direct

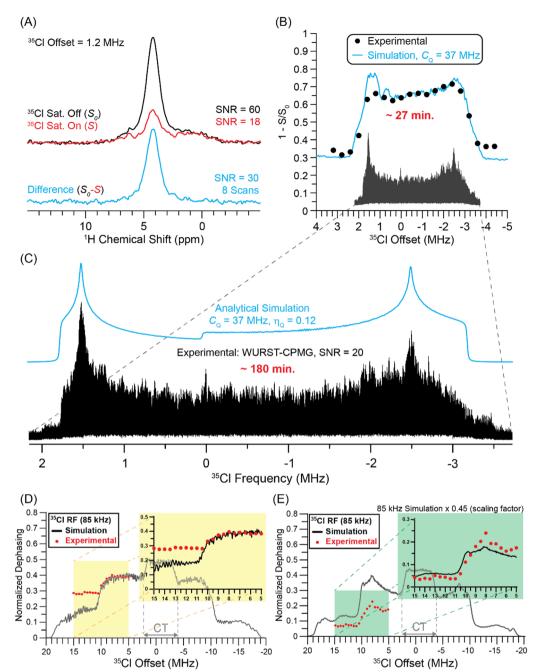


Fig. 3 Summary of ³⁵Cl solid-state NMR experiments on transplatin performed with a 9.4 T magnetic field. (A) 1D ¹H(³⁵Cl) DE-RESPDOR spectra recorded with (red) or without (black) 80 μs rectangular ³⁵Cl saturation pulses. The difference spectrum (cyan) is shown below. 8 scans were acquired for each spectrum, the MAS frequency was 50 kHz, and the total duration of $SR4_1^2$ dipolar recoupling was 3.84 ms. (B) Plot of ${}^1H({}^{35}Cl)$ DE-RESPDOR normalized signal dephasing ($\Delta S/S_0$) as a function of the ³⁵Cl pulse offset over the CT region. The circles and lines correspond to experimental data points and numerical simulations, respectively. The same experimental parameters were used for the experiments shown in Fig. 3A and B. (C) VOCS WURST-CPMG static ³⁵Cl NMR spectrum of transplatin and simulation (cyan). Comparison of experimental and SIMPSON simulated ¹H(³⁵Cl) DE-RESPDOR dephasing for (D) rectangular ³⁵Cl saturation pulses 80 μs in duration and (E) tanh/tan pulses that are 40 μs in duration. The ³⁵Cl pulse offset was varied in steps of 500 kHz over the range of +5 MHz to +15 MHz.

acquisition WURST-CPMG NMR spectra, leading to reduced precision in the extraction of the $C_{\rm Q}$ and $\eta_{\rm Q}$ values. Fitting of the WURST-CPMG spectrum was reported to gives uncertainties of 0.1 to 0.3 MHz and 0.02 on the measured $C_{\rm Q}$ and $\eta_{\rm Q}$ values, respectively.⁵⁶ Simulations of the RESPDOR dephasing profiles with variable $C_{\rm Q}$ values suggest that the uncertainties on the measured values of $C_{\rm Q}$ are on the order of 1 MHz (Fig. S4, ESI†). The simulations suggest the $\eta_{\rm O}$ value is between 0.0 and 0.25. Thus, there is likely a loss of precision in measurement of C_Q and η_Q as compared to direct detection methods. However, as is shown below, it is possible to improve the precision of the measured η_Q values by mapping out the ST powder patterns with RESPDOR experiments.

Additional ¹H(³⁵Cl) DE-RESPDOR experiments on transplatin were performed where the offset of the ³⁵Cl saturation pulse.

73. The spectra show

tin were performed where the offset of the ³⁵Cl saturation pulse varied in steps of 500 kHz over a range of +15 to +5 MHz in order to detect parts of the ³⁵Cl ST powder patterns. Corresponding SIMPSON simulated normalized dephasing profiles with 85 kHz RF field saturation pulses (black) are shown in Fig. 3D. Plotting the signal dephasing as a function of the ³⁵Cl saturation pulse offset enables the reconstruction of the partial MAS ST powder pattern for the transplatin. In Fig. 3D, there is a discrepancy between the experimental and simulated dephasing at different positions of the satellite transitions. The higher frequency part of the ST shows higher than expected dephasing. There are a number of reasons that explain this discrepancy. First, numerical simulations with a ¹H-³⁵Cl two-spin system show that the ratio of dephasing at the inner and outer part of the ST depends upon the recoupling duration (Fig. S5, ESI†). Second, the crystal structure of transplatin shows that each ¹H spin is coupled to several ³⁵Cl spins, meaning that a two-spin simulation is not an accurate representation of the experiments. Finally, the experimental 35Cl RF field likely changes as the probe is retuned. While all of these factors could change the dephasing at different offsets, the most important constraint on the $\eta_{\rm O}$ value is the position of the "step" arising from the overlap of the two satellite transitions.

Fig. 3E shows the simulated and experimental RESPDOR dephasing profiles obtained with ^{35}Cl tanh/tan saturation pulses with an 85 kHz RF field. The DE-RESPDOR experiments with the 40 μ s tanh/tan pulses give well-defined ST discontinuities in both simulation and experiment, enabling η_Q to be more accurately determined. Fitting the ST region of the RESPDOR dephasing profile indicates that η_Q is between 0.0 and 0.1 (Fig. S3, ESI†). This is an important observation because the indirectly detected CT powder pattern is not very sensitive to η_Q . Therefore, if increased precision is required on measured values of η_Q then RESPDOR experiments can be performed to locate the ST discontinuities.

Comparison of direct detection and indirect detection for acquisition of the 35 Cl solid-state NMR spectrum of MAPbCl₃

Next, we investigated the use of indirect detection methods for acquisition of the $^{35}{\rm Cl}$ solid-state NMR spectrum of methylammonium lead chloride (MAPbCl₃). Michaelis and co-workers have recently shown that $^{35}{\rm Cl}$ solid-state NMR spectroscopy can be used to probe the structure of lead chloride perovskites and related phases. 58 The VOCS $^{35}{\rm Cl}$ WURST-CPMG spectrum of MAPbCl₃ was obtained with 5 sub-spectra (Fig. 4A). Blue lines are numerically simulated spectra with a $^{35}{\rm Cl}$ $C_{\rm Q}$ of 16.5 MHz (with $\eta_{\rm Q}=0$), which is consistent with the 16.34 MHz $^{35}{\rm Cl}$ $C_{\rm Q}$ value reported by Sarkar $et~al.^{58}$ The total experimental time to acquire the WURST-CPMG spectrum was 51 minutes, and the signal-to-noise ratio is approximately 160 at the most intense part of the CT powder pattern.

Fig. 4B depicts ¹H{³⁵Cl} DE-RESPDOR spectra with saturation pulses (red) and spectra without saturation pulses (black). With 16 scans, the control and dephasing spectra have signal-to-noise ratios of 150 and 52, respectively. The difference

spectrum (cyan) shown below has a signal-to-noise ratio of 73. The spectra shown in Fig. 4B were obtained with a 0 MHz 35 Cl offset. All spectra were collected at $B_0 = 9.4$ T using a 35 Cl saturation pulse length of four rotor cycles (80 µs) with an 80 kHz RF field and 3.84 ms of SR4² dipolar recoupling.⁵⁵ Fig. S2 (ESI†) illustrates how to choose the optimal recoupling duration. Fig. S6 (ESI†) shows how varying the recoupling duration affects the quality of the indirectly detected 35Cl NMR spectrum. The ³⁵Cl spectrum was indirectly detected with ¹H{³⁵Cl} DE-RESPDOR by varying the offset of the 35Cl saturation pulse in 100 kHz steps over a range of +1.5 to -2 MHz (Fig. 4C). The ¹H detected ³⁵Cl NMR spectrum of MAPbCl₃ was obtained in *ca*. 25 minutes at $B_0 = 9.4$ T. However, as was seen above for transplatin, due to the RF field used for the 35Cl saturation pulses, the CT pattern seen in the RESPDOR dephasing profile does not perfectly match the directly acquired CT powder pattern. Numerical simulations of the ¹H{³⁵Cl} DE-RESPDOR dephasing profile indicate that the 35 Cl C_{O} is ca. 16.5 MHz (with $\eta_{\rm O} = 0$), consistent with the static WURST-CPMG spectrum. We note that the offset of the 35Cl pulses was stepped in 100 kHz increments, resulting in lower resolution for the experimental RESPDOR dephasing profile as compared to the simulated one.

For MAPbCl₃ the sensitivity with ¹H detection is worse than the directly detected ³⁵Cl NMR spectrum. The gains in signal-tonoise ratio and time savings provided by ¹H detection is likely limited because the 1 H T_{1} of MAPbCl₃ ($T_{1} = 30$ s) is much longer than the 35 Cl T_1 (optimal recycle delays of 0.15 s). Furthermore, the ³⁵Cl homogeneous transverse relaxation time constant (T_2) is long enough to allow CPMG echoes to be acquired for ca. 50 ms, making CPMG detection efficient for MAPbCl₃. The relatively narrow breadth of the CT selective spectrum also means that only 5 WURST-CPMG sub-spectra need to be acquired. Thus, the results for MAPbCl₃ suggest that if the CT is less than 1 MHz in breadth and the 35 Cl T_2' is sufficiently long to allow efficient CPMG detection then direct detection is likely to be the preferred acquisition method. But we note that the ¹H{³⁵Cl} RESPDOR experiments may still be worthwhile since they provide valuable structural information by confirming that the ¹H spins of the MA cations are dipole coupled (spatially proximate) to the Cl anions.

We also attempted ²⁰⁷Pb{³⁵Cl} *J*-resolved experiments to establish if ²⁰⁷Pb could also be used as a spy nucleus for ³⁵Cl detection. Fig. 4D shows ²⁰⁷Pb{³⁵Cl} *J*-resolved spectra recorded with (red) saturation pulses and without (black) saturation pulses. The pulse sequence for the J-resolved experiments is shown in Fig. 1C. The J-resolved experiments were performed at a field of 9.4 T with an MAS frequency of 25 kHz. The control and dephasing spectra have signal-to-noise ratios of 13 and 4, respectively. Each spectrum was obtained with 2048 scans and a 2 s recycle delay. The difference spectrum (cyan) shown below has an adequate signal-to-noise ratio of 5. The 35Cl saturation pulse was two rotor periods in duration (80 µs) with a 41.7 kHz RF field, and the spin echo had a total duration of 0.64 ms. In this sample, the ²⁰⁷Pb T_2' limits the echo duration and the achievable dephasing. ²⁰⁷Pb{³⁵Cl} *J*-resolved experiments on MAPbCl₃ were performed with 35Cl saturation pulse offsets varying in 200 kHz steps over a

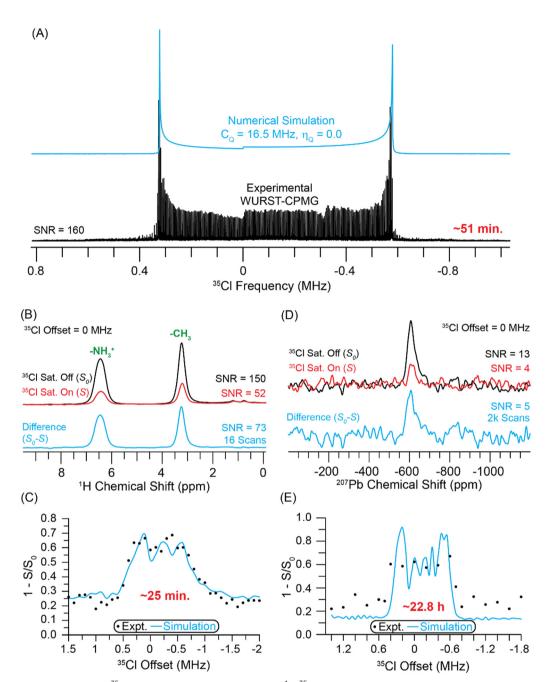


Fig. 4 (A) Static VOCS WURST-CPMG ³⁵Cl NMR spectrum of MAPbCl₃. (B) 1D ¹H(³⁵Cl) DE-RESPDOR spectra recorded with (red) or without (black) a ³⁵Cl saturation pulse and 3.84 ms of SR4² dipolar recoupling and a 50 kHz MAS frequency. A difference spectrum (cyan) is shown below. (C) Plot of ¹H(³⁵Cl) DE-RESPDOR signal dephasing as a function of the ³⁵Cl transmitter. (D) 1D ²⁰⁷Pb(³⁵Cl) J-resolved spectra recorded (red) with or (black) without a ³⁵Cl saturation pulse and 0.64 ms of total J evolution time. (E) The plot of 207Pb(35Cl) J-resolved signal dephasing as a function of the 35Cl transmitter recorded with a 25 kHz MAS frequency. In (C) and (E), the circles and lines correspond to experimental data points and numerical simulations, respectively. The simulation used a 35 Cl C $_{\rm Q}$ of 16.5 MHz. All experiments were performed with a magnetic field of 9.4 T.

range of +1.4 to -1.8 MHz. Plotting the signal dephasing as a function of the ³⁵Cl saturation pulse offset enables reconstruction of the MAS ³⁵Cl CT quadrupolar powder pattern for MAPbCl₃. The ²⁰⁷Pb{³⁵Cl} *J*-resolved experiments required *ca.* 22.8 hours at $B_0 = 9.4$ T. In this case, ²⁰⁷Pb detection would not be used to enhance the sensitivity of the 35Cl NMR experiments, rather it would be used to obtain structural information because the ²⁰⁷Pb{³⁵Cl} *J*-resolved experiments confirm that the lead atoms

are covalently bound to chlorine atoms and that the $C_{\rm O}$ of the chlorine atoms matches that observed in the directly acquired ³⁵Cl solid-state NMR spectrum.

¹H{⁸¹Br} DE-RESPDOR and direct WURST-CPMG experiments on MAPbBr₃

We investigated the use of indirect detection methods for acquisition of the 81Br solid-state NMR spectrum of methylammonium Paper PCCP

lead bromide (MAPbBr₃). Previously, it was reported that the total ⁷⁹Br CT solid-state NMR spectrum of MAPbBr₃ required days of spectrometer time to acquire. ²² Due to the breadth of the ⁸¹Br CT solid-state NMR spectrum (*ca.* 16 MHz), we only acquired a few VOCS sub-spectra close to the discontinuities of the ⁸¹Br CT powder pattern (Fig. 5A). Blue lines are numerically simulated ⁸¹Br solid-state NMR spectra with a ⁸¹Br C_Q of 118 MHz (with η_Q = 0). The experimental time to acquire the two WURST-CPMG spectra was 41 minutes and the signal-to-noise ratio is approximately 117 at the most intense horn.

Fig. 5B depicts 1 H{ 81 Br} DE-RESPDOR spectra with (red) and without (black) 81 Br saturation pulses. All spectra were collected at B_0 = 14.1 T using a 81 Br saturation pulse length of four rotor cycles (80 μ s) with a 50 kHz RF field and 1.92 ms of SR4 255 dipolar recoupling. With 8 scans, the control and dephasing spectra have signal-to-noise ratios of 420 and 340, respectively. The difference spectrum (cyan) shown below has a signal-to-noise ratio of 75. The spectra shown in Fig. 5B were obtained with a 81 Br pulse offset of -5 MHz. The 81 Br spectrum was then

indirectly detected with $^{1}H\{^{81}Br\}$ DE-RESPDOR by varying the offset of the ^{81}Br saturation pulse in 1 MHz steps over a range of $^{+10}$ to $^{-14}$ MHz (Fig. 5C). The complete ^{1}H detected ^{81}Br solid-state NMR spectrum of MAPbBr $_{3}$ was obtained in ca . 64 minutes. Numerical simulations of the $^{1}H\{^{81}Br\}$ DE-RESPDOR dephasing profile indicate that the ^{81}Br C_{Q} is ca . 118 MHz (with $\eta_{Q}=0$), consistent with the static VOCS WURST-CPMG spectrum. Note, a simulation of the $^{1}H\{^{81}Br\}$ DE-RESPDOR dephasing profile that also accounts for additional dephasing from ^{79}Br explains why the dephasing profile in Fig. 5C is asymmetric; at lower ^{81}Br transmitter offsets there is dephasing from the ^{79}Br ST (Fig. S7, ESI†).

Comparing the sensitivity of the indirectly detected ¹H{⁸¹Br} DE-RESPDOR and the directly detected ⁸¹Br WURST-CPMG reveals a slight sensitivity gain with ¹H detection. While the ⁸¹Br WURST-CPMG spectrum of the high frequency horn has a signal-to-noise ratio of 117, this sub-spectrum required 20.5 minutes to acquire, corresponding to a sensitivity of 26 min^{-1/2}. In comparison, the ¹H{⁸¹Br} DE-RESPDOR difference spectrum had a signal-

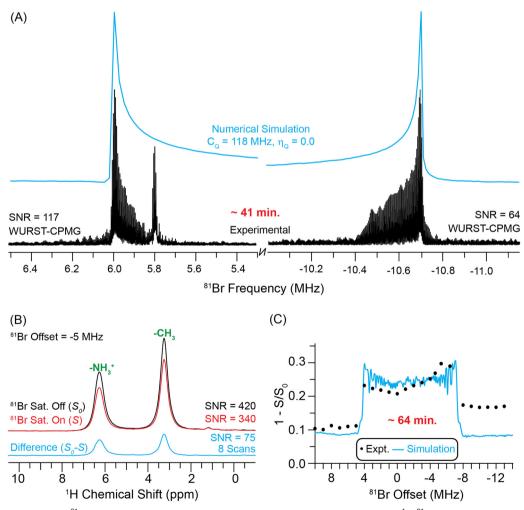


Fig. 5 (A) Static WURST-CPMG 81 Br NMR spectra of MAPbBr $_{3}$ obtained at a magnetic field of 9.4 T. (B) 1D 1 H(81 Br) DE-RESPDOR spectra recorded with (red) or without (black) a 81 Br saturation pulse, 1.92 ms of SR4 $^{2}_{1}$ dipolar recoupling, a 25 kHz MAS frequency and a 14.1 T magnetic field. A difference spectrum (cyan) is shown below. (C) Plot of 1 H(81 Br) DE-RESPDOR dephasing as a function of the 81 Br transmitter offset. The circles and a line correspond to experimental data points and numerical simulations, respectively. The simulation used a 81 Br C_{Q} of 118 MHz.

PCCP

to-noise ratio of 75 in 3.2 minutes, corresponding to a sensitivity of $42 \text{ min}^{-1/2}$. Therefore, in this case the RESPDOR experiments provide a 1.6-fold improvement in sensitivity and 2.6-fold reduction in experiment time. For MAPbBr3 the gain in signal-tonoise provided by ${}^{1}H$ detection is likely limited because the ${}^{1}H$ T_{1} of MAPbBr₃ ($T_1 = 24$ s) is much longer than the ⁸¹Br T_1 (optimal recycle delays of 0.12 s). However, we stress again that indirect detection also gives additional structural information by confirming that the ¹H spins of the MA⁺ cations are dipole-coupled to the Br anions. We also note that the ¹H detected experiments required only a few µL of material, while we used 100 µL of material for the direct 81Br WURST-CPMG experiments.

Indirect detection of the ⁶³Cu solid-state NMR spectrum of triphosCuI complex by ¹H → ³¹P{⁶³Cu} J-resolved experiment

We studied the use of indirect detection methods for acquisition of the ⁶³Cu solid-state NMR spectrum of the copper(1) phosphine complex, CH₃C(CH₂PPh₂)₃CuI (triphosCuI, Fig. S8, ESI†). Phosphines are common ligands coordinated to copper centers and phospine copper complexes are important catalysts, for example, for Sonogashira C-C cross-coupling reactions.⁵⁹ Therefore, it is interesting to determine whether ³¹P-detection can be used as a method to obtain ⁶³Cu NMR spectra of copper complexes with phosphine ligands. The ⁶³Cu solid-state NMR signals of triphos-CuI were narrow enough to obtain a CT MAS NMR spectrum that was free of spinning sidebands (Fig. 6A). Note, to acquire this spectrum we used the DEPTH pulse sequence⁶⁰ (with CT selective pulses) because the conventional spin echo NMR spectrum showed an intense 63Cu NMR signal from copper metal components of the probe. A fit of the 63Cu MAS NMR spectrum gave 63 Cu $C_{\rm O}$ = 3.2 MHz, $\eta_{\rm O}$ = 0.57 and $\delta_{\rm iso}$ = 322 ppm. The total experimental time to acquire the DEPTH NMR spectrum was 205 minutes, and the signal-to-noise ratio was approximately 50. In this case, the 63Cu NMR spectrum is quite narrow, and therefore, ³¹P detection is not technically needed to study this compound. However, it is difficult to accurately determine the value of η_O by only fitting the CT lineshape. Below, we show that indirect detections allow both the 63Cu CT and ST powder patterns to be obtained and confirms the accuracy of the fitted value of $\eta_{\rm O}$.

Fig. 6B shows the MAS $^{1}H \rightarrow ^{31}P\{^{63}Cu\}$ *J*-resolved NMR spectra obtained with (red) and without (black) a ⁶³Cu saturation pulse. The ³¹P NMR spectrum shows two sets of NMR signals centered at -35 ppm and -43 ppm. Each set of signals in the 31 P NMR spectrum is composed of a 4-component multiplet that arises due to the combined effects of J-coupling and residual dipolar coupling to 63Cu and 65Cu nuclei that experience quadrupolar broadening (see a simulated spectrum in Fig. S10, ESI†). ³¹P solid-state NMR spectra similar in appearance to the ones shown in Fig. 6B have been reported for other Cu(I) phosphine compounds. 61-63 The single crystal X-ray structure of triphosCuI shows that all three P atoms are crystallographically distinct (CCDC: 2250183†). The Cu-P bonds are similar in length for all P atoms (2.274 Å to 2.288 Å). However, two of the phosphorus atoms have similar I-Cu-P bond angles (126.1° and 123°), while the other I-Cu-P bond angle is 115.8°. Gauge-including

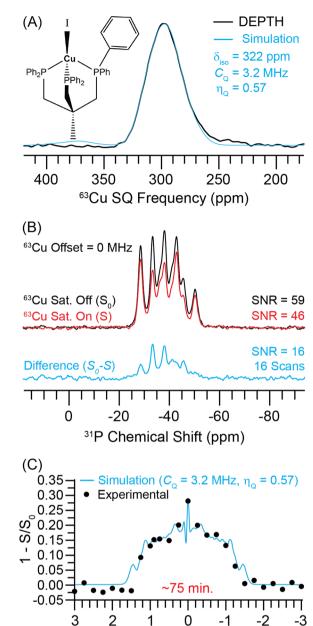


Fig. 6 (A) Experimental ⁶³Cu DEPTH NMR spectrum (black) and a simulation with a $^{63}{\rm Cu}~C_{\rm Q}$ = 3.2 MHz and $\eta_{\rm Q}$ = 0.57 (cyan). (B) $^1{\rm H}~\to~^{31}{\rm P}\{^{63}{\rm Cu}\}~J{\rm -resolved}$ NMR spectra recorded with (red) or without (black) a 63 Cu saturation pulse and 1.44 ms of total J evolution time. (C) $^{1}H \rightarrow ^{31}P\{^{63}Cu\}$ J-resolved signal dephasing as a function of the 63 Cu transmitter recorded at $B_0 = 9.4$ T with 25 kHz MAS frequency. The circles and a line correspond to experimental data points and numerical simulation for a 63 Cu $C_Q = 3.2$ MHz and $\eta_Q = 0.57$ (cyan).

63Cu Offset (MHz)

projector-augmented wave (GIPAW)⁶⁴ calculations implemented in the CASTEP⁶⁵ program was used to predict the ³¹P magnetic shielding and differences in chemical shifts. The calculation predicts that two of the 31P nuclei have similar magnetic shielding (σ_{iso} = 318.6 ppm and 320.5 ppm), while the third ³¹P nucleus which has the I-Cu-P bond angle of 115.8° is approximately 15 ppm more shielded (σ_{iso} = 335.0 ppm). The predicted shieldings are in reasonable agreement with the

experimental spectrum which shows higher intensity for the higher frequency ³¹P NMR signals.

With 16 scans, the control and dephased ³¹P NMR spectra have signal-to-noise ratios of 59 and 46, respectively. The difference spectrum (cyan) shown below has a signal-to-noise ratio of 16. The spectra shown in Fig. 6B were obtained with a 0 MHz ⁶³Cu offset. All spectra were collected at $B_0 = 9.4$ T using a 63 Cu saturation pulse length of one rotor cycle (40 s) and a total spin echo duration of 1.44 ms. The 63Cu NMR spectrum was then indirectly detected with ${}^{1}H \rightarrow {}^{31}P_{1}^{63}Cu$ *J*-resolved experiments by varying the offset of the 63Cu saturation pulse in 250 kHz steps over a range of +3 to -3 MHz (Fig. 6C). In Fig. 6C, we have integrated over all ³¹P peaks. The ³¹P detected ⁶³Cu NMR spectrum of triphosCuI was obtained in ca. 75 minutes at $B_0 = 9.4$ T. Numerical simulations of the ${}^{1}H \rightarrow {}^{31}P\{{}^{63}Cu\} J$ -resolved dephasing profile indicate that the 63 Cu $C_{\rm O}$ is ca. 3.2 MHz (with $\eta_{\rm O}$ = 0.57), in good agreement with the 63Cu DEPTH NMR spectrum. Numerical simulations with different 63Cu saturation pulse RF fields and different values of $\eta_{\rm O}$ are shown in the ESI† (Fig. S9). With the current optimized saturation pulse condition of 30 kHz RF field, the dephasing profile remains sensitive to the value of $\eta_{\rm O}$.

Given the narrow width of the central transition ⁶³Cu NMR spectrum of triphosCuI, 31P detection is not useful for sensitivity enhancement. However, the J-resolved experiments are still helpful in this case because they confirm the presence of coordinative bonds between the Cu and P atoms and confirms that the copper observed in the directly detected ⁶³Cu NMR spectrum gives rise to the observed dephasing.

Numerical simulations of dephasing in ¹H{³⁵Cl} DE-RESPDOR experiments as a function of 35Cl Co

The dependence of the dephasing in a ¹H{³⁵Cl} DE-RESPDOR experiment on 35 Cl $C_{\rm Q}$ was investigated with numerical SIMP-SON simulations. Fig. 7 shows normalized dephasing as a function of $^{35}\mathrm{Cl}~C_\mathrm{O}$ for a 50 kHz MAS frequency with a magnetic

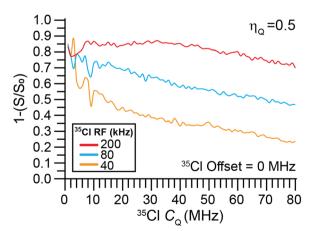


Fig. 7 SIMPSON simulated dependence of the normalized ${}^{1}H({}^{35}Cl)$ DE-RESPDOR dephasing (1 - S/S₀) on the 35 Cl $C_{\rm Q}$. Simulations were performed with a 50 kHz magic angle spinning (MAS) frequency with a magnetic field of 9.4 T. Simulations used 80 μ s 35 Cl saturation pulses with RF fields of 200 kHz, 80 kHz, or 40 kHz. All simulations used a $^{1}H-^{35}Cl$ spin system with a 2 kHz dipolar coupling constant and $\eta_Q = 0.5$.

field of 9.4 T for 200 kHz, 80 kHz, and 40 kHz saturation pulse RF fields. The ³⁵Cl saturation pulse was 80 μs in duration. Each curve was constructed by varying C_0 from 1 to 80 MHz with 1 MHz increments while maintaining $\eta_{\rm O}$ constant at 0.5 and considering the dephasing at ³⁵Cl transmitter offset = 0 MHz for each data point. The dephasing is significantly higher at 200 kHz RF field for the 35 Cl $C_{\rm Q}$ range considered in this simulation. However, such a high 35Cl RF field may not be possible to achieve experimentally. For the other two saturation pulse RF fields of 80 kHz and 40 kHz, the dephasing gradually decreases as the 35 Cl $C_{\rm O}$ increases. But, even if the 35 Cl pulse RF field was limited to 40 kHz appreciable dephasing is still predicted. Notably, Cl covalently bonded to Cl has a Co on the order of 75 MHz.⁶⁶ Therefore, the ¹H{³⁵Cl} DE-RESPDOR experiments could even be applicable to detection of covalently bonded chlorine atoms in organic systems.

Numerical simulations of RESPDOR experiments with I = 5/2and 7/2 nuclei

One obvious question that arises from the previous results is whether or not the indirect detection methods can potentially be applied to quadrupolar nuclei with spins greater than 3/2. To address this question, we have performed SIMPSON simulations of DE RESPDOR experiments for representative 5/2 (127 I, Fig. 8) and 7/2 nuclei (51V, Fig. 8). Fig. 8 shows SIMPSON simulated 127I and 51V NMR spectra and DE RESPDOR dephasing plots for the two test cases of BaI₂·2H₂O²⁶ and V₂O₂(OH)₃,⁶⁷ respectively. The 127 I $C_{\rm O}$ and $\eta_{\rm O}$ of BaI₂·2H₂O has been previously measured, while the $C_{\rm O}$ and $\eta_{\rm O}$ of $V_2O_2({\rm OH})_3$ were obtained from a plane-wave DFT calculation. The SIMPSON simulations clearly suggest that the frequency stepped RESPDOR experiments should be applicable to higher spin nuclei. However, we note that it is possibly more challenging to resolve the CT from the ST since there are more ST for higher spin quadrupolar nuclei. Additionally, there may be significant broadening of the powder patterns, especially if higher RF fields are used for the saturation pulses. For example, in the simulated ¹H{⁵¹V} RESPDOR dephasing profiles the powder pattern is significantly broadened due to off-resonance saturation effects. We plan to experimentally test these approaches for I = 5/2 and I = 7/2 nuclei in future work.

Conclusions

In conclusion, we have demonstrated that frequency-stepped dephasing experiments can be used for the indirect detection of wideline solid-state NMR spectra of abundant spin-3/2 nuclei. For the test cases considered in this paper, significant time savings and gains in sensitivity were realized in some cases. The exact gains in sensitivity that are achievable with indirect detection depend upon the ratio of the ${}^{1}H$ T_{1} and quadrupolar nucleus T_1 and the spin quantum number and γ of the quadrupolar nucleus. Additional factors that influence the gains in sensitivity include the magnitude of the dipolar or scalar couplings and T_2' of the quadrupolar nucleus, with the latter

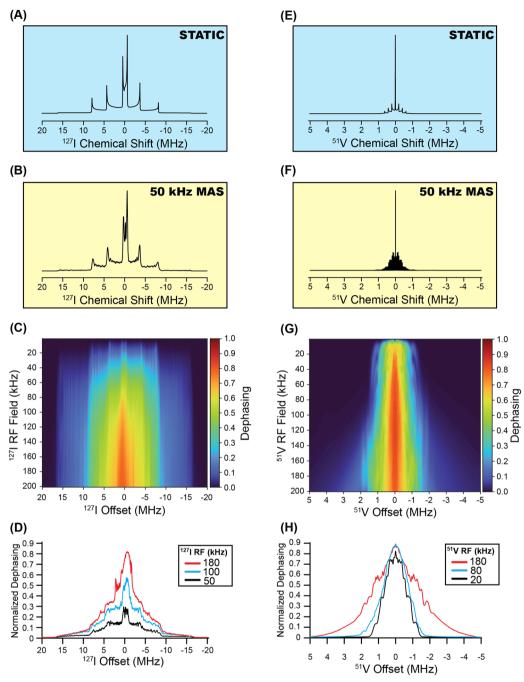


Fig. 8 SIMPSON simulated ¹²⁷I solid-state NMR spectra of Bal₂·2H₂O ($C_Q = 53.8$ MHz and $\eta_Q = 0$) shown for (A) a stationary sample and (B) for a 50 kHz MAS frequency. (C) Heat plot showing the simulated dephasing for ¹H(¹²⁷I) DE-RESPDOR experiments as a function of the ¹²⁷I saturation pulse RF field with conventional rectangular pulses that are 80 μ s in duration. (D) Dephasing profiles extracted from the heat plot for 127 I saturation pulse RF fields of 180 kHz, 100 kHz, and 50 kHz. SIMPSON simulated 51 V solid-state NMR spectra of $V_2O_2(OH)_3$ ($C_Q=5.8$ MHz and $\eta_Q=0.33$) shown for (E) a stationary sample and (F) for a 50 kHz MAS frequency. (G) Heat plot showing the simulated dephasing for ¹H(⁵¹V) DE-RESPDOR experiments as a function of the ⁵¹V saturation pulse RF field with conventional rectangular pulses that are 80 µs in duration. (H) Dephasing profiles extracted from the heat plot for 51V saturation pulse RF fields 180 kHz, 80 kHz, and 20 kHz.

parameter determining how efficient CPMG detection can be. The breadth of the quadrupolar powder pattern is also an important consideration, with indirect detection likely preferred for wider spectra and direct detection preferred for narrower quadrupolar powder patterns. Even in cases where the indirect detection dephasing experiments do not provide

absolute gains in sensitivity, they may still be helpful as they provide valuable structural information by confirming the presence of dipolar or scalar couplings between the detected nucleus and the quadrupolar nucleus of interest. We also note that much smaller sample volumes are required for the indirect detection experiments, so they should be useful for limited

quantity samples. Numerical simulations suggest that the RESPDOR methods are applicable to samples with very large C_{O} .

We anticipate that the indirect detection experiments demonstrated here can be readily combined with dynamic nuclear polarization (DNP) to further enhance sensitivity.⁶⁸ Under MAS conditions DNP-enhanced ¹H spin polarization can be efficiently transferred to spin-1/2 nuclei such as ¹H, ¹³C and ³¹P, whereas direct DNP or indirect DNP of quadrupolar nuclei is often more challenging. Hence, the indirect detection approach is potentially easier to implement in DNP experiments. We are pursuing further research along these lines. Another interesting direction to consider would be to incorporate phase-modulated (PM) saturation pulses^{69,70} into the DE-RESPDOR experiments. The PM saturation pulses have been shown to provide enhanced dephasing in REDOR experiments with quadrupolar nuclei that exhibit large quadrupolar coupling constants. 69,70 For samples with very large $C_{\rm O}$, the PM pulses may be beneficial. We are actively using these indirect detection methods to study materials that contain quadrupolar nuclei that give rise to wideline solid-state NMR spectra.

4. Experimental

Transplatin was purchased from Alfa Aesar and used without further purification. Methylammonium bromide (CH3NH3Br) was purchased from DyeSol. Methylammonium chloride (CH₃NH₃Cl, 99.0%) and lead chloride (PbCl₂, 99.999%) were purchased from Sigma-Aldrich. Lead bromide (PbBr₂, 98 + %) was purchased from Acros. N,N-Dimethylformamide (DMF) and toluene were purchased from Fisher Scientific. Copper(1) iodide (CuI, 95 + %) was purchased from Alfa Aesar and used after purification. 1,1,1-Tris(diphenylphosphinomethyl)ethane (triphos, 97 + %) was purchased from Strem. Chloroform was purchased from BeanTown Chemical and used after vacuum distillation over sieves. MAPbCl3, MAPbBr3 and triphosCuI were prepared according to the following procedures:

Synthesis of methylammonium lead halides

CH₃NH₃PbBr₃ and CH₃NH₃PbCl₃ were synthesized by a slightly modified literature procedure. 71,72 Briefly, CH₃NH₃Br (1.5 mmol) and PbBr₂ (1.5 mmol) were dissolved in DMF (30 mL). After stirring until the mixture became homogeneous (<30 min), excess toluene (100 mL) was added. Crystalline CH₃NH₃PbBr₃ was collected by centrifugation at 4000 rpm for 10 min. After washing 3 times with toluene (30 mL), the material was dried under vacuum. CH3NH3PbCl3 was synthesized from CH₃NH₃Cl and PbCl₂ following a similar procedure. Synthesis of CH₃NH₃PbBr₃ and CH₃NH₃PbCl₃ was confirmed by powder X-ray diffraction (PXRD, Fig. S11, ESI†). PXRD patterns were recorded using Cu Ka radiation on a Rigaku Ultima IV diffractometer (40 kV, 44 mA).

Synthesis of the complex triphosCuI

A flask was charged with 1,1,1-tris(diphenylphosphinomethyl)ethane (111.3 mg, 0.1782 mmol), CuI (32.5 mg, 0.171 mmol),

and 25 mL of chloroform under nitrogen. The reaction mixture was stirred overnight, forming a crystalline precipitate. The mixture was filtered, and the solids were washed with 3 mL of chloroform, then dried in vacuo. A colorless powder (103.5 mg, 0.1270 mmol, 71.3%) was collected. Solution ¹H NMR spectra and single crystal X-ray diffraction data are included in the ESI.† The single-crystal X-ray diffraction structure of triphosCuI can be accessed from the Cambridge Crystallographic Data Centre (CCDC code: 2250183).

Solid-state NMR spectroscopy

Solid-state NMR spectroscopy experiments were performed on a 9.4 T Bruker wide-bore magnet equipped with a Bruker AVANCE III HD console (1H{35Cl} DE-RESPDOR,49 35Cl and ⁸¹Br WURST-CPMG, ^{19 207}Pb{³⁵Cl} *J*-resolved, ⁶³Cu DEPTH⁶⁰ and ${}^{1}H \rightarrow {}^{31}P\{{}^{63}Cu\}$ *J*-resolved) and equipped with a Bruker 1.3 mm HX (¹H{³⁵Cl} experiments of transplatin and MAPbCl₃), Bruker 2.5 mm HXY probe (207 Pb{ 35 Cl} of MAPbCl₃ and 1 H \rightarrow ³¹P{⁶³Cu} of triphosCuI complex) or a Bruker 4.0 mm HXY magic angle spinning (MAS) NMR probe (all WURST-CPMG experiments). ¹H{⁸¹Br} experiments were performed with a 14.1 T Bruker wide-bore magnet equipped with a Bruker AVANCE NEO console and a Bruker 2.5 mm HXY MAS NMR probe. All experiments utilized N₂ gas for spinning. ¹H chemical shifts were referenced to neat tetramethylsilane by using adamantane $(\delta_{iso}(^{1}H) = 1.72 \text{ ppm})$ as a secondary chemical shift reference. 207Pb and 31P chemical shifts were indirectly referenced to neat TMS using the IUPAC recommended relative NMR frequency.73 NMR spectra were processed and analyzed with Bruker Topspin version 3.6.4 (AVANCE III HD data) or 4.1.4 (AVANCE NEO data) software.

The following experimental details are with respect to data acquired at $B_0 = 9.4$ T with the 1.3 mm HX NMR probe (${}^{1}H{}^{35}Cl$) experiments), 2.5 mm HXY NMR probe (207 Pb $\{^{35}$ Cl $\}$ and 1 H \rightarrow ³¹P{⁶³Cu} experiments) and 4 mm HXY NMR probe (WURST-QCPMG experiments). ¹H{³⁵Cl} DE-RESPDOR spectra of transplatin were recorded with the 1.3 mm HX NMR probe and a 50 kHz MAS frequency. The ¹H longitudinal relaxation time constant (T_1) of transplatin was ca.17 s; all experiments utilized a 5 s recycle delay. ¹H{³⁵Cl} DE-RESPDOR experiments were performed with 35 Cl saturation pulses that were 80 μ s (4 $\times \tau_{rot}$) in duration with an 80 kHz RF field. 49 Additional experiments on transplatin were performed with tanh/tan ³⁵Cl saturation pulses 40 µs in duration. The sweep width of the tanh/tan pulses was set to 5 MHz. The SR412 heteronuclear dipolar recoupling sequence was applied to the ¹H spins to reintroduce the ¹H-³⁵Cl dipolar interaction under MAS.55 A control (without a 35Cl saturation pulse) and dephased (with a 35Cl saturation pulse) point were recorded at each ³⁵Cl offset. Similarly, ¹H{³⁵Cl} DE-RESPDOR spectra of MAPbCl₃ were recorded with the 1.3 mm HX NMR probe and a 50 kHz MAS frequency. The 1 H T_{1} of $MAPbCl_3$ was ca. 24 s and 30 s for high-frequency (NH₃) and lowfrequency ¹H NMR signal (-CH₃), respectively; all experiments utilized a 5 s recycle delay and the high-frequency ¹H NMR signal was used to map out the ³⁵Cl spectrum. ¹H{³⁵Cl} DE-RESPDOR experiments were performed with 35Cl saturation

pulses that were 80 μs (4 \times τ_{rot}) in duration with an 80 kHz radio frequency (RF) field. 49 The SR412 heteronuclear dipolar recoupling sequence was applied to the ¹H spins to reintroduce the ¹H-³⁵Cl dipolar interaction under MAS.⁵⁵ A control (without a ³⁵Cl saturation pulse) and dephased (with a 35Cl saturation pulse) point was recorded at each ³⁵Cl offset. ²⁰⁷Pb{³⁵Cl} *J*-resolved spectra of MAPbCl₃ were recorded with the 2.5 mm HXY NMR probe and a 25 kHz MAS frequency. All experiments utilized a 2 s recycle delay. ²⁰⁷Pb{³⁵Cl} *J*-resolved experiments were performed with ³⁵Cl saturation pulses that were 80 μs (2 \times $\tau_{rot})$ in duration with a 14 kHz RF field. A control (without a 35Cl saturation pulse) and dephased (with a 35Cl saturation pulse) point were recorded at each 35 Cl offset. 1 H \rightarrow 31 P $_{1}^{63}$ Cu $_{1}$ J-resolved spectra of triphosCuI were recorded with the 2.5 mm HXY NMR probe and a 25 kHz MAS frequency. The ${}^{1}H$ T_{1} of triphosCuI complex was ca. 6.4 s; all experiments utilized an 8 s recycle delay. ¹H → ³¹P₁⁶³Cu} J-resolved experiments were performed with ⁶³Cu saturation pulses that were 40 μs (1 \times $\tau_{rot})$ in duration with a 30 kHz RF field. A control (without a 63Cu saturation pulse) and dephased (with a 63Cu saturation pulse) point were recorded at each ⁶³Cu offset. The ⁶³Cu DEPTH⁶⁰ spectrum was recorded with 3 s recycle delay and 4096 scans. Static WURST-QCPMG spectra of MAPbCl3 were recorded with the 4 mm HXY NMR probe with WURST pulses that were 25 μs in duration and with a sweep width of 800 kHz. 19,24,74 Each echo in the CPMG train was 50 µs in duration. A total of 30 echoes were acquired. 50 kHz ¹H RF field SPINAL-64 decoupling was performed throughout the entire static CPMG experiments.⁷⁵ Similarly, static WURST-QCPMG spectra of transplatin were recorded with the 4 mm HXY NMR probe with WURST pulses that were 50 µs in duration and with a sweep width of 800 kHz. 19,24,74 Each echo in the CPMG train was 90 µs in duration. A total of 100 echoes were acquired. High-frequency and low-frequency ends were recorded for static WURST-QCPMG spectra of MAPbBr3 with the 4 mm HXY NMR probe with WURST pulses that were 25 µs in duration and with a sweep width of 800 kHz. 19,24,74 Each echo in the CPMG train was 50 µs in duration. A total of 10 echoes were acquired.

The following experimental details are for data collected with the Bruker 2.5 mm HXY NMR probe and B_0 = 14.1 T (1H{81Br} experiments). 1H{81Br} DE-RESPDOR spectra of MAPbBr₃ were recorded with a 25 kHz MAS frequency. The ¹H T_1 of MAPbBr₃ was ca. 24 s and 23 s for high-frequency (-NH₃) and low-frequency signal (-CH₃), respectively. All experiments applied a 10 s recycle delay and considered highfrequency signal to map out the 81Br spectrum. 1H{81Br} DE-RESPDOR experiments were performed with 81Br saturation pulses that were 80 μs (2 \times τ_{rot}) in duration with a 50 kHz RF field.⁴⁹ The SR4₁² heteronuclear dipolar recoupling sequence was applied to the ¹H spins to reintroduce the ¹H-⁸¹Br dipolar interaction under MAS.55 A control (without a 81Br saturation pulse) and dephased (with a 81Br saturation pulse) point was recorded at each 81Br offset.

Numerical solid-state NMR spectroscopy simulations

SIMPSON v4.1.1 was used to perform numerical solid-state NMR simulations. 50-52 The archived data includes the SIMP-SON input codes. Except for the ${}^{1}H$ $\pi/2$ pulses, all the pulses in

the files were finite in duration. All 2D heat maps were created using the rep678 crystal file. Static and MAS ideal ³⁵Cl NMR spectra were simulated using the zcw28656 crystal file. The number of gamma angles was 15 for the MAS spectrum simulations. In Fig. 2C and D, the 35Cl offset was incremented in steps of 50 kHz over a frequency range of ± 20 MHz to ± 20 MHz while the 35Cl saturation RF field was increased in steps of 2 kHz from 0 to 200 kHz. The simulations in Fig. 2E were extracted from the simulation corresponding to Fig. 2C. The simulation in Fig. 2F was extracted from corresponding simulations shown in Fig. 2D. MATLAB R2021B was used to create all heat maps. The simulated spectra were processed in ssNake v1.3.⁵⁷ The DE-RESPDOR heat maps were normalized by dividing each dephasing intensity by the maximum dephasing exhibited in each heat map. All the other numerical simulations were run with identical parameters (RF fields, transmitter offsets, and B_0) to those used experimentally. The other numerical simulations for ¹H{³⁵Cl} DE-RESPDOR in Fig. 2B and 4C were performed with a two-spin ¹H-³⁵Cl spin system, the zcw4180 crystal file, 13 γ -angles, and a 0.5 μ s time step where the Hamiltonian was considered time-independent. ¹H{⁸¹Br} DE-RESPDOR numerical simulations were done with a two-spin $^{1}\text{H-}^{81}\text{Br}$ spin system, the zcw4180 crystal file, 13 γ -angles, and a 0.1 µs time step where the Hamiltonian was considered timeindependent. Numerical simulations of static 35Cl/81Br solidstate NMR spectra were performed with the zcw28656 crystal file and assumed ideal excitation of the powder pattern (start operator I_{1x} , detect operator I_{1c}). In Fig. 8, all 2D heat maps were created using the rep678 crystal file. Static and MAS ideal 35Cl NMR spectra were simulated using the zcw28656 crystal file. The number of gamma angles was 15 for the MAS spectrum simulations. In Fig. 8C, the ¹²⁷I offset was incremented in steps of 50 kHz over a frequency range of +20 MHz to -20 MHz while the ¹²⁷I saturation RF field was increased in steps of 2 kHz from 0 to 200 kHz. The simulation in Fig. 8D was extracted from the simulation corresponding to Fig. 8C.

In Fig. 8G, the ⁵¹V offset was incremented in steps of 50 kHz over a frequency range of +5 MHz to -5 MHz while the 51V saturation RF field was increased in steps of 1 kHz from 0 to 200 kHz. The simulation in Fig. 8H was extracted from the simulation corresponding to Fig. 8G. MATLAB R2021B was used to create all heat maps. The simulated spectra were processed in ssNake v1.3.57

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Material synthesis, solid-state NMR experiments and simulations were supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division (A. J. R., J. V., S. N. S. L, B. A. A., R. W. D., and E. G.). The Ames Laboratory is operated for the US DOE by

Iowa State University under Contract DE-AC02-07CH11358. Synthesis, characterization and NMR experiments on triphosCuI were supported by grant CHE-1900100 from the US NSF (J. B. and M. R. K). A. J. R. acknowledges additional support from the Alfred P. Sloan Foundation through a Sloan research fellowship.

References

- 1 S. P. Brown and H. W. Spiess, Advanced solid-state NMR methods for the elucidation of structure and dynamics of molecular, macromolecular, and supramolecular systems, Chem. Rev., 2001, 101, 4125-4155.
- 2 P.-H. Chien, K. J. Griffith, H. Liu, Z. Gan and Y.-Y. Hu, Recent Advances in Solid-State Nuclear Magnetic Resonance Techniques for Materials Research, Annu. Rev. Mater. Res., 2020, 50, 493-520.
- 3 T. K. Karamanos, A. P. Kalverda and S. E. Radford, Generating Ensembles of Dynamic Misfolding Proteins, Front. Neurosci., 2022, 16, 1-14.
- 4 D. L. Bryce, New frontiers for solid-state NMR across the periodic table: A snapshot of modern techniques and instrumentation, Dalton Trans., 2019, 48, 8014-8020.
- 5 S. E. Ashbrook, Solid-state NMR spectroscopy, Phys. Chem. Chem. Phys., 2009, 11, 6875.
- 6 R. W. Schurko, Ultra-wideline solid-state NMR spectroscopy, Acc. Chem. Res., 2013, 46, 1985-1995.
- 7 S. E. Ashbrook and S. Sneddon, New methods and applications in solid-state NMR spectroscopy of quadrupolar nuclei, J. Am. Chem. Soc., 2014, 136, 15440-15456.
- 8 A. Medek, V. Frydman and L. Frydman, Central Transition Nuclear Magnetic Resonance in the Presence of Large Quadrupole Couplings: Cobalt-59 Nuclear Magnetic Resonance of Cobaltophthalocyanines, J. Phys. Chem. A, 1999, 103, 4830-4835.
- 9 D. Massiot, I. Farnan, N. Gautier, D. Trumeau, A. Trokiner and J. P. Coutures, 71Ga and 69Ga nuclear magnetic resonance study of beta-Ga₂O₃: resolution of four- and six-fold coordinated Ga sites in static conditions, Solid State Nucl. Magn. Reson., 1995, 4, 241-248.
- 10 C. P. Slichter, NMR Study of Platinum Catalysis, Surf. Sci., 1981, 106, 382-396.
- 11 T. J. Bastow, M. E. Smith and S. N. Stuart, Observation of ⁹¹Zr NMR in zirconium-based metals and oxides, Chem. Phys. Lett., 1992, 19, 125-129.
- 12 T. J. Bastow and M. E. Smith, 91Zr NMR characterisation of phases in transformation toughened zirconia, Solid State Nucl. Magn. Reson., 1992, 1, 165-174.
- 13 F. H. Larsen, J. Skibsted, H. J. Jakobsen and N. C. Nielsen, Solid-state QCPMG NMR of low-y quadrupolar metal nuclei in natural abundance, J. Am. Chem. Soc., 2000, 122, 7080-7086.
- 14 F. H. Larsen, H. J. Jakobsen, P. D. Ellis and N. C. Nielsen, High-field QCPMG-MAS NMR of half-integer quadrupolar nuclei with large quadrupole couplings, Mol. Phys., 1998, **95**, 1185-1195.

- 15 A. S. Lipton, M. D. Smith, R. D. Adams and P. D. Ellis, Zn solid-state and single-crystal NMR spectroscopy and X-ray crystal structure of zinc formate dihydrate, J. Am. Chem. Soc., 2002, 124, 410-414.
- 16 A. S. Lipton, R. W. Heck, M. Hernick, C. A. Fierke and P. D. Ellis, Residue ionization in LpxC directly observed by ⁶⁷Zn NMR spectroscopy, J. Am. Chem. Soc., 2008, 130, 12671-12679.
- 17 H. Nagashima, J. Trébosc, Y. Kon, K. Sato, O. Lafon and J. P. Amoureux, Observation of Low-γ Quadrupolar Nuclei by Surface-Enhanced NMR Spectroscopy, J. Am. Chem. Soc., 2020, 142, 10659-10672.
- 18 B. E. G. Lucier, K. E. Johnston, W. Xu, J. C. Hanson, S. D. Senanayake, S. Yao, M. W. Bourassa, M. Srebro, J. Autschbach and R. W. Schurko, Unravelling the structure of Magnus' pink salt, I. Am. Chem. Soc., 2014, 136, 1333-1351.
- 19 L. A. O'Dell and R. W. Schurko, QCPMG using adiabatic pulses for faster acquisition of ultra-wideline NMR spectra, Chem. Phys. Lett., 2008, 464, 97-102.
- 20 A. J. Rossini, R. W. Mills, G. A. Briscoe, E. L. Norton, S. J. Geier, I. Hung, S. Zheng, J. Autschbach and R. W. Schurko, Solid-state chlorine NMR of group IV transition metal organometallic complexes, J. Am. Chem. Soc., 2009, 131, 3317-3330.
- 21 D. Laurencin, F. Ribot, C. Gervais, A. J. Wright, A. R. Baker, L. Campayo, J. V. Hanna, D. Iuga, M. E. Smith, J. M. Nedelec, G. Renaudin and C. Bonhomme, ⁸⁷Sr, ¹¹⁹Sn, ¹²⁷I Single and { ¹H/¹⁹F}-Double Resonance Solid-State NMR Experiments: Application to Inorganic Materials and Nanobuilding Blocks, ChemistrySelect, 2016, 1, 4509-4519.
- 22 L. Piveteau, M. Aebli, N. Yazdani, M. Millen, L. Korosec, F. Krieg, B. M. Benin, V. Morad, C. Piveteau, T. Shiroka, A. Comas-Vives, C. Copéret, A. M. Lindenberg, V. Wood, R. Verel and M. V. Kovalenko, Bulk and Nanocrystalline Cesium Lead-Halide Perovskites as Seen by Halide Magnetic Resonance, ACS Cent. Sci., 2020, 6, 1138-1149.
- 23 D. L. Bryce and G. D. Sward, Solid-state NMR spectroscopy of the quadrupolar halogens: Chlorine-35/37, bromine-79/ 81, and iodine-127, Magn. Reson. Chem., 2006, 44, 409-450.
- 24 L. A. O'Dell, A. J. Rossini and R. W. Schurko, Acquisition of ultrawideline NMR spectra from quadrupolar nuclei by frequency stepped WURST-QCPMG, Chem. Phys. Lett., 2009, 468, 330-335.
- 25 A. S. Lipton, J. A. Sears and P. D. Ellis, A general strategy for the NMR observation of half-integer quadrupolar nuclei in dilute environments, J. Magn. Reson., 2001, 151, 48-59.
- 26 C. M. Widdifield and D. L. Bryce, Solid-state 127 I NMR and GIPAW DFT study of metal iodides and their hydrates: Structure, symmetry, and higher-order quadrupoleinduced effects, J. Phys. Chem. A, 2010, 114, 10810-10823.
- 27 L. Müller, Sensitivity Enhanced Detection of Weak Nuclei Sensitivity Enhanced Detection of Weak Nuclei Using Heteronuclear Multiple Quantum Coherence, J. Am. Chem. Soc., 1979, 101, 4481-4484.
- 28 S. Cavadini, A. Abraham and G. Bodenhausen, Protondetected nitrogen-14 NMR by recoupling of heteronuclear dipolar interactions using symmetry-based sequences, Chem. Phys. Lett., 2007, 445, 1-5.

PCCP

29 S. Cavadini, A. Lupulescu, S. Antonijevic and G. Bodenhausen, Nitrogen-14 NMR spectroscopy using residual dipolar splittings in solids, J. Am. Chem. Soc., 2006, 128, 7706-7707.

- 30 Z. Gan, Measuring amide nitrogen quadrupolar coupling by high-resolution ¹⁴N/¹³C NMR correlation under magic-angle spinning, J. Am. Chem. Soc., 2006, 128, 6040-6041.
- 31 Y. Nishiyama, Y. Endo, T. Nemoto, H. Utsumi, K. Yamauchi, K. Hioka and T. Asakura, Very fast magic angle spinning ¹H-¹⁴N 2D solid-state NMR: Sub-micro-liter sample data collection in a few minutes, J. Magn. Reson., 2011, 208, 44-48.
- 32 S. Cavadini, S. Antonijevic, A. Lupulescu and G. Bodenhausen, Indirect detection of nitrogen-14 in solids via protons by nuclear magnetic resonance spectroscopy, J. Magn. Reson., 2006, 182, 168-172.
- 33 S. Cavadini, A. Abraham, S. Ulzega and G. Bodenhausen, Evidence for dynamics on a 100 ns time scale from singleand double-quantum nitrogen-14 NMR in solid peptides, J. Am. Chem. Soc., 2008, 130, 10850-10851.
- 34 M. Grüne, R. Luxenhofer, D. Iuga, S. P. Brown and A. C. Pöppler, ¹⁴N-¹H HMQC solid-state NMR as a powerful tool to study amorphous formulations-an exemplary study of paclitaxel loaded polymer micelles, J. Mater. Chem. B, 2020, 8, 6827-6836.
- 35 A. S. Tatton, T. N. Pham, F. G. Vogt, D. Iuga, A. J. Edwards and S. P. Brown, Probing hydrogen bonding in cocrystals and amorphous dispersions using 14N-1H HMQC solid-state NMR, Mol. Pharm., 2013, 10, 999-1007.
- 36 C. D. Makowka, C. P. Slichter and J. H. Sinfelt, NMR of platinum catalysts: Double NMR of chemisorbed carbon monoxide and a model for the platinum NMR line shape, Phys. Rev. B: Condens. Matter Mater. Phys., 1985, 31, 5663-5679.
- 37 C. D. Makowka, C. P. Slichter and J. H. Sinfelt, Probe of the Surface of a Heterogeneous Catalyst: Double NMR of Carbon Monoxide Chemisorbed on Highly Dispersed Platinum, Phys. Rev. Lett., 1982, 49, 379-382.
- 38 P. K. Wang, J. P. Ansermet, S. L. Rudaz, Z. Wang, S. Shore, C. P. Slichter and J. H. Sinfelt, NMR Studies of Simple Molecules on Metal Surfaces, Science, 1986, 234, 35-41.
- 39 C. P. Grey and A. J. Vega, Determination of the Quadrupole Coupling Constant of the Invisible Aluminum Spins in Zeolite HY with ¹H/²⁷A1 TRAPDOR NMR, J. Am. Chem. Soc., 1995, 117, 8232-8242.
- 40 M. Kalwei and H. Koller, Quantitative comparison of REAP-DOR and TRAPDOR experiments by numerical simulations and determination of H-Al distances in zeolites, Solid State Nucl. Magn. Reson., 2002, 21, 145-157.
- 41 C. Schroeder, V. Siozios, C. Mück-Lichtenfeld, M. Hunger, M. R. Hansen and H. Koller, Hydrogen Bond Formation of Brønsted Acid Sites in Zeolites, Chem. Mater., 2020, 32, 1564-1574.
- 42 R. W. Dorn, B. J. Ryan, S. N. S. Lamahewage, M. V. Dodson, J. B. Essner, R. Biswas, M. G. Panthani and A. J. Rossini, Chlorination of Hydrogenated Silicon Nanosheets Revealed by Solid-State Nuclear Magnetic Resonance Spectroscopy, Chem. Mater., 2023, 35, 539-548.
- 43 N. T. Duong and Y. Nishiyama, Detection of remote protonnitrogen correlations by 1H-detected 14N overtone solid-

- state NMR at fast MAS, Phys. Chem. Chem. Phys., 2022, 24, 10717-10726.
- 44 Z. Gan, Rotary resonance echo double resonance for measuring heteronuclear dipolar coupling under MAS, J. Magn. Reson., 2006, 183, 235-241.
- 45 C. P. Grey, W. S. Veeman and A. J. Vega, Rotational echo ¹⁴N/¹³C/¹H triple resonance solid-state nuclear magnetic resonance: A probe of ¹³C-¹⁴N internuclear distances, J. Chem. Phys., 1993, 98, 7711-7724.
- 46 A. Venkatesh, D. Gioffrè, B. A. Atterberry, L. Rochlitz, S. L. Carnahan, Z. Wang, G. Menzildjian, A. Lesage, C. Copéret and A. J. Rossini, Molecular and Electronic Structure of Isolated Platinum Sites Enabled by the Expedient Measurement of 195Pt Chemical Shift Anisotropy, J. Am. Chem. Soc., 2022, 144, 13511-13525.
- 47 T. Wolf, A. Eden-Kossoy and L. Frydman, Indirectly detected satellite-transition quadrupolar NMR via progressive saturation of the proton reservoir, Solid State Nucl. Magn. Reson., 2023, 125, 101862.
- 48 M. J. Jaroszewicz, A. R. Altenhof, R. W. Schurko and L. Frydman, Sensitivity Enhancement by Progressive Saturation of the Proton Reservoir: A Solid-State NMR Analogue of Chemical Exchange Saturation Transfer, J. Am. Chem. Soc., 2021, 143, 19778-19784.
- 49 B. A. Atterberry, S. L. Carnahan, Y. Chen, A. Venkatesh and A. J. Rossini, Double echo symmetry-based REDOR and RESPDOR pulse sequences for proton detected measurements of heteronuclear dipolar coupling constants, J. Magn. Reson., 2022, 336, 107147.
- 50 M. Bak, J. T. Rasmussen and N. C. Nielsen, SIMPSON: A General Simulation Program for Solid-State NMR Spectroscopy, J. Magn. Reson., 2000, 147, 296-330.
- 51 Z. Tošner, T. Vosegaard, C. Kehlet, N. Khaneja, S. J. Glaser and N. C. Nielsen, Optimal control in NMR spectroscopy: Numerical implementation in SIMPSON, J. Magn. Reson., 2009, 197, 120-134.
- 52 Z. Tošner, R. Andersen, B. Stevensson, M. Edén, N. C. Nielsen and T. Vosegaard, Computer-intensive simulation of solid-state NMR experiments using SIMPSON, J. Magn. Reson., 2014, 246, 79-93.
- 53 T. L. Hwang, P. C. M. Van Zijl and M. Garwood, Fast Broadband Inversion by Adiabatic Pulses, J. Magn. Reson., 1998, 133, 200-203.
- 54 A. Pankowska, K. Kochalska, A. Łazorczyk, K. Dyndor, P. Kozioł, B. Zieńczuk, M. Toborek and R. Pietura, Chemical exchange saturation transfer (CEST) as a new method of signal obtainment in magnetic resonance molecular imaging in clinical and research practice, Pol. J. Radiol., 2019, 84, e147-e152.
- 55 A. Brinkmann and A. P. M. Kentgens, Proton-selective ¹⁷O-¹H distance measurements in fast magic-angle-spinning solidstate NMR spectroscopy for the determination of hydrogen bond lengths, J. Am. Chem. Soc., 2006, 128, 14758-14759.
- 56 B. E. G. Lucier, A. R. Reidel and R. W. Schurko, Multinuclear solid-state NMR of square-planar platinum complexes Cisplatin and related systems, Can. J. Chem., 2011, 89, 919-937.

57 S. G. J. van Meerten, W. M. J. Franssen and A. P. M. Kentgens, ssNake: A cross-platform open-source NMR data processing and fitting application, J. Magn. Reson., 2019,

- 301, 56-66. 58 D. Sarkar, R. W. Hooper, A. Karmakar, A. Bhattacharya, A. Pominov, V. V. Terskikh and V. K. Michaelis, Metal Halide Perovskite and Perovskite-like Materials through the Lens of Ultra-wideline 35/37Cl NMR Spectroscopy, ACS
- 59 K. Sonogashira, Y. Tohda and N. Hagihara, A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines, Tetrahedron Lett., 1975, 50, 4467-4470.

Mater. Lett., 2022, 4, 1255-1263.

- 60 D. G. Cory and W. M. Ritchey, Suppression of Signals from the Probe in Bloch Decay Spectra, J. Magn. Reson., 1988, 80, 128-160.
- 61 B. E. G. Lucier, J. A. Tang, R. W. Schurko, G. A. Bowmaker, P. C. Healy and J. V. Hanna, Solid-state ⁶⁵Cu and ³¹P NMR spectroscopy of bis(triphenylphosphine) copper species, J. Phys. Chem. C, 2010, 114, 7949-7962.
- 62 J. A. Tang, B. D. Ellis, T. H. Warren, J. V. Hanna, C. L. B. Macdonald and R. W. Schurko, Solid-state ⁶³Cu and ⁶⁵Cu NMR spectroscopy of inorganic and organometallic copper(1) complexes, J. Am. Chem. Soc., 2007, 129, 13049-13065.
- 63 H. Yu, X. Tan, G. M. Bernard, V. V. Terskikh, J. Chen and R. E. Wasylishen, Solid-State 63Cu, 65Cu, and 31P NMR Spectroscopy of Photoluminescent Copper(1) Triazole Phosphine Complexes, J. Phys. Chem. A, 2015, 119, 8279-8293.
- 64 C. J. Pickard and F. Mauri, All-electron magnetic response with pseudopotentials: NMR chemical shifts, Phys. Rev. B: Condens. Matter Mater. Phys., 2001, 63, 2451011.
- 65 S. J. Clark, M. D. Segall, C. J. Pickard Ii, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, First principles methods using CASTEP, Z. Kristallogr., 2005, 220, 567-570.
- 66 F. A. Perras and D. L. Bryce, Direct investigation of covalently bound chlorine in organic compounds by solidstate 35Cl NMR spectroscopy and exact spectral line-shape simulations, Angew. Chem., Int. Ed., 2012, 51, 4227-4230.

- 67 A. M. Callegari and M. Boiocchi, Häggite from the Gambatesa mine, Liguria, Italy: a refinement of the crystal structure, Neues Jahrb. Mineral., Abh., 2015, 192, 33-38.
- 68 T. Maly, G. T. Debelouchina, V. S. Bajaj, K. N. Hu, C. G. Joo, M. L. Mak-Jurkauskas, J. R. Sirigiri, P. C. A. Van Der Wel, J. Herzfeld, R. J. Temkin and R. G. Griffin, Dynamic nuclear polarization at high magnetic fields, J. Chem. Phys., 2008, 128, 052211.
- 69 E. Nimerovsky and A. Goldbourt, Efficient rotational echo double resonance recoupling of a spin-1/2 and a quadrupolar spin at high spinning rates and weak irradiation fields, J. Magn. Reson., 2010, 206, 52-58.
- 70 E. Nimerovsky, R. Gupta, J. Yehl, M. Li, T. Polenova and A. Goldbourt, Phase-modulated LA-REDOR: A robust, accurate and efficient solid-state NMR technique for distance measurements between a spin-1/2 and a quadrupole spin, J. Magn. Reson., 2014, 244, 107-113.
- 71 B. A. Rosales, L. Men, S. D. Cady, M. P. Hanrahan, A. J. Rossini and J. Vela, Persistent Dopants and Phase Segregation in Organolead Mixed-Halide Perovskites, Chem. Mater., 2016, 28, 6848-6859.
- 72 F. Zhu, L. Men, Y. Guo, Q. Zhu, U. Bhattacharjee, P. M. Goodwin, J. W. Petrich, E. A. Smith and J. Vela, Shape evolution and single particle luminescence of organometal halide perovskite nanocrystals, ACS Nano, 2015, 9, 2948-2959.
- 73 R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow and P. Granger, NMR nomenclature. Nuclear spin properties and conventions for chemical shifts (IUPAC recommendations 2001), Pure Appl. Chem., 2001, 73, 1795-1818.
- 74 A. J. Rossini, R. W. Mills, G. A. Briscoe, E. L. Norton, S. J. Geier, I. Hung, S. Zheng, J. Autschbach and R. W. Schurko, Solid-state chlorine NMR of group IV transition metal organometallic complexes, J. Am. Chem. Soc., 2009, 131, 3317-3330.
- 75 B. M. Fung, A. K. Khitrin and K. Ermolaev, An Improved Broadband Decoupling Sequence for Liquid Crystals and Solids, J. Magn. Reson., 2000, 142, 97-101.