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Abstract
Organolead halide and mixed halide perovskites (CH3NH3PbX3, CH3NH3PbX3–nYn, X and Y = Cl−, Br− or I−), are promising materials for photovoltaics and optoelectronic devices. 207Pb solid-state NMR spectroscopy has previously been applied to characterize phase segregation and halide ion speciation in mixed halide perovskites. However, NMR spectroscopy is an insensitive technique that often requires large sample volumes and long signal averaging periods. This is especially true for mixed halide perovskites, which give rise to extremely broad 207Pb solid-state NMR spectra. Here, we quantitatively compare the sensitivity of the various solid-state NMR techniques on pure and mixed halide organolead perovskites and demonstrate that both fast MAS and DNP can provide substantial gains in NMR sensitivity for these materials. With fast MAS and proton detection, high signal-to-noise ratio two-dimensional (2D) 207Pb-1H heteronuclear correlation (HETCOR) NMR spectra can be acquired in less than half an hour from only ca. 5 µL of perovskite material. Modest relayed DNP enhancements on the order of 1 to 20 were obtained for perovskites. The cryogenic temperatures (110 K) used for DNP experiments also provide a significant boost in sensitivity. Consequently, it was possible to obtain the 207Pb solid-state NMR spectrum of a 300 nm thick model thin film of CH3NH3PbI3 in 34 hours by performing solid-state NMR experiments with a sample temperature of 110 K. This result demonstrates the possibility of using NMR spectroscopy for characterization of perovskite thin films.

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Sensitivity-Enhanced $^{207}\text{Pb}$ Solid-State NMR Spectroscopy for the Rapid, Non-Destructive Characterization of Organolead Halide Perovskites

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Abstract

Organolead halide and mixed halide perovskites (CH$_3$NH$_3$PbX$_3$, CH$_3$NH$_3$PbX$_{3-n}$Y$_n$, X and Y = Cl$^-$, Br$^-$ or I$^-$), are promising materials for photovoltaics and optoelectronic devices. $^{207}$Pb solid-state NMR spectroscopy has previously been applied to characterize phase segregation and halide ion speciation in mixed halide perovskites. However, NMR spectroscopy is an insensitive technique that often requires large sample volumes and long signal averaging periods. This is especially true for mixed halide perovskites, which give rise to extremely broad $^{207}$Pb solid-state NMR spectra. Here, we quantitatively compare the sensitivity of the various solid-state NMR techniques on pure and mixed halide organolead perovskites and demonstrate that both fast MAS and DNP can provide substantial gains in NMR sensitivity for these materials. With fast MAS and proton detection, high signal-to-noise ratio two-dimensional (2D) $^{207}$Pb-$^1$H heteronuclear correlation (HETCOR) NMR spectra can be acquired in less than half an hour from only ca. 5 µL of perovskite material. Modest relayed DNP enhancements on the order of 1 to 20 were obtained for perovskites. The cryogenic temperatures (110 K) used for DNP experiments also provide a significant boost in sensitivity. Consequently, it was possible to obtain the $^{207}$Pb solid-state NMR spectrum of a 300 nm thick model thin film of CH$_3$NH$_3$PbI$_3$ in 34 hours by performing solid-state NMR experiments with a sample temperature of 110 K. This result demonstrates the possibility of using NMR spectroscopy for characterization of perovskite thin films.
TOC Graphic

Introduction

Lead halide perovskites have attracted considerable interest for applications in photovoltaics and optoelectronic devices due to the fact that they possess tunable band gaps, high photo-conversion efficiencies (PCE) up to 22% and they are solution processable.\textsuperscript{1-2} Lead halide perovskites have the general formula APbX\textsubscript{3}, where A is either an inorganic or organic cation (Cs\textsuperscript{+}, CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}, CH(NH\textsubscript{2})\textsubscript{2}\textsuperscript{+}), and X are the halides (Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}). Perovskites with mixed cations and/or halides (A\textsubscript{1-m}B\textsubscript{m}PbX\textsubscript{3-n}Y\textsubscript{n} A, B = Rb\textsuperscript{+}, Cs\textsuperscript{+}, CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+} or CH(NH\textsubscript{2})\textsubscript{2}\textsuperscript{+} and X, Y = Cl\textsuperscript{−}, Br\textsuperscript{−} or I\textsuperscript{−}) currently provide the best performance and stability in photovoltaic devices.\textsuperscript{1,3} Powder X-ray diffraction (PXRD) is commonly applied to characterize pure and mixed lead halide perovskites. However, PXRD often provides limited insight into the structures of mixed phased lead halide perovskites which may show short range phase segregation and even give rise to amorphous phases. For these reasons we have previously applied \textsuperscript{207}Pb solid-state nuclear magnetic resonance (NMR) spectroscopy to determine the local lead coordination environment and probe phase segregation and mixing within mixed halide perovskites.\textsuperscript{4-5} Many other research groups have also used solid-state NMR and nuclear quadrupole resonance (NQR) spectroscopy of the elements commonly found in lead halide perovskites (\textsuperscript{1}H, \textsuperscript{2}H, \textsuperscript{13}C, \textsuperscript{14}N, \textsuperscript{35}Cl, \textsuperscript{79}Br, \textsuperscript{127}I, \textsuperscript{133}Cs, \textsuperscript{207}Pb, etc.) to probe structure, observe hydration and measure the dynamics of cations and anions.\textsuperscript{4-40}
NMR spectroscopy is an insensitive technique that often requires large sample volumes and long signal averaging periods. This is especially true for mixed halide perovskites, which give rise to extremely broad $^{207}$Pb solid-state NMR spectra because the $^{207}$Pb chemical shift is dependent upon the identity and number of coordinating halogen atoms. Previous $^{207}$Pb solid-state NMR experiments on lead halide perovskites were performed with large sample volume rotors (3.2-4.0 mm rotors with 30-100 µL sample volume), and either slow magic angle spinning (MAS) or static conditions. In the past decade, the solid-state NMR technologies of dynamic nuclear polarization (DNP) and fast MAS have emerged as methods to enhance the sensitivity of solid-state NMR experiments by several orders of magnitude.

Here, we present an in-depth investigation of the NMR sensitivity enhancements that can be obtained with fast MAS or DNP for $^{207}$Pb solid-state NMR experiments on pure and mixed phase lead halide perovskites. Note that we have previously presented preliminary data on the application of DNP, fast MAS and proton detection to improve the sensitivity of solid-state NMR experiments on lead halide perovskites. A quantitative comparison of the sensitivity of the various NMR techniques demonstrates that both fast MAS and DNP can provide substantial gains in sensitivity. Fast MAS and proton detection allow $^{207}$Pb solid-state NMR spectra to be rapidly obtained from less than 5 µL samples of perovskites. Using these methods, high quality $^{207}$Pb solid-state NMR spectra of both pure and mixed halide organolead perovskites can typically be obtained in less than half an hour. With low temperature (ca. 110 K) NMR experiments it is possible to obtain a $^{207}$Pb solid-state NMR spectrum of a CH$_3$NH$_3$PbI$_3$ model thin film (less than 500 nm film thickness) in 35 hours.
Results and Discussion

Figures 1-3 compare the $^{207}$Pb solid-state NMR spectra of pure and mixed halide perovskites obtained with different NMR methods and the sensitivity ($S$) of each spectrum is indicated. In order to assess and quantitatively compare the different methods for obtaining $^{207}$Pb NMR spectra, $S$ was measured for each of the different $^{207}$Pb NMR experiments (Equation 1):$^{56}$

$$S = SNR \times t^{-1/2}$$ \hspace{1cm} (1)

Where, SNR is the signal-to-noise ratio, $t$ is the total experimental time (in minutes) and $S$ is given in units of min$^{-1/2}$. The sensitivity allows the SNR of NMR spectra acquired with different methods to be compared and normalizes for different experiment times.
Figure 1. (A) Comparison of $^{207}$Pb solid-state NMR spectra of CH$_3$NH$_3$PbBr$_3$ obtained with different NMR methods: (blue, top trace) DNP enhanced, 110 K $^1$H→$^{207}$Pb CPMAS, (green) proton detected, 40 kHz MAS 2D $^{207}$Pb→$^1$H CP-HETCOR, (red) 50 kHz MAS direct detection $^{207}$Pb spin echo, (yellow) 2D $^1$H{$^{207}$Pb} D-HMQC, (purple, lower trace) static $^{207}$Pb spin echo. (B) 2D $^{207}$Pb→$^1$H CP-HETCOR spectrum with 40 kHz MAS and (C) 2D $^1$H{$^{207}$Pb} D-HMQC spectrum with 40 kHz MAS. In (A) the $^{207}$Pb NMR sensitivity for each experiment is noted beside each spectrum. For (B) and (C) the $^1$H sensitivity of the first $t_1$ increment of the 2D NMR experiment is displayed to the left of the $^1$H spectrum, the $^{207}$Pb sensitivity is displayed in the bottom left corner of the correlation experiment and the total experiment time is indicated in the lower right hand corner.

Comparison of the Sensitivity of $^{207}$Pb Solid-State NMR Experiments. Here we focus on CH$_3$NH$_3$PbBr$_3$ as a model to investigate the sensitivity of the different NMR methods. The trends observed for the other perovskites are similar to those observed for CH$_3$NH$_3$PbBr$_3$. The first method tested to enhance the sensitivity of $^{207}$Pb solid-state NMR experiments was fast MAS at a frequency of 50 kHz. A 1.3 mm double resonance NMR probe was used for these experiments. In addition to the fast MAS rates that can be achieved, small diameter rotors are advantageous because minimal sample volumes on the order of 5 µL are required. The small solenoidal coil in the fast MAS probe also produces high radiofrequency (RF) fields that enable uniform excitation of the broad $^{207}$Pb NMR spectra of mixed halide perovskites (see below). A direct $^{207}$Pb spin echo solid-state NMR spectrum of CH$_3$NH$_3$PbBr$_3$ obtained from a stationary sample (without MAS)
with 4.6 hours of signal averaging gave a sensitivity of 0.7 min$^{-1/2}$ (Figure 1A, lower trace, see Table S1). The $^{207}$Pb solid-state NMR spectra of lead halide perovskites are often very broad. Spin echo pulse sequences are preferred over Bloch decay pulse sequences for acquisition of broad NMR signals. It is challenging to capture the full FID in Bloch decay experiments due to signal dephasing during the pulse ring-down period (receiver delay), while in the echo experiment the NMR signal is refocused after the receiver delay. The spin echo pulse sequence also helps to suppress $^{207}$Pb NMR signals that arise from lead metal within the probe components. With a 50 kHz MAS frequency a direct $^{207}$Pb spin echo NMR spectrum was obtained with a sensitivity of 5.7 min$^{-1/2}$, which corresponds to more than an order of magnitude improvement in sensitivity compared to the spin echo spectrum of the stationary sample. A similar gain in sensitivity was provided by fast MAS for CH$_3$NH$_3$PbI$_3$ (Table S1 and Figure S2). However, for CH$_3$NH$_3$PbCl$_3$ there is negligible gain in the sensitivity under MAS (Figure S3, see below).

Fast MAS provides a large gain in sensitivity for the bromide and iodide perovskites because MAS causes enhanced $^{207}$Pb longitudinal relaxation due to longitudinal spin exchange of $^{207}$Pb with the high-abundance, fast-relaxing, NMR-active halogen nuclei, $^{127}$I or $^{79/81}$Br. This effect is not expected for chloride perovskites because $^{35/37}$Cl does not have a similar Larmor frequency to $^{207}$Pb. For example, for CH$_3$NH$_3$PbBr$_3$ the $^{207}$Pb longitudinal relaxation times ($T_1$) are 0.1 s under 50 kHz MAS and 1.5 s under stationary conditions (Table S3). Fast MAS is required for the spin echo experiments because the echo delays must be rotor synchronized to avoid lineshape distortions. The $^{207}$Pb transverse relaxation times ($T_2$) observed in most of the CH$_3$NH$_3$PbX$_3$ are extremely short (less than 90 µs for bromide and iodide perovskites and ca. 1 ms for chloride perovskites). Slower MAS frequencies will lead to reduced echo signal intensity because longer echo delays are required. Short echo delays of arbitrary duration can be used for
static experiments because the sample is not rotating, however, the $^{207}\text{Pb} \ T_1$ will be longer in the static experiments.

Next, proton detection was tested to enhance the sensitivity of $^{207}\text{Pb}$ solid-state NMR experiments on lead halide perovskites containing organic cations. Proton detection in combination with fast MAS is widely employed to enhance the sensitivity of solid-state NMR experiments by exploiting the high sensitivity associated with detection of $^1\text{H}$ spins (Figure S1).\textsuperscript{48-49} Normally, proton detected solid-state NMR spectra of spin-1/2 nuclei are obtained with a cross-polarization heteronuclear correlation (CP-HETCOR) pulse sequence which uses forwards ($^1\text{H} \rightarrow X$) and backwards ($X \rightarrow ^1\text{H}$) CP steps for coherence transfer.\textsuperscript{48-49} However, the proton $T_1$ of the methylammonium cations are between 8 s and 25 s (Table S4) at room temperature, which is up to three orders of magnitude longer than the $^{207}\text{Pb} \ T_1$ under fast MAS conditions (0.02 to 1.0 s, see above). The proton $T_1$ are relatively long at room temperature because the dynamic reorientation of the methylammonium cations likely occurs at a frequency greater than the $^1\text{H}$ Larmor frequency.\textsuperscript{14} Note that at reduced temperatures (ca. 110 K) the proton $T_1$ are reduced to a few seconds, likely because the dynamic reorientation of the methylammonium cations is slowed and occurs at a frequency near to the $^1\text{H}$ Larmor frequency (\textit{vide infra}).\textsuperscript{14} Therefore, at room temperature it is much more efficient to skip the initial forward $^1\text{H} \rightarrow ^{207}\text{Pb}$ CP step and directly excite the fast-relaxing $^{207}\text{Pb}$ nucleus, then use a $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP transfer, followed by detection of the $^1\text{H}$ spins. With this scheme, the gain in sensitivity achievable with proton detection as compared to direct $^{207}\text{Pb}$ excitation and detection can be estimated with the following equation:\textsuperscript{48, 56}

$$\xi_{\text{CP-HETCOR}} \approx f \times \left( \frac{\gamma_{^1\text{H}}}{\gamma_{^{207}\text{Pb}}} \right)^{3/2} \times \left( \frac{W_{^{207}\text{Pb}}}{W_{^1\text{H}}} \right)^{1/2} \times \left( \frac{N_{^{207}\text{Pb}}}{N_{^1\text{H}}} \right)$$ (2)
Where $\xi$ is the sensitivity gain from proton detection, $f$ is the CP transfer efficiency, $\gamma_{1\text{H}}$ and $\gamma_{207\text{Pb}}$ are the gyromagnetic ratios for the $^1\text{H}$ and $^{207}\text{Pb}$ nuclei, respectively, $W_{1\text{H}}$ and $W_{207\text{Pb}}$ are the experimentally observed linewidths for the $^1\text{H}$ and $^{207}\text{Pb}$ NMR signals $N_{1\text{H}}$ and $N_{207\text{Pb}}$ are the number of $^1\text{H}$ and $^{207}\text{Pb}$ resonances (peaks). Considering the $\gamma$ of $^1\text{H}$ and $^{207}\text{Pb}$, proton detection can approximately provide a factor 10 gain in sensitivity, which corresponds to a 100-fold reduction in experiment time. We also note that in methylammonium perovskites the $^1\text{H}$ NMR signals tend be narrower than the $^{207}\text{Pb}$ NMR signals, which also favors proton detection. In agreement with equation (2) we find that the first increment of a $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR experiment on CH$_3$NH$_3$PbBr$_3$ gives a sensitivity of 51.5 min$^{-1/2}$, which corresponds to nearly a 10-fold improvement in sensitivity compared to the MAS $^{207}\text{Pb}$ spin echo NMR spectrum ($S = 5.7$ min$^{-1/2}$). The sensitivities and SNR are noted in Table S5 for the first increment of the $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR and $^1\text{H}\{^{207}\text{Pb}\}$ dipolar heteronuclear multiple quantum correlation (D-HMQC) experiments. In order to obtain the $^{207}\text{Pb}$ NMR spectrum, a full 2D NMR spectrum must be acquired and this usually leads to a slight reduction in sensitivity. For this reason, the $^{207}\text{Pb}$ NMR spectrum extracted from the positive projection of the indirect dimension of the 2D CP-HETCOR spectrum has a sensitivity of 28.5 min$^{-1/2}$. However, this still corresponds to ca. 5 times higher sensitivity than was obtained with the direct detected fast MAS $^{207}\text{Pb}$ spin echo experiment. With the high sensitivity provided by proton detection and the relatively short $^{207}\text{Pb}$ $T_1$ relaxation times, complete 2D $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR could typically be acquired in a few minutes (Figure 1B).

The constant time D-HMQC pulse sequence$^{58}$ (Figure S1) was also used to obtain proton detected $^{207}\text{Pb}$ solid-state NMR spectra. However, the recycle delay in the D-HMQC experiments is governed by the longer proton $T_1$ and the 2D NMR spectrum often contains substantial $t_1$-noise.
For these reasons, direct detection fast MAS $^{207}\text{Pb}$ spin echo experiments or the proton detected $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR are preferred and yield the highest sensitivity (Figures 1 and S2-S5).

For CH$_3$NH$_3$PbBr$_3$, the absolute sensitivity of the $^{207}\text{Pb}$ solid-state NMR experiments performed with a 1.3 mm rotor (ca. 4 µL of sample) were also compared to static and MAS experiments performed with a 4.0 mm rotor (ca. 100 µL of sample). Both static and MAS $^{207}\text{Pb}$ NMR experiments with a 4.0 mm rotor were performed with the DEPTH pulse sequence$^{59}$ to suppress probe background signals and to avoid lengthy echo delays that result in transverse relaxation. As was observed for the 1.3 mm rotor, 10 kHz MAS with the 4.0 mm rotor provided a substantial gain in sensitivity as compared to static experiment because of the reduction in the $^{207}\text{Pb} T_1$ (Figure S6). Consequently, an MAS $^{207}\text{Pb}$ DEPTH NMR spectrum with a sensitivity of 25.6 min$^{-1/2}$ was obtained with the 4.0 mm rotor. The sensitivity of the MAS $^{207}\text{Pb}$ DEPTH spectrum obtained with the 4.0 mm rotor is about 4.5 times that of the MAS spin echo $^{207}\text{Pb}$ spectrum obtained with the 1.3 mm rotor, with the gain in sensitivity attributed to the 20-fold increase in sample volume in the 4.0 mm rotor as compared to the 1.3 mm rotor. However, the MAS $^{207}\text{Pb}$ DEPTH NMR spectrum has slightly lower sensitivity than the proton detected $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR spectrum obtained with the 1.3 mm rotor. In summary, DEPTH MAS experiments with large diameter rotors also provide good $^{207}\text{Pb}$ NMR sensitivity, but, the 1.3 mm rotor offers numerous advantages such as a large reduction in required sample mass/volume, higher rf fields, elimination of spinning sidebands, improved $^1\text{H}$ resolution, and allows 2D spectra to be recorded in the same time as is required for a 1D $^{207}\text{Pb}$ spectrum. Furthermore, as we demonstrate below, the fast MAS experiments are especially advantageous for the mixed halide perovskites.
The results of the different $^{207}$Pb NMR experiments on CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbCl$_3$ are detailed in the SI (see Figures S2-S5 and Tables S1 and S3-S5). In general, similar trends in the sensitivity of the different NMR experiments were seen for these materials, with proton detected $^{207}$Pb→$^1$H CP-HETCOR experiments generally providing the best absolute sensitivity. The sensitivity gains provided by proton detection for CH$_3$NH$_3$PbI$_3$ are slightly lower than for CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbCl$_3$. The reduced sensitivity for CH$_3$NH$_3$PbI$_3$ is likely due to less efficient CP because of a shorter $^{207}$Pb rotating frame spin-lattice relaxation time constant ($T_1\rho$).

**DNP Enhanced $^{207}$Pb Solid-State NMR.** In a modern DNP experiment the large spin polarization of the unpaired electrons in stable exogenous radicals are transferred to the NMR active nuclei at cryogenic temperatures (typically 120 K or less).$^{41-43, 47, 60}$ DNP can provide maximum sensitivity enhancements ($\varepsilon$) of up to 658 for $^1$H.$^{42-43, 47}$ In order to prepare the lead halide perovskites for DNP experiments the powders were impregnated$^6$ with a 16 mM TEKPol 1,1,2,2-tetrachloroethane (TCE) radical solution. The radical solution coats the outside of the perovskite particles and DNP enhanced $^1$H polarization is relayed from the surface of the particles to the interior by proton spin diffusion.$^{62-64}$ This approach is referred to as relayed DNP. In order to obtain large DNP enhancements with relayed DNP, a long proton $T_1$ is required in the crystalline phase.$^{62-64}$ Unfortunately, for all of the perovskites examined the proton $T_1$ was on the order of 2 s at ca. 110 K and prevents the build-up of substantial DNP enhanced $^1$H magnetization (see Table S4). There is a reduction in the $^1$H $T_1$ of the organolead halide perovskites when going from room temperature to 110 K because the dynamic reorientation of the cation occurs at a similar frequency to the $^1$H Larmor frequency.$^{14}$ Consequently, $^1$H-$^{207}$Pb CPMAS DNP enhancements ($\varepsilon_{\text{Pb}}$) in this study were on the order of 1 – 16 due to the short $^1$H $T_1$ for the microcrystalline perovskites at 110 K.
For CH$_3$NH$_3$PbBr$_3$ the $\varepsilon_{\text{pb}}$ was approximately 3 which roughly corresponds to an NMR time savings factor of 9. Despite the low $\varepsilon_{\text{pb}}$ we found that DNP enhanced solid-state NMR provided the best absolute sensitivity for CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, likely because of the cryogenic sample temperatures,\textsuperscript{65} the gain in $^{207}$Pb polarization from CP and the moderate sample volume of the 3.2 mm diameter rotors used for DNP (ca. 30 $\mu$L). For CH$_3$NH$_3$PbCl$_3$, 110 K CP-TOSS MAS experiments were also performed on materials with and without addition of biradical solution (Figure S7). The addition of biradical solution causes a ca. 50% reduction in sensitivity for CP-TOSS MAS experiments on CH$_3$NH$_3$PbCl$_3$. The reduced sensitivity is attributed to well-known depolarization effects that occur when MAS is applied to samples containing nitrooxide biradicals.\textsuperscript{66-68} Although DNP tends to give the best sensitivities for CH$_3$NH$_3$PbX$_3$, another drawback of this approach is that the low temperatures (100-120 K) required for DNP NMR induce phase transitions in CH$_3$NH$_3$PbX$_3$.\textsuperscript{11, 16, 30-31, 36, 69} This phase transition is reflected in the $^{207}$Pb chemical shifts for CH$_3$NH$_3$PbX$_3$ which are shifted to much more negative $^{207}$Pb chemical shifts as compared to the room temperature NMR spectra. These effects need to be kept in mind when interpreting the $^{207}$Pb solid-state NMR spectra obtained at lower temperatures.

Between the microcrystalline perovskites, CH$_3$NH$_3$PbCl$_3$ gave the highest $\varepsilon_{\text{pb}}$ of 6 (Figures S3, S6). However, the DNP-enhanced $^{207}$Pb NMR spectra of CH$_3$NH$_3$PbCl$_3$ showed several isotropic lead peaks, when only a single peak was expected. The DNP $^{207}$Pb solid-state NMR spectra of CH$_3$NH$_3$PbCl$_3$ were obtained with a cross-polarization total suppression of spinning sidebands (CP-TOSS) pulse sequence\textsuperscript{70} (Figure S1) to eliminate spinning sidebands and ensure that only isotropic peaks were observed (Figures 2, S8). The CP-TOSS spectrum reveals a second $^{207}$Pb peak at a more positive chemical shift which possessed a higher $\varepsilon_{\text{pb}}$ of 16 (Figure S7). The larger relayed DNP enhancement for the more positive chemical shifts suggests that these signals
arise from a phase that is located at the surface of the perovskite crystallites or is associated with smaller diameter particles. We hypothesized that the second peak arises from CH$_3$NH$_3$PbCl$_3$ that is kinetically trapped in a higher temperature cubic or tetragonal phase. This hypothesis was confirmed by performing multiple variable temperature $^{207}$Pb NMR experiments on a single sample of CH$_3$NH$_3$PbCl$_3$ (Figure S9). The variable temperature $^{207}$Pb NMR spectra of CH$_3$NH$_3$PbCl$_3$ show that the intensity of the peaks depends upon the thermal history of the sample, confirming that reversible solid-solid phase transitions and trapping of high temperature phases occurs.

**Figure 2.** DNP enhanced $^{207}$Pb solid-state NMR spectra of micro- and nanocrystalline perovskites: (upper) Static CP spin echo $^{207}$Pb NMR spectrum of CH$_3$NH$_3$PbI$_3$, (middle) CPMAS $^{207}$Pb NMR spectrum of CH$_3$NH$_3$PbBr$_3$ and (lower) CPTOSS $^{207}$Pb NMR spectrum of CH$_3$NH$_3$PbCl$_3$. For CH$_3$NH$_3$PbI$_3$ spectra were obtained from a stationary sample and for CH$_3$NH$_3$Pb(Cl/Br)$_3$ the MAS frequency was 6 kHz.
Higher enhancements for relayed DNP experiments, can generally be obtained for samples with smaller particle sizes, i.e. nanocrystalline samples should give higher DNP enhancements.\textsuperscript{63} Nanocrystalline perovskites have shown great promise for optoelectronic devices (light emitting diodes, displays, lasers, etc.).\textsuperscript{71-73} Therefore, we performed relayed DNP NMR experiments on nanocrystalline perovskites\textsuperscript{74} to see if larger DNP enhancements could be obtained and to determine if there are any structural differences between the microcrystalline perovskites (see Figure S10 for TEM images of the nanocrystalline samples). Despite the very small grain size of the nanocrystalline samples (ca. 10 – 20 nm particle diameter) there was generally not a substantial improvement in the $e_{\text{Pb}}$ for the nanocrystalline samples.\textsuperscript{13}C CPMAS DNP enhancements ($e_{\text{C}}$) were also measured for the nanocrystalline and microcrystalline perovskites (Table S6). As expected, the nanocrystalline perovskites showed higher $e_{\text{C}}$ than the microcrystalline perovskites. In the DNP-enhanced $^{207}$Pb and $^{13}$C CPMAS experiments polarization is derived from the same bath of hyper-polarized $^1$H spins of the methylammonium cations. Therefore, the $^{13}$C and $^{207}$Pb CPMAS DNP signal enhancements should be the same, but, in all cases, $e_{\text{C}}$ was higher than $e_{\text{Pb}}$ (Table S6). It has previously been noted that microwave induced sample heating can cause differences in NMR relaxation time constants that causes apparently non-uniform CPMAS DNP enhancements to be measured for spins that share a common $^1$H spin bath.\textsuperscript{75} Sample temperature measurements indicated that the microwave typically heated the sample by ca. 15 K (Table S7). We speculate that the $^1$H or $^{207}$Pb $T_1\rho$ decrease at higher temperature, leading to less efficient $^1$H-$^{207}$Pb CP. $^{13}$C CP efficiency is unlikely to show a strong temperature dependence because much shorter contact times (ca. 1 ms) are used. Reduced CP efficiency at higher temperatures will cause the DNP-enhanced $^{207}$Pb CPMAS NMR spectra to have lower than expected intensity compared to the reference spectrum, which explains the apparent reduction in $e_{\text{Pb}}$ as compared to $e_{\text{C}}$. 


Figure 3. (A) Comparison of $^{207}\text{Pb}$ solid-state NMR spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_{1.5}\text{Cl}_{1.5}$ obtained with different NMR methods: (green, top trace) 2D $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR, (blue) DNP enhanced, 110 K $^1\text{H} \rightarrow ^{207}\text{Pb}$ CPMAS, (red) 50 kHz MAS direct detection $^{207}\text{Pb}$ spin echo, (yellow) 2D $^1\text{H}\{^{207}\text{Pb}\}$ D-HMQC, (purple, lower trace) static $^{207}\text{Pb}$ spin echo. (B) Full 2D $^{207}\text{Pb} \rightarrow ^1\text{H}$ 2D CP-HETCOR NMR spectrum of $\text{CH}_3\text{NH}_3\text{PbBr}_{1.5}\text{Cl}_{1.5}$. (C) Comparison of the 50 kHz MAS $^{207}\text{Pb}$ solid-state NMR spectra obtained with 2D $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR (green) and a direct spin echo (red). Dashed lines indicate the assignment of the $^{207}\text{Pb}$ isotropic chemical shifts to different lead coordination environments. In B) the $^1\text{H}$ sensitivity of the first $t_1$ increment of the 2D experiment is displayed to the left of the $^1\text{H}$ NMR spectrum and the $^{207}\text{Pb}$ sensitivity is displayed in the bottom left corner of the HETCOR spectrum.

Enhancing the Sensitivity of $^{207}\text{Pb}$ Solid-State NMR Experiments in Mixed Perovskites. We have previously demonstrated that $^{207}\text{Pb}$ solid-state NMR is a very useful technique for understanding the halogen atom distribution in mixed perovskites because the $^{207}\text{Pb}$ isotropic chemical shift depends upon the identity and number of coordinating halogen atoms.\(^4\) The $^{207}\text{Pb}$ solid-state NMR spectra of mixed perovskites are often extremely broad due to the large isotropic shift differences caused by coordination of different halides. As equation (2) suggests, broadening of the $^{207}\text{Pb}$ NMR signal will cause a substantial decrease in the sensitivity of $^{207}\text{Pb}$ detected NMR experiments. Note that it is not possible to apply Car-Purcell Meiboom-Gill (CPMG) techniques to improve the sensitivity of direct detection $^{207}\text{Pb}$ NMR experiments because the $^{207}\text{Pb}$ $T_2$ relaxation times are typically very short in perovskites. Therefore, different $^{207}\text{Pb}$ solid-state NMR
methods were tested on mixed halide perovskites of the formula CH$_3$NH$_3$PbX$_{3-n}$Y$_n$ (Figure 3 and Figures S11-S17). For all mixed halide perovskites the proton detected CP-HETCOR method provided the highest sensitivity. For CH$_3$NH$_3$PbBr$_{1.5}$Cl$_{1.5}$, the $^{207}$Pb NMR spectrum obtained with proton detected CP-HETCOR and a 1.3 mm rotor had nearly 1.5 times better sensitivity than a MAS DEPTH $^{207}$Pb NMR spectrum obtained with a 4.0 mm rotor (Figure S12). Importantly, for CH$_3$NH$_3$PbBr$_{1.5}$Cl$_{1.5}$, the proton detected $^{207}$Pb NMR spectrum was very similar to that obtained with a direct MAS $^{207}$Pb spin echo (Figure 3C). This result suggests that proton detection can improve sensitivity without a significant distortion of the relative peak intensities. This is important because the relative peak intensities can be used to quantify the halide ion distribution. For example, Figure 3C shows the assignment of the different $^{207}$Pb chemical shifts to different lead coordination environments of CH$_3$NH$_3$PbBr$_{1.5}$Cl$_{1.5}$ (see Figure S11 as well).

One potential limitation of CP based methods is that CP typically has a lower excitation bandwidth than direct excitation. However, it is well known that when the breadth of the NMR spectrum exceeds the excitation bandwidth of the pulse sequence it is possible to use frequency stepped acquisition protocols to obtain the NMR spectrum. For example, CH$_3$NH$_3$PbI$_{1.5}$Br$_{1.5}$ gives rise to a very broad $^{207}$Pb NMR spectrum that spans ca. 1300 ppm and exceeds the limited excitation bandwidth of the CP steps (ca. 20 kHz excitation bandwidth ~ 239 ppm). A complete 2D CP-HETCOR spectrum of CH$_3$NH$_3$PbI$_{1.5}$Br$_{1.5}$ was formed by co-adding 2D HETCOR spectra collected at four different $^{207}$Pb transmitter offsets, with the transmitter incremented in steps of 20 kHz (239 ppm). The $^{207}$Pb solid-state NMR spectra of CH$_3$NH$_3$PbI$_{1.5}$Br$_{1.5}$ obtained with the frequency stepped CP-HETCOR experiment was very similar in appearance to that obtained with the direct $^{207}$Pb spin echo spectrum, again suggesting that there are minimal intensity distortions with the proton detected CP-HETCOR pulse sequence. Two separate CP-HETCOR spectra were
acquired for CH$_3$NH$_3$PbI$_{1.5}$Cl$_{1.5}$ to observe the $^{207}$Pb NMR signals from the Cl$^-$ and I$^-$ ions because there is no mixing of the halide ions in this perovskite material and the signals from the different phases have a large isotropic chemical shift difference (Figure S14). DNP NMR gave the second best sensitivity for both CH$_3$NH$_3$PbBr$_{1.5}$Cl$_{1.5}$ and CH$_3$NH$_3$PbI$_{1.5}$Cl$_{1.5}$ (Figure 3A and S14). However, all of the $^{207}$Pb solid-state NMR spectra are extremely broad and required frequency stepped acquisition due to the limited excitation bandwidths associated with CP and the lower $^{207}$Pb RF fields available on the 3.2 mm DNP NMR probe. DNP NMR on CH$_3$NH$_3$PbI$_{1.5}$Br$_{1.5}$ gave the second worst sensitivity, most likely because of the unfavorable NMR properties associated with the $^{207}$Pb nuclei coordinated by iodine (Figure S15).

The fast MAS probe is especially advantageous for $^{207}$Pb solid-state NMR experiments on mixed halide perovskites because it provides large $^{207}$Pb RF fields that allow broadband excitation. This is demonstrated for the MAS/static spin echo spectra and the constant time 2D D-HMQC $^{207}$Pb spectra of CH$_3$NH$_3$PbI$_{1.5}$Br$_{1.5}$ and CH$_3$NH$_3$PbI$_{1.5}$Cl$_{1.5}$ (Figures S13-S17). For both CH$_3$NH$_3$PbBr$_{1.5}$Cl$_{1.5}$ and CH$_3$NH$_3$PbI$_{1.5}$Br$_{1.5}$, MAS was once again found to provide a large gain in sensitivity as compared to static spin echo experiments. For CH$_3$NH$_3$PbI$_{1.5}$Cl$_{1.5}$, fast MAS provides minimal gains in sensitivity because the CH$_3$NH$_3$PbCl$_3$ phase within the mixture does not undergo a reduction in $T_1$ upon MAS. Therefore, a 3 s recycle delay (*ca.* three times the $^{207}$Pb $T_1$ of CH$_3$NH$_3$PbCl$_3$) was required to obtain quantitative $^{207}$Pb peak intensities.
Figure 4. (A) 50 kHz MAS $^1$H solid-state NMR spectra of CH(NH$_2$)$_2$PbI$_3$ (upper) and CH$_3$NH$_3$PbI$_3$ (lower). (B) $^{207}$Pb solid-state NMR spin echo spectra acquired with a 50 kHz MAS frequency of (upper) CH(NH$_2$)$_2$PbI$_3$ and (lower) CH$_3$NH$_3$PbI$_3$. The dashed lines illustrate the slight differences in the $^{207}$Pb isotropic chemical shifts. (C) 50 kHz MAS 2D $^{207}$Pb→$^1$H CP-HETCOR spectrum of CH(NH$_2$)$_2$PbI$_3$ obtained in 12 minutes. For (C) the $^1$H sensitivity of the first $t_1$ increment of the 2D NMR experiment is displayed to the left of the $^1$H spectrum, the $^{207}$Pb sensitivity is displayed in the bottom left corner of the correlation experiment and the total experiment time is indicated in the lower right hand corner.

$^{207}$Pb Solid-State NMR Spectra of Methylammonium and Formamidinium Perovskites. MAS $^1$H and $^{207}$Pb NMR spectra were also obtained for CH$_3$NH$_3$PbI$_3$ and CH$_3$(NH$_2$)$_2$PbI$_3$ to see if $^1$H and $^{207}$Pb isotropic chemical shifts are sensitive to the organic cations (Figure 4). The $^{207}$Pb isotropic chemical shifts are 1561 ppm for CH$_3$NH$_3$PbI$_3$ and 1448 ppm for CH(NH$_2$)$_2$PbI$_3$. The $^{207}$Pb chemical shift of 1448 ppm observed here for CH(NH$_2$)$_2$PbI$_3$ is close to the value of 1495 ppm measured by Michaelis and co-workers with $^{207}$Pb NMR experiments on static samples, with the slight difference in $^{207}$Pb chemical shifts likely due to sample heating induced by the 50 kHz MAS. Given the breadth of the $^{207}$Pb NMR signals of CH(NH$_2$)$_2$PbI$_3$ and CH$_3$NH$_3$PbI$_3$ it would be challenging to differentiate signals from methylammonium and formamidinium on the basis of $^{207}$Pb NMR spectra alone. However, the $^1$H NMR spectra of the formamidinium and methylammonium cations are clearly distinct and show a ca. 1 ppm shift difference in the $^1$H ammonium signals. With 50 kHz MAS and proton detection it was possible to obtain a high quality
2D $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR spectrum of CH(NH$_2$)$_2$PbI$_3$ in only 12 minutes (Figure 4). These results illustrate that 2D $^{207}\text{Pb} \rightarrow ^1\text{H}$ CP-HETCOR experiments and simple $^1\text{H}$ fast MAS experiments could be used to probe cation speciation in mixed cation perovskites.

![Diagram of NMR spectra](image)

**Figure 5.** 110 K static $^{207}\text{Pb}$ solid-state NMR spectra of (upper trace) thin film of CH$_3$NH$_3$PbI$_3$ and (lower trace) microcrystalline CH$_3$NH$_3$PbI$_3$. The spectrum of the thin film was obtained with a 34 hour experiment time. A picture of a glass microscope slide coated with the model thin film is shown in the inset.

*Low Temperature $^{207}\text{Pb}$ Solid-State NMR of a Model CH$_3$NH$_3$PbI$_3$ Perovskite Thin Film.*

Perovskite-based solar cells are usually made by depositing a thin layer (less than 300-500 nm)$^{79}$ of perovskite material onto transparent conductive substrates. It has previously been shown that the specific procedure used for the thin layer deposition greatly affects the composition, crystallinity and substrate coverage of the film, all of which can greatly affect device performance.$^{80-82}$ Non-invasive methods for the characterization of deposited thin films are normally restricted to microscopy, PXRD and X-ray photoelectron spectroscopy (XPS), all of which provide an incomplete picture of the molecular structure of deposited thin films. For
example, in 2016 Rosales et. al. reported that different synthetic techniques for mixed halide perovskites showed similar PXRD patterns, however \(^{207}\text{Pb}\) solid-state NMR spectra detected that the halide distribution and local lead coordination environments were distinct.\(^4\) As a proof-of-concept demonstration of solid-state NMR spectroscopy for the molecular characterization of perovskite thin films, we have applied low temperature \(^{207}\text{Pb}\) solid-state NMR to a model CH\(_3\)NH\(_3\)PbI\(_3\) thin film deposited on No. 0 (0.085-0.13 mm) thick glass microscope slides. NMR experiments on the thin film are challenging because the content of CH\(_3\)NH\(_3\)PbI\(_3\) was estimated to be only about 1.0 wt.\%, with the microscope slide making up the remainder of the sample volume and mass. The coated microscope slide was broken into pieces in order to accommodate the thin film into the 3.2 mm MAS rotors (Figure S20). We note that static conventional and DNP-enhanced solid-state NMR experiments on planar substrates have previously been conducted with probes featuring rectangular solenoidal coils that can accommodate stacks of planar substrates.\(^83\)-\(^84\) Using this type of approach it could be possible to study intact thin films.

Since the DNP enhancements were negligible for experiments on powdered CH\(_3\)NH\(_3\)PbI\(_3\) the spectrum of the model thin film was obtained without addition of the radical polarization matrix and DNP. However, the sample temperature of \(ca.\) 110 K provides a substantial gain in sensitivity, allowing a \(^1\text{H}\rightarrow^{207}\text{Pb}\) CPMAS solid-state NMR spectrum of the model CH\(_3\)NH\(_3\)PbI\(_3\) thin film to be obtained in 34 hours (Figure 5). The \(^{207}\text{Pb}\) solid-state NMR spectrum of the thin film is identical to that of microcrystalline CH\(_3\)NH\(_3\)PbI\(_3\). This demonstrates that with the use of DNP or low temperature NMR it may be possible to use the \(^{207}\text{Pb}\) solid-state NMR to study perovskite thin films within devices.
Conclusions

In conclusion, with fast MAS and proton detection or DNP it is possible to significantly improve the $^{207}\text{Pb}$ sensitivity and reduce solid-state NMR experiment times. High quality $^{207}\text{Pb}$ NMR spectra of pure perovskite materials could be obtained in a matter of minutes with DNP/low temperature solid-state NMR experiments. However, the cooling of the samples leads to large differences in the $^{207}\text{Pb}$ isotropic chemical shifts when compared to the room temperature NMR spectra and possibly induces peak broadening/splitting. Proton detected CP-HETCOR experiments provide the best sensitivity for mixed halide perovskites ($< 30$ min. experimental times) and yield similar relative peak intensities as direct spin echo experiments. $^{207}\text{Pb}$ NMR spectra of mixed phases obtained with fast MAS and proton detection can be used to detect and quantify the different lead coordination environments. Using low temperature solid-state NMR, it was possible to obtain the $^{207}\text{Pb}$ solid-state NMR spectrum of a model thin film of $\text{CH}_3\text{NH}_3\text{PbI}_3$. We anticipate that the NMR techniques described here should also be applicable to other perovskite systems such as tin-based perovskite materials, mixed cation lead perovskite materials and perovskite thin films in model devices.

Experimental

$\text{CH}_3\text{NH}_3\text{PbX}_{3-n}Y_n$ samples were prepared using a slightly modified version of our previously reported methods. Ammonium Halides. Hydroiodic acid ($10 \text{ mL, } 0.075 \text{ mol}$) or hydrobromic acid ($8.6 \text{ mL, } 0.075 \text{ mol}$) or hydrochloric acid ($6.2 \text{ mL, } 0.075 \text{ mol}$) was added to a solution of excess methylamine ($24 \text{ mL, } 0.192 \text{ mol}$) in ethanol ($100 \text{ mL}$) at $0 \degree\text{C}$, and the mixture stirred for $2 \text{ h}$. The solution was concentrated under vacuum and the resulting powder dried under dynamic vacuum at $60 \degree\text{C}$ for $12 \text{ h}$, then recrystallized from ethanol. $n$-octylammonium iodide ($\text{CH}_3(\text{CH}_2)_7\text{NH}_3\text{I}$), $n$-octylammonium bromide ($\text{CH}_3(\text{CH}_2)_7\text{NH}_3\text{Br}$) and $n$-octylammonium
chloride (CH₃(CH₂)₇NH₃Cl) were washed repeatedly with diethyl ether and dried under dynamic vacuum before use. CH₃NH₃PbX₃ (X = Cl or Br) nanocrystals were prepared using previously reported synthesis.⁷⁴,⁸⁵ PbX₂ (0.08 mmol), CH₃NH₃X (0.04 mmol) and CH₃(CH₂)₇NH₃X (0.04 mmol) were added into DMF (2 mL). The precursor solution was rapidly mixed with 200 mL toluene while stirring. Samples were allowed to stand for 24 h before isolating the product by centrifugation (10 min at 4000 rpm) and washing with toluene (5 mL). For CH₃NH₃PbI₃ nanocrystals, PbI₂ (37 mg, 0.08 mmol), CH₃NH₃I (19 mg, 0.12 mmol) and CH₃(CH₂)₇NH₃I (31 mg, 0.12 mmol) were added into a mixture of acetonitrile (200 mL) and DMF (200 µL). The precursor solution was rapidly mixed with toluene (750 mL) while stirring. Samples were allowed to stand for 24 h before isolating the product by centrifugation (10 min at 4000 rpm) and washing with toluene (5 mL). Films. 300-500 nm thick CH₃NH₃PbI₃ thin films were prepared by spin-coating the precursor solution (1M PbI₂ + 1M CH₃NH₃I in DMF) at 6000 rpm for 45s on a 1” x 1” glass slide (No. 0, 0.085-0.13 mm thick, pre-cleaned by sonication in Alconox cleaning solution, conc. H₂SO₄, Millipore water, methanol, and acetone for 20 min each), followed by annealing at 100 °C for 1 h.⁷⁹

Conventional solid-state NMR experiments were performed on a Bruker wide-bore 9.4 T (ν₀(¹H) = 400 MHz) NMR spectrometer equipped with a Bruker Avance III HD console and Bruker 1.3 mm HX fast MAS probe. ¹H RF pulses were calibrated directly on the samples and the ²⁰⁷Pb RF pulses were calibrated using the ¹³C RF pulses for adamantane and scaled by the gyromagnetic ration of ¹³C and ²⁰⁷Pb. DNP enhanced solid-state NMR experiments were performed on a Bruker 9.4 T 400 MHz/263 GHz solid-state NMR spectrometer,⁶⁰ equipped with a Bruker Avance III console. A Bruker 3.2 mm triple resonance DNP probe configured in H-X double resonance mode, capable of tuning from ²⁰⁷Pb (83.682 MHz) to ¹³C (100.580 MHz) was used for the acquisition of
all DNP spectra. The sample temperature for DNP experiments was approximately 110 K. \(^1\)H and \(^{207}\)Pb RF pulses were calibrated directly on each sample for DNP experiments.

\(^1\)H chemical shifts were referenced to neat tetramethylsilane through the use of adamantane \((\delta_{iso}(^1\text{H}) = 1.82 \text{ ppm})\) as a secondary chemical shift standard. For DNP NMR experiments the \(^1\)H chemical shifts were referenced based on the DNP solvent 1,1,2,2-tetrachloroethane (TCE) chemical shift \((\delta_{iso}(^1\text{H}) = 6.2 \text{ ppm})\) as a secondary reference. \(^{207}\)Pb chemical shifts were indirectly referenced to the established chemical shift standards using the previously published relative NMR frequencies.\(^{86}\)

The \(^{207}\)Pb spin echo,\(^{87}\) \(^1\)H\{}\(^{207}\)Pb\} D-HMQC,\(^{58, 88-90}\) \(^{207}\)Pb\(\rightarrow\)\(^1\)H CP-HETCOR,\(^{48-49, 51, 53}\) \(^1\)H-\(^{207}\)Pb CPMAS,\(^{91}\) \(^1\)H-\(^{207}\)Pb CP-TOSS\(^{70}\) and \(^1\)H-\(^{207}\)Pb CP spin echo experiments were performed using previously described pulse sequences and are depicted in Figure S1. The recycle delays, number of scans and number of indirect acquisition points for all NMR experiments are all given in the SI (Tables S1-S2). The \(^1\)H and \(^{207}\)Pb \(T_1\) for each sample were measured with saturation recovery pulse sequences and the recycle delay was set to 1.3 times the relevant \(T_1\) to maximize sensitivity. For the \(^{207}\)Pb spin echo all \(^{207}\)Pb pulses used RF fields of 125-177 kHz for \(\text{CH}_3\text{NH}_3\text{PbX}_3\) and 250 kHz for \(\text{CH}_3\text{NH}_3\text{PbX}_{3-n}\text{Y}_n\). The mixed halide perovskites utilized larger RF fields to ensure uniform excitation of the entire \(^{207}\)Pb NMR spectrum. All of the MAS \(^{207}\)Pb spin echo experiments were performed using a MAS frequency of 50 kHz.

The CP-HETCOR experiments were performed at a MAS frequency of 50 kHz for all samples with the exception of \(\text{CH}_3\text{NH}_3\text{PbBr}_3\) which used a MAS frequency of 40 kHz. The RF field for the initial \(^1\)H excitation pulses was 125 kHz. The \(^1\)H and \(^{207}\)Pb CP spin lock pulses utilized RF fields of 130-200 kHz and 63-104 kHz and had a duration of 3-22 ms. Both the CP spin lock match condition and the duration were experimentally optimized on each sample to yield
maximum signal. The amplitude of the $^1$H CP spin lock pulses was linearly ramped from 80% to
100% of the applied RF field to improve the CP efficiency.\textsuperscript{91} Continuous wave decoupling was
applied on the $^1$H channel during the $t_1$ evolution period using the HORROR condition (25 kHz
$^1$H RF field).

The D-HMQC experiments were performed with a constant time pulse sequence developed
for the acquisition of wideline spectra.\textsuperscript{58} This fixes the total evolution time during the $t_1$ period
allowing for the indirect dimension spectral width to be set large enough to observe the entire $^{207}$Pb
NMR spectrum since the CH$_3$NH$_3$PbX$_{3-n}$Y$_n$ peak widths tend to be similar or larger than the MAS
frequency. All D-HMQC experiments utilized the symmetry based recoupling sequence
supercycled (S)R4\textsubscript{1} which was applied to the $^1$H nuclei for fixed durations to build-up and
reconvert the anti-phase coherences.\textsuperscript{92-93} The SR4\textsubscript{1} sequence was applied for a total duration of 24-78
rotor cycles on each side of the $^1$H \(\pi\) pulse. The recoupling time was experimentally optimized
on each sample. The MAS frequency used for the D-HMQC was 50 kHz for all samples with the
exception of CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_{1.5}$Cl$_{1.5}$ which used a MAS frequency of 40 kHz. The
$^1$H RF field for the recoupling scheme was two times the spinning rate (i.e. 100 kHz for all samples
except for CH$_3$NH$_3$PbI$_{1.5}$Cl$_{1.5}$ which was 80 kHz). The RF fields for the $^{207}$Pb $\pi/2$ pulses was
between 177-250 kHz.

DNP samples were prepared by massing out 20-30 mg of perovskite material on a watch
glass. The perovskite material was then impregnated\textsuperscript{61} with 15-20 $\mu$L of a 16 mM biradical solution
of TEKPol TCE.\textsuperscript{94-95} The nano perovskite samples followed the same sample preparation as the
bulk perovskites except only 5-10 mg of sample was massed out because the quantities of the nano
perovskites were limited. For the nanocrystalline perovskites 15-20 mg of boron nitride was mixed
into the sample to fill the volume of the rotor. The samples were not ground prior to the
impregnation step. After the wetness impregnation step the samples were packed into 3.2 mm sapphire rotors, with a teflon screw insert and a zirconia drive cap. The thin film of CH$_3$NH$_3$PbI$_3$ perovskite was crushed prior to packing into a 3.2 mm sapphire rotor, the sample was not ground in order to prevent separation of the perovskite from the glass slide. The thin film of CH$_3$NH$_3$PbI$_3$ was also not impregnated with the 16 mM TEKP01 TCE solution since the bulk CH$_3$NH$_3$PbI$_3$ had negligible DNP enhancements. For CH$_3$NH$_3$PbCl$_3$ and CH$_3$NH$_3$PbBr$_3$ CP-TOSS and CPMAS spectra were acquired with a MAS frequency of 6 kHz, respectively. The CP-TOSS pulse program was used on the CH$_3$NH$_3$PbCl$_3$ perovskite to suppress the spinning sidebands (Figure S8). DNP enhanced static NMR spectra of CH$_3$NH$_3$PbI$_3$ were obtained with a CP spin echo pulse program. The $^1$H-$^{207}$Pb CP experiments used spin lock pulses with RF fields of 63 kHz and 72 kHz respectively for the $^{207}$Pb and $^1$H nuclei. The $^1$H CP spin lock pulses were linearly ramped from 70% to 100% of the maximum spin lock RF field for CH$_3$NH$_3$PbCl$_3$ and CH$_3$NH$_3$PbBr$_3$. For the CH$_3$NH$_3$PbX$_{3-n}$Y$_n$ and CH$_3$NH$_3$PbI$_3$ the $^1$H contact pulse used a 90% to 100% linear ramp of the spin lock RF. The length of the CP spin lock was between 2-10 ms and was experimentally optimized to obtain maximum signal on each sample. SPINAL-64 heteronuclear $^1$H decoupling was applied during acquisition with an RF field of 100 kHz.$^{96}$

**Thin film preparation for NMR.** Using a mortar and pestle the CH$_3$NH$_3$PbI$_3$ coated microscope slide was crushed into small pieces that were then packed into a sapphire NMR rotor. After crushing, the majority of the perovskite film still appeared to be grafted onto the microscope slide (Figure S20).

**Data processing.** All 1D and 2D NMR spectra were processed using exponential multiplication for the line broadening, and the amount of line broadening applied to each sample was approximately 1/8 of the peak width at half height. For the exact amount of line broadening
applied to each spectrum please see Tables S8-10. For all of the 2D NMR spectra the amount of
$^1$H line broadening was 25 Hz, with the exception of CH(NH$_2$)$_2$PbI$_3$ which had 100 Hz of line
broadening applied to $^1$H. The acquisition time, number of time-domain points and number of
zero-fill points are given in Tables S8-10.

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Supporting Information

Additional supplementary information including data Tables, Figures of NMR spectra and NMR
experimental parameters can be found in the supporting information.

References

Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Gratzel, M., Cesium-Containing Triple
Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency. Energy
2. NREL Best Research-Cell Efficiencies Chart.
Correa-Baena, J. P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Gratzel, M., Incorporation of
Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance. Science 2016,
354, 206-209.
Dopants and Phase Segregation in Organolead Mixed-Halide Perovskites. Chem. Mater. 2016,
28, 6848-6859.
5. Rosales, B. A.; Hanrahan, M. P.; Boote, B. W.; Rossini, A. J.; Smith, E. A.; Vela, J., Lead
Halide Perovskites: Challenges and Opportunities in Advanced Synthesis and Spectroscopy. ACS
7. Volkov, A. F.; Venevtse.Yn; Semin, G. K., Nuclear Quadrupole Resonance(NQR) of $^{79}$Br and
$^{81}$Br in Perovskite and Orthorhombic Forms of CsPbBr$_3$ and CsPbI$_3$. Phys. Status Solidi 1969,
35, 167-169.


