Supporting Information

Short-range ion dynamics in methylammonium lead iodide by multinuclear solid state NMR and ¹²⁷I NQR

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1) X-Ray Analysis



Figure S1. XRD analysis of MAPI powders (a) pure (natural abundance of the isotopes) (b) 13 C, 15 N enriched (20 % abundance).

2) ¹H NMR



Figure S2. ¹H MAS NMR spectra of MAPbI₃, recorded at different T. No significant variation of the chemical shifts can be detected.



Figure S3. ¹H T_1 measurements in (¹³C,¹⁵N)-enriched MAPbI₃. Fit of inversion recovery at different T. Note the nearly perfect fit with a mono exponential function with only minor deviation at T<183 K.



Figure S4. Temperature dependence of ¹H T_1 in pure MAPbBr₃ shown in comparison to the data in pure (and (¹³C, ¹⁵N)-labelled MAPbI₃. Note that the behaviour is very similar, while the inflection point is distinctly shifted to the lower temperatures.

3) Calculation of the second moment M₂

The dipole-dipole interactions in solids can be quantified by the so-called second moment M_2 of the spectrum, which is defined as:

$$M_2 = M_2^{II} + M_2^{IS}$$
 (Eq. 1)

$$M_2^{II} = \frac{3}{5} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^4 \hbar^2 I(I+1) \frac{1}{N_I} \sum_{i\neq j}^{N_I} r_{ij}^{-6}$$
(Eq. 2)

$$M_2^{IS} = \frac{4}{15} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{1}{N_I} \sum_{i \neq k}^{N_I} r_{ik}^{-6}, \qquad (\text{Eq. 3})$$

where M_2^{II} and M_2^{IS} are the homonuclear and the heteronuclear contributions respectively, \hbar is the Planck's constant, μ_o is the permeability of vacuum, I and S are the nuclear spins of the resonating I -spins and non-resonating S-spins, respectively. N_I and N_S denote the numbers of resonating and non-resonating nuclei in the sample, γ_1 and γ_s are the gyromagnetic ratios of the resonating and non-resonating spins, and r_{ij} and r_{jk} are inter-nuclear distances. The theoretical equations above are specified for a completely rigid spin system and may or may not fully describe the specific molecular system under study. On the other hand, experimentally the second moment M₂ of the NMR signal (for a peak of Gaussian lineshape) is extracted from the FWHM (FWHM = $\pi^{-1}\sqrt{2\ln(2)M_2}$), therefore the experimental M₂ values are highly sensitive to internal molecular motions, and if they would substantially deviate from the calculated values, this would indicate the presence of intramolecular or intracrystalline reorientations. In this respect, variable temperature proton wide-line NMR experiments in solid methylammonium halides from the early 1970s form a well-documented set of relevant studies.¹⁻⁴ For a hypothetical case of entirely rigid tetragonal MAPbI₃, the calculated total second moments for CH₃ and NH₃ protons $(1.5 \times 10^{10} \text{ and } 4.1 \times 10^{10} \text{ rad}^2 \text{s}^{-2})$ yield static linewidths of 45.7 and 75.6 kHz, respectively. In a case of internal rotation around the C-N axis, the second moment is reduced by a factor of $F(\gamma) = \frac{1}{4} (3\cos^2\gamma - 1)^2$, with the angle γ between the internuclear axis and the axis of motion.⁵ With the rotational axis perpendicular to all internuclear vectors the second moment is only reduced by a factor of 4. In contrast, as shown in Fig. 1b and Fig. S3, we measure a much narrower linewidth of about 8 kHz coming from the overlap of CH₃ and NH₃ signals, corresponding to a M₂ of 4.8×10^8 $rad^{2}s^{-2}$. This relatively low value indicates that both CH₃ and NH₃⁺ groups are not only

involved in a rotation around the C-N axis, but must also undergo another reorientation with a symmetry axis higher than 2-fold.

4) ¹H T_1 relaxation time

Expression of T_1 *relaxation time with separate contributions:*

A spin-lattice relaxation time primarily caused by dipole-dipole interactions with other protons can be expressed as follows in BPP formalism:^{6,7}

$$\frac{1}{T_1} = \frac{3}{10} \gamma^4 \hbar^2 \sum_i r_i^{-6} \left(\frac{1}{1 + \omega^2 \tau_r^2} + \frac{4}{1 + 4\omega^2 \tau_r^2} \right) \tau_r , \qquad (Eq.4)$$

With ω , τ_{ρ} , γ and r_i being the resonance frequency, motional correlation time, proton gyromagnetic ratio and internuclear distances, respectively. In conditions of fast motion limit ($\tau_{\rho}\omega >> 1$), the equation is then reduced to

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 \sum_i r_i^{-6} \tau_r = \mathcal{C}(r) \tau_r .$$
 (Eq. 5)

Instead, spin-rotational relaxation time for protons can be expressed as:

$$\frac{1}{T_1^{SR}} = \frac{4\pi^2 I_0^2}{9\hbar^2} \left(2C_{\perp}^{1H} + C_{\parallel}^{1H} \right) \tau_r^{-1} , \qquad (\text{Eq. 6})$$

where I_0 is moment of inertia of the molecule or group, C_{\perp} and C_{\parallel} are spin-rotation tensors describing the coupling of the nuclear and molecular angular momenta along perpendicular and parallel axes. Eq. 6 directly gives the peculiar inverse temperature dependence of the spin-rotational relaxation.

T_1 relaxation time with MAS and in the rotating frame $(T_{1\rho})$:

As shown in Fig. S5a, when separating the CH₃ and NH₃ contributions from the ¹H NMR spectra using MAS and recording the respective relaxation times we obtained, as expected, very similar values. This is in an agreement with the considerations made in the main text regarding the behavior of MA-cation as a symmetrical rotor showing no preferential interaction of the CH₃ and NH₃ groups with the inorganic framework. We also note (Fig.

S5a), that at the higher temperatures the spinning induces a deviation from the monotonous behavior, which we are presently unable to explain. This is one of the reasons why we chose to measure the relaxation time under stationary conditions. A similar behavior is visible for $^{13}C T_1$ times under MAS conditions (Fig. S6).

The results on protons spin-lattice relaxation time in the rotating frame $T_{I\rho}$ at two spinlocking radio-frequency fields (RF) are shown in Fig. S5b. While the obtained magnitude of the $T_{I\rho}$ at the higher RF on the order of tens of milliseconds suggests the cross-polarization (CP) to ¹³C and ¹⁵N to be an attractive proposition, a very long T_I of protons efficiently wipes out the possible benefits of the cross-polarization experiments. For this reason, we used the direct excitation to collect both ¹³C and ¹⁵N NMR data presented in the main text.



Figure S5. Temperature dependence of (a) ¹H T_1 in pure MAPbI₃ under 10 kHz MAS. (b) ¹H Spinlattice relaxation time in the rotating frame ($T_{I\rho}$) at spin-locking radio-frequency fields of 15 and 50 kHz, as measured in a spin-locking experiment by varying the time of spin-lock.

5) ¹³C and ¹⁵N spectra and T_1 relaxation time

Expression of T_1 *relaxation time with separate contributions:*

$$\frac{1}{T_1^{13C}} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{CSA}} + \frac{1}{T_1^{SR}}.$$
(Eq. 7)

Where DD interactions refer primarily to C-H coupling. The full expressions for each of the three mechanisms above in the fast motion limit are given as follows:^{48,51}

$$\frac{1}{T_1^{DD}} = \gamma_{13C}^2 \gamma_{1H}^2 \hbar^2 \sum_j r_j^{-6} \tau_r = C \mathbf{1}(r) \tau_r,$$
(Eq. 8)

$$\frac{1}{T_1^{CSA}} = \frac{6}{45} \omega_{13C}^2 (\Delta \sigma) \tau_r = B \tau_r,$$
 (Eq. 9)

$$\frac{1}{T_1^{SR}} = \frac{4\pi^2 I_0^2}{9\hbar^2} \left(2C_{\perp}^{13C} + C_{\parallel}^{13C} \right) \tau_r^{-1}, \tag{Eq. 10}$$

where ω_{I3X} , τ_{ρ} , γ_{I3X} , $\Delta \alpha nd r_j$ being the ¹³C Larmor frequency, motional correlation time, gyromagnetic ratio, anisotropy of shielding ($\sigma_1 - \sigma_{\perp}$ for axially symmetric molecules in a solid spectrum without internal rotations) and proton-carbon internuclear distances, respectively. One should note that the rotational correlation times τ_{ρ} for ¹³C and ¹H can be related, but generally do not coincide.

Effect of MAS on T_1 *in* ${}^{13}C$ *and* ${}^{15}N$

Our preliminary experiments indicated that ¹³C spin-lattice relaxation times have been to a certain degree affected by the sample spinning in MAS. This effect was similar, although in a smaller magnitude, to that previously reported for spin-lattice relaxation of ²⁰⁷Pb in PbI₂ and PbBr₂,⁸ and was attributed to a MAS-assisted cross-relaxation of a spin 1/2 nucleus to a strongly quadrupolar nucleus. The effect is not observable for protons due to a very high difference in the Larmor frequencies between ¹²⁷I and ¹H (> 300 MHz at the used field of 9.4 T). The situation is different for ¹³C and ¹²⁷I because the difference in their Larmor frequencies is only ~20 MHz, and since the quadrupole constant of ¹²⁷I in MAPbI₃ is > 550 MHz,⁹ the nuclear energy levels of ¹³C will inevitably cross under MAS with greatly spread quadrupolar interactions in ¹²⁷I. This becomes evident when comparing the *T*₁s measured under MAS or stationary conditions as shown in Fig. S6.



Figure S6. Temperature dependence of ¹³C T_1 in pure MAPbI₃ with and without 5 kHz MAS.





Figure S7. Temperature dependence of (a) ¹³C and (b) ¹⁵N MAS spectra in (${}^{13}C$, ${}^{15}N$)-enriched MAPbI₃. In the tetragonal and cubic phase (233-353 K), the chemical shift trend behaves as expected, while a discontinuity is present in the orthorhombic phase (153 K). Unless specified, spinning was 5 kHz.

6) ¹⁴N NMR: DFT calculations



Figure S8. Structure of $MAPbI_3$ (a) before and (b) after the DFT MD simulations. Note that the lattice parameters are fixed, while the MA orientation and position varies.

Table S1. ¹⁴N NMR parameters in methylammonium cations as calculated in a 3x3x3 supercell of MAPbI₃ after a molecular dynamic simulation run for 1 ps 270 K with DFT CASTEP code (ZORA pseudopotentials).

			Asymmetry	Isotropic	Span	Skew
			parameter	shielding		
Filename	Atom(#)	χ _Q /MHz	$\eta_{ m Q}$	σ _{iso} /ppm	Ω /ppm	κ
	N(1)	-0.66	0.63	185.2	21.1	0.34
	N(2)	0.75	0.35	195.7	17.1	-0.24
	N(3)	0.85	0.35	188.5	20.2	0.31
	N(4)	0.70	0.56	188.1	11.2	-0.61
	N(5)	0.60	0.55	190.9	14.8	-0.59
	N(6)	0.61	0.72	190.5	22.1	0.49
	N(7)	0.70	0.45	196.7	12.0	-0.11
	N(8)	0.61	0.75	190.9	19.2	-0.53
	N(9)	0.74	0.29	195.3	12.7	-0.35
	N(10)	0.69	0.33	192.1	20.1	-0.31
	N(11)	0.69	0.75	189.1	16.0	0.09
	N(12)	0.61	0.50	190.7	12.0	0.05
	N(13)	0.81	0.55	193.9	11.8	-0.11
	N(14)	0.78	0.36	196.0	7.3	0.64
MAPbI ₃ icsd 250735 3x3						
SuperCell	N(15)	0.61	0.56	190.8	23.1	0.43
	N(16)	-0.44	0.91	195.0	8.4	-0.66
	N(17)	0.85	0.38	186.5	24.6	-0.47
	N(18)	0.75	0.08	197.1	12.5	-0.40
	N(19)	0.69	0.35	196.7	14.7	-0.03
	N(20)	0.73	0.25	192.5	14.6	-0.36
	N(21)	0.48	0.89	186.5	37.7	-0.21
	N(22)	0.40	0.31	191.4	15.1	-0.57
	N(23)	0.74	0.39	193.7	17.6	0.71
	N(24)	0.71	0.56	192.4	13.4	-0.05
	N(25)	0.74	0.70	193.4	10.6	0.19
	N(26)	0.62	0.81	192.3	17.4	0.08
	N(27)	0.85	0.62	189.4	12.9	0.45
Average absolute						
values:		0.68	0.52	191.9	16.3	-0.07

7) ²⁰⁷Pb NMR: DFT calculations

		Calculated Shielding parameters			Experimental isotropic chemical shift (from Ref. ¹⁰)
Compound	ICSD #	σ_{iso} , ppm	$\Delta \sigma$, ppm	η	δ_{iso} , ppm from PbMe ₄
$Pb(NO_3)_2$	62698	9763.07	-151.34	0	-3454
	174004	9768.89	-181.8	0	-3454
PbCl ₂	202130	8609.98	217.13	0.43	-1717
PbBr ₂	202134	8291.92	260.66	0.55	-979
PbO (Red)	15466	7153.28	868.64	0	1939
	15466	7153.28	868.64	0	1930
	15466	7153.28	868.64	0	1949
PbO (Yellow)	60135	7310.25	960.62	0.41	1527
	653900	7305.63	961.86	0.41	1527
	99776	7127.54	915.88	0	1527
Pb ₂ SnO ₄ SI	31482	7651.29	782.01	0.71	798
Pb ₂ SnO ₄ SII	31482	7675.21	812.94	0.74	662
PbCO ₃	36554	9310.49	685.24	0.27	-2630
	36554	9310.49	685.24	0.27	-2622
PbSO ₄	92609	9881.83	485.79	0.29	-3613
PbC ₂ O ₄	109830	8895.76	257.29	0.16	-1642
	109830	8895.76	257.29	0.16	-1659
PbSiO ₃ SI	250220	8256.85	517.23	0.11	93
SII	250220	8386.41	620.67	0.22	-166
SIII	250220	8457.58	384.32	0.65	-366
Pb ₃ (PO ₄) ₂ SI	92582	9163.35	-259.65	0.9	-2886
Pb ₃ (PO4) ₂ SII	92582	9023.33	-651.67	0.69	-2016
	14247	9315.19	-98.52	0.71	-2886
	14247	9238.85	628	0.65	-2016
PbMoO ₄	26784	9064.31	-116.74	0.06	-2004.9
	89034	9066.1	-112.13	0.07	-2004.9
PbTiO ₃	61168	8996.69	269.28	0	-1408
PbZrO ₃ SI	150699	8831.1	240.01	0.34	-1340
PbZrO ₃ SII	150699	8656.26	-475.09	0.95	-1000

 Table S2.
 ²⁰⁷Pb DFT CASTEP (ZORA) results in lead compounds for geometry optimized structures.

8) ¹²⁷I NQR



Analysis of the temperature dependent NQR frequencies

Figure S9. Temperature dependence of the ¹²⁷I NQR frequencies. Phase transition is visible at 327 K (blue line). Note the appreciable temperature dependence even after transition into the cubic phase.

The expressions for the temperature dependence of the NQR frequencies (Fig. S9) are similar to those previously derived by Ramakrishna:¹¹

$$\nu_T = \nu_Q \left[1 - \frac{3h}{8\pi^2 A_t f_t} - \frac{3h}{4\pi^2 A_t f_t} \frac{1}{e^{\frac{hf_t}{kT}} - 1} \right]$$
(Eq. 11)

$$\nu_{Q(\frac{1}{2}-\frac{3}{2})} = \frac{3eQq_{zz}}{10h}; \ \nu_{Q(\frac{3}{2}-\frac{5}{2})} = \frac{3eQq_{zz}}{20h}$$
 (Eq. 12)

The equations above assume an axially symmetric situation, i.e. when $\eta_Q \approx 0.0$, which is entirely valid for MAPbI₃, particularly in the cubic phase. We can therefore fit the appreciable temperature dependence observed after phase transition with these equations, and extract a torsional frequency $v_t \approx 1.15$ THz (≈ 38 cm⁻¹).

Expressions for the correlation time of the torsional vibrations

The Bayer theory¹² of spin-lattice relaxation in NQR state that the temperature dependence of the T_{IQ} can provide an accurate estimate of the correlation time τ_a of the rotational (torsional) vibrations. For a nucleus with spin 3/2 there is a single resonance transition that is uniquely described by a single relaxation time. This case has been extensively studied, and numerous experimental confirmations of the theory exist in the literature.¹³ For a spin 5/2 nucleus, however, the situation is not as straightforward, since the 2 resonance transitions have 2 different relaxation times, and in a general case the probabilities of transitions are not independent. For such a case, no closed form solution has yet been found.¹⁴ However, if the temperature is not too low (in most situations > 20 K), the relaxation is mainly defined by the transitions $|\Delta m|=2$, and the contribution of transitions with $|\Delta m|=1$ is negligibly small.^{12,14} In a special case of $\eta_Q=0$ and at sufficiently high temperatures, the expressions for pure NQR spin-lattice relaxation in spin 5/2 nucleus can be written as:¹⁵

$$T_{1,|\Delta m|=2}(\nu_1) = \frac{64}{10} \frac{(\pi J_1 \nu_t)^2}{(h\nu_{Q_1})^2 \tau_a} \frac{(e^{x}-1)^2}{\frac{2(ch(x)-1)}{1+\omega_1^2 \tau_a^2 (e^{x}-1)^2} + \frac{2ch(x)-1}{1+\omega_1^2 \tau_a^2}}$$
(Eq. 13)

$$T_{1,|\Delta m|=2}(\nu_2) = \frac{8}{9} \frac{(\pi J_1 \nu_t)^2}{(h\nu_{Q_1})^2 \tau_a} \frac{(e^x - 1)^2}{\frac{2(ch(x) - 1)}{1 + \omega_2^2 \tau_a^2 (e^x - 1)^2} + \frac{2ch(x) - 1}{1 + \omega_2^2 \tau_a^2}}$$
(Eq. 14)

with
$$v_1 = \frac{3}{10}eQq_{zz}$$
, $v_2 = \frac{3}{20}eQq_{zz}$ and $x = \frac{hv_t}{kT}$

Here v_t is the frequency rotational vibrations, J_I is the moment of inertia of the rotating part, and v_Q is the the frequency of the NQR in the absence of lattice vibrations, i.e. extrapolation to zero temperature. Evaluation of the correlation time τ_a can be easily done from the ratios of the experimental values of T_{IQ} for different transitions:

$$\frac{T_1(\nu_1)}{T_1(\nu_2)} = \frac{72}{10} \left(\frac{\nu_{Q2}}{\nu_{Q1}}\right)^2 \frac{\frac{2(ch(x)-1)}{1+\omega_2^2 \tau_a^2 (e^{x}-1)^2} + \frac{2ch(x)-1}{1+\omega_2^2 \tau_a^2}}{\frac{2(ch(x)-1)}{1+\omega_1^2 \tau_a^2 (e^{x}-1)^2} + \frac{2ch(x)-1}{1+\omega_1^2 \tau_a^2}}$$
(Eq. 15)

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