SUPPORTING INFORMATION FOR

Phase Evolution in Methylammonium Tin Halide Perovskites with Variable Temperature Solid-State ^{119}Sn NMR Spectroscopy

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Table S1: Density functional theory (DFT) calculated NMR parameters using ADF 2017, implementing a zero-order regular approximation, quadrupole-zeta basis set (ZORA/QZ4P).

Compound	σ_{iso} (ppm)	Span, Ω (ppm)	Skew, κ	Space Group	Crystal System	Temperature (K)
$[SnCl_6]^{4-}$	3567.27	0.001	-1.00	$Pm\bar{3}m$	Cubic	533
$[SnCl_6]^{4-}$	3518.17	20.30	1.00	$R3m$	Rhombohedral	350
$[SnCl_6]^{4-}$	3430.57	234.2	0.50	Pc	Monoclinic	318
$[SnCl_6]^{4-}$	3391.60	295.6	0.09	$P1$	Triclinic Sn1	250
$[SnCl_6]^{4-}$	3358.46	419.3	0.59	$P1$	Triclinic Sn2	250
$[SnBr_6]^{4-}$	3184.4	0.001	1.00	$Pm3m$	Cubic	295
$[SnBr_6]^{4-}$	3022.7	223.2	-0.39	$PmC21$	Orthorhombic	200
α-$[SnI_6]^{4-}$	2637.9	7.245	1.00	$Pm\bar{3}m$ $P4mm$[1]	Cubic	295
β-$[SnI_6]^{4-}$	2644.5	24.08	1.00	$I4cm$	Tetragonal	190

1. See discussion in Stoumpus et al., 2013, Inorg. Chem., 52, 9019-9038

Table S2: Calculated magnetic shielding parameters for SnX_6^{4-} (X = Cl, Br, I).

	σ_{11}				σ_{22}				σ_{33}				σ_{iso}			
	σ_{para}	σ_{dia}	σ_{SO}	σ_{tot}	σ_{para}	σ_{dia}	σ_{SO}	σ_{tot}	σ_{para}	σ_{dia}	σ_{SO}	σ_{tot}	σ_{para}	σ_{dia}	σ_{SO}	σ_{tot}
$SnCl_6^{4-}$																
Cubic	−1974	5106	436	3567	−1974	5106	436	3567	−1974	5106	436	3567	−1974	5106	436	3567
Mono.	−2133	5104	355	3333	−2074	5105	362	3391	−1977	5106	443	3567	−2061	5105	387	3431
Tric. A	−2240	5101	323	3190	−2153	5103	328	3275	−1961	5104	470	3609	−2118	5103	374	3358
Tric. B	−2178	5105	319	3248	−2086	5106	359	3383	−1970	5108	412	3544	−2078	5106	363	3392
$SnBr_6^{4-}$																
Cubic	−2195	5075	304	3184	−2195	5075	304	3184	−2195	5075	304	3184	−2195	5075	304	3184
Ortho.	−2206	5026	77	2897	−2181	5050	183	3051	−2129	5053	195	3120	−2172	5043	152	3023
SnI_6^{4-}																
Alpha	−2435	5091	−21	2635	−2435	5091	−21	2635	−2430	5091	−19	2643	−2434	5091	−20	2638
Beta	−2446	5091	−9	2637	−2446	5091	−9	2637	−2437	5091	6	2661	−2443	5091	−4	2645

Table S3: NMR parameters for other tin halide and oxide compounds.

Compound	δ_{iso} (ppm)	Ω (ppm)	κ	Properties	Source
$SnCl_2$	-915 (0.5)	350 (5)	0.6 (0.05)	Solid M_p = 247 °C	this work
$SnBr_2$	-580(50) -640	n.d.	n.d	Solid M_p = 215 °C	[1] [2]
SnI_2	-528	n.d.	n.d.	Solid M_p = 320 °C	this work
$SnCl_4$	-150 (2) Neat	-	-	Liquid M_p = -33 °C	[3]
$SnBr_4$	-638 (1) Neat	-	-	Liquid M_p = 31 °C	[3]
SnI_4	-1745	n.d.	n.d.	Solid M_p = 144 °C	this work
SnO	-208	1013	0.87	Solid M_p = 1080 °C	[4]
SnO_2	-604	121	0.84	Solid M_p = 1630 °C	[5]
Sn metal	7567 7500 6864	- - -	- - -	Solid M_p = 232 °C	[6] [7] [2]

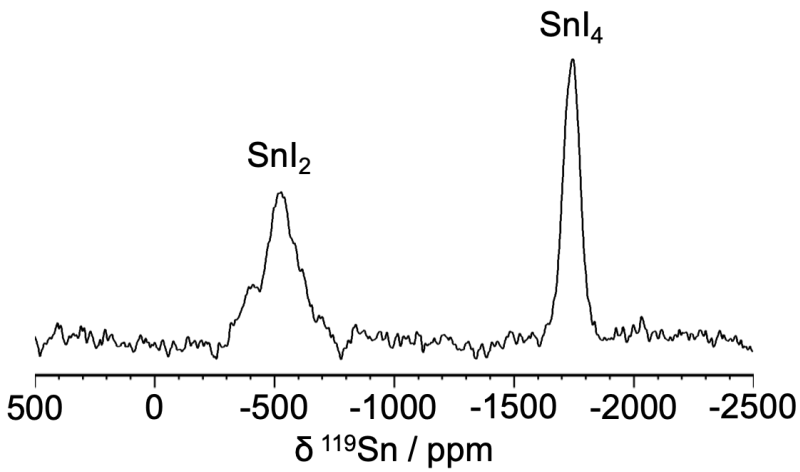

Figure S1: Solid-state ^{119}Sn MAS NMR spectrum of freshly purchased SnI_2 (purported to be 99%), T = 290 K; B_0 = 11.75 T; $\omega_r/2\pi$ = 12 kHz; 2048 co-added transients. The purchased material clearly contains nearly equivalent fractions of both SnI_2 and SnI_4.

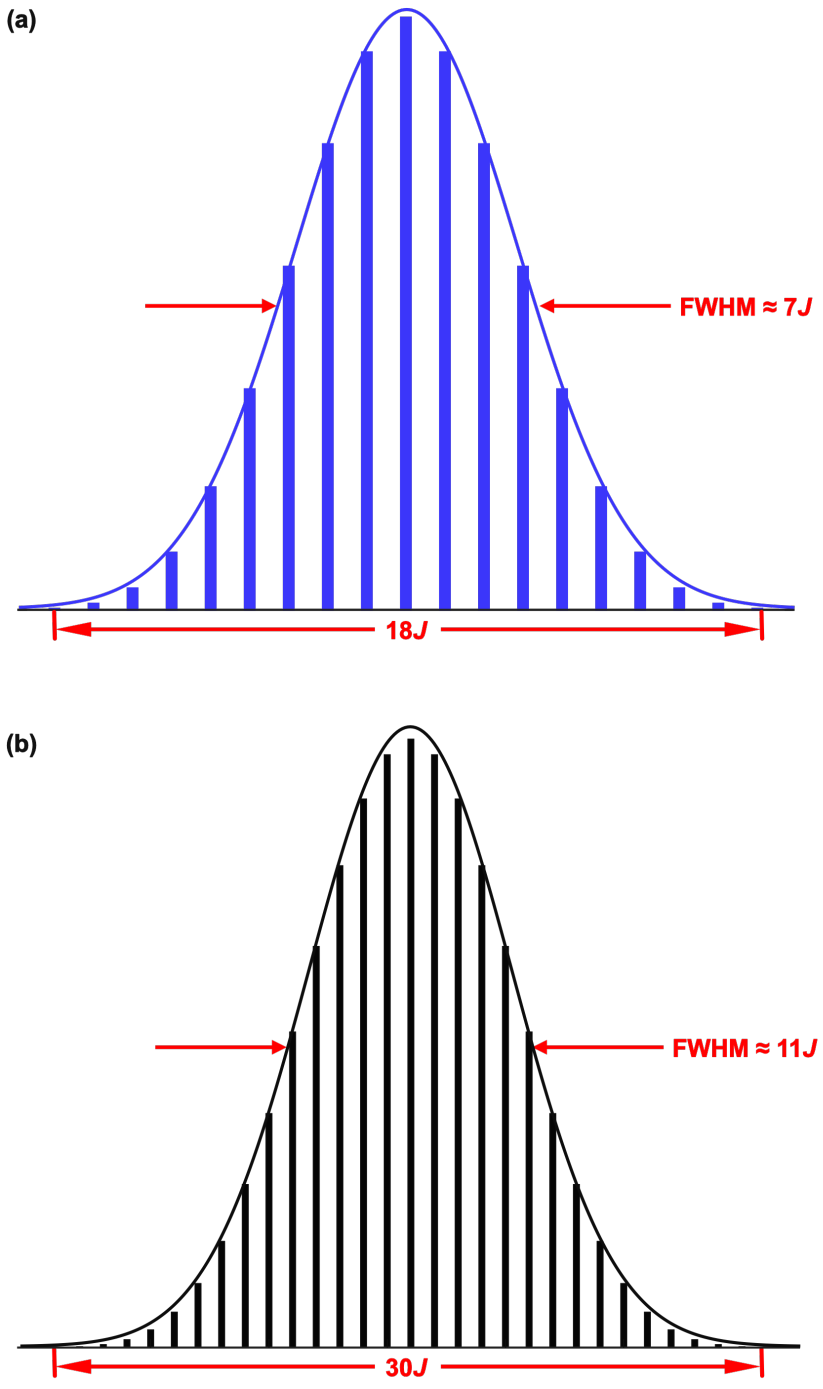

Figure S2: First-order *J*-coupling splitting pattern expected for an *I* = 1/2 nucleus coupled to six magnetically equivalent *I* = 3/2 nuclei (i.e., $^{35/37}$Cl or $^{79/81}$Br) with negligible quadrupolar interactions and with relative peak intensities of 1:6:21:56:120:216:336:456:546:580:546:456: 336:216:120:56:21:6:1(a)[8]; the trace above this pattern illustrates the Gaussian lineshape expected if individual peaks are not resolved. The corresponding pattern for an *I* = 1/2 nucleus indirectly spin-spin coupled to six *I* = 5/2 nuclei (i.e., ^{127}I) with relative peak intensity ratios of 1:6:21:56:126:252:456:756:1161:1666:2247:5856:3431:3906:4221:4332:4221:3906:3431:2856:2247:1666:1161: 756:456:252:126:56:21:6:1 (b)[8].

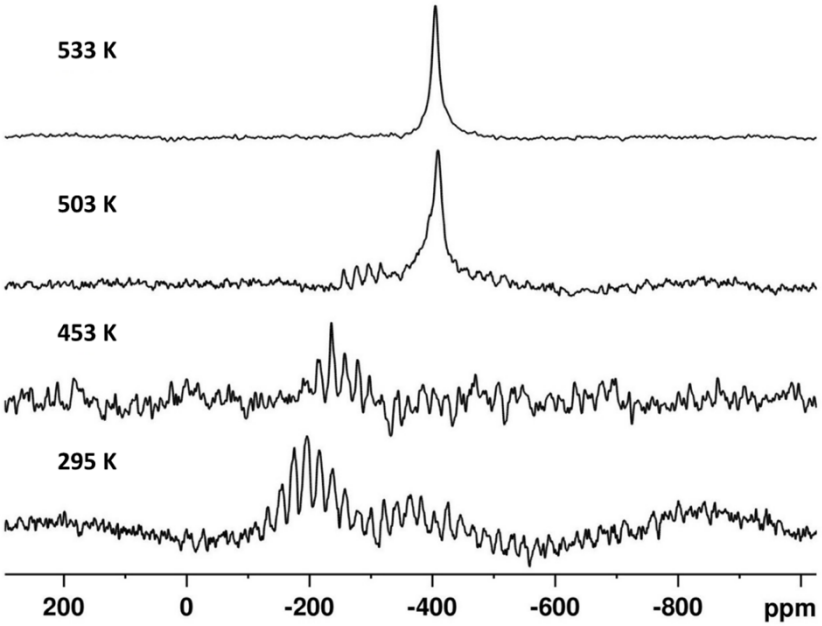

Figure S3: Variable temperature ^{119}Sn MAS NMR spectra of $MASnCl_3$ (B_0 = 9.4 T; $\omega_r/2\pi$ = 3 kHz).

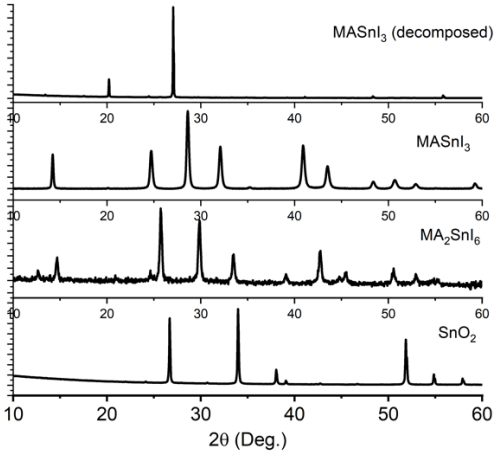

Figure S4: Powder X-ray diffraction patterns of decomposed $MASnI_3$, pristine $MASnI_3$, MA_2SnI_6 and SnO_2.

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