

## Supplementary Material

# Temperature-Dependent Evolution of Raman Spectra of Methylammonium Lead Halide Perovskites $\text{CH}_3\text{NH}_3\text{PbX}_3$ ( $\text{X} = \text{I}, \text{Br}$ )

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**Table S1.** Assignments of Raman bands of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>

No.	Wavenumber / cm <sup>-1</sup>				Assignments
	Orthorhombic	Tetragonal I	Tetragonal II	Cubic	
v <sub>1</sub>	328/296	325	326	326	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> -PbBr <sub>3</sub> <sup>-</sup> cage vibration
v <sub>2</sub>	916	918	917	916	CH <sub>3</sub> rocking and NH <sub>3</sub> <sup>+</sup> rocking
v <sub>3</sub>	971	973	971	969	C-N <sup>+</sup> stretching
v <sub>4</sub>	1259	1254	1253	—	CH <sub>3</sub> rocking and NH <sub>3</sub> <sup>+</sup> rocking
v <sub>5</sub>	1421	1424	1423	—	CH <sub>3</sub> symmetric deformation
v <sub>6</sub>	1456	1458	—	—	CH <sub>3</sub> degenerate deformation
v <sub>7</sub>	1461	—	—	—	CH <sub>3</sub> degenerate deformation
v <sub>8</sub>	1472	1482	1479	1478	NH <sub>3</sub> <sup>+</sup> symmetric deformation
v <sub>9</sub>	1590	1592	1592	1592	NH <sub>3</sub> <sup>+</sup> degenerate deformation
v <sub>10</sub>	2820	2823	2824	2829	combination
v <sub>11</sub>	2895	2893	2893	—	combination
v <sub>12</sub>	2965	2965	2965	2967	CH <sub>3</sub> symmetric stretching
v <sub>13</sub>	3032	3034	3036	—	CH <sub>3</sub> degenerate stretching
v <sub>14</sub>	3039	—	—	—	CH <sub>3</sub> degenerate stretching
v <sub>15</sub>	3105	3105	3107	—	NH <sub>3</sub> <sup>+</sup> symmetric stretching
v <sub>16</sub>	3144	—	—	—	NH <sub>3</sub> <sup>+</sup> degenerate stretching

**Table S2.** Assignments of Raman bands of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>

No.	Wavenumber / cm <sup>-1</sup>			Assignments
	Orthorhombic	Tetragonal	Cubic	
v <sub>1</sub>	~250	258	246	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> -PbI <sub>3</sub> <sup>-</sup> cage vibration
v <sub>2</sub>	918	909	908	CH <sub>3</sub> rocking and NH <sub>3</sub> <sup>+</sup> rocking
v <sub>3</sub>	969	965	959	C-N <sup>+</sup> stretching
v <sub>4</sub>	—	1249	—	CH <sub>3</sub> rocking and NH <sub>3</sub> <sup>+</sup> rocking
v <sub>5</sub>	1422	1421	1423	CH <sub>3</sub> symmetric deformation
v <sub>6</sub>	—	1450	—	CH <sub>3</sub> degenerate deformation
v <sub>7</sub>	—	—	—	CH <sub>3</sub> degenerate deformation
v <sub>8</sub>	1460	1469	1469	NH <sub>3</sub> <sup>+</sup> symmetric deformation
v <sub>9</sub>	1587	1583	1582	NH <sub>3</sub> <sup>+</sup> degenerate deformation