Supporting Information

Halogen Effects on Ordering and Bonding of $CH_3NH_3^+$ in $CH_3NH_3PbX_3$ (X = Cl, Br, I) Hybrid Perovskites: A vibrational spectroscopic study

Ralf G. Niemann,[a,b,§] Athanassios G. Kontos, [b§] Dimitrios Palles,[c] Efstratios I. Kamitsos,[c] Andreas Kaltzoglou,[b] Federico Brivio,[a] Polycarpos Falaras,[b] and Petra J. Cameron[a]*

[a] Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom

[b] Institute of Nanoscience and Nanotechnology, NCSR Demokritos, 15310 Athens, Greece

[c] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 11635 Athens, Greece

[§] These authors contributed equally.

* To whom correspondence should be addressed.

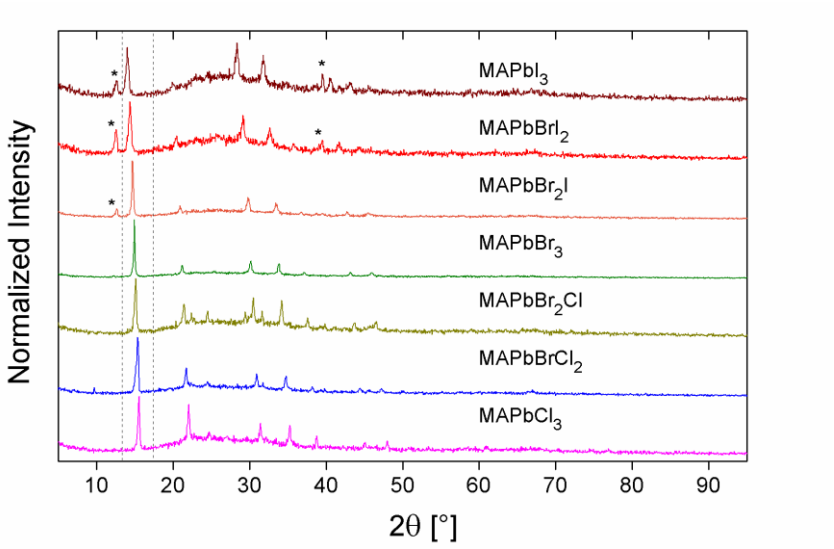

Figure S1: Full powder XRD patterns of all halide perovskites examined in this study. Reflections attributed to unconverted PbI_2 are denoted with asterisks.

Table S1: Lattice parameters from XRD data for $MAPbX_3$ perovskites

Composition	Crystal system	a = b (Å)	c (Å)
$MAPbCl_3$	Cubic	5.675(2)	5.675(2)
$MAPbBrCl_2$	Cubic	5.755(3)	5.755(3)
$MAPbBr_2Cl$	Cubic	5.849(3)	5.849(3)
$MAPbBr_3$	Cubic	5.954(2)	5.954(2)
$MAPbBr_2I$	Tetragonal	8.449(4)	11.997(4)
$MAPbBrI_2$	Tetragonal	8.682(6)	12.407(6)
$MAPbI_3$	Tetragonal	8.861(2)	12.653(2)

Table S2: Optical band gaps (E_g) and laser excitation energies for the Raman and PL investigation of perovskite materials. (Res) stands for Resonant, (Off-res) for off-resonance Raman excitation and (PL) for Photoluminescence which occurred upon excitation in the vicinity of E_g.

Perovskite	E_g (eV)	514 nm[t] *(2.41 eV)*	785 nm[t,w] *(1.58 eV)*	1064 nm *(1.17 eV)*
$MAPbCl_3$	3.06	Off-res	Off-res	Off-res
$MAPbBrCl_2$	2.78	Off-res	Off-res	Off-res
$MAPbBr_2Cl$	2.53	Off-res	Off-res	Off-res
$MAPbBr_3$	2.33	Res – PL	Off-res	Off-res
$MAPbBr_2I$	2.08	Res – PL	Off-res	Off-res
$MAPbBrI_2$	1.81	Res – PL	Off-res	Off-res
$MAPbI_3$	1.61	Res	PL	Off-res

[t] Extra Low-temperature measurements
[w] Extra Low-frequency range accessed

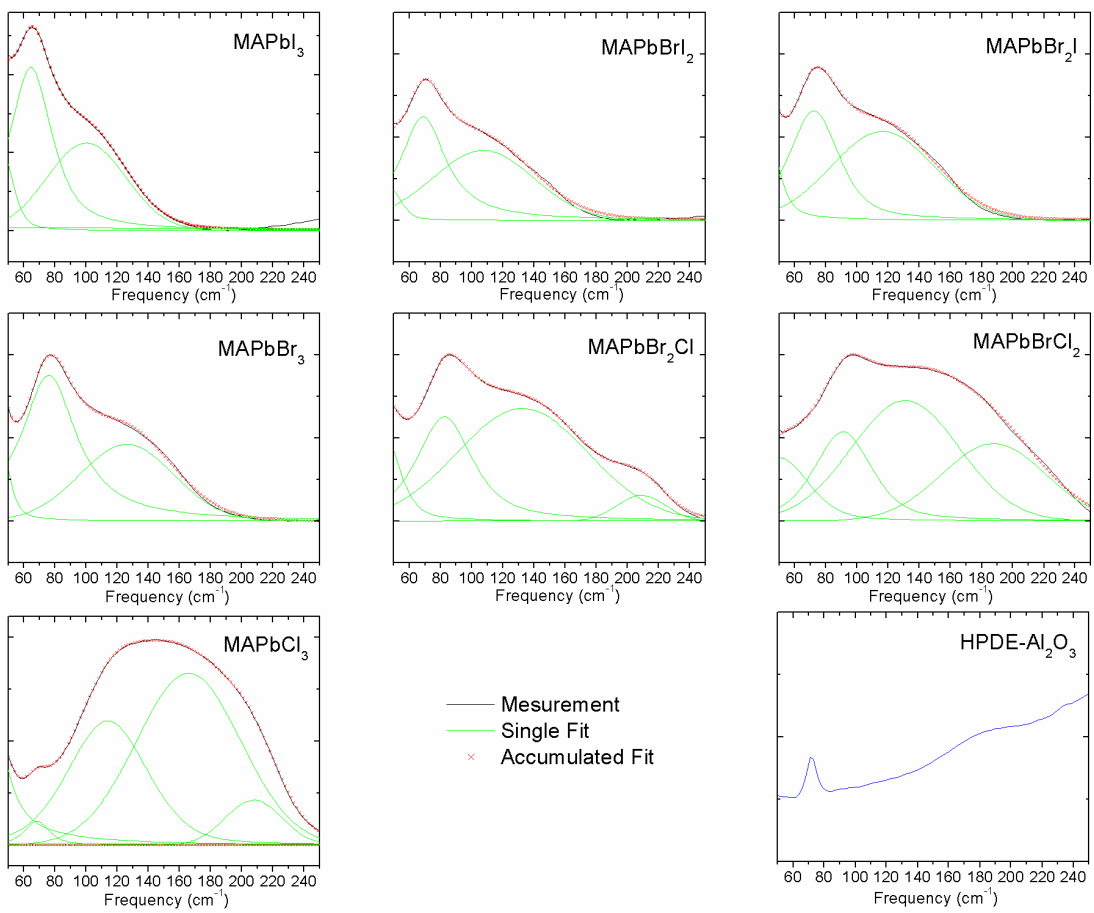

Figure S2: Fitting analysis of the far-IR absorption spectra (black lines). Fitting spectra are shown with red symbols and fitting components with green lines. Last graph shows spectrum of reference HPDE-Al_2O_3.

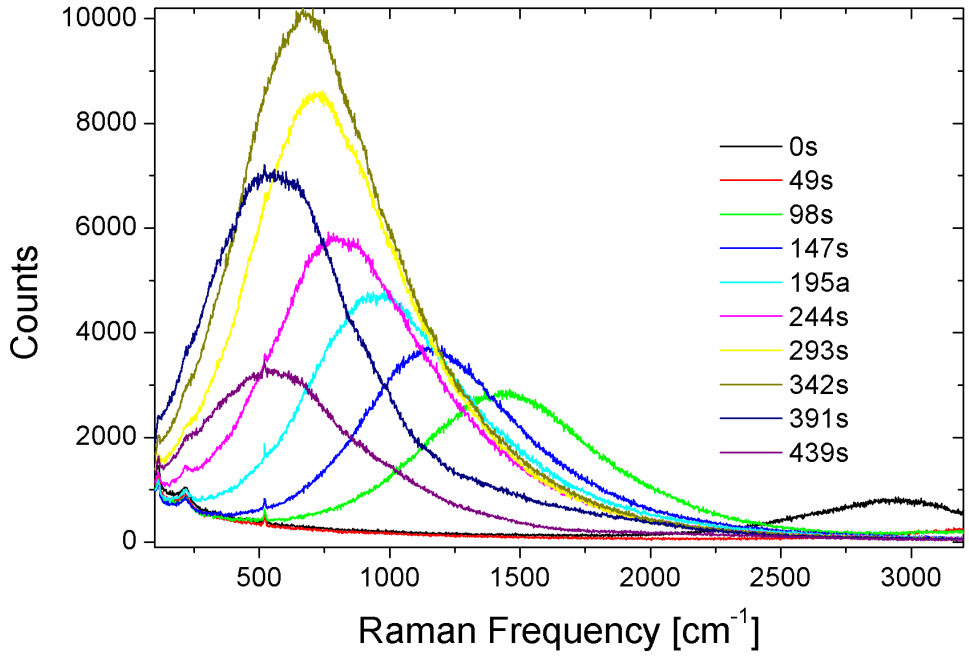

Figure S3: Spectra show shifting of PL during measuring $MAPbI_2Br$ under resonance (514 nm) conditions, indicating phase segregation.

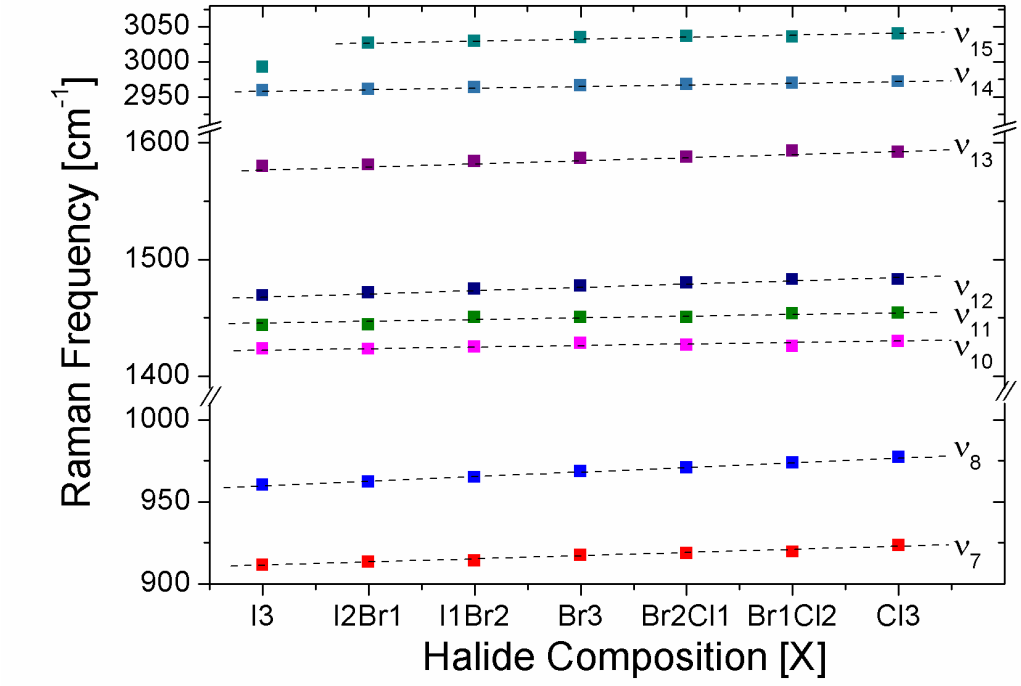

Figure S4: Raman frequency shifts of strongest MA modes above 900 cm^{-1} for various halogen contents in $MAPbX_3$.

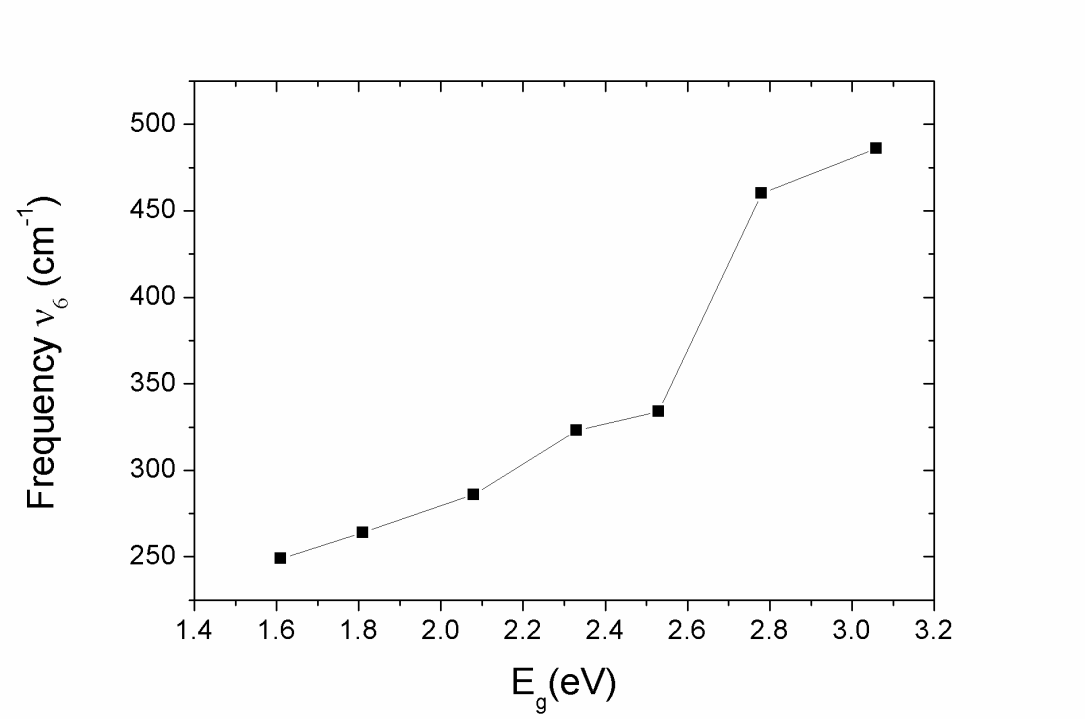

Figure S5: The frequency of the ν_6 torsional mode at RT against the band gaps for all measured $MAPbX_3$ derivatives.

Table S3: Overview of main MA Raman frequency peaks above 900 cm^{-1}, measured at 100 K by excitation at 785 nm, for MA lead derivatives MAPb[X].

Mode/[X]	I2Br	IBr2	Br3	Br2Cl	BrCl2	Cl3	Assignment
ν_7	912	915	918	923	925	927	ρ (MA)
ν_8	965	969	972	975	976	979	ν (CN)
ν_9	1250	1252	1253	1255	1255		ρ (MA)
ν_{10}	1420	1421	1428	1427	1426	1430	δ_s (CH_3)
ν_{11}	1454	1455	1463	1458	1458	1464	δ_a (CH_3)
ν_{12}	1472	1476	1483	1486	1488		δ_s (NH_3^+)