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## **Supporting Information**

Halogen Effects on Ordering and Bonding of  $\text{CH}_3\text{NH}_3^+$  in  $\text{CH}_3\text{NH}_3\text{PbX}_3$

(X = Cl, Br, I) Hybrid Perovskites: A vibrational spectroscopic study

*Ralf G. Niemann,<sup>a,b,§</sup> Athanassios G. Kontos,<sup>b,§\*</sup> Dimitrios Palles,<sup>c</sup> Efstratios I.*

*Kamitsos,<sup>c</sup> Andreas Kaltzoglou,<sup>b</sup> Federico Brivio,<sup>a</sup> Polycarpos Falaras,<sup>b</sup> and Petra J.*

*Cameron<sup>a</sup>*

<sup>a</sup> Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom

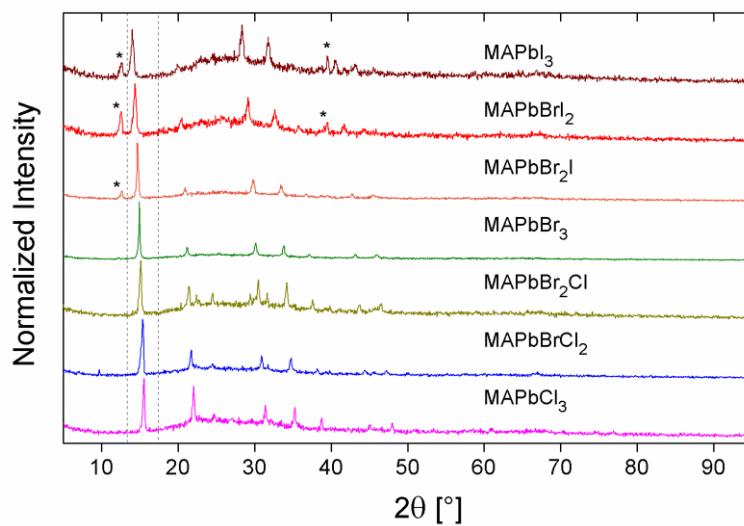
<sup>b</sup> Institute of Nanoscience and Nanotechnology, NCSR Demokritos, 15310  
Athens, Greece

<sup>c</sup> Theoretical and Physical Chemistry Institute, National Hellenic Research  
Foundation, 11635 Athens, Greece

§ These authors contributed equally.

\* To whom correspondence should be addressed.

Figure S1, Table S1	p. S2
Table S2, Figure S2	p. S3
Figure S3, Figure S4	p. S4
Figure S5, Table S3	p. S5



**Figure S1:** Full powder XRD patterns of all halide perovskites examined in this study. Reflections attributed to unconverted PbI<sub>2</sub> are denoted with asterisks.

**Table S1:** Lattice parameters from XRD data for MAPbX<sub>3</sub> perovskites

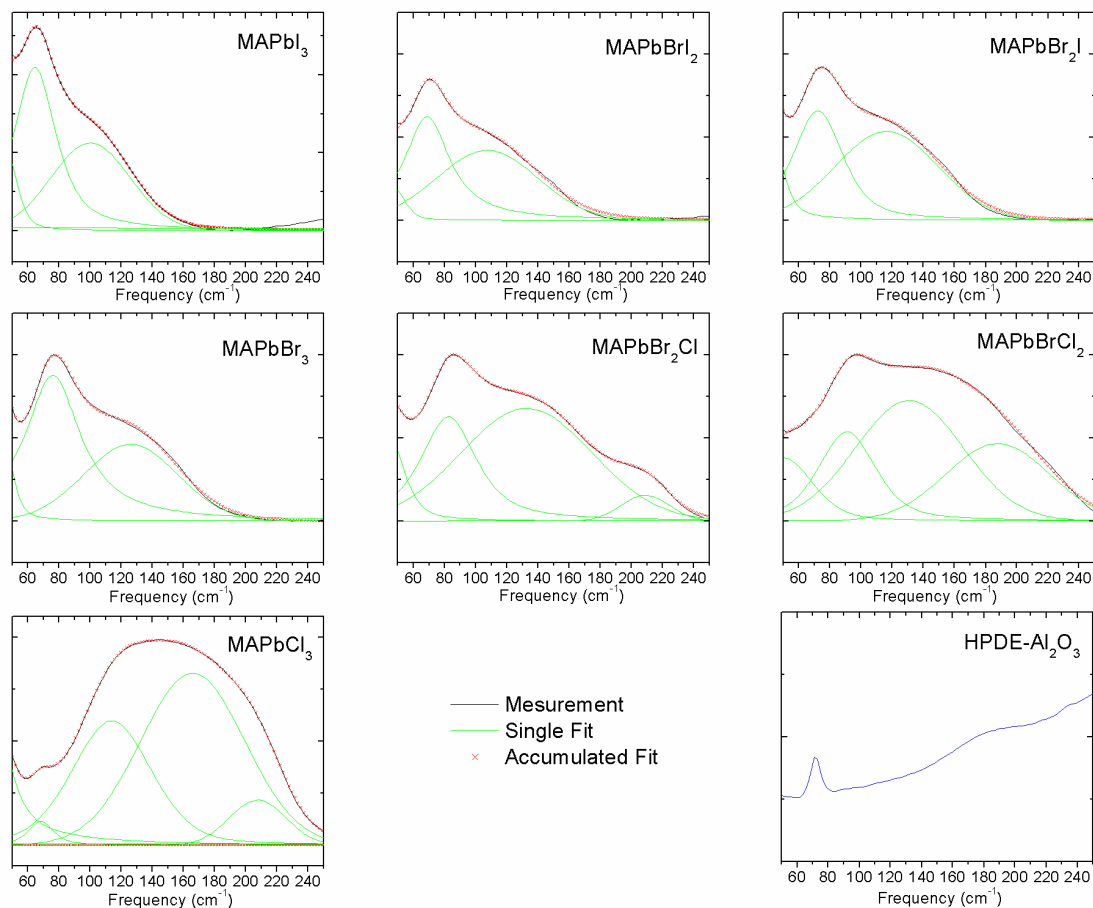
Composition	Crystal system	a = b (Å)	c (Å)
MAPbCl <sub>3</sub>	Cubic	5.675(2)	5.675(2)
MAPbBrCl <sub>2</sub>	Cubic	5.755(3)	5.755(3)
MAPbBr <sub>2</sub> Cl	Cubic	5.849(3)	5.849(3)
MAPbBr <sub>3</sub>	Cubic	5.954(2)	5.954(2)
MAPbBr <sub>2</sub> I	Tetragonal	8.449(4)	11.997(4)
MAPbBrI <sub>2</sub>	Tetragonal	8.682(6)	12.407(6)
MAPbI <sub>3</sub>	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 <sup>†</sup> (2.41 eV)	785 nm <sup>†,w</sup> (1.58 eV)	1064 nm (1.17 eV)
MAPbCl <sub>3</sub>	3.06	Off-res	Off-res	Off-res
MAPbBrCl <sub>2</sub>	2.78	Off-res	Off-res	Off-res
MAPbBr <sub>2</sub> Cl	2.53	Off-res	Off-res	Off-res
MAPbBr <sub>3</sub>	2.33	Res – PL	Off-res	Off-res
MAPbBr <sub>2</sub> I	2.08	Res – PL	Off-res	Off-res
MAPbBrI <sub>2</sub>	1.81	Res – PL	Off-res	Off-res
MAPbI <sub>3</sub>	1.61	Res	PL	Off-res

<sup>†</sup> Extra Low-temperature measurements

<sup>w</sup> 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<sub>2</sub>O<sub>3</sub>.**

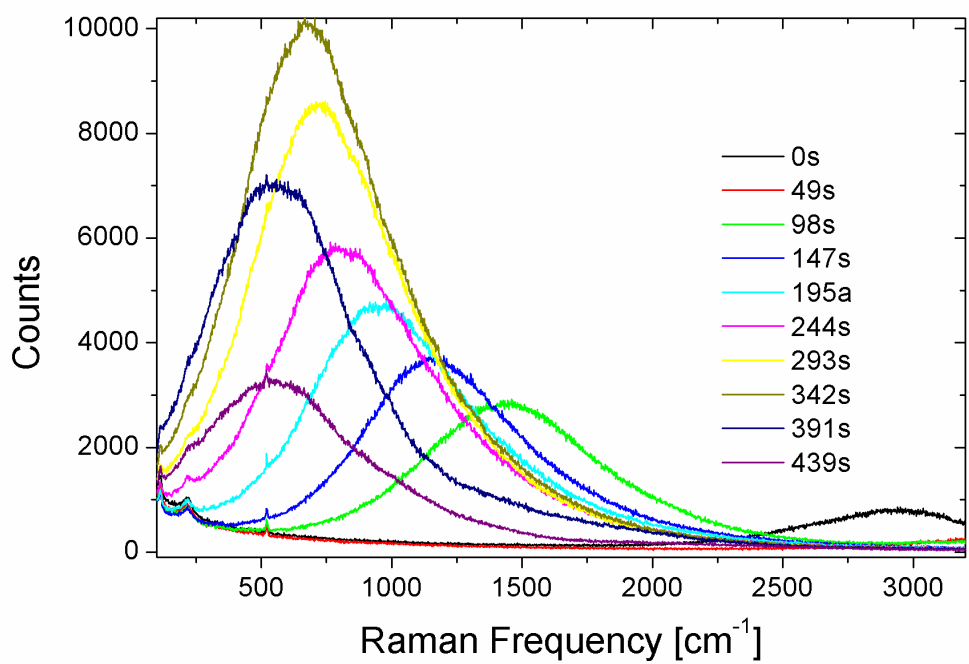


Figure S3: Spectra show shifting of PL during measuring MAPbI<sub>2</sub>Br under resonance (514 nm) conditions, indicating phase segregation.

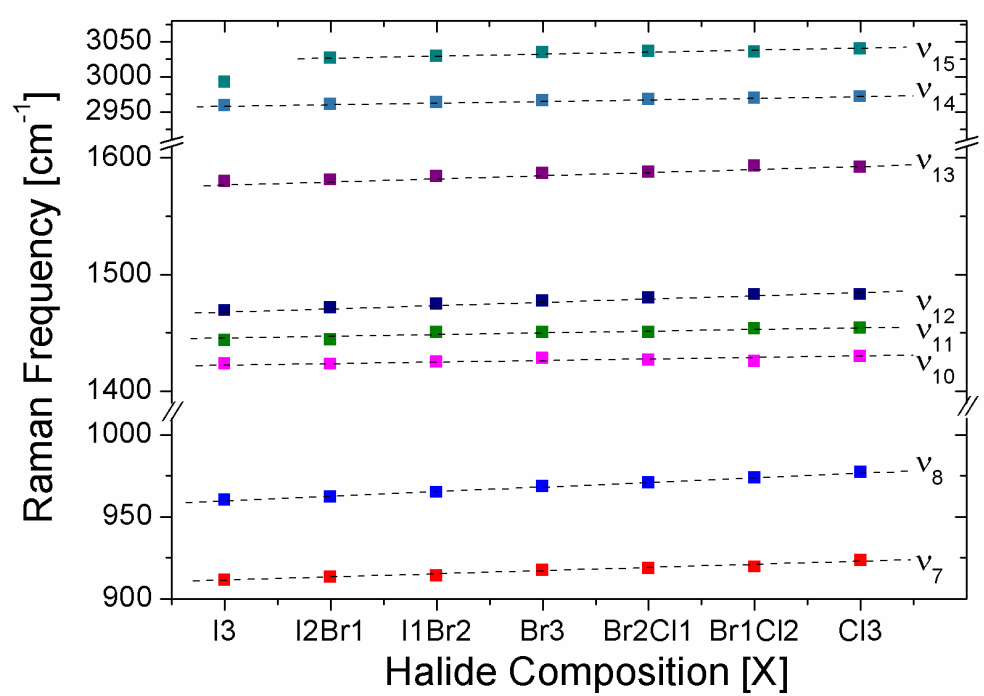
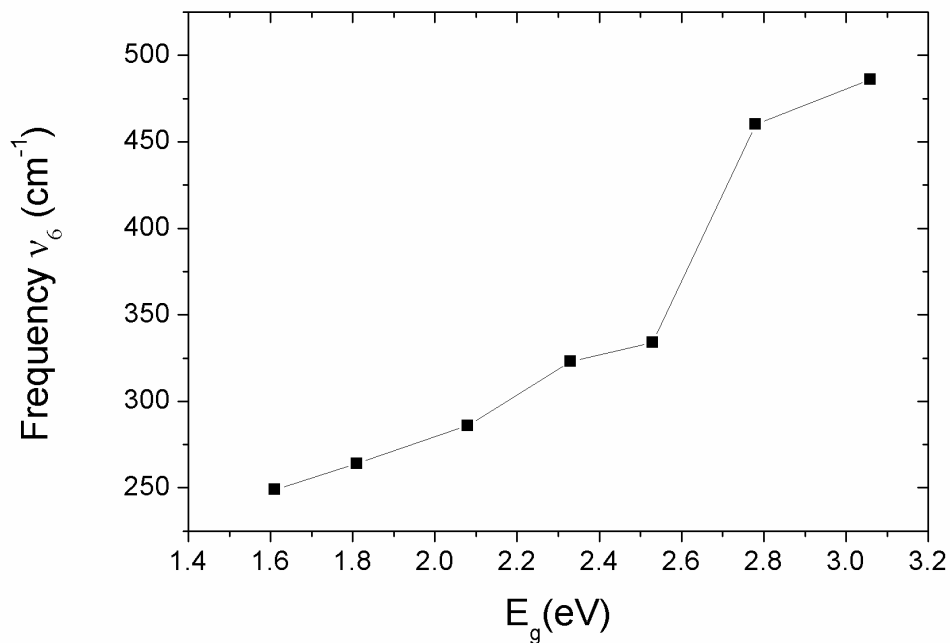


Figure S4: Raman frequency shifts of strongest MA modes above 900 cm<sup>-1</sup> for various halogen contents in MAPbX<sub>3</sub>.



**Figure S5:** The frequency of the  $\nu_6$  torsional mode at RT against the band gaps for all measured MAPbX<sub>3</sub> derivatives.

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

Mode/[X]	I2Br	IBr2	Br3	Br2Cl	BrCl2	Cl3	Assignment
$\nu_7$	912	915	918	923	925	927	$\rho$ (MA)
$\nu_8$	965	969	972	975	976	979	$\nu$ (CN)
$\nu_9$	1250	1252	1253	1255	1255		$\rho$ (MA)
$\nu_{10}$	1420	1421	1428	1427	1426	1430	$\delta_s$ (CH <sub>3</sub> )
$\nu_{11}$	1454	1455	1463	1458	1458	1464	$\delta_a$ (CH <sub>3</sub> )
$\nu_{12}$	1472	1476	1483	1486	1488		$\delta_s$ (NH <sub>3</sub> <sup>+</sup> )