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Supporting Information

Halogen Effects on Ordering and Bonding of CH_3NH_3^+ in $\text{CH}_3\text{NH}_3\text{PbX}_3$

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

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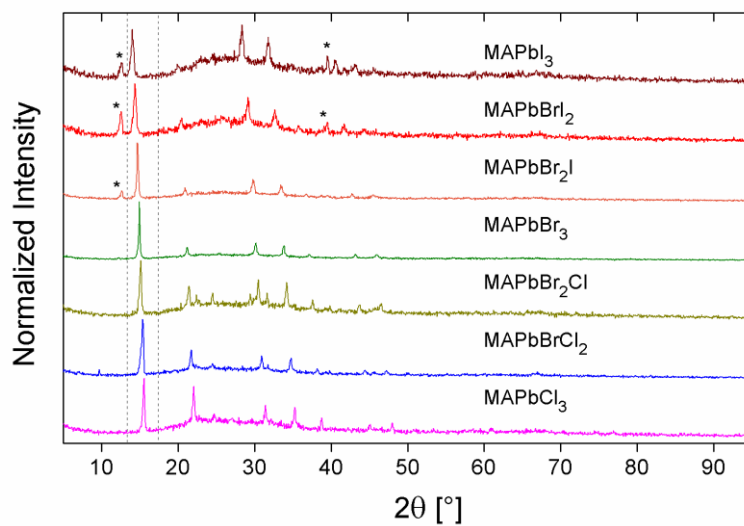


Figure S1: Full powder XRD patterns of all halide perovskites examined in this study. Reflections attributed to unconverted PbI₂ are denoted with asterisks.

Table S1: Lattice parameters from XRD data for MAPbX₃ 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 ₂ Cl | Cubic | 5.849(3) | 5.849(3) |
| MAPbBr ₃ | Cubic | 5.954(2) | 5.954(2) |
| MAPbBr ₂ I | 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 [†] (2.41 eV) | 785 nm ^{†,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 ₂ Cl | 2.53 | Off-res | Off-res | Off-res |
| MAPbBr ₃ | 2.33 | Res – PL | Off-res | Off-res |
| MAPbBr ₂ I | 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 |

[†] Extra Low-temperature measurements

^w Extra Low-frequency range accessed

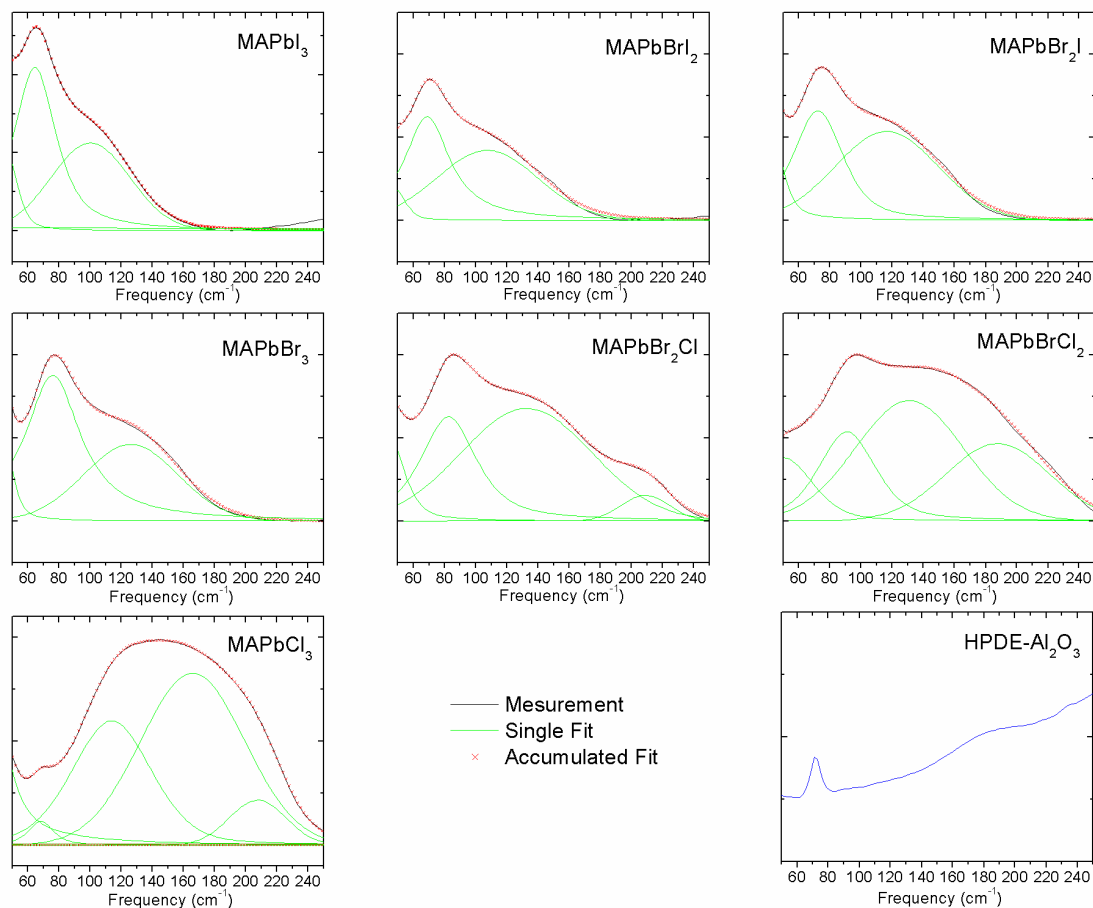


Figure S2: Fitting analysis of the far-IR absorption spectra (black lines). Fitting spectra are shown with red symbols and fitting components with green lines. Last graph shows spectrum of reference HPDE-Al₂O₃.

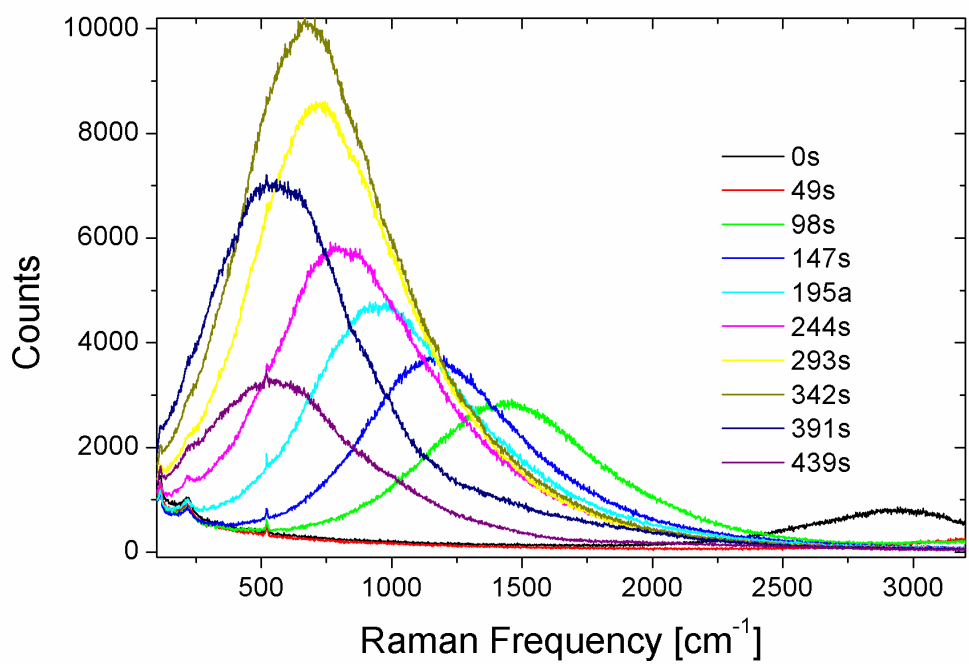


Figure S3: Spectra show shifting of PL during measuring MAPbI₂Br under resonance (514 nm) conditions, indicating phase segregation.

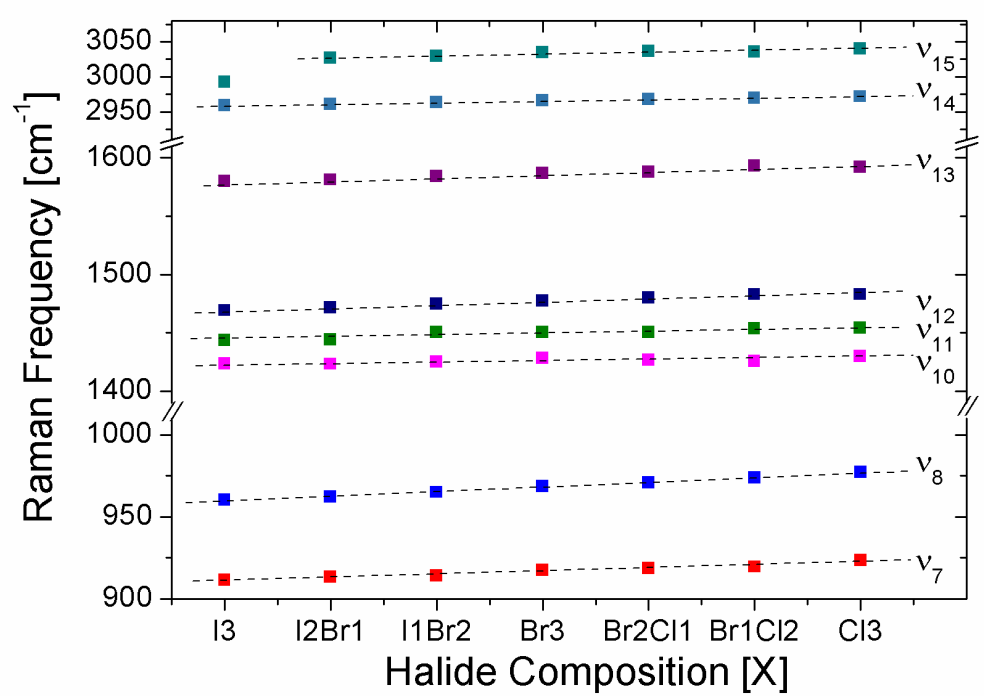


Figure S4: Raman frequency shifts of strongest MA modes above 900 cm⁻¹ for various halogen contents in MAPbX₃.

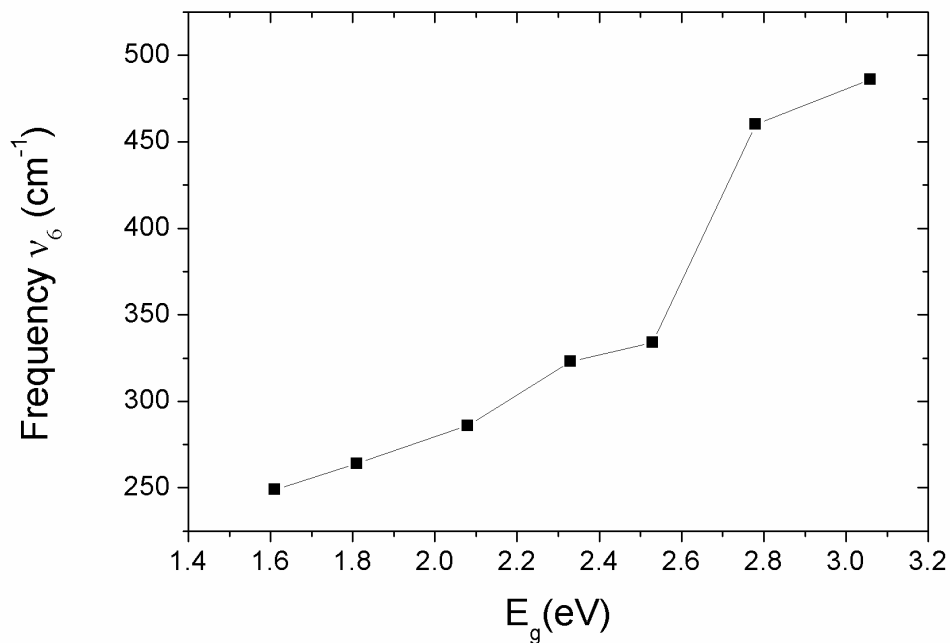


Figure S5: The frequency of the ν_6 torsional mode at RT against the band gaps for all measured MAPbX₃ derivatives.

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 ⁺) |