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SUPPLEMENTARY INFORMATION

Vibrational dynamics in lead halide perovskites investigated by Raman spectroscopy†

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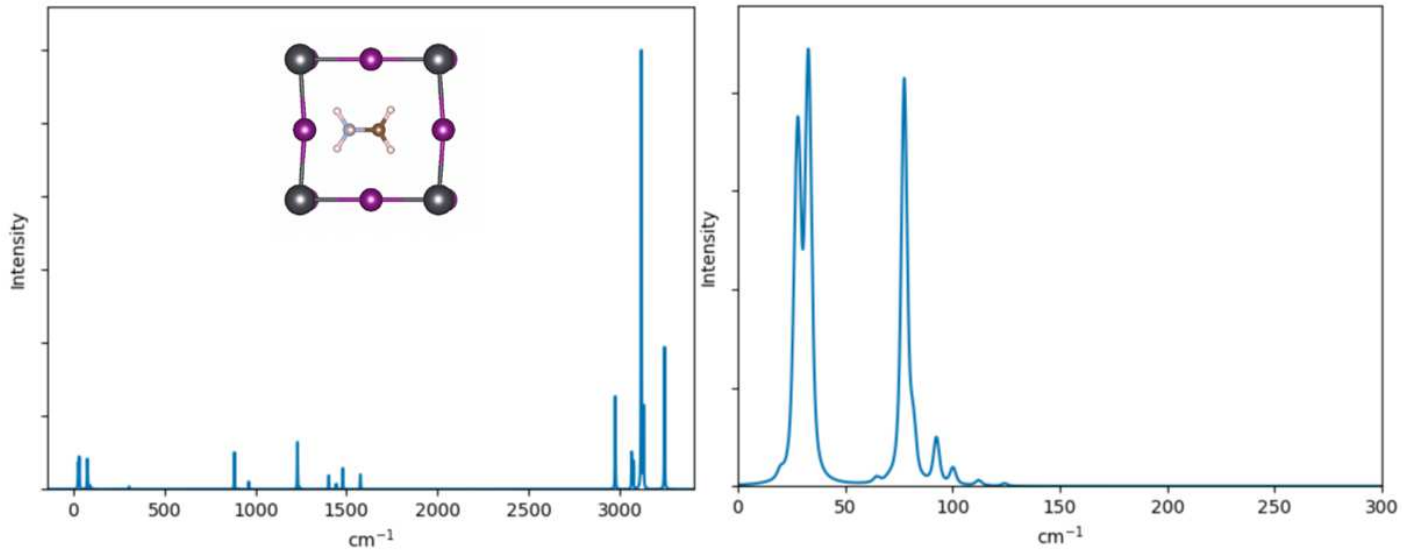

Fig. 1 DFT spectrum of $MAPbI_3$ in a) complete range 0-3500 cm^{-1} and b) low frequency region 0-300 cm^{-1}. The difference compared to the experimental spectrum is caused by different space groups: to simplify theoretical calculations, cubic $Pm\bar{3}m$ space group was taken whereas in fact $MAPbI_3$ has tetragonal I4/mcm symmetry at RT.

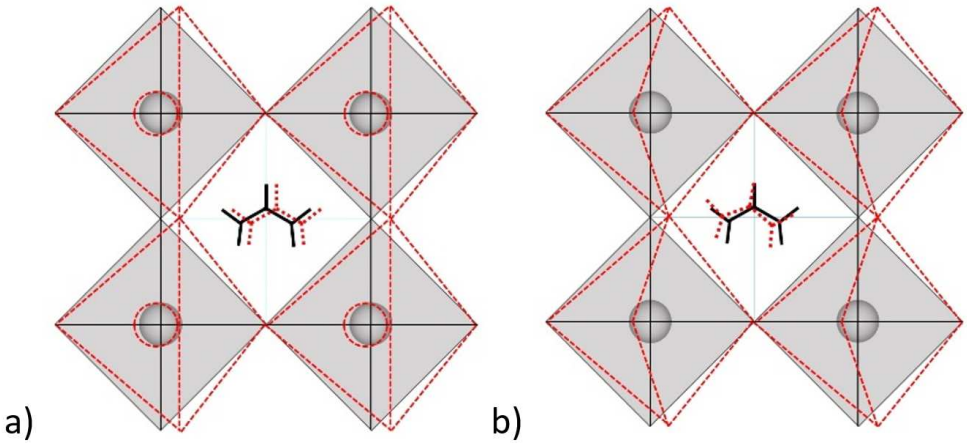

Fig. 2 Sublattice modes of the zone I: a) twist and b) distortion of octahedra.

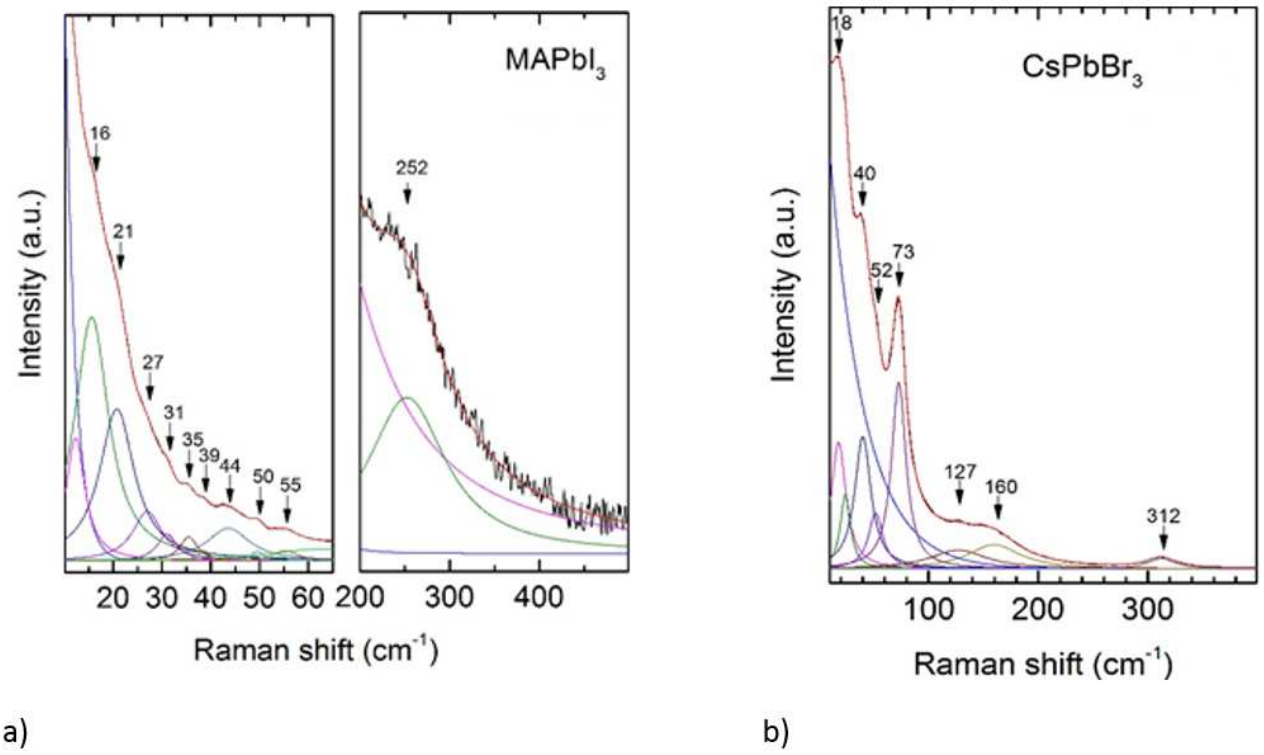

Fig. 3 Raman spectra of (a) $MAPbI_3$ and (b) $CsPbBr_3$ measured at RT with an excitation by laser with λ = 633 nm.

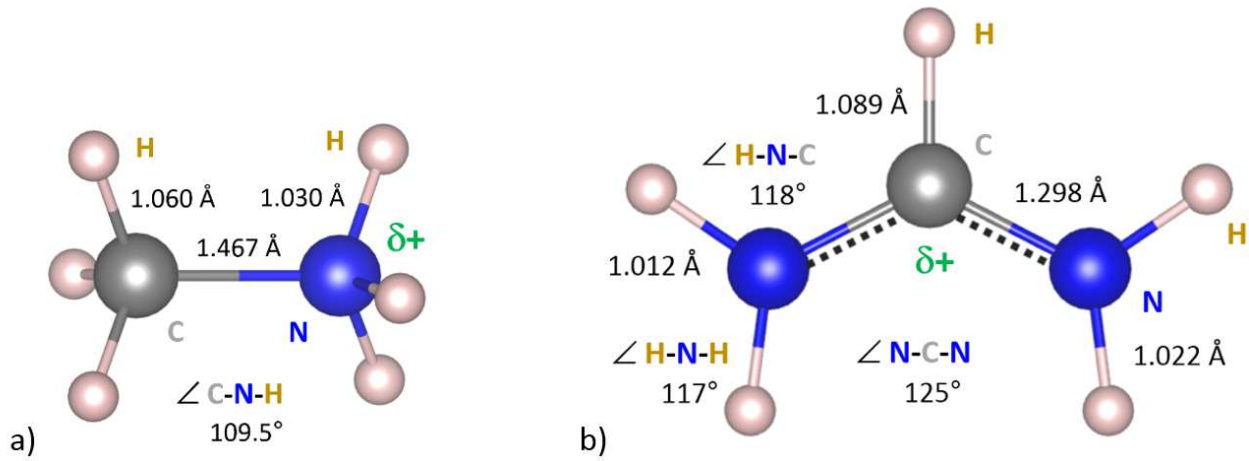

Fig. 4 Structural formulas of the molecular ions: a) methylammonium, b) formamidinium[? ?].

Table 1 Relevant ionic radii[? ? ? ?].

Material	Ionic Radius (Å)
FA^{+}	2.53
Cs^{+}	1.81
Pb^{+2}	1.19
I^{-}	2.20
Br^{-}	1.96

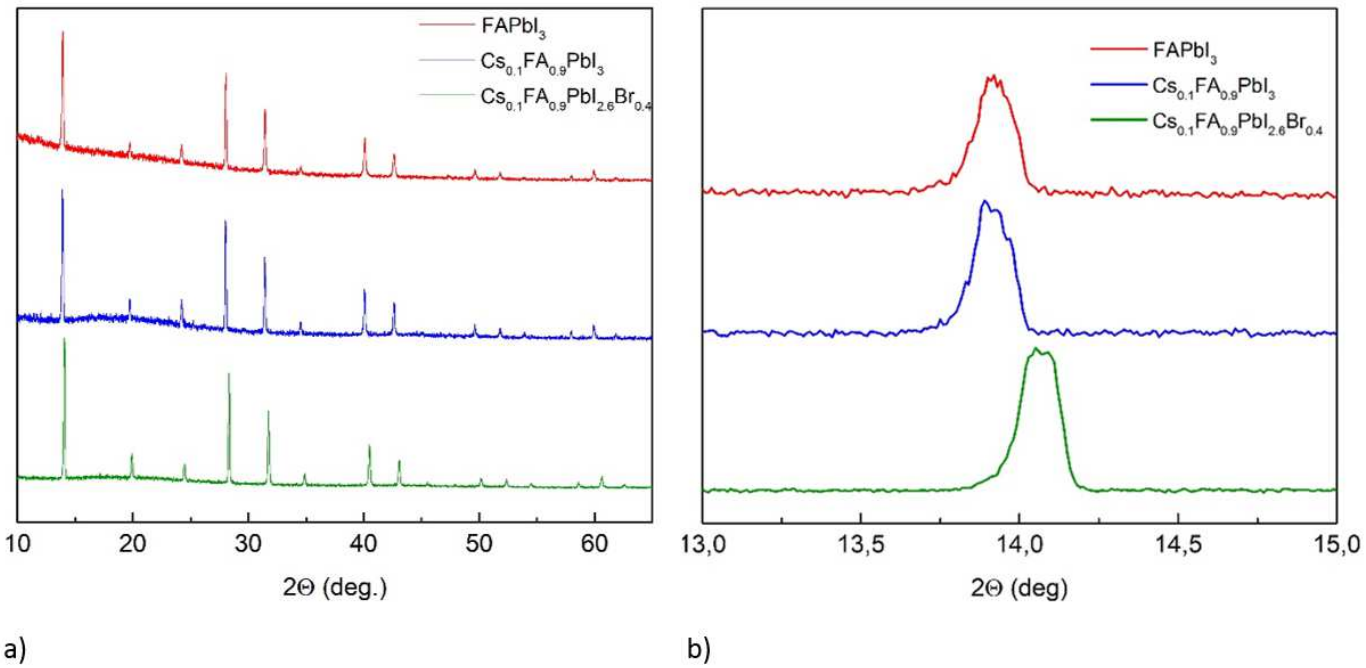

Fig. 5 Powder XRD patterns of as-prepared $FAPbI_3$-based perovskites: (a) wide range and (b) selected 2Θ area around (100) reflection in a cubic $Pm\bar{3}m$ system. Lattice constants were calculated on the basis of Rietveld refinement over the whole measured 2Θ range.

Table 2 Relevant Goldschmidt tolerance factors (GTFs)[??]

Material	GTF
$FAPbI_3$	0.987
$Cs_{0.1}FA_{0.9}PbI_3$	0.972
$Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$	0.974
$FAPbBr_3$	1.008
$CsPbI_3$	0.836
$CsPbBr_3$	0.974

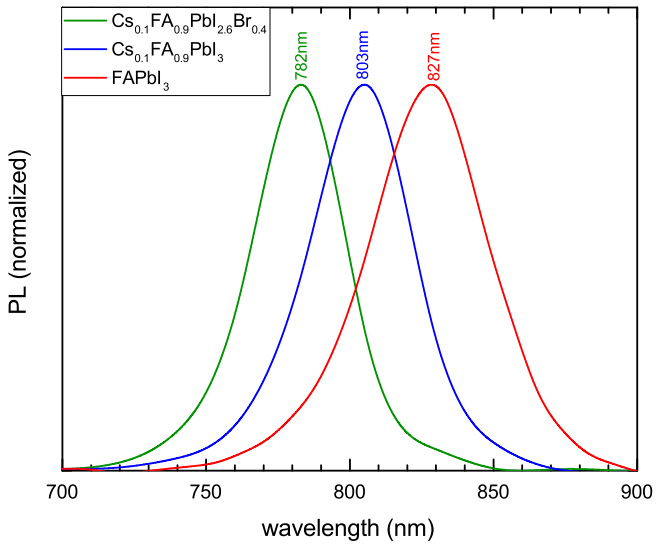

Fig. 6 PL signals (spline smoothed curve) for $Cs_{0.1}FA_{0.9}PbI_3$ and for $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ measured with an excitation source of 633 nm