

## Pseudospin-phonon pretransitional dynamics in lead halide hybrid perovskites

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### Supplemental Material

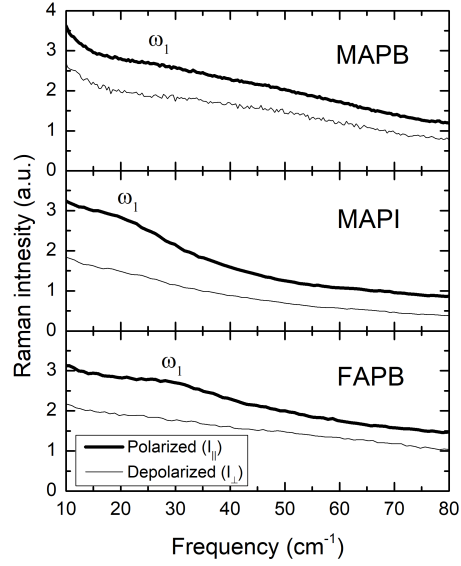


Figure S1: Polarized ( $I_{\parallel}$ ) and depolarized ( $I_{\perp}$ ) Raman spectra in MAPB, MAPI, and FAPB in the cubic phase with incident polarization parallel to  $[110]$  and  $q \parallel [001]$ , showing a stronger Raman activity of the mode  $\omega_1$  in the polarized spectra. The latter provides a favorable scattering geometry to follow the mode with temperature across the cubic to tetragonal transition.

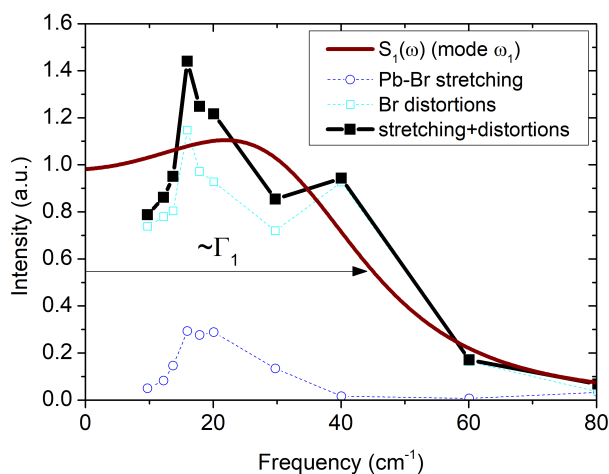


Figure S2: Raman spectral response of MAPB of the low frequency mode  $\omega_1$  in the cubic phase (our work) compared to *ab-initio* MD calculations of the frequency distribution of the Br modes [1]. The latter have been projected onto Pb-Br stretching and  $\text{Br}_6$  rotation eigenvectors. The remaining displacements are  $\text{Br}_6$  "distortions" and contain bending. Since in the cubic phase rotations are zone boundary vibrations, they do not contribute to the Raman signal and have not been considered here. The agreement between calculations and experiments suggests that the low-frequency response  $\omega_1$  fitted with one single DHO might contain a dominant contribution of bending-like motions together with possibly a weak contribution of stretching at low frequency.

Table S1: Literature data on the reorientational motions of the organic cation in APbX<sub>3</sub> samples (A=FA, MA; X=Br, I). When not specified the values are at room temperature. Values in meV and cm<sup>-1</sup> correspond to HWHM. One notices that at high temperature, the characteristic time scales of the reorientational motions are typically lower than ~ 10 ps, leading to HWHM of several wave numbers (few tens of meV).

Ref.	Techniques	Rotation of CH <sub>3</sub> and/or NH <sub>3</sub> around the C-N axis ps (meV, cm <sup>-1</sup> )	Reorientation of the C-N axis (residence time) ps (meV, cm <sup>-1</sup> )
Our work	INS single crystal	FAPB : 1.64 (0.40, 3.2)*	
Our work	Raman single crystal	MAPB : 0.8 (0.8, 6.4)*,** MAPI : 0.9 (0.7, 5.6)*,** FAPB : 0.47 (1.4, 11.3)*,**	
Swainson[2] (2015)	Powder QENS	MAPB : 1.0 (0.7, 5.6)*,***	
Leguy (2015)	Powder QENS	MAPI : 3.0 (0.2, 1.6)	MAPI : 14 (0.05, 0.4)
Chen (2015)	Powder QENS	MAPI : 1.0 (0.7, 5.6) 0.5 (1.3, 10.5) (370 K)	MAPI : 5 (0.13, 1.1) 2.4 (0.27, 2.2) (370 K)
Poglitsch (1987)	Powder mm-wave		MAPB : 2.7 (0.24, 1.9) MAPI : 5.4 (0.12, 1.0)
Ref.	Techniques	Wobbling of the C-N axis in a cone (precession) ps (meV, cm <sup>-1</sup> )	Reorientation of the C-N axis (residence time) ps (meV, cm <sup>-1</sup> )
Bakulin (2015)	Thin films t-resolved IR	MAPI : 0.3 (2.2, 17.7)	MAPI : 3 (0.22, 1.8)

\* Nature of the relaxations not specified

\*\* Error bar = ± 1 cm<sup>-1</sup>

\*\*\* Value extrapolated at room temperature

## References

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