Supplementary Information for "Prediction and understanding of barocaloric effects in orientationally disordered materials from molecular dynamics simulations"

Carlos Escorihuela-Sayalero,[1] Luis Carlos Pardo,[1] Michela Romanini,[1] Nicolas Obrecht,[2] Sophie Loehlé,[2] Pol Lloveras,[1] Josep-Lluís Tamarit,[1] and Claudio Cazorla[1, *]

[1] *Grup de Caracterització de Materials, Departament de Física,*
Universitat Politècnica de Catalunya, Campus Diagonal-Besòs,
Av. Eduard Maristany 10-14, 08019 Barcelona, Spain
Research Center in Multiscale Science and Engineering,
Universitat Politècnica de Catalunya, Campus Diagonal-Besòs,
Av. Eduard Maristany 10-14, 08019 Barcelona, Spain
[2] *TotalEnergies OneTech, 69369 Solaize, France*

The figures in this supplementary document are the following:

• Supplementary Figure 1: Angular autocorrelation function calculated across the order-disorder phase transition in MAPI.

• Supplementary Figure 2: Partial low-frequency phonon density of states calculated across the order-disorder phase transition in MAPI at zero pressure.

• Supplementary Figure 3: Three-dimensional sketch of the orientational paths followed by the molecular MA cations in MAPI at high temperatures ($T > T_t$).

• Supplementary Figure 4: Orientational probability density function of molecular MA cations in MAPI obtained from AIMD simulations.

• Supplementary Figure 5: Calculated entropy for a rigid free rotor consisting of a MA molecule.

* claudio.cazorla@upc.edu
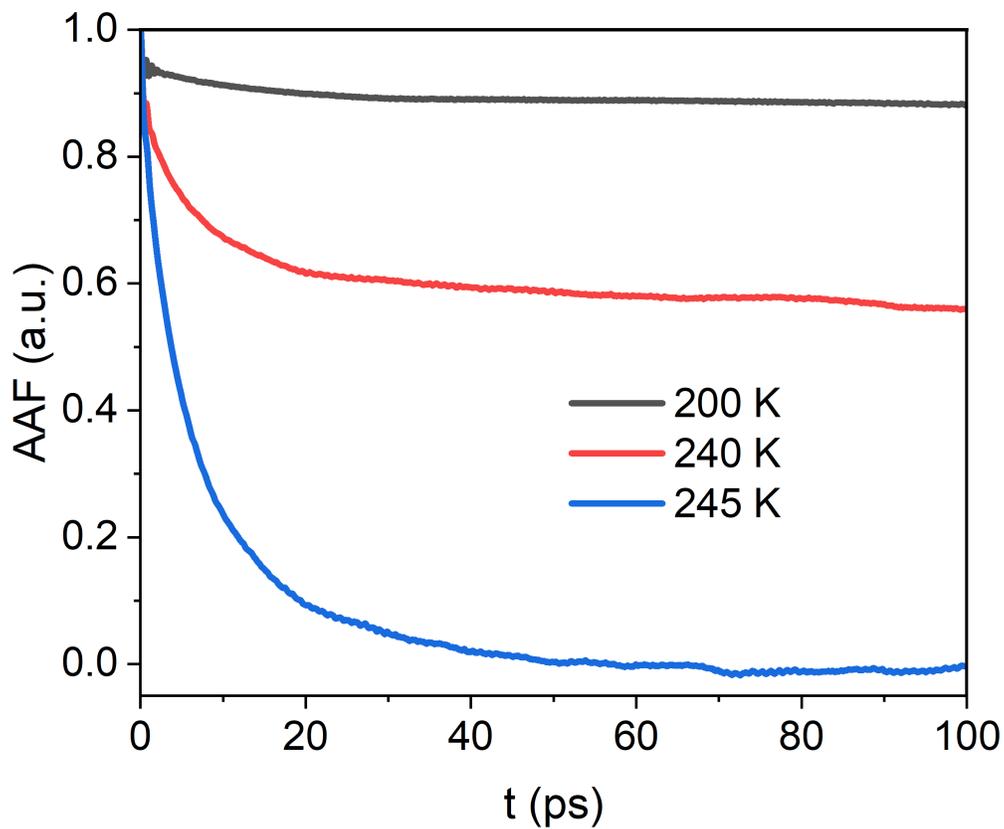
Supplementary Figure 1: **Angular autocorrelation function calculated across the order-disorder phase transition in MAPI.** The angular autocorrelation function is defined like $\phi_{\mathrm{MA}}(\tau) = \langle \hat{\mathbf{r}}(t) \cdot \hat{\mathbf{r}}(t+\tau) \rangle$, where $\hat{\mathbf{r}}$ is a unitary vector connecting the C and N atoms in each MA molecule and $\langle \cdots \rangle$ denotes statistical average in the NpT ensemble considering all the molecular cations. This function was calculated at temperatures above and below the transition temperature T_t, showing that it rapidly decays towards zero at temperatures $T > T_t$.
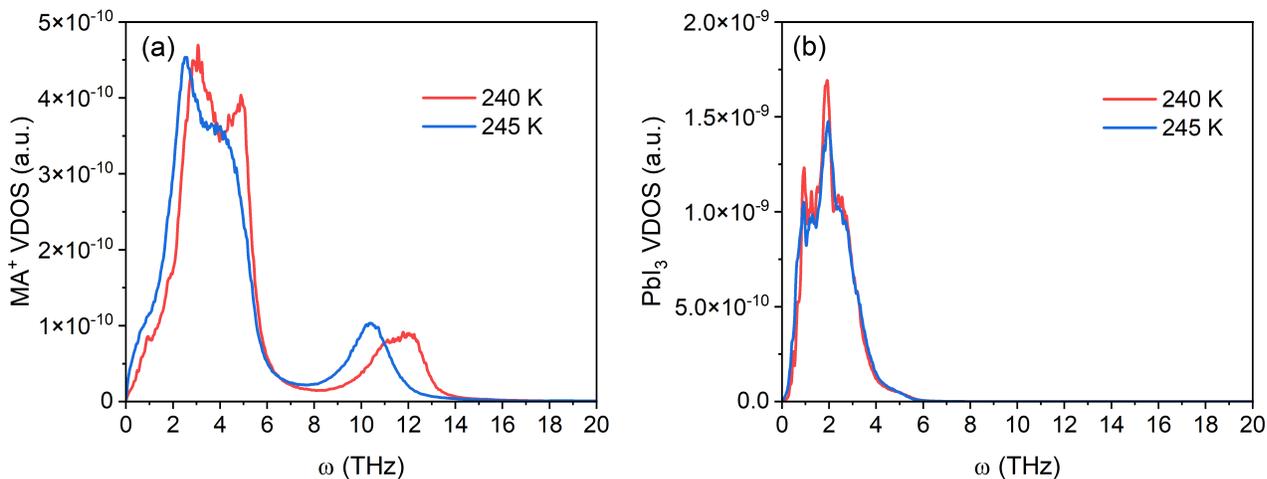
Supplementary Figure 2: **Low-frequency partial vibrational density of states calculated across the order-disorder phase transition in MAPI at zero pressure.** Vibrational density of states corresponding to (a) molecular MA cations and (b) PbI_3 groups across the order-disorder phase transition in MAPI. The larger T-induced phonon variations are observed for the MA molecules.
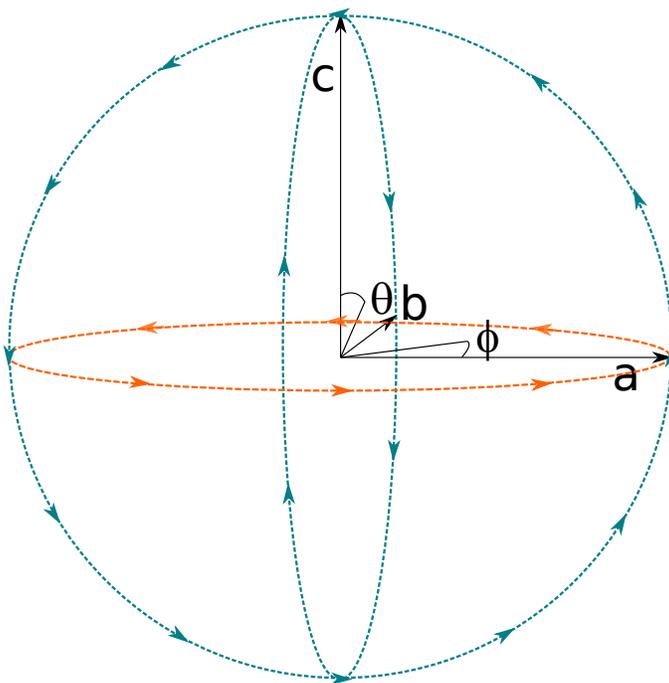
Supplementary Figure 3: **Three-dimensional sketch of the orientational paths followed by the MA^+ molecules in the disordered phase.** We depict the orientation of the molecular MA cations using big arrows in a spherical coordinate system, while the orientational paths are represented by circles on a sphere. The orientational trajectories do not correspond to maximum circles in the a–b plane. It becomes apparent that the number of available molecular orientational paths is quite limited.
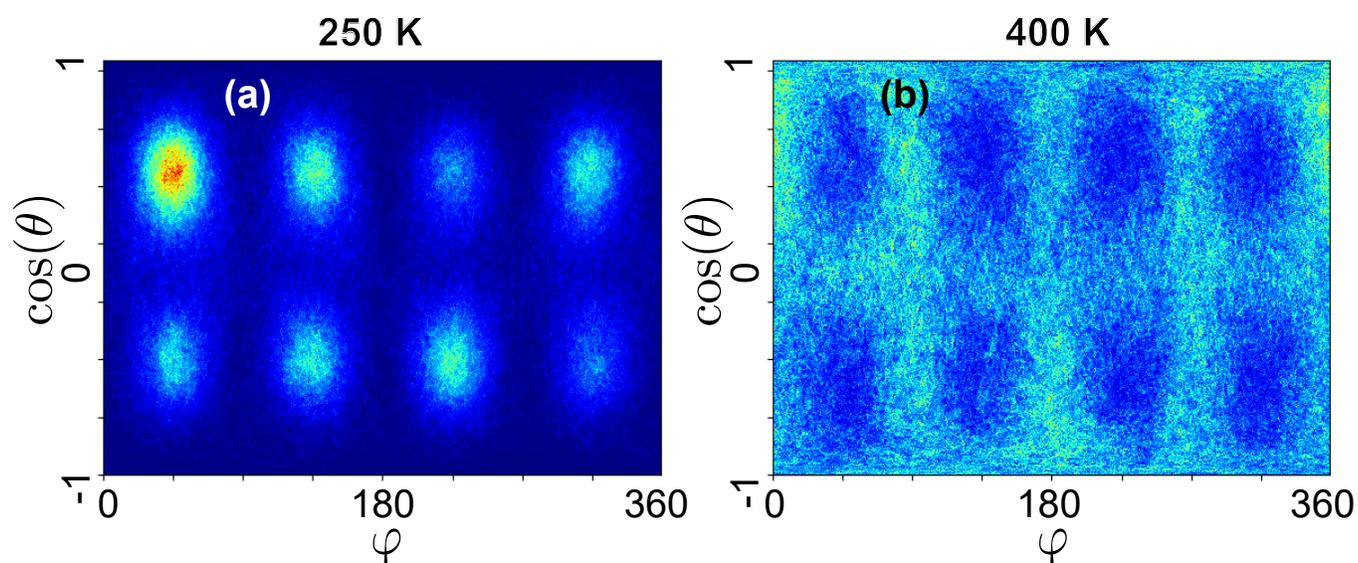
Supplementary Figure 4: **Angular probability density function calculated for molecular MA cations in MAPI from AIMD simulations based on DFT.** Histograms are calculated at (a) 250 K considering the tetragonal $I4cm$ phase and (b) 400 K considering the cubic $Pm\bar{3}m$ phase. Results are equivalent to those obtained using classical interatomic potentials. Differences in the location of the lobes and stripes with respect to the NpT–MD results (Fig. 4 in the main text) arise from a different choice of the crystal lattice orientation.
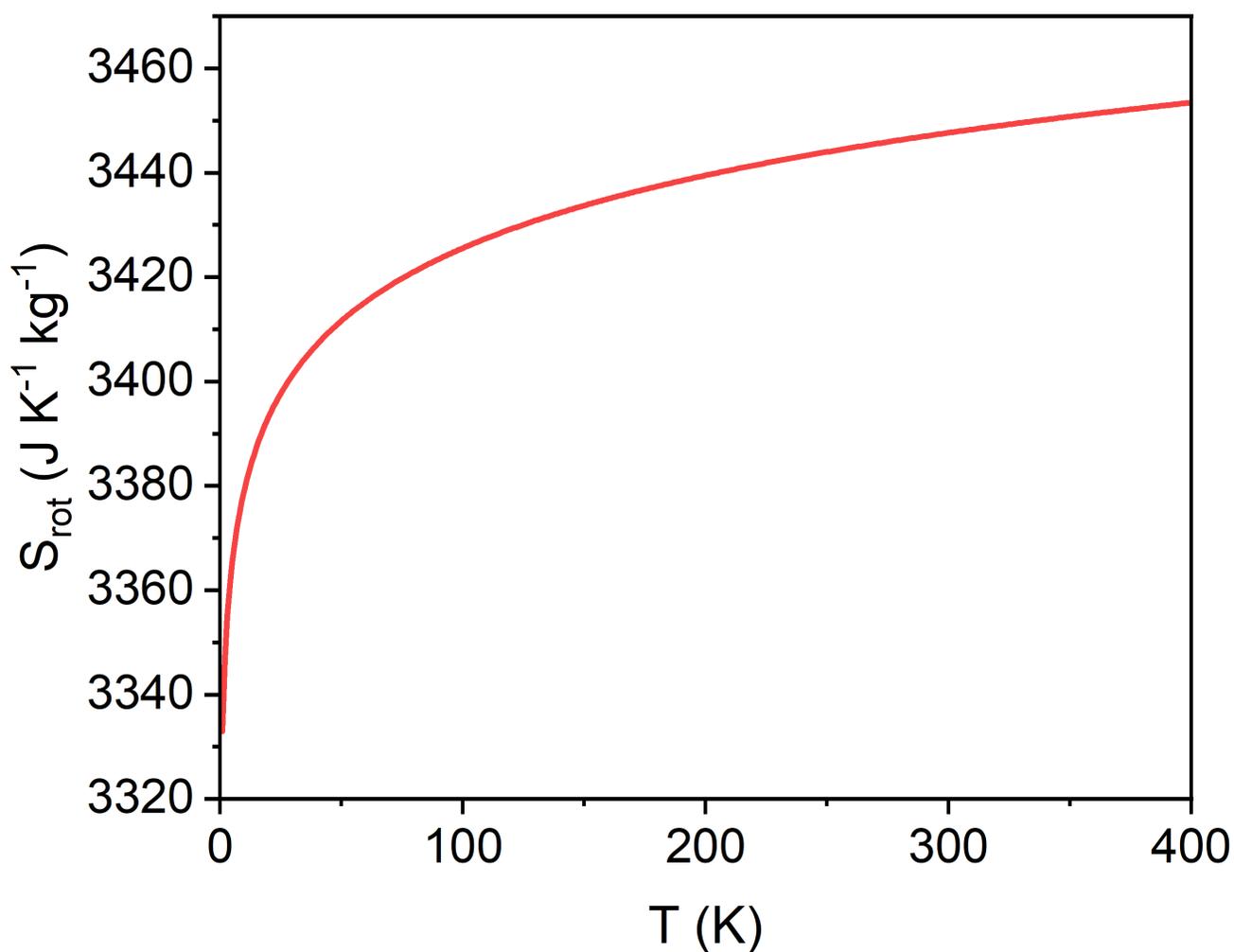
Supplementary Figure 5: **Calculated entropy for a rigid free rotor consisting of a MA^{+} molecule.** Note that this entropy function increases monotonically under increasing temperature, in contrast to the plateaus estimated for S_{ori} in MAPI above the phase transition temperature (Fig. 4 in the main text). The existing non-negligible discrepancies between the represented entropy function and S_{ori} point to the fact that the rigid molecular free rotor model is not physically adequate to describe molecular disorder in plastic crystals and/or organic-inorganic perovskites.