Cation dynamics and structural stabilization in formamidinium lead iodide perovskites

Kacper Druzbicki,^{1,2,*} Rasmus Lavén,³ Jeff Armstrong,⁴ Lorenzo Malavasi,⁵ Felix Fernandez-Alonso,^{2,6,7,8} and Maths Karlsson³

¹*Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Lodz, Poland*

²*Materials Physics Center, CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 Donostia - San Sebastian, Spain*

³*Department of Chemistry and Chemical Engineering,*

Chalmers University of Technology, SE-412 96 Göteborg, Sweden

⁴*ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, U. K.*

⁵*Department of Chemistry and INSTM, University of Pavia, Viale Taramelli 16, Pavia 27100, Italy*

⁶*IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain*

⁷*Donostia International Physics Center (DIPC),*

Paseo Manuel de Lardizabal 4, 20018 Donostia - San Sebastian, Spain

⁸*Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, U. K.*

The vibrational dynamics of pure and methylammonium-doped formamidinium lead iodide perovskites (FAPbI₃) has been investigated by high-resolution neutron spectroscopy. For the first time, we provide an exhaustive and accurate analysis of the cation vibrations and underlying local structure around the organic moiety in these materials using first-principles electronic-structure calculations validated by the neutron data. Inelastic Neutron Scattering experiments on FAPbI₃ provide direct evidence of the formation of a low-temperature orientational glass, unveiling the physico-chemical origin of phase metastability in the tetragonal structure. Further analysis of these data provides a suitable starting point to understand and explore the stabilization of the perovskite framework *via* doping with small amounts of organic cations. In particular, we find that hydrogen bonds in FAPbI₃ are strengthened in a synergistic manner as a result of cage deformation induced by the dynamics of the neighbouring methylammonium cations.

I. INTRODUCTION

Organometal Halide Perovskites (OHP's) have recently attracted an enormous interest due to their promising applications as absorbers in photovoltaic devices.[1] The prototypical OHP is methylammonium lead iodide (CH₃NH₃PbI₃, or MAPbI₃ for short). The main disadvantage of MAPbI₃ is, however, its poor long-term stability towards humidity and heat.[2–5] Formamidinium lead iodide (HC[NH₂]₂PbI₃, or FAPbI₃ for short) is currently attracting a lot of attention because it shows a much higher environmental stability, and its cubic phase has a close to ideal bandgap for photoabsorption (1.47 eV). [6, 7] However, FAPbI₃ shows a complex polymorphism behaviour which is currently considered to be a prime factor limiting its application potential. [8]

The structural picture of both MAPbI₃ and FAPbI₃ remains elusive to a great extent, since its better understanding is hindered by the presence of both static and dynamical disorder, as well as by the formation of domain structures of multiple origins. These idiosyncrasies have been highlighted, for instance, in the total-scattering experiments reported by Malavasi and co-workers, bringing to the fore the relevance and importance of ubiquitous short-range octahedral distortions in OHP's. [9–11]

The phase diagrams of both systems under interest and their mixtures is depicted in Fig. 1. In principle, it is commonly accepted that MAPbI₃ shows three

different crystal structures depending on the temperature, i.e. the low-temperature orthorhombic phase for $T < 160$ K; the tetragonal phase for $160 \text{ K} < T < 330 \text{ K}$; and the high-temperature cubic phase for $T > 330 \text{ K}$. [12] The space group assignment of each phase of MAPbI₃ has been, however, debatable from the very beginning. Poglitsch and Weber solved the orthorhombic structure in the non-centrosymmetric space group $Pna2_1$, [13] which has been eventually refined as the $Pnma$ structure by Baikie *et al.* [14] Using extensive *ab initio* modelling combined with inelastic neutron scattering (INS) experiments, Druzbicki *et al.* [15] showed that the $Pnma$ model is insufficient to describe the experimental data, pointing at the importance of octahedral deformations. Furthermore, with low-temperature X-ray diffraction, Baikie *et al.* [14] revealed the presence of some noticeable residual electron density at distances unreasonably close to the iodine positions, which leaves their space group assignment questionable. Similarly, the presence of high-residual electron density peaks was detected by Breternitz *et al.* [16] in the high-resolution X-ray study of the tetragonal phase. However, the commonly accepted centrosymmetric $I4/mcm$ model of the room-temperature phase has been recently questioned, following the discovery of ferroelectric behavior. [17] This has been further resolved by Breternitz *et al.* with the refinement of the structure within $I4cm$, which is the only polar maximal subgroup of $I4/mcm$. The average structure of the high-temperature cubic phase has been described with the $Pm\bar{3}m$ space group. However, recent high-resolution X-ray total-scattering studies postulate the system to be made up of small dynamic tetragonal

* E-mail: kacper.druzbicki@ehu.eus Tel: +34 943 01 5453

FIG. 1: The phase diagram of the perovskite solid solutions $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ across the temperature range of 10 - 365 K, according to Francisco-López *et al.* [18] Note that the mixtures studied in the present work correspond to the solutions $\text{MA}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ and $\text{MA}_{0.4}\text{FA}_{0.6}\text{PbI}_3$, respectively. The phase transition temperatures marked on the diagram refer to pure parent components. Note that the low-temperature structures are questionable (the space groups denoted with the question marks). For each phase considered (see the arrows), the corresponding crystal structures of pure MAPbI_3 and FAPbI_3 are presented as insets, with selected geometrical projections. Distortions of the PbI_6 octahedra are the characteristic features of the alternative $P1$ model of the low-temperature structure of MAPbI_3 . [15] The most-reliable model of the low-temperature γ -polymorph of FAPbI_3 published to date is of $P4bm$ symmetry. [19] This model is based on a $1 \times 1 \times 6$ expansion of the β -phase model ($P4/mbm$), where the FA^+ cation is rotated incrementally around the long cell axis.

domains at 350 K. [20, 21] Moreover, these domains were found to be left over from structural phase transitions that take place tens to hundreds of degrees below. [21] These considerations are in line with the conflicting evidence from various experimental and theoretical treatments of the degree of ordering of the organic cation in the orthorhombic phase. [22]

In the above context, the atomic structure of FAPbI_3 is far less understood. At room temperature (RT), FAPbI_3 has a stable hexagonal non-perovskite phase (yellow δ -polymorph, $P6_3mc$). [7, 23] However, a metastable cubic perovskite phase (black α -phase, $Pm\bar{3}m$), with an optimal band gap for photovoltaics, can be stabilized at RT for hours to weeks (depending on sample storage etc.) *via* heating above the hexagonal-to-cubic phase transition occurring around 410 K. [7, 8, 23] Upon cooling from the cubic phase, a tetragonal phase (β -phase, $P4/mbm$) is formed below 285 K, and yet another structure is found below 140 K (γ -phase). [19, 24–28] The structure of the low-temperature γ -polymorph is still under debate. Based on powder X-ray diffraction (PXRD), Fabini *et al.* [25] refined the γ -phase in a new primitive tetragonal unit cell retaining $P4/mbm$ symmetry, whilst Chen *et al.* [19] simultaneously refined the neutron and X-ray diffraction patterns in a $1 \times 1 \times 6$ super-

cell ($P4bm$) of the intermediate tetragonal phase, with the FA^+ cations rotated in increments around the c -axis. More recently, neutron powder diffraction experiments by Weber *et al.* [28] pointed towards a locally disordered γ -phase with possibly no long-range ordering of the FA^+ organic cations. The formation of an orientational glass at low temperatures has also been reported in previous studies. [22, 29] Therefore, a complete understanding of the low-temperature phase of FAPbI_3 remains elusive.

Due to aforementioned lack of phase stability in FAPbI_3 , considerable efforts have been focused on the study of the mixed-cation systems $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$, as they have been shown to stabilize the cubic perovskite structure of FAPbI_3 at RT even for relatively low concentrations of the MA dopant. [7] Additionally, these mixed systems show a higher stability towards humidity and heat than pure MAPbI_3 , and are currently among the materials with the highest photovoltaic efficiency. [30–33] Combining Raman scattering and photoluminescence (PL) spectroscopy, Francisco-López *et al.* have recently reported the compositional phase diagram of $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ solid solutions across the temperature range 10 – 365 K. [18]

Notwithstanding these recent developments, many fundamental aspects of FAPbI_3 remain poorly understood.

FIG. 2: INS spectra measured on (i) starting material of FAPbI₃ (orange curve; mixture of both perovskite and non-perovskite phases); (ii) after storage *in vacuo* for a period of three-months (blue curve; increased amount of the hexagonal phase); and (iii) after annealing at 165°C (black shaded curve; tetragonal phase). For ease of comparison, the spectra have been normalized and vertically shifted, and the spectral range of 60 – 80 meV is given as an inset. The atomic projections show the crystallographic structures of the low-temperature hexagonal (left) and tetragonal (right) phases according to Chen *et al.* [19].

In particular, we note important gaps in our knowledge concerning the low-temperature structure of FAPbI₃, which is believed to form an orientational glass, or how doping with small amounts of MA⁺ cations facilitates the stabilization of the perovskite framework of FAPbI₃. In addition, as compared to MAPbI₃, relatively little is known about the dynamics of the FA⁺ cation which, however, is believed to be more of an intricate nature. [34]

To date, FAPbI₃ has been primarily studied by diffraction techniques, [19, 24, 25, 27, 28] thereby providing information on the time-averaged structure. On the contrary, the use of spectroscopic techniques allows access to atomic and molecular correlation functions in both space and time and, thus, provide additional insights into the local structure and ensuing dynamics. Relative to other techniques, Inelastic Neutron Scattering (INS) is, in particular, superbly sensitive to the organic cation in OHP's, whose dynamics largely determines charge localization in these materials.[35] So far, the study of atomic motions in FAPbI₃ using INS spectroscopy has been primarily focused on the inorganic components Pb and I. This work has evinced the extreme softness of the Pb-I framework, leaving the hydrogen dynamics quite unexplored and limited to a narrow energy transfer range (0-15 meV). [36, 37] Further insights have been provided for the analogous FAPbBr₃ system, as recently reported by Mozur *et al.* [38]

As in the previous case of MAPbI₃ [15], we take the ensuing dynamics of the organic cation as a sensitive probe of local structure. In this work, the INS spectrum of FAPbI₃ is presented and extensively discussed for the first time. We focus on the low-temperature tetragonal structure observed upon cooling from the metastable cubic polymorph at RT. *Ab initio* modelling using time-dependent and time-independent methodologies provide an accurate description of the measured INS response of FAPbI₃. We extend this analysis onto the MA⁺-doped

FAPbI₃ mixtures, in order to provide new insights into the stabilisation of these solid solutions.

II. RESULTS AND DISCUSSION

It is known that FAPbI₃ decomposes into a non-perovskite hexagonal phase (δ -polymorph), which is the thermodynamically stable form at RT. [19, 28, 39] Our starting material is a physical mixture of the metastable perovskite (room-temperature cubic α -phase) and the stable non-perovskite δ -polymorph [19, 28]. Taking this knowledge into account, a first INS measurement was performed by cooling our starting material to base temperature (10 K), where the contributing polymorphs are transformed into their respective low-temperature phases – namely, the low-temperature perovskite γ -phase as well as the low-temperature hexagonal phase, hereafter denoted LT-Hex.[19] The experiment was repeated after three months, in order to increase the relative amount of the non-perovskite fraction. The perovskite structure of FAPbI₃ can be, however, restored by heating the sample above the hexagonal-to-cubic phase transition occurring around 400 K. [8, 24, 28] A third INS measurement was, hence, performed immediately after a heat treatment at 438 K for about 10 minutes. [40] The sample was then quenched down to base temperature in order to observe the pure (γ -phase) of FAPbI₃. [19] These INS data are presented in Fig. 2.

As shown in Fig. 2, thermal annealing results in rather subtle changes in spectral intensities, and in the disappearance of some shoulders. Most importantly, we note a downward shift of the intense feature at ca. 20 meV and the loss of its fine structure, as well as a clear growth in the intensity of the band at 15 meV. From an analysis of close contacts in both polymorphs (see the insets to Fig. 2), this effect appears to be related to the weakening of

specific interactions, e.g., hydrogen-bonds, due to the enhanced disorder of the FA^+ units in the tetragonal phase. The range above 50 meV is hardly sensitive to the underlying phase, only resulting in relatively minor frequency shifts and intensity modulations, which can be further linked to an increased cation disorder in the perovskite phase affecting the hydrogen-bond network.

At this juncture, we note that the resulting INS spectrum may depend on the way the dynamic structure factor $S(q, E)$ is probed via INS. These considerations are corroborated through a comparison of INS data for single-crystal and powder samples of an analogous FAPbBr_3 system, obtained with triple-axis and indirect-geometry neutron spectrometers, respectively. [37, 38] The overall intensity progression of the INS spectrum of FAPbI_3 presented in this work is very similar to that observed by Mozur *et al.* on powder FAPbBr_3 , collected on the VISION spectrometer (SNS, Oak Ridge). [38]

Figure 3 shows the INS spectra of the parent materials, along with the $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ mixtures of relevance to this work. In order to bring to the fore the relative contributions of either MAPbI_3 and FAPbI_3 to total intensities, these data have been normalized to the height of those spectral bands that are least affected by cation mixing. Using this normalization procedure, difference spectra ($\text{MA}_{1-x}\text{FA}_x\text{PbI}_3 - \text{FAPbI}_3$) were calculated to highlight MAPbI_3 contributions to the total intensity (see the red curves in Fig. 3).

The INS spectrum of MAPbI_3 shows several sharp peaks in the region below 40 meV. The vibrational dynamics of pure MAPbI_3 has already been studied extensively in a previous INS study. [15] Here, we emphasize the recent upgrade of the TOSCA spectrometer, [41–45], which has allowed us to explore the terahertz range with a much higher signal-to-noise ratio relative to previous work. [15] The sharp modes below 30 meV are governed by combined MA^+ librations and vibrations of the lead-iodide framework. [15] The peaks above 30 meV mainly consist of internal molecular vibrations. In particular, the sharp and intense peak at ~ 37 meV has been assigned to a torsional mode of MA and was found to be particularly sensitive to the local crystal environment of the MA^+ cation. [15]

Compared to MAPbI_3 , the INS spectrum of FAPbI_3 exhibits broader features in the low-energy region of ~ 6 –30 meV, corresponding to molecular librations combined with inorganic lattice deformations. These differences indicate that the orientation of the FA^+ cations are more disordered at 10 K, as compared to MA^+ in MAPbI_3 , where the cations arrange in highly preferable directions. [12] This observation is in agreement with previous studies by neutron diffraction, [28] thermophysical measurements, [22], and nuclear magnetic resonance, [29] which have indicated the formation of an FAPbI_3 orientational glass at temperatures below 100 K.

For the mixed stoichiometries, the INS features shown in Fig. 3 are also very similar to those of tetragonal FAPbI_3 , consistent with that both of the mixed stoi-

FIG. 3: INS spectra of FAPbI_3 and MAPbI_3 along with their mixtures, recorded on TOSCA at 10 K. The spectra of the mixtures were normalized w.r.t. the one for pure FAPbI_3 using the intensity of the band marked with the asterisk.

The spectrum of pure MAPbI_3 was normalized w.r.t. the spectrum of $\text{MA}_{0.4}\text{FA}_{0.6}\text{PbI}_3$, using the band marked with an arrow. Consequently, the difference spectra for the mixtures (the red curves) were calculated as $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3 - \text{FAPbI}_3$. The most prominent spectral shifts upon sample mixing are marked with red arrows. The same intensity scale has been used for all the spectra presented in this figure.

chiometries have the same low-temperature structure as FAPbI_3 . [46] The difference spectra, which are mainly highlighting the MA^+ features, reflect a strong damping of intensity in the low-frequency part of the spectrum. Noticeably, there is a progressive upward shift of the spectral peak at ca. 20 meV with increasing MAPbI_3 content (by ca. 2.5 meV), which, however cannot be unequivocally assigned at this stage. Also, the peak observed at ca. 37 meV in pure MAPbI_3 , assigned to a disrotary mode of the methyl and/or ammonia groups of MAPbI_3 (denoted as $\tau(-\text{C-N-})$), [15] is substantially modified in these mixtures (by ca. 4 meV). A similar shift and damping have been observed by Mozur *et al.* [47] for the case of $\text{MA}_{1-x}\text{Cs}_x\text{PbBr}_3$, where the formation of an orientational MA^+ glass was observed at low temperature for relatively low concentrations of the Cs^+ cation. Similarly, the most intense peak observed within the librational part of the spectrum (see Lib. MA^+) at ca. 10 meV for crystalline MAPbI_3 can be assigned to the mode arising from a reorientation of the whole MA^+ molecule about the long molecular axis. These molecular motions are modulated by well-defined hydrogen-bonding interactions between the organic cation and the inorganic lattice, giving rise to sharp spectral features in crystalline

MAPbI₃. From these considerations, we may conclude that MA⁺ in the mixtures experiences a largely disordered local environment, with little evidence to support the idea of long-range order for either FA⁺ or MA⁺.

To gain further and much-needed quantitative insights into the INS data, we have performed first-principles calculations. To this end, we have explored several computational models:

(i) The first one (hereafter, β -model) takes as starting point the structure of the FAPbI₃ tetragonal cell provided by Fabini *et al.* [25] This structure has been solved in the $P4/mbm$ space group, with the FA⁺ cation represented as a point mass. Since the cation is thought to be dynamically disordered between preferred orientations, we have considered different scenarios by transforming the initial $P4/mbm$ structure into a number of alternative lower-symmetry configurations. As further detailed in the SI, this approach had limited success in describing the experimental INS spectrum of the low-temperature phase of FAPbI₃. These calculations indicate that the total number of cations contained in the β -model per crystallographic cell is insufficient to account for all spectral features.

(ii) Based on the above results for the β -model, an extended model of the disordered low-temperature phase was used as initial input (hereafter γ -model, $P4bm$). This structure has been proposed by Chen *et al.* [19, 26], based on powder neutron diffraction experiments, and its reliability has been recently confirmed by Webber *et al.* [28] The cell constants were fixed to the values measured at 15 K ($a = 8.87740$ Å, $c = 37.67240$ Å), [19, 26] whereas the FA⁺ cations ($\times 12$ ions) were extracted from the crystallographic model and oriented randomly, to account for molecular disorder. This structure (with a resulting $P1$ symmetry) was found to be sufficient to account for all INS features and, therefore, it has been used for subsequent normal-mode analysis using Harmonic Lattice Dynamics (HLD). (iii) Finally, we have performed *Ab Initio* Molecular Dynamics (AIMD) simulations on an extended γ -model of FAPbI₃ consisting of a larger $2 \times 2 \times 1$ supercell containing 48 FA⁺ ions and with lattice parameters $a = b = 17.75480$ Å and $c = 37.67240$ Å. This model is compared with AIMD simulations on MAPbI₃ for a $2 \times 2 \times 2$ supercell containing 32 MA⁺ cations. This MAPbI₃ supercell uses the $P1$ model ($Z = 4$) of the low-temperature phase from previous work. [15] The primitive model used for reference HLD calculations of MAPbI₃ is described by the highest possible symmetry corresponding to the Cc space group ($Z = 2$).

The above computational models adopted throughout this work are summarised in Fig. 4, and more details are relegated to the SI. These can be used to provide a quantitative interpretation of the INS spectrum of FAPbI₃, which has been summarized in Table 1. The spectra resulting from both HLD and AIMD simulations are displayed in Fig. 5. For consistency, we confront these outputs with the theoretical calculations performed for

FIG. 4: The structural models of FAPbI₃ (a. – b.) and MAPbI₃ (c. – d.) adopted in the *ab initio* modelling detailed in the main text. The primitive cells used for HLD calculations are presented in panels a. and c., while the extended periodic models used for the AIMD simulations are given in panels b. and d. for FAPbI₃ and MAPbI₃, respectively.

MAPbI₃ using another computational approximation, ie. PBE-D3(BJ) [48–51] (see the SI for a detailed comparison of the results obtained with both PBE-TS and PBE-D3(BJ)). Since the INS spectrum of MAPI has been extensively analyzed in Ref. [15], we focus here on a detailed interpretation of the INS spectrum of FAPbI₃. However, we note that owing to an improved sensitivity of the TOSCA spectrometer, the assignment of a few weak bands in the low-frequency regime has been revised herein. This has been emphasized in Fig. 5, where six MA⁺ librations are now clearly assigned (see the bands labeled as *i*–*vi*). Particularly, we note that the highest-frequency external mode (denoted as libration *i*) is observed at 18.1 meV, whereas the feature at 23 meV is the first overtone of librational mode *v*, largely damped upon mixing. Consequently, the band at ca. 20 meV in the above-discussed difference spectrum does not correspond to MA⁺ vibrations.

By inspection of Fig. 5, one can find an excellent match of the predicted INS spectra of FAPbI₃ to the experimental one. Further improvement with the use of AIMD methodology, relying on a larger supercell, points at the importance of a larger number of different local configurations needed to properly describe the spectrum, supporting the finding that the low-temperature structure of FAPbI₃ is highly disordered. [28] At this stage, owing to an excellent reproduction of the spectral intensities over the entire frequency range, the assignment of the internal-mode range becomes straightforward, as summarized in Table 1. Despite the use of two different codes (CASTEP *vs* CP2K), both HLD and low-temperature

TABLE I: Experimentally observed (INS at 10 K) phonon frequencies of FAPbI₃ (in meV), as compared to the results of the first-principles calculations (PBE-D3(BJ)). [48–51]

The phonon frequencies are from HLD calculations (CASTEP), and AIMD simulations (CP2K). Spectral assignments: ν - stretching; δ - bending; γ - out-of-plane deformation; Lib. - libration. The mode numbering correspond to those shown in Fig. 5. (Roman and Arabic numerals for the external and internal modes, respectively).

Peak Position [meV]				Assignment
Notation	INS	HLD	MD	
1	419.3	428.2	433.7	ν [N-H] (<i>antisymmetric</i>)
2	406.9	416.8	417.4	ν [N-H] (<i>symmetric</i>)
3	391.0	385.3	395.7	ν [C-H]
4	213.9	211.0	214.0	ν [C-N] + δ [NH ₂] + δ [CH]
5	201.4	198.0	199.1	δ [NH ₂] (<i>symmetric</i>)
6	188.8	190.2	190.8	δ [NH ₂] (<i>antisymmetric</i>)
7	166.7	165.4	166.9	δ [NCH]
8	140.7	136.9	137.3	δ [CNH] (<i>symmetric</i>)
9	125.4	124.7	124.3	δ [CNH] + δ [NCH]
10	87.6	86.2	86.8	γ [NH ₂] + γ [CH]
11	74.7	75.8	74.4	γ [NH ₂]
12	72.1	72.0	72.0	γ [NH ₂]
13	67.2	67.6	68.7	γ [NH ₂]
14	63.3	61.9	62.0	δ [N-C-N]
<i>i</i>	19.9	22.1	24.9	FA ⁺ Lib. (<i>long-axis</i>)
<i>ii</i>	16.1	19.6	22.7	FA ⁺ Lib. (<i>long-axis</i>)
<i>iii</i>	13.3	14.9	16.6	FA ⁺ Lib. (<i>long-axis</i>)
<i>iv</i>	9.3	9.5	11.4	FA ⁺ Lib. (<i>in-plane</i>)
<i>v</i>	8.1	8.3	8.8	FA ⁺ Lib. (<i>short-axis</i>)
<i>vi</i>	7.2	6.9	6.1	FA ⁺ Lib. (<i>short-axis</i>)
δ Pb-I	3.9	3.5	3.2	δ [I-Pb-I] + FA ⁺ Lib.
δ Pb-I	1.4	1.6	1.7	δ [I-Pb-I] + FA ⁺ Lib.

AIMD simulations provide very similar frequencies. [55]

As indicated in Fig. 5, internal and external modes are separated by a large phonon gap of ca. 40 meV, which is roughly twice the value found for MAPbI₃. At this point, we note that for both parent compounds the low-frequency part of the spectrum is highly overlapping in terms of energy (ca. 0–20 meV), therefore, being considerably populated at elevated temperatures, where sample mixing is performed. We anticipate that this phenomenon is a key factor making both compounds good candidates for solid solutions.

Because of evident formation of the orientational glass, the analysis of the terahertz part of the INS spectrum of FAPbI₃ is far more challenging. Nevertheless, the computational outputs are sufficient to guarantee a general assignment of the respective features. A detailed inspection of the normal modes has allowed to classify the underlying librations into the three main types arising from rotations of an asymmetric top (as displayed as insets to Fig. 5). The normal mode analysis indicates that the range above 15 meV is due to librations along the long molecular axis; the in-plane librations contribute mainly to the most-intense feature at ca. 10 meV; whereas the reorientations along the short molecular axis mainly contribute as the low-frequency shoulder bands at ca. 7–8 meV. We note that this idealized picture is disturbed by

FIG. 5: Experimental (TOSCA 10 K) and theoretical (HLD and AIMD) spectra of FAPbI₃ (bottom panels) and MAPbI₃ (upper panels) calculated for the structural models presented in Fig. 4 using PBE-D3(BJ) level of theory. [48–54] The contributions from the fundamental transitions in the theoretical spectra are represented by thick lines. Simplified visualization of different types of librational modes is provided as insets to the figure, with the experimental bands assigned with Roman numerals. For FAPbI₃ the internal modes are further marked with Arabic numerals. See Table 1 for a detailed band assignment.

different local environments and variable strength of the specific forces affecting the FA⁺ cations.

In order to provide more insight into the low-lying features we rely on a detailed decomposition of the hydrogen-projected vibrational density of states (VDOS) into the contribution of each of 48 FA⁺ cations included in the extended γ -phase model. This has been presented in Figure 6, where two extreme cases have been highlighted. The analysis reveals that the upper part of the VDOS is particularly sensitive to the local environment of the FA⁺ cations. The related modes correspond to cation librations about the long molecular axis (see the inset to Fig. 6), giving the strongest

FIG. 6: (bottom panel) Partial hydrogen-projected VDOS spectra calculated for each of 48 FA^+ molecules included in the extended structural model of the γ -phase of FAPbI_3 (see Fig. 4 b). [56, 57]. The most-intense bands in the VDOS spectrum (spread over the range ca. 15 – 25 meV) correspond to the molecular libration depicted in the inset. The blue and red shaded curves correspond to two extreme cases of weakly (a.; blue) and strongly (b.; red) H-bonded FA^+ cations (see the upper panel for time-averaged (30 ps) structures with the same color-coding used). The time-averaged close-contacts between the hydrogen and iodine atoms are given in Angstroms.

partial contributions to the total intensity due to the largest molecular displacements. As evidenced from the analysis of the time-averaged volumes of the surrounding sub-units along with the H–I distances, this effect can be clearly attributed to the strength of the hydrogen-bonds, immobilizing the FA^+ cations.

Based on the above-given analysis, the INS spectra of the $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ mixtures (see Fig. 3) can be finally understood. With an increasing amount of the MA^+ dopant, the frequency of the lowest-lying internal vibration ($\tau(-\text{C}-\text{N}-)$) undergoes a progressive downward-shift in energy, due to an increasing orientational disorder, further attributed to the weakening of the MA^+ hydrogen bonding and the disorder-induced expansion of the surrounding cage. Simultaneously, there is an increasing fraction of the FA^+ cations subjected to stronger hydrogen-bonding interactions with a collapsed inorganic cage, manifested by the upward-shift in energy of the respective highest-energy librational modes. The mechanism is promoted by the extreme softness of the inorganic framework, [36, 37] and a strong overlap of the VDOSs of inorganic [58] and organic counterparts. We note that the INS experiments presented by Ferreira and co-workers [36, 37] link the unstable nature of α - FAPbI_3 to its very low bulk modulus and a negative C_{12} elastic

constant. Furthermore, the recently proposed transition pathway for the degradation of α - FAPbI_3 [59] highlights the importance of short-range octahedral distortions. We anticipate that the above-discussed synergistic strengthening of hydrogen-bonding interactions involving the FA^+ cations results in a locking-effect, which strongly inhibits degradation of the perovskite framework.

III. CONCLUSIONS

In conclusion, the combined use of high-resolution INS experiments and advanced *ab initio* modelling has provided, for the first time, a detailed and quantitative view of the local environment and vibrational dynamics of FA^+ cations in formamidinium lead-iodide perovskites. The formation of an orientational glass has been confirmed, and a realistic model of the low-temperature structure of FAPbI_3 has been proposed and validated by the neutron scattering data. An excellent match between experimental and simulated spectra has been achieved. We have also extended the analysis to heavily substituted solid-state $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ mixtures, revealing synergistic dynamics across both MA^+ and FA^+ cations, directly affecting the geometry of the surrounding inorganic framework. Based on these considerations, we have identified important factors contributing to the stabilization of FAPbI_3 perovskite structures. We anticipate that these will facilitate the design of efficient routes for the further optimisation of these solid solutions using criteria such as (i) the similarity of the vibrational profiles of the organic guests; (ii) the effective thermal population of low-energy vibrational motions; (iii) or a high molecular mobility of the organic dopants.

IV. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Sample Preparation: $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ ($x = 0.0, 0.1, 0.4$, and 1.0) powder samples were synthesized using protocols reported elsewhere.[7, 60, 61] The chemical composition and integrity of each sample was further corroborated with ^1H NMR following Ref. [7].

Neutron Scattering Experiments: The INS experiments were performed on the TOSCA spectrometer,[41–45] operating at the ISIS Neutron and Muon Source. The measurements were performed at $T = 10$ K. Standard corrections were applied to the data within the Mantid software package. [62]

Ab Initio Calculations: The modelling of the INS spectra was performed in terms of solid-state formulation of Density Functional Theory (DFT) as implemented in the CASTEP (versions 16.1 and 20.1) [63, 64] and CP2K (version 8.1) codes [65, 66], respectively. The calculations were performed under Periodic Boundary Conditions (PBCs). The Perdew-Burke-Ernzerhof (PBE) functional [48] was used all throughout this work. We adopted two different approximations to take into account of van-der-Waals (vdW) interactions in our calculations: Tkatchenko-Scheffler corrections, PBE-TS [67];

and the D3 correction method of Grimme *et al.* with Becke-Johnson (BJ) damping, PBE-D3(BJ). [48–51] The phonon eigenvalues and eigenvectors calculated using HLD served as an input for the further modelling of the INS spectra. [52, 53] For the MD simulations, production-run trajectories were used for modelling of the hydrogen-projected VDOS spectra *via* the explicit calculation of the Velocity AutoCorrelation Function (VACF). The analysis and the post-processing of the MD production runs was made with the help of the TRAVIS code. [56, 57] Alternatively, we have also followed the recently implemented strategy to model the $S(q, E)$ spectra from MD trajectories by means of an approximate treatment of the Debye-Waller factor which accounts for overtone and combination bands as well the specific configuration of the TOSCA spectrometer. [54]

More experimental and computational details are provided in the SI.

SUPPLEMENTARY INFORMATION

This Section includes further details on the INS experiments, *ab initio* modelling, calculations using simplified mod-

els of FAPbI₃, analysis of the influence of vdW corrections on the INS spectra, detailed analysis of the low-frequency phonon modes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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SUPPLEMENTARY INFORMATION:

Cation dynamics and structural stabilization in formamidinium lead iodide perovskites

Kacper Druzbicki,^{1,2,*} Rasmus Lavén,³ Jeff Armstrong,⁴ Lorenzo Malavasi,⁵ Felix Fernandez-Alonso,^{6,7,8,9} and Maths Karlsson¹⁰

¹*Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Lodz, Poland*

²*Materials Physics Center, CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 Donostia - San Sebastian, Spain*

³*Department of Chemistry and Chemical Engineering,*

Chalmers University of Technology, SE-412 96 Göteborg, Sweden

⁴*ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire OX11 0QX, U. K.*

⁵*Department of Chemistry and INSTM, University of Pavia, Viale Taramelli 16, Pavia 27100, Italy*

⁶*Materials Physics Center, CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 Donostia - San Sebastian, Spain*

⁷*IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain*

⁸*Donostia International Physics Center (DIPC),*

Paseo Manuel de Lardizabal 4, 20018 Donostia - San Sebastian, Spain

⁹*Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, U. K.*

¹⁰*Department of Chemistry and Chemical Engineering,*

Chalmers University of Technology, SE-412 96 Göteborg, Sweden

I. INELASTIC NEUTRON SCATTERING

The INS experiments were performed on the TOSCA spectrometer. [1–5] operating at the ISIS neutron and muon source. Powder samples of $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ ($x = 0.0, 0.1, 0.4, \text{ and } 1.0$) were loaded into rectangular Al sample cells which were sealed with In wire. The measurements were performed at $T = 10$ K. The pure FAPbI_3 sample was measured first as a mixture of the hexagonal and tetragonal polymorphs. A second measurement of FAPbI_3 was performed after annealing at 438 K to form the cubic phase directly prior to the measurements, followed by subsequent quenching to 10 K where the INS measurements were performed. In this way, the FAPbI_3 sample is then in the pure tetragonal phase at 10 K. [6, 7]

For a powder sample, within the incoherent approximation, the observed neutron-scattering intensity corresponding to the i -th vibrational mode at a momentum transfer $q[\text{\AA}^{-1}]$ is given by [8]:

$$I(q, nE_i) \propto \frac{(qU_i)^{2n} \sigma_{\text{inc}}}{n!} \exp[-(qU_{\text{Tot}})^2] \quad (1)$$

where n is the quantum number of an i -th mode ($n = 1$ for a fundamental; $n > 1, 2, 3$ and so forth for overtones and combination bands); σ_{inc} stands for the incoherent scattering cross-section. U_i is the mean square atomic displacement in the considered vibration, and the exponential term is known as the Debye-Waller Factor (DWF). U_{Tot} stands for the total root mean square displacement of all the atoms in all (both internal and external) modes, and its magnitude is partially determined by the thermal motion of the molecule. More

rigorous and formal considerations can be found in Ref. [9].

Thus, the INS spectrum of $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ will be dominated by contribution from the organic cations, both because of the large incoherent cross section of hydrogen and its low mass relative to other atoms present in the system.

TOSCA is a so-called inverted-geometry time-of-flight spectrometer with two fixed scattering angles. This means that one probes specific trajectories on the (q, E) plane in the forward and backward scattering hemispheres, *i.e.* with each E corresponding to a specific q value. For TOSCA, this relationship is approximately given by $E[\text{cm}^{-1}] \approx 16q^2[\text{\AA}^{-1}]$.

II. COMPUTATIONAL DETAILS

The modelling of the INS spectra was performed using both Harmonic Lattice Dynamics (HLD) and *Ab Initio* Molecular Dynamics (AIMD) under Periodic Boundary Conditions (PBCs). For the HLD calculations we employed the Plane-Wave Pseudo-Potential (PW-PP) formulation of Density Functional Theory (DFT) as implemented in the CASTEP code (versions 16.1 and 20.1), [10, 11]. The same numerical settings were the same as those used in the previously reported study on MAPbI_3 . [12] In brief, the Perdew-Burke-Ernzerhof (PBE) functional within the Generalized-Gradient-Approximation (GGA) was augmented with semi-empirical dispersion corrections (DFT-D). [13] The core electrons were described by a set of hard, norm-conserving PPs, while the electronic wave functions were defined using a PW basis set with a kinetic energy cutoff of 900 eV. A Monkhorst-Pack grid was used to maintain a constant k -spacing of $0.05 \text{\AA}^{-1}$. All structures were accurately relaxed to minimize all residual atomic forces. The convergence criteria in the variation of the

* E-mail: kacper.druzbicki@ehu.eus Tel: +34 943 01 5453

total energy, Hellmann–Feynman forces, external stress (as in the case of full cell-relaxation, unless otherwise stated), maximum displacement, and the self-consistent field (SCF) were defined as 1×10^{-12} eV/atom, 1×10^{-5} eV/Å, 0.0001 GPa, 1×10^{-6} Å, and 1×10^{-12} eV/atom, respectively.

We adopted two different approximations to account for van-der-Waals (vdW) interactions in our calculations: Tkatchenko-Scheffler corrections, DFT-vdW(TS) [14]; and the D3 correction method of Grimme *et al.* with Becke-Johnson (BJ) damping, DFT-D3(BJ). [15–17] Both DFT-vdW(TS) and DFT-D3(BJ) are atom-pair-wise DFT-D correction schemes, and we further augmented the latter to include three-body terms.

Following geometry optimization, phonon frequencies and eigenvectors were calculated within the harmonic approximation at the Γ point by diagonalizing the mass-weighted Hessian matrix, W , constructed by numerical differentiation of the analytical gradients with respect to atomic displacements. For the finite-difference calculations, we used a displacement amplitude of 0.01 Å. The calculated phonon eigenvalues and eigenvectors served as an input for the further modelling of the INS spectra. [18, 19]

In the second scheme, we used the CP2K code [20, 21] to perform AIMD simulations on supercell structures (see the main text for more details). These calculations used PBE-D3(BJ) [15–17, 22] in combination with plane-wave (500 Ry) / gaussian atom-centered double-zeta quality basis sets (DZVP-MOLOPT) along with Goedecker-Teter-Hutter (GTH) pseudopotentials. Convergence criteria were chosen to be consistent with the accuracy of the parallel CASTEP calculations. This approach provides a similar level of accuracy for both computational codes [23]. Such consistency has been further verified for MAPbI₃ via comparison with earlier published results (see Section IV) [12]. A set of classically-thermostatted (NVT; Nosé-Hoover) time-evolved simulations was performed in the framework of Born-Oppenheimer Molecular Dynamics (BOMD). In each case, 20-ps simulations at 150 K were followed by a 10-ps equilibration at 50 K, and a subsequent 30-ps production run. Using 576 processors at the Polish high-performance computing facility PROMETHEUS, [24] these calculations produced about 2.5 ps per day.

For the MD simulations, production-run trajectories served as input for the modelling of the hydrogen-projected Vibrational Densities Of States (VDOS) via the explicit calculation of the Velocity AutoCorrelation Function (VACF), for direct comparison with INS data. The VDOS for a particular atom j is given by the Fourier-transform of the VACF according to:

$$VDOS = \sum_j^N \int_0^\infty \frac{\langle \nu(t)_j \nu(0)_j \rangle}{\langle \nu(0)_j^2 \rangle} \exp(-i\omega t) dt, \quad (2)$$

where $\nu(t)_j$ is the velocity at time t . The analysis and the

post-processing of the BOMD production runs was made with the help of the TRAVIS code. [25, 26] Alternatively, we have also followed the recently implemented strategy to model the INS spectra from MD trajectories by means of an approximate treatment of the Debye-Waller factor which accounts for overtone and combination bands as well the specific configuration of the TOSCA spectrometer. [27]

III. THE SIMPLIFIED MODELS OF THE TETRAGONAL PHASE OF FAPbI₃

Using the structure of the β -tetragonal phase of FAPbI₃ reported by Weber *et al.* [7] as starting point, we found that it becomes necessary to consider a range of FA⁺ configurations within the unit cell. The transformation of the initial $P4/mbm$ structure into the alternative ones results in a lowered global symmetry. Following these considerations, we have examined a number of alternative models, with the internal coordinates constrained by symmetry in each case. These have been illustrated in Fig. S1. (see models *a.–f.*). Although a larger number of different configurations was tested, the discussed ones were selected as giving visibly distinct INS spectra.

(*a.*) The structure was simply derived from the initial $P4/mbm$ model, with only one FA⁺ molecule per asymmetric unit. This model has $P4_21m$ symmetry, based on the cell constants fixed to the experimental values (200 K). [7]

(*b.*) The model was built by running simple BOMD simulations with CASTEP (NVT at 200K), where the coordinates of the inorganic cage were fixed, and the preferred orientation of FA⁺ cation was found. The resulting structure was further symmetrized to the closest, Pc point group, and successively fully optimized at atmospheric pressure.

(*c.*) This is a $1 \times 1 \times 2$ supercell of (*a.*), with the FA⁺ cations reoriented by 180° in the c -direction, and by 90° in the ab -plane, respectively. This model consists of two cations per asymmetric unit, preserving the $P4_21m$ symmetry. The model was obtained based on the cell constants fixed to the experimental values. [7]

(*d.*) This is a variation of model (*b.*) above. It consists of one molecule per asymmetric unit, where the symmetry operators of the $P2_1$ space group transform the cations by 180° in the a -direction. The structure was further fully optimized at atmospheric pressure.

(*e.*) This is a variation of the $2 \times 1 \times 1$ supercell in model (*d.*), with two FA⁺ cations per asymmetric unit, thereby preserving $P2_1$ symmetry. The structure was also fully optimized at atmospheric pressure.

(*f.*) Finally, the structures is an analogue of model (*e.*), containing four, fully independent FA⁺ cations (global symmetry $P1$), being fully optimized at the atmospheric pressure without any symmetry constraints.

The INS spectra predicted with HLD for each structure

FIG. 1: Alternative, simple models of the tetragonal phase of FAPbI₃, obtained with CASTEP/PBE-TS calculations. See the main text for a detailed description. Note a different convention of the cell axes adopted in each case.

considered are presented in Fig. 2. These have been confronted with the experimental spectra recorded on TOSCA at 10 K. By inspection of the figure one can note that the INS spectrum of FAPbI₃ is highly sensitive to the cation orientation, particularly in the range below 400 cm⁻¹.

The local arrangement of the FA⁺ cations affects the high-frequency regime mainly in terms of the resulting transition intensities and the presence of the shoulder bands all across 500 - 1200 cm⁻¹. This range can be attributed to purely internal FA⁺ vibrations.

While each model facilitates a qualitative interpretation of the spectra above 400 cm⁻¹, none of them provides an acceptable reproduction of the low-frequency regime observed experimentally. This range can be attributed to external vibrations of the FA⁺ ions, where the rotational and translational degrees of freedom are transformed to a PbI₃-mixed lattice phonons. Such a discrepancy has been confirmed by Mozur et al., with the DFT calculations performed for an analogous FAPbBr₃ system, using a simplified model of the tetragonal phase. [28]

Closer inspection of the external modes in the a. and b. models also allows to exclude the presence of a highly ordered crystal structure with the cations

FIG. 2: Comparison of the experimental (TOSCA 10K) and theoretical INS spectra of FAPbI₃. The theoretical spectra correspond to the (a. - f.) models presented in Fig. S1. The calculations were performed with pair-wise vdW corrections to PBE (PBE-TS). The energy scale is given in inverse centimeters.

oriented preferentially along a unique direction. While extending the number of the nonequivalent FA⁺ cations, and so accounting for orientational disorder, we note a progression of the low-part of the VDOS toward higher wavenumbers.

We conclude that the simplified models of the tetragonal phase, derived from the model of an intermediate-temperature β -phase ($P4/mbm$), are insufficient to describe the INS response of FAPbI₃ in the low-temperature regime. For the low-temperature limit, one should consider the system as an orientational glass, for which no simple definition of local order appears to be possible. These results are in line with

the diffraction studies presented by Weber et al. [7] and supports the dielectric spectroscopy reported by Fabini et al. [29] In order to improve the agreement with the experimental data, we have employed alternative, more extended models of the low-temperature phase of MAPbI₃ presented in the main text.

IV. THE INFLUENCE OF THE VDW CORRECTIONS ON THE INS SPECTRA

The consistency of the HLD outputs obtained by means of the two different schemes used to correct for missing vdW energy contributions to the PBE functional has been examined by confronting the computational results with the experimental spectra measured on TOSCA for both MAPbI₃ and FAPbI₃. These results are collected in Figs. S3 - S5, respectively. The results were obtained through the calculations performed for the primitive cells described in the main text, where the unit cells of MAPbI₃ were fully-relaxed under atmospheric pressure, contrary to FAPbI₃, for which the cell constants were fixed to the values measured at 15 K by Chen et al. [6]

The excellent correlation between the phonon frequencies calculated with both approaches (Fig. S3) justify the use of both computational strategies for the computational modeling of the title systems. While providing nearly identical treatment of the vibrational properties, some deviations appear in the range below 30 meV, where the vibrational dynamics of the organic cations is largely dictated by the vibrations of inorganic framework due to the coupling of both organic and inorganic counterparts. This has been presented in more

detail in Fig. S4.

By referring to Fig. S4 and the intensity distributions provided therein, we note that both approaches provide a satisfying match to the experimental data. Some differences in the low-frequency region of the FAPbI₃ spectrum can be attributed to artificial stress present in the fixed-cell calculations, [6] where both PBE-D3(BJ) and PBE-TS structures are slightly off their equilibrium volumes at 0 K.

V. POTENTIAL ENERGY DISTRIBUTION ANALYSIS OF THE PHONON MODES OF FAPbI₃ AND MAPbI₃

To support our discussion in the main text, Fig. S5 gives a detailed analysis of the potential energy distribution for each normal mode of vibration predicted by both PBE-D3(BJ) and PBE-TS. This decomposition focuses on the low-energy motions of FAPbI₃ and MAPbI₃. We note that the vibrations of the inorganic cage largely dominate the potential energy landscape in the range below 8 meV. Librations predicted at ca. 8–16 meV also contain considerable contributions from the motions of the centre-of-mass of the organic cations (Transl.), therefore evincing strong couplings to the deformation of the inorganic framework.

At this point, we also address the question how the mass of the cation affects the terahertz range of vibrations in both compounds considered. This can be understood by focusing on the translational contributions. From comparison of the stacked histograms presented for MAPbI₃ and FAPbI₃, it appears that the shift is at the order of ca. 2 meV. This can be illustrated by a slight change in energy of the two upper-frequency phonon modes with dominating translational character, i.e. ca. 20 and 18 meV for MAPbI₃, and FAPbI₃, respectively. Further insight is, however, hindered by a highly-mixed nature of the modes.

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FIG. 3: Correlation between the phonon frequencies (in inverse centimeters) for the low-temperature phases of (left) MAPbI₃, and FAPbI₃, as calculated by means of different vdW corrections to PBE functional (Grimme's D3 with Becke-Johnson Damping, PBE-D3(BJ), and Tkatchenko-Scheffler, PBE-TS.)

FIG. 4: Comparison of the experimental (TOSCA 10K) and theoretical INS spectra of MAPbI₃ and FAPbI₃ calculated with PBE-D, using pair-wise (TS) and triple-wise (D3(BJ)) vdW corrections, respectively.

FIG. 5: Stacked histograms showing the energy decomposition of the low-frequency phonon modes of MAPbI₃ (upper panels) and FAPbI₃ (bottom panels), as calculated for their low-temperature phases by means of PBE-TS and PBE-D3(BJ). The percentage contributions arise from the translations (TRANSL.) and librations (LIBR.) and the internal molecular vibrations. See Ref. [30] for a detailed description of the numerical procedure applied for the decomposition of the dynamic matrix. The phonon frequencies are given in meV, in line with the data presented in the main text.

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FIG. 7: GRAPHICAL ABSTRACT